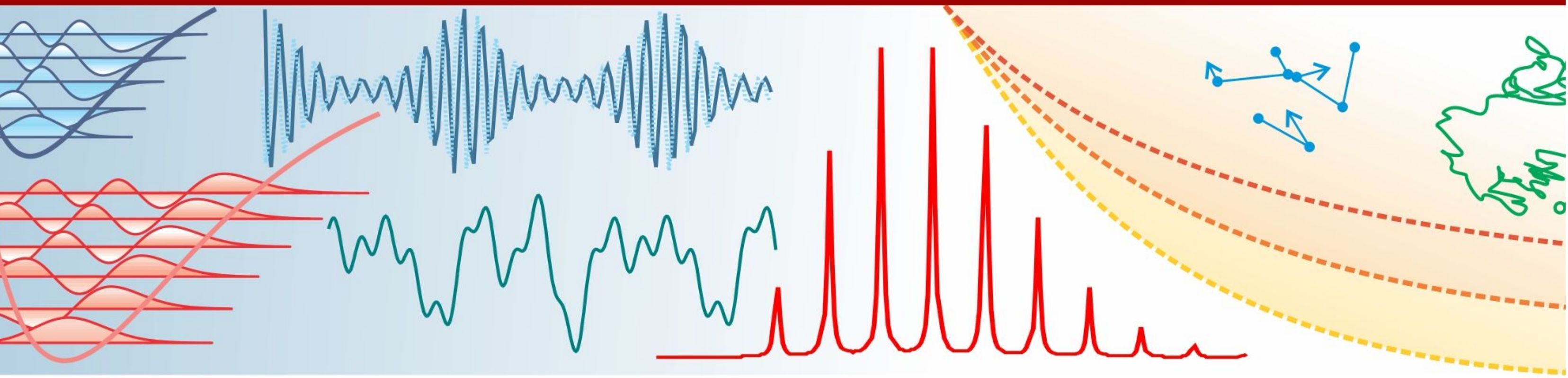
Time-Dependent Quantum Mechanics and Spectroscopy



Andrei Tokmakoff

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1. INTRODUCTION

1.1. Time Evolution with a Time-Independent Hamiltonian

The time evolution of the state of a quantum system is described by the time-dependent Schrödinger equation (TDSE):

$$i\hbar\frac{\partial}{\partial t}\psi(\bar{r},t)=\hat{H}(\bar{r},t)\psi(\bar{r},t) \tag{1.1}$$

$\hat{H}$ is the Hamiltonian operator which describes all interactions between particles and fields, and determines the state of the system in time and space. $\hat{H}$ is the sum of the kinetic and potential energy. For one particle under the influence of a potential

$$\hat{H}=-\frac{\hbar^2}{2m}\hat{\nabla}^2+\hat{V}(\bar{r},t) \tag{1.2}$$

The state of the system is expressed through the wavefunction $\psi(\bar{r},t)$. The wavefunction is complex and cannot be observed itself, but through it we obtain the probability density $P=\left|\psi(\bar{r},t)\right|^2$ which characterizes the spatial probability distribution for the particles described by $\hat{H}$ at time *t*. Also, it is used to calculate the expectation value of an operator $\hat{A}$

$$\left\langle\hat{A}(t)\right\rangle=\int\psi^*(\bar{r},t)\hat{A}\psi(\bar{r},t)\,d\bar{r}=\left\langle\psi(t)\middle|\hat{A}\middle|\psi(t)\right\rangle \tag{1.3}$$

Physical observables must be real, and therefore will correspond to the expectation values of Hermitian operators $\left(\hat{A}=\hat{A}^\dagger\right)$.

Our first exposure to time-dependence in quantum mechanics is often for the specific case in which the Hamiltonian $\hat{H}$ is assumed to be independent of time: $\hat{H}=\hat{H}(\bar{r})$. We then assume a solution with a form in which the spatial and temporal variables in the wavefunction are separable:

$$\psi(\bar{r},t)=\varphi(\bar{r})T(t) \tag{1.4}$$

$$i\hbar\frac{1}{T(t)}\frac{\partial}{\partial t}T(t)=\frac{\hat{H}(\bar{r})\varphi(\bar{r})}{\varphi(\bar{r})} \tag{1.5}$$

Here the left-hand side is a function only of time, and the right-hand side is a function of space only ($\bar{r}$, or rather position and momentum). Equation (1.5) can only be satisfied if both sides are equal to the same constant, E. Taking the right-hand side we have

$$\frac{\hat{H}(\bar{r})\varphi(\bar{r})}{\varphi(\bar{r})}=E \qquad\Rightarrow\qquad \hat{H}(\bar{r})\varphi(\bar{r})=E\varphi(\bar{r}) \tag{1.6}$$

This is the Time-Independent Schrödinger Equation (TISE), an eigenvalue equation, for which $\varphi(\bar{r})$ are the eigenstates and E are the eigenvalues. Here we note that $\langle\hat{H}\rangle=\langle\psi|\hat{H}|\psi\rangle=E$, so $\hat{H}$ is the operator corresponding to E and drawing on classical mechanics we associate $\langle\hat{H}\rangle$ with the expectation value of the energy of the system.

Now taking the left-hand side of (1.5) and integrating:

$$i\hbar\frac{1}{T(t)}\frac{\partial T}{\partial t}=E \quad \Rightarrow \quad \left(\frac{\partial}{\partial t}+\frac{iE}{\hbar}\right)T(t)=0 \tag{1.7}$$

$$T(t)=\exp(-iEt/\hbar) \tag{1.8}$$

So, in the case of a bound potential we will have a discrete set of eigenfunctions $\varphi_n(\bar{r})$ with corresponding energy eigenvalues E_n from the TISE, and there are a set of corresponding solutions to the TDSE.

$$\psi_n(\bar{r},\ t)=\varphi_n(\bar{r})\exp(-iE_nt/\hbar) \tag{1.9}$$

Since the only time-dependence is a phase factor, the probability density for an eigenstate is independent of time: $P=|\psi_n(t)|^2=$ constant. Therefore, the eigenstates $\varphi(\bar{r})$ do not change with time and are called *stationary states*.

However, more generally, a system may exist as a linear combination of eigenstates:

$$\psi(\bar{r},t)=\sum_n c_n\psi_n(\bar{r},t)=\sum_n c_n e^{-iE_nt/\hbar}\varphi_n(\bar{r}) \tag{1.10}$$

where c_n are complex amplitudes, with $\sum_n |c_n|^2=1$. For such a case, the probability density will oscillate with time. As an example, consider two eigenstates

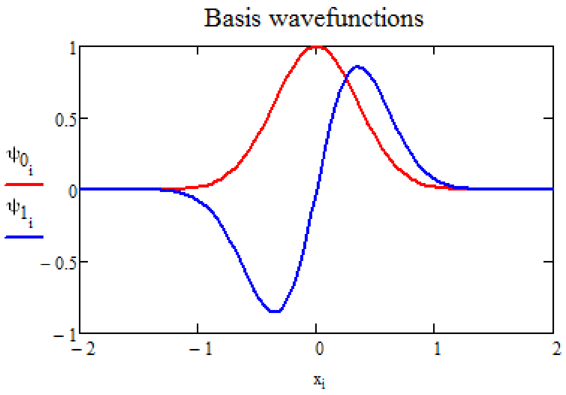
$$\psi(\bar{r},t)=\psi_1+\psi_2=c_1\varphi_1 e^{-iE_1t/\hbar}+c_2\varphi_2 e^{-iE_2t/\hbar} \tag{1.11}$$

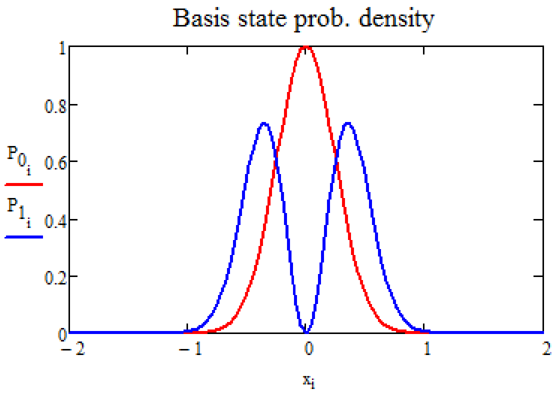
For this state the probability density oscillates in time as

$$\begin{aligned} P(t) &= |\psi|^2=|\psi_1+\psi_2|^2 \\ &= |c_1\varphi_1|^2+|c_2\varphi_2|^2+c_1^*c_2\varphi_1^*\varphi_2 e^{-i(\omega_2-\omega_1)t}+c_2^*c_1\varphi_2^*\varphi_1 e^{+i(\omega_2-\omega_1)t} \\ &= |\psi_1|^2+|\psi_2|^2+2|\psi_1\psi_2|\cos((\omega_2-\omega_1)t) \end{aligned} \tag{1.12}$$

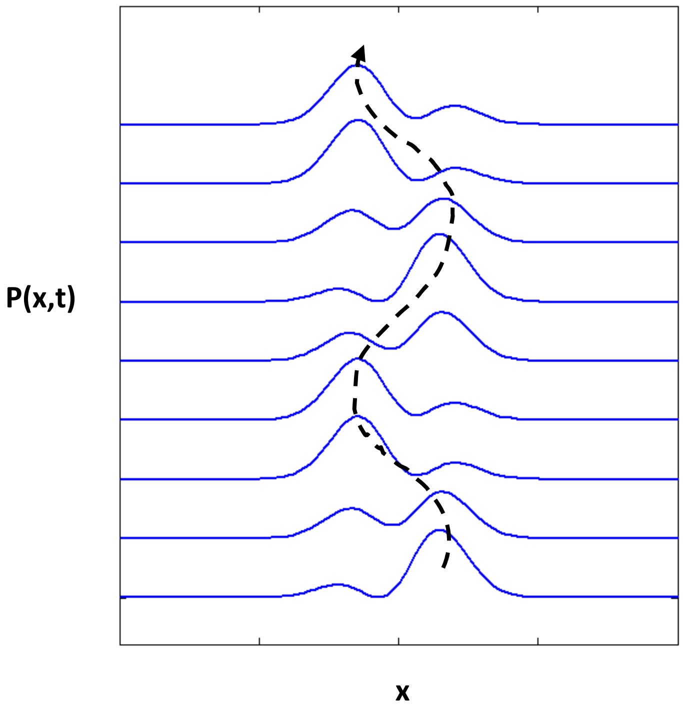
where $\omega_n=E_n/\hbar$. We refer to this state of the system that gives rise to this time-dependent oscillation in probability density as a coherent superposition state**,** or *coherence*. More generally, the oscillation term in eq. (1.12) may also include a time-independent phase factor ϕ that arises from the complex expansion coefficients.

As an example, consider the superposition of the ground and first excited states of the quantum harmonic oscillator. The basis wavefunctions, $\psi_0(x)$ and $\psi_1(x)$, and their stationary probability densities $P_i = \langle \psi_i(x) | \psi_i(x) \rangle$ are





If we create a superposition of these states with eqn. (1.11), the time-dependent probability density oscillates, with ⟨x(t)⟩ bearing similarity to the classical motion. (Here $c_0 = 0.5$ and $c_1 = 0.87$.)



Readings

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1.2. Exponential Operators

Throughout our work, we will make use of exponential operators of the form

$$\hat{T} = e^{-i\hat{A}}$$

We will see that these exponential operators act on a wavefunction to move it in time and space. Of particular interest to us is the time-propagator or time-evolution operator, $\hat{U} = e^{-i\hat{H}t/\hbar}$, which propagates the wavefunction in time. Note the operator $\hat{T}$ is a *function of an operator,* $f(\hat{A})$. A function of an operator is defined through its expansion in a Taylor series, for instance

$$\hat{T} = e^{-i\hat{A}} \;=\; \sum_{n=0}^{\infty} \frac{(-i\hat{A})^n}{n!} = 1 - i\hat{A} - \frac{\hat{A}\hat{A}}{2} - \cdots \tag{1.13}$$

Since we use them so frequently, let's review the properties of exponential operators that can be established with eq. (1.13). If the operator $\hat{A}$ is Hermitian, then $\hat{T} = e^{-i\hat{A}}$ is unitary, i.e., $\hat{T}^{\dagger} = \hat{T}^{-1}$. Thus the Hermitian conjugate of $\hat{T}$ reverses the action of $\hat{T}$. For the time-propagator $\hat{U}$, $\hat{U}^{\dagger}$ is often referred to as the time-reversal operator.

The eigenstates of the operator $\hat{A}$ also are also eigenstates of $f(\hat{A})$, and eigenvalues are functions of the eigenvalues of $\hat{A}$. Namely, if you know the eigenvalues and eigenvectors of $\hat{A}$, i.e., $\hat{A}\varphi_n = a_n\varphi_n$, you can show by expanding the function that

$$f\left(\hat{A}\right)\varphi_n = f\left(a_n\right)\varphi_n \tag{1.14}$$

Our most common application of this property will be to exponential operators involving the Hamiltonian. Given the eigenstates φ_n, then $\hat{H}\left|\varphi_n\right\rangle = E_n\left|\varphi_n\right\rangle$ implies

$$e^{-i\hat{H}t/\hbar}\left|\varphi_n\right\rangle = e^{-iE_nt/\hbar}\left|\varphi_n\right\rangle \tag{1.15}$$

Just as $\hat{U} = e^{-i\hat{H}t/\hbar}$ is the time-evolution operator, which displaces the wavefunction in time, $\hat{D}_x = e^{-i\hat{p}_x x/\hbar}$ is the spatial displacement operator that moves ψ along the x coordinate. If we define $\hat{D}_x(\lambda) = e^{-i\hat{p}_x\lambda/\hbar}$, then the action of is to displace the wavefunction by an amount λ.

$$\left|\psi\left(x-\lambda\right)\right\rangle = \hat{D}_x(\lambda)\left|\psi\left(x\right)\right\rangle \tag{1.16}$$

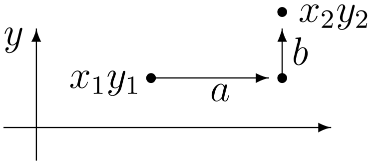
Also, applying $\hat{D}_x(\lambda)$ to a position operator shifts the operator by λ

$$\hat{D}_x^{\dagger}\hat{x}\hat{D}_x = \hat{x} + \lambda \tag{1.17}$$

Thus $e^{-i\hat{p}_x\lambda/\hbar}|x\rangle$ is an eigenvector of $\hat{x}$ with eigenvalue $x + \lambda$ instead of x. The operator $\hat{D}_x = e^{-i\hat{p}_x\lambda/\hbar}$ is a displacement operator for x position coordinates. Similarly, $\hat{D}_y = e^{-i\hat{p}_y\lambda/\hbar}$ generates displacements in y and $\hat{D}_z$ in z. Similar to the time-propagator $\hat{U}$, the displacement operator $\hat{D}$ must be unitary, since the action of $\hat{D}^\dagger\hat{D}$ must leave the system unchanged. That is if $\hat{D}$ shifts the system to x from x_0, then $\hat{D}^\dagger$ shifts the system from x back to x_0.

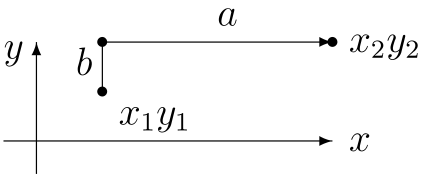
We know intuitively that linear displacements commute. For example, if we wish to shift a particle in two dimensions, x and y, the order of displacement does not matter. We end up at the same position. These displacement operators commute, as expected from $[p_x,p_y] = 0$.

$$|x_2y_2\rangle = e^{-ibp_y/\hbar}e^{-iap_x/\hbar}|x_1y_1\rangle \Rightarrow$$



first move along x by a, then along y by b.

$$= e^{-iap_x/\hbar}e^{-ibp_y/\hbar}|x_1y_1\rangle \Rightarrow$$

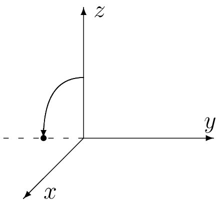


reverse order

Similar to the displacement operator, we can define rotation operators that depend on the angular momentum operators, L_x, L_y, and L_z. For instance, $\hat{R}_x(\phi) = e^{-i\phi L_x/\hbar}$ gives a rotation by angle ϕ about the x-axis. Unlike linear displacement, rotations about different axes do not commute. For example, consider a state representing a particle displaced along the z-axis, $|z_0\rangle$. Now the action of two rotations $\hat{R}_x$ and $\hat{R}_y$ by an angle of π/2 on this particle differs depending on the order of operation.

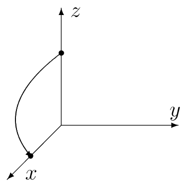
$$\underbrace{e^{-i\frac{\pi}{2}L_y/\hbar}}_{\text{rotation by }\frac{\pi}{2}\text{ about }y\text{-axis}} \quad \underbrace{e^{-i\frac{\pi}{2}L_x/\hbar}|z_0\rangle}_{\text{rotation by }\frac{\pi}{2}\text{ about }x\text{-axis}} \Rightarrow$$

particle on –y axis



$$\underbrace{e^{-i\frac{\pi}{2}L_x/\hbar}}_{\text{rotation by }\frac{\pi}{2}\text{ about }x\text{-axis}} \quad \underbrace{e^{-i\frac{\pi}{2}L_y/\hbar}|z_0\rangle}_{\text{rotation by }\frac{\pi}{2}\text{ about }y\text{-axis}} \Rightarrow$$

particle on +x axis



The results of these two rotations taken in opposite order differ by a rotation about the z–axis. Thus, because the rotations about different axes do not commute, we must expect the angular momentum operators, which generate these rotations, not to commute. Indeed, we know that $[L_x,L_y] = i\hbar L_z$, where the commutator of rotations about the x and y axes is related by a z-axis rotation. As with rotation operators, we will need to be careful with time-propagators to determine whether the order of time-propagation matters. This, in turn, will depend on whether the Hamiltonians at two points in time commute.

Finally, it is worth noting some relationships that are important in evaluating the action of exponential operators:

(1) The Baker–Hausdorff relationship:

$$\begin{aligned}\exp\left(i\hat{G}\lambda\right)\hat{A}\ \exp\left(-i\hat{G}\lambda\right) \;=\; & \hat{A}+i\lambda\left[\hat{G},\hat{A}\right] \;+\; \left(\frac{i^2\lambda^2}{2!}\right)\left[\hat{G},\left[\hat{G},\hat{A}\right]\right]+\ldots \\ & +\; \left(\frac{i^n\lambda^n}{n!}\right)\left[\hat{G},\left[\hat{G},\left[\hat{G}\ldots\left[\hat{G},\hat{A}\right]\right]\right]\ldots\right] \;+\; \ldots\end{aligned} \tag{1.18}$$

(2) If $\hat{A}$ and $\hat{B}$ do not commute, but $\left[\hat{A},\hat{B}\right]$ commutes with $\hat{A}$ and $\hat{B}$, then

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-\frac{1}{2}\left[\hat{A},\hat{B}\right]} \tag{1.19}$$

(3)

$$e^{\hat{A}}\,e^{\hat{B}} = e^{\hat{B}}\,e^{\hat{A}}\,e^{-\left[\hat{B},\hat{A}\right]} \tag{1.19}$$

Time-Evolution Operator

Since the TDSE is deterministic and linear in time, we can define an operator that describes the dynamics of the wavefunction:

$$\psi(t)=\hat{U}(t,t_0)\psi(t_0) \tag{1.20}$$

U is is the time-propagator or time-evolution operator that evolves the quantum system as a function of time. It represents the solution to the time-dependent Schrödinger equation. To investigate its form we consider the TDSE for a *time-independent Hamiltonian*:

$$\frac{\partial}{\partial t}\psi(\bar{r},t)+\frac{i\hat{H}}{\hbar}\psi(\bar{r},t)=0 \tag{1.21}$$

To solve this, we will define an exponential operator $\hat{T}=\exp\left(-i\hat{H}t/\hbar\right)$, which is defined through its expansion in a Taylor series:

$$\hat{T}=\exp\left(-i\hat{H}t/\hbar\right) \;=\; 1-\frac{i\hat{H}t}{\hbar}+\frac{1}{2!}\left(\frac{i\hat{H}t}{\hbar}\right)^2-\cdots \tag{1.22}$$

You can also confirm from the expansion that $\hat{T}^{-1}=\exp\left(i\hat{H}t/\hbar\right)$, noting that $\hat{H}$ is Hermitian and $\hat{H}$ commutes with $\hat{T}$. Multiplying eq. (1.21) from the left by $\hat{T}^{-1}$, we can write

$$\frac{\partial}{\partial t}\left[\exp\left(\frac{i\hat{H}t}{\hbar}\right)\psi(\bar{r},t)\right]=0, \tag{1.23}$$

and integrating $t_0 \rightarrow t$, we get

$$\exp\left(\frac{i\hat{H}t}{\hbar}\right)\psi(\bar{r},t)-\exp\left(\frac{i\hat{H}t_0}{\hbar}\right)\psi(\bar{r},t_0)=0 \tag{1.24}$$

$$\psi(\bar{r},t)=\exp\left(\frac{-i\hat{H}(t-t_0)}{\hbar}\right)\psi(\bar{r},t_0) \tag{1.25}$$

So, comparing to (1.20), we see that the time-propagator is

$$\hat{U}(t,t_0)=\exp\left(\frac{-i\hat{H}(t-t_0)}{\hbar}\right). \tag{1.26}$$

For the time-independent Hamiltonian for which we know the eigenstates φ_n and eigenvalues E_n, we can express this in a practical form using eq. (1.14)

$$\psi_n(\bar{r},t)=e^{-iE_n(t-t_0)/\hbar}\psi_n(\bar{r},t_0) \tag{1.27}$$

Alternatively, if we substitute the projection operator (or identity relationship)

$$\sum_n |\varphi_n\rangle\langle\varphi_n| = 1 \tag{1.28}$$

into eq. (1.26), we see

$$\begin{aligned}\hat{U}(t,t_0) &= e^{-i\hat{H}(t-t_0)/\hbar}\sum_n |\varphi_n\rangle\langle\varphi_n| \\ &= \sum_n e^{-i\omega_n(t-t_0)}|\varphi_n\rangle\langle\varphi_n|\end{aligned} \qquad \omega_n = \frac{E_n}{\hbar} \tag{1.29}$$

So now we can write our time-developing wave-function as

$$\begin{aligned}|\psi_n(\bar{r},t)\rangle &= |\varphi_n\rangle\sum_n e^{-i\omega_n(t-t_0)}\langle\varphi_n|\psi_n(\bar{r},t_0)\rangle \\ &= \sum_n e^{-i\omega_n(t-t_0)}\,c_n \\ &= \sum_n c_n(t)|\varphi_n\rangle\end{aligned} \tag{1.30}$$

As written in eq. (1.20), we see that the time-propagator $\hat{U}(t,t_0)$ acts to the right (on *kets*) to evolve the system in time. The evolution of the conjugate wavefunctions (*bras*) is under the Hermitian conjugate of $\hat{U}(t,t_0)$ acting to the left:

$$\langle\psi(t)| = \langle\psi(t_0)|\hat{U}^\dagger(t,t_0) \tag{1.31}$$

From its definition as an expansion and recognizing $\hat{H}$ as Hermitian, you can see that

$$\hat{U}^\dagger(t,t_0) = \exp\left[\frac{i\hat{H}(t-t_0)}{\hbar}\right] \tag{1.32}$$

Noting that $\hat{U}$ is unitary, $\hat{U}^\dagger = \hat{U}^{-1}$, we often refer to $\hat{U}^\dagger$ as the time reversal operator.

1.3. Two-Level System

Let's use the time-propagator in a model calculation that we will refer to often. It is common to reduce or map quantum problems onto a two level system (2LS). We will pick the most important states for our problem and find strategies for discarding or simplifying the influence of the remaining degrees of freedom. Consider a 2LS with two unperturbed or "zeroth order" states $|\varphi_a\rangle$ and $|\varphi_b\rangle$ with energies ε_a and ε_b, which are described by a zero-order Hamiltonian H_0:

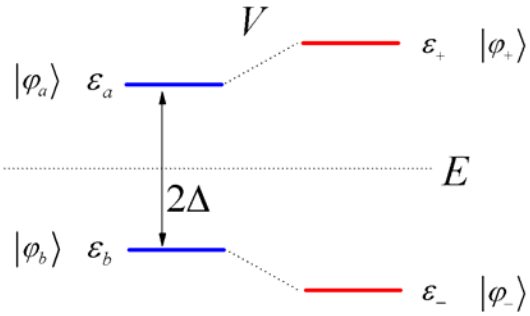
$$\begin{aligned}\hat{H}_0 &= |\varphi_a\rangle \varepsilon_a \langle\varphi_a| + |\varphi_b\rangle \varepsilon_b \langle\varphi_b| \\ &= \begin{pmatrix} \varepsilon_a & 0 \\ 0 & \varepsilon_b \end{pmatrix}\end{aligned} \tag{1.33}$$

These states interact through a coupling V of the form

$$\begin{aligned}\hat{V} &= |\varphi_a\rangle V_{ab} \langle\varphi_b| + |\varphi_b\rangle V_{ba} \langle\varphi_a| \\ &= \begin{pmatrix} 0 & V_{ab} \\ V_{ba} & 0 \end{pmatrix}\end{aligned} \tag{1.34}$$

The full Hamiltonian for the two coupled states is V_{ab}. The zero-order states are

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{V} \\ &= \begin{pmatrix} \varepsilon_a & V_{ab} \\ V_{ba} & \varepsilon_b \end{pmatrix}\end{aligned} \tag{1.35}$$



We will ask: If we prepare the system in state $|\varphi_a\rangle$, what is the time-dependent probability of observing it in $|\varphi_b\rangle$? The coupling mixes these states, leading to two eigenstates of $\hat{H}$, $|\varphi_+\rangle$ and $|\varphi_-\rangle$, with corresponding energy eigenvalues ε_+ and ε_-. Since $|\varphi_a\rangle$ and $|\varphi_b\rangle$ are not eigenstates of H, and since our time-propagation will be performed in the eigenbasis using eq. (1.29), we will need to find the transformation between these bases.

We start by searching for the eigenvalues of the Hamiltonian. Since the Hamiltonian is Hermitian, $\left(H_{ij} = H_{ji}^*\right)$, we write

$$V_{ab} = V_{ba}^* = V e^{-i\phi} \tag{1.36}$$

$$\hat{H} = \begin{pmatrix} \varepsilon_a & V e^{-i\phi} \\ V e^{+i\phi} & \varepsilon_b \end{pmatrix} \tag{1.37}$$

Often the couplings we describe are real, and we can neglect the phase factor ϕ. Now we define variables for the mean energy and energy splitting between the uncoupled states

$$E = \frac{\varepsilon_a + \varepsilon_b}{2} \tag{1.38}$$

$$\Delta = \frac{\varepsilon_a - \varepsilon_b}{2} \tag{1.39}$$

We can then obtain the eigenvalues of the coupled system by solving the secular equation

$$\det\left(H - \lambda I\right) = 0 \tag{1.40}$$

giving

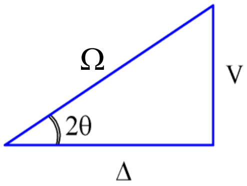
$$\varepsilon_{\pm} = E \pm \Omega \tag{1.41}$$

Here I defined another variable

$$\Omega = \sqrt{\Delta^2 + V^2} \tag{1.42}$$

To determine the eigenvectors of the coupled system $\left|\varphi_{\pm}\right\rangle$, it proves to be a great simplification to define a mixing angle θ that describes the relative magnitude of the coupling relative to the zero-order energy splitting through

$$\tan 2\theta = \frac{V}{\Delta} \tag{1.43}$$



We see that the mixing angle adopts values such that 0 ≤ θ≤ π/4. Also, we note that

$$\sin 2\theta = V/\Omega \tag{1.44}$$

$$\cos 2\theta = \Delta/\Omega \tag{1.45}$$

In this representation the Hamiltonian eq. (1.37) becomes

$$\hat{H} = E\bar{I} + \Delta\begin{pmatrix} 1 & \tan 2\theta e^{-i\phi} \\ \tan 2\theta e^{+i\phi} & -1 \end{pmatrix} \tag{1.46}$$

and we can express the eigenvalues as

$$\varepsilon_{\pm} = E \pm \Delta \sec 2\theta \tag{1.47}$$

Next we want to find *S*, the transformation that diagonalizes the Hamiltonian and which transforms the coefficients of the wavefunction from the zero-order basis to the eigenbasis. The eigenstates can be expanded in the zero-order basis in the form

$$\left|\varphi_{\pm}\right\rangle = c_a\left|\varphi_a\right\rangle + c_b\left|\varphi_b\right\rangle \tag{1.48}$$

So that the transformation can be expressed in matrix form as

$$\begin{pmatrix} \varphi_+ \\ \varphi_- \end{pmatrix} = S\begin{pmatrix} \varphi_a \\ \varphi_b \end{pmatrix} \tag{1.49}$$

To find S, we use the Schrödinger equation $\hat{H}\left|\varphi_{\pm}\right\rangle = \varepsilon_{\pm}\left|\varphi_{\pm}\right\rangle$ substituting eq. (1.48). This gives

$$S = \begin{pmatrix} \cos\theta \; e^{-i\phi/2} & \sin\theta \; e^{i\phi/2} \\ -\sin\theta \; e^{-i\phi/2} & \cos\theta \; e^{i\phi/2} \end{pmatrix} \tag{1.50}$$

Note that S is unitary since $S^{\dagger} = S^{-1}$ and $(S^{T})^{*} = S^{-1}$. Also, the eigenbasis is orthonormal: $\left\langle \varphi_{+} \middle| \varphi_{+} \right\rangle + \left\langle \varphi_{-} \middle| \varphi_{-} \right\rangle = 1$.

Now, let's examine the eigenstates in two limits:

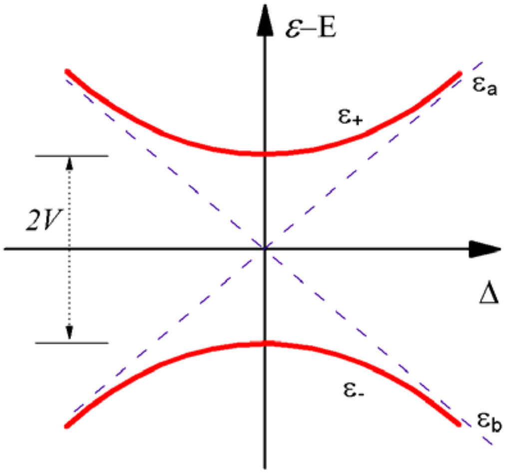
(1) Weak coupling (|V/Δ| ≪ 1). Here $\theta \approx 0$, and $\left|\varphi_{+}\right\rangle$ corresponds to $\left|\varphi_{a}\right\rangle$ weakly perturbed by the V_{ab} interaction. $\left|\varphi_{-}\right\rangle$ corresponds to $\left|\varphi_{b}\right\rangle$. In another way, as $\theta \to 0$, we find $\left|\varphi_{+}\right\rangle \to \left|\varphi_{a}\right\rangle$ and $\left|\varphi_{-}\right\rangle \to \left|\varphi_{b}\right\rangle$.

(2) Strong coupling (|V/Δ| ≫ 1). In this limit $\theta = \pi/4$, and the *a/b* basis states are indistinguishable. The eigenstates are symmetric and antisymmetric combinations:

$$\left|\varphi_{\pm}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\varphi_{b}\right\rangle \pm \left|\varphi_{a}\right\rangle\right) \tag{1.51}$$

Note from eq. (1.50) that the sign of V dictates whether $\left|\varphi_{+}\right\rangle$ or $\left|\varphi_{-}\right\rangle$ corresponds to the symmetric or antisymmetric eigenstate. For negative $V >> \Delta$, $\theta = -\pi/4$, and the correspondence in eq (1.51) changes to $\mp$.

We can schematically represent the energies of these states with the following diagram. Here we explore the range of $\varepsilon_{\pm}$ available given a fixed coupling V and varying the splitting Δ.



This diagram illustrates an avoided crossing effect. The strong coupling limit is equivalent to a degeneracy point (Δ~0) between the states $\left|\varphi_{a}\right\rangle$ and $\left|\varphi_{b}\right\rangle$. The eigenstates completely mix the unperturbed states, yet remain split by the strength of interaction *2V*. We will return to the discussion of avoided crossings when we describe potential energy surfaces and the adiabatic approximation, where the dependence of V and Δ on position R must be considered.

Now we can turn to describing dynamics. The time evolution of this system is given by the time-propagator

$$U(t) = |\varphi_+\rangle e^{-i\omega_+ t} \langle\varphi_+| + |\varphi_-\rangle e^{-i\omega_- t} \langle\varphi_-| \tag{1.52}$$

where $\omega_\pm = \varepsilon_\pm / \hbar$. Since φ_a and φ_b are not the eigenstates, preparing the system in state φ_a will lead to time evolution! Let's prepare the system so that it is initially in $|\varphi_a\rangle$.

$$|\psi(0)\rangle = |\varphi_a\rangle \tag{1.53}$$

Evaluating the time-dependent amplitudes of initial and final states with the help of S, we find

$$\begin{aligned} c_a(t) &= \langle\varphi_a|U(t)|\varphi_a\rangle \\ &= e^{-iEt}\left[\cos^2\theta e^{i\Omega_R t} + \sin^2\theta e^{-i\Omega_R t}\right] \end{aligned} \tag{1.54}$$

$$\begin{aligned} c_b(t) &= \langle\varphi_b|U(t)|\varphi_a\rangle \\ &= 2\sin\theta\cos\theta e^{-iEt}\sin\Omega_R t \end{aligned} \tag{1.55}$$

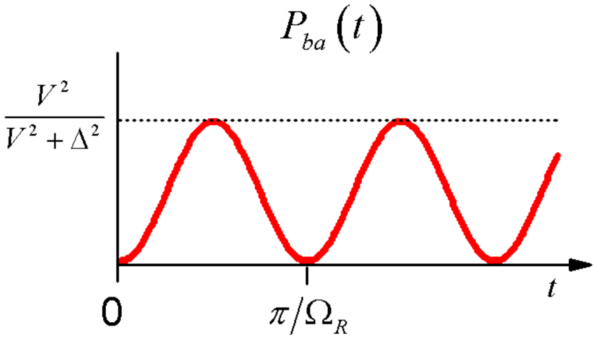
So, what is the probability that it is found in state $|\varphi_b\rangle$ at time t?

$$\begin{aligned} P_{ba}(t) &= |c_b(t)|^2 \\ &= \frac{V^2}{V^2+\Delta^2}\sin^2\Omega_R t \end{aligned} \tag{1.56}$$

where

$$\Omega_R = \frac{1}{\hbar}\sqrt{\Delta^2 + V^2} \tag{1.57}$$

Ω_R, the Rabi Frequency, represents the frequency at which probability amplitude oscillates between φ_a and φ_b states.



Notice for the weak coupling limit ($V \to 0$), $\varphi_\pm \to \varphi_{a,b}$ (the eigenstates resemble the stationary states), and the time-dependence disappears. In the strong coupling limit ($V >> \Delta$), amplitude is exchanged completely between the zero-order states at a rate given by the coupling: $\Omega_R \rightarrow V/\hbar$. Even in this limit it takes a finite amount of time for amplitude to move between states. To get $P = 1$ requires a time $\tau = \pi/2\Omega_R = \hbar\pi/2V$.

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2. TIME-EVOLUTION OPERATOR

Dynamical processes in quantum mechanics are described by a Hamiltonian that depends on time. Naturally the question arises how do we deal with a time-dependent Hamiltonian? In principle, the time-dependent Schrödinger equation can be directly integrated choosing a basis set that spans the space of interest. Using a potential energy surface, one can propagate the system forward in small time-steps and follow the evolution of the complex amplitudes in the basis states. In practice even this is impossible for more than a handful of atoms, when you treat all degrees of freedom quantum mechanically. However, the mathematical complexity of solving the time-dependent Schrödinger equation for most molecular systems makes it impossible to obtain exact analytical solutions. We are thus forced to seek numerical solutions based on perturbation or approximation methods that will reduce the complexity. Among these methods, time-dependent perturbation theory is the most widely used approach for calculations in spectroscopy, relaxation, and other rate processes. In this section we will work on classifying approximation methods and work out the details of time-dependent perturbation theory.

2.1. Time-Evolution Operator

Let's start at the beginning by obtaining the equation of motion that describes the wavefunction and its time evolution through the time propagator. We are seeking equations of motion for quantum systems that are equivalent to Newton's—or more accurately Hamilton's—equations for classical systems. The question is, if we know the wavefunction at time t0 $\left|\psi\left(\bar{r},t_0\right)\right\rangle$, how does it change with time? How do we determine $\left|\psi\left(\bar{r},t\right)\right\rangle$ for some later time $t>t_0$? We will use our intuition here, based largely on correspondence to classical mechanics). To keep notation to a minimum, in the following discussion we will not explicitly show the spatial dependence of wavefunction.

We start by assuming *causality*: $\left|\psi\left(t_0\right)\right\rangle$ precedes and determines $\left|\psi\left(t\right)\right\rangle$, which is crucial for deriving a deterministic equation of motion. Also, as usual, we assume time is a continuous variable:

$$\lim_{t\to t_0}\left|\psi\left(t\right)\right\rangle=\left|\psi\left(t_0\right)\right\rangle \tag{2.1}$$

Now define an "time-displacement operator" or "propagator" that acts on the wavefunction to the right and thereby propagates the system forward in time:

$$\left|\psi\left(t\right)\right\rangle=U\left(t,t_0\right)\left|\psi\left(t_0\right)\right\rangle \tag{2.2}$$

We also know that the operator U cannot be dependent on the state of the system $\left|\psi\right\rangle$. This is necessary for conservation of probability, i.e., to retain normalization for the system. If

$$\left|\psi\left(t_0\right)\right\rangle=a_1\left|\varphi_1\left(t_0\right)\right\rangle+a_2\left|\varphi_2\left(t_0\right)\right\rangle \tag{2.3}$$

$$\begin{aligned}\left|\psi(t)\right\rangle &= U(t,t_0)\left|\psi(t_0)\right\rangle \\ &= U(t,t_0)\,a_1\left|\varphi_1(t_0)\right\rangle + U(t,t_0)\,a_2\left|\varphi_2(t_0)\right\rangle \\ &= a_1(t)\left|\varphi_1\right\rangle + a_2(t)\left|\varphi_2\right\rangle\end{aligned} \tag{2.4}$$

This is a reflection of the importance of linearity and the principle of superposition in quantum mechanical systems. While $\left|a_i(t)\right|$ typically is not equal to $\left|a_i(0)\right|$,

$$\sum_n \left|a_n(t)\right|^2 = \sum_n \left|a_n(t_0)\right|^2 \tag{2.5}$$

This dictates that the differential equation of motion is linear in time.

Properties of *U*

We now make some important and useful observations regarding the properties of *U*.

1) **Unitary**. Note that for eq. (2.5) to hold and for probability density to be conserved, *U* must be unitary

$$P = \left\langle \psi(t) \middle| \psi(t) \right\rangle = \left\langle \psi(t_0) \right| U^\dagger U \left| \psi(t_0) \right\rangle \tag{2.6}$$

which holds if $U^\dagger = U^{-1}$.

2) **Time continuity**: The state is unchanged when the initial and final time-points are the same

$$U(t,t) = 1\,. \tag{2.7}$$

3) **Composition property**. If we take the system to be deterministic, then it stands to reason that we should get the same wavefunction whether we evolve to a target time in one step $(t_0 \rightarrow t_2)$ or multiple steps $(t_0 \rightarrow t_1 \rightarrow t_2)$. Therefore, we can write

$$U(t_2,t_0) = U(t_2,t_1)\,U(t_1,t_0) \tag{2.8}$$

Note, since *U* acts to the right, order matters:

$$\begin{aligned}\left|\psi(t_2)\right\rangle &= U(t_2,t_1)\,U(t_1,t_0)\left|\psi(t_0)\right\rangle \\ &= U(t_2,t_1)\left|\psi(t_1)\right\rangle\end{aligned} \tag{2.9}$$

Equation (2.8) is already very suggestive of an exponential form for *U*. Furthermore, since time is continuous and the operator is linear it also suggests that the time propagator is only a dependent on a time interval

$$U(t_1,t_0) = U(t_1 - t_0) \tag{2.10}$$

4) **Time-reversal**. The inverse of the time-propagator is the time reversal operator. From eq. (2.8):

$$U(t,t_0)U(t_0,t)=1 \tag{2.11}$$

$$\therefore U^{-1}(t,t_0)=U(t_0,t). \tag{2.12}$$

An equation of motion for *U*

Let's find an equation of motion that describes the time-evolution operator using the change of the system for an *infinitesimal* time-step, δt: $U(t+\delta t,t)$. Since

$$\lim_{\delta t\to 0} U(t+\delta t,t)=1 \tag{2.13}$$

We expect that for small enough δt, U will change linearly with δt. This is based on analogy to thinking of deterministic motion in classical systems. Setting t_0 to 0, so that $U(t,t_0)=U(t)$, we can write

$$U(t+\delta t)=U(t)-i\hat{\Omega}(t)\delta t \tag{2.14}$$

$\hat{\Omega}$ is a time-dependent Hermitian operator, which is required for U to be unitary. We can now write a differential equation for the time-development of $U(t,t_0)$, the equation of motion for U:

$$\frac{d\,U(t)}{dt}=\lim_{\delta t\to 0}\frac{U(t+\delta t)-U(t)}{\delta t} \tag{2.15}$$

So from (2.14) we have:

$$\frac{\partial U(t,t_0)}{\partial t}=-i\hat{\Omega}U(t,t_0) \tag{2.16}$$

You can now see that the operator needed a complex argument, because otherwise probability density would not be conserved; it would rise or decay. Rather it oscillates through different states of the system.

We note that $\hat{\Omega}$ has units of frequency. Since quantum mechanics fundamentally associates frequency and energy as $E=\hbar\omega$, and since the Hamiltonian is the operator corresponding to the energy, and responsible for time evolution in Hamiltonian mechanics, we write

$$\hat{\Omega}=\frac{\hat{H}}{\hbar} \tag{2.17}$$

With that substitution we have an equation of motion for U:

$$i\hbar\frac{\partial}{\partial t}U(t,t_0)=\hat{H}U(t,t_0) \tag{2.18}$$

Multiplying from the right by $|\psi(t_0)\rangle$ gives the TDSE:

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \tag{2.19}$$

If you use the Hamiltonian for a free particle $-(\hbar^2/2m)(\partial^2/\partial x^2)$, this looks like a classical wave equation, except that it is linear in time. Rather, this looks like a diffusion equation with imaginary diffusion constant. We are also interested in the equation of motion for $U^\dagger$ which describes the time evolution of the conjugate wavefunctions. Following the same approach and recognizing that $U^\dagger(t,t_0)$ acts to the left:

$$\langle\psi(t)| = \langle\psi(t_0)|U^\dagger(t,t_0) \tag{2.20}$$

we get

$$-i\hbar\frac{\partial}{\partial t}U^\dagger(t,t_0) = U^\dagger(t,t_0)\hat{H}\,. \tag{2.21}$$

Evaluating the time-evolution operator

At first glance it may seem straightforward to integrate eq. (2.18). If H is a function of time, then the integration of $i\hbar\, dU/U = H\,dt$ gives

$$U(t,t_0) = \exp\left[\frac{-i}{\hbar}\int_{t_0}^{t} H(t')\,dt'\right] \tag{2.22}$$

Following our earlier definition of the time-propagator, this exponential would be cast as a series expansion

$$U(t,t_0) \overset{?}{=} 1 - \frac{i}{\hbar}\int_{t_0}^{t} H(t')\,dt' + \frac{1}{2!}\left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t}\int_{t_0}^{t} dt'\,dt''H(t')H(t'') + \ldots \tag{2.23}$$

This approach is dangerous, since we are not properly treating H as an operator. Looking at the second term in eq. (2.23), we see that this expression integrates over both possible time-orderings of the two Hamiltonian operations, which would only be proper if the Hamiltonians at different times commute: $\left[H(t'),H(t'')\right] = 0$.

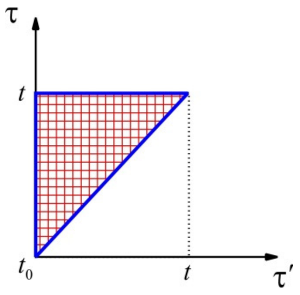
Now, let's proceed a bit more carefully assuming that the Hamiltonians at different times do not commute. Integrating equation (2.18) directly from t_0 to t gives

$$U(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)U(\tau,t_0) \tag{2.24}$$

This is the solution; however, it is not very practical since $U(t,t_0)$ is a function of itself. But we can make an iterative expansion by repetitive substitution of U into itself. The first step in this process is

$$
\begin{aligned}
U(t,t_0) &= 1-\frac{i}{\hbar}\int_{t_0}^{t} d\tau H(\tau)\left[1-\frac{i}{\hbar}\int_{t_0}^{\tau} d\tau' H(\tau')U(\tau',t_0)\right] \\
&= 1+\left(\frac{-i}{\hbar}\right)\int_{t_0}^{t} d\tau H(\tau)+\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t} d\tau\int_{t_0}^{\tau} d\tau' H(\tau)H(\tau')U(\tau',t_0)
\end{aligned}
\tag{2.25}
$$

Note in the last term of this equation, that the integration limits enforce a time-ordering; that is, the first integration variable τ' must precede the second τ. Pictorially, the area of integration is

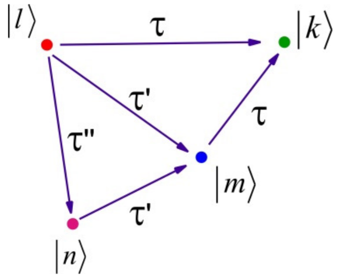


The next substitution step gives

$$
\begin{aligned}
U(t,t_0) = 1 &+ \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t} d\tau H(\tau) \\
&+ \left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t} d\tau\int_{t_0}^{\tau} d\tau' H(\tau)H(\tau') \\
&+ \left(\frac{-i}{\hbar}\right)^3\int_{t_0}^{t} d\tau\int_{t_0}^{\tau} d\tau'\int_{t_0}^{\tau'} d\tau'' H(\tau)H(\tau')H(\tau'')U(\tau'',t_0)
\end{aligned}
\tag{2.26}
$$

From this expansion, you should be aware that there is a time-ordering to the interactions. For the third term, τ'' acts before τ', which acts before τ: $t_0 \le \tau'' \le \tau' \le \tau \le t$.

What does this expression represent? Imagine you are starting in state $|\psi_0\rangle = |\ell\rangle$ and you want to describe how one evolves toward a target state $|\psi\rangle = |k\rangle$. The possible paths by which one can shift amplitude and evolve the phase, pictured in terms of these time variables are:



The first term in eq. (2.26) represents all actions of the Hamiltonian which act to directly couple $|\ell\rangle$ and $|k\rangle$. The second term described possible transitions from $|\ell\rangle$ to $|k\rangle$ via an intermediate state $|m\rangle$. The expression for *U* describes all possible paths between initial and final state. Each of these paths interferes in ways dictated by the acquired phase of our eigenstates under the time-dependent Hamiltonian.

The solution for U obtained from this iterative substitution is known as the positive time-ordered exponential

$$\begin{aligned} U(t,t_0) &\equiv \exp_+\left[\frac{-i}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)\right] \\ &\equiv \hat{T}\exp\left[\frac{-i}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)\right] \\ &= 1+\sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^{n}\int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau} d\tau_n \ldots \int_{t_0}^{t} d\tau_1\, H(\tau_n)H(\tau_{n-1})\ldots H(\tau_1) \end{aligned} \tag{2.27}$$

($\hat{T}$ is known as the Dyson time-ordering operator.) In this expression the time-ordering is

$$\begin{aligned} &t_0 \to \tau_1 \to \tau_2 \to \tau_3 \ldots. \tau_n \to t \\ &t_0 \to \quad \ldots \quad \tau'' \to \tau' \to \tau \end{aligned} \tag{2.28}$$

So, this expression tells you about how a quantum system evolves over a given time interval, and it allows for any possible trajectory from an initial state to a final state through any number of intermediate states. Each term in the expansion accounts for more possible transitions between different intermediate quantum states during this trajectory.

Compare the time-ordered exponential with the traditional expansion of an exponential:

$$1+\sum_{n=1}^{\infty}\frac{1}{n!}\left(\frac{-i}{\hbar}\right)^{n}\int_{t_0}^{t} d\tau_n \ldots \int_{t_0}^{t} d\tau_1\, H(\tau_n)H(\tau_{n-1})\ldots H(\tau_1) \tag{2.29}$$

Here the time-variables assume all values, and therefore all orderings for $H(\tau_i)$ are calculated. The areas are normalized by the $n!$ factor. (There are $n!$ time-orderings of the τ_n times.) (As commented above these points need some more clarification.)

We are also interested in the Hermitian conjugate of $U(t,t_0)$, which has the equation of motion in eq. (2.21). If we repeat the method above, remembering that $U^\dagger(t,t_0)$ acts to the left, then we obtain

$$U^\dagger(t,t_0) = 1+\frac{i}{\hbar}\int_{t_0}^{t} d\tau\, U^\dagger(t,\tau)H(\tau). \tag{2.30}$$

Performing iterative substitution leads to a negative-time-ordered exponential:

$$\begin{aligned} U^\dagger(t,t_0) &= \exp_-\left[\frac{i}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)\right] \\ &= 1+\sum_{n=1}^{\infty}\left(\frac{i}{\hbar}\right)^{n}\int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \ldots \int_{t_0}^{\tau_2} d\tau_1 H(\tau_1)H(\tau_2)\ldots H(\tau_n) \end{aligned} \tag{2.31}$$

Here the $H(\tau_i)$ act to the left.

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2.2. Integrating the TDSE Directly

Okay, how do we evaluate the time-propagator and obtain a time-dependent trajectory for a quantum system? Expressions such as eq. (2.27) are daunting, and there are no simple ways in which to handle this. One cannot truncate the exponential because usually this is not a rapidly converging series. Also, the solutions oscillate rapidly as a result of the phase acquired at the energy of the states involved, which leads to a formidable integration problem. Rapid oscillations require small time steps, when in fact the time scales. For instance in a molecular dynamics problem, the highest frequency oscillations may be as a result of electronically excited states with periods of less than a femtosecond, and the nuclear dynamics that you hope to describe may occur on many picosecond time scales. Rather than general recipes, there exist an arsenal of different strategies that are suited to particular types of problems. The choice of how to proceed is generally dictated by the details of your problem, and is often an art-form. Considerable effort needs to be made to formulate the problem, particularly choosing an appropriate basis set for your problem. Here it is our goal to gain some insight into the types of strategies available, working mainly with the principles, rather than the specifics of how it's implemented.

Let's begin by discussing the most general approach. With adequate computational resources, we can choose the brute force approach of numerical integration. We start by choosing a basis set and defining the initial state ψ_0. Then, we can numerically evaluate the time-dependence of the wavefunction over a time period t by discretizing time into n small steps of width $\delta t = t/n$ over which the change of the system is small. A variety of strategies can be pursed in practice.

One possibility is to expand your wavefunction in the basis set of your choice

$$|\psi(t)\rangle = \sum_n c_n(t)|\varphi_n\rangle \tag{2.32}$$

and solve for the time-dependence of the expansion coefficients. Substituting into the right side of the TDSE,

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \tag{2.33}$$

and then acting from the left by $\langle k|$ on both sides leads to an equation that describes their time-dependence:

$$i\hbar\frac{\partial c_k(t)}{\partial t} = \sum_n H_{kn}(t)c_n(t) \tag{2.34}$$

or in matrix form $i\hbar\dot{\mathbf{c}} = \mathbf{H}\mathbf{c}$. This represents a set of coupled first-order differential equations in which amplitude flows between different basis states at rates determined by the matrix elements of the time-dependent Hamiltonian. Such equations are straightforward to integrate numerically. We recognize that we can integrate on a grid if the time step forward (δt) is small enough that the Hamiltonian is essentially constant. Then eq. (2.34) becomes

$$i\hbar\,\delta c_k(t) = \sum_n H_{kn}(t)c_n(t)\,\delta t \tag{2.35}$$

and the system is propagated as

$$c_k(t+\delta t) = c_k(t) + \delta c_k(t) \tag{2.36}$$

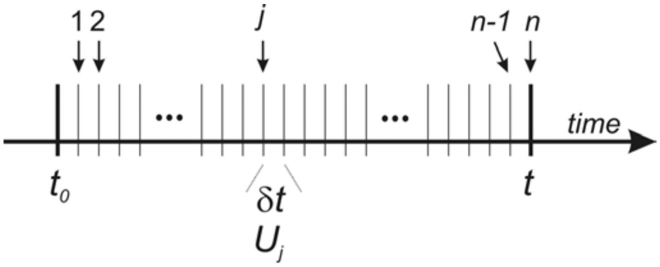
The downside of such a calculation is the unusually small time-steps and significant computational cost required.

Similarly, we can use a grid with short time steps to simplify our time-propagator as

$$\hat{U}(t+\delta t,t) = \exp\left[-\frac{i}{\hbar}\int_t^{t+\delta t} dt'\,\hat{H}(t')\right] \approx \exp\left[-\frac{i}{\hbar}\delta t\,\hat{H}(t)\right] \tag{2.37}$$

Therefore the time propagator can be written as a product of *n* propagators over these small intervals.

$$\begin{aligned}\hat{U}(t) &= \lim_{\delta t\to 0}\left[\hat{U}_n\hat{U}_{n-1}\cdots\hat{U}_2\hat{U}_1\right]\\ &= \lim_{n\to\infty}\prod_{j=0}^{n-1}{}_{+}\,\hat{U}_j\end{aligned} \tag{2.38}$$



Here the time-propagation over the j^{th} small time step is

$$\begin{aligned}\hat{U}_j &= \exp\left[-\frac{i}{\hbar}\delta t\,\hat{H}_j\right]\\ \hat{H}_j &= \hat{H}(j\,\delta t)\end{aligned} \tag{2.39}$$

Note that the expressions in (2.38) are operators time ordered from right to left, which we denote with the "+" subscript. Although (2.38) is exact in the limit δt→0 (or n→∞), we can choose a finite number such that $H(t)$ does not change much over the time δt. In this limit the time propagator does not change much and can be approximated as an expansion

$$\hat{U}_j \approx 1 - \frac{i}{\hbar}\delta t\,\hat{H}_j \tag{2.40}$$

In a general sense this approach is not very practical. The first reason is that the time step is determined by $\delta t \ll \hbar/|H|$ which is typically very small in comparison to the dynamics of interest.

The second complication arises when the potential and kinetic energy operators in the Hamiltonian don't commute. Taking the Hamiltonian to be $\hat{H} = \hat{T} + \hat{V}$,

$$\begin{aligned} e^{-i\hat{H}(t)\delta t/\hbar} &= e^{-i(\hat{T}(t)+\hat{V}(t))\delta t/\hbar} \\ &\approx e^{-i\hat{T}(t)\delta t/\hbar} e^{-i\hat{V}(t)\delta t/\hbar} \end{aligned} \tag{2.41}$$

The second line makes the Split Operator approximation, what states that the time propagator over a short enough period can be approximated as a product of independent propagators evolving the system over the kinetic and potential energy. The validity of this approximation depends on how well these operators commute and the time step, with the error scaling like $\frac{1}{2}[\hat{T}(t),\hat{V}(t)](\delta t/\hbar)^2$, meaning that we should use a time step, such that $\delta t < \{2\hbar^2/[\hat{T}(t),\hat{V}(t)]\}^{1/2}$.[1] This approximation can be improved by symmetrizing the split operator as

$$e^{-i\hat{H}(t)\delta t/\hbar} \approx e^{-i\hat{V}(t)\frac{\delta t}{2}/\hbar} e^{-i\hat{T}(t)\delta t/\hbar} e^{-i\hat{V}(t)\frac{\delta t}{2}/\hbar} \tag{2.42}$$

Here the error scales as $\frac{1}{12}(\delta t/\hbar)^3\{[\hat{T},[\hat{T},\hat{V}]] + \frac{1}{2}[\hat{V},[\hat{V},\hat{T}]]\}$. There is no significant increase in computational effort since half of the operations can be combined as

$$e^{-\frac{i\hat{V}}{\hbar}\frac{(j+1)\delta t}{2}} e^{-\frac{i\hat{V}}{\hbar}\frac{j\delta t}{2}/} \approx e^{-i\hat{V}j\delta t/\hbar} \tag{2.43}$$

to give

$$U(t) \approx e^{-i\hat{V}\frac{n\delta t}{2}/\hbar}\left[\prod_{j=1}^{n}{}_{+} e^{-i\hat{V}j\delta t/\hbar} e^{-i\hat{T}j\delta t/\hbar}\right] e^{-i\hat{V}\frac{\delta t}{2}/\hbar}. \tag{2.44}$$

Readings

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2.3. Transitions Induced by a Time-Dependent Potential

For many time-dependent problems, most notably in spectroscopy, we can often partition the problem so that the time-dependent Hamiltonian contains a time-independent part H_0 that we can describe exactly, and a time-dependent potential $V(t)$:

$$H = H_0 + V(t) \tag{2.45}$$

The remaining degrees of freedom are discarded, and then only enter in the sense that they give rise to the interaction potential with H_0. This is effective if you have reason to believe that the external Hamiltonian can be treated classically, or if the influence of H_0 on the other degrees of freedom is negligible. From (2.45), there is a straightforward approach to describing the time-evolving wavefunction for the system in terms of the eigenstates and energy eigenvalues of H_0.

To begin, we know the complete set of eigenstates and eigenvalues for the system Hamiltonian

$$H_0 |n\rangle = E_n |n\rangle \tag{2.46}$$

The state of the system can then be expressed as a superposition of these eigenstates:

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle \tag{2.47}$$

The TDSE can be used to find an equation of motion for the eigenstate coefficients

$$c_k(t) = \langle k|\psi(t)\rangle \tag{2.48}$$

Starting with

$$\frac{\partial |\psi\rangle}{\partial t} = \frac{-i}{\hbar} H\,|\psi\rangle \tag{2.49}$$

$$\frac{\partial\, c_k(t)}{\partial t} = -\frac{i}{\hbar}\langle k\,|H|\,\psi(t)\rangle \tag{2.50}$$

and from (2.50)

$$= -\frac{i}{\hbar}\sum_n \langle k\,|H|\,n\rangle\, c_n(t) \tag{2.51}$$

Already we see that the time evolution amounts to solving a set of coupled linear ordinary differential equations. These are rate equations with complex rate constants, which describe the feeding of one state into another. Substituting eq. (2.45) we have:

$$\begin{aligned}\frac{\partial\, c_k(t)}{\partial t} &= -\frac{i}{\hbar}\sum_n \left\langle k\left|\left(H_0 + V(t)\right)\right|n\right\rangle c_n(t) \\ &= -\frac{i}{\hbar}\sum_n \left[E_n\,\delta_{kn} + V_{kn}(t)\right] c_n(t)\end{aligned} \tag{2.52}$$

or, $$\frac{\partial c_k(t)}{\partial t}+\frac{i}{\hbar}E_k c_k(t)=-\frac{i}{\hbar}\sum_n V_{kn}(t)c_n(t). \tag{2.53}$$

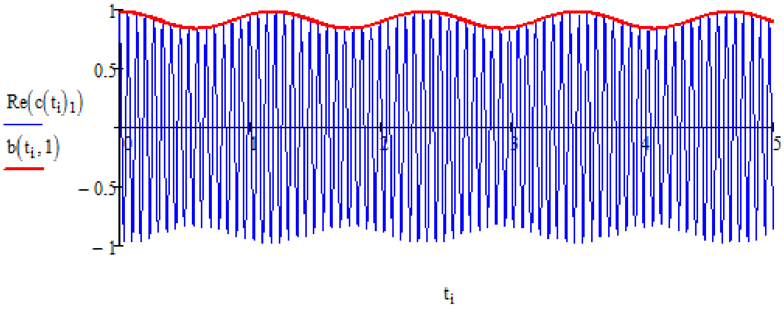
Next, we define and substitute

$$c_m(t)=e^{-iE_m t/\hbar}\,b_m(t) \tag{2.54}$$

which implies a definition for the wavefunction as

$$|\psi(t)\rangle=\sum_n b_n(t)e^{-iE_n t/\hbar}\,|n\rangle \tag{2.55}$$

This defines a slightly different complex amplitude, that allows us to simplify things considerably. Notice that $|b_k(t)|^2=|c_k(t)|^2$. Also, $b_k(0)=c_k(0)$. In practice what we are doing is pulling out the "trivial" part of the time evolution, the time-evolving phase factor, which typically oscillates much faster than the changes to the amplitude of *b* or *c*.



We will come back to this strategy which we discuss the interaction picture.

Now eq. (2.53) becomes

$$e^{-iE_k t/\hbar}\frac{\partial b_k}{\partial t}=-\frac{i}{\hbar}\sum_n V_{kn}(t)\;e^{-iE_n t/\hbar}b_n(t) \tag{2.56}$$

or $$i\hbar\frac{\partial b_k}{\partial t}=\sum_n V_{kn}(t)\,e^{-i\omega_{nk}t}\,b_n(t) \tag{2.57}$$

This equation is an exact solution. It is a set of coupled differential equations that describe how probability amplitude moves through eigenstates due to a time-dependent potential. Except in simple cases, these equations cannot be solved analytically, but it is often straightforward to integrate numerically.

When can we use the approach described here? Consider partitioning the full Hamiltonian into two components, one that we want to study H_0 and the remaining degrees of freedom H_1. For each part, we have knowledge of the complete eigenstates and eigenvalues of the Hamiltonian: $H_i\,|\psi_{i,n}\rangle=E_{i,n}\,|\psi_{i,n}\rangle$. These subsystems will interact with one another through H_{int}. If we are careful to partition this in such a way that H_{int} is small compared H_0 and H_1, then it should be possible to properly describe the state of the full system as product states in the sub-systems: $|\psi\rangle = |\psi_0\psi_1\rangle$. Further, we can write a time-dependent Schrödinger equation for the motion of each subsystem as:

$$i\hbar \frac{\partial|\psi_1\rangle}{\partial t} = H_1|\psi_1\rangle \tag{2.58}$$

Within these assumptions, we can write the complete time-dependent Schrödinger equation in terms of the two sub-states:

$$i\hbar|\psi_0\rangle \frac{\partial|\psi_1\rangle}{\partial t} + i\hbar|\psi_1\rangle \frac{\partial|\psi_0\rangle}{\partial t} = |\psi_0\rangle H_1|\psi_1\rangle + |\psi_1\rangle H_0|\psi_0\rangle + H_{\text{int}}|\psi_0\rangle|\psi_1\rangle \tag{2.59}$$

Then left operating by $\langle\psi_1|$ and making use of eq. (2.58), we can write

$$i\hbar \frac{\partial|\psi_0\rangle}{\partial t} = \left[H_0 + \langle\psi_1|H_{\text{int}}|\psi_1\rangle\right]|\psi_0\rangle \tag{2.60}$$

This is equivalent to the TDSE for a Hamiltonian of form (2.45) where the external interaction $V(t) = \langle\psi_1|H_{\text{int}}(t)|\psi_1\rangle$ comes from integrating the 1-2 interaction over the sub-space of $|\psi_1\rangle$. So this represents a time-dependent mean field method.

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 308.
2. Merzbacher, E., *Quantum Mechanics*. 3rd ed.; Wiley: New York, 1998; Ch. 14.
3. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Sec. 2.3.
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2.4. Resonant Driving of Two-level System

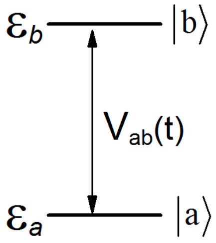
Let's describe what happens when you drive a two-level system with an oscillating potential.

$$V(t) = V\cos\omega t \tag{2.61}$$

$$V_{k\ell}(t) = V_{k\ell}\cos\omega t \tag{2.62}$$

Note, this is the form you would expect for an electromagnetic field interacting with charged particles, i.e. dipole transitions. In a simple sense, the electric field is $\bar{E}(t) = \bar{E}_0\cos\omega t$ and the interaction potential can be written as $V = -\bar{E}\cdot\bar{\mu}$, where $\bar{\mu}$ represents the dipole operator. We will look at the form of this interaction a bit more carefully later.

We now couple two states $|a\rangle$ and $|b\rangle$ with the oscillating field. Here the energy of the states is ordered so that $\varepsilon_b > \varepsilon_a$. Let's ask if the system starts in $|a\rangle$ what is the probability of finding it in $|b\rangle$ at time t?



The system of differential equations that describe this problem is:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}b_k(t) &= \sum_{n=a,b} b_n(t)V_{kn}(t)\,e^{-i\omega_{nk}t} \\ &= \sum_{n=a,b} b_n(t)V_{kn}\,e^{-i\omega_{nk}t}\cdot\frac{1}{2}\left(e^{-i\omega t}+e^{i\omega t}\right) \end{aligned} \tag{2.63}$$

Where I wrote *cos ωt* in its complex form. Writing this explicitly

$$i\hbar\dot{b}_b = \tfrac{1}{2}b_a V_{ba}\left[e^{i(\omega_{ba}-\omega)t}+e^{i(\omega_{ba}+\omega)t}\right]+\tfrac{1}{2}b_b\cancel{V_{bb}}\left[e^{i\omega t}+e^{-i\omega t}\right] \tag{2.64}$$

$$i\hbar\dot{b}_a = \tfrac{1}{2}b_a\cancel{V_{aa}}\left[e^{i\omega t}+e^{-i\omega t}\right]+\tfrac{1}{2}b_b V_{ab}\underbrace{\left[e^{i(\omega_{ab}-\omega)t}+e^{i(\omega_{ab}+\omega)t}\right]}_{\substack{\text{or} \\ \left[e^{-i(\omega_{ba}+\omega)t}+e^{-i(\omega_{ba}-\omega)t}\right]}} \tag{2.65}$$

Here the expressions have been written in terms of the frequency ω_{ba}. Two of these terms are dropped, since (for our case) the diagonal matrix elements $V_{ii}=0$. We also make the *secular approximation* (or *rotating wave approximation*) in which the nonresonant terms are dropped. When $\omega_{ba}\approx\omega$, terms like $e^{\pm i\omega t}$ or $e^{i(\omega_{ba}+\omega)t}$ oscillate very rapidly (relative to $|V_{ba}|^{-1}$) and so do not contribute much to change of c_n. (Remember, we take the frequencies ω_{ba} and ω to be positive). So now we have:

$$\dot{b}_b = \frac{-i}{2\hbar}b_a\,V_{ba}\,e^{i(\omega_{ba}-\omega)t} \tag{2.66}$$

$$\dot{b}_a = \frac{-i}{2\hbar} b_b \, V_{ab} \, e^{-i(\omega_{ba}-\omega)t} \tag{2.67}$$

Note that the coefficients are oscillating at the same frequency but phase shifted to one another. Now if we differentiate eq. (2.66):

$$\ddot{b}_b = \frac{-i}{2\hbar}\left[\dot{b}_a \, V_{ba} \, e^{i(\omega_{ba}-\omega)t} + i(\omega_{ba}-\omega) b_a \, V_{ba} \, e^{i(\omega_{ba}-\omega)t}\right] \tag{2.68}$$

Rewrite eq. (2.66):

$$b_a = \frac{2i\hbar}{V_{ba}} \dot{b}_b \, e^{-i(\omega_{ba}-\omega)t} \tag{2.69}$$

and substitute (2.69) and (2.67) into (2.68), we get linear second order equation for b_b.

$$\ddot{b}_b - i(\omega_{ba}-\omega)\dot{b}_b + \frac{|V_{ba}|^2}{4\hbar^2} b_b = 0 \tag{2.70}$$

This is just the second order differential equation for a damped harmonic oscillator:

$$a\ddot{x} + b\dot{x} + cx = 0 \tag{2.71}$$

$$\begin{aligned} x &= e^{-(b/2a)t}\left(A\cos\mu t + B\sin\mu t\right) \\ \mu &= \frac{1}{2a}\sqrt{4ac-b^2} \end{aligned} \tag{2.72}$$

With a little more manipulation, and remembering the initial conditions $b_k(0)=0$ and $b_\ell(0)=1$, we find

$$P_b(t) = |b_b(t)|^2 = \frac{|V_{ba}|^2}{|V_{ba}|^2 + \hbar^2(\omega_{ba}-\omega)^2}\sin^2\Omega_R t \tag{2.73}$$

Where the Rabi Frequency

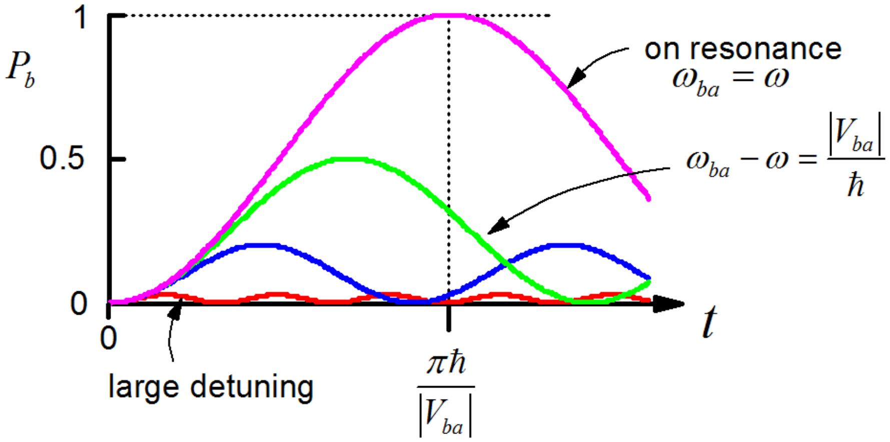
$$\Omega_R = \frac{1}{2\hbar}\sqrt{|V_{ba}|^2 + \hbar^2(\omega_{ba}-\omega)^2} \tag{2.74}$$

Also,

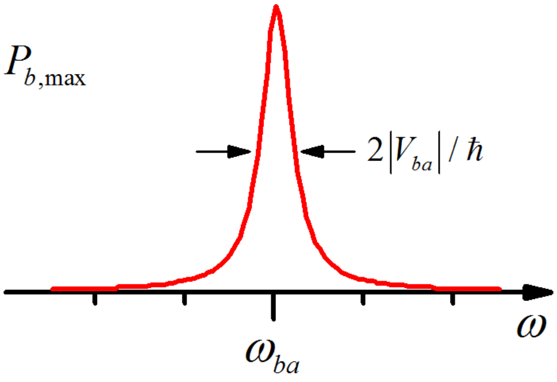
$$P_a = 1 - P_b \tag{2.75}$$

The amplitude oscillates back and forth between the two states at a frequency dictated by the coupling between them. [Note a result we will return to later: electric fields couple quantum states, creating coherences!]

An important observation is the importance of *resonance* between the driving potential and the energy splitting between states. To get transfer of probability density you need the driving field to be at the same frequency as the energy splitting. On resonance, you always drive probability amplitude entirely from one state to another.



The efficiency of driving between *a* and *b* states drops off with detuning. Here plotting the maximum value of P_b as a function of frequency:



2.5. Schrödinger and Heisenberg Representations

The mathematical formulation of quantum dynamics that has been presented is not unique. So far, we have described the dynamics by propagating the wavefunction, which encodes probability densities. Ultimately, since we cannot measure a wavefunction, we are interested in observables, which are probability amplitudes associated with Hermitian operators, with time-dependence that can be interpreted differently. Consider the expectation value:

$$\begin{aligned}\left\langle \hat{A}(t)\right\rangle &= \langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\psi(0)|U^\dagger \hat{A} U|\psi(0)\rangle \\ &= \left(\langle\psi(0)|U^\dagger\right)\hat{A}\left(U|\psi(0)\rangle\right) \\ &= \left\langle\psi(0)\middle|\left(U^\dagger \hat{A} U\right)\middle|\psi(0)\right\rangle\end{aligned} \tag{2.76}$$

The last two expressions are written to emphasize alternate "pictures" of the dynamics. The first, known as the Schrödinger picture, refers to everything we have done so far. Here we propagate the wavefunction or eigenvectors in time as $U|\psi\rangle$. Operators are unchanged because they carry no time-dependence. Alternatively, we can work in the Heisenberg picture. This uses the unitary property of U to time-propagate the operators as $\hat{A}(t) = U^\dagger \hat{A} U$, but the wavefunction is now stationary. The Heisenberg picture has an appealing physical picture behind it, because particles move. That is, there is a time-dependence to position and momentum.

Schrödinger Picture

In the Schrödinger picture, the time-development of $|\psi\rangle$ is governed by the TDSE or equivalently, the time propagator:

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle \quad \text{and} \quad |\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle \tag{2.77}$$

In the Schrödinger picture, operators are typically independent of time, $\partial A/\partial t = 0$. What about observables? For expectation values of operators $\langle A(t)\rangle = \langle\psi|A|\psi\rangle$:

$$\begin{aligned}i\hbar\frac{\partial}{\partial t}\left\langle \hat{A}(t)\right\rangle &= i\hbar\left[\left\langle\psi\middle|\hat{A}\middle|\frac{\partial\psi}{\partial t}\right\rangle + \left\langle\frac{\partial\psi}{\partial t}\middle|\hat{A}\middle|\psi\right\rangle + \left\langle\psi\middle|\cancel{\frac{\partial\hat{A}}{\partial t}}\middle|\psi\right\rangle\right] \\ &= \left\langle\psi\middle|\hat{A}H\middle|\psi\right\rangle - \left\langle\psi\middle|H\hat{A}\middle|\psi\right\rangle \\ &= \left\langle\left[\hat{A},H\right]\right\rangle\end{aligned} \tag{2.78}$$

If $\hat{A}$ is independent of time (as we expect in the Schrödinger picture), and if it commutes with H, it is referred to as a constant of motion.

Heisenberg Picture

From eq. (2.76), we can distinguish the Schrödinger picture from Heisenberg operators:

$$\hat{A}(t) = \left\langle \psi(t) \middle| \hat{A} \middle| \psi(t) \right\rangle_S = \left\langle \psi(t_0) \middle| U^\dagger \hat{A} U \middle| \psi(t_0) \right\rangle_S = \left\langle \psi \middle| \hat{A}(t) \middle| \psi \right\rangle_H \tag{2.79}$$

where the operator is defined as

$$\begin{aligned} \hat{A}_H(t) &= U^\dagger(t,t_0)\,\hat{A}_S U(t,t_0) \\ \hat{A}_H(t_0) &= \hat{A}_S \end{aligned} \tag{2.80}$$

Note, the pictures have the same wavefunction at the reference point t_0. Since the wavefunction should be time-independent, $\partial|\psi_H\rangle/\partial t = 0$, we can relate the Schrödinger and Heisenberg wavefunctions as

$$|\psi_S(t)\rangle = U(t,t_0)|\psi_H\rangle \tag{2.81}$$

So,

$$|\psi_H\rangle = U^\dagger(t,t_0)|\psi_S(t)\rangle = |\psi_S(t_0)\rangle \tag{2.82}$$

As expected for a unitary transformation, in either picture the eigenvalues are preserved:

$$\begin{aligned} \hat{A}\,|\varphi_i\rangle_S &= a_i\,|\varphi_i\rangle_S \\ U^\dagger \hat{A} U U^\dagger\,|\varphi_i\rangle_S &= a_i U^\dagger\,|\varphi_i\rangle_S \\ \hat{A}_H\,|\varphi_i\rangle_H &= a_i\,|\varphi_i\rangle_H \end{aligned} \tag{2.83}$$

The time evolution of the operators in the Heisenberg picture is:

$$\begin{aligned} \frac{\partial \hat{A}_H}{\partial t} = \frac{\partial}{\partial t}\left(U^\dagger \hat{A}_S U\right) &= \frac{\partial U^\dagger}{\partial t}\hat{A}_S U + U^\dagger \hat{A}_S \frac{\partial U}{\partial t} + U^\dagger \cancel{\frac{\partial \hat{A}_S}{\partial t}} U \\ &= \frac{i}{\hbar} U^\dagger H\,\hat{A}_S U - \frac{i}{\hbar} U^\dagger \hat{A}_S\,H U + \cancel{\left(\frac{\partial \hat{A}}{\partial t}\right)_H} \\ &= \frac{i}{\hbar} H_H\,\hat{A}_H - \frac{i}{\hbar}\hat{A}_H\,H_H \\ &= -\frac{i}{\hbar}\left[\hat{A}, H\right]_H \end{aligned} \tag{2.84}$$

The result

$$i\hbar \frac{\partial}{\partial t}\hat{A}_H = \left[\hat{A}, H\right]_H \tag{2.85}$$

is known as the Heisenberg equation of motion. Here I have written the odd looking $H_H = U^\dagger H U$. This is mainly to remind one about the time-dependence of *H*. Generally speaking, for a time-independent Hamiltonian $U = e^{-iHt/\hbar}$, *U* and *H* commute, and $H_H = H$. For a time-dependent Hamiltonian, *U* and *H* need not commute.

Classical equivalence for particle in a potential

The Heisenberg equation is commonly applied to a particle in an arbitrary potential. Consider a particle with an arbitrary one-dimensional potential

$$H = \frac{p^2}{2m} + V(x) \tag{2.86}$$

For this Hamiltonian, the Heisenberg equation gives the time-dependence of the momentum and position as

$$\dot{p} = -\frac{\partial V}{\partial x} \tag{2.87}$$

$$\dot{x} = \frac{p}{m} \tag{2.88}$$

Here, I have made use of

$$\left[\hat{x}^n, \hat{p}\right] = i\hbar n\hat{x}^{n-1} \tag{2.89}$$

$$\left[\hat{x}, \hat{p}^n\right] = i\hbar n\hat{p}^{n-1} \tag{2.90}$$

Curiously, the factors of $\hbar$ have vanished in equations (2.87) and (2.88), and quantum mechanics does not seem to be present. Instead, these equations indicate that the position and momentum operators follow the same equations of motion as Hamilton's equations for the classical variables. If we integrate eq. (2.88) over a time period t we find that the expectation value for the position of the particle follows the classical motion.

$$\langle x(t)\rangle = \frac{\langle p\rangle t}{m} + \langle x(0)\rangle \tag{2.91}$$

We can also use the time derivative of eq. (2.88) to obtain an equation that mirrors Newton's second law of motion, $F=ma$:

$$m\frac{\partial^2\langle x\rangle}{\partial t^2} = -\langle \nabla V\rangle \tag{2.92}$$

These observations underlie Ehrenfest's Theorem, a statement of the classical correspondence of quantum mechanics, which states that the expectation values for the position and momentum operators will follow the classical equations of motion.

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 312.
2. Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press: New York, 1995.
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2.6. Interaction Picture

The interaction picture is a hybrid representation that is useful in solving problems with time-dependent Hamiltonians in which we can partition the Hamiltonian as

$$H(t) = H_0 + V(t) \tag{2.93}$$

H_0 is a Hamiltonian for the degrees of freedom we are interested in, which we treat exactly, and can be (although for us usually will not be) a function of time. $V(t)$ is a time-dependent potential which can be complicated. In the interaction picture, we will treat each part of the Hamiltonian in a different representation. We will use the eigenstates of H_0 as a basis set to describe the dynamics induced by $V(t)$, assuming that $V(t)$ is small enough that eigenstates of H_0 are a useful basis. If H_0 is not a function of time, then there is a simple time-dependence to this part of the Hamiltonian that we may be able to account for easily.

Setting V to zero, we can see that the time evolution of the exact part of the Hamiltonian H_0 is described by

$$\frac{\partial}{\partial t} U_0(t,t_0) = -\frac{i}{\hbar} H_0(t) U_0(t,t_0) \tag{2.94}$$

where,

$$U_0(t,t_0) = \exp_+\left[-\frac{i}{\hbar}\int_{t_0}^{t} d\tau\, H_0(t)\right] \tag{2.95}$$

or, for a time-independent H_0,

$$U_0(t,t_0) = e^{-iH_0(t-t_0)/\hbar} \tag{2.96}$$

We define a wavefunction in the interaction picture $|\psi_I\rangle$ in terms of the Schrödinger wavefunction through:

$$|\psi_S(t)\rangle \equiv U_0(t,t_0)|\psi_I(t)\rangle \tag{2.97}$$

or

$$|\psi_I\rangle = U_0^\dagger |\psi_S\rangle \tag{2.98}$$

Effectively the interaction representation defines wavefunctions in such a way that the phase accumulated under $e^{-iH_0t/\hbar}$ is removed. For small V, these are typically high frequency oscillations relative to the slower amplitude changes induced by V.

Now we need an equation of motion that describes the time evolution of the interaction picture wavefunctions. We begin by substituting eq. (2.97) into the TDSE:

$$i\hbar\frac{\partial}{\partial t}|\psi_S\rangle = H|\psi_S\rangle \tag{2.99}$$

$$\frac{\partial}{\partial t} U_0(t,t_0)|\psi_I\rangle = \frac{-i}{\hbar} H(t)\, U_0(t,t_0)\,|\psi_I\rangle$$

$$\frac{\partial U_0}{\partial t}|\psi_I\rangle + U_0 \frac{\partial|\psi_I\rangle}{\partial t} = \frac{-i}{\hbar}\big(H_0 + V(t)\big)\, U_0(t,t_0)\,|\psi_I\rangle \tag{2.100}$$

$$\cancel{\frac{-i}{\hbar} H_0 U_0 |\psi_I\rangle} + U_0 \frac{\partial|\psi_I\rangle}{\partial t} = \frac{-i}{\hbar}\big(\cancel{H_0} + V(t)\big)\, U_0\,|\psi_I\rangle$$

$$\therefore \quad i\hbar \frac{\partial|\psi_I\rangle}{\partial t} = V_I\,|\psi_I\rangle \tag{2.101}$$

where
$$V_I(t) = U_0^\dagger(t,t_0)\, V(t)\; U_0(t,t_0) \tag{2.102}$$

$|\psi_I\rangle$ satisfies the Schrödinger equation with a new Hamiltonian in eq. (2.102): the interaction picture Hamiltonian, $V_I(t)$. We have performed a unitary transformation of $V(t)$ into the frame of reference of *H*0, using U_0. Note: Matrix elements in $V_I = \langle k|V_I|l\rangle = e^{-i\omega_{lk}t} V_{kl}$ where *k* and *l* are eigenstates of *H0*.

We can now define a time-evolution operator in the interaction picture:

$$|\psi_I(t)\rangle = U_I(t,t_0)\,|\psi_I(t_0)\rangle \tag{2.103}$$

where
$$U_I(t,t_0) = \exp_+\left[\frac{-i}{\hbar}\int_{t_0}^{t} d\tau\, V_I(\tau)\right] \tag{2.104}$$

Now we see that

$$\begin{aligned} |\psi_S(t)\rangle &= U_0(t,t_0)\,|\psi_I(t)\rangle \\ &= U_0(t,t_0)U_I(t,t_0)\,|\psi_I(t_0)\rangle \\ &= U_0(t,t_0)U_I(t,t_0)\,|\psi_S(t_0)\rangle \end{aligned} \tag{2.105}$$

$$\therefore \quad U(t,t_0) = U_0(t,t_0)U_I(t,t_0) \tag{2.106}$$

Also, the time evolution of conjugate wavefunction in the interaction picture can be written

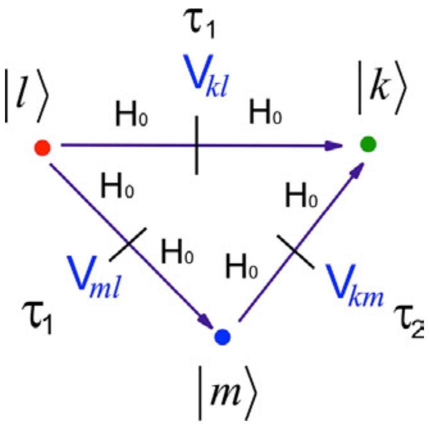
$$U^\dagger(t,t_0) = U_I^\dagger(t,t_0)\,U_0^\dagger(t,t_0) = \exp_-\left[\frac{i}{\hbar}\int_{t_0}^{t} d\tau\, V_I(\tau)\right]\exp_-\left[\frac{i}{\hbar}\int_{t_0}^{t} d\tau\, H_0(\tau)\right] \tag{2.107}$$

For the last two expressions, the order of these operators certainly matters.

So what changes about the time-propagation in the interaction representation? Let’s start by writing out the time-ordered exponential for *U* in eq. (2.106) using eq. (2.104):

$$\begin{aligned} U(t,t_0) &= U_0(t,t_0) + \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t} d\tau\, U_0(t,\tau)V(\tau)U_0(\tau,t_0) + \cdots \\ &= U_0(t,t_0) + \sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^{n} \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \ldots \int_{t_0}^{\tau_2} d\tau_1\, U_0(t,\tau_n)V(\tau_n)U_0(\tau_n,\tau_{n-1})\ldots \\ &\qquad \times U_0(\tau_2,\tau_1)V(\tau_1)U_0(\tau_1,t_0) \end{aligned} \tag{2.108}$$

Here I have used the composition property of $U(t,t_0)$. The same positive time-ordering applies. Note that the interactions $V(\tau_i)$ are not in the interaction representation here. Rather we used the definition in eq. (2.102) and collected terms. Now consider how U describes the time-dependence if I initiate the system in an eigenstate of H_0 $|l\rangle$ and observe the amplitude in a target eigenstate $|k\rangle$. The system evolves in eigenstates of H_0 during the different time periods, with the time-dependent interactions V driving the transitions between these states. The first-order term describes direct transitions between l and k induced by V, integrated over the full time period. Before the interaction phase is acquired as $e^{-iE_\ell(\tau-t_0)/\hbar}$, whereas after the interaction phase is acquired as $e^{-iE_\ell(t-\tau)/\hbar}$. Higher-order terms in the time-ordered exponential accounts for all possible intermediate pathways.



We now know how the interaction picture wavefunctions evolve in time. What about the operators? First of all, from examining the expectation value of an operator we see

$$\begin{aligned} \langle \hat{A}(t)\rangle &= \langle \psi(t)|\hat{A}|\psi(t)\rangle \\ &= \langle \psi(t_0)|U^\dagger(t,t_0)\,\hat{A}\,U(t,t_0)|\psi(t_0)\rangle \\ &= \langle \psi(t_0)|U_I^\dagger U_0^\dagger \hat{A} U_0 U_I|\psi(t_0)\rangle \\ &= \langle \psi_I(t)|\hat{A}_I|\psi_I(t)\rangle \end{aligned} \tag{2.109}$$

where
$$A_I \equiv U_0^\dagger\, A_S\, U_0 . \tag{2.110}$$

So the operators in the interaction picture also evolve in time, but under H_0. This can be expressed as a Heisenberg equation by differentiating A_I

$$\frac{\partial}{\partial t}\hat{A}_I = \frac{i}{\hbar}\left[H_0, \hat{A}_I\right] \tag{2.111}$$

Also, we know
$$\frac{\partial}{\partial t}|\psi_I\rangle = \frac{-i}{\hbar}V_I(t)|\psi_I\rangle \tag{2.112}$$

Notice that the interaction representation is a partition between the Schrödinger and Heisenberg representations. Wavefunctions evolve under V_I, while operators evolve under *H*0.

$$\begin{array}{llll} \text{For } H_0 = 0, V(t) = H & \Rightarrow & \dfrac{\partial \hat{A}}{\partial t} = 0; \quad \dfrac{\partial}{\partial t}|\psi_S\rangle = \dfrac{-i}{\hbar} H|\psi_S\rangle & \text{Schrödinger} \\ \text{For } H_0 = H, V(t) = 0 & \Rightarrow & \dfrac{\partial \hat{A}}{\partial t} = \dfrac{i}{\hbar}\left[H, \hat{A}\right]; \quad \dfrac{\partial \psi}{\partial t} = 0 & \text{Heisenberg} \end{array} \tag{2.113}$$

The relationship between *UI* and *bn*

Earlier we described how time-dependent problems with Hamiltonians of the form $H = H_0 + V(t)$ could be solved in terms of the time-evolving amplitudes in the eigenstates of *H*0. We can describe the state of the system as a superposition

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle \tag{2.114}$$

where the expansion coefficients $c_k(t)$ are given by

$$\begin{aligned} c_k(t) &= \langle k|\psi(t)\rangle = \langle k|U(t,t_0)|\psi(t_0)\rangle \\ &= \langle k|U_0 U_I|\psi(t_0)\rangle \\ &= e^{-iE_k t/\hbar}\langle k|U_I|\psi(t_0)\rangle \end{aligned} \tag{2.115}$$

Now, comparing equations (2.115) and (2.54) allows us to recognize that our earlier modified expansion coefficients *bn* were expansion coefficients for interaction picture wavefunctions

$$b_k(t) = \langle k|\psi_I(t)\rangle = \langle k|U_I|\psi(t_0)\rangle \tag{2.116}$$

Readings

1. Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press: New York, 1995.
2. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Ch. 4.

2.7. Time-Dependent Perturbation Theory

Perturbation theory refers to calculating the time-dependence of a system by truncating the expansion of the interaction picture time-evolution operator after a certain term. In practice, truncating the full time-propagator U is not effective, and only works well for times short compared to the inverse of the energy splitting between coupled states of your Hamiltonian. The interaction picture applies to Hamiltonians that can be cast as $H(t)=H_0+V(t)$ and, allows us to focus on the influence of the coupling. We can then treat the time evolution under *H0* exactly, but truncate the influence of $V(t)$. This works well for weak perturbations. Let's look more closely at this.

We know the eigenstates for $H_0 : H_0|n\rangle = E_n|n\rangle$, and we can calculate the evolution of the wavefunction that results from $V(t)$:

$$|\psi_I(t)\rangle = \sum_n b_n(t)|n\rangle \tag{2.117}$$

For a given state *k*, we calculate $b_k(t)$ as:

$$b_k = \langle k|U_I(t,t_0)|\psi(t_0)\rangle \tag{2.118}$$

where

$$U_I(t,t_0) = \exp_+\left[\frac{-i}{\hbar}\int_{t_0}^{t} V_I(\tau)\,d\tau\right] \tag{2.119}$$

Now we can truncate the expansion after a few terms. This works well for small changes in amplitude of the quantum states with small coupling matrix elements relative to the energy splittings involved ($|b_k(t)| \approx |b_k(0)|; |V| \ll |E_k - E_n|$) As we will see, the results we obtain from perturbation theory are widely used for spectroscopy, condensed phase dynamics, and relaxation.

Let's take the specific case where we have a system prepared in $|\ell\rangle$, and we want to know the probability of observing the system in $|k\rangle$ at time t due to $V(t)$: $P_k(t) = |b_k(t)|^2$.

Expanding

$$b_k(t) = \left\langle k\left|\exp_+\left[-\frac{i}{\hbar}\int_{t_0}^{t} d\tau\, V_I(\tau)\right]\right|\ell\right\rangle \tag{2.120}$$

$$\begin{aligned} b_k(t) = \langle k|\ell\rangle \; &- \frac{i}{\hbar}\int_{t_0}^{t} d\tau \langle k|V_I(\tau)|\ell\rangle \\ &+ \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle k|V_I(\tau_2)V_I(\tau_1)|\ell\rangle \;+\ldots \end{aligned} \tag{2.121}$$

Now, using

$$\langle k|V_I(t)|\ell\rangle = \langle k|U_0^\dagger\, V(t)\, U_0|\ell\rangle = e^{-i\omega_{\ell k}t}\, V_{k\ell}(t) \tag{2.122}$$

we obtain:

$$b_k(t) = \delta_{k\ell} - \frac{i}{\hbar}\int_{t_0}^{t} d\tau_1 \; e^{-i\omega_{\ell k}\tau_1} V_{k\ell}(\tau_1) \qquad \text{“first-order”} \tag{2.123}$$

$$+ \sum_m \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \; e^{-i\omega_{mk}\tau_2} \, V_{km}(\tau_2) \, e^{-i\omega_{\ell m}\tau_1} \, V_{m\ell}(\tau_1) \qquad \text{“second order”} \tag{2.124}$$

$$+ \ldots$$

The first-order term allows only direct transitions between $|\ell\rangle$ and $|k\rangle$, as allowed by the matrix element in *V*, whereas the second-order term accounts for transitions occurring through all possible intermediate states $|m\rangle$. For perturbation theory, the time-ordered integral is truncated at the appropriate order. Including only the first integral is first-order perturbation theory. The order of perturbation theory that one would extend a calculation should be evaluated initially by which allowed pathways between $|\ell\rangle$ and $|k\rangle$ you need to account for and which ones are allowed by the matrix elements.

For first-order perturbation theory, the expression in eq. (2.123) is the solution to the differential equation that you get for direct coupling between $|\ell\rangle$ and $|k\rangle$:

$$\frac{\partial}{\partial t} b_k = \frac{-i}{\hbar} \; e^{-i\omega_{\ell k} t} \; V_{k\ell}(t) \, b_\ell(0) \tag{2.125}$$

This indicates that the solution does not allow for the feedback between $|\ell\rangle$ and $|k\rangle$ that accounts for changing populations. This is the reason we say that validity dictates $\left|b_k(t)\right|^2 - \left|b_k(0)\right|^2 \ll 1$. If the initial state of the system $|\psi_0\rangle$ is not an eigenstate of H_0, we can express it as a superposition of eigenstates, $|\psi_0\rangle = \sum_n b_n(0)|n\rangle$ with

$$b_k(t) = \sum_n b_n(0) \langle k|U_I|n\rangle \tag{2.126}$$

Another observation applies to first-order perturbation theory. If the system is initially prepared in a state $|\ell\rangle$, and a time-dependent perturbation is turned on and then turned off over the time interval $t = -\infty$ to $+\infty$, then the complex amplitude in the target state $|k\rangle$ is just related to the Fourier transform of $V_{\ell k}(t)$ evaluated at the energy gap $\omega_{\ell k}$.

$$b_k(t) = -\frac{i}{\hbar}\int_{-\infty}^{+\infty} d\tau \; e^{-i\omega_{\ell k}\tau} \, V_{k\ell}(\tau) \tag{2.127}$$

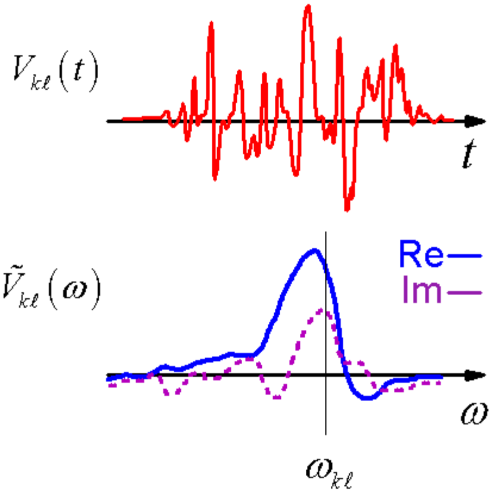
If the Fourier transform pair is defined in the following manner:

$$\tilde{V}(\omega) \equiv \tilde{\mathcal{F}}\left[V(t)\right] = \int_{-\infty}^{+\infty} dt \, V(t) \exp(i\omega t), \tag{2.128}$$

$$V(t) \equiv \tilde{\mathcal{F}}^{-1}\left[\tilde{V}(\omega)\right] = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \, \tilde{V}(\omega) \exp(-i\omega t) \tag{2.129}$$

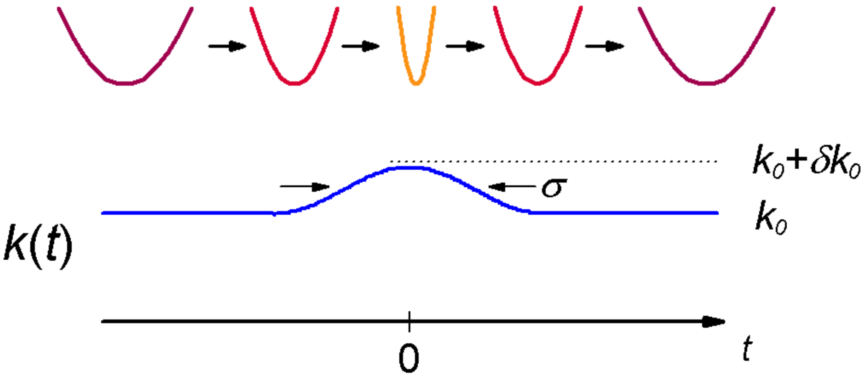
Then we can write the probability of transfer to state *k* as

$$P_{k\ell} = \frac{2\pi\left|\tilde{V}_{k\ell}\left(\omega_{k\ell}\right)\right|^2}{\hbar^2}. \tag{2.130}$$



Example: First-order Perturbation Theory

Let’s consider a simple model for vibrational excitation induced by the compression of harmonic oscillator. We will subject a harmonic oscillator initially in its ground state to a Gaussian compression pulse, which increases its force constant.



First, write the complete time-dependent Hamiltonian:

$$H(t) = T+V(t)=\frac{p^2}{2m}+\frac{1}{2}k(t)x^2 \tag{2.131}$$

Now, partition it according to $H=H_0+V(t)$ in such a manner that we can write H_0 as a harmonic oscillator Hamiltonian. This involves partitioning the time-dependent force constant into two parts:

$$k(t)=k_0+\delta k(t) \qquad k_0=m\Omega^2 \qquad \delta k(t)=\delta k_0 \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right) \tag{2.132}$$

$$H = \underbrace{\frac{p^2}{2m}+\frac{1}{2}k_0x^2}_{H_0} + \underbrace{\frac{1}{2}\delta k_0 x^2 \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right)}_{V(t)} \tag{2.133}$$

Here δk_0 is the magnitude of the induced change in the force constant, and σ is the time-width of the Gaussian perturbation. So, we know the eigenstates of H_0: $H_0|n\rangle = E_n|n\rangle$

$$H_0=\hbar\Omega\left(a^\dagger a+\frac{1}{2}\right) \qquad E_n=\hbar\Omega\left(n+\frac{1}{2}\right) \tag{2.134}$$

Now we ask, if the system is in $|0\rangle$ before applying the perturbation, what is the probability of finding it in state $|n\rangle$ after the perturbation?

For $n\neq 0$:
$$b_n(t)=\frac{-i}{\hbar}\int_{t_0}^{t} d\tau \;\; V_{n0}(\tau)\; e^{i\omega_{n0}\tau} \tag{2.135}$$

Using $\omega_{n0} = \left(E_n - E_0\right)/\hbar = n\Omega$, and recognizing that we can set the limits to $t_0 = -\infty$ and t = ∞,

$$b_n\left(t\right) = \frac{-i}{2\hbar}\delta k_0 \left\langle n\middle|x^2\middle|0\right\rangle \int_{-\infty}^{+\infty} d\tau \;\; e^{in\Omega\tau} e^{-\tau^2/2\sigma^2} \tag{2.136}$$

This leads to

$$b_n\left(t\right) = \frac{-i}{2\hbar}\delta k_0 \sqrt{2\pi}\sigma \left\langle n\middle|x^2\middle|0\right\rangle e^{-n^2\sigma^2\Omega^2/2} \tag{2.137}$$

Here we made use of an important identity for Gaussian integrals:

$$\int_{-\infty}^{+\infty} \exp\left(ax^2 + bx + c\right) dx = \sqrt{\frac{-\pi}{a}} \; \exp\left(c - \frac{1}{4}\frac{b^2}{a}\right) \tag{2.138}$$

$$\int_{-\infty}^{+\infty} \exp\left(-ax^2 + ibx\right) dx = \sqrt{\frac{\pi}{a}} \exp\left(-\frac{b^2}{4a}\right) \tag{2.139}$$

What about the matrix element?

$$x^2 = \frac{\hbar}{2m\Omega}\left(a + a^\dagger\right)^2 = \frac{\hbar}{2m\Omega}\left(aa + a^\dagger a + aa^\dagger + a^\dagger a^\dagger\right) \tag{2.140}$$

From these we see that first-order perturbation theory will not allow transitions to $n = 1$, only $n = 0$ and $n = 2$. Generally this would not be realistic, because you would certainly expect excitation to n=1 would dominate over excitation to n=2. A real system would also be anharmonic, in which case, the leading term in the expansion of the potential *V*(*x*), that is linear in *x*, would not vanish as it does for a harmonic oscillator, and this would lead to matrix elements that raise and lower the excitation by one quantum.

However for the present case,

$$\left\langle 2\middle|x^2\middle|0\right\rangle = \sqrt{2}\frac{\hbar}{2m\Omega} \tag{2.141}$$

So,

$$b_2 = \frac{-i\sqrt{\pi}\,\delta k_0\,\sigma}{2m\Omega} e^{-2\sigma^2\Omega^2} \tag{2.142}$$

and we can write the probability of occupying the n = 2 state as

$$P_2 = \left|b_2\right|^2 = \frac{\pi\delta k_0{}^2\sigma^2}{2m^2\Omega^2} e^{-4\sigma^2\Omega^2} \tag{2.143}$$

From the exponential argument, significant transfer of amplitude occurs when the compression pulse width is small compared to the vibrational period.

$$\sigma << \frac{1}{\Omega} \tag{2.144}$$

In this regime, the potential is changing faster than the atoms can respond to the perturbation. In practice, when considering a solid-state problem, with frequencies matching those of acoustic phonons and unit cell dimensions, we need perturbations that move faster than the speed of sound, i.e., a shock wave. The opposite limit, $\sigma\Omega >> 1$, is the adiabatic limit. In this case, the perturbation is so slow that the system always remains entirely in n=0, even while it is compressed.

Now, let's consider the validity of this first-order treatment. Perturbation theory does not allow for b_n to change much from its initial value. First we re-write eq. (2.143) as

$$P_2 = \sigma^2\Omega^2 \frac{\pi}{2}\left(\frac{\delta k_0^{\ 2}}{k_0^{\ 2}}\right) e^{-4\sigma^2\Omega^2} \tag{2.145}$$

Now for changes that don't differ much from the initial value, $P_2 << 1$

$$\sigma^2\Omega^2 \frac{\pi}{2}\left(\frac{\delta k_0^{\ 2}}{k_0^{\ 2}}\right) << 1 \tag{2.146}$$

Generally, the magnitude of the perturbation δk_0 must be small compared to k_0.

One step further…

The preceding example was simple, but it tracks the general approach to setting up problems that you treat with time-dependent perturbation theory. The approach relies on writing a Hamiltonian that can be cast into a Hamiltonian that you can treat exactly H_0, and time-dependent perturbations that shift amplitudes between its eigenstates. For this scheme to work well, we need the magnitude of perturbation to be small, which immediately suggests working with a Taylor series expansion of the potential. For instance, take a one-dimensional potential for a bound particle, $V(x)$, which is dependent on the form of an external variable y. We can expand the potential in x about its minimum $x = 0$ as

$$\begin{aligned} V(x) &= \frac{1}{2!}\frac{\partial^2 V}{\partial x^2}\bigg|_{x=0} x^2 + \frac{1}{2!}\frac{\partial^2 V}{\partial x \partial y}\bigg|_{x=0} xy + \frac{1}{3!}\sum_{y,z}\frac{\partial^3 V}{\partial x \partial y \partial z}\bigg|_{x=0} xyz + \cdots \\ &= \frac{1}{2}kx^2 + V^{(2)}xy + \left(V_3^{(3)}x^3 + V_2^{(3)}x^2y + V_1^{(3)}xy^2\right) + \cdots \end{aligned} \tag{2.147}$$

The first term is the harmonic force constant for x, and the second term is a bi-linear coupling whose magnitude $V^{(2)}$ indicates how much a change in the variable y influences the variable x. The remaining terms are cubic expansion terms. $V_3^{(3)}$ is the cubic anharmonicity of $V(x)$, and the remaining two terms are cubic couplings that describe the dependence of x on y. Introducing a time-dependent potential is equivalent to introducing a time-dependence to the operator y, where the form and strength of the interaction is subsumed into the amplitude V. In the case of the previous example, our formulation of the problem was equivalent to selecting only the $V_2^{(3)}$ term, so that $\delta k_0/2 = V_2^{(3)}$, and giving the value of y a time-dependence described by the Gaussian waveform.

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 1285.
2. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Ch. 4.
3. Sakurai, J. J., *Modern Quantum Mechanics, Revised Edition*. Addison-Wesley: Reading, MA, 1994; Ch. 2.

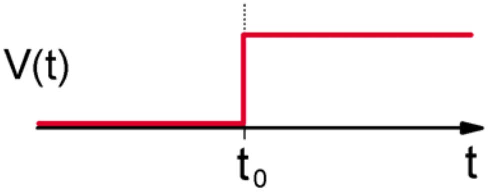
2.8. Fermi’s Golden Rule

A number of important relationships in quantum mechanics that describe rate processes come from first-order perturbation theory. These expressions begin with two model problems that we want to work through: (1) time evolution after applying a step perturbation, and (2) time evolution after applying a harmonic perturbation. As before, we will ask: if we prepare the system in the state $|\ell\rangle$, what is the probability of observing the system in state $|k\rangle$ following the perturbation?

Constant perturbation (or step perturbation)

The system is prepared such that $|\psi(-\infty)\rangle = |\ell\rangle$. A constant perturbation of amplitude V is applied at t_0:

$$V(t) = V\,\Theta(t-t_0) = \begin{cases} 0 & t < t_0 \\ V & t \geq t_0 \end{cases} \qquad (2.148)$$



Here $\Theta(t-t_0)$ is the Heaviside step response function, which is 0 for $t < t_0$ and 1 for $t \geq t_0$. Now, turning to first-order perturbation theory, the amplitude in $k \neq \ell$, we have:

$$b_k = -\frac{i}{\hbar}\int_{t_0}^{t} d\tau\, e^{i\omega_{k\ell}(\tau - t_0)} V_{k\ell}(\tau) \qquad (2.149)$$

Here $V_{k\ell}$ is independent of time. Setting $t_0 = 0$,

$$\begin{aligned} b_k &= -\frac{i}{\hbar} V_{k\ell} \int_0^t d\tau\, e^{i\omega_{k\ell}\tau} \\ &= -\frac{V_{k\ell}}{E_k - E_\ell}\left[exp(i\omega_{k\ell}t) - 1\right] \qquad (2.150) \\ &= -\frac{2i V_{k\ell}\, e^{i\omega_{k\ell}t/2}}{E_k - E_\ell}\, sin(\omega_{k\ell}t/2) \end{aligned}$$

In the last expression, I used the identity $e^{i\theta} - 1 = 2i\, e^{i\theta/2}\, sin(\theta/2)$. Now

$$P_k = |b_k|^2 = \frac{4|V_{k\ell}|^2}{|E_k - E_\ell|^2}\, sin^2\left(\frac{\omega_{k\ell}t}{2}\right) \qquad (2.151)$$

If we write this using the energy splitting variable we used earlier: $\Delta = (E_k - E_\ell)/2$,

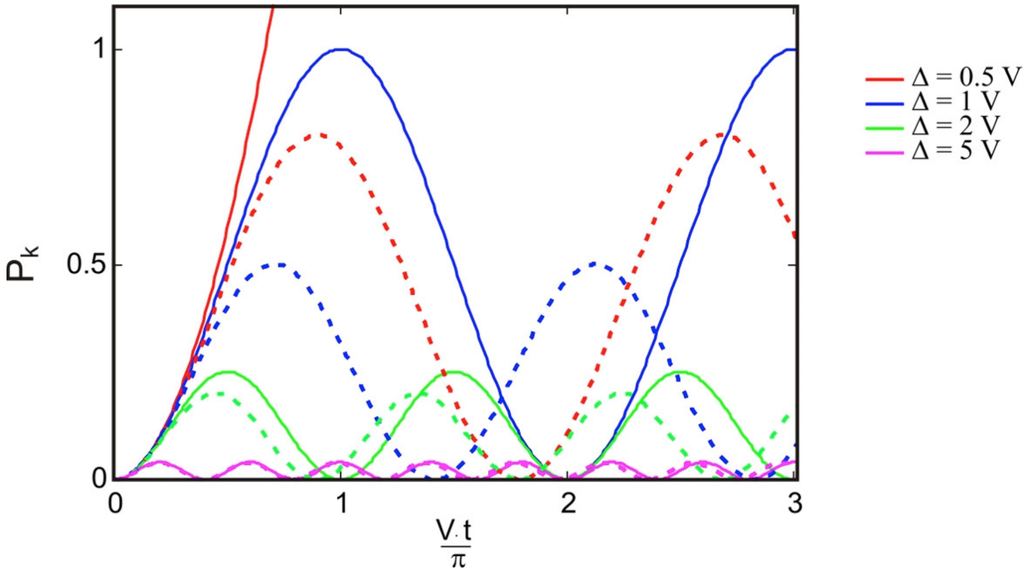
$$P_k = \frac{V^2}{\Delta^2}\sin^2(\Delta t/\hbar) \qquad (2.152)$$

Compare this with the exact result we have for the two-level problem:

$$P_k = \frac{V^2}{V^2 + \Delta^2} \sin^2\left(\sqrt{\Delta^2 + V^2}\, t / \hbar\right) \tag{2.153}$$

As expected, the perturbation theory result works well for $V \ll \Delta$.

Let's examine the time-dependence to P_k, and compare the perturbation theory (solid lines) to the exact result (dashed lines) for different values of Δ.

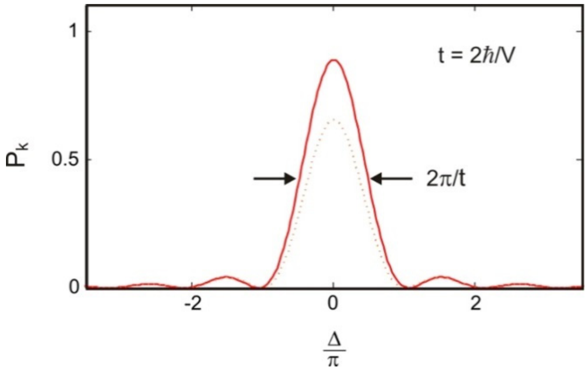


The worst correspondence is for Δ=0 for which the behavior appears quadratic and the probability quickly exceeds unity. It is certainly unrealistic, but we do not expect that the expression will hold for the "strong coupling" case: Δ ≪ V. One begins to have quantitative accuracy in for the regime $P_k(t) - P_k(0) < 0.1$ or $\Delta < 4V$.

Now let's look at the dependence on Δ. We can write the first-order result eq. (2.152) as

$$P_k = \frac{V^2 t^2}{\hbar^2} \operatorname{sinc}^2\left(\Delta t / 2\hbar\right) \tag{2.154}$$

where $\operatorname{sinc}(x) = \sin(x)/x$. If we plot the probability of transfer from $|\ell\rangle$ to $|k\rangle$ as a function of the energy level splitting $(E_k - E_\ell)$ we have:



The probability of transfer is sharply peaked where energy of the initial state matches that of the final state, and the width of the energy mismatch narrows with time. Since $\lim_{x\to 0}\operatorname{sinc}(x)=1$, we see that the short time behavior is a quadratic growth in P_k

$$\lim_{\Delta\to 0} P_k = V^2 t^2 / \hbar^2 \tag{2.155}$$

The integrated area grows linearly with time.

Since the energy spread of states to which transfer is efficient scales approximately as $E_k - E_\ell < 2\pi\hbar/t$, this observation is sometimes referred to as an uncertainty relation with $\Delta E \cdot \Delta t \geq 2\pi\hbar$. However, remember that this is really just an observation of the principles of Fourier transforms. A frequency can only be determined as accurately as the length of the time over which you observe oscillations. Since time is not an operator, it is not a true uncertainly relation like $\Delta p \cdot \Delta x \geq 2\pi\hbar$.

In the long time limit, the *sinc*^{2}(x) function narrows to a delta function:

$$\lim_{t\to\infty} \frac{\sin^2(ax/2)}{ax^2} = \frac{\pi}{2}\,\delta(x) \tag{2.156}$$

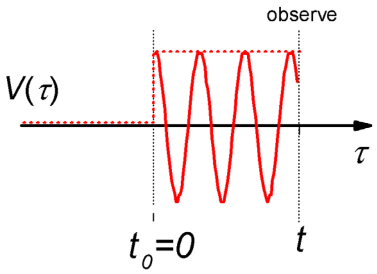
$$\lim_{t\to\infty} P_k(t) = \frac{2\pi}{\hbar}\left|V_{k\ell}\right|^2 \delta\left(E_k - E_\ell\right) t \tag{2.157}$$

The delta function enforces energy conservation, saying that the energies of the initial and target state must be the same in the long time limit. What is interesting in eq. (2.157) is that we see a probability growing linearly in time. This suggests a transfer *rate* that is independent of time, as expected for simple first-order kinetics:

$$w_k(t) = \frac{\partial P_k(t)}{\partial t} = \frac{2\pi\left|V_{k\ell}\right|^2}{\hbar}\,\delta\left(E_k - E_\ell\right) \tag{2.158}$$

This is one statement of Fermi's Golden Rule—the state-to-state form—which describes relaxation rates from first-order perturbation theory. We will show that this rate properly describes long time exponential relaxation rates that you would expect from the solution to $dP/dt = -wP$.

Harmonic perturbation



The second model calculation is the interaction of a system with an oscillating perturbation turned on at time $t_0 = 0$. The results will be used to describe how a light field induces transitions in a system through dipole interactions. Again, we are looking to calculate the transition probability between states ℓ and k:

$$V(t) = V\cos\omega t\ \Theta(t) \qquad (2.159)$$

$$\begin{aligned} V_{k\ell}(t) &= V_{k\ell}\cos\omega t \\ &= \frac{V_{k\ell}}{2}\left[e^{-i\omega t} + e^{i\omega t}\right] \end{aligned} \qquad (2.160)$$

Setting $t_0 \to 0$, first-order perturbation theory leads to

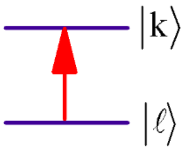
$$\begin{aligned} b_k &= \frac{-i}{\hbar}\int_{t_0}^{t} d\tau\, V_{k\ell}(\tau)\, e^{i\omega_{k\ell}\tau} \\ &= \frac{-iV_{k\ell}}{2\hbar}\int_0^t d\tau\left[e^{i(\omega_{k\ell}-\omega)\tau} + e^{i(\omega_{k\ell}+\omega)\tau}\right] \\ &= \frac{-iV_{k\ell}}{2\hbar}\left[\frac{e^{i(\omega_{k\ell}-\omega)t}-1}{\omega_{k\ell}-\omega} + \frac{e^{i(\omega_{k\ell}+\omega)t}-1}{\omega_{k\ell}+\omega}\right] \end{aligned} \qquad (2.161)$$

Using $e^{i\theta} - 1 = 2i\, e^{i\theta/2}\, sin(\theta/2)$ as before:

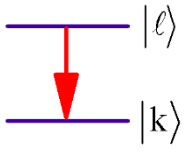
$$b_k = \frac{V_{k\ell}}{\hbar}\left[\frac{e^{i(\omega_{k\ell}-\omega)t/2}\,\sin\left[(\omega_{k\ell}-\omega)t/2\right]}{\omega_{k\ell}-\omega} + \frac{e^{i(\omega_{k\ell}+\omega)t/2}\,\sin\left[(\omega_{k\ell}+\omega)t/2\right]}{\omega_{k\ell}+\omega}\right] \qquad (2.162)$$

Notice that these terms are only significant when $\omega \approx \omega_{k\ell}$. The condition for efficient transfer is resonance, a matching of the frequency of the harmonic interaction with the energy splitting between quantum states. Consider the resonance conditions that will maximize each of these:

First Term	Second Term
max at : $\omega = +\omega_{k\ell}$	$\omega = -\omega_{k\ell}$
$E_k > E_\ell$	$E_k < E_\ell$
$E_k = E_\ell + \hbar\omega$	$E_k = E_\ell - \hbar\omega$



Absorption
(resonant term)



Stimulated Emission
(anti-resonant term)

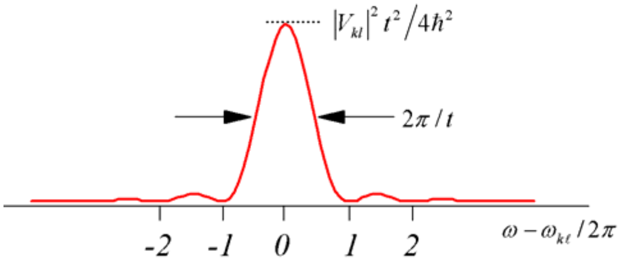
If we consider only absorption, $E_k > E_\ell$, we have:

$$P_{k\ell} = |b_k|^2 = \frac{|V_{k\ell}|^2}{\hbar^2 (\omega_{k\ell} - \omega)^2} \quad \sin^2\left[\tfrac{1}{2}(\omega_{k\ell} - \omega) t\right] \tag{2.163}$$

We can compare this with the exact expression:

$$P_{k\ell} = |b_k|^2 = \frac{|V_{k\ell}|^2}{\hbar^2 (\omega_{k\ell} - \omega)^2 + |V_{k\ell}|^2} \quad \sin^2\left[\frac{1}{2\hbar}\sqrt{|V_{k\ell}|^2 + (\omega_{k\ell} - \omega)^2}\ t\right]. \tag{2.164}$$

Again, we see that the first-order expression is valid for couplings $|V_{k\ell}|$ that are small relative to the detuning $\Delta\omega = (\omega_{k\ell} - \omega)$. The maximum probability for transfer is on resonance $\omega_{k\ell} = \omega$



Similar to our description of the constant perturbation, the long time limit for this expression leads to a delta function $\delta(\omega_{k\ell} - \omega)$. In this long time limit, we can neglect interferences between the resonant and antiresonant terms. The rates of transitions between k and ℓ states determined from $w_{k\ell} = \partial P_k / \partial t$ becomes

$$w_{k\ell} = \frac{\pi}{2\hbar^2} |V_{k\ell}|^2 \left[\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega)\right]. \tag{2.165}$$

We can examine the limitations of this formula. When we look for the behavior on resonance, expanding the sin(x) shows us that P_k rises quadratically for short times:

$$\lim_{\Delta\omega \to 0} P_k(t) = \frac{|V_{k\ell}|^2}{4\hbar^2} t^2 \tag{2.166}$$

This clearly will not describe long-time behavior, but it will hold for small P_k, so we require

$$t << \frac{2\hbar}{V_{k\ell}} \tag{2.167}$$

At the same time, we cannot observe the system on too short a time scale. We need the field to make several oscillations for this to be considered a harmonic perturbation.

$$t > \frac{1}{\omega} \approx \frac{1}{\omega_{k\ell}} \tag{2.168}$$

These relationships imply that we require $V_{k\ell} << \hbar\omega_{k\ell}$. (2.169)

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Laloë, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 1299.
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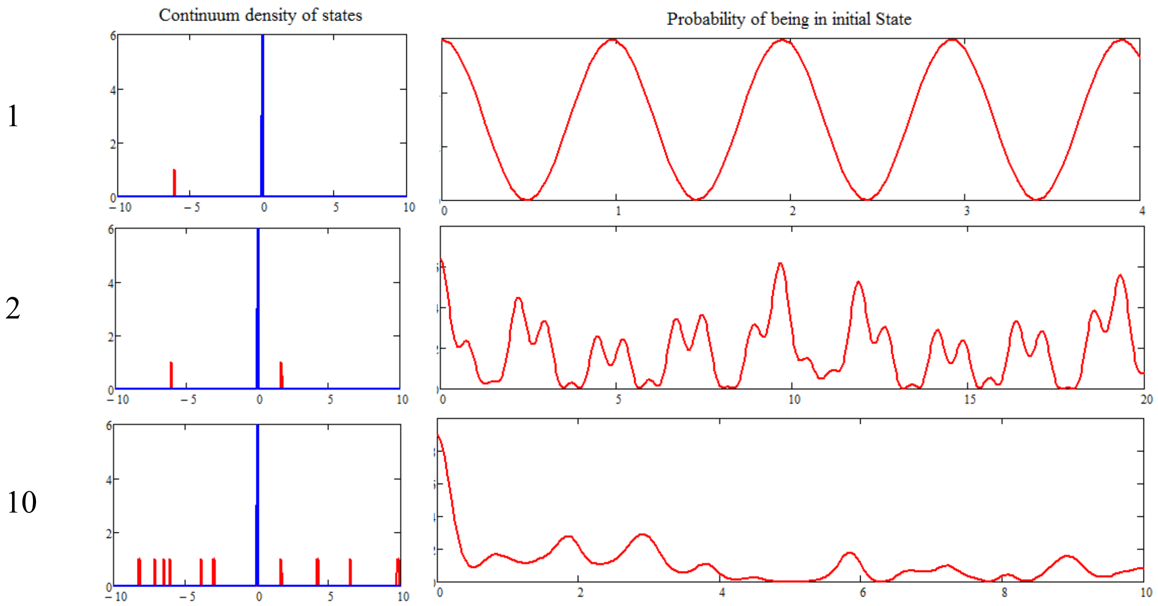
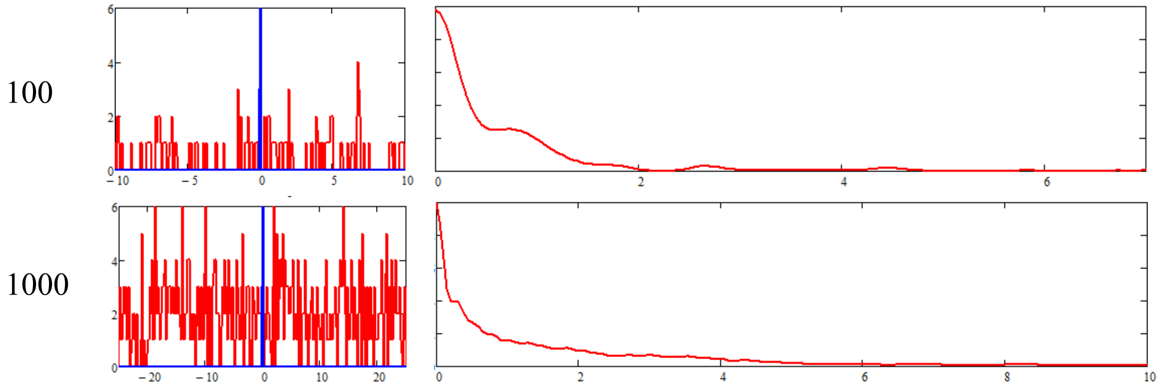
3. IRREVERSIBLE RELAXATION

At a fundamental level, the basic laws governing the time evolution of *isolated* quantum mechanical systems are invariant under time reversal. That is, there is no preferred direction to the arrow of time. The TDSE is reversible, meaning that one can find solutions for propagating either forward or backward in time. If one reverses the sign of time and thereby momenta of objects, we should be able to go back where the system was at an earlier time. We can see this in the exact solution to the two-level problem, where amplitude oscillates between the two states with a frequency that depends on the coupling. If we reverse the sign of the time, the motion is reversed. In contrast, when a quantum system is in contact with another system having many degrees of freedom, a definite direction emerges to the arrow of time, and the system's dynamics is no longer reversible. Such irreversible systems are dissipative, meaning they decay in time from a prepared state to a state where phase relationships between the basis states are lost.

How does irreversible behavior, a hallmark of chemical systems, arise from the deterministic TDSE? We will answer this question specifically in the context of quantum transitions from a given energy state of the system to energy states its surroundings. Qualitatively, such behavior can be expected to arise from destructive interference between oscillatory solutions of the system and the set of closely packed manifold of energy states of the bath. To illustrate this point, consider the following calculation for the probability amplitude for an initial state of the system coupled to a finite but growing number of randomly chosen states belonging to the bath.





Here, even with only 100 or 1000 states, recurrences in the initial state amplitude are suppressed by destructive interference between paths. Clearly in the limit that the accepting state are truly continuous, the initial amplitude prepared in ℓ will be spread through an infinite number of continuum states. We will look at this more closely by describing the relaxation of an initially prepared state as a result of coupling to a continuum of states of the surroundings. This is common to all dissipative processes in which the surroundings to the system of interest form a continuous band of states.

To begin, let us define a continuum. We are familiar with eigenfunctions being characterized by quantized energy levels, where only discrete values of the energy are allowed. However, this is not a general requirement. Discrete levels are characteristic of particles in bound potentials, but free particles can take on a continuous range of energies given by their momentum, $E = \langle p^2 \rangle / 2m$. The same applies to dissociative potential energy surfaces, and bound potentials in which the energy exceeds the binding energy. For instance, photoionization or photodissociation of a molecule involves a light field coupling a bound state into a continuum. Other examples are common in condensed matter. The intermolecular motions of a liquid, the lattice vibrations of a crystal, or the allowed energies within the band structure of a metal or semiconductor are all examples of a continuum.

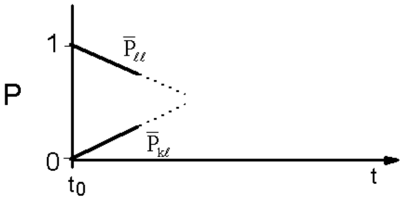
For a discrete state imbedded in such a continuum, the Golden Rule gives the probability of transition from the system state $|\ell\rangle$ to a continuum state $|k\rangle$ as:

$$\overline{w}_{k\ell} = \frac{\partial \overline{P}_{k\ell}}{\partial t} = \frac{2\pi}{\hbar} \left| V_{k\ell} \right|^2 \rho\left(E_k = E_\ell \right) \tag{3.1}$$

The transition rate $\overline{w}_{k\ell}$ is constant in time, when $\left| V_{k\ell} \right|^2$ is constant in time, which will be true for short time intervals. Under these conditions integrating the rate equation on the left gives

$$\overline{P}_{k\ell} = \overline{w}_{k\ell} \left(t - t_0 \right) \tag{3.2}$$

$$\overline{P}_{\ell\ell} = 1 - \overline{P}_{k\ell} \tag{3.3}$$



The probability of transition to the continuum of bath states varies linearly in time. As we noted, this will clearly only work for times such that $P_k(t) - P_k(0) << 1$.

What long time behavior do we expect? A time-independent rate with population governed by $\overline{w}_{k\ell} = \partial \overline{P}_{k\ell}/\partial t$ is a hallmark of first order kinetics and exponential relaxation. In fact, for exponential relaxation out of a state ℓ, the short time behavior looks just like the first order result:

$$\begin{aligned} \overline{P}_{\ell\ell}(t) &= \exp(-\overline{w}_{k\ell} t) \\ &= 1 - \overline{w}_{k\ell} t + \ldots \end{aligned} \tag{3.4}$$

So we might believe that $\overline{w}_{k\ell}$ represents the tangent to the relaxation behavior at $t = 0$. The problem we had previously was we did not account for depletion of initial state. In fact, we will see that when we look a touch more carefully, that the long time relaxation behavior of state ℓ is exponential and governed by the golden rule rate. The decay of the initial state is irreversible because there is feedback with a distribution of destructively interfering phases.

Let's formulate this problem a bit more carefully. We will look at transitions to a continuum of states $\{k\}$ from an initial state ℓ under a constant perturbation. These together form a complete set; so for $H(t) = H_0 + V(t)$ with $H_0|n\rangle = E_n|n\rangle$.

$$1 = \sum_n |n\rangle\langle n| = |\ell\rangle\langle\ell| + \sum_k |k\rangle\langle k| \tag{3.5}$$

As we go on, you will see that we can identify ℓ with the "system" and $\{k\}$ with the "bath" when we partition $H_0 = H_S + H_B$.

Now let's make some simplifying assumptions. For transitions into the continuum, we will assume that transitions only occur between ℓ and states of the continuum, but that there are no interactions between states of the continuum: $\langle k|V|k'\rangle = 0$. This can be rationalized by thinking of this problem as a discrete set of states interacting with a continuum of normal modes. Moreover, we will assume that the coupling of the initial to continuum states is a constant for all states k: $\langle\ell|V|k\rangle = \langle\ell|V|k'\rangle = \cdots$. For reasons that we will see later, we will also keep the diagonal matrix element $\langle\ell|V|\ell\rangle = 0$. With these assumptions, we can summarize the Hamiltonian for our problem as

$$\begin{aligned} H(t) &= H_0 + V(t) \\ H_0 &= |\ell\rangle E_\ell \langle\ell| + \sum_k |k\rangle E_k \langle k| \\ V(t) &= \sum_k \left[|k\rangle V_{k\ell} \langle\ell| + |\ell\rangle V_{\ell k} \langle k| \right] + |\ell\rangle V_{\ell\ell} \langle\ell| \end{aligned} \tag{3.6}$$

We are seeking a more accurate description of the occupation of the initial and continuum states, for which we will use the interaction picture expansion coefficients

$$b_k(t) = \langle k | U_I(t,t_0) | \ell \rangle \tag{3.7}$$

Earlier, we saw that the exact solution to U_I was:

$$U_I(t,t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} d\tau \, V_I(\tau) U_I(\tau,t_0) \tag{3.8}$$

This form was not very practical, since U_I is a function of itself. For first-order perturbation theory, we set the final term in this equation $U_I(\tau,t_0) \rightarrow 1$. Here, in order to keep the feedback between $|\ell\rangle$ and the continuum states, we keep it as is.

$$b_k(t) = \langle k | \ell \rangle - \tfrac{i}{\hbar} \int_{t_0}^{t} d\tau \, \langle k | V_I(\tau) U_I(\tau,t_0) | \ell \rangle \tag{3.9}$$

Inserting eq.(3.7), and recognizing $k \neq l$,

$$b_k(t) = -\frac{i}{\hbar} \sum_n \int_{t_0}^{t} d\tau \, e^{i\omega_{kn}\tau} \, V_{kn} \, b_n(\tau) \tag{3.10}$$

Note, V_{kn} is not a function of time. Equation (3.10) expresses the occupation of state k in terms of the full history of the system from $t_0 \rightarrow t$ with amplitude flowing back and forth between the states n. Equation (3.10) is just the integral form of the coupled differential equations that we used before:

$$i\hbar \frac{\partial b_k}{\partial t} = \sum_n e^{i\omega_{kn}t} \, V_{kn} \, b_n(t) \tag{3.11}$$

These exact forms allow for feedback between all the states, in which the amplitudes b_k depend on all other states. Since you only feed from ℓ into k, we can remove the summation in (3.10) and express the complex amplitude of a state within the continuum as

$$b_k = -\frac{i}{\hbar} V_{k\ell} \int_{t_0}^{t} d\tau \, e^{i\omega_{k\ell}\tau} \, b_\ell(\tau) \tag{3.12}$$

We want to calculate the rate of leaving $|\ell\rangle$, including feeding from continuum back into initial state. From eq. (3.11) we can separate terms involving the continuum and the initial state:

$$i\hbar \frac{\partial}{\partial t} b_\ell = \sum_{k \neq \ell} e^{i\omega_{\ell k}t} \, V_{\ell k} \, b_k + V_{\ell\ell} \, b_\ell \tag{3.13}$$

Now substituting (3.12) into (3.13), and setting $t_0 = 0$:

$$\frac{\partial b_\ell}{\partial t} = -\frac{1}{\hbar^2} \sum_{k \neq \ell} \left| V_{k\ell} \right|^2 \int_0^t b_\ell(\tau) \, e^{i\omega_{k\ell}(\tau - t)} \, d\tau - \frac{i}{\hbar} V_{\ell\ell} \, b_\ell(t) \tag{3.14}$$

This is an integro-differential equation that describes how the time-development of b_ℓ depends on the entire history of the system. Note we have two time variables for the two propagation routes:

$$\begin{aligned}\tau:&\ \ |\ell\rangle \to |k\rangle \\ t:&\ \ |k\rangle \to |\ell\rangle\end{aligned} \tag{3.15}$$

The next assumption is that b_ℓ varies slowly relative to $\omega_{k\ell}$, so we can remove it from integral. This is effectively a weak coupling statement: $\hbar\omega_{k\ell} >> V_{k\ell}$. b is a function of time, but since it is in the interaction picture it evolves slowly compared to the $\omega_{k\ell}$ oscillations in the integral.

$$\frac{\partial b_\ell}{\partial t} = b_\ell\left[-\frac{1}{\hbar^2}\sum_{k\neq\ell}\left|V_{k\ell}\right|^2\int_0^t e^{i\omega_{k\ell}(\tau-t)}\,d\tau - \frac{i}{\hbar}V_{\ell\ell}\right] \tag{3.16}$$

Now, we want the long time evolution of b, for times $\omega_{k\ell}t >> 1$, we will investigate the integration limit $t\to\infty$.

Complex integration of (3.16): Defining $t' = \tau - t \quad dt' = d\tau$

$$\int_0^t e^{i\omega_{k\ell}(\tau-t)}\,d\tau = -\int_0^t e^{i\omega_{k\ell}t'}\,dt' \tag{3.17}$$

The integral $\lim\limits_{T\to\infty}\int_0^T e^{i\omega t'}\,dt'$ is purely oscillatory and not well behaved. The strategy to solve this is to integrate:

$$\begin{aligned}\lim_{\varepsilon\to 0^+}\int_0^\infty e^{(i\omega+\varepsilon)t'}\,dt' &= \lim_{\varepsilon\to 0^+}\ \frac{1}{i\omega+\varepsilon} \\ &= \lim_{\varepsilon\to 0^+}\left(\frac{\varepsilon}{\omega^2+\varepsilon^2} + i\frac{\omega}{\omega^2+\varepsilon^2}\right)\end{aligned} \tag{3.18}$$

$$= \pi\delta(\omega) - i\mathbb{P}\frac{1}{\omega} \tag{3.19}$$

(This expression is valid when used under an integral)

In the final term we have written in terms of the Cauchy Principle Part:

$$\mathbb{P}\left(\frac{1}{x}\right) = \begin{cases}\frac{1}{x} & x\neq 0 \\ 0 & x = 0\end{cases} \tag{3.20}$$

Using eq. (3.19), eq. (3.16) becomes

$$\frac{\partial b_\ell}{\partial t} = b_\ell\left[\underbrace{-\frac{\pi}{\hbar^2}\sum_{k\neq\ell}\left|V_{k\ell}\right|^2\delta(\omega_{k\ell})}_{term\,1}\ \underbrace{-\frac{i}{\hbar}\left(V_{\ell\ell} + \mathbb{P}\sum_{k\neq\ell}\frac{\left|V_{k\ell}\right|^2}{E_k - E_\ell}\right)}_{term\,2}\right] \tag{3.21}$$

Note that Term 1 is just the Golden Rule rate, written explicitly as a sum over continuum states instead of an integral

$$\sum_{k\neq\ell}\delta\left(\omega_{k\ell}\right)\Rightarrow\hbar\rho\left(E_k=E_\ell\right) \tag{3.22}$$

$$\bar{w}_{k\ell}=\int dE_k\;\rho\left(E_k\right)\left[\frac{2\pi}{\hbar}\left|V_{k\ell}\right|^2\,\delta\left(E_k-E_\ell\right)\right] \tag{3.23}$$

Term 2 is just the correction of the energy of E_ℓ from second-order time-independent perturbation theory, ΔE_ℓ.

$$\Delta E_\ell=\langle\ell|V|\ell\rangle+\sum_{k\neq\ell}\frac{\left|\langle k|V|\ell\rangle\right|^2}{E_k-E_\ell} \tag{3.24}$$

So, the time evolution of b_ℓ is governed by a simple first-order differential equation

$$\frac{\partial b_\ell}{\partial t}=b_\ell\left(-\frac{\bar{w}_{k\ell}}{2}-\frac{i}{\hbar}\Delta E_\ell\right) \tag{3.25}$$

Which can be solved with $b_\ell\left(0\right)=1$ to give

$$b_\ell\left(t\right)=\exp\left(-\frac{\bar{w}_{k\ell}t}{2}-\frac{i}{\hbar}\Delta E_\ell\, t\right) \tag{3.26}$$

We see that one has exponential decay of amplitude of b_ℓ! This is a manner of irreversible relaxation from coupling to the continuum.

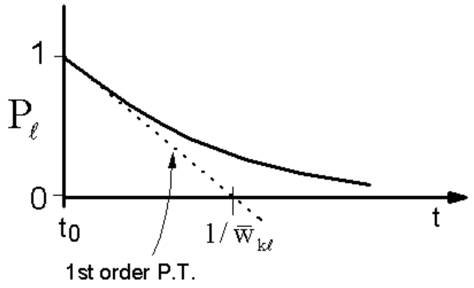
Now, since there may be additional interferences between paths, we switch from the interaction picture back to Schrödinger Picture, $c_\ell=b_\ell e^{-i\omega_\ell t}$:

$$c_\ell\left(t\right)=\exp\left[-\left(\frac{\bar{w}_{k\ell}}{2}+i\frac{E'_\ell}{\hbar}\right)t\right] \tag{3.27}$$

with the corrected energy $$E'_\ell\equiv E_\ell+\Delta E \tag{3.28}$$

and $$P_\ell=\left|c_\ell\right|^2=\exp\left[-\bar{w}_{k\ell}t\right]. \tag{3.29}$$

The solutions to the TDSE are expected to be complex and oscillatory. What we see here is a real dissipative component and an imaginary dispersive component. The probability decays exponentially from initial state. Fermi's Golden Rule rate tells you about long times!



Now, what is the probability of appearing in any of the states $\left|k\right\rangle$? Using eqn.(3.12):

$$\begin{aligned} b_k(t) &= -\frac{i}{\hbar}\int_0^t V_{k\ell}\, e^{i\omega_{k\ell}\tau}\, b_\ell(\tau)\, d\tau \\ &= V_{k\ell}\frac{1-\exp\left(-\frac{\overline{w}_{k\ell}}{2}t-\frac{i}{\hbar}\left(E'_\ell-E_k\right)t\right)}{E_k-E'_\ell+i\hbar\overline{w}_{k\ell}/2} \\ &= \quad V_{k\ell}\frac{1-c_\ell(t)}{E_k-E'_\ell+i\hbar\overline{w}_{k\ell}/2} \end{aligned} \tag{3.30}$$

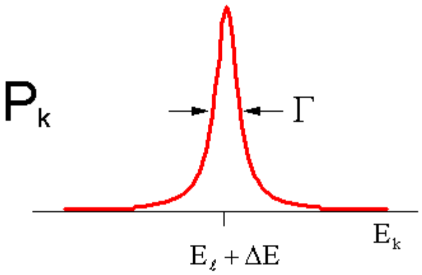
If we investigate the long time limit $\left(t\to\infty\right)$, noting that $P_{k\ell}=|b_k|^2$, we find

$$P_{k\ell}=\frac{\left|V_{k\ell}\right|^2}{\left(E_k-E'_\ell\right)^2+\Gamma^2/4} \tag{3.31}$$

with

$$\Gamma\equiv\overline{w}_{k\ell}\cdot\hbar \tag{3.32}$$

The probability distribution for occupying states within the continuum is described by a Lorentzian distribution with maximum probability centered at the corrected energy of the initial state E'_ℓ. The width of the distribution is given by the relaxation rate, which is proxy for $\left|V_{k\ell}\right|^2\rho(E_\ell)$, the coupling to the continuum and density of states.



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4. THE DENSITY MATRIX

The density matrix or density operator is an alternate representation of the state of a quantum system for which we have previously used the wavefunction. Although describing a quantum system with the density matrix is equivalent to using the wavefunction, one gains significant practical advantages using the density matrix for certain time-dependent problems—particularly relaxation and nonlinear spectroscopy in the condensed phase.

The density matrix is defined as the outer product of the wavefunction with its conjugate.

$$\rho(t) \equiv |\psi(t)\rangle\langle\psi(t)| \tag{4.1}$$

This implies that if you specify a state $|\chi\rangle$, $\langle\chi|\rho|\chi\rangle$ gives the probability of finding a particle in the state $|\chi\rangle$. Its name derives from the observation that it plays the quantum role of a probability density. If you think of the statistical description of a classical observable obtained from moments of a probability distribution P, then ρ plays the role of P in the quantum case:

$$\langle A\rangle = \int A\,P(A)\,dA \tag{4.2}$$

$$\langle A\rangle = \langle\psi|A|\psi\rangle = Tr[A\rho] \tag{4.3}$$

where $Tr[\ldots]$ refers to tracing over the diagonal elements of the matrix, $Tr[\cdots] = \sum_a \langle a|\cdots|a\rangle$.

The last expression is obtained as follows. If the wavefunction for the system is expanded as

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle \tag{4.4}$$

the expectation value of an operator is

$$\left\langle \hat{A}(t)\right\rangle = \sum_{n,m} c_n(t)\,c_m^*(t)\left\langle m\middle|\hat{A}\middle|n\right\rangle \tag{4.5}$$

Also, from eq. (4.1) we obtain the elements of the density matrix as

$$\begin{aligned}\rho(t) &= \sum_{n,m} c_n(t)\,c_m^*(t)|n\rangle\langle m| \\ &\equiv \sum_{n,m} \rho_{nm}(t)\,|n\rangle\langle m|\end{aligned} \tag{4.6}$$

We see that ρ_{nm}, the density matrix elements, are made up of the time-evolving expansion coefficients. Substituting into eq. (4.5) we see that

$$\begin{aligned}\left\langle \hat{A}(t)\right\rangle &= \sum_{n,m} A_{mn}\rho_{nm}(t) \\ &= Tr\left[\hat{A}\rho(t)\right]\end{aligned} \tag{4.7}$$

In practice this makes evaluating expectation values as simple as tracing over a product of matrices.

What information is in the density matrix elements, ρ_{mn}? The diagonal elements ($n = m$) give the probability of occupying a quantum state:

$$\rho_{nn} = c_n c_n^* = p_n \geq 0 \tag{4.8}$$

For this reason, diagonal elements are referred to as populations. The off-diagonal elements ($n \neq m$) are complex and have a time-dependent phase factor

$$\rho_{nm} = c_n(t)\, c_m^*(t) = c_n c_m^*\, \mathrm{e}^{-i\omega_{nm}t} \tag{4.9}$$

Since these describe the coherent oscillatory behavior of coherent superpositions in the system, these are referred to as coherences.

So why would we need the density matrix? It becomes a particularly important tool when dealing with mixed states, which we take up later. Mixed states refer to statistical mixtures in which we have imperfect information about the system, for which me must perform statistical averages in order to describe quantum observables. For mixed states, calculations with the density matrix are greatly simplified. Given that you have a statistical mixture, and can describe p_k, the probability of occupying quantum state $|\psi_k\rangle$, evaluation of expectation values is simplified with a density matrix:

$$\left\langle \hat{A}(t) \right\rangle = \sum_k p_k \left\langle \psi_k(t) \middle| \hat{A} \middle| \psi_k(t) \right\rangle \tag{4.10}$$

$$\rho(t) \equiv \sum_k p_k \left| \psi_k(t) \right\rangle \left\langle \psi_k(t) \right| \tag{4.11}$$

$$\left\langle \hat{A}(t) \right\rangle = Tr\left[\hat{A} \rho(t) \right] \tag{4.12}$$

Evaluating expectation value is the same for pure or mixed states.

Properties of the density matrix

We can now summarize some properties of the density matrix, which follow from the definitions above:

1) ρ is Hermitian since $\rho_{nm}^* = \rho_{mn}$
2) Since probability must be normalized, $Tr(\rho) = 1$
3) We can ascertain the degree of "pure-ness" of a quantum state from

$$Tr\left(\rho^2\right) \begin{cases} = 1 & \text{for pure state} \\ < 1 & \text{for mixed state} \end{cases}$$

In addition, when working with the density matrix it is convenient to make note of these trace properties:

1) The trace over a product of matrices is invariant to cyclic permutation of the matrices:

$$Tr\left(ABC\right)=Tr\left(CAB\right)=Tr\left(BCA\right)$$

2) From this result we see that the trace is invariant to unitary transformation:

$$Tr\left(S^{\dagger}AS\right)=Tr\left(S^{-1}AS\right)=Tr\left(A\right)$$

Time-evolution of the density matrix

The equation of motion for the density matrix follows naturally from the definition of ρ and the time-dependent Schrödinger equation.

$$\begin{aligned}\frac{\partial\rho}{\partial t}&=\frac{\partial}{\partial t}\big[|\psi\rangle\langle\psi|\big]\\&=\left[\frac{\partial}{\partial t}|\psi\rangle\right]\langle\psi|+|\psi\rangle\frac{\partial}{\partial t}\langle\psi|\\&=\frac{-i}{\hbar}H|\psi\rangle\langle\psi|+\frac{i}{\hbar}|\psi\rangle\langle\psi|H\end{aligned}\tag{4.13}$$

$$\frac{\partial\rho}{\partial t}=\frac{-i}{\hbar}\left[H,\rho\right]\tag{4.14}$$

Equation (4.14) is the Liouville-Von Neumann equation. It is isomorphic to the Heisenberg equation of motion, since ρ is also an operator. The solution to (4.14) is

$$\rho\left(t\right)=U\rho\left(0\right)U^{\dagger}\tag{4.15}$$

This can be demonstrated by first integrating eq. (4.14) to obtain

$$\rho(t)=\rho\left(0\right)-\frac{i}{\hbar}\int_0^t d\tau\left[H\left(\tau\right),\rho\left(\tau\right)\right]\tag{4.16}$$

If we expand eq. (4.16) by iteratively substituting into itself, the expression is the same as when we substitute

$$U=\exp_{+}\left[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)\right]\tag{4.17}$$

into eq. (4.15) and collect terms by orders of $H(\tau)$.

Note that eq. (4.15) and the cyclic invariance of the trace imply that the time-dependent expectation value of an operator can be calculated either by propagating the operator (Heisenberg) or the density matrix (Schrödinger or interaction picture):

$$\begin{aligned}\left\langle \hat{A}(t)\right\rangle &= Tr\left[\hat{A}\rho(t)\right]\\ &= Tr\left[\hat{A}U\,\rho_0\,U^\dagger\right]\\ &= Tr\left[\hat{A}(t)\,\rho_0\right]\end{aligned} \tag{4.18}$$

For a time-independent Hamiltonian it is straightforward to show that the density matrix elements evolve as

$$\rho_{nm}(t) = \left\langle n\middle|\rho(t)\middle|m\right\rangle = \langle n|U|\psi_0\rangle\langle\psi_0|U^\dagger|m\rangle \tag{4.19}$$

$$\rho_{nm}(t) = e^{-i\omega_{nm}(t-t_0)}\rho_{nm}(t_0) \tag{4.20}$$

From this we see that populations, $\rho_{nn}(t) = \rho_{nm}(t_0)$, are time-invariant, and coherences oscillate at the energy splitting ω_{nm}.

The density matrix in the interaction picture

For the case in which we wish to describe a material Hamiltonian H_0 under the influence of an external potential $V(t)$,

$$H(t) = H_0 + V(t) \tag{4.21}$$

we can also formulate the density operator in the interaction picture, ρ_I. From our original definition of the interaction picture wavefunctions

$$|\psi_I\rangle = U_0^\dagger|\psi_S\rangle \tag{4.22}$$

We obtain ρ_I as

$$\rho_I = U_0^\dagger\rho_S U_0 \tag{4.23}$$

Similar to the discussion of the density operator in the Schrödinger equation, above, the equation of motion in the interaction picture is

$$\frac{\partial\rho_I}{\partial t} = -\frac{i}{\hbar}\left[V_I(t),\rho_I(t)\right] \tag{4.24}$$

where, as before, $V_I = U_0^\dagger V U_0$.

Equation (4.24) can be integrated to obtain

$$\rho_I(t) = \rho_I(t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt' \left[V_I(t'), \rho_I(t')\right] \tag{4.25}$$

Repeated substitution of $\rho_I(t)$ into itself in this expression gives a perturbation series expansion

$$\begin{aligned}\rho_I(t) = \rho_0 &- \frac{i}{\hbar}\int_{t_0}^{t} dt_1 \left[V_I(t_1), \rho_0\right] \\ &+ \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \left[V_I(t_2), \left[V_I(t_1), \rho_0\right]\right] + \cdots \\ &+ \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \left[V_I(t_n), \left[V_I(t_{n-1}), \left[\ldots, \left[V_I(t_1), \rho_0\right]\ldots\right]\right]\right] \\ &+ \cdots\end{aligned} \tag{4.26}$$

$$\rho_I(t) = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \cdots + \rho^{(n)} + \cdots \tag{4.27}$$

Here $\rho_0 = \rho(t_0)$ and $\rho^{(n)}$ is the n$^{\text{th}}$-order expansion of the density matrix. This perturbative expansion will play an important role later in the description of nonlinear spectroscopy. An n^{th} order expansion term will be proportional to the observed polarization in an n^{th} order nonlinear spectroscopy, and the commutators observed in eq. (4.26) are proportional to nonlinear response functions. Similar to eq. (4.15), equation (4.26) can also be expressed as

$$\rho_I(t) = U_0\, \rho_I(0) U_0^{\dagger} \tag{4.28}$$

This is the solution to the Liouville equation in the interaction picture.

In describing the time-evolution of the density matrix, particularly when describing relaxation processes later, it is useful to use a superoperator notation to simplify the expressions above. The Liouville equation can be written in shorthand in terms of the Liovillian superoperator $\hat{\hat{\mathcal{L}}}$

$$\frac{\partial \hat{\rho}_I}{\partial t} = \frac{-i}{\hbar} \hat{\hat{\mathcal{L}}}\, \hat{\rho}_I \tag{4.29}$$

where $\hat{\hat{\mathcal{L}}}$ is defined in the Schrödinger picture as

$$\hat{\hat{\mathcal{L}}}\, \hat{A} \equiv \left[H, \hat{A}\right] \tag{4.30}$$

Similarly, the time propagation described by eq. (4.28) can also be written in terms of a superoperator $\hat{\hat{G}}$, the time-propagator, as

$$\rho_I(t) = \hat{\hat{G}}(t) \rho_I(0) \tag{4.31}$$

$\hat{\hat{G}}$ is defined in the interaction picture as

$$\hat{\hat{G}}\hat{A}_I \equiv U_0\,\hat{A}_I\,U_0^\dagger \tag{4.32}$$

Given the eigenstates of H_0, the propagation for a particular density matrix element is

$$\begin{aligned}\hat{\hat{G}}(t)\,\rho_{ab} &= e^{-iH_0t/\hbar}\left|a\right\rangle\left\langle b\right|e^{iH_0t/\hbar} \\ &= e^{-i\omega_{ab}t}\left|a\right\rangle\left\langle b\right|\end{aligned} \tag{4.33}$$

Using the Liouville space time-propagator, the evolution of the density matrix to arbitrary order in eq. (4.26) can be written as

$$\rho_I^{(n)} = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \ldots \int_{t_0}^{t_2} dt_1 \hat{G}(t-t_n)V(t_n)\hat{G}(t_n-t_{n-1})V(t_{n-1})\cdots\hat{G}(t_2-t_1)V(t_1)\rho_0\,. \tag{4.34}$$

5. THE ADIABATIC APPROXIMATION

In quantum mechanics, the adiabatic approximation refers to those solutions to the Schrödinger equation that make use of a time-scale separation between fast and slow degrees of freedom, and use this to find approximate solutions as product states in the fast and slow degrees of freedom. Perhaps the most fundamental and commonly used version is the Born–Oppenheimer (BO) approximation, which underlies much of how we conceive of molecular electronic structure and is the basis of potential energy surfaces. The BO approximation assumes that the motion of electrons is much faster than nuclei due to their large difference in mass, and therefore electrons adapt very rapidly to any changes in nuclear geometry. That is, the electrons "adiabatically follow" the nuclei. As a result, we can solve for the electronic state of a molecule for fixed nuclear configurations. Gradually stepping nuclear configurations and solving for the energy leads to a potential energy surface, or adiabatic state. Much of our descriptions of chemical reaction dynamics is presented in terms of propagation on these potential energy surfaces. The barriers on these surfaces are how we describe the rates of chemical reactions and transition state. The trajectories along these surfaces are used to describe mechanism.

More generally, the adiabatic approximation can be applied in other contexts in which there is a time-scale separation between fast and slow degrees of freedom. For instance, in the study of vibrational dynamics when the bond vibrations of molecules occur much faster than the intermolecular motions of a liquid or solid. It is also generally implicit in a separation of the Hamiltonian into a system and a bath, a method we will often use to solve condensed matter problems. As widely used as the adiabatic approximation is, there are times when it breaks down, and it is important to understand when this approximation is valid, and the consequences of when it is not. This will be particularly important for describing time-dependent quantum mechanical processes involving transitions between potential energy sources.

5.1. Born–Oppenheimer Approximation

As a starting point, it is helpful to review the Born–Oppenheimer Approximation (BOA). For a molecular system, the Hamiltonian can be written in terms of the kinetic energy of the nuclei (N) and electrons (e) and the potential energy for the Coulomb interactions of these particles.

$$\begin{aligned}\hat{H} &= \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{NN} + \hat{V}_{eN} \\ &= -\sum_{i=1}^{n} \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{J=1}^{N} \frac{\hbar^2}{2M_J}\nabla_J^2 \\ &\quad + \frac{1}{4\pi\varepsilon_0}\sum_{\substack{i,j=1 \\ j>i}}^{n} \frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} + \frac{1}{4\pi\varepsilon_0}\sum_{\substack{I,J=1 \\ J>I}}^{N} \frac{Z_I Z_J e^2}{\left|\mathbf{R}_I - \mathbf{R}_J\right|} - \frac{1}{4\pi\varepsilon_0}\sum_{i=1}^{n}\sum_{J=1}^{N} \frac{Z_J e^2}{\left|\mathbf{r}_i - \mathbf{R}_J\right|}\end{aligned} \tag{5.1}$$

Here and in the following, we will use lowercase variables to refer to electrons and uppercase to nuclei. The variables n, i, $\boldsymbol{r}$, ∇_r^2, and m_e refer to the number, index, position, Laplacian, and mass of electrons, respectively, and N, J, $\boldsymbol{R}$, and M refer to the nuclei. e is the electron charge, and Z is the atomic number of the nucleus. Note, this Hamiltonian does not include relativistic effects such as spin-orbit coupling.

The time-independent Schrödinger equation is

$$\hat{H}\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right)\Psi\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right)=E\Psi\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right) \tag{5.2}$$

$\Psi\left(\hat{\mathbf{r}},\hat{\mathbf{R}}\right)$ is the total vibronic wavefunction, where "vibronic" refers to the combined electronic and nuclear eigenstates. Exact solutions using the molecular Hamiltonian are intractable for most problems of interest, so we turn to simplifying approximations. The BO approximation is motivated by noting that the nuclei are far more massive than an electron ($m_e \ll M_I$). With this criterion, and when the distances separating particles is not unusually small, the kinetic energy of the nuclei is small relative to the other terms in the Hamiltonian. Physically, this means that the electrons move and adapt rapidly—adiabatically—in response to shifting nuclear positions. This offers an avenue to solving for Ψ by fixing the position of the nuclei, solving for the electronic wavefunctions ψ_i, and then iterating for varying $\boldsymbol{R}$ to obtain effective electronic potentials on which the nuclei move.

Since it is fixed for the electronic calculation, we proceed by treating $\boldsymbol{R}$ as a parameter rather than an operator, set $\hat{T}_N$ to 0, and solve the electronic TISE:

$$\hat{H}_{el}\left(\hat{\mathbf{r}},\mathbf{R}\right)\psi_i\left(\hat{\mathbf{r}},\mathbf{R}\right)=U_i\left(\mathbf{R}\right)\psi_i\left(\hat{\mathbf{r}},\mathbf{R}\right) \tag{5.3}$$

U_i are the electronic energy eigenvalues for the fixed nuclei, and the electronic Hamiltonian in the BO approximation is

$$\hat{H}_{el}=\hat{T}_e+\hat{V}_{ee}+\hat{V}_{eN} \tag{5.4}$$

In (5.3), ψ_i is the electronic wavefunction for fixed $\boldsymbol{R}$, with $i = 0$ referring to the electronic ground state. Repeating this calculation for varying $\boldsymbol{R}$, we obtain $U_i(\boldsymbol{R})$, an effective or mean-field potential for the electronic states on which the nuclei can move. These effective potentials are known as Born–Oppenheimer or adiabatic potential energy surfaces (PES).

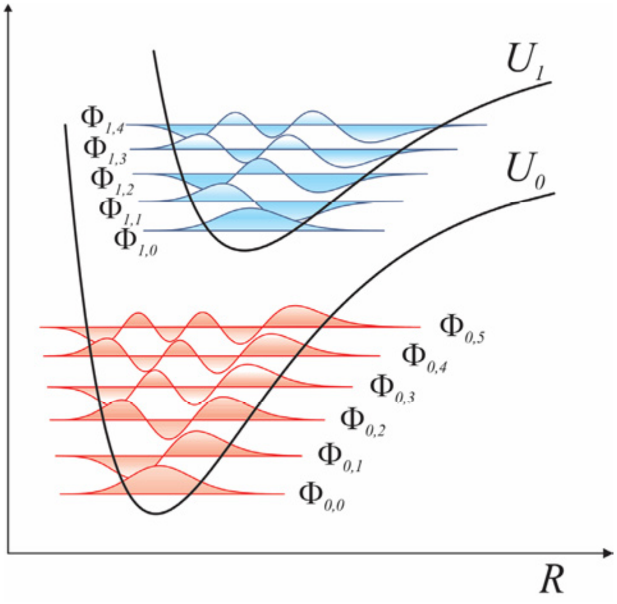
For the nuclear degrees of freedom, we can define a Hamiltonian for the i^{th} electronic PES:

$$\hat{H}_{Nuc,i}=\hat{T}_N+U_i(\hat{R}) \tag{5.5}$$

which satisfies a TISE for the nuclear wave functions $\Phi(R)$:

$$\hat{H}_{Nuc,i}\Phi_{iJ}(R) = E_{iJ}\Phi_{iJ}(R) \tag{5.6}$$

Here J refers to the J^{th} eigenstate for nuclei evolving on the i^{th} PES. Equation (5.5) is referred to as the BO Hamiltonian.



The BOA effectively separates the nuclear and electronic contributions to the wavefunction, allowing us to express the total wavefunction as a product of these contributions $\Psi(\mathbf{r},\mathbf{R}) = \Phi(\mathbf{R})\psi(\mathbf{r},\mathbf{R})$ and the eigenvalues as sums over the electronic and nuclear contribution: $E = E_N + E_e$. The BOA does not treat the nuclei classically. However, it is the basis for semiclassical dynamics methods in which the nuclei evolve classically on a potential energy surface, and interact with quantum electronic states. If we treat the nuclear dynamics classically, then the electronic Hamiltonian can be thought of as depending on **R** or on time as related by velocity or momenta. If the nuclei move infinitely slowly, the electrons will adiabatically follow the nuclei and systems prepared in an electronic eigenstate will remain in that eigenstate for all times.

5.2. Nonadiabatic Effects

Even without the BO approximation, we note that the nuclear-electronic product states form a complete basis in which to express the total vibronic wavefunction:

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_{i,J} c_{i,J}\Phi_{i,J}(\mathbf{R})\psi_i(\mathbf{r},\mathbf{R}) \tag{5.7}$$

We can therefore use this form to investigate the consequences of the BO approximation. For a given vibronic state, the action of the Hamiltonian on the wavefunction in the TISE is

$$\hat{H}\Psi_{i,J} = \left(\hat{T}_N(\mathbf{R}) + \hat{H}_{el}(\mathbf{R})\right)\Phi_{i,J}(\mathbf{R})\psi_i(\mathbf{R}) \tag{5.8}$$

Expanding the Laplacian in the nuclear kinetic energy via the chain rule as $\nabla^2 AB = (\nabla^2 A)B + 2(\nabla A)\nabla B + A\nabla^2 B$, we obtain an expression with three terms

$$\begin{aligned}\hat{H}\Psi_{i,J} &= \Phi_{i,J}(\mathbf{R})\left(\hat{T}_N(\mathbf{R}) + U_i(\mathbf{R})\right)\psi_i(\mathbf{R}) \\ &-\sum_J \frac{\hbar^2}{M_J}\nabla_R\Phi_{i,J}(\mathbf{R})\nabla_R\psi_i(\mathbf{R}) \\ &-\sum_J \frac{\hbar^2}{2M_J}\Phi_{i,J}(\mathbf{R})\nabla_R^2\psi_i(\mathbf{R})\end{aligned} \tag{5.9}$$

This expression is exact for vibronic problems, and is referred to as the coupled channel Hamiltonian. Note that if we set the last two terms in (5.9) to zero, we are left with $\hat{H} = \hat{T}_N + U$, which is just the Hamiltonian we used in the Born-Oppenheimer approximation, eq. (5.5). Therefore, the last two terms describe deviations from the BO approximation, and are referred to as nonadiabatic terms. These depend on the spatial gradient of the wavefunction in the region of interest, and act to couple adiabatic Born–Oppenheimer states.

The coupled channel Hamiltonian has a form that is reminiscent of a perturbation theory Hamiltonian in which the Born–Oppenheimer states play the role of the zero-order Hamiltonian being perturbed ay a nonadiabatic coupling *V*:

$$\hat{H} = \hat{H}_{BO} + \hat{V} \tag{5.10}$$

To investigate this relationship further, it is helpful to write this Hamiltonian in its matrix form. We obtain the matrix elements by sandwiching the Hamiltonian between two projection operators and evaluating

$$\hat{H}_{i,I,j,J} = \int\int d\mathbf{r}d\mathbf{R}\,\Psi_{i,I}^*(\mathbf{r},\mathbf{R})\hat{H}(\mathbf{r},\mathbf{R})\Psi_{j,J}(\mathbf{r},\mathbf{R})\,. \tag{5.11}$$

Making use of eq. (5.9) we find that the Hamiltonian can be expressed in three terms

$$\begin{aligned}\hat{H}_{i,I,j,J} &= \int d\mathbf{R}\,\Phi_{i,I}(\mathbf{R})\left(\hat{T}_N(\mathbf{R}) + U_j(\mathbf{R})\right)\Phi_{j,J}(\mathbf{R})\delta_{i,j} \\ &-\sum_I \frac{\hbar^2}{M_I}\int d\mathbf{R}\,\Phi_{i,I}(\mathbf{R})\nabla_R\Phi_{j,J}(\mathbf{R})\cdot\mathbf{F}_{ij}(\mathbf{R}) \\ &-\sum_I \frac{\hbar^2}{2M_I}\int d\mathbf{R}\,\Phi_{i,I}(\mathbf{R})\Phi_{j,J}(\mathbf{R})\mathbf{G}_{ij}(\mathbf{R})\end{aligned} \tag{5.12}$$

where

$$\begin{aligned}\mathbf{F}_{ij}(\mathbf{R}) &= \int d\mathbf{r}\,\psi_i^*(\mathbf{r},\mathbf{R})\nabla_R\psi_j(\mathbf{r},\mathbf{R}) \\ \mathbf{G}_{ij}(\mathbf{R}) &= \int d\mathbf{r}\,\psi_i^*(\mathbf{r},\mathbf{R})\nabla_R^2\psi_j(\mathbf{r},\mathbf{R})\end{aligned} \tag{5.13}$$

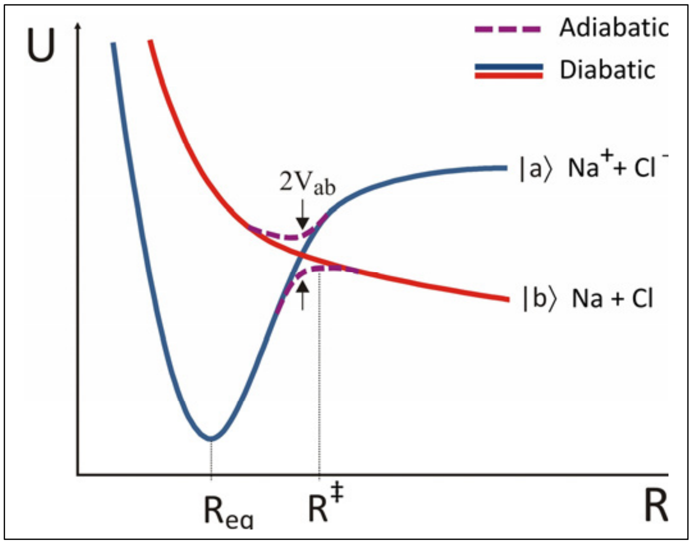
The first term in eqn. (5.12) gives the BO Hamiltonian. In the latter two terms, ***F*** is referred to as the nonadiabatic, first-order, or derivative coupling, and ***G*** is the second-order nonadiabatic coupling or diagonal BO correction. Although they are evaluated by integrating over electronic degrees of freedom, both depend parametrically on the position of the nuclei. In most circumstances the last term is much smaller than the other two, so that we can concentrate on the second term in evaluating couplings between adiabatic states. For our purposes, we can write the nonadiabatic coupling in equation (5.10) as

$$\hat{V}_{i,I,j,J}(\mathbf{R}) = -\sum_I \frac{\hbar^2}{M_I}\int d\mathbf{R}\,\Phi_{i,I}(\mathbf{R})\nabla_R\Phi_{j,J}(\mathbf{R})\cdot\mathbf{F}_{ij}(\mathbf{R}) \tag{5.14}$$

This emphasizes that the coupling between surfaces depends parametrically on the nuclear positions, the gradient of the electronic and nuclear wavefunctions, and the spatial overlap of those wavefunctions.

5.3. Diabatic and Adiabatic States

Although the Born–Oppenheimer surfaces are the most straightforward and commonly calculated, they may not be the most chemically meaningful states. As an example consider the potential energy curves for the diatomic NaCl. The chemically distinct potential energy surfaces one is likely to discuss have distinct atomic or ionic character at large separation between the atoms. These "diabatic" curves focus on physical effects, but are not eigenstates. In the figure, the ionic state $|a\rangle$ is influenced by the Coulomb attraction between ions that draws them together, leading to a stable configuration at R_{eq} once these attractive terms are balanced by nuclear repulsive forces. However, the neutral atoms (Na^0 and Cl^0) have a potential energy surface $|b\rangle$ which is dominated by repulsive interactions. The adiabatic potentials from the BO Hamiltonian will reflect significant coupling between the diabatic electronic states. BO states of the same symmetry will exhibit an avoided crossing where the electronic energy between corresponding diabatic states is equal. As expected from our earlier discussion, the splitting at the crossing for this one-dimensional system would be $2V_{ab}$, twice the coupling between diabatic states.



The adiabatic potential energy surfaces are important in interpreting the reaction dynamics, as can be illustrated with the reaction between Na and Cl atoms. If the neutral atoms are prepared on the ground state at large separation and slowly brought together, the atoms are weakly repelled until the separation reaches the transition state $R^{\ddagger}$. Here we cross into the regime where the ionic configuration has lower energy. As a result of the nonadiabatic couplings, we expect that an electron will transfer from Na^0 to Cl^0, and the ions will then feel an attractive force leading to an ionic bond with separation R_{eq}.

Diabatic states can be defined in an endless number of ways, but only one adiabatic surface exists. In that respect, the term "nonadiabatic" is also used to refer to all possible diabatic surfaces. However, diabatic states are generally chosen so that the nonadiabatic electronic couplings in eq. (5.13) are zero. This can be accomplished by making the electronic wavefunction independent of R.

As seen above, for coupled states with the same symmetry the couplings repel the adiabatic states and we get an avoided crossing. However, it is still possible for two adiabatic states to *cross*. Mathematically this requires that the energies of the adiabatic states be degenerate ($E_\alpha = E_\beta$) *and* that the coupling at that configuration be zero ($V_{\alpha\beta}=V_{\beta\alpha}=0$). This isn't possible for a one-dimensional problem, such as the NaCl example above, unless symmetry dictates that the nonadiabatic coupling vanishes. To accomplish this for a Hermitian coupling operator you need two independent nuclear coordinates, which enable you to independently tune the adiabatic splitting and coupling. This leads to a single point in the two-dimensional space at which degeneracy exists, which is known as a conical intersection (an important topic that is not discussed further here).

5.4. Adiabatic and Nonadiabatic Dynamics

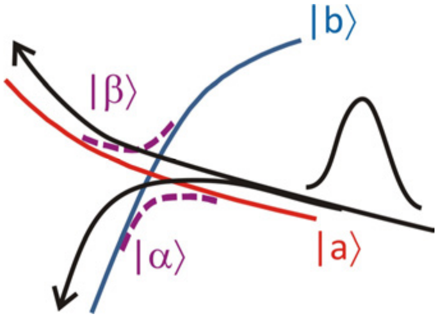
OK, so what does the discussion above mean for dynamics? The BO approximation never explicitly addresses electronic or nuclear dynamics, but neglecting the nuclear kinetic energy to obtain potential energy surfaces has implicit dynamical consequences. As we discussed for our NaCl example, moving the neutral atoms together slowly allows electrons to completely equilibrate about each forward step, resulting in propagation on the adiabatic ground state. This is the essence of the adiabatic approximation. If you prepare the system in Ψ_α, an eigenstate of H at the initial time t_0, and propagate slowly enough, that Ψ_α will evolve as an eigenstate for all times:

$$H(t)\Psi_\alpha(t) = E_\alpha(t)\Psi_\alpha(t) \tag{5.15}$$

Equivalently this means that the n^{th} eigenfunction of $H(t_0)$ will also be the n^{th} eigenfunction of $H(t)$. In this limit, there are no transitions between BO surfaces, and the dynamics only reflect the phases acquired from the evolving system. That is the time propagator can be expressed as

$$U(t,t_0)_{adiabatic} = \sum_\alpha |\alpha\rangle\langle\alpha| \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} dt'\, E_\alpha(t')\right) \tag{5.16}$$

In the opposite limit, we also know that if the atoms were incident on each other so fast (with such high kinetic energy) that the electron did not have time to transfer at the crossing, that the system would pass smoothly through the crossing along the diabatic surface. In fact it is expected that the atoms would collide and recoil. This implies that there is an intermediate regime in which the velocity of the system is such that the system will split and follow both surfaces to some degree.



In a more general sense, we would like to understand the criteria for adiabaticity that enable a time-scale separation between the fast and slow degrees of freedom. Speaking qualitatively about any time-dependent interaction between quantum mechanical states, the time-scale that separates the fast and slow propagation regimes is determined by the strength of coupling between those states. We know that two coupled states exchange amplitude at a rate dictated by the Rabi frequency Ω_R, which in turn depends on the energy splitting and coupling of the states. For systems in which there is significant nonperturbative transfer of population between two states *a* and *b*, the time scale over which this can occur is approximately $\Delta t \approx 1/\Omega_R \approx \hbar/V_{ab}$. This is not precise, but is provides a reasonable starting point for discussing "slow" versus "fast". "Slow" in an adiabatic sense would mean that a time-dependent interaction act on the system over a period such that $\Delta t \ll \hbar/V_{ab}$. In the case of our NaCl example, we would be concerned with the time scale over which the atoms pass through the crossing region between diabatic states, which is determined by the incident velocity between atoms.

Adiabaticity criterion

Let's investigate these issues by looking more carefully at the adiabatic approximation. Since the adiabatic states $\Psi_\alpha(t) \equiv |\alpha\rangle$ are orthogonal for all times, we can evaluate the time propagator as

$$U(t) = \sum_\alpha e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} |\alpha\rangle\langle\alpha| \tag{5.17}$$

and the time-dependent wavefunction is

$$\Psi(t) = \sum_\alpha b_\alpha(t)\, e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} |\alpha\rangle \tag{5.18}$$

Although these are adiabatic states we recognize that the expansion coefficients can be time-dependent in the general case. So, we would like to investigate the factors that govern this time-dependence. To make the notation more compact, let's define the time-rate of change of the eigenfunction as

$$|\dot{\alpha}\rangle = \frac{\partial}{\partial t}|\Psi_\alpha(t)\rangle \tag{5.19}$$

If we substitute the general solution eq. (5.18) into the TDSE, we get

$$i\hbar\sum_\alpha\left(\dot{b}_\alpha|\alpha\rangle + b_\alpha|\dot{\alpha}\rangle - \frac{i}{\hbar}E_\alpha b_\alpha|\alpha\rangle\right)e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} = \sum_\alpha b_\alpha E_\alpha|\alpha\rangle e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} \tag{5.20}$$

Note, the third term on the left hand side equals the right hand term. Acting on both sides from the left with $\langle\beta|$ leads to

$$-\dot{b}_\beta e^{-\frac{i}{\hbar}\int_0^t E_\beta(t')dt'} = \sum_\alpha b_\alpha\langle\beta|\dot{\alpha}\rangle e^{-\frac{i}{\hbar}\int_0^t E_\alpha(t')dt'} \tag{5.21}$$

We can break up the terms in the summation into one for the target state $|\beta\rangle$ and one for the remaining states.

$$-\dot{b}_\beta = b_\beta\langle\beta|\dot{\beta}\rangle + \sum_{\alpha\neq\beta} b_\alpha\langle\beta|\dot{\alpha}\rangle \exp\left[-\frac{i}{\hbar}\int_0^t dt'\, E_{\alpha\beta}(t')\right] \tag{5.22}$$

where $E_{\alpha\beta}(t) = E_\alpha(t) - E_\beta(t)$.

The adiabatic approximation applies when we can neglect the summation in eq. (5.22), or equivalently when $\langle\beta|\dot{\alpha}\rangle \ll \langle\beta|\dot{\beta}\rangle$ for all $|\alpha\rangle$. In that case, the system propagates on the adiabatic state $|\beta\rangle$ independent of the other states: $\dot{b}_\beta = -b_\beta\langle\beta|\dot{\beta}\rangle$. The evolution of the coefficients is

$$\begin{aligned} b_\beta(t) &= b_\beta(0)\exp\left[-\int_0^t \langle\beta(t')|\dot{\beta}(t')\rangle\, dt'\right] \\ &\approx b_\beta(0)\exp\left[\frac{i}{\hbar}\int_0^t E_\beta(t')\,dt'\right] \end{aligned} \tag{5.23}$$

Here we note that in the adiabatic approximation $E_\beta(t) = \langle\beta(t)\,|\,H(t)\,|\,\beta(t)\rangle$. Equation (5.23) indicates that in the adiabatic approximation the population in the states never changes, only their phase.

The second term on the right in eq. (5.22) describes the nonadiabatic effects, and the overlap integral

$$\langle\beta|\dot{\alpha}\rangle = \left\langle\Psi_\beta\left|\frac{\partial\Psi_\alpha}{\partial t}\right.\right\rangle \tag{5.24}$$

determines the magnitude of this effect. $\langle\beta|\dot{\alpha}\rangle$ is known as the nonadiabatic coupling (even though it refers to couplings between adiabatic surfaces), or as the geometrical phase. Note the parallels here to the expression for the nonadiabatic coupling in evaluating the validity of the Born-Oppenheimer approximation, however, here the gradient of the wavefunction is evaluated in time rather than the nuclear position. It would appear that we can make some connections between these two results by linking the gradient variables through the momentum or velocity of the particles involved.

So, when can we neglect the nonadiabatic effects? We can obtain an expression for the nonadiabatic coupling by expanding

$$\frac{\partial}{\partial t}\left[H\left|\alpha\right\rangle = E_\alpha\left|\alpha\right\rangle\right] \tag{5.25}$$

and acting from the left with $\left\langle\beta\right|$, which for $\alpha \neq \beta$ leads to

$$\left\langle\beta\middle|\dot{\alpha}\right\rangle = \frac{\left\langle\beta\middle|\dot{H}\middle|\alpha\right\rangle}{E_\alpha - E_\beta} \tag{5.26}$$

For adiabatic dynamics to hold $\left\langle\beta\middle|\dot{\alpha}\right\rangle << \left\langle\beta\middle|\dot{\beta}\right\rangle$, and so we can say

$$\frac{\left\langle\beta\middle|\dot{H}\middle|\alpha\right\rangle}{E_\alpha - E_\beta} << -\frac{i}{\hbar}E_\beta \tag{5.27}$$

So how accurate is the adiabatic approximation for a finite time-period over which the systems propagates? We can evaluate eq. (5.22), assuming that the system is prepared in state $|\alpha\rangle$ and that the occupation of this state never varies much from one. Then the occupation of any other state can be obtained by integrating over a period τ as

$$\begin{aligned}\dot{b}_\beta &= \left\langle\beta\middle|\dot{\alpha}\right\rangle \exp\left[-\frac{i}{\hbar}\int_0^\tau dt' E_{\alpha\beta}(t')\right] \\ b_\beta &\approx i\hbar\frac{\left\langle\beta\middle|\dot{H}\middle|\alpha\right\rangle}{E_{\alpha\beta}^2}\left\{\exp\left[-\frac{i}{\hbar}E_{\alpha\beta}\tau\right]-1\right\} \\ &= 2\hbar\frac{\left\langle\beta\middle|\dot{H}\middle|\alpha\right\rangle}{E_{\alpha\beta}^2}e^{-\frac{i}{\hbar}E_{\alpha\beta}\tau}\sin\left(\frac{E_{\alpha\beta}\tau}{2\hbar}\right)\end{aligned} \tag{5.28}$$

Here I used $e^{i\theta}-1 = 2i\,e^{i\theta/2}\sin(\theta/2)$. For $|b_\beta| << 1$, we expand the *sin* term and find

$$\left\langle\Psi_\beta\middle|\frac{\partial H}{\partial t}\middle|\Psi_\alpha\right\rangle \ll E_{\alpha\beta}/\tau \tag{5.29}$$

This is the criterion for adiabatic dynamics, which can be seen to break down near adiabatic curve crossings where $E_{\alpha\beta} = 0$, regardless of how fast we propagate through the crossing. Even away from curve crossing, there is always the possibility that nuclear kinetic energies are such that $(\partial H / \partial t)$ will be greater than or equal to the energy splitting between adiabatic states.

5.5. Landau–Zener Transition Probability

Clearly the adiabatic approximation has significant limitations in the vicinity of curve crossings. This phenomenon is better described through transitions between diabatic surfaces. To begin, how do we link the temporal and spatial variables in the curve crossing picture? We need a time-rate of change of the energy splitting, $\dot{E} = dE_{ab} / dt$. The Landau–Zener expression gives the transition probabilities as a result of propagating through the crossing between *diabatic* surfaces at a constant $\dot{E}$. If the energy splitting between states varies linearly in time near the crossing point, then setting the crossing point to $t = 0$ we write

$$E_a - E_b = \dot{E}t \tag{5.30}$$

If the coupling between surfaces V_{ab} is constant, the transition probability for crossing from surface *a* to *b* for a trajectory that passes through the crossing is

$$P_{ba} = 1 - \exp\left[-\frac{2\pi V_{ab}^2}{\hbar \left| \dot{E} \right|} \right] \tag{5.31}$$

and $P_{aa} = 1 - P_{ba}$. Note if $V_{ab} = 0$ then $P_{ba} = 0$, but if the splitting sweep rate $\dot{E}$ is small as determined by

$$2\pi V_{ab}^2 >> \hbar \left| \dot{E} \right| \tag{5.32}$$

then we obtain the result expected for the adiabatic dynamics $P_{ba} \approx 1$.

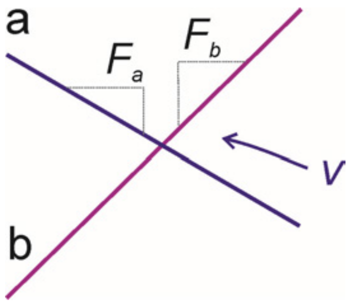
We can provide a classical interpretation to eq. (5.31) by equating $\dot{E}$ with the velocity of particles involved in the crossing. We define the velocity as $v = \partial R / \partial t$, and the slope of the diabatic surfaces at the crossing, $F_i = \partial E_i / \partial R$. Recognizing

$$\left(E_a - E_b \right) / t = v \left(F_a - F_b \right) \tag{5.33}$$

we find

$$P_{ba} = 1 - \exp\left[-\frac{2\pi V_{ab}^2}{\hbar v \left| F_a - F_b \right|} \right] \tag{5.34}$$

In the context of potential energy surfaces, what this approximation says is that you need to know the slopes of the potentials at their crossing point, the coupling and their relative velocity in order to extract the rates of chemical reactions.



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6. INTERACTION OF LIGHT AND MATTER

6.1 Electric Dipole Hamiltonian

One of the most important applications of time-dependent quantum mechanics for chemists is spectroscopy, which refers to the study of interaction of matter with electromagnetic radiation (called light for short). Classically, light–matter interactions are a result of an oscillating electromagnetic field resonantly interacting with charged particles in the matter (most often bound electrons). Quantum mechanically, a light field acts to couple the quantum states associated with the charged particles, as we have discussed earlier.

Our starting point is to write a general Hamiltonian for this problem as a sum of contributions from the matter H_M, the light H_L, and the light-matter interaction H_{LM},

$$H = H_M + H_L + H_{LM} \tag{6.1}$$

Although the Hamiltonian for the matter may be time dependent, the time-dependent phenomena of interest here are the electromagnetic field and its interaction with the matter. A quantum mechanical treatment of the light describes the light in terms of photons for different modes of electromagnetic radiation, which we will address later.

We will start with semiclassical treatment of the problem. For this approach we treat the matter quantum mechanically, and treat the light field classically. For the field we assume that the action of the light on the matter is a time-dependent potential, but the matter does not influence the light. (Energy conservation requires the change in the matter to be raised in the quantum state of the system and annihilation of a photon from the light field. We will deal with this in detail later). We are just interested in the effect that the light has on the matter. In that case, we can really ignore H_L, and we have a Hamiltonian for the system, which is

$$\begin{aligned} H &\approx H_M + H_{LM}(t) \\ &= H_0 + V(t) \end{aligned} \tag{6.2}$$

Now we derive an explicit expression for the Hamiltonian in the Electric Dipole approximation. The standard procedure is to first write down a classical Hamiltonian, and then replace the classical dynamical variables of matter with suitable quantum operators:

$$\begin{aligned} p &\rightarrow -i\hbar\hat{\nabla} \\ x &\rightarrow \hat{x} \end{aligned} \tag{6.3}$$

In order to get the classical Hamiltonian, we need to work through two steps: (1) We need to describe electromagnetic fields, specifically in terms of a vector potential, and (2) we need to describe how the electromagnetic field interacts with charged particles.

Brief summary of electrodynamics

Let's summarize the description of electromagnetic fields that we will use. A derivation of the plane wave solutions to the electric and magnetic fields and vector potential is described in the appendix. Also, it is helpful to review this material in Jackson[1] or Cohen-Tannoudji, et al.[2]

Maxwell's Equations describe electric and magnetic fields $\left(\overline{E}, \overline{B}\right)$; however, to construct a Hamiltonian, we must use the time-dependent interaction potential (rather than a field). To construct the potential representation of $\overline{E}$ and $\overline{B}$, you need a vector potential $\overline{A}\left(\overline{r},t\right)$ and a scalar potential $\varphi\left(\overline{r},t\right)$. For electrostatics we normally think of the field being related to the electrostatic potential through $\overline{E} = -\nabla\varphi$, but for a field that varies in time and in space, the electrodynamic potential must be expressed in terms of both $\overline{A}$ and φ.

In general an electromagnetic wave written in terms of the electric and magnetic fields requires six variables (the *x, y,* and *z* components of *E* and *B*). This is an over determined problem; Maxwell's equations constrain these. The potential representation has four variables (A_x, A_y, A_z and φ), but these are still not uniquely determined. We choose a constraint—a representation or guage—that allows us to uniquely describe the wave. Choosing a gauge such that $\varphi = 0$ (Coulomb gauge) leads to a unique description of $\overline{E}$ and $\overline{B}$:

$$-\overline{\nabla}^2\overline{A}\left(\overline{r},t\right) + \frac{1}{c^2}\frac{\partial^2\overline{A}\left(\overline{r},t\right)}{\partial t^2} = 0 \tag{6.4}$$

$$\overline{\nabla}\cdot\overline{A} = 0 \tag{6.5}$$

This wave equation for the vector potential gives a plane wave solution for free space:

$$\overline{A}\left(\overline{r},t\right) = A_0\hat{\varepsilon}\, e^{i\left(\overline{k}\cdot\overline{r}-\omega t\right)} + A_0^*\hat{\varepsilon}\, e^{-i\left(\overline{k}\cdot\overline{r}-\omega t\right)} \tag{6.6}$$

This describes the wave oscillating in time at an angular frequency ω and propagating in space in the direction along the wave vector $\overline{k}$, with a spatial period $\lambda = 2\pi/\left|\overline{k}\right|$. The wave has an amplitude A_0 which is directed along the polarization unit vector $\hat{\varepsilon}$. Since $\overline{\nabla}\cdot\overline{A} = 0$, we see that $\overline{k}\cdot\hat{\varepsilon} = 0$ or $\overline{k}\perp\hat{\varepsilon}$. From the vector potential we can obtain $\overline{E}$ and $\overline{B}$

$$\begin{aligned}\overline{E} &= -\frac{\partial\overline{A}}{\partial t} \\ &= i\omega A_0\,\hat{\varepsilon}\left(e^{i\left(\overline{k}\cdot\overline{r}-\omega t\right)} - e^{-i\left(\overline{k}\cdot\overline{r}-\omega t\right)}\right)\end{aligned} \tag{6.7}$$

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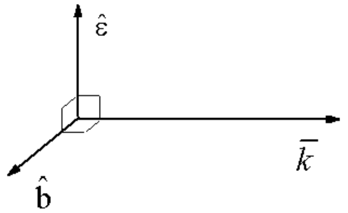
[1] Jackson, J. D. *Classical Electrodynamics* (John Wiley and Sons, New York, 1975).

[2] Cohen-Tannoudji, C., Diu, B. & Lalöe, F. *Quantum Mechanics* (Wiley-Interscience, Paris, 1977), Appendix III.

$$\begin{aligned}\bar{B} &= \bar{\nabla}\times\bar{A}\\ &= i\left(\bar{k}\times\hat{\varepsilon}\right)A_0\left(e^{i\left(\bar{k}\cdot\bar{r}-\omega t\right)}-e^{-i\left(\bar{k}\cdot\bar{r}-\omega t\right)}\right)\end{aligned}\tag{6.8}$$

If we define a unit vector along the magnetic field polarization as $\hat{b}=\left(\bar{k}\times\hat{\varepsilon}\right)/\left|\bar{k}\right|=\hat{k}\times\hat{\varepsilon}$, we see that the wave vector, the electric field polarization and magnetic field polarization are mutually orthogonal $\hat{k}\perp\hat{\varepsilon}\perp\hat{b}$.



Also, by comparing eq. (6.6) and (6.7) we see that the vector potential oscillates as *cos*(ωt), whereas the electric and magnetic fields oscillate as *sin*(ωt). If we define

$$\frac{1}{2}E_0 = i\omega A_0 \qquad 9)$$

$$\frac{1}{2}B_0 = i\left|k\right|A_0\tag{6.10}$$

then,

$$\bar{E}\left(\bar{r},t\right)=\left|E_0\right|\hat{\varepsilon}\sin\left(\bar{k}\cdot\bar{r}-\omega t\right)\tag{6.11}$$

$$\bar{B}\left(\bar{r},t\right)=\left|B_0\right|\hat{b}\sin\left(\bar{k}\cdot\bar{r}-\omega t\right)\tag{6.12}$$

Note, $E_0/B_0=\omega/\left|k\right|=c$.

Classical Hamiltonian for radiation field interacting with charged particle

Now, let's find a classical Hamiltonian that describes charged particles in a field in terms of the vector potential. Start with Lorentz force[3] on a particle with charge *q*:

$$\bar{F}=q\left(\bar{E}+\bar{v}\times\bar{B}\right)\tag{6.13}$$

Here $\bar{v}$ is the velocity of the particle. Writing this for one direction (*x*) in terms of the Cartesian components of $\bar{E}$, $\bar{v}$ and $\bar{B}$, we have:

$$F_x=q\left(E_x+v_yB_z-v_zB_y\right)\tag{6.14}$$

In Lagrangian mechanics, this force can be expressed in terms of the total potential energy *U* as

$$F_x=-\frac{\partial U}{\partial x}+\frac{d}{dt}\left(\frac{\partial U}{\partial v_x}\right)\tag{6.15}$$

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[3] See Schatz and Ratner, p.82-83.

Using the relationships that describe $\overline{E}$ and $\overline{B}$ in terms of $\overline{A}$ and φ, inserting into eq. (6.14), and working it into the form of eq. (6.15), we can show that:

$$U = q\varphi - q\overline{v}\cdot\overline{A} \tag{6.16}$$

This is derived in CTDL,[4] and you can confirm by replacing it into eq. (6.15).

Now we can write a Lagrangian in terms of the kinetic and potential energy of the particle

$$L = T - U \tag{6.17}$$

$$L = \frac{1}{2}m\overline{v}^2 + q\overline{v}\cdot\overline{A} - q\varphi \tag{6.18}$$

The classical Hamiltonian is related to the Lagrangian as

$$\begin{aligned} H &= \overline{p}\cdot\overline{v} - L \\ &= \overline{p}\cdot\overline{v} - \tfrac{1}{2}m\overline{v}^2 - q\overline{v}\cdot\overline{A} - q\varphi \end{aligned} \tag{6.19}$$

Recognizing
$$\overline{p} = \frac{\partial L}{\partial \overline{v}} = m\overline{v} + q\overline{A} \tag{6.20}$$

we write
$$\overline{v} = \tfrac{1}{m}\left(\overline{p} - q\overline{A}\right) \tag{6.21}$$

Now substituting (6.21) into (6.19), we have:

$$H = \tfrac{1}{m}\overline{p}\cdot\left(\overline{p} - q\overline{A}\right) - \tfrac{1}{2m}\left(\overline{p} - q\overline{A}\right)^2 - \tfrac{q}{m}\left(\overline{p} - q\overline{A}\right)\cdot A + q\varphi \tag{6.22}$$

$$H = \frac{1}{2m}\left[\overline{p} - q\overline{A}\left(\overline{r},t\right)\right]^2 + q\varphi\left(\overline{r},t\right) \tag{6.23}$$

This is the classical Hamiltonian for a particle in an electromagnetic field. In the Coulomb gauge $\left(\varphi = 0\right)$, the last term is dropped.

We can write a Hamiltonian for a single particle in a bound potential V_0 in the *absence* of an external field as

$$H_0 = \frac{\overline{p}^2}{2m} + V_0\left(\overline{r}\right) \tag{6.24}$$

and in the *presence* of the EM field:

$$H = \frac{1}{2m}\left(\overline{p} - q\overline{A}\left(\overline{r},t\right)\right)^2 + V_0\left(\overline{r}\right) \tag{6.25}$$

Expanding:
$$H = H_0 - \frac{q}{2m}\left(\overline{p}\cdot\overline{A} + \overline{A}\cdot\overline{p}\right) + \frac{q^2}{2m}\left|\overline{A}\left(\overline{r},t\right)\right|^2 \tag{6.26}$$

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[4] Cohen-Tannoudji, et al. app. III, p. 1492.

Generally the last term which goes as the square of A is small compared to the cross term which is proportional to first power of A. This term should be considered for extremely high field strength, which is non-perturbative and significantly distorts the potential binding molecules together, i.e., when it is similar in magnitude to V_0. One can estimate that this would start to play a role at intensity levels $>10^{15}$ W/cm^2, which may be observed for very high energy and tightly focused pulsed femtosecond lasers. So, for weak fields we have an expression that maps directly onto solutions we can formulate in the interaction picture:

$$H = H_0 + V(t) \tag{6.27}$$

$$V(t) = \frac{q}{2m}\left(\bar{p}\cdot\bar{A} + \bar{A}\cdot\bar{p}\right) \tag{6.28}$$

Quantum mechanical electric dipole Hamiltonian

Now we are in a position to substitute the quantum mechanical momentum for the classical. Here the vector potential remains classical, and only modulates the interaction strength.

$$\bar{p} = -i\hbar\bar{\nabla} \tag{6.29}$$

$$V(t) = \frac{i\hbar}{2m} q\left(\bar{\nabla}\cdot\bar{A} + \bar{A}\cdot\bar{\nabla}\right) \tag{6.30}$$

We can show that $\bar{\nabla}\cdot\bar{A} = \bar{A}\cdot\bar{\nabla}$. For instance, if we are operating on a wavefunction on the right, we can use the chain rule to write $\bar{\nabla}\cdot(\bar{A}\,|\psi\rangle) = \left(\bar{\nabla}\cdot\bar{A}\right)|\psi\rangle + \bar{A}\cdot\left(\bar{\nabla}|\psi\rangle\right)$. The first term is zero since we are working in the Coulomb gauge $\left(\bar{\nabla}\cdot\bar{A} = 0\right)$. Now we have:

$$\begin{aligned} V(t) &= \frac{i\hbar q}{m}\,\bar{A}\cdot\bar{\nabla} \\ &= -\frac{q}{m}\bar{A}\cdot\hat{p} \end{aligned} \tag{6.31}$$

Now we can generalize (6.31) for the case of multiple charged particles, as would be appropriate for interactions involving a molecular Hamiltonian:

$$V(t) = -\sum_j \frac{q_j}{m_j}\bar{A}\left(\bar{r}_j, t\right)\cdot\hat{p}_j \tag{6.32}$$

$$V(t) = -\sum_j \frac{q_j}{m_j}\left[A_0\hat{\varepsilon}\cdot\hat{p}_j\; e^{i\left(\bar{k}\cdot\bar{r}_j - \omega t\right)} + A_0^*\hat{\varepsilon}\cdot\hat{p}_j^\dagger\; e^{-i\left(\bar{k}\cdot\bar{r}_j - \omega t\right)}\right] \tag{6.33}$$

Under most of the circumstances we will encounter, we can neglect the wave vector dependence of the interaction potential. This applies if the wavelength of the field is much larger than the dimensions of the molecules we are interrogating, i.e. $(\lambda \to \infty)\left(|k| \to 0\right)$. To see this, let's define r_0 as the center of mass of a molecule and expand about that position

$$\begin{aligned} e^{i\bar{k}\cdot\bar{r}_i} &= e^{i\bar{k}\cdot\bar{r}_0}\, e^{i\bar{k}\cdot(\bar{r}_i-\bar{r}_0)} \\ &= e^{i\bar{k}\cdot\bar{r}_0}\, e^{i\bar{k}\cdot\delta\bar{r}_i} \end{aligned} \tag{6.34}$$

For interactions, with UV, visible, and infrared radiation, wavelengths are measured in hundreds to thousands of nanometers. This is orders of magnitude larger than the dimensions that describe charge distributions in molecules ($\delta\bar{r}_i = \bar{r}_i - \bar{r}_0$). Under those circumstances $|k|\delta r_i << 1$, and setting $\bar{r}_0 = 0$ means that $e^{i\bar{k}\cdot\bar{r}} \to 1$. This is known as the electric dipole approximation. Implicit in this is also the statement that all molecules within a macroscopic volume experience an interaction with a spatially uniform, homogeneous electromagnetic field.

Certainly there are circumstances where the electric dipole approximation is poor. In the case where the wavelength of light in on the same scale as molecular dimensions, the light will now have to interact with spatially varying charge distributions, which will lead to scattering of the light and interferences between the scattering between different spatial regions. We will not concern ourselves with this limit further.

We also retain the spatial dependence for certain other types of light–matter interactions. For instance, we can expand eq. (6.34) as

$$e^{i\bar{k}\cdot\bar{r}_i} \approx e^{i\bar{k}\cdot\bar{r}_0}\left[1 + i\bar{k}\cdot(\bar{r}_i - \bar{r}_0) + \ldots\right] \tag{6.35}$$

We retain the second term for quadrupole transitions: charge distribution interacting with gradient of electric field and magnetic dipole.

Now, using $A_0 = iE_0/2\omega$, we write (6.31) as

$$V(t) = \frac{-iqE_0}{2m\omega}\left[\hat{\varepsilon}\cdot\hat{p}\, e^{-i\omega t} - \hat{\varepsilon}\cdot\hat{p}\, e^{i\omega t}\right] \tag{6.36}$$

$$\begin{aligned} V(t) &= \frac{-qE_0}{m\omega}(\hat{\varepsilon}\cdot\hat{p})\sin\omega t \\ &= \frac{-q}{m\omega}\left(\bar{E}(t)\cdot\hat{p}\right) \end{aligned} \tag{6.37}$$

or for a collection of charged particles (molecules):

$$V(t) = -\left(\sum_j \frac{q_j}{m_j}(\hat{\varepsilon}\cdot\hat{p}_j)\right)\frac{E_0}{\omega}\sin\omega t \tag{6.38}$$

This is the interaction Hamiltonian in the electric dipole approximation.

Transition dipole matrix elements

In order to physically interpret eq. (6.38) it is first helpful to evaluate matrix elements in this Hamiltonian. Note in first order perturbation matrix element calculations one uses unperturbed wavefunctions. Thus we evaluate the matrix elements of the electric dipole Hamiltonian using the eigenfunctions of H_0:

$$V_{k\ell} = \langle k | V_0 | \ell \rangle = \frac{-qE_0}{m\omega} \langle k | \hat{\varepsilon} \cdot \hat{p} | \ell \rangle \tag{6.39}$$

We can evaluate $\langle k | \overline{p} | \ell \rangle$ using an expression that holds for any one-particle Hamiltonian:

$$\left[\hat{r}, \hat{H}_0 \right] = \frac{i\hbar \hat{p}}{m} \tag{6.40}$$

This expression gives

$$\begin{aligned} \langle k | \hat{p} | \ell \rangle &= \frac{m}{i\hbar} \langle k | \hat{r} \hat{H}_0 - \hat{H}_0 \hat{r} | \ell \rangle \\ &= \frac{m}{i\hbar} \left(\langle k | \hat{r} | \ell \rangle E_\ell - E_k \langle k | \hat{r} | \ell \rangle \right) \\ &= i m \omega_{k\ell} \langle k | \hat{r} | \ell \rangle . \end{aligned} \tag{6.41}$$

So we have

$$V_{k\ell} = -iqE_0 \frac{\omega_{k\ell}}{\omega} \langle k | \hat{\varepsilon} \cdot \overline{r} | \ell \rangle \tag{6.42}$$

or for many charged particles

$$V_{k\ell} = -iE_0 \frac{\omega_{k\ell}}{\omega} \left\langle k \middle| \hat{\varepsilon} \cdot \sum\nolimits_j q_j \hat{r}_j \middle| \ell \right\rangle \tag{6.43}$$

The matrix element includes an operator that describes the spatial distribution of charges, the dipole operator

$$\hat{\mu} = \sum\nolimits_j q_j \hat{r}_j \tag{6.44}$$

We can see that it is the quantum analog of the classical dipole moment, which describes the distribution of charge density ρ in the molecule:

$$\overline{\mu} = \int d\overline{r} \, \overline{r} \, \rho(\overline{r}) . \tag{6.45}$$

The matrix elements in the dipole operator μ_{kl} are known as transition dipole matrix elements:

$$\begin{aligned} V_{k\ell} &= -iE_0 \frac{\omega_{k\ell}}{\omega} \langle k | \hat{\varepsilon} \cdot \overline{\mu} | \ell \rangle \\ &= -iE_0 \frac{\omega_{k\ell}}{\omega} \mu_{kl} \end{aligned} \tag{6.46}$$

These expressions allow us to write in a simplified form the well-known interaction potential for a dipole in a field:

$$V(t) = -\,\bar{\mu}\cdot\bar{E}(t) \tag{6.47}$$

Here we note that we have reversed the order of terms, since they commute.

We are seeking to use this Hamiltonian to evaluate the transition rates induced by $V(t)$ from our first-order perturbation theory expression. For a perturbation $V(t) = V_0 \sin\omega t$ the rate of transitions induced by field is

$$w_{k\ell} = \frac{\pi}{2\hbar}\left|V_{k\ell}\right|^2\left[\delta\left(E_k - E_\ell - \hbar\omega\right) + \delta\left(E_k - E_\ell + \hbar\omega\right)\right] \tag{6.48}$$

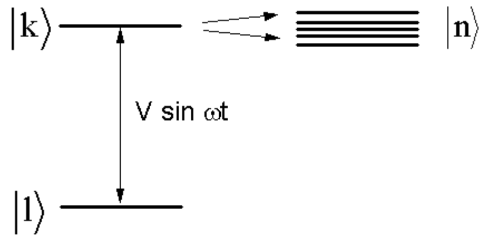
or

$$\begin{aligned} w_{k\ell} &= \frac{\pi}{2\hbar}\left|E_0\right|^2\frac{\omega_{k\ell}^2}{\omega^2}\left|\bar{\mu}_{kl}\right|^2\left[\delta\left(E_k - E_\ell - \hbar\omega\right) + \left(E_k - E_\ell + \hbar\omega\right)\right] \\ &= \frac{\pi}{2\hbar^2}\left|E_0\right|^2\left|\bar{\mu}_{kl}\right|^2\left[\delta\left(\omega_{k\ell} - \omega\right) + \delta\left(\omega_{k\ell} + \omega\right)\right] \end{aligned} \tag{6.49}$$

Equation (6.49) is an expression for the absorption and emission spectrum since the rate of transitions can be related to the power absorbed from or emitted to the field. The strength of interaction between light and matter is given by the matrix element μ_{kl}. In order that we have absorption, the part $\langle f|\mu|i\rangle$, which is a measure of change of charge distribution between $|f\rangle$ and $|i\rangle$, should be non-zero. In other words, the incident radiation has to induce a change in the charge distribution of matter to get an effective absorption rate. This matrix element is the basis of selection rules based on the symmetry of the matter charge eigenstates. The second part, namely the electric field polarization vector says that the electric field of the incident radiation field must project onto the matrix elements of the dipole moment between the final and initial sates of the charge distribution. Thus one can get information on the orientation of molecules using polarized light.

Relaxation leads to line-broadening

Let’s combine the results from the last two lectures, and describe absorption to a state that is coupled to a continuum. What happens to the probability of absorption if the excited state decays exponentially?



$|k\rangle$ relaxes exponentially
... for instance by coupling to continuum
$P_k \propto \exp\left[-\bar{w}_{nk} t\right]$

We can start with the first-order expression:

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{k\ell} t}\, V_{k\ell}\left(t\right) \tag{6.50}$$

where we make the approximation $b_\ell\left(t\right) \approx 1$. We can add irreversible relaxation to the description of b_k, using our earlier expression for the relaxation of $b_k\left(t\right) = \exp\left[-\bar{w}_{nk} t/2 - i\Delta E_k t/\hbar\right]$. In this case we will neglect the correction to the energy $\Delta E_k = 0$

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{k\ell} t}\, V_{k\ell}\left(t\right) - \frac{\bar{w}_{nk}}{2} b_k \tag{6.51}$$

Or using $V\left(t\right) = -iE_0 \bar{\mu}_{k\ell} \sin\omega t$

$$\begin{aligned} \frac{\partial}{\partial t} b_k &= \frac{-i}{\hbar} e^{i\omega_{k\ell} t} \sin\omega t\, V_{k\ell} - \frac{\bar{w}_{nk}}{2} b_k\left(t\right) \\ &= \frac{E_0\, \omega_{k\ell}}{2i\hbar\omega}\left[e^{i\left(\omega_{k\ell}+\omega\right)t} - e^{i\left(\omega_{k\ell}-\omega\right)t}\right]\bar{\mu}_{k\ell} - \frac{\bar{w}_{nk}}{2} b_k\left(t\right) \end{aligned} \tag{6.52}$$

The solution to the differential equation

$$\dot{y} + ay = b\,e^{i\alpha t} \tag{6.53}$$

is

$$y\left(t\right) = A\,e^{-at} + \frac{b\,e^{i\alpha t}}{a + i\alpha} \tag{6.54}$$

$$b_k\left(t\right) = A\,e^{-\bar{w}_{nk} t/2} + \frac{E_0\, \bar{\mu}_{k\ell}}{2i\hbar}\left[\frac{e^{i\left(\omega_{k\ell}+\omega\right)t}}{\bar{w}_{nk}/2 + i\left(\omega_{k\ell}+\omega\right)} - \frac{e^{i\left(\omega_{k\ell}-\omega\right)t}}{\bar{w}_{nk}/2 + i\left(\omega_{k\ell}-\omega\right)}\right] \tag{6.55}$$

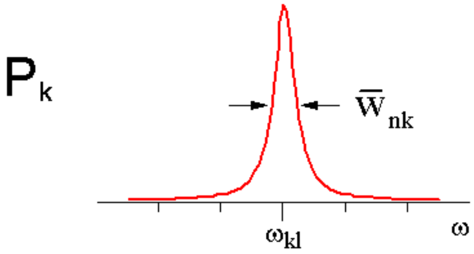
Let’s look at absorption only, in the long time limit:

$$b_k\left(t\right) = \frac{E_0 \bar{\mu}_{k\ell}}{2\hbar}\left[\frac{e^{i\left(\omega_{k\ell}-\omega\right)t}}{\omega_{k\ell} - \omega - i\bar{w}_{nk}/2}\right] \tag{6.56}$$

For which the probability of transition to *k* is

$$P_k = \left|b_k\right|^2 = \frac{E_0^2 \left|\mu_{k\ell}\right|^2}{4\hbar^2} \frac{1}{\left(\omega_{k\ell} - \omega\right)^2 + \overline{w}_{nk}{}^2 / 4} \tag{6.57}$$

The frequency dependence of the transition probability has a Lorentzian form:



The FWHM linewidth gives the relaxation rate from *k* into the continuum *n*. Also the linewidth is related to the system rather than the manner in which we introduced the perturbation. The line width or line shape is an additional feature that we interpret in our spectra, and commonly originates from irreversible relaxation or other processes that destroy the coherence first set up by the light field.

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; Appendix III.
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3. McHale, J. L., *Molecular Spectroscopy*. 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1999.
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6.2. Supplement: Review of Free Electromagnetic Field

Maxwell's Equations in SI units are:

(1) $$\bar{\nabla}\cdot\bar{B}=0$$

(2) $$\bar{\nabla}\cdot\bar{E}=\rho/\varepsilon_0$$

(3) $$\bar{\nabla}\times\bar{E}=-\frac{\partial\bar{B}}{\partial t}$$

(4) $$\bar{\nabla}\times\bar{B}=\mu_0\bar{J}+\varepsilon_0\mu_0\frac{\partial\bar{E}}{\partial t}$$

$\bar{E}$: electric field; $\bar{B}$: magnetic field; $\bar{J}$: current density; ρ: charge density; ε_0: electrical permittivity; μ_0: magnetic permittivity.

We are interested in describing $\bar{E}$ and $\bar{B}$ in terms of a scalar and vector potential. This is required for our interaction Hamiltonian.

Generally: A vector field $\bar{F}$ assigns a vector to each point in space. The divergence of the field

(5) $$\bar{\nabla}\cdot\bar{F}=\frac{\partial F_x}{\partial x}+\frac{\partial F_y}{\partial y}+\frac{\partial F_z}{\partial z}$$

is a scalar. For a scalar field ϕ, the gradient

(6) $$\nabla\phi=\frac{\partial\phi}{\partial x}\hat{x}+\frac{\partial\phi}{\partial y}\hat{y}+\frac{\partial\phi}{\partial z}\hat{z}$$

is a vector for the rate of change at one point in space. Here $\hat{x}^2+\hat{y}^2+\hat{z}^2=\hat{r}^2$ are unit vectors.

The Laplacian ∇^2 is the divergence of the gradient of a scalar field $\nabla^2 f=\bar{\nabla}\cdot\nabla f$, or in Cartesian coordinates

$$\nabla^2 f=\frac{\partial^2 f}{\partial x^2}+\frac{\partial^2 f}{\partial y^2}+\frac{\partial^2 f}{\partial z^2}$$

Also, the curl

(7) $$\bar{\nabla}\times\bar{F}=\begin{vmatrix}\hat{x} & \hat{y} & \hat{z}\\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z}\\ F_x & F_y & F_z\end{vmatrix}$$

is a vector whose *x*, *y*, and *z* components are the circulation of the field about that component.

Some useful identities from vector calculus are:

(8) $\overline{\nabla}\cdot\left(\overline{\nabla}\times\overline{F}\right)=0$

(9) $\nabla\times\left(\nabla\phi\right)=0$

(10) $\nabla\times\left(\overline{\nabla}\times\overline{F}\right)=\overline{\nabla}\left(\overline{\nabla}\cdot\overline{F}\right)-\overline{\nabla}^{2}\overline{F}$

We now introduce a vector potential $\overline{A}\left(\overline{r},t\right)$ and a scalar potential $\varphi\left(\overline{r},t\right)$, which we will relate to $\overline{E}$ and $\overline{B}$

Since $\overline{\nabla}\cdot\overline{B}=0$ and $\overline{\nabla}\left(\overline{\nabla}\times\overline{A}\right)=0$:

(11) $\overline{B}=\overline{\nabla}\times\overline{A}$

Using (3), we have:

$$\overline{\nabla}\times\overline{E}=-\overline{\nabla}\times\frac{\partial\overline{A}}{\partial t}$$

or

(12) $$\overline{\nabla}\times\left[\overline{E}+\frac{\partial\overline{A}}{\partial t}\right]=0$$

From (9), we see that a scalar product exists with:

(13) $$\overline{E}+\frac{\partial\overline{A}}{\partial t}=-\overline{\nabla}\varphi\left(\overline{r},t\right)$$

convention

or

(14) $$\overline{E}=\frac{\partial\overline{A}}{\partial t}-\nabla\varphi$$

So we see that the potentials $\overline{A}$ and φ determine the fields $\overline{B}$ and $\overline{E}$:

(15) $\overline{B}\left(\overline{r},t\right)=\overline{\nabla}\times\overline{A}\left(\overline{r},t\right)$

(16) $$\overline{E}\left(\overline{r},t\right)=-\overline{\nabla}\varphi\left(\overline{r},t\right)-\frac{\partial}{\partial t}\overline{A}\left(\overline{r},t\right)$$

We are interested in determining the wave equation for $\overline{A}$ and φ. Using (15) and differentiating (16) and substituting into (4):

(17) $$\overline{\nabla}\times\left(\overline{\nabla}\times\overline{A}\right)+\varepsilon_0\mu_0\left(\frac{\partial^2\overline{A}}{\partial t^2}+\overline{\nabla}\frac{\partial\varphi}{\partial t}\right)=\mu_0\overline{J}$$

Using (10):

(18) $$\left[-\overline{\nabla}^2\overline{A}+\varepsilon_0\mu_0\frac{\partial^2\overline{A}}{\partial t^2}\right]+\overline{\nabla}\left(\nabla\cdot\overline{A}+\varepsilon_0\mu_0\frac{\partial\varphi}{\partial t}\right)=\overline{\mu}_0\,\overline{J}$$

From (14), we have:

$$\overline{\nabla}\cdot\overline{E}=-\frac{\partial\overline{\nabla}\cdot\overline{A}}{\partial t}-\overline{\nabla}^2\varphi$$

and using (2):

(19) $$\frac{-\partial\overline{V}\cdot\overline{A}}{\partial t}-\overline{\nabla}^2\varphi=\rho/\varepsilon_0$$

Notice from (15) and (16) that we only need to specify <u>four</u> field components (A_x, A_y, A_z, φ) to determine all <u>six</u> $\overline{E}$ and $\overline{B}$ components. But $\overline{E}$ and $\overline{B}$ do not uniquely determine $\overline{A}$ and φ. So, we can construct $\overline{A}$ and φ in any number of ways without changing $\overline{E}$ and $\overline{B}$. Notice that if we change $\overline{A}$ by adding $\overline{\nabla}\chi$ where χ is any function of $\overline{r}$ and t, this will not change $\overline{B}$ $\left(\nabla\times\left(\nabla\cdot B\right)=0\right)$. It will change E by $\left(-\frac{\partial}{\partial t}\overline{\nabla}\chi\right)$, but we can change φ to $\varphi'=\varphi-\left(\partial\chi/\partial t\right)$. Then $\overline{E}$ and $\overline{B}$ will both be unchanged. This property of changing representation (gauge) without changing $\overline{E}$ and $\overline{B}$ is gauge invariance. We can transform between gauges with:

(20) $$\overline{A}'\left(\overline{r},t\right)=\overline{A}\left(\overline{r},t\right)+\overline{\nabla}\cdot\chi\left(\overline{r},t\right)$$

<u>gauge transformation</u>

(21) $$\varphi'\left(\overline{r},t\right)=\varphi\left(\overline{r},t\right)-\frac{\partial}{\partial t}\chi\left(\overline{r},t\right)$$

Up to this point, A' and Q are undetermined. Let's choose a χ such that:

(22) $$\overline{\nabla}\cdot\overline{A}+\varepsilon_0\mu_0\frac{\partial\varphi}{\partial t}=0$$

<u>Lorentz condition</u>

then from (17):

(23) $$-\nabla^2\overline{A}+\varepsilon_0\mu_0\frac{\partial^2\overline{A}}{\partial t^2}=\mu_0\overline{J}$$

The RHS can be set to zero for no currents.

From (19), we have:

(24) $$\varepsilon_0\mu_0\frac{\partial^2\varphi}{\partial t^2}-\nabla^2\varphi=\frac{\rho}{\varepsilon_0}$$

Eqns. (23) and (24) are wave equations for $\overline{A}$ and φ. Within the Lorentz gauge, we can still arbitrarily add another χ (it must only satisfy 22). If we substitute (20) and (21) into (24), we see:

$$(25)\qquad \nabla^2\chi-\varepsilon_0\mu_0\frac{\partial^2\chi}{\partial t^2}=0$$

So we can make further choices/constraints on $\overline{A}$ and φ as long as it obeys (25).

For a field far from charges and currents, $J=0$ and $\rho=0$.

$$(26)\qquad -\overline{\nabla}^2\overline{A}+\varepsilon_0\mu_0\frac{\partial^2\overline{A}}{\partial t^2}=0$$

$$(27)\qquad -\overline{\nabla}^2\varphi+\varepsilon_0\mu_0\frac{\partial^2\varphi}{\partial t^2}=0$$

We now choose $\varphi=0$ (Coulomb gauge), and from (22) we see:

$$(28)\qquad \overline{\nabla}\cdot\overline{A}=0$$

So, the wave equation for our vector potential is:

$$(29)\qquad -\overline{\nabla}^2\overline{A}+\varepsilon_0\mu_0\frac{\partial^2\overline{A}}{\partial t^2}=0$$

The solutions to this equation are plane waves.

$$(30)\qquad \overline{A}=\overline{A}_0\sin\left(\omega t-\overline{k}\cdot\overline{r}+\alpha\right)\qquad\qquad \alpha:\text{ phase}$$

$$(31)\qquad =\overline{A}_0\cos\left(\omega t-\overline{k}\cdot\overline{r}+\alpha'\right)$$

$\overline{k}$ is the wave vector which points along the direction of propagation and has a magnitude:

$$(32)\qquad k^2=\omega^2\mu_0\varepsilon_0=\omega^2/c^2$$

Since (28) $\overline{\nabla}\cdot\overline{A}=0$

$$-\overline{k}\cdot\overline{A}_0\cos\left(\omega t-\overline{k}\cdot\overline{r}+\alpha\right)=0$$

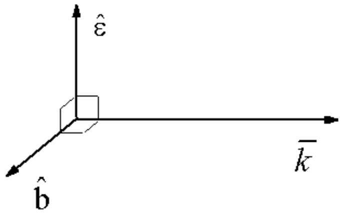
$$(33)\qquad \therefore\ \overline{k}\cdot\overline{A}_0=0\qquad\qquad \overline{k}\perp\overline{A}_0$$

A_0 is the direction of the potential → polarization. From (15) and (16), we see that for $\varphi=0$:

$$\overline{E} = -\frac{\partial \overline{A}}{\partial t} = -\,\omega \overline{A}_0 \cos\left(\omega t - \overline{k}\cdot\overline{r} + \alpha\right)$$

$$\overline{B} = \overline{\nabla}\times\overline{A} = -\left(\overline{k}\times\overline{A}_0\right)\cos\left(\omega t - \overline{k}\cdot\overline{r} + \alpha\right)$$

$$\therefore\quad \overline{k}\perp\overline{E}\perp\overline{B}$$



The Poynting vector describing the direction of energy propagation is $\overline{S} = \varepsilon_0 c^2\left(\overline{E}\times\overline{B}\right)$ and its average value, the intensity, is $I = \left\langle S\right\rangle = \frac{1}{2}\varepsilon_0 c E_0^2$.

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6.3. Absorption Cross Section

The rate of absorption induced by the field is

$$w_{k\ell}(\omega) = \frac{\pi}{2\hbar^2} \left| E_0(\omega) \right|^2 \left| \langle k | \hat{\varepsilon} \cdot \bar{\mu} | \ell \rangle \right|^2 \delta(\omega_{k\ell} - \omega) \tag{6.58}$$

The rate is clearly dependent on the strength of the field. The variable that you can most easily measure is the intensity *I*, the energy flux through a unit area, which is the time-averaged value of the Poynting vector, *S*

$$S = \varepsilon_0 c^2 \left(\bar{E} \times \bar{B} \right) \tag{6.59}$$

$$I = \langle S \rangle = \frac{1}{2} \varepsilon_0 c E_0^2 \tag{6.60}$$

Using this we can write

$$w_{k\ell} = \frac{4\pi}{3\varepsilon_0 c \hbar^2} I(\omega) \left| \langle k | \bar{\mu} | \ell \rangle \right|^2 \delta(\omega_{k\ell} - \omega) \tag{6.61}$$

where I have also made use of the uniform distribution of polarizations applicable to an isotropic field: $\left| \bar{E}_0 \cdot \hat{x} \right| = \left| \bar{E}_0 \cdot \hat{y} \right| = \left| \bar{E}_0 \cdot \hat{z} \right| = \frac{1}{3} \left| E_0 \right|^2$.

Now let's relate the rates of absorption to a quantity that is directly measured, an absorption cross section α:

$$\begin{aligned} \alpha &= \frac{\textit{total energy absorbed per unit time}}{\textit{total incident intensity}\left(\textit{energy / unit time / area}\right)} \\ &= \frac{\hbar\omega \; w_{k\ell}}{I} \end{aligned} \tag{6.62}$$

Note α has units of cm^{-2}. The golden rule rate for absorption also gives the same rate for stimulated emission. Given two levels $|m\rangle$ *and* $|n\rangle$:

$$\begin{aligned} & w_{nm} = w_{mn} \\ & \therefore \left(\alpha_A \right)_{nm} = \left(\alpha_{SE} \right)_{mn} \end{aligned} \tag{6.63}$$

We can now use a phenomenological approach to calculate the change in the intensity of incident light, due to absorption and stimulated emission passing through a sample of length *L* where the levels are initially thermally populated. Given that we have a thermal distribution of identical non-interacting particles, with quantum states such that the level $|m\rangle$ is higher in energy than $|n\rangle$:

$$\frac{dI}{dx} = -N_n \, \alpha_A \, I + N_m \, \alpha_{SE} \, I \tag{6.64}$$

$$\frac{dI}{I} = -\left(N_n - N_m\right)\alpha\, dx \tag{6.65}$$

Here N_n and N_m are population of the upper and lower states, but expressed as a population densities (*cm^{-3}*). If N is the molecular density,

$$N_n = N\left(\frac{e^{-\beta E_n}}{Z}\right) \tag{6.66}$$

Integrating (6.65) over a path length L we have

$$\begin{aligned} T = \frac{I}{I_0} &= e^{-\Delta N \alpha L} \\ &\approx e^{-N\alpha L} \end{aligned} \tag{6.67}$$

We see that the transmission of light through the sample decays exponentially as a function of path length. $\Delta N = N_n - N_m$ is the thermal population difference between states. The second expression in (6.67) comes from the high frequency approximation applicable to optical spectroscopy. Equation (6.67) can also be written in terms of the familiar Beer–Lambert Law:

$$A = -\log\frac{I}{I_0} = \epsilon C L \tag{6.68}$$

where A is the absorbance. C is the sample concentration in *$mol\ L^{-1}$*, which is related to the number density via Avagadro's number N_A

$$C[mol\, L^{-1}] = \frac{N[cm^{-3}]}{1000 N_A} \tag{6.69}$$

In eq. (6.68), the characteristic molecular quantity that describes the sample's ability to absorb the light is ϵ, the molar decadic extinction coefficient, given in *$L\ mol^{-1}\ cm^{-1}$*. With these units, we see that we can equate ϵ with the cross section as

$$\epsilon = \frac{N_A\, \alpha}{2303} \tag{6.70}$$

In the context of sample absorption characteristics, our use of the variable α for cross-section should not be confused with another use as an absorption coefficient with units of cm^{-1} that is equal to $N\alpha$ in eq. (6.67).

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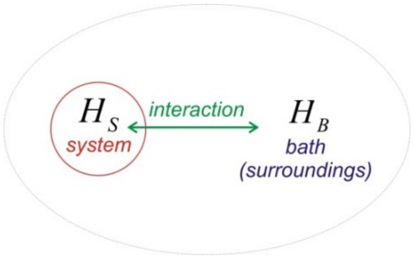
7. MIXED STATES AND THE DENSITY MATRIX

Conceptually we are now switching gears to develop tools and ways of thinking about condensed phase problems. What we have discussed so far is the time-dependent properties of *pure states*, the states of a quantum system that can be characterized by a single wavefunction. For pure states one can precisely write the Hamiltonian for all particles and fields in the system of interest. These are systems that are isolated from their surroundings, or isolated systems to which we introduce a time-dependent potential. For describing problems in condensed phases, things are different. Molecules in dense media interact with one another, and as a result no two molecules have the same state. Energy placed into one degree of freedom will ultimately leak irreversibly into its environment. We cannot write down an exact Hamiltonian for these problems; however, we can concentrate on a few degrees of freedom that are observed in a measurement, and try and describe the influence of the surroundings in a statistical manner.

These observations lead to the concept of *mixed states* or statistical mixtures. A mixed state refers to any case in which we describe the behavior of an ensemble for which there is initially no phase relationship between the elements of the mixture. Examples include a system at thermal equilibrium and independently prepared states. For mixed states we have imperfect information about the system, and we use statistical averages in order to describe quantum observables.



How does a system get into a mixed state? Generally, if you have two systems and you put these in contact with each other, the interaction between the two will lead to a new system that is inseparable. Consider two systems H_S and H_B for which the eigenstates of H_S are $|n\rangle$ and those of H_B are $|\alpha\rangle$.

$$H_0 = H_S + H_B \tag{0.1}$$

$$\begin{aligned} H_S|n\rangle &= E_n|n\rangle \\ H_B|\alpha\rangle &= E_\alpha|\alpha\rangle \end{aligned} \tag{0.2}$$

Before these systems interact, the state of the system $|\psi_0\rangle$ can be described as product states of $|n\rangle$ and $|\alpha\rangle$.

$$|\psi_0\rangle = |\psi_S^0\rangle|\psi_B^0\rangle \tag{0.3}$$

$$|\psi_S^0\rangle = \sum_n s_n|n\rangle \qquad |\psi_B^0\rangle = \sum_\alpha b_\alpha|\alpha\rangle \tag{0.4}$$

$$|\psi_0\rangle = \sum_{n,\alpha} s_n b_\alpha |n\alpha\rangle \tag{0.5}$$

where s and b are expansion coefficients. After these states are allowed to interact, we have a new state $|\psi(t)\rangle$. The new state can still be expressed in the zero-order basis, although this does not represent the eigenstates of the new Hamiltonian:

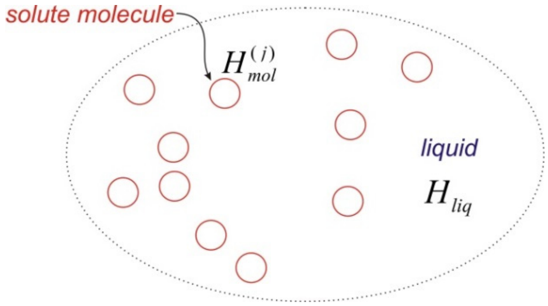
$$H = H_0 + V \tag{0.6}$$

$$|\psi(t)\rangle = \sum_{n,\alpha} c_{n,\alpha} |n\alpha\rangle \tag{0.7}$$

For any point in time, $c_{n,\alpha}$ is the complex amplitude for the mixed $|n\alpha\rangle$ state. Generally speaking, at any time after bringing the systems in contact $c_{n,\alpha} \neq s_n b_\alpha$. The coefficient $c_{n,\alpha}$ encodes $P_{n,\alpha} = |c_{n,\alpha}|^2$, the joint probability for finding particle of $|\psi_S\rangle$ in state $|n\rangle$ and simultaneously finding particle of $|\psi_B\rangle$ in state $|\alpha\rangle$. In the case of experimental observables, we are typically able to make measurements on the system H_S, and are blind to H_B. Then we are interested in the probability of occupying a particular eigenstate of the system averaged over the bath degrees of freedom:

$$P_n = \sum_\alpha P_{n,\alpha} = \sum_\alpha |c_{n,\alpha}|^2 = \langle |c_n|^2 \rangle \tag{0.8}$$

Now let's look at the thinking that goes into describing ensembles. Imagine a room temperature solution of molecules dissolved in a solvent. The same molecular Hamiltonian and wavefunctions can be used to express the state of any molecule in the ensemble. However, the details of the amplitudes of the eigenstates at any moment will also depend on the time-dependent local environment. We will describe this problem with the help of a molecular Hamiltonian $H^{(j)}_{mol}$, which describes the state of the molecule j within the solution through the wavefunction $|\psi^{(j)}\rangle$. We also have a Hamiltonian for the liquid H_{liq} into which we wrap all of the solvent degrees of freedom. The full Hamiltonian for the solution can be expressed in terms of a sum over N solute molecules and the liquid, the interactions between solute molecules H_{int}, and any solute-solvent interactions $H_{mol\text{-}liq}$:



$$\overline{H} = \sum_{j=1}^{N} H^{(j)}_{mol} + H_{liq} + \sum_{\substack{j,k=1 \\ j>k}}^{N} H^{(j,k)}_{\text{int}} + \sum_{j=1}^{N} H^{(j)}_{mol-liq} \tag{0.9}$$

For our purposes, we take the molecular Hamiltonian to be the same for all solute molecules, i.e., $H^{(j)}_{mol} = H_{mol}$ which obeys a TISE

$$H_{mol} |\psi_n\rangle = E_n |\psi_n\rangle \tag{0.10}$$

We will express the state of each molecule in this isolated molecule eigenbasis. For the circumstances we are concerned with, where there are no interactions or correlations between solute molecules, we are allowed to neglect H_{int}. Implicit in this statement is that we believe there is no quantum mechanical phase relationship between the different solute molecules. We will also drop H_{liq}, since it is not the focus of our interests and will not influence the conclusions. We can therefore write the Hamiltonian for any individual molecule as

$$H^{(j)} = H_{mol} + H^{(j)}_{mol-liq} \tag{0.11}$$

and the statistically averaged Hamiltonian

$$\overline{H} = \frac{1}{N}\sum_{j=1}^{N} H^{(j)} = H_{mol} + \left\langle H_{mol-liq} \right\rangle \tag{0.12}$$

This Hamiltonian reflects an ensemble average of the molecular Hamiltonian under the influence of a varying solute–solvent interaction.

To describe the state of any particular molecule, we can define a molecular wavefunction $\left|\psi_n^{(j)}\right\rangle$, which we express as an expansion in the isolated molecular eigenstates,

$$\left|\psi_n^{(j)}\right\rangle = \sum_n c_n^{(j)} \left|\psi_n\right\rangle \tag{0.13}$$

Here the expansion coefficients vary by molecule because of their interaction with the liquid, but they are all expressed in terms of the isolated molecule eigenstates. Note that this expansion is in essence the same as eq. (0.7), with the association $c_n^{(j)} \Leftrightarrow c_{n,\alpha}$. In either case, the mixed state arises from varying interactions with the environment. These may be static and appear from ensemble averaging, or time-dependent and arise from fluctuations in the environment.

Recognizing the independence of different molecules, the wavefunction for the complete system $\left|\Psi\right\rangle$ can be expressed in terms of the wavefunctions for the individual molecules under the influence of their local environment $\left|\psi^{(j)}\right\rangle$:

$$\overline{H}\left|\Psi\right\rangle = \overline{E}\left|\Psi\right\rangle \tag{0.14}$$

$$\left|\Psi\right\rangle = \left|\psi^{(1)}\psi^{(2)}\psi^{(3)}\cdots\right\rangle = \prod_{j=1}^{N}\left|\psi^{(j)}\right\rangle \tag{0.15}$$

$$\overline{E} = \sum_{j=1}^{N} E^{(j)} \tag{0.16}$$

We now turn out attention to expectation values that we would measure in an experiment. First we recognize that for the individual molecule *j*, the expectation value for an internal operator would be expressed

$$\left\langle A^{(j)}\right\rangle = \left\langle \psi^{(j)} \middle| \hat{A}\left(p_j, q_j\right) \middle| \psi^{(j)}\right\rangle \tag{0.17}$$

This purely quantum mechanical quantity is itself an average. It represents the mean value obtained for a large number of measurements made on an identically prepared system, and reflects the need to average over the intrinsic quantum uncertainties in the position and momenta of particles.

In the case of a mixed state, we must also average the expectation value over the ensemble of different molecules. In the case of our solution, this would involve an average of the expectation value over the *N* molecules.

$$\left\langle\left\langle A\right\rangle\right\rangle = \frac{1}{N}\sum_{j=1}^{N}\left\langle A^{(j)}\right\rangle \tag{0.18}$$

Double brackets are written here to emphasize that conceptually there are two levels of statistics in this average. The first involves the uncertainty over measurements of the same molecule in the identical pure state, whereas the second is an average over variations of the state of the system within an ensemble. However, we will drop this notation when we are dealing with ensembles, and take it as understood that expectation values must be averaged over a distribution.

Expanding eq. (0.18) with the use of eqs. (0.13) and (0.17) allows us to write

$$\begin{aligned}\left\langle A\right\rangle &= \frac{1}{N}\sum_{n,m}\underbrace{\sum_{j=1}^{N} c_m^{(j)}\left(c_n^{(j)}\right)^*}\left\langle \psi_n \middle| \hat{A} \middle| \psi_m\right\rangle \\ &= \sum_{n,m}\left\langle c_m c_n^*\right\rangle\left\langle \psi_n \middle| \hat{A} \middle| \psi_m\right\rangle\end{aligned} \tag{0.19}$$

The second term simplifies the first expression by performing an ensemble average over the complex wavefunction amplitudes. We use this expression to write a density matrix or density operator ρ, whose matrix elements are

$$\rho_{mn} = \left\langle c_m c_n^*\right\rangle \tag{0.20}$$

Then the expectation value becomes

$$\begin{aligned}\left\langle A\right\rangle &= \sum_{n,m}\rho_{mn}A_{nm} \\ &= Tr(\rho\hat{A})\end{aligned} \tag{0.21}$$

Here the trace *Tr*[...] refers to a trace over the diagonal elements of the matrix $\sum_a \langle a|\cdots|a\rangle$. Although these matrices were evaluated in the basis of the molecular eigenstates, we emphasize that the definition and evaluation of the density matrix and operator matrix elements are not specific to a particular basis set.

Although this is just one example, the principles are quite generally to mixed states in the condensed phase. The wavefunction is a quantity that is meant to describe a molecular or nanoscale object. To the extent that finite temperature, fluctuations, disorder, and spatial separation ensure that phase relationships are randomized between different nano-environments, one can characterize the molecular properties of condensed phases as mixed states in which ensemble-averaging is used to describe the interactions of these molecular environments with their surroundings.

The name density matrix derives from the observation that it plays the quantum role of a probability density. Comparing eq. (0.21) with the statistical determination of the mean value of A,

$$\langle A \rangle = \sum_{i=1}^{M} P(A_i) A_i \tag{0.22}$$

we see that ρ plays the role of the probability distribution function $P(A)$. Since ρ is Hermitian, it can be diagonalized, and in this diagonal basis the density matrix elements are in fact the statistical weights or probabilities of occupying a given state of the system.

Returning to our example, and comparing eq. (0.22) with eq. (0.18) also implies that $P_i(A) = 1/N$, i.e. that the contribution from each molecule to the average is statistically equivalent. Note also that the state of the system described by eq. (0.15) is a system of fixed energy. So, the probability density in (0.18) indicates that this expression applies to a microcanonical ensemble (N, V, E) in which any realization of a system at fixed energy is equally probable, and the statistical weight is the inverse of the number of microstates: $P = 1/\Omega$. In the case of a system in contact with a heat bath with temperature T, i.e., the canonical ensemble (N,V,T) we now express the average in terms of the probability that a member of an ensemble with fixed average energy can access a state of energy E.

Density matrix

Based on the discussion above, we are led to define the expectation value of an operator for a mixed state as

$$\left\langle \hat{A}(t)\right\rangle = \sum_j p_k \left\langle \psi^{(j)}(t)\middle|\hat{A}\middle|\psi^{(j)}(t)\right\rangle \tag{0.23}$$

where p_j is the probability of finding a system in the state defined by the wavefunction $|\psi^{(j)}\rangle$. Correspondingly, the density matrix for a mixed state is defined as:

$$\rho(t) \equiv \sum_j p_j \left|\psi^{(j)}(t)\right\rangle\left\langle\psi^{(j)}(t)\right| \tag{0.24}$$

For the case of a pure state, only one wavefunction $|\psi^{(k)}\rangle$ specifies the state of the system, and $p_j = \delta_{jk}$. Then the density matrix is as we described before,

$$\rho(t) = \left|\psi(t)\right\rangle\left\langle\psi(t)\right| \tag{0.25}$$

with the density matrix elements

$$\begin{aligned}\rho(t) &= \sum_{n,m} c_n(t)\,c_m^*(t)\left|n\right\rangle\left\langle m\right| \\ &\equiv \sum_{n,m} \rho_{nm}(t)\,\left|n\right\rangle\left\langle m\right|\end{aligned} \tag{0.26}$$

For mixed states, using the separation of system (a) and bath (α) degrees of freedom that we used above, the expectation value of an operator A can be expressed as

$$\begin{aligned}\left\langle A(t)\right\rangle &= \left\langle\psi(t)\middle|A\middle|\psi(t)\right\rangle \\ &= \sum_{\substack{a,\alpha \\ b,\beta}} c_{a,\alpha}^* c_{b,\beta} \left\langle a\,\alpha\middle|A\middle|b\,\beta\right\rangle \\ &= Tr\left[\rho A\right]\end{aligned} \tag{0.27}$$

Here, the density matrix elements are $\rho_{a,\alpha,b,\beta} = c_{a,\alpha}^* c_{b,\beta}$. We are now in a position, where we can average the system quantities over the bath configurations. If we consider that the operator A is only a function of the system coordinates, we can make further simplifications. An example is describing the dipole operator of a molecule dissolved in a liquid. Then we can average the expectation value of A over the bath degrees of freedom as

$$\begin{aligned}\langle A(t)\rangle &= \sum_{\substack{a,\alpha \\ b,\beta}} c^*_{a,\alpha} c_{b,\beta} \langle a|A|b\rangle \delta_{\alpha,\beta} \\ &= \sum_{a,b}\left(\sum_{\alpha} c^*_{a,\alpha} c_{b,\alpha}\right) A_{ab} \\ &\equiv \sum_{a,b} (\rho_S)_{ba} A_{ab} \\ &= Tr[\rho_S A]\end{aligned} \tag{0.28}$$

Here we have defined a density matrix for the system degrees of freedom (also called the reduced density matrix, σ)

$$\rho_s = |\psi_s\rangle\langle\psi_s| \tag{0.29}$$

with density matrix elements that traced over the bath states:

$$|b\rangle \rho_s \langle a| = \sum_{\alpha} c^*_{a,\alpha} c_{b,\alpha} \tag{0.30}$$

The "s" subscript should not be confused with the Schrödinger picture wavefunctions. To relate this to our similar expression for ρ, eq. (0.25), it is useful to note that the density matrix of the system are obtained by tracing over the bath degrees of freedom:

$$\begin{aligned}\rho_S &= Tr_B(\rho) \\ &= \sum_{a,b} (\rho_S)_{ba} A_{ab}\end{aligned} \tag{0.31}$$

Also, note that

$$Tr(A \times B) = Tr(A)Tr(B) \tag{0.32}$$

To interpret what the system density matrix represents, let's manipulate it a bit. Since ρ_S is Hermitian, it can be diagonalized by a unitary transformation T, where the new eigenbasis $|m\rangle$ represents the mixed states of the original $|\psi_S\rangle$ system.

$$\rho_S = \sum_m |m\rangle \rho_{mm} \langle m| \tag{0.33}$$

$$\sum_m \rho_{mm} = 1 \tag{0.34}$$

The density matrix elements represent the probability of occupying state $|m\rangle$, which includes the influence of the bath. To obtain these diagonalized elements, we apply the transformation T to the system density matrix:

$$\begin{aligned}(\rho_S)_{mm} &= \sum_{a,b} T_{mb} (\rho_S)_{ba} T^{\dagger}_{am} \\ &= \sum_{a,b,\alpha} c_{b,\alpha} T_{mb} c^{*}_{a,\alpha} T^{*}_{ma} \\ &= \sum_{\alpha} f_{m,\alpha} f^{*}_{m,\alpha} \\ &= \left| f_m \right|^2 = p_m \geq 0\end{aligned} \tag{0.35}$$

The quantum mechanical interaction of one system with another causes the system to be in a mixed state after the interaction. The mixed states, which are generally inseparable from the original states, are described by

$$\left| \psi_S \right\rangle = \sum_m f_m \left| m \right\rangle \tag{0.36}$$

If we only observe a few degrees of freedom, we can calculate observables by tracing over unobserved degrees of freedom. This forms the basis for treating relaxation phenomena.

Readings

1. Blum, K., *Density Matrix Theory and Applications*. Plenum Press: New York, 1981.
2. Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press: New York, 1995.

8. IRREVERSIBLE AND RANDOM PROCESSES

8.1. Concepts and Definitions

In condensed phases, intermolecular interactions and collective motions act to modify the state of a molecule in a time-dependent fashion. Liquids, polymers, and other soft matter experience intermolecular interactions that lead to electronic and structural motions. Atoms and molecules in solid form are subject to fluctuations that result from thermally populated phonons and defect states that influence electronic, optical, and transport properties. As a result, the properties and dynamics of an internal variable that we may observe in an experiment are mixed with its surroundings. In studying mixed states we cannot write down an exact Hamiltonian for these problems; however, we can describe the influence of the surroundings in a statistical manner. This requires a conceptual change.

As one change to our thinking, we now have to be concerned with ensembles. Most often, we will be concerned with systems in an equilibrium state with a fixed temperature for which many quantum states are accessible to the system. For comparing calculations of pure quantum states to experimental observables on macroscopic samples, we assume that all molecules have been prepared and observed in the same manner, so that the quantum expectation values for the internal operators can be compared directly to experimental observations. For mixed states, we have seen the need to perform an additional layer of averaging over the ensemble in the calculation of expectation values.

Perhaps the most significant change between isolated states and condensed matter is the dynamics. From the time-dependent Schrödinger equation, we see that the laws governing the time evolution of *isolated* quantum mechanical systems are invariant under time reversal. That is, there is no intrinsic directionality to time. If one reverses the sign of time and thereby momenta of objects, we should be able to exactly reverse the motion and propagate the system to where it was at an earlier time. This is also the case for classical systems evolving under Newton's equation of motion. In contrast, when a quantum system is in contact with another system having many degrees of freedom, a definite direction emerges for time, "the arrow of time," and the system's dynamics is no longer reversible. In such irreversible systems a well-defined prepared state decays in time to an equilibrium state where energy has been dissipated and phase relationships are lost between the various degrees of freedom.

Additionally, condensed phase systems on a local, microscopic scale all have a degree of randomness or noisiness to their dynamics that represent local fluctuations in energy on the scale of k_BT. This behavior is observed even through the equations of motion that govern the dynamics are deterministic. Why? It is because we generally have imperfect knowledge about all of the degrees of freedom influencing the system, or experimentally view its behavior through a highly restricted perspective. For instance, it is common in experiments to observe the behavior of condensed phases through a molecular probe imbedded within or under the influence of its surroundings. The physical properties of the probe are intertwined with the dynamics of the surrounding medium, and to us this appears as random behavior, for instance as Brownian motion. Other examples of the appearance of randomness from deterministic equations of motion include weather patterns, financial markets, and biological evolution. So, how do irreversible behavior and random fluctuations, hallmarks of all chemical systems, arise from the deterministic time-dependent Schrödinger equation? This fascinating question will be the central theme in our efforts going forward.

Definitions

Let's begin by establishing some definitions and language that will be useful for us. We first classify chemical systems of interest as equilibrium or non-equilibrium systems. An *equilibrium* system is one in which the macroscopic properties (i.e., the intensive variables) are invariant with time, or at least invariant on the time scales over which one executes experiments and observes the system. Further, there are no steady state concentration or energy gradients (currents) in the system. Although they are macroscopically invariant, equilibrium states are microscopically dynamic.

For systems at thermal equilibrium we will describe their time-dependent behavior as dynamically reversible or irreversible. For us, *reversible* will mean that a system evolves deterministically. Knowledge of the state of the system at one point in time and the equation of motion means that you can describe the state of the system for all points in time later or previously. *Irreversible* systems are not deterministic. That is, knowledge of the state of the system at one point in time does not provide enough information to precisely determine its past state.

Since all states are irreversible in the strictest sense, the distinction is often related to the time scale of observation. For a given system, on a short enough time scale dynamics will appear deterministic whereas on very long times appear random. For instance, the dynamics of a dilute gas appear ballistic on time scales short compared to the mean collision time between particles, whereas their motion appears random and diffusive on much longer time scales. *Memory* refers to the ability to maintain deterministic motion and reversibility, and we will quantify the decay of memory in the system with correlation functions. For the case of quantum dynamics, we are particularly interested in the phase relationships between quantum degrees of freedom that results from deterministic motion under the time-dependent Schrödinger equation.

Nonequilibrium states refers to open or closed systems that have been acted on externally, moving them from equilibrium by changing the population or energy of the quantum states available to the system. Thermodynamically, work is performed on the system, leading to a free-energy gradient that the nonequilibrium system will minimize as it re-equilibrates. For nonequilibrium states, we will be interested in *relaxation* processes, which refer to the time-dependent processes involved in re-equilibrating the system. *Dissipation* refers to the relaxation processes involving redistribution of energy as a nonequilibrium state returns toward a thermal distribution. However, there are other relaxation processes such as the randomization of the orientation of an aligned system or the randomization of phase of synchronized oscillations.

Statistics

With the need to describe ensembles, will use statistical descriptions of the properties and behavior of a system. The variable A, which can be a classical internal variable or quantum operator, can be described statistically in terms of the mean and mean-square values of A determined from a large number of measurements:

$$\langle A \rangle = \frac{1}{N}\sum_{i=1}^{N} A_i \tag{8.1}$$

$$\langle A^2 \rangle = \frac{1}{N}\sum_{i=1}^{N} A_i^2 \tag{8.2}$$

Here, the summation over i refers to averaging over N independent measurements. Alternatively, these equations can be expressed as

$$\langle A \rangle = \sum_{n=1}^{M} P_n A_n \tag{8.3}$$

$$\langle A^2 \rangle = \sum_{n=1}^{M} P_n A_n^2 \tag{8.4}$$

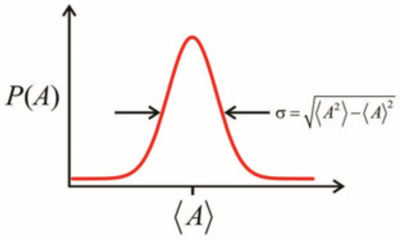
The sum over n refers to a sum over the M possible values that A can take, weighted by P_n, the probability of observing a particular value A_n. When the accessible values come from a continuous as opposed to discrete distribution, one can describe the statistics in terms of the moments of the distribution function, $P(A)$, which characterizes the probability of observing A between A and $A+dA$

$$\langle A \rangle = \int dA\, A\, P(A) \tag{8.5}$$

$$\langle A^2 \rangle = \int dA\, A^2\, P(A) \tag{8.6}$$

For time-dependent processes, we recognize that it is possible that these probability distributions carry a time dependence, $P(A,t)$. The ability to specify a value for A is captured in the variance of the distribution

$$\sigma^2 = \left\langle A^2 \right\rangle - \left\langle A \right\rangle^2 \tag{8.7}$$



We will apply averages over probability distributions to the description of ensembles of molecules; however, we should emphasize that a statistical description of a quantum system also applies to a pure state. A fundamental postulate is that the expectation value of an operator $\left\langle \hat{A} \right\rangle = \langle \psi | \hat{A} | \psi \rangle$ is the mean value of A obtained over many observations on identically prepared systems. The mean and variance of this expectation value represent the fundamental quantum uncertainty in a measurement.

To take this a step further and characterize the statistical relationship between two variables, one can define a joint probability distribution, $P(A,B)$, which characterizes the probability of observing A between A and $A+dA$ and B between B and $B+dB$. The statistical relationship between the variables can also emerges from moments of $P(A,B)$. The most important measure is a correlation function

$$C_{AB} = \left\langle AB \right\rangle - \left\langle A \right\rangle \left\langle B \right\rangle \tag{8.8}$$

You can see that this is the covariance—the variance for a bivariate distribution. This is a measure of the correlation between the variables A and B. That is, for a specific value of A, what are the associated statistics for B. To interpret this it helps to define a correlation coefficient

$$r = \frac{C_{AB}}{\sigma_A \sigma_B} \tag{8.9}$$

r can take on values from +1 to −1. If $r = 1$ then there is perfect correlation between the two distributions. If the variables A and B depend the same way on a common internal variable, then they are correlated. If no statistical relationship exists between the two distributions, then they are uncorrelated, $r = 0$, and $\left\langle AB \right\rangle = \left\langle A \right\rangle \left\langle B \right\rangle$. It is also possible that the distributions depend in an equal and opposite manner on an internal variable, in which case we call them anti-correlated with $r = -1$.

8.2. Thermal Equilibrium

For a statistical mixture at thermal equilibrium, individual molecules can occupy a distribution of energy states. An equilibrium system at temperature T has the canonical probability distribution

$$\rho_{eq} = \frac{e^{-\beta H}}{Z}. \tag{8.10}$$

Z is the partition function and $\beta = (k_B T)^{-1}$. Classically, we can calculate the equilibrium ensemble average value of a variable A as

$$\langle A \rangle = \int d\mathbf{p} \int d\mathbf{q} \;\; A(\mathbf{p},\mathbf{q};t)\, \rho_{eq}(\mathbf{p},\mathbf{q}) \tag{8.11}$$

In the quantum mechanical case, we can obtain an equilibrium expectation value of A by averaging $\langle A \rangle$ over the thermal occupation of quantum states:

$$\langle A \rangle = Tr\left(\rho_{eq} A\right) \tag{8.12}$$

where ρ_{eq} is the density matrix at thermal equilibrium. ρ_{eq} is a diagonal matrix characterized by Boltzmann weighted populations in the quantum states:

$$\rho_{nn} = p_n = \frac{e^{-\beta E_n}}{Z} \tag{8.13}$$

In fact, the equilibrium density matrix is defined by eq. (8.10), as we can see by calculating its matrix elements using $\hat{H}\left|n\right\rangle = E_n \left|n\right\rangle$,

$$\left(\rho_{eq}\right)_{nm} = \frac{1}{Z}\left\langle n\right| e^{-\beta \hat{H}} \left|m\right\rangle = \frac{e^{-\beta E_n}}{Z}\delta_{nm} = p_n \delta_{nm} \tag{8.15}$$

Note also that

$$Z = Tr\left(e^{-\beta \hat{H}}\right) \tag{8.16}$$

Eq. (8.12) can also be written as

$$\langle A \rangle = \sum_n p_n \left\langle n \middle| A \middle| n \right\rangle \tag{8.14}$$

It may not be obvious how this expression relates to our previous expression for mixed states $\langle A \rangle = \sum_{n,m} \left\langle c_n^* c_m \right\rangle A_{mn} = Tr\left(\rho \hat{A}\right)$. Remember that for an equilibrium system we are dealing with a statistical mixture in which no coherences (no phase relationships) are present in the sample. The lack of coherence is the important property that allows the equilibrium ensemble average of $\left\langle c_m c_n^* \right\rangle$ to be equated with the thermal population p_n. To evaluate this average we recognize that these are complex numbers, and that the equilibrium ensemble average of the expansion coefficients is equivalent to phase averaging over the expansion coefficients. Since at equilibrium all phases are equally probable

$$\left\langle c_n^* c_m \right\rangle = \frac{1}{2\pi}\int_0^{2\pi} c_n^* c_m \, d\phi = \frac{1}{2\pi}\left|c_n\right|\left|c_m\right|\int_0^{2\pi} e^{-i\phi_{nm}} d\phi_{nm} \tag{8.17}$$

where $c_n = \left|c_n\right| e^{i\phi_n}$ and $\phi_{nm} = \phi_n - \phi_m$. The integral in is quite clearly zero unless $\phi_n = \phi_m$, giving

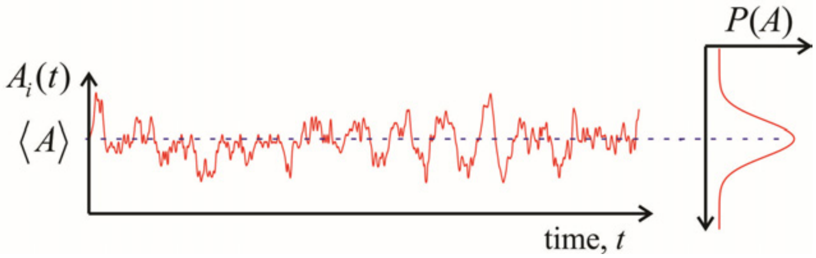
$$\left\langle c_n^* c_m \right\rangle = p_n = \frac{e^{-\beta E_n}}{Z} \tag{8.18}$$

8.3. Fluctuations

"Fluctuations" refers to the random or noisy time evolution of a microscopic subsystem imbedded an actively evolving environment. Randomness is a property of all chemical systems to some degree, but we will focus on an environment that is at or near thermal equilibrium. Systems at thermal equilibrium are macroscopically time-invariant; however, they are microscopically dynamic, with molecules exploring the range of microstates that are thermally accessible. Local variations in energy result in changes in molecular position, orientation, and structure, and are responsible for the activation events that allow chemical equilibria to be established.

If we wish to describe an internal variable A for a system at thermal equilibrium, we can obtain the statistics of A by performing ensemble averages described above. The resulting averages would be time-invariant. However, if we observe a member of the ensemble as a function of time, $A_i(t)$, the behavior is generally is observed to fluctuate randomly. The fluctuations in $A_i(t)$ vary about a mean value $\langle A\rangle$, sampling thermally accessible values which are described by an equilibrium probability distribution function $P(A)$. $P(A)$ describes the potential of mean force, the free energy projected as a function of A:

$$F(A) = -k_B T \ln P(A) \tag{8.19}$$



Given enough time, we expect that one molecule in a homogeneous medium will be able to sample all available configurations of the system. Moreover, a histogram of the values sampled by one molecule is expected to be equal to $P(A)$. Such a system is referred to as ergodic. Specifically, in an ergodic system, it is possible describe the macroscopic properties either by averaging over all possible values for a given member of the ensemble, or by performing an average over the realizations of A for the entire ensemble at one point in time. That is, the statistics for A can be expressed as a time-average or an ensemble average. For an equilibrium system, the ensemble average is

$$\langle A\rangle = Tr\left(\rho_{eq} A\right) = \sum_n \frac{e^{-\beta E_n}}{Z} \langle n|A|n\rangle \tag{8.20}$$

and the time average is

$$\overline{A} = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt\, A_i\left(t\right) \tag{8.21}$$

These quantities are equal for an <u>ergodic</u> system:

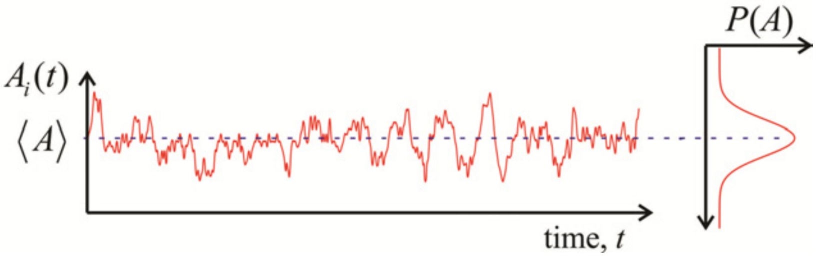
$$\left\langle A \right\rangle = \overline{A}$$

Equilibrium systems are ergodic. From eq. (8.21), we see that the term ergodic also carries a dynamical connotation. A system is ergodic if one member of the ensemble has evolved long enough to sample the equilibrium probability distribution. Experimental observations on shorter time scales view a nonequilibrium system.

9. TIME-CORRELATION FUNCTIONS

9.1. Definitions, Properties, and Examples

Time-correlation functions are an effective and intuitive way of representing the dynamics of a system, and are one of the most common tools of time-dependent quantum mechanics. They provide a statistical description of the time evolution of an internal variable or expectation value for an ensemble at thermal equilibrium. They are generally applicable to any time-dependent process, but are commonly used to describe random (or stochastic) and irreversible processes in condensed phases. We will use them extensively in the description of spectroscopy and relaxation phenomena. Although they can be used to describe the oscillatory behavior of ensembles of pure quantum states, our work is motivated by finding a general tool that will help us deal with the inherent randomness of molecular systems at thermal equilibrium. They will be effective at characterizing irreversible relaxation processes and the loss of memory of an initial state in a fluctuating environment.



Returning to the microscopic fluctuations of a molecular variable A, there seems to be little information in observing the trajectory for a variable characterizing the time-dependent behavior of an individual molecule. However, this dynamics is not entirely random, since they are a consequence of time-dependent interactions with the environment. We can provide a statistical description of the characteristic time scales and amplitudes to these changes by comparing the value of A at time t with the value of A at time t' later. With that in mind we define a time-correlation function (TCF) as a time-dependent quantity, $A(t)$, multiplied by that quantity at some later time, $A(t')$, and averaged over an equilibrium ensemble:

$$C_{AA}(t,t') \equiv \langle A(t)\,A(t')\rangle_{eq} \tag{9.1}$$

The classical for of the correlation function is evaluated as

$$C_{AA}(t,t') = \int d\mathbf{p} \int d\mathbf{q}\;\; A(\mathbf{p},\mathbf{q};t)\,A(\mathbf{p},\mathbf{q};t')\,\rho_{eq}(\mathbf{p},\mathbf{q}) \tag{9.2}$$

whereas the quantum correlation function can be evaluated as

$$\begin{aligned} C_{AA}(t,t') &= Tr\left[\rho_{eq} A(t) A(t')\right] \\ &= \sum_n p_n \left\langle n \middle| A(t) A(t') \middle| n \right\rangle \end{aligned} \tag{9.3}$$

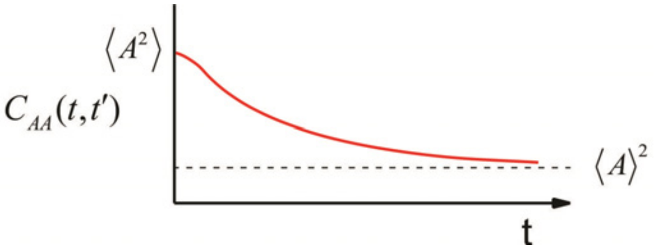
where $p_n = e^{-\beta E_n} / Z$. These are auto-correlation functions, which correlates the same variable at two points in time, but one can also define a cross-correlation function that describes the correlation of two different variables in time

$$C_{AB}(t,t') \equiv \left\langle A(t)\, B(t') \right\rangle \tag{9.4}$$

So, what does a time-correlation function tell us? Qualitatively, a TCF describes how long a given property of a system persists until it is averaged out by microscopic motions and interactions with its surroundings. It describes how and when a statistical relationship has vanished. We can use correlation functions to describe various time-dependent chemical processes. For instance, we will use $\left\langle \mu(t)\mu(0) \right\rangle$ –the dynamics of the molecular dipole moment– to describe absorption spectroscopy. We will also use them for relaxation processes induced by the interaction of a system and bath: $\left\langle H_{SB}(t) H_{SB}(0) \right\rangle$. Classically, you can use TCFs to characterize transport processes. For instance a diffusion coefficient is related to the velocity correlation function: $D = \frac{1}{3}\int_0^\infty dt \langle v(t)v(0)\rangle$.

Properties of Correlation Functions

A typical correlation function for random fluctuations at thermal equilibrium in the variable *A* might look like



It is described by a number of properties:

1. When evaluated at $t = t'$, we obtain the maximum amplitude, the mean square value of *A*, which is positive for an autocorrelation function and independent of time.

$$C_{AA}(t,t) = \left\langle A(t) A(t) \right\rangle = \left\langle A^2 \right\rangle \geq 0 \tag{9.5}$$

2. For long time separations, as thermal fluctuations act to randomize the system, the values of *A* become uncorrelated

$$\lim_{t\to\infty} C_{AA}(t,t') = \left\langle A(t) \right\rangle \left\langle A(t') \right\rangle = \left\langle A \right\rangle^2 \tag{9.6}$$

3. Since it is an equilibrium quantity, correlation functions are stationary. That means they do not depend on the absolute point of observation (*t* and *t'*), but rather the time interval between observations. A stationary random process means that the reference point can be shifted by an arbitrary value *T*

$$C_{AA}\left(t,t'\right)=C_{AA}\left(t+T,t'+T\right) \tag{9.7}$$

So, choosing $T=-t'$ and defining the time interval $\tau\equiv t-t'$, we see that only τ matters

$$C_{AA}\left(t,t'\right)=C_{AA}\left(t-t',0\right)=C_{AA}\left(\tau\right) \tag{9.8}$$

Implicit in this statement is an understanding that we take the time-average value of *A* to be equal to the equilibrium ensemble average value of *A*, i.e., the system is ergodic. So, the correlation of fluctuations can be expressed as either a time-average over a trajectory of one molecule

$$\overline{A(t)A(0)}=\lim_{T\to\infty}\frac{1}{T}\int_0^T d\tau\; A_i\left(t+\tau\right)A_i\left(\tau\right) \tag{9.9}$$

or an equilibrium ensemble average

$$\left\langle A(t)A(0)\right\rangle=\sum_n\frac{e^{-\beta E_n}}{Z}\left\langle n\middle|A(t)A(0)\middle|n\right\rangle \tag{9.10}$$

4. Classical correlation functions are real and even in time:

$$\begin{gathered}\left\langle A(t)A(t')\right\rangle=\left\langle A(t')A(t)\right\rangle\\ C_{AA}\left(\tau\right)=C_{AA}\left(-\tau\right)\end{gathered} \tag{9.11}$$

5. When we observe fluctuations about an average, we often redefine the correlation function in terms of the deviation from average

$$\delta A\equiv A-\left\langle A\right\rangle \tag{9.12}$$

$$C_{\delta A\delta A}\left(t\right)=\left\langle \delta A(t)\,\delta A(0)\right\rangle=C_{AA}\left(t\right)-\left\langle A\right\rangle^2 \tag{9.13}$$

Now we see that the long time limit when correlation is lost $\lim_{t\to\infty}C_{\delta A\delta A}\left(t\right)=0$, and the zero time value is just the variance

$$C_{\delta A\delta A}\left(0\right)=\left\langle \delta A^2\right\rangle=\left\langle A^2\right\rangle-\left\langle A\right\rangle^2 \tag{9.14}$$

6. The characteristic time scale of a random process is the correlation time, τ_c. This characterizes the time scale for TCF to decay to zero. We can obtain τ_c from

$$\tau_c = \frac{1}{\left\langle \delta A^2 \right\rangle} \int_0^\infty dt \left\langle \delta A(t) \delta A(0) \right\rangle \tag{9.15}$$

which should be apparent if you have an exponential form $C(t) = C(0)\exp(-t/\tau_c)$.

Examples of Time-Correlation Functions

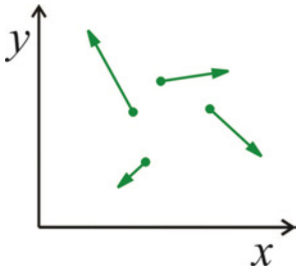
Example 1: Velocity autocorrelation function for gas

Let's analyze a dilute gas of molecules which have a Maxwell–Boltzmann distribution of velocities. We focus on the component of the molecular velocity along the $\hat{x}$ direction, v_x. We know that the average velocity is $\langle v_x \rangle = 0$. The velocity correlation function is

$$C_{v_x v_x}(\tau) = \left\langle v_x(\tau) v_x(0) \right\rangle$$

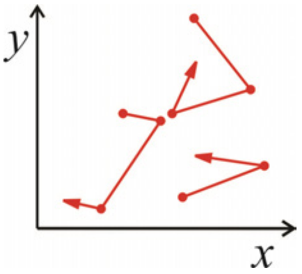
From the equipartition principle the average translational energy is $\frac{1}{2} m \left\langle v_x^2 \right\rangle = k_B T/2$, so

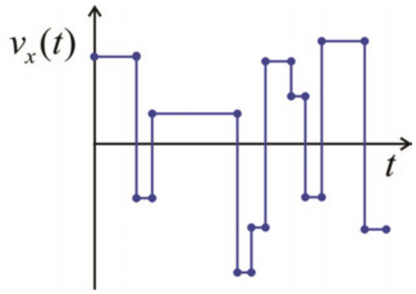
$$C_{v_x v_x}(0) = \left\langle v_x^2(0) \right\rangle = \frac{k_B T}{m}$$

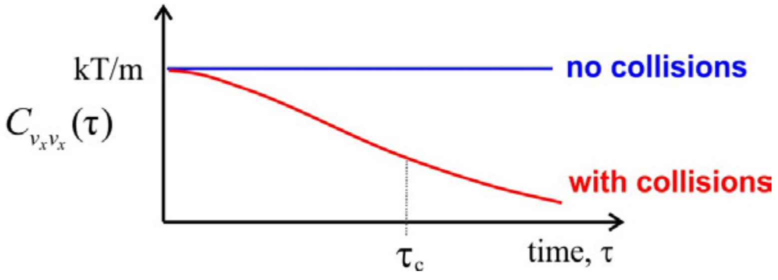


For time scales short compared to collisions between molecules, the velocity of any given molecule remains constant and unchanged, so the correlation function for the velocity is also unchanged at k_BT/m. This non-interacting regime corresponds to the behavior of an ideal gas.

For any real gas, there will be collisions that randomize the direction and speed of the molecules, so that any molecule over a long enough time will sample the various velocities within the Maxwell–Boltzmann distribution. From the trajectory of x-velocities for a given molecule we can calculate $C_{v_x v_x}(\tau)$ using time-averaging. The correlation function will drop on with a correlation time τ_c, which is related to mean time between collisions. After enough collisions, the correlation with the initial velocity is lost and $C_{v_x v_x}(\tau)$ approaches $\langle v_x^2 \rangle = 0$. Finally, we can determine the diffusion constant for the gas, which relates the time and mean square displacement of the molecules: $\langle x^2(t) \rangle = 2D_x t$. From $D_x = \int_0^\infty dt \langle v_x(t) v_x(0) \rangle$ we have $D_x = k_B T \tau_c / m$. In viscous fluids τ_c / m is called the mobility, μ.





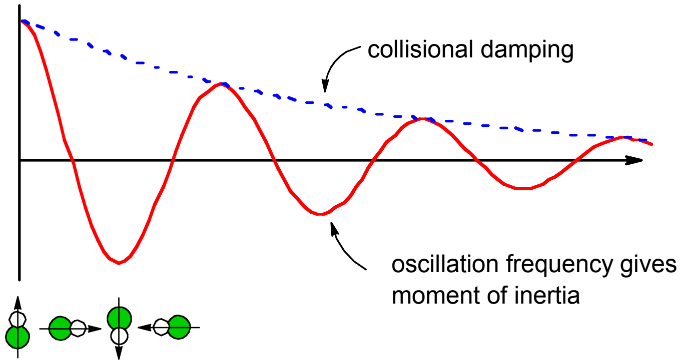


Example 2: Dipole moment correlation function

Now consider the correlation function for the dipole moment of a polar diatomic molecule in a dilute gas, $\bar{\mu}$. For a rigid rotating object, we can decompose the dipole into a magnitude and a direction unit vector: $\bar{\mu}_i = \mu_0 \cdot \hat{u}$. We know that $\langle \hat{\mu} \rangle = 0$ since all orientations of the gas phase molecules are equally probable. The correlation function is

$$\begin{aligned} C_{\mu\mu}(t) &= \langle \bar{\mu}(t)\bar{\mu}(0) \rangle \\ &= \langle \mu_0^2 \rangle \langle \hat{u}(t) \cdot \hat{u}(0) \rangle \end{aligned}$$

This correlation function projects the time-dependent orientation of the molecule onto the initial orientation. Free inertial rotational motion will lead to oscillations in the correlation function as the dipole spins. The oscillations in this correlation function can be related to the speed of rotation and thereby the molecule's moment of inertia (discussed below). Any apparent damping in this correlation function would reflect the thermal distribution of angular velocities. In practice a real gas would also have the collisional damping effects described in Example 1 superimposed on this relaxation process.



Example 3: Harmonic oscillator correlation function

The time-dependent motion of a harmonic vibrational mode is given by Newton's law in terms of the acceleration and restoring force as $m\ddot{q} = -\kappa q$ or $\ddot{q} = -\omega^2 q$ where the force constant is $\kappa = m\omega^2$. We can write a common solution to this equation as $q(t) = q(0)\cos\omega t$. Furthermore, the equipartition theorem says that the equilibrium thermal energy in a harmonic vibrational mode is

$$\frac{1}{2}\kappa\langle q^2 \rangle = \frac{k_B T}{2}$$

We therefore can write the correlation function for the harmonic vibrational coordinate as

$$\begin{aligned} C_{qq}(t) &= \langle q(t)q(0) \rangle = \langle q^2 \rangle \cos \omega t \\ &= \frac{k_B T}{\kappa} \cos \omega t \end{aligned}$$

9.2. Correlation Function from a Discrete Trajectory

In practice classical correlation functions in molecular dynamics simulations or single molecule experiments are determined from a time-average over a long trajectory at discretely sampled data points. Let's evaluate eq. (9.9) for a discrete and finite trajectory in which we are given a series of N observations of the dynamical variable A at equally separated time points t_i. The separation between time points is $t_{i+1}-t_i=\Delta t$, and the length of the trajectory is $T=N\Delta t$. Then we have

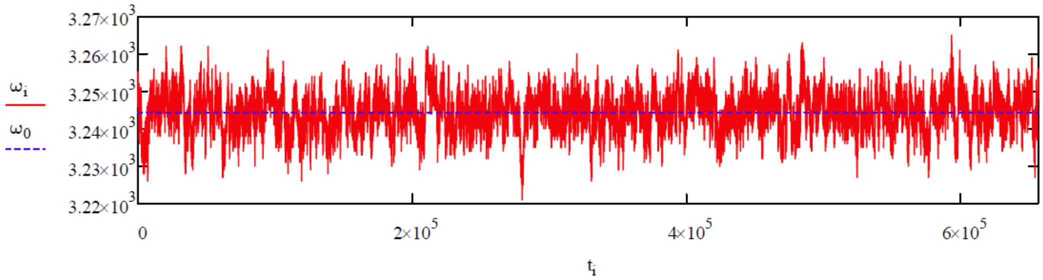
$$C_{AA}=\frac{1}{T}\sum_{i,j=1}^{N}\Delta t\,A(t_i)A(t_j)=\frac{1}{N}\sum_{i,j=1}^{N}A_iA_j \tag{9.16}$$

where $A_i=A(t_i)$. To make this more useful we want to express it as the time interval between points $\tau=t_j-t_i=\left(j-i\right)\Delta t$, and average over all possible pairwise products of A separated by τ. Defining a new count integer $n=j-i$, we can express the delay as $\tau=n\Delta t$. For a finite data set there are a different number of observations to average over at each time interval (n). We have the most pairwise products—N to be precise—when the time points are equal ($t_i=t_j$). We only have one data pair for the maximum delay $\tau = T$. Therefore, the number of pairwise products for a given delay τ is $N-n$. So we can write eq. (9.16) as

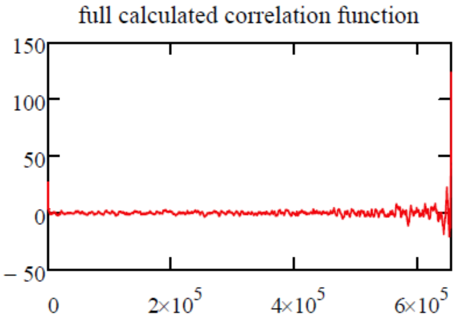
$$C_{AA}\left(\tau\right)=C\left(n\right)=\frac{1}{N-n}\sum_{i=1}^{N-n}A_{i+n}A_i \tag{9.17}$$

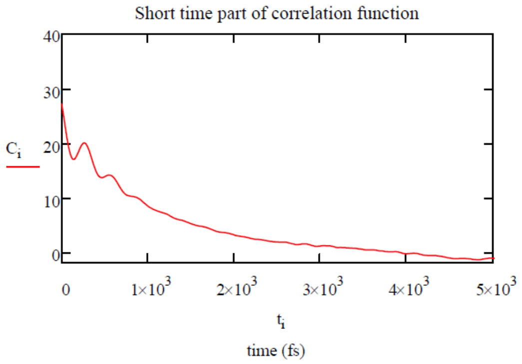
Note that this expression will only be calculated for positive values of n, for which $t_j \geq t_i$.

As an example consider the following calculation for fluctuations in a vibrational frequency $\omega(t)$, which consists of 32000 consecutive frequencies in units of cm^{-1} for points separated by 10 femtoseconds, and has a mean value of $\omega_0 = 3244\ \text{cm}^{-1}$. This trajectory illustrates that there are fast fluctuations on femtosecond time scales, but the behavior is seemingly random on 100 picosecond time scales



After determining the variation from the mean $\delta\omega(t_i) = \omega(t_i)-\omega_0$, the frequency correlation function is determined from eq. (9.17), with the substitution $\delta\omega(t_i) \rightarrow A_i$.


full calculated correlation function


Short time part of correlation function

We can see that the correlation function reveals no frequency correlation on the time scale of 10^4–10^5 fs, however a decay of the correlation function is observed for short delays signifying the loss of memory in the fluctuating frequency on the 10^3 fs time scale. From eq. (9.15) we find that the correlation time is $\tau_C = 785$ fs.

9.3. Quantum Time-Correlation Functions

Quantum correlation functions involve the equilibrium (thermal) average over a product of Hermitian operators evaluated two times. The thermal average is implicit in writing $C_{AA}(\tau)=\langle A(\tau)A(0)\rangle$. Naturally, this also invokes a Heisenberg representation of the operators, although in almost all cases, we will be writing correlation functions as interaction picture operators $A_I(t)=e^{iH_0t}Ae^{-iH_0t}$.

To emphasize the thermal average, the quantum correlation function can also be written as

$$C_{AA}(\tau)=\left\langle \frac{e^{-\beta H}}{Z}A(\tau)A(0)\right\rangle \tag{9.18}$$

with $\beta=(k_{\mathrm{B}}T)^{-1}$. If we evaluate this for a time-independent Hamiltonian in a basis of states $|n\rangle$, inserting a projection operator leads to our previous expression

$$C_{AA}(\tau)=\sum_n p_n\langle n|A(\tau)A(0)|n\rangle \tag{9.19}$$

with $p_n=e^{-\beta E_n}/Z$. Given the case of a time-independent Hamiltonian for which we have knowledge of the eigenstates, we can also express the correlation function in the Schrödinger picture as

$$\begin{aligned}C_{AA}(\tau)&=\sum_n p_n\langle n|U^\dagger(\tau)AU(\tau)A\,|\,n\rangle\\&=\sum_{n,m}p_n\,\langle n|A|m\rangle\langle m|A|n\rangle\,e^{-i\omega_{mn}\tau}\\C_{AA}(\tau)&=\sum_{n,m}p_n\,|A_{mn}|^2\,e^{-i\omega_{mn}\tau}\end{aligned} \tag{9.20}$$

Properties of Quantum Correlation Functions

There are a few properties of quantum correlation functions for Hermitian operators that can be obtained using the properties of the time-evolution operator. First, we can show that correlation functions are stationary:

$$\begin{aligned}\langle A(t)A(t')\rangle&=\langle U^\dagger(t)A(0)U(t)U^\dagger(t')A(0)U(t')\rangle\\&=\langle U(t')U^\dagger(t)AU(t)U^\dagger(t')A\rangle\\&=\langle U^\dagger(t-t')AU(t-t')A\rangle\\&=\langle A(t-t')A(0)\rangle\end{aligned} \tag{9.21}$$

Similarly, we can show

$$\langle A(-t)A(0)\rangle=\langle A(t)A(0)\rangle^*=\langle A(0)A(t)\rangle \tag{9.22}$$

or in short
$$C_{AA}^{*}(t)=C_{AA}(-t)\,. \tag{9.23}$$

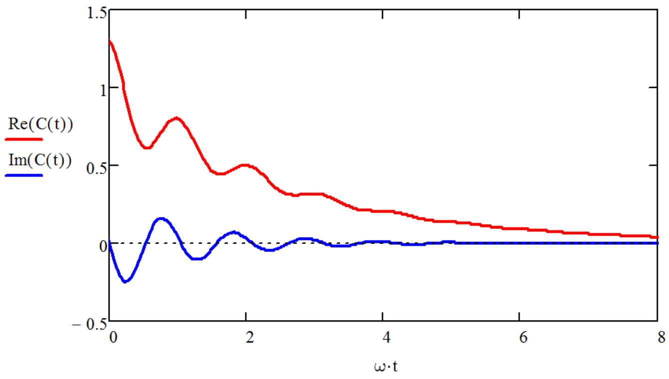
Note that the quantum $C_{AA}(t)$ is complex. You cannot directly measure a quantum correlation function, but observables are often related to the real or imaginary part of correlation functions. The real and imaginary parts of $C_{AA}(t)$ can be separated as

$$C_{AA}(t)=C'_{AA}(t)+i\,C''_{AA}(t) \tag{9.24}$$

$$\begin{aligned}C'_{AA}(t)&=\frac{1}{2}\left[C_{AA}(t)+C^{*}_{AA}(t)\right]=\frac{1}{2}\left[\langle A(t)A(0)\rangle+\langle A(0)A(t)\rangle\right]\\&=\frac{1}{2}\left\langle\left[A(t),A(0)\right]_{+}\right\rangle\end{aligned} \tag{9.25}$$

$$\begin{aligned}C''_{AA}(t)&=\frac{1}{2}\left[C_{AA}(t)-C^{*}_{AA}(t)\right]=\frac{1}{2}\left[\langle A(t)A(0)\rangle-\langle A(0)A(t)\rangle\right]\\&=\frac{1}{2}\left\langle\left[A(t),A(0)\right]\right\rangle\end{aligned} \tag{9.26}$$

Above $[A,B]_{+}\equiv AB+BA$ is the anticommutator. As illustrated below, the real part is even in time, and can be expanded as Fourier series in cosines, whereas the imaginary part is odd, and can be expanded in sines. We will see later that the magnitude of the real part grows with temperature, but the imaginary does not. At 0 K, the real and imaginary components have equal amplitudes, but as one approaches the high temperature or classical limit, the real part dominates the imaginary.



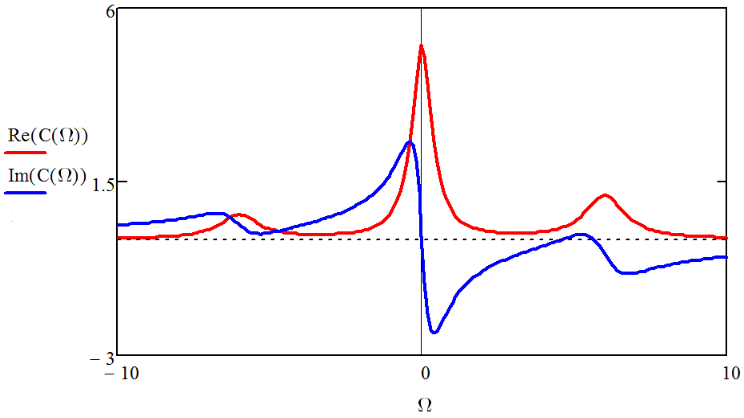
We will also see in our discussion of linear response that C'_{AA} and C''_{AA} are directly proportional to the step response function S and the impulse response function R, respectively. R describes how a system is driven away from equilibrium by an external potential, whereas S describes the relaxation of the system to equilibrium when a force holding it away from equilibrium is released. Classically, the two are related by $R\propto\partial S/\partial t$.

Since time and frequency are conjugate variables, we can also define a spectral or frequency-domain correlation function by the Fourier transformation of the TCF. The Fourier transform and its inverse are defined as

$$\tilde{C}_{AA}(\omega) = \tilde{\mathcal{F}}\left[C_{AA}(t)\right] = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, C_{AA}(t) \tag{9.27}$$

$$C_{AA}(t) = \tilde{\mathcal{F}}^{-1}\left[\tilde{C}_{AA}(\omega)\right] = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t}\, \tilde{C}_{AA}(\omega) \tag{9.28}$$

Examples of the frequency-domain correlation functions are shown below.



For a time-independent Hamiltonian, as we might have in an interaction picture problem, the Fourier transform of the TCF in eq. (9.20) gives

$$\tilde{C}_{AA}(\omega) = \sum_{n,m} p_n \left|A_{mn}\right|^2 \delta\left(\omega - \omega_{mn}\right) \tag{9.29}$$

This expression looks very similar to the Golden Rule transition rate from first-order perturbation theory. In fact, the Fourier transform of time-correlation functions evaluated at the energy gap gives the transition rate between states that we obtain from first-order perturbation theory. Note that this expression is valid whether the initial states *n* are higher or lower in energy than final states *m*, and accounts for upward and downward transitions. If we compare the ratio of upward and downward transition rates between two states *i* and *j*, we have

$$\frac{\tilde{C}_{AA}\left(\omega_{ij}\right)}{\tilde{C}_{AA}\left(\omega_{ji}\right)} = \frac{p_j}{p_i} = e^{\beta E_{ij}} \tag{9.30}$$

This is one way of showing the principle of detailed balance, which relates upward and downward transition rates at equilibrium to the difference in thermal occupation between states:

$$\tilde{C}_{AA}(\omega) = e^{\beta\hbar\omega}\, \tilde{C}_{AA}(-\omega) \tag{9.31}$$

This relationship together with a Fourier transform of eq. (9.23) allows us to obtain the real and imaginary components using

$$\tilde{C}_{AA}(\omega) \pm \tilde{C}_{AA}(-\omega) = \left(1 \pm e^{-\beta\hbar\omega}\right)\tilde{C}_{AA}(\omega) \tag{9.32}$$

$$\tilde{C}'_{AA}(\omega) = \tilde{C}_{AA}(\omega)\left(1 + e^{-\beta\hbar\omega}\right) \tag{9.33}$$

$$\tilde{C}''_{AA}(\omega) = \tilde{C}_{AA}(\omega)\left(1 - e^{-\beta\hbar\omega}\right) \tag{9.34}$$

9.4. Transition Rates from Correlation Functions

We have already seen that the rates obtained from first-order perturbation theory are related to the Fourier transform of the time-dependent external potential evaluated at the energy gap between the initial and final state. Here we will show that the rate of leaving an initially prepared state, typically expressed by Fermi's Golden Rule through a resonance condition in the frequency domain, can be expressed in the time-domain picture in terms of a time-correlation function for the interaction of the initial state with others.

The state-to-state form of Fermi's Golden Rule is

$$w_{k\ell} = \frac{2\pi}{\hbar} \left| V_{k\ell} \right|^2 \delta\left(E_k - E_\ell \right) \tag{9.35}$$

We will look specifically at the case of a system at thermal equilibrium in which the initially populated states ℓ are coupled to all states k. Time-correlation functions are expressions that apply to systems at thermal equilibrium, so we will thermally average this expression.

$$\overline{w}_{k\ell} = \frac{2\pi}{\hbar} \sum_{k,\ell} p_\ell \left| V_{k\ell} \right|^2 \delta\left(E_k - E_\ell \right) \tag{9.36}$$

where $p_\ell = e^{-\beta E_\ell} / Z$. The energy conservation statement expressed in terms of E or ω can be converted to the time domain using the definition of the delta function

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \; e^{i\omega t} \tag{9.37}$$

giving

$$\overline{w}_{k\ell} = \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell \left| V_{k\ell} \right| \int_{-\infty}^{+\infty} dt \; e^{i\left(E_k - E_\ell\right)t/\hbar} \tag{9.38}$$

Writing the matrix elements explicitly and recognizing that in the interaction picture, $e^{-iH_0 t/\hbar} \left| \ell \right\rangle = e^{-iE_\ell t/\hbar} \left| \ell \right\rangle$, we have

$$\overline{w}_{k\ell} = \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell \int_{-\infty}^{+\infty} dt \; e^{i\left(E_k - E_\ell\right)t/\hbar} \left\langle \ell \middle| V \middle| k \right\rangle \left\langle k \middle| V \middle| \ell \right\rangle \tag{9.39}$$

$$= \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell \int_{-\infty}^{+\infty} dt \; \left\langle \ell \middle| V \middle| k \right\rangle \left\langle k \middle| e^{iH_0 t/\hbar} \, V \, e^{-iH_0 t/\hbar} \middle| \ell \right\rangle \tag{9.40}$$

Then, since $\sum_k \left| k \right\rangle \left\langle k \right| = 1$

$$\overline{w}_{mn} = \frac{1}{\hbar^2} \sum_{\ell = m,n} p_\ell \int_{-\infty}^{+\infty} dt \left\langle \ell \middle| V_I(0) V_I(t) \middle| \ell \right\rangle \tag{9.41}$$

$$\overline{w}_{mn} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \left\langle V_I(t) V_I(0) \right\rangle \tag{9.42}$$

As before $V_I(t) = e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar}$. The final expression indicates that integrating over a correlation function for the time-dependent interaction of the initial state with its surroundings gives the relaxation or transfer rate. This is a general expression. Although the derivation emphasized specific eigenstates, eq. (9.42) shows that with a knowledge of a time-dependent interaction potential of any sort, we can calculate transition rates from the time-correlation function for that potential.

The same approach can be taken using the rates of transition in an equilibrium system induced by a harmonic perturbation

$$\bar{w}_{k\ell} = \frac{\pi}{2\hbar^2} \sum_{\ell,k} p_\ell \left|V_{k\ell}\right|^2 \left[\delta\left(\omega_{k\ell} - \omega\right) + \delta\left(\omega_{k\ell} + \omega\right)\right] \tag{9.43}$$

resulting in a similar expression for the transition rate in terms of a interaction potential time-correlation function

$$\begin{aligned} \bar{w}_{k\ell} &= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \left\langle V_I(0) V_I(t) \right\rangle \\ &= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \left\langle V_I(t) V_I(0) \right\rangle \end{aligned} \tag{9.44}$$

We will look at this closer in the following section. Note that here the transfer rate is expressed in terms of a Fourier transform over a correlation function for the time-dependent interaction potential. Although eq. (9.42) is not written as a Fourier transform, it can in practice be evaluated by a Fourier transformation and evaluating its value at zero frequency.

Readings on time-correlation functions

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10. LINEAR RESPONSE THEORY

10.1. Classical Linear Response Theory

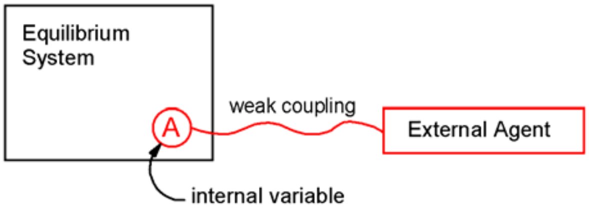
Correlation functions provide a statistical description of the dynamics of molecular variables; however, it remains unclear how they are related to experimental observables. You have probably sensed this from the perspective that correlation functions are *complex*, and how can observables be complex? Also, correlation functions describe equilibrium dynamics, but from a realistic point of view, exerting external forces should move the system away from equilibrium. What happens as a result? These questions fall into the realm of nonequilibrium statistical mechanics, an area of active research for which formal theories are limited and approximation methods are the primary tool. Linear response theory is the primary approximation method, which describes the evolution away or toward equilibrium under perturbative conditions.

We will use linear response theory as a way of describing a real experimental observable. Specifically this will tell us how an equilibrium system changes in response to an applied potential. The quantity that will describe this is a response function, a real observable quantity. We will go on to show how it is related to correlation functions. Embedded in this discussion is a particularly important observation. We will now deal with a nonequilibrium system, but we will show that when the changes are small away from equilibrium, the equilibrium fluctuations dictate the nonequilibrium response! Thus knowledge of equilibrium dynamics is useful in predicting the outcome of nonequilibrium processes.

So, the question is "How does the system respond if you drive it away from equilibrium?" We will examine the case where an *equilibrium* system, described by a Hamiltonian H_0 interacts weakly with an external agent, $V(t)$. The system is moved away from equilibrium by the external agent, and the system absorbs energy from the external agent.

How do we describe the time-dependent properties of the system? We first take the external agent to interact with the system through an internal variable A. So the Hamiltonian for this problem is given by

$$H = H_0 - f(t)\,A \tag{10.1}$$



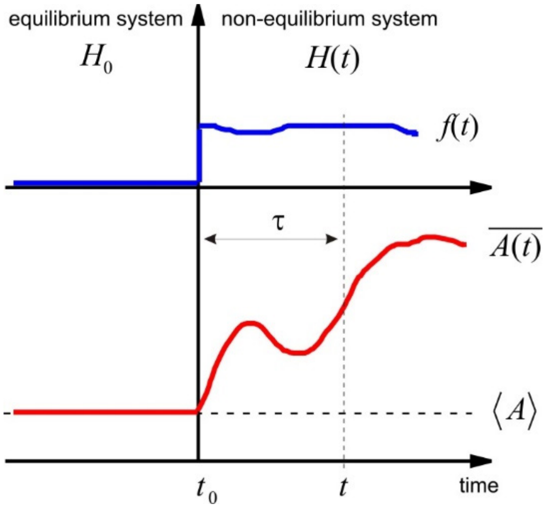
Here $f(t)$ is the time-dependent action of the external agent, and the deviation from equilibrium is linear in the internal variable. We describe the behavior of an ensemble initially at thermal equilibrium by assuming that each member of the ensemble is subject to the same interaction with the external agent, and then ensemble averaging. Initially, the system is described by H_0. It is at equilibrium and the internal variable is characterized by an equilibrium ensemble average $\langle A \rangle$. The external agent is then applied at time t_0, and the system is moved away from equilibrium, and is characterized through a nonequilibrium ensemble average, $\overline{A}$. $\langle A \rangle \neq \overline{A(t)}$ as a result of the interaction.

For a weak interaction with the external agent, we can describe $\overline{A(t)}$ by performing an expansion in powers of $f(t)$.

$$\overline{A(t)} = \left(terms\ f^{(0)} \right) + \left(terms\ f^{(1)} \right) + \ldots \tag{10.2}$$

$$\overline{A(t)} = \langle A \rangle + \int dt_0\, R(t,t_0)\, f(t_0) + \ldots \tag{10.3}$$

In this expression the agent is applied at t_0, and we observe the system at t. The leading term in this expansion is independent of f, and is therefore equal to $\langle A \rangle$. The next term in (10.3) describes the deviation from the equilibrium behavior in terms of a linear dependence on the external agent. $R(t,t_0)$ is the linear response function, the quantity that contains the microscopic information on the system and how it responds to the applied agent. The integration in the last term of eq. (10.3) indicates that the nonequilibrium behavior depends on the full history of the application of the agent $f(t_0)$ and the response of the system to it. We are seeking a quantum mechanical description of R.



Properties of the response function

1. Causal: Causality refers to the common sense observation that the system cannot respond before the force has been applied. Therefore $R(t,t_0) = 0$ for $t < t_0$, and the time-dependent change in A is

$$\delta\overline{A(t)} = \overline{A(t)} - \langle A \rangle = \int_{-\infty}^{t} dt_0\, R(t,t_0)\, f(t_0) \tag{10.4}$$

The lower integration limit is set to $-\infty$ to reflect that the system is initially at equilibrium, and the upper limit is the time of observation. We can also make the statement of causality explicit by writing the linear response function with a step response: $\Theta(t-t_0)R(t,t_0)$, where

$$\Theta(t-t_0) \equiv \begin{cases} 0 & (t < t_0) \\ 1 & (t \geq t_0) \end{cases} \tag{10.5}$$

2. Stationary: Similar to our discussion of correlation functions, the time-dependence of the system only depends on the time interval between application of the potential and observation. Therefore we write $R(t,t_0)=R(t-t_0)$ and

$$\delta\overline{A(t)}=\int_{-\infty}^{t}dt_0 R(t-t_0)\,f(t_0) \tag{10.6}$$

This expression says that the observed response of the system to the agent is a *convolution* of the material response with the time-development of the applied force.

Rather than the absolute time points, we can define a time-interval $\tau=t-t_0$, so that we can write

$$\delta\overline{A(t)}=\int_{0}^{\infty}d\tau\, R(\tau)\,f(t-\tau) \tag{10.7}$$

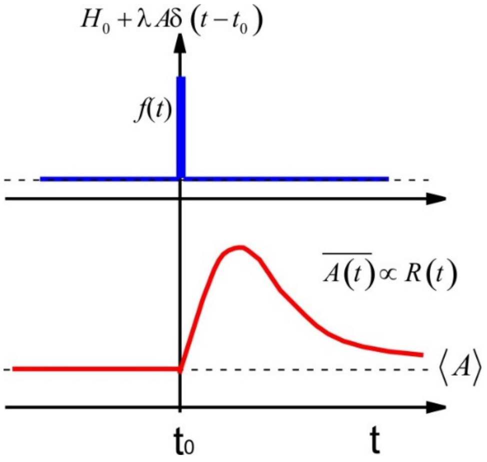
3. Impulse response: Note that for a delta function perturbation:

$$f(t)=\lambda\delta(t-t_0) \tag{10.8}$$

We obtain

$$\delta\overline{A(t)}=\lambda R(t-t_0) \tag{10.9}$$

Thus, R describes how the system behaves when an abrupt perturbation is applied and is often referred to as the impulse response function. An impulse response kicks the system away from the equilibrium established under H_0, and therefore the shape of a response function will always rise from zero and ultimately return to zero. In other words, it will be a function that can be expanded in *sines*. Thus the response to an arbitrary *f*(*t*) can be described through a Fourier analysis, suggesting that a spectral representation of the response function would be useful.



The susceptibility

The observed temporal behavior of the nonequilibrium system can also be cast in the frequency domain as a spectral response function, or susceptibility. We start with eq. (10.7) and Fourier transform both sides:

$$\begin{aligned}\delta\overline{A(\omega)} &\equiv \int_{-\infty}^{+\infty} dt\, \delta\overline{A(t)} e^{i\omega t} \\ &= \int_{-\infty}^{+\infty} dt \left[\int_0^{\infty} d\tau\, R(\tau) f(t-\tau)\right] e^{i\omega t}\end{aligned} \tag{10.10}$$

Now we insert $e^{-i\omega\tau}e^{+i\omega\tau}=1$ and collect terms to give

$$\delta\overline{A(\omega)} = \int_{-\infty}^{+\infty} dt \int_0^{\infty} d\tau\, R(\tau)\, f(t-\tau)\, e^{i\omega(t-\tau)}\, e^{i\omega\tau} \tag{10.11}$$

$$= \underline{\int_{-\infty}^{+\infty} dt'\, e^{i\omega t'}\, f(t')}\ \underline{\int_0^{\infty} d\tau\, R(\tau)\, e^{i\omega\tau}} \tag{10.12}$$

or

$$\delta\overline{A(\omega)} = \tilde{f}(\omega)\,\chi(\omega) \tag{10.13}$$

In eq. (10.12) we switched variables, setting $t'=t-\tau$. The first term $\tilde{f}(\omega)$ is a complex frequency domain representation of the driving force, obtained from the Fourier transform of $f(t')$. The second term $\chi(\omega)$ is the susceptibility which is defined as the Fourier–Laplace transform (single-sided Fourier transform) of the impulse response function. It is a frequency-domain representation of the linear response function. Switching between time and frequency domains shows that a convolution of the force and response in time leads to the product of the force and response in frequency. This is a manifestation of the convolution theorem:

$$A(t)\otimes B(t) \equiv \int_{-\infty}^{\infty} d\tau\, A(t-\tau)B(\tau) = \int_{-\infty}^{\infty} d\tau\, A(\tau)B(t-\tau) = \mathcal{F}^{-1}\left[\tilde{A}(\omega)\tilde{B}(\omega)\right] \tag{10.14}$$

Here $\otimes$ refers to convolution, $\tilde{A}(\omega)=\mathcal{F}\left[A(t)\right]$, $\mathcal{F}[\cdots]$ is a Fourier transform, and $\mathcal{F}^{-1}[\cdots]$ is an inverse Fourier transform.

Note that $R(\tau)$ is a real function, since the response of a system is an observable. The susceptibility $\chi(\omega)$ is complex:

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) \tag{10.15}$$

Since

$$\chi(\omega) = \int_0^{\infty} d\tau\, R(\tau) e^{i\omega\tau} \tag{10.16}$$

However, the real and imaginary contributions are not independent. We have

$$\chi' = \int_0^{\infty} d\tau\, R(\tau)\cos\omega\tau \tag{10.17}$$

and

$$\chi'' = \int_0^{\infty} d\tau\, R(\tau)\sin\omega\tau \tag{10.18}$$

χ' and χ'' are even and odd functions of frequency:

$$\chi'(\omega) = \chi'(-\omega) \tag{10.19}$$

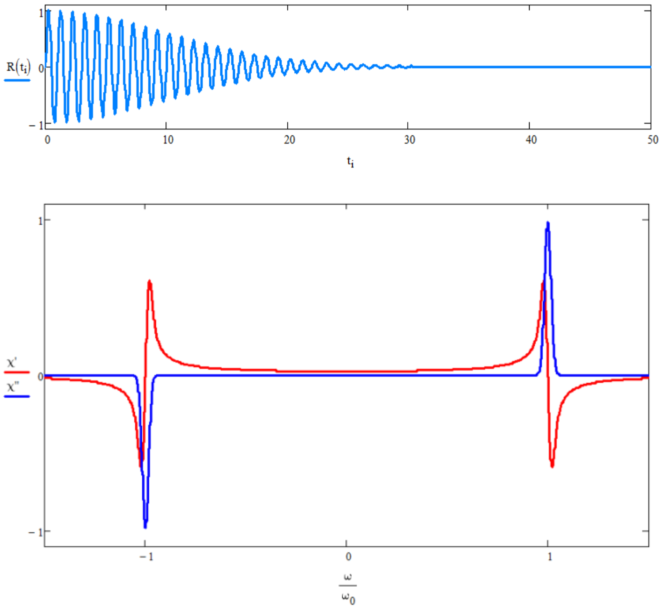
$$\chi''(\omega) = -\chi''(-\omega) \tag{10.20}$$

so that
$$\chi(-\omega)=\chi^*(\omega) \tag{10.21}$$

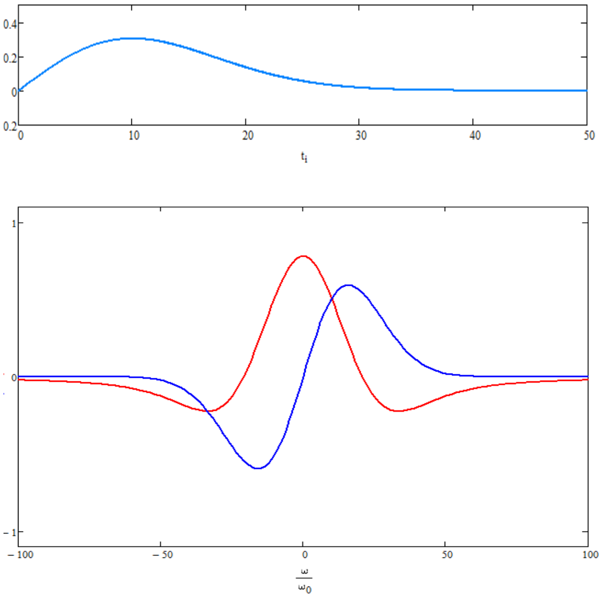
Notice also that eq. (10.21) allows us to write

$$\chi'(\omega)=\frac{1}{2}\left[\chi(\omega)+\chi(-\omega)\right] \tag{10.22}$$

$$\chi''(\omega)=\frac{1}{2i}\left[\chi(\omega)-\chi(-\omega)\right] \tag{10.23}$$



Example of a high frequency underdamped response function oscillating as sin($\omega_0 t$) and corresponding susceptibility



Example of a low frequency overdamped response function and corresponding susceptibility

Kramers–Krönig relations

Since they are cosine and sine transforms of the same function, $\chi'(\omega)$ is not independent of $\chi''(\omega)$. The two are related by the Kramers–Krönig relationships:

$$\chi'(\omega)=\frac{1}{\pi}\mathbb{P}\int_{-\infty}^{+\infty}\frac{\chi''(\omega')}{\omega'-\omega}d\omega' \tag{10.24}$$

$$\chi''(\omega)=-\frac{1}{\pi}\mathbb{P}\int_{-\infty}^{+\infty}\frac{\chi'(\omega')}{\omega'-\omega}d\omega' \tag{10.25}$$

These are obtained by substituting the inverse sine transform of eq. (10.18) into eq. (10.17):

$$\begin{aligned}\chi'(\omega) &= \frac{1}{\pi}\int_0^\infty dt\cos\omega t\int_{-\infty}^{+\infty}\chi''(\omega')\sin\omega' t\, d\omega' \\ &= \frac{1}{\pi}\lim_{L\to\infty}\int_{-\infty}^{+\infty} d\omega'\chi''(\omega')\int_0^L \cos\omega t\sin\omega' t\, dt\end{aligned} \tag{10.26}$$

Using $\cos ax \sin bx = \frac{1}{2}\sin(a+b)x + \frac{1}{2}\sin(b-a)x$, this can be written as

$$\chi'(\omega) = \frac{1}{\pi}\lim_{L\to\infty}\mathrm{P}\int_{-\infty}^{+\infty} d\omega'\chi''(\omega)\tfrac{1}{2}\left[\frac{-\cos(\omega'+\omega)L+1}{\omega'+\omega} - \frac{\cos(\omega'-\omega)L+1}{\omega'-\omega}\right] \tag{10.27}$$

If we choose to evaluate the limit $L\to\infty$, the cosine terms are hard to deal with, but we expect they will vanish since they oscillate rapidly. This is equivalent to averaging over a monochromatic field. Alternatively, we can average over a single cycle: $L = 2\pi/(\omega'-\omega)$ to obtain eq. (10.24). The other relation can be derived in a similar way. Note that the Kramers–Krönig relationships are a consequence of causality, which dictate the lower limit of $t_{initial} = 0$ on the first integral evaluated above.

Example: Driven harmonic oscillator

One can classically model the absorption of light through a resonant interaction of the electromagnetic field with an oscillating dipole, using Newton's equations for a forced damped harmonic oscillator:

$$\ddot{x} - \gamma\dot{x} + \omega_0^2 x = F(t)/m \tag{10.28}$$

Here the x is the coordinate being driven, γ is the damping constant, and $\omega_0 = \sqrt{k/m}$ is the natural frequency of the oscillator. We originally solved this problem is to take the driving force to have the form of a monochromatic oscillating source

$$F(t) = F_0\cos\omega t \tag{10.29}$$

Then, equation (10.28) has the solution

$$x(t) = \frac{F_0}{m}\left((\omega^2-\omega_0^2)^2 + \gamma^2\omega^2\right)^{-1/2}\sin(\omega t+\delta) \tag{10.30}$$

with
$$\tan\delta = \omega_0^2 - \omega^2/\gamma\omega \tag{10.31}$$

This shows that the driven oscillator has an oscillation period that is dictated by the driving frequency ω, and whose amplitude and phase shift relative to the driving field is dictated by its detuning from resonance. If we cycle-average to obtain the average absorbed power from the field, the absorption spectrum is

$$\begin{aligned} P_{avg}(\omega) &= \langle F(t)\cdot \dot{x}(t)\rangle \\ &= \frac{\gamma\omega^2 F_0^2}{2m}\left[\left(\omega_0^2-\omega^2\right)^2+\gamma^2\omega^2\right]^{-1/2} \end{aligned} \tag{10.32}$$

To determine the response function for the damped harmonic oscillator, we seek a solution to eq. (10.28) using an impulsive driving force $F(t) = F_0\delta(t-t_0)$. The linear response of this oscillator to an arbitrary force is

$$x(t) = \int_0^\infty d\tau\, R(\tau)\, F(t-\tau) \tag{10.33}$$

so that time-dependence with an impulsive driving force is directly proportional to the response function, $x(t) = F_0\ R(t)$. For this case, we obtain

$$R(\tau) = \frac{1}{m\Omega}\exp\left(-\frac{\gamma}{2}\tau\right)\sin\Omega\tau \tag{10.34}$$

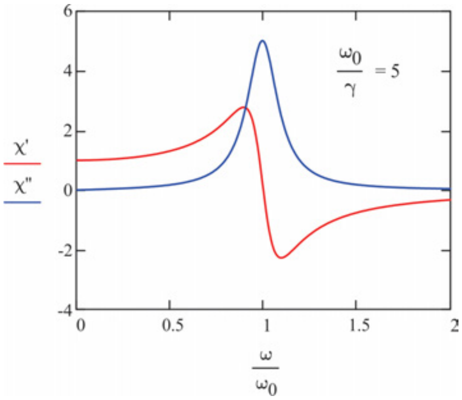
The reduced frequency is defined as

$$\Omega = \sqrt{\omega_0^2 - \gamma^2/4} \tag{10.35}$$

From this, we evaluate eq. (10.16) and obtain the susceptibility

$$\chi(\omega) = \frac{1}{m\left(\omega_0^2-\omega^2-i\gamma\omega\right)} \tag{10.36}$$

As we will see shortly, the absorption of light by the oscillator is proportional to the imaginary part of the susceptibility



$$\chi''(\omega) = \frac{\gamma\omega}{m\left[\left(\omega_0^2-\omega^2\right)^2+\gamma^2\omega^2\right]} \tag{10.37}$$

The real part is

$$\chi'(\omega) = \frac{\omega_0^2-\omega^2}{m\left[\left(\omega_0^2-\omega^2\right)^2+\gamma^2\omega^2\right]} \tag{10.38}$$

For the case of weak damping $\gamma << \omega_0$ commonly encountered in molecular spectroscopy, eq. (10.36) is written as a Lorentzian lineshape by using the near-resonance approximation

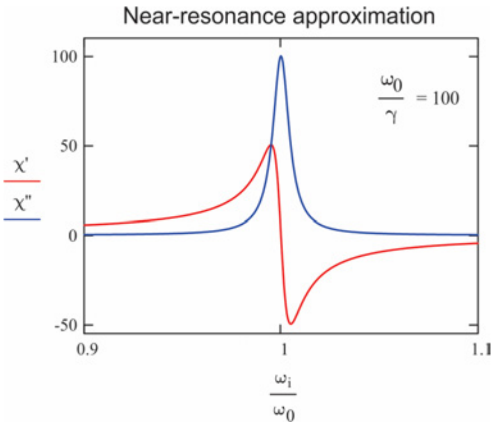
$$\omega^2-\omega_0^2 = (\omega+\omega_0)(\omega-\omega_0) \approx 2\omega(\omega-\omega_0) \tag{10.39}$$

$$\chi(\omega) \approx \frac{1}{2m\omega_0}\frac{1}{\omega-\omega_0+i\gamma/2}\,. \tag{10.40}$$

Then the imaginary part of the susceptibility shows asymmetric lineshape with a line width of γ, full width at half maximum.

$$\chi''(\omega) \approx \frac{1}{2m\omega_0} \frac{\gamma}{(\omega-\omega_0)^2 + \gamma^2/4} \tag{10.41}$$

$$\chi'(\omega) \approx \frac{1}{m\omega_0} \frac{(\omega-\omega_0)}{(\omega-\omega_0)^2 + \gamma^2/4} \tag{10.42}$$

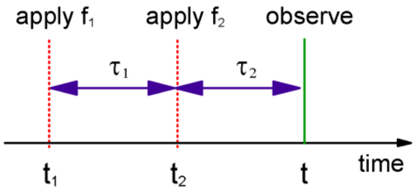


Nonlinear response functions

If the system does not respond in a manner linearly proportional to the applied potential but still perturbative, we can include nonlinear terms, i.e. higher expansion orders of $\overline{A(t)}$ in eq. (10.3). Let's look at <u>second order</u>:

$$\delta\overline{A(t)}^{(2)} = \int dt_1 \int dt_2 \; R^{(2)}(t;t_1,t_2)\, f_1(t_1)\, f_2(t_2) \tag{10.43}$$

Again we are integrating over the entire history of the application of two forces *f₁* and *f₂*, including any quadratic dependence on *f* .



In this case, we will enforce causality through a time ordering that requires (1) that all forces must be applied before a response is observed and (2) that the application of *f₂* must follow *f₁*. That is $t \geq t_2 \geq t_1$ or

$$R^{(2)}(t;t_1,t_2) \Rightarrow R^{(2)} \cdot \Theta(t-t_2) \cdot \Theta(t_2-t_1) \tag{10.44}$$

which leads to

$$\delta\overline{A(t)}^{(2)} = \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t_2} dt_1 R^{(2)}(t;t_1,t_2)\, f_1(t_1)\, f_2(t_2) \tag{10.45}$$

Now we will call the system *stationary* so that we are only concerned with the time intervals between consecutive interaction times. If we define the intervals between adjacent interactions

$$\begin{aligned} \tau_1 &= t_2 - t_1 \\ \tau_2 &= t - t_2 \end{aligned} \tag{10.46}$$

Then we have

$$\delta\overline{A(t)}^{(2)} = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \; R^{(2)}(\tau_1,\tau_2)\, f_1(t-\tau_1-\tau_2)\, f_2(t-\tau_2) \tag{10.47}$$

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10.2. Quantum Linear Response Functions

To develop a quantum description of the linear response function, we start by recognizing that the response of a system to an applied external agent is a problem we can solve in the interaction picture. Our time-dependent Hamiltonian is

$$H(t) = H_0 - f(t)\hat{A} \quad = \quad H_0 + V(t) \tag{10.48}$$

H_0 is the material Hamiltonian for the equilibrium system. The external agent acts on the equilibrium system through $\hat{A}$, an operator in the system states, with a time-dependence $f(t)$. We take $V(t)$ to be a small change, and treat this problem with perturbation theory in the interaction picture.

We want to describe the nonequilibrium response $\overline{A(t)}$, which we will get by ensemble averaging the expectation value of $\hat{A}$, i.e. $\overline{\langle A(t)\rangle}$. Remember the expectation value for a pure state in the interaction picture is

$$\begin{aligned}\langle A(t)\rangle &= \langle \psi_I(t)|A_I(t)|\psi_I(t)\rangle \\ &= \langle \psi_0|U_I^\dagger\, A_I\, U_I|\psi_0\rangle\end{aligned} \tag{10.49}$$

The interaction picture Hamiltonian for eq. (10.48) is

$$\begin{aligned}V_I(t) &= U_0^\dagger(t)V(t)U_0(t) \\ &= -f(t)A_I(t)\end{aligned} \tag{10.50}$$

To calculate an ensemble average of the state of the system after applying the external potential, we recognize that the nonequilibrium state of the system characterized by described by $|\psi_I(t)\rangle$ is in fact related to the initial equilibrium state of the system $|\psi_0\rangle$ through a time-propagator, as seen in eq. (10.49). So the nonequilibrium expectation value $\overline{A(t)}$ is in fact obtained by an equilibrium average over the expectation value of $U_I^\dagger\, A_I\, U_I$:

$$\overline{A(t)} = \sum_n p_n \langle n|U_I^\dagger\, A_I\, U_I|n\rangle \tag{10.51}$$

Again $|n\rangle$ are eigenstates of H_0. Working with the first order solution to $U_I(t)$

$$U_I(t-t_0) = 1 + \frac{i}{\hbar}\int_{t_0}^{t} dt'\, f(t')\, A_I(t') \tag{10.52}$$

we can now calculate the value of the operator *A* at time *t*, integrating over the history of the applied interaction $f(t')$:

$$\begin{aligned} A(t) &= U_I^\dagger\, A_I\, U_I \\ &= \left\{1-\frac{i}{\hbar}\int_{t_0}^{t} dt'\, f(t')\, A_I(t')\right\}\; A_I(t)\; \left\{1+\frac{i}{\hbar}\int_{t_0}^{t} dt'\, f(t')\, A_I(t')\right\} \end{aligned} \tag{10.53}$$

Here note that *f* is the time-dependence of the external agent. It does not involve operators in H_0 and commutes with *A*. Working toward the linear response function, we just retain the terms linear in $f(t')$

$$\begin{aligned} A(t) &\cong A_I(t) + \frac{i}{\hbar}\int_{t_0}^{t} dt'\, f(t')\left\{A_I(t)\,A_I(t') - A_I(t')\,A_I(t)\right\} \\ &= A_I(t) + \frac{i}{\hbar}\int_{t_0}^{t} dt'\, f(t')\left[A_I(t),\, A_I(t')\right] \end{aligned} \tag{10.54}$$

Since our system is initially at equilibrium, we set $t_0 = -\infty$ and switch variables to the time interval $\tau = t - t'$ and using $A_I(t) = U_0^\dagger(t)\, A\, U_0(t)$ obtain

$$A(t) = A_I(t) + \frac{i}{\hbar}\int_0^\infty d\tau\, f(t-\tau)\left[A_I(\tau),\, A_I(0)\right] \tag{10.55}$$

We can now calculate the expectation value of *A* by performing the ensemble-average described in eq. (10.51). Noting that the force is applied equally to each member of ensemble, we have

$$\overline{A(t)} = \langle A\rangle + \frac{i}{\hbar}\int_0^\infty d\tau\, f(t-\tau)\left\langle\left[A_I(\tau),\, A_I(0)\right]\right\rangle \tag{10.56}$$

The first term is independent of *f*, and so it comes from an equilibrium ensemble average for the value of *A*.

$$\langle A(t)\rangle = \sum_n p_n \langle n|A_I|n\rangle = \langle A\rangle \tag{10.57}$$

The second term is just an equilibrium ensemble average over the commutator in $A_I(t)$:

$$\left\langle\left[A_I(\tau),\, A_I(0)\right]\right\rangle = \sum_n p_n \left\langle n\left|\left[A_I(\tau),\, A_I(0)\right]\right|n\right\rangle \tag{10.58}$$

Comparing eq. (10.56) with the expression for the linear response function, we find that the quantum linear response function is

$$\begin{aligned} R(\tau) &= -\frac{i}{\hbar}\left\langle\left[A_I(\tau), A_I(0)\right]\right\rangle & \tau \geq 0 \\ &= 0 & \tau < 0 \end{aligned} \tag{10.59}$$

or as it is sometimes written with the unit step function in order to enforce causality:

$$R(\tau) = -\frac{i}{\hbar}\Theta(\tau)\left\langle\left[A_I(\tau), A_I(0)\right]\right\rangle \tag{10.60}$$

The important thing to note is that the time-development of the system with the applied external potential is governed by the dynamics of the equilibrium system. All of the time-dependence in the response function is under H_0.

The linear response function is therefore the sum of two correlation functions with the order of the operators interchanged, which is the imaginary part of the correlation function $C''(\tau)$

$$\begin{aligned} R(\tau) &= -\frac{i}{\hbar}\Theta(\tau)\left\{\left\langle A_I(\tau)A_I(0)\right\rangle - \left\langle A_I(0)A_I(\tau)\right\rangle\right\} \\ &= -\frac{i}{\hbar}\Theta(\tau)\left(C_{AA}(\tau) - C_{AA}^{*}(\tau)\right) \qquad (10.61) \\ &= \frac{2}{\hbar}\Theta(\tau)C''(\tau) \end{aligned}$$

As we expect for an observable, the response function is real. If we express the correlation function in the eigenstate description:

$$C(t) = \sum_{n,m} p_n \left|A_{mn}\right|^2 e^{-i\omega_{mn}t} \qquad (10.62)$$

then

$$R(t) = \frac{2}{\hbar}\Theta(t)\sum_{n,m} p_n \left|A_{mn}\right|^2 \sin\omega_{mn}t \qquad (10.63)$$

$R(\tau)$ can always be expanded in sines—an odd function of time. This reflects that fact that the impulse response must have a value of 0 (the deviation from equilibrium) at $t = t_0$, and move away from 0 at the point where the external potential is applied.

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10.3. The Response Function and Energy Absorption

Let’s investigate the relationship between the linear response function and the absorption of energy from the external agent—in this case an electromagnetic field. We will relate this to the absorption coefficient $\alpha = \dot{E}/I$ which we have described previously. For this case,

$$H = H_0 - f(t)A \quad = \quad H_0 - \mu \cdot E(t) \tag{10.64}$$

This expression gives the energy of the system, so the rate of energy absorption averaged over the nonequilibrium ensemble is described by:

$$\dot{E} = \frac{\partial \overline{H}}{\partial t} = -\frac{\partial f}{\partial t}\overline{A(t)} \tag{10.65}$$

We will want to cycle-average this over the oscillating field, so the time-averaged rate of energy absorption is

$$\begin{aligned} \dot{E} &= \frac{1}{T}\int_0^T dt \left[-\frac{\partial f}{\partial t}\overline{A(t)} \right] \\ &= \frac{1}{T}\int_0^T dt \frac{\partial f(t)}{\partial t}\left[\langle A \rangle + \int_0^\infty d\tau \, R(\tau) f(t-\tau) \right] \end{aligned} \tag{10.66}$$

Here the response function is $R(\tau) = -i\langle[\mu(\tau), \mu(0)]\rangle/\hbar$. For a monochromatic electromagnetic field, we can write

$$f(t) = E_0 \cos \omega t = \tfrac{1}{2}\left[E_0 e^{-i\omega t} + E_0^* e^{i\omega t} \right] \tag{10.67}$$

which leads to the following for the second term in (10.66):

$$\frac{1}{2}\int_0^\infty d\tau \, R(\tau)\left[E_0 \, e^{-i\omega(t-\tau)} + E_0^* \, e^{i\omega(t-\tau)} \right] \; = \; \frac{1}{2}\left[E_0 \, e^{-i\omega t}\chi(\omega) + E_0^* \, e^{i\omega t} \, \chi(-\omega) \right] \tag{10.68}$$

By differentiating (10.67), and using it with (10.68) in eq. (10.66), we have

$$\dot{E} = -\frac{1}{T}\langle A \rangle \left[f(T) - f(0) \right] - \frac{1}{4T}\int_0^T dt \left[-i\omega E_0 e^{-i\omega t} + i\omega E_0^* e^{i\omega t} \right]\left[E_0 e^{-i\omega t}\chi(\omega) + E_0^* e^{i\omega t}\chi(-\omega) \right] \tag{10.69}$$

We will now cycle-average this expression, setting $T = 2\pi/\omega$. The first term vanishes and the cross terms in second integral vanish, because $\frac{1}{T}\int_0^T dt \, e^{-i\omega t} \, e^{+i\omega t} = 1$ and $\int_0^T dt \, e^{-i\omega t} \, e^{-i\omega t} = 0$.

The rate of energy absorption from the field is

$$\begin{aligned} \dot{E} &= \frac{i}{4}\omega |E_0|^2 \left[\chi(-\omega) - \chi(\omega) \right] \\ &= \frac{\omega}{2}|E_0|^2 \, \chi''(\omega) \end{aligned} \tag{10.70}$$

So, the absorption of energy by the system is related to the imaginary part of the susceptibility. Now, from the intensity of the incident field, $I = c\left|E_0\right|^2 / 8\pi$, the absorption coefficient is

$$\alpha(\omega) = \frac{\dot{E}}{I} = \frac{4\pi\omega}{c}\chi''(\omega) \tag{10.71}$$

Readings

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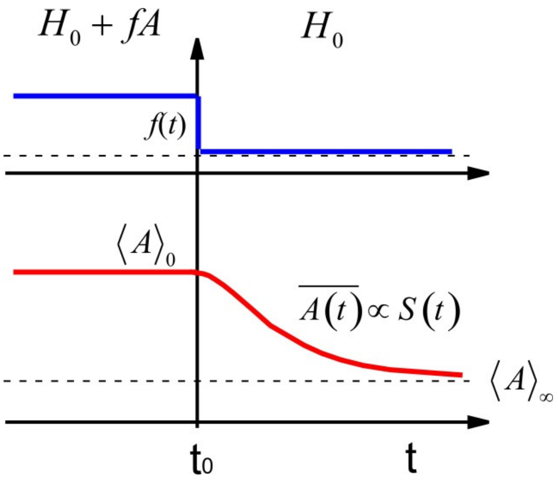
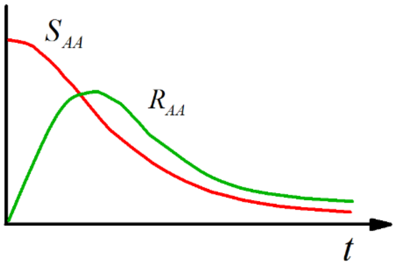
10.4. Relaxation of a Prepared State



The impulse response function $R(t)$ describes the behavior of a system initially at equilibrium that is driven by an external field. Alternatively, we may need to describe the relaxation of a prepared state, in which we follow the return to equilibrium of a system initially held in a nonequilibrium state. This behavior is described by step response function $S(t)$. The step response comes from holding the system with a constant field $H = H_0 - fA$ until a time *t0* when the system is released, and it relaxes to the equilibrium state governed by $H = H_0$.

We can anticipate that the forms of these two functions are related. Just as we expect that the impulse response to rise from zero and be expressed as an odd function in time, the step response should decay from a fixed value and look even in time. In fact, we might expect to describe the impulse response by differentiating the step response, as seen in the classical case.



$$R(t) = \frac{1}{kT}\frac{d}{dt}S(t) \qquad (10.72)$$

An empirical derivation of the step response begins with a few observations. First, response functions must be real since they are proportional to observables, however quantum correlation functions are complex and follow $C(-t) = C^*(t)$. Classical correlation functions are real and even, $C(t) = C(-t)$, and have the properties of a step response. To obtain the relaxation of a real observable that is even in time, we can construct a symmetrized function, which is just the real part of the correlation function:

$$\begin{aligned} S_{AA}(t) &= \tfrac{1}{2}\left\{\langle A_I(t)A_I(0)\rangle + \langle A_I(0)A_I(t)\rangle\right\} \\ &= \tfrac{1}{2}\left\{C_{AA}(t) + C_{AA}(-t)\right\} \\ &= C'_{AA}(t) \end{aligned} \qquad (10.73)$$

The step response function *S* defined as follows for $t \geq 0$.

$$S(\tau) \equiv \frac{1}{\hbar}\Theta(\tau)\left\langle\left[A_I(\tau), A_I(0)\right]\right\rangle_+ \qquad (10.74)$$

From the eigenstate representation of the correlation function,

$$C(t)=\sum_{n,m} p_n \left|A_{mn}\right|^2 e^{-i\omega_{mn}t} \tag{10.75}$$

we see that the step response function can be expressed as an expansion in cosines

$$S(t)=\frac{2}{\hbar}\Theta(t)\sum_{n,m} p_n \left|A_{mn}\right|^2 \cos\omega_{mn}t \tag{10.76}$$

Further, one can readily show that the real and imaginary parts are related by

$$\begin{aligned}\omega\frac{dC'}{dt}&=C''\\ \omega\frac{dC''}{dt}&=C'\end{aligned} \tag{10.77}$$

Which shows how the impulse response is related to the time-derivative of the step response.

In the frequency domain, the spectral representation of the step response is obtained from the Fourier–Laplace transform

$$S_{AA}(\omega)=\int_0^\infty dt\, S_{AA}(t)e^{i\omega t} \tag{10.78}$$

$$\begin{aligned}S_{AA}(\omega)&=\tfrac{1}{2}\left[C_{AA}(\omega)+C_{AA}(-\omega)\right]\\ &=\tfrac{1}{2}\left(1+e^{-\beta\hbar\omega}\right)C_{AA}(\omega)\end{aligned} \tag{10.79}$$

Now, with the expression for the imaginary part of the susceptibility,

$$\chi''(\omega)=\frac{1}{2\hbar}\left(1-e^{-\beta\hbar\omega}\right)C_{AA}(\omega) \tag{10.80}$$

we obtain the relationship

$$\chi''(\omega)=\frac{1}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)S_{AA}(\omega) \tag{10.81}$$

This is the formal expression for the fluctuation-dissipation theorem, proven in 1951 by Callen and Welton. It followed an observation made many years earlier (1930) by Lars Onsager for which he was awarded the 1968 Nobel Prize in Chemistry: "The relaxation of macroscopic nonequilibrium disturbance is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium state."

Noting that $\tanh(x)=\left(e^{x}-e^{-x}\right)/\left(e^{x}+e^{-x}\right)$ and $\tanh(x)\to x$ for x>>1, we see that in the high temperature (classical) limit

$$\chi''(\omega)\Rightarrow\frac{1}{2kT}\omega S_{AA}(\omega) \tag{10.82}$$

Appendix: Derivation of step response function

We can show more directly how the impulse and step response are related. To begin, let's consider the step response experiment,

$$H = \begin{cases} H_0 - fA & t < 0 \\ H_0 & t \geq 0 \end{cases} \tag{10.83}$$

and write the expectation values of the internal variable A for the system equilibrated under H at time $t = 0$ and $t = \infty$.

$$\langle A \rangle_0 = \left\langle \frac{e^{-\beta(H_0 - fA)}}{Z_0} A \right\rangle \qquad Z_0 = \left\langle e^{-\beta(H_0 - fA)} \right\rangle \tag{10.84}$$

$$\langle A \rangle_\infty = \left\langle \frac{e^{-\beta H_0}}{Z_\infty} A \right\rangle \qquad Z_\infty = \left\langle e^{-\beta H_0} \right\rangle \tag{10.85}$$

If we make the *classical* linear response approximation, which states that when the applied potential fA is very small relative to H_0, then

$$e^{-\beta(H_0 - fA)} \approx e^{-\beta H_0} \left(1 + \beta f A\right) \tag{10.86}$$

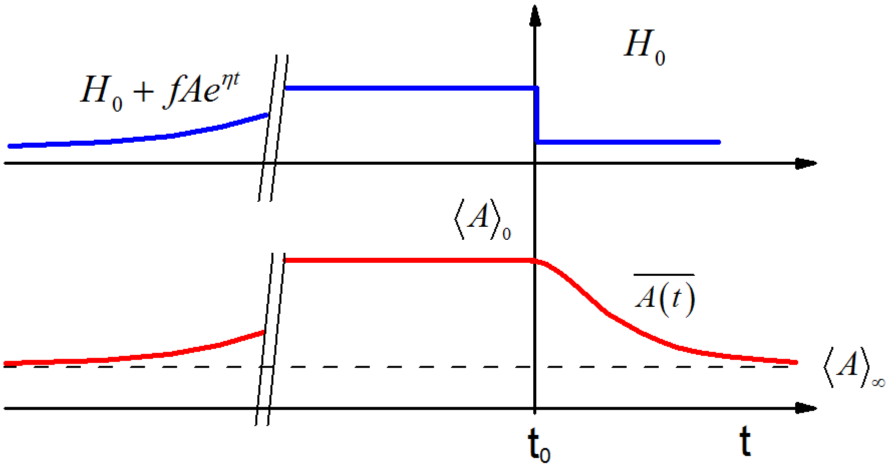
and $Z_0 \approx Z_\infty$, that

$$\delta A = \langle A \rangle_0 - \langle A \rangle_\infty \approx \beta f \left\langle A^2 \right\rangle \tag{10.87}$$

and the time dependent relaxation is given by the classical correlation function

$$\delta A(t) = \beta f \left\langle A(0) A(t) \right\rangle \tag{10.88}$$

For a description that works for the quantum case, let's start with the system under H_0 at t=–∞, ramp up the external potential at a slow rate η until t=0, and then abruptly shut off the external potential and watch the system. We will describe the behavior in the limit $\eta \to 0$.



$$H = \begin{cases} H_0 + fA\,e^{\eta t} & t < 0 \\ H_0 & t \geq 0 \end{cases} \tag{10.89}$$

Writing the time-dependence in terms of a convolution over the impulse response function *R*, we have

$$\overline{\delta A(t)} = \lim_{\eta \to 0} \int_{-\infty}^{0} dt' \Theta(t - t') R(t - t') e^{\eta t'} f \tag{10.90}$$

Although the integral over the applied force (*t'*) is over times t<0, the step response factor ensures that *t*≥0. Now, expressing *R* as a Fourier transform over the imaginary part of the susceptibility, we obtain

$$\begin{aligned} \overline{\delta A(t)} &= \lim_{\eta \to 0} \frac{f}{2\pi} \int_{-\infty}^{0} dt' \int_{-\infty}^{\infty} d\omega\, e^{(\eta - i\omega)t'} e^{i\omega t} \chi''(\omega) \\ &= \frac{f}{2\pi} \int_{-\infty}^{\infty} d\omega\, PP\left(\frac{1}{-i\omega}\right) \chi''(\omega) e^{i\omega t} \\ &= \frac{f}{2\pi i} \int_{-\infty}^{\infty} d\omega\, \chi'(\omega) e^{i\omega t} \\ &= f\,C'(t) \end{aligned} \tag{10.91}$$

A more careful derivation of this result that treats the quantum mechanical operators properly is found in the references.

Readings

1. Mazenko, G., *Nonequilibrium Statistical Mechanics*. Wiley-VCH: Weinheim, 2006.
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11. TIME-DOMAIN DESCRIPTION OF SPECTROSCOPY

11.1. A Classical Description of Spectroscopy

The traditional quantum mechanical treatment of spectroscopy is a static representation of a very dynamic process. An oscillating light field acts to drive bound charges in matter, which under resonance conditions leads to efficient exchange of energy between the light and matter. This dynamical picture emerges from a time-domain description, which shares many similarities to a classical description. Since much of the physical intuition that is helpful in understanding spectroscopy naturally emerges from the classical view, we will describe it first.

The classical view begins with the observation that atoms and molecules are composed of charged particles, and these charges are the handle by which an electromagnetic field exerts a force on the atom or molecule. The force exerted on the molecules depends on the form of the potential binding the charges together, the magnitude of the charges, and the strength of the external field.

The simplest elements of a model that captures what happens in absorption spectroscopy require us to consider a charged particle in a bound potential interacting with an oscillating driving force. The matter can be expressed in terms of a particle with charge *z* in a harmonic potential (the leading term in any expansion of the potential in the coordinate *Q*):

$$V_{res}(t)=\frac{1}{2}\kappa Q^2 \tag{11.1}$$

Here *k* is the restoring force constant. For the light field, we use the traditional expression

$$V_{ext}(t)=-\bar{\mu}\cdot\bar{E}(t) \tag{11.2}$$

for an external electromagnetic field interacting with the dipole moment of the system, $\bar{\mu}=zQ$. We describe the behavior of this system using Newton's equation of motion *F=ma*, which we write as

$$m\frac{\partial^2 Q}{\partial t^2}=F_{res}+F_{damp}+F_{ext} \tag{11.3}$$

On the right hand side of eq. (11.3) there are three forces: the harmonic restoring force, a damping force, and the driving force exerted by the light. Remembering that $F=-(\partial V/\partial Q)$, we can write eq. (11.3) as

$$m\frac{\partial^2 Q}{\partial t^2}=-\kappa Q-b\frac{\partial Q}{\partial t}+F_0\cos(\omega t) \tag{11.4}$$

Here, *b* describes the rate of damping. For the field, we have only considered the time-dependence $\bar{E}(t)=\bar{E}_0\cos(\omega t)$ and the amplitude of the driving force

$$F_0 = \left(\frac{\partial \overline{\mu}}{\partial Q}\right) \cdot \overline{E}_0 \tag{11.5}$$

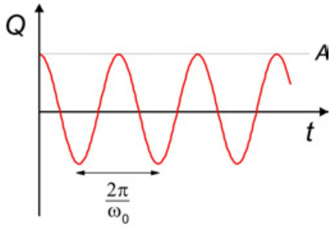
Eq. (11.5) indicates that increasing the force on the oscillator is achieved by raising the magnitude of the field, increasing how much the charge is displaced, or improving the alignment between the electric field polarization and the transition dipole moment.

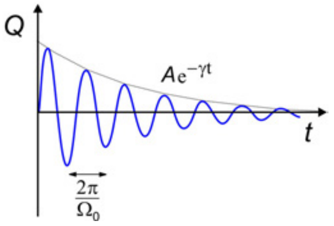
We can rewrite eq. (11.4) as the driven harmonic oscillator equation:

$$\frac{\partial^2 Q}{\partial t^2} + 2\gamma \frac{\partial Q}{\partial t} + \omega_0^2 Q = \frac{F_0}{m} \cos(\omega t) \tag{11.6}$$

Here the damping constant $\gamma = b/2m$ and the harmonic resonance frequency $\omega_0 = \sqrt{\kappa/m}$.

Let's look at the solution to eq. (11.6) for a couple of simple cases. First, for the case that there is no damping or driving force ($\gamma = F_0 = 0$), we have simple harmonic solutions in which oscillate at a frequency ω_0 : $Q(t) = A \sin(\omega_0 t) + B \cos(\omega_0 t)$. Let's just keep the *sin* term for now. Now if you add damping to the equation: $Q(t) = A e^{-\gamma t} \sin \Omega_0 t$. The coordinate oscillates at a reduced frequency $\Omega_0 = \sqrt{\omega_0{}^2 - \gamma^2}$. As we continue, let's assume a case with weak damping for which $\Omega_0 \approx \omega_0$.





The solution to eq. (11.6) takes the form

$$Q(t) = \frac{F_0/m}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2}} \sin(\omega t + \beta) \tag{11.7}$$

Where the phase factor is

$$\tan \beta = \left(\omega_0^2 - \omega^2\right) / 2\gamma\omega \tag{11.8}$$

So this solution to the displacement of the particle says that the amplitude certainly depends on the magnitude of the driving force, but more importantly on the resonance condition. The frequency of the driving field should match the natural resonance frequency of the system, $\omega_0 \approx \omega$ …like pushing someone on a swing. When you drive the system at the resonance frequency there will be an efficient transfer of power to the oscillator, but if you push with arbitrary frequency, nothing will happen. Indeed, that is what an absorption spectrum is: a measure of the power absorbed by the system from the field.

Notice that the coordinate oscillates at the driving frequency ω and not at the resonance frequency ω0. Also, the particle oscillates as a *sin*, that is, 90° out-of-phase with the field when driven on resonance. This reflects the fact that the maximum force can be exerted on the particle when it is stationary at the turning points. The phase shift β, depends varies with the detuning from resonance.

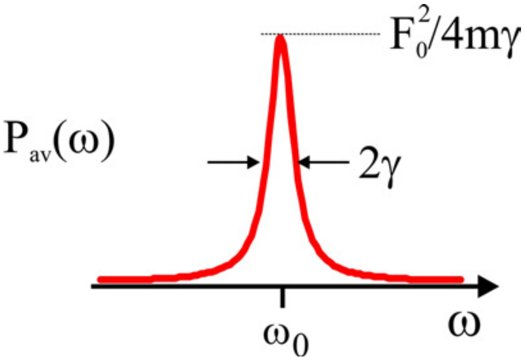
Now we can make some simplifications to eq. (11.7) and calculate the absorption spectrum. For weak damping $\gamma << \omega_0$ and near resonance $\omega_0 \approx \omega$, we can write

$$\left(\omega_0^2 - \omega^2\right)^2 = \left(\omega_0 - \omega\right)^2 \left(\omega_0 + \omega\right)^2 \approx 4\omega_0^2 \left(\omega_0 - \omega\right)^2 \tag{11.9}$$

The absorption spectrum is a measure of the power transferred to the oscillator, so we can calculate it by finding the power absorbed from the force on the oscillator times the velocity, averaged over a cycle of the field.

$$\begin{aligned} P_{avg} &= \left\langle F(t) \cdot \frac{\partial Q}{\partial t} \right\rangle_{avg} \\ &= \frac{\gamma F_0^2}{2m} \frac{1}{\left(\omega - \omega_0\right)^2 + \gamma^2} \end{aligned} \tag{11.10}$$

This is the Lorentzian lineshape, which is peaked at the resonance frequency and has a line width of 2γ (full width half-maximum, FWHM). The area under the lineshape is $\pi F_0^2 / 4m$.



11.2. Time-Correlation Function Description of Absorption Lineshape

The interaction of light and matter as we have described from Fermi's Golden Rule gives the rates of transitions between discrete eigenstates of the material Hamiltonian H_0. The frequency dependence to the transition rate is proportional to an absorption spectrum. We also know that interaction with the light field prepares a superposition of the eigenstates of H_0, and this leads to the periodic oscillation of amplitude between the states. Nonetheless, the transition rate expression really seems to hide any time-dependent description of motions in the system. An alternative approach to spectroscopy is to recognize that the features in a spectrum are just a frequency domain representation of the underlying molecular dynamics of molecules. For absorption, the spectrum encodes the time-dependent changes of the molecular dipole moment for the system, which in turn depends on the position of electrons and nuclei.

A time-correlation function for the dipole operator can be used to describe the dynamics of an equilibrium ensemble that dictate an absorption spectrum. We will make use of the transition rate expressions from first-order perturbation theory that we derived in the previous section to express the absorption of radiation by dipoles as a correlation function in the dipole operator. Let's start with the rate of absorption and stimulated emission between an initial state $\left|\ell\right\rangle$ and final state $\left|k\right\rangle$ induced by a monochromatic field

$$w_{k\ell} = \frac{\pi E_0^2}{2\hbar^2} \left|\left\langle k\left|\hat{\varepsilon}\cdot\bar{\mu}\right|\ell\right\rangle\right|^2 \left[\delta\left(\omega_{k\ell}-\omega\right)+\delta\left(\omega_{k\ell}+\omega\right)\right] \tag{11.11}$$

For shorthand we have written $\left|\bar{\mu}_{k\ell}\right|^2 = \left|\left\langle k\left|\hat{\varepsilon}\cdot\bar{\mu}\right|\ell\right\rangle\right|^2$. We would like to use this to calculate the experimentally observable absorption coefficient (cross-section) which describes the transmission through the sample

$$T = \exp\left[-\Delta N \alpha\left(\omega\right) L\right] \tag{11.12}$$

The absorption cross section describes the rate of energy absorption per unit time relative to the intensity of light incident on the sample

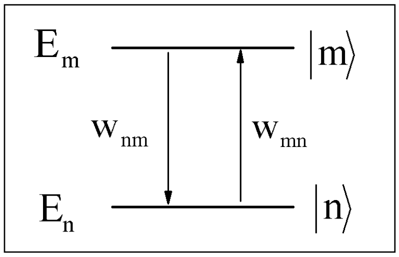
$$\alpha = \frac{-\dot{E}_{rad}}{I} \tag{11.13}$$

The incident intensity is

$$I = \frac{c}{8\pi} E_0^2 \tag{11.14}$$

If we have two discrete states $\left|m\right\rangle$ and $\left|n\right\rangle$ with $E_m > E_n$, the rate of energy absorption is proportional to the absorption rate and the transition energy

$$-\dot{E}_{rad} = w_{nn} \cdot \hbar\omega_{nm} \tag{11.15}$$



For an ensemble this rate must be scaled by the probability of occupying the initial state.

More generally, we want to consider the rate of energy loss from the field as a result of the difference in rates of absorption and stimulated emission between states populated with a thermal distribution. So, summing all possible initial and final states $|\ell\rangle$ and $|k\rangle$ over all possible upper and lower states $|m\rangle$ and $|n\rangle$ with $E_m > E_n$

$$\begin{aligned}-\dot{E}_{rad} &= \sum_{\ell,k\in\{m,n\}} p_\ell w_{k\ell} \hbar\omega_{k\ell} \\ &= \frac{\pi E_0^2}{2\hbar} \sum_{\ell,k\in\{m,n\}} \omega_{k\ell}\, p_\ell \left|\bar{\mu}_{k\ell}\right|^2 \left[\delta(\omega_{k\ell}-\omega)+\delta(\omega_{k\ell}+\omega)\right]\end{aligned} \tag{11.16}$$

The cross section including the net change in energy as a result of absorption $|n\rangle\rightarrow|m\rangle$ and stimulated emission $|m\rangle\rightarrow|n\rangle$ is:

$$\alpha(\omega)=\frac{4\pi^2}{\hbar c}\sum_{n,m}\left[\omega_{mn}\, p_n \left|\bar{\mu}_{mn}\right|^2 \delta(\omega_{mn}-\omega)+\omega_{nm}\, p_m \left|\bar{\mu}_{nm}\right|^2 \delta(\omega_{nm}+\omega)\right] \tag{11.17}$$

To simplify this we note:

1) Since $\delta(x)=\delta(-x)$, $\delta(\omega_{nm}+\omega)=\delta(-\omega_{mn}+\omega)=\delta(\omega_{mn}-\omega)$.
2) The matrix elements squared in the two terms are the same: $\left|\bar{\mu}_{mn}\right|^2=\left|\bar{\mu}_{nm}\right|^2$.
3) $\omega_{mn}=-\omega_{nm}=\omega$ as a result of the delta function enforcing this equality.

So,

$$\alpha(\omega)=\frac{4\pi^2\omega}{\hbar c}\sum_{n,m}(p_n-p_m)\left|\bar{\mu}_{mn}\right|^2\delta(\omega_{mn}-\omega) \tag{11.18}$$

Here we see that the absorption coefficient depends on the population difference between the two states. This is expected since absorption will lead to loss of intensity, whereas stimulated emission leads to gain. With equal populations in the upper and lower state, no change to the incident field would be expected. Since $p_\ell=\exp[-\beta E_\ell]/Z$

$$p_n-p_m=p_n\left(1-\exp[-\beta\hbar\omega_{mn}]\right) \tag{11.19}$$

$$\alpha(\omega)=\frac{4\pi^2}{\hbar c}\omega\left(1-e^{-\beta\hbar\omega}\right)\sum_{n,m}p_n\left|\bar{\mu}_{mn}\right|^2\delta(\omega_{mn}-\omega) \tag{11.20}$$

Again the ω_{mn} factor has been replaced with ω. We can now separate α into a product of factors that represent the field, and the matter, where the matter is described by $\sigma(\omega)$, the absorption lineshape.

$$\alpha(\omega)=\frac{4\pi^2}{\hbar c}\omega\left(1-e^{-\beta\hbar\omega}\right)\sigma(\omega) \tag{11.21}$$

$$\sigma(\omega)=\sum_{n,m}p_n\left|\bar{\mu}_{mn}\right|^2\delta\left(\omega_{mn}-\omega\right) \tag{11.22}$$

To express the lineshape in terms of a correlation function we use one representation of the delta function through a Fourier transform of a complex exponential:

$$\delta\left(\omega_{mn}-\omega\right)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\;e^{i\left(\omega_{mn}-\omega\right)t} \tag{11.23}$$

to write

$$\sigma(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\sum_{n,m}p_n\left\langle n\left|\bar{\mu}\right|m\right\rangle\left\langle m\left|\bar{\mu}\right|n\right\rangle e^{i\left(\omega_{mn}-\omega\right)t} \tag{11.24}$$

Now equating $U_0\left|n\right\rangle=e^{-iH_0t/\hbar}\left|n\right\rangle=e^{-iE_nt/\hbar}\left|n\right\rangle$, and recognizing that our expression contains the projection operator $\sum_m\left|m\right\rangle\left\langle m\right|=1$, we can write

$$\begin{aligned}\sigma(\omega)&=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\sum_{n,m}p_n\left\langle n\left|\bar{\mu}\right|m\right\rangle\left\langle m\left|U_0^{\dagger}\bar{\mu}U_0\right|n\right\rangle e^{-i\omega t}\\&=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\sum_{n,m}p_n\left\langle n\left|\bar{\mu}_I(0)\bar{\mu}_I(t)\right|n\right\rangle e^{-i\omega t}\end{aligned} \tag{11.25}$$

But this last expression is just a dipole moment correlation function: the equilibrium thermal average over a pair of time-dependent dipole operators:

$$\sigma(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{-i\omega t}\left\langle\bar{\mu}_I(0)\bar{\mu}_I(t)\right\rangle \tag{11.26}$$

The absorption lineshape is given by the Fourier transform of the dipole correlation function. The correlation function describes the time-dependent behavior or spontaneous fluctuations in the dipole moment in absence of *E* field and contains information on states of system and broadening due to relaxation. Additional manipulations can be used to switch the order of operators by taking the complex conjugate of the exponential

$$\sigma(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\;e^{i\omega t}\left\langle\bar{\mu}_I(t)\bar{\mu}_I(0)\right\rangle \tag{11.27}$$

and we can add back the polarization of the light field to the matrix element

$$\sigma(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{i\omega t}\left\langle\hat{\varepsilon}\cdot\bar{\mu}_I(t)\,\hat{\varepsilon}\cdot\bar{\mu}_I(0)\right\rangle \tag{11.28}$$

to emphasize the orientational component to this correlation function.

Here we have written operators emphasizing the interaction picture representation. As we move forward, we will drop this notation, and take it as understood that for the purposes of spectroscopy, the dipole operator is expressed in the interaction picture and evolves under the material Hamiltonian H_0.

Readings

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11.3. Different Types of Spectroscopy Emerge from the Dipole Operator

So the absorption spectrum in any frequency region is given by the Fourier transform over the dipole correlation function that describes the time-evolving change distributions in molecules, solids, and nanosystems. Let's consider how this manifests itself in a few different spectroscopies, which have different contributions to the dipole operator. In general the dipole operator is a relatively simple representation of the charged particles of the system:

$$\bar{\mu} = \sum_i q_i \left(\bar{r}_i - \bar{r}_0 \right) \tag{11.29}$$

The complexity arises from the time-dependence of this operator, which evolves under the full Hamiltonian for the system:

$$\bar{\mu}(t) = e^{iH_0 t/\hbar} \bar{\mu}(0) e^{-iH_0 t/\hbar} \tag{11.30}$$

$$\begin{aligned} H_0 &= H_{elec} + H_{vib} + H_{rot} + H_{trans} + H_{spin} + \cdots + H_{bath} + \cdots \\ &+ \sum_{i,j \in \{e,v,r,t,s,b,EM\}} H_{i-j} + \cdots \end{aligned} \tag{11.31}$$

The full Hamiltonian accounts for the dynamics of all electronic, nuclear, and spin degrees of freedom. It is expressed in eq. (11.31) in terms of separable contributions to all possible degrees of freedom and a bath Hamiltonian that contains all of the dark degrees of freedom not explicitly included in the dipole operator. We could also include an electromagnetic field. The last term describes pairwise couplings between different degrees of freedom, and emphasizes that interactions such as electron-nuclear interactions H_{e-v} and spin-orbit coupling H_{e-s}. The wavefunction for the system can be expressed in terms of product states of the wavefunctions for the different degrees of freedom,

$$\left| \psi \right\rangle = \left| \psi_{elec} \psi_{vib} \psi_{rot} \cdots \right\rangle \tag{11.32}$$

When the H_{i-j} interaction terms are neglected, the correlation function can be separated into a product of correlation functions from various sources:

$$C_{\mu\mu}(t) = C_{elec}(t) C_{vib}(t) C_{rot}(t) \cdots \tag{11.33}$$

which are each expressed in the form shown here for the vibrational states

$$C_{vib}(t) = \sum_{n=vib} p_n \left\langle \Phi_n \right| e^{iH_{vib}t} \mu \, e^{-iH_{vib}t} \mu \left| \Phi_n \right\rangle \tag{11.34}$$

Φ_n is the wavefunction for the nth vibrational eigenstate. The net correlation function will have oscillatory components at many frequencies and its Fourier transform will give the full absorption spectrum from the ultraviolet to the microwave regions of the spectrum. Generally speaking the highest frequency contributions (electronic or UV/Vis) will be modulated by contributions from lower frequency motions (…such as vibrations and rotations). However, we can separately analyze each of these contributions to the spectrum.

Examples

Atomic transitions

$H_0 = H_{atom}$. For hydrogenic orbitals, $|n\rangle \rightarrow |n\,\ell\,m_\ell\rangle$.

Rotational spectroscopy

From a classical perspective, the dipole moment can be written in terms of a permanent dipole moment with amplitude and direction

$$\bar{\mu} = \mu_0 \hat{u} \tag{11.35}$$

$$\sigma(\omega) = \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \mu_0^2 \left\langle \hat{\varepsilon}\cdot\hat{u}(0)\,\hat{\varepsilon}\cdot\hat{u}(t)\right\rangle \tag{11.36}$$

The lineshape is the Fourier transform of the rotational motion of the permanent dipole vector in the laboratory frame. μ_0 is the magnitude of the permanent dipole moment averaged over the fast electronic and vibrational degrees of freedom. The frequency of the resonance would depend on the rate of rotation—the angular momentum and the moment of inertia. Collisions or other damping would lead to the broadening of the lines.

Quantum mechanically we expect a series of rotational resonances that mirror the thermal occupation and degeneracy of rotational states for the system. Taking the case of a rigid rotor with cylindrical symmetry as an example, the Hamiltonian is

$$H_{rot} = \frac{\bar{L}^2}{2I} \tag{11.37}$$

and the wavefunctions are spherical harmonics $Y_{J,M}(\theta,\phi)$ which are described by

$$\begin{aligned} \bar{L}^2 \left|Y_{J,M}\right\rangle &= \hbar^2 J(J+1)\left|Y_{J,M}\right\rangle \quad && J = 0,1,2... \\ L_z \left|Y_{J,M}\right\rangle &= M\hbar\left|Y_{J,M}\right\rangle && M = -J,-J+1,...,J \end{aligned} \tag{11.38}$$

J is the rotational quantum number. M (or M_J) refers to its projection onto an axis (z), and has a degeneracy of $g_M(J)=2J+1$. The energy eigenvalues for H_{rot} are

$$E_{J,M} = \bar{B}J(J+1) \tag{11.39}$$

where the rotational constant, here in units of joules, is

$$\bar{B} = \frac{\hbar^2}{2I} \tag{11.40}$$

If we take a dipole operator in the form of eq. (11.35), then the far-infrared rotational spectrum will be described by the correlation function

$$C_{rot}(t)=\sum_{J,M} p_{J,M}\left|\mu_0\right|^2 \left\langle Y_{J,M}\left|e^{iH_{rot}t/\hbar}\left(\hat{u}\cdot\hat{\varepsilon}\right)e^{-iH_{rot}t/\hbar}\left(\hat{u}\cdot\hat{\varepsilon}\right)\right|Y_{J,M}\right\rangle \tag{11.41}$$

The evaluation of this correlation function involves an orientational average, which is evaluated as follows

$$\left\langle Y_{J',M'}\left|f(\theta,\phi)\right|Y_{J,M}\right\rangle=\frac{1}{4\pi}\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta\, d\theta\; Y^*_{J',M'}f(\theta,\phi)Y_{J,M} \tag{11.42}$$

Recognizing that $\left(\hat{u}\cdot\hat{\varepsilon}_Z\right)=\cos\theta$, we can evaluate eq. (11.41) using the reduction formula

$$\cos\theta\left|Y_{J,M}\right\rangle=c_{J+}\left|Y_{J+1,M}\right\rangle+c_{J-}\left|Y_{J-1,M}\right\rangle \tag{11.43}$$

$$c_{J+}=\sqrt{\frac{(J+1)^2-M^2}{4(J+1)^2-1}}\qquad c_{J-}=\sqrt{\frac{J^2+M^2}{4J^2-1}} \tag{11.44}$$

and the orthogonality of spherical harmonics

$$\left\langle Y_{J',M'}\middle|Y_{J,M}\right\rangle=4\pi\,\delta_{J',J}\,\delta_{M',M} \tag{11.45}$$

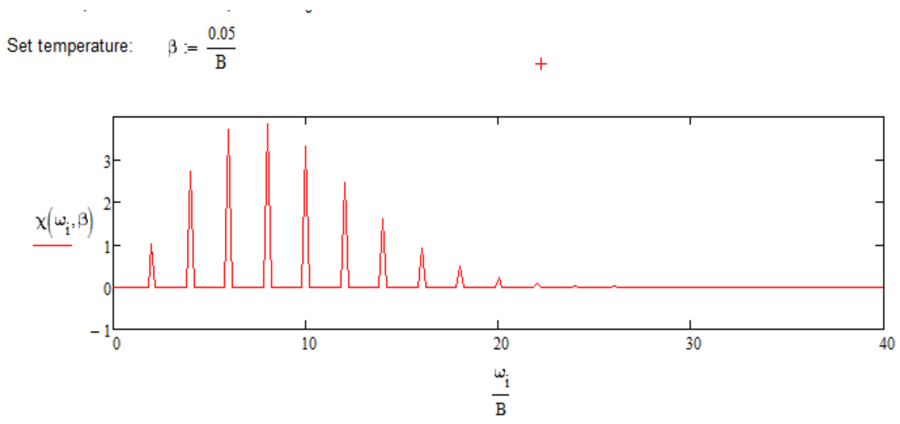
The factor $p_{J,M}$ in eq. (11.41) is the probability of thermally occupying a particular *J,M* level. For this we recognize that $p_{J,M}=g_M(J)e^{-\beta E_J}/Z_{rot}$, so that eq. (11.41) leads to the correlation function

$$C_{rot}(t)=\frac{\left|\mu_0\right|^2}{Z_{rot}}\sum_J(2J+1)e^{-\beta\bar{B}J(J+1)/\hbar}\left[e^{-i(J+1)2\bar{B}t/\hbar}+e^{iJ2\bar{B}t/\hbar}\right] \tag{11.46}$$

Fourier transforming eq. (11.46) leads to the lineshape

$$\sigma_{rot}(\omega)=\frac{\left|\mu_0\right|^2}{Z_{rot}}\hbar\sum_J(2J+1)e^{-\beta\bar{B}J(J+1)/\hbar}\left[\delta\left(\hbar\omega-2\bar{B}(J+1)\right)+\delta\left(\hbar\omega+2\bar{B}J\right)\right] \tag{11.47}$$

The two terms reflect the fact that each thermally populated level with $J > 0$ contributes both to absorptive and stimulated emission processes, and the observed intensity reflects the difference in populations.



IR vibrational spectroscopy

Vibrational spectroscopy can be described by taking the dipole moment to be weakly dependent on the displacement of vibrational coordinates q

$$\bar{\mu} = \bar{\mu}_0 + \left.\frac{\partial \bar{\mu}}{\partial q}\right|_{q=q_0} q + \cdots \tag{11.48}$$

Here the first expansion term is the permanent dipole moment and the second term is the transition dipole moment. If we are performing our ensemble average over vibrational states, the lineshape becomes the Fourier transform of a correlation function in the vibrational coordinate

$$\sigma(\omega) = \left|\frac{\partial \bar{\mu}}{\partial q}\right|^2 \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \left\langle q(0)\, q(t)\right\rangle \tag{11.49}$$

The vector nature of the transition dipole has been dropped here. So the time-dependent dynamics of the vibrational coordinate dictate the IR lineshape.

This approach holds for the classical and quantum mechanical cases. In the case of quantum mechanics, the change in charge distribution in the transition dipole moment is replaced with the equivalent transition dipole matrix element $|\partial\bar{\mu}/\partial q|^2 \Rightarrow |\bar{\mu}_{k\ell}|^2$. If we take the vibrational Hamiltonian to be that of a harmonic oscillator,

$$H_{vib} = \tfrac{1}{2m} p^2 + \tfrac{1}{2} m\omega_0^2 q^2 = \hbar\omega_0 \left(a^\dagger a + \tfrac{1}{2}\right) \tag{11.50}$$

then the time-dependence of the vibrational coordinate, expressed as raising and lowering operators is

$$q(t) = \sqrt{\frac{\hbar}{2m\omega_0}} \left(a^\dagger e^{i\omega_0 t} + a\, e^{-i\omega_0 t}\right) \tag{11.51}$$

The absorption lineshape is then obtained from eq. (11.49).

$$\sigma_{vib}(\omega) = \frac{1}{Z_{vib}} \sum_n e^{-\beta n\hbar\omega_0} \left[|\bar{\mu}_{(n+1)n}|^2 \left(\bar{n}+1\right) \delta\left(\omega - \omega_0\right) + |\bar{\mu}_{(n-1)n}|^2\, \bar{n}\, \delta\left(\omega + \omega_0\right)\right] \tag{11.52}$$

where $\bar{n} = (e^{\beta\hbar\omega_0} - 1)^{-1}$ is the thermal occupation number. For the low temperature limit applicable to most vibrations under room temperature conditions $\bar{n} \to 0$ and

$$\sigma_{vib}(\omega) = |\bar{\mu}_{10}|^2\, \delta\left(\omega - \omega_0\right) \tag{11.53}$$

Raman spectroscopy

Technically, we need second-order perturbation theory to describe Raman scattering, because transitions between two states are induced by the action of two light fields whose frequency difference equals the energy splitting between states. But much the same result is obtained is we replace the dipole operator with an induced dipole moment generated by the incident field: $\bar{\mu} \Rightarrow \bar{\mu}_{ind}$. The incident field E_i polarizes the molecule,

$$\bar{\mu}_{ind} = \bar{\bar{\alpha}} \cdot \bar{E}_i(t) \tag{11.54}$$

($\bar{\bar{\alpha}}$ is the polarizability), and the scattered light field results from the interaction with this induced dipole

$$\begin{aligned} V(t) &= -\bar{\mu}_{ind} \cdot \bar{E}_s(t) \\ &= \bar{E}_s(t) \cdot \bar{\bar{\alpha}} \cdot \bar{E}_i(t) \\ &= E_s(t) E_i(t) \left(\hat{\varepsilon}_s \cdot \bar{\bar{\alpha}} \cdot \hat{\varepsilon}_i \right) \end{aligned} \tag{11.55}$$

Here we have written the polarization components of the incident (*i*) and scattered (*s*) light projecting onto the polarizability tensor $\bar{\bar{\alpha}}$. Equation (11.55) leads to an expression for the Raman lineshape as

$$\begin{aligned} \sigma(\omega) &= \int_{-\infty}^{+\infty} dt \, e^{-i\omega t} \left\langle \hat{\varepsilon}_s \cdot \bar{\bar{\alpha}}(0) \cdot \hat{\varepsilon}_i \;\; \hat{\varepsilon}_s \cdot \bar{\bar{\alpha}}(t) \cdot \hat{\varepsilon}_i \right\rangle \\ &= \int_{-\infty}^{+\infty} dt \, e^{-i\omega t} \left\langle \bar{\bar{\alpha}}(0) \bar{\bar{\alpha}}(t) \right\rangle \end{aligned} \tag{11.56}$$

To evaluate this, the polarizability tensor can also be expanded in the nuclear coordinates

$$\bar{\bar{\alpha}} = \bar{\bar{\alpha}}_0 + \left. \frac{\partial \bar{\bar{\alpha}}}{\partial q} \right|_{q=q_0} q + \cdots \tag{11.57}$$

where the leading term would lead to Raleigh scattering and rotational Raman spectra, and the second term would give vibrational Raman scattering.

Also remember that the polarizability tensor is a second rank tensor that tells you how well a light field polarized along *i* can induce a dipole moment (light-field-induced charge displacement) in the *s* direction. For cylindrically symmetric systems which have a polarizability component $\alpha_{\parallel}$ along the principal axis of the molecule and a component $\alpha_{\perp}$ perpendicular to that axis, this usually takes the form

$$\bar{\bar{\alpha}} = \begin{pmatrix} \alpha_{\parallel} & & \\ & \alpha_{\perp} & \\ & & \alpha_{\perp} \end{pmatrix} = \alpha \mathbf{I} + \frac{1}{3}\beta \begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix} \tag{11.58}$$

where α is the isotropic component of polarizability tensor and β is the anisotropic component.

11.4. Ensemble Averaging and Line-Broadening

We have seen that an absorption lineshape can represent the dynamics of the dipole or be broadened by energy relaxation, for instance through coupling to a continuum. However, there are numerous processes that can influence the lineshape. These can be separated by dynamic processes intrinsic to the molecular system, which is termed homogeneous broadening, and static effects known as inhomogeneous broadening, which can be considered an ensemble averaging effect. To illustrate, imagine that the dipole correlation function has an oscillatory, damped form

$$C_{\mu\mu}(t) = \sum_{g,e} p_g \left|\mu_{eg}\right|^2 exp\left[-i\omega_{eg}t - \Gamma t\right] \tag{11.59}$$

Then the Fourier transform would give a lineshape

$$Re\left[\tilde{C}_{\mu\mu}(\omega)\right] = \sum_{g,e} p_g \frac{\left|\mu_{eg}\right|^2 \Gamma}{\left(\omega - \omega_{eg}\right)^2 - \Gamma^2} \tag{11.60}$$

Here the homogeneous effects are reflected in the factor Γ, the damping rate and linewidth, whereas inhomogeneous effects arise from averaging over the ensemble.

Homogeneous broadening

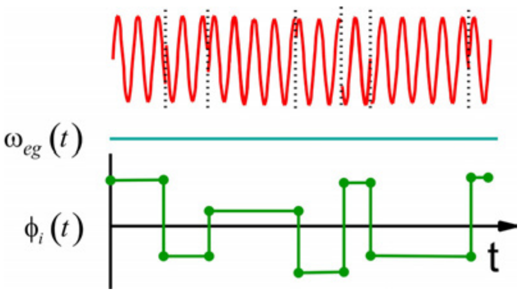
Several dynamical mechanisms can potentially contribute to damping and line-broadening. These intrinsically molecular processes, often referred to as homogeneous broadening, are commonly assigned a time scale $T_2 = \Gamma^{-1}$.

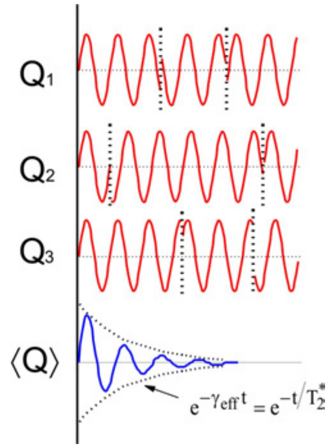
Population Relaxation. Population relaxation refers to decay in the coherence created by the light field as a result of the finite lifetime of the coupled states, and is often assigned a time scale T_1. This can have contributions from radiative decay, such as spontaneous emission, or non-radiative processes such as relaxation as a result of coupling to a continuum.

$$\frac{1}{T_1} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{NR}} \tag{11.61}$$

The observed population relaxation time depends on both the relaxation times of the upper and lower states (*m* and *n*) being coupled by the field: $1/T_1 = w_{mn} + w_{nm}$. When the energy splitting is high compared to $k_B T$, only the downward rate contributes, which is why the rate is often written $1/2T_1$.

Pure Dephasing. Pure dephasing is characterized by a time constant T_2^* that characterizes the randomization of phase within an ensemble as a result of molecular interactions. This is a dynamic effect in which memory of the phase of oscillation of a molecule is lost as a result of intermolecular interactions that randomize the phase. Examples include collisions in a dense gas, or fluctuations induced by a solvent. This process does not change the population of the states involved.





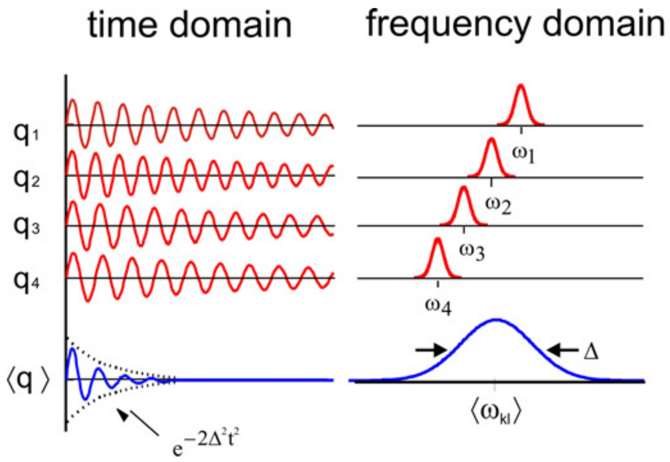
Orientational relaxation. Orientational relaxation (τ_{or}) also leads to relaxation of the dipole correlation function and to line-broadening. Since the correlation function depends on the projection of the dipole onto a fixed axis in the laboratory frame, randomization of the initial dipole orientations is an ensemble averaged dephasing effect. In solution, this process is commonly treated as an orientational diffusion problem in which τ_{or} is proportional to the diffusion constant.

If these homogeneous processes are independent, the rates for different processes contribute additively to the damping and line width:

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2^*} + \frac{1}{\tau_{or}} \tag{11.62}$$

Inhomogeneous broadening

Absorption lineshapes can also be broadened by a static distribution of frequencies. If molecules within the ensemble are influenced static environmental variations more than other processes, then the observed lineshape reports on the distribution of environments. This inhomogeneous broadening is a static ensemble averaging effect, which hides the dynamical content in the homogeneous linewidth. The origin of the inhomogeneous broadening can be molecular (for instance a distribution of defects in crystals) or macroscopic (i.e., an inhomogeneous magnetic field in NMR).



The inhomogeneous linewidth is dictated the width of the distribution Δ.

Total linewidth

The total observed broadening of the absorption lineshape reflects the contribution of all of these effects:

$$C_{\mu\mu} \propto \exp\left[-i\omega_{eg}t - \left(\frac{1}{T_2^*} + \frac{1}{2T_1} + \frac{1}{\tau_{or}}\right)t - \frac{\Delta^2}{2}t^2\right] \tag{11.63}$$

These effects can be wrapped into a lineshape function $g(t)$. The lineshape for the broadening of a given transition can be written as the Fourier transform over the oscillating transition frequency damped and modulated by a complex $g(t)$:

$$\sigma(\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, e^{-i\omega_{eg}t - g(t)} \tag{11.64}$$

All of these effects can be present simultaneously in an absorption spectrum.

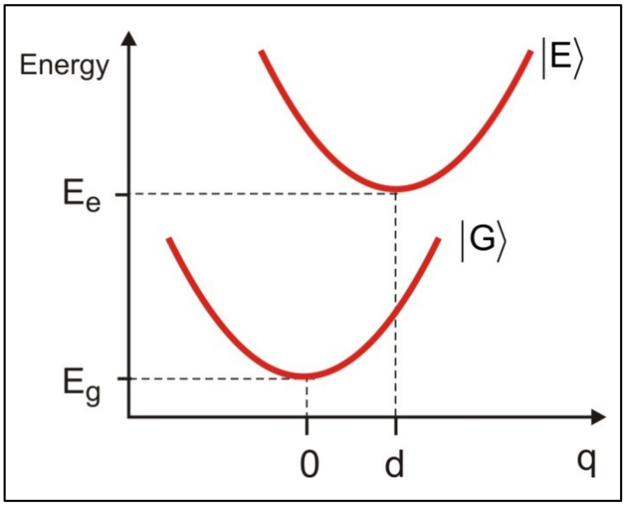
12. COUPLING OF ELECTRONIC AND NUCLEAR MOTION

12.1. The Displaced Harmonic Oscillator Model

Here we will discuss the displaced harmonic oscillator (DHO), a widely used model that describes the coupling of nuclear motions to electronic states. Although it has many applications, we will look at the specific example of electronic absorption experiments, and thereby gain insight into the vibronic structure in absorption spectra. Spectroscopically, it can also be used to describe wavepacket dynamics; coupling of electronic and vibrational states to intramolecular vibrations or solvent; or coupling of electronic states in solids or semiconductors to phonons. As we will see, further extensions of this model can be used to describe fundamental chemical rate processes, interactions of a molecule with a dissipative or fluctuating environment, and Marcus Theory for nonadiabatic electron transfer.

The DHO and Electronic Absorption

Molecular excited states have geometries that are different from the ground state configuration as a result of varying electron configuration. This parametric dependence of electronic energy on nuclear configuration results in a variation of the electronic energy gap between states as one stretches bond vibrations of the molecule. We are interested in describing how this effect influences the electronic absorption spectrum, and thereby gain insight into how one experimentally determines the coupling of between electronic and nuclear degrees of freedom. We consider electronic transitions between bound potential energy surfaces for a ground and excited state as we displace a nuclear coordinate q. The simplified model consists of two harmonic oscillators potentials whose 0-0 energy splitting is $E_e - E_g$ and which depends on q. We will calculate the absorption spectrum in the interaction picture using the time-correlation function for the dipole operator.



We start by writing a Hamiltonian that contains two terms for the potential energy surfaces of the electronically excited state $|E\rangle$ and ground state $|G\rangle$

$$H_0 = H_G + H_E \tag{12.1}$$

These terms describe the dependence of the electronic energy on the displacement of a nuclear coordinate q. Since the state of the system depends parametrically on the level of vibrational excitation, we describe it using product states in the electronic and nuclear configuration, $\left|\Psi\right\rangle = \left|\psi_{elec}, \Phi_{nuc}\right\rangle$, or in the present case

$$\left|G\right\rangle = \left|g, n_g\right\rangle \qquad \left|E\right\rangle = \left|e, n_e\right\rangle \tag{12.2}$$

Implicit in this model is a Born-Oppenheimer approximation in which the product states are the eigenstates of H_0, i.e. $H_G \,|\, G\rangle = (E_g + E_{n_g}) \,|\, G\rangle$.

The Hamiltonian for each surface contains an electronic energy in the absence of vibrational excitation, and a vibronic Hamiltonian that describes the change in energy with nuclear displacement.

$$\begin{aligned} H_G &= \left|g\right\rangle E_g \left\langle g\right| + H_g(q) \\ H_E &= \left|e\right\rangle E_e \left\langle e\right| + H_e(q) \end{aligned} \tag{12.3}$$

For our purposes, the vibronic Hamiltonian is harmonic and has the same curvature in the ground and excited states, however, the excited state is displaced by d relative to the ground state along a coordinate q.

$$H_g = \frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 \, q^2 \tag{12.4}$$

$$H_e = \frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 \left(q - d\right)^2 \tag{12.5}$$

The operator q acts only to changes the degree of vibrational excitation on the $|E\rangle$ or $|G\rangle$ surface.

We now wish to evaluate the dipole correlation function

$$\begin{aligned} C_{\mu\mu}(t) &= \left\langle \bar{\mu}(t)\bar{\mu}(0)\right\rangle \\ &= \sum_{\ell=E,G} p_\ell \left\langle \ell \middle| e^{iH_0 t/\hbar} \, \bar{\mu} \, e^{-iH_0 t/\hbar} \, \bar{\mu} \middle| \ell \right\rangle \end{aligned} \tag{12.6}$$

Here p_ℓ is the joint probability of occupying a particular electronic and vibrational state, $p_\ell = p_{\ell,elec} \, p_{\ell,vib}$. The time propagator is

$$e^{-iH_0 t/\hbar} = \left|G\right\rangle \, e^{-iH_G t/\hbar} \left\langle G\right| \quad + \quad \left|E\right\rangle \, e^{-iH_E t/\hbar} \left\langle E\right| \tag{12.7}$$

We begin by making the Condon Approximation, which states that there is no nuclear dependence for the dipole operator. It is only an operator in the electronic states.

$$\bar{\mu} = \left|g\right\rangle \mu_{ge} \left\langle e\right| + \left|e\right\rangle \mu_{eg} \left\langle g\right| \tag{12.8}$$

This approximation implies that transitions between electronic surfaces occur without a change in nuclear coordinate, which on a potential energy diagram is a vertical transition.

Under typical conditions, the system will only be on the ground electronic state at equilibrium, and substituting eqs. (12.7) and (12.8) into (12.6), we find:

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 \, e^{-i(E_e - E_g)t/\hbar} \left\langle e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \right\rangle \tag{12.9}$$

Here the oscillations at the electronic energy gap are separated from the nuclear dynamics in the final factor, the dephasing function:

$$\begin{aligned} F(t) &= \left\langle e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \right\rangle \\ &= \left\langle U_g^\dagger \, U_e \right\rangle \end{aligned} \tag{12.10}$$

The average ⟨ … ⟩ in equations (12.9) and (12.10) is only over the vibrational states $|n_g\rangle$. Note that physically the dephasing function describes the time-dependent overlap of the nuclear wavefunction on the ground state with the time-evolution of the same wavepacket initially projected onto the excited state

$$F(t) = \left\langle \varphi_g(t) \middle| \varphi_e(t) \right\rangle \tag{12.11}$$

This is a perfectly general expression that does not depend on the particular form of the potential. If you have knowledge of the nuclear and electronic eigenstates or the nuclear dynamics on your ground and excited state surfaces, this expression is your route to the absorption spectrum.[1]

To evaluate $F(t)$ for this problem, it helps to realize that we can write the nuclear Hamiltonians as

$$H_g = \hbar\omega_0 \left(a^\dagger a + \tfrac{1}{2} \right) \tag{12.12}$$

$$H_e = \hat{D} H_g \hat{D}^\dagger \tag{12.13}$$

Here $\hat{D}$ is the spatial displacement operator

$$\hat{D} = \exp\left(-i\hat{p}d/\hbar\right) \tag{12.14}$$

which shifts an operator in space as:

$$\hat{D}\hat{q}\hat{D}^\dagger = \hat{q} - d \tag{12.15}$$

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[1] For further on this see:
Schatz, G. C.; Ratner, M. A., *Quantum Mechanics in Chemistry*. Dover Publications: Mineola, NY, 2002; Ch. 9.
Reimers, J. R.; Wilson, K. R.; Heller, E. J., Complex time dependent wave packet technique for thermal equilibrium systems: Electronic spectra. *J. Chem. Phys.* **1983,** *79*, 4749-4757.

Note $\hat{p}$ is only an operator in the vibrational degree of freedom. We can now express the excited state Hamiltonian in terms of a shifted ground state Hamiltonian in eq. (12.13), and also relate the time propagators on the ground and excited states

$$e^{-iH_e t/\hbar} = \hat{D} e^{-iH_g t/\hbar} \hat{D}^\dagger \tag{12.16}$$

Substituting eq. (12.16) into eq. (12.10) allows us to write

$$\begin{aligned} F(t) &= \left\langle U_g^\dagger \, e^{-idp/\hbar} \, U_g \, e^{idp/\hbar} \right\rangle \\ &= \left\langle \hat{D}(t) \hat{D}^\dagger(0) \right\rangle \end{aligned} \tag{12.17}$$

This says that the effect of the nuclear motion in the dipole correlation function can be expressed as a time-correlation function for the displacement of the vibration.

To evaluate eq. (12.17) we write it as

$$F(t) = \left\langle e^{-id\hat{p}(t)/\hbar} \, e^{id\hat{p}(0)/\hbar} \right\rangle \tag{12.18}$$

since

$$\hat{p}(t) = U_g^\dagger \, \hat{p}(0) U_g \tag{12.19}$$

The time-evolution of $\hat{p}$ is obtained by expressing it in raising and lowering operator form,

$$\hat{p} = i\sqrt{\frac{m\hbar\omega_0}{2}} \left(a^\dagger - a \right) \tag{12.20}$$

and evaluating eq. (12.19) using eq. (12.12). Remembering $a^\dagger a = n$, we find

$$\begin{aligned} U_g^\dagger \, a U_g &= e^{in\omega_0 t} \, a \, e^{-in\omega_0 t} = a \, e^{i(n-1)\omega_0 t} e^{-in\omega_0 t} = a \, e^{-i\omega_0 t} \\ U_g^\dagger \, a^\dagger \, U_g &= a^\dagger \, e^{+i\omega_0 t} \end{aligned} \tag{12.21}$$

which gives

$$\hat{p}(t) = i\sqrt{\frac{m\hbar\omega_0}{2}} \left(a^\dagger e^{i\omega_0 t} - a \, e^{-i\omega_0 t} \right) \tag{12.22}$$

So for the dephasing function we now have

$$F(t) = \left\langle \exp\left[\underset{\sim}{d} \left(a^\dagger e^{i\omega_0 t} - a \, e^{-i\omega_0 t} \right) \right] \exp\left[-\underset{\sim}{d} \left(a^\dagger - a \right) \right] \right\rangle \tag{12.23}$$

where we have defined a dimensionless displacement variable

$$\underset{\sim}{d} = d\sqrt{\frac{m\omega_0}{2\hbar}} \tag{12.24}$$

Since $a^\dagger$ and a do not commute ($[a^\dagger, a] = -1$), we split the exponential operators using the identity

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}} e^{-\frac{1}{2}\left[\hat{A},\hat{B}\right]}. \tag{12.25}$$

or specifically for $a^\dagger$ and a, $$e^{\lambda a^\dagger + \mu a} = e^{\lambda a^\dagger}\, e^{\mu a}\, e^{\frac{1}{2}\lambda\mu} \tag{12.26}$$

This leads to

$$\begin{aligned} F(t) = \Big\langle &\exp\left[\underset{\sim}{d}\, a^\dagger e^{i\omega_0 t}\right] \exp\left[-\underset{\sim}{d}\, a\, e^{-i\omega_0 t}\right] \exp\left[-\tfrac{1}{2}\underset{\sim}{d}^2\right] \\ &\times \exp\left[-\underset{\sim}{d} a^\dagger\ \right] \exp\left[\underset{\sim}{d}\, a\ \right] \exp\left[-\tfrac{1}{2}\underset{\sim}{d}^2\right] \Big\rangle \end{aligned} \tag{12.27}$$

Now to simplify our work further, let's specifically consider the low temperature case in which we are only in the ground vibrational state at equilibrium $\left|n_g\right\rangle = \left|0\right\rangle$. Since $a\left|0\right\rangle = 0$ and $\left\langle 0\right| a^\dagger = 0$,

$$\begin{aligned} e^{-\lambda a}\left|0\right\rangle &= \left|0\right\rangle \\ \left\langle 0\right| e^{\lambda a^\dagger} &= \left\langle 0\right| \end{aligned} \tag{12.28}$$

and

$$F(t) = e^{-\underset{\sim}{d}^2} \left\langle 0\left| \exp\left[-\underset{\sim}{d}\, a\, e^{-i\omega_0 t}\right] \exp\left[-\underset{\sim}{d}\, a^\dagger\right] \right| 0\right\rangle \tag{12.29}$$

In principle these are expressions in which we can evaluate by expanding the exponential operators. However, the evaluation becomes much easier if we can exchange the order of operators. Remembering that these operators do not commute, and using

$$e^{\hat{A}}\, e^{\hat{B}} = e^{\hat{B}}\, e^{\hat{A}}\, e^{-\left[\hat{B},\hat{A}\right]} \tag{12.30}$$

we can write

$$\begin{aligned} F(t) &= e^{-\underset{\sim}{d}^2} \left\langle 0\left| \exp\left[-\underset{\sim}{d}\, a^\dagger\right] \exp\left[-\underset{\sim}{d} a\, e^{-i\omega_0 t}\right] exp\left[\underset{\sim}{d}^2\, e^{-i\omega_0 t}\right] \right| 0\right\rangle \\ &= \exp\left[\underset{\sim}{d}^2\left(e^{-i\omega_0 t} - 1\right)\right] \end{aligned} \tag{12.31}$$

So finally, we have the dipole correlation function:

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 \exp\left[-i\omega_{eg} t + D\left(e^{-i\omega_0 t} - 1\right)\right] \tag{12.32}$$

D is known as the Huang-Rhys parameter (which should be distinguished from the displacement operator $\hat{D}$). It is a dimensionless factor related to the mean square displacement

$$D = \underset{\sim}{d}^2 = d^2\,\frac{m\,\omega_0}{2\hbar} \tag{12.33}$$

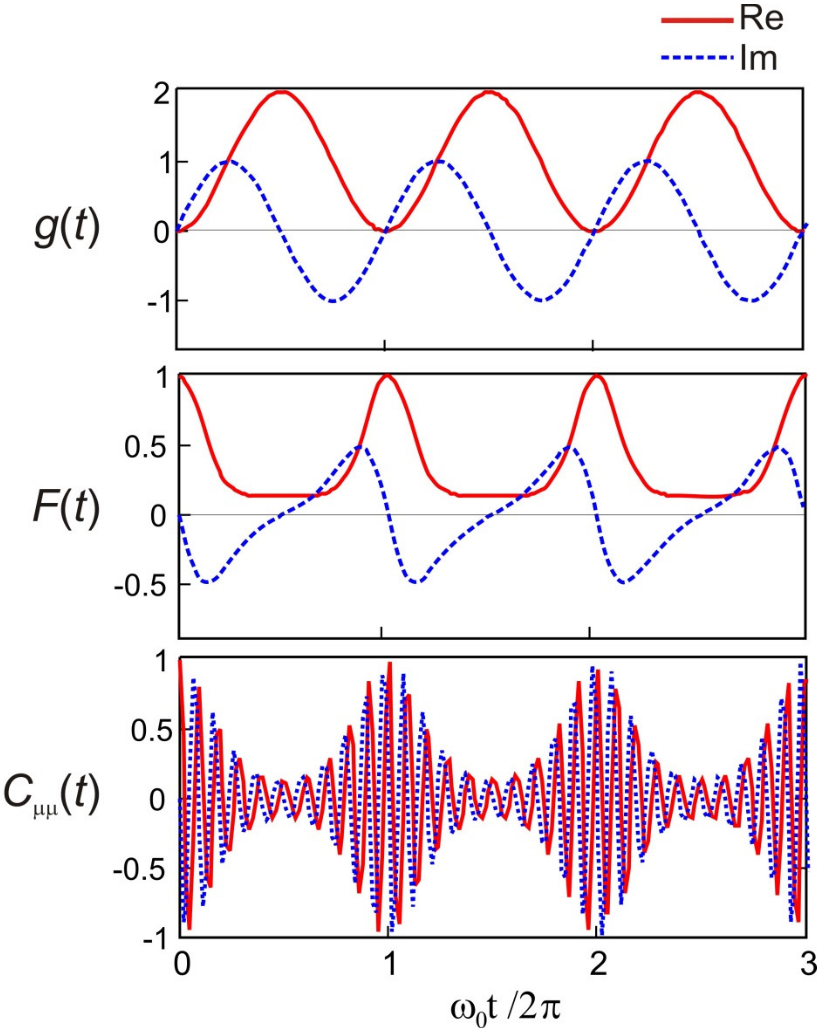
and therefore represents the strength of coupling of the electronic states to the nuclear degree of freedom. Note our correlation function has the form

$$C_{\mu\mu}(t) = \sum_n p_n \left|\mu_{mn}\right|^2 e^{-i\omega_{mn}t - g(t)} \tag{12.34}$$

Here $g(t)$ is our lineshape function

$$g\left(t\right) = -D\left(e^{-i\omega_0 t} - 1\right) \tag{12.35}$$

To illustrate the form of these functions, below is plotted the real and imaginary parts of $C_{\mu\mu}(t)$, $F(t)$, $g(t)$ for $D = 1$, and $\omega_{eg} = 10\omega_0$. $g(t)$ oscillates with the frequency of the single vibrational mode. $F(t)$ quantifies the overlap of vibrational wavepackets on ground and excited state, which peaks once every vibrational period. $C_{\mu\mu}(t)$ has the same information as $F(t)$, but is also modulated at the electronic energy gap ω_{eg}.



Absorption Lineshape and Franck-Condon Transitions

The absorption lineshape is obtained by Fourier transforming eq. (12.32)

$$\begin{aligned}\sigma_{abs}(\omega) &= \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, C_{\mu\mu}(t) \\ &= \left|\mu_{eg}\right|^2 e^{-D} \int_{-\infty}^{+\infty} dt\, e^{i\omega t} e^{-i\omega_{eg} t} \exp\left[D e^{-i\omega_0 t}\right]\end{aligned} \quad . \tag{12.36}$$

If we now expand the final term as

$$\exp\left[D\,\mathrm{e}^{-i\omega_0 t}\right] = \sum_{n=0}^{\infty} \frac{1}{n!} D^n \left(e^{-i\omega_0 t}\right)^n \tag{12.37}$$

the lineshape is

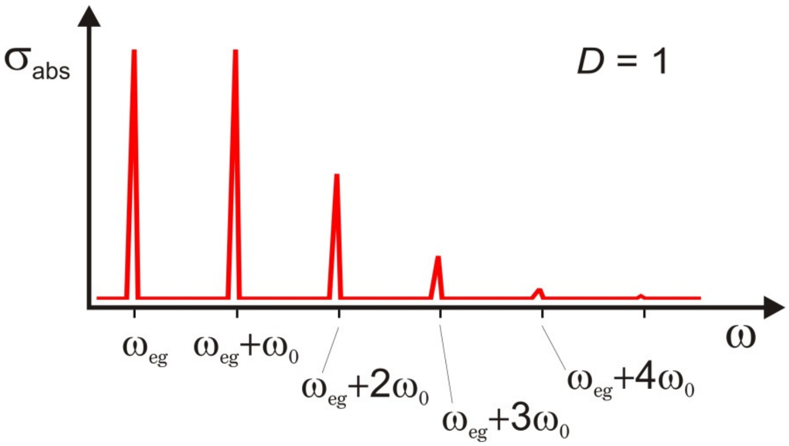
$$\sigma_{abs}(\omega) = \left|\mu_{eg}\right|^2 \sum_{n=0}^{\infty} e^{-D} \frac{D^n}{n!}\, \delta\left(\omega - \omega_{eg} - n\omega_0\right) \tag{12.38}$$

The spectrum is a progression of absorption peaks rising from ω_{eg}, separated by ω_0 with a Poisson distribution of intensities. This is a vibrational progression accompanying the electronic transition. The amplitude of each of these peaks are given by the Franck–Condon coefficients for the overlap of vibrational states in the ground and excited states

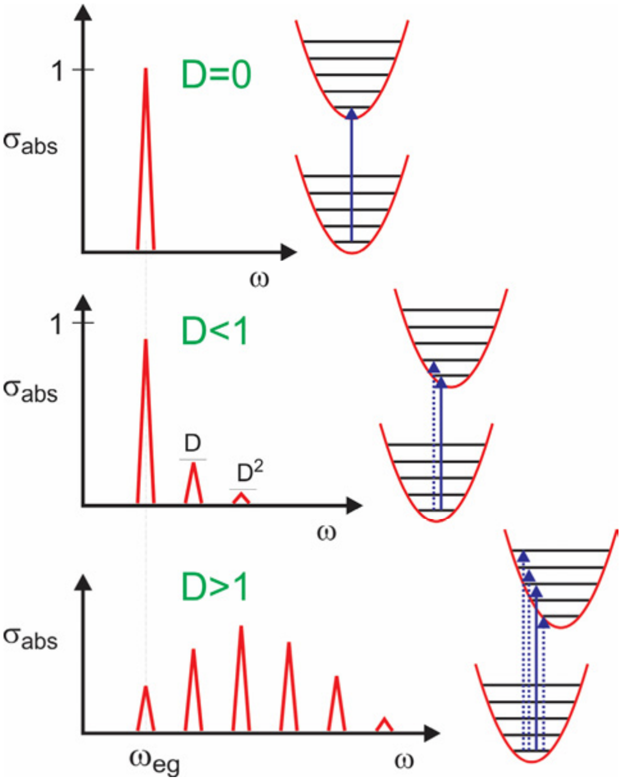
$$\left|\left\langle n_g = 0 \middle| n_e = n \right\rangle\right|^2 = \left|\left\langle 0 \middle| \hat{D} \middle| n \right\rangle\right|^2 = e^{-D} \frac{D^n}{n!} \tag{12.39}$$

The intensities of these peaks are dependent on D, which is a measure of the coupling strength between nuclear and electronic degrees of freedom.

Illustrated below is an example of the normalized absorption lineshape corresponding to the correlation function for D = 1 on the previous page.



Now let's investigate how the absorption lineshape depends on D.



For $D = 0$, there is no dependence of the electronic energy gap ω_{eg} on the nuclear coordinate, and only one resonance is observed. For $D < 1$, the dependence of the energy gap on q is weak and the absorption maximum is at ω_{eg}, with the amplitude of the vibronic progression falling off as D^n. For $D > 1$, the strong coupling regime, the transition with the maximum intensity is found for peak at $n \approx D$. So D corresponds roughly to the mean number of vibrational quanta excited from $q = 0$ in the ground state. This is the Franck-Condon principle, that transition intensities are dictated by the vertical overlap between nuclear wavefunctions in the two electronic surfaces.

To investigate the envelope for these transitions, we can perform a short time expansion of the correlation function applicable for $t < 1/\omega_0$ and for $D \gg 1$. If we approximate the oscillatory term in the lineshape function as

$$\exp(-i\omega_0 t) \approx 1 - i\omega_0 t - \tfrac{1}{2}\omega_0^2 t^2 \tag{12.40}$$

then the lineshape envelope is

$$\begin{aligned}\sigma_{env}(\omega) &= \left|\mu_{eg}\right|^2 \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\; e^{-i\omega_{eg}\, t} e^{D\left(\exp\left(-i\omega_0 t\right)-1\right)} \\ &\approx \left|\mu_{eg}\right|^2 \int_{-\infty}^{+\infty} dt\, e^{i\left(\omega-\omega_{eg} t\right)}\; e^{D\left[-i\omega_0 t-\frac{1}{2}\omega_0^2 t^2\right]} \\ &= \left|\mu_{eg}\right|^2 \int_{-\infty}^{+\infty} dt\, e^{i\left(\omega-\omega_{eg}-D\omega_0\right)t}\; e^{-\frac{1}{2}D\omega_0^2 t^2}\end{aligned} \tag{12.41}$$

This can be solved by completing the square, giving

$$\sigma_{env}(\omega) = \left|\mu_{eg}\right|^2 \sqrt{\frac{2\pi}{D\omega_0^2}}\; \exp\left[-\frac{\left(\omega-\omega_{eg}-D\omega_0\right)^2}{2D\omega_0^2}\right] \tag{12.42}$$

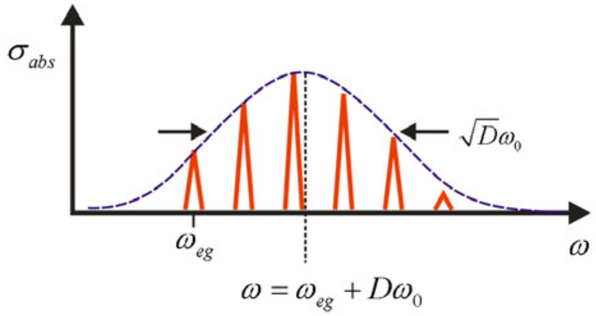
The envelope has a Gaussian profile which is centered at Franck–Condon vertical transition

$$\omega = \omega_{eg} + D\omega_0 \tag{12.43}$$

Thus we can equate D with the mean number of vibrational quanta excited in $|E\rangle$ on absorption from the ground state. Also, we can define the vibrational energy vibrational energy in $|E\rangle$ on excitation at $q = 0$

$$\lambda = D\hbar\omega_0 = \tfrac{1}{2} m\omega_0^2 d^2 \tag{12.44}$$

λ is known as the reorganization energy. This is the value of H_e at q=0, which reflects the excess vibrational excitation on the excited state that occurs on a vertical transition from the ground state. It is therefore the energy that must be dissipated by vibrational relaxation on the excited state surface as the system re-equilibrates following absorption.



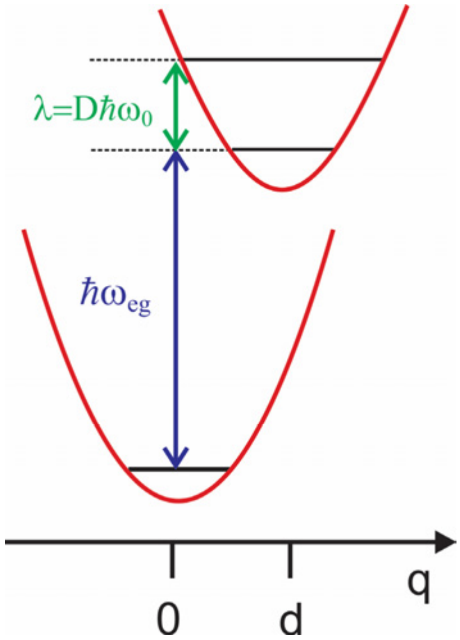
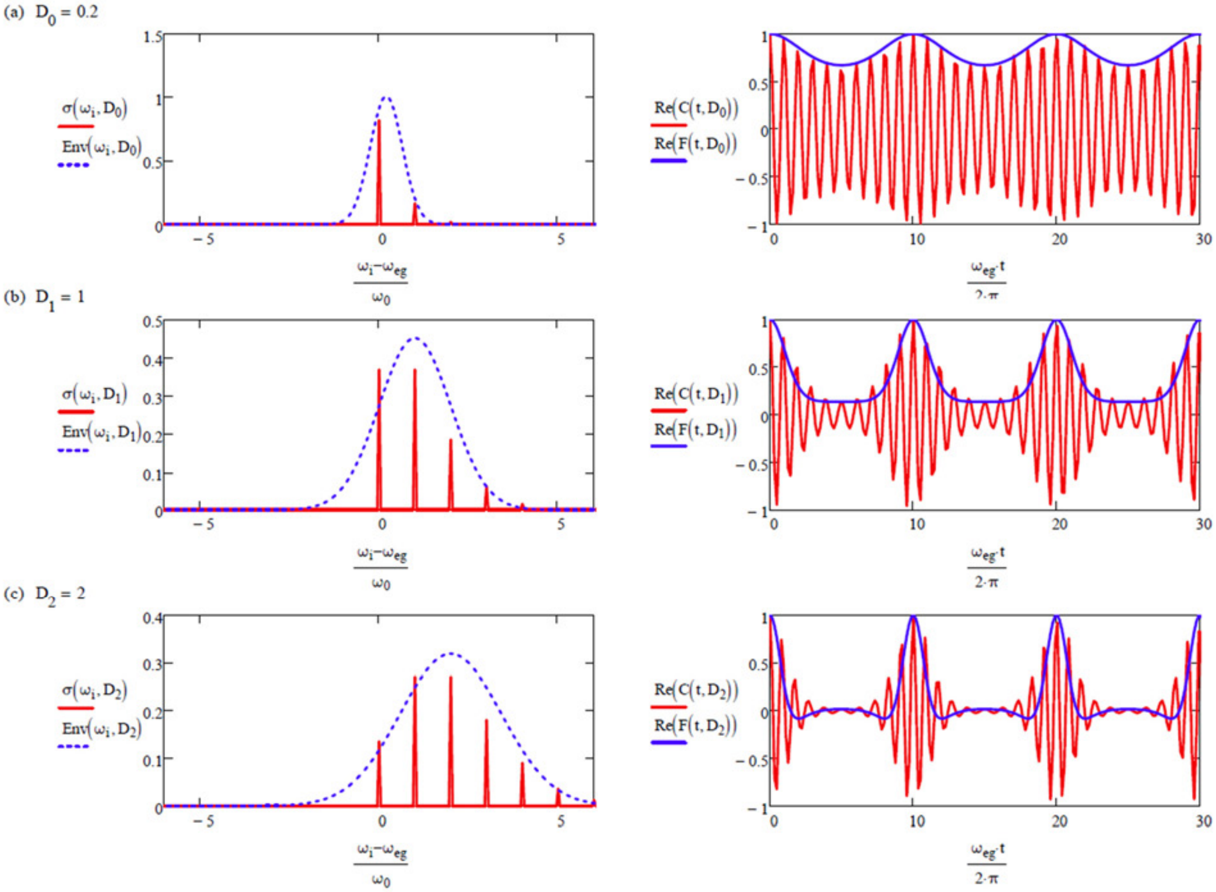
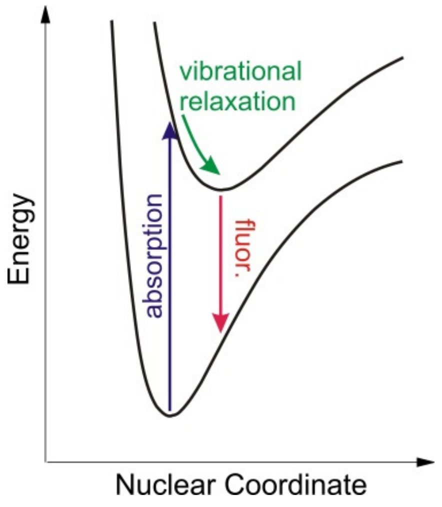


Illustration of how the strength of coupling D influences the absorption lineshape σ (12.38) and dipole correlation function $C_{\mu\mu}$ (12.32). Also shown, the Gaussian approximation to the absorption profile (12.42), and the dephasing function (12.31).

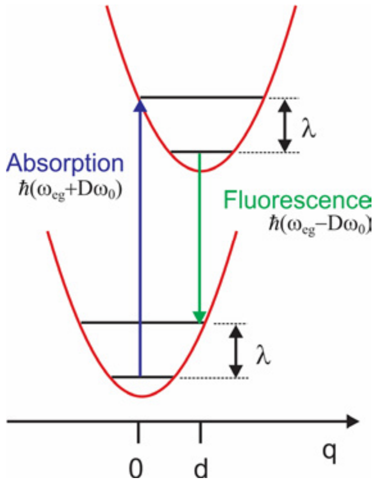


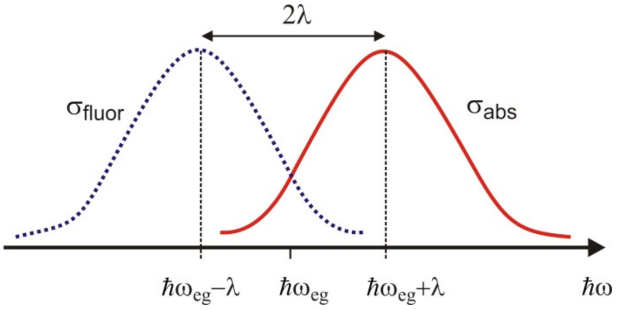
Fluorescence



The DHO model also leads to predictions about the form of the emission spectrum from the electronically excited state. The vibrational excitation on the excited state potential energy surface induced by electronic absorption rapidly dissipates through vibrational relaxation, typically on picosecond time scales. Vibrational relaxation leaves the system in the ground vibrational state of the electronically excited surface, with an average displacement that is larger than that of the ground state. In the absence of other non-radiative processes relaxation processes, the most efficient way of relaxing back to the ground state is by emission of light, i.e., fluorescence. In the Condon approximation this occurs through vertical transitions from the excited state minimum to a vibrationally excited state on the ground electronic surface. The difference between the absorption and emission frequencies reflects the energy of the initial excitation which has been dissipated non-radiatively into vibrational motion both on the excited and ground electronic states, and is referred to as the Stokes shift.

From the DHO model, the emission lineshape can be obtained from the dipole correlation function assuming that the initial state is equilibrated in $|e,0\rangle$, centered at a displacement $q=d$, following the rapid dissipation of energy λ on the excited state. Based on the energy gap at $q=d$, we see that a vertical emission from this point leaves λ as the vibrational energy that needs to be dissipated on the ground state in order to re-equilibrate, and therefore we expect the Stokes shift to be 2λ.





Beginning with our original derivation of the dipole correlation function and focusing on emission, we find that fluorescence is described by

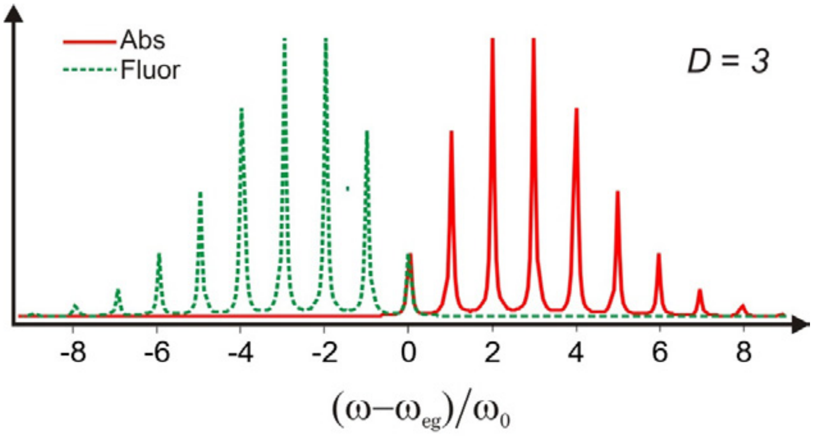
$$\begin{aligned} C_{fl} &= \langle e,0|\,\mu(t)\,\mu(0)\,|e,0\rangle = C^*_{\mu\mu}(t) \\ &= |\mu_{eg}|^2\, e^{-i\omega_{eg}t} F^*(t) \end{aligned} \tag{12.45}$$

$$\begin{aligned} C_{fl} &= \langle e,0|\,\mu(t)\,\mu(0)\,|e,0\rangle = C^*_{\mu\mu}(t) \\ &= |\mu_{eg}|^2\, e^{-i\omega_{eg}t} F^*(t) \\ F^*(t) &= \langle U_e^\dagger\, U_g \rangle \\ &= \exp\left[D\left(e^{i\omega_0 t}-1\right)\right] \end{aligned} \tag{12.46}$$

We note that $C^*_{\mu\mu}(t) = C_{\mu\mu}(-t)$ and $F^*(t) = F(-t)$. Then we can obtain the fluorescence spectrum

$$\begin{aligned} \sigma_{fl}(\omega) &= \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, C^*_{\mu\mu}(t) \\ &= |\mu_{eg}|^2 \sum_{n=0}^{\infty} e^{-D}\frac{D^n}{n!}\,\delta\left(\omega-\omega_{eg}+n\omega_0\right) \end{aligned} \tag{12.47}$$

This is a spectrum with the same features as the absorption spectrum, although with mirror symmetry about ω_{eg}.



A short time expansion confirms that the splitting between the peak of the absorption and emission lineshape envelopes is $2D\hbar\omega_0$, or 2λ. Further, one can establish that

$$\begin{aligned} \sigma_{abs}(\omega) &= \int_{-\infty}^{+\infty} dt\; e^{i(\omega-\omega_{eg})t+g(t)} \\ \sigma_{fl}(\omega) &= \int_{-\infty}^{+\infty} dt\; e^{i(\omega-\omega_{eg})t+g^*(t)} \\ g(t) &= D\left(e^{-i\omega_0 t}-1\right) \end{aligned} \tag{12.48}$$

Note that our description of the fluorescence lineshape emerged from our semiclassical treatment of the light–matter interaction, and in practice fluorescence involves spontaneous emission of light into a quantum mechanical light field. However, while the light field must be handled differently, the form of the dipole correlation function and the resulting lineshape remains unchanged. Additionally, we assumed that there was a time scale separation between the vibrational relaxation in the excited state and the time scale of emission, so that the system can be considered equilibrated in $\left|e,0\right\rangle$. When this assumption is not valid then one must account for the much more complex possibility of emission during the course of the relaxation process.

Readings

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12.2. Coupling to a Harmonic Bath

It is worth noting a similarity between the Hamiltonian for this displaced harmonic oscillator problem, and a general form for the interaction of an electronic "system" that is observed in an experiment with a harmonic oscillator "bath" whose degrees of freedom are invisible to the observable, but which influence the behavior of the system. This reasoning will in fact be developed more carefully later for the description of fluctuations. While the Hamiltonians we have written so far describe coupling to a single bath degree of freedom, the DHO model is readily generalized to many vibrations or a continuum of nuclear motions. Coupling to a continuum, or a harmonic bath, is the starting point for developing how an electronic system interacts with a continuum of intermolecular motions and phonons typical of condensed phase systems.

So, what happens if the electronic transition is coupled to many vibrational coordinates, each with its own displacement? The extension is straightforward if we still only consider two electronic states (*e* and *g*) to which we couple a set of independent modes, i.e., a bath of harmonic normal modes. Then we can write the Hamiltonian for *N* vibrations as a sum over all the independent harmonic modes

$$H_e = \sum_{\alpha=1}^{N} H_e^{(\alpha)} = \sum_{\alpha=1}^{N} \left(\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 \left(q_\alpha - d_\alpha \right)^2 \right) \tag{12.49}$$

each with their distinct frequency and displacement. We can specify the state of the system in terms of product states in the electronic and nuclear occupation, i.e.,

$$\begin{aligned} |G\rangle &= |g; n_1, n_2, \ldots, n_N\rangle \\ &= |g\rangle \prod_{\alpha=1}^{N} |n_\alpha\rangle \end{aligned} \tag{12.50}$$

Additionally, we recognize that the time propagator on the electronic excited potential energy surface is

$$U_e = \exp\left[-\frac{i}{\hbar} H_e t \right] = \prod_{\alpha=1}^{N} U_e^{(\alpha)} \tag{12.51}$$

where

$$U_e^{(\alpha)} = \exp\left[-\frac{i}{\hbar} H_e^{(\alpha)} t \right] \tag{12.52}$$

Defining $D_\alpha = d_\alpha^2 (m\omega_\alpha / 2\hbar)$

$$\begin{aligned} F^{(\alpha)} &= \left\langle \left[U_g^{(\alpha)} \right]^\dagger U_e^{(\alpha)} \right\rangle \\ &= \exp\left[D_\alpha \left(e^{-i\omega_\alpha t} - 1 \right) \right] \end{aligned} \tag{12.53}$$

the dipole correlation function is then just a product of multiple dephasing functions that characterize the time-evolution of the different vibrations.

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t} \cdot \prod_{\alpha=1}^{N} F^{(\alpha)}(t) \tag{12.54}$$

or

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t + g(t)} \tag{12.55}$$

with

$$g(t) = \sum_{\alpha} D_{\alpha}\left(e^{-i\omega_{\alpha}t} - 1\right) \tag{12.56}$$

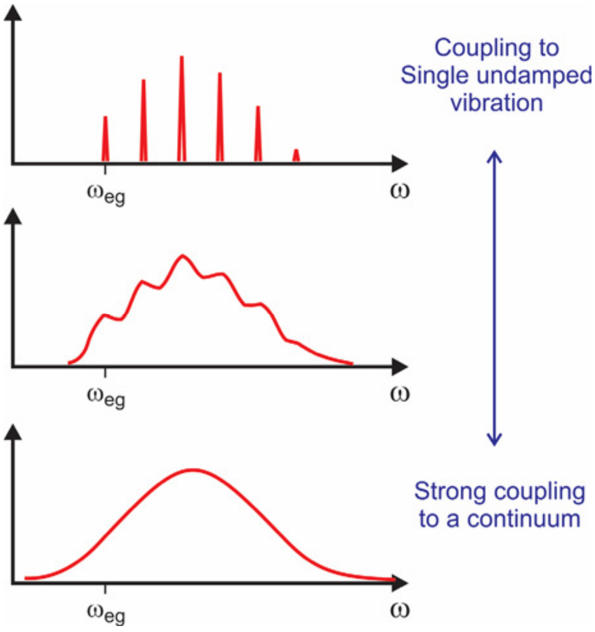
In the time domain this is a complex beating pattern, which in the frequency domain appears as a spectrum with several superimposed vibronic progressions that follow the rules developed above. Also, the reorganization energy now reflects to total excess nuclear potential energy required to make the electronic transition:

$$\lambda = \sum_{\alpha} D_{\alpha}\hbar\omega_{\alpha} \tag{12.57}$$

Taking this a step further, the generalization to a continuum of nuclear states emerges naturally. Given that we have a continuous frequency distribution of normal modes characterized by a density of states, $W(\omega)$, and a continuously varying frequency-dependent coupling, $D(\omega)$, we can change the sum in eq. (12.56) to an integral over the density of states:

$$g(t) = \int d\omega\; W(\omega)\; D(\omega)\left(e^{-i\omega t} - 1\right) \tag{12.58}$$

Here the product $W(\omega)\, D(\omega)$ is a coupling-weighted density of states, and is commonly referred to as a spectral density.



What this treatment does is provide a way of introducing a bath of states that the spectroscopically interrogated transition couples with. Coupling to a bath or continuum provides a way of introducing relaxation effects or damping of the electronic coherence in the absorption spectrum. You can see that if $g(t)$ is associated with a constant Γ, we obtain a Lorentzian lineshape with width Γ. This emerges under certain circumstances, for instance if the distribution of states and coupling is large and constant, and if the integral in eq. (12.58) is over a distribution of low frequencies, such that $e^{-i\omega t} \approx 1 - i\omega t$. More generally the lineshape function is complex, and the real part describes damping and the imaginary part modulates the primary frequency and leads to fine structure. We will discuss these circumstances in more detail later.

An Ensemble at Finite Temperature

As described above, the single mode DHO model above is for a pure state, but the approach can be readily extended to describe a canonical ensemble. In this case, the correlation function is averaged over a thermal distribution of initial states. If we take the initial state of the system to be in the electronic ground state and its vibrational levels (n_g) to be occupied as a Boltzmann distribution, which is characteristic of ambient temperature samples, then the dipole correlation function can be written as a thermally averaged dephasing function:

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t} F(t) \tag{12.59}$$

$$F(t) = \sum_{n_g} p(n_g) \left\langle n_g \left| U_g^\dagger U_e \right| n_g \right\rangle \tag{12.60}$$

$$p(n_g) = \frac{e^{-\beta\hbar n_g \omega_0}}{Z} \tag{12.61}$$

Evaluating these expressions using the strategies developed above leads to

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t} \exp\left[D\left[\underline{(\bar{n}+1)\left(e^{-i\omega_0 t}-1\right)} + \underline{\bar{n}\left(e^{+i\omega_0 t}-1\right)} \right]\right] \tag{12.62}$$

$\bar{n}$ is the thermally averaged occupation number of the harmonic vibrational mode.

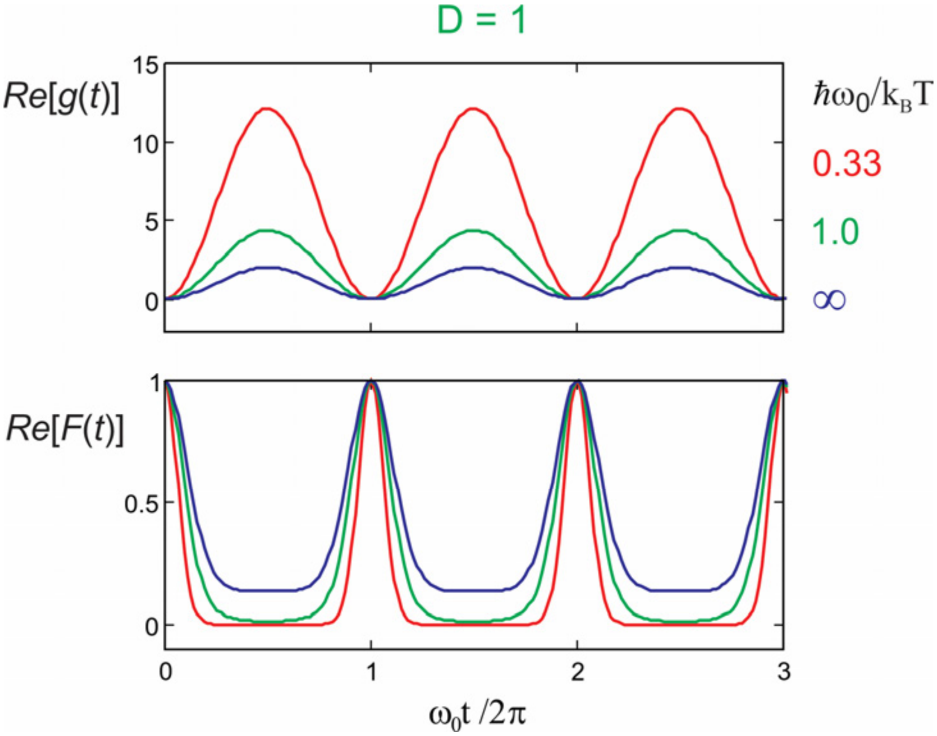
$$\bar{n} = \left(e^{\beta\hbar\omega_0} - 1\right)^{-1} \tag{12.63}$$

Note that in the low temperature limit, $\bar{n} \to 0$, and eq. (12.62) equals our original result eq. (12.32). The dephasing function has two terms underlined in (12.62), of which the first describes those electronic absorption events in which the vibrational quantum number increases or is unchanged ($n_e \geq n_g$), whereas the second are for those processes where the vibrational quantum number decreases or is unchanged ($n_e \leq n_g$). The latter are only allowed at elevated temperature where thermally excited states are populated and are known as “hot bands”.

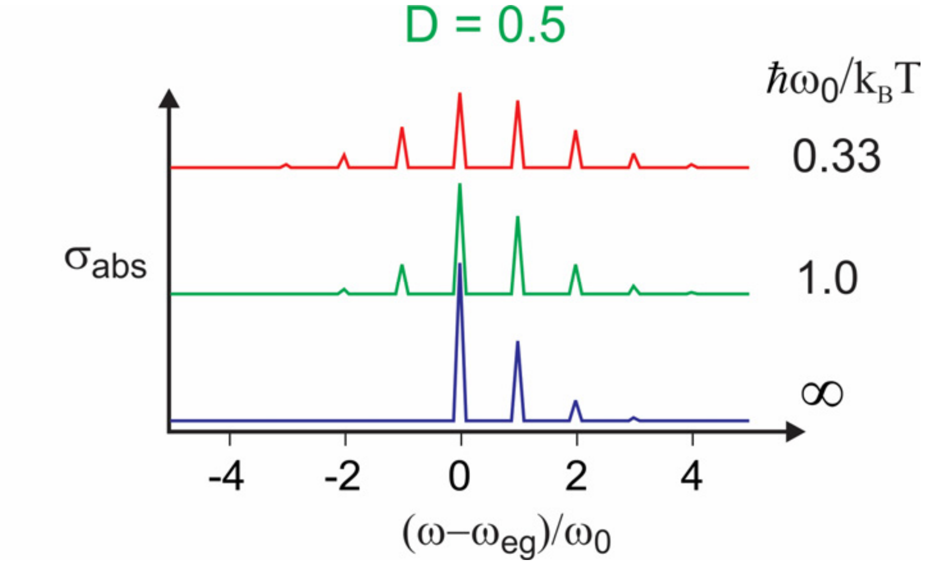
Now, let’s calculate the lineshape. If we separate the dephasing function into a product of two exponential terms and expand each of these exponentials, we can Fourier transform to give

$$\sigma_{abs}(\omega) = \left|\mu_{eg}\right|^2 \; e^{-D(2\bar{n}+1)} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \left(\frac{D^{j+k}}{j!k!} \right) (\bar{n}+1)^j \, \bar{n}^k \, \delta\left(\omega - \omega_{eg} - (j-k)\omega_0\right) \tag{12.64}$$

Here the summation over *j* describes $n_e \geq n_g$ transitions, whereas the summation over *k* describes $n_e \leq n_g$. For any one transition frequency, $(\omega_{eg}+n\omega_0)$, the net absorption is a sum over all possible combination of transitions at the energy splitting with n=(j–k). Again, if we set $\bar{n} \rightarrow 0$, we obtain our original result eq. (12.38). The contributions where k<j leads to the hot bands.



Examples of temperature dependence to lineshape and dephasing functions for D = 1. The real part changes in amplitude, growing with temperature, whereas the imaginary part is unchanged.



We can extend this description to describe coupling to a many independent nuclear modes or coupling to a continuum. We write the state of the system in terms of the electronic state and the nuclear quantum numbers, i.e., $|E\rangle = |e; n_1, n_2, n_3 \ldots\rangle$, and from that:

$$F(t) = \exp\left[\sum_j D_j \left[\left(\bar{n}_j + 1\right)\left(e^{-i\omega_j t} - 1\right) + \bar{n}_j \left(e^{i\omega_j t} - 1\right)\right]\right] \tag{12.65}$$

or changing to an integral over a continuous frequency distribution of normal modes characterized by a density of states, $W(\omega)$

$$F(t) = \exp\left[\int d\omega \; W(\omega) \; D(\omega)\left[\left(\bar{n}(\omega) + 1\right)\left(e^{-i\omega t} - 1\right) + \bar{n}(\omega)\left(e^{i\omega t} - 1\right)\right]\right] \tag{12.66}$$

$D(\omega)$ is the frequency dependent coupling. Let's look at the envelope of the nuclear structure on the transition by doing a short-time expansion on the complex exponential as in eq. (12.40)

$$F(t) = \exp\left[\int d\omega D(\omega) W(\omega)\left(-i\omega t - \left(2\bar{n} + 1\right)\frac{\omega^2 t^2}{2}\right)\right] \tag{12.67}$$

The lineshape is calculated from

$$\sigma_{abs}(\omega) = \int_{-\infty}^{+\infty} dt \, e^{i\left(\omega - \omega_{eg}\right)t} \; \exp\left[-i\left\langle\omega\right\rangle t\right] \exp\left[-\tfrac{1}{2}\left\langle\omega^2\right\rangle \; t^2\right] \tag{12.68}$$

where we have defined the mean vibrational excitation on absorption

$$\begin{aligned}\langle\omega\rangle &= \int d\omega W(\omega) D(\omega)\omega \\ &= \lambda / \hbar\end{aligned} \tag{12.69}$$

and

$$\left\langle\omega^2\right\rangle = \int d\omega \; W(\omega) D(\omega)\omega^2\left(2\bar{n}(\omega) + 1\right) \tag{12.70}$$

$\left\langle\omega^2\right\rangle$ reflects the thermally averaged distribution of accessible vibrational states. Completing the square, eq. gives

$$\sigma_{abs}(\omega) = \left|\mu_{eg}\right|^2 \sqrt{\frac{2\pi}{\left\langle\omega^2\right\rangle}} \; \exp\left[\frac{-\left(\omega - \omega_{eg} - \langle\omega\rangle\right)^2}{2\left\langle\omega^2\right\rangle}\right] \tag{12.71}$$

The lineshape is Gaussian, with a transition maximum at the electronic resonance plus reorganization energy. Although the frequency shift ⟨ω⟩ is not temperature dependent, the width of the Gaussian is temperature-dependent as a result of the thermal occupation factor in eq. (12.70).

12.3 Semiclassical Approximation to the Dipole Correlation Function

In introducing the influence of dark degrees of freedom on the spectroscopy of a bright state, we made some approximations that are not always valid, such as the Condon approximation and the Second Cumulant Approximation. To develop tools that allow us to work outside of these approximations, it is worth revisiting the evaluation of the dipole correlation function and looking at this a bit more carefully. In particular, we will describe the semiclassical approximation, which is a useful representation of the dipole correlation function when one wants to describe the dark degrees of freedom (the bath) using classical molecular dynamics simulations.

For a quantum mechanical material system interacting with a light field, the full Hamiltonian is

$$H = H_0 + V(t) \tag{12.72}$$

$$V(t) = -\overline{m} \cdot \overline{E}(t) \tag{12.73}$$

$\overline{m} = \sum_i z_i \overline{r}_i$ is the quantum mechanical dipole operator, where z_i are charges. The absorption lineshape is given by the Fourier transformation of the dipole autocorrelation function $C_{\mu\mu}$:

$$C_{\mu\mu}\left(\tau\right) = \left\langle \overline{m}(t)\overline{m}(0) \right\rangle = Tr\left(\rho_{eq}\overline{m}(t)\overline{m}(0)\right) \tag{12.74}$$

and the time dependence in $\overline{m}$ is expressed in terms of the usual time-propagator

$$\overline{m}(t) = \hat{U}_0^{\dagger}\overline{m}\hat{U}_0 \tag{12.75}$$

$$\hat{U}_0 = e_+^{-\frac{i}{\hbar}\int_0^t H_0(t')dt'} \tag{12.76}$$

In principle, the time development of the dipole moment for all degrees of freedom can be obtained directly from *ab initio* molecular dynamics simulations.

For a more practical expression in which we wish to focus on one or a few bright degrees of freedom, we next partition the Hamiltonian into system and bath

$$H_0 = H_S(Q) + H_B(q) + H_{SB}(Q,q) \tag{12.77}$$

For purposes of spectroscopy, the system H_S refers to those degrees of freedom (Q) with which the light will interacts, and which will be those in which we calculate matrix elements. The bath H_B refers to all of the other degrees of freedom (q), and the interaction between the two is accounted for in H_{SB}. Although the interaction of the light depends on how $\overline{m}$ varies with Q, the dipole operator remains a function of system and bath coordinates: $\overline{m}(Q,q)$.

We now use the interaction picture transformation to express the time propagator under the full material Hamiltonian $\hat{U}_0$ in terms of a product of propagators in the individual terms in *H₀*:

$$\hat{U}_0 = U_S U_B U_{SB} \tag{12.78}$$

$$\hat{U}_0 = e_+^{-\frac{i}{\hbar}\int_0^t H_0 \, dt'} = e^{-iH_S t} e_+^{-i\int_0^t H_B \, dt'} e_+^{-i\int_0^t \mathbf{H_{SB}}(t')\, dt'} \tag{12.79}$$

$$\mathbf{H_{SB}}(t) = e^{i(H_S+H_B)t} H_{SB} e^{-i(H_S+H_B)t} \tag{12.80}$$

Then the dipole autocorrelation function becomes

$$C_{\mu\mu} = \sum_n p_n \left\langle n \left| U_{SB}^\dagger U_B^\dagger U_S^\dagger \bar{m} U_S U_B U_{SB} \bar{m} \right| n \right\rangle \tag{12.81}$$

Where $p_n = \left\langle n \left| e^{-\beta H_0} \right| n \right\rangle / Tr\left(e^{-\beta H_0}\right)$.

Further, to make this practical, we make an adiabatic separation between the system and bath coordinates, and say that the interaction between the system and bath is weak. This allows us to write the state of the system as product states in the system (a) and bath (α), $|n\rangle = |a,\alpha\rangle$:

$$\left(H_S + H_B\right)|a,\alpha\rangle = \left(E_a + E_\alpha\right)|a,\alpha\rangle \tag{12.82}$$

With this we evaluate eq. (12.81) as

$$\begin{aligned} C_{\mu\mu} &= \sum_{a,\alpha} p_a p_\alpha \left\langle a,\alpha \left| U_{SB}^\dagger U_B^\dagger U_S^\dagger \bar{m} U_S U_B U_{SB} \bar{m} \right| a,\alpha \right\rangle \\ &= \sum_{\substack{a,b \\ \alpha}} p_a p_\alpha \left\langle \alpha \left| \left\langle a \left| U_{SB}^\dagger U_S^\dagger \; U_B^\dagger \bar{m} U_B \; U_S U_{SB} \right| b \right\rangle \bar{m}_{ba} \right| \alpha \right\rangle \end{aligned} \tag{12.83}$$

where $\bar{m}_{ba} = \left\langle b \left| \bar{m} \right| a \right\rangle$, and we have made use of the fact that H_S and H_B commute. Also, $p_a = e^{-E_a/kT} \big/ Q_S$. Now, by recognizing that the time propagators in the system and system-bath Hamiltonians describe time evolution at the system eigenstate energy plus any modulations that the bath introduces to it

$$U_S U_{SB} \left| b \right\rangle = e^{-iH_S t} \left| b \right\rangle e^{-i\int_0^t dt' \, \delta E_b(t')} = \left| b \right\rangle e^{-i\int_0^t dt' E_b(t')} \tag{12.84}$$

and we can write our correlation function as

$$C_{\mu\mu} = \sum_{\substack{a,b \\ \alpha}} p_a p_\alpha \left\langle \alpha \left| e^{i\int_0^t dt' E_a(t')} U_B^\dagger \bar{m}_{ab} U_B e^{-i\int_0^t dt' E_b(t')} \bar{m}_{ba} \right| \alpha \right\rangle \tag{12.85}$$

$$C_{\mu\mu} = \left\langle \bar{m}_{ab}(t) \bar{m}_{ba}(0) e^{-i\int_0^t dt' \, \omega_{ba}(t')} \right\rangle_B \tag{12.86}$$

$$\overline{m}_{ab}(t) = e^{-iH_B t}\,\overline{m}_{ab}\,e^{-iH_B t} \tag{12.87}$$

Equation (12.86) is the first important result. It describes a correlation function in the dipole operator expressed in terms of an average over the time-dependent transition moment, including its orientation, and the fluctuating energy gap. The time dependence is due to the bath and $\langle \ldots \rangle_B$ refers to a trace over the bath degrees of freedom.

Let's consider the matrix elements. These will reflect the strength of interaction of the electromagnetic field with the motion of the system coordinate, which may also be dependent on the bath coordinates. Since we have made an adiabatic approximation, to evaluate the matrix elements we would typically expand the dipole moment in the system degrees of freedom, *Q*. As an example for one system coordinate (*Q*) and many bath coordinates *q*, we can expand:

$$\overline{m}(Q,q) = \overline{m}_0 + \frac{\partial \overline{m}}{\partial Q} Q + \sum_\alpha \frac{\partial^2 \overline{m}}{\partial Q\, \partial q_\alpha} Q q_\alpha + \cdots \tag{12.88}$$

$\overline{m}_0$ is the permanent dipole moment, which we can take as a constant. In the second term, $\partial \overline{m}/\partial Q$ is the magnitude of the transition dipole moment. The third term includes the dependence of the transition dipole moment on the bath degrees of freedom, i.e., non-Condon terms. So now we can evaluate

$$\begin{aligned} \overline{m}_{ab} &= \left\langle a \left| \overline{m}_0 + \frac{\partial \overline{m}}{\partial Q} Q + \sum_\alpha \frac{\partial^2 \overline{m}}{\partial Q\, \partial q_\alpha} Q q_\alpha \right| b \right\rangle \\ &= \frac{\partial \overline{m}}{\partial Q} \langle a | Q | b \rangle + \sum_\alpha \frac{\partial}{\partial q_\alpha} \frac{\partial \overline{m}}{\partial Q} \langle a | Q | b \rangle q_\alpha \end{aligned} \tag{12.89}$$

We have set $\langle a | \overline{m}_0 | b \rangle = 0$. Now defining the transition dipole matrix element,

$$\overline{\mu}_{ab} = \frac{\partial \overline{m}}{\partial Q} \langle a | Q | b \rangle \tag{12.90}$$

we can write

$$\overline{m}_{ab} = \overline{\mu}_{ab} \left(1 + \sum_\alpha \frac{\partial \overline{\mu}_{ab}}{\partial q_\alpha} q_\alpha \right) \tag{12.91}$$

Remember that $\overline{\mu}_{ab}$ is a vector. The bath can also change the orientation of the transition dipole moment. If we want to separate the orientational and remaining dynamics this we could split the matrix element into an orientational component specified by a unit vector along $\partial \overline{m}/\partial Q$ and a scalar that encompasses the amplitude factors: $\overline{\mu}_{ab} = \hat{u}_{ab}\mu_{ab}$. Then eq. (12.86) becomes

$$C_{\mu\mu} = \left\langle \hat{u}_{ab}(t)\hat{u}_{ab}(0) m_{ab}(t) m_{ba}(0) e^{-i\int_0^t dt'\,\omega_{ba}(t')} \right\rangle_B \tag{12.92}$$

Mixed quantum-classical spectroscopy models apply a semiclassical approximation to equation (12.86). Employing the semiclassical approximation says that we will replace the quantum mechanical operator $\overline{m}_{ab}(t)$ with a classical $\overline{\mathcal{M}}_{ab}(t)$, i.e., we replace the time propagator U_B with classical propagation of the dynamics. Also, the trace over the bath in the correlation function becomes an equilibrium ensemble average over phase space.

How do you implement the semiclassical approximation? Replacing the time propagator U_B with classical dynamics amounts to integrating Newton's equations for all of the bath degrees of freedom. Then you must establish how the bath degrees of freedom influence $\omega_{ba}(t)$ and $\overline{m}_{ab}(t)$. For the quantum operator $\overline{m}(Q,q,t)$, only the system coordinate Q remains quantized, and following eq. (12.91) we can express the orientation and magnitude of the dipole moment and the dynamics depends on the classical degrees of freedom $\tilde{q}_\alpha$.

$$\overline{m}_{ab} = \overline{\mu}_{ab}\left(1 + \sum_{\alpha} a_\alpha \tilde{q}_\alpha\right) \tag{12.93}$$

a_α is a (linear) mapping coefficient, $a_\alpha = \partial\overline{\mu}_{ab}/\partial\tilde{q}_\alpha$, between the bath and the transition dipole moment.

In practice, use of this approximation has been handled in different ways, but practical considerations have dictated that $\omega_{ba}(t)$ and $\overline{m}_{ab}(t)$ are not separately calculated for each time step, but are obtained from a mapping of these variables to the bath coordinates q. This mapping may be to local or collective bath coordinates, and to as many degrees of freedom as are necessary to obtain a highly correlated single valued mapping of $\omega_{ba}(t)$ and $\overline{m}_{ab}(t)$. Examples of these mappings include correlating ω_{ba} with the electric field of the bath acting on the system coordinate.

Appendix

Let's evaluate the dipole correlation function for an arbitrary H_{SB} and an arbitrary number of system eigenstates. From eq. (12.83) we have

$$C_{\mu\mu} = \sum_{\substack{abcd\\ \alpha}} p_a p_\alpha \left\langle \alpha \middle| \left\langle a \middle| U_{SB}^\dagger \middle| c \right\rangle U_B^\dagger \left\langle c \middle| U_S^\dagger \overline{m} U_S \middle| d \right\rangle U_B \left\langle d \middle| U_{SB} \middle| b \right\rangle \left\langle b \middle| \overline{m} \middle| a \right\rangle \middle| \alpha \right\rangle \tag{12.94}$$

$$\left\langle c \middle| U_S^\dagger \overline{m} U_S \middle| d \right\rangle = e^{-i\left(E_d - E_c\right)t}\, \overline{m}_{cd} \tag{12.95}$$

$$\overline{m}_{cd}(t) = U_B^\dagger \overline{m}_{cd} U_B \tag{12.96}$$

$$\left\langle a \middle| U_{SB}^\dagger \middle| c \right\rangle = \left\langle a \middle| e^{i\int_0^t dt' \mathbf{H}_{\mathbf{SB}}(t')} \middle| c \right\rangle = \exp\left[i\int_0^t dt' \left[\mathbf{H}_{\mathbf{SB}}\right]_{ac}(t') \right] \tag{12.97}$$

$$C_{\mu\mu} = \sum_{abcd} p_a \left\langle e^{-i\omega_{dc}t} e^{i\int_0^t dt'\left[H_{SB}\right]_{ac}(t')} \bar{m}_{cd} e^{-i\int_0^t dt'\left[H_{SB}\right]_{db}(t')} \bar{m}_{ba} \right\rangle_B \tag{12.98}$$

$$C_{\mu\mu} = \left\langle \bar{m}_{cd}(t)\bar{m}_{ba}(0) \exp\left[-i\omega_{dc}t - i\int_0^t dt'\left[H_{SB}\right]_{db}(t') - \left[H_{SB}\right]_{ac}(t') \right] \right\rangle_B \tag{12.99}$$

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13. FLUCTUATIONS IN SPECTROSCOPY

Here we will describe how fluctuations are observed in experimental observables, as is common to experiments in molecular condensed phases. As our example, we will focus on absorption spectroscopy and how environmentally induced dephasing influences the absorption lineshape. Our approach will be to calculate a dipole correlation function for transition dipole interacting with a fluctuating environment, and show how the time scale and amplitude of fluctuations are encoded in the lineshape. Although the description here is for the case of a spectroscopic observable, the approach can be applied to any such problems in which the deterministic motions of an internal variable of a quantum system are influenced by a fluctuating environment.

We also aim to establish a connection between this problem and the Displaced Harmonic Oscillator model. Specifically, we will show that a frequency-domain representation of the coupling between a transition and a continuous distribution of harmonic modes is equivalent to a time-domain picture in which the transition energy gap fluctuates about an average frequency with a statistical time scale and amplitude given by the distribution of coupled modes. Thus an absorption spectrum is merely a spectral representation of the dynamics experienced by a experimentally probed transition.

13.1. Fluctuations and Randomness: Some Definitions

"Fluctuations" is my word for the time-evolution of a randomly perturbed system at or near equilibrium. For chemical problems in the condensed phase we constantly come up against the problem of random fluctuations to dynamical variables as a result of their interactions with their environment. It is unreasonable to think that you will come up with an equation of motion for the internal deterministic variable, but we should be able to understand the behavior statistically and come up with equations of motion for probability distributions. Models of this form are commonly referred to as stochastic. A stochastic equation of motion is one which includes a random component to the time-development.

When we introduced correlation functions, we discussed the idea that a statistical description of a system is commonly formulated in terms of probability distribution functions P. Observables are commonly described by moments of this distribution, which are obtained by integrating over P, for instance

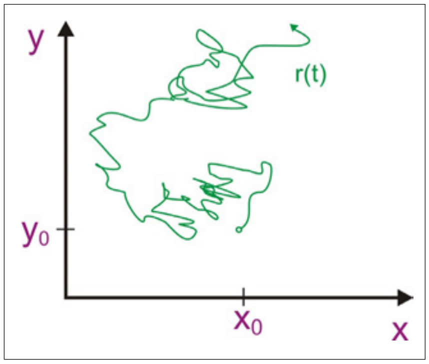
$$\begin{aligned}\langle x\rangle &= \int dx\, x\,\mathrm{P}(x)\\ \langle x^2\rangle &= \int dx\, x^2\,\mathrm{P}(x)\end{aligned}\tag{13.1}$$

For time-dependent processes, we recognize that it is possible that the probability distribution carries a time-dependence.

$$\begin{aligned} \langle x(t)\rangle &= \int dx\, x(t)\, \mathrm{P}(x,t) \\ \langle x^2(t)\rangle &= \int dx\, x^2(t)\, \mathrm{P}(x,t) \end{aligned} \tag{13.2}$$

Correlation functions go a step further and depend on joint probability distributions $\mathrm{P}(t'',A;t',B)$ that give the probability of observing a value of A at time t'' and a value of B at time t':

$$\langle A(t'')B(t')\rangle = \int dA \int dB\, A\, B\;\; \mathrm{P}(t'',A;t',B) \tag{13.3}$$



The statistical description of random fluctuations are described through these time-dependent probability distributions, and we need a stochastic equation of motion to describe their behavior. A common example of such a process is Brownian motion, the fluctuating position of a particle under the influence of a thermal environment. It is not practical to describe the absolute position of the particle, but we can formulate an equation of motion for the probability of finding the particle in time and space given that you know its initial position. Working from a random walk model, one can derive an equation of motion that takes the form of the well-known diffusion equation, here written in one dimension:

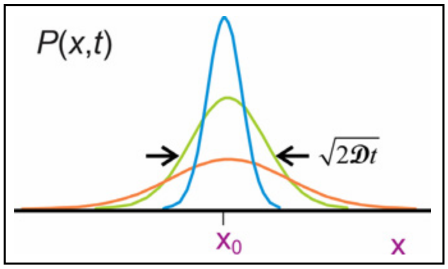
$$\frac{\partial \mathrm{P}(x,t)}{\partial t} = \mathcal{D}\frac{\partial^2}{\partial x^2}\mathrm{P}(x,t) \tag{13.4}$$

Here $\mathcal{D}$ is the diffusion constant which sets the time scale and spatial extent of the random motion. [Note the similarity of this equation to the time-dependent Schrödinger equation for a free particle if $\mathcal{D}$ is taken as imaginary]. Given the initial condition $\mathrm{P}(x,t_0)=\delta(x-x_0)$, the solution is a conditional probability density

$$\mathrm{P}(x,t;x_0,t_0) = \frac{1}{\sqrt{2\pi\mathcal{D}(t-t_0)}}\exp\left(-\frac{(x-x_0)^2}{4\mathcal{D}(t-t_0)}\right) \tag{13.5}$$

The probability distribution describes the statistics for fluctuations in the position of a particle averaged over many trajectories. Analyzing the moments of this probability density using eq. (13.2) we find that

$$\begin{aligned} \langle x(t)\rangle &= x_0 \\ \langle \delta x(t)^2\rangle &= 2\mathcal{D}t \end{aligned} \tag{13.6}$$



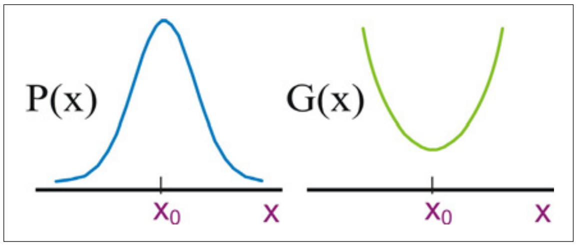
where $\delta x(t) = x(t) - x_0$. So, the distribution maintains a Gaussian shape centered at x_0, and broadens with time as $\sqrt{2\mathcal{D}t}$.

Brownian motion is an example of a Gaussian-Markovian process. Here Gaussian refers to cases in which we describe the probability distribution for a variable $P(x)$ as a Gaussian normal distribution. Here in one dimension:

$$\mathrm{P}(x) = A\, e^{-(x-x_0)^2/2\Delta^2}$$
$$\Delta^2 = \langle x^2 \rangle - \langle x \rangle^2 \qquad (13.6)$$

The Gaussian distribution is important, because the central limit theorem states that the distribution of a continuous random variable with finite variance will follow the Gaussian distribution. Gaussian distributions also are completely defined in terms of their first and second moments, meaning that a time-dependent probability density $P(x,t)$ is uniquely characterized by a mean value in the observable variable x and a correlation function that describes the fluctuations in x. Gaussian distributions for systems at thermal equilibrium are also important for the relationship between Gaussian distributions and parabolic free energy surfaces:

$$G(x) = -k_B T \ln \mathrm{P}(x) \qquad (13.7)$$



If the probability density is Gaussian along x, then the system's free energy projected onto this coordinate (often referred to as a potential of mean force) has a harmonic shape. Thus Gaussian statistics are effective for describing fluctuations about an equilibrium mean value x_0.

Markovian means that the time-dependent behavior of a system does not depend on its earlier history, statistically speaking. Naturally the state of any one molecule depends on its trajectory through phase space, however we are saying that from the perspective of an ensemble there is no memory of the state of the system at an earlier time. This can be stated in terms of joint probability functions as

$$\mathrm{P}(x_2,t_2;x_1,t_1;x_0,t_0) = \mathrm{P}(x_2,t_2;x_1,t_1)\,\mathrm{P}(x_1,t_1;x_0,t_0) \qquad (13.7)$$

or

$$\mathrm{P}(t_2;t_1;t_0) = \mathrm{P}(t_2;t_1)\,\mathrm{P}(t_1;t_0)$$

The probability of observing a trajectory that takes you from state 1 at time 1 to state 2 at time 2 does not depend on where you were at time 0. Further, given the knowledge of the probability of executing changes during a single time interval, you can exactly describe P for any time interval. Markovian therefore refers to time-dependent processes on a time scale long compared to correlation time for the internal variable that you care about. For instance, the diffusion equation only holds after the particle has experienced sufficient collisions with its surroundings that it has no memory of its earlier position and momentum: $t > \tau_c$.

Readings

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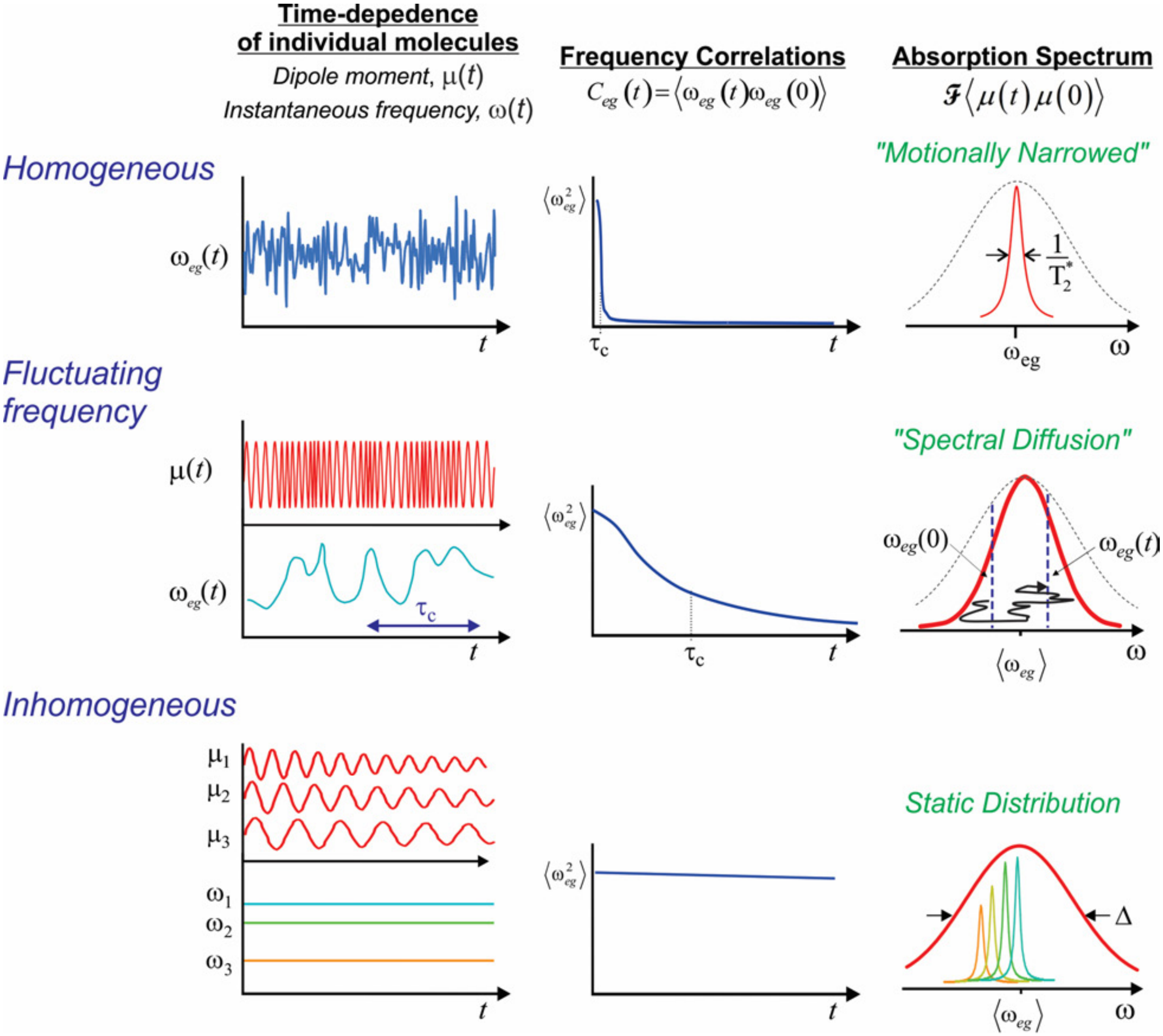
13.2. Line-Broadening and Spectral diffusion

We will investigate how a fluctuating environment influences measurements of an experimentally observed internal variable. Specifically we focus on the spectroscopy of a chromophore, and how the chromophore's interactions with its environment influence its transition frequency and absorption lineshape. In the absence of interactions, the resonance frequency that we observe is ω_{eg}. However, we have seen that interactions of this chromophore with its environment can shift this frequency. In condensed matter, time-dependent interactions with the surroundings can lead to time-dependent frequency shifts, known as spectral diffusion. How these dynamics influence the line width and lineshape of absorption features depends on the distribution of frequencies available to your system (Δ) and the time scale of sampling varying environments (τ_c). Consider the following cases of line broadening:

1) **Homogeneous.** Here, the absorption lineshape is *dynamically* broadened by rapid variations in the frequency or phase of dipoles. Rapid sampling of a distribution of frequencies acts to average the experimentally observed resonance frequency. The result in a "motionally narrowed" line width that is narrower than the distribution of frequencies available and proportional to the rate of fluctuation induced dephasing.
2) **Inhomogeneous.** In this limit, the lineshape reflects a *static* distribution of resonance frequencies, and the width of the line represents the distribution of frequencies, Δ, which arise, from different structural environments available to the system.
3) **Spectral Diffusion.** More generally, every system lies between these limits. Given a distribution of configurations that the system can adopt, for instance an electronic chromophore in a liquid, an equilibrium system will be ergodic, and over a long enough time any molecule will sample all configurations available to it. Under these circumstances, we expect that every molecule will have a different "instantaneous frequency" $\omega_i(t)$ which evolves in time as a result of its interactions with a dynamically evolving system. This process is known as spectral diffusion. The homogeneous and inhomogeneous limits can be described as limiting forms for the fluctuations of a frequency $\omega_i(t)$ through a distribution of frequencies Δ. If $\omega_i(t)$ evolves rapidly relative to Δ^{-1}, the system is homogeneously broadened. If $\omega_i(t)$ evolves slowly the system is inhomogeneous. This behavior can be quantified through the transition frequency time-correlation function

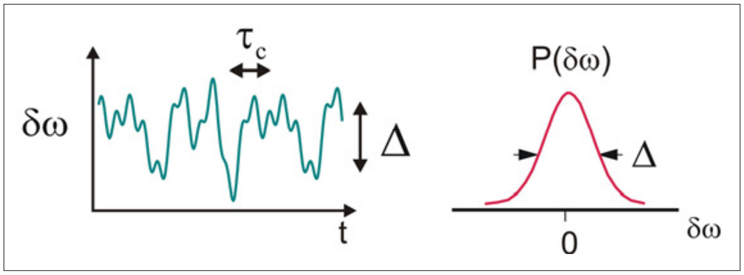
$$C_{eg}(t) = \langle \omega_{eg}(t)\,\omega_{eg}(0) \rangle \tag{13.8}$$

Our job will be to relate the transition frequency correlation function $C_{eg}(t)$ with the dipole correlation function that determines the lineshape, $C_{\mu\mu}(t)$.


Time-depedence of individual molecules
Dipole moment, μ(t)
Instantaneous frequency, ω(t)
Frequency Correlations
$C_{eg}(t)=\langle\omega_{eg}(t)\omega_{eg}(0)\rangle$
Absorption Spectrum
$\mathcal{F}\langle\mu(t)\mu(0)\rangle$
Homogeneous
$\omega_{eg}(t)$
t
$\langle\omega_{eg}^2\rangle$
τ_c
t
"Motionally Narrowed"
$\frac{1}{T_2^*}$
ω_{eg}
ω
Fluctuating frequency
$\mu(t)$
$\omega_{eg}(t)$
τ_c
t
$\langle\omega_{eg}^2\rangle$
τ_c
t
"Spectral Diffusion"
$\omega_{eg}(0)$
$\omega_{eg}(t)$
$\langle\omega_{eg}\rangle$
ω
Inhomogeneous
μ_1
μ_2
μ_3
ω_1
ω_2
ω_3
t
$\langle\omega_{eg}^2\rangle$
t
Static Distribution
Δ
$\langle\omega_{eg}\rangle$
ω

13.3. Gaussian-Stochastic Model for Spectral Diffusion

We will begin with a *classical* description of how random fluctuations in frequency influence the absorption lineshape, by calculating the dipole correlation function for the resonant transition. This is a Gaussian stochastic model for fluctuations, meaning that we will describe the time-dependence of the transition energy as *random* fluctuations about an average value through a Gaussian distribution.



$$\omega(t) = \langle\omega\rangle + \delta\omega(t) \tag{13.9}$$

$$\langle\delta\omega(t)\rangle = 0 \tag{13.10}$$

The fluctuations in ω allow the system to explore a Gaussian distribution of transitions frequencies characterized by a variance:[1]

$$\Delta = \sqrt{\langle\omega^2\rangle - \langle\omega\rangle^2} = \sqrt{\langle\delta\omega^2\rangle} \tag{13.11}$$

The time scales for the frequency shifts will be described in terms of a frequency correlation function

$$C_{\delta\omega\delta\omega}(t) = \langle\delta\omega(t)\delta\omega(0)\rangle \tag{13.12}$$

Furthermore, we will describe the time scale of the random fluctuations through a correlation time τ_c.

The absorption lineshape is described with a dipole time-correlation function. Let's treat the dipole moment as an internal variable to the system, whose value depends on that of ω. Qualitatively, it is possible to write an equation of motion for μ by associating the dipole moment with the displacement of a bound particle (x) times its charge, and using our intuition regarding how the system behaves. For a unperturbed state, we expect that x will oscillate at a frequency ω, but with perturbations, it will vary through the distribution of available frequencies. One function that has this behavior is

$$x(t) = x_0 e^{-i\omega(t)t} \tag{13.13}$$

If we differentiate this equation with respect to time and multiply by charge we have

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[1] In many figures the width of the Gaussian distribution is labeled with the standard deviation (here Δ). This is meant to symbolize that Δ is the parameter that determines the width, and not that it is the line width. For Gaussian distributions, the full line width at half maximum amplitude (FWHM) is 2.35Δ.

$$\frac{\partial \mu}{\partial t} = -i\omega(t)\,\mu(t) \tag{13.14}$$

Although it is a classical equation, note the similarity to the quantum Heisenberg equation for the dipole operator: $\partial\mu/\partial t = iH(t)\,\mu/\hbar + h.c.$ The correspondence of $\omega(t)$ with $H(t)/\hbar$ offers some insight into how the quantum version of this problem will look.

The solution to eq. (13.14) is

$$\mu(t) = \mu(0)\exp\left[-i\int_0^t d\tau\ \omega(\tau)\right] \tag{13.15}$$

Substituting this expression and eq. (13.9) into the dipole correlation function gives

or
$$C_{\mu\mu}(t) = \ |\mu|^2\ e^{-i\langle\omega\rangle t}\ F(t) \tag{13.16}$$

where
$$F(t) = \left\langle \exp\left[-i\int_0^t d\tau\,\delta\omega(\tau)\right]\right\rangle \tag{13.17}$$

The dephasing function here is obtained by performing an equilibrium average of the exponential argument over fluctuating trajectories. For ergodic systems, this is equivalent to averaging long enough over a single trajectory.

The dephasing function is a bit complicated to work with as written. However, for the case of Gaussian statistics for the fluctuations, it is possible to simplify F(t) by expanding it as a *cumulant expansion of averages* (see Appendix)

$$F(t) = \exp\left[-i\int_0^t d\tau'\left\langle\delta\omega(\tau')\right\rangle + \frac{i^2}{2!}\int_0^t d\tau'\int_0^t d\tau''\left\{\left\langle\delta\omega(\tau')\,\delta\omega(\tau'')\right\rangle - \left\langle\delta\omega(\tau')\right\rangle\left\langle\delta\omega(\tau'')\right\rangle\right\}\right] \tag{13.18}$$

In this expression, the first term is zero, since $\langle\delta\omega\rangle = 0$. Only the second term survives for a system with Gaussian statistics. Now recognizing that we have a stationary system, we have

$$F(t) = \exp\left[-\tfrac{1}{2}\int_0^t d\tau'\int_0^t d\tau''\left\langle\delta\omega(\tau'-\tau'')\,\delta\omega(0)\right\rangle\right] \tag{13.19}$$

We have rewritten the dephasing function n terms of a correlation function that describes the fluctuating energy gap. Note that this is a classical exception, so there is no time-ordering to the exponential. F(t) can be rewritten through a change of variables ($\tau = \tau' - \tau''$):

$$F(t) = \exp\left[-\int_0^t d\tau\ (t-\tau)\left\langle\delta\omega(\tau)\,\delta\omega(0)\right\rangle\right] \tag{13.20}$$

So the Gaussian stochastic model allows the influence of the frequency fluctuations on the lineshape to be described by $C_{\delta\omega\delta\omega}(t)$ a frequency correlation function that follows Gaussian statistics. Note, we are now dealing with two different correlation functions $C_{\delta\omega\delta\omega}$ and $C_{\mu\mu}$. The frequency correlation function encodes the dynamics that result from molecules interacting with the surroundings, whereas the dipole correlation function describes how the system interacts with a light field and thereby the absorption spectrum.

Now, we will calculate the lineshape assuming that $C_{\delta\omega\delta\omega}$ decays with a correlation time τ_c and takes on an exponential form

$$C_{\delta\omega\delta\omega}(t) = \Delta^2 \exp\left[-t/\tau_c\right] \tag{13.21}$$

Then eq. (13.20) gives

$$F(t) = \exp\left[-\Delta^2\tau_c^2\left(\exp(-t/\tau_c)+t/\tau_c-1\right)\right] \tag{13.22}$$

which is in the form we have seen earlier $F(t)=\exp(-g(t))$

$$g(t) = \Delta^2\tau_c^2\left(\exp(-t/\tau_c)+t/\tau_c-1\right) \tag{13.23}$$

To interpret this lineshape function, let's look at its limiting forms:

1) **Long correlation times** $(t \ll \tau_c)$. This corresponds to the inhomogeneous case where $C_{\delta\omega\delta\omega}(t) = \Delta^2$, a constant. For $t \ll \tau_c$ we can perform a short time expansion of exponential

$$e^{-t/\tau_c} \approx 1 - \frac{t}{\tau_c} + \frac{t^2}{2\tau_c^2} + \ldots \tag{13.24}$$

and from eq. (13.23) we obtain

$$g(t) = \Delta^2 t^2/2 \tag{13.25}$$

At short times, the dipole correlation function will have a Gaussian decay with a rate given by Δ^2: $F(t)=\exp(-\Delta^2 t^2/2)$. This has the proper behavior for a classical correlation function, i.e., even in time $C_{\mu\mu}(t)=C_{\mu\mu}(-t)$.

In this limit, the absorption lineshape is:

$$\begin{aligned}\sigma(\omega) &= |\mu|^2 \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, e^{-i\langle\omega\rangle t - g(t)} \\ &= |\mu|^2 \int_{-\infty}^{+\infty} dt\, e^{i(\omega-\langle\omega\rangle)t}\, e^{-\Delta^2 t^2/2} \\ &= \sqrt{\frac{2\pi}{\Delta^2}}\,|\mu|^2 \exp\left(-\frac{(\omega-\langle\omega\rangle)^2}{2\Delta^2}\right)\end{aligned} \tag{13.26}$$

We obtain a Gaussian inhomogeneous lineshape centered at the mean frequency with a width dictated by the frequency distribution.

2) **Short correlation times** $\left(t >> \tau_c\right)$. This corresponds to the homogeneous limit in which you can approximate $C_{\delta\omega\delta\omega}\left(t\right) = \Delta^2\delta\left(t\right)$. For $t >> \tau_c$ we set $e^{-t/\tau_c} \approx 0$, $t/\tau_c >> 1$ and eq. (13.23) gives

$$g\left(t\right) = -\Delta^2\tau_c\ t \tag{13.27}$$

If we define the constant

$$\Delta^2\tau_c \equiv \Gamma \tag{13.28}$$

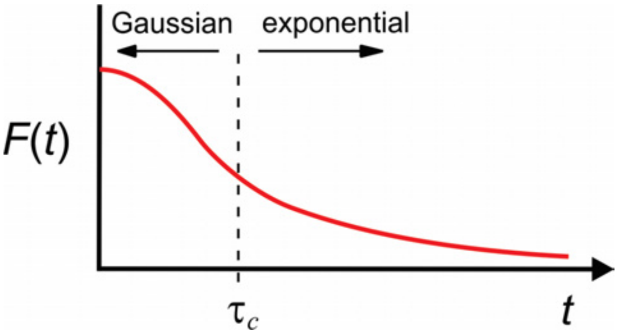
we see that the dephasing function has an exponential decay:

$$F\left(t\right) = \exp\left[-\Gamma t\right] \tag{13.29}$$

The lineshape for short correlation times (or fast fluctuations) takes on a Lorentzian shape

$$\begin{aligned} \sigma\left(\omega\right) &= \left|\mu\right|^2 \int_{-\infty}^{+\infty} dt\, e^{i\left(\omega - \langle\omega\rangle\right)t}\ e^{-\Gamma t} \\ \operatorname{Re}\sigma\left(\omega\right) &= \left|\mu\right|^2 \frac{\Gamma}{\left(\omega - \langle\omega\rangle\right)^2 + \Gamma^2} \end{aligned} \tag{13.30}$$

This represents the homogeneous limit. Even with a broad distribution of accessible frequencies, if the system explores all of these frequencies on a time scale fast compared to the inverse of the distribution ($\Delta\ \tau_c > 1$), then the resonance will be "motionally narrowed" into a Lorentzian line.

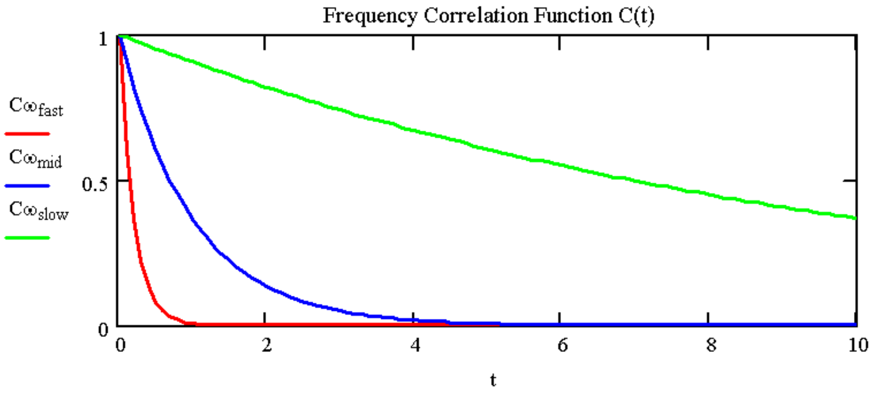


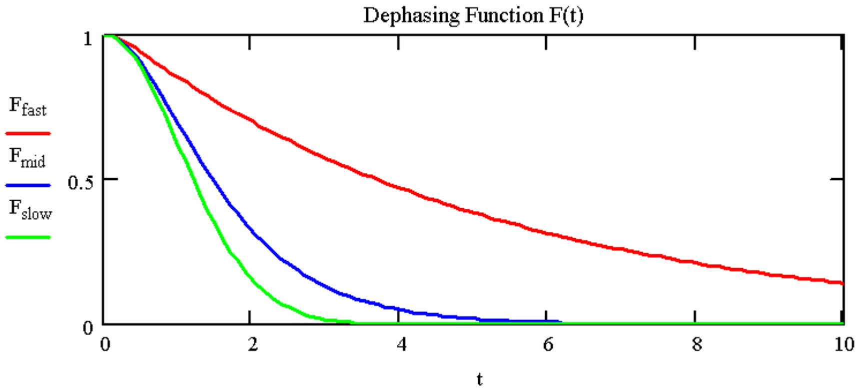
More generally, the envelope of the dipole correlation function will look Gaussian at short times and exponential at long times. The correlation time is the separation between these regimes. The behavior for varying time scales of the dynamics (τ_c) are best characterized with respect to the distribution of accessible frequencies (Δ). So we can define a factor

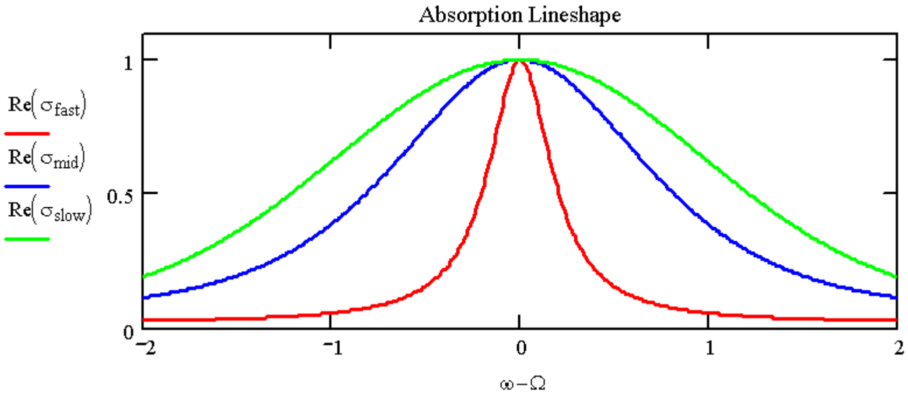
$$\kappa = \Delta \cdot \tau_c \tag{13.31}$$

$\kappa << 1$ is the fast modulation limit and $\kappa >> 1$ is the slow modulation limit. Let's look at how $C_{\delta\omega\delta\omega}$, $F\left(t\right)$, and $\sigma_{abs}\left(\omega\right)$ change as a function of κ.

$$\Delta = 1 \qquad \tau_c = \begin{pmatrix} 0.2 \\ 1 \\ 10 \end{pmatrix} \qquad \kappa = \begin{pmatrix} 0.2 \\ 1 \\ 10 \end{pmatrix} \quad \begin{matrix} \text{fast} \\ \text{mid} \\ \text{slow} \end{matrix}$$


Frequency Correlation Function C(t)


Dephasing Function F(t)

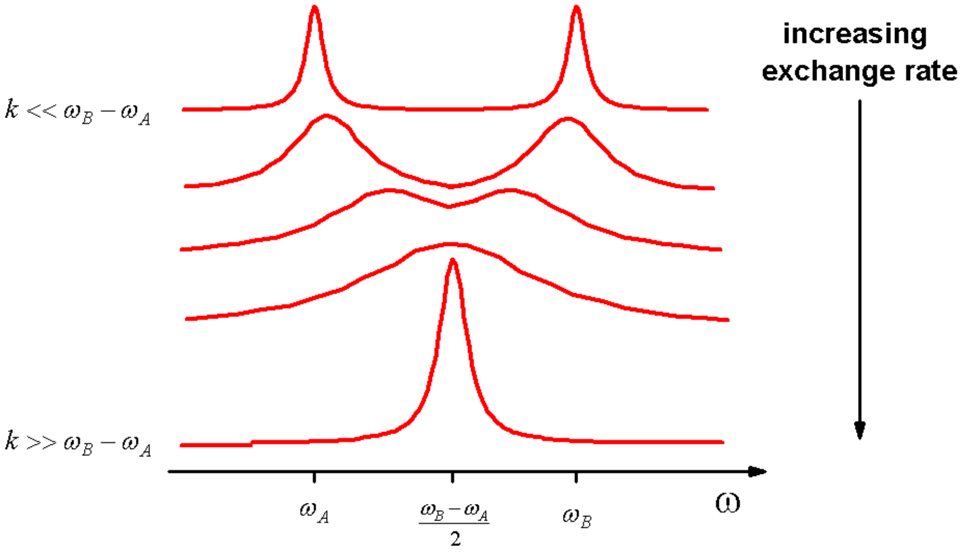

Absorption Lineshape

We see that for a fixed distribution of frequencies Δ the effect of increasing the time scale of fluctuations through this distribution (decreasing τ_c) is to gradually narrow the observed lineshape from a Gaussian distribution of static frequencies with width (FWHM) of 2.35·Δ to a motionally narrowed Lorentzian lineshape with width (FWHM) of $\Delta^2\tau_c/\pi = \Delta\cdot\kappa/\pi$.

This is analogous to the motional narrowing effect first described in the case of temperature dependent NMR spectra of two exchanging species. Assume we have two resonances at ω_A and ω_B associated with two chemical species that are exchanging at a rate k_{AB}

$$A \underset{k_{BA}}{\overset{k_{AB}}{\rightleftarrows}} B$$

If the rate of exchange is slow relative to the frequency splitting, $k_{AB} \ll \omega_A - \omega_B$, then we expect two resonances, each with a linewidth dictated by the molecular relaxation processes (T_2) and transfer rate of each species. On the other hand, when the rate of exchange between the two species becomes faster than the energy splitting, then the two resonances narrow together to form one resonance at the mean frequency.[2]



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[2] Anderson, P. W. A mathematical model for the narrowing of spectral lines by exchange or motion. *J. Phys. Soc. Japan* **9**, 316 (1954).; Kubo, R. in *Fluctuation, Relaxation, and Resonance in Magnetic Systems* (ed. Ter Haar, D.) (Oliver and Boyd, London, 1962).

Appendix: The Cumulant Expansion

For a statistical description of the random variable *x*, we wish to characterize the moments of *x*: $\langle x \rangle, \langle x^2 \rangle, \ldots$ Then the average of an exponential of *x* can be expressed as an expansion in moments

$$\langle e^{ikx} \rangle = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle \tag{13.31}$$

An alternate way of expressing this expansion is in terms of cumulants $c_n(x)$

$$\langle e^{ikx} \rangle = \exp\left(\sum_{n=1}^{\infty} \frac{(ik)^n}{n!} c_n(x) \right) \tag{13.32}$$

where the first few cumulants are:

$$c_1(x) = \langle x \rangle \qquad \textit{mean} \tag{13.33}$$

$$c_2(x) = \langle x^2 \rangle - \langle x \rangle^2 \qquad \textit{variance} \tag{13.34}$$

$$c_3(x) = \langle x^3 \rangle - 3\langle x \rangle \langle x^2 \rangle + 2\langle x \rangle^3 \qquad \textit{skewness} \tag{13.35}$$

An expansion in cumulants converges much more rapidly than an expansion in moments, particularly when you consider that *x* may be a time-dependent variable. Particularly useful is the observation that all cumulants with $n > 2$ vanish for a system that obeys Gaussian statistics.

We obtain the cumulants above by expanding eq. (13.31) and (13.32), and comparing terms in powers of *x*. We start by postulating that, instead of expanding the exponential directly, we can instead expand the exponential argument in powers of an operator or variable *H*

$$F = \exp[c] = 1 + c + \tfrac{1}{2}c^2 + \cdots \tag{13.36}$$

$$c = c_1 H + \tfrac{1}{2} c_2 H^2 + \cdots \tag{13.37}$$

Inserting eq. (13.37) into eq. (13.36) and collecting terms in orders of *H* gives

$$\begin{aligned} F &= 1 + \left(c_1 H + \tfrac{1}{2}c_2 H^2 + \cdots\right) + \tfrac{1}{2}\left(c_1 H + \tfrac{1}{2} c_2 H^2 + \cdots\right)^2 + \cdots \\ &= 1 + (c_1) H + \tfrac{1}{2}\left(c_2 + c_1^2\right) H^2 + \cdots \end{aligned} \tag{13.38}$$

Now comparing this with the expansion of the exponential

$$\begin{aligned} F &= \exp[fH] \\ &= 1 + f_1 H + \tfrac{1}{2} f_2 H^2 + \cdots \end{aligned} \tag{13.39}$$

allows one to see that

$$\begin{aligned} c_1 &= f_1 \\ c_2 &= f_2 - f_1^2 \end{aligned} \tag{13.40}$$

The cumulant expansion can also be applied to time-correlations. Applying this to the time-ordered exponential operator we obtain:

$$\begin{aligned} F(t) &= \left\langle \exp_+ \left[-i \int_0^t dt\, \omega(t) \right] \right\rangle \\ &\approx \exp\left[c_1(t) + c_2(t) \right] \end{aligned} \tag{13.41}$$

$$c_1 = -i \int_0^t d\tau \left\langle \omega(\tau) \right\rangle \tag{13.42}$$

$$\begin{aligned} c_2 &= -\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \left\{ \left\langle \omega(\tau_2)\, \omega(\tau_1) \right\rangle - \left\langle \omega(\tau_2) \right\rangle \left\langle \omega(\tau_1) \right\rangle \right\} \\ &= -\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \left\langle \delta\omega(\tau_2)\, \delta\omega(\tau_1) \right\rangle \end{aligned} \tag{13.43}$$

For Gaussian statistics, all higher cumulants vanish.

Readings

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13.4. The Energy Gap Hamiltonian

Introduction

In describing fluctuations in a quantum mechanical system, we describe how an experimental observable is influenced by its interactions with a thermally agitated environment. For this, we work with the specific example of an electronic absorption spectrum and return to the Displaced Harmonic Oscillator model. We previously described this model in terms of the eigenstates of the material Hamiltonian H_0, and interpreted the dipole correlation function and resulting lineshape in terms of the overlap between two wave packets evolving on the ground and excited surfaces $|E\rangle$ and $|G\rangle$.

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 \, e^{-i(E_e - E_g)t/\hbar} \langle \varphi_g(t) | \varphi_e(t) \rangle \tag{13.43}$$

It is worth noting a similarity between the DHO Hamiltonian, and a general form for the interaction of an electronic two-level "system" with a harmonic oscillator "bath" whose degrees of freedom are dark to the observation, but which influence the behavior of the system.

Expressed in a slightly different physical picture, we can also conceive of this process as nuclear motions that act to modulate the electronic energy gap ω_{eg}. We can imagine rewriting the same Hamiltonian in a form with a new physical picture that describes the electronic energy gap's dependence on q, i.e., its variation relative to ω_{eg}. If we define an Energy Gap Hamiltonian:

$$H_{eg} = H_e - H_g \tag{13.43}$$

we can rewrite the DHO Hamiltonian

$$H_0 = |e\rangle E_e \langle e| + |g\rangle E_g \langle g| + H_e + H_g \tag{13.44}$$

as an electronic transition linearly coupled to a harmonic oscillator:

$$H_0 = |e\rangle E_e \langle e| + |g\rangle E_g \langle g| + H_{eg} + 2H_g \tag{13.44}$$

Noting that

$$H_g = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 \tag{13.44}$$

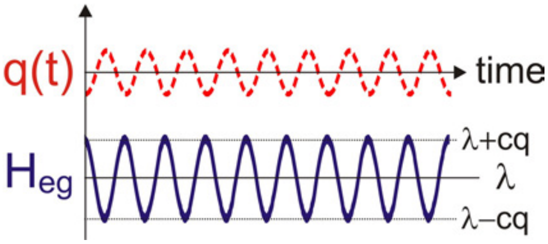
we can write this as a system-bath Hamiltonian:

$$H_0 = H_S + H_B + H_{SB} \tag{13.44}$$

where H_{SB} describes the interaction of the electronic system (H_S) with the vibrational bath (H_B). Here $H_S = |e\rangle E_e \langle e| + |g\rangle E_g \langle g|$, $H_B = 2H_g$ and

$$\begin{aligned} H_{SB} = H_{eg} &= \frac{1}{2} m\omega_0^2 \left(q-d\right)^2 - \frac{1}{2} m\omega_0^2\, q^2 \\ &= -m\omega_0^2\, d\, q + \frac{1}{2} m\omega_0^2\, d^2 \\ &= -c\, q + \lambda \end{aligned} \tag{13.44}$$

The Energy Gap Hamiltonian describes a linear coupling between the electronic transition and a harmonic oscillator. The strength of the coupling is *c* and the Hamiltonian has a constant energy offset value given by the reorganization energy. Any motion in the bath coordinate q introduces a proportional change in the electronic energy gap.



In an alternate form, the Energy Gap Hamiltonian can also be written to incorporate the reorganization energy into the system:

$$\begin{aligned} H_0 &= H'_S + H'_B + H'_{SB} \\ H'_S &= |e\rangle \left(E_e + \lambda\right) \langle e| + |g\rangle E_g \langle g| \\ H'_B &= \frac{p^2}{2m} + \frac{1}{2} m\omega_0^2\, q^2 \\ H'_{SB} &= -\, m\omega_0^2\, d\;\; q \end{aligned} \tag{13.44}$$

This formulation describes fluctuations about the average value of the energy gap $\hbar\omega_{eg}+\lambda$, however, the observables calculated are the same.

From the picture of a modulated energy gap one can begin to see how random fluctuations can be treated by coupling to a harmonic bath. If each oscillator modulates the energy gap at a given frequency, and the phase between oscillators is random as a result of their independence, then time-domain fluctuations and dephasing can be cast in terms of a Fourier spectrum of couplings to oscillators with continuously varying frequency.

Energy Gap Hamiltonian

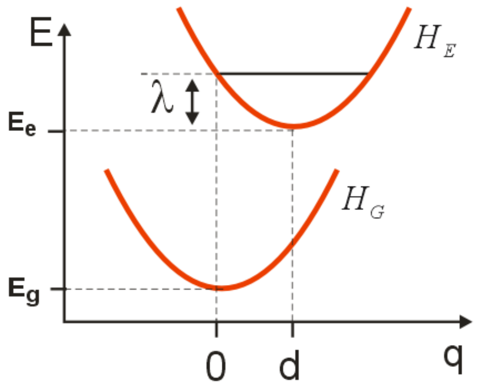
Now let's work through the description of electronic spectroscopy with the Energy Gap Hamiltonian more carefully. Working from eqs. (13.43) and (13.44) we express the energy gap Hamiltonian through reduced coordinates for the momentum, coordinate, and displacement of the oscillator

$$\underset{\sim}{p} = \hat{p}\,(2\hbar\omega_0 m)^{-1/2} \tag{13.45}$$

$$\underset{\sim}{q} = \hat{q}\,(m\omega_0/2\hbar)^{1/2} \tag{13.46}$$

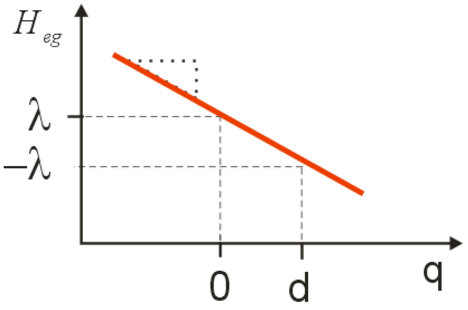
$$\underset{\sim}{d} = d\,(m\omega_0/2\hbar)^{1/2} \tag{13.47}$$

$$\begin{aligned} H_e &= \hbar\omega_0\left(\underset{\sim}{p}^2 + \left(\underset{\sim}{q} - \underset{\sim}{d}\right)^2\right) \\ H_g &= \hbar\omega_0\left(\underset{\sim}{p}^2 + \underset{\sim}{q}^2\right) \end{aligned} \tag{13.48}$$



From eq. (13.43) we have

$$\begin{aligned} H_{eg} &= -2\hbar\omega_0 \underset{\sim}{d}\,\underset{\sim}{q} + \hbar\omega_0 \underset{\sim}{d}^2 \\ &= -m\omega_0^2 d\, q + \lambda \end{aligned} \tag{13.49}$$



The energy gap Hamiltonian describes a linear coupling of the electronic system to the coordinate *q*. The slope of H_{eg} versus *q* is the coupling strength, and the average value of H_{eg} in the ground state, $H_{eg}(q=0)$, is offset by the reorganization energy λ. We note that the average value of the energy gap Hamiltonian is $\langle H_{eg}\rangle = \lambda$.

To obtain the absorption lineshape from the dipole correlation function

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t}\,F(t) \tag{13.50}$$

we must evaluate the dephasing function.

$$F(t) = \left\langle e^{iH_g t}\,e^{-iH_e t}\right\rangle = \left\langle U_g^\dagger U_e\right\rangle \tag{13.51}$$

We want to rewrite the dephasing function in terms of the time dependence to the energy gap H_{eg}; that is, if $F(t) = \left\langle U_{eg}\right\rangle$, then what is U_{eg}? This involves a unitary transformation of the dynamics to a new frame of reference. The transformation from the DHO Hamiltonian to the EG Hamiltonian is similar to our derivation of the interaction picture.

Transformation of time-propagators

If we have a time dependent quantity of the form

$$e^{iH_A t}\,A\,e^{-iH_B t} \tag{13.52}$$

we can also express the dynamics through the difference Hamiltonian $H_{BA}=H_B-H_A$

$$A\,e^{-i(H_B-H_A)t}=A\,e^{-iH_{BA}t} \tag{13.53}$$

using a commonly performed unitary transformation. If we write

$$H_B=H_A+H_{BA} \tag{13.54}$$

we can use the same procedure for partitioning the dynamics in the interaction picture to write

$$e^{-iH_B t}=e^{-iH_A t}\exp_+\left[-\frac{i}{\hbar}\int_0^t d\tau\,H_{BA}(\tau)\right] \tag{13.55}$$

where

$$H_{BA}(\tau)=e^{iH_A t}\,H_{BA}\,e^{-iH_A t} \tag{13.56}$$

Then, we can also write:

$$e^{iH_A t}e^{-iH_B t}=\exp_+\left[-\frac{i}{\hbar}\int_0^t d\tau\,H_{BA}(\tau)\right] \tag{13.57}$$

Noting the mapping to the interaction picture

$$H_e=H_g+H_{eg} \qquad \Leftrightarrow \qquad H=H_0+V \tag{13.58}$$

we see that we can represent the time dependence of the electronic energy gap H_{eg} using

$$\begin{aligned} e^{-iH_e t/\hbar}&=e^{-iH_g t/\hbar}\exp_+\left[\frac{-i}{\hbar}\int_0^t d\tau\,H_{eg}(\tau)\right] \\ U_e&=U_g U_{eg} \end{aligned} \tag{13.59}$$

where

$$\begin{aligned} H_{eg}(t)&=e^{iH_g t/\hbar}\,H_{eg}\,e^{-iH_g t/\hbar} \\ &=U_g^\dagger H_{eg} U_g \end{aligned} \tag{13.60}$$

Remembering the equivalence between the harmonic mode H_g and the bath mode(s) H_B indicates that the time dependence of the EG Hamiltonian reflects how the electronic energy gap is modulated as a result of the interactions with the bath. That is $U_g \Leftrightarrow U_B$.

Equation (13.59) immediately implies that

$$F(t)=\left\langle e^{iH_g t/\hbar}e^{-iH_e t/\hbar}\right\rangle=\left\langle \exp_+\left[\frac{-i}{\hbar}\int_0^t d\tau\, H_{eg}(\tau)\right]\right\rangle \tag{13.61}$$

Now the quantum dephasing function is in the same form as we saw in our earlier classical derivation. Using the second-order cumulant expansion allows the dephasing function to be written as

$$\begin{aligned}F(t)=\exp\Bigg[&\frac{-i}{\hbar}\int_0^t d\tau\left\langle H_{eg}(\tau)\right\rangle\\&+\left(\frac{-i}{\hbar}\right)^2\int_0^t d\tau_2\int_0^{\tau_2}d\tau_1\left\langle H_{eg}(\tau_2)H_{eg}(\tau_1)\right\rangle-\left\langle H_{eg}(\tau_2)\right\rangle\left\langle H_{eg}(\tau_1)\right\rangle\Bigg]\end{aligned} \tag{13.62}$$

Note that the cumulant expansion is here written as a time-ordered expansion. The first exponential term depends on the mean value of H_{eg}

$$\left\langle H_{eg}\right\rangle=\hbar\omega_0 \underset{\sim}{d}^2=\lambda \tag{13.63}$$

This is a result of how we defined H_{eg}. Alternatively, the EG Hamiltonian could have been defined relative to the energy gap at $Q=0$: $H_{eg}=H_e-H_g+\lambda$. In this case the leading term in (13.62) would be zero, and the mean energy gap that describes the high frequency (system) oscillation in the dipole correlation function is $\omega_{eg}+\lambda$.

The second exponential term in (13.62) is a correlation function that describes the time dependence of the energy gap

$$\begin{aligned}&\left\langle H_{eg}(\tau_2)H_{eg}(\tau_1)\right\rangle-\left\langle H_{eg}(\tau_2)\right\rangle\left\langle H_{eg}(\tau_1)\right\rangle\\&=\left\langle \delta H_{eg}(\tau_2)\delta H_{eg}(\tau_1)\right\rangle\end{aligned} \tag{13.64}$$

where

$$\begin{aligned}\delta H_{eg}&=H_{eg}-\left\langle H_{eg}\right\rangle\\&=-m\omega_0^2 d\, q\end{aligned} \tag{13.65}$$

Defining the time-dependent energy gap transition frequency in terms of the EG Hamiltonian as

$$\delta\hat{\omega}_{eg}\equiv\frac{\delta H_{eg}}{\hbar} \tag{13.66}$$

we can write the energy gap correlation function

$$C_{eg}(\tau_2,\tau_1)=\left\langle \delta\hat{\omega}_{eg}(\tau_2-\tau_1)\delta\hat{\omega}_{eg}(0)\right\rangle \tag{13.67}$$

It follows that

$$F(t)=e^{-i\lambda t/\hbar}e^{-g(t)} \tag{13.68}$$

$$g(t)=\int_0^t d\tau_2\int_0^{\tau_2}d\tau_1\, C_{eg}(\tau_2,\tau_1) \tag{13.69}$$

and the dipole correlation function can be expressed as

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\left(E_e - E_g + \lambda\right)t/\hbar} e^{-g(t)} \tag{13.70}$$

This is the correlation function expression that determines the absorption lineshape for a time-dependent energy gap. It is a general expression at this point, for all forms of the energy gap correlation function. The only approximation made for the bath is the second cumulant expansion.

Now, let's look specifically at the case where the bath we are coupled to is a single harmonic mode. The energy gap correlation function is evaluated from

$$\begin{aligned} C_{eg}(t) &= \sum_n p_n \left\langle n \middle| \delta\hat{\omega}_{eg}(t)\,\delta\hat{\omega}_{eg}(0) \middle| n \right\rangle \\ &= \frac{1}{\hbar^2} \sum_n p_n \left\langle n \middle| e^{iH_g t/\hbar}\, \delta H_{eg}\, e^{-iH_g t/\hbar}\, \delta H_{eg} \middle| n \right\rangle \end{aligned} \tag{13.71}$$

Noting that the bath oscillator correlation function

$$C_{qq}(t) = \left\langle q(t) q(0) \right\rangle = \frac{\hbar}{2m\omega_0}\left[\left(\bar{n}+1\right)e^{-i\omega_0 t} + \bar{n}\, e^{i\omega_0 t}\right] \tag{13.72}$$

we find

$$C_{eg}(t) = \omega_0^2\, D\left[\left(\bar{n}+1\right)e^{-i\omega_0 t} + \bar{n}\, e^{i\omega_0 t}\right] \tag{13.73}$$

Here, as before, $D = d^2\left(m\,\omega_0/2\hbar\right)$, $\bar{n}$ is the thermally averaged occupation number for the oscillator

$$\bar{n} = \sum\nolimits_n p_n \left\langle n \middle| a^\dagger a \middle| n \right\rangle = \left(e^{\beta\hbar\omega_0} - 1\right)^{-1} \tag{13.74}$$

and β = 1/k

$\beta = 1/k_B T$. Note that the energy gap correlation function is a complex function. We can separate the real and imaginary parts of C_{eg} as

$$C_{eg}(t) = C_{eg}{}' + iC_{eg}{}'' \tag{13.75}$$

$$\begin{aligned} C'_{eg}(t) &= \omega_0^2\, D \coth\left(\beta\hbar\omega_0/2\right)\cos\left(\omega_0 t\right) \\ C''_{eg}(t) &= \omega_0^2\, D \sin\left(\omega_0 t\right) \end{aligned} \tag{13.76}$$

where we have made use of the relation

$$2\bar{n}(\omega) + 1 = \coth\left(\beta\hbar\omega/2\right) \tag{13.77}$$

and $\coth(x) = \left(e^x + e^{-x}\right)/\left(e^x - e^{-x}\right)$. We see that the imaginary part of the energy gap correlation function is temperature independent. The real part has the same amplitude at T=0, and rises with temperature. We can analyze the high and low temperature limits of this expression from

$$\lim_{x\to\infty} \coth(x) = 1$$
$$\lim_{x\to 0} \coth(x) \approx \frac{1}{x} \tag{13.78}$$

Looking at the low temperature limit, $\coth(\beta\hbar\omega_0/2) \to 1$ and $\bar{n} \to 0$, we see that eq. (13.82) reduces to eq. (13.84). In the high temperature limit, $kT >> \hbar\omega_0$, $\coth(\hbar\omega_0/2kT) \to 2kT/\hbar\omega_0$, and we recover the expected classical result. The magnitude of the real component dominates the imaginary part $\left|C_{eg}{}'\right| >> \left|C_{eg}{}''\right|$, and the energy gap correlation function $C_{eg}(t)$ becomes real and even in time.

Similarly, we can evaluate (13.69), the lineshape function

$$g(t) = -D\left[(\bar{n}+1)\left(e^{-i\omega_0 t}-1\right)+\bar{n}\left(e^{i\omega_0 t}-1\right)\right]-iD\omega_0 t \tag{13.79}$$

The leading term in eq. (13.79) gives us a vibrational progression, the second term leads to hot bands, and the final term is the reorganization energy ($-iD\omega_0 t = -i\lambda t/\hbar$). The lineshape function can be written in terms of its real and imaginary parts

$$g(t) = g' + ig'' \tag{13.80}$$

$$g'(t) = D\coth(\beta\hbar\omega_0/2)(1-\cos\omega_0 t)$$
$$g''(t) = D(\sin\omega_0 t - \omega_0 t) \tag{13.81}$$

Because these enter into the dipole correlation function as exponential arguments, the imaginary part of g(t) will reflect the bath-induced energy shift of the electronic transition gap and vibronic structure, and the real part will reflect damping, and therefore the broadening of the lineshape. Similarly to $C_{eg}(t)$, in the high temperature limit $g' >> g''$.

Now, using eq. (13.68), we see that the dephasing function is given by

$$F(t) = \exp\left[D\left((\bar{n}+1)\left(e^{-i\omega_0 t}-1\right)+\bar{n}\left(e^{i\omega_0 t}-1\right)\right)\right]. \tag{13.82}$$

$$= \exp\left[D\left(\coth\left(\frac{\beta\hbar\omega}{2}\right)(1-\cos\omega t)+i\sin\omega t\right)\right] \tag{13.83}$$

Let's confirm that we get the same result as with our original DHO model, when we take the low temperature limit. Setting $\bar{n} \to 0$ in (13.83), we have our original result

$$F_{kT=0}(t) = \exp\left[D\left(e^{-i\omega_0 t}-1\right)\right] \tag{13.84}$$

In the high temperature limit $g' >> g''$, and from eq. (13.78) we obtain

$$
\begin{aligned}
F(t) &= \exp\left[\frac{2DkT}{\hbar\omega_0}\cos(\omega_0 t)\right] \\
&= \sum_{j=0}^{\infty}\frac{1}{j!}\left(\frac{2DkT}{\hbar\omega_0}\right)^j \cos^j(\omega_0 t)
\end{aligned}
\tag{13.85}
$$

which leads to an absorption spectrum which is a series of sidebands equally spaced on either side of ω_{eg}.

Spectral representation of energy gap correlation function

Since time- and frequency-domain representations are complementary, and one form may be preferable over another, it is possible to express the frequency correlation function in terms of its spectrum. For a complex spectrum of vibrational motions composed of many modes, representing the nuclear motions in terms of a spectrum rather than a beat pattern is often easier. It turns out that calculation are often easier performed in the frequency domain.

To start we define a Fourier transform pair that relates the time and frequency domain representations:

$$\tilde{C}_{eg}(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t}\, C_{eg}(t)\, dt \tag{13.86}$$

$$C_{eg}(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-i\omega t}\, \tilde{C}_{eg}(\omega)\, d\omega \tag{13.87}$$

Since the energy gap correlation function has the property $C_{eg}(-t) = C_{eg}^{\;*}(t)$, it also follows from (13.86) that the energy gap correlation *spectrum* is entirely real:

$$\tilde{C}_{eg}(\omega) = 2\,\mathrm{Re}\int_{0}^{\infty} e^{i\omega t}\, C_{eg}(t)\, dt \tag{13.88}$$

or

$$\tilde{C}_{eg}(\omega) = \tilde{C}'_{eg}(\omega) + \tilde{C}''_{eg}(\omega) \tag{13.89}$$

Here $\tilde{C}'_{eg}(\omega)$ and $\tilde{C}''_{eg}(\omega)$ are the Fourier transforms of the real and imaginary components of $C_{eg}(t)$, respectively. $\tilde{C}'_{eg}(\omega)$ and $\tilde{C}''_{eg}(\omega)$ are even and odd in frequency. Thus while $\tilde{C}_{eg}(\omega)$ is entirely real valued, it is asymmetric about ω=0.

With these definitions in hand, we can write the spectrum of the energy gap correlation function for coupling to a single harmonic mode spectrum (eq. (13.71)):

$$\tilde{C}_{eg}(\omega_\alpha) = \omega_\alpha^2 D(\omega_\alpha)\left[(\overline{n}_\alpha + 1)\,\delta(\omega - \omega_\alpha) + \overline{n}_\alpha\,\delta(\omega + \omega_\alpha)\right] \tag{13.90}$$

This is a spectrum that characterizes how bath vibrational modes of a certain frequency and thermal occupation act to modify the observed energy of the system. The first and second terms in (13.90) describe upward and downward energy shifts of the system, respectively. Coupling to a vibration typically leads to an upshift of the energy gap transition energy since energy must be put into the system and bath. However, as with hot bands, when there is thermal energy available in the bath, it also allows for down-shifts in the energy gap. The net balance of upward and downward shifts averaged over the bath follows the detailed balance expression

$$\tilde{C}(-\omega)=e^{-\beta\hbar\omega}\tilde{C}(\omega) \tag{13.91}$$

The balance of rates tends toward equal with increasing temperature. Fourier transforms of eqs. (13.76) gives two other representations of the energy gap spectrum

$$\tilde{C}'_{eg}(\omega_\alpha)=\omega_\alpha^2 D(\omega_\alpha)\coth(\beta\hbar\omega_\alpha/2)\left[\delta(\omega-\omega_\alpha)+\delta(\omega+\omega_\alpha)\right] \tag{13.92}$$

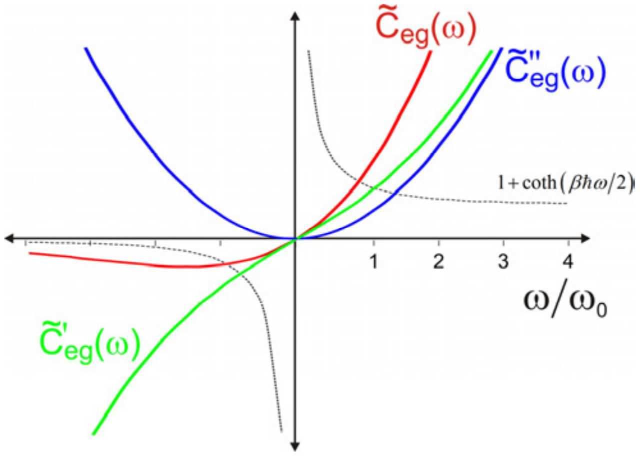
$$\tilde{C}''_{eg}(\omega_\alpha)=\omega_\alpha^2 D(\omega_\alpha)\left[\delta(\omega-\omega_\alpha)+\delta(\omega+\omega_\alpha)\right]. \tag{13.93}$$

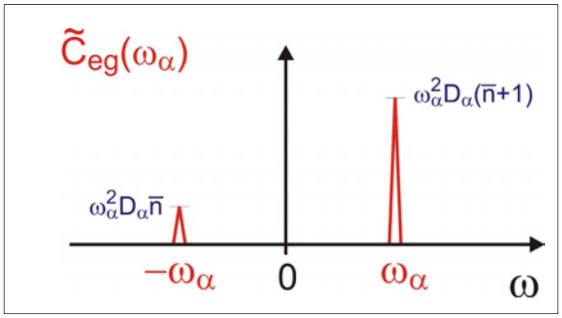
The representations in eqs. (13.90), (13.92), and (13.93) are not independent, but can be related to one another through

$$\tilde{C}'_{eg}(\omega_\alpha)=\coth(\beta\hbar\omega_\alpha/2)\tilde{C}''_{eg}(\omega_\alpha) \tag{13.94}$$

$$\tilde{C}_{eg}(\omega_\alpha)=\left(1+\coth(\beta\hbar\omega_\alpha/2)\right)\tilde{C}''_{eg}(\omega_\alpha) \tag{13.95}$$

That is, given either the real or imaginary part of the energy gap correlation spectrum, we can predict the other part. As we will see, this relationship is one manifestation of the fluctuation-dissipation theorem that we address later. Due to its independence on temperature, the spectral density $\tilde{C}''_{eg}(\omega_\alpha)$ is the commonly used representation.





Also from eqs. (13.69) and (13.87) we obtain the lineshape function as

$$\begin{aligned} g(t) &= \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi} \frac{\tilde{C}_{eg}(\omega)}{\omega^2} \left[\exp(-i\omega t) + i\omega t - 1 \right] \\ &= \int_0^{\infty} d\omega \frac{\tilde{C}''_{eg}(\omega)}{\pi\omega^2} \left[\coth\left(\frac{\beta\hbar\omega}{2} \right) (1 - \cos\omega t) + i(\sin\omega t - \omega t) \right] \end{aligned} . \tag{13.96}$$

The first expression relates $g(t)$ to the complex energy gap correlation function, whereas the second separates the real and the imaginary parts and relates them to the imaginary part of the energy gap correlation function.

Coupling to a Harmonic Bath

More generally for condensed phase problems, the system coordinates that we observe in an experiment will interact with a continuum of nuclear motions that may reflect molecular vibrations, phonons, or intermolecular interactions. We describe this continuum as continuous distribution of harmonic oscillators of varying mode frequency and coupling strength. The Energy Gap Hamiltonian is readily generalized to the case of a continuous distribution of motions if we statistically characterize the density of states and the strength of interaction between the system and this bath. This method is also referred to as the Spin-Boson Model used for treating a two-level spin-½ system interacting with a quantum harmonic bath.

Following our earlier discussion of the DHO model, the generalization of the EG Hamiltonian to the multimode case is

$$H_0 = \hbar\omega_{eg} + H_{eg} + H_B \tag{13.97}$$

$$H_B = \sum_\alpha \hbar\omega_\alpha \left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{q}_\alpha^2 \right) \tag{13.98}$$

$$H_{eg} = \sum_\alpha 2\hbar\omega_\alpha \underset{\sim}{d}_\alpha \underset{\sim}{q}_\alpha + \lambda \tag{13.99}$$

$$\lambda = \sum_\alpha \hbar\omega_\alpha \underset{\sim}{d}_\alpha^2 \tag{13.100}$$

Note that the time-dependence to H_{eg} results from the interaction with the bath:

$$H_{eg}(t) = e^{iH_B t/\hbar} H_{eg} e^{-iH_B t/\hbar} \tag{13.101}$$

Also, since the harmonic modes are normal to one another, the dephasing function and lineshape function are obtained from

$$F(t) = \prod_\alpha F_\alpha(t) \qquad g(t) = \sum_\alpha g_\alpha(t) \tag{13.102}$$

For a continuum, we assume that the number of modes are so numerous as to be continuous, and that the sums in the equations above can be replaced by integrals over a continuous distribution of states characterized by a density of states $W(\omega)$. Also the interaction with modes of a particular frequency are equal so that we can simply average over a frequency dependent coupling constant $D(\omega) = \underset{\sim}{d}^2(\omega)$. For instance, eq. (13.102) becomes

$$g(t) = \int d\omega_\alpha \, W(\omega_\alpha) \, g(t,\omega_\alpha) \tag{13.103}$$

Coupling to a continuum leads to dephasing resulting from interaction to a continuum of modes of varying frequency. This will be characterized by damping of the energy gap frequency correlation function $C_{eg}(t)$

$$C_{eg}(t) = \int d\omega_\alpha \, C_{eg}(\omega_\alpha, t) W(\omega_\alpha). \tag{13.104}$$

Here $C_{eg}(\omega_\alpha, t) = \langle \delta\omega_{eg}(\omega_\alpha, t) \delta\omega_{eg}(\omega_\alpha, 0) \rangle$ refers to the energy gap frequency correlation function for a single harmonic mode given in eq. (13.71).

While eq. (13.104) expresses the modulation of the energy gap in the time domain, we can alternatively express the continuous distribution of coupled bath modes in the frequency domain:

$$\tilde{C}_{eg}(\omega) = \int d\omega_\alpha \, W(\omega_\alpha) \tilde{C}_{eg}(\omega_\alpha). \tag{13.105}$$

An integral of a single harmonic mode spectrum over a continuous density of states provides a coupling weighted density of states that reflects the action spectrum for the system-bath interaction. We evaluate this with the single harmonic mode spectrum, eq. (13.90). We see that the spectrum of the correlation function for positive frequencies is related to the product of the density of states and the frequency dependent coupling

$$\tilde{C}_{eg}(\omega) = \omega^2 D(\omega) W(\omega) (\bar{n} + 1) \qquad (\omega > 0) \tag{13.106}$$

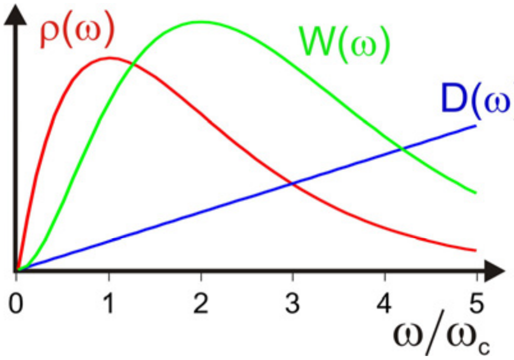
$$\tilde{C}_{eg}(\omega) = \omega^2 D(\omega) W(\omega) \bar{n} \qquad (\omega < 0) \tag{13.107}$$

This is an action spectrum that reflects the coupling weighted density of states of the bath that contributes to the spectrum.

In practice, the unusually symmetry of $\tilde{C}_{eg}(\omega)$ and its growth as ω^2 make it difficult to work with. Therefore we choose to express the frequency domain representation of the coupling-weighted density of states in eq. (13.106) as a *spectral density*, defined as

$$\begin{aligned}\rho(\omega) &\equiv \frac{\tilde{C}''_{eg}(\omega)}{\pi\omega^2} \\ &= \frac{1}{\pi}\int d\omega_\alpha\, W(\omega_\alpha) D(\omega_\alpha)\delta(\omega-\omega_\alpha) \\ &= \frac{1}{\pi} W(\omega) D(\omega)\end{aligned} \tag{13.108}$$

This expression is real and defined only for positive frequencies. Note $\tilde{C}''_{eg}(\omega)$ is an odd function in ω, and therefore ρ(ω) is also.



Example of spectral density using an ohmic density of states, $W(\omega)=\omega\exp[-\omega/\omega_C]$ and a linearly varying frequency dependent coupling.

The reorganization energy can be obtained from the first moment of the spectral density

$$\lambda = \hbar\int_0^\infty d\omega\ \omega\ \rho(\omega) \tag{13.109}$$

Furthermore, from eqs. (13.69) and (13.105) we obtain the lineshape function in two forms

$$\begin{aligned}g(t) &= \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi}\frac{\tilde{C}_{eg}(\omega)}{\omega^2}\left[\exp(-i\omega t)+i\omega t-1\right] \\ &= -\frac{i\lambda t}{\hbar}+\int_0^\infty d\omega\ \rho(\omega)\left[\coth\left(\frac{\beta\hbar\omega}{2}\right)(1-\cos\omega t)+i\sin\omega t\right]\end{aligned}. \tag{13.110}$$

In this expression the temperature dependence implies that in the high temperature limit, the real part of *g*(*t*) will dominate, as expected for a classical system. This is a perfectly general expression for the lineshape function in terms of an arbitrary spectral distribution describing the time scale and amplitude of energy gap fluctuations. Given a spectral density $\rho(\omega)$, you can calculate various spectroscopic observables and other time-dependent processes in a fluctuating environment.

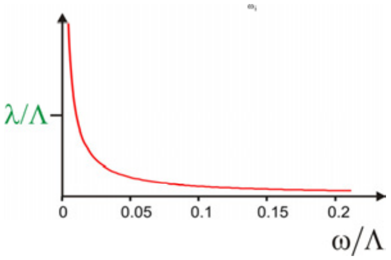
Now, let's evaluate the behavior of the lineshape function and absorption lineshape for different forms of the spectral density. To keep things simple, we will consider the high temperature limit, $k_BT \gg \hbar\omega$. Here $\coth(\beta\hbar\omega/2)\to 2/\beta\hbar\omega$ and we can neglect the imaginary part of the frequency correlation function and lineshape function. These examples are motivated by the spectral densities observed for random or noisy processes. Depending on the frequency range and process of interest, noise tends to scale as $\rho \sim \omega^{-n}$, where $n = 0$, 1 or 2. This behavior is often described in terms of a spectral density of the form

$$\rho(\omega) \propto \omega_c^{1-s}\omega^{s-2}e^{-\omega/\omega_c} \tag{13.111}$$

where ω_c is a cut-off frequency, and the units are inverse frequency. These spectral densities have the desired property of being an odd function in ω, and can be integrated to a finite value. The case $s = 1$ is known as the Ohmic spectral density, whereas $s > 1$ is super-ohmic and $s < 1$ is sub-ohmic.

1) Let's first consider the example when ρ drops as $1/\omega$ with frequency, which refers to the Ohmic spectral density with a high cut-off frequency. This is the spectral density that corresponds to an energy gap correlation function that decays infinitely fast: $C_{eg}(t) \sim \delta(t)$. To choose a definition consistent with eq. (13.109), we set

$$\rho(\omega) = \lambda / \Lambda\hbar\omega \tag{13.112}$$



where Λ is a finite high frequency integration limit that we enforce to keep ρ well behaved. Λ has units of frequency, it is equated with the inverse correlation time for the fast decay of $C_{eg}(t)$. Now we evaluate

$$\begin{aligned} g(t) &= \int_0^\infty d\omega \frac{2k_BT}{\Lambda\hbar\omega}\rho(\omega)(1-\cos\omega t) \ -\frac{i\lambda t}{\hbar} \\ &= \int_0^\infty d\omega \frac{2\lambda k_BT}{\Lambda\hbar^2}\frac{(1-\cos\omega t)}{\omega^2} \ -\frac{i\lambda t}{\hbar} \\ &= \lambda\frac{\pi k_BT}{\Lambda\hbar^2}t \ -\frac{i\lambda t}{\hbar} \end{aligned} \tag{13.113}$$

Then we obtain the dephasing function

$$F(t) = e^{-\Gamma t} \tag{13.114}$$

where we have defined the exponential damping constant as

$$\Gamma = \lambda\frac{\pi kT}{\Lambda\hbar^2} \tag{13.115}$$

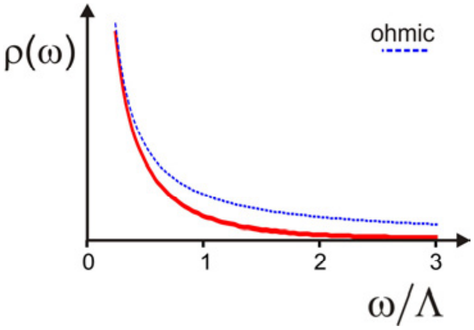
From this we obtain the absorption lineshape

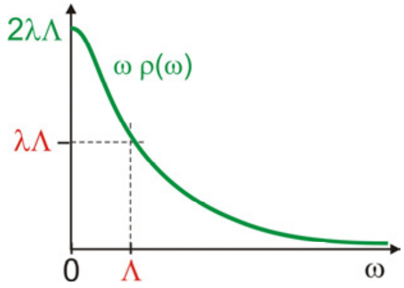
$$\sigma_{abs} \propto \frac{|\mu_{eg}|^2}{(\omega-\omega_{eg})+i\Gamma} \tag{13.116}$$

Thus, a spectral density that scales as $1/\omega$ has a rapidly fluctuating bath and leads to a homogeneous Lorentzian lineshape with a half-width Γ.

2) Now take the case that we choose a Lorentzian spectral density centered at $\omega = 0$. To keep the proper odd function of ω and definition of λ we write:

$$\rho(\omega) = \frac{\lambda}{\hbar\omega}\frac{\Lambda}{\omega^2 + \Lambda^2} \tag{13.117}$$





Note that for frequencies ω≪Λ, this has the ohmic form of eq. (13.112). This is a spectral density that corresponds to an energy gap correlation function that drops exponentially as $C_{eg}(t) \sim \exp(-\Lambda t)$. Here, in the high temperature (classical) limit $kT >> \hbar\Lambda$, neglecting the imaginary part, we find

$$g(t) \approx \frac{\pi\lambda kT}{\hbar^2\Lambda^2}\left[\exp(-\Lambda t) + \Lambda t - 1\right] \tag{13.118}$$

This expression looks familiar. If we equate

$$\Delta^2 = \lambda\frac{\pi kT}{\hbar^2} \tag{13.119}$$

and

$$\tau_c = \frac{1}{\Lambda} \tag{13.120}$$

we obtain the same lineshape function as the classical Gaussian-stochastic model:

$$g(t) = \Delta^2\tau_c^2\left[\exp(-t/\tau_c) + t/\tau_c - 1\right] \tag{13.121}$$

So, the interaction of an electronic transition with a harmonic bath leads to line broadening that is equivalent to random fluctuations of the energy gap. As we noted earlier, for the homogeneous limit, we find $\Gamma = \Delta^2\tau_c$.

Readings

1. Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press: New York, 1995; Ch. 7 and Ch. 8.

13.5. Correspondence of Harmonic Bath and Stochastic Equations

So, why does the mathematical model for coupling of a system to a harmonic bath give the same results as the classical stochastic equations of motion for fluctuations? Why does coupling to a continuum of bath states have the same physical manifestation as perturbation by random fluctuations? The answer is that in both cases, we really have imperfect knowledge of the behavior of all the particles present. Observing a small subset of particles will have dynamics with a random character. These dynamics can be quantified through a correlation function or a spectral density for the time-scales of motion of the bath. In this section, we will demonstrate a more formal relationship that illustrates the equivalence of these pictures.

To take our discussion further, let's again consider the electronic absorption spectrum from a classical perspective. It's quite common to think that the electronic transition of interest is coupled to a particular nuclear coordinate Q which we will call a *local coordinate*. This local coordinate could be an intramolecular normal vibrational mode, an intermolecular rattling in a solvent shell, a lattice vibration, or another motion that influences the electronic transition. The idea is that we take the observed electronic transition to be linearly dependent on one or more local coordinates. Therefore describing Q allows us to describe the spectroscopy. However, since this local mode has further degrees of freedom that it may be interacting with, we are extracting a particular coordinate out or a continuum of other motions, the local mode will appear to feel a fluctuating environment—a friction.

Classically, we describe fluctuations in Q as Brownian motion, typically through a Langevin equation. In the simplest sense, this is an equation that restates Newton's equation of motion $F=ma$ for a fluctuating force acting on a particle with position Q. For the case that this particle is confined in a harmonic potential,

$$m\ddot{Q}(t)+m\omega_0^2 Q^2+m\gamma\dot{Q}=f_R(t) \tag{13.122}$$

Here the terms on the left side represent a damped harmonic oscillator. The first term is the force due to acceleration of the particle of mass m ($F_{acc}=ma$). The second term is the restoring force of the potential, $F_{res}=-\partial V/\partial Q=m\omega_0^2$. The third term allows friction to damp the motion of the coordinate at a rate γ. The motion of Q is under the influence of $f_R(t)$, a random fluctuating force exerted on Q by its surroundings.

Under steady-state conditions, it stands to reason that the random force acting on Q is the origin of the damping. The environment acts on Q with stochastic perturbations that add and remove kinetic energy, which ultimately leads to dissipation of any excess energy. Therefore, the Langevin equation is modelled as a Gaussian stationary process. We take $f_R(t)$ to have a time-averaged value of zero,

$$\left\langle f_R(t)\right\rangle = 0 \tag{13.123}$$

and obey the classical fluctuation-dissipation theorem:

$$\gamma = \frac{1}{2mk_BT}\int_{-\infty}^{\infty}\left\langle f_R(t)\,f_R(0)\right\rangle \tag{13.124}$$

This shows explicitly how the damping is related to the correlation time for the random force. We will pay particular attention to the Markovian case

$$\left\langle f_R(t)\,f_R(0)\right\rangle = 2m\gamma k_BT\ \delta(t) \tag{13.125}$$

which indicate that the fluctuations immediately lose all correlation on the time scale of the evolution of *Q*.

The Langevin equation can be used to describe the correlation function for the time dependence of *Q*. For the Markovian case, eq. (13.122) leads to

$$C_{QQ}(t) = \frac{k_BT}{m\omega_0^2}\left(\cos\zeta t + \frac{\gamma}{2\zeta}\sin\zeta t\right)e^{-\gamma t/2} \tag{13.126}$$

where the reduced frequency $\zeta = \sqrt{\omega_0^2 - \gamma^2/4}$. The frequency domain expression, obtained by Fourier transformation, is

$$\tilde{C}_{QQ}(\omega) = \frac{\gamma kT}{m\pi}\frac{1}{\left(\omega_0^2-\omega^2\right)^2+\omega^2\gamma^2} \tag{13.127}$$

Remembering that the absorption lineshape was determined by the quantum mechanical energy gap correlation function $\left\langle \underset{\sim}{q}(t)\,\underset{\sim}{q}(0)\right\rangle$, one can imagine an analogous classical description of the spectroscopy of a molecule that experiences interactions with a fluctuating environment. In essence this is what we did when discussing the Gaussian stochastic model of the lineshape.

A more general description of the position of a particle subject to a fluctuating force is the Generalized Langevin Equation. The GLE accounts for the possibility that the damping may be time-dependent and carry memory of earlier configurations of the system:[1]

$$m\ddot{Q}(t) + m\omega_0^2Q^2 + m\int_0^t d\tau\,\gamma(t-\tau)\dot{Q}(\tau) = f(t) \tag{13.128}$$

The memory kernel, $\gamma(t-\tau)$, is a correlation function that describes the time-scales over which the fluctuating force retains memory of its previous state. The force due to friction on *Q* depends on the history of the system through τ, the time preceding *t*, and the relaxation of $\gamma(t-\tau)$. The

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[1] Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006.

classical fluctuation-dissipation relationship relates the magnitude of the fluctuating forces on the system coordinate to the damping

$$\langle f_R(t) f_R(\tau)\rangle = 2mk_BT\ \gamma(t-\tau) \tag{13.129}$$

As expected, for the case that $\gamma(t-\tau) = \gamma\delta(t-\tau)$, the GLE reduces to the Markovian case, eq. (13.122).

To demonstrate that the classical dynamics of the particle described under the GLE is related to the quantum mechanical dynamics for a particle interacting with a harmonic bath, we will outline the derivation of a quantum mechanical analog of the classical GLE. To do this we will derive an expression for the time-evolution of the system under the influence of the harmonic bath. We work with a Hamiltonian with a linear coupling between the system and the bath

$$H_{HB} = H_S(P,Q) + H_B(p_\alpha, q_\alpha) + H_{SB}(Q,q) \tag{13.130}$$

We take the system to be a particle of mass M, described through variables P and Q, whereas m_α, p_α and q_α are bath variables. For the present case, we will take the system to be a quantum harmonic oscillator,

$$H_s = \frac{P^2}{2M} + \frac{1}{2}M\Omega^2 Q^2 \tag{13.131}$$

and the Hamiltonian for the bath and its interaction with the system is written as[2]

$$H_B + H_{SB} = \sum_\alpha \left(\frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2}{2}\left(q_\alpha - \frac{c_\alpha}{m_\alpha \omega_\alpha^2} Q \right)^2 \right) \tag{13.132}$$

This expression explicitly shows that each of the bath oscillators is displaced with respect to the system by an amount dependent on their mutual coupling. In analogy to our work with the Displaced Harmonic Oscillator, if we define a displacement operator[3]

$$\hat{D} = \exp\left(-\frac{i}{\hbar} \sum_\alpha \underset{\sim}{\hat{p}}_\alpha \xi_\alpha \right) \tag{13.133}$$

where
$$\xi_\alpha = \frac{c_\alpha}{m_\alpha \omega_\alpha^2} Q \tag{13.134}$$

then
$$H_B + H_{SB} = \hat{D}^\dagger H_B \hat{D} \tag{13.135}$$

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[2] Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006.; Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press: New York, 1995.

[3] Calderia, A. O.; Legget, A. J., *Ann. Phys* **1983,** *149*, 372-456.

Eqn. (13.132) is merely a different representation of our earlier harmonic bath model. To see this we write (13.132) as

$$H_B + H_{SB} = \sum_\alpha \hbar\omega_\alpha \left(\underset{\sim}{p}_\alpha^2 + (\underset{\sim}{q}_\alpha - \underset{\sim}{c}_\alpha \underset{\sim}{Q})^2 \right) \tag{13.136}$$

where the coordinates and momenta are written in reduced form

$$\begin{aligned} \underset{\sim}{Q} &= Q\sqrt{m\omega_0/2\hbar} \\ \underset{\sim}{q}_\alpha &= q_\alpha\sqrt{m_\alpha\omega_\alpha/2\hbar} \\ \underset{\sim}{p}_\alpha &= p_\alpha\Big/\sqrt{2\hbar m_\alpha\omega_\alpha} \end{aligned} \tag{13.137}$$

Also, the reduced coupling is of the system to the αth oscillator is

$$\underset{\sim}{c}_\alpha = c_\alpha\Big/\omega_\alpha\sqrt{m_\alpha\omega_\alpha m\omega_0} \tag{13.138}$$

Expanding (13.136) and collecting terms, we find that we can separate terms as in the harmonic bath model

$$H_B = \sum_\alpha \hbar\omega_\alpha \left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{q}_\alpha^2 \right) \tag{13.139}$$

$$H_{SB} = -2\sum_\alpha \hbar\omega_\alpha \underset{\sim}{d}_\alpha \underset{\sim}{q}_\alpha \ + \ \lambda_B \tag{13.140}$$

The reorganization energy due to the bath oscillators is

$$\lambda_B = \sum_\alpha \hbar\omega_\alpha \underset{\sim}{d}_\alpha^2 \tag{13.141}$$

and the unitless bath oscillator displacement is

$$\underset{\sim}{d}_\alpha = \underset{\sim}{Q}\underset{\sim}{c}_\alpha \tag{13.142}$$

For our current work we regroup the total Hamiltonian (eq. (13.130)) as

$$H_{HB} = \left[\frac{P^2}{2M} + \frac{1}{2}M\bar{\Omega}^2 Q^2 \right] + \sum_\alpha \hbar\omega_\alpha \left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{q}_\alpha^2 \right) - 2\sum_\alpha \hbar\omega_\alpha \underset{\sim}{c}_\alpha \underset{\sim}{Q} \underset{\sim}{q}_\alpha \tag{13.143}$$

where the renormalized frequency is

$$\bar{\Omega}^2 = \Omega^2 + \Omega\sum_\alpha \omega_\alpha \underset{\sim}{c}_\alpha^2 \tag{13.144}$$

To demonstrate the equivalence of the dynamics under this Hamiltonian and the GLE, we can derive an equation of motion for the system coordinate *Q*. We approach this by first expressing these variables in terms of ladder operators

$$\underset{\sim}{\hat{P}} = i\left(\hat{a}^{\dagger} - \hat{a}\right) \qquad \underset{\sim}{\hat{p}}_{\alpha} = i\left(\hat{b}_{\alpha}^{\dagger} - \hat{b}_{\alpha}\right) \tag{13.145}$$

$$\underset{\sim}{\hat{Q}} = \left(\hat{a}^{\dagger} + \hat{a}\right) \qquad \underset{\sim}{\hat{q}}_{\alpha} = \left(\hat{b}_{\alpha}^{\dagger} + \hat{b}_{\alpha}\right) \tag{13.146}$$

Here $\hat{a}\,,\hat{a}^{\dagger}$ are system operators, $\hat{b}$ and $\hat{b}^{\dagger}$ are bath operators. If the observed particle is taken to be bound in a harmonic potential, then the Hamiltonian in eq. (13.130) can be written as

$$H_{HB} = \hbar\bar{\Omega}\left(\hat{a}^{\dagger}\hat{a} + \frac{1}{2}\right) + \sum_{\alpha}\hbar\omega_{\alpha}\left(\hat{b}_{\alpha}^{\dagger}\hat{b}_{\alpha} + \frac{1}{2}\right) - \left(\hat{a}^{\dagger} + \hat{a}\right)\sum_{\alpha}\hbar\omega_{\alpha}\underset{\sim}{c}_{\alpha}\left(\hat{b}_{\alpha}^{\dagger} + \hat{b}_{\alpha}\right) \tag{13.147}$$

The equations of motion for the operators in eqs. (13.145) and (13.146) can be obtained from the Heisenberg equation of motion.

$$\dot{\hat{a}} = \frac{i}{\hbar}\left[H_{HB}, \hat{a}\right] \tag{13.148}$$

from which we find

$$\dot{\hat{a}} = -i\bar{\Omega}\hat{a} + i\sum_{\alpha}\omega_{\alpha}\underset{\sim}{c}_{\alpha}\left(\hat{b}_{\alpha}^{\dagger} + \hat{b}_{\alpha}\right) \tag{13.149}$$

$$\dot{\hat{b}}_{\alpha} = -i\omega_{\alpha}\hat{b}_{\alpha} + i\omega_{\alpha}\underset{\sim}{c}_{\alpha}(\hat{a}^{\dagger} + \hat{a}) \tag{13.150}$$

To derive an equation of motion for the system coordinate, we begin by solving for the time-evolution of the bath coordinates by directly integrating eq. (13.150),

$$\hat{b}_{\alpha}(t) = e^{-i\omega_{\alpha}t}\int_{0}^{t} e^{i\omega_{\alpha}t'}\left(i\omega_{\alpha}\underset{\sim}{c}_{\alpha}\left(\hat{a}^{\dagger} + \hat{a}\right)\right)dt' + \hat{b}_{\alpha}(0)e^{-i\omega_{\alpha}t} \tag{13.151}$$

and insert the result into eq. (13.149). This leads to

$$\dot{\hat{a}} + i\bar{\Omega}\hat{a} - i\sum_{\alpha}\omega_{\alpha}\underset{\sim}{c}_{\alpha}^{2}(\hat{a}^{\dagger} + \hat{a}) + i\int_{0}^{t} dt'\,\kappa(t-t')\left(\dot{\hat{a}}^{\dagger}(t') + \dot{\hat{a}}(t')\right) = iF\left(t\right) \tag{13.152}$$

where
$$\kappa(t) = \sum_{\alpha}\omega_{\alpha}\underset{\sim}{c}_{\alpha}^{2}\cos(\omega_{\alpha}t) \tag{13.153}$$

and
$$F(t) = \sum_{\alpha}\underset{\sim}{c}_{\alpha}\left[\hat{b}_{\alpha}(0) - \omega_{\alpha}\underset{\sim}{c}_{\alpha}\left(\hat{a}^{\dagger}(0) + \hat{a}(0)\right)\right]e^{-i\omega_{\alpha}t} + h.c. \tag{13.154}$$

Now, recognizing that the time-derivative of the system variables is given by

$$\dot{\underset{\sim}{P}} = i\left(\dot{\hat{a}}^{\dagger} - \dot{\hat{a}}\right) \tag{13.155}$$

$$\dot{\underset{\sim}{Q}}\left(\dot{\hat{a}}^{\dagger} + \dot{\hat{a}}\right) \tag{13.156}$$

and substituting eq. (13.152) into (13.155), we can write an equation of motion

$$\underset{\sim}{\dot{P}}(t)+\left(\bar{\Omega}-2\sum_{\alpha}\frac{2\underset{\sim}{c}_{\alpha}^{2}}{\omega_{\alpha}}\right)\underset{\sim}{Q}+\int_{0}^{t}dt'\,2\kappa(t-t')\underset{\sim}{\dot{Q}}(t')=F\left(t\right)+F^{\dagger}\left(t\right) \tag{13.157}$$

Equation (13.157) bears a striking resemblance to the classical GLE, eq. (13.128). In fact, if we define

$$\begin{aligned}\gamma(t)&=2\bar{\Omega}\kappa(t)\\&=\frac{1}{M}\sum_{\alpha}\frac{c_{\alpha}^{2}}{m_{\alpha}\omega_{\alpha}^{2}}\cos\omega_{\alpha}t\end{aligned} \tag{13.158}$$

$$\begin{aligned}f_{R}(t)&=\sqrt{2\hbar M\Omega}\left[F\left(t\right)+F^{\dagger}\left(t\right)\right]\\&=\sum_{\alpha}c_{\alpha}\left[q_{\alpha}(0)\cos\omega_{\alpha}t+\frac{p_{\alpha}(0)}{m_{\alpha}\omega_{\alpha}}\sin\omega_{\alpha}t\right]\end{aligned} \tag{13.159}$$

then the resulting equation is isomorphic to the classical GLE

$$\dot{P}(t)+M\Omega^{2}Q(t)+M\int_{0}^{t}dt'\gamma(t-t')\dot{Q}(t')=f_{R}(t) \tag{13.160}$$

This demonstrates that the quantum harmonic bath acts a dissipative environment, whose friction on the system coordinate is given by eq. (13.158). What we have shown here is an outline of the proof, but detailed discussion of these relationships can be found elsewhere.[4]

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[4] Weiss, U. *Quantum Dissipative Systems*. 3rd ed.; World Scientific: Hackensack, N.J. , 2008; Leggett, A. J.; Chakravarty, S.; Dorsey, A. T.; Fisher, M. P. A.; Garg, A.; Zwerger, W. Dynamics of the dissipative two-state system. *Reviews of Modern Physics* **1987,** *59* (1), 1-85; Yan, Y.; Xu, R. Quantum Mechanics of Dissipative Systems. *Annual Review of Physical Chemistry* **2005,** *56* (1), 187-219.

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2. Fleming, G. R.; Cho, M., Chromophore-Solvent Dynamics. *Annual Review of Physical Chemistry* **1996,** *47* (1), 109-134.
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14. ENERGY AND CHARGE TRANSFER

14.1. Electronic Interactions

In this section we will describe processes that result from the interaction between two or more molecular electronic states, such as the transport of electrons or electronic excitation. This problem can be formulated in terms of a familiar Hamiltonian

$$H = H_0 + V$$

in which H_0 describes the electronic states (including any coupling to nuclear motion), and V is the interaction between the electronic states. In formulating such a problem we will need to consider some basic questions: Is V strong or weak? Are the electronic states described in a diabatic or adiabatic basis? How do nuclear degrees of freedom influence the electronic couplings? For weak couplings, we can describe the transport of electrons and electronic excitation with perturbation theory drawing on Fermi's Golden Rule:

$$\overline{w} = \frac{2\pi}{\hbar} \sum_{k,\ell} p_\ell \left| V_{k\ell} \right|^2 \delta\left(E_k - E_\ell \right)$$

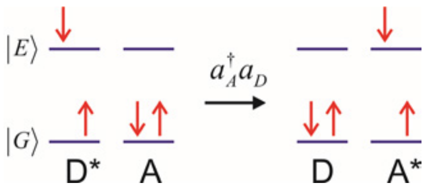
$$\overline{w} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \left\langle V_I(t) V_I(0) \right\rangle$$

This approach underlies common descriptions of electronic energy transport and non-adiabatic electron transfer. We will discuss this regime concentrating on the influence of vibrational motions they are coupled to. However, the electronic couplings can also be strong, in which case the resulting states become delocalized. We will discuss this limit in the context of excitons that arise in molecular aggregates.

To begin, it is useful to catalog a number of electronic interactions of interest. We can use some schematic diagrams to illustrate them, emphasizing the close relationship between the various transport processes. However, we need to be careful, since these are not meant to imply a mechanism or meaningful information on dynamics. Here are a few commonly described processes involving transfer from a donor molecule D to an acceptor molecule A:

a) **Resonance energy transfer**

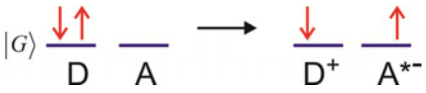
Applies to the transfer of energy from the electronic excited state of a donor to an acceptor molecule. Arises from a Coulomb interaction that is operative at long range, i.e., distances large compared to molecular dimensions. Requires electronic resonance. Named for the first practical derivations of expressions describing this effect: Förster Resonance Energy Transfer (FRET)



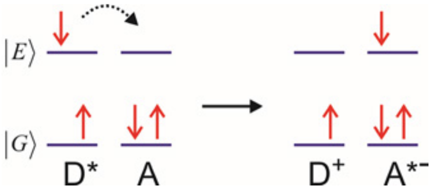
b) Electron transfer

Marcus theory. Nonadiabatic electron transfer. Requires wavefunction overlap.

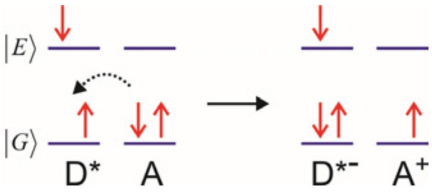
Ground state:



Excited state:

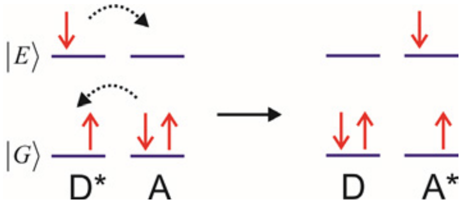


Hole transfer:

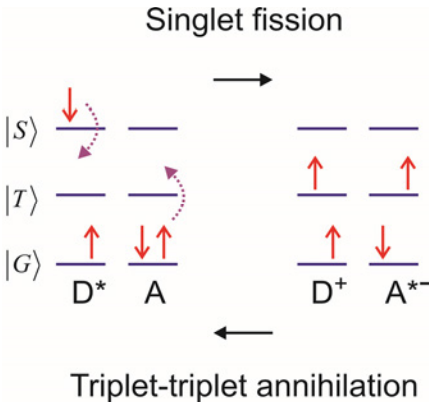


c) Electron-exchange energy transfer

Dexter transfer. Requires wavefunction overlap. Singlet or triplet



d) Singlet fission



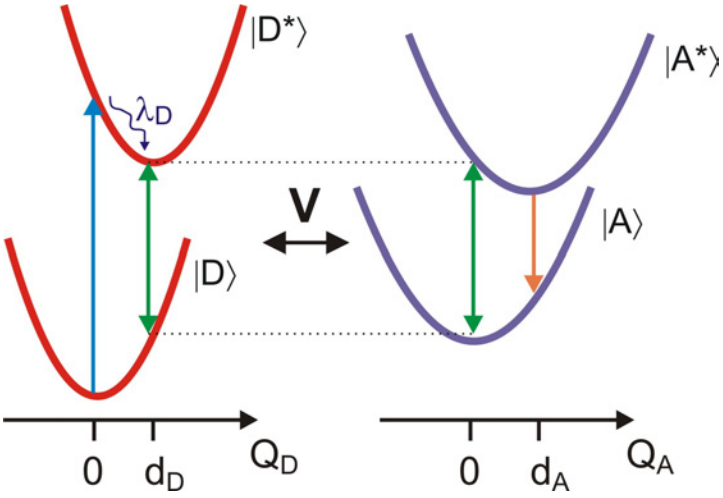
14.2. Förster Resonance Energy Transfer

Förster resonance energy transfer (FRET) refers to the nonradiative transfer of an electronic excitation from a donor molecule to an acceptor molecule:

$$D^* + A \rightarrow D + A^* \tag{14.1}$$

This electronic excitation transfer, whose practical description was first given by Förster, arises from a dipole–dipole interaction between the electronic states of the donor and the acceptor, and does not involve the emission and reabsorption of a light field. Transfer occurs when the oscillations of an optically induced electronic coherence on the donor are resonant with the electronic energy gap of the acceptor. The strength of the interaction depends on the magnitude of a transition dipole interaction, which depends on the magnitude of the donor and acceptor transition matrix elements, and the alignment and separation of the dipoles. The sharp $1/r^6$ dependence on distance is often used in spectroscopic characterization of the proximity of donor and acceptor.

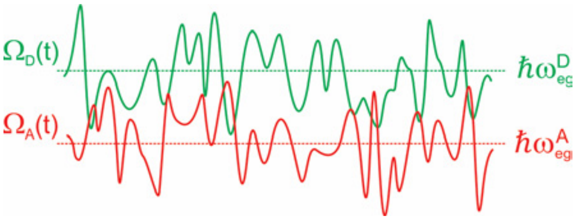
The electronic ground and excited states of the donor and acceptor molecules all play a role in FRET. We consider the case in which we have excited the donor electronic transition, and the acceptor is in the ground state. Absorption of light by the donor at the equilibrium energy gap is followed by rapid vibrational relaxation that dissipates the reorganization energy of the donor λ_D over the course of picoseconds. This leaves the donor in a coherence that oscillates at the energy gap in the donor excited state $\omega_{eg}^{D}\left(q_D = d_D\right)$. The time scale for FRET is typically nanoseconds, so this preparation step is typically much faster than the transfer phase. For resonance energy transfer we require a resonance condition, so that the oscillation of the excited donor coherence is resonant with the ground state electronic energy gap of the acceptor $\omega_{eg}^{A}\left(q_A = 0\right)$. Transfer of energy to the acceptor leads to vibrational relaxation and subsequent acceptor fluorescence that is spectrally shifted from the donor fluorescence. In practice, the efficiency of energy transfer is obtained by comparing the fluorescence emitted from donor and acceptor.

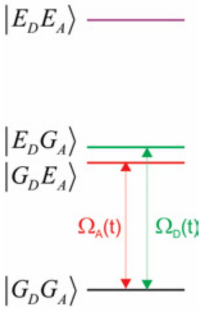


This description of the problem lends itself naturally to treating with a DHO Hamiltonian, However, an alternate picture is also applicable, which can be described through the EG Hamiltonian. FRET arises from the resonance that occurs when the fluctuating electronic energy gap of a donor in its excited state matches the energy gap of an acceptor in its ground state. In other words

$$\underbrace{\hbar\omega_{eg}^{D}-\lambda_D}_{\Omega_D(t)}=\underbrace{\hbar\omega_{eg}^{A}-\lambda_A}_{\Omega_A(t)} \tag{14.2}$$

These energy gaps are time-dependent with occasion crossings that allow transfer of energy.





Our system includes the ground and excited potentials of the donor and acceptor molecules. The four possible electronic configurations of the system are

$$|G_DG_A\rangle, |E_DG_A\rangle, |G_DE_A\rangle, |E_DE_A\rangle$$

Here the notation refers to the ground (*G*) or excited (*E*) vibronic states of either donor (*D*) or acceptor (A). More explicitly, the states also include the vibrational excitation:

$$|E_DG_A\rangle=|e_Dn_D;g_An_A\rangle$$

Thus the system can have no excitation, one excitation on the donor, one excitation on the acceptor, or one excitation on both donor and acceptor. For our purposes, let's only consider the two electronic configurations that are close in energy, and are likely to play a role in the resonance transfer in eq. (14.2)

$$|E_DG_A\rangle \text{ and } |G_DE_A\rangle$$

Since the donor and acceptor are weakly coupled, we can write our Hamiltonian for this problem in a form that can be solved by perturbation theory ($H=H_0+V$). Working with the DHO. approach, our material Hamiltonian has four electronic manifolds to consider:

$$\begin{aligned}H_0&=|E_D\rangle H_D^E\langle E_D|+|G_D\rangle H_D^G\langle G_D|\\&+|E_A\rangle H_A^E\langle E_A|+|G_A\rangle H_A^G\langle G_A|\end{aligned} \tag{14.3}$$

Each of these is defined as we did previously, with an electronic energy and a dependence on a displaced nuclear coordinate. For instance

$$H_D^E=|e_D\rangle E_e^D\langle e_D|+H_e^D \tag{14.4}$$

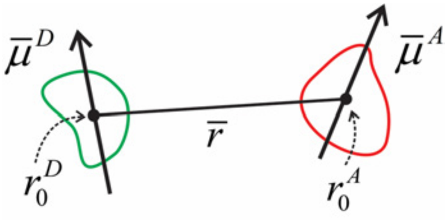
$$H_e^D = \hbar\omega_0^D\left(\tilde{p}_D^2 + \left(\tilde{q}_D - \tilde{d}_D\right)^2\right) \tag{14.5}$$

E_e^D is the electronic energy of donor excited state.

Then, what is *V*? Classically it is a Coulomb interaction of the form

$$V = \sum_{i,j} \frac{q_i^D q_j^A}{\left|r_i^D - r_j^A\right|} \tag{14.6}$$

Here the sum is over all electrons and nuclei of the donor (*i*) and acceptor (*j*). As is, this is challenging to work with, but at large separation between molecules, we can recast this as a dipole–dipole interaction. We define a frame of reference for the donor and acceptor molecule, and assume that the distance between molecules is large. Then the dipole moments for the molecules are



$$\begin{aligned} \bar{\mu}^D &= \sum_i q_i^D\left(r_i^D - r_0^D\right) \\ \bar{\mu}^A &= \sum_j q_j^A\left(r_J^A - r_0^A\right) \end{aligned} \tag{14.7}$$

The interaction between donor and acceptor takes the form of a dipole–dipole interaction:

$$V = \frac{3\left(\bar{\mu}_A \cdot \hat{r}\right)\left(\bar{\mu}_D \cdot \hat{r}\right) - \bar{\mu}_A \cdot \bar{\mu}_D}{\bar{r}^3} \tag{14.8}$$

where *r* is the distance between donor and acceptor dipoles and $\hat{r}$ is a unit vector that marks the direction between them. The dipole operators here are taken to only act on the electronic states and be independent of nuclear configuration, i.e., the Condon approximation. We write the transition dipole matrix elements that couple the ground and excited electronic states for the donor and acceptor as

$$\bar{\mu}_A = \left|A\right\rangle \bar{\mu}_{AA^*}\left\langle A^*\right| + \left|A^*\right\rangle \bar{\mu}_{A^*A}\left\langle A\right| \tag{14.9}$$

$$\bar{\mu}_D = \left|D\right\rangle \bar{\mu}_{DD^*}\left\langle D^*\right| + \left|D^*\right\rangle \bar{\mu}_{D^*D}\left\langle D\right| \tag{14.10}$$

For the dipole operator, we can separate the scalar and orientational contributions as

$$\bar{\mu}_A = \hat{u}_A\,\mu_A \tag{14.11}$$

This allows the transition dipole interaction in eq. (14.8) to be written as

$$V = \mu_A\mu_B\frac{\kappa}{r^3}\left[\left|D^*A\right\rangle\left\langle A^*D\right| + \left|A^*D\right\rangle\left\langle D^*A\right|\right] \tag{14.12}$$

All of the orientational factors are now in the term *κ*:

$$\kappa = 3(\hat{u}_A \cdot \hat{r})(\hat{u}_D \cdot \hat{r}) - \hat{u}_A \cdot \hat{u}_D \tag{14.13}$$

We can now obtain the rates of energy transfer using Fermi's Golden Rule expressed as a correlation function in the interaction Hamiltonian:

$$w_{k\ell} = \frac{2\pi}{\hbar^2} \sum_{\ell} p_\ell \left|V_{k\ell}\right|^2 \delta(\omega_k - \omega_\ell) = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \left\langle V_I(t) V_I(0) \right\rangle \tag{14.14}$$

Note that this is not a Fourier transform! Since we are using a correlation function there is an assumption that we have an equilibrium system, even though we are initially in the excited donor state. This is reasonable for the case that there is a clear time scale separation between the ps vibrational relaxation and thermalization in the donor excited state and the time scale (or inverse rate) of the energy transfer process.

Now substituting the initial state $\ell = \left|D^* A\right\rangle$ and the final state $k = \left|A^* D\right\rangle$, we find

$$w_{ET} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \frac{\left\langle \kappa^2 \right\rangle}{r^6} \left\langle D^* A \right| \mu_D(t) \mu_A(t) \mu_D(0) \mu_A(0) \left| D^* A \right\rangle \tag{14.15}$$

where $\mu_D(t) = e^{iH_D t/\hbar} \mu_D e^{-iH_D t/\hbar}$. Here, we have neglected the rotational motion of the dipoles. Most generally, the orientational average is

$$\left\langle \kappa^2 \right\rangle = \left\langle \kappa(t) \kappa(0) \right\rangle \tag{14.16}$$

However, this factor is easier to evaluate if the dipoles are static, or if they rapidly rotate to become isotropically distributed. For the static case $\left\langle \kappa^2 \right\rangle = 0.475$. For the case of fast loss of orientation: $\left\langle \kappa^2 \right\rangle \rightarrow \left\langle K(t) \right\rangle \left\langle K(0) \right\rangle = \left\langle \kappa \right\rangle^2 = 2/3$.

Since the dipole operators act only on $\left|A\right\rangle$ or $\left|D^*\right\rangle$, and the D and A nuclear coordinates are orthogonal, we can separate terms in the donor and acceptor states.

$$\begin{aligned} w_{ET} &= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \frac{\left\langle \kappa^2 \right\rangle}{r^6} \left\langle D^* \right| \mu_D(t) \mu_D(0) \left| D^* \right\rangle \left\langle A \right| \mu_A(t) \mu_A(0) \left| A \right\rangle \\ &= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \frac{\left\langle \kappa^2 \right\rangle}{r^6} \mathrm{C}_{\mathrm{D}^* D^*}(t) \mathrm{C}_{\mathrm{AA}}(t) \end{aligned} \tag{14.17}$$

The terms in this equation represent the dipole correlation function for the donor initiating in the excited state and the acceptor correlation function initiating in the ground state. That is, these are correlation functions for the donor emission (fluorescence) and acceptor absorption. Remembering that $\left|D^*\right\rangle$ represents the electronic and nuclear configuration $\left|d^* n_{D^*}\right\rangle$, we can use the displaced harmonic oscillator Hamiltonian or energy gap Hamiltonian to evaluate the correlation functions. For the case of Gaussian statistics we can write

$$C_{D^*D^*}(t) = \left|\mu_{DD^*}\right|^2 e^{-i\left(\omega_{DD^*}-2\lambda_D\right)t-g_D^*(t)} \tag{14.18}$$

$$C_{AA}(t) = \left|\mu_{AA^*}\right|^2 e^{-i\omega_{AA^*}t-g_A(t)} \tag{14.19}$$

Here we made use of

$$\omega_{D^*D} = \omega_{DD^*} - 2\lambda_D \tag{14.20}$$

which expresses the emission frequency as a frequency shift of $2\lambda_D$ relative to the donor absorption frequency.

The dipole correlation functions can be expressed in terms of the inverse Fourier transforms of a fluorescence or absorption lineshape:

$$C_{D^*D^*}(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\; e^{-i\omega t}\,\sigma_{fluor}^{D}(\omega) \tag{14.21}$$

$$C_{AA}(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\; e^{-i\omega t}\,\sigma_{abs}^{A}(\omega) \tag{14.22}$$

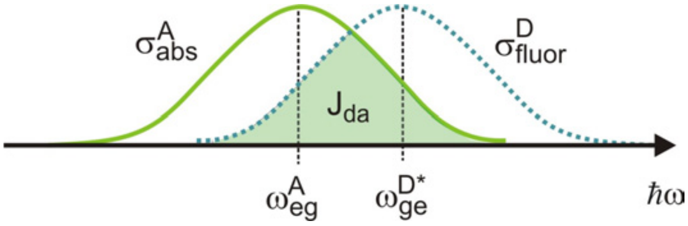
To express the rate of energy transfer in terms of its common practical form, we make use of Parsival's Theorem, which states that if a Fourier transform pair is defined for two functions, the integral over a product of those functions is equal whether evaluated in the time or frequency domain:

$$\int_{-\infty}^{\infty} f_1(t)\,f_2^*(t)\,dt = \int_{-\infty}^{\infty} \tilde{f}_1(\omega)\,\tilde{f}_2^*(\omega)\,d\omega \tag{14.23}$$

This allows us to express the energy transfer rate as an overlap integral J_{DA} between the donor fluorescence and acceptor absorption spectra:

$$w_{ET} = \frac{1}{\hbar^2}\frac{\langle\kappa^2\rangle}{r^6}\left|\mu_{DD^*}\right|^2\left|\mu_{AA^*}\right|^2\int_{-\infty}^{+\infty} d\omega\; \underset{\sim}{\sigma}_{abs}^{A}(\omega)\,\underset{\sim}{\sigma}_{fluor}^{D}(\omega) \tag{14.24}$$

Here $\underset{\sim}{\sigma}$ is the lineshape normalized to the transition matrix element squared: $\underset{\sim}{\sigma} = \sigma/\left|\mu\right|^2$. The overlap integral is a measure of resonance between donor and acceptor transitions.



So, the energy transfer rate scales as r^{-6}, depends on the strengths of the electronic transitions for donor and acceptor molecules, and requires resonance between donor fluorescence and acceptor absorption. One of the things we have neglected is that the rate of energy transfer will also depend on the rate of excited donor state population relaxation. Since this relaxation is typically dominated by the donor fluorescence rate, the rate of energy transfer is commonly written in terms of an effective distance R_0, and the fluorescence lifetime of the donor τ_D:

$$w_{ET} = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6 \tag{14.25}$$

At the critical transfer distance R_0 the rate (or probability) of energy transfer is equal to the rate of fluorescence. R_0 is defined in terms of the sixth-root of the terms in eq. (14.24), and is commonly written as

$$R_0^6 = \frac{9000\ln(10)\phi_D\left\langle\kappa^2\right\rangle}{128\pi^5 n^4 N_A}\int_0^\infty d\bar{\nu}\,\frac{\underset{\sim}{\sigma}_{\text{fluor}}^D\left(\bar{\nu}\right)\varepsilon_A\left(\bar{\nu}\right)}{\bar{\nu}^4} \tag{14.26}$$

This is the practical definition that accounts for the frequency dependence of the transition-dipole interaction and non-radiative donor relaxation in addition to being expressed in common units. $\bar{\nu}$ represents units of frequency in cm^{-1}. The fluorescence spectrum $\underset{\sim}{\sigma}_{fluor}^D$ must be normalized to unit area, so that $\underset{\sim}{\sigma}_{\text{fluor}}^D\left(\bar{\nu}\right)$ is expressed in cm (inverse wavenumbers). The absorption spectrum $\varepsilon_A\left(\bar{\nu}\right)$ must be expressed in molar decadic extinction coefficient units (liter/mol·cm). n is the index of refraction of the solvent, N_A is Avagadro's number, and ϕ_D is the donor fluorescence quantum yield.

Appendix: Transition Dipole Interaction

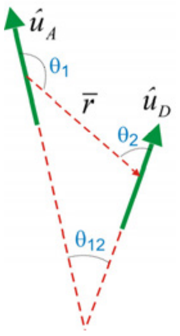
FRET is one example of a quantum mechanical transition dipole interaction. The interaction between two dipoles, *A* and *D*, in eq. (14.12) is

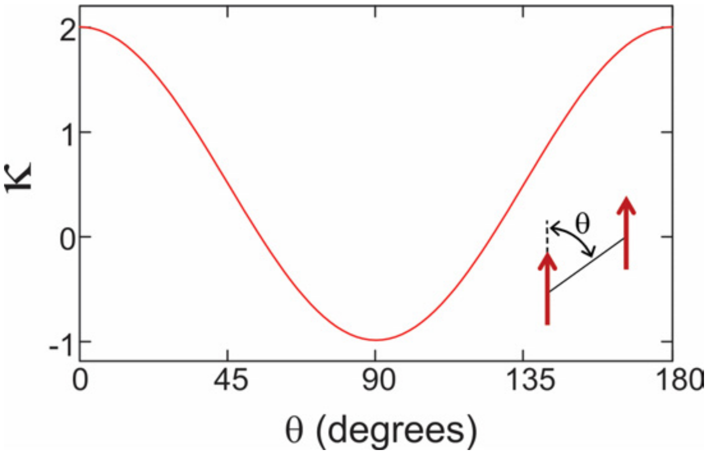
$$V = \frac{\kappa}{r^3}\langle e|\mu_A|g\rangle\langle g|\mu_D|e\rangle \tag{14.27}$$

Here, $\langle g|\mu_D|e\rangle$ is the transition dipole moment in Debye for the ground-to-excited state transition of molecule *A*. r is the distance between the centers of the point dipoles, and κ is the unitless orientational factor

$$\kappa = 3\cos\theta_1\cos\theta_2 - \cos\theta_{12}$$

The figure below illustrates this function for the case of two parallel dipoles, as a function of the angle between the dipole and the vector defining their separation.





In the case of vibrational coupling, the dipole operator is expanded in the vibrational normal coordinate: $\mu = \mu_0 + (\partial\mu/\partial Q_A)Q_A$, and harmonic transition dipole matrix elements are

$$\langle 1|\mu_A|0\rangle = \sqrt{\frac{\hbar}{2c\omega_A}}\frac{\partial\mu}{\partial Q_A} \tag{14.28}$$

where ω_A is the vibrational frequency. If the frequency ν_A is given in cm^{-1}, and the transition dipole moment $\partial\mu/\partial Q_A$ is given in units of D Å^{-1} amu$^{-1/2}$, then the matrix element in units of D is $|\langle 1|\mu_A|0\rangle| = 4.1058\,\nu_A^{-1/2}(\partial\mu/\partial Q_A)$. If the distance between dipoles is specified in Ångstroms, then the transition dipole coupling from (14.27) in cm^{-1} is $V(cm^{-1}) = 5034\kappa r^{-3}$. Experimentally, one can determine the transition dipole moment from the absorbance *A* as

$$A = \left(\frac{\pi N_A}{3c^2}\right)\left(\frac{\partial\mu}{\partial Q_A}\right)^2 \tag{14.29}$$

Readings

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14.3. Excitons in Molecular Aggregates

The absorption spectra of periodic arrays of interacting molecular chromophores show unique spectral features that depend on the size of the system and disorder of the environment. We will investigate some of these features, focusing on the delocalized eigenstates of these coupled chromophores, known as excitons. These principles apply to the study of molecular crystals, J-aggregates, photosensitizers, and light-harvesting complexes in photosynthesis. Similar topics are used in the description of properties of conjugated polymers and organic photovoltaics, and for extended vibrational states in IR and Raman spectroscopy.

Energy transfer in the strong coupling limit

Strong coupling between molecules leads to the delocalization of electronic or vibrational eigenstates, under which weak coupling models like FRET do not apply. From our studies of the coupled two-state system, we know that when the coupling between states is much larger that the energy splitting between the states ($\varepsilon_1 - \varepsilon_2 \ll 2V$) then the resulting eigenstates $|\pm\rangle$ are equally weighted symmetric and antisymmetric combinations of the two, whose energy eigenvalues are split by $2V$. Setting $\varepsilon_1 = \varepsilon_2 = \varepsilon$

$$E_\pm = \varepsilon \pm V$$

$$|\pm\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle \pm |2\rangle\right)$$

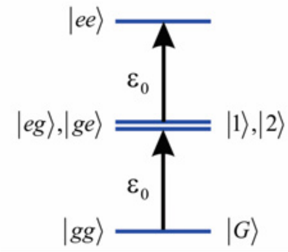
If we excite one of these molecules, we expect that the excitation will flow back and forth at the Rabi frequency. So, what happens with multiple coupled chromophores, focusing particular interest on the placement of coupled chromophores into periodic arrays in space? In the strong coupling regime, the variation in the uncoupled energies is small, making this a problem of coupled quasi-degenerate states. With a spatially period structure, the resulting states bear close similarity to simple descriptions of electronic band structure using the tight-binding model.

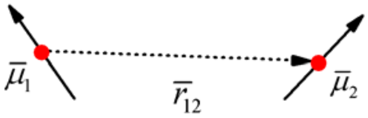
Excitons

Excitons refer to electronic excited states that are not localized to a particular molecule. But beyond that there are many flavors. We will concentrate on **Frenkel excitons**, which refer to excited states in which the excited electron and the corresponding hole (or electron vacancy) reside on the same molecule. All molecules remain electrically neutral in the ground and excited states. This corresponds to what one would expect when one has resonant dipole–dipole interactions between molecules. When there is charge transfer character, the electron and hole can reside on different molecules of the coupled complex. These are referred to as Mott–Wannier excitons.

Absorption spectrum of molecular dimer

To describe the spectroscopy of an array of many coupled chromophores, it is first instructive to work through a pair of coupled molecules. This is in essence the two-level problem from earlier. We consider a pair of molecules (*1* and *2*), which each have a ground and electronically excited state ($|e\rangle$ and $|g\rangle$) split by an energy gap ε_0, and a transition dipole moment $\bar{\mu}$. In the absence of coupling, the state of the system can be specified by specifying the electronic state of both molecules, leading to four possible states: $|gg\rangle, |eg\rangle, |ge\rangle, |ee\rangle$, whose energies are 0, ε_0, ε_0, and $2\varepsilon_0$, respectively.





For shorthand we define the ground state as $|G\rangle$ and the excited states as $|1\rangle$ and $|2\rangle$ to signify the the electronic excitation is on either molecule 1 or 2. In addition, the molecules are spaced by a separation r_{12}, and there is a transition dipole interaction that couples the molecules.

$$V = J\left(|2\rangle\langle 1| + |1\rangle\langle 2|\right)$$

Following our description of transition dipole coupling in Eqn. (14.8), the coupling strength J is given by

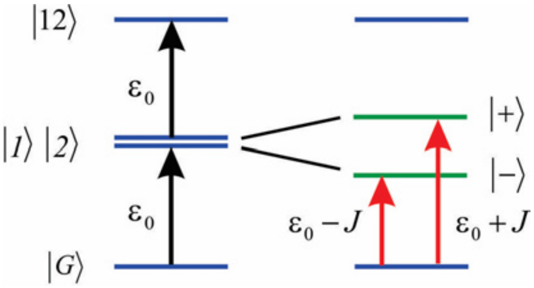
$$J = \frac{(\bar{\mu}_1 \cdot \bar{\mu}_2)|\bar{r}_{12}|^2 - 3(\bar{\mu}_1 \cdot \bar{r}_{12})(\bar{\mu}_2 \cdot \bar{r}_{12})}{|\bar{r}_{12}|^5} = \frac{\mu_1 \mu_2}{r_{12}^3}\kappa$$

where the orientational factor is

$$\kappa = (\hat{\mu}_1 \cdot \hat{\mu}_2) - 3(\hat{\mu}_1 \cdot \hat{r}_{12})(\hat{\mu}_2 \cdot \hat{r}_{12})$$

We assume that the coupling is not too strong, so that we can just concentrate on how it influences $|1\rangle$ and $|2\rangle$ but not $|G\rangle$. Then we only need to describe the coupling induced shifts to the singly excited states, which are described by the Hamiltonian

$$H = \begin{pmatrix} \varepsilon_0 & J \\ J & \varepsilon_0 \end{pmatrix}$$



As stated above, we find that the eigenvalues are

$$E_\pm = \varepsilon_0 \pm J$$

and that the eigenstates are:

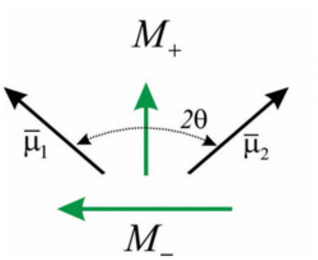
$$|\pm\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle \pm |2\rangle\right)$$

These symmetric and antisymmetric states are delocalized across the two molecules, and in the language of Frenkel excitons are referred to as the one-exciton states. Furthermore, the dipole operator for the dimer is

$$\bar{M} = \bar{\mu}_1 + \bar{\mu}_2$$

and so the transition dipole matrix elements are:

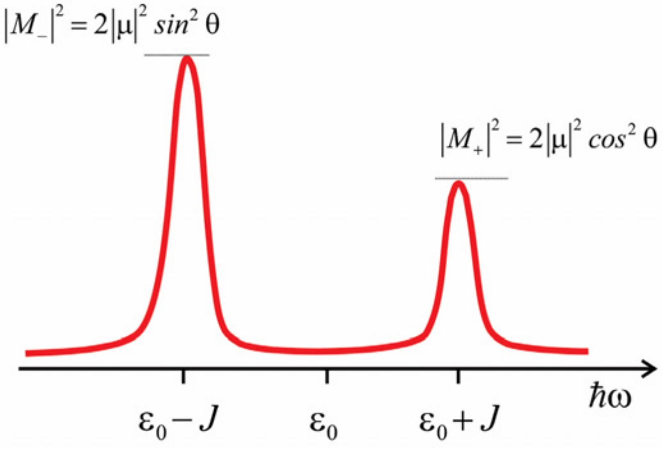
$$M_\pm = \left\langle \pm \middle| \bar{M} \middle| G \right\rangle = \frac{1}{\sqrt{2}}\left(\bar{\mu}_1 \pm \bar{\mu}_2\right)$$



M_+ and M_- are oriented perpendicular to each other in the molecular frame. If we confine the molecular dipoles to be within a plane, with an angle 2θ between them, then the amplitude of M_+ and M_- is given by

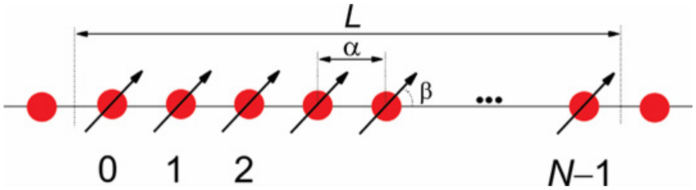
$$M_+ = 2\mu\cos\theta$$
$$M_- = 2\mu\sin\theta$$

We can now predict the absorption spectrum for the dimer. We have two transitions from the ground state and the $|\pm\rangle$ states which are resonant at $\hbar\omega = \varepsilon_0 \pm J$ and which have an amplitude $|M_\pm|^2$. The splitting between the peaks is referred to as the Davydov splitting. Note that the relative amplitude of the peaks allows one to infer the angle between the molecular transition dipoles. Also, note for θ = 0° or 90°, all amplitude appears in one transition with magnitude $2|\mu|^2$, which is referred to as superradiant.



Frenkel Excitons with Periodic Boundary Conditions

Now let's consider linear aggregate of N periodically arranged molecules. We will assume that each molecule is a two-level electronic system with a ground state and an excited state. We will assume that electronic excitation moves an electron from the ground state to an unoccupied orbital of the same molecule. We will label the molecules with integer values (n) between *0* and *N-1*:



If the molecules are separated along the chain by a lattice spacing α, then the size of the chain is $L=\alpha N$. Each molecule has a transition dipole moment μ, which makes an angle β with the axis of the chain.

In the absence of interactions, we can specify the state of the system exactly by identifying whether each molecule is in the electronically excited or ground state. If the state of molecule n within the chain is φ_n, which can take on values of g or e, then

$$|\psi\rangle = |\varphi_0, \varphi_1, \varphi_2 \cdots \varphi_n \cdots \varphi_{N-1}\rangle$$

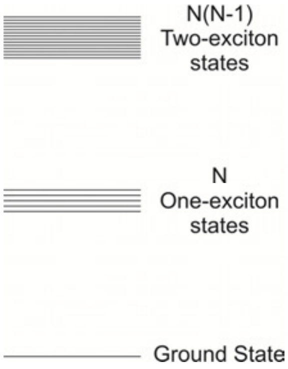
This representation of the state of the system is referred to as the *site basis*, since it is expressed in terms of each molecular site in the chain. For simplicity we write the ground state of the system as

$$|G\rangle = |g, g, g \ \ldots, g\rangle$$

If we excite one of the molecules within the aggregate, we have a singly excited state in which the n^{th} molecule is excited, so that

$$|\psi\rangle = |g, g, g, \ldots, e, \ \ldots, g\rangle \equiv |n\rangle$$

For shorthand, we identify this product state as $|n\rangle$, which is to be distinguished from the molecular eigenfunction at site n, φ_n.



The singly excited state is assigned an energy ε_0 corresponding to the electronic energy gap. In the absence of coupling, the singly excited states are N-fold degenerate, corresponding to a single excitation at any of the N sites. If two excitations are placed on the chain we can see that there are $N(N-1)$ possible states with energy $2\varepsilon_0$, recognizing that the Pauli principle does not allow two excitations on the same site. When coupling is introduced, the mixing of these degenerate states leads to the one-exciton and two-exciton bands. For this discussion, we will concentrate on the one-exciton states.

The coupling between molecule *n* and molecule *n′* is given by the matrix element $V_{nn'}$. We will assume that a molecule interacts only with its neighbors, and that each pairwise interaction has a magnitude *J*

$$V_{nn'} = J\,\delta_{n,n'\pm 1}$$

If *V* is a dipole–dipole interaction, the orientational factor κ dictates that when the transition dipole angle $\beta < 54.7°$ then the sign of the coupling $J < 0$, which is the case known as J-aggregates (after Edwin Jelley), and implies an offset stack of chromophores or head-to-tail arrangement. If $\beta > 54.7°$ then $J > 0$, and the system is known as an H-aggregate.

To begin, we also apply periodic boundary conditions to this problem, which implies that we are describing the states of an *N*-molecule chain within an infinite linear chain. In terms of the Hamiltonian, the molecules at the beginning and end of our chain feel the same symmetric interactions to two neighbors as the other molecules. To write this in terms of a finite *N*×*N* matrix, one couples the first and last member of the chain: $J_{0,N-1} = J_{N-1,0} = J$.

With these observations in mind, we can write the Frenkel Exciton Hamiltonian for the linear aggregate in terms of a system Hamiltonian that reflects the individual sites and their couplings

$$\begin{aligned} H_0 &= H_S + V \\ H_S &= \sum_{n=1}^{N} \varepsilon_0 \left|n\right\rangle\left\langle n\right| \\ V &= \sum_{n=1}^{N} J\left\{\left|n'\right\rangle\left\langle n\right| + \left|n\right\rangle\left\langle n'\right|\right\}\delta_{n,n'\pm 1} \end{aligned} \tag{14.30}$$

Here periodic boundary conditions imply that we replace $\left|N\right\rangle \Rightarrow \left|0\right\rangle$ and $\left|-1\right\rangle \Rightarrow \left|N-1\right\rangle$ where they appear.

The optical properties of the aggregate will be obtained by determining the eigenstates of the Hamiltonian. We look for solutions that describe one-exciton eigenstates as an expansion in the site basis.

$$\left|\psi(x)\right\rangle = \sum_{n=0}^{N-1} c_n(\mathrm{x})\left|\varphi_n(x - x_n)\right\rangle \tag{14.31}$$

which is written in order to point out the dependence of these wavefunctions on the lattice spacing *x*, and the position of a particular molecule at x_n. Such an expansion should work well when the electronic interactions between sites is weak enough to treat perturbatively. For the electronic structure of solids, this is known as the tight binding model, which describes band structure as a linear combinations of atomic orbitals.

Rather than diagonalizing the Hamiltonian, we can take advantage of its translational symmetry to obtain the eigenstates. The symmetry of the Hamiltonian is such that it is unchanged by any integral number of translations along the chain. That is the results are unchanged for any summation in eqs. (14.30) and (14.31) over N consecutive integers. Similarly, the molecular wavefunction at any site is unchanged by such a translation. Written in terms of a displacement operator $D = e^{ip_x\alpha/\hbar}$ that shifts the molecular wavefunction by one lattice constant α,

$$\left|\varphi\left(x+n\alpha\right)\right\rangle = D^n\left|\varphi\left(x\right)\right\rangle \tag{14.32}$$

These observations underlie Bloch's theorem, which states that the eigenstates of a periodic system will vary only by a phase shift when displaced by a lattice constant.

$$\left|\psi(x+\alpha)\right\rangle = e^{ik\alpha}\left|\psi(x)\right\rangle \tag{14.33}$$

Here k is the wavevector, or reciprocal lattice vector, a real quantity. Thus the expansion coefficients in eq. (14.31) will have an amplitude that reflects an excitation spread equally among the N sites, and only vary between sites by a spatially varying phase factor. Equivalently, the eigenstates are expected to have a form that is a product of a spatially varying phase factor and a periodic function:

$$\left|\psi(x)\right\rangle = e^{ikx}u(x) \tag{14.34}$$

These phase factors are closely related to the lattice displacement operators. If the linear chain has N molecules, the eigenstates must remain unchanged with a translation by the length of the chain $L = \alpha N$:

$$\left|\psi(x_n+L)\right\rangle = \left|\psi(x_n)\right\rangle$$

Therefore, we see that our wavefunctions must satisfy $e^{ikL} = 1$, or

$$Nk\alpha = 2\pi m \tag{14.35}$$

where m is an integer. Furthermore, since there are N sites on the chain, unique solutions to eq. (14.35) require that m can only take on N consecutive integer values. Like the site index n, there is no unique choice of m. Rewriting eq. (14.35), the wavevector is

$$k_m = \frac{2\pi}{\alpha}\frac{m}{N} \tag{14.36}$$

We see that for an N site lattice, m can take on the N consecutive integer values, so that $k_m\alpha$ varies over a 2π range of angles. The wavevector index m labels the N one-exciton eigenstates of an N molecule chain. By convention, k_m is chosen such that $-\pi/\alpha < k_m \leq \pi/\alpha$. Then the corresponding values of m are integers from $-(N-1)/2$ to $(N-1)/2$ if there are an odd number of lattice sites or $-(N-2)/2$ to $N/2$ for an even number of sites. For example, a 20 molecule chain would have $m = -9, -8, \ldots 9, 10$.

These findings lead to the general form for the m one-exciton eigenstates

$$\left|k_m\right\rangle = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ink_m\alpha} \left|n\right\rangle \tag{14.37}$$

The factor of $N^{-1/2}$ assures proper normalization of the wavefunction, $\langle\psi|\psi\rangle=1$. Comparing eqs. (14.37) and (14.31) we see that the expansion coefficients for the n^{th} site of the m^{th} eigenstate is

$$c_{m,n} = \frac{1}{\sqrt{N}} e^{ink_m\alpha} = \frac{1}{\sqrt{N}} e^{i2\pi nm/N} \tag{14.38}$$

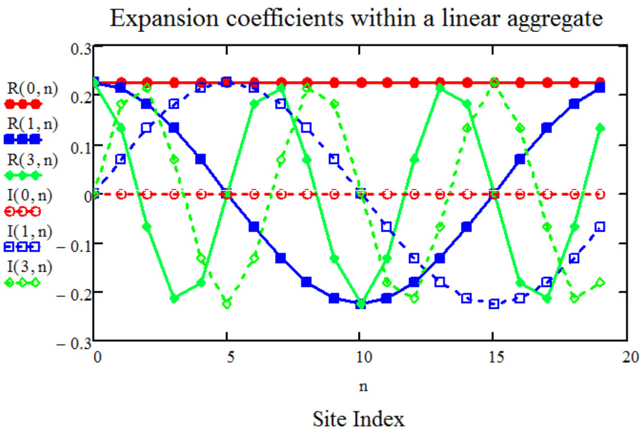
We see that for state $\left|k_0\right\rangle$, with $m = 0$, the phase factor is the same for all sites. In other words, the transition dipoles of the chain will oscillate in-phase, constructively adding for all sites. For the case that $k_m = \pi/\alpha$, we see that each site is out-of-phase with its nearest neighbors. Looking at the case of the dimer, $N = 2$, we see that $m = 0$ or 1, $k_m = 0$ or π/α, and we recover the expected symmetric and antisymmetric eigenstates:

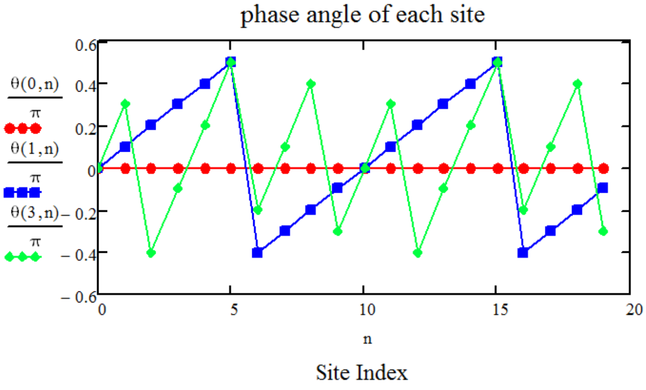
$$\left|k_0\right\rangle = \frac{1}{\sqrt{2}} \sum_{n=0}^{1} e^{in\cdot 0} \left|n\right\rangle = \frac{1}{\sqrt{2}}\left(\left|0\right\rangle + \left|1\right\rangle\right) \qquad (k=0)$$

$$\left|k_1\right\rangle = \frac{1}{\sqrt{2}} \sum_{n=0}^{1} e^{in\pi} \left|n\right\rangle = \frac{1}{\sqrt{2}}\left(\left|0\right\rangle - \left|1\right\rangle\right) \qquad (k=\pi/\alpha)$$

Schematically for $N = 20$, we see how the dipole phase varies with k_m, plotting the real and imaginary components of the expansion coefficients

$N = 20$ $\qquad R(m,n) := \frac{1}{\sqrt{N}} \cdot \mathrm{Re}\left(e^{i \cdot n \cdot k_m \cdot \alpha}\right)$ $\qquad I(m,n) := \frac{1}{\sqrt{N}} \cdot \mathrm{Im}\left(e^{i \cdot n \cdot k_m \cdot \alpha}\right)$





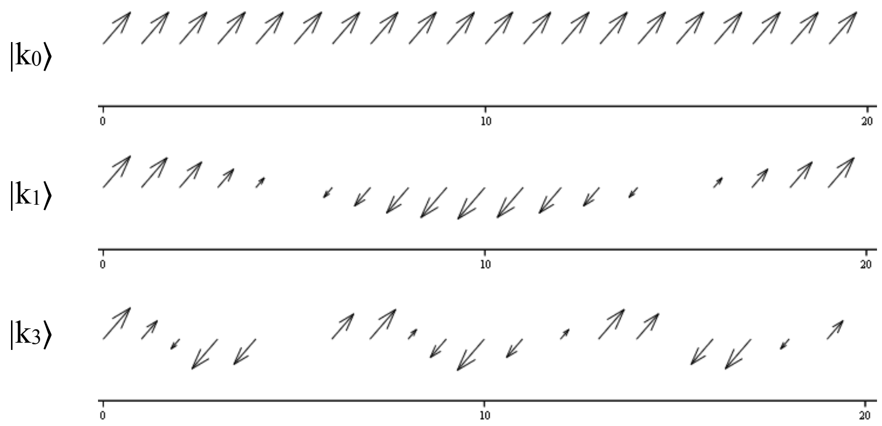
$$\theta_m(n) = \arctan\left(\frac{\mathrm{Im}(c_{m,n})}{\mathrm{Re}(c_{n.m})}\right)$$

Also, we can evaluate the one-exciton transition dipole matrix elements, $M(k_m)$, which are expressed as superpositions of the dipole moments at each site, $\bar{\mu}_n$:

$$\bar{M} = \sum_{n=0}^{N-1} \bar{\mu}_n \tag{14.39}$$

$$\begin{aligned} M_m &= \langle k_m | \bar{M} | G \rangle \\ &= \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ink_m\alpha} \langle n | \bar{\mu}_n | G \rangle \end{aligned} \tag{14.40}$$

The phase of the transition dipoles of the chain matches their phase within each k state. Thus for our problem, in which all of the dipoles are parallel, transitions from the ground state to the k_m=0 state will carry all of the oscillator strength. Plotted below is an illustration of the phase relationships between dipoles in a chain with $N = 20$.



Finally, let's solve for the one-exciton energy eigenvalues by calculating the expectation value of the Hamiltonian operator, eq. (14.30)

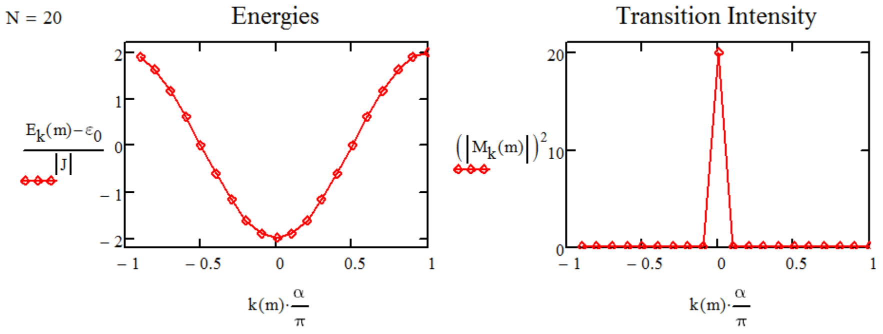
$$\begin{aligned} E(k_m) &= \langle k | H_0 | k \rangle \\ &= \frac{1}{N}\sum_{n,m=0}^{N-1} e^{i(n-m)k\alpha} \langle m | H_0 | n \rangle \end{aligned} \tag{14.41}$$

$$\langle k_m | H_S | k_m \rangle = \frac{1}{N}\sum_{n=0}^{N-1} \varepsilon_0 = \varepsilon_0$$

$$\begin{aligned} \langle k_m | V | k_m \rangle &= \frac{1}{N}\sum_{n=0}^{N-1} \left\{ e^{ik_m\alpha} \langle n-1 | V | n \rangle + e^{-ik_m\alpha} \langle n+1 | V | n \rangle \right\} \\ &= 2J\cos(k_m\alpha) \end{aligned}$$

$$E(k_m) = \varepsilon_0 + 2J\cos(k_m\alpha) \tag{14.42}$$

You predict that the one-exciton band of states varies in energy between $\varepsilon_0 - 2J$ and $\varepsilon_0 + 2J$. If we take J as negative, as expected for the case of J-aggregates (negative couplings), then $k = 0$ is at the bottom of the band. Examples are illustrated below for the N=20 aggregate.

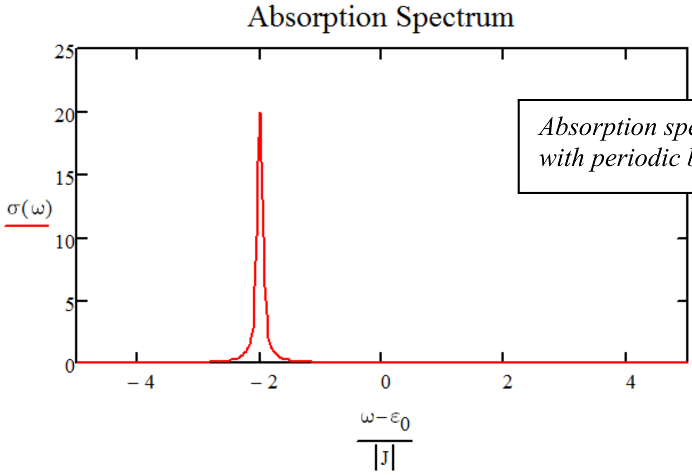


Note that the result in eq. (14.42) gives you a splitting of *4J* between the two states of the dimer, unlike the expected *2J* splitting from earlier. This is a result of the periodic boundary conditions that we enforce here.

We are now in a position to plot the absorption spectrum for aggregate, summing over eigenstates and assuming a Lorentzian lineshape for the system:

$$\sigma(\omega) = \sum_m |M_m|^2 \frac{\Gamma^2}{(\hbar\omega - E(k_m)) + \Gamma^2}$$

For a 20 oscillator chain with negative coupling, the spectrum is plotted below. We have one peak corresponding to the *k*0 mode that is peaked at $\hbar\omega = \varepsilon_0 - 2J$ and carries the oscillator strength of all 20 dipoles.



Absorption spectrum for N = 20 aggregate with periodic boundary conditions and J < 0.

Open Boundary Conditions

Similar types of solutions appear without using periodic boundary conditions. For the case of open boundary conditions, in the molecules at the end of the chain are only coupled to the one nearest neighbor in the chain. In this case, it is helpful to label on the sites from $n = 1, 2 \ldots N$. Furthermore, $m = 1, 2 \ldots N$. Under those conditions, one can solve for the eigenstates using use the boundary condition that $\psi = 0$ at sites 0 and *N*+1. The change in boundary condition gives *sine* solutions:

$$|k_m\rangle = \sqrt{\frac{2}{N+1}} \sum_{n=1}^{N} \sin\left(\frac{\pi m n}{N+1}\right) |n\rangle$$

The energy eigenvalues are

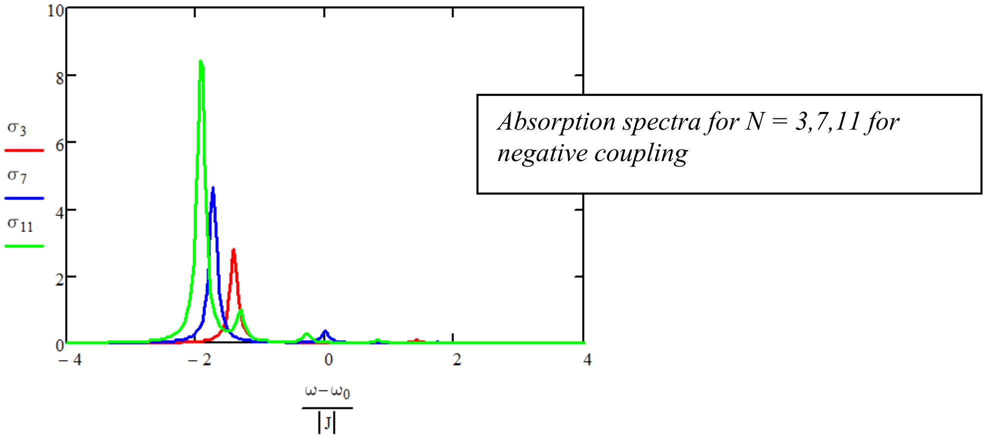
$$E_m = \omega_0 + 2J\cos\left(\frac{\pi m}{N+1}\right)$$

Returning to the case of the dimer (*N*=2), we can now confirm that we recover the symmetric and anti-symmetric eigenstates, with an energy splitting of *2J*.

If you calculate the oscillator strength for these transitions using the dipole operator in eq. (14.39), one finds:

$$M_m^2 = \left|\langle k_m | \bar{M} | G \rangle\right|^2 = \left(\frac{1-(-1)^m}{2}\right)^2 \frac{2\mu^2}{N+1}\cot^2\left(\frac{\pi m}{2(N+1)}\right)$$

This result shows that most of the oscillator strength lies in the $m=1$ state, for which all oscillators are in phase. For large *N*, M_1^2 carries 81% of the oscillator strength, with approximately 9% in the transition to the $m=3$ state.



Absorption spectra for N = 3,7,11 for negative coupling

The shift in the peak of the absorption relative to the monomer gives the coupling J. Including long-range interactions has the effect of shifting the exciton band asymmetrically about ω_0.

$\Omega_1 = \omega_0 + 2.4J$ (*m*=1, bottom of the band with *J* negative)

$\Omega_N = \omega_0 - 1.8J$ (Top of band)

Exchange Narrowing

If the chain is ***not*** homogeneous, i.e., all molecules do not have same site energy ε0, then we can model this effect as Gaussian random disorder. The energy of a given site is

$$\varepsilon_n = \varepsilon_0 + \delta\omega_n$$

We add as an extra term to our earlier Hamiltonian, eq. (14.30), to account for this variation.

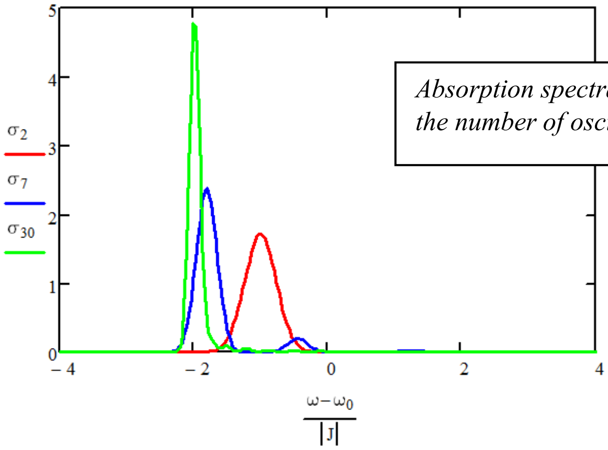
$$H_0 = H_S + H_{dis} + V$$

$$H_{dis} = \sum_n \delta\omega_n |n\rangle\langle n|$$

The effect is to shift and mix the homogeneous exciton states.

$$\delta\Omega_k = \langle k | H_{dis} | k \rangle = \frac{2}{N+1} \sum_n \sin^2\left(\frac{\pi k n}{N+1}\right) \delta\omega_n$$

We find that these shifts are also Gaussian random variables, with a standard deviation of $\Delta\sqrt{3/2(N+1)}$, where Δ is the standard deviation for site energies. So, the delocalization of the eigenstate averages the disorder over N sites, which reduces the distribution of energies by a factor scaling as $\sqrt{N}$. The narrowing of the absorption lineshape with delocalization is called exchange narrowing. This depends on the distribution of site energies being relatively small: $\Delta << 3\pi |J| / N^{3/2}$.



Absorption spectra for N = 2,6,30 normalized to the number of oscillators. 3Δ = J and J < 0.

Readings

1. Knoester, J., Optical Properties of Molecular Aggregates. In *Proceedings of the International School of Physics "Enrico Fermi" Course CXLIX*, Agranovich, M.; La Rocca, G. C., Eds. IOS Press: Amsterdam, 2002; pp 149-186.

14.4. Multiple Particles and Second Quantization

In the case of a large number of nuclear or electronic degrees of freedom (or for photons in a quantum light field), it becomes tedious to write out the explicit product-state form of the state vector, i.e.,

$$|\psi\rangle = |\varphi_1,\varphi_2,\varphi_3\ldots\rangle$$

Under these circumstances it becomes useful to define creation and annihilation operators. If $|\psi\rangle$ refers to the state of multiple harmonic oscillators, then the Hamiltonian has the form

$$H = \sum_\alpha \left(\frac{p_\alpha{}^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 q_\alpha^2 \right) \tag{14.43}$$

which can also be expressed as

$$H = \sum_\alpha \hbar\omega_\alpha \left(a_\alpha^\dagger a_\alpha + \frac{1}{2} \right) \tag{14.44}$$

and the eigenstates represented in through the occupation of each oscillator $|\psi\rangle = |n_1, n_2, n_3\ldots\rangle$. This representation is sometimes referred to as "second quantization", because the classical Hamiltonian was initially quantized by replacing the position and momentum variables by operators, and then these quantum operators were again replaced by raising and lowering operators.

The operator $a_\alpha^\dagger$ raises the occupation in mode $|n_\alpha\rangle$, and a_α lowers the excitation in mode $|n_\alpha\rangle$. The eigenvalues of these operators, $n_\alpha \to n_\alpha \pm 1$, are captured by the commutator relationships:

$$\left[a_\alpha, a_\beta^\dagger \right] = \delta_{\alpha\beta} \tag{14.45}$$

$$\left[a_\alpha, a_\beta \right] = 0 \tag{14.46}$$

Eqn. (14.45) indicates that the raising and lower operators do not commute if they are operators in the same degree of freedom (α=β), but they do otherwise. Written another way, these expression indicate that the order of operations for the raising and lowering operators in different degrees of freedom commute.

$$a_\alpha a_\beta^\dagger = a_\beta^\dagger a_\alpha \tag{14.47}$$

$$\begin{gathered} a_\alpha a_\beta = a_\beta a_\alpha \\ a_\alpha^\dagger a_\beta^\dagger = a_\beta^\dagger a_\alpha^\dagger \end{gathered} \tag{14.48}$$

These expressions also imply that the eigenfunctions operations of the forms in eq. (14.47) and (14.48) are the same, so that these eigenfunctions should be symmetric to interchange of the coordinates. That is, these particles are bosons.

This observations proves an avenue to defining raising and lowering operators for electrons. Electrons are fermions, and therefore antisymmetric to exchange of particles. This suggests that electrons will have raising and lowering operators that change the excitation of an electronic state up or down following the relationship

$$b_\alpha b_\beta^\dagger = -b_\beta^\dagger b_\alpha \tag{14.49}$$

or

$$\left[b_\alpha, b_\beta^\dagger \right]_+ = \delta_{\alpha\beta} \tag{14.50}$$

where $[\ldots]_+$ refers to the anti-commutator. Further, we write

$$\left[b_\alpha, b_\beta \right]_+ = 0 \tag{14.51}$$

This comes from considering the action of these operators for the case where $\alpha = \beta$. In that case, taking the Hermetian conjugate, we see that eq. (14.51) gives

$$2 b_\alpha^\dagger b_\alpha^\dagger = 0 \quad \text{or} \quad b_\alpha^\dagger b_\alpha^\dagger = 0 \tag{14.52}$$

This relationship says that we cannot put two excitations into the same state, as expected for Fermions. This relationship indicates that there are only two eigenfunctions for the operators $b_\alpha^\dagger$ and b_α, namely $\left| n_\alpha = 0 \right\rangle$ and $\left| n_\alpha = 1 \right\rangle$. This is also seen with eq. (14.50), which indicates that $b_\alpha^\dagger b_\alpha \left| n_\alpha \right\rangle + b_\alpha b_\alpha^\dagger \left| n_\alpha \right\rangle = \left| n_\alpha \right\rangle$

or

$$b_\alpha b_\alpha^\dagger \left| n_\alpha \right\rangle = \left(1 - b_\alpha^\dagger b_\alpha \right) \left| n_\alpha \right\rangle \tag{14.53}$$

If we now set $\left| n_\alpha \right\rangle = \left| 0 \right\rangle$, we find that eq. (14.53) implies

$$\begin{gathered} b_\alpha b_\alpha^\dagger \left| 0 \right\rangle = \left| 0 \right\rangle \\ b_\alpha^\dagger b_\alpha \left| 0 \right\rangle = 0 \\ b_\alpha b_\alpha^\dagger \left| 1 \right\rangle = 0 \\ b_\alpha^\dagger b_\alpha \left| 1 \right\rangle = \left| 1 \right\rangle \end{gathered} \tag{14.54}$$

Again, this reinforces that only two states, $|0\rangle$ and $|1\rangle$, are allowed for electron raising and lowering operators. These are known as Pauli operators, since they implicitly enforce the Pauli exclusion principle. Note, in eq. (14.54), that $|0\rangle$ refers to the eigenvector with an eigenvalue of zero $|\varphi_0\rangle$, whereas “0” refers to the null vector.

Frenkel Excitons

For electronic chromophores, we use the notation |g⟩ and |e⟩ for the states of an electron in its ground or excited state. The state of the system for one excitation in an aggregate

$$|n\rangle = |g,g,g,g\ldots e\ldots g\rangle$$

can then be written as $a_n^\dagger|G\rangle$, or simply $a_n^\dagger$, and the Frenkel exciton Hamiltonian is

$$H_0 = \sum_{n=0}^{N-1} \varepsilon_0 |n\rangle\langle n| + \sum_{n,m} J_{n,m} |n\rangle\langle m| \tag{14.55}$$

or

$$= \sum_{n} \varepsilon_0 b_n^\dagger b_n + \sum_{n,m} J_{n,m} b_n^\dagger b_m \tag{14.56}$$

Readings

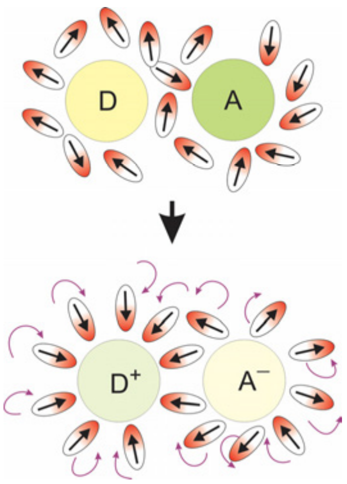
1. Schatz, G. C.; Ratner, M. A., *Quantum Mechanics in Chemistry*. Dover Publications: Mineola, NY, 2002; p. 119.

14.5. Marcus Theory For Electron Transfer

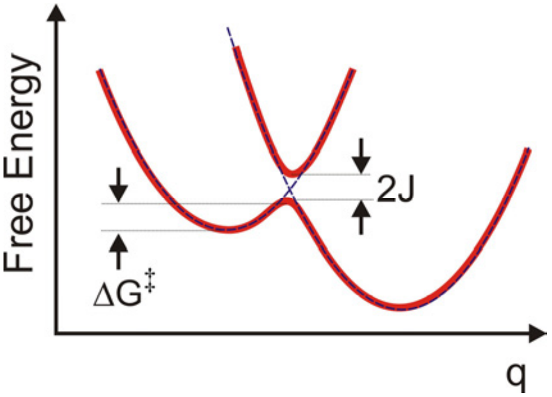
The displaced harmonic oscillator (DHO) formalism and the Energy Gap Hamiltonian have been used extensively in describing charge transport reactions, such as electron and proton transfer. Here we describe the rates of electron transfer between weakly coupled donor and acceptor states when the potential energy depends on a nuclear coordinate, i.e., nonadiabatic electron transfer. These results reflect the findings of Marcus' theory of electron transfer.

We can represent the problem as calculating the transfer or reaction rate for the transfer of an electron from a donor to an acceptor

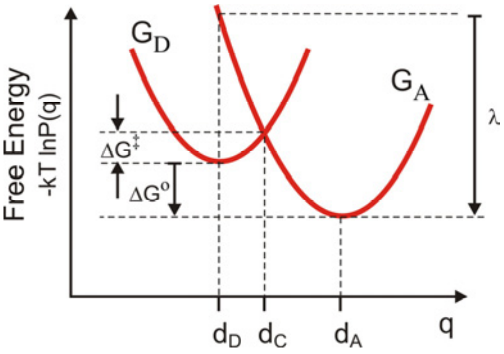
$$D + A \rightarrow D^{+} + A^{-} \tag{14.57}$$



This reaction is mediated by a nuclear coordinate q. This need not be, and generally isn't, a simple vibrational coordinate. For electron transfer in solution, we most commonly consider electron transfer to progress along a solvent rearrangement coordinate in which solvent reorganizes its configuration so that dipoles or charges help to stabilize the extra negative charge at the acceptor site. This type of *collective* coordinate is illustrated in the figure to the right. The external response of the medium along the electron transfer coordinate is referred to as "outer shell" electron transfer, whereas the influence of internal vibrational modes that promote ET is called "inner shell". The influence of collective solvent rearrangements or intramolecular vibrations can be captured with the use of an electronic transition coupled to a harmonic bath.



Normally we associate the rates of electron transfer with the free-energy along the electron transfer coordinate q. Pictures such as the ones above that illustrate states of the system with electron localized on the donor or acceptor electrons hopping from donor to acceptor are conceptually represented through diabatic energy surfaces. The electronic coupling J that results in transfer mixes these diabatic states in the crossing region. From this adiabatic surface, the rate of transfer for the forward reaction is related to the flux across the barrier. From classical transition state theory we can associate the rate with the free energy barrier using $k_f = A\exp(-\Delta G^{\dagger}/k_B T)$. If the coupling is weak, we can describe the rates of transfer between



donor and acceptor in the diabatic basis with perturbation theory. This accounts for nonadiabatic effects and tunneling through the barrier.

To begin we consider a simple classical derivation for the free-energy barrier and the rate of electron transfer from donor to acceptor states for the case of weakly coupled diabatic states. First we assume that the free energy or potential of mean force for the initial and final state, $G(q) = -k_BT \ln P(q)$, is well represented by two parabolas.

$$\begin{aligned} G_D(q) &= \frac{1}{2} m\omega_0^2 \left(q - d_D\right)^2 \\ G_A(q) &= \frac{1}{2} m\omega_0^2 \left(q - d_A\right)^2 + \Delta G^0 \end{aligned} \tag{14.58}$$

To find the barrier height $\Delta G^\ddagger$, we first find the crossing point d_C where $G_D(d_C) = G_A(d_C)$. Substituting eq. and solving for d_C gives

$$\frac{1}{2} m\omega_0^2 \left(d_C - d_D\right)^2 = \Delta G^\circ + \frac{1}{2} m\omega_0^2 \left(d_C - d_A\right)^2$$

$$\begin{aligned} d_C &= \frac{\Delta G^\circ}{m\omega_0^2}\left(\frac{1}{d_A - d_D}\right) + \frac{d_A + d_D}{2} \\ &= \frac{\Delta G^\circ}{2\lambda}\left(d_A - d_D\right) + \frac{d_A + d_D}{2} \end{aligned}$$

The last expression comes from the definition of the reorganization energy, which is the energy to be dissipated on the acceptor surface if the electron is transferred at d_D,

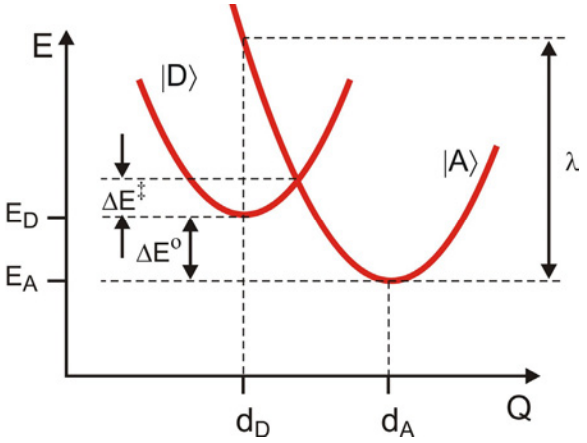
$$\begin{aligned} \lambda &= G_A\left(d_D\right) - G_A\left(d_A\right) \\ &= \frac{1}{2} m\omega_0^2 \left(d_D - d_A\right)^2 \end{aligned} \tag{14.59}$$

Then, the free energy barrier to the transfer $\Delta G^\ddagger$ is

$$\begin{aligned} \Delta G^\ddagger &= G_D\left(d_C\right) - G_D\left(d_D\right) \\ &= \frac{1}{2} m\omega_0^2 \left(d_C - d_D\right)^2 \\ &= \frac{1}{4\lambda}\left[\Delta G^\circ + \lambda\right]^2 \end{aligned}$$

So the Arrhenius rate constant is for electron transfer via activated barrier crossing is

$$k_{ET} = A \exp\left[\frac{-(\Delta G^\circ + \lambda)^2}{4\lambda kT}\right] \tag{14.60}$$



This curve qualitatively reproduced observations of a maximum electron transfer rate under the conditions $-\Delta G^\circ = \lambda$, which occurs in the barrierless case when the acceptor parabola crosses the donor state energy minimum.

We expect that we can more accurately describe nonadiabatic electron transfer using the DHO or Energy Gap Hamiltonian, which will include the possibility of tunneling through the barrier when donor and acceptor wavefunctions overlap. We start by writing the transfer rates in terms of the potential energy as before. We recognize that when we calculate thermally averaged transfer rates that this is equivalent to describing the diabatic free energy surfaces. The Hamiltonian is

$$H = H_0 + V \tag{14.61}$$

$$H_0 = |D\rangle H_D \langle D| + |A\rangle H_A \langle A| \tag{14.62}$$

Here $|D\rangle$ and $|A\rangle$ refer to the potential where the electron is either on the donor or acceptor, respectively. Also remember that $|D\rangle$ refers to the vibronic states $|d,n_d\rangle$. These are represented through the same harmonic potential, displaced from one another vertically in energy by

$$\Delta E = E_A - E_D$$

and horizontally along the reaction coordinate q:

$$\begin{aligned} H_D &= |d\rangle E_D \langle d| + H_d \\ H_A &= |a\rangle E_A \langle a| + H_a \end{aligned} \tag{14.63}$$

$$\begin{aligned} H_d &= \hbar\omega_0 \left(\underset{\sim}{p}^2 + (\underset{\sim}{q} - \underset{\sim}{d}_D)^2 \right) \\ H_a &= \hbar\omega_0 \left(\underset{\sim}{p}^2 + (\underset{\sim}{q} - \underset{\sim}{d}_A)^2 \right) \end{aligned} \tag{14.64}$$

Here we are using reduced variables for the momenta, coordinates, and displacements of the harmonic oscillator. The diabatic surfaces can be expressed as product states in the electronic and nuclear configurations: $|D\rangle = |d,n\rangle$. The interaction between the surfaces is assigned a coupling J

$$V = J\left[|d\rangle\langle a| + |a\rangle\langle d| \right] \tag{14.65}$$

We have made the Condon approximation, implying that the transfer matrix element that describes the electronic interaction has no dependence on nuclear coordinate. Typically this electronic coupling is expected to drop off exponentially with the separation between donor and acceptor orbitals;

$$J = J_0 \exp\left(-\beta_E \left(R - R_0\right)\right) \tag{14.66}$$

Here β_E is the parameter governing the distance dependence of the overlap integral. For our purposes, even though this is a function of donor-acceptor separation (R), we take this to vary slowly over the displacements investigated here, and therefore be independent of the nuclear coordinate (Q).

Marcus evaluated the perturbation theory expression for the transfer rate by calculating Franck-Condon factors for the overlap of donor and acceptor surfaces, in a manner similar to our treatment of the DHO electronic absorption spectrum. Similarly, we can proceed to calculate the rates of electron transfer using the Golden Rule expression for the transfer of amplitude between two states

$$w_{k\ell} = \frac{1}{\hbar^2}\int_{-\infty}^{+\infty} dt \left\langle V_I\left(t\right) V_I\left(0\right)\right\rangle \tag{14.67}$$

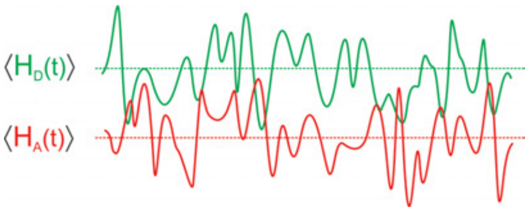
Using $V_I\left(t\right) = e^{iH_0 t/\hbar}\, V\, e^{-iH_0 t/\hbar}$, we write the electron transfer rate in the DHO eigenstate form as

$$w_{ET} = \frac{\left|J\right|^2}{\hbar^2}\int_{-\infty}^{+\infty} dt\, e^{-i\Delta E t/\hbar} F(t) \tag{14.68}$$

where

$$F(t) = \left\langle e^{iH_d t/\hbar} e^{-iH_a t/\hbar}\right\rangle \tag{14.69}$$

This form emphasizes that the electron transfer rate is governed by the overlap of vibrational wavepackets on the donor and acceptor potential energy surfaces.



Alternatively, we can cast this in the form of the Energy Gap Hamiltonian. This carries with is a dynamical picture of the electron transfer event. The energy of the two states have time-dependent (fluctuating) energies as a result of their interaction with the environment. Occasionally the energy of the donor and acceptor states coincide that is the energy gap between them is zero. At this point transfer becomes efficient. By integrating over the correlation function for these energy gap fluctuations, we characterize the statistics for barrier crossing, and therefore forward electron transfer.

Similar to before, we define a donor-acceptor energy gap Hamiltonian

$$H_{AD} = H_A - H_D \tag{14.70}$$

which allows us to write
$$F(t)=\left\langle \exp_{+}\left[-\frac{i}{\hbar}\int_{0}^{t} dt' H_{AD}(t')\right]\right\rangle \tag{14.71}$$

and
$$H_{AD}(t)=e^{iH_d t/\hbar} H_{AD}\ e^{-iH_d t/\hbar} \tag{14.72}$$

These expressions and application of the cumulant expansion to eq. allows us to express the transfer rate in terms of the lineshape function and correlation function

$$F(t)=\exp\left[\frac{-i}{\hbar}\langle H_{AD}\rangle t-\ g(t)\right] \tag{14.73}$$

$$g(t)=\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1\, C_{AD}(\tau_2-\tau_1) \tag{14.74}$$

$$C_{AD}(t)=\frac{1}{\hbar^2}\left\langle \delta H_{AD}(t)\,\delta H_{AD}(0)\right\rangle \tag{14.75}$$

$$\langle H_{AD}\rangle=\lambda \tag{14.76}$$

The lineshape function can also be written as a sum of many coupled nuclear coordinates, q_α. This expression is commonly applied to the vibronic (inner shell) contributions to the transfer rate:

$$\begin{aligned} g(t) &= -\sum_{\alpha}\left(\underset{\sim}{d}_{\alpha}^{A}-\underset{\sim}{d}_{\alpha}^{D}\right)^2\left[\left(\overline{n}_\alpha+1\right)\left(e^{-i\omega_\alpha t}-1+i\omega_0 t\right)+\overline{n}_\alpha\left(e^{i\omega_\alpha t}-1-i\omega_0 t\right)\right] \\ &= -\sum_{\alpha}\left(\underset{\sim}{d}_{\alpha}^{A}-\underset{\sim}{d}_{\alpha}^{D}\right)^2\left[\coth\left(\beta\hbar\omega_\alpha/2\right)\left(\cos\omega_\alpha t-1\right)-i\left(\sin\omega_\alpha t-\omega_\alpha t\right)\right] \end{aligned} \tag{14.77}$$

Substituting the expression for a single harmonic mode into the Golden Rule rate expression eq. gives

$$\begin{aligned} w_{ET} &= \frac{|J|^2}{\hbar^2}\int_{-\infty}^{+\infty} dt\, e^{-i\Delta E t/\hbar-g(t)} \\ &= \frac{|J|^2}{\hbar^2}\int_{-\infty}^{+\infty} dt\, e^{-i(\Delta E+\lambda)t/\hbar}\ \exp\left[D\left(\coth\left(\beta\hbar\omega_0/2\right)\left(\cos\omega_0 t-1\right)-i\sin\omega_0 t\right)\right] \end{aligned} \tag{14.78}$$

where
$$D=\left(\underset{\sim}{d}_A-\underset{\sim}{d}_D\right)^2 \tag{14.79}$$

This expression is very similar to the one that we evaluated for the absorption lineshape of the Displaced Harmonic Oscillator model. A detailed evaluation of this vibronically mediated transfer rate is given in Jortner.

To get a feeling for the dependence of *k* on *q*, we can look at the classical limit $\hbar\omega << kT$. This corresponds to the case where one is describing the case of a low frequency "solvent mode" or "outer sphere" effect on the electron transfer. Now, we neglect the imaginary part of $g(t)$ and take the limit $\coth(\beta\hbar\omega/2) \rightarrow 2/\beta\hbar\omega$:

$$w_{ET} = \frac{|J|^2}{\hbar^2}\int_{-\infty}^{+\infty} dt\, e^{-i(\Delta E+\lambda)t} \exp\left(-\left(\frac{2Dk_BT}{\hbar\omega_0}\right)(1-\cos\omega_0 t)\right) \tag{14.80}$$

Note that the high temperature limit also means the low frequency limit for ω_0. This means that we can expand $\cos\omega_0 t \approx 1-(\omega_0 t)^2/2$, and find

$$w_{ET} = \frac{|J|^2}{\hbar}\sqrt{\frac{\pi}{\lambda kT}}\exp\left[\frac{-(\Delta E+\lambda)^2}{4\lambda kT}\right] \tag{14.81}$$

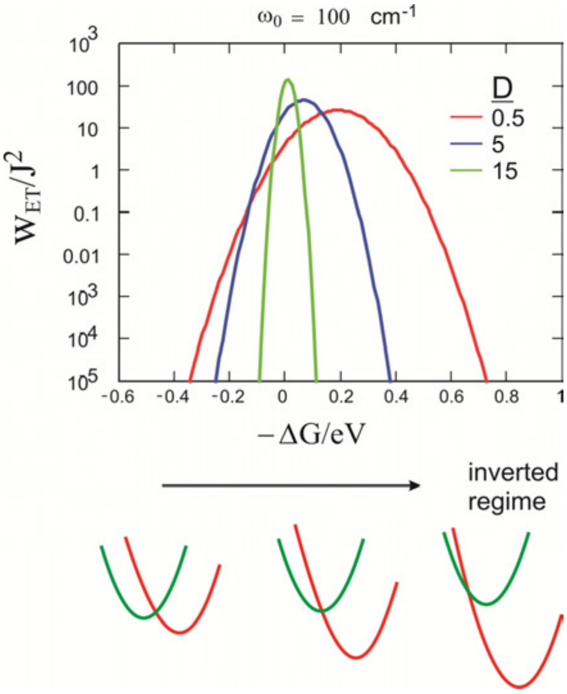
where $\lambda = D\hbar\omega_0$. Note that the activation barrier $\Delta E^\dagger$ for displaced harmonic oscillators is $\Delta E^\dagger = \Delta E + \lambda$. For a thermally averaged rate it is proper to associate the average energy gap with the standard free energy of reaction, $\langle H_A - H_D\rangle - \lambda = \Delta G^0$. Therefore, this expression is equivalent to the classical Marcus' result for the electron transfer rate

$$k_{ET} = A\exp\left[\frac{-(\Delta G^o+\lambda)^2}{4\lambda kT}\right] \tag{14.82}$$

where the pre-exponential is

$$A = 2\pi|J|^2/\hbar\sqrt{4\pi\lambda kT} \tag{14.83}$$

This expression shows the nonlinear behavior expected for the dependence of the electron transfer rate on the driving force for the forward transfer, i.e., the reaction free energy. This is unusual because we generally think in terms of a linear free energy relationship between the rate of a reaction and the equilibrium constant: $\ln k \propto \ln K_{eq}$. This leads to the thinking that the rate should increase as we increase the driving free energy for the reaction $-\Delta G^0$. This behavior only hold for a small region in ΔG^0. Instead, eq. shows that the ET rate will increase with $-\Delta G^0$, until a maximum rate is observed for $-\Delta G^0 = \lambda$ and the rate then decreases. This decrease of k with increased $-\Delta G^0$ is known as the "inverted regime". The inverted

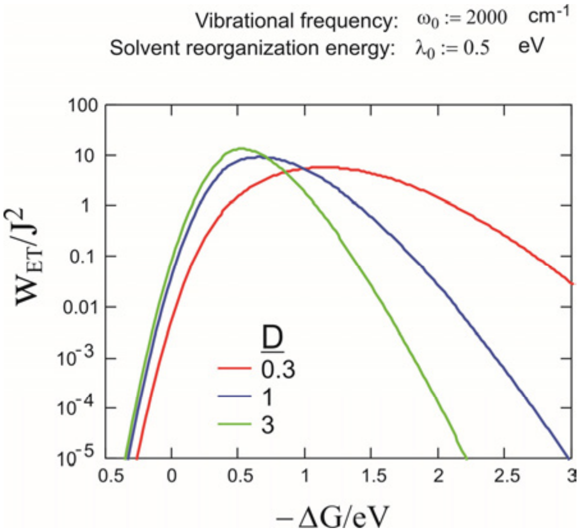


behavior means that extra vibrational excitation is needed to reach the curve crossing as the acceptor well is lowered. The high temperature behavior for coupling to a low frequency mode (100 cm^{-1} at 300 K) is shown at right, in addition to a cartoon that indicates the shift of the curve crossing at ΔG^0 is increased.

Particularly in intramolecular ET, it is common that one wants to separately account for the influence of a high frequency intramolecular vibration (inner sphere ET) that is not in the classical limit that applies to the low frequency classical solvent response. If an additional mode of frequency ω_0 and a rate in the form eq. is added to the low frequency mode, Jortner has given an expression for the rate as:

$$w_{ET} = \frac{|J|^2}{\hbar}\sqrt{\frac{\pi}{\lambda_0 kT}}\sum_{j=0}^{\infty}\left(\frac{e^{-D}}{j!}D^j\right)\exp\left[\frac{-\left(\Delta G^o + \lambda_0 + j\hbar\omega_0\right)^2}{4\lambda_0 kT}\right] \tag{14.84}$$

Here λ_0 is the solvation reorganization energy. For this case, the same inverted regime exists; although the simple Gaussian dependence of k on ΔG^0 no longer exists. The asymmetry here exists because tunneling sees a narrower barrier in the inverted regime than in the normal regime. Examples of the rates obtained with eq. are plotted in the figure below (T= 300K).



As with electronic spectroscopy, a more general and effective way of accounting for the nuclear motions that mediate the electron transfer process is to describe the coupling weighted density of states as a spectral density. Then we can use coupling to a harmonic bath to describe solvent and/or vibrational contributions of arbitrary form to the transfer event using

$$g(t) = \int_0^{\infty} d\omega\ \rho(\omega)\left[\coth\left(\frac{\beta\hbar\omega}{2}\right)(1-\cos\omega t) + i(\sin\omega t - \omega t)\right] \tag{14.85}$$

Readings

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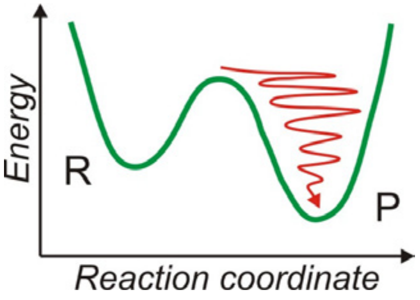
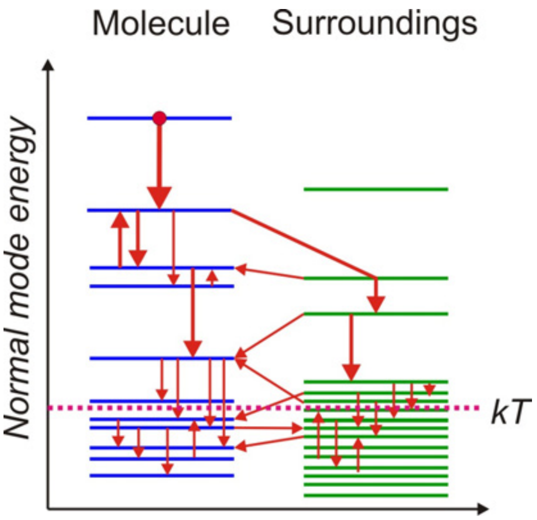
15. QUANTUM RELAXATION PROCESSES

15.1. Vibrational Relaxation

Here we want to address how excess vibrational energy undergoes irreversible energy relaxation as a result of interactions with other intra- and intermolecular degrees of freedom. Why is this process important? It is the fundamental process by which nonequilibrium states thermalize. As chemists, this plays a particularly important role in chemical reactions, where efficient vibrational relaxation of an activated species is important to stabilizing the product and not allowing it to re-cross to the reactant well. Further, the rare activation event for chemical reactions is similar to the reverse of this process. Although we will be looking specifically at vibrational couplings and relaxation, the principles are the same for electronic population relaxation through electron–phonon coupling and spin–lattice relaxation.



For an isolated molecule with few vibrational coordinates, an excited vibrational state must relax by interacting with the remaining internal vibrations or the rotational and translational degrees of freedom. If a lot of energy must be dissipated, radiative relaxation may be more likely. In the condensed phase, relaxation is usually mediated by the interactions with the environment, for instance, the solvent or lattice. The solvent or lattice forms a continuum of intermolecular motions that can absorb the energy of the vibrational relaxation. Quantum mechanically this means that vibrational relaxation (the annihilation of a vibrational quantum) leads to excitation of solvent or lattice motion (creation of an intermolecular vibration that increases the occupation of higher lying states).



For polyatomic molecules it is common to think of energy relaxation from high lying vibrational states ($kT << \hbar\omega_0$) in terms of cascaded redistribution of energy through coupled modes of the molecule and its surroundings leading finally to thermal equilibrium. We seek ways of describing these highly non-equilibrium relaxation processes in quantum systems.

Classically vibrational relaxation reflects the surroundings exerting a friction on the vibrational coordinate, which damps its amplitude and heats the sample. We have seen that a Langevin equation for an oscillator experiencing a fluctuating force $f(t)$ describes such a process:

$$\ddot{Q}(t)+\omega_0^2 Q^2-\gamma\dot{Q}=f(t)/m \tag{15.1}$$

This equation assigns a phenomenological damping rate γ to the vibrational relaxation we wish to describe. However, we know in the long time limit, the system must thermalize and the dissipation of energy is related to the fluctuations of the environment through the classical fluctuation-dissipation relationship. Specifically,

$$\langle f(t)f(0)\rangle = 2m\gamma k_B T\ \delta(t) \tag{15.2}$$

More general classical descriptions relate the vibrational relaxation rates to the correlation function for the fluctuating forces acting on the excited coordinate.

In these classical pictures, efficient relaxation requires a matching of frequencies between the vibrational period of the excited oscillator and the spectrum of fluctuation of the environment. Since these fluctuations are dominated by motions are of the energy scale of k_BT, such models do not work effectively for high frequency vibrations whose frequency $\omega \gg k_BT/\hbar$. We would like to develop a quantum model that allows for these processes and understand the correspondence between these classical pictures and quantum relaxation.

Let's treat the problem of a vibrational system H_S that relaxes through weak coupling V to a continuum of bath states H_B using perturbation theory. The eigenstates of H_S are $|a\rangle$ and those of H_B are $|\alpha\rangle$. Although our earlier perturbative treatment did not satisfy energy conservation, here we can take care of it by explicitly treating the bath states.

$$H = H_0 + V \tag{15.3}$$

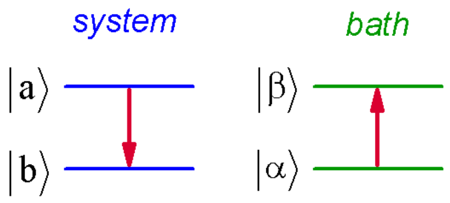
$$H_0 = H_S + H_B \tag{15.4}$$

$$H_S = |a\rangle E_a \langle a| + |b\rangle E_b \langle b| \tag{15.5}$$

$$H_B = \sum_\alpha |\alpha\rangle E_\alpha \langle\alpha| \tag{15.6}$$

$$H_0|a\alpha\rangle = (E_a + E_\alpha)|a\alpha\rangle \tag{15.7}$$

We will describe transitions from an initial state $|i\rangle = |a\alpha\rangle$ with energy $E_a + E_\alpha$ to a final state $|f\rangle = |b\beta\rangle$ with energy $E_b + E_\beta$. Since we expect energy conservation to hold, this undoubtedly requires that a change in the system states will require an equal and opposite change of energy in the bath. Initially, we take $p_a = 1 \quad p_b = 0$. If the interaction potential is V, Fermi's Golden Rule says the transition from $|i\rangle$ to $|f\rangle$ is given by



$$k_{fi} = \frac{2\pi}{\hbar} \sum_{i,f} p_i \left| \langle i | V | f \rangle \right|^2 \delta\left(E_f - E_i\right) \tag{15.8}$$

$$= \frac{2\pi}{\hbar} \sum_{a,\alpha,b,\beta} p_{a,\alpha} \left| \langle a\alpha | V | b\beta \rangle \right|^2 \delta\left(\left(E_b + E_\beta\right) - \left(E_a + E_\alpha\right) \right) \tag{15.9}$$

$$= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \sum_{\substack{a,\alpha \\ b,\beta}} p_{a,\alpha} \, \langle a\alpha | V | b\beta \rangle \langle b\beta | V | a\alpha \rangle \, e^{-i\left(\left(E_b - E_a\right) + \left(E_\beta - E_\alpha\right)\right)t/\hbar} \tag{15.10}$$

Equation (15.10) is just a restatement of the time domain version of (15.8)

$$k_{fi} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \left\langle V(t) V(0) \right\rangle \tag{15.11}$$

$$V(t) = e^{iH_0 t} \, V \, e^{-iH_0 t} \tag{15.12}$$

Now, the matrix element involves both evaluation in both the system and bath states, but if we write this in terms of a matrix element in the system coordinate $V_{ab} = \langle a | V | b \rangle$:

$$\langle a\alpha | V | b\beta \rangle = \langle \alpha | V_{ab} | \beta \rangle \tag{15.13}$$

Then we can write the rate as

$$k_{ba} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \sum_{\alpha,\beta} p_\alpha \left\langle \alpha \left| e^{+iE_\alpha t} \, V_{ab} \, e^{-iE_\beta t} \right| \beta \right\rangle \langle \beta | V_{ba} | \alpha \rangle \, e^{-i\omega_{ba} t} \tag{15.14}$$

$$k_{ba} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \left\langle V_{ab}(t) V_{ba}(0) \right\rangle_B e^{-i\omega_{ba} t} \tag{15.15}$$

$$V_{ab}(t) = e^{iH_B t} \, V_{ab} \, e^{-iH_B t} \tag{15.16}$$

Equation (15.15) says that the relaxation rate is determined by a correlation function

$$C_{ba}(t) = \left\langle V_{ab}(t) V_{ba}(0) \right\rangle \tag{15.17}$$

which describes the time-dependent changes to the coupling between *b* and *a*. The time dependence of the interaction arises from the interaction with the bath; hence its time evolution under H_B. The subscript $\langle \cdots \rangle_B$ means an equilibrium thermal average over the bath states

$$\langle \cdots \rangle_B = \sum_\alpha p_\alpha \, \langle \alpha | \cdots | \alpha \rangle \tag{15.18}$$

Note also that eq. (15.15) is similar but not quite a Fourier transform. This expression says that the relaxation rate is given by the Fourier transform of the correlation function for the fluctuating coupling evaluated at the energy gap between the initial and final state states.

Alternatively we could think of the rate in terms of a vibrational coupling spectral density, and the rate is given by its magnitude at the system energy gap ω_{ba}.

$$k_{ba} = \frac{1}{\hbar^2}\tilde{C}_{ba}\left(\omega_{ab}\right) \tag{15.19}$$

where the spectral representation $\tilde{C}_{ba}\left(\omega_{ab}\right)$ is defined as the Fourier transform of $C_{ba}\left(t\right)$.

Vibration coupled to a harmonic bath

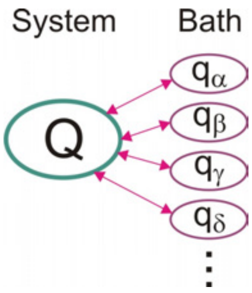
To evaluate these expressions, let's begin by consider the specific case of a system vibration coupled to a harmonic bath, which we will describe by a spectral density. Imagine that we prepare the system in an excited vibrational state in $v = |1\rangle$ and we want to describe relaxation to $v = |0\rangle$.[1]

$$H_S = \hbar\omega_0\left(\underset{\sim}{P}^2 + \underset{\sim}{Q}^2\right) \tag{15.20}$$

$$H_B = \sum_\alpha \hbar\omega_\alpha\left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{q}_\alpha^2\right) = \sum_\alpha \hbar\omega_\alpha\left(a_\alpha^\dagger a_\alpha + \tfrac{1}{2}\right) \tag{15.21}$$

We will take the system–bath interaction to be linear in the bath coordinates:

$$V = H_{SB} = \sum_\alpha c_\alpha \underset{\sim}{Q}\,\underset{\sim}{q}_\alpha \tag{15.22}$$



Here c_α is a coupling constant which describes the strength of the interaction between the system and bath mode α. Note, that this form suggests that the system vibration is a local mode interacting with a set of normal vibrations of the bath.

For the case of single quantum relaxation from $|a\rangle = |1\rangle$ to $b = |0\rangle$, we can write the coupling matrix element as

$$V_{ba} = \sum_\alpha \xi_{ab,\alpha}\left(a_\alpha^\dagger + a_\alpha\right) \tag{15.23}$$

where

$$\xi_{ab,\alpha} = c_\alpha \frac{\sqrt{m_Q m_q \omega_0 \omega_\alpha}}{2\hbar}\langle b|Q|a\rangle \tag{15.24}$$

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[1] Note that we are using an equilibrium property, the coupling correlation function, to describe a nonequilibrium process, the relaxation of an excited state. Underlying the validity of the expressions are the principles of linear response. In practice this also implies a time scale separation between the equilibration of the bath and the relaxation of the system state. The bath correlation function should work fine if it has rapidly equilibrated, even though the system may not have. An instance where this would work well is electronic spectroscopy, where relaxation and thermalization in the excited state occurs on picosecond time scales, whereas the electronic population relaxation is on nanosecond time scales.

Here the matrix element $\langle b|Q|a\rangle$ is taken in evaluating $\xi_{ab,\alpha}$. Evaluating eq. (15.17) is now much the same as problems we've had previously:

$$\begin{aligned}\left\langle V_{ab}(t)V_{ba}(0)\right\rangle_B &= \left\langle e^{iH_Bt}\,V_{ab}\,e^{-iH_Bt}\,V_{ba}\right\rangle_B \\ &= \sum_\alpha \xi_\alpha^2\left[\left(\bar{n}_\alpha+1\right)e^{-i\omega_\alpha t}+\bar{n}_\alpha\,e^{+i\omega_\alpha t}\right]\end{aligned} \tag{15.25}$$

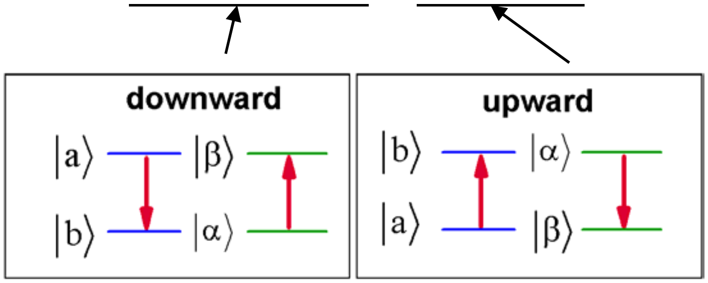
here $\bar{n}_\alpha=\left(e^{\beta\hbar\omega_\alpha}-1\right)^{-1}$ is the thermally averaged occupation number of the bath mode at ω_α. In evaluating this we take advantage of relationships we have used before

$$\begin{aligned}e^{iH_Bt}\,a_\alpha\,e^{-iH_Bt}&=a_\alpha e^{-i\omega_\alpha t}\\ e^{iH_Bt}\,a_\alpha^\dagger\,e^{-iH_Bt}&=a_\alpha^\dagger e^{+i\omega_\alpha t}\end{aligned} \tag{15.26}$$

$$\begin{aligned}\left\langle a_\alpha a_\alpha^\dagger\right\rangle&=\bar{n}_\alpha+1\\ \left\langle a_\alpha^\dagger a_\alpha\right\rangle&=\bar{n}_\alpha\end{aligned} \tag{15.27}$$

So, now by Fourier transforming (15.25) we have the rate as

$$k_{ba}=\frac{1}{\hbar^2}\sum_\alpha\left[\xi_\alpha\right]_{ab}^2\left[\underline{\left(\bar{n}_\alpha+1\right)\delta\left(\omega_{ba}+\omega_\alpha\right)}+\underline{\bar{n}_\alpha\delta\left(\omega_{ba}-\omega_\alpha\right)}\right] \tag{15.28}$$



This expression describes two relaxation processes which depend on temperature. The first is allowed at $T = 0$ K and is obeys $-\omega_{ba}=\omega_\alpha$. This implies that $E_a > E_b$, and that a loss of energy in the system is balanced by an equal rises in energy of the bath. That is $|\beta\rangle = |\alpha+1\rangle$. The second term is only allowed for elevated temperatures. It describes relaxation of the system by transfer to a higher energy state $E_b > E_a$, with a concerted decrease of the energy of the bath ($|\beta\rangle = |\alpha-1\rangle$). Naturally, this process vanishes if there is no thermal energy in the bath.[2]

To more accurately model the relaxation due to a continuum of modes, we can replace the explicit sum over bath states with an integral over a density of bath states W

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[2] There is an exact analogy between this problem and the interaction of matter with a quantum radiation field. The interaction potential is instead a quantum vector potential and the bath is the photon field of different electromagnetic modes. Equation (15.28) describes has two terms that describe emission and absorption processes. The leading term describes the possibility of spontaneous emission, where a material system can relax in the absence of light by emitting a photon at the same frequency.

$$k_{ba} = \frac{1}{\hbar^2} \int d\omega_\alpha W(\omega_\alpha) \xi_{ba}^2(\omega_\alpha) \Big[\big(\bar{n}(\omega_\alpha)+1\big) \delta(\omega_{ba}+\omega_\alpha) + \bar{n}(\omega_\alpha) \delta(\omega_{ba}-\omega_\alpha) \Big] \qquad (15.29)$$

We can also define a spectral density, which is the vibrational coupling-weighted density of states:

$$\rho(\omega_\alpha) \equiv W(\omega_\alpha) \xi_{ba}^2(\omega_\alpha) \qquad (15.30)$$

Then the relaxation rate is:

$$\begin{aligned} k_{ba} &= \frac{1}{\hbar^2} \int d\omega_\alpha W(\omega_\alpha) \xi_{ba}^2(\omega_\alpha) \Big[\big(\bar{n}(\omega_\alpha)+1\big) \delta(\omega_{ba}+\omega_\alpha) + \bar{n}(\omega_\alpha) \delta(\omega_{ba}-\omega_\alpha) \Big] \\ &= \frac{1}{\hbar^2} \Big[\big(\bar{n}(\omega_{ba})+1\big) \rho_{ba}(\omega_{ab}) + \bar{n}(\omega_{ba}) \rho_{ba}(-\omega_{ab}) \Big] \end{aligned} \qquad (15.31)$$

We see that the Fourier transform of the fluctuating coupling correlation function, is equivalent to the coupling-weighted density of states, which we evaluate at ω_{ba} or $-\omega_{ba}$ depending on whether we are looking at upward or downward transitions. Note that $\bar{n}$ still refers to the occupation number for the bath, although it is evaluated at the energy splitting between the initial and final system states. Equation (15.31) is a full quantum expression, and obeys detailed balance between the upward and downward rates of transition between two states:

$$k_{ba} = \exp(-\beta\hbar\omega_{ab}) k_{ab} \qquad (15.32)$$

From our description of the two level system in a harmonic bath, we see that high frequency relaxation ($kT << \hbar\omega_0$) only proceeds with energy from the system going into a mode of the bath at the same frequency, but at lower frequencies ($kT \approx \hbar\omega_0$) that energy can flow both into the bath and from the bath back into the system. When the vibration has energies that are thermally populated in the bath, we return to the classical picture of a vibration in a fluctuating environment that can dissipate energy from the vibration as well as giving kicks that increase the energy of the vibration. Note that in a cascaded relaxation scheme, as one approaches *kT*, the fraction of transitions that increase the system energy increase. Also, note that the bi-linear coupling in eq. (15.22) and used in our treatment of quantum fluctuations can be associated with fluctuations of the bath that induce changes in energy (relaxation) and shifts of frequency (dephasing).

Multiquantum relaxation of polyatomic molecules[3]

Vibrational relaxation of polyatomic molecules in solids or in solution involves anharmonic coupling of energy between internal vibrations of the molecule, also called IVR (internal vibrational energy redistribution). Mechanical interactions between multiple modes of vibration

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[3] V. M. Kenkre, A. Tokmakoff and M. D. Fayer, "Theory of vibrational relaxation of polyatomic molecules in liquids,"*J. Chem. Phys.,* **101**, 10618 (1994).

of the molecule act to rapidly scramble energy deposited into one vibrational coordinate and lead to cascaded energy flow toward equilibrium.

For this problem the bilinear coupling above doesn't capture the proper relaxation process. Instead we can express the molecular potential energy in terms of well-defined normal modes of vibration for the system and the bath, and these interact weakly through small anharmonic terms in the potential. Then we can extend the perturbative approach above to include the effect of multiple accepting vibrations of the system or bath. For a set of system and bath coordinates, the potential energy for the system and system–bath interaction can be expanded as

$$V_S + V_{SB} = \frac{1}{2}\sum_a \frac{\partial^2 V}{\partial Q_a^2} Q_a^2 + \frac{1}{6}\sum_{a,\alpha,\beta} \frac{\partial^3 V}{\partial Q_a \partial q_\alpha \partial q_\beta} Q_a q_\alpha q_\beta + \frac{1}{6}\sum_{a,b,\alpha} \frac{\partial^3 V}{\partial Q_a \partial Q_b \partial q_\alpha} Q_a Q_b q_\alpha \cdots \tag{15.33}$$

Focusing explicitly on the first cubic expansion term, for one system oscillator:

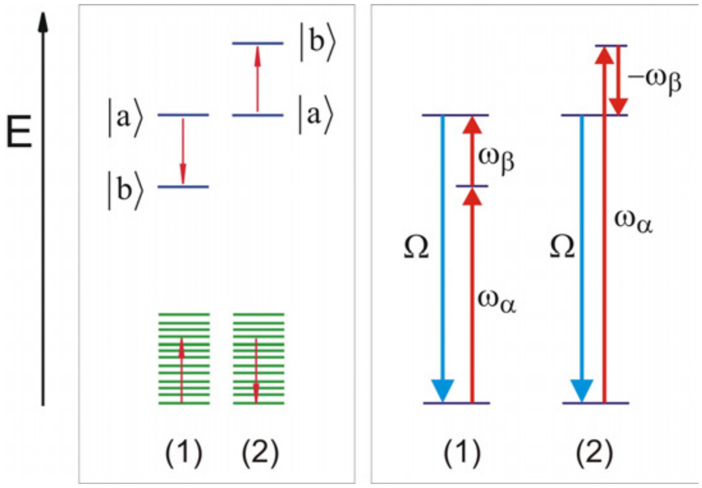
$$V_S + V_{SB} = \frac{1}{2} m\Omega^2 \underset{\sim}{Q}^2 + V^{(3)} \underset{\sim}{Q}\,\underset{\sim}{q}_\alpha \underset{\sim}{q}_\beta \tag{15.34}$$

Here, the system–bath interaction potential describes the case for a cubic anharmonic coupling that involves one vibration of the system Q interacting weakly with two vibrations of the bath $\underset{\sim}{q}_\alpha$ and $\underset{\sim}{q}_\beta$, so that $\hbar\Omega >> V^{(3)}$. Energy deposited in the system vibration will dissipate to the two vibrations of the bath, a three quantum process. Higher-order expansion terms would describe interactions involving four or more quanta.

Working specifically with the cubic example, we can use the harmonic bath model to calculate the rate of energy relaxation. This picture is applicable if a vibrational mode of frequency Ω relaxes by transferring its energy to another vibration nearby in energy (ω_α), and the energy difference ω_β being accounted for by a continuum of intermolecular motions. For this case one can show

$$k_{ba} = \frac{1}{\hbar^2}\Big[\big(\bar{n}(\omega_\alpha)+1\big)\big(\bar{n}(\omega_\beta)+1\big)\rho_{ba}(\omega_{ab}) + \big(\bar{n}(\omega_\alpha)+1\big)\bar{n}(\omega_\beta)\rho_{ba}(\omega_{ab})\Big] \tag{15.35}$$

where $\rho(\omega) \equiv W(\omega)\big(V^{(3)}(\omega)\big)^2$. Here we have taken $\Omega, \omega_\alpha >> \omega_\beta$. These two terms describe two possible relaxation pathways, the first in which annihilation of a quantum of Ω leads to a creation of one quantum each of ω_α and ω_β. The second term describes the dissipation of energy by coupling to a higher energy vibration, with the excess energy being absorbed from the bath. Annihilation of a quantum of Ω leads to a creation of one quantum of ω_α and the annihilation of one quantum of ω_β. Naturally this latter term is only allowed when there is adequate thermal energy present in the bath.



Rate calculations using classical vibrational relaxation

In general, we would like a practical way to calculate relaxation rates, and calculating quantum correlation functions is not practical. How do we use classical calculations for the bath, for instance drawing on a classical molecular dynamics simulation? Is there a way to get a quantum mechanical rate?

The first problem is that the quantum correlation function is complex $C_{ab}^{*}(t)=C_{ab}(-t)$ and the classical correlation function is real and even $C_{Cl}(t)=C_{Cl}(-t)$. In order to connect these two correlation functions, one can derive a quantum correction factor that allows one to predict the quantum correlation function on the basis of the classical one. This is based on the assumption that at high temperature it should be possible to substitute the classical correlation function with the real part of the quantum correlation function

$$C_{Cl}(t) \Rightarrow C'_{ba}(t) \tag{15.36}$$

To make this adjustment we start with the frequency domain expression derived from the detailed balance expression $\tilde{C}(-\omega)=e^{-\beta\hbar\omega}\tilde{C}(\omega)$

$$\tilde{C}(\omega)=\frac{2}{1+\exp(-\beta\hbar\omega)}\tilde{C}'(\omega) \tag{15.37}$$

Here $\tilde{C}'(\omega)$ is defined as the Fourier transform of the real part of the quantum correlation function. So the vibrational relaxation rate is

$$k_{ba}=\frac{4}{\hbar^2\left(1+\exp\left(-\hbar\omega_{ba}/kT\right)\right)}\int_0^\infty dt\, e^{-i\omega_{ba}t}\,\mathrm{Re}\left[\left\langle V_{ab}(t)V_{ba}(0)\right\rangle\right] \tag{15.38}$$

Now we will assume that one can replace a classical calculation of the correlation function here as in eq. (15.36). The leading term out front can be considered a "quantum correction factor" that accounts for the detailed balance of rates encoded in the quantum spectral density.

In practice such a calculation might be done with molecular dynamics simulations. Here one has an explicit characterization of the intermolecular forces that would act to damp the excited vibrational mode. One can calculate the system–bath interactions by expanding the vibrational potential of the system in the bath coordinates

$$\begin{aligned} V_S + V_{SB} &= V_0 + \sum_\alpha \frac{\partial V^\alpha}{\partial Q} Q + \sum_\alpha \frac{\partial^2 V^\alpha}{\partial Q^2} Q^2 + \cdots \\ &= V_0 + FQ + GQ^2 + \cdots \end{aligned} \tag{15.39}$$

Here V^α represents the potential of an interaction of one solvent coordinate acting on the excited vibrational system coordinate Q. The second term in this expansion FQ depends linearly on the system Q and bath α coordinates, and we can use variation in this parameter to calculate the correlation function for the fluctuating interaction potential. Note that F is the *force* that molecules exert on Q! Thus the relevant classical correlation function for vibrational relaxation is a force correlation function

$$C_{Cl}(t) = \langle F(t) F(0) \rangle \tag{15.40}$$

$$k_{Cl} = \frac{1}{kT} \int_0^\infty dt \cos \omega_{ba} t \langle F(t) F(0) \rangle \tag{15.41}$$

Readings

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15.2. A DENSITY MATRIX DESCRIPTION OF QUANTUM RELAXATION

Here we will more generally formulate a quantum mechanical picture of coherent and incoherent relaxation processes that occur as the result of interaction between a prepared system and its environment. This description will apply to the case where we separate the degrees of freedom in our problem into a system and a bath that interact. We have limited information about the bath degrees of freedom. As a statistical mixture, we only have knowledge of the probability of occupying states of the bath and not of the phase relationships required to describe a deterministic quantum system. For such problems, the density matrix is the natural tool.

Mixed States

How does a system get into a mixed state? Generally, if you have two systems and you put these in contact with each other, interaction between the two will lead to a new system that is inseparable. Imagine that I have two systems H_S and H_B for which the eigenstates of H_S are $|a\rangle$ and those of H_B are $|\alpha\rangle$.

$$H_0 = H_S + H_B \tag{15.42}$$

$$\begin{aligned} H_S|a\rangle &= E_a|a\rangle \\ H_B|\alpha\rangle &= E_\alpha|\alpha\rangle \end{aligned} \tag{15.43}$$

In general, before these systems interact, they can be described in terms of product states in the eigenstates of H_S and H_B:

$$|\psi(t_0)\rangle = |\psi_S^0\rangle|\psi_B^0\rangle \tag{15.44}$$

$$|\psi_S^0\rangle = \sum_a s_a|a\rangle \qquad |\psi_B^0\rangle = \sum_\alpha b_\alpha|\alpha\rangle \tag{15.45}$$

$$|\psi_0\rangle = \sum_{a,\alpha} s_a b_\alpha |a\rangle|\alpha\rangle \tag{15.46}$$

After these states are allowed to interact, we have a new state vector $|\psi(t)\rangle$. The new state can still be expressed in the zero-order basis, although this does not represent the eigenstates of the new Hamiltonian

$$H = H_0 + V \tag{15.47}$$

$$|\psi(t)\rangle = \sum_{a,\alpha} c_{a\alpha}|a\alpha\rangle \tag{15.48}$$

For any point in time, $c_{a\alpha}$ is the joint probability amplitude for finding particle of $|\psi_S\rangle$ in $|a\rangle$ and simultaneously finding particle of $|\psi_B\rangle$ in $|\alpha\rangle$. At $t = t_0$, $c_{a\alpha} = s_a b_\alpha$.

Now suppose that you have an operator *A* that is only an operator in the $\left|\psi_S\right\rangle$ coordinates. This might represent an observable for the system that you wish to measure. Let's calculate the expectation value of *A*

$$\left\langle A(t)\right\rangle = \left\langle \psi(t)\middle|A\middle|\psi(t)\right\rangle = \left\langle \psi_S\middle|A\middle|\psi_S\right\rangle \tag{15.49}$$

$$\begin{aligned}\left\langle A(t)\right\rangle &= \sum_{\substack{a,\alpha\\b,\beta}} c^*_{a\alpha} c_{b\beta} \left\langle a\alpha\middle|A\middle|b,\beta\right\rangle \\ &= \sum_{\substack{a,\alpha\\b,\beta}} c^*_{a\alpha} c_{b\beta} \left\langle a\middle|A\middle|b\right\rangle \delta_{\alpha\beta} \\ &= \sum_{a,b}\left(\sum_{\alpha} c^*_{a\alpha} c_{b\alpha}\right) A_{ab} \\ &\equiv \sum_{a,b} \left(\rho_S\right)_{ba} A_{ab} \\ &= Tr\left[\rho_S A\right]\end{aligned} \tag{15.50}$$

Here we have defined a density matrix for the degrees of freedom in $\left|\psi_S\right\rangle$

$$\rho_S = \left|\psi_S\right\rangle\left\langle\psi_S\right| \tag{15.51}$$

with density matrix elements that traced over the $\left|\psi_B\right\rangle$ states, that is, that are averaged over the probability of occupying the $\left|\psi_B\right\rangle$ states.

$$\left|b\right\rangle \rho_S \left\langle a\right| = \sum_{\alpha} c^*_{a\alpha} c_{b\alpha} \tag{15.52}$$

Here the matrix elements in direct product states involve elements of a four-dimensional matrix, which are specified by the tetradic notation.

We have defined a trace of the density matrix over the unobserved degrees of freedom in $\left|\psi_B\right\rangle$, i.e. a sum over diagonal elements in α. To relate this to our similar prior expression: $\left\langle A(t)\right\rangle = Tr\left[\rho A\right]$, the following definitions are useful:

$$\begin{aligned}\rho_S &= Tr_B\left(\rho\right) \\ &= \sum_{a,b} \left(\rho_S\right)_{ba} A_{ab} \\ &= Tr\left(\rho_S A\right)\end{aligned} \tag{15.53}$$

Also,

$$Tr\left(A\times B\right) = Tr\left(A\right) Tr\left(B\right) \tag{15.54}$$

Since ρ_S is Hermitian, it can be diagonalized by a unitary transformation *T*, where the new eigenbasis $\left|m\right\rangle$ represents the mixed states of the $\left|\psi_S\right\rangle$ system.

$$\rho_S = \sum_m |m\rangle\langle m|\, \rho_{mm} \tag{15.55}$$

$$\sum_m \rho_{mm} = 1 \tag{15.56}$$

The density matrix elements represent the probability of occupying state $|m\rangle$ averaged over the bath degrees of freedom

$$\begin{aligned}\rho_{mm} &= \sum_{a,b} T_{mb}\rho_{ba}\, T^{\dagger}_{am} \\ &= \sum_{a,b,\alpha} a_{b\alpha} T_{mb} a^{*}_{a\alpha}\, T^{*}_{ma} \\ &= \sum_{\alpha} f_{m\alpha} f^{*}_{m\alpha} \\ &= \sum_{\alpha} |f_{m\alpha}|^2 = p_m \geq 0\end{aligned} \tag{15.57}$$

The quantum mechanical interaction of one system with another causes the system to be in a mixed state after the interaction. The mixed states are generally not separable into the original states. The mixed state is described by

$$|\psi_S\rangle = \sum_m d_m |m\rangle \tag{15.58}$$

$$d_m = \sum_{\alpha} f_{m\alpha} \tag{15.59}$$

If we only observe a few degrees of freedom, we can calculate observables by tracing over unobserved degrees of freedom. This forms the basis for treating relaxation phenomena. A few degrees of freedom that we observe, coupled to many other degrees of freedom, which lend to irreversible relaxation.

Equation of motion for the reduced density matrix

So now to describe irreversible processes in quantum systems, let's look at the case where we have partitioned the problem so that we have a few degrees of freedom that we are most interested in (the system), which is governed by H_S and which we observe with a system operator A. The remaining degrees of freedom are a bath, which interact with the system. The Hamiltonian is given by eqs. (15.42) and (15.47). In our observations, we will be interested in expectation values in A which we have seen are written

$$\begin{aligned}\langle A_S\rangle &= Tr\left[\rho(t)A\right]\\ &= Tr_S\left[\sigma(t)A\right]\\ &= \sum_{a,b}\sigma_{ab}(t)A_{ba}\\ &= Tr_S Tr_B\left[\rho(t)A\right]\end{aligned} \tag{15.60}$$

Here σ is the reduced density operator for the system degrees of freedom. This is the more commonly variable used for ρ_S.

$$\sigma_{ab} = \sum_{\alpha}\langle a\alpha|\rho|b\alpha\rangle = Tr_B\rho_{ab} \tag{15.61}$$

Tr_B and Tr_S are partial traces over the bath and system respectively. Note, that since $Tr(A\times B) = TrA\,TrB$ for direct product states, all we need to do is describe time evolution of σ to understand the time dependence to A.

We obtain the equation of motion for the reduced density matrix beginning with

$$\rho(t) = U(t)\rho(0)U^{\dagger}(t) \tag{15.62}$$

and tracing over bath:

$$\sigma(t) = Tr_B\left[U\rho U^{\dagger}\right] \tag{15.63}$$

We can treat the time evolution of the reduced density matrix in the interaction picture. From our earlier discussion of the density matrix, we integrate the equation of motion

$$\dot{\rho}_I = -\frac{i}{\hbar}\left[V_I(t),\rho_I(t)\right] \tag{15.64}$$

to obtain

$$\rho_I(t) = \rho_I(0) - \frac{i}{\hbar}\int_0^t d\tau\left[V_I(\tau),\rho_I(\tau)\right] \tag{15.65}$$

Remember that the density matrix in the interaction picture is

$$\rho_I(t) = U_0^{\dagger}\rho(t)U_0 = e^{i(H_S+H_B)t/\hbar}\,\rho(t)e^{-i(H_s+H_B)t/\hbar} \tag{15.66}$$

and similarly

$$V_I(t) = U_0^{\dagger}VU_0 = e^{i(H_S+H_B)t/\hbar}\,V(t)e^{-i(H_s+H_B)t/\hbar} \tag{15.67}$$

Substituting (15.65) into (15.64) we have

$$\dot{\rho}_I(t) = -\frac{i}{\hbar}\left[V_I(t),\rho_I(t_0)\right] - \frac{1}{\hbar^2}\int_0^t dt'\left[V_I(t),\left[V_I(t'),\rho_I(t')\right]\right] \tag{15.68}$$

Now taking a trace over the bath states

$$\dot{\sigma}_I(t) = -\frac{i}{\hbar}Tr_B\left[V_I(t),\rho_I(t_0)\right] - \frac{1}{\hbar^2}\int_0^t dt'\,Tr_B\left[V_I(t),\left[V_I(t'),\rho_I(t')\right]\right] \tag{15.69}$$

If we assume that the interaction of the system and bath is small enough that the system cannot change the bath

$$\rho_I(t) \approx \sigma_I(t)\,\rho_B(0) = \sigma_I(t)\,\rho_{eq}^B \tag{15.70}$$

$$\rho_{eq}^B = \frac{e^{-\beta H_B}}{Z} \tag{15.71}$$

Then we obtain an equation of motion for σ to second order:

$$\dot{\sigma}_I(t) = -\frac{i}{\hbar} Tr_B\left[V_I(t), \sigma_I(0)\,\rho_{eq}^B\right] - \frac{1}{h^2}\int_0^t dt'\, Tr_B\left[V_I(t), \left[V_I(t'), \sigma_I(t')\,\rho_{eq}^B\right]\right] \tag{15.72}$$

The last term involves an integral over a correlation function for a fluctuating interaction potential. This looks similar to a linear response function, and also the same form as the relaxation rates from Fermi's Golden Rule that we just discussed. The first term in eq. (15.72) involves a thermal average over the interaction potential, $\langle V\rangle_B = Tr_B\left[V\rho_{eq}^B\right]$. If this average value is zero, which would be the case for an off-diagonal form of *V*, we can drop the first term in the equation of motion for σ_I. If it were not zero, it is possible to redefine the Hamiltonian such that $H_0 \to H_0 + \langle V\rangle_B$ and $V(t) \to V(t) - \langle V\rangle_B$, which recasts it in a form where $\langle V\rangle_B \to 0$ and the first term can be neglected.

Now let's evaluate the equation of motion for the case where the system–bath interaction can be written as a product of operators in the system $\hat{A}$ and bath $\hat{\beta}$:

$$H_{SB} = V = \hat{A}\hat{\beta} \tag{15.73}$$

This is equivalent to the bilinear coupling form that was used in our prior description of dephasing and population relaxation. There we took the interaction to be linearly proportional to the system and bath coordinate(s): $V = c\underset{\sim}{Q}\underset{\sim}{q}$. The time evolution in the two variables is separable and given by

$$\begin{aligned} \hat{A}(t) &= U_S^\dagger \hat{A}(t_0)\, U_S \\ \hat{\beta}(t) &= U_B^\dagger \hat{\beta}(t_0)\, U_B \end{aligned} \tag{15.74}$$

The equation of motion for σ_I becomes

$$\begin{aligned} \dot{\sigma}_I(t) = \frac{1}{\hbar^2}\int_0^t dt' &\left[\hat{A}(t)\hat{A}(t')\sigma(t') - \hat{A}(t')\sigma(t')\hat{A}(t)\right] Tr_B\left(\hat{\beta}(t)\hat{\beta}(t')\rho_{eq}^B\right) \\ &-\left[\hat{A}(t)\sigma(t')\hat{A}(t') - \sigma(t')\hat{A}(t')\hat{A}(t)\right] Tr_B\left(\hat{\beta}(t')\hat{\beta}(t)\rho_{eq}^B\right) \end{aligned} \tag{15.75}$$

Here the history of the evolution of $\hat{A}$ depends on the time dependence of the bath variables coupled to the system. The time dependence of the bath enters as a bath correlation function

$$C_{\beta\beta}(t-t') = Tr_B\left(\hat{\beta}(t)\hat{\beta}(t')\rho_{eq}^B\right) \\ = \left\langle \hat{\beta}(t)\hat{\beta}(t')\right\rangle_B = \left\langle \hat{\beta}(t-t')\hat{\beta}(0)\right\rangle_B \tag{15.76}$$

The bath correlation function can be evaluated using the methods that we have used in the Energy Gap Hamiltonian and Brownian Oscillator Models. Switching integration variables to the time interval prior to observation

$$\tau = t - t' \tag{15.77}$$

we obtain

$$\dot{\sigma}_I(t) = -\frac{1}{\hbar^2}\int_0^t d\tau \left[\hat{A}(t), \hat{A}(t-\tau)\sigma_I(t-\tau)\right] C_{\beta\beta}(\tau) - \left[\hat{A}(t), \sigma_I(t-\tau)\hat{A}(t-\tau)\right] C_{\beta\beta}^*(\tau). \tag{15.78}$$

Here we have made use of $C_{\beta\beta}^*(\tau) = C_{\beta\beta}(-\tau)$. For the case that the system–bath interaction is a result of interactions with many bath coordinates

$$V = \sum_\alpha \hat{A}\hat{\beta}_\alpha \tag{15.79}$$

then eq. (15.78) becomes

$$\dot{\sigma}_I(t) = -\frac{1}{\hbar^2}\sum_{\alpha,\beta}\int_0^t d\tau \left[\hat{A}(t), \hat{A}(t-\tau)\sigma_I(t-\tau)\right] C_{\alpha\beta}(\tau) - \left[\hat{A}(t), \sigma_I(t-\tau)\hat{A}(t-\tau)\right] C_{\alpha\beta}^*(\tau)$$

(15.80)

with the bath correlation function

$$C_{\alpha\beta}(\tau) = \left\langle \hat{\beta}_\alpha(\tau)\hat{\beta}_\beta(0)\right\rangle_B \tag{15.81}$$

Equation (15.78) or (15.80) indicates that the rates of exchange of amplitude between the system states carries memory of the bath's influence on the system, that is, $\sigma_I(t)$ is dependent on $\sigma_I(t-\tau)$. If we make the Markov approximation, for which the dynamics of the bath are much faster than the evolution of the system and where the system has no memory of its past, we would replace

$$\sigma(t') = \sigma(t')\delta(t-t') \Rightarrow \sigma(t) \tag{15.82}$$

in eq. (15.75), or equivalently in eq. (15.78) set

$$\sigma_I(t-\tau) \Rightarrow \sigma_I(t) \tag{15.83}$$

For the subsequent work, we use this approximation. Similarly, the presence of a time scale separation between a slow system and a fast bath allows us to change the upper integration limit in eq. (15.78) from *t* to ∞.

Evaluating the equation of motion: Redfield equations

Do describe the exchange of amplitude between system states induced by the bath, we will want to evaluate the matrix elements of the reduced density matrix in the system eigenstates. To begin, we use eq. (15.78) to write the time-dependent matrix elements as

$$\begin{aligned}\dot{\sigma}^I_{ab}(t) = -\sum_{c,d}\frac{1}{\hbar^2}\int_0^\infty d\tau \Big[\hat{A}_{ac}(t)\hat{A}_{cd}(t-\tau)\sigma^I_{db}(t) - \hat{A}_{ac}(t-\tau)\,\sigma^I_{cd}(t)\,\hat{A}_{db}(t)\ \Big]C_{\beta\beta}(\tau) \\ -\Big[\hat{A}_{ac}(t)\sigma^I_{cd}(t)\,\hat{A}_{db}(t-\tau) - \sigma^I_{ac}(t)\,\hat{A}_{cd}(t-\tau)\,\hat{A}_{db}(t)\Big]\,C^*_{\beta\beta}(\tau)\end{aligned} \tag{15.84}$$

Now, let's convert the time dependence expressed in terms of the interaction picture into a Schrodinger representation using

$$\left\langle a\middle|A(t)\middle|b\right\rangle = e^{i\omega_{ab}t}A_{ab}$$

$$\left\langle a\middle|\sigma^I\middle|b\right\rangle = e^{i\omega_{ab}t}\sigma_{ab} \tag{15.85}$$

To see how this turns out, consider the first term in eq. (15.84):

$$\dot{\sigma}^I_{ab} = \frac{\partial}{\partial t}\left\langle a\middle|\sigma^I\middle|b\right\rangle$$

$$\dot{\sigma}^I_{ab}(t) = -\sum_{c,d}\frac{1}{\hbar^2}\int_0^\infty d\tau\,\hat{A}_{ac}(t)\hat{A}_{cd}(t-\tau)\sigma^I_{db}(t)\,C_{\beta\beta}(\tau) \tag{15.86}$$

$$\dot{\sigma}_{ab}(t)e^{i\omega_{ab}\tau} + i\omega_{ab}e^{i\omega_{ab}\tau}\sigma_{ab} = -\sum_{c,d}\frac{1}{\hbar^2}\,\hat{A}_{ac}\hat{A}_{cd}\,\sigma_{db}(t)\,e^{i\omega_{ac}t+i\omega_{cd}t+i\omega_{db}t}\int_0^\infty d\tau e^{-i\omega_{cd}\tau}\,C_{\beta\beta}(\tau) \tag{15.87}$$

Defining the Fourier-Laplace transform of the bath correlation function:

$$\tilde{C}_{\beta\beta}(\omega) = \int_0^\infty d\tau e^{i\omega\tau}\,C_{\beta\beta}(\tau) \tag{15.88}$$

We have

$$\dot{\sigma}_{ab}(t) = -i\omega_{ab}\sigma_{ab} - \sum_{c,d}\frac{1}{\hbar^2}\,\hat{A}_{ac}\hat{A}_{cd}\,\sigma_{db}(t)\,\tilde{C}_{\beta\beta}(\omega_{dc}) \tag{15.89}$$

Here the spectral representation of the bath correlation function is being evaluated at the energy gap between system states ω_{dc}. So the evolution of coherences and populations in the system states is governed by their interactions with other system states, governed by the matrix elements, and this is modified depending on the fluctuations of the bath at different system state energy gaps. In this manner, eq. (15.84) becomes

$$\begin{aligned}\dot{\sigma}_{ab}(t) = -i\omega_{ab}\sigma_{ab}(t) - \frac{1}{\hbar^2}\sum_{c,d}\Big[\,\hat{A}_{ac}\hat{A}_{cd}\,\sigma_{db}(t)\,\tilde{C}_{\beta\beta}(\omega_{dc}) - \hat{A}_{ac}\hat{A}_{db}\,\sigma_{cd}(t)\,\tilde{C}_{\beta\beta}(\omega_{ca}) \\ - \hat{A}_{ac}\hat{A}_{db}\,\sigma_{cd}(t)\,\tilde{C}^*_{\beta\beta}(-\omega_{db}) + \hat{A}_{cd}\hat{A}_{db}\,\sigma_{ac}(t)\,\tilde{C}^*_{\beta\beta}(-\omega_{cd})\Big]\end{aligned} \tag{15.90}$$

$$= -i\omega_{ab}\sigma_{ab}(t) - \sum_{c,d}\Big[\Gamma^+_{ac,cd}\,\sigma_{db}(t) - \Gamma^-_{ac,db}\,\sigma_{cd}(t) - \Gamma^+_{ac,db}\,\sigma_{cd}(t) + \Gamma^-_{cd,db}\,\sigma_{ac}(t)\Big]. \tag{15.91}$$

The rate constants are defined through:

$$\Gamma^{+}_{ab,cd}=\frac{1}{\hbar^2}A_{ab}A_{cd}\,\tilde{C}_{\beta\beta}(\omega_{dc}) \tag{15.92}$$

$$\Gamma^{-}_{ab,cd}=\frac{1}{\hbar^2}A_{ab}A_{cd}\,\tilde{C}_{\beta\beta}(\omega_{ba}) \tag{15.93}$$

Here we made use of $\tilde{C}^{*}_{\beta\beta}(\omega)=\tilde{C}_{\beta\beta}(-\omega)$. Also, it is helpful to note that

$$\Gamma^{+}_{ab,cd}=[\Gamma^{-}_{dc,ba}]^{*} \tag{15.94}$$

The coupled differential equations in eq. (15.91) express the relaxation dynamics of the system states almost entirely in terms of the system Hamiltonian. The influence of the bath only enters through the bath correlation function.

The common alternate way of writing these expressions is in terms of the relaxation superoperator **R**

$$\dot{\sigma}_{ab}(t)=-i\omega_{ab}\sigma_{ab}-\sum_{c,d}R_{ab,cd}\,\sigma_{cd}(t) \tag{15.95}$$

or in the interaction picture

$$\dot{\sigma}^{I}_{ab}(t)=\sum_{c,d}\sigma^{I}_{cd}(t)\,R_{ab,cd}\;e^{i(E_a-E_b-E_c+E_d)t/\hbar} \tag{15.96}$$

Equation (15.95), the reduced density matrix equation of motion for a Markovian bath, is known as the Redfield equation. It describes the irreversible and oscillatory components of the amplitude in the $|a\rangle\langle b|$ coherence as a result of dissipation to the bath and feeding from other states. **R** describes the rates of change of the diagonal and off-diagonal elements of σ_I and is expressed as:

$$R_{ab,cd}=\delta_{db}\sum_k\Gamma^{+}_{ak,kc}-\Gamma^{+}_{db,ad}-\Gamma^{-}_{db,ad}+\delta_{ac}\sum_k\Gamma^{-}_{dk,kb} \tag{15.97}$$

where *k* refers to a system state.

The derivation described above can be performed without assuming a form to the system–bath interaction potential as we did in eq. (15.73). If so, one can write the relaxation operator in terms of a correlation function for the system–bath interaction

$$\Gamma^{+}_{ab,cd}=\frac{1}{\hbar^2}\int_0^\infty d\tau\,\langle V_{ab}(\tau)V_{cd}(0)\rangle_B\,e^{-i\omega_{cd}\tau} \tag{15.98}$$

$$\Gamma^{-}_{ab,cd}=\frac{1}{\hbar^2}\int_0^\infty d\tau\,\langle V_{ab}(0)V_{cd}(\tau)\rangle_B\,e^{-i\omega_{ab}\tau} \tag{15.99}$$

The tetradic notation for the Redfield relaxation operator allows us to identify four classes of relaxation processes, depending on the number of states involved:

aa,aa : Population relaxation (rate of loss of the population in *a*)

ab,ab : Coherence relaxation or dephasing (damping of the coherence *ab*)

aa,bb : Population transfer (rate of transfer of population from state *b* to state *a*)

ab,cd : Coherence transfer (rate at which amplitude in an oscillating superposition between two states (*c* and *d*) couples to form oscillating amplitude between two other states (*a* and *b*)

The origin and meaning of these terms will be discussed below.

Secular Approximation

From eq. (15.96) we note that the largest changes in matrix elements of σ_I result from a resonance condition:

$$\begin{aligned} \exp\left[i\left(E_a - E_b - E_c + E_d\right)t/\hbar\right] &\approx 1 \\ E_a - E_b - E_c + E_d &\approx 0 \end{aligned} \tag{15.100}$$

which is satisfied when:

$$\begin{aligned} a = c\ ;\ b = d \qquad & \Rightarrow R_{ab,ab} \\ a = b\ ;\ c = d \qquad & \Rightarrow R_{aa,cc} \\ a = b = c = d \qquad & \Rightarrow R_{aa,aa} \end{aligned} \tag{15.101}$$

In evaluating relaxation rates, often only these *secular* terms are retained. Whether this approximation is valid must be considered on a case by case basis and depends on the nature of the system eigenvalues and the bath correlation function.

Population Relaxation and the Master Equation

To understand the information in the relaxation operator and the classification of relaxation processes, let's first consider the relaxation of the diagonal elements of the reduced density matrix. Using the secular approximation,

$$\dot{\sigma}_{aa}\left(t\right) = -\sum_b R_{aa,bb}\sigma_{bb}\left(t\right) \tag{15.102}$$

Considering first the case that $a \neq b$, eq. (15.97) gives the relaxation operator as

$$R_{aa,bb} = -\Gamma^{+}_{ba,ab} - \Gamma^{-}_{ba,ab} \tag{15.103}$$

Recognizing that Γ^{+} and Γ^{-} are Hermitian conjugates,

$$\begin{aligned} R_{aa,bb} &= -\frac{1}{\hbar^2}\left|A_{ab}\right|^2 \int_0^{\infty} d\tau C_{\beta\beta}\left(\tau\right) e^{-i\omega_{ba}\tau} + c.c. \\ &= -\frac{1}{\hbar^2}\int_0^{\infty} d\tau \left\langle V_{ba}\left(\tau\right) V_{ab}\left(0\right)\right\rangle_B e^{-i\omega_{ab}\tau} + c.c. \end{aligned} \tag{15.104}$$

So $R_{aa,bb}$ is a real valued quantity. However, since $\left\langle V_{ba}\left(\tau\right)V_{ab}\left(0\right)\right\rangle = \left\langle V_{ba}\left(0\right)V_{ab}\left(-\tau\right)\right\rangle$,

$$R_{aa,bb} = -\frac{1}{\hbar^2}\int_{-\infty}^{+\infty} dt \left\langle V_{ba}\left(\tau\right) V_{ab}\left(0\right)\right\rangle_B e^{i\omega_{ba}\tau} \tag{15.105}$$

So we see that the relaxation tensor gives the population relaxation rate between states *a* and *b* that we derived from Fermi's Golden rule:

$$R_{aa,bb} = -w_{ab} \qquad \left(a \neq b\right). \tag{15.106}$$

For the case that *a* = *b*, eq. (15.97) gives the relaxation operator as

$$\begin{aligned} R_{aa,aa} &= -\left(\Gamma^{+}_{aa,aa} + \Gamma^{-}_{aa,aa}\right) + \sum_{k}\left(\Gamma^{+}_{ak,ka} + \Gamma^{-}_{ak,ka}\right) \\ &= \sum_{k\neq a}\left(\Gamma^{+}_{ak,ka} + \Gamma^{-}_{ak,ka}\right) \end{aligned} \tag{15.107}$$

The relaxation accounts for the bath-induced dissipation for interactions with all states of the system (last term), but with the influence of self-relaxation (first term) removed. The net result is that we are left with the net rate of relaxation from *a* to all other system states (*a* ≠ *k*)

$$R_{aa,aa} = \sum_{k\neq a} w_{ka} \tag{15.108}$$

This term $R_{aa,aa}$ is also referred to as the inverse of T_1, the population lifetime of the *a* state.

The combination of these observations shows that the diagonal elements of the reduced density matrix follow a master equation that describes the net gain and loss of population in a particular state

$$\dot{\sigma}_{aa}\left(t\right) = \sum_{b\neq a} w_{ab}\,\sigma_{bb}\left(t\right) - \sum_{k\neq a} w_{ka}\,\sigma_{aa}\left(t\right) \tag{15.109}$$

Coherence Relaxation

Now let's consider the relaxation of the off-diagonal elements of the reduced density matrix. It is instructive to limit ourselves at first to one term in the relaxation operator, so that we write the equation of motion as

$$\dot{\sigma}_{ab}\left(t\right) = -i\omega_{ab}\sigma_{ab}\left(t\right) - R_{ab,ab}\,\sigma_{ab}\left(t\right) + \cdots \tag{15.110}$$

The relaxation operator gives

$$R_{ab,ab} = -\left(\Gamma^{+}_{aa,bb} + \Gamma^{-}_{aa,bb}\right) + \sum_{k}\left(\Gamma^{+}_{ak,ka} + \Gamma^{-}_{bk,kb}\right) \tag{15.111}$$

$$= -\left(\Gamma^{+}_{aa,bb} + \Gamma^{-}_{aa,bb} - \Gamma^{+}_{aa,aa} - \Gamma^{-}_{bb,bb}\right) + \left(\sum_{k\neq a}\Gamma^{+}_{ak,ka} + \sum_{k\neq b}\Gamma^{-}_{bk,kb}\right) \tag{15.112}$$

In the second step, we have separated the sum into two terms, one involving relaxation constants for the two coherent states, and the second involving all other states. The latter term looks very similar to the relaxation rates in eq. (15.107). In fact, if we factor out the imaginary parts of these terms and add them as a correction to the frequency in eq. (15.110), $\omega_{ab} \to \omega_{ab} + \mathrm{Im}[term\,2]$, then the remaining expression is directly related to the population lifetimes of the *a* and *b* states:

$$\begin{aligned}\mathrm{Re}\left(\sum_{k\neq a}\Gamma^{+}_{ak,ka} + \sum_{k\neq b}\Gamma^{-}_{bk,kb}\right) &= \frac{1}{2}\sum_{k\neq b} w_{kb} - \frac{1}{2}\sum_{k\neq a} w_{ka} \\ &= \frac{1}{2}\left(\frac{1}{T_{1,a}} + \frac{1}{T_{1,b}}\right)\end{aligned} \tag{15.113}$$

This term accounts for the decay of the coherence as a sum of the rates of relaxation of the *a* and *b* states.

The meaning of the first term on the right hand side of eq. (15.112) is a little less obvious. If we write out the four contributing relaxation factors explicitly using the system–bath correlation functions in eqs. (15.98) and (15.99), the real part can be written as

$$\begin{aligned}\mathrm{Re}\left(\Gamma^{+}_{aa,bb} + \Gamma^{-}_{aa,bb} - \Gamma^{+}_{aa,aa} - \Gamma^{-}_{bb,bb}\right) &= \int_0^\infty d\tau \left\langle \left[V_{bb}(\tau) - V_{aa}(\tau)\right]\left[V_{bb}(0) - V_{aa}(0)\right]\right\rangle_B \\ &\equiv \int_0^\infty d\tau \left\langle \Delta V(\tau)\Delta V(0)\right\rangle_B\end{aligned} \tag{15.114}$$

In essence, this term involves an integral over a correlation function that describes variations in the *a-b* energy gap that varies as a result of its interactions with the bath. So this term, in essence, accounts for the fluctuations of the energy gap that we previously treated with stochastic models. Of course in the current case, we have made a Markovian bath assumption, so the fluctuations are treated as rapid and only assigned an interaction strength Γ which is related to the linewidth. In an identical manner to the fast modulation limit of the stochastic model we see that the relaxation rate is related to the square of the amplitude of modulation times the correlation time for the bath:

$$\begin{aligned}\int_0^\infty d\tau \left\langle \Delta V(\tau)\Delta V(0)\right\rangle_B &= \left\langle \Delta V^2\right\rangle \tau_c \\ &\equiv \Gamma \\ &= \frac{1}{T_2^*}\end{aligned} \qquad (15.115)$$

As earlier this is how the pure dephasing contribution to the Lorentzian lineshape is defined. It is also assigned a time
scale T_2^*.

So to summarize, we see that the relaxation of coherences has a contribution from pure-dephasing and from the lifetime of the states involved. Explicitly, the equation of motion in eq. (15.110) can be re-written

$$\dot{\sigma}_{ab}(t) = -i\underset{\sim}{\omega}_{ab}\sigma_{ab}(t) - \frac{1}{T_2}\sigma_{ab}(t) \qquad (15.116)$$

where the dephasing time is

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2}\left(\frac{1}{T_{1,a}} + \frac{1}{T_{1,b}}\right) \qquad (15.117)$$

and the frequency has been corrected as a result interactions with the bath with the (small) imaginary contributions to $R_{ab,ab}$:

$$\underset{\sim}{\omega}_{ab} = \omega_{ab} + \mathrm{Im}\left[R_{ab,ab}\right] \qquad (15.118)$$

Readings

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