

# Quantum Vibronic Effects on the Electronic Properties of Molecular Crystals

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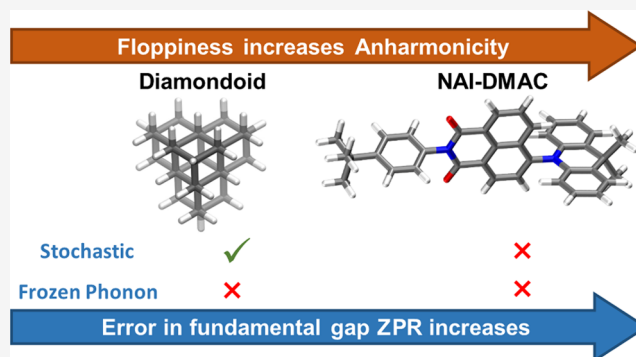


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**ABSTRACT:** We present a study of molecular crystals, focused on the effect of nuclear quantum motion and anharmonicity on their electronic properties. We consider a system composed of relatively rigid molecules, a diamondoid crystal, and one composed of floppier molecules, NAI-DMAC, a thermally activated delayed fluorescence compound. We compute fundamental electronic gaps at the density functional theory (DFT) level of theory, with the Perdew–Burke–Erzenhof (PBE) and strongly constrained and approximately normed (SCAN) functionals, by coupling first-principles molecular dynamics with a nuclear quantum thermostat. We find a sizable zero-point renormalization (ZPR) of the band gaps, which is much larger in the case of diamondoids (0.6 eV) than for NAI-DMAC (0.22 eV). We show that the frozen phonon (FP) approximation, which neglects intermolecular anharmonic effects, leads to a large error ( $\sim 50\%$ ) in the calculation of the band gap ZPR. Instead, when using a stochastic method, we obtain results in good agreement with those of our quantum simulations for the diamondoid crystal. However, the agreement is worse for NAI-DMAC where intramolecular anharmonicities contribute to the ZPR. Our results highlight the importance of accurately including nuclear and anharmonic quantum effects to predict the electronic properties of molecular crystals.



## 1. INTRODUCTION

Quantum vibronic effects play an important role in determining the temperature dependence of the electronic properties of molecules and solids, including their fundamental electronic gaps, as reported for small molecules,<sup>1,2</sup> nanoclusters,<sup>3–6</sup> and crystalline<sup>6–14</sup> and amorphous solids.<sup>15</sup> Hence, predicting quantum vibronic effects is critical to understanding the physical behavior of systems used in applications ranging from bioelectronics, thermoelectrics, and photovoltaics, to optical fiber technologies, spintronics, and quantum sensing.

In the first-principles electronic structure calculations of electron–phonon interactions, quantum vibronic effects are included using perturbative<sup>16</sup> or nonperturbative methods<sup>17</sup> such as frozen phonon (FP) and stochastic methods. All of these techniques rely on the harmonic approximation of the potential energy surface (PES). In addition, the FP method assumes that electronic eigenenergies are quadratic with respect to given phonon modes' coordinates, and perturbative methods also invoke the rigid ion approximation to represent the nuclear Hamiltonian. Previous work showed that the rigid ion approximation is not adequate to compute the renormalization of the fundamental gap of isolated molecules<sup>6,18</sup> and that the quadratic approximation is not sufficiently accurate for molecular crystals composed of small molecules.<sup>12</sup> Furthermore, recently, the validity of the harmonic approximation has been

questioned in the case of perovskites,<sup>19</sup> organic molecular crystals,<sup>14</sup> and amorphous carbon.<sup>15</sup>

The stochastic method is an interesting alternative to the FP technique, especially the so-called one-shot implementation<sup>20,21</sup> proposed by Zacharias et al. Using such a method, Monserrat et al. reported very large (1–2 eV) zero phonon renormalizations (ZPR) of the fundamental gap of molecular crystals composed of small molecules: CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, and HF, and discussed the limitations of the quadratic approximation within the FP method.<sup>12</sup> Using path-integral molecular dynamics simulations and a machine-learned potential, Alvertis et al. showed that the harmonic approximation, which underlies both the stochastic and FP methods, fails catastrophically for acene molecular crystals,<sup>14</sup> and their results challenged the validity of the stochastic method, at least for some molecular crystals. However, the authors of ref 14 also pointed out that the short-range nature of the machine-learned potentials employed in

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their study may introduce non-negligible residual error in band gap renormalizations.

First-principles molecular dynamics (FPMD) simulations<sup>22</sup> can fully account for anharmonic vibronic effects, but only at the classical level, yielding reliable results near or above the Debye temperature. Path-integral FPMD simulations<sup>23–25</sup> constitute an accurate framework to describe nuclear quantum effects (NQEs); however, due to their computational cost, they are rarely adopted to study electron–phonon interactions in molecules and solids. Recently, we showed that using a colored noise generalized Langevin equation thermostat (also known as quantum thermostat<sup>26–28</sup>), in conjunction with FPMD simulations, one can accurately predict the impact of NQEs on the electronic properties of several carbon-based systems with an affordable computational cost.<sup>6</sup>

Here, we use FPMD simulations with a quantum thermostat to accurately include anharmonic quantum vibronic effects and study their impact on the electronic properties of molecular crystals. We then compare FPMD results with those obtained using the FP and the stochastic one-shot methods to assess the validity of the approximations adopted when using these techniques. We investigate in detail two molecular crystals: one composed of a rigid diamondoid molecule, [1(2,3)4]-pentamantane,<sup>29</sup> and one composed of a floppy molecule, NAI-DMAC,<sup>30</sup> which has important applications for third-generation organic light-emitting diodes (OLED).<sup>30</sup> We found that for both crystals, the frozen phonon method performs poorly. For the pentamantane crystal, the stochastic method yields much improved results compared to those of FP. In contrast, for NAI-DMAC, the stochastic method does not lead to any substantial improvement. To understand the origin of the breakdown of the different approximations, we also perform calculations for isolated molecules which shed light on the importance of intra- and intermolecular anharmonicities on the vibronic coupling, and hence on their impact on electronic properties.

The rest of the paper is organized as follows. In Section 2, we describe the methods adopted in our work. We present our results for the pentamantane molecule and molecular crystal in Sections 3.1 and 3.2, respectively. The results obtained for both the isolated molecule and the crystal of NAI-DMAC are discussed in Section 3.3. Finally, we give our summary and conclusions in Section 4.

## 2. METHODS

**2.1. Theory.** Within the Born–Oppenheimer (BO) approximation, the Schrödinger equation of a system with  $N$  nuclei can be expressed as<sup>17</sup>

$$\begin{aligned} \hat{H}|\chi_k(\mathbf{R})\rangle &= \left( -\frac{1}{2} \sum_I \frac{1}{M_I} \nabla_{R_I}^2 + \mathcal{V}(\mathbf{R}) \right) |\chi_k(\mathbf{R})\rangle \\ &= \varepsilon_k |\chi_k(\mathbf{R})\rangle \end{aligned} \quad (1)$$

where  $M_I$  and  $\mathbf{R} = (R_{1x}, R_{1y}, \dots, R_{Nx})$  are the mass of the  $I$ -th nucleus and the Cartesian position vector of all nuclei with respect to a chosen origin, respectively. Here,  $\mathbf{r}$  and  $|\psi(\mathbf{r}; \mathbf{R})\rangle$  are the electronic coordinates and wave function, respectively.  $\mathcal{V}(\mathbf{R})$  and  $|\chi_k(\mathbf{R})\rangle$  represent the  $3N$ -dimensional adiabatic potential energy surface and the wave function for the  $k$ -th nuclear state, respectively. For simplicity, we consider only the vibrational modes at the  $\Gamma$ -point of the simulation supercell.

When the system is at equilibrium at a temperature  $T$ , the effect of electron–phonon interaction on the electronic property  $O(\mathbf{R})$  can be included by performing an ensemble average over all adiabatic nuclear states  $k$

$$\begin{aligned} \langle O \rangle_T &= \frac{1}{Q(T)} \sum_{k=0}^{\infty} \langle \chi_k(\mathbf{R}) | \hat{O}(\mathbf{R}) | \chi_k(\mathbf{R}) \rangle \exp\left(-\frac{\varepsilon_k}{k_B T}\right) \\ &= \int d\mathbf{R} W(\mathbf{R}, T) O(\mathbf{R}) \end{aligned} \quad (2)$$

Here

$$W(\mathbf{R}, T) = \frac{1}{Q(T)} \sum_{k=0}^{\infty} \langle \chi_k(\mathbf{R}) | \chi_k(\mathbf{R}) \rangle \exp\left(-\frac{\varepsilon_k}{k_B T}\right) \quad (3)$$

denotes the probability of finding the system with the nuclear coordinates within  $\mathbf{R}$  and  $\mathbf{R} + d\mathbf{R}$ . The partition function  $Q(T)$  is defined as  $Q(T) = \sum_{k=0}^{\infty} \exp\left(-\frac{\varepsilon_k}{k_B T}\right)$ , where  $k_B$  is the Boltzmann constant.

A molecular dynamics simulation with either a path-integral approach<sup>23,25</sup> or quantum thermostat approach<sup>26–28</sup> utilizes eq 2 to compute the electron–phonon-renormalized electronic properties. However, being computationally expensive, such simulations are not often adopted for computing electron–phonon renormalizations of electronic properties from first principles. Commonly used approaches in solid-state physics employ the harmonic approximation (HA) to  $\mathcal{V}(\mathbf{R})$

$$\begin{aligned} \mathcal{V}^H(\mathbf{R}) &= \frac{1}{2} \sum_{I\alpha, J\alpha'} (R_{I\alpha} \sqrt{M_I}) D_{I\alpha, J\alpha'} (\sqrt{M_J} R_{J\alpha'}) \\ &= \frac{1}{2} \mathbf{R}^T \mathbf{M}^{1/2} \mathbf{D} \mathbf{M}^{1/2} \mathbf{R} \end{aligned} \quad (4)$$

with  $\mathbf{M}$  representing a  $3N \times 3N$  diagonal matrix of nuclear masses. The elements of the dynamical matrix, also known as the mass-weighted Hessian matrix, are given by

$$D_{I\alpha, J\alpha'} = \frac{1}{\sqrt{M_I M_J}} \left. \frac{\partial^2 \mathcal{V}(\mathbf{R})}{\partial R_{I\alpha} \partial R_{J\alpha'}} \right|_{\mathbf{R}=\mathbf{0}} \quad (5)$$

where  $\alpha, \alpha'$  denote the cartesian axes  $x, y, \text{ or } z$ , and  $I, J$  denote the indices of the nuclei.

A spectral decomposition of the dynamical matrix,  $\mathbf{D} = \mathbf{U} \boldsymbol{\Omega}^2 \mathbf{U}^T$ , returns a unitary matrix,  $\mathbf{U}$ , and a  $3N \times 3N$  diagonal matrix of normal-mode frequencies,  $\boldsymbol{\Omega}$ , with diagonal elements:  $\omega_1, \omega_2, \dots, \omega_{3N}$ . The total nuclear Hamiltonian can be separated into 3 independent translational degrees of freedom,  $d_t$  number of independent global rotational degrees of freedom, and  $3N - 3 - d_t$  number of independent vibrational degrees of freedom. For solid, linear, and nonlinear isolated molecules, the number of rotational degrees of freedom ( $d_r$ ) is 0, 2, and 3, respectively. Since the translations and global rotations, which appear as the first  $3 + d_r$  lowest eigenvalues of  $\boldsymbol{\Omega}$ , do not affect the electronic properties, we focus on the vibrational Hamiltonian

$$\hat{H}^H = \sum_{\nu=3+d_r+1}^{3N} \left( -\frac{1}{2} \nabla_{X_\nu}^2 + \frac{1}{2} \omega_\nu^2 X_\nu^2 \right) \quad (6)$$

with  $X_\nu$  denoting the  $\nu$ -th normal mode. The partition function for the  $\nu$ -th harmonic oscillator is

$$Q_\nu^H(T) = \sum_{k=0}^{\infty} \exp\left[-\frac{\omega_\nu}{k_B T} \left(k + \frac{1}{2}\right)\right] \\ = \exp\left(\frac{\omega_\nu}{2k_B T}\right) n_B(\omega_\nu, T) \quad (7)$$

where the Bose occupation factor is given by

$$n_B(\omega, T) = \frac{1}{\exp(\omega/k_B T) - 1} \quad (8)$$

As a consequence of the separable form of the Hamiltonian, eq 2 can be simplified

$$\langle O \rangle_T^H = \int d\mathbf{X} W^H(\mathbf{X}, T) O(\mathbf{X}) \\ = \int d\mathbf{X} \left[ \prod_{\nu=3+d_r+1}^{3N} G(X_\nu; \sigma_{\nu,T}) \right] O(\mathbf{X}) \quad (9)$$

where the harmonic probability density,  $W^H(\mathbf{X}, T)$ , reduces to a product of independent Gaussian functions,

$G(X_\nu; \sigma_{\nu,T}) = \frac{1}{\sqrt{2\pi\sigma_{\nu,T}^2}} \exp\left(-\frac{X_\nu^2}{2\sigma_{\nu,T}^2}\right)$ , with widths related to the Bose occupation factor

$$\sigma_{\nu,T} = \sqrt{\frac{2n_B(\omega_\nu, T) + 1}{2\omega_\nu}} \quad (10)$$

We note that though eq 9 is valid under the harmonic approximation, it does not assume any explicit dependence of the electronic observable  $O$  on nuclear coordinates ( $\mathbf{R}$ ) or normal mode coordinates ( $\mathbf{X}$ ). To further simplify the expression, we Taylor expand  $O(\mathbf{X})$

$$O(\mathbf{X}) = O(\mathbf{0}) + \sum_{\nu} \frac{\partial O}{\partial X_\nu} \Big|_0 X_\nu + \sum_{\nu\nu'} \frac{\partial^2 O}{\partial X_\nu \partial X_{\nu'}} \Big|_0 X_\nu X_{\nu'} + \dots \quad (11)$$

and truncate the expansion after the second order. After inserting the resulting expression into eq 9, we obtain the phonon-renormalized electronic observable within the quadratic (Q) approximation

$$\langle O \rangle_T^Q = O(\mathbf{0}) + \sum_{\nu=3+d_r+1}^{3N} \frac{1}{2\omega_\nu} \frac{\partial^2 O}{\partial X_\nu^2} \Big|_0 \left[ n_B(\omega_\nu, T) + \frac{1}{2} \right] \quad (12)$$

We note that terms of odd order in  $X_\nu$  or cross-coupling terms such as  $X_\nu X_{\nu'}$ , with  $\nu \neq \nu'$ , do not appear because in the harmonic approximation, the density is symmetric with respect to  $\mathbf{X} = \mathbf{0}$ . For systems with strong anharmonicity, the vibrational density would no longer be symmetric, and hence both odd-order terms and cross-coupling terms would become important.

**2.2. Stochastic Approach.** The stochastic approach employs Monte Carlo sampling to evaluate  $W(\mathbf{X}, T)$  and eq 9 to compute phonon-renormalized electronic properties. At each Monte Carlo step, a displaced normal mode coordinate is obtained,  $\mathbf{X}^i = \boldsymbol{\tau}^i$ , where, for  $\nu > 3 + d_r$ , the matrix elements,  $\tau_\nu^i$ , are a Gaussian distributed random number with zero mean and width  $\sigma_{\nu,T}$ , while the first  $3 + d_r$  matrix elements are set to zero. Then, the  $\mathbf{X}^i$ 's are back-transformed to Cartesian coordinates, and  $\mathbf{R}^i$  and the electronic observable  $O(\mathbf{R}^i)$  are computed. After  $M$  Monte Carlo steps, eq 9 can be rewritten as

$$\langle O \rangle_T^{\text{MC}} = \frac{1}{M} \sum_{i=1}^M O(\mathbf{X}^i) = \frac{1}{M} \sum_{i=1}^M O(\mathbf{R}^i) \quad (13)$$

Based on the mean value (MV) theorem and utilizing a quadratic (Q) approximation, Monserrat showed that there exists  $2^{3N-3-d_r}$  mean-value positions,  $\mathbf{X}_{\text{MVQ}}$ , for which  $O(\mathbf{X}_{\text{MVQ}}) \simeq \langle O \rangle_T^{\text{MC}}$ ,<sup>31</sup> with  $\mathbf{X}_{\text{MVQ}}^i = \mathbf{s}^i \boldsymbol{\sigma}_T$ , where the matrix elements of  $\boldsymbol{\sigma}_T$  is given by eq 10, and  $\mathbf{s}^i$  is a matrix with the first  $3 + d_r$  elements set to zero and the remaining  $3N - 3 - d_r$  elements being either +1 or -1. It was shown that a Monte Carlo algorithm that samples random signs,  $\mathbf{s}^i$ , has a faster convergence for the value of  $\langle O \rangle_T^{\text{MC}}$  than the one that samples random numbers,  $\boldsymbol{\tau}^i$ , from a Gaussian distribution.<sup>31</sup> Following Monserrat's work, Zacharias and Giustino proposed a one-shot (OS) algorithm,<sup>21</sup> in which the signs are chosen according to

$$s_\nu = (-1)^{\nu-4-d_r} \text{ for } \nu > 3 + d_r \\ = 0, \text{ for } \nu \leq 3 + d_r \quad (14)$$

and they showed that only a single first-principles calculation for the atomic configuration,  $\mathbf{X} = \mathbf{s} \boldsymbol{\sigma}_T$  is sufficient to converge the value of  $\langle O \rangle_T$ . They also proposed that an additional first-principles calculation on the antithetic pair of the chosen atomic configuration, i.e.,  $\mathbf{X} = -\mathbf{s} \boldsymbol{\sigma}_T$ , can improve the result, and this is the approximation adopted here.

$$\langle O \rangle_T^{\text{OS}} = \frac{1}{2} [O(\mathbf{s} \boldsymbol{\sigma}_T) + O(-\mathbf{s} \boldsymbol{\sigma}_T)] \quad (15)$$

**2.3. Frozen Phonon Approach.** A frozen phonon (FP) approach utilizes eq 12 to compute phonon-renormalized electronic properties. Throughout this work, our electronic observables ( $O$ ) are either the valence and conduction band (VB) energies ( $E_n$ ) or the band gap ( $E_g$ ). The second derivative of the  $n$ -th band energy with respect to  $\nu$ -th phonon mode scaled by the phonon frequency (see eq 12 when  $O = E_n$ ) is called the electron–phonon coupling energy (EPCE).

$$\text{EPCE}_{n,\nu} = \frac{1}{2\omega_\nu} \frac{\partial^2 E_n}{\partial X_\nu^2} \Big|_0 \quad (16)$$

It is evident from eq 12 that the electron–phonon renormalization of the  $n$ -th band

$$\Delta E_n(T) = \langle E_n \rangle_T - E_n(\mathbf{0}) \quad (17)$$

reduces to

$$\Delta E_n^Q(0) = \sum_{\nu=3+d_r+1}^N \text{EPCE}_{n,\nu} \quad (18)$$

within the quadratic approximation at 0 K. The EPCEs can be computed using the FP method (see Section S1.3 in the Supporting Information for more details).

**2.4. Computational Details.** We used the Qbox code<sup>32</sup> for the optimization of the geometry and cell parameters of all systems studied here. For molecular dynamics (MD) simulations with a quantum thermostat (QT), which in the following we call “QTMD” simulations, we used Qbox coupled<sup>6</sup> to the i-PI code, where the i-PI driver<sup>33</sup> moves the nuclear coordinates and Qbox compute forces from density functional theory (DFT). To obtain the zero-point renormalization (ZPR)

of electronic energies,  $\Delta E_n(0)$ , the electron–phonon renormalizations at finite  $T$ ,  $\Delta E_n(T)$  are fitted with the Viña model<sup>34</sup>

$$\Delta E_n(T) = \Delta E_n(0) - A[1 + 2/(e^{B/T} - 1)] \quad (19)$$

For the frozen phonon and stochastic calculations, we used the PyEPFD package<sup>35</sup> to generate displaced structures and Qbox for DFT calculations. Specifically, the Qbox outputs were post-processed with the PyEPFD package to compute the dynamical matrix, phonon frequencies, phonon eigenvectors, and renormalized energy gaps. Throughout this work, we used a Cartesian displacement of 0.005 a.u. to compute the dynamical matrix elements. To compute the first and second derivatives,  $O'$  and  $O''$  we used a normal mode displacement that corresponds to a potential energy change,  $\delta V^H = 0.001$  a.u., see eqs S23–S25 in the Supporting Information. In addition, we used PyEPFD to calculate the anharmonic measure<sup>36</sup> and vibrational densities along a phonon mode by post-processing quantum molecular dynamics trajectories obtained from QTMD simulations.

For the pentamantane molecule, we used a generalized gradient approximated (GGA) Perdew–Burke–Erzenhof (PBE) functional<sup>37,38</sup> and strongly constrained and approximately normed (SCAN)<sup>39</sup> meta-GGA functional. For the molecular crystal of pentamantane, we only used the SCAN functional. For both the molecule and the crystal of NAI-DMAC, we used only the PBE functional in order to be consistent with our previous study.<sup>40</sup> We used norm-conserving pseudopotentials<sup>41</sup> with 50 and 60 Ry kinetic energy cutoffs for pentamantane and NAI-DMAC, respectively.

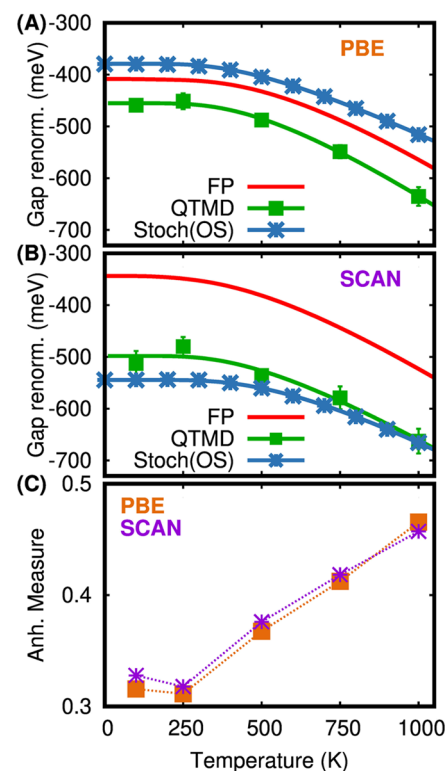
### 3. RESULTS AND DISCUSSION

**3.1. Electron–Phonon Renormalization of the Electronic Properties of the Pentamantane Molecule: Validation of Stochastic One-Shot Method for Finite Systems.** Using the PBE and SCAN functionals, we compare the results obtained with the stochastic one-shot method with those obtained with QTMD simulations and the FP method.<sup>6</sup>

The static highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap computed using the SCAN functional (5.71 eV) is 680 meV larger than that computed using PBE. The gap of pentamantane estimated from optical absorption measurements in the gas phase (which naturally include electron–phonon interactions) is 5.81 eV at ambient temperatures.<sup>42</sup> The computed exciton binding energy of the molecule is about 2.5 eV<sup>4</sup> and hence the estimated fundamental gap is  $\approx 8.3$  eV. At 250 K, QTMD simulations with the PBE and SCAN functionals underestimate the fundamental gap and yield 4.58 and 5.23 eV, respectively. The QTMD simulations predict a ZPR value of  $-498$  meV with the SCAN functional, 42 meV larger than the PBE value ( $-456$  meV). To obtain the ZPR value from experiments, measurements should be performed at a wide range of temperatures and the data extrapolated to 0 K. Unfortunately such data are not available at present in the literature.

When using PBE (see Figure 1A), the stochastic one-shot and FP results are in good agreement with each other, but they deviate by 15% from those of QTMD simulations, which fully account for anharmonic effects.

When using SCAN (see Figure 1B), we find that the FP method underestimates the gap renormalization by  $\approx 35\%$ , while the stochastic one-shot method only slightly overestimates it. To investigate the reason for the overall good agreement of the



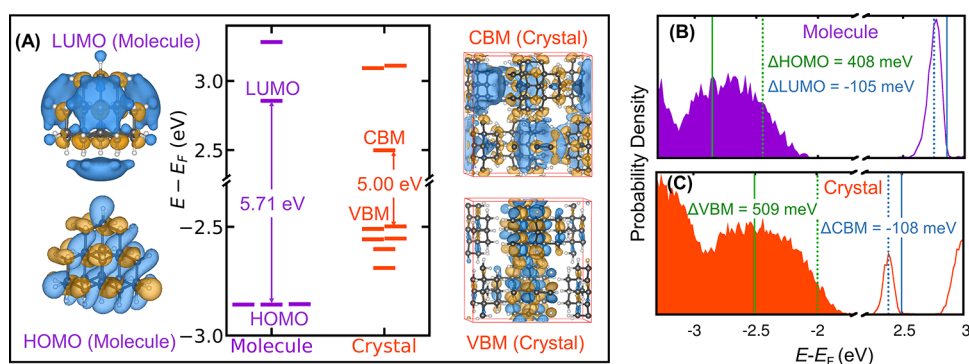
**Figure 1.** (A, B): Electron–phonon renormalization of the HOMO–LUMO gap of the pentamantane molecule as a function of temperature as computed using PBE (A) and SCAN (B) functionals. The gap renormalizations are computed using frozen phonon (FP), stochastic one-shot (Stoch(OS)), and first-principles molecular dynamics coupled with a quantum thermostat (QTMD). For Stoch(OS) and QTMD results, symbols represent the results obtained from simulations, while the solid lines represent the Viña model fit of the simulation results. (C): Anharmonic measure for the pentamantane molecule at different temperatures computed from the trajectories obtained with QTMD simulations using the PBE and SCAN functionals. Broken lines are a guide to the eyes.

stochastic and QTMD results for both the PBE and SCAN functionals and the worse agreement of FP and QTMD results in the case of SCAN, we computed an anharmonic measure proposed by Knupp et al.<sup>36</sup>

$$a_x(T) = \sqrt{\frac{\sum_{x \in \mathbf{A}} \langle (F_x - F_x^H)^2 \rangle_T}{\sum_{x \in \mathbf{A}} \langle F_x^2 \rangle_T}} \quad (20)$$

for the configurations obtained from QTMD simulations. For a specific configuration,  $F_x$  and  $F_x^H$  denote the forces obtained for a coordinate  $x$  from a first-principles calculation and from the harmonic approximation, respectively, and  $\mathbf{A}$  denotes a subspace of Cartesian ( $\mathbf{R}$ ) coordinates for a set of specified nuclei or a subspace of normal-mode ( $\mathbf{X}$ ) coordinates. The total anharmonic measure is computed by including all atoms (or normal modes) in the subspace  $\mathbf{A}$ , while the anharmonic measure for a particular group of atoms or normal modes is computed by properly selecting the subspace  $\mathbf{A}$ . From eq 20, it is easy to see that anharmonic measure values larger than one indicate a breakdown of the harmonic approximation.

Total anharmonic measures for the isolated pentamantane molecule as a function of  $T$  are shown in Figure 1C (see also Figure S1 in the Supporting Information for a normal-mode-resolved anharmonic measures at 100 K). We found similar



**Figure 2.** (A) HOMO and LUMO levels relative to the Fermi level computed with the SCAN functional for an isolated pentamantane molecule and its molecular crystal when nuclei are at rest. (B, C) Electronic density of states at 100 K for the molecule and the crystal, respectively, computed using QTMD simulations with the SCAN functional. The green (blue) vertical lines represent the average energies of the HOMO or VBM (LUMO or CBM) when atoms are at rest (solid line) and at 100 K (broken line).

values with the PBE and SCAN functional (below 0.5) up to high temperatures, indicating that the harmonic approximation should perform relatively well and hence it is likely not the reason of the worse performance of the FP method with the SCAN functional. Within the FP method, one employs the quadratic approximation for the HOMO–LUMO energies, which is not satisfied for the SCAN functional. Instead, the stochastic one-shot method does not rely on the quadratic approximation and includes electron–phonon couplings to any order, thus yielding results in reasonable agreement with QTMD simulations for both functionals. The slight deviation (below 15%) originates from the harmonic approximation adopted in the stochastic method.

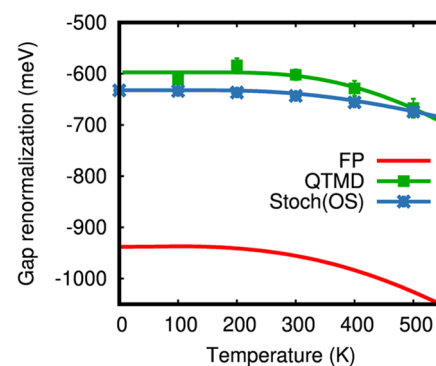
The stochastic one-shot method had been tested for several extended systems, but to the best of our knowledge, it has not yet been applied to finite systems. Our results show that, as long as the harmonic approximation is valid, the one-shot method should also be applicable to finite systems and should perform better than the FP method at a cheaper computational cost. Indeed, the FP method requires an order of  $6N$  calculations to compute the second derivatives appearing in eq 12, while the stochastic one-shot method requires only two calculations per temperature. Our results also indicate that the validity of the quadratic approximation depends on the choice of the functional. The inclusion of intermediate range van der Waals interactions in the meta-GGA scan functional may be a reason for a stronger nonquadratic electron–phonon coupling obtained with the SCAN functional.

**3.2. Pentamantane Molecular Crystal.** Now we turn to discuss the results for the molecular crystal of pentamantane. We used a unit cell containing 4 molecular units, with 232 atoms in total. Figure 2A compares the HOMO (LUMO) of the molecule with the VBM (CBM) of the crystal unit cell when nuclei are at rest. In the molecule, the HOMO is threefold degenerate, while the LUMO is singly degenerate. In the crystal, there are several valence band states close in energy to the VBM, the CBM remains singly degenerate. The static fundamental gap of the crystal is 0.71 eV smaller than that of the molecule when the SCAN functional is used. We also computed the inverse participation ratios (IPR)  $\int |\psi|^4 d^3r / (\int |\psi|^2 d^3r)^2$  for the molecule's HOMO, LUMO and crystal's VBM, CBM which are  $2.5 \times 10^{-4}$ ,  $1.1 \times 10^{-5}$ ,  $1.5 \times 10^{-4}$ , and  $1.7 \times 10^{-5}$ , respectively, suggesting that the LUMO(CBM) is more delocalized. Figure 2A also shows that the LUMO(CBM) is a surface state, with the CBM delocalized over two molecular units. In contrast, the

HOMO(VBM) is localized between the C–C and C–H bonds, though the VBM is also spread out over two molecules.

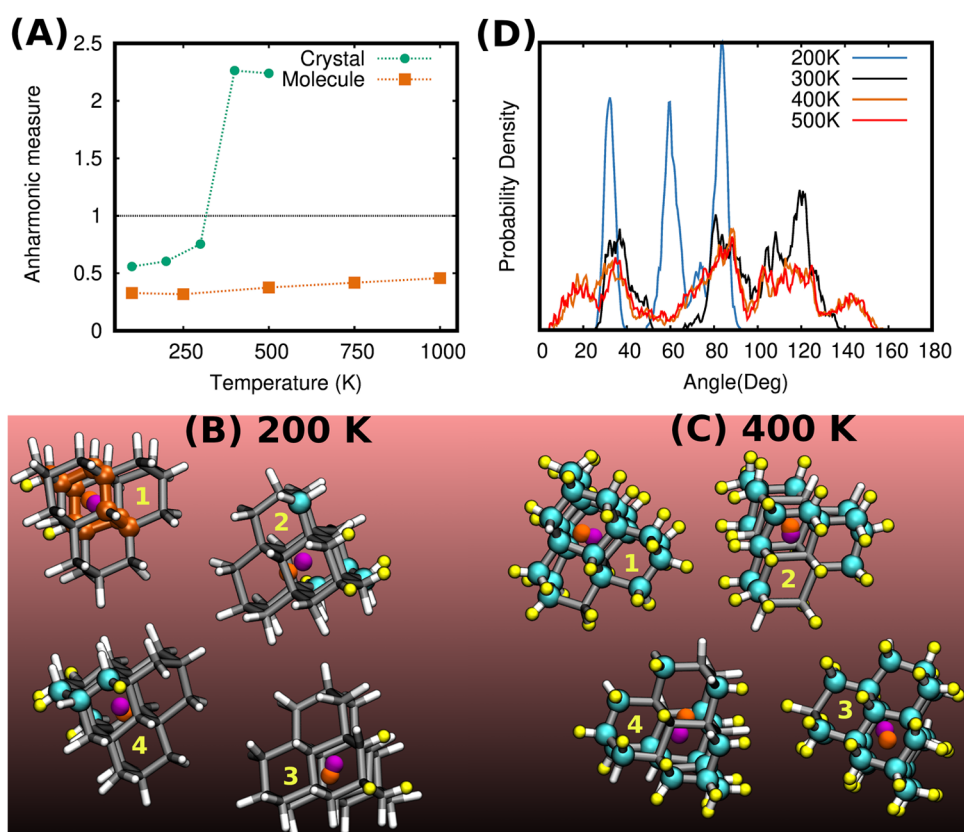
Figure 2B,C shows the electronic density of states for the molecule and the crystal, respectively, obtained by including quantum nuclear vibrations at 100 K with QTMD simulations. In both cases, HOMO(VBM) and LUMO(CBM) move toward the Fermi level and consequently, the gap decreases when adding quantum vibronic effects. Moreover, the value of the HOMO(VBM) renormalization is much larger than that of the LUMO(CBM), due to its delocalized character. The renormalization of the LUMO (CBM) of the molecule and the crystal are very similar, while the renormalization of the VBM of the crystal ( $-509$  meV) is about 100 meV larger than the HOMO of the molecule. The VBM of the crystal is localized on two molecular units and therefore, it is affected by both intra- and intermolecular vibrations.

Figure 3 compares the band gap renormalizations of the pentamantane crystal as a function of temperature when



**Figure 3.** Electron–phonon band gap renormalization of the pentamantane crystal, computed at the SCAN level of theory, as a function of temperature. The gap renormalizations are computed using frozen phonon (FP), stochastic one-shot (Stoch(OS)), and first-principles molecular dynamics coupled with a quantum thermostat (QTMD). For Stoch(OS) and QTMD results, symbols represent the results obtained from simulations, while the solid lines represent the Viña model fit of the simulation results.

different methods are used to describe the quantum nuclear vibrations. Compared to QTMD results, the FP method overestimates the gap renormalization by more than 300 meV (>50%), while the stochastic one-shot method yields only a slight (<6%) overestimate. To understand these differences, we



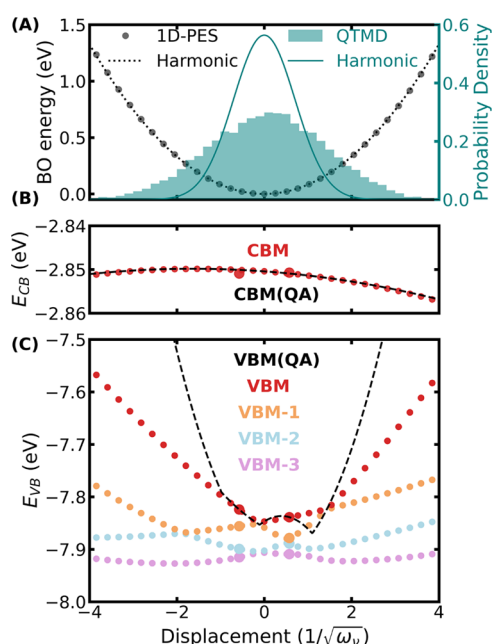
**Figure 4.** (A): Anharmonic measures of the pentamantane molecule and crystal at different temperatures as obtained from QTMD simulations using the SCAN functional. (B, C): Atoms with anharmonic measure greater than 1 are highlighted as cyan (C) and yellow (H) spheres for the pentamantane crystal at 200 and 400 K. Within the crystal unit cell, there are four molecules which are designated as 1, 2, 3, and 4. In molecule-1 of (B), a 10-membered  $C_{10}$  ring is highlighted with orange balls and sticks. The vector joining the center of mass of the  $C_{10}$  ring (orange spheres) and that of the molecule (pink spheres) defines a unique molecular axis that is minimally affected by the internal vibration of the molecule. (D): Angular distribution between molecular axes at different temperatures as obtained from QTMD simulations.

computed again the crystal's total anharmonic measure using the QTMD trajectories, and our results are shown in Figure 4A (see Figure S2 in the Supporting Information for the mode-resolved anharmonic measures at 100 K).

Though the total anharmonic measure of the crystal is larger than that of the isolated molecule, its value is smaller than one. At  $T > 300$  K, however, the total anharmonic measure becomes larger than 1, and consequently, the harmonic approximation is expected to break down. Yet, the stochastic OS method predicts a ZPR value that is in agreement with that of QTMD. To understand this apparent contradiction, we computed the atom-resolved anharmonic measures. Figure 4B,C highlights as cyan (C) and yellow (H) spheres those atoms whose anharmonic measure value is greater than one. At 200 K, we found only a handful of such atoms, while at 400 K, most of the atoms have an anharmonic measure value greater than 1. This sharp transition indicates that at  $T > 300$  K, the crystal's phonon modes become strongly anharmonic due to coupling with rigid body rotations of the molecule. To accumulate further evidence, we defined the axis of a molecular unit by defining a vector joining the centers of mass of a molecule (shown as pink spheres) and the center of mass (shown as orange spheres) of a unique  $C_{10}$  ring (shown by orange balls and sticks, see molecule-1 of Figure 4B) within that molecule. Such a definition of the molecular axis is least sensitive toward intramolecular vibrations. From QTMD trajectories, we computed the probability distribution of the angles between the axes of different molecules within the crystal's unit cell using the

TRAVIS trajectory analyzer<sup>43,44</sup> and these results are shown in Figure 4D. At 200 K, the angular distribution has only three sharp peaks, while at  $T > 300$  K, a very broad distribution stems from large-amplitude rigid body rotations of pentamantane molecules within the crystal. Such hindered rotations have a nonparabolic potential energy surface and are, therefore, strongly anharmonic. However the VBM and CBM states are not localized within the molecules and consequently, they are not much affected by such intermolecular motions. This is the reason why, even at  $T > 300$  K, the harmonic approximation does not introduce a large error and the stochastic OS results are in good agreement with QTMD simulations.

Unlike the stochastic method, FP calculations overestimate the gap renormalizations by more than 50% compared to the reference QTMD results, and this large deviation is attributed to the quadratic approximation. To illustrate the importance of nonquadratic electron–phonon coupling terms, we consider the phonon mode along which the electron–phonon coupling energy for the HOMO is the highest when computed using the FP approximation. We performed a scan of the one-dimensional potential energy surface (PES) and of the Kohn–Sham eigenvalues of the HOMO and LUMO levels along this normal mode. Moreover, we also computed the probability distribution by projecting the XYZ coordinates obtained from QTMD trajectories to the normal mode vector. In Figure 5A, we compared the probability density obtained from a QTMD simulation at 100 K with the analytical expression obtained from



**Figure 5.** One-dimensional scan of the Born–Oppenheimer (BO) potential energy surface (PES),  $\mathcal{V}(\mathbf{R})$ , and Kohn–Sham eigenenergies ( $E_n$ ) of CBM and VBM along a normal mode with a harmonic frequency of  $1336\text{ cm}^{-1}$ . (A) Comparison of the 1D PES computed using SCAN DFT (circles) with that obtained from the harmonic approximation (dotted line). A comparison of the probability densities at 100 K as obtained from a QTMD simulation and the harmonic approximation is also shown. The circles in (B, C) show the energies of the Kohn–Sham eigenstates of the conduction band minimum (CBM) and the four highest eigenvalues of the valence band (VB), respectively, as calculated using SCAN DFT. The black dashed line represents the VBM(CBM) eigenenergies computed with the quadratic approximation (QA), using the first and second derivatives of the eigenenergies with respect to the phonon mode. The two points that are used to compute these derivatives are shown with larger symbols.

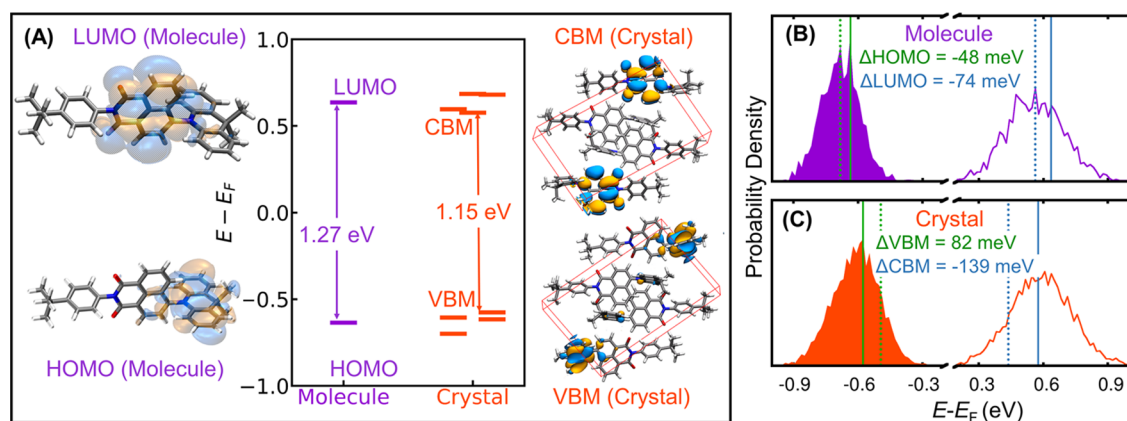
the harmonic approximation at the same temperature, which is a Gaussian distribution.

Figure 5A shows that the vibrational energy within the harmonic approximations is in excellent agreement with the Born–Oppenheimer energies obtained by displacing the ions

along the normal mode. However, the normal mode probability density obtained with the harmonic approximation is narrower compared to that obtained from the QTMD sampling. This is due to the anharmonic cross-coupling between normal modes which is included in a QTMD sampling but not when the ions are displaced along a normal mode. Therefore, sampling a one-dimensional potential energy surface to include anharmonicity, as done in many previous studies<sup>45–47</sup> is not necessarily accurate. Despite the broadening of the anharmonic vibrational density of the pentamantane crystal, the harmonic approximation to the density is still valid. Therefore, the stochastic method where ions are displaced following the harmonic vibrational density, predicts electron–phonon renormalizations in close agreement with the fully anharmonic QTMD simulations.

Figure 5B shows that the CBM eigenenergy surface is flat as a function of phonon mode coordinates, consistent with a small EPCE value (only  $-0.2\text{ meV}$ ) as computed using the FP approach. The CBM eigenenergy surface computed using the quadratic approximation is in excellent agreement with that obtained from DFT with the SCAN functional. Close to the VBM (see Figure 5C), there are four nearby Kohn–Sham states exhibiting crossing as a function of phonon displacements. Because of these crossings, the VBM state is not always a pure state, and the eigenenergy surface is only a piecewise continuous function with respect to the phonon displacement. Such state crossing introduces additional complexity in using the quadratic approximation, as previously observed also for isolated diamondoid molecules.<sup>48</sup> Therefore, the quadratic approximation overestimates the VBM energies at displacements larger than the value used to compute the first and second derivatives of the eigenenergies. Hence, the FP method predicts a large  $72.6\text{ meV}$  contribution toward the ZPR for this phonon mode. In contrast, if we apply stochastic OS displacements only to this mode, the computed ZPR contribution reduces to  $20.9\text{ meV}$ . This shows the limitations of the quadratic approximation and of the FP method for the calculations of eigenvalues and energy gaps, and we expect a similar trend for other electronic properties.

Both the isolated molecule and the crystal of pentamantane have large ZPR values,  $-500$  and  $-600\text{ meV}$ , which are comparable to those of diamond. The frozen phonon method



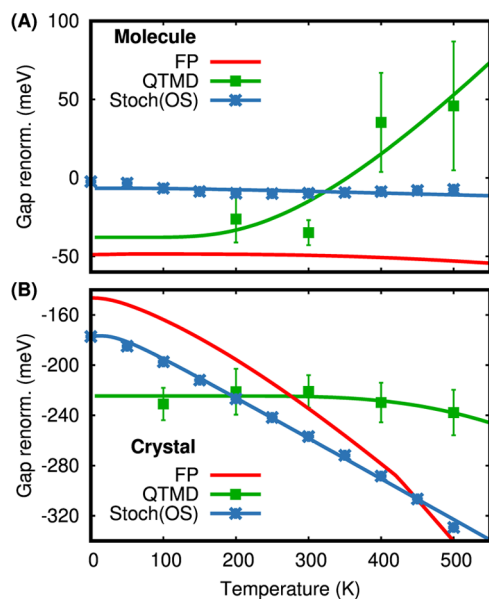
**Figure 6.** (A) HOMO and LUMO levels relative to the Fermi level computed with the PBE functional for an isolated NAI-DMAC molecule and its molecular crystals when nuclei are at rest. (B, C) Electronic density of states at 200 K for the molecule and crystal, respectively, computed using QTMD simulations. The green (blue) vertical lines represent the average energies of the HOMO or VBM (LUMO or CBM) when atoms are at rest (solid line) or in motion at 200 K (broken line).

overestimates the ZPR value of the crystal by 50% due to the quadratic approximation, whereas the stochastic one-shot method, which does not rely on that approximation, agrees well with the reference QTMD results.

**3.3. Electron–Phonon Renormalization of NAI-DMAC Molecule and Crystal.** We turn to discussing the results for the NAI-DMAC molecule and crystal. Figure 6A compares the HOMO(LUMO) of the molecule with the VBM(CBM) of the crystal as obtained employing the PBE functional when the nuclei are at rest. The LUMO and HOMO of the molecule, both singly degenerate, are localized on the acceptor unit NAI and donor unit DMAC, respectively. The unit cell of the NAI-DMAC crystal has four molecules and 4 Kohn–Sham eigenstates for both CBM and VBM that are very close in energy. The CBM and VBM of the crystal are also localized on the NAI(acceptor) and DMAC (donor) units of two molecules, respectively. With the PBE functional, we obtained a 0.12 eV smaller band gap in the crystal than in the molecule.

Figure 6B,C shows the EDOS for the isolated molecule and the crystal, respectively, when quantum nuclear vibrations at 200 K are included using QTMD simulations. The LUMO(CBM) moves toward the Fermi level by an amount of 74 meV (139 meV); instead, the HOMO of the molecule moves downward from the mid-gap by an amount of 48 meV, and the VBM of the crystal toward the Fermi level by an amount of 82 meV.

Figure 7 compares the fundamental gap renormalizations as a function of temperature for the isolated molecule (A) as well as

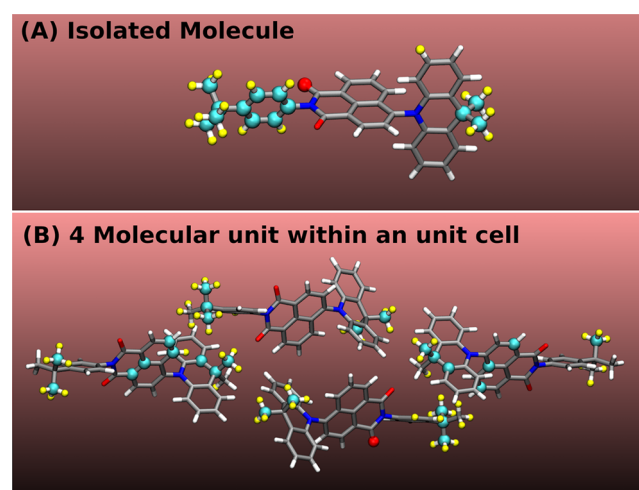


**Figure 7.** Electron–phonon renormalizations of the fundamental gap of the NAI-DMAC molecule (A) and crystal (B) as a function of temperature. The gap renormalizations are computed using the PBE functional and three different approaches: (i) frozen phonon (FP), (ii) stochastic one-shot (Stoch(OS)), and (iii) first-principles molecular dynamics coupled with a quantum thermostat (QTMD). Symbols represent the results of simulations, while the solid lines represent the Viña model fit of the simulation results.

the crystal (B) obtained with QTMD simulations, stochastic OS, and FP methods. For the isolated molecule, surprisingly, the gap renormalization values are rather small,  $\approx -40$  meV below 300 K; however, they change sign (i.e., the gap increases) when the temperature is above 400 K and the slope of the gap renormalization with respect to temperature is positive. Indeed,

with increasing  $T$ , the HOMO level decreases in energy while the LUMO level remains approximately constant. In contrast, for the crystal, up to almost 500 K, the band gap renormalizations remain constant at  $\approx -220$  meV with very small variations observed for the CBM and VBM.

For both the molecule and the crystal, the FP and stochastic methods predict an incorrect temperature dependence of the fundamental gap, and at variance with the pentamantane crystal's results, we find that the stochastic method does not improve the FP results. We find that the anharmonic measure from the QTMD simulations is 7.29 units and 2.99 units for the molecule and the crystal, respectively, even at a very low temperature of 200 K. (Figures S3 and S4 in the Supporting Information show the mode-resolved anharmonic measures of the molecule and the crystal). There are several modes with very high values of the anharmonic measure (in the range of 10–50) showing that the harmonic approximation breaks down. Figure 8

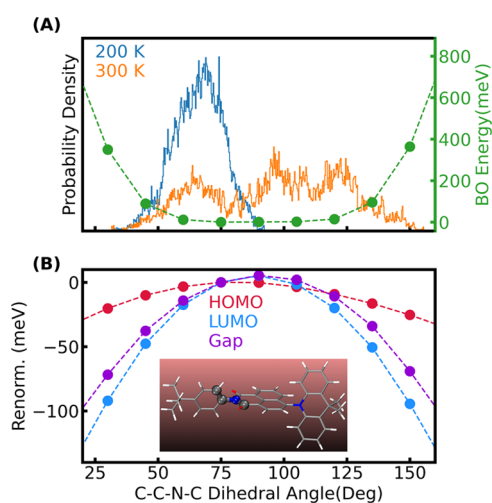


**Figure 8.** Atom-resolved anharmonic measure of an isolated NAI-DMAC molecule (A) and the crystal (B). The atoms with an anharmonic measure greater than 1 are highlighted as cyan (C) and yellow (H) spheres.

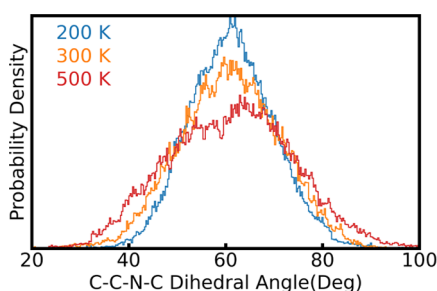
shows the atoms for which the anharmonic measure value is larger than 1 for the molecule (A) and the crystal (B). We note that for the isolated molecule, the atoms of the tertiary-butyl-phenyl group of the NAI subunit and the methyl groups of the DMAC subunit exhibit a large anharmonic measure, suggesting a likely free rotation of these groups.

To understand the effects of free rotations, we scanned the PES and HOMO, LUMO eigenenergies by rotating the tertiary-butyl-phenyl group relative to the naphthalimide group. We note that such a one-dimensional scan neglects the coupling between these rotations with other rotational and/or vibrational degrees of freedom and such a one-dimensional PES scan should only be used to gain a qualitative understanding. Figure 9 shows the BO energies (A) and renormalization of the HOMO and LUMO energies and their gap as a function of C–C–N–C dihedral angle (B). In addition, the probability distributions of this dihedral angle at different temperatures as obtained from QTMD simulations are reported for the molecule (Figure 9A) and the crystal (Figure 10).

In the isolated molecule, the rotation of the tertiary-butyl-phenyl group is characterized by a very flat PES, see Figure 9A. Although at 200 K, the dihedral angle is restricted within 40–100°, at  $T > 300$  K, the rotation becomes almost free, and a wide



**Figure 9.** (A): Probability distribution of the C–C–N–C dihedral angle highlighted as spheres in the inset of (B) for the isolated molecule at different temperatures as obtained from QTMD simulations. The green circles represent the Born–Oppenheimer energy when PES is scanned by varying the dihedral angle of the isolated molecule. (B): Renormalizations for the HOMO, and LUMO levels as well as the gap for the isolated molecule when only the dihedral angle is varied.



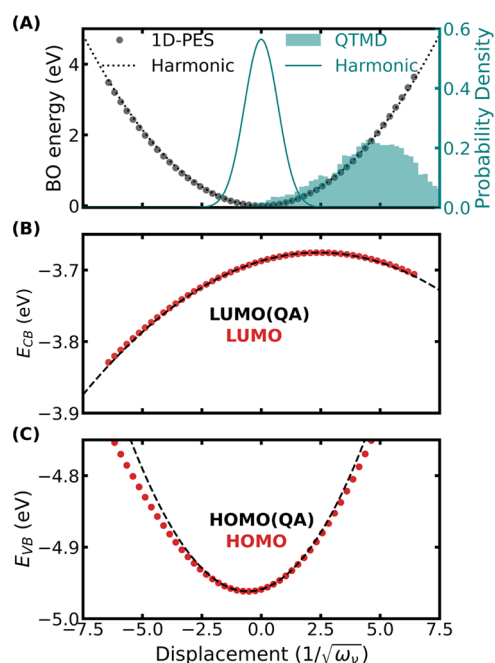
**Figure 10.** Probability distribution of the C–C–N–C dihedral angle (highlighted as spheres in the inset of Figure 9B) for the NAI-DMAC crystal at different temperatures, as obtained from QTMD simulations.

range of dihedral angles ( $25\text{--}160^\circ$ ) are explored by the torsional motion. Both LUMO and HOMO levels are coupled to this rotational degree of freedom and their energy decreases as the dihedral angle moves further away from its equilibrium value ( $\approx 75^\circ$ ); however, the energy decrease is faster for the LUMO than the HOMO and the resulting gap renormalization is negative. We note that the LUMO and HOMO are strongly coupled to the rotation of the NAI unit relative to the DMAC unit as well (see Figure S5 in the Supporting Information), but the former increases in energy while the latter decreases in energy as the C–C–N–C dihedral angle moves away from its equilibrium value ( $\approx 90^\circ$ ), and consequently, the gap opens with this rotation. These two torsional motions have opposite effects on the renormalization of the HOMO–LUMO gap at finite temperatures; they also lead to large fluctuations of the gap during our QTMD simulations, resulting in overall small ZPR values with large uncertainties, see Figure 7A. We also scanned the PES for the rotation of the methyl groups, but the effects on the HOMO–LUMO gap are much smaller, 5 meV at most, for a methyl group; see Figures S6–S8 in the Supporting Information. Such torsional and rotational motions are strongly anharmonic because (i) the PES is sinusoidal and hence cannot be modeled with a parabola, and (ii) curvilinear rotational displacements

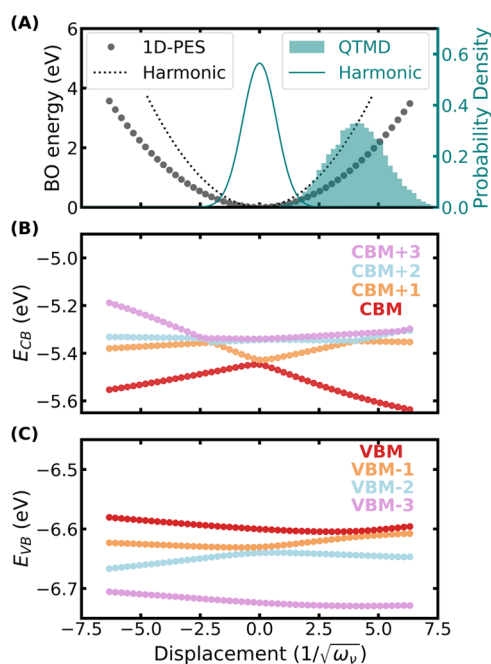
cannot be described by rectilinear normal modes when the angle variation is large.

In the crystal, contrary to the isolated molecule, the torsional motion of the tertiary-butyl-phenyl group is restricted due to packing constraints. The dihedral angle distribution varies weakly with increasing temperature and, the carbon atoms of the phenyl rings of the tertiary-butyl-phenyl group do not exhibit a large anharmonic measure. Despite the packing constraints, the methyl groups are still free to rotate and consequently, their motions remain strongly anharmonic. Therefore, the strong anharmonic phonon–phonon interactions originating within an isolated NAI-DMAC molecule also persist within the molecular crystal, and these interactions cannot be accurately represented using the stochastic method.

To understand the consequences of the (i) harmonic and (ii) quadratic approximations, we considered the phonon modes with the highest electron–phonon coupling energy for the molecule’s HOMO and the crystal’s CBM, respectively. We performed a scan of the one-dimensional potential energy surface (PES), and Kohn–Sham eigenvalues of the HOMO (VBM) and LUMO (CBM) levels along this normal mode (see Figures 11 and 12). In addition, we also computed the vibrational density of these normal modes by projecting the XYZ coordinates obtained from QTMD trajectories to the normal mode vectors. In Figures 11A and 12A, we compared



**Figure 11.** One-dimensional scan of the Born–Oppenheimer (BO) potential energy surface (PES),  $\mathcal{V}(\mathbf{R})$ , and Kohn–Sham eigenenergies ( $E_n$ ) of CBM and VBM along a normal mode with a harmonic frequency of  $1329\text{ cm}^{-1}$ . (A) Comparison of the 1D PES computed using PBE (circles) with that obtained from the harmonic approximation (dotted line). A comparison of the probability densities at 200 K as obtained from a QTMD simulation and the harmonic approximation is also shown. The circles in (B, C) show the energies of the Kohn–Sham eigenstates of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), respectively, as calculated using DFT with PBE functional. The black dashed line represents the HOMO (LUMO) eigenenergies computed with the quadratic approximation (QA), using the first and second derivatives of the eigenenergies with respect to the normal mode.



**Figure 12.** One-dimensional scan of the Born–Oppenheimer (BO) potential energy surface (PES),  $\mathcal{V}(\mathbf{R})$ , and Kohn–Sham eigenenergies ( $E_n$ ) of CBM and VBM along a normal mode with a harmonic frequency of  $1371\text{ cm}^{-1}$ . (A) Comparison of the 1D PES computed using PBE (circles) with that obtained from the harmonic approximation (dotted line). A comparison of the probability densities at 200 K as obtained from a QTMD simulation and the harmonic approximation is also shown. The circles in (B, C) show the energies of the Kohn–Sham eigenstates of the conduction band (CB) with the four lowest eigenvalues (CBM, to CBM + 3) and the valence band (VB) with the four highest eigenvalues (VBM to VBM - 3), respectively, as calculated using DFT with the PBE functional.

such a vibrational density obtained from a QTMD simulation at 200 K with the analytical expression obtained from the harmonic approximation at the same temperature, which is a Gaussian distribution.

First, we consider the isolated molecule. Figure 11A shows again an excellent agreement between the harmonic potential energy and the Born–Oppenheimer energies obtained by displacing the ions along the normal mode. We note that the estimation of the anharmonic measure for this mode as obtained from QTMD simulation at 200 K (3.02) is larger than 1, indicating the inadequacy of the normal mode to describe the internuclear motion within the molecule. This stems from a strong anharmonic coupling between the chosen normal mode and other ones, resulting in an asymmetric vibrational density along this mode. This observation reiterates the limitations of the one-dimensional scans along normal modes to include anharmonic coupling effects. Figure 11B,C shows the LUMO and HOMO energies as a function of normal mode displacements, respectively. In both cases, we observe a reasonable agreement between the results obtained using the quadratic approximation and those of the first-principles calculations. As the anharmonic vibrational density for the NAI-DMAC molecule is not a Gaussian distribution, both FP and stochastic methods become inaccurate to compute the electron–phonon renormalization of the band gap.

Figure 12A shows that the harmonic approximation overestimates the vibrational energy compared to the reference first-principles calculations when ions are displaced along the normal

mode. We note that the true anharmonic vibrational density is not a Gaussian distribution and it is asymmetric and shifted toward a positive value of  $x$ . Figure 12B,C shows the energies of the Kohn–Sham eigenstates with four lowest and highest eigenvalues of the conduction and valence bands, respectively, as a function of normal mode displacements. As for the pentamantane crystal, we observe crossings between valence and conduction band states which make the quadratic approximation unreliable for the electronic states. Therefore, both FP and stochastic methods predict inaccurate results for the electron–phonon renormalization of the band gap as neither the quadratic nor the harmonic approximation hold for the NAI-DMAC molecular crystal.

#### 4. SUMMARY AND CONCLUSIONS

We investigated the effect of quantum vibronic coupling and anharmonicity on the electronic properties of two molecular crystals, pentamantane, composed of rigid molecules, and NAI-DMAC, composed of floppier units. Specifically, we analyzed the validity of common approximations used in the literature when applying the stochastic and frozen phonon methods, by comparing the results of these techniques with those of first-principles molecular dynamics simulations with a quantum thermostat. We found that for both the isolated diamondoid molecule and corresponding molecular crystal the ZPR of their electronic gaps is rather large,  $-500$  and  $-600$  meV (at the SCAN level) respectively, comparable to that of diamond. In contrast, the NAI-DMAC molecule has a small ZPR of  $-38$  meV (at the PBE level), despite consisting of light first and second-row elements. Due to packing constraints, the molecular crystal of NAI-DMAC has a relatively larger ZPR of  $-224$  meV.

Our calculations showed that in spite of PBE and SCAN functionals giving a similar anharmonic measure for an isolated diamondoid molecule, results with the SCAN functional exhibit more pronounced higher-order electron–phonon coupling effects. In fact, the quadratic approximation and resulting frozen phonon results are poorer approximations when using SCAN, which includes van der Waals interactions.

We also found that the presence of nearly degenerate states close to the valence band maxima (conduction band minima) of the molecular crystals studied here made the frozen phonon calculations inaccurate, leading to incorrect predictions of the VBM, CBM, and gap renormalizations. A stochastic calculation may improve over the frozen phonon methods, provided the anharmonic phonon–phonon scattering is relatively weak. However, when the anharmonic phonon–phonon scattering is substantial, then both frozen phonon and stochastic methods fail to appropriately describe electron–phonon renormalizations. A strong anharmonic coupling is expected for floppy molecules and their molecular crystals and the frozen phonon or stochastic method should not be used for such systems.

Finally, we found that sampling one-dimensional phonon modes to incorporate anharmonic effects, as in many earlier studies, may be inaccurate, as it fails to account for anharmonic couplings between normal modes. Our work highlights the importance of including quantum vibronic effects to accurately describe the electronic properties of molecular crystals composed of light elements.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.3c00424>.

Methods, theory, stochastic approach, frozen phonon approach, and additional figures; mode-resolved EPCEs and anharmonic measures; and effect of torsion on the potential energy surface and band gap of NAI-DMAC molecule (PDF)

(PDF)

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### Notes

The authors declare no competing financial interest.

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