

# Generalization of dielectric dependent hybrid functionals to finite systems

Nicholas P. Brawand

*Institute for Molecular Engineering, University of Chicago, Chicago, Illinois 60637, United States*

Márton Vörös, Marco Govoni, and Giulia Galli

*Institute for Molecular Engineering, University of Chicago, Chicago, Illinois 60637, United States and*

*Argonne National Laboratory, Lemont, Illinois 60439, United States*

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## DETAILS OF STATISTICAL ANALYSIS

The mean absolute error (MAE) is a good statistic to compare the accuracies of different electronic structure methods. In order to compute the MAE, one must first pick a sample or a small set of test systems which are supposedly representative of an entire population of systems which one is interested in but, for practical reasons, unable to compute. We will call the MAE calculated using the sample, the sample MAE and the MAE calculated using all the systems in the population, the population MAE. When the sample MAE's of two methods are compared, it is usually implied that the difference in the sample MAE's is approximately the difference in population MAE's. This assumption is often used to make conclusions about the relative accuracies of different methods regarding population statistics based on inferences drawn from the sample statistics. However, in order to make inferences about the population MAE's using the sample MAE's, one must go beyond reporting descriptive statistics (e.g. standard deviations and averages) and in addition report inferential statistics (e.g. p-values and confidence intervals) [1]. Below we outline the steps we took to evaluate the statistical and practical significance of our results.

In order to determine if the MAE's of different methods differ significantly, Friedman [2] and post hoc Wilcoxon signed rank tests [3] were performed. These tests are non-parametric [4], statistical methods designed to test the null hypothesis. The null hypothesis is expressed as:

$$H_o : \mu_1 = \mu_2 \dots = \mu_n \quad (1)$$

where  $\mu_i$  represents the mean absolute error of the  $i$ th method and  $n$  is the number of methods one is considering; this hypothesis was rejected (and hence two or more sets were considered different) if the p-value obtained from the Friedman test was  $< 0.05$ . The Friedman test is widely supported by many software packages like scipy [5] and R [6] and it was designed to test the null hypothesis for multiple meth-

ods (more than two) simultaneously.

After determining if at least one *pair* of methods differed significantly, post hoc Wilcoxon signed rank tests (similar to the Friedman test but designed to compare only two methods at one time) were performed for each *pair* of methods. As more Wilcoxon signed rank tests are performed, the chances of committing a type I error (i.e. rejection of the null hypothesis when it is actually true) increases. To avoid this potential issue, two methods were considered to differ significantly only if the p-value returned by the Wilcoxon signed rank test was greater than  $\alpha/N$ , where  $\alpha = 0.05$  and  $N$  is the number of Wilcoxon tests performed. Finally, in order to give a measure of practical significance, we provided 95% confidence intervals of the differences in mean absolute errors. Friedman, post hoc Wilcoxon tests and confidence intervals were computed using functions provided by the python scipy library [5] and R [6]. We point the reader to Ref. [7] for further information.

## G2/97 DATA

Vertical ionization potentials (VIP) of the G2/97 subset consisting of 36 of closed shell molecules from Ref. [8] predicted by the SX hybrid functional and  $G_0W_0$  starting from SX wavefunctions ( $G_0W_0@SX$ ) are provided in Table II. Geometries were taken from the NIST Computational Chemistry Comparison and Benchmark Database [9].

## OPEN SHELL SYSTEMS

We also tested the SX method on a few open shell systems where we found good agreement with experiment. Vertical ionization potentials results are provided in Table V below.

	Photoemission	
	p-value	95% CI [eV]
SX-PBE0	$5.93 \times 10^{-6}$	[-2.05, -1.77]
SX-G <sub>0</sub> W <sub>0</sub> @PBE0	$9.92 \times 10^{-5}$	[0.15, 0.29]
	Absorption	
	p-value	95% CI [eV]
TDSX-TDPBE0 <sup>‡</sup>	0.362	[-0.07, 0.24]
TDSX-BSE@G <sub>0</sub> W <sub>0</sub> @PBE0 <sup>‡</sup>	$1.94 \times 10^{-4}$	[-0.55, -0.23]

<sup>‡</sup> data from Ref. [10]

TABLE I. Post hoc Wilcoxon signed rank test results comparing the accuracy of the SX functional to alternative schemes based on many body perturbation theory (BSE@G<sub>0</sub>W<sub>0</sub>) and global hybrid density functionals (PBE0) for both photoemission and absorption of Thiel’s test set. Unscaled p values were calculated using the Wilcoxon signed rank test comparing the two methods listed in the first column. CI is the unscaled 95% confidence interval of the differences of the mean absolute errors between methods. See text for further details.

### THIEL DATA

Vertical ionization potentials (VIP) of the G2/97 subset predicted by the SX hybrid functional and by G<sub>0</sub>W<sub>0</sub> calculations starting from SX wavefunctions (G<sub>0</sub>W<sub>0</sub>@SX) are provided in Table III.

The first lowest optical singlet excitations predicted by the time dependent SX hybrid functional method (TDSX) compared to the revised best theoretical estimates of Thiel’s test set are provided in Table IV. p-values and confidence intervals for this data are provided in Table I.

### SI QUANTUM DOT GEOMETRIES

See provided XYZ files.

### PHOTOEMISSION SPECTRA

Photoemission spectra of benzene and pyridine predicted by the SX method, G<sub>0</sub>W<sub>0</sub> and experiment are presented in figures S1 and S2. The SX spectra are the Kohn-Sham states relative to vacuum using Eq. 6 of the manuscript, where  $i$  is the index of the highest occupied molecular orbital. Even though we used the mixing fraction optimized for the highest occupied state, we still find agreement with experiment and a significant improvement over other global hybrids such as PBE0 which predicts the position of the first peak of benzene and pyridine to be 7.23 and 7.49 eV respectively. Though we find good

agreement with G<sub>0</sub>W<sub>0</sub> and experiment for most of the spectra, the deepest states appear to be too deep in energy, thus stretching the spectra over a wider range of energies. This is characteristic of global hybrids [11] and can be remedied by adding additional parameters to the hybrid form, such as adopting a range separated hybrid formalism.

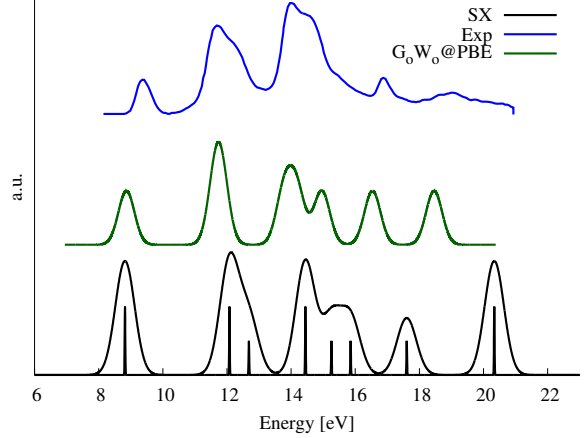


FIG. S1. Photoemission spectrum (approximated by a broadened density of states) of benzene predicted by the SX hybrid functional (SX), G<sub>0</sub>W<sub>0</sub> starting from PBE wavefunctions (G<sub>0</sub>W<sub>0</sub>@PBE) and experiment (Exp). Both G<sub>0</sub>W<sub>0</sub> and experimental results are taken from Ref. [12].

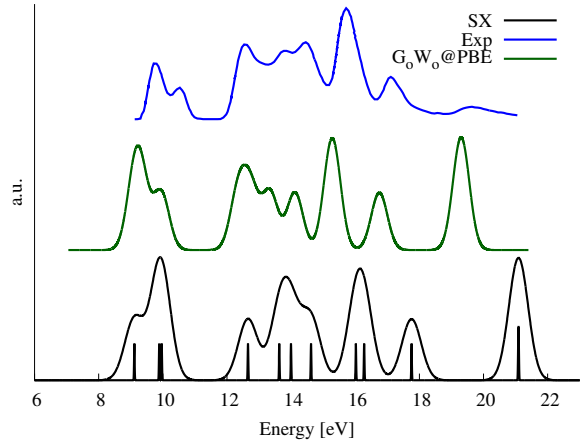


FIG. S2. Photoemission spectrum (approximated by a broadened density of states) of pyridine predicted by the SX hybrid functional (SX), G<sub>0</sub>W<sub>0</sub> starting from PBE wavefunctions (G<sub>0</sub>W<sub>0</sub>@PBE) and experiment (Exp). Both G<sub>0</sub>W<sub>0</sub> and experimental results are taken from Ref. [12].

## CELL SIZES

Every molecule from the G2 test set was placed in a supercell of side length 15.87 angstroms. Every molecule from Thiel’s test set was placed in a supercell of side length  $[2 \times D + 5]$  angstroms where  $D$  is the greatest distance between two atoms. Silicon nanocrystals were placed in cells such that the smallest distance of vacuum between images was 9.5 angstroms or greater.

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- [1] The p-value is the probability of obtaining the observed results when the null hypothesis is true; the hypothesis that an observed difference is due to chance alone, in this case that the observed difference in mean absolute errors is due to sampling error. We consider a p-values less than 0.05% enough evidence to reject the null hypothesis. The confidence interval provides a good estimate of the difference between the population mean absolute errors.
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Molecule	Exp.	G <sub>0</sub> W <sub>0</sub> @SX	SX	$\alpha_{i=\text{HOMO}}^{\text{SX}}$
C <sub>2</sub> H <sub>2</sub>	11.49	11.62	10.98	0.76
C <sub>2</sub> H <sub>4</sub>	10.68	10.73	10.12	0.75
C <sub>4</sub> H <sub>4</sub> S	8.86	9.34	8.79	0.68
C <sub>6</sub> H <sub>6</sub>	9.25	9.45	8.93	0.67
CH <sub>3</sub> Cl	11.29	11.83	11.13	0.71
CH <sub>3</sub> OH	10.96	11.35	10.84	0.68
CH <sub>3</sub> SH	9.44	9.79	9.15	0.72
CH <sub>4</sub>	14.4	14.69	14.19	0.76
Cl <sub>2</sub>	11.49	12.06	11.33	0.71
ClF	12.77	13.21	12.43	0.71
CO	14.01	14.65	14.03	0.73
CO <sub>2</sub>	13.78	14.17	13.56	0.68
CS	11.33	12.18	11.54	0.68
F <sub>2</sub>	15.7	16.12	15.88	0.69
H <sub>2</sub> CO	10.89	11.28	10.74	0.69
H <sub>2</sub> O	12.62	12.81	12.39	0.7
H <sub>2</sub> O <sub>2</sub>	11.7	11.95	11.56	0.68
HCl	12.74	13.08	12.38	0.74
HCN	13.61	13.91	13.15	0.75
HF	16.12	16.2	15.89	0.71
HOCl	11.12	11.67	10.98	0.69
Li <sub>2</sub>	5.11	5.4	5.13	0.82
LiF	11.3	11.38	11.09	0.67
LiH	7.9	8.19	7.6	0.73
N <sub>2</sub>	15.58	16.19	15.68	0.7
N <sub>2</sub> H <sub>4</sub>	8.98	10.11	9.56	0.69
Na <sub>2</sub>	4.89	4.89	4.77	0.86
NaCl	9.8	9.46	8.73	0.68
NH <sub>3</sub>	10.82	11.13	10.64	0.71
P <sub>2</sub>	10.62	10.75	10.07	0.75
PH <sub>3</sub>	10.59	10.9	10.29	0.76
SH <sub>2</sub>	10.5	10.73	10.1	0.75
Si <sub>2</sub> H <sub>6</sub>	10.53	10.98	10.43	0.72
SiH <sub>4</sub>	12.3	13.22	12.68	0.76
SiO	11.49	11.91	11.1	0.68
SO <sub>2</sub>	12.5	12.92	12.26	0.67

TABLE II. Vertical ionization potentials (VIP) in eV of the G2/97 subset predicted by the SX hybrid functional and G<sub>0</sub>W<sub>0</sub> calculations starting from SX wavefunctions (G<sub>0</sub>W<sub>0</sub>@SX) and values of the screened exchange constant ( $\alpha_{i=\text{HOMO}}^{\text{SX}}$ ) using Eq. 6 of the manuscript. Experimental values and geometries were taken from the NIST Computational Chemistry Comparison and Benchmark Database.

Molecule	Exp.	SX	PBE0	G <sub>0</sub> W <sub>0</sub> @PBE0	$\alpha_{i=\text{HOMO}}^{\text{SX}}$
ethene [C <sub>2</sub> H <sub>4</sub> ]	10.68	10.16	7.87	10.53	0.76
butadiene [C <sub>4</sub> H <sub>6</sub> ]	9.07	8.68	6.81	9.03	0.72
hexatriene [C <sub>6</sub> H <sub>8</sub> ] <sup>‡</sup>	8.3	7.85	6.25	8.19	0.69
octatetraene [C <sub>8</sub> H <sub>10</sub> ] <sup>[13]</sup>	7.79	7.33	5.91	7.65	0.67
cyclopropene [C <sub>3</sub> H <sub>4</sub> ]	9.86	9.52	7.22	9.91	0.75
cyclopentadiene [C <sub>5</sub> H <sub>6</sub> ]	8.61	8.14	6.33	8.53	0.7
norbornadiene [C <sub>7</sub> H <sub>8</sub> ] <sup>‡</sup>	8.38	8.32	6.42	8.64	0.72
benzene [C <sub>6</sub> H <sub>6</sub> ]	9.25	8.97	7.3	9.26	0.68
naphthalene [C <sub>10</sub> H <sub>8</sub> ] <sup>‡</sup>	8.14	7.72	6.33	8.05	0.66
furan [C <sub>4</sub> H <sub>4</sub> O]	8.9	8.5	6.67	8.90	0.7
pyrrole [C <sub>4</sub> H <sub>5</sub> N]	8.23	7.89	6.14	8.26	0.69
imidazole [C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> ]	8.96	8.53	6.71	8.93	0.7
pyridine [C <sub>5</sub> H <sub>5</sub> N]	9.51	9.15	7.5	9.66	0.64
pyrazine [C <sub>4</sub> H <sub>4</sub> N]	9.63	9.56	7.45	9.71	0.65
pyrimidine [C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> ]	9.73	9.95	7.52	9.73	0.64
pyridazine [C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> ]	9.31	9.56	7.07	9.28	0.63
triazine [C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> ] <sup>[14]</sup>	10.4	10.64	8.15	10.45	0.64
tetrazine [C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> ] <sup>[15]</sup>	9.7	10.0	7.47	9.83	0.64
formaldehyde [CH <sub>2</sub> O]	10.88	10.81	7.87	10.85	0.69
acetone [C <sub>3</sub> H <sub>6</sub> O] (B2)	9.8	9.86	7.26	9.66	0.65
benzoquinone [C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> ] <sup>[16]</sup>	10.11	10.43	8.03	10.04	0.61
formamide [CH <sub>3</sub> NO] <sup>‡</sup>	10.16	10.38	7.65	10.21	0.66
acetamide [C <sub>2</sub> H <sub>5</sub> NO]	10.0	10.01	7.38	9.75	0.64
cytosine [C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O] <sup>†</sup>	8.9	8.6	6.84	8.76	0.63
thymine [C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> ] <sup>†</sup>	9.1	8.96	7.16	9.14	0.65
uracil [C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> ] <sup>†</sup>	9.5	9.22	7.52	9.54	0.62
adenine [C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> ] <sup>†</sup>	8.4	8.0	6.48	8.31	0.64

<sup>‡</sup> Adiabatic ionization potentials

<sup>†</sup> Average experimental values from Ref. [17]

TABLE III. Vertical ionization potentials (VIP) in eV of the Thiel's set (with the exception of propanamide due to lack of experimental data) predicted by the SX hybrid (SX) functional, PBE0 and G<sub>0</sub>W<sub>0</sub> calculations starting from PBE0 wavefunctions (G<sub>0</sub>W<sub>0</sub>@PBE0) and values of the screened exchange constant ( $\alpha_{i=\text{HOMO}}^{\text{SX}}$ ) using Eq. 6 of the manuscript. Experimental values were taken from the NIST Computational Chemistry Comparison and Benchmark Database unless noted otherwise. Molecular geometries taken from Ref. [18].

Molecule	Irrep.	BTE2	TDSX	TDPBE0	BSE@G <sub>0</sub> W <sub>0</sub> @PBE0
ethene [C <sub>2</sub> H <sub>4</sub> ]	B <sub>1u</sub>	7.8	7.6	7.48	7.02
butadiene [C <sub>4</sub> H <sub>6</sub> ]	B <sub>u</sub>	6.18	5.95	5.65	5.36
hexatriene [C <sub>6</sub> H <sub>8</sub> ]	B <sub>u</sub>	5.1	5.01	4.68	4.41
octatetraene [C <sub>8</sub> H <sub>10</sub> ]	B <sub>u</sub>	4.66	4.37	4.03	3.8
cyclopropene [C <sub>3</sub> H <sub>4</sub> ]	B <sub>2</sub>	6.68	6.56	6.18	5.82
cyclopentadiene [C <sub>5</sub> H <sub>6</sub> ]	B <sub>2</sub>	5.55	5.23	5.02	4.58
norbornadiene [C <sub>7</sub> H <sub>8</sub> ] (B <sub>1</sub> ) <sup>‡</sup>	B <sub>2</sub>	6.21	6.55	5.57	5.45
benzene [C <sub>6</sub> H <sub>6</sub> ]	E <sub>1u</sub>	7.13	7.27	6.99	6.35
naphthalene [C <sub>10</sub> H <sub>8</sub> ]	B <sub>2u</sub>	4.82	4.73	4.38	3.96
furan [C <sub>4</sub> H <sub>4</sub> O]	B <sub>2</sub>	6.32	6.2	6.02	5.5
pyrrole [C <sub>4</sub> H <sub>5</sub> N]	B <sub>2</sub>	6.57	6.32	6.65	6.38
imidazole [C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> ]	2A''	6.65	6.81	6.56	5.74
pyridine [C <sub>5</sub> H <sub>5</sub> N]	B <sub>1</sub>	4.59	5.44	4.83	4.34
pyrazine [C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> ]	B <sub>3u</sub>	4.13	4.49	3.96	3.49
pyrimidine [C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> ]	B <sub>1</sub>	4.43	5.03	4.31	3.8
pyridazine [C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> ]	B <sub>1</sub>	3.85	4.24	3.65	3.11
triazine [C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> ]	A <sub>2</sub> ''	4.71	5.4	4.62	4.16
tetrazine [C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> ]	B <sub>3u</sub>	2.46	2.81	2.29	1.73
formaldehyde [CH <sub>2</sub> O] (B <sub>2</sub> ) <sup>‡</sup>	A <sub>1</sub>	9.29	9.35	9.21	8.34
acetone [C <sub>3</sub> H <sub>6</sub> O] (B <sub>2</sub> ) <sup>‡</sup>	2A <sub>1</sub>	8.9	9.07	8.61	8.16
benzoquinone [C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> ]	B <sub>1u</sub>	5.47	5.47	4.91	4.58
formamide [CH <sub>3</sub> NO]	A''	5.55	5.91	5.61	5.01
acetamide [C <sub>2</sub> H <sub>5</sub> NO]	A''	5.62	6.0	5.64	5.02
propanamide [C <sub>3</sub> H <sub>7</sub> NO]	A''	5.65	6.01	5.67	5.04
cytosine [C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O] (1A') <sup>‡</sup>	A''	4.87	5.89	4.89	4.49
thymine [C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> ]	A''	4.82	5.52	4.76	4.2
uracil [C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> ]	A''	5.0	5.45	4.7	4.16
adenine [C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> ]	2A'	5.25	5.76	5.04	4.59

<sup>‡</sup> Data for lowest predicted transition not available; the character is provided in parenthesis.

TABLE IV. The first lowest optical singlet excitations in eV, predicted by the time dependent SX hybrid functional method (TDSX) compared to the revised best theoretical estimates of Thiel's test set (BTE2). Values predicted for the same transitions by TDPBE0 and BSE/G<sub>0</sub>W<sub>0</sub>@PBE0 are taken from Ref. [10]. The irreducible representations of the transitions (Irrep.) are given in the 2nd column. Molecular geometries taken from Ref. [18].

Molecule	Exp. <sup>‡</sup>	SX	G <sub>0</sub> W <sub>0</sub> @PBE <sup>‡</sup>	$\alpha_{i=\text{HOMO}}^{\text{SX}}$
Al	5.99	5.71	5.64	0.81
N	14.53	14.21	13.51	0.76
O2	12.3	13.12	11.68	0.71
OH	13.02	12.70	12.44	0.72
Mean Absolute Error		0.44	0.64	

<sup>‡</sup> data from Ref. [19]

TABLE V. Vertical ionization potentials (VIP) in eV of a few open shell systems from the G2/97 test set predicted by the SX hybrid functional and G<sub>0</sub>W<sub>0</sub> calculations starting from PBE wavefunctions (G<sub>0</sub>W<sub>0</sub>@PBE) and values of the screened exchange constant ( $\alpha_{i=\text{HOMO}}^{\text{SX}}$ ) using Eq. 6 of the manuscript. Experimental geometries were taken from the NIST Computational Chemistry Comparison and Benchmark Database.