Supporting Information: Accurate ionization potentials from Kohn-Sham eigenvalues with the help of potential adjustors

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A. Geometries of the molecules of test set TS12

24

Antracene

C -2.4927437 1.4151026 0.0000000

C -3.6849291 0.7153027 0.0000000

C -3.6849291 -0.7153027 0.0000000

C -2.4927437 -1.4151026 0.0000000

C -1.2327018 -0.7279406 0.0000000

C -1.2327018 0.7279406 0.0000000

H -2.4915355 2.5165432 0.0000000

H -4.6429169 1.2575675 0.0000000

H -4.6429169 -1.2575675 0.0000000

H -2.4915355 -2.5165432 0.0000000

C 0.0000000 -1.4127552 0.0000000

C 0.0000000 1.4127552 0.0000000

C 1.2327018 -0.7279406 0.0000000

C 1.2327018 0.7279406 0.0000000

H 0.0000000 -2.5149158 0.0000000

H 0.0000000 2.5149158 0.0000000

C 2.4927437 -1.4151026 0.0000000

C 2.4927437 1.4151026 0.0000000

H 2.4915355 -2.5165432 0.0000000

H 2.4915355 2.5165432 0.0000000

C 3.6849291 -0.7153027 0.0000000

C 3.6849291 0.7153027 0.0000000

H 4.6429169 -1.2575675 0.0000000

H 4.6429169 1.2575675 0.0000000

12

Benzene

C 1.3892220 0.0000000 0.0000000

C 0.6946110 1.2031015 0.0000000

C -0.6946110 1.2031015 0.0000000

C -1.3892220 0.0000000 0.0000000

C -0.6946110 -1.2031015 0.0000000

C 0.6946110 -1.2031015 0.0000000

H 2.4672443 0.0000000 0.0000000

H 1.2336222 2.1366963 0.0000000

H -1.2336222 2.1366963 0.0000000

H -2.4672443 0.0000000 0.0000000

H -1.2336222 -2.1366963 0.0000000

H 1.2336222 -2.1366963 0.0000000

3

CO2

C 0.0000000 0.0000000 0.0000000

O 0.5291771 1.0486261 0.0000000

O -0.5291771 -1.0486261 0.0000000

6

Ethylene

C 0.0000000 0.0000000 0.6608153

C 0.0000000 0.0000000 -0.6608153

H 0.9228996 0.0000000 1.2316760

H -0.9228996 0.0000000 1.2316760

H 0.9228996 0.0000000 -1.2316760

H -0.9228996 0.0000000 -1.2316760

2

F2

F 0.0000000 0.0000000 -0.6670322

F 0.0000000 0.0000000 0.6670322

3

H2O

O 0.0000000 0.0000000 -0.0644484

H 0.7499149 0.0000000 0.5114912

H -0.7499149 0.0000000 0.5114912

5

Methane

C 0.0000000 0.0000000 0.0000000

H 0.6289005 0.6289005 0.6289005

H -0.6289005 0.6289005 -0.6289005

H -0.6289005 -0.6289005 0.6289005

H 0.6289005 -0.6289005 -0.6289005

2

N2

N 0.0000000 0.0000000 -0.5559659

N 0.0000000 0.0000000 0.5559659

30

Naphthacene

C -3.7321288 1.4166040 0.0000000

C -4.9214673 0.7163523 0.0000000

C -4.9209221 -0.7177123 0.0000000

C -3.7311047 -1.4170460 0.0000000

C -2.4676344 -0.7303946 0.0000000

C -2.4680387 0.7308193 0.0000000

H -3.7317315 2.5180365 0.0000000

H -5.8803104 1.2571074 0.0000000

H -5.8793431 -1.2592179 0.0000000

H -3.7298667 -2.5184317 0.0000000

C -1.2417998 -1.4148941 0.0000000

C -1.2421482 1.4158254 0.0000000

C -0.0000513 -0.7308406 0.0000000

C 0.0000139 0.7319581 0.0000000

H -1.2421126 -2.5168765 0.0000000

H -1.2427819 2.5178834 0.0000000

C 2.4676541 -0.7304211 0.0000000

C 2.4679173 0.7308013 0.0000000

C 1.2417685 -1.4149873 0.0000000

C 1.2421702 1.4158665 0.0000000

H 1.2420119 -2.5169637 0.0000000

H 1.2428012 2.5178997 0.0000000

C 3.7312785 -1.4170211 0.0000000

C 3.7320472 1.4165786 0.0000000

H 3.7297314 -2.5184167 0.0000000

H 3.7316515 2.5180226 0.0000000

C 4.9210550 -0.7176896 0.0000000

C 4.9214072 0.7164320 0.0000000

H 5.8795553 -1.2590280 0.0000000

H 5.8801980 1.2572359 0.0000000

18

Naphthalene

C -1.2485059 1.4004909 0.0000000

C -2.4321204 0.7109279 0.0000000

C -2.4321204 -0.7109279 0.0000000

C -1.2485059 -1.4004909 0.0000000

C 0.0000000 -0.7097052 0.0000000

C 0.0000000 0.7097052 0.0000000

H -1.2450605 2.4830537 0.0000000

H -3.3730175 1.2448992 0.0000000

H -3.3730175 -1.2448992 0.0000000

H -1.2450605 -2.4830537 0.0000000

C 1.2485059 -1.4004909 0.0000000

C 1.2485059 1.4004909 0.0000000

C 2.4321204 -0.7109279 0.0000000

C 2.4321204 0.7109279 0.0000000

H 1.2450605 -2.4830537 0.0000000

H 1.2450605 2.4830537 0.0000000

H 3.3730175 -1.2448992 0.0000000

H 3.3730175 1.2448992 0.0000000

4

NH3

N 0.0000000 0.0000000 0.0683541

H 0.9293009 0.0000000 -0.3166152

H -0.4646504 0.8047982 -0.3166152

H -0.4646504 -0.8047982 -0.3166152

5

SiH4

Si 0.0529177 0.1058354 0.1587531

H 0.9220329 0.9749506 1.0278684

H -0.8161975 0.9749506 -0.7103621

H -0.8161975 -0.7632798 1.0278684

H 0.9220329 -0.7632798 -0.7103621

B. Geometries of the molecules of test set TS13

24

Anthracene

C -2.4721263 1.4020368 -0.0004871

C -3.6481428 0.7109722 0.0024572

C -3.6481503 -0.7109659 0.0025000

C -2.4721375 -1.4020378 -0.0004201

C -1.2195496 -0.7201792 -0.0025312

C -1.2195473 0.7201646 -0.0025489

H -2.4716766 2.4859475 -0.0006353

H -4.5914575 1.2428756 0.0047490

H -4.5914691 -1.2428606 0.0048350

H -2.4716932 -2.4859472 -0.0005104

C 0.0000007 -1.3988594 -0.0034467

C -0.0000007 1.3988504 -0.0034413

C 1.2195511 -0.7201776 -0.0029223

C 1.2195471 0.7201656 -0.0029016

H -0.0000001 -2.4836876 -0.0034526

H 0.0000006 2.4836809 -0.0034375

C 2.4721372 -1.4020372 -0.0007031

C 2.4721266 1.4020369 -0.0006397

H 2.4716921 -2.4859465 -0.0009770

H 2.4716767 2.4859476 -0.0008735

C 3.6481494 -0.7109650 0.0025415

C 3.6481433 0.7109721 0.0025820

H 4.5914680 -1.2428603 0.0050871

H 4.5914582 1.2428741 0.0051763

12

Benzene

C 1.3913772 0.0000000 0.0000001

C 0.6956918 1.2049666 0.0000002

C -0.6956918 1.2049666 -0.0000002

C -1.3913772 -0.0000000 -0.0000000

C -0.6956918 -1.2049666 0.0000003

C 0.6956918 -1.2049666 -0.0000004

H 2.4745466 -0.0000000 0.0000006

H 1.2372684 2.1430289 0.0000006

H -1.2372684 2.1430289 -0.0000008

H -2.4745466 0.0000000 -0.0000003

H -1.2372684 -2.1430289 0.0000015

H 1.2372684 -2.1430289 -0.0000016

10

Butadien

C -1.2606961 3.6260241 0.0000185

C -0.2683574 2.7333136 0.0000984

C 1.1435950 3.0766046 -0.0001620

C 2.1359340 2.1838943 0.0000276

H -2.2988349 3.3210772 0.0002141

H -1.0627965 4.6920810 -0.0002381

H -0.5061256 1.6725777 0.0003892

H 1.3813631 4.1373406 -0.0005613

H 1.9380345 1.1178374 0.0003894

H 3.1740727 2.4888413 -0.0001759

3

CO2

C -0.0000146 -0.0000289 -0.0000000

O 0.5226021 1.0355971 0.0000000

O -0.5225876 -1.0355682 0.0000000

6

Ethylene

C -0.0000000 -0.0000000 0.6624749

C 0.0000000 0.0000000 -0.6624749

H 0.9214984 0.0000000 1.2328188

H -0.9214984 0.0000000 1.2328188

H 0.9214984 -0.0000000 -1.2328188

H -0.9214984 -0.0000000 -1.2328188

2

F2

F 0.0000000 0.0000000 -0.6984809

F 0.0000000 0.0000000 0.6984809

4

Formaldehyde

C 0.1060421 1.8574566 0.0830974

O -0.5468136 2.8601598 0.0047932

H 1.1343154 1.8560924 0.4954012

H -0.2820540 0.8755591 -0.2524419

3

Water

O -0.0000000 0.0000000 -0.0701342

H 0.7652256 0.0000000 0.5143340

H -0.7652256 0.0000000 0.5143340

5

Methane

C 0.0000000 0.0000000 -0.0000000

H 0.6290115 0.6290115 0.6290115

H -0.6290115 0.6290115 -0.6290115

H -0.6290115 -0.6290115 0.6290115

H 0.6290115 -0.6290115 -0.6290115

2

N2

N 0.0000000 0.0000000 -0.5455256

N 0.0000000 0.0000000 0.5455256

18

Naphthalene

C -1.2413210 1.3975438 -0.0000080

C -2.4251180 0.7061743 0.0000199

C -2.4251168 -0.7061761 0.0000110

C -1.2413184 -1.3975422 -0.0000204

C -0.0000001 -0.7142492 -0.0000348

C -0.0000001 0.7142545 -0.0000347

H -1.2396619 2.4815397 -0.0000091

H -3.3669575 1.2407746 0.0000503

H -3.3669548 -1.2407789 0.0000299

H -1.2396559 -2.4815380 -0.0000365

C 1.2413194 -1.3975422 -0.0000089

C 1.2413222 1.3975438 -0.0000213

C 2.4251180 -0.7061763 0.0000199

C 2.4251192 0.7061745 0.0000114

H 1.2396526 -2.4815381 -0.0000114

H 1.2396591 2.4815397 -0.0000401

H 3.3669558 -1.2407798 0.0000504

H 3.3669583 1.2407760 0.0000324

4

NH3

N 0.0000006 0.0000000 0.0585414

H 0.9430360 -0.0000000 -0.3133441

H -0.4715182 0.8166956 -0.3133443

H -0.4715182 -0.8166956 -0.3133443

5

SiH4

Si 0.0529177 0.1058354 0.1587531

H 0.9080464 0.9609641 1.0138819

H -0.8022111 0.9609641 -0.6963757

H -0.8022111 -0.7492934 1.0138819

H 0.9080464 -0.7492934 -0.6963757

C. Test set TS13: Ionization potentials obtained directly from unshifted eigenvalues and list of potential adjustors

TABLE I. Deviations of ionization potentials obtained directly, i.e., without applying potential adjustors, as negatives of PBE, B3LYP, and PBE0 eigenvalues from experimental values. The mean values are taken over all molecules and (i) only the first IPs, (ii) the first three different IPs, and (iii) all IPs below 40 eV. All values in eV.

TS13	PBE	B3LYP	PBE0
First IPs			
mean signed error	-4.28	-3.16	-2.84
mean absolute error	4.28	3.16	2.84
root mean squared error	4.43	3.24	2.93
First three IPs			
mean signed error	-4.41	-3.19	-2.83
mean absolute error	4.41	3.19	2.83
root mean squared error	4.55	3.28	2.92
All IPs up to 40 eV			
mean signed error	-4.26	-2.90	-2.50
mean absolute error	4.26	2.90	2.50
root mean squared error	4.39	3.01	2.61

TABLE II. Values of the potential adjustor $\Delta_{\rm xc}^{N-}[\bar{v}_{\rm xc}]$ for the molecules of the test set TS13 for the PBE, B3LYP, and PBE0 functional. All values in eV.

Molecules	$\Delta_{\rm xc}^{N-}[\bar{v}_{\rm xc}]$PBE	$\Delta_{\rm xc}^{N-}[\bar{v}_{\rm xc}]$B3LYP	$\Delta_{\rm xc}^{N-}[\bar{v}_{\rm xc}]$PBE0
H_2O	-5.708	-4.079	-3.624
Benzene	-2.971	-2.199	-1.971
F2	-5.998	-4.474	-4.095
NH_3	-4.929	-3.600	-3.169
N_2	-5.168	-3.893	-3.566
CO_2	-4.620	-3.378	-3.053
Ethylene	-3.917	-2.928	-2.611
Methane	-4.512	-3.499	-3.096
SiH4	-3.627	-2.966	-2.708
Naphthalene	-2.434	-1.825	-1.655
Anthracene	-2.121	-1.590	-1.441
Formaldehyde	-4.530	-3.252	-2.960
Butadien	-3.063	-2.286	-2.053
Average	-4.123	-3.075	-2.769

D. paB3LYP and paPBE0 ionization potentials of the molecules of the test set TS13 compared to G_0W_0 data

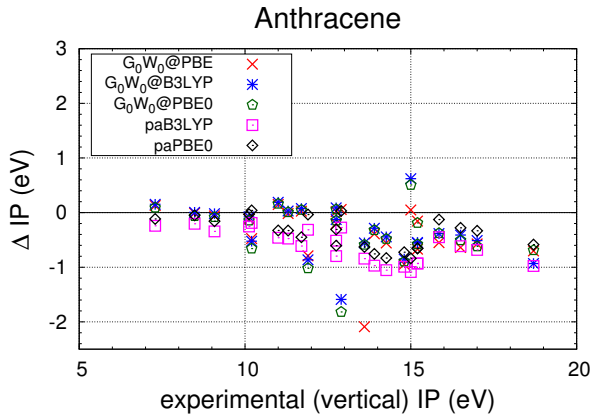

FIG. 1. Deviations of paB3LYP, paPBE0, G_0W_0@PBE, G_0W_0@B3LYP, and G_0W_0@PBE0 IPs from experimental IPs.[1,2,3,4,5,6]

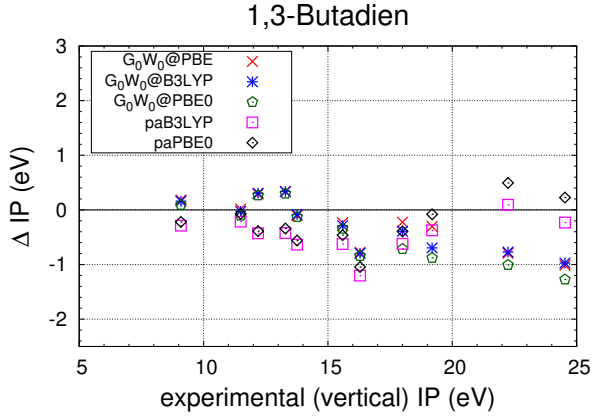

FIG. 2. Deviations of paB3LYP, paPBE0, G_0W_0@PBE, G_0W_0@B3LYP, and G_0W_0@PBE0 IPs from experimental IPs.[7]

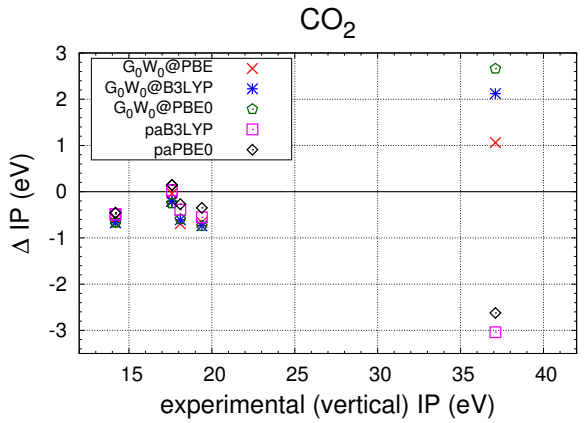

FIG. 3. Deviations of paB3LYP, paPBE0, G_0W_0@PBE, G_0W_0@B3LYP, and G_0W_0@PBE0 IPs from experimental IPs.[8]

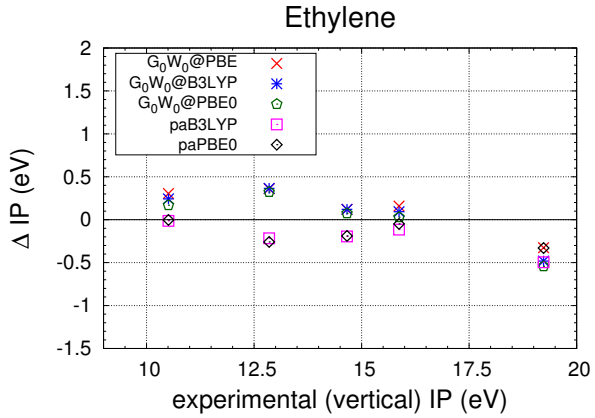

FIG. 4. Deviations of paB3LYP, paPBE0, G_0W_0@PBE, G_0W_0@B3LYP, and G_0W_0@PBE0 IPs from experimental IPs.[9]

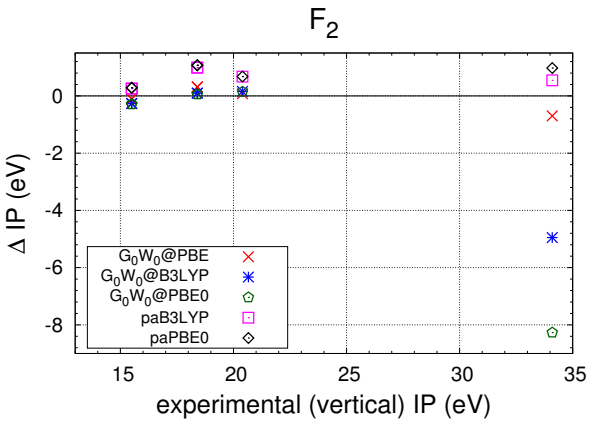

FIG. 5. Deviations of paB3LYP, paPBE0, G_0W_0@PBE, G_0W_0@B3LYP, and G_0W_0@PBE0 IPs from experimental IPs.[10]

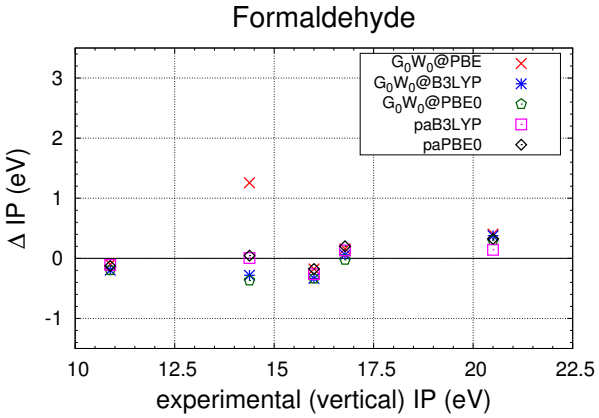

FIG. 6. Deviations of paB3LYP, paPBE0, G_0W_0@PBE, G_0W_0@B3LYP, and G_0W_0@PBE0 IPs from experimental IPs.[11]

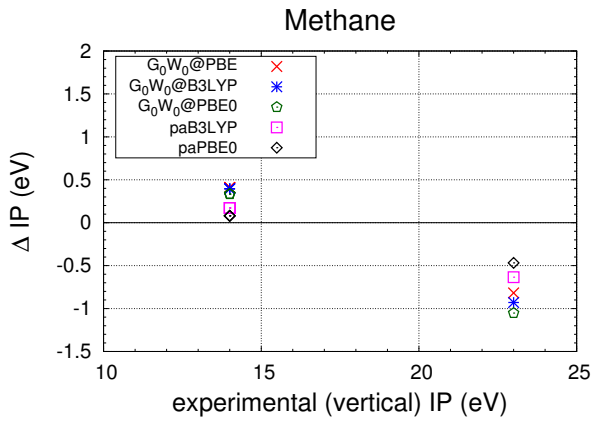

FIG. 7. Deviations of paB3LYP, paPBE0, G_0W_0@PBE, G_0W_0@B3LYP, and G_0W_0@PBE0 IPs from experimental IPs.[12]

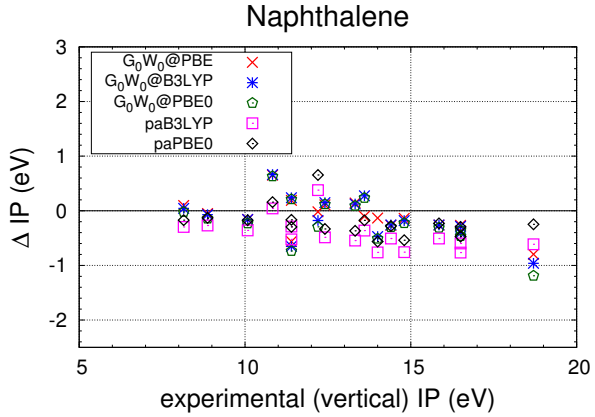

FIG. 8. Deviations of paB3LYP, paPBE0, G_0W_0@PBE, G_0W_0@B3LYP, and G_0W_0@PBE0 IPs from experimental IPs.[1,5,6,13,14,15,16,17]

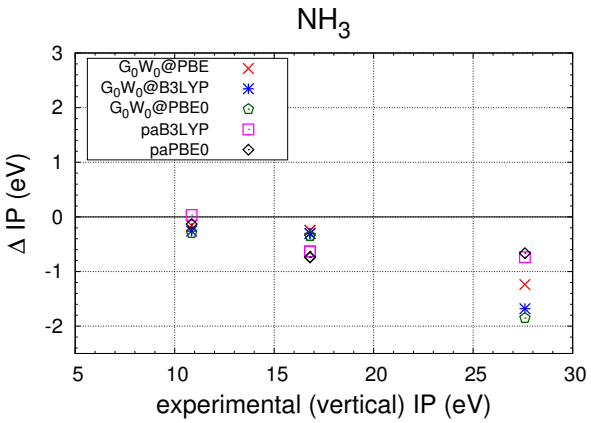

FIG. 9. Deviations of paB3LYP, paPBE0, G_0W_0@B3LYP, and G_0W_0@PBE IPs from experimental IPs.[18]

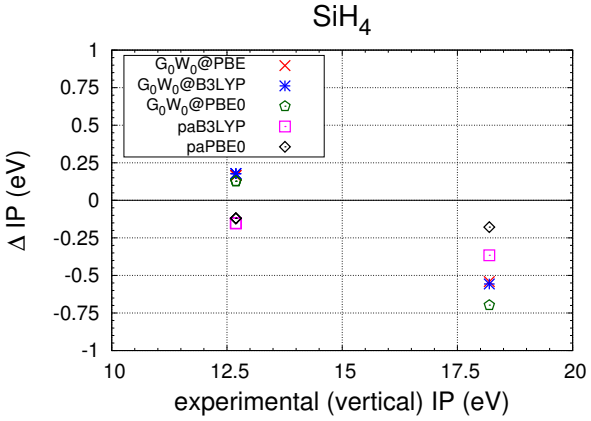

FIG. 10. Deviations of paB3LYP, paPBE0, G_0W_0@B3LYP, and G_0W_0@PBE IPs from experimental IPs.[19]

E. Plots of difference between best fit to experimental spectra and calculated spectra after aligning ionization potential of HOMO for the medium size acceptor molecules

1. Phenazine

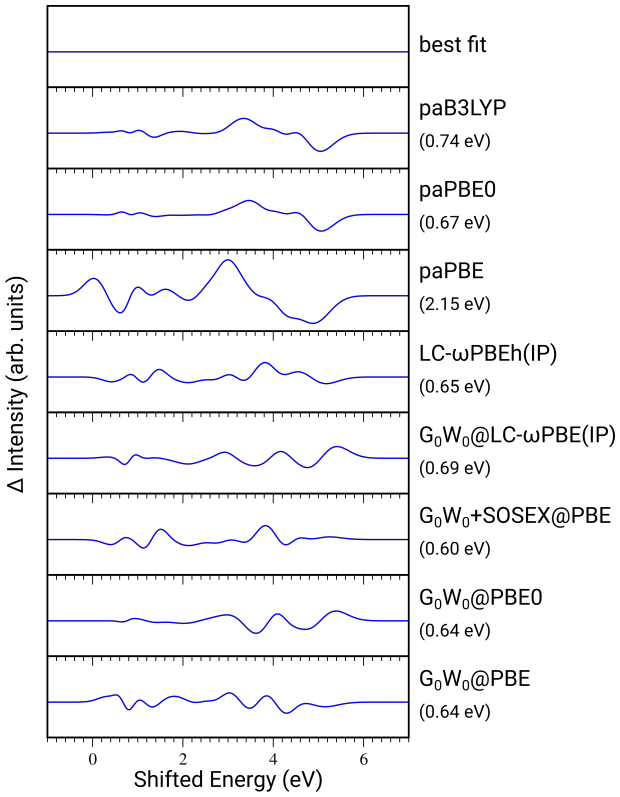

FIG. 11. Difference spectra to best fit for phenazine where the HOMO of each method is shifted to 0 eV.

2. Benzoquinone

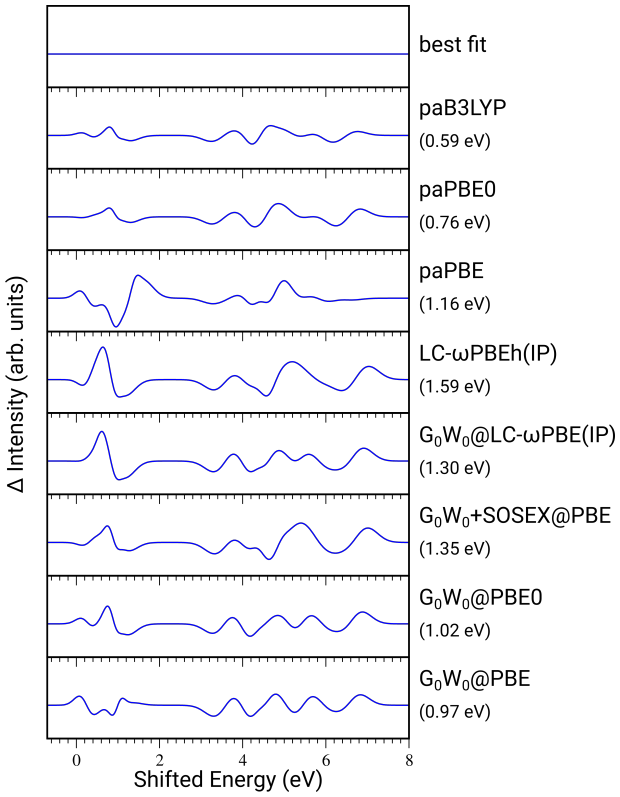

FIG. 12. Difference spectra to best fit for benzoquinone where the HOMO of each method is shifted to 0 eV.

3. Maleic anhydride

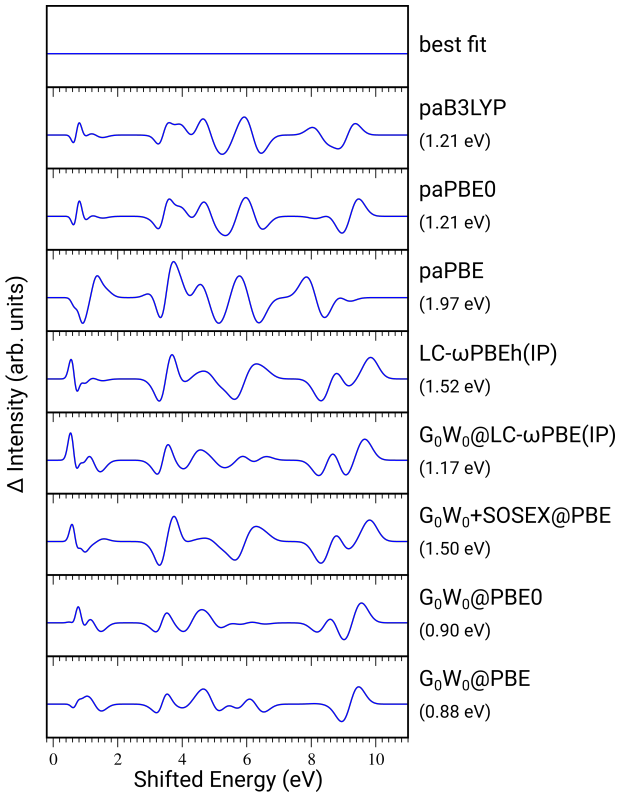

FIG. 13. Difference spectra to best fit for maleic anhydride where the HOMO of each method is shifted to 0 eV.

4. Nitrobenzene

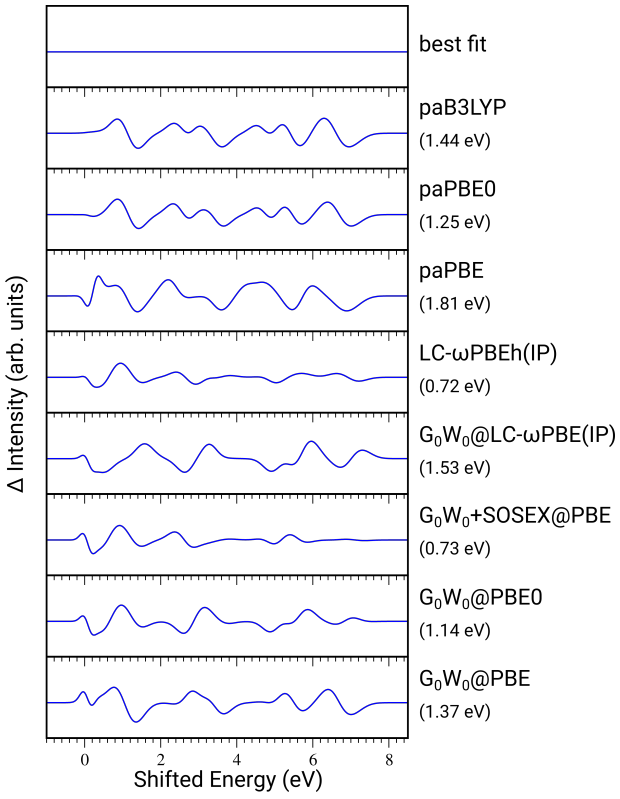

FIG. 14. Difference spectra to best fit for nitrobenzene where the HOMO of each method is shifted to 0 eV.

5. Tetrachloro-benzoquinone

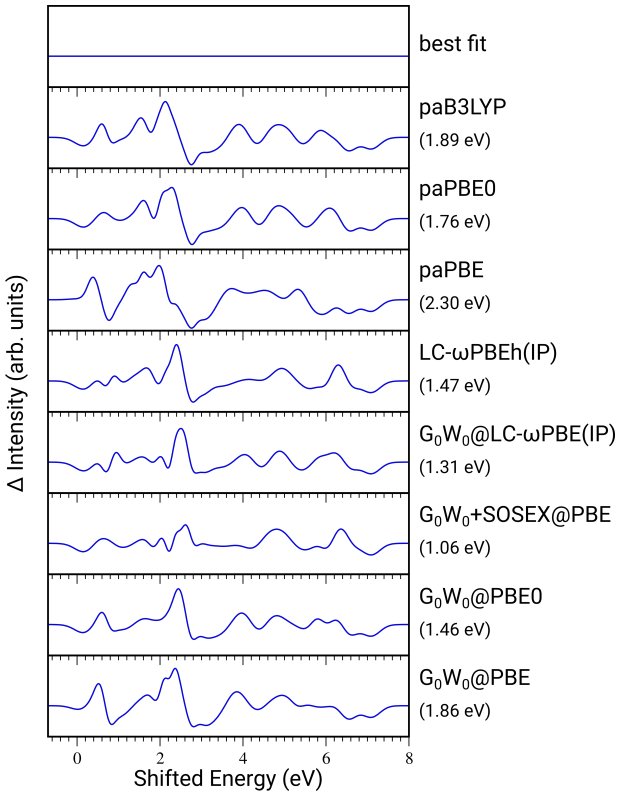

FIG. 15. Difference spectra to best fit for tetrachloro-benzoquinone where the HOMO of each method is shifted to 0 eV.

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[1] R. Boschi, J. Murrell, and w. Schmidt, Faraday Discuss. Chem. Soc. **54**, 116 (1972).

[2] P. A. Clark, F. Brogli, and E. Heilbronner, Helv. Chim. Acta **55**, 1415 (1972).

[3] D. G. Streets and T. A. Williams, J. Electron Spectrosc. Relat. Phenom. **3**, 71 (1974).

[4] N. Hush, A. Cheung, and P. Hilton, J. Electron Spectrosc. Relat. Phenom. **7**, 385 (1975).

[5] W. Schmidt, J. Chem. Phys. **66** (1977).

[6] M. Yamauchi, Y. Yamakita, H. Yamakado, and K. Ohno, J. Electron Spectrosc. Relat. Phenom. **88-91**, 155 (1998).

[7] M. P. Keane, A. N. de Brito, N. Correia, S. Svensson, L. Karlsson, B. Wannberg, U. Gelius,

S. Lunell, W. R. Salaneck, M. Lgdlund, D. B. Swanson, and A. G. MacDiarmid, Phys. Rev. B **45**, 6390 (1992).

[8] C. J. A. U.Gelius, D. A. Allison, G. Johansson, H. Siegbahn, and K. Siegbahn, J. Electron Spectrosc Relat. Phenom. **1**, 131 (1972).

[9] D. W. Turner, C. Baker, A. Baker, and C. R. Brundle, Wiley-Inter-science. London **268** (1970).

[10] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. Heden, K. Hamrin, U. Gelius, T. Bergmank, L. Werme, R. Manne, and Y. Baer, Amsterdam: North-Holland (1969).

[11] L. Cederbaum, G. Hohlneicher, and S. Peyerimhoff, Chem. Phys. Lett. **11**, 421 (1971).

[12] S. T. Hood, A. Hamnett, and C. E. Brion, J. Electron Spectrosc Relat. Phenom. **11**, 205 (1977).

[13] J. Eland and C. Dandy, Z. Naturforsch. **A 23a**, 355 (1968).

[14] S. Obenland and W. Schmidt, J. Am. Soc. **97**, 6633 (1975).

[15] T. Munakata, K. Ohno, Y. Harada, and K. Kuchitsu, Chem. Phys. Lett. **83**, 243 (1981).

[16] T. Kajiwara, S. Masuda, K. Ohno, and Y. Harada, J. Chem. Soc., Perkin Trans. 2 , 507 (1988).

[17] T. Bally, C. Carra, M. P. Fülscher, and Z. Zhu, J. Chem. Soc., Perkin Trans. 2 , 1759 (1998).

[18] A. O. Bawagan, R. Mueller-Fiedler, and C. E. Brion, Chem. Phys. **120**, 335 (1988).

[19] B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. Schweitzer, W. Bull, and F. A. Grimm, J. Chem. Phys. **53**, 768 (1970).