Explicitly Correlated Frequency-Independent Second-Order Green's Function for Accurate Ionization Energies

Yu-ya Ohnishi[a] and Seiichiro Ten-no[a,b]

Explicitly correlated second-order Green's function (GF2-F12) is presented and applied to polycyclic aromatic hydrocarbons (PAHs), oligothiophene, and porphyrins. GF2 suffers from slow convergence of orbital expansions as in the ordinary post Hartree–Fock methods in *ab initio* theory, albeit the method is capable of providing quantitatively accurate ionization energies (IE) near the complete basis set limit. This feature is significantly mitigated by introducing F12 terms of explicitly correlated electronic structure theory. It is demonstrated that GF2-F12 presents accurate IE with augmented triple-zeta quality of basis sets. The errors from experimental results are typically less than 0.15 eV for PAHs. © 2016 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.24468

Introduction

Ionization energies (IE) and electron affinities (EA) (or electron detachment and attachment energies) are fundamental quantities to elucidate the electronic properties of atoms and molecules. They are important indices to rationalize the reactivities of molecules, and are often employed to design new functional materials such as organic light-emitting diodes and organic photovoltaic devices. Gas phase photoelectron spectroscopy is a tool to directly measure the IE/EA of atoms and molecules experimentally. There are several ways to calculate these quantities theoretically, while each of the methods has drawbacks and advantages.

The use of Koopmans' theorem[1] in Hartree–Fock (HF) or Kohn–Sham orbital energies is the simplest way of the evaluation of IE/EA at small computational costs. However, the accuracy is unsatisfactory in many cases because the electron correlation and orbital relaxation (OR) effects are absent in the mean field descriptions. For example, the HF fails to predict the correct ordering of $3\sigma_g$ and $1\pi_u$ orbital energies of N_2 molecule.[2] Alternatively, Kohn–Sham orbital energies often present reasonable results when a range separation is introduced in the functional.[3,4] Nevertheless, it is difficult to systematically improve the accuracy due to the strong functional and system dependencies. Another class of methods for IE/EA are the so-called ΔSCF and its post HF variants, in which the difference between the total energies for the $(N\pm1)-$ and $N-$ electron systems is deemed to be the vertical IE or EA. These methods are capable of incorporating both the OR and electron correlation effects when a post HF is employed. If a highly sophisticated electronic structure method such as full configuration interaction,[5] coupled cluster (CC),[6] or multireference theory[7] is available to evaluate total energies, this procedure should lead to precise IE/EA. The accuracy can be systematically improved by employing a higher level of theory and increasing the size of basis set. Direct calculations of IE/EA are also possible by the symmetry adapted cluster-configuration interaction (SAC-CI)[8] and equation-of-motion (EOM) CC.[9]

Unfortunately, these methods are computationally demanding for large molecules, and the applicability is relatively limited for the present.

One-electron many-body Green's function (GF) or electron propagator theory[10–19] has been also employed to calculate the IE/EA of solids, polymers, and molecules.[20–22] The quasiparticle energies from the Dyson equation can be systematically improved by incorporating higher-order perturbative contributions. Readers can refer to textbooks and reviews for several practical methods based on GF theory.[10,18,19] One of the most successful models both in terms of accuracy and computational cost is the outer-valence Green's function (OVGF), in which higher-order effects are included effectively at the cost of third-order perturbation theory.[15,23–25] OVGF gives significantly accurate vertical IEs on occupied orbitals near the Fermi levels. The algebraic diagrammatic construction[18,26] is also an important framework for inner-valence ionizations in the situation that the diagonal approximation in perturbative GF is poor. More recently, Hirata and coworkers have suggested that the energy differences between N- and (N±1)-electronic systems from the nth-order Møller–Plesset perturbation (MPn) theory in the same set of molecular orbitals define an alternative diagrammatic expansion of Koopmans-like electron binding energies, which converge to those of the full GF methods as $n \rightarrow \infty$.[27] In this wise, the effects of higher-order perturbation have been studied

[a] Yu-ya Ohnishi, S. Ten-no
    Graduate School of System Informatics, Kobe University, Nada-Ku, Kobe
    657-8501, Japan
[b] S. Ten-no
    Graduate School of Science, Technology, and Innovation, Kobe University,
    Nada-Ku, Kobe 657-8501, Japan
    E-mail: tenno@garnet.kobe-u.ac.jp

extensively, while much less is known about the basis set convergence, albeit the triple-zeta basis set practically recommended.[28] However, a strong basis set dependency should be observed in the GF expansions since the working equations of GF are closely related to the MP series.

In what follows, the slow basis set convergences of the second-order GF (GF2) quasi-particle energy is revealed for occupied orbitals under the diagonal and frequency-independent approximations. Then, we shall incorporate F12 theory, which has been successfully applied to accelerate the convergence of *ab initio* methods,[29–34] into GF2. The developed GF2-F12 are numerically examined on the IEs of polycyclic aromatic hydrocarbons (PAHs), oligothiophene, and porphyrins.

Theory

The GF2 quasi-particle energy for the kth occupied orbital of an N-electronic closed-shell system under the diagonal and frequency-independent approximations, ϵ_k^{GF2}, is given by

$$\epsilon_k^{GF2} = \epsilon_k^{HF} + \Sigma_k^{OR} + \Sigma_k^{CD} \tag{1}$$

$$\Sigma_k^{OR} = \sum_{i,j}^{occ.} \sum_{a}^{vir.} \frac{\langle ij|ka \rangle (2\langle ka|ij \rangle - \langle ak|ij \rangle)}{\epsilon_k^{HF} + \epsilon_a^{HF} - \epsilon_i^{HF} - \epsilon_j^{HF}} \tag{2}$$

$$\Sigma_k^{CD} = \sum_{i}^{occ.} \sum_{a,b}^{vir.} \frac{\langle ik|ab \rangle (2\langle ab|ik \rangle - \langle ba|ik \rangle)}{\epsilon_k^{HF} + \epsilon_i^{HF} - \epsilon_a^{HF} - \epsilon_b^{HF}}, \tag{3}$$

where the indices $i, j, \ldots$ and $a, b, \ldots$ represent occupied and virtual orbitals, respectively, and ϵ_p^{HF} stands for the HF orbital energy for the pth orbital. According to the classification by Pickup and Goscinski,[35,36] the GF2 self-energy can be decomposed into the orbital relaxation, pair relaxation, and pair removal contributions, while we have defined a couple of components, OR and correlation difference (CD) in eqs. (2) and (3), respectively. OR is the contribution from the OR or the Fock difference, corresponding to the sum of orbital relaxation and pair relaxation of the Pickup–Goscinski classification. CD is the MP2 correlation energy difference between the N- and $(N-1)$-electronic systems, that is equivalent to the pair removal of Pickup–Goscinski.

It should be stressed that the set of orbitals for the MP2 correlation energies of $(N-1)$-electron systems coincide with those for the N-electron system.[27,35–39] Therefore, given the MP2 pair energy, e_{ij} for the N-electron system,

$$e_{ij} = \sum_{a,b}^{vir.} \frac{\langle ij|ab \rangle (2\langle ab|ij \rangle - \langle ba|ij \rangle)}{\epsilon_i^{HF} + \epsilon_j^{HF} - \epsilon_a^{HF} - \epsilon_b^{HF}}, \tag{4}$$

CD can be expressed in terms of e_{ij} as

$$\Sigma_k^{CD} = \sum_{i,j}^{occ.} e_{ij} - \sum_{i,j}^{occ.} e_{ij}(1 - \delta_{jk}) = \sum_{i}^{occ.} e_{ik}, \tag{5}$$

where δ_{jk} is the Kronecker delta function. As the MP2 pair energy e_{ij} exhibits a slow convergence due to the double
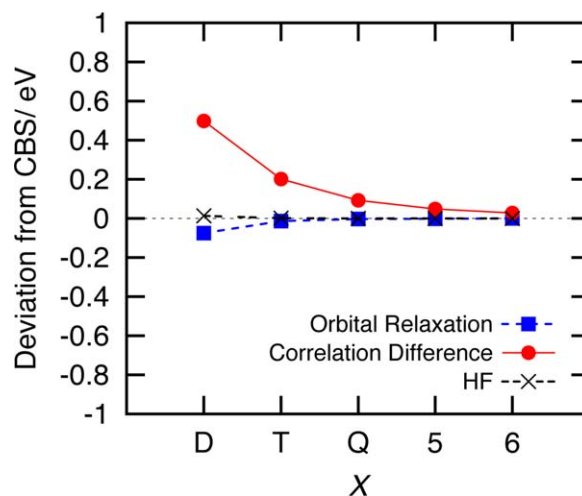

Figure 1. The deviations from CBS limits of the HF (black cross), orbital relaxation (OR; blue square), and correlation difference (CD; red circle) components in the quasi-particle energy for benzene in aug-cc-pV XZ basis sets. (See the text for CBS.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

summation over virtual orbitals in (4), so does the CD contribution to ϵ_k^{GF2}. Figure 1, shows the basis set convergences of ϵ_i^{HF}, ϵ_i^{OR}, and ϵ_i^{CD} from their complete basis set (CBS) limits for benzene in aug-cc-pV XZ.[40–42] For the maximum angular momentum of the expansion L and that for occupied orbitals $L_{occ.}$, Σ_k^{CD} goes as $(L+1)^{-3}$, while the expansion for Σ_k^{OR} is a terminating series at $3L_{occ.}$ in the virtual index. It is considered that the convergence of Σ_k^{CD} can be accelerated by replacing the pair energy by the MP2-F12 one,

$$\epsilon_k^{GF2-F12} = \epsilon_k^{HF} + \Sigma_k^{OR} + \Sigma_k^{CD-F12} \tag{6}$$

$$\Sigma_k^{CD-F12} = \sum_{i}^{occ.} (e_{ik} + d_{ik}), \tag{7}$$

where d_{ik} stands for the F12 corrections to the second-order pair energies. We examine practical approximations corresponding to the previously developed MP2-F12 methods[43,44] using the Slater correlation factor,[45]

$$f(r_{12}) = -\gamma^{-1} \exp(-\gamma r_{12}), \tag{8}$$

and the s- and p-wave cusp conditions for single and triplet pairs (SP Ansatz).[46]

Computational Details

GF2-F12 is implemented in our GELLAN program package.[47] Many-electron integrals are calculated exploiting numerical quadratures,[43,46] and a massively parallel implementation is achieved in the previous hybrid MPI/OpenMP parallelizations.[44] We examine A, A*, B, and B* approximations corresponding to those of MP2-F12,[43] where A and A* neglect the contribution from the exchange commutator and the asterisked methods assume the extended Brillouin condition (EBC).[48] The aug-cc-

pV XZ (X = D, T, Q, 5, and 6) basis sets[40–42] are employed for all GF calculations performed on K computer at RIKEN in Japan.

In addition to GF2-F12, we employ the frequency-dependent second- and third-order GF methods, GF2(ω) and GF3(ω), as well as the OVGF. We also test the DFT orbital energies from BLYP,[49,50] B3LYP,[50–53] LC-BLYP,[54] CAM-B3LYP,[55] and ωB97X-D[56] functionals using the 6-311G(d,p)[57] basis set for comparisons. The geometries are optimized at ωB97X-D/6-31G(d),[58,59] which usually give reasonable geometrical and electronic properties for π-conjugated systems of DFT.[4] DFT, GF2(ω), GF3(ω), and OVGF calculations are performed with the Gaussian09 program suite on Intel Xeon clusters. The CBS limits of the GF methods are estimated in terms of the two-point extrapolation scheme of Helgaker[60,61] with aug-cc-pV(56)Z.

Figure 2 presents Σ_k^{CD-F12} in various approximations as functions of the length-scale parameter $r_c = 1/\gamma$. There are close resemblances between Σ_k^{CD-F12} and the corresponding MP2-F12 energies.[43] GF2-F12/A and A* do not necessarily give an upper bound of the CBS limit due to the absence of the exchange commutator in the so-called B-intermediate. The use of aug-cc-pVTZ preserves the tendencies, though the dependencies on the approximations and r_c are much smaller. Figure 3 illustrates the Brandow (or antisymmetrized Goldstone) diagrams[62] for the contributions of OR and CD, and the V- and B-term contributions GF2-F12 under EBC, respectively.[63,64] The two upgoing arrows in Σ_k^{CD} indicate that the summation is a nonterminating series, and the wave operator is augmented by the vertex for the rational generator in (c) connected by double arrows spanned by CBS.[33,65] This contribution defines GF2-F12/V*, which does not contains a term contribution (d) quadratic to the geminal, leading to an error linear in the F12 amplitudes exhibiting stronger r_c dependencies as in CCSD-F12-0.[66] It is also noted that supplementary literatures are available for the perturbational analysis of the composition of EBC in CCSD(F12)[67] and an implementation of EOM-CC-F12 for IEs.[68] The length-scale parameter does not influence the results strongly as far a basis larger than as aug-cc-pVTZ is employed. We therefore use the default parameter $r_c = 2/3$ in GELLAN henceforth.

Results

Polycyclic aromatic hydrocarbons

First, we investigate the basis set convergence of GF2-F12 for the first IE of benzene in Table 1. As observed in the previous section, HF (Koopmans' theorem) exhibits a very small basis set dependence. The convergence of GF2 is considerably slow and gives results more deviated from the experimental IE, 9.244 eV, compared to HF especially for a small basis. The accuracy of GF2 is improved with the size of the basis set, and its CBS agrees with the experimental value only within 0.01 eV. The IE of GF2/aug-cc-pVTZ is 9.053 eV in the experimental geometry, and it is considered that the geometrical effect to the IE is in the order of another 0.01 eV. It is evident that F12 corrections significantly improve the convergence of GF2. GF2-F12/A* and B in aug-cc-VTZ results are very close to the CBS limit 9.255 eV. It is noted that all F12 corrections involving GF2-F12/V* are virtually
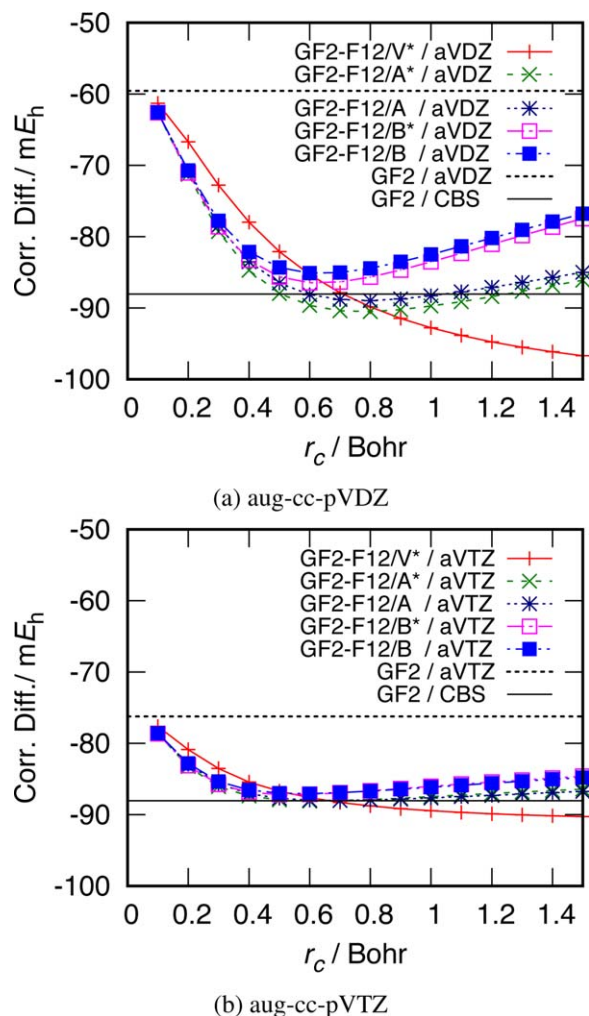
Figure 2. Σ_k^{CD-F12} (mE_h) in aug-cc-pVDZ (a) and aug-cc-pVTZ (b) for the neon atom as functions of length-scale parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

identical in a basis larger than aug-cc-pVTZ. The convergence of GF2 (ω) resembles the one of frequency-independent GF2, while GF3 (ω) and OVGF show much smaller basis set dependencies. This is rather controversial, since no cancelation between the second and higher-order components with respect to the basis set is observed in the standard MPn and CC series.[70] We therefore leave investigations on the convergence of the higher-order GFs for future works.
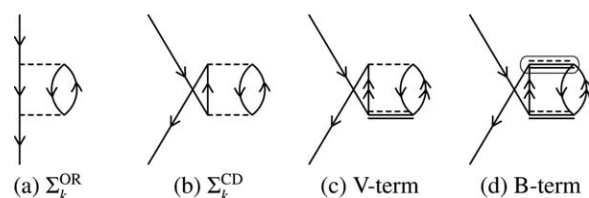
Figure 3. GF2 self-energies corresponding to OR (a), CD (b), and V- (c) and B-term (d) contributions of F12 corrections, where the resolvent lines are omitted from the (a) and (b). The vertex in the horizontal double straight line with single dashed-line represents the integrals over the rational generator $\hat{\mathcal{R}}_{12}$ of F12 theory,[32,33,46] and the same vertex is augmented by ellipse for the commutator integrals $[\hat{F}_{12}, \hat{\mathcal{R}}_{12}]$ in (d).

Table 1. The basis set dependence of the first IE (eV) of benzene from HF (Koopmans), GF2, GF2-F12, GF2(ω), GF3(ω), and OVGF in aug-cc-pV XZ (X = D, T, Q, 5, and 6) basis sets compared to those in the CBS limits.

| X	HF (Koopmans)	GF2	GF2-F12/A*	GF2-F12/B	GF2(ω)	GF3(ω)	OVGF
D	9.165	8.820	9.246	9.205	8.863	9.360	9.226
T	9.176	9.066	9.252	9.235	9.080	9.393	9.304
Q	9.177	9.166	9.252	9.245	9.168	9.393	9.328
5	9.178	9.208	9.253	9.249	9.204	9.389	9.334
6	9.178	9.228	9.254	9.252	9.221	9.385	9.336
CBS[a]	9.178	9.255	9.255	9.255	9.244	9.380	9.339

The experimental IE is 9.244 eV.[69] [a] The CBS limit from GF2 is also used for GF2-F12/A* and /B.

Table 2. The first IEs (eV) of PAHs from HF, GF2, GF2-F12/A*, GF2-F12/B, BLYP, B3LYP, CAM-B3LYP, LC-BLYP, and ωB97X-D.

Compound	HF	GF2	GF2-F12/A*	GF2-F12/B	BLYP	B3LYP	LC-BLYP	CAM-B3LYP	ωB97X-D	Exptl.
Benzene	9.176	9.066	9.252	9.235	6.015	6.982	9.846	8.429	9.005	9.244[a]
Naphthalene	7.917	7.874	8.063	8.045	5.198	6.066	8.670	7.378	7.948	8.144[b]
Anthracene	7.100	7.116	7.306	7.289	4.711	5.507	7.916	6.721	7.285	7.439[c]
Pyrene	7.160	7.141	7.332	7.314	4.833	5.612	7.965	6.787	7.335	7.426[c]
Coronene	7.124	7.009	7.202	7.185	4.959	5.721	7.976	6.853	7.398	7.29[d]
Ovalene	6.376	6.386	6.580	6.563	4.532	5.220	7.274	6.242	6.764	6.71[d]
RMSD	0.252	0.281	0.098	0.114	2.691	1.877	0.570	0.656	0.154	–
ME	−0.233	−0.277	−0.086	−0.104	−2.667	−1.857	0.566	−0.640	−0.086	–

[a] Ref. [69]. [b] Ref. [71]. [c] Ref. [72]. [d] Ref. [73].

We compare the IEs of PAHs, benzene, naphthalene, anthracene, pyrene, coronene, and ovalene from HF, GF2, GF2-F12, and DFT with those of ultraviolet photoelectron spectroscopy (UPS) in Table 2 along with the statistical measures, root mean square deviations (RMSD) and mean errors (ME). The Koopmans absolute of orbital energies are regarded as IEs for HF and DFT. The aug-cc-pVTZ basis set is used for the HF, GF2, and GF2-F12 and 6-311G(d,p) for DFT. Among the methods examined, the GF2-F12/A* and GF2-F12/B present the smallest root-mean-square-deviations (RMSDs), 0.098 eV and 0.114 eV, respectively. In accord with the previous work,[3] the pure and hybrid GGA functionals, BLYP and B3LYP, significantly underestimates the IEs. The Coulomb-attenuating method, CAM-B3LYP, somewhat improves B3LYP but still the IEs are underestimated. LC-BLYP overcorrects the BLYP result. ωB97X-D presents a considerably small RMSD, 0.154 eV, and this functional is seemingly practically useful among the DFT examined in this work. One notes that GF2-F12 slightly underestimates the IE for all the molecules.

(a)

(b)
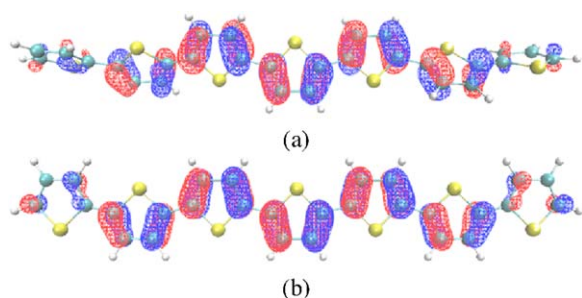
Figure 4. HOMO of thiophene heptamer of fully optimized (a) and in which S—C—C—S dihedral angles are fixed to be 180° (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(a) Absolute value of HOMO energy vs S-C-C-S Angle

(b) MP2-F12/B energy vs S-C-C-S Angle
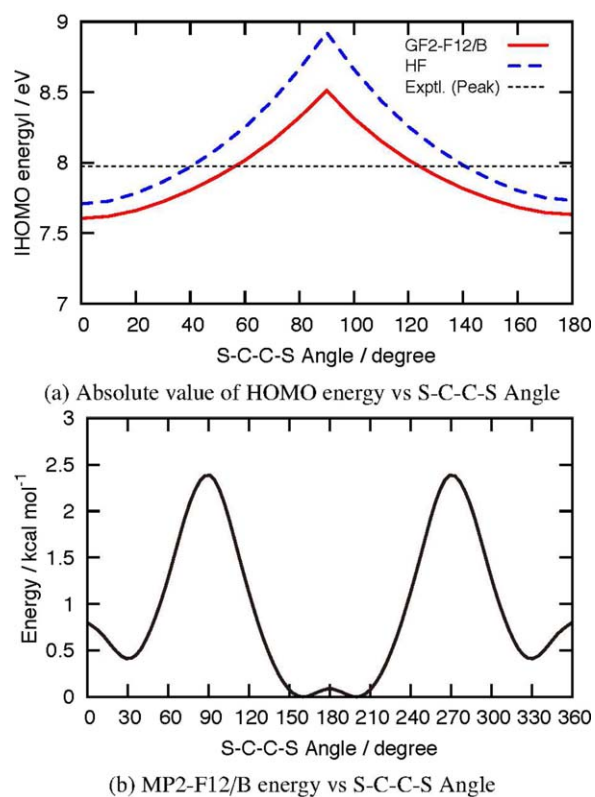
Figure 5. Absolute value of HOMO energy (eV) calculated by the HF and GF2-F12/B methods (a) and the potential energy curve calculated by the MP2-F12 method (kcal mol^{-1}) (b) as a functions of S—C—C—S dihedral angle of 2,2′-bithiophene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
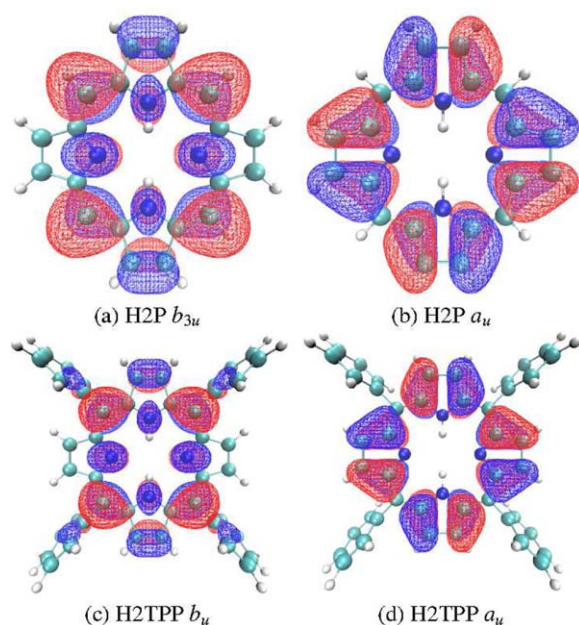
Figure 6. Molecular orbitals of b_{3u} (a) and a_u (b) symmetries of free-base porphyrin (H2P), and b_u (c) and a_u (d) symmetries of tetraphenylporphyrin (H2TPP). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conversely, ωB97X-D underestimates IEs for small PAHs but starts to overestimate them for coronene and ovalene. Thus, further investigations are needed to examine the accuracy of the ωB97X-D functional for IEs of larger PAHs.

Oligothiophene

We next investigate the IEs of another series of π-conjugated systems, oligothiophenes from monomer to heptamer (see Fig. 4). The UPS results show a sharp peak for the thiophene molecule, while the spectra for 2,2′-bithiophene contains a broad peak with the full-width at half-maximum 0.6 eV.[74,75] This is because the monomer unit easily rotates and the HOMO energy changes along the rotation in the oligothiophenes. For example, the GF2-F12/B IE of the S-C-C-S dihedral angle for 2,2′-bithiophene in Figure 5a displays the minimum and maximum of IEs, around 7.6 and 8.5 eV, at 180° and 90°, respectively. The small rotational barrier, 2.5 kcal/mol at MP2-F12/aug-cc-pVTZ as shown in Figure 5b indicates the rotation of monomer

Table 3. The first IE (eV) from HF, GF2, GF2-F12/B, and ωB97X-D of thiophene N-mers.

N	HF	GF2	GF2-F12/B	ωB97X-D	Exptl.
1	8.965	8.715	8.914	8.669	8.87[a]
2	7.888/7.733	7.558/7.443	7.747/7.632	7.778/7.651	7.95/7.5[a]
3	7.435/7.218	7.065/6.906	7.257/7.098	7.410/7.232	7.43/7.0[a]
4	7.227/6.954	6.833/6.631	7.026/6.824	7.246/7.019	7.28/6.7[a]
5	7.015/6.800	6.631/6.471	6.825/6.664	7.074/6.895	7.11/6.4[a]
6	6.970/6.705	6.573/6.371	6.767/6.565	7.041/6.819	7.1/6.5[b]
7	6.895/6.641	6.501/6.305	6.695/6.499	6.982/6.767	

The numbers before and after the slashes stand for those for (the fully optimized)/(flat) conformers, respectively, for $N \geq 2$, corresponding to the (peak)/(lower edge) values from the UPS spectra in the experimental column. The aug-cc-pVTZ basis set is employed for the HF, GF2, and GF2-F12 and 6-311G(d,p) for the DFT methods. [a] The peak values are from Figure 3 and the lower edge values are read from Figure 2 of Ref. [74]. [b] The peak and lower edge values are read off from Figures 4 and 6, respectively, of Ref. [75].

unit is one of the reasons for the broadening of the spectra, in addition to the contribution of adiabatic ionization process. Therefore, we calculate the IEs in the most stable and fully flat conformations of oligomers as shown in Figure 4 for comparisons with the observed peak and lower edge values of the UPS spectra, respectively.

Table 3 shows that GF2-F12/B improves the IE of the monomer compared to HF, while the absence of the F12 correction in GF2 even deteriorates the result. For $N \geq 2$, GF2-F12/B tends to underestimate the peak values by ca. 0.2–0.3 eV. The IEs of GF2-F12/B in flat conformers are underestimated compared to the experimental lower edge values by 0.1 eV on average. This is reasonable because the experimental values correspond to those from adiabatic ionization processes, and the theoretical IEs in the flat geometries should be always larger than the experimental values. The ωB97X-D IEs in the most stable geometries agree well with the experimental peak values especially for $N \geq 3$. The method also presents reasonable IEs for the flat geometries, which are larger than the experimental lower edge value by 0.1-0.3 eV in accord with the observation of Salzner et al. on the performance of the ωB97X-D functional.[4]

Porphyrins

As the final example, we show the IEs of unsubstituted free-base porphyrin (H2P) and tetraphenylporphyrin (H2TPP) in

Table 4. The IEs of frontier orbitals (eV) calculated by the HF, GF2, GF2-F12/B, LC-BLYP, CAM-B3LYP, and ωB97X-D and experimental values of H2P and H2TPP.

state	HF	GF2	GF2-F12/B	LC-BLYP	CAM-B3LYP	ωB97X-D	NR2[a]	P3[a]	OVGF[a]	Exptl.
H2P										
$^2B_{3u}$	6.777	6.540	6.718	7.388	6.415	6.912	6.68	6.96	6.66	6.9[b]
^2A_u	6.187	6.919	7.095	7.251	6.424	6.922	6.78	7.02	6.72	7.1sh[b]
H2TPP										
^2B_u	6.483	5.970	6.155	7.099	6.148	6.633	–	–	–	6.43[c]
^2A_u	6.124	6.580	6.754	7.189	6.346	6.842	–	–	–	6.70[c]

The aug-cc-pVTZ basis set is employed for the HF, GF2, and GF2-F12 and 6-311G(d,p) for the DFT methods. [a] Ref. [82]. Geometries were optimized by the B3LYP/6-311G(d,p). NR2 and P3 indicate nondiagonal, renormalized second-order approximation and partial third order, respectively. For the OVGF, the recommended values are presented. [b] Ref. [83]. [c] Ref. [84].

Figure 6. The IEs of various porphyrins have been investigated using DFT,[76–78] the SAC-CI,[79,80] equation-of-motion coupled-cluster (EOM-CC), and perturbation (EOM-PT),[81] and various electron propagators such as NR2, P3, and OVGF.[82] However, the basis sets employed in these works are not sufficiently large due to the relatively large molecular size, and hence, it is worthy to estimate the CBS limits using GF2-F12. As shown in Table 4, HF fails to predict the correct ordering of IEs concerning the HOMO and HOMO-1 both for H2P and H2TPP. Although GF2 corrects the incorrect ordering, the results are worsened compared to HF for $^2B_{3u}$ (H2P) and ^2B_u (H2TPP). The incorporation of the F12/B correction significantly improves the results for H2P in a balanced manner retaining the accuracy for $^2A_{1u}$. The method also presents qualitatively accurate IEs for H2TPP, though the deviation for the ^2B_u is somewhat increased compared to HF. The results of NR2 and OVGF[82] lie in between those of HF and GF2. This can be attributed to the smaller basis set and virtual space employed in the previous work. P3 gives precise results though a further investigation is needed for the basis set convergence of the method. The IEs of DFT are considerably dependent on the functionals and systems as far as the Kohn–Sham orbital energies are employed. All functionals give correct ordering for H2TPP. LC-BLYP however fails the prediction for H2P, and CAM-B3LYP and ωB97X-D lead to almost identical orbital energies for $^2B_{3u}$ and ^2A_u of the H2P.

Conclusion

GF2-F12 is implemented under the diagonal and frequency independent approximations and has been tested for IEs of PAH, oligothiophene, and porphyrins. It is clearly demonstrated that the incorporation of F12 significantly improve the basis set convergence of GF2. The IEs of GF2-F12/aug-cc-pVTZ are satisfactorily accurate and virtually identical to the CBS limits of GF2. The maximum deviations from the experimental IEs are 0.15 eV for PAHs and 0.3 eV for oligothiophenes and porphyrins. For IEs examined in this article, GF2-F12 systematically underestimates the experimental IEs, while DFT with ωB97X-D functional, which is often as accurate as GF2-F12, overshoots them in some cases. It will be possible to incorporate F12 into other GF methods, and we are working on this line of subject.

Acknowledgment

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