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So Hirata, *Pacific Northwest National Laboratory*

Chang-Guo Zhan, *Pacific Northwest National Laboratory*

Edoardo Apra, *Pacific Northwest National Laboratory*

Theresa L. Windus, *Pacific Northwest National Laboratory*

David A. Dixon, *Pacific Northwest National Laboratory*



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# A New, Self-Contained Asymptotic Correction Scheme To Exchange-Correlation Potentials for Time-Dependent Density Functional Theory

So Hirata,\* Chang-Guo Zhan,† Edoardo Aprà, Theresa L. Windus, and David A. Dixon

William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352

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By combining the asymptotic correction scheme of Casida and Salahub for exchange-correlation potentials and the phenomenological linear correlation between experimental ionization potentials and highest occupied Kohn–Sham (KS) orbital energies found by Zhan, Nichols, and Dixon, we propose a new, expedient, and self-contained asymptotic correction to exchange-correlation potentials in KS density functional theory (DFT) for use in time-dependent density functional theory (TDDFT) that does not require an ionization potential as an external parameter from a separate calculation. The asymptotically corrected (TD)DFT method is implemented in the quantum chemistry program suite NWChem for both sequential and massively parallel execution. The asymptotic correction scheme combined with the B3LYP functional [B3LYP(AC)] is shown to be well balanced for both valence- and Rydberg-type transitions, with average errors in excitation energies of CO, N<sub>2</sub>, CH<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub> being smaller than those of uncorrected BLYP and B3LYP TDDFT by factors of 4 and 2, respectively, consistent with the improved orbital energies found for B3LYP(AC). We demonstrate the general applicability and accuracy of the method for the Rydberg excited states of mono- to tetrafluorinated methanes, the valence and Rydberg excited states of benzene, and the *Q*, *B*, *N*, and *L* band positions of free-base porphyrin.

## Introduction

Time-dependent density functional theory (TDDFT)<sup>1–7</sup> is becoming widely used as a reliable method for the prediction of electronic excitation processes and other fast time-dependent phenomena involving the electronic response to an external perturbation. Density functional theory (DFT) accounts for the electron correlation of a system in the ground state by virtue of approximations to the exact but unknown exchange-correlation functional. Thus, TDDFT can also, in principle, incorporate a large fraction of the effects of electron correlation in an excited state within the framework of single-excitation theory. In practice, the accuracy of TDDFT employing the most widely available exchange-correlation functionals, which are approximations to the true functional, and the so-called adiabatic approximation has been varied.<sup>8,9</sup> For vertical excitation energies to low-lying valence excited states, TDDFT with these approximate functionals has proven quite accurate, significantly outperforming the Hartree–Fock-based analogues, such as configuration-interaction singles (CIS) and time-dependent Hartree–Fock (TDHF). However, for high-lying excited states or Rydberg excited states, TDDFT underestimates the excitation energies by up to 1 eV or more.

Casida et al.<sup>10</sup> identified the cause of the breakdown of TDDFT for high-lying excited states to be the incorrect asymptotic behavior of most of the exchange-correlation potentials currently in use. This problem is closely related to the self-interaction problem of DFT and the fact that DFT with the present-day functionals significantly underestimates the

orbital energies and, thus, Koopmans' ionization potentials. Unlike the exact exchange-correlation potential, which must have a slow  $-1/r$  asymptotic decay, most present-day approximations to the exchange-correlation functional result in fast exponential decay of the associated potentials in the asymptotic region. This leads to errors in the excitation energies and other properties that probe this region. A very simple and effective way to rectify this problem was proposed by Tozer and Handy<sup>11</sup> and by Casida and Salahub.<sup>10,12</sup> They proposed to splice a  $-1/r$  asymptotic tail to an exchange-correlation potential that does not have the correct asymptotic behavior. Because the approximate exchange-correlation potentials are too shallow everywhere, a negative constant must be added to them before they are spliced to the  $-1/r$  tail seamlessly in a region that is not sensitive to chemical effects or to the long-range behavior. The negative constant or the shift is often discussed in terms of the derivative discontinuity problem with approximate functionals.<sup>11</sup> The shift is usually taken to be the difference of the HOMO energy from the true ionization potential, which can be obtained either from experiment or from a  $\Delta$ SCF calculation. In either the Tozer–Handy or the Casida–Salahub asymptotic correction schemes, the amount of the shift is determined by a separate  $\Delta$ SCF calculation of the ionization potential prior to a TDDFT calculation. It would be preferable if the shift could be computed within a single KS DFT calculation, rather than supplied as an external parameter obtained from two separate calculations. Such an approach has the advantage of being more expedient and self-contained, and can be regarded as a new functional in the broadest definition, where the functional is geared toward accurate descriptions of excited states and time-dependent phenomena as well as those of ground states. Baerends et al. also proposed two schemes that lead to exchange-correlation potentials with correct asymptotic decay behavior:

\* Corresponding author. E-mail address: so.hirata@pnl.gov.

† Permanent address: Division of Pharmaceutical Sciences, College of Pharmacy, University of Kentucky, Lexington, Kentucky 40536. E-mail address: zhan@uky.edu.

the method of statistical averaging of orbital potentials (SAOP)<sup>13</sup> and the gradient-regulated connection (GRAC).<sup>14</sup> The former does not require the knowledge of ionization potential, and hence can be considered as a successful example in this category.

Recently, we found that there is a strong linear correlation between the highest occupied KS orbital energies ( $\epsilon_{\text{HOMO}}$ ) and experimental ionization potentials (IP), even though the KS orbital energies significantly underestimate the experimental or  $\Delta$ SCF IPs.<sup>15</sup> With the Becke3–Lee–Yang–Parr (B3LYP) functional and the aug-cc-pVTZ+ basis set (“+” stands for an additional set of diffuse functions), a linear relationship was found for 52 representative atomic or molecular systems (with  $R = 0.993$ ) and can be written as

$$\text{IP} = -\epsilon'_{\text{HOMO}} = -1.3042 \epsilon_{\text{HOMO}} + 0.411 \quad (1)$$

in units of eV.<sup>15</sup> Assuming that a shift ( $\Delta$ ) is the difference between  $-\text{IP}$  and  $\epsilon_{\text{HOMO}}$  for an uncorrected potential and that  $\epsilon'_{\text{HOMO}}$  approaches  $-\text{IP}$  for a corrected potential, i.e.,

$$-\epsilon'_{\text{HOMO}} = -1.3042 (\epsilon'_{\text{HOMO}} - \Delta) + 0.411 \quad (2)$$

we find

$$\Delta = 0.2332 \epsilon'_{\text{HOMO}} - 0.315 \quad (3)$$

We can now use the shift ( $\Delta$ ) determined by this formula self-consistently in the KS DFT cycles. Below, we demonstrate that the combination of this formula and the asymptotic correction scheme of Casida and Salahub leads to a self-contained asymptotically corrected Kohn–Sham SCF that is rapidly convergent for the shift as well as for the KS orbitals, and that the subsequent TDDFT calculations produce excitation energies that are dramatically improved for high-lying and Rydberg excited states. The results of asymptotically corrected TDDFT calculations for the vertical excitation energies of carbon monoxide, nitrogen, formaldehyde, ethylene, methane, fluorinated methanes, benzene, and free-base porphyrin are found to be in good agreement with the available gas-phase experimental data (the porphyrin data were obtained in vapor or solution) over a wide energy range.

### Computational Approach

The asymptotic correction scheme has been implemented in the KS DFT module of NWChem,<sup>16</sup> which supports both sequential and massively parallel executions. This module employs Gaussian-type basis functions. In each iteration of the KS SCF, a KS Hamiltonian matrix is built with the density matrix from the previous iteration. The exchange-correlation contribution to the KS Hamiltonian matrix elements, written as

$$X_{\mu\nu} = \int \phi_{\mu}(\mathbf{r}) V_{\text{xc}}(\mathbf{r}) \phi_{\nu}(\mathbf{r}) \, d\mathbf{r} \quad (4)$$

where  $\phi_{\mu}(\mathbf{r})$  and  $\phi_{\nu}(\mathbf{r})$  are basis functions and  $V_{\text{xc}}(\mathbf{r})$  is an exchange-correlation potential, are computed numerically by using a multi-center grid. Formally, the exchange-correlation potential is the functional derivative of an exchange-correlation functional with respect to the electron density,

$$V_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}} / \delta \rho(\mathbf{r}) \quad (5)$$

which often suffers from the nonphysical fast decay. Following Casida and Salahub and eq 3, we redefine the exchange-correlation potential, hereafter referred to as B3LYP(AC), as

$$V_{\text{xc}}(\mathbf{r}) = \max[V_{\text{B3LYP}}(\mathbf{r}) + \Delta, 0.8 \times V_{\text{LB94}}(\mathbf{r})], \quad (6)$$

where  $\Delta$  is a negative constant given by eq 3 and  $V_{\text{B3LYP}}(\mathbf{r})$  and  $V_{\text{LB94}}(\mathbf{r})$  are, respectively, the uncorrected exchange-correlation potential of the B3LYP functional (containing nonlocal HF exchange) and the van-Leeuwen–Baerends (LB94) potential,<sup>17</sup> which has the correct long-range decay. The asymptotic correction will shift down the occupied orbital energies uniformly (by  $|\Delta|$ ) without significantly altering the distributions or the shapes of the occupied orbitals and at the same time drastically improve the shapes, distributions, and ranges of virtual orbitals.

Several important remarks about eq 6 are in order. (i) Because the relationships expressed by eqs 1–3 are determined for the B3LYP functional, it should be used only for the asymptotic correction of the B3LYP potential. We anticipate that a similar relationship holds between  $\epsilon_{\text{HOMO}}$  and the IP for any other approximate functional, but with different numerical values for the constants in eqs 1–3. (ii) It is reasonable to scale the LB94 potential by a factor of 0.8 to compensate for the HF exchange contribution with a prefactor of 0.2 in the B3LYP functional that contributes partially to the correct long-range decay. The numerical constant  $\Delta$  does not need to be scaled, however. (iii) Like the original Casida–Salahub scheme or the Tozer–Handy scheme, the modified exchange correlation potential no longer has a rigorous mathematical connection (via the variational principle) to the energy functional. Nevertheless, we use the B3LYP functional to compute the total energy, which is justified because the density that defines the energy of a molecule in the ground state is not affected significantly by the asymptotic correction. The total energy differences obtained by using the B3LYP and B3LYP(AC) functionals are a few milliHartree for the majority of molecules studied in this paper. (iv) We apply the asymptotic correction to the local part of the exchange-correlation potential and compute the gradient-correction contributions to the KS Hamiltonian matrix elements by integration by parts. Thus, eq 6 can be interpreted as referring to just the local (as opposed to gradient-corrected or HF exchange) part of the B3LYP potential. We expect this approach to have a negligibly small numerical consequence from the approach that corrects both local and gradient-corrected parts of the potentials.<sup>11</sup>

With the asymptotic correction scheme, the TDDFT calculations of excitation energies and other time-dependent phenomena benefit from the improved orbitals and orbital energies. In addition, no particular change in the TDDFT program is needed. We report here a new parallel implementation of TDDFT in NWChem. The TDDFT module of NWChem implements the LCAO TDDFT algorithm first outlined by Bauernschmitt and Ahlrichs<sup>8</sup> for spin-restricted systems and by Hirata and Head-Gordon<sup>18</sup> for spin-unrestricted systems, and invokes Davidson’s iterative subspace method. The performance critical section of the calculation is the contraction of a trial vector with the so-called A and B matrices. This step, which is also a kernel of the coupled-perturbed KS method, is carried out in the AO basis and several trial vectors can be processed at a time so that the number of direct integral evaluations can be minimized.<sup>19</sup> The parallel execution of this step ensures load balancing across processors in a dynamical setting.<sup>19</sup> The TDDFT module calculates the vertical excitation energies, oscillator strengths, and  $S^2$  expectation values of excited states by TDDFT, Tamm–Dancoff TDDFT,<sup>20</sup> TDHF, and CIS.

### Applications

We first illustrate the effectiveness of the present asymptotic correction scheme for the vertical IPs and excitation energies

**TABLE 1: Vertical Ionization Potentials (in eV)**

state	BLYP	B3LYP	B3LYP(AC)	expt
CO <sup>a</sup>	9.00	10.52	13.98	14.01 <sup>d</sup>
N <sub>2</sub> <sup>a</sup>	10.23	11.94	15.67	15.60 <sup>d</sup>
CH <sub>2</sub> O <sup>a</sup>	6.19	7.66	10.40	10.88 <sup>e</sup>
C <sub>2</sub> H <sub>4</sub> <sup>a</sup>	6.57	7.63	10.47	10.68 <sup>f</sup>
CH <sub>4</sub> <sup>b</sup>	9.37	10.76	14.21	14.01 <sup>f</sup>
CH <sub>3</sub> F <sup>b</sup>	8.00	9.63	12.90	13.29 <sup>g</sup>
CH <sub>2</sub> F <sub>2</sub> <sup>b</sup>	8.12	9.75	13.02	13.27 <sup>g</sup>
CHF <sub>3</sub> <sup>b</sup>	9.50	11.18	14.85	14.80 <sup>g</sup>
CF <sub>4</sub> <sup>b</sup>	10.33	12.32	16.42	16.20 <sup>g</sup>
C <sub>6</sub> H <sub>6</sub> <sup>c</sup>	6.12	7.06	9.74	9.08 <sup>f</sup>

<sup>a</sup> Geometries are taken from ref 18. <sup>b</sup> Geometries are taken from ref 34. <sup>c</sup> The B3LYP/cc-pVDZ optimized geometry. <sup>d</sup> Reference 22. <sup>e</sup> Reference 23. <sup>f</sup> Reference 24. <sup>g</sup> Reference 35.

of small molecules (CO, N<sub>2</sub>, CH<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub>) that have low-lying valence and Rydberg excited states. We use the aug-cc-pVDZ+ basis set, which has an additional set of diffuse functions with exponents 1/3 of the most diffuse functions of the original aug-cc-pVDZ basis set.<sup>21</sup> Table 1 compares the vertical IPs of these molecules computed by Koopmans' theorem with the experimental data.<sup>22–24</sup> Such a comparison is a valid test of the method by virtue of the theorem that states that the highest occupied KS orbital energy of exact KS DFT of a molecule is the negative of the IP.<sup>25,26</sup> The IPs computed by using the BLYP and B3LYP functionals are far too small, consistent with the results of many other reports.<sup>27</sup> However, our new asymptotic correction scheme as shown in the table, labeled as B3LYP(AC), is very effective in rectifying the severe underestimation of the IP by the other functionals. It must be emphasized that no external parameter such as the  $\Delta$ SCF result for the IP enters the B3LYP(AC) calculations, and hence the agreement between the computed and measured IPs is not a trivial consequence of the preceding  $\Delta$ SCF calculation. The degree of agreement is as good as that obtained by Casida and Salahub, attesting to the accuracy of the phenomenological linear relationship of Zhan et al.<sup>15</sup> With the particular implementation of KS DFT in NWChem, it took 5 to 7 SCF iterations to converge the B3LYP density matrices and energies for these molecules. Turning on the asymptotic correction scheme, we introduce the additional variable  $\Delta$  [the shift defined by eq 3], and this caused an increase in the number of SCF iterations by only 2 in all cases. Thus, our B3LYP(AC) approach does not add significant computational cost considering the significant improvement in the orbital energies.

Because the BLYP and B3LYP functionals underestimate the IPs considerably, the BLYP and B3LYP calculated excitation energies for Rydberg states converge to limits that are too low. As shown in Tables 2 to 5, whereas the BLYP and B3LYP excitation energies for the valence excited states of CO, N<sub>2</sub>, CH<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub> are remarkably accurate, they quickly deviate from the experimental data<sup>28–33</sup> as they approach the calculated IPs. As expected from the improved IPs in Table 1, the B3LYP(AC) method rectifies this shortcoming of the typical functionals used in TDDFT and gives accurate excitation energies throughout the energy range studied in these tables. The standard deviations from the experimental data for these four molecules are 1.33 eV for BLYP, 0.74 eV for B3LYP, and 0.34 eV for B3LYP(AC). The contribution of HF exchange in B3LYP delays the breakdown of the TDDFT excitation energies to a slightly higher energy side relative to the BLYP results, which is why B3LYP has been used in a number of studies. Our new asymptotic correction scheme corrects the remaining large errors

**TABLE 2: Vertical Excitation Energies (in eV) of CO**

state	BLYP	B3LYP	B3LYP(AC)	expt <sup>a</sup>
V <sup>3</sup> Π	5.84	5.88	5.86	6.32
V <sup>1</sup> Π	8.24	8.40	8.38	8.51
V <sup>3</sup> Σ <sup>+</sup>	8.08	7.94	7.99	8.51
V <sup>3</sup> Δ	8.70	8.66	8.70	9.36
V <sup>1</sup> Σ <sup>-</sup>	9.77	9.72	9.76	9.88
V <sup>3</sup> Σ <sup>-</sup>	9.77	9.72	9.76	9.88
V <sup>1</sup> Δ	10.02	10.05	10.09	10.23
R <sup>3</sup> Σ <sup>+</sup>	8.82	9.56	10.23	10.4
R <sup>1</sup> Σ <sup>+</sup>	9.05	9.86	10.75	10.78
R <sup>3</sup> Σ <sup>+</sup>	9.40	10.19	11.23	11.3
R <sup>1</sup> Σ <sup>+</sup>	9.45	10.22	11.46	11.40
R <sup>1</sup> Π	9.57	10.31	11.52	11.53
R <sup>3</sup> Π	9.52	10.28	11.40	11.55
R <sup>1</sup> Σ <sup>+</sup>	10.38	11.24	12.71	12.4

<sup>a</sup> References 28, 29.

**TABLE 3: Vertical Excitation Energies (in eV) of N<sub>2</sub>**

state	BLYP	B3LYP	B3LYP(AC)	expt <sup>a</sup>
V <sup>3</sup> Σ <sub>u</sub> <sup>+</sup>	7.49	7.11	7.09	7.75
V <sup>3</sup> Π <sub>g</sub>	7.46	7.59	7.43	8.04
V <sup>3</sup> Δ <sub>u</sub>	8.27	8.02	8.00	8.88
V <sup>1</sup> Π <sub>g</sub>	9.09	9.27	9.08	9.31
V <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	9.59	9.35	9.33	9.67
V <sup>1</sup> Σ <sub>u</sub> <sup>-</sup>	9.59	9.35	9.33	9.92
V <sup>1</sup> Δ <sub>u</sub>	9.89	9.75	9.73	10.27
V <sup>3</sup> Π <sub>u</sub>	10.37	10.69	10.72	11.19
R <sup>3</sup> Σ <sub>g</sub> <sup>+</sup>	10.07	11.01	11.77	12.0
R <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	10.30	11.30	12.26	12.2
R <sup>1</sup> Π <sub>u</sub>	10.74	11.78	12.99	12.90
R <sup>1</sup> Σ <sub>u</sub> <sup>+</sup>	10.54	11.76	12.95	12.98
R <sup>1</sup> Π <sub>u</sub>	11.43	12.09	13.07	13.24
R <sup>1</sup> Π <sub>u</sub>	12.65	13.49	13.75	13.63
R <sup>1</sup> Σ <sub>u</sub> <sup>+</sup>	11.81	13.26	14.01	14.25

<sup>a</sup> Reference 32.

**TABLE 4: Vertical Excitation Energies (in eV) of CH<sub>2</sub>O**

state	BLYP	B3LYP	B3LYP(AC)	expt <sup>a</sup>
V <sup>3</sup> A <sub>2</sub>	3.02	3.10	3.05	3.50
V <sup>1</sup> A <sub>2</sub>	3.73	3.83	3.78	3.94
V <sup>3</sup> A <sub>1</sub>	5.58	5.22	5.21	5.53
R <sup>3</sup> B <sub>2</sub>	5.53	6.33	6.54	6.83
R <sup>1</sup> B <sub>2</sub>	5.61	6.44	6.72	7.09
R <sup>3</sup> A <sub>1</sub>	6.25	7.18	7.60	7.79
R <sup>3</sup> B <sub>2</sub>	6.30	7.11	7.45	7.96
R <sup>1</sup> A <sub>1</sub>	6.27	7.23	7.72	7.97
R <sup>1</sup> B <sub>2</sub>	6.34	7.19	7.60	8.12
R <sup>1</sup> A <sub>2</sub>	6.55	7.47	8.18	8.38
V <sup>1</sup> B <sub>1</sub>	8.34	8.86	8.75	8.68
R <sup>1</sup> A <sub>2</sub>	7.69	8.61	9.56	9.22

<sup>a</sup> References 30, 31.

in the B3LYP excitation energies for Rydberg states, without leading to deterioration of the excitation energies for the valence states.

We next examined the performance of B3LYP(AC) TDDFT for methane and mono-, di-, tri-, and tetrafluorinated methanes (Table 6). The excited states of these molecules are predominantly of Rydberg character and are therefore particularly suitable tests for the asymptotic correction scheme. They are important species in atmospheric chemistry and have been the subject of recent studies in connection to semiconductor technology, where they serve as models for photoresist polymers which are transparent in the region of 157 nm (7.9 eV), the excitation energy of the F<sub>2</sub> laser.<sup>34</sup> For these molecules, TDDFT with the BLYP functional gives excitation energies that are too low,<sup>34</sup> and the errors from the experimental data<sup>35</sup> can be as large as a few electronvolts. The B3LYP functional roughly



**TABLE 5: Vertical Excitation Energies (in eV) of C<sub>2</sub>H<sub>4</sub>**

state	BLYP	B3LYP	B3LYP(AC)	expt <sup>a</sup>
V <sup>3</sup> B <sub>1u</sub>	4.31	4.07	4.06	4.36
R <sup>3</sup> B <sub>3u</sub>	6.10	6.50	6.89	6.98
R <sup>1</sup> B <sub>3u</sub>	6.15	6.57	7.02	7.15
V <sup>1</sup> B <sub>1u</sub>	7.08	7.34	7.47	7.66
R <sup>3</sup> B <sub>2g</sub>	6.53	7.04	7.52	7.79
R <sup>3</sup> B <sub>1g</sub>	6.58	7.07	7.24	7.79
R <sup>1</sup> B <sub>1g</sub>	6.60	7.10	7.66	7.83
R <sup>1</sup> B <sub>2g</sub>	6.56	7.09	7.64	8.0
R <sup>3</sup> A <sub>g</sub>	6.89	7.35	8.15	8.15
R <sup>1</sup> A <sub>g</sub>	6.92	7.44	8.38	8.29
R <sup>3</sup> B <sub>3u</sub>	7.13	7.78	8.65	8.57
R <sup>1</sup> B <sub>3u</sub>	7.17	7.81	8.70	8.62

<sup>a</sup> Reference 33.**TABLE 6: Vertical Excitations (in eV) of Methane and Fluorinated Methanes**

state <sup>a</sup>	BLYP	B3LYP	B3LYP(AC)	expt <sup>b</sup>
CH <sub>4</sub>				
3s ← HOMO	8.9	9.6	10.1	9.7, 10.4
3p ← HOMO	9.8	10.5	11.5	10.9
CH <sub>3</sub> F				
3s ← HOMO	7.5	8.4	8.8	9.36
3p ← HOMO	8.2	9.3	10.2	10.42
3d ← HOMO	9.3	10.4	11.3	11.21
CH <sub>2</sub> F <sub>2</sub>				
3s ← HOMO	7.6	8.5	8.9	9.28
3p ← HOMO	8.3	9.3	10.0	10.45
3d ← HOMO,	9.1	10.2	11.7	11.50
3p ← HOMO-1				
CHF <sub>3</sub>				
3s ← HOMO	9.0	10.0	10.7	10.92
3p ← HOMO	9.6	10.7	11.5	11.91
CF <sub>4</sub>				
3s ← HOMO	9.8	11.1	12.0	12.51
3s ← HOMO-1	11.1	12.4	13.3	13.59
3p ← HOMO	10.6	12.0	13.6	13.89

<sup>a</sup> The most intense calculated transition of each category is listed.<sup>b</sup> References 34, 35.

halves these large errors, but there still remain significant errors, especially for higher lying states. In previous work, these errors have been accounted for by an empirical scaling function applied after the calculation is complete. The B3LYP(AC) accounts for most of the remainder of the errors, and the calculated excitation energies are now in quite good agreement with the observed band positions. Table 6 illustrates that the stepwise fluorination of methane alters the excitation energy to the lowest state in a nonsystematic fashion, in part due to changing of the symmetries of the molecules, and that fluorination does tend to shift the absorption spectrum to the blue. The B3LYP(AC) method is capable of reproducing the nonsystematic changes upon fluorination at least semiquantitatively. In parallel with the TDDFT results for excitation energies, the vertical IPs computed by B3LYP(AC) are dramatically improved relative to those computed by BLYP or B3LYP (Table 1). The IPs obtained from B3LYP(AC) are within 0.4 eV of the experimental data.<sup>24,35</sup>

**TABLE 7: Vertical Excitation Energies (in eV) of Benzene<sup>a</sup>**

state	BLYP	B3LYP	B3LYP(AC)	expt <sup>b</sup>
V <sup>1</sup> B <sub>2u</sub>	5.17	5.37	5.38	4.90
R <sup>1</sup> E <sub>1g</sub>	5.55, 5.55	5.98, 5.98	6.34, 6.34	6.33
V <sup>1</sup> B <sub>1u</sub>	5.87	6.02	6.04	6.19, 6.19
R <sup>1</sup> E <sub>2u</sub> , <sup>1</sup> A <sub>1u</sub> , <sup>1</sup> A <sub>2u</sub>	6.00, 6.00, 6.01, 6.02	6.46, 6.48, 6.48, 6.53	6.96, 6.99, 6.99, 7.06	6.93, 6.95
V <sup>1</sup> E <sub>1u</sub>	6.77, 6.77	6.98, 6.98	6.93, 6.93	6.94, 6.96
R <sup>1</sup> E <sub>1u</sub>	6.33, 6.33	6.74, 6.74	7.41, 7.41	7.41, 7.59
R <sup>1</sup> E <sub>1g</sub> , <sup>1</sup> B <sub>1g</sub> , <sup>1</sup> B <sub>2g</sub>	6.53, 6.54, 6.54, 6.54	7.04, 7.04, 7.05, 7.05	7.66, 7.66, 7.66, 7.68	7.46, 7.54, 7.62

<sup>a</sup> The aug-cc-pVDZ+ basis set is used on each C atom and the aug-cc-pVDZ basis set on each H atom. <sup>b</sup> References 36–41.

Our new method improves the usefulness of TDDFT as a tool for the design of next-generation polymers for photoresist and pellicle applications.<sup>34</sup>

We also applied our B3LYP(AC) scheme to the larger, conjugated  $\pi$ -electron systems benzene (Table 7) and free-base porphyrin (Table 8). The former has both valence and Rydberg excited states and mixtures of these states in the low energy region and are a challenging problem for an excitation theory. In this example, again we find that the agreement between theory and experiment<sup>36–41</sup> improves in the order of B3LYP(AC) > B3LYP > BLYP, particularly for Rydberg states. The agreement obtained at the B3LYP(AC) level is quite satisfactory for benzene, and the errors are less than 0.2 eV for all states shown in the table with an exception of the lowest lying state which has an error of 0.5 eV with the calculated value being too high. The asymptotic correction also decreases the errors in the calculated IPs of benzene (Table 1), although in this example, it tends to overestimate the correction slightly. As noted above, all of the functionals do reasonably well for this lowest excited state. In contrast to benzene, the low-lying excited states of porphyrin are dominantly of valence character (for previous TDDFT results of porphyrin, see refs 8, 42, 43). The BLYP TDDFT excitation energies tend to be systematically lower than experimental data for the *N* and *L* bands. The B3LYP functional raises the BLYP excitation energies for the *N* and *L* bands, and consequently the B3LYP excitation energies are in good agreement with experimental data<sup>44–47</sup> for all *Q*, *B*, *N*, and *L* bands. Given the fact that the B3LYP functional, which has partially correct asymptotic behavior, improves on the BLYP results for the *N* and *L* bands, leads us to raise the question as to whether the full asymptotic correction may overshoot the excitation energies for these bands, leading to the conclusion that the agreement at the B3LYP level may be due to some cancellation of errors. We can address this question by performing the B3LYP(AC) calculation for the same system, and we find that this is not the case. The B3LYP(AC) does not increase the B3LYP excitation energies of these states any further, despite a large shift in the potential by the AC, and the agreement at the B3LYP level is retained at the B3LYP(AC) level. The asymptotic correction does not significantly alter the oscillator strengths from the B3LYP TDDFT calculation, either, which are in qualitative agreement with experiment. This result suggests that the HF contribution in B3LYP shifts the energy threshold higher so that errors come at higher energies rather than partially correcting the excitation energies of higher-lying states.

We note that CO, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub> were included in the original training set of molecules used to determine the linear relationship (eq 1). The fact that the proposed B3LYP(AC) method performs reasonably well for other molecules that are not among the training set attests to the wide applicability of the present method. We note that the studies so far are restricted to organic molecules, and further tests of the general applicabil-

**TABLE 8: Vertical Excitation Energies (in eV) and Oscillator Strengths (in parentheses) of Porphin at the B3LYP/cc-pVDZ Optimized Geometry<sup>a</sup>**

state	BLYP	B3LYP	B3LYP(AC)	expt <sup>b</sup>
V <sup>1</sup> B <sub>3u</sub>	2.16 (0.0007)	2.27 (0.00004)	2.27 (0.00001)	1.98–2.02 ( <i>Q<sub>x</sub></i> ) (0.01)
V <sup>1</sup> B <sub>2u</sub>	2.29 (0.0004)	2.42 (0.00006)	2.42 (0.00002)	2.33–2.42 ( <i>Q<sub>y</sub></i> ) (0.06)
V <sup>1</sup> B <sub>3u</sub>	2.98 (0.126)	3.31 (0.466)	3.31 (0.458)	3.13–3.33 ( <i>B</i> ) (1.15)
V <sup>1</sup> B <sub>2u</sub>	3.02 (0.038)	3.46 (0.702)	3.46 (0.694)	
V <sup>1</sup> B <sub>2u</sub>	3.41 (0.875)	3.73 (0.416)	3.72 (0.413)	3.65 ( <i>N</i> ) (<0.1)
V <sup>1</sup> B <sub>3u</sub>	3.47 (0.754)	3.81 (0.709)	3.81 (0.706)	
V <sup>1</sup> B <sub>2u</sub>	3.77 (0.141)	4.34 (0.100)	4.33 (0.102)	4.25 ( <i>L</i> ) (~0.1)
V <sup>1</sup> B <sub>3u</sub>	3.78 (0.115)	4.45 (0.104)	4.44 (0.105)	

<sup>a</sup> The aug-cc-pVDZ+ basis set is used on each N atom and the cc-pVDZ basis set on each of C and H atoms. <sup>b</sup> Measured in vapor or solution. References 44–47.

ity of the method for inorganic, metallic, and organometallic compounds and to charge-transfer-type excited states will be needed.

### Concluding Remarks

We have proposed and implemented an asymptotically corrected DFT and TDDFT that is a combination of the Casida–Salahub asymptotic correction<sup>10,12</sup> and the phenomenological linear correlation of Zhan, Nichols, and Dixon,<sup>15</sup> and have shown that (i) it requires only a marginal additional computational effort (typically a few additional SCF iterations in our particular implementation), (ii) it gives considerably improved IPs, (iii) it corrects the excitation energies to Rydberg states effectively, (iv) it does not lead to deterioration in the prediction of the excitation energies of valence states, which are usually already reasonable with uncorrected TDDFT, and (v) it is applicable not only to molecules that are among the training set of Zhan et al. but also to other molecules of different sizes and properties.

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