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Comparison of DFT Methods for Molecular Orbital Eigenvalue Calculations

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We report how closely the Kohn−Sham highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) eigenvalues of 11 density functional theory (DFT) functionals, respectively, correspond to the negative ionization potentials (−IPs) and electron affinities (EAs) of a test set of molecules. We also report how accurately the HOMO−LUMO gaps of these methods predict the lowest excitation energies using both time-independent and time-dependent DFT (TD−DFT). The 11 DFT functionals include the local spin density approximation (LSDA), five generalized gradient approximation (GGA) functionals, three hybrid GGA functionals, one hybrid functional, and one hybrid meta GGA functional. We find that the HOMO eigenvalues predicted by KMLYP, BH&HLYP, B3LYP, PW91, PBE, and BLYP predict the −IPs with average absolute errors of 0.73, 1.48, 3.10, 4.27, 4.33, and 4.41 eV, respectively. The LUMOs of all functionals fail to accurately predict the EAs. Although the GGA functionals inaccurately predict both the HOMO and LUMO eigenvalues, they predict the HOMO−LUMO gap relatively accurately (~0.73 eV). On the other hand, the LUMO eigenvalues of the hybrid functionals fail to predict the EA to the extent that they include HF exchange, although increasing HF exchange improves the correspondence between the HOMO eigenvalue and −IP so that the HOMO−LUMO gaps are inaccurately predicted by hybrid DFT functionals. We find that TD−DFT with all functionals accurately predicts the HOMO−LUMO gaps. A linear correlation between the calculated HOMO eigenvalue and the experimental −IP and calculated HOMO−LUMO gap and experimental lowest excitation energy enables us to derive a simple correction formula.

Introduction

The molecular orbital (MO) is an important concept in chemistry, and molecular orbital theory is employed extensively to describe chemical behavior. Not only has MO theory become a ubiquitous set of tools used to explain chemical behavior, such as reactivity and kinetics, but it also provides an indispensable conceptual construct for the description of other phenomenon involving molecular electronic structure including charge-transfer processes, photoexcitation, magnetism, and molecular electronics.[1] In fact, it is quite common to extract trends in molecular behavior based on simple MO properties. For example, molecules with large HOMO−LUMO gaps are generally stable and unreactive; while those with small gaps are generally reactive. Unfortunately, although MO theory is of immense utility, commonly used DFT functionals that can economically calculate the electronic structure of molecules may not predict orbital energies accurately. Consequently, the application of quantum chemical methods for designing molecular components that act as molecular transistors, dyes, and catalysts often produces sub par results and thus quantum chemistry's utility has generally been limited for these endeavors.[1,2] Furthermore, methods that have been developed to describe phenomena involving the electronic structure and which use the energy levels and electronic structure predicted by quantum chemistry as input have been hindered by the quality of these properties provided by current quantum chemical methods.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the two most important molecular orbitals. At the Hartree−Fock (HF) level, Koopmans' theorem suggests that the energy of the HOMO is a good approximation to the negative experimental ionization potential (−IP).[1] Similarly, it suggests that the electron affinity (EA) for an *N*-electron system is equal to the negative of the LUMO energy, assuming that the orbitals do not relax. In general, the prediction of the EA using Koopmans' theorem is unreliable due to the generally large effect of orbital relaxation on the LUMO eigenvalue. In fact, the HF LUMO energy goes to zero in the complete basis set limit.[3] In addition to the question of the effect of relaxation on the validity of Koopmans' theorem, there has been substantial uncertainty as to the degree of physical significance of the Kohn Sham (KS) orbitals of density functional theory (DFT) applied within the KS framework[4,5] and thus how well their eigenvalues correspond to physical observables.[6] This question has persisted despite the fact that DFT has become a widely used class of quantum chemical methods because of its ability to predict relatively accurate molecular properties at a reasonable computational cost. Several observations lend support to the idea that the KS orbitals are physically significant. First, the shape and symmetry properties of the KS orbitals have been found to be very similar to those calculated by HF.[7] Second, the long-range behavior of the electron density of the exact KS potential results in a HOMO eigenvalue equal to the −IP on the electron deficient side of the exact KS potential integer discontinuity and a LUMO eigenvalue equal to the −EA on the electron abundant side.[8−11] However, commonly used DFT exchange-correlation functionals that are continuum approximations, such as conventional GGA functionals, do not exhibit an integer discontinuity. Thus, their HOMO eigenvalues are shifted up from the −IP by half of the magnitude of the discontinuity and similarly their LUMO eigenvalues are shifted down from −EA by the same amount.[9,12,13] Furthermore, for finite systems, true KS eigenvalues corresponding to unoccupied orbitals can be directly related to excited-state energies, and the HOMO−LUMO gap gives a

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reasonable approximation to the lowest excitation energy.[14−17] Consequently, sufficient evidence exists to establish a reasonable expectation that the KS orbitals are physically significant objects to the extent that exchange-correlation functionals approach the exact exchange-correlation functional and thus provide a good theoretical and practical basis for qualitative interpretation of molecular orbitals as suggested by Baerends.[7,18]

Unfortunately, the exact exchange-correlation functional is not known. Previous studies have established that for most available exchange-correlation functionals the calculated HOMO eigenvalue differs substantially from the experimental −IP.[19−21] Zhan et al. investigated the MO eigenvalues and related properties with the B3LYP functional. They found that a generally applicable linear correlation exists between both the B3LYP calculated HOMO eigenvalues and HOMO−LUMO gaps and relevant experimental properties.[19] In this paper, we present the results of a systematic investigation of the HOMO and LUMO eigenvalues calculated using the functionals from five different categories of DFT methods: LSDA, GGA, hybrid LSDA, hybrid GGA, and hybrid meta GGA methods. The LSDA functionals depend only on the electron density; the GGA functionals depend on the density as well as the gradient of the electron density; hybrid LSDA functionals mix LDA and HF exchange but are not gradient corrected; hybrid GGA functionals mix LDA and HF exchange with a gradient correction to exchange; the hybrid meta GGA functionals mix LDA and HF exchange with a gradient correction to exchange and employ a kinetic energy functional. We will write LSDA, GGA, HLSDA, HGGA, and HMGGA when specifically referring to one of the above subsets of “DFT functionals”. In this paper, we examine the SVWN LSDA functional,[22,23] the BLYP, BP86, BPW91, PW91, and PBE GGA functionals,[24−28] the KMLYP hybrid LSDA functional,[29] the B3LYP, BH&HLYP, and O3LYP hybrid GGA functionals,[24,25,30−32] and the B1B95 hybrid meta GGA functional.[24,33] KMLYP has been shown to accurately predict reaction energies, activation barriers, ionization potentials, and electron affinities.[29,34−37] One aim of this paper is to compare how well the HOMO and LUMO eigenvalues correspond to −IP and EA, respectively. Another goal is to find approaches to improve the accuracy of commonly used methods and to prescribe an approach for predicting accurate HOMO and LUMO eigenvalues and consequently HOMO−LUMO gaps without relying on an empirical correction. However, we also develop an alternative empirical relationship between the predicted HOMO and LUMO eigenvalues and their related experimental values. For example, if one could obtain a relationship between the calculated HOMO eigenvalues and the experimental IPs, then the calculated HOMO eigenvalues could be corrected empirically to predict accurate IPs. Determination of such a relationship requires DFT calculations on a set of representative molecular systems. In this investigation, we use a set of 27 molecules for the −IP and 10 molecules for the EA. These systems are selected because good experimental data exists to serve as benchmarks for these systems and because these molecules contain a variety of chemical bonds between first and second row atoms. The test set also covers a range of molecular sizes extending from diatomic molecules to anthracene ($C_{14}H_{10}$).

Results and Discussion

To study the accuracy of MO eigenvalues predicted by different DFT functionals, we need to choose benchmarks for each property. We use the negative of the experimental IP as the benchmark for the HOMO eigenvalue. Two candidates that can be used as the HOMO−LUMO gap benchmark are the following: the theoretical near-exact HOMO−LUMO eigenvalue differences determined from the correlated electron densities using the Zhao−Morrison−Parr (ZMP) approach[38] which was used by Allen and Tozer[9] or the experimental lowest excitation energy which was used by Dixon et al.[19] In this paper, we have selected experimental data as benchmarks. The LUMO benchmark is calculated as the negative of the experimental IP plus the experimental lowest excitation energy. We use the 6-311+G(d,p) basis set[39−41] for all calculations reported. We test the basis set dependence of the HOMO and LUMO energies using the 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), and AUG-cc-pVTZ basis sets and find that the calculated HOMO energies and TD−DFT HOMO−LUMO gaps are generally insensitive to the basis set. On the other hand, the LUMO energies are sensitive to the basis set for cases where the LUMO eigenvalues are positive. Therefore, we use the relatively economical 6-311+G(d,p) basis set as its accuracy is sufficient for these calculations. All eigenvalues are for structures optimized using the same basis set and method. Gaussian 03 is used for all calculations.[42] Analysis of the computed results and comparison with experiment is used to derive simple empirical corrections to the HOMO eigenvalues and HOMO−LUMO gaps.

DFT HOMO Eigenvalues. A DFT calculation within the KS framework results in the eigenvalues of occupied and unoccupied (virtual) orbitals. Table 1 shows the calculated HOMO eigenvalues and the experimental −IP[43,44] for the test set of 27 molecules. We also list the largest absolute and average absolute errors of these calculations. By the use of the experimental −IPs as benchmarks for the quality of the HOMO eigenvalues of these DFT functionals, KMLYP results in an average absolute error in the predicted −IPs of 0.73 eV, followed by BH&HLYP with an error of 1.48 eV. SVWN, O3LYP, B3LYP, and B1B95 predict the −IPs with absolute errors of 3.73, 3.68, 3.10, and 2.86 eV, respectively. These results are consistent with previous reports that because conventional GGA and LSDA functionals are continuum functionals their HOMO eigenvalues are shifted upward by half of the integer discontinuity.[9,12,13] The HOMO eigenvalues predicted by hybrid functionals are generally better than those predicted by nonhybrid functionals and are relatively sensitive to the fraction of HF exchange in the exchange-correlation functional with functions with higher fractions of HF exchange resulting in more accurate HOMO eigenvalues. The explanation is that the hybrid functionals include a fraction of exact orbital exchange.[13] The percentages of HF exchange for the five hybrid functionals in this paper are as follows: KMLYP (55.7%), BH&HLYP (50%), B1B95 (28%), B3LYP (20%), and O3LYP (11.61%). The relatively small percentages of HF exchange in B3LYP, O3LYP, and B1B95 limit the accuracy of their HOMO eigenvalues. It has been shown previously that increasing the fraction of HF exchange improves the accuracy of both atomization energies and barrier heights over non-hybrid functionals.[45−47] Note that the negative of the DFT HOMO eigenvalues predicted using the exchange-correlation functionals examined herein underestimate the experimental IPs indicating a systematic error in the HOMO eigenvalues.

Figure 1 shows that the correlation between the negative of the calculated HOMO eigenvalues and the experimental IPs is linear. We only show the correlation curves of nine DFT functionals with the relevant correlation curves for the BP86 and PBE functionals included in the Supporting Information as the results for all five GGA functionals are very similar.

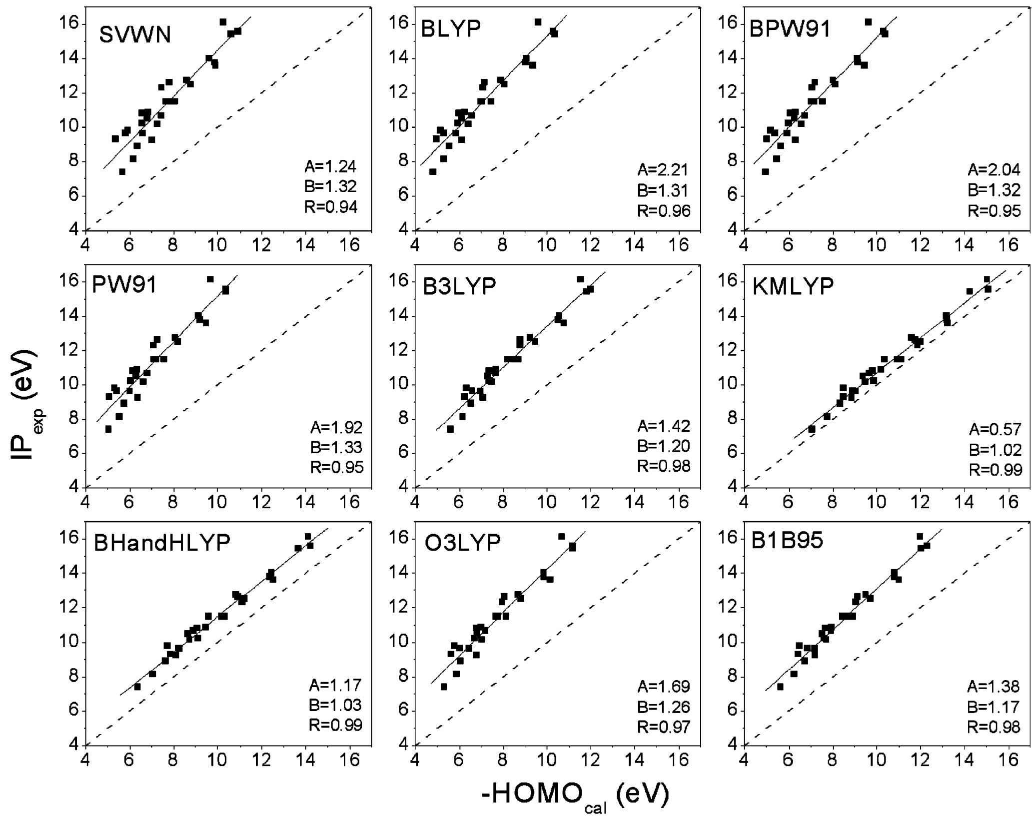

Figure 1. Absolute value of calculated HOMO eigenvalues vs experimental IPs. The dashed line indicates an ideal 1.0 correlation between experimental and calculated values.

TABLE 1: HOMO Eigenvalues (in electronvolts), before and after Correction Using the Correction Formula in eq 1 with Values Given in Figure 1

	SVWN	BLYP	BP86	BPW91	PW91	PBE	B3LYP	KMLYP	BH&H	O3LYP	B1B95	EXP
HCO	-5.36	-4.96	-5.11	-5.02	-5.06	-5.00	-6.23	-8.47	-7.87	-5.62	-6.40	-9.31
CO_2	-9.86	-9.02	-9.23	-9.13	-9.19	-9.12	-10.50	-13.19	-12.36	-9.85	-10.80	-13.78
C_2H_2	-7.83	-7.01	-7.26	-7.15	-7.21	-7.16	-8.20	-10.37	-9.59	-7.68	-8.45	-11.49
H_2CO	-6.83	-6.24	-6.39	-6.29	-6.34	-6.27	-7.67	-10.20	-9.47	-7.00	-7.92	-10.88
CH_4	-9.92	-9.35	-9.52	-9.43	-9.48	-9.41	-10.76	-13.23	-12.51	-10.14	-11.00	-13.60
H_2CCO	-6.60	-5.83	-6.05	-5.94	-6.00	-5.94	-6.96	-9.01	-8.27	-6.43	-7.16	-9.64
Cl_2	-8.06	-7.44	-7.63	-7.52	-7.56	-7.52	-8.70	-10.91	-10.21	-8.13	-8.89	-11.49
CO	-9.63	-9.05	-9.22	-9.11	-9.15	-9.08	-10.55	-13.17	-12.43	-9.85	-10.80	-14.01
H_2	-10.63	-10.35	-10.45	-10.38	-10.39	-10.32	-11.81	-14.25	-13.65	-11.16	-12.03	-15.43
N_2	-10.94	-10.27	-10.43	-10.31	-10.37	-10.29	-12.00	-15.08	-14.22	-11.17	-12.30	-15.58
O_2	-7.46	-7.07	-7.12	-7.04	-7.08	-6.99	-8.79	-11.85	-11.11	-7.94	-9.06	-12.30
CH_3NH_2	-5.81	-5.29	-5.48	-5.37	-5.41	-5.36	-6.59	-8.90	-8.22	-6.02	-6.83	-9.65
CH_3CHO	-6.56	-5.94	-6.10	-5.98	-6.05	-5.98	-7.34	-9.86	-9.11	-6.68	-7.59	-10.24
C_4H_4O	-6.35	-5.54	-5.77	-5.66	-5.73	-5.67	-6.53	-8.33	-7.62	-6.05	-6.72	-8.90
HF	-10.27	-9.59	-9.72	-9.62	-9.69	-9.60	-11.53	-15.04	-14.09	-10.67	-11.97	-16.12
C_2H_4	-7.44	-6.57	-6.82	-6.72	-6.79	-6.74	-7.66	-9.66	-8.89	-7.18	-7.91	-10.68
C_4H_2	-7.25	-6.41	-6.67	-6.57	-6.62	-6.58	-7.49	-9.48	-8.73	-7.01	-7.70	-10.17
C_6H_6	-7.03	-6.11	-6.39	-6.29	-6.36	-6.31	-7.08	-8.85	-8.10	-6.77	-7.18	-9.25
$C_{10}H_8$	-6.18	-5.29	-5.57	-5.46	-5.53	-5.48	-6.15	-7.74	-7.04	-5.86	-6.23	-8.14
$C_{14}H_{10}$	-5.67	-4.80	-5.07	-4.96	-5.03	-4.99	-5.58	-7.04	-6.36	-5.30	-5.64	-7.40
H_2O	-7.80	-7.14	-7.30	-7.19	-7.26	-7.18	-8.79	-11.75	-10.91	-8.05	-9.12	-12.62
H_2S	-6.80	-6.11	-6.34	-6.24	-6.29	-6.25	-7.28	-9.37	-8.66	-6.81	-7.50	-10.50
HCl	-8.60	-7.88	-8.12	-8.01	-8.06	-8.02	-9.22	-11.60	-10.84	-8.68	-9.49	-12.74
NaCl	-5.91	-5.15	-5.32	-5.19	-5.31	-5.26	-6.31	-8.48	-7.73	-5.77	-6.48	-9.80
NH_3	-6.55	-5.98	-6.18	-6.07	-6.12	-6.07	-7.35	-9.81	-9.08	-6.78	-7.64	-10.82
HCOOH	-7.65	-6.98	-7.13	-7.02	-7.10	-7.02	-8.44	-11.12	-10.32	-7.74	-8.72	-11.50
SO_2	-8.79	-8.04	-8.23	-8.12	-8.20	-8.12	-9.46	-11.99	-11.21	-8.81	-9.71	-12.50
					errors before correction							
largest error	5.85	6.53	6.40	6.50	6.43	6.52	4.59	1.32	2.07	5.45	4.15	
average error	3.73	4.41	4.22	4.32	4.27	4.33	3.10	0.73	1.48	3.68	2.86	
					errors after correction							
largest error	1.35	1.31	1.36	1.37	1.34	1.36	0.85	0.62	0.66	1.02	0.82	
average error	0.62	0.53	0.56	0.56	0.56	0.57	0.37	0.24	0.25	0.45	0.33	

The negative of the calculated HOMO energies of the 11 functionals investigated and especially KMLYP and BH&HLYP exhibits a high degree of linear correlation with the experimental IPs, indicative of a simple, systematic error in these HOMO eigenvalues. The linear correlation implies that Koopmans' identification of the HOMO energy with the negative IP is approximately correct and is thus evidence that the HOMO eigenvalues calculated by DFT have physical significance for

TABLE 2: LUMO Eigenvalues (in electronvolts)[a]

	SVWN	BLYP	BP86	BPW91	PW91	PBE	B3LYP	KMLYP	BH&HLYP	O3LYP	B1B95	exp
C_2H_2	-1.02	-0.36	-0.50	-0.37	-0.48	-0.43	0.33	1.03	1.03	0.06	0.80	-6.26
CH_4	-0.31	-0.09	0.13	0.21	-0.15	-0.01	0.26	0.88	0.88	-0.12	0.73	-2.70
CO	-2.77	-2.09	-2.23	-2.12	-2.19	-2.14	-1.16	0.33	0.41	-1.44	-0.56	-7.61
H_2	0.59	1.01	1.12	1.25	1.00	1.10	1.56	2.53	2.58	1.32	2.16	-3.63
HF	-0.86	-0.64	-0.31	-0.23	-0.60	-0.44	0.05	1.23	1.14	-0.30	0.79	-5.82
C_6H_6	-1.85	-1.10	-1.32	-1.19	-1.28	-1.23	-0.48	0.57	0.76	-0.71	-0.18	-4.53
$C_{10}H_8$	-2.75	-1.95	-2.19	-2.07	-2.15	-2.10	-1.40	-0.44	-0.19	-1.63	-1.14	-4.15
$C_{14}H_{10}$	-3.34	-2.50	-2.76	-2.64	-2.72	-2.67	-2.03	-1.18	-0.90	-2.24	-1.79	-4.09
H_2O	-0.51	-0.17	0.05	0.19	-0.15	-2.31	0.52	1.71	1.69	0.28	1.25	-5.52
NH_3	-0.50	-0.19	-0.003	0.13	-0.26	-0.11	0.30	1.14	1.16	-0.01	0.88	-5.10

[a] The experimental benchmarks are subtracted from the experimental ionization potential and lowest excitation energy.

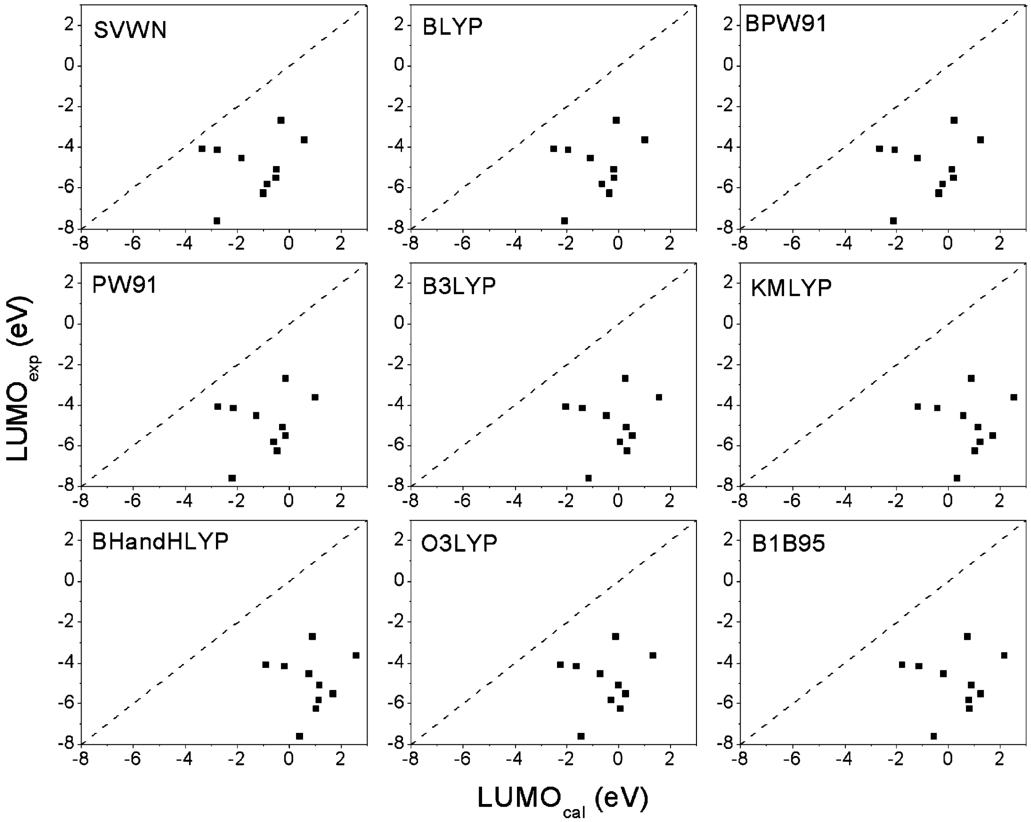

Figure 2. Calculated LUMO eigenvalues (in electronvolts) vs experimental results. The experimental result is determined from the difference between the experimental IP and the experimental lowest excitation energy. The dashed line indicates an ideal 1.0 correlation between experimental and calculated values.

quality exchange-correlation functionals. Of practical consequence is the fact that from the linear correlation curves we can extract a linear correction equation for the calculated HOMO energies to obtain more accurate predictions of the IP. The parameters for each functional for the correction formula shown below are given in Figure 1:

$$-\mathrm{HOMO}_{\mathrm{corr}} = A + B \times (-\mathrm{HOMO}_{\mathrm{cal}}) \qquad (1)$$

Here, $\mathrm{HOMO}_{\mathrm{corr}}$ is the corrected HOMO energy, and $\mathrm{HOMO}_{\mathrm{cal}}$ is the calculated HOMO eigenvalue, Although this empirical correction is a simple linear correlation, it significantly improves the accuracy of functionals with significant differences between the HOMO energies and −IPs. We show the largest and average absolute errors of corrected HOMO energies in Table 1 and the corrected HOMO energies in the Supporting Information. The average absolute energy differences between the corrected HOMO energies and −IPs range from 0.24 eV for KMLYP to 0.62 eV for SVWN, whereas the uncorrected differences between the HOMO energies and −IPs ranged from 0.73 eV for KMLYP to 4.41 eV for BLYP. Although the KMLYP HOMO energies are improved modestly from their already relatively accurate prediction of IP, the HOMO energies of all other functionals are significantly improved by their respective empirical corrections.

DFT LUMO Eigenvalues. In this paper, the experimental benchmark for the LUMO eigenvalue is determined by taking the difference between the experimental ionization potential and the experimental lowest excitation energy (approximately the HOMO−LUMO gap).[19,43,44] Because of the scarcity of accurate experimental excitation energies, we only list comparisons between the LUMO energies and the set of 10 molecules (Table 2). The calculated LUMO eigenvalues are shown in Table 2. Compared with the HOMO results, the errors in the LUMO eigenvalues are significantly larger with the calculated LUMO eigenvalues being much higher in energy than those determined experimentally. As expected, the virtual orbitals are generally more difficult to describe theoretically than the occupied orbitals. Figure 2 shows the calculated LUMO energies vs the LUMO benchmark energies determined using the experimental IP and lowest excitation energy. The data exhibits almost no correlation,

TABLE 3: HOMO−LUMO Gaps Calculated Directly from the Energy Difference between the HOMO and LUMO Eigenvalues, before and after Correction[a]

	SVWN	BLYP	BP86	BPW91	PW91	PBE	B3LYP	KMLYP	BH&HLYP	O3LYP	B1B95	exp
C_2H_2	6.81	6.66	6.75	6.79	6.73	6.73	8.53	11.39	10.62	7.74	9.26	5.23
CH_4	9.60	9.26	9.64	9.64	9.32	9.40	11.02	14.11	13.40	10.03	11.73	10.9
CO	6.86	6.96	6.99	6.99	6.96	6.94	9.39	13.51	12.84	8.41	10.24	6.4
H_2	11.22	11.36	11.56	11.63	11.39	11.43	13.37	16.78	16.23	12.48	14.18	11.8
HF	9.41	8.95	9.41	9.39	9.09	9.16	11.59	16.26	15.23	10.37	12.75	10.3
C_6H_6	5.18	5.01	5.07	5.09	5.09	5.08	6.60	9.42	8.86	6.06	7.01	4.72
$C_{10}H_8$	3.43	3.34	3.37	3.39	3.38	3.38	4.75	7.30	6.85	4.23	5.09	3.99
$C_{14}H_{10}$	2.34	2.30	2.31	2.32	2.32	2.32	3.55	5.86	5.47	3.06	3.85	3.31
H_2O	7.29	6.97	7.35	7.39	7.11	7.16	9.31	13.47	12.60	8.33	10.37	7.1
NH_3	6.05	5.79	6.17	6.20	5.86	5.96	7.65	10.95	10.24	6.77	8.51	5.72
					errors before correction							
largest error	1.58	1.64	1.52	1.56	1.58	1.50	3.30	7.11	6.44	2.51	4.03	
average error	0.73	0.76	0.72	0.72	0.74	0.73	1.63	4.96	4.29	1.03	2.35	
					errors after correction							
largest error	1.71	1.71	1.60	1.62	1.72	1.69	1.68	2.28	2.23	1.71	1.87	
average error	0.71	0.73	0.71	0.72	0.73	0.72	0.85	1.00	0.95	0.83	0.92	

[a] Equation 1 with values given in Figure 3.

most likely because the calculated LUMO is not accurate and experimental benchmarks are not direct measurements of the LUMO eigenvalue, because of extensive relaxation of the occupied orbitals. Consequently, the DFT calculated LUMO energies and the experimentally derived LUMO energies show little correlation. Although a direct calculation of the LUMO energies leads to large errors, the LUMO eigenvalue might be calculated more correctly by first calculating the HOMO−LUMO gap and then subtracting the HOMO eigenvalue. This calculation is more robust because both the HOMO and gap are well defined and of physical significance, which in turn might lead to improvement in the accuracy of the calculated LUMO.

HOMO−LUMO Gaps. The HOMO−LUMO gaps calculated directly as the difference in HOMO and LUMO eigenvalues using the 11 DFT functionals are reported in Table 3. It is immediately apparent that the HOMO−LUMO gaps of the two nonhybrid functionals (LSDA, GGA) are notably better than those calculated using hybrid functionals (HLSDA, HGGA, HMGGA). Our results for GGA are consistent with those of Allen and Tozer who found that GGA HOMO−LUMO gaps accurately reproduced the theoretical benchmark, although they did not examine non-GGA functionals.[9] Also, of the five hybrid functionals, the B3LYP, O3LYP, and B1B95 HOMO−LUMO gaps are markedly better than those of KMLYP and BH&HLYP. These results indicate that there is in effect an anticorrelation between the accuracy of the HOMO−LUMO gaps and the accuracy of the HOMO energies of DFT functionals. The two hybrid functionals (KMLYP and BH&HLYP) perform significantly worse than other functionals for calculating HOMO−LUMO gaps, while they were significantly more accurate in predicting HOMO eigenvalues. Consequently, it is the fact that KMLYP and BH&HLYP have small errors in their predicted HOMO eigenvalues and significant errors in their LUMO eigenvalues that results in their less accurate HOMO−LUMO gaps. On the other hand, the three hybrid functionals B3LYP, O3LYP, and B1B95 have moderate accuracy because they have low percentages of HF exchange. These results are consistent with the idea that even the true exchange-correlation functional would lead to a poor prediction for both the LUMO and HOMO−LUMO gap because the LUMO is a poor physical description of the EA. The difficulty lies in the difference between the definition of the LUMO, a virtual orbital and thus a purely theoretical entity, and the electron affinity, an experimentally measured property. Thus, although the LUMO eigenvalue and the electron affinity are related, the LUMO eigenvalue corresponds only weakly to the measured EA of the molecule. A possible solution to the inability of LUMO energies to predict the EA is the use of TD−DFT to predict HOMO−LUMO gaps from which a prediction for the EA is obtained by adding the HOMO energies to the HOMO−LUMO gaps.

Figure 3 shows HOMO−LUMO gaps calculated from the difference in HOMO and LUMO eigenvalues and the experimental lowest excitation energies. The linear correlation coefficients are not as high as those determined for the HOMO, although a linear correlation relationship is apparent. Consequently, we can empirically correct the calculated HOMO−LUMO gaps. Table 3 lists the absolute errors for corrected results with the corrected values reported in the Supporting Information. This simple correction decreases both the largest errors and average errors, with the average unsigned errors predicted within approximately 1 eV of the experimental gap while the average *uncorrected* unsigned errors are as large as 5 eV. After correction, the residual error is still significant. As mentioned above, to describe the gap accurately, time-dependent (TD) calculations are required. With TD calculations,[48−50] we obtain excitation energies directly, rather than as the indirect byproducts of solving the secular equation using a basis set that provides a set of virtual orbitals and eigenvalues. We perform time-dependent DFT (TD−DFT) calculations using the same basis set to determine the lowest excitation energy. The excitation energy of the first singlet excited state is a reasonable approximation to the HOMO−LUMO gap.[14−17] This definition of the HOMO−LUMO gap has a more physical essence than that calculated directly from the energy difference between HOMO and LUMO eigenvalues. From the excitation energies calculated this way and the calculated HOMO eigenvalues, we can determine the LUMO eigenvalues. Therefore, to calculate LUMO energies, we shall first calculate HOMO eigenvalues and then use TD−DFT to calculate the HOMO−LUMO gaps and thus obtain the LUMO eigenvalues as the HOMO energies plus the HOMO−LUMO gaps.

Table 4 shows the HOMO−LUMO gaps (lowest excitation energies) calculated using TD−DFT. The TD−DFT HOMO−LUMO gaps are significantly better than those determined from the energy differences between the HOMO and LUMO eigenvalues. In contrast to the directly calculated HOMO−LUMO gaps, the differences between TD−DFT gaps calculated with different functionals are small. For instance, although KMLYP and BH&HLYP gaps calculated as the orbital energy differences were the most inaccurate, TD-KMLYP and TD−BH&HLYP predict relatively good HOMO−LUMO gaps with errors of 1.38

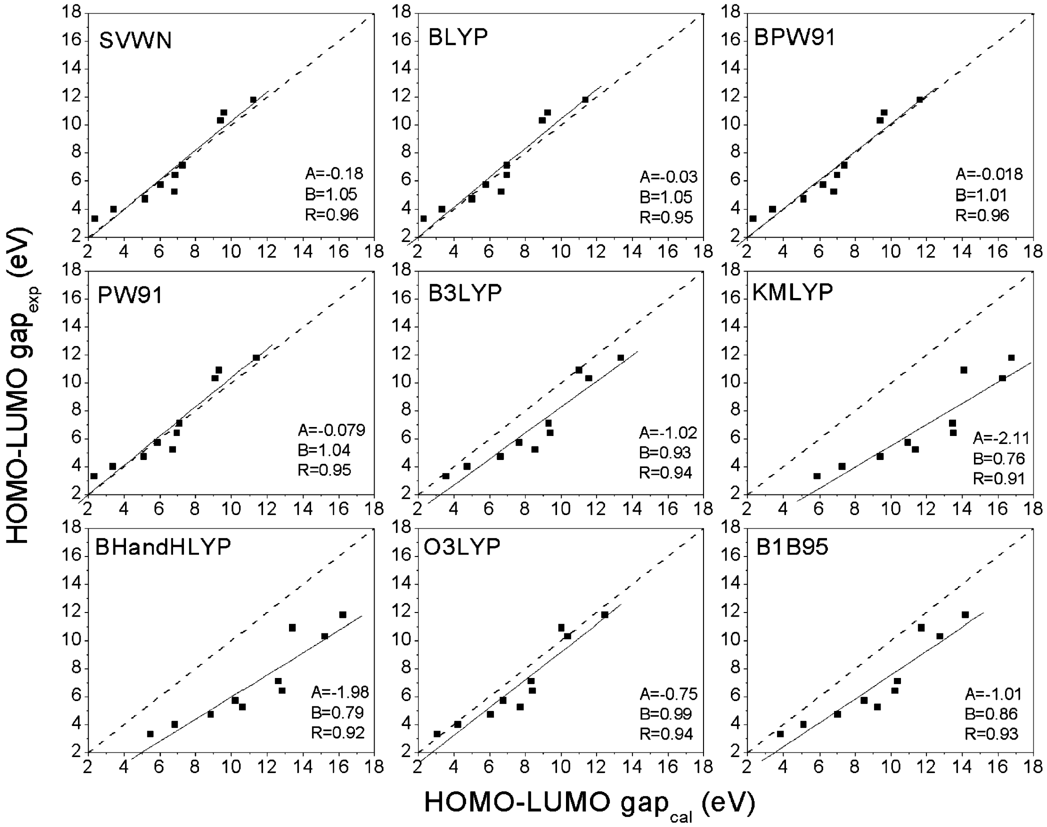

Figure 3. Calculated HOMO−LUMO gaps (in electronvolts) vs experimental lowest excitation energies. The dashed line indicates an ideal 1.0 correlation between experimental and calculated values.

TABLE 4: HOMO−LUMO Gaps (in electronvolts) Calculated Using TD−DFT Before and After Correction Using the Correction Formula[a]

	SVWN	BLYP	BP86	BPW91	PW91	PBE	B3LYP	KMLYP	BH&HLYP	O3LYP	B1B95	exp
C_2H_2	7.90	6.76	7.67	7.65	7.43	7.50	6.88	8.61	8.19	7.33	8.00	5.23
CH4	9.70	9.39	9.71	9.72	9.43	9.51	9.96	10.93	10.61	9.51	10.20	10.9
CO	8.21	8.17	8.20	8.21	8.19	8.18	8.41	8.78	8.72	8.35	8.44	6.4
H_2	12.38	12.63	12.61	12.74	12.69	12.64	12.89	13.22	13.23	12.88	12.95	11.8
HF	9.63	9.15	9.58	9.57	9.29	9.36	9.90	11.26	10.80	9.52	10.30	10.3
C_6H_6	6.96	5.34	6.80	6.83	6.56	6.68	5.37	5.84	7.22	6.68	7.06	4.72
$C_{10}H_8$	4.12	4.18	4.02	4.04	4.04	4.04	4.34	4.87	4.75	4.30	4.46	3.99
$C_{14}H_{10}$	2.92	3.02	2.87	2.88	2.88	2.88	3.20	3.73	3.64	3.11	3.29	3.31
H_2O	7.55	7.23	7.54	7.59	7.37	7.41	7.76	8.71	8.39	7.58	8.07	7.1
NH_3	6.20	6.02	6.26	6.33	6.14	6.16	6.46	7.25	7.01	6.31	6.73	5.72
					errors before correction							
largest error	2.70	1.77	2.47	2.45	2.23	2.30	2.01	3.41	2.99	2.13	2.80	
Average error	1.07	0.84	1.05	1.08	1.04	1.05	0.87	1.38	1.37	1.09	1.15	
					errors after correction							
largest error	2.08	1.73	1.88	1.85	1.96	1.91	1.53	2.02	1.68	2.00	1.79	
average error	0.98	0.78	0.94	0.95	0.97	0.97	0.68	0.69	0.79	0.93	0.86	

[a] Equation 1 with values given in Figure 4.

and 1.37 eV, respectively. Also notice that most of the calculated gaps are larger than the experimental gaps, indicating a systematic error that might be corrected.

The TD−DFT calculated gaps plotted vs experimental excitation energies shown in Figure 4 indicate that the linear correlations between calculated results and experimental results are appreciably better than those calculated using time-independent DFT which should increase the utility of the linear correction equation. Again, the linear correlation is likely due to the definition of the calculated HOMO−LUMO gap using TD−DFT being more consistent with the physical process. This results in errors that are more systematic. Table 4 shows the errors for the corrected HOMO−LUMO gaps with the corrected values tabulated in the Supporting Information. The small errors in the corrected HOMO eigenvalues and corrected HOMO−LUMO gaps indicate that prediction of MO energies is expected to be reliable. It can be seen that, after correction, the errors in the corrected HOMO−LUMO gaps range from 0.71 to 1.00 eV for the 11 functionals while the errors for the corrected TD HOMO−LUMO gaps range from 0.68 to 0.98 eV. Thus, predicting HOMO−LUMO gaps using time-independent DFT and our linear correction formula seems to be an alternative route to TD−DFT for accurate predictions of the lowest excitation energy.

Conclusions

In this paper, we have reported HOMO and LUMO eigenvalues predicted employing 11 DFT functionals. We use the negative of the experimental ionization potential and the lowest experimental excitation energy to compare with the calculated

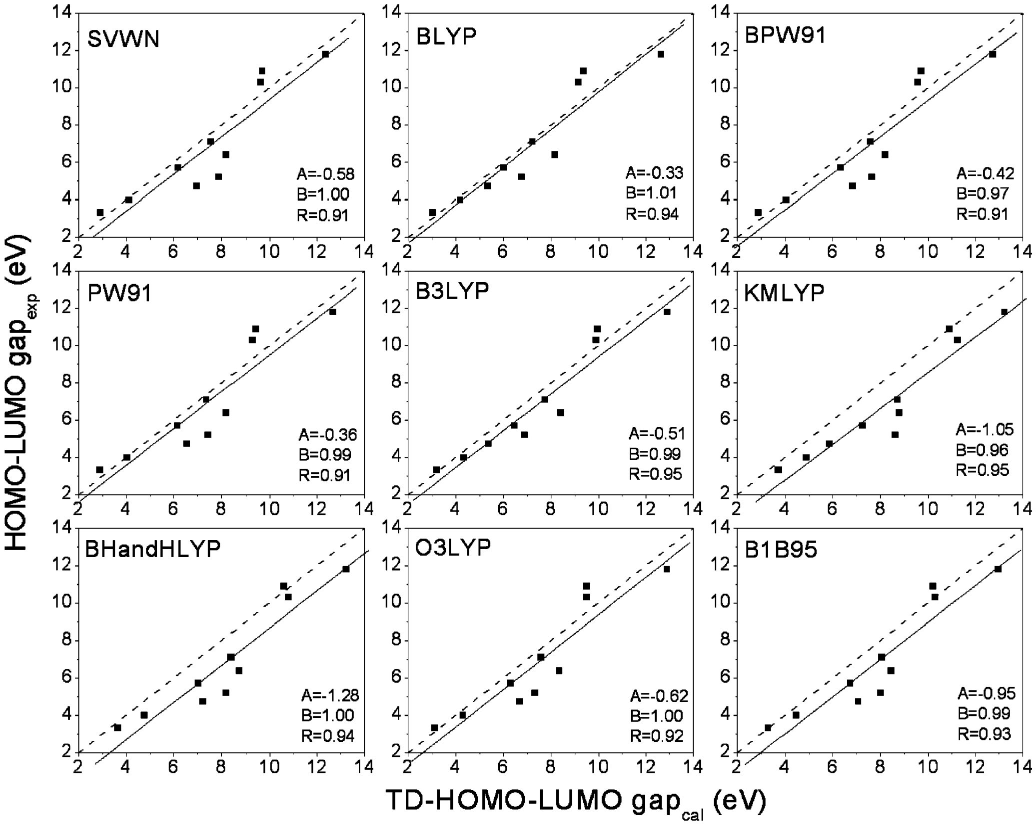

Figure 4. TD−DFT calculated HOMO−LUMO gaps (in electronvolts) vs experimental lowest excitation energies. The dashed line indicates an ideal 1.0 correlation between experimental and calculated values.

HOMO eigenvalue and the HOMO−LUMO gap. We find that the KMLYP and BH&HLYP HOMO energies predict the most accurate −IPs with errors of 0.73 and 1.48 eV, respectively. The B1B95, B3LYP, and O3LYP hybrid functionals include less HF exchange and result in errors in their HOMO energies of 2.86, 3.10, and 3.68 eV, respectively. The HOMO eigenvalues predicted by hybrid functionals are better than those predicted by nonhybrid functionals with the pure DFT methods resulting in errors in the HOMO energy ranging from 3.73 to 4.41 eV. On the other hand, after an empirical correction, all 11 functionals result in accurate HOMO eigenvalues with errors ranging from 0.24 to 0.62 eV. The calculated LUMO eigenvalues of all 11 functionals are considerably larger than the experimental EAs as a result of the poor description of virtual orbitals by time-independent quantum chemical methods. However, the predicted HOMO−LUMO gaps by nonhybrid functionals are relatively accurate with errors ranging from 0.72 to 0.76 eV. Unfortunately, the large fraction of HF exchange in KMLYP and BH&HLYP that results in accurate HOMO eigenvalues degrades the accuracy of the LUMO eigenvalues, thus resulting in inaccurate HOMO−LUMO gaps. Consequently, KMLYP and BH&HLYP have errors in their HOMO−LUMO gaps of 4.96 and 4.29 eV. The smaller percentage of HF exchange in the O3LYP, B3LYP, and B1B95 hybrid functionals leads to errors in the HOMO−LUMO gaps of 1.03, 1.63, and 2.35 eV.

To obtain better predictions for the HOMO−LUMO gap, we performed time-dependent calculations. The first excitation energy from the TD−DFT calculation leads to accurate predictions of the HOMO−LUMO gap for all 11 DFT methods with errors ranging from 0.84 to 1.38 eV. The calculated HOMOs, HOMO−LUMO gaps, and TD−DFT HOMO−LUMO gaps all have high linear correlations with the respective experimental values, and consequently, empirical formulas are determined to correct the calculated results. As has been shown, the DFT-calculated HOMO and LUMO eigenvalues are generally less sensitive to the basis set.[19] So although these correction formulas are based on results using the 6-311+G(d,p) basis set, they should be similar to results one might obtain using a different basis set. After correction, the errors in the HOMO energies over our 27 molecule test set range from 0.24 to 0.62 eV. The average error in the corrected HOMO−LUMO gaps ranges from 0.71 to 1.00 eV while the errors for the corrected TD HOMO−LUMO gaps range from 0.68 to 0.98 eV. This implies that the corrected HOMO−LUMO gaps are as accurate as the TD−DFT and corrected TD−DFT gaps. In conclusion, all 11 functionals predict accurate HOMO orbital energies when corrected and accurate HOMO−LUMO gaps either by using TD−DFT or by empirically correcting the HOMO−LUMO energy differences. Accurate LUMO orbital eigenvalues can be obtained by adding the corrected HOMO energies to the corrected or TD−DFT HOMO−LUMO gaps. Thus, these methods can be powerful tools for the prediction of MO eigenvalues and may be useful for simulation of molecular electronics and for understanding charge transfer in photoexcitation and redox chemistry.

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Supporting Information Available: Correlation curves of nine DFT functionals with the relevant correlation curves for the BP86 and PBE functionals. Corrected HOMO energies including the largest and average absolute errors. Corrected

HOMO−LUMO gaps and corrected TD-DFT HOMO−LUMO gaps are also presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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