

Assessment of Handy–Cohen Optimized Exchange Density Functional (OPTX)

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Received: June 14, 2004; In Final Form: July 27, 2004

In this paper we present a systematic assessment of the Handy–Cohen optimized exchange density functional (OPTX), comparing results from OLYP and O3LYP with those from BLYP and B3LYP. We find that OPTX significantly outperforms Becke88 in the calculations of the atomic exchange energies, and O3LYP leads to the best total atomic energies (H to Ar) among these four functionals. We find OLYP and O3LYP are competitive or even better than BLYP and B3LYP in the predictions of ionization potentials, electron affinities, and proton affinities against the extended G2 set of 75 atoms and molecules. For thermochemistry of the extended G2 set of 148 molecules, we find that the mean absolute deviation (in kcal/mol) follows the order BLYP (7.10) > OLYP (4.66) > O3LYP (4.13) > B3LYP (3.14). Thus OLYP is the best pure DFT, but B3LYP is the best overall. The histogram of error distribution of the G2 set indicates that O3LYP has more predictive power than B3LYP, although O3LYP has a tendency for overbinding. OLYP and O3LYP significantly outperform BLYP and B3LYP in describing van der Waals interactions, but OLYP and O3LYP underestimate hydrogen bond strengths even more than BLYP and B3LYP and, hence, cannot be recommended for studying hydrogen bond systems.

I. Introduction

Density functional theory (DFT) is the method of choice for first principles quantum chemical calculations of the electronic structure and properties of many molecular and solid systems. With the exact exchange-correlation functional, DFT would take into full account all complex many-body effects at a computation cost characteristic of mean field approximations. Unfortunately, the exact exchange-correlation functional is unknown, making it essential to pursue the quest of finding more accurate and reliable functionals. Currently, two popular functionals for thermochemistry would be BLYP and B3LYP.^{1–5} BLYP is a pure GGA (generalized gradient approximation) functional, consisting of the B88 exchange functional due to Becke¹ and the LYP correlation functional due to Lee–Yang–Parr.²

$$\text{BLYP} = 1.0E_x^{\text{Slater}} + 1.0\Delta E_x^{\text{B88}} + 1.0E_c^{\text{LYP}} \quad (1)$$

Here $E_x^{\text{Slater}} = -\sum_{\sigma}(3/4)(6/\pi)^{1/3} \int \rho_{\sigma}^{4/3}(r) dr$ is the major part of exchange energy E_x based on the uniform electron gas (UEG) approximation.^{6,7}

The Becke gradient correction takes the form,¹

$$\Delta E_x^{\text{B88}} = - \sum_{\sigma} \int \frac{\beta \rho_{\sigma}^{4/3} x_{\sigma}^2}{1 + 6\beta x_{\sigma} \sinh^{-1}(x_{\sigma})} dr \quad (2)$$

where $x_{\sigma} = |\nabla \rho_{\sigma}| \rho_{\sigma}^{-4/3}$. The parameter $\beta = 0.0042$ was determined by fitting to the Hartree–Fock (HF) values of noble gas atoms from He to Rn.¹

B3LYP is a hybrid functional which uses a small proportion of “exact exchange” based on the adiabatic connection formula.⁵

$$\text{B3LYP} = a_0 E_x^{\text{HF}} + (1 - a_0) E_x^{\text{Slater}} + a_x \Delta E_x^{\text{B88}} + a_c E_c^{\text{VWN}} + (1 - a_c) E_c^{\text{LYP}} \quad (3)$$

where $a_0 = 0.20$, $a_x = 0.72$, and $a_c = 0.19$ are taken from Becke’s linear least-squares fit to 56 atomization energies, 42 ionization potentials, and 8 proton affinities.⁴ Here $E_c(\text{VWN})$ is a local correlation functional, due to Vosko, Wilks, and Nusair, based on the random phase approximation (RPA).⁸

It is now well documented that GGA significantly improves over LDA (local density approximation) for thermochemistry leading to a mean absolute deviation (MAD) of 7.1 kcal/mol for BLYP compared to 90.9 kcal/mol for LDA (SVWN: $E_x^{\text{Slater}} + E_c^{\text{VWN}}$), whereas the hybrid GGA (B3LYP) leads to a MAD of 3.1 kcal/mol, all based on calculations for the extended G2 set of 148 molecules.^{9–11}

Recently, Handy and Cohen (hereafter HC) proposed a new exchange functional, OPTX¹²

$$\begin{aligned} E_x^{\text{OPTX}} &= a_1 E_x^{\text{Slater}} - a_2 \sum_{\sigma} \int \frac{\rho_{\sigma}^{4/3} (\gamma x_{\sigma}^2)^2}{(1 + \gamma x_{\sigma}^2)^2} dr \\ &= a_1 E_x^{\text{Slater}} + \Delta E_x^{\text{OPTX}} \end{aligned} \quad (4)$$

where $a_1 = 1.05151$, $a_2 = 1.43169$, and $\gamma = 0.006$, with the parameters determined by fitting to the unrestricted HF energies of first- and second-row atoms. In particular, they drop the usual requirement that the E_x^{Slater} term has the value of 1.0 to recover the UEG condition. This extra freedom makes OPTX better than B88 by a factor of 2 for the prediction of atomic exchange

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energies of atoms from H to Ar. When combined with LYP, HC found that OLYP (OPTX + LYP, MAD = 3.3 kcal/mol) significantly outperforms BLYP (MAD = 4.5 kcal/mol) for thermochemistry of 93 atomic and molecular systems.^{12,13}

A new hybrid functional, O3LYP, has also been proposed¹³

$$\text{O3LYP} = aE_x^{\text{HF}} + bE_x^{\text{Slater}} + c\Delta E_x^{\text{OPTX}} + a_c E_c^{\text{VWN5}} + (1 - a_c)E_c^{\text{LYP}} \quad (5)$$

where $a = 0.1161$, $b = 0.9262$, $c = 0.8133$, and $a_c = 0.19$. Important differences from B3LYP are that the proportion of “exact exchange” in O3LYP is 0.1161 as compared to 0.20 in B3LYP and that O3LYP uses E_c^{VWN5} (the local correlation functional due to Vosko, Wilks, and Nusair from fitting to the Ceperley–Alder Monte Carlo results on the electron gas⁸) instead of using E_c^{VWN} as in B3LYP. HC found that O3LYP is substantially better than B3LYP for the 93 systems.¹³

Baker and Pulay (hereafter BP) performed an independent assessment of OLYP and O3LYP for organic reactions and for first-row transition metals.^{14,15} On the basis of the results for geometries, heats of reactions, and barrier heights for twelve organic reactions, BP support the finding by HC that OLYP is superior to BLYP, essentially rendering BLYP obsolete, whereas O3LYP is overall better than B3LYP, albeit not by much.¹⁴ For transition metals, however, BP found that OLYP and O3LYP are clearly worse than both BLYP and B3LYP for predicting atomic excitation and 4s ionization energies and concluded that there is no real incentive to use either OLYP and O3LYP in place of B3LYP for calculations involving first-row transition metals.¹⁵

In this paper we present a systematic assessment using the well-established G2 set and compare results from OLYP and O3LYP with those from BLYP and B3LYP. We find that OPTX significantly outperforms B88 in the calculation of the atomic exchange energies, and that for atoms from H to Ar O3LYP leads to the best total atomic energies among these four functionals. We find that OLYP and O3LYP are competitive or even better than BLYP and B3LYP in the predictions of ionization potentials, electron affinities, and proton affinities against the extended G2 sets. For thermochemistry, we find that the mean absolute error follows the order that BLYP (7.10) > OLYP (4.66) > O3LYP (4.13) > B3LYP (3.14 kcal/mol); hence OLYP is the best pure DFT with an accuracy approaching that of hybrid functional B3LYP. The histogram of error distribution of the G2 set indicates that O3LYP has more predictive power than B3LYP, although O3LYP has a tendency for overbinding. In particular, OLYP and O3LYP significantly outperform BLYP and B3LYP in the description of the van der Waals interactions; but the OLYP and O3LYP functionals do worse than BLYP and B3LYP for hydrogen bonding and hence cannot be recommended for the study of hydrogen bond systems.

II. Computational Details

We use the well-known extended G2 set as the testing set,^{9–11} which contains heats of formation of 148 molecules, 42 ionization potentials, 25 electron affinities, and 8 proton affinities. This 148 molecule set includes inorganic compounds and organic compounds and it includes radicals, saturated hydrocarbons, and unsaturated (aromatic) rings. Heats of formation of these molecules provide a good test of the functionals for the covalent systems. We also include the total atomic energies of first 18 atoms.^{16,17}

In addition, we use He₂, Ne₂, and Ar₂ as probes of the van der Waals systems and (H₂O)₂ as a prototypical system of hydrogen bonded interactions.

For the G2 set, we use the same MP2 molecular geometries as in G2 theory,^{9–11} and we use the scaled Hartree–Fock vibrational frequencies for zero-point energies and finite-temperature corrections. The 6-311+G(3df,2p) basis sets are employed for all cases.^{9–11} This choice of geometries and basis sets allows a direct comparison of our results with previously published data obtained with other functionals.^{10,11,18–22}

For He₂ and Ne₂, we use the aug-cc-pVTZ basis sets.^{23,24} For (H₂O)₂, we use the aug-cc-pVTZ(-f) basis sets.^{23,24} The bonding energies are corrected for BSSE (basis set superposition error).²⁵

All calculations are performed with Jaguar.²⁶ We did not use the pseudospectral method to facilitate the direct comparison with the literature data. Ultrafine DFT grids of Jaguar are used in all calculations.

III. Results and Discussion

A. Atomic Data. Table 1 compares the total energies (in Hartree) calculated self-consistently by Hartree–Fock (HF) and the DFT-exchange-only methods with the total energies of HF limit¹⁷ for the first 18 atoms from H to Ar. Comparing these results to the HF limit, we find an error of 1.8 kcal/mol (MAD: mean absolute deviation), which may be interpreted as the basis set error associated with aug-cc-pVTZ for the atomic calculations. B88 yields MAD = 7.3 kcal/mol, which was the best result at the time B88 was developed. OPTX substantially improves over Becke88, leading to MAD = 2.6 kcal/mol. This is the best result to date.

B3LYP has been successfully applied to a wide range of systems of different properties. However, the B3LYP hybrid exchange functional ($0.20E_x^{\text{HF}} + 0.80E_x^{\text{Slater}} + 0.72\Delta E_x^{\text{B88}}$), leads to a huge error of 54.8 kcal/mol for the atoms. The new hybrid functional, O3 = $0.1161E_x^{\text{HF}} + 0.9262E_x^{\text{Slater}} + 0.8133\Delta E_x^{\text{OPTX}}$, behaves better than B3, but still leads to MAD = 44.4 kcal/mol.

Table 2 presents another way of gauging the quality of an exchange functional. Taking the HF exchange energies as a reference, post-DFT calculations with HF densities give the following errors (MADs) for the exchange energies: 9.5 (B88), 3.3 (OPTX), 57.0 (B3), and 45.8 (O3). Note here that although the MADs associated with hybrid functionals B3 and O3 are significantly larger than those of Becke88 and OPTX, the errors increase systematically with the atomic number. Thus errors associated with hybrid exchange functional may be more systematic.

Table 3 summarizes the correlation energies for the first 18 atoms from H to Ar¹⁷ and the correlation energies calculated self-consistently by DFT methods. BLYP and OLYP share the same correlation functional; thus the slight difference in the correlation energies between these two reflects the effect of changes in density from different exchange functionals. The correlation functionals in B3LYP and O3LYP are similar. O3LYP borrows the mixing parameters from B3LYP, but O3LYP uses VWN version V based on the accurate Monte Carlo calculations,⁸ whereas B3LYP uses VWN version III based on the random phase approximation.⁸ The LYP correlation functional gives a MAD of 7.5 in BLYP and 7.2 in OLYP, whereas substantially higher errors are associated with the hybrid correlation functionals, giving MAD = 69.4 (in B3LYP) and 47.0 (in O3LYP).

TABLE 1: Total Energies (in Hartree) of the 18 Atoms from H to Ar^a

atom	$E(\text{HF limit})$	$E(\text{HF})$	$\Delta E(\text{B}^b)$	$\Delta E(\text{O}^c)$	$\Delta E(\text{B3}^d)$	$\Delta E(\text{O3}^e)$
H	-0.500000	-0.499821	-0.002278	-0.001576	-0.005298	-0.004360
He	-2.861704	-2.861183	0.001105	0.001608	-0.010846	-0.008502
Li	-7.432730	-7.432705	-0.005295	-0.001201	-0.023299	-0.017527
Be	-14.57303	-14.57288	-0.008004	-0.001397	-0.034189	-0.025191
B	-24.52906	-24.53217	-0.005234	-0.000972	-0.039415	-0.032205
C	-37.68864	-37.69181	-0.003129	-0.001590	-0.047494	-0.040451
N	-54.40096	-54.40116	-0.004642	-0.001185	-0.060107	-0.048253
O	-74.80942	-74.81298	0.014026	0.007580	-0.054020	-0.048916
F	-99.40932	-99.40689	0.024382	0.009676	-0.058295	-0.056259
Ne	-128.54710	-128.53327	0.027750	0.012174	-0.070712	-0.063966
Na	-161.85892	-161.85804	0.016043	0.007327	-0.087449	-0.075861
Mg	-199.61457	-199.61335	0.009578	0.000341	-0.104289	-0.091453
Al	-241.87642	-241.87917	0.002747	-0.001484	-0.119351	-0.102628
Si	-288.85433	-288.85663	-0.005342	-0.004140	-0.137662	-0.114974
P	-340.71907	-340.71649	-0.016942	-0.006998	-0.161145	-0.128136
S	-397.50477	-397.50987	-0.015408	0.002035	-0.168140	-0.129829
Cl	-459.48172	-459.48597	-0.018325	0.006514	-0.183054	-0.136442
Ar	-526.81790	-526.81335	-0.027793	0.007251	-0.207452	-0.147397
MAD ^f		1.8	7.3	2.6	54.8	44.4

^a Here the HF limit¹⁷ is for Hartree–Fock with a complete basis set. The total energies were calculated self-consistently using the aug-cc-pVTZ basis set for HF and the DFT-exchange-only methods, and the error is defined as $\Delta E = E(\text{HF limit}) - E(\text{DFT})$. The best DFT results are in boldface. ^b References 1, 6, 7: $1.0E_x^{\text{Slater}} + 1.0\Delta E_x^{\text{B88}}$. ^c References 6, 7, 12: $1.05151E_x^{\text{Slater}} + 1.0\Delta E_x^{\text{OPTX}}$. ^d References 1, 4–7: $0.20E_x^{\text{HF}} + 0.80E_x^{\text{Slater}} + 0.72\Delta E_x^{\text{B88}}$. ^e References 6, 7, 13: $0.1161E_x^{\text{HF}} + 0.9262E_x^{\text{Slater}} + 0.8133\Delta E_x^{\text{OPTX}}$. ^f Mean absolute deviations (MADs) as compared to HF limit are given in kcal/mol.

TABLE 2: Hartree–Fock (HF) Exchange Energies (in Hartree) of the 18 Atoms from H to Ar and the Differential DFT Exchange-Only Exchange Energies [$\Delta E_x = E_x(\text{HF}) - E_x(\text{DFT Exchange-Only})$] (in Hartree)^a

atom	$E_x(\text{HF})$	$\Delta E_x(\text{B})$	$\Delta E_x(\text{O})$	$\Delta E_x(\text{B3})$	$\Delta E_x(\text{O3})$
H	-0.312190	-0.002722	-0.001846	-0.005512	-0.004527
He	-1.025447	-0.000282	0.000430	-0.011535	-0.009291
Li	-1.781214	-0.005939	-0.001686	-0.023743	-0.017925
Be	-2.666716	-0.009071	-0.001775	-0.034888	-0.025528
B	-3.759184	-0.016429	-0.005847	-0.044554	-0.036829
C	-5.066702	-0.014794	-0.007347	-0.053704	-0.045804
N	-6.604576	-0.010437	-0.003976	-0.063970	-0.050655
O	-8.204931	-0.001149	-0.000559	-0.062863	-0.056284
F	-10.031048	0.013588	0.006162	-0.062572	-0.058739
Ne	-12.102300	0.029706	0.019552	-0.064565	-0.055464
Na	-14.017379	0.012864	0.006072	-0.089266	-0.076810
Mg	-15.994046	0.006193	-0.000033	-0.106144	-0.091688
Al	-18.079161	-0.011412	0.006776	-0.125697	-0.107546
Si	-20.292187	-0.018780	-0.009435	-0.144127	-0.119811
P	-22.640536	-0.020320	-0.006773	-0.162559	-0.127595
S	-25.019285	-0.033620	-0.006695	-0.178398	-0.138043
Cl	-27.530263	-0.035312	-0.002134	-0.193020	-0.144414
Ar	-30.183224	-0.031304	0.007898	-0.208276	-0.146153
MAD ^b		9.5	3.3	57.0	45.8

^a The DFT energies were calculated using HF densities. The basis sets used is aug-cc-pVTZ. The best DFT results are in boldface. ^b Mean absolute deviations (MADs) as compared to HF limit are given in kcal/mol.

The exchange-correlation total atomic energies calculated self-consistently with various DFT methods are summarized in Table 4. MADs are calculated as compared to the exact atomic total energies.¹⁷ Here BLYP and OLYP lead to similar errors of 7.2 and 7.7 kcal/mol, respectively. The MADs for B3LYP and O3LYP are 14.6 and 2.9 kcal/mol, respectively.

Summarizing O3LYP leads to the best results for atomic calculations. This impressive performance, however, is achieved by error cancellation between the exchange part and the correlation part. Such error cancellation also occurs in B3LYP.

B. Heats of Formation. Table 5 lists the experimental heats of formation (298 K) for the extended G2 set of 148 molecules.^{10,11} The deviations from experiment (theory-expt.) for BLYP, OLYP, B3LYP, and O3LYP are presented. Figure 1a shows the histogram of errors for OLYP as compared to that

TABLE 3: Correlation Energies (in Hartree) for the 18 Atoms from H to Ar¹⁷ and the Correlation Energies Calculated Self-Consistently by DFT Methods^a

atom	$E_c(\text{exact})$	$E_c(\text{BLYP}^b)$	$E_c(\text{OLYP}^c)$	$E_c(\text{B3LYP}^d)$	$E_c(\text{O3LYP}^d)$
H	0	0	0	-0.007558	-0.004174
He	-0.04202	-0.043702	-0.043704	-0.063836	-0.056727
Li	-0.04533	-0.053744	-0.053700	-0.082626	-0.072264
Be	-0.09436	-0.095093	-0.094874	-0.133606	-0.119560
B	-0.12484	-0.126493	-0.125271	-0.174244	-0.156397
C	-0.15636	-0.159615	-0.158634	-0.217913	-0.196440
N	-0.18834	-0.192206	-0.192051	-0.262037	-0.237002
O	-0.25798	-0.257834	-0.256873	-0.338772	-0.309262
F	-0.32478	-0.321458	-0.320964	-0.415110	-0.381286
Ne	-0.39120	-0.382886	-0.383101	-0.489896	-0.451787
Na	-0.39648	-0.408679	-0.408462	-0.525547	-0.483699
Mg	-0.43943	-0.460218	-0.459657	-0.587469	-0.541699
Al	-0.47058	-0.495496	-0.493906	-0.632719	-0.583331
Si	-0.50567	-0.531469	-0.530154	-0.680100	-0.627130
P	-0.54093	-0.567003	-0.566951	-0.728331	-0.671757
S	-0.60623	-0.630705	-0.629171	-0.802696	-0.741750
Cl	-0.66828	-0.691984	-0.690955	-0.876693	-0.811592
Ar	-0.72610	-0.751098	-0.751262	-0.949564	-0.880289
MAD ^f		7.5	7.2	69.4	47.0

^a Here $E_c(\text{DFT}) = E_{\text{cor}}(\text{DFT}) - E(\text{exchange-only})$. The aug-cc-pVTZ basis sets were used. ^b References 1, 2, 6, 7: $1.0E_x^{\text{Slater}} + 1.0\Delta E_x^{\text{B88}} + 1.0E_c^{\text{LYP}}$. ^c References 2, 6, 7, 12: $1.05151E_x^{\text{Slater}} + 1.0\Delta E_x^{\text{OPTX}} + 1.0E_c^{\text{LYP}}$. ^d References 1, 2, 4–8: $0.20E_x^{\text{HF}} + 0.80E_x^{\text{Slater}} + 0.72\Delta E_x^{\text{B88}} + 0.19E_c^{\text{VWN3}} + 0.81E_c^{\text{LYP}}$. ^e References 2, 6–8, 13: $0.1161E_x^{\text{HF}} + 0.9262E_x^{\text{Slater}} + 0.8133\Delta E_x^{\text{OPTX}} + 0.19E_c^{\text{VWN5}} + 0.81E_c^{\text{LYP}}$. ^f Mean absolute deviations (MADs) are given in kcal/mol.

for BLYP, and Figure 1b shows the histogram of errors for O3LYP as compared to that for B3LYP. From Table 1 and Figure 1, it is clear that OLYP (MAD = 4.66 kcal/mol) clearly outperforms BLYP (MAD = 7.10 kcal/mol).

The inclusion of exact exchange in B3LYP (MAD = 3.14) significantly improves over BLYP (MAD = 7.10), whereas the difference is small as compared OLYP (MAD = 4.66) to O3LYP (MAD = 4.13). The errors are more equally distributed around the error peak for OLYP and O3LYP, indicating improved predictive power for these two functionals as compared to the classic functionals BLYP and B3LYP.

On the other hand, errors cluster at the “-2 to -3” interval for OLYP (17/148) and the “-3 to -4” interval for O3LYP

TABLE 4: Total Atomic Energies (in Hartree) of the 18 Atoms from H to Ar, Calculated Self-Consistently with DFT Methods^a

atom	exact	$\Delta E(\text{BLYP})$	$\Delta E(\text{OLYP})$	$\Delta E(\text{B3LYP})$	$\Delta E(\text{O3LYP})$
H	-0.5	-0.002278	-0.001577	0.002260	-0.000185
He	-2.903724	0.002787	0.003292	0.010970	0.006206
Li	-7.478060	0.003119	0.007169	0.013997	0.009407
Be	-14.66739	-0.007271	-0.000883	0.005057	0.000009
B	-24.65390	-0.003581	-0.000540	0.009989	-0.000648
C	-37.8450	0.000127	0.000684	0.014058	-0.000371
N	-54.5893	-0.000776	0.002526	0.013590	0.000409
O	-75.0674	0.013880	0.006473	0.026772	0.002366
F	-99.7341	0.021059	0.005859	0.032036	0.000247
Ne	-128.9383	0.019436	0.004074	0.027985	-0.003380
Na	-162.2554	0.028242	0.019308	0.041618	0.011358
Mg	-200.054	0.030366	0.020568	0.043750	0.010815
Al	-242.347	0.027663	0.021843	0.042789	0.010123
Si	-289.360	0.020457	0.020344	0.036768	0.006486
P	-341.260	0.009131	0.019024	0.026256	0.002691
S	-398.111	0.009067	0.024977	0.028325	0.005691
Cl	-460.150	0.005380	0.029188	0.025359	0.006870
Ar	-527.544	-0.002794	0.032412	0.016013	0.006792
MAD		7.2	7.7	14.6	2.9

^a The differences between the exact total atomic energies¹⁷ and DFT [$\Delta E = E(\text{exact}) - E(\text{DFT})$] are given. The aug-cc-pVTZ basis sets are used. The best DFT results are in boldface.

(29/148), showing a clear overbinding tendency. In OLYP, BLYP, and O3LYP, the maximum negative deviations (-22.0, -27.6, and -9.4 kcal/mol, respectively) occur at NO₂, whereas in B3LYP, the maximum negative deviation (-8.2 kcal/mol) occurs at BeH. In OLYP, O3LYP, and B3LYP, the maximum positive deviations (26.1, 25.9, and 20.0 kcal/mol, respectively) occur at SiF₄, whereas in BLYP, the maximum positive deviation (25.3 kcal/mol) occurs at SiCl₄.

For the subset of inorganic hydrides (X_nH_m, X = H, Li, N, O, F, Si, P, S, Cl; *n* = 1, 2; *m* = 1-6), MADs are 3.12 (BLYP), 2.37 (OLYP), 1.81 (B3LYP), and 1.68 (O3LYP). For Si₂H₆ the hybrid functionals are significantly better than pure DFT. In this case, deviations are 10.30 (BLYP), 6.61 (OLYP), -0.11 (B3LYP), and -0.35 (O3LYP).

The performance of BLYP for larger hydrocarbons (nos. 78-94 in Table 5) is less satisfactory. The MAD of hydrocarbon subset is 8.22 kcal/mol, with the maximum error of 18.54 kcal/mol for isobutane. The OLYP functional performs much better. The MAD of this subset is 3.39 kcal/mol. Whereas BLYP generally underbinds, OLYP has a tendency to overbind. The maximum error (-6.11 kcal/mol) occurs at methylenecyclopropane. On average, B3LYP is the best for this subset with MAD = 2.88 kcal/mol and a maximum error of 7.40 kcal/mol at bicyclobutane. Instead of improving, O3LYP is poorer than OLYP, leading to an enhanced overbinding propensity. The MAD for O3LYP is 4.31 with a maximum error of -8.97 kcal/mol.

For a subset of substituted hydrocarbons (e.g., nos. 95-136 in Table 5), the performance of BLYP is not satisfactory (MAD = 6.07), showing large variation from overbinding (-18.24 at nitromethane) to underbinding (14.21 at propyl chloride). The hybrid B3LYP functional significantly improves over BLYP, leading to a MAD of 2.14 kcal/mol. The maximum error (9.2 kcal/mol) occurs at HCCl₃. OLYP outperforms BLYP, but the hybrid O3LYP (MAD = 3.27 kcal/mol over this subset) has an overall accuracy similar to OLYP (MAD = 3.58 kcal/mol). However, including exact exchange does reduce the maximum error of -15.18 for OLYP to -7.01 kcal/mol for O3LYP.

For a subset of radicals (e.g., nos. 138-148 in Table 5), OLYP leads to MAD = 4.93 kcal/mol, with a maximum error of -22.04 kcal/mol at NO₂. O3LYP (MAD = 4.60) is slightly

improved. However, the maximum error reduces to -9.42 kcal/mol. Whereas BLYP (MAD = 6.13) is the worst, B3LYP (MAD = 2.94) is the best among these four. BLYP is also problematic with an error of -27.61 kcal/mol for NO₂, which is reduced to -4.47 kcal/mol in B3LYP.

Fluorine and chlorine-containing compounds are notoriously problematic systems in the G2 set. The MADs obtained from these compounds (nos. 57-77 in Table 5) are 14.44, 12.44, 7.24, and 7.65 kcal/mol for BLYP, OLYP, B3LYP, and O3LYP, respectively. The largest errors encountered are 25.31 (SiCl₄, BLYP), 26.06, 19.97, and 25.89 for OLYP, B3LYP, and O3LYP, respectively, at SiF₄.

OLYP generally improves over BLYP for thermochemistry, but there are a few cases where the results are considerably worse. Thus for AlF₃, BLYP underbinds by 7.25 kcal/mol, and OLYP underbinds by 14.86.

Based on MADs in Table 5, the accuracy for thermochemistry follows the order BLYP \ll OLYP < O3LYP < B3LYP. Hence we conclude that

•OLYP is clearly superior to BLYP, being the best pure DFT method for thermochemistry;

•O3LYP results for molecules are no better than B3LYP, providing no real incentive to use O3LYP in place of B3LYP.

C. Ionization Potentials, Electron Affinities, and Proton Affinities. Table 6 lists the experimental ionization potentials (IPs) and the deviations from experiments for 18 atoms and 24 molecules,^{9,11} and Table 7 lists the results of electron affinities (EAs) for 7 atoms and 18 molecules.^{9,11} We calculated IPs and EAs as energy differences between the neutral species and the corresponding ionic species.

C.1. Ionization Potentials. Very accurate experimental IPs for atoms are available, providing a good test of the functionals at handling positively charged systems. For the atomic systems, the MADs for OLYP and O3LYP are 0.112 and 0.109 eV, respectively, which are better than the corresponding BLYP value (0.188) and B3LYP value (0.203 eV).

For molecular systems, the MADs for OLYP and O3LYP are 0.240 and 0.161 eV, respectively, which are worse than for BLYP (0.187) and B3LYP (0.141 eV).

The overall MADs for the 42 systems are 0.187 (BLYP) > 0.185 (OLYP) > 0.168 (B3LYP) > 0.139 (O3LYP). The problematic cases are O (0.56 eV) for BLYP, C₂H₄ (0.91) for OLYP, and O₂ (0.80, 0.58 eV) for B3LYP and O3LYP, respectively.

C.2. Electron Affinities. There has been some debate in the literature concerning whether DFT methods are suitable for calculating electron affinities.²⁷⁻²⁹ However, the numerical results demonstrate that DFT methods lead to electron affinities with an accuracy comparable to conventional ab initio calculations.^{11,29}

For the atomic systems, MADs for OLYP and O3LYP are 0.089 and 0.067 eV, respectively.

For the molecular systems, MADs for OLYP and O3LYP are 0.149 and 0.123 eV, respectively. EA of O₂ (-0.33 eV) is problematic for OLYP, whereas EA of NO is problematic for O3LYP.

The MADs for the total 25 systems are 0.133 (OLYP) and 0.107 (O3LYP) eV. For BLYP and B3LYP, similar calculations lead to 0.106 (BLYP) and 0.103 (B3LYP).

C.3. Proton Affinities. Table 8 lists the proton affinities (PAs) at 0 K for 8 systems of the G2 set and the deviations (theory-exptl) obtained from BLYP, OLYP, B3LYP, and O3LYP. OLYP leads to MAD = 1.380 kcal/mol with a maximum deviation of 3.42 kcal/mol for C₂H₂. The PAs are more often

TABLE 5: Experimental Heats of Formation (kcal/mol, 298 K) for the G2 Test Set (148 Molecules)^{9,10} and the Deviations (theory-exptl) Obtained from BLYP, OLYP, B3LYP, and O3LYP^a

no.	molecule	exptl	$\Delta E(\text{BLYP})$	$\Delta E(\text{OLYP})$	$\Delta E(\text{B3LYP})$	$\Delta E(\text{O3LYP})$
1	H ₂	0.00	-0.215	-2.595	-0.998	-3.123
2	LiH	33.30	-0.051	1.028	-0.410	0.356
3	BeH	81.70	-7.309	-5.442	-8.180	-6.520
4	CH	142.50	-1.783	-0.906	-1.666	-1.168
5	CH ₂ (³ B ₁)	93.70	0.047	-3.551	-2.066	-4.833
6	CH ₂ (¹ A ₁)	102.75	0.622	0.399	-0.222	-0.519
7	CH ₃	35.00	-0.396	-3.436	-3.289	-5.446
8	CH ₄	-17.90	2.387	-2.500	-1.593	-5.075
9	NH	85.20	-6.035	-3.009	-4.575	-2.755
10	NH ₂	45.10	-8.029	-4.573	-6.448	-4.533
11	NH ₃	-10.97	-4.342	-3.106	-3.532	-3.465
12	OH	9.40	-3.484	-2.140	-1.894	-1.710
13	H ₂ O	-57.80	-0.609	-1.493	1.321	-0.852
14	HF	-65.14	-0.410	-1.953	1.573	-0.953
15	SiH ₂ (¹ A ₁)	65.20	-0.427	-0.124	-2.179	-1.695
16	SiH ₂ (³ B ₁)	86.20	0.351	-4.228	-2.262	-5.532
17	SiH ₃	47.90	1.031	-1.827	-3.100	-4.500
18	SiH ₄	8.20	4.020	2.234	-1.877	-1.905
19	PH ₂	33.10	-4.838	-3.902	-5.957	-5.090
20	PH ₃	1.30	-0.876	-0.842	-3.225	-2.845
21	H ₂ S	-4.90	1.747	-1.243	0.378	-2.030
22	HCl	-22.06	1.540	-1.564	0.961	-1.689
23	Li ₂	51.60	3.639	2.216	3.514	2.318
24	LiF	-80.10	-3.044	1.776	0.379	2.791
25	C ₂ H ₂	54.19	0.320	0.623	2.614	1.221
26	H ₂ C=CH ₂	12.54	1.795	-1.835	-0.540	-3.733
27	H ₃ C-CH ₃	-20.08	6.483	-1.420	-0.591	-5.905
28	CN	104.90	-8.059	-1.744	2.548	3.446
29	HCN	31.50	-7.317	-1.105	0.331	2.160
30	CO	-26.42	-3.185	-0.380	3.929	3.232
31	HCO	10.00	-9.122	-7.725	-2.170	-4.224
32	H ₂ C=O	-25.96	-4.886	-4.951	-0.361	-2.915
33	CH ₃ -OH	-48.00	0.511	-2.224	-0.115	-3.373
34	N ₂	0.00	-10.108	1.090	1.923	6.572
35	H ₂ N-NH ₂	22.79	-9.388	-3.902	-5.916	-3.574
36	NO	21.58	-13.383	-7.341	-2.461	-1.809
37	O ₂	0.00	-15.315	-14.654	-1.987	-7.176
38	HO-OH	-32.53	-7.541	-4.096	1.796	0.020
39	F ₂	0.00	-9.721	-6.408	2.573	0.007
40	CO ₂	-94.05	-12.595	-10.647	0.269	-3.784
41	Na ₂	33.96	-0.895	-3.883	-0.129	-2.964
42	Si ₂	139.87	1.325	2.014	5.346	4.235
43	P ₂	34.31	-4.889	2.503	1.392	5.145
44	S ₂	30.74	-5.668	-6.128	-1.302	-3.447
45	Cl ₂	0.00	0.309	-0.993	2.914	0.654
46	NaCl	-43.56	5.526	5.124	4.416	4.492
47	SiO	-24.64	-2.592	5.245	5.461	8.520
48	CS	66.90	-1.025	-0.158	4.993	3.239
49	SO	1.20	-9.626	-6.959	-0.596	-2.210
50	ClO	24.19	-10.532	-8.153	-1.618	-3.346
51	ClF	-13.24	-5.738	-4.220	0.994	-0.677
52	H ₃ Si-SiH ₃	19.10	10.295	6.610	-0.111	-0.345
53	CH ₃ Cl	-19.56	3.888	-1.397	0.854	-3.182
54	H ₃ C-SH	-5.50	5.302	-0.482	1.306	-2.928
55	HOCl	-17.80	-4.487	-3.143	1.493	-0.280
56	SO ₂	-70.95	-7.170	-2.737	9.912	6.398
57	BF ₃	-271.41	-0.056	6.130	3.939	6.699
58	BCl ₃	-96.30	8.809	2.973	6.475	2.298
59	AlF ₃	-289.03	7.251	14.858	11.818	15.481
60	AlCl ₃	-139.72	15.533	12.000	10.363	9.194
61	CF ₄	-223.04	-3.661	-5.418	4.463	-1.026
62	CCl ₄	-22.94	12.277	7.475	14.101	9.014
63	O=C=S	-33.08	-10.877	-10.274	-0.330	-4.330
64	CS ₂	27.95	-7.546	-8.518	0.483	-3.646
65	COF ₂	-152.70	-2.462	-2.041	9.061	4.094
66	SiF ₄	-385.98	16.046	26.062	19.972	25.889
67	SiCl ₄	-158.40	25.307	19.064	19.083	16.134
68	N ₂ O	19.61	-25.286	-16.338	-2.234	-4.259
69	ClNO	12.36	-22.535	-15.545	-1.587	-4.450
70	NF ₃	-31.57	-25.162	-19.503	-4.042	-8.255

TABLE 5: Cont'd

no.	molecule	exptl	$\Delta E(\text{BLYP})$	$\Delta E(\text{OLYP})$	$\Delta E(\text{B3LYP})$	$\Delta E(\text{O3LYP})$
71	PF ₃	-229.07	-1.524	8.238	7.008	11.321
72	O ₃	34.10	-23.553	-17.689	8.619	-0.004
73	F ₂ O	5.86	-20.963	-14.495	0.323	-3.388
74	ClF ₃	-37.97	-23.987	-18.707	-2.032	-7.083
75	C ₂ F ₄	-157.40	-16.258	-15.578	-2.997	-8.785
76	C ₂ Cl ₄	-2.97	8.287	2.667	11.782	5.209
77	CF ₃ CN	-118.40	-11.570	-5.308	4.121	2.412
78	C ₃ H ₄ (propyne)	44.20	2.726	-0.405	2.062	-1.564
79	C ₃ H ₄ (allene)	45.50	-2.059	-5.148	-1.847	-5.746
80	C ₃ H ₄ (cyclopropene)	66.20	5.144	-3.513	3.479	-4.360
81	C ₃ H ₆ (propylene)	4.78	6.085	-0.540	0.729	-4.314
82	C ₃ H ₆ (cyclopropane)	12.70	9.739	-2.176	2.364	-6.313
83	C ₃ H ₈ (propane)	-25.00	11.757	1.142	1.467	-5.372
84	C ₄ H ₆ (butadiene)	26.30	4.937	-0.299	1.703	-3.128
85	C ₄ H ₆ (2-butyne)	34.80	6.317	-0.231	2.651	-3.184
86	C ₄ H ₆ (methylenecyclopropane)	47.90	5.063	-6.110	0.201	-8.967
87	C ₄ H ₆ (bicyclobutane)	51.90	14.363	-2.497	7.404	-5.690
88	C ₄ H ₆ (cyclobutene)	37.40	11.951	0.003	6.180	-3.247
89	C ₄ H ₈ (cyclobutane)	6.80	16.293	1.278	5.323	-5.018
90	C ₄ H ₈ (isobutene)	-4.00	11.752	2.501	3.147	-3.335
91	C ₄ H ₁₀ (trans butane)	-30.00	17.202	3.907	3.676	-4.649
92	C ₄ H ₁₀ (isobutane)	-32.07	18.540	5.610	4.871	-3.100
93	C ₅ H ₈ (spiropentane)	44.30	16.142	-3.081	5.866	-8.422
94	C ₆ H ₆ (benzene)	19.74	9.090	1.499	4.736	-1.852
95	H ₂ CF ₂	-107.71	-3.100	-4.793	-0.030	-3.580
96	HCF ₃	-166.60	-3.686	-5.181	2.203	-2.215
97	H ₂ CCl ₂	-22.83	6.302	0.732	4.709	0.029
98	HCCl ₃	-24.66	9.092	3.638	9.188	4.133
99	H ₃ C-NH ₂ (methylamine)	-5.50	-0.949	-2.138	-3.003	-4.377
100	CH ₃ -CN (methyl cyanide)	18.00	-4.748	-1.952	-0.197	-0.534
101	CH ₃ -NO ₂ (nitromethane)	-17.80	-18.239	-15.179	-1.896	-7.009
102	CH ₃ -O-N=O (methyl nitrite)	-15.90	-17.800	-12.136	-0.853	-3.927
103	CH ₃ -SiH ₃ (methylsilane)	-7.00	9.960	5.150	1.014	-0.879
104	HCOOH (formic acid)	-90.50	-7.108	-6.283	0.912	-2.571
105	HCOOCH ₃ (methyl formate)	-85.00	-4.985	-5.010	0.312	-3.341
106	CH ₃ CONH ₂ (acetamide)	-57.00	-4.322	-3.898	-1.388	-3.669
107	CH ₂ -NH-CH ₂ (aziridine)	30.20	0.878	-4.544	-0.698	-5.913
108	NCCN (cyanogen)	73.30	-18.046	-3.846	1.090	5.078
109	(CH ₃) ₂ NH (dimethylamine)	-4.40	3.286	-0.166	-1.793	-4.361
110	CH ₃ -CH ₂ -NH ₂ (<i>trans</i> -ethylamine)	-11.30	3.144	-0.749	-2.032	-4.954
111	H ₂ C=C=O (ketene)	-11.35	-9.252	-9.604	-2.347	-6.259
112	CH ₂ -O-CH ₂ (oxirane)	-12.57	0.826	-5.830	1.440	-5.655
113	CH ₃ CHO (acetaldehyde)	-39.70	-1.295	-4.446	0.315	-4.194
114	O=CH-CH=O (glyoxal)	-50.70	-8.906	-6.831	1.665	-1.829
115	CH ₃ CH ₂ OH (ethanol)	-56.21	5.709	0.286	1.900	-2.863
116	CH ₃ -O-CH ₃ (dimethyl ether)	-44.00	3.357	-0.889	0.055	-3.932
117	CH ₂ -S-CH ₂ (thiooxirane)	19.60	6.945	-2.798	3.375	-4.433
118	CH ₃ CH ₂ SO (dimethyl sulfoxide)	-36.20	7.424	0.899	6.554	-0.239
119	CH ₃ -CH ₂ -SH (ethanethiol)	-11.10	10.953	2.490	3.774	-1.961
120	CH ₃ -S-CH ₃ (dimethyl sulfide)	-8.90	9.492	0.895	2.791	-3.250
121	H ₂ C=CHF	-33.20	-3.192	-5.345	-1.453	-5.026
122	CH ₃ -CH ₂ -Cl (ethyl chloride)	-26.80	9.044	1.157	2.865	-2.633
123	H ₂ C=CHCl (vinyl chloride)	8.90	-0.514	-5.028	-1.475	-5.734
124	H ₂ C=CHCN (acrylonitrile)	43.20	-4.540	-0.303	2.438	2.214
125	CH ₃ -CO-CH ₃ (acetone)	-51.93	3.822	-1.980	2.057	-3.858
126	CH ₃ COOH (acetic acid)	-103.40	-1.816	-3.746	2.619	-2.279
127	CH ₃ COF (acetyl fluoride)	-105.70	-3.610	-5.865	1.624	-3.564
128	CH ₃ COCl (acetyl chloride)	-58.00	-1.191	-4.743	2.644	-3.036
129	CH ₃ CH ₂ CH ₂ Cl (propyl chloride)	-31.52	14.210	3.625	4.791	-2.208
130	(CH ₃) ₂ CH-OH (2-propanol)	-65.20	11.683	3.897	4.557	-1.391
131	C ₂ H ₅ -O-CH ₃ (methyl ethyl ether)	-51.70	8.119	1.204	1.606	-3.873
132	(CH ₃) ₃ N (trimethylamine)	-5.70	8.200	3.093	0.004	-3.232
133	C ₄ H ₄ O (furan)	-8.30	2.231	-2.921	4.310	-2.407
134	C ₄ H ₄ S (thiophene)	27.50	9.394	0.503	7.997	-0.180
135	C ₄ H ₄ NH (pyrrole)	25.90	1.392	-2.469	1.128	-3.595
136	C ₅ H ₅ N (pyridine)	33.60	-0.691	-1.915	0.639	-2.535
137	SH	34.18	-0.872	-1.658	-1.336	-2.013
138	CCH	135.10	0.579	0.578	3.548	1.855
139	C ₂ H ₃ (² A')	71.60	-2.499	-4.950	-3.197	-5.856
140	CH ₃ CO (² A')	-2.40	-6.119	-7.813	-2.015	-6.049

TABLE 5: Cont'd

no.	molecule	exptl	$\Delta E(\text{BLYP})$	$\Delta E(\text{OLYP})$	$\Delta E(\text{B3LYP})$	$\Delta E(\text{O3LYP})$
141	H ₂ COH (² A)	-4.08	-3.753	-4.926	-2.355	-4.897
142	CH ₃ O (² A')	4.10	-4.557	-5.303	-3.637	-5.461
143	CH ₃ CH ₂ O (² A'')	-3.70	3.596	0.147	1.314	-2.015
144	CH ₃ S (² A')	29.80	0.903	-2.735	-1.633	-4.424
145	C ₂ H ₅ (² A')	28.90	2.716	-3.415	-2.779	-7.032
146	(CH ₃) ₂ CH (² A')	21.50	6.631	-2.485	-1.707	-7.863
147	(CH ₃) ₃ C	12.30	12.541	0.684	1.174	-6.608
148	NO ₂	7.91	-27.612	-22.044	-4.472	-9.417
MAD			7.096	4.660	3.135	4.126

^a The 6-311+G(3df,2p) basis sets are used. The best DFT results are in boldface.

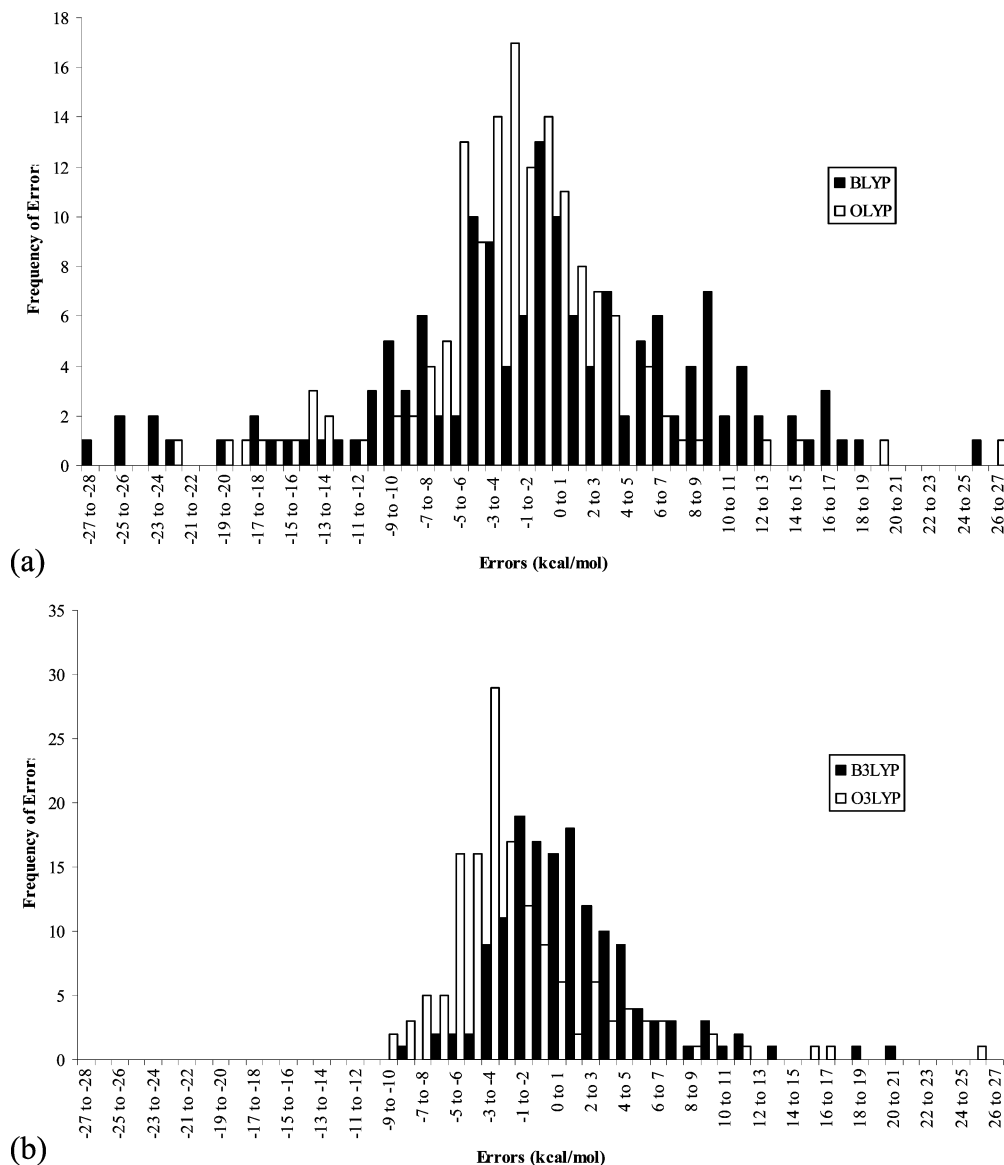


Figure 1. Histogram of (a) BLYP and OLYP. (b) B3LYP and O3LYP deviation for the heats of formation of the G2 testing set. Each vertical bar represents deviations in 1 kcal/mol range.

overestimated in OLYP as shown by the greater number of positive deviations with this functional. The MADs for these 8 systems are 1.380 (OLYP), and 1.128 kcal/mol (O3LYP). For comparison, one has MAD = 1.904 for BLYP and 1.369 for B3LYP. These error statistics are fairly impressive, although the sample space (8 data) might be too small to draw definitive conclusions.

D. Bonding Properties of Rare-Gas Dimers. Noble-gas dimers are the best test molecules to assess accuracy in describing van der Waals interactions.³⁰ Table 9 summarizes

the bonding properties of He₂, Ne₂, and Ar₂ calculated by different flavors of DFT functionals. Although the B88 exchange functional has been quite successful in describing covalently bonded systems, it fails completely in describing van der Waals interactions.^{31,32} Thus every DFT method using B88 as the exchange functional, pure or hybrid, gives unbounded noble-gas dimers. The binding energies (all negative) calculated with BLYP at the experimental distances are $\Delta E(\text{He-He}) = -0.084$, $\Delta E(\text{Ne-Ne}) = -0.139$, and $\Delta E(\text{Ar-Ar}) = -0.411$ kcal/mol. Including exact exchange reduces the repulsion, leading to

TABLE 6: Ionization Potentials (IP, in eV) at 0 K of the 42 Systems in the G2 Set^{9,11} and the Deviations (theory-exptl) Obtained from BLYP, OLYP, B3LYP, and O3LYP^a

no.	system	exptl	<i>E</i> (BLYP)	<i>E</i> (OLYP)	<i>E</i> (B3LYP)	<i>E</i> (O3LYP)
1	H → H ⁺	13.60	-0.06	-0.05	0.06	-0.01
2	He → He ⁺	24.59	0.20	0.17	0.34	0.26
3	Li → Li ⁺	5.39	0.13	0.16	0.23	0.19
4	Be → Be ⁺	9.32	-0.34	-0.29	-0.20	-0.24
5	B → B ⁺	8.30	0.32	0.19	0.44	0.26
6	C → C ⁺	11.26	0.15	0.12	0.29	0.20
7	N → N ⁺	14.54	-0.03	0.07	0.13	0.14
8	O → O ⁺	13.61	0.56	0.07	0.55	0.13
9	F → F ⁺	17.42	0.32	0.02	0.34	0.07
10	Ne → Ne ⁺	21.56	0.16	0.07	0.21	0.11
11	CH ₄ → CH ₄ ⁺	12.62	-0.25	-0.30	-0.06	-0.20
12	NH ₃ → NH ₃ ⁺	10.18	-0.06	-0.10	0.01	-0.07
13	OH → OH ⁺	13.01	0.18	-0.07	0.23	-0.01
14	H ₂ O → H ₂ O ⁺	12.62	-0.07	-0.12	0.00	-0.08
15	HF → HF ⁺	16.04	0.00	-0.05	0.06	-0.02
16	Na → Na ⁺	5.14	0.21	0.10	0.28	0.13
17	Mg → Mg ⁺	7.65	-0.02	-0.11	0.08	-0.06
18	Al → Al ⁺	5.98	-0.11	-0.07	0.04	0.00
19	Si → Si ⁺	8.15	-0.21	-0.12	-0.04	-0.05
20	P → P ⁺	10.49	-0.31	-0.15	-0.11	-0.07
21	S → S ⁺	10.36	0.05	-0.07	0.18	0.01
22	Cl → Cl ⁺	12.97	-0.06	-0.11	0.10	-0.03
23	Ar → Ar ⁺	15.76	-0.15	-0.08	0.04	0.00
24	SiH ₄ → SiH ₄ ⁺	11.00	-0.34	-0.44	-0.09	-0.30
25	PH → PH ⁺	10.15	-0.17	-0.04	0.02	0.03
26	PH ₂ → PH ₂ ⁺	9.82	-0.06	0.02	0.12	0.09
27	PH ₃ → PH ₃ ⁺	9.87	-0.15	-0.23	-0.03	-0.17
28	SH → SH ⁺	10.37	-0.05	-0.11	0.10	-0.03
29	H ₂ S → H ₂ S ⁺ (² B ₁)	10.47	-0.20	-0.19	-0.05	-0.12
30	H ₂ S → H ₂ S ⁺ (² A ₁)	12.78	-0.31	-0.31	-0.12	-0.22
31	HCl → HCl ⁺	12.75	-0.17	-0.14	0.00	-0.06
32	C ₂ H ₂ → C ₂ H ₂ ⁺	11.40	-0.27	-0.33	-0.16	-0.27
33	C ₂ H ₄ → C ₂ H ₄ ⁺	10.51	-0.23	0.91	-0.15	-0.24
34	CO → CO ⁺	14.01	-0.10	-0.27	0.13	-0.13
35	N ₂ → N ₂ ⁺ (² Σ _g ⁻)	15.58	-0.21	-0.32	0.28	-0.03
36	N ₂ → N ₂ ⁺ (² Π _u)	16.70	-0.25	-0.30	-0.06	-0.19
37	O ₂ → O ₂ ⁺	12.07	0.41	0.36	0.80	0.58
38	P ₂ → P ₂ ⁺	10.53	0.08	0.16	0.41	0.32
39	S ₂ → S ₂ ⁺	9.36	-0.08	0.04	0.23	0.18
40	Cl ₂ → Cl ₂ ⁺	11.50	-0.44	-0.43	-0.12	-0.26
41	ClF → ClF ⁺	12.66	-0.34	-0.39	-0.05	-0.23
42	CS → CS ⁺	11.33	-0.07	-0.13	0.10	-0.05
	MAD		0.187	0.185	0.168	0.139

^a IP is calculated as the total energy difference between a neutral system and the corresponding cation. The 6-311+G(3df,2p) basis sets are used. The best DFT results are in boldface.

binding energies for B3LYP (at the experimental distances) of $\Delta E(\text{He-He}) = -0.045$, $\Delta E(\text{Ne-Ne}) = -0.061$, and $\Delta E(\text{Ar-Ar}) = -0.237$ kcal/mol.

The London dispersion interaction responsible for the bonding in these systems arises from the interaction of fluctuating dipoles on each atom, which arises completely from electron correlation. For the noble gas dimers the proper exchange functional should lead to a repulsive interaction similar to Hartree-Fock.^{33,34} Replacing B88 with OPTX leads to overbinding in the noble gas dimers. Thus for He₂, OLYP yields $R = 2.887$ Å and $\Delta E = 0.079$ kcal/mol, which can be compared to the experimental data of $R(\text{He-He}) = 2.970$ Å, and $\Delta E(\text{He-He}) = 0.022$ kcal/mol,³⁰ overestimating $\Delta E(\text{He-He})$ by 259%. O3LYP gives satisfactory results for Ne₂, leading to $R(\text{Ne-Ne}) = 3.225$ Å, and $\Delta E(\text{Ne-Ne}) = 0.109$ kcal/mol, which can be compared to the experimental values of $R(\text{Ne-Ne}) = 3.091$ Å and $\Delta E(\text{Ne-Ne}) = 0.084$ kcal/mol.³⁰ Interactions in Ar₂ are underestimated by 82.5% and 88.8% with OLYP and O3LYP, respectively.

With conventional density functionals the long-range potential and hence the density are not correct,³⁵⁻⁴⁰ so that a correct description of long-range London dispersion interactions will

TABLE 7: Electron Affinities (EA, in eV) at 0 K of 25 Systems of G2 Set^{9,11} and the Deviations (theory-exptl) Obtained from BLYP, OLYP, B3LYP, and O3LYP^a

no.	system	exptl	<i>E</i> (BLYP)	<i>E</i> (OLYP)	<i>E</i> (B3LYP)	<i>E</i> (O3LYP)
1	C ← C ⁻	1.26	0.05	0.03	0.10	0.05
2	CH ← CH ⁻	1.24	0.08	0.05	0.12	0.07
3	³ CH ₂ ← CH ₂ ⁻	0.65	0.16	-0.04	0.13	-0.05
4	CH ₃ ← CH ₃ ⁻	0.08	-0.04	-0.15	-0.06	-0.16
5	NH ← NH ⁻	0.38	0.13	-0.14	0.07	-0.15
6	NH ₂ ← NH ₂ ⁻	0.74	0.00	-0.15	-0.04	-0.16
7	O ← O ⁻	1.46	0.24	-0.07	0.14	-0.09
8	OH ← OH ⁻	1.83	0.01	-0.16	-0.06	-0.18
9	F ← F ⁻	3.40	0.16	-0.02	0.06	-0.06
10	O ₂ ← O ₂ ⁻	0.44	0.06	-0.33	0.12	-0.25
11	NO ← NO ⁻	.02	0.25	0.10	0.32	0.16
12	CN ← CN ⁻	3.82	-0.01	-0.17	0.21	-0.04
13	Si ← Si ⁻	1.38	-0.19	-0.18	-0.06	-0.11
14	P ← P ⁻	0.75	0.12	-0.09	0.19	-0.04
15	S ← S ⁻	2.08	0.02	-0.11	0.11	-0.06
16	Cl ← Cl ⁻	3.62	-0.05	-0.12	0.06	-0.06
17	SiH ← SiH ⁻	1.28	-0.15	-0.14	-0.03	-0.08
18	¹ SiH ₂ ← SiH ₂ ⁻	1.12	-0.07	-0.07	0.05	-0.02
19	SiH ₃ ← SiH ₃ ⁻	1.44	-0.09	-0.23	-0.02	-0.18
20	PH ← PH ⁻	1.00	0.02	-0.15	0.10	-0.09
21	PH ₂ ← PH ₂ ⁻	1.26	-0.10	-0.20	0.00	-0.14
22	SH ← SH ⁻	2.31	-0.08	-0.15	0.02	-0.10
23	PO ← PO ⁻	1.09	-0.05	-0.09	0.07	-0.03
24	S ₂ ← S ₂ ⁻	1.66	-0.16	-0.25	0.01	-0.15
25	Cl ₂ ← Cl ₂ ⁻	2.39	0.37	0.12	0.45	0.20
	MAD		0.106	0.133	0.103	0.107

^a The EA is calculated as the total energy difference between the neutral and the corresponding anionic system. The 6-311+G(3df,2p) basis sets are used. The best DFT results are in boldface.

TABLE 8: Proton Affinities (PA, in kcal/mol) at 0 K for the 8 Systems in the G2 Set^{9,11} and the Deviations (theory-exptl) Obtained from BLYP, OLYP, B3LYP, and O3LYP^a

no.	system	exptl	<i>E</i> (BLYP)	<i>E</i> (OLYP)	<i>E</i> (B3LYP)	<i>E</i> (O3LYP)
1	H ₂ ← H ₃ ⁺	100.8	-3.10	-0.32	-2.80	-0.59
2	NH ₃ ← NH ₄ ⁺	202.5	-2.40	1.32	-0.66	1.74
3	H ₂ O ← H ₃ O ⁺	165.1	-3.87	-0.70	-2.33	-0.31
4	C ₂ H ₂ ← C ₂ H ₃ ⁺	152.3	0.55	3.42	1.28	3.25
5	SiH ₄ ← SiH ₅ ⁺	154.0	0.11	2.23	-0.62	1.45
6	PH ₃ ← PH ₄ ⁺	187.1	-2.97	-0.74	-1.15	-0.04
7	H ₂ S ← H ₃ S ⁺	168.8	-1.50	0.53	-1.11	0.44
8	HCl ← H ₂ Cl ⁺	133.6	-0.74	1.76	-0.99	1.21
	MAD		1.904	1.380	1.369	1.128

^a PA is calculated as the total energy difference between the neutral and the corresponding cationic system. The 6-311+G(3df,2p) basis sets are used. The best DFT results are in boldface.

likely require a fundamental improvement in the correlation functional.

E. Bonding Properties of Water Dimer. Water dimer is the prototypical hydrogen bonded system,⁴¹⁻⁴⁹ and it has been studied thoroughly with both experiment and theory. Unfortunately, it has been very difficult to obtain accurate experimental determinations of R_e and D_e , because of the large fluctuations in structure within the zero-point motions. Microwave spectroscopy leads directly to a vibrationally averaged O...O distance $R_0 = 2.976$ Å, and the data have been extrapolated to estimate that $R_e = 2.952$ Å.⁴⁵ The widely accepted experimental value of $D_e = 5.44 \pm 0.7$ kcal/mol⁴⁹ was based on measurements of the thermal conductivity of the water vapor and involved a number of assumptions.

The best ab initio calculations are quite complete. Thus coupled cluster single and double excitations with triple corrections (CCSD(T)(Full)) has been used with a sequence of basis sets so that the basis effects can be extrapolated to the complete basis. This leads to $R_e(\text{O...O}) = 2.912 \pm 0.005$ Å and $D_e = 5.02 \pm 0.10$ kcal/mol,⁴³ which we consider as exact.

TABLE 9: Bonding Properties of He₂, Ne₂, and Ar₂ Calculated by BLYP, OLYP, B3LYP, and O3LYP Using the aug-cc-pVTZ(-f) Basis Set^a

	$R(\text{He-He})$	$\Delta E(\text{He-He})$	$R(\text{Ne-Ne})$	$\Delta E(\text{Ne-Ne})$	$R(\text{Ar-Ar})$	$\Delta E(\text{Ar-Ar})$
BLYP ^b		-0.084		-0.139		-0.411
OLYP	2.887	+0.079	3.283	+0.123	4.836	+0.050
B3LYP ^b		-0.045		-0.061		-0.237
O3LYP	2.860	+0.072	3.225	+0.109	4.473	+0.032
exptl ^c	2.970	+0.022	3.091	+0.084	3.757	+0.285

^a The bond energies are corrected for BSSE effects.²⁵ bond lengths are in Å and bond energies are in kcal/mol. ^b The potential energy curves of BLYP and B3LYP are repulsive. The “bond energies” are calculated at the experimental distances. ^c Reference 30.

TABLE 10: Bonding Properties of Water Dimer^a

	D_e	$R_e(\text{O}\cdots\text{O})$	$\Delta R_d(\text{OH})^b$	$\Delta\nu_d(\text{OH})^c$
BLYP	4.18	2.952	0.008	-182
OLYP	2.76	3.175	0.004	-107
B3LYP	4.57	2.926	0.008	-173
O3LYP	3.20	3.095	0.005	-119
best <i>ab initio</i>	<i>5.02 ± 0.10^d</i>	<i>2.912 ± 0.005^d</i>	<i>0.007^e</i>	<i>-121^e</i>
exptl	5.44 ± 0.7 ^h	2.952 ^f		-170 ^g

^a Calculations are performed with BLYP, OLYP, B3LYP, and O3LYP with aug-cc-pVTZ(-f). The reference data are in italics. The best DFT result is in boldface. ^b The elongation of the O–H bond in the donor water. ^c The red shift of the donor O–H stretching mode experienced upon forming a hydrogen bridge. ^d Reference 43, CCSD(T)(FULL)/IO275 → ∞ (IO275: interaction optimized basis set with 275 basis functions for H₂O dimer. O: 7s5p5d3f2g1h. H_d: 2s4p1d. H: 2s3p. BF:3s3p2d1f). ^e Reference 44, MP4/VTZ(2df) on O and VTZ(2p) on H. ^f Reference 45. ^g References 46–48. ^h Reference 49. Experimental D_e was estimated by adding the zero-point energy calculated at HF/4-21G level.

Table 10 lists the calculated bonding properties of (H₂O)₂ by various DFT methods. It is well-known that BLYP and B3LYP do not do well in describing hydrogen bonds. Thus we see that BLYP leads to $R_e(\text{O}\cdots\text{O}) = 2.952$ Å (0.040 Å too high) with $D_e = 4.18$ kcal/mol (0.84 kcal/mol or 16.7% too low) whereas B3LYP gives $R_e(\text{O}\cdots\text{O}) = 2.926$ Å (0.014 Å too high) with $D_e = 4.57$ kcal/mol (0.45 kcal/mol or 9.0% too low).

Replacing B88 with OPTX degrades the performance of the functionals for hydrogen bonding. Thus OLYP gives $R_e(\text{O}\cdots\text{O}) = 3.175$ Å, which is 0.263 Å too long, whereas D_e is 2.76 kcal/mol (2.26 kcal/mol or 45.0% too small). This indicates that hydrogen bonding is significantly underestimated by OLYP. O3LYP performs slightly better but leads to a calculated $R_e(\text{O}\cdots\text{O}) = 3.095$ Å (0.183 Å too long) and $D_e = 3.20$ kcal/mol (1.82 kcal/mol or 36.3% too small), still underestimating hydrogen bonding.

The elongation of the donor O–H bond from the monomer to the dimer is also of interest. The best *ab initio* result, $\Delta R_d(\text{OH}) = 0.007$ Å, is based on MP4/VTZ(2df) on O and VTZ(2p) on H from Bleiber and Sauer.⁴⁴ OLYP and O3LYP lead to $\Delta R_d(\text{OH}) = 0.004$ and 0.005 Å, respectively, underestimating this quantity by 43% and 29%, respectively.

Another parameter of interest is the red shift, $\Delta\nu_d(\text{OH})$ in the donor O–H stretching mode upon forming a hydrogen bridge. Because the monomer has two OH modes (symmetric and the asymmetric) that are split significantly, we use the arithmetic mean of the symmetric and the asymmetric harmonic stretching modes of the free monomer in comparing to the donor O–H stretching mode of the dimer.⁴⁴ The experimental harmonic frequencies of the water monomer and dimer lead to $\Delta\nu_d(\text{OH}) = -170$ cm⁻¹.^{46–48} The best *ab initio* value obtained by Bleiber and Sauer at the MP4/VTZ(2df,2p) level is -121 cm⁻¹,⁴⁴ underestimating the frequency shift by 49 cm⁻¹ or 28.8%. OLYP and O3LYP underestimate $\Delta\nu_d(\text{OH})$ by 63 and 51 cm⁻¹ or 37.1 and 30.0%, respectively, whereas BLYP and

B3LYP lead to satisfactory results with shifts of 12 and 3 cm⁻¹ or 7.1 and 1.7%, respectively.

IV. Concluding Remarks

We report here a systematic assessment of the Handy–Cohen optimized exchange density functional (OPTX). We present the results of OLYP and O3LYP for predicting atomic data (exchange energies, correlation energies and total energies for atoms from H to Ar) and the heats of formation, ionization potentials, electron affinities, and proton affinities for the extended G2 set. We also tested OLYP and O3LYP for describing van der Waals interactions in noble gas dimers (He₂, Ne₂, and Ar₂) and for describing hydrogen bond interactions in water dimer. The results of OLYP and O3LYP are compared with those from the BLYP and B3LYP functionals.

As compared to BLYP, OLYP shows much improved quality in the predictions of the atomic data (exchange energies) and the heats of formation of molecular systems. Although OLYP is marginally better than BLYP in the predictions of ionization potentials, and proton affinities, OLYP is slightly worse than BLYP in the description of electron affinities. However, OLYP significantly outperforms BLYP in the description of the van der Waals interactions, but OLYP is inferior to BLYP in the prediction of hydrogen bonding.

As compared to OLYP, O3LYP leads to larger errors in the calculations of atomic exchange energies and atomic correlation energies. However, the errors in the exchange part partly cancel those in the correlation part, leading to a good description of the total atomic energies. The same is true for B3LYP, but B3LYP performs generally worse than O3LYP for atomic data. Though B3LYP is a significant improvement over BLYP in thermochemistry, the effect of including exact exchange is less significant on going from OLYP to O3LYP. Thus the MAD decreases in the order BLYP (7.10) > OLYP (4.66) > O3LYP (4.13) > B3LYP (3.14). On the basis of the histogram of error distributions, we conclude that O3LYP has more predictive power than B3LYP, but O3LYP has a tendency to overbind. O3LYP outperforms B3LYP in predicting ionization potentials and proton affinities; and O3LYP is competitive with B3LYP for predicting electron affinities. O3LYP significantly outperforms B3LYP in describing van der Waals interactions, but O3LYP is clearly worse at describing hydrogen bonding.

Our conclusion is that OLYP provides the best overall nonhybrid functional currently available. Although O3LYP does provide some attractive features, they do not in our mind improve upon B3LYP

Acknowledgment. This research was funded by DOE (ASCI), National Institutes of Health (HD 36385-02), National Natural Science Foundation of China (20021002), National Natural Science Foundation of Fujian (2002F010), the Ministry of Science and Technology of China (2001CB610506) and TRAPOYT from the Ministry of Education of China. The

facilities of the Materials and Process Simulation Center (MSC) used in these studies were funded by DURIP-ARO, DURIP-ONR, IBM (SUR), NSF (MRI), and the Beckman Institute. In addition, the MSC is funded by grants from DOE-FETL, ARO-MURI, ONR-MURI, NIH, ChevronTexaco, Aventis Pharma, General Motors, Seiko-Epson, Berlex Biopharma, and Asahi Kasei.

Supporting Information Available: Table of total energies of the G2 test set. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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