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The performance of the Becke–Lee–Yang–Parr (B–LYP) density functional theory with various basis sets

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The performance of a recently introduced hybrid of density functional theory and Hartree–Fock theory, the B–LYP/HF procedure, has been examined with a variety of basis sets. We have found that even the relatively small 6-31G* basis set yields atomization energies, ionization potentials and proton affinities whose mean absolute error, compared with a large body of accurate experimental data, is only 6.45 kcal/mol. We have also found that the addition of a "higher-level correction" (of the type used in G2 theory) to the B–LYP/HF total energies reduces the mean absolute error to 4.14 kcal/mol.

1. Introduction

The computation of total molecular energy is often handled by an initial study at the Hartree–Fock (single-configuration) level, followed by a treatment of the remaining (correlation) energy, using perturbation or configuration interaction techniques with Hartree–Fock as a starting point. However, a major impediment to progress is that, although determination of the Hartree–Fock (HF) energy is quite efficient, the correlation techniques are complex and involve computational costs which escalate rapidly with the size of the system. If N is the size of the basis used for orbital expansion, the HF cost is formally $\mathcal{O}(N^4)$ but this can be reduced to a lower order by neglect of small integrals. The cost of the subsequent correlation calculation, on the other hand, is $\mathcal{O}(N^7)$ for fourth-order perturbation theory, MP4 [1], or for related coupled-cluster-type methods, such as QCISD(T) [2] or CCSD(T) [3]. Since the correlation energy is numerically much smaller than the HF energy, this situation is somewhat unbalanced and there is a need for techniques which can give a satisfactory description of the total energy, including correlation, at lower cost.

Density functional theory [4] shows promise in providing reasonable estimates of correlation energy [5]. In this type of theory, general functionals of the electron density are used for this purpose. They may be applied directly to a HF density already derived by conventional methods or they may be used to determine the density in a self-consistent manner by solution of the Kohn–Sham equations [6]. Over the last few years, a number of groups have published studies [7,8] of correlation functionals using the HF density and, in a very recent study [9], we have proposed such a correlation functional (B–LYP) based on a combination of previous proposals for exchange by Becke [10] and for correlation by Lee, Yang and Parr [11] as transformed by Miehlich et al. [8]. Using a big orbital basis, we were able to show that a

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large experimental dataset of atomization energies, ionization energies, electron affinities and proton affinities could be reproduced by this B-LYP/HF procedure with an overall mean absolute error of only 3.86 kcal/mol.

In the present paper, we explore the performance of B-LYP/HF models using smaller basis sets. Since the cost of computing the B-LYP correlation energy is less than that of the underlying HF procedure, such a model might lead to an energy theory, with documented correlation performance, that could be extended to much larger molecules. Our initial purpose here is not to report calculations for large molecules but, rather, to lay the groundwork by testing several basis sets against the full experimental dataset used in validating G2 theory.

2. Method

The computational procedure is straightforward. Equilibrium structures are found at the MP2/6-31G(d) level and harmonic frequencies at HF/6-31G(d). The latter are scaled by an empirical factor [12] of 0.8929 and used to compute zero-point vibrational energies E_{ZPV} where appropriate. The structures are then used for single-point computations with a variety of basis sets. The unrestricted HF equations are solved to give the α and β components of the HF electron density $\rho_{\mathrm{HF}}=\rho_\alpha+\rho_\beta$ and corresponding energy

$$E_{\mathrm{HF}}=E_T+E_V+E_J+E_K\,, \tag{1}$$

where E_T is the kinetic energy, E_V is the potential energy involving nuclei and E_J and E_K are the Coulomb and exchange parts of the electron–electron repulsion energy. In the present procedure, the exchange energy E_K is replaced by an exchange-correlation functional $E_{\mathrm{XC}}^{\mathrm{B-LYP}}[\rho_{\mathrm{HF}}]$ to give a total energy

$$E_0^{\mathrm{B-LYP}}=E_{\mathrm{HF}}-E_K+E_{\mathrm{XC}}^{\mathrm{B-LYP}}+E_{\mathrm{ZPV}}\,.$$

The functional $E_{\mathrm{XC}}^{\mathrm{B-LYP}}$ is written as a sum of parallel-spin (αα+ββ) and antiparallel-spin (αβ) parts,

$$E_{\mathrm{XC}}^{\mathrm{B-LYP}}=E_{\mathrm{P}}[\rho_\alpha]+E_{\mathrm{P}}[\rho_\beta]+E_{\mathrm{A}}[\rho_\alpha,\rho_\beta]\,. \tag{3}$$

In (3), E_{P} is the well-known Becke exchange formula [9],

$$E_{\mathrm{P}}[\rho]=-\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\int\rho^{4/3}\,\mathrm{d}r-\int\rho^{4/3}\frac{bx^2}{1+6bx\sinh^{-1}x}\,\mathrm{d}r\,, \tag{4}$$

$$x=\rho^{-4/3}|\nabla\rho|\,, \tag{5}$$

with $b=0.0042$ to fit exchange energies of inert gas atoms. The antiparallel part $E_{\mathrm{A}}[\rho_\alpha,\rho_\beta]$ is the Lee, Yang and Parr correlation functional [11], as transformed by Miehlich, Savin, Stoll and Preuss [8].

Three basis sets are used for orbital expansion. The largest is 6-311+G(2df, p) [#1]. This starts with the standard 6-311G set, adds diffuse functions (+) and also two sets of d functions and one set of f functions to heavy (i.e. $Z\geqslant3$) atoms. In addition, one set of p functions is added to hydrogen and helium. This basis (which, for brevity, we will henceforth designate B1) is not quite as large as the one (6-311+G(3df, 2p) (footnote 1), henceforth designated B0) used in our previous paper [9] but it does reduce the cost of the computations by a factor of about two. The objective here is to test whether the highest polarization functions have a significant effect on the $E_0^{\mathrm{B-LYP}}$ energies. The other two basis sets are 6-31+G(d) and 6-31G(d). These are much smaller and might be useful for studies on larger molecules. The 6-31+G(d) basis (which we will designate B2) has diffuse functions as well as d-polarization functions on heavy atoms; it should have some value as a general-purpose basis. In 6-31G(d) (which we will designate B3), the diffuse functions are eliminated, leading to only 15 functions per heavy atom and two per non-heavy atom. This is likely to perform poorly for anions, but is worth testing elsewhere.

In our previous paper [9], we gave details of a scheme, closely related to that of Becke [15], for the numerical integration of the Becke and Lee, Yang and Parr functionals. Since then, we have discovered deficiencies in the procedure described and have improved upon it. Specifically, we now perform the angular integrations using the 194-point formula of Lebedev [16] and, for the radial integrations, we use

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[#1] Hitherto, the 6-311+G(df, p) basis set has not been defined for Ne and Ar. We have defined the diffuse function exponents for Ne and Ar to be 0.13 and 0.06, respectively, and the f function exponent for Ar to be 0.85.

the 50-point Euler–Maclaurin scheme described recently by Murray, Handy and Laming [17,18]. Our working formula for the radial integration is

$$\int_0^\infty r^2F(r)\,dr \approx \sum_{i=1}^{n-1} w_iF(r_i)\,, \qquad (6)$$

where

$$w_i = 2R^3ni^5(n-i)^{-7}\,, \qquad (7)$$

$$r_i = Ri^2(n-i)^{-2}\,, \qquad (8)$$

and R is the "atomic radius" as defined in ref. [9].

Finally, we propose that the abbreviation F1/F2/B be used to denote the energy obtained by evaluating the functional F1 using the density obtained by solving the self-consistent field equations appropriate for the functional F2 with the basis set B. The level of theory used in our earlier study is then B-LYP/HF/B0 and the levels used in the present work are (in order of decreasing sophistication) B-LYP/HF/B1, B-LYP/HF/B2 and B-LYP/HF/B3. We also suggest that the abbreviation F1/B be understood to be equivalent to F1/F1/B.

3. Results and discussion

We have computed the B-LYP/HF/B1, B-LYP/HF/B2 and B-LYP/HF/B3 energies of the 152 atoms, molecules and ions needed for comparison with the experimental G2 data set (which we have extended here to include H_2, H_3^+, He, He^+, Ne, Ne^+, Ar and Ar^+) using a modified version of the GAUSSIAN 92 suite of programs [19].

In table 1, we list the total energies of the atoms with $Z \leqslant 18$ and compare these, where possible, with the "exact" total energies obtained by Davidson and co-workers in a recent, and very thorough, study [20]. We have previously found that the B-LYP/HF/B0 level of theory [9] yields total atomic energies which agree to within 10 mhartree, for the atoms with $Z \leqslant 10$, with the exact results and it is apparent from table 1 that this accuracy is also achieved using the B1 basis. We see, however, that the B2 and B3 levels are significantly less successful in reproducing the exact energies: the worst case is the neon atom (40 and 61 mhartree errors, respectively) whose 6-31G basis is much poorer than the corresponding 6-311G basis.

In table 2, we present the total atomization energies which follow from the data in table 1. As was found for the total atomic energies, there is little dif-

Table 1
B-LYP/HF total energies (hartree) for neutral atoms

Atom	Exact	B1	B2	B3
H	−0.500000	−0.4970	−0.4954	−0.4954
He	−2.903724	−2.9031	−2.8978	−2.8978
Li	−7.47806	−7.4795	−7.4794	−7.4792
Be	−14.66736	−14.6575	−14.6569	−14.6545
B	−24.65393	−24.6467	−24.6444	−24.6388
C	−37.8450	−37.8398	−37.8344	−37.8293
N	−54.5893	−54.5809	−54.5692	−54.5665
O	−75.067	−75.0722	−75.0506	−75.0441
F	−99.734	−99.7434	−99.7143	−99.6994
Ne	−128.939	−128.9414	−128.8999	−128.8783
Na	–	−162.2654	−162.2638	−162.2638
Mg	–	−200.0719	−200.0614	−200.0613
Al	–	−242.3631	−242.3495	−242.3489
Si	–	−289.3690	−289.3518	−289.3508
P	–	−341.2556	−341.2367	−341.2357
S	–	−398.1060	−398.0831	−398.0815
Cl	–	−460.1404	−460.1137	−460.1118
Ar	–	−527.5263	−527.4945	−527.4920

Table 2
B-LYP/HF total atomization energies $\sum D_0$ (kcal/mol)

Molecule	Expt.	B1	B2	B3	Molecule	Expt.	B1	B2	B3
H_2	103.3	103.1	103.3	103.3	HCN	301.8	303.5	298.6	299.4
LiH	56.0	55.2	53.8	53.8	CO	256.2	252.8	248.3	250.5
BeH	46.9	53.0	52.7	52.9	HCO	270.3	270.7	267.3	269.1
CH	79.9	80.0	79.0	78.3	H_2CO	357.2	354.3	352.2	354.2
CH_2 ($^3B_1$)	179.6	177.0	176.1	176.3	H_3COH	480.8	473.1	469.4	470.1
CH_2 ($^1A_1$)	170.6	167.5	165.2	164.2	N_2	225.1	229.2	224.2	224.0
CH_3	289.2	287.1	286.3	286.9	H_2NNH_2	405.4	406.9	400.3	396.0
CH_4	392.5	387.0	387.3	389.3	NO	150.1	154.7	150.7	152.1
NH	79.0	82.3	80.5	79.4	O_2	118.0	124.1	122.6	126.9
NH_2	170.0	174.3	170.3	168.1	HOOH	252.3	252.2	245.8	245.2
NH_3	276.7	277.1	272.0	268.0	F_2	36.9	41.5	40.4	47.7
OH	101.3	102.5	99.2	97.1	CO_2	381.9	379.5	371.5	376.9
OH_2	219.3	216.5	210.0	205.4	Na_2	16.6	16.2	16.3	16.3
FH	135.2	133.5	128.7	123.3	Si_2	74.0	68.3	66.3	66.7
SiH_2 ($^1A_1$)	144.4	142.0	140.5	139.9	P_2	116.1	113.8	108.7	108.8
SiH_2 ($^3B_1$)	123.4	119.0	118.4	118.1	S_2	100.7	100.3	94.9	96.0
SiH_3	214.0	207.2	206.3	205.8	Cl_2	57.2	54.0	47.7	48.9
SiH_4	302.8	294.4	293.2	292.6	NaCl	97.5	91.0	88.9	87.3
PH_2	144.7	144.9	142.6	142.3	SiO	190.5	185.3	179.6	178.6
PH_3	227.4	222.7	220.0	219.6	SC	169.5	164.2	160.1	160.5
SH_2	173.2	168.7	164.5	164.5	SO	123.5	123.4	117.0	117.5
ClH	102.2	99.5	95.6	95.5	ClO	63.3	58.5	53.4	54.6
Li_2	24.0	19.6	19.3	19.2	ClF	60.3	59.9	56.5	57.8
LiF	137.6	135.1	131.8	129.3	Si_2H_6	500.1	481.6	480.2	480.0
HCCH	388.9	383.1	376.3	377.6	CH_3Cl	371.0	362.7	361.5	364.4
H_2CCH_2	531.9	524.0	521.0	523.7	CH_3SH	445.1	433.9	430.9	433.6
H_3CCH_3	666.3	653.4	653.7	658.4	HOCl	156.3	154.4	147.7	147.9
CN	176.6	162.7	156.6	157.6	SO_2	254.0	241.3	222.2	223.6

ference between the B0 and B1 atomization energies. As we proceed to the cheaper B2 and B3 bases, the atomization energies of most of the species considered decrease by 1-6 kcal/mol. However, in systems for which polarization functions are particularly important, the loss of binding is more severe: the B1 and B2 atomization energies of SO_2, for example, differ by nearly 20 kcal/mol.

In table 3, we compare B-LYP/HF ionization potentials. The data obtained using the B0, B1 and B2 basis sets are very similar but B3 generally yields ionizations potentials which are somewhat smaller. This reflects the fact that neutral systems usually benefit more from the presence of diffuse functions in the basis set than do their ionized counterparts.

In table 4, we compare B-LYP/HF electron affinities. Once again, the B0 and B1 basis sets yield very similar results and the affinities computed using the B2 basis are in fairly satisfactory agreement with these. In contrast, it is well known that ab initio calculations on anions are of little value if diffuse functions are not present in the basis set and the electron affinities computed using the B3 basis are hopelessly inadequate.

Table 5 reveals that even the small basis sets in our study are capable of yielding proton affinities in good agreement with experimental data. As we indicated in our earlier paper [9], the computation of proton affinities is the least demanding of the four tasks we have considered here because, in many cases, the electronic structures of A and AH^+ are substantially similar.

In table 6, we summarize the performance of B-LYP/HF theory as a function of basis set. For comparison purposes, we have included the results obtained in our earlier study using the large B0 basis set. It appears that the use of the B1 basis in place of the B0 basis has only a small effect on the com-

Table 3
B–LYP/HF ionization potentials (eV)

Molecule	Expt.	B1	B2	B3	Molecule	Expt.	B1	B2	B3
H	13.60	13.52	13.48	13.48	OH_2	12.62	12.49	12.41	12.04
He	24.59	24.77	24.71	24.71	FH	16.04	15.99	15.92	15.29
Li	5.39	5.51	5.52	5.51	SiH_4	11.00	10.69	10.81	10.77
Be	9.32	8.97	8.97	8.91	PH	10.15	9.96	9.99	9.96
B	8.30	8.56	8.54	8.39	PH_2	9.82	9.73	9.77	9.73
C	11.26	11.36	11.36	11.22	PH_3	9.87	9.72	9.70	9.65
N	14.54	14.48	14.54	14.48	SH	10.37	10.31	10.29	10.25
O	13.61	14.07	14.07	13.90	SH_2 ($^2B_1$)	10.47	10.27	10.25	10.21
F	17.42	17.65	17.67	17.25	SH_2 ($^1A_1$)	12.78	12.48	12.48	12.44
Ne	21.56	21.65	21.71	21.13	ClH	12.75	12.59	12.58	12.53
Na	5.14	5.31	5.31	5.31	HCCH	11.40	11.11	10.99	10.78
Mg	7.65	7.60	7.61	7.61	H_2CCH_2	10.51	10.25	10.13	9.96
Al	5.98	5.81	5.85	5.84	CO	14.01	14.29	14.37	14.17
Si	8.15	7.93	7.94	7.92	N_2 ($^2\Sigma_g$)	15.58	15.55	15.51	15.39
P	10.49	10.20	10.22	10.19	N_2 ($^2\Pi_u$)	16.70	16.44	16.38	16.26
S	10.36	10.32	10.31	10.28	O_2	12.07	12.42	12.48	12.34
Cl	12.97	12.89	12.89	12.84	P_2	10.53	10.15	10.22	10.18
Ar	15.76	15.64	15.67	15.60	S_2	9.36	9.29	9.39	9.36
CH_4	12.62	12.36	12.48	12.42	Cl_2	11.50	11.16	11.26	11.22
NH_3	10.18	10.06	9.96	9.71	ClF	12.66	12.65	12.79	12.52
OH	13.01	13.13	13.08	12.80	SC	11.33	12.04	12.19	12.03

Table 4
B–LYP/HF electron affinities (eV)

Molecule	Expt.	B1	B2	B3	Molecule	Expt.	B1	B2	B3
C	1.26	1.21	1.20	−0.26	Si	1.385	1.16	1.16	+0.75
CH	1.24	1.20	1.18	−0.12	SiH	1.277	1.07	1.08	+0.69
CH_2	0.65	0.72	0.63	−0.64	SiH_2	1.124	1.00	1.01	+0.66
CH_3	0.08	−0.06	−0.16	−1.44	SiH_3	1.44	1.33	1.31	+1.00
CN	3.82	4.58	4.65	+3.64	P	0.746	0.77	0.76	+0.09
NH	0.38	0.39	0.33	−1.29	PH	1.00	0.99	0.96	+0.33
NH_2	0.74	0.64	0.56	−0.98	PH_2	1.26	1.15	1.12	+0.53
NO	0.02	0.05	0.17	−0.88	PO	1.09	1.05	1.08	+0.35
O	1.46	1.56	1.56	−0.37	S	2.077	2.05	2.05	+1.46
OH	1.83	1.72	1.68	−0.21	SH	2.314	2.21	2.20	+1.63
O_2	0.44	0.46	0.50	−0.66	S_2	1.663	1.53	1.60	+1.25
F	3.40	3.42	3.46	+0.87	Cl	3.615	3.56	3.56	+2.97
					Cl_2	2.39	2.84	3.10	+2.69

puted results: the mean absolute deviations of the B0 and B1 values from 131 experimental data are 3.86 and 3.97 kcal/mol, respectively. The computational cost of these B-LYP/HF calculations is reduced by a factor of about five if the B2, rather than the B1, basis set is used but it appears from table 6 that relatively little predictive accuracy is sacrificed by this substitution: the overall mean absolute deviation for the B2 basis set is 5.45 kcal/mol. However, if diffuse functions are removed from the B2 basis, leading thereby to the B3 basis, the overall mean absolute deviation rises to 9.66 kcal/mol. Nonetheless, closer examination of table 6 reveals that most of this performance degradation can be traced to the extremely poor electron affinity results obtained using B3. If these are excluded, the mean absolute deviation of

Table 5
B-LYP/HF proton affinities (kcal/mol)

Molecule	Expt.	B1	B2	B3
H_2	100.8	97.3	90.1	90.1
HCCH	152.3	152.5	151.8	156.7
NH_3	202.5	200.8	202.2	207.7
H_2O	165.1	162.1	160.7	168.1
SiH_4	154	153.6	149.7	150.5
PH_3	187.1	183.2	182.6	183.7
H_2S	168.8	166.0	164.9	165.9
HCl	133.6	131.2	127.6	128.8

Table 6
Mean absolute deviations (kcal/mol) of B-LYP/HF results (excluding higher-level correction) from experiment

	B0	B1	B2	B3
atomization energies	3.94	4.32	7.03	7.14
ionization potentials	4.49	4.50	4.71	5.86
electron affinities	3.16	2.83	3.50	23.28
proton affinities	2.11	2.24	4.33	4.74
overall	3.86	3.97	5.45	9.66

Table 7
Mean absolute deviations (kcal/mol) of B-LYP/HF results (including higher-level correction) compared to experiment

	B0	B1	B2	B3
h_α (mhartree)	−3.0	−3.0	−4.6	−4.6
h_β (mhartree)	−4.8	−5.4	−9.1	−8.9
atomization energies	3.33	3.34	3.90	4.00
ionization potentials	3.96	4.05	4.89	4.22
electron affinities	2.83	3.39	5.17	18.91
proton affinities	2.11	2.24	4.33	4.74
overall	3.36	3.51	4.49	6.96

B3 from experiment falls to 6.45 kcal/mol, which is only slightly inferior to B2.

In the G2 procedure for estimating molecular energies [13,14], the final step is the addition of a "higher-level correction" (HLC) to the total energy

$$\Delta E(\mathrm{HLC}) = h_\alpha n_\alpha + h_\beta n_\beta \,, \qquad (9)$$

where n_α and n_β are the numbers of α and β valence electrons, respectively, h_α is chosen so that the total energy of the hydrogen atom is reproduced exactly and h_β is chosen to minimize the mean absolute deviation from experiment of the 55 atomization energies considered in ref. [14]. In the same way, we have computed values of h_α and h_β for each of the B-LYP/HF models which we have considered and have examined the effect of the correction (9) on the performances of the models. The resulting statistics are collected in table 7 and reveal, by comparison with table 6, that there are systematic errors for which the HLC can partly compensate, particularly for the B-LYP/HF models using small basis sets. In particular, the overall mean absolute deviation for the B3 basis falls from 9.66 to 6.96 kcal/mol when the HLC is included and if, as before, the electron affinities are excluded from consideration, this falls even further to 4.14 kcal/mol.

4. Conclusions

The B-LYP/HF theoretical model chemistry is in reasonable agreement with a wide range of experimental results, even when it is used in conjunction with modest basis sets. In particular, when augmented with a simple "higher-level correction", the mean absolute deviation of B-LYP/HF/6-31G(d) predictions from a set of 106 experimentally well-established atomization energies, ionization potentials and proton affinities is only 4.18 kcal/mol. Similar accuracy is achieved at the B-LYP/HF/6-31+G(d) level, even when electron affinities are included in the comparison. Although such deviations are only about three times greater than the corresponding mean absolute deviation of G2 theory, the relative computational inexpense of B-LYP/HF/6-31G(d) and B-LYP/HF/6-31+G(d) permits them to be applied to much larger chemical systems than is possible for G2 theory.

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