Empirical density functionals

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Abstract

Using a set of accurate experimental data for calibration, we have constructed an empirical exchange-correlation density functional, EDF1. When applied self-consistently with the $6\text{-}31 + G^*$ basis set, EDF1 yields results in significantly better agreement with the experimental data than either the B-LYP or B3-LYP functional. © 1998 Elsevier Science B.V.

1. Introduction

In spite of our incomplete knowledge of the properties of the true exchange-correlation (XC) functional, density functional theory (DFT) [1] has become a very popular computational tool. Approximate XC functionals are often tested by systematic comparison of computed total energies with high-quality experimental data. The large G2 set of atomization energies, ionization potentials, electron affinities and proton affinities [2] has been so used in several such studies [3–6]. These tests showed significantly improved agreement with experiment as functionals dependent only on local densities were replaced by those which also involve local density gradients. In recent years, DFT exchange functionals have been mixed with Fock exchange to yield what are often referred to as hybrid methods [7]. With some adjustment of parameters, mean absolute deviations between theory and experiment have begun to approach levels achieved by conventional ab initio methods, such as the G2 model itself [2].

In this Letter, we present a study of some simple XC functionals with three main objectives. In the first place, we increase the emphasis on empirical parameterization. Most previous studies have precisely satisfied certain limiting conditions, such as correct behaviour for the uniform free-electron gas and scaling at large distances, parameterization then being used to specify intermediate ranges. By releasing constraints and modestly increasing parameterization, it may be possible not only to obtain functionals of high practical value but also to get some indication of functional changes that are implied by the experimental data and so may point towards understanding further improvements.

Up to this point, it has been implicitly assumed that a functional that is optimal for a large orbital basis set will be equally suitable for smaller bases. This is probably not correct; the best functional with a small orbital basis may differ from the ultimate functional associated with an infinitely flexible basis. A second objective, therefore, is to search for an XC functional that is optimized for a relatively small basis set. Such a functional would obviously have practical value and, additionally, parameterization within a small basis may absorb some deficiencies of the basis itself.

The third objective is to evaluate the necessity of including Fock exchange in order to obtain good agreement with experiment. It has been alleged ''that a small exact-exchange component is a natural and necessary constituent of any exchange-correlation approximation aiming for accurate molecular energetics'' [8]. However, doing so introduces non-local effects and consequent computational complications [9,10]; it ought not to be incorporated unless it is really needed.

2. Methods

The orbital basis used is $6\text{-}31 + G^*$. This is a simple basis which accommodates the main types of distortions that occur for atoms in molecules. The 31 valence-shell split allows for atomic anisotropy in molecular environments, the $(+)$ diffuse functions are included so that anions can be treated and the $(^*)$ polarization functions permit 'sideways' electronic displacements. The basis is quite small (2 functions for H–He, 19 for Li–Ne and 23 for Na–Ar) and should be usable for quite large organic molecules. Equilibrium geometries are at the $MP2/6\text{-}31G^*$ level as in the original G2 work and zero-point vibrational energies are also calculated for Hartree–Fock harmonic frequencies in the same way. DFT calculations were performed by one of us (RDA) using the Q-Chem program [11].

The experimental database used for comparison is close to that used in the original G2 study [2]. It consists of 56 atomization energies, 40 ionization potentials, 25 electron affinities and 8 proton affinities. Two entries (for N_2^+ and SH_2^+) have been eliminated because they are excited states. Also some properties of H_2 and inert gas atoms have been added. (Note that, because there are no diffuse basis functions on H atoms in the $6\text{-}31 + G^*$ basis, the electron affinity of the hydrogen atom has been excluded.)

The quality of various functionals is judged by the root-mean-square (RMS) deviation of the theoretical from the experimental values for these 129 data points. The theoretical values are derived from full self-consistent Kohn–Sham calculations on 150 separate atoms and molecules. The RMS deviation is minimized with respect to parameters included in the

functionals. Among other variational schemes, we will consider linear combinations of different functionals or linear combinations of the same functionals with different parameters. Such linear optimization can be carried out in two ways. In the first, which may be termed 'internal' optimization, the full XC functional is written as a linear combination of component functionals

$$E_{XC} = \int \sum_i c_i f_i (\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta)\mathrm{d}r \qquad (1)$$

with adjustable coefficients c_i. This single functional is then used to carry out a set of 150 self-consistent Kohn–Sham calculations of total energies, leading to an RMS value for the deviation from experiment, which may then be minimized with respect to the c_i. If Hartree–Fock exchange is to be included, this can be done by adding another term to the sum in Eq. (1), with an additional c-coefficient. This is the conventional mixing method, introduced by Becke [7].

The second method used, termed 'external' optimization, carries out individual Kohn–Sham self-consistent calculations for *each* of the component XC functionals

$$E_{XC}^{(i)} = \int f_i (\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta)\mathrm{d}r \qquad (2)$$

applied to *each* member of the set of 150 molecules. Thus, if there are N individual functions f_i in Eq. (1), external optimization requires $150N$ such calculations. These energies may then be arranged as N vectors $E^{(i)}$ and then combined, using coefficients c_i, to give a single set of 150 energies in a vector

$$E(c) = \sum_i^N c_i E^{(i)}. \qquad (3)$$

Such a mixture describes a 'linear combination of model chemistries' defined by the coefficients c_i. Again its overall RMS deviation may be minimized with respect to c_i, by comparing predictions with the experimental database.

Clearly, the first type of model is ultimately preferable, since application to a new molecule will only require a single Kohn–Sham calculation, whereas the second model would require N such calculations. However, optimization by the second method only involves elementary quadratic mini-

mization and, as we will see, can help significantly in determining which combinations of functionals are worthwhile candidates for internal optimization.

The functionals used are based on the work of Becke [12] and of Lee, Yang and Parr (LYP) [13,14]. Most exchange functionals can be written in the form

$$E_X = E_X[\rho_\alpha] + E_X[\rho_\beta],$$

$$E_X[\rho_\sigma] = \int \rho_\sigma^{4/3}(r)\, g(x_\sigma)\mathrm{d}r, \tag{4}$$

where $g(x_\sigma)$ is a function of the dimensionless reduced density gradient

$$x_\sigma(r) = \frac{|\nabla \rho_\sigma(r)|}{\rho_\sigma^{4/3}(r)}. \tag{5}$$

The popular functional (B88) of Becke uses

$$g_{B88}(x_\sigma) = g(0) + \Delta B(\beta, x_\sigma), \tag{6}$$

where $g(0)$ has the free-electron value $C_0 = -3/2(3/4\pi)^{1/3}$ and $\Delta B(\beta, x_\sigma)$ is a correction function.

$$\Delta B(\beta, x_\sigma) = -\frac{\beta x_\sigma^2}{1 + 6\beta x_\sigma \sinh^{-1} x_\sigma} \tag{7}$$

Becke chose $\beta = 0.0042$ to fit the known Fock exchange energies of inert gas atoms.

The LYP functional [13] treats $\alpha\beta$-correlation using a form fitted to the wavefunction for the helium atom. We need not give the full analytical form other than to note that there are four parameters a, b, c, d with original values (0.04918, 0.132, 0.2533, 0.349). When added to B88 exchange, this leads to the full XC-functional B-LYP, which was introduced in 1992 [4] and is known to perform quite well in studies of this sort [4–6].

3. Results

Initial studies using internal mixing were carried out with parameter modifications within the B-LYP functional itself. The results are listed in Table 1. First the unmodified form gives an RMS deviation of 5.290 kcal/mol. The corresponding mean absolute deviation is 4.11. Next, the Becke parameter β was

Table 1
Modified B-LYP RMS deviations (kcal/mol)

Functional	RMS deviation
B(0.0042)-LYP	5.290
B(0.0035)-LYP	5.069
B(0.0042)+1.0431LYP	4.963
B-LYP (optimum)	4.848

optimized and it was found that a smaller value of 0.0035 gave improved agreement with experiment (5.069 kcal/mol). Third, an optimum linear combination of the original Becke and LYP parts lowers the RMS deviation further to 4.963. Finally, a fuller optimization lowers this further to 4.848 kcal/mol. (This has $g(0) = 1.0072 C_0$, a β-value in Eq. (7) of 0.003705 and LYP parameters of $\{a, b, c, d\} = \{0.049, 0.108, 0.24, 0.342\}$.) Such improvements are relatively modest.

The next step was to allow external linear mixing, including B-LYP functionals with different β-values. This led to a sharp lowering of the RMS error. Thus, if B(0.0035)-LYP and B(0.0042)-LYP are mixed with S-null and B(0.0042)-null), giving flexibility to the combined calculation, the RMS deviation falls to 4.543 kcal/mol. Clearly, the linear combination of the two Becke functions is a better exchange functional than either separately. The optimal external combination, which contains large and opposite coefficients for B(0.0035)-LYP and B(0.0042)-LYP, is

$$9.588\,B(0.0035)\text{-LYP} - 7.727\,B(0.0042)\text{-LYP}$$

$$- 0.861\,S\text{-null} + 0.743\,B(0.0042)\text{-null} \tag{8}$$

The combination (8) was next refined as an internal linear combination and, finally, the LYP parameters were redetermined. The complete XC functional is then

$$E_{XC} = \sum_{\sigma = \alpha, \beta} \int \{1.030952 C_0$$

$$+ 10.4017 \Delta B(0.0035, x_\sigma)$$

$$- 8.44793 \Delta B(0.0042, x_\sigma)\} \rho_\sigma^{4/3} \mathrm{d}r$$

$$+ \text{LYP}(0.055, 0.158, 0.25, 0.3505). \tag{9}$$

The RMS deviation is now lowered to 4.237 kcal/mol and the mean absolute deviation to 3.215

Table 2
External linear mixing of Hartree–Fock (kcal/mol)

Functional combination	RMS deviation
B-LYP + B(0.0042)-null + S-null	4.920
B-LYP + B(0.0042)-null + S-null + HF	4.499
EDF1 + B(0.0042)-null + B(0.0035)-null + S-null + LYP	4.211
EDF1 + B(0.0042)-null + B(0.0035)-null + S-null + LYP + HF	4.211

kcal/mol. We term the non-LYP part of Eq. (9) the double-Becke functional. We term the complete functional 'Empirical Density Functional 1' or EDF1.

The third stage of this investigation is admixture of Fock exchange. Table 2 gives the results of external mixing of Hartree–Fock with B-LYP and EDF1 plus their components. Clearly, there is strong HF mixing with B-LYP but virtually none with EDF1. This is confirmed by attempts to mix Fock exchange internally with EDF1. The mixing coefficient is less than 0.001 and there is no significant energy lowering.

Tables 3 and 4 contain the results of applying the B-LYP and EDF1 functionals, using the $6-31 + G^*$ basis set, to obtain the thermochemistry of the molecules in the G2 set. In addition, we have included results from the widely used B3LYP functional [8,15], again with the small $6-31 + G^*$ basis. B3LYP performs quite poorly and is inferior to B-LYP and EDF1. However, the parameterization within B3LYP was carried out [8] by Becke using (in effect) an infinite basis and the functional performance would be improved if the parameters were re-optimized at the $6-31 + G^*$ level. (A partial re-optimization along these lines indicates that Fock exchange participation is reduced to about 5%, leading to an RMS deviation of 4.65 kcal/mol, considerably inferior to EDF1.)

The overall improvement afforded by EDF1 is due largely to its significantly better atomization energies and proton affinities; electron addition and removal energies are only slightly superior. The worst EDF1 results are for the atomization energies of SO_2 and O_2, the ionization energy of O_2, the electron affinity of Cl_2 and the proton affinity of H_2 but it is interesting that each of these cases is also problematic for B-LYP and B3LYP.

Table 3
Deviations from experiment for various functionals

	Exp.	Exp.-BLYP	Exp.-B3LYP	Exp.-EDF1
atomization energies (kcal/mol)				
H_2	103.3	−0.1	−0.6	−3.1
LiH	56.0	1.0	1.0	1.3
BeH	46.9	−7.0	−7.9	−7.2
CH	79.9	−0.3	0.3	−0.4
CH_2 ($^3B_1$)	179.6	1.9	0.1	−2.3
CH_2 ($^1A_1$)	170.6	4.0	3.8	2.2
CH_3	289.2	1.5	−0.8	−3.7
CH_4	392.5	3.9	0.6	−3.7
NH	79.0	−3.5	−1.6	−2.7
NH_2	170.0	−2.6	−0.2	−2.6
NH_3	276.7	2.6	4.4	−0.2
OH	101.3	0.7	2.8	0.4
OH_2	219.3	7.6	10.3	4.6
FH	135.2	5.3	7.7	2.9
SiH_2 ($^1A1$)	144.4	1.5	0.2	−0.6
SiH_2 ($^3B1$)	123.4	1.7	−0.4	−2.7
SiH_3	214.0	4.4	1.0	−0.3
SiH_4	302.8	6.0	1.0	0.7
PH_2	144.7	−0.7	−1.0	−2.8
PH_3	227.4	4.4	3.0	0.4
SH_2	173.2	7.5	7.1	3.4
ClH	102.2	6.5	6.4	3.5
Li_2	24.0	4.2	4.2	5.4
LiF	137.6	2.3	5.8	4.4
HCCH	388.9	8.4	11.3	4.1
H_2CCH_2	531.9	7.0	5.6	−1.3
H_3CCH_3	666.3	9.5	3.7	−3.0
CN	176.6	−3.7	7.8	−2.1
HCN	301.8	−2.1	6.6	−1.5
CO	256.2	2.5	10.5	2.4
HCO	270.3	−4.4	3.6	−6.3
H_2CO	357.2	−1.0	4.9	−4.5
H_3COH	480.8	6.9	7.8	−0.1
N_2	225.1	−4.5	8.8	0.2
H_2NNH_2	405.4	−0.1	5.2	−2.4
NO	150.1	−8.5	3.6	−6.7
O_2	118.0	−13.1	1.3	−13.9
HOOH	252.3	0.5	11.3	−0.2
F_2	36.9	−9.1	3.8	−7.3
CO_2	381.9	−2.8	11.9	−5.4
Na_2	16.6	−0.7	−0.1	1.3
Si_2	74.0	1.9	9.0	0.8
P_2	116.1	2.5	10.4	3.7
S_2	100.7	1.8	7.4	0.0
Cl_2	57.2	7.7	10.9	6.6
NaCl	97.5	7.4	6.7	6.7
SiO	190.5	3.6	12.7	6.2
SC	169.5	3.6	10.8	2.6
SO	123.5	−1.1	9.0	−1.4
ClO	63.3	−3.5	5.8	−2.9
ClF	60.3	−0.9	6.1	−0.7
CH_3Cl	371.0	7.1	5.1	−0.2

Table 3 (continued)

	Exp.	Exp.-BLYP	Exp.-B3LYP	Exp.-EDF1
Si_2H_6	500.1	13.2	4.5	4.1
CH_3SH	445.1	11.1	8.4	2.1
HOCl	156.3	4.1	10.8	3.0
SO_2	254.0	16.3	35.9	15.3
ionization potentials (eV)				
H	13.60	0.12	0.08	0.06
He	24.59	−0.12	−0.19	−0.20
Li	5.39	−0.13	−0.15	−0.12
Be	9.32	0.33	0.29	0.36
B	8.30	−0.27	−0.30	−0.26
C	11.26	−0.13	−0.19	−0.18
N	14.54	−0.01	−0.09	−0.13
O	13.61	−0.54	−0.43	−0.31
F	17.42	−0.33	−0.26	−0.24
Ne	21.56	−0.22	−0.17	−0.28
Na	5.14	−0.19	−0.19	−0.07
Mg	7.65	0.02	0.00	0.14
Al	5.98	0.11	0.04	0.04
Si	8.15	0.20	0.11	0.12
P	10.49	0.29	0.17	0.16
S	10.36	−0.01	−0.05	0.01
Cl	12.97	0.07	0.00	0.04
Ar	15.76	0.11	0.01	0.00
CH_4	12.62	0.13	0.00	0.07
NH_3	10.18	0.19	0.20	0.13
OH	13.01	−0.11	−0.06	−0.04
OH_2	12.62	0.17	0.19	0.11
FH	16.04	0.08	0.11	0.00
SiH_4	11.00	0.21	0.02	0.18
PH	10.15	0.15	0.04	0.03
PH_2	9.82	0.05	−0.05	−0.05
PH_3	9.87	0.18	0.14	0.17
SH	10.37	0.09	0.03	0.08
SH_2	10.47	0.24	0.16	0.18
ClH	12.75	0.19	0.10	0.10
HCCH	11.40	0.40	0.36	0.32
H_2CCH_2	10.51	0.35	0.35	0.28
CO	14.01	0.01	−0.12	0.07
N_2	15.58	0.24	−0.15	0.21
O_2	12.07	−0.47	−0.79	−0.53
P_2	10.53	0.32	−0.36	0.20
S_2	9.36	−0.02	−0.26	−0.13
Cl_2	11.50	0.30	0.04	0.23
ClF	12.66	0.19	−0.02	0.16
SC	11.33	−0.06	−0.14	−0.05
electron affinities (eV)				
C	1.26	−0.07	−0.02	−0.06
CH	1.24	−0.07	−0.02	−0.07
CH_2	0.65	−0.07	0.05	0.05
CH_3	0.08	0.14	0.24	0.21
CN	3.82	−0.06	−0.18	0.02
NH	0.38	−0.07	0.09	0.07
NH_2	0.74	0.08	0.21	0.15
NO	0.02	−0.37	−0.36	−0.30

Table 3 (continued)

	Exp.	Exp.-BLYP	Exp.-B3LYP	Exp.-EDF1
O	1.46	−0.26	−0.06	−0.11
OH	1.83	0.02	0.19	0.08
O_2	0.44	−0.14	−0.11	0.07
F	3.40	−0.22	−0.02	−0.17
Si	1.38	0.19	0.13	0.18
SiH	1.28	0.14	0.09	0.13
SiH_2	1.12	0.08	0.04	0.08
SiH_3	1.44	0.11	0.11	0.17
P	0.75	−0.10	−0.07	−0.02
PH	1.00	0.01	0.02	0.08
PH_2	1.26	0.12	0.11	0.16
PO	1.09	−0.05	−0.17	−0.06
S	2.08	−0.04	−0.03	0.02
SH	2.31	0.07	0.07	0.09
S_2	1.66	0.07	−0.03	0.12
Cl	3.62	0.01	−0.01	0.00
Cl_2	2.39	−0.69	−0.70	−0.56
proton affinities (kcal/mol)				
H_2	100.8	10.7	11.5	8.5
HCCH	152.3	0.5	−0.2	−2.5
NH_3	202.5	1.1	−0.2	−1.7
H_2O	165.1	5.3	4.1	2.9
SiH_4	154.0	4.0	5.7	2.9
PH_3	187.1	4.0	2.8	1.5
H_2S	168.8	3.4	3.5	1.0
HCl	133.6	5.6	6.5	3.4

It is interesting to compare the double-Becke functional with the original B88 form. The new $g(x)$ is

$$g_{\text{doubleB}}(x) = 1.030952 C_0$$
$$+ 10.4017 \Delta B(0.0035, x)$$
$$- 8.44793 \Delta B(0.0042, x) \qquad (10)$$

This and the analogous B88 form are plotted in Fig. 1. We note the following:

(1) The value of double-Becke at $x = 0$ is slightly below that for the free electron gas.

Table 4
RMS errors for functionals

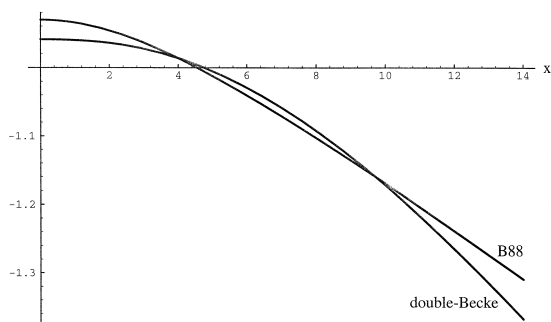| RMS errors (kcal/mol)	Exp.-BLYP	Exp.-B3LYP	Exp.-EDF1
atomization energies	5.75	8.10	4.41
ionization potentials	5.14	5.05	4.34
electron affinities	4.39	4.40	3.79
proton affinities	5.23	5.51	3.77

Fig. 1. The $g(x)$ functions for the B88 and double-Becke exchange functionals.

(2) The initial quadratic term in the Taylor expansion

$$g(x) = g(0) + \tfrac{1}{2}g''(0)x^2 + \dots \qquad (11)$$

is only $g''(0) = -0.00184$, compared with -0.0084 for the original B88 form. It may be noted that the new value is closer to, but smaller than, the ab initio value of -0.00378 for the almost uniform gas, due to Sham and Kleinman [16,17].

(3) In the range $0 < x < 4$, the double-Becke $g(x)$ lies below the old curve. At $x = 4$, there is a crossing and the new curve is higher. At $x = 9.7$, there is another crossing and the new curve is lower thereafter.

4. Conclusions

The principal conclusions to be drawn from these studies are:

(1) The function $g(x)$, specifying the dependence of the 'exchange' functional on density gradient, differs considerably from the original Becke88 form, if optimized with respect to experimental energies.

(2) For the small $6\text{-}31 + G^*$ basis used here, the resulting total functional, EDF1, is the best of which we are presently aware. It should be suitable for computations on large molecules.

(3) No significant improvement is found when mixing with proper Fock exchange is included in the

complete functional. It should be emphasized, however, that this result applies only to this rather small orbital basis and may change if larger bases were used.

Acknowledgements

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