

Assessment of exchange correlation functionals

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Abstract

We have examined the predictions of many of the generalised gradient approximation, and hybrid functionals, which are presently in the literature. Specifically we have looked at energetics and structures for two molecular sets, one with 93 systems and one with 147 systems. We find that recently developed functionals with more adjustable parameters give improved predictions when compared with less flexible functionals. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The determination of improved exchange-correlation functionals is all important if density functional theory (DFT) is to become an ever important tool of computational quantum chemistry. New DFT functionals are being presented at an increasing rate, at the risk of the subject being swamped and possibly the quality of such functionals not being reliably assessed and compared. We consider that it is of value if functionals which are presented by one research group are independently validated by another group.

In this Letter, we are going to investigate several functionals to see how they perform on a set of 93 systems. Their performance will be measured on both energies and energy gradients. The values reported are

$$d_E = \sum_{A_1, A_2, M} |E_i - E_i^{\text{exact}}| / N_1, \quad (1)$$

$$r_E = \sqrt{\left(\sum_{A_1, A_2, M} (E_i - E_i^{\text{exact}})^2 / N_1 \right)}, \quad (2)$$

$$d_G = 500 \sum_{M, \alpha} |\nabla_\alpha E_i| / N_2, \quad (3)$$

$$r_G = 500 \sqrt{\left(\sum_{M, \alpha} (\nabla_\alpha E_i)^2 \right) / N_2}, \quad (4)$$

$$Q = 750 \sum_{A_1, A_2, M} (E_i - E_i^{\text{exact}})^2 + 500 \sum_{M, \alpha} (\nabla_\alpha E_i)^2, \quad (5)$$

d_E and r_E (in kcal mol⁻¹) are a measure of how well the energy quantities are fitted, and d_G and r_G (in au) are a measure of how small the gradient vectors are for the molecules. N_1 is the number of energies E_i , and N_2 is the number of gradient components $\nabla_\alpha E_i$.

Q is the quantity (in au) which is actually minimised in any self-consistent Kohn–Sham refinement which we undertake. The relative weights for energies and gradients were adjusted to give a reasonable balance.

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It is of course vital that our set of 93 systems is representative of aspects of chemistry. Essentially our atoms and molecules are a subset of Pople's G2-1 set of first- and second-row systems. The full set is given in A_1 contains 18 atoms and cations from the first row. The exact total energies of these 18 atoms are included in the set, taken from Ref. [1]. This means that first-row ionisation energies are included.

A_2 contains seven second-row atoms. This time, only ionisation energies ($A_2^+ - A_2$) are in the set. Separate calculations have to be performed on A_2 and A_2^+ .

M contains 61 molecules from the first and second rows. The atomisation energies of these 61 molecules are in the set, the accurate values of which are obtained from Ref. [2]. Note that eight molecular ionisation energies are included as a result.

For the gradient terms (3) and (4), all 61 molecules are included, and specifically $\nabla_{j\alpha} E_i$ is evaluated with $j = 1, 2 \dots (N_i - 1)$, $\alpha = x, y, z$ where N_i is the number of atoms in the molecule. All calculations are performed at experimental geometries, where $\nabla_{j\alpha} E_i^{\text{exact}} = 0$. For the 93 set, we have $N_1 = 86$ and $N_2 = 537$.

We think that it is reasonable to include first-row atomic energies in the set. In a molecule, these electrons become valence electrons, and thus their energetic aspects are important. We think that the $1s^2$ electrons should be included because of their polarisation effects. For similar reasons, we believe that the inclusion of cationic energies is important. We do not think that the inclusion of second-row

atomic energies is sensible because most of these energies are in the far inside $1s^2$ core. Thus we revert to ionisation energies (following Becke).

We hope that the molecular set is representative of much of first- and second-row chemistry: there are open- and closed-shell molecules, there are molecules with single, double and triple bonds, there are ionic systems, and systems which the quantum chemist would classify as multi-configurational.

There are deficiencies in our testing set, the major one being that there are no anions or diffuse systems. We have not included any proton affinities from the Pople sets. There are no H-bonded systems. There are of course no molecules from transition-metal chemistry. There are no charge-transfer (CT) molecules. No properties such as dipole moments are included. No systems akin to those studied by physicists (solids) are included.

For these reasons, we have also tested some of the functionals on a larger set, the details of which are given in Table 1.

We already have a new HCTH functional the parameters of which were determined by fitting to a 147 system training set [4]. We report the performance of a subset of our functionals using this larger 147 set (it includes 24 anions, eight proton affinities and additional molecules from the Pople G2 set [9]). For the 147 set, $N_1 = 136$ and $N_2 = 909$.

In Section 2, we give some details of all the functionals that we have examined. In Section 3, we analyse these functionals according to their performance for Eqs. (1) and (5), and as a result we present some advice on the use of these functionals.

Table 1

The systems in the (a) 93 set and (b) 147 set

(a) 93 Set:

(1) A_1 : H, He, Li, Be, B, C, N, O, F, Ne, Li^+ , Be^+ , B^+ , C^+ , N^+ , O^+ , F^+ , Ne^+ {18}(2) A_2 : Na, Mg, Al, Si, P, S, Cl {7}(3) A_2^+ : Na^+ , Mg^+ , Al^+ , Si^+ , P^+ , S^+ , Cl^+ {7}(4) M : H_2 , LiH, BeH, CH, $\text{CH}_2(^1\text{A})$, $\text{CH}_2(^3\text{B})$, CH_3 , CH_4 , NH, NH_2 , NH_3 , OH, H_2O , HF, Li_2 , LiF, C_2H_2 , C_2H_4 , C_2H_6 , CN, HCN, CO, HCO, H_2CO , CH_3OH , N_2 , N_2H_4 , O_2 , H_2O_2 , F_2 , CO_2 , $\text{SiH}_2(^1\text{A})$, $\text{SiH}_2(^3\text{B})$, SiH_3 , SiH_4 , PH_2 , PH_3 , HCl, Na_2 , Si_2 , P_2 , S_2 , Cl_2 , NaCl, SiO, CS, SO, ClO, ClF, CH_3Cl , CH_3SH , HOCl, SO_2 , HF^+ , HCl^+ , CO^+ , N_2^+ , O_2^+ , P_2^+ , S_2^+ , Cl_2^+ {61}

(b) Extra systems in 147 set:

(5) H_2S , Si_2H_6 (6) H_3^+ , NH_4^+ , H_3O^+ , C_2H_3^+ , PH_4^+ , H_3S^+ , H_2Cl^+ , PH_2^+ , SiH_3^+ , NH_3^+ , $\text{H}_2\text{S}^+(^2\text{B}_1)$, H_2O^+ , CH_4^+ , SiH_4^+ , C_2H_4^+ , ClF^+ , PH_3^+ , C_2H_2^+ , $\text{H}_2\text{S}^+(^2\text{A}_1)$, $\text{N}_2^+(^2\Pi_u)$, PH^+ , SH^+ (7) C^- , O^- , F^- , Si^- , P^- , Cl^- , S^- , CH_3^- , NH_2^- , OH^- , CN^- , SiH_3^- , PH_2^- , CH^- , CH_2^- , O_2^- , SiH_2^- , Cl_2^- , S_2^- , NH^- , SiH^- , PH^- , PO^- , SH^- (8) $(\text{HF})_2$, $(\text{H}_2\text{O})_2$

2. Functionals

The functionals fall into three main categories:

- (1) GGAs: the generalised gradient approximation, where E_{xc} is approximated by a local functional of just ρ and $\nabla\rho$ generally in the form

$$E_{xc} = \int \rho^{4/3} g(s^2) d\mathbf{r} \text{ where } s = \frac{|\nabla\rho|}{\rho^{4/3}};$$

- (2) Hybrid GGAs: include a fraction of exact Hartree–Fock exchange

$$E_x^{\text{HF}} = - \sum_{i>j} \iint \frac{\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \times d\mathbf{r}_1 d\mathbf{r}_2;$$

- (3) Meta-GGAs: go beyond first-order approximation of the GGA by introducing second-order derivatives, the Laplacian of the density, $\nabla^2\rho$, or the kinetic energy density, $\tau = \sum_i (\nabla\phi_i)^2$.

$$E_{xc}^{\text{MGGA}} = \int F_{xc}(\rho, \nabla\rho, \nabla^2\rho, \tau) d\mathbf{r}.$$

The group of meta-GGAs in this Letter also include hybrid meta-GGAs which include exact exchange as well.

The functionals investigated were:

- LDA: the local density approximation with Dirac exchange (LDAX) [10] and VWN-5 correlation [11];
- GGAs
 - BLYP: the most commonly used GGA functional comprising LDAX + Becke's 1988 gradient exchange functional (B88X) [12] with Lee, Yang and Parr's correlation functional (LYP) [13];
 - BP86: LDAX + B88X + VWN-5 and Perdew's 1986 non-local correction (P86) [14] to LDA correlation;
 - BP91: LDAX + B88X + Perdew and Wang's 1991 correlation functional (PW91) which is based on a slowly varying electron density [15,16];
 - PBE: Perdew, Burke and Ernzerhof's simpler exchange and correlation functionals, based on the slowly varying electron gas [17,18];
 - HCTH: based on Becke's 1997 expansion form [23] for an exchange-correlation functional but

with 15 parameters and not including any exact exchange [19].

- Hybrid GGAs
 - B3P91: Becke's original 3 parameter fit including exact exchange, LDAX, B88X and PW91 [20];
 - B3P86: the same fit using VWN-5 and P86 correlation instead of PW91 [21];
 - B3LYP: the same fit using LYP correlation – the most widely used hybrid functional [21];
 - PBE0: an hybrid functional based on PBE with a theoretically determined value of 1/4 for exact exchange [22];
 - B97: Becke's original 10 parameter functional obtained by fitting to the G1 set [23].
- Meta-GGAs
 - B98: another 10-parameter functional, the terms of which include $\nabla^2\rho$, τ and exact exchange [24];
 - PKZB: based upon PBE but extended to include τ [25];
 - VS98: based on the second-order density matrix expansion with 21 parameters [26].

The parameters in Becke's functionals (B97 and B98) were optimised in a post-LDA manner with an infinite numerical basis. We reoptimised these parameters in a self-consistent manner with our TZ2P basis (see below) against our fitting (testing) set. Similarly, we also reoptimised the linear parameters in VS98. Reoptimised functionals are labeled with a '–1'.

We have implemented all of these functionals in this Letter and have taken care to ensure that all subroutines have been programmed correctly. In all cases, we have checked that energies are consistent with those in the parent papers and have also performed finite-field checks both on the subroutines and on the evaluation of the dipole moment. We have taken the approach of Neumann et al. [27] to perform self-consistent calculations with τ by considering the contribution to the Fock matrix element

$$\int \nabla\eta_r \left(2 \frac{\partial G}{\partial \tau} \right) \nabla\eta_s d\mathbf{r}.$$

For all calculations, we have also used high-accuracy grids as these are especially important for functionals involving τ and $\nabla^2\rho$.

We have used the same basis set in all calculations. This is defined as a TZ2P basis set by the following.

1. For hydrogen, we used the PVTZ contraction given in Ref. [3] but with no d-set.
2. For first-row atoms, we used the 5S4P contraction given in Ref. [5–7], and two sets of d-polarisation were used.
3. For Na, Mg and Al, we used a 631G2DP basis [8] and for the remaining second-row atoms a 9S6P contraction of Huzinaga's original 12S9P set [5–7]; three sets of d-polarisations were used.

These basis sets form part of the CADPAC library; our software package CADPAC was used for all of these calculations [28].

3. Results and discussion

In Table 2 are given the values for the performance parameters d_E , r_E , d_G , r_G and Q as defined in Eqs. (1) and (5) together with the value for the

coefficient of exact Hartree–Fock exchange c_x . We also give the value for Q excluding the total energies, A_1 , which we call Q_1 . We now will discuss the performance of each functional

- LDA: The value of the geometry parameter is better than for many of the GGA functionals and this is why LDA has been used with some success for geometries but unfortunately the energetics are very poor.
- BLYP: This is the most commonly used GGA functional; the performance parameters indicate that geometries are relatively poor (too long) and energies are significantly worse than more recent GGA functionals. The Q parameter is 4 times as large as for the best GGA functional. The clear message is that there are superior GGA functionals to BLYP.
- BP86: The performance of BP86 is rather similar to that of BLYP as measured by Q , with energy predictions being slightly worse and geometrical predictions being slightly better.
- BP91: BP91 is an improvement over BP86, mainly with the energy predictions.

Table 2

Values for the performance parameters Eqs. (1) and (5) for the functionals examined. The final column is the value of Q_1 which excludes the 18 total energies of first-row atoms and cations (A_1)

Functional	c_x	d_E	d_G	r_E	r_G	Q	Q_1
(a) Non-Hybrid functionals							
LDA	0	74.04	1.70	131.02	3.04	2821.83	184.36
PKZB	0	11.73	2.56	26.43	4.75	138.70	27.05
PBE	0	11.94	1.86	17.71	3.51	64.62	23.87
BLYP	0	4.46	2.08	5.99	4.37	26.39	24.57
VS98	0	6.32	0.97	11.18	2.18	25.57	6.62
BP86	0	6.74	1.84	8.45	3.56	25.29	21.88
BP91	0	4.72	1.74	6.09	3.41	18.57	17.05
B98 ^{GGA-1}	0	3.01	1.29	3.99	2.86	11.40	10.88
VS98-1	0	2.80	1.17	3.69	2.57	9.30	8.45
HCTH	0	3.49	1.09	4.57	2.17	8.50	7.48
B97 ^{GGA-1}	0	3.26	1.01	4.39	2.04	7.61	6.34
(b) Hybrid functionals							
PBE0	0.25	8.00	1.09	13.78	2.75	39.19	10.54
B3P86	0.2	4.36	1.00	5.55	2.29	10.70	9.73
B3P91	0.2	3.49	0.99	4.56	2.33	9.24	7.74
B3LYP	0.2	3.40	0.91	4.42	2.32	8.98	7.93
B98	0.1985	2.10	1.16	2.94	2.45	7.86	7.49
B98-1	0.21	1.97	0.93	2.72	2.10	5.98	5.77
B97	0.1943	2.51	0.91	3.20	1.97	5.86	5.43
B97-1	0.15	2.02	0.91	2.70	1.91	5.10	4.74

- PBE: This functional does not perform well for our 93 chemical systems, energy predictions being more than twice as bad as BLYP while geometries are marginally better. Its position in the Table 2 is explained because the functional contains no free parameters and has been determined from the consideration of a perturbed uniform electron gas. It cannot be recommended for chemistry.
- HCTH: This 15-term GGA functional should perform well as it has been parametrised by fitting to these 93 systems (together with fitting to exchange correlation potentials). The values of the performance parameters show an improvement in energies of 1 kcal mol⁻¹ and a factor of 2 reduction in bond length error. The fact that it is a good functional follows from its performance with the 147 systems discussed below.
- B97^{GGA}-1: Here we have taken Becke's 97 expansion and reoptimised its nine parameters without exact exchange for the 93 systems. Table 2 shows that it gives an improvement over HCTH as expected because of its specific refinement.
- B98^{GGA}-1: This is as for B97^{GGA}-1 but with Becke's 98 expansion our results conclude that B98 is an inferior expansion to B97. This is encouraging because B98 involves the Laplacian of the density, and thus the results suggest that it is not fruitful to include it in more advanced functionals.
- PKZB: This meta-GGA arises from a consideration of the perturbed uniform electron gas energetically; its performance for energies is similar to that of PBE but its geometrical predictions are inferior. There seems to be no argument for it to be used in place of PBE.
- VS98: This meta-GGA designed for molecules appears to give similar energetic predictions to BP86 but much improved geometrical predictions.
- VS98-1: Our reparameterisation of the 18 linear coefficients in VS98 shows a substantial improvement of the energetic predictions, indeed the best of all the non-hybrid functionals. Geometrical predictions are not as good as B97^{GGA}-1 however.
- PBE0: Exact exchange has been added to PBE, giving an improvement over PBE by a factor of 2 as measured by Q . It is still inferior to BLYP in energetic predictions and cannot be recommended.
- B3P91: The first hybrid functional, the results supporting the great improvement noticed by Becke, geometries are improved by a factor of 2 and energies are improved by more than 1 kcal mol⁻¹.
- B3P86: This is marginally worse than B3P91, mainly due to the energy predictions.
- B3LYP: Our analysis shows that its performance is indistinguishable from that of B3P91; however, it is the hybrid functional which is most widely used.
- B97: This hybrid functional due to Becke does perform significantly better than B3LYP; in particular, energy predictions are improved by 1 kcal mol⁻¹ and the Q value is decreased from 8.98 to

Table 3

Performance parameters d_E , d_G , and Q for selected functionals using the larger 147 system testing set

Functional	c_x	d_E	d_G	Q_{147}	$Q_{147}-Q$
BLYP	0	4.89	2.12	43.22	16.83
VS98	0	6.04	1.00	35.69	10.12
HCTH	0	4.30	1.15	19.46	10.96
B98	0.1985	3.20	1.22	18.71	10.85
B3LYP	0.2	3.30	1.05	18.16	9.18
B97 ^{GGA} -1	0	4.08	1.02	17.23	9.62
B97	0.1943	3.38	1.01	15.02	9.16
B98-1	0.21	2.85	1.00	14.45	8.47
B97-1	0.15	3.00	0.98	13.60	8.50

Table 4
Parameters for the B97^{GGA}-1 and B97-1 functionals

	Exchange	$\alpha\beta$ correlation	$\sigma\sigma$ correlation
(a) B97 ^{GGA} -1			
c_0	1.1068	0.7961	0.4883
c_1	-0.8765	5.7060	-2.117
c_2	4.2639	-14.9820	2.3235
c_x		0.0	
(b) B97-1			
c_0	0.8773	0.9253	0.2228
c_1	0.2149	2.0270	1.3678
c_2	1.5204	-7.3431	-1.5068
c_x		0.15	

5.86. We must recommend the use of this hybrid functional.

- B98: This later hybrid functional of Becke would appear to give improved energetics (as Becke himself found) but inferior geometrical predictions. Because functionals are often used to predict structures, we do not recommend B98.
- B97-1: We have found that a lower value of c_x considerably improves the energetic predictions of B97, with reparameterisation. Note this is not the same B97-1 as in Ref. [19].
- B98-1: Again we find that B98-type functionals are inferior to the B97 functionals.

We now will comment on the values of Q_1 in Table 3 (the values of Q without the total energies of first-row atoms and cations). We see that Q_1 is substantially lower than Q for LDA, PKZB, PBE and PBE0. This underlines the fact that functionals determined from the electron gas give very poor atomic energies. Furthermore, we note that the VS98 value of Q_1 is also substantially lower than Q because van Voorhis and Scuseria did not include atomic energies in their parameterisation of this functional. The values of Q and Q_1 are similar for all remaining functionals.

We now will look at the performance of some of the functionals with the 147 systems as presented in This is important primarily because of the much wider chemistry but also because it is an independent assessment of our refined functionals (indicated by -1). As expected for this larger set, d_E has increased a little (this is mainly due to the inclusion of

anions which are described poorly by all the functionals) as also d_G has increased a little. However, the quality of the predictions for energetics and structures is very good for B97.

The key message is that the ordering of the functional performance has not significantly changed from that of the 93 set. In particular, BLYP is inferior to B97^{GGA}-1 and B3LYP is inferior to B97 and B97-1, although a closer examination suggests that B3LYP and B97 give similar predictions for the additional systems. Our recommendations therefore remain unchanged.

In summary, we suggest that there has been progress in functional development in recent years. In particular, we suggest that for chemical problems the BLYP and BP GGA functionals may give inferior predictions to the B97^{GGA}-1 (because this is not generally available we include its parameters in Table 4, using exactly the same form as presented by Becke in his table for B97). We also suggest that the often used B3P86, B3P91 and B3LYP functionals may give inferior predictions to Becke's B97 functional (and possibly the B97-1 functional whose parameters are again given in Table 4). We understand that the B97 class of functional is being made available in widely used software packages.

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