An Investigation of the Performance of a Hybrid of Hartree-Fock and Density Functional Theory

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Abstract

We explore a hybrid methodology in which the Hartree-Fock energy and density are combined with the nonlocal exchange functional of Becke (1988) and the nonlocal correlation functional of Lee, Yang and Parr (1988) to yield an estimate of the Schrödinger total energy. The resulting mean absolute deviation from a large number of experimental atomization energies, ionization potentials, electron affinities, and proton affinities is 3.86 kcal/mol. Performance comparisons are made with the recently developed G2 theory and nonconventional interpretations of the density functionals are discussed. © 1992 John Wiley & Sons, Inc.

Introduction

Systematic prediction of molecular energy by quantum mechanical methods is one of the principal objectives of theoretical chemistry. In the last few years, there has been some success in developing methods which will reproduce experimental energies, such as dissociation energies, ionization potentials, and electron affinities, to an accuracy of ± 2 kcal/mol or 0.1 eV. The GAUSSIAN-1 (G1) and GAUSSIAN-2 (G2) models [1,2] achieve this by *ab initio* procedures, supplemented by a single small semiempirical parameter to allow for higher-order basis functions and higher-order correlation corrections. However, this level of accuracy is only reached at a cost that rapidly increases with the size of the system (an iterative N^6 step followed by a single N^7 step, where N scales as the molecular size). There is, therefore, interest in methods which might reach similar precision more efficiently.

Density functional theory has recently shown promise in this direction. In particular, Becke [3] has proposed an algorithm which, when applied to the same experimental data set as used in G1 theory, gives total atomization energies of neutral molecules with an average absolute error of 3.7 kcal/mol. This result compares with 1.6 kcal/mol for G1 and 1.2 kcal/mol for G2 theory, but is obtained at lower cost and is more easily extendable to larger molecules. Other density functional theories have also shown promise in this direction [4,5].

Most density functional theories attempt to express the exchange and/or correlation energies as functionals of the one-electron density $\rho(r)$ (or of the α- and β-densities $\rho_\alpha(r)$, $\rho_\beta(r)$ for open-shell systems). Exact functionals are unknown,

but some general properties have been elucidated and many explicit forms have been tried. The densities ρ_α, ρ_β are obtained usually via a self-consistent procedure, based on the potential derived from the exchange-correlation functional (Kohn-Sham equations). However, it is quite possible to apply the same energy functionals to electron densities derived by standard (HF) theory. An extensive study of this sort, using several functionals, has been published by Clementi and Chakravorty [6]. Such comparative studies should help our understanding of both the densities and functionals as well as pointing the way towards improved treatments.

Our principal objective is to apply a combination of energy functionals from the recent literature to a large set of Hartree-Fock densities. This set consists of the atoms, molecules, and ions used in the G2 study [2], where they were tested against well-known atomization energies, ionization potentials, electron affinities, and proton affinities. Here we make a parallel study, using a Hartree-Fock density and a combination of exchange-correlation functionals due to Becke [7] and Lee et al. [8]. Emphasis is on the development of a unique procedure for all species, with well-defined total energies, which may be compared directly with Schrödinger total energies, insofar as they are known. Such total energies, which are rarely reported in the current density functional literature, can then be used to calculate energy differences, directly comparable to experimental data (as is possible with G2 theory).

Method

In order to facilitate comparison with previous calculations, we shall use molecular structures and frequencies exactly as in G2 theory. All geometrical parameters are found at the MP2/6-31G(d) level and harmonic frequencies at HF/6-31G(d). These frequencies (scaled by the usual 0.893 empirical factor [9]) are used to calculate zero-point vibrational energies. Single-point Hartree-Fock calculations are then carried out with the largest basis used in G2 theory, 6-311 + G($3df,2p$) [10]. Restricted (RHF) and unrestricted Hartree-Fock (UHF) methods are used for closed and open shell systems, respectively. The electron density, ρ, may be described in conventional notation as HF/6-311 + G($3df,2p$)//MP2/6-31G(d). This is then used for density functional calculations.

In density functional theory, the total energy is written

$$E = E_T + E_V + E_J + E_{XC} \tag{1}$$

where E_T is the kinetic energy of independent electrons having the density ρ, E_V is the potential energy involving nuclei (nuclear–electron + nuclear–nuclear) and E_J is the overall coulomb repulsive energy

$$E_J = \frac{1}{2} \int\int \rho(r_1) r_{12}^{-1} \rho(r_2) \, dr_1 \, dr_2 \tag{2}$$

The remaining term E_{XC} is the exchange-correlation energy, representing the energy lowering due to the fact that the complete electron–electron interaction is less than E_J, partly because this incorrectly includes the interaction of a particular electron with its own smoothed distribution, and partly because the relative motion of other electrons is correlated, not independent as implicit in Eq. (2).

In Hartree-Fock theory, the energy is calculated as the expectation value of the Hamiltonian using the optimized single-determinant wavefunction with occupied spin orbitals χ_i. This gives an energy

$$E_{\mathrm{HF}} = E_T + E_V + E_J + E_X \tag{3}$$

where E_X is the exchange energy

$$E_X = -\frac{1}{2} \sum_{i,j}^{\mathrm{occ}} \int\int \chi_i(1)\chi_j(1)r_{12}^{-1}\chi_i(2)\chi_j(2)\, d\tau_1\, d\tau_2 \tag{4}$$

integration being over cartesian and spin coordinates. This expression takes some account of the tendency of electrons of parallel spin to be kept spatially apart by virtue of the antisymmetry principle. However, as is well known, the Hartree-Fock energy E_{HF} takes no account of the correlation between electrons of antiparallel spin. The remaining part of the energy is the correlation energy E_C, which deals with α-β correlation and also the remaining α-α and β-β correlation effects not included in the exchange part of E_{HF}. E_C is difficult and frequently expensive to compute. In G2 theory, it is treated by a combination of Møller-Plesset (MP) and quadratic configuration interaction methods.

A common recommendation in density functional theory is to treat E_X and E_C together as a single correction E_{XC}, determined by a functional $E_{XC}[\rho]$. There is some point to this, since the exchange energy by itself is not clearly defined for densities other than Hartree-Fock. Nevertheless, in practice, E_{XC} often *is* split into two parts, one of which has the *appearance* of an exchange correction and the other the *appearance* of a correlation correction. However, the two do not necessarily correspond to exact exchange and correlation, in the normal meaning of these terms. Ziegler [11], for example, notes that poor results are often obtained if exact (i.e., HF) exchange energies are used in conjunction with certain functionals for correlation. Instead, it is better to use a different density functional theory (DFT) functional for exchange to go along with the correlation calculation. Since the exchange energy is well-defined (at least for ρ_{HF}), we prefer to denote this partition of E_{XC} as a division into a *parallel*-spin ($\alpha\alpha + \beta\beta$) part E_P and an *antiparallel*-spin ($\alpha\beta$) part E_A,

$$E_{XC} = E_P[\rho_\alpha] + E_P[\rho_\beta] + E_A[\rho_\alpha, \rho_\beta] \tag{5}$$

The parallel part, which is exchange-like, is the sum of an α- and a β-part, determined solely by their respective densities ρ_α and ρ_β. The antiparallel part, which is correlation-like, is a single functional $E_A[\rho_\alpha, \rho_\beta]$ which vanishes unless ρ_α and ρ_β are both nonvanishing and overlapping. A possible interpretation is that E_P takes account of both elimination of self-interaction and effects of full correlation of parallel ($\alpha\alpha + \beta\beta$) electrons (including exchange), while E_A takes into account of the remaining correlation between antiparallel ($\alpha\beta$) electrons. We shall return to this hypothesis in a later section.

We now turn to specification of the functionals. For the parallel part, we use the expression introduced by Becke in 1988 [7], and also used by Becke [3] in his recent study of atomization energies. We shall write this as

$$E_P^{B88} = E_P[\rho_\alpha] + E_P[\rho_\beta] \tag{6}$$

where

$$E_P[\rho] = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3} \int \rho^{4/3}\, dr - \int \rho^{4/3} \frac{bx^2}{1 + 6bx \sinh^{-1}x}\, dr \tag{7}$$

$$x = \rho^{-4/3}|\nabla\rho| \tag{8}$$

The first term in (7) is designed to reproduce the exchange energy of a uniform electron gas. The second term introduces a correction for nonuniformity through the density gradient $\nabla\rho$, the particular analytic form being such that correct asymptotic behaviour is achieved far from the molecular centre. The parameter b is chosen by Becke as 0.0042 to fit the known exchange energies for the inert gas atoms.

The Becke functional (7) is parameterized to give good *atomic* exchange energies. However, as noted above, it may not always lead to good exchange energies for molecules. It is useful to introduce a quantity

$$\Delta E_P^{B88} = E_P^{B88} - E_X \tag{9}$$

which measures the "Becke 88 excess," or excess exchange energy implied by (7). As will be seen in the next section, this excess is quite large for many molecules. Since we are using a Hartree-Fock density, the values of E_P^{B88} and E_X are both computable and ΔE_P^{B88} is easily obtained.

It remains to add the antiparallel correlation correction $E_A[\rho_\alpha, \rho_\beta]$. Here we use the form introduced by Lee, Yang and Parr (LYP) [8]. This originates in an older study of $\alpha\beta$ correlation in the helium atom by Colle and Salvetti [12]. The actual form programmed is one equivalent to LYP presented by Miehlich, Savin, Stoll, and Preuss (MSSP) [13]. It is given fully by eq. (2) of this reference and need not be reproduced in full. It does have the property of vanishing if either ρ_α or ρ_β is nonexistent, so has the appearance of representing only $\alpha\beta$ correlation. We denote it by E_A^{LYP}.

It should be noted that both LYP and MSSP applied the LYP functional to a number of other atomic and molecular systems and sometimes obtained good results when compared with known *total* correlation energies. Since E_A^{LYP} does not incorporate effects of $\alpha\alpha$ or $\beta\beta$ correlation in any direct manner, the significance of this is somewhat unclear. We shall use E_A^{LYP} only to represent the antiparallel part.

The (Becke 88 + Lee, Yang and Parr) correlation energy is then given by

$$E_C^{BLYP} = \Delta E_P^{B88} + E_A^{LYP} \tag{10}$$

and the corresponding total energy E_0^{BLYP} is obtained by adding the HF and zero-point vibrational energies

$$E_0^{BLYP} = E_{HF} + E_C^{BLYP} + E_{ZPV} \tag{11}$$

The actual procedure is:
1. Obtain the Hartree-Fock energy E_{HF};
2. Remove the Hartree-Fock exchange energy E_X;
3. Compute E_P^{B88} and E_A^{LYP} by numerical quadrature and add to give E_e^{BLYP};
4. Compute E_{ZPV} and add to give E_0^{BLYP}.

Details of the numerical integration scheme are given in the Appendix.

Results and Discussion

The BLYP procedure just described has been applied to 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 [14]. The source data listed in Table I are:

1. The proper (unrestricted Hartree-Fock) exchange energy, E_X, with the large 6-311+G($3df,2p$) basis;
2. The Becke-88 excess, ΔE_P^{B88}, given by Eq. (9), measuring the amount by which the Becke functional (7) gives an energy contribution additional to E_X;
3. The estimate of the total correlation energy, E_C^{BLYP}, given in this theory as the sum of ΔE_P^{B88} and the antiparallel part due to Lee, Yang and Parr;
4. The total energy, E_0^{BLYP}, obtained by adding the correlation to the Hartree-Fock energy, to give E_e and then further modified by addition of the zero-point energy, as listed elsewhere [1,2].

This set of data should prove of value in assessing the role of various energy contributions; it is more comprehensive than most of the data published in the density functional literature.

We begin with information about the total energies of atoms. For small atoms, the total energy (corresponding to full solution of the Schrödinger equation) is moderately well known, either by high-level theory, or by some combination of experimental and theoretical ionization potentials. The BLYP results are compared with some such values in Table II. Agreement is generally achieved within 10 millihartrees (mh), although there is some variation. The Becke-88 functional fails to give the correct exchange energy for the hydrogen atom (-312.5 mh) by 2.8 mh, leading to a significant error of 3 mh. For the heavier atoms, such as oxygen, fluorine, and neon, there are some partly compensating errors. On the one hand, incompleteness of the orbital basis results in a Hartree-Fock energy that is too positive by about 20 mh for the neon atom (based on the HF limit of -128.5470 given by Veillard and Clementi [15]). On the other hand, the magnitude of the correlation energy is overestimated in this treatment. Here, we have -31.1 mh from ΔE_P^{B88} and -383.4 mh from E_A^{BLYP}, giving a total of -414.5 mh. The actual correlation energy of neon is close to -390 mh [16].

Table III lists the total atomization energies, ΣD_0, from the present theory, together with G2 and experimental data. This consists of the 55 molecules of the G2 set plus H_2. The mean absolute difference between BLYP and experiment is 3.94 kcal/mol, which may be compared with 1.16 kcal/mol for G2 theory. The BLYP

TABLE I. Source data.

Molecule	E_X (mh)	ΔE_P^{B88} (mh)	E_C^{BLYP} (mh)	E_0^{BLYP} (ht)	Molecule	E_X (mh)	ΔE_P^{B88} (mh)	E_C^{BLYP} (mh)	E_0^{BLYP} (ht)
H	−312.5	+2.8	+2.8	−0.4970					
He	−1026.2	+1.0	−42.8	−2.9027	He⁺	−623.2	+5.2	+5.2	−1.9929
Li	−1781.0	+5.9	−47.5	−7.4796	Li⁺	−1651.1	+6.2	−41.4	−7.2772
Be	−2666.2	+9.0	−85.5	−14.6575	Be⁺	−2504.9	+9.5	−51.6	−14.3278
B	−3768.6	+9.2	−115.7	−24.6467	B⁺	−3491.3	+10.2	−96.4	−24.3320
C	−5074.6	+8.7	−149.6	−37.8398	C⁺	−4745.2	+9.8	−129.4	−37.4224
N	−6603.5	+10.0	−181.9	−54.5808	N⁺	−6212.0	+12.1	−161.2	−54.0488
O	−8212.3	−6.0	−262.7	−75.0721	O⁺	−7911.6	+18.3	−188.4	−74.5550
F	−10037.0	−20.3	−341.4	−99.7432	F⁺	−9670.6	+3.2	−269.8	−99.0946
Ne	−12098.3	−31.1	−414.5	−128.9411	Ne⁺	−11656.5	−7.1	−344.6	−128.1457
Na	−14017.6	−12.4	−420.8	−162.2668	Na⁺	−13902.2	−8.1	−407.4	−162.0717
Mg	−15991.7	−1.0	−460.5	−200.0671	Mg⁺	−15859.7	+3.5	−423.8	−199.7877
Al	−18090.4	+8.0	−485.1	−242.3591	Al⁺	−17892.2	+3.1	−477.7	−242.1457
Si	−20303.1	+12.2	−517.0	−289.3690	Si⁺	−20071.1	+8.3	−506.6	−289.0779
P	−22641.0	+15.1	−551.2	−341.2604	P⁺	−22368.4	+10.7	−540.3	−340.8855
S	−25033.0	+18.3	−609.4	−398.1123	S⁺	−24791.3	+18.2	−569.3	−397.7331
Cl	−27541.1	+19.9	−669.9	−460.1471	Cl⁺	−27262.2	+20.4	−629.0	−459.6734
Ar	−30183.4	+25.9	−724.9	−527.5318	Ar⁺	−29854.7	+25.2	−685.7	−526.9571
C⁻	−5265.3	−5.2	−176.1	−37.8833	Si⁻	−20455.1	+9.9	−528.8	−289.4119
					P⁻	−22766.0	+7.9	−591.9	−341.2884
O⁻	−8387.7	−42.0	−339.4	−75.1274	S⁻	−25194.6	+9.9	−652.4	−398.1876
F⁻	−10276.6	−60.2	−421.2	−99.8669	Cl⁻	−27748.0	+12.1	−712.4	−460.2778
H₂	−659.7	+3.1	−35.3	−1.1588	CN	−11757.7	−36.9	−450.4	−92.6806
LiH	−2140.2	+7.3	−81.1	−8.0642	HCN	−12013.2	−53.7	−515.9	−93.4024
BeH	−3084.3	+16.2	−91.1	−15.2387	CO	−13301.6	−62.4	−545.4	−113.3162
CH	−5423.0	+5.5	−190.4	−38.4649	HCO	−13685.4	−59.2	−564.7	−113.8419
CH₂ (³B₁)	−5874.6	+14.8	−196.4	−39.1166	H₂CO	−14071.2	−49.6	−588.9	−114.4723
CH₂ (¹A₁)	−5789.6	+6.3	−226.1	−39.1020	H₃COH	−14843.6	−22.9	−618.3	−115.6567
CH₃	−6227.3	+15.7	−240.6	−39.7895	N₂	−13050.9	−79.8	−560.6	−109.5275
CH₄	−6592.4	+17.6	−276.4	−40.4460	H₂NNH₂	−14623.2	−33.2	−629.3	−111.8009
NH	−6936.7	−1.6	−236.8	−55.2100	NO	−14736.1	−83.2	−609.2	−129.9006
NH₂	−7286.4	−9.4	−287.2	−55.8548	O₂	−16291.3	−115.7	−682.9	−150.3423
NH₃	−7661.6	−13.3	−330.9	−56.5160	HOOH	−17063.7	−103.6	−739.1	−151.5425
OH	−8557.3	−24.5	−324.2	−75.7339	F₂	−19936.3	−138.7	−813.4	−199.5522
OH₂	−8930.3	−38.0	−378.2	−76.4142	CO₂	−21591.1	−113.1	−901.6	−188.5912
FH	−10411.9	−45.9	−408.2	−100.4547	Na₂	−28022.9	−27.4	−868.0	−324.5593
SiH	−20652.8	+17.5	−545.7	−289.9765	Si₂	−40558.6	−6.1	−1101.4	−578.8468
SiH₂ (¹A₁)	−21007.6	+22.9	−573.8	−290.5898	P₂	−45181.0	−16.4	−1227.8	−682.7032
SiH₂ (³B₁)	−21053.3	+30.8	−543.5	−290.5525	S₂	−50051.0	+1.8	−1301.0	−796.3851
SiH₃	−21413.4	+39.9	−573.2	−291.1907	Cl₂	−55078.7	+14.3	−1398.1	−920.3803
SiH₄	−21780.7	+49.8	−598.6	−291.8275	NaCl	−41688.8	+8.7	−1123.5	−622.5593
PH	−22984.8	+19.7	−583.1	−341.8698	SiO	−28548.5	−55.6	−906.8	−364.7374
PH₂	−23328.5	+23.0	−617.2	−342.4866	PO	−30807.7	−60.7	−952.0	−416.5567
PH₃	−23682.7	+27.6	−647.7	−343.1085	SC	−30084.0	−23.3	−869.9	−436.2151
SH	−25371.7	+17.7	−647.5	−398.7414	SO	−33218.2	−54.4	−990.6	−473.3827
SH₂	−25720.4	+18.0	−683.2	−399.3773	ClO	−35736.7	−31.5	−1019.8	−535.3139
ClH	−27889.4	+15.6	−711.0	−460.8045	ClF	−37554.7	−52.6	−1098.2	−559.9862
Li₂	−3560.7	+12.2	−120.6	−14.9903	Si₂H₆	−42883.6	+89.9	−1170.4	−582.4896
LiF	−11994.2	−43.3	−461.2	−107.4382	CH₃Cl	−33809.1	+28.6	−953.5	−500.0574
HCCH	−10963.1	−22.4	−465.2	−77.2852	CH₃SH	−31641.5	+30.4	−927.4	−438.6342
H₂CCH₂	−11743.2	+5.5	−491.5	−78.5046	HOCl	−36077.7	−43.3	−1067.7	−535.9644
H₃CCH₃	−12514.1	+32.7	−518.5	−79.7048	SO₂	−41427.7	−125.5	−1377.1	−548.6482

TABLE I. (Continued)

Molecule	E_X (mh)	ΔE_P^{B88} (mh)	E_C^{BLYP} (mh)	E_0^{BLYP}(ht)	Molecule	E_X (mh)	ΔE_P^{B88} (mh)	E_C^{BLYP} (mh)	E_0^{BLYP}(ht)
H_3^+	-712.8	+3.2	-35.0	-1.3145	SH_2^+ ($^2A_1$)	-25443.6	+14.6	-649.9	-398.9182
CH_4^+	-6267.4	+12.1	-245.3	-39.9922	SH_3^+	-25825.0	+22.7	-678.2	-399.6427
NH_3^+	-7405.9	+2.2	-275.9	-56.1456	ClH^+	-27605.1	+17.2	-671.3	-460.3416
NH_4^+	-7772.7	-3.3	-321.5	-56.8355	ClH_2^+	-27958.1	+14.9	-710.9	-461.0148
OH^+	-8254.7	-4.4	-258.0	-75.2509	$HCCH^+$	-10693.0	-12.1	-415.8	-76.8770
OH_2^+	-8617.9	-20.2	-318.8	-75.9544	$HCHCH^+$	-11058.1	-11.8	-454.4	-77.5290
OH_3^+	-9010.7	-30.8	-371.3	-76.6726	$H_2CCH_2^+$	-11491.0	+20.6	-436.9	-78.1279
FH^+	-10042.3	-24.6	-343.5	-99.8670	CO^+	-13074.2	-60.5	-493.9	-112.7915
SiH_4^+	-21493.4	+34.9	-575.4	-291.4343	N_2^+ ($^2\Sigma_g$)	-12627.8	-124.5	-565.7	-108.9565
SiH_5^+	-21858.4	+45.9	-599.6	-292.0725	N_2^+ ($^2\Pi_u$)	-12672.8	-79.2	-516.3	-108.9239
PH^+	-22712.6	+14.0	-572.2	-341.5041	O_2^+	-15805.1	-162.8	-701.6	-149.8867
PH_2^+	-23062.8	+17.9	-602.6	-342.1292	P_2^+	-44940.9	-16.8	-1193.3	-682.3300
PH_3^+	-23468.1	+34.3	-604.8	-342.7509	S_2^+	-49725.4	-25.8	-1305.4	-796.0443
PH_4^+	-23834.3	+43.7	-631.3	-343.4005	Cl_2^+	-54756.5	-9.9	-1389.6	-919.9705
SH^+	-25132.4	+20.2	-605.6	-398.3625	ClF^+	-37256.5	-57.4	-1067.1	-559.5236
SH_2^+ ($^2B_1$)	-25473.5	+20.9	-643.7	-398.9995	SC^+	-29976.7	-0.4	-792.4	-435.7734
CH^-	-5605.3	-6.8	-217.1	-38.5079	SiH^-	-20808.6	+19.4	-554.4	-290.0130
CH_2^-	-5954.2	-7.6	-257.7	-39.1421	SiH_2^-	-21161.9	+24.9	-585.0	-290.6231
CH_3^-	-6324.1	-6.1	-293.6	-39.7860	SiH_3^-	-21525.1	+30.9	-613.0	-291.2379
NH^-	-7060.3	-31.7	-304.5	-55.2229	PH^-	-23107.9	+12.3	-623.5	-341.9039
NH_2^-	-7420.9	-38.3	-350.3	-55.8777	PH_2^-	-23459.1	+15.8	-654.8	-342.5264
OH^-	-8736.9	-60.1	-396.7	-75.7963	SH^-	-25537.2	+9.3	-688.4	-398.8217
O_2^-	-16524.2	-125.7	-725.7	-150.3576	PO^-	-31051.7	-45.6	-954.7	-416.5931
NO^-	-14985.7	-79.1	-624.0	-129.9011	S_2^-	-50242.9	+5.5	-1326.0	-796.4407
CN^-	-11848.8	-56.9	-516.2	-92.8482	Cl_2^-	-55271.4	+10.2	-1417.2	-920.4807

TABLE II. Energies for neutral atoms[a].

Atom	E(UHF)	E(BLYP)	E(Sch)[b]	ΔE(BLYP-Sch)
H	-0.4998	-0.4970	-0.5000	+3.0
He	-2.8599	-2.9026	-2.9042	+1.6
Li	-7.4320	-7.4796	-7.4781	-1.5
Be	-14.5719	-14.6574	-14.6673	+9.9
B	-24.5311	-24.6467	-24.6539	+7.2
C	-37.6903	-37.8399	-37.8451	+5.2
N	-54.3989	-54.5809	-54.5895	+8.6
O	-74.8093	-75.0721	-75.0673	-4.8
F	-99.4018	-99.7432	-99.7313	-11.9
Ne	-128.5266	-128.9411	-128.937	-4.

[a] Total energies in hartrees; differences in millihartrees.
[b] Based on Hartree-Fock and correlation estimates [15], but with the Lamb Shift correction reversed in sign as pointed out [16].

mean accuracy is quite close to that obtained by Becke [3], 3.7 kcal/mol, based on the original 55 compounds. He uses a combination of B88 and a correlation correction based on the paramatrization of the free-electron gas by Vosko et al. [17]. We shall refer to this procedure as B92.

A detailed examination of the entries in Table III shows little correlation with errors reported for B92, even though the overall performance is comparable. The BLYP binding energies are mostly too small, whereas B92 tends to overbind. A large BLYP error occurs for the CN radical, for which D_0 is 13.4 kcal/mol too low; B92 gives a value 6.1 kcal/mol too high. This radical is known to be highly spin-contaminated at the UHF level. It is therefore of interest to note that the restricted ROHF density leads to a BLYP binding of 174.0 kcal/mol, in much better agreement with experiment. Other large BLYP errors are found for C_2H_6 and Si_2H_6, the latter giving an atomization energy 17.2 kcal/mol too small. These errors are spread over seven bonds, however. B92 gives good agreement for these molecules.

TABLE III. Total atomization energies ΣD_0 (in kcal/mol).

Molecule	BLYP	G2	Expt	Molecule	BLYP	G2	Expt
H_2	103.4	104.4	103.3	HCN	304.2	302.8	301.8
LiH	55.0	56.6	56.0	CO	253.7	258.0	256.2
BeH	52.8	45.5	46.9	HCO	271.7	271.4	270.3
CH	80.4	80.5	79.9	H_2CO	355.4	359.3	357.2
CH_2 ($^3B_1$)	177.5	178.6	179.6	H_3COH	474.9	482.3	480.8
CH_2 ($^1A_1$)	168.3	172.0	170.6	N_2	229.6	223.8	225.1
CH_3	287.8	289.1	289.2	H_2NNH_2	408.7	404.4	405.4
CH_4	387.9	393.2	392.5	NO	155.4	150.6	150.1
NH	83.0	77.9	79.0	O_2	124.3	115.6	118.0
NH_2	175.7	170.1	170.0	HOOH	253.7	252.1	252.3
NH_3	278.7	276.5	276.7	F_2	41.3	36.6	36.9
OH	103.4	101.6	101.3	CO_2	381.0	384.6	381.9
OH_2	218.4	219.6	219.3	Na_2	16.1	19.2	16.6
FH	134.6	136.3	135.2	Si_2	68.3	73.6	74.0
SiH_2 ($^1A_1$)	142.3	147.1	144.4	P_2	114.5	114.7	116.1
SiH_2 ($^3B_1$)	118.9	123.8	123.4	S_2	100.7	97.4	100.7
SiH_3	207.5	213.5	214.0	Cl_2	54.0	55.8	57.2
SiH_4	295.2	304.8	302.8	NaCl	91.2	98.8	97.5
PH_2	145.7	144.9	144.7	SiO	185.9	188.8	190.5
PH_3	224.1	226.4	227.4	SC	165.0	170.5	169.5
SH_2	170.1	173.0	173.2	SO	124.4	120.8	123.5
ClH	100.7	102.6	102.2	ClO	59.4	61.2	63.3
Li_2	19.5	25.9	24.0	ClF	60.2	61.0	60.3
LiF	135.2	137.5	137.6	Si_2H_6	482.9	503.0	500.1
HCCH	383.8	387.2	388.9	CH_3Cl	363.6	372.1	371.0
H_2CCH_2	525.2	531.7	531.9	CH_3SH	435.6	445.0	445.1
H_3CCH_3	654.6	666.6	666.3	HOCl	155.7	156.8	156.3
CN	163.2	176.0	176.6	SO_2	245.8	248.9	254.0

Table IV gives ionization energies for the same G2 set plus values for the hydrogen atom and the three inert gases helium, neon and argon. The mean absolute difference between BLYP and experiment is 0.195 eV (4.49 kcal/mol), compared with 0.054 eV (1.24 kcal/mol) by the G2 procedure. We note that the majority (30 of 42) of the BLYP ionization energies are smaller than experiment. In particular, the result for the hydrogen atom is significantly too small (by 0.08 eV). This may be traced to the failure of the Becke-88 formula to give the correct exchange energy for the hydrogen atom. On the other hand, the worst error in Table IV is for carbon monosulfide, for which the BLYP value is 0.69 eV too large. Our results show comparable accuracy to a smaller set of ionization energies of another DFT study reported by Ziegler [11], using different functionals.

Table V lists electron affinities for the G2 dataset. The mean error for BLYP is found to be 0.137 eV (3.16 kcal/mol), compared with 0.056 eV (1.29 kcal/mol) for G2 theory. The majority (20 of 25) of the values are numerically too small. However, the result more seriously in error is the cyano radical, for which the BLYP electron affinity is 0.74 eV too high. This large error evidently is due to the poor description of the neutral radical, as already noted in the discussion of atomization energies. Our results may be compared with a DFT study of electron affinities due to Ziegler and Gutsev [18], using different functionals. They studied many of the same molecules and also found an average error of about 0.2 eV. However, for the cyano radical, they obtain an electron affinity which is too small, whereas ours is

TABLE IV.   Ionization potentials (eV).

Molecule	BLYP	G2	Expt	Molecule	BLYP	G2	Expt
H	13.52	13.60	13.60	OH_2	12.51	12.63	12.62
He	24.76	24.54	24.59	FH	15.99	16.08	16.04
Li	5.51	5.34	5.39	SiH_4	10.70	11.01	11.00
Be	8.97	9.41	9.32	PH	9.95	10.09	10.15
B	8.56	8.20	8.30	PH_2	9.73	9.72	9.82
C	11.36	11.18	11.26	PH_3	9.73	9.87	9.87
N	14.48	14.48	14.54	SH	10.31	10.31	10.37
O	14.07	13.52	13.61	SH_2 ($^2B_1$)	10.28	10.43	10.47
F	17.65	17.39	17.42	SH_2 ($^2A_1$)	12.49	12.75	12.78
Ne	21.64	21.61	21.56	ClH	12.60	12.71	12.75
Na	5.31	4.95	5.139	HCCH	11.11	11.42	11.40
Mg	7.60	7.65	7.646	H_2CCH_2	10.25	10.58	10.51
Al	5.81	5.93	5.984	CO	14.28	14.01	14.01
Si	7.92	8.10	8.15	N_2 ($^2\Sigma_g$)	15.54	15.56	15.58
P	10.20	10.44	10.49	N_2 ($^2\Pi_u$)	16.42	16.67	16.70
S	10.32	10.20	10.36	O_2	12.40	12.17	12.07
Cl	12.89	12.85	12.97	P_2	10.16	10.54	10.53
Ar	15.64	15.69	15.76	S_2	9.27	9.28	9.36
CH_4	12.35	12.68	12.62	Cl_2	11.15	11.51	11.50
NH_3	10.08	10.19	10.18	ClF	12.59	12.65	12.66
OH	13.14	12.98	13.01	SC	12.02	11.42	11.33

TABLE V.   Electron affinities (eV).

Molecule	BLYP	G2	Expt.	Molecule	BLYP	G2	Expt.
C	1.18	1.19	1.26	Si	1.17	1.35	1.385
CH	1.17	1.13	1.24	SiH	0.99	1.18	1.277
CH$_2$	0.69	0.66	0.65	SiH$_2$	0.91	0.99	1.124
CH$_3$	−0.10	0.04	0.08	SiH$_3$	1.28	1.42	1.44
CN	4.56	3.97	3.82	P	0.76	0.64	0.746
NH	0.35	0.30	0.38	PH	0.93	0.96	1.00
NH$_2$	0.62	0.77	0.74	PH$_2$	1.08	1.25	1.26
NO	0.01	−0.07	0.02	PO	0.99	1.04	1.09
O	1.50	1.40	1.46	S	2.05	2.00	2.077
OH	1.70	1.87	1.83	SH	2.19	2.30	2.314
O$_2$	0.42	0.47	0.44	S$_2$	1.51	1.66	1.663
F	3.37	3.48	3.40	Cl	3.56	3.60	3.615
				Cl$_2$	2.73	2.38	2.39

much too large. Like us, they use spin-unrestricted methods. The reasons for this anomaly are hard to pursue further as Ziegler and Gutsev do not report their detailed energy components for the separate species CN and CN$^-$.

Table VI gives eight proton affinities that are compared with G2 theory and experiment. Here the performance of BLYP is quite good, the mean error of 2.11 kcal/mol being not much greater than the value of 1.04 kcal/mol obtained at the G2 level. This superior performance is not surprising, since no change in the number of electrons is involved and the electron configurations of the protonated species are closely related to those of the neutral molecules.

Combining all of the 130 experimental comparisons in Tables III to VI, we obtain an overall mean absolute error of 3.86 kcal/mol for the BLYP model. This is not much greater than the value of 3.7 kcal/mol obtained by Becke [3] for atomization energies only.

Parallel and Antiparallel Contributions

We return now to the interpretation of the separation of E_{XC} into parallel and antiparallel parts, E_P^{B88} and E_A^{LYP}. As noted earlier, one possibility is that the parallel

TABLE VI.   Proton affinities (kcal/mol).

Molecule	BLYP	G2	Expt	Molecule	BLYP	G2	Expt
H$_2$	97.7	99.2	100.8	SiH$_4$	153.7	153.0	154.
HCCH	153.0	153.6	152.3	PH$_3$	183.2	186.2	187.1
NH$_3$	200.5	202.5	202.5	H$_2$S	166.5	167.7	168.8
H$_2$O	162.1	163.1	165.1	HCl	132.0	133.0	133.6

part represents the full exchange energy plus further energy lowering due to extra (non-Hartree-Fock) correlation energy between $\alpha\alpha$ and $\beta\beta$ pairs. Inspection of Table I, clearly shows that this cannot be correct in all cases because the Becke-88 excess ΔE_P^{B88} is sometimes *positive*, indicating an energy lowering of *less* than the exchange energy. This cannot be correct. It shows up for the hydrogen atom, where there is no electron correlation, but the Becke-88 energy fails to cancel the coulomb energy E_J, as it should. This may, of course, be a fault of the particular analytic form of the Becke-88 energy. Indeed, the constant b in Eq. (7) could be increased so that ΔE_P^{B88} is zero for the hydrogen atom; all values of ΔE_P^{B88} for other systems then become negative. However, we will not investigate modified functionals here.

Another possibility is that the partition of correlation into ΔE_P^{B88} and E_A^{LYP} gives the breakdown of *correlation binding* into parallel and antiparallel parts, even though this does not work fully for the isolated atoms. We have tested this idea by evaluating some of these binding contributions from Table I (they turn out all to be positive) and compare them with the corresponding parallel ($\alpha\alpha + \beta\beta$) and antiparallel ($\alpha\beta$) contributions from an MP2 treatment (frozen core or valence electrons only with the same basis), where the parallel-antiparallel partition is unequivocal. This comparison as displayed in Table VII shows moderate success for the simple hydrides CH$_4$, NH$_3$, OH$_2$, and FH. However, for the two heavy-atom molecules N$_2$ and F$_2$, the comparison is much less successful. For F$_2$, the satisfactory reproduction of the total correlation binding (as evidenced by the good dissociation energy in Table III) is ascribed mainly to the parallel (Becke-88) part rather than to the antiparallel (LYP) part. At the MP2 level, the opposite is true. Evidently, the success of the BLYP procedure cannot be fully understood along these lines; new insight is needed.

Conclusions

The following conclusions are drawn from this work:

1. The BLYP procedure described, based on existing energy functionals and using the Hartree-Fock density, is capable of giving total energies in reasonable agreement ($\sim$20 mh) with exact Schrödinger energies, insofar as these are known.

TABLE VII. Parallel and antiparallel binding energies (mh).

Molecule	Parallel		Antiparallel	
	MP2($\alpha\alpha + \beta\beta$)	$\Delta(\Delta E^{B88})$	MP2($\alpha\beta$)	$\Delta(E^{LYP})$
CH$_4$	23.4	2.9	103.4	135.8
NH$_3$	22.8	31.4	114.1	125.9
OH$_2$	28.6	37.5	89.9	83.5
FH	21.5	28.3	52.0	41.3
N$_2$	40.1	99.6	153.1	97.0
F$_2$	34.7	97.9	90.5	32.8

2. Various differences of BLYP total energies reproduce good experimental data on atomization energies, ionization energies, electron affinities and proton affinities to an accuracy of about 4 kcal/mol or 0.2 eV. Even though this does not match the greater accuracy achieved by G2 theory, it is a significant achievement for a method of moderate computational cost. The use of a single, well-defined, theoretical procedure for all of these physical properties gives some coherence to the theory.

3. The partition of the electron correlation into parallel (B88) and antiparallel (LYP) parts does not always match the corresponding partition in simple Møller-Plesset theory. The significance of the individual components of BLYP (or other comparable density functional treatments) is not fully understood.

Acknowledgments

Appendix: Numerical Integration in Three Dimensions

Our preliminary method for evaluating density functionals such as (7) is closely related to that described by Becke [19] but, for various reasons, we have made a number of modifications to his scheme which we now describe.

(1) Our cell functions $P_i(r)$ are identical to Becke's for homonuclear systems, but we have *not* found it necessary to adopt the "atomic size adjustments" which Becke suggests for heteronuclear systems.

(2) We employ Gauss-Laguerre, rather than Gauss-Chebyshev, quadrature for the single-center radial subintegrations. This choice was motivated by the fact that the true electron density is known to decay exponentially at large distances from the molecule.

(3) We use 31 radial points on each center, scaled so that the 16th (middle) point lies at the maximum of the radial probability function $4\pi r^2 \varphi^2(r)$ of the valence atomic orbital $\varphi(r)$ given by Slater's well known rules [20]. For example, the 16th radial point for a hydrogen atom lies at $r = 1.0$ au and that for a carbon atom lies at $r = 16/13$ au.

(4) We use 72 angular points at each radial point. The distribution of these is given by a special set of 12 points corresponding to the vertices of a regular icosahedron inscribed in the sphere (the axes of the icosahedron follow the "standard orientation" conventions of the GAUSSIAN program), plus a general set of 60 points generated by the rotation subgroup of the icosahedral group. Such formulae, based on finite rotation subgroups of the sphere, are highly efficient in the sense that the number of surface harmonics exactly integrated by them is close to one per angular point. A clear exposition of the theory of

this approach to quadrature on the surface of a sphere can be found in the literature [21].

If the electron density $\rho(r)$ itself is integrated using this preliminary scheme, the results agree with the total number of electrons to within a few thousandths of an electron for all of the molecules studied. Furthermore, we have observed that both the B88 and LYP functional values are comparatively insensitive to further improvements in the grid. Nonetheless, further work is underway to construct even more efficient integration schemes.

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