Density-functional thermochemistry. III. The role of exact exchange

Axel D. Becke

Articles you may be interested in

Efficient exact exchange approximations in density-functional theory
J. Chem. Phys. **123**, 164116 (2005); 10.1063/1.2072887

Density-functional theory (hyper)polarizabilities of push-pull π -conjugated systems: Treatment of exact exchange and role of correlation
J. Chem. Phys. **123**, 014319 (2005); 10.1063/1.1926275

Accurate polymer polarizabilities with exact exchange density-functional theory
J. Chem. Phys. **119**, 11001 (2003); 10.1063/1.1630011

Density-functional thermochemistry. V. Systematic optimization of exchange-correlation functionals
J. Chem. Phys. **107**, 8554 (1997); 10.1063/1.475007

Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exact-exchange mixing
J. Chem. Phys. **104**, 1040 (1996); 10.1063/1.470829
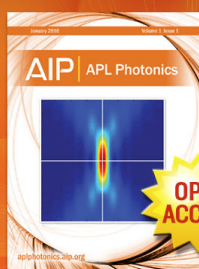
Density-functional thermochemistry. III. The role of exact exchange

Axel D. Becke
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Despite the remarkable thermochemical accuracy of Kohn–Sham density-functional theories with gradient corrections for exchange-correlation [see, for example, A. D. Becke, J. Chem. Phys. **96**, 2155 (1992)], we believe that further improvements are unlikely unless *exact-exchange* information is considered. Arguments to support this view are presented, and a semiempirical exchange-correlation functional containing local-spin-density, gradient, and exact-exchange terms is tested on 56 atomization energies, 42 ionization potentials, 8 proton affinities, and 10 total atomic energies of first- and second-row systems. This functional performs significantly better than previous functionals with gradient corrections only, and fits experimental atomization energies with an impressively small average absolute deviation of 2.4 kcal/mol.

I. INTRODUCTION

This is the third in a series of papers on the assessment of density-functional theory (DFT) on the atoms and molecules of the Gaussian-1 (G1) database of Pople and co-workers.[1,2] In the first paper,[3] hereafter referred to as paper I, we demonstrated that the well-known overbinding tendency of the local-spin-density exchange-correlation approximation (LSDA) is nicely compensated by the exchange-only density-gradient correction of Becke.[4] Our second paper[5] (paper II) indicated that the exchange-only gradient correction by itself gives extremely poor ionization potentials, and must be accompanied by a gradient correction for *dynamical correlation* if a generally reliable thermochemical procedure is desired. For this purpose, we adopted the gradient-corrected correlation functional of Perdew and Wang.[6]

Motivated by a reexamination of the *adiabatic connection* formula for exchange-correlation energy,[7] we have also recently investigated[8] a novel "half-and-half" mixing of *exact*-exchange energy and the LSDA for exchange-correlation *potential* energy which performs as well on the G1 thermochemical tests as the gradient-corrected DFT of paper II. We found, in addition, that a simple two-parameter semiempirical generalization[8] accurately fits the G1 data, for atomization only, with an average absolute deviation from experiment of 2.6 kcal/mol, thus offering a tantalizing hint of the future potential of this approach.

Unfortunately, our half-and-half theory of Ref. 8 is defective in several respects. Though energy differences of thermochemical interest are well obtained, *total* energies are rather poor. The uniform electron-gas limit is not obtained, a disturbing failure from a formal density-functional perspective. Also, our semiempirical generalization gives good atomization energies only, while ionization potentials and proton affinities are extremely poor. In the present work, we address these problems by incorporating the gradient corrections for exchange and correlation examined in papers I and II into our exact-exchange–local-DFT approach. With the added flexibility of gradient correction terms, an impressive overall fit to G1 thermo-chemical data, total atomic energies, and even the uniform electron gas is achieved.

A review of the Kohn–Sham DFT formalism, on which this work is based, was presented in paper I and will not be repeated here. Excellent expositions of density-functional theory in general are also available elsewhere.[9] Instead, we begin the following section with a discussion of the adiabatic connection formula[7] and its physical content. The most important implication of this discussion is the undeniable role of exact exchange. Despite the well-intentioned efforts of density-functional researchers to circumvent the calculation of exact-exchange energies, we shall see that a small exact-exchange component is a natural and necessary constituent of any exchange-correlation approximation aiming for accurate molecular energetics.

II. THE ADIABATIC CONNECTION

The exchange-correlation energy E_{XC} of Kohn–Sham density-functional theory is given by a rigorous *ab initio* formula known as the "adiabatic connection" formula.[7] Of the many possible forms that this important result may take, the following is most convenient for our purposes:

$$E_{XC} = \int_0^1 U_{XC}^\lambda \, d\lambda, \qquad (1)$$

where λ is an interelectronic coupling-strength parameter that "switches on" the $1/r_{12}$ Coulomb repulsion between electrons, and U_{XC}^λ is the *potential energy* of exchange-correlation at intermediate coupling strength λ. This formula "connects" the noninteracting Kohn–Sham reference system (defined by $\lambda = 0$) to the fully interacting real system ($\lambda = 1$) through a continuum of *partially* interacting systems ($0 \leqslant \lambda \leqslant 1$), all of which share a common density ρ (the density of the real, fully interacting system). Though the integrand of Eq. (1) refers explicitly to *potential* energy only, the *kinetic* part of the exchange-correlation energy is generated, in effect, by the λ integration. A simple derivation of this adiabatic connection formula using first-order perturbation theory may be found in the Appendix of Ref. 10.

We believe that careful consideration of the λ dependence of the integrand in Eq. (1) is important in understanding the successes and failures of current density-functional theories. In particular, the $\lambda = 0$ lower limit, corresponding to the noninteracting Kohn–Sham reference system, is of major relevance. Here, the exchange-correlation potential energy U_{XC}^0 is the *pure exchange energy of the Slater determinant of the Kohn–Sham orbitals*, with no dynamical correlation whatsoever. This Kohn–Sham exchange energy will be designated E_X from now on, and is essentially, though not exactly, equal in value to the conventional Hartree–Fock exchange energy. We refer the reader to Ref. 8 and references therein for further discussion of this point.

The conventional exchange-correlation LSDA substitutes for each U_{XC}^λ in Eq. (1) a model value from local uniform-electron-gas theory. Unfortunately, the local electron-gas model is physically inappropriate near the $\lambda = 0$ exchange-only limit in molecular bonds. The problem may be understood by considering, for the sake of argument, H_2. In this simplest conceivable case, the exact (restricted) *exchange hole* is the negative of the σ_g orbital density and is reference-point independent. This static hole, uniformly distributed over both centers, implies a complete absence of left–right correlation in the H_2 bond. The electron-gas model hole, on the other hand, is reference-point centered, relatively localized, and thus "follows" its reference electron around. The effect is a crude simulation of left–right correlation which, though desirable in the *interacting* system, clearly misrepresents the noninteracting $\lambda = 0$ limit. Consequently, we believe that the principal source of the overbinding error of the LSDA is the $\lambda = 0$ end of the coupling-strength integration.

Furthermore, Gunnarsson and Jones[11] have argued convincingly that density-functional energy differences suffer conspicuous errors if orbital *nodes* are created or lost in the process (e.g., antibonding orbitals). The intricacies of exact-exchange-energy differences corresponding to changes in orbital nodality are particularly poorly described by local electron-gas models. Again, the problem is most acute at $\lambda = 0$.

These arguments apply to density-functional exchange-correlation approximations with gradient corrections as well. We therefore suspect that gradient-corrected DFT, no matter how sophisticated and no matter how well *atomic* total energies are reproduced, will always display at least slight overbinding tendencies. Indeed, perusal of the atomization energy data in paper II reveals a distinct overbinding tendency for the *nonhydride* systems, though hydrides are well treated.

Our "half-and-half" theory of Ref. 8 approximates Eq. (1) as the *average* of the *exact*-exchange energy at $\lambda = 0$ and the LSDA for exchange-correlation *potential* energy at $\lambda = 1$. Thus, we employ the electron-gas model at full interaction strength only, and discard its problematic $\lambda = 0$ limit altogether. This approximation performs quite well on the thermochemical tests of the G1 database (average absolute deviation of 6.5 kcal/mol and maximum deviation of -22.5 kcal/mol for atomization energies) and, indeed,

rivals the gradient-corrected DFT of paper II (average absolute deviation of 5.7 kcal/mol and maximum deviation of $+18.4$). In the following section, we extend the work of Ref. 8 by relaxing the linear λ dependence underlying the half-and-half model, and by including gradient corrections.

III. THE PRESENT MODEL

To reiterate the arguments of the preceding section: the $\lambda = 0$ limit of the coupling-strength integration of Eq. (1) is *nothing more* and *nothing less* than *exact exchange*. Surely, therefore, exact exchange energy must play a role in highly accurate density-functional theories. Accordingly, we propose the following exchange-correlation approximation:

$$E_{XC} = E_{XC}^{LSDA} + a_0(E_X^{exact} - E_X^{LSDA}) + a_X \Delta E_X^{B88} + a_C \Delta E_C^{PW91}, \tag{2}$$

where a_0, a_X, and a_C are *semiempirical coefficients* to be determined by an appropriate fit to experimental data, E_X^{exact} is the *exact* exchange energy, ΔE_X^{B88} is Becke's 1988 gradient correction (to the LSDA) for exchange,[4] and ΔE_C^{PW91} is the 1991 gradient correction for correlation of Perdew and Wang.[6] These are the same gradient corrections considered in papers I and II. For the correlation component of the leading term E_{XC}^{LSDA}, we use the electron-gas parametrization of Ref. 12.

Equation (2) is motivated by reasonable physical arguments. The second term replaces *some* electron-gas exchange with *exact* exchange to capture the proper small-λ limit of Eq. (1). The coefficient a_0 thus reflects the relative importance of a system's independent-particle character, or, equivalently, the rate of onset of correlation as λ increases from zero. We assume as a first approximation in this work, that its value is constant. The third and fourth terms allow optimum admixtures of exchange and correlation-type gradient corrections. Clearly, the coefficient a_X has value less than unity, since the presence of the E_X^{exact} term reduces the need for the gradient correction ΔE_X^{B88}. For good measure, we allow flexibility in the coefficient a_C as well. Notice, also, that Eq. (2) is the simplest possible mixture of exact exchange, the LSDA for exchange-correlation, and gradient corrections of exchange and correlation type, that exactly recovers the uniform electron-gas limit.

This functional has been applied to the atoms and molecules of the G1 database, following exactly the same basis-set-free, post-LSDA computational procedure as in papers I and II and in Ref. 8. We refer the interested reader to these previous publications for descriptions of the methodology. The semiempirical coefficients of Eq. (2) have been determined by a linear least-squares fit to the 56 atomiza-

tion energies, 42 ionization potentials, 8 proton affinities, and the 10 first-row total atomic energies of Ref. 13. The resulting optimum values are

$$a_0 = 0.20, \quad a_X = 0.72, \quad a_C = 0.81, \tag{3}$$

TABLE I. Atomization energies D_0 (kcal/mol).

	Expt.[a]	Eq. (2)	Δ[b]
H_2	103.5	101.6	−1.9
LiH	56.0	52.9	−3.1
BeH	46.9	54.5	+7.6
CH	79.9	79.9	0.0
$CH_2(^3B_1)$	179.6	184.1	+4.5
$CH_2(^1A_1)$	170.6	168.2	−2.4
CH_3	289.2	292.6	+3.4
CH_4	392.5	393.5	+1.0
NH	79.0	81.3	+2.3
NH_2	170.0	173.1	+3.1
NH_3	276.7	276.8	+0.1
OH	101.3	101.9	+0.6
H_2O	219.3	217.0	−2.3
HF	135.2	133.3	−1.9
Li_2	24.0	17.9	−6.1
LiF	137.6	131.7	−5.9
C_2H_2	388.9	389.0	+0.1
C_2H_4	531.9	534.3	+2.4
C_2H_6	666.3	668.7	+2.4
CN	176.6	176.7	+0.1
HCN	301.8	302.4	+0.6
CO	256.2	253.4	−2.8
HCO	270.3	273.7	+3.4
H_2CO	357.2	357.9	+0.7
CH_3OH	480.8	480.8	0.0
N_2	225.1	223.0	−2.1
N_2H_4	405.4	407.2	+1.8
NO	150.1	151.5	+1.4
O_2	118.0	123.1	+5.1
H_2O_2	252.3	249.8	−2.5
F_2	36.9	35.6	−1.3
CO_2	381.9	385.1	+3.2
$SiH_2(^1A_1)$	144.4	142.8	−1.6
$SiH_2(^3B_1)$	123.4	126.4	+3.0
SiH_3	214.0	213.3	−0.7
SiH_4	302.8	300.0	−2.8
PH_2	144.7	146.8	+2.1
PH_3	227.4	225.6	−1.8
H_2S	173.2	172.7	−0.5
HCl	102.2	102.0	−0.2
Na_2	16.6	13.2	−3.4
Si_2	74.0	76.3	+2.3
P_2	116.1	112.2	−3.9
S_2	100.7	105.8	+5.1
Cl_2	57.2	58.6	+1.4
NaCl	97.5	92.6	−4.9
SiO	190.5	184.2	−6.3
CS	169.5	166.9	−2.6
SO	123.5	126.5	+3.0
ClO	63.3	66.6	+3.3
ClF	60.3	60.7	+0.4
Si_2H_6	500.1	496.7	−3.4
CH_3Cl	371.0	373.2	+2.2
CH_3SH	445.1	446.2	+1.1
HOCl	156.3	156.2	−0.1
SO_2	254.0	251.4	−2.6

[a]From Refs. 13 and 14.
[b]Deviation from experiment for theory of Eq. (2).

TABLE II. Ionization potentials (eV).

	Expt.[a]	Eq. (2)	Δ[b]
H	13.60	13.71	+0.11
He	24.59	24.71	+0.12
Li	5.39	5.56	+0.17
Be	9.32	9.02	−0.30
B	8.30	8.71	+0.41
C	11.26	11.58	+0.32
N	14.54	14.78	+0.24
O	13.61	13.95	+0.34
F	17.42	17.58	+0.16
Ne	21.56	21.60	+0.04
Na	5.14	5.27	+0.13
Mg	7.65	7.57	−0.08
Al	5.98	6.12	+0.14
Si	8.15	8.25	+0.10
P	10.49	10.57	+0.08
S	10.36	10.48	+0.12
Cl	12.97	13.04	+0.07
Ar	15.76	15.80	+0.04
CH_4	12.62	12.47	−0.15
NH_3	10.18	10.12	−0.06
OH	13.01	13.09	+0.08
H_2O	12.62	12.54	−0.08
HF	16.04	15.99	−0.05
SiH_4	11.00	10.85	−0.15
PH	10.15	10.31	+0.16
PH_2	9.82	10.03	+0.21
PH_3	9.87	9.81	−0.06
SH	10.37	10.43	+0.06
$SH_2(^2B_1)$	10.47	10.42	−0.05
$SH_2(^2A_1)$	12.78	12.64	−0.14
HCl	12.75	12.74	−0.01
C_2H_2	11.40	11.23	−0.17
C_2H_4	10.51	10.36	−0.15
CO	14.01	14.05	+0.04
$N_2(^2\Sigma_g)$	15.58	15.77	+0.19
$N_2(^2\Pi_u)$	16.70	16.65	−0.05
O_2	12.07	12.46	+0.39
P_2	10.53	10.41	−0.12
S_2	9.36	9.58	+0.22
Cl_2	11.50	11.35	−0.15
ClF	12.66	12.55	−0.11
CS	11.33	11.34	+0.01

[a]From Refs. 13 and 14.
[b]Deviation from experiment for theory of Eq. (2).

TABLE III. Proton affinities (kcal/mol).

	Expt.[a]	Eq. (2)	Δ[b]
H_2	100.8	100.9	+0.1
C_2H_2	152.3	157.0	+4.7
NH_3	202.5	204.4	+1.9
H_2O	165.1	165.7	+0.6
SiH_4	154.0	153.9	−0.1
PH_3	187.1	186.1	−1.0
H_2S	168.8	168.9	+0.1
HCl	133.6	134.6	+1.0

[a]From Refs. 13 and 14.
[b]Deviation from experiment for theory of Eq. (2).

TABLE IV. Total atomic energies (hartrees).

	Exact[a]	Eq. (2)	Δ[b]
H	−0.500	−0.504	−0.004
He	−2.904	−2.908	−0.004
Li	−7.478	−7.484	−0.006
Be	−14.667	−14.657	+0.010
B	−24.654	−24.644	+0.010
C	−37.845	−37.837	+0.008
N	−54.590	−54.582	+0.008
O	−75.067	−75.066	+0.001
F	−99.731	−99.735	−0.004
Ne	−128.937	−128.935	+0.002

[a]From Ref. 13.
[b]Deviation from exact energy for theory of Eq. (2).

and the overall *root-mean-square* deviation from experiment for the complete set of 116 data points is 3.35 kcal/mol.

We omit electron affinities from consideration here because the LSDA exchange-correlation potential does not bind negative ions, a well-known failure of the local-spin-density approximation. Anions must therefore be stabilized by Watson-sphere-like potentials in the present post-LSDA framework, and, given the somewhat arbitrary nature of such stabilizing potentials, we choose not to include electron affinities in this work.

In Tables I–IV, we list all atomization energies, ionization potentials, proton affinities, and total atomic energies, respectively, of the present tests. Tables V and VI summarize average absolute and maximum deviations. For energies of atomization, the results of our optimized Eq. (2) have an average absolute deviation from experiment of only 2.4 kcal/mol, and a maximum deviation of 7.6. This is less than half the error of the gradient-corrected DFT of paper II (5.7 kcal/mol average), and only twice the error of the Gaussian-2 theory of Pople and co-workers[14] (1.2 kcal/mol average[13]). We concede, however, that the present results are generated by a three-parameter least-squares fit, and therefore represent the *best possible* performance of this class of exchange-correlation functionals.

For ionization potentials, our average absolute deviation is 0.14 eV, compared with 0.15 in paper II and 0.05 for Gaussian-2.[13] Our proton affinities have an average deviation of only 1.2 kcal/mol, compared with 1.5 in paper II and 1.0 for Gaussian-2.[13] Maximum deviations are listed in

TABLE V. Average absolute deviations.

	G2[a]	Eq. (2)	GC[b]
Atomization energies (kcal/mol)	1.2	2.4	5.7
Ionization potentials (eV)	0.05	0.14	0.15
Proton affinities (kcal/mol)	1.0	1.2	1.5
Total energies (mhartree)		6.0	11.0

[a]G2: Gaussian-2 theory (Refs. 13 and 14).
[b]GC: Gradient-corrected DFT of Ref. 5.

TABLE VI. Maximum absolute deviations.

	G2[a]	Eq. (2)	GC[b]
Atomization energies (kcal/mol)	5.1	7.6	18.4
Ionization potentials (eV)	0.19	0.41	0.44
Proton affinities (kcal/mol)	2.0	4.7	4.2
Total energies (mhartree)		10.0	29.0

[a]G2: Gaussian-2 theory (Refs. 13 and 14).
[b]GC: Gradient-corrected DFT of Ref. 5.

Table VI. Even the *total* energies of the first-row atoms H through Ne are well reproduced, with an average error of 6 mhartree and a maximum error of 10. Recalling, also, that Eq. (2) contains the exact uniform-electron-gas limit, it is fair to say that our functional fits an impressive variety of experimental and theoretical data.

IV. CONCLUSIONS AND OUTLOOK

We have revealed in this work the important and potentially powerful role of exact exchange in density-functional thermochemistry. The semiempirical combination of exact exchange, the LSDA, and gradient correction terms in Eq. (2) performs significantly better than the gradient-corrected exchange-correlation functional of paper II (Ref. 5), and approaches an average precision of order 2 kcal/mol (or 0.1 eV, 10 kJ/mol). This is the accuracy considered by Pople and co-workers[1] as a desirable target for quantum thermochemical methods, and which is comfortably met by the composite *ab initio* Gaussian-2 procedure.[14] The same target accuracy now appears realistic for density-functional theory.

In future studies, we hope to eliminate the semiempirical aspects of the present model through detailed analysis of λ dependence in the adiabatic connection formula, or perhaps through insights from perturbation theory. Given the encouraging level of precision achieved here, we feel that the extra computational effort (for some!) of exact-exchange evaluation is well rewarded.

[1]J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, J. Chem. Phys. **90**, 5622 (1989).
[2]L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **93**, 2537 (1990).
[3]A. D. Becke, J. Chem. Phys. **96**, 2155 (1992).
[4]A. D. Becke, Phys. Rev. A **38**, 3098 (1988); in *The Challenge of d and f Electrons*, edited by D. R. Salahub and M. C. Zerner, Vol. 394 in ACS Symposium Series (American Chemical Society, Washington, DC, 1989), p. 165.
[5]A. D. Becke, J. Chem. Phys. **97**, 9173 (1992).

[6] J. P. Perdew, in *Electronic Structure of Solids*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991); J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992); J. P. Perdew and Y. Wang (unpublished).

[7] J. Harris and R. O. Jones, J. Phys. F **4**, 1170 (1974); O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976); D. C. Langreth and J. P. Perdew, *ibid.* **15**, 2884 (1977); J. Harris, Phys. Rev. A **29**, 1648 (1984).

[8] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).

[9] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[10] A. D. Becke, J. Chem. Phys. **88**, 1053 (1988).

[11] O. Gunnarsson and R. O. Jones, Phys. Rev. B **31**, 7588 (1985).

[12] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[13] P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch, Int. J. Quantum Chem. Quantum Chem. Symp. **26**, 319 (1992).

[14] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, J. Chem. Phys. **94**, 7221 (1991).