

The adiabatic connection method: A non-empirical hybrid

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For systems in which generalized gradient approximations (GGA's) work better for exchange-correlation energies than for exchange alone, a simple hybrid of GGA energies with the exact exchange energy is derived which improves the GGA result. A criterion is given which shows when this hybrid makes the greatest improvement. Results for molecules are given, showing that multiply-bonded systems are most improved.

I. INTRODUCTION

The generalized gradient approximations (GGA's) [1–4] of density functional theory [5,6] have become popular for calculating chemical reaction energies, because they combine accuracy with computational efficiency [7]. However, they have not yet achieved reliable chemical accuracy [8].

Since GGA's can be divided into exchange and correlation contributions to the energy, one can compare both the exchange and the exchange-correlation energies with more accurate calculations for small systems. Typically, the GGA error is *smaller* for the exchange-correlation energy than for the exchange energy. Loosely, when correlation is turned on, the hole around a point in the system becomes deeper and more short-ranged, so that approximations that use local information (the density and its gradient) to estimate the energy improve [9,10]. This has led to suggestions for improving the accuracy of density functionals, by replacing a fraction of the density functional exchange energy with the exact exchange energy [9,11]. As a working hypothesis, the amount of mixing may be taken to be constant, and empirical fits on limited data sets of atomization energies usually yield about 25% for the optimal mixing parameter [12]. However, some systems and properties seem to require more or less mixing than about 25%. For example, as the bond length of an H_2 molecule is stretched [13–15] to infinity, the fraction of exact exchange needed changes to 0% in a spin-restricted calculation. It has also been shown that multiple-bonded molecules have greater exchange-correlation energy errors because of relatively large errors at the exchange level [16].

In the present work, we show that by making several simple assumptions about the relation of exchange to exchange-correlation, we can derive a hybrid of GGA energies with the exact exchange energy (evaluated on the GGA Kohn-Sham orbitals) with no empirical input, and

in which the mixing parameter is a functional of the density. This hybrid improves GGA atomization energies of molecules by about a factor of 3.

II. THE ADIABATIC CONNECTION

The ground state energy of a (non-relativistic) many-electron system may be written as

$$E = T + V_{ee} + V_{ext} \quad (1)$$

where T is the interacting kinetic energy, V_{ee} is the expectation value of the Coulomb repulsion between electrons, and V_{ext} is the expectation value of the external potential between the electrons and nuclei. In Kohn-Sham density functional theory [17], Eq. (1) is rewritten in terms of a non-interacting reference wavefunction with the same density, the Kohn-Sham wavefunction, so that

$$E = T_s + U + V_{ext} + E_{xc} \quad (2)$$

where T_s is the non-interacting kinetic energy, U is the classical or Hartree energy, and E_{xc} is the exchange-correlation energy. From Eq. (2),

$$E_{xc} = V_{ee} - U + T_c, \quad (3)$$

where $T_c = T - T_s$ is the difference between the interacting and non-interacting kinetic energies. Thus E_{xc} contains both potential ($V_{ee} - U$) and kinetic contributions.

The adiabatic connection relates the physical and Kohn-Sham systems in a continuous fashion. Consider the Hamiltonian

$$\hat{H} = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}_{ext,\lambda}, \quad (4)$$

where $v_{ext,\lambda}(\mathbf{r})$ is the local external potential chosen at each λ to keep the density fixed (at its physical value). At

$\lambda = 0$, the electrons are not interacting, the wavefunction is the Kohn-Sham wavefunction, and the external potential is the Kohn-Sham potential. At $\lambda = 1$, we return to the correlated interacting system. Using the Hellmann-Feynman theorem, one can show [18]

$$E_{\text{xc}} = \int_0^1 d\lambda E_{\text{xc},\lambda}, \quad (5)$$

where

$$E_{\text{xc},\lambda} = V_{ee,\lambda} - U, \quad (6)$$

and $V_{ee,\lambda}$ is the expectation value of the Coulomb electron-electron repulsion for the ground state wavefunction with coupling-constant λ . At $\lambda = 0$, there is no correlation, and $E_{\text{xc},\lambda=0} = E_{\text{x}}$. At $\lambda = 1$, combining Eqs. (3) and (6), we find $E_{\text{xc},\lambda=1} = E_{\text{xc}} - T_{\text{c}}$, i.e., the potential energy contribution to exchange-correlation. Since the actual E_{xc} is an average between these two limits, we naturally find

$$E_{\text{x}} \geq E_{\text{xc}} \geq E_{\text{xc},\lambda=1}. \quad (7)$$

The λ -dependence of the energy can be extracted from the exchange-correlation energy functional itself via the scaling relation:

$$E_{\text{xc},\lambda}[\rho] = \frac{d}{d\lambda} \left(\lambda^2 E_{\text{xc}}[\rho(\mathbf{r}/\lambda)/\lambda^3] \right) \quad (8)$$

This was first derived (in slightly different form) in Ref. [19,20], for the integrated quantity $E_{\text{xc}}^\lambda = \int_0^\lambda d\lambda E_{\text{xc},\lambda}$. E.g., if

$$E_{\text{xc}}^{\text{GGA}} = \int d^3r \rho(\mathbf{r}) \epsilon_{\text{xc}}^{\text{GGA}}(\rho, \nabla\rho), \quad (9)$$

then

$$\epsilon_{\text{xc},\lambda}^{\text{GGA}} = \frac{d}{d\lambda} \left\{ \lambda^2 \epsilon_{\text{xc}}^{\text{GGA}}(\rho(\mathbf{r})/\lambda^3, \nabla\rho(\mathbf{r})/\lambda^4) \right\}, \quad (10)$$

is the energy per electron of $E_{\text{xc},\lambda}^{\text{GGA}}$. The smooth curve of Fig. 1 is $-\Delta E_{\text{xc},\lambda} = E_{\text{xc},\lambda}(\text{molecule}) - E_{\text{xc},\lambda}(\text{atoms})$ for the atomization of N_2 , calculated [16] for the PW91 functional [1,2] (including spin-polarization for the atoms).

In terms of the adiabatic connection, local and semilocal density functionals should become more accurate as λ increases. For such approximations, we expect the errors to be ordered as

$$\delta E_{\text{x}}^{\text{GGA}} \geq \delta E_{\text{xc}}^{\text{GGA}} \geq \delta E_{\text{xc},\lambda=1}^{\text{GGA}}, \quad (11)$$

where $\delta E = |E^{\text{GGA}} - E^{\text{exact}}|$. For many problems of chemical interest, we can relatively easily calculate all three GGA results. With little extra effort, we can also calculate the (almost) exact exchange ($\lambda = 0$) energy, by inserting the GGA orbitals into the Fock integral. We cannot calculate the exact values for E_{xc} and $E_{\text{xc},\lambda=1}$ without doing a correlated wavefunction calculation. We show below how to combine the information from such calculations to improve the GGA estimate of the exchange-correlation energy.

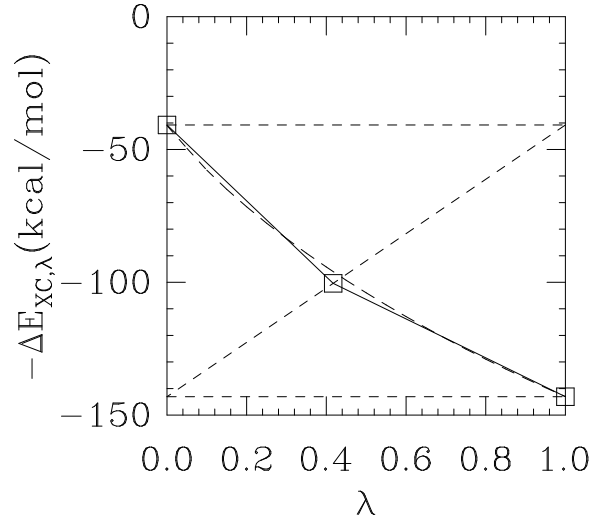


FIG. 1. Two-legged representation (solid line) of the λ -dependence of the exchange-correlation contribution to the atomization energy (ΔE) of N_2 in PW91 (dashed curve). The legs are chosen to pass through the $\lambda = 0$ (ΔE_{x}) and $\lambda = 1$ ($\Delta E_{\text{xc},\lambda=1}$) points, while meeting along the opposite diagonal at $\lambda = b$, so as to reproduce the correct λ -average (ΔE_{xc}), each marked by a square.

III. TWO-LEGGED REPRESENTATION

Before we construct our hybrid, we introduce a simple geometric construction which represents the λ -dependent curve of any functional (exact or approximate). We approximate the curve by two straight line segments, one passing through $\lambda = 0$, the other through $\lambda = 1$, and meeting at some value $\lambda = b$ in between (see Figure 1 for an application to an energy difference). If we restrict the meeting point to be somewhere along the opposite diagonal, i.e., along the dashed line running from $(\lambda = 0, E_{\text{xc},\lambda=1})$ to $(\lambda = 1, E_{\text{x}})$ then the area under this “two-legged” curve is simply the energy at which the two legs meet. We determine the positions of these legs using the three energies discussed above: At $\lambda = 0$, the first segment passes through E_{x} , at $\lambda = 1$, the second leg passes through $E_{\text{xc},\lambda=1}$, while their meeting point is chosen at E_{xc} . Thus

$$b = \frac{E_{\text{xc}} - E_{\text{xc},\lambda=1}}{E_{\text{x}} - E_{\text{xc},\lambda=1}}. \quad (12)$$

So long as E_{xc} is closer to $E_{\text{xc},\lambda=1}$ than to E_{x} , i.e., the curve is concave upward, we find $0 \leq b \leq 1/2$. This two-legged construction thus provides a simple representation of the full λ -dependent curve, based on just three energies, while b is a measure of the concavity of the curve. Note that under uniform scaling to high densities [21,16], $b \rightarrow 1/2$, and the two legs form a single straight

line, while for low densities, or systems with strong static correlation, $b \rightarrow 0$, and the first leg drops precipitously [16].

To construct the two-legged representation of a λ -dependent GGA curve, the only energies needed are the exchange, exchange-correlation, and the $\lambda = 1$ value of the GGA, which can easily be calculated from Eq. (10).

IV. HYBRID CONSTRUCTION AND FORMULA

We wish to construct a non-empirical hybrid formula which combines the most accurate GGA energies (near $\lambda = 1$) with the exact exchange energy at $\lambda = 0$. Eq. (12) suggests an obvious candidate: Calculate b^{GGA} from the GGA energies, and combine it with E_x and $E_{xc,\lambda=1}^{\text{GGA}}$ to find:

$$E_{xc}^I = b^{\text{GGA}} E_x + (1 - b^{\text{GGA}}) E_{xc,\lambda=1}^{\text{GGA}}. \quad (13)$$

This possibility has already been investigated [16,15], but yields little or no improvement over GGA energies. The reason for this is straightforward. Since the $\lambda = 1$ region of the GGA curve is more accurate than the $\lambda = 0$ end, when there is a significant error at $\lambda = 0$, the exact adiabatic curve must drop more rapidly, i.e. have greater curvature, than its GGA counterpart. In terms of the two-legged representation, $b \leq b^{\text{GGA}}$, where b is the exact value, defined by applying Eq. (12) to the exact energies. This is especially important if static correlation becomes relatively large, where b drops to zero.

To construct a more accurate hybrid from the same information, we still represent the hybrid by two legs, one of which passes through the exact exchange value, the other through $E_{xc,\lambda=1}^{\text{GGA}}$.

$$E_{xc}^{\text{hyb}} = b^{\text{hyb}} E_x + (1 - b^{\text{hyb}}) E_{xc,\lambda=1}^{\text{GGA}} \quad (14)$$

It only remains to choose where to connect the two legs, i.e. what should be the value of b^{hyb} . We treat only the case $E_x > E_x^{\text{GGA}}$. It appears unlikely that the exact and GGA λ -dependent curves cross [16], so we impose this restraint on their two-legged representations. We also make b as small as possible, so that the hybrid most closely approximates the GGA curve near $\lambda = 1$. This leads to the simple result that the hybrid legs meet on the two-legged representation of the GGA curve (see Figure 2 for an application to an energy difference). (The less accurate choice of Eq. (13) can be constructed by drawing a vertical line through $\lambda = b^{\text{GGA}}$; where it crosses the dashed diagonal is E_{xc}^I .) Elementary geometry yields the formula

$$b^{\text{hyb}} = \frac{E_x^{\text{GGA}} - E_{xc,\lambda=1}^{\text{GGA}}}{E_x - E_{xc,\lambda=1}^{\text{GGA}} - dE_{xc,\lambda}^{\text{GGA}}/d\lambda|_{\lambda=0}}, \quad (15)$$

assuming $E_x \geq E_x^{\text{GGA}}$, so that the meeting point is on the first leg of the GGA curve, for which

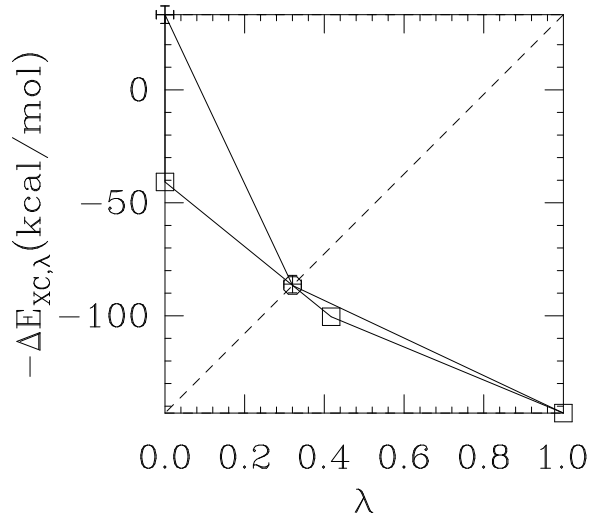


FIG. 2. Two-legged hybrid (higher solid line) for the N_2 atomization energy (ΔE), constructed from the exact exchange at $\lambda = 0$, the PW91 value for $\Delta E_{xc,\lambda=1}$, and b chosen as small as possible, without going below the PW91 curve. Squares denote GGA energies, a circle denotes the hybrid exchange-correlation energy, while pluses denote exact energies.

$$\left. \frac{dE_{xc,\lambda}^{\text{GGA}}}{d\lambda} \right|_{\lambda=0} = \frac{E_{xc}^{\text{GGA}} - E_x^{\text{GGA}}}{b^{\text{GGA}}}, \quad (16)$$

where b^{GGA} is determined by Eq. (12) above, applied to the GGA energies.

To understand how this hybrid works, we discuss several limits, referring to the geometric construction of Figure 2. If $E_x = E_x^{\text{GGA}}$, i.e., no error in the exchange energy, the hybrid and GGA two-legged representations become identical, i.e., $b^{\text{hyb}} = b^{\text{GGA}}$, and $E_{xc}^{\text{hyb}} = E_{xc}^{\text{GGA}}$. In the opposite extreme of strong static correlation, in which the GGA two-legged curve appears relatively flat along the bottom of a figure like Fig. 2, and $\delta E_x \gg |E_x^{\text{GGA}} - E_{xc,\lambda=1}^{\text{GGA}}|$, then the hybrid curve touches the GGA two-legged curve at $b^{\text{hyb}} \rightarrow 0$, giving a hybrid energy $E_{xc}^{\text{hyb}} \rightarrow E_x^{\text{GGA}}$. While this may not be precisely the correct result in this limit, the important feature is that E_{xc}^{hyb} is close to E_{xc}^{GGA} , rather than to E_x . A simple indicator of how large a correction the hybrid can be expected to make to a GGA calculation is given by

$$\phi = \frac{E_x - E_x^{\text{GGA}}}{E_x^{\text{GGA}} - E_{xc,\lambda=1}^{\text{GGA}}}. \quad (17)$$

When $\phi \ll 1$, the hybrid and GGA curves are almost identical, so that the hybrid only slightly changes the GGA result, and the exchange error is not necessarily the dominant error. For $\phi \gtrsim 1$, the exchange error is relatively large, and the hybrid should noticeably improve E_{xc} . Cases might also arise in which there is a large

TABLE I. Exchange-correlation contributions to atomization energies of molecules, in kcal/mol (1eV=23.06 kcal/mol). E_{XC} has been evaluated on LSD densities at experimental geometries [23,24]. Nonspherical densities and Kohn-Sham potentials have been used for open-shell atoms [25]. The calculations are performed with a modified version of the CADPAC program [26]. The experimental values for ΔE (with zero point vibration removed) are taken from Ref. [27,28]. Hyb denotes the two-legged hybrid of Eq. (14). ΔE_x was evaluated using LSD orbitals. The error in E_x^{PW91} is measured relative to E_x , all others relative to E_{XC}^{exp} . (m.a.e.=mean absolute error)

mol.	ΔE_x	ΔE_x^{PW91}	$\Delta E_{XC}^{\text{PW91}}$	$\Delta E_{XC,\lambda=1}^{\text{PW91}}$	$\Delta E_{XC}^{\text{hyb}}$	$\Delta E_{XC}^{\text{exp}}$
H ₂	32	33	53	68	53	56
LiH	26	28	45	58	45	50
CH ₄	201	211	296	355	294	294
NH ₃	107	136	211	265	205	206
OH	33	50	76	95	72	72
H ₂ O	88	117	168	205	162	164
HF	56	78	103	122	99	100
Li ₂	0	4	18	26	17	22
LiF	90	120	143	161	137	144
C ₂ H ₂	173	216	299	356	289	288
C ₂ H ₄	259	292	409	489	401	398
HCN	68	131	201	251	188	186
CO	44	99	144	176	133	134
N ₂	-33	41	100	143	87	86
NO	-41	36	85	120	71	67
O ₂	-33	46	85	112	72	62
F ₂	-75	2	22	37	12	6
P ₂	-39	4	53	84	45	50
Cl ₂	13	35	59	75	55	53
m.a.e.		37	8.4		3.3	-

GGA exchange error, but in which the slope of the exact curve is not as steep as suggested by this construction [22]. In these circumstances, our hybrid does correct the GGA result in the right direction, but not by enough (see the case of F₂ below).

Note that we are not suggesting the true adiabatic curves consist of line segments. The two-legged representation is simply a convenient geometric representation of these curves, yielding a simple prescription for the construction of a hybrid (Eqs. (14)-(16)).

V. RESULTS AND CONCLUSIONS

The new hybrid can be applied to the atomization energy of molecules, because the *energy difference* (ΔE) curves usually have much larger errors at $\lambda = 0$ than $\lambda = 1$ [16]. We now apply our hybrid to the atomization of molecules, i.e., we insert $\Delta E_{XC,\lambda}$ in all parts of the construction of Section III, where $\Delta E_{XC,\lambda}$ is the adiabatic curve for the energy *difference* between the constituent atoms and the molecule. The hybrid should prove most

useful for such energy differences, in which the core is cancelled, so that the exchange error is far more noticeable than in the total energies, i.e., ϕ will be greater than for the total energies.

In Table I, we list results for 19 molecules, using the PW91 GGA. The mean absolute error (m.a.e.) is reduced from 8.4 kcal/mol in the GGA to 3.3 kcal/mol in the hybrid. Furthermore, ignoring energy differences of less than 2 kcal/mol (since our hybrid is limited by the accuracy of $E_{XC,\lambda=1}$) the hybrid almost always reduces the GGA error. Consistent with earlier speculation [16], the usefulness of the hybrid is greatest for multiple-bonded systems. We find $\phi \lesssim 0.5$ for single bonds, and $\phi \gtrsim 0.5$ for multiple bonds. If we define

$$a = \frac{E_{XC}^{\text{hyb}} - E_{XC}^{\text{GGA}}}{E_x - E_x^{\text{GGA}}}, \quad (18)$$

as the amount of mixing of exact exchange, as used by Becke, we find $0.13 \leq a \leq 0.29$ for all the molecules in the table, in rough agreement with Becke's single empirical value [8,12]. However, we also find that a is typically higher for single bonds than for multiple bonds, illustrating the non-universal nature of a .

Finally, we compare our hybrid with others. The Becke half-and-half [9] is a simple straight line (one-legged) interpolation between E_x and $E_{XC,\lambda=1}^{\text{GGA}}$, i.e., it has $b = 1/2$, applied to LSD. It thus uses only two inputs, and fails to capture a key ingredient of atomization energies, namely the rapid drop in the curve near $\lambda = 0$. The simple approximation of $b = b^{\text{GGA}}$ improves this somewhat [16], but still fails to capture this drop, because b remains finite as the exchange error becomes large. The hybrid suggested here cures these problems, and is probably the best estimate of E_{XC} , given only the four inputs ($E_x, E_x^{\text{GGA}}, E_{XC}^{\text{GGA}}, E_{XC,\lambda=1}^{\text{GGA}}$) and the assumption that the error along the adiabatic curve is greatest at $\lambda = 0$. An alternative approach to hybrid construction uses the slope of the exact curve at $\lambda = 0$, rather than the GGA value at $\lambda = 1$. This can be estimated from general arguments about the convergence of perturbation theory for these systems [29], yielding results of comparable accuracy for the molecules given here, but requiring as input knowledge of the performance of perturbation theory. Lastly, one can calculate the slope of the exact curve at $\lambda = 0$ using Levy-Görling perturbation theory [20], combine it with E_x , and with $E_{XC,\lambda}^{\text{GGA}}$ near $\lambda = 1$, and so produce the potentially most accurate hybrid yet [22]. However, this is at the cost of greater computational effort to do the perturbation calculation (comparable to second-order Møller-Plesset perturbation theory).

To summarize, we have shown that when the principal source of error in a GGA energy calculation comes from the exchange or $\lambda = 0$ end of the adiabatic connection curve, a simple non-empirical hybrid of exact exchange and GGA energies eliminates most of this error.

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