

MIXING EXACT EXCHANGE WITH GGA: WHEN TO SAY WHEN

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INTRODUCTION

The local spin density (LSD) approximation [1] has long been the method of choice for solid-state physics calculations. With the advent of generalized gradient approximations (GGA's) [2, 3, 4, 5, 6, 7], density functional calculations for bond energies became an inexpensive alternative to traditional *ab-initio* quantum chemical calculations [8]. The recently derived PBE approximation [9] reduces the mean absolute error on a set of 20 small molecules from 31 kcal/mol in LSD to 8 kcal/mol. Both LSD and PBE approximations are non-empirical, in that all their parameters (other than the exchange-correlation energy per electron of a uniform gas) are fundamental constants. PBE is a simplification of the PW91 GGA [5, 6, 7].

GGA is not more accurate than LSD for every property of every system, but is usually better for energy differences between more and less inhomogeneous ground states, for reasons that are well-understood [10]. (GGA also provides employment for aspiring young theorists.)

However, Becke [11, 12] showed how to do even better, using a mixture of exact exchange and GGA. He reduced errors to about 3 kcal/mol, finding the optimum mixture to lie in the range of 16 -28 % of exact exchange, depending on the choice of GGA. Further empirical parameters were introduced via "B3LYP" [13], arguably the most-used functional in chemistry today.

The present work describes the formal underpinning behind such

mixtures in terms of the adiabatic connection, and summarizes recent work in which the validity and accuracy of several hybrid schemes were explored [14, 15, 16, 17]. The upshot is a non-empirical prescription for "when to say when." We use atomic units ($e^2 = \hbar = m = 1$) throughout, except for exchange-correlation contributions to atomization energies of molecules, which are in kcal/mol. (1 hartree = 27.21, 1 eV = 627.5 kcal/mol.)

ADIABATIC CONNECTION

The total ground-state energy of a non-relativistic electronic system is:

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

where T is the kinetic energy, V_{ee} the Coulomb repulsion energy between electrons, and V_{ext} the external potential energy. In the Kohn-Sham scheme [1], in which the wavefunction is non-interacting, the ground-state energy is rewritten as

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

where T_s is the kinetic energy of the Kohn-Sham wavefunction, and U is the Hartree energy,

$$U = \frac{1}{2} \int d^3r' \int d^3r \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (3)$$

Thus the exchange-correlation energy is

$$E_{xc} = V_{ee} - U + T - T_s, \quad (4)$$

and contains both a potential and a kinetic contribution.

To construct the adiabatic connection, we simply generalize the constrained-search definition of the universal functional [18]

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \quad (5)$$

to [19, 20, 21]

$$F_\lambda[n] = \min_{\Psi_\lambda \rightarrow n} \langle \Psi_\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_\lambda \rangle. \quad (6)$$

Thus Ψ_λ is the ground-state wavefunction of a problem with interelectronic repulsion $\lambda \hat{V}_{ee}$, but which yields n . At $\lambda = 1$, we have the regular

interacting wavefunction, while at $\lambda = 0$, we recover the Kohn-Sham non-interacting wavefunction. Note also that the external potential is then λ -dependent, in order to keep the density fixed as λ changes. Inserting this definition into Eq. (4), we have

$$\begin{aligned} E_{xc} &= F_{\lambda=1} - F_{\lambda=0} - U \\ &= \int_0^1 d\lambda \frac{dF_{\lambda}}{d\lambda} - U \\ &= \int_0^1 d\lambda E_{xc,\lambda}, \end{aligned} \quad (7)$$

where

$$E_{xc,\lambda} = \langle \Psi_{\lambda} | \hat{V}_{ee} | \Psi_{\lambda} \rangle - U, \quad (8)$$

since only the dependence of the Hamiltonian on λ contributes. Thus we have expressed the exchange-correlation energy in terms of a purely potential contribution, at the price of having to perform an integral over coupling constant.

Figure 1 shows the adiabatic connection curve for the two-electron Hooke's atom [22], in which the electrons are held to a center by a harmonic potential of radial frequency $\omega = 1/2$. Note that $\lambda = 0$ is the

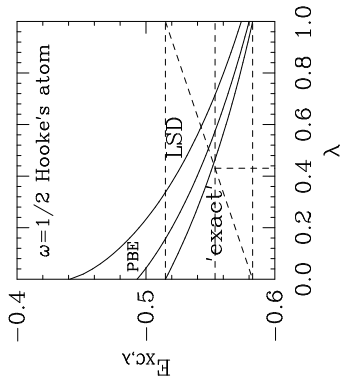


Figure 1. Solid lines: adiabatic connection curves for $\omega = 1/2$ Hooke's atom, within the local density approximation (LSD), the PBE generalized gradient approximation, and "exactly" (see text). The dashed lines show how to construct the correlation parameter b geometrically for the "exact" curve.

exchange limit, i.e., $E_{xc,\lambda=0} = E_x$. At $\lambda = 1$ we have the fully interacting system, and $E_{xc,\lambda=1}$ is the pure potential contribution to exchange-correlation. The average over λ , which is the area under the curve, gives the actual exchange-correlation energy, $E_{xc} = \int_0^1 d\lambda E_{xc,\lambda}$.

Since correlation reduces the energy, these are always ordered:

$$E_x \geq E_{xc} \geq E_{xc,\lambda=1}. \quad (9)$$

Furthermore, since the exchange-correlation energy contains a kinetic component, it is related to the potential contribution via

$$E_{xc} = E_{xc,\lambda=1} + T_c, \quad (10)$$

where $T_c = T - T_s$ is the kinetic contribution to the correlation energy (or the correlation contribution to the kinetic energy).

The 'exact' curve was constructed by fitting three energies known from the exact solution, viz. E_x , E_{xc} , and $E_{xc} - T_c$, to a [1,1]-Padé form in λ [17]. Because it is fitted to the exact values, we expect it to be highly accurate in the range $0 \leq \lambda \leq 1$.

A simple measure of the strength of the correlation in a system is given by the curvature of the adiabatic connection curve in the range $\lambda = 0$ to 1. We write

$$E_{xc} = bE_x + (1 - b)E_{xc,\lambda=1}, \quad (11)$$

and find $0 \leq b \leq 1$ (see problem 1). In fact, for all cases we are aware of, the adiabatic curve is concave upwards, i.e.,

$$\frac{d^2 E_{xc,\lambda}}{d\lambda^2} \geq 0, \quad (12)$$

so that $b \leq 1/2$, as conjectured by Levy [23]. Solving Eq. (11) for b yields

$$b = \frac{T_c}{T_c - E_c}. \quad (13)$$

For high density (relatively low correlation) systems, the adiabatic curve is almost a straight line, and b is close to $1/2$, as in Fig. 1. For low density (relatively strong correlation) systems, the adiabatic curve drops rapidly toward its $\lambda = \infty$ limit, and b is closer to zero. Thus b^{-1} is a measure of the strength of correlation. Figure 2 demonstrates this

is usually associated with low densities. But for atomization energies of molecules, there is strong static correlation even at typical valence densities.

Although it is barely visible in Fig. 1, note that the LSD approximation has an incorrect logarithmic divergence in its slope as $\lambda \rightarrow 0$. This singular behavior is due to the long-range nature of the Coulomb interaction in the extended uniform gas system, and contributes to the LSD overestimate of static correlation in finite systems. For a finite system with non-degenerate Kohn-Sham determinant this slope should be finite, and $E_{xc,\lambda}$ may be written as [23]

$$E_{xc,\lambda} = E_x + \lambda E_c^{(2)} + \dots \quad (\lambda \rightarrow 0). \quad (14)$$

The real-space construction of a GGA corrects this problem [7], but the PW91 parametrization of its results does not [24]. The recent PBE [9], derived in a simpler fashion, recovers this correct behavior.

CORRELATION MAKES THE HOLE GROW DEEPER

In this section, we analyze the behavior of approximate functionals over the range of the adiabatic curve. The λ -dependent curve can be calculated for any approximate density functional by scaling the density [25, 26]:

$$E_{xc,\lambda}[n] = \frac{d}{d\lambda} (\lambda^2 E_{xc}[n(\mathbf{r}/\lambda)/\lambda^3]). \quad (15)$$

In Fig. 1 we show both the LDA and PBE curves alongside the sketch of the exact curve. We see that both approximate functionals improve their performance as λ grows.

This behavior can be understood in very general terms by considering these approximations as approximations for the (system- and spherically-averaged) exchange-correlation hole [27]. As λ is turned on, correlation deepens the on-top hole [15]. Because the hole is normalized to -1 , this implies parts of the hole are being drawn in to smaller separations. Since the LDA and PBE approximations work best for small separations, their accuracy in describing the hole (and therefore in predicting the energy) improves as the hole gets deeper and more short-ranged. Thus they work best at the $\lambda = 1$ end. This explains the well-known cancellation of errors between exchange and correlation for approximate functionals.

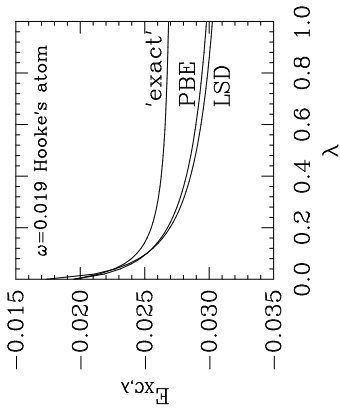


Figure 2. Adiabatic connection curve for $\omega = 0.019$ Hooke's atom, within the local density approximation (LSD), the PBE generalized gradient approximation, and "exactly" (see text).

Table 1. Energies in hartrees and b for the $\omega = 1/2$ Hooke's atom

energy	exact	LSD	PBE
E_x	-0.515	-0.441	-0.493
E_{xc}	-0.554	-0.527	-0.544
$E_{xc,\lambda=1}$	-0.583	-0.574	-0.580
b	0.43	0.35	0.41

behavior for $\omega = 0.019$, a low-density analytic solution to Hooke's atom, where $b = 0.12$. The numbers for the $\omega = 1/2$ solution are tabulated in Table I. A simple geometric interpretation can be given to b , and is illustrated for the "exact" curve of Fig. 1 by the dashed lines. Draw a horizontal line at E_{xc} for the adiabatic curve, so that the net area between the horizontal line and the curve is zero. Next draw a backwards diagonal from the point ($\lambda = 0, E_{xc,\lambda=1}$) to the point ($\lambda = 1, E_{xc,\lambda=0}$). The value of λ where these two lines intersect is b .

We conclude this section with a working definition of the nebulous concept of "static" correlation. By static correlation we will mean correlation with little kinetic contribution. From Eq. (13), a system with strong static correlation will have b close to zero. For total energies, this

Since the relative error reduces as correlation is turned on, splitting the exchange-correlation energy into an exchange and a correlation contribution produces larger errors in each than in their sum. In Fig. 3, we show percentage errors in LDA (relative to PW91) for closed-shell atoms. We

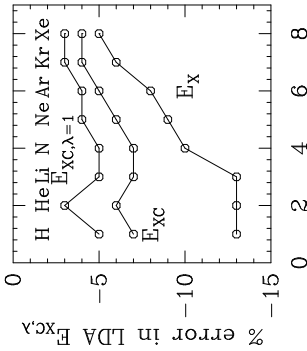


Figure 3. Percent errors made in the three energies discussed in the text for LSD relative to PW91.

find

$$|\Delta E_X| \geq |\Delta E_{XC}| \geq |\Delta E_{XC, \lambda=1}|, \quad (16)$$

consistent with our hole arguments.

NON-EMPIRICAL HYBRID CONSTRUCTION

Consider a situation in which we can calculate any approximate functional energy, and know also the ‘exact’ exchange energy. Here, by ‘exact’, we mean the Fock integral evaluated on the Kohn-Sham orbitals, and we ignore small errors in these orbitals from their exact counterparts. Thus we get an approximate adiabatic connection curve from an approximate E_{XC} functional via Eq. (15), plus an exact value at just one point along the curve, $\lambda = 0$. How can we best utilize the additional information in that one point?

A convenient way to express the result of any such procedure is to write the exchange-correlation energy as

$$E_{XC}^{\text{hyb}} = a(E_X - E_X^{\text{DEA}}) + E_{XC}^{\text{DEA}}, \quad (17)$$

where DFA denotes density functional approximation. When the exact exchange energy lies above the DFA exchange-correlation energy, this expression defines a value for $0 \leq a \leq 1$. Becke [12] fitted this form to the atomization energies of many molecules, ionization potentials and proton affinities, finding $0.16 \leq a \leq 0.3$ and reducing the mean error to 2-3 kcal/mol.

Exact exchange plus approximate correlation

A naive solution would be simply to shift the entire approximate curve downward, by the amount of error at $\lambda = 0$. This is equivalent to adding the approximate correlation energy to the exact exchange energy, thereby destroying the cancellation of errors between exchange and correlation mentioned above, and typically producing a larger error than in the original approximation itself. Such a construction ignores the fact that the approximation improves as λ grows.

Half and half

Another crude but more effective scheme is to use a straight line to connect the exact exchange value with the approximation at $\lambda = 1$,

$$E_{XC, \lambda}^{1/2 \& 1/2} = E_X + \lambda(E_{XC, \lambda=1}^{\text{DFA}} - E_X) \quad (18)$$

which, when integrated over λ , yields

$$E_{XC}^{1/2 \& 1/2} = \frac{1}{2}E_X + \frac{1}{2}E_{XC, \lambda=1}^{\text{DFA}}. \quad (19)$$

This model was used by Becke [28], with DFA=LSD, to improve upon LSD results. It has the merit of having a finite slope as $\lambda \rightarrow 0$, and becomes exact if $E_{XC, \lambda=1}^{\text{DFA}}$ is exact and the system has high density.

Levy had in fact written an exact half-and-half formula earlier, in the context of the total energy [29]. For the exchange-correlation energy alone, this is

$$E_{XC} = \frac{1}{2}(E_{XC} + T_c) + \frac{1}{2}E_{XC, \lambda=1}. \quad (20)$$

The first term has the importance that, *if the exact density is known*, the exchange-correlation potential can be constructed by any of several schemes, and its virial is precisely $E_{XC} + T_c$. Thus when the exact density is known, an extremely accurate estimate is possible[30], since $E_{XC, \lambda=1}^{\text{DFA}}$ is more accurate than E_{XC}^{DFA} , and only half of its error appears in Eq. (20).

Two-legged mixing

More recently, we have constructed and tested several non-empirical hybrid schemes. Two of these can be best pictured by mimicking the adiabatic curve by two straight line segments, chosen so that they meet at $\lambda = b$ and $E_{xc,\lambda=b} = E_{xc}$, i.e., the kink in the curve is at exactly the average. In Fig. 4, the solid lines show both the two-legged representation for the ‘exact’ and LSD curves for the $\omega = 1/2$ Hooke’s atom.

The simplest scheme can be constructed by approximating both b and $E_{xc,\lambda=1}$ in Eq. (11) by their density functional approximations, but using the exact exchange value [31, 14]:

$$E_{xc}^I = b^{\text{DFA}} E_x + (1 - b^{\text{DFA}}) E_{xc,\lambda=1}^{\text{DFA}} \quad (21)$$

This approximation, applied to LSD, is shown by the line marked I on Fig. 4 and the results listed in Table I. Although it yields almost the

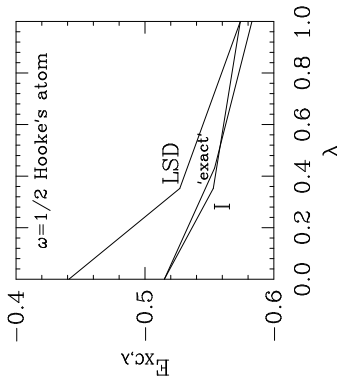


Figure 4. Two-legged line segment representation of adiabatic curves of Fig. 1, and hybrid approximation I (see text).

exact exchange-correlation energy in this case, the agreement is somewhat fortuitous. The value $b^{\text{LSD}} = 0.35$ is too low, due to the excessive static correlation in LSD for this system, but the error is cancelled by the remnant LSD error at $\lambda = 1$. The same fortuitous cancellation often occurs when the hybrid of Eq. 21 is applied to LSD atomization energies of molecules, as shown in Ref. [14].

The atomization energies of molecules are of more practical interest. We apply our reasoning directly to the adiabatic curve of the energy difference between the separated atoms and the molecule. The situation is different from that of Fig. 4, as now $-\Delta E_x$ is always above $-\Delta E_{xc,\lambda}^{\text{GGA}}$. In Fig. 5, we plot both the PW91 curve for the atomization of N_2 and the

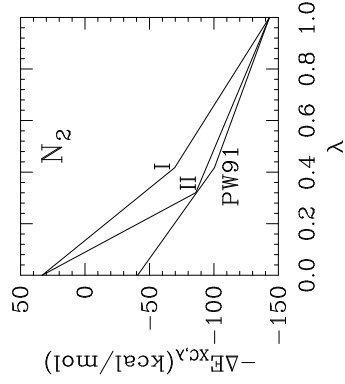


Figure 5. Construction of two-legged line segments representing the adiabatic connection curve for the atomization of N_2 . For each case, the average, ΔE_{xc} , is the value at the kink in the curve, $\lambda = b$. The two hybrid curves (I+II) employ the exact ΔE_x at $\lambda = 0$ and the PW91 $\Delta E_{xc,\lambda}$ at $\lambda = 1$, but I uses the PW91 value of b , while II is chosen to be as close to PW91 as possible.

hybrid I discussed above. Since the exact $-\Delta E_{xc}$ is about -85 kcal/mol, we see that the error in the PW91 curve must be largely coming at the small λ end. We can therefore construct a better hybrid than I, using exactly the same inputs, but now requiring the second line segment to be as close as possible to its GGA counterpart, without actually crossing it. This construction leads to a simple non-empirical hybrid (see Eqs. (15) and (16) of Ref. [15]), and produces the curve marked II in Fig. 5, whose average is -85 kcal/mol. Application of this scheme to many small molecules produces mean errors of about 3-4 kcal/mol, comparable to those of Becke [11, 12], and also typically gives a between 0.1 and 0.3. Thus this non-empirical scheme may be viewed as a derivation of Becke’s value for a .

Connection to perturbation theory

An alternative construction for the difference between the exact and approximate adiabatic atomization curves provides a heuristic relation between a and n , the approximate order of perturbation theory needed to estimate accurately the atomization energy of molecules. Using the same general idea that the curves should be most similar at the $\lambda = 1$ end, we write [16]

$$E_{xc,\lambda}^{\text{III}}(n) = E_{xc,\lambda}^{\text{DFA}} + (E_x - E_x^{\text{DFA}})(1 - \lambda)^{n-1} \quad (22)$$

and choose n as the lowest order in perturbation theory needed to provide a realistic description of the shape of the adiabatic curve. For many small molecules, second order perturbation theory is insufficient, but fourth order is reasonably accurate, so $n = 4$. When we average Eq (22) over λ , we find:

$$E_{xc}^{\text{hyb}} = E_{xc}^{\text{DFA}} + \frac{1}{n}(E_x - E_x^{\text{DFA}}). \quad (23)$$

Thus the need for 4th-order perturbation theory implies $a \approx 1/4$.

An even better hybrid

An additional piece of information about the adiabatic connection curve is provided by the boundary condition [32, 33]

$$\lim_{\lambda \rightarrow \infty} E_{xc,\lambda} = \text{const.} \quad (24)$$

Since all the schemes discussed so far were designed solely for the range $0 \leq \lambda \leq 1$, none take advantage of this information. On the other hand, the [1/1]-Padé ansatz [17]

$$\Delta E_{xc,\lambda} = a \frac{[1 + \lambda b]}{[1 + \lambda c]} \quad (25)$$

obeys this condition and provides an analytical model for $E_{xc,\lambda}$. The non-empirical parameters in Eq. (25) are obtained with the exact exchange energy, i.e. $E_{xc,\lambda=0}$ and with the value and the derivative with respect to λ of $E_{xc,\lambda}^{\text{DFA}}$ at $\lambda = 1$.

For molecules with weak to moderate correlation, this yields similar results to the two-legged hybrid. But for molecules with very strong static correlation this model leads to more accurate atomization energies

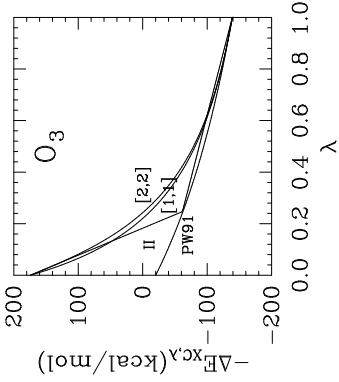


Figure 6. Adiabatic connection curves for O_3 in PW91, two-legged hybrid, [1,1]-Padé, and [2,2]-Padé. The last of these yields essentially the exact atomization energy.

[34]. To understand why this is so, consider the atomization of the ozone molecule. In Fig. 6, we plot the adiabatic curves from PW91, the two-legged hybrid, the [1,1]-Padé, and the [2,2]-Padé, discussed below. These yield values of $-\Delta E_{xc}$ of -90, -62, -55, and -50 kcal/mol, respectively, while the exact value is -50 kcal/mol. The two-legged model produces too negative a result because it relies too heavily on the incorrect $\lambda = 0$ information of the PW91 curve.

More sophisticated hybrids

The schemes discussed so far have been limited in how much they can improve upon the DFA result by a paucity of information about the exact adiabatic curve: Just one point at $\lambda = 0$ and general arguments about the nature of the error in the DFA curves. (The silver lining in this cloud is the ease with which they can be implemented – hence the current popularity of such schemes in quantum chemistry.) We can both test the current schemes and hope to improve upon them in cases where they fail by employing more exact information, but at the price of doing a more expensive calculation.

The simplest next step is to use second-order Görling-Levy perturbation theory [35] to find the exact value for the slope of the adiabatic

curve at $\lambda = 0$. This information can be incorporated into a [2/2]-Padé model [17] analogous to Eq. (25), but now including the correct slope at $\lambda = 0$. The necessary calculations are technically no more expensive than standard second-order Möller-Plesset perturbation theory. One of us (M. E.) has performed such calculations for small molecules [17]. In most cases, the exact slopes coincide reasonably well with those predicted by the hybrid schemes II, III and Eq. (25). However, in some cases, such as O_3 , for which none of the simpler hybrids work so well, the [2/2]-Padé scheme improves the atomization energy significantly. The [2/2]-Padé curve for O_3 is shown in Fig. 6, and yields essentially the exact atomization energy.

CONCLUSIONS

To summarize, we have shown that hybrids of exact exchange and density functional GGA's can be constructed non-empirically. The basic input is the GGA calculation of $E_{xc,\lambda}$ and the exact E_x . Note that some insight into the source of error in the GGA calculation is needed, and that the resulting hybrid only works (i.e., improves on the GGA result) when that insight is correct.

For atoms, Fig. 2 for the low density Hooke's atom indicates a system where the approximate functionals do *worse* at $\lambda = 1$ than $\lambda = 0$. This should also be the case for the $Z \rightarrow \infty$ limit of the Be atom36. In neither case do we expect our current hybrids to work.

For molecules, our schemes have been developed specifically for atomization energies, where strong non-locality of the exchange hole leads to larger errors at $\lambda = 0$ than at $\lambda = 1$. These schemes will fail when the error does not follow this pattern, e.g., in H_2 where the $\lambda = 0$ end of the adiabatic connection is much better approximated by PW91 and PBE than the $\lambda = 1$ end [37], implying that a more general form of hybrid is required to include these cases. Another difficulty arises when the hybrid is applied directly to energy differences, as this leads to non-unique values for total energies (see problem 3).

The hybrid schemes employed here use only the energy at $\lambda = 0$ (and, in one case, its derivative with respect to λ). However, much more detail at $\lambda = 0$ can easily be calculated, such as the exchange hole of Ref. [27]. Using information from this hole may make possible more

sophisticated and accurate hybrid calculations, producing, e.g., a hybrid hole [38].

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EXERCISES

1. Show that b , defined in Eq. (11), is always between 0 and 1.
2. Prove that b is never greater than $1/2$.
3. Show that if a , defined by Eq. (17), is system-dependent, then applying the hybrid scheme to energy differences leads to different results than applying it to total energies, and then taking differences. This is a formal shortfall for all the non-empirical hybrids discussed here,
4. Construct a hybrid scheme which overcomes this problem [39].

Answers to odd-numbered problems

1. From the variational principle, one may easily show [25] that

$$T_c \geq 0, \quad E_c \leq 0 \quad (26)$$

for all densities. Inserting these inequalities into Eq. (13), we find $0 \leq b \leq 1$.

3. Consider a homogeneous diatomic molecule, A_2 . The hybrid I defined in Eq. (21), applied directly to the atomization energy yields:

$$\Delta E_{xc}^I = b\Delta E_x + (1 - b)\Delta E_{xc,\lambda=1}^{DFA} \quad (27)$$

where $\Delta E = 2E(A) - E(A_2)$, and

$$b = \Delta T_c / (\Delta T_c - \Delta E_c). \quad (28)$$

On the other hand, if we write

$$\Delta E_{xc} = 2E_{xc}^I(A) - E_{xc}^I(A_2), \quad (29)$$

we find

$$\Delta E_{xc} = b(A)2E_x(A) - b(A_2)E_x(A_2) + [1 - b(A)]2E_{xc,\lambda=1}^{\text{DFA}}(A) - [1 - b(A_2)]E_{xc,\lambda=1}^{\text{DFA}}(A_2) \quad (30)$$

with $b(A)$ given by Eq. (13) evaluated within the DFA for A , and similarly for $b(A_2)$. Only if all values for b are equal will the two methods yield the same result. The same reasoning applies to all the energy difference hybrids discussed here, and also to the parameter a in Eq. (17).

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