Rationale for mixing exact exchange with density functional approximations

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Density functional approximations for the exchange-correlation energy E_{xc}^{DFA} of an electronic system are often improved by admixing some exact exchange E_x: $E_{xc} \approx E_{xc}^{DFA} + (1/n)(E_x - E_x^{DFA})$. This procedure is justified when the error in E_{xc}^{DFA} arises from the $\lambda = 0$ or exchange end of the coupling-constant integral $\int_0^1 d\lambda\ E_{xc,\lambda}^{DFA}$. We argue that the optimum integer n is approximately the lowest order of Görling–Levy perturbation theory which provides a realistic description of the coupling-constant dependence $E_{xc,\lambda}$ in the range $0 \leq \lambda \leq 1$, whence $n \approx 4$ for atomization energies of typical molecules. We also propose a continuous generalization of n as an index of correlation strength, and a possible mixing of second-order perturbation theory with the generalized gradient approximation. © *1996 American Institute of Physics.* [S0021-9606(96)01846-6]

Kohn–Sham density functional theory[1-3] typically makes a local or semilocal approximation for the exchange-correlation energy functional $E_{xc}[\rho_\uparrow, \rho_\downarrow]$ of the electron spin densities, even though it also provides orbitals from which a Fock integral or "exact" exchange energy may be constructed. Given any pair of spin densities $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$, there is usually a unique Slater determinant Ψ_0 of Kohn–Sham orbitals which yields those densities and minimizes[4,5] the expectation value of the kinetic energy operator $\hat{T}$, and thus an exact Kohn–Sham exchange energy $E_x = \langle \Psi_0 | \hat{V}_{ee} | \Psi_0 \rangle - (e^2/2)\int d^3r\, d^3r'\ \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}'-\mathbf{r}|$, where $\hat{V}_{ee}$ is the electron–electron repulsion operator and $\rho = \rho_\uparrow + \rho_\downarrow$. Hybrids[6-9] which incorporate some of this exact exchange provide a simple and accurate description of the atomization energies, bond lengths, and vibration frequencies of most molecules.[10-17] The current popularity of hybrids in quantum chemistry demands a simple rationale for how much exact exchange should be included for a particular system or property. Such a rationale might motivate further improvements in calculational methods.

Becke[6] showed that the proper starting point for hybrid theory is the adiabatic connection formula,[18-20]

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

where

$$E_{xc,\lambda} = \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle - \frac{e^2}{2}\int d^3r \int d^3r'\, \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\qquad(2)$$

is λ^{-1} times the potential energy of exchange and correlation for electron–electron interaction $\lambda e^2/|\mathbf{r}-\mathbf{r}'|$, in a system whose external potential $v_\lambda(\mathbf{r})$ is adjusted to hold the electron density $\rho(\mathbf{r})$ fixed at its physical $\lambda=1$ value. Ψ_λ is the ground-state wave function of this system. At $\lambda=0$, the Kohn–Sham noninteracting system is recovered. From the Hellmann–Feynman theorem, the coupling-constant integral of Eq. (1) incorporates the kinetic energy of correlation. A simple two-point approximation to this integral is $(E_{xc,\lambda=0} + E_{xc,\lambda=1})/2$, where $E_{xc,\lambda=0} = E_x$ is the exchange energy of the Kohn–Sham orbitals. Becke[6] reasoned that local or semilocal density functionals are more accurate at $\lambda=1$ (where the exchange-correlation hole is deeper and thus more localized around its electron[21]) than at $\lambda=0$. His half-and-half hybrid[6,22]

$$E_{xc}^{hyb} = \frac{1}{2}(E_x + E_{xc,\lambda=1}^{DFA}),\qquad(3)$$

where E_x is the exact exchange energy and DFA is a density functional approximation, uses the local spin density (LSD) approximation for $E_{xc,\lambda=1}^{DFA}$. The underlying ideas about $\lambda=0$ and $\lambda=1$ can also be implemented in other ways.[23-25]

Becke[7] later proposed the three-parameter hybrid

$$E_{xc}^{hyb} = E_{xc}^{LSD} + a_0(E_x - E_x^{LSD}) + a_x(E_x^{GGA} - E_x^{LSD})$$
$$+ a_c(E_c^{GGA} - E_c^{LSD}),\qquad(4)$$

where $E_{xc}^{GGA} = \int d^3r f(\rho_\uparrow, \rho_\downarrow, \nabla\rho_\uparrow, \nabla\rho_\downarrow)$ is a generalized gradient approximation, and $E_{xc}^{LSD} = \int d^3r f(\rho_\uparrow, \rho_\downarrow, 0, 0)$ is its LSD piece. The parameters $a_0 = 0.20$, $a_x = 0.72$, and $a_c = 0.81$ were determined by fitting to a data set of measured atomization energies. If E_x^{GGA} and E_c^{GGA} are correct for the uniform gas [as they were in Becke's original B3PW91,[26-28] but not[21,29] in the popular B3LYP (Refs. 26, 30, 31)], then the resulting hybrid of Eq. (4) is also correct in the uniform-gas limit. A recent (B1) simplification[8,29] sets $a_x = 1 - a_0$ and $a_c = 1$, i.e.,

$$E_{xc}^{hyb} = E_{xc}^{DFA} + a_0(E_x - E_x^{DFA}),\qquad(5)$$

with $a_0 = 0.16$ or 0.28 (depending on the choice of GGA) (Ref. 8) and DFA=GGA. The errors in GGA atomization energies are most severe for multiply-bonded molecules like N_2; for evidence that these errors arise principally from the $\lambda \to 0$ or exchange limit, see Ref. 25.

Previous work[6-8,10-17] establishes the usefulness of the hybrid of Eq. (5), but does not provide a qualitative physical explanation for this form or for the empirical value of the parameter a_0. The aim of this work is to provide such an explanation. We will show that $a_0 \approx 1/4$ is to be expected for

the atomization energies of most molecules, but also that larger values of a_0 may be more appropriate for total energies of atoms and molecules, and smaller values for atomization energies of molecules with nearly degenerate ground states of the unperturbed ($\lambda=0$) problem.

Every density functional approximation $E_{xc}^{DFA}[\rho_\uparrow,\rho_\downarrow]$ has a coupling-constant decomposition $E_{xc,\lambda}^{DFA}$ like Eq. (1) [see Eq. (13)], which permits us to define $E_x^{DFA}=E_{xc,\lambda=0}^{DFA}$ and $E_c^{DFA}=E_{xc}^{DFA}-E_x^{DFA}$. We propose a simple model for the hybrid coupling-constant dependence,

$$E_{xc,\lambda}^{hyb}(n)=E_{xc,\lambda}^{DFA}+(E_x-E_x^{DFA})(1-\lambda)^{n-1}, \qquad (6)$$

where $n\geq1$ is an integer to be determined. Equation (6) reduces to the exact E_x at $\lambda=0$, as it should, and to $E_{xc,\lambda}^{DFA}$ at or near $\lambda=1$, where $E_{xc,\lambda}^{DFA}$ is most trustworthy. The integer n controls how rapidly the correction to DFA vanishes as $\lambda\rightarrow1$. Then

$$E_{xc}^{hyb}=\int_0^1 d\lambda E_{xc,\lambda}^{hyb}=E_{xc}^{DFA}+\frac{1}{n}(E_x-E_x^{DFA}). \qquad (7)$$

We now argue that the optimum integer n should be the lowest order of perturbation theory which provides a realistic description of the shape or λ-dependence of the exact $E_{xc,\lambda}$,

$$E_{xc,\lambda}\approx e^2(c_0+c_1\lambda+\cdots+c_{n-1}\lambda^{n-1}) \quad (0\leq\lambda\leq1). \qquad (8)$$

This choice maximizes the similarity of $E_{xc,\lambda}^{hyb}$ to $E_{xc,\lambda}^{DFA}$ near $\lambda=1$, while ensuring that no unnecessary powers of λ are introduced into Eq. (6). For example, if the curve of $E_{xc,\lambda}$ vs λ is constant ($n=1$), then the best correction to $E_{xc,\lambda}^{DFA}$ in Eq. (6) is a constant shift; if this curve is a straight line ($n=2$), then the best correction is a straight line; if this curve is a cubic ($n=4$), then the best correction is a cubic, etc. In other words, we assume that $E_{xc,\lambda}^{DFA}$ and $E_{xc,\lambda}^{hyb}$ can each be fitted accurately by a polynomial like Eq. (8), with an index n no higher than that needed for an accurate representation of the exact $E_{xc,\lambda}$.

The appropriate zero-order problem is the Kohn–Sham noninteracting Hamiltonian, and the perturbation is constructed to hold the density fixed.[32–34] However, we expect that in most cases n can be estimated by examining the convergence of the traditional Møller–Plesset perturbation expansion, in which the zero-order problem is the Hartree–Fock Hamiltonian.

The $n=1$ case is exemplified by Kr^{26+}, a strongly positive closed-shell ion. Although $E_{xc,\lambda}^{hyb}$ of Eq (6) will not match $E_{xc,\lambda}^{DFA}$ for any λ, $n=1$ is clearly the best choice for the exchange-dominated case.[35] Equation (7) becomes

$$E_{xc}^{hyb}(n=1)=E_x+E_c^{DFA}, \qquad (9)$$

which incorporates 100% of exact exchange plus GGA correlation. Equation (9) has been tested for molecular atomization energies by Clementi and Chakravorty;[36] the results are superior to Hartree–Fock values, but inferior to values calculated from GGA exchange and correlation without exact exchange. Clearly, molecular atomization energies are not exchange dominated. Equation (9) has also been applied to insulating solids.[37]

The $n=2$ case might apply when second-order perturbation theory is adequate. Equation (7) becomes

$$E_{xc}^{hyb}(n=2)=E_{xc}^{DFA}+\frac{1}{2}(E_x-E_x^{DFA}), \qquad (10)$$

which reduces to the half-and-half hybrid[6,23] of Eq. (3) when $E_{xc\lambda}^{DFA}$ is also a straight line. An unsatisfactory and artificial feature of the $n=2$ model is that, although $E_{xc\lambda}^{hyb}$ matches $E_{xc\lambda}^{DFA}$ at $\lambda=1$, the first derivative is not matched. In reality, $\lambda=1$ is not a special point, but simply one which falls in the large-λ range where density functional approximations work best.

The $n=4$ case is exemplified by typical molecules like the 32 in the G1 data set, for which fourth-order Møller–Plesset perturbation theory (MP4) yields atomization energies[38] with a small mean absolute error of 2.6 kcal/mol. For this case,

$$E_{xc}^{hyb}(n=4)=E_{xc}^{DFA}+\frac{1}{4}(E_x-E_x^{DFA}). \qquad (11)$$

Moreover, $E_{xc,\lambda}^{hyb}$ matches $E_{xc,\lambda}^{DFA}$ in value, slope, and second derivative at $\lambda=1$. Equation (11) constitutes our rationale for the hybrid of Eq. (5) and our explanation of the value of the semiempirical parameter $a_0=0.16$ or 0.28.[8]

Finally, the case $n\geq4$ arises when there is a degenerate or nearly-degenerate ground-state of the unperturbed ($\lambda=0$) problem, as exemplified to some extent by the molecule O_3 (Ref. 13) or by "stretched" H_2,[24,39]

$$E_{xc}^{hyb}(n\geq4)\approx E_{xc}^{DFA}. \qquad (12)$$

In this case, $E_{xc,\lambda}^{hyb}$ of Eq. (6) has a very negative ($\approx-\infty$) slope at $\lambda=0$, so the full density functional approximation is recovered, as expected on the basis of arguments[6–8,25,39–41] that a local or semilocal functional for the exchange energy incorporates an estimate of "static correlation," while the corresponding approximation for the correlation energy models "dynamic correlation." The geometry and vibration frequencies of ozone (O_3) are better described[13] by GGA alone than by a Becke hybrid with 20% or 25% of exact exchange.

An ideal hybrid would be sophisticated enough to optimize n for each system and property, but the accuracy of MP4 (Ref. 38) for most molecules suggests $n=4$ as the best single choice. Table I shows the atomization energies of 19 molecules constructed from this rationalized value of n, using as a density functional the nonempirical GGA of Perdew and Wang (PW91).[27,28] Since Rayleigh–Schrödinger perturbation theory is size-consistent,[47] this hybrid could also work for insulating solids.

Figure 1 displays the λ-dependence of $E_{xc,\lambda}^{hyb}(n=4)$ from Eq. (6), in comparison with $E_{xc,\lambda}^{DFA}$. What is actually shown is $-\Delta E_{xc,\lambda}=E_{xc,\lambda}(N_2)-2E_{xc,\lambda}(N)$, appropriate to the atomization energy ΔE of N_2. $E_{xc,\lambda}^{DFA}$ has been evaluated from the relationship[22,32,48]

$$E_{xc,\lambda}[\rho_\uparrow,\rho_\downarrow]=\frac{d}{d\lambda}\{\lambda^2 E_{xc}[\rho_{\uparrow\alpha},\rho_{\downarrow\alpha}]\}, \qquad (13)$$

TABLE I. Atomization energies of molecules, in kcal/mol (1 eV=23.06 kcal/mol). E_{XC} has been evaluated on LSD densities at experimental geometries (Refs. 42, 43). Nonspherical densities and Kohn–Sham potentials have been used for open-shell atoms (Ref. 44). The calculations are performed with a modified version of the CADPAC program (Ref. 45); for details of the calculation, see Ref. 25. The experimental values for ΔE (with zero point vibration removed) are taken from Refs. 38 and 46. Hyb denotes the $n=4$ hybrid of exact exchange with the PW91 density functional. UHF is self-consistent unrestricted Hartree–Fock, for comparison.

System	ΔE^{UHF}	ΔE^{LSD}	ΔE^{PW91}	ΔE^{hyb}	ΔE^{exp}
H_2	84	113	105	105	109
LiH	33	60	53	52	58
CH_4	328	462	422	419	419
NH_3	201	337	303	296	297
OH	68	124	111	107	107
H_2O	155	266	236	228	232
HF	97	162	143	138	141
Li_2	3	23	20	19	24
LiF	89	153	137	130	139
C_2H_2	294	460	416	405	405
C_2H_4	428	632	574	565	563
HCN	199	361	327	311	312
CO	174	299	269	255	259
N_2	115	267	242	225	229
NO	53	199	171	152	153
O_2	33	175	144	124	121
F_2	−20	79	55	36	39
P_2	41	142	120	109	117
Cl_2	17	80	64	58	58
mean abs. error	73.2	32.3	8.4	3.1	…

where $\rho_{\sigma\alpha}(\mathbf{r})$ is the uniformly-scaled spin density $\alpha^3\rho_\sigma(\alpha\mathbf{r})$ and $\alpha=\lambda^{-1}$. The shape of the curve $-\Delta E_{\text{xc},\lambda}^{\text{hyb}}$ is smooth and plausible.

To contrast the hybrid presented here from those of Refs. 49 and 50, we note that the two-legged hybrid of Ref. 49 and the [1/1]-Padé of Ref. 50 estimate the curvature of the exact λ-dependence using GGA results near $\lambda=1$, while the [2/2]-Padé hybrid of Ref. 50 inputs yet another piece of information, the exact initial slope $dE_{\text{xc},\lambda}/d\lambda|_{\lambda=0}$ from perturbation theory. In the present work, our single parameter n is determined only from knowledge of the convergence of perturba-
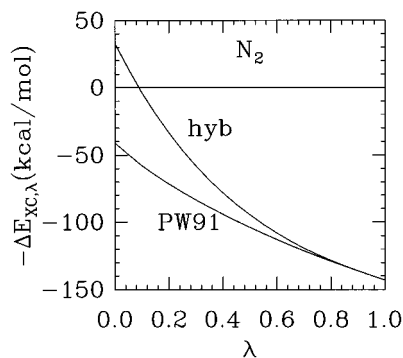
tion theory. Furthermore, once n is chosen, Eq. (7) requires only exact exchange and GGA exchange-correlation energies, just as in Eq. (5).

In a more speculative vein, we propose a continuous generalization of the parameter n of Eq. (6) as an index of ''correlation strength;'' for other definitions, see Refs. 47 and 51. This index n would be determined by fitting the left-hand side of

$$dE_{\text{xc},\lambda}^{\text{hyb}}/d\lambda|_{\lambda=0}=dE_{\text{xc},\lambda}^{\text{DFA}}/d\lambda|_{\lambda=0}-(n-1)(E_{\text{x}}-E_{\text{x}}^{\text{DFA}}) \quad (14)$$

to the exact $dE_{\text{xc},\lambda}/d\lambda|_{\lambda=0}$ given by second-order density functional theory perturbation theory.[32–34] This value of n predicts the optimum amount of exact exchange to be admixed with a density functional approximation, and might also predict the convergence of the perturbation expansion. [If the n predicted by Eq. (14) were $\lesssim2$, we could drop the density functional contribution altogether, and simply use second-order perturbation theory.] Note that n can be defined either for a system (e.g., an atom or molecule) using $E_{\text{xc},\lambda}$ in Eq. (14) or a process (e.g., atomization of a molecule) using the energy change $\Delta E_{\text{xc},\lambda}$ in Eq. (14). We are currently testing hybrids of second-order perturbation theory with GGA. Proper implementation may require a nonempirical GGA which has a perturbation expansion in powers of λ about $\lambda=0$ for a finite system, unlike LSD or PW91. We have recently developed such a GGA.[52] Within this GGA, the derivative on the right-hand side of Eq. (14) is given by twice Eq. (9) of Ref. 52.

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FIG. 1. Dependence of $E_{\text{xc},\lambda}$ of Eq. (1) upon coupling constant λ in the PW91–GGA density functional approximation and $n=4$ hybrid (hyb) of Eq. (6). What is actually shown is $-\Delta E_{\text{xc},\lambda}=E_{\text{xc},\lambda}(N_2)-2E_{\text{xc},\lambda}(N)$, appropriate for the atomization energy ΔE of N_2.

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