

A novel form for the exchange-correlation energy functional

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A new approximate form for the exchange-correlation energy functional is developed. The form is based on the density matrix expansion (DME) for the exchange functional [R. M. Koehl, G. K. Odom, and G. E. Scuseria, *Mol. Phys.* **87**, 835 (1996)]. The nonlocal portion of the correlation energy is assumed to have the same general form as that derived for exchange, while the local portion is taken to be that of the uniform electron gas. The resulting formula does not resort to the use of exact-exchange mixing. A Kohn-Sham implementation of this functional is constructed and the parameters within the functional are adjusted to minimize the difference between the theoretical and the experimental data for a large set of atomic and molecular systems. The results are found to compare favorably with existing functionals, even those which include exact-exchange mixing.
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I. INTRODUCTION

The fundamental theorem of most modern applications of density functional theory (DFT) is the theorem of Kohn and Sham¹⁻³ which states that the exact ground state energy of any many-electronic system is given by

$$E_0[\rho] = T_s[\rho] + J[\rho] + E_{ne}[\rho] + E_{xc}[\rho], \quad (1)$$

where $T_s[\rho]$ is the noninteracting kinetic energy

$$T_s[\rho] = \int \sum_i^{occ} |\nabla \psi_i|^2 d\mathbf{r} \equiv \int \tau d\mathbf{r}, \quad (2)$$

$J[\rho]$ is the classical Coulomb repulsion energy, $E_{ne}[\rho]$ is the energy of the electrons in the external field of the nuclei and $E_{xc}[\rho]$ is the exchange-correlation (XC) energy. The wonderful thing about Eq. (1) is that the first three terms on the right hand side of the equation are well-known and readily calculable functionals of the electronic density. The disheartening fact is that the analytic form of the XC functional is not, and probably cannot ever be, known. The goal of this article is to develop better approximations to the exact $E_{xc}[\rho]$.

One useful approximation to the true XC functional is the so-called generalized-gradient approximation (GGA).⁴⁻⁶ This approximation assumes that the exchange-correlation functional is given by:

$$E_{xc}[\rho] = \int f(\rho, \nabla \rho) d\mathbf{r}, \quad (3)$$

where f is simply a function of the values of the density and its gradient at the point \mathbf{r} . Functionals of this form have been shown to give very good results. Further, Neumann and Handy have shown⁷ that simple methods of adding higher-order derivatives of the density to existing approximations of the general form of Eq. (3) do not seem to significantly improve the agreement with the exact results. This seems to

indicate that the errors inherent in current functionals should be corrigible without appealing to higher than first derivatives of the density.

Becke has investigated various methods of using the exact, Hartree-Fock-style exchange energy to improve approximations to the true XC functional. Such forms are often referred to as “hybrid” functionals, and Becke has found⁸⁻¹⁰ that exact-exchange mixing can significantly improve the results obtained from GGA-style functionals. There are, however, drawbacks to using exact exchange. Most importantly, the Hartree-Fock (HF) exchange energy is known to give qualitatively incorrect results for transition-metal complexes and other systems in which there are a number of low-lying virtual orbitals whose interactions with the occupied orbitals are not treated. Density functionals do not seem to suffer from this difficulty, since they compute the energy based on density and not orbital fluctuations.

In a pair of articles,^{11,12} we have investigated the utility of a Taylor series-like density matrix expansion (DME), first introduced by Negele and Vautherin¹³ to approximate HF exchange. The resulting functional has a GGA-like dependence on ρ and $\nabla \rho$ but also includes terms that depend on the noninteracting kinetic energy density τ . Since the Kohn-Sham energy functional already depends on τ through the definition of $T_s[\rho]$ in Eq. (2), such a term does not require any additional information about the electron distribution, but merely defines a more flexible form for the XC-functional. It was found¹² that such a form gives very encouraging results for the approximation of the exact-exchange energy.

In the present work, we investigate the possibility of applying the form that arises from the DME to approximate the entirety of the XC-functional instead of the exchange part alone. Because we have already seen that the DME possesses the ability to approximate the HF exchange-energy, one circumvents the use of exact-exchange mixing. Nonetheless, the accuracy of the resulting functional is shown to be competitive with established XC-functionals.

II. THE DENSITY MATRIX EXPANSION

The Hartree-Fock exchange energy for a closed shell system can be written as

$$E_x[\rho] \equiv -\frac{1}{4} \int \int \frac{|\rho(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (4)$$

where the density matrix is given by

$$\rho(\mathbf{r}_1, \mathbf{r}_2) \equiv \sum_i^{occ} \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}_2). \quad (5)$$

One can perform a density matrix expansion using Bessel functions j_n for the inter-electronic distance coordinate $s = |\mathbf{r}_1 - \mathbf{r}_2|$ and Legendre polynomials in the derivative operator for the remaining coordinate $\mathbf{r} = a\mathbf{r}_1 + (1-a)\mathbf{r}_2$, where a is adjustable, to obtain the second order approximation

$$\begin{aligned} \rho(\mathbf{r}, s) = & 3 \frac{j_1(ks)}{ks} \rho(\mathbf{r}) + \frac{35j_3(ks)}{2k^3s} \left(\left[a^2 - a + \frac{1}{2} \right] \nabla^2 \rho(\mathbf{r}) \right. \\ & \left. - \tau(\mathbf{r}) + \frac{3}{5} k^2 \rho(\mathbf{r}) \right) + \dots, \end{aligned} \quad (6)$$

where k has dimensions of inverse length.

The benefits of the particular choice of Bessel functions and Legendre polynomials is now clear, since Eq. (6) recovers the exact LDA density matrix when truncated to zeroth order; no other set of expansion functions will accomplish this. One might expect this expansion to be slowly convergent in a delocalized system, such as a metal. However, because of the use of Bessel functions in the DME, one obtains an excellent approximation (LDA) to delocalized exchange even at zeroth order. The convergence to the exact result upon addition of subsequent terms may still be slow, so that the second order approximation we are discussing may not be as accurate for very delocalized systems. However, the DME expansion *must* eventually account for the long range behavior of the density matrix because the expansion functions $j_n(ks)/k^n s$ form a complete basis, so that the dependence of the density matrix on s (or, indeed any function of s) can be expanded in terms of these nondivergent functions. The importance of higher-order terms in the DME will be the subject of a subsequent work.

Using Eq. (6) to approximate the density matrix, we can do the s integral in Eq. (4) analytically, and integrate by parts to get rid of the Laplacian term¹² to obtain

$$\begin{aligned} E_x^{\text{DME}}[\rho] = & -\pi \int \left(\frac{9\rho^2}{4k^2} + \frac{35\rho^{8/3}}{12k^4} g_2(x, z) \right. \\ & \left. + \frac{1225\rho^{10/3}}{96k^6} g_2^2(x, z) \right) d\mathbf{r}, \end{aligned} \quad (7)$$

where

$$g_2(x, z) = (a^2 - a + \frac{1}{2})x^2/3 - z \quad (8)$$

is the second order correction to the density matrix and x and z are given by

$$x = \frac{|\nabla \rho|}{\rho^{4/3}}, \quad z = \frac{\tau}{\rho^{5/3}} - C_F, \quad (9)$$

and C_F is the Fermi constant

$$C_F = \frac{3}{5} (3\pi^2)^{2/3}. \quad (10)$$

In the previous papers, the square of the second order term was neglected on the grounds that it would give a much smaller contribution to the total exchange energy. In the current work, we retain this term since it should, at the very least, not make our results any worse.

Now, one would nominally choose k to be the Fermi momentum,

$$k_F \equiv (3\pi^2 \rho)^{1/3}. \quad (11)$$

However, in accord with our previous work,¹² we have found a significant improvement is gained by using the more general form

$$k^2$$

ing requirements. The only way for this to be true, however, is for $\gamma^\lambda(x, z)$ to scale as the limiting value of the above sequence, $\lambda^{4/3}$. The simplest form that scales in this fashion and satisfies the requirement that the Fermi momentum be recovered for uniform densities is

$$\gamma(x, z) = 1 + \alpha(x^2 + z). \quad (18)$$

This is the form that we have selected for the present study. One might nominally expect that different coefficients for the x^2 and z terms would give an improved description of the exchange energy, but we have found empirically that this is not the case, and so we retain the form of Eq. (18) for simplicity. One consequence of using this $\gamma(x, z)$ is that for any *truncated* version of the DME, one finds that the approximate exchange energy scales to zero under nonuniform scaling. Hence, while the true exchange as given by the infinite order DME using this $\gamma(x, z)$ scales to a negative constant under nonuniform scaling, the form of the DME seems to indicate that it is more appropriate to require that any finite-order approximate functional scale to zero in this limit.

It is very important to note that even though the expansion in Eq. (6) contains the correct second order coefficient for $j_3(ks)/ks$ it does not include all the terms that depend on x and z . This is because the exact expansion uses Legendre polynomials for the derivative operator. Even the highest order polynomials from this family have terms that are low order in its argument, and hence every term in the expansion of Eq. (6) will depend partly on x^2 and z . If one were somehow able to reexpress the (infinite) expansion simply in terms of the powers of the differential operator, one would obtain an equation with the exact contributions of x^2 and z . However, since the mathematical identity^{11,13} that allows us to perform the DME applies exclusively to Legendre polynomials and spherical Bessel functions, and the Bessel functions must be retained in order to obtain the LDA density matrix as in Eq. (6), it is at the very least not a straightforward task to do this transformation analytically. However, since all the higher order terms will look precisely like the terms we have already obtained, the total effect of all higher order terms is just to alter the coefficients of the terms in Eq. (7). To account for this effect, we insert adjustable parameters in front of each term to obtain, after some simplification and absorbing any multiplicative constants into the parameter set

$$E_x^{\text{GVT4}}[\rho] = \int \rho^{4/3} \left(\frac{a}{\gamma(x, z)} + \frac{bx^2 + cz}{\gamma^2(x, z)} + \frac{dx^4 + ex^2z + fz^2}{\gamma^3(x, z)} \right) d\mathbf{r}. \quad (19)$$

We will, for convenience, call this the GVT4 functional due to the similarity to the GMVT functional defined in Ref. 12 except that the current form includes some of the effects of the squares of the second order terms (fourth order terms).

We note that a very similar choice for k^2 was made in Ref. 12 in order to force the exchange energy density $U_x(r)$, defined by

$$E_x[\rho] \equiv \int \rho U_x d\mathbf{r}, \quad (20)$$

to converge exponentially to zero for large r . The exchange energy density for the DME with k modified by the factor of Eq. (18) also has an exponentially decaying behavior. This differs from the known exact form¹⁵

$$\lim_{r \rightarrow \infty} U_x^{\text{exact}} = -\frac{1}{r}. \quad (21)$$

However, we note that for a functional of the form

$$E_x[\rho] = \int \rho^{4/3} g(x, z) d\mathbf{r} \quad (22)$$

this condition is *incompatible* with the exact nonuniform scaling requirements of Eqs. (13) and (14). Specifically, Eq. (21) requires that for large r , or equivalently large x , the enhancement function $g(x, z)$ take the asymptotic form

$$g(x, z) \propto x / \log(x) \quad (23)$$

which is easily seen to violate both Eqs. (13) and (14). Hence, the best we can hope for from our general approach is an exchange energy density that goes to zero exponentially, which is achieved by the current form.

It is clear that, in principle, the ratios of the coefficients d , e , and f are fixed by the values of b and c , since this fourth order term is proportional to the square of the second order term. However, we choose to allow these ratios to vary with the expectation that if the constraint that fixes these ratios is physically significant, our parameter selection scheme should discover this independent of our derivation. Also, since we have inserted a parameter in front of the LDA term, our functional will not retain the correct result for the uniform electron gas limit. However, it has been shown in our previous investigations^{11,12} that a small violation of this limit drastically improves results for molecular systems, and so we include it here. It is also instructive to present the trivial generalization of Eq. (19) to open shells,

$$K^{\text{GVT4}}[\rho_\alpha, \rho_\beta] = \sum_\sigma \int \rho_\sigma^{4/3} \left(\frac{a}{\gamma_\sigma(x, z)} + \frac{bx_\sigma^2 + cz_\sigma}{\gamma_\sigma^2(x, z)} + \frac{dx_\sigma^4 + ex_\sigma^2z_\sigma + fz_\sigma^2}{\gamma_\sigma^3(x, z)} \right) d\mathbf{r}, \quad (24)$$

where

$$\gamma_\sigma(x, z) \equiv 1 + \alpha(x_\sigma^2 + z_\sigma) \quad (25)$$

and x_σ and z_σ are the same as x and z , merely evaluated for the α and β densities as opposed to the total density. We note that the GVT4 form above gives results comparable to the exchange functional of Ref. 12.

III. CONSTRUCTION OF THE EXCHANGE-CORRELATION FORM

It has been shown^{11,12} that the DME forms discussed above are sufficiently flexible to accurately describe the exact-exchange energy. One would, of course, like to find a

way to confer this same flexibility and accuracy on a correlation functional. To this end, we note that the exchange functional in Eq. (24) has the general form

$$E^x[\rho_\alpha, \rho_\beta] \propto \sum_\sigma \int \rho_\sigma e^{\text{LDA}} f(x_\sigma, z_\sigma) d\mathbf{r}, \quad (26)$$

if we choose

$$f(x_\sigma, z_\sigma) = \left(\frac{a}{\gamma_\sigma(x, z)} + \frac{bx_\sigma^2 + cz_\sigma}{\gamma_\sigma^2(x, z)} + \frac{dx_\sigma^4 + ex_\sigma^2 z_\sigma + fz_\sigma^2}{\gamma_\sigma^3(x, z)} \right). \quad (27)$$

That is, our exchange functional can be expressed up to an overall numerical prefactor as the exchange energy for the uniform electron gas times a dimensionless, nonlocal function $f(x_\sigma, z_\sigma)$. Since this function is dimensionless, and therefore independent of the energy scale of the problem, one expects that it should be, in some sense, transferable between different types of energy functional. The only difficulty in our case lies in how this function may be incorporated into a correlation functional in a consistent, physical manner.

The correlation formalism we shall use to accomplish this is the one proposed by Becke.⁹ Becke defines same-spin and opposite-spin correlation functionals,

$$E_c^{\sigma\sigma'} = \int f^{\sigma\sigma'}(x, z) e_{c\sigma\sigma'}^{\text{LDA}} d\mathbf{r}, \quad (28)$$

$$E_c^{\sigma\sigma} = \int f^{\sigma\sigma}(x_\sigma, z_\sigma) D_\sigma e_{c\sigma\sigma}^{\text{LDA}} d\mathbf{r}, \quad (29)$$

where

$$x^2 \equiv x_\alpha^2 + x_\beta^2, \quad z \equiv z_\alpha + z_\beta \quad (30)$$

and the same-spin and opposite spin LDA correlation parts are as defined by Stoll *et al.*¹⁶ The factor D_σ is a dimensionless factor given by

$$D_\sigma = 1 - \frac{x_\sigma^2}{4(z_\sigma + C_F)}. \quad (31)$$

D_σ is easily seen to be zero for any system with only one orbital. Since our same-spin correlation is multiplied by this factor, this term guarantees that the correlation energy is zero for any one-electron system, which is certainly a desirable trait for a correlation functional. With these definitions, one constructs the correlation energy as

$$E_c = E_c^{\alpha\beta} + E_c^{\alpha\alpha} + E_c^{\beta\beta}. \quad (32)$$

Our approach is to simply utilize the same function $f(x, z)$ as was used to describe exchange and insert it into each of the correlation forms above, where we use the recent parameterization of Perdew and Wang for the local correlation form.¹⁷ This choice is not in any way motivated by physical concerns, but should rather be considered a convenient approximation. The bulk of the difference between the exchange and correlation energies should be accounted for by the presence of the uniform electron gas functional multiplying each of the dimensionless $f(x, z)$'s. We attempt to account for any further differences by allowing the parameters in each of the three terms (exchange, same-spin and opposite-spin correla-

tion) to vary independently. Since we know this form is flexible enough to describe exchange, one hopes that it will also be sufficiently flexible to describe correlation phenomena. Hence we define our exchange-correlation form to be the exchange functional of Eq. (24) together with the correlation form Eq. (32) with the dimensionless nonlocal factor of Eq. (27). This functional form will be referred to as the VSXC form.

Now, this functional form has the drawback that the number of parameters is quite large. Handy and collaborators¹⁸ have shown recently that a large number of parameters does not necessarily guarantee proportionally better results, but that it is more important that the terms that are included via the parametrization are *physically significant*. The primary hurdle that having so many parameters invokes is that it becomes necessary to fit them over a very large number of systems in order to be certain that the results thus obtained are not simply due to the numerical fit, and to ensure that the resulting parameters are robust. However, noting that there are essentially an infinite number of systems this functional may be applied to, one can increase the fitting set without bound until the number of parameters ceases to be a concern.

We also note here that our definition of D_σ is slightly different from that given by Becke.^{9,19} We have modified his definition so that D_σ is pseudo-zeroth order in the derivatives of the density. This is significant because our DME expansion is essentially a Taylor expansion, and should therefore begin with a term that is of order zero in the differential.

IV. COMPUTATIONAL METHOD

The first thing that must be done in order to determine the quality of the VSXC form is to obtain the optimal values of the parameters in the functional. For this purpose, we have constructed an extensive set of experimental values against which the results obtained by the VSXC functional will be compared. Our set includes the G2 set of molecules²⁰ and also a large number of other species as described in the Appendix. All the fitting calculations are performed at the experimental geometries using a 6-311+G(3df,2p) basis. Further details on how the calculations were done are also discussed in the Appendix.

Now, several authors have proposed the use of certain standard atomic and molecular densities as the testing grounds for novel functionals.^{8-10,21-23} This has the obvious advantage of being significantly faster than a full Kohn-Sham treatment, but the major drawback is that an excellent functional at any given fixed density does not necessarily translate into an excellent functional in a Kohn-Sham scheme. Further, it is not altogether clear that a fixed density should be appropriate for the comparison of two XC functionals, since density relaxation, which would be accounted for in a KS treatment, may be an important phenomenon for any given chemical system. For these reasons, we have decided to use only fully self-consistent Kohn-Sham densities for our comparisons.

Since our functional depends on the kinetic energy density, τ , a traditional KS scheme employing the functional derivative of the energy with respect to the density to obtain

self-consistency becomes very complicated. However, it has been shown²⁴ that this difficulty can be circumvented by considering the contribution of the functional to a given element of the Fock matrix. Specifically, it can be shown that the presence of τ in the functional G gives rise to only one additional term in the rs element of the Fock matrix:

$$\int \nabla \chi_r \left(2 \frac{\partial G}{\partial \tau} \right) \nabla \chi_s d\mathbf{r}, \quad (33)$$

where χ is an atomic orbital. We have implemented our functional self-consistently using the above correction in a developmental version of the Gaussian suite of programs.²⁵

Now, it becomes necessary to optimize the parameters in an SCF fashion over our training set. However, the parameter optimization is not so easy in this case as it is for the post-SCF case, since the density now *changes* each time the parameters are changed. This nonlinear interaction has the potential to foul up any attempts to optimize parameters within a functional, but we have found that a simple iterative procedure works very nicely. First, a set of guess parameters are generated by a typical post-SCF fit to, say, LDA densities. Then, as the first step in the iterative procedure, a full SCF calculation is performed using these parameters. Once this has been done, another post-SCF parameter optimization is performed at the SCF density of the *previous* set of parameters. Another SCF run is then performed and the procedure is repeated until the energy and parameters become stable. We have found, empirically, that this process tends to converge within three iterative cycles.

VSXC satisfies the Lieb-Oxford bound for exchange.^{6,28} The Lieb-Oxford bound requires that the exact LDA-exchange enhancement factor, in our case $f(x,z)$, should satisfy

$$f(x,z) > -2.12 \quad (34)$$

for all possible values of x and z . Since our enhancement factor is a function of two variables, it is not easily displayed for examination, nor is the equation for the minimum value easily solved analytically. However, it is possible to verify that the minimum value of our exchange enhancement factor is attained when $x \sim 26$ and $z \sim 40$, where the enhancement factor is about -1.88 . The enhancement factor for the whole of LDA XC should also satisfy this bound, but it would be extremely difficult to examine the behavior of the total XC enhancement factor, since there are different enhancement factors for each piece, and such an analysis would therefore require evaluation of the relative magnitudes of the various terms. Hence we refrain from this in the present paper. However, it is very encouraging that the exchange part, which makes up the majority of the XC energy, satisfies this important bound.

The results obtained with the optimal parameters over the training set are listed in Tables II–V together with the results with the standard functionals BLYP,^{21,22} B3LYP,⁸ and B1B95.⁹ The lattermost of these was specifically implemented for this work following Ref. 24. In Table VI, we list the overall statistics for each method. The results presented in these tables must be taken with a grain of salt, since our functional has been *optimized* to give the best possible results over this set. With this *caveat*, we note that the results given by the rather naive VSXC form are very encouraging. They compare favorably to the results of the established functionals, even B1B95 and B3LYP, which include exact exchange mixing. In fact, the standard deviation of 6.2 mE_h over the entire set for VSXC is actually lower than that obtained by any of the other functionals. The average absolute errors for B1B95 and VSXC are essentially the same, 4.6 mE_h compared to 4.7 , and both are significantly better than B3LYP, with an average absolute error of 6.3 mE_h . A comparison of the results of our functional to those of B1B95 and B3LYP over this set is probably fair in spite of the fact that our functional was optimized over this set, since the latter two were, themselves, fitted to a set which included about 70% of the molecules in our full set. As far as functionals that do not employ exact-exchange mixing go, we see that VSXC offers a very significant improvement over the BLYP functional, giving errors that are generally less than half as large as those for the established form.

It is important to note that certain molecules in the training set are described poorly by all of the XC functionals examined herein. Most notably, the atomization energy of C_2 is significantly underestimated by all the functionals. This is understandable, since the proper description of the ground state of C_2 is known to involve a significant amount of non-dynamical correlation,²⁹ a phenomenon which is very difficult to account for in density functional theory.³⁰ We think that the identification of molecules such as this are crucial to the systematic improvement of existing density functionals.

TABLE II. Energy Differences (kcal/mol) from experimental atomization energies (D_e) for the G2 set (ZPVE corrected).

Molecule	Expt.	BLYP	B3LYP	B1B95	VSXC
LiH	-57.7	-0.1	-0.6	3.6	2.6
BeH	-49.6	-7.4	-8.2	-4.4	0.1
CH	-83.7	-1.8	-1.6	1.4	0.3
$\text{CH}_2 \ ^3\text{B}_1$	-189.8	-0.0	-2.1	0.0	-1.8
$\text{CH}_2 \ ^1\text{A}_1$	-180.5	0.5	-0.2	3.5	0.9
CH_3	-306.4	-0.5	-3.3	0.6	-3.6
CH_4	-419.1	2.3	-1.6	1.1	-1.9
NH	-83.4	-6.0	-4.5	0.2	0.5
NH_2	-181.5	-7.9	-6.4	0.3	-1.1
NH_3	-297.3	-3.6	-2.9	2.5	1.9
OH	-106.3	-3.3	-1.8	0.4	-0.9
H_2O	-232.1	-0.5	1.1	2.6	0.9
FH	-140.7	-0.2	1.3	1.3	-0.9
LiF	-138.8	-1.6	1.6	5.2	1.0
C_2H_2	-405.3	0.0	2.0	1.7	-1.6
C_2H_4	-562.4	3.4	1.1	2.4	-0.1
C_2H_6	-710.7	6.5	-0.5	1.3	0.5
HCN	-316.3	-4.2	2.6	5.0	4.8
CO	-259.2	-3.3	3.0	0.8	0.5
HCO	-278.3	-9.5	-3.0	-2.7	-4.4
H_2CO	-373.4	-5.1	-0.7	-0.2	-1.1
CH_3OH	-511.6	0.3	-0.3	1.1	2.5
N_2	-228.5	-11.6	-0.9	2.8	6.7
N_2H_4	-437.8	-9.6	-6.2	2.0	7.5
CO_2	-388.9	-12.4	-0.8	-5.2	-5.9
$\text{SiH}_2 \ ^1\text{A}_1$	-151.4	-0.3	-2.0	0.4	-0.6
$\text{SiH}_2 \ ^3\text{B}_1$	-130.7	0.3	-2.1	-1.3	-1.7
SiH_3	-226.7	3.0	-0.8	1.5	-0.2
SiH_4	-321.4	3.9	-1.8	1.7	-1.8
PH_2	-152.8	-4.9	-5.9	-2.1	-2.8
PH_3	-242.0	-0.8	-3.0	0.0	-0.7
SH_2	-182.3	1.6	0.3	-0.6	-2.4
HCl	-106.2	1.5	0.8	-0.6	-1.1
NaCl	-97.8	5.4	4.2	2.3	-3.1
SiO	-192.2	-2.3	4.8	5.0	2.6
SC	-171.2	-1.1	4.6	0.2	-2.1
Si_2H_6	-529.5	10.0	-0.2	1.8	-5.8
CH_3Cl	-393.6	4.1	1.5	-0.1	1.3
CH_3SH	-472.7	10.2	7.4	6.2	5.9
Li_2	-24.4	3.5	3.4	6.7	-0.0
CN	-179.0	-12.3	-0.5	1.5	-2.4
NO	-152.9	-13.9	-2.7	-1.0	1.0
O_2	-120.4	-15.2	-3.5	-4.5	-7.3
H_2O_2	-268.6	-5.7	3.0	5.0	5.1
F_2	-38.5	-9.6	2.3	3.0	-0.1
Si_2	-74.7	1.1	4.9	1.3	-5.2
P_2	-117.2	-4.8	0.5	-0.6	1.8
Na_2	-16.8	-1.2	-0.5	1.7	-6.3
S_2	-101.6	-5.2	-1.3	-7.2	-6.8
Cl_2	-57.9	0.5	2.8	-2.6	3.0
SO	-125.1	-9.0	-1.2	-3.3	-4.4
ClO	-64.3	-10.3	-2.0	-3.8	-2.2
ClF	-61.4	-5.2	0.8	-1.6	0.8
HOCl	-164.3	-4.0	1.2	-0.5	2.9
SO_2	-258.5	-6.1	7.7	2.3	3.5
G2 totals	Expt.	BLYP	B3LYP	B1B95	VSXC
$\overline{ x }$	—	4.8	2.5	2.3	2.5
σ_x	—	9.3	4.2	3.2	3.3
Max. Dev. (+)	—	10.2	7.7	6.7	7.5
Max. Dev. (—)	—	15.2	8.2	7.2	7.3

TABLE III. Energy differences (eV) from experimental ionization potentials (ZPVE corrected).

Molecule	Expt.	BLYP	B3LYP	B1B95	VSXC
H	13.60	-0.06	0.05	-0.05	0.06
He	24.59	0.19	0.32	0.09	0.21
Li	5.39	0.12	0.22	0.05	0.07
Be	9.32	-0.34	-0.20	-0.42	-0.18
B	8.30	0.32	0.43	0.13	0.19
C	11.26	0.14	0.28	0.08	0.30
N	14.54	-0.03	0.12	0.05	0.32
O	13.61	0.55	0.54	0.12	0.01
F	17.42	0.30	0.33	0.04	0.06
Ne	21.56	0.15	0.19	0.01	0.21
Na	5.14	0.20	0.27	0.00	-0.12
Mg	7.56	0.06	0.16	-0.11	0.04
Al	5.98	-0.11	0.03	-0.10	0.05
Si	8.15	-0.20	-0.03	-0.11	0.13
P	10.49	-0.31	-0.11	-0.11	0.14
S	10.36	0.04	0.17	-0.04	0.01
Cl	12.97	-0.06	0.09	-0.04	0.06
Ar	15.76	-0.15	0.03	-0.03	0.05
CH ₄	12.80	-0.25	-0.06	-0.17	-0.21
NH ₃	10.22	-0.09	-0.01	-0.12	-0.09
OH	13.04	0.17	0.22	-0.04	0.01
H ₂ O	12.69	-0.07	0.00	-0.13	-0.08
FH	16.10	-0.00	0.05	-0.10	0.01
SiH ₄	11.08	-0.35	-0.09	-0.23	-0.05
PH ₂	9.80	-0.06	0.10	0.00	0.21
PH ₃	9.86	-0.14	-0.02	-0.10	-0.01
SH ₂ ² B ₁	10.47	-0.21	-0.05	-0.11	-0.04
HCl	12.76	-0.18	-0.00	-0.07	-0.01
C ₂ H ₂	11.42	-0.27	-0.14	-0.20	-0.24
C ₂ H ₄	10.55	-0.31	-0.23	-0.27	-0.27
CO	14.01	-0.11	0.15	0.00	-0.03
N ₂ ² σ	15.59	-0.23	0.25	0.14	-0.16
O ₂	12.04	0.23	0.51	0.28	0.30
P ₂					

Unfortunately, it is clear from the data that our approach has not been wholly successful in improving the results for this particular molecule.

We also present in Table VII the KS total atomic energies obtained using the large basis sets of Ref. 31 for each functional together with the nonrelativistic atomic energies as computed in Ref. 32 for comparison. It is clear from the table that VSXC shows a systematic overestimation of the total energies. As a general rule, the other functionals also overestimate total energies, but to a lesser extent. However, since this systematic overestimation does not seem to affect

TABLE V. Energy differences (kcal/mol) from experimental results for some additional atomization energies. The experimental energies are shown in the first column. Subsequent columns show $E_{\text{SCF}} - E_{\text{Expt}}$ for each of the functionals discussed.

Molecule	Expt.	BLYP	B3LYP	B1B95	VSXC
H ₂	-109.3	-0.0	-0.8	1.8	2.9
BH	-82.2	-0.9	-1.6	0.1	-1.0
BO	-193.7	-8.0	-2.0	-1.7	-2.1
PO	-143.6	-9.5	-1.1	0.5	1.9
MgH	-33.0	0.5	-0.3	0.4	1.0
C ₂	-145.8	10.7	26.1	24.1	12.7
SH	-87.2	-0.3	-0.8	-0.4	-2.1
O ₃	-147.6	-23.1	7.2	8.9	-0.7
OCS	-333.3	-10.8	-1.0	-7.8	-9.5
NO ₂	-227.4	-27.8	-6.4	-5.7	-7.3
N ₂ O	-270.5	-26.7	-6.0	-4.0	-3.4
C ₂ N ₂	-501.0	-20.6	-3.5	-1.8	-1.1
SO ₃	-344.0	-4.3	12.1	2.1	4.4
CINO	-191.3	-22.3	-3.0	-2.5	-5.2
FNO	-209.5	-29.7	-8.6	-6.7	10.8
FOF	-93.2	-20.6	0.0	1.2	-3.2
FCIO ₃	-236.5	-6.1	16.7	3.3	7.4
BF ₃	-469.6	0.1	3.4	-0.8	-3.8
CF ₄	-475.7	-3.3	3.8	-6.7	-1.5
CCl ₄	-312.4	12.2	13.6	-5.7	1.8
C ₂ F ₄	-582.9	8.4	20.6	7.9	9.7
SiF ₄	-572.6	18.1	20.1	13.4	0.4
SiCl ₄	-382.0	23.8	17.5	-3.8	-2.9
NF ₃	-205.1	-23.7	-3.7	-4.2	-4.8
ClF ₃	-125.6	-21.6	-1.3	-4.5	-7.6
PF ₅	-556.4	14.9	20.8	8.4	5.0
SF ₆	-478.4	11.1	21.8	0.2	-1.5

Totals

$\overline{ x }$	—	13.3	8.3	4.8	4.3
σ_x	—	24.6	10.7	8.0	5.4
Max. Dev. (+)	—	23.8	26.1	24.1	12.7
Max. Dev. (-)	—	29.7	8.6	7.8	9.5

the energy differences obtained by VSXC, one can assert that the surplus energy is probably localized to the core electrons, which do not play a major role in most chemical processes.

In light of the excellent results obtained by our functional in the absence of exact-exchange mixing, one might hope that even better results would be obtained by allowing some admixture of exact exchange in our functional. We have investigated this possibility by evaluating the functional

$$E_{\text{XC}}[\rho] = E_{\text{XC}}^{\text{VSXC}}[\rho] + c_{\text{ex}} E_{\text{x}}^{\text{exact}}, \quad (35)$$

where c_{ex} is an adjustable parameter. It is implicit in our definition that all of the parameters in this new XC expression will be varied independently to minimize the error with respect to experimental results. We note that this is the most general way to attempt to include the exact-exchange energy, and is identical to the method used by Becke.¹⁰ When this functional is optimized, one finds the remarkably low value of 0.000 035 for the exact-exchange mixing parameter c_{ex} , which results, of course, in no noticeable change in the results given by the functional. This result *strongly* supports our assertion that the exact-exchange energy is not necessary for a proper description of the thermochemistry of atomic and molecular systems, or at minimum, that the DME contains a good enough description of exact exchange to preclude its *explicit* inclusion in the functional form. Our conclusion would seem to be at odds with the results of Becke⁸⁻¹⁰ which provide several examples of cases where exact-exchange mixing is necessary to obtain reasonable results. However, we note that all of Becke's functionals utilize the B88 exchange functional²¹ or some form of similar quality. Hence one might conclude that the apparent need for exact-exchange mixing with current density functionals is merely a relic of the relatively poor quality of past exchange functionals.

TABLE IX. Statistical deviations (mE_h) from Hartree-Fock total energies over the G2 set.

	Becke-88	VSX
$\overline{ x }$	45.0	7.1
σ_x	61.6	9.0
Max. Dev. (+)	54.1	19.3
Max. Dev. (−)	165.3	21.1

statistical summary of the results, presented in Table X. For comparison, the same results for BLYP, B3LYP and B1B95 are also presented, along with the results for the G2 method itself.³³ All calculations used MP2/6-31G* optimized geometries and scaled HF/6-31G* zero-point energies as in Ref. 33. As can be seen from the table, the thermochemistry predicted by VSXC is the most accurate of any of the density-functional methods considered. The results for VSXC are almost a factor of 3 better than for BLYP and also somewhat better than for B3LYP or B1B95, but noticeably worse than those given by the more sophisticated G2 method, with VSXC giving an average absolute error of 2.7 kcal/mol compared to 1.6 for the G2 method. The results for VSXC could probably be improved somewhat if the Kohn-Sham optimized geometries were used instead of the MP2/6-31G* geometries, but only by a few percent. Hence while VSXC falls short of the excellent results of the G2 method, our results strongly indicate that it offers competitive thermochemistry when compared to some of the best existing functionals.

It is also instructive to see how well our method predicts optimized structures. For this purpose, we have calculated the optimized geometries provided by VSXC over the set of diatomic molecules in the G2 set and presented the results in Table XI. This set has previously been proposed by Handy^{7,24} and furnishes a simple measure of the accuracy of the geometries provided by a given method. As can be seen from the table, the average absolute error of 0.013 Å for VSXC is somewhat worse than that provided by the hybrid methods B3LYP and B1B95, which give average absolute errors of 0.010 and 0.009, respectively. On the other hand, it shows some improvement over the results for BLYP, which has an average absolute error of 0.019 Å. It is interesting to note that VSXC performs very comparably to the hybrid methods with the exception of the two alkali metal diatomics Na₂ and Li₂ for which it severely overestimates the bond lengths. It is not clear why these molecules should present such difficulty for an otherwise accurate method. The challenge involved in improving the bond lengths without resorting to the use of Hartree-Fock exchange has been noted by other authors.^{18,24,26} We see here that VSXC succeeds in part

TABLE XI. Optimized diatomic bond lengths in angstroms for various functionals using a 6-311+G(3df,2p) basis set.

Molecule	Exact	BLYP	B3LYP	B1B95	VSXC
BeH	1.343	1.347	1.341	1.344	1.362
CH	1.120	1.132	1.122	1.122	1.129
Cl2	1.988	2.040	2.010	1.979	2.006
ClF	1.628	1.673	1.642	1.619	1.648
CIO	1.570	1.600	1.576	1.557	1.576
CN	1.172	1.174	1.162	1.159	1.170
CO	1.128	1.136	1.124	1.121	1.131
F2	1.412	1.431	1.394	1.375	1.413
FH	0.917	0.932	0.922	0.916	0.918
H2	0.741	0.746	0.743	0.741	0.741
HCl	1.275	1.289	1.280	1.274	1.273
Li2	2.673	2.708	2.700	2.713	2.735
LiF	1.564	1.584	1.572	1.573	1.594
LiH	1.595	1.597	1.590	1.596	1.617
N2	1.098	1.103	1.091	1.087	1.097
Na2	3.079	3.047	3.040	3.061	3.154
NaCl	2.361	2.385	2.371	2.370	2.395
NH	1.036	1.050	1.039	1.037	1.041
NO	1.151	1.161	1.144	1.138	1.151
O2	1.208	1.228	1.203	1.191	1.211
OH	0.971	0.985	0.974	0.969	0.971
P2	1.893	1.910	1.888	1.875	1.889
S2	1.889	1.928	1.903	1.883	1.899
SC	1.535	1.548	1.531	1.525	1.540
SiO	1.510	1.530	1.511	1.505	1.519
SO	1.481	1.512	1.488	1.477	1.494
$\overline{ x }$	—	0.019	0.009	0.010	0.013

in improving these results, but some insight is needed to make the improvement universal for all types of bonds.

We have also applied our implementation of the VSXC form to try to predict the electron affinities of two very difficult atoms, O and F. Electron affinities were not considered as part of our fitting set as a matter of convenience, as some methods give very unstable results for negative ions. In spite of the fact that our method was not calibrated to these systems, we see in Table XII that the results given by VSXC for these electron affinities are excellent, giving comparable results to a large-basis coupled-cluster single double (triple) [CCSD(T)] calculation. Additionally, we have looked at the activation energy for the reaction $H_2 + H \rightarrow H + H_2$. As can be seen from Table XIII, BLYP *severely* underestimates the barrier for this reaction, as compared to the accurate quadratic configuration interaction [QCISD(T)] result. This is, in fact, typical of GGA functionals. B3LYP and B1B95 both

TABLE X. Statistical deviations (kcal/mol) over the G2/97 set of Ref. 33.

	BLYP	B3LYP	B1B95	VSXC	G2
$\overline{ x }$	7.1	3.1	2.9	2.7	1.6
σ_x	9.5	4.5	3.9	3.6	2.1
Max. Dev. (+)	28.4	8.2	14.3	11.6	8.2
Max. Dev. (−)	24.8	20.1	14.2	9.5	7.1

TABLE XII. Electron affinities (eV) of O and F using various methods. Coupled-cluster results from Ref. 34 and experimental results from Ref. 20.

Method	O	F
BLYP	1.70	3.65
B3LYP	1.60	3.46
B1B95	1.63	3.59
VSXC	1.42	3.44
CCSD	1.25	3.19
CCSD(T)	1.42	3.36
Expt.	1.46	3.40

TABLE XIII. Activation energies (kcal/mol) for the reaction $\text{H}_2 + \text{H}$ using various methods. All calculations performed with the 6-311+G(3df,2p) basis, except for the QCISD(T) calculation, which utilized the CC-VQZ basis.

Method	H_2 R_e	TS R_e	E_a
HF	0.734	0.932	17.7
BLYP	0.746	0.935	2.9
B3LYP	0.743	0.929	4.3
B1B95	0.741	0.929	7.5
VSXC	0.741	0.929	5.5
QCISD(T)	0.741	0.929	9.8

give improved results by using exact exchange, which severely overestimates this barrier height, to bring the severe underestimate given by the generalized gradient expansion closer to the true result. The predicted barrier for VSXC is comparable to the results given by the hybrid functionals, lying somewhere between the more accurate B1B95 and the less accurate B3LYP. Work to examine the results obtained by this functional for other activation energies is in progress, but this initial result indicates that our form may offer competitive barrier heights as well.

VII. CONCLUSIONS

In this paper, we have presented a novel form for the XC functional and implemented it in a Kohn-Sham fashion. This functional does not appeal to knowledge of the exact exchange energy to compute the XC energy, but rather relies on a more accurate representation of the exchange-energy functional that includes the kinetic energy density τ to improve overall energetics. Hence our approach provides a possible alternative to the current “hybrid” *ansatz* of exact-exchange mixing^{9,8,10,35} which has, to date, offered by far the best results available within the framework of density functional theory. By assessing the accuracy of the VSXC functional over a very large set of systems, including both a large training set and numerous other chemically interesting species, it is concluded that VSXC appears to offer approximately the same energetic accuracy as the “hybrid” methods mentioned previously without resorting to the use of exact exchange. This is in accord with the conclusions reached in Ref. 26 using a B88-type exchange functional and a correlation functional that models the Coulomb hole.³⁶

There are certain shortcomings of the VSXC form. The optimized geometries are in general quite good, but VSXC shows a strong overestimation of the bond lengths for the alkali metal diatomics. Additionally, there are still certain “difficult” molecules such as C_2 and FNO whose energetics are not treated well by any of the XC functionals considered in this paper. These shortcomings indicate that some improvements still need to be made in order to obtain truly uniformly satisfactory results from DFT. Future work may investigate the possibility of addressing these difficulties within a similar framework. Most notably, it would be instructive to take into consideration the uniform and nonuniform scaling requirements for the correlation energy.¹⁴ This would offer a much more physical approximation to the cor-

relation energy, in contrast to the admittedly simplistic form we have used.

Hence we conclude that the functional form proposed in this paper shows great promise for the fast and accurate evaluation of exchange-correlation energies within a Kohn-Sham framework. Our results also strongly indicate that excellent thermochemistry can be obtained using functionals that do not contain HF exchange, contrary to the conclusions that have been drawn previously.^{8–10,35} Further work is warranted to evaluate more precisely the utility of this functional as a general alternative to exact-exchange mixing. It is, for example, unclear whether our prescription will mimic the benefits of exact exchange on the magnetic couplings of antiferromagnetic materials.³⁷ However, the initial results presented herein are very encouraging.

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APPENDIX: CONSTRUCTION OF THE TRAINING SET

Several previous works^{8,9,26} have used the G2 set of atomization energies and ionization potentials²⁰ to optimize and test various functionals. However, this set includes only 55 atomization energies and 42 ionization potentials. Since our functional has no less than 21 different parameters that may be adjusted, it seems to us that this set is too small, so that it needs to be augmented. Recently, the so-called “G2/97” set has been introduced,³³ which adds a large number of heats of formation to the original set. However, most of these molecules are substituted organic species, and it is even noted in Ref. 33 that density functional methods seem to uniformly perform well for these systems. Further, many of the molecules are quite large (10–20 atoms) which is a significant computational expense for a single element of a fitting set. Hence we eschew the full G2/97 set as a fitting set. Instead, we begin with the original G2 set of atomization energies²⁰ and ionization potentials, and attempt to add to it *small* species that are expected to be more stringent tests for density functionals.

As far as ionization potentials (IPs) go, the G2 set is a nearly exhaustive list of the accurately known values. We had difficulty obtaining with consistency the ionization potentials for N_2 ($^2\Pi$) and SH_2 3B_1 because certain steps in our fitting procedure required the calculations to be run without symmetry which made converging to anything other than the ground state difficult. For this reason, we removed these two values from the set and compensated by adding the IPs of F_2 , NO and C_2 . Additionally, there are a number of molecules in the G2/97 set which are shown in Ref. 33 to be “difficult” cases for DFT. We have selected several of these systems, and also several additional molecules from the literature for which the heats of formation are accurately known. This procedure produced 28 additional atomization energies.

It is wise to use stretched and shortened bonds to give a more precise measure of the quality of a functional. In the same spirit, we have utilized the Rydberg-Kleine-Rees procedure^{30,38} to generate the experimental potential surfaces for several of the diatomics in the original G2 set whose vibrations are typically described poorly by DFT methods. Since most chemical phenomena occur in the vicinity of equilibrium, however, we choose a stretching factor of only 1.1, compared to Handy's choice of 1.5. The energy we calculate is the difference between the equilibrium energy and those of the bond stretched and shortened by 10%. This set should obviously test the accuracy of the equilibrium geometry and harmonic vibrational frequencies for these diatomics. Additionally, these cases should improve the prediction of activation energies, since these usually involve slightly distorted bond lengths.

Finally, in general, we have chosen to perform all the calculations at the experimental geometries. It would be best to obtain the energies at the SCF optimized geometries, but this entails a significantly larger amount of computational effort, and the energetic difference between the experimental and SCF optimized geometries is expected to be minimal. Experimental geometries are as found in Refs. 39–47 and references therein. In cases where no reliable experimental result was found, a QCISD(T) calculation with a polarized triple-zeta (cc-pVTZ) basis was used as the “experimental” geometry. All experimental energetics are as derived from Refs. 20, 33, 40, 41, and 45. In cases where the experimental zero-point energy was not available, the scaled HF/6-31G* results of Ref. 33 were used.

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