

# Density functional calculations of molecular bond energies

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The calculation of molecular bond energies is a sensitive test of exchange-correlation approximations in density functional theory. The well known local density approximation (LDA) gives excellent bond lengths and vibrational frequencies, but seriously overestimates dissociation energies. Therefore, we have investigated the effect on bond energies of nonlocal corrections to the LDA exchange-correlation functional. We consider the nonlocal correction term of Langreth and Mehl, and also a new semiempirical exchange energy correction. Significant improvements over the LDA dissociation energies are obtained in calculations on first-, second-, and third-row homonuclear diatomic systems.

## I. INTRODUCTION

The calculation of molecular bond energies is a particularly interesting application of density functional methods. Even though *ab initio* quantum chemical techniques are able to provide reliable dissociation energies for small molecular systems, the complexity of *ab initio* calculations escalates rapidly with increasing molecular size or in systems containing very heavy atoms. Density functional calculations, on the other hand, do not share these difficulties. In fact, density functional computations have recently been performed on transition metal dimers such as Cr<sub>2</sub> and Mo<sub>2</sub> with encouraging results.<sup>1-3</sup> At the same time, the calculation of molecular bond energies is an extremely sensitive test of density functional theories, and, in particular, of local exchange-correlation approximations.

In this communication, we discuss an extensive series of density functional bond energy calculations for the first- and second-row dimers H<sub>2</sub> through Cl<sub>2</sub> and also Cr<sub>2</sub>. These calculations have been carried out using a completely numerical computational scheme (i.e., no LCAO basis sets) developed by us for diatomic systems several years ago.<sup>4,5</sup> The purpose of this work is to assess the local density approximation (LDA) for exchange-correlation energy and the effect of various nonlocal gradient-type corrections.

Section II contains a brief outline of the density functional formalism of Hohenberg, Kohn, and Sham<sup>6,7</sup> and the local density exchange-correlation approximation. This is followed in Sec. III by a review of our computational procedure and a discussion of the resulting LDA bond energies for 15 selected dimers. We shall see that the LDA results leave much room for improvement, and therefore the nonlocal exchange-correlation correction of Langreth and Mehl<sup>8</sup> is examined in Sec. IV. The Langreth-Mehl bond energies are significantly better than the LDA values, but the discrepancies with experiment are still large enough that further refinements are necessary.

Unfortunately, the theory of nonlocal correction terms for the exchange-correlation energy of an inhomogeneous electron gas is rather difficult, and we wonder, therefore, if a *semiempirical* approach might be useful. To this end, we analyze separately the exchange and correlation energy com-

ponents of typical atomic systems in Sec. V. We find that the LDA most poorly represents the exchange energy component, and a semiempirical attempt to rectify the problem is then discussed in Sec. VI. The resulting semiempirical exchange-correlation functional provides excellent bond energies for the 15 molecules of this study, and we present these in Sec. VII. Finally, we offer concluding remarks in Sec. VIII.

Before proceeding, however, we note that the following equations and data are given in atomic units ( $\hbar = e = m_e = 1$ ) unless otherwise indicated.

## II. BASIC THEORY

We assume that the total electronic energy of an atomic or molecular system containing  $N$  electrons is given by the following expression:

$$E = \frac{1}{2} \sum_{i=1}^N \int |\nabla\psi_i|^2 d^3\mathbf{r} + \int \rho V_{\text{ext}} d^3\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d^3\mathbf{r}_1 d^3\mathbf{r}_2 + E_{\text{XC}}(\rho\uparrow, \rho\downarrow), \quad (1)$$

where the  $\psi_i$  are integrally occupied orthonormal single-particle orbitals,  $\rho$  is the total electron density,

$$\rho = \sum_{i=1}^N |\psi_i|^2, \quad (2)$$

$V_{\text{ext}}$  is the external potential due to the atomic nuclei, and  $E_{\text{XC}}$  is called the exchange-correlation energy. It can be shown<sup>6</sup> that  $E_{\text{XC}}$  is, in fact, a unique functional of the spin densities  $\rho\uparrow$  and  $\rho\downarrow$ .

In the local density approximation (LDA) the exchange-correlation energy is estimated as follows:

$$E_{\text{XC}}^{\text{LDA}} = \int \rho \epsilon_{\text{XC}}(\rho\uparrow, \rho\downarrow) d^3\mathbf{r}, \quad (3)$$

where  $\epsilon_{\text{XC}}$  is the exchange-correlation energy per particle of a *uniform* electron gas with "up" and "down" electron spin densities given by the *local* values of  $\rho\uparrow$  and  $\rho\downarrow$ , respectively. The quantity  $\epsilon_{\text{XC}}$  can be calculated by a variety of many-body theoretical techniques such as the random phase approximation, Monte Carlo methods, etc. In the present

work, we use for  $\epsilon_{XC}(\rho\uparrow, \rho\downarrow)$  the Monte Carlo data of Ceperley and Alder<sup>9</sup> as parametrized by Vosko, Wilk, and Nusair (VWN).<sup>10</sup>

The single-particle orbitals  $\psi_i$  are determined by applying the variational principle to the total energy of expression (1). One obtains the following Schrödinger-like equation for  $\psi_i$ :

$$-\frac{1}{2}\nabla^2\psi_i + (V_{\text{ext}} + V_{\text{el}} + V_{\text{XC}}^\sigma)\psi_i = \epsilon_i\psi_i, \quad (4)$$

where  $V_{\text{el}}$  is the Coulomb potential arising from the total electron density,

$$V_{\text{el}}(1) = \int \frac{\rho(2)}{r_{12}} d^3r_2 \quad (5)$$

and  $V_{\text{XC}}^\sigma$  is the exchange-correlation potential given by the functional derivative of  $E_{\text{XC}}$ :

$$V_{\text{XC}}^\sigma = \frac{\delta E_{\text{XC}}}{\delta \rho_\sigma}. \quad (6)$$

In the local density approximation, this functional derivative is simply

$$V_{\text{XC}}^\sigma(\text{LDA}) = \frac{\partial}{\partial \rho_\sigma} [\rho\epsilon_{\text{XC}}(\rho\uparrow, \rho\downarrow)], \quad (7)$$

an explicit VWN-based expression for which may be found in Ref. 11. Notice, also, that the exchange-correlation potential is spin dependent and is therefore given the spin label  $\sigma$ . This formulation of the inhomogeneous many-electron problem is due to Hohenberg, Kohn, and Sham,<sup>6,7</sup> and hence the single-particle equation (4) is often referred to as the Kohn–Sham equation.

### III. LDA BOND ENERGIES

In the present work, the Kohn–Sham orbitals are computed using a discrete numerical method previously developed by us for calculations on diatomic systems.<sup>4,5</sup> We use no LCAO, muffin-tin, or cellular approximations of any kind. Instead, all functions are defined on a discrete, two-dimensional mesh in prolate spheroidal coordinates, which are related to the elliptical coordinate system familiar to chemists. Integration and partial differentiation are performed on this mesh using 2D cubic spline analysis. Interested readers are referred to Ref. 4 for a detailed description of our procedure.

The dissociation energy  $D_e$  of a diatomic molecule AB is given by the difference

$$D_e = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}, \quad (8)$$

where  $E_{\text{AB}}$ ,  $E_{\text{A}}$ , and  $E_{\text{B}}$  are the total energies of the molecule AB and the separated constituent atoms A and B, respectively. In our calculations, the free atomic energies  $E_{\text{A}}$  and  $E_{\text{B}}$  are computed using exactly the same code and the same discrete mesh as used for the computation of  $E_{\text{AB}}$ . We do this in order to take advantage of cancellation of numerical errors that occurs in the energy difference (8). In this regard, though, it should be noted that the atomic density functional energies have a slight dependence on  $M_L$ , the  $Z$  component of total angular momentum. This is due to the fact that, for a given  $L$ , the complex spherical harmonic functions  $Y_{LM}(\theta, \phi)$  do not have equivalent densities for all possible values

of  $M$  (see the Appendix of Ref. 12 for a discussion of this point). In the present work, then, we have assumed that  $M_L = 0$  in all of our atomic calculations.

It should also be noted that these calculations are completely spin unrestricted (i.e., we use different exchange-correlation potentials for spin-up and spin-down orbitals in the case of a spin-polarized system). This is important here, as we deal with spin-polarized separated atoms, and a few molecular triplet states as well. Furthermore, our  $\text{Cr}_2$  calculation assumes an “antiferromagnetic” ground state wave function as described in several recent publications<sup>1–3</sup> to which we refer the reader for details.

In Table I, we present LDA bond energies, calculated for the experimental ground state symmetry and at the experimental internuclear separation, for a selection of 15 first-, second-, and third-row homonuclear diatomic systems. The numerical accuracy of these results is 0.1 eV (0.01 eV for  $\text{Be}_2$ ), based on their convergence as a function of the number of mesh points used in the calculations. Also in Table I, we compare the LDA bond energies with experiment.

It is clear that the LDA results tend to overestimate the exact bond energies by as much as several electron volts in the worst cases. For the 15 molecules in the table, the rms deviation from experiment is 1.2 eV, certainly very much larger than we would like. In the following sections, therefore, we examine the effect on these dissociation energies of nonlocal correction terms to the local density approximation.

### IV. LANGRETH–MEHL BOND ENERGIES

A comprehensive study by Langreth, Perdew, and Mehl of nonlocal corrections to the LDA in inhomogeneous systems has culminated recently in the work of Langreth and Mehl (see Ref. 8 and references therein). These authors have deduced a gradient-type correction term for the LDA exchange-correlation energy which offers substantial improvements over the LDA in applications to various atomic

TABLE I. Dissociation energies (eV).

	Expt <sup>a</sup>	LDA <sup>b</sup>	LM <sup>c</sup>	SE <sup>d</sup>
H <sub>2</sub>	4.8	4.9	5.0	5.1
Li <sub>2</sub>	1.1	1.0	0.6	1.0
B <sub>2</sub>	3.0	3.9	3.3	2.6
C <sub>2</sub>	6.3	7.3	6.1	5.5
N <sub>2</sub>	9.9	11.6	10.2	10.1
O <sub>2</sub>	5.2	7.6	6.4	5.4
F <sub>2</sub>	1.7	3.4	2.4	1.7
Na <sub>2</sub>	0.8	0.9	0.3	0.9
Al <sub>2</sub>	1.8	2.0	1.7	1.1
Si <sub>2</sub>	3.1	4.0	3.5	3.1
P <sub>2</sub>	5.1	6.2	5.3	4.9
S <sub>2</sub>	4.4	5.9	5.2	4.2
Cl <sub>2</sub>	2.5	3.6	3.0	2.1
Cr <sub>2</sub>	1.6	3.0	0.9	1.7
Be <sub>2</sub>	0.10	0.56	0.36	0.17

<sup>a</sup>Reference 26, Ref. 27 for Cr<sub>2</sub>, Ref. 28 for Be<sub>2</sub>.

<sup>b</sup>LDA: local density approximation.

<sup>c</sup>LM: Langreth–Mehl.

<sup>d</sup>SE: present semiempirical approximation.

and solid-state problems. For a non-spin-polarized system, the Langreth-Mehl (LM) exchange-correlation energy is given by

$$E_{XC}^{LM} = E_{XC}^{LDA}(RPA) + a \int \frac{(\nabla\rho)^2}{\rho^{4/3}} \left( e^{-F} - \frac{7}{18} \right) d^3r, \quad (9)$$

where

$$F = b \frac{|\nabla\rho|}{\rho^{7/6}} \quad (10)$$

and "a" and "b" are constants to be specified later. The LDA term is necessarily expressed in the random phase approximation for which we use the RPA parametrization of Vosko, Wilk, and Nusair.<sup>10</sup>

Of course, a *spin-polarized* version of the LM theory is required for the calculation of molecular bond energies. The necessary spin-dependent generalization has very recently been provided by Hu and Langreth,<sup>13</sup> and appears as follows:

$$E_{XC}^{LM} = E_{XC}^{LDA}(RPA) + A \int \left[ \left( \frac{\rho^\uparrow}{\rho} \right)^{5/3} + \left( \frac{\rho^\downarrow}{\rho} \right)^{5/3} \right]^{-1/2} \frac{(\nabla\rho)^2}{\rho^{4/3}} e^{-F} - \frac{7}{18} \left[ \frac{(\nabla\rho^\uparrow)^2}{\rho^{\uparrow 4/3}} + \frac{(\nabla\rho^\downarrow)^2}{\rho^{\downarrow 4/3}} \right] d^3r, \quad (11)$$

where

$$F = B \frac{|\nabla\rho|}{\rho^{7/6}} \quad (12)$$

and the constants *A* and *B* are given by

$$A = \frac{\pi}{4(6\pi^2)^{4/3}}, \quad (13)$$

$$B = (9\pi)^{1/6} f. \quad (14)$$

The parameter *f* in the last equation is discussed at length in the papers of Langreth and Mehl,<sup>8,14</sup> and in these calculations we use their theoretical estimate  $f = 1/6$ .

The dissociation energies of our 15 test molecules have been recalculated using the spin-dependent LM exchange-correlation functional (11) and the results are presented in the third column of Table I. We consider these to be preliminary values, as they have been calculated using LDA orbitals. Previous experience with gradient-corrected potentials indicates that this approximation has a negligible effect on the resulting bond energies (less than 0.1 eV). At any rate, calculations utilizing the full nonlocal exchange-correlation potential will be undertaken at a future time.

We see that the LM bond energies agree significantly better with experiment than do the LDA results. The rms deviation is only 0.5 eV, compared to 1.2 eV for the LDA. Roughly speaking, then, the Langreth-Mehl nonlocal correction removes about one-half of the discrepancy with experiment. Nevertheless, 0.5 eV is still a rather large error and further refinements of the theory are clearly necessary.

However, given the complexity of the theory of nonlocal exchange-correlation approximations, we suggest that a semiempirical approach to the problem might provide useful information. We develop such an approach in the following sections.

TABLE II. Atomic exchange energies (a.u.).

	Exact	LDA <sup>a</sup>	$X\alpha\beta\gamma^b$
H	-0.313	-0.268	-0.310
He	-1.026	-0.884	-1.027
Li	-1.781	-1.538	-1.780
Be	-2.667	-2.312	-2.669
B	-3.744	-3.272	-3.744
C	-5.045	-4.459	-5.050
N	-6.596	-5.893	-6.608
O	-8.174	-7.342	-8.192
F	-10.00	-9.052	-10.04
Ne	-12.11	-11.03	-12.16
Na	-14.02	-12.79	-14.06
Mg	-15.99	-14.61	-16.03
Al	-18.07	-16.53	-18.10
Si	-20.28	-18.59	-20.30
P	-22.64	-20.79	-22.65
S	-25.00	-23.00	-25.01
Cl	-27.51	-25.35	-27.52
Ar	-30.19	-27.86	-30.18
Kr	-93.89	-88.62	-93.82
Xe	-179.2	-170.6	-178.9

<sup>a</sup>Equation (15).

<sup>b</sup>Equation (20), with  $\alpha = 2/3$ ,  $\beta = 0.0036$ , and  $\gamma = 0.004$ .

## V. ATOMIC EXCHANGE AND CORRELATION ENERGIES

In this section, we analyze separately the exchange and correlation energy components of typical atomic systems. The reason for this will be evident by the end of the section. For an excellent discussion of the meaning of exchange and correlation energy components in the context of density functional theory, the reader is referred to the article of Langreth and Mehl<sup>8</sup>, and references therein.

In Tables II and III, the ground state exchange and correlation energies, respectively, of some typical atomic systems are tabulated. The exchange energies are computed us-

TABLE III. Atomic correlation energies (a.u.).

	Exact <sup>a</sup>	LDA <sup>b</sup>	Stoll <sup>c</sup>
H	0.0	-0.022	0.0
He	-0.042	-0.113	-0.059
Li	-0.045	-0.151	-0.072
Be	-0.094	-0.225	-0.116
B	-0.124	-0.291	-0.148
C	-0.155	-0.360	-0.177
N	-0.186	-0.430	-0.204
O	-0.254	-0.539	-0.272
F	-0.316	-0.644	-0.331
Ne	-0.381	-0.746	-0.386
Na	-0.386	-0.805	-0.410
Mg	-0.428	-0.892	-0.461
Al	-0.459	-0.966	-0.497
Si	-0.494	-1.042	-0.530
P	-0.521	-1.119	-0.562
S	-0.595	-1.227	-0.627
Cl	-0.667	-1.330	-0.685
Ar	-0.732	-1.431	-0.738

<sup>a</sup>Reference 16 (without radiative corrections).

<sup>b</sup>Equation (16).

<sup>c</sup>Equation (17).

ing the Hartree–Fock orbitals of Clementi and Roetti,<sup>15</sup> and the correlation energies are taken from the work of Veillard and Clementi<sup>16</sup> (without radiative corrections). Also, we show the corresponding exchange and correlation energy components calculated in the local density approximation:

$$E_X^{\text{LDA}} = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \int (\rho^\uparrow{}^{4/3} + \rho^\downarrow{}^{4/3}) d^3r, \quad (15)$$

$$E_C^{\text{LDA}} = \int \rho \epsilon_C(\rho^\uparrow, \rho^\downarrow) d^3r, \quad (16)$$

where  $\epsilon_C$  is the correlation energy per particle of a uniform electron gas for which we employ, as usual, the VWN parametrization<sup>10</sup> (in this case, the parametrization of Ceperley and Alder data<sup>9</sup>). The Hartree–Fock densities of Clementi and Roetti<sup>15</sup> are also used for the LDA calculations.

Notice that the LDA typically underestimates atomic exchange energies by something in the order of 10%, and overestimates atomic correlation energies by a factor of roughly 2. This latter discrepancy is rather alarming, but insightful interpretations of the problem have been offered by Langreth and Mehl<sup>8</sup> and by Stoll *et al.*<sup>17,18</sup> We believe that the LM and the Stoll interpretations are essentially equivalent, the former being based on momentum-space arguments and the latter on a coordinate-space point of view. We shall pursue the Stoll interpretation here, however, because it retains the simplicity of the local density approximation.

Stoll argues that in finite systems such as atoms and molecules the correlation energy of the like-spin electron pairs is very small compared to the correlation energy of the opposite-spin pairs. This is not the case in a homogeneous system, where the like-spin components account for about one-half of the total correlation energy. In finite systems, therefore, the usual LDA functional must be corrected by explicitly subtracting out the like-spin correlation energy components:

$$E_C^{\text{Stoll}} = E_C^{\text{LDA}} - \int \rho^\uparrow \epsilon_C(\rho^\uparrow, 0) d^3r - \int \rho^\downarrow \epsilon_C(0, \rho^\downarrow) d^3r. \quad (17)$$

In the last column of Table III we show that this opposite-spins-only functional does, in fact, give atomic correlation energies in very good agreement with the exact values. The original factor of 2 discrepancy has certainly been eliminated. Although there are many other approaches to the problem of correlation energy approximations in the literature, we will not consider them here. A good review of the subject has been provided by Stoll and Savin.<sup>19</sup>

Notice that, if we use Stoll's approximation, then the absolute errors in the atomic correlation energies of Table III are very much smaller than the absolute errors in the LDA exchange energies of Table II, by at least an order of magnitude. For the time being, then, we shall ignore nonlocal correlation energy corrections and concentrate entirely on nonlocal corrections for the exchange energy. The situation is rather fortunate, because exchange energy has a trivial  $e^2$  dependence (i.e., simply proportional to  $e^2$ , where  $e$  is the electronic charge) and also a trivial spin dependence. Consequently, exchange energy functionals can be studied

empirically, using dimensional analysis as a guide in choosing appropriate functional forms. On the other hand, purely empirical studies of correlation energy are not possible.

## VI. SEMIEMPIRICAL GRADIENT-CORRECTED EXCHANGE ENERGY FUNCTIONALS

Empirical studies of approximate exchange energy functionals have a history beginning with the well known  $X\alpha$  approximation of Slater (see Ref. 20 for a good review):

$$E_{X\alpha} = -\frac{9}{4} \alpha \left( \frac{3}{4\pi} \right)^{1/3} \int (\rho^\uparrow{}^{4/3} + \rho^\downarrow{}^{4/3}) d^3r. \quad (18)$$

The form of this functional is fixed by dimensional analysis alone, and  $\alpha$  is a parameter empirically chosen to give agreement with exact atomic exchange energies. Its value is in the range 0.7–0.8 for typical atomic systems, and is exactly  $\alpha = 2/3$  for the uniform electron gas. The  $X\alpha$  approximation has been extremely useful in applications to numerous atomic, molecular, and solid-state problems. Nevertheless, the parameter  $\alpha$  has a strong  $Z$  dependence, and this is an undesirable aspect of the theory.

In an attempt to improve on the  $X\alpha$  approximation, Herman *et al.*<sup>21,22</sup> introduced on the basis of dimensional arguments a gradient-corrected exchange energy functional of the form

$$E_{X\alpha\beta} = E_{X\alpha} - \beta \int \left[ \frac{(\nabla\rho^\uparrow)^2}{\rho^\uparrow{}^{4/3}} + \frac{(\nabla\rho^\downarrow)^2}{\rho^\downarrow{}^{4/3}} \right] d^3r, \quad (19)$$

where  $\beta$  is a new parameter, and the value of  $\alpha$  is fixed at  $\alpha = 2/3$  in order to obtain the proper homogeneous gas limit. The empirical value for  $\beta$  is typically in the order of 0.003 in atomic systems.<sup>23</sup>

The gradient correction term of the  $X\alpha\beta$  functional was derived, at about the same time, by Sham<sup>24</sup> on the basis of density functional theory, and more recently by several other authors as well (see Ref. 25 and references therein). Unfortunately, the density functional value of  $\beta$  is less than *one-half* the empirical atomic value, and this discrepancy has troubled the  $X\alpha\beta$  theory for many years. Langreth and Mehl, however, have recently explained the origin of this discrepancy<sup>8</sup> and we are therefore confident that the empirical atomic  $\beta$  is meaningful.

Unfortunately, the  $X\alpha\beta$  exchange *potential* [i.e., the functional derivative of expression (19)] *diverges* asymptotically in the exponential tails of atomic and molecular charge distributions,<sup>21,22</sup> as does the Langreth–Mehl potential.<sup>8</sup> Therefore, it is necessary in atomic and molecular applications to cut off the  $X\alpha\beta$  and the LM potentials in some appropriate manner. Divergences occur at nuclear cusps also, but these are not a serious problem.

A further difficulty with the  $X\alpha\beta$  approximation is its lack of universality. Just as the  $\alpha$  parameter of the  $X\alpha$  functional has a strong  $Z$  dependence, the  $\beta$  parameter of the  $X\alpha\beta$  functional is also strongly  $Z$  dependent. In order to illustrate this, we present in Table IV empirical  $\beta$  parameters for some typical atomic systems (i.e., the value of  $\beta$  which, for a given atom, gives perfect agreement between  $E_{X\alpha\beta}$ , with  $\alpha = 2/3$ , and the exact exchange energy). These empirical  $\beta$ 's show a strong  $Z$  dependence, ranging from 0.0022 for light atoms to something in the order of 0.0035 for

TABLE IV. Empirical  $\beta$  parameters (a.u.).

	$X\alpha\beta^a$	$X\alpha\beta\gamma^b$
H	0.0023	0.0038
He	0.0022	0.0036
Li	0.0023	0.0036
Be	0.0025	0.0036
B	0.0026	0.0036
C	0.0026	0.0036
N	0.0026	0.0035
O	0.0027	0.0035
F	0.0027	0.0035
Ne	0.0027	0.0034
Na	0.0028	0.0035
Mg	0.0029	0.0035
Al	0.0030	0.0035
Si	0.0030	0.0036
P	0.0030	0.0036
S	0.0030	0.0036
Cl	0.0030	0.0036
Ar	0.0031	0.0036
Kr	0.0033	0.0036
Xe	0.0034	0.0037

<sup>a</sup>Equation (19), with  $\alpha = 2/3$ .

<sup>b</sup>Equation (20), with  $\alpha = 2/3$  and  $\gamma = 0.004$ .

very heavy atoms. Clearly, the  $X\alpha\beta$  approximation is no more universal than the  $X\alpha$  approximation.

Regarding the first of these difficulties, we feel that the asymptotic divergence problem is more than just a numerical inconvenience. It is a fundamental failure of the theory. One can imagine slightly pathological density distributions (step functions, for example) for which the  $X\alpha\beta$  exchange energy itself, let alone its functional derivative, will diverge. Obviously, the gradient correction term must be suitably cut off in cases where the density gradient becomes too large. We are therefore motivated to introduce the following modified gradient-corrected exchange energy functional:

$$E_{X\alpha\beta\gamma} = E_{X\alpha} - \beta \int \frac{(\nabla\rho\uparrow)^2}{\rho\uparrow^{4/3}} \left[ 1 + \gamma \frac{(\nabla\rho\uparrow)^2}{\rho\uparrow^{8/3}} \right]^{-1} - \beta \int \frac{(\nabla\rho\downarrow)^2}{\rho\downarrow^{4/3}} \left[ 1 + \gamma \frac{(\nabla\rho\downarrow)^2}{\rho\downarrow^{8/3}} \right]^{-1}, \quad (20)$$

where  $\alpha = 2/3$ , and we now have two parameters  $\beta$  and  $\gamma$ . This functional contains the  $X\alpha\beta$  expression as a special case (i.e.,  $\gamma = 0$  or density gradients very small) but assumes a  $\rho^{4/3}$  integrand in the case of large  $\gamma$ , large density gradients, or in the exponential tails of atomic and molecular charge distributions. Hence, this  $X\alpha\beta\gamma$  functional is divergence free. In our opinion, this is the simplest conceivable dimensionally consistent expression having all of these desirable properties.

The parameters  $\beta$  and  $\gamma$  have been empirically determined by a least squares fit to the Hartree-Fock exchange energies of the 20 atomic systems H through Ar, Kr, and Xe (using the Hartree-Fock orbitals and densities of Clementi and Roetti<sup>15</sup>). We find that a suitable value for parameter  $\gamma$  is 0.004, with a corresponding best-fit  $\beta$  of 0.0036. It happens that the least squares error of this fit is surprisingly small. In fact, the  $X\alpha\beta\gamma$  functional fits the exact atomic exchange energies almost an *order of magnitude better* than

does the  $X\alpha\beta$  functional, and we feel that this is a very significant improvement.

In order to demonstrate the quality of the  $X\alpha\beta\gamma$  fit, we present in Table IV the associated empirical  $\beta$ 's, defined in the usual manner, for  $\alpha = 2/3$  and  $\gamma = 0.004$ . It is obvious that the empirical  $\beta$  is virtually independent of  $Z$ . In other words, the  $X\alpha\beta\gamma$  functional is not only divergence free, but is also *universal* (at least in finite systems). These results strongly support the functional form introduced in expression (20).

## VII. SEMIEMPIRICAL BOND ENERGIES

In the last column of Table II, atomic  $X\alpha\beta\gamma$  exchange energies are presented and compared with the exact results. Notice that, in absolute terms, the error in the  $X\alpha\beta\gamma$  exchange energy is of the same order as the error in the Stoll correlation energy approximation (see Table III). This is a logical stage, then, at which to pause and recalculate our dissociation energies.

Let us consider the following exchange-correlation approximation:

$$E_{XC}^{SE} = E_{X\alpha\beta\gamma} + E_C^{\text{Stoll}}. \quad (21)$$

Since the parameters of the  $X\alpha\beta\gamma$  exchange functional have been determined empirically, we shall call this a semiempirical (SE) exchange-correlation approximation. A third set of molecular bond energies have been calculated using this SE approximation and the results are presented in the last column of Table I. As with our LM calculation, we have used LDA orbitals to compute the new bond energies, but this is not expected to affect our results by more than 0.1 eV or so.

The agreement between the SE bond energies and experiment for our entire range of dimers is very good, typically in the order of a few tenths of an electron volt. The rms deviation from the experimental values is only 0.3 eV, compared to 0.5 eV for the LM theory and 1.2 eV for the LDA. The improvement in the semiempirical bond energies over the LDA and even the LM results is substantial.

## VIII. CONCLUSIONS

Several important conclusions can be drawn as a result of these calculations. First of all, it appears that nonlocal exchange-correlation corrections of the *gradient-type* are very useful in calculating molecular bond energies, though much more work is required on their theoretical aspects. In particular, refinements of the Langreth-Mehl theory<sup>8</sup> would be welcome, not only in its spin dependence, but also in its basic functional form. The present work indicates that special emphasis on the exchange part of the total exchange-correlation energy is essential and that the large-gradient behavior of existing density functionals must be carefully considered.

These calculations also demonstrate the value of a semiempirical approach to the density functional theory of molecular binding energies. Our philosophy is quite simple: use *atomic* systems to help us find (empirically or otherwise) universal exchange-correlation parameters, and then apply these without further adjustment to the calculation of *molecular* properties. This approach has produced in the

present work an exchange-correlation approximation which gives excellent dissociation energies. Our results are very encouraging, as severe overbinding of molecular systems is currently an outstanding problem in density functional theory.

We are now attempting to implement the full gradient-corrected LM and SE *potentials* in our 2D numerical code. This is not an easy task, however, as the numerical computation of the necessary higher-order derivatives is extremely difficult. When this has been accomplished, we shall undertake bond length and vibrational frequency calculations for the molecules of the present study. Results will be published as soon as possible.

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