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Weighted density approximation applied to diatomic molecules

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Early investigations into the weighted spin-density approximation (WSDA) report atomic energies which err by more than those in the much simpler local-spin-density approximation (LSDA). More recent work has refined the WSDA to obtain substantial improvement over the LSDA in atomic energies. These results suggest that a WSDA may improve quantum-chemistry calculations. The extension of the method from atoms to molecules is nontrivial, however, and we know of no published work applying a WSDA to molecules. We develop an energy functional which treats correlation locally, and exchange in the WSDA. The functional achieves a substantial improvement over the LSDA in atomic energies. We calculate bond lengths, dissociation energies, and vibrational frequencies for some first-row dimers. In particular, the hydrogen dimer is described well with this functional. Dissociation energies are also relatively accurate for the heavier dimers. Except for H_2, however, bond lengths tend to be longer than experiments indicate. We discuss features of the WSDA necessary to improve these findings. [S0163-1829(96)07844-7]

I. INTRODUCTION

The weighted density approximation (WDA) is one of the earliest attempts to develop an energy density functional which accounts for nonlocal contributions to the exchange-correlation energy.[1–3] The approximation is applied within the framework of the density-functional theory of Hohenberg and Kohn,[4,5] which states that the energy of an electronic system is given by the minimum of $E[\rho]$, a functional of the electron density $\rho(\mathbf{r})$. The Kohn-Sham method[6] of minimizing $E[\rho]$ separates the functional into the noninteracting kinetic T, electron-nuclear, electron-electron repulsion, and exchange-correlation E_{xc} energies

$$E[\rho]=T[\rho]-\sum_i Z_i\int d\mathbf{r}\frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_i|}+\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+E_{\mathrm{xc}}[\rho]. \tag{1}$$

By definition, E_{xc} is the difference between $E[\rho]$ and the other three terms, and it is the only one which needs to be approximated. One simple form is the local-density approximation (LDA)

$$E_{\mathrm{xc}}^{\mathrm{lda}}[\rho]=\int d\mathbf{r}\rho(\mathbf{r})\epsilon_{\mathrm{xc}}^{\mathrm{lda}}(\rho(\mathbf{r})), \tag{2}$$

where $\epsilon_{\mathrm{xc}}^{\mathrm{lda}}(\rho(\mathbf{r}))$ depends only on the density at $\mathbf{r}$, and is the exchange-correlation energy density in a homogeneous electron-gas of density $\rho(\mathbf{r})$, typically found from Monte Carlo studies.[7] While it is easy to implement, this approximation suffers from a number of problems such as spurious self-correlation in hydrogen and over binding in molecules.[8] These errors largely arise because of the suppression of nonlocality in $\epsilon_{\mathrm{xc}}^{\mathrm{lda}}$; the true ϵ_{xc} is not just a function of the local density $\rho(\mathbf{r})$, but rather a functional of the density everywhere. The WDA attempts to correct the problems of the LDA by incorporating this essential nonlocality.

Early applications of the WDA to atoms found that exchange could be treated more accurately[2,3] than in the LDA, although correlation tends not to be improved. Total atomic energies calculated in the LDA are more accurate than either the correlation or exchange energies separately, because its tendency to overestimate correlation is compensated for by an underestimate of exchange. In earlier applications of the WDA this compensation typically does not occur, so that the calculated energies for lighter atoms are poorer than in the much simpler LDA.[8] For this reason, as well as the computational difficulty in applying a WDA to nonspherical systems, we know of no published accounts of a WDA tested on molecules.

A more recent investigation,[9] however, finds that a functional which treats exchange in the weighted spin-density approximation (WSDA, the spin-polarized extension to WDA), but treats correlation in a local-spin-density approximation (LSDA) achieves significant improvements over the LSDA alone in atomic energies. Others[10–13] have had success using similar variants of the WDA to calculate properties of solids. These results suggest that such a WSDA-based functional may be a route to include nonlocal effects in quantum-chemistry calculations.

In this paper we present a formalism in which we treat exchange in the WSDA and correlation in the LSDA. Our formulation is particularly well suited to evaluation in a Gaussian basis set, and makes molecular calculations feasible. In Sec. II we develop our functional, and in Sec. III we present the computational details. In Sec. IV we report our results. We find significant improvements over the LSDA in atomic energies. However, this functional yields only mixed success in describing small molecules. Finally, in Sec. V we interpret these results.

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II. ENERGY FUNCTIONAL

One may split E_{xc} in Eq. (1) into correlation and exchange terms. For the present functional, exchange will be treated in the WSDA. This approximation begins by expressing E_x in terms of a density pair-correlation function $g_x^\sigma(\mathbf{r},\mathbf{r}')$,

$$E_x^{\mathrm{WDA}}[\rho_\uparrow,\rho_\downarrow]=\tfrac{1}{2}\sum_\sigma \int d\mathbf{r}\int d\mathbf{r}'\rho_\sigma(\mathbf{r}) \times\frac{[g_x^\sigma(\mathbf{r},\mathbf{r}';[\rho_\sigma])-1]}{|\mathbf{r}-\mathbf{r}'|}\rho_\sigma(\mathbf{r}'), \tag{3}$$

where $g_x^\sigma(\mathbf{r},\mathbf{r}';[\rho_\sigma])$ is itself a functional of the density ρ_σ for each spin σ. This equation is exact, but requires knowledge of g_x. Except for the homogeneous electron-gas,[7,14] exact determination of $g_x^\sigma(\mathbf{r},\mathbf{r}';[\rho_\sigma])$ is difficult or impossible.[15–17] The hope of the WSDA, however, is that the functional dependence of $g_x^\sigma(\mathbf{r},\mathbf{r}')$ can be determined from the sum rule

$$\int d\mathbf{r}'[1-g_x^\sigma(\mathbf{r},\mathbf{r}';[\alpha_\sigma])]\rho_\sigma(\mathbf{r}')=1, \tag{4}$$

as well as a number of exact conditions[18] which suggest the form of g_x. Here the functional dependence of $g_x^\sigma(\mathbf{r},\mathbf{r}';[\rho_\sigma])$ on ρ_σ has been formally replaced by some scalar field $\alpha_\sigma(\mathbf{r})$, which parametrizes $g_x^\sigma(\mathbf{r},\mathbf{r}')$. This $\alpha_\sigma(\mathbf{r})$ is adjusted so that the sum rule (4) is obeyed throughout space.

Variants of the WSDA differ in the way in which $g_x^\sigma(\mathbf{r},\mathbf{r}';[\alpha_\sigma])$ is parametrized by $\alpha_\sigma(\mathbf{r})$. We choose a form which is particularly well suited for evaluation in a Gaussian basis set, namely a Gaussian,

$$g_x^\sigma(\mathbf{r},\mathbf{r}';\alpha_\sigma)=1-e^{-\alpha_\sigma(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^2}. \tag{5}$$

Unlike many previously used pair-correlation holes,[2,3] this form satisfies the exact conditions that $g_x^\sigma(\mathbf{r}\to\mathbf{r}')=1$, $dg_x/dr_{\mathbf{r}\to\mathbf{r}'}=0$, and $1-g_x^\sigma(\mathbf{r},\mathbf{r}')>0$. In addition, it will always be possible to find some $\alpha_\sigma(\mathbf{r})$ to satisfy Eq. (4) since this integral varies monotonically between zero as $\alpha_\sigma(\mathbf{r})\to\infty$, and N_σ (the number of spin σ electrons) when $\alpha(\mathbf{r})=0$.

In the limit of constant density, when $\rho_\sigma(\mathbf{r})=\rho_\sigma$, Eq. (4) gives $\alpha_\sigma(\mathbf{r})=\pi\rho_\sigma^{2/3}$ Figure 1 shows that this $g_x^\sigma(\mathbf{r},\mathbf{r}')$ approximates well the exact homogeneous expression[4]

$$g_x^{\mathrm{hom}}(r_{12};\rho_\sigma)=1-\left[3\frac{j_1(r_{12}(6\pi^2\rho_\sigma)^{1/3})}{r_{12}(6\pi^2\rho_\sigma)^{1/3}}\right]^2. \tag{6}$$

Integrating Eq. (3) in this limit using our approximate form (5) gives

$$E_x^{\mathrm{hom}}[\rho_\uparrow,\rho_\downarrow]=-\sum_\sigma \int d\mathbf{r}[\rho_\sigma(\mathbf{r})]^{4/3}. \tag{7}$$

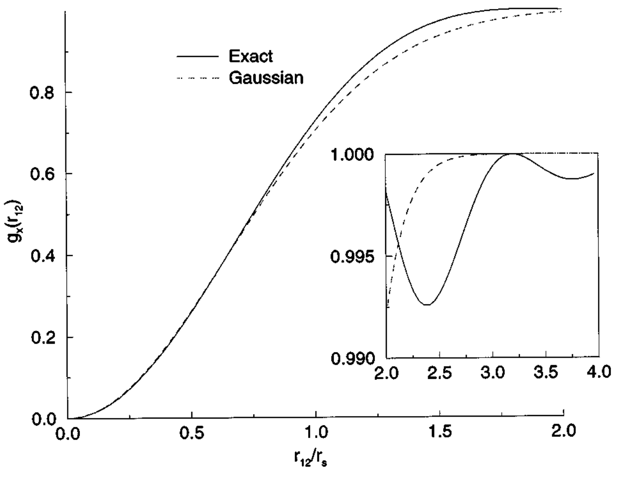

FIG. 1. The exact [Eq. (6)] and approximate [Eq. (5)] correlation functions $g_x(r_{12})$ in the limit of constant density. Here $r_s=(3/4\pi\rho_\sigma)^{1/3}$.

This differs by about 7% from the exact expression obtained by inserting Eq. (6) into Eq. (3). To ensure that E_x properly reproduces the exact result in the homogeneous limit, a correction ΔE_x augments Eq. (3) to arrive at the final form for the exchange functional used here,

$$\Delta E_x[\rho_\uparrow,\rho_\downarrow]=\sum_\sigma\left[1-\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\right]\int d\mathbf{r}[\rho_\sigma(\mathbf{r})]^{4/3}, \tag{8}$$

$$E_x[\rho_\uparrow,\rho_\downarrow]=E_x^{\mathrm{WDA}}[\rho_\uparrow,\rho_\downarrow]+\Delta E_x[\rho_\uparrow,\rho_\downarrow]. \tag{9}$$

Adding this term $\Delta E_x[\rho_\uparrow,\rho_\downarrow]$ should not be confused with shell partitioning,[2,10] where the WSDA is applied only to density-density interactions with the same atomic shell while intershell interactions are treated as in the LSDA. In the present functional, the term $\Delta E_x[\rho_\uparrow,\rho_\downarrow]$ is added to ensure that the functional reduces to the correct value in the limit of constant density; core and valence electrons remain on the same footing. The effects of shell partitioning, which may provide a more physical description of intershell interactions,[2] are left for future study.

The inclusion of $\Delta E_x[\rho_\uparrow,\rho_\downarrow]$ in $E_x[\rho_\uparrow,\rho_\downarrow]$ does not interfere with sum rule (4), since it can be interpreted as the energy (3) resulting from the difference of two LDA-type pair-correlation functions

$$\delta g_x(\mathbf{r},\mathbf{r}')=\frac{\rho_\sigma(\mathbf{r})}{\rho_\sigma(\mathbf{r}')}[g_x^{\mathrm{hom}}(\mathbf{r},\mathbf{r}';\rho_\sigma(\mathbf{r})) -g_x(\mathbf{r},\mathbf{r}';\alpha_\sigma(\mathbf{r})=\pi\rho_\sigma^{2/3}(\mathbf{r}))]. \tag{10}$$

Both of these g_x satisfy Eq. (4), so their difference satisfies a sum rule integrating to zero. In this sense, this correction behaves like a correlation term; this analogy appears again when calculating the energy of hydrogen, since there it nearly cancels the spurious LSDA self-correlation.

Correlation is treated as in the LSDA, using the Vosko-Wilk-Nusair (VWN) parametrization of the homogeneous electron-gas correlation energy[19]

$$E_c[\rho_\uparrow,\rho_\downarrow]=\int d\mathbf{r}\;\rho(\mathbf{r})\epsilon_c^{\mathrm{lda}}(\rho_\uparrow(\mathbf{r}),\rho_\downarrow(\mathbf{r})). \tag{11}$$

As mentioned above, merely adding this correlation energy to the WSDA exchange (3) leads to poorer total energies for lighter atoms.[8] The correction $\Delta E_x[\rho_\uparrow,\rho_\downarrow]$, however, in-

TABLE I. The total ground state energies in hartree calculated with the present functional compared to those from LSDA (Ref. 19) and similar theory in Ref. 9, and experiment (Ref. 33,34).

Atom	Experiment	This work	% Error	Ref. 9	% Error	LSDA	% Error
H	−0.500	−0.502	−0.4			−0.479	4.2
He	−2.904	−2.907	−0.10	−2.909	−0.17	−2.835	2.4
Li	−7.478	−7.474	0.05	−7.473	0.07	−7.344	1.79
Be	−14.667	−14.645	0.15	−14.605	0.42	−14.447	1.50
B	−24.653	−24.636	0.07	−24.583	0.28	−24.354	1.24
C	−37.844	−37.839	0.01	−37.779	0.17	−37.470	0.988
N	−54.587	−54.593	−0.01	−54.530	0.10	−54.137	0.824
O	−75.015	−75.108	−0.12	−75.011	0.00	−74.527	0.65
F	−99.725	−99.812	−0.09	−99.695	0.03	−99.114	0.61
Ne	−128.928	−129.044	−0.09	−128.914	0.01	−128.233	0.54
Na	−162.245	−162.386	−0.09	−162.270	−0.01	−161.444	0.49
Mg	−200.043	−200.230	−0.09	−200.108	−0.03	−199.135	0.45
Al	−242.336	−242.540	−0.08	−242.425	−0.04	−241.315	0.42
Si	−289.374	−289.558	−0.06	−289.452	−0.04	−288.215	0.40
P	−341.240	−341.449	−0.06	−341.356	−0.03	−339.995	0.36
S	−398.14	−398.33	−0.05	−398.23	−0.03	−396.73	0.35
Cl	−460.20	−460.39	−0.04	−460.29	−0.03	−458.66	0.33
Ar	−527.55	−527.77	−0.04	−527.68	−0.02	−525.94	0.31

cludes enough LSDA-type exchange energy to maintain the compensation in errors between LSDA correlation and exchange needed to obtain the accurate atomic energies presented in Sec. IV.

The overall energy functional developed here is a simplified version of that in Ref. 9, which produced promising results for atoms. It differs mainly in that $1-g_x^\sigma(\mathbf{r},\mathbf{r}')$ is a Gaussian instead of $e^{-\alpha(\mathbf{r}-\mathbf{r}')^{3/2}}$ (which leads to an unphysical second derivative at $\mathbf{r}\rightarrow\mathbf{r}'$), $E_c[\rho_\uparrow,\rho_\downarrow]$ is just the VWN functional, and the present functional is correct in the homogeneous density limit.

III. COMPUTATIONAL METHODS

We minimize the energy functional (1) by the usual Kohn-Sham[6] scheme using a modified version of the DEFT computer code.[20,21] The spin-density ρ_σ is expressed as a sum over orbitals $\rho_\sigma(\mathbf{r})=\Sigma_i^{N\sigma}|\psi_i(\mathbf{r})|^2$. The orbitals themselves are expanded in a set of Cartesian Gaussian functions, $\psi_i(\mathbf{r})=\Sigma_\ell c_\ell^i g_i(\mathbf{r})$, where $g_\ell(\mathbf{r})\equiv f(\mathbf{r})e^{\beta_\ell r^2}$ and $f(\mathbf{r})\equiv x^i y^j z^k$ are simple polynomials of degree less than 2. c_ℓ^i are the eigenvectors of the Fock matrix H_{ij}^σ for spin σ,

$$H_{ij}^\sigma=\langle g_i|-\tfrac{1}{2}\nabla^2-\sum_i\frac{Z_i}{|\mathbf{r}-\mathbf{R}_i|}+\sum_{\sigma'}\int d\mathbf{r}'\frac{\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+v_x^\sigma(\mathbf{r})$$
$$+v_c^\sigma(\rho_\uparrow(\mathbf{r}),\rho_\downarrow(\mathbf{r}))|g_j\rangle. \tag{12}$$

The only part of this matrix which differs from a LSDA calculation is the functional derivative with respect to exchange. This derivative is expandable in four terms,

$$v_x^\sigma(\mathbf{r})=\frac{\delta E_x[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma(\mathbf{r})}\equiv v_{\mathrm{lda}}^\sigma(\mathbf{r})+v_1^\sigma(\mathbf{r})+v_2^\sigma(\mathbf{r})+v_3^\sigma(\mathbf{r}), \tag{13}$$

where

$$v_{\mathrm{lda}}^\sigma(\mathbf{r})=\frac{4}{3}\left[1-\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\right][\rho_\sigma(\mathbf{r})]^{1/3}, \tag{14}$$

$$v_1^\sigma(\mathbf{r})=\tfrac{1}{2}\int d\mathbf{r}'\rho_\sigma(\mathbf{r}')\frac{[g_x^\sigma(\mathbf{r},\mathbf{r}';\alpha_\sigma(\mathbf{r}))-1]}{|\mathbf{r}-\mathbf{r}'|}, \tag{15}$$

$$v_2^\sigma(\mathbf{r})=\tfrac{1}{2}\int d\mathbf{r}'\rho_\sigma(\mathbf{r}')\frac{[g_x^\sigma(\mathbf{r}',\mathbf{r};\alpha_\sigma(\mathbf{r}'))-1]}{|\mathbf{r}-\mathbf{r}'|} \tag{16}$$

$$=v_1^\sigma(\mathbf{r})+\tfrac{1}{2}\int d\mathbf{r}'\rho_\sigma(\mathbf{r}')$$
$$\times\frac{[g_x^\sigma(\mathbf{r}',\mathbf{r};\alpha_\sigma(\mathbf{r}'))-g_x^\sigma(\mathbf{r},\mathbf{r}';\alpha_\sigma(\mathbf{r}))]}{|\mathbf{r}-\mathbf{r}'|}, \tag{17}$$

$$v_3^\sigma(\mathbf{r})=\tfrac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2\frac{\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\,\frac{\delta g_x^\sigma(\mathbf{r}_1,\mathbf{r}_2;\alpha_\sigma(\mathbf{r}_1))}{\delta\rho_\sigma(\mathbf{r})} \tag{18}$$

$$=\tfrac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)|\mathbf{r}_1-\mathbf{r}_2|$$
$$\times e^{-\alpha_\sigma(\mathbf{r}_1)|\mathbf{r}_1-\mathbf{r}_2|^2}\frac{\delta\alpha_\sigma(\mathbf{r}_1)}{\delta\rho_\sigma(\mathbf{r})}. \tag{19}$$

The field α depends on the density through the sum rule (4), so the functional derivative of this equation yields

$$\delta\rho_\sigma(\mathbf{r})e^{-\alpha_\sigma(\mathbf{r}')|\mathbf{r}'-\mathbf{r}_1|^2}$$
$$=\delta\alpha(\mathbf{r}')\int d\mathbf{r}_1\rho_\sigma(\mathbf{r}_1)(\mathbf{r}_1-\mathbf{r}')^2 e^{-\alpha_\sigma(\mathbf{r}')|\mathbf{r}'-\mathbf{r}_1|^2}, \tag{20}$$

resulting in

TABLE II. Equilibrium separations in bohr for first-row dimers calculated using the functional presented here compared to experimental, LSDA, and GGA values (Ref. 35). The GGA in Ref. 35 uses the Perdew-Wang exchange (Refs. 36 and 37) with the VWN correlation (Ref. 19).

Dimer	Experiment	This work	GGA	LSDA
H_2 [a]	1.40	1.39		1.44
Li_2	5.05	6.57	5.11	5.13
N_2	2.07	2.14	2.09	2.07
O_2	2.28	2.42	2.33	2.29
F_2	2.67	2.83	2.71	2.62

[a]Experimental and LSDA values for H_2 are from Ref. 38.

$$v_3^\sigma(\mathbf{r}) = \tfrac{1}{2}\int d\mathbf{r}'\rho_\sigma(\mathbf{r}')\frac{m_1(\mathbf{r}')}{m_2(\mathbf{r}')}e^{-\alpha_\sigma(\mathbf{r}')|\mathbf{r}'-\mathbf{r}|^2}, \tag{21}$$

$$m_n(\mathbf{r}) \equiv \int d\mathbf{r}'\rho_\sigma(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^n e^{-\alpha_\sigma(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^2}. \tag{22}$$

The asymptotic behavior of this potential is important to the discussion in Sec. V. It can be shown[2] that at a large distance r from a neutral charge distribution containing more than one-electron per spin, $v_1^\sigma \rightarrow -1/2r$, while v_2^σ and v_3^σ go to zero exponentially. This differs from the exact behavior, obtained if if $g_x^\sigma(\mathbf{r},\mathbf{r}')$ were symmetric on interchange of $\mathbf{r}$ and $\mathbf{r}'$, in that v_2^σ should also go to $-1/2r$.

In a Gaussian basis set, Eqs. (4), (15), and (22) may be evaluated analytically as three center integrals.[22] The remaining integrals are performed numerically on a grid.[23] By fitting the density to a set of Gaussians, even further simplification is achieved in the obvious manner.

The calculations presented here use an uncontracted basis,[24,25] which for atoms boron through neon include eight s-type functions, 13 p-type functions, and two ‘‘diffuse’’ d-type functions. When used for Hartree-Fock calculations, these basis sets converge the energy to better than 0.01%.[26]

Our calculations do not use any pseudopotential method to describe the core electrons, but rather incorporate all the electrons directly. Therefore, we avoid a subtle issue which plagues many studies on solids.[10–13,27]

IV. RESULTS

TABLE III. Dissociation energies in eV for first-row dimers calculated at the equilibrium separation given in Table II. For comparison, we also present experimental measurements and these energies calculated with GGA and LSDA functionals, as well as experimental results (Ref. 35).

Dimer	Experiment	This work	GGA	LSDA
H_2 [a]	4.75	4.95		4.91
Li_2	1.07	0.42	0.95	1.01
N_2	9.86	9.23	10.50	11.34
O_2	5.21	5.22	6.00	7.54
F_2	1.72	1.69	2.22	3.32

[a]Experimental and LSDA values for H_2 are from Ref. 38.

TABLE IV. Vibrational frequencies in 10^2 cm^{-1} for first-row dimers. Also presented are calculations performed using GGA and LSDA functionals as well as experimental results (Ref. 35).

Dimer	Experiment	This work	GGA	LSDA
H_2 [a]	44.0	45.9		42.0
Li_2	3.5	1.9	3.4	3.3
N_2	23.6	21.3	23.5	24.1
O_2	15.8	13.2	15.1	16.1
F_2	9.2	8.2	9.9	10.9

[a]Experimental and LSDA values for H_2 are from Ref. 38.

Table I shows the total energies for a group of lighter atoms, calculated using the functional developed here. These energies are comparable to those in Ref. 9, and both improve significantly on the LSDA energies. The energies from Ref. 9 are better for some of the heavier atoms; however, their correlation functional did include one parameter which was adjusted to fit some of these energies.

Noteworthy in Table I is the accurate energy calculated for hydrogen. For a one-electron system, Eq. (4) gives a solution $\alpha_\sigma(\mathbf{r})=0$, so that Eq. (3) is the exact exchange energy. The correction added in Eq. (9) to reproduce the homogeneous limit now almost cancels the LSDA correlation energy, resulting in a nearly self-interaction-free theory.

In Tables II, III, and IV we present the equilibrium bond lengths, dissociation energies, and vibrational frequencies for the first row diatomic molecules. Except for H_2, bond lengths are longer than those measured experimentally, and err by more than those calculated in either a generalized gradient approximation (GGA) or LSDA. However, Fig. 2 shows that even for Li_2, where the calculated discrepancies are largest, the total ground-state energy is still more accurate than the LSDA. This more accurate description of the total energy leads to better dissociation energies for the heavier dimers.

V. DISCUSSION

The WSDA energy functional developed here clearly improves upon the LSDA for atomic energies. In addition, because it readily lends itself to evaluation in a basis set of Gaussian-type orbitals, we are able to extend these results to small molecules, but with mixed results. Using the functional presented here, total molecular energies are improved, generally leading to good dissociation energies, although the bond lengths are not similarly improved. Much of this error is due to the behavior of the exchange energy with increasing separation.

We may understand the observed behavior by examining the gradient of the exchange energy.[20,28] The change in E_x, caused by displacing one nucleus δR and therefore resulting in a change in the density, $\delta\rho_\sigma(\mathbf{r})$, is just

$$\delta E_x = \sum_\sigma \int v_x^\sigma(\mathbf{r})\,\delta\rho_\sigma(\mathbf{r}). \tag{23}$$

From the form of Eq. (3) as well as v_x^σ, it is evident that, as the atoms in a dimer are distantly separated, this change will result from each atom moving in the asymptotic exchange potential resulting from the other.[29] As mentioned in Sec. III, this asymptotic potential is half of the exact limit for all the

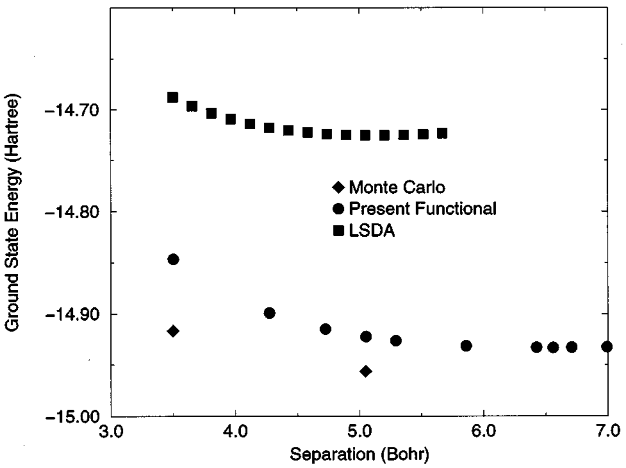

FIG. 2. The total ground-state energy of Li_2 as a function of the nuclear separation compared to LSDA (Ref. 19), and two points from Monte Carlo calculations (Ref. 32).

dimers except H_2. Since the rate of decay of $-E_x$ as r increases is less than expected, these dimers achieve lower energies by increasing the nuclear separation, without suffering as much increase in the exchange energy as they should. In the special case of H_2, however, there is only one-electron per spin, so Eq. (4) is satisfied by $\alpha(\mathbf{r})=0$. Consequently, $g_x(\mathbf{r},\mathbf{r}')$ possess the the symmetry of the exact correlation function

$$g_x^{\mathrm{exact}}(\mathbf{r},\mathbf{r}')=g_x^{\mathrm{exact}}(\mathbf{r}',\mathbf{r}), \tag{24}$$

so both v_1^σ and v_2^σ are identical, leading to the true $-1/r$ decay of the exchange potential. This symmetry explains why the bond length for H_2 was better than for the other molecules.

It is important to note that the v_x which enters into the energy gradient[28] is the true exchange potential, irrespective of the potential used to calculate the density. Therefore, one cannot ameliorate these problems by simply using a nonconsistent v_x, designed to have the correct asymptotic behavior, in the self-consistent procedure.[9,30,31]

The contrast between H_2 and the other dimers suggests that a form of g_x having the proper symmetry on interchange might improve these calculations. Such calculations are much more difficult. Preliminary investigations on several forms which incorporate this symmetry, however, produce atomic energies which are even higher than in the LSDA, although work is in progress to improve these results.

Some improvement might be obtained by refining the form of the g_x in Eq. (5). In WDA studies on solids comparing several hole parametrizations,[27] however, no one form was able to achieve systematic improvement over the LDA when calculating such parameters as lattice constants and bulk moduli. It was found there that the behavior of E_x^{WDA} is determined by the overall decay length scale in g_x, set by Eq. (4), rather than by the detailed structure of g_x. In addition, only fairly small changes can be made to g_x if one retains the exact conditions presented in Sec. II.

The calculations presented here help answer a long standing question about how well the WSDA will treat molecules. In summary, we find that the total energies calculated using the WSDA more accurate than with the LSDA, while the position and curvature of energy minima are not. Despite the mixed results, we hope that this work leads to additional insight into how to describe exchange and correlation accurately.

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