Energies of Atoms with Nonspherical Charge Densities Calculated with Nonlocal Density-Functional Theory

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Calculations using nonlocal density-functional theory show that the total energies of atoms in states characterized by partially filled degenerate subshells are substantially lower when the charge density is not spherically averaged. This is in contrast to the case with local density theory in which spherical and nonspherical treatments of atoms give essentially identical energies. A cooperative effect of nonlocality in the exchange-correlation functional and nonsphericity in the charge density lowers the atomic total energies and greatly improves the calculated binding energies of B_2, C_2, O_2, and F_2.

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Calculations of atomic total energies using the local spin-density approximation (LSDA) are usually carried out with the further approximation of spherically averaging the electron density in the open shell. For atoms with partially filled, degenerate sublevels (p or d), a spherical charge density is enforced by use of fractional population numbers.

There are two reasons for imposition of spherical averaging in atomic calculations. First, when the spherical approximation is used, the radial and angular equations are separable. Solutions to the radial differential equation can be obtained by direct one-dimensional numerical integration. Without variable separation, the radial functions must be obtained variationally by use of a basis set. Second, Janak and Williams[1] have shown that within the LSDA the nonspherical corrections are quite small in spin-polarized calculations for first-row atoms and can be accurately calculated by first-order perturbation theory for cases where the corrections are significant (transition-metal atoms and nonspin polarized treatments). For total energy calculations there is thus no strong motivation for our dispensing with the approximation of spherical symmetry.

Variational considerations lead one to expect that removing the constraint of spherical symmetry would lower the atomic energy. In fact, however, most atoms studied by Janak and Williams showed slightly higher energies when the nonspherical charge densities were used. This was attributed to incomplete cancellation of the self-interaction, a problem with local density functionals which arises because of the approximate treatment of exchange. Thus calculations for nonspherical atoms in local density theory have revealed the inadequacy of current descriptions of self-interaction in the LSDA, but have not yielded better atomic reference energies.

A local exchange-correlation energy density and potential at a point in space depends only on the charge density at that point.[2,3] In the past few years advances have been made in the development of nonlocal density functionals.[4–7] A nonlocal exchange-correlation energy density and potential depend not only on the charge density at the point of interest, but also on the gradient of the charge density at that point. The nonlocal extension of density-functional theory improves the predicted correlation energies,[8] one-electron energies,[4] and binding energies.[9,10]

Improved descriptions of the energetics of atoms are important for more than simply the achievement of a better understanding of the stability and structure of atoms, for the atomic energies serve as references for the calculation of the binding energies of molecules and solids. In this Letter, we report results from nonlocal calculations which show that the total energies of nonspherical atoms are quite systematically lower than those for spherical atoms, a result which leads to appreciably improved molecular binding energies. Specifically, we present results of calculations of the binding energies of all first-row dimers in which the component atoms have open p shells: B_2, C_2, O_2, and F_2.

The nonspherical calculations were performed with the augmented-Gaussian-basis (AGB) method of Painter and Averill.[11] Atomic-orbital solutions in this method are determined variationally as linear combinations of Gaussian-basis functions. Electron-electron matrix elements are evaluated semianalytically with use of a combination of Gaussian integral algorithms and numerical sampling.

We present results for two types of nonlocal functionals—one developed by Langreth and Mehl (LM)[4,7] and the other, the generalized gradient approximation

(GGA), by Perdew and Yue.[5,6] In both cases, the total exchange energy can be written in the form

$$E_x[n] = -0.738\,56 \int d^3r\, n^{4/3}(r) F(s), \qquad (1)$$

where n = charge density, $s = |\nabla n| / 2(3\pi^2)^{1/3} n^{4/3}$, and $F(s) = (1 + as^2 + bs^4 + cs^5)^m$.

For the LM functional, $a = (1 + 23.140 f^2)(0.0864)$, $b = c = 0$, and $m = 1$, where f is the adjustable wave-vector cutoff parameter, which has the suggested range of 0.13–0.17. For the Perdew GGA functional, $a = 1.2975$, $b = 14.0$, $c = 0.2$, and $m = \frac{1}{15}$.

The correlation energy is separated into a local term plus a nonlocal correction. The LM nonlocal correction to the correlation energy is, in Hartree atomic units,

$$E_c^{\mathrm{LM}}[n] = 0.004\,287 \int d^3r\, |\nabla n|^2 [e^{-F} + 9f^2] / n^{4/3}, \qquad (2)$$

$F = 1.745 f |\nabla n| / n^{7/6}$, f = wave-vector cutoff parameter (0.13–0.17), and the Perdew nonlocal correlation energy term is given by

$$E_c^{\mathrm{P}}[n] = \int d^3r\, e^{-\phi} C(n) |\nabla n|^2 / n^{4/3}, \qquad (3)$$

where

$$\phi = 1.745 f [C(\infty)/C(n)] |\nabla n| / n^{7/6}, \quad C(n) = 0.001\,667 + (0.002\,568 + \alpha r_s + \beta r_s^2)/(1 + \gamma r_s + \delta r_s^2 + 10^4 \beta r_s^3),$$

$$n = (4\pi r_s^3/3)^{-1}, \quad \alpha = 0.023\,266, \quad \beta = 7.389 \times 10^{-6}, \quad \gamma = 8.723, \quad \delta = 0.472, \quad f = 0.11.$$

In the calculations with use of the LM nonlocal functional, we used the Vosko-Wilk-Nusair (VWN)[12] fit to the random-phase approximation for the local correlation. With the GGA functional of Perdew, we used two parametrizations of the Ceperly-Alder[13] results for the local correlation function: the VWN parametrization[14] (denoted in the tables as GGA-VWN) and that of Perdew and Zunger[15] (denoted in the tables as GGA-PZ). Spin-dependent forms[6,7] of Eqs. (2) and (3) and the related expressions for the nonlocal exchange-correlation potential were used in the calculations reported here.

Self-consistent spin-polarized atomic total energies were obtained for the four open p-shell atoms in the first row: boron, carbon, oxygen, and fluorine. Spherical and nonspherical results with use of the four previously described functionals are summarized in Table I. The VWN exchange-correlation functional was used for the local density calculations, and nonlocal calculations were carried out (again for both nonspherical and spherical models) with the LM functional and the GGA of Perdew.[6] The electron configurations in the open-shell scheme were p_z^1 for B, $p_x^1 p_y^1$ for C, $p_x^1 p_y^1 p_z^2$ for O, and $p_x^2 p_y^2 p_z^1$ for F.

TABLE I. Effect of the removal of the spherical approximation on the atomic energies of B, C, O, and F with use of four density functionals. (NS = nonspherical, S = spherical; energies in Hartrees, except for energy differences, as noted.)

Atom	GGA-VWN[a]	GGA-PZ[b]	LM[c]	VWN[d] (local)
B(NS)	−24.687 28	−24.685 07	−24.573 84	−24.354 46
B(S)	−24.681 01	−24.679 10	−24.568 66	−24.352 77
Diff (eV)	0.171	0.162	0.141	0.046
C(NS)	−37.895 61	−37.891 03	−37.741 99	−37.467 98
C(S)	−37.891 22	−37.886 89	−37.739 59	−37.468 59
Diff (eV)	0.119	0.113	0.065	−0.001
O(NS)	−75.158 75	−75.151 75	−74.905 18	−74.525 54
O(S)	−75.146 22	−75.139 77	−74.894 79	−74.523 30
Diff (eV)	0.341	0.326	0.283	0.061
F(NS)	−99.847 00	−99.840 66	−99.536 58	−99.109 33
F(S)	−99.837 93	−99.832 16	−99.531 05	−99.110 79
Diff (eV)	0.247	0.231	0.150	−0.040

[a] Perdew's GGA local plus nonlocal exchange (Ref. 5) and nonlocal correlation (Ref. 6). The local correlation is the parametrization by Vosko, Wilk, and Nusair of the Ceperly-Alder results (Ref. 12).

[b] Same exchange and nonlocal correlation as in GGA-VWN, but using Perdew-Zunger parametrization (Ref. 15) for local correlation.

[c] Langreth-Mehl functional (Refs. 4 and 7) for nonlocal exchange and correlation, and the Vosko, Wilk, and Nusair (Ref. 12) parametrization of the exchange and correlation from the random-phase approximation.

[d] Vosko, Wilk, and Nusair parametrization of the Ceperly-Alder results (Ref. 12).

TABLE II. Binding energies (in electronvolts) of first-row dimers using spherical and nonspherical atom energies. The binding energy is calculated from the minimum of the state experimentally observed to be the ground state (e.g., $^1\Sigma_g^+$ and $^3\Sigma_g^-$ for C_2 and B_2, respectively).

		Nonspherical			Spherical		
	Expt.	GGA-VWN[a]	LM[b]	VWN	GGA-VWN	LM	VWN
B_2	2.9	3.22	3.38	3.84	3.56	3.66	3.93
C_2	6.2	6.18	6.18	7.22	6.42	6.31	7.19
O_2	5.2	5.94	6.30	7.49	6.62	6.87	7.54
F_2	1.65	2.19	2.39	3.39	2.68	2.69	3.32

[a] See Table I for meaning of exchange-correlation abbreviations.

[b] See Ref. 9. The values in this column are in good agreement with the results in Ref. 9, which were calculated without the effect of nonlocality on the atomic and molecular densities.

Oxygen shows the largest nonspherical effect with use of the local VWN calculation with the total energy in the nonspherical treatment lying 0.061 eV lower than the result in the spherical approximation. Likewise, the nonspherical boron-atom energy is lower than that obtained in the spherical central-field model, while both carbon and fluorine atomic energies were slightly lower in the approximation of spherical symmetry. The results are in good quantitative agreement with results of Janak and Williams, who treated B and C with an unspecified local functional.

When we use a nonlocal exchange-correlation functional, the atomic energies of all four atoms are significantly lowered by including the nonspherical corrections. The largest difference is again observed in the oxygen atom in which the Perdew functional gives an energy lowering of about 0.34 eV for the nonspherical atom compared with that in the spherical approximation. The smallest effect occurs in the carbon atom. The LM functional also results in a lowering of the total energies in the nonspherical case, but the effect is only 60% and 80% as large for carbon and oxygen, respectively, as with the GGA functional of Perdew. The greater lowering with the GGA functional results in better binding energies from GGA than from LM.

One of the more important implications of these results is in the calculation of binding energies of solids and molecules, where the LSDA often shows a pronounced tendency toward overbinding. Using as exemplary cases the diatomic molecules formed from the four nonspherical atoms of the first row, we see from Table II that the inclusion of both nonlocal and nonspherical corrections gives much closer agreement between theory and experiment. (The binding energies are calculated from the minimum of the experimental ground-state configuration of the molecules.) While nonlocality alone effects some improvement in molecular binding energies calculated within the spherical central-field model, inclusion of nonsphericity in the atom calculations leads to significant corrections to the tendency of overbinding. The overbinding is reduced by 70% in the O_2 molecule which is most overbound (2.3 eV) in the LSDA. The discrepancy in the nonlocal, nonspherical treatment remains the largest for O_2 (0.7 eV). The dramatic overbinding by 100% in the LSDA description of F_2 is reduced to 30% in the combined nonlocal, nonspherical treatment. As can be seen by comparison of spherical and nonspherical results for C_2 (and F_2), going beyond the central-field model within the LSDA (VWN) does not guarantee an improved binding energy—improvement is systematically obtained only with the nonlocal functionals (LM or GGA).

Calculations within the LSDA have characteristically been in greatest disagreement with experiment in binding energies, and it has been recognized that the greater self-interaction error in the atomic limit is the major source of this problem. Here we demonstrate that a full treatment of both nonlocal *and* nonspherical terms in open-shell atoms allows a cooperative effect between the two and provides atomic reference energies that define greatly improved binding energies in representative first-row diatomic molecules. Comparable improvement should be obtained in more general applications to molecules and solids.

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