PHYSICAL REVIEW B VOLUME 37, NUMBER 2 15 JANUARY 1988-I

Chemical bond as a test of density-gradient expansions for kinetic and exchange energies

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(Received 8 December 1986; revised manuscript received 21 September 1987)

Errors in kinetic and exchange contributions to the molecular bonding energy are assessed for approximate density functionals by reference to near-exact Hartree-Fock values. From the molecular calculations of Allan *et al.* and of Lee and Ghosh, it is demonstrated that the density-gradient expansion does not accurately describe the noninteracting kinetic contribution to the bonding energy, even when this expansion is carried to fourth order and applied in its spin-density-functional form to accurate Hartree-Fock densities. In a related study, it is demonstrated that the overbinding of molecules such as N_2 and F_2, which occurs in the local-spin-density (LSD) approximation for the exchange-correlation energy, is not attributable to errors in the self-consistent LSD densities. Contrary to expectations based upon the Gunnarsson-Jones nodality argument, it is found that the LSD approximation for the exchange energy can seriously overbind a molecule even when bonding does not create additional nodes in the occupied valence orbitals. LSD and exact values for the exchange contribution to the bonding energy are displayed and discussed for several molecules.

I. INTRODUCTION AND SUMMARY

The density-functional theory[1] of electronic structure aspires to chemical accuracy (chemical energies in error by less than 0.01 hartree), and in its Kohn-Sham[2] incarnation comes close[3,4] to achieving it within the local-spin-density approximation for exchange and correlation.[2] Density-gradient expansions[1,2] have always provided the most systematic means to generate density-functional approximations, starting from the local approximation in order zero. In this paper we show that the density-gradient expansions of the noninteracting kinetic[5] and exchange[2] energies (through fourth and zero order, respectively), which have given remarkably accurate total energies when applied to realistic atomic[6,7] and molecular[8–10] densities, are nevertheless seriously deficient in their description of the energetics of the chemical bond. It is hoped that this observation will stimulate the development of improved density functionals, and the testing of such functionals against chemical data.

The noninteracting kinetic and exchange energies of an electronic ground state are those of a Slater determinant which yields the true density. Hartree-Fock wave functions, available for many atoms and molecules, are Slater determinants with densities which often closely approximate the corresponding true densities (even when the true wave function is strongly Coulomb correlated).[11] If Hartree-Fock densities were to be used with exact density functionals, then close-to-exact dissociation energies would probably be obtained as a consequence of the Hohenberg-Kohn variational principle.[1] Although exchange and correlation are usually treated together in Kohn-Sham theory (and correlation is needed for chemical accuracy), we have several reasons to consider exchange alone, which will be discussed in Sec. III.

Thus our approach is to start with Hartree-Fock densities for the molecules and their constituent atoms. The density functionals to be tested are evaluated for these densities, and the resulting contributions to the molecular bonding energy are compared with nearly exact Hartree-Fock values. For any energy term E, we define

$$\Delta E = E(\text{molecule}) - \sum E(\text{isolated atoms}) . \tag{1}$$

The noninteracting kinetic energy makes a large and important contribution ΔT to the molecular bonding energy. We will show that this contribution is described very poorly by the density-gradient expansion. This conclusion holds in zero, second, and fourth order,[5] and it holds even when spin polarization[12] is taken into account.

The zero-order term in the gradient expansion for the exchange energy is the popular local-spin-density (LSD) approximation.[2] We will show that the exchange contribution ΔE_x to the molecular bonding energy is also described rather poorly within LSD for a number of molecules. For N_2 and F_2, even the sign is wrong. The LSD exchange energy functional tends to overbind molecules,[3,4] and it overbinds by about the same amount whether the electron densities employed are Hartree-Fock or self-consistent LSD densities. Contrary to expectations based upon the Gunnarsson-Jones nodality argument,[4] we find serious LSD overbinding even in the exchange-only description of N_2, a molecule which forms without the creation of antibonding orbitals in the $2p$ valence shell. Serious LSD overbinding is also found in the exchange-only description of a C_2 excited state which has no occupied antibonding valence orbital at all. We conclude that orbital nodality is not always a reliable predictor of LSD chemical errors.

II. KINETIC ENERGY

The Hohenberg-Kohn theorem[1] in principle permits the ground-state energy of a system to be constructed from its electron density, bypassing the need for a wave function. In practice a major stumbling block has been the construction of an accurate density functional for the noninteracting electron kinetic energy T. In recent years, the fourth-order density gradient expansion $T_0+T_2+T_4^H$ in the Hodges form[5] has been applied to Hartree-Fock densities of atoms[6,7] and molecules,[8–10] and has been found to overestimate T typically by less than 1% in comparison with Hartree-Fock values. Since the absolute errors are still usually much larger than chemical bonding energies, it is sometimes believed (cf. Ref. 9) that the gradient expansion is not useful for most applications to quantum chemistry and solid-state physics (although modifications of this expansion do account for the repulsion between overlapping closed shells.[13]) However, this conventional belief has not yet been verified. Could it be that these errors cancel out of bonding energy differences after all? Most of the kinetic energy resides in the atomic core; if most of the error of the gradient expansion also resides there, such a cancellation of errors could occur. Indeed it is sometimes asserted that gradient expansions, based on the electron gas of slowly varying density, are more appropriate to the valence electrons than to the tightly bound core electrons (and this assertion is supported by numerical results in the case of the exchange-correlation energy). We shall present evidence that, unfortunately, no precise systematic cancellation of errors occurs. The original gradient expansion gives a poor account of molecular bond-

TABLE I. Noninteracting electron kinetic energy contribution ΔT to the energy of formation of a molecule (with bond length R) from separate atoms. The density-functional (DF) and spin-density functional (SDF) gradient expansions $T_0+T_2+T_4$ are compared with exact Hartree-Fock (HF) values. (Energies in hartrees, distances in bohrs.) The molecular geometries employed are *not* precisely the Hartree-Fock equilibrium geometries.

Molecule	R	$\Delta(T_0+T_2+T_4^H)_{\rm DF}$	$\Delta(T_0+T_2+T_4^H)_{\rm SDF}$	$\Delta T^{\rm HF}$
H_2	1.4017[a]	0.44	0.12	0.128
BH	2.3501[b,c]	0.31	0.09	0.091
HF	1.7325[b]	0.75	0.40	0.16
	1.733[a]	0.8	0.5	0.1
	1.8342[c]	0.62	0.27	0.012
BF	2.3905[a]	1.0	0.8	0.3
N_2	2.068[b]	1.07	−0.78	−0.01
	2.0741[a]	1.1	−0.7	−0.1
	2.124[c]	0.89	−0.96	−0.19
F_2	2.680[b]	0.3	−0.1	−0.25
	2.68[a]	0.3	−0.1	−0.3
	2.75[c]	0.2	−0.2	−0.31
CO	2.124[c]	1.1	0.3	0.16
	2.132[a]	1.2	0.4	0.2
	2.1322[b]	1.0	0.2	0.14
H_2O	a	1.26	0.39	0.27
CO_2	a	1.7	0.3	0.2
BH_3	a	0.89	0.35	0.31
CH_4	a	1.47	0.52	0.48
NH_3	a	1.30	−0.10	0.26
NNO	a	2.3	−0.1	0.0
C_2H_2	a	1.27	0.32	0.32
H_2CO	a	1.7	0.5	0.3
HBe^+	2.124[c]	0.47	0.20	0.266

[a] Reference 10.
[b] Reference 8.
[c] Reference 9.

TABLE II. A study of ΔT by orders of the gradient expansion for the molecules H_2 and N_2. (See caption of Table I.) Note that T_0 is the Thomas-Fermi kinetic energy.

H_2[a]	$\Delta(T_0)_{DF}$	0.403	$\Delta(T_0)_{SDF}$	0.063
	$\Delta(T_0+T_2)_{DF}$	0.418	$\Delta(T_0+T_2)_{SDF}$	0.078
	$\Delta(T_0+T_2+T_4^H)_{DF}$	0.439	$\Delta(T_0+T_2+T_4^H)_{SDF}$	0.118
		$\Delta T^{HF}=0.128$		
N_2[b]	$\Delta(T_0)_{DF}$	1.33	$\Delta(T_0)_{SDF}$	-0.37
	$\Delta(T_0+T_2)_{DF}$	1.19	$\Delta(T_0+T_2)_{SDF}$	-0.59
	$\Delta(T_0+T_2+T_4^H)_{DF}$	1.07	$\Delta(T_0+T_2+T_4^H)_{SDF}$	-0.78
		$\Delta T^{HF}=-0.01$		

[a]Reference 10.

[b]Reference 8.

ing energies, which is substantially improved by the *spin*-density gradient expansion,[12] but even this modified version is far from chemical accuracy.

Recently Allan *et al.*[8,9] and Lee and Ghosh[10] have reported Hartree-Fock kinetic energies T^{HF} and gradient expansion values $T_0+T_2+T_4^H$ for a number of molecules. In Table I we have selected those molecules which have a spin-unpolarized (singlet) ground state, and calculated the noninteracting kinetic energy contribution ΔT to the energy of formation of the molecule from separate atoms. For the atoms, we used numerical Hartree-Fock densities calculated with the Froese Fischer program.[14]

For each atom considered here, the ground state is the multiplet of highest spin S, and of highest orbital angular momentum L consistent with this value of S. The Hohenberg-Kohn theorem applies even to a degenerate ground state.[15] However, since gradient expansions are expected to be less accurate for multideterminant states,[16] the multiplet-member chosen here was the single Slater determinant with z components $M_s=S$ and $M_L=L$. The density of this ground state was *not* spherically averaged. Calculations were performed both with the density-functional (DF) (Ref. 5) gradient expansion $T_0+T_2+T_4^H$, and with the *spin*-density functional (SDF) (Ref. 12) expansion. [Note that the spherical approximation for the atomic density would overestimate $\Delta(T_0+T_2+T_4^H)$ by as much as 0.1 hartree.]

By comparison with the "exact" Hartree-Fock value ΔT^{HF} in Table I, the density-functional (DF) gradient expansion seriously overestimates ΔT. This overestimation is partially corrected by the spin-density functional (SDF) gradient expansion (since the separated atoms are all spin polarized), but the remaining error is often large and apparently random. For example, there is a serious underestimation for N_2 and a serious overestimation for BF.

Table II presents a study of ΔT by orders of the gradient expansion for the molecules H_2 and N_2. For H_2, the spin-density gradient expansion gives a good account of ΔT, with systematic improvements from higher orders of the expansion. But for N_2, the description is poor in all orders. Referring back to Table I, we can see that this expansion also works fairly well for the other s-electron-bonded molecule (HBe^+) tabulated there, but it works erratically for the p-electron-bonded molecules.

For rare-gas diatomics with Hartree-Fock densities, the quantitative failure of the gradient expansion was demonstrated by Shih[17] and by Pearson and Gordon.[13] As far as we know, the only other previous study of molecular bonding energies via density-gradient expansion was made by Yonei,[18] who used $(T_0+T_2)_{DF}$ for the kinetic energy, and the local density approximation for the exchange energy. At each internuclear separation R, Yonei constructed a density which approximately minimized this total-energy functional. The resultant binding energy curve for the molecule N_2 minimized at $R=2.56$ bohr (24% greater than the experimental bond length of 2.068 bohr), but with about the experimental bonding energy (for $R=2.068$ bohr).

The molecular densities of Refs. 8–10 are claimed to be of near-Hartree-Fock quality, as are the atomic densities employed here. Table I indicates a good general agreement[10] between molecular kinetic energies calculated with a Gaussian orbital basis[10] and those calculated with a basis of Slater-type orbitals.[8,9]

Four points of principle must be addressed. The first is that, even for the Hartree-Fock density, T^{HF} is not precisely the noninteracting kinetic energy[2] T which the gradient expansion is trying to approximate. The difference is associated with the fact that the Hartree-Fock potential is not a local potential $V(\mathbf{r})$. Atomic calculations[19,20] suggest that this difference (which is usually overlooked) is much smaller than the chemical bonding energies of interest here. In fact, $T^{HF}-T$ is second-order[15] in the difference between the Hartree-Fock and Kohn-Sham determinants for the same density. If somehow it turns out that this difference is not small, then it would very likely mean that $\Delta T<\Delta T^{HF}$, which still supports our assertion that the gradient expansion often seriously overestimates ΔT. The inequality would arise if T^{HF} is sufficiently greater than T in the molecule. (In the atom[19,20] $T\simeq T^{HF}$, and in the molecule T^{HF} is never less[15] than the exact noninteracting kinetic energy for the Hartree-Fock density.)

The second point of principle (also conventionally overlooked) is that the Hodges form of the gradient expansion should be applied only to *analytic* electron densities.[21] There is a correction[21] to the fourth-order term T_4^H due to the cusps at the nuclei which is comparable in size to T_4^H itself. However, this cusp correction should almost cancel out of the energy differences $\Delta(T_0+T_2$

$+T_4^H$) considered here. The third point is that the next term in the gradient series (T_6) diverges for atoms and molecules.[22] Fourth and finally, we dissent from the characterization[9] of the SDF gradient expansion[12,21] as an "interpolation" between unpolarized and fully polarized limits; for better or worse, the spin dependence is determined by the requirement that the gradient expansion be exact in the limit of slowly varying density. (For each atom and molecule considered here, the Hartree-Fock ground state that we have chosen decomposes into independent spin-up and spin-down electron densities.)

With reasonable security, we can conclude that the gradient expansion does not in fact have chemical accuracy. We cannot say whether this situation would be improved by applying the local asymptotic truncation of Pearson and Gordon[13] to the gradient expansion of the proper kinetic energy density.[21] However, it appears from Table II that this situation would *not* be improved by the global asymptotic truncation ($T_0+T_2+0.5T_4^H$) of Ref. 8. We note interesting recent progress[23,24] toward the construction of nonlocal approximations to $T[n]$.

Why does the gradient expansion fail for the valence electrons in atoms and molecules? A partial answer might be found in the behavior of the "small" parameter $|\nabla n|/2k_F n$ where $k_F=(3\pi^2 n)^{1/3}$. This parameter is less than unity over most of the interior of an atom, but diverges exponentially as $|\mathbf{r}|\to\infty$ in an atom or molecule.[19] In a bulk solid (especially a metal), this parameter is better behaved and the gradient expansion might still provide a useful description of the valence electrons.

III. EXCHANGE ENERGY

Chemical accuracy is more nearly approached by the Kohn-Sham[2] version of spin-density functional theory, in which the noninteracting kinetic energy is treated exactly and only the exchange-correlation energy E_{xc} is approximated. In the commonly used local-spin-density approximation,[2] the SDF gradient expansion for E_{xc} is truncated at order zero. A worrisome overbinding (at worst 0.08 hartree for O_2) results for first-row *sp*-bonded diatomics, although H_2 and the alkali dimer Li_2 are accurately described.[3] In their study of the sources of error in the LSD approximation, Gunnarsson and Jones[4] have emphasized that errors in the exchange energy are a major cause of the discrepancies with experiment. This conclusion was also reached in an earlier study of refinements to the correlation energy in the H_2 molecule.[25] It is useful to compare results from exchange-only LSD calculations for selected systems with results from near-exact Hartree-Fock calculations in order to distinguish these errors from those that are due to approximations in the treatment of Coulomb correlation. Then errors often appear in an exaggerated form, and effects due to improvements in the treatment of exchange can be isolated. This is apparent in the exchange-only bonding energies ΔE_{tot} for N_2 and F_2 recalculated here self-consistently for $\alpha=\frac{2}{3}$ by the method of Ref. 3, and compared with Hartree-Fock bonding energies[26] in Table III. The LSD overbinding for each of these two cases is ~ 0.15 hartree. (The exchange-only LSD approximation is the same as the spin-polarized $X\alpha$ method[27] with $\alpha=\frac{2}{3}$.)

In search of the explanation for this error, it is natural to question the role of differences in the density alone. The LSD valence-electron densities for atoms are known to decay much too slowly into the vacuum.[28] Nevertheless, the Hartree-Fock and exchange-only LSD orbitals are sufficiently similar that first-row atomic exchange energies calculated from the Fock integral with the two types of orbitals agree within 0.005 hartree.[4] Similarities have also been observed between the LSD and Hartree-Fock molecular orbitals in ozone.[29]

These previous findings are consistent with the results for molecules displayed in Table III, where the exchange contribution ΔE_x to the bonding energy is calculated in the LSD approximation and compared to exact Hartree-Fock values. Molecular exchange energies were taken from Table I of Ref. 9, while atomic values were computed here. For each molecule in Table III, the LSD and Hartree-Fock values of ΔE_x were calculated with the same (Hartree-Fock) density, while the LSD and Hartree-Fock values of ΔE_{tot} were calculated with different (respectively, self-consistent) densities. For the cases tested (N_2 and F_2), the LSD error for ΔE_{tot} is found to be essentially the same as that for ΔE_x. Clearly, this error arises directly from the error of the LSD

TABLE III. Changes ΔE_{tot} and ΔE_x in the total and exchange energies, respectively, upon molecule formation. The exchange-only description presented here neglects electron Coulomb correlation. All values were calculated with accurate Hartree-Fock densities, except for the local-spin-density (LSD) value of ΔE_{tot}, which was calculated with the self-consistent LSD density. Note that the dissociation energy is $-\Delta E_{\mathrm{tot}}$. (Energies in hartrees. Note that the spherical approximation for the atomic density would have underestimated the LSD value of ΔE_x by as much as 0.01 hartrees.)

	ΔE_{tot}			ΔE_x		
Molecule	LSD	Hartree-Fock	LSD error	LSD	Hartree-Fock	LSD error
Li_2	−0.010	−0.006	−0.004			
N_2	−0.33	−0.19	−0.14	−0.02	0.13	−0.15
F_2	−0.11	0.04	−0.15	−0.06	0.07	−0.13
BH				−0.07	−0.07	−0.00
HF				−0.14	−0.09	−0.05
CO				−0.23	−0.12	−0.11
HBe^+				−0.09	−0.10	0.01

exchange energy functional, and *not* from the error of the self-consistent LSD density.

Gunnarsson and Jones[4] have proposed a rationale for the errors of LSD exchange in molecules and other systems. Simply stated, their argument is this: Since the LSD exchange energy functional does not retain in detail the orbital nodal structure that arises in the Fock integral, errors will ensue with a size depending upon how greatly the nodal structures differ in cases being compared (e.g., molecule and constituent atoms). Thus the errors of the LSD bonding energy are expected to be much smaller in Li_2, BH, and HBe^+, where the occupied valence molecular orbitals are all bonding orbitals, than they are in F_2, where some of the orbitals are antibonding with additional nodes. These expectations are confirmed in Table III. However, the isoelectric molecules N_2 and CO are surprising: They display large LSD exchange-only overbinding (comparable to that in F_2), even though all of their 2*p*-derived occupied orbitals are bonding. This unexpected result has been uncovered here because our study of these molecules is exchange only; N_2 does not look so anomalous when correlation is included.[4]

If the Gunnarsson-Jones rationale applies to N_2 and CO, then it must be the 2*s*-derived antibonding molecular orbitals which are responsible for the exchange-only LSD overbinding. We have excluded this possibility via an exchange-only study of an excited singlet state of the carbon molecule C_2^* $(1\sigma_g)^2$ $(1\sigma_u)^2$ $(2\sigma_g)^2$ $(1\pi_u)^4$ $(3\sigma_g)^2$, which dissociates to excited carbon atoms $C^*(1s)^2$ $(2s\uparrow)^1$ $(2p\uparrow)^3$. This molecule is like N_2 but without the antibonding $(2\sigma_u)^2$ electrons. We first performed unrestricted Hartree-Fock calculations with a 6-311G^{**} basis[30] for C_2^* and C^*, and obtained a bond length $R=2.14$ bohr with a bonding energy $\Delta E_{\text{tot}}(\text{HF}) = +0.01$ hartree. We then performed exchange-only LSD calculations with the basis of Ref. 3 and the same bond length, and obtained a bonding energy $\Delta E_{\text{tot}}(\text{LSD}) = -0.21$ hartree. There is a pronounced LSD overbinding despite the absence of occupied antibonding orbitals in the valence shell. We conclude that orbital nodality alone is not always a reliable predictor of LSD chemical errors.

The substantial errors of the LSD approximation for ΔE_x often are largely canceled[4] by compensating errors in the LSD approximation for ΔE_c, the correlation contribution to the bonding energy. A similar cancellation of errors occurs for the jellium surface energy and many other problems, and is partially understood.[31,32] This cancellation of errors should not be neglected in any effort to understand the reasons for the success of the LSD approximation for exchange and correlation, or to go beyond it. In particular, it bodes well for the eventual success of *generalized* gradient approximations (e.g., Refs. 32 and 33) for exchange and correlation taken *together*. Improvements over LSD in chemical bonding energies have already been achieved[34,35] by such approximations.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation under Grant No. DMR-84-20964, by the Donors of the Petroleum Research Fund administered by the American Chemical Society, by the U.S. Department of Energy, (Division of Materials Sciences), under Contract No. DE-84OR21400 with Martin Marietta Energy Systems, Inc., and by the Natural Sciences and Engineering Research Council of Canada (under Grant No. A6294).

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