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Momentum space properties and local density approximations in small molecules: A critical appraisal

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Electron densities obtained from high-quality wave functions are used to assess critically functionals for a variety of molecular properties. We concentrate mainly on those linking the electron density to the moments of momentum, since these relate directly to experimental observables. We also examine exchange and Coulomb functionals, gradient corrections, and information entropies. We determine whether any of the functionals can be considered useful for chemical applications. We examine a range of light molecules near equilibrium geometry, a series of light diatomic hydrides over a range of internuclear distance, and atoms in a range of chemical environments. Closed- and open-shell systems are considered. Large basis sets are used throughout and, for the studies dependent on internuclear separation, we employ correlated wave functions with proper dissociation.

I. INTRODUCTION

We have used high-quality wave functions to assess critically the applicability of expressions predicted by electron gas theory, which is the basis of modern density functional theory. There are currently two major strands to density functional theory. The older approach is based on the well-known Thomas–Fermi method but continues to be refined to account for exchange, correlation, density gradients, and relativistic effects. The newer, now dominant strategy considers exchange and correlation together, frequently in terms of exchange–correlation potentials; recent accounts of the general theory have been given by Kohn and Vashishta[1] and of a variety of applications by Williams and von Barth.[2] This paper is concerned with the first approach and concentrates on local density approximations to momentum space properties, which relate directly to experimental observables. Even a cursory glance at the literature reveals a vast number of publications on such local density approximations for atoms and molecules (for recent reviews see Refs. 3 and 4). Many functionals have been proposed for a variety of atomic and molecular properties but have mostly been employed for studies of global trends across wide ranges of usually atomic systems. It is important, and timely, to determine whether any of these approximations can be considered valid to chemical accuracy. We reach some very definite conclusions and also present findings of general interest concerning momentum space properties in molecules. Our results for open-shell systems suggest some worrying comments on the generalization of the exchange–correlation approach to spin-polarized systems.

It is important that we make a specific comment concerning "accuracy." Many of the functionals that have been tested in the literature are found to be correct to small percentage errors. To put such results in context, we note that the total energy of BH^+ is around -25 hartree; an error of

only one tenth of one percent is quite substantial when compared to the binding energy of about 0.07 hartree. Similar arguments can be made for properties other than the total energy. The functionals should yield high accuracy for individual molecules over wide ranges of nuclear separations. If this is not achieved then it is essential that the deviations reflect directly the nature of the chemical binding. Also, to be considered useful, we require that the momentum and position space information entropies recently examined in the literature should show systematic differences for different molecules.

The structure of this paper is as follows. In Sec. II, we review the local density functionals that we have chosen to test. In Sec. III we consider a series of light diatomics, each close to its equilibrium bond length R_e, using Hartree–Fock wave functions obtained with a very large basis set. Both open- and closed-shell molecules are examined. A multiconfigurational self-consistent field (MCSCF) wave function is used in Sec. IV for the OH ($X\,^2\Pi_i$) radical for a range of internuclear distances, R. The results are also compared with those from SCF calculations. We proceed to more extensive tests in Sec. V where spin-coupled wave functions with very large basis sets are employed for three molecules that have very different bonding characteristics: $BH^+(X\,^2\Sigma^+)$, $LiH(X\,^1\Sigma^+)$, and $LiH^+(X\,^2\Sigma^+)$. In Sec. VI we use the zero-flux surface partitioning scheme to study oxygen and hydrogen atoms in a small range of chemical environments. We present a summary and our conclusions in Sec. VII.

II. LOCAL DENSITY APPROXIMATIONS

The Hohenberg–Kohn theorem[5] has been said to be "of transcendent importance in chemistry".[4] It states that the ground state energy of a many-electron system is a unique functional of the electron density. This is the driving force behind density functional theory. In this section we review

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some of the functionals that have been proposed for various properties, including components of the total energy.

We start by considering the moments of momentum $\langle p^m \rangle$ defined by

$$\langle p^m \rangle = \int p^m \rho(\mathbf{p}) d\mathbf{p} , \qquad (2.1)$$

where $\rho(\mathbf{p})$ is the momentum space density, the analog in momentum space of the position space density $\rho(\mathbf{r})$. In the Thomas–Fermi theory these are related[3,6] to the electron density $\rho(\mathbf{r})$ by

$$\langle p^m \rangle = \frac{3(3\pi^2)^{m/3}}{m+3} \int \rho(\mathbf{r})^{(m+3)/3} \, d\mathbf{r}$$

$$\equiv \frac{3(3\pi^2)^{m/3}}{m+3} I_m \qquad (2.2)$$

in atomic units, which we use throughout. These moments are related directly to the experimentally observable Compton profile $J(q)$.[7] Explicitly, for $m \geqslant 0$,

$$\langle p^m \rangle = 2(m+1) \int_0^\infty q^m J(q) dq . \qquad (2.3)$$

$\langle p^2 \rangle$ is simply twice the electronic kinetic energy T, $\langle p \rangle$ is usually called the mean momentum, and $\langle p^{-1} \rangle$ is just twice the maximum in the Compton profile. If we find that Eq. (2.2) is obeyed well for an individual molecule in a number of rovibrational levels then we have additional information for inverting Compton profile data to obtain an *experimental* electron density.

The Dirac–Slater exchange energy is given by[8]

$$K[\rho] = \tfrac{3}{4} (3/\pi)^{1/3} \int \rho(\mathbf{r})^{4/3} \, d\mathbf{r} \qquad (2.4)$$

and so, as originally pointed out by Pathak and Gadre,[9] we should expect

$$K[\rho] = \langle p \rangle / \pi . \qquad (2.5)$$

It has also been suggested[10–12] that the Coulomb energy for an N-electron system is given by

$$J[\rho] = B_0 N^{2/3} \int \rho(\mathbf{r})^{4/3} d\mathbf{r} , \qquad (2.6)$$

where B_0 is a purely numerical constant whose exact value depends on the range of systems fitted in a least-squares sense. It follows from Eq. (2.6) that $J[\rho]/N^{2/3}$ should also be proportional to $\langle p \rangle$.

A common correction to Thomas–Fermi theory is the inclusion of gradient terms to allow for the inhomogeneity of the electron density.[13] For the kinetic energy

$$T = T_0 + T_2 + T_4 , \qquad (2.7)$$

where

$$T_0 = \frac{3}{10} (3\pi^2)^{2/3} \int \rho(\mathbf{r})^{5/3} d\mathbf{r} , \qquad (2.8)$$

$$T_2 = \frac{1}{72} \int \frac{(\nabla\rho)^2}{\rho} \, d\mathbf{r} , \qquad (2.9)$$

$$T_4 = \frac{1}{540(3\pi^2)^{2/3}} \int \rho^{1/3}$$

$$\times \left\{ \left(\frac{\nabla^2\rho}{\rho}\right)^2 - \frac{9}{8} \left(\frac{\nabla^2\rho}{\rho}\right) \left(\frac{\nabla\rho}{\rho}\right)^2 + \frac{1}{3} \left(\frac{\nabla\rho}{\rho}\right)^4 \right\} d\mathbf{r} . \qquad (2.10)$$

Note that, whereas the integrands for T_0 and T_2 are always positive, that for T_4 can be of either sign.

This gradient expansion has been used with fair success to calculate the total kinetic energy of atoms, ions, and molecules[14,15] substituting Hartree–Fock densities into the right-hand side of Eqs. (2.8)–(2.10). Such an approach is not altogether satisfactory. The proper local behavior of the kinetic energy density[16–18] may not be necessarily reproduced. In addition, since the electron density decays exponentially, the gradient expansion of the kinetic energy does not converge; T_6 diverges for atoms in the regions close to the nucleus and far from it.[19] Such an expansion is not suitable for a component of a total energy functional which is then variationally minimized to determine the electron density since $\delta T_4/\delta\rho$ imparts physically unacceptable properties to the Euler equation.[16] This latter aspect is not of immediate concern in the present work.

An alternative kinetic energy functional has also been proposed[20,21] for an N-electron system,

$$T = 9T_2 + \tau(N)T_0 , \qquad (2.11)$$

where T_0 and T_2 are defined in Eqs. (2.8) and (2.9). $9T_2$ is the full Weizäcker correction,[22] which is the correct kinetic energy functional for a one- or two-electron Hartree–Fock atom. The functional derivative $\delta T/\delta\rho$ now has acceptable properties. Various functions have been suggested[20,21] for $\tau(N)$; however, they all involve numerical constants obtained from various fits to Hartree–Fock values.

Gordon and co-workers, who are mostly interested in applying electron gas models to intermolecular forces,[23] have suggested an alternative means[24] for dealing with divergence of the gradient expansion. At each point in space, the gradient corrections are considered as terms in an asymptotic series which is then truncated at the smallest term. Pearson and Gordon,[24] who refer to their scheme as a local asymptotic summation, have also examined scaling the smallest gradient correction by a factor between 0 and 1.

T_2 requires one further comment. It has been suggested for N-electron diatomics that T_2 should be large when the dissociation energy D is large and even that D/N should increase linearly with T_2.[25] It has been shown in our previous work[15] that such a correlation is not observed. It was, however, noticed that D/N^2 tends to be *small* when T_2 is large, but the empirical inverse relationship between these two quantities was rather rough. We investigate these proposals further by examining the variation of T_2 with R for different molecules.

Lastly, information "entropies" have been defined[26] as

$$S_r = - \int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r} , \qquad (2.12)$$

$$S_p = - \int \rho(\mathbf{p}) \ln \rho(\mathbf{p}) d\mathbf{p} , \qquad (2.13)$$

and Gadre[27] has encouraged the systematic study of these for atoms and molecules.

III. RESULTS FOR DIATOMICS NEAR R_e USING HARTREE–FOCK WAVE FUNCTIONS

Instead of obtaining rather poor electron densities by solving the Thomas–Fermi or related equations, we have used SCF wave functions to test the expressions predicted by electron gas theory. This approach was first used for atoms by Kim and Gordon[28] and subsequently by Shih, Wang, Parr, and others.[14] In our previous work[15,29] we generalized this approach to a series of first-row diatomic molecules testing not only the density functional energy equations and their gradient corrections, but also the related expressions linking the moments of momentum to the electron density. The present paper is partly an extension of our previous work, but we include the necessary detail to make the present account self-contained.

We tested Eq. (2.2) for $m = -1, 1, 2$ for a series of neutral diatomic systems and singly charged positive ions. For all the atoms and diatomic molecules that were studied, we employed a large, flexible basis set—namely a universal even-tempered (UET) basis set of $9s/6p/3d$ Slater-type functions on each center.[30] The values of $\langle p^m \rangle$ were evaluated via the Fourier transform of $\psi(\mathbf{r})$. It was found[29] that the linear relationships between $\langle p^m \rangle$ and I_m were obeyed fairly well: The root-mean square (rms) percentage errors for positive m were $\sim\frac{1}{2}\%$ and for $m = -1$ was $\sim 2\frac{1}{2}\%$. However, the gradients differed from the proportionality constants predicted by Eq. (2.2) by up to 10%.

An important point that we did not mention previously is that no distinction was made between closed- and open-shell molecules. The equations we have used have been derived for closed-shell systems in the sense that each cell in phase space contains two electrons; when there are unpaired electrons there is no mention of spin. It is clearly possible to derive alternative equations for the case where all electrons have the same spin (complete spin polarization). The correct approach for a molecule that is between these two extremes (partial spin polarization) is not clear. The simple correction that has been proposed by Kim and Gordon[28] is in fact the same as the starting point for spin-density functional theory.[3,31] In such an approach, the electron density is divided into two noninteracting electron gases and for systems with N_α electrons of α spin and N_β of β spin it is written as

$$\rho(N_\alpha, N_\beta) = \rho(N_\alpha, 0) + \rho(0, N_\beta) \qquad (3.1)$$

so that

$$T[N_\alpha, N_\beta] = T[N_\alpha, 0] + T[0, N_\beta] . \qquad (3.2)$$

The two terms on the right-hand side of Eq. (3.2) are then evaluated using the equations for complete spin polarization. It does not seem realistic to consider partitioning of the total Hartree–Fock density into noninteracting α-spin and β-spin components. However, the expressions used in spin-density functional theory, which depend on the *degree* of spin polarization x, can also be considered as merely an interpolation between $x = 0$ and $x = 1$. We note that Kim and

Gordon obtained rather mixed results and also that they mentioned the failure of their spin correction when $N_\alpha - N_\beta$ was small compared with the total number of electrons.

The Hartree–Fock density, unlike the Thomas–Fermi density, depends not only on the spatial occupancy of the orbitals but also on the spins (and the precise coupling of these) in the open shells. We realize that Eq. (2.2) is derived without taking any explicit account of electron spin. Nonetheless, we substituted open-shell restricted Hartree–Fock wave functions directly into this equation and found, rather surprisingly, that the errors were no larger than for the closed-shell molecules. Equation (2.2) appears to have a wider range of applicability than might be supposed from a consideration of its underlying assumptions. For our present purposes we do not find it necessary to distinguish between open- and closed-shell molecules in any way.

It is possible, by including appropriate self-interaction energies, to link the Dirac–Slater exchange energy $K[\rho]$ with Hartree–Fock energy terms E_K in a consistent manner for both open- and closed-shell molecules. Explicitly,

$$E_K = \sum_{i<j}^{N}{}' K_{ij} + \frac{1}{2} \sum_i^N J_{ii} , \qquad (3.3)$$

where the summations extend over all N electrons. The first term represents the usual definition of exchange energy, and the prime indicates that the summation is only over pairs of electrons of the same spin. The second term is the self-interaction contribution; it dominates the first term for low atomic number. This is the natural extension of the expression we used in previous work for closed shells.[29]

Our use of E_K differs from the approach of previous authors[28,14] who subtracted the classical potential energy $U_c[\rho]$ from the Hartree–Fock potential energy. For an atom or ion with nuclear charge Z,

$$U_c[\rho] = Z \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r} + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} \, d\mathbf{r}' . \qquad (3.4)$$

Instead, we merely sum the required elements of the Coulomb $\mathbf{J}$ and exchange $\mathbf{K}$ matrices. Our value of E_K for the neon atom agrees well with the corresponding value given by Shih *et al.*[14] but differs somewhat from that given by Kim and Gordon.[28]

We show in Fig. 1 a plot of E_K vs $\langle p \rangle$. For convenience, the values are also recorded in Table I. It can be seen that Eq. (2.5) is obeyed well, the rms percentage error being 0.7%. A similar test of Eq. (2.6) for our series of diatomics produces very disappointing results as should be clear from Fig. 2 where we plot E_J vs $N^{2/3}I_1$. The E_J values differ from the usual definition of Coulomb energy by the self-interaction terms and are recorded in Table I. Note that E_J–E_K reproduces the total two-electron contribution to the energy. The rms percentage error in Fig. 2 is 6.6%. We have also plotted $E_J/N^{2/3}$ against $\langle p \rangle$ and the results were no better.

To a large extent, the linear relationship discussed by Gadre and Bendale[11] is a manifestation of the very large range of atomic number considered: it is a question of scale. Bartolotti and Parr[12] have plotted essentially E_J/I_1 vs $N^{2/3}$. Our corresponding plot, which we do not reproduce here, is no better than Fig. 2—the rms percentage error is 5.7%. We
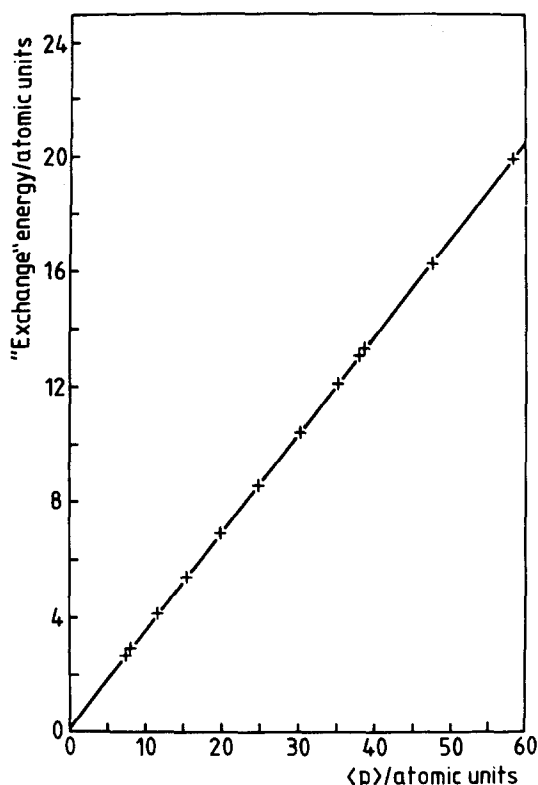
FIG. 1. "Exchange energy" E_K vs $\langle p \rangle$. The line drawn through the points was chosen by a least-squares fit. The gradient is 0.34 and the intercept is 0.13. The Thomas–Fermi predicted slope [Eq. (2.5)] is 0.32.

FIG. 2. "Coulomb energy" E_J vs $N^{2/3}I_1$. The line shown has gradient 0.76 and intercept 4.6 and was chosen by a least-squares fit.

feel that global plots must be treated with great caution. Furthermore, it is absolutely essential that a *meaningful* estimate of the deviation from linearity be quoted.

It might be possible to obey Eq. (2.6) rather better by scaling the self-interaction energies by a numerical factor λ. This is presumably related to the problem of the incomplete cancellation between $J[\rho]$ and $K[\rho]$ for singly occupied orbitals.[32] We are very concerned that the price of any such procedure is that the sum of the Coulomb and exchange energies is no longer equal to the total Hartree–Fock two-elec-
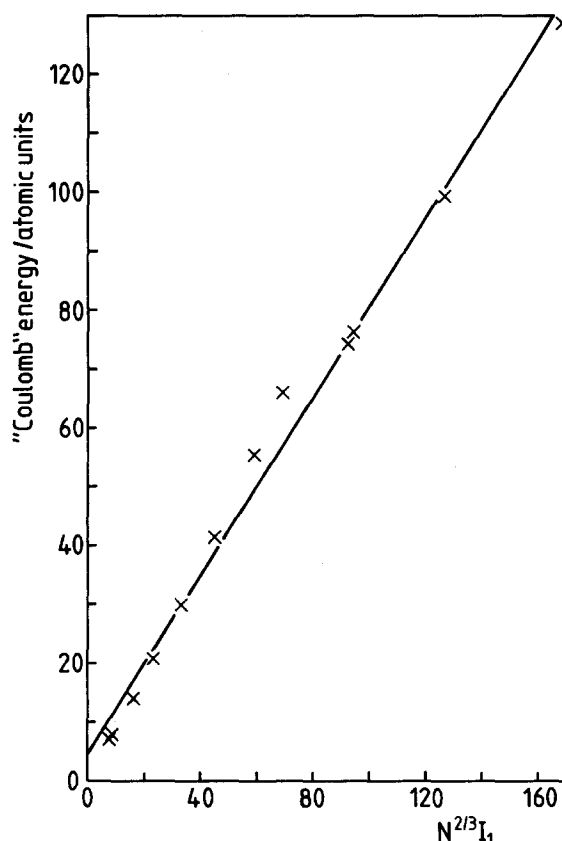
tron energy. We found that least-squares fitting of B_0 and λ was not satisfactory.

As is well known, simple rearrangement of the energy expression for a closed-shell SCF calculation leads to

$$E_{\text{SCF}} = \sum_i (\epsilon_i^N + \epsilon_i^{\text{SCF}}) + V_{nn} , \qquad (3.5)$$

where the summation is over doubly occupied orbitals and V_{nn} is the total nuclear–nuclear repulsion term. The ϵ^{SCF} are orbital energies which are the eigenvalues of the orbital equations

$$\left[\hat{H}^N + \sum_i (2\hat{J}_i - \hat{K}_i) \right] \phi_j = \epsilon_j^{\text{SCF}} \phi_j \qquad (3.6)$$

in which $\hat{H}^N$ is the one-electron Hamiltonian with eigenvalues ϵ^N.

The well-documented successes of simple uses of orbital energies such as Walsh's rules are rather surprising given that the change in the sum of the orbital energies (E_S) with geometry may be swamped by the other terms. However, Ruedenberg[33] has shown that an energy relationship suggested by Fraga[34] for atoms, and subsequently by Politzer[35] for molecules, leads to the approximate relation

$$E_{\text{SCF}} \cong \frac{3}{2} E_S \equiv \frac{3}{2} \sum_i 2\epsilon_i^{\text{SCF}} \qquad (3.7)$$

for molecules close to their equilibrium geometry. In a fit to actual calculations, he found that a better value for $\alpha \equiv E_{\text{SCF}}/E_S$ is ~ 1.55. There has been much published concerning this relation and on the best value for α; several similar relationships have also been investigated and it is inappropriate to list them here. However, since we have

TABLE I. Values of I_1, $\langle p \rangle$, E_K, E_J, and the self-interaction term in atomic units for the systems studied. Each atom or molecule was in its ground electronic state. The bond lengths used are given (in brackets) in bohr; some of these are slightly different from those used in our previous work (Refs. 15 and 29). There are a few minor errors in Table I of Ref. 29. I_2 for BeH$^+$ should have read 4.735 instead of 4.753. In addition, reading from left to right, the values for F_2 should have been 62.879, 397.02, 24.613, 58.338, 24.985, 10.785, 19.931.

System	I_1	$\langle p \rangle$	E_K	E_J	"Self-interaction"
Be	3.131	7.434	2.667	7.156	2.616
BeH$^+$(2.124)	3.420	8.072	2.916	7.880	2.870
BH(2.3501)	4.898	11.682	4.129	14.024	3.912
CH(2.124)	6.446	15.508	5.411	20.899	4.939
NH(2.0)	8.280	19.911	6.911	29.920	6.100
OH(1.8342)	10.410	24.853	8.555	41.448	7.391
HF(1.8342)	12.817	30.304	10.399	55.541	8.781
Ne	14.939	35.197	12.108	66.147	10.104
N$_2$(2.124)	15.983	37.939	13.061	74.180	7.626
CO(2.124)	16.307	38.639	13.334	76.327	11.715
O$_2$(2.3501)	19.973	47.578	16.248	99.410	8.925
F$_2$(2.75)	24.613	58.338	19.931	128.52	10.211

near-Hartree–Fock-limit wave functions available for several systems it does seem worthwhile to test Ruedenberg's energy expressions for them. We find a range of values for α: 1.26 (BeH$^+$), 1.45 (BH), 1.54 (N$_2$), 1.56 (CO), 1.66 (F$_2$), and 1.67 (HF). The value for BeH$^+$ is especially disappointing; we note that Fraga found poorer values for atomic ions than for neutral atoms.

Mucci and March[36] have examined the absolute error, $\Delta = E - \frac{1}{2}E_s$, and have related this to the chemical potential and subsequently to electronegativity. Kemister and March[37] have suggested that the change in Δ on going from free atoms to a molecule containing them might reflect the nature of the chemical binding. We have a number of serious reservations.

The most obvious failing of SCF wave functions is that they generally dissociate to incorrect fragments: ionic products are common. Connected with this question is that of avoided crossings. As an example, we shall consider the two lowest $^2\Sigma^+$ states of BeH which arise out of the avoided crossing[38] of diabatic curves dissociating to the Be(^1S) + H(^2S) and Be(^3P) + H(^2S) limits. The "crossing" occurs close to R_e for the upper state; the minima are at ~ 2.5 bohr for $X\,^2\Sigma^+$ and ~ 4.3 bohr for $C\,^2\Sigma^+$. In any test of the change in Δ on bond formation, it is not at all clear whether we should use Be(^1S) or Be(^3P) values. We have also mentioned and shall reconsider later, the possibility that the dissociation energy might be directly connected to kinetic energy gradients in the SCF wave function at R_e. For a molecule such as BeH, this would appear to be very unlikely given the switching between diabatic curves beyond R_e. A more extreme example is the $^1\Sigma^+$ potential of KI dissociating to K(^2S) + I($^2P_{1/2}$); there is a crossing at large R and until ~ 100 Å the molecule is ionic. It is difficult to believe that the SCF wave function contains much information about the binding energy or that the change in Δ from R_e to ∞ is meaningful. A further problem is that many molecules dissociate to open-shell fragments. There are many Fock operators in common use for open-shell systems yielding different sets of orbital energies. It is not at all clear which of these should be used in Eq. (3.7) or to evaluate Δ.

We now turn to gradient expansions for the kinetic energy [Eqs. (2.7)–(2.11)]. As can be seen from Table II, $T_0 + T_2 + T_4$ is an overestimate of the Hartree–Fock value T_{HF} for all of the molecules we have studied. Similar results were found in work on atomic systems[14]; the T_4 values seem to be too large by a factor of 2 or more. Of the alternative functionals that have been proposed, the least successful were those based on Eq. (2.11). The forms for $\tau(N)$ suggested by Acharya[20] and by Gasquez and Robles[21] gave rms errors of $5\frac{1}{2}\%$ and $3\frac{1}{2}\%$, respectively. Much better results were obtained using two other schemes which take some account of T_4. For the molecules for which $T_0 + T_2$ is an underestimate, the modified functional[15] $T_m = T_0 + T_2 + \gamma T_4$ (with $\gamma \sim \frac{1}{2}$ from a least-squares fit) gave an rms error of 0.3%; note that there is a typographical error in Ref. 15 in that we referred to $T_0 + T_2$ as an overestimate. Comparable accuracy (0.3%) was achieved using the local asymptotic summation suggested by Pearson and Gordon[24]; the values of T_L from this approach are listed in Table

TABLE II. Values in atomic units of T_0, T_2, T_4, T, T_m, and T_L; $T = T_0 + T_2 + T_4$. $T_m = T_0 + T_2 + \gamma T_4$ (from a least squares percentage fit, $\gamma \sim \frac{1}{2}$). T_L are the values obtained using the local asymptotic method (Ref. 24) with the expansion truncated locally at the smallest term. All molecules are in their ground electronic states and bond lengths are as in Table I. The Hartree–Fock kinetic energies T_{HF} are also given.

Molecule	T_0	T_2	T_4	T	T_m	T_L	T_{HF}
BeH$^+$	13.60	1.57	0.34	15.51		15.27	15.040
BeH	13.63	1.56	0.31	15.50		15.34	15.151
BH	22.63	2.50	0.49	25.62		25.40	25.120
BH$^+$	22.23	2.48	0.50	25.21	24.94	24.98	24.784
CH	34.35	3.59	0.70	38.64	38.26	38.33	38.254
NH	49.35	4.89	0.95	55.19	54.68	54.77	54.916
OH	68.13	6.40	1.25	75.78	75.11	75.22	75.380
LiO	74.41	7.14	1.39	82.94	82.19	82.34	82.294
HF	91.11	8.12	1.58	100.8	99.96	100.1	99.921
N$_2$	98.39	9.61	1.87	109.9	108.9	109.0	108.61
CO	102.3	9.82	1.91	114.0	113.0	113.2	112.66
O$_2$	135.0	12.7	2.46	150.2	148.8	149.1	149.29
F$_2$	180.5	16.2	3.12	199.8	198.1	198.6	198.51

II together with those of T_m. Pearson and Gordon have also suggested scaling the smallest correction by a factor of 1/2. We found that this gave better results for the lightest hydrides but tended to underestimate T_{HF} for the heavier ones.

There are two important caveats. First, the differences between the Hartree–Fock kinetic energies and those from the most successful gradient expansions are on the order of tenths of hartree. Second, approaches which involve least-squares fitting detract from the utility of the gradient expansion approach and its ability to predict. Using data for narrower ranges of N and Z, thereby reducing even further the applicability of the expansions, γ could be refitted to further reduce the errors in T_m. Similarly it would be possible to fit a scale factor for the smallest correction in T_L. However, these simple gradient expansions do not achieve chemical accuracy. Functionals based on partitioning of the charge density[16] might be more successful (see also Sec. VI). In addition, the gradient expansions are likely to have smaller percentage errors for heavier systems: in the asymptotic limit $Z \to \infty$, T_0 becomes the exact nonrelativistic kinetic energy functional.[39]

Our approach has revealed interesting trends and empirical relationships; we are particularly impressed by the success of Eq. (2.2) for open- and closed-shell molecules. It is important to examine whether similar features hold at the much finer level of an individual molecule. This is the subject of the next section.

IV. RESULTS FOR OH USING MCSCF WAVE FUNCTIONS

The failing of SCF wave functions, that they generally dissociate to incorrect fragments as R is increased, can be remedied by adding additional configurations whose weights are optimized simultaneously with the orbitals in an MCSCF procedure. The orbitals which diagonalize the one-particle density matrix [the natural orbitals $\phi_i(\mathbf{r})$] may then be used, for example, to construct large configuration interaction (CI) calculations.

Here we employ the same valence MCSCF expansion, consisting of just ten configurations, as was used previously[40] to compute the radial dependence of the spin-orbit coupling $A(R)$. The $X\,{}^2\Pi_i$ ground state of the OH radical is interesting to us because its wave function demonstrates a large and rapid change between about 3–5 bohr. For example, $A(R)$ changes from a molecular value to an atomic value in an almost stepwise fashion. This change is preceded by a minimum close to 2.8 bohr.

The momentum space density was calculated via the expansion of the density matrix $\rho(\mathbf{p},\mathbf{p}')$ according to

$$\rho(\mathbf{p},\mathbf{p}') = \sum_i n_i\,\phi_i^*(\mathbf{p})\phi_i(\mathbf{p}'),\qquad(4.1)$$

where the ϕ_i ($\mathbf{p}$) are the Fourier transforms of the ϕ_i ($\mathbf{r}$) and the n_i are the natural orbital occupation numbers. The expectation value of a one-electron property Ω in the momentum representation is then simply

$$\langle\Omega\rangle = \sum_i n_i\langle\phi_i(\mathbf{p})|\widehat{\Omega}|\phi_i(\mathbf{p})\rangle.\qquad(4.2)$$

Values of $\langle p^m\rangle$ and I_m were evaluated for $m = 2, 1, -1$ over a wide range of internuclear distance using the MCSCF wave functions and these are plotted in Figs. 3 (a)–3(c). The point marked A is very close to R_e (1.8342 bohr); we also mark 3.0 bohr as B and 6.0 bohr as C to clarify the direction in which R increases. For comparison, $\langle p^m\rangle$ and I_m were also computed using restricted Hartree–Fock SCF wave functions at three distances. These are marked by triangles: A', B', and C' are 1.8342, 3.0, and 6.0 bohr, respectively. The differences we find between the SCF and MCSCF values of $\langle p^m\rangle$ at R_e are consistent with previous work.[41] For positive m, the MCSCF values are slightly larger than those from SCF wave functions; the reverse is true for $m = -1$. The differences between the SCF and MCSCF values at larger R are merely a reflection of the inadequacies

of the SCF wave function; any similar systematic study of local density functionals based on SCF electron densities would be meaningless.

All of the plots of $\langle p^m\rangle$ vs I_m for OH are linear around R_e (point A). There is a clear minimum in the plot for $m = 2$ at larger R corresponding to the minimum in the kinetic energy at R_c (a little before point B). There is a marked change in curvature before R_c is reached. The curve for $R > R_c$ is not superimposed on that for $R < R_c$; if it were, then the plot would have an appearance similar to that of a bandhead. Similar remarks apply to the plot of $\langle p\rangle$ vs I_1 except that the minimum is less marked and occurs at slightly larger R. The plot of $\langle p^{-1}\rangle$ vs I_{-1} is linear over a wider range of R near R_e; there is a marked change near R_c. We are tempted to suggest that the shapes of these plots, and in particular the changes in curvature, are reflections of the changes in the wave function. Only by investigating more molecules with different bonding characteristics will be able to confirm or deny this suggestion. We shall return to this question in Sec. V.

We now briefly assess the applicability of the gradient expansions for the kinetic energy. In view of the comments in Sec. III, we have not attempted an exhaustive study. Fitting the data between 1.6 and 2.1 bohr to a functional of the form $T_m = T_0 + T_2 + \gamma T_4$ gives $\gamma \sim 0.7$ and typical errors of about 0.02 hartree. For comparison, the binding energy from the lowest vibrational level is $D_0 \sim 0.16$ hartree. Attempts to fit functionals over more extended ranges of R resulted in much larger errors. The inclusion of points at large R, where the kinetic energy increases with R, gave particularly poor results. We recognize again the restrictions of the fitting approach, particularly over such a narrow range of R, and we shall not consider further this aspect of gradient expansions. The first correction term T_2 is interesting for reasons we shall now outline and a study of its radial variation is very worthwhile.
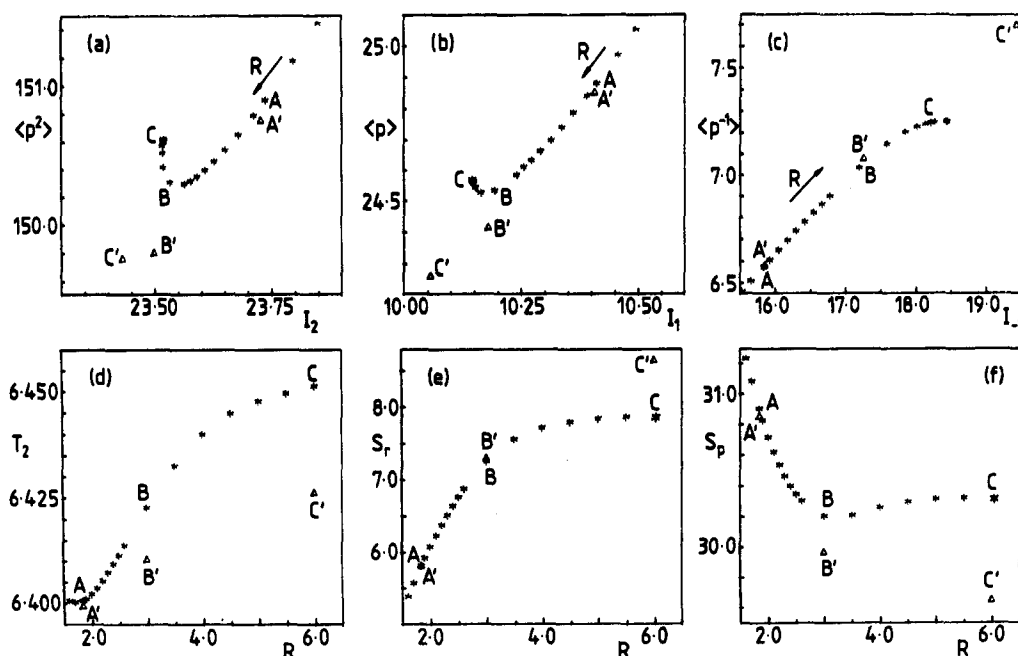

FIG. 3. Local density functionals for the $X\,{}^2\Pi_i$ state of OH ($R_e \simeq 1.8$ bohr) using MCSCF (*) and SCF (△) wave functions. All the quantities are expressed in atomic units and are as defined in the text. The individual frames are (a) $\langle p^2\rangle$ vs I_2, (b) $\langle p\rangle$ vs I_1, (c) $\langle p^{-1}\rangle$ vs I_{-1}, (d) the first gradient correction T_2 to the kinetic energy, (e) the position space entropy S_r, (f) the momentum space entropy S_p. The direction of increasing internuclear distance R is marked for the first three frames. The R values in these can be identified by reference to one of the other frames since the MCSCF calculations were performed for one set of distances. The bond lengths marked are 1.8342 bohr (A,A'), 3.0 bohr (B,B'), and 6.0 bohr (C,C').

According to Teller's theorem,[42] there can be no molecular binding in a local density functional theory that neglects electron density gradients. This is the basis of the qualitative argument of Mucci and March[25] that D/N should increase linearly with T_2. With this in mind, we have investigated the variation of T_2 with R, which we plot in Fig. 3(d). Starting at R_e, T_2 increases with R and the binding energy decreases. This appears to be in keeping with our previous findings[15] for a series of molecules but is totally opposed to the proposals of Ref. 25. We have also examined the variation of binding energy with T_2 and have concluded, at least for OH, that there is no meaningful dependence of one on the other.

Lastly, we plot in Figs. 3(e) and 3(f) the information entropies defined by Eqs. (2.12)–(2.13). Without comparison with similar plots for other molecules there is little that can be said at this stage about the variation of these quantities with R. We thus defer the discussion until Sec. V.

The proportionality between $\langle p^m \rangle$ and I_m near R_e is encouraging. In addition, the possible reflection of the chemistry of bond formation in the shapes of the corresponding plots suggest that it would be worthwhile to consider them for a range of molecules which display different bonding characteristics.

V. RESULTS FOR LIGHT HYDRIDES USING SPIN-COUPLED WAVE FUNCTIONS

We now present tests of the various functionals for a variety of diatomic systems, namely BH^+, LiH, and LiH^+. The spin-coupled method,[43] which we use to describe these molecules may be unfamiliar and so we start with a brief description of the salient features important to the current work. For reviews and summaries of recent results see Ref. 44.

Spin-coupled valence-bond theory[45] provides visuality without sacrificing accuracy. For small systems, the shortcomings of classical valence bond (VB) theory are overcome while an accuracy comparable to the highest quality MCSCF-CI calculations is obtained. Spin-coupled valence-bond computations are performed in two stages. First, the spin-coupled wave function is obtained from a rapidly convergent iterative procedure[43] and virtual orbitals are calculated.[45] These are used to construct small numbers of additional structures in the VB stage. Although it is based on just one spatial configuration, the spin-coupled wave function dissociates correctly, gives an accurate value for R_e, and typically provides more than 75% of the binding energy. This simple wave function is more than adequate for our present purposes since it displays all the qualitative features of the larger VB calculations.

The spin-coupled wave function for an N-electron system may be written[43]

$$\psi_{SM} = \sum_k C_{Sk} \sqrt{N!} \mathbf{A}\{\phi_1(1)\phi_2(2)\cdots\phi_N(N)\,\Theta^N_{S,M;k}\}$$

$$\equiv \{\phi_1\phi_2\cdots\phi_N\} . \qquad (5.1)$$

The orbitals $\phi_\mu(i) \equiv \phi_\mu(\mathbf{r}_i)$ are a set of N distinct, singly occupied nonorthogonal spatial orbitals. The $\Theta^N_{S,M;k}$ are a set of orthogonal spin functions in which the spins of the N electrons are coupled to give resultant S and projection M. In the current work we use the standard genealogical (branching diagram) functions and the index k labels the specific mode of coupling. A is the idempotent N-electron antisymmetrizing operator. The spatial orbitals are expanded as linear combinations of m basis functions

$$\phi_\mu = \sum_{p=1}^m C_{\mu p} X_p \qquad (5.2)$$

and the coefficients $C_{\mu p}$ are optimized simultaneously with the spin-coupled coefficients C_{Sk}. In the present work we use the same UET basis set as above.

The one-electron component of the energy is given by

$$E_1 = \frac{1}{\Delta} \sum_{\mu,\nu=1}^N D(\mu,\nu) \langle \phi_\mu(\mathbf{r}) | \hat{h} | \phi_\nu(\mathbf{r}) \rangle \qquad (5.3)$$

in which $\hat{h}$ is the one-electron Hamiltonian, $D(\mu,\nu)$ is a one-electron density matrix, and Δ is the normalization integral. These last two are connected by[43]

$$\Delta = \sum_{\nu=1}^N D(\mu,\nu) \langle \phi_\mu | \phi_\nu \rangle . \qquad (5.4)$$

Similar relationships exist linking higher-order density matrices all the way up to the N-electron density matrix; this is a list of purely group theoretical quantities and is the starting point for the spin-coupled method.

The position and momentum densities were calculated directly from $D(\mu,\nu)$. For example

$$\rho(\mathbf{p}) = \frac{1}{\Delta} \sum_{\mu,\nu=1}^N D(\mu,\nu)\,\phi_\mu^*(\mathbf{p})\phi_\nu(\mathbf{p}) , \qquad (5.5)$$

where the $\phi_i(\mathbf{p})$, which are the Fourier transforms of $\phi_i(\mathbf{r})$, are nonorthogonal.

We now consider each molecule in turn.

A. BH^+

The variation of $\langle p^m \rangle$ with I_m for the $X\,^2\Sigma^+$ ground state of BH^+ is shown in Figs. 4(a)–4(c). The points A, B, and C marked on the plots are at 2.3501, 3.3, and 6.0 bohr, respectively. The behavior is similar to that observed for OH in that the proportionality between $\langle p^m \rangle$ and I_m holds for approximately 1 bohr around $R_e \simeq 2.3$ bohr. The plot for $m = 2$ has a pronounced minimum near $R_c \simeq 3.3$ bohr. If the gradients before and after the minimum in the kinetic energy are a reflection of the electronic configuration, then Fig. 4(a) suggests a dramatic change between two of these. This manifests itself in MCSCF-CI calculations as a change from $1\sigma^2 2\sigma^2 3\sigma^1$ to $1\sigma^2 3\sigma^2 2\sigma^1$ near R_C: note that this is reflected in the character of the orbitals rather than in the CI coefficients.[46] The $m = +1, -1$ plots are roughly linear for $R < R_C$ but show marked curvature for $R > R_C$.

Extensive spin-coupled VB calculations of the asymptotic portions of the potential surfaces for the reaction of $B^+(^1S,^3P)$ with H_2 have been reported recently.[47] The various low-lying states of BH and of BH^+ are given by suitable cuts through these surfaces. The net spin of the two core electrons on boron was fixed to a singlet so that only two spin couplings remained active. As shown in Fig. 4 of Ref. 47, there is a rapid crossover of these spin-coupling coefficients over a fairly narrow range of R. This displays the essential
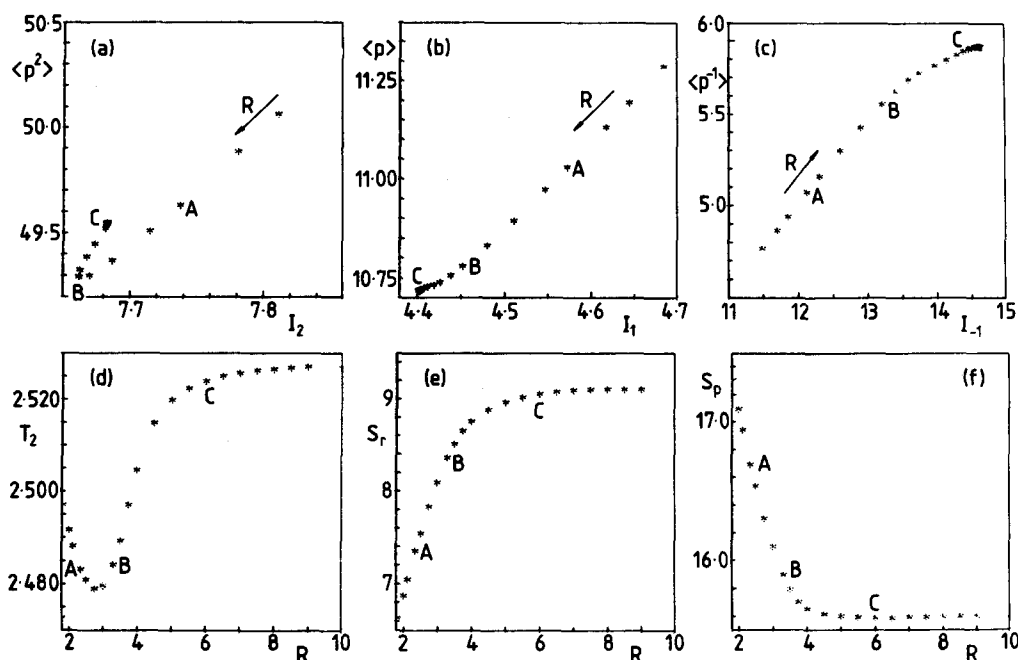
FIG. 4. Local density functionals for the $X^2\Sigma^+$ state of BH^+ ($R_e \simeq 2.3$ bohr) using spin-coupled wave functions. The individual frames are as listed for Fig. 3. There is a one-to-one correspondence between the points in each plot as to the bond lengths used. The R values marked are 2.3501 bohr (A), 3.3 bohr (B), and 6.0 bohr (C).

chemistry of the formation of the chemical bond and represents the change from an atomic situation to a molecular one. The distance R_c appears to correspond directly to the change in spin coupling; indeed, the point at which the two coefficients are equal is very close to R_c.

We have examined electron density contour maps for each orbital of BH^+ at several values of R. The effects of bond formation are obviously visible both in position space and in momentum space. The momentum space distributions for the valence electrons change from spherical to ovaloid on bond formation and the molecular geometry can affect the momentum density significantly by introducing a series of nodal planes. We shall publish separately an account of these studies.

For distances greater than R_e, the radial dependence of T_2 is similar to that for OH. There is different behavior at smaller R, as shown in Fig. 4(d). For BH^+ ($R_e \sim 2.3$ bohr) there is a minimum near $R = 2.75$, whereas for OH ($R_e \sim 1.8$ bohr) there is only an exceptionally shallow minimum near 1.7 bohr. Beyond the minima, T_2 increases with R so that T_2 is larger in the separated atoms than at R_e. Considering the molecule (or pair of atoms) as a whole, the electron density would be expected to be more homogeneous at R_e than for larger nuclear separations. Although T_2 is a crude average of the gradients, it thus appears reasonable that it should increase with R. Superimposed on this general trend of T_2 increasing with R we see other features which we cannot yet rationalize.

Finally, as part of the suggested[27] systematic study of S_r and S_p we display in Figs. 4(e) and 4(f) the variation of these two quantities with R. While detailed discussion of these is again deferred until we have more of them to compare, an obvious initial comment is that the plots for OH and for BH^+ do not seem to reflect the changes in character of the wave functions over certain ranges of R.

B. LiH

The $X^1\Sigma^+$ state of LiH has a binding energy of ~ 0.09 hartree and a bond length $R_e = 3.015$ bohr. The ground state of LiH is substantially different to that of BH^+ in that the spatial wave function at R_e can be described as mostly ionic, whereas at large R it is essentially covalent. The effect of this change in spatial configuration is particularly clear in the dipole moment function $\mu(R)$ which increases from R_e until it reaches a maximum value near 5 bohr—it then decreases rapidly towards zero. A spin-coupled VB study of $\mu(R)$ has recently been reported[48] demonstrating the rapid convergence of this approach. For four electrons coupled to a singlet there are just two spin-coupling coefficients. $|C_{02}|^2$, corresponding to singlet coupling of the Li core orbitals, is very close to unity for all R and $|C_{01}|^2$ never exceeds 10^{-5}. Denoting the wave function $\{\sigma_1\sigma_2\sigma_3\sigma_4\}$ as in Eq. (5.1) then σ_1 and σ_2 are the Li core orbitals, which change very little on bonding. σ_4 is mostly a $H(1s)$ orbital which distorts remarkably little. The binding energy arises largely due to the exchange interaction between σ_4 and σ_3; this last is a $Li(2s)$ orbital at very large R but acquires $H(1s)$ character fairly gradually at shorter R contributing to the large variation in $\mu(R)$ and leading to substantial ionic character near R_e. Unlike OH and BH^+, there is essentially no change in the spin coupling.

The gradual change in character just mentioned would appear to be reflected in the plots of $\langle p^m \rangle$ against I_m as shown in Figs. 5(a)–5(c). The points marked are A = 3.0, B = 5.0, and C = 7.0 bohr. Whereas for OH and BH^+ the proportionality between these pairs of quantities holds for about 1 bohr around R_e, this is not the case for LiH and all the plots are gently curved in this region. The behavior of these plots at larger R is rather more similar to that of OH. The minimum in the $m = 2$ curve, and thus the minimum in
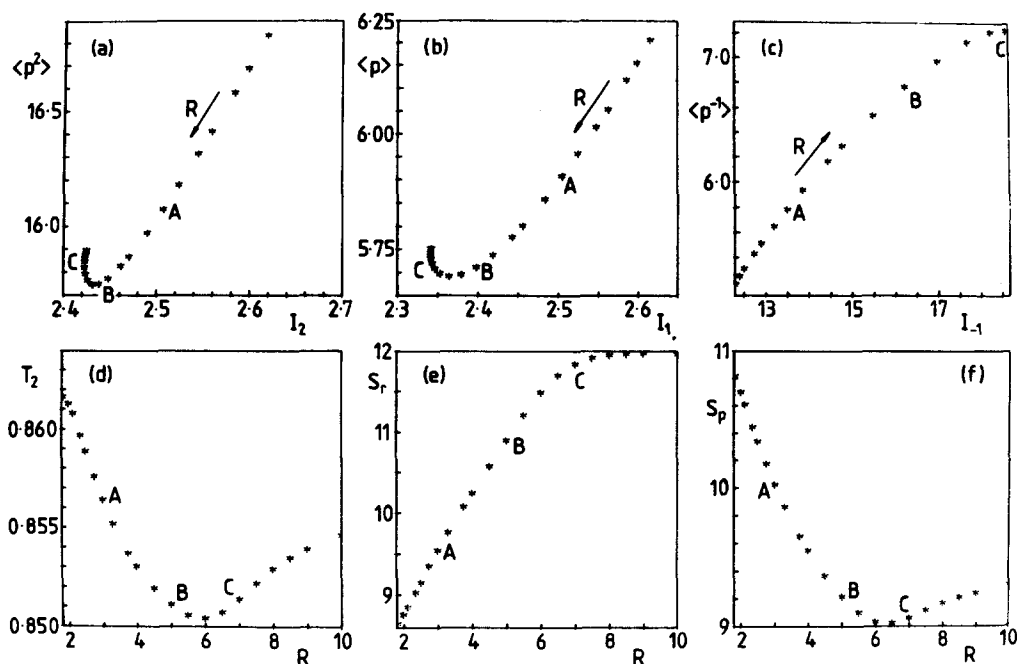
FIG. 5. Local density functionals for the $X\,^1\Sigma^+$ state of LiH ($R_e \simeq 3.0$ bohr) using spin-coupled wave functions. The individual frames are as listed for Fig. 3. Again there is a one-to-one correspondence between the points in each plot as to the R values. The bond lengths marked are 3.0 bohr (A), 5.0 bohr (B), and 7.0 bohr (C).

the kinetic energy, occurs between 5.0–5.5 bohr, where $\mu(R)$ has started to decrease.

The variation of T_2 with R is shown in Fig. 5(d). As for BH$^+$ there is a minimum in T_2 which occurs close to the minimum in the kinetic energy. This occurs at a much larger value of R than for BH$^+$. The value of T_2 at 30 bohr has not quite attained the value at R_e; this is the first case we have found where T_2 is (slightly) larger at R_e than for the separated atoms. However, it is not at all clear whether T_2 in the molecule should be compared with values for the neutral atoms or with the values for Li$^+$ and H$^-$ ions (cf. the discussion in Sec. III). Moreover, T_2 does increase with R beyond about 5.5 bohr so that smaller gradients correspond to larger binding in this region.

LiH is the last of the chemically bound molecules studied in this work and it is now opportune to examine the information entropies S_r and S_p to see how they reflect the different bonding characteristics. The radial variation of these two quantities is shown in Figs. 5(e) and 5(f) [cf. Figs. 3(e) and 3(f) for OH and Figs. 4(e) and 4(f) for BH$^+$]. Using a qualitative argument based on the uncertainty principle Gadre has suggested[27] that expansion in r space, with a corresponding increase in S_r, leads to contraction in p space and thus a reduction in S_p. In keeping with this suggestion we find a general increase in S_r and a general decrease in S_p as the atoms are separated. Whereas for OH and LiH there are minima in S_p which occur at the minima in the kinetic energy, there are no corresponding maxima in S_r. Neither S_r nor S_p seems to reflect the change in character of the wave functions. We find this disappointing and find nothing to commend these entropies. However, it might be interesting to see whether the techniques of entropy maximization (subject to a series of constraints) developed by Gadre[26] can yield expectation values or can predict Compton profiles to chemical accuracy.

C. LiH$^+$

Spin-coupled studies of the $X\,^2\Sigma^+$ state of LiH$^+$ suggests that this state is only very weakly bound: $D_e \cong 0.005$ hartree (~ 1060 cm^{-1}) and $R_e \cong 4.2$ bohr. The well depth is increased by only about 20 cm^{-1} at the VB stage indicating that the binding arises largely from induction with only a small contribution from dispersion. There is no marked change in the spin-coupling coefficients or in the spatial wave function as R is decreased. It is rather perverse that the linear relationships between $\langle p^m \rangle$ and I_m [Figs. 6(a)–6(c)] are obeyed best for this system which has the least chemical binding of our series of molecules. The points marked on the plots are 2.3501 bohr (A), 5.5 bohr (B), and 8.0 bohr (C). The curve for $m = 2$ now does fold back on itself after the minimum in $\langle p^2 \rangle$, giving the appearance of a bandhead. Similar behavior is seen for $\langle p \rangle$. It is tempting to link this behavior with the absence of any significant change in bonding character with R.

For completeness, the variation of T_2 with R and of the entropies with R are shown in Figs. 6(d)–6(f). There is little that can be added to our previous remarks.

VI. RESULTS FOR ATOMS IN MOLECULES

The linear relationship between $\langle p^2 \rangle$ and I_2 for the open-shell system of LiH$^+$ is remarkable. Throughout this work we have not found it necessary to make any distinction between open-shell and closed-shell molecules, and it is worthwhile to present further tests of Eq. (2.2) for $m = +2$. We have used the zero-flux surface partitioning scheme[49] to divide the total electron density $\rho(r)$ into atomic fragments. This scheme gives rigorously and uniquely defined fragments which satisfy an equation of motion and an atomic virial theorem, both of which mirror exactly those for the total system.
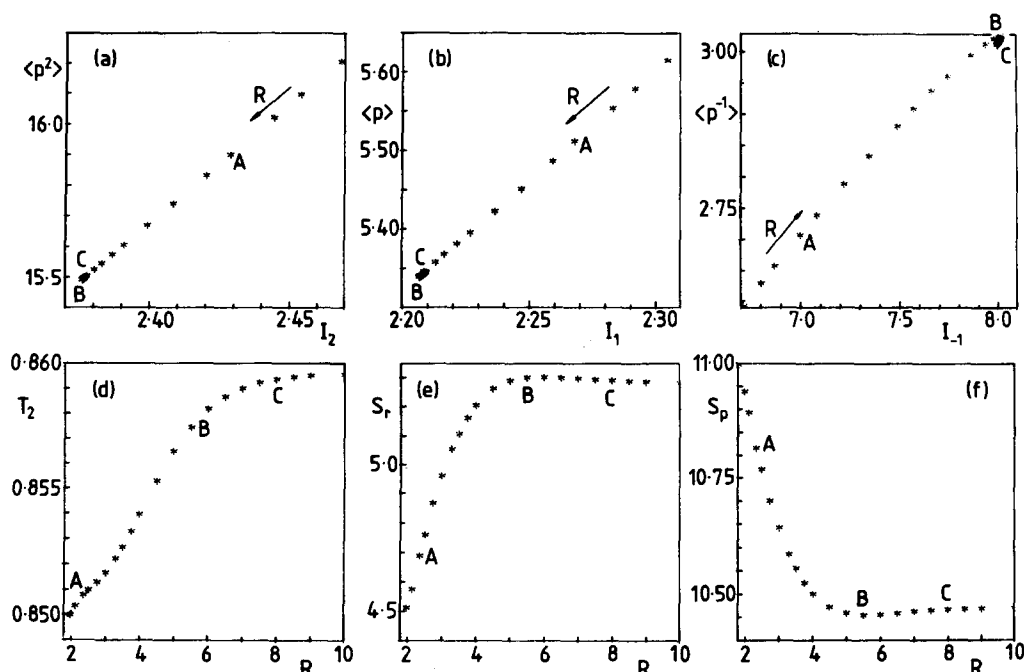
FIG. 6. Local density functionals for the very weakly bound $X\,^2\Sigma^+$ state of LiH$^+$ ($R_e \simeq 4.2$ bohr) using spin-coupled wave functions. The individual frames are identified in the caption for Fig. 3. There is a one-to-one correspondence between the points in each plot as to the internuclear distances. The bond lengths marked are 2.3501 bohr (A), 5.5 bohr (B), and 8.0 bohr (C).

We have considered hydrogen and oxygen atoms in CO_2, H_2O, H_2CO, and CH_3OH at equilibrium geometry. Note that we might expect the corrections embodied in spin-density functional theory to be especially important for hydrogen atoms. The basis sets and some of the wave functions are the same as used by one of us previously.[50] Values of $\langle p^2 \rangle$ and I_2 were obtained by suitable integration over the atomic fragments and are collected in Table III.

For the hydrogen atoms the ratio of $\langle p^2 \rangle$ to I_2 varies between approximately 6 and 8.5. Nonetheless, it is clear from a plot of these data that a reasonable linear relationship does indeed hold giving an rms error of less than 5×10^{-3}. However, such a least-squares fit has a nonzero intercept. For each of the oxygen atoms, the ratio of $\langle p^2 \rangle$ to I_2 is 6.30 which is very similar to the numerical slope (6.33) for the series of open- and closed-shell molecules considered in Ref. 29. Equation (2.2) appears to hold rather well for $m = 2$ for

atoms in molecules, although the predicted gradient (5.74) is inaccurate.

VII. SUMMARY AND CONCLUSIONS

Inspired by the extensive literature on density functional theory we have tested functionals of the electron density that relate to molecular properties. Our main motive was the examination of the accuracy of these functionals for light molecules. In particular we were interested to ascertain whether any of these functionals were capable of high accuracy over a wide range of nuclear separations.

For a range of light diatomics, each near its equilibrium bond length, we found that the functional $K[\rho]$ [Eq. (2.4)] was quite successful (errors $< 1\%$), whereas the functional $J[\rho]$ [Eq. (2.6)] was a notable failure (errors $> 6\%$). We were particularly interested in moments of momentum because these are related to information obtained in Compton and $(e, 2e)$ scattering experiments. The functionals for $\langle p^2 \rangle$ and $\langle p \rangle$ [Eq. (2.2)] were quite reliable ($\sim\frac{1}{2}\%$). The functional for $\langle p^{-1} \rangle$ was poorer ($\sim 2\frac{1}{2}\%$). Using the functionals derived for closed-shell molecules we found no larger errors for open-shell molecules than for closed shells. This was somewhat unexpected. In this sort of application it does not seem necessary to incorporate any explicit account of spin polarization as in spin-density functional theory.

Gradient corrections to the kinetic energy [Eqs. (2.7)–(2.10)] were considered. For the light molecules studied, two approaches were notably much more successful than the others. The simplest of these was the modified functional[15] $T = T_0 + T_2 + \frac{1}{2}T_4$. Similar accuracy was obtained using the local asymptotic modification suggested by Pearson and Gordon,[24] in which the expansion is truncated locally according to the relative magnitude of the terms. During the course of this work we have also investigated the gradient corrections to the mean momentum $\langle p \rangle$ (see also Ref. 15)

TABLE III. Values in atomic units of $\langle p^2 \rangle$ and I_2 for hydrogen and oxygen atoms in molecules. Further details are given in the text. For methanol, H_h is the hydroxyl hydrogen and H_t and H_g are the *trans* and two *gauche* hydrogen atoms of the methyl group. Least-squares fits were performed to a linear relationship for each element and give the "fitted $\langle p^2 \rangle$" values.

	I_2	$\langle p^2 \rangle$	$\langle p^2 \rangle / I_2$	Fitted $\langle p^2 \rangle$
H_2O	0.0837	0.7182	8.58	0.719
$CH_3OH(H_h)$	0.0848	0.7278	8.58	0.725
$CH_3OH (H_t)$	0.2080	1.2780	6.14	1.284
$CH_3OH (H_g)$	0.2186	1.3298	6.08	1.332
H_2CO	0.2452	1.4598	5.95	1.453
O atoms				
H_2O	23.92	150.62	6.30	150.65
CH_3OH	23.94	150.86	6.30	150.80
H_2CO	23.96	150.92	6.30	150.95
CO_2	24.01	151.32	6.30	151.32

and we have found similar behavior to the gradient expansion for T. It is possible that the various functionals we have mentioned might be more accurate for heavier systems, but we have not examined this. Much of the previous work has indeed been on light systems. Other motives for concentrating on lighter molecules include the Gordon–Kim electron gas model and the study of light molecules on surfaces.

We also investigated the functionals for moments of momentum over a range of internuclear separation for a range of molecules. The functionals are generally accurate over a range of R around R_e which would be sampled by the lowest few vibrational levels. The deviations can be attributed to changes in wave function for the molecules studied. The differences between the molecules are most striking in the $\langle p^2 \rangle$ vs I_2 plots. It would be very interesting to investigate a molecule for which there is an avoided crossing between the ground state and an excited state of the same symmetry. In the case of the covalent/ionic crossing in LiF, Werner and Meyer[51] found that the matrix which diagonalizes the dipole matrix was very similar to that which effects the adiabatic to p-diabatic transformation. We wonder whether the shape of the plot of $\langle p^2 \rangle$ and I_2 for, say, the $X\,^2\Sigma^+$ and $C\,^2\Sigma^+$ of BeH could be used in a similar fashion. Based on preliminary investigations, we see no reason why this functional should not be useful for excited states.

We examined the radial dependence of the first correction term T_2 in the gradient expansion of the kinetic energy, since it has been suggested[25] that an increase in T_2 accompanies molecular binding. We found this not to be the case and we believe that the qualitative argument is spurious. In addition, the R dependence of the entropies S_r and S_p was not very interesting and showed no systematic variations from molecule to molecule. Perhaps we are expecting too much from such crude averages.

Since completing our studies we have become aware of the elegant work of Chelikowsky[52] who showed that the cohesive energies of simple metals can be accurately predicted solely from atomic kinetic energy terms. He argued from Teller's theorem that if both the atom and the metal were true Thomas–Fermi systems (no electron density gradients) then there would be no cohesion. In his model, it is the increased homogeneity of the kinetic energy of the valence electrons that leads to binding. Although inhomogeneous kinetic energy terms are not negligible in molecules, our findings for $T_2(R)$ are consistent with this work on metals.

Finally we turn to the question of spin-density functional theory. As we have mentioned we did not find it necessary for any of the functionals to make any distinction between closed and open shells. It is widely accepted that the formulas we used do not apply to open-shell systems and that the modifications in spin-density functional theory are necessary. However, by using a spin-dependent electron density, we appear to have obviated the need for any explicit account of spin polarization. All of the expressions seem to have a wider range of applicability than their underlying assumptions suggest; more general derivations of the same expressions ought to be possible. The results for atoms in molecules are probably not surprising since it can be argued that they are closed-shell systems in a general sense. A gener-

alized idea of closed shells also arises in the effective medium approach to adsorption on metal surfaces.[53] We wonder whether it would be appropriate throughout density functional theory to employ a formalism based on spin-dependent electron densities, when available, rather than to attempt an interpolation between zero and full spin polarization which is at best dubious.

VIII. FINAL REMARKS

Local density approximations have been successful in a wide range of applications including solid state physics, surface science, and intermolecular forces. We do not wish to criticize exchange–correlation potentials or nonlocal approximations since we have not considered these in this work. It is necessary to make a few pertinent comments regarding the application of local density approximations to "global trends" across wide ranges of atoms or molecules. We seriously question the merits of such work, the "success" of which has often been a matter of scale; the percentage errors are often excessive for chemical applications. We feel that the focus of attention should move from these gross trends to the investigation of functionals that can achieve chemical accuracy. The Hohenberg–Kohn rainbow is well worth following to the pot of gold at its end. We expect that any progress along this road using this approach to density functional theory will be better aided by studies of individual molecules, or of small ranges of very similar molecules, than by studying extended series of atoms. We are referring not just to total energies but rather to chemically interesting properties such as multipole moments, ionization potentials, electron affinities, and spectroscopic constants. Even if they could not be used predictively, functionals that could be used convincingly to rationalize experimental data would make a valuable contribution.

[1] W. Kohn and P. Vashishta, in *Theory of the Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York 1983).
[2] A. R. Williams, and U. von Barth, in *Theory of the Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).
[3] N. H. March, Theor. Chem. Spec. Per. Rep. **4**, 92 (1981).
[4] R. G. Parr, Annu. Rev. Phys. Chem. **34**, 631 (1983).
[5] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).
[6] N. L. Allan and N. H. March, Int. J. Quantum Chem. Symp. **17**, 227 (1983).
[7] B. G. Williams, *Compton Scattering* (McGraw–Hill, New York 1977); M. J. Cooper, Rep. Prog. Phys. **48**, 415 (1985).
[8] J. C. Slater, Phys. Rev. **81**, 385 (1951); J. C. Slater and J. H. Wood, Int. J. Quantum Chem. Symp. **4**, 3 (1971).
[9] R. K. Pathak and S. R. Gadre, J. Chem. Phys. **74**, 5929 (1981); **77**, 1073 (1982).

[10] S. R. Gadre, L. J. Bartolotti, and N. C. Handy, J. Chem. Phys. **72**, 1034 (1980).

[11] S. R. Gadre and R. D. Bendale, J. Chem. Phys. **78**, 996 (1983).

[12] L. J. Bartolotti and R. G. Parr, J. Chem. Phys. **75**, 4553 (1981).

[13] G. I. Plindov and I. K. Dmitrieva, J. Phys. Lett. (Paris) **45**, 419 (1984), and references therein; C. H. Hodges, Can. J. Phys. **51**, 1428 (1973).

[14] C. C. Shih, Phys. Rev. A **14**, 919 (1976); W. Wang, R. G. Parr, D. R. Murphy, and G. Henderson, Chem. Phys. Lett. **43**, 409 (1976); D. R. Murphy and W. Wang, J. Chem. Phys. **72**, 429 (1980); C. C. Shih, *ibid.* **72**, 1404 (1980); W. Wang, *ibid.* **73**, 416 (1980); C. C. Shih, D. R. Murphy, and W. Wang, *ibid.* **73**, 1340 (1980).

[15] N. L. Allan, C. G. West, D. L. Cooper, P. J. Grout, and N. H. March, J. Chem. Phys. **83**, 4562 (1985).

[16] Y. Tal and R. F. W. Bader, Int. J. Quantum Chem. Symp. **12**, 153, (1978).

[17] J. A. Alonso and L. A. Girifalco, Chem. Phys. Lett. **53**, 190 (1978); D. R. Murphy and R. G. Parr, *ibid.* **60**, 377 (1979); Y. A. Borisov and V. V. Surikov, J. Struct. Chem. USSR **22**, 280 (1981).

[18] M. L. Zorita, J. A. Alonso, and L. C. Balbas, Int. J. Quantum Chem. **27**, 393 (1985).

[19] D. R. Murphy, Phys. Rev. A **24**, 1682 (1981).

[20] P. K. Acharya, L. J. Bartolotti, S. B. Sears, and R. G. Parr, Proc. Natl. Acad. Sci. U. S. A. **77**, 6978 (1980).

[21] J. L. Gazquez and J. Robles, J. Chem. Phys. **76**, 1467 (1982); P. K. Acharya, *ibid.* **78**, 2101 (1983).

[22] C. F. von Weizäcker, Z. Phys. **96**, 431 (1935).

[23] Y. S. Kim and R. G. Gordon, J. Chem. Phys. **56**, 3122 (1972).

[24] E. W. Pearson and R. G. Gordon, J. Chem. Phys. **82**, 881 (1985).

[25] J. F. Mucci and N. H. March, J. Chem. Phys. **78**, 6187 (1983).

[26] S. R. Gadre and S. B. Sears, J. Chem. Phys. **71**, 432 (1979); **75**, 4625 (1980); T. Koga and M. Morita, *ibid.* **79**, 1933 (1983); S. R. Gadre, R. D. Bendale, and S. P. Gejii, Chem. Phys. Lett. **117**, 138 (1985); S. R. Gadre and R. D. Bendale, Int. J. Quantum Chem. **28**, 311 (1985).

[27] S. R. Gadre, Phys. Rev. A **30**, 620 (1984); S. R. Gadre, S. B. Sears, S. J. Chakravorty, and R. D. Bendale, *ibid.* **32**, 2602, (1985).

[28] Y. S. Kim and R. G. Gordon, J. Chem. Phys. **60**, 1842 (1974).

[29] N. L. Allan, D. L. Cooper, C. G. West, P. J. Grout, and N. H. March, J. Chem. Phys. **83**, 239 (1985).

[30] D. L. Cooper and S. Wilson, J. Chem. Phys. **76**, 6008 (1982).

[31] G. L. Oliver and J. P. Perdew, Phys. Rev. A **20**, 387 (1979).

[32] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[33] K. Ruedenberg, J. Chem. Phys. **66**, 375 (1977).

[34] S. Fraga, Theor. Chim. Acta **2**, 406 (1964). See also: E. B. Priestly and S. Fraga, Can. J. Phys. **44**, 1933 (1966).

[35] P. Politzer, J. Chem. Phys. **64**, 4239 (1976).

[36] J. F. Mucci and N. H. March, J. Chem. Phys. **71**, 1495 (1979).

[37] G. Kemister and N. H. March (to be published).

[38] See: D. L. Cooper, J. Chem. Phys. **80**, 1961 (1984); R. Colin, C. Dreze, and M. Steinhauer, Can. J. Phys. **61**, 641 (1983).

[39] E. H. Lieb and B. Simon, Phys. Rev. Lett. **31**, 681 (1973).

[40] D. L. Cooper, Mol. Phys. **54**, 439 (1985).

[41] See for example: V. H. Smith, Jr., G. H. F. Diercksen, and W. P. Kraemer, Phys. Lett. A **54**, 319 (1975); R. A. Tawil and S. R. Langhoff, J. Chem. Phys. **63**, 1572 (1975); V. H. Smith Jr., A. J. Thakkar, W. H. Henneker, J. W. Liu, B. Liu, and R. E. Brown, *ibid.* **67**, 3676 (1977); **73**, 4150 (1980); K. E. Banyard and J. C. Moore, J. Phys. B **10**, 2781 (1977).

[42] E. Teller, Rev. Mod. Phys. **34**, 627 (1962).

[43] J. Gerratt, Adv. At. Mol. Phys. **7**, 141 (1971).

[44] D. L. Cooper, J. Gerratt, and M. Raimondi, Faraday Symp. Chem. Soc. **19**, 149, (1984); J. Gerratt, M. Raimondi, and D. L. Cooper, Adv. Chem. Phys. (to be published); Comput. Phys. Rep. (to be published).

[45] J. Gerratt and M. Raimondi, Proc. R. Soc. London Ser. A **371**, 525 (1980).

[46] R. Klein, P. Rosmus, and H. J. Werner, J. Chem. Phys. **77**, 3559, (1982).

[47] D. L. Cooper, J. Gerratt, and M. Raimondi, Chem. Phys. Lett. (in press).

[48] D. L. Cooper, J. Gerratt, and M. Raimondi, Chem. Phys. Lett. **118**, 6 (1985).

[49] R. W. F. Bader and T. T. Nguyen-Dang, Adv. Quantum Chem. **14**, 63 (1981); R. W. F. Bader, T. T. Nguyen-Dang, and Y. Tal, Rep. Prog. Phys. **14**, 893 (1981); S. Srebrenik, R. W. F. Bader, and T. T. Nguyen-Dang, J. Chem. Phys. **68**, 3667 (1978).

[50] D. L. Cooper and N. C. J. Stutchbury, Chem. Phys. Lett. **120**, 167 (1985).

[51] H. J. Werner and W. Meyer, J. Chem. Phys. **74**, 5802 (1981).

[52] J. R. Chelikowsky, Phys. Rev. Lett. **47**, 387 (1981).

[53] B. Chakraborty, S. Holloway, and J. K. Nørskov, Sur. Sci. **152**, 660 (1985), and references therein. See also pp. 299–302 of Ref. 2.