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Investigation of the spin-density functional method for calculating spin-magnetic-moment densities*

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The spin-density functional formalism is investigated with the objective of producing practical methods for calculating the spin (magnetic moment) density, $m(\vec{r})$, of atoms, molecules, and metals. Calculations are performed for the atoms Li, Na, K, N, P, Mn, and As in their spherically symmetric ground states using two approximations for the exchange-correlation functional: (i) the exact treatment of exchange with a local approximation for correlation (referred to as "SUHF-C"), (ii) the local spin-density (LSD) approximation for both exchange and correlation. The "SUHF-C" values of $m(0)$ for Li, Na, K, N, P, Mn, and As are 108, 99, 91, 200, -30, 108, and 93% of experiment, respectively. For Li, Na, and K the LSD approximation yields 98, 109, and 106%, respectively. Away from the nucleus, in all the cases studied, the LSD and "SUHF-C" results for $m(\vec{r})$ are in close agreement. We conclude that for systems where there is a large direct contribution the LSD approximation should give better than 90% accuracy, even at the origin. The results using "SUHF-C" suggest that it has the capability of yielding accurate values of $m(\vec{r})$ for atoms and molecules.

I. INTRODUCTION

The electron spin (magnetic moment) density $m(\vec{r})$ enters a number of phenomena that are of current interest: (i) magnetic form factors as determined from neutron scattering experiments,[1,2] which are related to the Fourier transform of $m(\vec{r})$, i.e., $m(\vec{q})$; (ii) hyperfine interactions[3,4] in atoms, molecules, and metals (Knight shifts), i.e., dipole-dipole and Fermi contact terms. The latter is especially difficult to calculate accurately since it depends on the value of the spin density at the nucleus, $m(0)$, where $m(\vec{r})$ has a cusp behavior which tends to amplify any absolute errors introduced by approximations in the theory.

There have been a number of calculations[5-10] of $m(0)$ for atoms using many-body perturbation theory (MBPT). Although quite accurate, this procedure involves a great deal of computation even for relatively small atomic systems and it is unlikely that it can be extended to more complicated systems in the near future. In contrast, the spin-unrestricted Hartree-Fock (SUHF) method[11] is relatively simple to apply. However, after a number of initial successes in calculating $m(0)$ (for a recent review see Ref. 12) it has fallen out of favor as a procedure for obtaining reliable estimates of this quantity. In particular the precise numerical solutions of the SUHF equations by Bagus *et al.*[13] emphasized its inadequacies. On the other hand, it is clear from the spin-density functional (SDF) formalism[14-17] that exact values of the spin density can, in principle, be obtained from the self-consistent solutions of a set of single-particle equations which contain the effects of exchange and correlation (XC) through the appropriate functional of the electron number and spin densities $E_{xc}[n, m]$ $(=E_{xc}[n_+, n_-])$.

The central problem in the SDF approach is that the exact $E_{xc}[n_+, n_-]$ is unknown. Most efforts at practical applications of the SDF formalism have concentrated on making the local spin-density (LSD)[16,18] approximation for $E_{xc}[n_+, n_-]$. Although this approximation has proved to be quite useful in a number of applications,[19-21] we shall see that it is not adequate for all situations.

One purpose of this work is to establish the analog of the SUHF procedure from the viewpoint of the SDF formalism[22] as an accurate method for calculating $m(\vec{r})$ in atoms and molecules. Since, in general, exchange is more important than correlation in such systems, we treat exchange exactly and correlation in the LSD approximation. Our results indicate that this procedure has the capacity to produce accurate values of $m(\vec{r})$ for $\vec{r}$ in the vicinity of the origin, the region presenting the greatest difficulty.

We wish to emphasize that the Slater-determinant formed from the wave functions of the single-particle SDF equations is an auxiliary quantity and is not related (nor an approximation) to the true ground-state wave function. These single-particle wave functions should only be used to calculate the electron number and spin densities. Thus the problem of S^2 not being a good quantum number in the usual SUHF theory[23,24] does not exist in the SDF formalism. Since the single-particle SDF and SUHF equations are identical when correlation is neglected and only differ in interpretation, we shall refer to this approach as the "SUHF" method. When correlation is included by the LSD approximation the method shall be referred to as "SUHF-C". (We prefer to use the quotes to distinguish between SDF and Hartree-Fock theory so as to avoid new nomenclature.)

We also evaluate the accuracy of the LSD approximation for spin-density calculations with the intent of applying it to spin-polarized metals where the comparable importance of exchange and correlation dictates that they should be treated on the same level of approximation. We shall see that the LSD scheme works quite well for $m(r)$ where $r>0$ but is inadequate for $m(0)$ in situations where $m(0)$ arises solely from XC core polarization.

Attention in this work will be focused on the neutral atoms Li, Na, K, N, P, Mn, and As, having spherically symmetric ground states of nonzero total spin. In the tables we present values for $m(0)$ in various approximations for $E_{xc}[n_+,n_-]$ and compare these results with the Slater approximation, MBPT calculations, and with experiment. Graphs of $m(r)$ for Li, Na, K, and Mn are also presented for some of these approximations. Section II summarizes the theory, and Sec. III contains a discussion of the results and conclusions.

II. THEORY

Consider a nonrelativistic inhomogeneous atomic system of N electrons in the presence of the nuclear potential $v(\vec{r})=-Z/r$ (Z is the atomic number) and a constant magnetic field B in the z direction which couples only to the spins. In the absence of spin-orbit interactions the density functional theory of Hohenberg, Kohn, and Sham,[22,25] as elaborated by von Barth and Hedin,[16] leads to a self-consistent set of single-particle Schrödinger equations (atomic units) for the ground state:

$$\{-\tfrac{1}{2}\nabla^2 - Z/r + v_H(\vec{r}) + v_{xc}^{(\sigma)}[\vec{r};n_+,n_-] - \sigma\mu_e B\}\psi_{i\sigma}(\vec{r}) = \epsilon_{i\sigma}\psi_{i\sigma}(\vec{r}), \qquad (2.1)$$

$$n_\sigma(\vec{r}) = \sum_i |\psi_{i\sigma}(\vec{r})|^2\theta(\mu-\epsilon_{i\sigma}), \qquad (2.2)$$

$$n(\vec{r}) = n_+(\vec{r}) + n_-(\vec{r}),$$

$$v_H(\vec{r}) = \int d\vec{r}'\,\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}, \qquad (2.3a)$$

$$v_{xc}^{(\sigma)}[\vec{r};n_+,n_-] = \frac{\delta E_{xc}[n_+,n_-]}{\delta n_\sigma(\vec{r})}, \qquad (2.3b)$$

where the quantity $n_\sigma(\vec{r})$, $\sigma=+/-$ is the number density for spin-up/down electrons, $n(\vec{r})$ is the total number density, and μ_e is the electron Bohr magneton. The chemical potential μ in (2.2) is determined by the constraint

$$N = \sum_{i\sigma}\theta(\mu-\epsilon_{i\sigma}),$$

where i denotes a complete set of quantum numbers excluding spin. A complete knowledge of the usual exchange-correlation energy functional $E_{xc}[n_+,n_-]$, and hence its functional derivative, would enable one in principle to solve Eqs. (2.1) to (2.3) iteratively for the exact ground-state number densities $n_\sigma(\vec{r})$, in terms of which the total spin density (or spin-magnetic-moment density in units of μ_e) is $m(\vec{r})=n_+(\vec{r})-n_-(\vec{r})$. Note that in the above $\epsilon_{i\sigma}$ and $\psi_{i\sigma}(\vec{r})$ are to be regarded as auxiliary quantities used to construct the necessary functionals.

The derivation of these equations was based upon the generalized Hohenberg-Kohn theorems which require that the ground state of the system be nondegenerate. For the spherically symmetric atoms that we will be considering, the presence of the magnetic field B ensures the fulfillment of this condition and at the same time fixes the total numbers N_+ and N_- of spin-up and spin-down electrons, respectively. Having applied the field and obtained Eqs. (2.1) to (2.3), we then can let B be infinitesimally small.

The functional $E_{xc}[n_+,n_-]$ is not known for a general system. The simplest approximation is the LSD,

$$E_{xc}^{loc}[n_+,n_-] = \int d\vec{r}\,n(\vec{r})\epsilon_{xc}(n_+(\vec{r}),n_-(\vec{r})), \qquad (2.4)$$

where $\epsilon_{xc}(n_+(\vec{r}),n_-(\vec{r}))$ is the exchange-correlation energy per particle at the position $\vec{r}$ in a homogeneous electron gas characterized by constant spin number densities equal to the $n_+(\vec{r})$ and $n_-(\vec{r})$ of the inhomogeneous gas. Hence the exchange-correlation potential of (2.3b) becomes

$$v_{xc}^{(\sigma)}[\vec{r};n_+,n_-] = \frac{\partial}{\partial n_\sigma(\vec{r})}[n(\vec{r})\epsilon_{xc}(n_+(\vec{r}),n_-(\vec{r}))]; \qquad (2.5)$$

the energy $\epsilon_{xc}(n_+(\vec{r}),n_-(\vec{r}))$ can be written

$$\epsilon_{xc} = \epsilon_x + \epsilon_c, \qquad (2.6)$$

where ϵ_x and ϵ_c are exchange and correlation contributions, respectively. The exchange term is the usual Hartree-Fock result for a spin-polarized Fermi system

$$\epsilon_x = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\frac{1}{n(\vec{r})}[n_+(\vec{r})^{4/3}+n_-(\vec{r})^{4/3}]. \qquad (2.7)$$

Since the energy ϵ_c will be a function of $n_+(\vec{r})$, $n_-(\vec{r})$, and $n(\vec{r})$, we can write

$$v_{\mathrm{xc}}^{(\sigma)}(\vec{r}) = v_x^{(\sigma)}(\vec{r}) + v_c^{(\sigma)}(\vec{r}), \tag{2.8}$$

where

$$v_x^{(\sigma)}(\vec{r}) = -2(3/4\pi)^{1/3}[n_\sigma(\vec{r})]^{1/3}, \tag{2.9}$$

$$v_c^{(\sigma)}(\vec{r}) = \epsilon_c(r_s, x_\sigma) + (1 - x_\sigma)\frac{\partial \epsilon_c(r_s, x_\sigma)}{\partial x_\sigma} - \frac{r_s}{3}\frac{\partial \epsilon_c(r_s, x_\sigma)}{\partial r_s}, \tag{2.10}$$

with $x_\sigma(\vec{r}) = n_\sigma(\vec{r})/n(\vec{r})$ being the fractional spin-σ electron density at $\vec{r}$ and $r_s(\vec{r}) = [3/4\pi n(\vec{r})]^{1/3}$. Note that for convenience we have transformed the dependence of ϵ_c on $n_+(\vec{r})$, $n_-(\vec{r})$, and $n(\vec{r})$ to the variables r_s and x_σ. All future references to Eq. (2.1) will imply the use of the potential defined in (2.8).

In the above, both exchange and correlation effects have been treated approximately. We may expect better results for atoms and molecules, however, if we make use of an alternate procedure which includes exchange effects exactly. Following Kohn and Sham[22] we take, *a priori*,

$$E_{\mathrm{xc}}[n_+, n_-] = E_x[n_+, n_-] + \int d\vec{r}\, n(\vec{r})\epsilon_c(n_+(\vec{r}), n_-(\vec{r})), \tag{2.11}$$

where $E_x[n_+, n_-]$ is the Hartree-Fock exchange energy of a system with number densities $n_\sigma(\vec{r})$ and where we have made the LSD approximation for the correlation energy. Then using the previous notation, we get

$$\left(-\frac{\nabla^2}{2} - \frac{Z}{r} + v_H(\vec{r}) + v_c^{(\sigma)}[\vec{r}; n_+, n_-] - \sigma\mu_e B\right)\psi_{i\sigma}(\vec{r}) - \int d\vec{r}\,'\frac{\rho(\vec{r}, \vec{r}\,')}{|r - r'|}\psi_{i\sigma}(\vec{r}\,') = \epsilon_{i\sigma}\psi_{i\sigma}(\vec{r}), \tag{2.12}$$

where

$$\rho(\vec{r}, \vec{r}\,') = \sum_{i\sigma}\psi_{i\sigma}(\vec{r})\psi_{i\sigma}^*(\vec{r}\,') \tag{2.13}$$

and $v_c^{(\sigma)}[\vec{r}; n_+, n_-]$ is given by (2.10).

Equations (2.12) have the form of the Hartree-Fock equations, but they have two advantages. Correlation is included explicitly (albeit in a local approximation, but in principle could be improved[26,27]) which should improve the results, and the auxiliary wave functions $\psi_{i\sigma}(\vec{r})$ and their associated Slater determinant are not related to the true ground-state wave function. Because of this latter property, such a determinant does not have to be an eigenfunction of the operators representing constants of motion. Specifically, we do not face the problem, which arises in the conventional SUHF method, of the Slater determinant failing to be an eigenfunction of the total electron spin angular momentum operator $\vec{S}^2$.[11] This explains why the SUHF method works so well in many cases in spite of this apparent drawback and why efforts to improve it by projecting out that part of the determinant which is not the appropriate eigenfunction of $\vec{S}^2$ have often led to worse results.[23,24] Equations (2.12) and (2.1) differ solely in their treatment of the exchange term. The exact nonlocal treatment in (2.12) removes whatever electron self-interactions are incorrectly present in the local exchange term of (2.1). Because of this nonlocality, an exact solution of (2.12) even for small-N systems is a nontrivial computational problem, yet a relatively simple one when compared with the computations required by the MBPT method. For the atomic systems under consideration the equations can be solved by assuming orbitals $\psi_{i\sigma}(\vec{r})$ of the form

$$\psi_{i\sigma}(\vec{r}) = (1/r)P(n_i l_i \sigma; r)Y_{l_i m_{li}}(\theta, \phi)\chi_\sigma \tag{2.14}$$

subject to the orthonormality requirement

$$\int_0^\infty dr\, P(nl\sigma; r)P(n'l\sigma; r) = \delta_{nn'}. \tag{2.15}$$

where $Y_{lm}(\theta, \phi)$ is a spherical harmonic and χ_σ is a spin eigenfunction. The quantum numbers n, l, and m_l have their usual meaning. For the spherically symmetric atoms that we will be considering, the separation of the spatial wave function into a product of a radial part, independent of the magnetic quantum number m_l, and an angular part is an exact procedure and will reduce (2.1) and (2.12) to sets of equations for the radial functions $P(nl\sigma; r)$. As a result, for each (nl) shell there will be only one radial equation for each spin. If the atom has unequal numbers of spin-up and spin-down electrons, the presence of the spin-dependent potentials in these equations will yield different radial functions for electrons which differ only in their spin quantum numbers. Hence the spin densities at the nucleus from closed shells of such atoms will generally be nonzero. An often used approximation in which the P's are taken to be independent of spin leads to a "restricted Hartree-Fock" (RHF) set of equations with the undesirable feature of yielding no contribution to spin densities from closed shells for any atoms.

In order to include correlation effects in (2.1) and (2.12), we need to know the $\epsilon_c(r_s, x_\sigma)$ in (2.10). Using the random phase approximation, von Barth and Hedin[16] computed a correlation energy $\epsilon_c^{\mathrm{VH}}(r_s, x_\sigma)$ for total densities in the metallic range $r_s = 1$ to $r_s = 6$ and for several values of x_σ. For atomic systems we require a knowledge of $\epsilon_c(r_s, x_\sigma)$ outside this density range. Our procedure will be to use $\epsilon_c^{\mathrm{VH}}(r_s, x_\sigma)$ between $r_s = 1$ and $r_s = 6$ and then, keeping the von Barth–Hedin x_σ dependence at

TABLE I. Spin densities (a.u.) at the nucleus for Li, Na, and K atoms.

	$1s$	$2s$	$3s$	$4s$	Total
Li(^2S)					
LSD-X	−0.0092	0.2108			0.2106
LSD-XC	−0.0006	0.2278			0.2272
"SUHF"	0.0609	0.1638			0.2247
"SUHF-C"	0.0720	0.1772			0.2492
Slater	−0.0142	0.2760			0.2618
MBPT[a]					0.230
Experiment[b]					0.2313
Na(^2S)					
LSD-X	0.0197	−0.0405	0.7540		0.7332
LSD-XC	0.0069	−0.0311	0.8414		0.8172
"SUHF"	0.0463	0.0746	0.5265		0.6474
"SUHF-C"	0.0480	0.1004	0.5900		0.7384
Slater	0.0416	−0.0806	1.0220		0.9830
MBPT[c]					0.7255
Experiment[d]					0.7492
K(^2S)					
LSD-X	0.0139	−0.0013	−0.0475	1.0327	0.9978
LSD-XC	0.0136	−0.0011	−0.0290	1.1860	1.1695
"SUHF"	0.0342	0.0409	0.0875	0.6908	0.8534
"SUHF-C"	0.0368	0.0504	0.1211	0.8032	1.0115
Slater	0.0298	−0.0021	−0.0949	1.4309	1.3637
Experiment[b]					1.1068

[a] Reference 7.

[b] Reference 36.

[c] Reference 9.

[d] References 35 and 36.

these end points, to extrapolate for small and large r_s values according to the r_s dependence given by Carr and Maradudin[28] and Carr *et al.*,[29] respectively, for the case $x_\sigma = \frac{1}{2}$.

III. DISCUSSION AND CONCLUSIONS

We have considered the atoms Li, Na, K, N, P, Mn, and As in their ground-state configurations. The multiplets of lowest energy are ^2S for the alkalis Li, Na, and K; ^4S for N, P, and As; and ^6S for Mn, and because they correspond to atomic states of zero total orbital angular momentum the electron distribution for each atom is spherically symmetric. These multiplets are twofold, fourfold, and sixfold degenerate, respectively, because of the possible orientations of the total spin. Application of an external magnetic field $\vec{B}$, which couples only to the spins, lifts these degeneracies and gives a unique ground state which corresponds to $S_z = \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$, respectively, for the above systems. Thus if $E_{xc}[n, m]$ were known exactly, the $n(\vec{r})$ and $m(\vec{r})$ calculated from the SDF method correspond to the ground state with these values for S_z and the corresponding values of $\vec{S}^2$.

In each case we have computed the self-consistent spin-density $m(\vec{r})$ within various approximations for $E_{xc}[n_+, n_-]$. At the nucleus the same quantity has been evaluated using MBPT for most of these atoms. In the absence of relativistic corrections this quantity may be obtained from hyperfine measurements. However, it has recently been shown by Andriessen *et al.*[10] that relativistic corrections are important (~20%) for atoms with relatively low atomic number (e.g., Mn). At present there is no equivalent experimental data away from the nucleus. In Tables I and II we present the results for $m(0)$.

Before discussing our results in detail, we wish to emphasize that due to the auxiliary nature of the one-electron spin orbitals only the total spin and number densities are meaningful quantities. In the presentation of our data the decomposition of the spin densities into contributions from various atomic shells is for illustrative purposes only, and should not be interpreted as assigning any physical significance to them.

Solutions of (2.1) were obtained using an appropriate modification of the Wood-Boring self-consistent-field program.[30] Equations (2.12) were solved using a modified SUHF program based on a multiconfiguration Hartree-Fock program due to Froese Fischer.[31]

TABLE II. Spin densities (a.u.) at the nucleus for N, P, As, and Mn atoms.

	1*s*	2*s*	3*s*	4*s*	Total
N(^4S)					
LSD-X	−0.6668	0.6149			−0.0519
LSD-XC	−0.5734	0.5379			−0.0355
"SUHF"	−0.7432	0.9307			0.1875
"SUHF-C"	−0.6633	0.8577			0.1944
Slater	−1.1350	1.0692			−0.0658
MBPT [a]					0.0975
Experiment [b]					0.0971
P(^4S)					
LSD-X	−0.1818	−0.0466	−0.0528		−0.2812
LSD-XC	−0.1751	−0.0145	0.0225		−0.1671
"SUHF"	−0.3548	0.2347	−0.0193		−0.1394
"SUHF-C"	−0.3504	0.2737	0.0497		−0.0270
Slater	−0.3145	−0.0952	0.0328		−0.3769
MBPT [c]					0.0826
Experiment [d]					0.0913
As(^4S)					
LSD-X	−0.1184	0.0380	−0.0965	−0.8205	−0.9974
LSD-XC	−0.1186	0.0320	−0.0581	−0.4862	−0.6309
"SUHF"	−0.2681	0.0329	0.2812	−0.6429	−0.5969
"SUHF-C"	−0.2697	0.0289	0.3594	−0.3596	−0.2410
Slater	−0.2124	0.0815	−0.2051	−1.1244	−1.4604
Experiment [e]					−0.2595
Mn(^6S)					
LSD-X	−0.0457	−1.8767	0.6959	1.5178	0.2913
LSD-XC	−0.0511	−1.6978	0.7838	1.0731	0.1080
"SUHF"	−0.0318	−2.6769	1.3222	1.1486	−0.2379
"SUHF-C"	−0.0465	−2.5127	1.3879	0.8161	−0.3552
Slater	−0.0748	−3.1755	1.4299	2.1602	0.3398
MBPT [f]					−0.412
Experiment [g]					−0.3285

[a] Reference 5.
[b] Reference 37.
[c] Reference 8.
[d] References 34 and 38.
[e] References 38 and 39.
[f] Reference 10.
[g] Reference 39.

Each of the alkali metals Li, Na, and K has a single valence *s* electron outside closed shells which polarizes the core electrons via a spin-dependent potential. From Table I we see that the local spin-density approximation with and without correlation (denoted by LSD-XC and LSD-X respectively) yields about 90% accuracy for the contact spin density. Inclusion of correlation gives improvement for Li and K but not for Na. We also observe that the dominant contribution (about 95%) comes from the unpaired *s* electron. Using "SUHF-C" we obtained pronounced improvement over "SUHF" for Na and K, in particular "SUHF-C" gives 99% and 91% of the experimental values in comparison to 86% and 71% for "SUHF", respectively. If the relativistic corrections on SUHF found by Desclaux[32] (1% and 5% increases for Na and K respectively) are assumed to apply here then the agreement with experiment would be further improved. The excellent agreement between "SUHF-C" and MBPT for Li and Na at $\vec{r}=0$ where the absolute error in $m(\vec{r})$ due to the LSD approximation for $E_c[n_+,n_-]$ is largest because of the cusp[33] in the *s*-state wave functions suggests that "SUHF-C" gives very reliable values for $m(\vec{r})$ ($\vec{r}\neq 0$) for Li, Na, and K (Figs. 1, 2, and 3). Hence the "SUHF-C" and LSD-XC spin densities differ most in the region near the nucleus. Beyond the outermost minimum the agreement is quite good.

Also shown are the results of using the local density approximation for exchange and correlation (LD-XC) in which one assumes $E_{xc}[n_+,n_-]=E_{xc}[n]$, and the results for the Slater approximation which is LSD-X with the v_x of (2.9) multiplied by $\frac{3}{2}$. In their overall ability to reproduce the "SUHF-C"

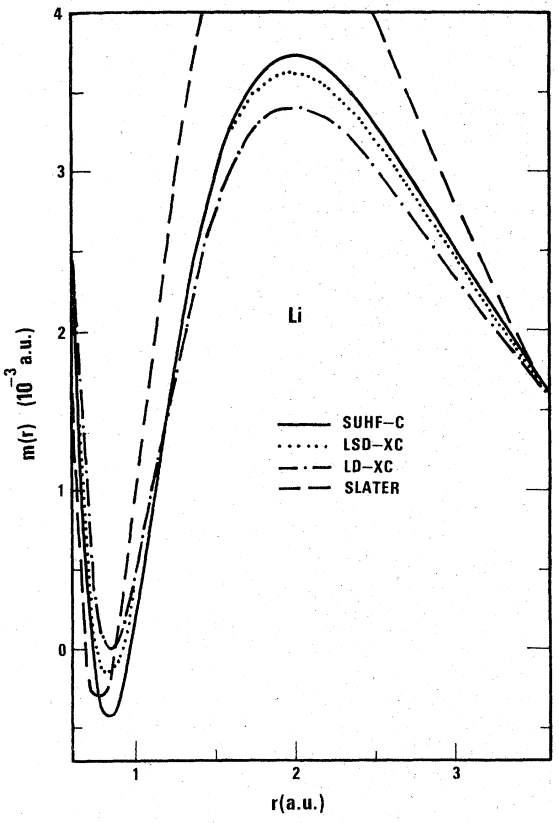

FIG. 1. Li-atom spin densities.

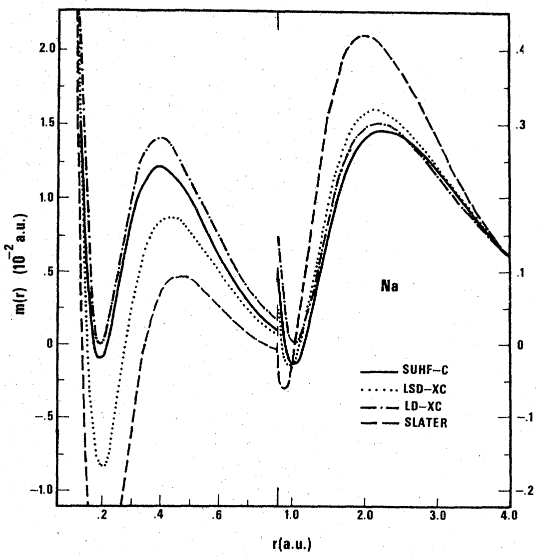

FIG. 2. Na-atom spin densities.

spin densities the LD-XC and LSD-XC approximations are comparable. A notable difference, however, is the inability of LD-XC to reproduce the negative minima which are characteristic of the "SUHF", "SUHF-C," and LSD curves. The Slater approximation is significantly worse than the others.

N, P, and As are examples of atoms which have an imbalance of spin due to three parallel-spin *p* electrons in the same open shell outside a closed-shell core. The Mn atom has an open 3*d* shell containing five parallel-spin electrons. Table II summarizes the results obtained for $m(0)$ for these cases. In both LSD and "SUHF" treatments the addition of correlation improves the resultant values of $m(0)$ considerably except for N where the already poor SUHF result is made slightly worse. P is especially noteworthy in that it was the first case where SUHF failed to give the correct sign of $m(0)$. We note that the inclusion of correlation by the LSD approximation is nearly sufficient to reverse the sign of $m(0)$ given by "SUHF." For Mn and As the "SUHF-C" values are in close agreement with the experimental values and the theoretical value in Mn.[10] These results suggest that a small improvement over the local approximation (possibly the next term in a gradient expansion) for $E_c[n_+, n_-]$ should be sufficient to calculate $m(\vec{r})$ accurately for atoms and molecules where relativistic effects are small. Generally the results from the local approximations differ considerably from the true values, suggesting that where "core polarization" is the sole contribution to $m(0)$ the LSD approximation is inadequate.

As an example of $m(\vec{r})$ away from the nucleus for such systems, we have plotted it for Mn in Fig. 4. The difficulty in calculating $m(\vec{r})$ in the vicinity of the nucleus can be appreciated by an

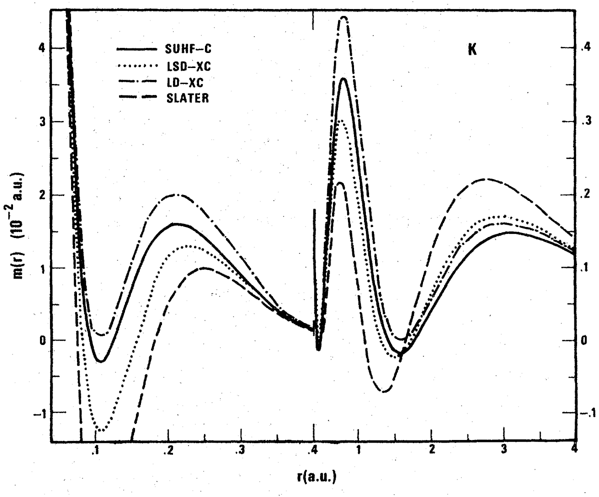

FIG. 3. K-atom spin densities.

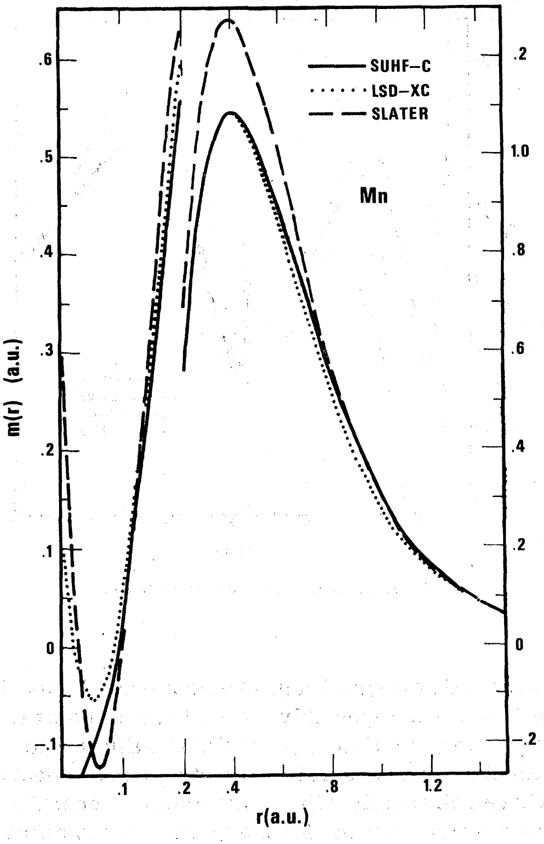

FIG. 4. Mn-atom spin densities.

examination of this figure. For $r \geq 0.05$ a.u. the LSD-XC parallels the "SUHF-C" results. However, for smaller values of r the "SUHF-C" result continues to be negative with a strong cusp behavior while the LSD-XC curve reverses direction and becomes positive as r approaches zero.

As mentioned previously, only the total spin densities have physical meaning. This fact is well illustrated in the tables where we note that, although individual "shell" contributions vary widely according to the approximation used for $E_{xc}[n_+,n_-]$, the totals are in relatively close agreement.

We conclude that for regions not too close to the nucleus the LSD-XC and "SUHF-C" approximations of the density functional theory yield magnetic moment distributions which agree quite well with one another. Taking the "SUHF-C" as a standard, this implies that the LSD-XC is a good procedure for calculating $m(\vec{r})$ over most of the volume for all systems. Thus, LSD-XC should give good results for the magnetic form factor. At the nucleus an accuracy of better than 90% should be expected from the LSD-XC for atoms having unpaired s electrons and relatively small core polarization effects. If the accuracies obtained here for $m(0)$ reflect how well one can expect to do in metallic systems where there is a large direct contribution, then the relative simplicity of the LSD approach makes meaningful calculations in such cases quite practical. In atomic and molecular systems where core-polarization dominates, our results suggest that the "SUHF-C" method presents a practical alternative to complicated MBPT calculations, although an improvement in the LSD approximation for $E_c[n_+,n_-]$ will be necessary if one insists on errors of less than ±0.1 a.u.

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[1] A. J. Freeman, B. N. Harmon, and T. J. Watson-Yang, Phys. Rev. Lett. 34, 281 (1975).

[2] W. C. Koehler and R. M. Moon, Phys. Rev. Lett. 36, 616 (1976).

[3] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. IIA.

[4] *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967).

[5] L. Goodman, G. Nöldeke, and H. Walther, Z. Phys. 167, 26 (1962).

[6] H. P. Kelly, Phys. Rev. 173, 142 (1968).

[7] E. S. Chang, Robert T. Pu, and T. P. Das, Phys. Rev. 174, 1 (1968).

[8] N. C. Dutta, C. Matsubara, R. T. Pu, and T. P. Das, Phys. Rev. 177, 33 (1969).

[9] T. Lee, N. C. Dutta, and T. P. Das, Phys. Rev. A 1, 995 (1970).

[10] J. Andriessen, S. N. Ray, Taesul Lee, T. P. Das, and D. Ikenberry, Phys. Rev. A 13, 1669 (1976).

[11] G. W. Pratt, Phys. Rev. 102, 1303 (1956).

[12] R. E. Watson and A. J. Freeman, in Ref. 4.

[13] P. S. Bagus, B. Liu, and H. F. Schaefer III, Phys. Rev. A 2, 555 (1970).

[14] J. C. Stoddart and N. H. March, Ann. Phys. (N.Y.) 64, 174 (1971).

[15] M. M. Pant and A. K. Rajagopal, Solid State Commun. 10, 1157 (1972).

[16] U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).

[17] A. K. Rajagopal and J. Callaway, Phys. Rev. B 7, 1912 (1973).

[18] O. Gunnarson, B. I. Lundqvist, and J. Wilkins, Phys. Rev. B 10, 1319 (1974).

[19] O. Gunnarson and B. I. Lundqvist, Phys. Rev. B 13,

4274 (1976).

[20] S. H. Vosko, J. P. Perdew, and A. H. MacDonald, Phys. Rev. Lett. 35, 1725 (1975).

[21] A. H. MacDonald and S. H. Vosko, J. Low Temp. Phys. 25, 27 (1976).

[22] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[23] W. Marshall, Proc. Phys. Soc. (London) 78, 113 (1961).

[24] V. Heine, Czech. J. Phys. B 13, 619 (1963); Phys. Rev. 107, 1002 (1957). In fact the SDF formalism explains the success of the SUHF method in calculating exchange polarization and answers the question raised on p. 628 in the former reference.

[25] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[26] S. Ma and K. A. Brueckner, Phys. Rev. 165, 18 (1968).

[27] D. J. W. Geldart and M. Rasolt, Phys. Rev. B 13, 1477 (1976).

[28] W. J. Carr and A. A. Maradudin, Phys. Rev. 133, A371 (1964).

[29] W. J. Carr, Jr., R. A. Coldwell-Horsfall, and A. E. Fein, Phys. Rev. 124, 747 (1961).

[30] J. H. Wood and M. Boring, Comp. Phys. Commun. 7, 73 (1974).

[31] C. Froese Fischer, Comp. Phys. Commun. 1, 151 (1969).

[32] J. P. Desclaux, Int. J. Quant. Chem. 6, 26 (1972).

[33] In the vicinity of $r=0$, $P_{ns\sigma}(r) \simeq C_{ns\sigma} r(1-Zr)$, $[P_{ns\sigma}(r)/r]^2_{r=0} = [P_{ns\sigma}(r_m)/r_m(1-Zr_m)]^2$, and $Zr_m \simeq 0.5$. Thus any absolute error in $P_{ns\sigma}(r_m)$ due to the LSD approximation is amplified at $r=0$.

[34] R. H. Lambert and F. M. Pipkin, Phys. Rev. 128, 198 (1962).

[35] M. Arditi and R. T. Carver, Phys. Rev. 109, 1012 (1958).

[36] P. Kusch and H. Taub, Phys. Rev. 75, 1477 (1949).

[37] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. 116, 87 (1959).

[38] J. M. Pendlebury and K. F. Smith, Proc. Phys. Soc. 84, 849 (1964).

[39] G. K. Woodgate and J. S. Martin, Proc. Phys. Soc. 70A, 485 (1957).