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The Fermi hole and the exchange parameter in X_α theory*

M. S. Gopinathan, M. A. Whitehead, and R. Bogdanović
Department of Chemistry, McGill University, Montréal, Québec, Canada, H3C 3G1

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In Slater's statistical exchange approximation, the Fermi hole is assumed to be spherical and uniform in density. This leads to an exchange potential that depends on an adjustable parameter α which is different for each atom. The value of this parameter is determined empirically for each atom, usually by equalizing the total energy of the atom calculated by the X_α method to that calculated by Hartree-Fock theory. In this paper an explicit dependence of α on the atomic number Z is developed by considering a linear variation of the Fermi-hole density, with the proper boundary values. This permits the calculation of theoretical α values for all atoms in the periodic table; these are reported. These theoretical α values reproduce the Z dependence of the empirical α values in all details. Further, it is shown that electrons of opposite spin should have different α values—a result that has important consequences in X_α calculations of magnetic properties and hyperfine interactions.

I. INTRODUCTION

Slater's statistical approximation to the exchange potential has proved[1] a practical and reasonably accurate method of obtaining approximate one-electron solutions to the Schrödinger equation for atoms, molecules, and solids. In the statistical approximation, the exchange potential is proportional to the $\frac{1}{3}$ power of the local charge density; the proportionality constant contains an adjustable parameter α which has to be determined for each atom. Several criteria are used to determine these α values.[2] The different α values for different atoms, and the possibility of determining these values in several ways, reduces the stature of the X_α theory to a parametric theory. Therefore it is desirable to enquire whether the proportionality constant in the exchange potential can be derived for each atom from purely theoretical considerations. Such an enquiry would lead to a greater understanding of electron exchange in atoms. This is the purpose of this paper.

The one-electron Schrödinger equation in the X_α method determining the spin orbitals u_i is easily derived.[1] The nonrelativistic Hamiltonian is

$$H=\sum_i f_i+\sum_{i<j} r_{ij}^{-1}\ , \tag{1}$$

where f_i is the one-electron operator consisting of the kinetic and potential energies in the field of the nucleus (or nuclei for molecules), and the second term is the coulomb interaction between pairs of electrons. The total electron density at a point $1, \rho(1)$, can be written as the sum of the density due to the spin-up electrons, $\rho_\uparrow(1)$, and that due to the spin-down electrons, $\rho_\downarrow(1)$. These charge densities are defined by

$$\rho_\uparrow(1)=\sum_i n_{i\uparrow}u_{i\uparrow}^*(1)u_{i\uparrow}(1), \tag{2}$$

and similarly for $\rho_\downarrow(1)$. Here $n_{i\uparrow}$ is the occupation number of the spin orbital $u_{i\uparrow}$. The expectation value of the total energy is then given by,

$$\begin{aligned}E=&\sum_i n_i\int u_i^*(1)f_1u_i(1)\,d\tau_1\\&+\frac{1}{2}\int\rho_\uparrow(1)\left(\int\rho(2)r_{12}^{-1}\,d\tau_2+U_\uparrow(1)\right)d\tau_1\\&+\frac{1}{2}\int\rho_\downarrow(1)\left(\int\rho(2)r_{12}^{-1}\,d\tau_2+U_\downarrow(1)\right)d\tau_1.\end{aligned} \tag{3}$$

The first term is the sum of the kinetic and nuclear-electron attraction energies. The second and third terms correspond to the electron-electron interaction energy written separately for spin-up, ↑, and spin-down, ↓, electrons. In each term, $\int\rho(2)r_{12}^{-1}\,d\tau_2$ represents the electron-electron Coulomb potential at point 1, and $U_\uparrow(1)$ is called the exchange potential acting on a spin-up electron at this point. $U_\uparrow(1)$ is a negative term which removes the self-interaction energy of electrons wrongly included in the Coulomb term, and also accounts for all exchange effects. Slater's statistical approximation sets $U_\uparrow(1)$ (in rydberg units) as

$$U_\uparrow(1)=-9\alpha[(3/4\pi)\rho_\uparrow(1)]^{1/3}, \tag{4}$$

with a similar expression for $U_\downarrow(1)$; α is the parameter discussed above. When this form of $U(1)$ is substituted into Eq. (3) and the variational principle applied to minimize E with respect to the u_i's, then the one-electron Schrödinger equations determining the $u_{i\uparrow}$'s are

$$[-\nabla_1^2+V_C(1)+V_{X\uparrow}(1)]u_{i\uparrow}(1)=\xi_{i\uparrow}u_{i\uparrow}(1), \tag{5}$$

with similar equations for $u_\downarrow$. Here $V_{X\uparrow}(1) = \frac{2}{3}U_\uparrow(1)$. These are the self-consistent-field equations of the X_α method, which can be solved iteratively.

Slater has shown[2] that the $\rho_\uparrow^{1/3}(1)$ dependence of the exchange potential $U_\uparrow(1)$, Eq. (4), is easily obtained by certain simplifying assumptions regarding the distribution of the exchange charge which produces the exchange potential $U_\uparrow(1)$.

The exchange potential being negative means that the exchange charge is removed from the total electron distribution as far as our reference electron is concerned; this is commonly called the Fermi hole. Here, we adopt the sign convention that the exchange charge is negative, and this corresponds to the Fermi-hole density being positive. It will be shown in Sec. II that the total amount of the exchange charge is -1 and that its value at the position of the electron in question, namely, point 1, is $-\rho_\uparrow(1)$. Slater assumes that the exchange charge is distributed with a uniform density equal to $-\rho_\uparrow(1)$ within a sphere centered at point 1. If the radius of this Fermi sphere is r_s, then from the requirement that the total exchange charge be -1,

$$\tfrac{4}{3}\pi r_s^3 \rho_\uparrow(1) = 1 . \tag{6}$$

The electrostatic potential at the center of the sphere due to this exchange charge is $-3/r_s$ (in rydberg units); thus

$$U_\uparrow(1) = -3[\tfrac{4}{3}\pi\rho_\uparrow(1)]^{1/3} . \tag{7}$$

Comparison with Eq. (4) gives a theoretical value of $\alpha = 0.87$. However, to empirically obtain the spin orbitals u_i's with Hartree-Fock accuracy requires different α values to be used for different atoms; these empirical values are considerably less than 0.87. Consequently, the α value in Eq. (4) has always been treated as an adjustable parameter. Schwarz[3] has determined the α values for atoms H through Rn, using the criterion that the total energy computed by the X_α method be equal to the Hartree-Fock energy for the atom. These values, denoted α_{HF}, show a smooth variation with atomic number Z. α_{HF} falls with atomic number, being around 0.78 for the two-electron atoms, decreasing to a range of 0.72–0.70 for the $3d$ transition elements and remaining almost constant thereafter at 0.69 (see Table II and Fig. 3). Further, the plot of α_{HF} vs Z (Fig. 3) shows distinct breaks in the slope as each new subshell is filled; the slope remains almost constant within a subshell.

Other criteria have been used[4,5] to determine α, but they lead to a rather random variation with Z and their use is not usually recommended.[6] Hence we do not consider such values in this paper.

Lindgren and Schwarz[7] have analyzed the variation of α with atomic number. They decomposed the total exchange potential in an atom into contributions from the various shells, as well as into self-interaction and interelectronic parts. These quantities were found to vary differently with atomic number and the variation in α_{HF} with Z represents an average of these individual variations. Such an analysis, accomplished by introducing more empirical α parameters, one for each shell, is only a detailed description of the Z dependence of α_{HF}.

What is required is a quantitative explanation of the Z dependence of α_{HF} and, if possible, a method of determining the α values nonempirically. It has been shown above that the simple form of the Fermi hole assumed by Slater does not lead to any Z dependence of α. Therefore we examine in detail the nature of the Fermi hole in atoms, and show that a simple modification of the exchange charge distribution in the Fermi hole from the distribution assumed by Slater leads to an exchange potential that depends explicitly on the number of electrons, making α Z dependent. This permits calculation of α values for all atoms (Sec. II). Such a calculation is done for all atoms in the periodic table and the results are compared with the α_{HF} values (Sec. III).

II. DENSITY FUNCTIONS, FERMI HOLE, AND EXCHANGE PARAMETER

It is well known[8-10] that the electron-electron interaction energy corresponding to the Hamiltonian of Eq. (1) can be described in terms of the spatial part of the reduced density matrix elements. Only the diagonal elements of the one- and two-particle density matrices are needed here and these are defined as[8-10]

$$\rho(1) = n \int |\psi(1, 2, \ldots, n)|^2 \, d\tau_2 \cdots d\tau_n \, ds_1 \, ds_2 \cdots ds_n , \tag{8}$$

$$\pi(1,2) = n(n-1) \times \int |\psi(1, 2, \ldots, n)|^2 \, d\tau_3 \cdots d\tau_n \, ds_1 \, ds_2 \cdots ds_n . \tag{9}$$

Here, $d\tau_i$ stands for the volume element of the ith electron and ds_i for the spin coordinate. $\rho(1)$ gives the charge density at point 1 and is the probability of finding any of the n electrons at this point. Equation (8) defines this as the number of electrons times the probability of finding a specific electron at point 1. $\pi(1,2)$ is the pair density and gives the probability of finding any of the n particles at point 1 and simultaneously another at point 2. According to Eq. (9) this is equal to the number of pairs times the probability of finding simultaneously a specific pair at points 1 and 2. It follows from Eqs. (8) and (9) and the normalization of ψ that

$$\int \rho(1)\, d\tau_1 = n, \tag{10}$$

$$\int \pi(1,2)\, d\tau_1\, d\tau_2 = n(n-1), \tag{11}$$

and that

$$\int \pi(1,2)\, d\tau_2 = (n-1)\rho(1). \tag{12}$$

All information about electron exchange and correlation of their motion is contained in $\rho(1)$ and $\pi(1,2)$. When the electrons move independently of each other, the corresponding pair-density distribution, which we denote as $\pi^{\rm ind}(1,2)$, is usually but *wrongly* written as

$$\pi^{\rm ind}(1,2) = \rho(1)\rho(2). \tag{13}$$

This expression is wrong since it does not preserve normalization. This is easily seen by integrating both sides of Eq. (13) over $d\tau_1$ and $d\tau_2$, which leads to $n^2 - n = n^2$. Therefore Eq. (13) is approximately valid only for systems with very large n and not for finite systems such as atoms and molecules, with which we are concerned. Kutzelnigg, Del Re, and Berthier[11] have shown that the correct form of the independent pair function is, instead of Eq. (13),

$$\pi^{\rm ind}(1,2) = \rho(1)\rho(2) - \rho(1)\rho(2)/n. \tag{14}$$

Following McWeeny,[8] for a system of definite spin, $\rho(1)$ and $\pi(1,2)$ may be broken into their spin components,

$$\rho(1) = \rho_\uparrow(1) + \rho_\downarrow(1) \tag{15}$$

and

$$\pi(1,2) = \pi_{\uparrow\uparrow}(1,2) + \pi_{\uparrow\downarrow}(1,2) + \pi_{\downarrow\uparrow}(1,2) + \pi_{\downarrow\downarrow}(1,2), \tag{16}$$

where, for instance, $\pi_{\uparrow\downarrow}(1,2)$ gives the probability of finding an electron with spin up at point 1 and another with spin down *simultaneously* at point 2. It is easily seen that

$$\int \rho_\uparrow(1)\, d\tau_1 = n_\uparrow, \quad \int \rho_\downarrow(1)\, d\tau_1 = n_\downarrow, \tag{17}$$

$$\begin{gathered}\int \pi_{\uparrow\uparrow}(1,2)\, d\tau_1\, d\tau_2 = n_\uparrow(n_\uparrow - 1),\\ \int \pi_{\downarrow\downarrow}(1,2)\, d\tau_1\, d\tau_2 = n_\downarrow(n_\downarrow - 1),\end{gathered} \tag{18}$$

$$\int \pi_{\uparrow\uparrow}(1,2)\, d\tau_2 = (n_\uparrow - 1)\rho_\uparrow(1), \tag{19}$$

$$\int \pi_{\uparrow\downarrow}(1,2)\, d\tau_1\, d\tau_2 = \int \pi_{\downarrow\uparrow}(1,2)\, d\tau_1\, d\tau_2 = n_\uparrow n_\downarrow, \tag{20}$$

where $n = n_\uparrow + n_\downarrow$; $n_\uparrow$ is the number of spin-up electrons and $n_\downarrow$ is the number of spin-down electrons. Also, analogous to Eq. (14), for the independent pair functions,

$$\pi^{\rm ind}_{\uparrow\uparrow}(1,2) = \rho_\uparrow(1)\rho_\uparrow(2) - \rho_\uparrow(1)\rho_\uparrow(2)/n_\uparrow, \tag{21}$$

and similarly for $\pi^{\rm ind}_{\downarrow\downarrow}(1,2)$;

$$\pi^{\rm ind}_{\uparrow\downarrow}(1,2) = \rho_\uparrow(1)\rho_\downarrow(2), \tag{22}$$

and similarly for $\pi^{\rm ind}_{\downarrow\uparrow}(1,2)$. The pair functions, when the electronic motion is correlated, may be written as[8]

$$\pi_{\uparrow\uparrow}(1,2) = \rho_\uparrow(1)\rho_\uparrow(2) + \rho_\uparrow(1)\rho_\uparrow(2) f_{\uparrow\uparrow}(1,2), \tag{23}$$

and similarly for $\pi_{\downarrow\downarrow}(1,2)$;

$$\pi_{\uparrow\downarrow}(1,2) = \rho_\uparrow(1)\rho_\downarrow(2) + \rho_\uparrow(1)\rho_\downarrow(2) f_{\uparrow\downarrow}(1,2), \tag{24}$$

and similarly for $\pi_{\downarrow\uparrow}(1,2)$. The f's are the "correlation factors." This name has to be qualified; for the pair distribution of electrons of *unlike* spins, f represents the fractional change in π from $\pi^{\rm ind}$ owing to correlation, as is seen by comparing Eq. (24) with (22). However, for *like*-spin (e.g., $\uparrow\uparrow$) electrons, $(f_{\uparrow\uparrow} + 1/n_\uparrow)$ is really the *correlation factor*, as follows from Eqs. (21) and (23).

The correlation between electrons of unlike spins is not considered in either the Hartree-Fock or X_α theory; in these approximations, $\pi^{\rm ind}_{\uparrow\downarrow}$ and $\pi^{\rm ind}_{\downarrow\uparrow}$ [Eq. (22)] are used so that $f_{\uparrow\downarrow}(1,2) = f_{\downarrow\uparrow}(1,2) = 0$ for all positions 1 and 2. However, it is possible to include such correlations in the X_α theory by considering the properties of the "Coulomb hole," so that the solution of the resulting one-electron X_α equations leads to fully correlated spin orbitals and eigenvalues. The theory and results of such a study will be presented elsewhere.[12] Here we consider only the correlation between electrons of the same spin.

The conditional probability of finding an electron of $\uparrow$ spin at position 2, when one is known to be at position 1 with $\uparrow$ spin, is, from Eq. (23),

$$\pi_{\uparrow\uparrow}(1,2)/\rho_\uparrow(1) = \rho_\uparrow(2) + \rho_\uparrow(2) f_{\uparrow\uparrow}(1,2); \tag{25}$$

$\rho_\uparrow(2) f_{\uparrow\uparrow}(1,2)$ thus represents the modification in the charge distribution $\rho_\uparrow(2)$ stemming from the presence of a spin-up electron at position 1.

Now, the total electron-electron interaction energy can be written

$$\left\langle \sum_{i<j} r_{ij}^{-1} \right\rangle = \frac{1}{2} \int r_{12}^{-1} \pi(1,2)\, d\tau_1\, d\tau_2. \tag{26}$$

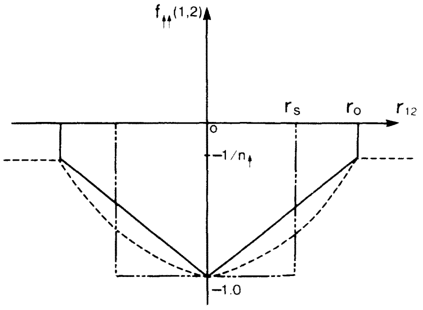

FIG. 1. Forms of the approximations to the like-spin correlation factor $f_{\uparrow\uparrow}(1,2)$. ------: Slater's approximation (Ref. 1); —: present approximation; – – –: correct form (Ref. 14).

Using the spin components of (1, 2) given by Eqs. (22) and (23) in Eq. (26), and comparing the result with the corresponding terms in Eq. (3), it is seen that for the exchange potential,

$$U_\uparrow(1)=\int r_{12}^{-1}\rho_\uparrow(2)f_{\uparrow\uparrow}(1,2)\,d\tau_2. \tag{27}$$

This corresponds to an exchange charge ρ^{ex} at position 2, given by

$$\rho_\uparrow^{ex}(2)=\rho_\uparrow(2)f_{\uparrow\uparrow}(1,2). \tag{28}$$

Furthermore, by integrating Eq. (25) over $d\tau_2$ and using Eq. (19),

$$\int\rho_\uparrow^{ex}(2)\,d\tau_2=\int\rho_\uparrow(2)f_{\uparrow\uparrow}(1,2)\,d\tau_2=-1. \tag{29}$$

That is, the total amount of exchange charge, which is effectively removed from the distribution as far as the reference electron at position 1 is concerned, is -1. Also, from the Pauli exclusion principle, $\pi_{\uparrow\uparrow}(1,1)=0$, so that from Eq. (25) the exchange charge at position 1 of the reference electron is

$$\rho_\uparrow^{ex}(1)=\rho_\uparrow(1)f_{\uparrow\uparrow}(1,1)=-\rho_\uparrow(1). \tag{30}$$

Thus the Fermi hole has a density at the position of the reference electron equal to the density of the electrons of the same spin at that point. But at any other point, it may be considerably different from this value, as follows from Eq. (28). This will be especially so in regions of strongly varying electron density. In general, the Fermi hole has a varying density and is not necessarily centered at the position of the reference electron.[8,13] Slater's assumption of uniform spherical distribution for the Fermi-hole density is therefore rather severe for atoms and molecules.

We now consider the value of the exchange density when positions 1 and 2 are far apart. In this case, we may expect $\pi_{\uparrow\uparrow}(1,2)$ to reduce to the independent pair distribution, $\pi_{\uparrow\uparrow}^{ind}(1,2)$ of Eq. (21). Then

$$\rho_\uparrow^{ex}(2)=-\rho_\uparrow(2)/n_\uparrow, \tag{31}$$

for r_{12} large. Physically, this means that when one electron of spin up is far removed from the distribution, the probability of finding a similar electron is reduced by a factor of $1/n_\uparrow$ everywhere. The same result may be obtained[14] by considering $f_{\uparrow\uparrow}(1,2)$ as a slowly varying function for large r_{12}, so that $\rho_\uparrow^{ex}(2)$ has the form (const) × $\rho_\uparrow(2)$. From Eq. (29), the value of this constant is $-1/n_\uparrow$; this leads to Eq. (31). Thus the Fermi hole has a density equal to $\rho_\uparrow(1)$ for $r_{12}=0$, and $\rho_\uparrow(2)/n_\uparrow$ for large r_{12}.

We now assume that the electron density is slowly varying around the point 1, so that we may replace $\rho_\uparrow(2)/n_\uparrow$ by $\rho_\uparrow(1)/n_\uparrow$. This is equivalent to saying that the electron density is uniform within the Fermi hole, but the exchange density, Eq. (28), changes owing to the change in $f_{\uparrow\uparrow}(1,2)$ from -1 at $r_{12}=0$ to $-(1/n_\uparrow)$ at large r_{12} (Fig. 1). We further assume that the Fermi hole is spherical, with radius r_0, and is centered at position 1, but the density of the hole varies *linearly* with r, the distance from the center, and is equal to $\rho_\uparrow(1)/n_\uparrow$ at the boundary and zero outside. In Fig. 2, this Fermi-hole density distribution is compared schematically with that assumed by Slater. Other, more complicated forms for variation of hole density have been suggested; but these require the introduction of additional arbitrary parameters and are not of much practical value (see Ref. 6 for comments on such methods).

Thus

$$\rho_\uparrow^{ex}(r)=ar+b. \tag{32}$$

Determining the constants a and b using the boundary conditions, $\rho_\uparrow^{ex}(r=0)=-\rho_\uparrow(1)$ and $\rho_\uparrow^{ex}(r=r_0)=-\rho_\uparrow(1)/n_\uparrow$, gives

$$\rho_\uparrow^{ex}(r)=-\{[\rho_\uparrow(1)/r_0](1/n_\uparrow-1)r+\rho_\uparrow(1)\}. \tag{33}$$

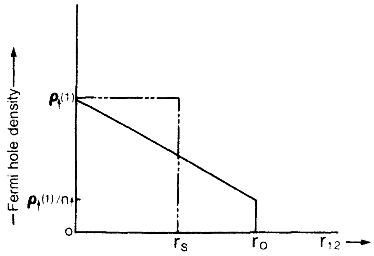

FIG. 2. Approximations to the Fermi-hole density distribution (schematic). ------: Slater's approximation (Ref. 1); —: present approximation. r_s and r_0 are the radii of the Fermi sphere in the two approximations.

Also, Eq. (29) then becomes

$$4\pi\int_0^{r_0}\rho_\uparrow^{\text{ex}}(r)r^2\,dr=-1. \tag{34}$$

Substituting for $\rho_\uparrow^{\text{ex}}(r)$ from Eq. (33) and integrating, we find the radius of the Fermi sphere,

$$r_0=[\pi(1/n_\uparrow+\tfrac{1}{3})\rho_\uparrow(1)]^{-1/3}. \tag{35}$$

Notice that in Slater's approximation, the radius of the Fermi sphere is, from Eq. (6), $r_s=[\frac{4}{3}\pi\rho_\uparrow(1)]^{-1/3}$. This is always smaller than r_0 [Eq. (35)]. Thus one of the effects of the present treatment is to enlarge the Fermi sphere, as shown in Fig. 2.

The potential at the center of the sphere owing to the exchange density is

$$\begin{aligned}U_\uparrow(1)&=4\pi\int_0^{r_0}\rho_\uparrow^{\text{ex}}(r)r\,dr\\&=\tfrac{4}{3}\pi r_0^2(1/n_\uparrow+\tfrac{1}{2})\rho_\uparrow(1),\end{aligned} \tag{36}$$

using Eq. (33). Substituting for r_0 from Eq. (35),

$$U_\uparrow(1)=\frac{8\pi^{1/3}}{3}\,\frac{1/n_\uparrow+\frac{1}{2}}{(1/n_\uparrow+\frac{1}{3})^{2/3}}\,\rho_\uparrow^{1/3}(1), \tag{37}$$

with a similar expression for $U_\downarrow(1)$, in rydberg units.

Thus the exchange potential for a spin-up electron has an explicit dependence on the number of spin-up electrons in the system, in addition to its dependence on this number through $\rho_\uparrow(1)$; Eqs. (4) or (7) have no such explicit dependence.

Writing Eq. (37) in the form of Eq. (4) yields

$$\alpha_{t\uparrow}=\frac{8}{27}\left(\frac{4\pi^2}{3}\right)^{1/3}\frac{1/n_\uparrow+\frac{1}{2}}{(1/n_\uparrow+\frac{1}{3})^{2/3}} \tag{38}$$

for the exchange parameter for spin-up electrons, and

$$\alpha_{t\downarrow}=\frac{8}{27}\left(\frac{4\pi^2}{3}\right)^{1/3}\frac{1/n_\downarrow+\frac{1}{2}}{(1/n_\downarrow+\frac{1}{3})^{2/3}} \tag{39}$$

for the spin-down electrons. The notation α_t is introduced to denote that these are theoretically derived quantities.

III. EVALUATION OF THEORETICAL α VALUES FOR ATOMS

According to Eqs. (38) and (39), the spin-up and spin-down electrons have different α values when their numbers are different in an atom. The values of $\alpha_{t\uparrow}$ (or equivalently $\alpha_{t\downarrow}$) are computed from Eq. (38) for $n_\uparrow$ values from 1 to 55. These results are given in Table I, column 2. It is seen that the $\alpha_{t\uparrow}$ values steadily decrease with increasing $n_\uparrow$, being around 0.8 for small $n_\uparrow$ and approaching a constant value of 0.728 for large $n_\uparrow$. This range of values is remarkably close to the

TABLE I. Theoretical exchange parameter $\alpha_{t\uparrow}$ and scaled theoretical exchange parameter $\alpha'_{t\uparrow}$ from Eqs. (38) and (42) as a function of the number of electrons $n_\uparrow$.

$n_\uparrow$	$\alpha_{t\uparrow}$	$\alpha'_{t\uparrow}$
1	0.866 172	0.841 991
2	0.789 938	0.767 885
3	0.763 868	0.742 543
4	0.751 489	0.730 509
5	0.744 568	0.723 781
6	0.740 288	0.719 621
7	0.737 450	0.716 862
8	0.735 470	0.714 937
9	0.734 031	0.713 538
10	0.732 952	0.712 490
11	0.732 122	0.711 683
12	0.731 470	0.711 049
13	0.730 948	0.710 542
14	0.730 523	0.710 129
15	0.730 174	0.709 789
16	0.729 883	0.709 507
17	0.729 638	0.709 268
18	0.729 428	0.709 064
19	0.729 249	0.708 890
20	0.729 095	0.708 740
21	0.728 960	0.708 609
22	0.728 842	0.708 491
23	0.728 738	0.708 394
24	0.728 646	0.708 304
25	0.728 565	0.708 225
26	0.728 491	0.708 154
27	0.728 426	0.708 090
28	0.728 367	0.708 033
29	0.728 314	0.707 981
30	0.728 265	0.707 934
31	0.728 222	0.707 892
32	0.728 182	0.707 853
33	0.728 145	0.707 817
34	0.728 111	0.707 784
35	0.728 081	0.707 754
36	0.728 052	0.707 726
37	0.728 026	0.707 708
38	0.728 002	0.707 678
39	0.727 979	0.707 656
40	0.727 958	0.707 636
41	0.727 939	0.707 617
42	0.727 921	0.707 599
43	0.727 904	0.707 583
44	0.727 888	0.707 567
45	0.727 874	0.707 553
46	0.727 859	0.707 539
47	0.727 846	0.707 527
48	0.727 834	0.707 515
49	0.727 822	0.707 503
50	0.727 812	0.707 493
51	0.727 801	0.707 483
52	0.727 792	0.707 474
53	0.727 782	0.707 464
54	0.727 774	0.707 457
55	0.727 766	0.707 448

TABLE II. Theoretical exchange parameters for atoms α_{ta} and α'_{ta} calculated from Eqs. (38), (40), and (42); α_{HF} values are from Ref. 3.

Atomic number	Atom	Electronic configuration	$n_\uparrow$, $n_\downarrow$	α_{ta}	α'_{ta}	α_{HF}
1	H	$1s^1$	$\frac{1}{2}$, $\frac{1}{2}$	0.994 095	0.966 343	0.978 04
2	He	$1s^2$	1, 1	0.866 172	0.841 991	0.772 98
3	Li	He $2s^1$	2, 1	0.815 349	0.792 587	0.781 47
4	Be	He $2s^2$	2, 2	0.789 938	0.767 885	0.768 23
5	B	He $2s^2 2p^1$	3, 2	0.774 296	0.752 680	0.765 31
6	C	He $2s^2 2p^2$	4, 2	0.764 305	0.742 967	0.759 28
7	N	He $2s^2 2p^3$	5, 2	0.757 531	0.736 382	0.751 97
8	O	He $2s^2 2p^4$	5, 3	0.751 805	0.730 817	0.744 77
9	F	He $2s^2 2p^5$	5, 4	0.747 644	0.726 771	0.737 32
10	Ne	He $2s^2 2p^6$	5, 5	0.744 568	0.723 781	0.730 81
11	Na	Ne $3s^1$	6, 5	0.742 233	0.721 152	0.731 15
12	Mg	Ne $3s^2$	6, 6	0.740 288	0.719 621	0.729 13
13	Al	Ne $3s^2 3p^1$	7, 6	0.738 760	0.718 135	0.728 53
14	Si	Ne $3s^2 3p^2$	8, 6	0.737 535	0.716 944	0.727 51
15	P	Ne $3s^2 3p^3$	9, 6	0.736 534	0.715 971	0.726 20
16	S	Ne $3s^2 3p^4$	9, 7	0.735 527	0.714 992	0.724 75
17	Cl	Ne $3s^2 3p^5$	9, 8	0.734 708	0.714 196	0.723 25
18	Ar	Ne $3s^2 3p^6$	9, 9	0.734 031	0.713 538	0.721 77
19	K	Ar $4s^1$	10, 9	0.733 463	0.712 986	0.721 17
20	Ca	Ar $4s^2$	10, 10	0.732 952	0.712 490	0.719 84
21	Sc	Ar $3d^1 4s^2$	11, 10	0.732 517	0.712 067	0.718 41
22	Ti	Ar $3d^2 4s^2$	12, 10	0.732 144	0.711 704	0.716 98
23	V	Ar $3d^3 4s^2$	13, 10	0.731 819	0.711 389	0.715 56
24	Cr	Ar $3d^5 4s^1$	15, 9	0.731 620	0.711 195	0.713 52
25	Mn	Ar $3d^5 4s^2$	15, 10	0.731 285	0.710 870	0.712 79
26	Fe	Ar $3d^6 4s^2$	15, 11	0.730 998	0.710 590	0.711 51
27	Co	Ar $3d^7 4s^2$	15, 12	0.730 750	0.710 349	0.710 18
28	Ni	Ar $3d^8 4s^2$	15, 13	0.730 533	0.710 139	0.708 96
29	Cu	Ar $3d^{10} 4s^1$	15, 14	0.730 392	0.709 953	0.706 97
30	Zn	Ar $3d^{10} 4s^2$	15, 15	0.730 174	0.709 789	0.706 77
31	Ga	Ar $3d^{10} 4s^2 4p^1$	16, 15	0.730 024	0.709 643	0.706 90
32	Ge	Ar $3d^{10} 4s^2 4p^2$	17, 15	0.729 889	0.709 512	0.706 84
33	As	Ar $3d^{10} 4s^2 4p^3$	18, 15	0.729 767	0.709 393	0.706 65
34	Se	Ar $3d^{10} 4s^2 4p^4$	18, 16	0.729 642	0.709 272	0.706 38
35	Br	Ar $3d^{10} 4s^2 4p^5$	18, 17	0.729 530	0.709 163	0.706 06
36	Kr	Ar $3d^{10} 4s^2 4p^6$	18, 18	0.729 428	0.709 064	0.705 74
37	Rb	Kr $5s^1$	19, 18	0.729 336	0.708 975	0.705 53
38	Sr	Kr $5s^2$	19, 19	0.729 249	0.708 890	0.705 04
39	Y	Kr $4d^1 5s^2$	20, 19	0.729 170	0.708 813	0.704 65
40	Zr	Kr $4d^2 5s^2$	21, 19	0.729 097	0.708 742	0.704 24
41	Nb	Kr $4d^4 5s^1$	23, 18	0.729 041	0.708 688	0.703 83
42	Mo	Kr $4d^5 5s^1$	24, 18	0.728 981	0.708 630	0.703 41
43	Tc	Kr $4d^5 5s^2$	24, 19	0.728 912	0.708 563	0.702 99
44	Ru	Kr $4d^7 5s^1$	24, 20	0.728 850	0.708 502	0.702 53
45	Rh	Kr $4d^8 5s^1$	24, 21	0.728 792	0.708 446	0.702 17
46	Pd	Kr $4d^{10}$	23, 23	0.728 738	0.708 394	0.701 58
47	Ag	Kr $4d^{10} 5s^1$	24, 23	0.728 691	0.708 346	0.701 45
48	Cd	Kr $4d^{10} 5s^2$	24, 24	0.728 646	0.708 304	0.701 14
49	In	Kr $4d^{10} 5s^2 5p^1$	25, 24	0.728 605	0.708 264	0.701 02
50	Sn	Kr $4d^{10} 5s^2 5p^2$	26, 24	0.728 565	0.708 226	

TABLE II. *(continued)*

Atomic number	Atom	Electronic configuration	$n_\uparrow$, $n_\downarrow$	α_{ta}	α'_{ta}	α_{HF}
51	Sb	Kr $4d^{10}5s^25p^3$	27, 24	0.728 530	0.708 191	
52	Te	Kr $4d^{10}5s^25p^4$	27, 25	0.728 491	0.708 155	
53	I	Kr $4d^{10}5s^25p^5$	27, 26	0.728 458	0.708 112	
54	Xe	Kr $4d^{10}5s^25p^6$	27, 27	0.728 426	0.708 090	0.699 84
55	Cs	Xe $6s^1$	28, 27	0.728 396	0.708 061	0.699 61
56	Ba	Xe $6s^2$	28, 28	0.728 367	0.708 033	0.699 27
57	La	Xe $5d^16s^2$	29, 28	0.728 340	0.708 007	0.698 98
58	Ce	Xe $4f^26s^2$	30, 28	0.728 314	0.707 982	0.698 45
59	Pr	Xe $4f^36s^2$	31, 28	0.728 291	0.707 959	0.697 65
60	Nd	Xe $4f^46s^2$	32, 28	0.728 268	0.707 937	
61	Pm	Xe $4f^56s^2$	33, 28	0.728 247	0.707 916	
62	Sm	Xe $4f^66s^2$	34, 28	0.728 227	0.707 896	
63	Eu	Xe $4f^76s^2$	35, 28	0.728 208	0.707 878	0.695 75
64	Gd	Xe $4f^75d^16s^2$	36, 28	0.728 189	0.707 860	0.6956
65	Tb	Xe $4f^85d^16s^2$	36, 29	0.728 168	0.707 840	0.695 25
66	Dy	Xe $4f^{10}6s^2$	35, 31	0.728 147	0.707 819	0.694 53
67	Ho	Xe $4f^{11}6s^2$	35, 32	0.728 129	0.707 801	
68	Er	Xe $4f^{12}6s^2$	35, 33	0.728 112	0.707 785	
69	Tm	Xe $4f^{13}6s^2$	35, 34	0.728 053	0.707 769	
70	Yb	Xe $4f^{14}6s^2$	35, 35	0.728 081	0.707 754	0.693 17
71	Lu	Xe $4f^{14}5d^16s^2$	36, 35	0.728 066	0.707 740	0.693 24
72	Hf	Xe $4f^{14}5d^26s^2$	37, 35	0.728 053	0.707 727	
73	Ta	Xe $4f^{14}5d^36s^2$	38, 35	0.728 040	0.707 714	
74	W	Xe $4f^{14}5d^46s^2$	39, 35	0.728 027	0.707 702	
75	Re	Xe $4f^{14}5d^56s^2$	40, 35	0.728 015	0.707 691	
76	Os	Xe $4f^{14}5d^66s^2$	40, 36	0.728 002	0.707 679	
77	Ir	Xe $4f^{14}5d^76s^2$	40, 37	0.727 990	0.707 668	
78	Pt	Xe $4f^{14}5d^96s^1$	40, 38	0.727 979	0.707 656	0.693 06
79	Au	Xe $4f^{14}5d^{10}6s^1$	40, 39	0.727 968	0.707 646	0.693 01
80	Hg	Xe $4f^{14}5d^{10}6s^2$	40, 40	0.727 958	0.707 636	0.692 90
81	Tl	Xe $4f^{14}5d^{10}6s^2\,6p^1$	41, 40	0.727 948	0.707 626	0.692 89
82	Pb	Xe $4f^{14}5d^{10}6s^26p^2$	42, 40	0.727 939	0.707 617	
83	Bi	Xe $4f^{14}5d^{10}6s^26p^3$	43, 40	0.727 930	0.707 609	
84	Po	Xe $4f^{14}5d^{10}6s^26p^4$	43, 41	0.727 921	0.707 600	
85	At	Xe $4f^{14}5d^{10}6s^26p^5$	43, 42	0.727 912	0.707 591	
86	Rn	Xe $4f^{14}5d^{10}6s^26p^6$	43, 43	0.727 904	0.707 583	0.692 48
87	Fr	Rn $7s^1$	44, 43	0.727 896	0.707 575	
88	Ra	Rn $7s^2$	44, 44	0.727 888	0.707 567	
89	Ac	Rn $6d^17s^2$	45, 44	0.727 881	0.707 560	
90	Th	Rn $6d^27s^2$	46, 44	0.727 873	0.707 553	
91	Pa	Rn $5f^26d^17s^2$	47, 44	0.727 866	0.707 546	
92	U	Rn $5f^36d^17s^2$	48, 44	0.727 860	0.707 540	
93	Np	Rn $5f^57s^2$	49, 44	0.727 853	0.707 533	
94	Pu	Rn $5f^67s^2$	50, 44	0.727 847	0.707 527	
95	Am	Rn $5f^77s^2$	51, 44	0.727 841	0.707 522	
96	Cm	Rn $5f^76d^1\,7s^2$	52, 44	0.727 836	0.707 517	
97	Bk	Rn $5f^86d^17s^2$	52, 45	0.727 830	0.707 511	
98	Cf	Rn $5f^{10}7s^2$	51, 47	0.727 822	0.707 504	
99	Es	Rn $5f^{11}7s^2$	51, 48	0.727 817	0.707 500	
100	Fm	Rn $5f^{12}7s^2$	51, 49	0.727 811	0.707 493	
101	Md	Rn $5f^{13}7s^2$	51, 50	0.727 806	0.707 488	
102	Lw	Rn $5f^{14}7s^2$	51, 51	0.727 801	0.707 483	
103	No	Rn $5f^{14}6d^17s^2$	52, 51	0.727 796	0.707 478	

empirically determined α_{HF} values for atoms (see Table II). As $n_\uparrow \to \infty$, Eq. (39) gives a limiting value of 0.7275, which may be compared with the α value of $\frac{2}{3}$ for an electron gas of uniform density.[15,16]

In the X_α method, different α values for electrons of different spin are not generally used, whereas, according to Eqs. (42) and (43), when $n_\uparrow$ and $n_\downarrow$ are different, different α values must be used. This result may be of particular importance in the spin-polarized X_α calculations,[1(a)] and we will return to this point in Sec. IV. For open-shell atoms, the α_{HF} value is determined by making the total energy of the atom calculated by the X_α equal to an average of the energies of the various multiplets; this average is calculated using the hyper-Hartree-Fock method.[1(b)]

Within the present theory, to compute an average theoretical α value for the atom (α_{ta}) for comparison with the α_{HF} values, the following simple averaging is used:

$$\alpha_{ta} = (n_\uparrow \alpha_{t\uparrow} + n_\downarrow \alpha_{t\downarrow})/(n_\uparrow + n_\downarrow), \tag{40}$$

where $n_\uparrow$ and $n_\downarrow$ refer to the number of spin-up and spin-down electrons in the ground-state configuration of the atom, and $\alpha_{t\uparrow}$ and $\alpha_{t\downarrow}$ are the corresponding values calculated using Eqs. (38) and (39). These average values α_{ta} are given in Table II for all atoms in the Periodic Table. The available[3] α_{HF} values are also given in Table II for comparison. The α_{ta} and α_{HF} are plotted as a function of the atomic number Z in Fig. 3.

The Z dependence of α_{ta} given by Eqs. (38)–(40) is seen to be in very good agreement with the empirically found Z dependence of α_{HF} (Fig. 3). This shows that the nature of the Fermi hole assumed in Sec. II to derive Eqs. (35)–(40) is essentially correct and adequately describes the situation in atoms. Quantitatively, the α_{ta} values, although close to the α_{HF} values, are consistently higher. Thus the limiting value of α_{HF} for large Z is around 0.69, while the theoretical limiting value is 0.7275. To compare the theoretical α_{ta} values with the α_{HF} values, this theoretical limiting value can be adjusted and the corresponding α values for atoms computed. For this purpose, Eq. (38) is expressed by

$$\alpha_{t\uparrow} = C \frac{1/n_\uparrow + \frac{1}{2}}{(1/n_\uparrow + \frac{1}{3})^{2/3}}, \tag{41}$$

where $C = 0.699\,53$ reduces Eq. (41) to (38) and corresponds to the limiting value of 0.7275 for $\alpha_{t\uparrow}$. Reducing the value of C to 0.680, i.e., using

$$\alpha'_{t\uparrow} = 0.68 \frac{1/n_\uparrow + \frac{1}{2}}{(1/n_\uparrow + \frac{1}{3})^{2/3}}, \tag{42}$$

corresponds to a limiting value of 0.7072. These $\alpha'_{t\uparrow}$ values are also given in Table I, column 3. The corresponding average α values for atoms, denoted as α'_{ta} and computed using the averaging process of Eq. (40), are given in Table II and plotted in Fig. 3. These are seen to be in closer agreement with α_{HF}.

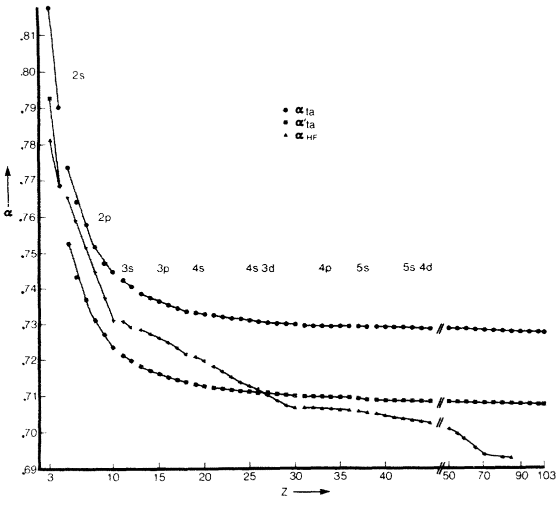

FIG. 3. Plot of α_{ta}, α'_{ta}, and α_{HF} vs atomic number.

We now turn to the fact, mentioned in Sec. I, that the slope $\partial\alpha_{\mathrm{HF}}/\partial Z$ is discontinuous at every atomic subshell. This is evident from Fig. 3. The theoretical slope, $\partial\alpha_{ta}/\partial Z$ or $\partial\alpha'_{ta}/\partial Z$, is seen from Fig. 3 to have exactly the same behavior as $\partial\alpha_{\mathrm{HF}}/\partial Z$; the magnitudes of the slopes are also in good agreement. The apparent linearity of the slope within each subshell is a direct consequence of the dependence of α on the number of electrons, Eqs. (38) and (39), of the *Aufbau* principle and of Hund's rule, which determine the ground-state configuration of atoms. From Eq. (38) and the numerical values of Table I it is seen that $\alpha_{t\uparrow}$ falls nonlinearly with $n_\uparrow$; so does $\alpha_{t\downarrow}$ with $n_\downarrow$. When a subshell is being filled with electrons, $n_\uparrow$ increases with atomic number while $n_\downarrow$ remains constant until the subshell is one-half filled, according to Hund's rule for the ground state, and $n_\uparrow$ remains constant while $n_\downarrow$ increases until the two values are equal when the subshell is full. Consequently, $\alpha_{t\uparrow}$ falls nonlinearly and $\alpha_{t\downarrow}$ remains constant until the subshell is one-half filled; then $\alpha_{t\uparrow}$ remains constant and $\alpha_{t\downarrow}$ falls nonlinearly until the subshell is full. Thus *within the subshell* the atomic α_{ta} value is an appropriate average [cf. Eq. (40)] of a nonlinearly varying quantity and a constant; consequently, the variation in α_{ta} becomes almost linear. This is schematically shown in Fig. 4. The discontinuity in the slope $\partial\alpha_{ta}/\partial Z$ at the beginning of every subshell arises

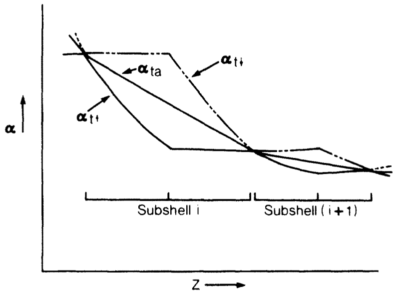

FIG. 4. Variation of $\alpha_{t\uparrow}$, $\alpha_{t\downarrow}$, and α_{ta} in atomic subshells according to Eqs. (42)–(44), showing approximate linearity (idealized in the figure) of α_{ta} within each subshell and the discontinuity in slope $\partial\alpha_{ta}/\partial Z$ at the beginning of each subshell. (Purely schematic.)

from the fact that α_{ta} is dependent on both $n_\uparrow$ and $n_\downarrow$ and the ratio of these two changes at every subshell. These breaks will be more pronounced for light atoms (small $n_\uparrow$) for which the variation in $\alpha_{t\uparrow}$ is large. These facts are easily verified from Fig. 3.

From the $n_\uparrow$ and $n_\downarrow$ values in Table II, which reflect the ground-state electronic configuration of elements, note that slight deviation from the regular behavior of α vs Z is predicted for Cr, Nb, Dy, and Cf. The available α_{HF} values show these predicted deviations (Table II).

Thus all details of the empirical Z dependence of the α_{HF} values are well reproduced by the present theoretical α_{ta} values. This confirms that the model of the Fermi hole assumed in Sec. II is essentially correct and is sufficient to describe the hole in atoms, and hopefully in molecules and solids as well.

IV. DISCUSSION

It has been shown that the Fermi sphere has a density $\rho_\uparrow(1)$ at the center and $\rho_\uparrow(1)/n_\uparrow$ at points far from the center. Assuming a linear variation of the hole density within the sphere with these boundary values leads to an expression for the exchange potential which retains the simple $\rho_\uparrow^{1/3}(1)$ dependence of the X_α theory, but shows that α values depend explicitly on the $n_\uparrow$, the number of electrons. These theoretical values of α are found to reproduce almost quantitatively the empirically determined α_{HF} values as well as all details of their dependence on atomic number.

Efforts have been made[17] to arrive at a single, Z-independent α value that could be used for all atoms, but this involves the introduction of another Z-dependent parameter β and terms involving the derivative of ρ in the exchange potential. It is clear from the present study that the Z dependence of α has a theoretical basis, and arises naturally without introducing any arbitrary parameters. Therefore the use of a Z-independent α value is unjustified.

Another important result from the present work is that for an atom or ion with a different number of spin-up ($n_\uparrow$) and spin-down ($n_\downarrow$) electrons, there are two different values of α, namely, $\alpha_{t\uparrow}$ for spin-up electrons and $\alpha_{t\downarrow}$ for spin-down electrons, Eqs. (38) and (39). Thus the difference in the exchange potential for the two types of electrons arises not merely from the difference in the electron densities $\rho_\uparrow(1)$ and $\rho_\downarrow(1)$, but also from the difference in $\alpha_{t\uparrow}$ and $\alpha_{t\downarrow}$. This fact has important consequences in calculations of properties such as magnetic behavior and contact hyperfine interaction using the spin-polarized X_α method. As an illustration, we take the case of the contact hyperfine interaction in the Mn^{2+} ion discussed by Slater.[1(c)] The magnitude of the contact hyperfine structure is a measure of the spin density at the nucleus arising from the s electrons and is a stringent test of the exchange approximation. In the particular case of the Mn^{2+} ion the sign of the hyperfine structure corresponds to an excess of spin-down electrons over spin-up electrons at the nucleus. The spin-polarized X_α calculations predict the correct sign, but underestimate the magnitude; Slater has therefore concluded that this feature will prevent the use of the X_α method if very accurate calculations of contact hyperfine structure are desired. The deficiency of the X_α method can be removed if the dependence of α on the number of electrons is considered. In the spin-polarized X_α method a single average α value is normally used for both spin-up and spin-down electrons. But in the Mn^{2+} ion $n_\uparrow(=14) > n_\downarrow(=9)$ and consequently (see Table I) $\alpha_{t\uparrow} < \alpha_{ta} < \alpha_{t\downarrow}$. Thus, for instance, the spin-up electrons will have a less negative exchange potential and higher energy, compared to the use of the average α_{ta}. This would result in increasing the density of the spin-down electrons at the nucleus and decreasing that of the spin-up electron there, from the corresponding values obtained by the use of a simple average α. Thus the magnitude of the spin density at the nucleus and hence that of the contact hyperfine structure would be increased. Numerical calculations are underway to test these qualitative predictions. Wilson *et al.*[18] used in a calculation on the Mn^{+2} ion different α values, $\alpha_{\mathrm{HF}}(\uparrow)$ and $\alpha_{\mathrm{HF}}(\downarrow)$ for different spins, the two α values being empirically determined. Contrary to the present theoretical results, they used $\alpha_{\mathrm{HF}}(\uparrow) > \alpha_{\mathrm{HF}}(\downarrow)$, which leads to the wrong sign for the spin density at the nucleus.

Finally, the use of different α values for electrons of opposite spin is of paramount importance in describing the whole range of magnetic properties that depend on the small energy differences between spin-up and spin-down electrons.

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[1] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4, (a) p. 56, (b) p. 293, (c) p. 65. This volume is concerned mainly with the X_α method and contains an extensive bibliography.

[2] J. C. Slater, Adv. Quantum Chem. 6, 1 (1972).

[3] K. Schwarz, Phys. Rev. B 5, 2466 (1972); Theor. Chim. Acta (Berlin) 34, 225 (1974).

[4] I. Lindgren, Phys. Lett. 19, 382 (1965); Ark. Fys. 31, 59 (1966).

[5] E. A. Kmetko, Phys. Rev. A 7, 37 (1970).

[6] J. C. Slater, Phys. Rev. B 5, 844 (1972); J. C. Slater and J. H. Wood, Int. J. Quantum Chem. 4S, 3 (1971).

[7] I. Lindgren and K. Schwarz, Phys. Rev. A 5, 542 (1972).

[8] R. McWeeny, Rev. Mod. Phys. 32, 335 (1960).

[9] P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

[10] W. Kutzelnigg, *Topics in Current Chemistry* (Springer, Berlin, 1973), Vol. 41, p. 31.

[11] W. Kutzelnigg, G. Del Re, and G. Berthier, Phys. Rev. 172, 49 (1968).

[12] M. S. Gopinathan and M. A. Whitehead (unpublished).

[13] V. W. Maslen, Proc. Phys. Soc. Lond. A 69, 734 (1956).

[14] R. McWeeny, Int. J. Quantum Chem. 1S, 351 (1967).

[15] R. Gaspar, Acta Phys. Hung. 3, 263 (1954).

[16] W. Kohn and L. J. Sham, Phys. Rev. 140, A1113 (1965).

[17] F. Herman and K. Schwarz, *Computational Solid State Physics* (Plenum, New York, 1972), p. 245.

[18] T. M. Wilson, J. H. Wood, and J. C. Slater, Phys. Rev. A 2, 620 (1970).