PHYSICAL REVIEW A VOLUME 24, NUMBER 1 JULY 1981

Self-consistent-field–Ξa method: The atomic properties of several atoms using theoretical a parameters derived from the Fermi hole

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(Received 1 May 1980)

Theoretical parameters a_t for the self-consistent-field–Ξa (SCF-Ξa) method are derived by considering the Fermi hole, modified from the form used to generate the theoretical α parameters in the $X\alpha$ method, because of including explicit self-interaction in the Hamiltonian, which scales the exchange potential. The a_t for all elements in the Periodic Table are given, to compare with previous compilations. For $Z > 30$ they are in error due to relativistic effects becoming important. The results from the SCF-Ξa method with a_t have been compared with those previously calculated for Cu^+, Mn^{2+}, Ne, and Ar for the one-electron energies $-\epsilon_i$, the total energies E, the Fermi contact terms χ, and the core-spin densities.

I. INTRODUCTION

Gopinathan[1] improved the approximate representation of the atomic Hartree-Fock (HF) potentials, by calculating the self-interaction term explicitly and scaling the remaining exchange potential to the charge density ρ as in the $X\alpha$ method.[2]

This new method, named the self-consistent-field-Ξa (SCF-Ξa) hereafter the Ξa method, has been applied to Cu^+ and Mn^{2+} by Gopinathan[1] using parameters α_{t_a} derived[3] theoretically within the $X\alpha$ scheme. The Ξa one-electron energies $-\epsilon i$ and other properties such as the Fermi contact term χ of Mn^{2+} were closer to the HF results than those of the $X\alpha$ method using α_{t_a}. However, the Ξa total energies[4] E from Ne to Ar of the even-Z atoms were all lower than the corresponding exact nonrelativistic energies[5] when α_{t_a} was used, suggesting that the α_{t_a}, derived within the $X\alpha$ scheme, are unsuitable for use in the Ξa method.

When the total energy of Eq. (1), $\langle E_{\Xi a}\rangle$, is set equal to the atomic energy of the HF limit, $E_{\text{limit}}^{\text{HF}}$, a corresponding parameter, a_{HF} is obtained. This follows closely the derivation of α_{HF} by Schwarz[6] for the $X\alpha$ method. The numerical values of a_{HF} were distinctly less than α_{HF}, e.g.,[7] for Li: $a_{\text{HF}} = 0.322\,37$ and $\alpha_{\text{HF}} = 0.781\,47$; for Ar: $a_{\text{HF}} = 0.479\,16$ and $\alpha_{\text{HF}} = 0.721\,77$. However, since $\alpha_{t_a} \simeq \alpha_{\text{HF}}$, it would be expected that $a_{t_a} \simeq a_{\text{HF}}$. Therefore, it is obvious that the α_{t_a}'s are too large to be used in the Ξa scheme, and consequently it is necessary to reformulate the parameter, a_{t_a}, if theoretical parameters are to be used in calculations.

While the Ξa one-electron energies with a_{t_a} are expected to be much better than the $X\alpha$ values, from previous experience,[8,9] it should not be expected that a drastic change will occur from the values from Ξa when α_{t_a} is used, because the quality of the wave function and the related physical properties depend very much on the method and less on the parameter. Nevertheless large-value parameters such as α_{t_a} when used in the Ξa scheme will be not only energetically unfavorable for atoms but also for molecules. For example, since the total atomic energy is linearly dependent on the parameter, large-value parameters lower the dissociation limit. If the energy lowering is not retained for all internuclear distances, not only is the potential curve affected, but in the worst case a bound state may turn out to be unbound.[10]

II. TOTAL ENERGY AND EXCHANGE ENERGY

The total energy in the Ξa method[1] is (distances in a.u., energies in Ry)

$$\langle E_{\Xi a}\rangle = \sum_i n_i \int u_i^*(1) f_1 u_i(1)\, d\tau_1 + \tfrac{1}{2}\int \rho(1)\rho(2) g_{12}\, d\tau_1 d\tau_2 - \tfrac{1}{2}\int \sum_i \rho_{i\uparrow}(1)\rho_{i\uparrow}(2) g_{12}\, d\tau_1 d\tau_2$$

$$- \tfrac{9}{2} C a_\uparrow \int \sum_i \rho'_{i\uparrow}(1)\rho_\uparrow^{-2/3}(1)\rho_{i\uparrow}(1)\, d\tau_1 + (\downarrow) \qquad (1)$$

where $(\downarrow)$ represents terms with down spins. The u_i's are the spin orbitals with orbital occupancy n_i, $f_1 = -\nabla^2 - 2Z/r$, $g_{12} = 2/r_{12}$, and $C = (3/4\pi)^{1/3}$. $\rho_\uparrow(1)$ is the total charge density, $\rho_{i\uparrow}(1)$ is the charge density of the electron in spin orbital $u_{i\uparrow}$, and $\rho'_{i\uparrow}$ is the difference between $\rho_\uparrow(1)$ and $\rho_{i\uparrow}(1)$,

$$\rho_{i\uparrow}(1) = n_{i\uparrow} u_{i\uparrow}^*(1) u_{i\uparrow}(1), \quad \rho_\uparrow(1) = \sum_{i\uparrow} n_i u_i^*(1) u_i(1),$$

$$p'_{i\uparrow}(1) = \rho_\uparrow(1) - \rho_{i\uparrow}(1) = \sum_{j \neq i\uparrow} n_j u_j^*(1) u_j(1). \qquad (2)$$

In Eq. (1), $a_\uparrow$ could be determined empirically for each atomic system, but will be derived theoretically. Integrals 2 to 6 on the right-hand side of Eq. (1), account for the electron-electron interaction energies. The third integral is the self-interaction integral which is wrongly included in the second integral, the Coulomb interaction energy, in the $X\alpha$ scheme, but is evaluated exactly in the Ξa scheme. The negative sign means that this term is subtracted from the second term. The algebraic sum of the second and the third terms plus the necessary contribution from the down-spin terms will be the usual Coulomb interaction energy in the HF method. Therefore, the fourth term, which is $a_\uparrow$ dependent, must be equivalent to the exchange energy when the self-interaction term is excluded. This is the fundamental difference from the $X\alpha$ method where the third and fourth terms are combined to give the exchange-correlation integral which depends on the parameter, α.

Minimizing the total energy [Eq. (1)] variationally with respect to u_i's, gives a set of one-electron Schrödinger equations to be solved[1] in the Ξa scheme,

$$[f_1 + V_c(1) + V^{s}_{i\uparrow}(1) + V^{ex}_{i\uparrow}(1)]u_{i\uparrow}(1) = \epsilon_{i\uparrow} u_{i\uparrow}(1)\,, \tag{3}$$

where V_c is the Coulomb potential; $V^{s}_{i\uparrow}$ is the self-interaction potential for the ith spin orbital, and $V^{ex}_{i\uparrow}$ is the exchange potential.

By defining[1]

$$U^{ex}_{\uparrow}(1) = \Big(-9Ca_\uparrow \sum_i \rho_i'(1)\rho_\uparrow^{-2/3}(1)\rho_{i\uparrow}(1)\Big)\Big/\rho_\uparrow(1)\,, \tag{4}$$

the Ξa electron-electron interaction terms in Eq. (1) can be written as

$$\begin{aligned}\Big\langle \sum_{i<j} g_{12}\Big\rangle = \tfrac{1}{2}\int \rho(1)\rho(2) g_{12}\, d\tau_1 d\tau_2 \\ -\tfrac{1}{2}\int \sum_i \rho_{i\uparrow}(1)\rho_{i\uparrow}(2) g_{12}\, d\tau_1 d\tau_2 \\ +\tfrac{1}{2}\int \rho_\uparrow(1) U^{ex}_{\uparrow}(1)\, d\tau_1 + (\downarrow)\,.\end{aligned} \tag{5}$$

The exchange potential of Eq. (4) can also be reformulated by means of definitions given in Eq. (2), i.e.,

$$U^{ex}_{\uparrow}(1) = -9Ca_\uparrow\Big(\rho_\uparrow^{1/3}(1) - \rho_\uparrow^{-5/3}(1)\sum_i \rho^2_{i\uparrow}(1)\Big)\,. \tag{6}$$

Clearly, the first term on the right-hand side of Eq. (6) has exactly the same form as the exchange-correlation potential $U^{xc}_{\uparrow}(1)$ in the $X\alpha$ theory. The second term is the self-interaction energy in the Ξa theory. It is removed from $U^{xc}_{\uparrow}(1)$ because the self-interaction energy, the second term of Eq. (5), is now evaluated exactly.

III. ONE- AND TWO-PARTICLE DENSITY MATRICES

The electron-electron interaction energy can also be written in terms of the one- and two-particle density matrices defined as[11-13]

$$\rho(1) = n\int |\psi(1,2,\ldots,n)|^2 d\tau_2\cdots d\tau_n ds_1\cdots ds_n\,, \tag{7}$$

$$\pi(1,2) = n(n-1)\int |\psi(1,2,\ldots,n)|^2 d\tau_3\cdots d\tau_n ds_1\cdots ds_n\,, \tag{8}$$

and

$$\Big\langle \sum_{i>j} r_{12}^{-1}\Big\rangle = \tfrac{1}{2}\int r_{12}^{-1}\pi(1,2)\, d\tau_1 d\tau_2\,. \tag{9}$$

For a system of definite spin, $\rho(1)$ and $\pi(1,2)$ can be written as[11]

$$\rho(1) = \rho_\uparrow(1) + \rho_\downarrow(1)\,, \tag{10}$$

$$\begin{aligned}\pi(1,2) = \pi_{\uparrow\uparrow}(1,2) + \pi_{\uparrow\downarrow}(1,2) \\ + \pi_{\downarrow\uparrow}(1,2) + \pi_{\downarrow\downarrow}(1,2)\,,\end{aligned} \tag{11}$$

$\rho_\uparrow(1)$, the total charge density of up-spin electrons $n_\uparrow$, is the probability density of finding any of the $n_\uparrow$ electrons at point 1. The pair density $\pi_{\uparrow\uparrow}(1,2)$ is the probability density of finding any of the $n_\uparrow$ electrons at point 1 and simultaneously another up-spin electron at point 2. When two electrons are far apart, they can be treated as independent particles, and the pair density can be written as[3,14]

$$\pi^{ind}_{\uparrow\uparrow}(1,2) = \rho_\uparrow(1)\rho_\uparrow(2) - \rho_\uparrow(1)\rho_\uparrow(2)/n_\uparrow\,, \tag{12}$$

and similarly for $\pi^{ind}_{\downarrow\downarrow}(1,2)$ for electrons with the same spins; or

$$\pi^{ind}_{\uparrow\downarrow}(1,2) = \rho_\uparrow(1)\rho_\downarrow(2)\,, \tag{13}$$

and similarly for $\pi^{ind}_{\downarrow\uparrow}(1,2)$ for electrons with the opposite spins. It was also suggested by McWeeny[11] that when two electrons are correlated, the pair density may be written as

$$\pi_{\uparrow\uparrow}(1,2) = \rho_\uparrow(1)\rho_\uparrow(2) + \rho_\uparrow(1)\rho_\uparrow(2) f_{\uparrow\uparrow}(1,2)\,, \tag{14}$$

and similarly for $\pi_{\downarrow\downarrow}(1,2)$ for electrons with the parallel spins, and

$$\pi_{\uparrow\downarrow}(1,2) = \rho_\uparrow(1)\rho_\downarrow(2)\,, \tag{15}$$

and similarly for $\pi_{\downarrow\uparrow}(1,2)$ for electrons with the opposite spins. In Eq. (15), $\rho_\uparrow(1)\rho_\downarrow(2) f_{\uparrow\downarrow}(1,2)$ is not included, because it accounts for the correlation between electrons of unlike spins. Such correlation is not considered in the HF theory nor in the Ξa method.

IV. EXCHANGE DENSITY AND THE THEORETICAL α PARAMETER

Assuming the particles are indistinguishable, then $\rho_i(1)$, the probability density of finding the ith particle at point 1, in Eq. (2) can be written[14] as $\rho_i(1)=\rho(1)/n$. The self-interaction term in Eq. (5) can then be written as

$$\tfrac{1}{2}\int \sum_i \rho_{i\uparrow}(1)\rho_{i\uparrow}(2)g_{12}d\tau_1 d\tau_2$$
$$=\frac{1}{2n_\uparrow}\int \rho_\uparrow(1)\rho_\uparrow(2)g_{12}d\tau_1 d\tau_2\,. \tag{16}$$

The same result can be achieved if $\sum_i \rho_{i\uparrow}(1)\rho_{i\uparrow}(2)$ is replaced by $\rho_\uparrow(1)\rho_\uparrow(2)-2\sum_{i<j}\pi^{\text{ind}}_{i\uparrow j\uparrow}(1,2)$, where $\pi^{\text{ind}}_{i\uparrow j\uparrow}(1,2)$ is defined as[11] the product of $\rho_{i\uparrow}(1)\rho_{j\uparrow}(2)$; and the relation $\pi^{\text{ind}}_{\uparrow\uparrow}(1,2)=n_\uparrow(n_\uparrow-1)\pi^{\text{ind}}_{i\uparrow j\uparrow}(1,2)$ is used.[14] Therefore Eq. (5) becomes

$$\left\langle\sum_{i<j} g_{12}\right\rangle=\tfrac{1}{2}\int \rho(1)\rho(2)g_{12}d\tau_1 d\tau_2$$
$$-\frac{1}{2n_\uparrow}\int \rho_\uparrow(1)\rho_\uparrow(2)g_{12}d\tau_1 d\tau_2$$
$$+\tfrac{1}{2}\int \rho_\uparrow(1)U^{ex}_\uparrow(1)d\tau_1+(\downarrow)\,. \tag{17}$$

By comparing to Eq. (9), the exchange potential can be written as (in a.u.):

$$U^{ex}_\uparrow(1)=\int r_{12}^{-1}\left(f_{\uparrow\uparrow}(1,2)+\frac{1}{n_\uparrow}\right)\rho_\uparrow(2)d\tau_2\,. \tag{18}$$

This exchange potential is produced by an exchange-charge density at position 2:

$$\rho^{ex}_\uparrow(2)=\left(f_{\uparrow\uparrow}(1,2)+\frac{1}{n_\uparrow}\right)\rho_\uparrow(2)\,, \tag{19}$$

$(f_{\uparrow\uparrow}(1,2)+1/n_\uparrow)$ is in fact the correlation factor[3] for like-spin electrons changing from the independent case, $\pi^{\text{ind}}_{\uparrow\uparrow}(1,2)$ to the correlated density function $\pi_{\uparrow\uparrow}(1,2)$. Furthermore, $f_{\uparrow\uparrow}(1,2)$ was shown[3] to be negative within the Fermi hole. In the case of the $X\alpha$ theory, the exchange-correlation charge density $\rho^{ext}_\uparrow(2)$ was shown to be $f_{\uparrow\uparrow}(1,2)\rho_\uparrow(2)$. Consequently, Eq. (19) means that when the self-interaction is evaluated exactly and the corresponding portion is removed from the exchange-correlation potential, the exchange-charge density, $\rho^{ex}_\uparrow(2)$, at position 2 will be reduced by $\rho_\uparrow(2)/n_\uparrow$ as compared to $\rho^{ex}_\uparrow(2)$. Now, from Eq. (14) and the conditional probability of finding an ↑ spin electron at position 2 when $\rho_\uparrow(1)$ is known, one has[3] $f_{\uparrow\uparrow}(1,1)\rho_\uparrow(1)=-\rho_\uparrow(1)$, so that the exchange-charge density at position 1 is

$$\rho^{ex}_\uparrow(1)=-\left(1-\frac{1}{n_\uparrow}\right)\rho_\uparrow(1)=-\sum_{j\neq i}\rho_{j\uparrow}(1)\,. \tag{20}$$

Following the same argument, but with the two electrons far apart, it follows that

$$\rho^{ex}_\uparrow(2)=0\,. \tag{21}$$

The above two equations show that the exchange charge density around a reference electron is equal to the charge density due to other electrons at the reference point. When an up-spin electron is far from the distribution, the probability of finding a similar electron at that position is zero.

By assuming that the Fermi hole is spherical[3] and is centered at position 1, and that the density varies linearly within the hole, then from Eqs. (20) and (21) one can obtain

$$\rho^{ex}_\uparrow(r)=-\left(1-\frac{1}{n_\uparrow}\right)\rho_\uparrow(1)\left(1-\frac{r}{r_0}\right), \tag{22}$$

where r is the distance between positions 1 and 2, and r_0 is the radius of the Fermi sphere.

Now, it is known[3] that the total amount of the *exchange-correlation charge*,

$$\int \rho^{exc}_\uparrow(2)d\tau_2=\int \rho_\uparrow(2)f_{\uparrow\uparrow}(1,2)d\tau_2\,,$$

removed from the charge distribution is -1 when the reference electron at position 1 is considered. Therefore from Eq. (19) one can show that the amount of the *exchange charge*, $\int\rho^{ex}_\uparrow(2)d\tau_2$, is *zero* since $\int(1/n_\uparrow)\rho_\uparrow(2)d\tau_2=1$. It is then mathematically impossible to determine r_0 from the condition $\int\rho^{ex}_\uparrow(2)d\tau_2=0$ with $\rho^{ex}_\uparrow$ defined by Eq. (22) unless a nonlinear relation between $\rho^{ex}_\uparrow$ and r is assumed. However the Fermi hole radius, r_0, defined by $\rho^{exc}_\uparrow$ in Ref. 3 is not altered in the present work provided the same definition is taken. The Fermi hole does not depend on whether or not the self-interaction exchange is considered explicitly, consequently r_0 is determined by

$$\int_0^{r_0}\rho^{exc}_\uparrow(r)d\tau=-1\,. \tag{23}$$

It is obvious that according to the definition by Gopinathan, Whitehead, and Bogdanovic,[3] and Eq. (19), one can obtain

$$\rho^{exc}_\uparrow(r)=\rho^{ex}_\uparrow(r)-\frac{1}{n_\uparrow}\rho_\uparrow(1)$$
$$=-\left[\frac{1}{r_0}\rho_\uparrow(1)\left(\frac{1}{n_\uparrow}-1\right)r+\rho_\uparrow(1)\right]. \tag{24}$$

Equation (24) is based on a further assumption[3] that the electron density is slowly varying around the center, the point 1, so that $\rho_\uparrow(2)/n_\uparrow$ in Eq. (19) may be replaced by $\rho_\uparrow(1)/n_\uparrow$.

Now Eqs. (23) and (24), give a result similar to that in Ref. 3:

$$r_0=[\pi(1/n_\uparrow+1/3)\rho_\uparrow(1)]^{-1/3}\,. \tag{25}$$

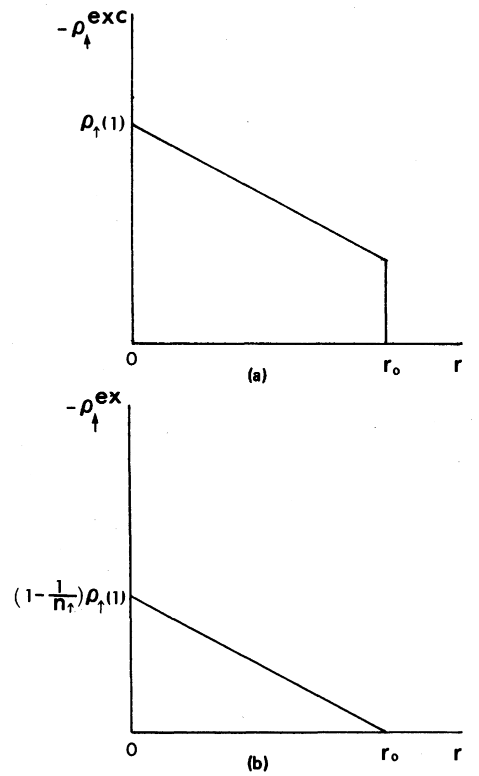

FIG. 1. (a) The schematic exchange-correlation charge distribution (taken from Ref. 3). (b) The schematic exchange-charge distribution (present work).

It is worth mentioning that since r_0 is defined as in Eq. (25) in the present work, then dependence of $\rho_\uparrow^{ex}$ on r, and $\rho_\uparrow^{exc}$ on r are parallel. The difference between their density distribution function (Fig. 1) is only a constant shift, $\rho_\uparrow(1)/n_\uparrow$. The exchange-charge potential at the center of the sphere due to the exchange-charge density will be

$$U_\uparrow^{ex}(1)=4\pi\int_0^{r_0}\rho_\uparrow^{ex}(r)r\,dr\,.$$

The exchange potential in Ry units will be

$$U_\uparrow^{ex}(1)=-\frac{4}{3}\pi^{1/3}\left(1-\frac{1}{n_\uparrow}\right)\left(\frac{1}{n_\uparrow}+\frac{1}{3}\right)^{-2/3}\rho_\uparrow^{1/3}(1)\,. \tag{26}$$

Consequently, to generate theoretical $a_{t\uparrow}$ similar to the $\alpha_{t\uparrow}$ it is necessary to replace $\rho_{t\uparrow}(1)$ by $\rho_\uparrow(1)/n_\uparrow$ in Eq. (6), and compare with Eq. (26):

$$a_{t\uparrow}=\frac{4}{27}\left(\frac{4\pi^2}{3}\right)^{1/3}\left(\frac{1}{n_\uparrow}+\frac{1}{3}\right)^{-2/3},\quad(n_\uparrow\neq 1)\,. \tag{27}$$

When $n_\uparrow=1$, $U_\uparrow^{ex}(1)=0$, which means that there is no exchange term, and, therefore, $a_{t\uparrow}$ is undefined. The average theoretical a value is defined as

$$a_{ta}=(n_\uparrow a_{t\uparrow}+n_\downarrow a_{t\downarrow})/(n_\uparrow+n_\downarrow)\,. \tag{28}$$

The value $a_{t\uparrow}$ is related to $\alpha_{t\uparrow}$, the theoretical α value derived in the $X\alpha$ theory by

$$a_{t\uparrow}=[n_\downarrow/(n_\uparrow+2)]\alpha_{t\uparrow}\,.$$

For large $n_\uparrow$ values $a_{t\uparrow}\simeq\alpha_{t\uparrow}$. This can be justified by looking at Eq. (6) where the second term, $\rho_\uparrow(1)/n_\uparrow$, in the brackets is negligible compared to the first term for large $n_\uparrow$ values. On the other hand, $a_{t\uparrow}$ is significantly different from $\alpha_{t\uparrow}$ for small $n_\uparrow$'s.

V. RESULTS

The calculated values for $a_{t\uparrow}$ and $a_{t\downarrow}$ and the average values a_{ta} for atoms are given in Table I. The one-electron energies $-\epsilon i$ and the total energy $-E$ calculated for Mn^{2+} ($Ar\,3d^5$) by the Ξ method are given in Table II. The corresponding core-spin density of Mn^{2+} with parameters a_t and α_t are plotted in Fig. 4. Results of $-\epsilon i$ and $-E$ for Ne, Ar, and Cu^+ are given in Table III.

VI. DISCUSSION

From Table I, it is seen that values of a_t and a_{ta} within the Ξa scheme increase with Z. The values are significantly smaller than α_t and α_{ta}, the theoretical parameters[3] derived within the $X\alpha$ theory. The values of a_{ta} are closer to the a_{HF} values[7] (Fig. 2). Li: $a_{ta}=0.263\,31$, $a_{HF}=0.322\,37$, and $\alpha_{HF}=0.781\,47$; Ar: $a_{ta}=0.600\,57$, $a_{HF}=0.479\,16$, and $\alpha_{HF}=0.721\,77$. The trend of a_{ta} follows essentially that of a_{HF}; the trend of α_{ta} is similar to the trend of α_{HF}; but a_{ta} or a_{HF} has the opposite trend to α_{ta} or α_{HF}. The values of a_{ta} also support the argument in Sec. IV that the difference between a_{ta} and α_{ta} is more pronounced for light atoms, decreasing for heavier atoms.

A plot of $a_{t\uparrow}$ or $a_{t\downarrow}$ versus the number of electrons (Table I) clearly indicates its nonlinearity. The variation in $a_{t\uparrow}$, $a_{t\downarrow}$, and a_{ta} follows a similar pattern opposite to that in $\alpha_{t\uparrow}$, $\alpha_{t\downarrow}$, and α_{ta} observed in Ref. 3. The slope of $\partial a_{ta}/\partial Z$ is discontinuous at the beginning of every subshell. The breaks are significant for small atoms where the change in a_{ta} is large. Following Hund's rule that determines the ground-state configuration of atoms, for the first half subshell $a_{t\uparrow}$ is increased nonlinearly as the number of up-spin electrons increases (Fig. 3), while $a_{t\downarrow}$ is kept constant because the number of down-spin electrons remains constant. For the remaining half subshell, $a_{t\uparrow}$ is a constant because of the constant $n_\uparrow$, but $a_{t\downarrow}$ is increased nonlinearly as the number of down-spin electrons increases. The value of a_{ta} within the subshell is therefore an appropriate average

TABLE I. Theoretical exchange parameter $a_{t\uparrow}$ or $a_{t\downarrow}$ and the average value $a_{ta} = (n_\uparrow a_{t\uparrow} + n_\downarrow a_\downarrow)/(n_\uparrow + n_\downarrow)$ as a function of the number of the electrons.

$n_\uparrow$ or $n_\downarrow$	$a_{t\uparrow}$ or $a_{t\downarrow}$	Z	Atom configuration		$n_\uparrow$	$n_\downarrow$	a_{ta}	Z	Atom configuration		$n_\uparrow$	$n_\downarrow$	a_{ta}
2	0.394 969							51	Sb	Kr $4d^{10}5s^25p^3$	27	24	0.675 558
3	0.458 321	3	Li	He $2s^1$	2	1	0.263 313	52	Te	Kr $4d^{10}5s^25p^4$	27	25	0.676 463
4	0.500 992	4	Be	He $2s^2$	2	2	0.394 969	53	I	Kr $4d^{10}5s^25p^5$	27	26	0.677 340
5	0.531 834	5	B	He $2s^22p^1$	3	2	0.432 980	54	Xe	Kr $4d^{10}5s^25p^6$	27	27	0.678 190
6	0.555 216	6	C	He $2s^22p^2$	4	2	0.465 651	55	Cs	Xe $6s^1$	28	27	0.679 015
7	0.573 573	7	N	He $2s^22p^3$	5	2	0.492 730	56	Ba	Xe $6s^2$	28	28	0.679 810
8	0.588 376	8	O	He $2s^22p^4$	5	3	0.504 267	57	La	Xe $5d^16s^2$	29	28	0.680 581
9	0.600 570	9	F	He $2s^22p^5$	5	4	0.518 127	58	Ce	Xe $4f^26s^2$	30	28	0.681 330
10	0.610 793	10	Ne	He $2s^22p^6$	5	5	0.531 834	59	Pr	Xe $4f^36s^2$	31	28	0.682 057
11	0.619 488	11	Na	Ne $3s^1$	6	5	0.544 588	60	Nd	Xe $4f^46s^2$	32	28	0.682 763
12	0.626 974	12	Mg	Ne $3s^2$	6	6	0.555 216	61	Pm	Xe $4f^56s^2$	33	28	0.683 449
13	0.633 488	13	Al	Ne $3s^23p^1$	7	6	0.565 101	62	Sm	Xe $4f^66s^2$	34	28	0.684 115
14	0.639 208	14	Si	Ne $3s^23p^2$	8	6	0.574 164	63	Eu	Xe $4f^76s^2$	35	28	0.684 763
15	0.644 272	15	P	Ne $3s^23p^3$	9	6	0.582 429	64	Gd	Xe $4f^75d^16s^2$	36	28	0.685 392
16	0.648 785	16	S	Ne $3s^23p^4$	9	7	0.588 759	65	Tb	Xe $4f^85d^16s^2$	36	29	0.685 983
17	0.652 833	17	Cl	Ne $3s^23p^5$	9	8	0.594 832	66	Dy	Xe $4f^{10}6s^2$	35	31	0.686 547
18	0.656 486	18	Ar	Ne $3s^23p^6$	9	9	0.600 570	67	Ho	Xe $4f^{11}6s^2$	35	32	0.687 112
19	0.659 797	19	K	Ar $4s^1$	10	9	0.605 951	68	Er	Xe $4f^{12}6s^2$	35	33	0.687 663
20	0.662 813	20	Ca	Ar $4s^2$	10	10	0.610 793	69	Tm	Xe $4f^{13}6s^2$	35	34	0.688 201
21	0.665 572	21	Sc	Ar $3d^14s^2$	11	10	0.615 348	70	Yb	Xe $4f^{14}6s^2$	35	35	0.688 725
22	0.668 105	22	Ti	Ar $3d^24s^2$	12	10	0.619 619	71	Lu	Xe $4f^{14}5d^16s^2$	36	35	0.689 237
23	0.670 439	23	V	Ar $3d^34s^2$	13	10	0.623 621	72	Hf	Xe $4f^{14}5d^26s^2$	37	35	0.689 736
24	0.672 597	24	Cr	Ar $3d^54s^1$	15	9	0.627 884	73	Ta	Xe $4f^{14}5d^36s^2$	38	35	0.690 223
25	0.674 597	25	Mn	Ar $3d^54s^2$	15	10	0.630 880	74	W	Xe $4f^{14}5d^46s^2$	39	35	0.690 698
26	0.676 457	26	Fe	Ar $3d^64s^2$	15	11	0.633 786	75	Re	Xe $4f^{14}5d^56s^2$	40	35	0.691 162
27	0.678 190	27	Co	Ar $3d^74s^2$	15	12	0.636 584	76	Os	Xe $4f^{14}5d^66s^2$	40	36	0.691 608
28	0.679 810	28	Ni	Ar $3d^84s^2$	15	13	0.639 265	77	Ir	Xe $4f^{14}5d^76s^2$	40	37	0.692 044
29	0.681 326	29	Cu	Ar $3d^{10}4s^1$	15	14	0.641 827	78	Pt	Xe $4f^{14}5d^96s^1$	40	38	0.692 470
30	0.682 749	30	Zn	Ar $3d^{10}4s^2$	15	15	0.644 272	79	Au	Xe $4f^{14}5d^{10}6s^1$	40	39	0.692 886
31	0.684 087	31	Ga [a]	Ar $3d^{10}4s^24p^1$	16	15	0.646 601	80	Hg	Xe $4f^{14}5d^{10}6s^2$	40	40	0.693 294
32	0.685 348	32	Ge	Ar $3d^{10}4s^24p^2$	17	15	0.648 820	81	Tl	Xe $4f^{14}5d^{10}6s^26p^1$	41	40	0.693 693
33	0.686 537	33	As	Ar $3d^{10}4s^24p^3$	18	15	0.650 934	82	Pb	Xe $4f^{14}5d^{10}6s^26p^2$	42	40	0.694 083
34	0.687 661	34	Se	Ar $3d^{10}4s^24p^4$	18	16	0.652 862	83	Bi	Xe $4f^{14}5d^{10}6s^26p^3$	43	40	0.694 464
35	0.688 725	35	Br	Ar $3d^{10}4s^24p^5$	18	17	0.654 712	84	Po	Xe $4f^{14}5d^{10}6s^26p^4$	43	41	0.694 835
36	0.689 734	36	Kr	Ar $4d^{10}4s^24p^6$	18	18	0.656 486	85	At	Xe $4f^{14}5d^{10}6s^26p^5$	43	42	0.695 198
37	0.690 692	37	Rb	Kr $5s^1$	19	18	0.658 186	86	Rn	Xe $4f^{14}5d^{10}6s^26p^6$	43	43	0.695 553
38	0.691 602	38	Sr	Kr $5s^2$	19	19	0.659 797	87	Fr	Rn $7s^1$	44	43	0.695 901
39	0.692 468	38	Y	Kr $4d^15s^2$	20	19	0.661 344	88	Ra	Rn $7s^2$	44	44	0.696 241
40	0.693 294	40	Zr	Kr $4d^25s^2$	21	19	0.662 829	89	Ac	Rn $6d^17s^2$	45	44	0.696 574
41	0.694 082	41	Nb	Kr $4d^45s^1$	23	18	0.664 313	90	Th	Rn $6d^27s^2$	46	44	0.696 901
42	0.694 834	42	Mo	Kr $4d^55s^1$	24	18	0.665 692	91	Pa	Rn $5f^26d^17s^2$	47	44	0.697 221
43	0.695 553	43	Tc	Kr $4d^55s^2$	24	19	0.666 941	92	U	Rn $5f^36d^17s^2$	48	44	0.697 535
44	0.696 241	44	Ru	Kr $4d^75s^1$	24	20	0.668 150	93	Np	Rn $5f^57s^2$	49	44	0.697 843
45	0.696 900	45	Rh	Kr $4d^85s^1$	24	21	0.669 319	94	Pu	Rn $5f^67s^2$	50	44	0 698 144
46	0.697 532	46	Pd	Kr $4d^{10}$	23	23	0 670 439	95	Am	Rn $5f^77s^2$	51	44	0.698 440
47	0.698 139	47	Ag	Kr $4d^{10}5s^1$	24	23	0.671 541	96	Cm	Rn $5f^76d^17s^2$	52	44	0.698 730
48	0.698 721	48	Cd	Kr $4d^{10}5s^2$	24	24	0.672 597	97	Bk	Rn $5f^86d^17s^2$	52	45	0.699 011
49	0.699 281	49	In	Kr $4d^{10}5s^25p^1$	25	24	0.673 617	98	Cf	Rn $5f^{10}7s^2$	51	47	0.699 283
50	0.699 819	50	Sn	Kr $4d^{10}5s^25p^2$	26	24	0.674 604	99	Es	Rn $5f^{11}7s^2$	51	48	0.699 554
51	0.700 337							100	Fm	Rn $5f^{12}7s^2$	51	49	0.699 820
52	0.700 837							101	Md	Rn $5f^{13}7s^2$	51	50	0.700 081
53	0.701 318							102	No	Rn $5f^{14}7s^2$	51	51	0.700 337
54	0.701 782							103	Lr	Rn $5f^{14}6d^17s^2$	52	51	0.700 590
55	0.702 230												

[a] The values of a_{ta} for $Z > 30$ are in error because spin-orbit coupling invalidates the $n_\uparrow$ and $n_\downarrow$ separation. This failure is also true of the previously tabulated α_{ta} of the $X\alpha$ theory (Ref. 3). The a_{HF} (Ref. 6) and α_{HF} (Ref. 7) also suffer this inaccuracy since they are developed to make $\langle E_{\Xi a}\rangle$ or $\langle E_{X\alpha}\rangle = E^{\mathrm{HF}}_{\mathrm{lim}}$, and spin-orbit coupling is not present in the nonrelativistic Hartree-Fock Hamiltonian. This criticism is not true of parameterizations which equate a or α to experimental energies (Ref. 9).

TABLE II. One-electron energies $-\epsilon_i$ and the total energy $-E$ for the ground state of Mn^{2+} (Ar $3d^5$) by SPHF and Ξa methods, in Ry.

Orbital	SPFH (Ref. 12)	$\Xi a(a_t)$[a]	Diff.[c]	$\Xi a(\alpha_t)$[b]	Diff.[c]
$1s\uparrow$	482.369	482.304	0.065	480.774	1.595
$1s\downarrow$	482.374	482.111	0.263	480.797	1.577
$2s\uparrow$	59.633	60.359	−0.726	59.359	0.274
$2s\downarrow$	59.363	59.798	−0.435	59.094	0.269
$2p\uparrow$	51.044	49.319	1.725	52.303	−1.259
$2p\downarrow$	50.781	48.907	1.874	52.144	−1.363
$3s\uparrow$	9.323	9.425	−0.102	8.991	0.332
$3s\downarrow$	8.494	8.708	−0.214	8.320	0.174
$3p\uparrow$	6.753	6.395	0.358	6.749	0.004
$3p\downarrow$	5.745	5.373	0.372	6.099	−0.354
$3d\uparrow$	2.576	2.276	0.300	3.093	−0.517
$-E_{\text{tot}}$	2298.222[d]	2307.019	−8.797	2313.891	−15.669

[a] Calculated using Eq. (1) with $a_{t\uparrow} = 0.639\,21$ and $a_{t\downarrow} = 0.600\,57$ [Eq. (24)].
[b] Calculated using Eq. (1) with $\alpha_{t\uparrow} = 0.730\,52$ and $\alpha_{t\downarrow} = 0.734\,03$ by Gopinathan (Refs. 1 and 3).
[c] The difference between the SPHF and the energy given in the preceding column.
[d] Averaged total energy over the states with different possible magnetic quantum numbers.

TABLE III. One-electron energies $-\epsilon_i$ and the total energy $-E$ for the ground state of Ne, Ar, and Cu^+ by HF and Ξa methods, in Ry.

Orbital		HF[a]	$\Xi a(a_{ta})$[b]	Diff.[d]	$\Xi a(\alpha_{ta})$[c]	Diff.[d]
Ne	$1s$	65.5455	65.5456	−0.0001	65.3954	0.1501
	$2s$	3.8610	4.0658	−0.2048	4.5557	−0.6947
	$2p$	1.7010	1.3574	0.3436	1.4054	0.2956
$-E^{e}_{\text{tot}}$	*e*	257.0942	257.7638	−0.6696	259.8514	−2.7572
		(257.855)				
Ar	$1s$	237.2213	237.0765	0.1448	237.0887	0.1326
	$2s$	24.6449	25.0113	−0.3664	25.6437	−0.9988
	$2p$	19.1435	17.9787	1.1648	18.0200	1.1235
	$3s$	2.5550	2.6992	−0.1442	2.8904	−0.3354
	$3p$	1.1823	0.9653	0.2170	0.9962	0.1861
$-E^{e}_{\text{tot}}$	*e*	1053.6350	1057.4771	−3.8421	1061.7662	−8.1312
		(1055.098)				
Cu^+	$1s$	658.22	658.09	0.13	656.18	2.04
	$2s$	82.26	83.12	−0.86	81.66	0.60
	$2p$	71.86	69.78	2.08	73.08	−1.22
	$3s$	10.65	10.86	−0.21	10.07	0.58
	$3p$	7.28	6.94	0.34	7.11	0.17
	$3d$	1.62	1.38	0.24	2.06	−0.44
$-E^{e}_{\text{tot}}$	*e*	3277.46	3289.91	−12.45	3292.78	−15.32

[a] E. Clementi, IBM J. Res. Dev. Suppl. 9, 2 (1965).
[b] Calculated by Eq. (1) with $a_\uparrow$ and $a_\downarrow$ given by Eq. (24).
[c] Calculated by Eq. (1) with (Ref. 3) $\alpha_\uparrow$ and $\alpha_\downarrow$.
[d] The difference between the HF energy and the energy given in the preceding column.
[e] J. B. Mann, LASL Report No. LA-3690 (1967) (unpublished). Values in brackets are the nonrelativistic exact energy quoted by Keller and Gázquez, Phys. Rev. A 20, 1289 (1979).

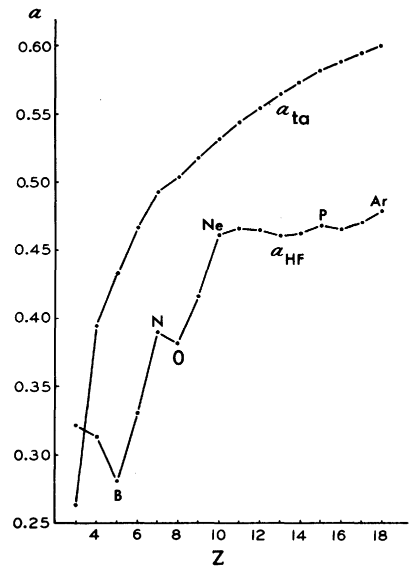

FIG. 2. Comparison of a_{ta} and a_{HF} (Ref. 7) in the Ξa method.

of a nonlinearly varying quantity and a constant, and is approximately linear.

Consequently, the modified model used to develop the a_t must be essentially correct, and should be valid in atoms, molecules, and solids.[3]

The Ξa one-electron energies using a_t (Eq. 27) are much better than the $X\alpha$ results,[1] for example, in the case of Mn^{2+} the $X\alpha$ results are: $1s_{\uparrow} = -469.59$ Ry., $2s_{\uparrow} = -55.20$ Ry., $3d_{\uparrow} = -1.93$ Ry., etc, they are far away from the spin-polarized HF(SPHF) results,[13] whereas the Ξa results (Table II) are very close to the SPHF,[15] ones. Within the Ξa scheme, results using a_t do differ from those using α_t, Table II, however, there is no significant improvement as compared to the SPHF results.[16,17,18] The total energy $\langle E_{\Xi a}\rangle$ with a_t for Mn^{2+} is lowered by -8.797 Ry from the SPHF $\langle E\rangle$, whereas $\langle E_{\Xi a}\rangle$ with α_t is lowered by -15.669 Ry. Thus $\langle E_{\Xi a}\rangle$ with a_t is significantly closer to the corresponding HF results and closer to the nonrelativistic exact energy. These conclusions also apply to Ne, Ar, and Cu^+ (Table III) for closed shell atoms.

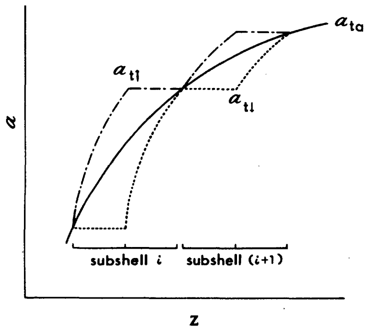

FIG. 3. Variation of $a_{t\uparrow}$, $a_{t\uparrow}$, and a_{ta} in atomic subshells (purely schematic).

The Ar core-spin densities (Fig. 4) in Mn^{2+} calculated using a_t in the Ξa method are closer to the SPHF results than those calculated using α_t for r from 0.1 to 0.2 a.u. and from 1.4 to 2.1 a.u.; but between 0.4 and 0.8 a.u. and 0.95 to 1.3 a.u., α_t gives a closer fit, but both calculations are off from the SPHF results.

The polarization of the s-electronic charge density causes a nonvanishing spin density at the nucleus. It gives rise to a nonzero Fermi contact term for systems like Mn^{2+} (see Fig. 4). Results of the present work using Ξa method with a_t for Mn^{2+} is compared to that[1] using α_t. The quantity is defined as[16]

$$\chi = \frac{4}{n_{\uparrow} - n_{\downarrow}} \sum_{n} \left[\rho_{n_s\uparrow}(0) - \rho_{n_s\downarrow}(0)\right]. \qquad (30)$$

The calculated χ in the present work, $\Xi a(a_t)$, is -2.31 a.u., and that[1] of $\Xi a(\alpha_t)$ is -4.54 a.u. The experimental measurement by Abragam *et al.*[18] is -3.10 a.u. According to Watson and Freeman[16] the relativistic correction would increase the theoretical values by several percent, therefore the present result with a_t will be even closer to the experimental and that using α_t will be further off from the experimental value after the correction.

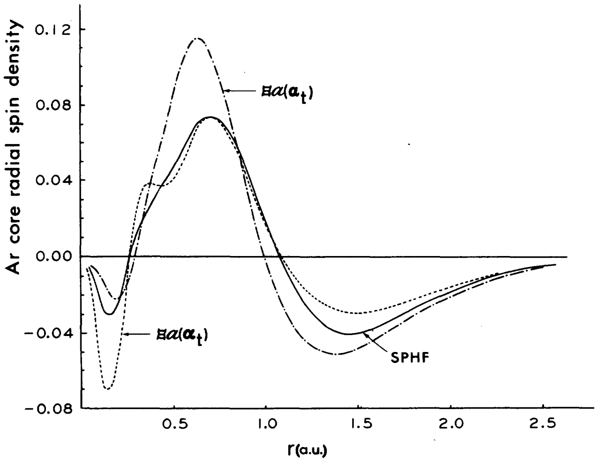

FIG. 4. The Ar core spin-density distribution in Mn^{2+} by the Ξa method with $a_{t(\uparrow \text{ and } \uparrow)}$ and $a_{t(\uparrow \text{ and } \uparrow)}$ values compared to the result with the SPHF calculations.

TABLE IV. Fermi contact term in Mn^{2+}.

	SPHF[a] (Ref. 13)	$X\alpha$ (Ref. 12)	$X\alpha(\xi)$ (Ref. 12)	$\Xi a(\alpha_t)^1$	$\Xi a(a_t)$	Expt. (Ref. 15)
χ_{1s}	−0.191	−0.158	+6.527	+0.300	−4.609	
χ_{2s}	−7.154	−5.376	−3.520	−8.046	−1.582	
χ_{3s}	+3.218	+2.004	+2.758	+3.209	+3.879	
χ_{total}	−4.127	−3.530	+5.765	−4.537	−2.312	−3.10

[a] Varies haphazardly with size of basis set (Ref. 13).

CONCLUSION

The theoretical a_t for the Ξa method have been established and calculated, from a Fermi hole formulation. The a_t have the opposite trend with Z to the α_t of the $X\alpha$ method, but a similar pattern of dependence on the $n_\uparrow$ and $n_\downarrow$, including discontinuity at the beginning of every subshell and linearity of a_{t_a} with Z within a subshell. The Ξa one-electron energies using a_{t_a} but much better than the $X\alpha$ one electron energies using α_{t_a} or α_{HF}. The $\langle E\Xi a\rangle$ is improved when a_{t_a}. The Ar core spin densities in Mn^{2+} have essentially the same shape as from SPHF. The Fermi contact total $\chi(\Xi a)$ with a_t is significantly closer to experimental than the $\chi(\Xi a)$ with α_t (Table IV).

ACKNOWLEDGMENT

This research was supported by the NSERC (Canada). The McGill Computing Centre provided facilities on their Amdahl/V7 computer.

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