PHYSICAL REVIEW A VOLUME 8, NUMBER 3 SEPTEMBER 1973

Correction Functions to Hartree-Fock Orbitals Derived from Correlated Wave Functions for He-, Li-, and Be-Like Ions

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(Received 31 October 1972)

Using energetically reliable configuration-interaction and Hartree-Fock wave functions for He(^1S state)-, Li(^2S and ^2P states)-, and Be(^1S state)-like ions, we applied the method of successive partial orthogonalizations to determine orbital correction f functions (introduced by Sinanoğlu in his many-electron theory) which arise from electron-correlation effects. The addition of an f function to an appropriate Hartree-Fock orbital gives an improved orbital representation as far as the one-particle density is concerned. Hence, changes in the corresponding radial density distributions were obtained and their characteristics and Z-dependent trends were rationalized in terms of the fluctuation potential proposed by Sinanoğlu. For He-like ions, changes in the K-shell density showed strong split-shell characteristics. This also held for the K shell of the Be-like ions; however, as Z increased, the perturbative influence of the L shell became more apparent. In the L shells for the Be-like systems, because of the $2s$-$2p$ near degeneracy, angular correlation is relatively high and, consequently, the fluctuation potential gave rise to an f effect which produced an over-all density contraction towards the nucleus. These density changes for the $2s$ electrons are considerably larger than the changes associated with the K shells. At a low-Z value for Li(^2S)-like ions, spin polarization of the K shell owing to the unpaired L-shell electron is small, the changes in density being predominantly intrashell effects. For high Z, spin-polarization effects are greatly increased. The L-shell electron in the ^2S state experiences only an intershell fluctuation potential—which is purely attractive. For this state, the density changes for the outer electron are about 25% of the L-shell effect in the Be(^1S)-like ion and they are almost four times larger than the corresponding K-shell effect. In the Li(^2P) series of ions, the K-shell density shifts due to the f functions are dominated by intrashell effects for $Z=3$ whereas, at higher-Z values, an exchange effect becomes the major influence. Our results for the L shell appear less satisfactory and suggest that a further such study of the excited state of these ions would be of interest.

I. INTRODUCTION

The energy improvement arising from electron correlation in a many-electron system is expressed with respect to the energy of the Hartree-Fock (HF) wave function. The influence of electron correlation on other physical properties can be similarly defined. Starting from the HF wave function, Sinanoğlu has reformulated the exact wave function in such a way that correlation effects are systematically separated into several parts: f_i functions—corrections to the ith HF orbital; U_{ij} functions—electron-pair correlations; and also higher many-electron correlation terms such as U_{ijk}, U_{ijkl}, ...[1] In the present article we study the functions f_i derived from accurate configuration-interaction (CI) wave functions for the ground state of a series of two-, three-, and four-electron atomic ions. For the three-electron series, f_i functions are also derived for the first excited state.

The correlation effect in a many-electron system is due to the residual fluctuation potentials which remain between electrons after the average long-range Coulomb repulsions have been accounted for by the HF treatment. The orbital correction parts of the correlation effect—the f_i functions—arise from averaging all the two-, three-, etc. particle correlations over all electrons involved except the ith electron. In terms of CI nomenclature the f_i functions depend on the presence of configurations in the wave function which arise from single excitations within a basis set of HF orbitals. The omission of such substitutions in CI calculations is equivalent to the neglect of the f_i functions in Sinanoğlu's presentation of many-electron theory. Although Sinanoğlu and Tuan[2] have shown that f_i functions make only negligible contributions to the total energy, it is now known that these correction functions can have significance when determining certain properties other than the energy. Stanton[3] suggested that orbital corrections could be important when evaluating electron densities—particularly in regions close to the nucleus. Such changes would influence, for example, the calculation of nuclear magnetic shielding properties, Fermi contact potentials, etc. In a correlation study of the molecular ion H_3^+, Duben and Lowe[4] have shown that singly substituted configurations cause a small contraction of the electron density similar to that arising from initial atomic-molecular formation. CI calculations by Bender and Davidson[5] and by Grimaldi[6] for the electric dipole moment of several diatomic molecules were also found to be influenced by the presence of single excitations in the wave functions. Recently, coherent and, in particular, incoherent x-ray scattering factors have been found to be sensitive to such correlation effects.[7,8] Finally, single substitutions within a CI wave function become of particular importance in systems like Be which possess low-lying formally vacant orbitals. Early calculations by Watson[9] for Be-like ions revealed that correlation effects produced some interesting shifts in the spatial distribution of the 2*s* orbitals.

II. CALCULATION OF *f* FUNCTIONS

The *f* functions reported here are derived from the CI wave functions of Weiss.[10] For the two-electron atomic ions, Weiss expressed the ground-state wave function $\Psi(^1S)$ as the interaction of 35 configurations using a basis set of Slater-type orbitals (STO's) extending as far as 5*g* orbitals. This basis set was also used to form the 45-term CI wave functions for the ^2S and ^2P states of the Li-like ions. Finally, Weiss used a basis set involving orbitals up to 4*f* to construct a 55-term wave function for the ground states of the four-electron series. In each instance, partial optimization of orbital exponents was carried out along with a complete determination of all configuration coefficients. The calculated energies were in very good agreement with the "exact" results, and, in addition, as can be seen by inspection, the wave functions contain a significant number of those configurations[11] needed for the description of the *f* functions. This suggests that, in general, the Weiss wave functions should provide a realistic representation of the true wave functions in order to determine and examine the characteristics of *f* functions. Such an examination requires a knowledge of the HF wave functions: it was most convenient, computationally, to use the 12-term analytical functions of Roothaan, Sachs, and Weiss.[12] For H^-, we used the five-term analytical HF orbitals of Curl and Coulson.[13] Such wave functions are quoted by their authors to be an accurate representation of the true HF orbitals to at least four decimal places within a point-by-point comparison.

Following Sinanoğlu, the exact wave function Ψ for an N-electron closed-shell system can be written as

$$\Psi(1,2,\ldots,N)=c\mathfrak{A}\left[(\phi_1,\phi_2,\ldots,\phi_i,\ldots,\phi_N)\left(1+\sum_i^N\frac{f_i}{\phi_i}+\frac{1}{\sqrt{(2!)}}\sum_{i>j}^N\frac{U_{ij}}{\phi_i\phi_j}+\frac{1}{\sqrt{(3!)}}\sum_{i>j>k}^N\frac{U_{ijk}}{\phi_i\phi_j\phi_k}+\cdots\right)\right], \tag{1}$$

where $\mathfrak{A}$ is the antisymmetrizer, $(\phi_1,\phi_2,\ldots,\phi_l,\ldots,\phi_N)$ is a product of N normalized HF spin-orbitals ϕ and $\langle f_i|\phi_l\rangle=0$, $\langle U_{ij}|\phi_l\rangle=0$, $\langle U_{ijk}|\phi_l\rangle=0$, etc., for $l=1,2,\ldots,N$. Sinanoğlu's formulation uses an intermediate normalization condition $\langle\Psi|\mathrm{HF}\rangle=1$, whereas our introduction of the constant c ensures that $\langle\Psi|\Psi\rangle=1$. From (1), the scalar product of Ψ with the simple product function $[\phi_1(1)\cdots\phi_{i-1}(i-1)\phi_{i+1}(i+1)\cdots\phi_N(N)]$ gives

$$\langle\Psi|\phi_1(1)\cdots\phi_{i-1}(i-1)\phi_{i+1}(i+1)\cdots\phi_N(N)\rangle=[c/\sqrt{(N!)}][\phi_i(i)+f_i(i)]. \tag{2}$$

But

$$\langle\Psi|\phi_1(1)\cdots\phi_{i-1}(i-1)\phi_i(i)\phi_{i+1}(i+1)\cdots\phi_N(N)\rangle=c/\sqrt{(N!)}$$

and hence

$$f_i(i)=\frac{\langle\Psi|\phi_1(1)\cdots\phi_{i-1}(i-1)\phi_{i+1}(i+1)\cdots\phi_N(N)\rangle}{\langle\Psi|\phi_1(1)\cdots\phi_N(N)\rangle}-\phi_i(i)\,. \tag{3}$$

Sinanoğlu refers to this technique as the method of successive partial orthogonalizations (MSPO).[14] The *f* functions were evaluated by using the Weiss wave functions for Ψ and the analytical HF orbitals mentioned above: The results are expressed as corrections to the normalized HF radial component $R(r)$.

Although, for purposes of discussion, the presentation of all results would be helpful, space limitations oblige us to keep diagrams and tables to a minimum. In Fig. 1 we show the $f(r)$ curves for the 1*s* orbitals for selected two-electron ions, and in Fig. 2 similar curves are shown for the 1*s* and 2*s* orbitals for Be.[15] For reference, Table I contains a comparison of $f(r)$ and $R(r)$ evaluated at the nucleus for all orbitals and ions examined here. Also we quote values for $\|f\|$ —the norm of $f(r)$. When an orbital-correction function is added to the corresponding HF orbital, it produces an approximate representation of the principal natural orbital[16-18] and also of the corresponding Brueckner orbital.[14,1(a)] The relationship between natural orbitals and Brueckner orbitals has been discussed by Smith and Kutzelnigg,[19] and these authors have shown that the single determinant, whose overlap with the exact wave function is a maximum, is composed of Brueckner orbitals or, as they are sometimes called, "best-overlap" orbitals. Consequently, the redistribution of the HF one-particle radial density $D(r)$ due to the influence of $f(r)$ is, to first order, given by the expression $2r^2R(r)f(r)$. These radial difference densities are denoted by Δ along with a reference

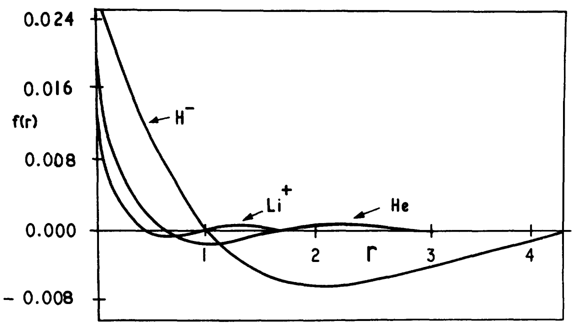

FIG. 1. Orbital-correction function $f_{1s}(r)$ for some He(^1S)-like ions.

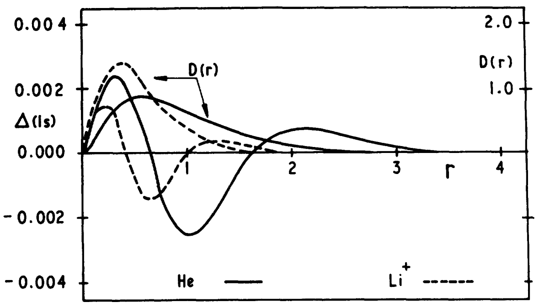

FIG. 3. HF orbital radial distribution $D(r)$ and the associated Δ curve for the ^1S state of He and Li$^+$.

to the spin-orbital under examination. We note that, by definition,

$$\int_0^\infty D(r)\,dr = 1 \quad\text{and}\quad \int_0^\infty \Delta(r)\,dr = 0\,.$$

In Fig. 3 we show $\Delta(1s\alpha) \equiv \Delta(1s\beta)$ and $D(r)$ for He and Li$^+$ in the ^1S state. Figures 4 and 5 show the difference densities and the $D(r)$ curves for the 1s and 2s orbitals, respectively, for Be(^1S) and C^{++}(^1S). Figures 6 and 7 illustrate some typical results for the ground state and first excited state of the three-electron atomic ion series.

III. DISCUSSION

The addition of $f(r)$ to the HF radial function $R(r)$ provides an improved one-particle orbital representation. For the He-, Li-, and Be-like isoelectronic series of atomic ions, we have obtained redistributions in the HF radial density $D(r)$ due to $f(r)$. The characteristics and Z-dependent trends of the Δ curves are now examined and rationalized in terms of the fluctuation potential introduced by Sinanoğlu.[20]

The fluctuation potential is that part of the instantaneous repulsion between two electrons which remains after the average, long-range Coulomb repulsions have been accounted for by the HF treatment. For a He-like system with the two electrons i and j initially occupying HF spin-orbitals ϕ_i and ϕ_j, the fluctuation potential m_{ij} is defined as

$$m_{ij} = \frac{1}{r_{ij}} - \int \phi_j^*(j)\frac{1}{r_{ij}}\phi_j(j)\,d(j) + \phi_j(i)\int \phi_j^*(j)\frac{1}{r_{ij}}\phi_i(j)\,d(j) - \int \phi_i^*(i)\frac{1}{r_{ij}}\phi_i(i)\,d(i) + \phi_i(j)\int \phi_j^*(i)\frac{1}{r_{ij}}\phi_j(i)\,d(i) + J_{ij} - K_{ij}\,,$$

where J_{ij} and K_{ij} are Coulomb and exchange integrals. Considering the nucleus as the origin of coordinates, Fig. 8 shows a typical fluctuation potential (following Sinanoğlu) experienced by an electron as it moves along a line (drawn through the origin) which passes through the location of a second or "fixed" electron. A more general cross section of the fluctuation potential surface is shown by the dotted line which represents the effect experienced by an electron moving along a line through the origin which does *not* pass through the second electron.

For convenience we will first discuss the closed-shell systems and then follow with a discussion of the ^2S and ^2P states of the Li-like ions.

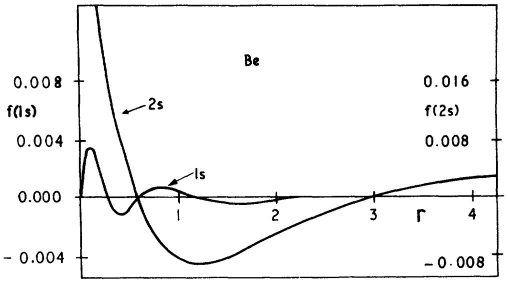

FIG. 2. Orbital-correction functions $f_{1s}(r)$ and $f_{2s}(r)$ for Be(^1S).

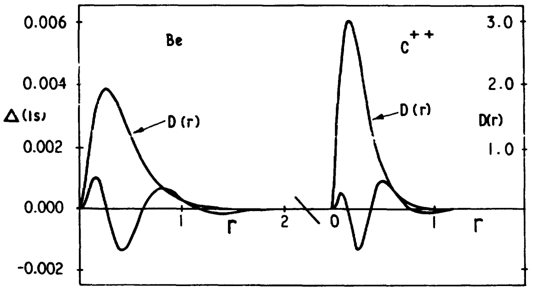

FIG. 4. HF orbital radial distribution $D(r)$ and the associated Δ curve for the K shell of Be(^1S) and C^{++}(^1S).

^1S State of Two-Electron Systems

From Fig. 1, a comparison of the $f(r)$ curve for He with that given in Ref. 2 shows that our choice of an energetically reliable CI wave function and HF wave function leads to a smaller f effect, in agreement with the expectation of Sinanoğlu and Tuan. The value of $f_{1s}(r)/R_{1s}(r)$ at the origin obtained by those workers from two wave functions of differing accuracy[21] was 4.0% and 2.8% while our calculations, based on the wave functions of Weiss, yield a value of 0.5%. In all instances the shape of the f curve is essentially the same.

The shape of the $\Delta(1s)$ curves in Fig. 3 for He and Li^+ can be related to the fluctuation potentials. Reference to a typical fluctuation potential shown in Fig. 8 indicates that close to the nucleus the potential is negative; in the region approaching $\langle r\rangle_{1s}$ an electron will experience a positive or negative potential depending on whether or not both electrons are on the same side of the nucleus. However, the very large positive-potential peak should be dominant. Further out from the origin we again have a balance of positive and negative potentials, but now of more comparable magnitudes, and since the electrons have, *a priori*, a higher probability of being on opposite sides of the nucleus, the negative effect will dominate. Given a fluctuation-potential pattern of this form, the density changes we expect, and indeed observe, are an increase of density in the region close to the nucleus, a decrease in the region approaching $\langle r\rangle_{1s}$, and a further increase in density in the outer region of the charge cloud. Density shifts arising from electron-correlation effects are compensated into stability via changes in the electron-nuclear attraction energy and, in particular, in the kinetic energy.[22] As the nuclear charge Z increases in value, absolute changes in the individual energy components will become more sensitive to such variations in the wave function. Consequently, we expect to observe larger density shifts for low Z than for high Z. This is clearly demonstrated in Table I: The value for $\|f\|$ falls from

TABLE I. Orbital-correction function $f(r)$ and the radial part $R(r)$ of the HF orbital evaluated at the nucleus as origin. Also given are values of $\|f\|$ — the norm of $f(r)$.

Z	1	2	3	4	5	6	7	8
He(^1S)-like ions								
$f_{1s}(0)$	0.0280	0.0219	0.0178	0.0166	0.0183	0.0148	0.0151	0.0113
$R_{1s}(0)$	1.3926	4.7536	9.2691	14.6934	20.8914	27.7818	35.2954	43.3912
$\|f_{1s}\|$	0.0527	0.0020	0.0008	0.0005	0.0003	0.0002	0.0002	0.0002
Li(^2S)-like ions[a]								
$f_{1s\alpha}(0)$	···	···	0.0269	0.0428	0.0557	···	0.0757	0.0885
$f_{1s\beta}(0)$	···	···	0.0047	−0.0109	−0.0257	···	−0.0521	−0.0639
$R_{1s}(0)$	···	···	9.2624	14.6745	20.8644	···	35.2519	43.3360
$\|f_{1s\alpha}\|$	···	···	0.0012	0.0013	0.0013	···	0.0013	0.0013
$\|f_{1s\beta}\|$	···	···	0.0018	0.0021	0.0020	···	0.0017	0.0016
$f_{2s\alpha}(0)$	···	···	0.0217	0.0186	0.0157	···	0.0108	−0.0040
$R_{2s}(0)$	···	···	1.4471	3.1874	5.2048	···	9.9755	12.6855
$\|f_{2s}\|$	···	···	0.0095	0.0041	0.0028	···	0.0015	0.0014
Li(^2P)-like ions[b]								
$f_{1s\alpha}(0)$	···	···	0.0137	−0.0019	−0.0150	−0.0257	−0.0364	···
$f_{1s\beta}(0)$	···	···	0.0222	0.0322	0.0384	0.0407	0.0390	···
$R_{1s}(0)$	···	···	9.2625	14.6666	20.8462	27.7161	35.2130	···
$\|f_{1s\alpha}\|$	···	···	0.0011	0.0017	0.0018	0.0017	0.0016	···
$\|f_{1s\beta}\|$	···	···	0.0012	0.0017	0.0016	0.0015	0.0012	···
$\|f_{2p}\|$[c]	···	···	0.0090	0.0060	0.0020	0.0025	0.0032	···
Be(^1S)-like ions								
$f_{1s}(0)$	···	···	0.0039	−0.0004	−0.0039	−0.0046	−0.0076	−0.0047
$R_{1s}(0)$	···	···	9.2639	14.6710	20.8563	27.7310	35.2359	43.3155
$\|f_{1s}\|$	···	···	0.0010	0.0007	0.0006	0.0005	0.0005	0.0004
$f_{2s}(0)$	···	···	0.0952	0.0865	0.0920	0.0972	0.1015	0.0978
$R_{2s}(0)$	···	···	1.0035	2.6739	4.6304	6.8436	9.2905	11.9587
$\|f_{2s}\|$	···	···	0.1336	0.0321	0.0189	0.0143	0.0117	0.0098

[a] CI wave function for $Z = 6$ unreliable.

[b] CI wave function for $Z = 8$ unreliable.

[c] $R_{2p}(0)$ and $f_{2p}(0)$ zero for all Z.

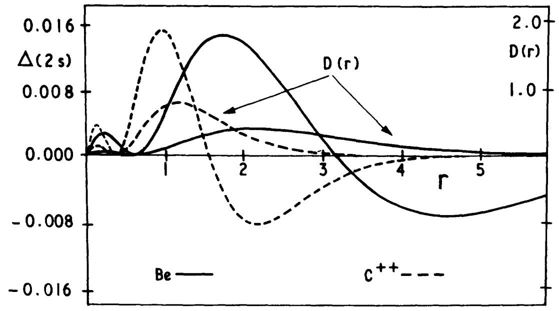

FIG. 5. HF orbital radial distribution $D(r)$ and the associated Δ curve for the L shell of Be(^1S) and C^{++} (^1S).

0.0527 at $Z = 1$ to 0.0002 when $Z = 8$. For He(^1S)-like ions the correlation-induced changes occurring in $D(r)$ are in accord with Sinanoğlu's description of dynamical correlation and possess the characteristics of a simple split-shell model ($1s1s'$). Larsson[23] has developed an iterative method for obtaining Brueckner orbitals and has presented radial difference densities between Brueckner and HF orbitals for Li$^+$. These differences should, of course, be comparable with the Δ($1s$) curve for Li$^+$ given in Fig. 3: a close comparison shows that the two sets of results are almost identical.

^1S State of Four-Electron Systems

K Shell

For the ^1S state of a four-electron atomic ion, the fluctuation potential experienced by a K-shell electron arises from the other K electron plus the effect due to the two L-shell electrons. The HF orbital densities $D(r)$ for $1s$ and $2s$ are sufficiently distinct to suggest that, since $R_{1s}(r)$ is virtually indistinguishable from its two-electron counterpart, the fluctuation potential for the K shell will bear a strong resemblance to that in-

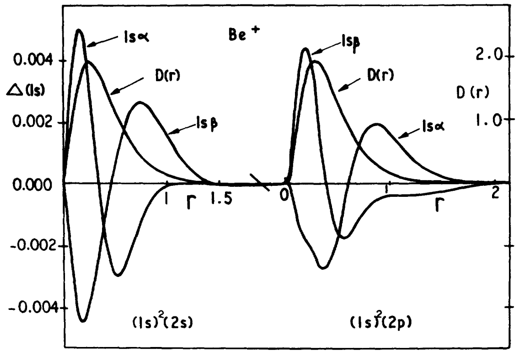

FIG. 6. HF orbital radial distribution $D(r)$ and the Δ($1s\alpha$) and Δ($1s\beta$) curves for the K shell of the ^2S and ^2P states of Be$^+$.

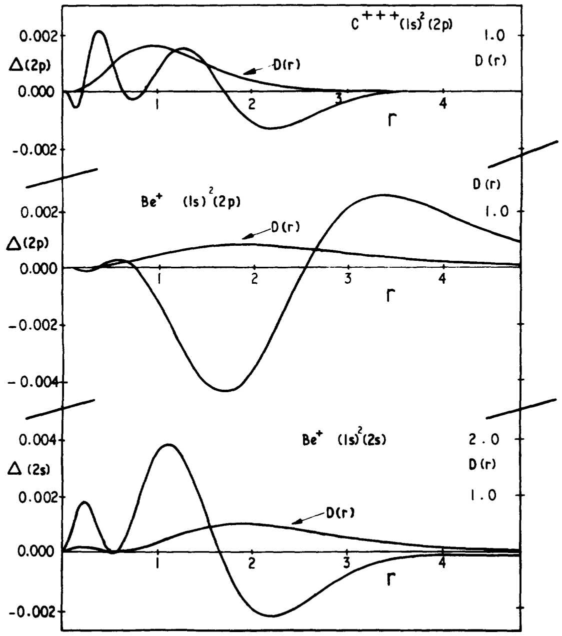

FIG. 7. $D(r)$ curve and Δ($2s$) and Δ($2p$) curves for the ^2S and ^2P states of Be$^+$, respectively. Also shown are the $D(r)$ and Δ($2p$) curves for $C^{+++}(^2P)$.

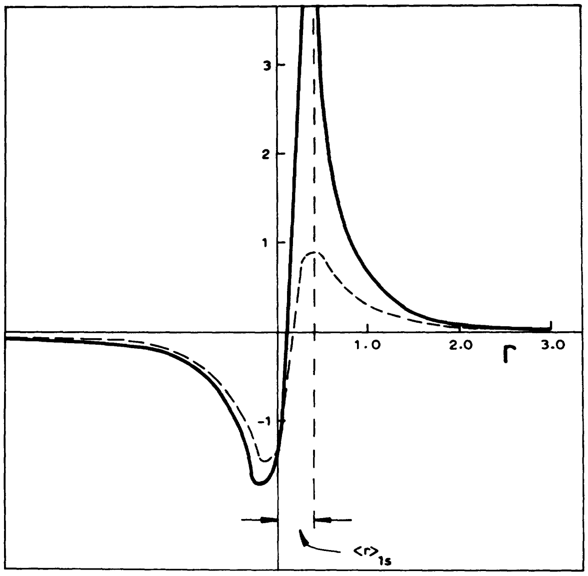

FIG. 8. Cross sections of the fluctuation-potential surface which arises from a $1s$ electron in beryllium "fixed" at $\langle r \rangle_{1s} = 0.41$ a.u.: Solid line is cross section along nucleus-"fixed" electron line; dashed line is cross section passing through the nucleus at 45° to the nucleus-"fixed" electron line.

voked for the corresponding He-like ion. However, a small perturbation effect does exist due to the $2s$ electrons. The fluctuation potential due to the $2s$ electrons is much shallower than that arising from a $1s$ electron, since the former are considerably less localized in their spatial distribution. In addition, the potential is negative throughout the bulk of the $1s$ region and has a positive peak at about $\langle r\rangle_{2s}$. Therefore, compared with a two-electron example, the total fluctuation potential felt by a $1s$ electron in a Be(^1S)-like ion is slightly increased in depth in the negative regions, decreased in magnitude in the positive region, and also possesses the additional feature of having a small but definite positive peak in the $1s \sim 2s$ transition region. Such observations lead us to predict density shifts which are essentially of the split-shell pattern associated with the two-electron ions, but with the second peak in the Δ curve increased along with the appearance of a small second minimum occurring in the outer region. An increase of Z gives rise to a greater localization of the $2s$ electrons and, consequently, the positive peak in the $1s \sim 2s$ region for the total fluctuation potential for $1s$ is increased. This leads to a more pronounced second minimum occurring in the Δ curve. These effects are illustrated in the $\Delta(1s\alpha) \equiv \Delta(1s\beta)$ curves for Be and C^{++} given in Fig. 4.

We note that Fig. 2 shows the $f_{1s}(r)$ function obtained for Be. This is indeed very similar to the Be^{++} result except close to the nucleus where the curve turns over. Table I shows that $f_{1s}(0)$ for Be(^1S) is actually negative; such a result is in disagreement with Stanton's suggestion that the HF orbital and corresponding $f(r)$ function have the same sign close to the nucleus.[3] However, from a natural orbital analysis of several wave functions for the Be atom, Barnett, Linderberg, and Shull[24] suggest that the description of the inner shell afforded by the Weiss wave function is rather less accurate than that provided by certain other correlated wave functions.[9,25] (This point will be discussed further in a subsequent paper now in preparation.) Such a deficiency could account for the apparent anomolous behavior of $f_{1s}(r)$ close to the origin for the four-electron ions.

L Shell

The fluctuation potential acting on a $2s$ electron is due to the other L-shell electron plus a smaller effect arising from the K-shell electrons. As already discussed, the $2s$ fluctuation potential is much shallower and has a much less marked positive peak than the $1s$ fluctuation potential. Because the $2s$ orbital possesses near-degeneracy with the $2p$ orbital, the mixing of corresponding configurations in a CI correlated wave function is quite large. This causes an unusually high degree of angular correlation.[26] Consequently, in contrast to the $1s$ example, the high probability of a large interelectronic angle between the two L-shell electrons removes the ability of the repulsive peak in the fluctuation potential to dominate at *any* r value. Thus, the fluctuation potential due to the other $2s$ electron is purely attractive towards the nucleus. The K shell makes its greatest contribution to the total fluctuation potential experienced by a $2s$ electron in the inner regions of the charge cloud where, of course, $D_{2s}(r)$ is small; when $r \gtrsim \langle r\rangle_{2s}$ the K-shell effect is small and, for the four-electron series, its influence is swamped by the $2s$ fluctuation potential. Because the L shell is shielded from the nucleus by the $1s$ charge cloud, $\Delta(2s)$ can become much larger than $\Delta(1s)$ before stability is achieved by the compensating effect of changes in the kinetic and potential energy. The difference in magnitude between the Δ curves for $1s$ and $2s$, at a common Z value, is shown by inspection of Figs. 4 and 5. In addition, since the shielding of the nucleus reduces the effective Z, we expect that, for the $2s$ shells, the greatest density shifts will occur at low-Z values. For Li^-, we found changes as large as 10% of the HF orbital density. This inward movement of charge is in agreement with the results of Benesch and Smith[7] and of Tanaka and Sasaki[8] in connection with their studies of the effect of electron correlation on x-ray scattering factors. They found that, for small-angle scattering, the x-ray scattering factor derived from a correlated wave function is significantly larger than that derived from HF calculations. Watson,[9] Linderberg and Shull,[27] and other workers[28] have also observed appreciable changes in the $2s$ orbital density for four-electron atomic ions as a consequence of correlation effects. Inspection of Table I shows that $f_{2s}(0)$ remains a sizable fraction of $R_{2s}(0)$ even for fairly large Z. Figure 2 shows $f_{2s}(r)$ for Be.

Although energy changes due to adding $f(r)$ to $R(r)$ are only fourth-order quantities,[3] the L-shell energy changes which range from −0.0018 a.u. (Li^-) to −0.0005 a.u. (Be) to −0.0003 a.u. (O^{4+}) are very much greater than the K-shell values—none of which exceed −0.000 04 a.u.[29]

^2S State of Three-Electron Systems

K Shell

The HF reference state is obtained from a restricted calculation in which the $1s\alpha$ and $1s\beta$ orbitals are spatially identical. No such restriction operates on the orbital correction functions.

Consequently, the corresponding radial density shifts $\Delta(1s\alpha)$ and $\Delta(1s\beta)$ not only reflect K-shell effects but also reveal the influence of intershell correlation in the form of polarization effects due to the spin imbalance in the L shell. Insight into the nature of the polarization effects was obtained by carrying out unrestricted HF calculations and comparing the $1s\alpha$ and $1s\beta$ orbital densities with those derived from a restricted HF calculation using the same basis set. For an L-shell electron with α spin, it was found that polarization caused a spatial contraction of $1s\alpha$ towards the nucleus together with an expansion—of roughly equal magnitude—for the $1s\beta$ orbital. Such charge redistributions are very similar to the $\Delta(1s\alpha)$ and $\Delta(1s\beta)$ curves, derived from the Weiss CI wave function and the restricted HF reference state, for the Li(^2S)-like series when $Z \geqslant 4$. In Fig. 6 we show the Δ curves for $1s\alpha$ and $1s\beta$ for Be$^+$ as a typical example. However, for $Z=3$, the CI wave function provides a $\Delta(1s\alpha)$ curve which resembles $\Delta(1s\alpha) \equiv \Delta(1s\beta)$ found for Li$^+$ plus some enhancement at the nucleus, whereas $\Delta(1s\beta)$, although similar to the Li$^+$ curve in the outer regions, is depressed in value close to the nucleus. The *mean* of $\Delta(1s\alpha)$ and $\Delta(1s\beta)$ for Li(^2S) is very close to the $\Delta(1s)$ curve for Li$^+$.

Although it is not possible to separate rigorously K intrashell correlation effects from spin polarization, the above results are in close accord with the notion that, for low Z, the large spatial distribution of the $2s$ orbital causes only a slight polarization of the K shell, the major changes in $D(r)$ being due to the intrashell correlation splitting. For high Z, the contraction of the $2s$ shell results in spin polarization being the dominant effect. In addition, using the model of the $2s$ perturbative fluctuation potential—as applied to the K shell of the four-electron series—we would expect to observe a similar second minimum appearing at high Z as before. Such an effect was found in the $\Delta(1s\beta)$ curves as Z increases.

L Shell

In this instance the fluctuation potential is purely intershell in origin; its influence is no longer masked by an intrashell effect as occurred in the study of the L shell in the Be-like series. Within the $2s$ region the HF potential arising from a $1s$ electron is closely equivalent to that due to an electron placed at the origin. Consequently, if the instantaneous $1s$-$2s$ interelectronic distance exceeds the distance of the $2s$ electron from the origin, the fluctuation potential acting on the $2s$ electron will be negative and *vice versa*. Trivial geometrical considerations indicate that the fluctuation potential arising from the $1s$ charge cloud has, effectively, an over-all attractive influence on the L-shell electron. This is illustrated for the Be$^+$ ion in Fig. 7. The magnitude of this effect is of interest, being roughly a quarter of that found for $\Delta(2s)$ in Be(^1S) but about four times larger than the $\Delta(1s)$ effect.

For the L shell of Li(^2S), Larsson and Smith[30] have shown the change in radial density which arises from the difference between the Brueckner orbital and the spin-polarized HF orbital. Our $\Delta(2s)$ curve for Li is in close agreement with their curve in the K-shell region but differs in magnitude in the outer region.

^2P State of Three-Electron Systems

K Shell

The reference orbitals for the ^2P state of the Li-like ions are taken from an HF calculation of restricted form. The marked differences between the Δ curves for the excited and ground states of the ions, as illustrated for $Z=4$ in Fig. 6, must obviously be associated with the difference in symmetry states. For the ^2S state, the orthogonality requirement arising from the use of HF reference orbitals demands that a form of spatial distinctness be preserved between the $1s\alpha$ and $2s\alpha$ orbitals.[31] However, for the ^2P state, the orthogonality requirement between $1s\alpha$ and $2p\alpha$ is always satisfied due to their different symmetry type. Therefore, since similar orthogonality requirements operate for the orbital-correction functions, the spatial behavior of $f(r)$ will, in turn, be less constrained in the ^2P state than in the ^2S state. Hence, a gain in exchange energy can be achieved if the $1s\alpha$ orbital expands slightly to produce an increased radial overlap with the $2p\alpha$ orbital. Correspondingly, the $1s\beta$ orbital will contract slightly to maintain an over-all balance among energy components. Both orbital shifts are measured relative to the HF description. As with the ^2S state, orbital densities derived from an unrestricted HF calculation were compared with the results of the restricted treatment: As anticipated, an expansion of the $1s\alpha$ orbital was observed together with a contraction of almost equal magnitude of the $1s\beta$ orbital. In addition to the above exchange effect—a form of spin polarization—the K electrons will, of course, experience the normal intrashell correlation effects as discussed previously for the ground state.

As Z decreases in value the excited orbital will become increasingly diffuse and, in the limit of low Z the system will ionize; consequently, intrashell correlation effects will dominate the shape of the Δ curves. Hence, for the Li(^2P)-like ions, it was found that as Z became smaller the $\Delta(1s\alpha)$ and $\Delta(1s\beta)$ curves showed a convergence towards the $\Delta(1s\alpha) \equiv \Delta(1s\beta)$ curve for the appropriate two-electron ion. Our curves for $Z = 3$ show this effect—the mean was in fact almost indistinguishable from the $\Delta(1s)$ curve for Li^+: This is illustrated in Table I for the origin. However, at $Z = 4$, it is clear from the expansion of the $1s\alpha$ orbital shown in Fig. 6 that the exchange effect must now be the leading influence.

Although the general characteristics of the $\Delta(1s\alpha)$ and $\Delta(1s\beta)$ curves can be rationalized as described above, their detailed behavior will obviously reflect any restrictions imposed by Weiss in the determination of his wave functions. The ^2P functions contain only those configurations which couple a ^1S or ^3S description of the K shell with an outer p orbital. Brown and Smith[32] comment that radial distortions of the K shell will be described by such a wave function but that the omission of configurations of the form (spd), (sdf), (d^2f), etc., which arise as a consequence of the over-all ^2P character of the state, excludes any description of axial distortions. The inclusion of such configurations in $\Psi(^2P)$ would give rise to improved f functions for the K shell orbitals, and hence Δ curves, which were an admixture of terms with s-, and d-type symmetry.

L Shell

The $\Delta(2p\alpha)$ curves for the $Li(^2P)$-like ions present something of an enigma. Figure 7 shows that the curves possess a complicated structure and also a marked variation with Z. From previous arguments we expected the $2p\alpha$ orbital to show a simple contraction towards the origin. Broadly speaking, such an over-all effect is apparent at large Z; however, other factors must surely be involved. We recall that the calculation of $f_{2p}(r)$ requires the evaluation of $\langle\Psi(^2P)\,|\,\phi_{1s}(1)\phi_{1s}(2)\rangle$, where $\Psi(^2P)$ is represented by the CI wave function of Weiss. Clearly, only those configurations in $\Psi(^2P)$ constructed from s, s, p-type basis orbitals can contribute to this function. Since only three p-type STO basis orbitals occur in the formation of such configurations, it could be that the shape of the $\Delta(2p\alpha)$ curves is less reliable than the other Δ curves examined here. Nevertheless, the magnitude of the effect is of the order expected as can be seen by inspection of the $\|f\|$ values in Table I. Extending the $\Psi(^2P)$ wave functions of Weiss to include all missing configurations will clearly improve the behavior of the f_{2p} functions; however, it is easily seen from Eq. (3) that, in this instance, their symmetry character will remain pure p type.

For the ^2S and ^2P state of the Li-like ions, the energy contributions arising from the f functions are all small. However, it is of interest to note that the f_{2p} contributions increased rapidly from $-0.000\,02$ a.u. ($Z = 3$) to $-0.000\,13$ a.u. ($Z = 5$) to $-0.000\,35$ a.u. ($Z = 7$). Although such figures should not be taken too literally, no such sharp increase was observed for other orbital correction functions.

IV. SUMMARY

In a many-electron theory using HF spin orbitals ϕ_i as a reference basis set, Sinanoğlu has systematically separated electron correlation effects into correction functions f_i for the one-particle orbitals ϕ_i, electron pair-correlation functions U_{ij}, and higher correlation terms. We have applied the method of successive partial orthogonalizations to determine f functions arising from correlated wave functions for isoelectronic ions of the type He(^1S state), Li(^2S and ^2P states), and Be(^1S state). We used the CI wave functions of Weiss which, in each instance, account for a very large fraction of the correlation energy. Although energetically not important, the addition of an orbital-correction function to the appropriate HF orbital produces an improved representation of the one-particle density. The subsequent changes in radial density are referred to here as Δ curves and their gross characteristics are rationalized by inspection of the fluctuation potential proposed by Sinanoğlu. Clearly, the *detailed* behavior of such curves will also reflect any limitations or restrictions imposed by Weiss in the determination of his wave functions.

The Δ curves for the K orbitals of both the He- and Be-like ions show strong evidence of dynamical correlation effects of the simple split-shell form. Larger changes in density occur at low Z than at high-Z values as a consequence of any shift in density being compensated into stability through an energy requirement. As Z increases for the Be-like ions, the perturbative effect of the L shell on the $1s$ electrons becomes progressively more influential and is clearly shown in the outer region of the $\Delta(1s)$ curves. For both states of the Li-like ions, the $\Delta(1s)$ curves at a low-Z value possess strong similarities with the He-like curves. However, when Z becomes larger, changes in density for the K-shell orbitals of the ^2S state become markedly affected by spin-polarization effects, whereas for the ^2P state $\Delta(1s)$ becomes dominated by an exchange effect.

Correlation effects for the $2s$ electrons in the Be-like ions are, essentially, of an intrashell character. The presence of $2p$ orbitals in a CI basis set influences $\Delta(2s)$ even though the $2p$ orbitals are unable to contribute directly to f_{2s}

owing to the different symmetry. This occurs because the near degeneracy of the $2s$-$2p$ orbitals gives rise to considerable angular correlation and, as a consequence, the total fluctuation potential acting on a $2s$ electron has a purely attractive character. Hence, the orbital-correction part of the correlation effect produces an over-all contraction of the orbital density towards the nucleus. The screening of the nucleus by the K-shell electrons permits the $\Delta(2s)$ curves to become considerably larger than $\Delta(1s)$ before being compensated into stability by means of concomitant energy changes. By contrast, the $\Delta(2s)$ curves for the Li(^2S)-like series arise solely from intershell effects which are now no longer masked by intrashell correlation. An over-all attractive effect occurs which, when compared with the corresponding Be(^1S)-like ion, is roughly speaking about a quarter of that found for $\Delta(2s)$ but about four times the $\Delta(1s)$ effect.

For the $2p$ orbital, the Δ curves for the three-electron ions will again arise solely from intershell correlation. However, although the magnitude of the norm of f_{2p} is not out of keeping with that for f_{2s} in the ^2S state, the $\Delta(2p)$ curves possess a complicated structure which is difficult to rationalize in terms of the fluctuation potential. This could originate, in particular, from the limited number of p orbitals used to construct those configurations which contribute to f_{2p} and, as such, a redetermination of the ^2P state wave functions for the Li-like ions may be helpful.

To obtain physical insight into the correlation effects contained within a CI wave function demands some systematic partitioning of the wave function. The method of successive partial orthogonalizations represents an excellent, albeit little used, alternative to the natural orbital mode of analysis. In a following paper we shall use the same method to extract the pair-correlation functions U_{ij}.

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