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Exposition of atomic pair correlation functions and associated energies obtained by analysis of correlated wave functions

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Using Sinanoğlu's method of successive partial orthogonalizations, pair correlation functions have been extracted from the energetically accurate configuration-interaction wave functions of Weiss for a series of two-, three-, and four-electron ions. For selected systems, the pair correlation functions are examined by constructing contour diagrams which explicitly reveal the relative corrections to the Hartree-Fock wave functions brought about by inclusion of pairwise correlation interactions. For each pair function, an associated pair correlation energy is evaluated. The characteristics of both the pair functions and the pair energies are examined together with (i) their Z dependence for a constant number of electrons and (ii) their dependence upon the number of electrons for constant Z. The small differences which occur between the K shells for ions of a constant Z have been rationalized in terms of an orthogonality requirement, while the slight but smooth variation of the K-shell pair energies with Z has enabled us to comment on the stability of the ion He$^-$. Our pictorial representation has highlighted differences between the L- and K-shell correlation effects within the Be-like ions. In particular, the large degree of angular correlation in the L shell, brought about by the near degeneracy of the $2s$ and $2p$ orbitals, is clearly apparent from the contour diagrams. Also revealed is a nearly linear variation of the L-shell pair energies with Z. Comparison of the pair energies for the four-electron ions with the results of other workers shows that the wave functions analyzed here provide a good description of the correlation effect within the K- and L-shells, the description of the latter being superior to that of the former. The intershell correlation behavior, however, is accounted for only very approximately. For the Be-like series as a whole, the L-shell pair energies are expected to be highly reliable.

I. INTRODUCTION

Electron correlation arises from residual fluctuation potentials which remain between electrons after the average of the Coulomb repulsions have been accounted for by the Hartree-Fock (HF) model. Correlation effects are known to be important in the calculation of several atomic and molecular properties. For example, electron affinities, transition probabilities, oscillator strengths, Fermi contact potentials, Compton profiles, and binding energies are each sensitive to such effects.

To obtain physical insight into the structure of a correlated wave function which describes a many-electron system demands some systematic partitioning technique. The method of successive partial orthogonalizations[1] suggested by Sinanoğlu represents an appropriate mode of analysis since it enables the correlation effect to be systematically separated into several parts: f_i functions—corrections to the ith HF orbital; U_{ij} functions—electron pair correlations, and also higher multielectron correlation terms such as U_{ijk}, U_{ijkl}, etc. In a recent paper,[2] this technique was used to derive orbital correction functions f_i from the energetically accurate configuration-interaction (CI) wave functions of Weiss[3] for the ground state of a series of two-, three-, and four-electron atomic ions. Also, for the three-electron series, f_i functions were obtained for the first excited state. The characteristics and Z-dependent trends of the concomitant changes in the orbital radial density distributions were rationalized in terms of the fluctuation potential.

In the present article we extend our analysis of the Weiss wave functions mentioned above in order to examine the pair correlation functions U_{ij} which, as is well known, make the dominant contribution to the correlation energy. As well as examining the characteristics of the U_{ij} functions we have also evaluated the associated pair correlation energies ϵ_{ij}. For the Be-like ions, a comparison can be made with the calculations of Webster and Stewart[4] who, during the course of the present investigation, reported pair correlation energies determined by means of a variational perturbation procedure.

II. ANALYSIS AND RESULTS

A wave function Ψ for an N-electron closed-shell system (or for an open-shell system for which the HF approximation takes the form of a single determinant) can be expressed as

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

where $\mathcal{A}$ is the antisymmetrization operator, $\Pi(1, 2, \ldots, N)$ 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 $l = 1, 2, \ldots, N$ and, of course, from our definitions $\mathcal{A}\Pi(1, 2, \ldots, N)$ represents the normalized N-particle HF wave function Φ. Following our previous analysis,[2] the constant c has been introduced to ensure that we have the normalization condition $\langle \Psi | \Psi \rangle = 1$. The method of successive partial orthogonalizations enables the pair correlation function U_{ij} to be written as

$$U_{ij} = \frac{1}{\sqrt{2}}\left(\frac{\langle \Psi | \Pi_{ij} \rangle}{\langle \Psi | \Pi \rangle} - \phi_i\phi_j + \phi_j\phi_i - f_i\phi_j + \phi_j f_i - \phi_i f_j + f_j\phi_i\right), \tag{2}$$

where Π_{ij} is equivalent to Π but with the omission of the orbitals $\phi_i(\vec{x}_i)$ and $\phi_j(\vec{x}_j)$ and where the dependence on electron coordinates is indicated, for instance, by

$$\phi_i\phi_j - \phi_j\phi_i \equiv \phi_i(\vec{x}_i)\phi_j(\vec{x}_j) - \phi_j(\vec{x}_i)\phi_i(\vec{x}_j). \tag{3}$$

The f_i function for the ϕ_i orbital, for example, is given by the relation

$$f_i(\vec{x}_i) = \langle \Psi | \Pi_i \rangle / \langle \Psi | \Pi \rangle - \phi_i(\vec{x}_i). \tag{4}$$

For the exact wave function it is easy to show that the total correlation energy E_{corr} may be represented by the sum of the pair correlation energies ϵ_{ij} defined by

$$\epsilon_{ij} = \langle \phi_i\phi_j | (1/r_{ij}) | U_{ij} \rangle, \tag{5}$$

where U_{ij} is given by Eq. (2).

As in our previous paper,[2] we have regarded the Weiss wave functions as a representation of Ψ. Equations (2) and (5) were used to evaluate the pair correlation functions U_{ij} and their associated energies ϵ_{ij}. Clearly, such quantities will reflect any limitations or restrictions imposed by Weiss in the construction and determination of his wave functions. Nevertheless, for nearly all of the two-, three-, and four-electron ions, these wave functions accounted for over 90% of the total correlation energy.

Following our earlier work, the normalized HF wave function for each atomic state examined here was written in the form of a single determinant. For H^-, we used the five-term analytical HF orbitals of Curl and Coulson[5] and for all other systems and states we used the 12-term analytical functions of Roothaan, Sachs, and Weiss.[6] Such wave functions are quoted by their authors to be equivalent to the solutions of the integrodifferential HF equations to four decimal places. In the nomenclature of Sinanoğlu and his co-workers,[1,7-9] the pair correlation functions for closed-shell states consist only of "all-external" contributions whereas, for an atomic system in a nonclosed shell state, an analysis of electron correlation based on the use of restricted HF (RHF) wave functions means that a pair function so derived can be regarded as composed of "internal," "semi-internal," and "all-external" contributions. Though not required for the systems examined in this paper a detailed discussion of the complications which arise when a state cannot be represented by a single determinant has been given by Silverstone and Sinanoğlu[8] and Sinanoğlu and Oksuz.[9]

In Fig. 1 we plot contour diagrams of the function $U_{1s1s}(\vec{x}, \vec{R})/\phi_{1s}(\vec{x})\phi_{1s}(\vec{R})$ for a number of different values of $\vec{R}$ for the systems He(^1S) and Be^{++}(^1S). This function measures the fractional change in the HF wave function at the point $\vec{x}$ brought about by the correlation interaction with an electron "fixed" at the point $\vec{R}$. The distances are measured with respect to the nucleus as origin. Similar diagrams are presented in Fig. 2 for the U_{1s1s} and U_{2s2s} pair functions for Be(^1S). Figure 3 contains a number of cross sections of the contour diagrams shown in Fig. 1 for He(^1S). For the K-shell diagrams, contours in the range -0.1 to $+0.1$ have been plotted at intervals of 0.02, while for the L shell the range selected for the contours was -0.5 to $+0.5$ at intervals of 0.1. The regions within which the various contours have been plotted were chosen to represent the physically significant regions of the appropriate orbital charge density; for large values of either $\vec{x}$ or $\vec{R}$ both $U_{ij}(\vec{x}, \vec{R})$ and the HF wave function tend to zero and hence the ratio of these functions becomes unreliable. In Table I we present values of $\| U_{ij} \|$—the norm of U_{ij}. This quantity gives a measure of the over-all distortion of that part of the total HF wave function associated with the orbitals ϕ_i and ϕ_j.

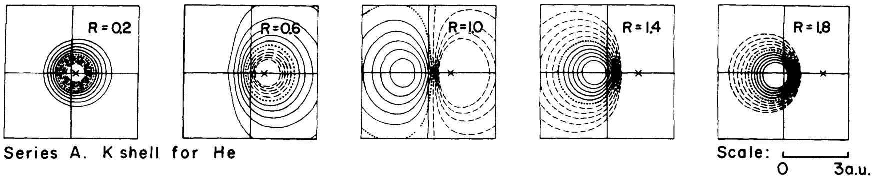
In Table II we list the pair correlation energies ϵ_{ij} for the He(^1S)-, Li (^2S and ^2P)-, and Be(^1S)-like ions. For the two-electron systems we have simply quoted as the pair energy the total correlation energy obtained by Weiss. For Be(^1S), a comparison of pair correlation energies obtained by various workers can be made by inspection of Table III. In Fig. 4 we plot ϵ_{1s1s} against the atomic number Z for the three series of ions.

III. DISCUSSION

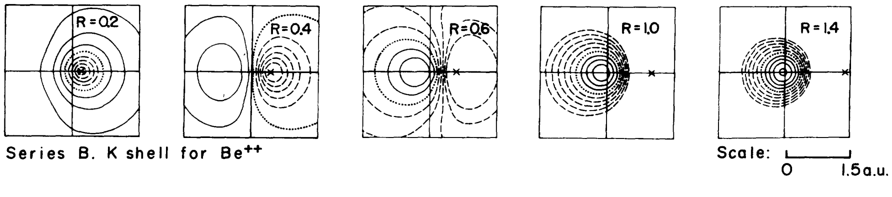
Let us first consider the diagrams for He in Fig. 1. As the magnitude of $\vec{R}$ tends to zero or to infinity, the contours approximate to circles centered on the nucleus; clearly this result is required by symmetry. At these extreme values of R the pair function U_{ij} is behaving, essentially, as a form of the orbital correction function. When $R=0$, the fixed electron will exactly screen one unit of nuclear charge. Because of this reduction in the effective nuclear charge, the free electron will now be described by a hydrogenlike orbital which will be expanded relative to the original HF orbital since the latter took into account only partial screening of the nucleus. The difference in these orbitals will be represented by the function U_{ij}. On the other hand, when $R=\infty$ the screening is reduced to zero. Consequently, in this instance, the function U_{ij} will now represent a contraction of the original HF orbital to produce the hydrogenlike orbital appropriate to the unscreened nucleus. Thus, as the position of the fixed electron is moved away from the origin, the contours must change from being negative in the region surrounding the nucleus and positive in the outer region of the charge cloud, to being positive close to the nucleus and negative in the outer zone. Figure 1 clearly demonstrates this trend for both He and Be^{++}.

When the fixed electron is placed in the vicinity of $\langle r\rangle_{1s}$, which for He is 0.93 a.u.[10] and for Be^{++} is 0.41 a.u.,[11] the pair function now acts in its more generally accepted role as a correlation function exhibiting, specifically, a two-particle nature. The contour and profile diagrams for He when $R=1.0$ a.u., shown in Figs. 1 and 3, respectively, indicate that, in the neighborhood of the fixed electron, the HF wave function takes on too large a value, i.e. the HF treatment yields too high a value for the probability of finding the two electrons close together. For positions on the opposite side of the nucleus from the fixed electron the HF wave function underestimates this probability. The profile shows that the error in the wave function is about 25% at $x=1.0$ a.u. and about 10% at $x=-1.0$ a.u. Such changes in relative errors for diametrically opposite positions are also to be found in the work of Banyard and Ellis[12] on the interelectronic angular distribution of electrons in He. Consideration of the form of the coutours presented here leads us to the conclusion that for the ground state of He no obvious distinction can be made between the extent to which angular or radial correlation is dominant. That both factors are involved to an almost equal degree is shown by inspection of the coefficients in the natural expansion of the Weiss wave function.[10]

The diagrams for Be^{++} exhibit the same trends as discussed above, namely, as we proceed from large to small values of the fixed electron distance the positive and negative regions of the contours interchange. When the fixed electron is located at the $\langle r\rangle_{1s}$ value for Be^{++}, i.e., $R\sim 0.4$ a.u., examination of the countour diagram shows that the error in the HF wave function due to the neglect of electron correlation is about 12% in the vicinity of the fixed electron and, at most, 6% in those regions where the HF wave function is too small. Thus, compared with the He situation, the percentage error is noticeably reduced as we pass to Be^{++}. This effect is also illustrated in Table I where the values of $\lVert U_{ij}\rVert$ for He and Be^{++} are seen to be 0.09 and 0.04, respectively. Clearly, an increase in nuclear charge causes the fluctuation potential to be a smaller perturbation than was the case for He. However, when the nuclear charge is reduced, the particular importance of correlation for $Z=1$ is immediately apparent since the value for $\lVert U_{ij}\rVert$ is 0.26 compared with that of unity for the HF—or uncorrelated—part of Ψ. As is well known, allow-



Series A. K shell for He



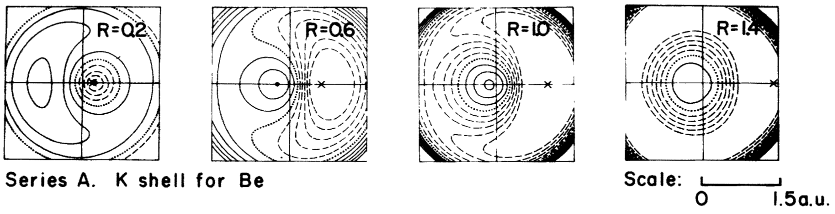
Series B. K shell for Be^{++}

FIG. 1. Contour diagrams of $U_{ij}(\vec{x},\vec{R})/\phi_i(\vec{x})\phi_j(\vec{R})$ for He, series A, and Be^{++}, series B. The "fixed" electron is shown by the cross at a distance R from the nucleus. All the contours are drawn within the range of values -0.1 to $+0.1$ at intervals of 0.02. The zero contour is shown dotted, positive contours are drawn as full lines and negative contours as dashed lines.

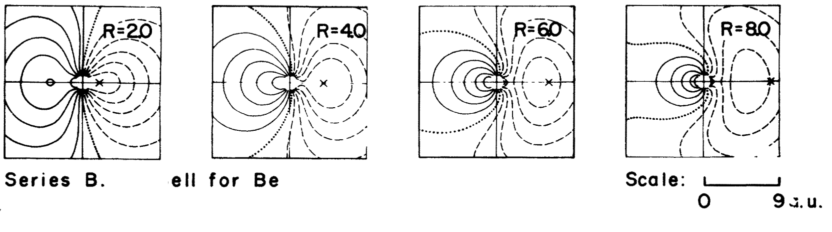
ance for electron correlation is essential in order to predict the stability of H^- from an energy point of view.[13]

In Fig. 2 we present a number of contour diagrams for the K- and L-shell pair correlation functions of Be. The diagrams for the K shell resemble those of Fig. 1 for Be^{++} in the inner regions of space. However, compared with Be^{++}, we note that a certain contraction of the diagrams seems to have taken place. This is evidenced by the outer circular contours which are apparent in Fig. 2 but which fall outside the grid for Be^{++} (clearly at a sufficiently large distance from the fixed electron and from the nucleus the contours are all circular). This difference is brought about by the presence of the $2s$ electrons which can affect the K-shell pair function in two ways. Firstly, the HF $1s$ orbital of Be differs from that of Be^{++}—this difference, however, is actually very small. Secondly, the orthogonality requirement demands that the K-shell pair function for Be must be strongly orthogonal to the $2s$ orbital, though no such restriction operates for the Be^{++} pair function. Byron and Joachain[14] suggest that it is the orthogonality requirement alone that is responsible for the difference in correlation between the K-shell electrons of Be and Be^{++}. It should be noted, however, that, as will be discussed later, the Weiss wave functions for the Be-like ions give a description of the K shells which is somewhat less reliable than that for the He-like ions and, no doubt, some of the differences between the corresponding diagrams of Figs. 1 and 2 are also attributable to this difference in reliability. Nevertheless, the over-all similarity of the K-shell pair functions is indicated by the closeness of the appropriate $\|U_{ij}\|$ values. The similarity of the K-shell pair functions for the corresponding He- and Li-like ions is even more marked as seen by inspection of Table I.

Since the $2s$ orbital has a node, a singularity is introduced into the contour diagrams for the L-shell. However, as the major part of the orbital density lies at some distance from the nodal radius, we have simply omitted in Fig. 2 any contours close to this region. Examination of the L-shell contours shows marked changes from those observed for the K shells. Over the chosen range of R values, the diagrams reveal little evidence of any trend towards purely circular contours which, as we have seen, must occur for very large or small values of R. The fractional change, relative to the HF wave function, is generally about 5 times that which occurs for the inner shell. The $\|U_{ij}\|$ values suggest that as Z increases the degree of correlation between the $2s$ electrons is reduced, but much less markedly than was the case for the $1s$ electrons. Similar observations have been made concerning the influence of correlation on the Z dependence of the angular distribution for the $2s$ electrons.[12] Table I also shows that the absolute values of $\|U_{ij}\|$ are very much larger than the corresponding K-shell values. This is a consequence of the near $2s$-$2p$ degeneracy which occurs for the $Be(^1S)$-like ions and implies that in a CI wave function, based on HF orbitals, the configuration $(1s^2 2p^2)^1S$ has a particularly large coefficient. Consequently, in terms of the cluster formulation of Ψ, the U_{2s2s} pair function will have a very large p wave contribution indicating a high degree of angular correlation between the $2s$ electrons. Such an effect is apparent in Fig. 2. As the nuclear charge is increased, the fluctuation potential again becomes a smaller



Series A. K shell for Be



Series B. ell for Be

FIG. 2. Contour diagrams of $U_{ij}(\vec{x},\vec{R})/\phi_i(\vec{x})\phi_j(\vec{R})$ for the K shell, series A, and L shell, series B, of Be. The "fixed" electron is shown by the cross at a distance R from the nucleus. The zero contour is shown dotted, positive contours are drawn as full lines, and negative contours as dashed lines. For the K shell the contours are drawn within the range of values −0.1 to +0.1 at intervals of 0.02; for the L shell the contours are drawn within the range of values −0.5 to +0.5 at intervals of 0.1.

perturbation, but this is partially offset by the increased near degeneracy of the 2*s* and 2*p* orbitals. Hence, the decrease in importance of the correlation behavior is less marked than was observed for the *K* shell. The $\Vert U_{2s2s}\Vert$ value obtained by Sinanoğlu[15] from analysis of the Watson[16] Be wave function was 0.30 which compares closely with our value of 0.31 obtained from the Weiss wave function.

The values of $\Vert U_{ij}\Vert$ for the various intershell pairs are all much less than the corresponding intrashell values. However, as we shall see later, the description of the intershell behavior afforded by the Weiss wave functions is very approximate, consequently, the magnitude of the intershell $\Vert U_{ij}\Vert$ values is somewhat questionable.

We have determined the various pair correlation energies which are implicitly contained in the three- and four-electron Weiss wave functions by substitution of the pair correlation functions into Eq. (5). Inspection of the pair energies in Table II again indicates the similarity of the *K*-shell correlation effect within the different systems. The difference in magnitude between the various *K*-shell pair energies is, at most, only about 10%. As discussed previously,[2] the Weiss wave functions for the systems examined here differ to some extent in their reliability, for example, we commented on the relative poorness of the Li-like wave functions for the ^2P state. Nevertheless, the ordering of the *K*-shell pair correlation energies for any particular *Z* is as might reasonably be expected from *a priori* considerations: the effect of the orthogonality requirement implies that the form of the pair function for the Be-like ions is more restricted than that for the corresponding two-electron ion, whereas, for the appropriate Li-like ion, the presence of a single outer electron results in an intermediate situation. For the excited state of the Li-like ions the effect of a 2*p* electron results in a situation which, in this instance, is intermediate between that of the corresponding two- and three-electron ions in their respective ground states. As *Z* decreases, the description of the outer electron, or electrons, becomes more spatially diffuse and it is to be expected that the distinction between the *K* shells of different systems would become less marked. This behavior is clearly apparent from Fig. 4. Extrapolation of the *K*-shell pair energies for the Li- and Be-like ions to *Z* values less than 3 shows that these curves intersect with the pair energy curve appropriate to the two electron ions. From the general reasoning given above it is anticipated that the pair energy curve for the Li-like ions, for example, will intersect the pair energy curve for the He-like ions only when the electron of the outer shell is so far removed from that of the *K* shell that its presence has no effect on the inner-shell electrons. This implies that the system has effectively ionized. Examination of Fig. 4 shows that the Li-like ^2S-state pair energy curve intersects the He-like pair energy curve at a *Z* value of 2.06, while the Li-like ^2P-state pair energy curve crosses the He-like pair energy curve at a *Z* value of about 2.7. Since both intersections occur at $Z > 2$, these results are suggestive that no $(1s^2 2p)$ excited state of the He^- ion exists and that the ground state is actually just unstable with respect to dissociation to a free electron and an He atom. Such comments are in accord with the results of the investigation of Weiss[3] who concluded that the He^- ion "is probably unstable, and, if it is stable, it is bound by no more than 0.026 eV."

Definitions of pair correlation energies depend on the way in which the higher linked-cluster terms are accounted for. Consequently, within these different definitions, the results of even exact deter-

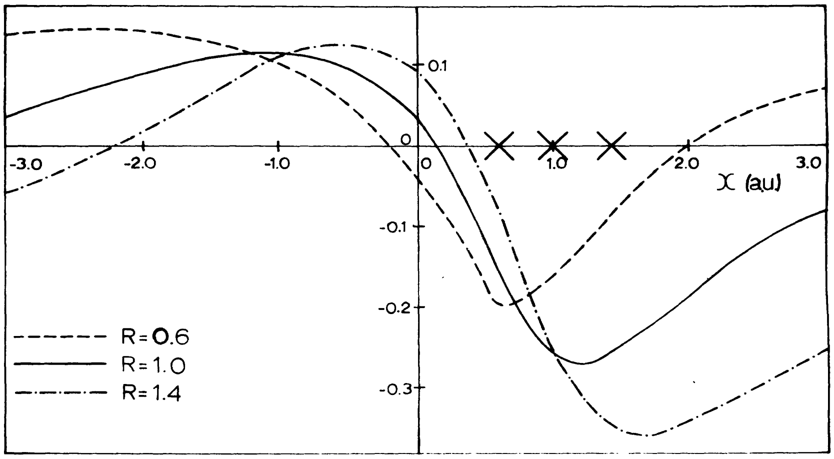


FIG. 3. Cross sections of the *R* = 0.6, *R* = 1.0, and *R* = 1.4 He contour diagrams of Fig. 1. The cross sections are taken along the nucleus-"fixed" electron line and the position of the fixed electron is shown by the cross at a distance *R* from the nucleus.

TABLE I. Values of $||U_{ij}||$.

Electron Pair i,j	Z 1	2	3	4	5	6	7	8
			He(^1S)-like ions					
$1s\alpha 1s\beta$	0.2551	0.0900	0.0571	0.0422	0.0332	0.0271	0.0227	0.0198
			Li(^2S)-like ions [a]					
$1s\alpha 1s\beta$	···	···	0.0566	0.0411	0.0323	···	0.0225	0.0195
$1s\beta 2s\alpha$	···	···	0.0177	0.0171	0.0151	···	0.0118	0.0106
$1s\alpha 2s\alpha$	···	···	0.0120	0.0105	0.0089	···	0.0067	0.0059
			Li(^2P)-like ions [b]					
$1s\alpha 1s\beta$	···	···	0.0574	0.0421	0.0332	0.0274	0.0233	···
$1s\beta 2p\alpha$	···	···	0.0062	0.0079	0.0073	0.0064	0.0055	···
$1s\alpha 2p\alpha$	···	···	0.0085	0.0102	0.0089	0.0076	0.0064	···
			Be(^1S)-like ions					
$1s\alpha 1s\beta$	···	···	0.0562	0.0402	0.0313	0.0256	0.0217	0.0188
$2s\alpha 2s\beta$	···	···	0.3718	0.3141	0.2882	0.2722	0.2610	0.2526
$1s\beta 2s\alpha$	···	···	0.0072	0.0096	0.0100	0.0093	0.0085	0.0077
$1s\alpha 2s\alpha$	···	···	0.0014	0.0008	0.0006	0.0005	0.0004	0.0004

[a] Wave function for $Z = 6$ unreliable.
[b] Wave function for $Z = 8$ unreliable.

minations of the pair energies would differ. However, for the Be-like ions, the distinctness between the K- and L-shells implies that the three- and four-particle linked-cluster terms will be of negligible importance and, hence, although the results in Table III are derived by different means, a meaningful comparison is still possible. We see from Table III that the values of ϵ_{1s1s} for Be derived from the CI calculations of Watson,[16] Nesbet,[17] Bunge[21] and Weiss are consistently smaller than the other values listed there which, for example, have been derived from the use of explicitly cor-

TABLE II. Pair correlation energies ϵ_{ij} derived from the wave functions of Weiss (Ref. 3). All energies are negative and measured in atomic units.

Electron Pair i,j	Z 1	2	3	4	5	6	7	8
			He(^1S)-like ions					
$1s\alpha 1s\beta$	0.0395	0.0415	0.0428	0.0435	0.0439	0.0442	0.0444	0.0446
			Li(^2S)-like ions [a]					
$1s\alpha 1s\beta$	···	···	0.0419	0.0419	0.0419	···	0.0418	0.0417
$1s\beta 2s\alpha$	···	···	0.0017	0.0030	0.0038	···	0.0048	0.0051
$1s\alpha 2s\alpha$	···	···	0.0006	0.0010	0.0012	···	0.0014	0.0015
			Li(^2P)-like ions [b]					
$1s\alpha 1s\beta$	···	···	0.0427	0.0432	0.0434	0.0435	0.0437	···
$1s\beta 2p\alpha$	···	···	0.0002	0.0005	0.0007	0.0008	0.0009	···
$1s\alpha 2p\alpha$	···	···	0.0003	0.0008	0.0012	0.0013	0.0014	···
			Be(^1S)-like ions					
$1s\alpha 1s\beta$	···	···	0.0413	0.0410	0.0406	0.0404	0.0402	0.0400
$2s\alpha 2s\beta$	···	···	0.0261	0.0447	0.0593	0.0725	0.0847	0.0962
$1s\beta 2s\alpha$	···	···	0.0004	0.0012	0.0019	0.0024	0.0028	0.0031
$1s\alpha 2s\alpha$	···	···	$<10^{-5}$	$<10^{-5}$	$<10^{-4}$	$<10^{-4}$	$<10^{-4}$	$<10^{-4}$

[a] Wave function for $Z = 6$ unreliable.
[b] Wave function for $Z = 8$ unreliable.

related trial functions or the direct numerical solution of pair-function equations. Clearly, this is a reflection of the well-known convergence difficulty associated with CI wave functions in the description of correlation effects. Recently, Webster and Stewart[4] have reported calculations of the pair correlation energies of the Be-like ions for $Z = 3-10$. Their values for ϵ_{1s1s} differ from the present results by 2.4% for $Z=3$ and 5.4% for $Z=8$. This suggests that the description of the K shell in the Be-like ions provided by the Weiss wave functions is inferior to that achieved by Weiss in his two-electron studies since, in that instance, errors in the K-shell correlation energy ranged from 1.6% at $Z=3$ to 2.0% at $Z=8$. For Be itself, the relatively unreliable description of the K shell arising from the Weiss wave function has also been noted by Barnett, Linderberg, and Shull[23] and by Olympia and Smith.[24]

Turning our attention to the pair correlation energies for the L shells of the four-electron ions, given in Table II, we note immediately a very marked variation with Z. This is a manifestation of the $2s$-$2p$ degeneracy which occurs in the limit of infinite Z and inspection indicates that this variation is almost exactly linear as predicted by Linderberg and Shull[25] and discussed by Alper.[26] Inspection of Table III reveals that the description of the L shell of Be provided by the Weiss wave function is more in keeping with the results of the other calculations that was the case for the K shell. The superiority of the L-shell description over that of the K shell is further exemplified by reference to the calculation of Byron and Joachain[14] for B^+. These workers obtained K- and L-shell pair energies of -0.0425 and -0.0596 a.u., respectively, compared with the present values of -0.0410 and -0.0593 a.u. The results of Webster and Stewart for the L-shell energies are, unfortunately, very inaccurate and so comparisons for the other ions cannot be made.

TABLE III. Comparison of pair correlation energies for Be. All energies are measured in atomic units.

Source	$-\epsilon_{1s\,1s}$	$-\epsilon_{2s\,2s}$	$-\epsilon_{1s\,2s}$
Watson[a]	0.0376	0.0418	0.0051
Nesbet[b]	0.0418	0.0454	0.0059
Geller, Taylor, and Levine[c]	0.0421	0.0444	•••
Kelly[d]	0.0421	0.0449	0.0050
Szasz and Byrne[e]	0.0424	0.0445	•••
Webster and Stewart[f]	0.0424	0.0379	0.0061
Byron and Joachain[g]	0.0425	0.0448	0.0052
Bunge[h]	0.0409	0.0451	0.0052
Tuan and Sinanoğlu[i]	0.0440	0.0439	0.0065
Present calculation (Weiss)	0.0410	0.0447	0.0024

[a] See Ref. 16.
[b] See Ref. 17.
[c] See Ref. 18.
[d] See Ref. 19.
[e] See Ref. 20.
[f] See Ref. 4.
[g] See Ref. 14.
[h] See Ref. 21.
[i] See Ref. 22.

In Table II we have also listed the values obtained for the various intershell pair correlation energies. For Be, Table III shows that the intershell correlation energy evaluated here is less than half of that obtained in the other calculations. For B^+, Byron and Joachain achieved a value of -0.0075 a.u. for the $1s$-$2s$ intershell correlation energy compared with the present value of -0.0038 a.u. Clearly, the description of the intershell correlation behavior provided by the Weiss four-electron wave functions is very approximate.

IV. SUMMARY

Pair correlation functions U_{ij} and their associated pair energies ϵ_{ij} have been examined for He(^1S)-, Li(^2S and ^2P)-, and Be(^1S)-like ions by analyzing the elaborate CI wave functions of Weiss according to the many-electron theory of Sinanoğlu. Pair functions, which collectively represent the most important correlation term in the cluster expansion of a wave function, have been presented in a pictorial form which highlights their importance relative to the appropriate HF wave function. For Be and B^+, the pair energies have been compared with those derived by other workers.

A series of contour diagrams for He and Be^{++} showing the ratio $U_{ij}(\vec{x}, \vec{R})/\phi_i(\vec{x})\phi_j(\vec{R})$, where $\vec{R}$ and $\vec{x}$ are the vector positions of a fixed and a free electron, respectively, revealed several interesting features. At very large and small values for R the U_{ij} function essentially fulfills the role of turning the $1s$ HF orbital into the appropriate hydrogenlike wave function. Even in the region $R \sim \langle r \rangle_{1s}$ the U_{ij} function represents a significant correction to the HF wave function, the ratio being

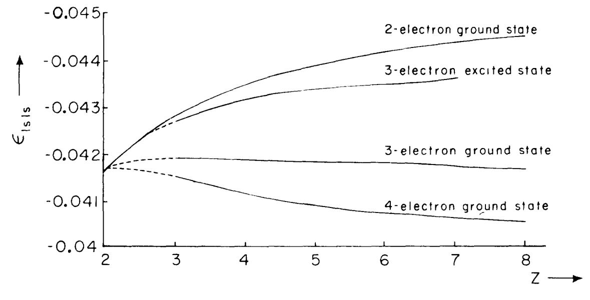


FIG. 4. Variation with the nuclear charge Z of the $1s^2$ pair correlation energy $\epsilon_{1s\,1s}$ derived from the Weiss wave functions for the ^1S states of the He-like and Be-like ions and for the ^2S and ^2P states of the Li-like ions.

about 25% for He and 12% for Be^{++} near to the fixed electron. A natural orbital study has suggested that for He there is no clear-cut distinction between the importance of angular and radial correlation and it is pleasing to observe that our pictorial representation of the correlation effect is in accord with this interpretation. Turning to the Be-like ions, the occupancy of the L shell influences the $U_{1s1s}(\vec{x}, \vec{R})$ functions through an orthogonality requirement. Taking Be as an example, this is shown as a slight contraction of the K-shell contour diagrams in the outer regions whereas, in the inner regions, a notable similarity is retained between the Be and Be^{++} diagrams. The over-all resemblance between the pair functions is indicated by the closeness of the corresponding values for $\|U_{ij}\|$. The norm U_{ij} values also show that this resemblance exists for each of the corresponding two- and four-electron ions and that, in addition, the similarity extends to include both states of the appropriate three-electron ion. Examination of the pair energies for the K shells reveals that, at a constant Z, the values differ by, at most 10%: it was found that the ordering of the pair energies could be rationalized in terms of the orthogonality requirement. The variation of ϵ_{1s1s} with respect to Z, although small for each of the four series, does, nevertheless, allow us to comment on the stability of the ion He^-. Our results lead to the inference that such a system is unstable in both the ground and the $1s^2 2p$ excited state, however, in accord with the general comments of Weiss, we found that for the ground state the instability is only marginal. Although the values for the K-shell pair energies for the Be-like series are less satisfactory than those achieved for the two-electron series they are, nevertheless, in reasonable general agreement with the results of other workers.

The contour diagrams for the L shell in Be show marked differences when compared with those for the K shell. Firstly, the influence of correlation is seen to be considerably more important and, secondly, the pictorial representation now reveals the large degree of angular correlation which occurs for the L shell as a consequence of the near $2s$-$2p$ degeneracy. For each of the four-electron ions, the increased importance of correlation within the L shell is apparent from a comparison of $\|U_{2s2s}\|$ with $\|U_{1s1s}\|$. The pair energies reflect the near degeneracy in the L shell by revealing an almost linear variation of ϵ_{2s2s} with Z. This behavior is, once again, in marked contrast with that observed for the K shell. For Be and B^+, a comparison of the pair energies for the L shells with the results obtained by other workers shows very good agreement, being superior to the corresponding comparison for the K shells.

The intershell pair energies for the systems examined here are all considerably smaller than the intrashell values. It should be noted, however, that in those instances where a comparison with other workers is possible, the present results were found to be only very approximate.

The present work has illustrated the power and usefulness of the method of successive partial orthogonalizations in partitioning the correlation effect and hence indicating how the wave function may be improved. In this connection it is proposed to extend our analysis to include other well-correlated wave functions for such systems which, as one aspect of the project, will then allow us to make a comparison of the resulting pair correlation functions with those presented here. Finally, in an article now in preparation, we report the development of a series of pair correlated wave functions for the Be-like ions which enable us to examine systematically the effect of correlation on the generalized oscillator strengths for the ^1S-^1P transition.

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[1] O. Sinanoğlu, Rev. Mod. Phys. 35, 517 (1963). For a general review of Sinanoğlu's many-electron theory see O. Sinanoğlu and K. A. Brueckner, *Three Approaches to Electron Correlation in Atoms* (Yale U. P., New Haven, Conn., 1970).

[2] G. K. Taylor and K. E. Banyard, Phys. Rev. 8, 1157 (1973).

[3] A. W. Weiss, Phys. Rev. 122, 1826 (1961), wave functions for ground state of two-, three-, four-electron ions; A. W. Weiss, Astrophys. J. 138, 1262 (1963), wave functions for ^2P state of three-electron ions.

[4] B. C. Webster and R. F. Stewart, Theor. Chim. Acta. 27, 355 (1972).

[5] R. F. Curl and C. A. Coulson, Proc. Phys. Soc. Lond. 85, 647 (1965); corrections to the analytical SCF wave functions for H^- have been given by these authors in J. Phys. B 1, 325 (1968).

[6] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960).

[7] V. McKoy and O. Sinanoğlu, J. Chem. Phys. 41, 2689 (1964).

[8] H. J. Silverstone and O. Sinanoğlu, J. Chem. Phys. 44, 1899 (1966).

[9] O. Sinanoğlu and I. Oksuz, Phys. Rev. Lett. 21, 507 (1968).

[10] K. E. Banyard and C. C. Baker, J. Chem. Phys. 51, 2680 (1969).

[11] C. C. Baker and K. E. Banyard, Phys. Rev. 188, 57 (1969).

[12] K. E. Banyard and D. J. Ellis, Mol. Phys. 24, 1291

(1972).

[13] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).

[14] F. W. Byron and C. J. Joachain, Phys. Rev. 157, 7 (1967).

[15] O. Sinanoğlu, J. Chem. Phys. 36, 706 (1962).

[16] R. E. Watson, Phys. Rev. 119, 170 (1960).

[17] R. K. Nesbet, Phys. Rev. 155, 51 (1967).

[18] M. Geller, H. S. Taylor, and H. B. Levine, J. Chem. Phys. 43, 1727 (1965).

[19] H. P. Kelly, Phys. Rev. 131, 684 (1963); 136, B896 (1964).

[20] L. Szasz and W. Byrne, Phys. Rev. 158, 34 (1967).

[21] C. F. Bunge, Phys. Rev. 168, 92 (1968).

[22] D. F. Tuan and O. Sinanoğlu, J. Chem. Phys. 41, 2677 (1964).

[23] G. P. Barnett, J. Linderberg, and H. Shull, J. Chem. Phys. 43, S80 (1965).

[24] P. L. Olympia, Jr. and D. W. Smith, J. Chem. Phys. 52, 67 (1970).

[25] J. Linderberg and H. Shull, J. Mol. Spectrosc. 5, 1 (1960).

[26] J. S. Alper, Phys. Rev. 177, 86 (1969).