PHYSICAL REVIEW A VOLUME 13, NUMBER 2 FEBRUARY 1976

Some expectation values for Be-like ions derived from pair-correlated wave functions

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(Received 11 February 1975; revised manuscript received 14 October 1975)

Pair-correlated energies are reported for the ground states of a series of Be-like ions and, in particular, an assessment is made of the influence which *individual* pair correlations alone have on various one-particle expectation properties. The small changes which occur were, generally, heavily dominated by the L-shell effect, which became more pronounced as Z became larger.

For Be-like ions, we have shown[1] that allowances for pair correlations in the electronic description give significant improvements in the calculated values of off-diagonal quantities such as generalized oscillator strengths. Besides reporting briefly on the formation of our pair-correlation functions, the present article follows the theme of earlier work[2] for He-like ions by examining the influence of some ground-state correlation effects on several one-particle expectation values. In particular, although the changes will be only of second order according to Møller and Plesset,[3] the mode of construction of the correlated wave function Ψ allows us to assess specifically the relative importance of the individual K-, L- and intershell pair correlations *alone* when evaluating such properties. Finally, we note that no other comprehensive list of expectation values for Be-like ions appears to exist.

The correlated wave function was expressed in terms of the many-electron theory of Sinanoğlu[4] and the leading term in the expansion was chosen to be the Hartree-Fock (HF) function. As a simplification and because of their energy importance, only the pair-correlation functions U_{ij} were retained in our correlated description of Ψ. Following the Nesbet-Bethe-Goldstone approach,[5] each pair function was written as an orbital expansion

$$U_{ij}(\vec{x}_1, \vec{x}_2) = \left(\sum_{a,b} C^{i,j}_{a,b} \phi_a(\vec{r}_1)\phi_b(\vec{r}_2) \right) \Theta(s_1, s_2), \quad (1)$$

where $\Theta(s_1, s_2)$ is a two-electron spin eigenfunction; $\vec{x}_k$ and $\vec{r}_k$ are the space-spin and space coordinates, respectively, of electron k. Subject to the symmetry requirements imposed on Ψ, the coefficients $C^{i,j}_{a,b}$ form a set of independent variational parameters which, for each pair, were obtained by the minimization of the pair energy functional given by Levine *et al.*[6] We used the minimization procedure of Fletcher and Powell[7] based on an iterative technique due to Davidon.[8] The functions ϕ_a, ϕ_b, etc., were chosen to be virtual HF orbitals obtained from a Hartree-Fock-Roothaan (HFR) calculation within a given basis set, and hence the various orthogonality constraints of the many-electron theory are automatically satisfied. Although computationally attractive from the orthogonality viewpoint, the use of virtual orbitals has the drawback that it can give a description which is spatially too diffuse when compared with occupied orbitals. However, unless the basis set is excessive, all symmetry-allowed possibilities can be used in the representation of each pair function. Thus, the present approach not only maximizes the usefulness of the basis set, but also indicates that our results are limited essentially by its nature and size.

For each ion we used the 7 s-type and 15 p-type basis functions employed by Weiss[9] in his construction of a 55-term configuration-interaction (CI) wave function. Besides providing 20 virtual orbitals for the representation of each U_{ij}, our HFR calculations gave ground-state energies which, compared with those of Roothaan, Sachs, and Weiss,[10] showed a discrepancy of 10^{-3} a.u. for Li^-, whereas for Be the agreement was to within 10^{-4} a.u. and continued to improve as Z, the atomic number, was increased in value. (All results are expressed here in atomic units.) Therefore, our basis set satisfies the basic criteria for a correlation calculation of being able to reproduce a satisfactory HF energy. The evaluation of pair functions by a direct minimization of their energies ϵ_{ij} necessitates a decoupling procedure within the wave function which implies that any rigorous condition of an upper bound on the total energy has been relaxed. This is well known and has been discussed by several workers (see, for example,

TABLE I. Approximate Hartree-Fock energies $E_{\rm HF}$, pair-correlation energies ϵ_{ij} and the total energy $E_{\rm Tot}$ for the ground-state of the Be-like ions. Atomic units are used throughout.

Z	3	4	5	6	7	8
$-E_{\rm HF}$	7.4270	14.5729	24.2375	36.4085	51.0823	68.2577
$-\epsilon_{1s1s}$	0.0385	0.0379	0.0375	0.0373	0.0371	0.0370
$-\epsilon_{2s2s}$	0.0274	0.0443	0.0597	0.0730	0.0855	0.0975
$-\epsilon_{1s2s}$ $(S=0)$	0.0011	0.0031	0.0045	0.0054	0.0060	0.0065
$-\epsilon_{1s2s}$ $(S=1)$	0.0003	0.0007	0.0010	0.0012	0.0013	0.0014
$-E_{\rm Tot}$ [a]	7.4949	14.6603	24.3422	36.5278	51.2148	68.4029

[a] $E_{\rm Tot} = E_{\rm HF} + \epsilon_{1s1s} + \epsilon_{2s2s} + \epsilon_{1s2s}\ (S=0) + 3\epsilon_{1s2s}\ (S=1)$.

Szasz,[11] Krauss and Weiss,[12] Byron and Joachain,[13] and Nesbet[5]).

Energies are given in Table I. The expectation values listed in Table II were evaluated using, in turn, the HF orbitals, the HF orbitals and the K-shell pair function, the HF orbitals and the L-shell pair function and, finally, the HF orbitals plus the K-, L- and intershell functions. The quantity Δr gives a measure of the diffuseness of the radial density distribution $D(r)$.[14(a)] Although not presented here, the coherent x-ray scattering factors were also determined.[14(b)]

Comparisons of ϵ_{1s1s}, ϵ_{2s2s} and our total intershell pair energy $\epsilon_{1s2s} = \epsilon_{1s2s}(S=0) + 3\epsilon_{1s2s}(S=1)$ with other workers are most conveniently made for Be and B^+; see, respectively, results summarized in Table III of Banyard and Taylor[1] and Byron and Joachain.[13] For both systems our re-

TABLE II. Expectation values for the Be-like ions in the ground state and the changes due to the inclusion in the wave function of individual pair correlation, expressed as a percentage of the HF value.

Z	Wave function	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\langle r\rangle$	$\langle r^2\rangle$	$\langle r^4\rangle$	$\langle -\frac{1}{2}\sum_{i=1}^{4}\nabla_i^2\rangle$	$\langle \delta^3(\vec{r})\rangle$	Δr
3	HF	30.2453	5.8836	11.7845	70.4761	4886.31	7.4350	3.4560	2.9899
	HF + all pairs	30.2024	5.8779	11.7953	70.5838	4892.28	7.4685	3.4516	2.9917
	% change due to $K_{\rm corr}$	−0.04	−0.04	+0.01	+0.01	0.00	+0.41	−0.01	0.00
	$L_{\rm corr}$	−0.10	−0.06	+0.09	+0.16	+0.12	+0.08	−0.12	+0.07
	all pairs	−0.14	−0.10	+0.09	+0.15	+0.12	+0.45	−0.13	+0.06
4	HF	57.6260	8.4113	6.0960	17.0081	252.573	14.5771	8.8523	1.3890
	HF + all pairs	57.4386	8.4021	6.0745	16.8831	249.037	14.6045	8.8177	1.3837
	% change due to $K_{\rm corr}$	−0.03	−0.04	0.00	+0.01	+0.01	+0.15	−0.01	0.00
	$L_{\rm corr}$	−0.29	−0.08	−0.36	−0.73	−1.39	−0.01	−0.36	−0.37
	all pairs	−0.33	−0.11	−0.35	−0.73	−1.39	+0.19	−0.39	−0.38
5	HF	94.0452	10.9194	4.2420	7.9036	51.6031	24.2397	18.1677	0.9226
	HF + all pairs	93.7454	10.9094	4.2256	7.8372	50.7696	24.2570	18.0951	0.9183
	% change due to $K_{\rm corr}$	−0.02	−0.01	0.00	+0.01	0.00	+0.12	−0.01	0.00
	$L_{\rm corr}$	−0.29	−0.08	−0.39	−0.84	−1.61	−0.05	−0.38	−0.46
	all pairs	−0.32	−0.09	−0.39	−0.84	−1.61	+0.07	−0.40	−0.47
6	HF	139.478	13.4230	3.2774	4.6147	17.0354	36.4098	32.4737	0.6945
	HF + all pairs	139.008	13.4127	3.2614	4.5656	16.6921	36.4181	32.3318	0.6904
	% change due to $K_{\rm corr}$	−0.01	0.00	0.00	0.00	0.00	+0.08	−0.01	0.0
	$L_{\rm corr}$	−0.32	−0.06	−0.49	−1.06	−2.01	−0.06	−0.42	−0.59
	all pairs	−0.34	−0.08	−0.49	−1.06	−2.01	+0.02	−0.44	−0.59
7	HF	193.918	15.9249	2.6775	3.0382	7.2340	51.0831	52.8450	0.5581
	HF + all pairs	193.253	15.9147	2.6629	3.0021	7.0741	51.0833	52.6045	0.5544
	% change due to $K_{\rm corr}$	−0.01	0.00	0.00	0.00	0.00	+0.06	−0.01	0.00
	$L_{\rm corr}$	−0.33	−0.05	−0.55	−1.18	−2.21	−0.06	−0.44	−0.66
	all pairs	−0.34	−0.06	−0.55	−1.19	−2.21	0.00	−0.46	−0.66
8	HF	257.363	18.4261	2.2660	2.1559	3.5913	68.2588	80.3562	0.4670
	HF + all pairs	256.476	18.4162	2.2528	2.1288	3.5082	68.2523	79.9822	0.4639
	% change due to $K_{\rm corr}$	−0.01	0.00	0.00	0.00	0.00	+0.04	−0.01	0.00
	$L_{\rm corr}$	−0.33	−0.05	−0.58	−1.26	−2.31	−0.06	−0.45	−0.66
	all pairs	−0.34	−0.05	−0.58	−1.26	−2.31	−0.01	−0.47	−0.66

sults for ϵ_{2s2s} and ϵ_{1s2s} are in excellent agreement with previous values but the comparisons for ϵ_{1s1s} were somewhat less good. Our K-shell pair energies may be influenced by the omission from our basis set of d- and f-type orbitals whereas, for L-shell correlation effects in Be-like ions, the p-orbital contribution—which we have allowed for—is known to be dominant.

As anticipated, Table II shows only small changes in the expectation values; nevertheless, several interesting trends emerge concerning the influence of the individual pair functions. For Δr the main cause of change arises from the L-shell pair function which, with the exception of Li^-, marginally enhances the charge cloud contraction normally observed as Z increases; K-shell correlation leaves Δr unaffected. The influence on the detailed form of $D(r)$ can be judged from the behavior of $\langle r^n \rangle$. In all instances the major change occurs as a consequence of L-shell correlation which, except for Li^-, gives reductions for $\langle r^n \rangle$ which become more significant as n increases beyond $n=1$. This clearly indicates a contraction of the 2s orbital density and, as Table II shows, this contraction increases in relative importance as Z becomes larger. The lack of convergence between the correlated and noncorrelated values as Z increases is in contrast to the behavior exhibited by He-like ions and is a manifestation, in the present case, of the increase in near-degeneracy of the 2s and 2p orbitals.

The nuclear magnetic shielding factor and electron-nuclear potential energy depend on $\langle r^{-1} \rangle$ which is seen here to exhibit a remarkably high degree of independence to all pair-correlation effects. A similar observation has been made by Davidson[15] for He. For $\langle r^{-2} \rangle$, pair correlations cause a total relative change which remains almost constant for $Z > 3$, the effect being dominated once again by the L shell.

Expectation values of $\delta^3(\vec{r}_1)$ are a measure of the electron density at the nucleus and assume importance in the calculation of relativistic and certain radiative corrections.[16] It is significant to note from inspection of Table II that the influence of K-shell pair correlation is virtually negligible, the present overall change is almost totally due to the L-shell effect and causes a reduction in value which increases slightly in magnitude as Z becomes larger. However, for $\langle -\frac{1}{2}\sum_{i=1}^{4} \nabla_i^2 \rangle$, the relative importance found so far for the K- and L-shell pair correlations is seen to have been reversed at low to intermediate Z values. K-shell correlation causes the expected increase in kinetic energy for each ion: the relative effect becomes smaller as Z gets larger and, except for Li^-, always opposes the change produced by the L-shell pair function. For $Z \geq 5$, the net effect of all pair correlations is one of approximate cancellation.

Throughout the series, our HF values for the x-ray scattering factors were found to be in excellent agreement with the corresponding results of Benesch, Singh, and Smith.[17] Although correlation within the L shell proved to be considerably more important than that in the K shell, the total changes were, nevertheless, quite small. The correlation trends, which became more pronounced with Z, followed those found for Be by Tanaka and Sasaki[18] and by Benesch and Smith.[19]

Generally, it was observed that, for the ground states of the Be-like ions, changes in the present expectation properties due to L-shell pair correlations were, relatively, considerably larger than those due to either K- or intershell pair correlations: the intershell effects having a negligible influence in each instance. These pair characteristics were particularly noticeable when examining the changes in the density at the nucleus. For $\langle r^{-1} \rangle$, however, the results were virtually insensitive to all such correlation effects for all Z values.

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