PHYSICAL REVIEW VOLUME 188, NUMBER 1 5 DECEMBER 1969

Analysis of Electron Correlation in Two-Electron Systems. II. Be^{++}, B^{3+}, C^{4+}, N^{5+}, and O^{6+}

C. C. Baker and K. E. Banyard
Department of Physics, University of Leicester, Leicester, England

(Received 2 June 1969)

The analysis of correlation effects within two-electron systems is extended to Be^{++}, B^{3+}, C^{4+}, N^{5+}, and O^{6+}. These ions are the remaining members of the isoelectronic series studied by both an extended configuration-interaction (CI) treatment and wave functions which involve Hylleraas-type correlation factors. Values are determined for $\langle \cos\gamma_{12}\rangle$, $\langle \vec{r}_1 \cdot \vec{r}_2\rangle$, and $\langle r^n\rangle$, where $-2 \leq n \leq 4$. The two-particle radial density differences $\Delta D(r_1; r_2)$, relative to the uncorrelated approach, were examined for the CI wave functions. Radial and angular correlation effects were also examined by means of a natural-orbital analysis. This revealed that, for correlation, configurations involving angular basis functions were dominant, although the *relative* importance of correlation effects decreases with increasing Z. Values obtained for the diamagnetic susceptibility χ and $\langle \vec{r}_1 \cdot \vec{r}_2\rangle$ give excellent support for the inverse-Z expansion formulas derived by Dalgarno and Stewart. As Z increases, the comparatively simple r_{12} wave functions appear to overemphasize the influence of correlation effects on certain expectation values.

I. INTRODUCTION

In a previous paper[1] (part I of the series), wave functions containing electron correlation effects were analyzed for the two-electron systems H^-, He, and Li^+. The correlated wave functions were formulated either by means of a configuration-interaction (CI) treatment, or by the inclusion of explicit correlation factors. The CI wave functions were those of Weiss,[2] and the r_{12} functions were those of Green *et al.*[3] A pictorial representation of the influence of electron correlation on the two-particle radial density distribution $D(r_1; r_2)$ was given by means of density difference maps, $\Delta D(r_1; r_2)$, each expressed with respect to the corresponding Hartree-Fock density. We also determined several one- and two-particle expectation values which allowed us to examine radial and angular correlation effects. This was further facilitated by expressing each CI wave function in terms of natural orbitals,[4] and examining selected expectation values as a function of the degree of truncation within the natural expansion.

A comparison with the results available from the excellent calculations of Pekeris[5] for H^-, He, and Li^+ indicated that, as Z increased, the wave functions of Green *et al.* contained a slightly greater emphasis of both angular and radial correlation effects. Similar trends were not apparent for the CI wave functions of Weiss, which compared favorably with the Pekeris calculations.

Our investigation has now been extended to the remaining members of the isoelectronic series studied by Weiss and by Green *et al.*, namely, Be^{++}, B^{3+}, C^{4+}, N^{5+}, and O^{6+}. The procedure parallels our previous investigation quite closely. As before, a comparison is made with the analytical Hartree-Fock functions of Roothaan, Sachs, and Weiss,[6] which, for our two-electron systems, are the "best" noncorrelated functions of greatest computational convenience. Natural expansions for the CI wave functions are also presented.

II. WAVE FUNCTIONS AND ENERGIES

The normalized symmetric space functions $\Psi(1, 2)$ arising from the ground-state treatments considered here are: (a) function I, the CI wave function of Weiss[2] involving the superposition of 35 configurations with Slater-type basis orbitals extending as far as $5g$ and employing seven variable orbital exponents; (b) function II, the energetically "best" wave function obtained by Gree *et al.*[3] which includes correlation effects explicitly by means of Hylleraas-type correlation factors; and (c) function III, the Hartree-Fock functions provided by Roothaan, Sachs, and Weiss.[6]

The energies[7] obtained from each treatment are quoted in Table I. The results of Frankowski and Pekeris[8] are taken as the criteria when calculating the "exact" correlation energy. Although the total energies given by the treatments of Weiss and of Green *et al.* are in general agreement with the results of Frankowski and Pekeris, we note that, as Z increases, the percentage correlation energy provided by the functions of Green *et al.* shows a steady decrease, whereas the Weiss treatment maintains an almost constant percentage value for $Z \geq 4$. Consequently, in the present paper, we have placed slightly greater emphasis on the analysis of the Weiss functions.

Correlation effects were also studied by analyzing each CI wave function in terms of natural orbitals χ_i. The coefficients c_i associated with the

TABLE I. Wave functions and energies.

Z	4 Be^{2+}		5 B^{3+}		6 C^{4+}		7 N^{5+}		8 O^{6+}	
Wave function	Energy $-E$ (a.u.)	% corr.[a]	Energy $-E$ (a.u.)	% corr.[a]	Energy $-E$ (a.u.)	% corr.[a]	Energy $-E$ (a.u.)	% corr.[a]	Energy $-E$ (a.u.)	% corr.[a]
I. Weiss (35-CI)[b]	13.6548	98.2	22.0302	98.1	32.4054	98.2	44.7806	98.2	59.1557	98.0
II. Green *et al.*[c] (r_{12})	13.6533	94.8	22.0284	94.2	32.4034	93.8	44.7785	93.6	59.1535	93.2
III. Hartree-Fock[d]	13.6113	0[e]	21.9862	0[e]	32.3612	0[e]	44.7362	0[e]	59.1112	0[e]
χ_1 (Weiss)[f]	13.6113	...	21.9862	...	32.3612	...	44.7362	...	59.1111	...
Frankowski and Pekeris[g]	13.6556	100[e]	22.0310	100[e]	32.4062	100[e]	44.7814	100[e]	59.1566	100[e]

[a] % correlation = $100\,[(E - E_{(\mathrm{HF})})/(E_{\mathrm{PEKERIS}} - E_{(\mathrm{HF})})]$.

[b] Reference 2.

[c] Reference 3.

[d] Reference 6.

[e] By definition

[f] The first natural orbital in the appropriate natural expansion.

[g] Reference 8.

χ_i in the natural expansion[4] are given in Table II. Each term in the natural expansion of $\Psi(1, 2)$ is a configuration of S-type symmetry composed of basis orbitals whose symmetry-type is represented by λ_i. For each system, the energy expectation value corresponding to the first natural orbital χ_1 is given in Table I.

III. ELECTRON DENSITIES AND EXPECTATION VALUES

The density functions and expectation values mentioned here are all as defined in paper I. Although the present work does not include contour diagrams for $\Delta D(r_1;\, r_2)$, the general behavior of such surfaces as Z increases may be judged by inspection of Table III, where we present the coordinates of the maxima and minima of the $\Delta D(r_1;\, r_2)$ surfaces for the Weiss functions. For comparison, Table III contains the appropriate values for the Hartree-Fock two-particle density, namely, $D(r_1;\, r_2)_{\mathrm{III}}$. Values of $\langle r^n \rangle$ are listed in Table IV for $-2 \leq n \leq 4$. Included in parentheses for the Weiss functions are the number of terms required in the natural expansion for convergence to that value for $\langle r^n \rangle$. Table V gives results for the one-particle density $\rho(r)$ evaluated at the nucleus from the treatments I, II, and III for H^- through 0^{6+}. In Table VI, we present values for Δr – which provides a measure of the diffuseness of each $D(r)$, σ – the nuclear diamagnetic shielding factor, χ – the atomic diamagnetic susceptibility,[9] $\langle \cos\gamma_{12} \rangle$, and $\langle \vec{r}_1 \circ \vec{r}_2 \rangle$. Included in parentheses are values of χ and $\langle \vec{r}_1 \circ \vec{r}_2 \rangle$ derived from the inverse-Z expansions of Dalgarno and Stewart.[10]

IV. DISCUSSION

The excellent agreement found in paper I between the energies derived from the first natural orbital χ_1 and the Hartree-Fock treatment is seen from Table I to be maintained throughout the two-electron series. The effect of neglecting all higher terms, i.e., $i > 1$, in each natural expansion of the Weiss wave functions gives energy changes ranging from 0.0406 (H^-), 0.0428 (Li^+), and 0.0440 (B^{3+}), increasing slowly to 0.0446 (0^{6+}). The "exact" correlation energy, defined here as the difference between the Pekeris[5,8] and Hartree-Fock energies,[6] has values ranging from 0.0398 $\times$(H^-), 0.0435 (Li^+), and 0.0448 (B^{3+}), to 0.0454 $\times$(0^{6+}).

In Table II, the coefficients c_i in the natural expansion provide a measure of the relative importance of configurations derived from basis orbitals of symmetry type λ_i. As Z increases, we observe that $i > 1$ each c_i decreases in value, hence indicating that correlation effects become *relatively* less important. The coefficients also indicate that, for correlation terms within each

TABLE II. Coefficients c_i, and symmetry λ_i of the basis orbitals, associated with each χ_i in the natural expansion of the Weiss CI wave functions.[a]

Z	4 Be^{2+}	5 B^{3+}	6 C^{4+}	7 N^{5+}	8 O^{6+}
χ_i	c_i λ_i	c_i λ_i	c_i λ_i	c_i λ_i	c_i λ_i
1	−0.99916 (*s*)	−0.99947 (*s*)	−0.99967 (*s*)	−0.99978 (*s*)	−0.99984 (*s*)
2	0.03112 (*p*)	0.02489 (*p*)	0.02072 (*p*)	0.01775 (*p*)	0.01554 (*p*)
3	0.02637 (*s*)	0.02052 (*s*)	0.01679 (*s*)	0.01422 (*s*)	0.01233 (*s*)
4	0.00694 (*d*)	0.00564 (*d*)	0.00476 (*d*)	0.00409 (*d*)	0.00361 (*d*)
5	0.00594 (*p*)	0.00479 (*p*)	0.00400 (*p*)	0.00346 (*p*)	0.00303 (*p*)
6	0.00388 (*s*)	0.00309 (*s*)	0.00256 (*s*)	0.00219 (*s*)	0.00191 (*s*)
7	0.00254 (*f*)	0.00201 (*f*)	0.00172 (*f*)	0.00150 (*f*)	0.00131 (*f*)
8	0.00215 (*d*)	0.00174 (*d*)	0.00147 (*d*)	0.00127 (*d*)	0.00112 (*d*)
9	0.00175 (*p*)	0.00140 (*p*)	0.00117 (*p*)	0.00101 (*p*)	0.00088 (*p*)
10	0.00099 (*s*)	0.00081 (*s*)	0.00067 (*g*)	0.00058 (*s*)	0.00050 (*g*)
11	0.00098 (*g*)	0.00080 (*g*)	0.00066 (*s*)	0.00057 (*g*)	0.00049 (*s*)
12	0.00089 (*f*)	0.00065 (*f*)	0.00056 (*f*)	0.00049 (*f*)	0.00044 (*f*)
13	0.00068 (*d*)	0.00054 (*d*)	0.00046 (*d*)	0.00039 (*d*)	0.00034 (*d*)
14	0.00040 (*p*)	0.00031 (*p*)	0.00026 (*p*)	0.00021 (*p*)	0.00019 (*p*)
15	0.00034 (*s*)	0.00028 (*s*)	0.00023 (*s*)	0.00020 (*s*)	0.00017 (*s*)
$\sum_{i\neq 1} c_i^2(\lambda_i = s)$	0.00071	0.00043	0.00028	0.00021	0.00015
$\sum_i c_i^2(\lambda_i \neq s)$	0.00106	0.00068	0.00047	0.00035	0.00027

[a] Transformation matrices between the basis and the natural orbitals may be obtained from C. C. B. on request.

natural expansion, the relative importance of configurations derived from angular orbitals with respect to those derived from radial orbitals increases as Z becomes larger. As a general guide, Table II contains some assessment of the total radial correlation "character" and total angular correlation "character" contained in each natural expansion. The increase in nuclear charge thus shows its effect by decreasing the radial freedom of the electrons, hence causing a relative increase in correlation by means of angular separation.

Correlation effects create a drop in $D(r_1 = r_2)$ with respect to the Hartree-Fock value. We see from Table III that the minima in $\Delta D(r_1 = r_2)$ become deeper and closer to the nucleus as Z increases, however, their depth expressed as a fraction of the Hartree-Fock value for $D(r_1 = r_2)$ becomes considerably smaller. Similar type features occur for the maxima in $\Delta D(r_1; r_2)$. Certain of the tendencies are illustrated in Fig. 1

TABLE III. Maxima and minima which occur in the $\Delta D(r_1, r_2)$ surfaces of Weiss relative to the Hartree-Fock density.

System	Maxima				Minima		
Z	r_1	r_2	$\Delta D(r_1; r_2)$	$D(r_1; r_2)_{\text{III}}$	$r_1 = r_2$	$\Delta D(r_1 = r_2)$	$D(r_1 = r_2)_{\text{III}}$
4 Be^{2+}	0.18	0.60	0.16798	2.96398	0.16	−0.38410	4.96692
					0.58	−0.07606	1.74415
5 B^{3+}	0.14	0.46	0.21534	5.04726	0.14	−0.48429	9.35218
					0.46	−0.09774	2.72393
6 C^{4+}	0.12	0.38	0.26033	7.58689	0.10	−0.58485	11.14324
					0.38	−0.11935	3.97193
7 N^{5+}	0.08	0.32	0.29951	8.91667	0.10	−0.68493	19.56631
					0.32	−0.14110	5.74086
8 O^{6+}	0.08	0.28	0.35607	13.05398	0.08	−0.80293	23.04324
					0.28	−0.16366	7.39508

TABLE IV. Values of $\langle r^n \rangle$ for $4 \le Z \le 8$.

Z System	Wave function	$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r^{1} \rangle$	$\langle r^{2} \rangle$	$\langle r^{3} \rangle$	$\langle r^{4} \rangle$
4 Be^{2+}	Weiss[a]	55.686 (4)	7.3755 (4)	0.82852 (5)	0.46400 (6)	0.32811 (6)	0.28044 (6)
	Hartree-Fock	55.649	7.3748	0.82827	0.46365	0.32780	0.28029
	χ_1 (Weiss)	55.701	7.3774	0.82814	0.46352	0.32758	0.27983
5 B^{3+}	Weiss[a]	89.517 (6)	9.3754 (5)	0.64909 (6)	0.28388 (5)	0.15641 (5)	0.10400 (5)
	Hartree-Fock	89.476	9.3749	0.64897	0.28376	0.15634	0.10399
	χ_1 (Weiss)	89.533	9.3770	0.64890	0.28370	0.15626	0.10386
6 C^{4+}	Weiss[a]	131.34 (3)	11.375 (2)	0.53358 (6)	0.19145 (3)	0.08641 (3)	0.04702 (3)
	Hartree-Fock	131.31	11.375	0.53351	0.19140	0.08639	0.04703
	χ_1 (Weiss)	131.36	11.376	0.53347	0.19137	0.08636	0.04698
7 N^{5+}	Weiss[a]	181.17 (3)	13.375 (2)	0.45298 (5)	0.13779 (3)	0.05268 (6)	0.02426 (3)
	Hartree-Fock	181.14	13.375	0.45294	0.13777	0.05267	0.02426
	χ_1 (Weiss)	181.19	13.376	0.45291	0.13775	0.05265	0.02424
8 O^{6+}	Weiss[a]	239.00 (3)	15.375 (2)	0.39354 (5)	0.10390 (3)	0.03445 (3)	0.01375 (3)
	Hartree-Fock	238.97	15.375	0.39351	0.10389	0.03445	0.01376
	χ_1 (Weiss)	239.02	15.376	0.39349	0.10387	0.03443	0.01374

[a] Figures in parenthesis represent the number of terms in the natural expansion required for convergence to the recorded CI values.

where the maxima and minima in $\Delta D(r_1 ; r_2)$ are plotted against Z for $1 \leqslant Z \leqslant 8$. We also note that $(r_2 - r_1)$ obtained from the maxima in $\Delta D(r_1 ; r_2)$ is roughly proportional to $Z^{-1.2}$.

Differences between $\langle r^n \rangle$ values determined from χ_1 and the Hartree-Fock orbitals are seen from Table IV to be small. However, a general pattern of behavior is apparent. For $\langle r^{-2} \rangle$ and $\langle r^{-1} \rangle$, the χ_1 values are consistently larger than the Hartree-Fock results, whereas for larger n the converse is true. A similar pattern existed for Li^+ but the change-over occurred at $\langle r^3 \rangle$ instead of $\langle r^1 \rangle$ as found for $Z \geqslant 4$. Going to He and H^-, χ_1 (Weiss) gave larger values than the Hartree-Fock treatment for *all* $\langle r^n \rangle$. Variations between χ_1 and the Hartree-Fock functions are not too surprising since Nazaroof and Hirschfelder[11] have shown that the first natural orbital begins to differ from the Hartree-Fock orbitals in the second order. Such differences, although small, might be expected to be most noticeable for low Z values. Table IV also reveals that χ_1 and the Hartree-Fock orbitals give values for $\langle r^{-2} \rangle$ and $\langle r^{-1} \rangle$ which span the corresponding CI results. A similar behavior, based on the Weiss functions, occurred for Li^+ and He.

Although details are not given, it was found that, as before,[1] the addition of configurations involving s orbitals within the natural expansion of $\Psi(1,2)$ caused the resulting $D(r)$ to expand. The effect decreased considerably as Z increased. The influence of the angular orbitals was less clear-cut.

The CI wave functions of Weiss give a one-particle density $\rho(r)$ evaluated at the nucleus which is larger than the Hartree-Fock result for all Z values. A similar effect has been found in our investigation of the influence of correlation in molecules.[12] Table V shows that, except for H^-, the percentage change with respect to the Hartree-Fock result is small and decreases markedly with the increase of Z. The values of Green *et al.* for $\rho(0)$ do not follow the trend shown by the CI results and at present no explanation can be offered.

The CI values for χ and $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$ given in Table VI strongly support the findings of Dalgarno and Stewart.[10] For completeness, the appropriate comparisons for χ taken from the Weiss CI results of paper I are: -18.850 (-12.00) for H^-, -1.8891 (-1.879) for He, and -0.70685 (-0.711) for Li^+. The corresponding values for $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$ were: -0.67622 (-0.619) for H^-, -0.06455 (-0.0624) for He, and -0.01717 (-0.0170) for Li^+. As in Table VI, the quantities in parentheses are those obtained by Dalgarno and Stewart. On the whole, the high accuracy anticipated by these workers was well justified; possible exceptions occur at low Z values which is only to be expected.

The over-all trends which were seen to develop in Table VI of paper I are continued here. In particular, as Z increases, the values for $\langle \cos\gamma_{12} \rangle$,

TABLE V. Electron density $\rho(r)$ evaluated at the nucleus.

Z	System	I, Weiss	II, Green *et al.*	III, Hartree-Fock
1	H^-	0.33109	0.33344	0.30928
2	He	3.63118	3.61853	3.59642
3	Li^+	13.7332	13.6669	13.6740
4	Be^{2+}	34.4338	32.7607	34.3585
5	B^{3+}	69.5780	66.2518	69.4564
6	C^{4+}	122.964	121.805	122.825
7	N^{5+}	198.434	196.793	198.242
8	O^{6+}	299.805	297.660	299.609

$\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$, and Δr derived from the functions of Green *et al.* are all larger in magnitude than the CI results, suggesting, in the former, a possible overemphasis of the influence of correlation effects.

V. CONCLUSION

The results presented here show the further development of trends which appeared for H^-, He, and Li^+ in paper I. It was noticed there that the natural orbital coefficients indicated that, for correlation, a configuration involving *s* orbitals was initially most important for H^- whereas, for Li^+, a configuration based on angular orbitals was dominant. The coefficients in Table II of this paper show that a configuration composed of angular basis functions continues to prevail as Z increases. As before, the relative importance of all correla-

TABLE VI. Some expectation values for $4 \leq Z \leq 8$.

Z System	Wave function	Δr	$\sigma \times 10^5$	χ [a]	$\langle \cos\gamma_{12} \rangle$	$\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$
4 Be^{2+}	I, Weiss	0.24574	13.0915	−0.36714 (−0.36976)[b]	−0.03292	−0.00686 (−0.00686)[b]
	II, Green *et al.*	0.25166	12.8576	−0.38342	−0.04273	−0.00997
	III, Hartree-Fock	0.24560	13.0903	−0.36734	c	c
	χ_1 (Weiss)	0.24558	13.0949	−0.36724	c	c
5 B^{3+}	I, Weiss	0.19136	16.6413	−0.22491 (−0.22596)	−0.02641	−0.00340 (−0.00342)
	II, Green *et al.*	0.19720	16.3117	−0.23671	−0.03470	−0.00513
	III, Hartree-Fock	0.19131	16.6404	−0.22482	...	...
	χ_1 (Weiss)	0.19128	16.6442	−0.22477	...	...
6 C^{4+}	I, Weiss	0.15668	20.1906	−0.15168 (−0.15223)	−0.02203	−0.00193 (−0.00194)
	II, Green *et al.*	0.15832	20.1108	−0.15383	−0.02810	−0.00278
	III, Hartree-Fock	0.15668	20.1906	−0.15164	...	...
	χ_1 (Weiss)	0.15665	20.1924	−0.15162	...	...
7 N^{5+}	I, Weiss	0.13266	23.7406	−0.10916 (−0.10947)	−0.01890	−0.00119 (−0.00120)
	II, Green *et al.*	0.13391	23.6625	−0.11050	−0.02379	−0.00173
	III, Hartree-Fock	0.13266	23.7406	−0.10915	...	...
	χ_1 (Weiss)	0.13266	23.7424	−0.10913	...	...
8 O^{6+}	I, Weiss	0.11506	27.2906	−0.08231 (−0.08250)	−0.01657	−0.00079 (−0.00080)
	II, Green *et al.*	0.11587	27.2143	−0.08313	−0.02079	−0.00115
	III, Hartree-Fock	0.11502	27.2906	−0.08231	...	...
	χ_1 (Weiss)	0.11502	27.2924	−0.08229	...	...

[a] See Ref. 9.

[b] The figures in parentheses are derived from the inverse-Z expansion of Dalgarno and Stewart.

[c] Due to the independent-particle nature of the Hartree-Fock treatment and to the fact that χ_1 is composed of *s*-type orbitals, this quantity is identically zero.

tion terms within each natural expansion decreases as Z becomes larger. Support for such a conclusion can be drawn from the values of $\Delta D(r_1; r_2)$ at the maxima and minima.

Values of χ and $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$ obtained from the Weiss CI functions for $1 \leq Z \leq 8$ give excellent support to the expansion formulas for these quantities deduced by Dalgarno and Stewart. Finally, although the wave functions of Green *et al.* indicate that, in general, correlation becomes relatively less important as Z increases, the functions appear to overemphasize the *influence* of correlation effects on certain expectation values.

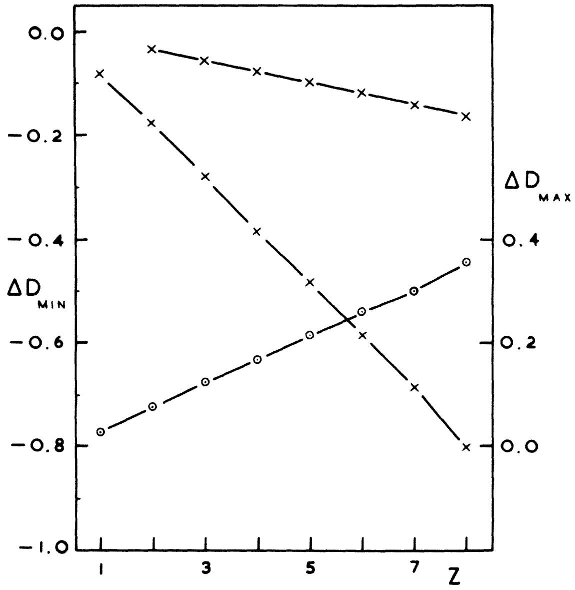

FIG. 1. Values of the minima, $\Delta D_{\min}$(−×−×−), and the maxima, $\Delta D_{\max}$(−⊙−⊙−), which occur in the $\Delta D(r_1; r_2)$ surfaces, derived from the Weiss CI wave functions relative to the Hartree-Fock density, for various Z for the heliumlike series.

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