# Compact and accurate integral-transform wave functions. II. The $2^{1}S$ , $2^{3}S$ , $2^{1}P$ , and $2^{3}P$ states of the helium-like ions from He through Mg<sup>10+</sup>

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The method of the preceding paper is used to construct compact and accurate integral-transform wave functions for the four lowest excited states of the helium-like ions. Convergence studies of the energy and various expectation values are presented for the  $2^{1}S$  and  $2^{3}S$  states of the helium atom. Parallelotope parameters and energies are given for the  $2^{1}S$ ,  $2^{3}S$ ,  $2^{1}P$ , and  $2^{3}P$  states of the ions from He through Mg<sup>10+</sup>. A brief discussion of the prospects for extending the method to many-electron systems is included.

#### I. INTRODUCTION

In the preceding paper<sup>1</sup> (hereafter referred to as I) we pointed out that a systematic collection of compact and accurate wave functions expressed in a relatively simple basis set would greatly facilitate the analysis of correlation effects in two-electron atoms. We demonstrated that a suitable variant of the integral-transform or generator coordinate method can be used to provide such wave functions, and a set of wave functions for the ground 1 <sup>1</sup>S state of the helium isoelectronic series was presented.

It is the purpose of this paper to demonstrate the usefulness of the method presented in I for excited states, and to provide a set of compact wave functions for the  $2^{1}S$ ,  $2^{3}S$ ,  $2^{1}P$ , and  $2^{3}P$  states of the heliumlike ions.

A brief outline of the method, the ansatz of I for S states, and a new ansatz for P states are presented in Sec. II. Convergence studies for the energy and a variety of other properties are presented for the  $2^{1}S$  and  $2^{3}S$  states of the helium atom in Sec. III. Wave functions for the  $2^{1}S$  and  $2^{3}S$  states of the ions from Li<sup>\*</sup> through Mg<sup>10\*</sup>, and for the  $2^{3}P$  and  $2^{1}P$  states of the ions from He through Mg<sup>10+</sup>, are also presented in Sec. III. A brief summary of results is presented in Sec. IV, along with a discussion of the prospects of extending the method to many-electron systems.

# **II. THEORETICAL DETAILS**

A full discussion of our method has been presented in I. Here we restrict ourselves to the barest of details. The variational ansatz that we use for S states is

$$\Psi(r_1, r_2, r_{12}) = (4\pi)^{-1} \sum_{k=1}^{N} C_k (1 \pm P_{12}) \exp(-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}),$$
(1)

where  $P_{12}$  is the permutation operator defined by

$$P_{12}f(r_1, r_2, r_{12}) = f(r_2, r_1, r_{12}).$$
<sup>(2)</sup>

For P states, the ansatz we employ is

$$\Psi(r_{1}, r_{2}, \theta_{1}, \theta_{2}, r_{12})$$

$$= \sqrt{3} (4\pi)^{-1} \sum_{k=1}^{N} C_{k} (1 \pm P_{12})$$

$$\times [r_{1} \cos \theta_{1} \exp(-\alpha_{k} r_{1} - \beta_{k} r_{2} - \gamma_{k} r_{12})].$$
(3)

In Eqs. (1) and (3), the plus and minus signs correspond to the singlet and triplet states, respectively. The linear coefficients are found by solving the usual secular equations, and the nonlinear parameters are chosen to be the lattice points of a pseudorandom number quadrature formula (scheme P in the notation of I). Specifically the nonlinear parameters are generated by the following equations:

$$\alpha_{k} = \eta \left[ (A_{2} - A_{1}) \langle \frac{1}{2} k(k+1) \sqrt{2} \rangle + A_{1} \right], \qquad (4a)$$

$$\beta_{k} = \eta \left[ (B_{2} - B_{1}) \langle \frac{1}{2} k(k+1) \sqrt{3} \rangle + B_{1} \right], \qquad (4b)$$

$$\gamma_k = \eta \left[ (G_2 - G_1) \langle \frac{1}{2} k(k+1) \sqrt{5} \rangle + G_1 \right], \qquad (4c)$$

for k = 1, 2, ..., N. In the above  $\langle x \rangle$  is defined to be the fractional part of x. The parameters  $A_1, A_2, B_1, B_2, G_1$ , and  $G_2$  define a parallelotope in  $\alpha - \beta - \gamma$ space and are chosen variationally to minimize the energy. Since we are dealing with bound states we

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$$\min \alpha_k > 0, \qquad (5a)$$

and

 $\min \beta_k > 0.$  (5b)

As in I we allow negative values of  $\gamma_k$ , and hence to guarantee existence of all of the integrals required for the computation of the energy and other properties we must impose the following constraints:

$$\min_{k, l} (\alpha_k + \alpha_l + \gamma_k + \gamma_l) > 0, \qquad (6a)$$

$$\min_{\substack{k,l\\k\neq l}} (\beta_k + \beta_l + \gamma_k + \gamma_l) > 0, \qquad (6b)$$

$$\min_{k,l} (\alpha_k + \beta_l + \gamma_k + \gamma_l) > 0.$$
 (6c)

In Eqs. (4),  $\eta = 1$  in principle, but in practice  $\eta$  is chosen to ensure that our wave functions satisfy the virial theorem (see I for a fuller discussion).  $\eta$  does not differ from unity by more than 10<sup>-5</sup> for our wave functions.

The S-state ansatz of Eq. (1) was used in I, and references to previous usage were given there. The P-state ansatz of Eq. (3) has, to our knowledge, not been used previously. The ansatz of Pritchard and Wallis<sup>2</sup> is the most similar to Eq. (3) of all those that we have found in the literature.

The methods we use for computing the requisite integrals, for solving the secular equation, and for optimizing the parallelotope parameters are described in I. The angular momentum analysis required for the P-state integrals is described elsewhere.<sup>3</sup>

### **III. RESULTS**

The  $2^{1}S$  state is not the lowest state of singlet S symmetry. The second-lowest eigenvalue and corresponding eigenvector, respectively, of the singlet S-symmetry secular equation provide<sup>4</sup> the desired upper bound to the energy and the approximate wave function for the  $2^{1}S$  state.

As we pointed out in I, separate optimization of the parallelotope parameters is required for each state of interest. For example, the second root of the  $60 \times 60$  secular equation with the parallelotope parameters optimized for the ground state (Table II of I) is -2.13 a.u., as compared with the "exact" result of -2.14597 a.u. Hence the parallelotope parameters that we present in this paper have all been separately optimized for each state, ion, and expansion length.

Table I lists the parallelotope parameters,  $1 - \eta$ , the energy, and various expectation values for a

sequence of wave functions with increasing numbers of terms, N, for the 2 <sup>1</sup>S state of helium. The quantities  $C_{\rm EN}$  and  $C_{\rm EE}$  are measures of deviations from the electron-nuclear and electronelectron cusp conditions respectively. The definitions of these quantities may be found in I. For an exact wave function,  $C_{\rm EN}$  should<sup>5,6</sup> be equal to the nuclear charge Z, and  $C_{\rm EE}$  should<sup>3,5,7</sup> be equal to  $\frac{1}{2}$ .

Note that the intuitive inequalities (based upon hydrogenic ideas)

$$A_1 < \frac{1}{2}Z < A_2$$
, (7a)

$$B_1 < Z < B_2 , \qquad (7b)$$

are satisfied in almost all cases, negative  $\gamma_k$ 's occur, confirming our arguments in I that they should, and  $\eta$  is very close to unity, indicating that our optimization of the parallelotope parameters was relatively successful in locating at least a local minimum. It should be evident that inequalities (7) are equally meaningful upon interchange of the A's and B's because of the spatial symmetry of the wave functions.

The energies are seen to converge smoothly toward the "exact" values of Pekeris<sup>8</sup> and Frankowski.<sup>9</sup> The 55-term energy is roughly  $2 \times 10^{-7}$ a.u. too large. Since no bounding principle is being used for them, the other expectation values do not converge monotonically.  $\langle r^{-1} \rangle$  and  $\langle r_{12}^{-1} \rangle$ , which are a part of  $\langle H \rangle$ , converge most rapidly, and  $\langle r^{-2} \rangle$  and  $\langle r_{12}^{-2} \rangle$ , which are a part of  $\langle H^2 \rangle$ , converge least rapidly. The deviations from the cusp conditions are larger than they were in the case of the ground state (see I). The higher moments  $\langle r^4 \rangle$ and  $\langle r_{12}^4 \rangle$  also converge slowly, presumably because the diffuse distributions of the excited state are harder to reproduce than the more compact ones of the ground state.

A similar convergence study for the  $2^{3}S$  state of helium is presented in Table II. The inequalities of Eq. (7) are almost always satisfied, negative  $\gamma_{k}$ 's occur, and  $\eta$  is very close to unity. The 55term energy is only  $2 \times 10^{-9}$  a.u. too high as compared with the best available results.<sup>8,9</sup> The other expectation values are converging fairly rapidly, and the electron-nuclear cusp-condition deviations are of the order of 0.0001. Since this is a state of maximum multiplicity, there is no electronelectron cusp.

The facts that the  $2^{3}S$  state is the lowest of its symmetry type, that there is no electron-electron cusp, and that the "open-shell" character of the one-particle part of our basis functions is well suited to describing the diffuse charge distribution all help in making the functions in Table II more accurate than our functions for the other states.

Ν	20	30	40	55	Exact
<i>A</i> <sub>1</sub>	0.3670	0.5180	0.4743	0.5133	
<b>A</b> <sub>2</sub>	1.1340	0.9310	1.2430	1.4077	
B <sub>1</sub>	1.8750	2.0140	1.9530	1.9962	
<i>B</i> <sub>2</sub>	2,3310	2.0360	2.0920	2.0708	
$G_1$	-0.3250	-0.3710	-0.4729	-0.2107	
$G_2$	0.5940	0.8800	0.5630	0.7688	
$1 - \eta$	-1.939-5	-1.354-6	7.629-7	8.023-7	
-E	2.145966060	2.145971291	2.145972811	2.145973824	2.14597404
$\langle r^{-2} \rangle$	8.293 565	8.293697	8.293430	8.293 566	
$\langle r^{-1} \rangle$	2.27080315	2.27081469	2.27081614	2.27081551	
$\langle r \rangle$	5.947 0617	5.9459508	5.9458568	5.9460770	5.94612
$\langle r^2 \rangle$	32,19986	32.17273	32.17326	$32.177\ 62$	32.1782
$\langle r^3  angle$	216.517	216.006	216.036	216.107	
$\langle r^4  angle$	1658.3	1649.5	1650.2	1651.3	
$\langle r_{12}^{-2}  angle$	0.143891	0.143766	0.143775	0.143743	
$\langle r_{12}^{-1}  angle$	0.24967417	0.24968680	0.24968666	0.24968338	
$\langle r_{12} \rangle$	5.270 599 9	5.2694547	$5.269\ 458\ 4$	5.2696574	5.26969
$\langle \pmb{r}_{12}^2  angle$	32.323 57	32.296 51	32,297 43	32.30160	32.302
$\langle r_{12}^3  angle$	224.424	223.918	223.949	224.018	
$\langle r_{12}^4  angle$	1744.2	1735.4	1736.2	1737.3	
$\langle \cos \theta_{12} \rangle$	-0.14652977 - 1	-0.14657261 - 1	-0.14663552-1	-0.14658852-1	
$\langle \delta({f r}_1) \rangle$	1.309 260	1.309 248	1.309189	$1.309\ 272$	$1.309\ 45$
$C_{\rm EN}$	1.999718	1.999403	1.999439	1.999626	2
$\langle  \delta({f r}_{12})  \rangle$	0.008 818	0.008700	0.008 707	0.008 679	0.008 65
$C_{\mathrm{EE}}$	0.429167	0.470780	0.469962	0.479629	0.5

TABLE I. Parallelotope parameters, expectation values, and cusp checks for the 2<sup>1</sup>S state of helium. The exact values of  $C_{EN}$  and  $C_{EE}$  are from the cusp conditions, and all other "exact" values are from Ref. 8. Note that in this table, as in Tables II–VI, all quantities are in atomic units and the exponent notation is  $7.629-7=7.629\times10^{-7}$ .

In view of the current interest<sup>10</sup> in the interpretation of Hund's rules, we remark that  $\langle r_{12}^k \rangle$  (for k=1,2,3,4) is larger in the singlet than in the triplet, and that the interelectronic repulsion is greater in the triplet than in the singlet. The fact that  $\langle r_{12}^{-2} \rangle$  does not follow the above trend merely reflects the aphorism that a few moments are not sufficient to characterize a distribution, and reminds one of the local nature of the Pauli principle. We shall defer further discussion of these points to a later paper, where the full electron-electron distribution functions will be analyzed in detail.

In I we pointed out that the simple ansatz of Thorhallsson, Fisk, and Fraga<sup>11</sup> (TFF) for the perturbative correction to the wave function in

the presence of an uniform static electric field was not suitable for the excited states of helium. This is borne out by our calculations of the dipole polarizability using the wave functions of Tables I and II as the unperturbed functions and the TFF ansatz for the perturbative correction. The required formalism has been outlined in I. The resulting polarizabilities of 170 and 334 a.u. for 2<sup>3</sup>S and  $2^{1}S$  states respectively are completely ruled out by Weinhold's lower bounds<sup>12</sup> of 315 and 792 a.u. for the 2<sup>3</sup>S and 2<sup>1</sup>S states, respectively. This is not particularly surprising, since the TFF ansatz weights regions of space close to the nucleus and is therefore not suited to describing distortions of the diffuse charge distributions of the excited states of helium.

N	20	30	40	55	Exact
 A <sub>1</sub>	0.4930	0.4860	0.4490	0.4280	
$A_2$	1.0200	0.8910	1.1110	1.2059	
B <sub>1</sub>	1.9220	1.9230	1.7370	1.9360	
<i>B</i> <sub>2</sub>	2.2290	2.2420	2.5750	2.1574	
G <sub>1</sub>	-0.1320	-0.2150	-0.2330	-0.1728	
$G_2$	0.2520	0.5580	0.4220	0.4819	
$1 - \eta$	7.684-8	3.746-8	-4.900-9	4.179-9	
-E	2.175229193	2.175229343	2.175229363	2.175229376	2.175229378
$\langle r^{-2}  angle$	8.340 935	8.340 915	8.340 904	8.340 900	
$\langle r^{-1} \rangle$	2,309 328 28	2.30932834	2.309 328 29	2.30932831	
$\langle r \rangle$	5.100 902 9	5.100 907 3	5.100 930 8	5.100 924 6	5.1009254
$\langle r^2  angle$	22.92819	22.92817	22.928 84	22.928 63	22.92864
$\langle r^3 \rangle$	130.423	130.421	130.435	130.430	
$\langle r^4 \rangle$	856.68	856.65	856.91	856.81	
$\langle r_{12}^{-2}  angle$	0.889077-1	0.889065-1	0.889061-1	0.889060-1	
$\langle r_{12}^{-1} \rangle$	0.26819817	0.26819800	0.26819786	0.26819787	
$\langle r_{12} \rangle$	4.4475148	4.4475175	4.4475405	4.4475345	4.447 535
$\langle r^2_{12}  angle$	23.04573	23.04575	23.04640	23.04619	23.04620
$\langle r_{12}^3  angle$	136.734	136.734	136.748	136.742	
$\langle r_{12}^4  angle$	916.23	916.25	916.50	916.39	
$\langle \cos\theta_{12} \rangle$	-0.15839181 - 1	-0.15839377-1	-0.15839228-1	-0.15839224-1	
$\langle \delta(\mathbf{\tilde{r}_{i}}) \rangle$	1.320 389	1.320370	1.320369	1.320 364	1.320 355
CEN	2.000 093	2.000 027	2.000 053	2.000 032	2

TABLE II. Parallelotope parameters, expectation values, and cusp checks for the  $2^{3}S$  state of helium. The "exact" value of  $C_{EN}$  is from the cusp condition, and all other "exact" values are from Ref. 8. Note that units and exponent notation are the same as in Table I.

Tables III and IV list parallelotope parameters and energies for the 2<sup>1</sup>S and 2<sup>3</sup>S states of the ions from Li<sup>\*</sup> through Mg<sup>10+</sup>. As can be seen from the  $\Delta = (E - E_{exact}) \times 10^7$  values, the functions for the 2<sup>3</sup>S state are more accurate than the corresponding functions for the 2<sup>1</sup>S state. The 40-term function for 2<sup>1</sup>S Li<sup>\*</sup> has an energy error of 13 × 10<sup>-7</sup> a.u. The 20- and 25-term 2<sup>1</sup>S functions for the rest of the ions have energy errors of the order of 10<sup>-5</sup> a.u. All of the 2<sup>3</sup>S functions for the ions have 20 or 25 terms and energy errors of the order of 10<sup>-6</sup> a.u.

In Tables V and VI we present parallelotope parameters and energies for the  $2^{3}P$  and  $2^{1}P$ states of the ions from He through Mg<sup>10\*</sup>. The helium functions have 30 terms, and all the rest are 20-term functions. The energies for helium have errors of roughly  $5 \times 10^{-7}$  a.u., and the energies for the other ions have errors of the order of  $5 \times 10^{-6}$  a.u. The somewhat larger errors for the  $2^{1}P$  functions for Be<sup>2+</sup> and Ne<sup>8+</sup> reflect convergence problems with the optimization process. Note that inequalities (7) are generally satisfied, that  $\eta$  is close to unity, and that negative  $\gamma_{k}$ 's occur.

We searched for and did not find a bound  $2^{1}S$ ,  $2^{3}S$ ,  $2^{1}P$ , or  $2^{3}P$  state for  $H^{-}$ .

#### IV. DISCUSSION

In Sec. III we presented relatively accurate functions for the four lowest excited states of the heliumlike ions. They are also very compact. For the 2 <sup>1</sup>S state of He, our 55-term energy lies be-

TABLE III. Parallelotope parameters and energies for the 2<sup>1</sup>S states of the ions from Li<sup>+</sup> to Mg<sup>10<sup>+</sup></sup>.  $\Delta = 10^7 (E - E_{\text{exact}})$ , where the "exact" values are from Refs. 8 and 9. Units and exponent notation are as in Table I.

Z	N	$A_1$	$A_2$	B 1	B 2	<i>G</i> <sub>1</sub>	G <sub>2</sub>	$1 - \eta$	<i>E</i>	Δ
3	40	2,772	3.522	0.748	2.605	-0.747	1.027	5.009 - 8	5.04087542	13.2
4	25	3.402	4.925	1.341	3.621	-0.081	0.595	1.525 - 5	9.18485800	159
5	25	4.810	5.236	1.915	4.956	-0.104	0.972	4.516 - 7	14.5785199	80.9
6	25	5.477	6.893	1.841	6.625	-0.161	0.537	2.693 - 8	21.2220025	152
7	25	6.750	7.299	2.889	6.909	-0.123	1.272	-2.260 - 7	29.1154048	109
8	25	7.948	8.081	2.724	6.402	-0.614	2.687	3.702 - 7	38.2587448	125
9	20	8.392	9.072	2.195	8.471	-0.234	1.152	-5.388 - 8	48.6520116	500
10	20	9.346	10.076	2.510	9.392	-0.261	1.257	-5.201 - 8	60.2952874	526
11	20	3.174	10.925	10.532	10.764	-0.350	0.379	6.702-8	73.1885276	
12	20	2.998	16.837	11.922	12.045	-0.803	1.312	1.234 - 5	87.3318119	

tween the 47- and 98-term energies of Frankowski,<sup>9</sup> who used logarithmic terms in his ansatz, and between the 308- and 444-term perimetric coordinate method-B wave functions of Pekeris.<sup>8</sup> For the  $2^{3}S$  state of He, our 55-term energy is better than the 98-term energy of Frankowski's function<sup>9</sup> (-2.175 229 375 a.u.), and lies between the 252- and 444-term method-B energies of Pekeris.<sup>8</sup>

The fact that our 55-term  $2^{3}S$  function for helium is better than Frankowski's 98-term function containing logarithmic terms is probably largely due to the use of a single exponent in the latter. For the  $2^{1}S$  state of Li<sup>+</sup>, our 40-term energy lies between the 125- and 203-term method-B energies of Pekeris,<sup>8</sup> and between the 19- and 47-term energies of Frankowski. For the  $2^{1}S$  states of Be<sup>2+</sup> through Ne<sup>8+</sup>, and the  $2^{3}S$  states of Li<sup>+</sup> through Ne<sup>8+</sup>, our 20- or 25-term energies all lie between the 19- and 47-term energies of Frankowski.

For the  $2^{3}P$  state of He, our 30-term energy lies between the 120- and 165-term energies ob-

tained<sup>13</sup> with a standard Hylleraas basis, and between the 69- and 111-term energies obtained by Schwartz<sup>13</sup> with a Hylleraas basis augmented with fractional powers of  $r_1 + r_2$ . The 30-term energies for the  $2^{3}P$  and  $2^{1}P$  states lie between the 56- and 120-term energies obtained by Pekeris<sup>8</sup> with perimetric coordinate wave functions having two variable exponents (method D in his notation). Comparison with Pekeris's convergence studies indicates that our 20-term energies for the 2<sup>3</sup>P states of the ions from Li<sup>+</sup> through Ne<sup>8+</sup> lie between the 20- and 56-term energies of Pekeris. Our 20term energies for the  $2^{1}P$  states of the ions from  $Li^+$  to  $Ne^{8+}$  have nonuniform errors; some of them are better and some are poorer than the 20-term results of Pekeris.

Note that for the 2<sup>1</sup>S and 2<sup>3</sup>S states of He our 55-term energies are better than the 84-term energies of Winkler and Porter.<sup>14</sup> The latter used exponents only from the totally positive octant of the  $\alpha$ - $\beta$ - $\gamma$  parameter space. This demonstrates once again the importance of optimizing the par-

TABLE IV. Parallelotope parameters and energies for the 2<sup>3</sup>S states of the ions from Li<sup>+</sup> to Mg<sup>10<sup>+</sup></sup>.  $\Delta = 10^7 (E - E_{\text{exact}})$ , where "exact" values are from Refs. 8 and 9. Units and exponent notation are as in Table I.

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Z	N	$A_1$	$A_2$	<i>B</i> <sub>1</sub>	B 2	G <sub>1</sub>	$G_2$	$1 - \eta$	- E	Δ
3	25	2.993	3.102	1.275	2.025	-0.210	-0.029	6.412-8	5.11072694	4.26
4	25	3.900	3.990	1.710	2.360	-0.210	-0.050	-4.9997	9.297 165 90	6.78
5	25	4.634	5.685	1.949	3.307	-0.137	1.012	3.571 - 8	14.7338972	1.26
6	25	5.671	6.275	1.965	3.073	-0.648	1.578	4.915-9	21.4207557	1.47
7	25	6.653	7.294	2.471	3.563	-0.770	1.776	5.115 - 9	29.3576816	1.47
8	25	7.820	8.316	3.143	3.807	-0.320	1.834	-2.007 - 8	38.5446472	1.28
9	20	8.938	9.154	4.288	4.500	-0.300	0.308	-1.720 - 7	48.9816368	15.0
10	20	9.906	10.092	4.700	4.889	-0.300	1.392	-6.244-8	60.6686460	5.24
11	<b>20</b>	10.960	11.134	5.249	5.691	-0.942	1.732	-5.133-8	73.6056664	
12	20	11.794	12.452	4.926	8.081	-1.569	2.351	-2.168 - i0	87.7926961	

$\boldsymbol{Z}_{i}$	N	<b>A</b> <sub>1</sub> <sup>*</sup>	$A_2$	B <sub>1</sub>	<b>B</b> <sub>2</sub>	$G_1$	$G_2$	$1 - \eta$	- <i>E</i>	Δ
2	30	0.067	1.202	1.496	2.164	-0.232	0.687	-4.005-7	2.13316372	4.72
3	<b>20</b>	0.700	2.685	2.661	3.660	-0.175	0.409	5.293-7	5.02771241	32.7
4	20	0.751	3.424	3.402	4.625	-0.096	0.735	5.671 - 8	9.17497016	29.9
5	20	1.532	3.317	4.805	5.151	-0.389	1.459	4.791-8	14.5731338	38.9
6	20	1.528	5.052	5.366	6.794	-0.187	1.191	4.716 - 9	21.2217077	30.1
7	20	1.874	5.885	6.314	7.866	-0.221	1.423	1.999 - 9	29.1204987	30.0
8	20	2.220	6.707	7.261	8.934	-0.253	1.655	3.397-9	$38.269\ 419\ 7$	30.0
9	20	2.564	7.526	8.203	10.000	-0.284	1.889	1.713 - 9	48.6684243	30.0
10	20	3.448	6.467	8.934	10.476	-0.765	3.000	2.524 - 9	60.3174854	34.6
11	20	3.991	9.624	10.347	12.382	-0.967	2.099	1.338 - 8	73.2165876	
12	20	3.723	9.713	11,133	13.137	-0.405	2.621	-2.008-8	87.3657198	

TABLE V. Parallelotope parameters and energies for the  $2^{3}P$  states of the ions from He to  $Mg^{10^{+}}$ .  $\Delta = 10^{7}(E - E_{exact})$ , where the "exact" values are from Ref. 8. Units and exponent notation are as in Table I.

allelotope parameters.

From the above discussion it is evident that we have largely succeeded in providing a systematic collection of compact and accurate wave functions expressed in a relatively simple basis set. These results and those of  $I^1$  provide a set of such wave functions for the five lowest states of the two-electron ions. As discussed in I these functions should now be analyzed in order to gain further insight into the electron correlation problem. Analysis of the electron-electron distribution functions is underway in our laboratory.

An intriguing possibility is the extension of these methods to many-electron systems. Full optimization of the parallelotope parameters for an explicitly correlated wave function for an atom with three or more electrons would be prohibitively expensive. The ideas of Somorjai and Grimaldi,<sup>15</sup> and Kukulin<sup>16</sup> seem to offer promising possibilities for overcoming these problems. We feel it would be worthwhile to devote some effort to the exploration of the usefulness of such ideas in the construction of wave functions containing interelectronic coordinates. Clearly small atomic systems, such as Li and Be, are natural starting points. We hope to be able to report such calculations in the future.

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TABLE VI. Parallelotope parameters and energies for the 2<sup>1</sup>P states of the ions from He to  $Mg^{10^+}$ .  $\Delta = 10^7 (E - E_{exact})$ , where the "exact" values are from Ref. 8. Units and exponent notation are as in Table I.

Z	N	$A_1$	$A_2$	B <sub>1</sub>	B 2	G <sub>1</sub>	G <sub>2</sub>	$1 - \eta$	<i>E</i>	Δ
2	30	0.282	1.851	1.608	2.836	-0.174	0.287	3.977-7	2,12384265	4.38
3	<b>20</b>	0.773	2.210	2.668	3.751	-0.342	0.682	6.172 - 8	4.99334812	29.5
4	<b>20</b>	0.357	2.923	3.940	3.980	-0.300	2.050	3.019-5	9.11072739	442.
5	20	0.225	4.505	3.723	5.437	-0.548	1.716	-1.275 - 7	14.4772777	55.4
6	<b>20</b>	0.372	5.512	4.412	6.549	-0.680	2.123	1.372 - 8	21.0933262	60.6
7	<b>20</b>	1.680	5.700	5.629	8.172	-0.220	1.998	-9.082-9	28.9591100	64.2
8	20	0.827	7.283	5.696	8.810	-0.942	2.943	-2.427 - 8	38.0747282	69.9
9	<b>20</b>	3.575	6.697	8.482	9.866	-2.426	4.372	-3.847 - 10	48.4402382	61.0
10	20	2.783	7.323	9.685	11.144	-3.162	4.010	1.603 - 9	60.0556560	207.
11	<b>20</b>	4.285	9.162	9.117	15.118	-1.858	3.454	8.672-10	72.9210467	
<b>12</b>	20	1.282	11.493	8.614	13.205	-1.445	4.543	1.611 - 7	87.036 381.1	

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