

calculated values for  $C_3H_8$  are higher by about an order of magnitude than those obtained by Vestal.<sup>6</sup> Although the rate constants themselves may be in error, the computed isotope effects on the rate constants should be fairly accurate, since any errors in the assumed models (frequencies, moments of inertia, etc.) should partly cancel out for the two isotopic molecules. The computed isotope effects are the following:

$$k_{A,C_3H_8}/k_{A,C_3D_8}=5, \quad k_{B,C_3H_8}/k_{B,C_3D_8}=15,$$

where  $k_{A,C_3H_8}$  denotes the rate constant of Reaction (A) in  $C_3H_8$ ,  $k_{A,C_3D_8}$  the rate constant of Reaction (A) in  $C_3D_8$  with similar notations for the rate constants of Reaction (B), and where the isotope effects are computed for the threshold energies. The reaction rate constants increase very rapidly with energy above

threshold,<sup>6</sup> the isotope effects remaining, however, fairly constant in the range of metastable rate constants.

Although Reaction (B) is 15 times faster for  $C_3H_8$  than for  $C_3D_8$  at threshold, both molecules will give metastable ions due to this reaction, since at threshold the rate constants are lower than  $10^4 \text{ sec}^{-1}$  and they reach the metastable range at  $\sim 0.01 \text{ eV}$  above threshold. We propose, however, that Reaction (A) contributes strongly to the metastable peak only in  $C_3D_8$  and not in  $C_3H_8$ . This explains the isotope effect on the yield of the metastable ion as well as the occurrence of two rate constants in  $C_3D_8$ , while the high rate constant is missing in  $C_3H_8$ .

We plan to study isotope effects on parent-ion metastable transitions in the molecules  $CH_3CD_2CH_3$  and  $CD_3CH_2CD_3$ . In these molecules, Reactions (A) and (B) should give metastable ions of different masses which could, therefore, be studied separately.

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## Configuration Interaction in Two- and Three-Electron Atoms\*

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The ground states of the first four members of the helium isoelectronic series and the  $2^2S$  and  $2^2P$  states of lithium are calculated using a configuration-interaction expansion in a complete denumerable set of single-particle functions, with one adjustable scale parameter. The best energies for the two-electron systems, obtained with 120-term expansions, are  $E(H^-) = -0.52748$ ,  $E(He) = -2.90335$ ,  $E(Li^+) = -7.27945$ , and  $E(Be^{++}) = -13.65504$ , in units of  $e^2/a_0$ . The energies for all but He are lower than any heretofore obtained with a configuration-interaction approach. The dependence of energy on scale factor is found to be very pronounced, in contrast to the corresponding behavior for wavefunctions which contain the interparticle coordinates explicitly. The best energies for the lithium states, obtained with 208-term expansions, are  $E(2^2S) = -7.47369$  and  $E(2^2P) = -7.40366$ . The  $2^2S$  energy is not as good as has been obtained with either expansions in terms of interparticle coordinates or configuration interaction with many nonlinear parameters. The  $2^2P$  energy is of approximately the same accuracy but is lower than any previously published.

### INTRODUCTION

THE Hartree-Fock solutions to the wave equation for a many-electron atom can never be more than approximations to the exact solution because the inter-electron repulsion, or correlation, is not correctly represented. An exact solution to the Schrödinger equation, with the Hamiltonian given by

$$\mathcal{H} = \sum_i \left[ -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{i < j} (1/r_{ij}), \quad (1)$$

can in principle be obtained by representing the solu-

tion by a trial function  $\Psi$  which is then varied until the total energy, given by

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle / \langle \Psi | \Psi \rangle, \quad (2)$$

is a minimum. If the trial function is of the form

$$\Psi = \sum_j C_j \psi_j, \quad (3)$$

then this variational principle leads to the matrix eigenvalue equation

$$\sum_j (H_{ij} - ES_{ij}) C_j = 0, \quad (4)$$

where

$$H_{ij} = \langle \psi_i | \mathcal{H} | \psi_j \rangle \quad (5)$$

and

$$S_{ij} = \langle \psi_i | \psi_j \rangle.$$

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The lowest eigenvalue of the matrix equation (4) gives the energy  $E$ , and the components of the corresponding eigenvector are the expansion coefficients  $C_j$ . Thus, the choice of a trial function in the form (3) gives a straightforward way of minimizing the energy with respect to a large number of parameters.

Methods of applying the variational principle to a many-electron atom fall into two general classes, depending on the type of functions used in the expansion (3). In application, the most straightforward method is the method of configuration interaction, in which the solution is represented as a superposition of antisymmetrized products of single-particle functions. Then, if these functions are members of a complete set, the exact solution can be approximated as closely as desired by the inclusion of enough terms. However, this method is found to provide very slow convergence to the exact solution, the reason being that functions of single-particle coordinates provide a very poor means of representing an effect which depends on the interparticle coordinates.<sup>1</sup> The other variation method, in which the interparticle coordinates  $r_{ij}$  are explicitly included in the trial function, does give much faster convergence but extreme computational difficulties arise in the calculation of the matrix elements (5). Thus, the choice is between working with a very large matrix containing elements which are relatively easy to calculate, or quite a small matrix with elements which are extremely difficult to calculate. For states with zero angular momentum, the solution in terms of interparticle coordinates depends only on the relative coordinates of the particles, and even though this form is still more difficult to work with than a product of single-particle functions, quite accurate results were obtained (long before the advent of electronic computers) by Hylleraas<sup>2</sup> for the ground state of helium and by James and Coolidge<sup>3</sup> for the ground state of lithium. In recent years, the ground-state energies of two-electron atoms have been determined with extreme accuracy by this method.<sup>4,5</sup> The ground-state energy of lithium has also been determined very accurately.<sup>6</sup> For  $P$  states of two-electron atoms the method is still tractable,<sup>7</sup> and very good results have been obtained for the  $2P$  states of helium.<sup>8,9</sup> However, for larger atoms in higher angular momentum states it is important to investigate the applicability of configuration interaction before attempting to use the more complicated method. In addition, the use of

product configurations provides a wavefunction in a more usable form for the calculation of expectation values of operators other than the nonrelativistic energy, such as fine-structure and hyperfine-structure splittings.

The purpose of this investigation is the application of configuration interaction to the  $2^3P$  state of lithium with preliminary calculations, for comparison purposes, of the ground states of two-electron atoms and the  $2^3S$  state of lithium. A secondary purpose, which developed during the course of the research, is an investigation of the effect of a varying scale parameter on the calculated ground-state energies of two-electron atoms.

### CHOICE OF FUNCTIONS

In addition to the coefficients  $C_j$  in the expansion (3), variational parameters may also be included in the configurations themselves. However, this inclusion of nonlinear parameters requires that a new linear variational problem be set up and solved for each new choice of these parameters. This was done by Weiss,<sup>10</sup> for  $S$  states of two-, three- and four-electron atoms, with the single-particle functions in the form of Slater orbitals, but containing up to 12 nonlinear parameters. The simplicity of the functions in this case makes it feasible to recalculate the matrix elements every time the parameters are varied. Results of comparable accuracy have been obtained by Nesbet and Watson,<sup>11</sup> who used a truncated complete set of polynomials containing four nonlinear parameters. With this type of function, the calculation of matrix elements is much more complicated and any continuation in this direction would be quite difficult. Another possibility is to use such a complete set, including as many terms as possible, with one nonlinear parameter which is the same for each member of the set. This was done by Tycho, Thomas, and King<sup>12</sup> for the  $1^1S$  and  $2^3S$  states of helium, but without a complete minimization of the energy. With only one nonlinear parameter, the building up of the total function  $\Psi$  from the set can be done in a straightforward way, and there is little or no question of the uniqueness of the minimization. Another advantage of this method is that with the single nonlinear parameter chosen as a scale factor, the Hamiltonian (1) can be written in terms of the scaled variables,  $\xi_i = 2kr_i$ , as

$$\mathcal{H} = 2k^2 \sum_i [\nabla_i^2 + (Z/k)\xi_i^{-1}] + 2k \sum_{i < j} \xi_{ij}^{-1}. \quad (6)$$

The appearance of  $k$  as a multiplicative factor means that matrix elements need to be calculated only once

<sup>1</sup> J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., Inc., New York, 1960), Vol. 2, p. 48.

<sup>2</sup> E. A. Hylleraas, *Z. Physik* **54**, 347 (1929).

<sup>3</sup> H. M. James and A. S. Coolidge, *Phys. Rev.* **49**, 688 (1936).

<sup>4</sup> C. L. Pekeris, *Phys. Rev.* **112**, 1649 (1958); **115**, 1216 (1959).

<sup>5</sup> Charles Schwartz, *Phys. Rev.* **128**, 1146 (1962).

<sup>6</sup> E. A. Burke, *Phys. Rev.* **130**, 1871 (1963).

<sup>7</sup> G. Breit, *Phys. Rev.* **35**, 569 (1930).

<sup>8</sup> C. L. Pekeris, B. Schiff, and H. Lifson, *Phys. Rev.* **126**, 1057 (1962).

<sup>9</sup> C. Schwartz, *Phys. Rev.* **134**, A1181 (1964).

<sup>10</sup> A. W. Weiss, *Phys. Rev.* **122**, 1826 (1961).

<sup>11</sup> R. K. Nesbet and R. E. Watson, *Phys. Rev.* **110**, 1073 (1958).

<sup>12</sup> D. H. Tycho, L. H. Thomas, and K. M. King, *Phys. Rev.* **109**, 369 (1958).

for a given state of a system, and then a variation over a wide range of scale factors can be carried out quite easily.

The choice of hydrogenic functions as the basis set in the expansion (3) has the disadvantages that both discrete and continuum states must be included, and that the appearance of the principal quantum number  $n$  in the argument of the functions leads to very slow convergence.<sup>13</sup> The reason for the slow convergence is that with increasing  $n$ , the nodes of the function get shifted away from the origin, while the function to be represented is expected to be concentrated at small values of  $r$ . The functions which result when the  $n$  is removed from the argument of the hydrogenic radial functions do not have these disadvantages. They are denumerably complete, with no continuum states, and have nodes concentrated at small values of  $r$ .<sup>14</sup> The functions are

$$\phi_{nlm}(\xi, \theta, \phi) = \{[\Gamma(n-l)]^{1/2} / [\Gamma(n+l+1)]^{1/2}\} \xi^l \times \exp(-\xi/2) L_{n-l-1}^{2l+1}(\xi) Y_l^m(\theta, \phi), \quad (7)$$

and satisfy the differential equation

$$[\nabla^2 + (n/\xi) - \frac{1}{4}] \phi_{nlm}(\xi, \theta, \phi) = 0, \quad (8)$$

where  $n=1, 2, 3, \dots$ ;  $l=0, 1, 2, \dots, (n-1)$  and  $-l \leq m \leq l$ . This is not a Schrödinger equation, except for  $n=1$ , the difference being that the energy is a constant while the strength of the potential is different for different eigenfunctions. Thus, higher eigenvalues of the matrix equation (4) do not correspond to excited states of a physical system represented by an expansion in these functions.

The many-particle Hamiltonian (6) may be written as

$$\mathcal{H} = 2k^2 H_1 + 2k H_2, \quad (9)$$

where

$$H_1 = - \sum_i [\nabla_i^2 + (Z/k)(1/\xi_i)] \quad (10)$$

and

$$H_2 = \sum_{i < j} (1/\xi_{ij}). \quad (11)$$

It follows immediately from (10) and the differential equation (8) that the matrix elements of the operator  $H_1$  are given by

$$\begin{aligned} \langle n'l'm' | H_1 | nlm \rangle \\ = \sum_i \int \phi_{n'l'm'}^* \left[ \left( n - \frac{Z}{k} \right) \xi_i^{-1} + \frac{1}{4} \right] \phi_{nlm} d\tau. \end{aligned} \quad (12)$$

The integrals needed for the evaluation of this matrix

element are<sup>15</sup>

$$\int \phi_{n'l'm'}^* \xi^{-1} \phi_{nlm} d\tau = \delta_{n'n} \delta_{l'l} \delta_{m'm} \quad (13)$$

and

$$\begin{aligned} \int \phi_{n'l'm'}^* \phi_{nlm} d\tau = \delta_{l'l} \delta_{m'm} \\ \times \{ 2n\delta_{n'n} - \delta_{n',n+1} [(n-l)(n+l+1)]^{1/2} \\ - \delta_{n',n-1} [(n+l)(n-l-1)]^{1/2} \}. \end{aligned} \quad (14)$$

The integral given by (14) is also required for the overlap matrix  $S_{ij}$ . The functions (7) are therefore not orthonormal in the usual sense, but this presents no difficulty since both (13) and (14) are required anyway. While  $S_{ij}$  is not the unit matrix, for the systems considered in this study it is approximately 90% empty, and a scheme of matrix packing was used in order to make fullest possible use of the available computer storage.

The matrix elements of the two-particle operator  $H_2$  are much more complicated than those of  $H_1$ , but are independent of  $Z$  and  $k$ , so that they need be calculated only once. It is of course also possible to write the one-particle operator  $H_1$  in the form of a sum of two terms each of which is independent of  $Z$  and  $k$ , but because of the extreme simplicity of the integrals (13) and (14) it was found that the matrix elements of  $H_1$  could be calculated as needed faster than they could be read from cards.

## GROUND STATES OF TWO-ELECTRON ATOMS

The general form of the configurations used for the ground states of heliumlike atoms is the linear combination of Slater determinants<sup>16</sup>

$$\begin{aligned} \psi_{LM} = \sum_{m_1} C(l_1 l_2 L; m_1 m_2 M) \\ \times [ | \phi_{n_1 l_1 m_1}(1) \alpha \phi_{n_2 l_2 m_2}(2) \beta | \\ \pm | \phi_{n_2 l_2 m_2}(1) \alpha \phi_{n_1 l_1 m_1}(2) \beta | ], \end{aligned} \quad (15)$$

where the plus and minus signs indicate singlet and triplet states, respectively.

For  $^1S$  states, the configurations are specified by only three quantum numbers, namely  $n_1$ ,  $n_2$ , and  $l$ . The expansion of the trial function (3) may then be written in the form

$$\Psi_{^1S} = \sum_{n_1=1}^n \sum_{n_2=1}^{n_1} \sum_{l=0}^{n_2-1} A(n_1, n_2, l) \psi_{^1S}(n_1, n_2, l), \quad (16)$$

<sup>15</sup> P. R. Fontana, Phys. Rev. **123**, 1871 (1961). This paper gives a more general expression for the matrix element of any power of  $r$ .

<sup>16</sup> Unless otherwise indicated, the notation for all angular-momentum-coupling symbols is that of M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

<sup>13</sup> Reference 1, Vol. 2, p. 45.

<sup>14</sup> M. Rotenberg, Ann. Phys. (N.Y.) **19**, 262 (1962).

where  $n$  is the maximum principal quantum number in the expansion and the limits on the sums express the fact that  $A(n_1, n_2, l) = A(n_2, n_1, l)$ . This particular form of the expansion gives a straightforward way of building up the total wavefunction  $\Psi$  from the configurations (15) for a two-electron atom. For a given maximum principal quantum number  $n$ , the number of terms  $N$  in the expansion is  $N = \frac{1}{6}n(n+1)(n+2)$ . However, there is no reason to assume that this is the best way of forming the total function  $\Psi$ , given the maximum number of terms which can be included. It is quite possible that faster convergence might be obtained by specifying a maximum  $l$ , thus allowing higher values of  $n_1$  and  $n_2$  to be included. But if this is done there is the question of just how many values of  $n$  should go with a given  $l$ , whereas if the configurations are ordered by  $n$  there is no difficulty in including all possible values of  $l$ .

For the first application of this method, the preliminary 20-term variational calculation of Tycho, Thomas, and King<sup>12</sup> was repeated. It had originally been intended to do this only as a check of the matrix element and eigenvalue computer programs, since this part of their work uses a method completely equivalent to that used here. The preliminary results of Tycho *et al.* were reproduced, as expected. As an additional result, the energies obtained by Shull and Löwdin<sup>17</sup> with a 20-term expansion were also reproduced. In this latter case the configurations are specified by the same set of  $n$  and  $l$  values as those used here, but with different radial functions. Different eigenvectors are therefore obtained with the two expansions, the reason for the equal eigenvalues being that the two types of radial functions can be expressed as contiguous hypergeometric series and the two expansions are therefore linearly dependent.

The results obtained with the 20-term expansion, shown in Table I, make it evident that the energy is not at all insensitive to variations in the scale parameter, but has a definite minimum near  $k=2.20$ . There

TABLE I. Preliminary calculation of helium ground-state energy.<sup>a</sup>

$n=3$ (10 terms)		$n=4$ (20 terms)	
$k$	$E$	$k$	$E$
1.80	-2.898176	1.90	-2.900750
1.90	-2.898927	2.00	-2.900991
1.95	-2.899120	2.10	-2.901157
2.00	-2.899185	2.20	-2.901230
2.05	-2.899111	2.30	-2.901180
2.10	-2.898888	2.40	-2.900960
2.20	-2.897935	2.50	-2.900516

<sup>a</sup> All energies are in units of  $e^2/a_0$ .

<sup>17</sup> H. Shull and P.-O. Löwdin, J. Chem. Phys. 30, 617 (1959).

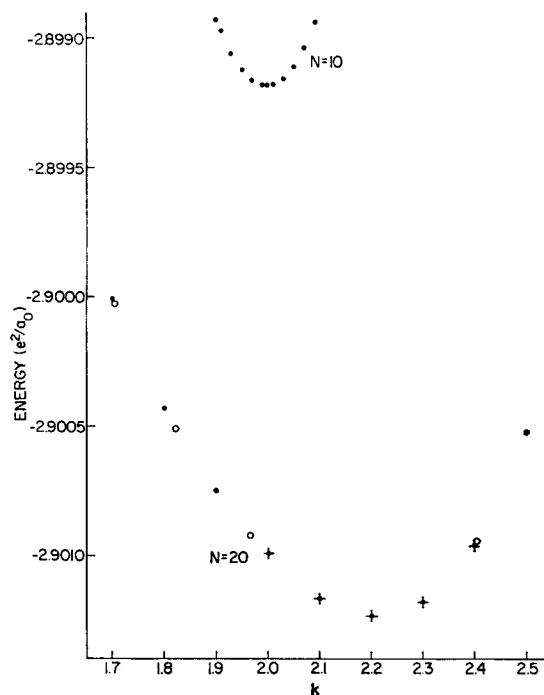


FIG. 1. Preliminary calculation of helium ground-state energy. +, Results of Shull and Löwdin; O, results of Tycho, Thomas, and King; ●, results of present calculation.

remains the question of how the optimum scale parameter changes as the number of terms in the expansion is changed. It is of course obvious that there is some such dependence, since a one-term function gives the well-known result  $E_{\min}(k) = E(Z - \frac{5}{18})$ , which for helium means  $k=1.6875$ . In order to investigate this, the next smaller set was used with  $n=3$  and, therefore, containing 10 terms. These results are also shown in Table I. The minimum has moved to  $k=2.00$ . It is thus clear that variations in scale parameter can have an important effect, at least for small sets of configurations. These results are shown even more clearly in Fig. 1, in which the energies for the two expansions are plotted as functions of the scale parameter. It should be noted that for  $n=4$  the energy minimum occurs at a value of  $k$  which is greater than  $Z$ . Thus, the interpretation of this parameter as a "screened effective nuclear charge" is no longer valid.

In view of the above results it was decided that an extensive investigation should be made of the variation of the ground-state energy of a two-electron atom both with respect to scale parameter  $k$  and nuclear charge  $Z$ . The energies of the first four members of the helium isoelectronic series were calculated, with systematically increasing expansion lengths, and with a range of  $k$  hopefully wide enough to exclude the possibility of multiple minima.

The resulting energies are given in Table II and in Fig. 2 are shown all energies calculated for the

TABLE II. Ground-state energies of two-electron atoms.

$n$	$N$	$Z=1$		$Z=2$		$Z=3$		$Z=4$	
		$k$	$E$	$k$	$E$	$k$	$E$	$k$	$E$
2	4	0.75	-0.49970	1.77	-2.87544	2.78	-7.25049	3.79	-13.62548
3	10	0.74	-0.52454	2.00	-2.89918	3.19	-7.27441	4.36	-13.64951
4	20	0.75	-0.52572	2.20	-2.90123	3.50	-7.27693	4.80	-13.65229
5	35	0.80	-0.52690	2.40	-2.90237	3.90	-7.27826	5.30	-13.65373
6	56	0.90	-0.52718	2.70	-2.90292	4.30	-7.27891	5.90	-13.65444
7	84	0.90	-0.52739	2.90	-2.90318	4.70	-7.27924	6.40	-13.65481
8	120	0.95	-0.52748	3.20	-2.90335	5.10	-7.27945	6.90	-13.65504
Exact <sup>a</sup>			-0.52775		-2.90372		-7.27991		-13.65557
error			0.00027		0.00037		0.00046		0.00053
			(0.05%)		(0.013%)		(0.006%)		(0.004%)

<sup>a</sup> The exact values are those of Pekeris, Ref. 4, which when corrected for relativistic effects and nuclear motion, predict the ionization energies within experimental error.

helium ground state with wavefunction expansions ranging from 20 to 120 terms. Similar sets of curves were obtained for  $Z=1, 3,$  and  $4$ . Figure 2 also shows the results of Tycho *et al.*, including their final calculated energy obtained with a 680-term wavefunction, but with no variation in scale parameter. The solid curves through the points actually calculated do not represent numerical fitting, but are intended to be illustrative only. As can be seen from Table II, the scale parameter for minimum energy increases monotonically with increasing  $n$ , and increases more rapidly with larger  $Z$ . If a complete set is used in the expansion, then in the limit it should make no difference what

scale parameter is used, since the same value of the energy would be obtained. However, in practice, where a truncated set must be used, the choice of an optimum scale parameter is very important.

In Fig. 3 the optimum  $k$  is shown as a function of  $n$ . The values were obtained from curves such as those of Fig. 2, with uncertainties as indicated. No attempt was made to determine the optimum  $k$  with a finer variation near the minimum since in this region it is true that the energy is very insensitive to variations in  $k$ . The result is that the scale parameter for minimum energy seems to increase linearly with increasing  $n$ , for  $n$  greater than 2 or 3. From the way the scale parameter appears in the argument,  $\xi=2kr$ , of the radial function, it can be seen that increasing  $k$  means decreasing  $r$ , or a shifting of the function toward the origin. As  $n$  is increased, the number of nodes in the function increases, and the effect of the increasing  $k$  is to keep the nodes at small values of  $r$ .

### LITHIUM $2^2S$ AND $2^2P$ STATES

The general form of the configurations used for the calculation of the lithium energies is complicated by the fact that there are two possibilities for coupling the spins of the electrons, giving a singlet or triplet intermediate state. If  $L-S$  coupling is assumed, then the most general form of a three-electron configuration is given by the following linear combination of Slater determinants:

$$\begin{aligned} & \psi_{LM_L S M_S}((l_a l_b)^{2\gamma+1j}, l_c) \\ &= \sum_{m_a m_b, \mu_a \mu_b} C(l_a l_b j; m_a m_b) C(j l_c L; m_a + m_b, M_L - m_a - m_b) \\ & \quad \times C(\frac{1}{2} \frac{1}{2} \gamma; \mu_a \mu_b) C(\gamma \frac{1}{2} S; \mu_a + \mu_b, M_S - \mu_a - \mu_b) \\ & \times |\phi_a(1) \chi_{\frac{1}{2} \mu_a}(1) \phi_b(2) \chi_{\frac{1}{2} \mu_b}(2) \phi_c(3) \chi_{\frac{1}{2} M_S - \mu_a - \mu_b}(3)|. \quad (17) \end{aligned}$$

In this representation the angular momenta  $l_a$  and  $l_b$  are coupled to form an intermediate state  $j$ , which is then coupled with  $l_c$  to form the final state  $L$ . The

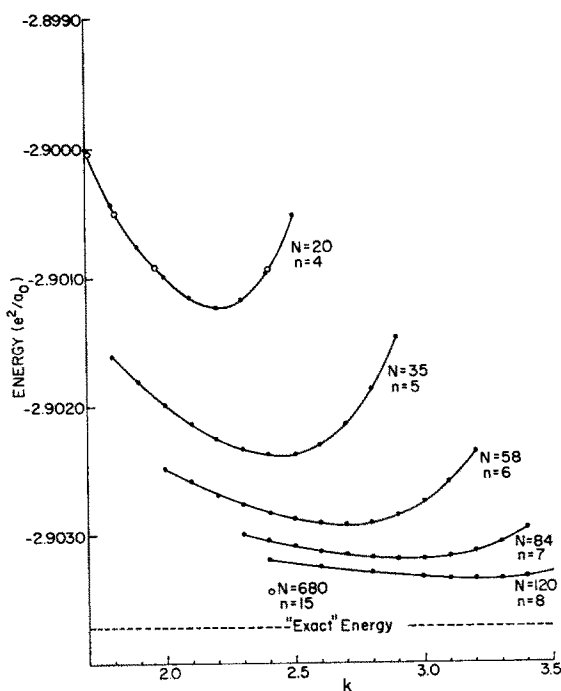
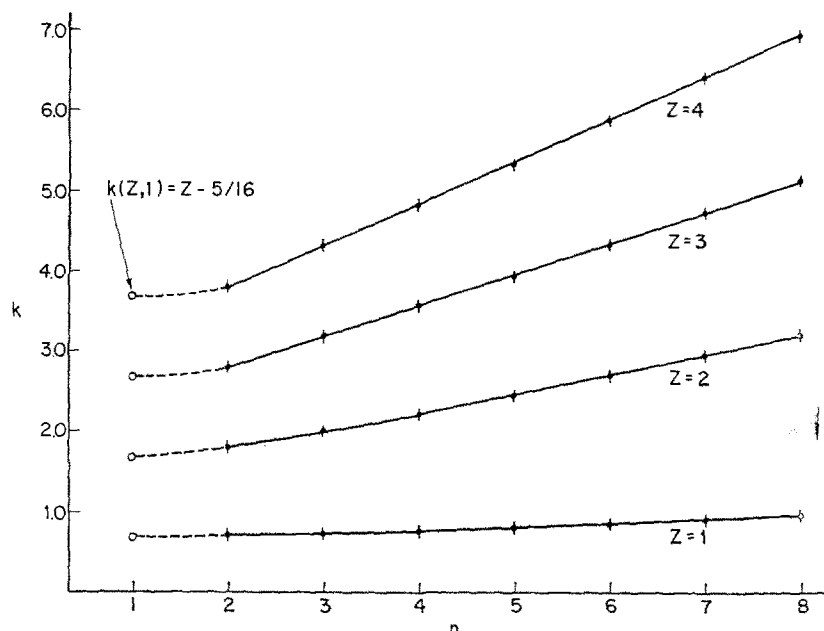


FIG. 2. Energy of  $1^1S$  He as a function of scale parameter and maximum principal quantum number in the expansion. The open circles are the results of Tycho, Thomas, and King.<sup>12</sup>

FIG. 3. Optimum scale parameter for ground states of two-electron atoms as a function of maximum principal quantum number.



intermediate spin quantum number  $\gamma$  has the value 0 for a singlet intermediate state and the value 1 for a triplet intermediate state. The two cases can be considered separately, with the spin coupling written out explicitly, since only matrix elements of spin-independent operators have to be calculated. The various types of spin coupling will then lead to different linear combinations of the same spatial integrals.

The choice of configurations is not at all as straightforward as in the two-electron calculations, where there were only three quantum numbers to be specified. In that case, quite good results were obtained simply by increasing the maximum value of  $n$  and including all possible values of  $l$ . However, for lithium there are eight quantum numbers to be specified, once the total  $L$  has been fixed. Of course not all combinations of the eight numbers are possible. There are triangle conditions on the angular-momentum quantum numbers  $l_1$ ,  $l_2$ , and  $j$  and on  $j$ ,  $l_3$ , and  $L$ , and there is the condition that all configurations be of the same parity. Finally, there are configurations which are linearly dependent, but not in such an obvious manner as was the case in the two-electron calculations. There still remain many choices for the types of configuration to be included. There is the question of whether the triplet-core configurations should be included on an equal basis with those with a singlet core, or whether they can be neglected. There is also the question of the relative importance of configurations with  $j \neq 0$ , the open shell type. And, since this is a system of inequivalent particles, there is the question of the relative ranges of  $n$  and  $l$  values for the three electrons. Since the resulting energy is to be the criterion for the "goodness" of the wavefunction, it is a matter of trial and error to decide on the importance of various

possible types of configurations, based on their relative contributions to the energy. It was found that, as expected, the most significant contribution to the energy for the two states comes from the closed-shell singlet configurations  $(n_1 n_2 l) ^1S, n_3 s$  and  $(n_1 n_2 l) ^1S, n_3 p$ . It was also found that with this type of configuration a very wide range of  $n_3$  must be included for a given core  $(n_1 n_2 l)$ . This is not too surprising since for these states the part of the solution describing the outer electron will be very different from that part describing the inner electrons. Therefore, the requirement that the scale factor be the same for all three electrons is quite unrealistic and it is only when very many terms are added to the expansion that one can expect that the rigidity of this requirement will be overcome and that the expansion in a complete set will begin to represent the true solution to the wave equation accurately. The triplet-core configurations  $(n_1 n_2 l) ^3S, n_3 s$  and  $(n_1 n_2 l) ^3S, n_3 p$  were found to give small but not negligible contributions to the energies, but the open shell, the most general type of configuration possible, was found to give an insignificant contribution.

In the final calculation of the lithium ground-state energy, configurations of the type  $(n_1 n_2 l) ^{2\gamma+1}S, n_3 s$  with a fixed  $l$  were added to the expansion until it became evident that a practical limit had been reached. The addition of terms with  $l=0$  was carried to 95 terms and then cut back to 79 terms, because at this point it appeared that the improvement in energy with the addition of configurations had reached a very small but finite constant value of approximately 0.00002 a.u. per configuration, independent of the precise description of the configuration. Similar results were obtained for  $l=1$  terms and  $l=2$  terms,

TABLE III. Energy of the  $2^2S$  state of the Li atom.

	$N$	$k$	$E$	$\Delta E$
$S$	79	2.95	-7.44722	
$S+P$	142	3.08	-7.47085	0.02341
$S+P+D$	184	3.10	-7.47268	0.00183
$S+P+D+F$	190	3.10	-7.47273	0.00005
$S+P+D$	189	3.10	-7.47279	0.00194
$S+P+D+$ Triplet core	208	3.10	-7.47369	0.00090
Exact*			-7.47805	
error			0.00436 (0.058%)	

\* See Ref. 18.

but with decreasing improvement in the energy with increasing  $l$ . Thus, no evidence was found for a "radial limit" or for "angular-correlation limits." For triplet-core configurations, the behavior with respect to  $n_3$  was found to be different from that of the singlet core in that the optimum range of  $n_3$  turned out to be quite small. The first few terms give a noticeable improvement in the energy, but the contribution decreases rapidly with increasing  $n_3$ . The final results for the lithium ground state are shown in Table III, in which the notations  $S$ ,  $S+P$ , etc., indicate the values of  $l$  included in the configurations. The exact energy is that of Scherr, Silverman, and Matsen.<sup>18</sup>

The building up of the  $2^2P$  function did not require quite as much trial and error as the ground state, since that calculation had provided some insight into the kind of behavior to be expected. The results for the  $2^2P$  state are shown in Table IV. In this case the set labeled  $S$  contains both singlet and triplet cores. The contribution from triplet-core configurations with  $l$  other than zero was found to be negligible. This is in contrast to the ground state, in which triplet cores with  $l=1$  were found to be most important, with small but significant contributions from triplet cores with  $l=0$  and  $l=2$ . As was the case for the ground

TABLE IV. Energy of the  $2^2P$  state of the Li atom.

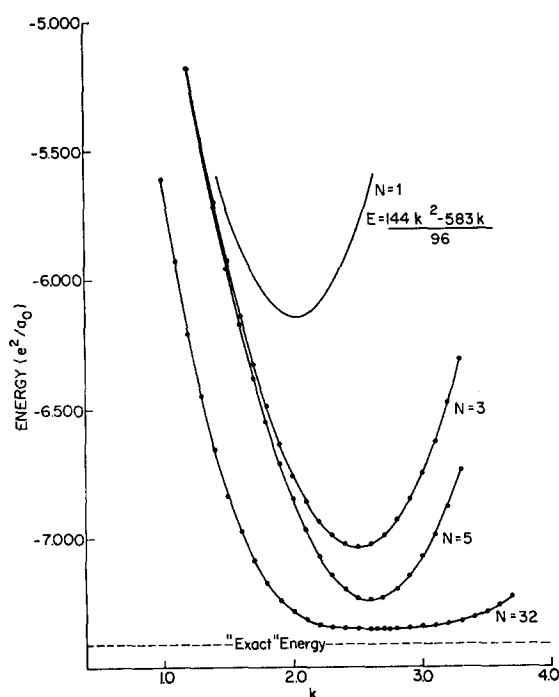
	$N$	$k$	$E$	$\Delta E$
$S$	79	3.00	-7.37962	
$S+P$	150	3.00	-7.40164	0.02202
$S+P+D$	196	3.10	-7.40360	0.00196
$S+P+D+F$	208	3.10	-7.40366	0.00006
Exact*			-7.41013	
error			0.00647 (0.087%)	

\* See text preceding Ref. 19.

<sup>18</sup> C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962). The exact energy is obtained by adding to the two-electron energy of Pekeris, Ref. 5, the experimental ionization energy corrected for relativistic effects and nuclear motion.

state, the open-shell configurations were found to give no significant contribution to the energy. The exact energy of the  $2^2P$  state was found by adding to the  $2^2S$  energy the observed  $2^2S-2^2P$  energy difference.<sup>19</sup> No corrections were made because the accuracy of the calculation does not seem to warrant it.

The change in optimum scale parameter  $k$  as the expansions are increased is seen from Tables III and IV to be very similar for the two states, and to be very small when compared with the corresponding behavior for two-electron atoms. However, the final optimum  $k$  is again greater than  $Z$ , so that  $k$  cannot be interpreted as a screened effective nuclear charge. At each point in the expansion at which energies were calcu-

FIG. 4. Energy of  $2^2P$  Li as a function of scale parameter and expansion length.

lated, four different values, of  $k$ , at most, were found to be sufficient for finding the energy minimum. There is the possibility, however, that this minimization is not unique and that multiple minima might occur. In order to investigate this possibility, the energy of the  $2^2P$  state was calculated with a wide range of scale parameters and with expansions up to 32 terms. The result is shown in Fig. 4. The energy given by a one-term function is just a parabola similar to that obtained from a one-term calculation for helium. As the number of terms is increased, the curve flattens out as expected, passing through zero for zero  $k$ ,

<sup>19</sup> *Atomic Energy Levels*, C. E. Moore, Ed. (U.S. Government Printing Office, Washington, D.C., 1949) Natl. Bur. Std. Circ. No. 467.

and in the limit of a complete set would be a step function with the exact value of the energy for any value of  $k$  greater than zero.

### CONCLUSIONS

It is clear that the method of configuration interaction, with one scale parameter, does work quite well for the ground states of two-electron atoms. In fact, much better results are obtainable than would be expected from the work of Tycho, Thomas, and King.<sup>13</sup> Unfortunately, from the results obtained for other systems, it appears that this is the only state for which this method will give good results, and that the ground state of helium is a singularly poor one on which to test a method of calculating the energies of atomic systems. The spatial equivalence of the two electrons just happens to allow a function with one scale parameter to represent the system quite well.

For a system of inequivalent particles, such as lithium, one scale parameter does not allow enough flexibility. There are two ways in which this might be overcome. The rapidly decreasing improvement in energy with increasing  $l$  in the core functions, as shown by Tables III and IV, indicates that an improved result might be obtained by using different scale parameters for single-particle functions with different values of  $l$ , as was done for the ground state of helium by Nesbet and Watson.<sup>11</sup> However, the results obtained for helium in the present investigation make it appear likely that a more profitable method would be the use of different scale parameters for the inner and outer electrons. Unfortunately, in introducing more than one scale parameter, one loses the advantage of having to calculate the matrix elements for a given set of configurations only once. If several scale parameters are used, assigned either to different functions or to different particles, all matrix elements have to be recalculated for every set of values of the scale parameters for which the energy is desired. Thus, for example, for higher states of helium the calculation of the energy for each set of values of the scale parameters would take as much effort as is required for the entire ground-state calculation.

In order to investigate the improvement which might be expected, a trial calculation was made of the ground-state energy of lithium using one- and two-term functions with different scale parameters for the inner and outer electrons. The trial functions are then of the form  $(1s1s) {}^1S$ ,  $2s'$  and  $A(1s1s) {}^1S$ ,  $1s' + B(1s1s) {}^1S$ ,  $2s'$ , where the prime indicates the different scale parameter. The results are compared in Table V with what can be obtained from an expansion in configurations of the form  $(1s1s) {}^1S$ ,  $ns$ . The expansion must be carried to 17 terms, or through the configuration  $(1s1s) {}^1S$ ,  $18s$  before the rigidity imposed by the single scale parameter is overcome. This gives some indica-

TABLE V. Improvement in lithium ground-state energy with two scale parameters.

$N$	$k_1 = k_2$	$k_2$	$E$	Error
1	2.68	0.94	-7.3935	0.084(1.1%)
2	2.70	0.70	-7.4190	0.059(0.8%)
17	$(k_1 = k_2 = k_3 = 2.70)$		-7.4191	0.058(0.8%)

tion both of the improvement which might be obtained by the use of two scale parameters, and the size of the expansion which would be necessary with one scale parameter in order to get results comparable to those of other methods.

Finally, it is clear that when a solution is approximated by an expansion in a complete set of single-particle functions, the effect of scaling is very important, and that the optimum scale parameter changes significantly when the expansion is increased. This has also been noted by Shull and Löwdin<sup>17</sup> for truncated complete sets containing up to 20 terms. They drew the conclusion that no physical significance should be attached to the scale parameter; that it is merely a mathematical parameter which is to be adjusted so as to provide the best result. However, physical significance is often attached to scale parameters. For instance, Pekeris<sup>4</sup> required that the scale factor be equal to  $(-E)^{\frac{1}{2}}$ , so that the solution to the helium wave equation would have the same asymptotic behavior as a product of hydrogen functions. But, when a minimization with respect to scale parameter is included in this type of calculation, the optimum value is generally found to be greater than  $(-E)^{\frac{1}{2}}$ .<sup>20-22</sup> Ignoring the possible effect of a changing scale parameter does seem to work much better in calculations with  $r_{ij}$  functions than in configuration-interaction calculations. Davidson<sup>21</sup> and Schwartz<sup>22</sup> have noted some dependence of optimum scale parameter on expansion length when  $r_{ij}$  functions are used, but the type of dependence does not seem to be the same as that found with configuration interaction. When single-particle configurations are used, the optimum scale parameter for two-electron ground states appears to tend to a large value as the exact solution is approached. On the other hand, the results of Davidson and Schwartz seem to show that with  $r_{ij}$  functions the scale parameter rises slowly, with an optimum value somewhere in the vicinity of  $Z$ , but not necessarily less than  $Z$ . Thus, the two types of expansion seem to be fundamentally different, but in neither case can the effect of scaling be ignored or given a simple physical interpretation.

<sup>20</sup> T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

<sup>21</sup> E. R. Davidson, J. Chem. Phys. **39**, 875 (1963).

<sup>22</sup> H. M. Schwartz, Phys. Rev. **130**, 1029 (1963).