

but *not* as in Eq. (3.4). Here the Hulthén method need not provide an upper bound while, as we have just seen, the Kohn method is guaranteed to do so. In this case, it is no longer true that the Kohn estimate must be more accurate. Indeed, an example of the reverse situation is provided by some of Seaton's⁹ results. Nevertheless, one would certainly use the Kohn prin-

ciple, since it possesses the very desirable minimum property.

Similar considerations hold when more than one bound state exists. If no bound states exist case (b) does not arise and, as we have pointed out previously,⁵ the Kohn method should be used to obtain the bound on the scattering length.

Approximate Wave Functions for Atomic Be†

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A configuration interaction calculation, involving thirty-seven configurations and including the $(1s)^2(2s)^2$ Hartree-Fock function, has been done for the ground state of atomic Be. Approximately ninety percent of the correlation energy has been incorporated into the final total energy. The results indicate that the correlation energy is associated with two effects, namely that of the "correlation hole" as has been observed for He and that of "orbital degeneracy" (which does not appear in the two-electron He case). The former effect is best handled by the Hylleraas approach and the latter by the configuration interaction method, and the results suggest that an admixture of the two methods would lead to the most rapidly convergent description of the exact four-electron wave function. The errors introduced by handling "high-lying" configurations by second-order perturbation theory rather than by exact configuration interaction are also investigated.

I. INTRODUCTION

THE Hartree-Fock formalism¹ yields approximate solutions of the many-electron Hamiltonian. These solutions are in considerable error if one wishes to use them to predict almost any physically observable quantity. Not only are the solutions in error, but small improvements in the wave functions, as evidenced by a lowering of the expectation values of the total energies, will lead to poorer predictions of some of the observables. The lithium hyperfine interaction² is an example of this. The two standard methods for improving on the Hartree-Fock wave function are (1) that of Hylleraas³ where interelectronic coordinates (r_{ij}) are explicitly included in the wave function and (2) that of configuration interaction where the variational principle is applied to a trial wave function which is a linear combination of Slater determinants. The Hylleraas approach has been very successfully applied to the two-electron (three-particle) ions^{4,5} where total

energies and wave functions of accuracy sufficient to assist in supplying information concerning the nucleus have been obtained.⁴ The configuration interaction approach has yielded much less accurate results for the same problem.^{6,7}

The difference between the He Hartree-Fock function and the exact eigenfunction for the two-electron (nonrelativistic) Hamiltonian occurs because the Hartree-Fock function inadequately describes the behavior of the two electrons when they are close together, i.e., the "correlation hole" is omitted. The comparative success of the Hylleraas method, when applied to He, is due to the fact that it supplies a more rapidly convergent method for describing the "correlation hole."

Both methods increase in difficulty with increasing numbers of particles. This increase is most serious for the Hylleraas approach since the number of interelectronic r_{ij} coordinates increases quadratically with the number of particles while the number of independent one-electron (r_i) coordinates increases only linearly. When going from the Hartree-Fock to more exact eigenfunctions for systems of four or more electrons there often is, as has been suggested by

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¹ For example, see D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley and Sons, New York, 1957).

² L. M. Sachs (to be published); R. K. Nesbet (to be published).

³ E. Hylleraas, *Z. Physik* **65**, 209 (1930); E. Hylleraas and J. Midtal, *Phys. Rev.* **103**, 829 (1956).

⁴ C. L. Pekeris, *Phys. Rev.* **112**, 1649 (1958).

⁵ S. Chandrasekhar and G. Herzberg, *Phys. Rev.* **98**, 1050 (1955); T. Kinoshita, *Phys. Rev.* **105**, 1490 (1956); J. F. Hart and G. Herzberg, *Phys. Rev.* **106**, 79 (1957); and E. A. Hylleraas and J. Midtal, *Phys. Rev.* **109**, 1013 (1958).

⁶ R. K. Nesbet and R. E. Watson, *Phys. Rev.* **110**, 1073 (1958).

⁷ G. R. Taylor and R. G. Parr, *Proc. Natl. Acad. Sci. (U.S.)* **38**, 154 (1952); L. C. Green, M. M. Mulder, M. N. Lewis, and J. W. Wall, *Phys. Rev.* **93**, 757 (1954); H. Shull and P. -O. Löwdin, *J. Chem. Phys.* **23**, 1362 (1955); P. -O. Löwdin and H. Shull, *Phys. Rev.* **101**, 1730 (1955); E. Holgöien, *Phys. Rev.* **104**, 1301 (1956); and D. H. Tycko, L. H. Thomas, and K. M. King, *Phys. Rev.* **109**, 369 (1958).

Nesbet⁸ and Jorgensen,⁹ a problem of "orbital degeneracy" along with that of the "correlation hole." We will see that the "orbital degeneracy" problem is important for the ground state of Be which in this case involves the near degeneracy of the Be $2s$ and $2p$ one-electron functions (orbitals). The method of configuration interaction is the more appropriate way of handling the "orbital degeneracy."

The writer has used the method of configuration interaction for the $1S$ ground state of atomic Be. The primary purpose of the work is to investigate the nature of the problems one will face when attempting to deal with electronic systems involving more than one doubly filled shell. The calculation uses a set of orthogonal Slater determinants (in turn constructed from an orthonormal set of one-electron orbitals) with the Hartree-Fock $1s^2 2s^2$ function as the first or "ground" configuration. The combining coefficients of the linear combination of Slater determinants are just the components of an eigenvector of a matrix eigenvalue equation. For a finite set of Slater determinants, this eigenvalue equation can be solved by standard methods.

The correlation energy is defined to be the difference between the Hartree-Fock total energy and the true nonrelativistic eigenvalue. It is convenient to measure the quality of a wave function (superior to the Hartree-Fock) by observing what percentage of the correlation energy is included in the wave function's total energy. We will use this yardstick in our discussion of Be.

Configuration interaction calculations have already been done for Be. Boys¹⁰ obtained a ten configuration Be wave function whose total energy included approximately one-half of the correlation energy. Boys did not use a Hartree-Fock function as the "ground" configuration. Kibartas, Kavetskis, and Yutsis¹¹ obtained two-thirds of the correlation energy with three *nonorthogonal* configurations one of which being the numerical $1s^2 2s^2$ Hartree-Fock function of the Hartrees.¹² Their (Kibartas, Kavetskis, and Yutsis) better result was due to using the Hartree-Fock function as one of the three configurations and to a very good choice of the other two configurations. These two configurations were a $1s^2 p_1^2$ and a $2s^2 p_2^2$. The p_1 was a numerical Hartree-Fock one-electron solution for a p function in Be $1s^2 p_1^2$ where the $1s$ function of the Hartrees' calculation was used and likewise p_2 was a solution for a $2s^2 p_2^2$ environment with a fixed (the Hartrees' solution) $2s$ function. The p_1 resembles a Be $2p$ function and no such identification can be made of the p_2 . Szász¹³ has used the Hylleraas approach,

starting with a Hartree function and obtained similar energy values.

In the course of the calculation it was discovered that the published value of the Be correlation energy is incorrect, and this is discussed in the following section. This is followed by a description of the one-electron orbitals and how they were obtained. There is then a description of the configurations actually used, a few details of the calculation and finally the results.

II. THE Be CORRELATION ENERGY

As has already been indicated, it is convenient to measure the quality of wave functions, superior to Hartree-Fock ones, by observing what percentage of the correlation energy has been incorporated into their total energies. Accurate values of the correlation energies are desirable in themselves since they aid in our understanding of how exact eigenfunctions differ from Hartree-Fock functions.

Fröman¹⁴ reports a Be correlation energy of 0.087 a.u. (1 a.u.=27.2023 ev. using the value of the rydberg appropriate for Be) and Kibartas, Kavetskis, and Yutsis¹¹ report one of 0.088 a.u. I have also computed it and obtained a value of 0.0944 a.u. This disagreement is due to two causes. First the earlier estimates rely on the Hartree-Fock total energy obtained by the Hartrees¹² and there are several values of the energy available from their results. The commonly chosen^{10,14} value is in error. Secondly, and less in magnitude but greater in interest, there are experimental uncertainties which affect the estimate of the true eigenvalue.

The Hartree calculation was done using numerical procedures and yielded numerical one-electron functions. They obtained a total energy ranging between -14.56 to -14.58 a.u. with -14.58 a.u. usually being quoted. It is difficult to obtain an accurate value for the total energy of such a function. This is particularly due to errors associated with the kinetic energy integrals and this problem has been a matter of some concern.¹⁵ Roothaan, Sachs, and Weiss¹⁶ have obtained an analytic Hartree-Fock solution for Be. The total energy can be accurately evaluated for such a function but the quality of the function is limited by the basis set from which the function is constructed. Large basis sets assist in avoiding this problem and Roothaan, Sachs, and Weiss did calculations with a number of large sets. The best total energy obtained was -14.57302 a.u. which lies within the range of values obtained by the Hartrees and which I believe is a more accurate estimate than -14.58 a.u. The Hartree-Fock solution used by me as the "ground" configuration is also analytic and has a total energy of -14.57299 a.u. or 0.00003 a.u. poorer than that of Roothaan and co-workers.

⁸ R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

⁹ C. K. Jorgensen (private correspondence).

¹⁰ S. F. Boys, Proc. Roy. Soc. (London) **A201**, 125 (1950).

¹¹ V. V. Kibartas, V. I. Kavetskis, and A. P. Yutsis, Zhur. éksp. i teoret. Fiz. **29**, 623 (1955) [translation: Soviet Phys.—JETP **2**, 476 (1956)].

¹² D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A150**, 9 (1935); **A154**, 588 (1936).

¹³ L. Szász, doctoral dissertation, Ludwig-Maximilians Universität, Munich, 1959 (unpublished).

¹⁴ A. Fröman, Phys. Rev. **112**, 870 (1958).

¹⁵ A. J. Freeman and P. -O. Löwdin, Phys. Rev. **111**, 1212 (1958).

¹⁶ C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss (to be published).

Of greater interest than the Hartree-Fock total energy is the true eigenvalue. For electronic systems where all the ionization energies have been observed (this is true for atoms through F) the energies are added up and relativistic corrections are subtracted giving a nonrelativistic total energy. Unfortunately, even for an atom as small as Be, the ionization energies are not all accurately known. For the small atoms this uncertainty is generally associated with the $1s^2 1S$ to $1s^2 S$ ionization process, the value for Be being ± 0.00044 a.u.¹⁷ To avoid this I have used Pekeris¹⁴ theoretical value for the $Be^{++}1s^2$ total energy. It is accurate to several more digits than are of interest here (and it falls within the stated experimental uncertainty). Using the Pekeris nonrelativistic energy and adding to it the observed Be^0 to Be^{++} ionization energies one needs only make a relativistic correction for the $2s$ shell. A crude estimate of this correction has been obtained by using the equation for hydrogenic functions;

$$\frac{\alpha^2 Z^4}{n^3} \left(-\frac{1}{j+1/2} + \frac{3}{4n} \right) + \dots, \quad (1)$$

where n and j are the one-electron quantum numbers. A screening constant (Z) of 1.95, which was obtained by Slater's rules,¹⁸ was used. This yields a $2s$ shell relativistic correction of 0.00002 a.u., a Be total energy of -14.66745 a.u. and in turn a correlation energy of 0.0944 a.u.

III. THE ONE-ELECTRON FUNCTIONS

The Slater determinants are constructed from an orthonormal set of one-electron functions of the form;

$$\psi_i(\mathbf{r}_a) = [u_i(r_a)/r_a] S_i(\theta_a \phi_a) X_i(s_a), \quad (2)$$

where the S_i is a normalized spherical harmonic (with quantum numbers l and m_l) and X_i is a spin function with eigenvalues $m_s = +1/2$ or $-1/2$. The u_i is a normalized radial function which, so that integrals can be easily and accurately obtained, is of analytic form, i.e.;

$$u_i = \sum_j C_{ij} \eta_j, \quad (3)$$

where normalized basis functions of the form

$$\eta_j = N_j r^{l+n_j+1} e^{-Z_j r} \quad (4)$$

have been used. The l is the angular quantum number, Z_j and n_j are assigned parameters and N_j is a normalization constant and is given by

$$N_j = \left(\frac{(2Z_j)^{2l+2n_j+3}}{(2l+2n_j+2)!} \right)^{\frac{1}{2}}. \quad (5)$$

The basis set is listed in Table I. The choice of the number of functions for a particular l value, of the screening constants (Z_j 's), including the relationship between Z_j 's of different l values and of the powers of r (n_j 's) relied heavily on earlier work on He.⁶ For example, it had been observed that little was gained by an extensive investigation where individual Z_j 's were varied so as to obtain a best basis set so this was not done for Be. Care was taken to make sure that no two basis functions were too much alike with the resultant errors that can occur, e.g., if η_9 had an appreciably smaller valued Z_j or η_2 a larger one, the two basis functions would overlap each other more and their C_{ij} 's would tend to become large in magnitude and opposite in sign introducing errors in the integrals involving ψ_i 's (which are obtained as linear combinations of integrals involving the basis functions). Variation of the two s function Z_j 's was done where a Hartree-Fock calculation was done for each choice of Z_j 's and the Hartree-Fock $1s^2 2s^2$ total energy was used as a criterion of the quality of the choice. Limited variation of the other Z_j 's was also done with criteria based on crude estimates of the configuration interaction that could be done with the resulting functions.

Having chosen the η_j 's there was then the problem of choosing the ψ_i 's (or u_i 's) constructed from them. If n ψ_i 's of a given l value had been obtained, the next was obtained by using the Schmidt process to orthogonalize the η_j 's to the n u_i 's, observing which of the orthogonalized η_j 's would be most effective for configuration interaction, choosing that one as the radial part of ψ_{n+1} and then repeating the process (with the "principle" η_i of ψ_{n+1} omitted) for ψ_{n+2} . When deter-

TABLE I. Be basis function parameters.

For the construction of s functions ($l=0$)			For the construction of p functions ($l=1$)		
j	n_j	Z_j	j	n_j	Z_j
1	0	6.0	10	0	9.0
2	0	1.0	11	0	1.5
3	1	6.0	12	1	9.0
4	1	1.0	13	1	1.5
5	2	6.0	14	2	9.0
6	2	1.0	15	2	1.5
7	3	6.0	16	3	9.0
8	3	1.0			
9	4	6.0			
For the construction of d functions ($l=2$)			For the construction of f functions ($l=3$)		
j	n_j	Z_j	j	n_j	Z_j
17	0	12.0	22	0	15.0
18	0	2.0	23	0	2.5
19	1	12.0	24	1	15.0
20	1	2.0			
21	2	12.0			
For the construction of g functions ($l=4$)					
j	n_j	Z_j			
25	0	18.0			
26	0	3.0			
27	1	18.0			

¹⁷ *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1.

¹⁸ J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

TABLE II. The combining coefficients (C_{ij}) which define the one-electron functions ($U_i(r)$) in terms of the basis set (η_j).

i	Title of function	Principal configuration ^a	C_{ij}						
			1	2	3	4	5	6	7
1	1s		0.4848470	0.2176069	0.2641661	-0.2683019	0.1682250	0.1675844	0.0451277
2	2s		-0.0811293	-0.1473455	-0.0511496	1.3329117	-0.0410639	-0.3867802	-0.0075224
3	3s	2s ² s _I ²	-0.9541767	-0.4130058	-0.5189231	0.3510279	1.9029536	-0.2805105	-0.0888150
4	3s _I	1s ² s _{II} ²	-0.0677193	0.1087583	-0.0281226	-1.5781781	0.3466395	0.4265845	-0.0063392
5	3s _{II}	2s ² s _{III} ²	-2.3388370	-1.1340586	4.7935430	2.2736416	-2.2116885	-1.0811843	-0.2176680
6	3s _{IV}	2s ² s _{IV} ²	-2.9639258	-1.2260328	8.6993974	0.4300532	-8.1693479	-0.6874241	-0.2758978
7	p _I	1s ² p _I ²	0.0018150	0.6344460	-0.0110284	-0.1694747	0.0200795	0.6245963	-0.0222008
8	p _{II}	2s ² p _{II} ²	-0.0002912	-0.1017717	1.0145531	0.0271855	-0.0032210	-0.1001917	0.0035612
9	p _{III}	2s ² p _{III} ²	-0.0003976	-0.1389909	-2.6698253	0.0371276	2.8894414	-0.1368331	0.0048636
10	p _{IV}	2s ² p _{IV} ²	4.6212002	-0.0858183	-8.4893539	0.0229240	4.5872141	-0.0844860	0.0030030
11	p _V	1s ² p _V ²	-1.1619175	1.4598108	2.9832901	0.4827560	-2.5193588	-1.7791890	0.0632400
12	d _I	1s ² d _I ²	0.0266365	-0.6000319	-0.0826493	1.5380263	0.0949354		
13	d _{II}	2s ² d _{II} ²	-0.0004037	0.0090939	1.0013675	-0.0233099	-0.0014388		
14	d _{III}	2s ² d _{III} ²	-0.0008029	0.0180874	-2.9984135	-0.0463623	3.1608514		
15	d _{IV}	2s ² d _{IV} ²	6.0010095	0.0140180	-11.227852	-0.0359314	5.9176949		
16	f _I	1s ² f _I ²	0.0180241	1.0012089	-0.0313172				
17	f _{II}	2s ² f _{II} ²	-0.0009270	-0.0514960	1.0029326				
18	f _{III}	2s ² f _{III} ²	3.1698447	0.0639022	-3.0113646				
19	g _I	1s ² g _I ²	0.0000000	1.0000000	0.0000000				
20	g _{II}	2s ² g _{II} ²	0.0000000	-0.0323967	1.0005246				
21	g _{III}	2s ² g _{III} ²	3.4667482	0.0391222	-3.3204254				

^a As predicted for the function by second-order perturbation theory.

mining which orthogonalized η_j was most effective for configuration interaction, the sets of $1s1s\eta_j^2$, $1s2s\eta_j^2$, and $2s^2\eta_j^2$ functions were constructed and second order perturbation theory was then used to observe which set had the greatest effect on the Be total energy. Successive ψ_i 's were obtained until further ones had predicted energy contributions of less than 0.00005 a.u. Except for the 1s and 2s, ψ_i 's are labelled with roman numerals and are numbered in the order they were obtained.

With a method for obtaining successive ψ_i 's there remained only the choice of the first for each l value. There was no problem for $l=0$ since 1s and 2s orbitals were obtained from a Hartree-Fock calculation. Investigation showed that, other than the $1s^22s^2$, the most important configuration is a $1s^2p^2$ where the p function resembles a Be $2p$ function. The p_I (in accordance with the labeling system) used in this configuration was a Hartree-Fock solution for a p function in an environment consisting of a $\text{Be}^{++}1s^2$ ion. This led to a p function which is similar but not identical to the p function of Kibartas, Kavetskis, and Yutsis in their $1s^2p_I^2$ configuration. Second order perturbation theory predicted that d_I , f_I and g_I functions which were also Hartree-Fock solutions for a Be^{++} ion environment would yield the best configuration interaction energy contributions so such functions were used as the first of each of their respective l values (actually a rough approximation to such a solution was used for g_I). In all, six s -like (including the 1s and 2s), five p -like, four d -like, three f -like and three g -like one-electron orbitals were constructed. In general their charge densities are concentrated either into the region where the 1s is concentrated or into the region of the 2s. The ones (x) concentrated in the 1s region were chosen for their effectiveness when used in $2s^2x^2$ con-

figurations where the overlap of x and the 1s in large part determines the effectiveness of the configuration for configuration interaction. The other one-electron functions, with their charge densities concentrated in the 2s region are (according to second order perturbation theory) of greatest importance for the construction of $1s^2x^2$ configurations. Table II lists the combining coefficients (C_{ij}) which define the u_i 's or ψ_i 's in terms of the η_j 's. The third column of the table designates the second order perturbation theory prediction of whether the function is more important when used in $1s^2x^2$ or in $2s^2x^2$ configurations.

The technique of building up a set of localized one-electron functions, useful for configuration interaction, by successive applications of the Schmidt orthogonalization procedure is moderately effective if a realistic method is used to determine which of a set of ψ_i 's is most important for use in configuration interaction. We will see that second order perturbation theory was, unfortunately, not an adequate measuring device.

IV. THE CHOICE OF CONFIGURATIONS

Except for the case of two doubly occupied s orbitals, such as $1s^22s^2$ or $2s^2s_I^2$, a single Slater determinant is not a $1S$ state for a four electron system. It is most convenient to deal with the $1S$ functions which are constructed from sets of Slater determinants which differ in only their one-electron m_l and m_s values (i.e., with fixed assignments of i and l). Such $1S$ functions have been illustrated elsewhere⁶ for the two-electron case. With a few exceptions, which will be discussed below, only one unique $1S$ four-electron function can be constructed with a specific assignment of i 's (here denoting the Roman numeral values) and l 's. Such functions are, except for a phase factor of ± 1 , uniquely defined when the four i and four l values are given. In

this work the phase factor has been chosen so that the Slater determinant where *all* the m_i 's equal zero is of positive sign in the 1S function. This differs by a factor of minus one from the convention used for two-electron determinants involving p and f functions in reference 6.

One hundred and seventy-seven 1S functions or configurations can be constructed for which two or more of the electrons are $1s$ and/or $2s$ and the remainder are chosen from the other nineteen ψ_i 's. Hundreds of 1S functions can be constructed in which the $1s$ and $2s$ appear once or not at all. A calculation which utilizes more than a small fraction of these configurations would unduly tax both the digital computer used in the calculation and the person responsible for the calculation. As a result, one stage of the calculation becomes a search for the 1S configurations which will be most important for use in configuration interaction. Before indicating the history of this search it would be well to review the types of 1S configurations which can occur. One useful way to catalog configurations is by the number of ψ_i 's which differ from those in the "ground" $1s^22s^2$ configuration. The resulting four types are discussed below. In this discussion x and y are used to denote ψ_i 's other than the $1s$ and $2s$.

Single Substitution Configurations

The $1s^22sx$ and $1s2s^2x$ are the two types of configurations of this category. In order to be 1S functions, x must be an s -like orbital. Because the $1s$ and $2s$ are Hartree-Fock orbitals and since x is orthogonal to them, the configurations have zero valued matrix elements connecting them to the $1s^22s^2$ configuration. Second order perturbation theory would thus predict that their inclusion would have no effect on the configuration interaction energy. Since these states have appreciable matrix elements connecting them to other (than the $1s^22s^2$) low-lying configurations, it is possible that their inclusion would have some effect. Several single substitution configurations were included in a calculation where all elements of the configuration interaction matrix were computed and then the matrix was diagonalized. These configurations produced energy effects of less than 0.000001 a.u., effects so small that configurations of this type have not been included in the final configuration interaction calculation.

Double Substitution Configurations

This type of configuration plays the leading role in configuration interaction. It takes the form of $1s^2xy$, $2s^2xy$ and $1s2sxy$ where x and y may have differing or identical l and i values. These configurations have nonzero matrix elements with the ground configuration and it was with these that the second order perturbation theory investigation was done. Except for the $1s2sxy$, with x and y of differing i (their l values cannot differ for a 1S configuration), only a single 1S function can be constructed for a given assignment of i and l values.

The $1s2sxy$ of differing x and y plays the smallest role in configuration interaction and only one, the $1s2sp_Ip_{II}$, has been used in the final configuration interaction calculation. Two linearly independent $1s2sp_Ip_{II}$ 1S functions can be constructed and only one has been used. It is

$$\begin{aligned} \Psi(1s2sp_Ip_{II}) = & \frac{1}{3}[1s\alpha 2s\beta p_I^0\alpha p_{II}^0\beta] \\ & - \frac{1}{3}[1s\alpha 2s\beta p_I^1\alpha p_{II}^{-1}\beta] - \frac{1}{3}[1s\alpha 2s\beta p_I^{-1}\alpha p_{II}^1\beta] \\ & + \frac{1}{3}[1s\beta 2s\alpha p_I^0\beta p_{II}^0\alpha] - \frac{1}{3}[1s\beta 2s\alpha p_I^1\beta p_{II}^{-1}\alpha] \\ & - \frac{1}{3}[1s\beta 2s\alpha p_I^{-1}\beta p_{II}^1\alpha] - \frac{1}{6}[1s\alpha 2s\alpha p_I^0\beta p_{II}^0\beta] \\ & + \frac{1}{6}[1s\alpha 2s\alpha p_I^1\beta p_{II}^{-1}\beta] + \frac{1}{6}[1s\alpha 2s\alpha p_I^{-1}\beta p_{II}^1\beta] \\ & - \frac{1}{6}[1s\beta 2s\beta p_I^0\alpha p_{II}^0\alpha] + \frac{1}{6}[1s\beta 2s\beta p_I^1\alpha p_{II}^{-1}\alpha] \\ & + \frac{1}{6}[1s\beta 2s\beta p_I^{-1}\alpha p_{II}^1\alpha] - \frac{1}{6}[1s\alpha 2s\beta p_I^0\beta p_{II}^0\alpha] \\ & + \frac{1}{6}[1s\alpha 2s\beta p_I^1\beta p_{II}^{-1}\alpha] + \frac{1}{6}[1s\alpha 2s\beta p_I^{-1}\beta p_{II}^1\alpha] \\ & - \frac{1}{6}[1s\beta 2s\alpha p_I^0\alpha p_{II}^0\beta] + \frac{1}{6}[1s\beta 2s\alpha p_I^1\alpha p_{II}^{-1}\beta] \\ & + \frac{1}{6}[1s\beta 2s\alpha p_I^{-1}\alpha p_{II}^1\beta], \quad (6) \end{aligned}$$

where α and β denote one-electron spin assignments of $+1/2$ and $-1/2$, respectively, and the p superscripts denote one-electron m_l values. Each bracket indicates a single four-electron Slater determinant. Other functions of this type, including the other $1s2sp_Ip_{II}$, were investigated but they gave energy contributions of less than 0.00006 a.u. and have not been used in the final calculation.

Triple Substitution Configurations

These configurations have matrix elements which are zero with the $1s^22s^2$ configuration but sizable with other important configurations. Their contributions to the configuration interaction energy are smaller than 0.000001 a.u. and thus no configurations of this type appear in the final calculation.

Quadruple Substitution Configurations

These also have zero valued matrix elements connecting them to the $1s^22s^2$ configuration but unlike the single and triple substitution configurations these give important energy contributions via their nonzero matrix elements with important configurations other than the $1s^22s^2$. Only configurations of the form x^2y^2 have been considered. Investigation shows that other types would be less important. If neither x nor y is an s -like function, several linearly independent $^1Sx^2y^2$ functions can be constructed. The simplest is one where two-electron $^1Sx^2$ and $^1Sy^2$ functions are constructed and then combined into a four-electron 1S function. Such a function has nonzero matrix elements with other configurations used in the calculation while the other linearly independent x^2y^2 1S functions *do not*. These other x^2y^2 functions do have large matrix elements with the $x^2(^1S)y^2(^1S)$. Investigation has shown that their configuration interaction energy contributions [via their interaction with the $x^2(^1S)y^2(^1S)$] are effectively zero.

Shortly after the start of the work on Be it became apparent that second-, or higher, order perturbation theory gave poor estimates of the relative importance of different 1S configurations. To avoid this problem I constructed the ("basic") configuration interaction matrix for the most important configurations, then increased the matrix to include additional configurations of uncertain importance and diagonalized the resultant matrix to discover the effect of the additions. Any configuration which proved to be important was added to the "basic" matrix. The importance of the n th configuration would be observed by diagonalizing the n by n and the $(n-1)$ by $(n-1)$ matrices and interpreting the difference in energies as being the n th configuration's contribution. In the final thirty-seven configuration calculation, all matrices down to the two by two have been diagonalized with the differences in successive diagonalizations again being interpreted as the contributions from specific configurations. This process is costly in computer time but gives us data which aids us in obtaining insight into the configuration interaction process.

In the discussion of results, configurations of the $1s^2xy$ form will be interpreted as contributing to the correlation energy effects of the $2s$ shell since the xy replaces the $2s^2$ of the $1s^22s^2$ configuration. Similarly the $2s^2xy$ configurations will be associated with the $1s$ shell correlation and the $1s2sxy$ and quadruple substitution configurations with intershell effects. This interpretation is not strictly realistic but it is a convenient crutch when interpreting results.

Of the thirty-seven configurations of the final calculation, roughly the first twenty were chosen solely for their importance in improving the Be total energy. The later configurations were chosen partially for their energy contributions and partially for the assistance they give in answering questions such as how effective was the choice of the ψ_i 's used in the half-dozen most important configurations.

V. THE COMPUTATIONS

The computations were started on the Whirlwind computer at M.I.T. but the majority of the work was done on the 704 computer in the M.I.T. Computation Center. The computer was used to generate the one and two-electron integrals used for the construction of matrix elements. These integrals were computed for each stage of the Schmidt orthogonalization in search of ψ_i 's. The computer was also used for the matrix diagonalizations.

Matrix elements were computed by hand, using the well known relationships^{8,19} for matrix elements of the nonrelativistic many (four)-electron Hamiltonian between Slater determinants. These were combined to give matrix elements between multideterminantal 1S

functions. The matrix elements are as accurate as the one and two-electron integrals from which they are constructed. These integrals, which are in terms of the ψ_i 's, are obtained as linear combinations of the integrals in terms of the basis functions (η_j 's). The latter integrals are obtained analytically. The ability to compute integrals analytically rather than numerically yields integrals in terms of the ψ_i 's which are comparatively accurate. This is the great strength of the analytic approach. The integrals involving ψ_i 's of low Roman numeral value are accurate to seven digits while those of higher Roman numeral values tend to be somewhat less accurate. This is due to the increasing magnitude of the C_{ij} 's for the high values of i .

VI. RESULTS

The results are tabulated in Table III. The table's first column lists the contributing configurations (Ψ_n) and the second their n values. The next column gives the energy contributions as predicted by second order perturbation theory. The fourth column lists the actual energy contribution for the n th configuration. This is obtained by taking the difference between the n configuration energy and that of the $(n-1)$ configuration wave function. The next (fifth) column lists the eigenvector coefficients (K_n) which define the thirty-seven configuration function (Φ) in terms of the individual configurations (Ψ_n), i.e.,

$$\Phi = \sum_{n=1}^{37} K_n \Psi_n. \quad (7)$$

The first four configurations are the really important ones and a Φ constructed from these alone may be of interest to some readers. For this reason the four configuration eigenvector appears in the sixth column. The next column gives the energies (E_n 's) of the n configuration Φ 's. These energies will be compared with those in the last two columns. These columns will be discussed later.

Table III contains a number of items of interest. First we see that the thirty-seven configuration function's energy (E_{37}) includes slightly less than ninety percent, and the four configuration energy (E_4) seventy-four percent of the correlation energy. Appreciable energy contributions stop after the inclusion of the fourth configuration. Secondly, there is the failure of second order perturbation theory to make accurate energy contribution predictions. This is particularly so with the $1s^2xy$ type of configuration such as the $n=13$ case. This failure is so severe that $1s^2xy$ configurations involving the s_{II} , f_I , and g_I orbitals have been left out of the calculation. For example, second order perturbation theory predicts that the $1s^2s_{II}^2$ configuration would contribute an energy improvement of -0.00117 a.u., an appreciable contribution. In a correct handling of the configuration interaction, with

¹⁹ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), in particular p. 171.

TABLE III. The results of the thirty-seven configuration calculation for Be.

The n th configuration (Ψ_n)	n value	Second-order perturbation theory prediction of the energy contribution Ψ_n (a.u.)	Actual energy contribution of Ψ_n , i.e., $E_n - E_{n-1}$ (a.u.)	Eigenvector (K_n 's) of the thirty-seven configuration wave function	Eigenvector (K_n 's) of the four-configuration wave function	Energy (E_n) of the n configuration wave function (a.u.)	Two-column ^b border determinant E_n (a.u.)	Four-column ^b border determinant E_n (a.u.)
$1s^2 2s^2$	1		-14.57299	0.9575824	0.9597008	-14.57299		
$1s^2 p_1^2$	2	-0.04555	-0.04116	-0.2844586	-0.2793724	-14.61414		
$2s^2 p_{II}^2$	3	-0.01937	-0.01769	-0.0262111	-0.0238793	-14.63183		
$2s^2 s_1^2$	4	-0.01185	-0.01071	-0.0232595	-0.0188478	-14.64254		
$2s^2 d_{II}^2$	5	-0.00268	-0.00213	-0.0059003		-14.64467		
$p_1^2(^1S)p_{II}^2(^1S)$	6	0.00000	-0.00157	0.0070633		-14.64624		
$2s^2 p_{III}^2$	7	-0.00144	-0.00111	-0.0051437		-14.64735	-14.64801	-14.64737
$2s^2 p_I p_{II}$	8	-0.00117	-0.00106	-0.0073743		-14.64841		
$p_1^2(^1S)s_1^2(^1S)$	9	0.00000	-0.00100	0.0056508		-14.64941		
$1s 2s s_1^2$	10	-0.00088	-0.00084	-0.0055013		-14.65025		
$1s 2s p_{II}^2$	11	-0.00070	-0.00063	-0.0047417		-14.65088		
$2s^2 p_{II} p_{III}$	12	-0.00142	-0.00065	-0.0051990		-14.65153	-14.65280	-14.65115
$1s^2 d_1^2$	13	-0.00431	-0.00040	-0.0182294		-14.65203		
$1s 2s p_I p_{II}^a$	14	-0.00040	-0.00062	-0.0062031		-14.65265		
$2s^2 p_{II}^2$	15	-0.00064	-0.00048	-0.0018353		-14.65313		
$2s^2 s_{III}^2$	16	-0.00042	-0.00031	0.0003207		-14.65344		
$2s^2 d_{III}^2$	17	-0.00042	-0.00031	-0.0019705		-14.65375	-14.65527	-14.65344
$2s^2 p_{IV}^2$	18	-0.00034	-0.00027	-0.0009703		-14.65402		
$p_1^2(^1S)d_{II}^2(^1S)$	19	0.00000	-0.00019	0.0015848		-14.65421		
$2s^2 s_{IIV}^2$	20	-0.00034	-0.00038	0.0102900		-14.65459		
$1s 2s p_1^2$	21	-0.00034	-0.00020	0.0065906		-14.65479		
$2s^2 g_{II}^2$	22	-0.00022	-0.00016	-0.0008295		-14.65495	-14.65672	-14.65452
$2s^2 p_{III} p_{IV}$	23	-0.00029	-0.00001	0.0000858		-14.65496		
$2s^2 s_{IIIV}^2$	24	-0.00020	-0.00023	-0.0057483		-14.65519		
$2s^2 s_{IIV}^2$	25	-0.00018	-0.00068	-0.0049320		-14.65587		
$2s^2 p_{II} p_{IV}$	26	-0.00015	-0.00071	-0.0021912		-14.65658		
$1s^2 p_V^2$	27	-0.00009	-0.00001	-0.0008337		-14.65659	-14.65749	-14.65532
$1s^2 p_I p_V$	28	-0.00006	-0.00003	0.0013765		-14.65662		
$2s^2 d_{III} d_{III}$	29	-0.00015	-0.00018	-0.0015543		-14.65680		
$2s^2 f_{III}^2$	30	-0.00012	-0.00010	-0.0004808		-14.65690		
$2s^2 d_{IV}^2$	31	-0.00011	-0.00009	-0.0004351		-14.65698		
$p_1^2(^1S)d_1^2(^1S)$	32	0.00000	-0.00000 _s	0.0004639		-14.65698	-14.65787	-14.65565
$2s^2 s_{IV}^2$	33	-0.00008	-0.00026	0.0020928		-14.65724		
$2s^2 g_{IIV}^2$	34	-0.00006	-0.00004	-0.0002745		-14.65728		
$2s^2 p_1^2$	35	-0.00006	-0.00003	-0.0018990		-14.65731		
$1s^2 p_I p_{II}$	36	-0.00008	-0.00009	0.0025567		-14.65740		
$1s^2 p_{II}^2$	37	-0.00000 ₁	-0.00000 ₁	-0.0003084		-14.65740	-14.65814	-14.65590
Experimental energy =						-14.66745		

^a See Eq. (6).^b See text.

the $1s^2 2p^2$ configuration already present, the $1s^2 s_{II}^2$ makes a contribution of -0.000002 a.u.

Of the correlation energy that has been incorporated into the Be function, about half of it is associated with the $1s^2 p_1^2$ configuration, slightly less than half with correlation in the $1S$ shell (the $2s^2 xy$ configurations), about five percent representing correlation between shells and about one percent associated with the $2s$ shell correlation after the $2s-p_1$ (which is $2p$ -like) near degeneracy is resolved.

Inspection of the contributions to the $1s$ shell correlation correction shows a pattern which is similar to that observed in the He configuration interaction.⁶ The $2s^2 xy$ configurations are acting to expand, in one-electron spherical harmonics and radial functions, an interelectronic r_{ij} singularity or "correlation hole" in the $1s$ shell region. A similar interpretation cannot be made of the $1s^2 xy$ configuration contributions where ninety-five percent of the energy contribution comes from a single configuration, the $1s^2 p_1^2$. Instead it appears

that most of the energy improvement is associated with the "orbital degeneracy" between the Be $2s$ and p_1 (i.e., $2p$) and that, at most, ten percent of the $2s$ shell correlation energy is due to a correction for a "correlation hole" in the $2s$ shell region. The energy associated with the correlation between the two shells, as indicated by the $1s 2s xy$ and quadruple substitution configuration energy contributions, appears to be larger than the $2s$ shell "correlation hole" energy.

Several double substitution configurations (notably those for $n=25, 26$, and 33) show energy contributions which are larger than predicted by second order perturbation theory. The large contributions occur because these configurations act in conjunction with configurations already present. For example, the addition of the $2s^2 s_{IV}^2$ ($n=33$) configuration caused appreciable increases in the eigenvector coefficients (K_n 's) of the $2s^2 s_{IIV}^2$, $2s^2 s_{IIIV}^2$, $2s^2 s_{III}^2$ and $2s^2 s_1^2$ and a decrease for the $2s^2 2_{III}^2 K_n$.

One purpose of the higher n valued configurations is

that they serve as a crude test on the ψ_i 's appearing in the important configurations. The small energy contributions of the $1s^2p_v^2$, $1s^2p_vp_I$, $1s^2p_Ip_{II}$, and $1s^2p_{II}^2$, despite large matrix elements with the $1s^2p_I^2$, suggest that the p_I orbital was a very good choice for use in the $1s^2p_I^2$ configuration. Similar observations suggest that it would be possible to obtain somewhat better p_{II} and s_I orbitals for use in the important $2s^2p_{II}^2$ and $2s^2s_I^2$ configurations.

The contributions to the Be total energy have been the sole criterion of the importance of the configurations. Other criteria could be used such as the magnitude of the eigenvector coefficients (K_n 's). Such a criterion would make the $2s$ shell, $1s^2xy$ type of configuration appear more important (note K_{13}). Second order perturbation theory is as inadequate for predicting K_n 's as it is in predicting energy contributions.

One question of interest is when can second order perturbation theory be accurately used instead of the full handling of the configuration interaction problem. Table III indicates that perturbation theory applied to the single configuration $1s^22s^2$ function gives poor results. It seemed desirable to find out what happened if perturbation theory were used *after* the two configuration, $1s^22s^2$ and $1s^2p_I^2$ problem was handled exactly. Such a treatment corresponds to setting all matrix elements but those in the first two columns and on the diagonal equal to zero and the diagonalizing the resultant configuration interaction matrix. The eighth column of table III gives the result of such a "two-column" treatment. In the interest of conserving computer time, diagonalizations were restricted to every fifth n value. It also seemed desirable to do a similar calculation where the four important configurations are handled exactly. The last column of Table III lists the results of the "four-column" treatment of the configuration interaction matrix. The "two column" results show a conflict between the common tendency of perturbation theory to overestimate and the loss of the energy contributions due to interactions between the higher configurations. The former effect dominates and a total energy which is low results. The "four-column" case yields an energy which is high, i.e., it underestimates the effect of configuration interaction. Its energy is in poorer agreement with the exact treatments (column seven) energy than is the "two-column" energy. This is due to a closer cancellation of errors in the "two-column" case. I leave it to the reader²⁰

²⁰ Footnote added in proof.—It seemed desirable to insert the writer's opinions. I believe that *after* the $2s$ - $2p$ (or equivalent)

to decide how far one should carry out an exact treatment of configuration interaction before resorting to perturbation theory. It might interest the reader to know that in the slightly larger atomic system of C, there are ten configurations²¹ which are as important as the first four in Be. This suggests that, even with the "early" use of second order perturbation theory, the problem rapidly becomes huge in size.

VII. CONCLUSIONS

The primary purpose of this work was to obtain information concerning the problems that will have to be faced when one attempts to deal accurately with electronic systems which are appreciably larger than He. This Be calculation indicates that an "orbital degeneracy" problem, as well as the "correlation hole" problem of He, will be met and must be dealt with. The "orbital degeneracy" problem is not a small effect in Be and this will be the case for many other electronic systems. The Be results also suggest than an effective approach would be one where one starts with the Hartree-Fock ground configuration, uses configuration interaction to resolve the "orbital degeneracy" and then goes on and treats the "correlation hole" effects either using the Hylleraas approach, which would not be trivial, or using additional configuration interaction. While doing such a calculation it must be remembered that the energy associated with the "correlation hole" between shells is liable to be as large as that associated with an outer shell.

In conclusion, I would like to point out that, with a better choice of ψ_i 's and with a criterion for choosing Ψ_n 's which is based solely on energy considerations, a noticeably better Be energy could be obtained in a calculation with as many configurations as have been used here.

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"orbital degeneracy" is resolved, second-order perturbation theory can be very satisfactorily used to predict the relative importance of configurations and, for many purposes, it is quite reasonable to use it in place of full configuration interaction.

²¹ R. K. Nesbet (private conversation).