

Electronic Structure of Atomic Boron*

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The electronic structure of the 2P ground state of the boron atom has been studied using configuration interaction. A 187-configuration function yielded an energy of -24.6392 hartrees, which corresponds to 88.3% of the correlation energy. The separability of different types of single and double excitations from the Hartree-Fock ground state was investigated. The sum of the energy increments found for single and double excitations amounted to 88.1% of the correlation energy; when the same functions were used simultaneously in a full configuration interaction, the calculated energy included 86.3% of the correlation energy. Triple and quadruple excitations accounted for 2% of the correlation energy. A relatively good five-configuration wave function is also given.

INTRODUCTION

THE need for atomic wave functions of better than Hartree-Fock accuracy has long been recognized. For smaller atoms, it has proved practical to use configuration-interaction (CI) methods, and such studies have recently been reported for atoms containing as many as four electrons.¹ However, the difficulty of carrying out calculations increases rapidly with the number of electrons, and few authoritative studies exist for atoms larger than Be. A five-electron atom already illustrates most of the added difficulties which must be overcome in order to make CI calculations for the remaining first-row atoms. These difficulties include the effect of an increased variety of intra- and intershell correlations involving electrons in p orbitals, and the problems associated with the description of an angular momentum eigenfunction for five electrons in an open-shell state. Accordingly, we present in this paper an accurate CI study of the five-electron 2P ground state of atomic boron.

The experimental value of the correlation energy of boron (the difference between the nonrelativistic exact energy and the Hartree-Fock energy) has been placed by Clementi² at 0.125 hartrees, based on his accurate Hartree-Fock calculation³ with an energy of -24.52905 hartrees. Two-configuration calculations have been made on boron both by Iutsis *et al.*⁴ and by Clementi and Veillard.⁵ Both of these calculations use the Hartree-Fock ground-state configuration $1s^2 2s^2 2p$ plus the "degeneracy effect" configuration $1s^2 2p^3$, and both obtain about 25% of the correlation energy. A more complete CI study of boron was made by Boys.⁶ He obtained an energy of -24.600 hartrees, or 57% of the

correlation energy, using an 11-configuration wave function.

Our study of boron is aimed toward three objectives. First, we wish to obtain as accurate a CI wave function and energy as can be reached with reasonable amounts of effort. Secondly, we wish to analyze our results in terms of different single excitations and pair correlations, to identify the main contributions to the correlation energy, and to help evaluate the quantitative accuracy of approximate theories of correlation. Finally, we wish to present a simple wave function which is accurate enough for many purposes. We have found a five-configuration function of energy -24.608 hartrees. This result compares favorably with the 11-configuration result of Boys.

Our calculations are based on CI expansions whose first configuration is the analytical Hartree-Fock function of Clementi.³ This function is probably quite accurate, as it gives an energy within 0.0001 hartree of the numerical Hartree-Fock value obtained in a careful investigation by Froese⁷ (-24.52913 hartrees). The use of an accurate Hartree-Fock wave function (rather than, for example, a double- ζ function) as a first configuration allows one to speak legitimately of excitations of various types from the Hartree-Fock zero-order state.

ATOMIC ORBITALS

The $1s$, $2s$, and $2p$ atomic orbitals or one-electron functions were taken to be the Hartree-Fock orbitals as given by Clementi. Additional atomic orbitals were obtained by adding Slater-type basis orbitals to the existing basis set and using the Gram-Schmidt procedure to orthogonalize these new one-electron functions to all previously adopted atomic orbitals of the same angular momentum. Our total basis set contained ten s , seven p , and four d Slater-type orbitals. From this basis six s , five p , and four d atomic orbitals were constructed. Following the notation used by Watson⁸ in his Be calculation, the occupied Hartree-Fock orbitals are referred to as $1s$, $2s$, and $2p$, while the

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¹ See, for example, C. Bunge, *Phys. Rev.* (to be published).

² E. Clementi, *IBM J. Res. Develop.* **9**, 2 (1965).

³ E. Clementi, *IBM J. Res. Develop. Suppl.* **9**, 2 (1965).

⁴ G. K. Tsunaitis and A. P. Iutsis, *Zh. Eksperim. i Teor. Fiz.* **28**, 452 (1955) [English transl.: *Soviet Phys.—JETP* **1**, 358 (1955)]; I. I. Glembotskii, V. V. Kibartas, and A. P. Iutsis, *Zh. Eksperim. i Teor. Fiz.* **29**, 617 (1955) [English transl.: *Soviet Phys.—JETP* **2**, 476 (1956)].

⁵ E. Clementi and A. Veillard, *J. Chem. Phys.* **44**, 3050 (1966).

⁶ S. F. Boys, *Proc. Roy. Soc. (London)* **A217**, 235 (1953).

⁷ C. Froese, *J. Chem. Phys.*, Suppl. **45**, 1417 (1966).

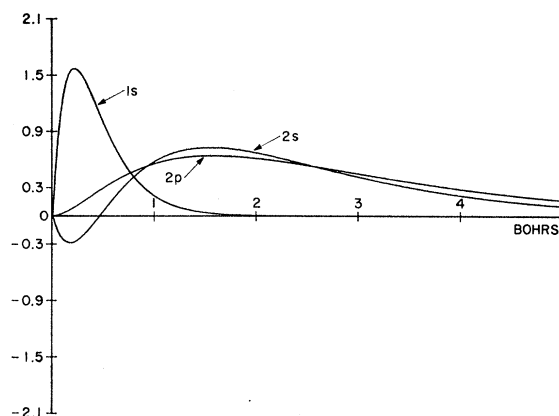
⁸ R. E. Watson, *Phys. Rev.* **119**, 170 (1960).

TABLE I. Basis set of Slater-type orbitals.

Orbital	n	l	ζ
φ_a	1	0	4.4661
φ_b	1	0	7.85
φ_c	2	0	0.832
φ_d	2	0	1.1565
φ_e	2	0	1.91197
φ_f	2	0	3.5213
φ_g	2	0	5.05
φ_h	3	0	2.03
φ_i	3	0	10.6
φ_j	4	0	2.76
φ_k	2	1	0.8783
φ_l	2	1	1.3543
φ_m	2	1	2.2296
φ_n	2	1	5.3665
φ_p	3	1	10.28
φ_q	4	1	11.8
φ_r	3	1	2.25
φ_s	3	2	1.71
φ_t	4	2	13.2
φ_u	4	2	1.31
φ_v	3	2	13.2

remaining "virtual" orbitals are designated s_{I} , s_{II} , s_{III} , s_{IV} , etc. The basis orbitals and the coefficients of the basis orbitals in the resulting atomic orbitals are listed in Tables I and II.

The screening parameter of each added basis orbital was chosen to optimize its effect in describing a particular type of correlation. For example, basis orbital φ_g , the main contributor to s_{I} , was selected to optimize a CI containing the configurations $1s^2 2s^2 2p$, $1s^2 2p^3$, and $s_{\text{I}}^2 2s^2 2p$. Atomic orbital s_{I} was thereby made particularly suited for describing $1s^2$ correlation. By adding to the above configurations $p_{\text{I}}^2 2s^2 2p$ and thereafter $1s^2 d_{\text{I}}^2 2p$, atomic orbitals p_{I} and d_{I} were then respec-

FIG. 1. Occupied Hartree-Fock orbitals for the 2P ground state of atomic boron. Plot is of $P_{nl}(r)$ as defined in the text.

tively optimized for $1s^2$ and $2s^2$ correlation. Continuing in a similar way, atomic orbitals d_{II} , p_{II} , and s_{II} were successively optimized for $1s^2$, $2s^2 + 2s^2 2p$, and $2s^2$ correlations, respectively. It became too cumbersome to continue this process further, so the remaining orbitals (s_{III} , s_{IV} , p_{III} , p_{IV} , d_{III} , and d_{IV}) were optimized in CI's containing only the configurations $1s^2 2s^2 2p$ and $1s^2 2p^3$, plus configurations characterizing the relevant correlated pair ($1s^2$ for s_{III} , p_{III} , and d_{IV} ; $2s^2$ for s_{IV} , p_{IV} , and d_{III}). It is planned to describe this process elsewhere in more detail.⁹

The atomic orbitals we have obtained by the process described in the two foregoing paragraphs have the general form

$$\varphi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \varphi), \quad (1)$$

where $R_{nl}(r)$ results from the linear combinations

TABLE II. Expansion of atomic orbitals in terms of the normalized Slater-type orbitals given in Table I. Atomic orbitals $1s$, $2s$, and $2p$ are occupied Hartree-Fock orbitals; the remaining atomic orbitals are virtual orbitals used in excited configurations.

$(1s) = 0.92109$	$15557 \varphi_a + 0.07847$	$01325 \varphi_b - 0.00036$	$00006 \varphi_c + 0.00085$	$00014 \varphi_d + 0.00002$	$00000 \varphi_e + 0.01146$	$00194 \varphi_f$
$(2s) = -0.19400$	$97071 \varphi_a - 0.01242$	$99723 \varphi_b + 0.01800$	$00119 \varphi_c + 0.71580$	$04782 \varphi_d + 0.38903$	$02597 \varphi_e - 0.11030$	$00684 \varphi_f$
$(s_{\text{I}}) = -1.97116$	$75695 \varphi_a - 0.16935$	$22976 \varphi_b - 0.00545$	$55774 \varphi_c - 0.25051$	$55350 \varphi_d - 0.13517$	$44781 \varphi_e + 0.01294$	$96046 \varphi_f$
	$+ 2.45334$	$34755 \varphi_g$				
$(s_{\text{II}}) = 0.22922$	$38820 \varphi_a - 0.00214$	$48809 \varphi_b - 0.09488$	$02107 \varphi_c - 3.78618$	$89654 \varphi_d - 2.05737$	$27695 \varphi_e + 0.57339$	$97311 \varphi_f$
	$- 0.21881$	$92910 \varphi_g + 5.51658$	$98361 \varphi_h$			
$(s_{\text{III}}) = -2.43246$	$06704 \varphi_a - 0.20935$	$21436 \varphi_b - 0.00834$	$17195 \varphi_c - 0.37342$	$96007 \varphi_d - 0.20173$	$97512 \varphi_e + 0.02566$	$72642 \varphi_f$
	$- 0.77510$	$88894 \varphi_g + 0.87663$	$14221 \varphi_h + 3.45323$	$11270 \varphi_i$		
$(s_{\text{IV}}) = -0.38297$	$21483 \varphi_a + 0.00811$	$44440 \varphi_b + 0.17833$	$63144 \varphi_c + 7.11729$	$12698 \varphi_d + 3.86743$	$35439 \varphi_e - 1.07727$	$59014 \varphi_f$
	$+ 0.38827$	$26863 \varphi_g - 27.96700$	$93488 \varphi_h + 0.32522$	$55427 \varphi_i + 18.02623$	$27118 \varphi_j$	
$(2p) = 0.54004$	$95918 \varphi_k + 0.38244$	$97109 \varphi_l + 0.13207$	$99002 \varphi_m + 0.00956$	$99928 \varphi_n$		
$(p_{\text{I}}) = -0.09263$	$75883 \varphi_k - 0.06560$	$36398 \varphi_l - 0.02265$	$63701 \varphi_m - 0.00164$	$15919 \varphi_n + 1.01460$	$55251 \varphi_p$	
$(p_{\text{II}}) = -2.63387$	$41273 \varphi_k + 3.12164$	$99115 \varphi_l - 0.64416$	$64563 \varphi_m - 0.04667$	$37809 \varphi_n - 0.04890$	$46063 \varphi_p$	
$(p_{\text{III}}) = 0.12813$	$48061 \varphi_k - 0.27459$	$17875 \varphi_l + 0.03133$	$79228 \varphi_m + 0.00227$	$06233 \varphi_n - 5.43508$	$45248 \varphi_p + 5.55154$	$02179 \varphi_q$
$(p_{\text{IV}}) = 4.35399$	$84954 \varphi_k - 12.69661$	$04231 \varphi_l + 1.06485$	$71822 \varphi_m + 0.07715$	$53849 \varphi_n + 0.29326$	$23310 \varphi_p - 0.16627$	$78297 \varphi_q$
	$+ 8.09098$	$57262 \varphi_r$				
$(d_{\text{I}}) = 1.00000$	$00000 \varphi_s$					
$(d_{\text{II}}) = -0.07088$	$92555 \varphi_s + 1.00250$	$94945 \varphi_t$				
$(d_{\text{III}}) = -1.18793$	$52764 \varphi_s + 0.07364$	$82957 \varphi_t + 1.55056$	$15836 \varphi_u$			
$(d_{\text{IV}}) = 0.14626$	$18019 \varphi_s - 2.66717$	$33250 \varphi_t - 0.10350$	$88284 \varphi_u + 2.84101$	$05144 \varphi_v$		

⁹ In the Ph.D. dissertation to be written by H. F. Schaefer (unpublished).

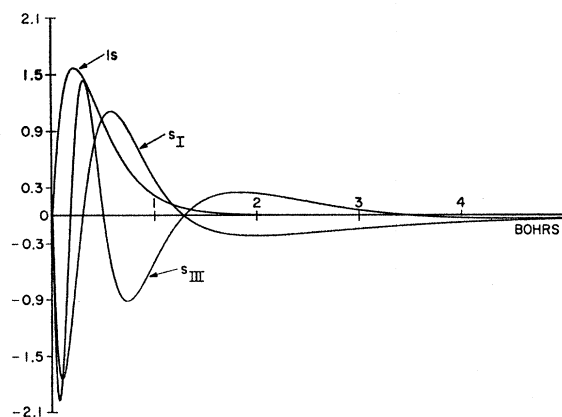


FIG. 2. Hartree-Fock $1s$ orbital and corresponding virtual s orbitals. Plot is of $P_{nl}(r)$ as defined in the text.

indicated in Table II. To aid in visualizing these atomic orbitals, we have plotted their radial parts in the form $P_{nl}(r) = rR_{nl}(r)$. Figure 1 shows the relative locations of the Hartree-Fock orbitals $1s$, $2s$, and $2p$, for orientation purposes. As expected, the $2s$ and $2p$ atomic orbitals have rather similar radial dependences. Figure 2 shows the $1s$ orbital and the two other s orbitals, s_I and s_{III} , which were optimized for describing the configurations with the $1s^2$ pair excited. We note that these two virtual orbitals also lie in the $1s$ region of space and have the nodal properties predicted by Nesbet¹⁰ to have optimum effect. Figures 3-7 show the remaining virtual orbitals, together with the Hartree-Fock orbitals which occupy the same regions of space. The curves show that there is a very definite separation between the orbitals which contribute primarily to the K -shell correlation energy and those which contribute primarily to L -shell correlation.

ANGULAR MOMENTUM

The five-electron angular momentum eigenfunctions are far more complicated than those of smaller systems.

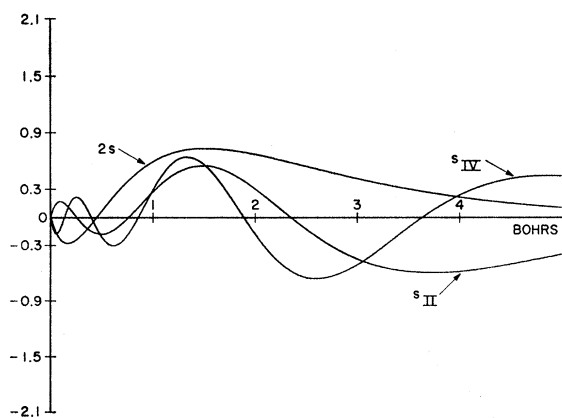


FIG. 3. Hartree-Fock $2s$ orbital and corresponding virtual s orbitals. Plot is of $P_{nl}(r)$ as defined in the text.

¹⁰ R. K. Nesbet, Proc. Roy. Soc. (London) A230, 312 (1955).

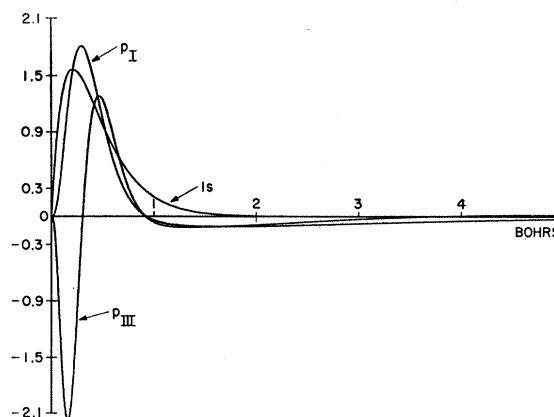


FIG. 4. Hartree-Fock $1s$ orbital and corresponding virtual p orbitals. Plot is of $P_{nl}(r)$ as defined in the text.

The complexity is due to the fact that many sets of five spin orbitals can couple to form L - S eigenfunctions in more than one way. Consider, for example, the configuration formed by the excitation of a $2s$ electron to a d_I orbital to give $1s^2 2s 2p d_I$. This configuration has an s , a p , and a d electron outside of closed shells, and these may couple to form two linearly independent 2P eigenfunctions. And the problem can get far worse. The configuration $1s 2s 2p p_I p_{II}$, which is important in our best wave function, leads to 15 linearly independent 2P states.¹¹ Clearly, if we include all linearly independent terms of the same orbital occupancy as separate configurations, the resulting CI will rapidly become so large as to make the matrix diagonalization a very difficult task and to obscure the interpretation of the wave function. In addition, the construction of the linearly independent L - S eigenfunctions is a major problem in itself.

Our approach to this problem was to develop a method for identifying a nearly optimal mixture of the full set of linearly independent eigenfunctions corre-

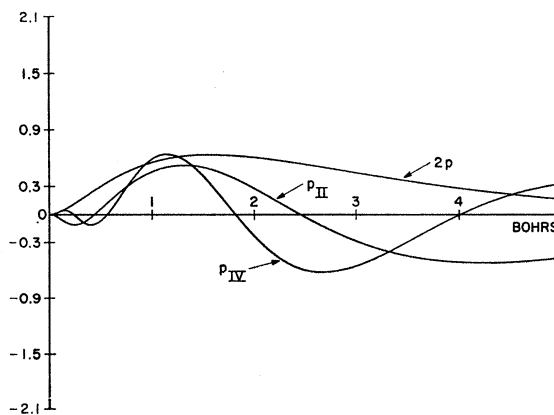


FIG. 5. Hartree-Fock $2p$ orbital and corresponding virtual p orbitals. Plot is of $P_{nl}(r)$ as defined in the text.

¹¹ Calculated with a computer program written by A. Rotenberg. The method is described in J. Chem. Phys. 39, 512 (1963).

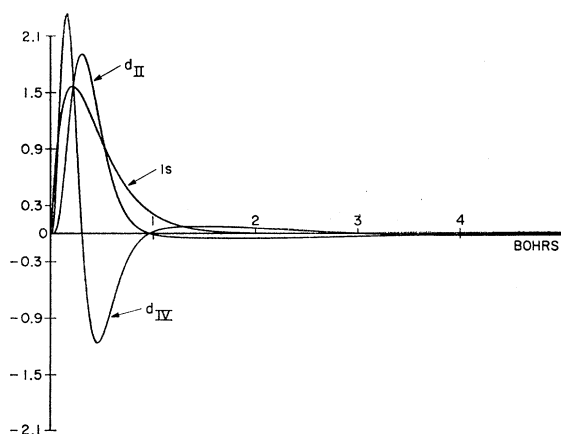


FIG. 6. Hartree-Fock 1s orbital and corresponding virtual d orbitals. Plot is of $P_{ni}(r)$ as defined in the text.

sponding to a given orbital occupancy. The optimal mixture, of course, is that which is present in the exact wave function. We approximated the optimal mixture by determining it from a CI including all eigenfunctions of the set in question, together with enough other configurations to establish the relationship of this set to the leading terms of the over-all wave function. This means that we assumed that small refinements in the final wave function would not cause serious readjustment in the relative weights of the set of eigenfunctions coming from a particular orbital occupancy. In applying this procedure, we determined the optimum L - S eigenfunction for each singly or doubly excited configuration from a CI which included the leading configuration $1s^2 2s^2 2p$, plus all other configurations of the same excitation type as the configuration under study.

Fortunately, it is possible to carry out the prescription of the preceding paragraph without first explicitly constructing the L - S eigenfunctions. Instead, we may include in the CI all the Slater determinants needed to form these eigenfunctions. The coefficients found for

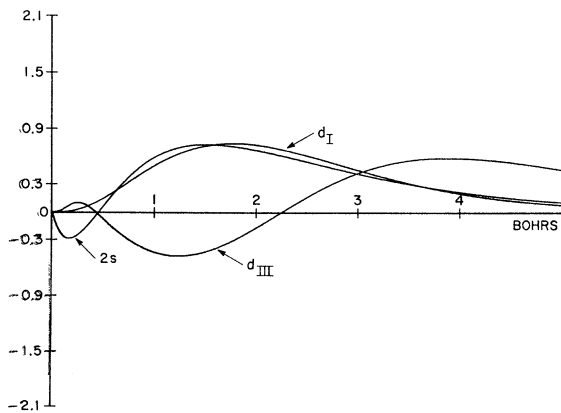


FIG. 7. Hartree-Fock 2s orbital and corresponding virtual d orbitals. Plot is of $P_{ni}(r)$ as defined in the text.

these determinants in the CI will be those of the approximately optimal L - S eigenfunction. For example, the configuration $1s^2 2s^2 2p d_I$ has 2P eigenfunctions which can be formed from nine Slater determinants. From a CI which included $1s^2 2s^2 2p$, the nine Slater determinants, and all other configurations involving excitation of one or both 2s electrons, an "optimal" $1s^2 2s^2 2p d_I$ eigenfunction was determined as

$$\begin{aligned}
 1s^2 2s^2 2p d_I = & -0.39175520 \det(1s\alpha, 1s\beta, 2s\alpha, 2p_{-\alpha}, d_{I+\beta}) \\
 & +0.62587283 \det(1s\alpha, 1s\beta, 2s\alpha, 2p_{-\beta}, d_{I+\alpha}) \\
 & -0.23411763 \det(1s\alpha, 1s\beta, 2s\beta, 2p_{-\alpha}, d_{I+\alpha}) \\
 & +0.27701257 \det(1s\alpha, 1s\beta, 2s\alpha, 2p_{0\alpha}, d_{I+\beta}) \\
 & -0.44255892 \det(1s\alpha, 1s\beta, 2s\alpha, 2p_{0\beta}, d_{I+\alpha}) \\
 & +0.16554617 \det(1s\alpha, 1s\beta, 2s\beta, 2p_{0\alpha}, d_{I+\alpha}) \\
 & -0.15993339 \det(1s\alpha, 1s\beta, 2s\alpha, 2p_{+\alpha}, d_{I0\beta}) \\
 & +0.25551151 \det(1s\alpha, 1s\beta, 2s\alpha, 2p_{+\beta}, d_{I0\alpha}) \\
 & -0.09557812 \det(1s\alpha, 1s\beta, 2s\beta, 2p_{+\alpha}, d_{I0\alpha}),
 \end{aligned} \quad (2)$$

where the subscripts to $2p$ and d_I indicate m quantum numbers.

For the remainder of this paper, the term "configuration" and the corresponding orbital occupancy symbols will be taken to mean an optimal eigenfunction, generated as described in this section. We plan to record elsewhere the coefficients of the Slater determinants in each of the 187 configurations used in this work.⁹

CHOICE OF CONFIGURATIONS

The separability of electron pair correlations has been much discussed recently,¹² and some calculations based on this approach have been carried out. In particular, Nesbet¹³ has obtained accurate solutions for atoms of what he calls generalized Bethe-Goldstone equations. Although we had serious reservations about the quantitative validity of separated-correlation methods, we felt that the concept was at least satisfactory enough to be used in deciding which configurations to use in a large CI. Since the Nesbet-Bethe-Goldstone formulation is conceptually straightforward and no more difficult to apply to open-shell systems than to closed-shell systems, it was chosen for this purpose. Our approach to the Bethe-Goldstone equations was slightly different from Nesbet's, since we used angular momentum eigenfunctions rather than determinants as the basis for our calculation. For example, to describe the single excitation $2s \rightarrow d_I$, we use an L - S eigenfunction which is a linear combination of determinants, some of which differ [see Eq. (2)] by two spin orbitals from the Hartree-Fock state $1s\alpha 1s\beta 2s\alpha 2s\beta 2p_{+\alpha}$. Nesbet would consider these determinants to be double

¹² See, for example, D. F. Tuan and O. Sinanoglu, *J. Chem. Phys.* **41**, 2677 (1964).

¹³ R. K. Nesbet, *Phys. Rev.* **155**, 51 (1967).

excitations, whereas for us they are parts of a single excitation.

We used second-order Bethe-Goldstone equations, in which the energy is approximated as

$$E = \sum_i e_i + \sum_{ij} e_{ij}, \quad (3)$$

where e_i is the correlation energy obtained by single excitations of the i th Hartree-Fock orbital and e_{ij} is the correlation energy obtained by simultaneous excitation of the i th and j th Hartree-Fock orbitals. For boron, these single and double-excitation energies are e_{1s} , e_{2s} , e_{2p} , e_{1s2} , e_{2s2} , e_{1s2s} , e_{1s2p} , and e_{2s2p} . Each correlation energy is obtained from CI calculations involving only configurations with the indicated excitations. Thus,

$$\begin{aligned} e_i &= E_i - E_0 \\ e_{ii} &= E_{ii} - e_i - E_0 \\ e_{ij} &= E_{ij} - e_i - e_j - E_0, \quad i \neq j \end{aligned} \quad (4)$$

where E_0 is the Hartree-Fock energy, E_i is the energy of a CI which includes the Hartree-Fock state and all configurations in which orbital i is excited, and E_{ij} refers to a CI which includes the Hartree-Fock state, all single excitations of orbitals i or j , and all their double excitations.

For the set of orbitals we used, there are 237 possible single- and double-excitation configurations. Of these, 164 were chosen for use in a final 187-configuration function. We selected configurations for the final CI on the basis of their contributions to the second-order Bethe-Goldstone energy, rejecting all doubly excited configurations which failed to contribute at least 0.00001 hartrees to a pair-correlation energy. All possible singly excited configurations were retained, since these can be viewed as corrections to the Hartree-Fock state and omissions here might result in an incorrect electron distribution.

An enormous number of triple and quadruple excitations were possible. The configurations included were formed by simultaneous use of the single and double excitations which had proved to be most important. Twenty-two of the most important of these configurations were used. Several triple excitations of the L -shell electrons, thought likely to be important but not of the above type, were examined but proved to be negligible.

RESULTS AND DISCUSSION

The main results of our CI studies are shown in Table III. The Bethe-Goldstone energy increments were calculated as indicated in Eq. (4). The 165-configuration "full second-order CI" includes in a single calculation all the configurations used in the Bethe-Goldstone computations, and therefore provides a measure of the extent to which the energy increments are truly

TABLE III. Configuration-interaction and Bethe-Goldstone calculations of the 2P ground state of atomic boron.

Calculation	Number of configurations	Energy, hartrees
Best CI (all types excitations)	187	-24.639194
Full second-order CI	165	-24.636707
Most important configurations of best CI	91	-24.637839
Best simple function	5	-24.608469
Analytical Hartree-Fock ^a	1	-24.529053
Bethe-Goldstone energy increments		
e_{1s}	8	-0.0001840
e_{2s}	8	-0.0218187
e_{2p}	4	-0.0000002
e_{1s}^2	38	-0.0387831
e_{2s}^2	29	-0.0392773
e_{1s2s}	31	-0.0034801
e_{1s2p}	23	-0.0012473
e_{2s2p}	23	-0.0050644
Sum of energy increments	...	-0.1098551
Experiment (nonrelativistic) ^b	...	-24.654

^a Reference 3.

^b Reference 2.

additive. We see that the full second-order CI yields a correlation energy of 0.107654 hartrees, which is 86.3% of the experimentally observed value. To this result, we may compare the sum of the Bethe-Goldstone energies, 0.109855 hartrees, or 88.1% of the experimental correlation energy. We thus see that the pair correlations in this system are additive to within approximately 2% of the total correlation energy, confirming nearly quantitatively the approach of Nesbet.

Proceeding beyond second order, we note that when the 22 triple and quadruple excitations were added to the 165-configuration function, the energy was lowered to -24.639194 hartrees, yielding 88.3% of the correlation energy. This was our best wave function for boron. We believe that this final function nearly exhausts the basis set we have used. We estimate that it may be possible to obtain a maximum of an additional 0.001 hartrees from triple and higher excitations. This is the one area in which a small improvement might have been made by adding further configurations. Rather than the 2% which we found, we predict that the true contribution of triple, quadruple, and quintuple excitations is 3% of the experimental correlation energy.

Using the method we have described, it appears that total configuration-interaction calculations can be made on the rest of the first-row atoms and that these calculations will yield 85-90% of the correlation energy. Nesbet^{13,14} has reported Bethe-Goldstone calculations on Be and Ne which obtain over 97% of the correlation energy. From our work, it appears that about 2% of this is due to overestimation which occurs when energy increments are added together. The remainder of the difference between Nesbet's work and our second-order

¹⁴ R. K. Nesbet, Phys. Rev. **155**, 56 (1967).

TABLE IV. A 91-configuration wave function for the 2P ground state of atomic boron, with the energy contribution of each configuration.

Configuration No. n	Configuration	Energy contribution $E(n) - E(n-1)$, hartrees	Coefficient in 91-configuration eigenvector	Energy $E(n)$ of n -configuration function, hartrees
1	$1s^2 2s^2 2p$...	0.96334095	-24.52905264
2	$1s^2 2p^3$	-0.03038760	-0.20464261	-24.55944024
3	$1s^2 2s d_I 2p$	-0.01899592	0.13023436	-24.57843615
4	$1s^2 2p^2 p_{II}$	-0.00393242	0.06558376	-24.58236857
5	$1s^2 2s s_{II} p_{II}$	-0.00124417	0.04181398	-24.58361275
6	$1s^2 2p d_I^2$	-0.00291758	0.03501298	-24.58653032
7	$1s^2 2s d_{III} 2p$	-0.00089961	0.03147605	-24.58742993
8	$1s^2 2s p_{II} d_I$	-0.00150179	0.02914062	-24.58893171
9	$1s^2 2s s_{II} 2p$	-0.00040438	0.02838392	-24.58933610
10	$p_I^2 2s^2 2p$	-0.01895619	0.02112794	-24.60829229
11	$1s^2 s_{II}^2 2p$	-0.00036332	-0.02102822	-24.60865561
12	$1s^2 p_{II}^2 2p$	-0.00059559	0.01966275	-24.60925120
13	$s_I^2 2s^2 2p$	-0.01088668	-0.01751313	-24.62013787
14	$1s^2 2s s_I p_{II}$	-0.00068963	0.01584036	-24.62082750
15	$1s^2 s_I s_{II} 2p$	-0.00030354	0.01156785	-24.62113104
16	$1s^2 2s s_{II} p_{IV}$	-0.00008930	0.01039813	-24.62122034
17	$1s^2 2s s_{IV} p_{II}$	-0.00000138	0.00987524	-24.62122172
18	$1s^2 s_{II} s_{IV} 2p$	-0.00000666	0.00853489	-24.62122838
19	$1s^2 p_{II} p_{IV} 2p$	-0.00013703	0.00766610	-24.62136542
20	$1s^2 2s s_I 2p$	-0.00015141	0.00700073	-24.62151683
21	$1s^2 2s s_{II} p_I$	-0.00038187	0.00681641	-24.62189870
22	$1s^2 2s s_{IV} p_{IV}$	-0.00005863	0.00656446	-24.62195733
23	$1s^2 s_I^2 2p$	-0.00018720	-0.00628013	-24.62214453
24	$1s^2 2s s_I p_{IV}$	-0.00008333	0.00620866	-24.62222786
25	$1s^2 2s s_I^2 2p$	-0.00113725	0.00591257	-24.62336511
26	$1s^2 2s p_{IV} d_{III}$	-0.00012426	0.00586677	-24.62348937
27	$1s^2 2s s_{III} p_{II}$	-0.00051753	0.00582674	-24.62400690
28	$2s^2 2p^2 p_I$	-0.00086882	0.00549949	-24.62487572
29	$1s^2 p_{II} d_I^2$	-0.00007390	0.00546162	-24.62494962
30	$1s^2 s_I s_{IV} 2p$	-0.00000724	0.00532383	-24.62495686
31	$1s^2 2s 2p^2 p_I$	-0.00042668	0.00529647	-24.62538354
32	$1s^2 2p^2 p_I$	-0.00034684	0.00525507	-24.62573038
33	$d_{II}^2 2s^2 2p$	-0.00234082	0.00499777	-24.62807120
34	$1s^2 p_{IV}^2 2p$	-0.00008671	0.00489237	-24.62815792
35	$1s^2 s_{II} d_I 2p$	-0.00003800	0.00461525	-24.62819592
36	$p_I^2 2p^3$	-0.00083850	0.00452551	-24.62903442
37	$1s^2 s_{II} s_{III} 2p$	-0.00032556	0.00446902	-24.62935998
38	$1s^2 s_{IV}^2 2p$	-0.00000511	-0.00439936	-24.62936509
39	$1s^2 d_{III}^2 2p$	-0.00005010	0.00413495	-24.62941519
40	$1s^2 2s s_I p_I$	-0.00025793	0.00413289	-24.62967312
41	$1s^2 2s p_I^2 2p$	-0.00067400	0.00381442	-24.63034713
42	$1s^2 2s 2p^3$	-0.00010157	0.00373768	-24.63044870
43	$1s^2 2s p_I p_{II} 2p$	-0.00029017	0.00364480	-24.63073887
44	$s_I^2 2p^3$	-0.00050558	0.00358968	-24.63124445
45	$1s^2 2s^2 s_I p_I$	-0.00029890	0.00355242	-24.63154336
46	$1s^2 2s p_{II} d_{III}$	-0.00002833	0.00345355	-24.63157169
47	$1s^2 s_I s_{III} 2p$	-0.00020143	0.00342084	-24.63177312
48	$p_{III}^2 2s^2 2p$	-0.00163580	0.00339221	-24.63340892
49	$1s^2 2s 2p^2 p_{II}$	-0.00009892	0.00338595	-24.63350784
50	$1s d_I 2s^2 2p$	-0.00008715	0.00328750	-24.63359499
51	$1s^2 s_{II} d_{III} 2p$	-0.00002451	0.00322902	-24.63361951
52	$1s^2 2s^2 p_I d_I$	-0.00020417	0.00312626	-24.63382367
53	$1s^2 s_{II}^2 p_{II}$	-0.00002348	-0.00296303	-24.63384716
54	$1s^2 2s s_{III} p_{IV}$	-0.00018068	0.00295444	-24.63402783
55	$p_I^2 2s d_I 2p$	-0.00033516	0.00289503	-24.63436299
56	$1s^2 2s p_I p_{IV} 2p$	-0.00015606	0.00287090	-24.63451905
57	$s_{III}^2 2s^2 2p$	-0.00069405	-0.00277175	-24.63521310
58	$1s^2 2s d_{II} 2p$	-0.00023677	0.00264394	-24.63544987
59	$1s^2 s_{III} s_{IV} 2p$	-0.00006815	0.00260533	-24.63551802
60	$1s^2 2s 2p^2 p_{IV}$	-0.00004343	0.00249160	-24.63556145
61	$1s^2 s_{II} p_{II} d_I$	-0.00001686	0.00242657	-24.63557831
62	$s_I^2 2s d_I 2p$	-0.00020470	0.00227599	-24.63578301
63	$1s^2 p_I p_{II} 2p$	-0.00006133	0.00208914	-24.63584434
64	$1s^2 2p^2 p_{IV}$	-0.00000592	0.00199995	-24.63585025
65	$1s^2 2s^2 p_I d_{III}$	-0.00006075	0.00187663	-24.63591100
66	$1s^2 2s s_{IV} p_I$	-0.00002244	0.00185962	-24.63593344
67	$1s^2 2s^2 p_I d_{II}$	-0.00020933	0.00184817	-24.63614277
68	$1s^2 2s^2 p_{II} d_I$	-0.00002823	0.00175515	-24.63617100
69	$1s^2 2s p_I d_I$	-0.00004088	0.00170929	-24.63621188
70	$1s^2 p_{II}^2$	-0.00000631	0.00167190	-24.63621819
71	$1s^2 2s^2 p_{II}$	-0.00000277	0.00161275	-24.63622096

TABLE IV. (continued).

Configuration No. n	Configuration	Energy contribution $E(n) - E(n-1)$, hartrees	Coefficient in 91-configuration eigenvector	Energy $E(n)$ of n -configuration function, hartrees
72	$1s^2 2s s_{III} p_I$	-0.00013211	0.00159206	-24.63635307
73	$1s 2s p_{II}^2 2p$	-0.00002222	-0.00153646	-24.63637529
74	$1s 2s d_I^2 2p$	-0.00002278	0.00147430	-24.63639807
75	$1s^2 2s s_{III} 2p$	-0.00005505	0.00147172	-24.63645313
76	$p_I^2 2p^2 p_{II}$	-0.00008845	0.00146973	-24.63654158
77	$s_I s_{III} 2s^2 2p$	-0.00012006	0.00145468	-24.63666163
78	$1s 2s p_I p_{III} 2p$	-0.00017377	0.00145369	-24.63683540
79	$1s d_{III} 2s^2 2p$	-0.00001759	0.00143681	-24.63685300
80	$1s 2s 2p^2 p_{III}$	-0.00010861	0.00130629	-24.63696160
81	$1s 2s^2 p_{IV} d_I$	-0.00001424	0.00120907	-24.63697584
82	$1s 2s d_I d_{III} 2p$	-0.00001410	0.00120128	-24.63698994
83	$1s^2 2s s_{II} p_{III}$	-0.00007267	0.00119699	-24.63706261
84	$1s^2 s_{III}^2 2p$	-0.00011114	-0.00118942	-24.63717375
85	$1s 2s^3 s_{III} p_I$	-0.00008440	0.00116313	-24.63725815
86	$s_I^2 2p^2 p_{II}$	-0.00005299	0.00116104	-24.63731114
87	$d_{IV}^2 2s^2 2p$	-0.00039084	0.00110177	-24.63770198
88	$d_{II}^2 2p^3$	-0.00010648	-0.00107305	-24.63780846
89	$1s 2s p_{II} p_{IV} 2p$	-0.00001116	0.00107166	-24.63781962
90	$1s^2 p_I p_{IV} 2p$	-0.00001764	0.00106568	-24.63783725
91	$1s^2 2s^2 p_{IV}$	-0.00000140	0.00100968	-24.63783865

result arises from the fact that each Bethe-Goldstone pair can be treated much more elaborately if it is not subsequently necessary to include all pairs in a final large calculation. Nesbet therefore uses larger (and different) basis sets for each pair calculation.

Let us next consider the simpler wave functions which can be used to approximate that of the full CI. Starting from the full CI, we eliminated all configurations with coefficients less than 0.001 in absolute value, leaving the 91-configuration function described in Table IV. Most of the remaining configurations in the full 187-configuration wave function have coefficients of magnitude between 0.0005 and 0.001. The 91-configuration function still contains 87.2% of the correlation energy and is therefore very little worse than that of the full CI. After arranging the configurations in order of the magnitude of their coefficients, we successively removed configurations one by one, starting from that of least weight, until the Hartree-Fock function was reached. In this way we obtained an estimate of the energy contribution of each configuration. These data are also presented in Table IV.

A far simpler but rather good wave function can be obtained by using the five configurations of Table IV which make the largest energy contributions (all greater than 0.01 hartrees). After these five configurations, the correlation energy contributions fall off rapidly. This five-configuration function gives 64% of the correlation energy and may be suitable for many calculations where extreme accuracy is not needed.

The function is

$$\Psi = 0.96934910 1s^2 2s^2 2p - 0.21351798 1s^2 2p^3 + 0.11843417 1s^2 2s d_I 2p + 0.02147963 p_I^2 2s^2 2p - 0.01686341 s_I^2 2s^2 2p. \quad (5)$$

The linear combination of Slater determinants used for the configuration $1s^2 2s d_I 2p$ is that given in Eq. (2); the optimum L - S eigenfunction for the configuration $p_I^2 2s^2 2p$ was found (to a good approximation) to be that commonly denoted $p_I^2(^1S)2s^2 2p$, i.e., the eigenfunction in which the two p_I electrons are coupled to form a 1S two-electron function.

All computations were carried out on the Stanford IBM System 360 Model 67 computer. All arithmetic operations were performed in double precision, and the program plus working storage required a total of approximately 25 000 double-precision words. Typical over-all computation times were, for the 187-configuration CI, 9 min; for the 91-configuration CI, 4 min; and for the five-configuration wave function, 50 sec. We plan to provide more details with respect to the computational methods and the 165-configuration and 187-configuration wave functions.⁹

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