

Nature of the Configuration-Interaction Method in *Ab Initio* Calculations.

I. Ne Ground State

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(Received 14 August 1969)

A detailed study of the correlation energy of Ne has been made in order to analyze the nature of the configuration-interaction (CI) method in *ab initio* calculations. Both the Bethe-Goldstone method of Nesbet and the total-pair-excitation-block method (TPEB) were examined. A series of calculations was made using both "atom-centered" and "shell-centered" basis sets. The most detailed calculations gave -0.333 a.u. (88%) for the correlation energy by the TPEB method, and -0.396 a.u. (104%) by the sum-of-the-pairs technique. The difference between these two values is mainly the so-called pair-pair interactions, which have been considered too small to be important to other investigators. A series of perturbation calculations on the triple and quadruple excitations gives $\sim 1.5\%$ of the total correlation energy. A complete CI calculation with a very limited basis set was done on the p block of Ne. The results of this calculation are in agreement with our total-atom calculation, except that now the TPEB calculation gave about 98.5%, and the sum of the pairs about 115% of the complete CI result. The effect on the pair correlation energy of a unitary transformation of the outer-shell occupied self-consistent-field orbitals was also studied. Only a small difference in the results was obtained.

I. INTRODUCTION

The methods employed in *ab initio* calculations have been, for the most part, either the traditional variation¹ or perturbation² procedures using a configuration-interaction (CI) representation of the state function of the system. Recently, however, some dissatisfaction with these methods has arisen because they represent what one might term "gross" quantum mechanics, and in many ways they fail to incorporate the physical aspects of the problem. In particular, it was hoped that the "grossness" could be removed from the above procedures, and in its place a method employed which partitions the calculation in such a manner that the most important contributions appear first in the simplest possible way. Perturbation theory provides the facade of this progression, but the standard techniques fail to converge with the necessary speed.³ More rapid convergence can apparently be achieved by modifying the perturbation partitioning.⁴ A similar enhancement of convergence has been sought for the variation method. In recent years variational procedures developed largely by Sinanoğlu⁵ and Nesbet⁶ have emerged which partition the CI-variation procedure in a manner similar to that employed in perturbation theory. As a result of this partitioning the procedures of Sinanoğlu and Nesbet place great emphasis on the so-called pair correlation energies. This emphasis has culminated in the recent results of Nesbet in which the pair correlation energies are calculated for all of the second-row atoms.⁷ These re-

sults appear to be so good that Nesbet calls them the total correlation energy, e.g., to quote Nesbet, "the total correlation energies range from 98.5–100.3% of the empirical correlation energy."⁷ The implication being that the omitted parts of a total calculation (i.e., pair-pair interactions, triple excitations, quadruple excitations, etc.), which Nesbet notes in previous results,⁶ are either very small, or almost totally self-canceling, or both. If the conclusions of Nesbet are valid, then the large-scale variation methods such as those of Bender and Davidson,⁸ and Schaefer and Harris⁹ may be unnecessarily complex. A detailed examination of the Nesbet method is, therefore, a necessity.

That Nesbet's conclusions need to be thoroughly examined goes without saying, but another more important implication of his work must be even more closely scrutinized. If one accepts the fact that Nesbet's Ne calculation is even more converged than the Be one (100.3% for Ne to 99% for Be), then one can visualize a time in the near future when any atom or molecule no matter how complex could have its correlation energy calculated with great accuracy by the relatively simple procedure of summing the pair correlation energies. Obviously this raises many questions which have quite fundamental significance to the method of CI calculations in general. In this research the authors have been exploring three of these pertinent questions. First, is the summation of pair correlations a valid (very accurate) procedure for determining the total correlation energy of atoms

or molecules? Second, are the other types of correlations (pair-pair, other three-body, etc.) small or self-canceling or perhaps neither? Third, even if the sum of the pairs method is insufficient for complex systems, is there a cutoff point at a comparatively low order of excitation, or do the more complex effects become important as the size of the system increases?

The present paper reports the results of a series of calculations on the ground state of Ne. These results appear to provide answers to the first two questions presented above. They also provide enough information to speculate about the third. In another paper to follow this one,¹⁰ more general mathematical reasoning will be employed to answer these questions. Specifically in this paper, in Sec. II, the simple theoretical arguments behind the calculations are presented. Particular attention is paid to the pair correlation method of Nesbet and a more traditional procedure designed to truncate the variation calculation at the end of the pair excitation block. In Sec. III we briefly outline the computational techniques used in this work. Section IV contains the results and discussion of the calculations of the Ne ground state. Included are a variety of pair summations and also diagonalizations of the total pair block. Some of these calculations are also done with basis sets rotated from delocalized to localized. Total excitation calculations within a particular limited basis for a part of the Ne atom are also included. A series of perturbation calculations of the triple and quadruple excitations is presented in order to try to determine the importance of higher excitations. Section V includes further discussion and a summary of the conclusions reached as a result of this work.

II. THEORY

In this section, the basic theoretical arguments are presented. The more fundamental theory will be presented in another article.¹⁰

We will begin by assuming that our concern is for atomic systems¹¹ so that our Hamiltonian can be expressed as

$$H = - \sum_{\mu=1}^N \left(\frac{1}{2} \nabla_{\mu}^2 + Z/r_{\mu} \right) + \sum_{\mu < \nu} \frac{1}{r_{\mu\nu}} \quad (1)$$

The state function for the atom in question is always represented in terms of the configuration-interaction method, i. e.,

$$\Psi = \sum_{I=0}^{\infty} C_I \phi_I \quad (2)$$

where each of the configurations in the orthonormal set $\{\phi_I\}$ is a partially symmetrized linear com-

bination of Slater determinants, i. e., ϕ_I is an eigenfunction of S^2 , S_Z , and L_Z but not of L^2 .¹²

In order to better appreciate the emphasis which will be placed upon the various separate block excitations, Eq. (2) is expressed below in an equivalent, but more tractable form:

$$\begin{aligned} \Psi = & \phi_0 + \sum_{i,a} C_i^a \phi_i^a + \sum_{\substack{i,j \\ a,b}} C_{ij}^{ab} \phi_{ij}^{ab} \\ & + \sum_{\substack{i,j,k \\ a,b,c}} C_{ijk}^{abc} \phi_{ijk}^{abc} + \dots, \end{aligned} \quad (3)$$

where in (3), $\phi_{ijk}^{abc} \dots$ represents the many electron configuration in which the electrons from space orbitals $i, j, k \dots$ of ϕ_0 have been excited to the orbitals $a, b, c \dots$. Note that in our procedure the excitations are from space orbitals rather than from spin orbitals. It is also possible to represent each group of excitations with separate designations, e. g.,

$$\begin{aligned} \Psi_{ij} = & \phi_0 + \sum_a C_i^a \phi_i^a \\ & + \sum_b C_i^b \phi_j^b + \sum_{a,b} C_{ij}^{ab} \phi_{ij}^{ab}, \end{aligned} \quad (4)$$

where the so-called occupied orbitals i and j are being replaced by the virtual "excited" sets a and b .

Returning to Eqs. (1) and (2), the standard secular equation may be set up, i. e.,

$$\sum_J (H_{IJ} - S_{IJ} E) C_J = 0 \quad (5)$$

where $H_{IJ} = \langle \phi_I | H | \phi_J \rangle$,

and $S_{IJ} = \langle \phi_I | \phi_J \rangle = \delta_{IJ}$.

For convenience we designate the term in brackets as

$$M_{IJ} = H_{IJ} - S_{IJ} E \quad (6)$$

One can modify the indexing in Eq. (6) so that it represents the particular type of block correlation energy rather than expressing each individual term separately. Thus the secular determinant becomes

$$\begin{vmatrix} \underline{M}_{00} & \underline{M}_{01} & \underline{M}_{02} \cdots \\ \underline{M}_{10} & \underline{M}_{11} & \underline{M}_{12} \cdots \\ \underline{M}_{20} & \underline{M}_{21} & \underline{M}_{22} \cdots \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix} = 0, \quad (7)$$

where in (7) 1 and 2 represent all of the single and double excitations collectively.

We may, of course, simplify the above expression by noting that our Hamiltonian contains nothing more complex than pair interactions. Thus (7) becomes

$$\begin{vmatrix} \underline{M}_{00} & \underline{M}_{01} & \underline{M}_{02} & \underline{0} & \underline{0} \cdots \\ \underline{M}_{10} & \underline{M}_{11} & \underline{M}_{12} & \underline{M}_{13} & \underline{0} \cdots \\ \underline{M}_{20} & \underline{M}_{21} & \underline{M}_{22} & \underline{M}_{23} & \underline{M}_{24} \cdots \\ \underline{0} & \underline{M}_{31} & \underline{M}_{32} & \underline{M}_{33} & \underline{M}_{34} \cdots \\ \cdot & \underline{0} & \underline{M}_{42} & \underline{M}_{43} & \underline{M}_{44} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0. \quad (8)$$

The standard practice of what we might term the

total variation procedure is to directly solve Eq. (8). In actual practice the equation must, of course, be truncated at some reasonable point, usually that indicated by the dashed lines. This subblock we shall designate the total pair excitation block (TPEB).^{13, 14} In addition to the partitioning, there is also the necessity to truncate the expansion basis. As a result the reasonableness of the TPEB approximation depends upon whether it is too crude, and also whether the CI basis used to calculate the upper bound to the total TPEB result is a nearly complete one. This latter fact is very important and will be one of the features emphasized in this study. The difficulty is, of course, that the total TPEB result is unknown. One of the fundamental questions of any TPEB calculation is, therefore, to determine whether the difference between the approximate result and the exact ground-state energy is due mainly to the truncation of the variational blocks (8), or mainly to the truncation of the TPEB basis.

These difficulties and other aspects led to the development of the methods of Sinanoğlu⁵ and Nesbet.⁶ The Nesbet Bethe-Goldstone procedure⁶ tries to circumvent these problems by noting that Eq. (8) may be further subdivided by separating each particular excitation within a total excitation block. In this manner Nesbet is able, at least in principle, to transform what appears to be an extremely untenable calculation into a rather tractable one. An example of how this is done through the pair block is shown below with Be, selected for convenience, as the example. Note that our indexing has been modified again so that it refers to the orbitals omitted from ϕ_0 ,

$$\begin{vmatrix} \underline{M}_{0,0} & \underline{M}_{0,1} & \underline{M}_{0,2} & \underline{M}_{0,12} & \underline{M}_{0,22} & \underline{M}_{0,11} \\ \underline{M}_{1,0} & \underline{M}_{1,1} & \underline{M}_{1,2} & \underline{M}_{1,12} & \underline{M}_{1,22} & \underline{M}_{1,11} \\ \underline{M}_{2,0} & \underline{M}_{2,1} & \underline{M}_{2,2} & \underline{M}_{2,12} & \underline{M}_{2,22} & \underline{M}_{2,11} \\ \underline{M}_{12,0} & \underline{M}_{12,1} & \underline{M}_{12,2} & \underline{M}_{12,12} & \underline{M}_{12,22} & \underline{M}_{12,11} \\ \underline{M}_{22,0} & \underline{M}_{22,1} & \underline{M}_{22,2} & \underline{M}_{22,12} & \underline{M}_{22,22} & \underline{M}_{22,11} \\ \underline{M}_{11,0} & \underline{M}_{11,1} & \underline{M}_{11,2} & \underline{M}_{11,12} & \underline{M}_{11,22} & \underline{M}_{11,11} \end{vmatrix} = 0 \quad (9)$$

where

$$\begin{aligned} 0 &= 1s^2 2s^2, \\ 1 &= \{1s - \phi_i\} i \geq 3, \\ 2 &= \{2s - \phi_i\} i \geq 3, \\ 11 &= \{1s^2 - \phi_i \phi_j\} i, j \geq 3, \\ 22 &= \{2s^2 - \phi_i \phi_j\} i, j \geq 3, \end{aligned}$$

$$12 = \{1s 2s - \phi_i \phi_j\} i, j \geq 3.$$

To calculate the specific contribution of say the 12 pair by the Nesbet method one need only solve the variation calculation outlined in the dashed lines. This gives what Nesbet calls the gross 12 increment ($\Delta \epsilon_{12}$). From this we subtract the results of the calculations of the contributions of lower blocks which presumably have already been

computed. The result of this calculation is the specific or "net" 12 increment (ϵ_{12}), i. e. ,

$$\epsilon_{12} = \Delta\epsilon_{12} - \epsilon_1 - \epsilon_2 - \epsilon_0 . \quad (10)$$

In general one obtains, for the individual pairs,

$$\epsilon_{ij} = \Delta\epsilon_{ij} - \epsilon_i - \epsilon_j - \epsilon_0 \quad (11)$$

and, for the sum of the pairs,

$$\epsilon = \sum_{i < j} \epsilon_{ij} . \quad (12)$$

This method may (by following Nesbet's lead⁶) be continued to include higher and higher blocks, until one has computed, through the Nth order, all net increments for an N-electron system. The result of this total Bethe-Goldstone calculation would be the same as that obtained by solving the total variation, Eq. (7), within the same orbital basis set. *It is important to note that the accuracy of this calculation is also dependent upon the completeness of the basis sets employed.* This last statement, which is well known to the users of perturbation methods, will play an important role in the results to follow. In the paper to follow this one, we will be particularly concerned with the nature of the term "completeness" and its complexity.¹⁰

As pointed out in the Introduction, Nesbet has used the sum of all of the net pair increments [Eq. (12)] to represent an accurate approximation to the exact ground-state correlation energy. Advocates of the TPEB method find it difficult to appreciate how the Nesbet method, by ignoring pair-pair interactions (such terms as $\overline{M}_{12,11}$, etc.), is able to get better results than the TPEB method (with the same basis set) which includes these interactions. Obviously either (1) these interactions are small and the TPEB method is, for some reason, more poorly converged to its limit than the Nesbet method, or (2) the pair-pair interactions are almost totally canceled by terms from higher excitations, or (3) the Bethe-Goldstone results of Nesbet are not converged and in effect mask the size of these pair-pair interactions. Some of the answers to these questions will be presented in Sec. IV.

III. METHODOLOGY

This section is designed to outline the specific procedures employed in our calculations so that no misunderstandings should arise as to possible differences between our results and those of others.

A. General

First, all calculations were done on the IBM 7094/7040 direct coupled system of the University

of Washington Computation Center. The programs employed were all developed in this research group.

The single-particle basis functions used in these calculations were normalized Slater-type orbitals. The size of the sets and their screening constants ξ were used as variables. The limitations employed included; $l \leq 4$, no more than 20 functions with the same m value, no more than 9 functions with the same ξ and m values.

After the one- and two-electron integrals were computed, the basis set was used to generate the self-consistent-field (SCF) result. This was accomplished in the usual manner (Roothaan) with close scrutiny being paid to problems of overcompleteness and linear dependency. In this manner the best basis sets were developed. Due to the nature of the Nesbet method, the SCF result was often poorer than could be obtained by other methods using similar numbers of orbitals. If one is not expecting great accuracy, this fact is not necessarily a critical feature of the CI results.¹⁵ A more detailed analysis of this problem will be presented in subsequent sections. The methods employed in these stages to optimize the ξ values were largely *ad hoc* procedures designed to completely span the expansion space of the basis. Due to the comparatively simple nature of the atomic system, more elaborate optimization procedures, such as Ransil's,¹⁶ were deemed unnecessary.

Functions which were to be employed in the correlation calculations, but which due to symmetry ($l \geq 2$) did not affect the SCF result, were included in many of the sets.

The CI calculations were performed by an eigenvalue algorithm based on an extension of the method of Nesbet¹⁷ and Shavitt.¹⁸ Initially these calculations were made using the SCF basis of occupied and virtual orbitals. The density matrix was then formed and the natural orbitals generated. The frozen form of these natural orbitals¹⁹ was then employed to repeat these CI calculations. The results of these calculations were compared and their relative merits analyzed. As will be seen in Sec. IV, the differences between the SCF orbitals and natural orbitals were not as pronounced as those obtained by Bender and Davidson on the first-row diatomics.¹

The CI calculations were, in general, performed by the TPEB and Nesbet pair scheme. Calculations were also made omitting the single excitations so that their contribution could be determined. Because Nesbet's results were obtained from configurations constructed entirely from single Slater determinants,⁷ rather than eigenfunction of S^2 , our results differed somewhat from his. These differences are easily determined (see Sec. IV) by employing the same basis as Nesbet and noting the magnitude in those cases where the results differ. These differences can then be added to any of our

calculations performed with larger basis sets because the larger sets would produce differences of about the same size.

B. Limitations of the Number of Configurations

Under certain circumstances it was necessary to limit the number of configurations employed in the CI calculations. When very large basis sets were used (~60 functions), the number of possible double excitations generated was untenably large. In order to circumvent this difficulty the contribution of these configurations was first calculated by second-order perturbation theory. (This method will be discussed in Sec. IIIC.) The terms were then ordered and the 1000 largest-orbital product contributors were employed to form configurations in the TPEB calculations. A perturbation calculation was done to test the effect of this truncation and this is reported in Sec. IV.

A different CI-variation procedure, which is not restricted to single and double excitations, was employed for some of these calculations. This method is, however, restricted to 50 spin configurations. It was used to calculate the total result of all excitations generated within a limited basis on selected subblocks of the Ne atom. It was also used as the variation initiator in a perturbation calculations of the triple and quadruple excitations.

C. Perturbation Method

The perturbation calculations were all done by a scheme developed in this group and described in detail elsewhere.²⁰ The technique is similar to the conventional Rayleigh-Schrödinger method, but differs because there is no initial partitioning of the Hamiltonian operator. Instead the perturbative matrix is partitioned so that all diagonal terms appear in the denominator. It is also arranged so that the scheme may be used to culminate a variation calculation. The basic equation is

$$\epsilon^{(2)} = \sum_{i \neq 0} \frac{\langle \phi_0 | H | \phi_i \rangle \langle \phi_i | H | \phi_0 \rangle}{\langle \phi_0 | H | \phi_0 \rangle - \langle \phi_i | H | \phi_i \rangle},$$

where $|\phi_0\rangle$ is an approximation to the wave function and may consist of several configurations. Note that expectation values appear in the denominator in place of the usual eigenvalues of H_0 .

D. Rotation of the Basis Set

It is well known that the Hartree-Fock wave function is independent of a unitary transformation on the orbitals in ϕ_0 . In some methods, however, the correlation energy is not independent of this transformation. This somewhat disturbing fact was

pointed out in calculations carried out in their research group by Bender and Davidson on LiH²¹ and BH.²² In those calculations the sum of the pairs was found to be very dependent upon a unitary transformation of the SCF orbitals. A similar procedure was developed for our calculations. This was used to test whether rotating the basis in ϕ_0 from the ordinary complex atomic orbitals to a localized tetrahedral basis would affect the pair results. Unfortunately the nature of this rotation was such that it destroyed the symmetry properties of the basis orbitals, and our programs were restricted to handling only 20 basis functions. This placed a severe restriction on the extent of our results.

IV. RESULTS AND DISCUSSION

We begin with an analysis of the results obtained by Nesbet using the summation of pairs technique (Bethe-Goldstone).⁷ This is done in order to establish a basis with which to compare our results. Nesbet's calculation is the only detailed study of Ne previously reported. The results of Sinanoğlu²³ and Kestner,²⁴ which will be discussed later, are concerned with specific fragmentary aspects of the total calculations. Nesbet's results are presented in Table I. They are listed in terms of collected spin-symmetrized pair groups, rather than the manner of their actual calculation. This listing is employed in order to make the comparison with our results more convenient. Also included in Table I are our results for a calculation of the L shell of Ne. These were obtained using a basis identical to Nesbet's L -shell basis. The basis employed in Nesbet's calculations consists of the basic double-zeta set of Clementi (CDZ) $\xi_{1s} = 8.9141, 12.3545; \xi_{2s} = 2.1839, 3.4921; \xi_{2p} = 2.0514, 4.6748$,²⁵ plus three separate additional sets of functions designed for calculations on different shells.

Several very important peculiarities of these pair calculations should be noted before they are accepted on an equal basis with those of more traditional methods. First, there are essentially four different ϕ_0 's in these calculations. There is the Hartree-Fock ϕ_0 which is used to obtain the SCF result ($\langle \phi_0 | H | \phi_0 \rangle$). Then there is also a unique ϕ_0 for each of the three different shells. How this should affect the interpretation of the results is not totally understood. The four different ϕ_0 's are also accompanied by the four different basis sets which are used to implement the pair calculations. Further, the SCF orbitals from one set are not quite orthogonal to those from another set so the $1s^2$ and $2s^2$ pairs, as calculated, are not quite mutually exclusive. Also a lack of completeness in the s - and p -type basis functions is reflected in the poor SCF energy obtained with the L -shell set. One should not, however, be too quick to criticize the

TABLE I. Nesbet Ne results and our L -shell results obtained with the same basis.^a

Type of pair	Nesbet's results	Our results	Symmetry difference
$2s^2$	-0.01083	-0.01084	...
$2s2p_0$	-0.02724	-0.02611	-0.00113
$2s2p_+$	-0.02715	-0.02604	-0.00111
$2s2p_-$	-0.02715	-0.02604	-0.00111
$2p_0^2$	-0.02581	-0.02583	...
$2p_02p_+$	-0.04928	-0.04615	-0.00313
$2p_02p_-$	-0.04928	-0.04615	-0.00313
$2p_+^2$	-0.01650	-0.01651	...
$2p_+2p_-$	-0.06753	-0.06356	-0.00397
$2p_-^2$	-0.01650	-0.01651	...
Sum (L shell)	-0.31727	-0.30374	-0.01358
$1s^2$ (K shell)	-0.03993		
$1s2s$	-0.005136		
$1s2p_0$	-0.006630		
$1s2p_+$	-0.006630		
$1s2p_-$	-0.006630		
Sum (K - L shell)	-0.025026		
Total sum of pairs	-0.38223		
SCF energy	(Varies with basis)	-128.53662 (Clementi H. F. energy = -128.5470)	
Basis = Clementi double zeta ^b plus			
	K shell	K - L shell	L shell
	$\zeta = 21.63:$	$\zeta = 4.214:$	$\zeta = 21.63:$ $\zeta = 4.214:$
	$2s, 2p$	$3s, 3p, 3d$	$2s, 2p$ $3s, 3p, 3d$
	$4s, 4p, 4d, 4f$	$4s, 4p, 4d$	$3s, 3p, 3d$ $4s, 4p, 4d$
	$5s, 5p, 5d, 5f$	$4f$	$4d, 4f$ $4f$

^aAll of the results reported in this table and all subsequent tables are in atomic units.^bSee Ref. 25.

method due to these peculiarities, because the unique nature of these calculations may make these difficulties inconsequential in the evaluation of the results.

The differences between the two sets of L -shell results reported in Table I are due, as was stated previously, to our using spin-symmetrized configurations, while Nesbet's configurations are all constructed from single Slater determinants. These differences, which we have called symmetry differences (SD), are itemized in Table I. The two sets of results agree (within the accuracy of the method) for those pairs in which the spin-symmetrized configurations are single Slater determinants (i. e. , $2s^2$, $2p_0^2$, $2p_+^2$, and $2p_-^2$). Therefore, one may conclude that the two calculations are equivalent except for the SD's. Close scrutiny shows that the SD's arise due to the "internal" pair-pair interactions between the Slater determinants which make up a particular degenerate set. These interactions are all positive in sign and would be omitted in any Bethe-Goldstone pair calculation. Thus, in order to bring our pair method in line with Nesbet's we need to add a contribution approximately equal to the SD's to results obtained from basis sets larger than Nesbet's.

To see what effect Nesbet's shell centering approach has on the results, we decided to do a series of increasingly complex calculations in which the basis is as evenly spread over all of the shells as possible. With an even spread we also hoped to get the best possible TPEB result. This is assuming that a balanced set is necessary for the TPEB method. As stated previously, we were also concerned with the very poor SCF result obtained with the Nesbet L -shell centered set. It was hoped that a balanced set could correct this difficulty. The results of these balanced calculations are presented in Table II. Of particular importance are the results obtained with the CDZ set. By noting the difference between these results and those of Table I, one can determine the importance of the additional sets of functions employed by Nesbet. The last column gives the results obtained when the SD's from Table I are added to our best results in Table II. These results indicate that the Nesbet values were obtained with an unexpanded basis, with the possible exception of the $1s^2$ pair. The TPEB results were obtained from the 60-function set using both the virtual SCF orbitals and the frozen natural orbitals. Note that the SCF energy obtained with this set also indicates that the s - and p -shell part of the results should be more converged than those obtained with the Nesbet set.

It is also interesting to compare the CDZ results reported in Table II with those reported in Table III. The latter numbers were obtained from sets based upon the one used by Clementi in his Hartree-Fock calculations of Ne.²⁶ The second column of Table III lists the results obtained using Clementi's set

(CHF). The third column has values generated from a basis set which was designed to "improve" as much as possible upon the CHF set. The set is called the pseudo-Clementi basis (PCS). A careful scrutiny of the set was maintained to ensure that no linear dependencies were created. This latter set should nearly span the s - and p -orbital spaces for Ne. One can, therefore, use the results in Table III as an indication of how well the CDZ set is converged. The PCS set was subsequently employed as the basic part of the basis set used in our most detailed calculations. These are discussed below.

Having already exhibited that a well-balanced, large basis set could produce an "excess" of pair correlation energy, we next tried to determine if even more could be obtained by the Nesbet method of using different basis sets centered on different shells. We considered the Nesbet $1s^2$ pair and our balanced KL pairs to be fairly well converged. Therefore, we decided to try to specifically increase the sum of the L -shell pair energies. Table IV lists the results obtained when the CHF basis and the additional L -shell functions used by Nesbet were combined. A 43-function (two functions centered on the K shell and 41 on the L shell) set is formed. The third column of this table includes the SD corrections. Once again the Nesbet set appears to be incomplete. It is interesting to note, however, how the additional s - and p -type functions used by Nesbet improve upon the CDZ set. By noting the difference between the CDZ and CHF results (Tables II and III) and the appropriate differences in Tables I and IV, this improvement and its reasons become apparent. Obviously the functions added to CDZ by Nesbet enhance the spanning of the s and p spaces, but they apparently fail to completely do so by a significant amount. Perhaps the most significant result to be noted in Table IV is that by using the Nesbet shell centering method, one is able to get pair results equivalent to those obtained using far more complex balanced sets. In particular, one should note that the low $2s2p$ pair results reported in Table II were quite substantially increased by the Clementi-Nesbet set (Table IV). Realizing this we decided to develop an even more complex L -shell centered basis set.

An attempt was made to provide a spanning of the rest of the l -type spaces in a manner similar to that used for the s and p spaces. A set was developed composed of the PCS s and p functions, plus members which at least partially span the d - and f -type spaces. This set and the L -shell results obtained using it are reported in Table V. The second column contains the result of the pair correlation calculations and the third, the sums of the second column results and the SD's. These results indicate that all of the previous sets used in L -shell calculations on Ne were incomplete. It is perhaps surprising to note that this basis, which is sup-

TABLE II. Series of balanced shell total Ne pair and TPEB calculations.

Type of pair	CDZ	20-function set	60-function set	60-function set + SD
$2s^2$	-0.00406	-0.00838	-0.01085	-0.01085
$2s2p_0$	-0.01349	-0.01677	-0.02570	-0.02683
$2s2p_-$	-0.01351	-0.01676	-0.02564	-0.02675
$2s2p_+$	-0.01351	-0.01676	-0.02564	-0.02675
$2p_0^2$	-0.01105	-0.01985	-0.02600	-0.02600
$2p_0^2p_+$	-0.02106	-0.03694	-0.04713	-0.05026
$2p_0^2p_-$	-0.02106	-0.03694	-0.04713	-0.05026
$2p_+^2$	-0.00813	-0.01292	-0.01687	-0.01687
$2p_+^2p_-$	-0.02664	-0.05009	-0.06412	-0.06809
$2p_+^2p_+$	-0.00813	-0.01292	-0.01687	-0.01687
Sum (L shell)	-0.14064	-0.22833	-0.30595	-0.31953
$1s^2$ (K shell)	-0.01197	-0.03170	-0.03842	-0.03842
$1s2s$	-0.00181	-0.00398	-0.00528	-0.00528
$1s2p_0$	-0.00063	-0.00422	-0.00709	-0.00709
$1s2p_+$	-0.00063	-0.00422	-0.00709	-0.00709
$1s2p_-$	-0.00063	-0.00422	-0.00709	-0.00709
Sum ($K-L$ shell)	-0.00370	-0.01664	-0.02655	-0.02655
Total sum of pairs	-0.15631	-0.27667	-0.37092	-0.38450
SCF energy	-128.53478	-128.53891	-128.54703	
TPEB	-0.13356	-0.24760	-0.33239 ^a (-0.33014 ^b)	
$E^{(2)}$ (second-order pert energy)			-0.37512 ^a (-0.45522 ^b)	
Basis	Clementi double zeta	Clementi double zeta plus	Clementi H. F. set ^c plus	
		$\xi 2p = 12.3543$	$\xi = 21.630$ for $3s, 3p, 3d$	
		$\xi 2s = 8.9141$	$\xi = 17.50$ for $2p$	
		$\xi 3s = 2.1839$	$\xi = 14.50$ for $2s$	
		$\xi 3d = 4.6748$	$\xi = 12.00$ for $4f$	
			$\xi = 8.4$ for $3d$	
			$\xi = 6.0$ for $4f$	
			$\xi = 4.20$ for $3d$	
			$\xi = 2.10$ for $3d$	

^a SCF virtual orbitals.^b Frozen natural orbitals.^c See Ref. 26.

TABLE III. Pair correlation energies for the Clementi-Hartree-Fock (CHF) and pseudo-Clementi (PCS) basis sets.

Type of pair	Results CHF			Results PCS		
$2s^2$	-0.00514			-0.00552		
$2s2p_0$	-0.01566			-0.01601		
$2s2p_+$	-0.01568			-0.01602		
$2s2p_-$	-0.01568			-0.01602		
$2p_0^2$	-0.01317			-0.01356		
$2p_02p_+$	-0.02477			-0.02510		
$2p_02p_-$	-0.02477			-0.02510		
$2p_+^2$	-0.00975			-0.00997		
$2p_+2p_-$	-0.03124			-0.03191		
$2p_-^2$	-0.00975			-0.00997		
Sum L shell)	-0.16561			-0.16918		
$1s^2$ (K Shell)	-0.02821			...		
$1s2s$	-0.00370			...		
$1s2p_0$	-0.00207			...		
$1s2p_+$	-0.00207			...		
$1s2p_-$	-0.00207			...		
Sum (K - L Shell)	-0.00991					
Total sum of pairs	-0.20373					
SCF energy	-128.54699			-128.54704		
TPEB	-0.17465					
Basis	ξ_{1s}	ξ_{2s}	ξ_{2p}	ξ_{1s}	ξ_{2s}	ξ_{2p}
Basis	15.4496	7.7131	9.4550	15.4496	10.125	10.125
	9.5735	4.7746	4.4545	9.5735	6.75	6.75
		2.8462	2.3717		4.50	4.50
		1.9550	1.4700		3.00	3.00
					2.00	2.00
					1.33	1.33

TABLE IV. Pair correlation energies obtained from Clementi-Nesbet basis set (L shell only).^a

Type of pair	Clementi-Nesbet results	Clementi-Nesbet + SD
$2s^2$	-0.01077	-0.01077
$2s2p_0$	-0.02649	-0.02762
$2s2p_+$	-0.02645	-0.02756
$2s2p_-$	-0.02645	-0.02756
$2p_0^2$	-0.02601	-0.02601
$2p_02p_+$	-0.04678	-0.04991
$2p_02p_-$	-0.04678	-0.04991
$2p_+^2$	-0.01676	-0.01676
$2p_+2p_-$	-0.06407	-0.06804
$2p_-^2$	-0.01676	-0.01676
Sum of L Shell pairs	-0.30732	-0.32090
SCF Energy	-128.54705	

^aThe basis set consists of the CHF functions and those functions added by Nesbet to the CDZ set for the L shell.

TABLE V. Correlation energies obtained with "unbalanced" 60-function set centered on L shell.

Type of pair	Results for unbalanced 60	Unbalanced 60 + SD
$2s^2$	-0.01117	-0.01117
$2s2p_0$	-0.02719	-0.02832
$2s2p_+$	-0.02712	-0.02823
$2s2p_-$	-0.02712	-0.02823
$2p_0^2$	-0.02678	-0.02678
$2p_02p_+$	-0.04807	-0.05120
$2p_02p_-$	-0.04807	-0.05120
$2p_+^2$	-0.01738	-0.01738
$2p_+2p_-$	-0.06554	-0.06951
$2p_-$	-0.01738	-0.01738
Sum (L shell)	-0.31582	-0.32940
$1s^2$ (K shell)	-0.03374	-0.03374
$1s2s$	-0.00485	-0.00485
$1s2p_0$	-0.00671	-0.00671
$1s2p_+$	-0.00671	-0.00671
$1s2p_-$	-0.00671	-0.00671
Sum (K - L shell)	-0.02498	-0.02498
Total sum of pairs	-0.37454	-0.38812
SCF energy	-128.54703	
TPEB	-0.33328 ^a (-0.33268 ^b)	
$E^{(2)}$	-0.37786 ^a (-0.47093 ^b)	
Basis	Pseudo-Clementi plus	
	ξ_{3d}	ξ_{4d}
	8.00	3.85
	4.00	3.00
	2.00	

^aSCF virtual orbitals.^bFrozen natural orbitals.

posedly centered on the L shell, gives essentially the same TPEB result as that obtained with the "balanced" 60-function set reported in Table II. This is due, we believe, to the greater importance of the L -shell pairs in the total result (i. e., $L \sim 82\%$, $K \sim 11\%$, and $KL \sim 7\%$). The insufficient treatment of the K shell in this unbalanced 60-function set is indicated by the poor K - and K - L -shell results also reported in Table V. This insufficiency is indicative of the nature of the shell-centered method.

An analysis was also made of one of the approximations used in the TPEB calculations. Recall that due to the extremely large numbers of configurations generated by our 60-function set, it was necessary to selectively truncate our many electron basis using perturbation theory. A perturbation calculation was used to test the effect of this truncation. The calculation was made employing the truncated (natural-orbital-generated) set

used to obtain the TPEB result reported in Table V. This gave the value $E^{(2)} = -0.4657$ a. u., whereas the total (untruncated) many electron basis produced an $E^{(2)} = -0.4709$ a. u. The differential ($\sim 1\%$) is probably also reflected in our variation calculation, so that one may assume our TPEB results nearly converged within the limits of the orbital basis employed.

In Table VI we imitate Nesbet and add together results from different calculations to obtain the best possible total sum of the pair correlation energies (Berthe-Goldstone). Since Nesbet's K -shell calculation is more detailed than any of ours, we use his value for $1s^2$. This summation is $\sim 104\%$ of the total correlation energy of Ne (0.381 a. u.) reported by Clementi.²⁷ Although this value gives the appearance of near convergence, there is reason to believe that quite a bit more can be obtained by employing an even more complete basis set. A further discussion of this point will appear in Sec. V.

TABLE VI. Our best summation of pair correlation results.

Type of pair	Best result
$2s^2$	-0.01117
$2s2p_0$	-0.02832
$2s2p_+$	-0.02823
$2s2p_-$	-0.02823
$2p_0^2$	-0.02678
$2p_02p_+$	-0.05120
$2p_02p_-$	-0.05120
$2p_+^2$	-0.01738
$2p_+2p_-$	-0.06951
$2p_-^2$	-0.01738
Sum (L shell)	-0.32940 ^a
$1s^2$ (K shell)	-0.03993 ^b
$1s2s$	-0.00528
$1s2p_0$	-0.00709
$1s2p_+$	-0.00709
$1s2p_-$	-0.00709
Sum (K - L shell)	-0.02655 ^c
Sum of pair correlation energies	-0.39588

^aTaken from Table V.^bTaken from Table I.^cTaken from Table II.

Perhaps the most significant single feature of these results is obtained by comparing the total sum of the pairs with the corresponding TPEB results. The difference between these two values is 0.04–0.06 a. u., and is all due to the so-called pair-pair interactions. This difference is roughly proportional to the total correlation energy obtained from the largest pairs. Thus, the pair-pair interactions for Ne constitute ~15% of the total correlation energy. It might seem reasonable to conclude from the above results that the approximate convergence values of the sum of the pairs and the

TPEB methods are ~105% and ~90%, respectively (with ~15% for the pair-pair interactions). If this were true it would be necessary for triple and quadruple (and perhaps higher) excitations to contribute ~10% to the total correlation energy. Thus, if these ratios were true, then the triple and quadruple excitations for Ne would not be small. In order to examine this point, we made a series of calculations of these higher excitations. The perturbative method for doing this was outlined in Sec. III. Specifically, we selected the 50 most important double excitations constructed from our unbalanced 60 natural orbital set, and performed a variation calculation using these 50 functions. We then constructed nearly all of the possible triple and quadruple excitations which could be generated from simultaneous excitations of different pairs. Finally, using the lowest-energy eigenfunction of the variation calculation as ϕ_0 , we performed a second-order perturbation calculation on these higher excitations. The results of these calculations are reported in Table VII. The significant feature of these results is the small size of the contributions of the triples and quadruples. Thus, despite the fact that our small variation calculation generates approximately $\frac{2}{3}$ of the eventual TPEB value, the $E^{(2)}$ perturbation calculation gives less than 2% of the total correlation energy. From these results the only interpretation is that it is a mistake to expect to get anywhere near 10% from the higher-excitation contribution to the correlation energy of Ne. It is also interesting that the ideas of Sinanoğlu about unlinked clusters are borne out.⁵ Thus the largest contributors to the energy from the higher excitations are the so-called S -type unlinked clusters.²⁸ Kestner's conclusions about the smallness of the triple excitations of Ne are also borne out by this study.²⁴ We do not agree with Kestner, however, in concluding that the small size of the triples is indicative of the exactness of Nesbet's results.

The accuracy of standard second-order perturbation calculations must always be considered somewhat suspect. Therefore, we did another

TABLE VII. Contribution of triple and quadruple excitations by perturbation theory (in a.u.).

Size of second-order perturbation	Perturbation results
19 triples and 1099 quadruples	-0.005699
329 triples ^a	-0.000156
19 triples ^b	-0.0001125
Total triples	-0.000156
Total quadruples	-0.005587
Total quadruples + triples	-0.005743
Correlation energy of ϕ_0	-0.22343

^aMost of the possible triple excitations from orbitals in ϕ_0 .^b S -type unlinked triples constructed from double excitations in ϕ_0 . See Refs. 5 and 28.

TABLE VIII. Total calculation using limited basis on p block of Ne.

No. of configurations	Block variation increment	Bethe-Goldstone
1 SCF	-128.47833	
14 singles + doubles	-0.08069	Pairs -0.09411
15 triples	-0.00016	3 body +0.01407
11 quadruples	-0.00091	4 body -0.00205
4 Pent. + Hex. (complete)	-0.00001	5 body +0.00053
		6 body -0.00021
Total correlation energy	-0.08177	-0.08177
Singles + doubles	-0.08069 (98.68%)	
The higher blocks	-0.00108 (1.32%)	
Pair energies		-0.09411 (115.2%)

Basis: Single zeta for $1s$ and $2s$ + CDZ for $2p$ (only $p \rightarrow p$ excitation considered)

series of calculations, the results of which we consider very important. These calculations were performed using a limited basis set on just the p block of Ne. Because the size of the basis set was very limited (we used the CDZ p -block set), we were able to calculate the contribution of all possible excitations (up through hexuples) by both the Bethe-Goldstone and the total excitation block methods. The results of these calculations are reported in Table VIII. Three features of these results are extremely important. First, the pair-pair interactions given by these calculations are once again $\sim 15\%$ of the total result. Second, the contributions of the true triple, quadruple, etc., excitations are also still small as they were before (i. e., less than 2%), and once again the quadruple excitation terms are much larger than the triples. Third, the TPEB result for this total "subspace" calculation is $\sim 98\%$ of the limit of the basis set while the sum of the pairs gives $\sim 115\%$.

Finally, selected results of a series of calculations are reported in Table IX, in which the basis sets are rotated from complex to tetrahedral. The motivation for this type of study was the results obtained by Bender and Davidson on LiH^{21} and BH^{22} . Their work indicated that the sum of the pairs method could be quite susceptible to the nature of the basis employed to make the calculations. The results exhibited in Table IX indicate that a similar, but much less pronounced effect is occurring for Ne. Unfortunately these results are not as accurate as one might desire. This is due to an inherent restriction of the programs. One should not necessarily conclude that the agreement between Nesbet's results⁶ and Sinanoğlu's tetrahedral results²³ disproves these ideas. It can be shown that whereas the sum of the pair energies for Bethe-Goldstone pairs is not invariant under a unitary transformation of ϕ_0 , the total pair energy for the exact Sinanoğlu MET pairs is invariant under these transformations (although not for the first

approximation to these pairs).

V. CONCLUSIONS

It has been conclusively shown that, at least for Ne, the sum of the pairs method designed by Nesbet overshoots the limiting energy of the basis set by a significant amount. The present calculations produce by this method approximately 104% of the correlation energy of Ne. It is suspected that the method will produce an even greater percentage if a more complete basis is employed. Before amplifying this statement, we should point out that the additional contributions produced with more complete basis sets will all be negative in sign. Thus, one should not expect the percentage to decrease if the sets are made more complete. More will be said on this subject in a subsequent paper.¹⁰

The significant differential ($\sim 15\%$) between the sum of the pairs and the TPEB result is due to the so-called pair-pair interactions. The size of these contributions (which are always positive in sign¹⁰) is perhaps surprising, because many researchers have long considered them an insignificant part of any calculation.²⁹ It should be pointed out that we do not agree with the conclusions of Freed,²⁸ in which he postulates that the pair-pair interactions will go to zero when one rotates to a totally localized basis set. It is true that this rotation will greatly reduce the contributions of totally disjoint pairs (e. g., t_1^2 with t_2^2 or in the parlance of Kelly²⁹ and Freed²⁵ the so-called nondiagonal hole-hole diagrams). The rotation does not, however, necessarily diminish the size of the interactions between semidisjoint pairs (e. g., $2p_0 2p_{+1}$ with $2p_0 2p_{-1}$ or particle-hole and ring diagrams). A more extensive treatment of this problem will be presented in the second paper of this study.¹⁰

It is also interesting to note that the improvement of the Nesbet method over second-order Rayleigh-Schrödinger perturbation theory is due to

TABLE IX. Effect of rotating the basis on the sum of the pairs.

Complex pairs	Complex results	Real pairs	Real results	Tetrahedral (<i>L</i> shell) pairs	Tetrahedral results
$2s^2$	-0.00838	$2s^2$	-0.00838	t_1^2	-0.01880
$2s2p_0$	-0.01677	$2s2p_x$	-0.01677	t_1t_2	-0.02542
$2s2p_+$	-0.01676	$2s2p_y$	-0.01677	t_1t_3	-0.02542
$2s2p_-$	-0.01676	$2s2p_z$	-0.01677	t_1t_4	-0.02542
$2p_0^2$	-0.01985	$2p_x^2$	-0.01985	t_2	-0.01880
$2p_02p_+$	-0.03694	$2p_x2p_y$	-0.03694	t_2t_3	-0.02542
$2p_02p_-$	-0.03694	$2p_x2p_z$	-0.03694	t_2t_4	-0.02542
$2p_+2$	-0.01292	$2p_y^2$	-0.01985	t_3	-0.01880
$2p_+2p_-$	-0.05009	$2p_y2p_z$	-0.03694	t_3t_4	-0.02542
$2p_-^2$	-0.01292	$2p_z^2$	-0.01985	t_4^2	-0.01880
Sum (<i>L</i> shell)	-0.22833	Sum	-0.22906	Sum	-0.22772
$1s^2$ (<i>K</i> shell)	-0.03170	$1s^2$	-0.03170	$1s^2$	-0.03170
$1s2s$	-0.00398	$1s2s$	-0.00398	$1st_1$	-0.00416
$1s2p_0$	-0.00422	$1s2p_x$	-0.00422	$1st_2$	-0.00416
$1s2p_+$	-0.00422	$1s2p_y$	-0.00422	$1st_3$	-0.00416
$1s2p_-$	-0.00422	$1s2p_z$	-0.00422	$1st_4$	-0.00416
Sum (<i>K-L</i> shell)	-0.01664	Sum	-0.01664	Sum	-0.01664
Total sum of pairs	-0.27667		-0.27740		-0.27606
TPEB	-0.24760				
SCF	-128.53891				

Basis set: $CDZ + \zeta_{2s} = 8.9141 + \zeta_{2p} = 12.3543 + \zeta_{3s} = 2.1839 + \zeta_{3d} = 4.6748$

the former's inclusion of the interacting virtual-state terms (i. e., the particle-particle and hole-hole ladder diagrams) to all orders. Interestingly these terms contribute (positive in sign) about 19% (i. e., $E^{(2)} \approx 123\%$ while $\sum \epsilon_{ij} \approx 104\%$) to the calculations reported in Table V. Thus, we see that contrary to the conclusions reached by many others,²⁹ the pair-pair interactions are, at least for Ne, almost as important as these ladder diagrams.¹⁰

The results of our higher-excitation and total *p*-block calculations indicate that the contribution of these higher-excitation terms is of the order of 2%. This small size plus the results of the total *p*-block calculation lead us to believe that the significant error present in our best calculations resides in the inherent incompleteness of the basis sets employed. Thus, if we were to scale a total calculation we would predict for the correlation energy of Ne:

	Sign
Sum of the pairs $\approx 113\%$	(-)
Pair-pair interactions $\approx 15\%$	(+)
TPEB $\approx 98\%$	(-)

Higher excitations $\approx 2\%$ (-) .

That this has not been obtained is indicative of the difficulty in obtaining a complete basis set for a relatively complex atomic system (10 electrons). The question that immediately arises is, if the basis set is incomplete, where are these "gaps" located? As stated previously the *s* and *p* spaces are (for our unbalanced 60-function calculation) almost completely saturated. Tests indicate that the *d* space is also nearly saturated. Thus the incompleteness of our best basis set is apparently due to the unsaturated nature of the *f* space, plus the omission of higher *l*-type spaces (*g*, *h*, etc.). That the contribution of these higher *l* spaces should be so large is not very surprising. A series of calculations made on Be by perturbation theory produced a contribution from higher *l*-type spaces of approximately 2%.^{30, 4b} One must, of course, be wary about transferring contributions obtained in different calculations using completely different basis sets.

One can legitimately question the appropriateness of simply scaling our results as was done above. As the size of the basis set is increased, the fraction of the connecting matrix elements be-

tween different pair excitations which are nonzero decreases rapidly. Hence it is possible that the relative accuracy of the sum of the pairs might improve somewhat as a more complete basis was used. It is unlikely that the absolute error would decrease, however, so that the difference of 0.04 is likely to be preserved. If the higher excitations contribute 2%, this would set a lower bound of about 108% for the pair energy limit compared with the upper bound of 113% obtained by scaling.

No firm conclusions can be drawn concerning the unitary rotations of ϕ_0 . A definite change in the sum of the "Nesbet" pairs was noted, but this was not as pronounced as the changes found by Bender and Davidson on molecular systems.^{21,22} Perhaps this differential will shrink as one goes to more and more complete basis sets, but the results reported in Table IX seem to preclude this possibility.

We have now discussed enough results to be able to answer, at least for this particular case, the three questions presented in the Introduction to this paper.

(a) The summation-of-pairs (Nesbet type) method is *not* an *extremely* accurate method for obtaining the exact correlation energy. The excellent percentages reported by Nesbet (100.3%), and even our 104%, are we feel far too low. They result from the use of an incomplete expansion basis. The TPEB method would, we feel, give better answers than the sum of the pairs method, if the basis sets employed were complete. This incompleteness is a difficult problem to solve, however, so that the ~10% error noted for our TPEB results will be difficult to remove. It should be pointed out that we do not feel the sum of the pairs method is without merit; in fact it represents what is probably the quickest and best technique yet developed to obtain accurate estimates of the total correlation energy. With the inclusions of the extensions as suggested by Nesbet,⁶ the method may prove particularly accurate. It should also be noted that our results do not necessarily preclude the use of the summation of pairs technique as an accurate scheme to calculate physical properties other than the correlation energy. (b) We have shown that for Ne the pair-pair interactions are quite large, on a relative scale in which one hopes for quantitative accuracy. We have also indicated that higher-excitation terms (triple, quadruple, etc.) are not large and contribute not more than 2% to the total correlation energy. The transferability

of these results is in part an answer to the third question. (c) Since all of our results are for Ne, we can only speculate on the transferability of these results to more complex systems. The fact that the pair-pair interactions are much smaller for Be is probably due to the small penetration of the 1s and 2s orbitals. Nesbet's results for pair energies indicate that all pairs of orbitals with large penetrations are strongly correlated. It seems likely that all pairs of pairs with large pair penetration, defined by something like

$$\int |\phi_i(1)\phi_j(2) \pm \phi_j(1)\phi_i(2)| |\phi_k(1) \times \phi_l(2) \pm \phi_l(1)\phi_k(2)| d\xi_1 d\xi_2,$$

will have large pair-pair interactions.

It is instructive to apply these ideas to the results obtained by others using methods other than the Bethe-Goldstone technique of Nesbet. Since no comparable results exist for the Ne atom, it is necessary to use results obtained for other atoms.³¹ The boron results of Schaefer and Harris⁹ and the oxygen results of Kelly²⁹ are interesting examples. In the former case totally symmetrized configurations were employed and no compensation was made for the SD's in obtaining their sum of the pairs. If this compensation were used it is probable that the Schaefer-Harris sum for *B* would be very close to Nesbet's.⁷ An extension of the Schaefer-Harris basis to get even more pair energy seems to be possible. Kelly's oxygen results were obtained by the Brueckner-Goldstone perturbation theory.²⁸ For this calculation Kelly ignores some of the nondiagonal ladder diagrams (most of which are positive in sign) as well as all pair-pair interaction diagrams. It is thus not surprising that Kelly gets a value for E_{corr} which is ~107%. Had he included these omitted diagrams his results would most certainly be closer to the true value.

ACKNOWLEDGMENTS

The contributions of Dr. Charles F. Bender of Battelle Memorial Institute, Columbus, Ohio are greatly appreciated; his programming skills and understanding of the problem were invaluable to its culmination. Thanks are also due the National Science Foundation for financial support.

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¹¹This is, of course, an unnecessary but expedient restriction.

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²⁸K. Freed, *Phys. Rev.* **173**, 1, 24 (1968).

²⁹H. P. Kelly, in *Perturbation Theory and Its Application to Quantum Mechanics*, edited by C. H. Wilcox (John Wiley & Sons, Inc., New York, 1966), pp. 215-241. In all fairness to Kelly and Nesbet we should point out that we do agree with their conclusion that pair-pair interactions are very small for Be.

³⁰F. L. Brooks and W. T. Simpson, *J. Chem. Phys.* **41**, 909 (1964).

³¹Subsequent to the completion of this work it was discovered that similar studies of Ne were being independently carried out by H. F. Schaefer, James Viers, and F. E. Harris, [H. F. Schaefer (private communication)]. Their results, although incomplete at this time, seem in general to verify our conclusions.