

Atomic Bethe-Goldstone Equations. III. Correlation Energies of Ground States of Be, B, C, N, O, F, and Ne

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A variational formulation of Brueckner's theory has been used to solve Bethe-Goldstone equations and to compute electronic pair-correlation energies for the atoms listed in the title. One-electron effective correlation energies, needed for open-shell atomic states, are also computed. An approximate Hartree-Fock function is used for the reference state in each case. Individual pair-correlation energies are computed to an expected accuracy of 0.001 Hartree a.u. The total correlation energies range from 98.5 to 100.3% of the empirical correlation energy. For comparison with many-particle perturbation theory, definitions of the hierarchy of n th-order Bethe-Goldstone equations and of the concepts of gross and net mean-value increments used in this work are restated in terms of linked Goldstone diagrams.

I. INTRODUCTION

The many-particle theory of Brueckner¹ is based on the idea that the two-particle problem can be solved exactly for each pair of particles in an N -particle system, if the two-particle wave function is constrained to be orthogonal to the remaining $N-2$ orbital functions describing particles in an assumed Fermi sea. The occupied orbitals of the Fermi sea are to be computed by a Hartree-Fock calculation using the modified two-body interaction that results from independent solution of all of the two-particle equations.

The two-particle equations were first derived by Brueckner as integral equations¹ using multiple-scattering theory.² The equivalent differential equations were derived by Bethe and Goldstone,³ and the pair-correlation equations are usually referred to as Bethe-Goldstone equations. A third form of these equations, a sum to infinite order of so-called ladder diagrams in perturbation theory, has been derived by Goldstone.⁴

The extensive literature on Brueckner's theory has been reviewed by Thouless⁵ and by Kumar.⁶ Although the theory was originally developed to deal with the hard-core interaction between nucleons in nuclear matter, much of the formalism is directly applicable to finite systems with arbitrary two-body interactions. Papers that are relevant to the present calculations on electronic wave functions include work by Brenig,⁷ Rodberg,⁸ Nesbet,⁹ Gomes, Walecka, and Weisskopf,¹⁰ Brout,¹¹ and Szasz.¹² It was pointed out by Szasz that an earlier variational method proposed for calculations on divalent atoms by Fock, Veselov, and Petrashen¹³ involves a form of the Bethe-Goldstone equation. A critical review of this theory and of its applicability to electronic correlation in atoms and molecules has been given by the present author.¹⁴

The proposal by Sinanoğlu¹⁵ for solution of "exact-pair" equations is closely related to the method of Brueckner, Bethe, and Goldstone. Except for a possibly unimportant difference in the treatment of the one-particle operator that must occur in the theory, the method of Sinanoğlu is equivalent to the use of Bethe-Goldstone equations.¹⁴ The calculations by Geller, Taylor, and Levine¹⁶ on the Be atom, based on Sinanoğlu's formalism,

are in fact a variational solution of the Bethe-Goldstone equations, using two-particle functions that depend explicitly on relative coordinates. An earlier variational calculation on Be, with somewhat different numerical results, was carried out by Tuan and Sinanoğlu.¹⁷

An alternative variational formulation of Brueckner's theory can be developed by expressing the Bethe-Goldstone equations in terms of Slater determinants for an N -particle system.¹⁴ This approach has been used to define the concept of an n -particle (or n th-order) Bethe-Goldstone equation, for n any integer less than N .¹⁸⁻²⁰ This hierarchy of n th-order Bethe-Goldstone equations can be used to compute successive net increments of the mean value of any many-particle operator, including the energy. By definition, the sum to N th order of all net increments is the exact mean value of the given operator.

Calculations by this method of the electronic correlation energy of the ground states of Be¹⁹ and Ne,²⁰ and of the correlation energy and magnetic hyperfine-structure constant of Li (²S) and of N (⁴S),¹⁸ have been previously reported. In the present paper this work is extended to a survey of the one- and two-particle net increments of correlation energy for the ground states of atoms from Be to Ne.

The earlier calculations on Be, N, and Ne included three-particle net-correlation energies, which were found to be negligible within the accuracy of the calculations (0.001 Hartree a.u. for each pair-correlation energy). For this reason three-particle terms were not computed for the other atoms considered here.

Recent work by Kelly^{21,22} has been concerned with the application of the Brueckner-Goldstone perturbation expansion⁴ to the electronic structure of atoms. In order to compare results of the present work with those of Kelly, it is convenient to have an alternative definition of n th-order Bethe-Goldstone equations in terms of the linked-cluster perturbation diagrams introduced by Goldstone.⁴ In the two-particle case, the basic definition of a Bethe-Goldstone equation is that stated by Gomes *et al.*¹⁰ and characterized by them as the "independent-pair model." The interaction between any pair of particles is to be considered as exactly as possible, but the interaction of all other

particles among themselves is neglected. The energy of the system is then approximated by adding the energy corrections obtained independently for each pair. When this definition is modified to take account of single-particle excitations, needed whenever Φ_0 is not an exact unrestricted Hartree-Fock function,²³ it leads to the one- and two-particle stages of the hierarchy of Bethe-Goldstone equations considered here. The equivalent definition of an n -particle Bethe-Goldstone equation in terms of Goldstone diagrams will be given in Sec. II following a formal description of the present method.

The third-order (or three-particle) Bethe-Goldstone equations considered in the present work are closely related to the summation of three-particle diagrams considered by Bethe.²⁴ Use of this idea in the theory of nuclear matter has recently been reviewed by Rajaraman and Bethe.²⁵

Because of the success in recent years in carrying out Hartree-Fock calculations for small molecules,²⁶ it has become of considerable interest to obtain quantitative estimates of correlation energy corrections to the Hartree-Fock approximation. While a Hartree-Fock calculation gives a total energy of high percentage accuracy, the energies of physical or chemical interest are usually expressed as small differences between total energies, in the form of dissociation or excitation energies. Net changes of correlation energy can make a substantial contribution to such energy differences.^{27,28} For example, roughly half of the dissociation energy of the very stable nitrogen molecule is due to the correlation energy difference between the molecule and the separated neutral atoms.²⁹ Recent work on the correlation-energy contribution to the ionization energy of N_2 is an example of the need for quantitative data on pair-correlation energies in light atoms.³⁰ The present work is intended to provide this data to an accuracy useful for applications.

II. OUTLINE OF THE COMPUTATIONAL METHOD

If a Fermi sea is defined by the occupied orbitals ϕ_i of a reference-state Slater determinant Φ_0 , the Bethe-Goldstone equation for pair ij is a two-particle Schrödinger equation, constrained by the orthogonality of the wave function to the $N-2$ orbitals ϕ_k with $k \neq i, j$.^{3, 10, 12} This is equivalent to a variational calculation with an N -particle trial function,^{14, 18}

$$\Psi_{ij} = \Phi_0 + \sum_a \Phi_i^a c_i^a + \sum_b \Phi_j^b c_j^b + \sum_{ab} \Phi_{ij}^{ab}. \quad (1)$$

In the notation used here, a Slater determinant obtained from Φ_0 by replacing occupied orbitals $\phi_i, \phi_j, \phi_k, \dots$ ($i < j < k \dots \leq N$) by occupied orbitals $\phi_a, \phi_b, \phi_c, \dots$ ($N < a < b < c \dots$), taken from a postulated complete set of orbital functions, is denoted by $\Phi_{ijk} \dots^{abc} \dots$. In Eq. (1), the summations extend over all values of the indices a and b , but indices i and j are fixed and denote specific occupied orbitals in Φ_0 . The summation over ab denotes a double sum with $a < b$.

A first-order or one-particle Bethe-Goldstone equation is equivalent to a calculation with trial function

$$\Psi_i = \Phi_0 + \sum_a \Phi_i^a c_i^a, \quad (2)$$

where index i is specified, but a takes on all possible values.

If Slater determinants $\Phi_{ij} \dots^{ab} \dots$ are denoted in general by Φ_μ , then the coefficients c_μ are obtained as components of an eigenvector of the configuration-interaction matrix $H_{\mu\nu}$, where H is the N -particle Hamiltonian. As indicated by Eq. (1) or (2), it is convenient to normalize the wave function by setting the coefficient of Φ_0 equal to unity.

In practice, the set of unoccupied orbitals ϕ_a is finite. Orbital sets are used that can be extended to completeness, and this extension is carried out until computed quantities are observed to stabilize within a specified error. The present calculations were carried out to an accuracy of 0.001 Hartree a. u. (e^2/a_X for Atom X) for each computed pair-correlation energy.

The general definition of an n th-order Bethe-Goldstone equation, as used here, is the equivalent of a variational calculation with a trial function that is a linear combination of Φ_0 and of all Slater determinants $\Phi_{ijk} \dots^{abc} \dots$ whose indices $ijk \dots$ are any subset of a specified list of n -occupied orbital indices. If the mean value H_{00} of the energy of the reference state Φ_0 is subtracted from each diagonal element of the configuration-interaction matrix (matrix of H), then the energy eigenvalue computed for the trial function $\Psi_{ij} \dots$ will be an energy increment $\Delta E_{ij} \dots$ with respect to H_{00} . These quantities will be referred to as *gross* energy increments. In order to make use of a hierarchy of Bethe-Goldstone equations of increasing order, it is convenient to define a *net* energy increment $e_{ij} \dots$ as the difference between the corresponding gross increment and the sum of all net increments of lower order whose indices form a subset of the set $ij \dots$. For example, the net energy increment for pair 25 is defined by

$$e_{25} = \Delta E_{25} - e_2 - e_5, \quad (3)$$

where ΔE_{25} is the directly computed lowest eigenvalue of the configuration-interaction matrix for Ψ_{25} , and e_2 and e_5 are net increments obtained from first-order Bethe-Goldstone equations for Ψ_2 and Ψ_5 , respectively. Thus e_{25} is that part of ΔE_{25} not contained in e_2 and e_5 separately. If carried to N th order, this method of bookkeeping gives the exact correlation energy (energy in addition to H_{00}) in the form

$$\Delta E = \sum_i e_i + \sum_{ij} e_{ij} + \sum_{ijk} e_{ijk} + \dots + e_{1 \dots N}. \quad (4)$$

In terms of Goldstone diagrams,⁴ the wave function defined by Eq. (1) is represented by the sum, to all orders in the perturbation theory, of linked cluster diagrams in which the occupied orbital indices (labels on backward directed lines) are restricted to i and j only. Because diagrams that apparently

violate the exclusion principle must be included in the linked cluster expansion,^{4,21} the indices i and j may be repeated any number of times within a given diagram. The unoccupied orbital indices [labels on forward directed lines, represented by a, b, \dots in Eq. (1)] take on all possible values.

The gross energy increment ΔE_{ij} , corresponding to Eq. (1), is given by the sum of all connected linked diagrams with no external lines in which the labels on backward directed lines are restricted to i and j . The gross increment of some other operator F is represented by a similar sum of connected graphs, but with one additional vertex to represent a matrix element of F .

The generalization to an n th-order Bethe-Goldstone equation is obvious. The wave function $\Psi_{ijk\dots}$, for a specified set of indices ($ijk\dots$), is represented by the sum to infinite order in the perturbation theory of all linked diagrams in which the labels on backward directed lines are limited to indices from the specified set. Gross increments of energy or of any other mean value are represented by the corresponding sum of connected graphs with no external lines.

Net increments of mean values can be defined exactly as they are in the present configuration-interaction formalism; as the difference between a gross increment and the sum of all net increments of lower order that have indices which are a subset of those labelling the gross increment. This defines each net increment as a specific sum of connected linked diagrams. For a set of indices ($ijk\dots$), this sum consists of all connected linked diagrams with no external lines in which backward directed lines are labelled by just this set of indices, with the restriction that every index in ($ijk\dots$) must appear at least once. This is to be contrasted with the sum for a *gross* increment, which includes all diagrams with backward directed lines labelled by subsets of the given set of occupied orbital indices.

The atoms considered here have single determinant wave functions in their ground-state configurations, if M_L and M_S are taken equal to L and S , respectively. Because there is at most one open-shell $2p^n$, the traditional Hartree-Fock equations are identical with the truncated Hartree-Fock equations solved by matrix methods as a preliminary stage in the present work.^{14,31} The constraints inherent in the traditional Hartree-Fock method (symmetry and equivalence restrictions on the orbitals) introduce one-particle configuration-interaction matrix elements for states other than 1S .²³ These matrix elements, which cannot be eliminated without destroying the spherical symmetry properties of the Hartree-Fock orbitals, lead to nonzero one-particle net correlation-energy contributions. Except for this, the computational procedure followed here is identical with that used for the 1S states of Be and Ne.^{19,20} The configuration interaction matrix is constructed in a basis of Slater determinants, taking into account only the quantum numbers M_L , M_S , and parity, and the lowest eigenvalue and corresponding eigenvector are obtained by a rapidly converging iterative algorithm.³²

Orbital basis sets capable of giving a reasonable approximation to an atomic Hartree-Fock calculation, using the matrix Hartree-Fock method,^{31,33}

are extended by including additional orbitals in the form of exponential functions $e^{-\zeta r}$ multiplied by powers of r and by spherical harmonics. Optimal values of the exponents ζ were determined by preliminary calculations on Be, N, and Ne. It was found that the best results obtained with exponents different for each value of angular quantum number l could be duplicated, to within the criterion of accuracy used in the present work, by basis sets with a common value of ζ for all values of l . Different values of ζ must still be used to represent perturbations of atomic orbitals with different principal quantum number n . Exponents ζ_K and ζ_L were obtained variationally for perturbations of the K and L shells, respectively, of Be, N, and Ne. These exponents for N were found to be very close to values found by linear interpolation between the exponents for Be and Ne, using nuclear charge Z as a parameter. Because of this result, exponents for the other atoms considered here, listed in Table I, were taken to be equal to values obtained from those for Be and N, or for N and Ne, by linear interpolation.

From earlier configuration-interaction calculations, it was predicted¹⁴ that an orbital basis set capable of representing perturbing orbitals with all combinations of up to three nodal surfaces superimposed on occupied Hartree-Fock orbitals should give energy values accurate to within 0.001 a.u. for individual Bethe-Goldstone equations. For K -shell perturbations, this requires basis orbitals with radial and angular factors indicated by quantum numbers nl up to $4s, 4p, 4d, 4f$, multiplying $e^{-\zeta_K r}$, in addition to basis orbitals needed to represent the occupied Hartree-Fock orbitals. The computer programs were designed to allow the inclusion of arbitrary nl values, and higher values were used when there was any question of convergence of an energy eigenvalue to 0.001 a.u. The specific basis sets used consisted of the "double-zeta" basis set of Clementi³⁴ augmented by perturbing orbitals with exponents ζ_K and ζ_L as described above. All basis orbitals of s and p symmetry were included in the preliminary matrix Hartree-Fock calculations.

III. RESULTS OF COMPUTATIONS

The reference-state Slater determinants for the atomic ground states considered here are explicitly

$$\Phi_0(\text{Be}, ^1S) = \det(1s\beta 1s\alpha 2s\beta 2s\alpha),$$

$$\Phi_0(\text{B}, ^2P) = \det(1s\beta 1s\alpha 2s\beta 2s\alpha 2p_1\alpha),$$

TABLE I. Exponents used for orbital basis sets.

Z	Atom	ζ_K	ζ_L
4	Be	7.814	1.419
5	B	10.085	1.860
6	C	12.355	2.302
7	N	14.626	2.743
8	O	16.961	3.233
9	F	19.295	3.724
10	Ne	21.630	4.214

$$\begin{aligned}\Phi_0(\text{C}, {}^3P) &= \det(1s\beta 1s\alpha 2s\beta 2s\alpha 2p_0\alpha 2p_1\alpha), \\ \Phi_0(\text{N}, {}^4S) &= \det(1s\beta 1s\alpha 2s\beta 2s\alpha 2p_{-1}\alpha 2p_0\alpha 2p_1\alpha), \quad (5) \\ \Phi_0(\text{O}, {}^3P) &= \det(1s\beta 1s\alpha 2s\beta 2s\alpha 2p_1\beta 2p_{-1}\alpha 2p_0\alpha 2p_1\alpha), \\ \Phi_0(\text{F}, {}^2P) &= \det(1s\beta 1s\alpha 2s\beta 2s\alpha \\ &\quad \times 2p_0\beta 2p_1\beta 2p_{-1}\alpha 2p_0\alpha 2p_1\alpha), \\ \Phi_0(\text{Ne}, {}^1S) &= \det(1s\beta 1s\alpha 2s\beta 2s\alpha \\ &\quad \times 2p_{-1}\beta 2p_0\beta 2p_1\beta 2p_{-1}\alpha 2p_0\alpha 2p_1\alpha).\end{aligned}$$

One-particle net correlation-energy increments, computed as indicated in Sec. II, above, are listed in Table II. Two-particle net correlation energies, computed as in Eq. (3) by subtracting one-particle net correlation energies from the directly computed gross energy increments, are tabulated for electron pairs involving K -shell orbitals ($1s\beta$ or $1s\alpha$) in Table III. The remaining two-particle net correlation energies, representing pairs of L -shell orbitals, are given in Table IV. These results are summarized and compared with empirical non-relativistic correlation energies³⁵ in Table V. The sum of one- and two-particle net correlation-energy increments is uniformly within 1.5% of the empirical correlation energy. This result is consistent with the accuracy expected from orbital basis sets of the kind used here.¹⁴

It is important to note that this level of accuracy holds for all of the atoms considered. There is no evidence for any systematic error (due to neglect of three-particle correlations) as the number of electrons increases from four to ten.

In a previous paper on Ne (1S), it was shown that the entire set of $2p^2$ pair-correlation energy increments could be expressed as linear combinations of only three independent parameters, to within the accuracy of the present calculations.²⁰ Because Slater determinants, rather than symmetry-adapted functions, are used in these calculations, this result is only approximate. In Ne (1S) it depends on the numerical accuracy of the matrix diagonalization. The three independent $2p^2$ energy parameters correspond to coupling a two-particle function to a pure 3P , 1D , or 1S eigenfunction. More precisely, the $(N-2)$ -particle Slater determinant obtained by removing two specified $2p$ orbitals from Φ_0 is a function of mixed symmetry which can be combined with $2p^2({}^3P, {}^1D, {}^1S)$ to form a symmetry-adapted N -particle function with quantum numbers

L, S appropriate to the atomic state in question.

Except for 1S states, the pair correlation energies given in Tables III and IV depend significantly on the quantum numbers M_L and M_S because the effective potential field of the open $2p$ shell is not spherically symmetrical. In general, the number of independent parameters cannot be reduced by considering symmetry-adapted pair functions. However, the various $2p^2$ energies could in all cases be represented by linear combinations of only three parameters, using coefficients given previously,²⁰ to within the accuracy of the present work. The values used for these parameters are listed in Table VI.

IV. COMPARISON WITH PREVIOUS WORK

The correlation energy for the $2s^2$ electron pair for several of the atoms considered here has been computed by McKoy and Sinanoğlu³⁶ using the formalism of Sinanoğlu.¹⁵ Their results, obtained with a simple variational function containing the relative coordinate r_{12} , are listed in Table VII, and compared with the $(2s\beta 2s\alpha)$ net correlation-energy increments from Table IV. Although the present results, obtained with much more elaborate variational trial functions, are more accurate, the main qualitative conclusion of McKoy and Sinanoğlu is verified, in that the $2s^2$ pair correlation decreases significantly as the $2p$ shell is filled. This is due, in part, to suppression of the $2s^2$ - $2p^2$ near degeneracy.³⁶

The specific effect of this near degeneracy was computed by Clementi and Veillard,³⁷ using two-configuration Hartree-Fock calculations. Optimal orbitals and configuration mixing coefficients were obtained for the configurations $1s^2 2s^2 2p^n$ and $1s^2 2p^{n+2}$, for the atomic states in which both configurations occur. The computed correlation energies are given in Table VII. Because the multi-configuration Hartree-Fock method allows for relaxation of the orbitals as well as for superposition of configurations, this method can include more of the correlation energy than is represented by the $2s^2$ net correlation energy obtained from a Bethe-Goldstone equation. Thus the Clementi and Veillard result for Be (1S) is somewhat larger in magnitude than the present result. For B (2P) and C (3P), the degeneracy effect apparently becomes a successively smaller fraction of the $2s^2$ pair

TABLE II. One-particle net increments of correlation energy, e_i , in Hartree units (e^2/a_X) for Atom X.

i	Be (1S)	B (2P)	C (3P)	N (4S)	O (3P)	F (2P)	Ne (1S)
$1s\beta$	-0.0	-0.000 008	-0.000 032	-0.000 076	-0.000 043	-0.000 018	-0.0
$1s\alpha$	-0.0	-0.000 010	-0.000 035	-0.000 076	-0.000 041	-0.000 015	-0.0
$2s\beta$	-0.0	-0.000 455	-0.000 982	-0.001 759	-0.001 126	-0.000 629	-0.0
$2s\alpha$	-0.0	-0.000 594	-0.000 995	-0.001 283	-0.000 848	-0.000 448	-0.0
$2p_{-1}\beta$							
$2p_0\beta$						-0.000 194	-0.0
$2p_1\beta$					-0.001 054	-0.000 194	-0.0
$2p_{-1}\alpha$				-0.0	-0.000 129	-0.000 229	-0.0
$2p_0\alpha$			-0.0	-0.0	-0.000 479	-0.000 134	-0.0
$2p_1\alpha$		-0.0	-0.0	-0.0	-0.000 129	-0.000 229	-0.0

TABLE III. Two-particle net increments of correlation energy, e_{ij} , in Hartree units, for KK and KL pairs.

ij	Be (1S)	B (2P)	C (3P)	N (4S)	O (3P)	F (2P)	Ne (1S)
$1s\beta 1s\alpha$	-0.041827	-0.041108	-0.040867	-0.040362	-0.040178	-0.039784	-0.039932
$1s\beta 2s\beta$	-0.000813	-0.000882	-0.000920	-0.000927	-0.000810	-0.000649	-0.000469
$2s\alpha$	-0.002119	-0.002283	-0.002234	-0.001800	-0.002120	-0.002122	-0.002099
$2p_{-1}\beta$							-0.001481
$2p_0\beta$						-0.001443	-0.001481
$2p_1\beta$					-0.001406	-0.001469	-0.001481
$2p_{-1}\alpha$				-0.001609	-0.001846	-0.001865	-0.001834
$2p_0\alpha$			-0.001708	-0.001609	-0.001944	-0.001847	-0.001834
$2p_1\alpha$		-0.001458	-0.001720	-0.001609	-0.001919	-0.001945	-0.001834
$1s\alpha 2s\beta$	-0.002119	-0.002375	-0.002422	-0.002194	-0.002352	-0.002246	-0.002099
$2s\alpha$	-0.000813	-0.000751	-0.000622	-0.000416	-0.000467	-0.000471	-0.000469
$2p_{-1}\beta$							-0.001834
$2p_0\beta$						-0.001764	-0.001834
$2p_1\beta$					-0.001675	-0.001781	-0.001834
$2p_{-1}\alpha$				-0.001284	-0.001410	-0.001465	-0.001481
$2p_0\alpha$			-0.001270	-0.001284	-0.001436	-0.001440	-0.001481
$2p_1\alpha$		-0.001125	-0.001289	-0.001284	-0.001410	-0.001465	-0.001481

correlation energy. A similar calculation on boron was carried out by Glembotskii *et al.*³⁸

Multiconfiguration Hartree-Fock calculations have been carried out on the three states, 3P , 1D , and 1S of the carbon atom ground-state configuration, $1s^2 2s^2 2p^2$, by Hinze and Roothaan³⁹ and by Bagus and Moser.⁴⁰ For configurations affecting only the $2p^2$ electron pair, their results are essentially identical, giving $2p^2$ pair correlation ener-

gies -0.009, -0.013, and -0.036 a.u. for the states 3P , 1D , and 1S , respectively. These results are in good qualitative agreement with the $2p^2$ pair-correlation parameters shown in Table VI, which appear to be roughly constant throughout the series of atoms considered here.

A detailed study of the 2P ground state of boron has recently been published by Schaefer and Harris.⁴¹ Their best variational calculation, us-

TABLE IV. Two-particle net increments of correlation energy, e_{ij} , for LL pairs.

ij	Be (1S)	B (2P)	C (3P)	N (4S)	O (3P)	F (2P)	Ne (1S)
$2s\beta 2s\alpha$	-0.045351	-0.039923	-0.028450	-0.013633	-0.012928	-0.011919	-0.010834
$2p_{-1}\beta$							-0.003294
$2p_0\beta$						-0.004633	-0.003302
$2p_1\beta$					-0.007374	-0.006013	-0.003294
$2p_{-1}\alpha$				-0.024944	-0.016560	-0.012208	-0.010283
$2p_0\alpha$			-0.024624	-0.024944	-0.020729	-0.014681	-0.010317
$2p_1\alpha$		-0.024528	-0.025680	-0.024944	-0.022856	-0.018548	-0.010283
$2s\alpha 2p_{-1}\beta$							-0.010283
$2p_0\beta$						-0.010892	-0.010317
$2p_1\beta$					-0.012285	-0.011860	-0.010283
$2p_{-1}\alpha$				-0.002869	-0.003065	-0.003162	-0.003294
$2p_0\alpha$			-0.004156	-0.002869	-0.002984	-0.003252	-0.003302
$2p_1\alpha$		-0.006886	-0.005538	-0.002869	-0.003065	-0.003162	-0.003294
$2p_{-1}\beta 2p_0\beta$							-0.010906
$2p_1\beta$							-0.010927
$2p_{-1}\alpha$							-0.016498
$2p_0\alpha$							-0.013732
$2p_1\alpha$							-0.022837
$2p_0\beta 2p_1\beta$						-0.010831	-0.010906
$2p_{-1}\alpha$						-0.013803	-0.013732
$2p_0\alpha$						-0.025813	-0.025813
$2p_1\alpha$						-0.013877	-0.013732
$2p_1\beta 2p_{-1}\alpha$					-0.022878	-0.023240	-0.022837
$2p_0\alpha$					-0.014204	-0.014011	-0.013732
$2p_1\alpha$					-0.017408	-0.017438	-0.016498
$2p_{-1}\alpha 2p_0\alpha$				-0.009948	-0.010295	-0.010675	-0.010906
$2p_1\alpha$				-0.009973	-0.010381	-0.010623	-0.010927
$2p_0\alpha 2p_1\alpha$			-0.009685	-0.009948	-0.010295	-0.010675	-0.010906

TABLE V. Summary of one- and two-particle correlation energies, in Hartree units.

	Be (¹ S)	B (² P)	C (³ P)	N (⁴ S)	O (³ P)	F (² P)	Ne (¹ S)
$\sum e_i$	-0.0	-0.001 067	-0.002 043	-0.003 194	-0.003 849	-0.002 090	-0.0
$\sum e_{ij}$	-0.041 827	-0.041 108	-0.040 867	-0.040 362	-0.040 178	-0.039 784	-0.039 932
(KK)							
$\sum e_{ij}$	-0.005 864	-0.008 874	-0.012 185	-0.014 015	-0.018 795	-0.021 970	-0.025 026
(KL)							
$\sum e_{ij}$	-0.045 351	-0.071 337	-0.098 133	-0.126 940	-0.187 306	-0.251 316	-0.317 269
(LL)							
E_C	-0.093 042	-0.122 385	-0.153 228	-0.184 512	-0.250 127	-0.315 160	-0.382 227
$E_C(\text{obs})^a$	-0.0940	-0.1240	-0.1551	-0.1861	-0.2539	-0.316	-0.381
%	99.0	98.7	98.8	99.1	98.5	99.7	100.3

^a A. Veillard and E. Clementi, to be published, IBM Technical Report No. RJ 447, 1967 (unpublished). This work revises and supersedes earlier data by E. Clementi, J. Chem. Phys. **38**, 2248 (1963). The empirical correlation energies are not corrected for the Lamb shift (radiative corrections).

ing a configuration-interaction function with up to four-particle excitations from a Hartree-Fock reference state, yielded 88.3% of the correlation energy. One- and two-particle net-energy increments were obtained by solving Bethe-Goldstone equations. The sum of these terms, listed in Table VIII, gave 88.1% percent of the correlation energy, indicating that the net three- and four-particle energy effects are very small. Schaefer and Harris used symmetry-adapted functions (²P eigenfunctions) throughout, instead of simple Slater determinants as used here. For this reason, their definition of the hierarchy of Bethe-Goldstone equations is based on configurations (given by *nl* values only) rather than on the structure of single determinants, and this changes the definition of the net energy increments. For example, in terms of configurational excitations, the 2s Bethe-Goldstone equation includes the effects of determinants obtained by single excitation of either 2sβ or 2sα as well as by double excitations such as 2sβ, 2p₁α to 2p₋₁β, 3d₂α. Except for these differences in definition, the results shown in Table VIII are in good quantitative agreement. The present results are more accurate because more terms are included in the individual variational calculations. For example, 171 Slater determinants were included in the trial wave function for the 1sβ, 1sα Bethe-Goldstone equation in the present work, and 139 Slater determinants for 2sβ, 2sα. The unoccupied orbital sets used to represent excitations of these two different orbital pairs are completely different, and except for Φ₀, there are no Slater determinants common to the two wave functions.

When all triply and quadruply excited configurations were removed from the full configuration-

interaction calculation of Schaefer and Harris, the correlation energy was reduced to 86.3% of its full value. Contrary to the discussion given by these authors, this loss of 2.0% of the correlation energy, compared with the full configuration-interaction function, should not be identified with the net three- or four-particle correlation energy, as defined in the present work. As shown in discussions of the structure of a many-particle wave function by Brenig,⁷ Iutsis,⁴² and Sinanoğlu,¹⁵ this error must be attributed to a constraint imposed on the wave function by failure to include three- and four-particle excited Slater determinants whose coefficients are approximated as functions of the coefficients of the dominant two-particle excitations. Because such product terms are not included, the coefficients of two-particle excitations are unnecessarily constrained from taking on values appropriate to noninteracting pair excitations. This result is one of the first quantitative indications of a clear advantage of the Brueckner-Bethe-Goldstone theory, which leads to a relative error of only 0.2% in this example, over the use of a variational trial function expressed as a sum of all possible pair excitations, a form proposed as an extension of first-order perturbation theory for the wave function.⁴³

Earlier configuration-interaction calculations by Boys on boron and carbon⁴⁴ gave roughly half of the correlation energy in each case. Boys' calculations, done before the introduction of electronic computers, have stood for a number of years as the most accurate calculations reported for these atoms.

The Brueckner-Goldstone perturbation theory has been used by Kelly to compute the correlation energy of the ³P ground state of oxygen.²² Results

TABLE VI. Parameters for 2p² pair-correlation energies, in Hartree units.

	C (³ P)	N (⁴ S)	O (³ P)	F (² P)	Ne (¹ S)
2p ² (³ P)	-0.009 685	-0.009 961	-0.010 323	-0.010 744	-0.010 913
2p ² (¹ D)			-0.017 408	-0.017 438	-0.016 498
2p ² (¹ S)			-0.044 445	-0.042 562	-0.044 076

TABLE VII. Comparison of $2s^2$ pair correlation energies (Hartree atomic units).

	Clementi and Veillard ^a	McKoy and Sinanoğlu ^b	Present work
Be (¹ S)	-0.047 542	-0.032 78	-0.045 351
B (² P)	-0.031 113	-0.025 80	-0.039 923
C (³ P)	-0.017 330	-0.014 99	-0.018 450
N (⁴ S)		-0.006 10	-0.013 633
O (³ P)			-0.012 928
F (² P)			-0.011 919
Ne (¹ S)		-0.010 00	-0.010 534

^aE. Clementi and A. Veillard, J. Chem. Phys. 44, 3050 (1966). Hartree-Fock calculation with two-configuration wave function, $1s^2 2s^2 2p^n$ and $1s^2 2p^{n+2}$.

^bV. McKoy and O. Sinanoğlu, J. Chem. Phys. 41, 2689 (1964).

are compared with the present work in Table IX. Because the formalism used by Kelly is equivalent to the use of single Slater determinants, represented by excitations of individual orbitals, rather than of symmetry-adapted functions, the individual correlation terms computed by Kelly should be identical with the particular sums of net correlation energies from the present calculations listed in Table IX. As can be seen from the Table, there is a nearly constant ratio of 1.1 between the two sets of results. In the case of the largest terms, $e(1s^2)$, $e(2s2p)$, and $e(2p^2)$, this discrepancy is greater than the expected error of the present results, where variational calculations have been carried out to within 0.001 a. u. for each net energy increment. Since the present calculations represent a sum to infinite order of perturbation series, it can be concluded that terms of higher order in these series should be included in Kelly's work in order to reach the level of accuracy of the present results. It should be noted that Kelly computed 107.9% of the correlation energy, compared with 98.5% obtained here.

V. DISCUSSION AND CONCLUSIONS

The results of the present calculations show a

TABLE VIII. Comparison of results for B (²P). Energy parameters in Hartree a. u.

	Schaefer and Harris ^a	Present work ^b
$e(1s)$	-0.000 184	-0.000 018
$e(2s)$	-0.021 819	-0.001 049
$e(2p)$	-0.000 000	-0.000 000
$e(2s^2)$	-0.039 277	-0.039 923
$e(1s2s)$	-0.003 480	-0.006 291
$e(1s2p)$	-0.001 247	-0.002 583
$e(2s2p)$	-0.005 064	-0.031 414
Total	-0.109 855	-0.122 385

^aH. F. Schaefer, III, and F. E. Harris, Phys. Rev. 167, 67 (1968).

^bNet energy increments listed in Tables II-IV are summed over m_l and m_s quantum numbers to give total increments indexed only by quantum numbers n and l .

very satisfactory internal consistency, as indicated by the summary given in Table V, especially when it is considered that each entry in Tables II, III, and IV represents an independent variational calculation. For this reason, it should be satisfactory for semiempirical use of the net correlation parameters to scale up each computed net correlation energy by dividing by the percentage error given for the total correlation energies in Table V. The ability of the present method to give quantitative results has been demonstrated.

The exact correspondence between the present formulation, in terms of Slater determinants and individual orbital excitations, and the Brueckner-Goldstone perturbation theory has been shown here in Sec. II, where net increments of any mean-value quantity have been defined in terms of linked diagrams.

The comparison with Kelly's calculation on O (³P), discussed in Sec. IV, suggests the conclusion that the Brueckner-Goldstone perturbation theory must be carried to somewhat higher order to give results of the present accuracy. The residual error in Kelly's calculation appears to be roughly twice as great as it is in the present work.

In extending the present method to excited states,

TABLE IX. Comparison of results for O (³P). Energy parameters in Hartree a. u.

	Kelly ^a	Present work ^b
$e(1s)$	-0.000 09	-0.000 084
$e(2s)$	-0.001 61	-0.001 974
$e(2p)$	-0.001 13	-0.001 791
$e(1s^2)$	-0.043 83	-0.040 178
$e(2s^2)$	-0.015 00	-0.012 928
$e(1s2s)$	-0.006 29	-0.005 749
$e(1s2p)$	-0.015 00	-0.013 046
$e(2s2p)$	-0.100 44	-0.088 918
$e(2p^2)$	-0.090 58	-0.085 461
Total	-0.273 97	-0.250 127

^aH. P. Kelly, Phys. Rev. 144, 39 (1966).

^bNet energy increments summed as in Table VIII.

some provision must be made for wave functions which cannot be approximated by a single Slater determinant in the Hartree-Fock approximation. A simple example of this is the 1S state in the $2s^22p^2$ ground-state configuration of carbon. The simplest approach, retaining the present organization of computer programs in terms of Slater determinants, is to choose, arbitrarily, one determinant from the zeroth-order symmetry-adapted function as reference state, and then always to include all determinants from this configuration in each variational trial function. Coefficients appropriate to the desired symmetry-adapted function would be used to initiate the iterative matrix-diagonalization algorithm.

Another approach, already used by Schaefer and Harris,⁴¹ is to reformulate the method in terms of

configurations rather than single Slater determinants, so that net increments, etc., are defined in terms of excitations of configurations rather than of individual orbitals. Then symmetry-adapted functions can be used at each stage of the computations. This approach is no longer in exact correspondence with the linked diagram expansion of the Brueckner-Goldstone perturbation theory. It would be an interesting theoretical exercise to reformulate the perturbation theory in terms of configurational excitations and symmetry-adapted functions. That this exercise may not be trivial is indicated by the fact that even the antisymmetry of the wave function must be ignored in deriving the linked diagram expansion, resulting in the so-called EPV (exclusion principle violating) diagrams.²¹

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