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Method of successive approximations for many-electron wave functions

Edward J. Kansa*
Vanderbilt University, Nashville, Tennessee 37203

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Assuming that there exists a correspondence between the methods of the superposition of configurations and linked-cluster perturbation-theory expansions, a method of successive approximations was used to generate the coefficients of the superposition-of-configurations expansion and the correlation energy of a many-electron wave function. The algorithm was applied to the ground state of Be. Using an excited *s,p,d* orbital basis set calculated in the V^N potential, and estimating the truncation error of the remaining pair-correlation energies of the partial-wave expansion, a correlation energy of −0.09312 a.u. was obtained.

I. INTRODUCTION

The methods of superposition-of-configurations (SC) expansion and the linked-cluster perturbation-theory (LCPT) expansion, which was developed by Brueckner[1] and Goldstone,[2] have been two approaches to the many-electron problem.

Recently, successful SC calculations have been performed on atoms such as (a) Be by Watson,[3] Bunge,[4] and Sims and Hagstrom[5]; (b) C by Bunge and Bunge[6]; (c) Ne by Barr and Davidson,[7] Bunge and Pelxeto,[8] and Viers and co-workers.[9] Nesbet[10] has developed a generalized Bethe-Goldstone approach in which a pair SC calculation is performed rather than the traditional sum-of-pairs SC calculation. Sinanoglu[11] had developed a powerful semiempirical approach to electron correlation which was based on SC and perturbation theories.

Pu, Chang, and Das,[12] and Kelly and coworkers[13,14] have performed successful LCPT calculations on a variety of atoms and molecules. Among the techniques developed by Kelly are (a) geometric summation of certain classes of terms by energy denominator shifts and ratios, (b) the choice of a V^{N-1} potential which enables the excited states to resemble physical one-particle excitations, (c) summations over bound states by discrete sums and the n^{-3} rule and the numerical integration over the continuous states, and (d) the explicit numerical calculation of a complete set of radial wave functions for the significant l values.

Nesbet,[15] Kelly and Sessler,[16] and Kelly[17] have demonstrated that there exists a correspondence between the pair-excitation terms of the SC and LCPT expansions of the exact wave function. This paper will extend this correspondence for all possible n-tuple excitations, and develop a method of successive approximations of an iterative-perturbative nature. In addition, it will be argued that the pair and pair-product excitations are the dominant corrections for closed-shell systems, while the non-pair-excitation terms are much less significant owing to a considerable cancellation of terms.

II. REVIEW OF THE BRUECKNER-GOLDSTONE LINKED-CLUSTER PERTURBATION THEORY

Consider a system of N identical fermions moving in some central-field potential and interacting through the two-body potential v_{ij}. For atoms, the Hamiltonian is given by

$$H=\sum T_i+\sum_{i<j} v_{ij}\,, \tag{1}$$

where

$$T_i=-\tfrac{1}{2}\nabla_i^2-Z/r_i\,.$$

(Atomic units will be used throughout, $e=m=\hbar=1$.)

To simplify the problem, it is assumed that an effective potential V can be constructed to represent the average interaction potential on the ith particle due to the other $N-1$ interacting particles.

The Hamiltonian can be separated into two parts as

$$H=H_0+H_1, \tag{2}$$

where

$$H_0=\sum_{i=1}^{N} h_i\,, \tag{3}$$

$$h_i=T_i+V_i\,,$$

and where

$$H_1=\sum_{i<j}^{N} v_{ij}-\sum_{i=1}^{N} V_i\,. \tag{4}$$

There exists an infinite number of single-particle solutions of the single-particle Schrödinger equation

$$h_i u_i = \epsilon_i u_i \,. \tag{5}$$

For a closed-shell system, the N lowest-lying solutions are used in the construction of the reference antisymmetrized product wave function $|\phi\rangle$:

$$|\phi\rangle = 1/(N!)^{1/2}\det[u_1(\vec{x}_1)\cdots u_N(\vec{x}_N)]\,. \tag{6}$$

The unoccupied states of $|\phi\rangle$ denoted by $\alpha, \beta, \gamma, \ldots$ are called holes and the occupied states of $|\phi\rangle$ denoted by $a, b, c, \ldots$ are called particles.

In the second-quantization notation, the Hamiltonian is written as

$$H_0 = \sum_n \epsilon_n \eta_n^\dagger \eta_n \,, \tag{7}$$

and

$$H_1 = \sum_{wxyz} \langle wx|v|yz\rangle \eta_w^\dagger \eta_x^\dagger \eta_z \eta_y - \sum_{wx} \langle w|V|x\rangle \eta_w^\dagger \eta_x \,, \tag{8}$$

where the summations are over distinct matrix elements. The operators $\eta_n^\dagger$ and η_n are the creation and destruction operators of u_n which satisfy the usual Fermi-Dirac anticommutation relations.

Goldstone[2] assumed that the exact solution of the many-body system $|\Psi\rangle$ could be adiabatically generated from $|\phi\rangle$ by the perturbation H_1. It is assumed that there exists an operator $U_\alpha(t)$ such that

$$|\Psi\rangle = e^{-iH_0 t} U_\alpha(t)|\phi\rangle \,. \tag{9}$$

Goldstone[2] used Wick's theorem to represent the series expansion for $U_\alpha|\phi\rangle$ by Feynman diagrams. The ith particle a_i is represented by a line directed upwards, and the ith hole α_i is represented by a line directed downward. The direction of time is increasing.

Two classes of diagrams arise from the use of Wick's theorem in the expansion of $U_\alpha(t)|\phi\rangle$: linked and unlinked. Further, diagrams may be connected or disconnected. A connected diagram cannot be decomposed into two or more diagrams of lower order without breaking any hole or particle lines. A connected unlinked diagram has no external free lines and it diverges as $\alpha \to 0$. A linked diagram is nondivergent and it has no disconnected unlinked components.

Disconnected diagrams may differ from one another only by having the interactions of the components in different positions relative to each other. Sums over the relative time orderings are equivalent to carrying out the time integrations with only the time-ordering restrictions in each component separately. The result is a factorization into a product of the separate disconnected components of the diagram. It can be shown that the sum of all the unlinked diagrams is given by $\langle\phi|U_\alpha(0)|\phi\rangle$. Choosing the intermediate normalization $\langle\phi|\Psi\rangle = 1$, one can then show that

$$|\Psi\rangle = \sum_{n=0}^{\infty} \left[\frac{1}{(E_0 - H_0)} H_1\right]_L^n |\phi\rangle, \tag{10}$$

where L restricts the summations to linked terms only. It is convenient to define $|\chi\rangle$ to be the correlated part of $|\Psi\rangle$,

$$|\chi\rangle = |\Psi\rangle - |\phi\rangle \,. \tag{11}$$

Then the correlation energy is given by

$$\begin{aligned} E_C &= \langle\phi|H_1|\chi\rangle \\ &= \sum_{n=1}^{\infty} \langle\phi|H_1 \left[\frac{1}{(E_0 - H_0)} H_1\right]_L^n |\phi\rangle \,. \end{aligned} \tag{12}$$

It is possible to regroup the series expansion of $|\chi\rangle$ according to the number of open loops or $[\eta_{a_i}^\dagger \eta_{\alpha_i}]$ pairs which will be called excitations. Both connected and disconnected linked diagrams are allowed in the expansion $|\chi\rangle$ to all orders of perturbation theory, whereas only linked connected diagrams are allowed to all orders in the expansion of the correlation energy. Figure 1 illustrates the expansion of $|\chi\rangle$ according to excitation number.

III. LINKED-CLUSTER AND SUPERPOSITION-OF-CONFIGURATIONS EXPANSION

It seems intuitively obvious that the SC and LCPT expansions are related. However, in considering the iterative expressions for the coefficients of the superposition of configurations as a means of generating the LCPT expansion, one must ensure that only linked connected or disconnected terms are generated and that the symmetry restrictions of a closed-shell Fermi system are satisfied.

This section relies heavily on the previous works

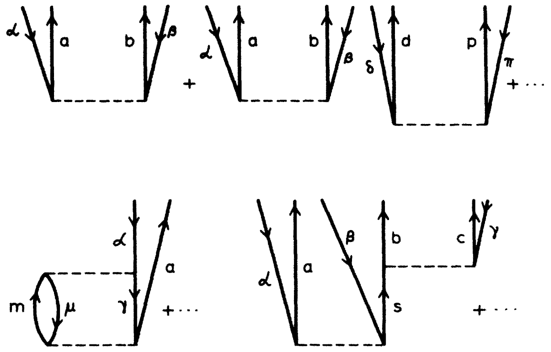

FIG. 1. Illustrative expansion of the correlated wave function which contains a pair excitation, a disconnected quadruple excitation, a single excitation, and a connected triple excitation.

of Nesbet,[15] Kelly and Sessler,[16] and Kelly[17] in order to generalize their results for the connected pair-excitation part of $|\Psi\rangle$ to all excitation numbers. Using the correspondence between the SC and LCPT expansions, an algorithm is proposed and numerically tested on the beryllium atom.

It is convenient to work in the notation of second quantization. The kth configuration of the space of j excitations can be written in terms of j-particle and hole creation operators chosen in such a manner that the symmetry restrictions are preserved:

$$|\Omega_k^j\rangle=[\eta^\dagger_{a_{k(1)}}\eta_{\alpha_{k(1)}}]\cdots[\eta^\dagger_{a_{k(j)}}\eta_{\alpha_{k(j)}}]|\phi\rangle, \tag{13}$$

where $1\leqslant j\leqslant N$.

The exact wave function can be expanded in terms of a complete set of symmetry-adapted configurations:

$$|\Psi\rangle=\sum_{j=0}^{N}\sum_{k=1}^{\infty} f_k^j|\Omega_k^j\rangle, \tag{14}$$

where k ranges over all the allowed configurations and j ranges from zero to N excitations, and where

$$f_1^0=1 \tag{15}$$

and

$$|\Omega_1^0\rangle=|\phi\rangle.$$

In order to take into account that the correlated wave function can be written in terms of linked connected or linked disconnected diagrams, define the SC coefficient f_k^j to be written as a sum of products of connected SC coefficients $F^i_{m_i}$ such that the product

$$\left[\left(\prod F^1_{m_1}\right)\left(\prod F^2_{m_2}\right)\cdots\right]^j_k \tag{16}$$

vanishes if the symmetry is not preserved in a closed-shell system.

The first few SC coefficients written in terms of products of distinct sums are given by

$$\begin{aligned}
f_k^1&=F_k^1,\\
f_k^2&=F_k^2+\sum[F^1_{m_1}F^1_{n_1}]^2_k,\\
f_k^3&=F_k^3+\sum[F^2_{m_2}F^1_{n_1}]^3_k+\sum[F^1_{m_1}F^1_{n_1}F^1_{o_1}]^3_k.
\end{aligned} \tag{17}$$

Following closely the procedures of Nesbet,[15] Kelly and Sessler,[16] and Kelly[17] the coefficients of the SC expansion are generated by considering those variations in $|\Psi\rangle$ which make the total energy a minimum, subject to the intermediate normalization constraint:

$$\delta\langle\Psi|(H-E)|\Psi\rangle=0,\quad \langle\phi|\Psi\rangle=1. \tag{18}$$

Following Nesbet,[15] it is convenient to impose the Hartree-Fock Brillouin condition upon the variations. In addition, for all unitary transformations which do not mix particle and hole states, one has for the SC matrix element between the Hartree-Fock reference configuration and all single-excitation configurations:

$$\langle\Omega_k^1|H|\phi\rangle=\langle\Omega_k^1|H_0|\phi\rangle=\langle\Omega_k^1|H_1|\phi\rangle=0\quad\text{for all } k. \tag{19}$$

In addition, it shall be assumed that both the hole and particle states are calculated using the Hartree-Fock potential constructed from the N occupied fermions, although this assumption may be relaxed. Then the variations upon $|\Psi\rangle$ which minimize the total energy subject to the above conditions yield the following expression for the connected SC coefficient:

$$\begin{aligned}
F_k^j=\frac{1}{d_k^j}\Big\{&\langle\Omega_k^j|H_1|\phi\rangle\delta(j,2)+\sum_{\substack{C\\ m\neq k}} f_m^j\langle\Omega_k^j|H_1|\Omega_m^j\rangle+\sum_C f_m^{j+2}\langle\Omega_k^j|H_1|\Omega_m^{j+2}\rangle\,\xi(j,N-2)\\
&+\sum_C f_m^{j+1}\langle\Omega_k^j|H_1|\Omega_m^{j+1}\rangle\,\xi(j,N-1)+\sum_C f_m^{j-2}\langle\Omega_k^j|H_1|\Omega_m^{j-2}\rangle\,\omega(j-1,1)+\sum_C f_m^{j-1}\langle\Omega_k^j|H_1|\Omega_m^{j-1}\rangle\,\omega(j-2,1)\Big\},
\end{aligned} \tag{20}$$

where $\sum_C$ restricts the summations to only distinct connected linked terms and where

$$\begin{aligned}
\omega(m,s)&=1\quad\text{if } m>s\\
&=0\quad\text{if } m\leqslant s
\end{aligned}$$

and

$$\begin{aligned}
\xi(m,s)&=1\quad\text{if } m\leqslant s,\\
&=0\quad\text{if } m>s.
\end{aligned}$$

The energy denominator is a generalization of the results reported by Kelly and Sessler,[16] and Kelly,[17] where

$$\begin{aligned}
d_k^j=&\sum(\epsilon_{\alpha_s}-\epsilon_{a_s})+\sum_{s,t}\langle a_{k_s}\alpha_{k_s}|v|\alpha_{k_s}a_{k_t}\rangle_x\\
&-\sum_{s<t}[\langle\alpha_{k_s}\alpha_{k_t}|v|\alpha_{k_s}\alpha_{k_t}\rangle_x\\
&\qquad+\langle a_{k_s}a_{k_t}|v|a_{k_s}a_{k_t}\rangle_x]\,\omega(j,1)\\
&+E_C-\sum_{n\neq k} f_n^2\langle\Omega_n^2|H_1|\phi\rangle\,\xi(j,N-2),
\end{aligned} \tag{21}$$

where the notation $\langle wx|v|yz\rangle_x$ represents the sum of the direct and exchange v-matrix elements.

The numerator of Eq. (20) contains three classes of SC matrix elements which can be decomposed into sums of v-matrix elements. Define a class-A SC matrix element which involves a change of two excitation numbers and which has the following decomposition:

$$\langle\Omega_k^j|H_1|\Omega_m^{j+2}\rangle=\sum_{s<t}\langle\alpha_{m_s}\alpha_{m_t}|v|a_{m_s}a_{m_t}\rangle_x\,. \tag{22}$$

Figure 2 illustrates a class-A v-matrix element which creates two excitations. Define a class-B SC matrix element which involves a change of one excitation number and which has the following decomposition:

$$\langle\Omega_k^j|H_1|\Omega_m^{j+1}\rangle=\sum_{st,np}[\langle a_{k_s}a_{m_t}|v|a_{k_p}\alpha_{m_n}\rangle_x - \langle\alpha_{m_s}\alpha_{m_t}|v|\alpha_{k_p}a_{m_n}\rangle_x]\,. \tag{23}$$

Figure 3 illustrates the class-B v-matrix elements which involve one excitation. Note that the three-hole one-particle v-matrix element tends to cancel the contribution from the three-particle one-hole v-matrix element. Define a class-C SC matrix element which involves no change of excitation number and which has the following decomposition:

$$\langle\Omega_k^j|H_1|\Omega_m^j\rangle=\sum_{st}\langle a_{k_s}\alpha_{m_t}|v|\alpha_{k_s}a_{m_t}\rangle_x + \sum_{s<t}[\langle\alpha_{m_s}\alpha_{m_t}|v|\alpha_{k_s}\alpha_{k_t}\rangle_x + \langle a_{m_s}a_{m_t}|v|a_{k_s}a_{k_t}\rangle_x]\,\omega(j,1). \tag{24}$$

Figure 4 illustrates the class-C v-matrix elements which involve no change in excitation number. The class-C v-matrix elements include the particle-particle, the hole-hole, and the particle-hole ladder diagrams, and the ring diagrams which are the exchange diagrams of the particle-hole ladder diagrams.

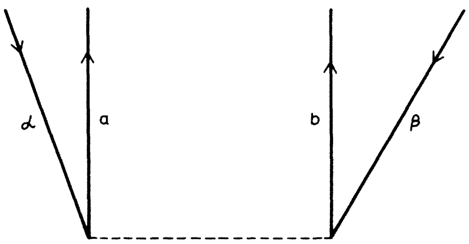

FIG. 2. Class-A v-matrix diagram which creates a pair of excitations.

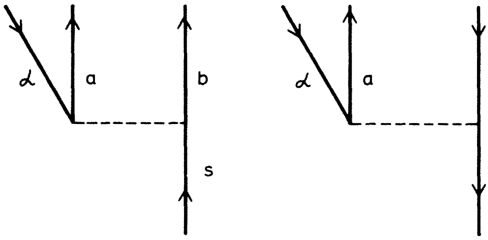

FIG. 3. Two class-B v-matrix diagrams which create an excitation.

The expression, Eq. (20), for the connected SC coefficients represents a set of coupled nonlinear equations. Under specific circumstances, the solutions may be generated by iteration as described by Nesbet,[15] Kelly and Sessler,[16] and Kelly.[17] For a closed-shell system in which the Hartree-Fock wave function is used as the reference vector, only the connected pair coefficient has a first-order contribution, whereas all other SC coefficients begin to have their contributions appearing from the second order or higher. It is also noted the second-order pair-excitation contributions arising from the class-C v-matrix elements are much more important than the corresponding second-order contributions to the single and connected triple excitations formed from class-B v-matrix elements, indicating that a considerable amount of cancellation of terms may take place. Kelly[13] has observed that the inclusion of all orders of class-C v-matrix elements is needed to obtain accurate LCPT results for closed-shell systems. Bunge[4] has also reported in his SC calculation of Be that the nonpair SC contributions amount to about 1% of the total calculated correlation energy, perhaps supporting the conjecture that there is a cancellation of terms in the formation of nonpair SC coefficients. Kelly[13,14] appears to be justified in neglecting the nonpair SC contributions in his calculations for

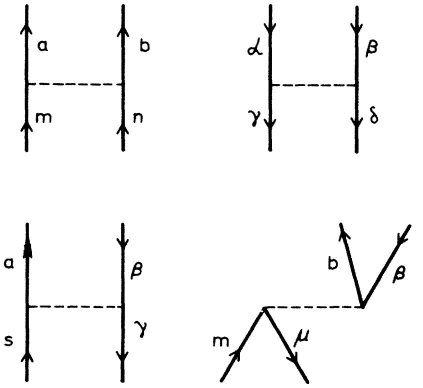

FIG. 4. Four class-C v-matrix diagrams which create no new excitations and which are solely internal modifications to a diagram.

closed-shell atoms and molecules, but he does include the single-excitation corrections in his treatment of open-shell atoms.

As pointed out previously, the expression for the connected SC coefficient was obtained by using the same procedures used by Nesbet,[15] Kelly and Sessler,[16] and Kelly[17] except that the decomposition of the SC matrix elements were done in more detail. Kelly[17] has pointed out in his paper that his energy denominator could be obtained from either the consideration of the exclusion-principle-violating (EPV)[13,17] terms of the LCPT expansion, or from SC theory by restricting the summations in the numerator to exclude the diagonal terms and the factorization of a certain subset of disconnected SC contributions and its inclusion into the energy denominator. The numerator of Eq. (20) for F_k^j restricts the summations over the decompositions of the SC matrix elements to include only distinct, linked, connected contributions to F_k^j.

In the same manner as Nesbet,[15] Kelly and Sessler,[16] and Kelly,[17] one assumes that the successive iterations of the sets of coupled SC coefficients converge. The result for a particular SC coefficient, F_k^j, will be a series expansion of linked distinct diagrams with "modified" energy denominators. Again following the method of Kelly,[17] the energy denominators may be again expanded to yield the original Brueckner-Goldstone LCPT expansion. From another point of view, Nesbet[10] has shown that the net increments in the Bethe-Goldstone hierarchy are related to sums to infinite order of subsets of linked diagrams. Since the Bethe-Goldstone and SC methods are related, Nesbet also establishes the correspondence between the LCPT and SC methods.

Since Nesbet,[15] Kelly and Sessler,[16] and Kelly[17] have established the correspondence between the LCPT and SC theories, this correspondence will be utilized in order to propose an algorithm using successive approximations. Using the insight from the LCPT expansion, it is possible to neglect on the first approximation the contribution of the nonpair SC coefficients in the expression for the connected-pair SC coefficients, thereby decoupling and linearizing Eq. (20) for the pair SC coefficients. One can then solve either a system of linear equations or else solve the system of pair SC coefficients iteratively if the system of equations requires an excessive amount of computer storage. In the latter case, making use of the correspondence between the LCPT and SC expansions may provide a means of obtaining rapid convergence by a good initialization, such as the method of "coefficients of enhancement" proposed by Kelly.[13] Having a good approximation to the pair SC coefficients, one can then construct the nonpair SC coefficients from the pair-connected SC coefficients. The procedure can then be repeated successively using the entire set of nonlinear coupled SC coefficients. This algorithm is based on the assumption that the pair SC coefficients are the dominant corrections, and that the nonpair SC coefficients are only small corrections.

The exact energy or the correlation energy is not the only interesting property obtainable from the exact wave function. Bethe and Salpeter[18] have pointed out that the accuracy of the wave function also affects the accuracy of the expectation values of the relativistic corrections, since the relativistic corrections are quite sensitive to the accuracy of the wave function in the vicinity of the atomic nucleus. It is convenient now to modify the notation somewhat.

Let

$$|\phi^{abc\cdots k}_{\alpha\beta\gamma\cdots\kappa}\rangle = \eta_a^\dagger \eta_\alpha \cdots \eta_k^\dagger \eta_\kappa |\phi\rangle , \tag{25}$$

where $[a\alpha]$ corresponds to the first excitation, $\eta_a^\dagger \eta_\alpha$, etc., and where

$$C^{abc\cdots k}_{\alpha\beta\gamma\cdots\kappa} \tag{26}$$

is the corresponding connected SC coefficient, and

$$c^{abc\cdots k}_{\alpha\beta\gamma\cdots\kappa} \tag{27}$$

is the corresponding SC coefficient composed of sums of products of disconnected SC coefficients.

Given the Hermitian operators O_1 and O_2, representing some one- and two-electron operators, respectively, their expectation values in terms of the exact SC wave function are given approximately by

$$\begin{aligned}\langle O_1\rangle &= \frac{\langle\Psi|O_1|\Psi\rangle}{\langle\Psi|\Psi\rangle} \\ &\simeq \frac{\langle\phi|O_1|\phi\rangle + 2\sum C^a_\alpha \langle\phi^a_\alpha|O_1|\phi\rangle + \sum\sum C^{ab}_{\alpha\beta} C^{st}_{\sigma\tau}\langle\phi^{ab}_{\alpha\beta}|O_1|\phi^{st}_{\sigma\tau}\rangle}{1+\sum|C^{ab}_{\alpha\beta}|^2\cdots} , \\ \langle O_2\rangle &= \frac{\langle\Psi|O_2|\Psi\rangle}{\langle\Psi|\Psi\rangle} \\ &\simeq \frac{\langle\phi|O_2|\phi\rangle + 2\sum C^{ab}_{\alpha\beta}\langle\phi^{ab}_{\alpha\beta}|O_2|\phi\rangle}{1+\sum|C^{ab}_{\alpha\beta}|^2\cdots} .\end{aligned} \tag{28}$$

In the expression for $\langle O_1 \rangle$, both the single excitation and the product of two pair SC coefficients were included since they would be expected to have the same magnitude. That is, a single-excitation coefficient first appears in the second-order LCPT, whereas the pair-connected SC coefficient appears for the first time in first-order LCPT. The use of the correspondence between the two theories has many applications.

IV. OUTLINE OF THE COMPUTATIONAL METHODS

The spectrum of virtual states of Be was calculated in the field of N electrons. Kelly[13] has shown that for the cases he considered the V^n potential is too weak to support any bound excited states. The virtual states were calculated for $l=0$, 1, and 2, ranging from a momentum value of $k=0.0$ a.u. to $k=126$ a.u. The atom was enclosed in a large sphere of radius 50 a.u., where the radial wave function was forced to vanish. The V^N potential is effectively quite small beyond 10 a.u., where the radial wave function behaves as a phase-shifted spherical Bessel function of orbital angular momentum l. In the region where the V^N potential is not negligible, the radial wave functions were calculated numerically using a modification of the algorithm developed by Robertson.[19] The analytical and numerical solutions were required to match at $r=10$ a.u.

The expressions for the SC coefficients are coupled sets of nonlinear integral equations which are transformed into a large number of coupled nonlinear equations when finite difference methods are used. On the first approximation, these equations were decoupled and linearized.

The nonpair SC coefficients, to a good approximation, can be formed from the unknown pair SC coefficients. One could estimate the pair SC coefficients by the first-order contribution or by means of Kelly's[13] method of the coefficients of enhancement $Ce(\alpha\beta, l)$, which account for an infinite number of EPV hole-particle, higher-order EPV terms, and the l-constant particle-particle ladder diagrams.

Using Kelly's[13] coefficients of enhancement, the approximate pair SC coefficient can be estimated from the first-order perturbation contribution by

$$C^{ab}_{\alpha\beta}(l) = Ce(\alpha\beta, l)\langle ab, l|v|\alpha\beta\rangle_x / d^{ab}_{\alpha\beta}\,. \tag{29}$$

Using the approximate expression for the connected-pair SC coefficient given by Eq. (29), the connected single- and triple-excitation terms were calculated by the following approximations:

$$C^{a}_{\alpha} = \sum C^{st}_{\sigma\tau}\langle \phi^{a}_{\alpha}|H_1|\phi^{st}_{\sigma\tau}\rangle / d^{a}_{\alpha}\,, \tag{30}$$

$$C^{abc}_{\alpha\beta\gamma} = \sum C^{st}_{\sigma\tau}\langle \phi^{abc}_{\alpha\beta\gamma}|H_1|\phi_{\sigma\tau}\rangle / d^{abc}_{\alpha\beta\gamma}\,,$$

where the higher-order corrections were neglected.

The contribution of the single, triple, and disconnected triple excitations first appears in second-order perturbation theory, and third order in their contributions to the pair SC coefficient, or fourth order in the correlation energy. The single- and triple-excitation contributions to $C^{ab}_{\alpha\beta}(l)$ appear to exhibit a considerable amount of cancellation, in addition to being small in magnitude. The contributions from the quadruple excitations are small from the results of Kelly[17] since the disconnected terms have been factored out and included in the energy denominator.

Kelly[13] has shown in his calculations for Be that the three-body terms are small corrections to the total correlation energy. For this reason, it was sufficient to calculate the three-body corrections once.

It was found to be convenient to lump the small corrections which were only iterated once, such as the three-body, single, triple, and quadruple contributions to $C^{ab}_{\alpha\beta}(l)$, by the sum $NP^{ab}_{\alpha\beta}(l)$,

$$NP^{ab}_{\alpha\beta}(l) = \frac{1}{d^{ab}_{\alpha\beta}}\Big\{\sum C^{ab}_{\gamma\delta}\langle\gamma\delta|v|\alpha\beta\rangle_x + \sum_{\delta,d}\left[C^{ad}_{\alpha\delta}(l)\langle d\beta|v|\delta b\rangle_x + C^{db}_{\delta\beta}(l)\langle d\alpha|v|\delta a\rangle_x\right]$$
$$+ \sum_{C} c^{s}_{\sigma}\langle\phi^{ab}_{\alpha\beta}|H_1|\phi^{s}_{\sigma}\rangle + \sum_{C} c^{rst}_{\rho\sigma\tau}\langle\phi^{ab}_{\alpha\beta}|H_1|\phi^{rst}_{\rho\sigma\tau}\rangle + \sum_{C} c^{prst}_{\pi\rho\sigma\tau}\langle\phi^{ab}_{\alpha\beta}|H_1|\phi^{prst}_{\pi\rho\sigma\tau}\rangle\Big\}\,, \tag{31}$$

where the energy denominator is given by Kelly's[13] prescription when the virtual states are in the continuum.

The contribution of the set of coefficients $[NP^{ab}_{\alpha\beta}(l)]$ to the pair-correlation energy of Be is −0.00029 a.u. for the 1s-1s pair and −0.00052 a.u. for the 2s-2s pair, which is in good agreement with the results of Bunge[4] and Kelly.[13] Since these corrections are small, they were iterated only once.

The "exact" pair SC coefficients are given by

$$C^{ab}_{\alpha\beta}(l) = \langle ab, l|v|\alpha\beta\rangle_x / d^{ab}_{\alpha\beta} + NP^{ab}_{\alpha\beta}(l) + L^{ab}_{\alpha\beta}(l) + \lambda(l) DL^{ab}_{\alpha\beta}(l), \tag{32}$$

where

$$L^{ab}_{\alpha\beta}(l_i)=\frac{1}{d^{ab}_{\alpha\beta}}\left\{\frac{2}{\pi}\int dk\{c^{kb}_{\alpha\beta}(l_i)[\langle k\alpha, l_i|v|\alpha a, l_i\rangle_x+\langle k\beta, l_i|v|\beta a, l_i\rangle_x]+c^{ak}_{\alpha\beta}(l_i)[\langle k\alpha, l_i|v|\beta b, l_i\rangle_x\right.$$
$$\left.+\langle k\beta, l_i|v|\beta b, l_i\rangle_x]\}+\left(\frac{2}{\pi}\right)^2\int dk_1\,dk_2\,c^{k_1k_2}_{\alpha\beta}(l_i)\langle k_1\,k_2, l_i|v|ab, l_i\rangle_x\right\}, \tag{33}$$

and where

$$DL^{ab}_{\alpha\beta}(l_i)=\frac{1}{d^{ab}_{\alpha\beta}}\sum_{j\neq i}\left(\frac{2}{\pi}\right)^2\iint dk_1\,dk_2\,c^{k_1k_2}_{\alpha\beta}(l_j)\langle k_1\,k_2, l_j|v|ab, l_i\rangle_x, \tag{34}$$

where $\lambda(l_i)$ is a parameter between zero and one, which is chosen to accelerate convergence in the iterative cycling of Eq. (32). $\lambda(l_i)$ is brought up slowly from zero to unity as the iteration number increases. The methods of analytic continuation and invariant imbedding are discussed by Laasonen[20] and by Ortega and Rheinboldt.[21]

The coefficients $\{L^{ab}_{\alpha\beta}(l_i)\}$ are the contributions from the l-constant particle-particle and hole-particle EPV interactions, and the coefficients $\{DL^{ab}_{\alpha\beta}(l_i)\}$ are the contributions from the l-changing particle-particle interactions. The set of SC coefficients converged rapidly in the iterative scheme except for that of the Be $2s$-$2s$ pair. Because the l-changing corrections are large in the Be $2s$-$2s$ pair, it was required to introduce the acceleration parameter λ and iterate longer.

Bunge[4] used the first three partial waves to obtain his set of virtual orbitals, and used the Slater-type s, p, d orbitals to finally generate his set of natural orbitals. A comparison of the results obtained by Bunge using natural orbitals and by this work are presented in Table I.

Table II presents the results of the Be calculations using the approximate SC scheme. In this calculation, the total correlation energy of Be (using an S, P, D basis) is −0.09092 a.u. with respect to Clementi's[22] RHF wave function, $E_{\mathrm{RHF}}(\mathrm{Be})=-14.573\,020$ a.u. The total energy of Be using the *spd* basis as determined by this calculation is −14.66394 a.u.

Byron and Joachain[23] have estimated the contributions to the pair-correlation energies of Be for the partial waves $l \geq 3$. Their pair-correlation energies are accurate to second order in perturbation. (See Table III.)

Byron and Joachain[23] obtained their second-order pair energies without considering the shifted energy denominators. Kelly[13] has shown that the use of shifted energy denominators affects the second-order pair energies. Further, the inclusion of the EPV hole-particle and l-constant particle-particle interactions tends to lower the pair energies, whereas the l-changing particle-particle interactions have a pronounced effect on increasing the Be $2s$-$2s$ pair energies, but are only of minor importance with the Be $1s$-$1s$ and $1s$-$2s$ pair-correlation energies.

It is observed that the S and P waves account for most of the $1s$-$1s$ pair-correlation energy. However, only the P waves are significant in the considerations of the Be $2s$-$2s$ pair energy. The D-wave contributions may be considered to be the first term in the asymptotic expansion of the remaining l partial waves, and one may speculate on the behavior of the remaining partial-wave correlation energies. It is noticed that the second-order D-wave pair energy for the $1s$-$1s$ correlation is approximately the same as the so-called exact terms of Kelly and of this work. But the so-called D-wave contribution to the $2s$-$2s$ pair energy is roughly one-third that of the second-order result.

Bunge[4] used the results of Ahlrichs and Kutzelnigg[24] to estimate the f- and g-orbital contributions to the $2s$-$2s$ pair energy; the sum of these energies is −0.0040 a.u. This result is likely to be too high since the l-changing diagrams have not been accounted for. It is assumed that the $1s$-$1s$ and $1s$-$2s$ asymptotic l-pair energies are essentially correct, and that −0.0018 a.u. is a reasonable estimate for the remaining l-corre-

TABLE I. *spd* limits of the pair-correlation energies of Be.

	E_c ($1s$-$1s$)	E_c ($2s$-$2s$)	E_c ($1s$-$2s$)	Total
Bunge[a]	−0.041 21	−0.045 10	−0.005 24	−0.091 55
This work	−0.040 72	−0.044 60	−0.005 1	−0.090 92

[a] Reference 4.

TABLE II. Pair-correlation energies of Be (SC formalism of this work).

Pair	S wave	P wave	D wave	Total
$1s$-$1s$	−0.013 11	−0.023 65	−0.003 96	−0.040 72
$2s$-$2s$	−0.002 40	−0.040 97	−0.001 21	−0.044 6
$1s$-$2s$	−0.000 9	−0.003 9	−0.000 3	−0.005 1

TABLE III. Second-order pair correlations of Be for $l \geq 3$, taken from Byron and Joachain. (The estimated E_C from Tables II and III is −0.094 42 a.u., which is an overestimate.)

Pair	$\sum_{l=3}^{\infty} E_C(ms,ns,l)$
1s-1s	−0.001 78
2s-2s	−0.002 20
1s-2s (triplet)	−0.000 006
1s-2s (singlet)	−0.000 034

TABLE IV. Comparison of the numerical Be correlation energy.

Author (Ref.)	E_C (1s, 1s)	E_C (2s, 2s)	E_C (1s, 2s)	E_C
Kelly (13)	−0.042 12	−0.044 88	−0.005 0	−0.092 0
Byron and Joachain (23)	−0.042 47	−0.044 82	−0.005 24	−0.092 5
Bunge (4)	−0.042 61	−0.045 50	−0.005 30	−0.093 4
Nesbet (10)	−0.041 83	−0.041 83	−0.005 86	−0.092 05
Sims and Hagstrom (5)	···	···	···	−0.093 52
This work[a]	−0.042 52	−0.045 40	−0.005 20	−0.093 12
Reference (25)	···	···	···	−0.094 4

[a] The results include estimates of the calculated *spd* and $l \geq 3$ correlation effects.

lation energy of the 1s-1s pair. However, a conservative estimate of the Be 2s-2s pair energy for $l \geq 3$ would be −0.0008 a.u. Table IV lists the sum of the *spd*-limit pair-correlation energies and the estimated corrections to the remaining partial waves.

V. CONCLUSIONS

The algorithm presented in this paper was based on the assumption that the reference wave function is a symmetry-adapted closed-shell Hartree-Fock wave function and that the Hartree-Fock potential V^N was used to generate the spectrum of virtual states. Kelly[13,14] has shown that the V^{N-1} potential is more physically realistic and that the LCPT expansion will converge much more quickly with virtual states calculated from this potential. Silverstone and Yin[26] and Huzinaga and Arnau[27] have discussed the arbitrariness of the virtual states in Hartree-Fock theory. There is a great deal of arbitrariness in the choice of these orbitals with the restriction that they be orthogonal to the ground-state orbitals and to themselves. It appears that the optimal choice of these orbitals has not been settled.

A point of concern is the slow convergence of the l expansion of the Be 2s-2s pair-correlation energies. Although the s, p, and d virtual orbitals do account for most of the Be 2s-2s pair-correlation energy, the asymptotic l series is quite important. The remaining correlation energy is most likely a poor estimate of the higher l-value corrections and the effect of the l-changing diagrams upon these corrections, rather than a poor estimate of the nonpair SC terms to the pair correlation energy. Perhaps the method of Sims and Hagstrom,[5] which directly used the r_{ij} term, should be incorporated in further LCPT and SC calculations to speed up the slow convergence of the partial-wave correlation energies.

The amount of cancellation exhibited in the construction of the nonpair SC terms would depend upon the physics of the many-body system. It would be advisable to study this on a larger atom such as Ne. (See Fig. 5 and Fig. 6 for examples of singly and triply excited diagrams.) It was pointed out by Kelly[13] that although the three-body diagrams are small in Be, they become increasingly more important in larger atoms. Micha[28] also reached the same conclusion as Kelly in his study of Ne. Since the single- and triple-excitation terms contribute to the self-energy corrections of the hole and particle states, it would be safe to assume that for atomic Hartree-Fock closed-shell wave functions, such corrections would most likely be small corrections.

Bethe and Salpeter[18] pointed out that the accuracy

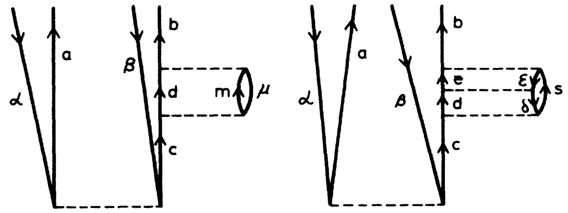

FIG. 5. Two diagrams which illustrate the "self-energy" corrections to a particle line.

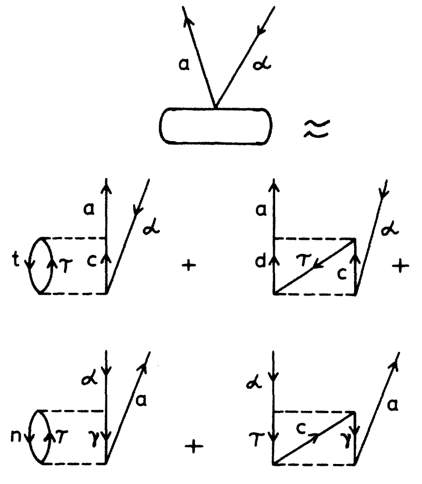

FIG. 6. Single-excitation SC diagram which is approximated by four Feynman diagrams of second-order perturbation theory.

of the relativistic energy corrections obtained from a nonrelativistic wave function depends strongly on the amount of correlation included. This would suggest that the relativistic corrections should be calculated using correlated wave functions, thereby yielding better estimates of the correlation energy.[29]

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*Present address: U. S. Bureau of Mines, 4800 Forbes Ave., Pittsburgh, Pa. 15213.

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