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Multiconfiguration Hartree-Fock method and many-body perturbation theory: A unified approach

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The multiconfiguration Hartree-Fock theory and many-body perturbation theory are combined in a calculation of the correlation energy of the ground state of the neutral beryllium atom. For this purpose the two-component Be multiconfiguration Hartree-Fock wave function is treated as a reference state and perturbation theory is used to systematically improve upon the accuracy of this function. The correlation energy of each pair of occupied orbitals is determined by solving numerically a coupled set of two-particle inhomogeneous equations. A detailed comparison is made with other beryllium calculations.

I. INTRODUCTION

Over the years extensive atomic calculations have been carried out using the multiconfiguration Hartree-Fock method (MCHF) and many-body perturbation theory (MBPT). Although accurate calculations can be performed with either scheme, these methods are clearly at their best under quite different circumstances. The MCHF method is most effective at capturing the dominant correlation effects which describe the dynamics of a many-electron state at a qualitative level; however, one often encounters difficulties with the method in dealing with a series of weakly interacting states. In Fig. 1 we show the percent of outer correlation that is included by MCHF expansions of varying length for the ground state of Be. While the first few configurations capture appreciable amounts of correlation, one rapidly approaches a region of diminishing returns in which increasing the length of the expansion by an order of magnitude only has a marginal effect.

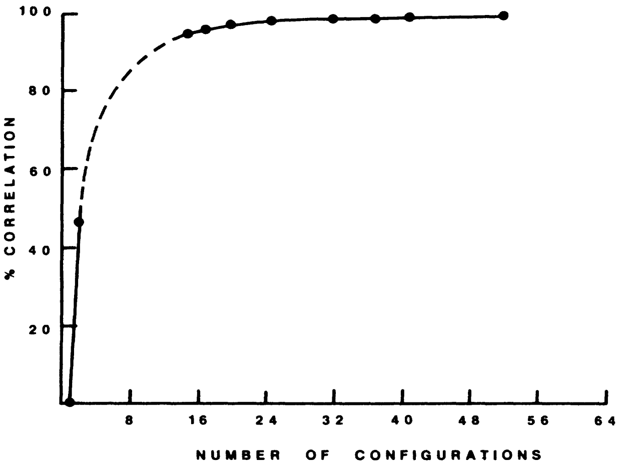

FIG. 1. Plot of percentage of correlation vs the number of configurations.

Perturbation theory, on the other hand, has exactly the opposite characteristics—large correlation effects are difficult to incorporate but a large number of small effects can readily be included. In a perturbation calculation on Be, for instance, Lindgren and Salmonson[1] found it necessary to go to 12th order in the perturbation theory to obtain convergence for the correlation energy of the $2s^2$ pair. The reason for this, of course, is that the $1s^22s^2$ and $1s^22p^2$ configurations of beryllium interact quite strongly and perturbation theory is poorly suited for calculating such a strong effect. The ideal approach could very well be a combination of these two methods.

Although this paper describes an atomic calculation, we would like to point out that the formal difficulties associated with combining the MCHF and MBPT approaches is quite relevant for molecular calculations as well. Perturbation theory has the advantage over the ordinary configuration-interaction (CI) approach that it is size consistent, that is, by including diagrams corresponding to disconnected pairs (so-called coupled-cluster diagrams) the theory has the proper asymptotic dependence in the limit in which the molecule separates into two parts. For this reason perturbation theory is ideally suited to the calculation of disassociation processes. Since the weight of the various electronic configurations in the ground-state wave function of a molecule depends generally upon the internuclear distances, however, it is important to use multiconfigurational wave functions to study molecular disassociation and coupled-cluster effects. These fundamental considerations are, of course, widely recognized and are responsible for the large number of multireference calculations that have been reported recently.[2] The point which we would like to emphasize here is that due to the relative ease and flexibility of atomic calculations, atomic theory provides a good testing ground for the most suitable ways of combining the MCHF and MBPT approaches. Even though our calculation here is on an atomic system, we shall take care to preserve the size consistency of the theory. In any case, to be effective we must use a form of many-body theory that is concise and well suited to the MCHF method.

The many-body perturbation formalism was developed by Brueckner[3] and Goldstone[4] and first applied to atomic systems by Kelly.[5] In these early calculations, Kelly explicitly constructed a complete set of eigenfunctions of the approximate Hamiltonian (H_0 say), and then treated the difference between H and H_0 as a perturbation. Perturbation calculations for bound-state systems can be carried out much more readily, however, by solving inhomogeneous one- and two-particle equations for the linear combinations of excited states that contribute to the Goldstone diagrams. Single-particle equations have been used by Sternheimer[6] to evaluate the effect of quadrupole shielding, by Dalgarno and Lewis[7] in their study of dipole polarizability, and by others.[8] Accurate methods for solving the two-particle equation were first developed by Musher and Schulman[9] and also by McKoy and Winter.[10] Such equations have been applied in perturbation calculations by Schulman and Lee[11] and by Morrison.[12] More recently, this approach has been used extensively by Garpman and co-workers at Chalmers University of Technology, Gothenburg, Sweden, where the numerical methods have been improved considerably.[13] The solution subroutines of the pair program which we have used in this calculation are essentially the same as those in Mårtensson-Pendrill's recent version of the Gothenburg code.[14] We have modified these subroutines slightly and altered them to read wave functions and lists of angular coefficients produced by our software package.[15]

In this paper, we combine the MCHF and MBPT approaches in a calculation of the correlation energy of Be. Some preliminary results of this calculation have been reported recently.[16] In the next section we consider the excitations from the valence shell from quite a general point of view in order to gain some insight into the general structure of the theory. Then in the following section we derive equations for the valence excitations by explicitly adding the Goldstone diagrams for excitations from the $2s^2$ and $2p^2$ pairs. One of the surprising features of the theory which emerges is that the ground state of Be, $a\mid 1s^22s^2\,{}^1S\rangle+b\mid 1s^22p^2\,{}^1S\rangle$, is coupled to the other linear combination of the $\mid 1s^22s^2\,{}^1S\rangle$ and $\mid 1s^22p^2\,{}^1S\rangle$ states by the approximate Hamiltonian H_0. In Sec. IV we consider excitations of the core orbitals.

II. GENERAL STRUCTURE OF THE THEORY

Our aim now is to obtain an approximate solution of the Schrödinger equation

$$H\Psi_\alpha=E_\alpha\Psi_\alpha \tag{1}$$

for the neutral beryllium atom. For this purpose, we separate the Hamiltonian into an approximate or model Hamiltonian H_0 and a perturbation V:

$$H=H_0+V\,. \tag{2}$$

We shall suppose that H_0 and V are of the general form

$$H_0=\sum_i\left[-\tfrac{1}{2}\nabla_i^2-\frac{Z}{r_i}+u_i\right]=\sum_i h_0(i)\,, \tag{3}$$

$$V=\sum_{\substack{i,j\\(i<j)}}1/r_{ij}-\sum_i u_i\,, \tag{4}$$

and the eigenstates of h_0 may be written

$$\psi(nlm_sm_l)=r^{-1}P_{nl}(r)Y^l_{m_l}(\theta,\psi)\chi_{m_s}\,. \tag{5}$$

The eigenstates of H_0, for which a certain number of the single-particle states (5) are occupied, can be used to partition the Hilbert space into a model space and an orthogonal space.

Since the $\mid 1s^22p^2\,{}^1S\rangle$ state of Be mixes strongly with the $\mid 1s^22s^2\,{}^1S\rangle$ state, we include both of these states in our model space. The lowest eigenstate of H then has its two leading components in the model space

$$\Psi_\alpha=a\mid 1s^22s^2\,{}^1S\rangle+b\mid 1s^22p^2\,{}^1S\rangle+\cdots\,. \tag{6}$$

We shall denote the component of Ψ_α within the model space by Ψ_α^0

$$\Psi_\alpha^0=P\Psi_\alpha=a\mid 1s^22s^2\,{}^1S\rangle+b\mid 1s^22p^2\,{}^1S\rangle \tag{7}$$

and suppose that it is normalized

$$\langle\Psi_\alpha^0\mid\Psi_\alpha^0\rangle=1\,. \tag{8}$$

A two-configuration MCHF calculation for the lowest ${}^1S$ state of Be yields

$$a=0.950\,034\,4,\quad b=0.312\,145\,1\,. \tag{9}$$

What we would like to do now is to develop a perturbative procedure for calculating corrections to the MCHF method. For this purpose it is convenient to introduce a wave operator, Ω which acts upon the model space and generates the corresponding eigenfunctions of H,

$$\Psi_\alpha=\Omega\Psi_\alpha^0\,. \tag{10}$$

The projection operator (7) and the wave operator (10) are illustrated in a simple way in Fig. 2. The operator P projects the eigenfunctions of H upon the model space and Ω generates them back from the model functions. A thorough treatment of these aspects of perturbation theory is given in a recent book.[17]

In order to obtain the Rayleigh-Schrödinger expansion, we must eliminate the energy from our basic equations. To do this we multiply the Schrödinger equation (1) first with P and then with Ω to obtain

$$\Omega PH\Omega\Psi_\alpha^0=E\Psi_\alpha\,, \tag{11}$$

where we have used Eqs. (7) and (10). Now subtracting Eq. (1) from Eq. (11) and using the properties of the projection operators we obtain

$$(\Omega H_0-H_0\Omega)\Psi_\alpha^0=V\Omega\Psi_\alpha^0-\Omega PV\Omega\Psi_\alpha^0\,. \tag{12}$$

This generalized form of the Bloch equation was first obtained by Lindgren.[18]

We can now use Eq. (12) to evaluate the matrix elements of the wave operator Ω between the model and the orthogonal spaces. However, when H_0 operates on the

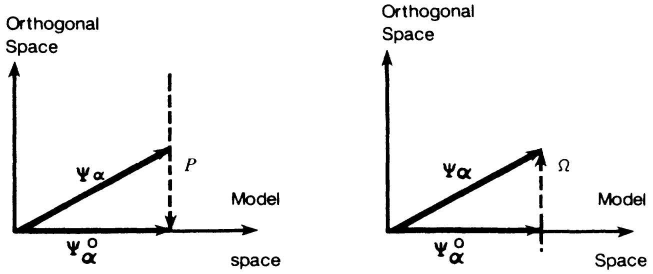

FIG. 2. Illustration of the wave operation (Ω) and the projection operator (*P*). *P* projects out of any function the component in the model space, and the wave operator generates the exact wave function Ψ_α by operating on the model function Ψ^0_α.

model function (7) to the right, it will produce

$$H_0\Psi^0_\alpha=2\epsilon_{2s}a \mid 1s^2 2s^2\,{}^1S\rangle +2\epsilon_{2p}b \mid 1s^2 2p^2\,{}^1S\rangle+2\epsilon_{1s}\Psi^0_\alpha\,. \qquad (13)$$

Thus because Ψ^0_α is not an eigenfunction of H_0, we cannot use Eq. (12) without decomposing Ψ^0_α into its component parts. This is certainly a disadvantage. We would like to treat the MCHF state as a single reference function, and we know that any decomposition of this kind will inevitably lead to intruder state problems. In order to avoid this difficulty we insert a complete set of states between Ω and H_0 in the first term of Eq. (12),

$$\Omega H_0\Psi^0_\alpha=\Omega\sum_\beta \mid\beta\rangle\langle\beta\mid H_0\mid\alpha\rangle =\Omega\langle\alpha\mid H_0\mid\alpha\rangle\Psi^0_\alpha+\Omega P_\perp H_0\Psi^0_\alpha\,, \qquad (14)$$

where $P_\perp$ is the projection operator for the linear combination of the states $\mid 1s^2 2s^2\,{}^1S\rangle$ and $\mid 1s^2 2p^2\,{}^1S\rangle$ that is orthogonal to the MCHF ground state. Substituting Eq. (14) into Eq. (12) and taking the term $\Omega P_\perp H_0\Psi^0_\alpha$ over to the right-hand side we obtain the basic equation

$$(\Omega\langle\alpha\mid H_0\mid\alpha\rangle-H_0\Omega)\Psi^0_\alpha=V\Omega\Psi^0_\alpha-\Omega PV\Omega\Psi^0_\alpha -\Omega P_\perp H_0\Psi^0_\alpha\,. \qquad (15)$$

In the next section we shall derive equations of this kind by explicitly adding together the Goldstone diagrams for excitations from the $2s^2$ and $2p^2$ pairs. At this point we only make a few observations.

When Eq. (15) is expressed in diagrams the additional term $\Omega P_\perp H_0$ will generally be linked and so our basic equation leads to a linked diagram theorem and size consistency is preserved. This would not be true if, for instance, we had added $\Omega PV\Psi^0$ to each side of the equation in order to transform $\Omega H_0\Psi^0_\alpha$ into $\Omega PH\Psi^0_\alpha$.

Equation (15) differs from the generalized Bloch equation by the last term on the right. This term couples the MCHF functions to the orthogonal linear combination of the states $\mid 1s^2 2s^2\,{}^1S\rangle$ and $\mid 1s^2 2p^2\,{}^1S\rangle$ by means of the approximate Hamiltonian H_0. As we shall see this leads to a two-component theory.

III. EXCITATIONS FROM THE VALENCE SHELL

Figure 3(a) shows a Goldstone diagram which describes the excitation of a pair of valence electrons (p,q) into excited states (r,t). This diagram corresponds to the two-particle wave function

$$\eta(pq\rightarrow(l_r l_t)^1S) =\sum_{n_r,n_t} \mid(n_r l_r,n_t l_t)^1S\rangle \times\frac{\langle(n_r l_r,n_t l_t)^1S\mid 1/r_{12}\mid(n_p l_p,n_q l_q)^1S\rangle}{\varepsilon_p+\varepsilon_q-\varepsilon_r-\varepsilon_r}\,. \qquad (16)$$

In addition to the wave function for the excited state, $\mid(n_r l_r,n_t l_t)^1S\rangle$, there is a matrix element corresponding to the dotted interaction line and an energy denominator, which is the negative of the excitation energy. Both the valence electrons and the excited electrons are coupled together to form an *S* state. Clearly this is a two-particle function that does not explicitly depend on the 1*s* electrons. We shall refer to the two valence electrons by 1 and 2.

By multiplying Eq. (16) from the left with $[\varepsilon_p+\varepsilon_q-h_0(1)-h_0(2)]$ we obtain the pair equation

$$[\varepsilon_p+\varepsilon_q-h_0(1)-h_0(2)]n(pq\rightarrow(l_r l_t)^1S) =\sum_{n_r n_t} \mid(n_r l_r,n_t l_t)^1S\rangle \times\langle(n_r l_r,n_t l_t)^1S\mid 1/r_{12}\mid(n_p l_p,n_q l_q)^1S\rangle\,. \qquad (17)$$

The sum over n_r and n_t may be removed by making use of the completeness relation for the single-particle states.

We are interested now in deriving an equation which describes the excitation of a pair of electrons from the MCHF state described by Eqs. (7) and (9). So we multiply Eq. (17) for the case, $p=q=2s$, by *a* and add Eq. (17) for the case, $p=q=2p$, times *b*

$$[2\varepsilon_{2s}-h_0(1)-h_0(2)]a\eta(2s^2\rightarrow(l_r l_t)^1S)+[2\varepsilon_{2p}-h_0(1)-h_0(2)]b\eta(2p^2\rightarrow(l_r l_t)^1S) =\sum_{n_r,n_t} \mid(n_r l_r,n_t l_t)^1S\rangle\langle(n_r l_r,n_t l_t)^1S\mid 1/r_{12}\mid a\psi(2s^2\,{}^1S)+b\psi(2p^2\,{}^1S)\rangle\,. \qquad (18)$$

We note here that the right-hand sides have combined to produce a matrix element involving the state $a\psi(2s^2\,{}^1S)+b\psi(2p^2\,{}^1S)$; however, due to the fact that the single-particle energies, $2\varepsilon_{2s}$ and $2\varepsilon_{2p}$ are not the same, it has not been possible to combine the two terms on the left-hand side of this equation. To deal with this problem we first take the inner product of Eq. (18) from the left with a particular excited state $\langle(n_r l_r,n_t l_t)^1S\mid$ to obtain

$$(2\varepsilon_{2s}-\varepsilon_r-\varepsilon_t)a\langle(n_r l_r,n_t l_t)^1S\mid\Omega^{(1)}\mid 2s^2\,{}^1S\rangle+(2\varepsilon_{2p}-\varepsilon_r-\varepsilon_t)b\langle(n_r l_r,n_t l_t)^1S\mid\Omega^{(1)}\mid 2p^2\,{}^1S\rangle =\langle(n_r l_r,n_t l_t)^1S\mid 1/r_{12}\mid a\psi(2s^2\,{}^1S)+b\psi(2p^2\,{}^1S)\rangle\,, \qquad (19)$$

where $\Omega^{(1)}$ is the first-order term in the expansion of the wave operator. We now make use of the fact that ε_{2s} and ε_{2p} are *different* eigenvalues of the *same* operator, h_0, and write Eq. (19) in the following way:

$$\langle (n_r l_r, n_t l_t)^1S \mid \Omega^{(1)}[h_0(1)+h_0(2)] \mid a\psi(2s^2\,{}^1S)+b\psi(2p^2\,{}^1S)\rangle$$
$$-(\varepsilon_r+\varepsilon_t)\langle (n_r l_r, n_t l_t)^1S \mid \Omega^{(1)} \mid a\psi(2s^2\,{}^1S)+b\psi(2p^2\,{}^1S)\rangle = \langle (n_r l_r, n_t l_t)^1S \mid 1/r_{12} \mid a\psi(2s^2\,{}^1S)+b\psi(2p^2\,{}^1S)\rangle \ . \tag{20}$$

This last equation is fairly simple, but we have here the same problem that we encountered in the last section: $[h_0(1)+h_0(2)]$ will mix into the model function the orthogonal linear combination of the states $2s^2$ and $2p^2$. Since it should be clear by now that we are being led into a two-component theory we make the following definitions:

$$\psi_- = a\psi(2s^2\,{}^1S)+b\psi(2p^2\,{}^1S) \ , \tag{21a}$$

$$\psi_+ = -b\psi(2s^2\,{}^1S)+a\psi(2p^2\,{}^1S) \ . \tag{21b}$$

Here ψ_- is related to the MCHF ground state and ψ_+ is the model function that is orthogonal to this state. Our notation is analogous to that used for two spin states. With this notation we again insert a complete set of states between the operators $\Omega^{(1)}$ and $[h_0(1)+h_0(2)]$ in Eq. (20) and carry the nondiagonal term over to the right-hand side to obtain

$$(\langle \psi_- \mid H_0 \mid \psi_- \rangle - \varepsilon_r - \varepsilon_t)\langle (n_r l_r, n_t l_t)^1S \mid \Omega^{(1)} \mid \Psi_- \rangle$$
$$= \langle (n_r l_r, n_t l_t)^1S \mid 1/r_{12} \mid \psi_- \rangle - \langle (n_r l_r, n_t l_t)^1S \mid \Omega^{(1)} \mid \psi_+ \rangle \langle \psi_+ \mid H_0 \mid \psi_- \rangle \ . \tag{22}$$

Finally, we multiply this last equation by $\mid (n_r l_r, n_t l_t)^1S \rangle$ and sum over n_r and n_t to obtain

$$[\langle \psi_- \mid H_0 \mid \psi_- \rangle - h_0(1) - h_0(2)]\eta_-({}^1S \to (l_r l_t)^1S)$$
$$= \sum_{n_r, n_t} \mid (n_r l_r, n_t l_t)^1S \rangle \langle (n_r l_r, n_t l_t)^1S \mid 1/r_{12} \mid \psi_- \rangle - \langle \psi_+ \mid H_0 \mid \psi_- \rangle \eta_+({}^1S \to (l_r l_t)^1S) \ , \tag{23}$$

where $\eta_-({}^1S \to (l_r l_t)^1S)$ $[\eta_+({}^1S \to (l_r l_t)^1S)]$ is the pair function that describes the excitation of two electrons from the ψ_- $[\psi_+]$ state.

Equation (23) and the equation obtained by the interchange $- \leftrightarrow +$ are the basic equations we shall use to describe excitations from the valence shell. These equations may be solved iteratively by first solving the "uncoupled" equations obtained by neglecting the last term in Eq. (23).

$$[\langle \psi_\pm \mid H_0 \mid \psi_\pm \rangle - h_0(1) - h_0(2)]\eta_\pm^{\mathrm{uc}}({}^1S \to (l_r l_t)^1S)$$
$$= \sum_{n_r, n_t} \mid (n_r l_r, n_t l_t)^1S \rangle \langle (n_r l_r, n_t l_t)^1S \mid 1/r_{12} \mid \psi_\pm \rangle \tag{24}$$

and then solving for the difference between the "coupled" and "uncoupled" functions

$$[\langle \psi_- \mid H_0 \mid \psi_- \rangle - h_0(1) - h_0(2)]\Delta\eta_-$$
$$= \langle \psi_+ \mid -H_0 \mid \psi_- \rangle \eta_+ \ , \tag{25a}$$

$$[\langle \psi_+ \mid H_0 \mid \psi_+ \rangle - h_0(1) - h_0(2)]\Delta\eta_+$$
$$= \langle \psi_- \mid H_0 \mid \psi_+ \rangle \eta_- \ . \tag{25b}$$

Here $\Delta\eta_-$ and $\Delta\eta_+$ are given by the equation

$$\Delta\eta_\pm = \eta_\pm({}^1S \to (l_r l_t)^1S) - \eta_\pm^{\mathrm{uc}}({}^1S \to (l_r l_t)^1S) \ . \tag{26}$$

We thus solve the uncoupled equations (24) to obtain pair functions that describe excitations from the states ψ_- and ψ_+, and then used these functions to form the right-hand sides of Eqs. (25). Continuing in this manner we generally obtained convergence within a few iterations.

Once the solutions of Eq. (23) are known, the energy may readily be calculated using the effective Hamiltonian

$$H_{\mathrm{eff}} = PH\Omega P \ , \tag{27}$$

which represents the Hamiltonian within the model space. From Eqs. (1) and (10) it follows directly that the eigenvalues of H_{eff} are the exact energies. Using the relation

$$P\Omega P = P \tag{28}$$

and the fact that the projection operators commute with H_0, the effective Hamiltonian may be written

$$H_{\mathrm{eff}} = PH_0P + PV\Omega P \ . \tag{29}$$

Finally, decomposing the wave operator into a part which operates within the model space and a part which generates the component of the wave function in the space orthogonal to the model space

$$\Omega = 1 + \chi \ , \tag{30}$$

we obtain

$$H_{\mathrm{eff}} = PHP + PV\chi P \ . \tag{31}$$

Since the correlation operator χ generates the component of the wave function in the orthogonal space, it must have at least one perturbation. χ can then be expanded as

$$\chi = \Omega^{(1)} + \Omega^{(2)} + \cdots \tag{32a}$$

and the effective Hamiltonian to second order is

$$H_{\mathrm{eff}}^{(2)} = PHP + PV\Omega^{(1)}P \ . \tag{32b}$$

In the MCHF calculation, of course, H was diagonalized within our model space. So we have

$$\langle \psi(1s^2)\psi_\alpha \mid H \mid \psi(1s^2)\psi_\beta \rangle = \delta_{\alpha\beta} E_\alpha^{\mathrm{MCHF}} \ , \tag{33}$$

where α and $\beta = +, -$.

Using Eqs. (31)–(33), we can form the matrix of $H_{\mathrm{eff}}^{(2)}$ within the model space:

$$\begin{bmatrix} E_{-}^{\mathrm{MCHF}}+\langle\psi_{-}\,|\,V\,|\,\eta_{-}({}^1S\rightarrow(l_rl_t)^1S)\rangle & \langle\psi_{-}\,|\,V\,|\,\eta_{+}({}^1S\rightarrow(l_rl_t)^1S)\rangle \\ \langle\psi_{+}\,|\,V\,|\,\eta_{-}({}^1S\rightarrow(l_rl_t)^1S)\rangle & E_{+}^{\mathrm{MCHF}}+\langle\psi_{+}\,|\,V\,|\,\eta_{+}({}^1S\rightarrow(l_rl_t)^1S)\rangle \end{bmatrix} . \tag{34}$$

We shall thus solve Eq. (25) iteratively for η_- and η_+ and then determine the second-order contribution to the correlation energy by diagonalizing the matrix (34) of $H_{\mathrm{eff}}^{(2)}$ within the model space. Before giving numerical results for excitations from the valence shell, however, we shall consider the effect of core excitations.

IV. EXCITATIONS FROM THE CORE

Excitations of the core orbitals can most effectively be studied by using the general approach based on the Bloch equation adopted in Sec. II. A perturbation expansion of the wave function can be generated by substituting the expansion (32a) of Ω into Eq. (12) and identifying terms of the same power on the left- and right-hand sides. In particular we obtain the first-order equation

$$\begin{aligned}(\Omega^{(1)}H_0-H_0\Omega^{(1)})\Psi_\alpha^0&=V\Psi_\alpha^0-PV\Psi_\alpha^0\\&=QV\Psi_\alpha\ .\end{aligned} \tag{35}$$

We shall use $|\psi_-\rangle$ to denote the MCHF ground state. Replacing Ψ_α^0 with $|\psi_-\rangle$ in Eq. (35) and taking the inner product from the left with $\langle 2s^{2\,1}S,(n_rl,n_tl)^1S,{}^1S\,|$ we obtain

$$\begin{aligned}(2\varepsilon_{1s}-\varepsilon_r-\varepsilon_t)&\langle 2s^{2\,1}S,(n_rl,n_tl)^1,{}^1S\,|\,\Omega^{(1)}\,|\,\psi_-\rangle\\&=\langle 2s^{2\,1}S,(n_rl,n_tl)^1S,{}^1S\,|\,V\,|\,\psi_-\rangle\\&=a\langle 2s^{2\,1}S,(n_rl,n_tl)^1S,{}^1S\,|\,V\,|\,1s^22s^{2\,1}S\rangle\ .\end{aligned} \tag{36}$$

Similarly,

$$\begin{aligned}(2\varepsilon_{1s}-\varepsilon_r-\varepsilon_t)&\langle 2p^{2\,1}S,(n_rl,n_tl)^1S\,|\,\Omega^{(1)}\,|\,\psi_-\rangle\\&=b\langle 2p^{2\,1}S,(n_rl,n_tl)^1S,{}^1S\,|\,V\,|\,1s^22p^{2\,1}S\rangle\ .\end{aligned} \tag{37}$$

Since the core excitations do not couple the various components of the MCHF wave functions, we can derive a pair equation for the excitation of the two core electrons from each component of the model function. For instance, using Eq. (36), one can readily show that the two-electron wave function

$$\psi=\sum_{n_r,n_t}|\,(n_rl,n_tl)^1S\,\rangle\times\langle 2s^{2\,1}S,(n_rl,n_tl)^1S,{}^1S\,|\,\Omega^{(1)}\,|\,\psi_-\rangle \tag{38}$$

satisfies the pair equation

$$\begin{aligned}&[2\varepsilon_{1s}-h_0(1)-h_0(2)]\psi\\&\quad=\sum_{n_r,n_t}|\,(n_rl,n_tl)^1S\,\rangle\langle 2s^{2\,1}S,(n_rl,n_tl)^1S\,|\,V\,|\,\psi_-\rangle\ .\end{aligned} \tag{39}$$

Here we have assumed that the state $|\,(n_rl,n_tl)^1S\,\rangle$ is antisymmetric. Also, the sums on the right-hand side of Eqs. (38) and (39) extend over the excited states.

Intershell correlation effects, for which one electron in the core and one electron in the valence shell are excited, are amenable to the same basic approach. Replacing Ψ_α^0 with $|\psi_-\rangle$ in Eq. (35) and taking the inner product from the left with

$$|\,(1s\,2s)^{1,3}S,(n_rl,n_tl)^{1,3}S,{}^1S\,\rangle$$

we obtain

$$(\varepsilon_{1s}+\varepsilon_{2s}-\varepsilon_r-\varepsilon_t)\langle(1s2s)^{1,3}S,(n_rl,n_tl)^{1,3}S,{}^1S\,|\,\Omega^{(1)}\,|\,\psi_-\rangle=\langle(1s\,2s)^{1,3}S,{}^1S\,|\,V\,|\,\psi_-\rangle\ . \tag{40}$$

The notation ${}^{1,3}S$ is meant to cover both the singlet and the triplet cases. In most instances the state $\langle(1s\,2s)^{1,3}S,(n_rl,n_tl)^{1,3}S,{}^1S\,|$ is joined by the perturbation only to the first component ($1s^22s^{2\,1}S$) of the MCHF wave function and we have the same kind of separation as before. The quantum numbers $n_r=2$, $l=1$, however, require special consideration since $\langle(1s\,2s)^{1,3}S,(2pnp)^{1,3}S,{}^1S\,|$ is joined both to $1s^22s^{2\,1}S$ and to $1s^22p^{2\,1}S$. Perturbing configurations of this kind, which contain a single excited orbital, are most suitably calculated using single-particle, perturbed functions. Since this lies outside the scope of the pair approach which we have adopted in this paper, we have used the MCHF method to evaluate this particular family of excitations. For all other possible combinations of quantum numbers, Eq. (40) leads immediately to the pair equation

$$[\varepsilon_{1s}+\varepsilon_{2s}-h_0(1)-h_0(2)]\psi'=\sum_{n_r,n_t}|\,(n_rl,n_tl)^{1,3}S\,\rangle\langle(1s2s)^{1,3}S(n_rl,n_tl)^{1,3}S,{}^1S\,|\,V\,|\,\psi_-\rangle \tag{41}$$

for the two-particle function

$$\psi'=\sum_{n_r,n_t}|\,(n_rl,n_tl)^{1,3}S\,\rangle\langle(1s\,2s)^{1,3}S,(n_rl,n_tl)^{1,3}S,{}^1S\,|\,\Omega^{(1)}\,|\,\psi_-\rangle\ . \tag{42}$$

The intershell $(1s\,2p)^1P$ and $(1s\,2p)^3P$ pairs can be treated similarly.

The contribution of the innershell and intershell excitations upon the energy can again be calculated by using Eq. (32b). We can write

$$E^{(2)}=\langle\psi_-\,|\,V\,|\,\psi^{(1)}\rangle \tag{43}$$

for the various contributions to the first-order wave function.

In order to entirely define our procedure we must specify the single-particle potential, u which appears in our approximate Hamiltonian, H_0. For this purpose we review briefly the MCHF theory for beryllium.

V. DEFINITION OF POTENTIAL AND INCLUSION OF SINGLE-PARTICLE EFFECTS

In order to derive the two-component MCHF equations for Be one considers the wave function

$$\psi^{\mathrm{MCHF}}=a\mid 1s^2 2s^2\,{}^1S\rangle+b\mid 1s^2 2p^2\,{}^1S\rangle\ . \tag{44}$$

Then

$$\begin{aligned}E&=a^2\langle 1s^2 2s^2\,{}^1S\mid H\mid 1s^2 2s^2\,{}^1S\rangle+2ab\langle 1s^2 2s^2\,{}^1S\mid H\mid 1s^2 2p^2\,{}^1S\rangle+b^2\langle 1s^2 2p^2\,{}^1S\mid H\mid 1s^2 2p^2\,S\rangle\\&=a^2[2I(1s)+2I(2s)+F^0(1s,1s)+4F^0(1s,2s)+F^0(2s,2s)-2G^0(1s,2s)]-2abG^1(2s,2p)/(3)^{1/2}\\&\quad+b^2[2I(1s)+2I(2p)+F^0(1s,1s)+4F^0(1s,2p)+F^0(2p,2p)+\tfrac{2}{5}F^2(2p,2p)-\tfrac{2}{3}G^1(1s,2p)]\ .\end{aligned} \tag{45}$$

This expression assumes that

$$\int_0^\infty P_{nl}(r)P_{n'l}(r)dr=\delta_{nn'}\ , \tag{46}$$

$$a^2+b^2=1\ . \tag{47}$$

Introducing a Lagrange multiplier for each constraint on the wave functions, we obtain the energy functional

$$W=E+\lambda_{1s,1s}\langle 1s\mid 1s\rangle+\lambda_{1s,2s}\langle 1s\mid 2s\rangle+\lambda_{2s,2s}\langle 2s\mid 2s\rangle+\lambda_{2p,2p}\langle 2p\mid 2p\rangle\ . \tag{48}$$

The requirement that δW be zero for all variations, δP_{nl}, of the radial part of the wave functions then leads to the MCHF equations for the $1s$ $2s$, and $2p$ orbitals[19]

$$\begin{aligned}LP_{1s}&=\frac{2}{r}Y_0(1s,1s;r)P_{1s}+\frac{2a^2}{r}[2Y^0(2s,2s;r)P_{1s}-Y^0(1s,2s;r)P_{2s}]\\&\quad+\frac{2b^2}{r}[2Y^0(2p,2p;r)P_{1s}-\tfrac{1}{3}Y^1(1s,2p;r)P_{2p}]+\varepsilon_{1s,1s}P_{1s}+\varepsilon_{1s,2s}P_{2s}\ ,\end{aligned} \tag{49}$$

$$LP_{2s}=\frac{2}{r}[2Y^0(1s,1s;r)+Y^0(2s,2s;r)]P_{2s}-\frac{2}{r}Y^0(1s,2s;r)P_{1s}-\frac{2}{\sqrt{3}}\left[\frac{b}{a}\right]\frac{1}{r}Y^1(2s,2p;r)P_{2p}+\varepsilon_{2s,2s}P_{2s}+\varepsilon_{2s,1s}P_{1s}\ , \tag{50}$$

$$LP_{2p}=\frac{2}{r}[2Y^0(1s,1s;r)+Y^0(2p,2p;r)+\tfrac{2}{5}Y^2(2p,2p;r)]P_{2p}-\tfrac{2}{3}Y^1(1s,2p;r)P_{1s}-\frac{2}{\sqrt{3}}\left[\frac{a}{b}\right]Y^1(2s,2p;r)P_{2s}+\varepsilon_{2p,2p}P_{2p}\ , \tag{51}$$

where the operator L is defined as

$$L=\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{l(l+1)}{r^2}\ , \tag{52}$$

the $Y^k(nl,n'l';r)$ functions are those introduced by Hartree,

$$\frac{1}{r}Y^k(nl,n'l;r)=\int_0^r\frac{s^k}{r^{k+1}}P_{nl}(s)P_{n'l'}(s)ds+\int_r^\infty\frac{r^k}{s^{k+1}}P_{nl}(s)P_{n'l'}(s)ds\ , \tag{53}$$

and the coefficients $\varepsilon_{nl,n'l}$ are related to the $\lambda_{nl,n'l}$ by the equations

$$\varepsilon_{nl,nl}=\frac{2\lambda_{nl,nl}}{q_{nl}} \tag{54}$$

and

$$\varepsilon_{nl,n'l}=\frac{\lambda_{nl,n'l}}{q_{nl}},\quad\langle nl\mid n'l\rangle=0\ . \tag{55}$$

Accordingly, for s and p states we made the following choice of potential:

$$\begin{aligned}u_s&=\frac{2}{r}Y^0(1s,1s;r)-K^0_{1s}+\frac{1}{r}Y^0(2s,2s;r)+\left[a^2\left[\frac{2}{r}Y^0(2s,2s;r)-K^0_{2s}\right]-\frac{1}{r}Y^0(2s,2s;r)\right]\mid P_{1s}\rangle\langle P_{1s}\mid\\&\quad-\frac{1}{\sqrt{3}}\left[\frac{b}{a}\right]K^1_{2p}\mid P_{2s}\rangle\langle P_{2s}\mid+b^2\left[\frac{2}{r}Y^0(2p,2p;r)-\tfrac{1}{3}K^1_{2p}\right]\mid P_{1s}\rangle\langle P_{1s}\mid\ ,\end{aligned} \tag{56}$$

$$u_p=\frac{2}{r}Y^0(1s,1s;r)-\tfrac{1}{3}K^1_{1s}+\frac{1}{r}[Y^0(2p,2p;r)+\tfrac{2}{5}Y^2(2p,2p;r)]-\frac{1}{\sqrt{3}}\left[\frac{a}{b}\right]K^1_{2s}\mid P_{2p}\rangle\langle P_{2p}\mid\ , \tag{57}$$

where

$$K^m_{nl}P_{n'l'}(r)=\frac{1}{r}Y^m(nl,n'l';r)P_{nl}(r)\ . \tag{58}$$

u_s and u_p are both $N-1$ potentials—as Kelly[5] found preferable in his early work on beryllium. Also if one defines

$$h_0=-\frac{1}{2}\frac{d^2}{dr^2}-\frac{Z}{r}+\frac{l(l+1)}{2r^2}+u \tag{59}$$

one can readily show that the eigenvalue equations for the $1s$, $2s$, and $2p$ orbitals

$$h_0\,|P_{nl}\rangle=\varepsilon_{nl}P_{nl}\rangle \tag{60}$$

are identical to the MCHF equations (49)—(51) except for the Lagrange multipliers associated with orthogonality. The fact that we have neglected these terms here will mean that we will have to deal with the orthogonality requirements explicitly when we solve the pair equations.

On the left-hand sides, of Eqs. (23), (39), and (41) we should clearly use the form which these potentials assume for excited states. Since the excited orbitals are orthogonal to the occupied functions, the defining equations (56) and (57), reduce in this case to

$$u_s=\frac{2}{r}Y^0(1s,1s;r)-K^0_{1s}+\frac{1}{r}Y^0(2s,2s;r)\ , \tag{61}$$

$$\begin{aligned}u_p=&\frac{2}{r}Y^0(1s,1s;r)-\frac{1}{3}K^1_{1s}\\&+\frac{1}{r}[Y^0(2p,2p;r)+\tfrac{2}{5}Y^2(2p,2p;r)]\ .\end{aligned} \tag{62}$$

For excited states with $l>1$, we chose to weight the $2s$ and $2p$ components of the potential with the coefficients of the respective configurations squared,

$$\begin{aligned}u_l=&\frac{2}{r}Y^0(1s,1s;r)-\frac{1}{2l+1}K^l_{1s}+a^2\frac{1}{r}Y^0(2s,2s;r)\\&+b^2\frac{1}{r}[Y^0(2p,2p;r)+\tfrac{2}{5}Y^2(2p,2p;r)]\ .\end{aligned} \tag{63}$$

This is reasonable since a^2 and b^2 correspond to probabilities that these configurations are occupied; however, one should emphasize that the MCHF potential can be chosen in a variety of different ways. Equations (49)—(51) only serve to define the potential within a three-dimensional manifold.

In some cases single-particle effects can readily be included in the pair function. Figures 3(b) and 3(c), for instance, show Goldstone diagrams which describe the excitation of a single valence electron by means of a direct and an exchange interaction with the $1s$ core. Figure 3(d) describes the excitation of a single electron by the potential. The diagrams shown in 3(b) and 3(c) will cancel the contribution from the potential diagram 3(d) that is due to the closed shell. What remains is a diagram of the same form as the diagram 3(d) with the matrix element of the part of the potential which is due to the valence shell, $\langle nl\,|-u^{\text{val}}\,|nl\rangle$. According to Eq. (4) a negative sign is associated with this potential interaction. This single-particle effect can be incorporated into the pair function. For this purpose, we denote by $\eta^{\text{I}}(1)$ and $\eta^{\text{I}}(2)$ single-particle functions that describe the excitation of the first and second electron, respectively, and we denote by $\eta^{\text{II}}(1,2)$ a pair function corresponding to a two-particle excitation. These functions satisfy the equations

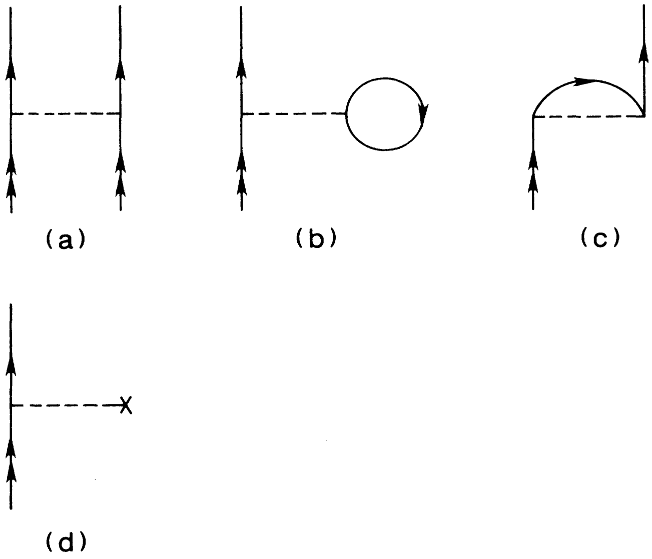

FIG. 3. Goldstone diagrams for the excitation of one or two valence electrons. (a) describes a two electron excitation, (b) and (c) describe the excitation of a single electron by means of a direct and an exchange interaction with the core, and (d) describes the excitation of an electron by the potential.

$$\begin{aligned}&[\varepsilon_{nl}-h_0(1)]\eta^{\text{I}}(1)\\&\quad=-u^{\text{val}}(1)P_{nl}(1)-\sum_{n'}P_{n'l}(1)\langle n'l\,|-u^{\text{val}}\,|nl\rangle\ ,\end{aligned} \tag{64}$$

$$\begin{aligned}&[\varepsilon_{nl}-h_0(1)]\eta^{\text{I}}(2)\\&\quad=-u^{\text{val}}(2)P_{nl}(2)-\sum_{n'}P_{n'l}(2)\langle n'l\,|-u^{\text{val}}\,|nl\rangle\ ,\end{aligned} \tag{65}$$

$$[\varepsilon_{nl}+\varepsilon_{nl}-h_0(1)-h_0(2)]\eta^{\text{II}}(1,2)=g(1,2)-X\ . \tag{66}$$

The last terms on the right in Eqs. (64) and (65) have the effect of forcing the orthogonality of the right-hand side with the solutions of the corresponding homogeneous equation. The right-hand side of Eq. (66), and in particular the orthogonality term X, have only been indicated schematically.

By multiplying Eq. (64) with $P_{nl}(2)$ and Eq. (65) with $P_{nl}(1)$ and adding these equations to Eq. (66), one may readily show that the pair function

$$\eta(1,2)=\eta^{\text{II}}(1,2)+\eta^{\text{I}}(1)P_{nl}(2)+P_{nl}(1)\eta^{\text{I}}(2) \tag{67}$$

satisfies the equation

$$\begin{aligned}&[\varepsilon_{nl}+\varepsilon_{nl}-h_0(1)-h_0(2)]\eta(1,2)\\&\quad=g(1,2)-[u^{\text{val}}(1)P_{nl}(1)]P_{nl}(2)\\&\quad\quad-P_{nl}(1)[u^{\text{val}}(2)P_{nl}(2)]-X'\ .\end{aligned} \tag{68}$$

Single-particle excitations from the valence shell can thus be included in the pair function by adding to the right-hand side of the pair equation terms for which the valence contribution to the potential operates on the occupied orbitals. Explicit expressions for these additional terms can be readily evaluated by making use of the defining equations for the potential, (56) and (57). We obtain

$$
\begin{aligned}
-u^{\mathrm{val}}P_{2s} &= -\frac{1}{r}Y^{0}(2s,2s;r) \\
&\quad +\frac{1}{\sqrt{3}}\left\{\frac{b}{a}\right\}\frac{1}{r}Y^{1}(2s,2p;r)P_{2p}\,, \qquad (69) \\
-u^{\mathrm{val}}P_{2p} &= -\frac{1}{r}\left[Y^{0}(2p,2p;r)+\tfrac{2}{5}Y^{2}(2p,2p;r)\right] \\
&\quad +\frac{1}{\sqrt{3}}\left\{\frac{a}{b}\right\}\frac{1}{r}Y^{1}(2s,2p;r)P_{2s}\,. \qquad (70)
\end{aligned}
$$

These terms generally have the effect of reducing the magnitude of excitations of the valence electrons to states having the same angular momentum. For correlation effects involving core orbitals single-particle effects can also generally be incorporated into the pair function; however, in the intershell case, as we have seen, single-particle excitations from the model space lead to a different interaction mechanism and they are best considered separately.

Thus far we have only considered the first-order corrections to the wave function. Among the various diagrams that occur in the next order is the ladder diagram for which the excited orbitals interact. As has been shown previously,[20] higher-order effects of this kind can be included in a systematic way by solving our basic equations iteratively. In our calculation we have taken these terms over to the left-hand side of the equation and included them with our potential.

VI. RESULTS AND DISCUSSION

For the excitation of valence electrons to s^2, p^2, d^2, f^2, and g^2 states, Eqs. (24) and (25) with the ladder correction mentioned above were solved in 35-, 60-, 85-, and 110-point grids and Richardson extrapolation was used to remove the numerical error due to grid size. In solving the pair equation we used an absolute convergence criterion of one part in 10^7. From this fact and from the consistency of our extrapolated results, it is reasonable to suppose that our numerical solution of the pair equation is generally accurate to a few parts in 10^6. However, we encountered some difficulty in solving the s^2 equation and our solutions are somewhat less accurate in that case. Apparently this instability is due to the presence of near-lying $P_{2s}P_{ns}$ states which are solutions of the corresponding homogeneous equation.

In Table I we show the results of separate MCHF calculations for the s^2, p^2, d^2, f^2, and g^2 series. In the MCHF calculations for the s^2 and p^2 series we allowed the $2s$ and $2p$ functions to relax to include single-particle excitations; however, for the other series the $1s$, $2s$, and $2p$ orbitals were held fixed to the value they have for the $1s^2(2s^2+2p^2)\,^1S$ MCHF calculation. The reason for this, of course, is that the relaxation of these orbitals is not included in the pair calculation. We note here also for later reference that the sum of the energy contributions of the individual MCHF calculations ($-0.002\,550\,3$) is greater than the energy contribution produced by the single large MCHF run ($-0.002\,363\,4$). Apparently in this case coupling effects between different pairs have the effect of lowering the overall energy contribution.

The result of these separate MCHF runs are compared with our pair calculations in rows three and four of Table II. The pair contributions are complete in the sense that all pairs of orbitals of that symmetry are included; however, these are still basically second-order results. To the extent that higher-order effects can be neglected the magnitude of the pair results should be somewhat larger than the corresponding MCHF value. This is true for all of the pair contributions except for the excitation to p^2 states. Our s^2 results may also be somewhat too large. The fact that our s^2 and p^2 results disagree slightly with what could be naturally inferred from the MCHF calculation is reasonable since the s^2 states give the dominant result and the contributions from this series is expected to converge rather slowly. The p^2 series is undoubtably more strongly coupled to the s^2 series than are the states with a larger value of the angular momentum. In the first two rows of Table II we also show results that were obtained by neglecting the coupling terms in Eq. (23) and by omitting the final matrix diagonalization. Clearly the coupling

TABLE I. A summary of MCHF calculations for the valence shell. The underlined orbitals were held fixed.

Configurations	Total energy (a.u.)	ΔE
$1s^2(2s^2+2p^2)\,^1S$	$-14.616\,845\,3$	
$\underline{1s}^2(2s^2+2p^2+3s^2+4s^2+5s^2)\,^1S$	$-14.618\,474\,1$	$-0.001\,628\,8$
$\underline{1s}^2(\underline{2s}^2+2p^2+3p^2+4p^2+5p^2)\,^1S$	$-14.617\,007\,1$	$-0.000\,161\,8$
$\underline{1s}^2(\underline{2s}^2+\underline{2p}^2+3d^2+4d^2+5d^2)\,^1S$	$-14.617\,344\,7$	$-0.000\,499\,4$
$\underline{1s}^2(\underline{2s}^2+\underline{2p}^2+4f^2+5f^2+6f^2)\,^1S$	$-14.617\,028\,8$	$-0.000\,183\,5$
$\underline{1s}^2(\underline{2s}^2+\underline{2p}^2+5g^2+6g^2+7g^2)\,^1S$	$-14.616\,922\,1$	$-0.000\,076\,8$
$\underline{1s}^2(2s^2+2p^2+3s^2+4s^2+5s^2$ $+3p^2+4p^2+5p^2+3d^2+4d^2+5d^2$ $+4f^2+5f^2+6f^2+5g^2+6g^2+7g^2)\,^1S$	$-14.619\,208\,7$	$-0.002\,363\,4$

TABLE II. Contribution to the correlation energy (a.u.) of beryllium from excitation of the valence orbitals.

	$s^2(10^{-3})$	$p^2(10^{-4})$	$d^2(10^{-4})$	$f^2(10^{-4})$	$g^2(10^{-5})$
Present calculation					
Without coupling terms in Eq. (23)	−1.66	−0.877	−3.944	−1.632	−7.296
Without 2×2 matrix diagonalization	−1.85	−1.416	−4.859	−1.849	−7.938
With coupling and matrix diagonalization	−1.86	−1.393	−5.051	−1.869	−7.972
MCHF	−1.629	−1.618	−4.994	−1.835	−7.680

TABLE III. Contribution to the correlation energy (a.u.) of beryllium from core excitations.

	$s^2(10^{-2})$	$p^2(10^{-2})$	$d^2(10^{-3})$	$f^2(10^{-4})$	$g^2(10^{-4})$
Present calculation	−1.526	−2.494	−3.737	−10.386	−3.931
MCHF	−1.400	−2.365	−3.651	−9.861	−3.600

TABLE IV. Intershell contribution to the correlation energy (a.u.) of beryllium.

$(1s2s)^1S$ pair	$s^2\,(10^{-4})$	$p^2\,(10^{-4})$	$d^2\,(10^{-4})$	$f^2\,(10^{-5})$	$g^2\,(10^{-5})$
Present calculation	−9.857	−9.810	−2.591	−6.861	−2.546
MCHF	−9.538	−9.391	−2.439	−6.079	−2.178
$(1s2s)^3S$ pair	$s^2\,(10^{-5})$	$p^2(10^{-4})$	$d^2\,(10^{-4})$	$f^2\,(10^{-5})$	$g^2\,(10^{-6})$
Present calculation	−4.610	−9.399	−1.707	−2.617	−6.201
MCHF	−4.092	−8.216	−1.495	−2.240	−5.077
$(1s2p)^1P$ pair	$sp\,(10^{-6})$	$pd\,(10^{-4})$	$df\,(10^{-5})$	$fg\,(10^{-6})$	
Present calculation	−4.820	−2.217	−2.545	−7.223	
MCHF	−3.844	−1.288	−1.947	−5.04	
$(1s2p)^3P$ pair	$sp\,(10^{-4})$	$pd\,(10^{-4})$	$df\,(10^{-5})$	$fg\,(10^{-6})$	
Present calculation	−1.491	−1.905	−1.576	−2.587	
MCHF	−1.301	−1.659	−1.113	−1.6	

TABLE V. Contributions to the intershell correlation energy (a.u.) due to single-particle excitations from the model space.

Excitation	ΔE
$(1s2s)^1S \rightarrow (2p\,np)^1S$	-4.02×10^{-4}
$(1s2s)^3S \rightarrow (2p\,np)^3S$	-8.96×10^{-4}

TABLE VI. A comparison of pair correlation energies (a.u.).

	$1s^2$	$1s2s$	$1s2p$	$2s^2$	Total
Fischer and Saxena, Ref. 22	−0.042 143	−0.004 126	−0.000 416	−0.046 161	−0.092 846
Kelly, Ref. 5	−0.042 12	−0.004 97		−0.044 88	−0.091 97
Bunge, Ref. 23	−0.042 564	−0.006 016		−0.046 731	−0.095 311
Lindgren and Salomonson, Ref. 24	−0.042 63	−0.005 54		−0.044 78	−0.092 96
Present	−0.045 372	−0.004 808	−0.000 617	−0.046 593	−0.097 390

terms are important in our calculation while the matrix diagonalization has only a marginal effect.

One of the few other correlation calculations with which our approach can be directly compared is the multiconfigurational model space calculation of Salonomson, Lindgren, and Mårtensson.[21] We redid their calculation using MCHF wave functions and including a ladder correction as we have in our calculation. In most cases the two calculations then agree quite closely. The principal difference between our approach and theirs is that they solve the pair equations for the pure $2s^2\,{}^1S$ and $2p^2\,{}^1S$ states and diagonalize the first- and second-order contributions together to obtain the energy levels, whereas we solve the pair equations for excitations from the linear combination of $2s^2\,{}^1S$ and $2p^2\,{}^1S$ states that is produced by the MCHF method.

In Table III we compare our results for excitations from the core. The agreement is quite good although our results may be slightly too large. In our calculation we included the third-order hole-hole and hole-particle diagrams as well as the ladder correction. The hole-particle diagrams have the effect of removing the core electrons from the single-particle potential. As a result our excited states interact only with two units of charge in the valence shell and in addition the two excited electrons interact with each other. Although this potential contains more third-order effects than we included in our valence-shell calculation, one can only appraise the accuracy of our results by carrying the calculation to higher orders or by comparing them to other accurate calculations. A more complete comparison with other beryllium calculations will be given presently.

In Table IV we compare our results with the MCHF for the intershell excitations. The MCHF calculations for the $(1s2s)^1S$ and $(1s2s)^3S$ pairs were performed with three excited orbitals in each case. It is partly due to the consistent way that the MCHF calculations were performed that the difference between the perturbation and MCHF calculations is so uniform in this case. The contributions from the $(1s2p)^1P$ and $(1s2p)^3P$ pairs were considerably smaller and in several cases the MCHF wave function only contained a single excited configuration of that symmetry. In cases such as these where there is a large number of small effects perturbation theory can provide useful information about the completeness of a MCHF calculation.

In Table V we give the contribution to the intershell correlation energy due to the particular effect involving a single excited orbital, which was discussed in Sec. IV. This correlation effect could also be included in the correlation energy of the $(1s2p)^1P$ and $(1s2p)^3P$ pairs. We follow here the assignment made in the earlier paper of Froese Fischer and Saxena.[22] Finally, in Table VI we compare our pair correlation energies with other accurate calculations that have been performed on beryllium. The agreement is quite good. This is encouraging since ours is still basically a second-order result while the calculations of Lindgren *et al.* and Bunge in particular are more extensive. The discrepancy for the $1s^2$ pair is probably mainly due to the same kind of higher-order coupling effect which we noted in conjunction with Table I. The contributions to the $1s^2$ correlation energy are quite large and we obtained the value shown in Table VI simply by adding up these individual contributions. In order to understand the coupling between the different components of the first-order wave function, the present calculation should be extended to higher order. Accurate second-order calculations, however, are interesting in their own right since the MCHF and MBPT theories can most easily be used in conjunction at low orders of the perturbation theory.

VII. CONCLUSION

We have seen that it is feasible to combine the MCHF and MBPT approaches. Using a formalism in which the multiconfiguration state is treated as a reference function we obtain a quite reasonable description of the correlation energy already at second order.

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[1] I. Lindgren and S. Salomonson, Phys. Scr. **21**, 335 (1980).

[2] See, e.g., W. D. Laidig and R. J. Bartlett, J. Chem. Phys. **104**, 424 (1984); B. Jeziorski and H. J. Monkhorst, Phys. Rev. A **24**, 1668 (1981); G. Hose and U. Kaldor, *ibid.* **30**, 2932 (1984); H. Sun, M. G. Sheppard, and K. F. Freed, J. Chem. Phys. Lett. **74**, 6842 (1981).

[3] K. A. Breuckner, Phys. Rev. **100**, 36 (1955).

[4] J. Goldstone, Proc. R. Soc. London, Ser. A **239**, 267 (1957).

[5] H. P. Kelly, Phys. Rev. **131**, 684 (1963); **136**, B896 (1964).

[6] R. M. Sternheimer, Phys. Rev. **80**, 102 (1951).

[7] A. Dalgarno and J. T. Lewis, Proc. R. Soc. London, Ser. A **233**, 70 (1955).

[8] J. Morrison, Phys. Rev. A **6**, 643 (1972); T. N. Chang and R. T. Poe, *ibid* **11**, 191 (1975); S. L. Carter and H. P. Kelly, *ibid.* **16**, 1525 (1977).

[9] J. I. Musher and J. M. Schulman, Phys. Rev. **173**, 93 (1968).

[10] V. McKoy and N. W. Winter, J. Chem. Phys. **48**, 5514 (1968).

[11] J. M. Schulman and W. S. Lee, Phys. Rev. A **5**, 13 (1972).

[12] J. Morrison, J. Phys. B **6**, 2205 (1973).

[13] S. Garpman, I. Lindgren, J. Lindgren, and J. Morrison, Phys. Rev. A **11**, 758 (1975).

[14] A. -M. Mårtensson-Pendrill (private communication).

[15] C. Froese Fischer, *An Atomic Structure Software Package*, Department of Energy Report No. DOE/ER/10618-11 (1983). Anyone interested in getting a recent version should contact the author.

[16] J. Morrison, Phys. Scr. **34**, 423 (1986).

[17] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed., Vol. 3 of *Springer Series on Atoms and Plasmas*, (Springer, Berlin, 1986).

[18] I. Lindgren, J. Phys. B **7**, 2441 (1974); Int. J. Quantum Chem. Symp. **12**, 33 (1978).

[19] C. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).

[20] S. Garpman, I. Lindgren, J. Lindgren, and J. Morrison, Z. Phys. A **276**, 167 (1976); A. -M. Mårtensson, J. Phys. B **12**, 3995 (1979).

[21] S. Salomonson, I. Lindgren, and A.-M. Mårtensson, Phys. Scr. **21**, 351 (1980).

[22] C. Froese Fischer and K. M. S. Saxena, Phys. Rev. A **9**, 1498 (1974).

[23] C. F. Bunge, Phys. Rev. A **14**, 1965 (1976); **17**, 486 (1978).

[24] I. Lindgren and S. Salomonson, Phys. Scr. **21**, 335 (1980).