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MULTIPLE PARTICLE EXCITATION EXPANSION

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Correlation Effects in Many Fermion Systems: Multiple Particle Excitation Expansion*

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ABSTRACT

The ground state wave function and energy of a finite system of interacting fermions are expanded in terms of multiple particle excitations on an uncorrelated zero order state. The resulting set of coupled equations constitutes a systematic variational

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6/63

generalization of Hartree-Fock theory. Comparison is made with many-body perturbation theory and it is shown that to any order the theory incorporates an infinite number of perturbation theory terms. Solutions of the equations for ground state atomic systems are discussed and related to previous work using many-body perturbation theory. It is shown that the sums of perturbation terms necessary for convergence are automatically included in the equations for two-particle excitations. Application of the equations to open shell atoms is described.

I. INTRODUCTION

Many systems of interacting fermions are well approximated by uncorrelated wave functions and in particular by determinants of single-particle states determined by Hartree-Fock theory. It is natural to attempt to expand the true wave function for such systems in multiple-particle excitations on the zero order approximation. We present here such a systematic expansion which corresponds to including firstly one-particle excitations, secondly two-particle excitations, and in succeeding orders excitations of more and more particles. The magnitudes of the excitations are determined by a variational approach. The resulting coupled equations are derived in Sec. II. Similar equations were previously derived by Nesbet[1]; our equations differ from his in that they show the explicit dependence upon the potential V which is used to determine the single-particle states for the expansion of the wave function $|\psi\rangle$. Section II also contains a treatment of the effect of choosing V as the Hartree-Fock

potential and the approximate inclusion of three-particle and higher excitations.

In Sec. III the solutions of the coupled equations are discussed and related to a previous calculation of the ground state of the beryllium atom using many-body perturbation theory.[2] In that calculation it was necessary to include high orders in the perturbation expansion. It is shown in Sec. III that the important infinite sums of perturbation terms are automatically included in the coupled equations for two-particle excitations. Application of the equations to open shell atoms is described at the end of Sec. III.

II. THE COUPLED EQUATIONS

1. Derivation

In order to solve the equation

$$H\,|\psi\rangle = E\,|\psi\rangle\,, \tag{1}$$

both H and $|\psi\rangle$ are expanded in terms of a complete set of single-particle states $|n\rangle$ which are determined from the eigenvalue equation

$$(T + V)\,|n\rangle = \epsilon_n\,|n\rangle\,.$$

The operator T represents the one-body operators of the Hamiltonian. In the atomic case,

$$T = -\hbar^2\,\nabla^2/2m - Ze^2/r\,.$$

The potential V is a one-body potential which approximately accounts for the effects of the interacting fermions. The particular choice of V is arbitrary except that it must be Hermitian; it is often chosen to be the Hartree-Fock potential.

The Hamiltonian H in second-quantized form is

$$H = \sum_a \epsilon_a \eta_a^+ \eta_a + \sum_{abcd} \langle ab| v |cd\rangle \eta_a^+ \eta_b^+ \eta_d \eta_c - \sum_{ab} \langle b| V |a\rangle \eta_b^+ \eta_a . \tag{2}$$

The sums are taken over all the single-particle states. In the second summation only distinct matrix elements are included; for example, $\langle ba| v |dc\rangle$ is not distinct from $\langle ab| v |cd\rangle$.[3] It is assumed for simplicity that the ground state wave function $|\psi\rangle$ may be approximated by an unperturbed solution $|\Phi_0\rangle$ which is a single determinant composed of the N states $|n\rangle$ which are lowest in energy. When it is necessary to express the unperturbed state $|\Phi_0\rangle$ as a linear combination of determinants, the following approach is still applicable, but it is then necessary to consider correction terms for each of the determinants and the equations become more lengthy.

The ground state wave function is expanded as

$$|\psi\rangle = |\Phi_0\rangle + \sum_{\alpha,k} f(k;\alpha) \eta_k^+ \eta_\alpha |\Phi_0\rangle + \sum_{\alpha\beta kk'} f(kk';\alpha\beta) \eta_k^+ \eta_{k'}^+ \eta_\beta \eta_\alpha |\Phi_0\rangle + \cdots \tag{3}$$

The states labeled k are excited states and not occupied in $|\Phi_0\rangle$. The states labeled with Greek letters are states which are occupied in $|\Phi_0\rangle$ and are called unexcited states. An unoccupied, unexcited state is called

a hole state. In all the sums only distinct terms are included. Terms which differ only in permutations of the excited states or the hole states are not distinct.

When Eqs. (2) and (3) are substituted into Eq. (1) an infinite set of coupled equations is obtained by equating terms with the same single-particle states. It is important in the appreciation of the theoretical basis of these equations to realize that this procedure is equivalent to a variational approach where the f's are determined by minimizing $\langle\psi|\ H\ |\psi\rangle$ subject to the constraint $\langle\psi\ |\ \psi\rangle$ = constant. Anticipating the rapid convergence of the approximation scheme, the following discussion is limited to one-particle and two-particle excitations. Higher order excitations are discussed in Sec. II 3.

The first equation in the system is obtained by taking the $|\Phi_0\rangle$ component of the result of inserting Eqs. (2) and (3) into Eq. (1):

$$\begin{aligned}
&\sum_{n=1}^{N} \epsilon_n + \sum_{\gamma<\delta}^{N} \langle\widetilde{\gamma\delta}|\ v\ |\gamma\delta\rangle - \sum_{\gamma=1}^{N} \langle\gamma|\ V\ |\gamma\rangle \\
&+ \sum_{\alpha,k} \left\{\sum_{\gamma} \langle\alpha\gamma|\ v\ |\widetilde{k\gamma}\rangle - \langle\alpha|\ V\ |k\rangle\right\} f(k;\alpha) \qquad (4) \\
&+ \sum_{\alpha\beta kk'} \langle\alpha\beta|\ v\ |\widetilde{kk'}\rangle\ f(kk';\alpha\beta) = E\ ,
\end{aligned}$$

where $\langle\widetilde{ab}|\ v\ |cd\rangle = \langle ab|\ v\ |cd\rangle - \langle ba|\ v\ |cd\rangle$. The $\eta_k^{+}\ \eta_\alpha\ |\Phi_0\rangle$ component yields:

$$\left(\epsilon_k + \sum_{n=1}^{N} \epsilon_n - \epsilon_\alpha\right) f(k;\alpha) + \sum_{\gamma=1}^{N} \langle \tilde{k\gamma}| v |\alpha\gamma\rangle - \langle k| V |\alpha\rangle$$

$$+ \sum_{k',\gamma\neq\alpha} \langle \tilde{\gamma k}| v |k'\alpha\rangle f(k';\gamma) + \sum_{k'} \left\{\sum_{\gamma\neq\alpha} \langle \tilde{k\gamma}| v |k'\gamma\rangle - \langle k| V |k'\rangle\right\} f(k';\alpha)$$

$$- \sum_{\gamma\neq\alpha} \left\{\sum_{\delta} \langle \tilde{\gamma\delta}| v |\alpha\delta\rangle - \langle\gamma| V |\alpha\rangle\right\} f(k;\gamma)$$

$$+ \sum_{\gamma\neq\alpha} \left\{\sum_{\delta\neq\alpha} \langle \tilde{\gamma\delta}| v |\gamma\delta\rangle - \langle\gamma| V |\gamma\rangle\right\} f(k;\alpha) \qquad (5)$$

$$+ \sum_{\beta\neq\alpha,\gamma\neq\alpha} \langle \tilde{\beta\gamma}| v |k'\alpha\rangle f(kk';\beta\gamma)$$

$$+ \sum_{k',\gamma} \left\{\sum_{\delta\neq\alpha} \langle \tilde{\gamma\delta}| v |k'\delta\rangle - \langle\gamma| V |k'\rangle\right\} f(kk';\alpha\gamma)$$

$$+ \sum_{k',k'',\gamma} \langle \tilde{k\gamma}| v |k'k''\rangle f(k'k'';\alpha\gamma) = E\, f(k;\alpha) \quad .$$

The third equation in the series is obtained by multiplying Eq. (1) from the left by $\langle\Phi_0|\, \eta_\alpha^+ \eta_\beta^+ \eta_{k'} \eta_k$. The result is:

$$\left(\epsilon_k + \epsilon_{k'} + \sum_{n=1}^{N} \epsilon_n - \epsilon_\alpha - \epsilon_\beta\right) f(kk';\alpha\beta)$$

$$+ \sum_{\gamma\neq\alpha,\beta} \left\{\sum_{\delta\neq\alpha,\beta} \langle \tilde{\gamma\delta}| v |\gamma\delta\rangle - \langle\gamma| V |\gamma\rangle\right\} f(kk';\alpha\beta)$$

$$+ \langle \tilde{kk'}| v |\alpha\beta\rangle + \sum_{k'',k'''} \langle \tilde{kk'}| v |k''k'''\rangle f(k''k''';\alpha\beta)$$

$$+ \sum_{k'',\gamma\neq\beta} \langle \tilde{\gamma}k' | v | k''\beta \rangle f(kk''; \alpha\gamma) + \sum_{\gamma\neq\alpha} \langle k^{\gamma}\gamma | v | \alpha k'' \rangle f(kk''; \gamma\beta)$$

$$+ \sum_{k''} \left\{ \sum_{\gamma\neq\alpha,\beta} \langle \tilde{\gamma}k' | v | \gamma k'' \rangle - \langle k' | V | k'' \rangle \right\} f(kk''; \alpha\beta)$$

$$+ \sum_{k'',\gamma\neq\beta} \langle \tilde{k}\gamma | v | k''\beta \rangle f(k'k''; \alpha\gamma) + \sum_{k'',\gamma\neq\alpha} \langle \tilde{\gamma}k | v | k''\alpha \rangle f(k''k'; \gamma\beta)$$

$$+ \sum_{k''} \left\{ \sum_{\gamma\neq\alpha,\beta} \langle \tilde{k}\gamma | v | k''\gamma \rangle - \langle k | V | k'' \rangle \right\} f(k''k'; \alpha\beta)$$

$$+ \sum_{\substack{\gamma\neq\alpha,\beta \\ \delta\neq\alpha,\beta}} \langle \tilde{\gamma}\delta | v | \alpha\beta \rangle f(kk'; \gamma\delta) + \sum_{\gamma\neq\beta} \left\{ -\sum_{\delta\neq\alpha} \langle \tilde{\gamma}\delta | v | \beta\delta \rangle + \langle \gamma | V | \beta \rangle \right\} f(kk'; \alpha\gamma)$$

$$+ \sum_{\gamma\neq\alpha} \left\{ -\sum_{\delta\neq\beta} \langle \tilde{\gamma}\delta | v | \alpha\delta \rangle + \langle \gamma | V | \alpha \rangle \right\} f(kk'; \gamma\beta)$$

$$- \sum_{\gamma\neq\alpha,\beta} \langle \tilde{\gamma}k' | v | \alpha\beta \rangle f(k; \gamma) - \sum_{\gamma\neq\alpha,\beta} \langle \tilde{k}\gamma | v | \alpha\beta \rangle f(k'; \gamma)$$

$$+ \sum_{k''} \langle \tilde{k}k' | v | k''\beta \rangle f(k''; \alpha) + \sum_{k''} \langle \tilde{k}k' | v | \alpha k'' \rangle f(k''; \beta)$$

$$+ \left\{ \sum_{\gamma\neq\alpha} \langle \tilde{\gamma}k' | v | \gamma\beta \rangle - \langle k' | V | \beta \rangle \right\} f(k; \alpha)$$

$$- \left\{ \sum_{\gamma\neq\alpha} \langle \tilde{\gamma}k | v | \gamma\beta \rangle - \langle k | V | \beta \rangle \right\} f(k'; \alpha)$$

$$+ \left\{ \sum_{\gamma\neq\beta} \langle \tilde{k}\gamma | v | \alpha\gamma \rangle - \langle k | V | \alpha \rangle \right\} f(k'; \beta)$$

$$- \left\{ \sum_{\gamma\neq\beta} \langle k^{\gamma}\gamma | v | \alpha\gamma \rangle - \langle k' | V | \alpha \rangle \right\} f(k; \beta) = E\, f(kk'; \alpha\beta) \,. \qquad (6)$$

2. The Hartree-Fock Potential

A great simplification in Eqs. (4), (5), and (6) results from choosing V to be the Hartree-Fock potential V_{HF}, defined by matrix elements

$$\langle a|\ V_{HF}\ |b\rangle = \sum_{n=1}^{N} \langle an|\ v\ |\tilde{bn}\rangle\ . \tag{7}$$

Equation (4) becomes

$$E - E_{HF} = \sum_{\alpha\beta kk'} \langle\alpha\beta|\ v\ |\tilde{kk'}\rangle\ f(kk';\ \alpha\beta)\ , \tag{8}$$

where

$$E_{HF} = \sum_{n=1}^{N} \epsilon_n + \sum_{\gamma<\delta}^{N} \langle\tilde{\gamma\delta}|\ v\ |\gamma\delta\rangle - \sum_{\gamma=1}^{N} \langle\gamma|\ V\ |\gamma\rangle = \sum_{n=1}^{N} \epsilon_n - \frac{1}{2}\sum_{\gamma=1}^{N} \langle\gamma|\ V\ |\gamma\rangle\ ; \tag{9}$$

while Eq. (5) for $f(k;\ \alpha)$ reduces to

$$\underset{(a)}{(\epsilon_k - \epsilon_\alpha)\ f(k;\ \alpha)} + \underset{(b)}{\sum_{\gamma,k'} \langle\tilde{\gamma k}|\ v\ |k'\alpha\rangle\ f(k';\ \gamma)}$$

$$+ \underset{(c)}{\sum_{\gamma,\beta,k'} \langle\tilde{\beta\gamma}|\ v\ |k'\alpha\rangle\ f(kk';\ \beta\gamma)} \tag{10}$$

$$+ \underset{(d)}{\sum_{k',k''} \langle\tilde{k\gamma}|\ v\ |k'k''\rangle\ f(k'k'';\ \alpha\gamma)} = (E - E_{HF})\ f(k;\ \alpha)\ .$$

The sums over unexcited states are no longer restricted because now there are additional terms arising from incomplete cancellations with the Hartree-Fock potential V_{HF}. They correspond to diagrams in perturbation theory in which the exclusion principle is violated in the intermediate states.[2] The terms of Eq. (10) are represented by diagrams in Fig. 1. The diagrams provide a connection with the corresponding terms of perturbation theory. In order to correspond more closely to the diagrams of Goldstone perturbation theory,[3] the term (a) of Eq. (10) should be brought to the rhs and then the equation divided by $(\epsilon_\alpha - \epsilon_k + E - E_{HF})$. In Goldstone's theory, the energy denominator would be $(\epsilon_\alpha - \epsilon_k)$. The term $(E - E_{HF})$ incorporates the summation of many higher-order terms in perturbation theory and corresponds to inclusion of the third class of EPV diagrams of reference 2. It is assumed in this paper that $(E - E_{HF})$ is not large relative to $(\epsilon_\alpha - \epsilon_k)$ and this assumption constitutes a restriction to finite systems.

When V is chosen as V_{HF}, Eq. (6) reduces to

$$(\epsilon_k + \epsilon_{k'} - \epsilon_\alpha - \epsilon_\beta)\, f(kk';\, \alpha\beta) + \langle \tilde{k}\tilde{k}' |\, v\, | \alpha\beta \rangle$$

$$+ \sum_{k''k'''} \langle \tilde{k}\tilde{k}' |\, v\, | k''k''' \rangle\, f(k''k''';\, \alpha\beta)$$

$$\text{(i)}$$

$$+ \sum_{k''\gamma} \langle \gamma\tilde{k}' |\, v\, | k''\beta \rangle\, f(kk'';\, \alpha\gamma) + \sum_{k''\gamma} \langle k''\gamma |\, v\, | \alpha k'' \rangle\, f(kk'';\, \gamma\beta)$$

$$\text{(ii)} \qquad\qquad \text{(iii)}$$

$$+ \sum_{k''\gamma} \langle \gamma\tilde{k} |\, v\, | k''\beta \rangle\, f(k''k';\, \alpha\gamma) + \sum_{k''\gamma} \langle \gamma\tilde{k} |\, v\, | k''\alpha \rangle\, f(k''k';\, \gamma\beta)$$

$$\text{(iv)} \qquad\qquad \text{(v)}$$

$$+ \sum_{\gamma\delta} \langle \widetilde{\gamma\delta} | v | \alpha\beta \rangle f(kk'; \gamma\delta) - \sum_{\gamma} \langle \widetilde{\gamma k'} | v | \alpha\beta \rangle f(k; \gamma)$$

(vi) (vii)

$$- \sum_{\gamma} \langle \widetilde{k\gamma} | v | \alpha\beta \rangle f(k'; \gamma) + \sum_{k''} \langle \widetilde{kk'} | v | k''\beta \rangle f(k''; \alpha)$$

(viii) (ix)

$$+ \sum_{k''} \langle \widetilde{kk'} | v | \alpha k'' \rangle f(k''; \beta) = (E - E_{HF}) f(kk'; \alpha\beta) . \qquad (11)$$

(x)

Again, as in Eq. (10), the sums over hole states are unrestricted because of contributions from the potential V_{HF}. The diagrams for Eq. (11) are given in Fig. 2.

3. Higher Excitations

The discussion so far has only included one- and two-particle excitations, and there are, of course, excitations up to N particles. When higher excitations are included, Eq. (4) still involves only one- and two-particle excitations directly. Equations (5) and (10) for $f(k; \alpha)$ must be modified to include coupling with $f(kk'k''; \alpha\beta\gamma)$ and Eqs. (6) and (11) for $f(kk'; \alpha\beta)$ must include terms coupling with $f(kk'k''; \alpha\beta\gamma)$ and $f(kk'k''k'''; \alpha\beta\gamma\delta)$. The importance of higher excitations depends both on the size of the system and the "goodness" of the single-particle wave functions used in the expansion. In perturbation theory, both one- and two-particle excitations enter in first order. Three- and four-particle excitations enter in second order. When good single-particle wave functions are used the matrix elements involving unexcited to excited states may be expected to be small, as found in reference 2. In Eq. (5) for $f(k; \alpha)$ and Eq. (6)

for $f(kk'; \alpha\beta)$, the three- and four-particle terms correspond to two higher orders of perturbation theory than do the lowest order terms. When N is not so large that the possible number of higher excitations can overcome the reductions due to terms reduced by two orders of perturbation theory, higher excitations are not expected to be very important.

When three-particle excitations are included, the term

$$\sum_{\beta\gamma k'k''} \langle\tilde{\beta\gamma}|\ v\ |k'k''\rangle\ f(kk'k''; \alpha\beta\gamma) \tag{12}$$

is added to the lhs of Eqs. (5) and (10) for $f(k; \alpha)$. The following terms are added to the lhs of Eq. (6) due to triple excitations:

$$\begin{aligned}
&\sum_{\gamma,k''} \left(\sum_{\delta\neq\alpha,\beta,\gamma} \langle\tilde{\gamma\delta}|\ v\ |k''\delta\rangle - \langle\gamma|\ V\ |k''\rangle \right) f(kk'k''; \alpha\beta\gamma) \\
&\quad - \sum_{\delta,\gamma\neq\beta;k''} \langle\tilde{\gamma\delta}|\ v\ |\beta k''\rangle\ f(kk'k''; \alpha\gamma\delta) \\
&\quad + \sum_{\gamma,k'',k'''} \langle\tilde{k''\gamma}|\ v\ |k''k'''\rangle\ f(kk''k'''; \alpha\beta\gamma) \\
&\quad - \sum_{\gamma,\delta\neq\alpha;k''} \langle\tilde{\gamma\delta}|\ v\ |\alpha k''\rangle\ f(kk'k''; \gamma\beta\delta) \\
&\quad + \sum_{\gamma,k'',k'''} \langle\tilde{k''\gamma}|\ v\ |k''k'''\rangle\ f(k''k'k'''; \alpha\beta\gamma)\ .
\end{aligned} \tag{13}$$

Coupling with four-particle excitations adds the term

$$\sum_{\gamma,\delta,k'',k'''} \langle\tilde{\gamma\delta}|\ v\ |k''k'''\rangle\ f(kk'k''k'''; \alpha\beta\gamma\delta) \tag{14}$$

to the lhs of Eq. (6) for $f(kk'; \alpha\beta)$. Equation (11) for $f(kk'; \alpha\beta)$, using V_{HF}, is modified on the lhs by the last four terms of Eq. (13) (without restrictions on the sums over hole states) and by Eq. (14).

The terms $f(kk'k''; \alpha\beta\gamma)$ and $f(kk'k''k'''; \alpha\beta\gamma\delta)$ are determined from equations which are similar to Eqs. (5) and (6). When N is not large, it should be quite valid to truncate terms beyond four excitations in the equations for $f(kk'k''; \alpha\beta\gamma)$ and $f(kk'k''k'''; \alpha\beta\gamma\delta)$ and to exclude all higher excitations. A simpler approximation is to approximate three- and four-particle excitations by products of one- and two-particle excitations and to omit three-body and higher clusters, as has been discussed by Sinanoglu.[4]

III. APPLICATIONS OF THE EQUATIONS TO ATOMIC STRUCTURE CALCULATIONS

1. Solutions and Perturbation Theory

The set of coupled equations (4), (5), and (6); or (8), (10), and (11) if V_{HF} is used; may be solved for the ground state energy E. That is, the matrix determined by the complete set of equations must be diagonalized. The lowest eigenvalue is the ground state energy and higher eigenvalues correspond to excited states with the same symmetry. The set has already been truncated because higher excitations have been omitted. The continuum may be divided into finite blocks such that the variation of f within any given block is small and the calculation is then reduced to that of a finite number of coupled equations provided a finite number of bound excited states is used.

When V_{HF} is used, the one-particle excitations $f(k; \alpha)$ are relatively unimportant compared to the two-particle excitations $f(kk'; \alpha\beta)$, and only the $f(kk'; \alpha\beta)$ are needed to determine $E - E_{HF}$.

The solution of Eq. (11) is, in the first approximation,

$$f(kk';\,\alpha\beta) = (\epsilon_\alpha + \epsilon_\beta - \epsilon_k - \epsilon_{k'} - \langle\tilde{\alpha\beta}|\ v\ |\alpha\beta\rangle + E - E_{HF})^{-1}\,\langle\tilde{kk'}|\ v\ |\alpha\beta\rangle\ . \tag{15}$$

The term $\langle\alpha\beta|\ v\ |\alpha\beta\rangle$ in Eq. (15) comes from the diagonal part of term (vi) of Eq. (11). It is the same term used in reference 1 to shift all energy denominators of the terms in perturbation theory. It might be expected on physical grounds because $\epsilon_\alpha + \epsilon_\beta - \langle\tilde{\alpha\beta}|\ v\ |\alpha\beta\rangle$ is just the effective two-particle energy for particles in states $|\alpha\rangle$ and $|\beta\rangle$. The ladder diagram term (i) of Eq. (11) accounts for the interaction of two particles in states $|k\rangle$ and $|k'\rangle$. Since the states $|k\rangle$ are determined by a potential in which all the unexcited states are filled (in the HF case), there is also a correction to account for the fact that $|k\rangle$ and $|k'\rangle$ are propagating with $|\alpha\rangle$ and $|\beta\rangle$ unoccupied. This correction comes from the terms $\gamma = \beta$ in (ii) and (iv) of Eq. (11) and from terms $\gamma = \alpha$ in (iii) and (v) of Eq. (11). These terms were called hole-particle EPV (exclusion principle violating) terms in reference 2 because they involve hole-particle interactions (and exchange) in which the exclusion principle is violated in going from one hole state to the same hole state.

In the numerical calculations on Be it was found necessary to include certain terms beyond second order in perturbation theory, namely the ladder diagrams and the hole-particle EPV diagrams.[5] If only these terms are retained, then Eq. (11) becomes

$$f(kk';\,\alpha\beta) = D^{-1}\,\langle\tilde{kk'}|\ v\ |\alpha\beta\rangle\ , \tag{16}$$

where

$$D = \epsilon_\alpha + \epsilon_\beta - \epsilon_k - \epsilon_{k'} - \langle \tilde{\alpha\beta} | \, v \, | \alpha\beta \rangle + E - E_{HF}$$

$$- \sum_{k''k'''} \langle \tilde{kk'} | \, v \, | k''k''' \rangle \, f(k''k'''; \alpha\beta) \Big/ f(kk'; \alpha\beta)$$

$$- \sum_{k''} \langle \tilde{\beta k'} | \, v \, | k''\beta \rangle \, f(kk''; \alpha\beta) \Big/ f(kk'; \alpha\beta) \qquad (17)$$

$$- \sum_{k''} \langle \tilde{k''\alpha} | \, v \, | \alpha k'' \rangle \, f(kk''; \alpha\beta) \Big/ f(kk'; \alpha\beta)$$

$$- \sum_{k''} \langle \tilde{\beta k} | \, v \, | k''\beta \rangle \, f(k''k'; \alpha\beta) \Big/ f(kk'; \alpha\beta)$$

$$- \sum_{k''} \langle \tilde{\alpha k} | \, v \, | k''\alpha \rangle \, f(k''k'; \alpha\beta) \Big/ f(kk'; \alpha\beta) \, .$$

The last four terms on the rhs of Eq. (17) are related to the expression (4a + 2b) which was used in reference 2 to sum the hole-particle EPV diagrams. The ladder term of Eq. (17) is related to the factor t of reference 2 which summed the ladder diagrams. Equations (16) and (17) are equivalent to the calculation of reference 2. The necessary higher order terms of perturbation theory are thus seen to be included in the multiple-particle excitation theory in a straightforward manner.

The last five terms on the rhs of Eq. (17) may have a dependence on k and k' which simplifies the calculations. This was found to be true in the numerical calculations for Be where each of the five terms could be written to a good approximation as $C_i(\epsilon_\alpha + \epsilon_\beta - \epsilon_k - \epsilon_{k'} - \langle \tilde{\alpha\beta} | \, v \, | \alpha\beta \rangle)$, where C_i is an appropriate constant for the ith term.[2]

2. Application to Open Shell Atoms

Since the Hamiltonian H commutes with the total orbital and spin angular momentum operators $\underset{\sim}{L}$ and $\underset{\sim}{S}$, the eigenstates for this Hamiltonian must be eigenstates of L^2 and S^2. The unperturbed eigenstate $|\Phi_0\rangle$ should have the correct symmetry (in L and S) of the true ground state $|\psi\rangle$ which may be written

$$|\psi\rangle = |\Phi_0\rangle + |\Delta\,\psi\rangle \; . \tag{18}$$

Equation (2) may be written as

$$H = H_0 + v - V \; , \tag{19}$$

where $v = \sum_{i<j}^{N} (r_{ij})^{-1}$, $V = \sum_{i=1}^{N} V(r_i)$, and $H_0\,|\Phi_0\rangle = E_0\,|\Phi_0\rangle$.

When Eqs. (18) and (19) are substituted into (1), there results:

$$|\Delta\,\Psi\rangle = (H - E)^{-1}\,[\Delta E - (v - V)]\,|\Phi_0\rangle \; , \tag{20}$$

where $\Delta E = E - E_0$. Since $\underset{\sim}{L}$ and $\underset{\sim}{S}$ commute with H and v, the calculated ground state $|\psi\rangle$ will be an eigenstate of L^2 and S^2 if $\underset{\sim}{L}$ and $\underset{\sim}{S}$ commute with V and $|\Phi_0\rangle$ is an eigenstate of L^2 and S^2. For closed-shell atoms, V_{HF} defined by Eq. (7) commutes with $\underset{\sim}{L}$ and $\underset{\sim}{S}$ and $|\Phi_0\rangle$ is a single determinant.

For open-shell atoms $\underset{\sim}{L}$ and $\underset{\sim}{S}$ in general do not commute with V_{HF} and so it is desirable to choose a V(r) which approximates V_{HF} as closely as possible but which commutes with $\underset{\sim}{L}$ and $\underset{\sim}{S}$. As described in Sec. II 1,

it is convenient but not necessary that $|\Phi_0\rangle$ be described by a single determinant. In calculating the ground state of many open-shell atoms it is possible to choose $|\Phi_0\rangle$ as a single determinant because the ground state usually has the maximum spin consistent with the exclusion principle. The energy is independent of M_L and M_S and the choice $M_L = L$ and $M_S = S$ often makes $|\Phi_0\rangle$ a single determinant.

Calculations for open-shell atoms, using Eqs. (4), (5), and (6), are planned. The numerical work described in reference 2 indicates the feasibility of these calculations.

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5. For example, the correlation energy among the 2S electrons was calculated to be -0.0285 a.u. in second order; when the ladder and hole-particle sums were included the 2S correlation energy was calculated to be -0.0439 a.u.

FIGURE CAPTIONS

Fig. 1. Diagrams corresponding to the terms of Eq. (10). (a) Diagrams for $f(k; \alpha)$ and $f(kk'; \alpha\beta)$. Diagrams (b), (c), and (d) correspond to the terms labeled (b), (c), and (d) in Eq. (10).

Fig. 2. Diagrams corresponding to terms of Eq. (11). (a) Ladder diagram for term (i). (b) Ring diagram and hole-particle diagram of term (ii). The diagrams for (iii), (iv), and (v) are similar. (c) Hole-hole interaction diagram of term (vi). (d) Diagram for coupling of one-particle and two-particle excitations of term (vii). The diagram for (viii) is similar. (e) Diagram for (ix) and (x). The exchange diagrams for (c), (d), and (e) have been omitted.

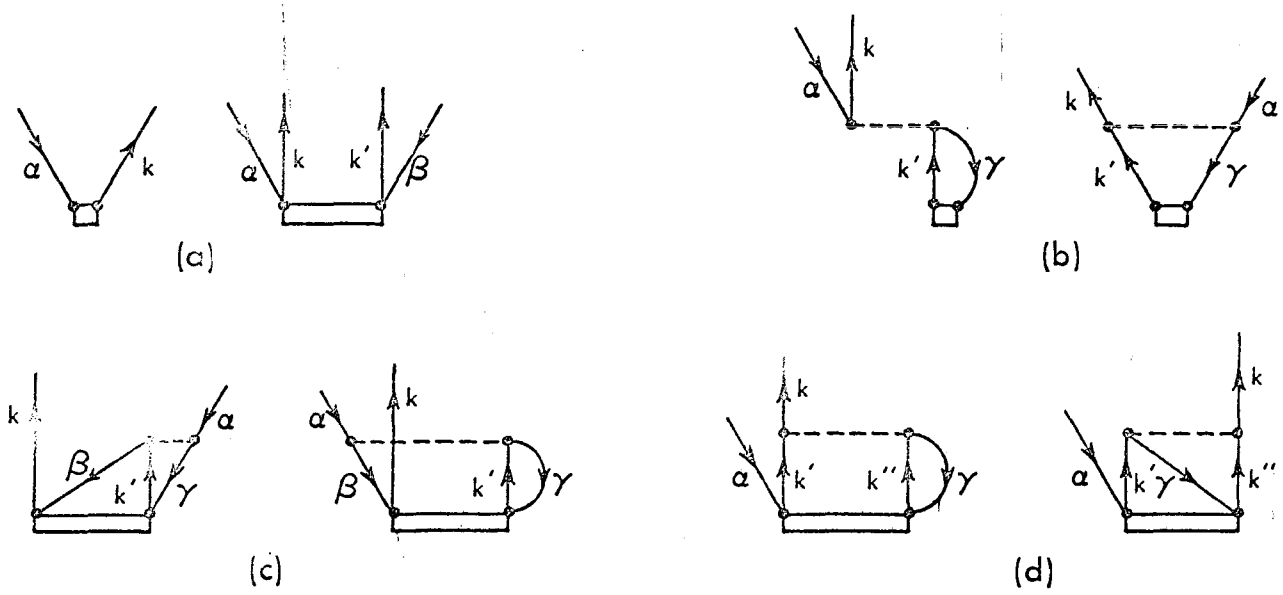

Figure 1

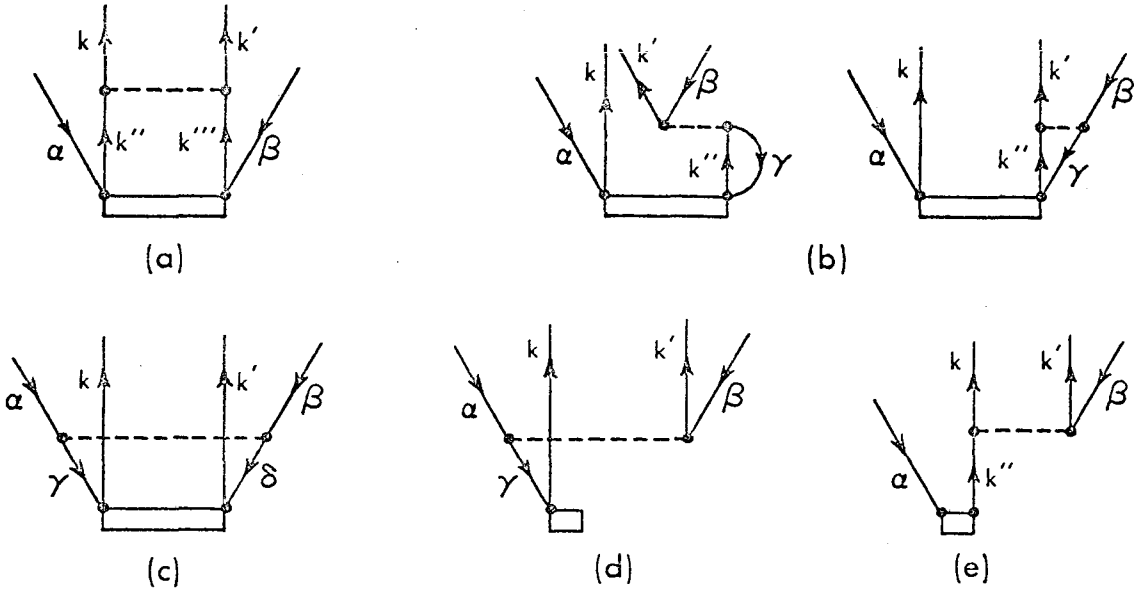

Figure 2

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