Theoret. chim. Acta (Berl.) 281—291 (1966)

Commentationes

Extension of the Separated Pair Theory

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Received August 16, 1966

Assuming that the separated pair ground state wave function of a $2N$-electron system is already known a method is given for constructing a suitable orthogonal complement to the set of product functions built up from strongly orthogonal geminals. All terms are explicitly given which may have nonzero matrix element with the separated pair ground state. Using perturbational techniques a second order correction is calculated. In the case of Be atom the magnitudes of contributions from terms omitted in the generalized separated pair theory are estimated and found to be appreciable.

Si l'on suppose connue la fonction d'onde à paires séparées pour l'état fondamental d'un système à $2N$ électrons, une méthode décrite ici permet de construire convenablement un complément orthogonal à l'ensemble des fonctions produits de géminales fortement orthogonales. Tous les termes ayant un élément dematrice non nul avec l'état fondamental sont donnés explicitement. Une correction du second ordre est calculée au moyen des techniques de perturbation. Dans le cas de l'atome de beryllium, la grandeur des contributions des termes omis dans la théorie généralisée des paires séparées est estimée et trouvée non négligeable.

Unter der Annahme, daß der Grundzustand eines $2N$-Elektronensystems in der Methode der getrennten Elektronenpaare bekannt ist, wird eine Methode angegeben, wie man den Basissatz von Produktfunktionen aus streng orthogonalen Geminalen geeignet vervollständigen kann. Alle mit dem Grundzustand kombinierenden Terme werden explizit angegeben. Mit Hilfe der Störungsrechnung wird eine Korrektur zweiter Ordnung berechnet. Im Falle des Be-Atoms wird die Größe der in der Theorie der getrennten Elektronenpaare vernachlässigten Beiträge abgeschätzt und als beträchtlich erwiesen.

Introduction

Although among other many-body theories going beyond the Hartree-Fock (HF) scheme the separated pair (SP) approach [*1, 7, 9—12, 15, 20—22, 24, 25*] offers the most simple formalism, it may be rightly criticized for lacking a clear prescription of how it should be systematically completed in order to get the exact solution of the problem. The method of cluster expansion of wave functions [*4, 17, 26*] and the HF method with complete configuration interaction (HF + CCI) (including the many-body perturbation theory) [*5, 14, 23*] while forced to use approximations in practical applications, are in principle able to give exact solutions within their framework. Calculations on four-electron systems (Be, LiH) have shown that at least for strongly localized systems the simple antisymmetrized product of strongly orthogonal geminals is a fairly good approximation for the ground state [*2, 7, 16, 21, 22, 27*]. It was these results which suggested to the author a closer investigation of the problem. The complete knowledge of a (nondegenerate) geminal product ground state is assumed from the beginning. First, a simple generalization of the SP theory is summarized, then the terms not taken into account by SP theory are discussed. Finally a method is given to obtain corrections to the SP theory by perturbational techniques.

Generalized SP Theory

ARAI [*3*] and LÖWDIN [*19*] have shown that for N antisymmetric (spin) geminals $\psi_K(1,2)$, satisfying the strong orthogonality conditions (SC's)

$$\int \psi_K^*(1,2)\,\psi_L(1,2')\,d1 = 0,\ K \neq L \tag{1}$$

there exists always at least one complete set of orthonormal one-electron functions $\{\varphi\}$, which can be partitioned into N subsets having no common elements

$$\varphi_{11}, \varphi_{12}, \varphi_{13}, \ldots \varphi_{K1}, \varphi_{K2}, \varphi_{K3}, \ldots \varphi_{N1}, \varphi_{N2}, \varphi_{N3}, \ldots$$

such that each geminal can be expanded in terms of its own subset only:

$$\psi_K(1,2) = \sum_{\varkappa,\lambda} a^K_{\varkappa\lambda}\,\varphi_{K\varkappa}(1)\,\varphi_{K\lambda}(2)\,. \tag{2}$$

The functions $\varphi_{K\varkappa}$ can be chosen to be natural orbitals of the total wave function of the system [*15*].

The best possible geminals (i.e. the $a^K_{\varkappa\lambda}$ and the $\varphi_{K\varkappa}$) are defined by an infinite set of coupled equations which can be derived variationally by using (2) and the energy expression [*9—11, 15, 20, 24, 25*]

$$E = H(0) + \sum_K \int \psi_K^*(1,2)\,[H(1) + H(2) + r_{12}^{-1}]\,\psi_K(1,2)\,d1\,d2 +$$
$$+ 2 \sum_K \sum_{L(\neq K)} \int d1\,d2\,d3\,d4\,r_{13}^{-1}\,[1 - P_{13}]\,\psi_K^*(1',2)\,\psi_K(1,2)\,\psi_L^*(3',4)\psi_L(3,4)\,. \tag{3}$$

For solving this set of equations an iteration procedure, directly in terms of natural spin orbitals, has been proposed by KUTZELNIGG [*15*].

When the one-electron functions $\varphi_{K\varkappa}$ are considered already known and fixed, it can be shown [*11*] that the best possible geminals $\psi_K(1,2)$ satisfy the coupled equations:

$$Q^K H^K(1,2)\,\psi_K(1,2) = E^K\,\psi_K(1,2)\,, \qquad K = 1,2, \ldots N\,, \tag{4}$$

where

$$H^K(1,2) = H(1) + H(2) + r_{12}^{-1} +$$
$$+ 2 \sum_{L(\neq K)} \int d3\,d4\,[r_{13}^{-1}(1 - P_{13}) + r_{23}^{-1}(1 - P_{23})]\,\psi_L^*(3',4)\,\psi_L(3,4)\,, \tag{5}$$

and the Q^K are two-electron projection operators

$$Q^K = q^K(1)\,q^K(2)\,,$$
$$q^K(1) = \sum_\varkappa \int d1\,\varphi_{K\varkappa}(1')\,\varphi^*_{K\varkappa}(1)\,. \tag{6}$$

Introducing the second subscript 1 to denote the best possible geminals, the ground state of a $2N$-electron system can be represented by the antisymmetrized geminal product

$$\Phi^{11\ldots1} = \left[\frac{2^N}{(2N)!}\right]^{\frac{1}{2}} \sum_P (-1)^p\,P\,\psi_{11}(1,2)\,\psi_{21}(3,4)\ldots\psi_{N1}(2N-1, 2N)\,. \tag{7}$$

For the sake of simplicity we assume, throughout this paper, that $\Phi^{11\ldots1}$ is nondegenerate.

This wave function takes into account N SP correlations and the corresponding unlinked clusters to all orders. These pair correlations are, however, not complete as compared to those defined by the cluster expansion of the wave function [*17*, *26*] because each of the pairs is required to lie within its own subspace.

When the $H^K(1,2)$, containing the best possible geminals $\psi_{L1}(1,2)$, are regarded as fixed, it can be easily shown that each of the operators $Q^K\, H^K(1,2)$ is Hermitian for all two-electron functions lying within the corresponding subspace. It means that its eigenfunctions form a complete set of two-electron functions there. When the dimension of the subspace K (i.e., the number of linearly independent one-electron functions $\varphi_{K\varkappa}$ in that subspace) equals to n_K, each of the operators $Q^K\, H^K(1,2)$ has, together with $\psi_{K1}(1,2)$, $\binom{n_K}{2}$ linearly independent eigenfunctions $\psi_{Kk}(1,2)$ with Lagrangian multipliers E^{Kk}, $k = 1,2,\ldots \binom{n_K}{2}$. They can be determined by solving N independent secular equations

$$|\, \boldsymbol{H}^K - E^K \mathbf{1}\, | = 0, \qquad K = 1,2,\ldots N\,, \tag{8}$$

where $\boldsymbol{H}^K$ has the following elements

$$\langle \varkappa\lambda \,|\, H^K(1,2)\,|\, \mu\nu\rangle = \int d1\; d2\; \varphi^*_{K\varkappa}(1)\varphi^*_{K\lambda}(2)\; H^K(1,2)\; \varphi_{K\mu}(1)\; \varphi_{K\nu}(2)\,.$$

The lowest roots E^{K1} and the corresponding eigenvectors $a^{K1}_{\varkappa\lambda}$ are, of course, identical to those of the best possible geminals $\psi_{K1}(1,2)$. The others represent "excited" separated pairs.

The geminals $\psi_{Kk}(1,2)$ and $\psi_{Ll}(1,2)$, $K \neq L$, are orthogonal in the strong sense

$$\int \psi^*_{Kk}(1,2)\; \psi_{Ll}(1,2')\; d1 = 0\;; \tag{9}$$

while $\psi_{Kk}(1,2)$ and $\psi_{Kl}(1,2)$, $k \neq l$, are automatically orthogonal in the usual sense

$$\int \psi^*_{Kk}(1,2)\; \psi_{Kl}(1,2)\; d1\; d2 = 0 \tag{10}$$

when $E^{Kk} \neq E^{Kl}$, or they can be orthogonalized when $E^{Kk} = E^{Kl}$.

The antisymmetrized geminal products $\Phi^{ij\ldots l}$ containing one geminal from each of the N subspaces

$$\Phi^{ij\ldots l} = \left[\frac{2^N}{(2N)!}\right]^{\frac{1}{2}} \sum_P (-1)^p\, P\, \psi_{1i}(1,2)\, \psi_{2j}(3,4)\ldots\psi_{Nl}(2N-1,\, 2N)\,, \tag{11}$$

when not all of the indices $i, j,\ldots l$ equal to 1, correspond to certain excited states of the system.

The best separated pair wave function Φ_{SP} can be obtained by combining all linearly independent $\Phi^{ij\ldots l}$

$$\Phi_{\text{SP}} = \sum_{i,j,\ldots l} A^{ij\ldots l}\, \Phi^{ij\ldots l}\,. \tag{12}$$

The Φ_{SP} and the corresponding energy E^{SP} could be determined by solving the secular equation

$$|\, \boldsymbol{H}^{\text{SP}} - E^{\text{SP}} \mathbf{1}\, | = 0\,, \tag{13}$$

where $\boldsymbol{H}^{\mathrm{SP}}$ is the matrix of the total Hamilton operator in the $\Phi^{ij\ldots l}$ representation.

The properties of the geminals $\psi_{Kk}(1,2)$ greatly simplify the calculation of the matrix elements of $\boldsymbol{H}^{\mathrm{SP}}$. Nonvanishing matrix elements arise only between geminal products $\Phi^{ij\ldots l}$ and $\Phi^{i'j'\ldots l'}$ differing in not more than two indices. In addition the ground state function $\Phi^{11\ldots 1}$ does not mix with singly excited configurations [*12*, *20*].

Now we introduce the idea of "simple excitation" which substitutes one of the geminals of $\Phi^{ij\ldots l}$ by another belonging to the same subspace: $\psi_{Kk}(1,2) \rightarrow \psi_{Kl}(1,2)$, $k \neq l$. By using it series (12) can be arranged by grouping the terms according to the minimum number of simple excitations needed to reach the actual state from the ground state $\Phi^{11\ldots 1}$. We then obtain the series

$$A^{(0)}\Phi^{11\ldots 1} + \sum A^{(1)}\Phi^{(1)}_{(S)} + \sum A^{(2)}\Phi^{(2)}_{(S)} + \cdots + \sum A^{(N)}\Phi^{(N)}_{(S)} \,. \tag{14}$$

When the convergence of (14) is sufficient we can terminate at a given order and solve the secular equation of this truncated series.

For systems with N large the Rayleigh-Schrödinger perturbation theory should be used [*5*, *12*, *18*, *20*]. It can be shown that each $\Phi^{ij\ldots l}$ is an eigenfunction of the following model Hamiltonian [*12*]

$$\mathscr{H} = \sum_P P \left\{ \sum_{K=1}^{N} Q^K H^K(2K-1,2K)\, Q^K \right\}$$

and belongs to the eigenvalue

$$E^{1i} + E^{2j} + \cdots + E^{Nl} \,.$$

Here, $\mathscr{H}$ is regarded as unperturbed Hamiltonian and the perturbation operator is $H - \mathscr{H}$.

The first and second order corrections have the following form

$$E_{(1)} = H(0) - 4 \sum_{K<2} \mathscr{J}^{KL}_{11\,11} \,,$$

$$E_{(2)} = -16 \sum_{K<L} \sum_{k,l>1} \frac{\left| \mathscr{J}^{K\;L}_{1k\,1l} \right|^2}{E^{Kk} + E^{Ll} - E^{K1} - E^{L1}} \,,$$

where

$$\mathscr{J}^{KL}_{ij\,kl} = \int d1\, d2\, d3\, d4\, r_{12}^{-1}\, [1 - P_{12}]\, \psi^*_{Ki}(1',3)\, \psi_{Kj}(1,3)\, \psi^*_{Lk}(2',4)\, \psi_{Ll}(2,4) \,.$$

Note that the $(n-1)$th and the nth order terms of (14) occur only in the nth and higher order energy corrections of the perturbation theory.

There is an apparent similarity between the above method and that of the HF + CCI. It is, however, of purely formal character as can be easily seen.

Introducing particle number operators $\mathscr{N}^K$ in each of the N subspaces

$$\mathscr{N}^K = \sum_{\alpha=1}^{2N} \sum_{\varkappa} \int d\alpha\, \varphi_{K\varkappa}(\alpha')\, \varphi^*_{K\varkappa}(\alpha)$$

which all commute with each other and with the total particle number operator $\mathscr{N} = \sum \mathscr{N}^K$, it can be shown that all the antisymmetrized geminal products of type (11) and any arbitrary linear combination of them are eigenfunctions of all of the $\mathscr{N}^K$ and belong to the eigenvalues $N_1 = N_2 = \cdots = N_N = 2$. Since none of the $\mathcal{N}^K$ commutes with the Hamiltonian H containing one- and two-particle operators, the $\mathcal{N}^K$ and H cannot have simultaneous eigenstates. Consequently Φ_{SP} cannot be exact eigenstate of the system. It is just the best possible approximate wave function required to be an eigenfunction of all of the $\mathcal{N}^K$ which belongs to the eigenvalues $N_1 = N_2 = \cdots = N_N = 2$. The Φ_{SP} takes into account all many-particle correlations compatible with this constraint.

Expansion of the Wave Function in Terms of Eigenfunctions of Operators $\mathcal{N}^K$

In so far as $\{\varphi\}$ is complete the total particle number operator $\mathcal{N}$ commutes with the Hamiltonian and they have simultaneous eigenstates. In this case any eigenstate of H can be expanded in terms of *all* linearly independent eigenstates of which belong to the eigenvalue $2N$. Since the set of the $\Phi^{ij\ldots l}$ comprises only a part of these eigenstates of $\mathcal{N}$ it should be completed with its "orthogonal complement". The choice of an orthogonal complement is not unique, of course. As two eigenstates of all of the $\mathcal{N}^K$ corresponding to different partitions of the occupation numbers $N_1, N_2, \ldots N_N$ are automatically orthogonal, the orthogonal complement consists of all linearly independent eigenstates of $\mathcal{N}$ which correspond to all possible partitions of the set $N_1, N_2, \ldots N_N$, $\sum N_K = 2N$, except for which $N_1 = N_2 = \cdots = N_N = 2$. It should be noted that the possible eigenvalues of the $\mathcal{N}^K$ are $0,1,2,\ldots 2N$, when $n_K > 2N$ or $0,1,2,\ldots n_K$, when $n_K \leq 2N$. To a given partition there exist $\prod\limits_K \binom{n_K}{N_K}$ linearly independent eigenstates of $\mathcal{N}$ which can be orthogonalized*.

For suitable building blocks we introduce the group functions $\overline{\psi}_{N_K k}$ defined as follows

$$\overline{\psi}_{N_K k} = (N_K!)^{-\frac{1}{2}} \sum_P (-1)^p P \sum_{\varkappa<\lambda<\cdots<\nu} a^{Kk}_{\varkappa\lambda\ldots\nu}\, \varphi_{K\varkappa}(1)\, \varphi_{K\lambda}(2) \ldots \varphi_{K\nu}(N_K)\,, \tag{15}$$

where

$$N_K = 0,1,2,\ldots n_K;\; k = 1,2,\ldots \binom{n_K}{N_K}\,;\; \varkappa,\lambda,\ldots\nu = 1,2,\ldots n_K\,.$$

Consequently the group functions belonging to different subspaces are orthogonal in the strong sense. As in every subspace there exist $\binom{n_K}{N_K}$ linearly independent N_K-particle functions they may be thought of as normalized and mutually orthogonal in the usual sense:

$$\int \overline{\psi}^{*}_{N_K k} \overline{\psi}_{N_K l}\, d1\, d2 \ldots dN_K = \delta_{kl}\,. \tag{16}$$

It should be noted that $\overline{\psi}_{N_K k} \equiv 1$, when $N_K = 0$. Obviously the $\overline{\psi}_{N_K k}$, with $N_K = 2$, are identified with the corresponding $\psi_{Kk}(1,2)$. The other group functions may be left temporarily unspecified.

It follows from the above definitions that the antisymmetrized product functions

$$\Psi^{ij\ldots l}_{N_2 N_1 \ldots N_N} = \left[\frac{N_1!N_2!\ldots N_N!}{(2N)!}\right]^{\frac{1}{2}} \sum_P (-1)^p\, P\, \overline{\psi}_{N_1 i}\, \overline{\psi}_{N_2 j} \ldots \overline{\psi}_{N_N l}\,, \tag{17}$$

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* The completeness of set $\{\varphi\}$ implies that at least one of the n_K is infinite.

$$i = 1,2,\ldots \binom{n_1}{N_1}, j = 1,2,\ldots \binom{n_2}{N_2}, \ldots l = 1,2,\ldots \binom{n_N}{N_N}, \quad \sum_K N_K = 2N ,$$

containing one group function from each of the N subspaces, form a complete set such that the exact wave function of the system Ψ can be expanded in terms of them

$$\Psi = \sum_{\substack{N_1 N_2, \ldots N_N \\ (\Sigma N_K = 2N)}} \sum_{i,j,\ldots l} A^{ij\ldots l}_{N_1 N_2 \ldots N_N} \Psi^{ij\ldots l}_{N_1 N_2 \ldots N_N} . \tag{18}$$

The $\Psi^{ij\ldots l}_{N_1 N_2 \ldots N_N}$, with $N_1 = N_2 = \cdots = N_N = 2$ are identical to the corresponding $\Phi^{ij\ldots l}$, whereas the others comprise the orthogonal complement. The exact energy values and the corresponding wave functions of the system are solutions of the secular equation

$$| \boldsymbol{H} - E \boldsymbol{1} | = 0 , \tag{19}$$

where matrix $\boldsymbol{H}$ has the following elements

$$\int \Psi^{*ij\ldots l}_{N_1 N_2 \ldots N_N} H \Psi^{i'j'\ldots l'}_{N_1' N_2' \ldots N_N} d1\, d2 \ldots d2N . \tag{20}$$

In order that all of the states (17) may be derived from the SP ground state in addition to the "simple excitation" a new elementary excitation should be introduced which transfers one electron from one of the subspaces to another, changing two group functions simultaneously

$$\overline{\psi}_{N_K i} \overline{\psi}_{N_L j} \to \overline{\psi}_{N_K - 1, k} \overline{\psi}_{N_L + 1, l} .$$

We call it "electron transfer excitation".

As H contains one- and two-particle operators, matrix element (20) is nonvanishing only when the minimum number of elementary excitations (simple + electron transfer) needed to transfer one of the states to the other is not more than 2.

By using the idea of the above elementary excitations we can arrange the series (18) in two different ways.

1. We can group the terms according to the minimum number of elementary electron transfer excitations needed to reach the actual term from one of the functions $\Phi^{ij\ldots l}$ which belong naturally to the first group. We then get the series

$$\sum_{i,j,\ldots l} B^{(0)} \Phi^{ij\ldots l} + \sum B^{(1)} \Psi^{(1)}_{(T)} + \sum B^{(2)} \Psi^{(2)}_{(T)} + \cdots + \sum B^{(2N-2)} \Psi^{(2N-2)}_{(T)} . \tag{21}$$

The generalized SP theory is equivalent to truncating this series to the first group. The consecutive smallness of the contributions of these groups with increasing order is ensured when the important $\varphi_{K\varkappa}$ are strongly localized spatially such that the differential overlap of every important pair $\varphi_{K\varkappa}$ and $\varphi_{L\lambda}$, $K \neq L$, is negligible [*13*]. In this case the matrix elements between functions belonging to different groups are either vanishing or negligible because they contain exchange-like integrals of the following type

$$\int \varphi^*_{K\varkappa}(1)\, \varphi^*_{K\lambda}(2)\, r_{12}^{-1}\, \varphi_{K\mu}(1)\, \varphi_{L\nu}(2)\, d1\, d2,\ K \neq L ,$$

$$\int \varphi^*_{K\varkappa}(1)\, \varphi^*_{K\lambda}(2)\, r_{12}^{-1}\, \varphi_{L\mu}(1)\, \varphi_{M\nu}(2)\, d1\, d2,\ L, M \neq K . \tag{22}$$

This grouping is reasonable only when the configurational mixing within the subspaces are much stronger than those between different subspaces, i.e., when the N pairs of the system are extremely localized spatially.

2. We can group the terms according to the minimum number of elementary excitations (simple + electron transfer) needed to reach the actual term from the SP ground state $\Phi^{11\ldots1}$.

We then obtain the series:

$$C^{(0)}\,\Phi^{11\ldots1} + \sum C^{(1)}\,\Psi^{(1)} + \sum C^{(2)}\,\Psi^{(2)} + \cdots + \sum C^{(2N-2)}\,\Psi^{(2N-2)}. \tag{23}$$

It treats the two kinds of elementary excitations on an equal footing.

Both series are exact in the sense that they are equivalent to some complete configuration interaction (e.g., HF + CCI) but it will be worth using them only when the convergence is suitably rapid, i.e., when the higher order terms can be neglected. The rate of the convergence may depend strongly on the nature of the system and cannot be determined without actual calculations.

Apart from requirements (15) and (16) the $\bar{\psi}_{N_K k}$, $N_K = 1$, and $N_K > 2$, are left unspecified so far. In principle, they may be defined as eigenfunctions of certain effective operators similar to (5) and can be determined by solving the corresponding secular equations. This choice may simplify the treatment to certain extent it would need, however, far to much labour in practical applications. Instead we use the simplest possible choice by identifying $\bar{\psi}_{N_K k}$, $N_K = 1$, with the corresponding $\varphi_{K\varkappa}$ and the $\bar{\psi}_{N_K k}$, $N_K > 2$, are represented by the following determinants

$$\bar{\psi}_{N_K k} \equiv \psi_{Kk}(1,2,\ldots N_K) = (N_K!)^{-\frac{1}{2}} \sum_P (-1)^p \, P\, \varphi_{K\varkappa}(1)\, \varphi_{K\lambda}(2) \ldots \varphi_{K\nu}(N_K)\,, \tag{24}$$

where

$$\varkappa < \lambda < \cdots < \nu, \qquad \varkappa,\lambda,\ldots\nu = 1,2,\ldots n_K\,.$$

In case of series (23) it is the terms of the second and third groups which may have nonvanishing matrix elements with $\Phi^{11\ldots1}$. We list all of them as follows (displaying only the factors being changed under "excitation"):

first group:

one simple excitation

$$\psi_{K1}(1,2) \to \psi_{Kk}(1,2)\,, \tag{25}$$

for all K and $k(k \neq 1)$;

one electron transfer excitation

$$\psi_{K1}(1,2)\,\psi_{L1}(3,4) \to \varphi_{K\varkappa}(1)\,\psi_{Ll}(2,3,4)\,, \tag{26}$$

for all K, $L(K \neq L)$, $\varkappa$ and l ;

second group:

two simple excitations

$$\psi_{K1}(1,2)\,\psi_{L1}(3,4) \to \psi_{Kk}(1,2)\,\psi_{Ll}(3,4)\,, \tag{27}$$

for all $K < L$, k and $l(k, l \neq 1)$;

one simple excitation + one electron transfer excitation

$$\psi_{K1}(1,2)\,\psi_{L1}(3,4)\,\psi_{M1}(5,6) \to \varphi_{K\varkappa}(1)\,\psi_{Ll}(2,3,4)\,\psi_{Mm}(5,6)\,, \tag{28}$$

for all K, L, $M(K \neq L \neq M)$, $\varkappa$, l and $m(m \neq 1)$;

two electron transfer excitations

$$\psi_{K1}(1,2)\,\psi_{L1}(3,4)\rightarrow\psi_{Ll}(1,2,3,4)\,,\quad \text{for all } K,\,L(K\neq L) \text{ and } l\;; \tag{29}$$

$$\psi_{K1}(1,2)\,\psi_{L1}(3,4)\,\psi_{M1}(5,6)\rightarrow\psi_{Ll}(1,3,4)\,\psi_{Mm}(2,5,6)\,,\quad \text{for all } K,\,L<M(K\neq L,\,M),\,l \text{ and } m\;; \tag{30}$$

$$\psi_{K1}(1,2)\,\psi_{L1}(3,4)\,\psi_{M1}(5,6)\rightarrow\varphi_{K\varkappa}(1)\,\varphi_{L\lambda}(3)\,\psi_{Mm}(2,4,5,6)\,,\quad \text{for all } K<L,\,M(M\neq K,\,L),\,\varkappa,\,\lambda \text{ and } m\;; \tag{31}$$

$$\psi_{J1}(1,2)\,\psi_{K1}(3,4)\,\psi_{L1}(5,6)\,\psi_{M1}(7,8)\rightarrow\varphi_{J\varkappa}(1)\,\psi_{Kk}(2,3,4)\,\varphi_{L\lambda}(5)\,\psi_{Mm}(6,7,8)\,,\quad \text{for all } J<L,\,K<M\;(J,\,L\neq K,\,M),\,\varkappa,\,k,\,\lambda \text{ and } m\,. \tag{32}$$

It should be emphasized that the states of type (26) do have nonvanishing matrix elements with $\Phi^{11\ldots1}$, because with respect to variations of this kind the antisymmetrized geminal products are not self-consistent.

For 4-electron systems (e.g. Be, LiH, etc.) there are no terms of third and higher order, consequently formulae (25), (26), (27) and (29) involve all possible configurations.

Calculation of Second Order Correction to the SP Ground State

In practical calculations the set $\{\varphi\}$ obtained by determining the best possible geminal product $\Phi^{11\ldots1}$ is a finite one of course. In this case, although the series (23) is also finite, it is still equivalent to a complete configuration interaction calculation based on $\{\varphi\}$. Even then, for systems with N large, it is necessary either to terminate the series at a certain order or to solve the corresponding secular equation by the perturbation theory. The partitioning method developed by LÖWDIN [*18*] is an excellent tool for this purpose because it does not need an unperturbed operator with the complete set of its eigenfunctions.

Let Ψ_0 be a function corresponding to the initial approximation and let Ψ_r, $r=1,2,3,\ldots$, be some excited configurations, by using the partitioning techniques, we can derive a perturbation series of Rayleigh-Schrödinger-type [*20, 29*] which is up to second order

$$H_{00}+\sum_{r>0}\frac{|H_{0r}|^2}{H_{00}-H_{rr}}\,, \tag{33}$$

where

$$H_{rs}=\int\Psi_r^*\,H\,\Psi_s\,d\tau\,,\quad\int\Psi_r^*\,\Psi_s\,d\tau=\delta_{rs}\,.$$

If $\Phi^{11\ldots1}$ is substituted for Ψ_0 configurations (26)—(32) may give nonvanishing matrix elements H_{0r}. They are listed in turn as follows

$$\begin{aligned}\sqrt{6}\,\Big\{&\int d1\,d2\,d3\,d4\,\psi_{K1}^*(1,2)\,\psi_{L1}^*(3,4)\,H(2)\,\varphi_{K\varkappa}(1)\,\psi_{Ll}(2,3,4)+\\&+\int d1\,d2\,d3\,d4\,\psi_{K1}^*(1,2)\,\psi_{L1}^*(3,4)\,[r_{12}^{-1}+2r_{23}^{-1}]\,\varphi_{K\varkappa}(1)\,\psi_{Ll}(2,3,4)+\\&+2\sum_{M(\neq K,L)}\int d1\,d2\ldots d6\,\psi_{K1}^*(1,2)\,\psi_{L1}^*(3,4)\,\psi_{M1}^*(5,6)\,r_{25}^{-1}\times\\&\times[1-P_{25}]\;\varphi_{K\varkappa}(1)\,\psi_{Ll}(2,3,4)\,\psi_{M1}(5,6)\Big\}\,,\end{aligned} \tag{34}$$

$$4 \int d1\, d2\, d3\, d4\, \psi^*_{K1}(1,2)\, \psi^*_{L1}(3,4)\, r^{-1}_{13}[1 - P_{13}]\, \psi_{Kk}(1,2)\, \psi_{Ll}(3,4)\,, \tag{35}$$

$$\begin{aligned}\sqrt{24} \int d1\, d2 \ldots d6\, \psi^*_{K1}(1,2)\, \psi^*_{L1}(3,4)\, \psi^*_{M1}(5,6)\, r^{-1}_{25} \times \\ \times [1 - P_{25}]\, \varphi_{K\varkappa}(1)\, \psi_{Ll}(2,3,4)\, \psi_{Mm}(5,6)\,,\end{aligned} \tag{36}$$

$$\sqrt{6} \int d1\, d2\, d3\, d4\, \psi^*_{K1}(1,2)\, \psi^*_{L1}(3,4)\, r^{-1}_{12}\, \psi_{Ll}(1,2,3,4)\,, \tag{37}$$

$$\sqrt{18} \int d1\, d2 \ldots d6\, \psi^*_{K1}(1,2)\, \psi^*_{L1}(3,4)\, \psi^*_{M1}(5,6)\, r^{-1}_{12}\, \psi_{Ll}(1,3,4)\, \psi_{Mm}(2,5,6,) \tag{38}$$

$$\begin{aligned}\sqrt{48} \int d1\, d2 \ldots d6\, \psi^*_{K1}(1,2)\, \psi^*_{L1}(3,4)\, \psi^*_{M1}(5,6)\, r^{-1}_{24}\, \varphi_{K\varkappa}(1) \times \\ \times\, \varphi_{L\lambda}(3)\, \psi_{Mm}(2,4,5,6)\,,\end{aligned} \tag{39}$$

$$\begin{aligned}6 \int d1\, d2 \ldots d8\, \psi^*_{J1}(1,2)\, \psi^*_{K1}(3,4)\, \psi^*_{L1}(5,6)\, \psi^*_{M1}(7,8)\, r^{-1}_{26} \times \\ \times [1 - P_{26}]\, \varphi_{J\varkappa}(1)\, \psi_{Kk}(2,3,4)\, \varphi_{L\lambda}(5)\, \psi_{Mm}(6,7,8)\,.\end{aligned} \tag{40}$$

The diagonal matrix elements in the denominator are to be calculated by the expression

$$\begin{aligned}H(0) + \sum_K \int d1\, d2 \ldots dN_K\, \psi^*_{Kk}(1,2,\ldots N_K)\, \left[N_K\, H(1) + \binom{N_K}{2} r^{-1}_{12}\right] \psi_{Kk}(1,2,\ldots N_K) + \\ + \sum_{K<L} N_K\, N_L \int d1\, d2 \ldots dN_K\, d1'\, d2' \ldots dN'_L\, \psi^*_{Kk}(1,2,\ldots N_K)\, \psi^*_{Ll}(1',2',\ldots N'_L) \times \\ \times\, r^{-1}_{11'}[\psi_{Kk}(1,2,\ldots N_K)\, \psi_{Ll}(1',2',\ldots N'_L) - \psi_{Kk}(1',2,\ldots N_K)\, \psi_{Ll}(1,2',\ldots N'_L)]\,.\end{aligned} \tag{41}$$

When spin and symmetry are explicitly taken into account the number of the nonvanishing terms will be further reduced. Other terms involving electron transfers between spatially strongly separated electron groups are negligible because they contain integrals of the type (22).

It can be easily seen that when the SP ground state is nondegenerate, as was assumed at the beginning, the inequality $H_{rr} > H_{00}$ always holds, i.e., the denominators in (33) do not vanish.

Matrix elements (34)—(41) are simple algebraic expressions of the coefficients of the geminals $a^{Kk}_{\varkappa\lambda}$, and of the integrals

$$\int \varphi^*_{K\varkappa}(1)\, H(1)\, \varphi_{L\lambda}(1)\, d1\,, \tag{42}$$

$$\int \varphi^*_{J\varkappa}(1)\, \varphi^*_{K\lambda}(2)\, r^{-1}_{12}\, \varphi_{L\mu}(1)\, \varphi_{M\nu}(2)\, d1\, d2\,. \tag{43}$$

Formulae (42) and (43) can be expressed in terms of integrals of the initial, nonorthogonal basis functions. The explicit calculation of the latter is necessary before the determination of the SP ground state. The only extra labour is the solution of the secular Eqs. (8) in order to obtain the coefficients of excited geminals.

Although the second term in (33) is formally a second order correction, it represents, in general, a much higher approximation than the corresponding term in the ordinary perturbation theory based on the solutions of the HF equations. Certain effects (e.g. the SP correlations) are included implicitly up to all orders. It can be shown, however, that when the geminals are simple antisymmetrized products of the HF functions of the system the first term of matrix elements (43) is cancelled by others and only the ordinary doubly excited configurations contribute in the rest.

In the case of the Be atom using Watson's results we can estimate the magnitudes of contributions from configurations (26) and (29) which violate the SC's. These can be approximately identified with the second order perturbation theory corrections of the corresponding configurations in Tab. 3 of Ref. [*28*]. The identification is equivalent to substituting the HF ground state for $\Phi^{11\ldots1}$. The contribution from the only two electron transfer configuration (configuration 37) is less than -10^{-6} a.u.; whereas that from the one electron transfer configurations (configurations 8, 10, 11, 20, 21, 35, 36) is about 4% of the total correlation energy. This clearly indicates that the electron transfer configurations cannot be omitted even if the pairs of the system are strongly localized. It may happen, particularly for systems with weakly localized pairs, that terms of higher than second order should also be added to Eq. (33).

Finally we remark that it is just configurations (25) and (26) which contribute to the corrections up to second order when the system is subject to a perturbation consisting of one-electron operators (external electric or magnetic fields). The first and second order corrections can still be represented as sum of contributions from N pairs. As a consequence of electron transfer configurations (26) a part of the contribution of a given pair originates, in contrast to the SP theory, from other subspaces.

Discussion

The basic assumption of the above method is that the SP correlations give the most significant part of the total correlation energy and the rest can be taken as correction. It restricts the applicability to systems which consist of strongly localizable pairs (or, generally, of strongly localizable groups) [*13*]. The extent of the fulfilment of this assumption can be determined only by concrete calculations.

The crucial point of the practical application of this method is the availability of SP ground state wave functions for systems with $N \gg 2$. This seems to be far beyond the reach of present day computing facilities. Similar difficulties are encountered in other methods, too. The method of HF + CCI is apparently more easily accessible; it has been proved, however, much less successful than that of using "configurational mixing with optimized configurations" which is very close to the SP theory [*6*]. The spatial localization and the transferability of electron groups in certain systems may give some help in the solution of this problem [*8*].

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