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The Configuration Interaction Method in the Second Quantization Representation

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The mathematical apparatus of the second quantization is applied to the configuration interaction method. The configurations are treated as a system of particles and holes against the vacuum state built by the closed shell of the ground configuration. Expressions for the operators of the basic physical quantities are derived using the hole formalism generalized on an arbitrary orthonormal system of orbitals. Rules for obtaining the result of application of the operator S^2 in the second quantization are formulated. An application of Wick's theorems for calculation of the matrix elements over configurations leads to a simple logical scheme of the configuration interaction method which is valid for configurations of an arbitrary complexity and can be easily programmed for a computer.

INTRODUCTION

The main merit of the configuration interaction (CI) method is the possibility of improving a trial wave function by extending considerably a set of basis configurations. Although only those few eigenvectors of the CI matrix which correspond to its lowest eigenvalues must be found, and although modern computers can solve secular equations of a very high order — several hundreds or even thousands — this possibility is not widely used.

The simple analytical expressions for the matrix elements of the Hamiltonian over the singly excited singlet and triplet configurations are widely known. Thus an interaction of these configurations became a standard method for computing excited states of molecules². Similarly an interaction between singly excited configurations is frequently used for the calculation of the electronic structure of radicals³⁻⁵, while doubly excited configurations have been used occasionally^{6,7}. Finally, not much is known about contributions of configurations involving an excitation of three and more electrons⁸.

Development of the expressions for the CI matrix elements can be considerably simplified when the second quantization representation is used instead of the usual method based on superposition of determinants. The former approach has been used⁹ in order to obtain the matrix elements over the doubly excited singlet configurations. A comparison with the corresponding elements of singly excited configurations shows that the expressions

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for the CI matrix elements become progressively complicated as configurations become more complex. The necessity to include more and more complicated formulae into the computer program is the main obstacle to a wider use of the configuration set. In order to overcome these difficulties it is necessary to abandon the derivation of the analytical expressions for the matrix elements and to delegate this work to a computer at an early stage of the calculation. The simple rules to compute the matrix elements in the second quantization representation which follow from Wick's theorem¹⁰ and are also good for configurations of a arbitrary complexity need to be programmed for a computer. The present paper is devoted to an actual realization of the above suggestion. Since the second quantization formalism has been described by many authors¹¹ we shall give only those formulae and statements which are necessary for our discussion.

In CI computations one first includes those configurations which do not differ much from the ground configuration. For example, the singly excited configurations are constructed from the Slater determinants built from the ground state determinant by changing a single row. To account for only the changes in an explicit form in the many-particle SCF theory, an elegant mathematical apparatus known as hole formalism has been developed. Besides offering a simple physical interpretation, the hole formalism reduces the calculations considerably. This formalism generalized on an arbitrary orthonormal orbital set will be exposed below.

THE SECOND QUANTIZATION AND CI METHOD

Let us consider a system of electrons in an external field, *e. g.* in a field of fixed nuclei. The Hamiltonian of this system is represented by a sum of one electron operators $\hat{h}(k)$, each of which acts on coordinates of one of the electrons and contains its kinetic energy operator and the external field potential, and a sum over all possible pairs of electrons of the electron interaction operators $\hat{U}(k, l)$. Let be given a complete orthonormal set of orbitals $\varphi_1, \varphi_2, \varphi_3, \dots$. Multiplying each orbital φ_i in turn by the spin functions η_+ and η_- which are eigenfunctions of the spin angular momentum operator with the eigenvalues $+1/2$ and $-1/2$ (in units of \hbar) one obtains a complete orthonormal system of spin orbitals

$$\psi_{i\sigma} : \psi_{1+}, \psi_{1-}, \psi_{2+}, \psi_{2-}, \dots \text{ where}$$

$$\psi_{i+} = \varphi_i \eta_+, \quad \psi_{i-} = \varphi_i \eta_-$$

In order to pass to the second quantization representation we shall now introduce creation $A_{i\sigma}^+$ and annihilation $A_{i\sigma}$ operators for an electron in a state $\psi_{i\sigma}$. They obey the anticommutation relations

$$[A_{i\sigma}, A_{j\sigma'}]_+ = [A_{i\sigma}^+, A_{j\sigma'}^+]_+ = 0, \quad [A_{i\sigma}, A_{j\sigma'}^+]_+ = \delta_{ij} \delta_{\sigma\sigma'}. \quad (1)$$

The many-electron spin-free Hamiltonian is then given by

$$H = \sum_{ij\sigma} A_{i\sigma}^+ A_{j\sigma} h_{ij} + \frac{1}{2} \sum_{\substack{ijkl \\ \sigma\sigma'}} (ij/kl) A_{i\sigma}^+ A_{j\sigma'}^+ A_{l\sigma'} A_{k\sigma} \quad (2)$$

where

$$h_{ij} = \langle \varphi_i | \hat{h} | \varphi_j \rangle, \quad (3)$$

$$(ij | kl) = \langle (\varphi_i \varphi_j | \hat{U} | \varphi_k \varphi_l) \rangle \quad (4)$$

Operators in the second quantization representation, including the Hamiltonian (2), act in a linear space (say R) basis. It can be constructed in the following way. First one introduces a vacuum state vector $|0\rangle$ defined for all i and σ by

$$A_{i\sigma} |0\rangle = 0, \quad \langle 0 | A_{i\sigma}^+ = 0 \quad (5)$$

The vacuum state is supposed to be normalized

$$\langle 0 | 0 \rangle = 1. \quad (6)$$

Acting on the vacuum state by each of the creation operators $A_{i\sigma}^+$ one obtains all one-particle states

$$|i\sigma\rangle = A_{i\sigma}^+ |0\rangle \quad (7)$$

The states with two electrons are generated by operator $A_{j\sigma'}$ acting on the state $|i\sigma\rangle$

$$|j\sigma', i\sigma\rangle = A_{j\sigma'}^+ |i\sigma\rangle = A_{j\sigma'}^+ A_{i\sigma}^+ |0\rangle. \quad (8)$$

It follows from the anticommutation relations (7) that only those vectors are linearly independent and not equal to zero for which $i = j$ and $\sigma = \sigma'$ are not valid simultaneously.

Following this procedure we obtain a set of linearly independent states with an arbitrary number N of electrons

$$|p\sigma\rangle = A_{p_1\sigma_1}^+ A_{p_2\sigma_2}^+ A_{p_3\sigma_3}^+ \dots A_{p_N\sigma_N}^+ |0\rangle \quad (9)$$

where symbol p covers a totality of numbers p_1, p_2, \dots, p_N , symbol σ of values $\sigma_1, \sigma_2, \dots, \sigma_N$, and if $p_n = p_{n+1}$ then $\sigma_n > \sigma_{n+1}$. A set of all these states with $N = 1, 2, 3, \dots$ determines the basis which we wished to construct.

Using the anticommutation relations (1) and definitions (5) and (6) one can show that all the basic vectors (9) form an orthonormal set. It may be also shown that each of the basis vectors is an eigenvector of an operator

$$N = \sum_{i\sigma} A_{i\sigma}^+ A_{i\sigma} \quad (10)$$

with an eigenvalue N . Thus the operator (10) is the operator of the number of particles.

The Hamiltonian (2) commutes with the number-of-particles operator N and each one of its eigenvectors belongs to one of the subspaces R_N of the space R built on the basis vectors with definite N . For this reason we fix a number of particles (N) in our system and shall construct corresponding eigenvectors.

The expansion coefficients of the eigenvectors of \mathbf{H} over the basis vectors are usually determined as solutions of the eigenvalue problem for a matrix with the elements $\langle p' \sigma' | \mathbf{H} | p \sigma \rangle$. For the practical determination of approximate eigenvectors the CI matrix is truncated before diagonalization.

The order of the CI matrix which is to be diagonalized can be decreased considerably if there are operators which commute with the Hamiltonian as well as between each other. Then using an appropriate unitary transformation one goes from the set of vectors $| p \sigma \rangle$ to a new set of the basis vectors which are eigenvectors of these operators, and an initial eigenvalue problem reduces into several eigenvalue problems of a smaller order. Each of them corresponds to a definite totality of eigenvalues of the operators mentioned.

The spin-free Hamiltonian always commutes with the total spin projection operator \mathbf{S}_z and with the square of the total spin operator \mathbf{S}^2 . The latter two commute with each other also. We shall first find the expressions for them both in the second quantization representation. Expression for \mathbf{S}_z is obtained from the general definition of an one-particle operator

$$\mathbf{Q} = \sum_{ij\sigma\sigma'} \mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma'} \langle \psi_{i\sigma} | \hat{\mathbf{Q}} | \psi_{j\sigma'} \rangle \quad (11)$$

where one should put $\hat{\mathbf{Q}} = \hat{\mathbf{S}}_z$. Using the orthonormality of the spin-orbitals and the definition

$$\hat{\mathbf{S}}_z \psi_{i\sigma} = \frac{1}{2} \sigma \psi_{i\sigma}$$

one obtains

$$\mathbf{S}_z = \frac{1}{2} \sum_{i\sigma} \sigma \mathbf{A}_{i\sigma}^+ \mathbf{A}_{i\sigma} \quad (12)$$

To construct an operator \mathbf{S}^2 we begin from the well known Dirac expression¹²

$$\hat{\mathbf{S}}^2 = \frac{1}{4} \mathbf{N} (4 - \mathbf{N}) + \sum_{k < l} \hat{\mathbf{P}}_{kl}^\sigma \quad (13)$$

In the second quantization representation the first term of (13) has the same pattern except that the total number of particles \mathbf{N} must be replaced by the corresponding operator \mathbf{N} defined by (10). The operator $\hat{\mathbf{P}}_{kl}^\sigma$ which interchanges the spin functions of two electrons k and l in the states $\psi_{i\sigma}$ and $\psi_{j\sigma'}$ corresponds to the two-particle operator

$$\sum_{\sigma} (\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma}^+ \mathbf{A}_{j\sigma} \mathbf{A}_{i\sigma} + \mathbf{A}_{i\sigma}^+ \mathbf{A}_{j,-\sigma}^+ \mathbf{A}_{j\sigma} \mathbf{A}_{i,-\sigma}). \quad (14)$$

Thus, finally

$$\mathbf{S}^2 = \frac{1}{4} \mathbf{N} (4 - \mathbf{N}) + \frac{1}{2} \sum_{ij\sigma} (\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma}^+ \mathbf{A}_{j\sigma} \mathbf{A}_{i\sigma} + \mathbf{A}_{i\sigma}^+ \mathbf{A}_{j,-\sigma}^+ \mathbf{A}_{j\sigma} \mathbf{A}_{i,-\sigma}). \quad (15)$$

Later we shall consider a construction of the eigenvectors of the operators \mathbf{S}_z and \mathbf{S}^2 .

HOLE FORMALISM

Consider the subset of the spin-orbitals $\{\psi\}_1$ which contains $2n_F$ first one-particle states $\psi_{i\sigma}$ with $i \leq n_F^*$, and form a vector

$$|\Phi_0\rangle = \prod_{i=1}^{n_F} (A_{i+}^+ A_{i-}^+) |0\rangle. \quad (16)$$

This vector corresponds to the Slater determinant built on the spin-orbitals chosen. A determinant built from the same spin-orbitals except $\psi_{j\sigma}$ corresponds to a vector

$$|\Phi'\rangle = A_{j,-\sigma}^+ \prod_{\substack{i=1 \\ (i \neq j)}}^{n_F} (A_{i+}^+ A_{i-}^+) |0\rangle. \quad (17)$$

Acting on $|\Phi'\rangle$ by a unit operator

$$A_{j\sigma}^+ A_{j\sigma} + A_{j\sigma} A_{j\sigma}^+$$

and using relations (1) and (5) one obtains

$$|\Phi'\rangle = \sigma A_{j\sigma} |\Phi_0\rangle \quad j \leq n_F \quad (18)$$

This means that action of an operator $A_{j\sigma}$ with $j \leq n_F$ on a vector $|\Phi_0\rangle$ leads to the annihilation of a particle in an occupied state $\psi_{j\sigma}$, *i. e.* to the creation of a hole in this state. Thus the operators $A_{i\sigma}$ and $A_{i\sigma}^+$ with $i \leq n_F$ can be interpreted as creation and annihilation operators respectively of the holes in the states of the subset $\{\Phi\}_1$. It can be shown that the Slater determinant with u rows changed by other v rows in the second quantization representation corresponds to a vector obtained from $|\Phi_0\rangle$ by action of u hole creation and v particle creation operators in the corresponding states. All basis vectors for the CI method can be presented in this way and we shall now indicate the corresponding formalism.

Using the anticommutation relations (1) and a definition of the vacuum (5) it is easy to see that

$$\begin{aligned} A_{i\sigma}^+ |\Phi_0\rangle &= 0, & \langle \Phi_0 | A_{i\sigma} &= 0, & i &\leq n_F \\ A_{i\sigma} |\Phi_0\rangle &= 0, & \langle \Phi_0 | A_{i\sigma}^+ &= 0, & i &> n_F \end{aligned} \quad (19)$$

i. e. $|\Phi_0\rangle$ is a vacuum state with respect to the creation and annihilation operators of the holes and particles. In the following discussion under the vacuum state we always imply the state $|\Phi_0\rangle$ and not the initial state $|0\rangle$.

We shall now introduce the important concept of a normal product (N-product) of the operators F_1, F_2, \dots denoted $N(F_1 F_2 \dots)$. In order to go from the usual product to a normal one we must transpose the operators in such a way that all the hole and particle creation operators are placed to the left of the annihilation operators, and each transposition of a pair of the operators must be followed by change of a sign. Under the sign of a N-product the operators can be arbitrary transposed. The sign depends only on the

* One can take n_F pairs of arbitrary spin-orbitals ψ_{i+} and ψ_{i-} with subsequent renumbering of them.

parity of transposition. An important property of the N-product, a consequence of (1), is that its average value over the vacuum is equal to zero

$$\langle \Phi_0 | N(\dots) | \Phi_0 \rangle = 0. \quad (20a)$$

An obvious exception is the case when under the sign of a N-product there is a constant or an expression not having creation or annihilation operators (c-number). Then its average over the vacuum is equal to itself

$$\langle \Phi_0 | N(c) | \Phi_0 \rangle = c. \quad (20b)$$

A reduction of operator products to a sum of the N-products is extremely useful as shown in calculating the vacuum average of the operator products by expressions (20). This reduction can be easily performed for a product of two operators using the N-products and the anticommutation relations (1)

$$\mathbf{AB} = N(\mathbf{AB}) + \overline{\mathbf{AB}}$$

The symbol $\overline{\mathbf{AB}}$ denotes a c-number called a convolution of the operators \mathbf{A} and \mathbf{B} . Only the following convolutions of the particle and hole operators are not equal to zero

$$\begin{aligned} \overline{\mathbf{A}_{i\sigma} \mathbf{A}_{i\sigma}^+} &= 1, & i > n_F \\ \overline{\mathbf{A}_{i\sigma}^+ \mathbf{A}_{i\sigma}} &= 1, & i \leq n_F \end{aligned} \quad (22)$$

Thus introducing the population numbers

$$n_i = \begin{cases} 1 & i \leq n_F \\ 0 & i > n_F \end{cases} \quad (23)$$

one obtains for all convolutions

$$\begin{aligned} \overline{\mathbf{A}_{i\sigma} \mathbf{A}_{j\sigma'}} &= \overline{\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma'}} = 0, \\ \overline{\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma'}} &= n_i \delta_{ij} \delta_{\sigma\sigma'}, \\ \overline{\mathbf{A}_{i\sigma} \mathbf{A}_{j\sigma}^+} &= (1 - n_i) \delta_{ij} \delta_{\sigma\sigma'}. \end{aligned} \quad (24)$$

The rules for reduction of the operator products to a sum of the N-products in a general case are given by the Wick theorems^{11*}.

Theorem 1. A product of the creation and annihilation operators is represented by a sum of the normal products with all possible convolutions including a normal product without convolutions. The sign of each term is determined by a number of the operator transpositions needed that the convoluting operators are grouped together

$$\begin{aligned} \mathbf{F}_1 \mathbf{F}_2 \mathbf{F}_3 \dots \mathbf{F}_n &= N(\mathbf{F}_1 \mathbf{F}_2 \mathbf{F}_3 \dots \mathbf{F}_n) + \overline{\mathbf{F}_1 \mathbf{F}_2} N(\mathbf{F}_3 \dots \mathbf{F}_n) - \overline{\mathbf{F}_1 \mathbf{F}_3} N(\mathbf{F}_2 \mathbf{F}_4 \dots \mathbf{F}_n) + \\ &\dots + \overline{\mathbf{F}_1 \mathbf{F}_2} \overline{\mathbf{F}_3 \mathbf{F}_4} N(\mathbf{F}_5 \dots \mathbf{F}_n) + \dots \end{aligned}$$

* The theorems given¹¹ have been formulated by Wick¹⁰ for the chronological products. We give a particular formulation of these theorems for the operators with equal times.

Theorem 2. If some operators in the product to be reduced stand from the beginning under the sign of the normal product then the reduction is made in the same way except that the convolutions must be omitted for those operators which from the beginning were standing under the sign of the same normal product.

EXPANSION OF THE PHYSICAL VALUE OPERATORS OVER THE N-PRODUCTS

For a one-particle operator \mathbf{Q} using (21) and (24) one obtains from (11)

$$\mathbf{Q} = \sum_{ij\sigma\sigma'} N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma'}) \langle \psi_{i\sigma} | \hat{\mathbf{Q}} | \psi_{j\sigma'} \rangle + \sum_{i\sigma} n_i \langle \psi_{i\sigma} | \hat{\mathbf{Q}} | \psi_{i\sigma} \rangle. \quad (25)$$

In particular, if an operator $\hat{\mathbf{Q}}$ does not act on the spin variables, then

$$\mathbf{Q} = \sum_{ij\sigma} N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma}) Q_{ij} + 2 \sum_i n_i Q_{ii} \quad (26)$$

where

$$Q_{ij} = \langle \varphi_{ij} | \hat{\mathbf{Q}} | \varphi_j \rangle. \quad (27)$$

One obtains in the same way from (12)

$$\mathbf{S}_Z = \frac{1}{2} \sum_{i\sigma} \sigma N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{i\sigma}). \quad (28)$$

The number-of-particles operator (10) becomes

$$\mathbf{N} = \sum_{i\sigma} N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{i\sigma}) + 2n_F. \quad (29)$$

Now we shall transform the Hamiltonian (2). The first sum in (2) is transformed according to (26) with $\hat{\mathbf{Q}} = \hat{h}$. In order to transform a sum corresponding to the electron interaction we use the first Wick theorem. Its application to a product of four operators gives

$$\begin{aligned} & \mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma'}^+ \mathbf{A}_{l\sigma'} \mathbf{A}_{k\sigma} = N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma'}^+ \mathbf{A}_{l\sigma'} \mathbf{A}_{k\sigma}) + \\ & + N(\mathbf{A}_{j\sigma'}^+ \mathbf{A}_{l\sigma'}) \overbrace{\mathbf{A}_{i\sigma}^+ \mathbf{A}_{k\sigma}} + N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{k\sigma}) \overbrace{\mathbf{A}_{j\sigma'}^+ \mathbf{A}_{l\sigma'}} - \\ & - N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{l\sigma'}) \overbrace{\mathbf{A}_{j\sigma'}^+ \mathbf{A}_{k\sigma}} - N(\mathbf{A}_{j\sigma'}^+ \mathbf{A}_{k\sigma}) \overbrace{\mathbf{A}_{i\sigma}^+ \mathbf{A}_{l\sigma'}} + \\ & + \overbrace{\mathbf{A}_{i\sigma}^+ \mathbf{A}_{k\sigma}} \overbrace{\mathbf{A}_{j\sigma'}^+ \mathbf{A}_{l\sigma'}} - \overbrace{\mathbf{A}_{i\sigma}^+ \mathbf{A}_{l\sigma'}} \overbrace{\mathbf{A}_{j\sigma'}^+ \mathbf{A}_{k\sigma}}, \end{aligned} \quad (30)$$

where only those terms are written down which can have non-zero convolutions. Putting this expansion into (2) and substituting all convolutions by their values according to (24), after the necessary summations one obtains

$$\mathbf{H} = E_0 + \sum_{ij\sigma} F_{ij} N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma}) + \frac{1}{2} \sum_{\substack{ijkl \\ \sigma\sigma'}} (ij|kl) N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma'}^+ \mathbf{A}_{l\sigma'} \mathbf{A}_{k\sigma}) \quad (31)$$

where

$$E_0 = 2 \sum_i n_i h_{ii} + \sum_{ij} n_i n_j [2(ij|ij) - (ij|ji)] \quad (32)$$

and

$$F_{ij} = h_{ij} + \sum_k n_k [2 (ik | jk) - (ik | kj)]. \quad (33)$$

Expression (32) is the well known equation for the energy in the Hartree-Fock approximation and F_{ij} are the matrix elements

$$\langle \varphi_i | \hat{F} | \varphi_j \rangle$$

of the Fock operator built on the orbitals $\varphi_1, \varphi_2, \dots, \varphi_{n_F}$. If these orbitals are eigenfunctions of the SCF Fock operator with eigenvalues ε_i then

$$F_{ij} = \varepsilon_i \delta_{ij}$$

and the Hamiltonian (31) becomes

$$\mathbf{H} = E_0 + \sum_{i\sigma} \varepsilon_i N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{i\sigma}) + \frac{1}{2} \sum_{\substack{ijkl \\ \sigma\sigma'}} (ij | kl) N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma'}^+ \mathbf{A}_{l\sigma'} \mathbf{A}_{k\sigma}). \quad (34)$$

This particular expression for the Hamiltonian is applicable only under the conditions mentioned. The general expression (31), however is valid for an arbitrary orthonormal set of orbitals.

Following the same procedure one can obtain an expression for the operator \mathbf{S}^2 given by (15). We present the final result:

$$\begin{aligned} \mathbf{S}^2 = & \frac{3}{4} \sum_{i\sigma} (1 - 2n_i) N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{i\sigma}) + \frac{1}{4} \sum_{ij\sigma} N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma}^+ \mathbf{A}_{j\sigma} \mathbf{A}_{i\sigma}) - \\ & - \frac{1}{4} \sum_{\substack{ij\sigma \\ (i \neq j)}} N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j,-\sigma}^+ \mathbf{A}_{j,-\sigma} \mathbf{A}_{i\sigma}) - \frac{3}{4} \sum_{i\sigma} N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{i,-\sigma}^+ \mathbf{A}_{i,-\sigma} \mathbf{A}_{i\sigma}) + \\ & + \frac{1}{2} \sum_{\substack{ij\sigma \\ (i \neq j)}} N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j,-\sigma}^+ \mathbf{A}_{j\sigma} \mathbf{A}_{i,-\sigma}). \end{aligned} \quad (35)$$

The fourth sum in (35) contains terms with $i = j$ from the third and fifth sums.

Having derived expressions for the operators \mathbf{S}_z and \mathbf{S}^2 in an appropriate form we can construct the basis vectors for the CI method which are eigenfunctions of these operators. First we note that any vector obtained as a result of the action of N_p particle and N_h hole creation operators on the vacuum state $|\Phi_0\rangle$ is an eigenvector of the operator \mathbf{N} with an eigenvalue $N_p - N_h + 2n_F$ which is equal to the total number of particles. By fixing this number we need consider only vectors with a definite value of the difference $N_p - N_h$. In most cases the vacuum state can be chosen in such a way that N_p is equal to N_h (the ground state of a molecule with closed shells) or differs from N_h by one (a radical).

Next we choose the electronic configurations. Let us set up the electronic configuration by selecting the orbital corresponding to N_p particles and N_h holes irrespective of their spins. We shall denote it as $(k_1 k_2 \dots k_{N_h}, m_1 m_2 \dots m_{N_p})$ where k_i corresponds to the hole orbitals, and m_i numerate the particle orbitals. These numbers are supposed to be arranged in a non-decreasing order (naturally $k_{N_h} < n_F, m_1 > n_F$). Furthermore, according to the Pauli principle each number cannot occur more than once.

Now for the configuration $(k_1 k_2 \dots, m_1 m_2 \dots)$ we construct all possible vectors as

$$\mathbf{A}_{k_1 \sigma_1} \mathbf{A}_{k_2 \sigma_2} \dots \mathbf{A}_{m_1 \sigma_1'}^+ \mathbf{A}_{m_2 \sigma_2'}^+ \dots | \Phi_0 \rangle \quad (36)$$

which in the following discussion are called the primitive vectors. Each of the spin indices $\sigma_1, \sigma_2, \dots, \sigma_1', \sigma_2', \dots$ independently assumes values $+1$ and -1 except those cases when $k_1 = k_{1+1}$ and $m_j = n_{j+1}$ for which necessarily $\sigma_1 = -\sigma_{1+1} = 1$ and $\sigma_j' = \sigma_{j+1}' = 1$. Under these conditions the primitive vectors constructed form an orthonormal system. Each of them is an eigenvector of the operator \mathbf{S}_z with an eigenvalue

$$M_S = \frac{1}{2} [(N_p^+ - N_p^-) - (N_h^+ - N_h^-)] \quad (37)$$

where $N_p^+, N_p^-, N_h^+, N_h^-$ is the number of particle and hole operators with the spin $+1$ and -1 correspondingly.

To determine the necessary basis vectors one selects for each configuration all primitive vectors (36) with a given value of the difference $(N_p^+ - N_p^-) - (N_h^+ - N_h^-)$, constructs a matrix of the operator \mathbf{S}^2 for them, and diagonalizes it. The result of the application of the operator \mathbf{S}^2 , on the primitive vector, represented at first sight by a cumbersome expression (35) is obtained by the following simple rules.

Rule 1. The action of the first four sums in (35) on a vector (36) reduces to a multiplication of it by a constant. Its value is equal to the value of M plus half the sum of N_p and N_h minus the number of orbitals occupied in pairs by particles or holes with opposite spins. All diagonal elements of the matrix \mathbf{S}^2 will be equal to the constant found.

Rule 2. The remaining part of the expression for \mathbf{S}^2 acts on a vector (36) converting it to a sum of the vectors orthogonal to (36). Each of them differs from the initial vector by change on opposite the spin indices of two particle-particle or hole-hole operators with different spins or the particle-hole operators with equal spins. In the latter case a vector enters a sum with a minus sign. It is necessary to consider all mentioned pairs of operators used to construct an initial vector except those operators which correspond in pairs to the same orbital.

CALCULATION OF THE MATRIX ELEMENTS

Previous treatment shows that the basis vectors are linear combinations of the primitive vectors, and the operators of the important physical values (see p. 7) reduce to three basic types

$$\Omega_0 = N(c), \quad (37a)$$

$$\Omega_1 = \sum_{ij\sigma} Q_{ij,\sigma} N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma}) \quad (37b)$$

$$\Omega_2 = \frac{1}{2} \sum_{\substack{ijk1 \\ \sigma\sigma'}} (ij/lk) N(\mathbf{A}_{i\sigma}^+ \mathbf{A}_{j\sigma'}^+ \mathbf{A}_{k\sigma'} \mathbf{A}_{l\sigma}) \quad (37c)$$

Take two primitive vectors corresponding to the same or to different configurations

$$\begin{aligned} |\Phi_1\rangle &= \mathbf{A}_{k_1\sigma_1} \mathbf{A}_{k_2\sigma_2} \cdots \mathbf{A}_{m_1\sigma_1'}^+ \mathbf{A}_{m_2\sigma_2'}^+ \cdots |\Phi_0\rangle, \\ |\Phi_2\rangle &= \mathbf{A}_{l_1\tau_1} \mathbf{A}_{l_2\tau_2} \cdots \mathbf{A}_{n_1\tau_1'}^+ \mathbf{A}_{n_2\tau_2'}^+ \cdots |\Phi_0\rangle. \end{aligned} \quad (38)$$

We shall calculate for them the matrix elements of each of the operators (37). Denoting

$$\begin{aligned} \mathbf{R}_1 &= \mathbf{A}_{k_1\sigma_1} \mathbf{A}_{k_2\sigma_2} \cdots \mathbf{A}_{m_1\sigma_1'}^+ \mathbf{A}_{m_2\sigma_2'}^+ \cdots \\ \mathbf{R}_1^+ &= \cdots \mathbf{A}_{m_2\sigma_2'}^+ \mathbf{A}_{m_1\sigma_1'}^+ \cdots \mathbf{A}_{k_2\sigma_2}^+ \mathbf{A}_{k_1\sigma_1}^+, \\ \mathbf{R}_2 &= \mathbf{A}_{l_1\tau_1} \mathbf{A}_{l_2\tau_2} \cdots \mathbf{A}_{n_1\tau_1'}^+ \mathbf{A}_{n_2\tau_2'}^+ \cdots \end{aligned} \quad (39)$$

the matrix element or an operator Ω , any of the operators (37), may be considered as the vacuum average

$$\langle \Phi_1 | \Omega | \Phi_2 \rangle = \langle \Phi_0 | \mathbf{R}_1^+ \Omega \mathbf{R}_2 | \Phi_0 \rangle. \quad (40)$$

To calculate (40), the product $\mathbf{R}_1^+ \Omega \mathbf{R}_2$ must be reduced applying the Wick's theorems to the sum of the N-products. As a result of the averaging according to (20) only those terms remain which are c-numbers, *i.e.* those terms in which all operators of $\mathbf{R}_1^+ \Omega \mathbf{R}_2$ enter the convolutions.

The advantage of the presentations of the physical value operators as a sum of N-products is now evident. Since \mathbf{R}_1^+ is a product of the particle and hole annihilation operators only, and \mathbf{R}_2 of the creation operators only, then $\mathbf{R}_1^+ = N(\mathbf{R}_1^+)$, $\mathbf{R}_2 = N(\mathbf{R}_2)$ and according to the second Wick theorem one must consider only the convolutions between the operators and \mathbf{R}_2 .

After this preliminary remark we continue the determination of the value of the matrix elements. First we find the maximum number of convolutions which can be construct between the operators from \mathbf{R}_1^+ and \mathbf{R}_2 . This number is equal to the number of particle and hole operators in \mathbf{R}_1 which are repeated in \mathbf{R}_2 . The operators in \mathbf{R}_1 as well as in \mathbf{R}_2 may be transposed in an arbitrary way multiplying the value of the matrix element by $(-1)^{p_1}$, where p_1 is the total number of transpositions. For this reason it is convinient to order the operators in \mathbf{R}_1 and \mathbf{R}_2 first, transposing them in such a way that the repeating operators are placed in \mathbf{R}_1 and \mathbf{R}_2 in the same order to the right of the non-repeating operators. We shall assume in the following that this ordering is performed. The total number of non-repeating operators in \mathbf{R}_1 and \mathbf{R}_2 will be denoted q . Because each of these q operators may be convoluted with one of the operators from Ω one can state *a priori* that the matrix element

$$\langle \Phi_0 | \mathbf{R}_1^+ \Phi \mathbf{R}_2 | \Phi_0 \rangle$$

will not be equal to zero only for $q = 0$ if $\Omega = \Omega_0$, for $q = 0, 2$ if $\Omega = \Omega_1$, and for $q = 0, 2, 4$ if $\Omega = \Omega_2$. We shall consider each of these cases separately*.

* In cases when the total number of the operators in \mathbf{R}_1 and \mathbf{R}_2 is less than 2 for $\Omega = \Omega_1$ or less than 4 for $\Omega = \Omega_2$ the value of the corresponding matrix elements is obviously equal to zero.

Case 1: $\Omega = \Omega_0, q = 0$. The convolution which gives a non-zero result can be done in a single way convoluting in pairs the repeating operators. When \mathbf{R}_1 and \mathbf{R}_2 are correctly ordered there is always an even number of other operators between the convoluting operators. Thus, the number of transpositions required by the first Wick theorem is also even and each convolution according to (24) is equal to 1. Finally the value of the matrix element will be equal to

$$\langle \Phi_1 | \Omega_0 | \Phi_2 \rangle = (-1)^{p_1} c. \tag{41}$$

Case 2: $\Omega = \Omega_1, q = 0$. In this case the vacuum average is equal to the sum of the terms each of which is the result of a convolution of two operators from Ω_1 with two equal operators from \mathbf{R}_1 and \mathbf{R}_2 . The other operators repeating in \mathbf{R}_1 and \mathbf{R}_2 (if there are any) convolute between them in pairs. The final result is

$$\langle \Phi_1 | \Omega_1 | \Phi_2 \rangle = (-1)^{p_1} \sum_{i\sigma} Q_{ii,\sigma} (1 - 2n_i) \tag{42}$$

where a pair of indices i, σ covers the interval met in \mathbf{R}_1 .

Case 3: $\Omega = \Omega_1, q = 2$. The single term in the expansion of $\mathbf{R}_1^+ \Omega \mathbf{R}_2$ over the N-products the vacuum average of which may be different from zero is obtained in the following way. All operators from \mathbf{R}_1 repeating in \mathbf{R}_2 convolute with the corresponding operators from \mathbf{R}_1^+ . Two non-repeating operators convolute with the operators from Ω_1 . The result is

$$\langle \Phi_1 | \Omega_1 | \Phi_2 \rangle = (-1)^{P_1+P_2} \delta_{\sigma_1\sigma_2} Q_{i_1i_2,\sigma_1} \tag{43}$$

where p_2 is the number of transpositions necessary to place in the product $\mathbf{R}_1 \mathbf{R}_2^+$ the non-repeating operator with a cross at the left of the non-repeating operator without a cross (p_2 is equal to 1 or 0), and a pair of indices $i_1 \sigma_1$ runs over the indices of the non-repeating operator with a cross, and a pair $i_1 \sigma_1$ — without a cross in the product $\mathbf{R}_1 \mathbf{R}_2^+$

Case 4: $\Omega = \Omega_2, q = 0$. For each pair of operators from \mathbf{R}_2 in the matrix element expression for this case there are possible four terms identical in pairs obtained by convoluting these operators and the corresponding pair of operators from \mathbf{R}_1^+ with four operators from Ω_2 .

$$\langle \Phi_1 | \Omega_2 | \Phi_2 \rangle = (-1)^{p_1} \sum_{ij\sigma\sigma'} (1 - 2n_i) (1 - 2n_j) \times [(ij/ij) - \delta_{\sigma\sigma'} (ij/ji)] \tag{44}$$

where a pair of indices i, σ , runs in the interval met in the operators from \mathbf{R}_1 and a pair j, σ' covers all values of indices of the operators from \mathbf{R}_1 placed to the right of the operator with indices i, σ .

Case 5: $\Omega = \Omega_2, q = 2$. In the expansion of each of the repeating operators in \mathbf{R}_2 four terms identical in pairs may not be equal to zero. They are obtained by the convoluting with the operators from Ω_2 of two non-repeating operators, and one of the operators in \mathbf{R}_2 repeating in \mathbf{R}_1 , and the corresponding operator from \mathbf{R}_1^+ . The final result is

$$\langle \Phi_1 | \Omega_2 | \Phi_2 \rangle = (-1)^{P_1+P_2} \delta_{\sigma_1\sigma_2} \sum_{i\sigma} (1 - 2n_i) \times [(ii_1 | ii_2) - \delta_{\sigma\sigma_1} (ii_1 | i_2i)] \tag{45}$$

where a pair of indices i, σ covers all values met in the repeating operators, and a value of p_2 and indices $i_1, i_2, \sigma_1, \sigma_2$ are defined as in case 3.

Case 6: $\Omega = \Omega_2$, $q = 4$. In this last case there may not be equal to zero the four in pairs identical terms obtained by convoluting four non-repeating operators from $\mathbf{R}_1^+ \mathbf{R}_2$ with four operators from Ω_2 . The result can be obtained in the following way. Let us write all non-repeating operators in the same order as they are placed in the product $\mathbf{R}_1 \mathbf{R}_2^+$ and order them in such a way that the cross operators stand to the left of the non-cross operators. Let p_3 be the number of transpositions made in order to obtain the standard order

$$A_{i_1\sigma_1}^+ A_{i_2\sigma_2}^+ A_{i_3\sigma_3} A_{i_4\sigma_4}$$

Then the value of the matrix element is

$$\langle \Phi_1 | \Omega_2 | \Phi_2 \rangle = (-1)^{P_1+P_3} [\delta_{\sigma_1\sigma_4} \delta_{\sigma_2\sigma_3} (i_1 i_2 | I_1 i_3) - \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} (i_4 i_2 | i_3 i_1)].$$

CONCLUSIONS

The second quantization method has been intensively developed recently and is widely used for treating many-particle problems. Recently, for example, Kouba and Öhrn have considered and solved some of the problems which we discuss in a different way¹⁷. We discussed in this paper only one aspect of the second quantization method, namely the construction of the multi-configurational wave functions. Our approach is alternative to the usual determinantal method but offers some advantages. The use of the second quantization representation allows the hole which is introduced naturally and which is a mathematical description of the interpretation of the excited configurations in terms of the particles and holes against the vacuum. The importance of this interpretation is obvious, particularly if the vacuum is chosen as the Hartree-Fock state. Then the terms with the N-products in the Hamiltonian (34) will describe the correlation of the electrons in an explicit form.

Introduction of the hole formalism allows the expressions for the CI matrix elements in a form when the integrals of interaction with the vacuum particles are already summed up, and the vacuum plays the role of an external field. The use of these expressions reduces the number of summations to a minimum which is essential when the number of particles is large. Despite the relative complexity of the second quantization method it reduces the procedure for the calculations of the matrix elements to a simple logical scheme which can be easily programmed for a computer. The corresponding algorithm is universal for all varieties of the matrix elements met in actual computations and is reduced to a few simple cases.

We composed a algorithm which is based on this logical scheme for the CI method. The corresponding program CI-2 is given in detail in our book¹³. We have used this program repeatedly, in particular for computing the π -electronic states of benzyl radical¹⁴, and glycine and tyrosine molecules and their neutral and charged radicals^{7,15}. Recently the same logical scheme, but without the use of the hole formalism, was incorporated in program CI-3 to perform a complete CI for the benzyl radical¹⁶.

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IZVOD

Metoda konfiguracijske interakcije u reprezentaciji druge kvantizacije

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Primijenjen je formalizam druge kvantizacije za formulaciju metode konfiguracijske interakcije. Konstrukcija matričnih elemenata Hamiltoniana osniva se na jednostavnim pravilima koja izlaze iz Wickovog teorema. Korelacija elektrona opisana je eksplicitno korištenjem formalizma čestica-rupa, posebno izabравši kao vakuum Hartree-Fockova stanje. Pristup je prikladan za obradu na računskim strojevima, a odgovarajući algoritam koristan je i za izračunavanje ostalih tipova matričnih elemenata.

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