

ФІЗИКО-МАТЕМАТИЧНІ НАУКИ

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CONFIGURATION INTERACTION IN THE SECOND QUANTIZATION REPRESENTATION: BASICS WITH APPLICATIONS UP TO FULL CI

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Mathematical formalism of the second quantization is applied to the configuration interaction (CI) method in quantum chemistry. Application of the Wick's theorems for calculation of the matrix elements over configurations leads to a simple logical scheme which is valid for configurations of an arbitrary complexity and can be easily programmed.

Keywords: second quantization, configuration interaction, Wick theorems, quantum chemistry, full CI, benzyl radical, electron density, spin density.

Математичний формалізм вторинного квантування застосований до методу конфігураційної взаємодії (КВ) в квантовій хімії. Застосування теореми Віка для розрахунку матричних елементів між конфігураціями дозволило сформулювати просту логічну схему обчислення матричних елементів у методі КВ, яка справедлива для конфігурацій довільної складності і може бути легко запрограмована.

Ключові слова: вторинне квантування, конфігураційна взаємодія, теореми Віка, квантова хімія, повне КВ, бензильний радикал, електронна щільність, спінова густина.

1. Introduction

The main advantage of the configuration interaction (CI) method [1] is the possibility of improving a trial wave function by extending considerably a set of basis configurations. The simple analytical expressions for the matrix elements of the Hamiltonian over the singly excited singlet and triplet configurations are well known. Thus an interaction of these configurations became a standard method for computing excited states of molecules [2]. Similarly, an interaction between singly excited configurations is frequently used for the calculation of the electronic structure of radicals [3], while doubly excited configurations have been still used occasionally. Finally, not much is still known about contributions of configurations involving an excitation of three and more electrons [4].

Development of the expressions for the CI matrix elements can be considerably simplified when the second quantization formalism [5] is used instead of the usual method based on superposition of determinants [1] (see also Appendix). The former approach has been used in order to obtain the matrix elements over the doubly excited singlet configurations [6]. A comparison with the corresponding elements over singly excited configurations shows that the expressions 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 extended configuration sets. 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 representations which follow from Wick's theorem [7] and are also good for configurations of an arbitrary complexity need to be programmed. The present review is devoted to an actual realization of the above suggestion [8, 9]. Since the second quantization formalism has been described by many authors [5] 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.

2. Review of 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 $\psi_{i\sigma}$:

$$\psi_{1+}, \psi_{1-}, \psi_{2+}, \psi_{2-}, \psi_{3+}, \psi_{3-}, \dots,$$

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

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

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

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

$$\hat{H} = \sum_{ij\sigma} \hat{A}_{i\sigma}^+ \hat{A}_{j\sigma} h_{ij} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} (ij|kl) \hat{A}_{i\sigma}^+ \hat{A}_{j\sigma'}^+ \hat{A}_{l\sigma'} \hat{A}_{k\sigma}, \quad (2)$$

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 , with basis which can be constructed in the following way. First, one introduces a vacuum state vector $|0\rangle$ defined for all i and σ by

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

with the vacuum state supposed to be normalized

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

Acting on the vacuum state by each of the creation operator one obtains all one-particle states

$$|i\sigma\rangle = \hat{A}_{i\sigma}^+ |0\rangle. \quad (7)$$

The states with two electrons are generated by operator $\hat{A}_{j\sigma'}^+$ acting on the state $|i\sigma\rangle$

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

It follows from the anticommutation relations (1) 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 of electrons

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

where symbol p covers a totality of numbers $p_1, p_2, p_3, \dots, p_N$, and symbol σ – a totality of numbers $\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N$, 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 we have wished to construct.

Using the anticommutation relations (1) and definitions (5) and (6) one can show that each of the basis vectors is an eigenvector of an operator

$$\hat{N} = \sum_{i\sigma} \hat{A}_{i\sigma}^+ \hat{A}_{i\sigma} \quad (10)$$

with an eigenvalue N .

The Hamiltonian (2) commutes with the number-of-particles operator \hat{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 will construct corresponding eigenvectors.

The expansion coefficients of the eigenvectors of \hat{H} over the basis vectors are usually determined as solutions of the eigenvalue problem for a matrix with the elements $\langle p'\sigma' | \hat{H} | p\sigma \rangle$. 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 \hat{S}_z and with the square of the total spin operator \hat{S}^2 . These two operators commute with each other also. We shall first find the expressions for them both in the second quantization representation. Expression for \hat{S}_z is obtained from the general definition of an one-particle operator

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

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

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

one obtains

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

To construct an operator \hat{S}^2 we begin with the well known Dirac expression [10]

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

In the second quantization representation the first term has the same pattern except that the total number of particles N must be replaced by the corresponding operator \hat{N} defined by (10). The operator \hat{P}_{kl}^σ 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

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

Thus, finally

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

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

3. Hole Formalism

Consider the subset of the spin-orbitals $\{\psi\}_1$, which contains first $2n_F$ one-particle states $\psi_{i\sigma}$ with $i \leq n_F$ or one can take n_F pairs of arbitrary spin-orbitals $\psi_{i,+1}$ and $\psi_{i,-1}$ with subsequent renumbering of them, and form a vector

$$|\Phi_0\rangle = \prod_{i=1}^{n_F} \left(\hat{A}_{i,+1}^+ \hat{A}_{i,-1}^+ \right) |0\rangle. \quad (16)$$

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

$$|\Phi'\rangle = \hat{A}_{j,-\sigma}^+ \prod_{i=1(i \neq j)}^{n_F} \left(\hat{A}_{i,+1}^+ \hat{A}_{i,-1}^+ \right) |0\rangle. \quad (17)$$

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

$$\hat{A}_{j\sigma}^+ \hat{A}_{j\sigma} + \hat{A}_{j\sigma} \hat{A}_{j\sigma}^+$$

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

$$|\Phi'\rangle = \sigma \hat{A}_{j\sigma} |\Phi_0\rangle. \quad (j \leq n_F) \quad (18)$$

This means that action of an operator $\hat{A}_{j\sigma}$ with $j \leq n_F$ on the 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 $\hat{A}_{i\sigma}$ and $\hat{A}_{i\sigma}^+$ with $i \leq n_F$ can be interpreted as creation and annihilation respectively of the holes in the states of the subset $\{\psi\}_1$.

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 describe the corresponding formalism.

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

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

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 N -product (normal product) of the operators $\hat{F}_1, \hat{F}_2, \hat{F}_3, \dots$ denoted as $N(\hat{F}_1 \hat{F}_2 \hat{F}_3 \dots)$. 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 parity of transposition. An important property of the N -product, a consequence of (1), is that its average value over the vacuum state is equal to zero

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

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 -numbers). Then its average over the vacuum state is equal to itself

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

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 expression (20). This reduction can be easily performed for a product of two operators using the N -products and the anticommutation relations (1):

$$\hat{A}\hat{B} = N(\hat{A}\hat{B}) + \overline{\hat{A}\hat{B}}. \quad (21)$$

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

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

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

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

The rules for reduction of the operator product to a sum of the N -products in a general case are given by the Wick's theorems [11]. The theorems given in [11] have been formulated by Wick [7] for the chronological products. We give a particular formulation of these theorems for the operators with equal times.

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 N -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:

$$\begin{aligned} \hat{F}_1 \hat{F}_2 \hat{F}_3 \dots \hat{F}_n &= N(\hat{F}_1 \hat{F}_2 \hat{F}_3 \dots \hat{F}_n) + \overline{\hat{F}_1 \hat{F}_2} N(\hat{F}_3 \hat{F}_4 \hat{F}_5 \dots \hat{F}_n) - \\ &- \overline{\hat{F}_1 \hat{F}_3} N(\hat{F}_2 \hat{F}_4 \hat{F}_5 \dots \hat{F}_n) + \dots + \overline{\hat{F}_1 \hat{F}_2} \overline{\hat{F}_3 \hat{F}_4} N(\hat{F}_5 \hat{F}_6 \hat{F}_7 \dots \hat{F}_n) + \dots \end{aligned}$$

Theorem 2. If some operators in the product to be reduced stand from the beginning under the sign of the N -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 N -product.

4. Expansion of the Physical Value Operators over the N -products

For a one-particle operator using (21) and (24) one obtains from (11)

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

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

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

where

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

One obtains in the same way from (12)

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

The number-of-particles operator (10) becomes

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

Now we shall transform the Hamiltonian (2). The first sum in (2) is transformed according to (26) with $\hat{Q} = \hat{h}$. 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

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

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

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

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

$$F_{ij} = \langle \varphi_i | \hat{F} | \varphi_j \rangle$$

of the Fock operator built on the orbitals $\varphi_1, \varphi_2, \varphi_3, \dots, \varphi_{n_F}$. 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

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

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 \hat{S}^2 given by (15). We present the final result

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

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

Having derived expressions for the operators \hat{S}_z and \hat{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 \hat{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 shell) or differs from N_h by one (a radical).

Next we choose the electronic configuration. Let us set up the electronic configuration by selecting the orbitals corresponding to N_p particles and N_h holes irrespective of their spins. We shall denote it as $(k_1 k_2 k_3 \dots k_{N_h}, m_1 m_2 m_3 \dots m_{N_p})$ 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 above $(k_1 k_2 \dots, m_1 m_2 \dots)$ we construct all possible vectors as

$$\hat{A}_{k_1 \sigma_1}^+ \hat{A}_{k_2 \sigma_2}^+ \dots \hat{A}_{m_1 \sigma'_1}^+ \hat{A}_{m_2 \sigma'_2}^+ \dots |\Phi_0\rangle, \quad (36)$$

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 $k_i = k_{i+1}$ and $m_i = m_{i+1}$ for which necessary $\sigma_i = -\sigma_{i+1} = 1$ and $\sigma'_i = -\sigma'_{i+1} = 1$. Under these conditions the primitive vectors constructed form an orthonormal system. Each of them is an eigenvector of the operator \hat{S}_z with the eigenvalue

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

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 $(N_p^+ - N_p^-) - (N_h^+ - N_h^-)$, construct a matrix of the operator \hat{S}^2 for them, and diagonalizes it. The result of

the application of the operator \hat{S}^2 on the primitive vector represented at first sight as a cumbersome expression (35) is obtained by the following 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_S^2 plus half the sum of N_p and N_h minus the number of orbitals occupied in pairs by particles and holes with opposite spins. All diagonal elements of the matrix of the operator \hat{S}^2 will be equal to the constant found so far.

Rule 2. The remaining part of the expression for \hat{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 later 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 orbitals.

5. General Approach to 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 reduce to three basic types:

$$\hat{\Omega}_0 = N(c),$$

$$\hat{\Omega}_1 = \sum_{ij\sigma} Q_{ij,\sigma} N(\hat{A}_{i\sigma}^+ \hat{A}_{j\sigma}), \quad (37)$$

$$\hat{\Omega}_2 = \frac{1}{2} \sum_{ijkl\sigma\sigma'} (ij | kl) N(\hat{A}_{i\sigma}^+ \hat{A}_{j\sigma'}^+ \hat{A}_{l\sigma} \hat{A}_{k\sigma}).$$

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

$$|\Phi_1\rangle = \hat{A}_{k_1 \sigma_1}^+ \hat{A}_{k_2 \sigma_2}^+ \dots \hat{A}_{m_1 \sigma'_1}^+ \hat{A}_{m_2 \sigma'_2}^+ \dots |\Phi_0\rangle, \quad (38)$$

$$|\Phi_2\rangle = \hat{A}_{l_1 \tau_1}^+ \hat{A}_{l_2 \tau_2}^+ \dots \hat{A}_{n_1 \tau'_1}^+ \hat{A}_{n_2 \tau'_2}^+ \dots |\Phi_0\rangle.$$

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

$$\hat{R}_1 = \hat{A}_{k_1 \sigma_1}^+ \hat{A}_{k_2 \sigma_2}^+ \dots \hat{A}_{m_1 \sigma'_1}^+ \hat{A}_{m_2 \sigma'_2}^+ \dots,$$

$$\hat{R}_1^+ = \dots \hat{A}_{m_2 \sigma'_2} \hat{A}_{m_1 \sigma'_1} \dots \hat{A}_{k_2 \sigma_2} \hat{A}_{k_1 \sigma_1}, \quad (39)$$

$$\hat{R}_2 = \hat{A}_{l_1 \tau_1}^+ \hat{A}_{l_2 \tau_2}^+ \dots \hat{A}_{n_1 \tau'_1}^+ \hat{A}_{n_2 \tau'_2}^+ \dots,$$

the matrix element of an operator $\hat{\Omega}$, any of the operators (37), may be considered as the vacuum average

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

To calculate (40), the product $\hat{R}_1^+ \hat{\Omega} \hat{R}_2$ 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 in $\hat{R}_1^+ \hat{\Omega} \hat{R}_2$ enter the convolutions.

The advantage of the presentations of the physical value operators as a sum of N -products is now evident. Since \hat{R}_1^+ is a product of the particle and hole annihilation operators only, and \hat{R}_2 – of the creation operators only, then $\hat{R}_1^+ = N(\hat{R}_1^+)$, $\hat{R}_2 = N(\hat{R}_2)$ and according to the second Wick's theorem one must consider only the convolutions between the operators \hat{R}_1^+ , $\hat{\Omega}$, and \hat{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 constructed between the operators from \hat{R}_1^+ and \hat{R}_2 . This number is equal to the number of particles and hole operators in \hat{R}_1^+ which are repeated in \hat{R}_2 . The operators in \hat{R}_1^+ as well as in \hat{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 convenient to order the operators in \hat{R}_1^+ and \hat{R}_2 first, transposing them in such a way that the repeating operators are placed in \hat{R}_1^+ and \hat{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 \hat{R}_1^+ and \hat{R}_2 will be denoted q . Because each of these q operators may be convoluted with one of the operators from $\hat{\Omega}$ one can state *a priori* that the matrix element

$$\langle \Phi_0 | \hat{R}_1^+ \hat{\Omega} \hat{R}_2 | \Phi_0 \rangle$$

will not be equal to zero only for $q=0$ if $\hat{\Omega} = \hat{\Omega}_0$, for $q=0,2$ if $\hat{\Omega} = \hat{\Omega}_1$, and for $q=0,2,4$ if $\hat{\Omega} = \hat{\Omega}_2$. We shall consider each of these cases separately. In cases when the total number of the operators in \hat{R}_1^+ and \hat{R}_2 is less than 2 for $\hat{\Omega} = \hat{\Omega}_1$ or less than 4 for $\hat{\Omega} = \hat{\Omega}_2$ the value of the corresponding matrix elements is obviously equal to zero.

Case 1: $\hat{\Omega} = \hat{\Omega}_0$, $q=0$. The convolution which gives a non-zero result can be done in a single way convoluting in pairs the repeating operators. When \hat{R}_1^+ and \hat{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 unity. Finally the value of the matrix element will be equal to

$$\langle \Phi_1 | \hat{\Omega}_0 | \Phi_2 \rangle = (-1)^{p_1} c. \tag{41}$$

Case 2: $\hat{\Omega} = \hat{\Omega}_1$, $q=0$. 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 $\hat{\Omega}_1$ with two equal operators from \hat{R}_1^+ and \hat{R}_2 . The other operators repeating in \hat{R}_1^+ and \hat{R}_2 , if there are any, convolute between them in pairs. The final result is

$$\langle \Phi_1 | \hat{\Omega}_1 | \Phi_2 \rangle = (-1)^{p_1} \sum_{i\sigma} Q_{i,\sigma} (1-2n_i), \tag{42}$$

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

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

$$\langle \Phi_1 | \hat{\Omega}_1 | \Phi_2 \rangle = (-1)^{p_1+p_2} \delta_{\sigma_1\sigma_2} Q_{i_1i_2,\sigma_1}, \tag{43}$$

where p_2 is the number of transpositions necessary to place in the product $\hat{R}_1^+ \hat{R}_2^+$ 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, σ_1 runs over the indices of the non-repeating operator with a cross, and a pair i_2, σ_2 – without a cross in the product $\hat{R}_1^+ \hat{R}_2^+$.

Case 4: $\hat{\Omega} = \hat{\Omega}_2$, $q=0$. For each pair of operators from \hat{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 \hat{R}_1^+ with four operators from $\hat{\Omega}_2$

$$\langle \Phi_1 | \hat{\Omega}_2 | \Phi_2 \rangle = (-1)^{p_1} \sum_{ij\sigma\sigma'} [(j|i)_{ij} - \delta_{\sigma\sigma'} (j|j)_{ji}] (1-2n_i)(1-2n_j), \tag{44}$$

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

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

$$\langle \Phi | \hat{\Omega}_2 | \Phi_2 \rangle = (-1)^{n+2} \delta_{\sigma\sigma_1} \sum_{i\sigma} (1-2t_i) \left[\langle \hat{u}_i | \hat{u}_i \rangle - \delta_{\sigma\sigma_1} \langle \hat{u}_i | \hat{u}_i \rangle \right], \quad (45)$$

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: $\hat{\Omega} = \hat{\Omega}_2, q = 4$. 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 $\hat{R}_1^+ \hat{R}_2^+$ with four operators from $\hat{\Omega}_2$. 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 $\hat{R}_1^+ \hat{R}_2^+$ 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 standard order

$$\hat{A}_{i_1\sigma_1}^+ \hat{A}_{i_2\sigma_2}^+ \hat{A}_{i_3\sigma_3}^+ \hat{A}_{i_4\sigma_4}^+.$$

Then the value of the matrix element is

$$\langle \Phi | \hat{\Omega}_2 | \Phi_2 \rangle = (-1)^{n+2} \left[\delta_{\sigma\sigma_1} \delta_{\sigma_2\sigma_3} \langle i_1 i_2 | i_3 i_4 \rangle - \delta_{\sigma\sigma_3} \delta_{\sigma_2\sigma_1} \langle i_1 i_2 | i_3 i_4 \rangle \right]. \quad (46)$$

6. Matrix Elements of the Physical Value Operators for Molecules and Radicals with Account of Singly and Doubly Excited Configurations as an Example of the General Approach

Analytical expressions for the matrix elements of the operators are useful only for simple configurations and for the derivation of various general statements. For complex configurations it is expedient to adopt a calculation scheme given above and suitable for programming. Now we give for the case of the singly and doubly excited configurations for molecules and radicals some basis vectors which will be useful in further applications [12]. They are given in a final form, and some of them are compared with the expressions available in the literature. When deriving analytical expressions for the matrix elements we did not assume any restrictions on an orthonormal orbital set used for the construction of the configurations. We also consider some general expressions for the SCF orbitals and will show that in the case of radicals some Hamiltonian matrix elements between the ground configuration and the singly excited configurations vanish. Finally, we shall give formulae for the calculation of some molecular and radical properties by the CI method such as electronic density of atoms, bond orders, transition moments, and spin distribution.

6. 1. Basis Vectors

Consider the singly excited configurations (k, m) of a molecule with closed shells in the ground state. In this case $N_p = N_h = 1$ and four primitive vectors are possible:

$$\begin{aligned} |\Phi_1\rangle &= \hat{A}_{k+} \hat{A}_{m+}^+ |\Phi_0\rangle, & |\Phi_3\rangle &= \hat{A}_{k-} \hat{A}_{m+}^+ |\Phi_0\rangle, \\ |\Phi_2\rangle &= \hat{A}_{k-} \hat{A}_{m-}^+ |\Phi_0\rangle, & |\Phi_4\rangle &= \hat{A}_{k+} \hat{A}_{m-}^+ |\Phi_0\rangle. \end{aligned} \quad (47)$$

Using the rules of # 4 above one obtains

$$\begin{aligned} \hat{S}^2 |\Phi_1\rangle &= |\Phi_1\rangle - |\Phi_2\rangle, & \hat{S}^2 |\Phi_3\rangle &= 2 |\Phi_3\rangle, \\ \hat{S}^2 |\Phi_2\rangle &= -|\Phi_1\rangle + |\Phi_2\rangle, & \hat{S}^2 |\Phi_4\rangle &= 2 |\Phi_4\rangle. \end{aligned} \quad (48)$$

As expected, the matrix of the operator \hat{S}^2 reduces to one two-row and two one-row matrices. By diagonalizing the former one obtains the following normalized basis vectors

$$\begin{aligned} |^1\Psi_1\rangle &= \frac{1}{\sqrt{2}} (|\Phi_1\rangle + |\Phi_2\rangle), & M_S &= 0, & S &= 0, \\ |^3\Psi_1\rangle &= \frac{1}{\sqrt{2}} (|\Phi_1\rangle - |\Phi_2\rangle), & M_S &= 0, & S &= 1, \\ |^3\Psi_2\rangle &= |\Phi_3\rangle, & M_S &= 1, & S &= 1, \\ |^3\Psi_3\rangle &= |\Phi_4\rangle, & M_S &= -1, & S &= 1. \end{aligned} \quad (49)$$

There are unusual signs in the first two vectors.

In the case of a radical the vacuum state $|\Phi_0\rangle$ is chosen as the closed shell of its ground state. Then one kind of the basis vectors is obviously

$$|^2\Psi_1\rangle = \hat{A}_{m+}^+ |\Phi_0\rangle. \quad (50)$$

Now we consider the basis vectors for the configuration (k, mn) of a radical limiting of ourselves to the vectors with $M_S = 1/2$. The corresponding primitive vectors are

$$\begin{aligned} |\Phi_5\rangle &= \hat{A}_{k-} \hat{A}_{m+}^+ \hat{A}_{n-}^+ |\Phi_0\rangle, \\ |\Phi_6\rangle &= \hat{A}_{k+} \hat{A}_{m+}^+ \hat{A}_{n+}^+ |\Phi_0\rangle, \\ |\Phi_7\rangle &= \hat{A}_{k-} \hat{A}_{m-}^+ \hat{A}_{n+}^+ |\Phi_0\rangle. \end{aligned} \quad (51)$$

When $n = m$, the vector $|\Phi_6\rangle$ vanishes, and the vector $|\Phi_5\rangle$ differs from $|\Phi_7\rangle$ only by sign and becomes another basis vector

$$|^2\Psi_2\rangle = \hat{A}_{k-} \hat{A}_{m+}^+ \hat{A}_{m-}^+ |\Phi_0\rangle. \quad (52)$$

Let be $n \neq m$. Writing

$$\hat{S}^2 |\Phi_i\rangle = \sum_{j=5}^7 S_{ij}^2 |\Phi_j\rangle, \quad (53)$$

and using the rules of # 4 one obtains a matrix

$$S^2 = \begin{bmatrix} 7/4 & -1 & 1 \\ -1 & 7/4 & -1 \\ 1 & -1 & 7/4 \end{bmatrix}. \quad (54)$$

Diagonalizing this matrix we obtain eigenvector $(1, -1, 1)$ corresponding to an eigenvalue $5/4$ and two vectors $(1, -1, -2)$ and $(1, 1, 0)$ for degenerated eigenvalue $3/4$. Therefore the normalized doublet and quartet basis vectors are, respectively,

$$|^2\Psi_3\rangle = \frac{1}{\sqrt{6}} (|\Phi_5\rangle - |\Phi_6\rangle - 2|\Phi_7\rangle), \quad (55)$$

$$|{}^2\Psi_4\rangle = \frac{1}{\sqrt{2}}(|\Phi_5\rangle + |\Phi_6\rangle) \quad (56)$$

and

$$|{}^4\Psi_1\rangle = \frac{1}{\sqrt{3}}(|\Phi_5\rangle - |\Phi_6\rangle + |\Phi_7\rangle).$$

The doublet basis vectors are determined up to a unitary transformation. We have chosen the vectors (55) to correspond to those found in the literature.

6. 2. Elements of the CI matrix

The final expressions for the matrix elements of the Hamiltonian (31) obtained by using the results of # 5 above are now given.

Molecule

$$\langle \Phi_0 | \hat{H} | {}^{1,3}\Phi_1 \rangle = -f\sqrt{2}F_{km}, \quad (57)$$

$$\langle {}^{1,3}\Phi_1 | \hat{H} | {}^{1,3}\Phi_1 \rangle = \delta_{kk'}\delta_{mm'}E_0 + \delta_{kk'}F_{m'm} - \delta_{mm'}F_{kk'} + 2f(km' | mk') - (km' | k'm) \quad (58)$$

where

$$f = \begin{cases} 0 & \text{for } S = 1, \\ 1 & \text{for } S = 0. \end{cases}$$

Here and in the following expressions the primes are used for numbers of those particles and holes which constitute the basis vectors placed at the left of the Hamiltonian.

Radical

$$\langle {}^2\Phi_1 | \hat{H} | {}^2\Phi_1 \rangle = \delta_{mm'}E_0 + F_{m'm}, \quad (59)$$

$$\langle {}^2\Phi_2 | \hat{H} | {}^2\Phi_2 \rangle = \delta_{kk'}\delta_{mm'}E_0 + \delta_{mm'}(2\delta_{kk'}F_{m'm} - F_{kk'}) + \delta_{kk'}(m'm' | mm) + \delta_{mm'}[(km' | mk') - 2(km' | k'm)], \quad (60)$$

$$\begin{aligned} \langle {}^2\Phi_3 | \hat{H} | {}^2\Phi_3 \rangle &= \delta_{kk'}(\delta_{mm'}\delta_{nn'} - \delta_{mn'}\delta_{nm'})E_0 + \\ &+ \frac{1}{2}\{\delta_{kk'}(2\delta_{mm'}F_{n'n} + 2\delta_{nn'}F_{m'm} + \delta_{mm'}F_{m'n} + \\ &+ \delta_{nn'}F_{n'm}) - F_{kk'}(2\delta_{mm'}\delta_{nn'} + \delta_{nn'}\delta_{mm'}) + \\ &\delta_{kk'}[2(m'n' | mn) + (m'n' | nm)] - 2\delta_{mm'}(kn' | k'n) + \\ &+ \delta_{nn'}[3(m'k | k'm) - 2(m'k | mk')] - \\ &- \delta_{mm'}(m'k | nk') - \delta_{nn'}(n'k | mk')\}, \end{aligned} \quad (61)$$

$$\begin{aligned} \langle {}^2\Phi_4 | \hat{H} | {}^2\Phi_4 \rangle &= \delta_{kk'}(\delta_{mm'}\delta_{nn'} - \delta_{mn'}\delta_{nm'})E_0 + \\ &+ \frac{1}{2}\{\delta_{kk'}(2\delta_{mm'}F_{n'n} + 2\delta_{nn'}F_{m'm} - \delta_{mm'}F_{m'n} - \delta_{nn'}F_{n'm}) - \\ &- F_{kk'}(2\delta_{mm'}\delta_{nn'} - \delta_{mn'}\delta_{nm'}) + \delta_{kk'}[2(m'n' | mn) - \\ &-(m'n' | nm)] + 2\delta_{mm'}[2(kn' | nk') - (kn' | k'n)] + \\ &+ \delta_{nn'}[(m'k | k'm) - 2(m'k | mk')] + \delta_{mm'}[(m'k | nk') - \\ &- 2(m'k | k'n)] + \delta_{nn'}[(n'k | mk') - 2(n'k | k'm)]\}, \end{aligned} \quad (62)$$

$$\langle {}^2\Phi_1 | \hat{H} | {}^2\Phi_2 \rangle = \delta_{mm'}F_{km} + (km' | mm), \quad (63)$$

$$\langle {}^2\Phi_1 | \hat{H} | {}^2\Phi_3 \rangle = \sqrt{\frac{3}{2}}\delta_{mm'}F_{km} + (km' | mn), \quad (64)$$

$$\begin{aligned} \langle {}^2\Phi_1 | \hat{H} | {}^2\Phi_4 \rangle &= \frac{1}{\sqrt{2}}[2\delta_{mm'}F_{kn} - \delta_{nm'}F_{km} + \\ &+ 2(km' | nm) - (km' | mn)] \end{aligned} \quad (65)$$

$$\begin{aligned} \langle {}^2\Phi_2 | \hat{H} | {}^2\Phi_3 \rangle &= \frac{1}{\sqrt{6}}\{\delta_{kk'}[(m'm' | mn) - (m'm' | nm)] + \\ &+ 2\delta_{mm'}(km' | nk') - 2\delta_{nn'}(m'k | k'm)\}, \end{aligned} \quad (66)$$

$$\begin{aligned} \langle {}^2\Phi_2 | \hat{H} | {}^2\Phi_4 \rangle &= \frac{1}{\sqrt{2}}\{\delta_{kk'}(\delta_{mm'}F_{m'n} + \delta_{nn'}F_{m'm}) - \\ &- \delta_{nm'}\delta_{mm'}F_{kk'} + \delta_{kk'}(m'm' | mn) + \delta_{mm'}[2(km' | nk') - \\ &-(km' | k'n)] - \delta_{nn'}[(m'k | k'm) + (m'k | mk')]\}, \end{aligned} \quad (67)$$

$$\begin{aligned} \langle {}^2\Phi_3 | \hat{H} | {}^2\Phi_4 \rangle &= \frac{1}{\sqrt{3}}\{\delta_{kk'}(\delta_{mm'}F_{n'n} + \delta_{nn'}F_{m'm} - \delta_{mm'}F_{m'n} - \delta_{nn'}F_{n'm}) - \\ &- F_{kk'}(\delta_{mm'}\delta_{nn'} - \delta_{mn'}\delta_{nm'}) + \delta_{kk'}[(m'n' | mn) - (m'n' | nm)] + \\ &+ \delta_{mm'}[2(kn' | nk') - (kn' | k'n)] + \delta_{nn'}[(m'k | k'm) - (m'k | mk')] + \\ &+ \delta_{mm'}[(m'k | nk') - 2(m'k | k'n)] + \delta_{nn'}[(n'k | mk') - (n'k | k'm)]\}. \end{aligned} \quad (68)$$

Formula (59) is well known, e.g. in [13, 14]. Particular cases of some of the general expressions above can be found in the quantum chemistry literature, e.g. formula (60) for $k' = k, m' = m$ and (62) for $k' = k, m' = m, n' = n$ in [13], formula (63) for $m' \neq m$ in [13] and for $m' = m$ in [14], formula (64) for $m' = m$ in [14].

6. 3. The Brillouin Theorem and its Analog for Radicals

The orthonormal orbitals for which the first variation of energy E_0 of the vacuum state $|\Phi_0\rangle$ vanishes according to [15] satisfy the operator equation

$$\hat{F}\hat{P}_1 - \hat{P}_1\hat{F} = 0, \quad (69)$$

where \hat{F} is the Fock operator, and \hat{P}_1 is the Fock – Dirac density operator

$$\hat{P}_1 = \sum_{i=1}^{n_F} |\varphi_i\rangle\langle\varphi_i|. \quad (70)$$

Calculating the matrix element of (69) over the orbitals φ_k and φ_m and using projection properties of the operator \hat{P}_1 one obtains from (57) if initial orbitals satisfy equation (69) that

$$\langle \Phi_0 | \hat{H} | {}^1\Phi_1 \rangle = 0. \quad (71)$$

The conditions used in deriving (71) are more comprehensive than the conditions of the well known Brillouin theorem [16, 17]. The content of this theorem is expressed by (71) if configurations are built on the SCF eigenfunctions of the operator \hat{F} .

In the case of a radical the orbitals for which the first variation of the energy of the configuration $(-, m)$ vanishes satisfy the operator equation [19]

$$\hat{F}_1\hat{P}_1 - \hat{P}_1\hat{F}_1 + \hat{F}_2\hat{P}_2 - \hat{P}_2\hat{F}_2 = 0, \quad (72)$$

where \hat{P}_1 is defined by (70), \hat{P}_2 is a projection operator for the orbital φ_m , and the operators \hat{F}_1 and \hat{F}_2 for a semi-open shell are determined as

$$\hat{F}_1 = \hat{F} + \hat{J}_0 - \frac{1}{2} \hat{K}_0, \quad (73)$$

$$\hat{F}_2 = \frac{1}{2} \hat{F} + \hat{J}_0 - \hat{K}_0 \quad (74)$$

with the Fock operator \hat{F} built on the vacuum orbitals, and Coulomb \hat{J}_0 and exchange \hat{K}_0 operators are built on the orbital φ_m .

Let us write down the expressions for the matrix elements (59) for $m' \neq m$ and (63), (65) for $m' \neq m, n \neq m$

$$\langle {}^2\Phi_1 | \hat{H} | {}^2\Phi_1' \rangle = F_{mm'}, \quad (75)$$

$$\langle {}^2\Phi_1 | \hat{H} | {}^2\Phi_2 \rangle = F_{km} + (\hat{J}_0)_{km}, \quad (76)$$

$$\langle {}^2\Phi_1 | \hat{H} | {}^2\Phi_4 \rangle = \sqrt{2} [F_{kn} + (\hat{J}_0)_{kn} - \frac{1}{2} (\hat{K}_0)_{kn}], \quad (77)$$

where the last two matrix elements are expressed over the matrix elements of the operators \hat{J}_0 and \hat{K}_0 on the orbitals φ_i .

Using projection properties of the operators \hat{P}_1 and \hat{P}_2

$$\hat{P}_1 |\varphi_k\rangle = |\varphi_k\rangle, \quad \hat{P}_1 |\varphi_m\rangle = \hat{P}_1 |\varphi_{m'}\rangle = \hat{P}_1 |\varphi_n\rangle = 0, \quad (78)$$

$$\hat{P}_2 |\varphi_m\rangle = |\varphi_m\rangle, \quad \hat{P}_2 |\varphi_k\rangle = \hat{P}_2 |\varphi_{m'}\rangle = \hat{P}_2 |\varphi_n\rangle = 0,$$

from equation (72) one obtains

$$\begin{aligned} \langle \varphi_m | \hat{F}_2 | \varphi_{m'} \rangle &= 0, \\ \langle \varphi_k | \hat{F}_1 - \hat{F}_2 | \varphi_m \rangle &= 0, \end{aligned} \quad (79)$$

$$\langle \varphi_k | \hat{F}_1 | \varphi_n \rangle = 0.$$

Substituting \hat{F}_1 and \hat{F}_2 according (73) to (79) and using the identity

$$\hat{J}_0 |\varphi_m\rangle \equiv \hat{K}_0 |\varphi_m\rangle \quad (80)$$

we see that relations (79) express that the right sides of the equations (75) – (77) are zero.

Thus, the following statement was proved. If the configurations are built on an orthonormal orbital set for which the first variation of an energy of the configuration $(-, m)$ vanishes, then the Hamiltonian matrix elements between this configuration and any of the configurations $(-, m')$ with $m' \neq m$, configuration (k, mm) , and of the vector (56) of the configuration (k, mn) with $n \neq m$ are equal to zero.

Generally the equation (72) has many solutions but the statement proved so far is valid for any particular solution irrespective of the procedure of its derivation. Thus, this statement remains valid for the SCF orbitals obtained by the Roothaan operator [19] or by the use of the one-electron Hamiltonian for one open shell [20].

6. 4. Calculation of Certain One-particle Properties

The wave function for the state λ in the CI method is expanded over the basis vectors

$$|\lambda\rangle = \sum_q X_{q\lambda} |\psi_q\rangle \quad (81)$$

and the MO φ_i used to construct the primitive vectors are usually expressed as linear combination of orthonormal AO

$$\varphi_i = \sum_{\mu} C_{\mu i} \chi_{\mu}. \quad (82)$$

Observable physical properties are determined by the matrix elements mostly of the one-particle operator \hat{Q}

$$\langle \kappa | \hat{Q} | \lambda \rangle = \sum_{pq} X_{p\kappa}^* X_{q\lambda} \langle \psi_p | \hat{Q} | \psi_q \rangle. \quad (83)$$

Thus, one first needs to calculate the matrix elements of \hat{Q} on the basis vectors.

If \hat{Q} is a spin-free operator, analytical expressions for the matrix elements $\langle \psi_p | \hat{Q} | \psi_q \rangle$ for the configurations considered so far are obtained directly from the Hamiltonian matrix elements (57) – (68) by ignoring two-electron terms and changing F_{ij} to Q_{ij} and F_0 to an average value Q_0 of the operator \hat{Q} in the vacuum state. In particular, for the calculation of the electronic density on atoms

$P_{\mu\mu}^{\lambda\lambda}$ and bond orders $P_{\mu\nu}^{\lambda\lambda}$ in a state λ as well as transition electronic density on atoms $P_{\mu\mu}^{\kappa\lambda}$ corresponding to a transition from state κ to state λ one must take $C_{\mu i}^* C_{\mu j}$ and correspondingly $C_{\mu i}^* C_{\nu j} \equiv P_{ij}$ instead of Q_{ij} and Q_0 must be put equal to

$$2 \sum_{i=1}^{n_F} C_{\mu i}^* C_{\nu i}.$$

In the zero differential overlap approximation a component of the transition moment are determined through corresponding atomic coordinates and transition density, for example:

$$\mu_{\chi}^{\kappa\lambda} = \sum_{\nu} \chi_{\nu} P_{\nu\nu}^{\kappa\lambda}. \quad (84)$$

When calculating the spin density $\rho_{\mu\nu}^{\lambda}$ in a state λ one meets with an operator \hat{Q} which according to formula (12) depends on the spin variables being diagonal over them. We give final expressions for the matrix elements needed to calculate the spin density denoting

$$C_{\mu i}^* C_{\nu j} \equiv P_{ij}, \quad (85)$$

namely:

$$\langle {}^3\Psi_1' | 2\hat{S}_z | {}^3\Psi_1 \rangle = \delta_{kk'} P_{m'm} + \delta_{mm'} P_{kk'}, \quad (86)$$

$$\langle {}^2\Psi_1' | 2\hat{S}_z | {}^2\Psi_1 \rangle = P_{m'm} \quad (87)$$

$$\langle {}^2\Psi_2' | 2\hat{S}_z | {}^2\Psi_2 \rangle = \delta_{mm'} P_{kk'} \quad (88)$$

$$\langle {}^2\Psi'_3 | 2\hat{S}_z | {}^2\Psi_3 \rangle = \frac{1}{6} [\delta_{kk'} (4\delta_{mm'} P_{n'n} - 2\delta_{nn'} P_{m'm} - \delta_{nn'} P_{m'n} - \delta_{mm'} P_{n'm}) - P_{kk'} (4\delta_{mm'} \delta_{nn'} - 5\delta_{nn'} \delta_{mm'})], \quad (89)$$

$$\langle {}^2\Psi'_4 | 2\hat{S}_z | {}^2\Psi_4 \rangle = \frac{1}{2} [\delta_{kk'} (2\delta_{mm'} P_{m'm} - \delta_{mm'} P_{m'n} - \delta_{nn'} P_{n'm}) - P_{kk'} (\delta_{mm'} \delta_{nn'} - \delta_{nn'} \delta_{mm'})], \quad (90)$$

$$\langle {}^2\Psi'_1 | 2\hat{S}_z | {}^2\Psi_2 \rangle = -\delta_{nn'} P_{km} \quad (91)$$

$$\langle {}^2\Psi'_1 | 2\hat{S}_z | {}^2\Psi_3 \rangle = -\frac{1}{\sqrt{6}} (2\delta_{mm'} P_{kn} + \delta_{nn'} P_{km}) \quad (92)$$

$$\langle {}^2\Psi'_1 | 2\hat{S}_z | {}^2\Psi_4 \rangle = -\frac{1}{\sqrt{2}} \delta_{nn'} P_{km} \quad (93)$$

$$\langle {}^2\Psi'_2 | 2\hat{S}_z | {}^2\Psi_3 \rangle = \frac{1}{\sqrt{6}} [\delta_{kk'} (\delta_{mm'} P_{m'n} - \delta_{nn'} P_{m'm}) + 3P_{kk'} \delta_{mm'} \delta_{nn'}], \quad (94)$$

$$\langle {}^2\Psi'_2 | 2\hat{S}_z | {}^2\Psi_4 \rangle = \frac{1}{\sqrt{2}} [\delta_{kk'} (-\delta_{nn'} P_{m'n} + \delta_{nn'} P_{m'm}) + P_{kk'} \delta_{mm'} \delta_{nn'}], \quad (95)$$

$$\langle {}^2\Psi'_3 | 2\hat{S}_z | {}^2\Psi_4 \rangle = \frac{1}{\sqrt{12}} [\delta_{kk'} (-\delta_{nn'} P_{m'n} + 3\delta_{nn'} P_{n'm}) + P_{kk'} (2\delta_{mm'} \delta_{nn'} + \delta_{nn'} \delta_{mm'})]. \quad (96)$$

The expression for ${}^3\rho_{\mu\mu}^{\hat{\lambda}}$ derived in [9, 21] by the determinantal method is obtained from (86) in a way described above.

7. Exact Solution for a Seven-electron System Using Full CI Method

General approach to calculation of the CI matrix elements (# 5 above) was also used to perform full CI computation which gives an exact solution for a model Hamiltonian used. The full CI calculation was done for π -electronic model of the benzyl radical containing seven π -electrons. The reason why just the benzyl radical was chosen to perform such a labor-consuming full CI computation is connected with a still not-resolved discrepancy between computed π -spin density distribution in benzyl radical and its ESR proton splitting well studied experimentally [22, 23]. This being the situation when it seems desirable to examine the different characteristics of the ground state of benzyl radical as the approximation for the wave function is improved and approaches an exact eigenfunction of a given π -electronic Hamiltonian. We focus in this review only on technique how the restricted up to the full CI calculations were practically performed.

For a π -electronic shell of benzyl radical we used the traditional model based on the zero differential overlap approximation. Introducing creation $\hat{a}_{\mu\sigma}^+$ and annihilation $\hat{a}_{\mu\sigma}$ operators for an electron in atomic state μ with the spin σ and using the second quantization representation, the corresponding Hamiltonian is

$$\hat{H} = \sum_{\mu\nu\sigma} h_{\mu\nu}^{core} \hat{a}_{\mu\sigma}^+ \hat{a}_{\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\sigma\sigma'} \gamma_{\mu\nu} \hat{a}_{\mu\sigma}^+ \hat{a}_{\nu\sigma'}^+ \hat{a}_{\nu\sigma'} \hat{a}_{\mu\sigma}, \quad (97)$$

where $h_{\mu\nu}^{core}$ are so called core integrals, and $\gamma_{\mu\nu}$ – electron repulsion integrals of π -electronic theory. Indexes μ and ν run over all AOs (in our case from 1 to 7), and spin indexes σ and σ' take values $+1/2$ or $-1/2$. Regular model of the benzyl radical with standard CC bond length was used. All data which define the Hamiltonian (97)

completely can be find in [22]. Full CI was also performed for “equilibrium” model of the benzyl radical [23].

Now it is proper for computations to pass from AOs to MOs. Formally, this can be done by the introduction of creation $\hat{a}_{\mu\sigma}^+$ and annihilation $\hat{a}_{\mu\sigma}$ operators for electrons in molecular states through the canonical transformation

$$\hat{a}_{\mu\sigma} = \sum_i C_{\mu i} \hat{A}_{i\sigma}, \quad \hat{a}_{\mu\sigma}^+ = \sum_i C_{\mu i}^* \hat{A}_{i\sigma}^+, \quad (98)$$

where $C_{\mu i}$ are expansion coefficients of MO i over AOs. It is necessary that these expansion coefficients form a unitary matrix. Thus, the MOs will be orthonormalized and the commutation properties of the operators $\hat{A}_{i\sigma}^+$ and $\hat{A}_{i\sigma}$ will have the standard form.

Substituting (98) into (97) one obtains

$$\hat{H} = \sum_{ij\sigma} h_{ij} \hat{A}_{i\sigma}^+ \hat{A}_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} (ij | kl) \hat{A}_{i\sigma}^+ \hat{A}_{j\sigma'}^+ \hat{A}_{i\sigma} \hat{A}_{k\sigma'}, \quad (99)$$

where

$$h_{ij} = \sum_{\mu\nu} C_{\mu i}^* C_{\nu j} h_{\mu\nu}^{core}, \quad (100)$$

$$(ij | kl) = \sum_{\mu\nu} C_{\mu i}^* C_{\mu k} C_{\nu j}^* C_{\nu l} \gamma_{\mu\nu}. \quad (101)$$

In our computations the Hamiltonian (99) was taken as initial one. For the MOs entering (100) and (101) we have chosen those which minimize the energy of the ground configuration of benzyl. The corresponding orbital coefficients were computed by the SCF method for an open shell configuration [9]. Choice of these orbitals seems to be most natural providing conservation of the alternant properties for the full as well as for certain truncated configurational sets. These orbitals possess proper symmetry and some of the CI matrix elements are zero [12] due to relations analogous to Brillouin's theorem. It should be noted that the results obtained with full CI are invariant to the choice of the basis orbitals [1].

7. 1. Configurations and Energy Results

In the framework of the CI method the wave function is improved simply by extension of the configurational set. With a full set of configurations, the number of which is finite in our case, one obtains an exact eigenfunction for a given model Hamiltonian.

The theory of the CI method is well known [1]. The wave function is expanded in Slater determinants. The expansion coefficients are determined by diagonalization of the CI matrix. Its order can be lowered essentially if instead of single Slater determinants their orthonormal linear combinations of proper symmetry and multiplicity are used. We utilized this general scheme using the second quantization formalism described above successively, which is equivalent to the traditional determinantal approach (see e.g. Appendix below).

The ground state configuration of benzyl has symmetry 2B_2 . In the π -electron approximation there are 212 excited configurations of the same symmetry. The distribution of these with the multiplicity of the excitation and with the number of unpaired electrons is given in Table 1.

Table 1

Number of excited configurations for the benzyl radical depending on their type with corresponding number of the basis vectors (in parenthesis)

Number of unpaired electrons	Multiplicity of excitation					
	1	2	3	4	5	6
1	4(4)	21(21)	24(24)	33(33)	12(12)	5(5)
3	5(10)	14(28)	36(72)	22(44)	13(26)	–
5	–	5(25)	8(40)	9(45)	–	–
7	–	–	1(14)	–	–	–
Σ	9(14)	40(74)	69(150)	64(122)	25(38)	5(5)

For each configuration one can form one or more orthonormal doublet basis vectors corresponding to a positive projection of the spin. Construction of such single vector for the configuration $(i)^2(j)^2(k)^2(l)^1$ is simple. This vector corresponds to a single Slater determinant and is written as

$$A_{i\alpha}^+ A_{i\beta}^+ A_{j\alpha}^+ A_{j\beta}^+ A_{k\alpha}^+ A_{k\beta}^+ A_{l\alpha}^+ |0\rangle, \quad (102)$$

where $|0\rangle$ is the vacuum state, and indices α and β denote values $+1/2$ and $-1/2$ of the spin variable σ .

The configuration $(i)^2(j)^2(k)^1(l)^1(m)^1$ with three unpaired electrons gives rise to three vectors of type (102) with $M_s = +1/2$:

$$A_{i\alpha}^+ A_{i\beta}^+ A_{j\alpha}^+ A_{j\beta}^+ \times \begin{cases} A_{k\alpha}^+ A_{l\alpha}^+ A_{m\beta}^+ |0\rangle \\ A_{k\alpha}^+ A_{l\beta}^+ A_{m\alpha}^+ |0\rangle \\ A_{k\beta}^+ A_{l\alpha}^+ A_{m\alpha}^+ |0\rangle \end{cases}. \quad (103)$$

A linear combination of these configurations is written symbolically as

$$C_1 \alpha\alpha\beta + C_2 \alpha\beta\alpha + C_3 \beta\alpha\alpha. \quad (104)$$

Two sets of coefficients $(1/\sqrt{6}, 1/\sqrt{6}, -2/\sqrt{6})$ and $(1/\sqrt{2}, -1/\sqrt{2}, 0)$ give the two orthonormal doublet basis vectors.

For configurations with five and seven unpaired electrons the number of different spin-configurations with $M_s = +1/2$ is equal to 10 and 35, and the number of possible mutually orthogonal basis vectors is equal to 5 and 14. The corresponding sets of coefficients in the linear combination of type (104) obtained by the VB method [24] with subsequent orthogonalization are collected in Table 2. For convenience of listing these vectors are not normalized.

Expansion coefficients of all 35 basis vectors with seven unpaired electrons over spin-configurations can be found in [22].

The number of possible doublet basis vectors corresponding to different types of configurations is indicated in parenthesis in Table 1. The total number of basis vectors related to singly excited configurations of symmetry 2B_2 is equal to 14, doubly – to 74, triply – to 150, quadruply – to 122, quintuply – to 38, and sextuply – to 5.

Computations were performed with seven sets of basis vectors – G, I, II, III, IV, V, and F. Set G represents only the ground state configuration of benzyl. Each of the other sets was extended compared with previous one at the expense of the basis vectors corresponding to configurations of the next higher order of excitation. Thus the size of the configurational sets used was equal to 1, 15, 89, 239, 361, and 404 correspondingly. Set F with 404 configurations corresponds to the wave function with full CI.

Table 2

Expansion coefficients of the basis vectors with five unpaired electrons over spin-configurations

Spin-configuration	Basis vectors				
$\alpha\alpha\alpha\beta\beta$	0	0	-1	-1	1
$\alpha\alpha\beta\alpha\beta$	0	0	1	1	1
$\alpha\beta\alpha\alpha\beta$	2	0	0	0	-1
$\beta\alpha\alpha\alpha\beta$	-2	0	0	0	-1
$\alpha\alpha\beta\beta\alpha$	0	0	-1	1	-1
$\alpha\beta\alpha\beta\alpha$	-1	1	1	0	0
$\beta\alpha\alpha\beta\alpha$	1	-1	1	0	0
$\alpha\beta\beta\alpha\alpha$	-1	-1	0	-1	0
$\beta\alpha\beta\alpha\alpha$	1	1	0	-1	0
$\beta\beta\alpha\alpha\alpha$	0	0	-1	1	1

In order to perform CI computations one usually finds analytical expressions for matrix elements of the Hamiltonian over the basis vectors of different types. In our case this traditional way is not acceptable for most of the expressions to be programmed are cumbersome and the number of them is too large.

The derivation of the analytical expressions for the Hamiltonian matrix elements were rejected and entrusted this job to a computer at an early stage. To do this it was necessary to program simple rules for calculation of the matrix elements in the second quantization representation which follow from Wick's theorems and are equally good for configurations of arbitrary complexity. Necessary rules are given in # 5 above.

Occupation numbers of one-particle states for electrons are equal to 0 or 1. Therefore the computer code is ideally suitable to record vectors of type (102). The first eigenvalues and corresponding eigenvectors of the CI matrix were computed by an algorithm proposed by Nesbet [25].

The energy of the ground state of the benzyl radical computed with different configurational sets is given in Table 3.

Table 3
Change in energy E of the ground state of the benzyl radical and of the overlap integrals S between its exact and approximate wave functions as the configurational set is extending

Configurational set	E, eV	S
G	0.929722	0.945313
I	0.760009	0.966577
II	0.058437	0.997981
III	0.021089	0.999471
IV	0.000394	0.999994
V	0.000082	0.999999
F	0*	1

* Energy of the benzyl radical computed with full CI was taken as zero and for parametrical Hamiltonian (97) was equal to $-211.756817 eV$

The difference between the energy corresponding to full CI and the energy obtained in the single-configuration approximation will be called the correlation energy for a given model Hamiltonian. It is seen from Table 3 that the correlation energy in our case is equal to $-0.929722 eV$. With the singly excited configurations only 18 % of this energy is taken into account. Extension of the basis to include doubly excited configurations leads to an account of almost all the correlation energy, namely 94 %.

We do not give many other demonstrative results which came out of these computations [22, 23]. Our purpose was just to illustrate the second quantization technique described above to perform large scale CI calculations. More detailed information including computer program in ALGOL may be found in [26].

8. Appendix. Determinantal Method to Derive the Electron Density – Bond Order Matrix and the Spin Density with an Account of All Singly and Doubly Excited Configurations for Molecular States

The inclusion of more than singly excited configurations leads to a closer description of reactivity, geometry, and other properties of molecules in the ground and excited states. The knowledge of the distribution of the electron density $P_{\mu\mu}$, the spin density $\rho_{\mu\mu}$, and the bond orders $P_{\mu\nu}$, computed with an account of doubly excited configurations is important.

It is not difficult to find in quantum chemistry literature computations when wrong or better to say non-complete formulae for electron distributions mentioned above are used. For example, formula for ${}^1P_{\mu\nu}$ used in [27] is valid only for the case of mixing of some particular doubly excited configurations, namely those of the types ${}^1\Phi_{i \rightarrow k, i \rightarrow k}$ and ${}^1\Phi_{i \rightarrow k, j \rightarrow l}$, and of the ground state

configuration ${}^1\Phi_0$. Here the occupied MO's of the ground state of a molecule are designated by i and j , and the unoccupied – by k and l . The single-configurational wave function of the ground state of a molecule with $2n$ electrons is

$${}^1\Phi_0 = (1 \bar{1} \dots \bar{i} \bar{i} \dots j \bar{j} \dots n \bar{n})$$

or for the brevity just ${}^1\Phi_0 = |i\bar{i} \dots j\bar{j}|$. An identical wrong formula was erroneously used in [28–31] where singly and/or doubly excited configurations of arbitrary types have been included. The correct formulae for ${}^{1,3}P_{\mu\nu}$ and $\rho_{\mu\mu}$ with the inclusion of only singly excited configurations can be found in [9] where also is mentioned that the use of the widely-spread simple formula [27–31] for mixing of configurations of arbitrary types leads to an even qualitatively incorrect electron density distribution, especially for the states of different multiplicity. This appendix summarizes the derivation of the general expressions for ${}^{1,3}P_{\mu\nu}$ of the ground and excited singlet and triplet molecular states and for $\rho_{\mu\mu}$ of the triplet states by the determinantal method in the frame of the CI method including all singly and all doubly excited configurations [21].

A1. The Wave Functions

The multi-configurational wave functions for the singlet and triplet states are

$${}^1\Psi = {}^1X_0 {}^1\Phi_0 + \sum {}^1X_{i \rightarrow k} {}^1\Phi_{i \rightarrow k} + \sum {}^1X_{i \rightarrow k, i \rightarrow k} {}^1\Phi_{i \rightarrow k, i \rightarrow k} + \sum {}^1X_{j \rightarrow k, j \rightarrow k} {}^1\Phi_{j \rightarrow k, j \rightarrow k} + \sum {}^1X_{i \rightarrow l} {}^1\Phi_{i \rightarrow l} + \sum {}^1X'_{i \rightarrow k, j \rightarrow l} {}^1\Phi'_{i \rightarrow k, j \rightarrow l} + \sum {}^1X''_{j \rightarrow l} {}^1\Phi''_{j \rightarrow l}$$

$${}^3\Psi = \sum {}^3X_{i \rightarrow k} {}^3\Phi_{i \rightarrow k} + \sum {}^3X_{i \rightarrow k, j \rightarrow k} {}^3\Phi_{i \rightarrow k, j \rightarrow k} + \sum {}^3X_{i \rightarrow k, i \rightarrow l} {}^3\Phi_{i \rightarrow k, i \rightarrow l} + \sum {}^3X'_{i \rightarrow k, j \rightarrow l} {}^3\Phi'_{i \rightarrow k, j \rightarrow l} + \sum {}^3X''_{j \rightarrow l} {}^3\Phi''_{j \rightarrow l} + \sum {}^3X'''_{j \rightarrow l} {}^3\Phi'''_{j \rightarrow l}$$

where here and in the following equations the summation indexes over MO's are omitted supposing that they run independently over all possible values, and

$$\begin{aligned} {}^1\Phi_{i \rightarrow k} &= \frac{1}{\sqrt{2}}(|i\bar{k}j\bar{j}| - |\bar{i}k j\bar{j}|), \quad {}^1\Phi_{i \rightarrow k, i \rightarrow k} = |kk\bar{j}\bar{j}|, \\ {}^1\Phi_{j \rightarrow k} &= \frac{1}{\sqrt{2}}(|i\bar{k}\bar{j}k| + |\bar{i}k j\bar{k}|), \quad {}^1\Phi_{i \rightarrow l} = \frac{1}{\sqrt{2}}(|k\bar{l}j\bar{j}| + |\bar{l}k j\bar{j}|), \\ {}^1\Phi'_{j \rightarrow l} &= \frac{1}{2}(|i\bar{k}\bar{j}l| + |\bar{i}k j\bar{l}| - |i\bar{k}j\bar{l}| - |\bar{i}k j\bar{l}|), \\ {}^1\Phi''_{j \rightarrow l} &= \frac{1}{\sqrt{12}}(|i\bar{k}\bar{j}l| + |\bar{i}k j\bar{l}| + |i\bar{k}j\bar{l}| + |\bar{i}k j\bar{l}| - 2|i\bar{k}j\bar{l}| - 2|\bar{i}k j\bar{l}|), \\ {}^3\Phi_{i \rightarrow k} &= |ikj\bar{j}|, \quad {}^3\Phi_{i \rightarrow k, j \rightarrow k} = |i\bar{k}jk|, \quad {}^3\Phi_{i \rightarrow k, i \rightarrow l} = |klj\bar{j}|, \\ {}^3\Phi'_{j \rightarrow l} &= \frac{1}{\sqrt{2}}(|\bar{i}k j\bar{l}| - |i\bar{k}j\bar{l}|), \quad {}^3\Phi''_{j \rightarrow l} = \frac{1}{\sqrt{6}}(|\bar{i}k j\bar{l}| + |i\bar{k}j\bar{l}| - 2|i\bar{k}j\bar{l}|), \\ {}^3\Phi'''_{j \rightarrow l} &= \frac{1}{\sqrt{12}}(|\bar{i}k j\bar{l}| + |i\bar{k}j\bar{l}| + |i\bar{k}j\bar{l}| - 3|i\bar{k}j\bar{l}|). \end{aligned}$$

A2. The Expectation Value of a One-electron Operator

Let the one-electron operator be given

$$\hat{Q} = \sum_t \hat{Q}(t).$$

There should be found its average values

$${}^1\langle \hat{Q} \rangle = \langle {}^1\Psi | \hat{Q} | {}^1\Psi \rangle$$

and

$${}^3\langle \hat{Q} \rangle = \langle {}^3\Psi | \hat{Q} | {}^3\Psi \rangle.$$

In order to calculate the matrix elements of \hat{Q} on the determinantal functions contained in ${}^1\Psi$ and ${}^3\Psi$ one may use the known expansion [1]

$$\langle U | \hat{Q} | V \rangle = \sum_{rs} \langle u_r | \hat{Q} | v_s \rangle D(r | s),$$

where

$$U = (u_1 u_2 u_3 \dots u_N),$$

$$V = (v_1 v_2 v_3 \dots v_N),$$

and $D(r | s)$ is a minor of the determinant

$$D = \langle U | V \rangle,$$

received by crossing in D the column r and the row s .

Tedious calculations lead to the following expressions for ${}^1\langle \hat{Q} \rangle$ through the matrix elements of \hat{Q} in the MO representation and for ${}^3\langle \hat{Q} \rangle$ in the spin-MO representations:

$$\begin{aligned} {}^1\langle \hat{Q} \rangle = & 2 \sum_{i=1}^n Q_{ii} + \sum {}^1X_{i \rightarrow k} {}^1X'_{i \rightarrow k'} (Q_{kk'} \delta_{ii'} - Q_{ii'} \delta_{kk'}) + 2 \sum {}^1X_{i \rightarrow k}^2 (Q_{kk} - Q_{ii}) + \sum {}^1X_{i \rightarrow k} {}^1X'_{i' \rightarrow k'} (2Q_{kk} \delta_{ii'} \delta_{jj'} - Q_{ii} \delta_{jj'} - Q_{jj'} \delta_{ii'}) + \\ & + \sum {}^1X_{i \rightarrow k} {}^1X_{i \rightarrow l} {}^1X'_{i \rightarrow k'} {}^1X'_{i \rightarrow l'} (-2Q_{ii} \delta_{kk'} \delta_{ll'} + Q_{ll'} \delta_{kk'} + Q_{kk'} \delta_{ll'}) + \sum \left({}^1X'_{i \rightarrow k} {}^1X'_{i \rightarrow k'} + {}^1X''_{i \rightarrow k} {}^1X''_{i \rightarrow k'} \right) (Q_{kk'} \delta_{ii'} \delta_{jj'} \delta_{ll'} + Q_{ll'} \delta_{ii'} \delta_{jj'} \delta_{kk'} - \\ & - Q_{ii} \delta_{jj'} \delta_{kk'} \delta_{ll'} - Q_{jj'} \delta_{ii'} \delta_{kk'} \delta_{ll'}) + 2\sqrt{2} \sum {}^1X_{i \rightarrow k} \left({}^1X_0 + {}^1X_{i \rightarrow k} \right) Q_{ik} - 2 \sum {}^1X_{i \rightarrow k} {}^1X_{i \rightarrow k} Q_{jk} + 2 \sum {}^1X_{i \rightarrow k} {}^1X_{i \rightarrow l} Q_{il} - \\ & - \sqrt{2} \sum {}^1X_{i \rightarrow k} \left({}^1X'_{i \rightarrow k} + \sqrt{3} {}^1X''_{i \rightarrow k} \right) Q_{il} + 2\sqrt{2} \sum \left({}^1X_{i \rightarrow k} {}^1X_{i \rightarrow k} + {}^1X_{i \rightarrow k} {}^1X'_{i \rightarrow k} \right) Q_{ij} + 2\sqrt{2} \sum \left({}^1X_{i \rightarrow k} {}^1X_{i \rightarrow l} + {}^1X_{i \rightarrow k} {}^1X'_{i \rightarrow l} \right) Q_{kl}, \end{aligned}$$

$$\begin{aligned} {}^3\langle \hat{Q} \rangle = & \sum_{i=1}^n (Q_{ii} + Q_{i\bar{i}}) + \sum {}^3X_{i \rightarrow k} {}^3X_{i \rightarrow k'} (Q_{kk'} \delta_{ii'} - Q_{ii'} \delta_{kk'}) + \sum {}^3X_{i \rightarrow k} {}^3X'_{i \rightarrow k'} [(Q_{kk} + Q_{k\bar{k}}) \delta_{ii'} \delta_{jj'} - Q_{i\bar{i}} \delta_{jj'} - Q_{j\bar{j}} \delta_{i\bar{i}}] + \\ & + \sum {}^3X_{i \rightarrow k} {}^3X_{i \rightarrow l} [- (Q_{ii} + Q_{i\bar{i}}) \delta_{kk'} \delta_{ll'} + Q_{kk'} \delta_{ll'} + Q_{ll'} \delta_{kk'}] + \sum {}^3X'_{i \rightarrow k} {}^3X'_{i \rightarrow k'} [Q_{kk'} \delta_{ii'} \delta_{jj'} \delta_{ll'} - Q_{j\bar{j}} \delta_{ii'} \delta_{kk'} \delta_{ll'} + \frac{1}{2} (Q_{ii} + Q_{i\bar{i}}) \delta_{ii'} \delta_{jj'} \delta_{kk'} - \\ & - \frac{1}{2} (Q_{ii} + Q_{i\bar{i}}) \delta_{ii'} \delta_{jj'} \delta_{kk'}] + \frac{1}{6} \sum {}^3X''_{i \rightarrow k} {}^3X''_{i \rightarrow k'} [6Q_{kk'} \delta_{ii'} \delta_{jj'} \delta_{ll'} + (5Q_{ii} + Q_{i\bar{i}}) \delta_{ii'} \delta_{jj'} \delta_{ll'} - (4Q_{j\bar{j}} + 2Q_{j\bar{j}}) \delta_{ii'} \delta_{kk'} \delta_{ll'} - \\ & - (Q_{ii} + 5Q_{i\bar{i}}) \delta_{jj'} \delta_{kk'} \delta_{ll'}] + \frac{1}{12} \sum {}^3X'''_{i \rightarrow k} {}^3X'''_{i \rightarrow k'} [(3Q_{kk'} + 9Q_{k\bar{k}}) \delta_{ii'} \delta_{jj'} \delta_{ll'} + (11Q_{ii} + Q_{i\bar{i}}) \delta_{ii'} \delta_{jj'} \delta_{kk'} - (Q_{ii} + 11Q_{i\bar{i}}) \delta_{jj'} \delta_{kk'} \delta_{ll'} - \\ & - (11Q_{j\bar{j}} + Q_{j\bar{j}}) \delta_{ii'} \delta_{kk'} \delta_{ll'}] - 2 \sum {}^3X_{i \rightarrow k} {}^3X_{i \rightarrow k} Q_{j\bar{k}} - 2 \sum {}^3X_{i \rightarrow k} {}^3X_{i \rightarrow k} Q_{ii} - \sqrt{2} \sum {}^3X_{i \rightarrow k} {}^3X'_{i \rightarrow k} Q_{i\bar{j}} + \sqrt{\frac{2}{3}} \sum {}^3X_{i \rightarrow k} {}^3X''_{i \rightarrow k} (2Q_{ji} + Q_{j\bar{i}}) + \\ & + \frac{1}{\sqrt{3}} \sum {}^3X_{i \rightarrow k} {}^3X'''_{i \rightarrow k} (Q_{j\bar{i}} - Q_{ji}) + \sqrt{2} \sum {}^3X'_{i \rightarrow k} \left({}^3X'_{i \rightarrow k} - \frac{1}{\sqrt{3}} {}^3X''_{i \rightarrow k} \right) Q_{k\bar{i}} - \frac{1}{\sqrt{3}} \sum {}^3X_{i \rightarrow k} {}^3X'''_{i \rightarrow k} (3Q_{ki} + Q_{k\bar{i}}) + \\ & + \sqrt{2} \sum {}^3X_{i \rightarrow k} {}^3X'_{i \rightarrow k} Q_{i\bar{j}} + \sqrt{\frac{2}{3}} \sum {}^3X_{i \rightarrow k} {}^3X''_{i \rightarrow k} (Q_{i\bar{j}} + 2Q_{ij}) + \frac{1}{\sqrt{3}} \sum {}^3X_{i \rightarrow k} {}^3X'''_{i \rightarrow k} (Q_{i\bar{j}} - Q_{ij}) + \\ & + \frac{1}{\sqrt{3}} \sum \left[{}^3X'_{i \rightarrow k} \left({}^3X''_{i \rightarrow k} + \frac{1}{\sqrt{2}} {}^3X'''_{i \rightarrow k} \right) \right] [(Q_{ii} - Q_{i\bar{i}}) \delta_{ii'} + (Q_{i\bar{i}} - Q_{ii}) \delta_{i\bar{i}}] + \\ & + \frac{\sqrt{2}}{6} \sum {}^3X''_{i \rightarrow k} {}^3X'''_{i \rightarrow k'} [(Q_{i\bar{i}} - Q_{ii}) \delta_{ii'} \delta_{jj'} + (Q_{i\bar{i}} - Q_{ii}) \delta_{jj'} \delta_{i\bar{i}} + 2(Q_{jj} - Q_{j\bar{j}}) \delta_{ii'} \delta_{i\bar{i}}]. \end{aligned} \tag{105}$$

A3. The Electron Density – Bond Order Matrix and the Spin Density

Expanding the MOs in linear combination of AOs

$$\varphi_r = \sum_{\mu} C_{\mu r} \chi_{\mu} \tag{106}$$

one can introduce the matrix elements

$$Q_{\mu\nu} = \langle \chi_{\mu} | \hat{Q} | \chi_{\nu} \rangle$$

and obtains an expression for ${}^1\langle \hat{Q} \rangle$ in terms of the expansion coefficients $C_{\mu r}$. Comparing it with the known expression

$${}^{1,3}\langle \hat{Q} \rangle = \sum_{\mu\nu} {}^{1,3}P_{\mu\nu} Q_{\mu\nu} \tag{107}$$

one finally obtains

$$\begin{aligned}
 {}^1P_{\mu\nu} = & 2\sum_{i=1}^n C_{\mu i} C_{\nu i} + \sum X_{i \rightarrow k} {}^1X_{i' \rightarrow k'} (C_{\mu k} C_{\nu k'} \delta_{ii'} - C_{\mu i} C_{\nu i'} \delta_{kk'}) + \\
 & + 2\sum_{i \rightarrow k} {}^1X_{i \rightarrow k}^2 (C_{\mu k} C_{\nu k} - C_{\mu i} C_{\nu i}) + \sum_{j \rightarrow k} {}^1X_{i \rightarrow k} {}^1X_{i' \rightarrow k'} (2C_{\mu k} C_{\nu k} \delta_{ii'} \delta_{jj'} - C_{\mu i} C_{\nu i'} \delta_{jj'} - \\
 & - C_{\mu j} C_{\nu j'} \delta_{ii'}) + \sum_{i \rightarrow l} {}^1X_{i \rightarrow k} {}^1X_{i' \rightarrow k'} (-2C_{\mu i} C_{\nu i} \delta_{kk'} \delta_{ll'} + C_{\mu k} C_{\nu k'} \delta_{ll'} + C_{\mu l} C_{\nu l'} \delta_{kk'}) + \\
 & + \sum \left({}^1X'_{i \rightarrow k} {}^1X'_{i' \rightarrow k'} + {}^1X''_{i \rightarrow k} {}^1X''_{i' \rightarrow k'} \right) (C_{\mu k} C_{\nu k'} \delta_{ii'} \delta_{jj'} \delta_{ll'} + C_{\mu l} C_{\nu l'} \delta_{ii'} \delta_{jj'} \delta_{kk'} - C_{\mu i} C_{\nu i'} \delta_{jj'} \delta_{kk'} \delta_{ll'} - \\
 & - C_{\mu j} C_{\nu j'} \delta_{ii'} \delta_{kk'} \delta_{ll'}) + 2\sqrt{2} \sum X_{i \rightarrow k} \left({}^1X_0 + {}^1X_{i \rightarrow k} \right) C_{\mu i} C_{\nu k} - 2\sum {}^1X_{i \rightarrow k} {}^1X_{i \rightarrow k} C_{\mu j} C_{\nu k} + \\
 & + 2\sum {}^1X_{i \rightarrow k} {}^1X_{i \rightarrow k} C_{\mu i} C_{\nu l} - \sqrt{2} \sum {}^1X_{i \rightarrow k} \left({}^1X'_{i \rightarrow k} + \sqrt{3} {}^1X''_{i \rightarrow k} \right) C_{\mu j} C_{\nu l} + \\
 & + 2\sqrt{2} \sum \left({}^1X_{i \rightarrow k} {}^1X_{i \rightarrow k} + {}^1X_{i \rightarrow l} {}^1X'_{i' \rightarrow k'} \right) C_{\mu i} C_{\nu j} + 2\sqrt{2} \sum \left({}^1X_{i \rightarrow k} {}^1X_{i \rightarrow l} + {}^1X_{i \rightarrow k} {}^1X'_{i' \rightarrow k'} \right) C_{\mu k} C_{\nu l}.
 \end{aligned} \tag{108}$$

In order to calculate $\rho_{\mu\mu}$ let put in (105)

$$\hat{Q} = \sum_t \hat{S}_z(t).$$

Taking into account that

$$(\hat{S}_z)_{ij} = -(\hat{S}_z)_{i\bar{j}}$$

and using the AO basis one obtains after some manipulations

$$\begin{aligned}
 \left\langle \sum_t \hat{S}_z(t) \right\rangle = & \frac{1}{2} \sum {}^3X_{i \rightarrow k} {}^3X_{i' \rightarrow k'} \sum_{\mu} (C_{\mu k} C_{\mu k'} \delta_{ii'} + C_{\mu i} C_{\mu i'} \delta_{kk'}) + \frac{1}{2} \sum {}^3X_{i \rightarrow k} {}^3X_{i' \rightarrow k'} \sum_{\mu} (C_{\mu j} C_{\mu j'} \delta_{ii'} + C_{\mu i} C_{\mu i'} \delta_{jj'}) \\
 & + \frac{1}{2} \sum {}^3X_{i \rightarrow k} {}^3X_{i' \rightarrow k'} \sum_{\mu} (C_{\mu k} C_{\mu k'} \delta_{ll'} + C_{\mu l} C_{\mu l'} \delta_{kk'}) + \frac{1}{2} \sum {}^3X'_{i \rightarrow k} {}^3X'_{i' \rightarrow k'} \sum_{\mu} (C_{\mu k} C_{\mu k'} \delta_{jj'} + C_{\mu j} C_{\mu j'} \delta_{kk'}) + \\
 & + \frac{1}{6} \sum {}^3X''_{i \rightarrow k} {}^3X''_{i' \rightarrow k'} \sum_{\mu} (3C_{\mu k} C_{\mu k'} \delta_{ii'} \delta_{jj'} \delta_{ll'} + 2C_{\mu l} C_{\mu l'} \delta_{ii'} \delta_{jj'} \delta_{kk'} + 2C_{\mu i} C_{\mu i'} \delta_{jj'} \delta_{kk'} \delta_{ll'} - C_{\mu j} C_{\mu j'} \delta_{ii'} \delta_{kk'} \delta_{ll'}) + \\
 & + \frac{1}{12} \sum {}^3X'''_{i \rightarrow k} {}^3X'''_{i' \rightarrow k'} \sum_{\mu} (5C_{\mu i} C_{\mu i'} \delta_{jj'} \delta_{kk'} \delta_{ll'} + 5C_{\mu j} C_{\mu j'} \delta_{ii'} \delta_{kk'} \delta_{ll'} + 5C_{\mu l} C_{\mu l'} \delta_{ii'} \delta_{jj'} \delta_{kk'} - \\
 & - 3C_{\mu k} C_{\mu k'} \delta_{ii'} \delta_{jj'} \delta_{ll'}) + \sum {}^3X_{i \rightarrow k} {}^3X_{i \rightarrow k} \sum_{\mu} C_{\mu j} C_{\mu k} - \sum {}^3X_{i \rightarrow k} {}^3X_{i \rightarrow l} \sum_{\mu} C_{\mu i} C_{\mu l} + \\
 & + \frac{1}{2} \sum {}^3X_{i \rightarrow k} \left(\sqrt{2} {}^3X'_{i \rightarrow k} + \sqrt{\frac{2}{3}} {}^3X''_{i \rightarrow k} - \frac{2}{\sqrt{3}} {}^3X'''_{i \rightarrow k} \right) \sum_{\mu} C_{\mu j} C_{\mu l} + \frac{1}{2} \sum {}^3X_{i \rightarrow k} (-\sqrt{2} {}^3X'_{i \rightarrow k} + \\
 & + \sqrt{\frac{2}{3}} {}^3X''_{i \rightarrow k} - \frac{2}{\sqrt{3}} {}^3X'''_{i \rightarrow k}) \sum_{\mu} C_{\mu k} C_{\mu l} + \frac{1}{2} \sum {}^3X_{i \rightarrow l} (-\sqrt{2} {}^3X'_{i \rightarrow k} + \sqrt{\frac{2}{3}} {}^3X''_{i \rightarrow k} - \frac{2}{\sqrt{3}} {}^3X'''_{i \rightarrow k}) \sum_{\mu} C_{\mu i} C_{\mu j} + \\
 & + \frac{1}{\sqrt{3}} \sum {}^3X'_{i \rightarrow k} \left({}^3X''_{i' \rightarrow k'} + \frac{1}{\sqrt{2}} {}^3X'''_{i' \rightarrow k'} \right) \sum_{\mu} (C_{\mu l} C_{\mu l'} \delta_{ii'} - C_{\mu i} C_{\mu i'} \delta_{ll'}) + \\
 & + \frac{\sqrt{2}}{6} \sum {}^3X''_{i \rightarrow k} {}^3X''_{i' \rightarrow k'} \sum_{\mu} (2C_{\mu j} C_{\mu j'} \delta_{ii'} \delta_{ll'} - C_{\mu i} C_{\mu i'} \delta_{jj'} \delta_{ll'} - C_{\mu l} C_{\mu l'} \delta_{ii'} \delta_{jj'}).
 \end{aligned}$$

On the other hand

$$\left\langle \sum_t \hat{S}_z(t) \right\rangle = \frac{1}{2} \sum_{\mu} \rho_{\mu\mu},$$

so that finally

$$\begin{aligned}
 \rho_{\mu\mu} = & \sum^3 X_{i \rightarrow k}^3 X_{i' \rightarrow k'}^3 (C_{\mu k} C_{\mu k'} \delta_{i i'} + C_{\mu i} C_{\mu i'} \delta_{k k'}) + \sum^3 X_{j \rightarrow k}^3 X_{j' \rightarrow k}^3 (C_{\mu j} C_{\mu j'} \delta_{i i'} + C_{\mu i} C_{\mu i'} \delta_{j j'}) + \\
 & + \sum^3 X_{i \rightarrow k}^3 X_{i \rightarrow l'}^3 (C_{\mu k} C_{\mu k'} \delta_{i l'} + C_{\mu l} C_{\mu l'} \delta_{k k'}) + \sum^3 X_{j \rightarrow l}^3 X_{j \rightarrow l'}^3 (C_{\mu k} C_{\mu k'} \delta_{j j'} + C_{\mu j} C_{\mu j'} \delta_{k k'}) + \\
 & + \frac{1}{3} \sum^3 X_{j \rightarrow l}^3 X_{j \rightarrow l'}^3 (3 C_{\mu k} C_{\mu k'} \delta_{i i'} \delta_{j j'} \delta_{l l'} + 2 C_{\mu l} C_{\mu l'} \delta_{i i'} \delta_{j j'} \delta_{k k'} + 2 C_{\mu i} C_{\mu i'} \delta_{j j'} \delta_{k k'} \delta_{l l'} - C_{\mu j} C_{\mu j'} \delta_{i i'} \delta_{k k'} \delta_{l l'}) + \\
 & + \frac{1}{6} \sum^3 X_{j \rightarrow l}^3 X_{j \rightarrow l'}^3 (5 C_{\mu i} C_{\mu i'} \delta_{j j'} \delta_{k k'} \delta_{l l'} + 5 C_{\mu j} C_{\mu j'} \delta_{i i'} \delta_{k k'} \delta_{l l'} + 5 C_{\mu l} C_{\mu l'} \delta_{i i'} \delta_{j j'} \delta_{k k'} - \\
 & - 3 C_{\mu k} C_{\mu k'} \delta_{i i'} \delta_{j j'} \delta_{l l'}) + 2 \sum^3 X_{i \rightarrow k}^3 X_{j \rightarrow k}^3 C_{\mu j} C_{\mu k} - 2 \sum^3 X_{i \rightarrow k}^3 X_{i \rightarrow l}^3 C_{\mu i} C_{\mu l} + \\
 & + \sqrt{\frac{2}{3}} \sum^3 X_{i \rightarrow k} \left(\sqrt{3}^3 X_{j \rightarrow l}^3 + {}^3 X_{j \rightarrow l}'' - \sqrt{2}^3 X_{j \rightarrow l}''' \right) C_{\mu j} C_{\mu l} + \sqrt{\frac{2}{3}} \sum^3 \left(-\sqrt{3}^3 X_{j \rightarrow l}^3 + {}^3 X_{j \rightarrow l}'' - \sqrt{2}^3 X_{j \rightarrow l}''' \right) \times \\
 & \times \left({}^3 X_{i \rightarrow k} C_{\mu k} C_{\mu l} + {}^3 X_{i \rightarrow l} C_{\mu i} C_{\mu j} \right) + \sqrt{\frac{2}{3}} \sum^3 X_{j \rightarrow l}^3 \left(\sqrt{2}^3 X_{j \rightarrow l}'' + {}^3 X_{j \rightarrow l}''' \right) \left(C_{\mu l} C_{\mu l'} \delta_{i i'} - C_{\mu i} C_{\mu i'} \delta_{l l'} \right) + \\
 & + \frac{\sqrt{2}}{3} \sum^3 X_{j \rightarrow l}^3 X_{j \rightarrow l'}^3 \left(2 C_{\mu j} C_{\mu j'} \delta_{i i'} \delta_{l l'} - C_{\mu i} C_{\mu i'} \delta_{j j'} \delta_{l l'} - C_{\mu l} C_{\mu l'} \delta_{i i'} \delta_{j j'} \right).
 \end{aligned} \tag{109}$$

The expression (105) also permits to obtain the formula for ${}^3 P_{\mu\nu}$. Let us carry out the summation in (105) over the spin variables taking the normalization condition of ${}^3 \Psi$ into account. Using the AO representation and comparing the expression derived so far with (107) one finally obtains

$$\begin{aligned}
 {}^3 P_{\mu\nu} = & 2 \sum_{i=1}^n C_{\mu i} C_{\nu i} + \sum^3 X_{i \rightarrow k}^3 X_{i' \rightarrow k'}^3 (C_{\mu k} C_{\nu k'} \delta_{i i'} - C_{\mu i} C_{\nu i'} \delta_{k k'}) + \sum^3 X_{j \rightarrow k}^3 X_{j' \rightarrow k}^3 (2 C_{\mu k} C_{\nu k'} \delta_{i i'} \delta_{j j'} - C_{\mu i} C_{\nu i'} \delta_{j j'} - C_{\mu j} C_{\nu j'} \delta_{i i'}) + \\
 & + \sum^3 X_{i \rightarrow k}^3 X_{i \rightarrow l'}^3 (-2 C_{\mu i} C_{\nu l'} \delta_{k k'} \delta_{l l'} + C_{\mu k} C_{\nu k'} \delta_{l l'} + C_{\mu l} C_{\nu l'} \delta_{k k'}) + \\
 & + \sum^3 \left({}^3 X_{j \rightarrow l}^3 X_{j \rightarrow l'}^3 + {}^3 X_{j \rightarrow l}'' X_{j \rightarrow l'}'' + {}^3 X_{j \rightarrow l}''' X_{j \rightarrow l'}''' \right) \left(C_{\mu k} C_{\nu k'} \delta_{i i'} \delta_{j j'} \delta_{l l'} + C_{\mu l} C_{\nu l'} \delta_{i i'} \delta_{j j'} \delta_{k k'} - \right. \\
 & - C_{\mu i} C_{\nu i'} \delta_{j j'} \delta_{k k'} \delta_{l l'} - C_{\mu j} C_{\nu j'} \delta_{i i'} \delta_{k k'} \delta_{l l'} \left. \right) + 2 \sum^3 X_{i \rightarrow k}^3 X_{j \rightarrow k}^3 C_{\mu j} C_{\nu k} - 2 \sum^3 X_{i \rightarrow k}^3 X_{i \rightarrow l}^3 C_{\mu i} C_{\nu l} - \\
 & - \sqrt{2} \sum^3 X_{i \rightarrow k} \left({}^3 X_{j \rightarrow l}^3 - \sqrt{3}^3 X_{j \rightarrow l}'' \right) C_{\mu j} C_{\nu l} + \sqrt{\frac{2}{3}} \sum^3 X_{j \rightarrow k}^3 \left(\sqrt{3}^3 X_{j \rightarrow l}^3 - {}^3 X_{j \rightarrow l}'' - 2\sqrt{2}^3 X_{j \rightarrow l}''' \right) C_{\mu k} C_{\nu l} + \\
 & + \sqrt{2} \sum^3 X_{j \rightarrow l}^3 \left({}^3 X_{j \rightarrow l}^3 + \sqrt{3}^3 X_{j \rightarrow l}'' \right) C_{\mu i} C_{\nu j}.
 \end{aligned} \tag{110}$$

The expressions (108) – (110) immediately lead to the formulae [9]

$${}^{1,3} P_{\mu\nu} = 2 \sum_{i=1}^n C_{\mu i} C_{\nu i} + \sum^3 X_{i \rightarrow k}^3 X_{i' \rightarrow k'}^3 (C_{\mu k} C_{\nu k'} \delta_{i i'} - C_{\mu i} C_{\nu i'} \delta_{k k'}) \tag{111}$$

and

$$\rho_{\mu\mu} = \sum^3 X_{i \rightarrow k}^3 X_{i' \rightarrow k'}^3 (C_{\mu k} C_{\nu k'} \delta_{i i'} - C_{\mu i} C_{\nu i'} \delta_{k k'}), \tag{112}$$

which are valid for the case of including only singly excited configurations.

The formula for ${}^1 P_{\mu\nu}$ erroneously used in [27 – 31] may be obtained from (A7) if the summation in the latter is restricted by the condition $i = i'$ and $k = k'$. The validity of the expression for ${}^1 P_{\mu\nu}$ used in [27] follows from (A4) when accounting only for some particular configurations, namely those of the type ${}^1 \Phi_0$, ${}^1 \Phi_{i \rightarrow k, i \rightarrow k}$ and ${}^1 \Phi_{i \rightarrow k, j \rightarrow l}$ which have been included by the authors.

9. Conclusions

The second quantization method has been intensively developed and is widely used for treating many-particle problems. Kouba and Ohn [32], for example, have considered and solved some of the problems which we discuss in a different way, namely a translation was made of spin projection methods into the language of second quantization. This leads to a new formula for the Sanibel coefficients and expressions convenient to use for automatic calculation of spin projections. We discussed in this review 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 state. The importance of this interpretation is obvious, particularly if the vacuum state 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 state 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. The corresponding algorithm is universal for all varieties of the matrix elements met in actual computations and reduces to a few simple cases.

Such an algorithm which is based on this logical scheme for CI method was developed. The corresponding program CI-2 is given in details in [26]. We have used this program repeatedly, in particularly for computing electronic states of benzyl radical [33], and glycine and tyrosine molecules and their neutral and charged radicals [34]. The same logical scheme, but without use of the hole formalism, was incorporated in program CI-3 to perform a complete CI for the benzyl radical [22, 23].

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