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Study of the Electronic Structure of Radicals by the CI Method. I. Matrix Elements of the Physical Value Operators*

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The results of a preceding paper which describes the *CI* method in the second quantization are used to construct basis vectors in the case of singly and doubly excited configurations for molecules and radicals. The matrix elements of the Hamiltonian are also given. A method for calculating the electronic density distribution in the *CI* method is formulated. An analog of the well known Brillouin theorem for radicals is obtained.

INTRODUCTION

In the preceding paper[1] a scheme based on the second quantization representation for the configuration interaction (*CI*) method is suggested. In order to perform an actual *CI* computation the basic vectors** which are the eigenfunctions of the operator must be constructed first. This may be acomplished by using the general rules already formulated[1]. In the present communication we give for the case of the singly and doubly excited configurations for molecules and radicals some basis vectors which will be useful in future applications.

As mentioned in the preceding paper, the 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 calculating scheme suitable for computer programming.

In the present paper we calculate the Hamiltonian matrix elements on some basis vectors using the results of[1]. 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 system used for the construction of the configurations. We considered some general expressions for the *SCF* orbitals and showed that in the case of radicals some Hamiltonian matrix elements between the ground configurations 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 on atoms, bond orders, transition moments, and spin distribution.

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** We shall use terminology and designations from the preceding paper[1].

BASIC 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.

$$|\Phi_1> = \mathbf{A}_{k+}\mathbf{A}_{m+}|\Phi_0>,\quad |\Phi_3> = \mathbf{A}_{k-}\mathbf{A}^{+}_{m+}|\Phi_0>,$$
$$|\Phi_2> = \mathbf{A}_{k-}\mathbf{A}^{+}_{m-}|\Phi_0>,\quad |\Phi_4> = \mathbf{A}_{k+}\mathbf{A}^{+}_{m-}|\Phi_0>. \tag{1}$$

Using the given rules[1] one obtains

$$\mathbf{S}^2|\Phi_1> = |\Phi_1> - |\Phi_2>,\qquad \mathbf{S}^2|\Phi_3> = 2|\Phi_3>,$$
$$\mathbf{S}^2|\Phi_2> = -|\Phi_1> + |\Phi_2>,\qquad \mathbf{S}^2|\Phi_4> = 2|\Phi_4> \tag{2}$$

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

$$|^1\psi_1> = \frac{1}{\sqrt{2}}(|\Phi_1> + |\Phi_2>),\qquad M_S = 0,\qquad S = 0 \tag{3a}$$

$$|^3\psi_1> = \frac{1}{\sqrt{2}}(|\Phi_1> - |\Phi_2>),\qquad M_S = 0,\qquad S = 1 \tag{3b}$$

$$|^3\psi_2> = |\Phi_3>,\qquad M_S = +1,\qquad S = 1 \tag{3c}$$

$$|^3\psi_3> = |\Phi_4>,\qquad M_S = -1,\qquad S = 1 \tag{3d}$$

There are unusual signs in the first two vectors. In the case of a radical the vacuum $|\Phi_0>$ is chosen as the closed shell of its ground state [see (16)].[1] Then one kind of the basis vectors is obviously

$$|^2\psi_1> = \mathbf{A}^{+}_{n+}|\Phi_0> \tag{4}$$

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

$$|\Phi_5> = \mathbf{A}_{k-}\mathbf{A}^{+}_{m+}\mathbf{A}^{+}_{n-}|\Phi_0>,$$
$$|\Phi_6> = \mathbf{A}_{k+}\mathbf{A}^{+}_{m+}\mathbf{A}^{+}_{n+}|\Phi_0>, \tag{5}$$
$$|\Phi_7> = \mathbf{A}_{k-}\mathbf{A}^{+}_{m-}\mathbf{A}^{+}_{n+}|\Phi_0>.$$

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

$$|^2\psi_2> = \mathbf{A}_{k-}\mathbf{A}^{+}_{m+}\mathbf{A}^{+}_{m-}|\Phi_0>. \tag{6}$$

Let be $n \neq m$. Writing

$$\mathbf{S}^2|\Phi_2> = \sum_{j=5}^{7}(\mathbf{S}^2)_{ij}|\Phi_j> \tag{7}$$

and using the rules[1] one obtains a matrix

$$(\mathbf{S}^2) = \begin{pmatrix} 7/4 & -1 & 1 \\ -1 & 7/4 & -1 \\ 1 & -1 & 7/4 \end{pmatrix}. \tag{8}$$

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,

$$|\,{}^2\psi_3 > = \frac{1}{\sqrt{6}} (|\,\Phi_5 > - |\,\Phi_6 > - 2\,|\,\Phi_7 >), \tag{9a}$$

$$|\,{}^2\psi_4 > = \frac{1}{\sqrt{2}} (|\,\Phi_5 > + |\,\Phi_6 >) \tag{9b}$$

and

$$|\,{}^4\psi_1 > = \frac{1}{\sqrt{3}} (|\,\Phi_5 > - |\,\Phi_6 > + |\,\Phi_7 >). \tag{10}$$

The doublet basis vectors are determined to a unitary transformation. We have chosen the vectors (9) to correspond to those found in the literature.

ELEMENTS OF THE CI MATRIX

The final expressions for the matrix elements of the Hamiltonian [see (31)][1] obtained by using the results of § 5[1] are now given.

Molecule

$$< \Phi_o\,|\,\mathbf{H}\,|^{1,3}\psi_1 > = -f\sqrt{2}\,F_{km'} \tag{11}$$

$$< {}^{1,3}\psi_1'\,|\,\mathbf{H}\,|\,{}^{1,3}\psi_1 = \delta_{kk'}\,\delta_{mm'}\,\mathbf{E}_o + \delta_{kk'}\,F_{m'm} - \delta_{mm'}\,F_{kk'} + 2\,f\,(km'\,|\,mk') - (km'\,|\,k'm) \tag{12}$$

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 operator **H**.

Radical

$$< {}^2\psi_1'\,|\,\mathbf{H}\,|\,{}^2\psi_1 > = \delta_{mm'}\,\mathbf{E}_o + F_{m'm'} \tag{13}$$

$$\begin{aligned} < {}^2\psi_2'\,|\,\mathbf{H}\,|\,{}^2\psi_2 > &= \delta_{kk'}\,\delta_{mm'}\,\mathbf{E}_o + \delta_{mm'}\,(2\,\delta_{kk'}\,F_{m'm} - F_{kk'}) \\ &+ \delta_{kk'}\,(m'm'\,|\,mm) + \delta_{mm'}\,[(km'\,|\,mk') - 2\,(km'\,|\,k'm)], \end{aligned} \tag{14}$$

$$\begin{aligned} < {}^2\psi_3'\,|\,\mathbf{H}\,|\,{}^2\psi_3 > &= \delta_{kk'}\,(\delta_{mm'}\,\delta_{nn'} - \delta_{mn'}\,\delta_{nm'})\,\mathbf{E}_o + \frac{1}{2}\,\{\delta_{kk'}\,(2\,\delta_{mm'}\,F_{n'n} + 2\,\delta_{nn'}\,F_{m'm} + \\ &+ \delta_{mn'}\,F_{m'n} + \delta_{nm'}\,F_{n'm}) - F_{kk'}\,(2\,\delta_{mm'}\,\delta_{nn'} + \delta_{mn'}\,\delta_{nm'}) + \\ &+ \delta_{kk'}\,[2\,(m'n'\,|\,mn) + (m'n'\,|\,nm)] - 2\,\delta_{mm'}\,(kn'\,|\,k'n) + \\ &+ \delta_{nn'}\,[3\,(m'k\,|\,k'm) - 2\,(m'k\,|\,mk')] - \delta_{mn'}\,(m'k\,|\,nk') - \delta_{nm'}\,(n'k\,|\,mk')\}, \end{aligned} \tag{15}$$

$$\begin{aligned} < {}^2\psi_4' \,|\, \mathbf{H} \,|\, {}^2\psi_4 > = {} & \delta_{kk'} (\delta_{mm'} \delta_{nn'} - \delta_{mn'} \delta_{nm'}) E_o + \frac{1}{2} \{\delta_{kk'} (2\,\delta_{mm'} F_{n'n} + \\ & + 2\,\delta_{nn'} F_{m'm} - \delta_{mn'} F_{m'n} - \delta_{nm'} F_{n'm}) - F_{kk'} (2\,\delta_{mm'} \delta_{nn'} - \delta_{mn'} \delta_{nm'}) + \\ & + \delta_{kk'} [2\,(m'n' \,|\, mn) - (m'n' \,|\, nm)] + 2\,\delta_{mm'} [2\,(kn' \,|\, nk') - (kn' \,|\, k'n)] + \\ & + \delta_{nn'} [(m'k \,|\, k'm) - 2\,(m'k \,|\, mk')] + \delta_{mn'} [(m'k \,|\, nk') - 2\,(m'k \,|\, k'n)] + \\ & + \delta_{nm'} [(n'k \,|\, mk') - 2\,(n'k \,|\, k'm)]\}, \end{aligned} \tag{16}$$

$$< {}^2\psi_1' \,|\, \mathbf{H} \,|\, {}^2\psi_2 > = \delta_{mm'} F_{km} + (km' \,|\, mm), \tag{17}$$

$$< {}^2\psi_1' \,|\, \mathbf{H} \,|\, {}^2\psi_3 > = [\delta_{nm'} F_{km} + (km' \,|\, mn)] \,/\, \sqrt{3/2} \tag{18}$$

$$< {}^2\psi_1' \,|\, \mathbf{H} \,|\, {}^2\psi_4 > = [2\,\delta_{mm'} F_{kn} - \delta_{nm'} F_{km} + 2\,(km' \,|\, nm) - (km' \,|\, mn)] \,/\, \sqrt{2}, \tag{19}$$

$$\begin{aligned} < {}^2\psi_2' \,|\, \mathbf{H} \,|\, {}^2\psi_3 > = {} & (1/\sqrt{6}) \{\delta_{kk'} [(m'm' \,|\, mn) - (m'm' \,|\, nm)] + \\ & + 2\,\delta_{mm'} (km' \,|\, nk') - 2\,\delta_{nm'} (m'k \,|\, k'm)\}, \end{aligned} \tag{20}$$

$$\begin{aligned} < {}^2\psi_2' \,|\, \mathbf{H} \,|\, {}^2\psi_4 > = {} & (1/\sqrt{2}) \{\delta_{kk'} (\delta_{mm'} F_{m'n} + \delta_{nm'} F_{m'm}) - \delta_{nm'} \delta_{mm'} F_{kk'} + \\ & + \delta_{kk'} (m'm' \,|\, mn) + \delta_{mm'} [2\,(km' \,|\, nk') - (km' \,|\, k'n)] - \delta_{nm'} [(m'k \,|\, k'm) + (m'k \,|\, mk')]\}, \end{aligned} \tag{21}$$

$$\begin{aligned} < {}^2\psi_3' \,|\, \mathbf{H} \,|\, {}^2\psi_4 > = {} & (1/\sqrt{3}) \{\delta_{kk'} (\delta_{mm'} F_{n'n} + \delta_{nn'} F_{m'm} - \delta_{mn'} F_{m'n} - \delta_{nm'} F_{n'm}) - \\ & - F_{kk'} (\delta_{mm'} \delta_{nn'} - \delta_{mn'} \delta_{nm'}) + \delta_{kk'} [(m'n' \,|\, mn) - (m'n' \,|\, nm)] + \\ & + \delta_{mm'} [2\,(kn' \,|\, nk') - (kn' \,|\, k'n)] + \delta_{nn'} [(m'k \,|\, k'm) - (m'k \,|\, mk')] + \\ & + \delta_{mn'} [(m'k \,|\, nk') - 2\,(m'k \,|\, k'n)] + \delta_{nm'} [(nk' \,|\, mk') - (n'k \,|\, k'm)]\}. \end{aligned} \tag{22}$$

Formula (13) may be found in ref. (2, 3). These papers contain also particular cases of some of the general expressions given so far: (14) for $k' = k$, $m' = m$, and (16) for $k' = k$, $m' = m$, $n' = n$ are in (2), (17) for $m' \neq m$ is in ref. (2) and for $m' = m$ — in ref. (3), (18) for $m' = m$ is in (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 $|\, \Phi_0 >$ vanishes according to (4) satisfy the operator equation

$$\hat{F} \hat{P}_1 - \hat{P}_1 \hat{F} = 0 \tag{23}$$

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

$$\hat{P}_1 = \sum_{l=1}^{n_F} |\, \varphi_l > < \varphi_l \,|. \tag{24}$$

Calculating the matrix element of (23) between the orbitals φ_k and φ_m and using projection properties of the operator P_1 one obtains from (11) if initial orbitals satisfy equation (23):

$$< \Phi_0 \,|\, \mathbf{H} \,|\, {}^1\psi_1 > = 0 \tag{25}$$

The conditions used in derivating the above expression are more comprehensive than the conditions of the well known Brillouin theorem (5). The content of the latter is expressed by the equation (25) 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 (6)

$$\hat{F}_1 \hat{P}_1 - \hat{P}_1 \hat{F}_1 + \hat{F}_2 \hat{P}_2 - \hat{P}_2 \hat{F}_2 = 0 \tag{26}$$

where $\hat{P}_1$ is defined by (24), $\hat{P}_2$ 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

$$\hat{F}_1 = \hat{F} + \hat{J}_0 - \frac{1}{2} \hat{K}_0, \tag{27}$$

$$\hat{F}_2 = \frac{1}{2} \hat{F} + \hat{J}_0 - \hat{K}_0 \tag{28}$$

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 (13) for $m' \neq m$ and (17), (19) for $m' \neq m$, $n \neq m$

$$< {}^2\psi_1 \,|\, \mathbf{H} \,|\, {}^2\psi_1' > = F_{mm'}, \tag{29}$$

$$< {}^2\psi_1 \,|\, \mathbf{H} \,|\, {}^2\psi_2 > = F_{km} + (\hat{J}_0)_{km}, \tag{30}$$

$$< {}^2\psi_1 \,|\, \mathbf{H} \,|\, {}^2\psi_4 > = \sqrt{2}\,[F_{kn} + (\hat{J}_0)_{nk} - \frac{1}{2} (\hat{K}_0)_{kn}] \tag{31}$$

where the two last 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 $\hat{P}_2$

$$\hat{P}_1 \,|\, \varphi_k > = |\, \varphi_k >, \quad \hat{P}_1 \,|\, \varphi_m > = \hat{P}_1 \,|\, \varphi_{m'} > = \hat{P}_1 \varphi_n > = 0,$$

$$\hat{P}_2 \,|\, \varphi_m > = |\, \varphi_m >, \quad \hat{P}_2 \,|\, \varphi_k > = \hat{P}_2 \,|\, \varphi_{m'} > = \hat{P}_2 \,|\, \varphi_n > = 0 \tag{32}$$

from equation (26), one obtains

$$< \varphi_m \,|\, \hat{F}_2 \,|\, \varphi_{m'} > = 0,$$

$$< \varphi_k \,|\, \hat{F}_4 - F_2 \,|\, \varphi_m = 0, \tag{33}$$

$$< \varphi_k \,|\, \hat{F}_1 \,|\, \varphi_n = 0.$$

Substituting $\hat{F}_1$ and $\hat{F}_2$ according to (27) into (33) and using the identity

$$\hat{J}_0 \,|\, \varphi_m > \equiv \hat{K}_0 \,|\, \varphi_m > \tag{34}$$

we see that relations (33) express that the right sides of the equations (29), (30), and (31) 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 $m' \neq m$, (k, mm), and of the vector (9b) of the configuration (k, mn) with $n \neq m$ are equal to zero.

Generally the equation (26) 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[7] or by the use of the one-electron Hamiltonian for one open shell.[8]

CALCULATION OF CERTAIN ONE-PARTICLE PROPERTIES

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

$$|\lambda> = \sum_{q} X_{q\lambda} \, |\psi_q> \tag{35}$$

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

$$\varphi_i = \sum C_{\mu i} \, \chi_{\mu} \; . \tag{36}$$

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

$$<\varkappa \,|\, \mathbf{Q} \,|\, \lambda> = \sum_{pq} X^{*}_{p\varkappa} \; X_{q\lambda} <\psi_p \,|\, \mathbf{Q} \,|\, \psi_q>. \tag{37}$$

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

If $\mathbf{Q}$ is a spin-free operator, analytical expressions for the matrix elements $<\psi_p \,|\, \mathbf{Q} \,|\, \psi_q>$ for the configurations considered so far are obtained directly from the Hamiltonian matrix elements (11)—(22) by ignoring two-electron terms and changing F_{ij} to Q_{ij} and F_0 to an average value Q_0 of the operator Q in the vacuum state. In particular, for the calculation of the electronic density on atoms $P^{\lambda\lambda}_{\mu\mu}$ and bond orders $P^{\lambda\lambda}_{\mu\nu}$ in a state λ as well as transition electronic density on atoms $P^{\varkappa\lambda}_{\mu\mu}$ corresponding to a transition from state $\varkappa$ to state λ one must take $C^{*}_{\mu i} \; C_{\mu j}$ and correspondingly $C^{*}_{\mu i} \; C_{\nu j}$ 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 component of the transition moment are determined through corresponding atomic coordinates and transition density, for example:

$$\mu^{\varkappa\lambda}_{\chi} = \sum_{\nu} \chi_{\nu} \; P^{\varkappa\lambda}_{\nu\nu} \tag{38}$$

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

$$P_{ij} = C^{*}_{\mu i} \; C_{\nu j} \tag{39}$$

$$< {}^{3}\psi_1' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{3}\psi_1 > \; = \delta_{kk'} P_{m'm} + \delta_{mm'} P_{kk'}, \tag{40}$$

$$< {}^{2}\psi_1' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_1 > \; = P_{m'm}, \tag{41}$$

$$< {}^{2}\psi_2' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_2 > \; = \delta_{mm'} P_{kk'}, \tag{42}$$

$$\begin{aligned} < {}^{2}\psi_3' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_3 > \; = [\delta_{kk'} (4\,\delta_{mm'} P_{n'n} - 2\,\delta_{nn'} P_{m'm} - \delta_{mn'} P_{m'n} - \delta_{nm'} P_{n'm}) - \\ - P_{kk'} (4\,\delta_{mm'} \delta_{nn'} - 5\,\delta_{nn'}\, \delta_{nm'})]/6 \end{aligned} \tag{43}$$

$$\begin{aligned} < {}^{2}\psi_4' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_4 > \; = [\delta_{kk'} (2\delta_{nn'} P_{m'm} - \delta_{mn'} P_{m'n} - \delta_{nm'} P_{n'm}) - \\ - P_{kk'} \; (\delta_{mm'} \delta_{nn'} - \delta_{mn'}\, \delta_{nm'})]/2 \end{aligned} \tag{44}$$

$$< {}^{2}\psi_1' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_2 > \; = -\,\delta_{mm'} P_{km}, \tag{45}$$

$$< {}^{2}\psi_1' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_3 > \; = -\,(2\,\delta_{mm'} P_{kn} + \delta_{nm'} P_{km})/\sqrt{6} \tag{46}$$

$$< {}^{2}\psi_1' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_4 > \; = -\,\delta_{nm'} P_{km}/\sqrt{2} \tag{47}$$

$$< {}^{2}\psi_2' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_3 > \; = [\delta_{kk'} (\delta_{mm'} P_{m'n} - \delta_{nm'} P_{m'm}) + 3\,\delta_{mm'}\, \delta_{nm'} P_{kk'}]/\sqrt{6} \tag{48}$$

$$< {}^{2}\psi_2' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_4 > \; = [\delta_{kk'} (-\,\delta_{mm'} P_{m'n} + \delta_{nm'}\, P_{m'm}) + \delta_{mm'}\, \delta_{nm'} P_{kk'}]/\sqrt{2} \tag{49}$$

$$\begin{aligned} < {}^{2}\psi_3' \,|\, 2\,\mathbf{S}_Z \,|\, {}^{2}\psi_4 > \; = \frac{1}{\sqrt{12}} [\delta_{kk'} (-\,\delta_{mn'} P_{m'n} + 3\,\delta_{nm'} P_{n'm}) + \\ + P_{kk'} (2\,\delta_{mm'} \delta_{nn'} + \delta_{mn'}\, \delta_{nm'})] \end{aligned} \tag{50}$$

The expression for $p_{\mu\mu}$ derived in ref. (9, 10) by the determinantal method is obtained from (40) in a way described above.

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IZVOD

Studij elektronske strukture radikala metodom konfiguracijske interakcije. I Matrični elementi fizikalnih operatora

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Bazični vektori za jednostruko i dvostruko pobuđene konfiguracije molekula i radikala dani su korištenjem rezultata metode konfiguracijske interakcije u formalizmu druge kvantizacije. Dani su također i opći izrazi za matrične elemente Hamiltoniana u metodi konfiguracijske interakcije koji se za neke specijalne slučajeve reduciraju na izraze koji su poznati iz literature. Formuliran je teorem koji vrijedi za radikale, a analogan je poznatom Brillouinovom teoremu za molekule. Promatra se izračunavanje određenih jednočestičnih svojstava, uključujući izračunavanje elektronske gustoće na atomima, red veza, prijelaznih momenata i raspodjele spinske gustoće na pojedinim atomima.

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