
ADDITIONAL CONSTANTS OF MOTION OF THE CNDO-LIKE MANY-ELECTRON HAMILTONIANS OF PLANAR MOLECULAR SYSTEMS. III.*
SPINLESS FIRST-ORDER DENSITY MATRICES AND APPLICATIONS

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In this paper the spinless first-order density matrices are examined for states which are solutions of the CNDO-hamiltonian for planar molecules. It is shown that the additional constants of motion (CM's) of that hamiltonian permit to find simplifications in calculations of density matrices. An actual example is given showing the construction of configurations which are eigen-functions of the additional CM's. Two treatments on the H—N=O molecule were performed, with and without the factorization due to existing additional CM's, to demonstrate a difference in dimensions of the respective CI matrices.

A many-electron CNDO-hamiltonian for planar molecular systems was studied¹. This "model" hamiltonian can be derived from the "accurate" one by neglecting the exchange integrals between σ and π orbitals. This is actually done in the semiempirical CNDO approach² (strict ZDO approximation) as well as if the Mulliken approximation³ for two-body atomic integrals is adopted. It was shown^{1,4} that there exist additional constants of motion (hereafter CM's) which permit: *a*) to elucidate some kind of degeneracy observed in eigen-values of the model hamiltonian; *b*) a further factorization in the CI method. These points made possible to carry out the full CI calculations on the H₂O and H₂O⁺ molecules in the framework of the CNDO/2 method.

In this paper the spinless first-order density matrices are studied for states which are solutions of the CNDO hamiltonian for planar molecular systems. Actual examples will be given showing the construction of configurations which are eigen-functions of the additional CM's. Exploiting the factorization due to these CM's a dimension of CI matrices can considerably be reduced; an application to the HNO molecule is presented.

THEORETICAL

In finite or infinite basis sets of one-electron functions from which the N-electron functions are built up, two subsets can clearly be distinguished, *viz.* σ - and π -orbitals being symmetric and antisymmetric with respect to the reflection in the molecular plane.

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This implies that each Slater determinant contains a σ -part and a π -part. Thus the CNDO-hamiltonian over the basis of all possible Slater determinants built up from a given one-electron functions basis set can be expressed as

$$\mathbf{H}_A = \mathbf{H}_\sigma + \mathbf{H}_\pi + \mathbf{V}_{\sigma\pi}, \quad (1)$$

where the first two terms are hamiltonians covering all one- and two-particle interactions in spaces generated by σ - and π -orbitals, respectively. The third term, $\mathbf{V}_{\sigma\pi}$, stands for coulombic interaction between σ and π -subsystems and all its matrix elements over the basis of Slater determinants are coulomb integrals of the type

$$\int \sigma_1^*(1) \sigma_2(1) (1/r_{12}) \pi_1^*(2) \pi_2(2) dV_1 dV_2.$$

The accurate formulation of (1) in the language of the second quantization was reported previously¹.

The main results reached in ref.¹ are as follows: A) The hamiltonian (1) possesses two alternative sets of the mutually commuting MC's:

$$\mathbf{S}^2, \mathbf{S}_z, \mathbf{N}_\pi, \mathbf{S}_\sigma^2, \mathbf{S}_\pi^2, \quad \text{or} \quad \mathbf{S}_z^\sigma, \mathbf{S}_z^\pi, \mathbf{N}_\pi, \mathbf{S}_\sigma^2, \mathbf{S}_\pi^2. \quad (2a, b)$$

The operators \mathbf{S}^2 and \mathbf{S}_z refer to the square and to the z -component of the total spin, respectively. \mathbf{N}_π is an operator of the number of π -electrons. It holds $\mathbf{N} = \mathbf{N}_\sigma + \mathbf{N}_\pi$, where \mathbf{N} and \mathbf{N}_σ are operators of the total number of electrons and of the number of σ electrons. \mathbf{S}_σ^2 and \mathbf{S}_z^σ are operators of the total spin for σ electrons, the former refers to its square, the latter to its z -component. Operators \mathbf{S}_π^2 and \mathbf{S}_z^π for π -electrons have the analogous meaning. Let us assume that the hamiltonian (1) for N electrons is defined over a linear space E which is represented by all possible N -electron Slater determinants. On exploiting the CM's (2a), we can divide E into orthogonal and non-interacting subspaces

$$E = \sum E(S, S_z, N_\pi, S_\sigma, S_\pi), \quad (3a)$$

where the summation runs over all compatible values of arguments: $N_\pi \leq N$, $|S_z| \leq S$, $|S_\sigma - S_\pi| \leq S \leq S_\sigma + S_\pi$. The expression $E(S, S_z, N_\pi, S_\sigma, S_\pi)$ represents a subspace which is at the same time an eigen-space of all operators (2a) with the eigen-values explicitly expressed in the argument.

If the CM's (2b) are employed, a similar splitting of E into orthogonal and non-interacting subspaces is obtained

$$E = \sum F(S_z^\sigma, S_z^\pi, N_\pi, S_\sigma, S_\pi), \quad (3b)$$

where similarly as in (3a) the summation runs over all compatible values of arguments. The subspace $F(S_z^\sigma, S_z^\pi, N_\pi, S_\sigma, S_\pi)$ is an eigen-space to all operators (2b) with eigen-values explicitly expressed in the argument. Both subspaces $E(\dots)$ and $F(\dots)$ are eigen-spaces of \mathbf{N}_π , \mathbf{S}_σ^2 , and \mathbf{S}_π^2 operators, but $E(\dots)$ is an eigen-space of \mathbf{S}^2 and \mathbf{S}_z^2 operators, in contrast to $F(\dots)$, which is an eigen-space of \mathbf{S}_z^σ and \mathbf{S}_z^π operators. It appears more appropriate to consider the hamiltonian (1)

represented by subspaces $E(\dots)$ because of the direct physical meaning of eigen-values \mathbf{S}^2 and \mathbf{S}_z , however the adoption of $F(\dots)$ subspaces is advantageous since the basis vectors are more simple than those in $E(\dots)$, as will be shown in the following.

B) The eigen-values (energies) set of the hamiltonian (I) is identical in the following set of subspaces

$$E(x, y, N_\pi, S_\sigma, S_\pi), \quad |S_\sigma - S_\pi| \leq x \leq S_\sigma + S_\pi, \quad |y| \leq x, \quad (4a)$$

$$F(x, y, N_\pi, S_\sigma, S_\pi), \quad |x| \leq S_\sigma, \quad |y| \leq S_\pi. \quad (4b)$$

This implies that for given eigen-values of \mathbf{N}_π , \mathbf{S}_σ^2 , and \mathbf{S}_π^2 operators, it is sufficient to choose only one of subspaces (4a) or (4b) and to solve the eigen-value problem of the hamiltonian (I) in that selected subspace.

Spinless First Order Density Matrices

Let us examine general properties of elements of spinless first-order density matrices, $\gamma_{pp'}^{AB}$. The superindices A, B denote two normalized N -electron states $|\Psi_{A,B}\rangle$, indices p, p' refer to space orbitals. In the second quantization formalism these matrix elements can be defined as⁵

$$\gamma_{pp'}^{AB} = \langle \Psi_A | G_{pp'} | \Psi_B \rangle, \quad \mathbf{G}_{pp'} = \mathbf{X}_{p\alpha}^+ \mathbf{X}_{p'\alpha} + \mathbf{X}_{p\beta}^+ \mathbf{X}_{p'\beta}, \quad (5a, b)$$

where $\mathbf{X}_{p\alpha}^+$, $\mathbf{X}_{p\beta}$, ... are creation and annihilation operators corresponding to spin-orbitals $|p\rangle |\alpha\rangle$, $|p'\rangle |\beta\rangle$, ... Using the definition of the \mathbf{N}_π operator we can write

$$[\mathbf{N}_\pi, \mathbf{G}_{pp'}]_- = \{\delta(p, \pi) - \delta(p', \pi)\} \mathbf{G}_{pp'}, \quad (6)$$

where

$$\delta(p, \pi) = \begin{cases} 1 & \text{if } p \in \pi, \\ 0 & \text{if } p \notin \pi. \end{cases} \quad (7)$$

Assuming the $|\Psi_{A,B}\rangle$ states are eigen-functions of the \mathbf{N}_π operator with the eigen-values $N_\pi^{A,B}$, we obtain from (5a-b) and (6)

$$(N_\pi^A - N_\pi^B) \gamma_{pp'}^{AB} = \{\delta(p, \pi) - \delta(p', \pi)\} \gamma_{pp'}^{AB}. \quad (8)$$

Thus Eq. (8) gives us

$$\gamma_{pp'}^{AB} = \delta_{N_\pi^A, N_\pi^B + t} \langle \Psi_A | G_{pp'} | \Psi_B \rangle, \quad (9)$$

where δ_{ij} is a Kronecker delta and for t it holds

$$t = \begin{cases} -1 & \text{if } p \in \sigma \quad \text{and } p' \in \pi, \\ 0 & \text{if } p, p' \in \sigma \quad \text{or } p, p' \in \pi, \\ +1 & \text{if } p \in \pi \quad \text{and } p' \in \sigma. \end{cases} \quad (10)$$

Eqs (9) and (10) imply the following statements: A) For $N_{\pi}^A = N_{\pi}^B \pm 2$, $N_{\pi}^B \pm 3, \dots$ the density matrix elements are zero. B) For $N_{\pi}^A = N_{\pi}^B \pm 1$, the density matrix elements are generally non-zero only if $p \in \sigma$, $p' \in \pi$ or $p \in \pi$, $p' \in \sigma$. C) For $N_{\pi}^A = N_{\pi}^B$ the density matrix elements are generally non-zero only if $p, p' \in \sigma$ or $p, p' \in \pi$.

We shall concern only the case C, *i.e.* only those density matrix elements which refer to two states having an equal number of π -electrons. Similarly¹ the following commutation relation

$$[\mathbf{G}_{pp'}, \mathbf{Q}]_- = 0 \quad (11)$$

can be proved, where $p, p' \in \sigma$ or $p, p' \in \pi$, and \mathbf{Q} is an operator from the series (2a, b). Thus, the $|\Psi_{A,B}\rangle$ states being the eigen-functions either of the (2a) or (2b) set of operators, the following factorization of the density matrix elements holds (for $p, p' \in \sigma$ or $p, p' \in \pi$)

$$\gamma_{pp'}^{AB} = \delta_{A,B} \langle \Psi_A | G_{pp'} | \Psi_B \rangle. \quad (12)$$

Here $\delta_{A,B}$ means that the right side in (12) is generally non-zero only for such two $|\Psi_{A,B}\rangle$ states, which have same eigen-values either of the CM's (2a) or of the CM's (2b) (we assume $N_{\pi}^A = N_{\pi}^B$). Let us now consider that the $|\Psi_{A,B}\rangle$ states are eigen-functions of the (2b) CM's set, *i.e.* they belong to one $F(S_z^{\sigma}, S_z^{\pi}, N_{\pi}, S_{\sigma}, S_{\pi})$ subspace from (3b). We shall use for them the designation $|\Psi_{A,B}(S_z^{\sigma}, S_z^{\pi}, N_{\pi}, S_{\sigma}, S_{\pi})\rangle$. By means of the operator product $\mathbf{S}_{\pm}^{\sigma} \mathbf{S}_{\pm}^{\pi}$ (and of a normalization constant, compare ref.¹) the following set of normalized vectors can be constructed.

$$|\Psi_{A,B}(S_z^{\sigma}, S_z^{\pi}, N_{\pi}, S_{\sigma}, S_{\pi})\rangle, \quad |S_z^{\sigma}| \leq S_{\sigma}, \quad |S_z^{\pi}| \leq S_{\pi}. \quad (13)$$

The commutation relations (11) also hold for $\mathbf{Q} = \mathbf{S}_{\pm}^{\sigma}, \mathbf{S}_{\pm}^{\pi}$, which implies the density matrix elements are independent on the actual eigen-values of $\mathbf{S}_z^{\sigma}, \mathbf{S}_z^{\pi}$. More accurately, the density matrix elements

$$\langle \Psi_{A,B}(S_z^{\sigma}, S_z^{\pi}, N_{\pi}, S_{\sigma}, S_{\pi}) | \mathbf{G}_{pp'} | \Psi_{B}(S_z^{\sigma}, S_z^{\pi}, N_{\pi}, S_{\sigma}, S_{\pi}) \rangle \quad (14)$$

are identical for all S_z^{σ}, S_z^{π} satisfying $|S_z^{\sigma}| \leq S_{\sigma}, |S_z^{\pi}| \leq S_{\pi}$. Hence, the one-to-one mapping defined by the $\mathbf{S}_{\pm}^{\sigma} \mathbf{S}_{\pm}^{\pi}$ product between subspaces (4b) preserves not only the matrix elements of the hamiltonian (1) but also the matrix elements (14), similarly as in ref.¹ The orthonormal functions set (13) can be converted to eigen-functions of CM's (2a) by a unitary transformation

$$|\Psi_{A,B}(S, S_z, N_{\pi}, S_{\sigma}, S_{\pi})\rangle, \quad |S_{\sigma} - S_{\pi}| \leq S \leq S_{\sigma} + S_{\pi}, \quad |S_z| \leq S. \quad (15)$$

Functions (15) expressed by means of (13) are obtained on the basis of the theory of addition of the two angular momenta⁶

$$\begin{aligned}
 & |\Psi_{A,B}(S, S_z, N_\pi, S_\sigma, S_\pi)\rangle = \\
 & = \sum_{S_z, S_z} \langle S_\sigma S_\pi S_z^{\sigma} S_z^{\pi} | S S_z \rangle |\Psi_{A,B}(S_z^{\sigma}, S_z^{\pi}, N_\pi, S_\sigma, S_\pi)\rangle, \quad (16)
 \end{aligned}$$

where $S_z = S_z^{\sigma} + S_z^{\pi}$, $|S_{\sigma} - S_{\pi}| \leq S \leq S_{\sigma} + S_{\pi}$

and the factors are Clebsch-Gordan coefficients⁷. Now, let us compute the matrix element

$$\langle \Psi_A(S, S_z, N_\pi, S_\sigma, S_\pi) | \mathbf{G}_{pp'} | \Psi_B(S, S_z, N_\pi, S_\sigma, S_\pi) \rangle. \quad (17)$$

Using the unitary transformation (16), the factorization (12), and the one-to-one mapping (14) we obtain

$$\begin{aligned}
 & \langle \Psi_A(S, S_z, N_\pi, S_\sigma, S_\pi) | \mathbf{G}_{pp'} | \Psi_B(S, S_z, N_\pi, S_\sigma, S_\pi) \rangle = \\
 & = \langle \Psi_A(S_z^{\sigma}, S_z^{\pi}, N_\pi, S_\sigma, S_\pi) | \mathbf{G}_{pp'} | \Psi_B(S_z^{\sigma}, S_z^{\pi}, N_\pi, S_\sigma, S_\pi) \rangle.
 \end{aligned}$$

for any $|S_z^{\sigma}| \leq S_{\sigma}$ and $|S_z^{\pi}| \leq S_{\pi}$. Thus, like in ref.¹, the one-to-one mapping due to the transformation (16) between subspaces (4a) preserved the value of the matrix element (17). These two one-to-one mapping (14) and (18) imply: a) also $|\Psi_{A,B}\rangle$ are eigen-functions of CM's (2a) or CM's (2b), and b) $|\Psi_{A,B}\rangle$ belong to one of subspaces (4a) or (4b). Let us assume that the functions $|\Psi_{A,B}\rangle$ are accurate or approximate eigen-functions of the hamiltonian (1) and that they belong to one of subspaces (4a) or (4b). Both these functions have their counterparts in each subspace (4a) or (4b), i.e. there exist function sets (13) and (15). Accordingly, density matrices γ^{AB} (for $N_{\pi}^A = N_{\pi}^B$) are identical for all functions (13) and (15). Thus, the average value of a spinless one-particle observable $\langle \Psi_A | \Omega | \Psi_B \rangle$ is identical with all functions from (13) and (15).

APPLICATIONS AND REMARKS

In the introductory section the additional CM's of the model hamiltonian (1) were defined and the consequences of their existence regarding the features of the eigen-value system of this hamiltonian were examined. Now, we present three examples indicating a possible use of these results in actual calculations.

Example 1. We selected the H—N=O molecule (planar, C_s symmetry) to demonstrate the additional factorization in the full CI CNDO calculation. The system treated has 12 valence electrons and the one-electron functions basis contains seven σ -type and two π -type orbitals. The entries in the first and the second columns of the Table I are the dimensions of full CI problems in a common factorization due to the spatial symmetry (states A' and A'') and the spin operators \mathbf{S}^2 and \mathbf{S}_z (for fixed $S_z = 0$). The third and the fourth columns of that Table refer to additional factorization due to CM's \mathbf{N}_{π} , \mathbf{S}_z^{σ} and \mathbf{S}_z^{π} . It can be noticed that the simplification of the problem is considerable, which permits, in some cases, to perform even a full CI CNDO calculation⁴. Moreover, owing to the degeneracy in the eigen-spectrum of the hamiltonian (1) (section B

in Theoretical ($4a-b$) indicated in the fourth column in Table I (number in parentheses), it is enough to solve the CI problem merely in a subspace with the simplest basis functions.

TABLE I

Splitting of All Characteristic Subproblems with $S_z = 0$ which Are Solved in the Full CNDO-CI Calculation of $\text{H}-\overline{\text{N}}=\overline{\text{O}}$ Molecule (C_s -symmetry)

Factorization due to spatial symmetry and $\mathbf{S}^2, \mathbf{S}_z$		Additional splitting due to the new CM's	
$(R, S)^a$	dimension	$(N_\pi, S, S_\sigma, S_\pi)^b$	dimension
$(A', 0)$	1 316	(0, 0, 0, -)	28
		(2, 0, 0, 0)	588
		(2, 0, 1, 1)	210
		(4, 0, 0, 0)	490
$(A'', 0)$	1 204	$(1, 0, \frac{1}{2}, \frac{1}{2})$	224
		$(3, 0, \frac{1}{2}, \frac{1}{2})$	980
$(A', 1)$	1 680	(0, 1, 1, -)	21
		(2, 1, 1, 1)	(210) ^c
		(2, 1, 1, 0)	630
		(2, 1, 0, 1)	196
		(2, 1, 2, 1)	35
		(4, 1, 1, 0)	588
$(A'', 1)$	1 722	$(1, 1, \frac{1}{2}, \frac{1}{2})$	(224)
		$(1, 1, \frac{3}{2}, \frac{1}{2})$	70
		$(3, 1, \frac{1}{2}, \frac{1}{2})$	980
		$(3, 1, \frac{3}{2}, \frac{1}{2})$	448
$(A', 2)$	490	(2, 2, 1, 1)	(210)
		(2, 2, 2, 0)	105
		(2, 2, 2, 1)	(35)
		(4, 2, 2, 0)	140
$(A'', 2)$	560	$(1, 2, \frac{3}{2}, \frac{1}{2})$	(70)
		$(3, 2, \frac{3}{2}, \frac{1}{2})$	(448)
		$(3, 2, \frac{5}{2}, \frac{1}{2})$	42
$(A', 3)$	42	(2, 3, 2, 1)	(35)
		(4, 3, 3, 0)	7
$(A'', 3)$	42	$(3, 3, \frac{5}{2}, \frac{1}{2})$	(42)

^a R Irreducible representation, S total spin. ^b N_π, S_σ, S_π eigen-values of the additional CM's $\mathbf{N}_\pi, \mathbf{S}_\sigma^2, \mathbf{S}_\pi^2$ of $(2a)$, S total spin. ^csubproblems with "()" may be obtained from the previous ones of the same dimension by mapping (see Theoretical).

Example 2. This simple example shows how the eigen-functions of CM's (2a) are constructed. Let us consider a hypothetical four-electron system with an one-electron orthonormal basis containing three σ -type and two π -type orbitals designated as $|\sigma_1\rangle$, $|\sigma_2\rangle$, $|\sigma_3\rangle$ and $|\pi_1\rangle$, $|\pi_2\rangle$. Using a common notation we obtain the following basis of ten spinorbitals

$$|\sigma_1\rangle, |\bar{\sigma}_1\rangle, |\sigma_2\rangle, \dots, |\pi_2\rangle, |\bar{\pi}_2\rangle, \quad (19)$$

where e.g. $|\sigma_1\rangle$ is a product of a spatial $|\sigma_1\rangle$ and spin $|\alpha\rangle$ parts, similarly $|\bar{\sigma}_1\rangle = |\sigma_1\rangle|\beta\rangle$, etc. Now, the orthonormal basis for subspaces

$$F(S_z^\sigma = x, S_z^\pi = y, N_\pi = 2, S_\sigma = 1, S_\pi = 1), \quad (20)$$

$$(x, y) = (-1, 1), (0, 0), (1, -1),$$

can be constructed; $S_z = S_z^\sigma + S_z^\pi = 0$. Each subspace from (20) possesses three basis vectors.

Subspace $F(-1, 1, 2, 1, 1)$:

$$|\Phi_{(i,j)}(-1, 1, 2, 1, 1)\rangle = |\bar{\sigma}_i\sigma_j\pi_1\pi_2\rangle, \quad (21a)$$

subspace $F(0, 0, 2, 1, 1)$:

$$|\Phi_{(i,j)}(0, 0, 2, 1, 1)\rangle = \frac{1}{2}\{|\sigma_i\bar{\sigma}_j\pi_1\bar{\pi}_2\rangle + |\sigma_i\bar{\sigma}_j\bar{\pi}_1\pi_2\rangle + |\bar{\sigma}_i\sigma_j\pi_1\bar{\pi}_2\rangle + |\bar{\sigma}_i\sigma_j\bar{\pi}_1\pi_2\rangle\}, \quad (21b)$$

subspace $F(1, -1, 2, 1, 1)$:

$$|\Phi_{(i,j)}(1, -1, 2, 1, 1)\rangle = |\sigma_i\sigma_j\bar{\pi}_1\bar{\pi}_2\rangle. \quad (21c)$$

The index $(i, j) = (1, 2)$, $(1, 3)$ and $(2, 3)$, the expression $|\bar{\sigma}_i\bar{\sigma}_j\pi_1\pi_2\rangle$ and the similar ones stand for four-electron normalized Slater determinants. By means of the $S_+^\sigma S_-^\pi$ product and of a suitable normalization factor we obtain (21b) from (21a) and (21c) from (21b). On performing the unitary transformation (16), we can pass from the subspaces set (20) to the following subspaces

$$E(S = x, S_z = 0, N_\pi = 2, S_\sigma = 1, S_\pi = 1), x = 0, 1, 2. \quad (22)$$

The dimension of these subspaces is identical with that of subspaces (20). The necessary Clebsch-Gordan coefficients are listed in Table II.

TABLE II
Clebsch-Gordan Coefficients for $\langle 11xy | t0 \rangle$ of Eq. (16)

x	y	t		
		0	1	2
1	-1	$3^{-1/2}$	$2^{-1/2}$	$6^{-1/2}$
0	0	$-3^{-1/2}$	0	$(\frac{2}{3})^{1/2}$
-1	1	$3^{-1/2}$	$-2^{-1/2}$	$6^{-1/2}$

Subspace $E(0, 0, 2, 1, 1)$:

$$\begin{aligned} |\Psi_{(i,j)}(0, 0, 2, 1, 1)\rangle = & 1/\sqrt{(12)}\{2|\sigma_i\sigma_j\bar{\pi}_1\bar{\pi}_2\rangle + 2|\bar{\sigma}_i\bar{\sigma}_j\pi_1\pi_2\rangle - |\sigma_i\bar{\sigma}_j\pi_1\bar{\pi}_2\rangle - \\ & - |\sigma_i\bar{\sigma}_j\bar{\pi}_1\pi_2\rangle - |\bar{\sigma}_i\sigma_j\pi_1\bar{\pi}_2\rangle - |\bar{\sigma}_i\sigma_j\bar{\pi}_1\pi_2\rangle\}, \end{aligned} \quad (23a)$$

subspace $E(1, 0, 2, 1, 1)$:

$$|\Psi_{(i,j)}(1, 0, 2, 1, 1)\rangle = 2^{-1/2}\{|\sigma_i\sigma_j\bar{\pi}_1\bar{\pi}_2\rangle - |\bar{\sigma}_i\bar{\sigma}_j\pi_1\pi_2\rangle\}, \quad (23b)$$

subspace $E(2, 0, 2, 1, 1)$:

$$\begin{aligned} |\Psi_{(i,j)}(2, 0, 2, 1, 1)\rangle = & 6^{-1/2}\{|\sigma_i\sigma_j\bar{\pi}_1\bar{\pi}_2\rangle + |\bar{\sigma}_i\bar{\sigma}_j\pi_1\pi_2\rangle + |\sigma_i\bar{\sigma}_j\pi_1\bar{\pi}_2\rangle + \\ & + |\sigma_i\bar{\sigma}_j\bar{\pi}_1\pi_2\rangle + |\bar{\sigma}_i\sigma_j\pi_1\bar{\pi}_2\rangle + |\bar{\sigma}_i\sigma_j\bar{\pi}_1\pi_2\rangle\}. \end{aligned} \quad (23c)$$

Here, similarly as in (21a-c), the index has three values: (1, 2), (1, 3) and (2, 3). As shown in the section Theoretical the eigen-spectrum of the hamiltonian (I) is identical in subspaces (20) and (22), therefore, it is enough to estimate eigen-values in one of them. Since the structure of basis vectors is more simple in subspaces $F(\dots)$ than in subspaces $E(\dots)$, it is advantageous to solve the eigen-value problem in one of the $F(\dots)$ subspaces. Furthermore, the eigen-spectrum of the model hamiltonian (I) was proved to be identical in the other subspaces

$$E(x, y, 2, 1, 1), \quad x = 0, 1, 2; \quad |y| \leq x, \quad (24a)$$

and

$$F(x, y, 2, 1, 1), \quad |x| \leq 1, \quad |y| \leq 1. \quad (24b)$$

Extremely simple basis vectors are those which refer to the so-called maximum multiplicity, *i.e.* in the case (24a) for $S = S_z = S_\sigma + S_\pi$ and in the case (24b) for $S_z^\sigma = S_\sigma, S_z^\pi = S_\pi$.

Subspace $F(1, 1, 2, 1, 1)$:

$$|\Phi_{(i,j)}(1, 1, 2, 1, 1)\rangle = |\sigma_i\sigma_j\pi_1\pi_2\rangle, \quad (25a)$$

subspace $E(2, 2, 2, 1, 1)$:

$$|\Psi_{(i,j)}(2, 2, 2, 1, 1)\rangle = |\sigma_i\sigma_j\pi_1\pi_2\rangle, \quad (25b)$$

where the index $(i, j) = (1, 2), (1, 3)$ and $(2, 3)$. From this simple example it becomes evident that for a given eigen-values set of CM's $\mathbf{N}_\pi, \mathbf{S}_\sigma^2$, and \mathbf{S}_π^2 the most convenient way to obtain the eigen-spectrum of the hamiltonian (I) is in general that of solving the eigen-problem in the subspace $F(S_\sigma, S_\pi, N_\pi, S_\sigma, S_\pi)$.

Example 3. This last example concerns a problem of calculating the mean values of a spinless one-particle observable Ω . In subspaces (24a) and (24b) we construct the state functions $|\Psi_{A,B}\rangle$ and $|\Phi_{A,B}\rangle$ by forming the linear combinations of basis functions of those subspaces

$$|\Psi_{A,B}(x, y, 2, 1, 1)\rangle = \sum_{(i,j)} C_{(i,j)}^{A,B} |\Psi_{(i,j)}(x, y, 2, 1, 1)\rangle, \quad (26a)$$

for $x = 0, 1, 2$ and $|y| \leq x$

$$|\Phi_{A,B}(x, y, 2, 1, 1)\rangle = \sum_{(i,j)} C_{(i,j)}^{A,B} |\Phi_{(i,j)}(x, y, 2, 1, 1)\rangle, \quad (26b)$$

for $|x| \leq 1$ and $|y| \leq 1$. Expansion coefficients in (26a) and (26b) are identical. This can be proved by the fact that the state functions $|\Psi_{A,B}\rangle$ and $|\Phi_{A,B}\rangle$ are solutions of the eigen-value problem

of the hamiltonian (I) in subspaces (24a) and (24b). Accordingly, these states are coupled by the one-to-one mapping changing the basis functions but not the expansion coefficients. From the foregoing section it follows: a) the mean value of an observable Ω is, in general, non-zero only between two states $|\Psi_{A,B}(\dots)\rangle$ or $|\Phi_{A,B}(\dots)\rangle$ belonging to the same subspace $E(\dots)$ or $F(\dots)$ (12), and b) the mean values

$$\langle \Psi_A(x, y, 2, 1, 1) | \Omega | \Psi_B(x, y, 2, 1, 1) \rangle, \quad (28a)$$

for $x = 0, 1, 2$, and $|y| \leq x$

$$\langle \Psi_A(x, y, 2, 1, 1) | \Omega | \Phi_B(x, y, 2, 1, 1) \rangle, \quad (28b)$$

for $|x| \leq 1$ and $|y| \leq 1$

are identical for all compatible x and y . This implies the simplest calculation of the expectation value of Ω (analogous to the calculation of the eigen-values of the hamiltonian (I)) is that for two states $|\Phi_{A,B}\rangle$ belonging to a subspace of the highest multiplicity, i.e. to $F(S_\sigma, S_\pi, N_\pi, S_\sigma, S_\pi)$.

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