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# REMARK ON THE MANY-BODY PROBLEM FOR COMPOSITE PARTICLES

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*Abstract*: The dependence of symmetry conditions related to the exchange of electron and nuclei between atoms in a Girardeau's theory for many atom problem, is studied. Effects of interatomic exchange of electrons are incorporated into the »projected Hamiltonian« so that, when exchanges of electrons between atoms vanish, it tends to the Hamiltonian in which only the permutations of atoms as a whole are incorporated.

## *1. Introduction*

Recently, in a series of papers,[1, 2, 3] M. D. Girardeau has formulated a representation of second quantisation for the nonrelativistic system of composite particles, in such a way as to take into account the existence of composite particles. We think that some proofs from that theory can be generalised and several remarks can be made. Therefore, we will express the principal ideas and results of papers[1, 2, 3] together with our new results.

For the sake of definiteness, as composite particles are considered identical atoms, each containing one nucleus and $l$ electrons. The wave function for the system of $n$ such atoms is a function of position and one spin component ($z$ component) of all nuclei $X_i = (R_i, \sum_i)$ and electrons $x_j = (r_j, \sigma_j)$ and can be expanded in terms of the single atom wave functions as follows

$$\psi(X_1 \ldots X_n\, x_1 \ldots x_{ln}) = \sum_{\alpha_1 \ldots \alpha_n} C(\alpha_1 \ldots \alpha_n)\, \varphi_{\alpha_1}(X_1\, x_1 \ldots x_l) \ldots \varphi_{\alpha_n}(X_n\, x_{ln-l+1} \ldots x_{ln}), \tag{1.1.}$$

with coefficients

$$C(\alpha_1 \dots \alpha_n) = \int \varphi^*_{\alpha_1}(X\, x_1 \dots x_l) \dots \varphi^*_{\alpha_n}(X_n\, x_{1n-l+1} \dots x_{1n}) \cdot \cdot \psi(X_1 \dots X_n\, x_1 \dots x_{1n})\, \mathrm{d}X_1 \dots \mathrm{d}X_n\, \mathrm{d}x_1 \dots \mathrm{d}x_{1n}. \tag{1.2}$$

Single atom wave functions $\varphi_\alpha(X\, x_1 \dots x_l)$ form an ortonormal and complete set

$$\int \varphi^*_\alpha(X\, x_1 \dots x_l)\, \varphi_\beta(X\, x_1 \dots x_l)\, \mathrm{d}X\, \mathrm{d}x_1 \dots \mathrm{d}x_l = \delta_{\alpha\beta}$$

$$\sum_\alpha \varphi^*_\alpha(X\, x_1 \dots x_l)\, \varphi_\alpha(X'\, x'_1 \dots x'_l) = (l!)^{-1}\, \delta(X - X') \cdot \cdot \sum_{P'} (-1)^{p(P')} P' [\delta(x_1 - x'_1) \dots \delta(x_l - x'_l)]. \tag{1.3}$$

Symbol $\int$ stands for the integration over space coordinates and summation over spins, $\sum_{P'}$ denotes a sum over all permutations $p'$ of primed variables, $p(P')$ is the parity of the permutation $P'$.

In order that the functions $\psi(X_1 \dots X_n\, x_1 \dots x_{1n})$ would be symmetric or antisymmetric in nuclear coordinates and antisymmetric in electron coordinates, author of referenced papers shows that it is necessary that functions $C(\alpha_1 \dots \alpha_n)$ satisfy the following conditions

$$C(\alpha_1 \dots \alpha_l \dots \alpha_k \dots \alpha_n) = (-1)^{2J+1}\, C(\alpha_1 \dots \alpha_k \dots \alpha_l \dots \alpha_n), \tag{1.4}$$

$$\sum_{\alpha\beta} (\alpha_p\, \alpha_q \mid I_{\mathrm{elec}} \mid \alpha\beta)\, C(\alpha_1 \dots \alpha_{p-1}\, \alpha\, \alpha_{p+1} \cdot \cdot \alpha_{q-1}\, \beta\alpha_{q+1} \dots \alpha_n) = = -C(\alpha_1 \dots \alpha_p \dots \alpha_q \dots \alpha_n), \tag{1.5}$$

$$\sum_{\alpha\beta} (\alpha_p\, \alpha_q \mid I_{\mathrm{nuc}} \mid \alpha\beta)\, C(\alpha_1 \cdots \alpha_{p-1}\, \alpha\, \alpha_{p+1} \cdots \alpha_{q-1}\, \beta\, \alpha_{q+1} \cdots \alpha_n) = = (-)^{2J} C(\alpha_1 \cdots \alpha_p \cdots \alpha_q \cdots \alpha_n). \tag{1.6}$$

J is the nuclear spin.

Matrix elements of the exchange operators $I_{\mathrm{nuc}}$ and $I_{\mathrm{elec}}$ for nuclei and electrons are defined in terms of nucleus and electron exchange integrals

$$(\alpha_p\, \alpha_q \mid I_{\mathrm{elec}} \mid \alpha\beta) = \int \varphi^*_{\alpha_p}(X\, x_1 \dots x_l)\, \varphi^*_{\alpha_q}(X'\, x'_1 \dots x'_l) \cdot \cdot \varphi_\alpha(X\, x'_1\, x_2 \dots x_l)\, \varphi_\beta(X'\, x_1\, x'_2 \dots x'_l)\, \mathrm{d}X\, \mathrm{d}x_1 \dots \mathrm{d}x_l\, \mathrm{d}X'\, \mathrm{d}x'_1 \dots \mathrm{d}x'_l \tag{1.7}$$

$$(\alpha_p\, \alpha_q \mid I_{\mathrm{nuc}} \mid \alpha\beta) = \int \varphi^*_{\alpha_p}(X\, x_1 \dots x_l)\, \varphi^*_{\alpha_q}(X'\, x'_1 \dots x'_l) \cdot \cdot \varphi_\alpha(X'\, x_1 \dots x_l)\, \varphi_\beta(X\, x'_1\, x'_2 \dots x'_l)\, \mathrm{d}X\, \mathrm{d}x_1 \dots \mathrm{d}x_l\, \mathrm{d}X'\, \mathrm{d}x'_1 \dots \mathrm{d}x'_l.$$

In that paper we will prove that the above three conditions are not mutually independent and we shall show to which consequences, in connection with the other results of the original theory, this leads.

In referenced papers has been developed a representation in terms of atomic annihilation and creation operators $a_\alpha$ and $a_\alpha^+$ for atoms in single atom states $\varphi_\alpha(X\, x_1 \dots x_l)$. These operators satisfy Bose or Fermi commutation relations

$$\begin{aligned} a_\alpha\, a_\beta^+ - (-1)^{2J+l}\, a_\beta^+\, a_\alpha &= \delta_{\alpha\beta}, \\ a_\alpha\, a_\beta - (-1)^{2J+l}\, a_\beta\, a_\alpha &= 0. \end{aligned} \tag{1.8}$$

Hamiltonian and total atom number operator in that representation are given by

$$H = T + V_0 + V', \tag{1.9}$$

$$T = \sum_{\alpha\beta} (\alpha \mid T \mid \beta)\, a_\alpha^+ a_\beta,$$

$$V = \sum_{\alpha\beta} (\alpha \mid V \mid \beta)\, a_\alpha^+ a_\beta, \tag{1.10}$$

$$V' = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} (\alpha\beta \mid V' \mid \gamma\ \delta)\, a_\alpha^+\, a_\beta^+\, a_\delta\, a_\gamma,$$

$$N = \sum_\alpha a_\alpha^+ a_\alpha, \tag{1.11}$$

where matrix elements are

$$(\alpha \mid T \mid \beta) = \int \varphi_\alpha^*(X\, x_1 \dots x_l) \left[T(X) + \sum_{j=1}^{l} T(x_j)\right] \varphi_\beta(X\, x_1 \dots x_l)\, \mathrm{d}X\, \mathrm{d}x_1 \dots \mathrm{d}x_l,$$

$$(\alpha \mid V \mid \beta) = \int \varphi_\alpha^*(X\, x_1 \dots x_l) \left[\sum_{j=1}^{l} V(X x_j) + \sum_{j<k=1}^{l} V(x_j x_k)\right] \varphi_\beta(X x_1 \dots x_l)\, \mathrm{d}X \mathrm{d}x_1 \dots \mathrm{d}x_l,$$

$$\begin{aligned} (\alpha\beta \mid V' \mid \gamma\delta) = \int \varphi_\alpha^*(X\, x_1 \dots x_l)\, \varphi_\beta^*(X'\, x_1' \dots x_l') \Big[V(XX') + \sum_{j=1}^{l} (V(X\, x_j') + \\ + V(X' x_j)) + \sum_{j,k=1}^{l} V(x_j\, x_k')\Big] \varphi_\gamma(X\, x_1 \dots x_l)\, \varphi_\delta(X'\, x_1' \dots x_l')\, \mathrm{d}X\, \mathrm{d}x_1 \dots \\ \dots \mathrm{d}x_l\, \mathrm{d}X'\, \mathrm{d}x_1' \dots \mathrm{d}x_l'. \end{aligned} \tag{1.12}$$

Subsidiary conditions (1.5) and (1.6) can be written in a new representation too:

$$I_{\text{elec}} \mid C_n > \equiv \left[\frac{1}{2} \sum_{\alpha\beta\gamma\delta} (\alpha\beta \mid I_{\text{elec}} \mid \gamma\delta)\, a_\alpha^+ a_\beta^+ a_\delta a_\gamma\right] \mid C_n > =$$

$$= -\left[n(n-1)/2\right] \mid C_n >, \tag{1.13}$$

$$I_{\text{nuc}} \mid C_n > \equiv \left[\frac{1}{2} \sum_{\alpha\beta\gamma\delta} (\alpha\beta \mid I_{\text{nuc}} \mid \gamma\delta)\, a_\alpha^+ a_\beta^+ a_\delta a_\gamma\right] \mid C_n > = (-1)^{2J} \frac{n(n-1)}{2} \mid C_n >. \tag{1.14}$$

The space of all $n$ atom wave functions $C(\alpha_1 \ldots \alpha_n) \equiv \langle \alpha_1 \ldots \alpha_n \mid C_n \rangle$ satisfying the last equations is completly equivalent to the space of all $n$ nuclei, $ln$ electrons wave functions $\psi(X_1 \ldots X_n\, x_1 \ldots x_{ln})$ (with proper statistics).

## 2. *The determination of independent symmetry conditions*

Affirmation:

If functions $C(\alpha_1 \ldots \alpha_n)$ satisfy Equs. (1.4) and (1.5) they satisfy automatically Equ. (1.6).

Proof:

As in Ref.[3] we define

$$(\alpha_p\, \alpha_q \mid I_j \mid \alpha\beta) \equiv \int \varphi^*_{\alpha_p}(X\, x_1 \ldots x_l)\, \varphi^*_{\alpha_q}(X'\, x'_1 \ldots x'_l) \cdot$$

$$\cdot\, \varphi_\alpha(X\, x_1 \ldots x'_j\, x_{j+1} \ldots x_l)\, \varphi_\beta(X\, x_1 \ldots x_j\, x'_{j+1} \ldots x'_l)\, \mathrm{d}X\, \mathrm{d}x_1 \ldots \mathrm{d}x_l\, \mathrm{d}X'\, \mathrm{d}x'_1 \ldots \mathrm{d}x'_l. \tag{2.1}$$

Also, we have

$$(\alpha_p\, \alpha_q \mid I_{nuc} \mid \alpha\, \beta) = (\alpha_p\, \alpha_q \mid I_l \mid \beta\, \alpha) = (\alpha_q\, \alpha_p \mid I_l \mid \alpha\, \beta), \tag{2.2}$$

$$(\alpha\, \beta \mid I_0 \mid \gamma\, \delta) = \delta_{\alpha\gamma}\, \delta_{\beta\delta}. \tag{2.3}$$

Using the completeness relation for the functions $\varphi_\alpha(X\, x_1 \ldots x_l)$ and their antisymmetry properties with respect to $x_i$, one shows that there exist some relations between matrix elements $(\alpha\, \beta \mid I_j \mid \gamma\, \delta)$ for different $j$. We will use the relation[3]

$$(\alpha\, \beta \mid I_j\, I_{1p} \mid \gamma\, \delta) \equiv \sum_{\alpha_p \alpha_q} (\alpha\, \beta \mid I_1 \mid \alpha_p\, \alpha_q)(\alpha_p\, \alpha_q \mid I_j \mid \gamma\, \delta) = \tag{2.4}$$

$$= (1/l^2)\{(l-j)^2 (\alpha\beta \mid I_{j+1} \mid \gamma\, \delta) - 2j(l-j)(\alpha\, \beta \mid I_j \mid \gamma\, \delta) + j^2 (\alpha\beta \mid I_{j-1} \mid$$

$$\mid \gamma\, \delta)\}, \quad j \leq l, \ (I_{l+1} = 0).$$

Now we can proceed in two steps. First, we prove:

If functions $C(\alpha_1 \dots \alpha_n)$ satisfy (1.5) they satisfy also the equation

$$\sum_{\alpha\beta} (\alpha_p \alpha_q \mid I_j \mid \alpha \beta)\, C(\alpha_1 \dots \alpha_{p-1}\, \alpha\, \alpha_{p+1} \dots \alpha_{q-1}\, \beta\, \alpha_{q+1} \dots \alpha_n) =$$

$$= -\sum_{\alpha\beta} (\alpha_p \alpha_q \mid I_{j-1} \mid \alpha \beta)\, C(\alpha_1 \dots \alpha_{p-1}\, \alpha\, \alpha_{p+1} \dots \alpha_{q-1}\, \beta\, \alpha_{q+1} \dots \alpha_n), \tag{2.5}$$

for all $j = 1 \dots, l$.

From the fact that Equ. (2.5) is true for $j = 1$ (Equ. (1.5)) and the prediction that it is true for some $j$, we prove that Equ. (2.5) is true also for $j + 1$.

Multiplying Equ. (1.5) with $(\gamma\ \delta \mid I_j \mid \alpha_p\, \alpha_q)$ and summing over $\alpha_p$, $\alpha_q$ one obtains

$$\sum_{\alpha\beta} C(\alpha_1 \dots \alpha_{p-1}\, \alpha\, \alpha_{p+1} \dots \alpha_{q-1}\, \beta\, \alpha_{q+1} \dots \alpha_n) \sum_{\alpha_p \alpha_q} (\gamma\delta \mid I_j \mid \alpha_p\, \alpha_q)(\alpha_p\, \alpha_q \mid I_1 \mid \alpha\beta) =$$

$$= -\sum_{\alpha_p \alpha_q} C(\alpha_1 \dots \alpha_p \dots \alpha_q \dots \alpha_n)(\gamma\ \delta \mid I_j \mid \alpha_p\, \alpha_q). \tag{2.6}$$

With the aid of Equ. (2.4), Equ. (2.6) becomes

$$\sum_{\alpha\beta} C(\alpha_1 \dots \alpha_{p-1}\, \alpha\, \alpha_{p+1} \dots \alpha_{q-1}\, \beta\, \alpha_{q+1} \dots \alpha_n)\,[1 - 2j(l-j)/\,l^2](\gamma\ \delta \mid I_j \mid \alpha\beta) =$$

$$= -(1/\,l^2) \sum_{\alpha\beta} C(\alpha_1 \dots \alpha_{p-1}\, \alpha\, \alpha_{p+1} \dots \alpha_{q-1}\ \beta\, \alpha_{q+1} \dots \alpha_n)\,[(l-j)^2\ \ (\gamma\delta \mid I_{j+1} \mid$$

$$\mid \alpha\ \beta) + j^2\,(\gamma\delta \mid I_{j-1} \mid \alpha\ \beta)]. \tag{2.7}$$

In Equ. (2.7) the expression $\sum_{\alpha\beta} C(\alpha_1 \dots \alpha \dots \beta \dots \alpha_n)(\gamma\ \delta \mid I_{j-1} \mid \alpha\ \beta)$ can be replaced by $-\sum_{\alpha\beta} C(\alpha_1 \dots \alpha \dots \beta \dots \alpha_n)(\gamma\ \delta \mid I_j \mid \alpha\ \beta)$. After elementary calculations one obtains

$$\sum_{\alpha\beta} C(\alpha_1 \dots \alpha_{p-1}\, \alpha\, \alpha_{p+1} \dots \alpha_{q-1}\, \beta\, \alpha_{q+1} \dots \alpha_q)(\gamma\ \delta \mid I_{j+1} \mid \alpha\ \beta) =$$

$$= -\sum_{\alpha\beta} C(\alpha_1 \dots \alpha_{p-1}\, \alpha\, \alpha_{p+1} \dots \alpha_{q-1}\, \beta\, \alpha_{q+1} \dots \alpha_n)(\gamma\ \delta \mid I_j \mid \alpha\ \beta). \tag{2.8}$$

It is proved therefore that: if (1.5) is satisfied, from the assumption that (2.5) is valid for arbitrary $j$ follows that it is valid for $j + 1$ too.

The second step is to combine Equ. (2.5) and Equ. (1.5)

$$\sum_{\alpha\beta} (\alpha_p\, \alpha_q \mid I_j \mid \alpha\ \beta)\, C(\alpha_1 \dots \alpha_{p-1}\, \alpha\alpha_{p+1} \dots \alpha_{q-1}\, \beta\, \alpha_{q+1} \dots \alpha_n) =$$

$$= (-1)^j\, C(\alpha_1 \dots \alpha_p \dots \alpha_q \dots \alpha_n). \tag{2.9}$$

For $j = l$ Equ. (2.9) becomes

$$\sum_{\alpha\beta} (\alpha_p \alpha_q \mid I_l \mid \alpha \beta) C(\alpha_1 \ldots \alpha_{p-1} \alpha \alpha_{p+1} \ldots \alpha_{q-1} \beta \alpha_{q+1} \ldots \alpha_n) = \\ = (-1)^l C(\alpha_1 \ldots \alpha_p \ldots \alpha_q \ldots \alpha_n). \tag{2.10}$$

Replacing $(\alpha_p \alpha_q \mid I_l \mid \alpha \beta)$ in (2.10) by $(\alpha_p \alpha_q \mid I_{\text{nuc}} \mid \beta \alpha)$ and using Equ. (1.4) one obtains Equ. (1.6).

Therefore, our proof is concluded.

The consequences are the following:

— the operator equation (1.13) is equivalent to the set of Equs. (1.4), (1.5) and (1.6) i. e. if $\mid C_n >$ satisfies eigenvalue problem (1.13) it satisfies (1.14 automatically;

— the zero-temperature $n$ atom problem is that of finding simultaneous eigenstates of Hamiltonian $H$

$$H \mid C_n > = i \frac{\partial}{\partial t} \mid C_n > \tag{2.11}$$

of total number operator $N$ with the eigenvalue $n$

$$N \mid C_n > = n \mid C_n >, \tag{2.12}$$

and of the operator $I_{\text{elec}}$ with the eigenvalue $-n(n-1)/2$

$$I_{\text{elec}} \mid C_n > = -\frac{1}{2} n(n-1) \mid C_n >; \tag{2.13}$$

— the identity

$$\mathscr{P}_{\text{elec}} = \mathscr{P}_{\text{nuc}} \mathscr{P}_{\text{elec}}, \tag{2.14}$$

proved in[3] for two atom subspace, is true for any number of atoms in the system. $\mathscr{P}_{\text{nuc}}$ and $\mathscr{P}_{\text{elec}}$ are the projection operators which project onto the subspace of eigenstates of $I_{\text{elec}}$ with eigen value $-n(n-1)/2$ and of $I_{\text{nuc}}$ with the eigen value $(-1)^{2J} n(n-1)/2$, respectively;

— since the independent constants of motion are $H$, $N$ and $I_{\text{elec}}$ the formulation of the non zero temperature problem is now some what different from what was originally given.

Namely, the usual grand partition function is generalized in the following way

$$Z = Tr \exp[-\beta(H - \mu N + \gamma_{\text{elec}} I_{\text{elec}})]. \tag{2.15}$$

The appropriate density operator is defined as

$$\varrho = Z^{-1} \exp\left[-\beta (H - \mu N + \gamma_{\text{elec}} I_{\text{elec}})\right], \tag{2.16}$$

$\beta = (kT)^{-1}$, $k$ Boltzmann constant, $T$ the absolute temperature, $\mu$ is the atomic chemical potential, $\gamma_{\text{elec}}$ is Lagrange multiplier associated with the subsidiary condition (1.13). $\mu$ and $\gamma_{\text{elec}}$ are determined by the coupled equations

$$-\left(\frac{\partial W}{\partial \mu}\right)_{\beta,\gamma_{\text{elec}}} = \langle N \rangle = n, \tag{2.17}$$

$$\left(\frac{\partial W}{\partial \gamma_{\text{elec}}}\right)_{\beta,\mu} = \langle I_{\text{elec}} \rangle = -\frac{1}{2} n (n-1), \tag{2.18}$$

and $W$ is the generalized thermodinamical potential related to $Z$ by

$$Z = \exp(-\beta W). \tag{2.19}$$

## 3. *The projected Hamiltonian*

Since the operator $I_{\text{elec}}$ has the same general structure as the interatomic interaction Hamiltonian $V'$, to satisfy the subsidiary condition (1.5) would be as difficult as solving interatomic interaction exactly. This is why in the paper[3] was defined a »projected Hamiltonian« in which the subsidiary conditions (1.5) and (1.6) are incorporated as additional effective interatomic exchange interactions, which can then be treated approximately along, with the interatomic Coulomb interactions V'. The projected Hamiltonian is defined as follows

$$\mathscr{H} = \mathscr{P}_{\text{nuc}}\, \mathscr{P}_{\text{elec}}\, H \equiv \mathscr{P}_{\text{elec}}\, H, \tag{3.1}$$

where

$$\mathscr{P}_{\text{elec}} \mid C_n > = \mid C_n >, \tag{3.2}$$

if

$$[I_1 + \frac{1}{2} n (n-1)] \mid C_n > = 0, \tag{3.3}$$

and

$$\mathscr{P}^2_{\text{elec}} = \mathscr{P}_{\text{elec}}, \tag{3.4}$$

$$[H, \mathscr{P}_{\text{elec}}] = [\mathscr{P}_{\text{elec}}, H]. \tag{3.5}$$

Using (3.4) and (3.5) one can easily show that for eigenstates of $\mathscr{H}$ the following set of equations is valid

$$\mathscr{H} \mid C_n > = H \mid C_n > = E \mid C_n >. \tag{3.6}$$

We think that two remarks can be made regarding the definition (3.1) of the projected Hamiltonian:

— the operator $\mathscr{P}_{\text{elec}} H$ with $\mathscr{P}^2_{\text{elec}} = \mathscr{P}_{\text{elec}}$ is not the unique operator whose eigenstates satisfy the subsidiary condition (1.13). Eigenstates of the operator

$$\mathscr{H}' \equiv \mathscr{P}'_{\text{elec}} H \equiv b\, \mathscr{P}_{\text{elec}} H, \tag{3.7}$$

where $b$ is a real number, satisfy the subsidiary condition (1.13) too.

Suppose that $|\, C_n\rangle$ is an eigenstate of $\mathscr{H}'$ with the eigenvalue $E'$

$$\mathscr{H}' \,|\, C_n > = E' \,|\, C_n >. \tag{3.8}$$

Using (3.4) and (3.5) one gets

$$\mathscr{P}_{\text{elec}} \,|\, C_n > = \mathscr{P}_{\text{elec}} \frac{1}{E'} \mathscr{P}'_{\text{elec}} H \,|\, C_n > = \frac{b}{E'} \mathscr{P}^2_{\text{elec}} H \,|\, C_n > =$$

$$= \frac{b}{E'} \mathscr{P}_{\text{elec}} H \,|\, C_n > = \frac{\mathscr{P}'_{\text{elec}} H}{E'} \,|\, C_n > = |\, C_n >. \tag{3.9}$$

Therefore $|\, C_n >$ satisfies (3.3) because $\mathscr{P}_{\text{elec}}$ is defined as the operator which projects onto the subspace of the operator $I_{\text{elec}}$ with eigenvalue $-n(n-1)/2$. But eigenvalues of $\mathscr{H}'$ for different $b$ have different values. (Especially, for $b = 1$ we have the Hamiltonian $\mathscr{H}$ as defined in Ref[3]), and

— Equ. (3.6) as the direct consequence of (3.1) and (3.4) means that $\mathscr{H}$ and $H$ have the same eigenvalue, or that exchanges of electrons between different atoms do not contribute to the total energy of the system, which, as we know from more elementary theories on the problem, is not true.

We think that the second problem can be resolved if we define the projected Hamiltonian as in (3.7) where $b$ is to be found from the condition that the limit of the operator $\mathscr{H}'$ when $I_j \to 0$ for all $j = 1, \ldots l$ (no exchanges of electrons between different atoms) is equal $H$

$$\lim_{I_j \to 0,\ j=1,\ \ldots,\ l} \mathscr{H}' = H. \tag{3.10}$$

Now, it is necessary to find an explicit expression for $\mathscr{P}_{\text{elec}}$. In the original paper dealing with this problem, it has been concluded that operators $I_0, I_1, \ldots, I_l$, within the two atom state space form an algebra; therefore, the projection operator $\mathscr{P}_{\text{elec}}$ (here after we work within a two atom subspace) can be supposed as a linear combination of these operators

$$\mathscr{P}_{\text{elec}} = I_0 + \sum_{j=1}^{l} c_j I'_j, \tag{3.11}$$

where

$$I'_j = I_j - (-1)^j I_0. \tag{3.12}$$

Constants $c_1, \ldots c_l$ should be found so that the Equ. (3.4) and the Equ.

$$\mathscr{P}_{\text{elec}} I'_1 = 0, \tag{3.13}$$

which is a consequence of Equs. (3.2) and (3.3), are satisfied.

In fact, it is shown in the Appendix that the operator

$$\mathscr{P}_{\text{elec}} = m_l (I_0 + \sum_{j=1}^{l} a_j I_j), \tag{3.14}$$

with coefficients

$$m_l = \frac{(l!)^2}{(2l)!}; \; a_j = (-1)^j \binom{l}{j}^2, \tag{3.15}$$

satisfies (3.13) and (3.4). In the two atom subspace the operator $I_0$ is the unit operator. Because of this, it is evident that

$$\lim_{I_j \to 0,, j=1,\ldots,l} H (I_0 + \sum_{j=1}^{l} a_j I_j) = H + \lim_{I_j \to 0} \sum_{j=1}^{l} a_j H I_j = H. \tag{3.16}$$

Therefore, the operator

$$\mathscr{H}' = H + \sum_{j=1}^{l} a_j H I_j, \tag{3.17}$$

satisfies the condition (3.10) and its eigenstates have a proper statistics with respect to the exchange of electrons between different atoms.

Putting all terms into normal order with the aid of (1.8) and truncating the terms of the order higher than four (in the two atom subspace these terms do not contribute) we obtain the following expression for the projected Hamiltonian:

$$\mathscr{H}' = H + V_{ex} = H_0 + V' + V_{ex}, \tag{3.18}$$

$$V_{ex} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta}^{l} (\alpha \beta \mid V_{ex} \mid \gamma \delta) a_\alpha^+ a_\beta^+ a_\delta a_\gamma. \tag{3.19}$$

The matrix elements of the exchange interaction $V_{ex}$ are

$$(\alpha \beta \mid V_{ex} \mid \gamma \delta) = \sum_{j=1}^{l} a_j (\alpha \beta \mid V_j \mid \gamma \delta) + (\varepsilon_\alpha + \varepsilon_\beta) \sum_{j=1} a_j (\alpha\beta \mid I_j \mid \gamma \delta), \tag{3.21}$$

$$(\alpha\beta \mid V_J \mid \gamma\ \delta) = \int \varphi_\alpha^* (X\, x_1 \ldots x_l)\, \varphi_\beta^* (X'\, x_1' \ldots x_l')\, V' (XX'\, x_1 \ldots x_l\, x_1' \ldots x_l').$$

$$\cdot\, \varphi_\gamma (X\, x_1' \ldots x_j'\, x_{j+1} \ldots x_l)\, \varphi_\delta (X'\, x_1 \ldots x_j\, x_{j+1}' \ldots x_l')\, \mathrm{d}X\, \mathrm{d}x_1 \ldots \mathrm{d}x_l\, \mathrm{d}X'\, \mathrm{d}x_1' \ldots \mathrm{d}x_l', \tag{3.22}$$

$$\varepsilon_\alpha = (\alpha \mid H_0 \mid \alpha) = (\alpha \mid T + V_0 \mid \alpha),$$

$V' (XX'\, x_1 \ldots x_l\, x_1' \ldots x_l')$ is the interatomic interaction

$$V'(XX'\, x_1 \ldots x_l\, x_1' \ldots x_l') = V (XX') + \sum_{j=1}^{l} [V (Xx_j') + V (X'\, x_j)] + \sum_{k,j=1}^{l} V (x_j\, x_k'). \tag{3.23}$$

The form of our operator (3.19) is the same as the form of the exchange operator given in Ref[3], but the corresponding matrix elements in these two operators are not equal. At the same time our exchange operator tends to zero when exchange integrals tend to zero, while the original $V_{ex}$ tends under she tame conditions to the operator $(m_l - 1)\, H$. On the other hand, eigenvalues of our operator $V_{ex}$ are different from zero, (exchanges of electrons between atoms contribute to the total energy of the system), until all eigenvalues of the original exchange operator are equal zero. It is evident that these distinctions come from the difference in the definition of the projected Hamiltonian in our and the referenced article.

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## *APPENDIX*

If $\mid C_n >$ is an eigenstate of $I_J$ with the eigenvalue $-n\,(n-1)/2$

$$I_1' \mid C_n > \equiv (I_1 + \frac{1}{2} n\,(n-1) \mid C_n > = 0, \tag{1}$$

it is necessary that

$$\mathscr{P}_{\mathrm{elec}} \mid C_n > \equiv (I_0 + \sum_{j=1}^{l} c_j\, I_j') \mid C_n > = \mid C_n >, \tag{2}$$

i. e. the first necessary condition which $\mathscr{P}_{\text{elec}}$ has to satisfy is

$$I_1' \mathscr{P}_{\text{elec}} = 0. \tag{3}$$

Another necessary condition is

$$\mathscr{P}_{\text{elec}}^2 = \mathscr{P}_{\text{elec}}. \tag{4}$$

Let us prove: the operator $\mathscr{P}_{\text{elec}}$ whose coefficients $c_j$ are determined so that it satisfies (3) will satisfy the condition (4) as well.

In the two atom subspace these relations are valid

$$(I_1')^2 = 2\, l^{-2}\, (l^2 - l + 1)\, I_1' + l^{-2}\, (l-1)^2\, I_2', \tag{5}$$

$$I_1' I_j' = -(-1)^j I_1' + \left(\frac{j}{l}\right)^2 I_{j-1}' + l^{-2}\, (l^2 - 2jl + 2j^2)\, I_j' +$$

$$+ l^{-2}\, (l-j)^2\, I_{j+1}';\quad j \geq 2\ [\text{for } j = l,\ I_{j+1} = 0]. \tag{6}$$

Equ. (5) means that within the two atom subspace $I_2'$ is a second order polinomial in $I_1'$ without a zero order term. Using Equs. (5) and (6) for $j = 2$ we have

$$I_3' = a_{33}\, I_1'^3 + a_{32}\, I_1'^2 + a_{31}\, I_1', \tag{7}$$

where $a_{33}$, $a_{32}$ and $a_{31}$ are constants. Similarly, using (6) we can show that

$$I_j' = a_{jj}\, I_1'^j + a_{jj-1}\, I_1'^{j-1} + \ldots + a_{j-1}\, I_1';\ j = 1, \ldots, l. \tag{8}$$

Equ. (8) can be written in the form

$$I_j' = I_1' \cdot A_{j-1}, \tag{9}$$

where $A_{j-1}$ is a $(j-1)$-th polinomial in $I_1'$.

Using the definition (3.11) of $\mathscr{P}_{\text{elec}}$ and the Equ. (9), $\mathscr{P}_{\text{elec}}^2$ becomes

$$\mathscr{P}_{\text{elec}}^2 = \mathscr{P}_{\text{elec}} + \sum_{j=1}^{l} c_j\, (I_1'\, \mathscr{P}_{\text{elec}})\, A_{j-1}. \tag{10}$$

Now, it is evident that if the coefficients $c_j$ are determined so that Equ (3) is satisfied, $\mathscr{P}_{\text{elec}}$ satisfies Equ. (4) too.

Finally, let us determine $c_j$. Substituting (3.11) in (3), using (5) and (6), equating the coefficients of $I_j^!$ $(j = 1, 2, \ldots, l)$ to zero, one finds an inhomogeneous set of $l$ linear equations in the $l$ unkowns $c_1, \ldots, c_l$.

$$c_1 \cdot l^{-2}(l^2 - 2l + 2) + 4\, c_2 \cdot l^{-2} + \sum_{j=1}^{l} c_j (-1)^{j+1} = -1, \tag{11}$$

$$c_{j+1}(j+1)^2 + c_j \cdot (l^2 - 2jl + 2j^2) + c_{j-1}(l - j + 1)^2 = 0, \tag{12}$$

$$j = 2, 3, \ldots, l.$$

The last equation for $j = l$ (we make $c_{l+1} = 0$) takes the following form

$$c_{l-1} = -l^2 c_l. \tag{13}$$

Substituting the last equation in (12) for $j = l - 1$ we obtain relation between $c_{l-1}$ and $c_{l-2}$, or finally

$$c_j = (-1)^j \binom{l}{j}^2 \frac{(2l)!}{(l!)^2}. \tag{14}$$

Using the definition of the operators $I_j^!$ and the identity

$$\sum_{j=0}^{l} \binom{l}{j}^2 = \frac{(2l)!}{(l!)^2}, \tag{15}$$

the terms in $\mathscr{P}_{\text{elec}}$ can be gathered in a following way

$$\mathscr{P}_{\text{elec}} = I_0 \left[1 - \frac{(l!)^2}{(2l)!}\left(\frac{(2l)!}{(l!)^2} - 1\right)\right] + \frac{(l!)^2}{(2l)!} \sum_{j=1}^{l} (-1)^j \binom{l}{j}^2 I_j. \tag{16}$$

The expression (3.15) then follows immediatly.

References:

1) M. D. Girardeau, J. Math. Phys. **4** (1963) 1096;

2) M. D. Girardeau, J. Math. Phys. **11** (1970) 681;

3) M. D. Girardeau, J. Math. Phys. **12** (1971) 1799.

# ZAPAŽANJA U VEZI FORMULACIJE PROBLEMA VIŠE TIJELA ZA SLOŽENE ČESTICE

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Sadržaj

Proučeni su uslovi simetrije koji su povezani sa izmenom elektrona i jezgara između atoma u Girardeauovoj formulaciji druge kvantizacije za višeatomske sisteme.

Efekti izmene elektrona između atoma ugrađeni su u »Projektorski Hamiltonijan« tako da kada matrični elementi koji opisuju izmenu elektrona između atoma teže nuli, »Projektorski Hamiltonijan« teži Hamiltonijanu u kome su uzeti u obzir samo efekti izmene atoma kao celine.