

Separated Pair Theory *via* Girardeau's Hamiltonian

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Received April 13, 1971

Girardeau's Hamiltonian is used to develop the separated pair theory. The method does not involve the strong orthogonality condition.

The separated pair theory (SP) is a very promising way to treat the correlation problem in atoms and molecules [1]. The aim of this work is to describe a similar approach with the use of the Hamiltonian proposed by Girardeau [2]. Girardeau has written the wave function as a product of the electron pair functions and his treatment does not involve a strong orthogonality condition normally introduced in the SP theory. The theory as formulated in this paper was obtained from the linearization (Hartree-Fock) of the Girardeau's Hamiltonian. Such an approach was suggested by Büti [3] without giving the detail procedure.

Girardeau has transformed the Hamiltonian for fermions to the form appropriate to describe pairs of fermions:

$$\begin{aligned} H &= H_0 + V, \\ H_0 &= \sum_{\alpha\beta} \langle \alpha | \mathbf{h}_0 | \beta \rangle a_\alpha^+ a_\beta \\ V &= \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | V | \gamma\delta \rangle a_\alpha^+ a_\beta^+ a_\gamma a_\delta \end{aligned} \quad (1)$$

with

$$\begin{aligned} \langle \alpha | \mathbf{h}_0 | \beta \rangle &= \int \varphi_\alpha(1, 2) \left[-A_1 + 2U(r_1) + \frac{1}{r_{12}} \right] \varphi_\beta(1, 2) dV_1 dV_2, \\ \langle \alpha\beta | V | \gamma\delta \rangle &= \int \varphi_\alpha(1, 2) \varphi_\beta(3, 4) \frac{4}{r_{13}} \varphi_\gamma(1, 2) \varphi_\delta(3, 4) dV_1 dV_2 dV_3 dV_4 \end{aligned}$$

and a^+ , a satisfies the boson commutation rules. The wave function has a form:

$$\Phi = \sum_{\alpha, \beta, \dots, \gamma} C(\alpha, \beta, \dots, \gamma) \varphi_\alpha(1, 2) \varphi_\beta(3, 4) \dots \varphi_\gamma(X_{2n-1}, X_{2n}) \quad (2)$$

where $\varphi_\alpha(j, j+1)$ is antisymmetric for exchange $j \rightleftharpoons (j+1)$

$$\varphi_\alpha(j, j+1) = -\varphi_\alpha(j+1, j).$$

Two subsidiary conditions on Φ are:

$$N|\Phi\rangle = N_z|\Phi\rangle, \quad (3)$$

$$I|\Phi\rangle = -\frac{1}{2}N_z(N_z - 1)|\Phi\rangle \quad (4)$$

where

$$N = \sum_{\alpha} a_{\alpha}^{\dagger} a_{\alpha},$$

$$I = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | I | \gamma\delta \rangle a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\gamma} a_{\delta}$$

and

$$\langle \alpha\beta | I | \gamma\delta \rangle = \int \varphi_{\alpha}(1, 2) \varphi_{\beta}(3, 4) \varphi_{\gamma}(3, 2) \varphi_{\delta}(1, 4) dV_1 dV_2 dV_3 dV_4,$$

$N_z = \frac{2n}{2}$ is the number of pairs.

The linearization of the Hamiltonian Eq. (1) can be done in a standard manner:

$$H_{\text{HF}} = \sum_{\alpha\beta} [\langle \alpha | \mathbf{h}_0 | \beta \rangle - \delta_{\alpha\beta} \mu] a_{\alpha}^{\dagger} a_{\beta} + \sum_{\alpha\beta} \langle \alpha | W' | \beta \rangle a_{\alpha}^{\dagger} a_{\beta}$$

where W' is a Hartree-Fock approximation to the potential $V' = V + \lambda I$. From H_{HF} one obtains the usual form of the Hartree-Fock equation [4]:

$$F |\varphi_{\alpha}\rangle = \varepsilon_{\alpha} |\varphi_{\alpha}\rangle \quad (5)$$

where $F = \mathbf{h}_0 - \mu + W$.

The further approach is analogous to the SP theory [1]:

$$|\varphi_{\alpha}\rangle = \sum_{ij} d_{ij}^{\alpha} \psi_i(1) \psi_j(2) = \sum_a D_a^{\alpha} \psi_a(1, 2).$$

The equation for D_a^{α} is

$$\sum_a D_a^{\alpha} [\langle b | F | a \rangle - \varepsilon \delta_{ab}] = 0. \quad (6)$$

The matrix elements $\langle b | F | a \rangle$ are:

$$\langle kl | \mathbf{h}_0 - \mu | ij \rangle = 2\delta_{ki} I_{lj} + V_{klij} - \mu \delta_{ki} \delta_{lj},$$

$$\langle kl | W' | ij \rangle = \sum_{\alpha} \sum_{p,n} \{ 4d_{ip}^{\alpha} d_{kn}^{\alpha} V_{lpnj} + \delta_{ki} T_{pn}^{\alpha} [2\lambda \delta_{pj} \delta_{in} + 4V_{lpjn}] \}$$

and

$$I_{ij} = \int \psi_i(1) \mathbf{H}_0(1) \psi_j(1) dV_1,$$

$$V_{klij} = \int \psi_k(1) \psi_l(2) \frac{1}{r_{12}} \psi_i(1) \psi_j(2) dV_1 dV_2,$$

$$T_{pn}^{\alpha} = \sum_m d_{mp}^{\alpha} d_{mn}^{\alpha},$$

$$\mathbf{h}_0 = \mathbf{H}_0(1) + \mathbf{H}_0(2) + \frac{1}{r_{12}}.$$

The subsidiary conditions Eqs. (3), (4) can be written as

$$\sum_{\gamma \dots \delta} [\langle \alpha \dots \beta | I | \gamma \dots \delta \rangle + \delta_{\alpha\gamma} \delta_{\beta\delta}] c(\gamma \dots \delta) = 0 \quad (7)$$

and

$$\sum_{\alpha \dots \beta}^{\text{occ.}} C^2(\alpha \dots \beta) = \frac{Nz}{2}. \quad (8)$$

The coefficients D are obtained by self-consistent procedure from Eq. (6) for a choosen set μ, λ that obey Eq. (7) and Eq. (8).

The above described procedure was applied to determine the ground state energy of trans-butadiene. The theoretical parameters were taken for ψ_i, ψ_j . The calculation is quite complicated and the calculated C did not obey Eq. (8) exactly (error of 3%). The energy was obtained from the expression:

$$E = \langle \Phi | H - \mu N + \lambda I | \Phi \rangle = E_0 - N_z \mu - \frac{N_z(N_z - 1)}{2} \lambda \quad (9)$$

where

$$E_0 = \langle \Phi | H | \Phi \rangle$$

and

$$|\Phi\rangle = \sum_{\alpha\beta} C(\alpha\beta) \varphi_\alpha(1, 2) \varphi_\beta(3, 4).$$

Through we could not obtain the full self-consistency in the solution we believe that this error does not change the calculated energy too much. The energy calculated from Eq. (9) is by 2.26 eV lower than the Hartree-Fock energy and is slightly lower than the one obtained from SP theory [5]. The procedure with Girardeau treatment of the Hamiltonian thus gives 95.5% of the correlation energy [5].

The calculation can be further extended with the use of $\{\varphi_\gamma(i, i+1), \varphi_\delta(j, j+1) \dots\}$ which are not occupied in the ground state but are known from the solution of Eq. (6). The procedure is thus similar to the well known configuration interaction (CI) method. In a future paper we hope to report such an extension using diagrammatic perturbation method instead of the CI one.

References

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