Department of Physics, IIT Madras

Hartree Fock formalism

PCD_STiAP_P04

1. For a two electron system, spin exchange operator is given by $\hat{V}_{ex} = -\frac{1}{2}K\left(1+4\hat{s}_1 \bullet \hat{s}_2\right)$

   Where K is the exchange integral and $\hat{s}_1$ and $\hat{s}_2$ are spin angular momentum operators of two electrons. This was first introduced by Dirac and has wide applications in Condensed Matter Physics.

   a) Show that $\hat{s}_1 \bullet \hat{s}_2 = \frac{1}{2}\left[\hat{S}^2 - \hat{s}_1^{\,2} - \hat{s}_2^{\,2}\right]$

      Where $\hat{S}$ is total spin operator.

   b) Show that eigenvalues of $\hat{s}_1 \bullet \hat{s}_2$ for triplet $(S=1)$ and singlet $(S=0)$ states are $\frac{1}{4}$ and $-\frac{3}{4}$ respectively.

   c) Find the eigenvalues of V_{ex} for triplet and singlet states.

   d) Show that $V_{\sin glet} - V_{triplet} = 2K.$

   e) Which is the ground state of the system?

2. Prove that the direct integral J and exchange integral K for a N electron atomic system are real and positive.

3. For the ground state of an atom or ion having N electrons,

$$H_1 = \sum_{i=1}^{N} f\left(q_i\right) = \sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i}\right)$$

$$H_2 = \frac{1}{2}\sum_{i,j=1,j\neq i}^{N} V\left(q_i, q_j\right) = \sum_{i>j}\frac{1}{r_{ij}}$$

   Where H_1 is the sum of the N identical one-body hydrogenic Hamiltonian and H_2 is the sum of $\frac{N\left(N-1\right)}{2}$ identical terms which represent the two-body interactions between each pair of electrons and ϕ_a and ϕ_b are Slater determinants,

$$\phi_a\left(q_1, q_2 ......q_N\right) = \frac{1}{N!}\sum_P (-1)^P P u_{\alpha_1}\left(q_1\right) u_{\alpha_2}\left(q_2\right) ....u_{\alpha_N}\left(q_N\right)$$

$$\phi_b\left(q_1, q_2 ......q_N\right) = \frac{1}{N!}\sum_P (-1)^P P u_{\beta_1}\left(q_1\right) u_{\beta_2}\left(q_2\right) ....u_{\beta_N}\left(q_N\right)$$

   where P is the permutation operator.

Prove that:

a) For $\phi_a = \phi_b$,

$$\langle \phi_a | H_1 | \phi_a \rangle = \sum_{i=1}^{N} \langle u_{\alpha_i}(q_i) | f | u_{\alpha_i}(q_i) \rangle$$

$$\langle \phi_a | H_2 | \phi_a \rangle = \frac{1}{2} \sum_{i,j=1}^{N} [\langle u_{\alpha_i}(q_i) u_{\alpha_j}(q_j) | V | u_{\alpha_i}(q_i) u_{\alpha_j}(q_j) \rangle$$

$$- \langle u_{\alpha_j}(q_i) u_{\alpha_i}(q_j) | V | u_{\alpha_i}(q_i) u_{\alpha_j}(q_j) \rangle].$$

b) For $\phi_a \neq \phi_b$

($\beta_k \neq \alpha_k$ and $\beta_i = \alpha_i$ for all $i \neq k$)

$$\langle \phi_b | H_1 | \phi_a \rangle = \langle u_{\beta_k}(q_k) | f | u_{\alpha_k}(q_k) \rangle$$

$$\langle \phi_b | H_2 | \phi_a \rangle = \sum_{i=1}^{N} \langle u_{\alpha_i}(q_i) u_{\beta_k}(q_k) | V | u_{\alpha_i}(q_i) u_{\alpha_k}(q_k) \rangle$$

$$- \langle u_{\beta_k}(q_i) u_{\alpha_i}(q_k) | V | u_{\alpha_i}(q_i) u_{\alpha_k}(q_k) \rangle]$$

c) For $\phi_a \neq \phi_b$

($\beta_k \neq \alpha_k; \beta_k \neq \alpha_l; \beta_l \neq \alpha_l; \beta_l \neq \alpha_k$ and $\beta_i = \alpha_i$ for all $i \neq k, l$

$$\langle \phi_b | H_1 | \phi_a \rangle = 0$$

$$\langle \phi_b | H_2 | \phi_a \rangle = \sum_{i=1}^{N} \langle u_{\beta_k}(q_k) u_{\beta_l}(q_l) | V | u_{\alpha_k}(q_k) u_{\alpha_l}(q_l) \rangle$$

$$- \langle u_{\beta_l}(q_k) u_{\beta_k}(q_l) | V | u_{\alpha_k}(q_k) u_{\alpha_l}(q_l) \rangle.$$

d) For $\phi_a \neq \phi_b$

(Differing in more than 2 sets of q labels.)

$$\langle \phi_b | H_1 | \phi_a \rangle = 0$$

$$\langle \phi_b | H_2 | \phi_a \rangle = 0$$

4. Prove that the matrix λ, made up of Lagrange variational multipliers which constraint the variation in the elements of Hartree-Fock Slater determinants, is self adjoint.

5.

a) Obtain the condition that $\langle H \rangle$, where H is the N-electron Hamiltonian, is an extremum subject to the constraint that the one-electron spin-orbitals in the variational N-electron antisymmetrized wave function are normalized and orthogonal.

b) Express the above condition in a form in which the matrix of the Lagrange variational multipliers is diagonal and demonstrate that this condition is expressed by:

$$f\left(\vec{r}_1\right)u_k\left(\vec{r}_1\right)+[\sum_j\int d\tau_2\frac{u_j^*\left(\vec{r}_2\right)u_j\left(\vec{r}_2\right)}{r_{12}}]u_k\left(\vec{r}_1\right)$$

$$-\sum_j\delta\left(m_{s_k},m_{s_j}\right)[\int d\tau_2\frac{u_j^*\left(\vec{r}_2\right)u_k\left(\vec{r}_2\right)}{r_{12}}]u_j\left(\vec{r}_1\right)$$

$$=-\lambda_{kk}u_k\left(\vec{r}_1\right)$$

$$=\varepsilon_k u_k\left(\vec{r}_1\right)$$

Where $\varepsilon_k=-\lambda_{kk}$

c) Comment on the factor $\delta\left(m_{s_k},m_{s_j}\right)$ in the above equation.

d) Find the function $U_k\left(\vec{r}_1,\vec{r}_2\right)$ such that;

$$\int d\tau_2 U_k\left(\vec{r}_1,\vec{r}_2\right)u_k\left(\vec{r}_2\right)=-\sum_j\delta\left(m_{s_k},m_{s_j}\right)[\int d\tau_2\frac{u_j^*\left(\vec{r}_2\right)u_k\left(\vec{r}_2\right)}{r_{12}}]u_j\left(\vec{r}_1\right)$$

e) Show that the one-electron Hartree-Fock equation is written in a form inclusive of the spin variables such that the spin-orbital $U_k\left(q\right)=\langle q|k\rangle$ has k which represents a set of 4 quantum numbers including spin is given by:

$$[\frac{-\nabla_i^2}{2}+V_{HF}\left(q_i\right)]u_k\left(q_i\right)=\varepsilon_k u_k\left(q_i\right)$$

Where

$$V_{HF}\left(q_i\right)=\frac{-Z}{r_i}+V^c\left(q_i\right)+V^{ex}\left(q_i\right)$$

$$V^c\left(q_i\right)=\sum_{j=1}^{N}\int dq_2\frac{u_j^*\left(q_2\right)u_j\left(q_2\right)}{r_{i2}}$$

$$V^{ex}u_k\left(q_i\right)=-\sum_{j=1}^{N}\int dq_2\frac{u_j^*\left(q_2\right)u_k\left(q_2\right)}{r_{i2}}u_j\left(q_i\right)$$

f) Is the Hartree-Fock equation given above an eigenvalues equation?

g) Can you define the Hartree-Fock potential V_{HF} as a function of a single coordinate (that is, one set of 3 space coordinates and 1 spin coordinate) alone?

6. Determine if the potential U in problem 5(d) is Hermitian.

7.

a) Prove that;

$$-\lambda_{kk}=n_k\langle k|f|k\rangle+n_k\sum_j n_j[\langle kj|V|kj\rangle-\langle jk|V|kj\rangle$$

b) If $-\lambda_{kk}$ is written as ε_k, prove that:

c) $E\left(\phi^{(N)}\right)-E\left(\phi_{n_k=0}^{(N-1)}\right)=\varepsilon_k$

[Ref : T.H. Koopmans Physics **1** **104** (1933)]

d) Write the Slater determinant for ground state $1s^2 2s^2\,{}^1S$ of beryllium.

e) The Hartree-Fock potential is given by:

$$V_{HF} = -\frac{4}{r_i} + V^d_{1s\uparrow} + V^d_{1s\downarrow} + V^d_{2s\uparrow} + V^d_{2s\downarrow} - \left(V^{ex}_{1s\uparrow} + V^{ex}_{1s\downarrow} + V^{ex}_{2s\uparrow} + V^{ex}_{2s\downarrow}\right)$$

Where V^d and V^{ex} are direct and exchange integrals respectively.
Obtain the two coupled integro-differential equation:

$$\left\{-\frac{1}{2}\nabla^2_r - \frac{4}{r} + V^d_{1s}(r) + 2V^d_{2s}(r) - V^{ex}_{2s}(r)\right\}u_{1s}(r) = E_{1s}u_{1s}(r)$$

$$\left\{-\frac{1}{2}\nabla^2_r - \frac{4}{r} + V^d_{2s}(r) + 2V^d_{1s}(r) - V^{ex}_{1s}(r)\right\}u_{2s}(r) = E_{2s}u_{2s}(r)$$

8. Prove that $[H, L] = 0$, where H is the Hamiltonian

$$H = \sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i}\right) + \sum_{i<j=1}^{N}\frac{1}{r_{ij}}$$

And $L = \sum_i L_i$ is the total orbital angular momentum of the electrons.

<u>Useful references</u>:

1. Bethe, H.A and Jackiw R; Intermediate Quantum Mechanics; West-view press (1986).
2. Brandsen aB.H and joachain C.J; Physics of atoms and molecules;Longman Group Limited (1983).
3. Landau L.D. and Lifshitz E.M; Quantum Mechanics Non-Relativistic Theory; Pergamon Oxford (1977)