Department of Physics
IIT-Madras

PCD_STiAP_Self_Assesment_3
20 marks

1. Write down the Hamiltonian for the N electron system. Describe each term in the Hamiltonian. -2 marks

A1. $H^{(N)} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^{\,2} - \frac{Z}{r_i}\right) + \sum_{i<j=1}^{N}\frac{1}{r_{ij}} \qquad m;\hbar = 1$

Kinetic energy term
Potential energy term of each electron in the field of Z nucleus.
Coulomb repulsion between every pair of electrons.

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2. What is the principle followed in Hartree Fock formalism to attain the self consistency? What are the constraints the method is subjected to? -2 marks

A2. The Variational principle is used in Hartree Fock formalism to attain self-consistency. The Constraints are

(i) Normalization of the spin orbitals $\langle u_i | u_j \rangle = 1$ for $j = i$

(ii) The orthogonality $\langle u_i | u_j \rangle = 0$ for $j \neq i$

Where *i, j* stand respectively for the Collective Complete set of good Quantum numbers n, l, m_l, m_s of the i[th] and j[th] occupied single-particle states.

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3. In the given wave function equation of N electron system what is $\hat{A}$ and how it is expressed. Explain the operator. – 3 marks

$\psi^{(N)}_{1,2,\ldots N}(q_1,..,q_N) = \quad \hat{A}\left[u_1(q_1)u_2(q_2)..u_N(q_N)\right]$

$\hat{A}$ is the Antisymmetriser operator expressed as $\frac{1}{\sqrt{N!}}\sum_{P=1}^{N!}(-1)^p P$. $\frac{1}{\sqrt{N!}}$ is the normalization factor. There are $N!$ ways of permuting the N indistinguishable electrons in the N quantum states. For every permutation there will be a sign change which is represented by $(-1)^p$ and since there is N! ways the summation of P going from 1 to N!. The operator takes the direct product of the diagonal element from the Slater Determinant and antisymmetrise it.

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4. Write down the wave function for a two electron system in the form of Slater determinant and explain the terms in each rows and columns. What are the principles included in Slater determinant form.

-3 marks

$\Psi(q_1, q_2) = N\left[u_1(q_1)u_2(q_2) - u_1(q_2)u_2(q_1)\right]$

$u_i(q_j) = \langle j \,|\, i \rangle = \langle \vec{r_j}, \zeta_j \,|\, n_i, l_i, m_{l_i}, m_{s_i} \rangle$

$u_i(q_j) = \langle \vec{r_j} \mid n_i, l_i, m_{l_i} \rangle \langle \zeta_j \mid m_{s_i} \rangle$

$\langle \vec{r_j} \mid n_i, l_i, m_{l_i} \rangle$ is the space part ; $\langle \zeta_j \mid m_{s_i} \rangle$ is the spin part

$$\Psi(q_1, q_2) = N\left[u_1(q_1)u_2(q_2) - u_1(q_2)u_2(q_1)\right]$$

$$= \frac{1}{\sqrt{2}} \begin{vmatrix} u_1(q_1) & u_1(q_2) \\ u_2(q_1) & u_2(q_2) \end{vmatrix}$$

Rows: occupied of single particle states (labelled by a set of 4 quantum numbers) in the many-electron system
Columns: set of (space, spin) coordinates

The principles included in the Slater determinant form are 1) Pauli's exclusion Principle 2) Antisymmetry of the wavefunction

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5. Consider 2-electron wavefunction $\psi(q_1, q_2) = \phi(\vec{r}_1, \vec{r}_2)\chi(\zeta_1, \zeta_2)$ made up as an antisymmetrized product of 1-electron spin-orbitals $\phi_{n_i, l_i, m_{l_i}}(\vec{r}_j)\ \chi_{m_{s_i}}(\zeta_j)$. – 1+2+2 marks
   a. What are the states corresponding to $S = 0$ and $S = 0,1$. How are they represented?
   b. Write the form of the wavefunction for Singlet and Triplet state.
   c. Which state has lower energy? What factor determines the energy of the state?

A5.a. The State corresponding to S=0 is Singlet state and S=0, 1 is Triple state

Consider a two electron system with coordinates q_1 and q_2. If the electrons are interchanged, the wave functions are given by in terms of spatial and spin part,

$$\psi(q_1, q_2) = \phi(\vec{r}_1, \vec{r}_2)\chi(\zeta_1, \zeta_2)$$

$$\psi(q_2, q_1) = -\psi(q_1, q_2) = -\left\{\phi(\vec{r}_1, \vec{r}_2)\chi(\zeta_1, \zeta_2)\right\}$$

$$\psi(q_2, q_1) = \left\{-\phi(\vec{r}_1, \vec{r}_2)\right\}\ \chi(\zeta_1, \zeta_2)$$

$$= \phi(\vec{r}_1, \vec{r}_2)\ \left\{-\chi(\zeta_1, \zeta_2)\right\}$$

Either the spatial part should be antisymmetric corresponding to Triplet state or the spin part should be antisymmetric corresponding to Single state.

b. $\phi(\vec{r}_2, \vec{r}_1) = +\phi(\vec{r}_1, \vec{r}_2) = N\left[\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) + \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right]$ antisymmetric spin part – Singlet state

$\phi(\vec{r}_2, \vec{r}_1) = -\phi(\vec{r}_1, \vec{r}_2) = N\left[\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right]$ antisymmetric spatial part – Triplet state

c. The triplet state has lower energy when compared to Singlet state. In above equation, If r_1 tends to r_2 the triplet state vanishes. For the triplet state to exist the distance between 2 electrons r_{12} should be large so that the columbic repulsion force $1/r_{12}$ reduces. Thus the triplet states have lower energy.

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6. True or false. – 4 marks
   a. Exchange correlations are included in Hartree formalism. – False
   b. Coulomb correlations are included in Hartree Fock formalism. – False
   c. For, exchange term to exist, we should have an overlap between the spatial parts. – True
   d. Exchange correlations are also called as Fermi Dirac statistical correlation. – True

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7. What is the physical significance of Lagrange multipliers – 1 mark

   It represents the ionization energy of that particular orbital from which the electron is removed.
