1. For a two electron system, spin exchange operator is given by

\[ \hat{V}_{ex} = -\frac{1}{2} K (1 + 4 \hat{s}_1 \cdot \hat{s}_2) \]

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 \( \hat{s}_1 \cdot \hat{s}_2 = \frac{1}{2} (\hat{S}^2 - \hat{s}_1^2 - \hat{s}_2^2) \)

Where \( \hat{S} \) is total spin operator.

b) Show that eigenvalues of \( \hat{s}_1 \cdot \hat{s}_2 \) 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 \( V_{singlet} - V_{triplet} = 2K \).

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,

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

\[ H_2 = \frac{1}{2} \sum_{i,j=1, i \neq j}^{N} V(q_i, q_j) = \sum_{i,j}^{N} \frac{1}{r_{ij}} \]

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

\[ \phi_a (q_1, q_2, \ldots, q_N) = \frac{1}{N!} \sum_{p} (-1)^p P u_{\alpha_1} (q_1) u_{\alpha_2} (q_2) \ldots u_{\alpha_N} (q_N) \]

\[ \phi_b (q_1, q_2, \ldots, q_N) = \frac{1}{N!} \sum_{p} (-1)^p P u_{\beta_1} (q_1) u_{\beta_2} (q_2) \ldots u_{\beta_N} (q_N) \]

where \( P \) is the permutation operator.
Prove that:

a) For \( \phi_a = \phi_b \),
\[
    \langle \phi_a | H_1 | \phi_a \rangle = \sum_{i=1}^{N} \langle u_{\alpha_i}(q_i) | f | u_{\alpha_i}(q_i) \rangle
\]
\[
    \langle \phi_a | H_2 | \phi_a \rangle = \frac{1}{2} \sum_{i,j=1}^{N} \left[ \langle u_{\alpha_i}(q_i) u_{\alpha_i}(q_j) | V | u_{\alpha_i}(q_i) u_{\alpha_i}(q_j) \rangle \right.
    \left. - \langle u_{\alpha_j}(q_j) u_{\alpha_j}(q_j) | V | u_{\alpha_j}(q_j) u_{\alpha_j}(q_j) \rangle \right].
\]

b) For \( \phi_a \neq \phi_b \)
(\( \beta_k \neq \alpha_k \) and \( \beta_i = \alpha_i \) for all \( i \neq k \))
\[
    \langle \phi_b | H_1 | \phi_a \rangle = \langle u_{\beta_k}(q_k) | f | u_{\alpha_i}(q_i) \rangle
\]
\[
    \langle \phi_b | H_2 | \phi_a \rangle = \sum_{i=1}^{N} \langle u_{\alpha_i}(q_i) u_{\beta_k}(q_k) | V | u_{\alpha_i}(q_i) u_{\alpha_i}(q_i) \rangle
    \left. - \langle u_{\beta_k}(q_k) u_{\beta_k}(q_k) | V | u_{\alpha_i}(q_i) u_{\alpha_i}(q_i) \rangle \right].
\]

c) For \( \phi_a \neq \phi_b \)
(\( \beta_k \neq \alpha_k \); \( \beta_k \neq \alpha_i \); \( \beta_i \neq \alpha_i \) and \( \beta_i = \alpha_i \) for all \( i \neq k, l \)
\[
    \langle \phi_b | H_1 | \phi_a \rangle = 0
\]
\[
    \langle \phi_b | H_2 | \phi_a \rangle = \sum_{i=1}^{N} \langle u_{\beta_k}(q_k) u_{\beta_k}(q_i) | V | u_{\alpha_i}(q_i) u_{\alpha_i}(q_i) \rangle
    \left. - \langle u_{\beta_k}(q_k) u_{\beta_k}(q_k) | V | u_{\alpha_i}(q_i) u_{\alpha_i}(q_i) \rangle \right].
\]

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 \( \lambda \), 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:
\[
f(\vec{r}_i)u_k(\vec{r}_i) + \left[ \sum_j \int d\tau_2 \frac{u_j^*(\vec{r}_j)u_j(\vec{r}_j)}{r_{12}} \right]u_k(\vec{r}_i) - \sum_j \delta(m_{k'}, m_{j'}) \left[ \int d\tau_2 \frac{u_j^*(\vec{r}_j)u_k(\vec{r}_j)}{r_{12}} \right]u_j(\vec{r}_i)
\]

\[= -\lambda_{kk} u_k(\vec{r}_i)
\]

\[= \varepsilon_k u_k(\vec{r}_i)
\]

Where \( \varepsilon_k = -\lambda_{kk} \)

c) Comment on the factor \( \delta(m_{k'}, m_{j'}) \) in the above equation.

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

\[
\int d\tau_2 U_k(\vec{r}_1, \vec{r}_2) u_k(\vec{r}_2) = -\sum_j \delta(m_{k'}, m_{j'}) \left[ \int d\tau_2 \frac{u_j^*(\vec{r}_j)u_k(\vec{r}_j)}{r_{12}} \right]u_j(\vec{r}_i)
\]

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

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

Where

\[ V_{HF}(q_i) = -\frac{Z}{r_i} + V^c(q_i) + V^{as}(q_i) \]

\[ V^c(q_i) = \sum_{j=1}^{N} \int dq_2 \frac{u_j^*(q_2)u_j(q_2)}{r_{12}} \]

\[ V^{as} u_k(q_i) = -\sum_{j=1}^{N} \int dq_2 \frac{u_j^*(q_2)u_k(q_2)}{r_{12}}u_j(q_i) \]

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;

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

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

c) \( E(\phi^{(N)}) - E(\phi_{a=0}^{(N-1)}) = \varepsilon_k \)

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

d) Write the Slater determinant for ground state 1s^2 2s^1 S of beryllium.
e) The Hartree-Fock potential is given by:
\[
V_{HF} = -\frac{4}{r_i} + V_{1s1\uparrow}^d + V_{1s1\downarrow}^d + V_{2s1\uparrow}^d + V_{2s1\downarrow}^d - \left( V_{1s1\uparrow}^{ex} + V_{1s1\downarrow}^{ex} + V_{2s1\uparrow}^{ex} + V_{2s1\downarrow}^{ex} \right)
\]
Where \( V^d \) and \( V^{ex} \) are direct and exchange integrals respectively.

Obtain the two coupled integro-differential equation:
\[
\begin{align*}
\left\{-\frac{1}{2} \nabla_r^2 - \frac{4}{r} + V_{1s1\uparrow}^d(r) + 2V_{2s1\uparrow}^d(r) - V_{1s1\downarrow}^{ex}(r)\right\}u_{1s}(r) &= E_{1s}u_{1s}(r) \\
\left\{-\frac{1}{2} \nabla_r^2 - \frac{4}{r} + V_{2s1\uparrow}^d(r) + 2V_{1s1\uparrow}^d(r) - V_{2s1\downarrow}^{ex}(r)\right\}u_{2s}(r) &= E_{2s}u_{2s}(r)
\end{align*}
\]

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.

Useful references: