Problem 5

An energy difference between the spin-singlet (S=0) state and the spin-triplet (S=1) state is given by

$$E(\uparrow\downarrow + \downarrow\uparrow) - E(\uparrow\uparrow, \leftarrow\leftarrow, \downarrow\downarrow) = 2J$$

on the basis of the atomic orbital method. Here, $2J = -4\underline{S}\,t + 2\,J'$.

$$J' = \iint \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2)\left(+ \frac{e^2}{r_{12}} \right)dv_1 dv_1$$

and $\underline{S}$ is the overlap integral.

This energy difference is described by the following effective Hamiltonian using the respective spin-operators S_a and S_b at the A and B sites.

$$H_{eff} = -2J\,s_a \cdot s_b$$

Noting that $S = s_a + s_b$ and $S(S+1) = S^2 = s_a{}^2 + s_b{}^2 + 2\,s_a \cdot s_b$, when $S=0$ and $S=1$, show that $s_a \cdot s_b = -3/4$ and $s_a \cdot s_b = 1/4$,

respectively, and the energy difference between $S=0$ and $S=1$ is given by $2J$. *The above Hamiltonian is known as the Heisenberg Hamiltonian is written by $H = -2J\Sigma_{ij}\,S_i \cdot S_j$*

Problem 6

We next consider a more realistic solution of the electronic state in H_2 beyond either Heitler—London or Molecular Orbital approximations, by assuming $H(1,2) = h(1) + h(2) + V(1,2)$ as a Hamiltonian for H_2 where $h(1) + h(2)$ is the sum of one-electron Hamiltonian and $V(1,2)$ is the Coulomb repulsive interaction between electrons. Several integrals are defined as the follows;

$$\varepsilon \equiv \int \phi_a(1)h(1)\phi_a(1)dv_1 = \int \phi_b(1)h(1)\phi_b(1)dv_1$$

$$t \equiv \int \phi_a(1)h(1)\phi_b(1)dv_1 = \int \phi_b(1)h(1)\phi_a(1)dv_1$$

$$U_0 \equiv \int \phi_a(1)^2\phi_a(2)^2 V(1,2)dv_1 dv_2 = \int \phi_b(1)^1\phi_b(2)^2 V(1,2)dv_1 dv_2$$

$$U_1 \equiv \int \phi_a(1)^2\phi_b(2)^2 V(1,2)dv_1 dv_2 = \int \phi_b(1)^2\phi_a(2)^2 V(1,2)dv_1 dv_2$$

$$J' \equiv \int \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2) V(1,2)dv_1 dv_2$$

Solve the next problems.

(6-1) The trial wave functions of Molecular Orbital and Heitler-London (HL) with spin-singlet and HL with spin-triplet are given by

$$\Phi_S = \phi_1(1)\phi_1(2)$$

$$\Phi_{HL} = \frac{\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)}{\sqrt{2}}$$

$$\Phi_T = \frac{\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)}{\sqrt{2}}$$

Show the respective expected eigen energies are given as follows;

$$E_S = 2(\varepsilon + t) + \frac{1}{2}U_0 + \frac{1}{2}U_1 + J'$$

$$E_{HL} = 2\varepsilon + U_1 + J'$$

$$E_T = 2\varepsilon + U_1 - J'$$

(6-2) In order to improve the HL wave function;

$$\Phi_{HL} = \frac{1}{\sqrt{2(1+S^2)}}[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)]$$

We incorporate the following states, using $\phi_a(1)\,\phi_a(2)$ and $\phi_b(1)\,\phi_b(2)$

$$\Phi' = \frac{1}{\sqrt{2}}[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)]$$

Then, the improved trial wave function is expressed by $\Phi = c_1\Phi_{HL} + c_2\Phi'$.

Show how to get the following relation and solve an eigen energy for this state

$$\begin{vmatrix} 2\varepsilon + U_1 + J' - E & 2t \\ 2t & 2\varepsilon + U_0 + J' - E \end{vmatrix} = 0$$

If $U_0 - U_1 >> |t|$ is valid for Mott insulator, show that the eigen energy is given as the follow;

$$E_{HL} = 2\varepsilon + U_1 + J' - \frac{4t^2}{U_0 - U_1}$$