Problem 1

Consider the electronic state of hydorgen molecule ion (H_2^+). The Hamiltonian [$\mathcal{H}(H_2^+)$] is given by,

$$\mathcal{H}(H_2^+) = \frac{-\hbar^2}{2m}\Delta - \frac{e^2}{|\mathbf{r}-\mathbf{R_a}|} - \frac{e^2}{|\mathbf{r}-\mathbf{R_b}|}$$

where $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the differential operetor of kinetic energy and $U_0 = -\frac{e^2}{\mathbf{r}-\mathbf{R_a}} - \frac{e^2}{\mathbf{r}-\mathbf{R_b}}$ is the Coulomb attractive potential energy between electron and nuclei. $\mathbf{r}$, $\mathbf{R_a}$, $\mathbf{R_b}$ are the position vectors at electron, and neclear A and B, respectively. e and m is the charge and mass of electron. $h(\hbar = h/2\pi)$ is the Plank's constant. When E_{1s} is the eigen energy for the 1s state of hydrogen atom and $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ are their eigen function for the nuclear A and B, respectively. Anser the following problems..
The transfer integral (t) and the Coulomb integral are respectively defined by

$$t = \int \psi_a(\mathbf{r})\frac{e^2}{|\mathbf{r}-\mathbf{R_a}|}\psi_b(\mathbf{r})d\mathbf{r} = \int \psi_b(\mathbf{r})\frac{e^2}{|\mathbf{r}-\mathbf{R_b}|}\psi_a(\mathbf{r})d\mathbf{r}$$

$$u = \int |\psi_a(\mathbf{r})|^2\frac{e^2}{|\mathbf{r}-\mathbf{R_b}|}d\mathbf{r} = \int |\psi_b(\mathbf{r})|^2\frac{e^2}{|\mathbf{r}-\mathbf{R_a}|}d\mathbf{r}$$

Then, the overlap integral (S) of the 1s wave function for the A and B nuclear is also defiend by $S = \int \psi_a(\mathbf{r})\psi_b(\mathbf{r})d\mathbf{r}$.

[**1**] Write down the following matrix elements of $\mathcal{H}(H_2^+)$, $<\psi_a(\mathbf{r})|\mathcal{H}(H_2^+)|\psi_a(\mathbf{r})>$, $<\psi_a(\mathbf{r})|\mathcal{H}(H_2^+)|\psi_b(\mathbf{r})>$, $<\psi_b(\mathbf{r})|\mathcal{H}(H_2^+)|\psi_a(\mathbf{r})>$, $<\psi_b(\mathbf{r})|\mathcal{H}(H_2^+)|\psi_b(\mathbf{r})>$ in terms of the basic functions of $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ and express them, using E_{1s}, t, u, S.

[**2**] Consider the electroninc state of H_2^+ by means of the molecular orbital method. Assume that it is given by

$$\Psi(\mathbf{r}) = c_a\psi_a(\mathbf{r}) + c_b\psi_b(\mathbf{r}),$$

When this Shorendinger equation is expressed by

$$\mathcal{H}(H_2^+)\Psi = E\Psi$$

Write down the eigen energy E_1, E_2, using E_{1s}, t, u, S and expess the corresponding eigen function, $\Psi_1(\mathbf{r})$ and $\Psi_2(\mathbf{r})$ in terms of $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$, S. Here $E_1 < E_2$.

~~[**3**] When one more electron is added to H_2^+, write down the Hamiltonian of hydrogen molecule.~~

Problem 2

Consider the electronic state of hydorgen molecule ion (H_2^+). The Hamiltonian [$\mathcal{H}(H_2^+)$] is given by,

$$\mathcal{H}(H_2^+) = \frac{-\hbar^2}{2m}\Delta - \frac{e^2}{|\mathbf{r}-\mathbf{R_a}|} - \frac{e^2}{|\mathbf{r}-\mathbf{R_b}|}$$

where $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the differential operetor of kinetic energy and $U_0 = -\frac{e^2}{\mathbf{r}-\mathbf{R_a}} - \frac{e^2}{\mathbf{r}-\mathbf{R_b}}$ is the Coulomb attractive potential energy between electron and nuclei. $\mathbf{r}$, $\mathbf{R_a}$, $\mathbf{R_b}$ are the position vectors at electron, and neclear A and B, respectively. e and m is the charge and mass of electron. $h(\hbar = h/2\pi)$ is the Plank's constant. When E_{1s} is the eigen energy for the 1s state of hydrogen atom and $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ are their eigen function for the nuclear A and B, respectively. Anser the following problems..
The transfer integral (t) and the Coulomb integral are respectively defined by

$$t = \int \psi_a(\mathbf{r})\frac{e^2}{|\mathbf{r}-\mathbf{R_a}|}\psi_b(\mathbf{r})d\mathbf{r} = \int \psi_b(\mathbf{r})\frac{e^2}{|\mathbf{r}-\mathbf{R_b}|}\psi_a(\mathbf{r})d\mathbf{r}$$

$$u = \int |\psi_a(\mathbf{r})|^2\frac{e^2}{|\mathbf{r}-\mathbf{R_b}|}d\mathbf{r} = \int |\psi_b(\mathbf{r})|^2\frac{e^2}{|\mathbf{r}-\mathbf{R_a}|}d\mathbf{r}$$

Then, the overlap integral (S) of the 1s wave function for the A and B nuclear is also defiend by $S = \int \psi_a(\mathbf{r})\psi_b(\mathbf{r})d\mathbf{r}$.

[**1**] Consider the spin state for hydrogen molecule H_2. Answer the size of total number of spin, $\mathbf{S} = \mathbf{s_1} + \mathbf{s_2}$.

[**2**] Write down all possibe electronic states $\Psi_{H_2}(\mathbf{r_1}, \mathbf{r_2})$ for hydrogen molecule H_2 corresponding to each the spin state obtained in [**1**] as functions of $\Psi_1(\mathbf{r_1})$, $\Psi_1(\mathbf{r_2})$, $\Psi_2(\mathbf{r_1})$ and $\Psi_2(\mathbf{r_2})$ and describe why it is so wirtten.

[**3**] Answer the eigen wave function $\Psi_{H_2}(\mathbf{r_1}, \mathbf{r_2})_g$ and eigen energy E_g at the ground state as functions of E_{1s}, t, u, S, U, K, J. Here all the integrals on the Coulomb repulsive interaction are defined as follows;

$$U = \int\int |\psi_a(\mathbf{r_1})|^2\frac{e^2}{|\mathbf{r_{12}}|}|\psi_a(\mathbf{r_2})|^2 d\mathbf{r_1}d\mathbf{r_2}$$

$$K = \int\int |\psi_a(\mathbf{r_1})|^2\frac{e^2}{|\mathbf{r_{12}}|}|\psi_b(\mathbf{r_2})|^2 d\mathbf{r_1}d\mathbf{r_2}$$

$$J = \int\int \psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2})\frac{e^2}{|\mathbf{r_{12}}|}\psi_b(\mathbf{r_1})\psi_a(\mathbf{r_2}) d\mathbf{r_1}d\mathbf{r_2}$$

, then all other integrals are ignored. Note $\mathbf{r_{12}} = \mathbf{r_1} - \mathbf{r_2}$.

Problem 3

$$\Phi_{\mathrm{HL}} = \frac{1}{\sqrt{2(1+S^2)}}[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)]$$

Show that the expectation value of eigen energy

$$<\Phi_{HL}|H=(H'_1 + H'_2 + e^2/r_{12})|\Phi_{HL}>=E_{HL}$$

$$E_{\mathrm{HL}} = \frac{1}{1+S^2}\iint \psi_a(1)\psi_b(2)H[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)]dv_1dv_2$$

is given by

$$E_{\mathrm{HL}} = 2E_{1s} + \frac{Q}{1+S^2} + \frac{J}{1+S^2}$$

where

$$Q = \iint \psi_a(1)^2 \psi_b(2)^2\left(-\frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{R}_b|} - \frac{e^2}{|\boldsymbol{r}_2 - \boldsymbol{R}_a|} + \frac{e^2}{r_{12}}\right)dv_1dv_2$$

$$J = \iint \psi_a(1)\psi_b(1)\psi_a(2)\psi_b(2)\left(-\frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{R}_b|} - \frac{e^2}{|\boldsymbol{r}_2 - \boldsymbol{R}_a|} + \frac{e^2}{r_{12}}\right)dv_1dv_2$$

Problem 4

We define the following integrals

$$U = \int\int |\psi_a(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_{12}|} |\psi_a(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$$

$$K = \int\int |\psi_a(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_{12}|} |\psi_b(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$$

$$J' = \int\int \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_{12}|} \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Other integrals are neglected. $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ とする。

Show that

$$E_{\mathrm{HL}} = 2E_{1s} + \frac{Q}{1+S^2} + \frac{J}{1+S^2} = 2E_{1s} - 2u - 2\underline{S}t + K + J'$$

$$Q = \iint \psi_a(1)^2 \psi_b(2)^2\left(-\frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{R}_b|} - \frac{e^2}{|\boldsymbol{r}_2 - \boldsymbol{R}_a|} + \frac{e^2}{r_{12}}\right)dv_1dv_2 = -2u + K$$

$$J = \iint \psi_a(1)\psi_b(1)\psi_a(2)\psi_b(2)\left(-\frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{R}_b|} - \frac{e^2}{|\boldsymbol{r}_2 - \boldsymbol{R}_a|} + \frac{e^2}{r_{12}}\right)dv_1dv_2 = -2\underline{S}t + J'$$

And then $E_g - E_{HL} = ?$