PH 585
AMO

Solutions of HW # 6

Problem # 1

(a) Li $\Rightarrow$ 3 electrons $\Rightarrow 1s^2 2s$

$$\underset{\text{a.u.}}{H} = \sum_{i=1}^{3} \left[-\frac{1}{2} \vec{\nabla}_{r_i}^{2} - \frac{\overset{Z}{3}}{r_i} \right] + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

(b)
$$\Psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} u_{100,\uparrow}(1) & u_{100,\uparrow}(2) & u_{100,\uparrow}(3) \\ u_{100,\downarrow}(1) & u_{100,\downarrow}(2) & u_{100,\downarrow}(3) \\ u_{200,\uparrow}(1) & u_{200,\uparrow}(2) & u_{200,\uparrow}(3) \end{vmatrix}$$

(c)
$$E^{(0)} = 2\underbrace{E_{1s}}_{=-E_I Z^2} + \underbrace{E_{2s}}_{=-E_I \frac{Z^2}{4}} = -E_I\left(2\cdot 9 + \frac{9}{4}\right) = -\frac{81}{4} \overset{13.6\,\text{eV}}{E_I}$$

exclude $\sum_{i<j} \frac{1}{r_{ij}}$ terms (although not a good approx.!)

(d) Need $\langle \Psi | \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} | \Psi \rangle$

$$\frac{1}{6}\left[u_{100,\uparrow}(1)\, u_{100,\downarrow}(2)\, u_{200,\uparrow}(3) + u_{200,\uparrow}(1)\, u_{100,\uparrow}(2)\, u_{100,\downarrow}(3) + u_{100,\downarrow}(1)\, u_{200,\uparrow}(2)\, u_{100,\uparrow}(3) - u_{100,\uparrow}(1)\, u_{200,\uparrow}(2)\, u_{100,\downarrow}(3) - \right.$$

(2)

$- u_{100,\downarrow}(1)\, u_{100,\uparrow}(2)\, u_{200,\uparrow}(3) -$

$- u_{200,\uparrow}(1)\, u_{100,\downarrow}(2)\, u_{100,\uparrow}(3) \Big]$

Direct integrals;

$$J(\underset{1s}{100}, \underset{2s}{200}) = \langle u_{100}(1)\, u_{200}(2) | \frac{1}{r_{12}} | u_{100}(1)\, u_{200}(2) \rangle =$$

$$= \int |u_{100}(\vec{r}_1)|^2 \frac{1}{r_{12}} |u_{200}(\vec{r}_2)|^2 d\vec{r}_1\, d\vec{r}_2$$

$$J(\underset{1s}{100}, \underset{1s}{100}) = \int |u_{100}(\vec{r}_1)|^2 \frac{1}{r_{12}} |u_{100}(\vec{r}_2)|^2 d\vec{r}_1\, d\vec{r}_2$$

Exchange integral;

$$K(\underset{1s}{100}, \underset{2s}{200}) = \int u^*_{100}(\vec{r}_1)\, u^*_{200}(\vec{r}_2) \frac{1}{r_{12}} u_{100}(\vec{r}_2) \cdot$$

$$\cdot\, u_{200}(\vec{r}_1)\, d\vec{r}_1\, d\vec{r}_2$$

Note that all other integrals can be expressed as the ones above.

(The actual $E^{(1)} = 2J(1s, 2s) + J(1s, 1s) - K(1s, 2s)$)