Problem set 1.

1. Atomic units

$$\left\{-\frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}\right\}\psi = E\psi$$

unit of length is Bohr $= a_0 = \dfrac{4\pi\epsilon_0\hbar^2}{m_e e^2}$

Insert $\nabla_r^2 \rightarrow \dfrac{1}{a_0^2}\nabla_Y^2$, $\quad r = a_0 Y \quad$ so that

$$\left\{\frac{-\hbar^2}{2m_e a_0^2}\nabla_Y^2 - \frac{e^2}{4\pi\epsilon_0 a_0}\frac{1}{Y}\right\} = H$$

but $\dfrac{\hbar^2}{m_e a_0^2} = \dfrac{\cancel{\hbar^2}\ \cancel{m_e} e^2}{\cancel{m_e} a_0(4\pi\epsilon_0 \cancel{\hbar^2})} = \dfrac{e^2}{4\pi\epsilon_0 a_0}$ so

$$\left(-\frac{1}{2}\nabla_Y^2 - \frac{1}{Y}\right)\psi = \underbrace{\frac{H\psi}{e^2/4\pi\epsilon_0 a}} = \hat{H}\psi$$

Hartree unit, energy

Time : $\quad E = h\nu$, $\quad \nu = \dfrac{1}{\text{time}} = \dfrac{E}{h} \Rightarrow \text{time} = \dfrac{h}{E} = \dfrac{2\pi\hbar}{\text{Hartree}}$

traditionally, time is $\dfrac{\hbar}{\text{Hartree}}$.

or $\quad -i\hbar\dfrac{\partial}{\partial t}\psi = H\psi \Rightarrow \dfrac{1}{\text{time}}\hbar = \text{Hartree}$

$\therefore$ time $= \hbar/\text{Hartree}$

2. Jacobian for spherical coords

$$dr\,d\theta\,d\phi\; J = dx\,dy\,dz$$

$$J = \begin{vmatrix} \left(\frac{\partial x}{\partial r}\right)_{\theta,\phi} & \left(\frac{\partial y}{\partial r}\right)_{\theta,\phi} & \left(\frac{\partial z}{\partial r}\right)_{\theta,\phi} \\ \left(\frac{\partial x}{\partial \theta}\right)_{r,\phi} & \left(\frac{\partial y}{\partial \theta}\right)_{r,\phi} & \left(\frac{\partial z}{\partial \theta}\right)_{r,\phi} \\ \left(\frac{\partial x}{\partial \phi}\right)_{r,\theta} & \left(\frac{\partial y}{\partial \phi}\right)_{r,\theta} & \left(\frac{\partial z}{\partial \phi}\right)_{r,\theta} \end{vmatrix}$$

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

$$J = \begin{vmatrix} \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \\ r\cos\theta\cos\phi & r\cos\theta\sin\phi & -r\sin\theta \\ -r\sin\theta\sin\phi & r\sin\theta\cos\phi & 0 \end{vmatrix} = \left[r^2\cos^2\theta\sin\theta\cos^2\phi + \left[r^2\sin^3\theta\sin^2\phi \right] + r^2\cos^2\theta\sin\theta\sin^2\phi + r^2\sin^3\theta\cos^2\phi \right]$$

$$= r^2\sin^3\theta + r^2\cos^2\theta\sin\theta = r^2\sin\theta$$

$$J = r^2\sin\theta$$

$$dx\,dy\,dz = r^2 dr\,\sin\theta\,d\theta\,d\phi$$

3. Polarizability of the H-atom

$\psi = C_a\, 1s + C_b\, 2P_z$

find the appropriate C_a + C_b in the presence of a static electric field.

$$H = \underbrace{H_0}_{H\text{-atom}} - \mu \cdot E \qquad \mu = e\hat{r}\,, \quad E = E_z \hat{z}$$

$$H = H_0 - (eE_z) z$$

$$\left.\begin{array}{l} \langle 1s | H | 1s \rangle = -1/2 \\ \langle 2P_z | H | 2P_z \rangle = -1/8 \end{array}\right\} = -\frac{1}{2n^2}$$

$$\langle 1s | 1s \rangle = 1$$

$$\langle 1s | 2P_z \rangle = 0$$

$$\langle 2P_z | 2P_z \rangle = 1$$

The secular determinant is

$$\begin{vmatrix} -1/2 - E & H_{ab} \\ H_{ab} & -\frac{1}{8} - E \end{vmatrix} = 0$$

$$H_{ab} = \langle 1s | (-F z) | 2P_z \rangle$$

$$1s = \frac{1}{\sqrt{\pi}} \exp(-r)\,, \qquad 2P_z = \frac{1}{\sqrt{32\pi}}\, r e^{-r/2} \cos\theta$$

$$H_{ab} = -F \cdot \frac{128\sqrt{2}}{243}$$

roots

$$\left(+\frac{1}{2}+E\right)\left(\frac{1}{8}+E\right)-H_{ab}^2=0$$

$$E^2+\frac{5}{8}E+\frac{1}{16}-H_{ab}^2=0$$

$$2E=-\frac{5}{8}\pm\sqrt{\frac{25}{64}-4\left[\frac{1}{16}-H_{ab}^2\right]}$$

$$=-\frac{5}{8}\pm\sqrt{\frac{9}{64}+4H_{ab}^2}$$

$$2E=-\frac{5}{8}\pm\frac{3}{8}\sqrt{1+\frac{256}{9}H_{ab}^2}$$

$$E_{1s}\Rightarrow\left(-\frac{5}{8}-\frac{3}{8}\sqrt{1+\frac{256}{9}H_{ab}^2}\right)/2 \rightarrow -\frac{1}{2} \text{ when } H_{ab}=0$$

Next, determine C_a + C_b corresponding to this energy

$$\left(-\frac{1}{2}-E\right)C_a+H_{ab}C_b=0$$

or on substituting E, we obtain

$$\left\{-\frac{1}{2}+\frac{5}{16}+\frac{3}{16}\sqrt{1+\frac{256}{9}H_{ab}^2}\right\}C_a+H_{ab}C_b=0$$

$$\left\{\underbrace{\frac{3}{16}\sqrt{1+\frac{256}{9}H_{ab}^2}}_{\text{expand}}-\frac{3}{16}\right\}C_a+H_{ab}C_b=0$$

$$\left\{\frac{3}{16}\left(1+\frac{128}{9}H_{ab}^2\right)-\frac{3}{16}\right\}C_a+H_{ab}C_b=0$$

$$\frac{3}{16}\cdot\frac{128}{9} H_{ab}^2 C_a + H_{ab} C_b = 0$$

or $$\frac{8}{3} H_{ab}^2 C_a + H_{ab} C_b = 0$$ or

$$C_b = -\frac{8}{3} H_{ab} C_a$$

and $$\psi = C_a\left\{ |1s\rangle - \frac{8}{3} H_{ab} |2P_z\rangle \right\}$$

if we normalize we obtain terms quadratic in H_{ab} which we drop.

Now calculate $\langle \mu_z \rangle = \langle ez \rangle = \langle \psi^*(r) | z | \psi(r) \rangle$

drop the e

From parity considerations

$$\langle \mu_z \rangle = -\frac{16}{3} H_{ab} \underbrace{\langle 1s | z | 2P_z \rangle}_{\frac{128}{243}\sqrt{2}}, \quad \text{but } H_{ab} = -F\left(\frac{128}{243}\right)\sqrt{2}$$

$$\langle \mu_z \rangle = \frac{16}{3}\left(\frac{128\sqrt{2}}{243}\right)^2 F = 2.95 F = 2.95 E$$

$$\alpha = 2.95\, a_0^3 = 2.95 \times (0.529\,\text{Å})^3 = 0.44\,\text{Å}^3$$

For He, $\alpha = 0.205\,\text{Å}^3$
Ne, $\alpha = 0.395\,\text{Å}^3$

Our value seems a little large.