Assignment 8

1) H_2 has 2 nuclei and 2 electrons
$\{H_A, H_B\}$ $\{e_1, e_2\}$

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2M_H}\nabla_A^2}_{\text{kinetic energy of nucleus A}} \underbrace{-\frac{\hbar^2}{2M_H}\nabla_B^2}_{\text{kinetic energy of nucleus B}} \underbrace{-\frac{\hbar^2}{2m_e}\nabla_1^2}_{\text{kinetic energy of electron 1}} \underbrace{-\frac{\hbar^2}{2m_e}\nabla_2^2}_{\text{kinetic energy of electron 2}} + \underbrace{\frac{1}{|\vec{R}_A-\vec{R}_B|}}_{\text{repulsion between nuclei A and B}} + \underbrace{\frac{1}{|\vec{r}_1-\vec{r}_2|}}_{\text{repulsion between electrons 1 and 2}} - \underbrace{\frac{1}{|\vec{r}_1-\vec{R}_A|}}_{\text{attraction between e}^-\text{1 and nucleus A}} - \underbrace{\frac{1}{|\vec{r}_1-\vec{R}_B|}}_{\text{attraction between e}^-\text{1 and nucleus B}} - \underbrace{\frac{1}{|\vec{r}_2-\vec{R}_A|}}_{\text{attraction between e}^-\text{2 and nucleus A}} - \underbrace{\frac{1}{|\vec{r}_2-\vec{R}_B|}}_{\text{attraction between e}^-\text{2 and nucleus B}}$$

2) $\hat{H} = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)$

a) r is constant, so derivatives with respect to r are zero.

$\hat{H} = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$

$\hat{H}\Phi\{\phi\} = -\frac{\hbar^2}{2m_e r^2}\frac{\partial^2}{\partial \phi^2}\left[Ae^{im\phi} + Be^{-im\phi}\right] = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\left[(im)^2 Ae^{im\phi} + (-im)^2 Be^{im\phi}\right]$

$\hat{H}\Phi(\phi) = \frac{\hbar^2}{2m_e r^2}[-m^2][Ae^{im\phi} + Be^{-im\phi}]$

$\hat{H}\Phi\{\phi\} = \underbrace{\frac{\hbar^2 m^2}{2m_e r^2}}\Phi\{\phi\}$

yes, Φ is an eigenfunction of $\hat{H}$ with eigenvalue $\frac{\hbar^2 m^2}{2m_e r^2}$

b) $\hat{H}\Phi\{\phi\} = \frac{\hbar^2 m^2}{2m_e r^2}\Phi\{\phi\} = E\Phi\{\phi\}$

$E = \frac{\hbar^2 m^2}{2m_e r^2}$ $\rightarrow$ m can take any value

c) $\Phi\{\phi + 2\pi\} = \Phi\{\phi\}$

$Ae^{im(\phi+2\pi)} + Be^{-im(\phi+2\pi)} = Ae^{im\phi} + Be^{-im\phi}$

$(Ae^{im\phi})\underbrace{(e^{i2\pi m})} + (Be^{-im\phi})\underbrace{(e^{-i2\pi m})} = Ae^{im\phi} + Be^{-im\phi}$

must be 1, so that the equality is valid.

$e^{i2\pi m} = 1$ $\quad e^{-i2\pi m} = 1$

$\underbrace{\cos 2\pi m}_{=1} + \underbrace{i\sin 2\pi m}_{=0i} = 1 + 0i$ $\quad \underbrace{\cos 2\pi m}_{=1} - \underbrace{i\sin 2\pi m}_{=0i} = 1 + 0i$

m must be $0, \pm 1, \pm 2, \pm 3, \ldots$

d) yes there is degeneracy for all the levels except the lowest $\{m = 0\}$

e) $E = 0$

3) $P_{n=1\to n=2} = \left|\int_0^a \sqrt{\frac{2}{a}}\sin\left\{\frac{2\pi x}{a}\right\}(-ex)\sqrt{\frac{2}{a}}\sin\left\{\frac{\pi x}{a}\right\}dx\right|^2 = \left|\frac{2}{a}(-e)\int_0^a x\left[\frac{1}{2}\cos\left\{\frac{\pi x}{a}\right\} - \frac{1}{2}\cos\left\{\frac{3\pi x}{a}\right\}\right]dx\right|^2$

$= \left|-\frac{e}{a}\int_0^a x\cos\left(\frac{\pi x}{a}\right) - x\cos\left(\frac{3\pi x}{a}\right)dx\right|^2 = \left|-\frac{e}{a}\left[\left(\frac{ax}{\pi}\right)\sin\left\{\frac{\pi x}{a}\right\}\Big|_0^a - \int_0^a\left(\frac{a}{\pi}\right)\sin\left\{\frac{\pi x}{a}\right\}dx - \left(\frac{ax}{3\pi}\right)\sin\left\{\frac{3\pi x}{a}\right\}\Big|_0^a + \int_0^a\left(\frac{a}{3\pi}\right)\sin\left\{\frac{3\pi x}{a}\right\}dx\right]\right|^2$

$u = x$ $\quad dv = \cos\left\{\frac{\pi x}{a}\right\}dx$
$du = dx$ $\quad v = \sin\left\{\frac{\pi x}{a}\right\}\left(\frac{a}{\pi}\right)$

$= \left|-\frac{e}{a}\left[\left(\frac{a^2}{\pi}\right)(0) + \left(\frac{a^2}{\pi^2}\right)\cos\left\{\frac{\pi x}{a}\right\}\Big|_0^a - \left(\frac{a^2}{3\pi}\right)(0) - \left(\frac{a}{3\pi}\right)^2\cos\left\{\frac{3\pi x}{a}\right\}\Big|_0^a\right]\right|^2 = \left|-\frac{e}{a}\left[\left(\frac{a^2}{\pi^2}\right)(-1-1) - \left(\frac{a^2}{9\pi^2}\right)(-1-1)\right]\right|^2$

$= \left|\left(-\frac{e}{a}\right)\left(\frac{a^2}{\pi^2}\right)\left(-2 + \frac{2}{9}\right)\right|^2 = \left|-\frac{16ae}{9\pi^2}\right|^2 = \boxed{\frac{256a^2e^2}{81\pi^4}}$

$P_{n=1\to n=3} = \left|\int_0^a\sqrt{\frac{2}{a}}\sin\left\{\frac{3\pi x}{a}\right\}(-ex)\sin\left\{\frac{\pi x}{a}\right\}dx\right|^2 = \left|-\frac{e}{a}\int_0^a\left[x\cos\left\{\frac{2\pi x}{a}\right\} - x\cos\left\{\frac{4\pi x}{a}\right\}\right]dx\right|^2$

$= \left|-\frac{e}{a}\left[\left(\frac{ax}{2\pi}\right)\sin\left\{\frac{2\pi x}{a}\right\} + \left(\frac{a^2}{4\pi^2}\right)\cos\left\{\frac{2\pi x}{a}\right\} - \left(\frac{ax}{4\pi}\right)\sin\left\{\frac{4\pi x}{a}\right\} - \left(\frac{a^2}{16\pi^2}\right)\cos\left\{\frac{4\pi x}{a}\right\}\right]_0^a\right|^2$

$= \left|-\frac{e}{a}\left[\left(\frac{a^2}{4\pi^2}\right)(1-1) + \left(\frac{a^2}{16\pi^2}\right)(1-1)\right]\right|^2 = 0$