CHEM 452 HW 3 Hand-in solutions

$\boxed{P6.9}$ Here, we need the operators $\hat{x}$ and $\hat{p}_x$:

$\hat{x} = x$ (multiply by x) ; $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

on a function $f(x)$, with derivative $f'(x)$,

$$[\hat{x}, \hat{p}_x] = \hat{x}\hat{p}_x[f(x)] - \hat{p}_x\hat{x}[f(x)]$$

$$= x\cdot\left(-i\hbar \frac{\partial}{\partial x}[f(x)]\right) + i\hbar \frac{\partial}{\partial x}[x\cdot f(x)]$$

$$= \underbrace{-xi\hbar f'(x)}_{} + i\hbar[f(x) + \underbrace{x f'(x)}_{}]$$

these terms cancel

$$= i\hbar f(x)$$

this is the commutator. for $[\hat{p}_x, \hat{x}]$, the reverse will be true, so $\boxed{[\hat{p}_x, \hat{x}] = -i\hbar}$

$\boxed{P9.21}$

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\langle r \rangle = \frac{\int_{-\infty}^{\infty} \psi_{100}^*(r)\, r\, \psi_{100}(r) r^2 dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi}{\int_{-\infty}^{\infty} \psi_{100}^*(r)\, \psi_{100}(r) r^2 dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi}$$

Where $\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi = 4\pi$ (a good thing to remember)

$$\langle r \rangle = \frac{\int_{-\infty}^{\infty} r^3 e^{-2r/a_0} dr}{\int_{-\infty}^{\infty} r^2 e^{-\frac{2r}{a_0}} dr}$$, and use $\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$

$a = \frac{2}{a_0}$

$$\langle r \rangle = \frac{2\cdot\left[\frac{3!}{\left(\frac{2}{a_0}\right)^4}\right]}{2\cdot\left[\frac{2!}{\left(\frac{2}{a_0}\right)^3}\right]} = 3\left(\frac{a_0}{2}\right) = \boxed{1.5 a_0}$$

$\boxed{\text{P9.11}}$

For H-atom, the energy depends only on n, not on l.

$E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2}$. For each value of n, there are

$\underline{\underline{w = n^2}}$ different orbitals : $n-1$ values of l, each of which contain $2l+1$ values of m_l. To see this, we will list them out.

$w = \sum_{l=0}^{n-1} 2l+1$

a) $E = -\frac{e^2}{32\varepsilon_0 a_0}$, so $n^2 = 4$, $\boxed{n=2}$

for $n=2$, you can have $l=0$ or $l=1$.

$\underbrace{\psi_{210} \quad \psi_{211} \quad \psi_{21-1} \quad \psi_{200}}_{n^2 = 4 \text{ total different states.}}$

b) $E = -\frac{e^2}{72\pi\varepsilon_0 a_0}$, so $n^2 = 9$, $\boxed{n=3}$

$$\left.\begin{array}{ll} \psi_{300} & l=0 \\ \psi_{310}, \psi_{311}, \psi_{31-1} & l=1 \\ \psi_{320}, \psi_{32-2}, \psi_{322}, \psi_{321}, \psi_{32-1} & l=2 \end{array}\right\} \begin{array}{l} 1+3+5=9 \\ \text{total different} \\ \text{states} \end{array}$$

c) $n^2 = 16$, so $\boxed{n=4}$ total degeneracy $= 16$ $(1+3+5+7)$

ψ_{400}, $\psi_{410}, \psi_{411}, \psi_{41-1}$, $\psi_{42-2}, \psi_{42-1}, \psi_{420}, \psi_{421}, \psi_{422}$,

$\psi_{43-3}, \psi_{43-2}, \psi_{43-1}, \psi_{430}, \psi_{431}, \psi_{432}, \psi_{433}$