HW #4 Chem 1410

1. Show that $\hat{H}$ for the hydrogen atom commutes with $\hat{L}^2$ and $\hat{L}_z$.

$$\hat{H} = -\frac{\hbar^2}{2m_e r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hat{L}^2}{2m_e r^2}$$

$[\hat{L}^2, \hat{H}] = 0$ since $\hat{L}^2$ is independent of r and $\hat{L}^2$ commutes with itself.

$[\hat{L}_z, \hat{H}] = \frac{1}{2m_e r^2}[\hat{L}_z, \hat{L}^2]$ since $\hat{L}_z$ is independent of r

$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$ commutes with $\hat{L}^2$ because it does nothing to the terms that depend on θ and $[\frac{\partial}{\partial\phi}, \frac{\partial^2}{\partial\phi^2}] = 0$

$\Rightarrow [\hat{L}_z, \hat{H}] = 0$

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2. Is the $2p_x$ orbital of the H atom an eigenfunction of $\hat{L}_z$? Of $\hat{L}^2$?

We need only consider the angular part of the orbital. $2p_x \sim \sin\theta\cos\phi$

$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \Rightarrow \hat{L}_z(2p_x) \sim -\sin\theta\,\underline{\sin\phi}$

This is not an eigenfunction of $\hat{L}_z$

$$\hat{L}^2 \sin\theta\cos\phi = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}\sin\theta\cos\phi$$

$$= -\hbar^2\left\{\frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\cos\theta)+\frac{1}{\sin^2\theta}\sin\theta(-\cos\phi)\right\}$$

$$= -\hbar^2\left\{\frac{\cos\phi}{\sin\theta}(\cos^2\theta-\sin^2\theta)+\frac{-1}{\sin\theta}\cos\phi\right\}$$

$$= -\hbar^2\left\{\frac{\cos^2\theta-\sin^2\theta-1}{\sin\theta}\right\}\cos\phi = -\hbar^2\left(\frac{-2\sin^2\theta}{\sin\theta}\right)\cos\phi$$

$$= 2\hbar^2\sin\theta\cos\phi$$

So the $2p_x$ orbital is an eigenfunction of $\hat{L}^2$.

Now consider the $2p_+$ orbital. Is it an eigenfunction of $\hat{L}_z$? Of $\hat{L}^2$?

$$\hat{L}_z \sin\theta e^{i\phi} = \frac{\hbar}{i}\sin\theta(i)e^{i\phi} = \hbar\sin\theta e^{i\phi}$$

Yes, $2p_+$ is an eigenfunction of $\hat{L}_z$.

$$\hat{L}^2\sin\theta e^{i\phi} = -\hbar^2\left\{\frac{\cos^2\theta-\sin^2\theta}{\sin\theta}+\frac{1}{\sin\theta}(i)^2\right\}e^{i\phi}$$

$$= -\hbar^2\left\{\frac{\cos^2\theta-\sin^2\theta-1}{\sin\theta}\right\}e^{i\phi}$$

$$= 2\hbar^2\sin\theta e^{i\phi}$$

Yes, $2p_+$ is an eigenfunction of $\hat{L}^2$.

3. Show that the 1s → 2s transition of the H atom is dipole forbidden.

The operator responsible for a dipole transition is proportional to x, y, or z.

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

The integrals factor into r, θ, ϕ integrals. We can show that they are zero by examining only the θ or ϕ parts.

$$\langle 1s|z|2s\rangle \propto \int_0^{\pi} \sin\theta\cos\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= 2\pi\int_0^{\pi} \cos\theta\, d(\cos\theta) = \frac{2\pi\cos^2\theta}{2}\Big|_0^{\pi} = 0$$

$$\langle 1s|x|2s\rangle \propto \int_0^{2\pi} \cos\phi\, d\phi \int_0^{\pi} \sin^2\theta\, d\theta$$

$$\int_0^{2\pi} \cos\phi\, d\phi = \sin\phi\Big|_0^{2\pi} = 0$$

So $\langle 1s|x|2s\rangle = 0$

$$\langle 1s|y|2s\rangle \propto \int_0^{2\pi} \sin\phi\, d\phi \int_0^{\pi} \sin^2\theta\, d\theta$$

$$\int_0^{2\pi} \sin\phi\, d\phi = -\cos\phi\Big|_0^{2\pi} = 0$$

So $\langle 1s|y|2s\rangle = 0$

4. What is the average of r for the 2s orbital of the H atom? How does this differ from the most probable value of r?

$$\langle r \rangle_{2s} = \int_0^\infty dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \; r^3 \psi_{2s}^2$$

$$= \frac{4\pi}{32\pi a_0^3} \int_0^\infty r^3 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} dr$$

$$= \frac{1}{8a_0^3} \int_0^\infty r^3 \left(4 - \frac{4r}{a_0} + \frac{r^2}{a_0^2}\right) e^{-r/a_0} dr$$

$$= \frac{1}{8a_0^3} \left\{ \int_0^\infty 4r^3 e^{-r/a_0} dr - \frac{4}{a_0}\int_0^\infty r^4 e^{-r/a_0} dr + \frac{1}{a_0^2}\int_0^\infty r^5 e^{-r/a_0} dr \right\}$$

$$= \frac{1}{8a_0^3} \left\{ 4 \cdot 3!\, a_0^4 - \frac{4}{a_0} \cdot 4!\, a_0^5 + \frac{1}{a_0^2}\, 5!\, a_0^6 \right\}$$

$$= \frac{a_0}{8} \left\{ 24 - 96 + 120 \right\} = 6a_0$$

Now lets find the most probable value of r.

$$P(r) \propto r^2 \psi^2 = r^2 \left(4 - \frac{4r}{a_0} + \frac{r^2}{a_0^2}\right) e^{-r/a_0}$$

$$P(r) \propto \left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}\right) e^{-r/a_0}$$

$$\frac{dP}{dr} = 0 = \left(8r - \frac{12r^2}{a_0} + \frac{4r^3}{a_0^2}\right) e^{-r/a_0} - \left(\frac{1}{a_0}\right)\left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}\right) e^{-r/a_0}$$

$$0 = 8r - \frac{12r^2}{a_0} + \frac{4r^3}{a_0^2}$$
$$- \frac{4r^2}{a_0} + \frac{4r^3}{a_0^2} - \frac{r^4}{a_0^3}$$

$$8r - \frac{16r^2}{a_0} + \frac{8r^3}{a_0^2} - \frac{r^4}{a_0^3} = 0$$

$$\Rightarrow \quad r\left(8 - \frac{16r}{a_0} + 8\frac{r^2}{a_0^2} - \frac{r^3}{a_0^3}\right) = 0$$

$$\Rightarrow \quad r = 0 \leftarrow \text{one solution}$$

$$\frac{r^3}{a_0^3} - 8\frac{r^2}{a_0^2} + \frac{16r}{a_0} - 8 = 0 \qquad \text{let } x = \frac{r}{a_0}$$

$$x^3 - 8x^2 + 16x - 8$$

By inspection, $x=2$ is a solution.

If we factor this out, get

$$x^2 - 6x + 4 = 0 \Rightarrow x = 3 \pm \tfrac{1}{2}\sqrt{20} = 0.77,\ 5.23$$

So the extrema occur at

$r_1 = 0$

$r_2 = 0.77a_0$

$r_3 = 2a_0$

$r_4 = 5.23a_0$