More Solved Problems in Quantum Chemistry

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1. Determine the radii for the nodal surfaces of the $3s$ orbital of the hydrogen atom. $\psi_{300} = \psi_{3s} = \frac{2}{81\sqrt{3\pi a_0^3}} \left(27 - 18\frac{r}{a_0} + 2\left(\frac{r}{a_0}\right)\right) \exp\left(-\frac{r}{a_0}\right)$

   Solution: For a $3s$ orbital, the factor $\left(27 - 18\frac{r}{a_0} + 2\left(\frac{r}{a_0}\right)^2\right)$ vanishes at $r = \frac{18 \pm \sqrt{108}}{4} a_0$ which gives the radii of the nodal surfaces.

2. Confirm that $Y_{lm} = -\left(\frac{3}{8\pi}\right) \sin\theta \exp i\phi$ is an eigen function of the $\hat{L^2}$ and $\hat{L_z}$ operators.
   Solution: From the form of the function we can identify that $l = 1$ and $m = 1$.

$$\hat{L^2} = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\begin{aligned}
\hat{L^2}Y_{lm} &= -\frac{3}{8\pi}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\cos\theta + \frac{1}{\sin^2\theta}\sin\theta\right)\exp i\phi \\
&= -\frac{3}{8\pi}\sin\theta\exp\pm i\phi\left(\frac{\cos^2\theta - \sin^2\theta}{\sin^2\theta} + \frac{1}{\sin^2\theta}\right) \\
&= 2\left(-\frac{3}{8\pi}\sin\theta\exp i\phi\right)
\end{aligned}$$

   As expected, we find that $\hat{L^2}Y_{lm} = l(l+1)Y_{lm} = 2Y_{lm}$ in this case. The $\hat{L_z}$ operator is $-i\hbar\left(\frac{\partial}{\partial\phi}\right)$.

$$\hat{L_z}Y_{lm} = -i\hbar\left(\frac{\partial}{\partial\phi}\right)\left(-\frac{3}{8\pi}\sin\theta\exp i\phi\right) = 1\hbar\left(-\frac{3}{8\pi}\sin\theta\exp i\phi\right)$$

   Once again, as expected, we find that $\hat{L_z}Y_{lm} = m\hbar Y_{lm}$.

3. Show that $\langle r_{2s}\rangle \neq \langle r_{2p_z}\rangle$. You are given that $R_{20} = \frac{1}{\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2}\left(1 - \frac{r}{2a_0}\right)e^{-\frac{r}{2a_0}}$ and $R_{21} = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-\frac{r}{2a_0}}$.

   Solution: From the expectation value postulate we know that $\langle Op\rangle = \int \psi^* \hat{Op}\psi d\tau$, which for this case is $\langle r\rangle = \int R^* r R r^2 \,dr$.

4. Consider a system whose state is given as $\psi = \frac{\sqrt{3}}{3}\phi_1 + \frac{2}{3}\phi_2 + \frac{\sqrt{2}}{3}\phi_3$, where ϕ_1, ϕ_2, and ϕ_3 are orthonormal. (a) Calculate the probability of finding the system in any of the states ϕ_1, ϕ_2, or ϕ_3. (b) Consider an ensemble of 810 systems on which measurements are made. How many systems will be found in each one of the states ϕ_1, ϕ_2, or ϕ_3?

   Solution: (a) We first verify whether the state ψ is normalized, which it is - 3/9 + 4/9 + 2/9 = 1. The probability of finding the system in any of the states ϕ_i is $|c_i|^2$. In this case it is 1/3, 4/9, and 2/9 respectively. (b) If a large number of measurements, (N say, are made, the number of systems being found in a state i is $p_i N$.

5. An electron is moving freely in a box which extends from 0 to a. The electron is in the ground state of the box. If the wall at a is suddenly moved to $4a$, what is the probability of finding the electron in the (a) ground state and (b) first excited state of the new box?

Solution: The electron is initially in the state $\psi = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)$. The ground and first excited states of the new box are $\phi_1 = \sqrt{\frac{2}{4a}}\sin\left(\frac{\pi x}{4a}\right)$ and $\phi_2 = \sqrt{\frac{2}{4a}}\sin\left(\frac{2\pi x}{4a}\right)$. The probability of finding the electron in the state ϕ_i is given by $|\int_0^a \phi_i \psi \, dx|^2$.

6. An electron in hydrogen atom is in the energy eigenstate $Nre^{-\frac{r}{2a_0}}\sin\theta e^{-i\phi}$. (a) Find N (b) If $\hat{L^2}$ and $\hat{L_z}$ are measured, what will be the results? (c) And if $\hat{L_x}$ is measured? (d) What is the probability per unit radial interval (dr) of finding the electron at $r = 2a_0$?

Solution: (a) $N^2 = \frac{1}{\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} r^2 e^{-\frac{r}{a_0}} \sin^2\theta r^2 \, dr \sin\theta \, d\theta \, d\phi}$ (b) The l and m values are, respectively, 1 and -1. If $\hat{L^2}$ is measured, one would get $l(l+1)\hbar^2 = 2\hbar^2$. Measurement of $\hat{L_z}$ yields $m\hbar = 1\hbar$. (c) The state is not an eigenfunction of L_x (you can verify this by finding the operator form of $\hat{L_x}$. The expectation value of $\hat{L_x}$ in this state is zero. (d) The desired probability is found by integrating ψ^2 over θ and ϕ and evaluating the resulting function of r at $r = 2a_0$.

7. If $\hat{A}$ is the operator $i(x^2+1)\frac{d}{dx} + ix$, find the state $\psi(x)$ for which $\hat{A}\psi(x) = 0$. Normalize $\psi(x)$. Calculate the probability of being in the region $-1 \leq x \leq 1$ if the particle in the state $\psi(x)$.

Solution: The state $\psi(x)$ is the solution of the differential equation $\frac{d\psi}{dx} = -\frac{x}{x^2+1}$, which is $\frac{N}{\sqrt{x^2+1}}$. The function is normalized as always, $N^2\int_{-\infty}^{\infty}\psi^*\psi \, dx = 1$ implying that $N = \frac{1}{\sqrt{\pi}}$. The probability of being found in the specified region is $\frac{1}{\pi}\int_{-1}^{1}\frac{1}{x^2+1}\, dx = 1/2$.