Quiz 7.3 – Fundamentals of Quantum Mechanics

Name: Key

Wavefunction Normalization

The wavefunction for a 1s electron orbital is:

$$\psi_{1s}(r,\theta,\phi) = e^{-r/a_0}$$

$1 = \iiint N^2 \psi^2 \, d\tau$

Note that this is a function in spherical polar coordinates, and that a_0 is the Bohr radius. Find the normalization constant, and give the complete normalized wavefunction $\psi_{1s}(r,\theta,\phi)$

$1 = N^2 \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{-2r/a_0} r^2 \sin\theta \, dr\, d\theta\, d\phi$

$1 = N^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} r^2 e^{-2r/a_0}\, dr$

Integral Table

$1 = N^2 \cdot 2\pi \cdot \underbrace{(-\cos\theta)\big|_0^{\pi}}_{2} \cdot \frac{a_0^3}{4} \rightarrow N^2 = \frac{1}{\pi a_0^3} \rightarrow N = (\pi a_0^3)^{-1/2}$

$\psi_{1s} = (\pi a_0^3)^{-1/2} e^{-r/a_0}$

Expectation Values

For electronic orbitals, we can define an orbital angular momentum operator: $\hat{l}^2$

Some eigenvalues are:

$$\hat{l}^2\psi_{3s} = 0$$
$$\hat{l}^2\psi_{3p} = 2\hbar^2\psi_{3p}$$
$$\hat{l}^2\psi_{3d} = 6\hbar^2\psi_{3d}$$

If an electron is in the superposition state $\Psi = \left(\frac{1}{\sqrt{2}}\psi_{3s} + \frac{1}{\sqrt{3}}\psi_{3p} + \frac{1}{\sqrt{6}}\psi_{3d}\right)$, what will be the expectation value $\langle \hat{l}^2 \rangle$?

$C_1 \cdot 3s$ $\quad C_2 \cdot 3p$ $\quad C_3 \cdot 3d$

$\langle \hat{l}^2 \rangle = \langle C_1 \cdot 3s + C_2 \cdot 3p + C_3\, 3d \,|\, \hat{l}^2 \,|\, C_1 \cdot 3s + C_2 \cdot 3p \cdot C_3 \cdot 3d \rangle$

$\langle \hat{l}^2 \rangle = \langle C_1 \cdot 3s + C_2\, 3p + C_3\, 3d \,|\, C_1 \cdot \emptyset \cdot 3s + C_2 \cdot 2\hbar^2 \cdot 3p + C_3 \cdot 6\hbar^2 \cdot 3d \rangle$

$\langle \hat{l}^2 \rangle = C_1^2 \cdot \emptyset \cdot \cancelto{1}{\langle 3s|3s\rangle} + C_1 C_2 \cdot 2\hbar^2 \cancelto{\emptyset}{\langle 3s|3p\rangle} + C_1 C_3 \cdot 6\hbar^2 \cancelto{\emptyset}{\langle 3s|3d\rangle} +$
$C_2 C_1 \cdot \emptyset \cdot \cancelto{\emptyset}{\langle 3p|3s\rangle} + C_2^2 \cdot 2\hbar^2 \cancelto{1}{\langle 3p|3p\rangle} + C_2 C_3 \cdot 6\hbar^2 \cancelto{\emptyset}{\langle 3p|3d\rangle} +$
$C_3 C_1 \cdot \emptyset \cdot \cancelto{\emptyset}{\langle 3d|3s\rangle} + C_3 C_2 \cdot 2\hbar^2 \cdot \cancelto{\emptyset}{\langle 3d|3p\rangle} + C_3^2 \cdot 6\hbar^2 \cancelto{1}{\langle 3d|3d\rangle}$

$\langle \hat{l}^2 \rangle = C_1^2 \cdot \emptyset + C_2^2 \cdot 2\hbar^2 + C_3^2 \cdot 6\hbar^2 = \frac{1}{3} \cdot 2\hbar^2 + \frac{1}{6} \cdot 6\hbar^2 = \frac{5}{3}\hbar^2$

Schrödinger Equation and Wavefunctions

For a particle confined in the region $0 \leq x \leq L$, the appropriate wavefunctions are:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

o Another function, $\phi(x) = -4x^2 + 4x$ has a similar shape and obeys the same boundary conditions. Prove whether or not this function is also a solution to the Schrödinger equation.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi = -\frac{\hbar^2}{2m}\frac{d}{dx}(-8x+4) = -\frac{\hbar^2}{2m}\cdot -8 = \frac{4\hbar^2}{m} \neq E\phi$$

i.e. ϕ is not an eigenfunction of $\hat{H}$ and not a solution to the Schrödinger equation

o Find the average position $\langle x \rangle$ for the states $n = 1$ and $n = 2$ $\langle x \rangle = \int_0^L \psi^* \cdot x \cdot \psi \, dx$ -or- $\langle \psi | x | \psi \rangle$

$$\langle x \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \cdot x \cdot \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L}\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx \xrightarrow{\text{Integral Tables}}$$

$$\langle x \rangle = \frac{2}{L}\left(\frac{L^2}{4} - \frac{L^2}{4n\pi}\underbrace{\sin\left(\frac{2n\pi L}{L}\right)}_{\to \emptyset} - \frac{L^2\pi^2}{n^2 8}\cdot\left[\underbrace{\cos\left(\frac{2n\pi L}{L}\right)}_{\to 1} - \underbrace{1}_{-1}\right]\right)$$

n is an integer

$$\langle x \rangle = \frac{2}{L}\frac{L^2}{4} = \frac{L}{2} \text{ for any } n$$

o Assume $L = 1$, and give the probability that the system is observed with $0.4 < x < 0.6$ for the states $n = 1$ and $n = 2$

$$P = \int_{0.4}^{0.6} \sqrt{\frac{2}{L}} \sin(n\pi x) \cdot \sqrt{\frac{2}{L}} \sin(n\pi x)\, dx = \frac{2}{L}\int_{0.4}^{0.6} \sin^2(n\pi x)\, dx$$

$$P = 2\left[\frac{1}{2}x - \frac{1}{4n\pi}\sin(2n\pi x)\right]_{0.4}^{0.6}$$

$$P_1 = 2\left(\frac{0.2}{2} - \frac{1}{4\pi}\left[\sin(1.2\pi) - \sin(0.8\pi)\right]\right) = 0.387 \quad (39\% \text{ probability})$$

$$P_2 = 2\left(\frac{0.2}{2} - \frac{1}{8\pi}\left[\sin(2.4\pi) - \sin(1.6\pi)\right]\right) = 0.0486 \quad (5\% \text{ probability})$$