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2. Derive expressions for the projections of the angular momentum operators

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The angular momentum operator in quantum mechanics is defined as:

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}},$$

where $\hat{\vec{r}} = (x, y, z)$ is the position operator and $\hat{\vec{p}} = -i\hbar\nabla$ is the momentum operator.

Using the cross product, the components of the angular momentum operator are given by:

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y, \quad \hat{L}_y = z\hat{p}_x - x\hat{p}_z, \quad \hat{L}_z = x\hat{p}_y - y\hat{p}_x.$$

Substituting $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, $\hat{p}_y = -i\hbar\frac{\partial}{\partial y}$, and $\hat{p}_z = -i\hbar\frac{\partial}{\partial z}$, we get:

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right),$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

16. How in quantum mechanics can be calculated the angle between the angular momentum vector $\vec{L}$ and the z-axis? Calculate the values of this angle for magnetic quantum numbers $m = -2$ and $+1$ for 3d orbitals.

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In quantum mechanics, the angle θ between the angular momentum vector $\vec{L}$ and the z-axis is found using the relation:

$$\cos\theta = \frac{L_z}{\left|\vec{L}\right|}$$

However, because $\vec{L}$ and L_z are operators with quantized eigenvalues, we instead use:

$$\cos\theta = \frac{\langle L_z\rangle}{\sqrt{\langle\vec{L}^2\rangle}} = \frac{m\hbar}{\sqrt{l(l+1)}\hbar} = \frac{m}{\sqrt{l(l+1)}}$$

For 3d orbitals, the orbital quantum number is $l = 2$.
Case 1: $m = -2$

$$\cos\theta = \frac{-2}{\sqrt{2(2+1)}} = \frac{-2}{\sqrt{6}} = -\frac{\sqrt{6}}{3}$$

$$\theta = \cos^{-1}\left(-\frac{\sqrt{6}}{3}\right) \approx 144.7^\circ$$

Case 2: $m = +1$

$$\cos\theta = \frac{1}{\sqrt{6}} \approx 0.408$$

$$\theta = \cos^{-1}(0.408) \approx 66.4^\circ$$

20. Obtain the equation for radial part of wave function

Schrödinger equation for the hydrogen atom in spherical coordinates:

$$-\frac{\hbar^2}{2M}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\hat{L}^2 - \frac{2M}{\hbar^2}U(r)\right]\psi_{nlm}(\vec{r}) = E\psi_{nlm}(\vec{r}),$$

where:

$$\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta,\phi).$$

The angular momentum operator $\hat{L}^2$ acts only on the angular part Y_{lm}, and satisfies:

$$\hat{L}^2 Y_{lm} = \hbar^2 l(l+1)Y_{lm}.$$

Substituting the form $\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)$ into the equation:

$$-\frac{\hbar^2}{2M}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_{nl}(r)}{dr}\right)Y_{lm} - \frac{l(l+1)}{r^2}R_{nl}(r)Y_{lm} - \frac{2M}{\hbar^2}U(r)R_{nl}(r)Y_{lm}\right] = ER_{nl}(r)Y_{lm}.$$

distributing $-\frac{\hbar^2}{2M}$ to each term:

$$-\frac{\hbar^2}{2M}\cdot\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_{nl}}{dr}\right)Y_{lm} + \frac{\hbar^2 l(l+1)}{2Mr^2}R_{nl}Y_{lm} + U(r)R_{nl}Y_{lm} = ER_{nl}Y_{lm}.$$

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Dividing both sides by Y_{lm}, we get the radial part of the equation:

$$-\frac{\hbar^2}{2M}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_{nl}(r)}{dr}\right)\right] + \left[\frac{\hbar^2 l(l+1)}{2Mr^2} + U(r)\right]R_{nl}(r) = ER_{nl}(r).$$

31. Calculate the possible maximum number of electrons in 4p and 2d orbitals for hydrogen atom.

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Each orbital is characterized by quantum numbers:

- Principal quantum number n
- Orbital quantum number l
- Magnetic quantum number $m = -l, \ldots, +l$ (total $2l + 1$ values)
- Each orbital can hold 2 electrons (due to spin quantum number $s = \pm\frac{1}{2}$)

For 4p orbital:

- $n = 4$, $l = 1$
- Number of orbitals: $2l + 1 = 3$
- Maximum number of electrons: $3 \times 2 = 6$

For 2d orbital:

- $n = 2$, $l = 2$
- But values of l must satisfy $l + 1 \leq n$, so $l = 2$ is not allowed for $n = 2$ therefore, the 2d orbital does not exist

40. Write the Schrödinger equation for third order approximation of perturbation theory.

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In time-dependent perturbation theory, we write the total wave function as:

$$\Psi(t) = \sum_n c_n(t) e^{-iE_n t/\hbar} \psi_n,$$

where $c_n(t)$ are time-dependent coefficients, and ψ_n are eigenfunctions of the unperturbed Hamiltonian $\hat{H}_0$:

$$\hat{H}_0 \psi_n = E_n \psi_n.$$

When a time-dependent perturbation $\hat{H}'(t)$ is applied, the total Hamiltonian becomes:

$$\hat{H}(t) = \hat{H}_0 + \hat{H}'(t).$$

We expand the coefficients $c_n(t)$ as a power series:

$$c_n(t) = c_n^{(0)} + c_n^{(1)}(t) + c_n^{(2)}(t) + c_n^{(3)}(t) + \cdots,$$

where $c_n^{(k)}(t)$ is the k-th order correction.

The perturbation theory (non degenerate case) and not time dependend

From perturbation theory, the differential equation for $c_m(t)$ is:

$$i\hbar \frac{dc_m(t)}{dt} = \sum_n H'_{mn}(t) e^{i\omega_{mn} t} c_n(t), \quad \text{where} \quad \omega_{mn} = \frac{E_m - E_n}{\hbar}.$$

Substituting the expansion of $c_n(t)$, we collect terms order by order. The third-order approximation is given by:

$$i\hbar \frac{dc_m^{(3)}(t)}{dt} = \sum_n H'_{mn}(t) e^{i\omega_{mn} t} c_n^{(2)}(t),$$

where $c_n^{(2)}(t)$ is the second-order correction obtained from the previous step.