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Quantum Mechanics

Lecture 7

Spherical coordinates;
Separation of variables;
Angular quantum numbers;
Intrinsic vs. orbital AM;
Spherical harmonics.

A quick recap

A two-body interacting Hamiltonian can be transformed to relative coordinates:

$$H = \frac{\hat{\mathbf{p}}_1^2}{2m_1} + \frac{\hat{\mathbf{p}}_2^2}{2m_2} + V(|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|) \qquad \Rightarrow \qquad H = \frac{\hat{\mathbf{p}}^2}{2\mu} + V(|\hat{\mathbf{r}}|)$$

Angular momentum commutes with *H*, so simultaneous eigenstates exist:

$$[L_z, H] = [L^2, H] = [L_z, L^2] = 0$$

$$\mathbf{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} \qquad L_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

(+ cyclic)

$$H|E, l, m\rangle = E|E, l, m\rangle$$

$$L^2|E, l, m\rangle = l(l+1)\hbar^2|E, l, m\rangle$$

$$L_z|E, l, m\rangle = m\hbar|E, l, m\rangle$$

Spherical coordinates

To exploit the symmetry of the reduced *H*, transform to spherical coordinates:

In cartesian coordinates $\mathbf{x} = (x, y, z)$

$$\langle \mathbf{x} \,|\, \hat{\mathbf{p}}^2 \,|\, \psi \rangle = -\hbar^2 \nabla^2 \psi(\mathbf{x}) \qquad \nabla^2 \psi(\mathbf{x}) = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}$$

In spherical coordinates $\mathbf{r} = (r, \theta, \phi)$

$$\nabla \psi(\mathbf{r}) = \left(\frac{\partial \psi}{\partial r}, \frac{1}{r}\frac{\partial \psi}{\partial \theta}, \frac{1}{r \sin \theta}\frac{\partial \psi}{\partial \varphi} \right)$$

$$\langle \mathbf{r} \,|\, \hat{\mathbf{p}}^2 \,|\, \psi \rangle = -\hbar^2 \nabla^2 \psi(\mathbf{r}) \qquad \nabla^2 \psi(\mathbf{r}) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta}\frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta}\frac{\partial^2 \psi}{\partial \varphi^2}$$

Spherical coordinates

Recall our expression for **L**:

$$\mathbf{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} \;\Rightarrow\; L^2 = \mathbf{L} \cdot \mathbf{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} \cdot \hat{\mathbf{r}} \times \hat{\mathbf{p}} = -\hbar^2 \hat{\mathbf{r}} \times \nabla \cdot \hat{\mathbf{r}} \times \nabla$$

Now use the gradient formula:

$$\nabla \psi(\mathbf{r}) = \left(\frac{\partial \psi}{\partial r}, \frac{1}{r}\frac{\partial \psi}{\partial \theta}, \frac{1}{r \sin \theta}\frac{\partial \psi}{\partial \varphi} \right)$$

$$\langle \mathbf{r} | L^2 | \psi \rangle = \frac{-\hbar^2}{\sin \theta}\frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{-\hbar^2}{\sin^2 \theta}\frac{\partial^2 \psi}{\partial \varphi^2}$$

Compare with the previous expression:

$$\nabla^2 \psi(\mathbf{r}) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta}\frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta}\frac{\partial^2 \psi}{\partial \varphi^2}$$

Spherical coordinates

We therefore have: In spherical coordinates $\mathbf{r} = (r, \theta, \phi)$

$$\langle \mathbf{r} | \hat{\mathbf{p}}^2 | \psi \rangle = -\hbar^2 \nabla^2 \psi(\mathbf{r}) = \frac{-\hbar^2}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \langle \mathbf{r} | \psi \rangle}{\partial r} \right) + \frac{1}{r^2} \langle \mathbf{r} | L^2 | \psi \rangle$$

For the simultaneous eigenstates:

$$\langle \mathbf{r} | \hat{\mathbf{p}}^2 | E, l, m \rangle = \frac{-\hbar^2}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \langle \mathbf{r} | E, l, m \rangle}{\partial r} \right) + \frac{l(l+1)\hbar^2}{r^2} \langle \mathbf{r} | E, l, m \rangle$$

The time-independent Schrödinger eq. in radial coordinates becomes:

$$\left(\frac{-\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right) \psi_{E,l,m}(\mathbf{r}) = E \, \psi_{E,l,m}(\mathbf{r}) \qquad \psi_{E,l,m}(\mathbf{r}) = \langle \mathbf{r} | E, l, m \rangle$$

Separation of variables

The L.H.S. is independent of (θ,ϕ), so solve via separation of variables.

$$\psi_{E,l,m}(\mathbf{r}) = \langle \mathbf{r} \,|\, E, l, m \rangle = R(r)F(\theta, \phi)$$

Canceling the angular parts yields an equation for the radial wave function:

$$\left(\frac{-\hbar^2}{2\mu r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right) R(r) = E\, R(r)$$

Now make a substitution: $R(r) = \frac{u(r)}{r}$

$$\left(\frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right) u(r) = E\, u(r)$$

Radial wave function

The radial equation is thus equivalent to

$$\left(\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V_{\text{eff}}(r)\right)u(r) = E\,u(r) \qquad V_{\text{eff}}(r) = \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \qquad R(r) = \frac{u(r)}{r}$$

This is the single-particle Schrödinger equation!

$$V_{\text{eff}}(r) = V_{\text{cf}}(r) + V(r)$$

$$V_{\text{cf}}(r) = \frac{l(l+1)\hbar^2}{2\mu r^2}$$

"Centrifugal barrier" term:
This is the fictitious centrifugal potential that arises from transforming to spherical coordinates.

Note that this is independent of m, the L_z eigenvalue.

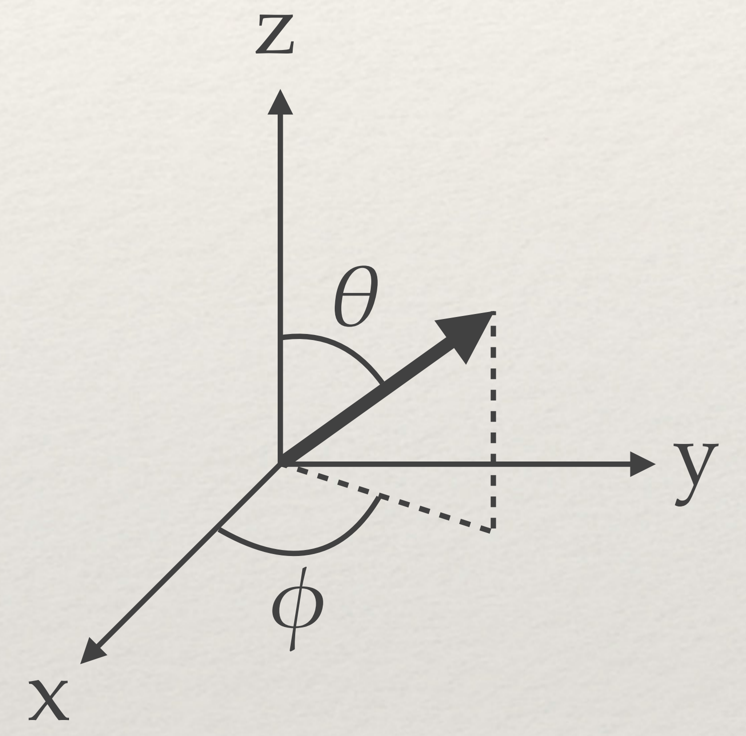
This implies that each value of l has $2l+1$ degenerate solutions

Angular quantum numbers

Recall our ansatz:

$$\psi_{E,l,m}(\mathbf{r}) = \langle \mathbf{r} | E, l, m \rangle = R(r)F(\theta, \phi) \qquad R(r) = \frac{u(r)}{r}$$

What about the angular part?
Recall, L_z is the generator of rotations around the z axis. Therefore:



$$\langle r, \theta, \phi | L_z | \psi \rangle = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \langle r, \theta, \phi | \psi \rangle \qquad L_z \xrightarrow{\text{sphere. coord.}} L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

Acting on the eigenstates we find:

$$\langle \mathbf{r} | L_z | E, l, m \rangle = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \langle \mathbf{r} | E, l, m \rangle = m\hbar \langle \mathbf{r} | E, l, m \rangle$$

First-order diff. eq. for ϕ only, $F(\theta,\phi) = \Theta(\phi)\Phi(\theta)$:

$$\frac{\partial}{\partial \phi} \Phi(\phi) = im\,\Phi(\phi) \;\Rightarrow\; \Phi(\phi) = C \exp(im\phi)$$

Angular quantum numbers

Recall our ansatz:

$$\psi_{E,l,m}(\mathbf{r}) = \langle \mathbf{r} \,|\, E, l, m \rangle = R(r)\Theta(\theta)\Phi(\phi) \quad R(r) = \frac{u(r)}{r} \qquad \Phi(\phi) \propto \exp(im\phi)$$

However, m must be quantized:

The variable ϕ is periodic, and our wave function must respect this symmetry. Therefore this single-value condition implies:

$$\exp(im\phi) = \exp(im(\phi + 2\pi)) \;\Rightarrow\; m = 0, \pm 1, \pm 2, \ldots$$

But m still depends on l:

For a given value of l, we have

$$m = -l, -l+1, \ldots, 0, \ldots, l-1, l$$

Important distinction: Orbital AM $\neq$ Spin AM

$$l = 0, 1, 2, \ldots$$

Orbital AM eigenvalues must be integers, and can never be half-integers.

Angular quantum numbers

Recall our ansatz:

$$\psi_{E,l,m}(\mathbf{r}) = \langle \mathbf{r} \,|\, E, l, m \rangle = R(r)\Theta(\theta)\Phi(\phi) \qquad R(r) = \frac{u(r)}{r} \qquad \Phi(\phi) \propto \exp(im\phi)$$

$$\left(\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V_{\text{eff}}(r) \right) u(r) = E\, u(r) \qquad V_{\text{eff}}(r) = \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)$$

What about the polar angle?

They are the **associated Legendre polynomials**:

$$\Theta(\theta) \propto P_l^m(\cos\theta)$$

Where does this come from?
The equation has spherical symmetry; this is the analog of Fourier decomposition for periodic functions.

Spherical harmonics:

$$Y_l^m(\theta, \phi) = N_{l,m} e^{im\phi} P_l^m(\cos\theta)$$

- normalization: $N_{l,m}$
- azimuthal component: $e^{im\phi}$
- polar component: $P_l^m(\cos\theta)$

Spherical harmonics

The form of the spherical harmonics can be found explicitly via ladder operators:

$$L_x = \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$L_y = \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$L_\pm = L_x \pm iL_y$$

$$\Rightarrow \quad L_\pm = \frac{\hbar}{i}e^{\pm i\phi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right)$$

Now use on the highest/lowest weight states:

$$\langle\theta,\phi\,|\,L_+\,|\,l,l\rangle = 0 = \frac{\hbar}{i}e^{i\phi}\left(i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right)\langle\theta,\phi\,|\,l,l\rangle$$

$$\left(i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right)\langle\theta,\phi\,|\,l,l\rangle = \left(\frac{\partial}{\partial\theta} - l\cot\theta\right)\langle\theta,\phi\,|\,l,l\rangle = 0$$

$$\Rightarrow \quad \langle\theta,\phi\,|\,l,l\rangle = c_l e^{il\phi}\sin^l\theta$$

Spherical harmonics

This must be normalized:

$$\int d\Omega \,|\langle \theta, \phi \,|\, l, l \rangle|^2 = 1 \;\Rightarrow\; \langle \theta, \phi \,|\, l, l \rangle = Y_l^l(\theta, \phi) = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)!}{4\pi}} e^{il\phi} \sin^l \theta$$

Use lowering operator to obtain other solutions:

$$L_- \,|\, l, m \rangle = \sqrt{l(l+1) - m(m-1)} \,|\, l, m \rangle$$

$$\Rightarrow \; Y_\ell^m(\theta, \varphi) = (-1)^m \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} P_{\ell m}(\cos\theta)\, e^{im\varphi}$$