

3. Principles of QM

Axiomatic principles

State vector axiom: State vector at t is ket $\psi(t)$, or $|\psi\rangle$, bra state.

Probability axiom: Given a system in state $|\psi\rangle$, a measurement will find it in state $|\phi\rangle$ with probability amplitude $\langle\phi|\psi\rangle$.

Hermitian operator axiom: Physical observable is represented by a linear and Hermitian operator.

Measurement axiom: Measurement of a physical observable results in eigenvalue of observable. Observable \hat{A} , we have $\hat{A}|a\rangle = a|a\rangle$, where a is eigenvalue and $|a\rangle$ is eigenvector. Measurement of the physical quantity represented by \hat{A} collapses the state $|\psi\rangle$ before measurement into an eigenstate $|a\rangle$ of \hat{A} .

Time evolution axiom: $i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$, w/o consider x or p .

Vector space

State vector is neither in position nor momentum space.

$$\text{Basis vectors: } |0\rangle = \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}, |1\rangle = \begin{bmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{bmatrix}, |n\rangle = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{bmatrix} \text{ (in } n\text{th pos).}$$

Linearity : Because the SE is linear, given two states $|\psi_1(t)\rangle$ and $|\psi_2(t)\rangle$, $|\psi(t)\rangle = c_1|\psi_1(t)\rangle + c_2|\psi_2(t)\rangle$ is also a sol. (c 's are complex).
Properties of a vector space

$$\text{Dual vector space } c|\psi\rangle \text{ is mapped to } c^* \langle\psi|. \text{ Given a vector, } |\psi\rangle = \begin{bmatrix} \vdots \\ \alpha \\ \vdots \end{bmatrix},$$

the dual vector is $\langle\psi| = [\cdots \quad \alpha^* \quad \cdots]$.

Dual basis vectors are $\langle 0| = [1 \quad 0 \quad \cdots]$, \cdots , $\langle n| [0 \quad \cdots \quad 1]$.

Inner product : $\langle\phi|\psi\rangle = c$, where c is complex.

$\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^* \rightarrow \langle\psi|\psi\rangle$ is real, positive, and finite for a normalizable ket vector. Can choose $\langle\psi|\psi\rangle = 1$. $\langle\psi_m|\psi_n\rangle = \delta_{mn}$

Operators

A matrix operator \hat{A} acting on a state vector $|\psi\rangle$ transforms it into another state vector $|\phi\rangle$, $\hat{A}|\psi\rangle = |\phi\rangle$. It is linear.

Properties of operators

Hermitian conjugate (Hermitian adjoint) operator in the dual space

Hermitian adjoint operator \hat{A}^\dagger acts on the dual vector $\langle\psi|$ from the right as $\langle\psi|\hat{A}^\dagger$, where $\hat{A}^\dagger = (\hat{A})^{T*}$.

$$(\hat{A}|\psi\rangle)^\dagger = |\psi\rangle^\dagger \hat{A}^\dagger = \langle\psi|\hat{A}^\dagger \quad \langle\psi| = |\psi\rangle^\dagger \quad \langle\psi|^\dagger = |\psi\rangle \\ (\hat{A}\hat{B})^\dagger = (\hat{A}\hat{B})^{T*} = (\hat{B}^T \hat{A}^T)^* = \hat{B}^{\dagger T} \hat{A}^{\dagger T} = \hat{B}^\dagger \hat{A}^\dagger, \quad (c\hat{A})^\dagger = c^* \hat{A}^\dagger$$

Outer product operators : $|\psi\rangle\langle\phi| \quad [|\psi\rangle\langle\phi|]\chi = |\psi\rangle\langle\phi|\chi$

Matrix elements of operators

$\langle\phi|\hat{A}|\psi\rangle$ (complex num)

Hermitian equiv to complex conj $\langle\phi|\hat{A}|\psi\rangle^\dagger = \langle\psi|\hat{A}^\dagger|\phi\rangle = \langle\phi|\hat{A}|\psi\rangle^*$

Hermitian operators : $\hat{A}^\dagger = \hat{A}$, so given $\hat{A}|\phi\rangle$ in the vector space, we have

$\langle\psi|\hat{A}^\dagger = \langle\phi|\hat{A}$ in the dual vector space.

Matrix elements of a Hermitian operator

$$\langle\phi|\hat{A}|\psi\rangle^\dagger = \langle\phi|\hat{A}|\psi\rangle^* = \langle\psi|\hat{A}^\dagger|\phi\rangle = \langle\psi|\hat{A}|\phi\rangle$$

Hermitian operator, real expectation vals: $\langle\psi|\hat{A}|\psi\rangle^* = \langle\psi|\hat{A}|\psi\rangle \equiv \langle\hat{A}\rangle$

Same result whether \hat{A} acts to right or left: $\langle\phi|\hat{A}|\psi\rangle = \langle\phi|\hat{A}^\dagger|\psi\rangle$

Eigenvals and eigenvcs of Hermitian operators : $\hat{A}|a_n\rangle = a_n|a_n\rangle$

Normalized eigvecs $\langle a_m|a_n\rangle = \delta_{mn}$. Gram-Schmidt, degenerate vec.

Completeness of eigenvector of a Hermitian operator Set $|a_n\rangle$ is complete if $\sum_n |a_n\rangle\langle a_n| = 1$. $\sum_n |a_n\rangle\langle a_n| = 1$ (identity operator)

Continuous spectra of a Hermitian operator Hermitian operator \hat{A} ,

$\hat{A}|a\rangle = a|a\rangle$, where a is continuous.

$\int da' \langle a'|\hat{A}|a\rangle = a \int da' \langle a'|\hat{A}|a\rangle = \int da' a' \langle a'|\hat{A}|a\rangle \rightarrow \langle a'|\hat{A}|a\rangle = \delta(a' - a)$

Continuous condition: $\int da |a\rangle\langle a| = 1$

Gram-Schmidt orthogonalization procedure Eigval (like energy level) is n -fold degenerate: n states w same eigval.

Orthogonal eigenstates \rightarrow no degeneracy.

1. Normalize each state and define $\alpha_i = \frac{\alpha_i}{\sqrt{\langle\alpha_i|\alpha_i\rangle}}$. 2. $|\alpha'_1\rangle = |\alpha_1\rangle$.

$$3. |\alpha'_2\rangle = \frac{|\alpha_2\rangle - \langle\alpha_1|\alpha_2\rangle \langle\alpha_1|\alpha_2\rangle}{\sqrt{\langle\alpha_2|\alpha_2\rangle - \langle\alpha_1|\alpha_2\rangle \langle\alpha_2|\alpha_1\rangle}} = \frac{|\alpha_2\rangle - \langle\alpha_1|\alpha_2\rangle \langle\alpha_1|\alpha_2\rangle}{\sqrt{1 - \langle\alpha_1|\alpha_2\rangle \langle\alpha_2|\alpha_1\rangle}}$$

4. Subtract components of $|\alpha_3\rangle$ along $|\alpha_1\rangle$ and $|\alpha_2\rangle$,

$|\alpha_3\rangle - \langle\alpha_1|\alpha_3\rangle \langle\alpha_1|\alpha_3\rangle - \langle\alpha_2|\alpha_3\rangle \langle\alpha_2|\alpha_3\rangle$, normalize and promote to $|\alpha'_3\rangle$

Position and momentum representation

$$\hat{r}|\vec{r}\rangle = \vec{r}|\vec{r}\rangle \quad \langle\vec{r}'|\vec{r}\rangle = \delta^3(\vec{r}' - \vec{r}), \int d^3\vec{r} |\vec{r}\rangle \langle\vec{r}| = 1, \langle\vec{r}'|\hat{r}|\vec{r}\rangle = \vec{r} \delta^3(\vec{r}' - \vec{r})$$

$$\hat{p}|\vec{p}\rangle = \vec{p}|\vec{p}\rangle \quad \langle\vec{p}'|\vec{p}\rangle = \delta^3(\vec{p}' - \vec{p}), \int d^3\vec{p} |\vec{p}\rangle \langle\vec{p}| = 1$$

State vector $|\psi(t)\rangle$ in position space (scalar): $\langle\vec{r}|\psi(x, t)\rangle \equiv \psi(\vec{r}, t)$

$$\langle\psi|\hat{p}|\psi\rangle = \frac{d}{dt} \langle\psi|\hat{r}|\psi\rangle m$$

Representation of momentum operator in position space: $\hat{p} = -i\hbar \vec{\nabla}$.

$$\langle x|\hat{p}|x'\rangle = -i\hbar \frac{\partial}{\partial x} \delta(x - x') = -i\hbar \frac{\partial}{\partial x} \langle x|x'\rangle.$$

$\hat{p} = -i\hbar \frac{\partial}{\partial x}$ is Hermitian, $\frac{\partial}{\partial x}$ is not.

$$\langle x|\hat{p}|p\rangle = p \langle x|p\rangle = -i\hbar \frac{\partial}{\partial x} \langle x|p\rangle. \text{ The solution is } \langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar} p x}.$$

$$\text{In 3D, } \langle\vec{r}|\vec{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar} \vec{p} \cdot \vec{r}}.$$

We can write the normalized wavefunction of definite position in momentum space, $\langle p|x\rangle = \langle x|p\rangle^*$. So, $\langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-\frac{i}{\hbar} p x}$ (particle moving to the left, or with momentum $-p$, in the momentum space).

Operators and wavefunction in position representation Position and momentum operators in pos space: $\hat{r} = \vec{r}$, $\hat{p} = -i\hbar \vec{\nabla}$.

\hat{r} is Hermitian and $\langle\phi|\hat{r}^\dagger|\psi\rangle = \langle\phi|\hat{r}|\psi\rangle$.

$$\hat{O}(\hat{r}, \hat{p}) = \hat{O}(\vec{r}, -i\hbar \vec{\nabla})$$

The expectation val of the observable should be indep of representation. In state $\psi(t)$, $\langle\hat{O}\rangle = \langle\psi(t)|\hat{O}|\psi(t)\rangle$.

Insert $\int d^2\vec{r} |\vec{r}\rangle \langle\vec{r}| = 1$ to get $\langle\hat{O}\rangle = \int d^2\vec{r} \langle\psi(t)|\vec{r}\rangle \langle\vec{r}|\hat{O}|\psi(t)\rangle$

$$\psi(\vec{r}, t) = \langle\vec{r}|\psi(t)\rangle, \quad \psi(\vec{r}, t)^* = \langle\vec{r}|\psi(t)\rangle^* = \langle\psi(t)|\vec{r}\rangle,$$

$$\langle\vec{r}|\hat{O}|\psi(t)\rangle = \hat{O}(\vec{r}, -i\hbar \vec{\nabla}) \psi(\vec{r}, t), \quad \langle\vec{O}\rangle = \int d^3\vec{r} \psi(\vec{r}, t)^* \hat{O}(\vec{r}, -i\hbar \vec{\nabla}) \psi(\vec{r}, t)$$

Operators and wavefunction in momentum representation $\hat{r} = i\hbar \vec{\nabla}_p$, or in

$$1D, \hat{x} = i\hbar \frac{\partial}{\partial p}, \hat{p} = \vec{p}, \text{ where } \vec{p}^* = \vec{p}.$$

$$\hat{O}(\hat{r}, \hat{p}) = \hat{O}(i\hbar \vec{\nabla}_p, \vec{p})$$

$$\langle\hat{O}\rangle = \langle\psi(t)|\hat{O}|\psi(t)\rangle \rightarrow \langle\hat{O}\rangle = \int d^2\vec{p} \langle\psi(t)|\vec{p}\rangle \langle\vec{p}|\hat{O}|\psi(t)\rangle.$$

$$\psi(\vec{p}, t) = \langle\vec{p}|\psi(t)\rangle, \quad \psi(\vec{p}, t)^* = \langle\vec{p}|\psi(t)\rangle^* = \langle\psi(t)|\vec{p}\rangle$$

$$\langle\vec{p}|\hat{O}|\psi(t)\rangle = \hat{O}(i\hbar \vec{\nabla}_p, \vec{p}), \quad \langle\vec{O}\rangle = \int d^3\vec{p} \psi(\vec{p}, t)^* \hat{O}(i\hbar \vec{\nabla}_p, \vec{p}) \psi(\vec{p}, t).$$

$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$, where $\hat{H} = \frac{\hat{p}^2}{2m} + V(\vec{r}, t)$ becomes

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi(\vec{r}, t) + V(\vec{r}, t) \psi(\vec{r}, t)$$

Commuting operators

If $[\hat{A}, \hat{B}] = 0$ and the states are nondegenerate, $|\psi\rangle$ is a simultaneous eigenstate of \hat{A} and \hat{B} .

$|\psi\rangle = |ab\rangle$, and $\hat{A}|ab\rangle = a|ab\rangle$, $\hat{B}|ab\rangle = b|ab\rangle$

Non-commuting operators and the general uncertainty principle

$$(\Delta A)^2 (\Delta B)^2 \geq (\frac{1}{2i} [\hat{A}, \hat{B}])^2$$

Cannot construct simultaneous eigenstates (which correspond to definite eigenvalues) of non-commuting observables.

Time evolution of expectation value of an operator and Ehrenfest's theorem

Ehrenfest's theorem: how observable \hat{O} 's expectation value in state $|\psi(t)\rangle$

evolves in time, $\frac{d}{dt} \langle\hat{O}\rangle = \langle\frac{\partial \hat{O}}{\partial t}\rangle + \frac{i}{\hbar} \langle[\hat{H}, \hat{O}]\rangle$

For $\hat{O} = \hat{p}$ and a Hamiltonian that is TI, $\frac{d}{dt} \langle\hat{p}\rangle = -\langle\vec{\nabla} V(\vec{r})\rangle$, which is just Newton's Second Law! \rightarrow QM contains all of classical mech.

The simple harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m \omega^2 \hat{x}^2$$

Raising and lowering operators Lowering op: $\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} (\hat{x} + \frac{i}{m\omega} \hat{p})$. Raising op: $\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} (\hat{x} - \frac{i}{m\omega} \hat{p})$.

$$[\hat{a}, \hat{a}^\dagger] = 1 \quad \hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}^\dagger + \hat{a}), \hat{p} = i\sqrt{\frac{m\omega\hbar}{2}} (\hat{a}^\dagger - \hat{a})$$

$$\hat{H} = (\hat{N} + \frac{1}{2}) \hbar \omega, \text{ where } \hat{N} = \hat{a}^\dagger \hat{a}. \text{ Now } \hat{N} \text{ is Hermitian, and } \hat{N}|n\rangle = n|n\rangle$$

$$[\hat{N}, \hat{a}] = -\hat{a}, [\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger$$

$$\hat{N}(\hat{a}|n\rangle) = (n-1)(\hat{a}|n\rangle), \hat{N}(\hat{a}^\dagger|n\rangle) = (n+1)(\hat{a}^\dagger|n\rangle)$$

Normalized number state vectors Energy levels are not degenerate, so $|n-1\rangle = c_n \hat{a}|n\rangle \rightarrow c_n = \frac{1}{\sqrt{n}} \rightarrow \hat{a}|n\rangle = \sqrt{n}|n-1\rangle$.

$$|n+1\rangle = d_n \hat{a}^\dagger|n\rangle \rightarrow d_n = \frac{1}{\sqrt{n+1}} \rightarrow \hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$$

Ground state: $|0\rangle$, excited state: $|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}} |0\rangle$, $n = 0, 1, 2, \dots$

$$\langle n'|\hat{x}|n\rangle = \sqrt{\frac{\hbar}{2m\omega}} \langle n'|(\hat{a}^\dagger + \hat{a})|n\rangle = \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{n+1} \delta_{n', n+1} + \sqrt{n} \delta_{n', n-1})$$

$$\langle n'|\hat{p}|n\rangle = i\sqrt{\frac{m\omega\hbar}{2}} \langle n'|(\hat{a}^\dagger - \hat{a})|n\rangle = i\sqrt{\frac{m\omega\hbar}{2}} (\sqrt{n+1} \delta_{n', n+1} - \sqrt{n} \delta_{n', n-1})$$

Wavefunctions in position representation $E_n = (n + \frac{1}{2}) \hbar \omega$, $n = 0, 1, 2, \dots$

The stationary wavefunctions of definite energy: $\psi_n(x) = \langle x|n\rangle$

$$\langle x'|\hat{a}^\dagger|x''\rangle = \delta(x' - x'') \frac{1}{\sqrt{2\sigma}} (x'' - \sigma^2 \frac{\partial}{\partial x''}), \text{ where } \sigma \equiv \sqrt{\frac{\hbar}{m\omega}}$$

$$\xi = \frac{x}{\sigma}, \quad \langle x|n\rangle = \frac{1}{\sqrt{\pi n! 2^n \sigma}} (\xi - \frac{\partial}{\partial \xi})^n e^{-\frac{1}{2} \xi^2}$$

$$\langle x|0\rangle = (\frac{m\omega}{\pi\hbar})^{1/4} e^{-\frac{m\omega}{2\hbar} x^2}, \quad \langle x|1\rangle = \sqrt{2} (\frac{m\omega}{\pi\hbar})^{1/4} x e^{-\frac{m\omega}{2\hbar} x^2}$$

Classical simple harmonic oscillator Hamiltonian of a simple harmonic is

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2. \quad \dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}, \quad \dot{p} = -\frac{\partial H}{\partial x} = -m \omega^2 x$$

Define $\sqrt{\hbar m \omega} \alpha = \sqrt{\frac{m\omega}{2}} x + \frac{i}{\sqrt{2m\omega}} p$, so $x = \sqrt{\frac{2\hbar}{m\omega}} \alpha_R$ and $p = \sqrt{2m\hbar\omega} \alpha_I$

Rewrite Hamiltonian, $H = \hbar \omega |\alpha|^2$, $\dot{\alpha} = -i \omega \alpha$. The sol is $\alpha = \alpha_0 e^{-i \omega t}$.

The quantum simple harmonic oscillator and coherent state Coherent state, superpos of stat states $|n\rangle$: $|\alpha\rangle = e^{-\frac{1}{2} |\alpha|^2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle$

$$P(n) = |\langle n|\alpha\rangle|^2 = |\alpha_n|^2 = \frac{\langle n\rangle^n e^{-\langle n\rangle}}{n!}, \text{ where } \langle n\rangle = \langle \alpha|a^\dagger a|\alpha\rangle = |\alpha|^2.$$

4. Three-dimensional systems

Three-dimensional infinite square well

$$-\frac{\hbar^2}{2m} (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) \psi(x, y, z) = E \psi(x, y, z) \text{ for } 0 \leq x \leq l_x, \dots$$

while $\psi(x, y, z) = 0$ outside.

Separation of vars: $\psi(x, y, z) = \psi_1(x) \psi_2(y) \psi_3(z)$

\rightarrow SE becomes $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_1(x) = E_1 \psi_1(x)$, ..., where $E = E_1 + E_2 + E_3$.

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} (\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}), \text{ with } n_x, n_y, n_z = 1, 2, \dots$$

Wave vector: $\vec{k} = (k_x, k_y, k_z) = (\frac{n_x \pi}{l_x}, \frac{n_y \pi}{l_y}, \frac{n_z \pi}{l_z})$

The Schrödinger equation in spherical coordinates

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi(\vec{r}, t) + V(\vec{r}) \psi(\vec{r}, t), \text{ where } \vec{r} = (r, \theta, \phi),$$

$\psi(\vec{r}, t) = \psi(r, \theta, \phi, t)$ and $\vec{\nabla}^2 = \frac{1}{r^2} \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$ is Laplacian operator.

For a TI and central potential, potential depends only on r , $V(\vec{r}) = V(r)$.

$$\frac{1}{R(r)} [\frac{d}{dr} [\frac{d}{dr} - \frac{2mr^2}{\hbar^2} (V(r) - E)]] = -Y(\theta, \phi) [\frac{1}{\sin \theta} \frac{d}{d\theta} + \frac{1}{\sin^2 \theta} \frac{d^2 Y(\theta, \phi)}{d\phi^2}]$$

Each side must be constant and equal.

$$\frac{1}{\sin \theta} \frac{d}{d\theta} + \frac{1}{\sin^2 \theta} \frac{d^2 Y(\theta, \phi)}{d\phi^2} = -l(l+1) Y(\theta, \phi)$$

$$\frac{d}{dr} - \frac{2mr^2}{\hbar^2} (V(r) - E) = l(l+1) R(r)$$

Orbital angular momentum $[\hat{L}_i, \hat{L}_j] = i\hbar \epsilon_{ijk} \hat{L}_k$, with $i = 1, 2, 3$

representing the x , y , and z components, and the epsilon tensor is

$\epsilon_{123} = \epsilon_{231} = \epsilon_{312} = 1$, which is -1 for odd perms of indicies, and vanishes when repeated.

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, [\hat{L}^2, \hat{L}_i] = 0$$

$$\text{In pos rep, } \hat{L} = \hat{r} \times \hat{p} = -i\hbar \vec{r} \times \vec{\nabla}$$

In sph coords,

$$\hat{L} = -i\hbar r \hat{r} \times (\frac{\partial}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial}{\partial \theta} \hat{\theta} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \hat{\phi}) = -i\hbar (\hat{\phi} \frac{\partial}{\partial \theta} - \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi})$$

Components along cartesian unit vectors:

$$\hat{r} = \sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y} + \cos \theta \hat{z}$$

$$\hat{\theta} = \cos \theta \cos \phi \hat{x} + \cos \theta \sin \phi \hat{y} - \sin \theta \hat{z}$$

$$\hat{\phi} = -\sin \phi \hat{x} - \cos \phi \hat{y}$$

$$\hat{L}_x = i\hbar (\sin \theta \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi}) \quad \hat{L}_y = i\hbar (-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi})$$

Spherical harmonics Find the sols to the angular eqn. Use sep of vars

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi).$$

$$\frac{1}{\Theta}[\sin\theta\frac{d}{d\theta} + l(l+1)\sin^2\theta = -\frac{1}{\Theta}\frac{d^2\Phi}{d\phi^2} = \text{constant} = m^2$$

$$\Psi(\psi) = e^{im\psi}$$

$\Psi(\psi)$ is periodic in ψ w period 2π gives the constraint $m = 0, \pm 1, \pm 2, \dots$

The eq for $\Theta(\theta)$ can be written in terms of $x \equiv \cos\theta$

$$(1-x^2)\frac{d^2P(x)}{dx^2} - 2x\frac{dP(x)}{dx} + (l(l+1) - \frac{m^2}{1-x^2})P(x) = 0$$

Associated Legendre functions: $P_l^{m_l}(x) = (1-x^2)^{|m_l|/2}(\frac{d}{dx})^{|m_l|}P_l(x)$,

where $P_l(x)$ is the l^{th} Legendre polynomial given by the Rodrigues formula $P_l(x) = \frac{1}{2^l l!}(\frac{d}{dx})^l(x^2-1)^l$, with l taking values $l = 0, 1, 2, \dots$

and for each l , m_l takes $2l+1$ values $m_l = -l, -l+1, \dots, l-1, l$.

Spherical harmonics, normalized angular wave functions:

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos\theta), \text{ where } \epsilon = (-1)^m \text{ for } m \geq 0 \text{ and } \epsilon = 1 \text{ for } m \leq 0.$$

The Legendre polynomials are normalized s.t. they satisfy the ortho relation $\int_{-1}^1 P_l P_l(x) dx = \int_0^\pi P_l(\theta) P_l(\theta) \sin\theta d\theta = \frac{2}{2l+1} \delta_{l'l}$

First few associated Legendre functions:

$$P_0^0(x) = 1, P_1^1(x) = \sqrt{1-x^2}, P_1^0(x) = x, P_2^2(x) = 3(1-x^2), P_2^1(x) = 3x\sqrt{1-x^2}, P_2^0(x) = \frac{1}{2}(3x^2-1)$$

$$P_0^0(\theta) = 1, P_1^1(\theta) = \sin\theta, P_1^0(\theta) = \cos\theta, P_2^2(\theta) = 3\sin^2\theta, P_2^1(\theta) = 3\cos\theta\sin\theta, P_2^0(\theta) = \frac{1}{2}(3\cos^2\theta-1)$$

with $P_l^{-m_l}(x) = P_l^{m_l}(x)$

$$\int_{-1}^1 P_l^{m_l'}(x) P_l^{m_l}(x) dx = \int_0^\pi P_l^{m_l'}(\theta) P_l^{m_l}(\theta) \sin\theta d\theta =$$

$$\frac{(l+m_l)!}{(2l+1)(l-m_l)!} \delta_{l'l} \delta_{m_l'm_l}$$

First few spherical harmonics:

$$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}, Y_1^{\pm 1}(\theta, \phi) = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}, Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

The spherical harmonics satisfy the orthogonality relation

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta Y_{l'}^{m_l'*}(\theta, \phi) Y_l^{m_l}(\theta, \phi) = \delta_{l'l'} \delta_{m_l'm_l}$$

$$\hat{L}^2 |lm_l\rangle = l(l+1)\hbar^2 |lm_l\rangle, \hat{L}_z |lm_l\rangle = m\hbar |lm_l\rangle$$

The spherical harmonics are the wavefunctions in pos rep,

$$Y_l^{m_l}(\theta, \phi) = \langle \vec{r} | lm_l \rangle$$

Parity of the spherical harmonics Cartesian coords:

$$\hat{P}\psi(x, y, z) = \psi(-x, -y, -z)$$

$$\text{Spherical coords: } \hat{P}\psi(r, \theta, \phi) = \psi(r, \pi - \theta, \phi + \theta)$$

For the Legendre polynomials, $\hat{P}P_l^{m_l}(\theta) = (-1)^{l-|m_l|}P_l^{m_l}(\theta) \rightarrow$ even for $l+|m_l|$ even and odd for $l+|m_l|$ odd.

Azimuthal part of the wavefunction, $\hat{P}e^{im_l\phi} = e^{im_l(\phi+\pi)} = (-1)^{m_l}e^{im_l\phi}$.

The spherical harmonics are products of two, and

$$\hat{P}Y_l^{m_l}(\theta, \phi) = Y_l^{m_l}(\pi - \theta, \phi + \pi) = (-1)^{l-|m_l|+m_l}Y_l^{m_l}(\theta, \phi) = (-1)^l Y_l^{m_l}(\theta, \phi)$$

The hydrogen atom

$$\text{Coulomb's law, } \hat{V} = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$\text{Let } u(r) \equiv rR(r), \text{ Radial eq: } -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + [-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}]u = Eu$$

The radial wave function $\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = [1 - \frac{m\epsilon^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{l(l+1)}{(\kappa r)^2}]u$$

$$\text{Introduce } \rho \equiv \kappa r, \rho_0 \equiv \frac{m\epsilon^2}{2\pi\epsilon\hbar^2\kappa}, \frac{d^2u}{d\rho^2} = [1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}]u$$

As $\rho \rightarrow \infty$, the constant term in the brackets dominates, so $\frac{d^2u}{d\rho^2} = u$.

General sol is $u(\rho) = Ae^{-\rho} + Be^{\rho}$, but $B = 0 \rightarrow u(\rho) \approx e^{-\rho}$ for large ρ .

As $\rho \rightarrow 0$, centrifugal term dominates, $\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u$

The general sol is $u(\rho) = C\rho^{l+1} + D\rho^{-l}$, but ρ^{-l} blows up as $\rho \rightarrow 0$, so $D = 0$. Thus, $u(\rho) \approx C\rho^{l+1}$ for small ρ .

Peel off the asymptotic behavior, $u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$

$$\text{Radial eq in terms of } v(\rho), \rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0$$

Assume the solution, $v(\rho)$, can be expressed as a power series in ρ :

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j.$$

$$c_{j+1} = \frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}c_j$$

$$\text{For large } j \text{ (corresponding to large } \rho), c_{j+1} = \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j$$

If this were exact, $c_j = \frac{2^j}{j!}c_0$, $v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!}\rho^j = c_0 e^{2\rho}$, and hence

$u(\rho) = c_0 \rho^{l+1}e^{\rho}$, which blows up at large ρ

Must exist $c_{j_{\max}+1} = 0$, beyond which all coefficients vanish automatically.

Define principle quantum number, $n \equiv j_{\max} + l + 1$, $\rho_0 = 2n$

$$E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{m\epsilon^3}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}$$

$$\text{Bohr formula: } E_n = -[\frac{m_e}{2\hbar^2}(\frac{e^2}{4\pi\epsilon})^2]\frac{1}{n^2} = \frac{E_1}{n^2} = \frac{-13.6 \text{ eV}}{n^2}, n = 1, 2, 3, \dots$$

$$\kappa = (\frac{m_e^2}{4\pi\epsilon_0\hbar^2})\frac{1}{n} = \frac{1}{an}, \text{ Bohr radius: } a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \text{ m}$$

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi)$$

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}$$

For arbitrary n , $l = 0, 1, 2, \dots, n-1$, so $d(n) = \sum_{l=0}^{n-1}(2l+1) = n^2$

$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$, where $L_{q-p}^p(x) \equiv (-1)^p(\frac{d}{dx})^p L_q(x)$ is an associated

Laguerre polynomial. $L_q(x) \equiv e^x(\frac{d}{dx})^q(e^{-x}x^q)$ is the q th Laguerre polynomial.

The normalized hydrogen wavefunctions are:

$$\psi_{nlm} = \sqrt{(\frac{2}{na})^3 \frac{(n-l-1)!}{2n[(n+1)!]^3}} e^{-r/na} (\frac{2r}{na})^l [L_{n-l-1}^{2l+1}(2r/na) Y_l^m(\theta, \phi)]$$

Wavefunctions are mutually orthogonal.

$$\text{Spectrum Transitions: } E_\gamma = E_i - E_f = -13.6\text{eV}(\frac{1}{n_i^2} - \frac{1}{n_f^2})$$

Planck formula, $E_\gamma = h\nu$, wavefunction is $\lambda = c/\nu$.

$$\text{Rydberg formula: } \frac{1}{\lambda} = R(\frac{1}{n_f^2} - \frac{1}{n_i^2})$$

$$\text{Rydberg constant: } R \equiv \frac{m}{4\pi c\hbar^3}(\frac{e^2}{4\pi\epsilon_0})^2 = 1.097 \times 10^7 \text{ m}^{-1}$$

General angular momentum

$$\hat{J} = (\hat{J}_x, \hat{J}_y, \hat{J}_z) = (\hat{J}_1, \hat{J}_2, \hat{J}_3)$$

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$$

The commutation relations are $[\hat{J}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{J}_k$, $[\hat{J}^2, J_i] = 0$

Take the commuting set to be \hat{J}^2 and \hat{J}_z . Now suppose we trade \hat{J}_x and \hat{J}_y for $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$

The commutation relations become $[\hat{J}_+, \hat{J}_-] = 2\hbar\hat{J}_z$ and $[\hat{J}_z, \hat{J}_\pm] = \pm\hbar\hat{J}_\pm$

and $[\hat{J}^2, \hat{J}_\pm] = 0$

Because \hat{J}^2 and \hat{J}_z commute, we can simultaneously diagonalize them. Let the

simultaneous eigenstate be $|ab\rangle$ s.t. $\hat{J}^2|ab\rangle = a|ab\rangle$, $\hat{J}_z|ab\rangle = b|ab\rangle$

$$\hat{J}^2(\hat{J}_\pm|ab\rangle) = a(\hat{J}_\pm|ab\rangle), \text{ so } \hat{J}_\pm|ab\rangle$$

$$(\hat{J}_z\hat{J}_\pm|ab\rangle) = (b \pm \hbar)(\hat{J}_\pm|ab\rangle)$$

Thus, \hat{J}_+ raises and \hat{J}_- lowers the eigenvalue b of \hat{J}_z . Therefore, assuming $|ab\rangle$ is normalized, $\hat{J}_\pm|ab\rangle = c_\pm|ab \pm \hbar\rangle$, where c_\pm are normalization constants.

$$\text{Define } j = \frac{n}{2}, \text{ then } a = b_{\max}^2 + \hbar b_{\max} = j^2\hbar^2 + \hbar^2j = j(j+1)\hbar^2$$

$$\hat{J}_\pm|jm_j\rangle = \hbar\sqrt{(j \mp m_j)(j \pm m_j + 1)}|jm_j \pm 1\rangle$$

The matrix elements of \hat{J}_\pm are

$$\langle j'm'_j|\hat{J}_\pm|jm_j\rangle = \hbar\sqrt{(j \mp m_j)(j \pm m_j + 1)}\langle j'm'_j|jm_j \pm 1\rangle =$$

$$\hbar\sqrt{(j \mp m_j)(j \pm m_j + 1)}\delta_{j'j}\delta_{m'_j m_j \pm 1}$$

Spin

Classical orbital and spinning motion Infinitesimal classical angular momentum corresponding to an infinite linear momentum $d\vec{p} = dm\vec{v}$ at position \vec{r} from the axis of rotation is $d\vec{L} = \vec{r} \times d\vec{p}$

$$\text{The total angular momentum is } \vec{L} = \int \vec{r} \times d\vec{p} = \int \vec{r} \times dm\vec{v}$$

Point particle of mass m at radius r spinning w constant angular velocity ω

about the z -axis, $\vec{L} = I\omega\hat{z} = m\omega r^2\hat{z}$

Considering a particle of mass m and charge q rotating with angular velocity ω at radius r about the z -axis, the angular momentum \vec{L} and the momentum dipole momentum $\vec{\mu}$ are given by $\vec{L} = m\omega r^2\hat{z}$, $\vec{\mu} = \frac{q}{2}\omega r^2\hat{z}$, where we used

$$\mu = I\pi r^2 \text{ with current } I = \frac{q}{2\pi/\omega} = \frac{q\omega}{2\pi}. \text{ Thus, } \vec{\mu} = \frac{q}{2m}\vec{L}$$

Spin

$$\text{Basis vectors are } |\frac{1}{2}, \frac{1}{2}\rangle \equiv |1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, |\frac{1}{2}, \frac{1}{2}\rangle \equiv |1\rangle = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

Construct the matrices for \hat{S}_x , \hat{S}_y , \hat{S}_z , and \hat{S}^2 .

The matrices \hat{S}_z and \hat{S}^2 are diagonal, since they are the ones that are simultaneously diagonalized. The matrix elements are

$$\langle s'm'_s|\hat{S}^2|sm_s\rangle = s(s+1)\hbar^2\delta_{s's}\delta_{m'_s m_s},$$

$$\langle s'm'_s|\hat{S}_z|sm_s\rangle = m_s\hbar\delta_{s's}\delta_{m'_s m_s}$$

$$\text{In matrix form, } \hat{S}^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \hat{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$\hat{S}_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \hat{S}_- = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-) \text{ and } \hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_-), \text{ we have } \hat{S}_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix},$$

$$\hat{S}_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

Spin angular momentum: $\vec{S} = \frac{\vec{\sigma}}{2}$

where the components of $\vec{\sigma}$ are called the Pauli matrices, and given by

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Observe that $[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k$ and $[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k$

A general state of a spin-half system is given by a spinor,

$$|\chi\rangle = \alpha|\frac{1}{2}, \frac{1}{2}\rangle + \beta|\frac{1}{2}, \frac{1}{2}\rangle = \begin{bmatrix} \alpha \\ \beta \end{bmatrix}, \text{ where } \alpha \text{ and } \beta \text{ are complex constants.}$$

Magnetic moment of the electron

Electron in a magnetic field

The Stern-Gerlach experiment

Addition of angular momentum

Triplet and singlet states of a system of two spin-halves

Addition of general angular momentum

Clebsch-Gordon coefficients