

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.

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

Dual vector space $c|\psi\rangle$ is mapped to $c^* \langle\psi|$. 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 $\langle 0| = [1 \quad 0 \quad \cdots]$, $\langle 1| = [0 \quad 1 \quad \cdots]$.

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 $\hat{A}^\dagger = (\hat{A})^T^*$.

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

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

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

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 evcs.

Completeness of eigenvector of a Hermitian operator Set $|a_n\rangle$ is complete if $\sum_n |\langle a_n|\psi\rangle|^2 = 1$. $\sum_n |a_n\rangle\langle a_n| = 1$ (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. $|\alpha'_i\rangle = |\alpha_i\rangle$.

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

4. Subtract components of $|\alpha_3\rangle$ along $|\alpha_1\rangle$ and $|\alpha_2\rangle$, $|\alpha_3\rangle - |\alpha_1\rangle\langle\alpha_1|\alpha_3\rangle - |\alpha_2\rangle\langle\alpha_2|\alpha_3\rangle$, normalize and promote to $|\alpha'_3\rangle$

Position and momentum representation

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

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

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

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

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.

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

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

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

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

$\langle\vec{r}|\hat{O}|\psi(t)\rangle = \hat{O}(\vec{r}, -i\hbar\vec{\nabla})\psi(\vec{r}, t)$, $\langle\hat{O}\rangle = \int d^2\vec{r}\psi(\vec{r}, t)^*\hat{O}(\vec{r}, -i\hbar\vec{\nabla})\psi(\vec{r}, t)$

Operators and wavefunction in momentum representation

$\hat{r} = i\hbar\vec{\nabla}_{\vec{p}}$, or in 1D, $\hat{x} = i\hbar\frac{\partial}{\partial p}$, $\hat{p} = \vec{p}$, where $\vec{p}^* = \vec{p}$.

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

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

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

$\langle\vec{p}|\hat{O}|\psi(t)\rangle = \hat{O}(i\hbar\vec{\nabla}_{\vec{p}}, \vec{p})\psi(\vec{p}, t)$, $\langle\hat{O}\rangle = \int d^2\vec{p}\psi(\vec{p}, t)^*\hat{O}(i\hbar\vec{\nabla}_{\vec{p}}, \vec{p})\psi(\vec{p}, t)$.

$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$, 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, $\frac{d}{dt}\langle\hat{O}\rangle = \langle\frac{\partial\hat{O}}{\partial t}\rangle + \frac{i}{\hbar}[\hat{H}, \langle\hat{O}\rangle]$

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: $\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} - \frac{i}{m\omega}\hat{p})$.

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

$\hat{H} = (\hat{N} + \frac{1}{2})\hbar\omega$, where $\hat{N} = \hat{a}^\dagger\hat{a}$. Now \hat{N} 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: $\psi_n(x) = \langle x|n\rangle$

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

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

$\langle x|0\rangle = (\frac{m\omega}{\pi\hbar})^{1/4}e^{-\frac{m\omega}{2\hbar}x^2}$, $\langle x|1\rangle = \sqrt{2}(\frac{m^3\omega^3}{\pi\hbar^3})^{1/4}xe^{-\frac{m\omega}{2\hbar}x^2}$

Classical simple harmonic oscillator Hamiltonian of a simple harmonic is

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

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

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 $|n\rangle$: $|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}|n\rangle$

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

4. Three-dimensional systems

Three-dimensional infinite square well

$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})\psi(x, y, z) = E\psi(x, y, z)$ 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 $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_1(x) = E_1\psi_1(x), \dots$, where $E = E_1 + E_2 + E_3$.

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

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

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

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

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

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

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

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

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

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

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

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

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

$\Psi(\psi)$ 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

$$P_l(x) = \frac{1}{2^l l!} (\frac{d}{dx})^l (x^2 - 1)^l, \text{ with } l \text{ taking values } l = 0, 1, 2, \dots$$

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,

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

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

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

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

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

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

$$\text{Introduce } \rho \equiv \kappa r, \rho_0 \equiv \frac{m e^2}{2\pi\epsilon_0 \hbar^2 \kappa}, \frac{d^2u}{d\rho^2} = [1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}]u$$

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, $n \equiv j_{\max} + l + 1$, $\rho_0 = 2n$

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

$$\text{Bohr formula: } E_n = -[\frac{m_e}{2\hbar^2} (\frac{e^2}{4\pi\epsilon_0})^2] \frac{1}{n^2} = \frac{E_1}{n^2} = \frac{-13.6 \text{ eV}}{n^2}, n = 1, 2, 3, \dots$$

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

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

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

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

$v(\rho) = L_{n-1}^{2l+1}(2\rho)$, 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.

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

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

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

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

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

