3. Principles of QM

Axiomatic principles

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

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

Time evolution axiom: $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \widehat{H}|\psi(t)\rangle$, 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 nth 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 $\langle\psi| = \begin{bmatrix}\cdots & \alpha^* & \cdots\end{bmatrix}$.

Dual basis vectors are $\langle 0| = \begin{bmatrix}1 & 0 & \cdots\end{bmatrix}, \cdots, \langle n| \begin{bmatrix}0 & \cdots & 1\end{bmatrix}$.

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

Properties of operators

Hermitian conjugate (Hermitian adjoint) operator in the dual space

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

$$(\widehat{A}|\psi\rangle)^\dagger = |\psi\rangle^\dagger\widehat{A}^\dagger = \langle\psi|\widehat{A}^\dagger \qquad \langle\psi| = |\psi\rangle^\dagger \qquad \langle\psi|^\dagger = |\psi\rangle$$

$$(\widehat{A}\widehat{B})^\dagger = (\widehat{A}\widehat{B})^{T*} = (\widehat{B}^T\widehat{A}^T)^* = \widehat{B}^{T*}\widehat{A}^{T*} = \widehat{B}^\dagger\widehat{A}^\dagger, \quad (c\widehat{A})^\dagger = c^*\widehat{A}^\dagger$$

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

Matrix elements of operators

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

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

Hermitian operators : $\widehat{A}^\dagger = \widehat{A}$, so given $\widehat{A}|\phi\rangle$ in the vector space, we have $\langle\psi|\widehat{A}^\dagger = \langle\phi|\widehat{A}$ in the dual vector space.

Matrix elements of a Hermitian operator

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

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

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

Eigenvals and eigenvecs of Hermitian operators : $\widehat{A}|a_n\rangle = a_n|a_n\rangle$

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

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

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

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 $\alpha_i = \frac{\alpha_i}{\sqrt{\langle a_i|a_i\rangle}}$. 2. $|\alpha_1'\rangle = |\alpha_1\rangle$.

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

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

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

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

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

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

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

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

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

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, $\langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{-\frac{i}{\hbar}px}$ (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: $\widehat{\vec r} = \vec r$, $\widehat{\vec p} = -i\hbar\vec\nabla$.

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

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

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

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

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

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

Operators and wavefunction in momentum representation $\widehat{\vec r} = i\hbar\vec\nabla_{\vec p}$, or in 1D, $\widehat x = i\hbar\frac{\partial}{\partial p}$, $\widehat{\vec p} = \vec p$, where $\vec p^* = \vec p$.

$\widehat O(\widehat{\vec r}, \widehat{\vec p}) = \widehat O(i\hbar\vec\nabla_{\vec p}, \vec p)$

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

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

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

$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \widehat H|\psi(t)\rangle$, where $\widehat H = \frac{\widehat{\vec p}^2}{2m} + V(\widehat{\vec r}, t)$ 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 $[\widehat A, \widehat B] = 0$ and the states are nondegenerate, $|\psi\rangle$ is a simultaneous eigenstate of $\widehat A$ and $\widehat B$.

$|\psi\rangle = |ab\rangle$, and $\widehat A|ab\rangle = a|ab\rangle$, $\widehat B|ab\rangle = b|ab\rangle$

Non-commuting operators and the general uncertainty principle

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

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 $\widehat O$'s expectation value in state $|\psi(t)\rangle$ evolves in time, $\frac{d}{dt}\langle\widehat O\rangle = \langle\frac{\partial\widehat O}{\partial t}\rangle + \frac{i}{\hbar}\langle[\widehat H, \widehat O]\rangle$

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

The simple harmonic oscillator

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

Raising and lowering operators Lowering op: $\widehat a = \sqrt{\frac{m\omega}{2\hbar}}(\widehat x + \frac{i}{m\omega}\widehat p)$,

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

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

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

$[\widehat N, \widehat a] = -\widehat a$, $[\widehat N, \widehat a^\dagger] = \widehat a^\dagger$

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

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

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

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

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

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

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

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

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

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

$\langle x|0\rangle = (\frac{m\omega}{\pi\hbar})^{1/4}e^{-\frac{m\omega}{2\hbar}x^2}, \qquad \langle x|1\rangle = \sqrt2(\frac{m^3\omega^3}{\pi\hbar^3})^{1/4}xe^{-\frac{m\omega}{2\hbar}x^2}$

Classical simple harmonic oscillator Hamiltonian of a simple harmonic is $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2. \qquad \dot x = \frac{\partial H}{\partial p} = \frac{p}{m}, \qquad \dot p = -\frac{\partial H}{\partial x} = -m\omega^2x$

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

Rewrite Hamiltonian, $H = \hbar\omega|\alpha|^2, \qquad \dot\alpha = -i\omega\alpha$. The sol is $\alpha = \alpha_0e^{-i\omega t}$.

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 $0 \leq x \leq l_x, ...$ 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 $E = E_1 + E_2 + E_3$.

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

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

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, $V(\vec r) = V(r)$.

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

Each side must be constant and equal.

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

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

Orbital angular momentum $[\widehat{L}_i, \widehat{L}_j] = i\hbar\epsilon_{ijk}\widehat{L}_k$, 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.
$\widehat{\vec{L}}^2 = \widehat{\vec{L}}_x^2+\widehat{\vec{L}}_y^2+\widehat{\vec{L}}_z^2$, $[\widehat{L^2},\widehat{L}_i]=0$
In pos rep, $\widehat{\vec{L}} = \widehat{\vec r}\times\widehat{\vec p} = -i\hbar\vec r\times\vec\nabla$
In sph coords,
$\widehat{\vec L} = -i\hbar r\hat r\times(\frac{\partial}{\partial r}\hat r + \frac1r\frac{\partial}{\partial\theta}\hat\theta + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\hat\phi = -i\hbar(\hat\phi\frac{\partial}{\partial\theta} - \hat\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$
Components along cartesian unit vectors:
$\hat r = \sin\theta\cos\psi\hat x + \sin\theta\sin\phi\hat y+\cos\theta\hat z$
$\hat\theta=\cos\theta\cos\phi\hat x+\cos\theta\sin\phi\hat y - \sin\theta\hat z$
$\hat\phi = -\sin\phi\hat x - \cos\phi\hat y$
$\widehat L_x = i\hbar(\sin\theta\frac{\partial}{\partial\theta}+\cot\theta\cos\phi\frac{\partial}{\partial\phi})$ $\widehat L_y = i\hbar(-\cos\phi\frac{\partial}{\partial\theta}+\cot\theta\sin\phi\frac{\partial}{\partial\phi})$
$\widehat L_z = -i\hbar\frac{\partial}{\partial\phi}$ $\widehat{\vec L}^2 = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}]$
$\widehat{\vec L}Y(\theta,\phi) = l(l+1)\hbar^2Y(\theta,\phi)$
$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr} - V_{\rm eff}(r)R(r) = ER(r)$, $V_{\rm eff}(r)=V(r)+\frac{l(l+1)\hbar^2}{2mr^2}$

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 $m=0,\pm1,\pm2,\cdots$
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 $l=0,1,2,...$ and for each l, m_l takes $2l+1$ values $m_l=-l,-l+1,...,l-1,l$.
Spherical harmonics, normalized angular wave functions:
$Y_l^m(\theta,\phi)=\epsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}e^{im\phi}P_l^m(\cos\theta)$, where $\epsilon=(-1)^m$ for $m\ge0$ and $\epsilon=1$ for $m\le0$.
The Legendre polynomials are normalized s.t. they satisfy the ortho relation $\int_{-1}1P_{l'}P_l(x)dx = \int_0^\pi P_{l'}(\theta)P_l(\theta)\sin\theta d\theta = \frac{2}{2l+1}\delta_{l'l}$
First few associated Legendre functions:
$P_0^0(x)=1, P_1^1(x)=\sqrt{1-x^2}, P_1^0(x)=x, P_2^2(x)=3(1-x^2), P_2^1(x)=3x\sqrt{1-x^2}, P_2^0=\frac12(3x^2-1)$
$P_0^0(\theta)=1, P_1^1(\theta)=\sin\theta, P_1^0(\theta)=\cos\theta, P_2^2(\theta)=3\sin^2\theta, P_2^1(\theta)=3\cos\theta\sin\theta, P_2^0(\theta)=\frac12(3\cos^2\theta-1)$
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:
$Y_0^0(\theta,\phi)=\frac{1}{\sqrt{4\pi}}, Y_1^{\pm1}(\theta,\phi)=\mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}, Y_1^0(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta$
The spherical harmonics satisfy the orthogonality relation
$\int_0^{2\pi}d\phi\int_0^\pi d\theta\sin\theta Y_{l'}^{m_l'*}(\theta,\phi)Y_l^{m_l}(\theta,\phi)=\delta_{l'l}\delta_{m_l'm_l}$
$\widehat{\vec L}^2|lm_l\rangle = l(l+1)\hbar^2|lm_l\rangle$, $\widehat L_z|lm_l\rangle = m\hbar|lm_l\rangle$
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:
$\widehat P\psi(x,y,z)=\psi(-x,-y,-z)$
Spherical coords: $\widehat P\psi(r,\theta,\phi)=\psi(r,\pi-\theta,\phi+\theta)$
For the Legendre polynomials, $\widehat PP_l^{m_l}(\theta)=(-1)^{l-|m_l|}P_l^{m_l}(\theta)\to$ even for $l+|m_l|$ even and odd for $l+|m_l|$ odd.
Azimuthal part of the wavefunction, $\widehat Pe^{im_l\phi}=e^{im_l(\phi+\pi)}=(-1)^{m_l}e^{im_l\phi}$.
The spherical harmonics are products of two, and
$\widehat PY_l^{m_l}(\theta,\phi)=Y_l^{m_l}(\pi-\theta,\phi+\pi)=(-1)^{l-|m_l|+m_l}Y_l^{m_l}(\theta,\phi)=(-1)^lY_l^{m_l}(\theta,\phi)$

The hydrogen atom

Coulomb's law, $\widehat V = -\frac{e^2}{4\pi\epsilon_0}\frac1r$
Let $u(r)\equiv rR(r)$, Radial eq: $-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+[-\frac{e^2}{4\pi\epsilon_0}\frac1r+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}]u=Eu$

The radial wave function
$\kappa\equiv\frac{\sqrt{-2mE}}{\hbar}$. Divide by E, $\frac{1}{\kappa^2}\frac{d^2u}{dr^2}=[1-\frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)}+\frac{l(l+1)}{(\kappa r)^2}]u$
Introduce $\rho\equiv\kappa r$, $\rho_0\equiv\frac{me^2}{2\pi\epsilon\hbar^2\kappa}$, $\frac{d^2u}{d\rho^2}=[1-\frac{\rho_0}{\rho}+\frac{l(l+1)}{\rho^2}]u$
As $\rho\to\infty$, 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 $B=0\to u(\rho)=Ae^{-\rho}$ for large ρ.
As $\rho\to0$, centriugal 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 $\rho\to0$, so $D=0$. Thus, $u(\rho)\approx Cp^{l+1}$ for small ρ.
Peel off the asymptotic behavior, let $u(\rho)=\rho^{l+1}e^{-\rho}v(\rho)$
$\frac{du}{d\rho}=\rho^le^{-\rho}[(l+1-\rho)v+\rho\frac{dv}{d\rho}]$
$\frac{d^2u}{d\rho^2}=\rho^le^{-\rho}\{[-2l-2+\rho+\frac{l(l+1)}{\rho}]v+2(l+1-\rho)\frac{dv}{d\rho}+\rho\frac{d^2v}{d\rho^2}\}$
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 $v(p)$ can be expressed as a power series in ρ: $v(\rho)=\sum_{j=0}^\infty c_j\rho^j$.
$\frac{dv}{d\rho}=\sum_{j=0}^\infty jc_j\rho^{j-1}=\sum_{j=0}^\infty(j+1)c_{j+1}\rho^j$,
$\frac{d^2v}{d\rho^2}=\sum_{j=0}^\infty j(j+1)c_{j+1}\rho^{j-1}$
$j(j+1)c_{j+1}+2(l+1)(j+1)c_{j+1}-2jc_j+[\rho_0-2(l+1)]c_j=0$
$c_{j+1}=\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}c_j$
For large j (corresponding to large ρ), $c_{j+1}=\frac{2j}{j(j+1)}c_j=\frac{2}{j+1}c_j$
If this were exact, $c_j=\frac{2^j}{j!}c_0$, $v(\rho)=c_0\sum_{j=0}^\infty\frac{2^j}{j!}\rho^j=c_0e^{2\rho}$, and hence $u(\rho)=c_0\rho^{l+1}e^\rho$, which blows up at large ρ
$\exists c_{j\max+1}=0$, so $2(j_{max}+l+1)-\rho_0=0$.
Define principle quantum number, $n\equiv j_{\max}+l+1$, so $\rho_0=2n$
$E=-\frac{\hbar^2\kappa^2}{2m}=-\frac{me^3}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}$
Bohr formula: $E_n=-[\frac{m}{2\hbar^2}(\frac{e^2}{4\pi\epsilon})^2]\frac{1}{n^2}=\frac{E_1}{n^2}=\frac{-13.6\text{ eV}}{n^2}$, $n=1,2,3,...$
$\kappa=(\frac{me^2}{4\pi\epsilon_0\hbar^2})\frac1n=\frac{1}{an}$, Bohr radius: $a\equiv\frac{4\pi\epsilon_0\hbar^2}{me^2}=0.529\times10^{-10}\text{m}$
$\psi_{nlm}(r,\theta,\phi)=R_{nl}(r)Y_l^m(\theta,\phi)$, $\psi_{100}(r,\theta,\phi)=\frac{1}{\sqrt{\pi a^3}}e^{-r/a}$
For arbitrary n, $l=0,1,...,n-1$, so $d(n)=2\sum_{l=0}^{n-1}(2l+1)=2n^2$
$v(\rho)=L_{n-l-1}^{2l+1}(2\rho)$, where $L_{q-p}^p(x)\equiv(-1)^p(\frac{d}{dx})^pL_q(x)$ is an associated Laguerre polynomial. $L_q(x)\equiv e^x(\frac{d}{dx})^q(e^{-x}x^q)$ is the qth Laguerre polynomial.
Normalized hydrogen wavefunctions:
$$\psi_{nlm}=\sqrt{(\frac{2}{na})^3\frac{(n-l-1)!}{2n[(n+1)!]^3}}e^{-r/na}(\frac{2r}{na})^l[L_{n-l-1}^{2l+1}(2r/na)Y_l^m(\theta,\phi)$$
Wavefunctions are mutually orthogonal.

Spectrum Transitions: $E_\gamma=E_i-E_f=-13.6eV(\frac{1}{n_i^2}-\frac{1}{n_f^2})$
Planck formula, $E_\gamma=h\nu$, wavefunction is $\lambda=c/\nu$.
Rydberg formula: $\frac1\lambda=R(\frac{1}{n_f^2}-\frac{1}{n_i^2})$
Rydberg constant: $R\equiv\frac{m}{4\pi c\hbar^3}(\frac{e^2}{4\pi\epsilon_0})^2=1.097\times10^7\ \text{m}^{-1}$

General angular momentum

$\widehat{\vec J}=(\widehat J_x,\widehat J_y,\widehat J_z)=(\widehat J_1,\widehat J_2,\widehat J_3)$
$\widehat{\vec J}^2=\widehat{\vec J}_x^2+\widehat{\vec J}_y^2+\widehat{\vec J}_z^2$
The commutation relations are $[\widehat J_i,\widehat J_j]=i\hbar\epsilon_{ijk}\widehat J_k$, $[\widehat{\vec J}^2,J_i]=0$
Take the commuting set to be $\widehat{\vec J}^2$ and $\widehat J_z$. Now suppose we trade $\widehat J_x$ and $\widehat J_y$ for $\widehat J_\pm=\widehat J_x\pm i\widehat J_y$
The commutation relations become $[\widehat J_+,\widehat J_-]=2\hbar\widehat J_z$ and $[\widehat J_z,\widehat J_\pm]=\pm\hbar\widehat J_\pm$ and $[\widehat{\vec J}^2,\widehat J_\pm]=0$

Because $\widehat{\vec J}^2$ and $\widehat J_z$ commute, we can simulaneously diagonalize them. Let the simultaneous eigenstate be $|ab\rangle$ s.t. $\widehat{\vec J}^2|ab\rangle=a|ab\rangle$, $\widehat J_z|ab\rangle=b|ab\rangle$
$\widehat{\vec J}^2(\widehat J_\pm|ab\rangle)=a(\widehat J_\pm|ab\rangle)$, so $\widehat J_\pm|ab\rangle$
$\widehat J_z(\widehat J_\pm|ab\rangle)=(b\pm\hbar)(\widehat J_\pm|ab\rangle)$
Thus, $\widehat J_+$ raises and $\widehat J_-$ lowers the eigenvalue b of $\widehat J_z$. Therefore, assuming $|ab\rangle$ is normalized, $\widehat J_\pm|ab\rangle=c_\pm|ab\pm\hbar\rangle$, where $c_\pm$ are normalization constants.
Define $j=\frac{n}{2}$, then $a=b_{\max}^2+\hbar b_{\max}=j^2\hbar^2+\hbar^2j=j(j+1)\hbar^2$
$\widehat J_\pm|jm_j\rangle=\hbar\sqrt{(j\mp m_j)(j\pm m_j+1)}|jm_j\pm1\rangle$
The matrix elements of $\widehat J_\pm$ are
$\langle j'm_j'|\widehat J_\pm|jm_j\rangle=\hbar\sqrt{(j\mp m_j)(j\pm m_j+1)}\langle j'm_j'|jm_j\pm1\rangle=\hbar\sqrt{(j\mp m_j)(j\pm m_j+1)}\delta_{j'j}\delta_{m_j'm_j\pm1}$

Spin

Classical orbital and spinning motion Infinitesimal classical angular momentum corresponsing to an infinite linear momentum $d\vec p=dm\vec v$ at position $\vec r$ from the axis of rotation is $d\vec L=\vec r\times d\vec p$
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 $\vec L=m\omega r^2\hat z$, $\vec\mu=\frac q2\omega r^2\hat z$, where we used $\mu=I\pi r^2$ with current $I=\frac{q}{2\pi/\omega}=\frac{q\omega}{2\pi}$. Thus, $\vec\mu=\frac{q}{2m}\vec L$

Spin
Basis vectors are $|\frac12,\frac12\rangle\equiv|1\rangle=\begin{bmatrix}1\\0\end{bmatrix}$, $|\frac12,-\frac12\rangle\equiv|2\rangle=\begin{bmatrix}0\\1\end{bmatrix}$
Construct the matrices for $\widehat S_x$, $\widehat S_y$, $\widehat S_z$, and $\widehat{\vec S}^2$.
The matrices $\widehat S_z$ and $\widehat{\vec S}^2$ are diagonal, since they are the ones that are simultaneously diagonalized. The matrix elements are
$\langle s'm_s'|\widehat{\vec S}^2|sm_s\rangle=s(s+1)\hbar^2\delta_{s's}\delta_{m_s'm_s}$,
$\langle s'm_s'|\widehat S_z|sm_s\rangle=m_s\hbar\delta_{s's}\delta_{m_s'm_s}$
In matrix form, $\widehat{\vec S}^2=\frac34\hbar^2\begin{bmatrix}1&0\\0&1\end{bmatrix}$, $\widehat S_z=\frac\hbar2\begin{bmatrix}1&0\\0&-1\end{bmatrix}$
$\widehat S_+=\hbar\begin{bmatrix}0&1\\0&0\end{bmatrix}$, $\widehat S_-=\frac\hbar2\begin{bmatrix}1&0\\0&-1\end{bmatrix}$, $\widehat S_x=\frac12(\widehat S_++\widehat S_-)$,
$\widehat S_y=\frac{1}{2i}(\widehat S_+-\widehat S_-)$, $\widehat S_x=\frac\hbar2\begin{bmatrix}0&1\\1&0\end{bmatrix}$, $\widehat S_y=\frac\hbar2\begin{bmatrix}0&-i\\i&0\end{bmatrix}$
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 $[\widehat S_i,\widehat S_j]=i\hbar\epsilon_{ijk}\widehat S_k$ and $[\sigma_i,\sigma_j]=2i\epsilon_{ijk}\sigma_k$
A general state of a spin-half system is given by a spinor,
$|\chi\rangle=\alpha|\frac12,\frac12\rangle+\beta|\frac12,\frac12\rangle=\begin{bmatrix}\alpha\\\beta\end{bmatrix}$, where α and β are complex constants.

Magnetic moment of the electron $\vec\mu=g\frac{q}{2m}\vec S$
For the electron, $q=-e$, and $\vec\mu=-g\frac{e}{2m}\vec S$
The corresponding operator: $\widehat{\vec\mu}=-g\frac{e}{2m}\widehat{\vec S}=-\frac g2\frac{e\hbar}{2m}\vec\sigma=-\frac g2\mu_B\vec\sigma$, where $\mu_B=\frac{e\hbar}{2m}$ is called Bohr magneton.

Electron in a magnetic field Free electron at rest in an external magnetic field $\vec B$. Electron has intrinsic magnetic moment due to intrinsic spin angular momentum, $\widehat H=\widehat V=-\widehat{\vec\mu}\cdot\vec B$
For a magnetic field along the z-axis, $\vec B=B\hat z$, and
$\widehat H=-\widehat\mu_zB=-(-\frac g2\frac em\vec S)\dot B\hat z=\frac g2\frac{eB}{m}S_z=\omega_sS_z=\frac g2\frac{eB\hbar}{2m}\sigma_z$, where $\omega_s=\frac g2\frac{eB}{m}=\frac g2\omega_c$ is called the spin precession (or Larmor) frequency and $w_c=\frac{eB}{m}$ is called cyclotron frequency. The g-factor has an approximate value $g\approx2$ (but not exactly). Therefore, the spin precession frequency ω_s is not equal to the cyclotron frequency.

Rewrite Hamiltonian as $\widehat{H} = \omega_s S_z$. In the bases in which $\widehat{\vec{S}}$ and $\widehat{S}_z$ are diagonalized, the eigenstates are given by
$\widehat{H}|\frac{1}{2},\frac{1}{2}\rangle = \omega_s \widehat{S}_z|\frac{1}{2},\frac{1}{2}\rangle = \frac{1}{2}\hbar\omega_s|\frac{1}{2},\frac{1}{2}\rangle$,
$\widehat{H}|\frac{1}{2},-\frac{1}{2}\rangle = \omega_s \widehat{S}_z|\frac{1}{2},-\frac{1}{2}\rangle = -\frac{1}{2}\hbar\omega_s|\frac{1}{2},-\frac{1}{2}\rangle$
The interaction of the spin of the electron w the external magentic field leads to two energy levls. Correspond to spin-up state and spin-down state, with a gap of $\hbar\omega_s$ btwn them.

The Stern-Gerlach experiment

Force on electron w spin-up: $\vec{F}_1 = -\vec{\boldsymbol{\nabla}} V_1 = \frac{1}{2}\hbar\vec{\boldsymbol{\nabla}}\omega_s = \frac{g}{2}\frac{e\hbar}{2m}\frac{\partial B(z)}{\partial z}$
Force on electron w spin-down: $\vec{F}_2 = -\vec{\boldsymbol{\nabla}} V_2 = -\frac{1}{2}\hbar\vec{\boldsymbol{\nabla}}\omega_s = -\frac{g}{2}\frac{e\hbar}{2m}\frac{\partial B(z)}{\partial z}$
Electrons are deflected up or down depending on whether they are spin-up or spin-down along $\vec{B}$.

Addition of angular momentum

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

$|j_1, m_{j1}\rangle \otimes |j_2, m_{j2}\rangle$
The total values of j ranges from the largest value of m_j to the smallest value of m_j in steps on unity.
$\widehat{\vec{J}}^2 = \widehat{\vec{J}}_1^2 \otimes 1 + 1 \otimes \widehat{\vec{J}}_2^2 + 2\widehat{J}_{1z} \otimes \widehat{J}_{2z} + \widehat{J}_{1+} \otimes \widehat{J}_{2-} + \widehat{J}_{1-} \otimes \widehat{J}_{2+}$
For spin angular momentum, we interchangeably use $\widehat{\vec{S}}$ for $\widehat{\vec{J}}$ as we mentioned earlier, and the quantum numbers s and m_s for j and m_j.

Addition of general angular momentum

$|j_1 + j_2, j_1 + j_2\rangle = |j_1, m_{j1}\rangle \otimes |j_2, m_{j2}\rangle$
$j = j_1 \otimes j_2 = j_1 + j_2 \oplus j_1 + j_2 - 1 \oplus j_1 + j_2 - 2 \oplus \cdots \oplus |j_1 - j_2|$
Clebsch-Gordon coefficients $|j_1, m_{j1}\rangle \otimes |j_2, m_{j2}\rangle = |j_1, m_{j1}; j_2, m_{j2}\rangle$
$|j, m_j\rangle = \sum_{m_j = m_{j1} + m_{j2}} \langle j_1, m_{j1}; j_2, m_{j2}|j, m_j\rangle |j_1, m_{j1}; j_2, m_{j2}\rangle$
where $\langle j_1, m_{j1}; j_2, m_{j2}; j, m_j\rangle$ are Clebsch-Gordon coefficients.