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 $\widehat{A}$, 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.
$\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^* \to \langle\psi|\psi\rangle$ 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.
$\int da'\langle a'|\widehat{A}|a\rangle = a\int da'\langle a'|a\rangle = \int da'a'\langle a'|a\rangle \to \langle a'|a\rangle = \delta(a'-a)$
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 $\to$ 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. $|\alpha_2'\rangle = \frac{|\alpha_2\rangle - |\alpha_1\rangle\langle\alpha_1|\alpha_2\rangle}{\sqrt{\langle\alpha_2|\alpha_2\rangle - \langle\alpha_1|\alpha_2\rangle\langle\alpha_2|\alpha_1\rangle}} = \frac{|\alpha_2\rangle - |\alpha_1\rangle\langle\alpha_1|\alpha_2\rangle}{\sqrt{1 - \langle\alpha_1|\alpha_2\rangle\langle\alpha_2|\alpha_1\rangle}}$
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 $\langle\widehat{O}\rangle = \int d^2\vec{r}\langle\psi(t)|\vec{r}\rangle\langle\vec{r}|\widehat{O}|\psi(t)\rangle$
$\psi(\vec{r},t) = \langle\vec{r}|\psi(t)\rangle, \qquad \psi(\vec{r},t)^* = \langle\vec{r}|\psi(t)\rangle^* = \langle\psi(t)|\vec{r}\rangle$,
$\langle\vec{r}|\widehat{O}|\psi(t)\rangle = \widehat{O}(\vec{r}, -i\hbar\vec{\nabla})\psi(\vec{r},t), \langle\vec{O}\rangle = \int d^3\vec{r}\psi(\vec{r},t)^*\vec{O}(\vec{r}, -i\hbar\vec{\nabla})\psi(\vec{r},t)$
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 $\vec{p}^* = \vec{p}$.
$\widehat{\vec{O}}(\widehat{\vec{r}},\widehat{\vec{p}}) = \widehat{O}(i\hbar\vec{\nabla}_{\vec{p}},\vec{p})$
$\langle\widehat{O}\rangle = \langle\psi(t)|\widehat{O}|\psi(t)\rangle \to \langle\widehat{O}\rangle = \int d^2\vec{p}\langle\psi(t)|\vec{p}\rangle\langle\vec{p}|\widehat{O}|\psi(t)\rangle$.
$\psi(\vec{p},t) = \langle\vec{p}|\psi(t)\rangle, \qquad \psi(\vec{p},t)^* = \langle\vec{p}\psi(t)\rangle^* = \langle\psi(t)|\vec{p}\rangle$
$\langle\vec{p}|\widehat{O}|\psi(t)\rangle = \widehat{O}(i\hbar\vec{\nabla}_{\vec{p}},\vec{p}), \langle\vec{O}\rangle = \int d^3\vec{p}\psi(\vec{p},t)^*\widehat{O}(i\hbar\vec{\nabla}_{\vec{p}},\vec{p})\psi(\vec{p},t)$.

$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \widehat{H}|\psi(t)\rangle$, 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! $\to$ 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
$|n-1\rangle = c_n\widehat{a}|n\rangle \to c_n = \frac{1}{\sqrt{n}} \to \widehat{a}|n\rangle = \sqrt{n}|n-1\rangle$.
$|n+1\rangle = d_n\widehat{a}^\dagger|n\rangle \to d_n = \frac{1}{\sqrt{n+1}} \to \widehat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$
Ground state: $|0\rangle$, excited state: $|n\rangle = \frac{(\widehat{a}^\dagger)^n}{\sqrt{n!}}|0\rangle$, $n = 0,1,2,\ldots$
$\langle n'|\widehat{x}|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle n'|(\widehat{a}^\dagger + \widehat{a})|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n+1}\delta_{n',n+1} + \sqrt{n}\delta_{n',n-1})$
$\langle n'|\widehat{p}|n\rangle = i\sqrt{\frac{m\omega\hbar}{2}}\langle n'|(\widehat{a}^\dagger - \widehat{a})|n\rangle = i\sqrt{\frac{m\omega\hbar}{2}}(\sqrt{n+1}\delta_{n',n+1} - \sqrt{n}\delta_{n',n-1})$
Wavefunctions in position representation
$E_n = (n + \frac{1}{2})\hbar\omega, n = 0,1,2,\ldots$
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 $\sigma \equiv \sqrt{\frac{\hbar}{m\omega}}$
$\xi = \frac{x}{\sigma}, \qquad \langle x|n\rangle = \frac{1}{\sqrt{\sqrt{\pi}n!2^n\sigma}}(\xi - \frac{\partial}{\partial\xi})^n e^{-\frac{1}{2}\xi^2}$
$\langle x|0\rangle = (\frac{m\omega}{\pi\hbar})^{1/4}e^{-\frac{m\omega}{2\hbar}x^2}, \qquad \langle x|1\rangle = \sqrt{2}(\frac{m^3\omega^3}{\pi\hbar^3})^{1/4}xe^{-\frac{m\omega}{2\hbar}x^2}$
Classical simple harmonic oscillator Hamiltonian of a simple harmonic is
$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2. \qquad \dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}, \qquad \dot{p} = -\frac{\partial H}{\partial x} = -m\omega^2x$
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 $0 \leq x \leq l_x, \ldots$
while $\psi(x,y,z) = 0$ outside.
Separation of vars: $\psi(x,y,z) = \psi_1(x)\psi_2(y)\psi_3(z)$
$\to$ SE becomes $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_1(x) = E_1\psi_1(x), \ldots$, 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 $n_x, n_y, n_z = 1,2,\ldots$.
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.
$\widehat{\vec{L}}^2 = \widehat{\vec{L}}_x^2 + \widehat{\vec{L}}_y^2 + \widehat{\vec{L}}_z^2$, $[\widehat{\vec{L}^2},\widehat{L}_i] = 0$
In pos rep, $\widehat{\vec{L}} = \widehat{\vec{r}} \times \widehat{\vec{p}} = -i\hbar\vec{r} \times \vec{\nabla}$
In sph coords,
$\widehat{\vec{L}} = -i\hbar r\widehat{r} \times (\frac{\partial}{\partial r}\widehat{r} + \frac{1}{r}\frac{\partial}{\partial\theta}\widehat{\theta} + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\widehat{\phi} = -i\hbar(\widehat{\phi}\frac{\partial}{\partial\theta} - \widehat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$
Components along cartesian unit vectors:
$\widehat{r} = \sin\theta\cos\psi\widehat{x} + \sin\theta\sin\phi\widehat{y} + \cos\theta\widehat{z}$
$\widehat{\theta} = \cos\theta\cos\phi\widehat{x} + \cos\theta\sin\phi\widehat{y} - \sin\theta\widehat{z}$
$\widehat{\phi} = -\sin\phi\widehat{x} - \cos\phi\widehat{y}$
$\widehat{L}_x = i\hbar(\sin\theta\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi})$ $\widehat{L}_y = i\hbar(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi})$
$\widehat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$ $\widehat{\vec{L}}^2 = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}]$
$\widehat{\vec{L}}Y(\theta,\phi) = l(l+1)\hbar^2Y(\theta,\phi)$
$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr} - V_{\text{eff}}(r)R(r) = ER(r)$, $V_{\text{eff}}(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2}$

Spherical harmonics

Find the sols to the angular eqn. Use sep of vars $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$.

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

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

$\Psi(\psi)$ 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 $x\equiv\cos\theta$

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

Associated Legendre functions: $P_l^{m_l}(x)=(1-x^2)^{|m_l|/2}(\frac{\mathrm{d}}{\mathrm{d}x})^{|m_l|}P_l(x)$, where $P_l(x)$ is the l^{th} Legendre polynomial given by the Rodrigues formula $P_l(x)=\frac{1}{2^l l!}(\frac{\mathrm{d}}{\mathrm{d}x})^l(x^2-1)^l$, 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 $m\geq0$ and $\epsilon=1$ for $m\leq0$.

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:

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

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

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:

$Y_0^0(\theta,\phi)=\frac{1}{\sqrt{4\pi}}, Y_1^{\pm1}(\theta,\phi)=\mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}, Y_1^0(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta$

The spherical harmonics satisfy the orthogonality relation

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

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

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, $\widehat{P}P_l^{m_l}(\theta)=(-1)^{l-|m_l|}P_l^{m_l}(\theta)\to$ even for $l+|m_l|$ even and odd for $l+|m_l|$ odd.

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

The spherical harmonics are products of two, and

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

The hydrogen atom

Coulomb's law, $\widehat{V}=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

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

The radial wave function

$\kappa\equiv\frac{\sqrt{-2mE}}{\hbar}$

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

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

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

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

As $\rho\to0$, centriugal term dominates, $\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2}=\frac{l(l+1)}{\rho^2}u$

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, $u(\rho)=\rho^{l+1}e^{-\rho}v(\rho)$

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

Assume the solution, $v(p)$, can be expressed as a power series in ρ: $v(\rho)=\sum_{j=0}^\infty c_j\rho^j$.

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

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

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

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

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

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

$\kappa=(\frac{me^2}{4\pi\epsilon_0\hbar^2})\frac{1}{n}=\frac{1}{an}$, Bohr radius: $a\equiv\frac{4\pi\epsilon_0\hbar^2}{me^2}=0.529\times10^{-10}\mathrm{m}$

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

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

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

$v(\rho)=L_{n-l-1}^{2l+1}(2\rho)$, where $L_{q-p}^p(x)\equiv(-1)^p(\frac{\mathrm{d}}{\mathrm{d}x})^pL_q(x)$ is an associated Laguerre polynomial. $L_q(x)\equiv e^x(\frac{\mathrm{d}}{\mathrm{d}x})^q(e^{-x}x^q)$ is the qth 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.

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

Rydberg constant: $R\equiv\frac{m}{4\pi c\hbar^3}(\frac{e^2}{4\pi\epsilon_0})^2=1.097\times10^7\ \mathrm{m}^{-1}$

General angular momentum

Spherical harmonics