$$\langle \chi' | \vec{J} | \chi \rangle = \sum_{m,m'} (\chi')^*_m (\vec{J}^{(j)})_{mm'} (\chi)_{m'}$$

or in matrix notation

$$= \chi'^{\dagger} \vec{J}^{(j)} \chi$$

$$= \begin{pmatrix} \chi'^*_\uparrow & \chi'^*_\downarrow \end{pmatrix} \frac{\hbar}{2} \vec{\sigma} \begin{pmatrix} \chi_\uparrow \\ \chi_\downarrow \end{pmatrix}$$ in the $j = \frac{1}{2}$ case.

5.3.6. ~~Spin and Orbital Angular Momentum Revisited~~

Finally suppose we recall again our physical discussion of angular momentum in the preceding section. We can use the definition of the orbital angular momentum operator $\vec{L} = \vec{R} \times \vec{P}$ to define the spin operator $\vec{S}$ by

$$\vec{J} = \vec{L} + \vec{S} \quad .$$

Since $\vec{R}, \vec{P}$ as well as $\vec{J}$ are vector operators

$$[J^i, J^j] = i\hbar \epsilon_{ijk} J^k$$

$$[J^i, X^j] = i\hbar \epsilon_{ijk} X^k$$

$$[J^i, P^j] = i\hbar \epsilon_{ijk} P^k$$

we have that $\vec{L}$ is a vector operator

$$[J^i, L^j] = i\hbar\epsilon_{ijk}L^k \,.$$ Hence

so is $\vec{S}$: $[J^i, S^j] = i\hbar\epsilon_{ijk}S^k$ which follows from the $[J^i, J^j] = i\hbar\epsilon_{ijk}J^k$ and $\vec{J}, \vec{L}$ commutators.

In addition we can calculate the commutator of $\vec{L}$ with $\vec{R}$ and $\vec{P}$ directly to find

$$[L^i, X^j] = i\hbar\epsilon_{ijk}X^k$$

$$[L^i, P^j] = i\hbar\epsilon_{ijk}P^k,$$

hence $[S^i, X^j] = 0 = [S^i, P^j]$ from the $\vec{J}$-$\vec{R}(\vec{P})$ commutators. Thus we have that $[L^i, S^j] = 0$. Further the $\vec{J}$-$\vec{J}$ commutator then yields

$$[S^i, S^j] = i\hbar\epsilon_{ijk}S^k,$$

$$[L^i+S^i, L^j+S^j] = \cancel{[L^i, L^j]} + \cancel{[S^i, L^j]}^{\,0} + \cancel{[L^i, S^j]}^{\,0} + [S^i, S^j]$$

$$= i\hbar\epsilon_{ijk}(\cancel{L^k} + S^k)$$

$$\Rightarrow [S^i, S^j] = i\hbar\epsilon_{ijk}S^k.$$

The spin angular momentum operator obeys the SU(2) algebra. Hence we can construct the eigenstates of the $\vec{S}^2$ and S_z operators, $|s, m_s\rangle$ with

$$\vec{S}^2 |s, m_s\rangle = s(s+1)\hbar^2 |s, m_s\rangle$$

$$S_z |s, m_s\rangle = m_s\hbar\, |s, m_s\rangle$$

where $s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ and $m_s = -s, \ldots, +s$.

The spin raising, S_+, and lowering, S_- operators can be defined as in the total angular momentum case

$$S_\pm \equiv S_x \pm i S_y$$

and the orthonormal standard spin basis can be constructed using them. Hence we have

$$S_+ |s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s+1)}\, |s, m_s+1\rangle$$

$$S_- |s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s-1)}\, |s, m_s-1\rangle$$

$$S_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle .$$

Hence the spin operators in the standard spin basis are represented by spin matrices

$$\vec{S}\,|s, m_s'\rangle = \sum_{m_s=-s}^{+s} \left(\vec{S}^{(s)}\right)_{m_s m_s'} |s, m_s\rangle$$

i.e. $\langle s, m_s|\vec{S}\,|s, m_s'\rangle = \left(\vec{S}^{(s)}\right)_{m_s m_s'}$.

Clearly the spin basis matrix elements of the spin operator are the same as ~~the~~ standard basis matrix elements of the angular momentum operator

$$\left(\vec{S}^{(s)}\right)_{m_s m_s'} = \left(\vec{J}^{(s)}\right)_{m_s m_s'} .$$

For example for $s=\frac{1}{2}$ $\vec{S}^{(\frac{1}{2})} = \frac{\hbar}{2}\vec{\sigma}$, the Pauli matrices. As well the spin basis can be represented by column vectors as discussed for the standard basis. For $s=\frac{1}{2}$ we have the spin-up, $e^{\uparrow} = \binom{1}{0}$, and spin-down, $e^{\downarrow} = \binom{0}{1}$, basis vectors.

As an illustration of the use of the spin basis, consider the interaction of a spin $\frac{1}{2}$ particle with an external magnetic field. Classically, a spinning charge has a magnetic moment $\vec{\mu}$ which interacts with the external magnetic field $\vec{B}$. The classical Hamiltonian describing the interaction is simply $H = -\vec{\mu}\cdot\vec{B}$. If the spinning charge has angular momentum $\vec{S}$ due to its spin then the magnetic moment is proportional to it, $\vec{\mu} = \gamma \vec{S}$ where the constant of proportionality γ, the gyromagnetic ratio, depends on the make up of the spinning charge.

Quantum mechanically, a particle with spin $\vec{S}$ has magnetic moment

$$\vec{\mu} = \gamma \vec{S} = \frac{q}{e} g \frac{e\hbar}{2mc} \frac{1}{\hbar} \vec{S}$$

$$\equiv g\left(\frac{q}{e}\right) \mu_B \frac{1}{\hbar} \vec{S}$$

where $\mu_B \equiv \frac{e\hbar}{2mc}$ is the Bohr magneton

and e is the magnitude of the electron charge, q is the electric charge of the particle, g depends on the particle being considered. (For neutral particles like neutron $\gamma \equiv g \frac{e\hbar}{2mc} = g\mu_B$.) g is called the Landé g-factor.

The interaction of the spin $\vec{S}$ with the external magnetic field $\vec{B}$ is again described by the Hamiltonian

$$H = -\vec{\mu}\cdot\vec{B} = -\gamma\vec{S}\cdot\vec{B}$$

$$= -g\frac{q}{e}\frac{\mu_B}{\hbar}\vec{S}\cdot\vec{B}.$$

For $\vec{B} = B\hat{z}$ this yields

$$H = -g\frac{q}{e}\frac{\mu_B B}{\hbar}S_z$$

$$\equiv \omega_B S_z$$

with the Bohr frequency $\omega_B \equiv -g\frac{q}{e}\frac{\mu_B B}{\hbar}$.

The spin basis vectors are the eigenstates of H

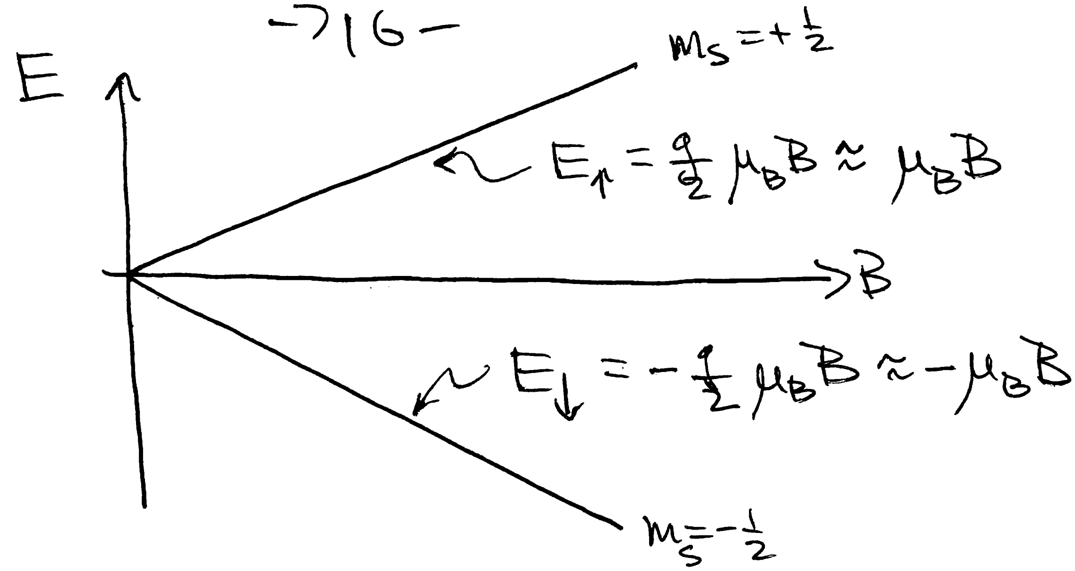
$$H|s=\tfrac{1}{2}, m_s\rangle = m_s\hbar\omega_B|s=\tfrac{1}{2}, m_s\rangle$$

with $m_s = \pm\frac{1}{2}$. Hence the energy eigenvalues are

$$E_{m_s} = m_s\hbar\omega_B = m_s\left(-g\frac{q}{e}\mu_B B\right)$$

For example for an electron, $\frac{q}{e} = -1$ and $\hbar\omega_B = g\mu_B B$. Experimentally we find $(g-2) = 0.002319312$ (i.e. $g = 2(1.001159656)$) which is known as the anomalous magnetic moment of the electron.

Hence



Suppose at time $t=0$, the spin is in the state

$$|\psi(0)\rangle = \cos\frac{\theta}{2}\, e^{-i\varphi/2} \left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle + \sin\frac{\theta}{2}\, e^{+i\frac{\varphi}{2}} \left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle$$

The state at time t is simply

$$|\psi(t)\rangle = \cos\frac{\theta}{2}\, e^{-\frac{i\varphi}{2}}\, e^{-\frac{i}{\hbar}E_{\frac{1}{2}}t} \left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle + \sin\frac{\theta}{2}\, e^{+\frac{i\varphi}{2}}\, e^{-\frac{i}{\hbar}E_{-\frac{1}{2}}t} \left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle$$

since $|\tfrac{1}{2}, m_s\rangle$ are energy eigenstates and

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = H|\psi(t)\rangle.$$

So

$$|\psi(t)\rangle = \cos\tfrac{\theta}{2}\, e^{-i\frac{(\varphi+\omega_B t)}{2}} |\tfrac{1}{2},\tfrac{1}{2}\rangle + \sin\tfrac{\theta}{2}\, e^{i\frac{(\varphi+\omega_B t)}{2}} |\tfrac{1}{2},-\tfrac{1}{2}\rangle .$$

The magnetic field $\vec{B}$ produces a phase shift between the coefficients of the spin eigenstates that depends on time.

Since $[H, S_z] = 0$, the observable S_z is a constant of the motion. The probability to measure spin $\pm\frac{1}{2}$ at t is

$$P_{\pm\frac{1}{2}} = |\langle \tfrac{1}{2}, \pm\tfrac{1}{2} | \psi(t)\rangle|^2 = \begin{cases} \cos^2\frac{\theta}{2} & \text{for } +\frac{1}{2} \\ \sin^2\frac{\theta}{2} & \text{for } -\frac{1}{2} \end{cases}$$

independent of t. However $S_{x,y}$ do not commute with H; $[H, S_{x,y}] \neq 0$ and hence are not constants of the motion. Their expectation values are

$$\langle \psi(t)|\vec{S}|\psi(t)\rangle =$$

$$= \begin{pmatrix} \cos\frac{\theta}{2} e^{+i\frac{(\varphi+\omega_B t)}{2}} & \sin\frac{\theta}{2} e^{-i\frac{(\varphi+\omega_B t)}{2}} \end{pmatrix} \frac{\hbar}{2}\vec{\sigma} \times$$

$$\times \begin{pmatrix} \cos\frac{\theta}{2} e^{-i\frac{(\varphi+\omega_B t)}{2}} \\ \sin\frac{\theta}{2} e^{+i\frac{(\varphi+\omega_B t)}{2}} \end{pmatrix}$$

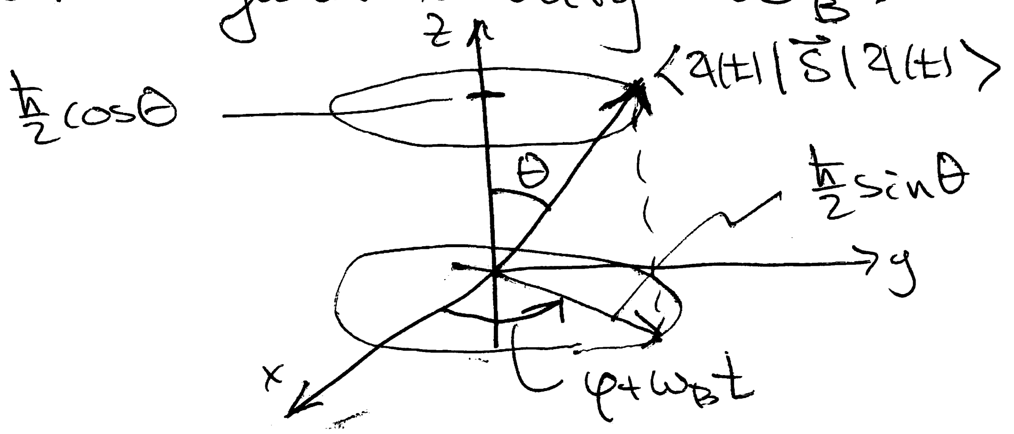
$\Rightarrow$

$$\langle\psi(t)|S_x|\psi(t)\rangle = \frac{\hbar}{2}\sin\theta\cos(\varphi+\omega_B t)$$

$$\langle\psi(t)|S_y|\psi(t)\rangle = \frac{\hbar}{2}\sin\theta\sin(\varphi+\omega_B t)$$

$$\langle\psi(t)|S_z|\psi(t)\rangle = \frac{\hbar}{2}\cos\theta \, .$$

The expectation values of $\vec{S}$ behave like classical angular momentum of magnitude $\frac{\hbar}{2}$ undergoing Larmor precession with angular velocity ω_B.



The standard basis consisted of the simultaneous eigenvectors of the CSCO $\{A, \vec{J}^2, J_z\}$, the $\{|k, j, m\rangle\}$.

Since $\vec{R}$ and $\vec{P}$ commute with $\vec{S}$, we may also use the sets $\{\vec{R}, \vec{S}^2, S_z\}$ or $\{\vec{P}, \vec{S}^2, S_z\}$ as CSCO. Since the $[S^i, X^j] = 0$, the eigenkets $|\vec{r}, s, m_s\rangle$ can be written as

$$|\vec{r}, s, m_s\rangle = |\vec{r}\rangle \otimes |s, m_s\rangle \quad .$$

Since these are complete, any state $|\psi\rangle$ may be expanded in terms of them

$$|\psi\rangle = \int d^3r \sum_{m_s=-s}^{+s} \psi^{(s)}_{m_s}(\vec{r})\, |\vec{r}, s, m_s\rangle$$

For a particular subspace $\mathcal{H}(s)$ with s fixed and we have the multi-component wavefunction

$$\psi^{(s)}_{m_s}(\vec{r}) = \langle \vec{r}, s, m_s | \psi\rangle \, .$$

Since $\vec{J} = \vec{L} + \vec{S}$ we have

$$\langle \vec{r}, s, m_s | \vec{J} | \psi\rangle = \langle \vec{r}, s, m_s | \vec{L} | \psi\rangle + \langle \vec{r}, s, m_s | \vec{S} | \psi\rangle .$$

Since $\vec{L} = \vec{R} \times \vec{P}$ we have

$$\langle \vec{r}, s, m_s | \vec{J} | \psi \rangle = \left(\vec{r} \times \frac{\hbar}{i} \vec{\nabla}_{\vec{r}}\right) \langle \vec{r}, s, m_s | \psi \rangle + \sum_{m_s'=-s}^{+s} \left(\vec{S}^{(s)}\right)_{m_s m_s'} \langle \vec{r}, s, m_s' | \psi \rangle$$

$$= \left[\left(\vec{r} \times \frac{\hbar}{i} \vec{\nabla}_{\vec{r}}\right) \delta_{m_s m_s'} + \left(\vec{S}^{(s)}\right)_{m_s m_s'}\right] \psi^{(s)}_{m_s'}(\vec{r})$$

as we found in our physical discussion of angular momentum. Since

$$|\psi'\rangle = U(R(\vec{\theta}))|\psi\rangle = e^{-\frac{i}{\hbar}\vec{\theta}\cdot\vec{J}}|\psi\rangle$$

we have that for infinitesimal angle $\vec{\theta} = \vec{\omega}$

$$\psi'^{(s)}_{m_s}(\vec{r}) = \langle \vec{r}, s, m_s | \psi' \rangle$$

$$= \langle \vec{r}, s, m_s | \mathbb{1} - \frac{i}{\hbar}\vec{\omega}\cdot\vec{J} | \psi \rangle$$

$$= \psi^{(s)}_{m_s}(\vec{r}) - \frac{i}{\hbar}\vec{\omega}\cdot\langle \vec{r}, s, m_s | \vec{J} | \psi \rangle$$

$$\boxed{\psi'^{(s)}_{m_s}(\vec{r}) = \psi^{(s)}_{m_s}(\vec{r}) - \frac{i}{\hbar}\vec{\omega}\cdot\left[\left(\vec{r} \times \frac{\hbar}{i}\vec{\nabla}_{\vec{r}}\right)\delta_{m_s m_s'} + \left(\vec{S}^{(s)}\right)_{m_s m_s'}\right]\psi^{(s)}_{m_s'}(\vec{r})}$$

and for finite rotations

$$\psi'^{(s)}_{m_s}(\vec{r}) = D^{(s)}_{m_s m_s'}(R(\vec{\theta}))\, \psi^{(s)}_{m_s'}(R^{-1}(\vec{\theta})\vec{r}) .$$

Since any basis is as good a basis as any other, we can imagine expanding the $|k, j, m\rangle$ states in terms of the $|\vec{r}, s, m_s\rangle$ states. Since $\vec{J} = \vec{L} + \vec{S}$, the relationship between the eigenstates of $\vec{J}^2, J_z$ and the orbital angular momentum and spin angular momentum that add up to be the total angular momentum we desire is complicated. We must first determine how to add angular momentum.

Before doing this, however, we can consider the case of spin zero particles. In this situation the total angular momentum is just the orbital angular momentum; $\vec{J} = \vec{L}$. (i.e. $\vec{J} = \vec{L} + \vec{0}$). So in the $\{|\vec{r}\rangle\}$ basis

$$\langle \vec{r}|\vec{J}|\psi\rangle = \langle \vec{r}|\vec{L}|\psi\rangle = \langle \vec{r}|\vec{R}\times\vec{P}|\psi\rangle$$

$$= \left(\vec{r} \times \frac{\hbar}{i}\vec{\nabla}_{\vec{r}}\right)\psi(\vec{r})$$

$pq \sim \hbar$ $\quad \{p\}\{q\} = \hbar$

When the particle has spin 0, the total ∡ momentum is just the orbital ∡ momentum. Now for orbital angular momentum

$\vec{J} = \vec{L} = \vec{R} \times \vec{P}$, we found in wavemechanics that l and m were integer valued only. This follows from the general properties of L, that is unlike spin $L = R \times P$.

Aside: In particular $L_z = X P_y - Y P_x$

and $[X_i, P_j] = i\hbar\delta_{ij}$.

Now define 4 operators that are hermitian:

$$q_1 \equiv \frac{X + P_y \frac{a^2}{\hbar}}{\sqrt{2}}$$

a = const. with dim. of length

i.e. $a = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$ Bohr radius

Problem 4.5c in Gr

$$q_2 \equiv \frac{X - P_y \frac{a^2}{\hbar}}{\sqrt{2}}$$

$$p_1 \equiv \left[\frac{\frac{a^2}{\hbar} P_x - Y}{\sqrt{2}}\right] \hbar/a^2$$

$$p_2 \equiv \left[\frac{\frac{a^2}{\hbar} P_x + Y}{\sqrt{2}}\right] \hbar/a^2$$

$$[q_1, p_2] = \frac{i\hbar}{\hbar 2i}[X, P_x] + \frac{\hbar a^2}{2\hbar}[P_y, Y]\frac{i}{2i} = 0$$

$$[q_2, p_1] = \frac{a^2\hbar}{2\hbar a^2}[X, P_x] + \frac{\hbar a^2}{2\hbar}[P_y, Y]\frac{i}{2} = 0$$

Now for $i = j$

$$\boxed{[q_i, p_j] = \frac{\hbar a^2}{2\hbar a^2}[X, P_x] - \frac{\hbar a^2}{2\hbar a^2}[P_y, Y] = i\hbar\delta_{ij}} = i\hbar\delta_{ij}$$

Further $[q_1, q_2] = 0 = [p_1, p_2]$

$\Rightarrow$

$$\boxed{\begin{aligned}[q_i, q_j] &= 0 = [p_i, p_j] \\ [q_i, p_j] &= i\hbar\delta_{ij}\end{aligned}}\quad \text{CCR.}$$

Further

$$X = \frac{1}{\sqrt{2}}(q_1 + q_2)$$
$$Y = \frac{1}{\sqrt{2}}\frac{a^2}{\hbar}(p_2 - p_1)$$
$$P_x = \frac{1}{\sqrt{2}}(p_1 + p_2)$$
$$a^2 P_y = \frac{\hbar}{\sqrt{2}}(q_1 - q_2)$$

$$L_z = X P_y - Y P_x$$
$$= \frac{\hbar}{a^2 2}[q_1^2 - q_2^2]$$
$$- \frac{a^2}{2\hbar}[p_2^2 - p_1^2]$$

let $a = 1$

$$\boxed{L_z = \left(\frac{a^2}{2\hbar}p_1^2 + \frac{1}{2}\frac{\hbar}{a^2}q_1^2\right) - \left(\frac{a^2}{2\hbar}p_2^2 + \frac{1}{2}\frac{\hbar}{a^2}q_2^2\right)}$$

This is just Hamiltonian for 2 independent 1-d SHO with $m = \hbar/a^2$, $\omega = 1$

$a^2/\hbar = \frac{1}{m}$,

Hence their individual ev. are

$$L_z = h_1 - h_2 \quad ; \quad h_1 \to E_1 = \hbar(n_1 + \tfrac{1}{2})$$
$$h_2 \to E_2 = \hbar(n_2 + \tfrac{1}{2})$$
$$n_{1,2} = 0, 1, 2, \dots$$

$\Rightarrow$

$$L_z \to m\hbar = E_1 - E_2$$
$$= \hbar(n_1 + \tfrac{1}{2}) - \hbar(n_2 + \tfrac{1}{2})$$
$$= \hbar(n_1 - n_2)$$

$\Rightarrow$

$$m = n_1 - n_2 = 0, \pm 1, \pm 2, \dots \Rightarrow \underline{\underline{\text{integer}}}$$

(<u>not</u> $\tfrac{1}{2}$ integer!)

Indeed this is what we found explicitly in the $\{|\vec{r}\rangle\}$ basis

$$\langle \vec{r} | \vec{J} | \psi \rangle = \langle \vec{r} | \vec{L} | \psi \rangle = \langle \vec{r} | \vec{R} \times \vec{P} | \psi \rangle$$
$$= \left(\vec{r} \times \frac{\hbar}{i} \vec{\nabla}_{\vec{r}}\right) \psi(\vec{r})$$

That is $\langle\vec{r}|\vec{J} = \langle\vec{r}|\vec{L} = (\vec{r}\times\frac{\hbar}{i}\vec{\nabla}_{\vec{r}})\langle\vec{r}|$ for the spin 0 subspace.

In spherical polar coordinates we have as found in wavemechanics

$$\langle\vec{r}|L_x = \frac{\hbar}{i}\left[-\sin\varphi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right]\langle r,\theta,\varphi|$$

$$\langle\vec{r}|L_y = \frac{\hbar}{i}\left[\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right]\langle r,\theta,\varphi|$$

$$\langle\vec{r}|L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}\langle r,\theta,\varphi|$$

Thus

$$\langle\vec{r}|L_\pm = \hbar e^{\pm i\varphi}\left[\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right]\langle r,\theta,\varphi|$$

and

$$\langle\vec{r}|\vec{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\langle r,\theta,\varphi|$$

Since these operators are independent of the radius r, they act **only** on the spherical angle variables we can introduce a spherical angle basis $|\theta,\varphi\rangle$, the action of L in this basis is given above. ($\{|\theta,\varphi\rangle\}$ is not complete, we need also the ~~radial~~ radial dependence of the wavefunction, but since it is not relevant for the following discussion we surpress it, as the k in the $|k,j,m\rangle$ basis).

Now since $\vec{J} = \vec{L}$ we know that the eigen states $|l,m\rangle$ of $\vec{L}^2$ and L_z are given by

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

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

with $l = 0,1,2,\ldots$ and $m = -l, -l+1, \ldots, l-1, l$.

Hence the $|l,m\rangle$ wavefunctions obey the angular differential equation

$$\langle \theta,\varphi | \vec{L}^2 | l,m\rangle = l(l+1)\hbar^2 \langle \theta,\varphi | l,m\rangle$$
$$= -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\langle \theta,\varphi | l,m\rangle$$

and

$$\langle \theta,\varphi | L_z | l,m\rangle = m\hbar \langle \theta,\varphi | l m\rangle$$
$$= \frac{\hbar}{i}\frac{\partial}{\partial\varphi}\langle \theta,\varphi | l,m\rangle .$$

The solutions to these differential equations, as we found in wave mechanics, are just the spherical harmonics.

$$\langle \theta,\varphi | l,m \rangle = Y_l^m(\theta,\varphi) \quad \text{with}$$

$l = 0, 1, 2, \ldots$ and $m = -l, -l+1, \ldots, l-1, l.$

Since $\langle l,m | l,m \rangle = 1$ we have

$$\int_{\varphi=0}^{2\pi} d\varphi \int_{\theta=0}^{\pi} \sin\theta \, d\theta \, |Y_l^m(\theta,\varphi)|^2 = 1.$$

Hence we have transformed from one basis $|l,m\rangle$ to another $|\theta,\varphi\rangle$; by means of the spherical harmonics

$$Y_l^m(\theta,\varphi) = \langle \theta,\varphi | l,m \rangle.$$

Finally any wavefunction for a spin 0 particle has the expansion in terms of the <u>standard basis wavefunctions</u>

$$\psi_{k,l,m}(\vec{r}) = \langle \vec{r} | k,l,m \rangle$$
$$= R_{k,l,m}(r) \, Y_l^m(\theta,\varphi)$$

Since $\vec{L}^2$ and L_z only act on the angular variables, $R_{klm}(r)$ acts as a constant factor in the $\langle \vec{r}|\vec{L}^2|k,l,m\rangle = l(l+1)\hbar^2\langle \vec{r}|k,l,m\rangle$ and $\langle \vec{r}|L_z|k,l,m\rangle = m\hbar\langle \vec{r}|k,l,m\rangle$ differential equations.

Using $L_\pm$ we find $R_{k,l,m\pm1}(r) = R_{k,l,m}(r)$ hence $R_{k,l,m}(r) = R_{kl}(r)$ is independent of m. So

$$\psi_{k,l,m}(\vec{r}) = R_{kl}(r)\, Y_l^m(\theta,\varphi)$$

form a complete set of spin 0 wave functions which are orthonormal (by convention)

$$\int d^3r\, \psi^*_{k,l,m}(\vec{r})\psi_{k',l',m'}(\vec{r})$$

$$= \int_0^\infty dr\, r^2 R^*_{kl}(r) R_{k'l'}(r) \times$$

$$\times \int_{4\pi} d\Omega\, Y_l^{m*}(\theta,\varphi) Y_{l'}^{m'}(\theta,\varphi)$$

$$= \langle k,l,m|k',l',m'\rangle = \delta_{kk'}\delta_{ll'}\delta_{mm'}$$

$\Rightarrow R_{kl}$ must be normalized to

$$\int_0^\infty dr\, r^2 R^*_{kl}(r) R_{k'l}(r) = \delta_{kk'}.$$

Hence any spin 0 wavefunction has the expansion

$$\psi(\vec{r}) = \langle \vec{r}|\psi\rangle = \sum_{k,l,m}\!\!\!\!\!\!\!\!\int\; \langle \vec{r}|k,l,m\rangle \underbrace{\langle k,l,m|\psi\rangle}_{\equiv C_{klm}}$$

$$= \sum_{k,l,m}\!\!\!\!\!\!\!\!\int\; C_{k,l,m} \langle \vec{r}|k,l,m\rangle$$

$$= \sum_{k,l,m}\!\!\!\!\!\!\!\!\int\; C_{k,l,m}\, \psi_{k,l,m}(\vec{r})$$

$$= \sum_{k,l,m}\!\!\!\!\!\!\!\!\int\; C_{k,l,m}\, R_{kl}(r)\, Y_l^m(\theta,\varphi)$$

In particular we can apply this to the case of the free particle with 0 spin. The Hamiltonian is

$$H = \frac{1}{2m}\vec{P}^2 .$$

On the one hand we can choose eigenstates of $\{H, \vec{P}\}$ as a basis

$$H|\vec{p}\rangle = E(\vec{p})|\vec{p}\rangle$$

$$\vec{P}|\vec{p}\rangle = \vec{p}\,|\vec{p}\rangle$$

and in the coordinate representation

This becomes

$$\langle \vec{r}|\vec{P}|\vec{p}\rangle = \frac{\hbar}{i}\vec{\nabla}_{\vec{r}}\langle \vec{r}|\vec{p}\rangle$$

$$= \vec{p}\langle \vec{r}|\vec{p}\rangle$$

$$\Rightarrow \langle \vec{r}|\vec{p}\rangle = c\, e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$$

and $\langle \vec{r}|H|\vec{p}\rangle = -\frac{\hbar^2}{2m}\nabla^2\langle \vec{r}|\vec{p}\rangle = E(\vec{p})\langle \vec{r}|\vec{p}\rangle$

$$= \frac{\vec{p}^{\,2}}{2m}\langle \vec{r}|\vec{p}\rangle$$

$$\Rightarrow \quad E(\vec{p}) = \frac{\vec{p}^{\,2}}{2m}.$$

Choosing the normalization factor $c = 1$ we have

$$\langle \vec{p}\,'|\vec{p}\rangle = \int d^3r\, e^{\frac{i}{\hbar}(\vec{p}-\vec{p}\,')\cdot\vec{r}}$$

$$= (2\pi\hbar)^3\delta^3(\vec{p}-\vec{p}\,'),$$

continuum orthonormality. Completeness is then given by

$$\mathbb{1} = \int\frac{d^3p}{(2\pi\hbar)^3}|\vec{p}\rangle\langle\vec{p}|$$

$\Rightarrow$

$$\langle \vec{r}\,'|\vec{r}\rangle = \int\frac{d^3p}{(2\pi\hbar)^3}\langle \vec{r}\,'|\vec{p}\rangle\langle\vec{p}|\vec{r}\rangle$$

$$= \int\frac{d^3p}{(2\pi\hbar)^3}e^{-\frac{i}{\hbar}\vec{p}\cdot(\vec{r}-\vec{r}\,')} = \delta^3(\vec{r}-\vec{r}\,').$$

As just discussed, we have that $\vec{J}=\vec{L}$ and $[\vec{L},\vec{P}^2]=0 \Rightarrow [\vec{L},H]=0$, so we can equally well consider $\{H,\vec{L}^2,L_z\}$ as our CSCO and expand our states in terms of their mutual eigenfunctions.

$$H|E,l,m\rangle = E|E,l,m\rangle \equiv \frac{\vec{p}^2}{2m}|E,l,m\rangle$$

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

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

where $E\geq 0$, $l=0,1,2,\ldots$, $m=-l,-l+1,\ldots,+l$.

Then
$$|\psi\rangle = \int_0^\infty \frac{dE}{\sqrt{\frac{2E\hbar^2}{m}}} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \langle E,l,m|\psi\rangle |E,l,m\rangle$$

Now if $|\psi\rangle$ is also an eigenstate of H with eigenvalue E we have

$$|\psi_E\rangle = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \langle E,l,m|\psi\rangle |E,l,m\rangle$$

In particular
$$|\vec{p}\rangle = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \langle E(p),l,m|\vec{p}\rangle \times |E(p),l,m\rangle$$

and

$$\langle \vec{r} | \vec{p} \rangle = e^{+\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$$

$$= \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \langle k, l, m | \vec{p} \rangle \psi_{k,l,m}(\vec{r})$$

$$= \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} C_{klm} R_{kl}(r) Y_l^m(\theta, \varphi)$$

where we have written

$$E(\vec{p}) = \frac{\vec{p}^2}{2m} \equiv \frac{\hbar^2 k^2}{2m} \quad ; k \geq 0.$$

Let's find the free particle energy eigenstates in the angular momentum basis $\psi_{k,l,m}(\vec{r})$ with completeness

$$\int_0^\infty \frac{dE}{\left(\frac{2E\hbar^2}{m}\right)^{1/2}} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} |E, l, m\rangle\langle E, l, m| = \mathbb{1}$$

and orthonormality

$$\int d^3r \, \psi^*_{k',l',m'}(\vec{r}) \psi_{k,l,m} = \delta(k-k') \delta_{ll'} \delta_{mm'}$$

Now $\delta(E-E') = \delta\left(\frac{\hbar^2}{2m}(k^2-k'^2)\right)$

$= \delta\left(\frac{\hbar^2}{2m}(k+k')(k-k')\right)$ with $k, k' \geq 0$

So $= \dfrac{1}{\frac{\hbar^2 k}{m}} \delta(k-k')$

$= \dfrac{1}{\left(\frac{2E\hbar^2}{m}\right)^{1/2}} \delta(k-k')$; i.e. $dE = \left(\frac{2E\hbar^2}{m}\right)^{1/2} dk$

So completeness becomes

$$\int_0^\infty dk \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \underbrace{|E(k), l, m\rangle\langle E(k), l, m|}_{\equiv |k,l,m\rangle\langle k,l,m|} = \mathbb{1}.$$

Now in spherical polar coordinates the we have that

$$H|k,l,m\rangle = \frac{\hbar^2 k^2}{2m}|k,l,m\rangle$$

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}\left(r\psi_{klm}(\vec{r})\right) - \frac{1}{\hbar^2 r^2}\vec{L}^2 \psi_{klm}(\vec{r})\right] = \frac{\hbar^2 k^2}{2m}\psi_{klm}(\vec{r})$$

which becomes, using orthogonality of $Y_\ell^m(\theta,\varphi)$

$$\frac{1}{r}\frac{d^2}{dr^2}\left(r R_{k\ell}(r)\right) - \frac{\ell(\ell+1)}{r^2} R_{k\ell}(r)$$

$$= -k^2 R_{k\ell}(r) .$$

This is just Bessel's equation $\Rightarrow$

$$R_{k\ell}(r) = N_{k\ell}\, j_\ell(kr)$$

where $j_\ell(kr)$ are the spherical Bessel functions. The normalization factor $N_{k\ell}$ is determined by

$$\int_0^\infty d^3r\, \psi^*_{k'\ell'm'}(\vec{r})\, \psi_{k\ell m}(\vec{r}) \equiv \delta(k'-k)\,\delta_{\ell\ell'}\,\delta_{mm'}$$

$$= \delta_{\ell'\ell}\,\delta_{m'm}\, N^*_{k'\ell} N_{k\ell} \underbrace{\int_0^\infty dr\, r^2\, j_\ell(k'r)\, j_\ell(kr)}_{=\frac{\pi}{2k^2}\delta(k-k')}$$

$\Rightarrow$ $\quad |N_{k\ell}|^2 = \dfrac{2k^2}{\pi}$ independent of ℓ.

Choosing $N_{k\ell}$ as real and positive $\Rightarrow$

$$N_{k\ell} = \sqrt{\tfrac{2}{\pi}}\, k, \quad \text{and } R_{k\ell}(r) = \sqrt{\tfrac{2}{\pi}}\, k\, j_\ell(kr)$$

Thus the complete set of free particle wavefunctions that are $\{H, \vec{L}^2, L_z\}$ eigenfunctions are

$$\boxed{\psi_{k\ell m}(\vec{r}) = \sqrt{\tfrac{2}{\pi}}\, k\, j_\ell(kr)\, Y_\ell^m(\theta,\varphi)}$$

$$= \langle \vec{r} \,|\, k, \ell, m\rangle .$$

Thus we have 2-sets of basis vectors. The plane ~~wave~~ eigenstates of $\{H, \vec{p}\}$

$$H|\vec{p}\rangle = \frac{\hbar^2 k^2}{2m}|\vec{p}\rangle = \frac{\vec{p}^{\,2}}{2m}|\vec{p}\rangle$$

$$\vec{P}|\vec{p}\rangle = \vec{p}\,|\vec{p}\rangle \qquad , \quad k^2 \geq 0, \quad \vec{p} \in \mathbb{R}^3$$

with wavefunctions

$$\psi_{\vec{p}}(\vec{r}) = \langle \vec{r}|\vec{p}\rangle = e^{+\frac{i}{\hbar}\vec{p}\cdot\vec{r}} .$$

On the other hand the eigenstates of $\{H, \vec{L}^2, L_z\}$ are $|k, \ell, m\rangle$

$$H|k,l,m\rangle = \frac{\hbar^2 k^2}{2m}|k,l,m\rangle$$

$$\vec{L}^2|k,l,m\rangle = l(l+1)\hbar^2|k,l,m\rangle$$

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

with $k^2 \geq 0$; $l = 0,1,2,\ldots$, $m = -l, -l+1, \ldots, +l$.

Their complete set of wave functions are

$$\psi_{klm}(\vec{r}) = \langle\vec{r}|k,l,m\rangle$$
$$= \sqrt{\frac{2}{\pi}}\, k\, j_l(kr)\, Y_l^m(\theta,\varphi).$$

Either set is a basis, so we can expand one in terms of the other

$$|\vec{p}\rangle = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\langle k,l,m|\vec{p}\rangle|k,l,m\rangle$$

where $\vec{p}^2 = \hbar^2 k^2$ and so

$$\langle\vec{r}|\vec{p}\rangle = e^{+\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$$
$$= \sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\overbrace{\langle k,l,m|\vec{p}\rangle}^{\equiv C_{klm}}\psi_{klm}(\vec{r})$$

So $$e^{+\frac{i}{\hbar}\vec{p}\cdot\vec{r}} = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} c_{klm}\sqrt{\frac{2k^2}{\pi}}\, j_l(kr)\, Y_l^m(\theta,\varphi)$$

and we are left to determine the coefficients c_{klm}. The result is given by

$$e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{+l} i^l\, Y_l^{m*}(\theta_{\vec{p}},\varphi_{\vec{p}})\, j_l(kr)\, Y_l^m(\theta,\varphi)$$

where $(\theta_{\vec{p}},\varphi_{\vec{p}})$ are the spherical angle coordinates of $\vec{p}$. We can obtain this general result by rotating the $\vec{p}$-vector so that it lies along the z-axis. In this new frame only $m=0$ states contribute since $\langle\vec{r}|\vec{p}\rangle = e^{ikr\cos\theta}$ and L_z becomes $\frac{\hbar}{i}\frac{\partial}{\partial\varphi} \Rightarrow L_z|p_z\rangle = 0$. Thus when $\vec{p}=\hbar k\hat{z}$ we have

$$e^{ikz} = \sum_{l=0}^{\infty} i^l\sqrt{4\pi(2l+1)}\, j_l(kr)\, Y_l^0(\theta)$$

$$\parallel$$

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l(2l+1)\, j_l(kr)\, P_l(\cos\theta)\,.$$

This can be rotated back to the original frame using the addition formula for spherical harmonics. In turn this

Consider the proof of the expansion

$$e^{ikz} = e^{ikr\cos\theta}$$

$$= \sum_{l=0}^{\infty} i^l (2l+1)\, j_l(kr)\, P_l(\cos\theta).$$

In general we had

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} C_{lm=0} \sqrt{\frac{2k^2}{\pi}}\, j_l(kr)\, Y_l^{m=0}(\theta,\varphi)$$

$$= \sum_{l=0}^{\infty} C_l \sqrt{\frac{2k^2}{\pi}}\, j_l(kr)\, Y_l^0(\theta,\varphi)$$

Now recall the recursion relation

$$Y_l^m(\theta,\varphi) = \sqrt{\frac{(l+m)!}{(2l)!\,(l-m)!}} \left(\frac{L_-}{\hbar}\right)^{l-m} Y_l^l(\theta,\varphi)$$

where

$$L_\pm \equiv L_x \pm i L_y$$

$$= \hbar e^{\pm i\varphi}\left(\pm \frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\varphi}\right)$$

$$\Rightarrow Y_l^0(\theta,\varphi) = \sqrt{\frac{1}{(2l)!}} \left(\frac{L_-}{\hbar}\right)^l Y_l^l(\theta,\varphi)$$

Since Y_ℓ^0 are orthonormal we have

$$C_\ell j_\ell(kr)\sqrt{\frac{2k^2}{\pi}} = \int d\Omega\, Y_\ell^{0*}(\theta,\varphi)\, e^{ikr\cos\theta}$$

$$= \frac{1}{\sqrt{(2\ell)!}}\int d\Omega \left[\left(\frac{L_-}{\hbar}\right)^\ell Y_\ell^\ell(\theta,\varphi)\right]^* e^{ikr\cos\theta}$$

$$= \frac{1}{\sqrt{(2\ell)!}}\int d\Omega\, Y_\ell^{\ell*}(\theta,\varphi)\left(\frac{L_+}{\hbar}\right)^\ell e^{ikr\cos\theta}$$

by definition of adjoint operator and L_+ is the adjoint of L_-, $L_+ = L_-^\dagger$.

Now

$$\left(\frac{L_+}{\hbar}\right)^\ell e^{ikr\cos\theta} = e^{i\ell\varphi}(-1)^\ell |\sin\theta|^\ell \frac{d^\ell}{d(\cos\theta)^\ell} e^{ikr\cos\theta}$$

$$= (-1)^\ell e^{i\ell\varphi} |\sin\theta|^\ell (ikr)^\ell e^{ikr\cos\theta}$$

But

$$Y_\ell^\ell(\theta,\varphi) = \frac{(-1)^\ell}{2^\ell \ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}}\, e^{i\ell\varphi}(\sin\theta)^\ell$$

So $$\left(\frac{L_+}{\hbar}\right)^\ell e^{ikr\cos\theta} = 2^\ell \ell! \sqrt{\frac{4\pi}{(2\ell+1)!}}\, Y_\ell^\ell(\theta,\varphi)\,(ikr)^\ell e^{ikr\cos\theta}$$

and so

$$C_\ell\, j_\ell(kr)\sqrt{\frac{2k^2}{\pi}} = \frac{2^\ell \ell!}{\sqrt{(2\ell)!}}\sqrt{\frac{4\pi}{(2\ell+1)!}}\,(ikr)^\ell \times$$

$$\times \int d\Omega\, Y_\ell^{\ell *}(\theta,\varphi)\, Y_\ell^\ell(\theta,\varphi)\, e^{ikr\cos\theta}$$

Now for $kr \to 0$ $\quad j_\ell(kr) \sim \dfrac{(kr)^\ell}{(2\ell+1)!!}$

So with $e^{ikr\cos\theta} \sim 1$ on the RHS due to the $(ikr)^\ell$ factor already and the normalization of Y_ℓ^m, we have

$$C_\ell \sqrt{\frac{2k^2}{\pi}}\,\frac{(kr)^\ell}{(2\ell+1)!!} = \frac{2^\ell \ell!}{\sqrt{(2\ell)!}}\sqrt{\frac{4\pi}{(2\ell+1)!}}\; i^\ell\,(kr)^\ell$$

$$\Rightarrow \boxed{\sqrt{\frac{2k^2}{\pi}}\, C_\ell = i^\ell \sqrt{4\pi(2\ell+1)}}$$

hence

$$e^{ikr\cos\theta} = \sum_{\ell=0}^{\infty} i^\ell \sqrt{4\pi(2\ell+1)}\; j_\ell(kr)\, Y_\ell^0(\theta,\varphi)$$

$$= \sum_{\ell=0}^{\infty} i^\ell (2\ell+1)\, j_\ell(kr)\, P_\ell(\cos\theta).$$

Now recall $\vec{k}$ could be in any direction in general instead of along the z-axis, but the above derivation will still be valid except that θ on the RHS is replaced by α, the ∡ between $\vec{r}$ and $\vec{k}$; Thus

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\alpha).$$

Next the addition theorem for spherical harmonics allows us to re-write $P_l(\cos\alpha)$ in terms of the angles $(\theta_{\vec{p}}, \varphi_{\vec{p}})$ and (θ, φ) as above.

Thus the plane wave state, the state of well defined momentum, involves a sum over all possible orbital ∡ momentum.

Likewise we can expand a state of well defined orbital angular momentum in terms of states with arbitrary direction of momentum (both sets of states have fixed energy ie $|\vec{k}|$.)

Using the orthonormality of the spherical harmonics we have

$$j_\ell(kr)\, Y_\ell^m(\theta,\varphi) = \frac{(-1)^\ell i^\ell}{4\pi} \int d\Omega_{\vec{p}}\, Y_\ell^m(\theta_{\vec{p}},\varphi_{\vec{p}})\, e^{i\vec{k}\cdot\vec{r}}$$

$$\| $$

$$\sqrt{\frac{\pi}{2k^2}}\, \psi_{k\ell m}(\vec{r}) = \sqrt{\frac{\pi}{2k^2}}\, \langle \vec{r} | k,\ell,m \rangle .$$

So a state of well-defined $\not\!\!L$ momentum involves all possible $\underline{\text{directions}}$ of the linear momentum.

As another example of the importance of symmetry groups, consider the O(4) symmetry of the Coulomb Potential:

Recall the Hamiltonian for the hydrogen atom for the relative particle is given by

$$H = +\frac{\vec{p}^{\,2}}{2m} + V(|\vec{r}|)$$

where $V(|\vec{r}|) = -\frac{e^2}{|\vec{r}|}$, the Coulomb potential.

As we know, the orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$ commutes with this Hamiltonian

$$[H, L_i] = 0.$$

As first pointed out by W. Pauli (Z. Physik 36 (1926) 336), there is a larger symmetry that this Hamiltonian has than just the SU(2) of angular momentum, and this larger symmetry can be exploited to find the energy eigenvalues of Hydrogen.

Suppose we introduce the Runge-Lenz vector operator

$$\vec{W} \equiv \sqrt{\frac{-m}{2H}}\left[\frac{1}{2m}(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})-\frac{e^2}{r}\vec{r}\right]$$

That is

$$W_i = \sqrt{\frac{-m}{2H}}\left[\frac{1}{2m}\epsilon_{ijk}(p_jL_k-L_jp_k)-\frac{e^2}{r}x_i\right]$$

Using the commutation relations of $[x_i, p_j] = i\hbar\delta_{ij}$ we find the following properties of $\vec{W}$:

1) $[W_i, H] = 0$

2) $[W_i, W_j] = i\hbar\epsilon_{ijk}L_k$

3) $[L_i, W_j] = i\hbar\epsilon_{ijk}W_k$

4) $\vec{L}\cdot\vec{W} = \vec{W}\cdot\vec{L} = 0$

5) $$\vec{W}^2 = -\left(\frac{m}{2H}\right)\left[\frac{2H}{m}(\vec{L}^2+\hbar^2)+(e^2)^2\right]$$
$$= -\vec{L}^2-\hbar^2-\frac{m}{2H}(e^2)^2$$
$$\Rightarrow \vec{W}^2+\vec{L}^2 = -\hbar^2-\frac{m}{2H}(e^2)^2$$

and of course

6) $[L_i, L_j] = i\hbar\epsilon_{ijk} L_k$.

The $(\vec{L}, \vec{W})$ algebra de-couples if we introduce their sum & difference

$$\vec{I} \equiv \frac{1}{2}(\vec{L} + \vec{W})$$

$$\vec{F} \equiv \frac{1}{2}(\vec{L} - \vec{W}) \quad .$$

Then we find

$$\boxed{\begin{aligned} [I_i, I_j] &= i\hbar\epsilon_{ijk} I_k \\ [F_i, F_j] &= i\hbar\epsilon_{ijk} F_k \\ [I_i, F_j] &= 0 \end{aligned}}$$

Thus the $\vec{I}$ and $\vec{F}$ separately obey the SU(2) commutation relations, hence they obey an algebra

$$\underset{3 X\text{'s}}{SU(2)} \times \underset{3 X\text{'s}}{SU(2)} = \underset{\substack{\text{rotations in 4 dimensions} \\ = 6 X\text{'s}}}{O(4)} \quad .$$

✓

Since $[H, \vec{L}] = 0 = [H, \vec{W}]$ we also have

$$[I_i, H] = 0 = [F_i, H].$$

Thus the hydrogen hamiltonian actually has an $O(4)$ symmetry.

Now any vector $\vec{J}$ that obeys the SU(2) algebra

$$[J_i, J_j] = i\hbar \epsilon_{ijk} J_k$$

has 1) $\vec{J}^2$ with eigenvalues $\hbar^2 j(j+1)$ where $j = 0, \frac{1}{2}, 1, \ldots$

2) J_z with eigenvalues for a given j $m = -j, -j+1, \ldots, j-1, +j$.

Thus

$\vec{I}^2$ has eigenvalues $i(i+1)\hbar^2$; $i = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$
$\vec{F}^2$ has eigenvalues $f(f+1)\hbar^2$; $f = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$

Since $[\vec{I}, H] = 0 \Rightarrow [\vec{I}^2, H] = 0$

$$[\vec{F}, H] = 0 \Rightarrow [\vec{F}^2, H] = 0$$

$$[I_i, F_j] = 0 \Rightarrow [\vec{I}^2, \vec{F}^2] = 0$$

Hence $\{H, \vec{I}^2, \vec{F}^2\}$ are a CSCO.

Their simultaneous eigenstates are defined by $|E, i, f\rangle$ with

$$H|E,i,f\rangle = E|E,i,f\rangle$$

$$\vec{I}^2|E,i,f\rangle = i(i+1)\hbar^2|E,i,f\rangle \;;\; i=0,\tfrac{1}{2},1,\ldots$$

$$\vec{F}^2|E,i,f\rangle = f(f+1)\hbar^2|E,i,f\rangle \;;\; f=0,\tfrac{1}{2},1,\ldots$$

Next consider the operators

$$\vec{I}^2 = \tfrac{1}{4}(\vec{W}+\vec{L})^2 = \tfrac{1}{4}(\vec{L}^2+\vec{W}^2+\vec{L}\cdot\vec{W}+\vec{W}\cdot\vec{L})$$

$$\vec{F}^2 = \tfrac{1}{4}(\vec{L}-\vec{W})^2 = \tfrac{1}{4}(\vec{L}^2+\vec{W}^2-\vec{L}\cdot\vec{W}-\vec{W}\cdot\vec{L})$$

But $\vec{L}\cdot\vec{W} = \vec{W}\cdot\vec{L} = 0$

$$\Rightarrow \quad \vec{I}^2 = \vec{F}^2 = \tfrac{1}{4}(\vec{L}^2+\vec{W}^2)$$

$$\Rightarrow \quad \vec{I}^2|E,i,f\rangle = \vec{F}^2|E,i,f\rangle$$

$$i(i+1)\hbar^2|E,i,f\rangle = f(f+1)\hbar^2|E,i,f\rangle$$

$$\Rightarrow \quad \boxed{i=f}$$

Further

$$\vec{I}^2|E,i,f\rangle = \tfrac{1}{4}(\vec{L}^2+\vec{W}^2)|E,i,f\rangle$$

$$\| \qquad = -\tfrac{1}{4}\left(\hbar^2+\frac{m}{2H}(e^2)^2\right)|E,i,f\rangle$$

$$i(i+1)\hbar^2|E,i,f\rangle = -\tfrac{1}{4}\left(\hbar^2+\frac{m(e^2)^2}{2E}\right)|E,i,f\rangle$$

$$\Rightarrow \quad \hbar^2 i(i+1) = -\tfrac{1}{4}\left(\hbar^2+\frac{me^4}{2E}\right)$$

$$\Rightarrow \quad E = -\frac{me^4}{2(\underbrace{4i(i+1)+1}_{=(2i+1)^2})\hbar^2} \quad ; i=0,\tfrac{1}{2},1\ldots$$

$$\Rightarrow \quad \boxed{E = -\frac{me^4}{2(2i+1)^2\hbar^2}, \quad i=0,\tfrac{1}{2},1,\ldots}$$

Now let

$$n = 2i+1 \quad \text{so for } i = 0, \tfrac{1}{2}, 1 \ldots$$

$n = 1, 2, 3, \ldots$, a positive integer.

$$\Rightarrow \boxed{E_n = -\frac{me^4}{2\hbar^2 n^2}} \quad , \; n = 1, 2, 3, \ldots$$

and defining the fine-structure constant

$$\alpha \equiv \frac{e^2}{\hbar c} \quad \Rightarrow$$

$$\boxed{E_n = -\frac{mc^2\alpha}{2n^2} \quad ; \; n = 1, 2, 3, \ldots}$$

as we found earlier.
