Angular Momentum

Recall from the old quantum theory, Bohr's hypothesis for the quantization of the atomic energy levels was that the angular momentum of the electron's orbit is quantized. This leads to the quantization of the energy level. He did not have any proof, but now we can prove it as well as understand and develop a a very profound and handy algebraic method to study those Hamiltonians in which angular momentum is conserved. Because spin is an intrinsic angular momentum of particles, the algebraic method that we will develop for angular momentum can also be used for spins. To distinguish these two types of angular momenta, one often refers the first as orbital or linear angular momentum which generates rotation of a particle in an orbit, and the spin angular momentum or simply spin for the intrinsic rotation of a particle w.r.t. to its own axis. They are denoted by $\vec{L}$ & $\vec{S}$, respectively. We will also learn a total angular momentum $\vec{J} = \vec{L} + \vec{S}$. When we say angular momentum, it may refer to the general properties for any of the three angular momentum.

Angular momentum vectors are different from other vectors like $\vec{r}$, $\vec{p}$, that they are called axial vectors. Because, angular momentum vectors are defined by the cross product of two other vectors, and by virtue of the cross product, the divergence of angular momentum vanishes. This is the reason they generate rotations. (Another example of an axial vector is magnetic field which hence can be described by the cross product of two vectors: $\vec{B} = \vec{\nabla} \times \vec{A}$, where $\vec{A}$ = vector potential). One common property of the axial vector is that its components do not commute with other, as we will see below, and in this chapter we want to take advantage of this property to define a Hilbert space and algebraic method that we developed for non-commuting position and momentum operators in the simple Harmonic oscillator case in the previous chapter.

Returning back to Bohr's hypothesis, Bohr assumed that the angular momentum is quantized in some integer (n) multiple of $\hbar$, and the same integer n (called the quantum number) appears in the energy as $1/n^2$. In our modern language, we interpret it as the eigenstates $|\psi_n\rangle$ of the angular momentum $|\psi_n\rangle$ with eigenvalues $n\hbar$, e.g. $L|\psi_n\rangle = n\hbar|\psi_n\rangle$, is also the eigenstates of the Hamiltonian $H|\psi_n\rangle = \frac{c}{n^2}|\psi_n\rangle$, where c is some constant. This means the angular momentum and the Hamiltonian share the same Hilbert space. This means, $\hat{L}$ & $\hat{H}$ commute with each other, or, $[H, \vec{L}] = 0$. From the Heisenberg's picture of the time evolution of an operator is given by $\frac{d\vec{L}}{\partial t} = \frac{i}{\hbar}[H, \vec{L}]$, we hence infer that $\frac{d\vec{L}}{dt} = 0$. This means $\vec{L}$ is a constant of motion. From classical mechanics, we have learned that angular momentum is the Noether charge of the rotation of the Lagrangian and if the Lagrangian is invariant under rotation, then angular momentum is conserved. This Noether theorem of conservation rule in the Poisson bracket language becomes $\frac{dL}{dt} = \{H, L\}_{P.B.}$, where H, L are classical variables, not operator. We again see that the Heisenberg's relation is a generalization of the Poisson bracket algebra for operators as Dirac said. We also said briefly that when an operator is conserved, it represents a symmetry for its conjugate variable, then the unitary operator $U = e^{iL\theta/\hbar}$ represents a translation of that variable (recall that we said $e^{iHt/\hbar}$, $e^{ipx/\hbar}$ are the time- & space translational unitary operators where the Hamiltonian and momentum are time-independent (conserved) respectively).

We do not want to discuss here the unitary transformation of the angular momentum operator, rather we want to go back to the case where

$$[\hat{H}, \vec{L}] = 0, \quad \text{--(1)}.$$

ie, for the Hamiltonian which is rotationally invariant or symmetric. Kinetic energy $K = p^2/2m = -\frac{\hbar^2 \nabla^2}{2m}$ is always rotationally symmetric (H.W.: Write the Laplacian operator ∇^2 and the angular momentum in spherical coordinates and show that $[\nabla^2, \vec{L}] = 0$). The most general potential that is rotationally symmetric are the ones that does not depend on angular coordinates, ie, $V(|\vec{r}|) = V(r)$. Such potentials are called central potential, which causes rotation of particles. Coulomb interation and gravitational potentials are two common examples of the central potentials. Since electron's orbit in an atom arises from Coulomb interaction, so angular momentum is indeed conserved, and Bohr was right in assuming that angular momentum & energy are quantized by the same quantum number.

So, we could just simply use the Hilbert space of the orbital angular momenta to solve the Hamiltonian for atoms. Well, we are almost right, but the problem arises from the fact that angular momenta are axial vectors and all three components do not commute. ☹. We can show that the three components of the axial vector follow this generic commutation relation:

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y. \text{--(2)}$$

This cyclic relation can be written in a compact form

$$\boxed{[L_i, L_j] = i\hbar\, \epsilon_{ijk} L_k,} \quad \text{---} (3).$$

where $i, j, k = x, y, z$, and
ϵ_{ijk} is the antisymmetric tensor defined as

$$\epsilon_{ijk} = \begin{cases} 1 & (ijk) \text{ are cyclic.} \\ -1 & ij \text{ are interchanged for a given } k. \\ 0 & \text{if } i=j \text{ or } j=k, \text{ or } i=k. \end{cases} \quad \text{—}(4)$$

The origin of this commutation relation is in its formula that the angular momentum is defined by the cross product of two vectors which are cannonically conjugate to each other and hence do not commute.

$$L_i = \epsilon_{ijk}\, r_j\, p_k \quad \text{---} (5).$$

in which $[r_j, p_k] = i\hbar\, \delta_{jk}$.

H.W. (i) Using eq (5), prove eq(3) in both cartesian and spherical coordinates.

(ii) Prove that if $\vec{L} = 0$, then all three components have simultaneous eigenfunctions.

(iii) Prove that the commutation relation (3) is equivalent to the vector commutation relation

$$\vec{L} \times \vec{L} = i\hbar \vec{L} \quad \text{---} (6)$$

which is another definition of an axial vector that the curl between itself don't vanish in the quantum limit. Does eq (3) & (6) have classical analog with Poisson Bracket?

- Now the trouble with non-vanishing commutator in quantum mechanics is that there exists an uncertainty in their measurements. As we saw in the previous case: eq (3) implies

$$\langle \Delta L_i \rangle^2 \langle \Delta L_j \rangle^2 \geq \frac{1}{4} |\langle [L_i, L_j] \rangle|^2$$
$$\geq \frac{1}{4} \langle L_k \rangle^2. \quad \cdots (7)$$

Since L_x, L_y, L_z are Hermitian operators each one has its own Hilbert space. But one's Hilbert space is not an Hilbert space for the two others. If we consider the Hilbert space of any L_k in eq (7), then $\langle L_k \rangle^2$ is some number and the uncertainty in the measurements of L_i & L_j are related by this number in such a way that if $\Delta L_i \to 0$, $\Delta L_j \to \infty$ and vice versa. Because, the Hamiltonian involves all three components of the angular momenta, and although the Hamiltonian also commutes with all three components, the Hilbert space of any one component is still not a good Hilbert space for the Hamiltonian.

So, what do we generally do? We will still go ahead and use the Hilbert space of any one component of the $\vec{L}$. We often choose L_z as a convention and also because L_z has a simpler form in the spherical coordinates $\hat{L}_z = i\hbar \frac{\partial}{\partial \phi}$. But what we call the z-component is a pure convention. Then one we choose the Hilbert space of L_z, this part of the Hamiltonian involving L_z is now fully solved. For the remaining part involving L_x, L_y, which do <u>not</u> commute, we need to construct a "wave packet" with minimum possible uncertainty in both L_x & L_y, such that $\langle \Delta L_x \rangle^2 \langle L_y \rangle^2 = \frac{1}{4} \langle L_z \rangle^2$. This is analogous to the wavepacket formulation we introduced for Hamiltonian involving x, p which do not commute. For the S.H.O Hamiltonian having a form: $p^2 + x^2$, we found it was convenient to even introduce raising and lowering operators $a = x + ip$, $a^+ = x - ip$, such that the Hamiltonian becomes proportional to the number operator $\hat{N} = aa^+$. The eigenfunctions of the number operator are the Gaussian states in both position and momentum domain, which is the wavepacket having least possible uncertainty in both position and momentum space.

Therefore, our approach will be along this line and we will use the Hilbert space of L_z and introduce raising and lowering operators $L_\pm = L_x \pm i L_y$. A distinction we will find here is that the Hilbert space of L_z is <u>finite dimensional</u>, whereas the Hilbert space of the number operator in the previous case was infinite dimensional. Both Hilbert spaces are discrete though.

So, we define the non-Hermitian raising and lowering operators as

$$L_\pm = L_x \pm i L_y . \quad \text{----} (8)$$

(Notice that $L_\pm^\dagger = L_\mp$, therefore they stand for $a^\dagger$, a like operators).
In analogy with the number operator $\hat{N} = a^\dagger a$, let us define a similar number like Hermitian operator

$$L_+ L_- = (L_x + iL_y)(L_x - iL_y) = L_x^2 + L_y^2 - i[L_x, L_y].$$
$$= L_x^2 + L_y^2 + \hbar L_z = L^2 - L_z^2 - \hbar L_z \quad \text{--} (9a)$$

$$\therefore \quad [L_+, L_-] = 2\hbar L_z \quad \text{--} (9b)$$

$$[L_z, L_\pm] = \pm \hbar L_\pm \quad \text{--} (9c).$$

$$[L_z, L_+L_-] = [L_z, L^2]$$
$$= [L_z, L_x^2] + [L_z, L_y^2]$$
$$= L_x[L_z, L_x] + [L_z, L_x]L_x + \cdots$$
$$= L_x i\hbar L_y + i\hbar L_y L_x - i\hbar L_y L_x - i\hbar L_x L_y$$
$$= 0. \quad \text{---} (9d)$$

$$[L^2, L_\pm] = 0 \quad \text{---} (9e)$$

Therefore we obtain our important clue that

$$[L_z, L_+L_-] = [L_z, L^2] = 0, \quad \text{-} (9d)$$

which means that L_z and L^2, and L_z and the "number" like operator share the same eigenstates and hence the ladder operators can be used to raise and lower between different eigenstates. Therefore, one can similarly start building the Hilbert space starting with the first state which is annihilated by L_-, i.e., $L_-|0\rangle = 0$. Notice that we are not calling it the ground state or the vaccum state, because, we do not have here a Hamiltonian. In general, the potential energy can depend on L differently and hence which state would correspond to the ground state is not known a priori.

But we have something else here that all eigenstates of the "number" operator are also eigenstates of L_z & L^2. Therefore, we can build the Hilbert space from these operators. We know the expressions of L_z, L^2 and we can solve for their eigenfunctions, but lets proceed with the abstract Hilbert space here. In the abstract case, we do not know the eigenvalues of L_z, L^2 yet, but we know their dimensions. From the commutation relations, as well as from the fact that $L_i \theta_i$ has the dimension of the phase space, i.e., $\hbar$ and the angular variable does not have a physical dimension, so the dimension of L_i is $\hbar$ and $L^2 \sim \hbar^2$. Therefore, the eigenvalues of L_z & L^2 will be $\hbar$ & $\hbar^2$ multiplied with some numbers, which are the quantum numbers. We denote the quantum numbers by 'm' & 'ℓ'. Then the eigenstates will be denoted by these two quantum number as $|\psi_{\ell m}\rangle \equiv |\ell, m\rangle$. The two eigenvalue equations are written as

$$L_z |\ell, m\rangle = m\hbar\, |\ell, m\rangle, \qquad \cdots (10a)$$

$$L^2 |\ell, m\rangle = \ell(\ell+1)\hbar^2 |\ell, m\rangle. \qquad \cdots (10b)$$

(We have written the eigenvalue of L^2 by a peculiar notation of $l(l+1)$. This is just for future convenience). At this stage, we do not have any knowledge of whether m & l are integers or not and if there is any bound on the allowed values and range of m & l. So, we will just treat them as some real numbers, because L_z, L^2 are Hermitian operators. (Of course we can guess that atleast m has to be discrete integers by the fact that $U = e^{iL_z\theta/\hbar}$ corresponds to rotation by angle θ about the z-axis and rotation is in build periodic. That means a rotation by $\theta = 2\pi$ should brings the unitary operator U back to an unit / identity operator $I \equiv e^{i2\pi m}$, since its equivalent to no rotation. Therefore, $L_z 2\pi/\hbar = 2\pi m \Rightarrow L_z = m\hbar$. The same constraint is there for the rotations along other axes and hence its reasonable to anticipate 'l' will also be integer. But there will be more concrete way to figure this things out.)

Lets take any component, say, L_x, and the inner product $\langle l,m | L_x^2 | l,m\rangle$
$= \langle L_x(l,m) | L_x(l,m)\rangle = \langle L_x \psi_{lm} | L_x \psi_{lm}\rangle$. Since this is an inner product of a state $|\psi'_{lm}\rangle = |L_x \psi_{lm}\rangle$, from the definition of an inner product, $\langle L_x \psi_{lm} | L_x \psi_{lm}\rangle \geq 0$. This means $\langle l,m | \vec{L}^2 | l,m\rangle \geq 0$. This implies that $l(l+1) \geq 0$. This would mean:

$$l \geq 0. \qquad \text{——(11)}.$$

(Alternatively, one can say $l \leq -1$, but since one can then redefine $l' = -(l+1)$ and get $l' \geq 0$ condition, so we are back to the same condition. Hence $l \leq -1$ being the same condition, we reject it).

From eq (9e), we get

$$L^2 \left(L_\pm \,|l,m\rangle\right) = L_\pm \left(L^2 |l,m\rangle\right) = l(l+1)\hbar^2 \left(L_\pm |l,m\rangle\right) \text{ --- } (12a)$$

Therefore, $L_\pm |l,m\rangle$ is also an eigenstate of L^2 with the same eigenvalue. There are two options for this to be true. (i) $L_\pm |l,m\rangle$ is linearly dependent on $|l,m\rangle$, i.e., $L_\pm |l,m\rangle = \lambda |l,m\rangle$, which means $|l,m\rangle$ is also an eigenstate of $L_\pm$. But remember that $L_\pm$ are not Hermitian operator. Or, (ii) $L_\pm |l,m\rangle$ & $|l,m\rangle$ are degenerate states of L^2, in which case $L_\pm |l,m\rangle$ & $|l,m\rangle$ are linearly independent, i.e. $\langle l,m| L_\pm |l,m\rangle = 0$. In the later case, $L_\pm |l,m\rangle$ would correspond to the other eigenstates of the same Hilbert space. Since, all states in the Hilbert space are also eigenstates of L_z, so, lets check whether the later is true. We know from eq (9c), that L_z & $L_\pm$ do not commute, but their commutation however returns back $L_\pm$ operator. So, we have hope.

$$\begin{aligned} L_z \left(L_\pm \,|l,m\rangle\right) &= \left(L_\pm L_z \pm \hbar L_\pm\right)|l,m\rangle \qquad \text{from eq (9c).} \\ &= L_\pm m\hbar |l,m\rangle \pm \hbar L_\pm |l,m\rangle \quad \text{from eq (10a).} \\ &= (m \pm 1)\hbar \left(L_\pm |l,m\rangle\right) \qquad \text{--- } (12b) \end{aligned}$$

So, $L_\pm |l,m\rangle$ are also eigenstates of L_z with <u>different</u> eigenvalues, this means $L_\pm |l,m\rangle$ are not linearly dependent to $|l,m\rangle$, and are different eigenstates within the same Hilbert space. We see that L^2 operator has lot of degeneracy which are not degenerate for L_z. In other words, if the Hamiltonian only has L^2 operator present, as we will see for the kinetic energy term, then it will have degeneracy. But in addition if there are terms proportional to L_z (as a matter of fact any component L_i), which has to be present in the potential energy term, then those degenerate energy levels will be lifted by this term. Physically, having a term proportional to L_z, means, we have broken the rotational symmetry of the orbitals, and there is an energy gain to have the orbitals oriented w.r.to the z-axis. Such a term can be obtained by applying an external magnetic field. In the context of spin angular momentum, as a magnetic field is applied, it orients the spins along this direction and we have a potential term $\sim \mu_B \vec{B}.\vec{S}$. Such a term is called Zeeman effect. In the Stern-Gerlach experiment, we had added the Zeeman term to allign the orbital and spin angular momentum).

Eq(12b) also indicate that $L_\pm$ does have the effect of taking the state $|l,m\rangle$ to another state $|l,m\pm1\rangle$, justifying its name raising and lowering operator. We can figure out how its done by choosing a form

$$L_\pm |l,m\rangle = c_\pm(l,m)\, |l, m\pm 1\rangle, \quad \cdots (13)$$

where $c_\pm(l,m)$ are the complex coefficients that we need to figure out now. Taking conjugation of eq(13), we have
$\langle l,m|(L_\pm)^\dagger = \langle l,m| L_\mp = \langle l, m\pm 1|\, c_\pm^*(l,m)$. Multiplying this in eq (13) we have

$$|c_+(l,m)|^2 \langle l,m+1|l,m+1\rangle = \langle l,m| L_- L_+ |l,m\rangle$$
$$= \langle l,m| \left(L^2 - L_z^2 - \hbar L_z \right) |l,m\rangle \quad \begin{pmatrix}\text{from} \\ \text{eq 9a}\end{pmatrix}$$
$$= \langle l,m| \left[l(l+1) - m^2 - m \right] \hbar^2 |l,m\rangle$$
$$= \left[l(l+1) - m(m+1) \right] \hbar^2 \langle l,m|l,m\rangle.$$

Recall that $|l,m\rangle$ states, being eigenstates of linear, Hermitian operators are orthonormalized, i.e. $\langle l',m'|l,m\rangle = \delta_{ll'}\delta_{mm'}$.
Hence we get

$$\boxed{c_+(l,m) = \hbar\sqrt{l(l+1) - m(m+1)}} \quad — (14a)$$

upto some arbitrary phase which we can set it to be zero by taking advantage of the fact that the eigenstates $|l,m\rangle$ are defined arbitrarily up to a phase. Similarly we get

$$\boxed{c_-(l,m) = \hbar\sqrt{l(l+1) - m(m-1)}} \quad — (14b)$$

(*) Now, given the fact that $|c_\pm(l,m)|^2 \geq 0$, we obtain

$$\hbar^2 \left[l(l+1) - m(m\pm 1) \right] \geq 0.$$

$$\Rightarrow \quad \boxed{\begin{aligned} l(l+1) &\geq m(m+1) \\ l(l+1) &\geq m(m-1) \end{aligned}}, \quad \cdots (15)$$

Therefore, from eq (15) and since $\ell \geq 0$ (from eq (11)), we obtain the bound on the Hilbert space :

$$\boxed{-\ell \leq m \leq \ell} \quad \text{— (16).}$$

Now, as we did for the case of Harmonic oscillator, the lowest state of the "number" operator is something that is annihilated by the lowering operator. Because, the job of a lowering operator is to lower the m-value to m-1. If we are at the lowest possible m_{min} state, there is no other state, and hence $|\ell, m_{min}-1\rangle$ must not exist. Therefore, the minimum value of m is something which is annihilated by L_- :

$$L_- |\ell, m_{min}\rangle = 0 . \quad \text{— (17)}$$

From eq (13), this means $\quad C_-(\ell, m_{min}) = 0.$

$$\Rightarrow \quad \ell(\ell+1) - m_{min}(m_{min}-1) = 0 .$$

$$\Rightarrow \quad \boxed{m_{min} = -\ell} \quad \text{— (18a).}$$

as also expected from eq (16).

Similarly, the maximum value of m, ie m_{max} is something which is annihilated by L_+ : $L_+|\ell, m_{max}\rangle = 0$, $C_+(\ell, m_{max}) = 0$.

This gives

$$\boxed{m_{max} = \ell} \quad \text{— (18b)}$$

Now, since starting from the minimum value of $m = -\ell$, one obtain all other states upto $m = \ell$, by repeated action of L_+, which raise the m-values by 1, so, the allowed values of m for a given ℓ is

$$\boxed{m \equiv -\ell, -\ell+1, -\ell+2, \cdots, \ell-2, \ell-1, \ell} \quad -(19).$$

Therefore, for a given value of ℓ, there are $\boxed{(2\ell+1) \text{ states.}}$ Because of this constraint in eq(19), and the fact that the total number of states has to be $(2\ell+1)$ which is an integer, there are two possible solutions - and hence two kind of particles:

$(2\ell+1) \equiv$ even integer $= 2, 4, 6, \cdots$ which gives $\ell = 1/2, 3/2, 5/2.$

Therefore, the angular momentum is half-integer multiples. Since we cannot think of orbital angular momentum being fractional which would correspond to a unitary rotation $e^{iL_z\theta/\hbar} = e^{i\ell\theta} = e^{i\frac{1}{2}2\pi} = e^{i\pi} = -1$. This is interesting, that under a 2π rotation, denoted by the unitary rotation on the Hilbert space $|\ell,m\rangle$, we do expect the state to come back to itself. But for the case of half-integer angular momentum, we obtain a phase of π, i.e., the state return to $-|\ell,m\rangle$ after a 2π rotation. This is very peculiar to happen for a particle orbiting in an orbit. But, such an angular momentum can be thought about to happen for the spin angular momentum. This is also precisely what Stern-Gerlach experiment reported for electrons. Therefore, we conclude that the spin angular momentum of electron is $1/2$, whose Hilbert space has two states $m_s = \pm 1/2$. Particles with half-integer spins are called <u>Fermions</u>. Electrons, protons, are examples of fermions. We will come back to the Hilbert space of spin $1/2$ particles below. This is clearly a quantum effect and it may not have any classical analog.

$\underline{(2l+1) = \text{odd integer} = 1, 3, 5, \cdots \text{ which gives } l = 0, 1, 2, \cdots}$.

Therefore, such states are achived for integer values of angular momentum. For angular momentum having integer l values, the 2π rotation leaves the states unchanged. Particles with integer spin angular momenta are called <u>Bosons</u>. Photon, phonon, etc are examples of Bosons. Ofcourse, for a particle (both fermions & bosons) rotating in space can have integer orbital angular momentum, as Bohr assumed.

To tabulate what we said above, we have.

$(2l+1)$	l	m	orbital or spin or both	Particles spin
0	×	×	×	×
1	0	0	Both	Boson if $l=s=0$.
2	$\frac{1}{2}$	$-\frac{1}{2}, \frac{1}{2}$	spin	Fermion
3	1	$-1, 0, 1$	Both	Boson if $s=1$.
4	$3/2$	$-3/2, -1/2, 1/2, 3/2$	spin	Fermions
5	2	$-2, -1, 0, 1, 2.$	Both	Boson if $s=2$
⋮	⋮	⋮	⋮	⋮

- All these states can be obtained by applying the raising or lowering operators $L\pm$ starting from the state with lowest or highest value of $m = \mp l$, respectively:

$$\left.\begin{aligned} |l, m\rangle &= N_+ (L+)^{m-m_{min}} \, |l, m_{min}\rangle \\ &= N_- (L-)^{m_{max}-m} \, |l, m_{max}\rangle, \end{aligned}\right\} \quad (20)$$

where the normalisation $N\pm$ can be fixed easily.

- Clearly, $|l,m\rangle$ form a finite dimensional Hilbert space of dimension $(2l+1)$. Any general state of rotationally symmetric Hamiltonian with angular momentum l can be expanded in this Hilbert space. We will see more of that later. On the other hand, a general state vector can be expanded in all values of l as

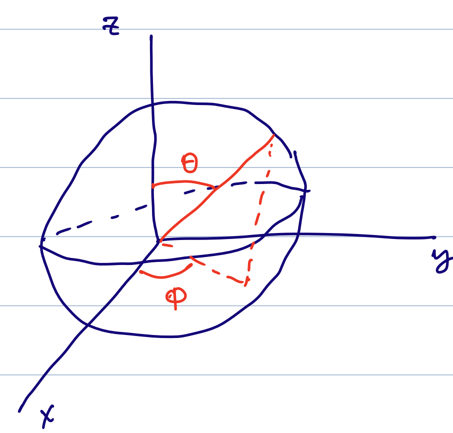
$$|\psi\rangle = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \psi_{lm} |l,m\rangle, \text{ where } \psi_{lm} = \langle l,m|\psi\rangle.$$

The closure property of this basis is $\sum_{l=0}^{\infty} \sum_{m=-l}^{l} |l,m\rangle\langle l,m| = \mathbb{I}$

- Another interesting property of the axial vectors following the commutation relation, we will show that any operator defined in this Hilbert space of same dimension can be expanded in terms of three angular momentum. This is shown by Wigner-Eckwart theorem which either we will see in this course or in QM-II.

(*) Representation of $|l,m\rangle$ states in spherical coordinates

Earlier we had momentum states $|p\rangle$ which we projected on the position states $|x\rangle$ to obtain plane wave solutions. Similarly, we can project the angular momentum states $|l,m\rangle$ onto its conjugate domain $|\theta,\phi\rangle$ and we denote those states $\Psi_{lm}(\theta,\phi) = Y_{lm}(\theta,\phi)$. Notice that we have three angular momenta L_x, L_y, L_z, but only two variables θ, ϕ. This is precisely because all three angular momenta are not independent, only two components are independent and the third one can be obtained from the commutation relation. You may also have learned somewhere else that the rotation on a Bloch sphere (on the surface of a fixed radius sphere), is denoted by two Euler angles. The commutation relation $L_x L_y - L_y L_x = i\hbar L_z$ is also telling us that if we make a rotation with respect to x-axis first and then w.r.t y-axis, or if we make a rotation w.r.t y-axis first followed by x-axis, we don't get to the same point, but we need another rotation w.r.t the z-direction to come to the same point.



Because of two Euler angle required for a rotation in 3 dimensions, we also have two quantum numbers $|l,m\rangle$.

• So, we want to evaluate $Y_{\ell m}(\theta,\phi)$ here. The reason for denoting them by function Y will be clear later that the result will turn out to be spherical harmonics functions.

$$\langle \theta,\phi | \ell, m\rangle = Y_{\ell m}(\theta,\phi) \quad --- (21).$$

The $|\theta,\phi\rangle$ eigenkets defined on the Bloch sphere are the eigenstates of angles $\hat{\theta}|\theta,\phi\rangle = \theta\,|\theta,\phi\rangle$, $\hat{\phi}|\theta,\phi\rangle = \phi|\theta,\phi\rangle$. It is a continuous, infinite dimensional Hilbert space for all values of $0 \leq \theta \leq \pi$ and $0 \leq \phi \leq 2\pi$, but the Hilbert space is periodic or called cyclic or compact, because for values of θ and ϕ outside those range can be brought back to the domain.

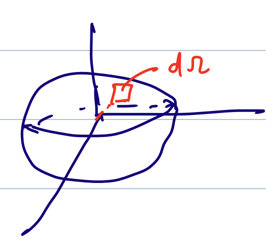
$\Rightarrow$ The closure or completeness relation is defined (in analogy with the position space case of $\int_{-\infty}^{\infty} dx\, |x\rangle\langle x| = \mathbb{I}$) as

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} d\Omega\; |\theta,\phi\rangle\langle\theta,\phi| = \mathbb{I} \quad --- (22)$$

where $d\Omega$ is the solid angle defined on the Bloch sphere as $d\Omega = \sin\theta\, d\theta\, d\phi$.

$\Rightarrow$ The inner product of $|\theta,\phi\rangle$ is hence defined as

$$\boxed{\langle\theta',\phi'|\theta,\phi\rangle = \frac{1}{\sin\theta}\,\delta(\theta-\theta')\,\delta(\phi-\phi') \quad — (23)}$$



$\Rightarrow$ Let us determine the abstract angular momentum operator in the angular space:

$$\langle \theta, \phi | \hat{L}_i | \theta, \phi' \rangle = L_i(\theta,\phi)\,\delta(\theta-\theta')\,\delta(\phi-\phi'), \text{ for } i = x, y, z.$$

We can simply evaluate these operators in the angle space starting from their expression in the coordinate space

$L_i = \epsilon_{ijk} r_j p_k = -i\hbar\, \epsilon_{ijk} r_j \frac{\partial}{\partial r_k}$. We know that

$$\langle \theta\phi | \hat{x} | \theta, \phi \rangle = x = r\sin\theta\cos\phi \qquad 0 \leq r \leq \infty$$

$$y = r\sin\theta\sin\phi \qquad 0 \leq \theta \leq \pi$$

$$z = r\cos\theta \qquad 0 \leq \phi \leq 2\pi.$$

Then we can evaluate:

$$L_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \quad \cdots (24a)$$

$$L_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \quad --(24b)$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi} \quad -(24c)$$

&

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad --(24d)$$

$$L_\pm = \hbar e^{\pm i\phi}\left[\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right]. \quad --- (24e)$$

From eq (24c). $\langle \theta, \phi | \hat{L}_z | l, m \rangle = -i\hbar \langle \theta, \phi | \frac{\partial}{\partial \phi} | l, m \rangle$

$$= -i\hbar \frac{\partial}{\partial \phi} \langle \theta, \phi | l, m \rangle$$

$$= -i\hbar \frac{\partial}{\partial \phi} Y_{lm}(\theta, \phi). \quad \text{---(25a)}.$$

We also know that $\hat{L}_z | l, m \rangle = m\hbar | l, m \rangle$. Applying $\langle \theta, \phi |$ on both sides we get $\langle \theta, \phi | \hat{L}_z | l m \rangle = m\hbar \langle \theta, \phi | l, m \rangle$ ---(25b)

Equating eq (25a) & (25b), we get

$$\frac{\partial}{\partial \phi} Y_{lm}(\theta, \phi) = i m \, Y_{lm}(\theta, \phi) \quad \text{--(26)}.$$

The solution of this first order differential equation is obtained by the ansatz:

$$Y_{lm}(\theta, \phi) = F_{lm}(\theta) \, e^{im\phi} \quad \text{---(27)}$$

which tells us a separation of variable method. We can now apply this ansatz to eq (24d), and recall again the fact that $\langle \theta, \phi | \hat{L}^2 | l, m \rangle = l(l+1)\hbar \langle \theta, \phi | l, m \rangle = l(l+1)\hbar \, Y_{lm}(\theta, \phi)$, we get a 2nd order differential equation as:

$$\frac{\partial^2}{\partial \theta^2} F_{lm} + \cot\theta \frac{\partial}{\partial \theta} F_{lm} + \left[l(l+1) - \frac{m^2}{\sin^2\theta} \right] F_{lm} = 0 \quad \text{---(28)}.$$

We won't solve this differential equations, but quote the result that the solution of this 2nd order PDE is the Legendre polynomials $F_{lm}(\theta) = P_l^m(\cos\theta)$. You can learn more about these polynomials from some standard math text book. Therefore, we get the eigenfunctions of the angular momentum operators as

$$\boxed{Y_{\ell m}(\theta,\phi) = P_\ell^m(\cos\theta)\, e^{im\phi}} \quad \cdots (29).$$

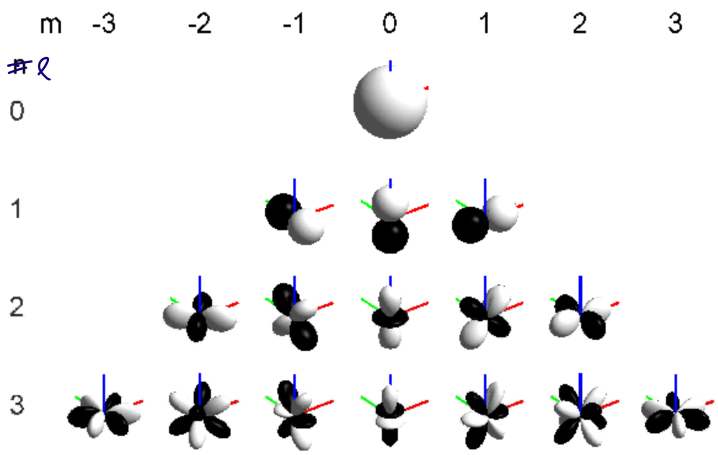
This wave function is not yet normalized. We can normalized it according to eq (23). ϕ part is normalized as $\frac{1}{\sqrt{2\pi}} e^{im\phi}$ and $P_\ell^m(\cos\theta)$ normalized form is

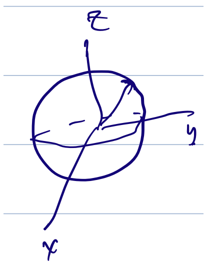
$$F_{\ell m}(\theta) = \left[\frac{2\ell + (\ell-m)!}{2(\ell+m)!}\right] P_\ell^m(\cos\theta).$$

Some of the spherical Harmonics are.

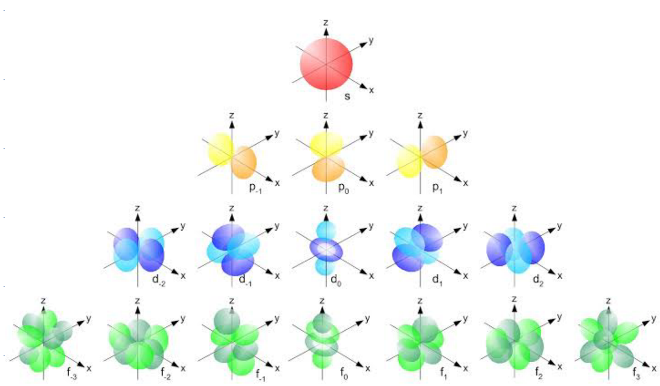
	Spherical	Cartesian	Rotating
$\ell=0$	$Y_{\ell=0}^{m=0}(\theta,\phi)=\sqrt{\frac{1}{4\pi}}$	$\sqrt{\frac{1}{4\pi}}$	$\sqrt{\frac{1}{4\pi}}$
$\ell=1$	$Y_{\ell=1}^{m=-1}(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\sin\phi\sin\theta$	$\sqrt{\frac{3}{4\pi}}\frac{y}{r}$	$-\sqrt{\frac{3}{4\pi}}\sin\theta\sin(-\omega t-\phi)$
	$Y_1^0(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta$	$\sqrt{\frac{3}{4\pi}}\frac{z}{r}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
	$Y_1^{+1}(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\phi\sin\theta$	$\sqrt{\frac{3}{4\pi}}\frac{x}{r}$	$\sqrt{\frac{3}{4\pi}}\sin\theta\cos(-\omega t+\phi)$
$\ell=2$	$Y_2^{-2}(\theta,\phi)=\sqrt{\frac{15}{16\pi}}\sin(2\phi)\sin^2\theta$	$\sqrt{\frac{15}{4\pi}}\frac{xy}{r^2}$	$-\sqrt{\frac{15}{16\pi}}\sin^2\theta\sin(-\omega t-2\phi)$
	$Y_2^{-1}(\theta,\phi)=\sqrt{\frac{15}{4\pi}}\sin\phi\sin\theta\cos\theta$	$\sqrt{\frac{15}{4\pi}}\frac{yz}{r^2}$	$-\sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\sin(-\omega t-\phi)$
	$Y_2^0(\theta,\phi)=\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$	$\sqrt{\frac{5}{16\pi}}\left(\frac{3z^2}{r^2}-1\right)$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
	$Y_2^{+1}(\theta,\phi)=\sqrt{\frac{15}{4\pi}}\cos\phi\sin\theta\cos\theta$	$\sqrt{\frac{15}{4\pi}}\frac{xz}{r^2}$	$\sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\cos(-\omega t+\phi)$
	$Y_2^{+2}(\theta,\phi)=\sqrt{\frac{15}{16\pi}}\cos(2\phi)\sin^2\theta$	$\sqrt{\frac{15}{16\pi}}\frac{x^2-y^2}{r^2}$	$\sqrt{\frac{15}{16\pi}}\sin^2\theta\cos(-\omega t+2\phi)$

- In (θ, ϕ) space, the spherical Harmonics look like





- The shape of these spherical Harmonics remind us of different orbitals, like s, p, d, f etc that we may have encountered in other courses. Indeed different orbitals symmetries atoms take for different values of l, m are indeed linear combinations of the spherical Harmonics.



S − Orbital $(L = 0)$:

- $Y_0^0(\theta, \emptyset) = \frac{1}{\sqrt{4\pi}}$ (12)

P − Orbital $(L = 1)$:

- $P_z = Y_1^0(\theta, \emptyset) = \sqrt{\frac{3}{4\pi}} \cos(\theta)$ (13)
- $P_x = \frac{1}{\sqrt{2}}\left(Y_1^{-1}(\theta, \emptyset) - Y_1^1(\theta, \emptyset)\right) = \sqrt{\frac{3}{4\pi}} \sin(\theta)\cos(\emptyset)$ (14)
- $P_y = \frac{i}{\sqrt{2}}\left(Y_1^{-1}(\theta, \emptyset) + Y_1^1(\theta, \emptyset)\right) = \sqrt{\frac{3}{4\pi}} \sin(\theta)\sin(\emptyset)$ (15)
  - *For:* $Y_1^{\pm 1}(\theta, \emptyset) = \mp\sqrt{\frac{3}{8\pi}} \sin(\theta)\, e^{\pm i\emptyset}$

D − Orbital $(L = 2)$:

- $d_{z^2} = Y_2^0(\theta, \emptyset) = \sqrt{\frac{5}{16\pi}}(3\cos^2(\theta) - 1)$ *with nodal* $\emptyset = 54.7^o$ (16)
- $d_{xz} = \frac{1}{\sqrt{2}}\left(Y_2^{-1}(\theta, \emptyset) - Y_2^1(\theta, \emptyset)\right) = \sqrt{\frac{15}{4\pi}} * \frac{xz}{r^2}$ (17)
- $d_{yz} = \frac{i}{\sqrt{2}}\left(Y_2^{-1}(\theta, \emptyset) + Y_2^1(\theta, \emptyset)\right) = \sqrt{\frac{15}{4\pi}} * \frac{yz}{r^2}$ (18)
- $d_{xy} = \frac{i}{\sqrt{2}}\left(Y_2^{-2}(\theta, \emptyset) - Y_2^2(\theta, \emptyset)\right) = \sqrt{\frac{15}{4\pi}} * \frac{xy}{r^2}$ (19)
- $d_{x^2-y^2} = \frac{1}{\sqrt{2}}\left(Y_2^{-2}(\theta, \emptyset) + Y_2^2(\theta, \emptyset)\right) = \sqrt{\frac{15}{16\pi}} * \frac{x^2-y^2}{r^2}$ (20)
  - $Y_2^{\pm 1}(\theta, \emptyset) = \mp\sqrt{\frac{15}{8\pi}} \sin(\theta)\cos(\theta) e^{\pm i\emptyset}$ (21)
  - $Y_2^{\pm 2}(\theta, \emptyset) = \sqrt{\frac{15}{32\pi}} \sin^2(\theta)\, e^{\pm 2i\emptyset}$ (22)

- H.W. Show that $(L^2)_{lm,l'm'} = \int d\Omega \, Y^*_{l'm'}(\theta,\varphi) \, L^2 \, Y_{lm}(\theta,\varphi)$

$$= l(l+1)\hbar^2 \, \delta_{ll'} \, \delta_{mm'}.$$

$$(L_z)_{lm,l'm'} = \int d\Omega \, Y^*_{l'm'}(\theta,\varphi) \, L_z \, Y_{lm}(\theta,\varphi)$$

$$= m\hbar \, \delta_{ll'} \, \delta_{mm'}.$$

& $(L_\pm)_{lm,l'm'} = \sqrt{l(l+1) - m(m\pm1)} \, \hbar \, \delta_{ll'} \, \delta_{m',m\pm1}.$

⊛ Matrix Representation of angular momentum operators.

The matrix representation is simply obtaining the matrix elements of the operators in the Hilbert space of $|l,m\rangle$. We know that the Hilbert space dimension here is $(2l+1)$ for a given value of l, and hence the matrix of the operator has also the dimension of $(2l+1)\times(2l+1)$. We know the following relations:

- $\langle l', m' | l m\rangle = \delta_{ll'}\,\delta_{mm'}$ --- (30a)

  $\langle l' m' | L_z | l m\rangle = m\hbar\,\delta_{ll'}\,\delta_{mm'}$ = diagonal matrix with entries $m\hbar$. (30b)

  $\langle l' m' | L^2 | l m\rangle = l(l+1)\hbar^2\,\delta_{ll'}\,\delta_{mm'}$ = diagonal matrix with entries $l(l+1)\hbar^2$. (30c)

  $\langle l' m' | L_\pm | l m\rangle = \sqrt{l(l+1) - m(m\pm 1)}\,\hbar\,\delta_{ll'}\,\delta_{m', m\pm 1}$ = off-diagonal matrix. —(30d)

  $\langle l m' | L_x | l m\rangle = ?$ <u>H.W.</u> —(30e)

  $\langle l m' | L_y | l m\rangle = ?$

- What about the eigenvectors $|l,m\rangle$? We can simply obtain it from the eigenvector of the diagonal matrix L_z. We will see some examples now.

- Examples:

$l=0$: $(2l+1)=1$. Here there dimension of the Hilbert space is 1.
So, $m=0$. $L_z = 0$, $L^2=0$. Null matrices.

$l=1/2$: $2l+1=2$: This is a two dimensional Hilbert space.
$m = \pm 1/2$.

$$L_z = \hbar\begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}, \quad L_+ = \hbar\begin{pmatrix} 0 & \frac{1}{2} \\ 0 & 0 \end{pmatrix}, \quad L_- = \hbar\begin{pmatrix} 0 & 0 \\ \frac{1}{2} & 0 \end{pmatrix}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad = \frac{\hbar}{2}\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$$L_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad L_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad L^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

The three matrices $\sigma_x, \sigma_y, \sigma_z = \frac{2}{\hbar}(L_x, L_y, L_z)$ are called the Pauli matrices for spin-1/2 particles. Show that the Pauli matrices are Hermitian and follow the commutation relation $[\sigma_i, \sigma_j] = 2\epsilon_{ijk}\sigma_k$. The eigen vector of L_z is

$$|l,m\rangle = |\tfrac{1}{2}, 1/2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |1/2, -1/2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

(Show that these two states are linearly indepenent).

H.W. obtain the eigenvalues and eigenvectors of L_x, L_y.

$\ell = 1$: $(2\ell+1) = 3$: We have a 3 dimensional Hilbert space with $m = 1, 0, -1$.

So, $L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$, $L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$, $L_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$

- Obtain the eigenvectors $|1,1\rangle$, $|1,0\rangle$, $|1,-1\rangle$.

Spin Angular Momentum

As shown by Stern-Gerlach experiment for electrons, and later on by many other experiments, most of the quantum particles possess internal precession with respect to its own axis. Therefore, they posses an internal spin angular momentum, which we often denote by $\vec{S}$. But unlike the orbital angular momentum which have an algebric expression in terms of two other operators in the domain space, the spin angular momentum $\vec{S}$ does not have any such algebric expression. However, it is confirmed by many experiments that spin angular momenta follow all the algebra obtained above for the orbital angular momenta. Therefore, $\vec{S}$ are axial vectors and have the commutation relation

$$[S_i, S_j] = i\hbar\, \epsilon_{ijk} S_k \quad \text{--- (31)}$$

All properties we obtained above for S_z, S^2, $S_\pm$ operators, and the Hilbert space $|s, m_s\rangle$ also hold for spin. One physical property that is distinct for spin compared to orbital momenta is that spin can take half-integer values as well as integer values, while the latter can only take integer values. We do not generally have a spin wavefunction written in the (θ, ϕ) domain, but it is customary to use the matrix representation for the spins. The results are same to what we have done for the general $\vec{L}$

operators above. We will elaborate that discussion little further here for spin $s=1/2$ case, which is the value electrons take.

For spin $s=1/2$, we have two dimensional Hilbert space. We express the spin operators by 2×2 Pauli matrices as $S_i = \hbar/2\, \sigma_i$, where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{--- (32)}$$

The commutation relation follows from that S operators as $[\sigma_i, \sigma_j] = 2\epsilon_{ijk}\sigma_k$. Show that their anti commutation relation satisfies

$$\{\sigma_i, \sigma_j\} = \sigma_i\sigma_j + \sigma_j\sigma_i = 2\delta_{ij} + 2i\epsilon_{ijk}\sigma_k \quad \text{--- (33)}$$

$$\Rightarrow \sigma_i^2 = \mathbb{I}, \qquad \sigma_i\sigma_j = i\epsilon_{ijk}\sigma_k \text{ for } i\neq j\neq k. \quad \text{--- (34)}$$

[The 2nd property has important consequence. If we define a unitary transformation with these Pauli matrices as $U = e^{i\vec{\sigma}\cdot\vec{\theta}} = e^{i(\sigma_x\theta_x + \sigma_y\theta_y + \sigma_z\theta_z)}$, where θ_i are the rotations of the spins w.r.to i^{th} direction, we see that all higher power terms in the expansion of the expansion gives back a single operator because of eq (34). This is the reason a large angle rotation θ_i can be obtained by many many infinitesimal rotation $\theta_i = N\delta\theta_i$ with $N\to\infty$. Therefore, such unitary operator indeed gives continuous rotation of spin. Eq (34) also satisfy some group theory axiom and σ_i for a continuous group.]

$\Rightarrow$ σ_i are Hermitian, Traceless, i.e. $\mathrm{Tr}\,\sigma_i = 0$ and $\det \sigma_i = -1$.

[σ_i following the commutation algebra, provides a complete set of 2x2 operators, in which any 2x2 operators can be expanded (c.f. Wigner-Eckwart theory. There is also a group theory argument for that that we may learn somewhere else). Remember, the complete set must also include 2x2 identity operator I.]

- We often use the eigenstates of σ_z as the Hilbert space. The two eigenstates are

$$|s, m_s\rangle = |1/2, 1/2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\0\end{pmatrix}; \quad |\tfrac{1}{2}, -1/2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\end{pmatrix}.$$

These two states are often denoted as spin up and spin down states $|\uparrow\rangle$, $|\downarrow\rangle$, respectively. When we say spin up or down, we do mean along the z-axis. But as we said earlier, z-axis is just a choice of convenience, but spin can be oriented along any arbitrary direction. We can obtain such states as a linear superposition of the $|\uparrow\rangle, |\downarrow\rangle$ states, which is to say, any other spinstate can be expanded in the 2-component Hilbert space of $|\uparrow\rangle$, $|\downarrow\rangle$.

$$|\chi\rangle = c_1|\uparrow\rangle + c_2|\downarrow\rangle \quad \text{---} \ (35)$$

where, of course, $c_1 = \langle\uparrow|\chi\rangle$, $c_2 = \langle\downarrow|\chi\rangle$, as usual.

- H.W.: (i) Show that $|\uparrow\rangle, |\downarrow\rangle$ states are orthonormalized. It also satisfies closure relation $|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| = \mathbb{I}$.

  (ii) Show that normalization condition on $|\chi\rangle$ gives $|c_1|^2 + |c_2|^2 = 1$.

  (iii) Find the eigenvectors of σ_x & σ_y operators. Can you expand these eigenvectors in the Hilbert space of σ_z operator?

  (iii) Consider a general operator in the x-y plane for a spin rotated with an angle ϕ as $S_\phi = S_x \cos\phi + S_y \sin\phi$. Find the eigenvalue and eigenvectors of S_ϕ. Obtain the expectation value of S_x, S_y & S_z in this basis.

  (iv) Repeat H.W. (iii) for a general 3D spin along $\hat{n}$ direction $S_n = S_x \sin\theta\cos\phi + S_y \sin\theta\sin\phi + S_z \cos\theta$.

  (v) Repeat the analysis for integer spin, say, $s=1$, as done above for $\ell=1$.

- <u>Magnetic moment and Zeeman Coupling.</u>

The existence of spin of electron has the physical consequence of giving intrinsic magnetic moment of a system. Of course, the same is true for proton & neutron which also possess spin (typically higher spin like 3/2, 5/2 etc) and can give large magnetic moment to the system. Let us only focus here to electrons with $s = 1/2$, although the formulas are easily generalized to higher spins.

We know that the magnetic moment of a charge particle $-e$ and mass m, moving in a closed orbit with angular momentum $\vec{L}$ produces a magnetic field at the center which is given by $\vec{M} = -\frac{e}{2m}\vec{L}$. Since, there is no classical expression for spin $\vec{S}$, we define the magnetic moment of spin similarly as,

$$\vec{M} = -\frac{eg}{2m}\vec{S} \quad \text{--- (36)}$$

where the extra factor g is called the gyromagnetic ratio, which is determined by experiment for spin to be $g=2$, whereas for orbital angular momentum $g=1$.

Such magnetic moment couples to an external magnetic field and gives a potential energy term as

$$H = -\vec{M}\cdot\vec{B} = \frac{eg}{2m}\vec{S}\cdot\vec{B} = \frac{eg\hbar}{4m}\vec{\sigma}\cdot\vec{B} \quad \text{--- (37)}$$

The Hamiltonian in eq (37) is called the Zeeman effect. We will solve eq (37) in a nicer and simpler method later.

⊛ Addition of angular momentum

Next we will study the properties of two or more angular momentum additions, such as $\vec{L}_1 + \vec{L}_2$, $\vec{S}_1 + \vec{S}_2$ for two interacting particles, or $\vec{L} + \vec{S}$ for a single particle with finite spin rotating in an orbit. We will denote the total angular momentum by $\vec{J}$ and the algebra is the same whether we are adding orbital or spin or both. Therefore, we basically want to study

$$\vec{J} = \vec{J}_1 + \vec{J}_2 .$$

- Since $\vec{J}_1$, $\vec{J}_2$ are axial vectors and have the above commutation relation for each of them, the total angular momentum is also an axial vector and have the same commutation relation $[J_1^i, J_1^j] = i\hbar \epsilon_{ijk} J_1^k$, and the same for $\vec{J}_2$, and $\vec{J}_1$ & $\vec{J}_2$ commute.

- Why do we want to work with the total angular momentum while we could simply work with indivial angular momentum?

Ans: The reason is that there are many occasions, especially for many particle Hamiltonian, like a He atom, that individual angular momenta are not conserved, ie, do not commute with the Hamiltonian, but the total angular momentum is conserved. This is expected for interacting particles, where the particles can exchange angular momentum between themselves but the total angular momentum of the system is conserved. Another example is when the Hamiltonian has terms like the spin orbit coupling term $\vec{L}\cdot\vec{S}$, we will see that the particle can exchange angular momentum between orbital and spin parts, but the total angular momentum $\vec{L}+\vec{S}$ remains conserved.

H.W. (i) Consider the Hamiltonian for a He atom with two electrons, where individually two electrons have the Hamiltonian of a Hydrogen atom H_1, H_2, but in addition, the two electrons also interact via the Coulomb repulsion $V(r_{12}) = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|}$. So, the total Hamiltonian is

$$H = H_1(r_1) + H(r_2) + V(r_{12}), \text{ where}$$

$$H(r_i) = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{2e^2}{4\pi\epsilon_0}\frac{1}{r_i}.$$

Show that L_1, L_2 for individual electrons are not conserved, but the total angular momentum $\vec{L} = \vec{L}_1 + \vec{L}_2$ is conserved.

(ii) Consider a single electron Hamiltonian with a spin-orbit coupling term $H = H_0 + \lambda\,\vec{L}\cdot\vec{S}$, where H_0 is as defined in the above example, and λ is a constant. Show that $\vec{J} = \vec{L} + \vec{S}$ is conserved here.

- If for a system of many particles, with indivial angular momentum being conserved, we can use the separation of variable method for the wave function and build the total wavefunction of all particles by a product of angular momentum states of individual particle. (In this case an additional modification has to be done to make the total wave function either symmetric or antisymmetric under the exchange of any two particles. The reason for that we will learn in QM-II course. In any case, we will not be concerned with this situation here and we do not need to bother it).

- Otherwise, when we have the total angular momentum being conserved, then we only have the option to use the Hilbert space of the total angular momentum $|j, m\rangle$. We want to learn here how to construct this Hilbert space by expanding it in the product state of indivial particles angular momentum states $|j_1, m_1\rangle |j_2, m_2\rangle \cdots$. The corresponding expansion coefficients are called Clebsch-Gordon coefficients.

- The allowed and forbidden values of j, m, in terms of $j_1, j_2, \cdots, m_1, m_2 \cdots$ are governed by the <u>selection rule</u>. One source of the selection rule that we can already anticipate is that for the total angular momentum case we have $(2j+1)$ dimensional Hilbert space. As we expand these states in the product state of individual angular momenta, the latter has a Hilbert space of $(2j_1+1)(2j_1+2), \ldots$ dimensional.

$\Rightarrow$ We start our analysis with two general angular momenta, which commute with each other, as

$$\vec{J} = \vec{J}_1 + \vec{J}_2 \quad \text{----} (38).$$

- Let $|j_i, m_i\rangle$ are the orthonormalized abstract simultaneous eigenstates of J_i^2 & J_{iz} for $i=1,2$, then we have

$$J_i^2 |j_i, m_i\rangle = j_i(j_i+1)\hbar\, |j_i, m_i\rangle \quad \text{---} (39a).$$

$$J_{iz} |j_i, m_i\rangle = m_i \hbar\, |j_i, m_i\rangle \quad \text{---} (39b)$$

- We want to now obtain a Hilbert space for the total angular momentum $\vec{J}$, by taking it into account that $\vec{J}$ is obtained from $\vec{J}_1$ & $\vec{J}_2$, rather than being an angular momentum by itself without any knowledge of $\vec{J}_1, \vec{J}_2$. In other words, in an ideal scenario, we would like to build an Hilbert space with states which are the simultaneous eigenstates of J^2, J_z, J_i^2, J_{iz}, so that in these eigenstates, all values of j, m, j_i, m_i are precisely specified. Obviously, this would have been possible if all these operators J^2, J_z, J_i^2, J_{iz} commute with each other. <u>But unfortunately they don't.</u>

- Let us first see their commutation relations first.

→ $\vec{J}^2 = \vec{J}_1^{\,2} + \vec{J}_2^{\,2} + 2\,\vec{J}_1\cdot\vec{J}_2$; since $[\vec{J}_1, \vec{J}_2] = 0$ ---- (40a)

→ $[\vec{J}^2, \vec{J}_i^{\,2}] = [\vec{J}_1^{\,2}, \vec{J}_i^{\,2}] + [\vec{J}_2^{\,2}, \vec{J}_i^{\,2}] + 2[\vec{J}_1\cdot\vec{J}_2, \vec{J}_i^{\,2}]$.

$= 2\,\underbrace{\vec{J}_1}_{}\cdot\underbrace{[\vec{J}_2, \vec{J}_i^{\,2}]}_{=0} + 2\underbrace{[\vec{J}_1, \vec{J}_i^{\,2}]}_{=0}\cdot\vec{J}_2$

$= 0$. —(40b)

→ $[J^2, J_{iz}] = \underbrace{[J_1^2, J_{iz}]}_{=0} + \underbrace{[J_2^2, J_{iz}]}_{=0} + 2[\vec{J}_1\cdot\vec{J}_2, J_{iz}]$.

$= 2[J_{1x}J_{2x}, J_{iz}] + 2[J_{1y}J_{2y}, J_{iz}] + 2\underbrace{[J_{1z}J_{2z}, J_{iz}]}_{=0}$

(Lets take $i=1$) $= 2\,J_{1x}\underbrace{[J_{2x}, J_{1z}]}_{=0} + 2[J_{1x}, J_{1z}]J_{2x} + (x\to y)$.

$= -2i\hbar\,J_{1y}J_{2x} + 2\,J_{1x}J_{2y}. \neq 0$ —(40c)

→ $[J_z, \vec{J}_i^{\,2}] = [J_{1z}, \vec{J}_i^{\,2}] + [J_{2z}, \vec{J}_i^{\,2}] = 0.$ —(40d)

→ $[J_z, J_{iz}] = 0$. —(40e)

$$\boxed{\text{So, } \vec{J}^2, J_z \text{ commute with } \vec{J}_i^{\,2}, \text{ but } J^2 \text{ does } \underline{\text{not}} \text{ commute } J_{iz}, \text{ and } J_z \text{ commutes with } J_i^2 \text{ \& } J_{iz}.}$$ —(41)

So, we won't get a simultaneous eigenstate for all six operators. We have to make a compromize. We can think about along the line of wavepacket or coherent state, that don't go for any one to eigenstate, rather construct a wavepacket like state in which we have the minimum uncertainties between those operators which do not commute. We are actually going to do similar here.

From (41), we have <u>two</u> possible, but distinct, states with maximum number of conserved operators. They are

(i) $\vec{J}_1^{\,2}, \vec{J}_2^{\,2}, \vec{J}^{\,2}, J_z$, with the corresponding quantum numbers are j_1, j_2, j, and m respectively, and the corresponding state is denoted by $\boxed{|j_1 j_2 j m\rangle}$. Thus according to this definition, we have

$$\vec{J}^{\,2}|j_1 j_2 j m\rangle = j(j+1)\hbar^2 |j_1 j_2 j m\rangle \qquad -(42a)$$
$$J_z |j_1 j_2 j m\rangle = m\hbar\, |j_1 j_2 j m\rangle \qquad -(42b)$$
$$\vec{J}_i^{\,2} |j_1 j_2 j m\rangle = j_i(j_i+1) |j_1 j_2 j m\rangle \qquad -(42c)$$

(notice that since $\vec{J}^{\,2}$ & $\vec{J}_i^{\,2}$ differ by $\vec{J}_1\cdot\vec{J}_2$ as in eq (40a), so we cannot relate j with j_1 & j_2 in this state. m_1 & m_2 values in this state are completely uncertain).

(ii) Another combination is $\vec{J}_1^{\,2}, \vec{J}_2^{\,2}, J_{1z}, J_{2z}$ (and J_z but J_z is not an independent operator in this state since $J_z = J_{1z}+J_{2z}$). The corresponding state carries quantum numbers j_1, j_2, m_1, and m_2 and the state is denoted as $\boxed{|j_1 j_2 m_1 m_2\rangle}$. We can build this state as a "direct product" state as

$$|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle \quad \text{--- (43)}$$

This is called a direct product state, because when we act this state by operators involving $\vec{J}_1$, the operator only acts on the Hilbert space of $|j_1 m_2\rangle$ and does not act on $|j_2 m_2\rangle$, and vice versa. Clearly, the state $|j_1 j_2 m_1 m_2\rangle$ is orthogonalized as

$$\langle j_1' j_2' m_1' m_2' | j_1 j_2 m_1 m_2\rangle = \langle j_1' m_1' | j_1 m_1\rangle \langle j_2' m_2' | j_2 m_2\rangle$$
$$= \delta_{j_1' j_1} \delta_{m_1' m_1} \delta_{j_2' j_2} \delta_{m_2' m_2}. \quad \text{--- (44a)}$$

And
$$J_1^2 |j_1 j_2 m_1 m_2\rangle = \left(J_1^2 |j_1 m_1\rangle\right) |j_2 m_2\rangle$$
$$= j_1(j_1+1)\hbar^2 |j_1 j_2 m_1 m_2\rangle.$$
$$J_2^2 |j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle \left(J_2^2 |j_2 m_2\rangle\right) \quad \text{--- (44b)}$$
$$= j_2(j_2+1)\hbar^2 |j_1 j_2 m_1 m_2\rangle.$$

$$J_{iz} |j_1 j_2 m_1 m_2\rangle = m_i |j_1 j_2 m_1 m_2\rangle \quad \text{--- (44c)}$$
$$J_z |j_1 j_2 m_1 m_2\rangle = (J_{1z} + J_{2z}) |j_1 j_2 m_1 m_2\rangle$$
$$= (m_1 + m_2)\hbar |j_1 j_2 m_1 m_2\rangle \quad \text{--- (44d)}$$

Therefore, in this state $m = m_1 + m_2$, but j is completely uncertain.
The dimension of the direct product Hilbert space is $(2j_1+1)(2j_2+1)$.

If you want to express the direct product state in the angular space $|\theta, \phi\rangle$ we will get

$$Y_{j_1 j_2 m_1 m_2}(\theta,\phi) = \langle \theta \phi | j_1 j_2 m_1 m_2\rangle$$
$$= Y_{j_1 m_1}(\theta,\phi)\, Y_{j_2 m_2}(\theta,\phi), \quad \text{for } \vec{J}_i \text{ being orb. ang. mom}$$
$$= \chi_{s_1 m_1}\, \chi_{s_2 m_2}, \quad \text{for } \vec{J}_i \text{ being spin ang. mom.}$$
$$= Y_{l_1 m_1}(\theta,\phi)\, \chi_{s_2 m_2}, \quad \text{for } J_1 = \text{orb. ang. mom}, \; s_2 = \text{spin. ang. mom}$$

(*) Now we have two possible, distinct states; one has few conserved quantities and few completely uncertain, and the other state has the complementary quantities conserved and uncertain. What do we do now?

[We had similar situation earlier. For a generic Hamiltonian, we had a choice of either position eigenstates or momentum eigenstates, but in position eigenstates position is completely known and momentum is completely uncertain. What we did was we expanded one state in another as $|x\rangle = \frac{V}{(2\pi\hbar)}\int dp\, \langle p|x\rangle |p\rangle = \frac{V}{(2\pi\hbar)}\int dp\, e^{ipx}\, |p\rangle$, where e^{ipx} are the expansion coefficients, called plane wave states. Then for any general wavefunction $\Psi(x)$ in position space we can expand in the momentum space as $\Psi(x) = \frac{V}{(2\pi\hbar)}\int dp\, \Psi(p)\, e^{ipx}$, where $\Psi(p)$ are the expansion coefficient, distributing different probability weight to different plane wave states. This is how we obtained a wave packet. Their we called it as the Fourier transformation because p, x happen to be cannonically conjugate to each other, but otherwise, essentially we were simply expanding one eigenstates (Hilbert space) into another Hilbert space of operators which do not commute.]

Clebsch-Gordon Coefficients:

So, we will follow the same strategy and expand one Hilbert space $|j_1 j_2 j m\rangle$ in the Hilbert space of $|j_1 j_2 m_1 m_2\rangle$:

$$|j_1 j_2 j m\rangle = \sum_{\substack{m_1=-j_1 \\ m_2=-j_2}}^{j_1, j_2} \underbrace{\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle}_{C^{j_1 j_2 j}_{m_1 m_2 m}} |j_1 j_2 m_1 m_2\rangle \quad \text{---(45)}$$

$\equiv$ Clebsch-Gordon Coeff.

(Notice that we only sum over m_1, m_2 indices, because the other two indices j_1, j_2 are common on both sides).

Selection Rules: We now need to find out the allowed values of j, m, for the given values of j_i, m_i.

(a) So, far we know $m_i = -j_i, -j_i+1, \text{----}, j_i-1, j_i$, and $m_1+m_2 = m$. Therefore, the C.G. coefficients are zero unless $m = m_1+m_2$. This gives our first selection rule:

$$\langle j_1 j_2 j m | j_1 j_2 m_1 m_2\rangle = \delta_{m, m_1+m_2}. \quad \text{---}(46a)$$

(b) Now we need to derive a relation between j_i & j.

m by definition runs between $-j, -j+1 \text{ ---} j-1, j$.

(i) The maximum value of m is j. The maximum values of m_i are j_i, and hence maximum value of $m = m_1+m_2$ is j_1+j_2. Therefore, the maximum possible value of j is j_1+j_2. So, when $m = j_1+j_2$, how

many possible values of m_1 & m_2 are allowed? Only one! $m_1 = j_1$, $m_2 = j_2$.
Hence, in this case we have from eq(45);

$$|j_1 j_2\; j\; j_1+j_2\rangle = \cancel{\sum_{\substack{m_1=j_1\\ m_2=j_2}}} \underbrace{\langle j_1 j_2\; j_1 j_2 \,|\, j_1 j_2\; j\; j_1+j_2\rangle}_{=1.} |j_1 j_2\; j_1 j_2\rangle$$

Since both states are normalized to unity, we have the C.G. coeff $C = 1$.

(ii) Next we consider $m = j_1+j_2-1$ case. Here we have two possible values of m_1 & m_2: Either $(m_1 = j_1,\, m_2 = j_2-1)$ or $(m_1 = j_1-1,\, m_2 = j_2)$.
So, here we will have two C.G. coefficients which we will evaluate later.

If $m = j_1+j_2-1$, what are the possible values of j? Recall, that $|m| \leq j$. Hence, we have two possible values $j = j_1+j_2$ or $j = j_1+j_2-1$.

(iii) Proceeding further to $m = j_1+j_2-2$, now we have three possible values combination of m_1, m_2; and also three possible values of j, which are, j_1+j_2, j_1+j_2-1, j_1+j_2-2.

(iv) Repeating this argument successively, we can obtain that the minimum possible positive value of j is not $-j_1-j_2$, which is a negative number, but $|j_1-j_2|$. Therefore, the possible values of j for a given j_1, j_2 is

$$|j_1-j_2| \leq j \leq j_1+j_2. \quad \text{—(46)}$$

So, we rewrite the two selection rules for given values of j_i, m_i

$$\boxed{\begin{gathered} |j_1 - j_2| \le j \le j_1 + j_2 \\ m = m_1 + m_2 . \end{gathered}} \quad \text{---} \quad (47)$$

We see that, for given m_1, m_2, m is already known, but for given $j_1 j_2$, j is unknown.

H.W. (i) How many values of j are there between $|j_1 - j_2|$ to $j_1 + j_2$, i.e. what's the dimension of the Hilbert space of $|j_1 j_2 j m\rangle$ states?

Show that
$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1) \quad \text{---} \quad (48).$$

Recall that $(2j_1+1)(2j_2+1)$ is also the dimension of the Hilbert space of the direct product state $|j_1 j_2 m_1 m_2\rangle$ that we obtained

(ii) Show that the inverse "Fourier transformation" or expansion to eq (45) is

$$\boxed{|j_1 j_2 m_1 m_2\rangle = \sum_{j=|j_1-j_2|}^{j_1+j_2} \cancel{\sum_{m=-j}^{j}} \left(C^{j_1 j_2 j}_{m_1 m_2 m}\right)^* |j_1 j_2 j m\rangle \quad \text{---} (49)}$$

since only one value of m is allowed.

* Summary so far:

Let us recap what we have so far. We have two Hilbert spaces of same dimensions $(2j_1+1)(2j_2+1)$, with complementary conserved quantities. Their Hilbert space properties are defined as

$|j_1 j_2 m_1 m_2\rangle$:

Orthogonality : $\langle j_1 j_2 m_1 m_2 | j_1 j_2 m_1' m_2'\rangle = \delta_{m_1 m_1'} \delta_{m_2 m_2'}$ — (50a)

Closure : $\displaystyle\sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 j_2 m_1 m_2\rangle\langle j_1 j_2 m_1 m_2| = \mathbb{I}.$ — (50b)

Ladder op: $J_i^{\pm}|j_1 j_2 m_1 m_2\rangle = \hbar\sqrt{j_i(j_i+1) - m_i(m_i \pm 1)}\,|j_1 j_2\, m_i \pm 1\; m_{j\neq i}\rangle$ — (50c)

$|j_1 j_2\, j\, m\rangle$:

Orthogonality : $\langle j_1 j_2\, j m | j_1 j_2\, j' m'\rangle = \delta_{jj'}\delta_{mm'}$ — (50d)

Closure : $\displaystyle\sum_{j=|j_1-j_2|}^{j_1+j_2} \sum_{m=-j}^{j} |j_1 j_2\, j m\rangle\langle j_1 j_2\, j m| = \mathbb{I}.$ — (50e)

Ladder op: $J^{\pm}|j_1 j_2\, j m\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)}\,|j_1 j_2\, j\, m\pm 1\rangle$ ... (50f)

$|j_1 j_2 m_1 m_2\rangle \Leftrightarrow |j_1 j_2 j m\rangle$:

$$|j_1 j_2 j m\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} C^{j_1 j_2 j}_{m_1 m_2} \, |j_1 j_2 \, m_1 m_2\rangle \quad \text{--- (50g)}$$

$$|j_1 j_2 \, m_1 m_2\rangle = \sum_{j=|j_1-j_2|}^{j_1+j_2} \cancel{\sum_{m=-j}^{j}} \left(C^{j_1 j_2 j}_{m_1 m_2 m}\right)^* |j_1 j_2 j m\rangle. \quad \text{--- (50h)}$$

since $m = m_1 + m_2$, only one m is allowed.

Since both $|j_1 j_2 m_1 m_2\rangle$ & $|j_1 j_2 j m\rangle$ are both orthonormalized, so we obtain the normalization condition on the C.G. coefficients as

$$\sum_{m_1=-}^{j_1} \sum_{m_2=-j_2}^{j_2} \left(C^{j_1 j_2 j}_{m_1 m_2 m}\right)^* C^{j_1 j_2 j'}_{m_1 m_2 m} = \delta_{j j'} \quad \text{--- (50i)}$$

And $$\sum_{j=|j_1-j_2|}^{j_1+j_2} \left(C^{j_1 j_2 j}_{m_1 m_2 m}\right)^* C^{j_1 j_2 j}_{m_1' m_2'} = \delta_{m_1 m_1'} \delta_{m_2 m_2'}. \quad \text{--- (50j)}$$

Both (50 i) & (50 j) combined gives us

$$\sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \left|C^{j_1 j_2 j}_{m_1 m_2}\right|^2 = \sum_{j=|j_1-j_2|}^{j_1+j_2} \left|C^{j_1 j_2 j}_{m_1 m_2 m}\right|^2 = 1 \quad \text{--- (50k)}$$

⊛ Recursion Relations of the C.G. Coefficients:

We make use of the ladder operator relations to obtain a recursion relation for the C.G. coefficients. Note that $J^{\pm} = J_1^{\pm} + J_2^{\pm}$. So, we apply J^- on eq(50g) and use eq(50f) to obtain

$$\sqrt{j(j+1) - m(m-1)}\,\cancel{\hbar}\,|j_1 j_2 j\, m-1\rangle = \sum_{m_1,m_2} C^{j_1 j_2 j}_{m_1 m_2 m}\left(J_1^- + J_2^-\right)|j_1 j_2\, m_1, m_2\rangle$$

$$= \sum_{m_1 m_2} C^{j_1 j_2 j}_{m_1 m_2 m}\Big[\sqrt{j_1(j_1+1) - m_1(m_1-1)}\,\cancel{\hbar}\,|j_1 j_2\, m_1-1\, m_2\rangle + \sqrt{j_2(j_2+1) - m_2(m_2-1)}\,\cancel{\hbar}\,|j_1 j_2\, m_1\, m_2-1\rangle\Big]$$

Then we multiply $\langle j_1 j_2\, m_1' m_2'|$ on both sides, we get

$$\sqrt{j(j+1) - m(m-1)}\; C^{j_1 j_2 j}_{m_1' m_2'\, m-1} = \sum_{m_1 m_2} C^{j_1 j_2 j}_{m_1 m_2 m}\Big[\sqrt{j_1(j_1+1) - m_1(m_1-1)}\,\underbrace{\langle j_1 j_2\, m_1' m_2'|j_1 j_2\, m_1-1, m_2\rangle}_{m_1' = m_1-1,\; m_2' = m_2}$$
$$+ \sqrt{j_2(j_2+1) - m_2(m_2-1)}\,\underbrace{\langle j_1 j_2\, m_1' m_2'|j_1 j_2\, m_1, m_2-1\rangle}_{m_1' = m_1,\; m_2' = m_2-1}\Big]$$

$$= \sqrt{j_1(j_1+1) - m_1'(m_1'+1)}\; C^{j_1 j_2 j}_{m_1'+1\, m_2'\, m} + \sqrt{j_2(j_2+1) - m_2'(m_2'+1)}\; C^{j_1 j_2 j}_{m_1'\, m_2'+1\, m} \quad \text{--(51a)}$$

Similarly applying J_+ operator we get (H.W.).

$$\sqrt{j(j+1)-m(m+1)}\; C^{j_1 j_2 j}_{m_1' m_2' m+1} = \sqrt{j_1(j_1+1)-m_1'(m_1'-1)}\; C^{j_1 j_2 j}_{m_1'-1\, m_2'\, m} + \sqrt{j_2(j_2+1)-m_2'(m_2'-1)}\; C^{j_1 j_2 j}_{m_1'\, m_2'-1\, m} \quad \text{--(51b)}.$$

(We will henceforth remove the prime and denote $m_1' \to m_1$, $m_2' \to m_2$).

- To obtain a recursion relation, we start with the $m=j$ value, which is the highest allowed value of m for a given j. Now we see from the L.H.S of eq(51b): $C^{j_1 j_2 j}_{m_1 m_2\, m+1} = \langle j_1 j_2 m_1 m_2 | j_1 j_2\, j\, m+1\rangle$ has to be zero for $m=j$, because $|j_1\, j_2\, j\, j+1\rangle$ state does not exist. Therefore, for $m=j$, we obtain from eq(51b):

$$\boxed{C^{j_1 j_2 j}_{m_1-1\, m_2\, j} = -\frac{\sqrt{j_2(j_2+1)-m_2(m_2-1)}}{\sqrt{j_1(j_1+1)-m_1(m_1-1)}}\; C^{j_1 j_2 j}_{m_1,\, m_2-1\, j}} \quad \text{--(51c)}$$

$\rightarrow$ This relates two nearest C.G. coefficients for the same value of $m = m_1+m_2 = j$, where $|j_1-j_2| \le j \le j_1+j_2$. Then once we find out the C.G. coefficient for the highest $m=j$ value, we can use (50a) to obtain all other C.G. coefficients for $m<j$, all the way upto $m=-j$.

→ Through a recursion relation, if we know any one C.G. coefficient, we can determine the rest. But the initial value is not determined here. But recall normalization eq (50k) which we can use to determine the remaining one. Therefore, all C.G. coefficients are completely determined here.

→ We however see two difficulties here.

(a) If any one of the C-G. coefficient is zero, all other coefficients are also zero due to the recursion relation. On the other hand, if we start with a finite value of coefficient, all other coefficients will be found to be non-zero.

This statement looks odd at a first glance to eq (51c). Because, from this equation, even if we start with $C^{j_1 j_2 j}_{m_1 m_2 - 1 m} \neq 0$ on the L-H-S, but $C^{j_1 j_2 j}_{m_1 - 1 m_2 m}$ can be zero if $m_2 = j_2$ from the numerator term. But, thanks to the selection rule, this says $m = m_1 + m_2 = m_1 + j_2 \Rightarrow m_1 = m - j_2$ and $|j_1 - j_2| \leq j = m \leq j_1 + j_2 \Rightarrow |j_1 - j_2| \leq m_1 + j_2 \leq j_1 + j_2$, which cannot be satisfied for any value of m_1 between $-j_1$ to $+j_1$. Therefore, for $j = m$, $m_2 = j_2$ value is not possible. This way we can convince that, thanks to the selection rule, all the coefficients are finite if we set one initial value to be finite.

So, we will set one initial value to be finite.

(b) Another difficulty is that if there is any constant phase in all c's, then it gets cancelled from both sides of the recursion relations (50a, 50b, 50c). Therefore, we cannot determine the C.G. coefficients upto a overall (global) phase factor.

No problem! The same problem we have from the eigenvalue equation of linear operators that the phase of the eigenvectors cannot be determined upto a global phase factor. We called it gauge freedom. But this gauge freedom does not change anything in the inner product and expectation values, therefore we can live with this undetermined global phase.

We can sometimes take this gauge freedom into our advantange. Since the physical properties does not depend on an overall phase in the eigenvectors, we can choose any global phase in which the problem becomes easier.

This is precisely what we are going to do here. We will take the phase of our initial C.G. coefficient, say, $c^{j_1 j_2 j}_{m_1 m_2 - 1 m} = |c^{j_1 j_2 j}_{m_1 m_2 - 1 m}| e^{i\phi}$, and devide all the coefficients by this phase term $e^{i\phi}$ as $c^{j_1 j_2 j}_{m_1 m_2 m} = c^{j_1 j_2 j}_{m_1 m_2 m} / e^{i\phi}$.

In simple term, this is just to say, we take our initial C.G. coefficient to be <u>real</u>.

Therefore, from (a) & (b), we impose the condition on the initial C.G. coefficient that

$C^{j_1 j_2 j}_{m_1, m_2 - 1, m}$ should be positive and real.

As we said, this makes no difference to the physical properties obtained from the Hilbert space. This particular gauge fixing choice was proposed by Condon, Shortley, and Wigner. Upto this gauge fixing, all other C.G. coefficients are now uniquely determined from the recursion relations [eq 50 a, b, c].

Symmetries of the C.G. coefficients :

- We notice that the value of $\vec{J} = \vec{J}_1 + \vec{J}_2$ does not change if we interchange between $\vec{J}_1$ & $\vec{J}_2$. So, how does the C.G. coefficient transform under the exchange of j_1 & j_2 quantum numbers?

(H.W.) : One can show that, the C.G. coefficient changes as -

$$C^{j_1 j_2 j}_{m_1 m_2 m} = (-1)^{j_1+j_2-j}\, C^{j_2 j_1 j}_{m_2 m_1 m}. \quad \text{---- (52a)}$$

$$= (-1)^{j_1+j_2-j}\, C^{j_1 j_2 j}_{-m_1 -m_2 -m} \quad \text{when } \vec{J}_1 \to -\vec{J}_1, \vec{J}_2 \to -\vec{J}_2, \vec{J} \to -\vec{J}.$$

$$= C^{j_2 j_1 j}_{-m_2 -m_1 -m} \quad \text{--- (52b)}$$

$$= (-1)^{j_1-m_1} \left(\frac{2j+1}{2j_2+1}\right)^{1/2} C^{j_1 j j_2}_{m_1 -m -m_2}; \quad \vec{J}_1 \to \vec{J}_1, \vec{J}_2 \to -\vec{J}, \vec{J} \to -\vec{J}_2$$

$$= (-1)^{j_2+m_2} \left(\frac{2j+1}{2j_1+1}\right)^{1/2} C^{j j_2 j_1}_{-m\, m_2 -m_1}; \quad \vec{J}_1 \to -\vec{J}, \vec{J}_2 \to \vec{J}_2, \vec{J} \to -\vec{J}_1.$$

- As we mentioned at the begining, there are mainly three cases of angular momentum addition we need to consider:

(a) $\vec{J}_1 = \vec{L}_1$, $\vec{J}_2 = \vec{L}_2 \Rightarrow \vec{J} = \vec{L}_1 + \vec{L}_2$ in which both $j_1 = l_1$, $j_2 = l_2$ are integer and hence $j = |l_1 - l_2|$ to $(l_1 + l_2)$ are all integers. Such cases arise for two or more particle case under central potential, so that total orbital angular commutes with the Hamiltonian. e.g. He-atom with two electrons case having electron-electron repulsion.

(b) $\vec{J}_1 = \vec{L}$, $\vec{J}_2 = \vec{S} \Rightarrow \vec{J} = \vec{L} + \vec{S}$. For the case of s = half-integer spin, $\vec{J}$ will also take half-integer spins. Such cases arises often in Hamiltonian with spin-orbit coupling term:

$$H = \lambda \vec{L} \cdot \vec{S} = \frac{\lambda}{2} (J^2 - L^2 - S^2).$$

(c) $\vec{J}_1 = \vec{S}_1$, $\vec{J}_2 = \vec{S}_2 \Rightarrow \vec{J} = \vec{S}_1 + \vec{S}_2$. For both integer and half-integer spins, we have integer $\vec{J}$ values. Such cases arise for Hamiltonians with spin-spin interactions, e.g., $H = \lambda \vec{S}_1 \cdot \vec{S}_2$ between two spins. We will consider such a case below.

<u>Solution to H.W.C</u> We consider two spin-1/2 particles here.

$s_1 = 1/2,\ m_1 = \pm 1/2,\ s_2 = 1/2,\ m_2 = \pm 1/2.$

- Direct product states $|s_1 s_2 m_1 m_2\rangle = |s_1 m_1\rangle |s_2 m_2\rangle$

$$|\tfrac{1}{2}\tfrac{1}{2}\ \tfrac{1}{2}\tfrac{1}{2}\rangle = |\uparrow\rangle\ |\uparrow\rangle = |\uparrow\uparrow\rangle \quad \text{(Denoting)}$$
$$-\tfrac{1}{2}\ -\tfrac{1}{2} \quad = |\downarrow\rangle\ |\downarrow\rangle = |\downarrow\downarrow\rangle$$
$$\tfrac{1}{2}\ -\tfrac{1}{2} \quad = |\uparrow\rangle\ |\downarrow\rangle = |\uparrow\downarrow\rangle$$
$$-\tfrac{1}{2}\ \tfrac{1}{2} \quad = |\downarrow\rangle\ |\uparrow\rangle = |\downarrow\uparrow\rangle$$

Since $|s_1 s_2 m_1 m_2\rangle$ is an eigenstate of S_z, we have

$$S_z |s_1 s_2 m_1 m_2\rangle = (S_{1z} + S_{2z}) |s_1 s_2 m_1 m_2\rangle$$
$$= (m_1 + m_2) |s_1 s_2 m_1 m_2\rangle$$
$$= m \quad |s_1 s_2 m_1 m_2\rangle.$$

So, m takes three values of $1, 0, -1$.

But $|s_1 s_2 m_1 m_2\rangle$ is not an eigenstate of $\vec{S}^2$. So, s is undefined but selection rule says $|s_1 - s_2| \leq s \leq s_1 + s_2 \Rightarrow s = 0, 1$.

- <u>For $s=0,\ m=0$:</u> we have

$$|s_1 s_2 s m\rangle = \sum_{m_1 m_2} C^{s_1 s_2 s}_{m_1 m_2 m} |s_1 s_2 m_1 m_2\rangle$$

$$\Rightarrow |\tfrac{1}{2}\tfrac{1}{2} 0 0\rangle = \overbrace{C^{1/2\ 1/2\ 0}_{\frac{1}{2}\ -\frac{1}{2}\ 0}}^{a} |\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\ -\tfrac{1}{2}\rangle$$
$$+ \underbrace{C^{\frac{1}{2}\ 1/2\ 0}_{-\frac{1}{2}\ \frac{1}{2}\ 0}}_{b.} |\tfrac{1}{2}\tfrac{1}{2}\ -\tfrac{1}{2}\ \tfrac{1}{2}\rangle$$

$$= a\,|\uparrow\downarrow\rangle + b\,|\downarrow\uparrow\rangle$$

From the symmetry rule we have $C^{\frac{1}{2}\frac{1}{2}0}_{\frac{1}{2}-\frac{1}{2}0} = -C^{\frac{1}{2}\frac{1}{2}0}_{-\frac{1}{2}\frac{1}{2}0}$

From the normalization we have $C^{\frac{1}{2}\frac{1}{2}0}_{\frac{1}{2}-\frac{1}{2}0} = \frac{1}{\sqrt{2}}$.

Therefore, we get $\left|\frac{1}{2}\frac{1}{2}\,0\,0\right\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$ --- (53)

Often we simply denote it by $|00\rangle$.

This is called a SINGLET state, because of single value of the m. This state is antisymmetric under the exchange of two spins. (This is also an entangled state, which means even if two particles live far far away, they are related to each other and if we measure the spin of one particle, the spin of other particle is also precisely known (check it). The interpretation of the state in eq(53) is that this is a superposition of two states with equal probability of spin ↑ particle in state 1 & spin down particle in state 2 and spin ↓ particle in state 2 & spin up particle in state 1, rather than having a precise value of spin in a given state. Recall the interpretation of double slit experiment in which the same particle has finite probability of passing through both slits and hence we took a superposition of both states.)

- For $s=1$, $m=1,0,-1$. We here denote $|sm\rangle \equiv |s_1 s_2\, s m\rangle$.

$$s=1,\quad m=1:\quad |11\rangle = \sum_{m_1 m_2} C^{1/2\,1/2\,1}_{m_1 m_2 1}\, |s_1 s_2\, m_1 m_2\rangle$$

$$= C^{1/2\,1/2\,1}_{1/2\,1/2\,1}\, \left|\tfrac{1}{2}\tfrac{1}{2}\,\tfrac{1}{2}\tfrac{1}{2}\right\rangle = C^{1/2\,1/2\,1}_{1/2\,1/2\,1}\, |\uparrow\uparrow\rangle$$

Due to normalization, $C^{1/2\,1/2\,1}_{1/2\,1/2\,1} = 1$.

So, $$\boxed{|11\rangle = |\uparrow\uparrow\rangle.} \quad \text{-- (54a)}$$

$$s=1,\quad m=-1:\quad \boxed{|1\,-1\rangle = C^{1/2\,1/2\,1}_{-1/2\,-1/2\,-1}\, |\downarrow\downarrow\rangle = |\downarrow\downarrow\rangle} \quad \text{-- (54b)}$$

$$s=1,\quad m=0:\quad |10\rangle = C^{1/2\,1/2\,1}_{1/2\,-1/2\,0}\, |\uparrow\downarrow\rangle + C^{1/2\,1/2\,1}_{-1/2\,1/2\,0}\, |\downarrow\uparrow\rangle$$

[Symmetry property $C^{s_1 s_2 s}_{m_1 m_2 m} = (-1)^{s_1+s_2-s}\, C^{s_2 s_1 s}_{m_2 m_1 m}$].

So, symmetry property says: $C^{1/2\,1/2\,1}_{1/2\,-1/2\,0} = +\,C^{1/2\,1/2\,1}_{-1/2\,1/2\,0}$
(from normalization) $= 1/\sqrt{2}$

$$\boxed{|10\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)} \quad \cdots \text{(54c)}$$

All three states are symmetric under the exchange of two spins. These three states are called triplet states, due to having 3 values of m. The total spin of the two spin is 1.

[This is also a superposition state but with same phase. This is <u>not</u> however an entangled state. ☹ Why.

<u>Check:</u> $S_{1z}|00\rangle = S_{1z}\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = \frac{1}{\sqrt{2}}\left(\hbar/2 - (-\frac{\hbar}{2})\right)$

$= \frac{\hbar}{\sqrt{2}}.$

$S_{2z}|00\rangle = -\hbar/\sqrt{2}.$

But $S_{1z}|10\rangle = S_{1z}\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = 0.$

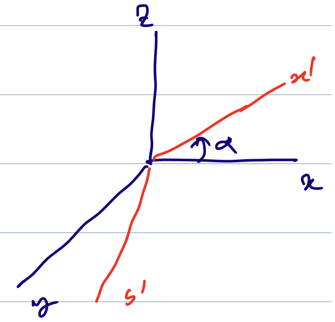
$S_{2z}|10\rangle = 0.$

So, in the triplet superposition state, if we make a measurement of spin in state 1 or 2, we always get the same value. Therefore, we cannot distinguish the two states. But in the singlet state, if we make a measurement in state 1 or 2, we get opposite spin and hence we immediately know the spin in the other state to be opposite.].

Rotation operators & Rotational invariance

Here we will discuss how the state vectors, operators transform under the rotation of the domain space. We have discussed in various occasions that rotations are generated by angular momentum. Let us see first how does that come along.

We know how the coordinate system changes under a rotation by α-angle with respect to the z-axis, say.



$$x' = x\cos\alpha + y\sin\alpha$$

$$y' = -x\sin\alpha + y\cos\alpha$$

$$z = z.$$

We can express this in the vector format.

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \underbrace{\begin{pmatrix} \cos\alpha & +\sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{R_z(\alpha)} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad \text{--- (1)}$$

We can write $R_z(\alpha)$ in terms of an matrix operator L_z as

$$R_z(\alpha) = e^{-iL_z\alpha} = \mathbb{I} - iL_z\alpha + \frac{i^2(L_z\alpha)^2}{2} + \cdots$$

$$= \left(\mathbb{I} - \frac{(L_z\alpha)^2}{2} + \cdots\right) - iL_z\alpha + \frac{i^3 L_z^3\alpha^3}{3!} \cdots$$

[We assume $L_z^2 = \mathbb{I}$]

$$= \left(\mathbb{I} - \frac{\alpha^2}{2} + \cdots\right) - iL_z\left(\alpha - \frac{\alpha^3}{3!} + \cdots\right)$$

$$= \cos\alpha - i L_z \sin\alpha. \quad --(2)$$

Equating eq (1) & (2), we get

$$L_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Therefore, L_z gives a rotation to the coordinate system by α w.r.t z axis. (We see that this L_z matrix is different from the one defined in the basis $|lm\rangle$) We can denote the general rotational operator for a rotation by angle θ with respect an arbitrary unit vector $\hat{n}$ as $R_n(\theta) = e^{-i\vec{J}.\hat{n}\,\theta}$, where $\vec{J}$ is the generalized angular momentum. (Notice that we have ignored the factor $\hbar$ in the exponential because of reference from classical mechanics, but it has to appear there in the exponential due to dimensional reason. In classical mechanics, any general rotation with respect to a reference unit vector is denoted by three Euler angles (α, β, γ), which is denoted by the product of three rotations $R(\alpha\beta\gamma) = R_z(\alpha) R_x(\beta) R_z(\gamma)$ $= e^{-iJ_z\alpha} e^{-iJ_y\beta} e^{-iJ_z\gamma}$). In quantum mechanics, the general angular momentum can be orbital, or spin, or total angular momentum whose components do not commute. Because, three components of the angular momentum are related to each other by the commutator relation one can say there are actually two independent angular momentum and hence two Euler angles are essentially required to govern any rotation in the constant radius sphere, called Bloch sphere. We often denote the

two angles by (θ, ϕ). We know how to define the radial coordinates in terms of these two angles. Then the abstract Hilbert space of the two commuting operators $\vec{J}^2$ & J_z, i.e., $|jm\rangle$ can be projected into the $|\theta, \phi\rangle$ domain, defined on the Bloch sphere gives us the spherical harmonics, which are the analogs of the wave functions of $\vec{J}^2, J_z$: $\langle \theta, \phi | jm \rangle = Y_{jm}(\theta, \phi)$.
(When we say spherical harmonics, we only refer to orbital angular momenta since they can be expressed in terms of position and momentum operators. For spin, no such expression is here and we simply denote χ_{sm} as the wavefunction.).

$R_z(\alpha) = e^{-i\frac{J_z}{\hbar}\alpha}$ is an operator which generates rotation by α-angle w.r.to the z-axis. Then we ask how does the wavefunction $Y_{lm}(\theta, \phi)$ transform under this rotation? For this particular rotational operator w.r.to z-axis, it rather easy to figure it out. As we said earlier, $R_z(\alpha)$ gives a "translation" of the variable ϕ by a value α. This is easy to see because $Y_{lm}(\theta, \phi)$ is an eigenstate of L_z & hence R_z:

$$
\begin{aligned}
R_z(\alpha)\, Y_{lm}(\theta, \phi) &= e^{-iL_z/\hbar\,\alpha}\, Y_{lm}(\theta, \phi) \\
&= e^{-im\alpha}\, F_l(\theta)\, e^{im\phi} \\
&= F_l(\theta)\, e^{-im(\phi+\alpha)} \\
&= Y_{lm}(\theta, \phi+\alpha).
\end{aligned}
$$

This formulation holds for the generalized angular momentum and corresponding wavefunction defined in some angular domain, although its not always possible to obtain a mathematical expression for spin angular momentum. Also, for rotation with respect to any arbitrary direction, say $\hat{n}$, we have $R_n(\alpha) = e^{-i\vec{J}\cdot\hat{n}/\hbar\,\alpha}$ $= e^{-i(J_x n_x + J_y n_y + J_z n_z)/\hbar\,\alpha}$, we cannot simply express as a "translation" by angle α, because the wavefunction is not the simultaneous wavefunction of J_x, J_y & J_z. Therefore, we simply express it by another wavefunction: $\Psi'_{jm}(\theta,\varphi) = R_n(\alpha)\,\Psi_{jm}(\theta,\varphi)$. In abstract notation, we denote it as $|jm\rangle' = \hat{R}_n(\alpha)\,|jm\rangle$.

- $R_n(\alpha)$ is actually a unitary operator: $R_n^{+} R_n = \mathbb{I}$. Therefore, under this unitary rotation, the inner product between any two states, the expectation values of operators remain invariant. To remind ourselves that $R_n(\alpha)$ is a unitary operator, many books denote it by $U_{R_n}(\alpha) \equiv R_n(\alpha)$. We will keep using the notation $R_n(\alpha)$ here. The states transform under the unitary rotations as given above. We also discussed briefly in the previous chapter that to keep the expectation value of an operator to be invariant under a unitary transformations, the operator A itself have to transform as $A' = R_n^{+} A R_n$. Let us see more of it here.

[Ref: Cohen-Tannoudji Complement B_{VI} (5c)]

(*) We will be considering a rotation by angle α with respect to the unit vector $\hat{n}$ in the domain/parameter space defined by a unitary operator

$$R_n(\alpha) = e^{-i\vec{J}\cdot\hat{n}/\hbar\,\alpha} \quad \text{---(3)}$$

acting on any abstract state vector.

- INNER PRODUCT: First we see that under this unitary transformation, the inner product is invariant.

Let's consider any two states $|\psi\rangle$ & $|\phi\rangle$ which transformed to $|\psi'\rangle = R_n(\alpha)|\psi\rangle$ & $|\phi'\rangle = R_n(\alpha)|\phi\rangle$. The inner product is

$$\langle\psi'|\phi'\rangle = \langle\psi|R_n^\dagger(\alpha)R_n(\alpha)|\phi\rangle = \langle\psi|\phi\rangle, \text{ since } R^\dagger R = \mathbb{I}. \quad \text{---(4)}$$

- ROTATION OF OBSERVABLES: Any observable in quantum mechanics is defined by the inner product of a corresponding linear, Hermitian operator. We consider an operator A. Let us say the expectation value of this operator, "a", being a measurable, does not depend on the coordinate system of the domain. In other words, under a rotation by α, the expectation value "a" should be the same. To achieve that we need the state vector $|\psi\rangle$ under which the expectation value is computed, and the operator $\hat{A}$ itself must be transformed. This means,

$$\text{We want } a = \langle\psi|A|\psi\rangle = \langle\psi'|A'|\psi'\rangle.$$

We know, $|\psi'\rangle = R_n(\alpha)|\psi\rangle$, so we need to figure out the relation

between A' & A. $\langle\psi'|A'|\psi'\rangle = \langle\psi|R_n^\dagger A' R_n|\psi\rangle = \langle\psi|A|\psi\rangle$.
Since this is true for any general state, therefore, the identity must hold at the operator level that

$$\boxed{A' = R_n A R_n^\dagger} \quad \text{---} \quad (5).$$

(*) Invariance of operators: The expectation value of an operator is always invariant under a unitary transformation. But when we say an "operator is invariant", ie $A' = A$ in eq(5), what do we get?
Let us consider a infinitesimal rotation $\delta\alpha$ only. (Actually an finite rotation α, can be obtained by applying n number of infinitesimal rotations by $\delta\alpha = \alpha/n$, with taking $n\to\infty$). For small $\delta\alpha$, we can do a Taylor's series expansion of eq(3).

$$R_n(\alpha) \approx \mathbb{I} - \frac{i}{\hbar}\vec{J}\cdot\hat{n}\,\delta\alpha + O(\delta\alpha)^2$$
$$R_n^\dagger(\alpha) \approx \mathbb{I} + \frac{i}{\hbar}\vec{J}\cdot\hat{n}\,\delta\alpha + \delta(\delta\alpha)^2 \quad \text{--}\ (6).$$

Then substituting eq (6) in eq (5) we get

$$A' = \left(\mathbb{I} - \frac{i}{\hbar}\vec{J}\cdot\hat{n}\,\delta\alpha\right) A \left(\mathbb{I} + \frac{i}{\hbar}\vec{J}\cdot\hat{n}\,\delta\alpha\right)$$

$$\boxed{A' = A - \frac{i}{\hbar}\left[\vec{J}\cdot\hat{n}, A\right]\delta\alpha + \delta(\delta\alpha)^2} \quad \text{---}(7)$$

- **SCALAR OPERATOR:** An operator A is said to be a scalar operator if the operator itself remains invariant under the unitary rotation. This means, if $A' = A$. From eq (5), it means A commutes with R_n & $R_n^\dagger$ $A' = R_n A R_n^\dagger = R_n R_n^\dagger A = A$. From, eq (2), it means, the operator A commutes with the generators of the rotation, ie, with the angular momentum operators.

$$[\vec{J}\cdot\hat{n}, A] = 0 .$$

e.g. Examples of scalar operator is J^2 itself, $\vec{L}\cdot\vec{S}$ term, $\vec{r}^2$, $\vec{p}^2$, $\vec{r}\cdot\vec{p}$, $V(r)$ (central potential). Most of the cases we study involve scalar operators, and when an operator $\hat{A}$ is invariant under a symmetry, defined by a unitary operator $\hat{U}$ which is defined by a generator $\hat{g}$ in the form $\hat{U} = e^{i\hat{g}s}$, where s is the domain and g is its canonical conjugate variable, then we say $\hat{A}$ is invariant under the symmetry if it satisfies the relation $UAU^\dagger = A$. This automatically, implies, the operator commutes with its generator $[A, g] = 0$. Since both A & g are linear and Hermitian operators, $[A, g] = 0$ means, both operators are simultaneously diagonalizable, ie, they have the same eigenvectors. A special case is when the variable $s =$ time (t) and the generator $g = H$ (Hamiltonian), then $U = e^{iH/\hbar t}$ generates time translation. $[H, A] = 0$ means A is a constant of motion. Similarly $s = x$, $g = p$ gives spatial translation.

- **VECTOR (TENSOR) OPERATORS** There is another type of operators which have components in the space, like, vectors $\vec{V} = \hat{V}_x \vec{e}_x + \hat{V}_y \vec{e}_y + \hat{V}_z \vec{e}_z$ or tensors (like conductivity tensor $\hat{\sigma}_{xx}, \hat{\sigma}_{xy}, \hat{\sigma}_{xz}, \cdots$). Our focus here will be only for vectors which is a tensor of rank 1. The analysis done here for the vector can hence be generalized in the future to tensor (in other courses).

The expectation value of a vector operator $\langle \hat{\vec{V}} \rangle$ is also invariant for any general state $|\psi\rangle$ under a unitary rotation. This is by definition, since the expectation values of a vector operator is an observable, which should not depend on the choice or orientation of the coordinate system. The expectation value is defined as $\vec{v} = \langle \psi | \hat{\vec{V}} | \psi \rangle$. Now, we make a rotation to the position domain defined by $R_n(\alpha)$ unitary operator. The state changes to $|\psi\rangle \to |\psi'\rangle = R_n(\alpha)$ as usual. The transformation of the vector operator to $\hat{\vec{V}} \to \hat{\vec{V}}'$ is obtained as

$$\vec{v} = \langle \psi' | \hat{\vec{V}}' | \psi' \rangle = \langle \psi | R_n^{+}(\alpha)\, \hat{\vec{V}}'\, R_n(\alpha) | \psi \rangle = \langle \psi | \hat{\vec{V}} | \psi \rangle .$$

So, we have $\quad \hat{\vec{V}}' = R_n(\alpha)\, \hat{\vec{V}}\, R_n(\alpha) \quad \cdots (8).$

This looks the usual as in eq(5). But the surprize lies in the fact that under the rotation $R_n(\alpha)$, the coordinate system has also rotated from $\hat{e}_\mu$ to $\hat{e}_\mu'$, where $\mu = x, y, z$. The $\vec{V}'$ vector is defined in the rotated reference frame as $\hat{\vec{V}}' = V_x' \hat{e}_x' + V_y' \hat{e}_y' + V_z' \hat{e}_z'$, while $\vec{V} = V_x \hat{e}_x + V_y \hat{e}_y + V_z \hat{e}_z$. Therefore, eq (8) can be written explicitly as:

$$\sum_{\mu=x,y,z} V'_\mu \hat{e}'_\mu = R_n(\alpha) \left[\sum_{\mu=x,y,z} V_\mu \hat{e}_\mu \right] R_n^{+}(\alpha) \quad \text{----} (9)$$

So, this his how the vector operator transform under a unitary rotation.

Now what does it mean when we say a vector operator itself is invariant under a rotation?

<u>Ans</u>: A vector operator is invariant under a unitary transformation if its all components V_μ remain invariants, i.e. $V'_\mu = V_\mu$. To find the condition under which this invariance is achieved, we have to write $\hat{e}'_\mu$ in terms of $\hat{e}_\mu$ in eq (9), then we can equate the coefficient of each unit vectors $\hat{e}_\mu$ on both sides, since $\hat{e}_\mu$ are linearly independent.

The expression becomes very long and ugly for rotation w.r.t a general direction $\hat{n}$. So, we will study for a rotation with respect to z-axis and use cyclic rule to obtain the result for other rotation. (For general rotation, see Merzbacher chapter 17, Sec 7, 432).

We consider rotation w.r.t z axis, $R_z(\alpha)$. We also consider infinitesimal rotation only, so that eq (7) is applicable. For the coordinate rotation we go back to eq (1) and substitute $\cos(\delta\alpha) \approx 1$ & $\sin(\delta\alpha) \approx \delta\alpha$ for infinitesimal rotation. Then we get

$$\left.\begin{aligned} \hat{e}_x' &= \hat{e}_x + \hat{e}_y\,\delta\alpha \\ \hat{e}_y' &= -\hat{e}_x\,\delta\alpha + \hat{e}_y \\ \hat{e}_z' &= \hat{e}_z \end{aligned}\right\} \quad -(9).$$

substituting eq (6) + (9) in eq (8), we get:

$$\begin{aligned} \vec{\hat{V}} = \vec{\hat{V}}' &= \left(\mathbb{I} - \tfrac{i}{\hbar}\,\delta\alpha\,\hat{J}_z\right)\hat{V}_x\left(\mathbb{I} + \tfrac{i}{\hbar}\,\delta\alpha\,\hat{J}_z\right)\left(\hat{e}_x + \hat{e}_y\,\delta\alpha\right) \\ &+ \left(\quad " \quad\right)\hat{V}_y\left(\quad " \quad\right)\left(-\hat{e}_x\,\delta\alpha + \hat{e}_y\right) \\ &+ \left(\quad " \quad\right)\hat{V}_z\left(\quad " \quad\right)\hat{e}_z \quad ---(10) \end{aligned}$$

Since $\hat{e}_x$ are linearly independent unit vectors, we can equate their coefficients on both sides:

$$\begin{aligned} \hat{e}_z: \quad \hat{V}_z' &= \left(\mathbb{I} - i/\hbar\,\delta\alpha\,\hat{J}_z\right)\hat{V}_z\left(\mathbb{I} + \tfrac{i}{\hbar}\,\delta\alpha\,\hat{J}_z\right) \\ &= \hat{V}_z - \tfrac{i}{\hbar}\underbrace{\delta\alpha\,[\hat{J}_z, \hat{V}_z]}_{=0.} + O(\delta\alpha)^2 \qquad \text{from eq (7).} \end{aligned}$$

For invariant operator, i.e., $\hat{V}_z' = V_z$: $\boxed{[\hat{V}_z, \hat{J}_z] = 0.}$ --- (11a)

$\hat{e}_x$: $\hat{V}_x' = (1)\,\hat{V}_x\,(1) - (1)\,\hat{V}_y\,(1)\,\delta\alpha$

$$= \hat{V}_x \underbrace{- \frac{i}{\hbar}\delta\alpha[\hat{J}_z, \hat{V}_x] - \hat{V}_y\,\delta\alpha}_{=0} + O(\delta\alpha)^2.$$

For $V_x' = V_x$: $\frac{i}{\hbar}[\hat{J}_z, \hat{V}_x] = -\hat{V}_y$.

$$\boxed{[\hat{V}_x, \hat{J}_z] = -i\hbar\,\hat{V}_y} \quad \cdots \text{(11b)}.$$

$\hat{e}_y$: $\hat{V}_y' = (1)\,\hat{V}_y\,(1) + (1)\,V_x\,(1)\,\delta\alpha$

$$= \hat{V}_y \underbrace{- \frac{i}{\hbar}\delta\alpha[\hat{J}_z, \hat{V}_y] + \hat{V}_x\,\delta\alpha}_{=0} + O(\delta\alpha)^2.$$

For $V_y' = V_y$:
$$\boxed{[\hat{V}_y, \hat{J}_z] = i\hbar\,\hat{V}_x} \quad \cdots \text{(11c)}.$$

(Notice that the invariance condition does not depend on the angle α).

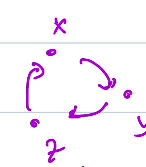
- Therefore, under a rotation about z-axis, the vector operator $\vec{V}$ is invariant if

$$\left.\begin{aligned} [\hat{V}_x, \hat{J}_z] &= -i\hbar\,\hat{V}_y \\ [\hat{V}_y, \hat{J}_z] &= i\hbar\,\hat{V}_x \\ [\hat{V}_z, \hat{J}_z] &= 0 \end{aligned}\right\} \text{—(11)}$$

and all cyclic combination

- For a rotation about x-axis we obtain from cyclic rule.

$$\left.\begin{aligned} [\hat{V}_x, \hat{J}_x] &= 0. \\ [\hat{V}_y, \hat{J}_x] &= -i\hbar\,\hat{V}_z \\ [\hat{V}_z, \hat{J}_x] &= i\hbar\,\hat{V}_y \end{aligned}\right\} \text{—(12)}$$



and all cyclic combination

- And for a rotation about y axis,

$$\left.\begin{aligned} [\hat{V}_x, \hat{J}_y] &= i\hbar\,\hat{V}_z \\ [\hat{V}_y, \hat{J}_y] &= 0. \\ [\hat{V}_z, \hat{J}_y] &= -i\hbar\,V_x \end{aligned}\right\} \text{—(13)}.$$

and all cyclic combination

(So essentially, eq (11), (12), (13) are combined for any general rotation).

The above cyclic rule indicate that there is a Levi-Chivita term on the right hand side, which means a cross product. We can write in general

$$[V_\mu, J_\nu] = i\hbar\, \epsilon_{\mu\nu\xi} V_\xi, \quad \text{where} \qquad ---(14)$$

$\mu, \nu, \xi = x, y, z$ for any arbitrary rotation. In fact, a better way to represent it for a rotation about any arbitrary direction $\hat{n}$, we have

$$\boxed{[\vec{V}, \hat{n}\cdot\vec{J}] = i\hbar\, \hat{n}\times\vec{V}}, \quad --(15).$$

- The rotational operator $\vec{J}$ itself is a vector operator. Then eq (14) reproduces the commutator algebra for any angular momentum.
- Other examples are $\vec{r}, \vec{p}, \vec{L}, \vec{S}$, etc which all transform under rotation as eq (14), (15).

(H.W.. (i) Consider a spatial rotation in which the generators are $\vec{J} = \vec{L} =$ orbital angular momentum. Then considering $\vec{V} = \vec{r}$ or $\vec{p}$, reproduce the commutator between $\vec{r}$ & $\vec{p}$.

(ii) Consider $\vec{J} = \vec{L}$, & $\vec{V} = \vec{S}$, then obtain the commutation relation between them.

(iii) Show that $\vec{V}\cdot\vec{W}$ & $\vec{V}\times\vec{W}$ transform as a scalar, vector respectively.

Matrix Elements of operators

Finally we want to study some matrix elements or expectation values of the scalar and vector operators in the angular momentum basis. Basically, the ultimate idea is that when such scalar or vector operators appear in some parts of the Hamiltonian, and hence we compute their expectation values. In other cases, such operators correspond to experimental effects such as applied electric/magnetic fields or potential terms responsible for scattering process which causes transition between different energy, momentum, and/or angular momentum states determined by matrix elements.

<u>Scalar Operator</u>: Let us start with the scalar operator A which commutes with all three components of the angular momentum, i.e., $[A, J_\mu] = 0$. Needless to say A commutes with J_z & $\vec{J}^2$ operators.

Since A is an observable, its linear and Hermitian. Therefore, the angular momentum states $|j,m\rangle$ are also eigenstates of A with the eigenvalues. Just to be more general, we assume there is some other quantum number we have associated with the energy eigenstates or momentum or any other operator which is denoted by the quantum number, say, k. Therefore, $|k\,j\,m\rangle$ is a generic eigenstate of A, J_z, J^2 as defined to be:

$$J_z \, |k j m\rangle = m\hbar \, |k j m\rangle \quad \text{---(1)}$$
$$J^2 \, |k j m\rangle = j(j+1)\hbar^2 \, |k j m\rangle \quad \text{--(2)}$$
$$A \, |k j m\rangle = a_{jm}(k) \, |k j m\rangle \quad \text{---(3).}$$

Now, since A commutes with J_x, J_y also, hence commutes with $J_\pm = J_x \pm i J_y$, applying $J_\pm$ from left in eq(3), we get

$$J_\pm A \, |k j m\rangle = J_\pm \, a_{jm}(k) \, |k j m\rangle$$
$$\Rightarrow \quad A\left(J_\pm \, |k j m\rangle\right) = a_{jm}(k) \left(J_\pm \, |k j m\rangle\right) \quad \text{--(4)}$$

Therefore, $J_\pm |kjm\rangle$ is also an eigenstate of A, with the same eigenvalue $a_{jm}(k)$. On the other hand, $J_\pm$ takes us to the state $|k j m\pm\rangle$, so, we have

$$A \, |k j m\pm 1\rangle = a_{jm}(k) \, |k j m \pm 1\rangle. \quad \text{--(5)}$$

Now, eq(3) is valid for the state $|k j m\pm 1\rangle$ with eigenvalues $a_{j m\pm 1}(k)$. Therefore, $a_{kj}(k)$ & $a_{jm\pm}(k)$ can be equal only if $a_{jm}(k)$ does not depend on the m-values: $\therefore$

$$\boxed{A \, |k j m\rangle = a_j(k) \, |k j m\rangle} \quad \text{--(6).}$$

In other words, when A commutes with all three components of $\vec{J}$, i.e., is rotationally invariant for rotations in all three directions, then all m-states are degenerate states of the A operator.

Examples of the A operator can be J^2, H here, but not J_z because J_z does not commute with J_x, J_y. We get:

$$H|kjm\rangle = E_j(k)\,|kjm\rangle.$$

$$J^2|kjm\rangle = j(j+1)\hbar^2\,|kjm\rangle.$$

For hydrogen atom, in which the potential $V(r)$ is rotationally invariant in all three directions, we will find in next chapter that all eigenstates have $(2j+1)$-fold degeneracy where $\vec{J} = \vec{L} + \vec{S}$. The generacy can be lifted by applying a magnetic field, because the magnetic field couples to $\vec{J}$ as $V = \mu\,\vec{B}\cdot\vec{J}$, which introduces a J component in the Hamiltonian, and hence the Hamiltonian is still invariant under a rotation with respect to the direction of magnetic field, say, z-direction, but is no longer invariant under the rotation w.r.to x & y-directions. Therefore, all the $(2j+1)$ fold degenerate states are now split. This is called Zeeman splitting.

- Finally, the matrix element of A between two states can be written, by using eq(6), as

$$\langle k'j'm'|\,A\,|kjm\rangle = a_j(k,k')\,\delta_{jj'}\,\delta_{mm'} \quad \text{--- (7)}.$$

where we have used the orthonormal condition on j & m states and we did not put that for the k-values though. Because, here we assume that k is a quantum number of the Hamiltonian, and A is some other term which causes a transition between two k-values. So, it gives a transition probability between the quantum numbers k & k', but for the same $j=j'$ & $m=m'$, since we continue to assume that A is rotationally invariant. If A also commutes with H, then we $a_j(k,k') = a_j(k)\,\delta(k-k')$ for continuous variable k, or $a_j(k)\,\delta_{kk'}$ when k is discrete. Then we will not have any transition.

⊛ MATRIX ELEMENT OF VECTOR OPERATORS.

We can anticipate that the matrix element calculations will be tricky for vector operators, because even if a vector operator is invariant under rotation in all three directions, but its components does not commute with all three components of the angular momentum. Here we will learn how to compute the matrix elements in the $|k\,j\,m\rangle$ states for a vector operator $\vec{V}$. Here again we assume that the rotation is obtained with respect to the z-axis, such that

$$\left.\begin{aligned} [V_z, J_z] &= 0, \\ [V_x, J_z] &= -i\hbar V_y, \\ [V_y, J_z] &= i\hbar V_x, \end{aligned}\right\} \quad \cdots (8).$$

and the commutation with J_x & J_y can be obtained by cyclic rule.

Therefore, $|k j m\rangle$ is an eigenstate of V_z, but not with V_x, V_y, and V_z also does not commute with J_x, J_y and hence its eigenvalue can not be considered to be independent of m-values yet.

We define, $V_\pm = V_x \pm i V_y$, which we will not yet call as raising & lowering operator.

Then $[J_z, V_\pm] = [J_z, V_x] \pm i [J_z, V_y]$

$$= i\hbar V_y \pm i(-i\hbar V_x)$$

$$= \pm \hbar (V_x \pm i V_y)$$

$$= \pm \hbar V_\pm \quad \text{---} \quad (9a)$$

$$[J_x, V_\pm] = [J_x, V_x] \pm i [J_x, V_y] = \pm i (i\hbar V_z) = \mp \hbar V_z \quad \text{---} (9b)$$

$$[J_y, V_\pm] = -i\hbar V_z \quad \text{---} \quad (9c)$$

$$[J_\pm, V_z] = [J_x, V_z] \pm i [J_y, V_z]$$

$$= -i\hbar V_y \pm i (i\hbar V_x)$$

$$= \mp \hbar V_\pm \quad \text{----} (9d)$$

(H.W). $$[J_\pm, V_\pm] = 0 \quad \text{--} \quad (9e)$$

$$[J_\pm, V_\mp] = \pm 2\hbar V_z \quad \text{---} (9f).$$

The commutation between V_x, V_y, V_z is not specified.

H.W. (i) Evaluate $[J^2, V_\mu]$, $[J^2, V^2]$, $[J_\mu, V^2]$, $[V^2, V_\mu]$.

(*) We see that V_z commutes with J_z, but it does <u>not</u> commute with J_x, J_y, and also does <u>not</u> commute with J^2. Therefore, V_z and J_z share the same eigenfunction, but not with J^2. Hence, in the expectation value / matrix element of V_z, m is conserved, but j is not. In fact, unlike the scalar operator A, we also cannot say that the expectation value of V_z does not depend on m. In fact, starting from the matrix element

$$\langle k'j'm' | [V_z, J_z] | kjm \rangle = 0.$$

we can only deduce the selection rule that

$$\langle k'j'm | V_z | kjm \rangle = v^z_{jj'}(k,k') \; \delta_{mm'} \quad \text{--- (10)}$$

where $v^z_{jj'}(k,k')$ is an unknown quantity

(*) How about $V_\pm$? Does it act as a raising / lowering operator or a transition from m to $m\pm1$ states? Needless to say what it does to k, j quantum number, we cannot deduce, but from the commutation relation (9b), we can actually say something about the change in the m-values.

For this we can use eq (9a), on the state $|kjm\rangle$:

$$[J_z, V_\pm]|kjm\rangle = \pm\hbar V_\pm |kjm\rangle$$

$$\Rightarrow \quad J_z\left(V_\pm |kjm\rangle\right) = (m\pm1)\hbar\left(V_\pm |kjm\rangle\right) \quad \text{--- (11a)}$$

And we also know: $J_z|kj\,m\pm1\rangle = (m\pm1)\hbar\,|kj\,m\pm1\rangle$ — (11b).

Eqs (11a) & (11b) suggest that $V_\pm|kjm\rangle$ & $|kj\,m\pm1\rangle$ are both eigenvectors of J_z with the same eigenvalue. This implies two possibilities: (i) $V_\pm|kjm\rangle$ and $|kj\,m\pm1\rangle$ are degenerate states, ie, they are orthogonal states. This would mean $\langle kj\,m\pm1|V_\pm|kjm\rangle = 0$. On the other hand, $|kj\,m\pm1\rangle$ & $|kjm\rangle$ are already orthogonal to each other since they are different eigenstates of the linear, Hermitian operator. So, to have both to be true $V_\pm$ operator have to come out from the matrix element, which would mean $|kjm\rangle$ is an eigenstate of $V_\pm$ also. This contradicts eq (9a). So, $V_\pm|kjm\rangle$ and $|kj\,m\pm1\rangle$ cannot be linearly independent. (ii) The other option is then they are linearly dependent, ie,

$$V_\pm|kjm\rangle \propto |kj\,m\pm1\rangle$$
$$= v_j^\pm(k)\,|kj\,m\pm1\rangle \quad \text{--- (11c)}$$

where $v_j^\pm(k)$ are some complex function.

In other words: $\langle kj\,m\pm1|V_\pm|kjm\rangle = v_j^\pm(k)$, which does not depend on m.

We can rewrite this equation for a generic matrix element form as

$$\langle k'j'm'|V_\pm|kjm\rangle = v_{jj'}^\pm(k,k')\,\delta_{m',m\pm1} \quad \text{--- (12)}$$

in which again we cannot specify the values of j & k.

We rewrite eq (10) & (12) together again

$$\boxed{\begin{aligned}\langle k'j'm'|V_z|kjm\rangle &= v^z_{jj'}(k,k')\,\delta_{m'm}\\ \langle k'j'm'|V_\pm|kjm\rangle &= v^\pm_{jj'}(k,k')\,\delta_{m'm\pm1}\end{aligned}} \quad \text{--- (13).}$$

So, the matrix representation of $\vec{V}$ operator in the $(2j+1)$ Hilbert space of a given $|kjm\rangle$ state, V_z is diagonal, while $V_\pm$ (hence hence V_x, V_y) are off-diagonal (only the nearest off diagonal term) matrix.

[The off diagonal matrix $V_\pm$ of this form is also called the circulant matrix. Such circulant matrices are diagonalizable with a discrete Fourier transformation. We will not do that here.].

- What are the values of $v^\pm_{jj'}(k,k')$? The situation is similar as the Clebsch-Gordon coefficients that we can get a recursion relation for them.

Let's make use of the commutator $[J_\pm, V_\pm]=0$ from eq (9e). Since $J_\pm$ & $V_\pm$ both increase/decrease m value by 1, their product will increase/decrease m values by 2. Therefore, the non-zero matrix elements for the same k, j values are

$$\langle kj\,m\pm2|J_\pm V_\pm|kjm\rangle = \langle kj\,m\pm|V_\pm J_\pm|kjm\rangle \quad \text{---(14).}$$

Insert the closure relation $\sum_{k',j',m'} |k'j'm'\rangle\langle k'j'm'| = \mathbb{I}$

And $\langle k'j'm'|J_\pm|kjm\rangle = \sqrt{j(j+1)-m(m\pm1)}\,\hbar\,\delta_{kk'}\delta_{jj'}\delta_{m'm\pm1}$, so we obtain

$$\langle kjm\pm2|J_\pm|kjm\pm1\rangle\langle kjm\pm1|V_\pm|kjm\rangle = \langle kjm\pm2|V_\pm|kjm\pm1\rangle\langle kjm\pm1|J_\pm|kjm\rangle.$$

$$\Rightarrow \boxed{\frac{\langle kj\,m\pm2|V_\pm|kj\,m\pm1\rangle}{\langle kj\,m\pm2|J_\pm|kj\,m\pm1\rangle} = \frac{\langle kj\,m\pm1|V_\pm|kj\,m\rangle}{\langle kj\,m\pm1|J_\pm|kj\,m\rangle}} \quad \text{---}(15).$$

Both the numerator and denominators are non-zero as long as $-j \leq m \leq j-2$. Lets say we can start with $m=-j$ value on the R.H.S. for V_+, and get ratio on L.H.S for $m+1$ to $m+2$, which then again can be put on the R.H.S and in its corresponding L.H.S we will get a ratio for $m+2$ to $m+3$, and so on. We notice this process the value of the ratio of eq(15) does not change, which means the ratio does not depend on m. Hence we denote:

$$\boxed{\begin{aligned} &\frac{\langle kj\,m\pm1|V_\pm|kj\,m\rangle}{\langle kj\,m\pm1|J_\pm|kj\,m\rangle} = \alpha_j^\pm(k) \quad \text{---}(16a) \\ &\Rightarrow \langle kj\,m\pm1|V_\pm|kj\,m\rangle = V_j^\pm(k) = \alpha_j^\pm(k)\langle kj\,m\pm1|J_\pm|kj\,m\rangle \quad \text{--}(16b) \\ &\qquad = \alpha_j^\pm(k)\sqrt{j(j+1)-m(m\pm1)}\,\hbar \quad \text{--}(16c) \end{aligned}}$$

* Next we want to compute $v^{z}_{j,j'}(k,k')$:

Here we will use eq (9f) $[J_{\mp}, V_{\pm}] = -2\hbar V_z$. Taking matrix element w.r.to $|kjm\rangle$ on both sides of $[J_-, V_+] = -2\hbar V_z$, we get.

$$-2\hbar \langle kjm | V_z | kjm\rangle = v^{z}_{j}(k) = \langle kjm | (J_- V_+ - V_+ J_-) | kjm\rangle$$

$$= \hbar\sqrt{j(j+1) - m(m+1)}\ \langle kjm+1 | V_+ | kjm\rangle$$
$$- \hbar\sqrt{j(j+1) - m(m-1)}\ \langle kjm | V_+ | kjm-1\rangle.$$

[using eq (16c)]
$$= \hbar^2\left[\cancel{j(j+1)} - m(m+1) - \cancel{j(j+1)} - m(m-1)\right]\alpha^{+}_{j}(k)$$
$$= -2m\hbar^2\, \alpha_j^{+}(k).$$

Therefore, $\boxed{\langle kjm | V_z | kjm\rangle = m\hbar\alpha^{+}_{j}(k)}$ --- (17).

We had chosen above the commutation $[J_-, V_+] = -2\hbar V_z$, to obtain eq(17). If we take $[J_+, V_-] = -2\hbar V_z$, we ~~get~~ get the same expression but with $\alpha_j^{-}(k)$ on the R.H.S. Therefore, the only one conclusion we have

$$\boxed{\alpha_j^{+}(k) = \alpha_j^{-}(k) = \alpha_j(k)} \quad --- (18).$$

Therefore, generalizing eqs (16) & (17) for a matrix element between two arbitrary values of m & m', we can write:

$$\langle k j m' | V_{\pm} | k j m \rangle = \alpha_j(k) \langle k j m' | J_{\pm} | k j m \rangle \quad \text{--- (18a)}$$

$$\langle k j m' | V_z | k j m \rangle = \alpha_j(k) \langle k j m' | J_z | k j m \rangle \quad \text{--- (18b)}$$

Therefore, this is true for all components of $\vec{V}$ vector. Therefore, we can write

$$\boxed{\langle k j m' | \vec{V} | k j m \rangle = \alpha_j(k) \langle k j m' | \vec{J} | k j m \rangle} \quad \text{--- (18c)}$$

Now, it becomes easy to compute the ratio $\alpha_j(k)$.

Lets take the matrix element of $\vec{J}\cdot\vec{V}$ operator:

$$\langle k j m' | \vec{J}\cdot\vec{V} | k j m \rangle = \sum_{k_1 j_1 m_1} \langle k j m' | \vec{J} | k_1 j_1 m_1 \rangle \cdot \langle k_1 j_1 m_1 | \vec{V} | k j m \rangle$$

[use eq (18c)]

$$= \sum_{k_1 j_1 m_1} \alpha_j(k) \langle k j m' | \vec{J} | k_1 j_1 m_1 \rangle \cdot \langle k_1 j_1 m_1 | \vec{J} | k j m \rangle \, \delta_{kk_1} \delta_{jj_1}$$

$$= \alpha_j(k) \langle k j m' | J^2 | k j m \rangle$$

$$= \alpha_j(k)\, j(j+1)\hbar^2 \delta_{mm'}.$$

Therefore, we get

$$\boxed{\alpha_j(k) = \frac{\langle k j m | \vec{J}\cdot\vec{V} | k j m \rangle}{j(j+1)\hbar^2}} \quad \text{--- (19)}$$

Again, we see that the L.H.S does not depend on the value of m, and hence the matrix element $\langle kjm|\vec{J}\cdot\vec{V}|kjm\rangle$ also does not depend on the value of m. We can simply denote it by $\langle\vec{J}\cdot\vec{V}\rangle$, and write $\alpha_j(k) = \frac{\langle\vec{J}\cdot\vec{V}\rangle}{j(j+1)\hbar^2}$.
Substituting α_j in eq (18c), and since α_j is a number which does not depend on m, we can slide it inside the matrix element term to reexpress eq (18c) as

$$\langle kjm'|\vec{V}|kjm\rangle = \langle kjm'|\frac{\langle\vec{J}\cdot\vec{V}\rangle}{j(j+1)\hbar^2}\vec{J}|kjm\rangle .$$

Since $|kjm\rangle$ states are chosen arbitrarily, the above identity must be true for any general state, i.e., the identity holds at the operator level and we have

$$\boxed{\vec{V} = \frac{\langle\vec{J}\cdot\vec{V}\rangle}{\langle J^2\rangle}\vec{J}} \quad \text{— (20).}$$

This identity is called the Wigner-Eckart Theorem. What this says is any vector operator which is rotationally invariant, where the rotation is defined by the angular momentum $\vec{J}$, one can express the vector operator in terms of the angular momentum operator. This is analogous to the Fourier expansion or expansion of a state in the orthogonal Hilbert space, but here its for a vector operator. Recall that all this was possible only for angular momentum case which follows the commutator $[J_\mu, J_\nu] = i\,\epsilon_{\mu\nu s} J_s$. This commutator relation is at the root of the expansion formula in eq(20). Therefore, this commutation relation is the replacement of the criterion for Hilbert space to be able to expand any normalizable state in a Hilbert space, that any vector operator can be expanded in the components of another vector operator provided the vector operator follows the commutator algebra $[J_\mu, J_\nu] = i\,\epsilon_{\mu\nu s} J_s$. This algebra is called the Lie Algebra and the rotational symmetry of the theory due to this Lie Algebra is called the $O(3)$ = three component orthogonal group.

H.W.

(i) Needless to say the components of $\vec{V}$ operator also follows a similar commutator

$$[V_\mu, V_\nu] = i\,\epsilon_{\mu\nu s} V_s \quad . \qquad (2.2.2)$$

(Please check. I have not checked myself and only assume it will hold following the form in eq 20).

(ii) Take another rotationally invariant operator $\vec{W}$ following eq (20). Then show that

$$\boxed{\vec{V} = \frac{\langle \vec{J}\cdot\vec{V}\rangle}{\langle \vec{J}\cdot\vec{W}\rangle}\,\vec{W}} \quad \cdots (21).$$

(iii) Show that $\vec{V}\cdot\vec{W}$ transforms as a scalar operator.

Any vector operator which does not necessarily have to be invariant under the rotation, but transform under the irreducible representation of the rotational group of $\vec{J}$ can be expanded in terms of $\vec{J}$ using the Wigner-Eckwart Theorem.

Application We have developed all the essential tools to make use of the rotational invariance and the angular momentum Hilbert space to compute various expectation values and matrix elements. We have not actually talked about any Hamiltonian in the above descriptions. We have however mentioned briefly and we will see more of it in the next chapter that the kinetic energy term $\frac{\hat{p}^2}{2m}$ is always rotationally invariant, as it becomes apparent as we write the momentum operator in the spherical coordinates. It actually depends on L^2 and hence l is a good quantum number and all m-values are degenerate. Any central potential $V(r)$ is also clearly rotationally invariant and have angular momenta as conserved quantity. Therefore, for such systems, angular momentum basis $|lm\rangle$ or $|jm\rangle$, where $\vec{J} = \vec{L} + \vec{S}$ is the total angular momentum if we include spin also, is a proper Hilbert space for the energy eigenvalue. Since within an atom the Coulomb interaction is a central field potential, therefore atomic spectra are governed by angular momentum states and Spherical Harmonics wave functions. Below we will study a couple of examples where under external magnetic & electric fields, we will see how the atomic energy levels are split which we can evaluate using the Wigner-Eckart theorem.

(A) Zeeman Splitting & Landé g-factor:

Let us say we have a particle, an electron mainly that we will concern, in an atom whose Hamiltonian is given by

$$H_0 = \frac{p^2}{2m} + V(r) \quad --(1).$$

As we mentioned above, its eigenspectrum can be obtained by the angular momentum Hilbert space $|n\,l\,m\rangle$, where n is another quantum number that we will discover in the next chapter. If we also want to include the spin state $|s, m_s\rangle$, then since in the Hamiltonian above spin angular momentum does not appear, so the orbital and spin angular momenta are individually conserved. Therefore, we do not even need to go to the total angular momentum basis, and we can simply take a product state as $|n\,l\,m\rangle|s\,m_s\rangle$ and then the spin states will be eliminated from the eigenvalue equation $H_0|n\,l\,m\rangle|s\,m_s\rangle = E_{nl}|n\,l\,m\rangle|s\,m_s\rangle$. So, we can just work with the orbital angular momentum states $|n\,l\,m\rangle$. The energy eigenvalues also do not depend on m-quantum number, since the Hamiltonian H commutes with all three components L_x, L_y, L_z of orbital angular momentum $\vec{L}$. Therefore, the orbital's axis of rotation around the nucleus in an atom is not fixed, so does the axis of spin of electrons.

Now, we apply a magnetic field to the atom. We choose the direction of the magnetic field along the z-direction. The result won't change by this choice of magnetic field direction, since the Hamiltonian without the magnetic field was fully rotationally invariant. Now, with the applied magnetic field along the z-axis, the electron's orbital angular momentum will be oriented along the magnetic field direction, and so does its internal spin angular momentum. The magnetic energy contribution should then be a dot product between $\vec{B}$ & $\vec{L}$ & $\vec{S}$ as they tend to be parallel and it should contribute a negative energy to the Hamiltonian because it lowers the total energy. We also assume that the magnetic field is sufficiently large so that in the $\vec{B}\cdot\vec{L}$ & $\vec{B}\cdot\vec{S}$ terms, only $B_z L_z$ & $B_z S_z$ terms contribute and L_x, L_y, S_x, S_y terms are negligible. This happens when the orbitals and spins are fully polarized towards the magnetic field direction. Therefore our full Hamiltonian is now

$$H = \underbrace{\frac{p^2}{2m} + V(r)}_{H_0} - \underbrace{\frac{\mu_B}{\hbar} B_z}_{H'} (L_z + 2 S_z) \quad \text{--(2)}$$

Extra factor of '2'.

$\mu_B = \frac{e\hbar}{2m}$ is the proportionality constant, called Bohr magneton that we have encountered in chapter 1. $W_L = \frac{\mu_B B_z}{\hbar}$ is called the Larmor's frequency. The factor of 2 that appears in front of S_z, is an extra factor that we know from experimental fact that internal spin angular momentum contributes twice the energy than the orbital angular momentum. It also has to do with how the spin angular momentum is defined. This factor is called the gyromagnetic ratio that we will see again below.

Its clear now that H' term breaks the full rotational symmetry that H_0 term enjoys, but L_z & S_z terms are still conserved, i.e. a 2-dimensional rotational symmetry for rotation w.r.t. the z-axis is still preserved. Therefore, the quantum numbers m & m_s for L_z & S_z are still good quantum numbers of the eigenvalues of the full Hamiltonian, but they are not degenerate anymore for different m-values. In fact, we can anticipate that the H' term will be proportional to m & m_s, and hence the energy levels will split.

Although both $\vec{L}^2, L_z$ & S^2, S_z are individually conserved in the Hamiltonian (2), and one can simply take a product state, but its convenient to go to the total angular momentum $\vec{J} = \vec{L} + \vec{S}$ state. Needless to say J_z & $\vec{J}^2$ are also conserved in H, as $[H, J_z] = [H, \vec{J}^2] = 0$.

Therefore, we will consider the $|j_1 j_2 j m\rangle$ state here which becomes here $|n \ell s j m\rangle$ by including the n-quantum number also. n quantum number will not contribute to any discussion here though, so one can simply ignore it.

We rewrite H' term in terms of $\vec{J}$ as.

$$H' = -\frac{\mu_B}{\hbar} B_z (L_z + 2S_z)$$
$$= -\frac{\mu_B}{\hbar} B_z (g_L L_z + g_s S_z)$$
$$= -\underbrace{\frac{\mu_B}{\hbar} B_z}_{w_L = \text{Larmor freq.}} g_J J_z \quad \text{--- (3)}$$

where we have introduced the Landé' g-factors for all angular momentum with values $g_L = 1$, $g_s = 2$ & g_J is something that we want to evaluate now.

Therefore, our task is to evaluate $\langle L_z \rangle$ and $\langle S_z \rangle$ in the total angular momentum basis $|n\, l\, s\, j\, m\rangle$. In this basis, L_z & S_z are not conserved operators, so, m_l, m_s are not known, only $m = m_l + m_s$ is known. So, we write L_z & S_z in terms of J_z using the Wigner-Eckart theorem as

$$\vec{L} = \frac{\langle \vec{L}\cdot\vec{J} \rangle_{njl}}{j(j+1)\hbar} \vec{J} \; ; \quad \vec{S} = \frac{\langle \vec{S}\cdot\vec{J} \rangle_{njs}}{j(j+1)\hbar^2} \vec{J} \quad \text{--- (4)}$$

Now, $\vec{L}\cdot\vec{J} = \vec{L}\cdot(\vec{L}+\vec{S}) = \vec{L}^2 + \vec{L}\cdot\vec{S} = \vec{L}^2 + \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$

$$= \frac{1}{2}(\vec{J}^2 + \vec{L}^2 - \vec{S}^2)$$

$$\vec{S}\cdot\vec{J} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 + \vec{S}^2)$$

So, $\langle \vec{L}\cdot\vec{J}\rangle = \frac{1}{2}\left[j(j+1) + l(l+1) - s(s+1)\right]\hbar^2$

$\langle \vec{S}\cdot\vec{J}\rangle = \frac{1}{2}\left[j(j+1) - l(l+1) + s(s+1)\right]\hbar^2.$

So, going back to eq (3), we have

$$g_J = \frac{1}{\langle J_z\rangle}\left[\langle L_z\rangle + 2\langle S_z\rangle\right]$$

$$= \frac{1}{\cancel{\langle J_z\rangle}}\left[\frac{\langle \vec{L}\cdot\vec{J}\rangle}{j(j+1)\hbar^2} + 2\frac{\langle \vec{S}\cdot\vec{J}\rangle}{j(j+1)\hbar^2}\right]\cancel{\langle J_z\rangle}$$

$$= \frac{1}{j(j+1)\hbar^2}\frac{1}{2}\left[3j(j+1) - l(l+1) + s(s+1)\right]\hbar^2.$$

$$\Rightarrow \boxed{g_J = \frac{3}{2} - \frac{l(l+1) - s(s+1)}{2j(j+1)}} \quad \text{--- (5).}$$

Therefore, the value of g_J depends on the value of l & s. Finally, the expectation value of H' is

$$\langle H'\rangle = w_L g_J \langle J_z\rangle = w_L g_J m\hbar \quad \text{--- (6).}$$

The total energy $E_{nesjm} = \langle H_0\rangle + \langle H'\rangle$

$$= E^{(0)}_{nesj} + w_L g_J \hbar m. \quad \text{--- (7).}$$

since due to rotational invariance of H_0, $E^{(0)}$ does not depend on m value. H' term lifts this degeneracy and split it into $(2j+1)$ states. The energy gap between them depends on g_J.

Lets take $l = 1$, $s = 1/2$. Then the possible j values are $-l-s \leq j \leq l+s$. That means $-3/2, -1/2, 1/2, 3/2$. Lets consider a $j = 3/2$ state, whose unperturbed energy $E^{(0)}_{n\,3/2\,1\,1/2}$ now splits to $(2j+1) = 4$ states. In this state, the Landé g-factor value is

$$g_j = \frac{3}{2} - \frac{l(l+1) - s(s+1)}{2j(j+1)}$$

$$= \frac{3}{2} - \frac{2 - 3/4}{2\,\frac{3}{2}\cdot\frac{5}{2}} =$$