VII. Central Potentials

Before going any further with angular momentum, it is best to begin *using* the relations we already have so that we can get some idea what they are good for. Perhaps the best application of the angular momentum eigenfunctions we dealt with in the previous section comes when one deals with a spherically symmetric (or central) potential. In this case, the potential energy is only a function of the distance r to the origin, and the knowledge we already have will tell us a great deal about the eigenstates of the system **irrespective of the particular potential**.
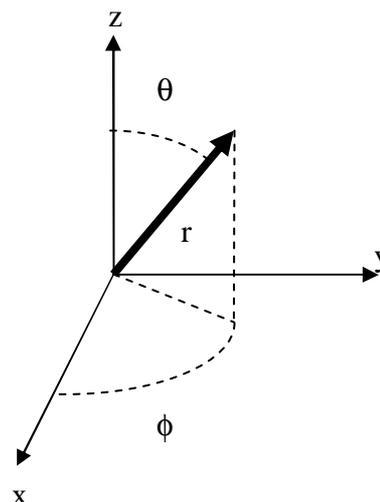
a. Spherical Polar Coordinates

Since we are dealing with a potential that is a function only of the distance r to the origin, it is by far preferable to work in a set of coordinates where r is one of the basic variables, rather than some function of x, y, z. To this end, we need to convert our equations to spherical polar coordinates - $x, y, z \rightarrow r, \theta, \phi$. In most **math** textbooks, ϕ is defined to be the angle relative to the z axis while the vast majority of quantum mechanics texts use θ in this capacity. We will use the latter definition, but be careful that any equations taken from other sources use this same convention! Here are some useful relations in spherical polar coordinates:

$$x \equiv r \cos\phi \sin\theta$$

$$y \equiv r \sin\phi \sin\theta$$

$$z \equiv r \cos\theta$$

$$\mathbf{e}_r \equiv \cos\phi\sin\theta\ \mathbf{i} + \sin\phi\sin\theta\ \mathbf{j} + \cos\theta\ \mathbf{k}$$

$$\mathbf{e}_\theta \equiv \cos\phi\cos\theta\ \mathbf{i} + \sin\phi\cos\theta\ \mathbf{j} - \sin\theta\ \mathbf{k}$$

$$\mathbf{e}_\phi \equiv -\sin\phi\ \mathbf{i} + \cos\phi\ \mathbf{j}$$

$$\nabla \equiv \mathbf{e}_r\frac{\partial}{\partial r} + \mathbf{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi} + \mathbf{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

b. Central Potentials

For an arbitrary potential $V(r)$, we can write

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\hat{r})$$

At this point, we convert the equations to **natural units** by choosing our unit of length and unit of mass so that $\hbar = m = 1$. Note that this leaves us one free standard unit (time, or, equivalently, energy). It is convenient to fix this dimension based on the problem at hand; for example, in a harmonic oscillator, it is useful to choose the energy so that $\hbar\omega = 1$, while for the Coulomb interaction it is useful to choose the unit of electron charge to be that of one electron. These units are merely out of convenience and in the end, once we have calculated an observable (such as the position) we will need to convert the result to a set of standard units (such as meters). The main benefit at the moment is that it removes the relatively unimportant factors of $\hbar$ and m from our equation, so that in natural units:

$$\hat{H} = -\frac{\nabla^2}{2} + V(\hat{r}) = \frac{-1}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) + V(\hat{r})$$

where the second equality just reinforces the gory details wrapped up in the Laplacian operator.

c. <u>Orbital Angular Momentum Operators</u>

In order to see what angular momentum has to do with this, we need to express the angular momentum operators in spherical polar coordinates, as well. In this case, the relevant type of angular momentum is that of the particle orbiting around the origin:

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = r\mathbf{e}_r \times -i\nabla = -i\left(\mathbf{e}_\phi \frac{\partial}{\partial \theta} - \mathbf{e}_\theta \frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right)$$

Plugging in our expressions for $\{\mathbf{e}_\theta, \mathbf{e}_\phi\}$ from above:

$$\hat{\mathbf{L}} = -i\left(\{-\sin\phi\ \mathbf{i} + \cos\phi\ \mathbf{j}\}\frac{\partial}{\partial\theta} - \{\cos\phi\cos\theta\ \mathbf{i} + \sin\phi\cos\theta\ \mathbf{j} - \sin\theta\ \mathbf{k}\}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$= \boxed{-i\left(-\sin\phi\frac{\partial}{\partial\theta} - \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)\mathbf{i}} \boxed{-i\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)\mathbf{j}} \boxed{+i\frac{\partial}{\partial\phi}\mathbf{k}}$$

$$\hat{L}_x \qquad\qquad\qquad \hat{L}_y \qquad\qquad\qquad \hat{L}_z$$

Further, after some algebra, one can show

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right).$$

At this point we notice that $\hat{\mathbf{L}}^2$ plays a conspicuous role in the Hamiltonian:

$$\hat{H} = \frac{-1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hat{\mathbf{L}}^2}{r^2} + V(\hat{r})$$

Hence, **all** of the angular dependence of $\hat{H}$ is contained in $\hat{\mathbf{L}}^2$ and we immediately conclude that:

$$[\hat{H}, \hat{\mathbf{L}}^2] = 0 \qquad\qquad [\hat{H}, \hat{L}_z] = 0$$

which means that the eigenfunctions of $\hat{H}$ are also angular momentum eigenfunctions! That is, for any fixed r,

$$|\psi_i\rangle \propto |l, m\rangle$$

Eigenfunction
of Hamiltonian

Quantum
Number for L^2

Quantum
Number for L_z
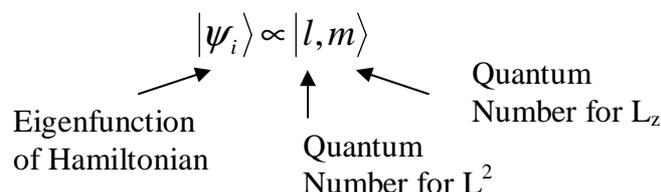
Of course, we really want to know what the eigenfunctions look like *in real space* rather than writing them as abstract vectors. First of all, notice that none of the angular momentum operators depend on r, and so the eigenfunctions depend only on the angles θ and ϕ. We will denote these functions by

$$Y_l^m(\theta,\phi) \equiv \langle \theta,\phi | l,m \rangle$$

where l indexes the eigenvalue of $\hat{\mathbf{L}}^2$ and m indexes the $\hat{L}_z$ eigenvalue. Then, we can write

$$\langle r,\theta,\phi | \psi_i \rangle = R_l^m(r) Y_l^m(\theta,\phi)$$

The radial function will depend on the form of $V(r)$, but the angular parts are **universal** – they are just the spatial representation of the orbital angular momentum eigenfunctions. They are called spherical harmonics and we proceed to define their precise form

d. <u>Spherical Harmonics</u>

The eigenvalue equations we derived previously for angular momentum now become partial differential equations that are not always easily solved. The $\hat{L}_z$ equation is trivial to solve:

$$\hat{L}_z Y_l^m(\theta,\phi) = m\hbar Y_l^m(\theta,\phi)$$

$$\Rightarrow -i\hbar \frac{\partial}{\partial \phi} Y_l^m(\theta,\phi) = m\hbar Y_l^m(\theta,\phi)$$

$$\Rightarrow Y_l^m(\theta,\phi) = P_l^m(\theta) e^{im\phi}$$

Unfortunately, the equations for $P_l^m(\theta)$ are more difficult. To solve for the P_l^m's, we follow two steps:

1) Recall that $\hat{L}_+ Y_l^{m=l}(\theta,\phi) = 0$. Or, in differential language:

$$\left(\cancel{e^{i\phi}} \frac{\partial}{\partial \theta} + i \cancel{e^{i\phi}} \cot\theta \cancel{\frac{\partial}{\partial \phi}} \right) P_l^{m=l}(\theta) e^{il\phi} = 0$$

$$il$$

$$\Rightarrow (\frac{\partial}{\partial \theta} - l\cot\theta) P_l^{m=l}(\theta) = 0$$

$$\Rightarrow P_l^{m=l}(\theta) \propto \sin^l \theta$$

2) Using this simple result for $m = l$, we can generate the spherical harmonics for other values of m by repeated application of the lowering operator:

$$P_l^m(\theta) \propto \left(\hat{L}_-\right)^{l-m} P_l^l(\theta)$$

The second step is rather tedious, and so we simply state that the result

$$P_l^m(\theta) = (-1)^l \sqrt{\frac{2l+1}{\pi 2^{2l+2}} \frac{\left(l+|m|\right)!}{\left(l-|m|\right)!(l!)^2}} \sin^{-|m|}\theta \frac{d^{l-|m|}}{d\cos\theta^{l-|m|}} \sin^{2l}\theta$$

$$\boxed{\Rightarrow Y_l^m(\theta,\phi) = (-1)^m P_l^m(\theta)e^{im\phi}}$$

These are the spherical harmonics and they are the eigenfunctions of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$. The normalization constant has been chosen so that

$$\iint Y_l^{m*}(\theta,\phi) Y_{l'}^{m'}(\theta,\phi) \sin\theta d\theta \, d\phi = \delta_{m,m'}\delta_{l,l'}$$

that is, we have chosen it so that the spherical harmonics are orthonormal.

Now, one important constraint on these solutions is that l **must be an integer**. To see this, note that half-integer l would imply half-integer m. In this case we have a problem, because as we seep around an angle $\Delta\phi = 2\pi$ the wavefunction needs to return to its original value; that is, it needs to be *periodic*. However, if m is half-integer, this is not true. For example, if $m = \frac{1}{2}$,

$$e^{i(\phi+2\pi)/2} = e^{i\phi/2}e^{i\pi} = -e^{i\phi/2} \neq e^{i\phi/2}$$

Because the half integer solutions do not obey the proper boundary conditions, they must be discarded.

Hence, even though our derivation above seemed to indicate that angular momentum could be half-integer, for the special case of orbital angular momentum, this is not possible. We will see shortly that half-integer angular momenta are crucial for the description of particle spins. In any case, this shows how the general quantization conditions $l = 0, \frac{1}{2}, 1, \frac{3}{2}...$ and $m = -l, -l+1,...l$ can be even further restricted when one is dealing with particular types of angular momentum. We will never have an l that is not an integer or half

integer, but often only certain integer or half integer values will be permissible.

e. **The Radial Equation**

Combining our expression for the spherical harmonics with the previous results, we find that the eigenfunctions for any central potential can be written

$$\langle r,\theta,\phi|\psi_i\rangle = R_l^m(r)P_l^m(\theta)e^{im\phi}$$

that is, the three dimensional wavefunction is *separable* into a product of three one dimensional wavefunctions. This is not generally the case, and is one of the particularly nice properties of spherically symmetric potentials. The radial function will generally depend on the form of the potential, but it will obey the equation:

$$\left(\frac{-1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{l(l+1)}{2r^2}+V(r)\right)R_l^m(r)=E_iR_l^m(r)$$

This equation can be solved exactly for only a few cases (the harmonic oscillator and the Coulomb potential are the most notable). Notice that the eigenvalue equation depends on the value of l, the quantum number for $\hat{\mathbf{L}}^2$, but not m, which indicates the projection of the angular momentum along the z axis. Hence the R_l^m's do not actually depend on m. Further, we anticipate the appearance of another quantum number (call it n) that indexes the solutions to this radial equation. Hence, we replace $R_l^m(r)\rightarrow R_{nl}(r)$ in what follows.

The radial equation can be simplified further if we look at the equation satisfied by the functions $\rho_{nl}(r)\equiv rR_{nl}(r)$:

$$\left(\frac{-1}{2}\frac{\partial^2}{\partial r^2}+\frac{l(l+1)}{2r^2}+V(r)\right)\rho_{nl}(r)=E_{nl}\rho_{nl}(r)$$

where, on the right, we have noted that the energies also depend on n and l. Notice that resemblance of this equation to the 1D Schrödinger equation. Indeed, if we define the effective potential by

$$V_{eff}(r)=\frac{l(l+1)}{2r^2}+V(r)$$

then this *is* a 1D Schrödinger equation, with the effective potential above. Note, however, that the boundary conditions are different than the typical 1D case:

$$\rho_{nl}(0) = 0 \qquad \rho_{nl}(\infty) = 0$$

Because the additional term in V_{eff} arises from the angular motion of the particle around the nucleus, it is usually called the "centrifugal potential".

f. **Hydrogen-like Atoms**

We are now ready to specialize to the particular case of the hydrogen-like atoms – that is, atomic ions with only one electron (H, He^{+}, Li^{+2}…). First, we will make the "infinite mass" approximation for the nucleus - we place the it at the origin and assume it never moves because it is much more massive than the electron. This is a fairly good approximation, since $m_p / m_e \approx 1800$, but if one wishes to be more precise, one merely needs to replace the electron mass with the reduced mass $\mu = \left(\frac{1}{m_e} + \frac{1}{m_N}\right)^{-1}$ in what follows. Hence, the nucleus only presents a potential in which the electron moves:

$$V(r) = -\frac{Ze^2}{r}$$

where $-e$ is the charge on the electron and $+Ze$ is the charge of the nucleus. At this point, we move from "natural units" ($\hbar = m_e = 1$)to "atomic units" ($\hbar = m_e = e = 1$). We can now explicitly state our fundamental units of mass, length and energy:

1 unit of mass $= m_e \approx 9.11 \times 10^{-28} g$

1 unit of length=1 Bohr $\equiv a_0 = \dfrac{\hbar^2}{m_e e^2} \approx 5.29 \times 10^{-9} m$

1 unit of energy=1Hartree $\equiv E_h = \dfrac{e^2}{a_0} \approx 4.36 \times 10^{-18} J$

The latter two units give the typical distance an electron is from the nucleus and a typical energy for an electron in a Coulomb potential.

Hence, we want to solve the equation

$$\left(\frac{-1}{2} \frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) \rho_{nl}(r) = E_{nl} \rho_{nl}(r).$$

Like the equation for $P_l^m(\theta)$, this is fairly tedious to solve, and we merely outline the steps

    1) Notice that for large r, the potential terms vanish and we just have

$$\rho_{nl}(r) \approx e^{\pm r\sqrt{-2E}}$$

    One must take the '-' solution, since otherwise the wavefunction will not go to zero at infinity.

    2) Write

$$\rho_{nl}(r) = f(r) e^{-r\sqrt{-2E}}$$

    and then expand $f(r)$ in a power series about the origin.

    3) Insert ρ_{nl} into the Schrödinger equation above and equate each term in the power series expansion for $f(r)$ to zero.

After a significant amount of algebra, one finds that ($\xi = 2Zr/n$)

$$R_{nl}(r) = \sqrt{\frac{(n-l-1)!4Z^3}{((n+l)!)^3 n^4}} e^{-\frac{\xi}{2}} (\xi)^l \frac{d^{2l+1}}{d\xi^{2l+1}} e^{\xi} \frac{d^{n+l}}{d\xi^{n+l}} e^{-\xi} \xi^{n+l}$$

which are known as the associated Laguerre polynomials. Examples for low values of n and l are reproduced in many textbooks.

There are two other very interesting things that come out of the algebra that leads up to the Legendre polynomials:

    1) One finds that solutions only exist if $l < n$. Hence, while a Hydrogenic atom can only have any integer angular momentum, these values are further restricted for fixed n. We typically denote the l states as 's', 'p', 'd', 'f', 'g', 'h' ... orbitals, for l=0,1,2,3,4,5.... Hence, we have 1s, 2s, 2p, 3s, 3p, 3d, etc orbitals, but not 1d orbitals or 3f orbitals.

    2) The energies of the Hydrogenic atom are $E_n = -\frac{1}{2} \frac{Z^2}{n^2}$, which were known experimentally long before Schrödinger ever

came along. The interesting thing here is that the energies *do not depend on l*! This is a feature peculiar to Hydrogenic potentials and is related to an additional symmetry possessed by the Coulomb potential. This is termed an "accidental" degeneracy of the levels.

Finally, before moving on, we note that these are only the bound states of the hydrogen atom. There are also positive energy states that are oscillatory instead of decaying. We will not concern ourselves with these states, except to say that the bound eigenfunctions by themselves are **not a complete basis** – only if the unbound solutions are included is completeness reached.

g. <u>Electron Spin</u>

Up to this point, we have been treating the electron as a structureless particle that has a mass and an electric charge. However, the electron actually has intrinsic angular momentum, as we now show.

It turns out that the electron has a magnetic moment. This can be measured experimentally in a Stern-Gerlach experiment. Here, one takes a beam of atoms that have one excess electron beyond a filled shell (most often Silver, but one could use Sodium, as well). The beam is passed through an inhomogeneous magnetic field. If the electron has a magnetic moment, the classical force on the electron is $\mathbf{F} \approx \mathbf{m} \cdot \nabla B$, where $\mathbf{m}$ is the magnetic moment and B is the magnitude of the magnetic field. Thus, particles with different moments will be deflected differing amounts by the magnetic field. When one performs the experiment, one observes:
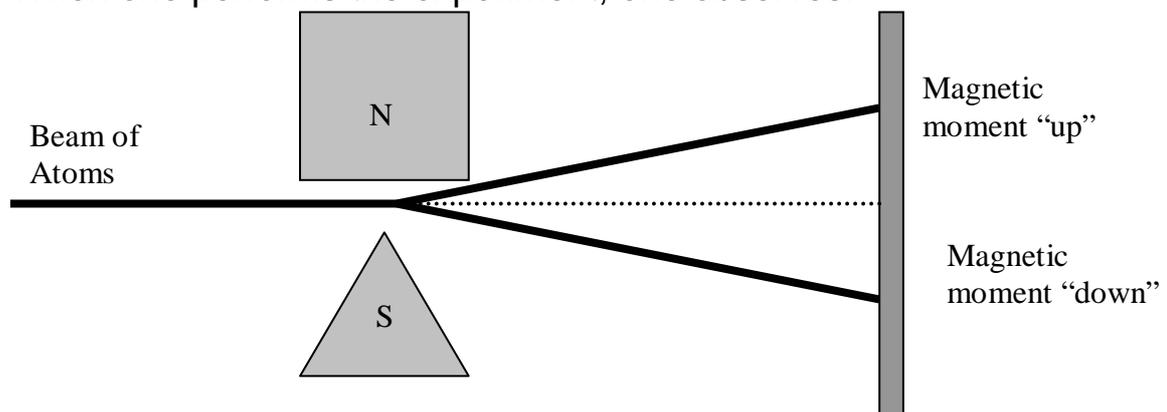
Thus, the magnitude magnetic moment of the electron is fixed, and the direction it points is *quantized* and can take on one of two values.

Now, how does this lead us to conclude that the electron has an intrinsic angular momentum? There are two arguments that lead to this conclusion:

1) Classically, magnetic moments are **always** due to circulating currents – this is known as Ampere's hypothesis. Thus the intrinsic magnetic moment of the electron leads us to postulate an associated angular momentum, called spin. The fact that there are only *two* possible orientations for the spin implies that the electron is spin-1/2 , for then the two orientations correspond to $m_s = \pm\frac{1}{2}$. Classically, one associates the magnetic moment with the angular momentum via $\mathbf{m} = -\dfrac{1}{2c}\mathbf{S}$. However, this turns out to be wrong for the electron; a full relativistic calculation shows that a large number of small corrections to this formula exist and the aggregate effect of these terms *renormalizes* the effective magnetic moment of the electron so that $\mathbf{m} = -\dfrac{g}{2c}\mathbf{S}$, where $g = 2.0022...$, or, for all practical purposes, $g = 2$.

2) Again, classically, a magnetic moment moving in a potential experiences a force $\mathbf{m}\cdot\mathbf{p}\times\nabla V(\mathbf{r})$. For the central potentials we are dealing with, the gradient of the potential will always point in the $\mathbf{r}$ direction. Thus the force is proportional to $\mathbf{m}\cdot\mathbf{p}\times\mathbf{r} \propto \mathbf{m}\cdot\mathbf{L}$. Now the different components of $\hat{\mathbf{L}}$ do not commute, and so it is clear that if we add the appropriate quantum correction for the interaction of the magnetic moment with the potential ($\hat{\mathbf{m}}\cdot\hat{\mathbf{L}}$) angular momentum will no longer be conserved! This can be ameliorated if we assume the electron carries an intrinsic angular momentum and that it is the sum of the spin and orbital angular momenta that is conserved.

For these reasons, we conclude that the electron has an intrinsic angular momentum of magnitude 1/2. We can thus work out the commutation relations and eigenvalue relations for spin by specializing our general results for angular momentum. First, there are the eigenvalue equations:

$$\hat{\mathbf{S}}^2 \left| s, m_s \right\rangle \equiv s(s+1) \left| s, m_s \right\rangle = \tfrac{3}{4} \left| \tfrac{1}{2}, m_s \right\rangle$$

$$S_z \left| s, m_s \right\rangle \equiv m_s \left| s, m_s \right\rangle = \pm \tfrac{1}{2} \left| \tfrac{1}{2}, \pm \tfrac{1}{2} \right\rangle$$

it is conventional to make the definitions

$$\left| \alpha \right\rangle \equiv \left| \tfrac{1}{2}, +\tfrac{1}{2} \right\rangle \qquad \left| \beta \right\rangle \equiv \left| \tfrac{1}{2}, -\tfrac{1}{2} \right\rangle.$$

Then, in the α, β-basis, the spin operators take the form of simple 2x2 matrices:

$$\hat{S}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{S}_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \hat{S}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

One can easily verify that these matrices satisfy the correct commutation relations. There are a lot of things one can learn about quantum mechanics even from a system as simple as this. But for the time being, we will be content with these relationships.

How does all this affect our previous calculations that neglected spin entirely? Thankfully, the effects are rather mild. To a good approximation, we can simply think of the spin as an additional degree of freedom. Operators that act in coordinate space will commute with the spin degree of freedom, and vice versa. Since none of our Hamiltonian operators, to this point, have involved spin, s and m_s have been good quantum numbers. Hence, we can simply think of each wavefunction as actually representing one of two degenerate components that are identical in coordinate space and differ only in spin space – one has spin α, the other spin β.

However, our previous arguments indicate that the Hamiltonian for a central potential should contain a term proportional to

$$\hat{\mathbf{m}} \cdot \hat{\mathbf{L}} = -\frac{g}{2c} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}$$

thus, there is an *interaction* between spin and orbital angular momentum. In order to deal with this, it is advantageous to first consider how one deals with multiple angular momenta, in general.