Total Angular Momentum for Hydrogen

Lecture 29

Physics 342
Quantum Mechanics I

Monday, April 12th, 2010

Note: This lies outside the main discussion in the course – it is for completeness, and to extend our discussion of angular momentum addition to the Hydrogen stationary states. For the angular momentum operators L^2 *and* L_z*, we know that* $[H, L_z] = [H, L^2] = [L^2, L_z] = 0$ *implies that we can find simultaneous eigenstates of all three, and our usual* $\psi_{n\ell m}$ *are already eigenstates of these. For total angular momentum, we know that* $[H, J_z] = [H, J^2] = [J^2, J_z] = 0$*, and so we should again be able to find simultaneous eigenstates of these three operators, but they are not "just" the* $\psi_{n\ell m}$*, this is an example where we have to make linear combinations to achieve the desired simultaneous eigenstates.*

We have the Hydrogen Hamiltonian – for central potential $\phi(r)$, we can write:

$$H_r = \frac{1}{2\,m}\,\mathbf{p}\cdot\mathbf{p} + \phi(r). \tag{29.1}$$

We know that L^2 and L_z commute with the Hamiltonian, and, trivially, so do S^2 and S_z. Our current goal is to establish the eigenfunctions of the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, or, more precisely, J^2 and J_z, and look at the parity of the result.

29.1 Angular Momentum Addition

We will need to be able to add two angular momenta to form a total angular momentum:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{29.2}$$

where $\mathbf{L}$, $\mathbf{S}$ and hence $\mathbf{J}$ are angular momentum operators of some sort. We assume that we have in our possession a set of states: $|\ell\,\ell_z\rangle$ and $|s\,s_z\rangle$ such that $L^2 \, |\ell \, \ell_z\rangle = \hbar^2 \, \ell \, (\ell + 1) \, |\ell \, \ell_z\rangle$, $L_z \, |\ell \, \ell_z\rangle = \hbar \, \ell_z \, |\ell \, \ell_z\rangle$, and similarly for $|s \, s_z\rangle$.

The plan is to combine the eigenkets from the **L** and **S** subspaces – our first question: How big is the space we need to span?

Think of the operators $L_\pm = L_x \pm i \, L_y$ – with $L_+ \, |\ell \, \ell_z\rangle = \alpha_+ \, |\ell \, \ell_z + 1\rangle$ – for some normalization α_+[1]. Our requirement is that the maximum value of ℓ_z is $|\ell|$, and the minimum value of ℓ_z is $-|\ell|$, so that for a given ℓ, we have $2 \, \ell + 1$ eigenvectors for L_z. So we need to span a combined space of size: $(2 \, \ell + 1) \, (2 \, s + 1)$.

We know, from the additive structure of $J_z = L_z + S_z$ that any eigenstate of L_z and S_z has eigenvalue $j_z = \ell_z + s_z$. But then, this eigenket must lie in a state of total $J > j_z$. For example, if we have $|\ell \, \ell_z\rangle = |1 \, 1\rangle$ and $|s \, s_z\rangle = |2 \, 2\rangle$, then the combination $|1 \, 1\rangle \, |2 \, 2\rangle$ has $j_z = 3$, but j itself (the total momentum) can then be at least $j = 3$, or any number greater than this (integer).

Now we do not know what the total j corresponding to a particular $j_z = \ell_z + s_z$ is. We do know that once we have one value for j, we can construct $2 \, j + 1$ total states with this angular momentum (the $2 \, j + 1$ eigenstates of J_z). So we are really asking for the number of distinct series of $2 \, j + 1$, j_z eigenkets associated with a particular j. We'll denote this number $N(j)$, and it corresponds to the number of available combinations $|\ell \, \ell_z\rangle \, |s \, s_z\rangle$ with total angular momentum j. In terms of the degeneracy $n(j_z)$, the number of ways of making a total j_z eigenket, we have

$$n(j_z) = \sum_{j \geq |j_z|} N(j). \tag{29.4}$$

In other words, we can relate the total degeneracy of the j angular momentum to the degeneracy of the j_z component. From our example, this says that $j_z = 3$ can be obtained by any allowed combination of total angular momenta with $j \geq 3$ (of which $j_z = 3$ could be a part). So we add the degeneracy of the total j for all possible j to get the degeneracy of the j_z.

[1] The normalization constant associated with $L_\pm$ is:

$$L_\pm \, |\ell \, \ell_z\rangle = \sqrt{\ell \, (\ell + 1) - \ell_z \, (\ell_z \pm 1)} \, |\ell \, \ell_z - 1\rangle \, . \tag{29.3}$$

Now consider the sums:

$$n(j) = \sum_{j' \geq j} N(j') \qquad n(j+1) = \sum_{j' \geq j+1} N(j') \tag{29.5}$$

subtracting gives us a way to count $N(j)$ using $n(j)$:

$$N(j) = n(j) - n(j+1). \tag{29.6}$$

The advantage here is that we *know* $n(j_z)$ – that's just the number of ways of picking ℓ_z and s_z so that $j_z = \ell_z + s_z$.

To count $n(j_z)$, for example, we just add up all the choices of ℓ_z and s_z that sum to j_z. We can do this graphically, as shown in Figure 29.1 – the points represent the z-component value of the spins (in this case, we have $\ell = 2$, $s = 1$, and the diagonals represent sums of constant j_z (the three available sums for $j_z = 1$ are shown). So, from the figure, there are 3 ways to get $j_z = 0$, $j_z = \pm 1$, 2 ways to have $j_z = \pm 2$ and 1 way to get $j_z = \pm 3$.

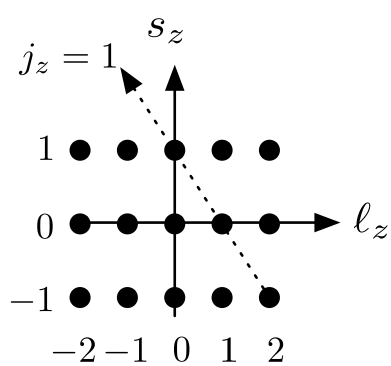

Figure 29.1: Example of counting degeneracy for addition of $\ell = 2$, $s = 1$ momenta.

In general, we have (order so that $\ell > s$):

$$n(j_z) = \begin{cases} 0 & |j_z| > \ell + s \\ \ell + s + (1 - |j_z|) & \ell + s \geq |j_z| \geq |\ell - s| \\ 2\,s + 1 & |\ell - s| \geq |j_z| \geq 0 \end{cases} \tag{29.7}$$

where the first line tells us that there are inaccessible values of j_z for a given ℓ and s, the third line covers the counting for the maximal orders ($j_z = \pm 1$, 0 in our example), and the middle line takes care of the rest of the terms.

Using this form, we can compute (29.6) – we learn, again assuming $\ell > s$, and looking at the form of the $n(j) - n(j+1)$, that only one of the terms depends at all on j – the middle conditional will return:

$$\ell + s + (1 - |j|) - (\ell + s + (1 - |j+1|)) \quad \ell + s \geq j \geq |\ell - s| \tag{29.8}$$

or

$$N(j) = 1 \quad j = \ell + s, \ell + s - 1, \ell + s - 2, \ldots, |\ell - s|. \tag{29.9}$$

So the recipe for success: In any angular momentum addition, there is a unique set ($N(j) = 1$) of eigenvectors $|j\, j_z\rangle$ with $j = \ell + s \longrightarrow |\ell - s|$ in integer steps, and for each j, $j_z = -j \longrightarrow j$ in integer steps.

29.2 Example

Take $\ell = 1$, and $s = \frac{1}{2}$. Our basis kets for each of these are:

$$\begin{aligned} &|1\ -1\rangle\ ,\ |1\,0\rangle\ ,\ |1\,1\rangle \\ &\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\ ,\ \left|\frac{1}{2}\,\frac{1}{2}\right\rangle. \end{aligned} \tag{29.10}$$

We know that there are combined states of total $j = \frac{3}{2}$, and $j = \frac{1}{2}$, so we'll pick a state with a $j_z = \frac{3}{2}$ first:

$$\left|j\,\frac{3}{2}\right\rangle = |1\,1\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle, \tag{29.11}$$

and this must be a state with $j = \frac{3}{2}$ as well. We can check this assertion – $J^2 = L^2 + S^2 + 2\,\mathbf{L}\cdot\mathbf{S}$, and

$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{4}\left(L_+ + L_-\right)\left(S_+ + S_-\right) - \frac{1}{4}\left(L_+ - L_-\right)\left(S_+ - S_-\right) + L_z\,S_z. \tag{29.12}$$

Then the operator J^2 acting on the composite state is:

$$\left(L^2 + S^2 + 2\,\mathbf{L}\cdot\mathbf{S}\right)|1\,1\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle = \hbar^2\left(2 + \frac{3}{4} + 1\right)|1\,1\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle \tag{29.13}$$

and this is just right for

$$J^2\left|\frac{3}{2}\,\frac{3}{2}\right\rangle = \hbar^2\,\frac{3}{2}\left(\frac{3}{2} + 1\right)\left|\frac{3}{2}\,\frac{3}{2}\right\rangle. \tag{29.14}$$

Now we can apply $J_- = L_- + S_-$ to this eigenket in order to lower the j_z. With normalization in place, we have

$$L_- \left|\ell\,\ell_z\right\rangle = \hbar\sqrt{(\ell+\ell_z)\,(\ell-\ell_z+1)}\,\left|\ell\,\ell_z-1\right\rangle, \tag{29.15}$$

and

$$J_-\left|\frac{3}{2}\,\frac{3}{2}\right\rangle = \hbar\left(\sqrt{2}\left|1\,0\right\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle + \left|1\,1\right\rangle\left|\frac{1}{2}\,-\frac{1}{2}\right\rangle\right). \tag{29.16}$$

We can normalize this:

$$\left|\frac{3}{2}\,\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left(\sqrt{2}\left|1\,0\right\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle + \left|1\,1\right\rangle\left|\frac{1}{2}\,-\frac{1}{2}\right\rangle\right). \tag{29.17}$$

The procedure continues, but is effectively covered by a Clebsch-Gordon table, this is basically how they are generated.

What about the net $j = \frac{1}{2}$ state? We can generate this by taking the most general linear combination of states with $j_z = \frac{1}{2}$ and projecting out the known $\left|\frac{3}{2}\,\frac{1}{2}\right\rangle$ state – that will leave us with a pure $j = \frac{1}{2}$, $j_z = \frac{1}{2}$, the top state of $j = \frac{1}{2}$, and we can once again apply the lowering operator to get the other.

Begin with

$$\left|j\,\frac{1}{2}\right\rangle = \alpha\left|1\,1\right\rangle\left|\frac{1}{2}\,-\frac{1}{2}\right\rangle + \beta\left|1\,0\right\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle, \tag{29.18}$$

then

$$\left\langle\frac{3}{2}\,\frac{1}{2}\middle|j\,\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left(\sqrt{2}\,a + b\right), \tag{29.19}$$

and to get this to be zero, and normalize the resulting state, we must have $\alpha = \frac{1}{\sqrt{3}}$, $\beta = -\frac{\sqrt{2}}{\sqrt{3}}$, giving us the state:

$$\left|j\,\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left(\left|1\,0\right\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle - \sqrt{2}\left|1\,1\right\rangle\left|\frac{1}{2}\,-\frac{1}{2}\right\rangle\right). \tag{29.20}$$

This state has $J^2\left|j\,\frac{1}{2}\right\rangle = \hbar^2\,\frac{3}{4}\left|j\,\frac{1}{2}\right\rangle$ as expected.

29.3 Total Angular Momentum

Since the Coulomb Hamiltonian H_r has

$$[L^2, H_r] = [L_z, H_r] = 0 \tag{29.21}$$

and, because there is no reference to spin at all,

$$[S^2, H_r] = [S_z, H_r] = 0 \tag{29.22}$$

we have, trivially:

$$[J^2, H_r] = [L^2 + 2\,\mathbf{L} \cdot \mathbf{S} + S^2, H_r] = 0 \tag{29.23}$$

and $[J_z, H_r] = 0$. So the Hamiltonian has eigenfunctions that are simultaneously eigenfunctions of J^2 and J_z. What do these look like? Since the Hydrogenic wave function is made up of an orbital part and a spin part, we can write

$$\Psi(\mathbf{r}) = \psi(\mathbf{r})\,\chi \tag{29.24}$$

for χ a two-component spinor associated with the Pauli matrix representation of spin – that is, $\mathbf{S} = \frac{1}{2}\,\hbar\,\boldsymbol{\sigma}$ has $S_z\,\chi_+ = \frac{1}{2}\,\hbar\,\chi_+$, $S_z\,\chi_- = -\frac{1}{2}\,\hbar\,\chi_-$ and $S^2\,\chi_\pm = \frac{3}{4}\,\hbar^2\,\chi_\pm$.

In addition, we know that the eigenfunctions of L^2 are, in spherical representation:

$$Y_\ell^m(\theta, \phi) = f_\ell^m\, e^{i\,m\,\phi}\, P_\ell^m(\cos\theta) \tag{29.25}$$

for f_ℓ^m a normalization factor introduced to ensure that

$$\int (Y_\ell^m(\theta, \phi))^*\; Y_{\ell'}^{m'}\, \sin\theta\, d\theta\, d\phi = \delta_{\ell\ell'}\delta_{mm'} \tag{29.26}$$

In this context, we have the operator eigenequation:

$$L^2\, Y_\ell^m = \hbar^2\,\ell\,(\ell+1)\, Y_\ell^m, \tag{29.27}$$

and $L_z\, Y_\ell^m = m\,\hbar\, Y_\ell^m$.

The eigenfunctions of J^2 are combinations of the Y_ℓ^m and χ_+ and χ_-, precisely the angular momentum addition we developed in the previous section. We know that there exist combinations, sometimes denoted $\mathcal{Y}_J^M$ that have:

$$J^2\,\mathcal{Y}_J^M = \hbar^2\,J\,(J+1)\,\mathcal{Y}_J^M \qquad J_z\,\mathcal{Y}_J^M = \hbar\,M\,\mathcal{Y}_J^M. \tag{29.28}$$

29.3.1 Computing $\mathcal{Y}_J^M$

Since we already know that the total angular momentum for an electron orbit and spin can come in only two combinations $\ell = J + \frac{1}{2}$, $\ell = J - \frac{1}{2}$, it is reasonable to try to write down the actual expressions. For a state $\mathcal{Y}_J^M$ with definite M, we can have:

$$\mathcal{Y}_J^M = \alpha\, Y_{J+\frac{1}{2}}^{M-\frac{1}{2}}\, \chi_- + \beta\, Y_{J+\frac{1}{2}}^{M+\frac{1}{2}} \chi_- + \gamma\, Y_{J-\frac{1}{2}}^{M-\frac{1}{2}}\, \chi_+ + \delta\, Y_{J-\frac{1}{2}}^{M+\frac{1}{2}}\, \chi_-, \tag{29.29}$$

where each term is constructed so as to have J_z component M (the total of $S_z + L_z$). It is tedious at this point to actually compute the constraints on these terms that lead to the final form – the line of reasoning is the same as in the above examples, you expand:

$$J^2 = L^2 + S^2 + 2\,\mathbf{L} \cdot \mathbf{S} \tag{29.30}$$

into ladder operators as in (29.12), combine terms and set the whole thing equal to $\hbar^2\, J\,(J+1)\,\mathcal{Y}_J^M$, then solve for $(\alpha, \beta, \gamma, \delta)$.

It is not surprising that the pairs (α, β) and (γ, δ) do not communicate (different ℓ values). Nor will it come as a shock to learn that you have an overall normalization factor. In the end, the combination that solves the eigenvalue problem is:

$$\mathcal{Y}_J^M = \alpha \left[Y_{J+\frac{1}{2}}^{M-\frac{1}{2}}\, \chi_+ - \sqrt{\frac{1+J+M}{1+J-M}}\, Y_{J+\frac{1}{2}}^{M+\frac{1}{2}}\, \chi_- \right] + \gamma \left[Y_{J-\frac{1}{2}}^{M-\frac{1}{2}}\, \chi_+ + \sqrt{\frac{J-M}{J+M}}\, Y_{J-\frac{1}{2}}^{M+\frac{1}{2}}\, \chi_- \right] \tag{29.31}$$

so we can divide this into two separate solutions (parity concerns, as we shall see below, suggest this) – one with $\ell = J + \frac{1}{2}$ and one with $\ell = J - \frac{1}{2}$.

In the end, after normalization, we get:

$$\begin{aligned} \mathcal{Y}_J^{M+} &= \frac{1}{\sqrt{2\,(J+1)}} \left(-\sqrt{1+J-M}\, Y_{J+\frac{1}{2}}^{M-\frac{1}{2}}\, \chi_+ + \sqrt{1+J+M}\, Y_{J+\frac{1}{2}}^{M+\frac{1}{2}}\, \chi_- \right) \\ \mathcal{Y}_J^{M-} &= \frac{1}{\sqrt{2\,J}} \left(\sqrt{J+M}\, Y_{J-\frac{1}{2}}^{M-\frac{1}{2}}\, \chi_+ + \sqrt{J-M}\, Y_{J-\frac{1}{2}}^{M+\frac{1}{2}}\, \chi_- \right). \end{aligned} \tag{29.32}$$

29.4 Parity for Spherical Harmonics

The parity operator P in one dimension changes the sign of the coordinates: $P\, f(x) = f(-x)$. The eigenfunctions of P are "even" and "odd" functions with eigenvalue ± 1. When we think of the Hamiltonian operator with central potential:

$$H = -\frac{\hbar^2}{2\,m}\,\nabla^2 + V(r), \tag{29.33}$$

it is clear that $[H, P] = 0$. So eigenfunctions of the Hamiltonian can be taken to be eigenfunctions of P. Since the spherical harmonics make up the angular solution, it is natural to ask if they are the desired simultaneous eigenfunction of P?

Spherical harmonics are products of $e^{i\,m\,\phi}$ and the associated Legendre polynomials $P_\ell^m(\cos\theta)$. The associated Legendre polynomials can be developed from the Legendre polynomials:

$$P_\ell^m(z) = \left(1 - z^2\right)^{|m|/2}\,\frac{d^{|m|}}{dz^{|m|}}\,P_\ell(z). \tag{29.34}$$

What does $\mathbf{x} \to -\mathbf{x}$ (the three-dimensional parity operation) do to θ and ϕ? For θ, we see that reflecting the vector shown in Figure 29.2 has $\theta' = \pi - \theta$.

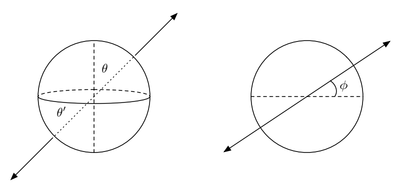

Figure 29.2: Relation of θ to θ' under spatial reflection.

Similarly, for the ϕ coordinate, we have $\phi' = \pi + \phi$. Now the Legendre polynomials have parity, from their definition:

$$P_\ell(x) = \frac{1}{2^\ell\,\ell!}\left(\frac{d}{dx}\right)^\ell \left(x^2 - 1\right)^\ell \tag{29.35}$$

of $+1$ when ℓ is even, -1 when ℓ is odd (set $y = -x$ and rewrite the above). That means, looking at the associated Legendre polynomials, that the parity of P_ℓ^m is $+1$ for $\ell + |m|$ even and -1 for $\ell + |m|$ odd. The parity of the phase $e^{i\,m\phi}$ is

$$e^{i\,m\,\phi'} = e^{i\,m\,(\pi+\phi)} = (-1)^m\,e^{i\,m\,\phi}, \tag{29.36}$$

so $+1$ for m even, -1 for m odd. Suppose we have two functions $f(x)$ and $g(x)$, with $P\,f(x) = (-1)^p\,f(x)$ and $P\,g(x) = (-1)^q\,g(x)$, then the product has $P\,(f(x)\,g(x)) = f(-x)\,g(-x) = (-1)^{(p+q)}\,f(x)\,g(x)$. In this case, we have

$$P\,Y_\ell^m = (-1)^{|m|}\,(-1)^{\ell+|m|} = (-1)^{\ell+2\,|m|} = (-1)^\ell, \tag{29.37}$$

and we see that our spherical harmonics are eigenstates of P as well.

29.5 Parity for $\mathcal{Y}_J^M$

The parity of the total angular momentum states is determined by the parity of the underlying Y_ℓ^m – all we know for sure is that there are two opposite parities here – since $\ell = J + \frac{1}{2}$ and $\ell = J - \frac{1}{2}$ are separated by an integer, we have one combination "even", the other "odd", but until we know J, we cannot say more than this. For example, if $J = \frac{3}{2}$, then there are $\ell = 1$ and $\ell = 2$ combinations in $\mathcal{Y}_J^M$ – the $\ell = 1$ form has parity -1, and $\ell = 2$ has parity $+1$.

Homework

Reading: Griffiths, pp. 185–200.

Problem 29.1

Griffiths 4.27. Practice calculating expectation values for spin operators.

Problem 29.2

If an electron is in the state $\chi = \chi_+$ (i.e. the spin up state w.r.t. S_z), what is the probability of obtaining a measurement of $\frac{\hbar}{2}$ for S_y?

Problem 29.3

Some issues associated with the Stern-Gerlach wave function.

a. Suppose you take the spin state:

$$\chi(t) = A\, e^{-i\,\frac{E_+\,t}{\hbar}}\,\chi_+ \qquad E_+ \equiv -\frac{1}{2}\,\hbar\,\gamma\,(B_0 + \alpha\,z)\,, \tag{29.38}$$

and treat it as a (potential) solution to Schrödinger's equation:

$$-\frac{\hbar^2}{2\,m}\,\frac{\partial^2}{\partial z^2}\,\chi(t) - \gamma\,\mathbf{B}\cdot\mathbf{S}\,\chi(t) = i\,\hbar\,\frac{\partial\chi(t)}{\partial t}. \tag{29.39}$$

Calculate the left and right-hand sides of this expression (take $\mathbf{B} = (B_0 + \alpha\,z)\,\hat{\mathbf{z}}$, just the z-component of the magnetic field), and show that they differ by terms of order α^2.

b. The magnetic field for the Stern-Gerlach experiment has an x component: $\mathbf{B} = -\alpha\,x\,\hat{\mathbf{x}} + (B_0 + \alpha\,z)\,\hat{\mathbf{z}}$ is the full magnetic field. Find the energies of the spin-portion of the Hamiltonian: $H = -\gamma\,\mathbf{B}\cdot\mathbf{S}$ ignoring the kinetic piece, so $H\,\chi = E\,\chi$. Show that they reduce to the Stern-Gerlach energies when α is small (technically, we can compare $\alpha\,x$ to $B_0 + \alpha\,z$, and the statement is $B_0 + \alpha\,z \gg \alpha\,x$ – Taylor expand your energies in the parameter $\epsilon \equiv \frac{\alpha\,x}{B_0 + \alpha\,z}$).