

# ADDITION OF ANGULAR MOMENTUM

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## 1 Adding apples to oranges?

We are going to be adding angular momenta in a variety of ways. We may add the *spin* angular momentum  $\mathbf{S}$  of a particle to its *orbital* angular momentum  $\mathbf{L}$ . Or we may want to add the spin angular momentum  $\mathbf{S}^{(1)}$  of a particle to the spin angular momentum  $\mathbf{S}^{(2)}$  of another particle. At first sight we may feel like we are trying to add apples to oranges! For a given particle its spin angular momentum has nothing to do with spatial wavefunctions, while its orbital angular momentum does. How could we ever add such things? Adding the spins of two different particles also seems unusual if, for example, the particles are far-away from each other. Vectors that live at different places are seldom added: you don't typically add the electric field at one point to the electric field at another point: the sum has no obvious interpretation. This is even more severe in general relativity: you *cannot* add vectors that 'live' at different points of space-time. To add them you need a procedure to first bring them to a common point. Once they both live at that common point you can add them.

I want to make clear, however, that at a basic algebraic level all angular momenta are apples (granny smith, red-delicious, macintosh, fuji, etc.) and therefore they can be added and it is natural to add them. We are not adding apples to oranges; we are adding apples to apples! The physics

requires it: we will see that energy eigenstates will also be eigenstates of operators in the sum of angular momenta. The mathematics allows it: the sum of angular momenta *is* an angular momentum acting in the appropriate *tensor* product. As we will see below, each angular momentum lives on a different vector space, but the sum finds a home in the tensor product of the vector spaces.

What is an angular momentum? It is a triplet  $\hat{J}_i$  of Hermitian linear operators on some complex vector space  $V$  satisfying the commutation relations

$$[\hat{J}_i, \hat{J}_j] = i\hbar \epsilon_{ijk} \hat{J}_k. \quad (1.1)$$

As we have learned, this is a very powerful statement. When coupled with the requirement that no negative norm-squared states exist, it implies that  $V$  can be decomposed into sums of representations of angular momentum, all of which are finite dimensional.

Let us now assume we have two angular momenta:

$$\begin{aligned} \text{Hermitian operators } J_i^{(1)} \text{ acting on } V_1 \text{ and satisfying } [\hat{J}_i^{(1)}, \hat{J}_j^{(1)}] &= i\hbar \epsilon_{ijk} \hat{J}_k^{(1)} \\ \text{Hermitian operators } J_i^{(2)} \text{ acting on } V_2 \text{ and satisfying } [\hat{J}_i^{(2)}, \hat{J}_j^{(2)}] &= i\hbar \epsilon_{ijk} \hat{J}_k^{(2)} \end{aligned} \quad (1.2)$$

Our claim is that the ‘sum’ of angular momenta is an angular momentum in the tensor product:

$$\hat{J}_i \equiv \hat{J}_i^{(1)} \otimes \mathbf{1} + \mathbf{1} \otimes \hat{J}_i^{(2)} \text{ satisfies } [\hat{J}_i, \hat{J}_j] = i\hbar \epsilon_{ijk} \hat{J}_k \text{ acting on } V_1 \otimes V_2. \quad (1.3)$$

Certainly the sum operator, as defined above, is an operator on  $V_1 \otimes V_2$ . It is in fact a Hermitian operator on  $V_1 \otimes V_2$ . We just need to check that the commutator holds

$$\begin{aligned} [\hat{J}_i, \hat{J}_j] &= [\hat{J}_i^{(1)} \otimes \mathbf{1} + \mathbf{1} \otimes \hat{J}_i^{(2)}, \hat{J}_j^{(1)} \otimes \mathbf{1} + \mathbf{1} \otimes \hat{J}_j^{(2)}] \\ &= [\hat{J}_i^{(1)} \otimes \mathbf{1}, \hat{J}_j^{(1)} \otimes \mathbf{1}] + [\mathbf{1} \otimes \hat{J}_i^{(2)}, \mathbf{1} \otimes \hat{J}_j^{(2)}], \end{aligned} \quad (1.4)$$

since the mixed terms, which represent commutators of the operators in the different spaces vanish:

$$[\hat{J}_i^{(1)} \otimes \mathbf{1}, \mathbf{1} \otimes \hat{J}_j^{(2)}] = 0, \quad [\mathbf{1} \otimes \hat{J}_i^{(2)}, \hat{J}_j^{(1)} \otimes \mathbf{1}] = 0. \quad (1.5)$$

(If this is not ‘obvious’, think about it and do the one-line computation that will make it obvious!).

Writing out the commutators we see that (1.4) becomes

$$[\hat{J}_i, \hat{J}_j] = [\hat{J}_i^{(1)}, \hat{J}_j^{(1)}] \otimes \mathbf{1} + \mathbf{1} \otimes [\hat{J}_i^{(2)}, \hat{J}_j^{(2)}]. \quad (1.6)$$

We can now use the independent algebras of angular momentum to find

$$\begin{aligned} [\hat{J}_i, \hat{J}_j] &= i\hbar \epsilon_{ijk} \hat{J}_k^{(1)} \otimes \mathbf{1} + i\hbar \epsilon_{ijk} \mathbf{1} \otimes \hat{J}_k^{(2)} \\ &= i\hbar \epsilon_{ijk} (\hat{J}_k^{(1)} \otimes \mathbf{1} + \mathbf{1} \otimes \hat{J}_k^{(2)}) \\ &= i\hbar \epsilon_{ijk} \hat{J}_k, \end{aligned} \quad (1.7)$$

which is what we set out to prove.

It is important to note that had we added the two angular momenta with some arbitrary coefficients we would not have got an angular momentum. Indeed, suppose we use two non-zero complex constants  $\alpha$  and  $\beta$  and write

$$\tilde{J}_i \equiv \alpha \hat{J}_j^{(1)} \otimes \mathbf{1} + \beta \mathbf{1} \otimes \hat{J}_j^{(2)}. \quad (1.8)$$

If either constant is zero we are not really summing. The commutator calculation above this time yields

$$[\tilde{J}_i, \tilde{J}_j] = i\hbar \epsilon_{ijk} (\alpha^2 \hat{J}_k^{(1)} \otimes \mathbf{1} + \beta^2 \mathbf{1} \otimes \hat{J}_k^{(2)}). \quad (1.9)$$

We have an algebra of angular momentum if the operator in parenthesis is  $\tilde{J}_k$ . This requires  $\alpha^2 = \alpha$  and  $\beta^2 = \beta$ . Since neither  $\alpha$  nor  $\beta$  is zero, the only solution is  $\alpha = \beta = 1$ . This confirms that we are using in (1.3) the *unique way* to add two angular momenta to form a new angular momentum.

By the same arguments that hold for any angular momentum on a vector space, the space  $V_1 \otimes V_2$  can be decomposed into sums of representations of the algebra of *total* angular momentum. This property gives us a powerful tool to understand the spectrum of the Hamiltonian in the physical state space  $V_1 \otimes V_2$ .

## 2 Adding two spin one-half angular momenta

To set up the notation recall that for a spin one-half particle and spin operators  $\mathbf{S}$  we write

$$\mathbf{S}^2 |s, m\rangle = \hbar^2 s(s+1) |s, m\rangle, \quad \hat{S}_z |s, m\rangle = \hbar m |s, m\rangle, \quad \text{with } s = \frac{1}{2}, \text{ and } m = \pm \frac{1}{2}. \quad (2.1)$$

The states that span the vector space are thus

$$|\frac{1}{2}, \frac{1}{2}\rangle, \quad |\frac{1}{2}, -\frac{1}{2}\rangle, \quad (2.2)$$

states that we used to label as  $|+\rangle$  and  $|-\rangle$ , respectively. The action of  $\mathbf{S}^2$  on any of these states gives  $\frac{3}{4}\hbar^2$  and the action of  $\hat{S}_z/\hbar$  gives  $\frac{1}{2}$  on the first and  $-\frac{1}{2}$  on the second.

We now consider the case in which our system features two spin one-half particles. For the first particle we have the triplet of spin operators  $\mathbf{S}^{(1)}$  acting on the vector space  $V_1$  spanned by

$$|\frac{1}{2}, \frac{1}{2}\rangle_1, \quad |\frac{1}{2}, -\frac{1}{2}\rangle_1, \quad (2.3)$$

For the second particle we have the triplet spin operators  $\mathbf{S}^{(2)}$  acting on the vector space  $V_2$  spanned by

$$|\frac{1}{2}, \frac{1}{2}\rangle_2, \quad |\frac{1}{2}, -\frac{1}{2}\rangle_2. \quad (2.4)$$

We now form the total spin

$$\hat{S}_i \equiv \hat{S}_i^{(1)} \otimes \mathbf{1} + \mathbf{1} \otimes \hat{S}_i^{(2)} \quad (2.5)$$

which we write, for brevity as

$$\hat{S}_i = \hat{S}_i^{(1)} + \hat{S}_i^{(2)}, \quad \text{for example, } \hat{S}_z = \hat{S}_z^{(1)} + \hat{S}_z^{(2)}, \quad (2.6)$$

with the understanding that each operator on the right-hand sides acts on the appropriate factor in the tensor product. The state space for the dynamics of the two particles must contain the tensor product  $V_1 \otimes V_2$  (more spaces might be needed if the particles have orbital angular momentum or they are moving). As we learned before,  $V_1 \otimes V_2$  is a four-dimensional complex vector space spanned by the products of states in (2.3) and (2.4):

$$|\frac{1}{2}, \frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, \frac{1}{2}\rangle_2, \quad |\frac{1}{2}, \frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, -\frac{1}{2}\rangle_2, \quad |\frac{1}{2}, -\frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, \frac{1}{2}\rangle_2, \quad |\frac{1}{2}, -\frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, -\frac{1}{2}\rangle_2. \quad (2.7)$$

It must be possible to organize these states into finite-dimensional representations of the total spin angular momentum, which is well-defined acting on these states. We have four basis states so the possibilities for multiplets of total spin  $s$  are

1. Four singlets ( $s = 0$ ).
2. Two doublets ( $s = \frac{1}{2}$ ).
3. One doublet ( $s = \frac{1}{2}$ ) and two singlets ( $s = 0$ ).
4. One triplet ( $s = 1$ ) and one singlet ( $s = 0$ ).
5. One  $s = \frac{3}{2}$  multiplet.

It may be instructive at this point if you pause to make sure no other option exists and then to consider which option is the only likely to be true! Guess it!

The main clue is that the states in the tensor product are eigenstates of  $\hat{S}_z$ , the total  $z$ -component of angular momentum. We see by inspection of (2.7) that the possible values of  $\hat{S}_z/\hbar$  are  $+1, 0$ , and  $-1$ . Since we have a state with  $m = +1$  and no state with higher  $m$  we must have a triplet  $s = 1$ . Thus the only option is the fourth one listed above: a triplet and a singlet. This is written as

$$(s = \frac{1}{2}) \otimes (s = \frac{1}{2}) = (s = 1) \oplus (s = 0) \quad (2.8)$$

Note that in the left-hand side we have the tensor product of the two state spaces, but in the right-hand side the *direct sum* of the representations of total spin angular momentum. This is a fundamental result and is written more briefly as

$$\boxed{\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0.} \quad (2.9)$$

Let us understand this very explicitly by organizing the basis states according to the eigenvalue  $m$  of  $\hat{S}_z/\hbar$ . We readily observe that

$$\begin{aligned} m = 1 &: & |\frac{1}{2}, \frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, \frac{1}{2}\rangle_2, \\ m = 0 &: & |\frac{1}{2}, \frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, -\frac{1}{2}\rangle_2, \quad |\frac{1}{2}, -\frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, \frac{1}{2}\rangle_2, \\ m = -1 &: & |\frac{1}{2}, -\frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, -\frac{1}{2}\rangle_2. \end{aligned} \quad (2.10)$$

We see that we get two states with  $m = 0$ . This is as it should be. One linear combination of these two states must correspond to the  $m = 0$  state of the triplet and another linear combination must correspond to the singlet  $s = m = 0$ . Those two states are in fact entangled states. Denoting by  $|s, m\rangle$  the eigenstates of  $\mathbf{S}^2$  and  $\hat{S}_z$  (total spin) we must have a triplet with states

$$\begin{aligned} |1, 1\rangle &= |\tfrac{1}{2}, \tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, \tfrac{1}{2}\rangle_2, \\ |1, 0\rangle &= \alpha |\tfrac{1}{2}, \tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_2 + \beta |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, \tfrac{1}{2}\rangle_2, \\ |1, -1\rangle &= |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_2. \end{aligned} \quad (2.11)$$

for some constants  $\alpha$  and  $\beta$ , as well as a singlet

$$|0, 0\rangle = \gamma |\tfrac{1}{2}, \tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_2 + \delta |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, \tfrac{1}{2}\rangle_2, \quad (2.12)$$

for some constants  $\gamma$  and  $\delta$ . We must determine these four constants. Let us begin with the state in the triplet. Recalling the general formula

$$J_{\pm}|j, m\rangle = \hbar\sqrt{j(j+1) - m(m\mp 1)}|j, m\pm 1\rangle \quad (2.13)$$

we quickly note that

$$\begin{aligned} J_-|1, 1\rangle &= \hbar\sqrt{2}|1, 0\rangle, \\ J_-|\tfrac{1}{2}, \tfrac{1}{2}\rangle &= \hbar\sqrt{\tfrac{1}{2} \cdot \tfrac{3}{2} - \tfrac{1}{2} \cdot (-\tfrac{1}{2})}|\tfrac{1}{2}, -\tfrac{1}{2}\rangle = \hbar|\tfrac{1}{2}, -\tfrac{1}{2}\rangle \\ J_+|\tfrac{1}{2}, -\tfrac{1}{2}\rangle &= \hbar\sqrt{\tfrac{1}{2} \cdot \tfrac{3}{2} - (-\tfrac{1}{2}) \cdot (\tfrac{1}{2})}|\tfrac{1}{2}, -\tfrac{1}{2}\rangle = \hbar|\tfrac{1}{2}, \tfrac{1}{2}\rangle \end{aligned} \quad (2.14)$$

In here  $J$  can be spin, of course. We now apply the lowering operator  $S_- = S_-^{(1)} + S_-^{(2)}$  to the top state in the triplet. We have

$$S_-|1, 1\rangle = (S_-^{(1)}|\tfrac{1}{2}, \tfrac{1}{2}\rangle_1) \otimes |\tfrac{1}{2}, \tfrac{1}{2}\rangle_2 + |\tfrac{1}{2}, \tfrac{1}{2}\rangle_1 \otimes (S_-^{(2)}|\tfrac{1}{2}, \tfrac{1}{2}\rangle_2), \quad (2.15)$$

Using the results in (2.14) we find

$$\sqrt{2}\hbar|1, 0\rangle = \hbar|\tfrac{1}{2}, -\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, \tfrac{1}{2}\rangle_2 + |\tfrac{1}{2}, \tfrac{1}{2}\rangle_1 \otimes \hbar|\tfrac{1}{2}, -\tfrac{1}{2}\rangle_2. \quad (2.16)$$

Cancelling the common factors of  $\hbar$  and switching the order of the terms we find that the  $|1, 0\rangle$  state takes the form

$$|1, 0\rangle = \frac{1}{\sqrt{2}} \left( |\tfrac{1}{2}, \tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_2 + |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, \tfrac{1}{2}\rangle_2 \right). \quad (2.17)$$

Having found the  $m = 0$  state of the  $s = 1$  multiplet there are a number of ways of finding the  $m = 0$  of the  $s = 0$  singlet. One way is orthogonality: the latter state must be orthogonal to the  $m = 0$  state above because these are two states with different  $s$ , thus different eigenvalues for the Hermitian operator  $\mathbf{S}^2$ . Since the overall sign or phase is irrelevant, we can simply take for the singlet

$$|0, 0\rangle = \frac{1}{\sqrt{2}} \left( |\tfrac{1}{2}, \tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_2 - |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}, \tfrac{1}{2}\rangle_2 \right). \quad (2.18)$$

You probably remember that we found this state in a previous chapter by requiring that it is annihilated by the sum of spin angular momentum operators. This is exactly the condition for a singlet.

As an interesting calculation and good practice with the operators, let us confirm that  $\mathbf{S}^2$  is zero acting on  $|0,0\rangle$ . For this it is useful to note that

$$\begin{aligned}\mathbf{S}^2 &= (\mathbf{S}^{(1)} + \mathbf{S}^{(2)})^2 = (\mathbf{S}^{(1)})^2 + (\mathbf{S}^{(2)})^2 + 2\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} \\ &= (\mathbf{S}^{(1)})^2 + (\mathbf{S}^{(2)})^2 + S_+^{(1)}S_-^{(2)} + S_-^{(1)}S_+^{(2)} + 2S_z^{(1)}S_z^{(2)}\end{aligned}\quad (2.19)$$

where in the second step we used the general result

$$\hat{\mathbf{J}}^{(1)} \cdot \hat{\mathbf{J}}^{(2)} = \frac{1}{2}(\hat{J}_+^{(1)}\hat{J}_-^{(2)} + \hat{J}_-^{(1)}\hat{J}_+^{(2)}) + \hat{J}_z^{(1)}\hat{J}_z^{(2)}\quad (2.20)$$

which is valid for arbitrary angular momenta. Written in explicit tensor notation it reads

$$\hat{\mathbf{J}}^{(1)} \cdot \hat{\mathbf{J}}^{(2)} \equiv \sum_{i=1}^3 \hat{J}_i^{(1)} \otimes \hat{J}_i^{(2)} = \frac{1}{2}(\hat{J}_+^{(1)} \otimes \hat{J}_-^{(2)} + \hat{J}_-^{(1)} \otimes \hat{J}_+^{(2)}) + \hat{J}_z^{(1)} \otimes \hat{J}_z^{(2)}\quad (2.21)$$

All states in the singlet have  $s_1 = s_2 = \frac{1}{2}$ , and therefore  $(\mathbf{S}^{(1)})^2 = (\mathbf{S}^{(2)})^2 = \frac{3}{4}\hbar^2$ . We thus have

$$\mathbf{S}^2 |0,0\rangle = \frac{3}{2}\hbar^2 |0,0\rangle + (S_+^{(1)}S_-^{(2)} + S_-^{(1)}S_+^{(2)} + 2S_z^{(1)}S_z^{(2)})|0,0\rangle\quad (2.22)$$

It is simple to see that

$$2S_z^{(1)}S_z^{(2)} |0,0\rangle = 2 \frac{\hbar}{2} \cdot \left(-\frac{\hbar}{2}\right) |0,0\rangle = -\frac{1}{2}\hbar^2 |0,0\rangle,\quad (2.23)$$

because the singlet is a superposition of tensor states where each has one state up and one state down. Similarly recalling that

$$S_{\pm}|\frac{1}{2}, \mp\frac{1}{2}\rangle = \hbar^2|\frac{1}{2}, \pm\frac{1}{2}\rangle\quad (2.24)$$

we quickly find that

$$(S_+^{(1)}S_-^{(2)} + S_-^{(1)}S_+^{(2)})|0,0\rangle = -\hbar^2 |0,0\rangle,\quad (2.25)$$

since each of the operators  $S_+^{(1)}S_-^{(2)}$  and  $S_-^{(1)}S_+^{(2)}$  kills one term in the singlet (call it the first) and acting on the other (the second) it gives  $\hbar^2$  times the first. Check it, anyway. Back in (2.26) we get

$$\mathbf{S}^2 |0,0\rangle = \frac{3}{2}\hbar^2 |0,0\rangle + (-\hbar^2 - \frac{1}{2}\hbar^2)|0,0\rangle = 0\quad (2.26)$$

as we wanted to show.

Let us summarize our results. The triplet states and singlet states are given by

$$\begin{aligned}|1,1\rangle &= |\frac{1}{2}, \frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, \frac{1}{2}\rangle_2, \\ |1,0\rangle &= \frac{1}{\sqrt{2}} \left( |\frac{1}{2}, \frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, -\frac{1}{2}\rangle_2 + |\frac{1}{2}, -\frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, \frac{1}{2}\rangle_2 \right) \\ |1,-1\rangle &= |\frac{1}{2}, -\frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, -\frac{1}{2}\rangle_2. \\ |0,0\rangle &= \frac{1}{\sqrt{2}} \left( |\frac{1}{2}, \frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, -\frac{1}{2}\rangle_2 - |\frac{1}{2}, -\frac{1}{2}\rangle_1 \otimes |\frac{1}{2}, \frac{1}{2}\rangle_2 \right).\end{aligned}\quad (2.27)$$

For briefer notation we replace

$$|\frac{1}{2}, \frac{1}{2}\rangle \rightarrow |\uparrow\rangle, \quad \text{and } |\frac{1}{2}, -\frac{1}{2}\rangle \rightarrow |\downarrow\rangle \quad (2.28)$$

We then have

$$\begin{aligned} |1, 1\rangle &= |\uparrow\rangle_1 \otimes |\uparrow\rangle_2, \\ |1, 0\rangle &= \frac{1}{\sqrt{2}} \left( |\uparrow\rangle_1 \otimes |\downarrow\rangle_2 + |\downarrow\rangle_1 \otimes |\uparrow\rangle_2 \right) \\ |1, -1\rangle &= |\downarrow\rangle_1 \otimes |\downarrow\rangle_2. \\ |0, 0\rangle &= \frac{1}{\sqrt{2}} \left( |\uparrow\rangle_1 \otimes |\downarrow\rangle_2 - |\downarrow\rangle_1 \otimes |\uparrow\rangle_2 \right). \end{aligned} \quad (2.29)$$

With the understanding that the first arrow refers to the first particle and the second arrow to the second particle, we can finally write all of this quite briefly

$$\begin{aligned} |1, 1\rangle &= |\uparrow\uparrow\rangle, \\ |1, 0\rangle &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \\ |1, -1\rangle &= |\downarrow\downarrow\rangle. \\ |0, 0\rangle &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \end{aligned}$$

(2.30)

This decomposition of the tensor product of two spin one-half state spaces is useful for the computation of the hyperfine splitting in the hydrogen atom, where the relevant spins are those of the proton and the electron.

### 3 Feynman-Hellman lemma

This is a nice and simple result that gives us insight into the way energy levels change under perturbations of the Hamiltonian.

Consider a Hamiltonian  $H(\lambda)$  with a parameter  $\lambda$  and some *normalized* energy eigenstate  $\psi(\lambda)$  with some energy  $E(\lambda)$ . We claim that

$$\frac{dE(\lambda)}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH(\lambda)}{d\lambda} \right| \psi(\lambda) \right\rangle.$$

(3.1)

This is the Feynman-Hellman (FH) lemma. Note that by assumption  $\psi(\lambda)$  is an eigenstate and is normalized for all values of  $\lambda$ . The proof of (3.1) is straightforward. Note that

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle, \quad (3.2)$$

and therefore

$$E(\lambda) = \langle \psi(\lambda) | H(\lambda) | \psi(\lambda) \rangle. \quad (3.3)$$

Now differentiate this relation with respect to  $\lambda$  to get

$$\frac{dE}{d\lambda}(\lambda) = \left( \frac{d}{d\lambda} \langle \psi(\lambda) | \right) H(\lambda) | \psi(\lambda) \rangle + \langle \psi(\lambda) | \frac{dH(\lambda)}{d\lambda} | \psi(\lambda) \rangle + \langle \psi(\lambda) | H(\lambda) \left( \frac{d}{d\lambda} | \psi(\lambda) \rangle \right) \quad (3.4)$$

Using the eigenstate equation for the first and last term,

$$\frac{dE}{d\lambda}(\lambda) = E(\lambda) \left( \frac{d}{d\lambda} \langle \psi(\lambda) | \right) | \psi(\lambda) \rangle + \langle \psi(\lambda) | \frac{dH(\lambda)}{d\lambda} | \psi(\lambda) \rangle + E(\lambda) \langle \psi(\lambda) | \left( \frac{d}{d\lambda} | \psi(\lambda) \rangle \right) \quad (3.5)$$

We thus have

$$\frac{dE}{d\lambda}(\lambda) = \langle \psi(\lambda) | \frac{dH(\lambda)}{d\lambda} | \psi(\lambda) \rangle + E(\lambda) \frac{d}{d\lambda} \langle \psi(\lambda) | \psi(\lambda) \rangle. \quad (3.6)$$

Since the state is normalized for all  $\lambda$  the last term vanishes and we are left with the result we wanted to prove. Note that the FH lemma is an exact result.

We can use the FH lemma to formulate an approximate result that is quite useful. Consider a Hamiltonian where the  $\lambda$  dependence is as follows

$$H(\lambda) = H(0) + \lambda H_1 = H(0) + \Delta H. \quad (3.7)$$

Here we have identified  $\lambda H_1$  with a perturbation  $\Delta H$  of the Hamiltonian. Let now  $\psi(\lambda)$  be the normalized eigenstate with energy  $E(\lambda)$  for all  $\lambda$ . Now by FH

$$\frac{dE(\lambda)}{d\lambda} = \langle \psi(\lambda) | H_1 | \psi(\lambda) \rangle \quad (3.8)$$

and evaluating at  $\lambda = 0$  we get

$$\left. \frac{dE(\lambda)}{d\lambda} \right|_{\lambda=0} = \langle \psi(0) | H_1 | \psi(0) \rangle \quad (3.9)$$

We now note that for small  $\lambda$

$$E(\lambda) = E(0) + \lambda \left. \frac{dE(\lambda)}{d\lambda} \right|_{\lambda=0} + \mathcal{O}(\lambda^2) \quad (3.10)$$

which we write as

$$E(\lambda) - E(0) = \langle \psi(0) | \Delta H | \psi(0) \rangle + \mathcal{O}(\Delta H^2) \quad (3.11)$$

The left-hand side is the shift  $\Delta E$  in energy and is given, finally, to first order in the perturbation  $\Delta H$  by

$$\boxed{\Delta E = \langle \psi(0) | \Delta H | \psi(0) \rangle.} \quad (3.12)$$

This is the simplest and most important result in perturbation theory. To compute the energy shift of a state we must just compute the expectation value of the change  $\Delta H$  of the Hamiltonian in the *unperturbed* state.

The above result can be used without concern when we have a single non-degenerate state of the original Hamiltonian  $H_0$ . We will have the situation, however, where we have a set of *degenerate* eigenstates of the Hamiltonian  $H_0$  and we want to figure out what happens to them. One cannot use directly (3.12) since the derivation assumes that the state smoothly evolves into an eigenstate as

$\lambda$  changes. The problem is that the original states we chose may not remain eigenstates under the perturbation: only certain linear combinations of the original eigenstates become the perturbed energy eigenstates. One must first figure out which are those particular linear combinations and then we can apply (3.12) to any of *those* states.

## 4 Hyperfine splitting

## 5 Spin-Orbit coupling

### 5.1 The physical interaction

### 5.2 Complete set of observables

### 5.3 Level splitting

### 5.4 Computation of $1 \otimes \frac{1}{2}$

## 6 General aspects of addition of angular momentum

The key formula is

$$j_1 \otimes j_2 = (j_1 + j_2) \oplus (j_1 + j_2 - 1) \oplus \dots \oplus |j_1 - j_2|. \quad (6.13)$$

This must be viewed as an equality between vector spaces. Or perhaps, more explicitly, as a way to write the vector space on the left-hand as a direct sum of interesting invariant subspaces. The vector space on the left-hand side is the tensor product of the vector space associated with the multiplet  $j_1$  of  $\mathbf{J}_1$  and the vector space associated with the multiplet  $j_2$  of  $\mathbf{J}_2$ . On the right-hand side we have a collection of multiplets of the angular momentum sum  $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$ . Thus each term on the right-hand side is an invariant subspace of the total angular momentum  $\mathbf{J}$ . Since various invariant subspaces appear, the representation is called reducible.

## 7 Hydrogen atom and hidden symmetry

Let us review the hydrogen atom spectrum we wish to derive by algebraic methods. We have energy levels with energies  $E_n$ , where

$$E_n = -\frac{e^2}{2a_0} \frac{1}{n^2}, \quad n = 1, 2, \dots \quad (7.1)$$

For each value  $n$  we have the following  $\ell$  multiplets of angular momentum  $\mathbf{L}$ :

$$\ell = 0, 1, \dots, n - 1. \quad (7.2)$$

A simple computation shows that this gives a total of  $n^2$  states. So at each  $n$  have a space  $\mathcal{H}_n$  of degenerate energy eigenstates. This space has dimension  $n^2$  and can be written as the direct sum of angular momentum multiplets

$$\mathcal{H}_n = (\ell = n - 1) \oplus (\ell = n - 2) \oplus \dots \oplus (\ell = 0). \quad (7.3)$$

We begin our analysis by recalling the hydrogen Hamiltonian, which takes the form

$$H = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{r}. \quad (7.4)$$

There are conserved orbital angular momentum operators  $\mathbf{L}$ :

$$[H, \mathbf{L}] = 0, \quad \mathbf{L} \times \mathbf{L} = i\hbar\mathbf{L}. \quad (7.5)$$

This Runge-Lenz vector  $\mathbf{R}$  is defined to be:

$$\mathbf{R} \equiv \frac{1}{2me^2}(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}) - \frac{\mathbf{r}}{r}. \quad (7.6)$$

As written this operator is Hermitian. It is also conserved, as it too commutes with the Hamiltonian (this was a practice problem!)

$$[H, \mathbf{R}] = 0. \quad (7.7)$$

Two alternative rewritings of  $\mathbf{R}$  are possible when we use the identity

$$\mathbf{p} \times \mathbf{L} = -\mathbf{L} \times \mathbf{p} + 2i\hbar\mathbf{p}. \quad (7.8)$$

These are

$$\mathbf{R} = \frac{1}{me^2}(\mathbf{p} \times \mathbf{L} - i\hbar\mathbf{p}) - \frac{\mathbf{r}}{r} = \frac{1}{me^2}(-\mathbf{L} \times \mathbf{p} + i\hbar\mathbf{p}) - \frac{\mathbf{r}}{r}. \quad (7.9)$$

If  $\mathbf{R}$  and  $\mathbf{L}$  are conserved, all of their scalar products are conserved too since the Hamiltonian would commute with them using the derivation property of commutators. We are already familiar with the Casimir  $\mathbf{L}^2$  that in fact commutes with all  $\hat{L}_i$ . Let us consider now  $\mathbf{R}^2$ , which must be a conserved scalar. Its evaluation is a practice problem (homework) and gives

$$\mathbf{R}^2 = 1 + \frac{2H}{me^4}(\mathbf{L}^2 + \hbar^2). \quad (7.10)$$

Notice that  $H$ , which appears in the above right-hand side can be moved, if desired, to the right of the parenthesis, as it commutes with  $\mathbf{L}$ . The right-hand side is indeed a conserved scalar. We now look into  $\mathbf{R} \cdot \mathbf{L}$ , which must also be conserved. First recall that

$$\mathbf{r} \cdot \mathbf{L} = 0, \quad \mathbf{p} \cdot \mathbf{L} = 0. \quad (7.11)$$

Using these and the first equality in (7.9) we find

$$\mathbf{R} \cdot \mathbf{L} = \frac{1}{me^2}(\mathbf{p} \times \mathbf{L}) \cdot \mathbf{L}. \quad (7.12)$$

But we now notice that

$$(\mathbf{p} \times \mathbf{L}) \cdot \mathbf{L} = \epsilon_{ijk} p_j L_k L_i = p_j \epsilon_{jki} L_k L_i = p_j (\mathbf{L} \times \mathbf{L})_j = \mathbf{p} \cdot (i\hbar\mathbf{L}) = 0. \quad (7.13)$$

As a result, we have shown that

$$\boxed{\mathbf{R} \cdot \mathbf{L} = 0.} \quad (7.14)$$

This relation is manifest classically where  $\mathbf{R}$  lies along the major axis of the ellipse and  $\mathbf{L}$  is perpendicular to the plane of the ellipse.

We now consider the commutation relations. First recall the definition of a vector (operator) under rotations. For such vector  $\mathbf{v}$  with components  $\hat{v}_i$  we have

$$[L_i, \hat{v}_j] = i\hbar\epsilon_{ijk}\hat{v}_k. \quad (7.15)$$

This relation can be written using cross products. For this consider the  $i$ -th component of the following vector

$$\begin{aligned} (\mathbf{L} \times \mathbf{v} + \mathbf{v} \times \mathbf{L})_i &= \epsilon_{ijk}(L_j \hat{v}_k + \hat{v}_j L_k) \\ &= \epsilon_{ijk}(L_j \hat{v}_k - \hat{v}_k L_j) \\ &= \epsilon_{ijk}[L_j, \hat{v}_k] \\ &= \epsilon_{ijk} i\hbar\epsilon_{jkl}\hat{v}_l \\ &= \epsilon_{ijk}\epsilon_{ljk} i\hbar\hat{v}_l \\ &= 2\delta_{il} i\hbar\hat{v}_l = 2i\hbar\hat{v}_i, \end{aligned} \quad (7.16)$$

which shows that the condition that  $\mathbf{v}$  is a vector under rotations reads

$$\mathbf{L} \times \mathbf{v} + \mathbf{v} \times \mathbf{L} = 2i\hbar\mathbf{v}. \quad (7.17)$$

The Runge-Lenz vector  $\mathbf{R}$  is a vector under rotations. This we know without any computation, since it is built using cross products from  $\mathbf{p}$  and  $\mathbf{L}$ , which are both vectors under rotations. Therefore we must have

$$\mathbf{L} \times \mathbf{R} + \mathbf{R} \times \mathbf{L} = 2i\hbar\mathbf{R}. \quad (7.18)$$

We also record the index form of the statement:

$$[L_i, R_j] = i\hbar\epsilon_{ijk}R_k. \quad (7.19)$$

*Exercise.* Show that  $\mathbf{R} \cdot \mathbf{L} = \mathbf{L} \cdot \mathbf{R}$ .

In order to understand the commutator of two  $\mathbf{R}$  operators we need a simple result: The commutator of two conserved operators is a conserved operator. To prove this consider two conserved operator  $S_1$  and  $S_2$ :

$$[S_1, H] = [S_2, H] = 0. \quad (7.20)$$

The Jacobi identity applied to the operators  $S_1, S_2$ , and  $H$  reads:

$$[[S_1, S_2], H] + [[H, S_1], S_2] + [[S_2, H], S_1] = 0. \quad (7.21)$$

This gives

$$[[S_1, S_2], H] = [[S_1, H], S_2] - [[S_2, H], S_1]. \quad (7.22)$$

Each term on the right-hand side vanishes, the first by conservation of  $S_1$  and the second by conservation of  $S_2$ . It follows that

$$[[S_1, S_2], H] = 0, \quad (7.23)$$

which, as desired, states the conservation of the commutator  $[S_1, S_2]$ . This result is useful, for it tells us that the commutator  $[R_i, R_j]$  must be some conserved object. We can focus, equivalently, on the cross product of two  $\mathbf{R}$ 's which encodes the commutator. We must have

$$\mathbf{R} \times \mathbf{R} = (\dots) \text{ "conserved vector" }, \quad (7.24)$$

where the dots represent some conserved scalar. Since  $\mathbf{L}$  and  $\mathbf{R}$  are conserved vectors, the possible vectors on the right-hand side are  $\mathbf{L}$ ,  $\mathbf{R}$ , and  $\mathbf{L} \times \mathbf{R}$ . To narrow down the options we examine the behavior of various vectors under the parity transformation

$$\mathbf{r} \rightarrow -\mathbf{r}. \quad (7.25)$$

Under this transformation we must have

$$\mathbf{p} \rightarrow -\mathbf{p}, \quad \mathbf{L} \rightarrow \mathbf{L}, \quad \mathbf{R} \rightarrow -\mathbf{R}. \quad (7.26)$$

The first follows from the preservation of the commutators between  $\mathbf{r}$  and  $\mathbf{p}$ . The second from  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ , and the third from the expression for  $\mathbf{R}$  in terms of  $\mathbf{r}$ ,  $\mathbf{p}$ ,  $\mathbf{L}$ . Since the left-hand side of (7.24) does not change sign under the parity transformation, nor should the right-hand side. From our choices  $\mathbf{L}$ ,  $\mathbf{R}$ , and  $\mathbf{L} \times \mathbf{R}$ , we can only have  $\mathbf{L}$ . We must therefore have

$$\mathbf{R} \times \mathbf{R} = (\dots)\mathbf{L}, \quad (7.27)$$

where, again, the expression in parenthesis must be a conserved scalar. A calculation (that we don't show here) gives

$$\mathbf{R} \times \mathbf{R} = i\hbar \left( -\frac{2H}{m\epsilon^4} \right) \mathbf{L}. \quad (7.28)$$

This completes the determination of all commutators relevant to  $\mathbf{L}$  and  $\mathbf{R}$ .

Now we come to the main point. We will derive algebraically the full characterization of the subspaces of degenerate energy eigenstates. For this we will assume we have one such subspace  $\mathcal{H}_\nu$  at some energy  $E_\nu$ , where  $\nu$  is a parameter to be specified below. We will look at our operators in that subspace. In our operator relations (7.10) and (7.28) we are actually allowed to replace  $H$  by the energy  $E_\nu$ , given that  $H$ , which commutes with  $\mathbf{L}$ , can be brought to the right, to be directly in front of the states. We can therefore set  $H$  equal to the energy, that we write in the form

$$H = E_\nu = -\frac{m\epsilon^4}{2\hbar^2} \frac{1}{\nu^2}, \quad \nu \in \mathbb{R}. \quad (7.29)$$

Here  $\nu$  is a unit-free, real constant, to be determined. The rest of the factors, except for a convenient factor of two, provide the right units. Of course, we know that the correct answer for these energies

emerge if  $\nu$  is a positive integer. This, however, is something we will be able to derive. It follows from the above equation that we can set

$$-\frac{2H}{me^4} = \frac{1}{\hbar^2\nu^2}. \quad (7.30)$$

We can use this expression to simplify our key relations (7.28) and (7.10):

$$\begin{aligned} \mathbf{R} \times \mathbf{R} &= i\hbar \frac{1}{\hbar^2\nu^2} \mathbf{L}, \\ \mathbf{R}^2 &= 1 - \frac{1}{\hbar^2\nu^2} (\mathbf{L}^2 + \hbar^2). \end{aligned} \quad (7.31)$$

A little further rearrangements give:

$$\begin{aligned} (\hbar\nu\mathbf{R}) \times (\hbar\nu\mathbf{R}) &= i\hbar \mathbf{L}, \\ \mathbf{L}^2 + \hbar^2\nu^2\mathbf{R}^2 &= \hbar^2(\nu^2 - 1). \end{aligned} \quad (7.32)$$

These are clear and simple algebraic relations between our operators. The first one shows that  $\hbar\nu\mathbf{R}$  has the units of angular momentum and kind of behaves like one, except that the operator to the right is not  $\hbar\nu\mathbf{R}$  but rather  $\mathbf{L}$ .

Our next step is to show that with the help of  $\mathbf{L}$  and  $\mathbf{R}$  we can construct two independent, commuting algebras of angular momentum. Of course, it is clear that  $\mathbf{L}$  is an algebra of angular momentum. But, using suitable linear combinations of  $\mathbf{L}$  and  $\mathbf{R}$  we will obtain two such algebras. Indeed, define

$$\begin{aligned} \mathbf{J}_1 &\equiv \frac{1}{2}(\mathbf{L} + \hbar\nu\mathbf{R}), \\ \mathbf{J}_2 &\equiv \frac{1}{2}(\mathbf{L} - \hbar\nu\mathbf{R}). \end{aligned} \quad (7.33)$$

Of course, we can solve for  $\mathbf{L}$  and  $\hbar\nu\mathbf{R}$  in terms of  $\mathbf{J}_1$  and  $\mathbf{J}_2$ :

$$\begin{aligned} \mathbf{L} &= \mathbf{J}_1 + \mathbf{J}_2 \\ \hbar\nu\mathbf{R} &= \mathbf{J}_1 - \mathbf{J}_2. \end{aligned} \quad (7.34)$$

It is important to realize that  $\mathbf{L}$  is nothing but the sum of  $\mathbf{J}_1$  and  $\mathbf{J}_2$ . We now claim that the operators  $\mathbf{J}_1$  and  $\mathbf{J}_2$  commute with each other. This is quickly confirmed by direct computation:

$$\begin{aligned} [J_{1i}, J_{2j}] &= \frac{1}{4} [L_i + \hbar\nu R_i, L_j - \hbar\nu R_j] \\ &= \frac{1}{4} (i\hbar \epsilon_{ijk} L_k - \hbar\nu [L_i, R_j] - \hbar\nu [L_j, R_i] - i\hbar \epsilon_{ijk} L_k) = 0, \end{aligned} \quad (7.35)$$

where we noted that the first and last terms on the right-hand side cancel each other out, and the second and third terms also cancel each other out using (7.19). Now we want to show that  $\mathbf{J}_1$  and  $\mathbf{J}_2$  are indeed angular momenta. We check both operators at the same time using the notation  $\mathbf{J}_{1/2}$  with

the subscripts '1' and '2' going with the top and bottom signs, respectively, on the right-hand side:

$$\begin{aligned}
\mathbf{J}_{1/2} \times \mathbf{J}_{1/2} &= \frac{1}{4}(\mathbf{L} \pm \hbar\nu\mathbf{R}) \times (\mathbf{L} \pm \hbar\nu\mathbf{R}) \\
&= \frac{1}{4}(i\hbar\mathbf{L} + i\hbar\mathbf{L} \pm (\mathbf{L} \times \hbar\nu\mathbf{R} + \hbar\nu\mathbf{R} \times \mathbf{L})) \\
&= \frac{1}{4}(2i\hbar\mathbf{L} \pm 2i\hbar\hbar\nu\mathbf{R}) \\
&= i\hbar\frac{1}{2}(\mathbf{L} \pm \hbar\nu\mathbf{R}) = \mathbf{J}_{1/2}.
\end{aligned} \tag{7.36}$$

In the first step we used the first equation in (7.32) and in the second step (7.18). In summary, we have confirmed that  $\mathbf{J}_1$  and  $\mathbf{J}_2$  are indeed two commuting angular momentum operators:

$$\begin{aligned}
\mathbf{J}_1 \times \mathbf{J}_1 &= i\hbar\mathbf{J}_1, \\
\mathbf{J}_2 \times \mathbf{J}_2 &= i\hbar\mathbf{J}_2, \\
[\mathbf{J}_1, \mathbf{J}_2] &= 0.
\end{aligned} \tag{7.37}$$

The constraint  $\mathbf{R} \cdot \mathbf{L} = 0$  gives us crucial information on the angular momenta. Using (7.34) and the commutativity of  $\mathbf{J}_1$  with  $\mathbf{J}_2$  we find

$$(\mathbf{J}_1 + \mathbf{J}_2)(\mathbf{J}_1 - \mathbf{J}_2) = 0 \quad \rightarrow \quad \mathbf{J}_1^2 = \mathbf{J}_2^2. \tag{7.38}$$

Both angular momenta have the same 'magnitude' on the subspace  $\mathcal{H}_\nu$  of degenerate energy eigenstates. Let us look at  $\mathbf{J}_1^2$ . Again, using  $\mathbf{R} \cdot \mathbf{L} = 0$  and the second of (7.32), we find

$$\mathbf{J}_1^2 = \frac{1}{4}(\mathbf{L}^2 + \hbar^2\nu^2\mathbf{R}^2) = \frac{1}{4}\hbar^2(\nu^2 - 1). \tag{7.39}$$

Note that the energy parameter  $\nu$  controls the magnitude of  $\mathbf{J}_1^2$ . Since both  $\mathbf{J}_1$  and  $\mathbf{J}_2$  commute with the Hamiltonian, the degenerate subspace  $\mathcal{H}_\nu$  must furnish a representation of both of these angular momenta! Any such representation must be specified by some  $j_1$  and some  $j_2$ , but the equality  $\mathbf{J}_1^2 = \mathbf{J}_2^2$  implies  $j_1 = j_2 \equiv j$ . We thus have

$$\mathbf{J}_1^2 = \mathbf{J}_2^2 = \frac{1}{4}\hbar^2(\nu^2 - 1) = \hbar^2 j(j+1). \tag{7.40}$$

Since  $j$  is an angular momentum it is quantized:  $2j \in \mathbb{Z}$ . This means we got the quantization of the energy! Solving for  $\nu$  in terms of  $j$  we find

$$\nu^2 = 1 + 4j(j+1) = 4j^2 + 4j + 1 = (2j+1)^2 \quad \rightarrow \quad \nu = 2j+1. \tag{7.41}$$

Note that as anticipated, the energy is determined by the value of  $j$ . This shows that in fact each subspace  $\mathcal{H}_\nu$  of degenerate energy eigenstates cannot carry more than one value of  $j$ . As  $j$  runs over all possible values  $\nu$  takes all positive integer values and thus can be identified with the principal quantum number  $n$ :

$$\begin{aligned}
j &= 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \\
n \equiv \nu &= 2j+1 = 1, 2, 3, 4, \dots
\end{aligned} \tag{7.42}$$

We have therefore recovered exactly the quantization of the energy levels in the hydrogen atom! What is the structure of the degenerate subspace  $\mathcal{H}_n$ ? We already know that each state must be an eigenstate of  $\mathbf{J}_1$  with eigenvalue  $\hbar^2 j(j+1)$  and *at the same time* an eigenstate of  $\mathbf{J}_2$  with the same eigenvalue. Since the two angular momenta are independent, the states must live in a tensor product of the space that carries the representation  $j$  of  $\mathbf{J}_1$  with the space that carries the representation  $j$  of  $\mathbf{J}_2$ . Therefore  $\mathcal{H}_n$ , with  $n = 2j + 1$ , must be  $j \otimes j$  where the first  $j$  is the value of  $\mathbf{J}_1$  and the second  $j$  the value of  $\mathbf{J}_2$ . More explicitly, the degenerate subspace has the structure

$$\mathcal{H}_n = j \otimes j \quad \text{with basis states} \quad |j_1 = j; m_1\rangle \otimes |j_2 = j; m_2\rangle, \quad -j \leq m_1, m_2 \leq j. \quad (7.43)$$

Since  $m_1$  and  $m_2$  each take  $2j + 1$  values, the dimension of  $\mathcal{H}_n$  is  $(2j + 1)^2 = n^2$ . This is indeed, the expected number of states that we have at the energy level. As we are familiar, the tensor product breaks into a sum of representations of the sum of angular momenta. But the sum here is simply the conventional angular momentum  $\mathbf{L} = \mathbf{J}_1 + \mathbf{J}_2$ . Since we know that

$$j \otimes j = 2j \oplus 2j - 1 \oplus \dots \oplus 0, \quad (7.44)$$

the representations on the right-hand side are the  $\ell$  multiplets that arise. Thus the degenerate subspace is a direct sum of the  $\ell$  values

$$(\ell = 2j) \oplus (\ell = 2j - 1) \oplus \dots \oplus 0. \quad (7.45)$$

Recalling that  $2j + 1 = n$ , we have obtained

$$\mathcal{H}_n = (\ell = n - 1) \oplus (\ell = n - 2) \oplus \dots \oplus (\ell = 0). \quad (7.46)$$

This is exactly the familiar set of  $\ell$  multiplets at the degenerate subspace labeled by the principal quantum number  $n$ . Done!

We should emphasize that the above algebraic analysis characterizes for us the *possible* subspaces  $\mathcal{H}_n$  of degenerate energy eigenstates. These subspaces are labeled by the values of  $j$ , with  $j \geq 0$  and  $2j \in \mathbb{Z}$  and  $n = 2j + 1$ . This gives an infinite list  $\{0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \dots\}$  of possible values of  $j$ . The algebraic analysis alone *cannot* tell us which values of  $j$  in the above list are used by the hydrogen atom. In physics, however, it is often the case that whatever is possible is in fact compulsory! Thus, it is not all that surprising that all possible values of  $j$  actually appear in the hydrogen atom spectrum.

As the simplest non-trivial example of the structure of subspaces of degenerate energies consider  $j = \frac{1}{2}$  which gives us  $n = 2$ . We then have  $\mathcal{H}_2 = \frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$ , where the right-hand side are the triplet  $\ell = 1$  and the singlet  $\ell = 0$ . The uncoupled basis states are of the form  $|\frac{1}{2}, m_1\rangle \otimes |\frac{1}{2}, m_2\rangle$  and thus the four of them can be written briefly as  $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$ . The singlet and triplet are therefore

$$\ell = 1 : \begin{cases} |1, 1\rangle = |\uparrow\uparrow\rangle, \\ |1, 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \\ |1, -1\rangle = |\downarrow\downarrow\rangle \end{cases}, \quad \ell = 0 : \quad |0, 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \quad (7.47)$$

These are the four states of the  $n = 2$  energy level. Note that we have built them out of spin-one-half states, but there is nowhere in sight such spin-one-half. In the hydrogen atom spectrum we were trying to reproduce the electron and the proton are treated as spinless.

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8.05 Quantum Physics II

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