

- (a) Construct the Hamiltonian matrix for this system.
- (b) The electron starts out (at $t = 0$) in the spin-up state with respect to the x -axis [that is, $\chi(0) = \chi_+^{(x)}$]. Determine $\chi(t)$ at any subsequent time. *Beware:* This is a time-dependent Hamiltonian, so you cannot get $\chi(t)$ in the usual way from stationary states. Fortunately, in this case you can solve the time-dependent Schrödinger equation (Equation 4.162) directly.
- (c) Find the probability of getting $-\hbar/2$ if you measure S_x . *Answer:*

$$\sin^2 \left(\frac{\gamma B_0}{2\omega} \sin(\omega t) \right).$$

- (d) What is the minimum field (B_0) required to force a complete flip in S_x ?

4.4.3 Addition of Angular Momenta

Suppose now that we have *two* spin-1/2 particles—for example, the electron and the proton in the ground state³⁵ of hydrogen. Each can have spin up or spin down, so there are four possibilities in all³⁶:

$$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow, \quad [4.175]$$

where the first arrow refers to the electron and the second to the proton. *Question:* What is the *total* angular momentum of the atom? Let

$$\mathbf{S} \equiv \mathbf{S}^{(1)} + \mathbf{S}^{(2)}. \quad [4.176]$$

Each of the four composite states is an eigenstate of S_z —the z -components simply *add*

$$\begin{aligned} S_z \chi_1 \chi_2 &= (S_z^{(1)} + S_z^{(2)}) \chi_1 \chi_2 = (S_z^{(1)} \chi_1) \chi_2 + \chi_1 (S_z^{(2)} \chi_2) \\ &= (\hbar m_1 \chi_1) \chi_2 + \chi_1 (\hbar m_2 \chi_2) = \hbar(m_1 + m_2) \chi_1 \chi_2, \end{aligned}$$

[note that $\mathbf{S}^{(1)}$ acts only on χ_1 , and $\mathbf{S}^{(2)}$ acts only on χ_2]. So m (the quantum number for the composite system) is just $m_1 + m_2$:

$$\begin{aligned} \uparrow\uparrow: m &= 1; \\ \uparrow\downarrow: m &= 0; \\ \downarrow\uparrow: m &= 0; \\ \downarrow\downarrow: m &= -1. \end{aligned}$$

³⁵I put them in the ground state so there won't be any *orbital* angular momentum to worry about.

³⁶More precisely, each particle is in a *linear combination* of spin up and spin down, and the composite system is in a *linear combination* of the four states listed.

At first glance, this doesn't look right: m is supposed to advance in integer steps, from $-s$ to $+s$, so it appears that $s = 1$ —but there is an extra state with $m = 0$. One way to untangle this problem is to apply the lowering operator $S_- = S_-^{(1)} + S_-^{(2)}$ to the state $\uparrow\uparrow$, using Equation 4.143:

$$\begin{aligned} S_-(\uparrow\uparrow) &= (S_-^{(1)}\uparrow)\uparrow + \uparrow(S_-^{(2)}\uparrow) \\ &= (\hbar\downarrow)\uparrow + \uparrow(\hbar\downarrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow). \end{aligned}$$

Evidently the three states with $s = 1$ are (in the notation $|s\ m\rangle$):

$$\left\{ \begin{array}{l} |1\ 1\rangle = \uparrow\uparrow \\ |1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\ -1\rangle = \downarrow\downarrow \end{array} \right\} \quad s = 1 \text{ (triplet)}. \quad [4.177]$$

(As a check, try applying the lowering operator to $|1\ 0\rangle$; what *should* you get? See Problem 4.35.) This is called the **triplet** combination, for the obvious reason. Meanwhile, the orthogonal state with $m = 0$ carries $s = 0$:

$$\left\{ |0\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \right\} \quad s = 0 \text{ (singlet)}. \quad [4.178]$$

(If you apply the raising or lowering operator to this state, you'll get zero. See Problem 4.35.)

I claim, then, that the combination of two spin-1/2 particles can carry a total spin of 1 or 0, depending on whether they occupy the triplet or the singlet configuration. To confirm this, I need to prove that the triplet states are eigenvectors of S^2 with eigenvalue $2\hbar^2$ and the singlet is an eigenvector of S^2 with eigenvalue 0. Now

$$S^2 = (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) \cdot (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) = (S^{(1)})^2 + (S^{(2)})^2 + 2\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}. \quad [4.179]$$

Using Equations 4.142 and 4.145, we have

$$\begin{aligned} \mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}(\uparrow\downarrow) &= (S_x^{(1)}\uparrow)(S_x^{(2)}\downarrow) + (S_y^{(1)}\uparrow)(S_y^{(2)}\downarrow) + (S_z^{(1)}\uparrow)(S_z^{(2)}\downarrow) \\ &= \left(\frac{\hbar}{2}\downarrow\right)\left(\frac{\hbar}{2}\uparrow\right) + \left(\frac{i\hbar}{2}\downarrow\right)\left(\frac{-i\hbar}{2}\uparrow\right) + \left(\frac{\hbar}{2}\uparrow\right)\left(\frac{-\hbar}{2}\downarrow\right) \\ &= \frac{\hbar^2}{4}(2\downarrow\uparrow - \uparrow\downarrow). \end{aligned}$$

Similarly,

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}(\downarrow\uparrow) = \frac{\hbar^2}{4}(2\uparrow\downarrow - \downarrow\uparrow).$$

It follows that

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}|1\ 0\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}}(2\downarrow\uparrow - \uparrow\downarrow + 2\uparrow\downarrow - \downarrow\uparrow) = \frac{\hbar^2}{4}|1\ 0\rangle, \quad [4.180]$$

and

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}|00\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}}(2\downarrow\uparrow - \uparrow\downarrow - 2\uparrow\downarrow + \downarrow\uparrow) = -\frac{3\hbar^2}{4}|00\rangle. \quad [4.181]$$

Returning to Equation 4.179 (and again using Equation 4.142), we conclude that

$$S^2|10\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2\frac{\hbar^2}{4}\right)|10\rangle = 2\hbar^2|10\rangle, \quad [4.182]$$

so $|10\rangle$ is indeed an eigenstate of S^2 with eigenvalue $2\hbar^2$; and

$$S^2|00\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} - 2\frac{3\hbar^2}{4}\right)|00\rangle = 0, \quad [4.183]$$

so $|00\rangle$ is an eigenstate of S^2 with eigenvalue 0. (I will leave it for you to confirm that $|11\rangle$ and $|1-1\rangle$ are eigenstates of S^2 , with the appropriate eigenvalue—see Problem 4.35.)

What we have just done (combining spin 1/2 with spin 1/2 to get spin 1 and spin 0) is the simplest example of a larger problem: If you combine spin s_1 with spin s_2 , what total spins s can you get?³⁷ The answer³⁸ is that you get every spin from $(s_1 + s_2)$ down to $(s_1 - s_2)$ —or $(s_2 - s_1)$, if $s_2 > s_1$ —in integer steps:

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \dots, |s_1 - s_2|. \quad [4.184]$$

(Roughly speaking, the highest total spin occurs when the individual spins are aligned parallel to one another, and the lowest occurs when they are antiparallel.) For example, if you package together a particle of spin 3/2 with a particle of spin 2, you could get a total spin of 7/2, 5/2, 3/2, or 1/2, depending on the configuration. Another example: If a hydrogen atom is in the state ψ_{nlm} , the net angular momentum of the electron (spin plus orbital) is $l + 1/2$ or $l - 1/2$; if you now throw in the spin of the proton, the atom's total angular momentum quantum number is $l + 1$, l , or $l - 1$ (and l can be achieved in two distinct ways, depending on whether the electron alone is in the $l + 1/2$ configuration or the $l - 1/2$ configuration).

The particular state $|s\ m\rangle$ with total spin s and z -component m will be some linear combination of the composite states $|s_1\ m_1\rangle|s_2\ m_2\rangle$:

$$|s\ m\rangle = \sum_{m_1+m_2=m} C_{m_1 m_2 m}^{s_1 s_2 s} |s_1\ m_1\rangle|s_2\ m_2\rangle \quad [4.185]$$

(because the z -components add, the only composite states that contribute are those for which $m_1 + m_2 = m$). Equations 4.177 and 4.178 are special cases of this general

³⁷I say *spins* for simplicity, but either one (or both) could just as well be *orbital* angular momentum (for which, however, we would use the letter l).

³⁸For a proof you must look in a more advanced text; see, for instance, Claude Cohen-Tannoudji, Bernard Diu, and Franck Lalœ, *Quantum Mechanics* (New York: John Wiley & Sons, 1977), Vol. 2, Chapter X.

Table 4.7: Clebsch-Gordan coefficients. (A square root sign is understood for every entry; the minus sign, if present, goes *outside* the radical.)

form, with $s_1 = s_2 = 1/2$ (I used the informal notation $\uparrow = |\frac{1}{2} \frac{1}{2}\rangle$, $\downarrow = |\frac{1}{2} (-\frac{1}{2})\rangle$). The constants $C_{m_1 m_2 m}^{s_1 s_2 s}$ are called **Clebsch-Gordan coefficients**. A few of the simplest cases are listed in Table 4.7.³⁹ For example, the shaded column of the 2×1 table tells us that

$$|2 \ 1\rangle = \frac{1}{\sqrt{3}}|2 \ 2\rangle|1 \ -1\rangle + \frac{1}{\sqrt{6}}|2 \ 1\rangle|1 \ 0\rangle - \frac{1}{\sqrt{2}}|2 \ 0\rangle|1 \ 1\rangle.$$

In particular, if two particles (of spin 2 and spin 1) are at rest in a box, and the total spin is 2, and its z -component is 1, then a measurement of $S_z^{(1)}$ could return the value $2\hbar$ (with probability $1/3$), or \hbar (with probability $1/6$), or 0 (with probability $1/2$). Notice that the probabilities add up to 1 (the sum of the squares of any column on the Clebsch-Gordan table is 1).

These tables also work the other way around:

$$|s_1 \ m_1\rangle|s_2 \ m_2\rangle = \sum_s C_{m_1 m_2 m}^{s_1 s_2 s} |s \ m\rangle. \tag{4.186}$$

For example, the shaded row in the $3/2 \times 1$ table tells us that

$$|\frac{3}{2} \ \frac{1}{2}\rangle|1 \ 0\rangle = \sqrt{\frac{3}{5}}|\frac{5}{2} \ \frac{1}{2}\rangle + \sqrt{\frac{1}{15}}|\frac{3}{2} \ \frac{1}{2}\rangle - \sqrt{\frac{1}{3}}|\frac{1}{2} \ \frac{1}{2}\rangle.$$

³⁹The general formula is derived in Arno Bohm, *Quantum Mechanics: Foundations and Applications*, 2nd ed. (New York: Springer-Verlag, 1986), p. 172.

If you put particles of spin $3/2$ and spin 1 in the box, and you know that the first has $m_1 = 1/2$ and the second has $m_2 = 0$ (so m is necessarily $1/2$), and you measured the total spin s , you could get $5/2$ (with probability $3/5$), or $3/2$ (with probability $1/15$), or $1/2$ (with probability $1/3$). Again, the sum of the probabilities is 1 (the sum of the squares of each row on the Clebsch-Gordan table is 1).

If you think this is starting to sound like mystical numerology, I don't blame you. We will not be using the Clebsch-Gordan tables much in the rest of the book, but I wanted you to know where they fit into the scheme of things, in case you encounter them later on. In a mathematical sense this is all applied **group theory**—what we are talking about is the decomposition of the direct product of two irreducible representations of the rotation group into a direct sum of irreducible representations. (You can quote that to impress your friends.)

***Problem 4.35**

- (a) Apply S_- to $|1\ 0\rangle$ (Equation 4.177), and confirm that you get $\sqrt{2}\hbar|1\ -1\rangle$.
- (b) Apply S_{\pm} to $|0\ 0\rangle$ (Equation 4.178), and confirm that you get zero.
- (c) Show that $|1\ 1\rangle$ and $|1\ -1\rangle$ (Equation 4.177) are eigenstates of S^2 , with the appropriate eigenvalue.

Problem 4.36 Quarks carry spin $1/2$. Three quarks bind together to make a **baryon** (such as the proton or neutron); two quarks (or more precisely a quark and an antiquark) bind together to make a **meson** (such as the pion or the kaon). Assume the quarks are in the ground state (so the *orbital* angular momentum is zero).

- (a) What spins are possible for baryons?
- (b) What spins are possible for mesons?

Problem 4.37

- (a) A particle of spin 1 and a particle of spin 2 are at rest in a configuration such that the total spin is 3 , and its z -component is 1 (that is, the eigenvalue of S_z is \hbar). If you measured the z -component of the angular momentum of the spin- 2 particle, what values might you get, and what is the probability of each one?
- (b) An electron with spin down is in the state ψ_{510} of the hydrogen atom. If you could measure the total angular momentum squared of the electron alone (not including the proton spin), what values might you get, and what is the probability of each?

Problem 4.38 Determine the commutator of S^2 with $S_z^{(1)}$ (where $\mathbf{S} \equiv \mathbf{S}^{(1)} + \mathbf{S}^{(2)}$). Generalize your result to show that

$$[S^2, \mathbf{S}^{(1)}] = 2i\hbar(\mathbf{S}^{(1)} \times \mathbf{S}^{(2)}). \quad [4.187]$$

Note: Because $S_z^{(1)}$ does not commute with S^2 , we cannot hope to find states that are simultaneous eigenvectors of both. To form eigenstates of S^2 , we need linear combinations of eigenstates of $S_z^{(1)}$. This is precisely what the Clebsch-Gordan coefficients (in Equation 4.185) do for us. On the other hand, it follows by obvious inference from Equation 4.187 that the sum $\mathbf{S}^{(1)} + \mathbf{S}^{(2)}$ *does* commute with S^2 , which only confirms what we already knew (see Equation 4.103).

FURTHER PROBLEMS FOR CHAPTER 4

***Problem 4.39** Consider the **three-dimensional harmonic oscillator**, for which the potential is

$$V(r) = \frac{1}{2}m\omega^2 r^2. \quad [4.188]$$

(a) Show that separation of variables in Cartesian coordinates turns this into three one-dimensional oscillators, and exploit your knowledge of the latter to determine the allowed energies. *Answer:*

$$E_n = (n + 3/2)\hbar\omega. \quad [4.189]$$

(b) Determine the degeneracy $d(n)$ of E_n .

*****Problem 4.40** Because the three-dimensional harmonic oscillator potential (Equation 4.188) is spherically symmetric, the Schrödinger equation can be handled by separation of variables in *spherical* coordinates as well as Cartesian coordinates. Use the power series method to solve the radial equation. Find the recursion formula for the coefficients, and determine the allowed energies. Check your answer against Equation 4.189.

****Problem 4.41**

(a) Prove the **three-dimensional virial theorem**

$$2\langle T \rangle = \langle \mathbf{r} \cdot \nabla V \rangle \quad [4.190]$$

(for stationary states). *Hint:* Refer to Problem 3.53.

(b) Apply the virial theorem to the case of hydrogen, and show that

$$\langle T \rangle = -E_n; \quad \langle V \rangle = 2E_n. \quad [4.191]$$

(c) Apply the virial theorem to the three-dimensional harmonic oscillator (Problem 4.39), and show that in this case

$$\langle T \rangle = \langle V \rangle = E_n/2. \quad [4.192]$$
