

## Lecture 20, March 8, 2006

## Solved Homework

We determined that the two coefficients in our two-gaussian wave function were  $c_1 = 0.3221$  and  $c_2 = 0.7621$ . We also determined that

$$\left\langle \psi_{1s}(r, \theta, \phi; c_1, \alpha_1, c_2, \alpha_2) \left| -\frac{1}{2} \nabla^2 \right| \psi_{1s}(r, \theta, \phi; c_1, \alpha_1, c_2, \alpha_2) \right\rangle = 1.5c_1^2 + 0.6435c_1c_2 + 0.3c_2^2$$

Using the normalized coefficient values, we have  $\langle T \rangle = 0.4873$ . Since  $\langle H \rangle$  was  $-0.4819$ ,  $\langle V \rangle$  must be  $-0.9692$ . We could also simply plug the coefficients into

$$\left\langle \psi_{1s}(r, \theta, \phi; c_1, \alpha_1, c_2, \alpha_2) \left| -\frac{1}{r} \right| \psi_{1s}(r, \theta, \phi; c_1, \alpha_1, c_2, \alpha_2) \right\rangle = -1.5958c_1^2 - 1.5908c_1c_2 - 0.7136c_2^2$$

which is also (as it must be)  $-0.9692$ . If we take  $-2\langle T \rangle$  we have  $-0.9746$ . So, although the virial theorem is *almost* satisfied, it is not quite. The error is less than 1%.

Exact wave functions *must* satisfy the virial theorem, but that is *not* true of approximate wave functions. As such, one may examine the virial ratio to assess the quality of an approximate wave function. As one gets closer to the exact wave function, one should get closer to a ratio of  $-2$ .

## Antisymmetry

Consider a quantum mechanical system consisting of two indistinguishable particles, e.g., two electrons. If we wanted to compute the probability that we would find electron 1 in some volume of space characterized by  $r_a \leq r \leq r_b$ ,  $\theta_a \leq \theta \leq \theta_b$ , and  $\phi_a \leq \phi \leq \phi_b$ , and at the same time find electron 2 in some volume of space characterized by  $r_c \leq r \leq r_d$ ,  $\theta_c \leq \theta \leq \theta_d$ , and  $\phi_c \leq \phi \leq \phi_d$ , we would compute this probability as

$$P[V_1(1), V_2(2)] = \int_{r_a}^{r_b} \int_{\theta_a}^{\theta_b} \int_{\phi_a}^{\phi_b} \int_{r_c}^{r_d} \int_{\theta_c}^{\theta_d} \int_{\phi_c}^{\phi_d} |\Psi[\psi_1(1), \psi_2(2)]|^2 r_1^2 dr_1 \sin \theta_1 d\theta_1 d\phi_1 r_2^2 dr_2 \sin \theta_2 d\theta_2 d\phi_2 \quad (20-1)$$

where the cumbersome notation is meant to emphasize that the probability has to do with electron 1 being in volume 1 and electron 2 being in volume 2, that  $\Psi$  depends (in an unspecified way) on two individual electron wave functions  $\psi$ , the first of which is

occupied by electron 1 and the second by electron 2, and that the first set of integration coordinates corresponds to electron 1 and the second set to electron 2.

Now, since the electrons are indistinguishable, we are not permitted to really label them. Put differently, the probability of finding electron 2 in volume 1 and electron 1 in volume 2 must be the same as the probability we've already discussed up to this point (that is, there is a single probability of finding "an" electron in volume one and "another" electron in volume 2). We would write the second probability just mentioned as

$$P[V_1(2), V_2(1)] = \int_{r_a}^{r_b} \int_{\theta_a}^{\theta_b} \int_{\phi_a}^{\phi_b} \int_{r_c}^{r_d} \int_{\theta_c}^{\theta_d} \int_{\phi_c}^{\phi_d} |\Psi[\psi_2(1), \psi_1(2)]|^2 r_1^2 dr_1 \sin\theta_1 d\theta_1 d\phi_1 r_2^2 dr_2 \sin\theta_2 d\theta_2 d\phi_2 \quad (20-2)$$

where the change is simply that we have swapped the coordinates that we used to use for electron 1 to now be associated with electron 2 and vice versa. Given that the probabilities in eqs. 20-1 and 20-2 are equal, and given that both integrations are over the identical volumes (we left integration over the spin coordinates out for simplicity, but nothing changes if they are included), then it must be the case that

$$|\Psi[\psi_1(1), \psi_2(2)]|^2 = |\Psi[\psi_1(2), \psi_2(1)]|^2 \quad (20-3)$$

In the absence of vector fields we may write any wave function as a real wave function, which gives

$$\Psi^2[\psi_1(1), \psi_2(2)] = \Psi^2[\psi_1(2), \psi_2(1)] \quad (20-4)$$

There are two solutions to this equation, namely

$$\Psi[\psi_1(1), \psi_2(2)] = \pm \Psi[\psi_1(2), \psi_2(1)] \quad (20-5)$$

That is, it could either be the case that switching the coordinates for electron 1 and electron 2 has no effect on  $\Psi$  or it could be the case that switching the coordinates changes the sign of  $\Psi$ .

All particles in the universe fall into one of these two classes. Particles whose wave functions are unchanged by coordinate exchange are called "bosons" and their wave functions are said to be "symmetric". Bosons are particles having integer spin. Examples of such particles are photons and  $\alpha$  particles (helium-4 nuclei). By contrast, particles with half-integer spin have their wave functions *change* sign upon coordinate exchange; such particles are called "fermions" and their wave functions are said to be "antisymmetric". Examples of fermions are electrons, protons, and neutrons.

It was Wolfgang Pauli who first proposed that electrons should be characterized by antisymmetric wave functions. This postulate is now known as the "Pauli principle".

Many of you may have heard this principle put differently, namely as “No two electrons can be characterized by all identical quantum numbers.” While that statement is often found in textbooks as the Pauli principle, it is not actually the correct postulate. Rather (as we will see below) it *follows* from the postulate that electrons have antisymmetric wave functions.

If this all seems terribly abstract, let us take a simple example of a wave function for two particles. In particular, let’s imagine two particles described by wave functions  $a$  and  $b$ . How might we write a wave function for both at the same time? We might try

$$\Psi(1,2) = a(1)b(2) \quad (20-6)$$

but we run into an immediate problem, namely that if we swap the particles (that’s what it means to swap their coordinates, it means to put particle 1 where particle 2 used to be, and vice versa) we have

$$\Psi(2,1) = a(2)b(1) \quad (20-7)$$

and just looking at eqs. 20-6 and 20-7 makes it clear that  $\Psi(2,1)$  is neither equal to  $\Psi(1,2)$  nor to  $-\Psi(1,2)$ —it’s just different. However, we could fix things up a bit by taking as our starting wave function instead

$$\Psi(1,2) = a(1)b(2) + a(2)b(1) \quad (20-8)$$

Now when we swap indices we have

$$\Psi(2,1) = a(2)b(1) + a(1)b(2) \quad (20-9)$$

and, sure enough,  $\Psi(2,1) = \Psi(1,2)$  (stare at it if you don’t see it), so we have a symmetric wave function—one that would be suitable for a pair of bosons.

What about an antisymmetric wave function? Let’s try

$$\Psi(1,2) = a(1)b(2) - a(2)b(1) \quad (20-10)$$

Swapping indices gives

$$\Psi(2,1) = a(2)b(1) - a(1)b(2) \quad (20-11)$$

and, huzzah,  $\Psi(2,1) = -\Psi(1,2)$  (you might need another stare), so the  $\Psi(1,2)$  of eq. 20-10 is indeed antisymmetric, and would be suitable for a pair of electrons.

Note that if the two electrons in question shared *all* the same quantum numbers (e.g.,  $n$ ,  $l$ ,  $m_l$ , and  $m_s$  in a hydrogenic orbital) then orbitals  $a$  and  $b$  would be *identical*. In that case,  $a = b$  and we would write eq. 20-10 as

$$\begin{aligned}\Psi(1,2) &= a(1)a(2) - a(2)a(1) \\ &= 0\end{aligned}\tag{20-12}$$

I.e., the wave function vanishes if both electrons have all the same quantum numbers. As noted above, this is a *consequence* of assuming electrons must have antisymmetric wave functions, not a postulate of its own.

This permits us to explain something that you all know, but that we have not yet proven. In particular, we now see why we cannot place more than 2 electrons in any one hydrogenic orbital. Specifying a single hydrogenic orbital fixes all of the quantum numbers for the electron except  $m_s$ ; the latter quantum number can only take on two values,  $\pm 1/2$ , so only two electrons can be put into the orbital. Other important consequences of antisymmetry will come up later in the course.

As for bosons, we should pause for a moment to note that there appears to be no restriction at all on having as many bosons as one would like all be characterized by identical quantum numbers (eq. 20-8 does not vanish when  $a = b$ ). At low temperatures, bosons do indeed exhibit a “collapse” into a single so-called “coherent” state that is called a Bose-Einstein condensate. Such condensates are like macroscopic atoms and can have bizarre properties. A more everyday boson coherence is exhibited by light when it is in the form of laser light. Laser beams are beams of light in which all of the photons are quantum-mechanically identical and they can thus be tightly focused and used for many specialized purposes.

We will not, however, return to bosons again in this course. Spin is too interesting to give up on. Indeed, let’s look at it more closely.

## Spin Operators

At a superficial level, spin and orbital angular momentum ( $\mathbf{L}$ ) are very similar to one another for a single electron. One has the relationships that  $\mathbf{S}$  is a vector quantity with components  $S_x$ ,  $S_y$ , and  $S_z$ , that

$$S^2 = S_x^2 + S_y^2 + S_z^2\tag{20-13}$$

and the commutation relationships

$$\begin{aligned}[S_x, S_y] &= i\hbar S_z \\ [S_y, S_z] &= i\hbar S_x \\ [S_z, S_x] &= i\hbar S_y\end{aligned}\tag{20-14}$$

Remember that those commutation relationships are consistent with the observation of half-integer values for the quantum numbers for  $S_z$ . In addition, they prevent us from

knowing more than one component of  $\mathbf{S}$  at any one time. The  $x$  and  $y$  components are usually the ones taken to be uncertain, just as for  $\mathbf{L}$ .

The odd thing about spin is that it has no classical physical analog, so coming up with an actual operator for use in evaluating trial wave functions is a serious challenge. In essence, we go about this empirically, taking advantage of the simplicity of there being only two apparent eigenfunctions for  $S_z$  for a single electron, namely  $\alpha$  and  $\beta$  where

$$S_z\alpha = \frac{1}{2}\hbar\alpha \quad \text{and} \quad S_z\beta = -\frac{1}{2}\hbar\beta \quad (20-15)$$

Trial and error indicates that all of the above equations involving spin are satisfied if we make the following definitions using small matrices

$$\begin{aligned} \alpha &= \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \text{and} \quad \beta = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \\ S_x &= \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \text{and} \quad S_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \text{and} \quad S_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \end{aligned} \quad (20-16)$$

(Note that  $\alpha$  and  $\beta$  are normalized if you recall that the complex conjugate of a matrix is its adjoint.) Let's verify one of the above equations.

$$\begin{aligned} S_z\alpha &= \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \\ &= \frac{\hbar}{2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \\ &= \frac{1}{2}\hbar\alpha \end{aligned} \quad (20-17)$$

It's a simple matter to verify the corresponding equation for  $\beta$ . What about a commutator?

$$\begin{aligned} [S_x, S_y] &= \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} - \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ &= \frac{\hbar^2}{4} \left( \begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} - \begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix} \right) \\ &= \frac{\hbar^2}{4} \begin{bmatrix} 2i & 0 \\ 0 & -2i \end{bmatrix} \\ &= \frac{i\hbar^2}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \\ &= i\hbar S_z \end{aligned} \quad (20-18)$$

Let's try something different. What's the result of applying  $S_x$  to a given spin?

$$\begin{aligned}
 S_x \alpha &= \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \\
 &= \frac{\hbar}{2} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \\
 &= \frac{1}{2} \hbar \beta
 \end{aligned}
 \tag{20-19}$$

You should verify the below relationships for yourself

$$S_x \beta = \frac{1}{2} \hbar \alpha \quad S_y \alpha = \frac{1}{2} i \hbar \beta \quad S_y \beta = -\frac{1}{2} i \hbar \alpha \tag{20-20}$$

Finally, to compute  $S^2$ , we can use the same relationship that we worked out for angular momentum (since the commutation relationships are the same), namely that

$$S^2 = S_+ S_- + S_z^2 - \hbar S_z \tag{20-21}$$

(see eq. 11-18 of lecture notes for  $L$  and rearrange). Recalling, again by analogy, the definitions for the raising and lowering operators, we have

$$\begin{aligned}
 S_+ &= S_x + i S_y \\
 &= \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + \frac{i \hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \\
 &= \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}
 \end{aligned}
 \tag{20-22}$$

Similarly, we can show

$$S_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \tag{20-23}$$

So, we now can evaluate eq. 20-21 as

$$\begin{aligned}
S^2 &= \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} + \frac{\hbar^2}{4} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} - \frac{\hbar^2}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \\
&= \hbar^2 \left( \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} + \frac{1}{4} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} - \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) \\
&= \hbar^2 \begin{bmatrix} 1 + 1/4 - 1/2 & 0 + 0 + 0 \\ 0 + 0 + 0 & 0 + 1/4 + 1/2 \end{bmatrix} \\
&= \hbar^2 \begin{bmatrix} 3/4 & 0 \\ 0 & 3/4 \end{bmatrix} \\
&= \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}
\end{aligned} \tag{20-24}$$

Note that the matrix part of the operator is the unit matrix. Since multiplication by the unit matrix leaves any matrix unchanged, the  $\alpha$  and  $\beta$  matrices will indeed be eigenfunctions of  $S^2$ , and they will have eigenvalue  $3/4 \hbar^2$ , which is indeed  $s(s+1)$  given that  $s = 1/2 \hbar$ .

### Spin in Many-electron Systems

Hydrogenic orbitals are eigenfunctions of the angular momentum operators  $L^2$  and  $L_z$  because of the spherical symmetry of the atomic system. When we place more than one electron into an atomic system, it turns out that no individual electron's angular momentum is a conserved quantum number any longer, but the sum of all of the electrons' angular momenta is. There are complicated rules for assigning quantum numbers  $L$  and  $M_L$ , which are the many electron analogs of  $l$  and  $m_l$ . However, we are not going to spend any time on them. Instead of focusing on many electron atoms, we are going to go straight to molecules. As polyatomic molecules do not have spherical symmetry, there are almost never any orbital angular momentum quantum numbers to worry about.

Wave functions of molecules can, however, still be eigenfunctions of the many electron operators  $S^2$  and  $S_z$ . As such, we will look more closely at how to compute these quantities for many-electron cases. The many-electron operators are

$$\begin{aligned}
S_z(1,2,\dots,N) &= \sum_i^N S_z(i) \\
S(1,2,\dots,N) &= \sum_i^N S(i)
\end{aligned} \tag{20-25}$$

where the operators in the sums are the one-electron operators we have already discussed up to this point.  $S_z$  is thus very simple. Every term in the sum is either  $\hbar/2$  (for  $\alpha$

electrons) or negative  $\hbar/2$  (for  $\beta$  electrons). So, if there are an equal number of both, the many-electron  $S_z$  has an eigenvalue of zero. For every excess  $\alpha$  electron the eigenvalue increases by  $\hbar/2$ , while for every excess  $\beta$  electron the eigenvalue decreases by  $\hbar/2$ .

$S$ , on the other hand, involves a vector sum. So, when we consider the many-electron  $S^2$ , we have the dot product

$$\begin{aligned} S^2(1,2,\dots,N) &= \left[ \sum_i^N S(i) \right] \cdot \left[ \sum_j^N S(j) \right] \\ &= \sum_i^N S^2(i) + 2 \sum_{i<j}^N [S_x(i)S_x(j) + S_y(i)S_y(j) + S_z(i)S_z(j)] \end{aligned} \quad (20-26)$$

Evaluation of this operator can be somewhat more challenging.

In the end, the eigenvalue equation for the many-electron quantum number associated with  $S^2$  is

$$\begin{aligned} S^2(1,2,\dots,N)\Psi(1,2,\dots,N) &= S(S+1)\hbar^2\Psi(1,2,\dots,N) \\ S &= \frac{1}{2}, \frac{3}{2}, \dots, \frac{N}{2} \quad N \text{ odd} \\ S &= 0, 1, \dots, \frac{N}{2} \quad N \text{ even} \end{aligned} \quad (20-27)$$

where  $S$  in eq. 20-27 is the many-electron quantum number (what we've called  $s$  for one-electron systems) *not* the spin *operator*. One just has to be savvy to avoid confusion about when we mean the operator and when we mean the quantum number.

With respect to  $S_z$ , the eigenvalue equation is

$$\begin{aligned} S_z(1,2,\dots,N)\Psi(1,2,\dots,N) &= M_S\hbar\Psi(1,2,\dots,N) \\ M_S &= \sum_{i=1}^N m_s(i) \end{aligned} \quad (20-28)$$

For a given value of  $S$ , we also have that allowed values of  $M_S$  are given by

$$M_S = -S, -(S-1), \dots, (S-1), S \quad (20-29)$$

Thus, when  $S = 0$ , there is only one possible value for  $M_S$ , namely 0, and we call such a state a "singlet", because it is singly degenerate. When  $S = 1/2$ , the allowed values for  $M_S$  are  $-1/2$  and  $1/2$ , and we call such a state a "doublet" because, in the absence of a magnetic field, the two states are degenerate in energy. I.e., the level is doubly



degenerate. Recall that this was the situation for one-electron hydrogenic atoms. There is one electron, for which  $S = s = 1/2$ . Recall also that we indicated this doublet degeneracy by the left superscript in the term symbol (see Lecture 15). Now, when  $S = 1$  you should be able to see that there will be 3 allowed values for  $M_S$ , so we call this state a triplet, and so on through quartet, quintet, sextet, etc.

Next lecture, we will examine some many-electron wave functions more closely.

### Homework

To be solved in class:

Working with matrices, verify all of the relations in eq. 20-20 and also verify that

$$\begin{aligned} S_+ \alpha &= \mathbf{0} & S_+ \beta &= \hbar \alpha \\ S_- \alpha &= \hbar \beta & S_- \beta &= \mathbf{0} \end{aligned}$$

To be turned in for possible grading Mar. 11:

What are the normalized eigenfunctions and eigenvalues for  $S_x$  and  $S_y$ , respectively? (Hint: Since  $S_x$  and  $S_y$  operate on  $\alpha$  and  $\beta$  in a way that transforms them to constants times  $\beta$  and  $\alpha$ , respectively, it might be good to consider functions of the form  $a\alpha + b\beta$ , where  $a$  and  $b$  are coefficients chosen to ensure that the functions are eigenvalues and also that they are normalized.)