

Lecture 21, March 10, 2006

(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 514-518.)

Solved Homework

We already showed that $S_x\alpha = (\hbar/2)\beta$ (eq. 20-19) For the operation on β we have

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

Working with the S_y operator involves

$$\begin{aligned} S_y\alpha &= \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \\ &= \frac{\hbar}{2} \begin{bmatrix} 0 \\ i \end{bmatrix} \\ &= \frac{1}{2} i\hbar\beta \end{aligned}$$

and

$$\begin{aligned} S_y\beta &= \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \\ &= \frac{\hbar}{2} \begin{bmatrix} -i \\ 0 \end{bmatrix} \\ &= -\frac{1}{2} i\hbar\alpha \end{aligned}$$

For the raising operator we have

$$S_+\alpha = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \\ = \mathbf{0}$$

and

$$S_+\beta = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \\ = \hbar \begin{bmatrix} 1 \\ 0 \end{bmatrix} \\ = \hbar\alpha$$

Similarly

$$S_-\alpha = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \\ = \hbar \begin{bmatrix} 0 \\ 1 \end{bmatrix} \\ = \hbar\beta$$

and

$$S_-\beta = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \\ = \mathbf{0}$$

Spin-Free Many-Electron Wave Functions and Antisymmetry

We have already seen that if we have two electrons in two orbitals a and b , then an acceptable antisymmetric wave function is

$$\Psi(1,2) = a(1)b(2) - a(2)b(1) \quad (21-1)$$

Note that a different, but completely equivalent way to write this is

$$\Psi(1,2) = \begin{vmatrix} a(1) & b(1) \\ a(2) & b(2) \end{vmatrix} \quad (21-2)$$

If the orbitals a and b are orthonormal, let's consider what needs to be done to normalize Ψ . We have

$$\begin{aligned}
& \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi^*(1,2)\Psi(1,2)dr_1dr_2 = \\
& \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} a^*(1)b^*(2)a(1)b(2)dr_1dr_2 \\
& - \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} a^*(1)b^*(2)a(2)b(1)dr_1dr_2 \\
& - \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} a^*(2)b^*(1)a(1)b(2)dr_1dr_2 \\
& + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} a^*(2)b^*(1)a(2)b(1)dr_1dr_2
\end{aligned} \tag{21-3}$$

Since a and b are orthogonal, anytime we have an integral over the coordinates of either electron 1 or electron 2 (or both) that involves the product a^*b , it will be zero. On the other hand, since a and b are normalized, if the only products in the integrals are a^*a or b^*b , they will be equal to one. Thus, the value of eq. 21-3 is $1-0-0+1=2$.

So, the normalized form for eq 21-2 is

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1) & b(1) \\ a(2) & b(2) \end{vmatrix} \tag{21-4}$$

Now, consider a case of more than two electrons. We might make a determinant along the lines of

$$\Psi(1,2,\dots,N) = \begin{vmatrix} a(1) & b(1) & \dots & n(1) \\ a(2) & b(2) & \dots & n(2) \\ \vdots & \vdots & \ddots & \vdots \\ a(N) & b(N) & \dots & n(N) \end{vmatrix} \tag{21-5}$$

Note that swapping the coordinates of any two electrons is equivalent to swapping two rows in the determinant (e.g., we could switch rows 1 and 2 and the effect would be that, in every term in the determinant, electrons 1 and 2 would have been swapped). It is a known feature of determinants that when two rows are swapped, the value of the determinant changes sign. So, this satisfies antisymmetry perfectly.

As for normalization, a bit of thinking about the orthonormality of the orbitals should make it clear that, when we integrate $\Psi^*\Psi$, the only products between pairs of terms in the determinants that will not be zero will be the square moduli of each term with itself, and each one of those will be equal to one. As there are $N!$ terms in a $N \times N$ determinant, that means that an acceptable, normalized, antisymmetric, many-electron wave function can be

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} a(1) & b(1) & \cdots & n(1) \\ a(2) & b(2) & \cdots & n(2) \\ \vdots & \vdots & \ddots & \vdots \\ a(N) & b(N) & \cdots & n(N) \end{vmatrix} \quad (21-6)$$

where the elements of the determinant are themselves individual, orthonormal, one-electron orbitals ("orbital" is just another word for a one-electron wave function). This form for a many-electron wave function is called a "Slater determinant", after John C. Slater, who first proposed it.

Note that this is not the only way in which one can form properly antisymmetric many-electron wave functions. All sorts of mathematical functions can be designed that properly change sign when electronic coordinates are interchanged. The Slater determinant form, however, has the advantage that it connects with the chemist's intuition of electrons occupying individual, distinct orbitals. Other antisymmetric functions do not admit to such a simple decomposition, so while they can be useful, they are not very intuitive.

Because eq. 21-6 is somewhat cumbersome to write out, the usual notation is to represent the Slater determinant as a ket, i.e.,

$$\Psi(1,2,\dots,N) = |ab\cdots n\rangle \quad (21-7)$$

where the normalization constant is not written but is taken as implicit in the ket. You just have to remember that it is there.

Note that a wave function that is written as a product of orbitals (as is each *individual* term of the determinant) is called a "Hartree product". Hartree was a theoretical physicist who was very much aided by his father in his research. His father was a retired mariner who enjoyed doing long, complicated arithmetic calculations—a perfect collaborator in the early part of the 20th century before computers were available (or even adding machines, the latter being mechanical computing devices that preceded computers).

One sometimes refers to a Slater determinant as an antisymmetrized Hartree product, and one can even define an operator, called the antisymmetrizer, that converts a Hartree product into a Slater determinant. However, we will not explore this in any further detail.

Spin Orbitals

Our discussion above has ignored any explicit discussion of spin. Recall that our ad hoc way of dealing with spin (which has the virtue of usually being useful!) is to form a complete wave function simply by multiplication of a spatial wave function by a spin

eigenfunction (either α or β). When we are using such a wave function as one of several in a many-electron calculation, we call it a spin orbital. Of course, for any one spatial function (say, a 2s orbital) there are only two possible spin orbitals: the $2s\alpha$ and the $2s\beta$. A Slater determinant involving spin orbitals might appear as

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} a(1)\alpha(1) & a(1)\beta(1) & b(1)\alpha(1) & b(1)\beta(1) & \dots \\ a(2)\alpha(2) & a(2)\beta(2) & b(2)\alpha(2) & b(2)\beta(2) & \dots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ a(N)\alpha(N) & a(N)\beta(N) & b(N)\alpha(N) & b(N)\beta(N) & \dots \end{vmatrix} \quad (21-8)$$

where there are N electrons and, at least in eq. 21-8, the first 4 doubly occupy spatial orbitals a and b while the rest occupy other orbitals until they are used up. Note that there is no *requirement* that any orbital be doubly occupied, that's just the form of the example. If there were to be an odd number of electrons, obviously there would have to be at least one orbital that was *not* doubly occupied, and in general there can be many.

Let's look rather carefully at the situation of 2 electrons in 2 orbitals. There are 6 ways to make a Slater determinant for this situation. They are:

$$\begin{aligned} \Psi^{\text{I}}(1,2) &= \frac{1}{\sqrt{2!}} \begin{vmatrix} a(1)\alpha(1) & a(1)\beta(1) \\ a(2)\alpha(2) & a(2)\beta(2) \end{vmatrix} & \Psi^{\text{II}}(1,2) &= \frac{1}{\sqrt{2!}} \begin{vmatrix} b(1)\alpha(1) & b(1)\beta(1) \\ b(2)\alpha(2) & b(2)\beta(2) \end{vmatrix} \\ \Psi^{\text{III}}(1,2) &= \frac{1}{\sqrt{2!}} \begin{vmatrix} a(1)\alpha(1) & b(1)\alpha(1) \\ a(2)\alpha(2) & b(2)\alpha(2) \end{vmatrix} & \Psi^{\text{IV}}(1,2) &= \frac{1}{\sqrt{2!}} \begin{vmatrix} a(1)\beta(1) & b(1)\beta(1) \\ a(2)\beta(2) & b(2)\beta(2) \end{vmatrix} \\ \Psi^{\text{V}}(1,2) &= \frac{1}{\sqrt{2!}} \begin{vmatrix} a(1)\alpha(1) & b(1)\beta(1) \\ a(2)\alpha(2) & b(2)\beta(2) \end{vmatrix} & \Psi^{\text{VI}}(1,2) &= \frac{1}{\sqrt{2!}} \begin{vmatrix} a(1)\beta(1) & b(1)\alpha(1) \\ a(2)\beta(2) & b(2)\alpha(2) \end{vmatrix} \end{aligned} \quad (21-9)$$

where the superscripts I–VI are simply labeling for further discussion. If it isn't obvious that these six determinants are all possibilities (because they are complicated to look at) just think about possible Hartree products. We can have (I) both electrons in orbital a (only possibility is one α and one β), (II) both electrons in orbital b (again, only possibility is one α and one β), (III) one α electron in each spatial orbital, (IV) one β electron in each spatial orbital, (V) an α electron in a and a β electron in b , and (VI) vice versa, a β electron in a and an α electron in b .

As these are just 2×2 determinants, let's expand them so that they fit on one line. Then we have

$$\begin{aligned}
\Psi^{\text{I}}(1,2) &= \frac{1}{\sqrt{2!}} a(1)a(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\
\Psi^{\text{II}}(1,2) &= \frac{1}{\sqrt{2!}} b(1)b(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\
\Psi^{\text{III}}(1,2) &= \frac{1}{\sqrt{2!}} [a(1)b(2) - a(2)b(1)]\alpha(1)\alpha(2) \\
\Psi^{\text{IV}}(1,2) &= \frac{1}{\sqrt{2!}} [a(1)b(2) - a(2)b(1)]\beta(1)\beta(2) \\
\Psi^{\text{V}}(1,2) &= \frac{1}{\sqrt{2!}} [a(1)\alpha(1)b(2)\beta(2) - a(2)\alpha(2)b(1)\beta(1)] \\
\Psi^{\text{VI}}(1,2) &= \frac{1}{\sqrt{2!}} [a(1)\beta(1)b(2)\alpha(2) - a(2)\beta(2)b(1)\alpha(1)]
\end{aligned} \tag{21-10}$$

You might quickly verify that these are, as they must be, all properly antisymmetric.

Now, since we have two electrons, we know that there can only be two possibilities for wave functions that are eigenfunctions of the total spin operator S^2 . One possibility is that the spins of the two electrons add constructively to give a total S value of 1 h-bar (quantum number $S = 1$) and the other possibility is that they add destructively to give a total S value of 0 (quantum number $S = 0$). The expectation value of S^2 for an eigenfunction is $S(S + 1)$ h-bar squared, so in this case the two possibilities are 2 ($S = 1$) and 0 ($S = 0$).

Let us see which, if any, of the wave functions above are indeed proper eigenfunctions of S^2 . (We care about this because the “true” wave function will indeed be one spin state or another, so trial functions that fail to be are not necessarily useful for much.) We’ll start with wave function I and use Dirac notation to try to keep things moderately tractable. Recall that S^2 does not operate on the spatial parts of the wave functions, so integration over the spatial coordinates simply involves overlap integrals—these will be 1 or 0 depending on whether the integration for each electron involves only one orbital or both, respectively, assuming a and b are orthonormal. Thus, we have for wave function I

$$\begin{aligned}
\langle \Psi^{\text{I}} | S^2 | \Psi^{\text{I}} \rangle &= \frac{1}{2} \langle |a(1)|^2 |a(2)|^2 \rangle \langle [\alpha(1)\beta(2) - \alpha(2)\beta(1)] | S^2 [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \rangle \\
&= \frac{1}{2} \left[\langle \alpha(1)\beta(2) | S^2 | \alpha(1)\beta(2) \rangle - \langle \alpha(1)\beta(2) | S^2 | \alpha(2)\beta(1) \rangle \right. \\
&\quad \left. - \langle \alpha(2)\beta(1) | S^2 | \alpha(1)\beta(2) \rangle + \langle \alpha(2)\beta(1) | S^2 | \alpha(2)\beta(1) \rangle \right]
\end{aligned} \tag{21-11}$$

So, the spatial portion of this wave function integrates to 1 and we are left needing to evaluate S^2 operating on the functions $\alpha(1)\beta(2)$ and on $\alpha(2)\beta(1)$. Expressing many-electron S^2 according to eq. 20-26, we find for the first case (in a.u., to save writing \hbar again and again)

$$\begin{aligned}
S^2\alpha(1)\beta(2) &= S^2(1)\alpha(1)\beta(2) + S^2(2)\alpha(1)\beta(2) + 2S_x(1)S_x(2)\alpha(1)\beta(2) \\
&\quad + 2S_y(1)S_y(2)\alpha(1)\beta(2) + 2S_z(1)S_z(2)\alpha(1)\beta(2) \\
&= \frac{1}{2}\left(\frac{1}{2} + 1\right)\alpha(1)\beta(2) + \frac{1}{2}\left(\frac{1}{2} + 1\right)\alpha(1)\beta(2) + \frac{1}{2}\beta(1)\alpha(2) + \frac{1}{2}\beta(1)\alpha(2) \quad (21-12) \\
&\quad - \frac{1}{2}\alpha(1)\beta(2)
\end{aligned}$$

where we have evaluated the components of S using eqs. 20-15, 20-19, and 20-20. Similarly, for the second spin product we find

$$\begin{aligned}
S^2\alpha(2)\beta(1) &= \frac{1}{2}\left(\frac{1}{2} + 1\right)\alpha(2)\beta(1) + \frac{1}{2}\left(\frac{1}{2} + 1\right)\alpha(2)\beta(1) + \frac{1}{2}\beta(2)\alpha(1) + \frac{1}{2}\beta(2)\alpha(1) \\
&\quad - \frac{1}{2}\alpha(2)\beta(1) \quad (21-13)
\end{aligned}$$

When we plug these results back into the remaining integrals in eq. 21-11, we find for the first of the four in brackets

$$\begin{aligned}
\langle \alpha(1)\beta(2) | S^2 | \alpha(1)\beta(2) \rangle &= \int \alpha(1)\beta(2) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(1)\beta(2) d\omega(1)d\omega(2) \\
&\quad + \int \alpha(1)\beta(2) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(1)\beta(2) d\omega(1)d\omega(2) \\
&\quad + \int \alpha(1)\beta(2) \frac{1}{2} \beta(1)\alpha(2) d\omega(1)d\omega(2) \\
&\quad + \int \alpha(1)\beta(2) \frac{1}{2} \beta(1)\alpha(2) d\omega(1)d\omega(2) \quad (21-14) \\
&\quad - \int \alpha(1)\beta(2) \frac{1}{2} \alpha(1)\beta(2) d\omega(1)d\omega(2) \\
&= \frac{1}{2} \left(\frac{1}{2} + 1 \right) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) + 0 + 0 - \frac{1}{2} \\
&= 1
\end{aligned}$$

where the orthonormality of the α and β spin functions for each electronic spin coordinate ω permits the trivial evaluation of the individual integrals. Since the fourth integral on the r.h.s. of the last equality in eq. 21-11 differs only by assignment of the electron labels 1 and 2, it also must have a value of 1. By the same symmetry argument, the second and third integrals must be equal to one another. Evaluating the second using eq. 21-13 gives

$$\begin{aligned}
\langle \alpha(1)\beta(2) | S^2 | \alpha(2)\beta(1) \rangle &= \int \alpha(1)\beta(2) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(2)\beta(1) d\omega(1)d\omega(2) \\
&+ \int \alpha(1)\beta(2) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(2)\beta(1) d\omega(1)d\omega(2) \\
&+ \int \alpha(1)\beta(2) \frac{1}{2} \beta(2)\alpha(1) d\omega(1)d\omega(2) \\
&+ \int \alpha(1)\beta(2) \frac{1}{2} \beta(2)\alpha(1) d\omega(1)d\omega(2) \quad (21-15) \\
&- \int \alpha(1)\beta(2) \frac{1}{2} \alpha(2)\beta(1) d\omega(1)d\omega(2) \\
&= 0 + 0 + \frac{1}{2} + \frac{1}{2} - 0 \\
&= 1
\end{aligned}$$

Thus, the expectation value of S^2 from eq. 21-11 for wave function I is simply $1/2(1-1-1+1)=0$. A lot of work to get zero, no? Nevertheless, this wave function is, then, a proper eigenfunction of S^2 . Since S is zero, the only allowed value for M_S (the component of the total spin along the z axis) is also zero. The energy of this wave function is thus singly degenerate with respect to the z component of the spin, and hence we call this state a “singlet”. Singlet wave functions are indicated by a superscript one to the left of the wave function symbol, i.e., $^1\Psi^I$ (recall the superscript 2 we used for doublet hydrogenic wave functions). Moreover, this is a special case of a singlet that involves all orbitals being doubly filled with one α and one β electron each. Such a singlet state is called a “closed-shell singlet”.

If we consider wave function II, we see that it is different only in the sense that the doubly occupied orbital is b instead of a . Since S^2 only operates on the spin part of the wave function, and since the spin part of wave function II is the same as that in wave function I, it is evident that this state, too, is a closed-shell singlet.

Next lecture we will focus on the status of the remaining wave functions. The homework leads in that direction.

Homework

To be solved in class:

Evaluate $\langle \alpha(1)\alpha(2) | S^2 | \alpha(1)\alpha(2) \rangle$. Remember to use eq. 20-26 to expand the operator.

To be turned in for possible grading Mar. 24:

Evaluate $\langle \beta(1)\beta(2) | S^2 | \beta(1)\beta(2) \rangle$. Remember to use eq. 20-26 to expand the operator.