

Lecture 22, March 20, 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**

When we expand the two-electron  $S^2$  operator into its individual components, we have

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

Note how the terms deriving from  $S_x$  and  $S_y$  become zero since these operators transform the  $\alpha$  spin function to the  $\beta$  spin function, and an integration over  $\alpha(i)\beta(i)d\omega(i)$  gives zero owing to the orthogonality of the spin functions.

## More Spin Algebra

The final result derived in the homework above, 2, is a proper eigenvalue of  $S^2$  corresponding to  $S = 1$ . That means that  $\alpha(1)\alpha(2)$  is an eigenfunction of  $S^2$ . Since  $S = 1$ , it must be the case that  $M_S$  can equal  $-1$ ,  $0$ , or  $1$ . Recall that evaluation of  $M_S$  is straightforward. One simply adds one-half for each  $\alpha$  electron and subtracts one-half for each  $\beta$  electron. So, for the case of  $\alpha(1)\alpha(2)$ , we have  $M_S = 1$ . The other two cases,  $-1$  and  $0$ , will be degenerate in energy in the absence of a magnetic field, so this state is triply degenerate. Such states are called “triplet” states, and indicated by a superscript 3 to the left of the wave function.

Technically, we did not prove that the expectation value of  $S^2$  over the *full* wave function  $\Psi^{\text{III}}$  is 2, we only showed it for the spin part of the wave function. It is a trivial matter, however, to show that the spatial portion of the wave function is normalized (it’s obviously a  $2 \times 2$  determinant of orthonormal spatial functions preceded by the square root of 2!, so that’s that). So, we should indicate the triplet character of  $\Psi^{\text{III}}$  by writing  ${}^3\Psi^{\text{III}}$ .

Some quick consideration of the symmetric nature of the  $\beta(1)\beta(2)$  case should convince one that

$$\langle \beta(1)\beta(2) | S^2 | \beta(1)\beta(2) \rangle = 2 \quad (22-1)$$

and that this is the  $M_S = -1$  component of the triplet,  ${}^3\Psi^{\text{IV}}$  (the homework to prove this will also, no doubt, be convincing...)

We now turn to  $\Psi^{\text{V}}$ . Evaluation of  $S^2$  proceeds in the fashion to which we should, by now, be accustomed

$$\langle \Psi^{\text{V}} | S^2 | \Psi^{\text{V}} \rangle = \frac{1}{2} \left[ \begin{aligned} &\langle a(1)\alpha(1)b(2)\beta(2) | S^2 | a(1)\alpha(1)b(2)\beta(2) \rangle \\ &- \langle a(1)\alpha(1)b(2)\beta(2) | S^2 | a(2)\alpha(2)b(1)\beta(1) \rangle \\ &- \langle a(2)\alpha(2)b(1)\beta(1) | S^2 | a(1)\alpha(1)b(2)\beta(2) \rangle \\ &+ \langle a(2)\alpha(2)b(1)\beta(1) | S^2 | a(2)\alpha(2)b(1)\beta(1) \rangle \end{aligned} \right] \quad (22-2)$$

Note that the second and third integrals on the r.h.s. are zero because of the orthonormality of the spatial orbitals  $a$  and  $b$ , whose products appear over the same electronic coordinate in those integrals. The spatial functions integrate to one in the first and fourth integrals, and the remaining spin expectation values are just those of eqs. 21-14 and 21-15. Thus, the expectation value of eq. 22-2 is  $1/2(1 - 0 - 0 + 1) = 1$ . There is no integer value of  $S$  for which  $S(S + 1) = 1$ , so evidently  $\Psi^{\text{V}}$  is *not* an eigenfunction of

$S^2$ . Symmetry arguments should make it clear that the same result will hold for  $\Psi^{VI}$ ; it too has  $\langle S^2 \rangle = 1$  and is not an eigenfunction of the total spin squared operator.

Note that the expectation value of 1 is exactly the average of a singlet ( $\langle S^2 \rangle = 0$ ) and a triplet ( $\langle S^2 \rangle = 2$ ), so it might be what we expect for a wave function that is a 50:50 mixture of singlet and triplet. If both  $\Psi^V$  and  $\Psi^{VI}$  are equal mixtures of singlet and triplet wave functions, that suggests that taking linear combinations of the two (and renormalizing) might give us pure spin states.

Indeed, if we examine the sum of the two, we consider

$$\begin{aligned}\Psi^{V+VI} &= \frac{1}{\sqrt{2}}(\Psi^V + \Psi^{VI}) \\ &= \frac{1}{\sqrt{2}} \left\{ \begin{aligned} &\frac{1}{\sqrt{2}}[a(1)\alpha(1)b(2)\beta(2) - a(2)\alpha(2)b(1)\beta(1)] \\ &+ \frac{1}{\sqrt{2}}[a(1)\beta(1)b(2)\alpha(2) - a(2)\beta(2)b(1)\alpha(1)] \end{aligned} \right\} \quad (22-3) \\ &= \frac{1}{2}[a(1)b(2) - a(2)b(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)]\end{aligned}$$

After integration over the spatial coordinates (which gives 2 times  $(1/2)^2$ , or  $1/2$ ), we may evaluate the expectation value of  $S^2$  as

$$\begin{aligned}\langle \Psi^{V+VI} | S^2 | \Psi^{V+VI} \rangle &= \frac{1}{2} \left[ \begin{aligned} &\langle \alpha(1)\beta(2) | S^2 | \alpha(1)\beta(2) \rangle + \langle \alpha(1)\beta(2) | S^2 | \alpha(2)\beta(1) \rangle \\ &+ \langle \alpha(2)\beta(1) | S^2 | \alpha(1)\beta(2) \rangle + \langle \alpha(2)\beta(1) | S^2 | \alpha(2)\beta(1) \rangle \end{aligned} \right] \\ &= \frac{1}{2}(1 + 1 + 1 + 1) \quad (22-4) \\ &= 2\end{aligned}$$

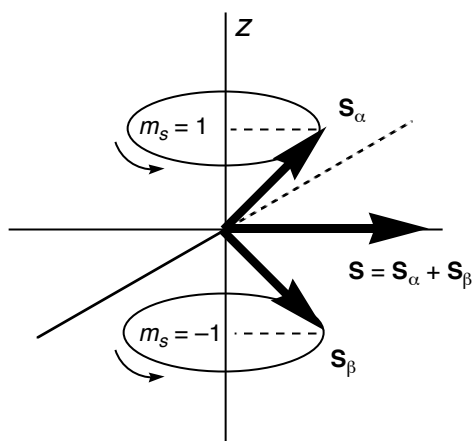
where the values of 1 for the spin integrals come from our prior evaluations (see eqs. 21-14 and 21-15).

So, the normalized sum of the two wave functions is indeed an eigenfunction of  $S^2$ . It is a triplet. The only component of the triplet left that we have not found is  $M_S = 0$ , and it would seem that eq. 22-3 is that wave function, since with one up and one down electron the expectation value of  $S_z$  will indeed be zero. If one likes a vector picture for this situation, it is as though the two electrons,  $\alpha$  and  $\beta$ , are precessing about the  $z$  axis in phase. One points up and one points down, so the net  $z$  component is zero, but the resultant vector has length square root 2, as it should for a triplet (see below figure).

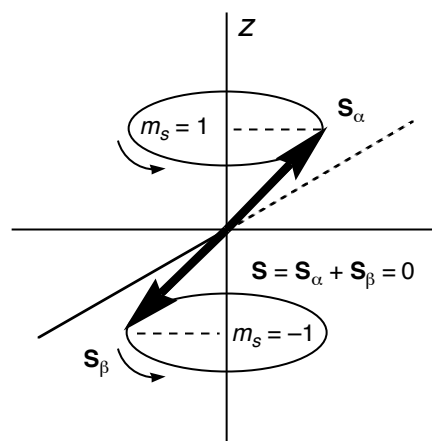
Now let's consider subtracting  $\Psi^{VI}$  from  $\Psi^V$ . That gives

$$\begin{aligned}
 \Psi^{V-VI} &= \frac{1}{\sqrt{2}} (\Psi^V - \Psi^{VI}) \\
 &= \frac{1}{\sqrt{2}} \left\{ \begin{aligned} &\frac{1}{\sqrt{2}} [a(1)\alpha(1)b(2)\beta(2) - a(2)\alpha(2)b(1)\beta(1)] \\ &-\frac{1}{\sqrt{2}} [a(1)\beta(1)b(2)\alpha(2) - a(2)\beta(2)b(1)\alpha(1)] \end{aligned} \right\} \quad (22-5) \\
 &= \frac{1}{2} [a(1)b(2) + a(2)b(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]
 \end{aligned}$$

We have previously evaluated  $\langle S^2 \rangle$  for the spin function in eq. 22-5. It is zero (see eq. 21-11 and subsequent discussion). So, this wave function is indeed a singlet spin eigenfunction. Note that two different orbitals are occupied, so one refers to this as an “open-shell” singlet to distinguish it from the closed-shell case, where all orbitals are completely filled. Returning to the geometric picture of spin, now we have two spin vectors pointing up and down but exactly out of phase with one another. In that case they completely cancel, and the total spin is indeed zero.



$\alpha$  and  $\beta$  electrons precessing in phase giving rise to resultant total spin squared of magnitude 2 (triplet)



$\alpha$  and  $\beta$  electrons precessing in opposite phase giving rise to resultant total spin squared of magnitude 0 (singlet)

### The Post-algebraic “Big Picture” of Two-electron Spin Functions

What were the key qualitative features of our two-electron wave functions? First, we found that all could be represented either as  $2 \times 2$  determinants or as linear combinations of  $2 \times 2$  determinants (thereby satisfying antisymmetry). It is a key observation that sometimes such linear combinations are required in order to form valid eigenfunctions of the total-spin-squared operator. The total number of wave functions

was 6, which is less than the limit of 10 that would arise from simple statistics of how many different ways to put two electrons that can be either of two spins in either of two orbitals—the reduction of 4 in possibilities is imposed by the Pauli exclusion principle, which prevents two electrons of the same spin from being in the same orbital (a consequence of antisymmetry, recall).

All determinants were eigenfunctions of  $S_z$ , with eigenvalues of either  $-1$ ,  $0$ , or  $1$ . The cases with eigenvalues of  $\pm 1$  must be triplets (since  $S$  must also be  $1$  in order for  $M_S$  to be allowed to take on the value of  $\pm 1$ ). The cases with eigenvalue  $0$  can be either singlets or the  $M_S = 0$  component of the triplet. The three triplet energies are degenerate in the absence of a magnetic field.

When one goes on to more spins than two, everything we've done up until now can be generalized, but as you might imagine, the spin algebra gets less pleasant for the most part. We will not plow through 3, 4, ... electrons. Rather, we will simply note that determinants analogous to those worked with above continue to be useful, either individually or in linear combinations, for the formation of simultaneous eigenfunctions of the Hamiltonian and the total spin squared operator.

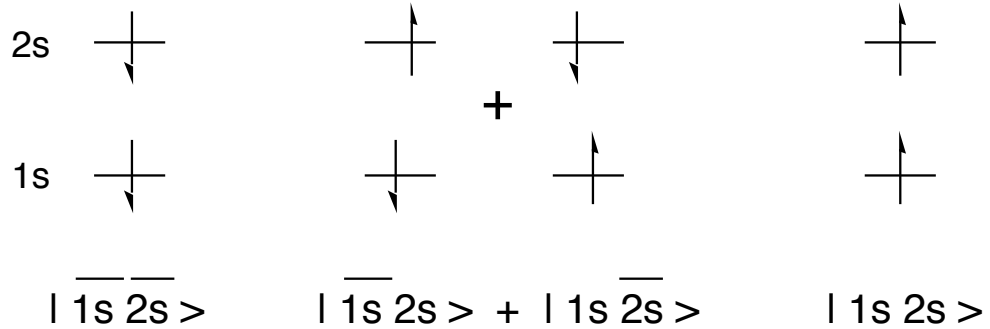
Of more interest, however, is the question of how the relative energies of these different spin states may be expected to compare. We will examine this question in the context of the helium atom.

## The Helium Atom

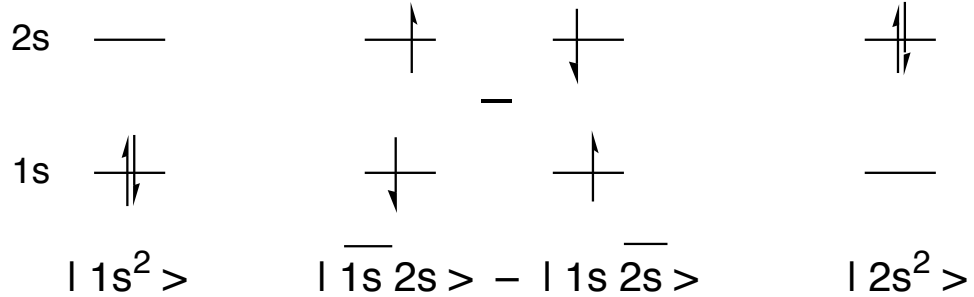
The He atom is a 2-electron system, so all our work above applies. Now, however, let's give actual names to the orbitals  $a$  and  $b$ . The low energy states of He will use the lowest energy orbitals, and the first two of these are the  $1s$  and  $2s$  orbitals (the  $2s$  will be lower than the  $2p$  set if the  $1s$  is occupied, since the electron in the  $1s$  will screen the nucleus from  $2p$  electrons (which have a node at the nucleus) more effectively than it does from  $2s$  electrons (which have non-zero amplitude at the nucleus). We could thus represent our 6 determinants outlined above as illustrated in the below figure.

Note that the figure shows the orbitals with  $1s$  below  $2s$  in recognition of the lower energy of the former compared to the latter. It shows the linear combinations required for the  $M_S = 0$  component of the triplet and the open-shell singlet, and it shows the shorthand notation one might use to represent these wave functions. A bar over an orbital means a  $\beta$  electron and no bar means an  $\alpha$  electron and a "squared" exponent means the orbital is occupied by one electron of each spin. The notation for the linear combinations is actually a bit more detailed than that usually employed. One usually writes only a single ket, and it is implicit that proper linear combinations will be employed to ensure a pure spin state if necessary (with the nature of the combination depending on the total spin desired).

### Triplets



### Singlets



As for the energies, it seems intuitively clear that the lowest energy state will be the  $|1s^2\rangle$  and the highest energy state the  $|2s^2\rangle$ , because these two states put both electrons in the lowest and highest energy orbitals, respectively. We know that the triplets are all the same energy (since they are degenerate in the absence of a magnetic field) but it is not obvious whether they are lower, higher, or equal to the energy of the open-shell singlet. Moreover, the quantitative differences are also not obvious.

Let us consider the energy of the ground state. If we evaluate it with the He Hamiltonian we have

$$\begin{aligned}
\langle 1s^2 | H | 1s^2 \rangle &= \langle 1s(1)1s(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)] | H | 1s(1)1s(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \rangle \\
&= \langle 1s(1)1s(2) | H | 1s(1)1s(2) \rangle \\
&= \left\langle 1s(1)1s(2) \left| -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right| 1s(1)1s(2) \right\rangle \\
&= \left\langle 1s(1) \left| -\frac{1}{2} \nabla_1^2 \right| 1s(1) \right\rangle + \left\langle 1s(1) \left| -\frac{2}{r_1} \right| 1s(1) \right\rangle \\
&\quad + \left\langle 1s(2) \left| -\frac{1}{2} \nabla_2^2 \right| 1s(2) \right\rangle + \left\langle 1s(2) \left| -\frac{2}{r_2} \right| 1s(2) \right\rangle \\
&\quad + \left\langle 1s(1)1s(2) \left| \frac{1}{r_{12}} \right| 1s(1)1s(2) \right\rangle \\
&= \varepsilon_{1s} + \varepsilon_{1s} + J_{1s1s}
\end{aligned} \tag{22-6}$$

Let's go through the steps in eq. 22-6 carefully. First, we expand our shorthand to the full blown determinant, except that we continue to regard normalization as implicit. Next, we insert the correct Hamiltonian for the He atom: kinetic energy of each electron, attraction of each electron to the nucleus (dependent on distance from the nucleus, defined as  $r_i$  where  $i$  tells which electron we are talking about), and the interelectronic repulsion (which depends on the distance between the electrons,  $r_{12}$ ). Since the Hamiltonian does not depend on spin, we can integrate out the spin coordinates (to one, since the singlet spin function is normalized) and be left with only spatial functions.

If we split this into 5 integrals, we can quickly see that most of those integrals only depend on the coordinates of *one* electron. In that case, integration over the coordinates of the other electron simply gives one (the 1s function is normalized), so we can drop it from the integrals. That is the simplification involved in the next to last equality. Finally, the energy of a single electron *all alone* in a 1s orbital is just the sum of its kinetic and potential energies,  $\varepsilon_{1s}$ , which we see appears twice (once for electron 1 and once for electron 2). The only remaining term is that for interelectronic repulsion. Such an integral is called a Coulomb integral, and it is usually abbreviated as  $J_{ab}$ , where  $a$  and  $b$  are the orbitals involved. Note that it is always non-negative (because the integral will end up as square modulus of one orbital (always non-negative) times square modulus of a second orbital (always non-negative) times inverse distance between integration coordinates (also always non-negative)).

Evaluation of the Coulomb integral is *not* particularly pleasant (it requires a careful transformation of coordinates). The value is, in the end 5/4 a.u. And, of course, we remember that the energy of a single electron in a 1s orbital is  $-Z^2/2$ , so for helium we have  $-2$ . Using this for  $\varepsilon_{1s}$ , the final value for our ground state He atom is  $(-2) + (-2) + (5/4) = -2.75$  a.u. (this is the value that was presented without derivation in lecture 18).

Entirely analogous work for the highest energy determinant  $|2s^2\rangle$  results in every term being divided by 4 (a  $1/n^2$  term where  $n$  is the principal quantum number). In that case, then, the energy is  $-0.6875$  a.u.

What about the triplet state? All three components have the same energy in the absence of a magnetic field, so it will suffice to compute the energy for any one. We determine for the  $M_S = 1$  state

$$\begin{aligned}
 \langle 1s2s|H|1s2s\rangle &= \langle [1s(1)2s(2) - 1s(2)2s(1)]\alpha(1)\alpha(2)|H|[1s(1)2s(2) - 1s(2)2s(1)]\alpha(1)\alpha(2)\rangle \\
 &= \langle [1s(1)2s(2) - 1s(2)2s(1)]|H|[1s(1)2s(2) - 1s(2)2s(1)]\rangle \\
 &= \frac{1}{2} \left[ \begin{aligned}
 &\left\langle 1s(1)\left|-\frac{1}{2}\nabla_1^2\right|1s(1)\right\rangle + \left\langle 1s(1)\left|-\frac{2}{r_1}\right|1s(1)\right\rangle \\
 &+ \left\langle 1s(2)\left|-\frac{1}{2}\nabla_2^2\right|1s(2)\right\rangle + \left\langle 1s(2)\left|-\frac{2}{r_2}\right|1s(2)\right\rangle \\
 &+ \left\langle 2s(1)\left|-\frac{1}{2}\nabla_1^2\right|2s(1)\right\rangle + \left\langle 2s(1)\left|-\frac{2}{r_1}\right|2s(1)\right\rangle \\
 &+ \left\langle 2s(2)\left|-\frac{1}{2}\nabla_2^2\right|2s(2)\right\rangle + \left\langle 2s(2)\left|-\frac{2}{r_2}\right|2s(2)\right\rangle \\
 &+ \left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)\right\rangle + \left\langle 1s(2)2s(1)\left|\frac{1}{r_{12}}\right|1s(2)2s(1)\right\rangle \\
 &- \left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|1s(2)2s(1)\right\rangle - \left\langle 1s(2)2s(1)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)\right\rangle
 \end{aligned} \right] \quad (22-7) \\
 &= \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} - K_{1s2s}
 \end{aligned}$$

Again, let's be crystal clear about steps. Step 1: insert the actual determinant with normalization implicit. Step 2: integrate over spin to arrive at a factor of one since spin is normalized. Step 3: Expand the Hamiltonian into its one-electron and two-electron terms. Since each one-electron term allows integration over the other electron's coordinates (to give one or zero) these integrals are simplified. Note, however, that because of the antisymmetric nature of the *spatial* wave function (for the singlets treated so far it's been the *spin* wave functions that were antisymmetric) there are 4 terms involving the  $1/r_{12}$  operator. Two of these terms we've seen before—they are Coulomb integrals—but one term is new. It is the integral involving the operator  $1/r_{12}$ , but now applied to an integral in which the indices of the electrons have been permuted over the spatial orbitals. The integral  $K$  is called an "exchange integral" (because the electronic coordinates are exchanged on either side of the operator). We've already established that  $\varepsilon_{1s}$  is  $-2$  a.u. and  $\varepsilon_{2s}$  is  $-0.5$  a.u.. Without going through the math, we'll accept that  $J_{1s2s}$  is  $0.420$  a.u. and  $K_{1s2s}$  is  $0.044$  a.u. In that case, the net energy of the triplet is  $-2.124$  a.u. (above the ground-state singlet, below the other closed shell singlet).



What about the open-shell singlet? It is left as tomorrow's homework that we have

$$\langle 1s2\bar{s} | H | 1s2\bar{s} \rangle = \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} + K_{1s2s} \quad (22-8)$$

in which case the energy of the open-shell singlet is higher than that of the triplet by  $2K_{1s2s}$  or 0.088 a.u. This difference is called the "singlet-triplet splitting". For a given pair of distinct orbitals  $a$  and  $b$ , the triplet will *always* be below the corresponding open-shell singlet unless the orbitals are so far apart in space that  $K_{ab}$  is zero, in which case the two states will be degenerate.

So, for the He atom, we have the ordering of energies

$${}^1|1s^2\rangle < {}^3|1s2s\rangle = {}^3|1s2\bar{s}\rangle = {}^3|1\bar{s}2\bar{s}\rangle < {}^1|1s2\bar{s}\rangle < {}^1|2s^2\rangle \quad (22-9)$$

If we compare our computed energy differences to experiment, we find that the ordering of eq. 22-9 is entirely correct, however, the quantitative predictions are not particularly good. That is because we failed to variationally optimize our wave functions, but that will not concern us here.

### Homework

To be solved in class:

Prove eq. 22-8 for the open-shell singlet.

To be turned in for possible grading Mar. 24:

Consider the fluorine atom. Its ground state is represented by the determinant  ${}^2|1s^2 2s^2 2p_x^2 2p_y^2 2p_z\rangle$ . Although fluorine is the most electronegative element, by applying a high enough voltage one can still strip an electron from it to generate  $F^+$ . If two electrons are always kept in the 1s orbital, what are all possible determinants that can be made by ionizing fluorine to  $F^+$ ? Put them in an energy ordering like that of eq. 22-9 and provide a short justification of your choice of order. Note that the F atom has spherical symmetry, so there is no difference between determinants that differ only in the labels  $x$ ,  $y$ , and  $z$  on the p orbitals (thus, for instance, there is no difference between  ${}^3|1s^2 2s^2 2p_x^2 2p_y^2 2p_z\rangle$  and  ${}^3|1s^2 2s^2 2p_x^2 2p_z^2 2p_y\rangle$ ). You can also ignore spin-orbit coupling.