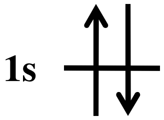
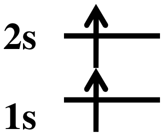
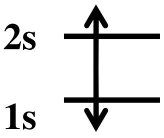
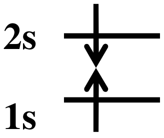
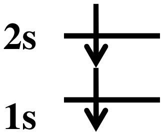
# TWO ELECTRONS: EXCITED STATES

In the last lecture, we learned that the independent particle model gives a reasonable description of the ground state energy of the Helium atom. Before moving on to talk about many-electron atoms, it is important to point out that we can describe many more properties of the system using the same type of approximation. By using the same independent particle prescription we can come up with wavefunctions for excited states and determine their energies, their dependence on electron spin, etc. by examining the wavefunctions themselves. That is to say, there is much we can determine from simply looking at $\Psi$ without doing any significant computation.

We will use the excited state 1s2s configuration of Helium as an example. For the ground state we had:

| | | $\Psi_{space}(\mathbf{r}_1,\mathbf{r}_2)$ | $\times$ | $\Psi_{spin}(\sigma_1,\sigma_2)$ |
|---|---|---|---|---|
|  | $\Rightarrow$ | $\psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)$ | | $\frac{1}{\sqrt{2}}\big(\alpha(\sigma_1)\beta(\sigma_2)-\beta(\sigma_1)\alpha(\sigma_2)\big)$ |

In constructing excited states it is useful to extend the stick diagrams we have used before to describe electronic configurations. Then there are four different configurations we can come up with:

| | $\Psi_{space}(\mathbf{r}_1,\mathbf{r}_2)$ | $\times$ | $\Psi_{spin}(\sigma_1,\sigma_2)$ |
|---|---|---|---|
|  | ? | | ? |
|  | ? | | ? |
|  | ? | | ? |
|  | ? | | ? |

Where the question marks indicate that we need to determine the space and spin wavefunctions that correspond to these stick diagrams. It is fairly easy to come up with a reasonable guess for each configuration. For example, in the first case we might write down a wavefunction like:

$$\psi_{1s\alpha}(\mathbf{r}_1\sigma_1)\psi_{2s\alpha}(\mathbf{r}_2\sigma_2)=\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\alpha(\sigma_1)\alpha(\sigma_2)$$

However, we immediately note that this wavefunction is not antisymmetric. We can perform the same trick as before to make an antisymmetric wavefunction out this:

$$\Rightarrow \tfrac{1}{\sqrt{2}}\Big(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\alpha(\sigma_1)\alpha(\sigma_2)-\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\alpha(\sigma_2)\alpha(\sigma_1)\Big)$$

$$\Rightarrow \underbrace{\tfrac{1}{\sqrt{2}}\Big(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)-\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\Big)}_{\Psi_{space}} \qquad \underbrace{\alpha(\sigma_1)\alpha(\sigma_2)}_{\Psi_{spin}}$$

Applying the same principle to the 1s↑2s↓ configuration gives us a bit of trouble:

$$\Rightarrow \tfrac{1}{\sqrt{2}}\Big(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\alpha(\sigma_1)\beta(\sigma_2)-\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\alpha(\sigma_2)\beta(\sigma_1)\Big)\neq\Psi_{space}\Psi_{spin}$$

Hence, the pure ↑↓ configuration can't be separated in terms of a space part and a spin part. We find a similar result for 1s↓2s↑:

$$\Rightarrow \tfrac{1}{\sqrt{2}}\Big(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\beta(\sigma_1)\alpha(\sigma_2)-\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\beta(\sigma_2)\alpha(\sigma_1)\Big)\neq\Psi_{space}\Psi_{spin}$$

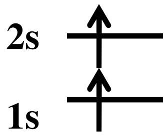
Since we know the wavefunction should separate, we have a problem. The solution comes in realizing that for an open shell configuration like this one, the 1s↑2s↓ and 1s↓2s↑ states are degenerate eigenstates and so we can make any linear combinations of them we like and we'll still obtain an eigenstate. If we make the "+" and "-" combinations of 1s↑2s↓ and 1s↓2s↑ we obtain:

$$\Rightarrow \big(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\alpha(\sigma_1)\beta(\sigma_2)-\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\alpha(\sigma_2)\beta(\sigma_1)\big)\pm$$
$$\big(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\beta(\sigma_1)\alpha(\sigma_2)-\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\beta(\sigma_2)\alpha(\sigma_1)\big)$$

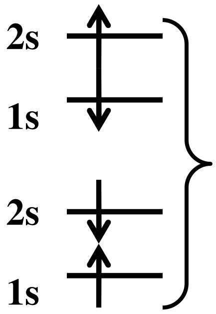
$$\Rightarrow \underbrace{\big(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\mp\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\big)}_{\Psi_{space}} \quad \underbrace{\big(\alpha(\sigma_1)\beta(\sigma_2)\pm\beta(\sigma_2)\alpha(\sigma_1)\big)}_{\Psi_{spin}}$$

which separates nicely. Performing similar manipulations for the ↓↓ configuration and taking care to make sure that all our spatial and spin wavefunctions are individually normalized allows us to complete the table we set out for the 1s2s excited states:

$$\Psi_{space}(\mathbf{r}_1,\mathbf{r}_2) \qquad \times \qquad \Psi_{spin}(\sigma_1,\sigma_2)$$



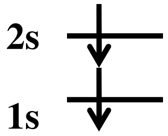
$$\Rightarrow \tfrac{1}{\sqrt{2}}\left(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)-\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\right) \qquad \times \qquad \alpha(\sigma_1)\alpha(\sigma_2)$$



$$\frac{1}{\sqrt{2}}\left(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)+\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\right)\times\frac{1}{\sqrt{2}}\left(\alpha(\sigma_1)\beta(\sigma_2)-\beta(\sigma_1)\alpha(\sigma_2)\right)$$

**and**

$$\frac{1}{\sqrt{2}}\left(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)-\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\right)\times\frac{1}{\sqrt{2}}\left(\alpha(\sigma_1)\beta(\sigma_2)+\beta(\sigma_1)\alpha(\sigma_2)\right)$$



$$\Rightarrow \tfrac{1}{\sqrt{2}}\left(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)-\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\right) \qquad \times \qquad \beta(\sigma_1)\beta(\sigma_2)$$

We notice several things about these wavefunctions:

- While the overall wavefunction is always antisymmetric by construction, the spatial part can be either antisymmetric (cases 1, 3 and 4) or symmetric (case 2). This effect is compensated for in the spin part, which can also be antisymmetric (case 2) or symmetric (cases 1,3 and 4). The resulting wavefunction always has a symmetric part times an antisymmetric part, resulting in an antisymmetric wavefunction.
- The spin part of Case 2 is exactly the same as the spin part of the ground state of the helium atom. Thus, just as we thought of the electrons in the ground state as being "paired", we say **the electrons in Case 2 are paired**.
- The spatial parts of three of the states above (cases 1,3 and 4) are the same. Case 2 has a different spatial part. Because the Hamiltonian only depends on spatial variables and not spin, we immediately conclude that 1,3 and 4 will be degenerate states – even when we take into account the electron-electron interaction. State 2, however, will generally have a different energy once we account for interactions. In common spectroscopic parlance the three degenerate states are called a **triplet** and the unique state is called a **singlet**. Further, because these states arise from degenerate spin states, they are called singlet and triplet spin states.

### Energies of Singlet and Triplet States

As we showed above, we expect the singlet and triplet states to have different energies once electron repulsion is taken into account. Which one will be lower? To decide this, we note that the triplet spatial wavefunction is zero when the two electrons are at the same position:

$$\mathbf{r}_1 = \mathbf{r}_2 \Rightarrow \Psi_T = \frac{1}{\sqrt{2}}\left(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_1) - \psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_1)\right) = 0$$

whereas the singlet wavefunction is non-zero:

$$\mathbf{r}_1 = \mathbf{r}_2 \Rightarrow \Psi_S = \frac{1}{\sqrt{2}}\left(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_1) + \psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_1)\right) = \sqrt{2}\ \psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_1) \neq 0$$

Because the electrons repel each other more when they are close to one another, we therefore expect the singlet to have more electron-electron repulsion and a higher energy. This rule turns out to hold quite generally and is called Hund's rule: **for degenerate non-interacting states, the configuration with highest spin multiplicity lies lowest in energy**. Hund actually has three rules (of which this is the first) concerning the ordering of degenerate non-interacting states. The others apply only to atoms and will not be discussed here, but see McQuarrie Section 9.11-9.12 for more on this topic.

So we expect the triplet to be lower. How much lower? To answer this question, we have to compute the average energies of the singlet and triplet wavefunctions. Recall that the spin part never matters for the energy:

$$\int \Psi^* \hat{H} \Psi d\mathbf{r} d\sigma = \int \Psi_{space}{}^* \Psi_{spin}{}^* \hat{H} \Psi_{space} \Psi_{spin} d\mathbf{r} d\sigma = \underbrace{\int \Psi_{spin}{}^* \Psi_{spin} d\sigma}_{\mathbf{1}} \int \Psi_{space}{}^* \hat{H} \Psi_{space} d\mathbf{r}$$
$$= \int \Psi_{space}{}^* \hat{H} \Psi_{space} d\mathbf{r}$$

The influence of the spin wavefunction is only indirect: if the spin part is antisymmetric (e.g. singlet) then the spatial part must be symmetric and *vice versa.* To simplify our algebra, it is convenient to create the obvious shorthand notation:

$$\Psi_T = \tfrac{1}{\sqrt{2}}\left(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) - \psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\right) \equiv \tfrac{1}{\sqrt{2}}(1s2s - 2s1s)$$
$$\Psi_S = \tfrac{1}{\sqrt{2}}\left(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) + \psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\right) \equiv \tfrac{1}{\sqrt{2}}(1s2s + 2s1s)$$

where we just need to remember that the first function in a product will be the one that has electron "1" while the second will have electron "2". Proceeding then:

$$E_{S/T} = \int \Psi_{S/T}^{*} \hat{H} \Psi_{S/T} d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{2}\int \left(1s2s \pm 2s1s\right)\left(\hat{H}_1 + \hat{H}_2 + \frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\right)\left(1s2s \pm 2s1s\right) d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \frac{1}{2}\int \left(1s2s \pm 2s1s\right)\left(-2 - \frac{1}{2} + \frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\right)\left(1s2s \pm 2s1s\right) d\mathbf{r}_1 d\mathbf{r}_2$$

$$= -\frac{5}{2} + \frac{1}{2}\int \left(1s2s \pm 2s1s\right)\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\left(1s2s \pm 2s1s\right) d\mathbf{r}_1 d\mathbf{r}_2$$

On the second line, we have used the fact that both $\Psi_S$ and $\Psi_T$ are eigenstates of the independent particle Hamiltonian (by construction) and on the third line, we have taken the independent particle energy outside the integral because $\Psi_S$ and $\Psi_T$ are normalized. Thus, we see that the average energy takes on the familiar form of (noninteracting energy)+(interactions). The interaction term can be simplified further:

$$\frac{1}{2}\int \left(1s2s \pm 2s1s\right)\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\left(1s2s \pm 2s1s\right) d\mathbf{r}_1 d\mathbf{r}_2$$

$$\Rightarrow \frac{1}{2}\int 1s2s\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}1s2s - 1s2s\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}2s1s - 2s1s\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}1s2s + 2s1s\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}2s1s \; d\mathbf{r}_1 d\mathbf{r}_2$$

We note that the first and last terms are the same if we just interchange the dummy integration variables:

$$\int 1s\left(\mathbf{r}_1\right)2s\left(\mathbf{r}_2\right)\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}1s\left(\mathbf{r}_1\right)2s\left(\mathbf{r}_2\right)d\mathbf{r}_1 d\mathbf{r}_2 \xrightarrow{1\leftrightarrow 2} \int 1s\left(\mathbf{r}_2\right)2s\left(\mathbf{r}_1\right)\frac{1}{\left|\mathbf{r}_2 - \mathbf{r}_1\right|}1s\left(\mathbf{r}_2\right)2s\left(\mathbf{r}_1\right)d\mathbf{r}_2 d\mathbf{r}_1$$

$$= \int 2s\left(\mathbf{r}_1\right)1s\left(\mathbf{r}_2\right)\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}2s\left(\mathbf{r}_1\right)1s\left(\mathbf{r}_2\right)d\mathbf{r}_1 d\mathbf{r}_2 \equiv J_{12}$$

Meanwhile the second and third terms are also the same:

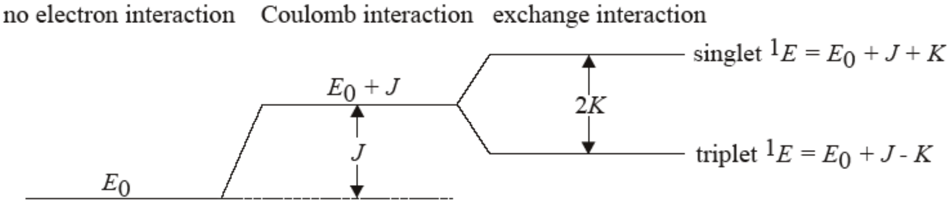
$$\int 1s\left(\mathbf{r}_1\right)2s\left(\mathbf{r}_2\right)\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}2s\left(\mathbf{r}_1\right)1s\left(\mathbf{r}_2\right)d\mathbf{r}_1 d\mathbf{r}_2 \xrightarrow{1\leftrightarrow 2} \int 1s\left(\mathbf{r}_2\right)2s\left(\mathbf{r}_1\right)\frac{1}{\left|\mathbf{r}_2 - \mathbf{r}_1\right|}2s\left(\mathbf{r}_2\right)1s\left(\mathbf{r}_1\right)d\mathbf{r}_2 d\mathbf{r}_1$$

$$= \int 2s\left(\mathbf{r}_1\right)1s\left(\mathbf{r}_2\right)\frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}1s\left(\mathbf{r}_2\right)2s\left(\mathbf{r}_1\right)d\mathbf{r}_1 d\mathbf{r}_2 \equiv K_{12}$$

These integrals are called **Coulomb**(J) and **exchange**(K) integrals, respectively. Both are positive numbers (because they arise from electron *repulsion*) and it can be rigorously proved that J>K always (i.e. no matter what functional form the 1s and 2s wavefunctions have). Thus, in terms of J and K the energies of the singlet and triplet states become:

$$E_{S/T} = -\frac{5}{2} + J_{12} \pm K_{12}$$

Thus we see that, as expected, the **singlet state is higher in energy than the triplet**. In fact, we can even give a numerical estimate for the splitting by evaluating $K_{12}$. Plugging in the forms of the 1s and 2s orbitals of helium and doing the integrals, we obtain $K_{12}$=32/729=1.2 eV and a splitting of 2$K_{12}$=2.4 eV. The latter is quite a bit larger than the experimental singlet-triplet splitting in helium, which comes out to only .8 eV. Once again, we see the independent particle model gives us a qualitatively correct picture (i.e. the sign of the splitting is correct and of the right order of magnitude) but we fail to obtain quantitative results. We therefore arrive at the following qualitative picture of the 1s2s excited state of Helium:



Helium 1s2s configuration energy: singlet and triplet states

It is interesting to note that the exchange interaction results from the fact that the electrons are indistinguishable. Notice that, if we had not antisymmetrized our wavefunctions, the spatial part would have just been a direct product 1s2s instead of the symmetric/antisymmetric 1s2s±2s1s combinations we obtained for the singlet and triplet. In the former case, the electrons are being treated as distinguishable (e.g. electron "1" is always 1s while electron "2" is always 2s) and the exchange term disappears from the interaction:

$$\frac{1}{2}\int(1s2s \pm 2s1s)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}(1s2s \pm 2s1s)\,d\mathbf{r}_1 d\mathbf{r}_2 \xrightarrow{\textit{distinguishable}} \int 1s2s\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}1s2s d\mathbf{r}_1 d\mathbf{r}_2 = J_{12}$$

Clearly exchange – which arises from the cross terms on the left – is absent on the right. Thus, the *K* integrals only arise when we have terms in the wavefunction where two electrons have exchanged places. Hence the name "exchange." It is important to note that, next to the Pauli exclusion principle, this is the biggest impact that antisymmetry has on chemistry.

There was a lot of interest in class about how we reconcile the fact that, in other chemistry courses you've been taught that there are only two spin states for a pair of electrons: ↑↓ and ↑↑. The former represented the singlet state and the latter the triplet state. You referred to the singlet electrons as being "paired" and the triplets as being "unpaired." However, how do these strange spin states we've derived connect with the "paired" and "unpaired" ideas? To answer this question, we first of all we should note that neither of the antiparallel states we've derived is strictly ↑↓. Instead, they look like ↑↓±↓↑, with ↑↓-↓↑ being the singlet and ↑↓+↓↑ being part of the triplet. The idea that the singlet state is ↑↓ is a white lie that we tell in order to simplify our arguments: as long as the subtle difference between ↑↓ and ↑↓-↓↑ isn't important, we can get away with explaining much (though not all) chemistry by treating the singlet state as ↑↓.

In the more precise picture we've derived here, it the **spin part of the wavefunction determines whether the electrons are paired or not**. An electron pair has the characteristic spin part $\alpha\beta-\beta\alpha$. That is to say, paired electrons form a singlet. Spin parts that look like $\alpha\alpha$, $\alpha\beta+\beta\alpha$, or $\beta\beta$ are unpaired triplet configurations. As we have seen above, **pairing two electrons raises the energy through the exchange integral**. In some situations, this is called the "pairing energy." The counterintuitive thing that we have to re-learn is that $\alpha\beta+\beta\alpha$ does **not** describe an electron pair. In every way it behaves like $\alpha\alpha$ or $\beta\beta$: the energies are the same and (as you will show on the homework) the eigenvalues of $\hat{S}^2_{total}$ are the same. This idea really does not fit into the simple qualitative picture of triplet states being ↑↑, but it is nonetheless true.

The fact that there are three elements of the triplet state is not a coincidence. As you will show, the eigenvalues of $\hat{S}^2_{total}$ for the triplet states are all $2\hbar^2$, which is consistent with a total spin of $S$=1, because the eigenvalues of $\hat{S}^2_{total}$ would then be $\hbar^2 S(S+1)=2\hbar^2$. This picture is also consistent with the idea that, if we add two spins with $s=\frac{1}{2}$ parallel to one another we should get a total $S$ of $S=\frac{1}{2}+\frac{1}{2}=1$. Given this picture, we note that the three triplet states would then correspond to the three possible z-projections of spin. That is to say the three triplet states should have $M_S$=+1,0 and-1, respectively. This gives us at least some qualitative picture of what the $\alpha\beta+\beta\alpha$ state means and why it corresponds to unpaired electrons. In the $\alpha\beta+\beta\alpha$ state the spins are oriented parallel to each other, but they are both oriented perpendicular to the z axis, so that on average you will always find one spin-up and one spin-down along z. This is a very simple example of the **addition of angular momentum**, a topic which is covered in much greater depth in McQuarrie.