

Helium Spectrum

Let's start by reminding ourselves of where we got to at the end of last term:

1. We used the Variational Principle to estimate the ionization energy. Using a wavefunction of the form

$$\psi = N e^{-Z_{eff} r_1/a} e^{-Z_{eff} r_2/a}$$

we were successful in getting close to the experimental value (and $Z_{eff} = 2 - 5/16$)

↑ nuclear charge ↑ effect of screening

This strongly suggests that the ground state is indeed one with both electrons in $l=0$ states, and with identical radial probability density. They are indeed behaving like identical particles in this picture.

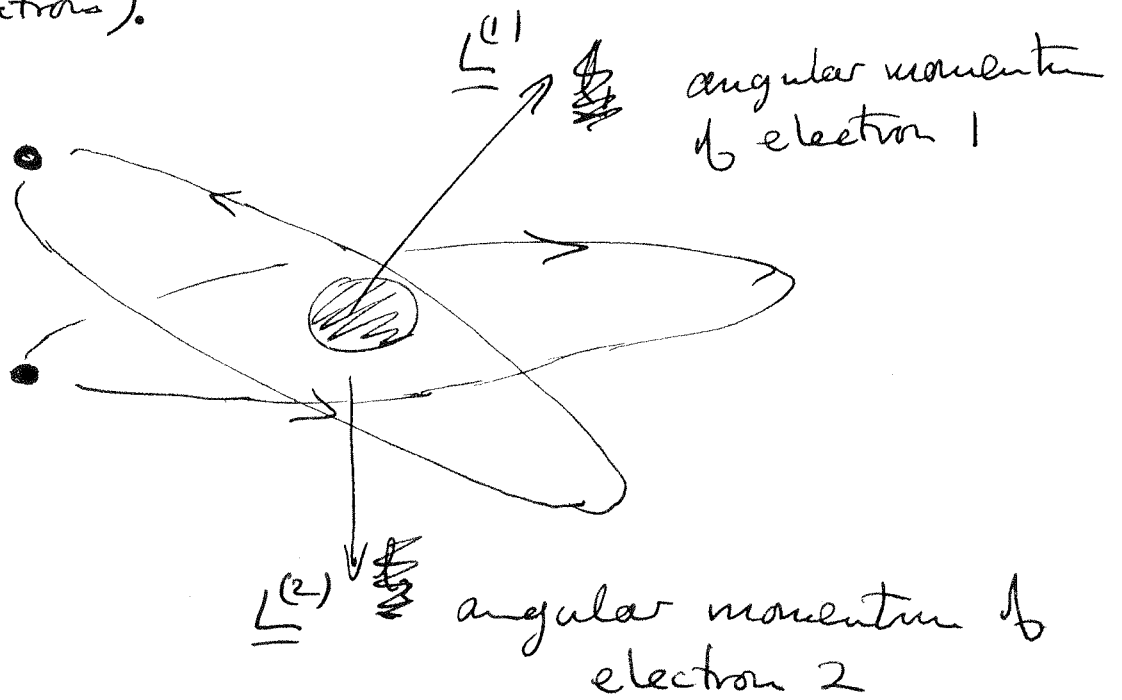
2. We considered the exchange principle which applies to wave-functions of identical particles. In particular wavefunctions for two identical electrons (which have spin $\frac{1}{2}$ and are therefore fermions) must be antisymmetric under exchange. i.e. $|1, 2\rangle = -|2, 1\rangle$

$$\begin{array}{c} \swarrow \quad \nwarrow \\ \text{particle 1} \quad \text{particle 2} \end{array}$$

We explored the implications of this for two fermions in an SHO potential and with no mutual interaction. Of course we have to apply this principle to the helium system as well. But before we do that we have to understand the angular ~~prop~~ momentum properties.

A. Orbital Angular Momentum in He

Let's consider for a moment a "classical Helium atom" — or if you like a star with two planets orbiting — (we'll assume the nucleus is infinitely heavy so we only have to consider motion of the electrons).



- Suppose that the electrons feel only the central potential. Then

$\underline{L}^{(1)}$ is conserved, i.e. a constant vector

$\underline{L}^{(2)}$ is "

The total angular momentum is

$$\underline{L} = \underline{L}^{(1)} + \underline{L}^{(2)} \quad \text{and}$$

\underline{L} is conserved, i.e. a constant vector.

Given the angular momenta of the two electrons we obtain the total angular momentum by vector addition.

- Now let's turn on the repulsion between the electrons (in the planetary system it would be an attraction of course). Electron 1 is no longer in a central potential so

$\underline{L}^{(1)}$ is not conserved, it is a time dependent vector.

similarly,

$\underline{L}^{(2)}$ is not

However there is no external couple on the entire system and therefore

$\underline{L} = \underline{L}^{(1)} + \underline{L}^{(2)}$ is conserved, it is a constant vector.

What happens quantum mechanically?

The time independent Sch equation takes the form

$$H \Phi(\underline{r}_1, \underline{r}_2) = E \Phi(\underline{r}_1, \underline{r}_2)$$

\downarrow position of electron 1 \swarrow position of electron 2

with

$$H = \frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2}$$

$$+ \frac{e^2}{4\pi\epsilon_0 |\underline{r}_1 - \underline{r}_2|}$$

$$= H_1 + H_2 + H_{int}$$

This looks nasty; because $\underline{r}_1, \underline{r}_2$ and $|\underline{r}_1 - \underline{r}_2|$ appear in the potential there is no way that this is separable - in fact it cannot be solved exactly as we noted last term.

However, our classical discussion suggests that we might be able to say something about the angular momenta of the system.

B. $[L, H]$

an angular momentum operator for
Start by noting that for electron 1

$$L_z^{(1)} = -i\hbar \left(x_1 \frac{\partial}{\partial y_1} - y_1 \frac{\partial}{\partial x_1} \right)$$

commutes with H_1 because this is just a copy of the hydrogen problem. It also commutes with H_2 because the latter is a function of x_2, y_2, z_2 only. So we need $[L_z^{(1)}, H_{int}]$ and it's sufficient to calculate

$$\begin{aligned} \left[L_z^{(1)}, \frac{1}{|\underline{r}_1 - \underline{r}_2|} \right] &= L_z^{(1)} \frac{1}{|\underline{r}_1 - \underline{r}_2|} - \frac{1}{|\underline{r}_1 - \underline{r}_2|} L_z^{(1)} \\ &= -i\hbar \left(x_1 \frac{\partial}{\partial y_1} - y_1 \frac{\partial}{\partial x_1} \right) \frac{1}{\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}} \\ &= -i\hbar \times -\frac{1}{2} \times 2 \times \frac{(x_1(y_1 - y_2) - y_1(x_1 - x_2))}{|\underline{r}_1 - \underline{r}_2|^3} \\ &= i\hbar \frac{(y_1 x_2 - x_1 y_2)}{|\underline{r}_1 - \underline{r}_2|^3} \end{aligned}$$

- as we might have expected it is not zero. By

swapping the labels $1 \leftrightarrow 2$ we also get

$$\left[L_z^{(2)}, \frac{1}{|\underline{r}_1 - \underline{r}_2|} \right] = \frac{i\hbar (y_2 x_1 - x_2 y_1)}{|\underline{r}_1 - \underline{r}_2|^3}$$

(7)

and we can deduce straightforwardly that

$$\left[\underbrace{L_z^{(1)} + L_z^{(2)}}_{L_z}, H_{\text{int}} \right] = 0$$

L_z
total ang. mom operator

and similarly for L_x and L_y . So at this level of approximation (ie no spin-orbit interaction terms in H) the levels of Helium are labelled by the total angular momentum quantum number L

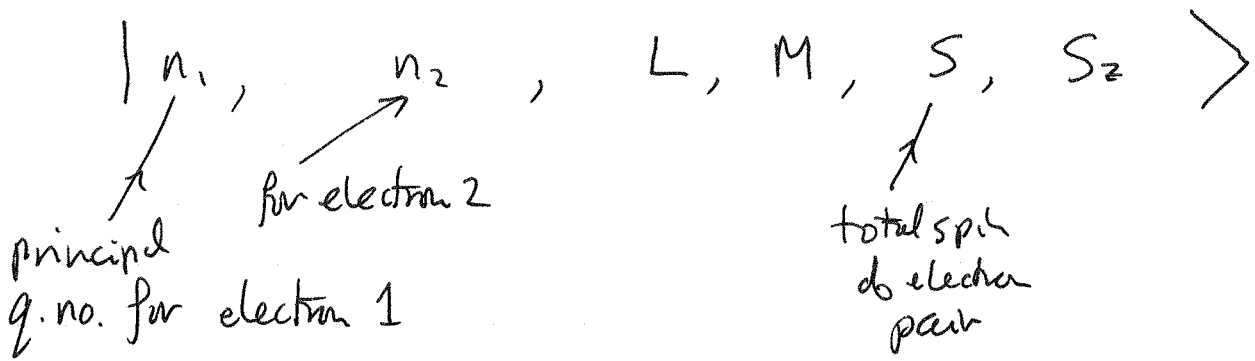
ie
$$\underline{L}^2 = L_z^2 + L_x^2 + L_y^2$$

$$\underline{L}^2 \Phi(r_1, r_2) = \hbar^2 L(L+1) \Phi(r_1, r_2)$$

and
$$L_z \Phi(r_1, r_2) = \hbar M \Phi(r_1, r_2)$$

C. Classification of levels

The quantum numbers are



Because we have no spin dependence in H the states will be factorized

$$|n_1, n_2, L, M\rangle \quad |S, S_z\rangle$$

spatial part
spin part

Let's start with

ground state

this is symmetric

$$|1, 1, 0, 0\rangle$$

antisymmetric

$$\frac{(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)}{\sqrt{2}}$$



from our remarks about the variational calculation

no angular momentum

$S=0$

NB. Only one spin state so this is a spin singlet

1st excited state

Obviously one of the electrons should stay in an $n=1$ state and the other be excited to $n=2$ so the spatial part could be

$$|1, 2, L, M\rangle$$

$$\text{or } |2, 1, L, M\rangle$$

with $L=1$ if the $n=2$ state has $l=1$
 $L=0$ " " " " " " " $l=0$

If we take the symmetric combination we get

$$\frac{1}{\sqrt{2}} (|1, 2, L, M\rangle + |2, 1, L, M\rangle) \quad |0, 0\rangle$$

↑ antisym spin
a singlet again

but now we could also take the antisym combination to get

$$\frac{1}{\sqrt{2}} (|1, 2, L, M\rangle - |2, 1, L, M\rangle) \quad |1, S_z\rangle$$

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

Higher excited states

It turns out that if we try to put both electrons in $n=2$ states the effect of the repulsion is so large that the total energy is positive and the atom ionized. Therefore all the excited states (and so $l=0$) take the form of one ~~is~~ electron in $n=1$ and one with principal quantum number $n > 1$. So they are either singlets

$$\frac{1}{\sqrt{2}} \left(|1, n, L, m\rangle + |n, 1, L, m\rangle \right) |0, 0\rangle$$

\swarrow
 $L=0, \dots, n-1$

or triplets

$$\frac{1}{\sqrt{2}} \left(|1, n, L, m\rangle - |n, 1, L, m\rangle \right) |1, S_z\rangle$$

Helium Spectrum 1

First three levels ignoring the effect of the mutual repulsion of electrons and not to scale!. Remember that one electron is always in the $n=1$ state.

Singlet $S=0$ Triplet $S=1$

○

$n=3$ $L=0,1,2$

$n=3$ $L=0,1,2$

$n=2$ $L=0,1$

$n=2$ $L=0,1$

○

$n=1$ $L=0$

D. Singlet-Triplet splitting

If we ignore the mutual repulsion term in the Hamiltonian

$$H_{int} = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}$$

then the singlet and triplet states are degenerate. We can see roughly what the effect of H_{int} is by using perturbation theory - however you should realise that H_{int} is big, as we discussed last term, and so this cannot give reliable answers for the splittings. More sophisticated methods are needed to do that.

Now H_{int} has no spin - angular dependent parts so the matrix element

$$\langle n_i n_l L M S S_z | H_{int} | n_i' n_l' L' M' S' S_z' \rangle$$

is non-zero only if $S=S'$ and $S_z=S_z'$ so the singlet and triplet states do not get mixed up by H_{int} .

To keep things simple let's consider the $n=2, L=0$

states; in the absence of Hint they take the form

$$\text{singlet: } \Phi_S = \left(\underset{\substack{\uparrow \\ n}}{\phi_{200}}(r_1) \underset{\substack{\uparrow \\ e}}{\phi_{100}}(r_2) + \phi_{200}(r_2) \underset{\substack{\uparrow \\ m}}{\phi_{100}}(r_1) \right) / \sqrt{2}$$

$$\text{triplet: } \Phi_T = \left(\phi_{200}(r_1) \phi_{100}(r_2) - \phi_{200}(r_2) \phi_{100}(r_1) \right) / \sqrt{2}$$

so the first order energy shift would be

$$\Delta E = \frac{e^2}{8\pi\epsilon_0} \int \frac{r_1^2 dr_1 r_2^2 dr_2 d\Omega_1 d\Omega_2}{|r_1 - r_2|} \left(\phi_{200}(r_1) \phi_{100}(r_2) \pm \phi_{200}(r_2) \phi_{100}(r_1) \right)^2$$

$$= \frac{e^2}{4\pi\epsilon_0} \int \frac{r_1^2 dr_1 r_2^2 dr_2 d\Omega_1 d\Omega_2}{|r_1 - r_2|} \left[\left(\phi_{200}(r_1) \right)^2 \left(\phi_{100}(r_2) \right)^2 \pm \left(\phi_{200}(r_1) \phi_{100}(r_1) \right) \left(\phi_{200}(r_2) \phi_{100}(r_2) \right) \right]$$

$$= \underset{\substack{\uparrow \\ \text{"direct"} \\ \text{term}}}{J_{20}} \pm \underset{\substack{\uparrow \\ \text{"exchange"} \\ \text{term}}}{K_{20}}$$

Note that since all the ϕ 's are positive in this case $\Rightarrow K_{20}$ is positive and so ΔE

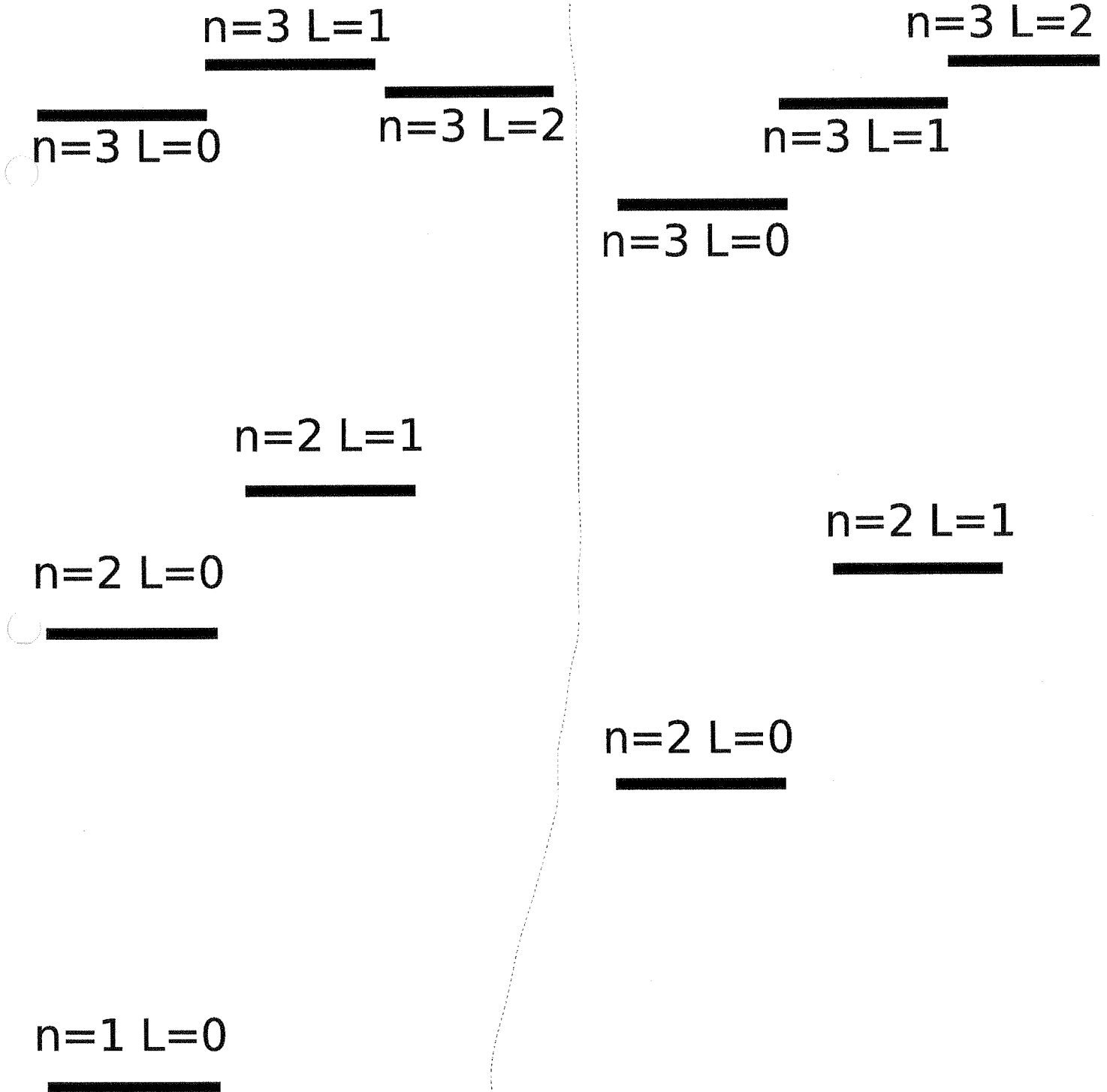
for the singlet is bigger than it is for the triplet and so the singlet level comes higher in the spectrum than the triplet one does transparency.

Helium Spectrum 2

First three levels including the effect of the mutual repulsion of electrons and not to scale!. Remember that one electron is always in the $n=1$ state.

Singlet $S=0$

Triplet $S=1$



It's not so obvious for the $L \neq 0$ states because now the ϕ 's are not positive as they have angle dependence of the $Y_{l,m}$. Nonetheless it turns out that for $n=2$, $L=1$ states it's still the case that the triplet level comes below the singlet.

E. Spectroscopic Notation

Our method of labelling the states is a little clumsy to write down so often the spectroscopic notation is used. ~~An example is~~ In this the orbital angular

is denoted by a letter

S	$L=0$
P	$L=1$
D	$L=2$
F	$L=3$

and the spin by the multiplicity $2S+1$. So

1S denotes the $L=0$ $S=0$ state

then the suffix is used for J ($J = L+S$) which in this case must be 0.

So its

$^{2S+1}L_J$
 \uparrow
 a letter

Of course anyone can do this. So what is

3P_2 ?

And what would the Singlet $L=2$ state be?

Move on Exchange

Before we move on to time-dependent physics there are a couple of topics on exchange that we should clear up.

A. Multiple particle wavefuns

The exchange principle remains true for states of more than two ^{identical} particles of course. Next year you will study systems like ^3He ; for example protons and neutrons are bound states of three constituent fermions called quarks.

There also states of multiple identical bosons - for example many photon systems, and liquid He^4 (the He^4 atom is a boson!). So how do we construct states with the required symmetry properties? Let's do it for three particles - then the generalization is obvious.

bosons start with three bosons^{1,2,3} in three states a, b, c then

$$\Phi = \phi_a(r_1) \phi_b(r_2) \phi_c(r_3)$$

we need to make this under $1 \leftrightarrow 2$ so form Φ'

by swapping $1 \leftrightarrow 2$ $\Phi' = \phi_a(r_2) \phi_b(r_1) \phi_c(r_3)$

now add Φ, Φ' ; the result will be symmetric under $1 \leftrightarrow 2$. To get something totally symmetric we keep swapping labels until we've run out of possibilities - it's easiest ~~to~~ to do this in tabular form

	a	b	c	
1	2	3	} no more possibilities with 3 in column a c	
2	1	3		
1	3	2	} no more with 3 in column b	
2	3	1		
3	1	2	} finished.	
3	2	1		

so

$$\Phi_S = \phi_a(r_1) \phi_b(r_2) \phi_c(r_3)$$

$$+ \phi_a(r_2) \phi_b(r_1) \phi_c(r_3)$$

$$+ \phi_a(r_1) \phi_b(r_3) \phi_c(r_2)$$

$$+ \phi_a(r_2) \phi_b(r_3) \phi_c(r_1)$$

$$+ \phi_a(r_3) \phi_b(r_1) \phi_c(r_2)$$

$$+ \phi_a(r_3) \phi_b(r_2) \phi_c(r_1)$$

each line is orthogonal to every other line so normalization factor is

$$\frac{1}{\sqrt{6}}$$

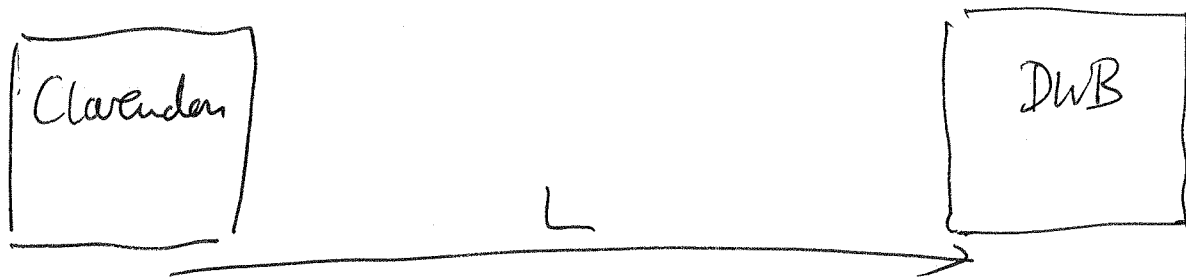
Fermions

This time when we swap $\rho_1 \leftrightarrow 2$ we want to subtract the two functions. So we use the same table but annotate to keep track of how many subtractions we have ~~had~~ made — since $(-1) \times (-1) = +1$ we need to do this. We get

$$\begin{aligned} \Phi_{1A} = & \left[\phi_a(r_1) \phi_b(r_2) \phi_c(r_3) \right. \\ & - \phi_a(r_2) \phi_b(r_1) \phi_c(r_3) \\ & - \phi_a(r_1) \phi_b(r_3) \phi_c(r_2) \\ & + \phi_a(r_2) \phi_b(r_3) \phi_c(r_1) \\ & + \phi_a(r_3) \phi_b(r_1) \phi_c(r_2) \\ & \left. - \phi_a(r_3) \phi_b(r_2) \phi_c(r_1) \right] \frac{1}{\sqrt{6}} \end{aligned}$$

B. When is "identical" distinguishable?

Although all electrons are identical you could legitimately argue that the electron in a hydrogen atom in the Clarendon Lab and the electron in a hydrogen atom in the DWB are distinguishable. How do we square this with quantum mechanics? The way to do it is to think about measurements.



Suppose we prepare an atom in the Clarendon with an electron in the ground state. Its wavefn is

$$\phi = \frac{2}{a^{3/2}} e^{-r/a} \cdot \frac{1}{\sqrt{4\pi}}$$

Now someone else observes an electron in the DWB. What is the probability that it is the electron observed in the CL?

Well it is \propto Vol of detector $|\phi|^2$

$$= \frac{1}{4\pi} \frac{\text{Vol}}{a^3} e^{-\frac{2L}{a}}$$

(5)

$$\sim \frac{1}{(10^{-10})^3} \exp(-2 \cdot 10^{12})$$

$$\sim \exp(-2 \cdot 10^{12} + \underbrace{30 \log 10}_{\text{negligible}})$$

very small!!

So we are for all practical purposes sure that it is a different electron that is observed in the DWB.

Note that in fact this is true even for a couple of atoms separated by a few tens of atomic sizes.