Atoms

The hamiltonian for a neutral atom of atomic number Z is

$$H = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0}\right) \frac{Ze^2}{r_j} \right\}$$
$$+ \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0}\right) \sum_{j \neq k}^{Z} \frac{e^2}{|\vec{r}_j - \vec{r}_i|}$$

In order to describe a neutral atom, we need to solve

$$H \psi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_Z) = E \psi(\vec{r}_1, \ldots, \vec{r}_Z)$$

with $\psi(\vec{r}_1, \ldots \vec{r}_Z)\chi(s_1, \ldots, s_Z)$ being antisymmetric w.r.t. interchange of any two electrons.

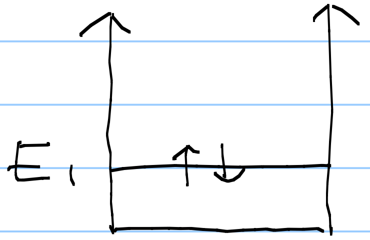
Solving this exactly is impossible. However, people have developed a number of approximation methods that yield solutions very close to the exact solution.

In this hamiltonian, the second term represents the interactions between electrons. What makes the hamiltonian unsolvable is this electron-electron interaction term (e-e)

Without the e-e interaction term, the solution is just that of hydrogen atom with the proton charge e replaced by Ze.

In order to get some feeling about the e-e interaction, let's take the infinite well potential as an example.

Last time we have found that the ground state of two-non interacting electrons (spin-$\frac{1}{2}$ particle) in the infinite square well is



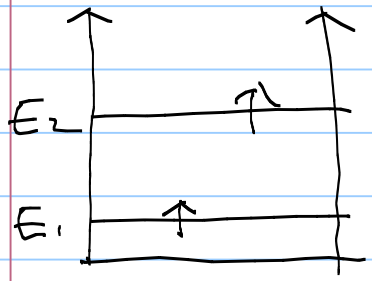
The singlet state with the two electrons occupying the ground state of the single electron state.

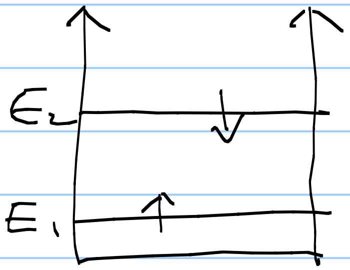
The ground state does not have any degeneracy. In other words, there is only one ground state written as

$$\psi_{n=1}(x_1)\,\psi_{n=1}(x_2)\,\underbrace{\chi_0(s_1, s_2)}_{\text{singlet state}}$$

$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

* Last time, we found that if we still neglect the electron-electron interaction the first excited states are degenerate with three triplet states and one singlet state like





triplet state → degeneracy three

singlet state → degeneracy one

Total degeneray of four with the energy of $E_1+E_2 = 5K$

The triplet state should look like

$$|\Psi\rangle_t = \frac{1}{\sqrt{2}}\left\{\psi_{n=1}(x_1)\,\psi_{n=2}(x_2) - \psi_{n=2}(x_1)\,\psi_{n=1}(x_2)\right\} \times \chi_1$$

, where χ_1 is one of $\begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{cases}$

So $|\Delta\rangle_t$ can be one of these three states.

Here note that for the triplet state, the spin part is symmetric w.r.t. the interchange of particles, and the spatial part is antisymmetric, the entire state being antisymmetric

Now the singlet state is

$$|\Delta\rangle_s = \psi_{n=1}(x_1)\,\psi_{n=2}(x_2)\,\chi_0$$

, where $\chi_0 = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$.

Again the spin part is antisymmetric w.r.t. the particle interchange. Therefore the spatial part should be symmetric.

So without electron-electron electrons, these four states have the same energy of $E = E_1 + E_2 = 5K$

; K was defined last time as $\frac{\hbar^2\pi^2}{2ma^2}$

✱ Now if we take into account e-e repulsion, what happens to the degeneracy and energy? Is the first excited state singlet state or triple state?

First, remember that e-e interaction results in an increase in the total energy because

$$V_{e-e} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} > 0.$$

If we look at the spatial part of an antisymmetric spatial wave ftn,

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}}\Big(\psi_{n=1}(x_1)\,\psi_{n=2}(x_2) - \psi_{n=2}(x_1)\,\psi_{n=1}(x_1)\Big)$$

we notice that if $x_1 = x_2$, ψ becomes zero.

In other words, the probability of finding two electrons at the same location simultaneously is zero.

So antisymmetric spatial wavefunctions tend to have two electrons further apart compared with symmetric spatial wave functions.

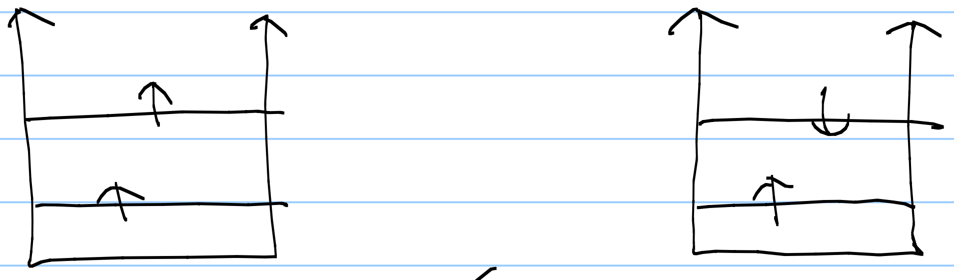
For a more formal proof of this conclusion, refer to section 5.1.2. of Griffiths.

So

triplet state ⇒ antisymmetric spatial wave function ⇒ electrons further apart than singlet state, which has symmetric spatial wave function ⇒ less e-e Coulomb repulsion in the triplet state ⇒ triplet state has lower energy than the singlet state

In other words,

with e-e interaction (Coulomb repulsion)



$E_{\text{triplet}} < E_{\text{singlet}}$

E (1st excited ~~state~~) = E triplet

$$= 5K + \Delta_{e-e}(\text{triplet})$$

The new degeneracy is now three for the 1st excited state, instead of 4.

This infinite well example is very similar to the parahelium (singlet) and the ortho helium (triplet) problem discussed in Griffiths section 5.2.1.
I recommend you to compare our example with the helium case.

* Periodic table

If neglect e-e interaction for a neutral atom of Z electrons, the energy of each electron filling the orbitals will be completely determined by n, because

$$E \propto -\frac{1}{n^2}$$

previously we have found that each n has n^2 degeneracy because $\sum_{\ell=0}^{n-1}(2\ell+1) = n^2$.

With the spins taken into account, The degeneracy of a shell indexed by "n" must be "$2n^2$".

In these imaginary atoms of non-interacting electrons, if the electrons were not fermions, in the ground state all electrons will reside in the lowest energy shell and there will not be a "periodic table".

But electrons are fermions and each orbital indexed by (n, ℓ, m) can occupy only two electrons, and that is why we have "$2n^2$" electrons for each shell.

If this were the case, the periodic table would be more like

1st row; $n=1$; 2 atoms

2nd row; $n=2$; $2\times 4 = 8$ atoms

3rd row; $n=3$; $2\times 9 = 18$ atoms

4th row; $n=4$; $2\times 16 = 32$ atoms, etc., But the actual periodic table looks like

1st row : 2 atoms
2nd row : 8 atoms
3rd row : 8 atoms
4th row : 18 atoms
5th row : 18 atoms
6th row : 32 atoms
7th row : 32 atoms.

This is because of so-called screening for the most part.

Traditionally, people use s for $\ell=0$, p for $\ell=1$, d for $\ell=2$, f for $\ell=3$, g for $\ell=4$, etc.

We call each "n" by "shell" and each "ℓ" by "subshell".

Each state represented by (n, ℓ, m) is called "orbital".

So $\underset{(\ell=2)}{d}$ subshell has five $(2\times\underset{\uparrow_{\ell}}{2}+1)$ orbitals.

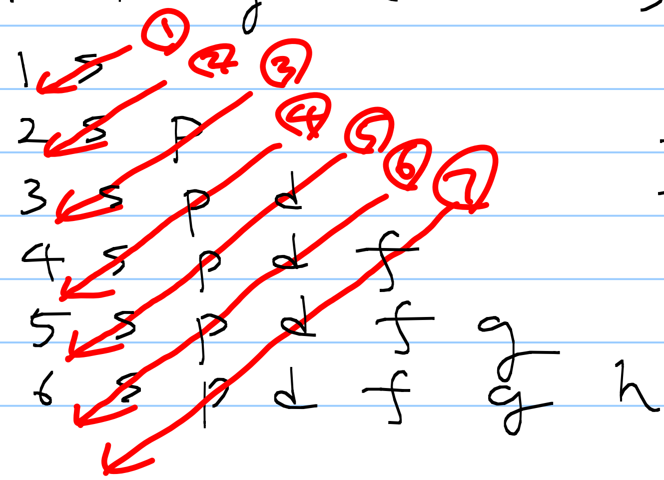
If we list the shells and subshells

1 s : 2 electrons
2 s p : 8 "
3 s p d : 18 "
4 s p d f : 32 "
5 s p d f g : 50 "
6 s p d f g h : 72 "

Because of the screening of other electrons, electrons in the higher "ℓ" state tend not to see the full attractive charge of the nucleus.

Therefore, higher "ℓ" state tends to push its energy value upward.

Because of this, the energy ordering in filling the orbitals appears as follows.



1s → 2s → 2p → 3s
→ 3p → 4s → 3d
→ 4p → 5s → 4d
→ 5p → 6s → 4f
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