ATOMS AND MULTI-PARTICLE SYSTEMS

Let us start with a simple, well-known system: one-dimensional quantum well, of width a. Let us throw a couple of electrons, of mass m, spin $1/2$, charge e^-, inside the well.

If we ignore indistinguishability (which requires $\psi(1,2) = \pm\psi(2,1)$), spin-statistic theorem (electrons are fermions: $\psi(1,2) = -\psi(2,1)$) and Coulomb repulsion, we get:

$$E_{n_1 n_2} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_1^2 + n_2^2\right) \qquad \psi(1,2) = \frac{2}{a}\sin\left(\frac{n_1\pi x_1}{a}\right)\sin\left(\frac{n_2\pi x_2}{a}\right)\chi(1,2)$$

we also ignore Pauli's exclusion principle, which required the two 1-particle states to be different

where $\chi(1,2)$ is spin part: it could be $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$ or $|\downarrow\downarrow\rangle$ while $\frac{2}{a}\sin\left(\frac{n_1\pi x_1}{a}\right)\sin\left(\frac{n_2\pi x_2}{a}\right) = |n_1 n_2\rangle$ using the same notation

	$\lvert n_1\, n_2\rangle$	degeneracy
ground	$\lvert 1,1\rangle$	4 $(\lvert\uparrow\uparrow\rangle, \lvert\uparrow\downarrow\rangle, \lvert\downarrow\uparrow\rangle, \lvert\downarrow\downarrow\rangle)$
1st excited	$\lvert 1,2\rangle$	4
	$\lvert 2,1\rangle$	4

Energy

$E_{12} = E_{21} = \frac{5}{2}E_{11}$ — 8 degenerate states

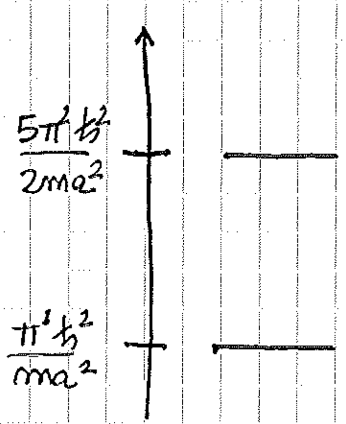
$E_{11} = \frac{\pi^2\hbar^2}{ma^2}$ — 4 degenerate states

Let us now add spin statistic / Pauli's exclusion principle:

among the twelve states above, only the anti-symmetric ones, for a $1 \leftrightarrow 2$ exchange, survive:

$\lvert n_1\, n_2\rangle$	spin	exchange parity: space · spin	degeneracy
$\lvert 1\,1\rangle$	$\frac{1}{\sqrt{2}}(\lvert\uparrow\downarrow\rangle - \lvert\downarrow\uparrow\rangle)$: singlet	symm · anti-symm	1
$\frac{1}{\sqrt{2}}(\lvert 12\rangle + \lvert 21\rangle)$	$\frac{1}{\sqrt{2}}(\lvert\uparrow\downarrow\rangle - \lvert\downarrow\uparrow\rangle)$: singlet	symm · anti-symm	1
$\frac{1}{\sqrt{2}}(\lvert 12\rangle - \lvert 21\rangle)$	$\lvert\uparrow\uparrow\rangle$, $\frac{1}{\sqrt{2}}(\lvert\uparrow\downarrow\rangle + \lvert\downarrow\uparrow\rangle)$, $\lvert\downarrow\downarrow\rangle$: triplet	anti-symm · symm	3

Here is the energy spectrum once we consider Pauli's exclusion principle:

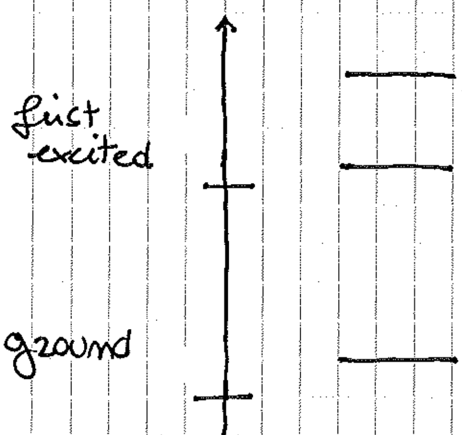


4 states : $\frac{1}{\sqrt{2}}(|12\rangle+|21\rangle)\cdot$ spin singlet : 1 state

$\frac{1}{\sqrt{2}}(|12\rangle-|21\rangle)\cdot$ spin triplet : 3 states

1 state : $|11\rangle\cdot$ spin singlet

Let us now add Coulomb repulsion, remembering that when two identical particles are in a symmetric (→ FOR PARTICLE EXCHANGE!) spatial wavefunction, they tend to stay closer to each other. This causes a split of the degeneracy of the first excited state: the spin-singlet state goes with a symmetric (for particle exchange) spatial wavefunction $\frac{1}{\sqrt{2}}(|12\rangle+|21\rangle)$: the two electrons are closer than in the $\frac{1}{\sqrt{2}}(|12\rangle-|21\rangle)$ state $\Rightarrow$ higher electrostatic energy. With Coulomb repulsion we obtain:



1 state : $\frac{1}{\sqrt{2}}(|12\rangle+|21\rangle)\cdot\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle)$ spin singlet

3 states : $\frac{1}{\sqrt{2}}(|12\rangle-|21\rangle)\cdot$ $|\uparrow\uparrow\rangle$ or $|\downarrow\downarrow\rangle$ or $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle)$ spin triplet

1 state : $|11\rangle\cdot\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle)$ spin singlet

Let us look at He atom. Ground state must have spatially symmetric and spin singlet: both electrons in $|n\,\ell\,m\rangle=|1\,0\,0\rangle$ spatial state:

$$\psi(1,2)=\psi_{100}(1)\psi_{100}(2)\cdot\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle)$$

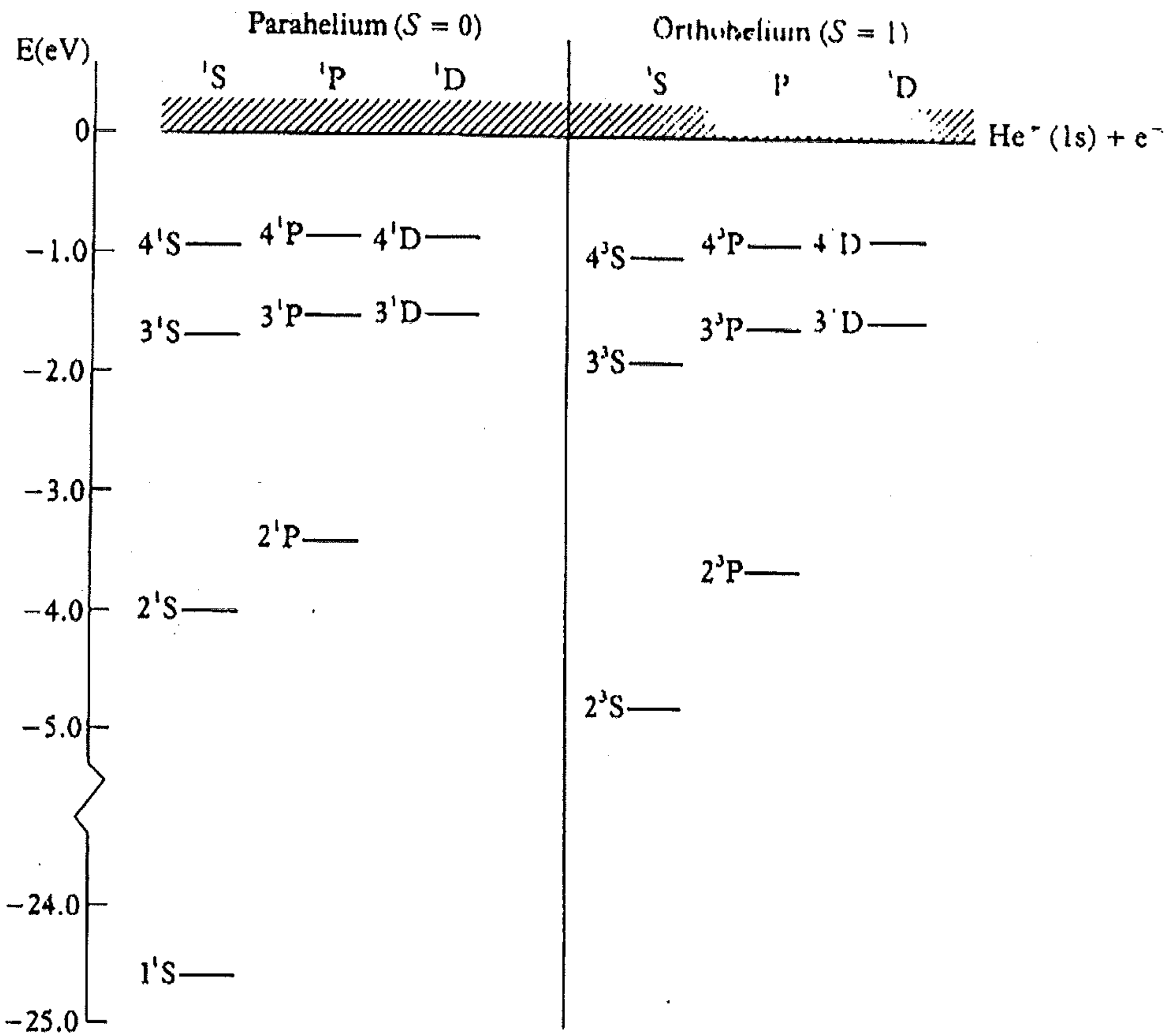
Neglecting Coulomb repulsion, the energy is just the sum of the energies of the two electrons: $E_1^{He}=Z^2E_1^H+Z^2E_1^H=8E_1^H=-8\cdot 13.6\,eV\cong-109\,eV$

where $Z = 2$ takes into account that He has two protons in its nucleus. We will see that in reality $E_1^{He} \sim -79\,eV$ due to screening effects.
What about He excited states? Now we can form both spatially symmetric (for particle exchange) or anti-symmetric superpositions of the single-particle states, and "fix" the symmetry of the full wavefunction by using either a spin singlet (anti-symmetric for particle exchange) or a spin triplet (symmetric for particle exchange) state.
There is a special name:

- PARAHELIUM: spin-singlet (total spin $=0$) $\cdot$ symmetric spatial superposition: electrons stay closer (attractive exchange force!): higher energy due to Coulomb attraction.

- ORTHOHELIUM: spin-triplet (total spin $= 1$) $\cdot$ anti-symmetric spatial superposition: repulsive exchange force, Coulomb interaction is smaller than in parahelium case

The lower Coulomb energy interaction makes orthohelium excited states favored with respect to the corresponding parahelium states. However, ground state has to be parahelium (both electrons are in same type of spatial wavefunction: $\psi_{100}(r, \theta, \phi)$ or $|n\,l\,m\rangle = |1\,0\,0\rangle$)



The experimental values of the lowest energy levels of helium.
$E = 0$ corresponds to the ionisation threshold.