Pauly exclusion principle

Non-distinguishable particles → their non-distinguishability must be reflected in their quantum state.

1 $\bullet$ $|a\rangle$ 2 $\bullet$ $|b\rangle$

Two-~~photon~~ particle wavefunction

$$|a\rangle_1 \otimes |b\rangle_2 = |a, b\rangle$$

Exchange operator $\hat{P}_{12}\,|a,b\rangle = |b,a\rangle =$

$$= |b\rangle_1 \otimes |a\rangle_2$$

Non-distinguishable → no measurement can determine if they are switches

$$\hat{P}_{12}\left[\hat{P}_{12}\,|a,b\rangle\right] = |a,b\rangle = |\psi\rangle \text{ identical}$$

One can formally show that either

$\hat{P}_{12}\,|\psi\rangle = |\psi\rangle$ symmetric under ~~inversion~~ exchange

or

$\hat{P}_{12}|\psi\rangle = -|\psi\rangle$ anti-symmetric under exchange

This seemingly trivial property rules our world!

<u>Bosons</u> (spin 1 particles) ~~are~~ have symmetric under exchange wavefunction

<u>Fermions</u> (spin ½ particles) have anti-symmetric under exchange wavefunction

Two electrons in an atom

electron 1: spin 1 $|s_1\rangle$; orbital 1 $|n_1, \ell_1, m_1\rangle$

electron 2: spin 2 $|s_2\rangle$; orbital 2 $|n_2, \ell_2, m_2\rangle$

Two-particle anti-symmetric wavefunction

$$|\psi_{12}\rangle = \frac{1}{\sqrt{2}}\Big[|s_1\rangle_1 |n_1, \ell_1, m_1\rangle_1 |s_2\rangle_2 |n_2, \ell_2, m_2\rangle_2 - $$
$$- |s_2\rangle_1 |n_2, \ell_2, m_2\rangle_1 |s_1\rangle_2 |n_1, \ell_1, m_1\rangle_2 \Big]$$

If $|s_1\rangle = |s_2\rangle$ (same spin state, both up or both down)

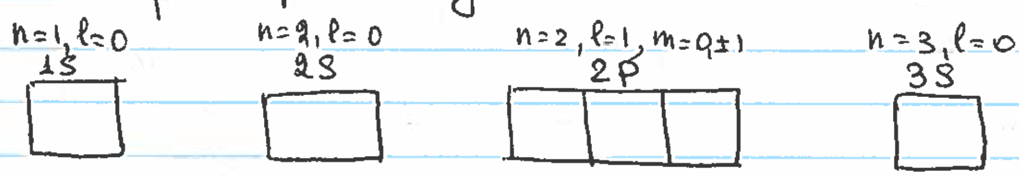
$$|\psi_{12}\rangle = \frac{1}{\sqrt{2}} |s_1\rangle_1 |s_1\rangle_2 \Big[|n_1, \ell_1, m_1\rangle_1 |n_2, \ell_2, m_2\rangle_2 - |n_2, \ell_2, m_2\rangle_1 |n_1, \ell_1, m_1\rangle_2 \Big]$$

if two electrons attempt to be on the same orbital, $|\psi_{12}\rangle = 0$ ⟶ impossible!

Pauli exclusion principle

No two electrons of the same atom can have identical values of <u>all</u> their quantum numbers

This principle governs our atomic structure



↑↓ He (2 electrons)

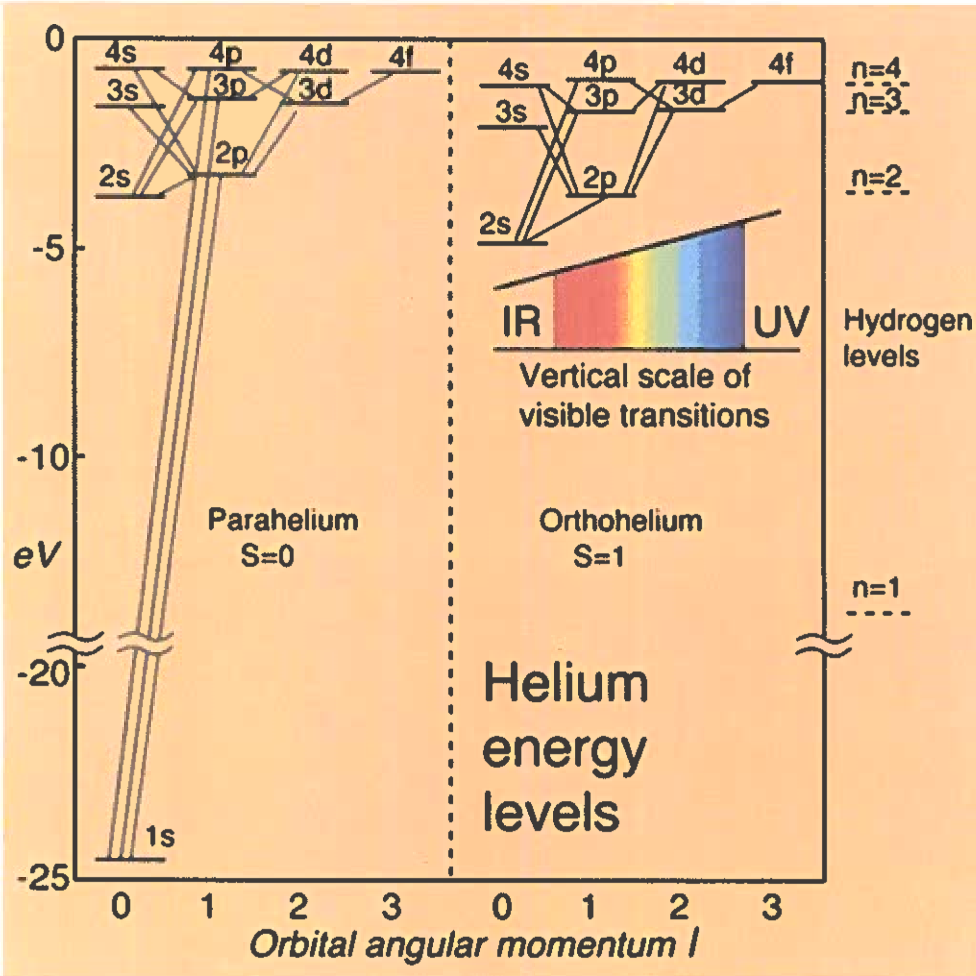
↑↓ ↑ Li (3 electrons)

↑↓ ↑↓ Be (4 electrons)

...

↑↓ ↑↓ ↑ ↑ ↑ N (7 electrons)

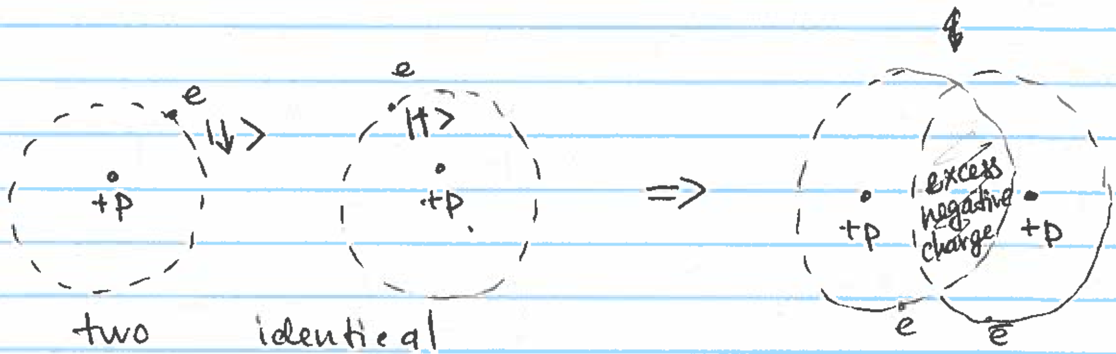
... Ne (10 electrons)



0
-5
-10
eV
-20
-25
4s
3s
2s
1s
4p
3p
2p
4d
3d
4f
Parahelium
S=0
4s
3s
2s
4p
3p
2p
4d
3d
4f
IR
UV
Vertical scale of
visible transitions
Orthohelium
S=1
Helium
energy
levels
n=4
n=3
n=2
Hydrogen
levels
n=1
0 1 2 3 0 1 2 3
Orbital angular momentum l

Pauli principle goes beyond just atoms

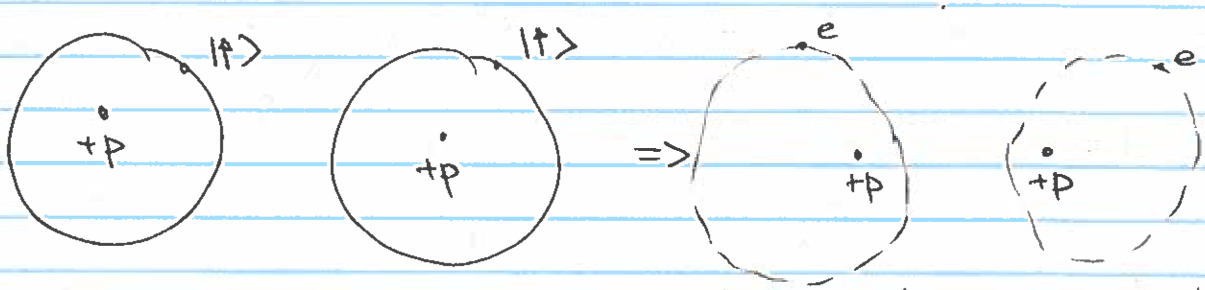
Molecular covalent bond



two identical hydrogen atoms

since spins are opposite, two electrons' spatial wavefunction is symmetric, so they have higher probability to be ~~th~~ between the two protons

but



~~less~~ ~~proba~~ two orbitals should not overlap, electrons are pushed away, molecular dissociation