Spin and Elements of Atomic Physics

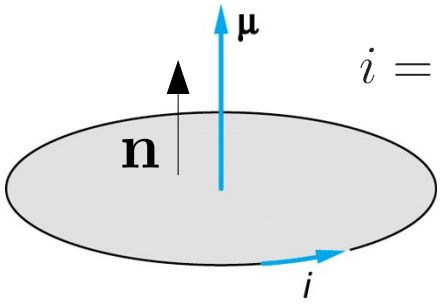
Outline

1. Magnetic Moment of a Particle in Orbital Motion
2. Stern-Gerlach Experiment and Electron's Spin
3. Total Angular Momentum. Spin-Orbit Coupling
4. Many-particle Quantum Systems. Bosons and Fermions.
5. Pauli Exclusion Principle
6. Periodic Table of Elements

Magnetic Moment of a Particle in Orbital Motion

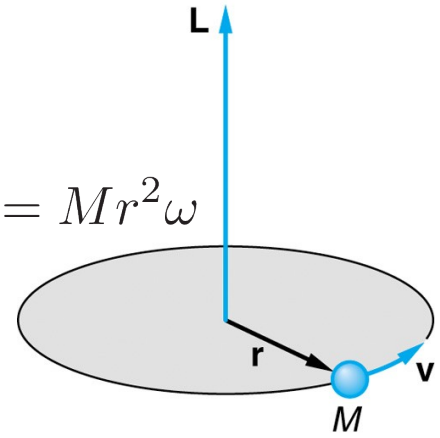
Magnetic Moment (Orbital Motion)

Recall: magnetic moment of a charged classical particle in orbital motion



$$i = \frac{q}{T} = \frac{q\omega}{2\pi}$$

$$\boldsymbol{\mu} = iA\,\mathbf{n} = \frac{q}{2M}\,\mathbf{L}$$



$$L = Mr^2\omega$$

Quantum-mechanics: *orbital angular momentum is quantized*

For an electron ($q = -e$, $M = m_e$)

$$|\boldsymbol{\mu}| = \frac{e\hbar}{2m_e}\sqrt{l(l+1)}, \qquad l = 0, 1, \ldots$$

$$\mu_z = \underbrace{-\frac{e\hbar}{2m_e}}_{\mu_B} m, \qquad m = 0, \pm 1, \ldots, \pm l$$

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24}\ [\mathrm{J/T}]$$ Bohr magneton

Magnetic Moment (Orbital Motion)

Hence, for an electron in *orbital motion*

$$|\boldsymbol{\mu}| = \mu_B \sqrt{l(l+1)}, \qquad l = 0, 1, \ldots$$

$$\mu_z = -m\mu_B, \qquad m = 0, \pm 1, \ldots, \pm l$$

In general, for any quantum particle in *orbital motion*

$$\boldsymbol{\mu} = -g_L \frac{\mu_B}{\hbar} \mathbf{L}$$

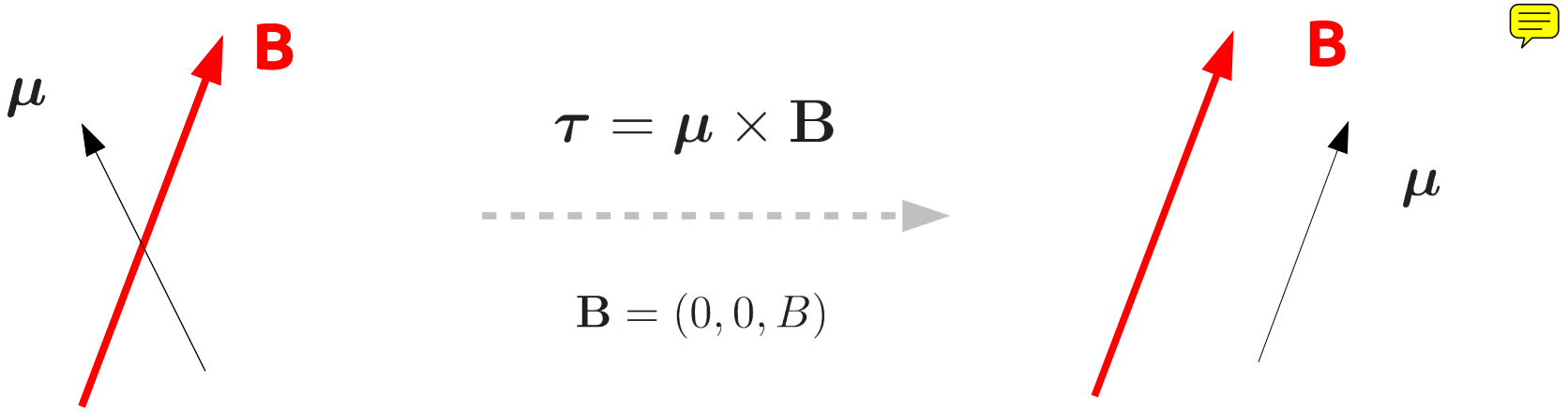
gyromagnetic factor (orbital Lande g-factor); equals one for electron in orbital motion

$$|\boldsymbol{\mu}| = g_L \mu_B \sqrt{l(l+1)}, \qquad l = 0, 1, \ldots$$

$$\mu_z = -m g_L \mu_B, \qquad m = 0, \pm 1, \ldots, \pm l$$

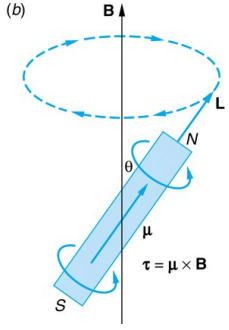
Magnetic Moment in a Magnetic Field

Recall: if we place a magnetic moment in a magnetic field there will be a torque trying to align the moment parallel to the field



so that the potential energy is minimized $U = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B$

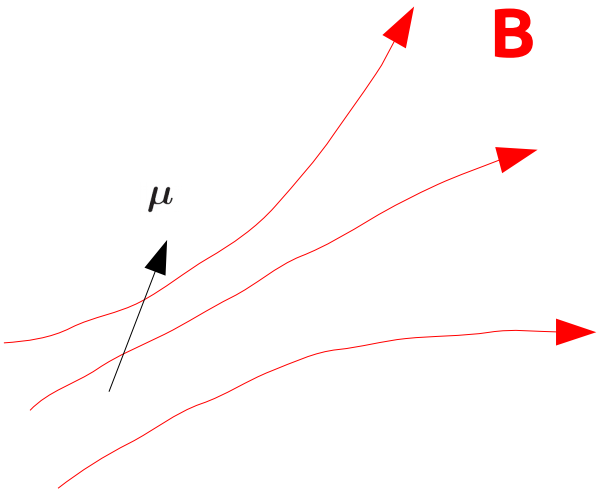
[* If the magnetic moment is spinning, additionally, precession around **B** will be observed.]



Stern-Gerlach Experiment and Electron Spin

Stern-Gerlach Experiment

Magnetic moment in an inhomogenous magnetic field



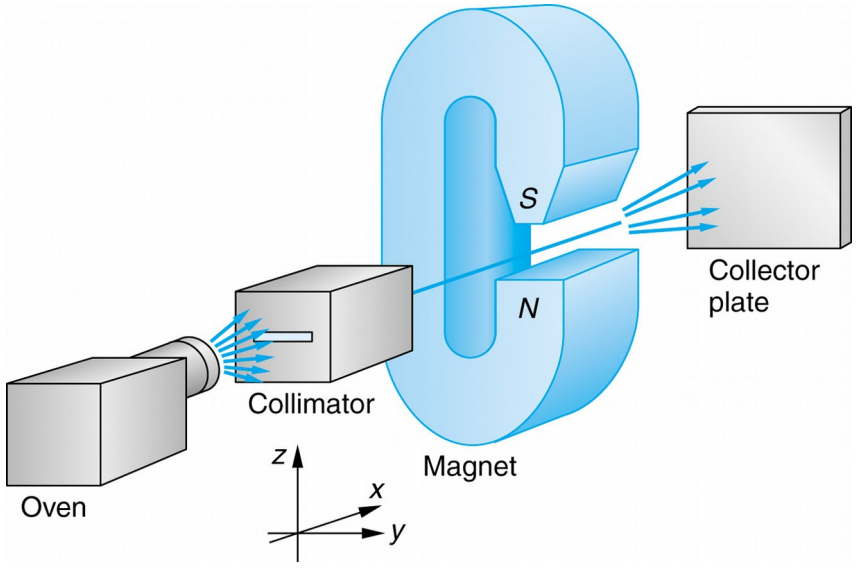
$$\mathbf{F} = -\nabla U = -\nabla(-\boldsymbol{\mu}\cdot\mathbf{B}) = \nabla(\boldsymbol{\mu}\cdot\mathbf{B})$$

Assuming that **B** is inhomogenous in the *z* axis direction we have

$$\nabla(\boldsymbol{\mu}\cdot\mathbf{B}) = \mu_z\frac{dB_z}{dz}$$

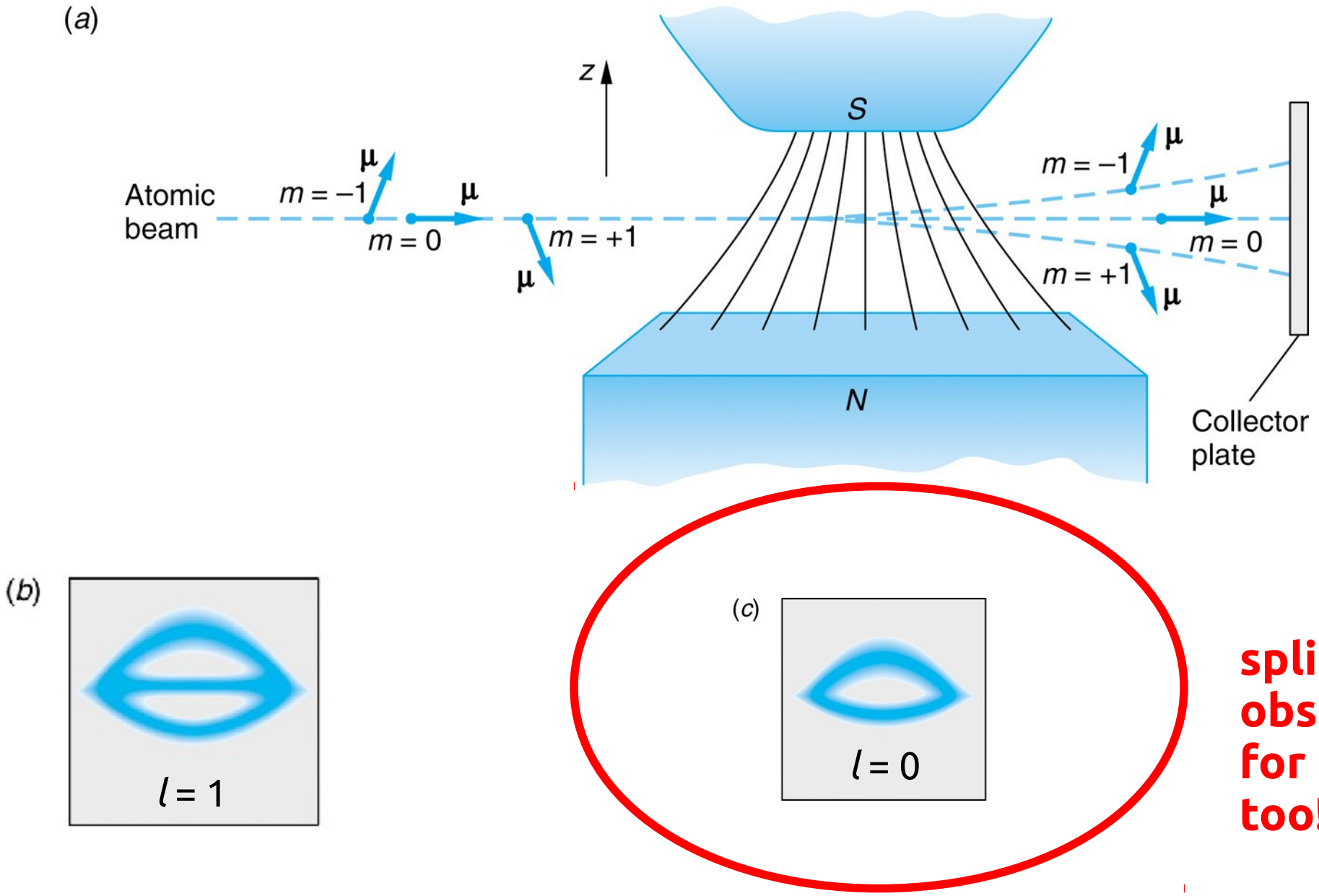
and the force

$$F_z = \mu_z\frac{dB_z}{dz} = -mg_L\mu_B\frac{dB_z}{dz}$$



For *l* = 1, 2,... the beam should split (quantum number *m has* 2*l* + 1different values -*l*, -*l* +1, ..., 0,.., *l*)

Stern-Gerlach Experiment ($l = 1$)

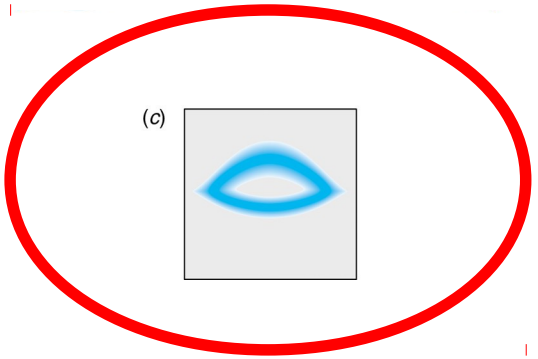


splitting observed for $l = 0$, too!!!

https://www.st-andrews.ac.uk/physics/quvis/simulations_chem/ch14-Experimental-proof-spin.html

Spin

For H atoms in the ground state
(n = 1, l =0) no splitting was expected



splitting observed also for *l=0*

Idea (Wolfgang Pauli)

*Electron has an additional intrinsic degree of freedom – **spin**.*

Spin operators have the same algebraic structure as the orbital angular momentum operators (e.g. the same commutation rules hold)

Eigenvalues

$$\hat{S}^2\chi = \hbar^2 s(s+1)\chi, \qquad s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$$

$$\hat{S}_z\chi = \hbar m_s \chi, \qquad m_s = -s, s+1, \ldots, s-1, s$$

HOWEVER half-integer values of *s* possible!

Electron's Spin

For the electron s =1/2, and m_s = -½, ½. The corresponding magnetic moment associated with the electron's spin

$$\mu_z = -m_s g_s \mu_B = \pm \mu_B$$

spin Lande factor $g_s \approx 2$

** Mathematically, the electron's spin operator is represented by the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\hat{\mathbf{S}} = \frac{\hbar}{2}\boldsymbol{\sigma} = \frac{\hbar}{2}(\sigma_x, \sigma_y, \sigma_z)$$

Full Hydrogen Atom Wave Functions

For the electron s=1/2. The complete set of quantum numbers of the Hydrogen atom consists of the: *principal*, *orbital*, *magnetic* and **spin quantum numbers**.

$$(n, l, m, m_s)$$

$$n = 1, 2, \ldots$$
$$l = 0, 1, 2, \ldots, n-1$$
$$m = -l, -l+1, \ldots, l-1, l$$
$$m_s = -\frac{1}{2}, \frac{1}{2}$$

Example: Hydrogen atom's ground-state wave function

$$\psi = C_1 \psi_{1,0,0,-\frac{1}{2}} + C_2 \psi_{1,0,0,+\frac{1}{2}}$$

$$\Pr\left(m_s = -\frac{1}{2}\right) = |C_1|^2, \qquad \Pr\left(m_s = \frac{1}{2}\right) = |C_2|^2$$

Total Angular Momentum. Spin-Orbit Coupling

Total Angular Momentum of an Electron

The electron in an atom has a combined *total angular momentum* with contributions due to both the orbital angular momentum and the spin.

The corresponding operator for the total angular momentum is

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

The eigenvalues of the operator $\hat{J}^2$ representing the magnitude of the total angular momentum (squared) are

$$\hbar^2 j(j+1), \qquad \text{with either } j = l + s \text{ or } j = |l - s|$$

and the $(2j+1)$ eigenvalues of the projection $\hat{J}_z$ are

$$m_j \hbar, \qquad m_j = -j, -j+1, \ldots, j-1, j$$

*** See Liboff 9.4-9.5 or Landau 31

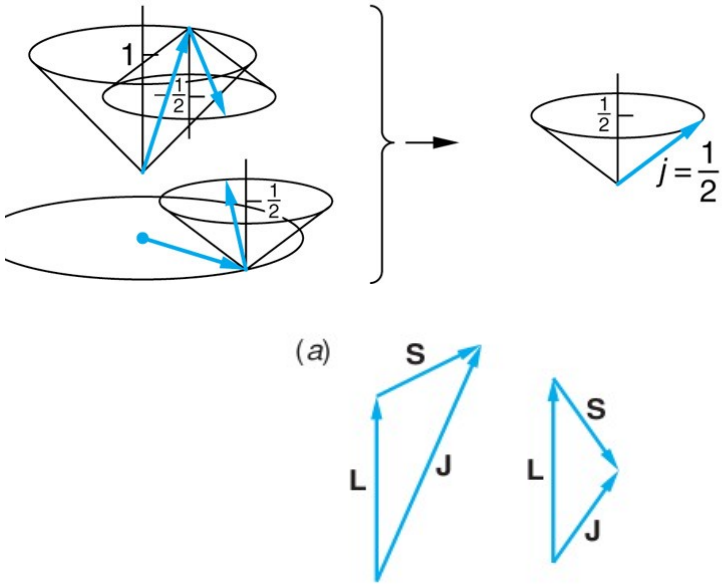
Example: Vector Model for $l = 1$, $s = ½$

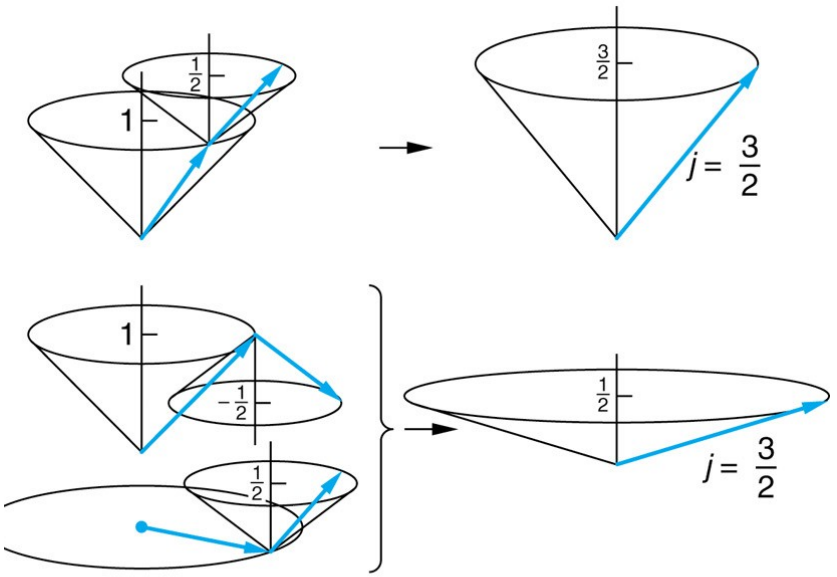
[Corresponds, e.g., to the electron in the first excited state of H atom, with $n = 2$, $l = 1$ (or any other excited state with $l = 1$)]

The possible values of j are: $|1 - ½| = ½$ and $1 + ½ = 3/2$.

For $j = ½$, the possible values of m_j are $-½$ and $½$.

For $j = 3/2$, the possible values of m_j are $-3/2$, $-½$, $½$, $3/2$.





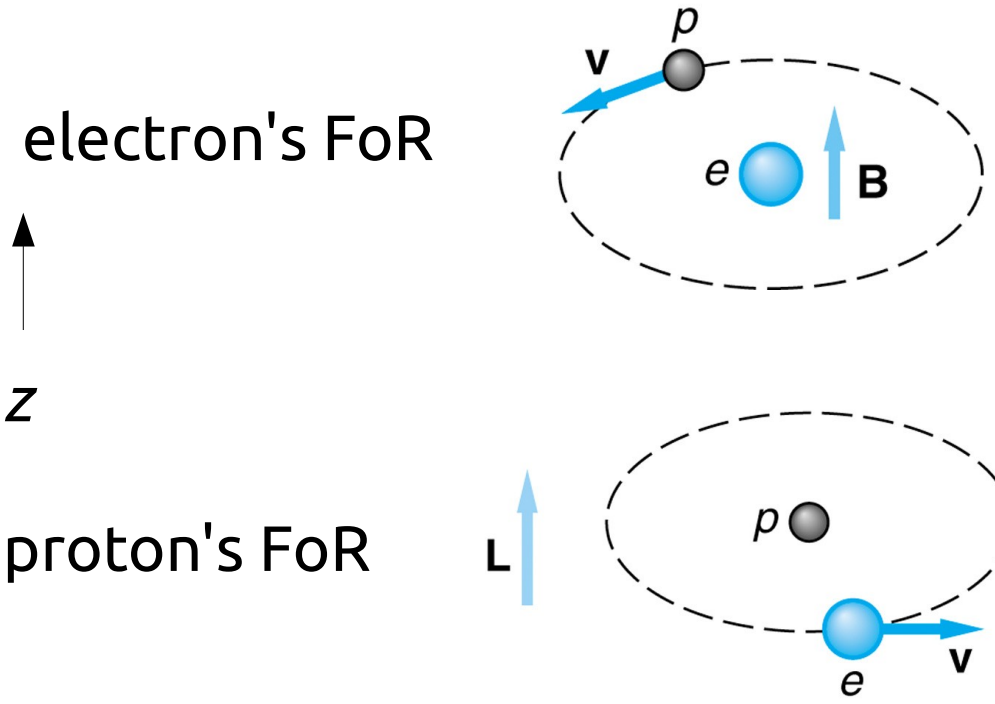
analogously for negative values of m_j

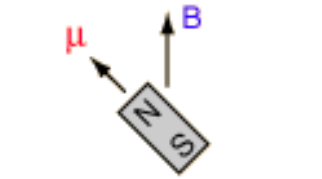
Spin-Orbit Coupling. Basic Explanation

Spectroscopic analysis of the H-atom spectrum shows two close lines corresponding to the transition from the first excited state (l =1) to the ground state (l = 0), the effect is known as the *fine structure splitting*.

What is the origin of this splitting?

Coupling between the orbital and the spin angular momenta.

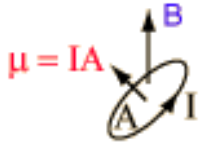


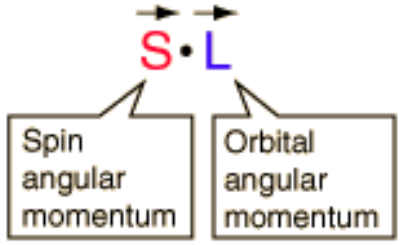


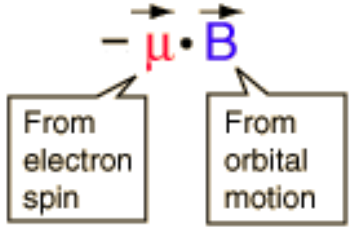
The interaction energy is of the form

$-\vec{\mu}\cdot\vec{B}$

like a magnet in an applied magnetic field.





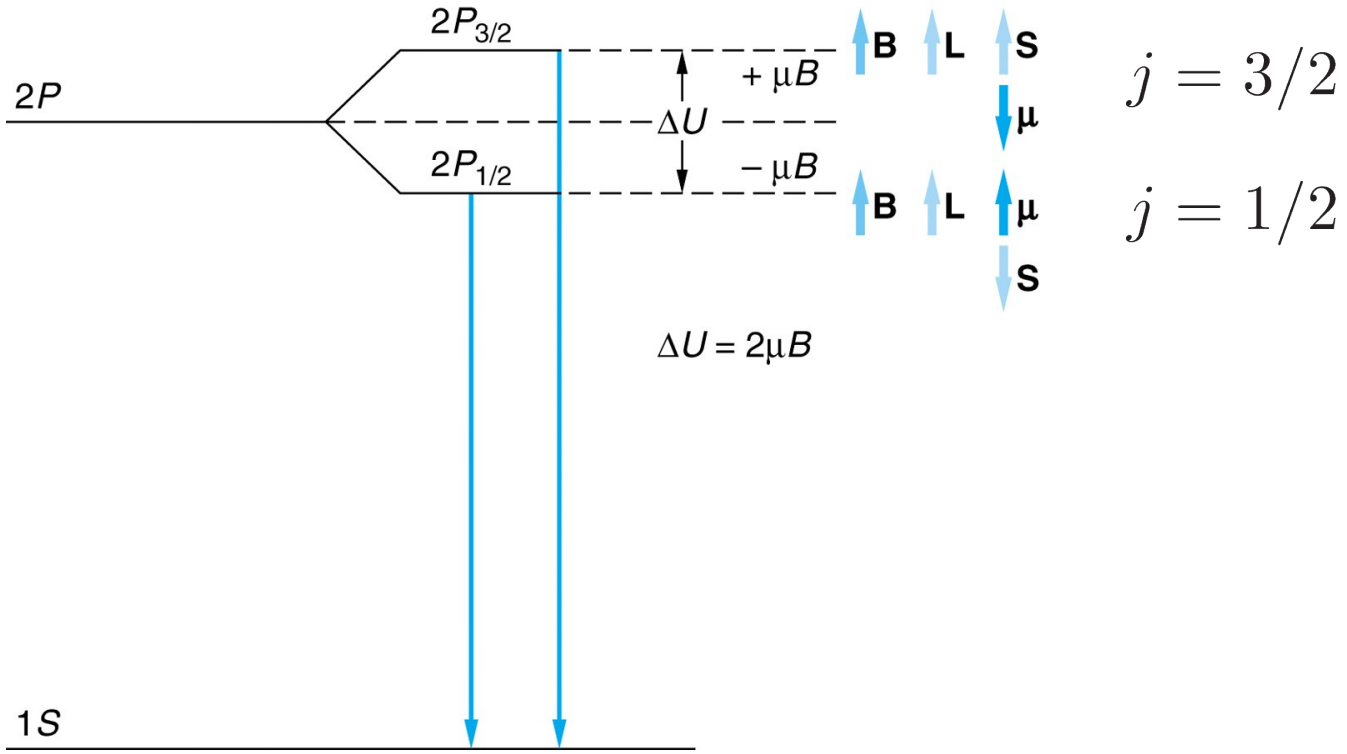


Source: hyperphysics.phy-astr.gsu.edu

Spin-Orbit Coupling. Basic Explanation

$$U = -\mu_z B = \pm \mu_B B$$

(upper sign – spin 'up';
lower sign – spin 'down')



$$j = 3/2$$

$$j = 1/2$$

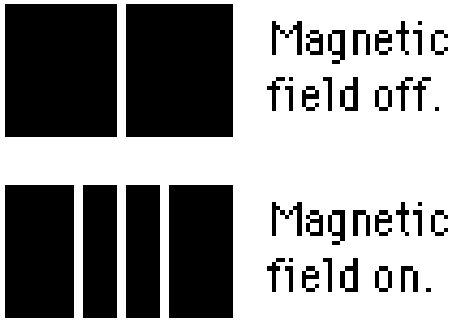
The two lines are 4.5 x 10^{-5} eV apart,
this corresponds to

$$B = \frac{\Delta U}{2\mu_B} \approx 0.39\ T$$

→ significant magnetic Field (10^4 stronger than that of the Earth)

Zeeman Effect

When an atom is placed in an **external magnetic field**, then the energy level with the quantum number j (corresponding to the total angular momentum) is split into $2j + 1$ energy levels corresponding to the possible values of the component of the total angular momentum along the field direction.



Sometimes the splitting due to spin-orbit coupling is referred to as the *internal Zeeman effect*.

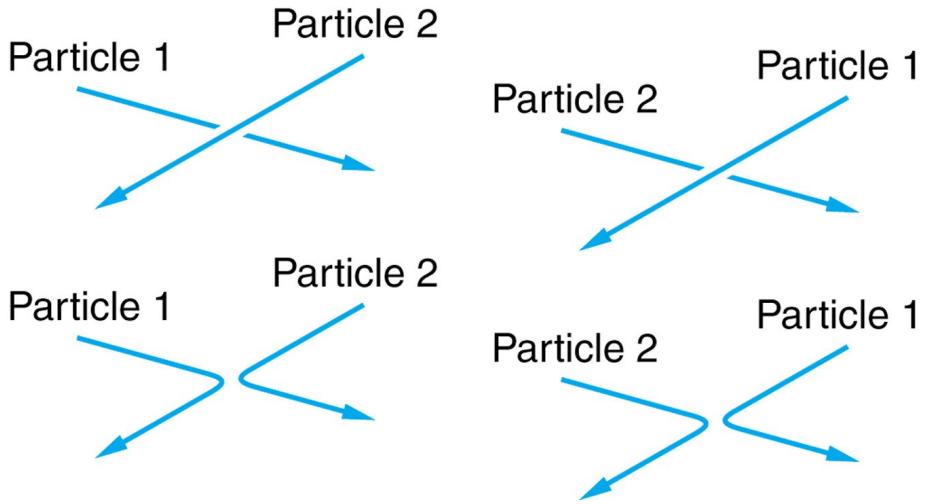
Many-particle Quantum Systems. Bosons and Fermions

Introduction

Recall that in quantum mechanics we cannot define trajectories of individual particles in the same sense as we do in classical mechanics.

We may label particles at t_0 but , since there is no well-defined trajectory (recall the Heisenberg uncertainty principle), we are not able to keep track of them for $t > t_0$.

An important consequence of this fact is **indistinguishability of identical quantum particles.**



equivalent scattering processes

We are only able to say that we detect **a** particle, we do not know if it is 1 or 2.

Two-particle Wave Function

$$\psi(\mathbf{r}_1, \mathbf{r}_2, t)$$

Interpretation

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2$$

probability of finding the particles in the infinitesimal elements of volume around points $\mathbf{r}_1$ and $\mathbf{r}_2$
(for the time being we are ignoring the spin variable)

Normalization condition

$$\int_{\text{all space}} |\psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 = 1$$

Time-Evolution

As always, time evolution is determined by the Schrödinger equation

$$i\hbar \frac{\partial \psi(\mathbf{r}_1, \mathbf{r}_2, t)}{\partial t} = \hat{H}\psi(\mathbf{r}_1, \mathbf{r}_2, t)$$

now with a two-particle Hamiltonian

$$\hat{H} = \frac{\hat{\mathbf{p}}_1^2}{2m_1} + \frac{\hat{\mathbf{p}}_2^2}{2m_2} + V(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, t) = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t)$$

If the potential energy is time-independent, we can find stationary states

$$\psi(\mathbf{r}_1, \mathbf{r}_2, t) = \varphi(\mathbf{r}_1, \mathbf{r}_2)e^{-\frac{i}{\hbar}Et}$$

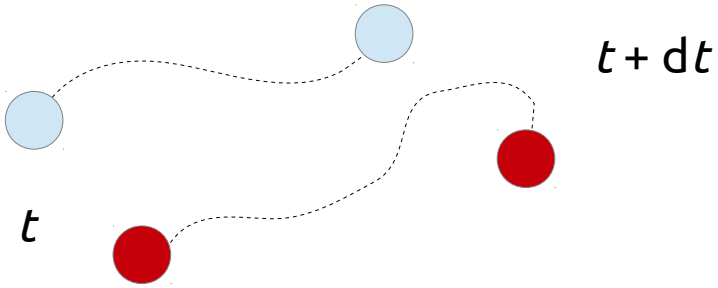
where the space-dependent part satisfies the stationary Schrödinger equation

$$\hat{H}\varphi(\mathbf{r}_1, \mathbf{r}_2) = E\varphi(\mathbf{r}_1, \mathbf{r}_2)$$

$$\left[-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V\right]\varphi(\mathbf{r}_1, \mathbf{r}_2) = E\varphi(\mathbf{r}_1, \mathbf{r}_2)$$

Wave Function of Identical Particles

classical mechanics



particles can be traced individually

quantum mechanics

even if we were able to distinguish the two particles at t, it cannot be said which is which at $t + \mathrm{d}t$ because of the Heisenberg uncertainty principle (lack of trajectories)

Conclusion: **Identical quantum particles are indistinguishable.**

Consider a 2-particle wave function

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2)$$

particle 1 in state α

particle 2 in state β

Wave Function of Identical Particles

In quantum mechanics we are only able to say that there is **a** particle in state α and **a** particle in state β, but we cannot say which is in which state.

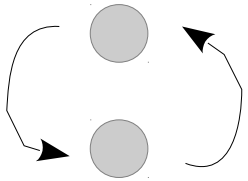
Therefore the wave function in this case should be

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = A\left[\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) \pm \psi_\beta(\mathbf{r}_1)\psi_\alpha(\mathbf{r}_2)\right]$$

Note. We can construct this wave function either with the plus or with the minus sign.

Exchange operator

$\hat{P}$ ⟶ interchanges two particles



Note that $\hat{P}^2 = \hat{I}$ (double interchange leaves the system unchanged), hence its eigenvalues are +1 and -1. Moreover, for identical particles, the exchange operator commutes with the Hamiltonian (remember that we assumed identical particles!).

Symmetry of two-particle wave function

Note that each of the two linear combinations (either with “+” or “-”) is an eigenfunction of the exchange operator.

$$\hat{P}\psi_+(\mathbf{r}_1,\mathbf{r}_2) = A\left[\psi_\alpha(\mathbf{r}_2)\psi_\beta(\mathbf{r}_1) + \psi_\beta(\mathbf{r}_2)\psi_\alpha(\mathbf{r}_1)\right] = \psi_+(\mathbf{r}_1,\mathbf{r}_2)$$

$$\hat{P}\psi_-(\mathbf{r}_1,\mathbf{r}_2) = A\left[\psi_\alpha(\mathbf{r}_2)\psi_\beta(\mathbf{r}_1) - \psi_\beta(\mathbf{r}_2)\psi_\alpha(\mathbf{r}_1)\right] = -\psi_-(\mathbf{r}_1,\mathbf{r}_2)$$

General observation (**symmetrization requirement**)

Wave functions of identical particles (in 3D) are either symmetric or antisymmetric with respect to exchange.

$$\hat{P}\psi(\mathbf{r}_1,\mathbf{r}_2) = -\psi(\mathbf{r}_1,\mathbf{r}_2)$$

FERMIONS

$$\hat{P}\psi(\mathbf{r}_1,\mathbf{r}_2) = \psi(\mathbf{r}_1,\mathbf{r}_2)$$

BOSONS

Fermions. Pauli Exclusion Principle

Pauli Exclusion Principle

Assume that two identical fermion particles are **in the same state**,

then $\hat{P}\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1, \mathbf{r}_2)$. On the other hand, for fermions, the wave function is antisymmetric under exchange, hence $\hat{P}\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_1, \mathbf{r}_2)$.

Both conditions can be satisfied if and only if $\psi(\mathbf{r}_1, \mathbf{r}_2) \equiv 0$, that is no such state can exist.

No two identical fermions can be found in the same state.

Pauli Exclusion Principle

No more than one electron may occupy a given quantum state specified by a particular set of quantum numbers (e.g. principal, orbital, magnetic, and spin quantum numbers for the hydrogen atom).

Spin-Statistics Theorem

Particles with half-integer spin (s = 1/2, 3/2, 5/2,...)
are fermions, i.e. subject to the Pauli exclusion principle.

Particles with integer spin (s = 0, 1, 2,...) are bosons.

Full wave function

The full wave function (including both spatial and spin part) is not a scalar, but rather a *spinor* (algebraically, a column vector)

$$\Psi(\mathbf{x}) = \psi(\mathbf{r})\chi(\mathbf{s})$$

and the general symmetrization requirement has the form

$$\hat{P}\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_1, \mathbf{x}_2)$$

FERMIONS
(*s* = 1/2, 3/2, 5/2,...)

$$\hat{P}\Psi(\mathbf{x}_1, \mathbf{x}_2) = \Psi(\mathbf{x}_1, \mathbf{x}_2)$$

BOSONS
(*s* = 0, 1, 2,...)

Symmetric and Antisymmetric Wave Functions

In solving many-particle problems, the multi-particle wave function is taken as a product of single-particle wave functions (this amounts to neglecting inter-particle interactions).

Then the product has to be made antisymmetric (in the case of fermions) or symmetric (in the case of bosons) in order to account for the proper statistics.

For a system of two particles, the normalized wave functions are

bosons
$$\Psi_+(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}}\left[\Psi_n(\mathbf{x}_1)\Psi_m(\mathbf{x}_2) + \Psi_n(\mathbf{x}_2)\Psi_m(\mathbf{x}_1)\right]$$

fermions
$$\Psi_-(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}}\left[\Psi_n(\mathbf{x}_1)\Psi_m(\mathbf{x}_2) - \Psi_n(\mathbf{x}_2)\Psi_m(\mathbf{x}_1)\right]$$

where *n* and *m* label one-particle states.

Example:
Electron Gas at the Absolute Zero

Example. Electron Gas at Absolute Zero

In solid state physics, many phenomena in metals, involving itinerant conduction electrons are surprisingly well described by using the free electron (electron gas) model, where the (Coulomb) interaction between electrons is completely neglected, while – however – their nature as fermion particles is still taken into account.

The Hamiltonian of such an **electron gas** is $$\hat{H} = \sum_{i=1}^{N} \frac{\hat{\mathbf{p}}_i^2}{2m}$$

The solution of the stationary Schrödinger equation is sought in the form

$$\varphi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \varphi^{(1)}(\mathbf{r}_1) \cdot \varphi^{(2)}(\mathbf{r}_2) \cdot \cdots \cdot \varphi^{(N)}(\mathbf{r}_N) = \prod_{i=1}^{N} \varphi^{(i)}(\mathbf{r}_i)$$

By plugging the product wave function into the Schrödinger equation, and invoking the standard separation-of-variables argument, the *N*-particle problem separates into *N* identical one-particle problems

$$\frac{\hat{\mathbf{p}}_i^2}{2m}\varphi(\mathbf{r}_i) = E^{(i)}\varphi(\mathbf{r}_i)$$

with the total energy of the electron gas $$E = \sum_{i=1}^{N} E^{(i)}$$

Example. Electron Gas at the Absolute Zero

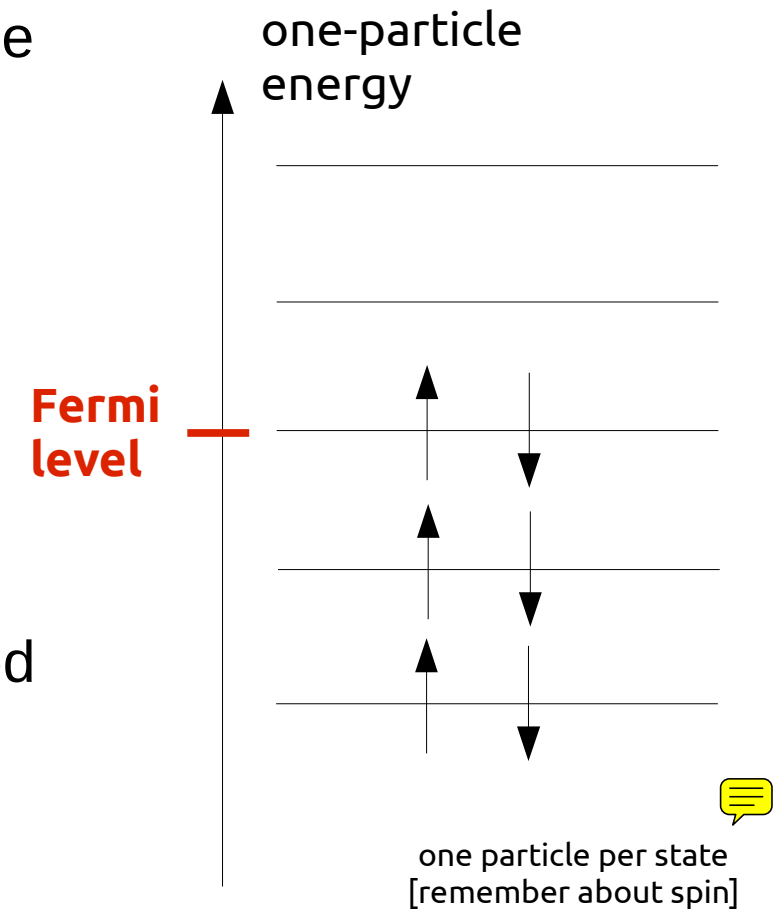
Solution of the one-particle Schrödinger equation gives a spectrum of one-particle energy levels (in this particular case usually periodic boundary conditions are imposed on a particle in a box).

Each of the electrons in the system can occupy any single-particle state, but in the way that does not violate the Pauli exclusion principle. [Formally, it means that the multiparticle wavefunction must be antisymmetric with respect to two-particle interchanges.]

At the absolute zero, the system assumes the configuration of minimum total energy.

This configuration is the configuration with the lowest [N/2] energy levels filled, and the higher ones completely empty.

The highest **one-particle** energy level that is filled at the absolute level is called the **Fermi level** of the system (in this case a metal).



Example. Electron Gas at the Absolute Zero

Given the **Fermi energy**, the corresponding temperature scale (**Fermi temperature**) may be defined as

$$T_F = \frac{E_F}{k_B}$$

k_B = 1.38 x 10^{-23} [J/K]
Boltzmann's constant

Element	*Fermi Energy* [eV]	*Fermi Temperature* x 10^4 [K]
Na	3.24	3.77
K	2.12	2.46
Cu	7.00	8.16
Ag	5.49	6.38
Au	5.53	6.42
Fe	11.1	13.0
Hg	7.13	8.29
Al	11.7	13.6

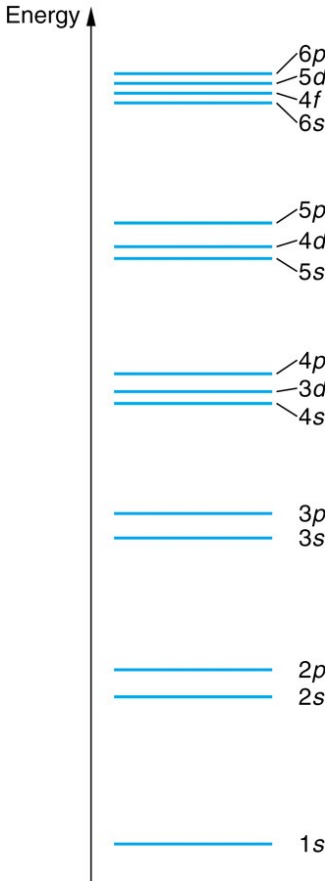
N.W. Ashcroft, N.D. Mermin, *Solid State Physics*

The Periodic Table of Elements

Multi-electron Atoms

Problem: Coulomb interaction between electrons implies that we need to solve a quantum-mechanical many-body problem. No analytical solution possible!

Idea: Take the full (many-particle) wave function to be a product of single-particle wave functions (atomic orbitals) labeled by the principal, orbital, magnetic, and spin quantum numbers.



Remember that this is an approximation!
Interaction between the electrons is neglected!

* *Can be refined by treating interaction as a perturbation within the perturbation theory.*

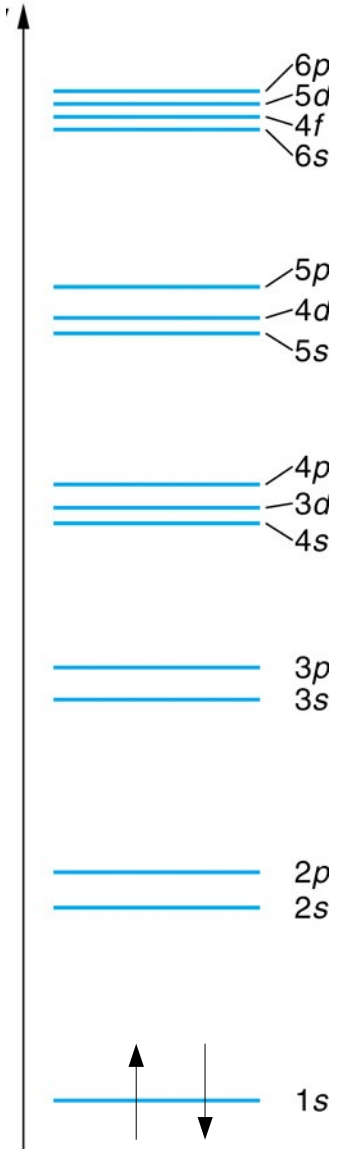
Fill the orbitals (also called *shells*) starting with these of the lowest energy. Make sure that the Pauli Exclusion Principle is not violated.

* **Question**: What is the order the non-completely filled shells are being filled in?

Keyword: *Hund's Rules*

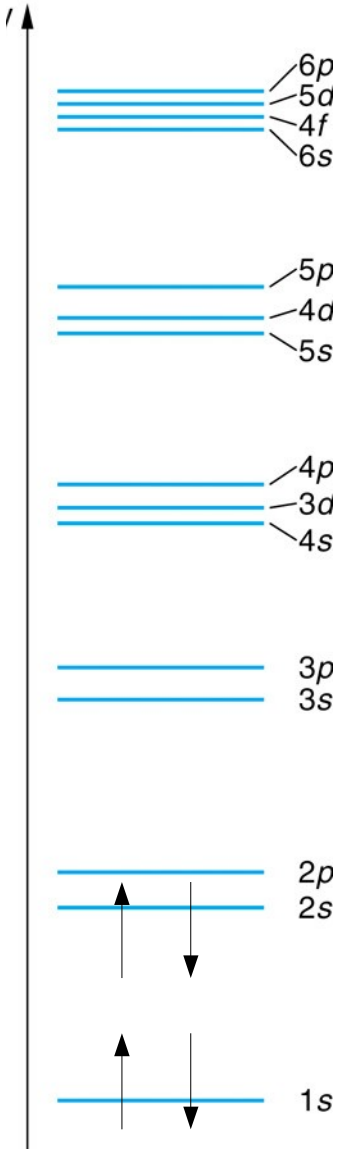
Examples

He



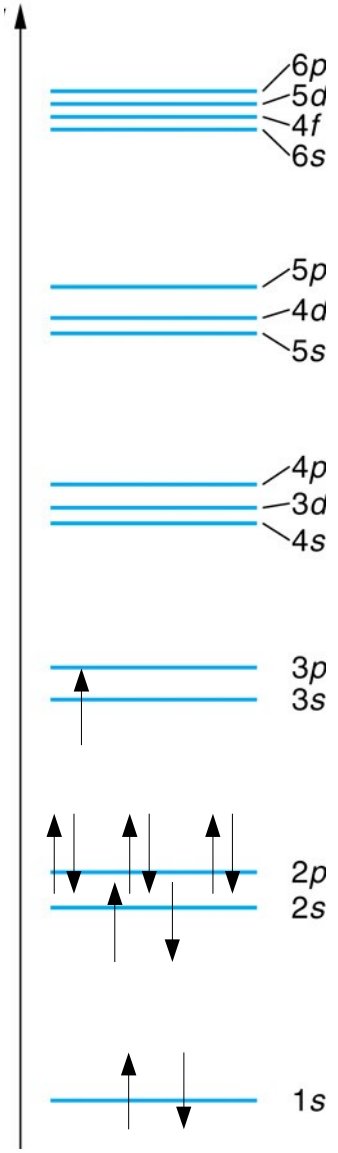
$1s^2$

Be



$1s^2 2s^2$

Na



$1s^2 2s^2 2p^6 3s^1$