Atomic and molecular physics Introduction

Introduction(atomic spectroscopy, energy scales, external fields, Bohr model, discrepancies of Bohr model).

Importance of atomic physics

- Fundamental test for Quantum theory.
- Other branches of physics heavily rely on atomic physics:
- Astrophysics, plasma physics, atmospheric physics, solid state physics, chemical physics and radiation physics.
- Chemistry (analysis, reaction rates).
- biology (molecular structure, physiology).
- Materials science, energy research, fusion studies.

Applications

- Lasers, X-ray technology, NMR, pollution detection, medical applications of devices
- (lasers, NMR etc.).

Atomic spectroscopy:

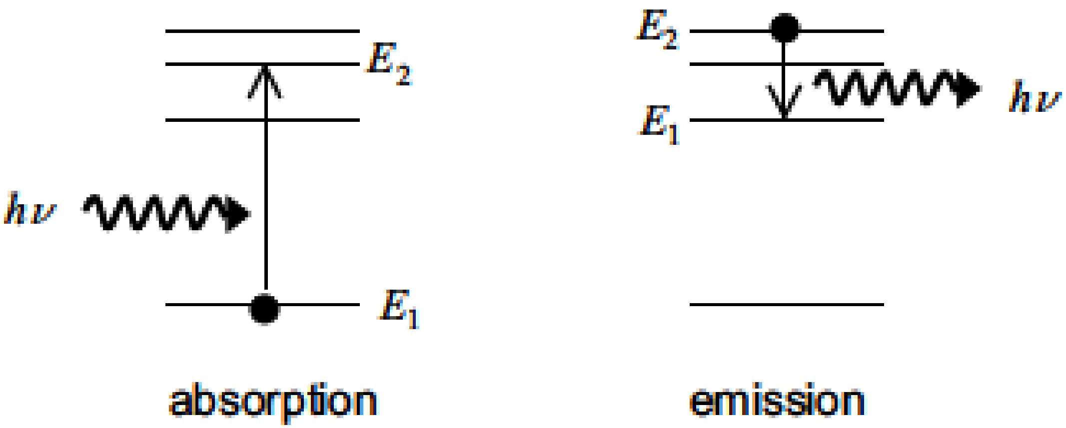
Most of our knowledge – from light matter interaction.

Optics and frequency measurements – the most precise evaluation of energy.

The optical lines of H atoms were extremely important in the development of quantum theory.

Radiative transitions:

- Absorption or emission of light between two quantum states:



- The frequency and wavelength of the light is related to the energy difference:

$$h\nu = \frac{hc}{\lambda} = E_2 - E_1 \, ,$$

Energy units

- 1 eV is the energy that is gained by an electron in a voltage of 1V.
- Energies of electrons in atoms few eV.
- 1eV = 1.6 x 10 $^{-19}$ J
- Another unit: wave numbers units: cm^{-1}

defined as:

$$\overline{\nu} = \frac{1}{\lambda\,(\text{in cm})} = \frac{\nu}{c} = \frac{E}{hc}\,.$$

*** $$1\,\text{eV} = (e/hc)\,\text{cm}^{-1} = 8066\,\text{cm}^{-1}.$$

Recall:

- $h=4x10^{-15}$ eV x s.
- $c=3x10^{8}$ m/sec = $3x10^{10}$ cm/sec.

- $1/hc = 1/(12x10^{-5}) = 8333$

- The advantage of this unit:

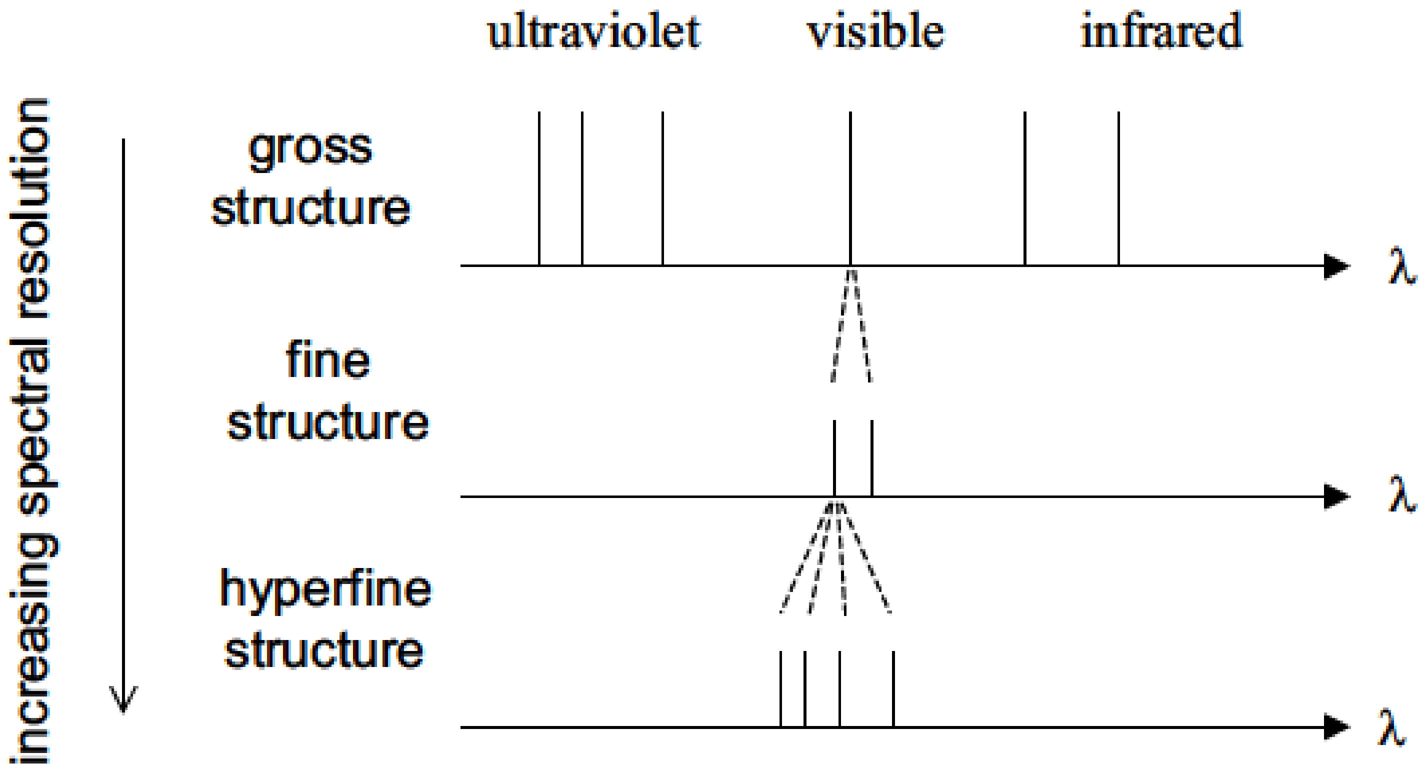
$$\frac{1}{\lambda} = \overline{\nu}_2 - \overline{\nu}_1 \,,$$

Rough energy scales

Energy scale	Energy (eV)	Energy (cm^{-1})	Contributing effects
Gross structure	$1 - 10$	$10^4 - 10^5$	electron–nuclear attraction electron-electron repulsion electron kinetic energy
Fine structure	$0.001 - 0.01$	$10 - 100$	spin-orbit interaction relativistic corrections
Hyperfine structure	$10^{-6} - 10^{-5}$	$0.01 - 0.1$	nuclear interactions

- $B = vXE/c^2$ origin of spin orbit coupling

Hierarchy of spectral lines observed with increasing spectral resolution.



Energy scales of atoms:

- Three level hierarchy:

1. Gross structure – largest interactions within the atoms:

- Kinetic energy of electrons.
- Attraction between the nucleus and the electrons.
- Repulsion between electrons
- Size 1-10 eV and larger. Goes from IR to x-rays.

Fine structure

- Many of the atomic spectral lines are multiplets. In the yellow sodium line:
- There are two lines with wavelengths of 589.0nm and 589.6 nm.
- fine structure energy splitting is 2*.1 x 10^{-3} eV or 17 cm^{-1}.*
- *Naïve description: Electron spin has a*
- *dipole moment of* $\mu_B = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24}\ \mathrm{J\,T^{-1}}$

Interaction with induced magnetic field

- Actually, it is a relativistic phenomenon induced by

- $B = vXE/c^2$ origin of spin orbit coupling.

- Real theories requires the Dirac Eqn.

Hyperfine structure

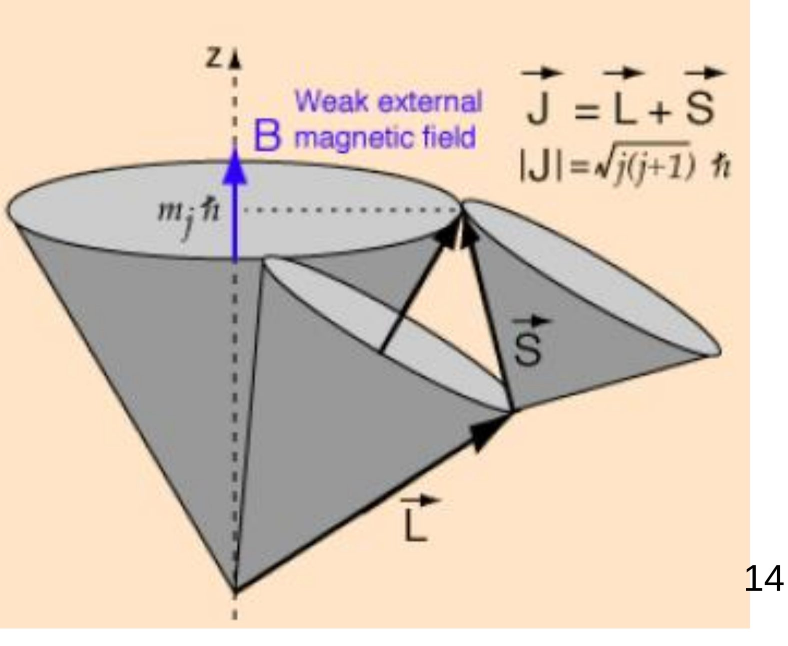
- Even higher resolution – fine structure lines are also multiplets.
- Hyperfine splitting – naively – the interaction of the nuclear spin magnetic moment (μ_B */ 2000*) with the magnetic field induced by the electron's motion.

- In reality – dipole – dipole and exchange interactions between the two spins

External magnetic field:

- Usually when the magnetic field is not so large, the coupling between the orbital angular momentum and the spin angular momentum – prevails:

- hv=gJ β H



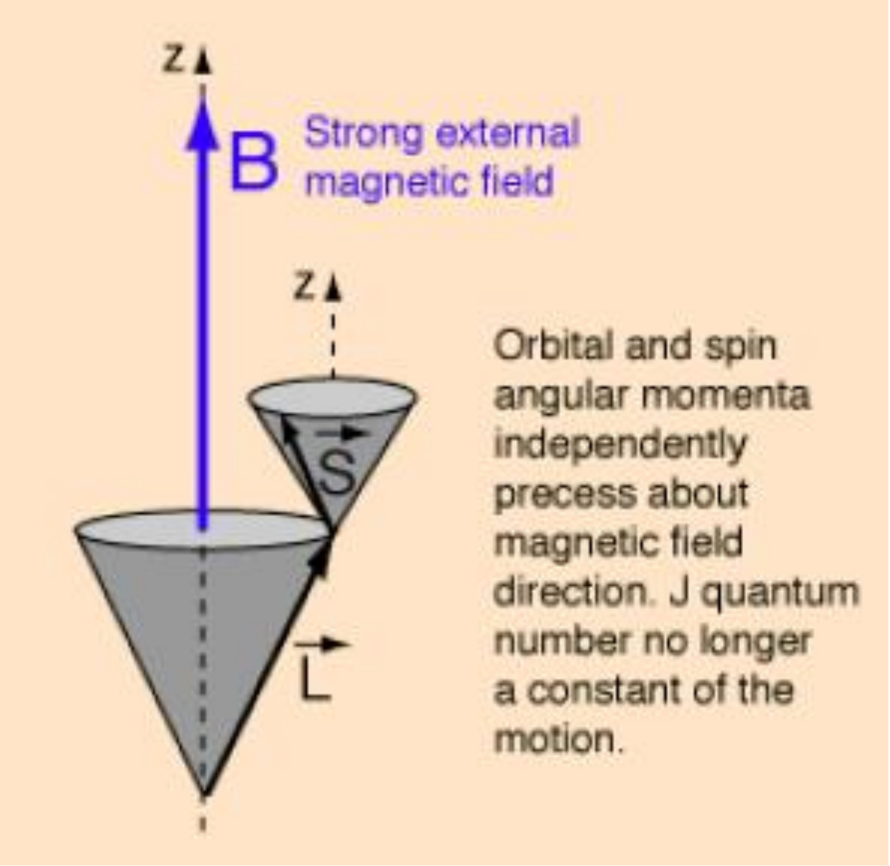
In strong magnetic field: Paschen back effect

- The strong field breaks the spin orbit coupling.

- The two spins precesse Independently.

  hv=gs β H

  hv=gL β H

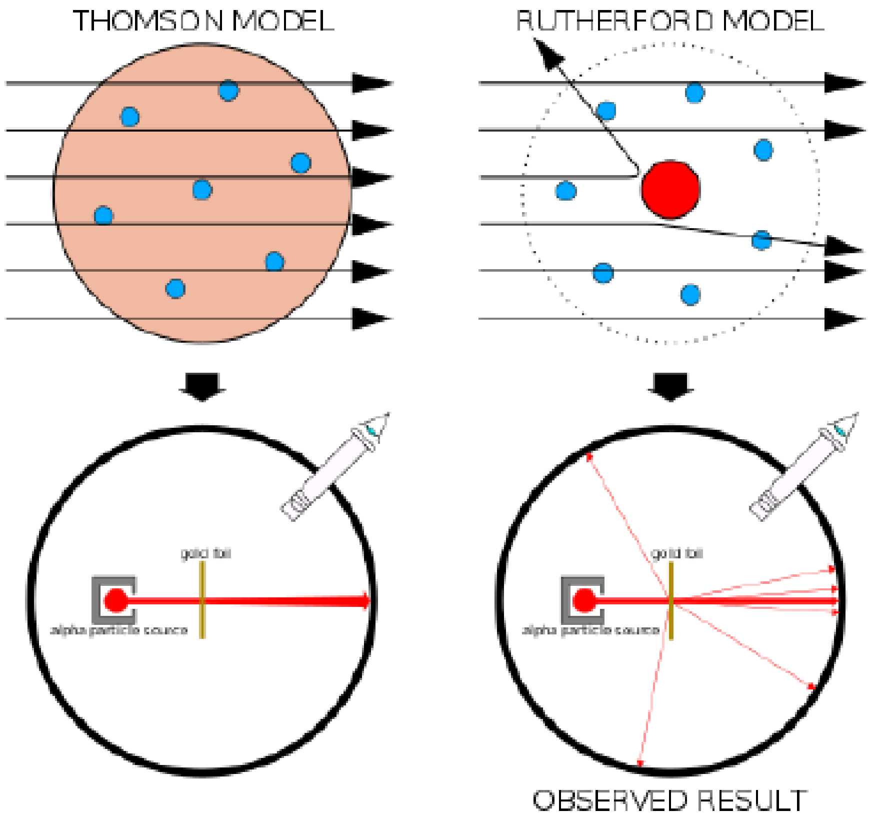


In strong electric fields – stark effect:

- Deformation of atomic structure – as a result of electric filed (The nucleus and the electrons are moving in opposite directions and their energy change.

The Bohr model

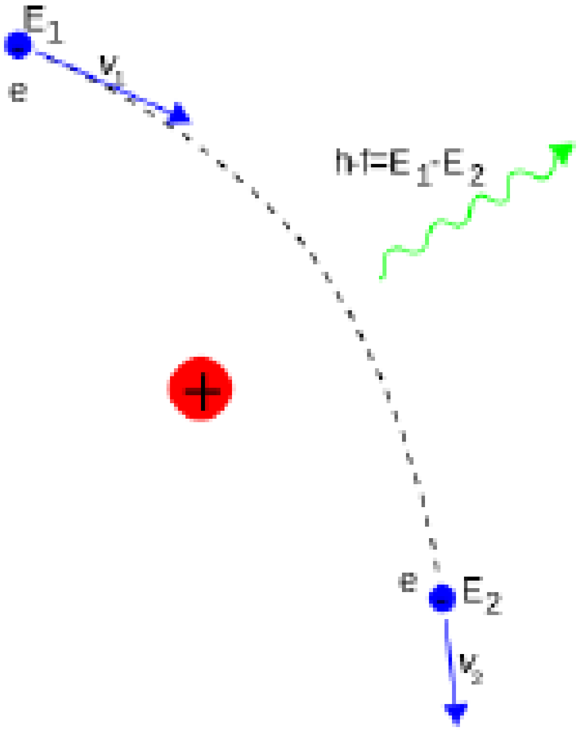
- 1911 – Rutherford experiment (actually the Geiger Marsden experiment).
- Scattering of α particle from a thin metal foil:
- Proof of the existence of positively charged nucleus



Left: Had Thomson's model been correct, all the alpha particles should have passed through the foil with minimal scattering.
Right: What Geiger and Marsden observed was that a small fraction of the alpha particles experienced strong deflection.

Bremsstrahlung is expected

- High energy electron is expected to slow down and emit radiation till it collides with the nucleus.



Bremsstrahlung produced by a high-energy electron deflected in the electric field of an atomic nucleus

The Bohr suggestion:

- Quantized angular momentum in units of $\hbar$ ($\hbar = h/2\pi$)

$$L = n\hbar,$$

- n is an integer.
- light is only emitted or absorbed when the electron jumps from one orbit to another.

The orbit must correspond to a fixed number of de Broglie wavelengths.

- For a circular orbit:

$$2\pi r = \text{integer} \times \lambda_{\text{deB}} = n \times \frac{h}{p} = n \times \frac{h}{mv};$$

In term of angular momentum:

$$L \equiv mvr = n \times \frac{h}{2\pi}.$$

Recall: The de Broglie wavelength

- The Einstein relation: $E = mc^2$
- The Planck Eqn: $E = h\nu$
- Equality: $mc^2 = h\nu$
- Particle do not propagate in the speed of light.

$$mv^2 = h\nu$$

$$mv^2 = \frac{hv}{\lambda} \qquad \lambda = \frac{hv}{mv^2} = \frac{h}{mv}$$

Energy quantization:

- Centripetal force – provided by the Coulomb interaction

$$F = \frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}.$$

- m is the reduced mass

Recall: the reduced mass

- Two interacting bodies:

$$\mathbf{F}_{12} = m_1 \mathbf{a}_1. \qquad \mathbf{F}_{21} = m_2 \mathbf{a}_2.$$

- Newton s third law:

$$\mathbf{F}_{12} = -\mathbf{F}_{21}. \qquad m_1 \mathbf{a}_1 = -m_2 \mathbf{a}_2.$$

$$\mathbf{a}_2 = -\frac{m_1}{m_2}\mathbf{a}_1.$$

Relative acceleration:

$$\mathbf{a}_{\rm rel} = \mathbf{a}_1 - \mathbf{a}_2 = \left(1 + \frac{m_1}{m_2}\right)\mathbf{a}_1 = \frac{m_2 + m_1}{m_1 m_2} m_1 \mathbf{a}_1 = \frac{\mathbf{F}_{12}}{m_{\rm red}}$$

E = -

The total energy:

- Kinetic + potential energy:

$$\frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

- Using $$F = \frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

we get: $$\frac{Ze^2}{4\pi\varepsilon_0 r^2} \; x \; \frac{r}{2} = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

- We get total energy $= - \dfrac{Ze^2}{8\pi\varepsilon_0 r}$

Kinetic energy can be written as:

$$\frac{mv^2}{2} = \frac{(mvr)^2}{2mr^2} = \frac{n^2h^2}{8\pi^2 mr^2} = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

Kinetic energy of electron	expressed in terms of angular momentum.	Use quantization of angular momentum.	Set equal to total energy of classical orbit.

USING: $r = \frac{n^2h^2\varepsilon_0}{Z\pi me^2}$ $E = -\frac{Z^2me^4}{8n^2h^2\varepsilon_0^2}$

We arrived to this equation by:

- By subsituting r in E we get:

$$\frac{Ze^2 \text{ x } Z\pi me^2}{8\pi\varepsilon_0 n^2 h^2 \varepsilon_0} = \frac{Z^2 e^4 \, m}{8\varepsilon_0{}^2 n^2 h^2}$$

The Rydberg energy:

- The formula

$$E = -\frac{Z^2 m e^4}{8 n^2 h^2 \varepsilon_0^2}$$

Can be written as: $$E_n = -\frac{R'}{n^2}$$

Where: $$R' = \left(\frac{m}{m_e} Z^2\right) R_\infty hc\,,$$

and $R_\infty hc$ is the Rydberg energy:

This is a fundamental constant

$$R_\infty hc = \frac{m_e e^4}{8\epsilon_0^2 h^2} \, .$$

Value of the Rydberg energy is:

2.17987×10^{-18} J = 13.606 eV.

R’ is the effective Rydberg constant

- The reduced mass of a proton and an electron:

$$m = m_e \times \frac{m_p}{m_e + m_p} = 0.9995\, m_e$$

- The effective Rydberg constant for the Hydrogen atom:

$$R_H = 0.9995\, R_\infty hc\,.$$

A difference 0.05% is detectable in spectroscopy.

Quantization of radius and velocity

- Using (observed before):

$$\frac{n^2h^2}{8\pi^2mr^2} = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

We got:

$$r = \frac{n^2h^2\varepsilon_0}{Z\pi me^2} = \frac{n^2a_0}{Z}$$

$$a_0 = 0.0529nm = Bohr\ \ radius$$

Velocity quantization:

- Recall: $$\frac{m_e v^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$
- Thus: $$v^2 = \frac{Ze^2}{m_e 4\pi\varepsilon_0 r}$$
- We found: $$r = \frac{n^2 h^2 \varepsilon_0}{Z\pi m e^2}$$
- Substitution: $$V^2 = \frac{Ze^2 Z\pi m e^2}{m_e 4\pi\varepsilon_0 n^2 h^2 \varepsilon_0} = \frac{Z^2 e^4}{4\varepsilon_0{}^2 n^2 h^2}$$

Fine structure term

- Velocity quantization: $V = \dfrac{Ze^2}{2\varepsilon_0 nh}$
- Can be written as: $v_n = \alpha \dfrac{Z}{n} c\,.$
- Where $\alpha = \dfrac{e^2}{2\epsilon_0 hc}\,.$
- Is the fine structure dimensionless constant $1/137.04$

Optical transitions:

- Recall: $$E_n = -\frac{R'}{n^2}$$
- Thus: $$h\nu = R_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$
- The emission with $n_1 = 1$
- Lyman series (in UV)

  and with $n_1 = 2$
- Balmer series (visible)

Problems with the Bohr model

- Inconsistence with the uncertainty principle:
- In the Bohr model:

$$p = mv = \left(\frac{\alpha Z}{n}\right) mc = \frac{n\hbar}{r_n} .$$

By substitution of α and using r_n definition:

$$\frac{e^2 Zmc}{2\varepsilon_0 hcn} = \frac{Ze^2 m}{2\varepsilon_0 hn} = \frac{Ze^2 m \cdot 2\pi h^2 n}{2\varepsilon_0 hn \cdot 2\pi h^2 n} = \frac{Z\pi me^2 \cdot hn}{n^2 h^2 \varepsilon_0 \cdot 2\pi}$$

The uncertainty principle gives:

$$\Delta p \sim \frac{\hbar}{\Delta x} \approx \frac{\hbar}{r_n} .$$

Classical and quantum limit:

- In other words we get:

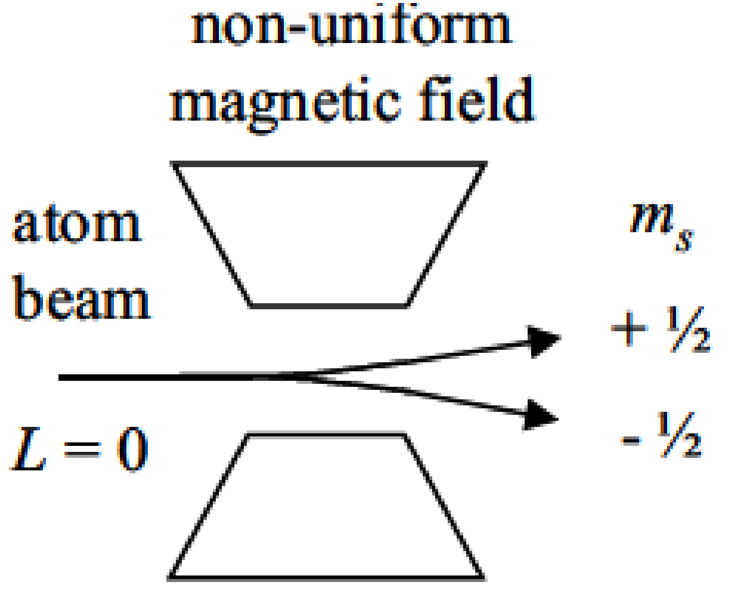
$$|p| \approx n\Delta p\,.$$

- The magnitude of p is undefined unless n is large.

- The Bohr model is a semiclassical model, and is more precise in the more classical regime (large n).

Spin-another limitation of the Bohr model.

- The Stern Gerlach experiment:



Atoms with L=0 still have angular momentum – The spin - a pure quantum phenomenon.

The spin

- Actually explained by the relativistic Dirac equation.
- Stern Gerlach experiment - The z component of the spin has 2 components.
- The electron is described by two quantum numbers: $s = 1/2 \quad m_s = \pm 1/2.$
- The magnitude of the spin angular momentum: $S = \sqrt{s(s+1)}\hbar$,

  and the z component: $S_z = m_s \hbar$

The Pauli exclusion principle

- Obeyed by particles with half integer spin.
- Particles with integer spin (alpha particles) do not obey it.
- The principle: only one electron can occupy a particular quantum state.