

Multielectron atoms

- Please fill out FCQs and return to the front.
- The last homework set will be out today and will be due on Thursday 4/30 (one day later than normal).
- HW11 average was 33 and HW12 average was 41.
- Final is on 5/2 from 1:30pm-4:00pm in G125 (this room)
- Rest of the semester:
 - Today we will finish spin and start thinking about multielectron atoms.
 - Friday we will cover the Pauli Exclusion Principle and find out where the periodic table comes from
 - Monday we will discuss the fundamentals of quantum mechanics
 - Wednesday and Friday of next week will be review.

Summary of hydrogen wave function

The hydrogen wave function is

$$\psi(r, \theta, \phi) = R_{nl}(r)\Theta_{\ell m}(\theta)e^{im\phi} \quad \text{or} \quad \psi(r, \theta, \phi) = R_{nl}(r)Y_{\ell m}(\theta, \phi)$$

The quantum numbers are:

$n = 1, 2, 3, \dots$ = principal quantum number

$$E_n = -Z^2 E_R / n^2$$

$\ell = 0, 1, 2, \dots, n-1$ = angular momentum quantum number

= s, p, d, f, ...

$$L = \sqrt{\ell(\ell + 1)}\hbar$$

$m = 0, \pm 1, \pm 2, \dots, \pm \ell$ is the z-component of angular momentum quantum number

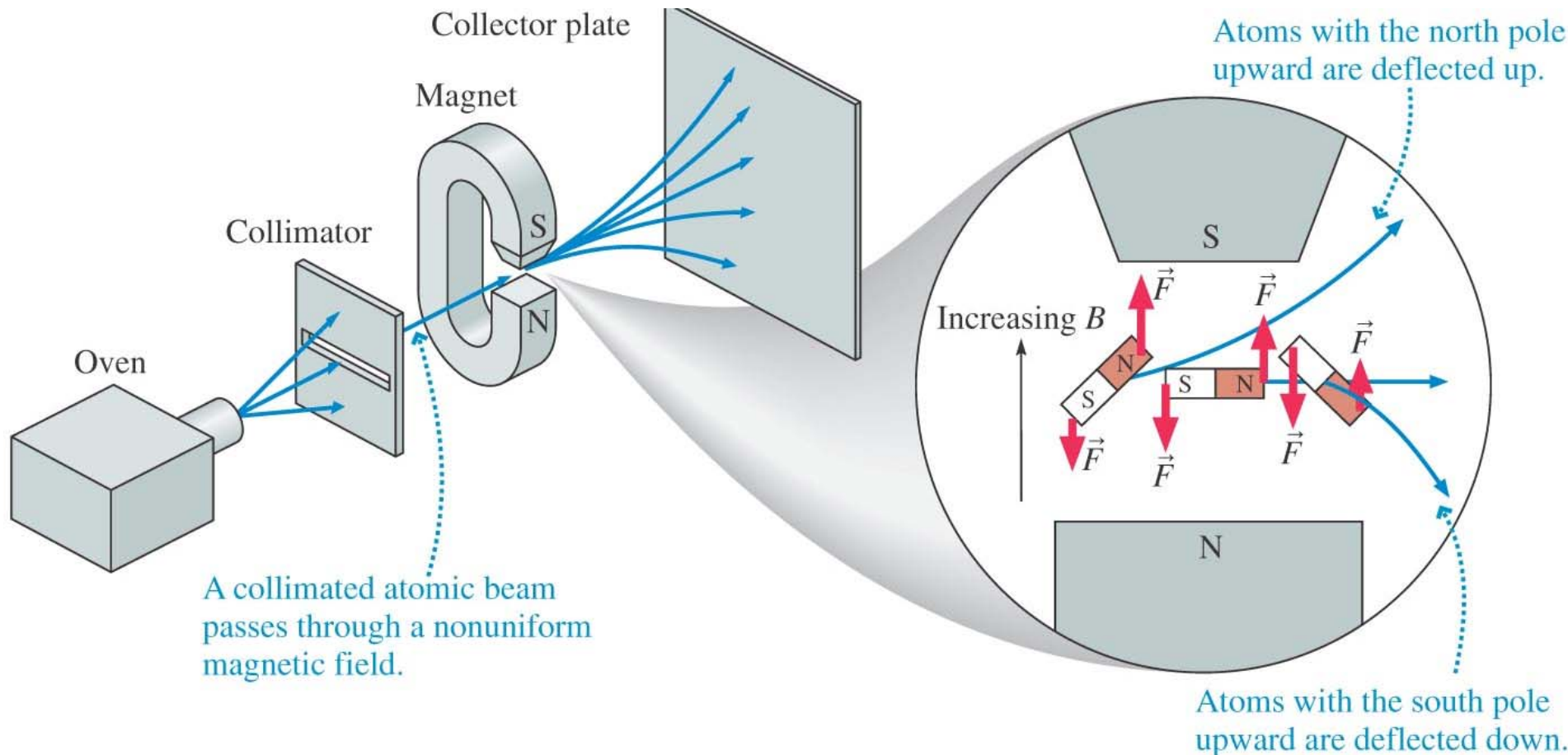
$$L_z = m\hbar$$

Note: For an angular momentum ℓ , there are $2\ell+1$ choices for m .

Stern-Gerlach experiment

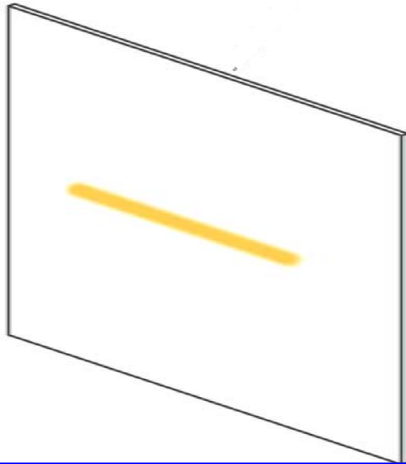
Placing a magnetic dipole in an external uniform magnetic field \vec{B} causes a torque on the dipole $\vec{\tau} = \vec{\mu} \times \vec{B}$ but no net force.

A Stern-Gerlach experiment sends atoms through a nonuniform magnetic field which can exert a net force on a magnetic dipole.

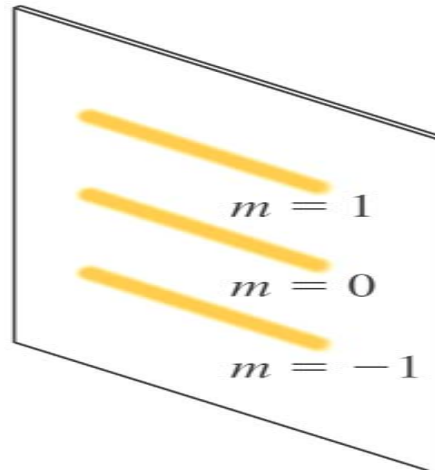


Result of Stern-Gerlach

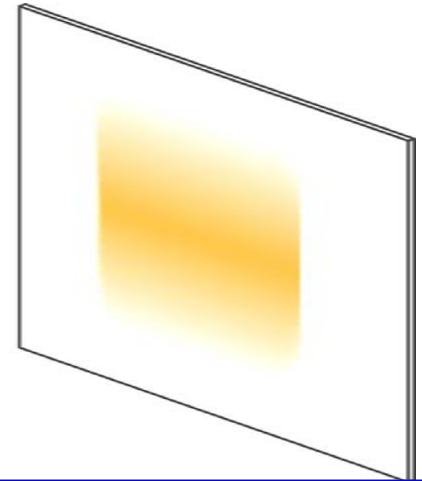
Sending in (ground state) hydrogen atoms which were believed to have $\ell=0$, one expects no deflection.



If $\ell \neq 0$, would find $2\ell+1$ bands (odd number)

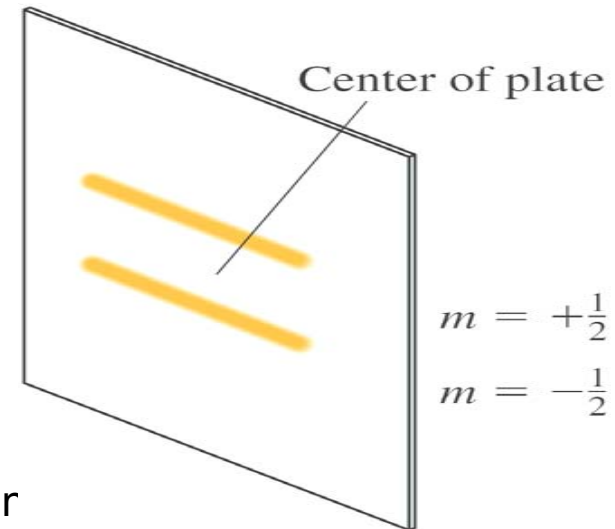


Classically, one would see a broad band



Doing the experiment gave two lines.

Interpretation: $\ell=0$ but the electron itself has some *intrinsic* angular momentum which can either be $-\hbar/2$ or $\hbar/2$.



Electron spin

$\ell = 0, 1, 2, \dots, n-1$ = orbital angular momentum quantum number

$m = 0, \pm 1, \pm 2, \dots, \pm \ell$ is the z-component of orbital angular momentum

$$L_z = m\hbar$$

$$L = \sqrt{\ell(\ell + 1)}\hbar$$

$s =$ spin (or intrinsic) angular momentum quantum number. The actual spin angular momentum is

$$S = \sqrt{s(s + 1)}\hbar$$

Electrons are $s = \frac{1}{2}$ (spin one-half) particles. Since this never changes, it is often not specified.

$m_s =$ z-component of spin angular momentum and can have values of $m_s = -s, -s+1, \dots, s-1, s$. The actual z-component of spin angular momentum is

$$S_z = m_s\hbar$$

For an electron only two possibilities: $m_s = \pm s = \pm \frac{1}{2}$

An electron with $m_s = +\frac{1}{2}$ is called spin-up or \uparrow

An electron with $m_s = -\frac{1}{2}$ is called spin-down or \downarrow

The full hydrogen wave function

The spatial part of the wave function is $\psi(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$ with quantum numbers n, ℓ, m giving energy $E_n = -Z^2 E_R / n^2$, orbital angular momentum $L = \sqrt{\ell(\ell + 1)}\hbar$ and z-component of orbital angular momentum $L_z = m\hbar$

To fully specify the wave function we also need the spin of the electron. This is set by the quantum number m_s which can be either $+1/2$ (spin up) or $-1/2$ (spin down).

So the full set of quantum numbers that describe the electron in an atom are n, ℓ, m, m_s .

Note, the electron is not really spinning. It is a helpful way of thinking about what is technically *intrinsic* angular momentum.

Also, the total angular momentum \vec{J} is the sum of orbital and intrinsic angular momentum: $\vec{J} = \vec{L} + \vec{S}$ and $J_z = L_z + S_z$

Remember degeneracy refers to multiple quantum number combinations with the same energy. For hydrogen, the energy is set by n . For a given n consider all of the combinations of quantum numbers ℓ , m , and m_s . Remember $\ell=0,1\dots n-1$ and $m=0,\pm 1,\pm 2\dots\pm 2\ell$ and $m_s=\pm 1/2$. How many combinations are there?

A. n

B. $2n$

C. n^2

D. $2n^2$

E. None of the above

Before we found out about spin we determined the number of degeneracies for the first three energy levels to be 1, 4, 9. In fact the degeneracy is n^2 .

For each of these ℓ and m combinations, there are now two possibilities for m_s and so the degeneracy is doubled to $2n^2$.

Multielectron atoms

So far we just considered an electron interacting with the nucleus.

When there are multiple electrons we have to consider the effect of the electrons on each other. This is difficult to do precisely.

So we need to make approximations.

The outer electrons are *screened* by the inner electrons so the effective charge they feel is less than Ze which we can write as $Z_{\text{eff}}e$. If one electron is well outside of the other $Z-1$ electrons it feels a charge of just $1e$ (i.e. $Z_{\text{eff}} = 1$).

This *screening* is basically just an application of Gauss' law

The innermost electrons feel nearly the full charge of Ze so $Z_{\text{eff}} \approx Z$.

We can use our findings for hydrogen-like ions by replacing Z with Z_{eff} so the energy is $E_n = -Z_{\text{eff}}^2 E_R / n^2$ and the most probable radius is $r_{\text{mp}} \approx n^2 a_B / Z_{\text{eff}}$

Clicker question 2

Set frequency to DA

Will the 1s orbital be at the same energy/radius for different atoms such as H, He, Li, Be, ...?

A. yes/yes

B. no/no

C. yes/no

D. no/yes

E. None of the above

$$E_n = -Z_{\text{eff}}^2 E_R / n^2$$

$$r_{\text{mp}} \approx n^2 a_B / Z_{\text{eff}}$$

The 1s state is always closest to the nucleus and thus will feel nearly the full force of all Z protons so $Z_{\text{eff}} \approx Z$.

Since $E_n = -Z_{\text{eff}}^2 E_R / n^2$, the energy will decrease (get more negative) as Z increases.

Since $r_{\text{mp}} \approx n^2 a_B / Z_{\text{eff}}$, the most probable radius will decrease (get smaller) as Z increases.