Hydrogen Atom Energies

The significance of the zero in energy is that the electron is free from the hydrogen nucleus.

Electron is free

Scaled plot of hydrogen levels in electron volts.

$$E = \frac{-13.6\ eV}{n^2}$$

The levels get closer together as they approach the ionization energy.

Electron is bound in atom

Ground state of the hydrogen electron

$$E_n = \{-me^4 / 32\pi^2\varepsilon_0^2\hbar^2\}\ \{1/n^2\} = -13.6\ eV\ /\ n^2$$

Selection Rules

E_2 Absorption can occur only when

E_1 $\Delta E = h\upsilon = E_2 - E_1$

A downward transition involves emissioin of a photon of energy:

$E_{photon} = h\upsilon = E_2 - E_1$
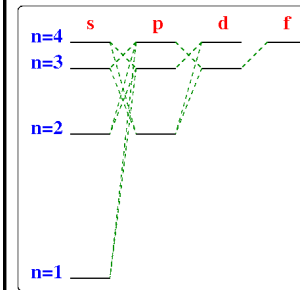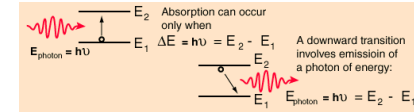
- Transitions can only occur between states that differ in ℓ by 1, i.e.

$$\Delta\ell = \pm 1$$

Hydrogen Atom Spectroscopy
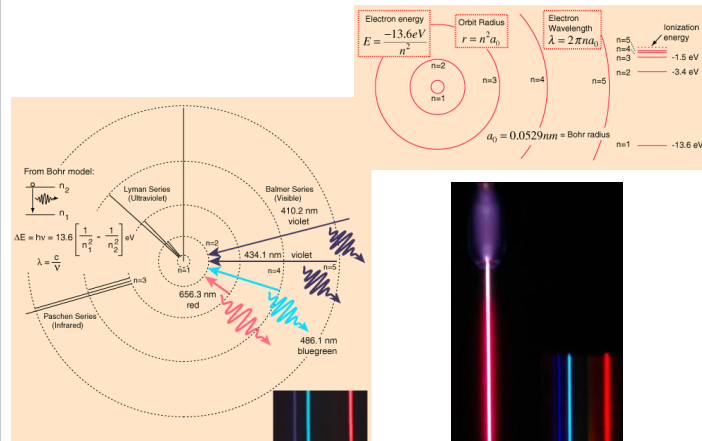
Where is the Electron ?

- Electron probability density:

$$|\psi|^2 = |RY|^2$$

- Probability of finding the electron in a small region of the atom volume:

$$r^2\ dr\ d\Omega = r^2\ dr\ d(\cos\theta)\ d\varphi \qquad \Omega = \text{solid angle}$$

is:

$$|R_{n\ell}(r)\ Y_{\ell m}(\theta,\varphi)|^2\ r^2\ dr\ d\Omega$$
$$= |rR_{n\ell}(r)|^2\ |Y_{\ell m}(\theta,\varphi)|^2\ dr\ d\Omega$$
$$= |\chi_{n\ell}(r)|^2\ |Y_{\ell m}(\theta,\varphi)|^2\ dr\ d\Omega$$

- Ask a mathematician !

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Radial Dependence

- Radius of first Bohr orbit:
  $$a_0 = 4\pi\varepsilon_0\hbar^2 / me^2 = 0.0529 \text{ nm}$$
- Radial wave functions $R_{n\ell}$:
  $$R_{10} = 2 \{1/a_0\}^{3/2} \exp\{-r/a_0\}$$
  $$R_{20} = [1/2\surd\{2\}] \{1/a_0\}^{3/2} \{2 - r/a_0\} \exp\{-r/a_0\}$$
- Radial probability density:
  $$P(r) = |\chi_{n\ell}|^2 = |rR_{n\ell}|^2$$
- As $r \Rightarrow 0$:
  $$\chi_{n\ell} = rR_{n\ell} \Rightarrow 0$$
  $$R_{n\ell=0} \nRightarrow 0 \qquad s \text{ wave density}$$
  $$R_{n\ell\neq0} \Rightarrow 0 \qquad p, d,... \text{ wave density}$$

Radial Distributions: n = 2

2s

2p
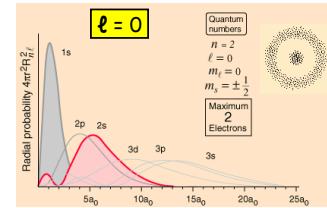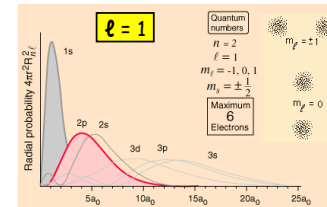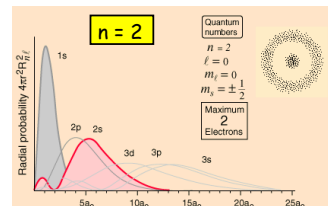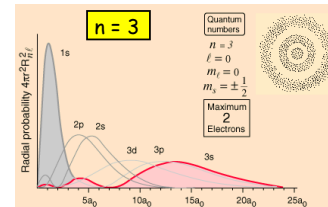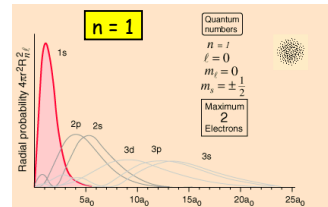
Radial Distributions: ℓ = 0

s waves

Radial Distributions: n = 3
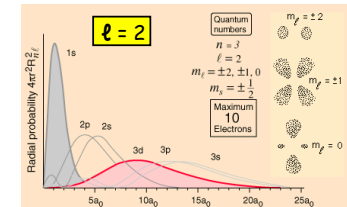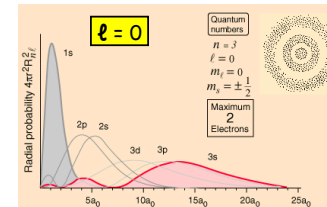
3s, 3p, 3d

H atom applet (also on VITAL)

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Angular Dependence

> Spherical harmonics $Y_{\ell m}$:

$Y_{00} = \sqrt{1/4\pi}$ $|\psi|^2$ isotropic

$Y_{11} = -\sqrt{3/8\pi}\ \sin\{\theta\}\ \exp\{i\varphi\}$ $|\psi|^2 \propto \sin^2\{\theta\}$

$Y_{10} = \sqrt{3/4\pi}\ \cos\{\theta\}$ $|\psi|^2 \propto \cos^2\{\theta\}$

$Y_{1-1} = \sqrt{3/8\pi}\ \sin\{\theta\}\ \exp\{-i\varphi\}$ $|\psi|^2 \propto \sin^2\{\theta\}$

$Y_{22} = \sqrt{15/32\pi}\ \sin^2\{\theta\}\ \exp\{2i\varphi\}$ $|\psi|^2 \propto \sin^4\{\theta\}$

$Y_{21} = -\sqrt{15/8\pi}\ \sin\{\theta\}\ \cos\{\theta\}\ \exp\{i\varphi\}$ $|\psi|^2 \propto \sin^2\{\theta\}\cos^2\{\theta\}$

$Y_{20} = \sqrt{5/16\pi}\ \{3\cos^2\{\theta\} - 1\}$ $|\psi|^2 \propto (3\cos^2\{\theta\} - 1)^2$

> In general $Y_{\ell m}$:
> > has φ dependence $\exp\{im\varphi\}$
> > has polynomials in sin/cos$\{\theta\}$ to order ℓ

Summary: Hydrogen Atom

> Electron moving under influence of central potential:
> > $V(r) = \{-e^2 / 4\pi\varepsilon_0 r\}$
> Energy quantisation:
> > $E_n = \{-me^4/8\varepsilon_0^2 h^2\}\{1/n^2\} = -Rhc/n^2 = -13.6\ eV / n^2$
> Accidental degeneracy on ℓ :
> > $\ell = 0, 1, 2 \ldots n-1$
> Degeneracy on m :
> > $m = -\ell, -\ell+1, \ldots 0, \ldots \ell-1, \ell$
> Photon emitted/absorbed for $\Delta\ell = \pm 1$ selection rule
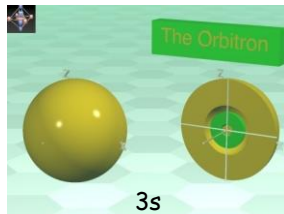> Electron wave function:
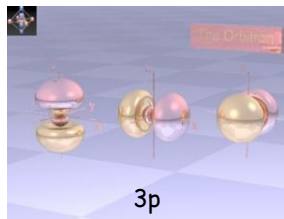> > $\psi_{n\ell m} = R_{n\ell}(r)\ Y_{\ell m}(\theta,\varphi)$

3D Atomic Orbitals (n=3)

The Orbitron

http://www.shef.ac.uk/chemistry/orbitron

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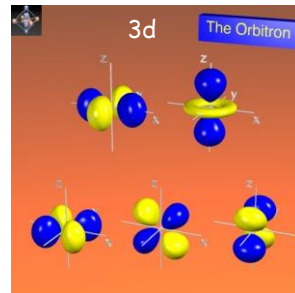
9. Wave Dynamics of Particles: Scattering

> 9.1 Potential Step
> 9.2 Potential Barrier
> 9.3 Attractive Potential Well

Scattering

> A particle moves under the influence of $V(x)$ (1D) but is not confined
> It is <u>unbound</u>:
$$|x| \rightarrow \infty \,, \; |\psi|^2 \not\rightarrow 0$$
> It has a <u>finite</u> (but not infinite) probability density $|\psi|^2$ when <u>far</u> from scattering centre ($V(x)$)
> It is (almost) a <u>free</u> particle <u>far</u> from region of $V(x)$
> Free particle:
$$\psi = A \exp\{ikx\} \text{ or } B \exp\{-ikx\} \quad \text{(or a combination)}$$
> Non-localised:
$$k > 0 \text{ and } \sqrt{\{2mE\}} / \hbar \text{ real} \Rightarrow E > 0 \quad \text{positive energy}$$
> Also remember:
$$\psi \text{ and } d\psi/dx \text{ are continuous}$$

Classical Scattering
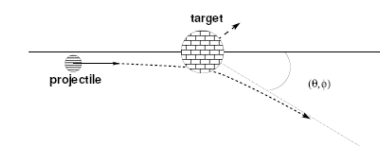
> A projectile hits a target and is scattered

> Particle scattering
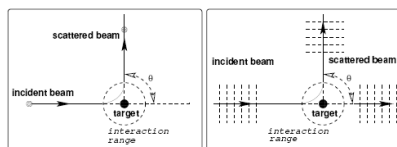
> Wave scattering

Scattering: What is Measured ?

> Incident particle:
> > Probability that it is scattered with a given energy, momentum

> Incident particle flux:
> > Flux that it is scattered with a given energy, momentum

> Flux is defined as the number of particles per unit time across unit perpendicular area

What is this in quantum physics ?

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Continuity of Flow

Velocity v
Area A
Density ρ

Changing density:
"flow" in = "flow" out

Constant density:
water in a pipe:
water in = water out

See QMIntro.pdf

- In classical physics, "flux" is conserved
- Current $J = n\, v\, A$
  - n = number density
    = particles per unit volume
- Current density $j = J / A$
  $$j = n\, v$$
- Conservation equation (1D)

$$\partial\rho/\partial t = -\partial j/\partial x$$

rate of change of density =
   - gradient of current density

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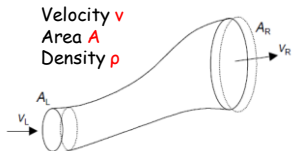

Quantum Flux Conservation

- Using the free particle solution:
  $\psi = A \exp\{ikx\} + B \exp\{-ikx\}$
- It is found that:
  $\psi^* \, d\psi/dx - \psi \, d\psi^*/dx = 2ik\,[|A|^2 - |B|^2]$
- Or:
  $-i[\psi^* \, d\psi/dx - \psi \, d\psi^*/dx] = 2k\,[|A|^2 - |B|^2]$ real
- Multiply by $\hbar/2m$ and remember $p = \hbar k$:
  $-\{i\hbar/2m\}\,[\psi^* \, d\psi/dx - \psi \, d\psi^*/dx] = \{p/m\}\,[|A|^2 - |B|^2]$

  dimension of velocity x prob density
- Conservation of probability current density
  - Quantum equivalent of flux !

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Scattering: Flux

- Start with time independent Schrödinger equation:
  $-\{\hbar^2/2m\}\, d^2\psi/dx^2 + V(x)\,\psi = E\,\psi$
- Multiply by ψ^* :
  $-\{\hbar^2/2m\}\,\psi^*\, d^2\psi/dx^2 + \psi^*\, V(x)\,\psi = \psi^*\, E\,\psi$
- Write down complex conjugate:
  $-\{\hbar^2/2m\}\,\psi\, d^2\psi^*/dx^2 + \psi\, V(x)\,\psi^* = \psi\, E\,\psi^*$
- Subtract:
  $\psi^*\, d^2\psi/dx^2 - \psi\, d^2\psi^*/dx^2 = 0$
- This is equivalent to:
  $d/dx\,[\psi^*\, d\psi/dx - \psi\, d\psi^*/dx] = 0$
- Implying:
  the quantity $\boxed{\psi^* \, d\psi/dx - \psi \, d\psi^*/dx}$ is conserved

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Quantum Scattering

- Using the free particle solution:
  $\psi = A \exp\{ikx\} + B \exp\{-ikx\}$

- Probability current density is conserved

- It has a component (in the +ve x direction of):
  $+p/m\,|A|^2$

- It has a component (in the -ve x direction of):
  $-p/m\,|B|^2$

- Quantum equivalent to classical conservation of flux

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9.1 Particle and Potential Step
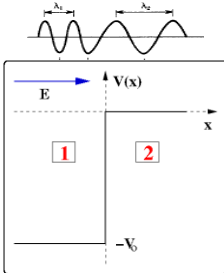
- Region 1 :
  - $x < 0$ $V = -V_0$
- Region 2 :
  - $x > 0$ $V = 0$

- Use time independent Schrödinger equation for solutions in regions 1 and 2

- Region 1 :
  - $\psi_1 = A_1 \exp\{ik_1x\} + B_1 \exp\{-ik_1x\}$ $k_1 = \sqrt{\{2m(E + V_0)\}} / \hbar$
- Region 2 :
  - $\psi_2 = A_2 \exp\{ik_2x\} + B_2 \exp\{-ik_2x\}$ $k_2 = \sqrt{\{2mE\}} / \hbar$
- Everywhere k_1 and k_2 are <u>real</u> and $E > 0$

Continuity of Waveforms

- Waveforms in Quantum Mechanics must be "continuous"
  - $\psi(x)$ must be single valued for all x
  - $d\psi/dx$ must be single valued for all x

  particularly at boundaries

Potential Step

- Apply continuity of ψ and $d\psi/dx$ at $x = 0$:
  - $A_1 + B_1 = A_2 + B_2$ two equations,
  - $k_1\{A_1 - B_1\} = k_2\{A_2 - B_2\}$ four unknowns
- Apply boundary conditions:
  - Far from scattering centre ($x = 0$) we have particle which was incident from left ($\Rightarrow$) now leaving (scattering) to right ($\Rightarrow$)
- Flux to right after scattering is only $\Rightarrow$, hence:
  - $\psi_2 = A_2 \exp\{ik_2x\}$ i.e. $B_2 = 0$
- Now we have:
  - $A_1 + B_1 = A_2$ two equations,
  - $\{k_1/k_2\} \{A_1 - B_1\} = A_2$ three unknowns
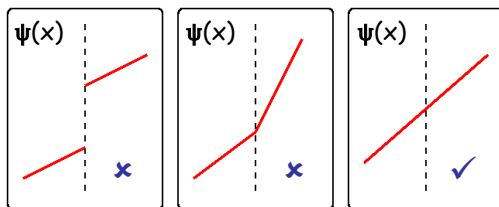
Potential Step

- Solving, we can determine the relative normalisation of each plane wave in ψ_1 and ψ_2 :
  - $B_1 = A_1 \{k_1 - k_2\} / \{k_1 + k_2\}$
  - $A_2 = A_1 2k_1 / \{k_1 + k_2\}$

- Hence in region 1 :
  - $\psi = A_1 \exp\{ik_1x\} + [A_1 \{k_1 - k_2\} / \{k_1 + k_2\}] \exp\{-ik_1x\}$
    - <u>incident</u> ($\Rightarrow$)   <u>reflected</u> or scattered ($\Leftarrow$)

- In region 2 :
  - $\psi = [A_1 2k_1 / \{k_1 + k_2\}] \exp\{ik_2x\}$
    - <u>transmitted</u> or unscattered ($\Rightarrow$)

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Potential Step

- Recall: Flux = $\{\hbar k/m\}\,|A|^2$
- Incident flux, region 1 :
  $$\{\hbar k_1/m\}\,|A_1|^2$$
- Reflected flux, region 1 :
  $$\{\hbar k_1/m\}\,|A_1|^2\,[\{k_1 - k_2\}/\{k_1 + k_2\}]^2$$
- Transmitted flux, region 2 :
  $$\{\hbar k_2/m\}\,|A_1|^2\,[2k_1/\{k_1 + k_2\}]^2$$
- It can be shown that the incident flux is <u>equal</u> to the sum of the reflected (scattered) and transmitted (unscattered) fluxes

  Probability current density is <u>conserved</u> !

Limit of Classical Physics

- No quantisation, i.e. $\hbar \Rightarrow 0$
  - $k_1 = \sqrt{2m(E + V_0)}/\hbar \Rightarrow \infty$ de Broglie wavelength
  - $k_2 = \sqrt{2mE}/\hbar \Rightarrow \infty$ gets small ($\Rightarrow 0$)
- Then:
  - $k_1 - k_2 \Rightarrow 0$ difference of two large numbers
  - $k_1 + k_2 \Rightarrow \infty$
- Therefore:
  - $R \Rightarrow 0,\ \ T \Rightarrow 1$
- The particle is in <u>no way or sense</u> "reflected" !
- It moves from the region (1) of kinetic energy ($E + V_0$) to the region (2) of kinetic energy E
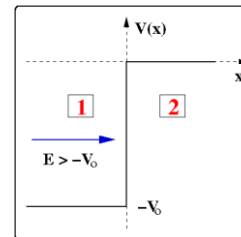
Reflectivity & Transmissivity

- Reflectivity R (due to scattering):
  - $R = \{flux \Leftarrow\}_{x<0} / \{flux \Rightarrow\}_{x<0}$
  - $= [\{k_1 - k_2\}/\{k_1 + k_2\}]^2$
  - $= [(\sqrt{E} - \sqrt{E + V_0})/(\sqrt{E} + \sqrt{E + V_0})]^2$
- Transmissivity T (not scattered):
  - $T = \{flux \Rightarrow\}_{x>0} / \{flux \Rightarrow\}_{x<0}$
  - $= 4k_1 k_2/(k_1 + k_2)^2$
  - $= 4\sqrt{E(E + V_0)}/(\sqrt{E} + \sqrt{E + V_0})^2$
- Large particle energy $E \gg V_0$
  - $R \sim 0,\ \ T \sim 1$ particle unaffected
- Small particle energy $E \sim 0$
  - $R \sim 1,\ \ T \sim 0$ particle confined to $x < 0$

Particle with Energy E < 0

- Region 1 :
  $$k_1 = \sqrt{2m(E + V_0)}/\hbar$$
- Region 2 :
  $$k_2 = \sqrt{2mE}/\hbar \quad \text{imaginary}$$
  $$= i\alpha_2$$

- Region 1 :
  $$\psi_1 = A_1 \exp\{ik_1 x\} + B_1 \exp\{-ik_1 x\}$$
- Region 2 :
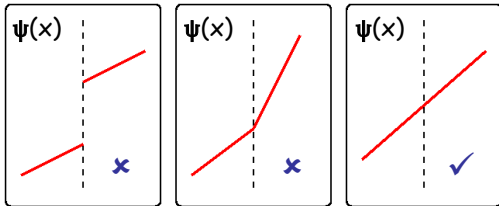 $$\psi_2 = A_2 \exp\{-\alpha_2 x\} + B_2 \exp\{\alpha_2 x\} \quad \text{i.e. } B_2 = 0$$

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Continuity of Waveforms

➢ Waveforms in Quantum Mechanics must be "continuous"
  ➢ $\psi(x)$ must be single valued for all x
  ➢ $d\psi/dx$ must be single valued for all x
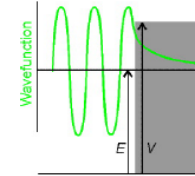 particularly at boundaries

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Potential Step

➢ Note that the wave function $\psi_2 \neq 0$ in region 2

➢ Probability density penetrates the barrier (cf finite square well)

➢ Reflectivity:
  $R = | \{\alpha_2 + ik_1\} / \{\alpha_2 - ik_1\} |^2 = 1$

➢ Particle is confined to $x < 0$

Potential Step

➢ Apply continuity of ψ and $d\psi/dx$ at $x = 0$:
  $$A_1 + B_1 = A_2$$
  $$ik_1\{A_1 - B_1\} = -\alpha_2 A_2$$
➢ Solve (as before):
  $$B_1 = -A_1 \{\alpha_2 + ik_1\} / \{\alpha_2 - ik_1\}$$
  $$A_2 = -A_1 \, 2ik_1 / \{\alpha_2 - ik_1\}$$

➢ Hence in region 1 :
  $$\psi_1 = A_1 \exp\{ik_1 x\} - [A_1 \{\alpha_2 + ik_1\} / \{\alpha_2 - ik_1\}] \exp\{-ik_1 x\}$$

➢ In region 2 :
  $$\psi_2 = [-A_1 \, 2ik_1 / \{\alpha_2 - ik_1\}] \exp\{-\alpha_2 x\}$$

Penetration Depth

➢ The penetration depth L represents an approximate measure of how far the wave-function of a quantum particle penetrates into the classically forbidden region
➢ Defined when the probability density falls to $1/e$ of its value at $x = 0$
  $$|\psi_2(x=L)|^2 / |\psi_2(x=0)|^2 = \exp\{-2\alpha_2 L\} = \exp\{-1\}$$
➢ So
  $$2\alpha_2 L = 1$$ Binding energy, energy below top of potential
➢ Or
  $$L = \hbar / [2\sqrt{2mE}]$$ Tutorial 3

➢ Note for $\hbar \Rightarrow 0$ (i.e. classical physics) $L = 0$

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Potential Step: Summary

➤ A change of the potential energy function $V(x)$ will cause the probability current density (flux) $\{p/m\}|A|^2$ of an otherwise <u>free</u> particle to be reflected or scattered

➤ The probability density of a particle will <u>penetrate</u> into "unphysical" regions where the total energy is less than the potential energy $V(x)$

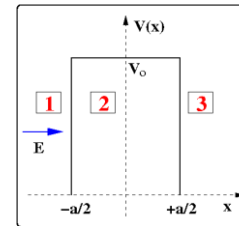➤ Can a particle <u>escape</u> from a region where its total energy is less than $V(x)$?

➤ Yes ! : <u>tunnelling</u>

9.2 Particle and Potential Barrier

➤ Potential is of the form:
$|x| > a/2$ $V = 0$
$|x| < a/2$ $V = V_0$
➤ Boundary conditions:
➤ Particle incident left to right
➤ Continuity of ψ and $d\psi/dx$

➤ Region 1 : $x < -a/2$
$\psi_1 = A_1 \exp\{ikx\} + B_1 \exp\{-ikx\}$ $k = \sqrt{\{2mE\}} / \hbar$
➤ Region 2 : $-a/2 < x < a/2$
$\psi_2 = A_2 \exp\{-\alpha x\} + B_2 \exp\{\alpha x\}$ $\alpha = \sqrt{\{2m(V_0 - E)\}} / \hbar$
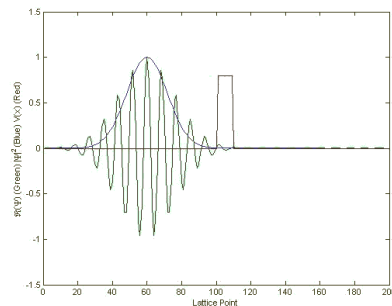➤ Region 3 : $a/2 < x$
$\psi_3 = A_3 \exp\{ikx\}$ $k = \sqrt{\{2mE\}} / \hbar$

Potential Barrier and Wave Packet

➤ Incident wave packet is partly reflected and partly transmitted

Potential Barrier

➤ Continuity of ψ at $x = -a/2$:
$A_1 \exp\{-ika/2\} + B_1 \exp\{ika/2\}$
$= A_2 \exp\{\alpha a/2\} + B_2 \exp\{-\alpha a/2\}$
➤ Continuity of ψ at $x = a/2$:
$A_3 \exp\{ika/2\} = A_2 \exp\{-\alpha a/2\} + B_2 \exp\{\alpha a/2\}$
➤ Continuity of $d\psi/dx$ at $x = -a/2$:
$ik[A_1 \exp\{-ika/2\} - B_1 \exp\{ika/2\}]$
$= \alpha[-A_2 \exp\{\alpha a/2\} + B_2 \exp\{-\alpha a/2\}]$
➤ Continuity of $d\psi/dx$ at $x = a/2$:
$ikA_3 \exp\{-ika/2\} = \alpha[-A_2 \exp\{-\alpha a/2\} + B_2 \exp\{\alpha a/2\}]$

Four equations, five unknowns

Potential Barrier

➢ Express the four unknowns B_1, A_2, B_2, A_3 in terms of A_1:

$$\exp\{ika/2\}\,B_1 - \exp\{\alpha a/2\}\,A_2 - \exp\{-\alpha a/2\}\,B_2 = -A_1\exp\{-ika/2\}$$
$$\exp\{-\alpha a/2\}\,A_2 + \exp\{\alpha a/2\}\,B_2 - \exp\{ika/2\}\,A_3 = 0$$
$$ik\,\exp\{ika/2\}\,B_1 - \alpha\,\exp\{\alpha a/2\}\,A_2 + \alpha\,\exp\{-\alpha a/2\}\,B_2 = ikA_1\exp\{-ika/2\}$$
$$\alpha\,\exp\{-\alpha a/2\}\,A_2 - \alpha\,\exp\{\alpha a/2\}\,B_2 + ik\,\exp\{ika/2\}\,A_3 = 0$$

➢ Solutions for B_1/A_1, A_2/A_1, B_2/A_1, A_3/A_1 follow after much tedious but straightforward algebra !

➢ In particular:
$$A_3/A_1 = 4ik\alpha\,\exp\{-ika\} \,/\, [\,(k+i\alpha)^2\exp\{\alpha a\} - (k-i\alpha)^2\exp\{-\alpha a\}\,]$$

➢ Finite free particle solution in region 3 !
$$\psi_3 = A_3\exp\{ikx\} \quad \text{for} \quad x \gg 0 \,!$$

Barrier Penetration

➢ Transmissivity T :
$$T = k|A_3|^2 \,/\, k|A_1|^2$$
$$= 16k^2\alpha^2\exp\{-2\alpha a\} \,/\, |(k + i\alpha)^2 - (k - i\alpha)^2\exp\{-2\alpha a\}|^2$$

➢ In most solutions:
$$\alpha a = \sqrt{\{2m(V_0 - E)\}}a \,/\, \hbar \text{ is large}$$

➢ Hence:
$$T \approx 16k^2\alpha^2\exp\{-2\alpha a\} \,/\, [(k^2 - \alpha^2)^2 + 4k^2\alpha^2]$$
$$= 16k^2\alpha^2\exp\{-2\alpha a\} \,/\, (k^2 + \alpha^2)^2$$

➢ Or:
$$T = \{16E(V_0 - E)\,/\,V_0\}\exp\{-2a\sqrt{\{2m(V_0 - E)\}}\,/\,\hbar\}$$

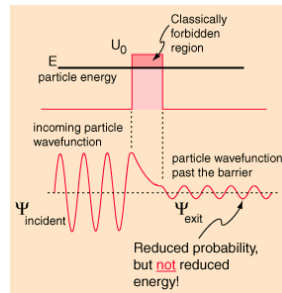➢ Dominant dependence on E is <u>exponential</u>

Barrier Penetration

➢ Region 1 :
Free particle + "backscattering"

➢ Region 2 :
"Exponential tunnelling"

➢ Region 3 :
Free particle (same energy)

➢ Classical limit $\hbar = 0$:
$$A_3 = 0$$

➢ Flux in region 1 :
$$|A_1|^2 + |B_1|^2 + 2\text{Re}[A_1^*B_1\cos\{2ka\}] \quad \text{interference}$$

➢ Flux in region 3 :
$$|A_3|^2 \neq 0 \quad \text{quantum effect}$$
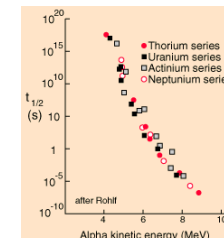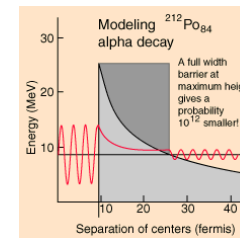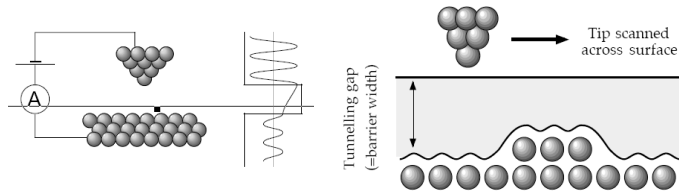
Alpha Decay of Atomic Nuclei

➢ Decay rate $\lambda \propto T$ varies over many orders of magnitude

➢ Energy of alpha particle varies over a few orders of magnitude

➢ Quantum <u>tunnelling</u> through Coulomb barrier

Scanning Tunnelling Microscope

> Current of electrons due to tunnelling through surface probe barrier
> Current $\propto T \propto \exp\{-\alpha a\}$
> Current very sensitive to a
>   Measurement of atomic structure near surface

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STM Images (Liverpool)
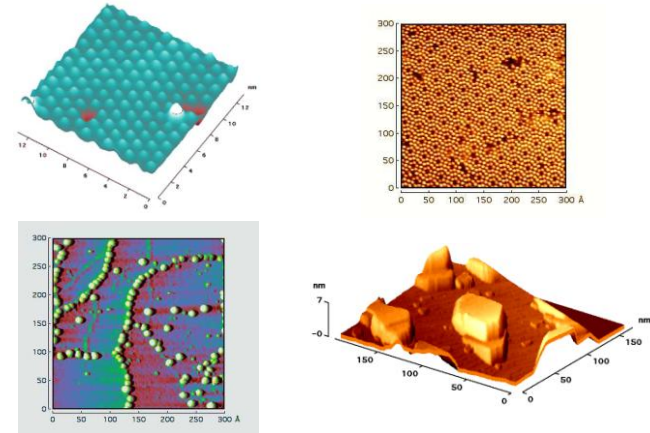
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Scanning Tunneling Microscope

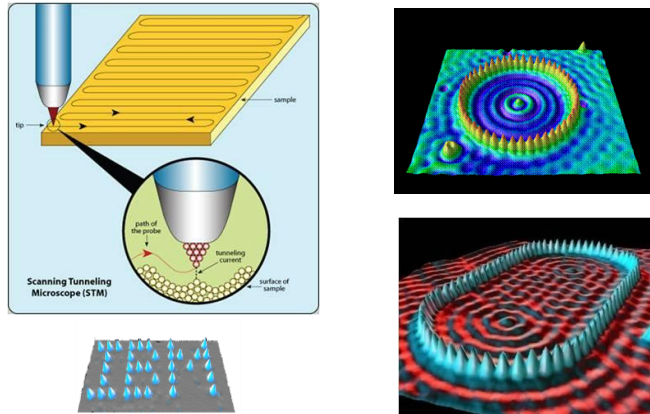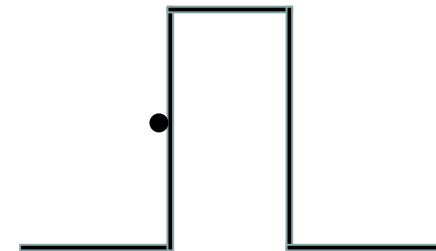07/09/2011   PHYS255: Quantum & Atomic Physics - E.S. Paul   242

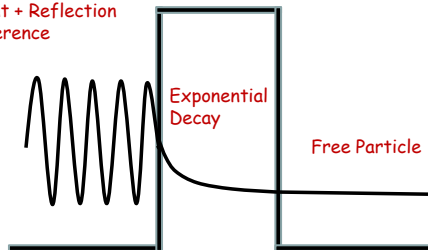## Summary: Barrier Penetration

Classical Picture

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Summary: Barrier Penetration
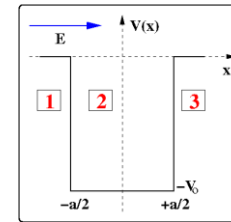
Incident + Reflection Interference

Exponential Decay

Free Particle

Quantum Picture

9.3 Particle & Attractive Potential Well

➢ Potential is of the form:

$|x| > a/2$ $V = 0$

$|x| < a/2$ $V = -V_0$

➢ Boundary conditions:

   ➢ Particle incident left to right

   ➢ Continuity of ψ and $d\psi/dx$

➢ Region 1 : $x < -a/2$

$\psi_1 = A_1 \exp\{ikx\} + B_1 \exp\{-ikx\}$ $k = \sqrt{2mE} / \hbar$

➢ Region 2 : $-a/2 < x < a/2$

$\psi_2 = A_2 \exp\{ik_0x\} + B_2 \exp\{-ik_0x\}$ $k_0 = \sqrt{2m(E + V_0)} / \hbar$

➢ Region 3 : $a/2 < x$

$\psi_3 = A_3 \exp\{ikx\}$ $k = \sqrt{2mE} / \hbar$

Attractive Potential Well

➢ After some tiresome algebra:

$A_3/A_1 = -4kk_0 \exp\{-ika\} / [(k - k_0)^2 \exp\{ik_0a\} – (k + k_0)^2 \exp\{-ik_0a\}]$

which can also be written:

$A_3/A_1 = -4kk_0 \exp\{-ika\} / [2(k^2 - k_0^2)^2 i \sin\{k_0a\} – 4kk_0 \cos\{k_0a\}]$

➢ Transmissivity T :

$T = k|A_3|^2 / k|A_1|^2$

$= 4k^2k_0^2 / [4k^2k_0^2 \cos^2\{k_0a\} + (k^2 + k_0^2)^2 \sin^2\{k_0a\}]$

$= 1 / [1 + X \sin^2\{k_0a\}]$ $X = (k^2 - k_0^2)^2 / 4k^2k_0^2$

➢ Maximum T when:

$\sin\{k_0a\} = 0$

$\therefore k_0a = 2\pi a / \lambda_0 = n\pi$ n integer

$n \lambda_0 /2 = a$

➢ Maximum when integer number of half wavelengths equals the width of the well

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Attractive Potential Well

- Maximum T occurs when:

  $[\sqrt{2m(E + V_0)} / \hbar] a = n\pi$

  where E is resonance energy
- Minimum T occurs when:

  $\sin\{k_0 a\} = \pm 1$ or $k_0 a = (n + \frac{1}{2})\pi$ n integer

  corresponding to:

  $[\sqrt{2m(E + V_0)} / \hbar] a = (n + \frac{1}{2})\pi$

  and energy E at minimum scattering
- Example: Ramsauer Townsend Effect
  - Electron transmission through (krypton) gas as a function of energy

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Attractive Potential Well & Wave Packet
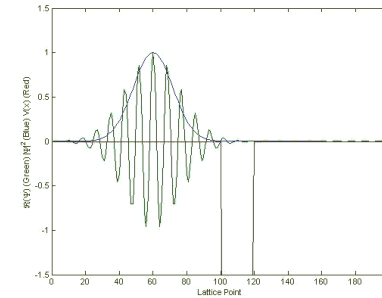
- Incident wave packet is partly reflected and partly transmitted

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Ramsauer Townsend Effect

$k_0 a = n\pi$

Ramsauer's Apparatus
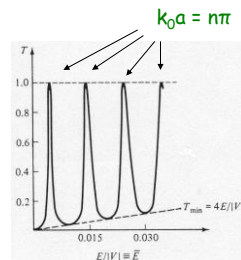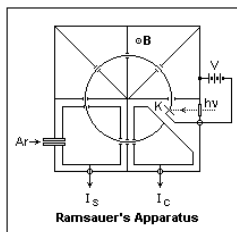
- Slits define orbit (velocity, energy) of electron
- "a" is diameter of gas atom

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Reflectionless Potential

- There is a shape of potential that prevents any reflection of a wave packet

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10. Atomic Structure

Hydrogen Atom Degeneracies

Energy / $\{me^4 / 32\pi^2\varepsilon_0^2\hbar^2\}$	n	ℓ	m	degeneracy
-1	1	0	0	one
-1/4	2	0	0	
-1/4	2	1	±1,0	four
-1/9	3	0	0	
-1/9	3	1	±1,0	nine
-1/9	3	2	±2,±1,0	

- Sub-shells within an energy shell are <u>degenerate</u>

Atomic Structure

- From quantum physics so far:
- If one particle moves in a central potential

$$V(\underline{r}) = V(r,\theta,\varphi) = V(r)$$

  then the energy is quantised according to
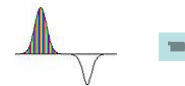
$$E = E_{n\ell}$$

- Here:

$$n \geq 1, \ell \geq 0$$

- ℓ specifies the quantised angular momentum^2 L^2

$$L^2 = \ell\{\ell+1\} \hbar^2$$

- m (-ℓ, -ℓ+1,... 0,... ℓ-1, ℓ) specifies the projection L_z of L on a fixed direction z

$$L_z = m \hbar$$

  Try to understand above in understanding atoms

---

n ℓ Quantum Numbers

- Principal quantum number n is written as a digit

- Angular momentum quantum number ℓ is written as:

ℓ = 0	s	"sharp"
ℓ = 1	p	"principal"
ℓ = 2	d	"diffuse"
ℓ = 3	f	"fundamental"
ℓ = 4	g	
ℓ = 5	h	now alphabetical
ℓ = 6	i	

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Central Field Approximation

➢ Neutral atom, atomic number Z
  ➢ nucleus + Z electrons in a bound state
➢ For electron i ($i = 1, 2,... Z$):
  $$V_i(\underline{r}_i) = -Ze^2 / 4\pi\varepsilon_0 r_i + \sum e^2 / 4\pi\varepsilon_0 r_{ij}$$
            e^- - nucleus e^- - e^- repulsion
               attraction
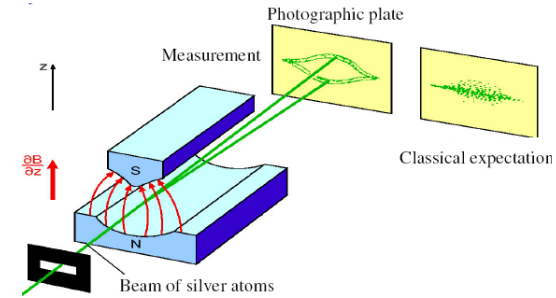➢ Definitely not central !
➢ Now write:
  $$V_i(\underline{r}_i) = V(r_i) + \Delta V(\underline{r}_i, r_{ij}) \qquad \Delta V(\underline{r}_i, r_{ij}) \text{ small}$$
➢ Approximate motion of an electron in an atom as that of an electron in a central potential and expect only small corrections ΔV

10.1 More than Orbital Angular Momentum

➢ <u>Stern Gerlach experiment</u>: a neutral ($\sum$charge = 0) atomic beam passes through a region of non-uniform magnetic field
  ➢ Beam is split into components !

Electrons in Atoms

➢ Each electron contributes an energy $E_{n\ell}$ to the total energy of the atom:
  $$E = \sum E_{i,n\ell} \qquad \text{summation } i = 1, Z$$
➢ Electrons in the atom can be specified by their configuration in sub-shells:

    $1s^2\ 2s^2\ 2p^2$

                  $n = 2, \ell = 1$ 2 electrons
             $n = 2, \ell = 0$ 2 electrons
       $n = 1, \ell = 0$ 2 electrons
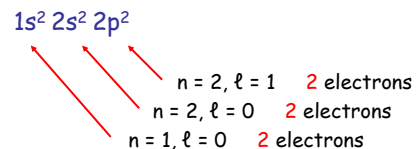
➢ And only small corrections need to be made

Stern Gerlach Experiment
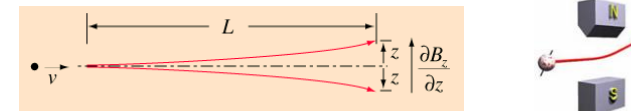
➢ How is a neutral atomic beam split ?
➢ Why is a non-uniform magnetic field necessary ?
➢ Force on a magnetic dipole $\underline{\mu}$ in a region of non-uniform field $\underline{B}$ is:
  $$\underline{F} = (\underline{\mu} \bullet \underline{\nabla})\,\underline{B} \qquad \text{if } B \text{ was uniform then any differential = 0 and hence } F = 0$$
➢ Atoms in beams must have magnetic dipole moments
  ➢ How ?

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Magnetic Dipole Moment

- Atoms are distributions in space of moving charge, i.e. current
- Atomic electrons are currents
- Currents interact with field B
- Current loops interact with changes in field B
- Current loops generate magnetic dipole moment

$\mu = IA$, A = area

- Consider a current loop of arbitrary shape with area A:
- Current I due to flow of n "lumps" per unit length of charge q at velocity v:
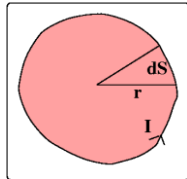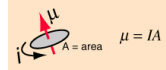$$I = n\,q\,v$$

Magnetic Dipole Moment

- Length dS contributes to angular momentum L
- If each lump of charge has mass m:
$$dL = n\,dS\,m\,v\,r$$
   total mass   velocity   distance

- The total angular momentum is then given by:
$$L = n\,m\,v\oint_s r\,dS \qquad dA = \tfrac{1}{2}\,r\,dS$$
$$= n\,m\,v\,2A \qquad \text{i.e. } 2\,dA = r\,dS$$

- Or, area:
$$A = L\,/\,2\,m\,n\,v$$

- Electromagnetism of current loop of any shape:
  magnetic moment: $\mu = I\,A = n\,q\,v\,A$

Magnetic Dipole Moment

- Substituting for A gives:
$$\mu = n\,q\,v\,L\,/\,2\,m\,n\,v$$

- Hence:
$$\boxed{\underline{\mu} = \{q/2m\}\,\underline{L}}$$
  no dependence on n, no dependence on shape of loop

- For atoms the loops of current are distributed everywhere, $q \Rightarrow -e$, m = electron mass
- The relation between total magnetic moment $\underline{\mu}$ and total orbital angular momentum $\underline{L}$ is thus:
$$\boxed{\underline{\mu} = -\{e/2m\}\,\underline{L}}$$

- Or:
$$\boxed{\underline{\mu} = g_\ell\,\{\mu_B/\hbar\}\,\underline{L}} \quad \text{where} \quad \boxed{\mu_B = -\{e\hbar/2m\}} \text{ Bohr magneton}$$

Magnetic Dipole Moment

- Atomic magnetic moments are best quoted in units of the Bohr magneton μ_B
- Note that "orbital g-factor" $g_\ell = 1$
- Back to atomic beam:
- Force in non-uniform field on atoms
$$\underline{F} = (\underline{\mu}\bullet\underline{\nabla})\,\underline{B}$$

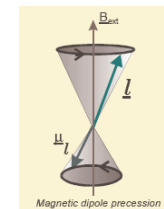Magnetic dipole precession

- The field is designed so that:
$$\underline{F} = (0,0,F_z)$$
- Then:
$$F_z = (\underline{\mu}\bullet\underline{\nabla})\,\underline{B} = \mu_z\,\partial B_z/\partial z \quad \text{if} \quad \partial B_z/\partial x = \partial B_z/\partial y = 0$$
- Or:
$$F_z = g_\ell\,\{\mu_B/\hbar\}\,L_z\,\partial B_z/\partial z$$
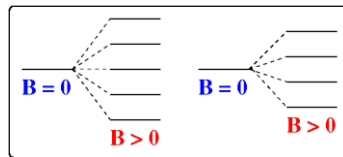
Force on Atomic Beam

- The non-uniform magnetic field establishes a direction for spatial quantisation:

$L_z = m\hbar$ $\qquad\qquad$ $m = -\ell, -\ell+1,... 0,... \ell-1, \ell$

$F_z = \{g_\ell \mu_B \, \partial B_z/\partial z\} \, m$

- The (neutral) atomic beam should split into $(2\ell + 1)$ components, provided $\ell > 0$

<u>BUT</u>: Some beams split into even number of components !

- <u>Problem:</u>
  $F \propto m$
  $(2\ell + 1)$ <u>odd</u>
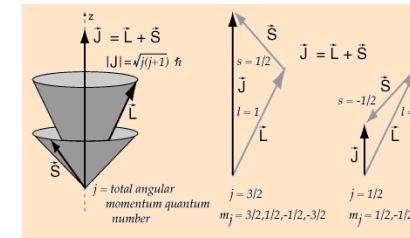 $m = 0$ no deflection
- Something is wrong !

Vector Model of Total Angular Momentum

- Orbital angular momentum <u>L</u> and electron intrinsic spin <u>S</u> are combined to produce total angular momentum <u>J</u>
- Both the <u>L</u> and <u>S</u> vectors <u>precess</u> around the direction of the <u>J</u> vector
- The vector <u>J</u> is a <u>constant</u> of the motion

Solution: Intrinsic Spin

- Uhlenbeck and Goudschmidt proposed that an additional contribution to the angular momentum of the atom, and therefore the magnetic moment of the atom, arises from the intrinsic spin of each electron

- The total angular momentum of the atom is:

$$\underline{J} = \underline{L} + \underline{S}$$
total   orbital   spin $\qquad\qquad$ vector addition

- The total magnetic moment of the atom is:

$$\underline{\mu} = \underline{\mu}_L + \underline{\mu}_S$$
$\qquad\qquad$ vector addition

Angular Momentum Quantum Numbers

- Orbital angular momentum:
  $L^2 = \ell\{\ell+1\} \hbar^2$ $\qquad$ $\ell = 0, 1, 2...$ $\qquad$ integer
- Spatial quantisation:
  $L_z = m \hbar$ $\qquad$ $m = -\ell, -\ell+1,... 0,... \ell-1, \ell$
- Spin:
  $S^2 = s\{s+1\} \hbar^2$ $\qquad$ $s = 1/2, 3/2,...$ $\qquad$ <u>half</u>-integer
- Spatial quantisation:
  $S_z = m_s \hbar$ $\qquad$ $m_s = -s, -s+1,... 0,... s-1, s$
- For one electron:
  Spin = $\frac{1}{2}$
- Hence:
  $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$

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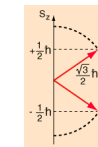
Angular Momentum Coupling

➤ Coupling $\underline{L}$ and $\underline{S}$ gives rise to the total angular momentum:

$$J = |\underline{L} + \underline{S}|$$

➤ Total angular momentum:

$$J^2 = j\{j+1\}\hbar^2 \qquad j = |\underline{\ell} + \underline{s}| \qquad \text{integer or half-integer}$$

➤ Spatial quantisation:

$$J_z = m_j \hbar \qquad m_j = -j, -j+1, \dots 0, \dots j-1, j$$

➤ We now know that any particle can have a degree of freedom called spin (s)

➤ This spin can be integer or half-integer

Electron Spin

➤ Electron spin S is a contribution to angular momentum
➤ It is quantised according to the rules for angular momentum:

$$S^2 = s\{s+1\}\hbar^2 \qquad s = 1/2$$
$$S_z = m_s \hbar \qquad m_s = \pm\tfrac{1}{2}$$

➤ The electron is a fermion
➤ Contribution to magnetic moment:

$$\underline{\mu}_s = g_s \{\mu_B/\hbar\} \underline{S} \qquad g_s \text{ is spin g-factor}$$

➤ Dirac:

$$g_s = 2 \qquad \text{remember } g_\ell = 1$$

➤ Full relativistic theory of quantum physics gives:

$$g_s = 2 + \text{very tiny additions}$$

Particles and Spin

➤ Spin arises because we live in a world in which Einstein's theory of special relativity holds
   ➤ The world is Lorentz invariant
➤ Particles with integer spin are called bosons

$$S_z = 0\hbar, (\pm\hbar, 0), (\pm 2\hbar, \pm\hbar, 0)$$

➤ Examples:
   some molecules, atoms, nuclei, hadrons, $W^\pm$, Z_0, photons
➤ Particles with half-integer spin are called fermions

$$S_z = \pm\tfrac{1}{2}\hbar, \dots$$

➤ Examples:
   electrons, quarks, protons, nuclei,…

Stern Gerlach Experiment & Hydrogen

➤ H atom ground state:

   $1s^1$ 1 electron in s subshell with $\ell = 0$

➤ Since it has no orbital angular momentum:

$$J = |\underline{L} + \underline{S}| = S$$
$$J_z = S_z = \pm\tfrac{1}{2}\hbar$$

➤ Magnetic dipole moment:

$$\mu_z = g_s \{\mu_B/\hbar\} S_z = \pm\tfrac{1}{2} g_s \mu_B = \pm\mu_B \qquad g_s = 2$$

➤ Force:

$$F_z = \pm\mu_B \, \partial B_z/\partial z$$

➤ H atom splits into two components (even) symmetrically due only to magnetic moment from electron spin
   ➤ Spin $\tfrac{1}{2}$ of electron confirmed !

10.2 Electron Spin & Hydrogen Atom

	s	p	d	f
n=4	___	___	___	___
n=3	___	___	___	
n=2	___	___		
n=1	___			

$$E_n = -13.6 \text{ eV} / n^2$$

➢ Exact solution of Schrödinger equation for one electron moving under the influence of Coulomb potential:
$$V(r) = \{-e^2 / 4\pi\varepsilon_0 r\}$$

➢ Accidental degeneracy in ℓ:
$$\ell = 0, 1, 2,\dots (n-1)$$

➢ Orbital angular momentum degeneracy in m:
$$m = -\ell, -\ell+1,\dots 0,\dots \ell-1, \ell$$

➢ And now spin $\frac{1}{2}$ angular momentum degeneracy in m_s:
$$m_s = -\tfrac{1}{2}, +\tfrac{1}{2}$$

Hydrogen Atom Degeneracy with Spin

Energy / $\{me^4 / 32\pi^2\varepsilon_0^2\hbar^2\}$	n	ℓ	m	m_s	degen.
-1	1	0	0	$\pm\tfrac{1}{2}$	two
-1/4	2	0	0	$\pm\tfrac{1}{2}$	
-1/4	2	1	±1,0	$\pm\tfrac{1}{2}$	eight
-1/9	3	0	0	$\pm\tfrac{1}{2}$	
-1/9	3	1	±1,0	$\pm\tfrac{1}{2}$	eighteen
-1/9	3	2	±2,±1,0	$\pm\tfrac{1}{2}$	

➢ Spin $\frac{1}{2}$ "degree of freedom" $\pm\tfrac{1}{2}$ multiplies degeneracy by 2

Spin-Orbit Coupling

➢ The (central) Coulomb potential:
$$V(r) = \{-e^2 / 4\pi\varepsilon_0 r\}$$
does <u>not</u> include the effects of the magnetic moments in the atom

➢ There is an interaction between $\underline{\mu}_s$ due to spin angular momentum of electron with $\underline{\mu}_\ell$ due to the orbital angular momentum of the electron

➢ When fixed in space relative to each other, the energy depends only on their relative orientation:
$$\Delta E \propto \underline{\mu}_s \cdot \underline{\mu}_\ell$$

➢ Here ΔE is the addition (or subtraction) to the total energy of the hydrogen atom due to this additional interaction

---

Spin-Orbit Energy

➢ Magnetic interaction between $\underline{\mu}_s$ and $\underline{\mu}_\ell$
  $\underline{\mu}_s$ is in magnetic field of $\underline{\mu}_\ell$ of orbital motion of electron

➢ Spin-orbit interaction energy:
$$\Delta E \propto \underline{\mu}_s \cdot \underline{\mu}_\ell \propto \underline{S} \cdot \underline{L}$$
$$\underline{\mu}_s = g_s \{\mu_B/\hbar\}\ \underline{S} \qquad \underline{\mu}_\ell = g_\ell \{\mu_B/\hbar\}\ \underline{L}$$

➢ The energy ΔE is added to the total energy of the H atom from solution of the Schrödinger equation with the electron in Coulomb potential function:
$$V(r) = \{-e^2 / 4\pi\varepsilon_0 r\}$$

➢ The energy levels are now:
$$E = E_{n\ell} + \Delta E$$

➢ What are the quantum numbers ?

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Spin-Orbit Energy

> Now:
$$\Delta E \propto g_s g_\ell \{\mu_B/\hbar\}^2 \, \underline{S} \cdot \underline{L}$$

> The total angular momentum of the hydrogen atom is:
$$\underline{J} = \underline{L} + \underline{S}$$

> Therefore:
$$\underline{J}^2 = (\underline{L} + \underline{S})^2 = \underline{L}^2 + \underline{S}^2 + 2\,\underline{S} \cdot \underline{L}$$

> And so:
$$\underline{S} \cdot \underline{L} = \tfrac{1}{2}(J^2 - L^2 - S^2)$$

> Hence the energy is:
$$\Delta E \propto \tfrac{1}{2} g_s g_\ell \{\mu_B/\hbar\}^2 (J^2 - L^2 - S^2)$$

> We can now substitute for J^2, L^2 and S^2

Spin-Orbit Splitting
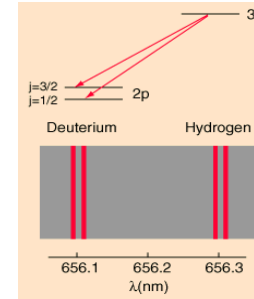
> The spin-orbit interaction "lifts" some of the degeneracy on ℓ of H atom energy

> Small shift and splitting of energy levels:
$$E = E_{n\ell} + \Delta E \Rightarrow E_{n\ell j}$$

> Notation:
$$n\ell_j \quad \text{e.g.} \quad 1s_{1/2}, \, 2p_{1/2}, \, 2p_{3/2}$$

> Spectral lines are split:
> "Fine structure"

> Selection rules for transitions:
$$\Delta\ell = \pm 1, \quad \Delta j = 0, \pm 1$$

Spin-Orbit Energy

> From quantum physics:
$$L^2 = \ell\{\ell+1\}\hbar^2$$
$$S^2 = s\{s+1\}\hbar^2 = \tfrac{1}{2}\{\tfrac{1}{2}+1\}\hbar^2 = \tfrac{3}{4}\hbar^2$$
$$J^2 = j\{j+1\}\hbar^2$$

> Where:
$$\ell = 0, 1, 2, \ldots$$
> j integrally spaced $\ell \pm \tfrac{1}{2}$

> Hence:
$$\Delta E \propto \tfrac{1}{2} g_s g_\ell \{\mu_B/\hbar\}^2 \left[j(j+1) - \ell(\ell+1) - \tfrac{3}{4} \right] \hbar^2$$
$$\propto j(j+1) - \ell(\ell+1) - \tfrac{3}{4}$$

> Each energy level $E_{n\ell}$ has ΔE, which depends on j and ℓ, added to it

Box:
$$L_z = m\,\hbar$$
$$S_z = m_s\,\hbar = \pm\tfrac{1}{2}\hbar$$
$$J_z = m_j\,\hbar$$

Spin-Orbit Splitting: Summary

> Spin-orbit coupling, due to the magnetic interaction of the electron spin and orbital angular momenta, gives rise to "fine structure" in atomic spectra of hydrogen

> It is "fine" because of the small, magnetic interaction between spin and orbital motion

> Full calculations based on relativity and quantum physics (Dirac) imply that the spin-orbit interaction and its effects are due to special relativity on the electron motion

> Final result for the hydrogen atom:
$$E = E_{n\ell} + \Delta E \Rightarrow E_{nj}$$

still (accidental) degeneracy on ℓ

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Example: H Atom s and p States

➢ Solution of Schrödinger equation with:
$$V(r) = \{-e^2 / 4\pi\varepsilon_0 r\}$$
yields energies:
$$E = E_{n\ell}$$
with accidental degeneracy on ℓ
e.g. $E_{3s} = E_{3p} = E_{3d}$

➢ Total angular momentum quantum number j specified by:
$$\underline{j} = \underline{\ell} + \underline{s}$$
e.g. $3s_{1/2}$ $3p_{1/2,3/2}$ $3d_{3/2,5/2}$
$$|\underline{0} + \tfrac{1}{2}| \qquad |\underline{1} + \tfrac{1}{2}| \qquad |\underline{2} + \tfrac{1}{2}|$$

➢ Small interaction, spin-orbit coupling:
$$E = E_{n\ell} \Rightarrow E_{nj}$$

H Atom Fine Structure

Electron in Coulomb potential	**+**	spin-orbit interaction of electron
Accidental degeneracy in ℓ		Accidental degeneracy in ℓ
Degeneracy in m and $m_s = \pm\tfrac{1}{2}$		Degeneracy in m_j and $m_j = m_\ell \pm \tfrac{1}{2}$
Transition: $2p \rightarrow 1s$ 1 line		Transitions: $2p_{1/2} \rightarrow 1s_{1/2}$ $2p_{3/2} \rightarrow 1s_{1/2}$
"singlet"		"doublet"

H Atom Fine Structure
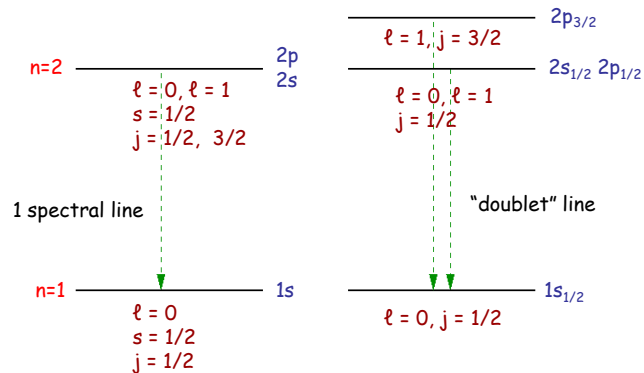
H Atom Degeneracy: Spin + $\underline{L} \cdot \underline{S}$ Coupling

Energy / $\{me^4 / 32\pi^2\varepsilon_0^2\hbar^2\}$	n	j	ℓ	m_j	degen.	label
$-1 + \text{"}s\cdot\ell\text{"}$	1	1/2	0	$\pm 1/2$	2	$1s_{1/2}$
$-1/4 + \text{"}s\cdot\ell\text{"}$	2	1/2	0	$\pm 1/2$	} 4	$2s_{1/2}$
$-1/4 + \text{"}s\cdot\ell\text{"}$	2	1/2	1	$\pm 1/2$		$2p_{1/2}$
$-1/4 + \text{"}s\cdot\ell\text{"}$	2	3/2	1	$\pm 3/2, \pm 1/2$	4	$2p_{3/2}$
$-1/9 + \text{"}s\cdot\ell\text{"}$	3	1/2	0	$\pm 1/2$	} 4	$3s_{1/2}$
$-1/9 + \text{"}s\cdot\ell\text{"}$	3	1/2	1	$\pm 1/2$		$3p_{1/2}$
$-1/9 + \text{"}s\cdot\ell\text{"}$	3	3/2	1	$\pm 3/2, \pm 1/2$	} 8	$3p_{3/2}$
$-1/9 + \text{"}s\cdot\ell\text{"}$	3	3/2	2	$\pm 3/2, \pm 1/2$		$3d_{3/2}$
$-1/9 + \text{"}s\cdot\ell\text{"}$	3	5/2	2	$\pm 5/2, \pm 3/2, \pm 1/2$	6	$3d_{5/2}$

Fine Structure Constant α

➢ The energies of the (fine structure) of the hydrogen atom may be expressed as:

$$E = -\{me^4 / 32\pi^2\varepsilon_0^2\hbar^2\} \{1/n^2\} [\, 1 + \alpha^2/n \, (1/\{j + \tfrac{1}{2}\} - 3/4n \,) \,]$$

which defines the "fine structure constant" α:

$$\alpha = e^2 / \hbar c$$

➢ Its value is:

$$\alpha \sim 1/137$$

10.3 Many-Electron Atoms

➢ In the central field approximation, each electron contributes an energy $E_{n\ell}$ where n is the principal quantum number and ℓ is the orbital angular momentum quantum number

  ➢ The quantum numbers n, ℓ specify an "energy sub-shell"

➢ In an atom with more than one electron, the minimum energy of the atom (ground state) would have all electrons in the lowest energy sub-shell: n = 1, ℓ = 0: 1s

➢ This is not consistent with observation

  ➢ E.g. zero orbital angular momentum of each electron and therefore also of atom ⇒ Stern-Gerlach splitting of 2 only !

Pauli Exclusion Principle

➢ In a many-electron system, only one electron may be assigned to one quantum state

  ➢ Quantum state = one (unique) set of quantum numbers
          = one (unique) wave function

➢ "Only one electron": probability density for two or more electrons is zero

➢ Pauli principle is fundamental

  ➢ It arises in the quantum field theory of particles where there is a distinction between half-integer particles (fermions) and integer spin particles (bosons)

          Proof is not straightforward !

Identical Particles

➢ Identical particles cannot be distinguished by means of any intrinsic properties

➢ This can lead to effects that have no classical analogue

➢ Two particles are identical if there are no interactions that can distinguish them

  ➢ A physical observable must be symmetric with respect to the interchange of any pair of particles

Fermions and Bosons

➢ Two identical fermions (e.g. two electrons with the same spin orientation) cannot occupy the same point in space, nor can they have the same value of momentum
  ➢ Pauli Exclusion Principle
  ➢ Each fermion has a unique set of quantum numbers

➢ Two non-interacting bosons can occupy the same point in space, or they can have the same value of momentum
  ➢ Boson condensation
  ➢ Bosons can all occupy the same (ground) state

Bosons and Fermions

➢ The time-dependent Schrödinger equation for two identical particles is:

$$\{i\hbar\, \partial/\partial t\}\, \Psi(\underline{r}_1, \underline{r}_2) = H(\underline{r}_1, \underline{r}_2)\, \Psi(\underline{r}_1, \underline{r}_2)$$

➢ As

$$H(\underline{r}_1, \underline{r}_2) = H(\underline{r}_2, \underline{r}_1)$$

there are two fundamentally different kinds of solution:

$$\Psi(\underline{r}_1, \underline{r}_2) = \Psi(\underline{r}_2, \underline{r}_1) \qquad \text{symmetric boson}$$
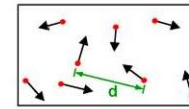
and

$$\Psi(\underline{r}_1, \underline{r}_2) = -\Psi(\underline{r}_2, \underline{r}_1) \qquad \text{antisymmetric fermion}$$

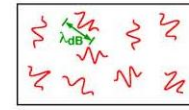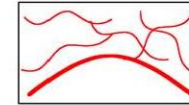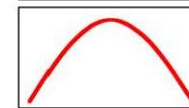## Bose-Einstein Condensate

➢ High temperature T
  Billiard balls
  Thermal velocity v, density d^{-3}
➢ Low temperature T
  Wave packets
  De Broglie wavelength $\lambda \propto T^{-1/2}$
➢ Critical Temperature T = T_{crit}
  Matter wave overlap
  De Broglie wavelength $\lambda \sim d$
➢ T = 0, Bose Condensate
  Giant matter wave

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Many-Electron Atoms

➢ Many-electron wave function:
  ➢ Each of the Z atomic electrons moves in the same potential V(r)
  ➢ All other interactions are small
➢ The quantum states are labelled by:

  n   principal quantum number

  ℓ orbital angular momentum quantum number

  m   spatial quantisation quantum number

  $s = \frac{1}{2}$ spin angular momentum quantum number

  $m_s = \pm\frac{1}{2}$ spatial quantisation quantum number

assigned to each electron

Electron Configurations

Electron configuration:
  (inert) closed-shell core + valence electrons

The Elements

The number of protons (or electrons) defines an element

(Valence) Electron Configurations

Electron configuration:
  (inert) closed-shell core + valence electrons

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Many-Electron Atoms

➢ Considering two electrons in quantum states (1) and (2), we can write the overall wave function:

$$\Psi = \psi_1^{(1)} \psi_2^{(2)}$$

➢ However this includes the possibility of "identical states", i.e. (1) = (2):

$$\Psi = \psi_1^{(1)} \psi_2^{(1)} \quad \text{so} \quad |\Psi|^2 \neq 0 \quad \text{violates Pauli principle}$$

➢ If the wave function of two electrons is written:

$$\Psi = \{1/\sqrt{2}\} [\ \psi_1^{(1)} \psi_2^{(2)} - \psi_1^{(2)} \psi_2^{(1)}\ ]$$
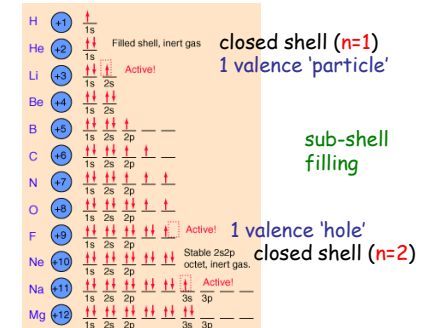
then if (1) = (2):

$$\Psi = 0 \quad \text{and} \quad |\Psi|^2 = 0 \quad \text{does not violates Pauli principle}$$

➢ Deeper statement of Pauli principle:

    ➢ Wave function of a many-electron (fermion) system must be antisymmetric ($\Psi \rightarrow -\Psi$) when any two electrons are interchanged

Electron Configurations

Sub-shell filling   Electron configurations
spin up, spin down

Many-Electron Atom in Central Field

➢ Atom with Z electrons:
➢ Each electron is assigned to a single wave function specified by a unique combination of the following quantum numbers:

$$n \qquad \ell \qquad m \qquad s = \tfrac{1}{2} \qquad m_s = \pm\tfrac{1}{2}$$

➢ Sub-shells are filled in order of increasing energy following the Pauli principle
➢ Energy of atom = sum of energies of each electron (specified by sub-shell)
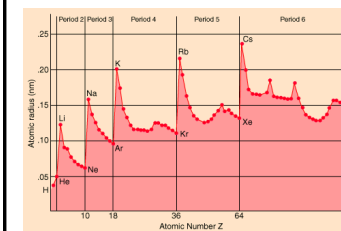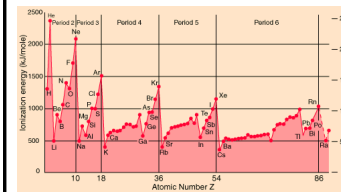➢ 'Capacity' of sub-shell $= 2(2\ell + 1)$

     Pauli principle $m_s = \pm\tfrac{1}{2}$ allowed values of m

Shell Structure (Magic Numbers)

➢ Full shells more bound
     highest ionisation energy
     smallest atomic radius

➢ Full shell + 1
     least bound
     largest atomic radius

➢ Closed shells define a set of magic numbers

     2 10 18 36 54 86…

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Closed (Full) Electron Shells

- A full (n,ℓ) sub-shell of 2(2ℓ + 1) electrons:
  - contributes to the energy of the atom
  - has each quantum state, wave function, assigned to an electron
  - Total $L_z = 0$ given by total sum of all m
  - Total $S_z = 0$ given by total sum of all m_s
  - Total $J_z = 0$ given by total sum of all m_j
- Hence it follows that a full sub-shell contributes <u>zero</u> to the (total angular momentum)^2 (J^2) and its projection $J_z = m_z \hbar$ of the atom
- There is also <u>no</u> contribution to the magnetic dipole moment

---

Ground State of Fe (Z=26)

- Optically active electrons are in the 3d sub-shell

	eV		Σ
4s	−7.9	2	
3d	−8.2	10	26
3p	−56	6	18
3s	−94	2	12
2p	−710	6	10
2s	−850	2	4
1s	−7130	2	2

- Large magnetic moment (iron !)
- Sub-shell ordering can change from atom to atom
  - more electrons change central field approximation
- Optical spectroscopy (ΔE ≤ few eV) specified by "outer" unfilled sub-shells and optically active electrons
- Inner sub-shell electrons have binding energies ~ keV
  - X ray active

Partially Filled Electron Shells

	electron capacity
3d	10
4s	2
3p	6
3s	2
2p	6
2s	2
1s	2

increasing energy ↑

- Partially filled sub-shell(s) contribute to the total angular momentum of an atom

  - J, m_j not necessarily zero
  - empty states accessible (to electrons if atom excited)

- Spectroscopy of many-electron atoms is determined by "optically active" electrons in partially filled sub-shells
- Structure of spectroscopy from sub-shells

10.4 Fine Structure in Optical Spectroscopy
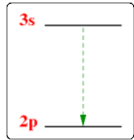
- Central field approximation:
- 1 optically active electron de-excites releasing a photon of energy:
$$E = E_{3s} - E_{2p}$$
- Example: $_6C$
  - ground state : $1s^2\ 2s^2\ 2p^2$ (capacity 2 2 6)
  - excited state : $1s^2\ 2s^2\ 2p^1\ 3s^1$ (capacity 2 2 6 2)
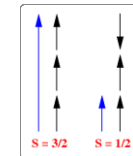   - closed   optically active
- Fine structure is observed: "splitting of energy levels"
  - Energy of atom = energy assuming central field approximation + small corrections (residual interactions)

Total Spin of Atomic Configurations

e.g. 3 electrons

e.g. $2p^2$ electrons

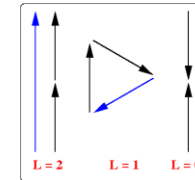- The total spin S of an atomic configuration is given by the vector sum of all optically active electrons:
$$S = |\Sigma\tfrac{1}{2}|$$
- The total orbital angular momentum L of an atomic configuration is given by the vector sum of all optically active electrons:
$$L = |\Sigma\ell|$$
- The total angular momentum J of an atomic configuration is given by the vector sum:
$$J = |\underline{L} + \underline{S}|$$

Fine Structure

- Residual interactions are ignored in the central field approximation
  - remaining non-central pieces of fields experienced by each atom
  - spin-orbit interactions (magnetic $\propto \underline{S}\cdot\underline{L}$)

- Configurations of electrons in partially filled sub-shells with different total spin S, total orbital angular momentum L, and total angular momentum J have different energies

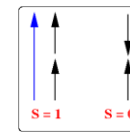- Full sub-shells, with only J = 0 contribution to atom have energies shifted

Carbon Ground State

- $_6C$ ground state : $1s^2\ 2s^2\ 2p^2$ (capacity 2 2 6)

- 2 valence electrons ($s = \tfrac{1}{2}$):
  - S = 0 requires electrons in different m_s states, antisymmetric under interchange of electrons
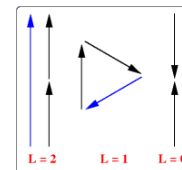 - S = 1 can have electrons in same m_s state, symmetric under interchange

- 2 electrons in 2p subshell ($\ell = 1$):
  - L = 0 symmetric under exchange
  - L = 1 antisymmetric under exchange
  - L = 2 symmetric under exchange

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Carbon Ground State

- We require overall antisymmetry under exchange
- (n,ℓ) sub-shell same for both electrons   symmetric
- Total spin $J = |\underline{L} + \underline{S}|$:

$$J = |\underline{0} + \underline{0}| \qquad |\underline{2} + \underline{0}| \qquad |\underline{1} + \underline{1}|$$

sym. anti.   sym. anti.   anti. sym.

$$^1S_0 \qquad\quad ^1D_2 \qquad\quad ^3P_2 \ ^3P_1 \ ^3P_0$$

highest energy   lowest energy

- Fine structure spectroscopic notation: $^{2S+1}L_J$
- Each with different energy:

  Largest S lowest energy ⎫ residual electrostatic

  Then largest L lowest energy ⎬ interactions
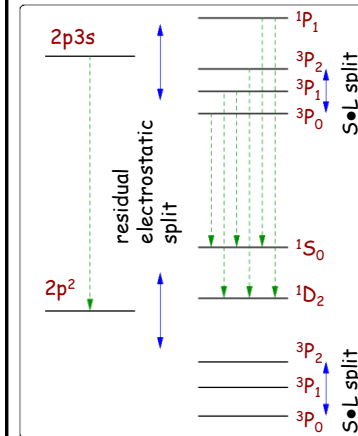
  Then smallest J lowest energy spin-orbit

  (Hund's Rules)

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Carbon Excited State

- $_6C$ excited state : $1s^2\ 2s^2\ 2p^1\ 3s^1$ (capacity 2 2 6 2)

- 2 electrons: S = 0, S = 1
- 1 electron in p subshell $\ell = 1$ ⎫
- 1 electron in s subshell $\ell = 0$ ⎬ L = 1
- n quantum numbers different (Pauli OK)   antisymmetric
- States $J = |\underline{L} + \underline{S}|$:

$$J = |\underline{1} + \underline{0}| \qquad\qquad |\underline{1} + \underline{1}|$$

$$^1P_1 \qquad\qquad ^3P_2 \ ^3P_1 \ ^3P_0$$

highest energy   lowest energy $^{2S+1}L_J$

- So what transitions are possible ?

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Carbon Fine Structure

2p3s

residual electrostatic split

$^1P_1$

$^3P_2$
$^3P_1$
$^3P_0$ $\underline{S}\bullet\underline{L}$ split

$^1S_0$

2p² $^1D_2$

$^3P_2$
$^3P_1$
$^3P_0$ $\underline{S}\bullet\underline{L}$ split

- One line (transition) becomes six !

- There are single lines for:
  - $\Delta L = \pm 1$
  - $\Delta J = 0, \pm 1$

- Other examples in other atoms can be more or can be less complicated

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Electron Configurations: Summary

- Single electron (hydrogen atom level energies)
  Couple ℓ and s to produce j
- Labels:

  $n\ \ell\ _j$ e.g. $1s_{1/2}$ ground state

- Multi electron configurations
  1 Split into inert core (filled shells) plus outer (valence) electrons
  2 Couple the ℓ values to produce L
  3 Couple the s values to produce S
  4 Couple L and S to produce J   (fermion asymmetry)
- Labels:

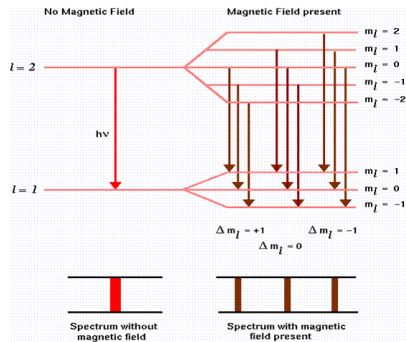 $^{2S+1}L_J$ e.g. $^3P_1$

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10.5 Zeeman Effect

- Atomic spectra change when subjected to an applied magnetic field
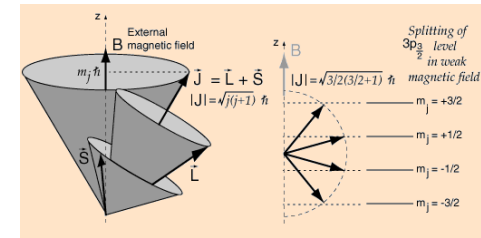- Fine structure splits into (yet more !) lines

---

Angular Momentum in a Magnetic Field

- Recall that the $\underline{L}$ and $\underline{S}$ vectors precess about the direction of the $\underline{J}$ vector
- Now the $\underline{J}$ vector precesses around the direction of the $\underline{B}$ field
- Now m_j is the constant of motion

Zeeman Effect

- The magnetic moment of the atom interacts with the applied magnetic field:

$$E_{atom} = E_{central\ field\ approx} + E_{residual} + \Delta E_{applied\ magnetic\ field}$$

- The interaction energy is:

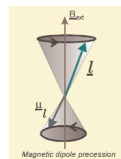$$\Delta E = -\underline{\mu} \bullet \underline{B}$$

- With:

$$\underline{\mu} = g_j \{\mu_B/\hbar\} \underline{J}$$

- Where:
  - μ_B is the Bohr magneton
  - g_j is the Landé g factor which depends on the atomic state (cf spin g factor of electron)

$$g_j = 1 + \{ [(j(j+1) + s(s+1) - \ell(\ell+1)] / 2j(j+1) \}$$

Interaction Energy

- For an atom in configuration $^{2S+1}L_J$:

$$\Delta E = g_j \{\mu_B/\hbar\} B\ J_z$$

  when the uniform magnetic field is applied along the z axis (spatial quantisation axis)
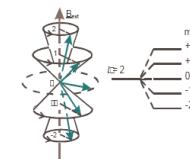- Now:

$$J_z = m_j \hbar$$

- Hence:

$$\Delta E = g_j\ \mu_B\ B\ m_j$$

- Splitting of energy level given by m_j (similar but not identical with Stern Gerlach experiment)
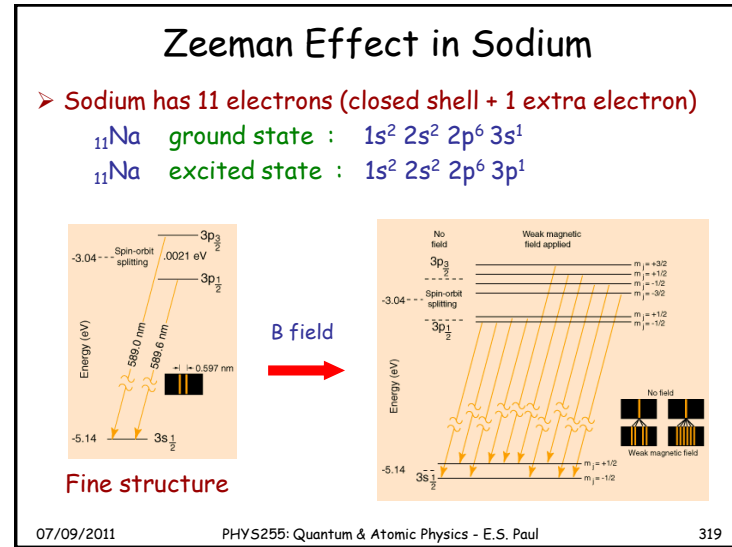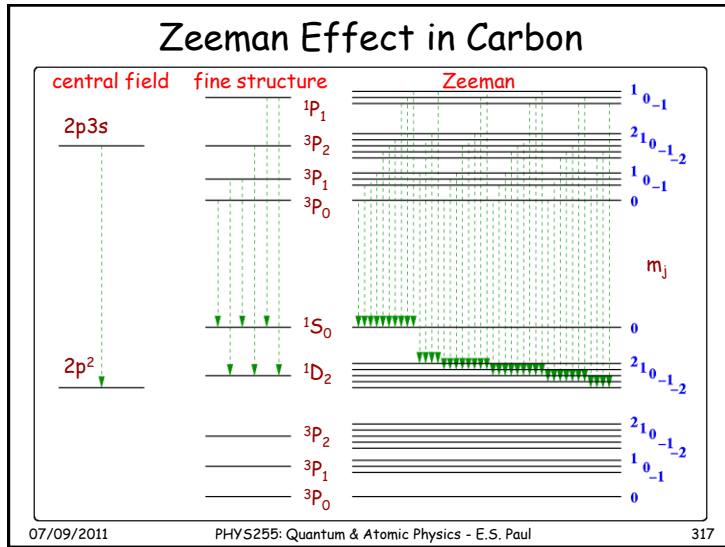 - proportional to B
  - depends on detailed atomic configuration (g_j)

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Zeeman Effect in Carbon

central field   fine structure   Zeeman

2p3s

$^1P_1$

$^3P_2$

$^3P_1$

$^3P_0$

m_j

$^1S_0$

$2p^2$

$^1D_2$

$^3P_2$

$^3P_1$

$^3P_0$

Zeeman Effect in Sodium

➢ Sodium has 11 electrons (closed shell + 1 extra electron)

$_{11}$Na   ground state : $1s^2\ 2s^2\ 2p^6\ 3s^1$

$_{11}$Na   excited state : $1s^2\ 2s^2\ 2p^6\ 3p^1$

Fine structure

Zeeman Effect: Selection Rules

➢ Transitions with:

$$\Delta L = \pm 1$$
$$\Delta J = 0, \pm 1$$

are now split according to:

$$\Delta m_j = 0, \pm 1$$

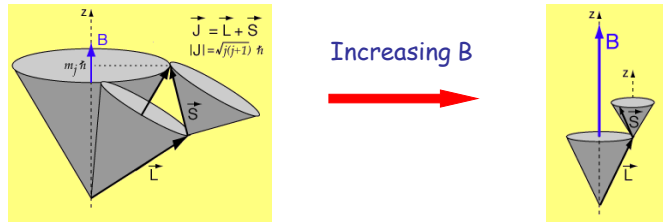leading to many different transitions !

➢ Note that if the applied magnetic field is large, i.e. much greater than the spin-orbit interaction, then the splitting can be different (Paschen-Back effect)

Paschen-Back Effect (Strong Field)

$\Delta E = \mu_B B$

Magnetic interaction energy $= (m_l + 2m_s)\mu_B B$

➢ The Zeeman splitting changes form in a strong magnetic field: the Paschen-Back Effect

➢ The field is strong enough disrupt the coupling between orbital L and spin S angular momenta

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Paschen-Back Effect

Increasing B

> Weak field (left):
>> The vectors L and S couple to form J which precesses around the direction of the magnetic field B
> Strong field (right):
>> The vectors L and S couple more strongly to the external field B rather than each other

---

10.6 Hyperfine Structure

> Yet more (very small) splitting of atomic transitions !
> Just as electrons in motion give rise to an atomic magnetic dipole moment, protons in motion give rise to a nuclear dipole magnetic moment

$$\underline{\mu} = g_I \{\mu_N/\hbar\} \, \underline{I} \quad \text{where} \quad \mu_N = \{e\hbar/2m_p\}$$

Nuclear magneton

> Note that: $\mu_N = \mu_B / 1836$ ratio of proton and e⁻ masses

> The proton dipole moment will interact with both the spin dipole moment of the electron and the orbital dipole moment of the electron

---

Proton and Neutron g Factors

> Consider orbital ℓ and intrinsic s angular momenta of the proton and neutron
> The orbital motion of the charged proton gives rise to a magnetic dipole moment and hence:

$$g_\ell \text{ (proton) = 1}$$

> The neutron is uncharged and hence:

$$g_\ell \text{ (neutron) = 0}$$

> Since the proton and neutron are composite objects, they have:

$$g_s \text{ (proton)} \approx 5.56 \quad \text{and} \quad g_s \text{ (neutron)} \approx -3.83 \; (!)$$

> Thus the intrinsic spin of the uncharged neutron can give magnetic effects !

Recall g_ℓ (electron) = 1   and g_s (electron) ≈ 2.00
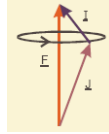
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Hyperfine Interaction

➢ The nuclear spin $\underline{I}$ (made up of orbital and intrinsic spins of the neutrons and protons) couples with the electron spin $\underline{J}$ (again made up of orbital and intrinsic spin) to give total spin $\underline{F}$:

$$\underline{F} = \underline{J} + \underline{I}$$

➢ The magnitude of $\underline{F}$ is:

$$|\underline{F}| = \sqrt{\{F(F+1)\}}\,\hbar$$

➢ The quantum number F can take the values:

$$F = J+I, J+I-1, \dots, J-I$$
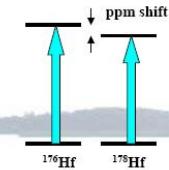
➢ There are:

$$(J+I) - |J-I| + 1$$

distinct components
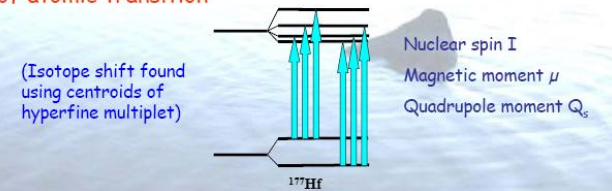

Isotope Shift & Hyperfine Structure

Isotope shift of atomic transition

Analysis yields the change in nuclear mean square charge radius

Nuclear size, static and dynamic deformations

Hyperfine structure of atomic transition

(Isotope shift found using centroids of hyperfine multiplet)

Nuclear spin I

Magnetic moment μ

Quadrupole moment Q_s

Hyperfine Interaction

➢ The interaction energy between the nuclear magnetic moment and the magnetic field produced by the electron angular momentum is given by:

$$E_{HF} = -\underline{\mu}_I \cdot \underline{B}_J = \{a/2\}\,[F(F+1) - I(I+1) - J(J+1)]$$

where:

$$a = \{g_I\,\mu_N\,B_J\} / \sqrt{\{J(J+1)\}}$$

➢ Hyperfine energy shifts are of the order:

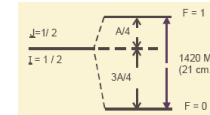$$\{m_e / m_p\}\,\alpha^2\,E_n \qquad \alpha \text{ fine structure constant}$$

➢ Measurement of the hyperfine structure of atomic transitions can yield the nuclear spin I if J is known

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Hyperfine Transition of Hydrogen

➢ For the ground state of hydrogen the hyperfine splitting between the F=1 and F=0 states is

$$\Delta E_{HF} = 5.9 \times 10^{-6}\ eV$$

➢ The photon corresponding to this transition has:

$$\nu = 1420.4057517667(10)\ MHz$$
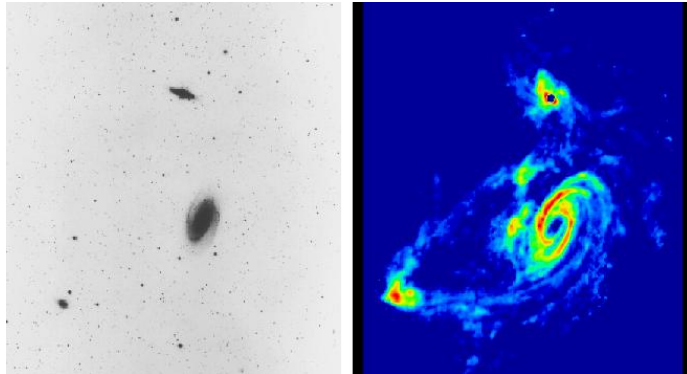$$\lambda = 21.1\ cm$$

which is in the range of radio frequencies

➢ This is the source of the famous 21 cm line which is extremely useful to radio astronomers for tracking hydrogen in the interstellar medium of galaxies

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Hydrogen in the Universe

Stellar light distribution   H 21 cm distribution

The Ring Nebula

Visible Light   21 cm Radiofrequency

Hyperfine Structure in an External Magnetic Field

➢ In a weak magnetic field the shift of the atomic energy levels due to hyperfine splitting is:

$$\Delta E_{HF} = g_F \, \mu_B \, B \, m_F$$

with:

$$g_F = g_J \left[\{F(F+1) + J(J+1) - I(I+1)\} / \{2F(F+1)\} \right]$$
$$- g_I \{\mu_N / \mu_B\} \left[\{F(F+1) + I(I+1) - J(J+1)\} / \{2F(F+1)\} \right]$$
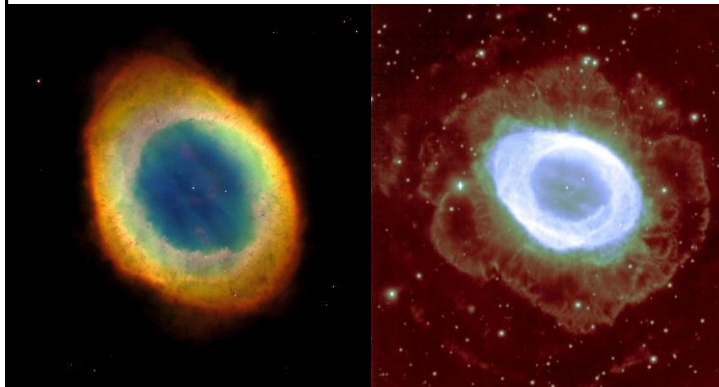
➢ We can neglect the second term since $\mu_N = \mu_B / 1836$

➢ The levels are split into $2F+1$ equidistant components

The Second & The Metre

➢ Hyperfine structure transitions are used to make very precise atomic clocks, usually with caesium or rubidium atoms

➢ One second is now defined to be exactly 9,192,631,770 cycles of the hyperfine structure transition frequency of caesium-133 atoms

➢ Since 1983 the metre is defined by declaring the speed of light in a vacuum to be exactly 299,792,458 m s^{-1}

➢ The metre is the length of the path travelled by light in vacuum during a time interval of 1 / 299,792,458 s

10.7 The Lamb Shift

➢ According to Schrödinger theory, electron states in the hydrogen atom with the same n and j quantum numbers ought to be degenerate (E_{nj}),

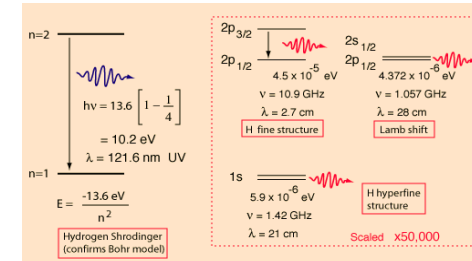e.g. $2s_{1/2}$ and $2p_{1/2}$ levels

➢ However a small energy shift is found, similar in size to the hyperfine structure

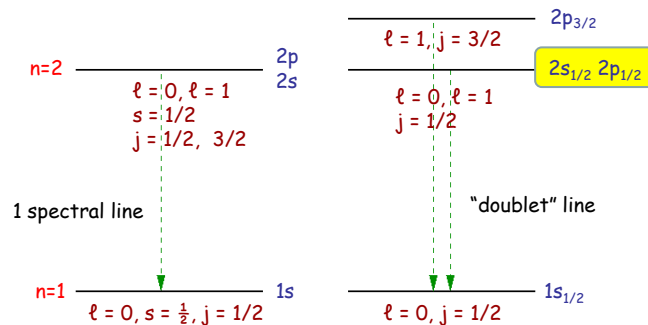➢ This is known as the Lamb Shift

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The Lamb Shift

➢ A very small difference in the energies of the $2s_{1/2}$ and $2p_{1/2}$ states in hydrogen exists, even smaller than the hyperfine structure, and corresponds to a frequency of 1.06 GHz

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H Atom Fine Structure (revisited)

➢ According to Schrödinger theory, the $2s_{1/2}$ and $2p_{1/2}$ levels in hydrogen should be degenerate

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The Electron g Factor

➢ The Lamb shift provided a high precision verification of theoretical calculations made with the quantum theory of electrodynamics (QED)

➢ These calculations predict that electrons continually exchange photons, this being the mechanism by which the electromagnetic force acts

➢ The effect is to smear out the electron's position slightly and perturbs the electron g factor from its expected value of 2

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Quantum Electrodynamics (QED)

➢ QED can be used to calculate the electron g factor with great precision:

g = 2.002319304386

➢ This value agrees to many decimal places with the value obtained from the tiny Lamb shift

➢ Triumph for QED !

10.8 Rydberg Atoms

➢ A Rydberg Atom is an excited atom with one or more of its electrons that have a very high principal quantum number n

➢ These atoms have a number of peculiar properties:

  ➢ exaggerated response to electric and magnetic fields

  ➢ long decay periods

  ➢ electron wave-functions that approximate classical orbits of electrons about the nucleus

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Rydberg Atoms

➢ Bohr's expression for the orbital radius r in terms of the principal quantum number n is

$r = a_0 n^2$ where $a_0 = 0.053$ nm is the Bohr radius

➢ For the n = 137 state in hydrogen, the atomic radius is

$r = 1$ μm   !

➢ Thus Rydberg atoms are extremely large with loosely bound valence electrons, easily perturbed or ionised by collisions or external fields