Atomic Physics

3rd year B1

P. Ewart

- ***Lecture notes***
- ***Lecture slides***
- ***Problem sets***

All available on Physics web site:

http:www.physics.ox.ac.uk/users/ewart/index.htm

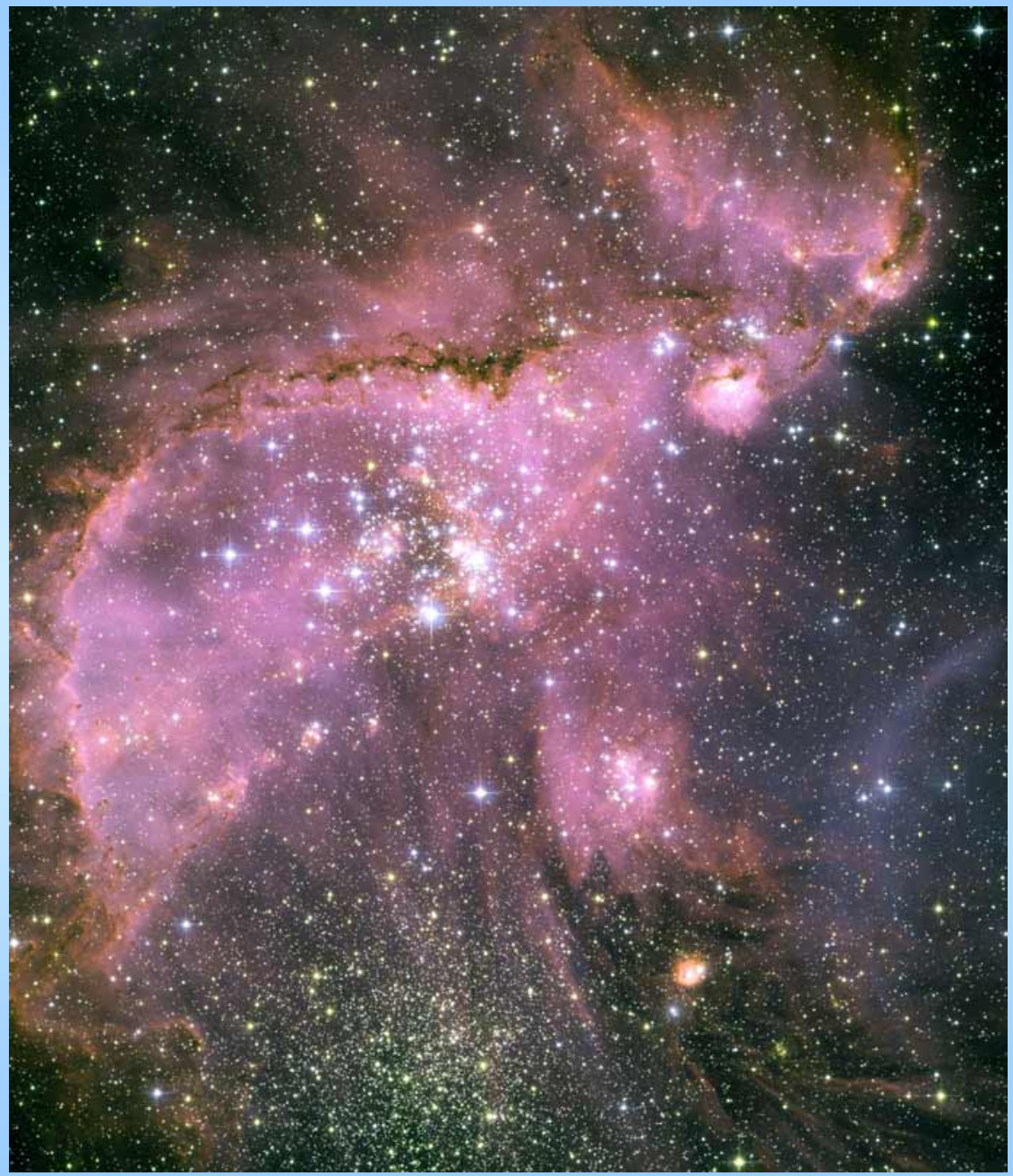
Atomic Physics:

- Astrophysics
- Plasma Physics
- Condensed Matter
- Atmospheric Physics
- Chemistry
- Biology

Technology

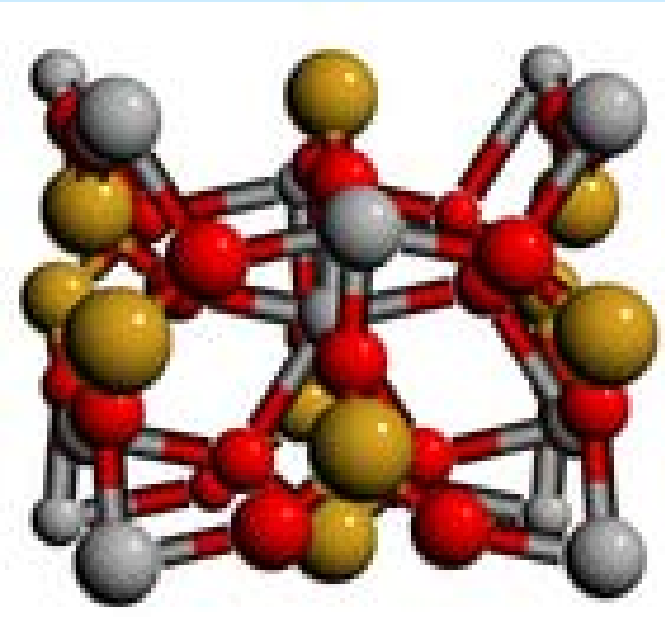
- Street lamps
- Lasers
- Magnetic Resonance Imaging
- Atomic Clocks
- Satellite navigation: *GPS*
- etc

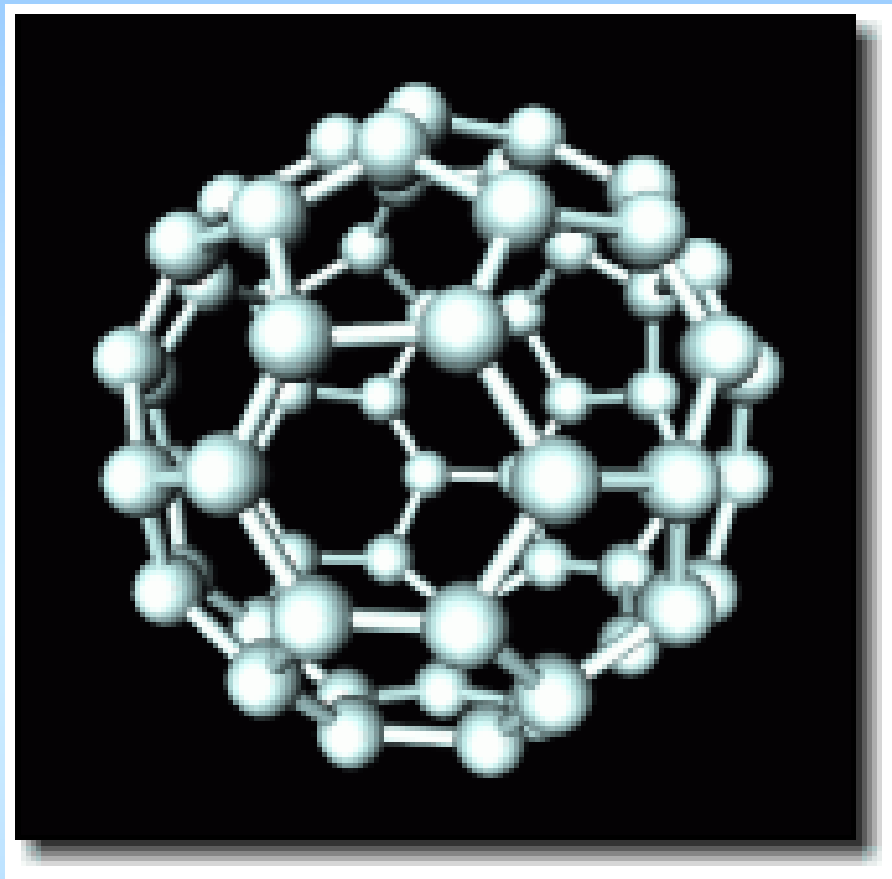
Astrophysics



Condensed Matter

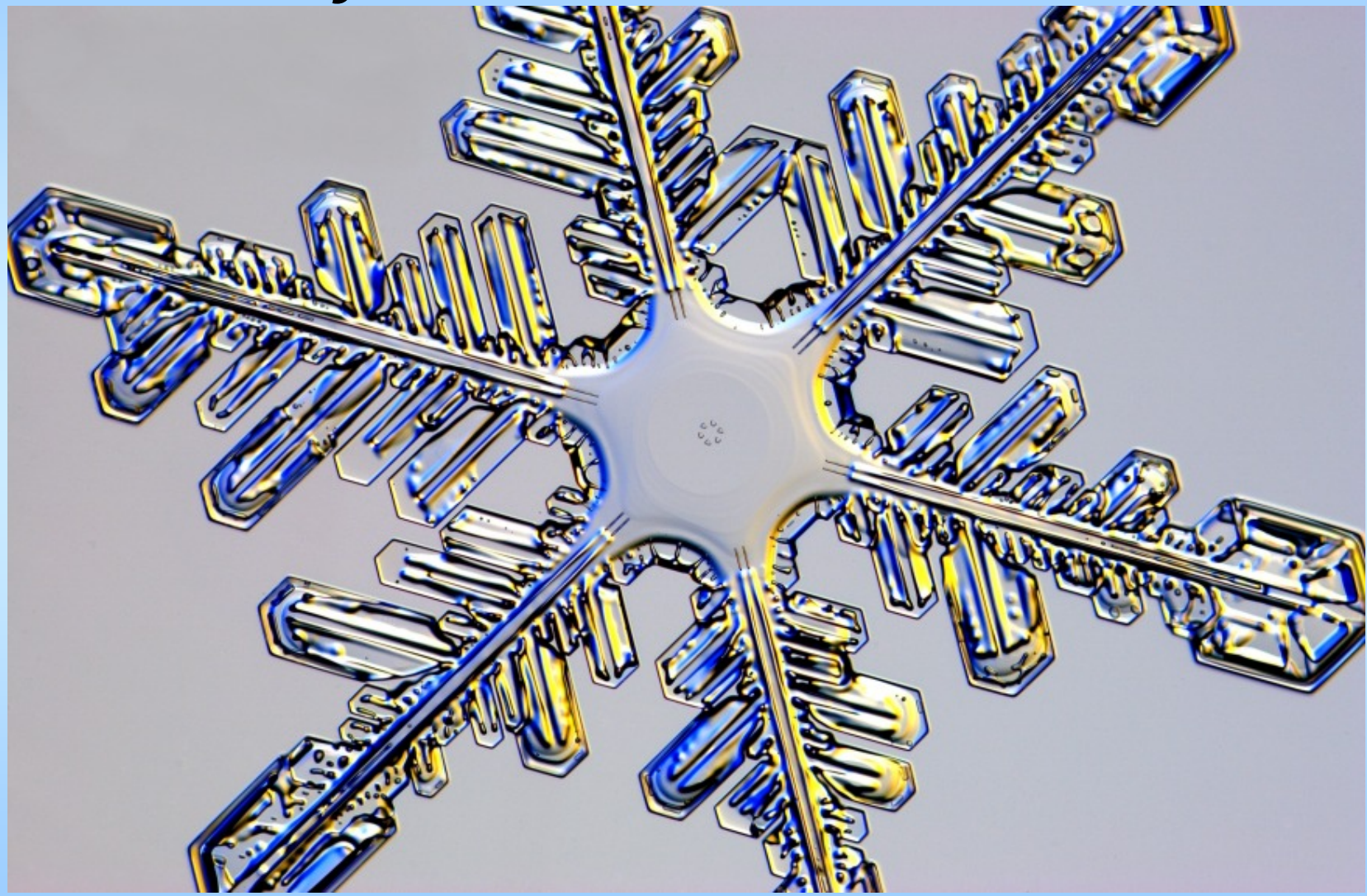
Zircon mineral crystal

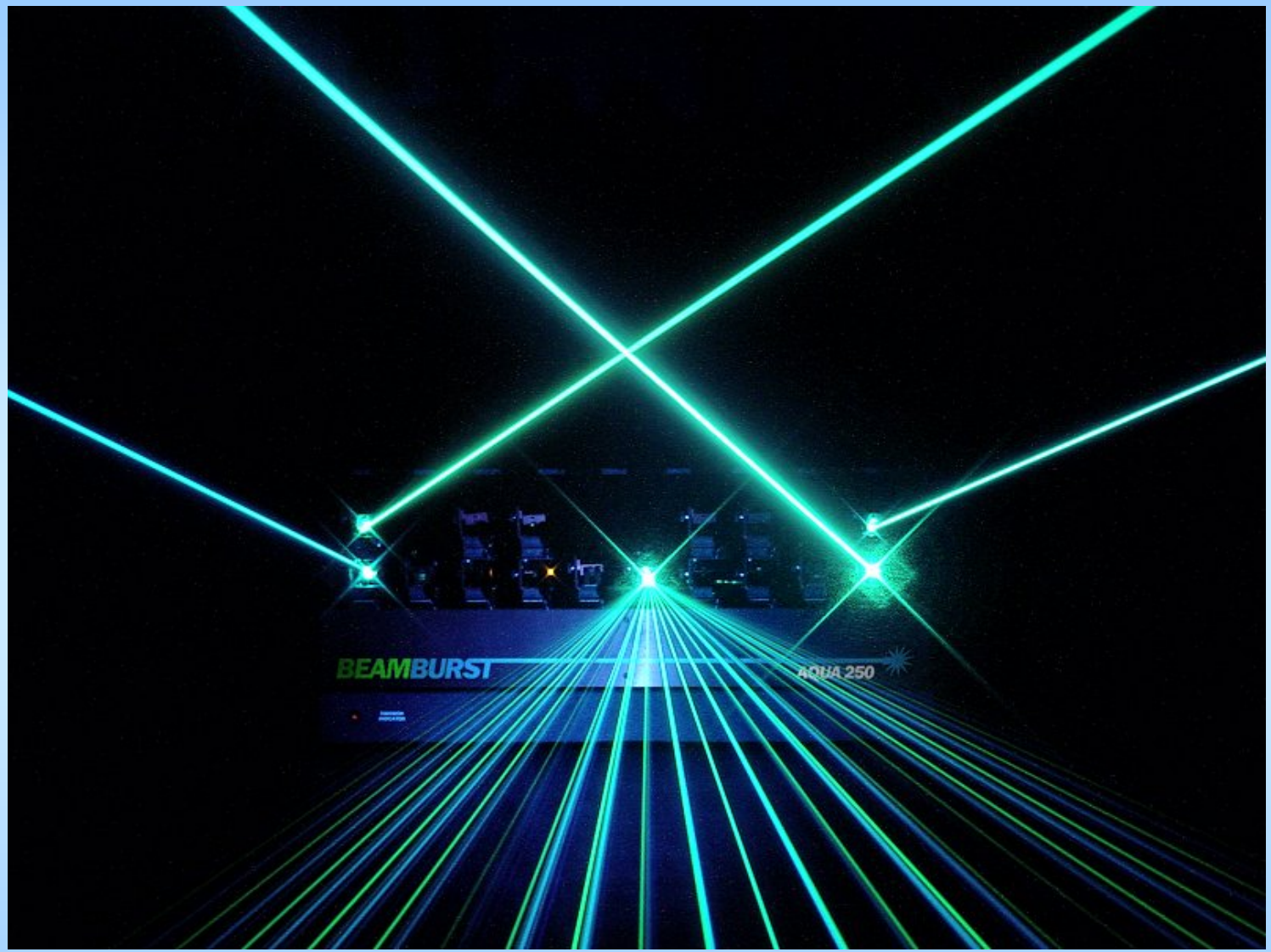




C_{60} Fullerene

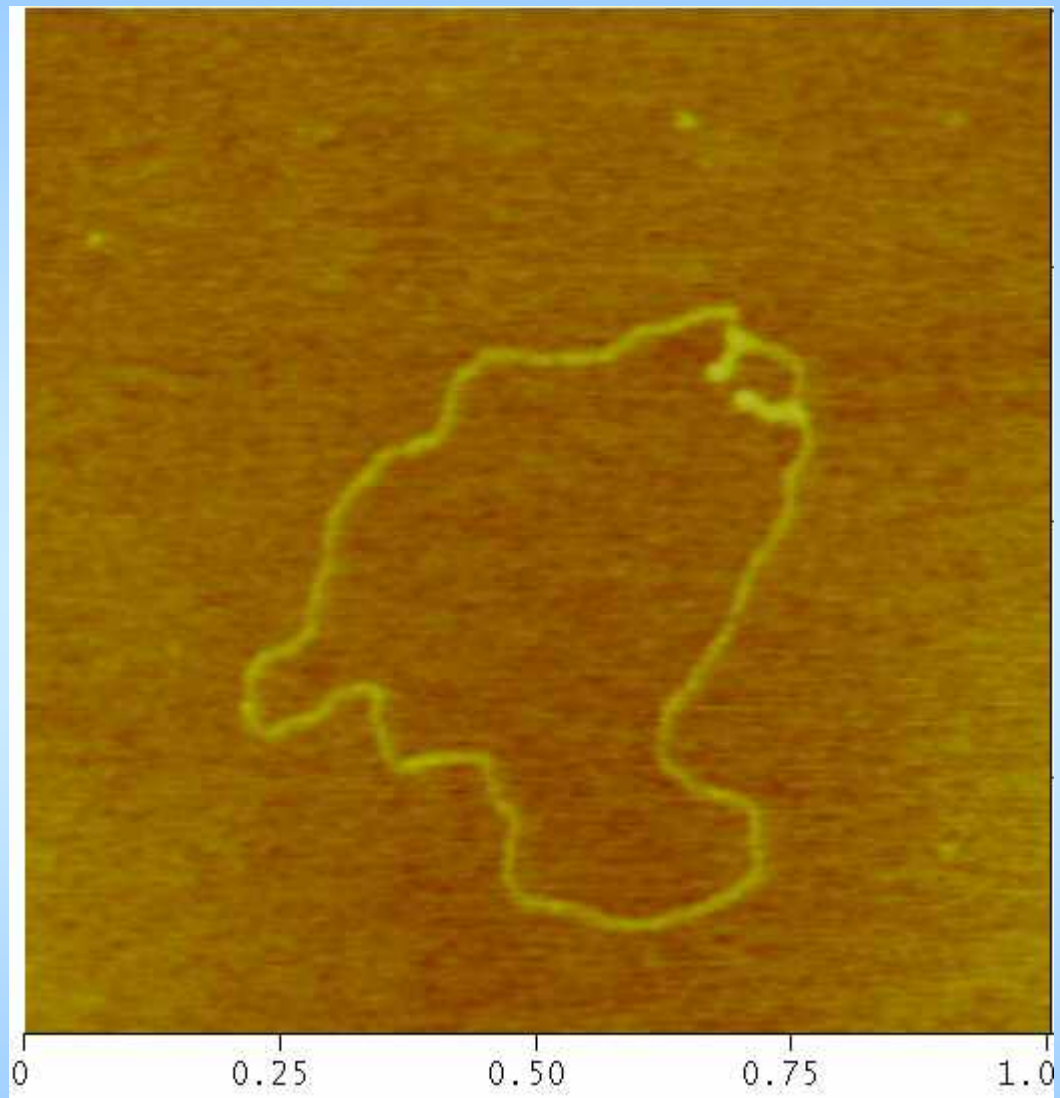
Snow crystal





Lasers

Biology

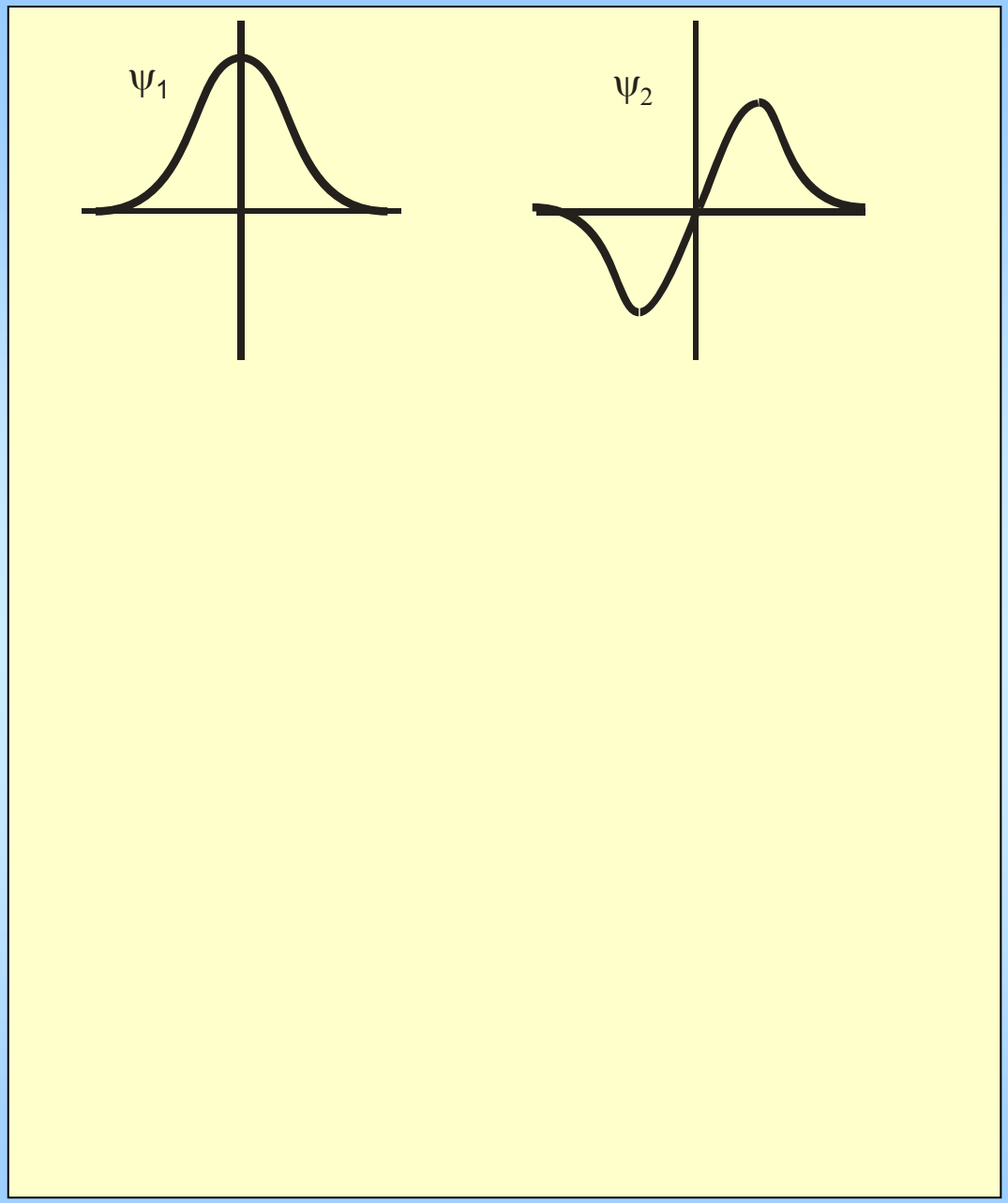


DNA strand

Lecture 1

- How we study atoms:
  - emission and absorption of light
  - spectral lines
- Atomic orders of magnitude
- Basic structure of atoms
  - approximate electric field inside atoms

Atomic radiation



Spectral Line Broadening

Homogeneous e.g.

Lifetime (Natural)

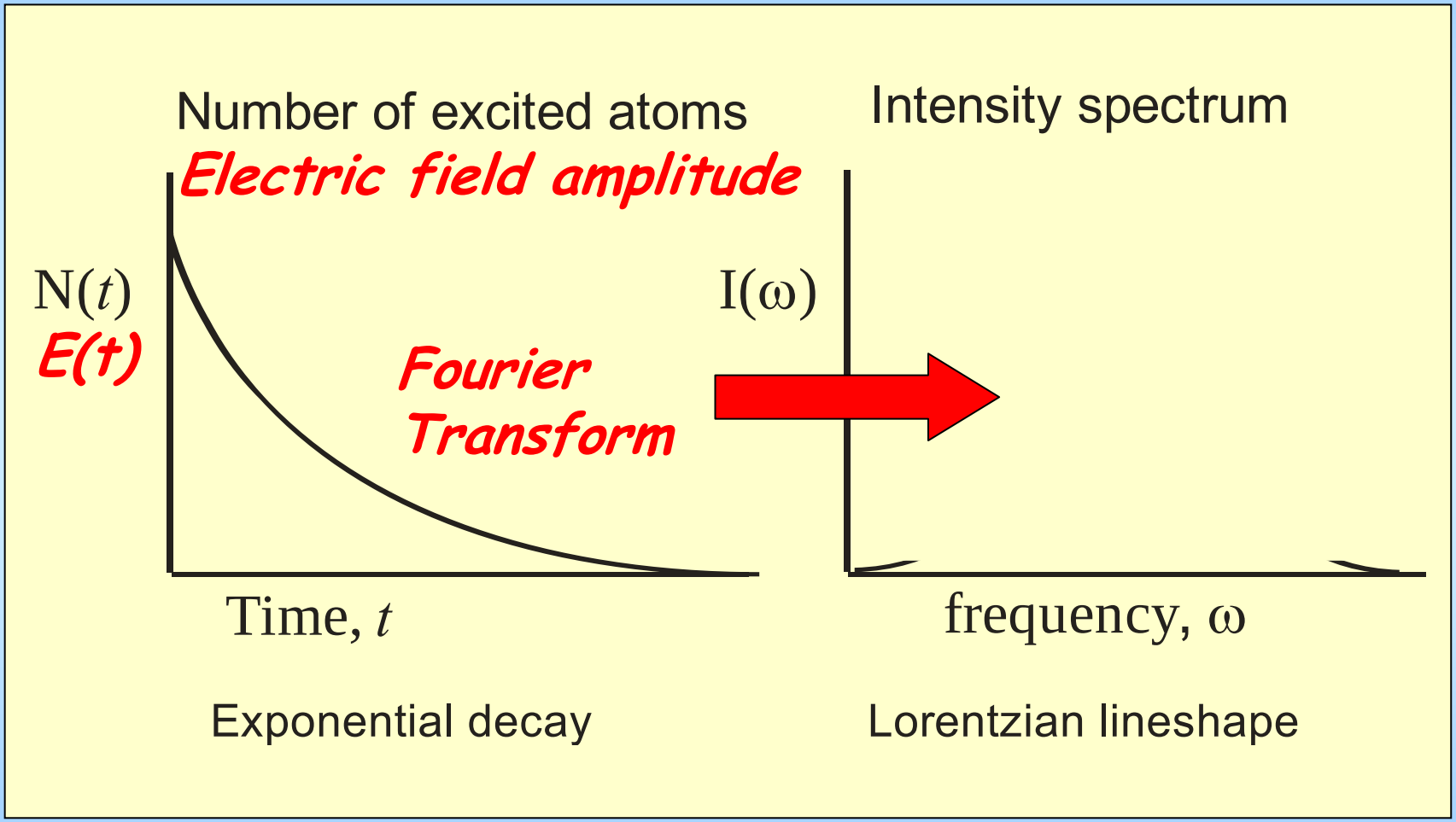
Collisional (Pressure)

Inhomogeneous e.g.

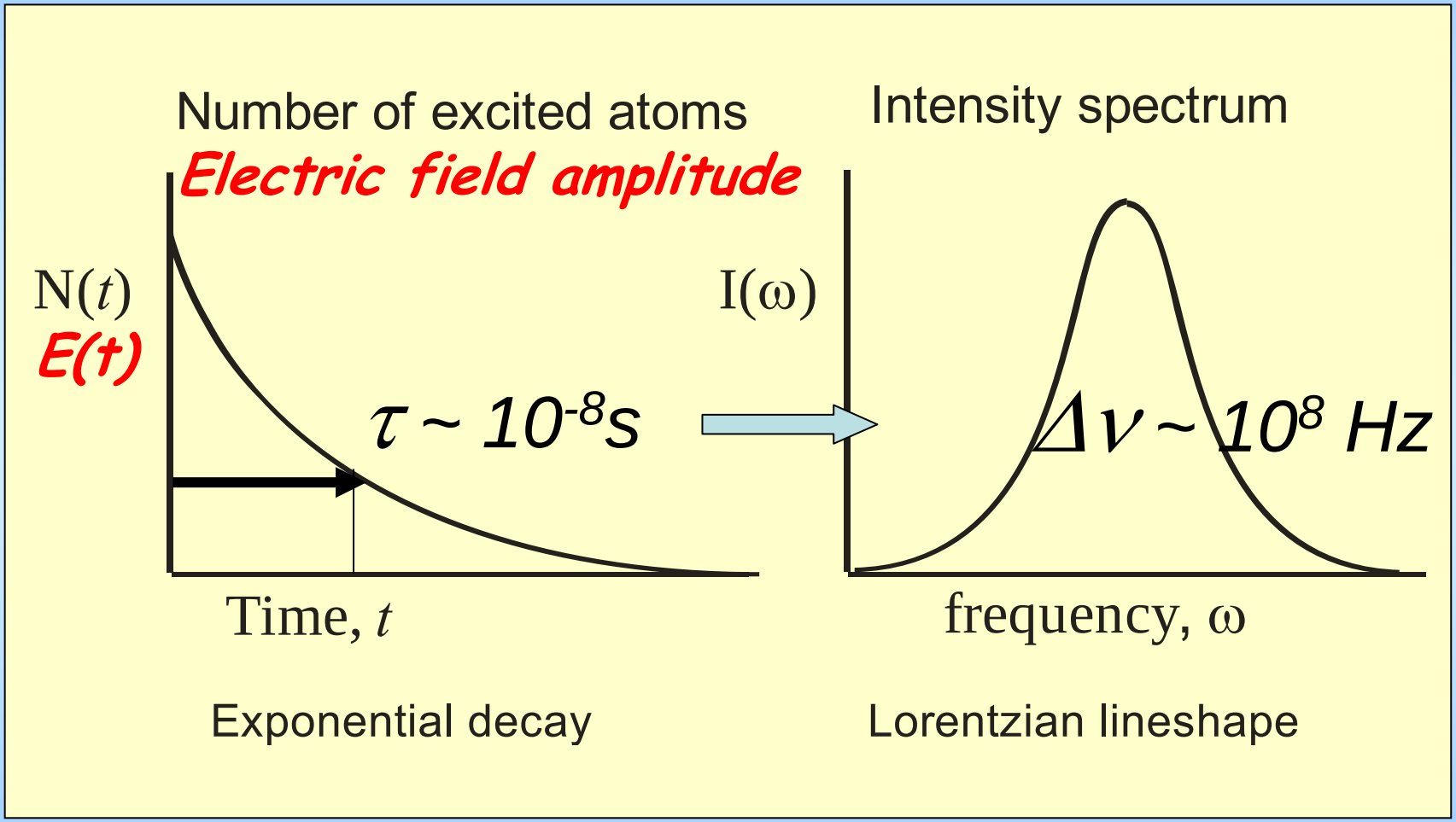
Doppler (Atomic motion)

Crystal Fields

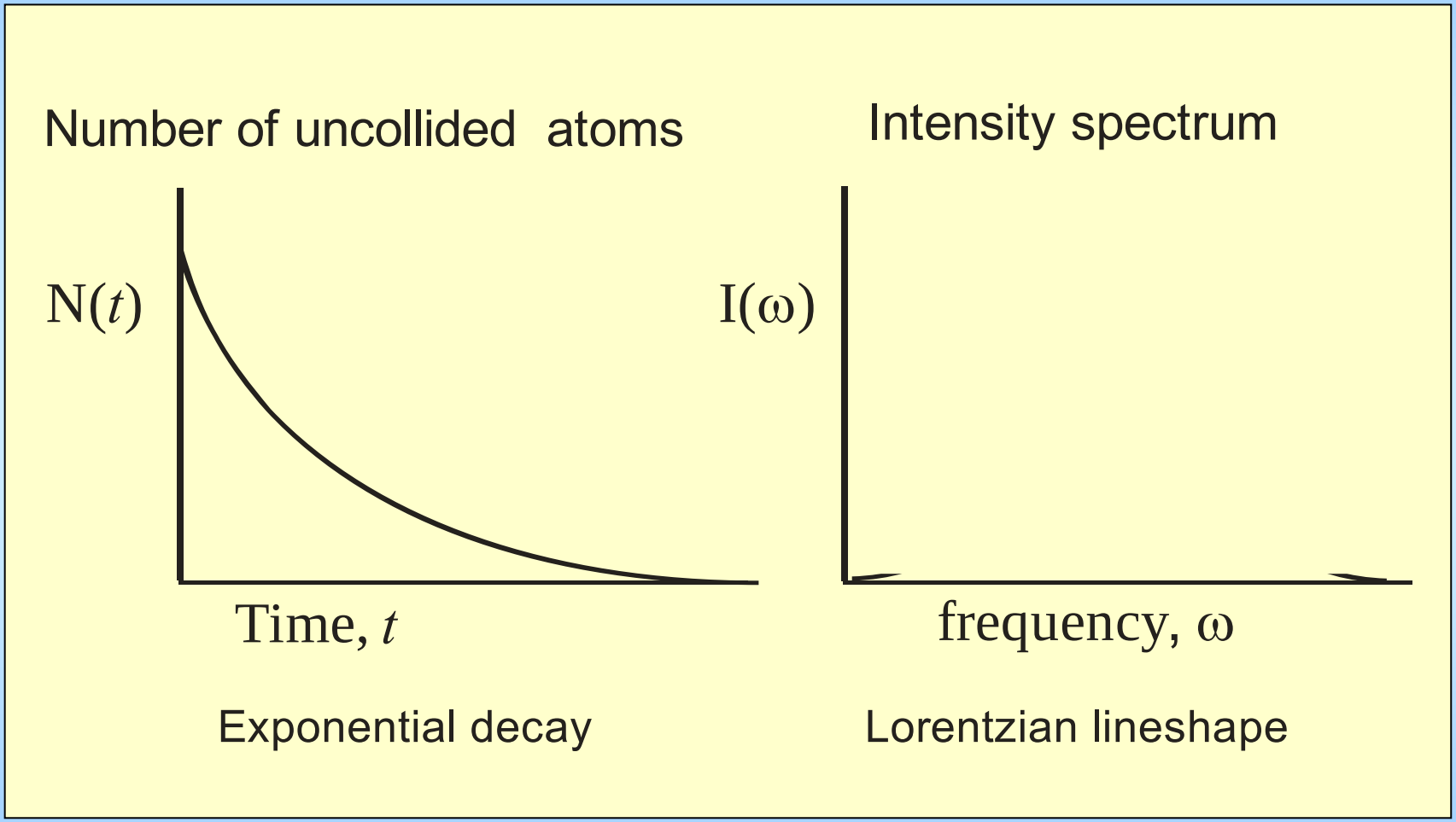
Lifetime (natural) broadening



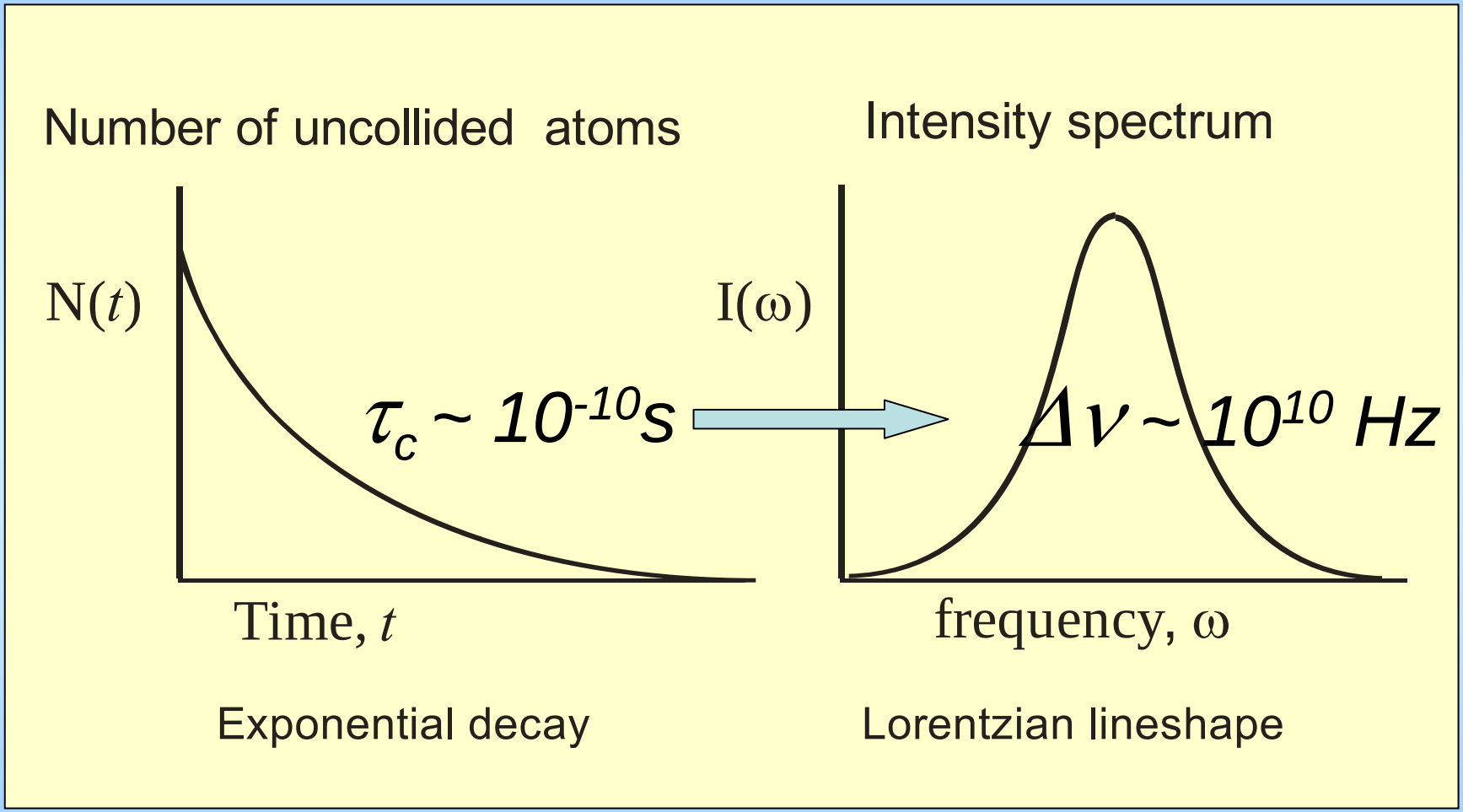
Lifetime (natural) broadening



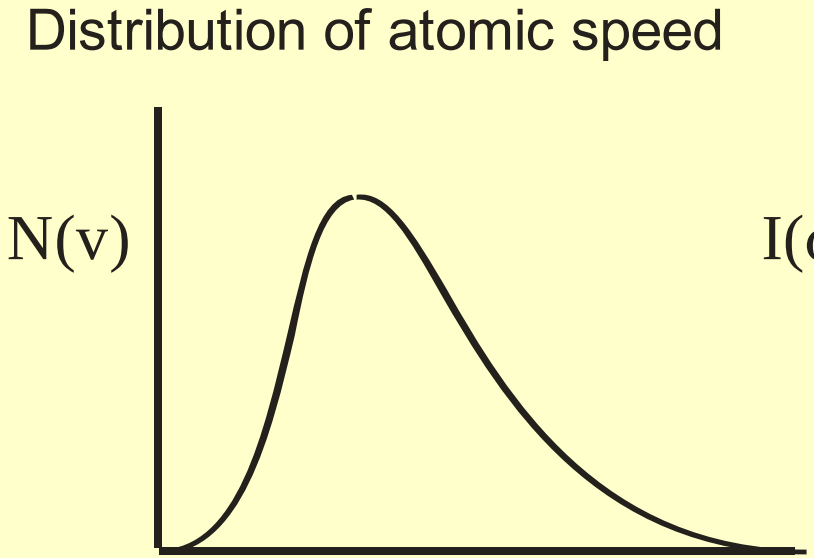
Collision (pressure) broadening

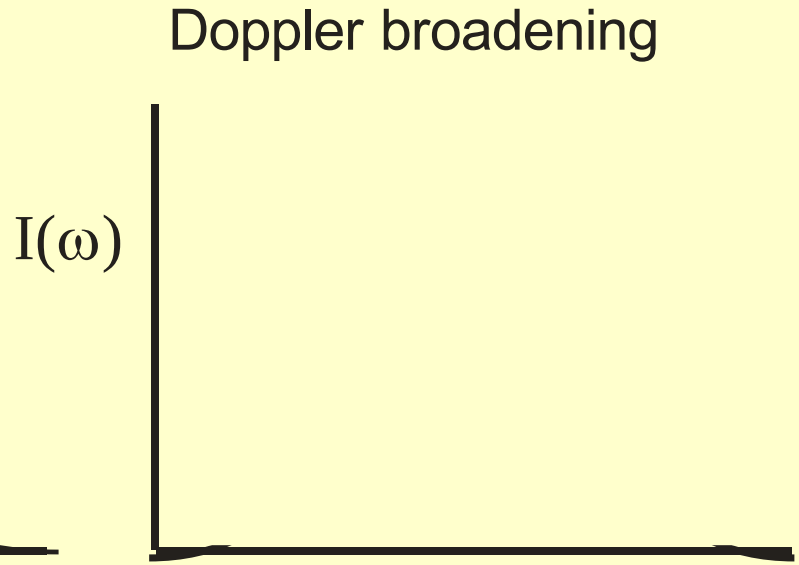


Collision (pressure) broadening



Doppler (atomic motion) broadening



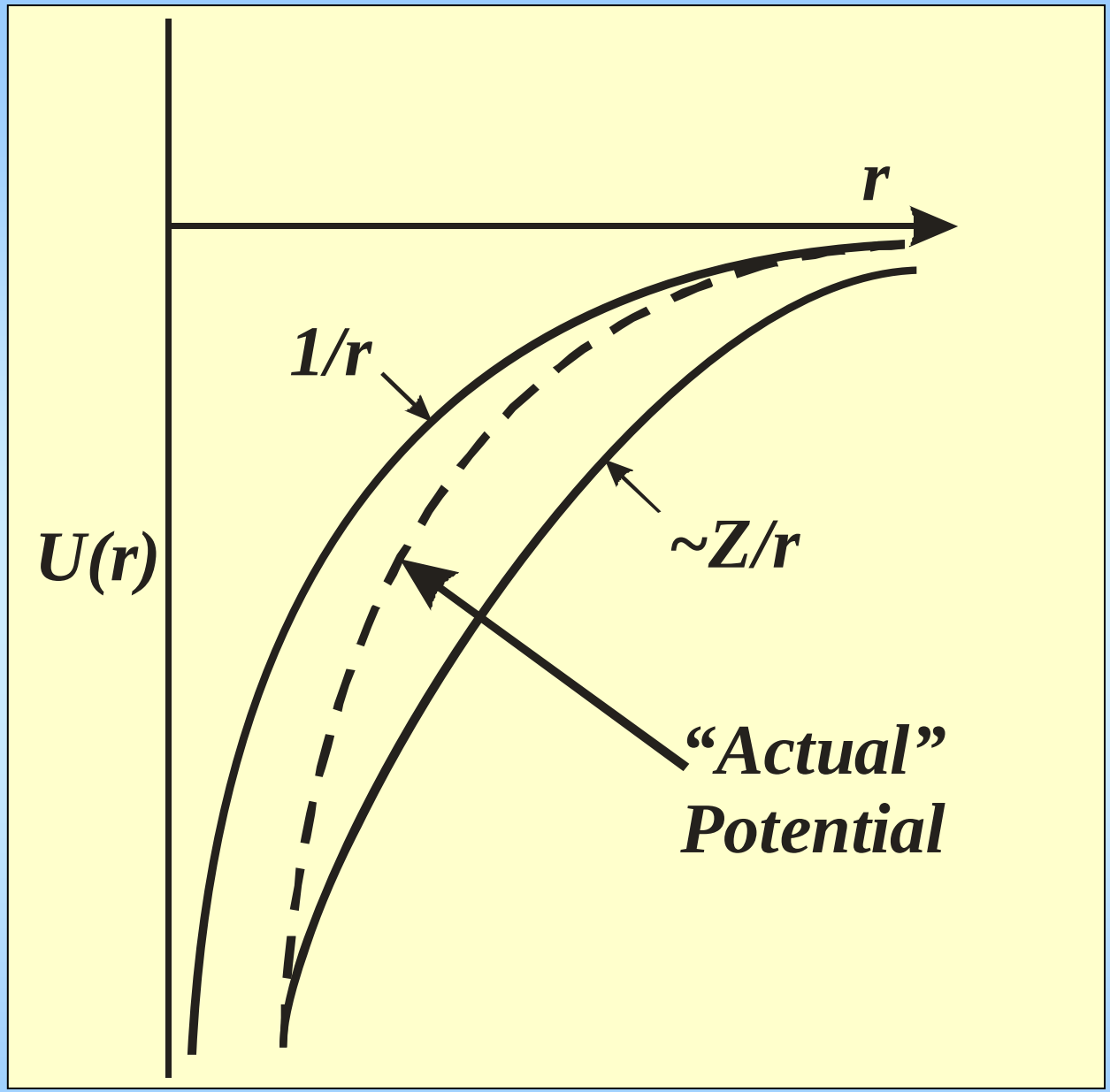


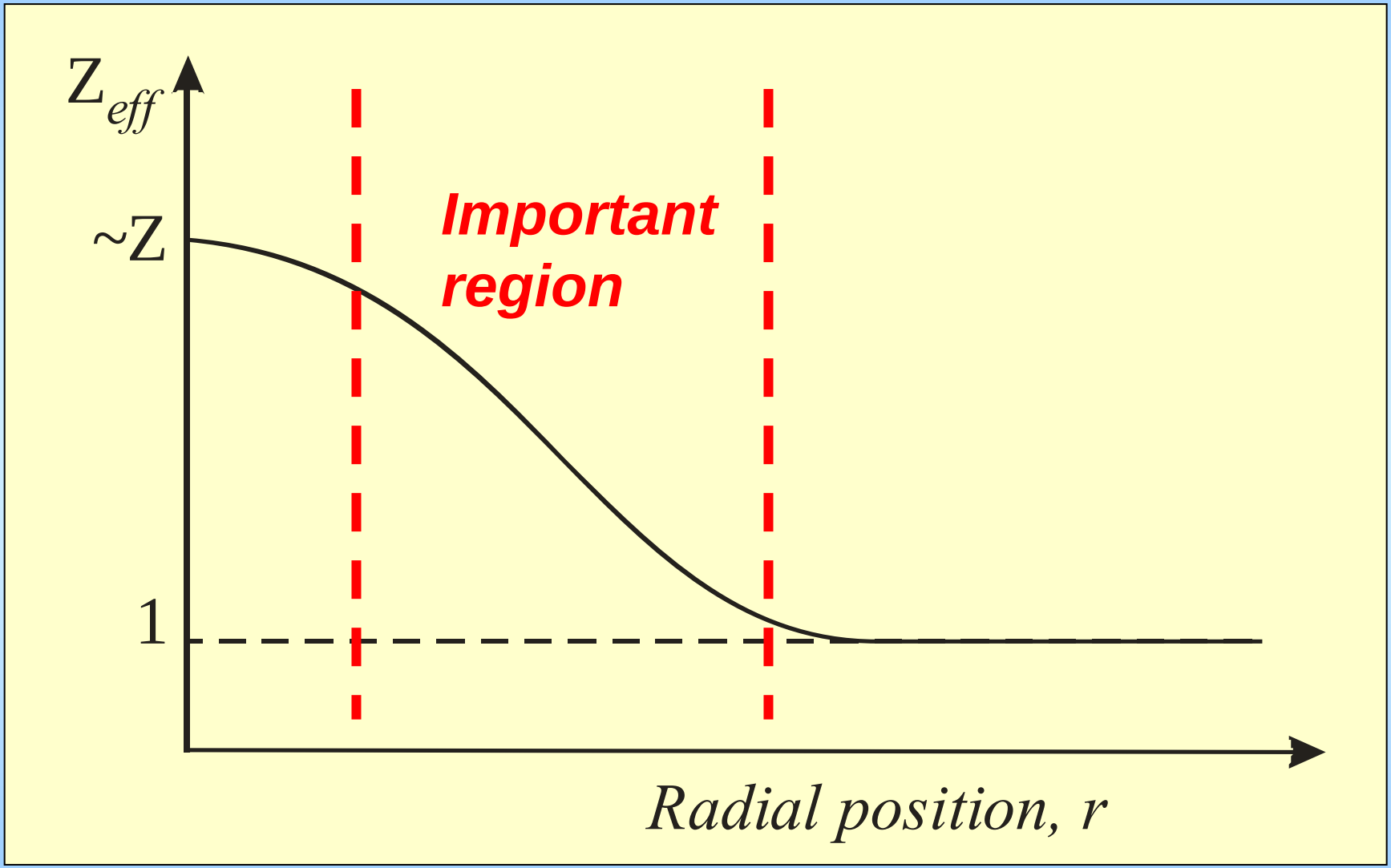
Typical $\Delta\nu \sim 10^9$ *Hz*

Atomic orders of magnitude

Atomic energy:	10^{-19} J $\rightarrow$ ~2 eV
Thermal energy:	$^1/_{40}$ eV
Ionization energy, H:	13.6 eV
= Rydberg Constant	109,737 cm^{-1}
Atomic size, Bohr radius:	5.3 x 10^{-11}m
Fine structure constant, $\alpha = v/c$:	1/137
Bohr magneton, μ_B:	9.27 x 10^{-24} JT^{-1}

The Central Field




Z_{eff}
~Z
1
Important region
Radial position, r

Lecture 2

- The Central Field Approximation:
  - physics of wave functions (Hydrogen)
- Many-electron atoms
  - atomic structures and the Periodic Table
- Energy levels
  - deviations from hydrogen-like energy levels
  - finding the energy levels; the quantum defect

Schrödinger Equation (1-electron atom)

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi$$

Hamiltonian for many-electron atom:

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i}\right) + \sum_{i>j}\frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Individual electron potential in field of nucleus

Electron-electron interaction

This prevents separation into Individual electron equations

Central potential in Hydrogen:

$$V(r) \sim 1/r,$$

separation of ψ into radial and angular functions:

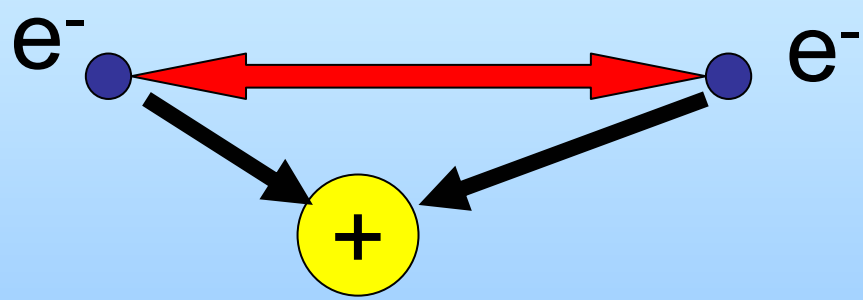
$$\psi = R(r) Y^{m}_{l}(\theta, \phi) \chi(m_s)$$

Therefore we seek a potential for multi-electron atom that allows separation into individual electron wave-functions of this form

Electron – Electron interaction term:

$$\sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Treat this as composed of two contributions:
(a)a centrally directed part
(b)a non-central ***Residual Electrostatic*** part



Hamiltonian for Central Field Approximation

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

$$\text{where} \quad \hat{H}_0 = \sum_i \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 + U(r_i) \right\}$$

Central Field Potential

$\hat{H}_1$ = residual electrostatic interaction

Perturbation Theory Approximation:
$\hat{H}_1 << \hat{H}_o$

Zero order Schrödinger Equation:

$$\hat{H}_0 \, \psi = E_0 \, \psi$$

$\hat{H}_0$ is spherically symmetric so equation is separable - solution for individual electrons:

$$\psi(n, l, m_l, m_s) = R'_{n,l}(r) Y_l^m(\theta, \phi) \chi(m_s)$$

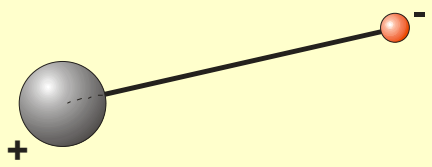
Radial Angular Spin

Central Field Approximation:

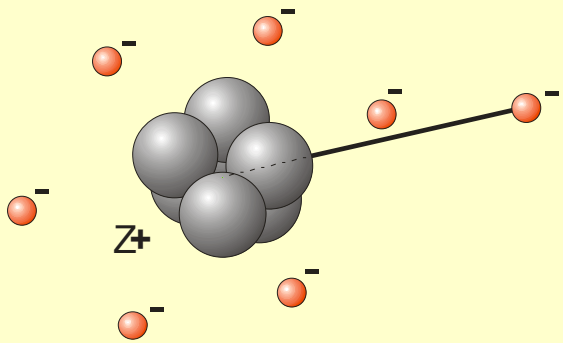
$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

$$\text{where } \hat{H}_0 = \sum_i \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 + U(r_i) \right\}$$

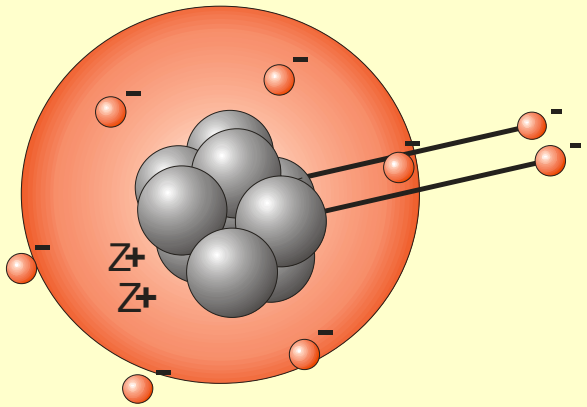
What form does $U(r_i)$ take?



Hydrogen atom

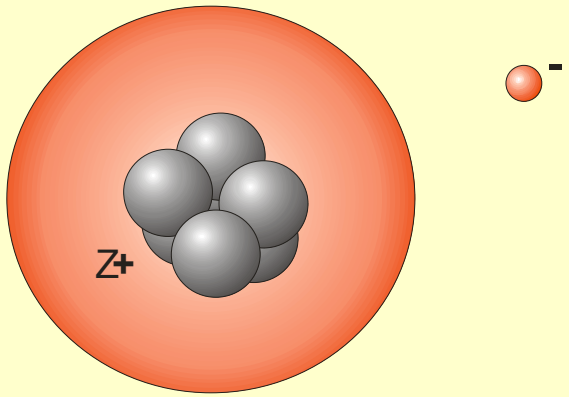


Many-electron atom



Z protons+ (Z – 1) electrons

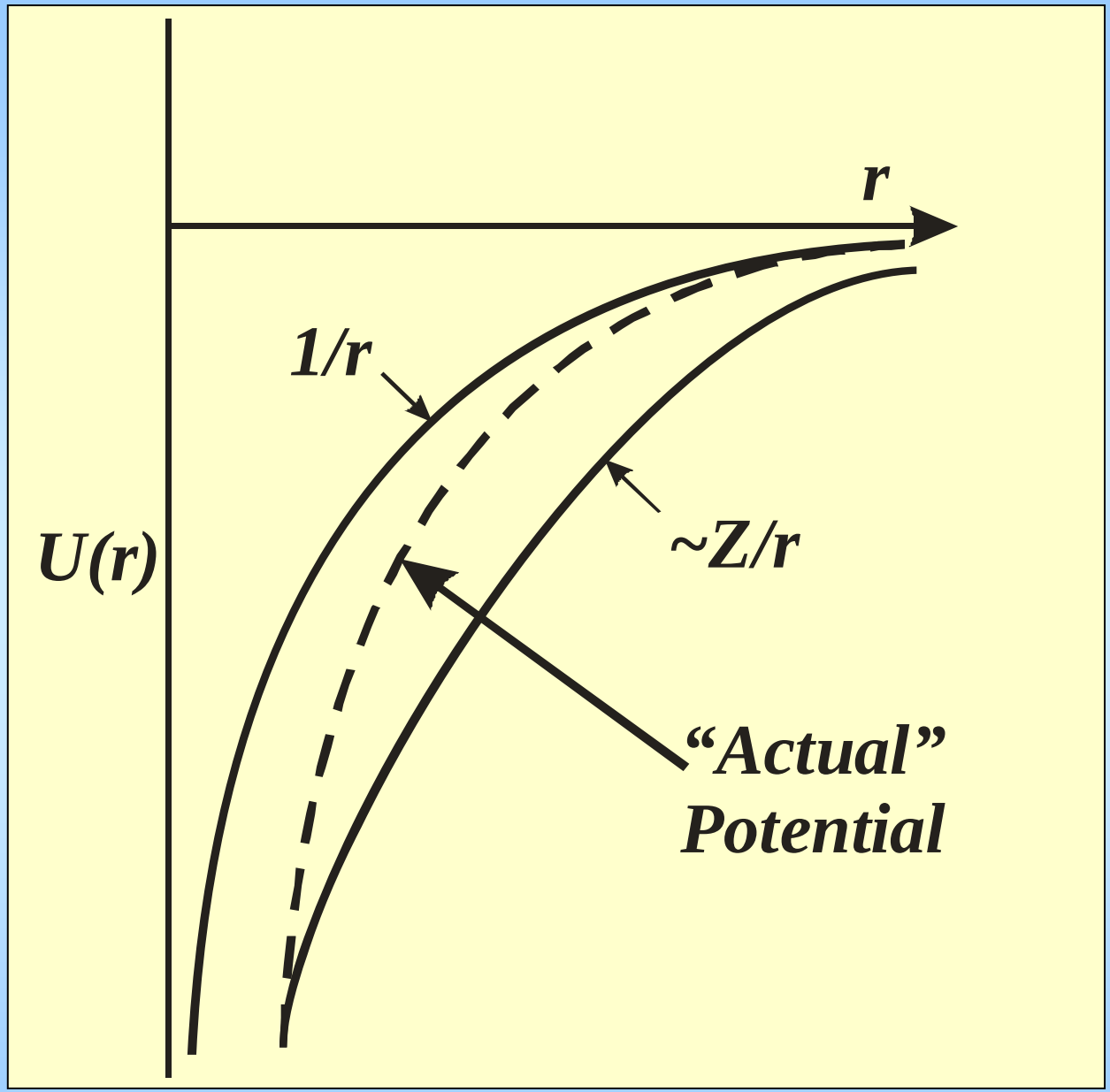
U(r) ~ 1/r

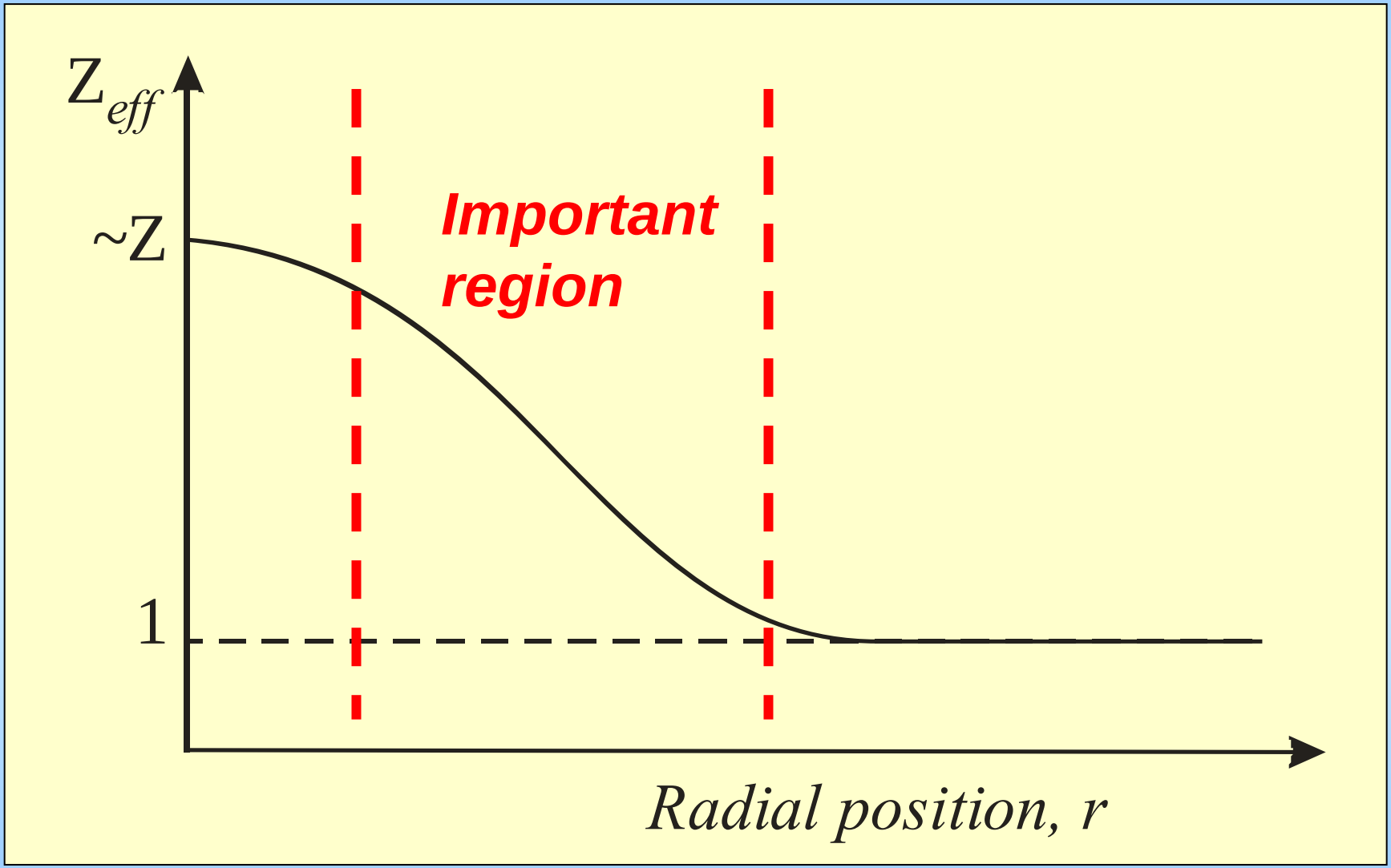


Z protons

U(r) ~ Z/r

The Central Field




Z_{eff}
~Z
1
Important region
Radial position, r

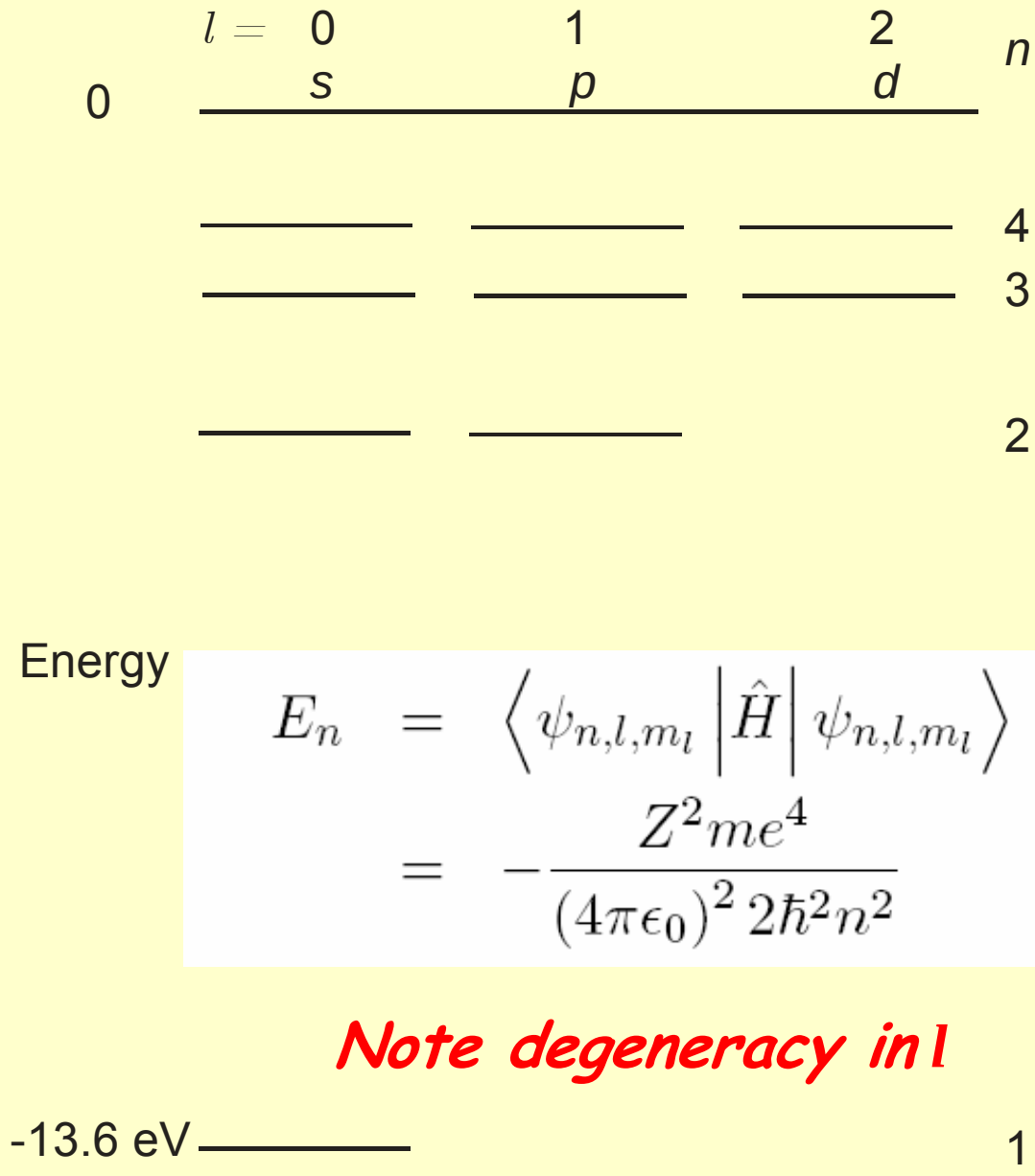
Finding the Central Field

- "Guess" form of U(r)
- Solve Schrödinger eqn. → Approx ψ.
- Use approx ψ to find charge distribution
- Calculate $U_c(r)$ from this charge distribution
- Compare $U_c(r)$ with U(r)
- Iterate until $U_c(r) = U(r)$

Energy eigenvalues for Hydrogen:

$$
\begin{aligned}
E_n &= \left\langle \psi_{n,l,m_l} \left| \hat{H} \right| \psi_{n,l,m_l} \right\rangle \\
&= -\frac{Z^2 m e^4}{(4\pi\epsilon_0)^2 \, 2\hbar^2 n^2}
\end{aligned}
$$

H Energy level diagram



Revision of Hydrogen solutions:

Product wavefunction:
Spatial x Angular function

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_l^{m_l}(\theta,\phi)$$

Normalization

$$\int R_{n,l}^2(r)r^2dr = 1 \qquad \int \left|Y_l^{m_l}(\theta,\phi)\right|^2 d\Omega = 1$$

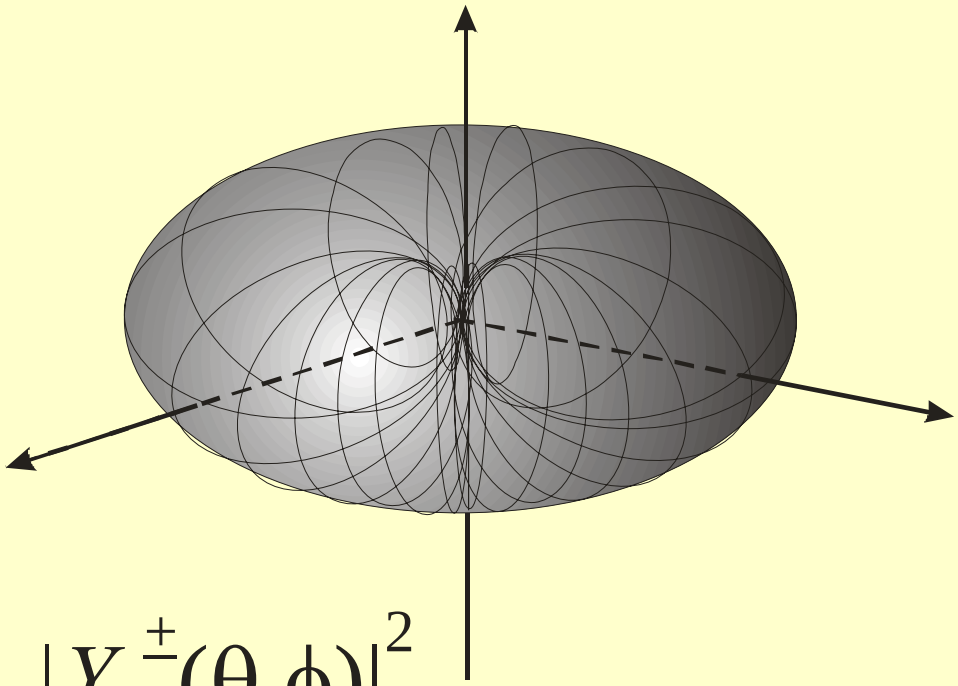
$Y_l^{m_l}(\theta,\phi)$: Eigenfunctions of angular momentum operators

$$\begin{aligned}\hat{l}^2 Y_l^{m_l}(\theta,\phi) &= l(l+1)\hbar^2 Y_l^{m_l}(\theta,\phi)\\ \hat{l}_z Y_l^{m_l}(\theta,\phi) &= m_l\hbar Y_l^{m_l}(\theta,\phi)\end{aligned}$$

Eigenvalues

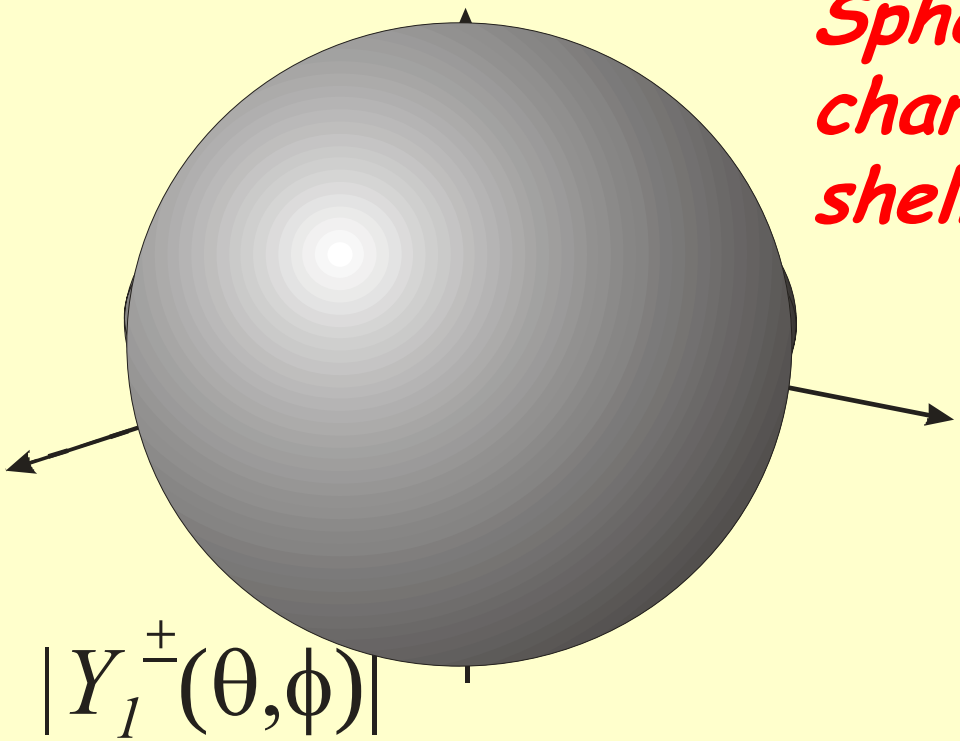
$$l = 0,1,2...(n-1) \qquad -l \le m_l \le l$$

Angular momentum orbitals



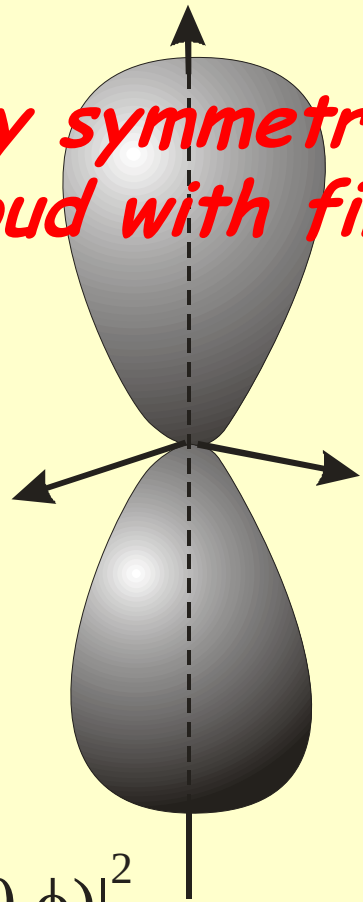
$$|Y_l^{\pm}(\theta,\phi)|^2$$

Angular momentum orbitals



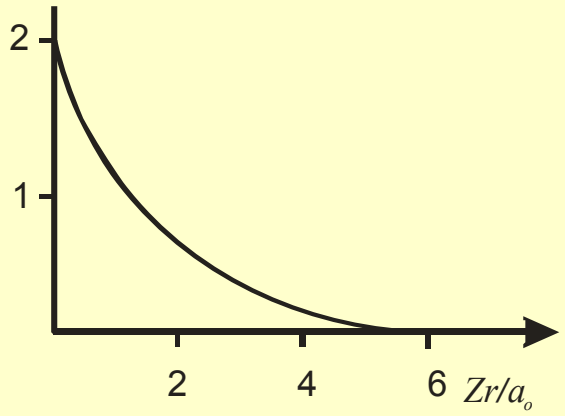
$|Y_1^{\pm}(\theta,\phi)|$

Spherically symmetric charge cloud with filled shell

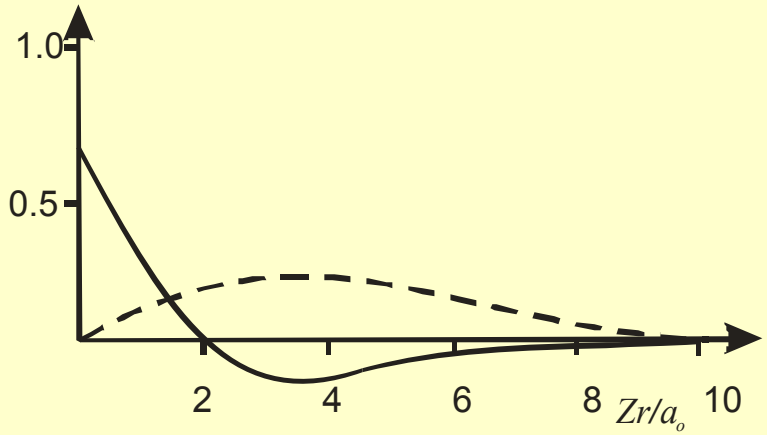


$|Y_1^{0}(\theta,\phi)|^2$

Radial wavefunctions

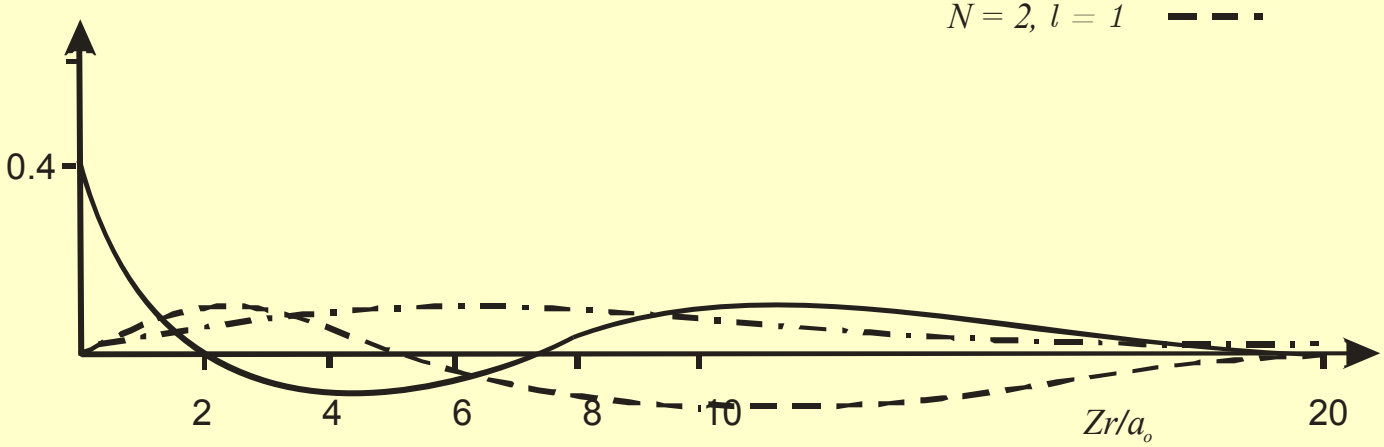


Ground state, $n = 1, l = 0$



1st excited state, $n = 2, l = 0$

$N = 2, l = 1$



2nd excited state, $n = 3, l = 0$

$n = 3, l = 1$

$n = 3, l = 2$

Radial wavefunctions

- $l = 0$ states do not vanish at $r = 0$
- $l \neq 0$ states vanish at $r = 0$,
  and peak at larger r as l increases
- Peak probability (size) ~ n^2
- $l = 0$ wavefunction has (n-1) nodes
- $l = 1$ has (n-2) nodes etc.
- Maximum $l=(n-1)$ has no nodes

Electrons arranged in “shells” for each n

The Periodic Table

Shells specified by n and l quantum numbers

H:	$1s$		
He:	$1s^2$	$2s$	
Li:	$1s^2$	$2s^2$	
Be:	$1s^2$	$2s^2 2p$	
C:	$1s^2$	$2s^2 2p^2$	
...			
Ne:	$1s^2$	$2s^2 2p^6$	
Na:	$1s^2$	$2s^2 2p^6$	$3s$

Electron configuration

The Periodic Table

K:	$1s^2 2s^2 2p^6$	$3s^2 3p^6$	$4s$
Ca:			$4s^2$

Va:	$3s^2 3p^6$	$3d^3 4s^2$
Cr:		$3d^5 4s$
Mn:		$3d^5 4s^2$

The Periodic Table
Rare gases

He:	$1s^2$
Ne:	$1s^2 2s^2 2p^6$
Ar:	$1s^2 2s^2 2p^6 3s^2 3p^6$
Kr:	$(\ldots) 4s^2 4p^6$
Xe:	$(\ldots..) 5s^2 5p^6$
Rn:	$(\ldots\ldots) 6s^2 6p^6$

The Periodic Table
Alkali metals

Li: $1s^2 2s$

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

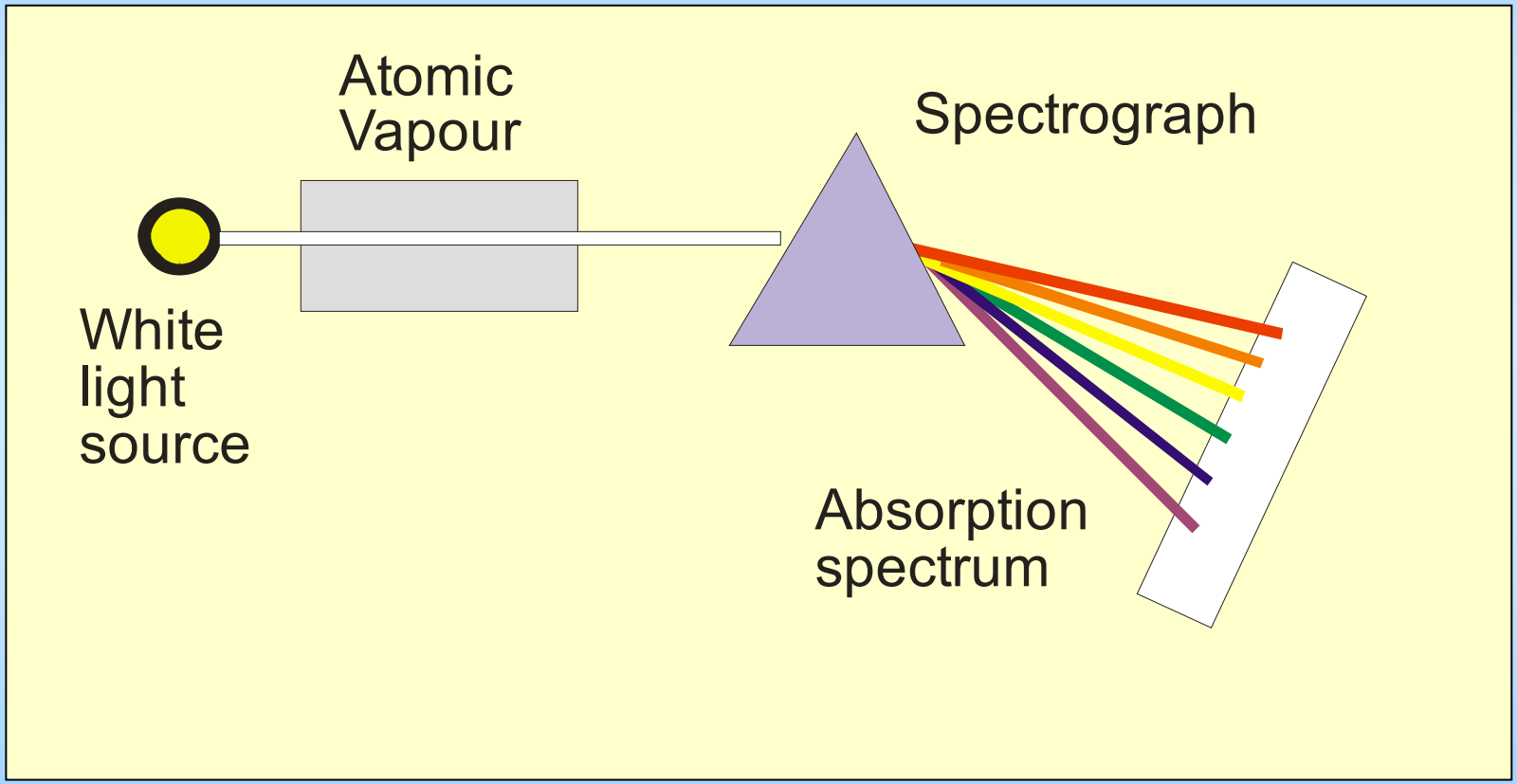
Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s$

Rb: $(\ldots) 4s^2 4p^6 5s$

Cs: $(\ldots..) 5s^2 5p^6 6s$

etc.

Absorption spectroscopy



Finding the Energy Levels

Hydrogen Binding Energy, Term Value $$T_n = \frac{R}{n^2}$$

Many electron atom, $$T_n = \frac{R}{(n - \delta(l))^2} .$$

$\delta(l)$ is the Quantum Defect

Finding the Quantum Defect

1. Measure wavelength λ of absorption lines

2. Calculate: $\bar{\nu} = 1/\lambda$

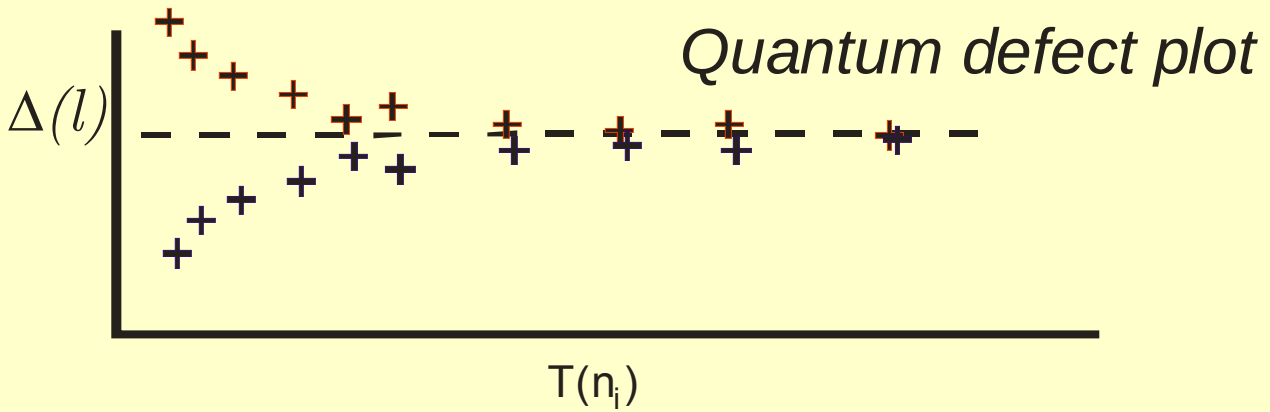
3. "Guess" ionization potential, $T(n_o)$ i.e. Series Limit

4. Calculate $T(n_i)$:

   $\bar{\nu}_i = T(n_o) - T(n_i)$

5. Calculate: n* or $\delta(l)$

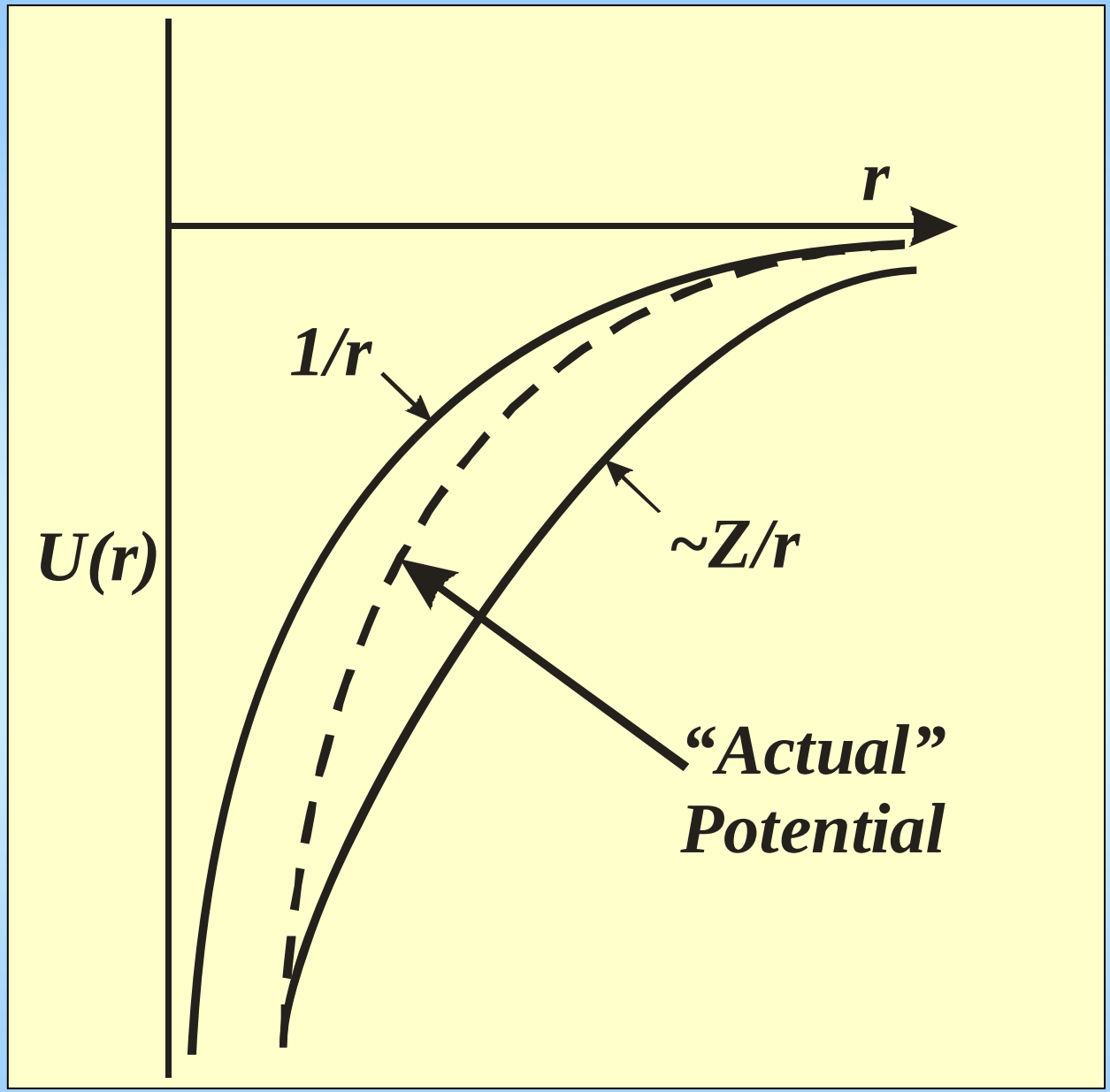
   $T(n_i) = R/(n - \delta(l))^2$



Lecture 3

- Corrections to the Central Field
- Spin-Orbit interaction
- The physics of magnetic interactions
- Finding the S-O energy – Perturbation Theory
- The problem of degeneracy
- The Vector Model (DPT made easy)
- Calculating the Spin-Orbit energy
- Spin-Orbit splitting in Sodium as example

The Central Field



Corrections to the Central Field

- Residual electrostatic interaction:

$$\hat{H}_1 = \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i \left\{ \frac{Ze^2}{4\pi\epsilon_0 r_i} + U(r_i) \right\}$$

- Magnetic spin-orbit interaction:

$$\hat{H}_2 = -\underline{\mu}.\underline{B}_{\text{orbit}}$$

Magnetic spin-orbit interaction

- Electron moves in Electric field of nucleus, so sees a Magnetic field B_{orbit}
- Electron spin precesses in B_{orbit} with energy:

  $-\mu.B$ which is proportional to $\underline{s}.\underline{l}$
- Different orientations of $\underline{s}$ and $\underline{l}$ give different total angular momentum $\underline{j} = \underline{l} + \underline{s}$.
- Different values of j give different $\underline{s}.\underline{l}$ so have different energy:

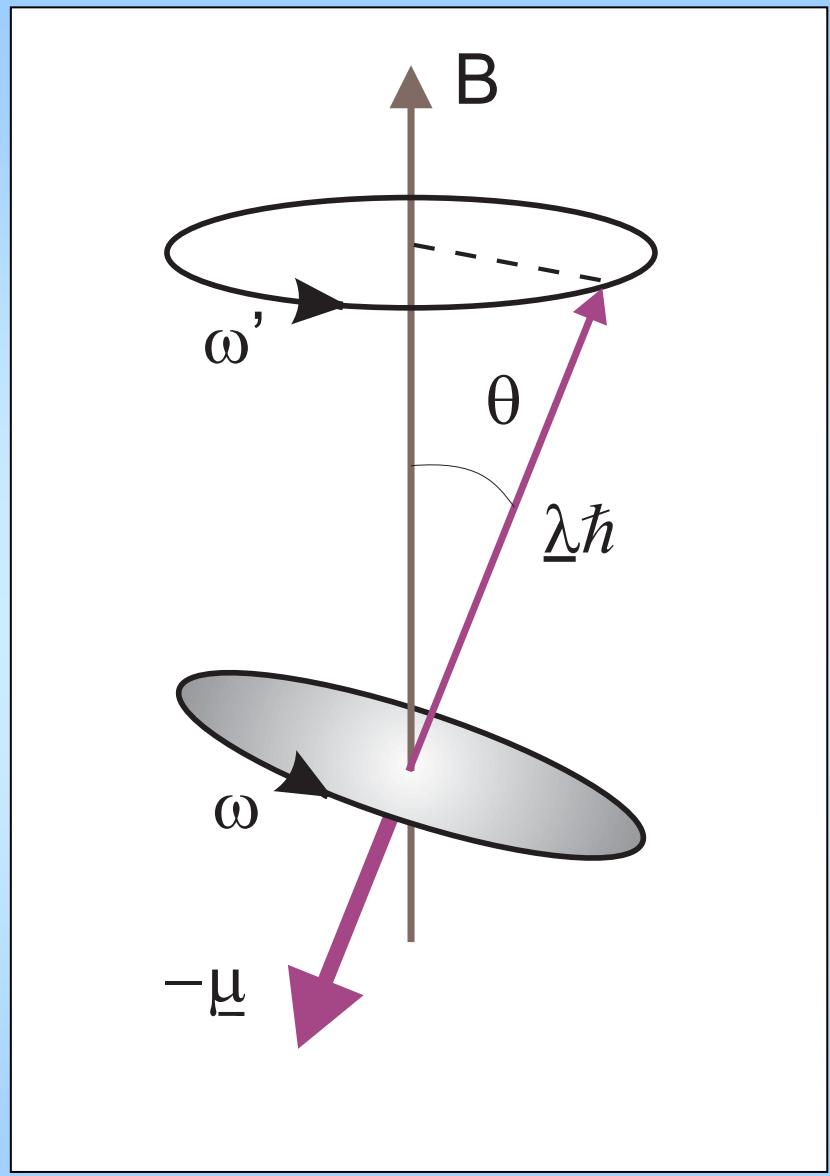
  The energy level is split for $l \pm 1/2$

Larmor Precession

Magnetic field B exerts a torque on magnetic moment $\underline{\mu}$ causing precession of $\underline{\mu}$ and the associated angular momentum vector $\underline{\lambda}$

The additional angular velocity ω' changes the angular velocity and hence energy of the orbiting/spinning charge

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



Spin-Orbit interaction: Summary

$$\underline{B} = -\frac{\underline{v} \times \underline{E}}{c^2}$$

$$\underline{B} = -\frac{1}{mc^2}\underline{p} \times \underline{r}\frac{|\underline{E}|}{|\underline{r}|}$$

$$\underline{B} = \frac{1}{mc^2}\frac{|\underline{E}|}{|\underline{r}|}\hat{\underline{l}}$$

$$|\underline{E}| = -\frac{\partial \phi(r)}{\partial r}$$

$$|\underline{E}| = -\frac{1}{e}\frac{\partial U(r)}{\partial r}$$

$$\underline{B} = \frac{1}{emc^2}\frac{1}{|\underline{r}|}\frac{\partial U(r)}{\partial r}\hat{\underline{l}}$$

$\underline{B}$ parallel to $\underline{l}$

$$\underline{\mu}_s = -g_s\frac{\mu_B}{\hbar}\hat{\underline{s}}$$

$\underline{\mu}$ parallel to $\underline{s}$

$$-\underline{\mu}_s \cdot \underline{B} \propto \frac{1}{r}\frac{\partial U(r)}{\partial r}\hat{\underline{s}} \cdot \hat{\underline{l}}$$

Perturbation energy

$$-\underline{\mu}_s \cdot \underline{B} = \frac{\mu_0}{4\pi} Z g_s \mu_B^2 \frac{1}{r^3} \frac{\hat{\underline{s}} \cdot \hat{\underline{l}}}{\hbar^3}$$

Radial integral

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{n^3 a_0^3 l(l+1/2)(l+1)}$$

Angular momentum operator

$$\hat{\underline{s}} \cdot \hat{\underline{l}} = \ ?$$

How to find $< \hat{\underline{s}} . \hat{\underline{l}} >$ using perturbation theory?

Perturbation theory with degenerate states

Perturbation Energy:

$$\Delta E = \langle \psi_i | \hat{H}' | \psi_i \rangle$$

Change in wavefunction:
So won't work if $E_i = E_j$
i.e. degenerate states.

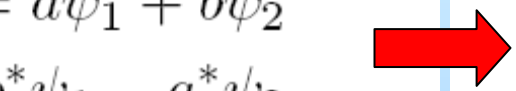
$$\Delta \psi_i = \sum_{j \neq i} \frac{\langle \psi_j | \hat{H}' | \psi_i \rangle}{E_i - E_j} \psi_j$$

We need a diagonal perturbation matrix,
i.e. off-diagonal elements are zero

$$\langle \psi_1 | \hat{H}' | \psi_2 \rangle = 0$$

New wavefunctions:

$$\phi_1 = a\psi_1 + b\psi_2$$
$$\phi_2 = b^*\psi_1 - a^*\psi_2$$



$$\langle \phi_1 | \hat{H}' | \phi_2 \rangle = 0$$

New eignvalues:

$$\Delta E_1 = \langle \phi_1 | \hat{H}' | \phi_1 \rangle \,, \quad \Delta E_2 = \langle \phi_2 | \hat{H}' | \phi_2 \rangle$$

The Vector Model

Angular momenta represented by vectors:

$\underline{l}^2$, $\underline{s}^2$ and $\underline{j}^2$, and $\underline{l}$, $\underline{s}$ $\underline{j}$ and with magnitudes:

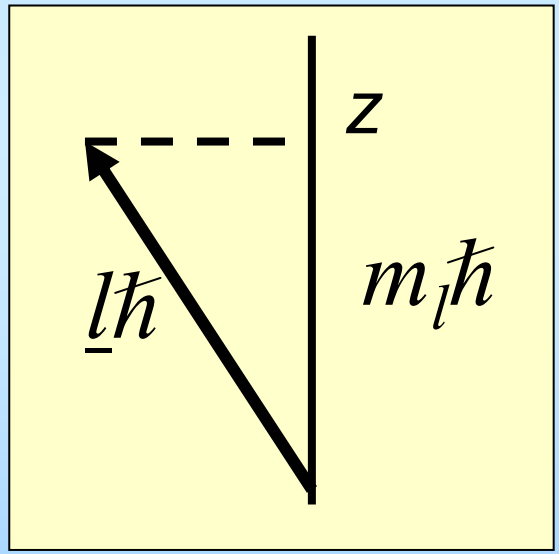
$l(l+1)$, $s(s+1)$ and $j(j+1)$. and

$\sqrt{l(l+1)}$,$\sqrt{s(s+1)}$ and $\sqrt{j(j+1)}$.

Projections of vectors:

$\underline{l}$, $\underline{s}$ and $\underline{j}$ on z-axis

are $\underline{m}_l$, $\underline{m}_s$ and $\underline{m}_j$



Constants of the Motion ➡ Good quantum numbers

Summary of Lecture 3: *Spin-Orbit coupling*

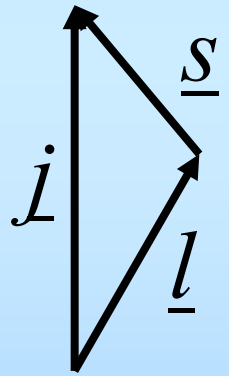
- Spin-Orbit energy

$$-\underline{\mu}_s \cdot \underline{B} \propto \frac{1}{r}\frac{\partial U(r)}{\partial r}\underline{\hat{s}} \cdot \underline{\hat{l}}$$

- Radial integral sets size of the effect.

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{n^3 a_0^3 l(l+1/2)(l+1)}$$

- Angular integral $< \underline{s} . \underline{l} >$ needs Degenerate Perturbation Theory
- New basis eigenfunctions: $\langle n, l, s, j, m_j |$
- $\underline{j}$ and $\underline{j}_z$ are constants of the motion



- Vector Model represents angular momenta as vectors
- These vectors can help identify constants of the motion
- These constants of the motion - represented by good quantum numbers

(a) No spin-orbit coupling

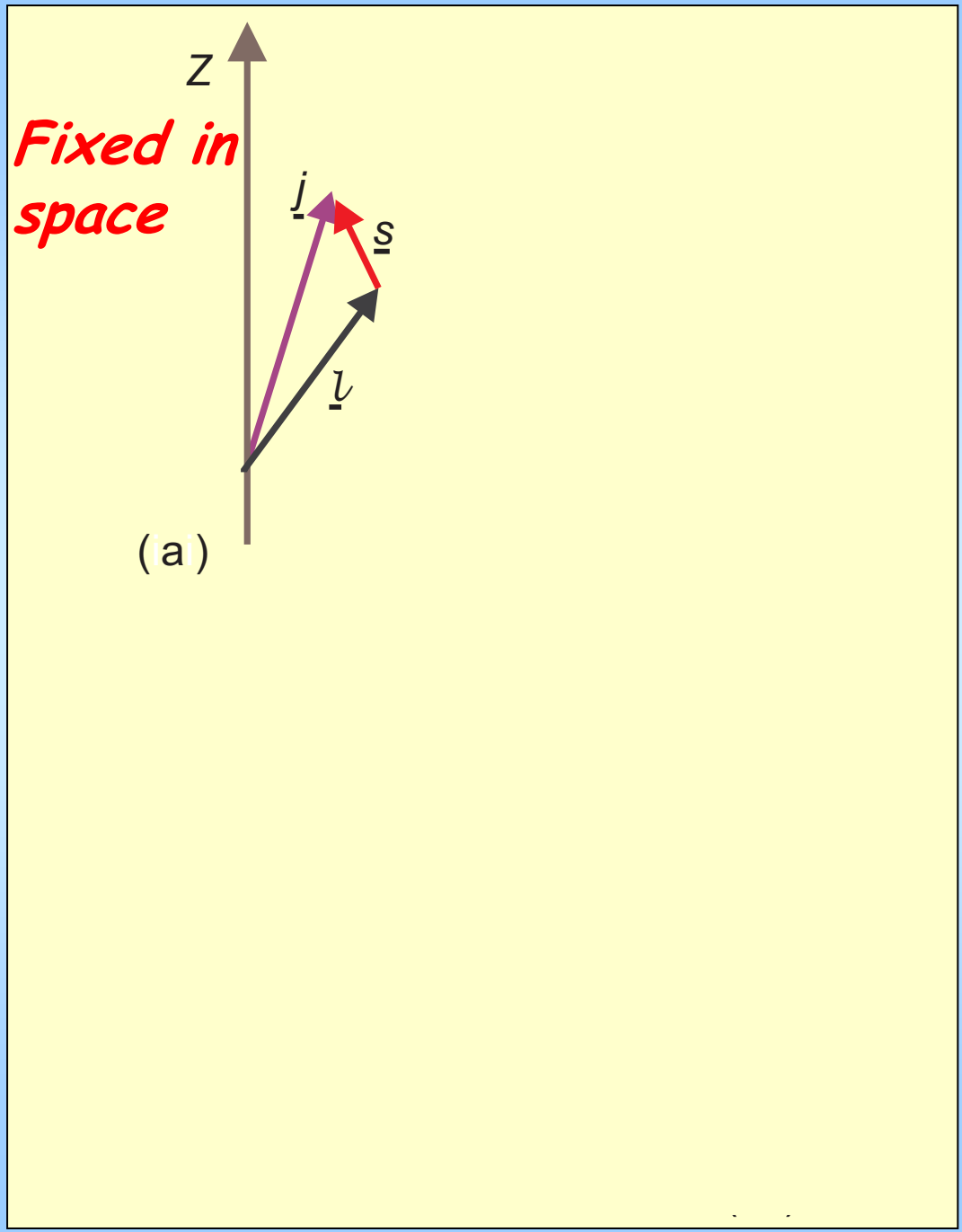
(b) Spin–orbit coupling gives precession around $\underline{j}$

(c) Projection of $\underline{l}$ on z is not constant

(d) Projection of $\underline{s}$ on z is not constant

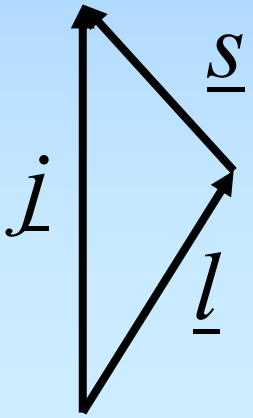
m_l and m_s are not good quantum numbers

Replace by j and m_j



Vector model defines:

$$\hat{\underline{j}}^2 = \left(\hat{\underline{l}} + \hat{\underline{s}}\right)^2 \qquad \hat{\underline{j}}_z = \hat{\underline{l}}_z + \hat{\underline{s}}_z$$



Vector triangle ⇒

$$\hat{\underline{s}} \cdot \hat{\underline{l}} = \frac{1}{2}\left(\hat{\underline{j}}^2 - \hat{\underline{l}}^2 - \hat{\underline{s}}^2\right)$$

Magnitudes

$j(j+1)$ $l(l+1)$ $s(s+1)$

$$\langle n, l, s, j, m_j | \, \hat{\underline{s}} \cdot \hat{\underline{l}} \, | n, l, s, j', m_j' \rangle = 0 \quad \text{unless} \quad j = j' \text{ and } m_j = m_j'$$

$$\langle n, l, s, j, m_j | \, \hat{\underline{s}} \cdot \hat{\underline{l}} \, | n, l, s, j, m_j \rangle = \frac{1}{2}\left\{ j(j+1) - l(l+1) - s(s+1) \right\} \hbar^2$$

$$-\underline{\mu}_s \cdot \underline{B} \propto \frac{1}{r}\frac{\partial U(r)}{\partial r}\underline{\hat{s}} \cdot \underline{\hat{l}} \qquad \sim \beta_{n,l} \times \langle \tfrac{1}{2} \{ \underline{j}^2 - \underline{l}^2 - \underline{s}^2 \} \rangle$$

Using basis states: $|\, n, l, s, j, m_j \rangle$ to find expectation value:

The spin-orbit energy is:

$$\Delta E = \beta_{n,l} \times (1/2)\{j(j+1) - l(l+1) - s(s+1)\}$$

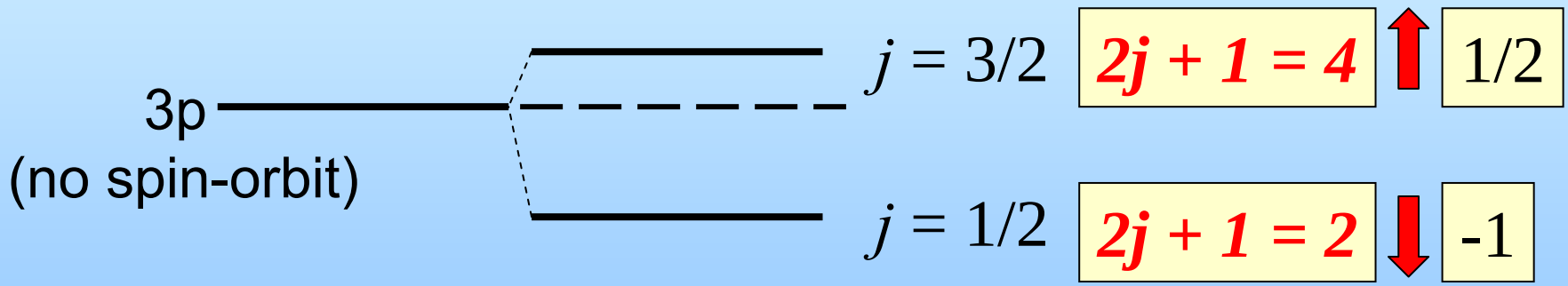
$$\Delta E = \beta_{n,l} \times (1/2)\{j(j+1) - l(l+1) - s(s+1)\}$$

Sodium

3s: n = 3, l = 0, no effect

3p: n = 3, l = 1, s = ½, -½, j = ½ *or* ³/₂

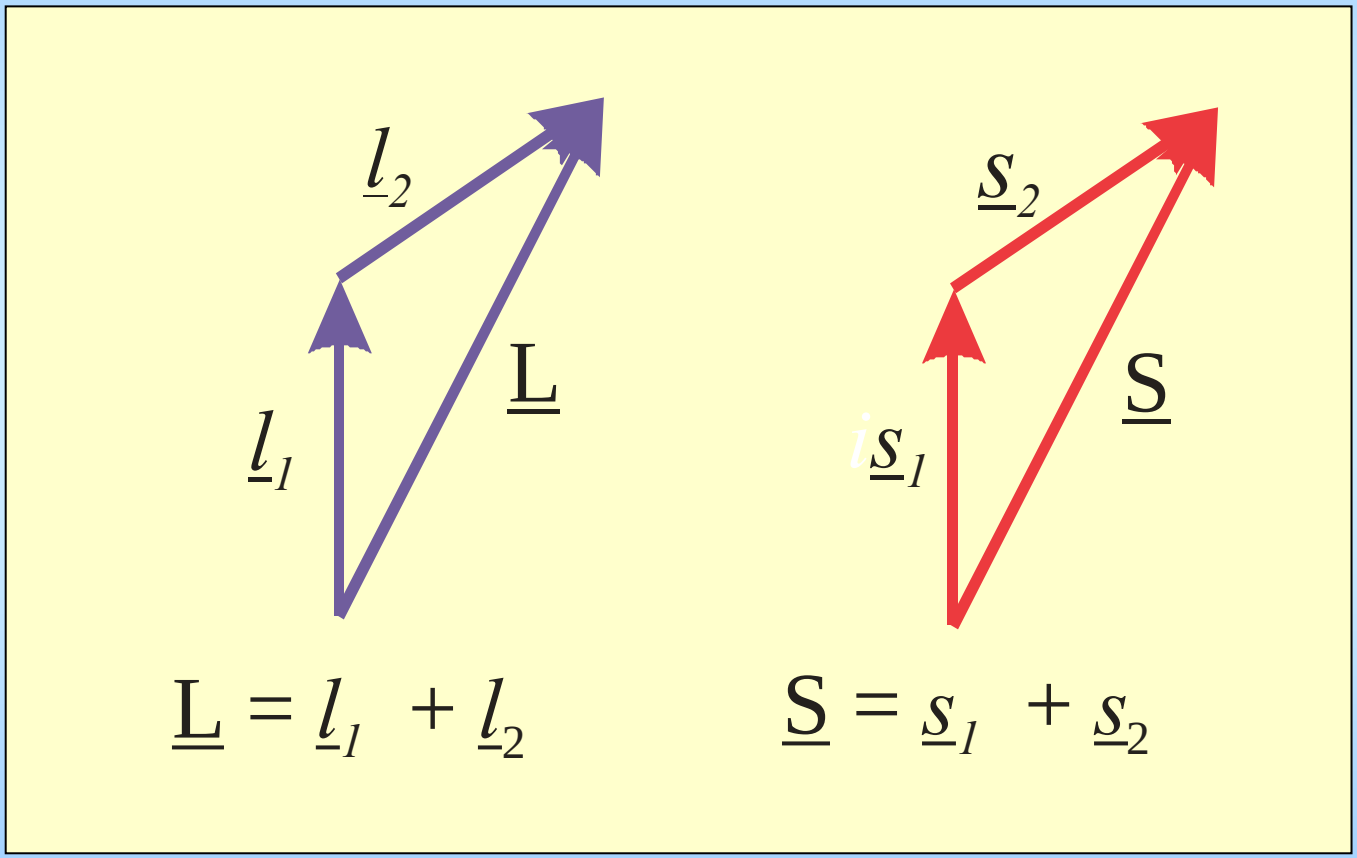
$\Delta E(1/2) = \beta_{3p} \times (-1)$; $\Delta E(3/2) = \beta_{3p} \times (1/2)$



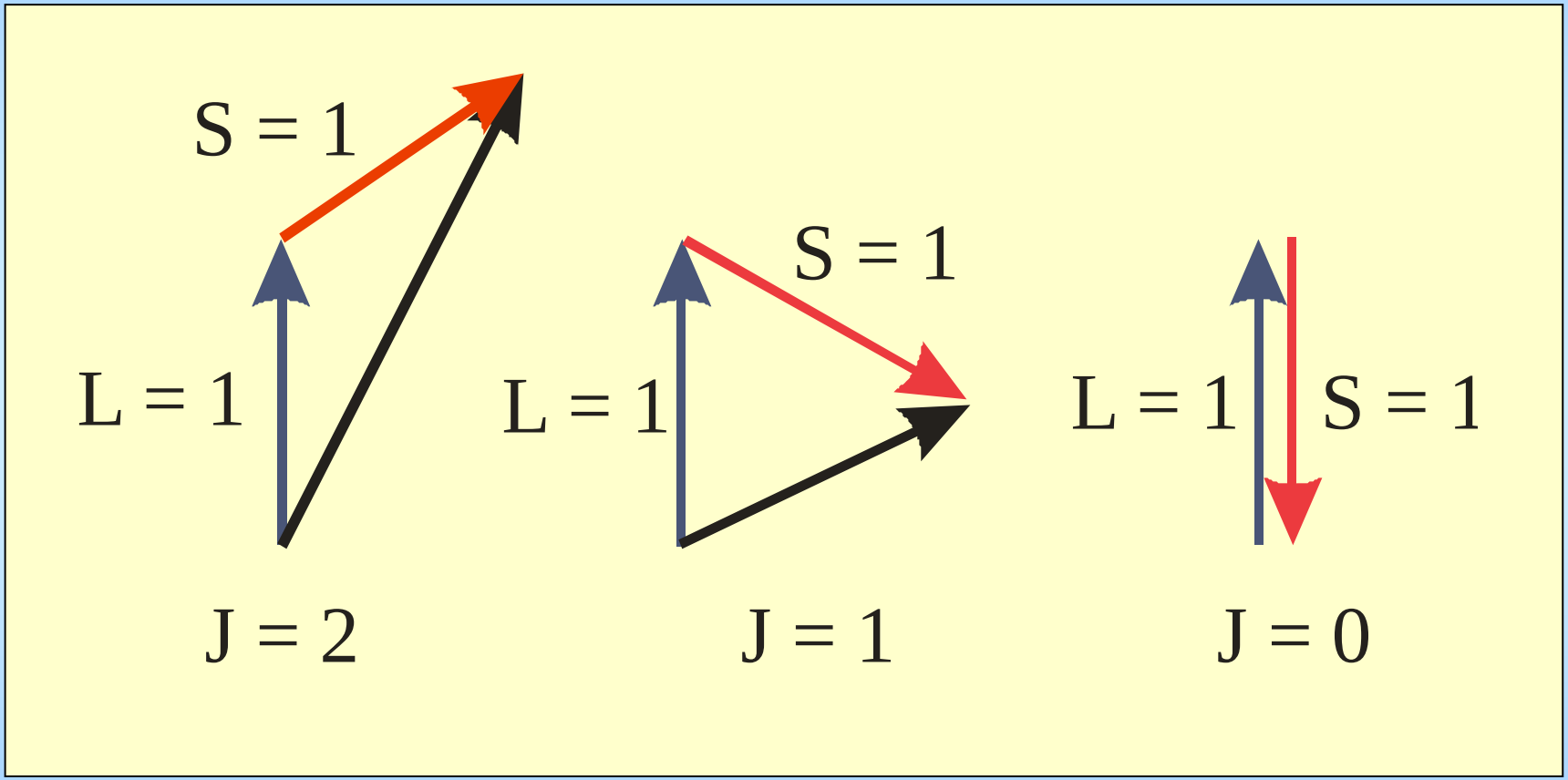
Lecture 4

- Two-electron atoms:
  the residual electrostatic interaction
- Adding angular momenta: LS-coupling
- Symmetry and indistinguishability
- Orbital effects on electrostatic interaction
- Spin-orbit effects

Coupling of $\underline{l}_i$ and $\underline{s}$ to form $\underline{L}$ and $\underline{S}$: *Electrostatic interaction dominates*



Coupling of L and S to form J



Magnesium: “typical” 2-electron atom

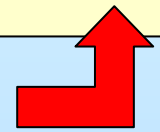
Mg Configuration:

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

Na Configuration:

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

“Spectator” electron in Mg



Mg energy level structure is like Na but levels are more strongly bound

Residual electrostatic interaction

$$\hat{H}_1 = -\sum_i \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i U(r_i)$$

3s4s state in Mg:
Zero-order wave functions

$$|\psi_1(3s)\psi_2(4s)\rangle$$

Perturbation energy:

$$\Delta E_1 \neq \langle\psi_1(3s)\psi_2(4s)|\,\hat{H}_1\,|\psi_1(3s)\psi_2(4s)\rangle \quad ?$$

Degenerate states

Linear combination of zero-order wave-functions

$$\phi_1 = \frac{1}{\sqrt{2}}\left(\psi_1(3s)\psi_2(4s) + \psi_1(4s)\psi_2(3s)\right)$$

$$\phi_2 = \frac{1}{\sqrt{2}}\left(\psi_1(3s)\psi_2(4s) - \psi_1(4s)\psi_2(3s)\right)$$

Off-diagonal matrix elements:

$$\frac{1}{2}\left\langle \psi_1(3s)\psi_2(4s) + \psi_1(4s)\psi_2(3s)\right| V \left|\psi_1(3s)\psi_2(4s) - \psi_1(4s)\psi_2(3s)\right\rangle$$

$1\uparrow$ $2\uparrow$ $3\uparrow$ $4\uparrow$

Off-diagonal matrix elements:

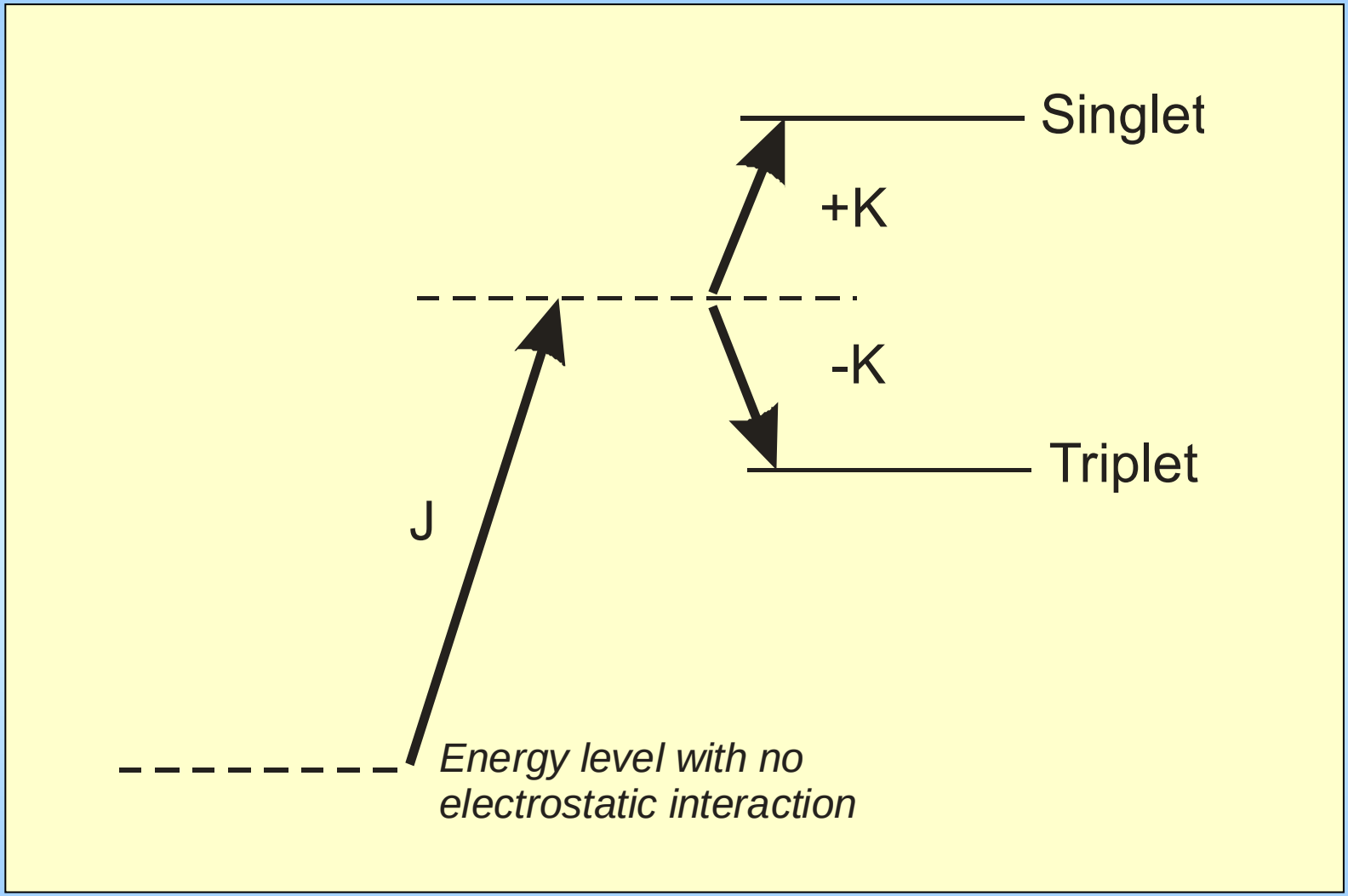
$$\frac{1}{2}\left\langle \psi_1(3s)\psi_2(4s) + \psi_1(4s)\psi_2(3s)\right| V \left|\psi_1(3s)\psi_2(4s) - \psi_1(4s)\psi_2(3s)\right\rangle$$

$1\uparrow$ $2\uparrow$ $3\uparrow$ $4\uparrow$

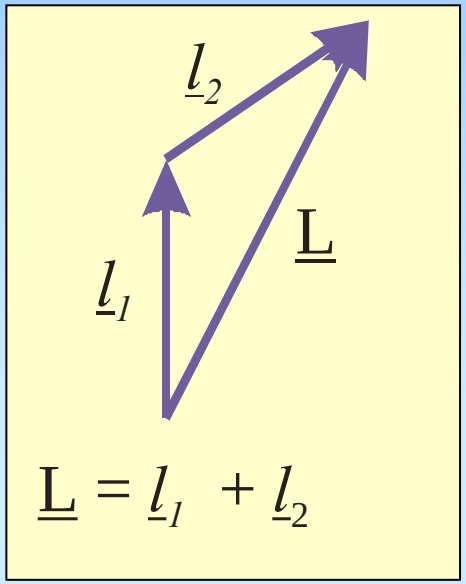
$$\begin{aligned}
1\times 3 &= \left\langle \psi_1(3s)\psi_2(4s)\right| V \left|\psi_1(3s)\psi_2(4s)\right\rangle = \mathrm{J} \\
2\times 4 &= -\left\langle \psi_1(4s)\psi_2(3s)\right| V \left|\psi_1(4s)\psi_2(3s)\right\rangle = -\mathrm{J} \\
2\times 3 &= \left\langle \psi_1(4s)\psi_2(3s)\right| V \left|\psi_1(3s)\psi_2(4s)\right\rangle = \mathrm{K} \\
1\times 4 &= -\left\langle \psi_1(3s)\psi_2(4s)\right| V \left|\psi_1(4s)\psi_2(3s)\right\rangle = -\mathrm{K}
\end{aligned}$$

Therefore $\left\langle \phi_1\right| V \left|\phi_2\right\rangle = 0$ as required!

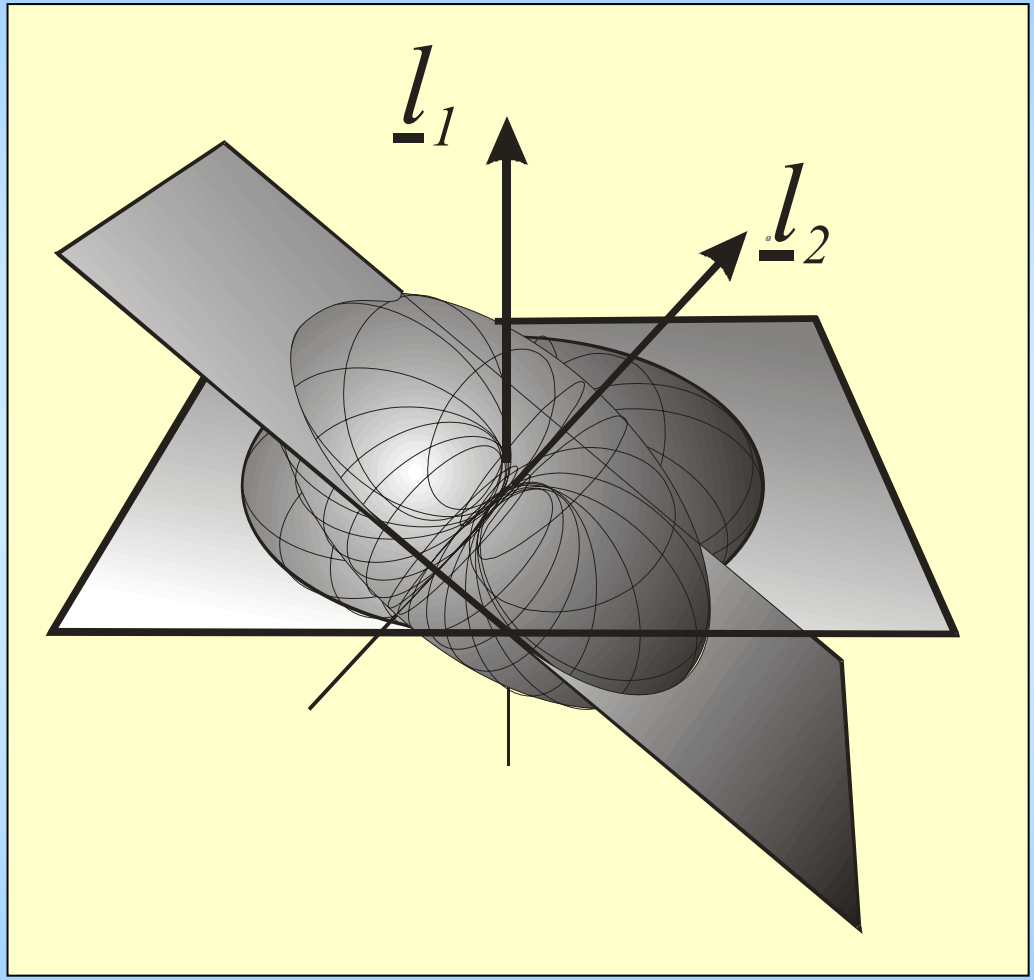
Effect of Direct and Exchange integrals



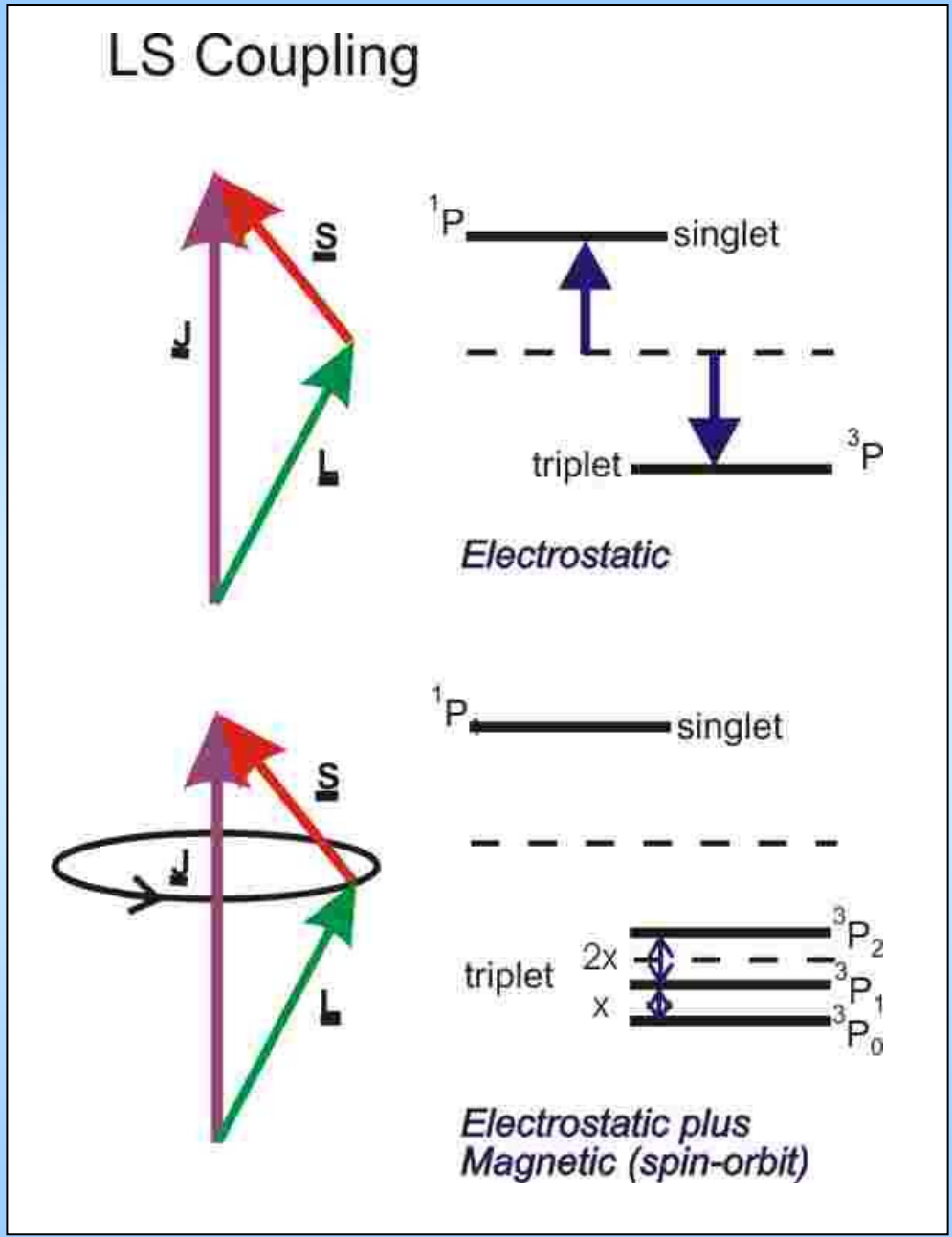
Orbital orientation effect on electrostatic interaction



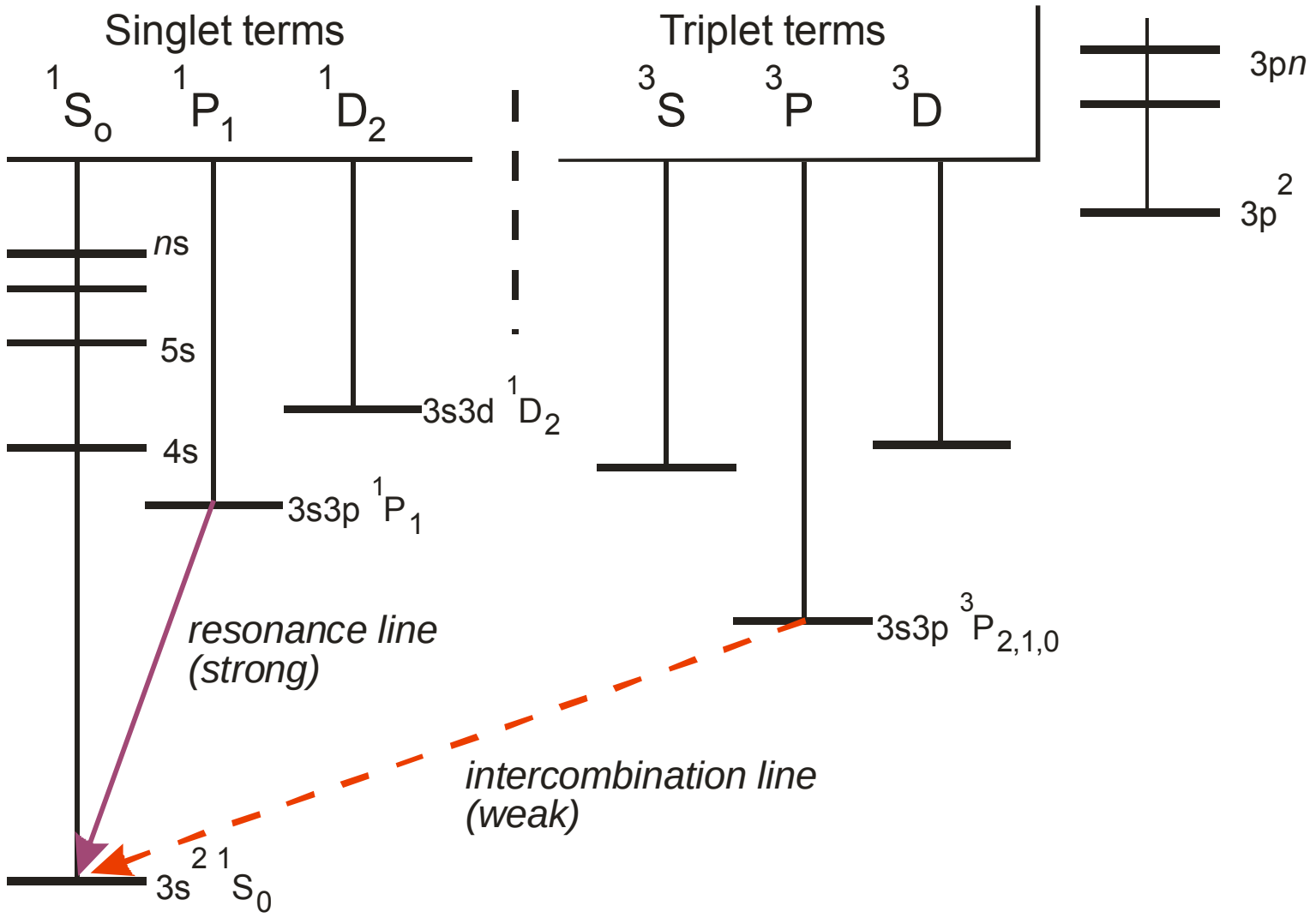
Overlap of electron wavefunctions depends on orientation of orbital angular momentum: so electrostatic interaction depends on $\underline{L}$



Residual Electrostatic and Spin-Orbit effects in LS-coupling



Term diagram of Magnesium



The story so far:
Hierarchy of interactions

Central Field configuration, $n_1 l_1 n_2 l_2 \ldots$ H_O

Residual Electrostatic $\rightarrow$ Terms, $L = S, P, D \ldots$ H_1

Spin-Orbit $\rightarrow$ Level, $J = |L - S| \rightarrow L + S$ H_2

H_3: Nuclear Effects on atomic energy

$H_3 << H_2 << H_1 << H_O$

Lecture 5

- Nuclear effects on energy levels
  - Nuclear spin
  - addition of nuclear and electron angular momenta
- How to find the nuclear spin
- Isotope effects:
  - effects of finite nuclear mass
  - effects of nuclear charge distribution
- Selection Rules

Nuclear effects in atoms

Nucleus:

Corrections

- stationary — Nuclear spin → magnetic dipole interacts with electrons
- infinite mass — orbits centre of mass with electrons
- point — charge spread over nuclear volume

Nuclear Spin interaction

Magnetic dipole ~ angular momentum

$$\underline{\mu} = - \gamma \underline{\lambda} \hbar$$

$$\underline{\mu}_{\underline{l}} = - g_l \, \mu_B \underline{l} \qquad \underline{\mu}_s = - g_s \mu_B \underline{s}$$

$$\underline{\mu}_I = - g_I \mu_N \underline{I}$$

$$g_I \sim 1 \qquad \mu_N = \mu_B \times m_e / m_P \sim \mu_B / 2000$$

Perturbation energy:

$$\hat{H}_3 = - \underline{\mu}_I . \underline{B}_{el}$$

$$\hat{H}_3 = -\underline{\hat{\mu}}_I \cdot \underline{\hat{B}}_{\mathrm{el}}$$

Magnetic field of electrons: Orbital and Spin

Closed shells: zero contribution

s orbitals: largest contribution – short range ~$1/r^3$

$l > 0$, smaller contribution - neglect

$$B_{\mathrm{el}} \sim \frac{\mu_0}{4\pi}\mu_B \left\langle \frac{1}{r^3} \right\rangle .$$

$$B_{\mathrm{el}} \sim \frac{\mu_0}{4\pi}\frac{\mu_B}{a_0^3} \sim 6\mathrm{T}$$

$$\hat{H}_3 = -\underline{\hat{\mu}}_I \cdot \underline{\hat{B}}_{\mathrm{el}}$$

$$\underline{B}_{el} = (scalar\ quantity) \times \underline{J}$$

Usually dominated by spin contribution in s-states:

Fermi “contact interaction”.

Calculable only for Hydrogen in ground state, 1s

Coupling of $\underline{I}$ and $\underline{J}$

$$\hat{H}_3 = -\underline{\hat{\mu}}_I \cdot \underline{\hat{B}}_{\mathrm{el}}$$

Depends on I Depends on J

$$\hat{H}_3 = A_J \underline{I} \cdot \underline{J}$$

Nuclear spin interaction energy:

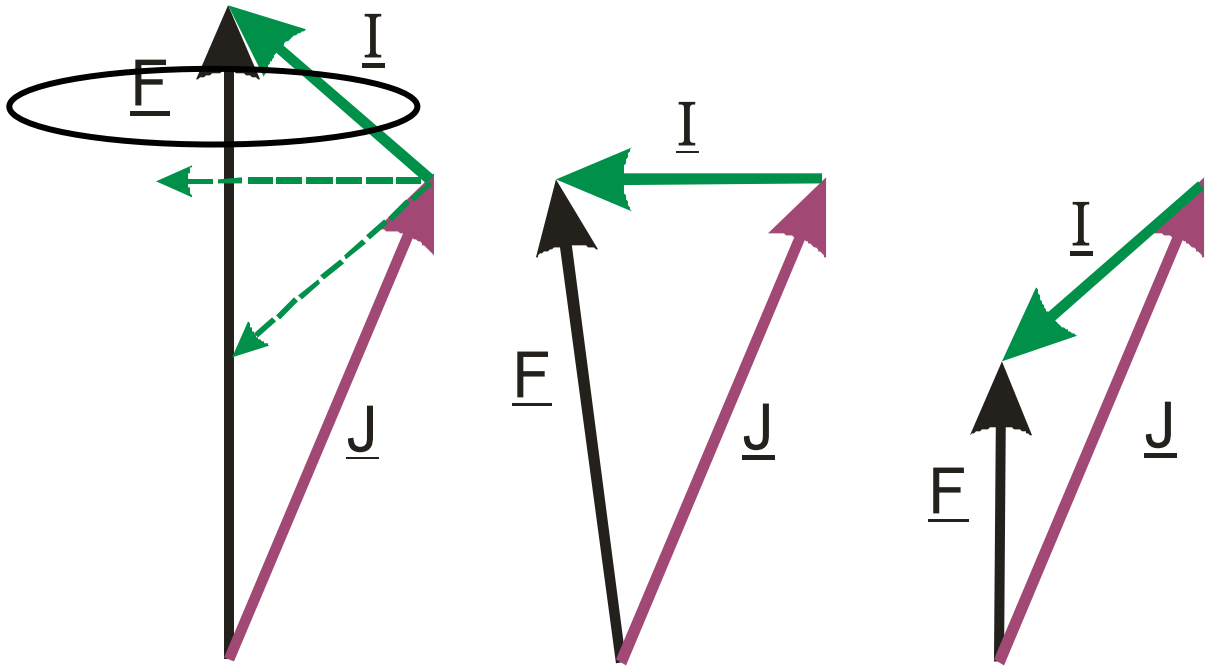
$$\Delta E = A_J \left\langle \underline{\hat{I}} \cdot \underline{\hat{J}} \right\rangle$$

empirical *Expectation value*

Vector model of nuclear interaction

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

$\underline{I}$ and $\underline{J}$ precess around $\underline{F}$



$$\underline{I} \cdot \underline{J} = \frac{1}{2}\left\{\underline{F}^2 - \underline{I}^2 - \underline{J}^2\right\}$$

Hyperfine structure

Hfs interaction energy: $\Delta E = A_J \left\langle \hat{\underline{I}} \cdot \hat{\underline{J}} \right\rangle$

Vector model result: $\underline{I} \cdot \underline{J} = \frac{1}{2} \left\{ \underline{F}^2 - \underline{I}^2 - \underline{J}^2 \right\}$

Hfs energy shift:

$$\Delta E = \frac{A_J}{2} \left\{ F(F+1) - I(I+1) - J(J+1) \right\}$$

Hfs interval rule:

$$\Delta E_{F'} = \Delta E(F') - \Delta E(F'-1) \sim A_J F'$$

Finding the nuclear spin, I

- Interval rule – finds F, then for known J $\rightarrow$ I
- Number of spectral lines

  $(2I + 1)$ for $J > I$, $(2J + 1)$ for $I > J$
- Intensity

  Depends on statistical weight $(2F + 1)$

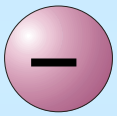
  finds F, then for known J $\rightarrow$ I

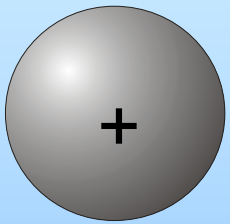
Isotope effects

$$E_n \sim \frac{Z^2 e^4 m_r}{2\hbar^2 n^2}$$

reduced mass

Orbiting about
Fixed nucleus,
infinite mass





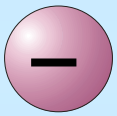
Orbiting about
centre of mass

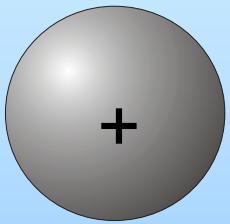
Isotope effects

$$E_n \sim \frac{Z^2 e^4 m_r}{2\hbar^2 n^2}$$

reduced mass

Orbiting about
Fixed nucleus,
infinite mass



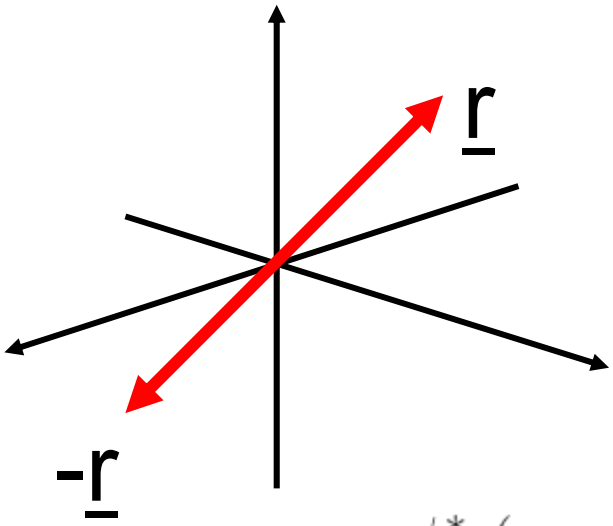


Orbiting about
centre of mass

Lecture 6

- Selection Rules
- Atoms in magnetic fields
  - basic physics; atoms with no spin
  - atoms with spin: anomalous Zeeman Effect
  - polarization of the radiation

Parity selection rule



$$-e\cdot\phi^{*}_{nl}(x,y,z)\left[\hat{\underline{i}}x+\hat{\underline{j}}y+\hat{\underline{k}}z\right]\ \phi_{n'l'}(x',y',z')$$

N.B. Error in notes eqn (161)

Parity $(-1)^{l}$ must change

$\Delta l = \pm 1$

Configuration

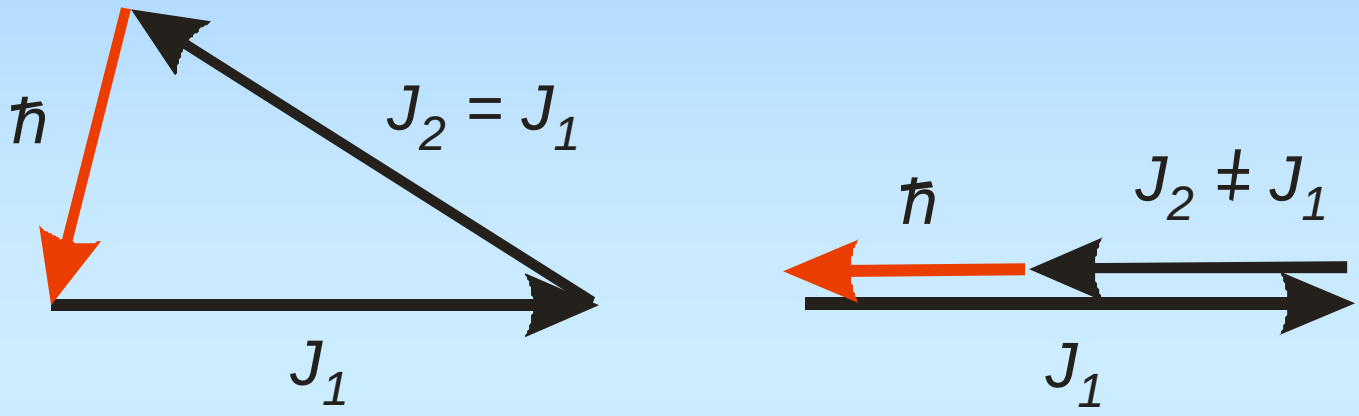
$$
\begin{aligned}
& \langle \psi_1(1s)\psi_2(2p)| \, \underline{r}_1 + \underline{r}_2 \, |\psi_1(3p)\psi_2(3d)\rangle \\
= \; & \langle \psi_1(1s)| \, \underline{r}_1 \, |\psi_1(3p)\rangle \times \langle \psi_2(2p)|\psi_2(3d)\rangle + \langle \psi_2(2p)| \, \underline{r}_2 \, |\psi_2(3d)\rangle \times \langle \psi_1(1s)|\psi_1(3p)\rangle \\
= \; & 0
\end{aligned}
$$

Only one electron “jumps”

$$
\begin{aligned}
\Delta n &= \text{anything} \\
\Delta l &= \pm 1
\end{aligned}
$$

Selection Rules:

Conservation of angular momentum



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

$$\Delta S = 0$$

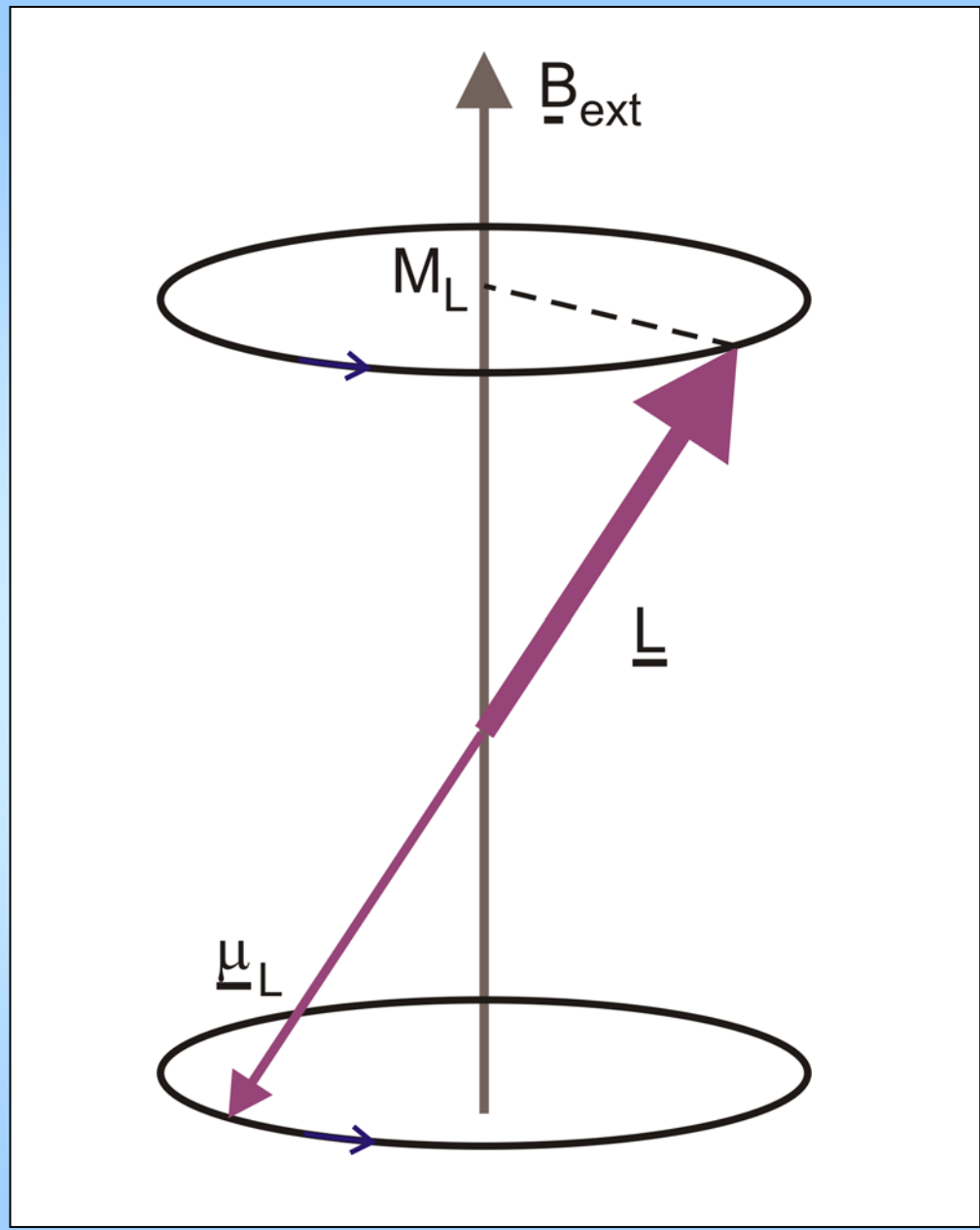
$$\Delta M_J = 0, \pm 1$$

Atoms in magnetic fields

Effect of B-field on an atom with no spin

Interaction energy - Precession energy:

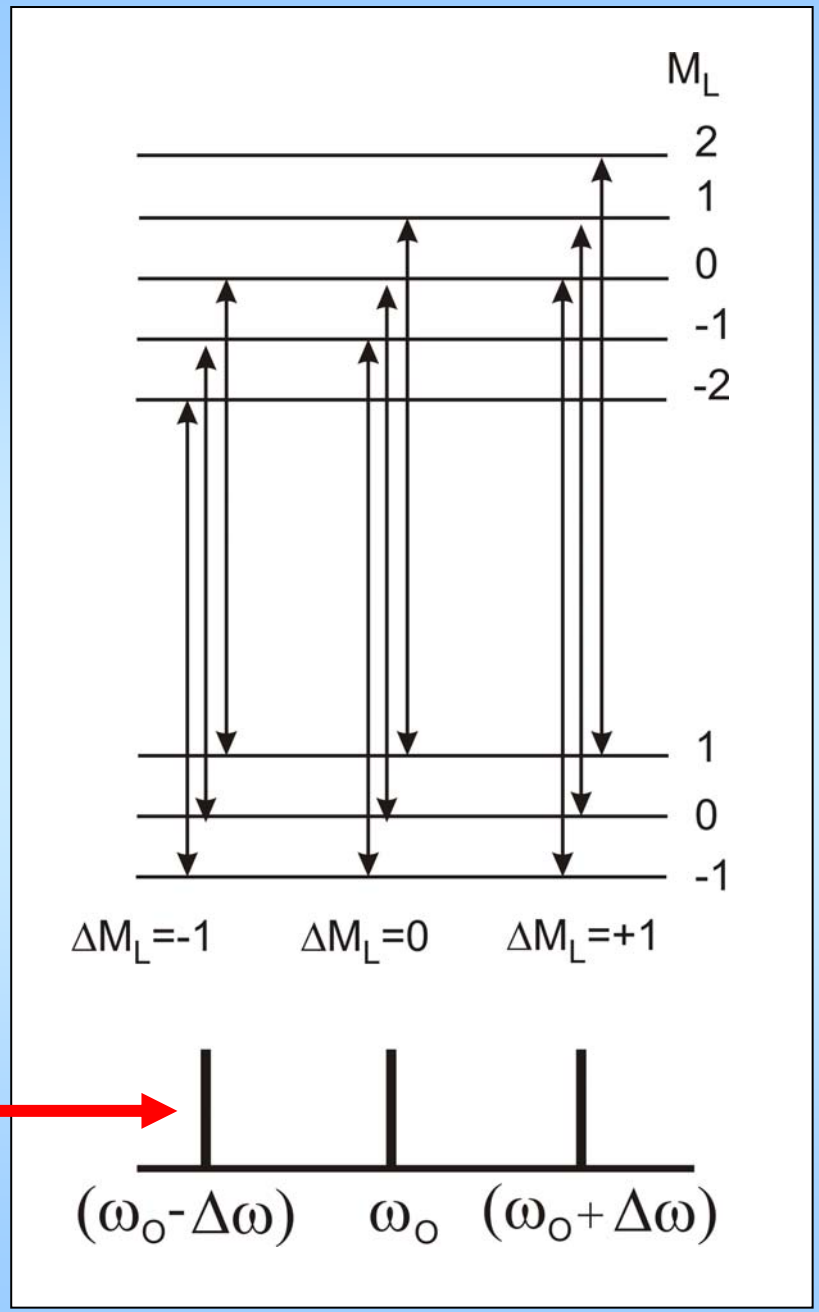
$$\Delta E_Z = -\underline{\mu}_L \cdot \underline{B}_{\text{ext}}$$



Normal Zeeman Effect

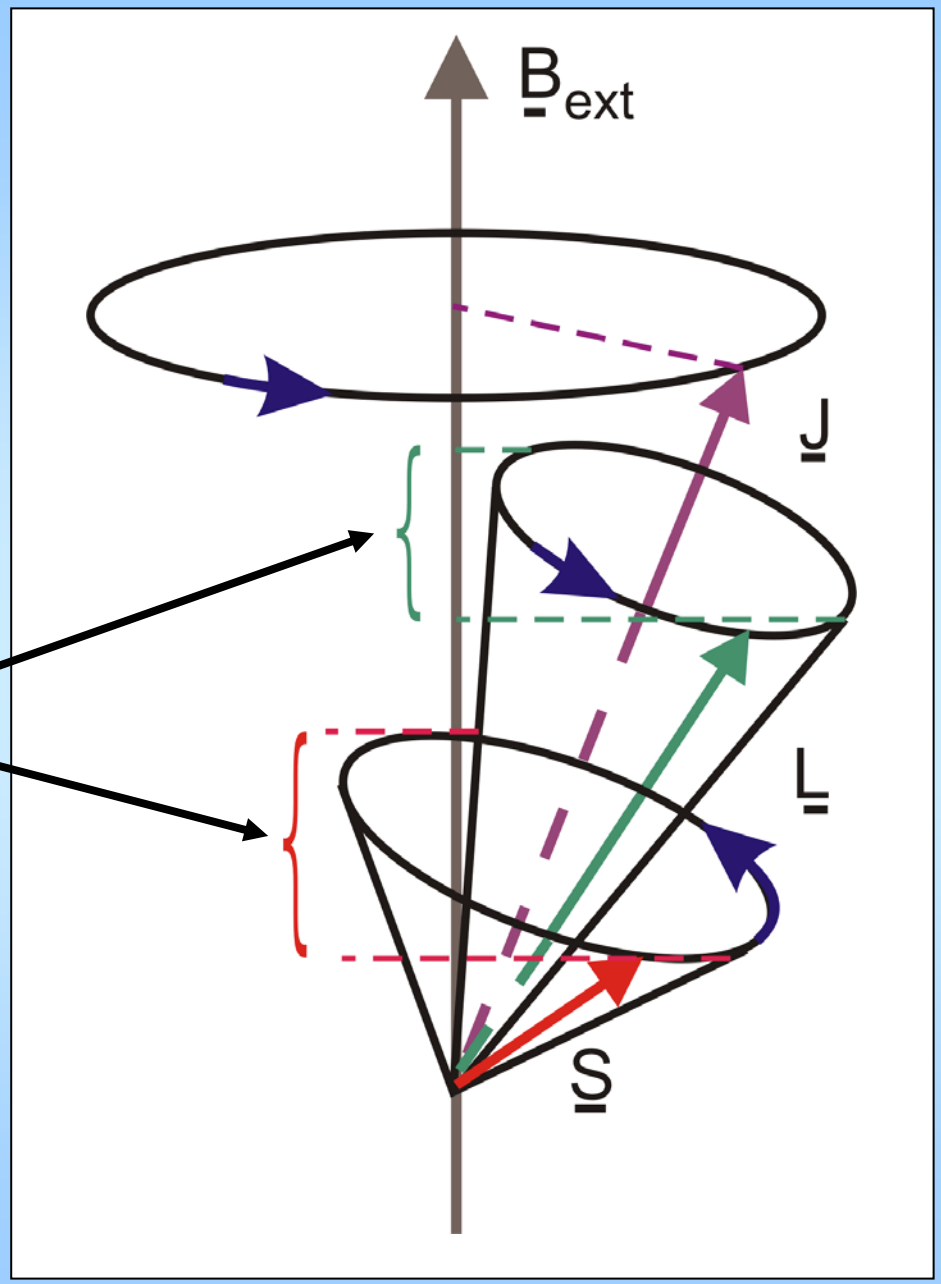
Level is split into equally Spaced sub-levels (states)

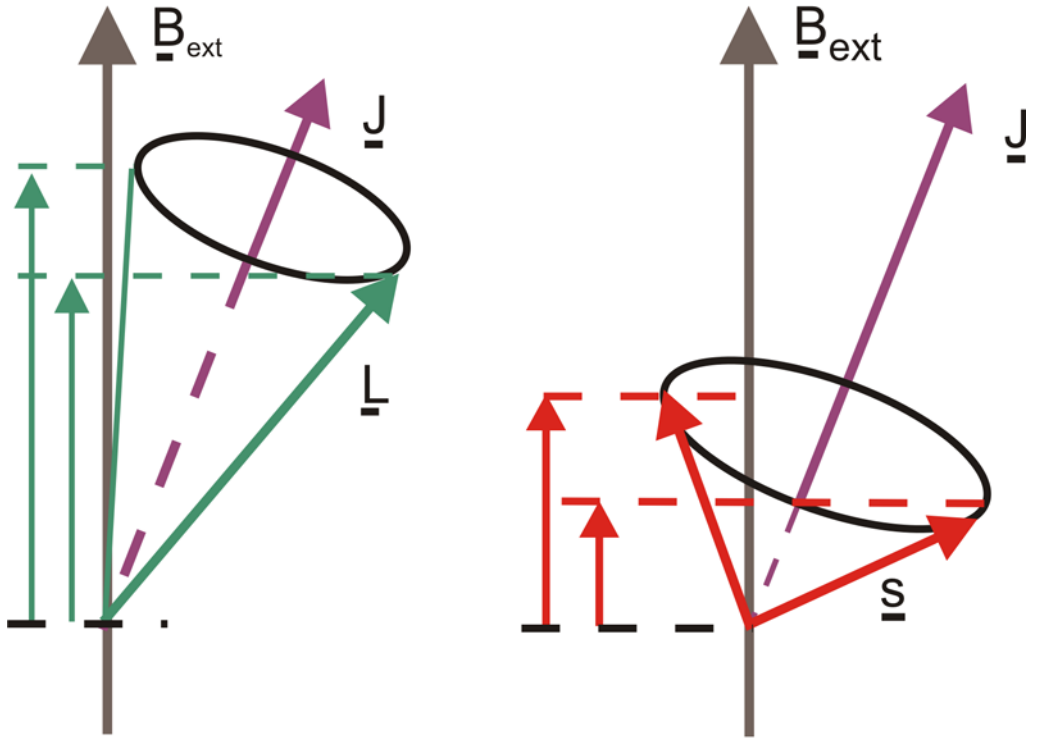
Selection rules on M_L give a spectrum of the normal Lorentz Triplet



Effect of B-field on an atom with spin-orbit coupling

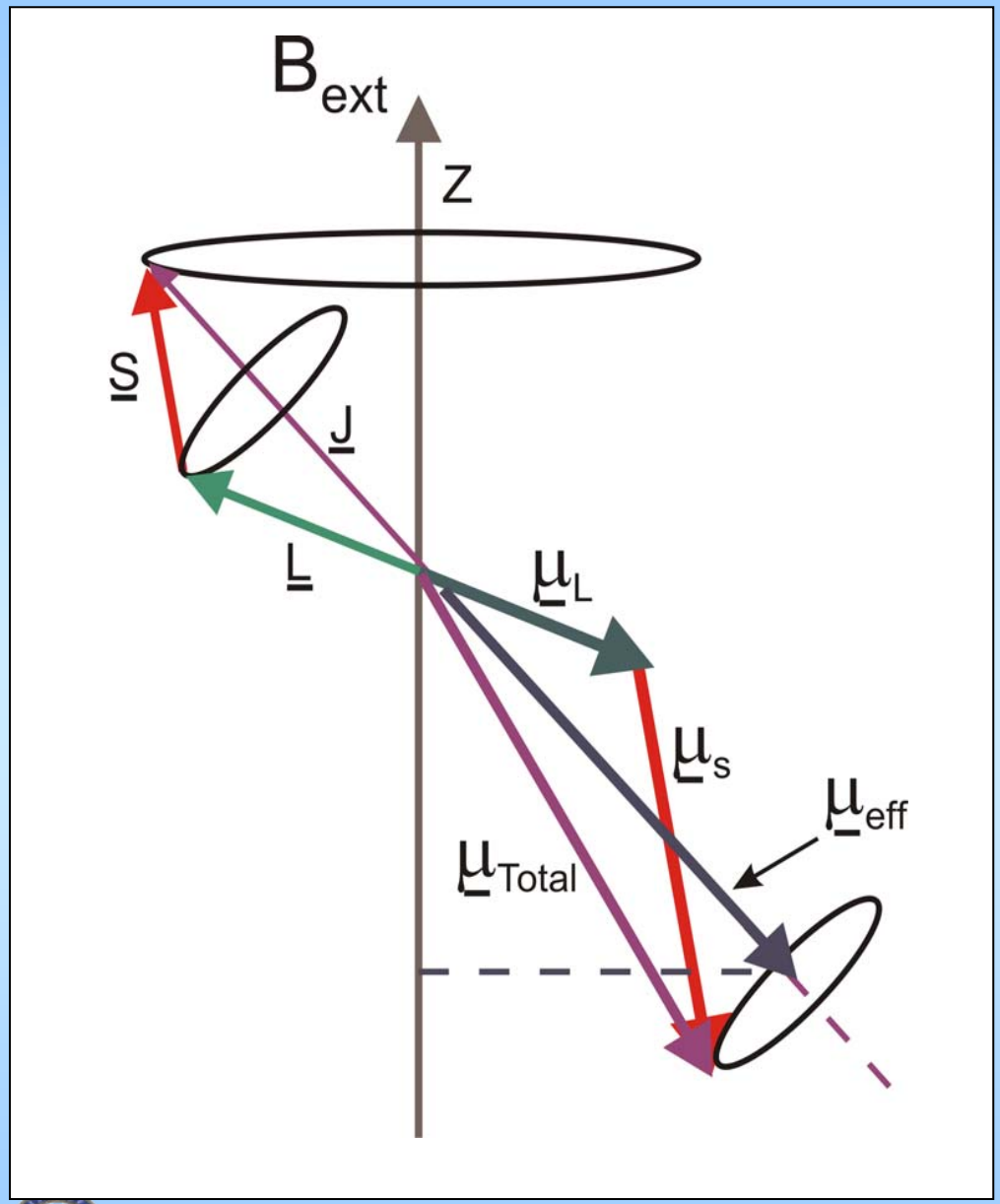
Precession of L and S around the resultant J leads to variation of projections of L and S on the field direction





Projections of L and S on z axis vary owing to precession around J.

m_L and m_s are no longer good quantum numbers



Total magnetic moment does not lie along axis of $\underline{J}$.

Effective magnetic moment *does* lie along axis of $\underline{J}$, hence has constant projection on B_{ext} axis

$$\underline{\mu}_{\text{eff}} = g_J \mu_B \underline{J}$$

Perturbation Calculation of B_{ext} effect on spin-orbit level

Interaction energy

$$\hat{H}_{\mathrm{mag}} = -\underline{\mu}_{\mathrm{atom}} \cdot \underline{B}_{\mathrm{ext}}$$

Effective magnetic moment

$$\underline{\mu}_{\mathrm{eff}} = g_J \mu_B \underline{J}$$

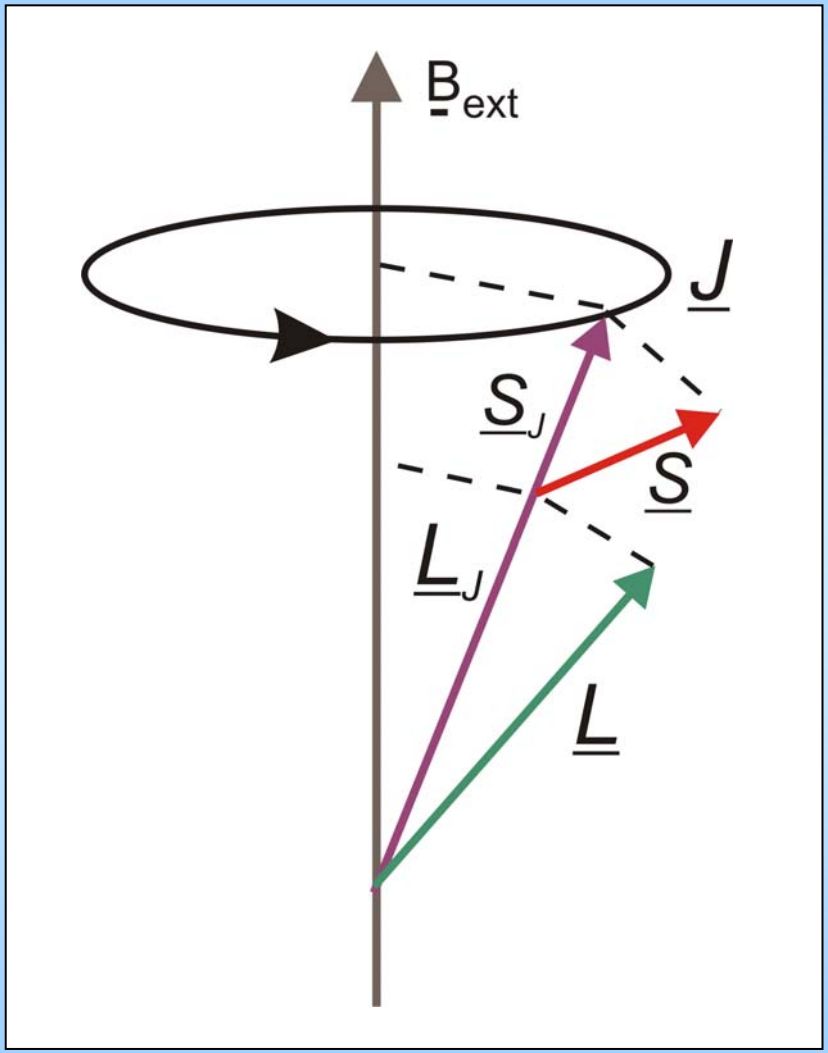
Perturbation Theory:
expectation value of energy

$$\Delta E_{\mathrm{AZ}} = g_J \mu_B \left\langle \underline{\hat{J}} \cdot \underline{\hat{B}}_{\mathrm{ext}} \right\rangle$$

Energy shift of M_J level

$$\Delta E_{\mathrm{AZ}} = g_J \mu_B \underline{B}_{\mathrm{ext}} M_J$$

Vector Model Calculation of B_{ext} effect on spin-orbit level



Projections of $\underline{L}$ and $\underline{S}$ on $\underline{J}$ are given by

$$\frac{|\underline{L}\cdot\underline{J}|\underline{J}}{|\underline{J}|^2} = \underline{L}_J$$

$$\frac{|\underline{S}\cdot\underline{J}|\underline{J}}{|\underline{J}|^2} = \underline{S}_J$$

Vector Model Calculation of B_{ext} effect on spin-orbit level

$$\begin{aligned}\Delta E_{\rm AZ} &= g_L\mu_B \underline{L}_J \cdot \underline{B}_{\rm ext} + g_S\mu_B \underline{S}_J \cdot \underline{B}_{\rm ext} \\ &= g_L\mu_B \frac{|\underline{L}\cdot\underline{J}|}{|\underline{J}|^2}\underline{J}\cdot\underline{B}_{\rm ext} + g_S\mu_B \frac{|\underline{S}\cdot\underline{J}|}{|\underline{J}|^2}\underline{J}\cdot\underline{B}_{\rm ext}\end{aligned}$$

$$\Delta E_{\rm AZ} = \mu_B \frac{\left[3\underline{J}^2 - \underline{L}^2 + \underline{S}^2\right]}{2|\underline{J}|^2} J_z B_{\rm ext}$$

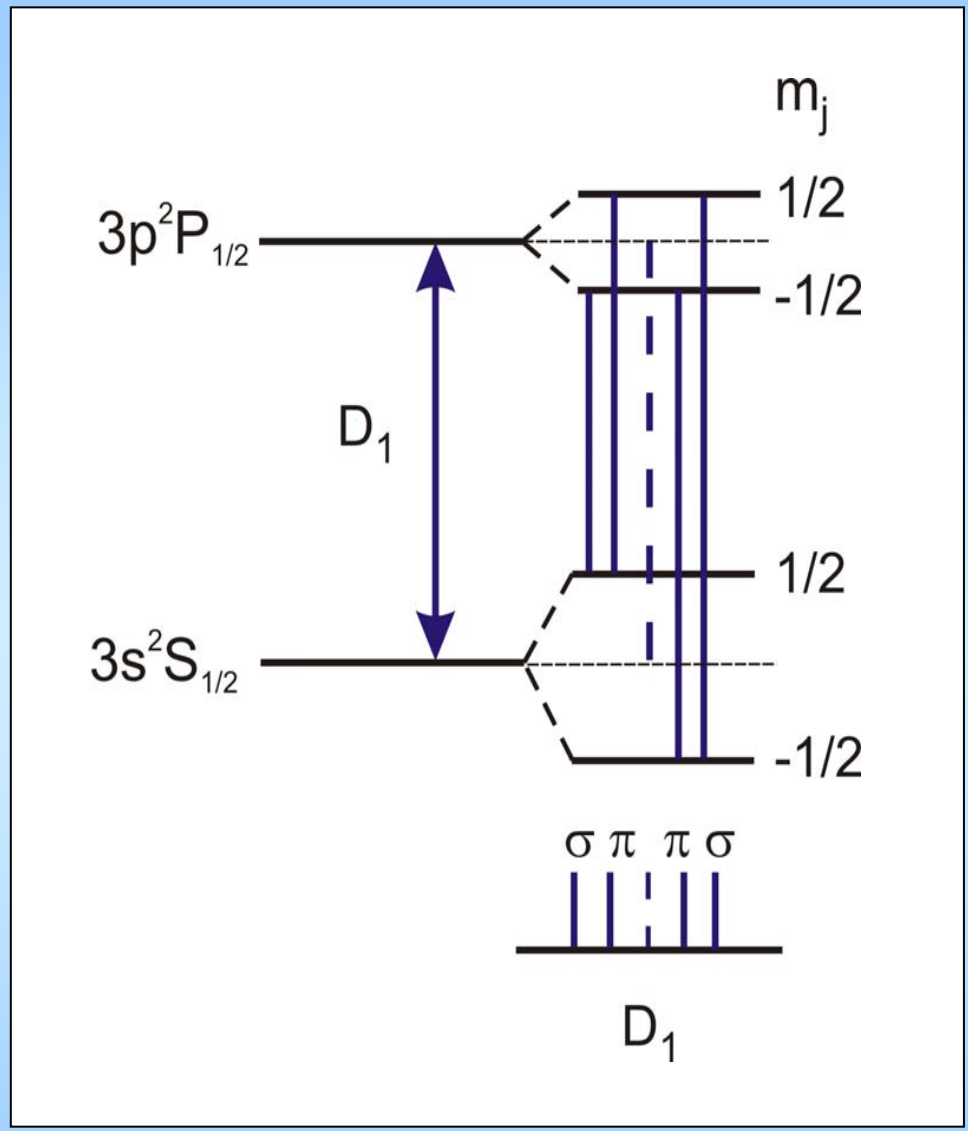
$$\Delta E_{\rm AZ} = \frac{[3J(J+1) - L(L+1) + S(S+1)]}{2J(J+1)} \mu_B B_{\rm ext} M_J$$

Perturbation Theory result

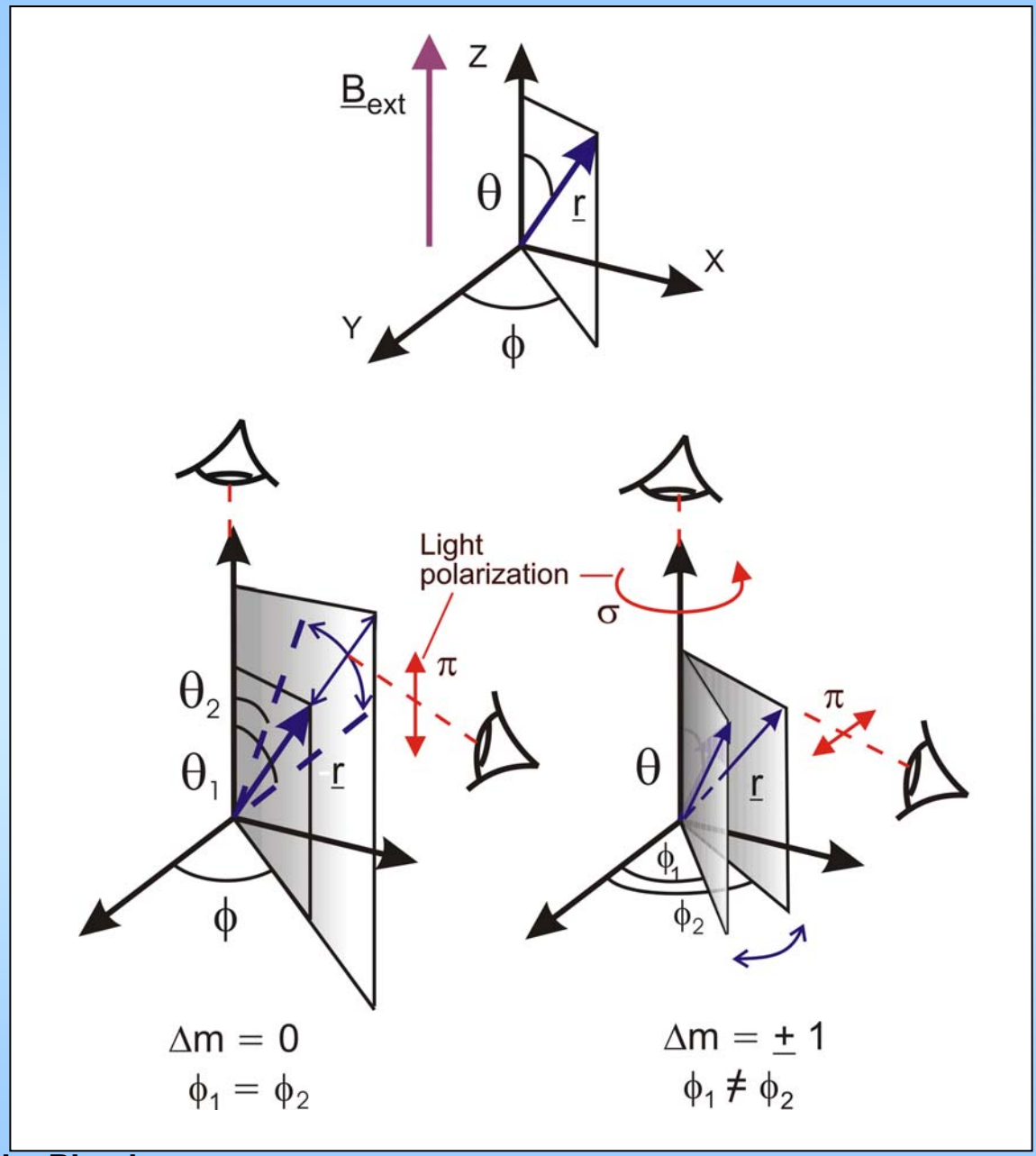
$$\Delta E_{\rm AZ} = g_J \mu_B \underline{B}_{\rm ext} M_J$$

Anomalous Zeeman Effect:

$3s^2S_{1/2} – 3p^2P_{1/2}$ in Na



Polarization of Anomalous Zeeman components associated with Δm selection rules

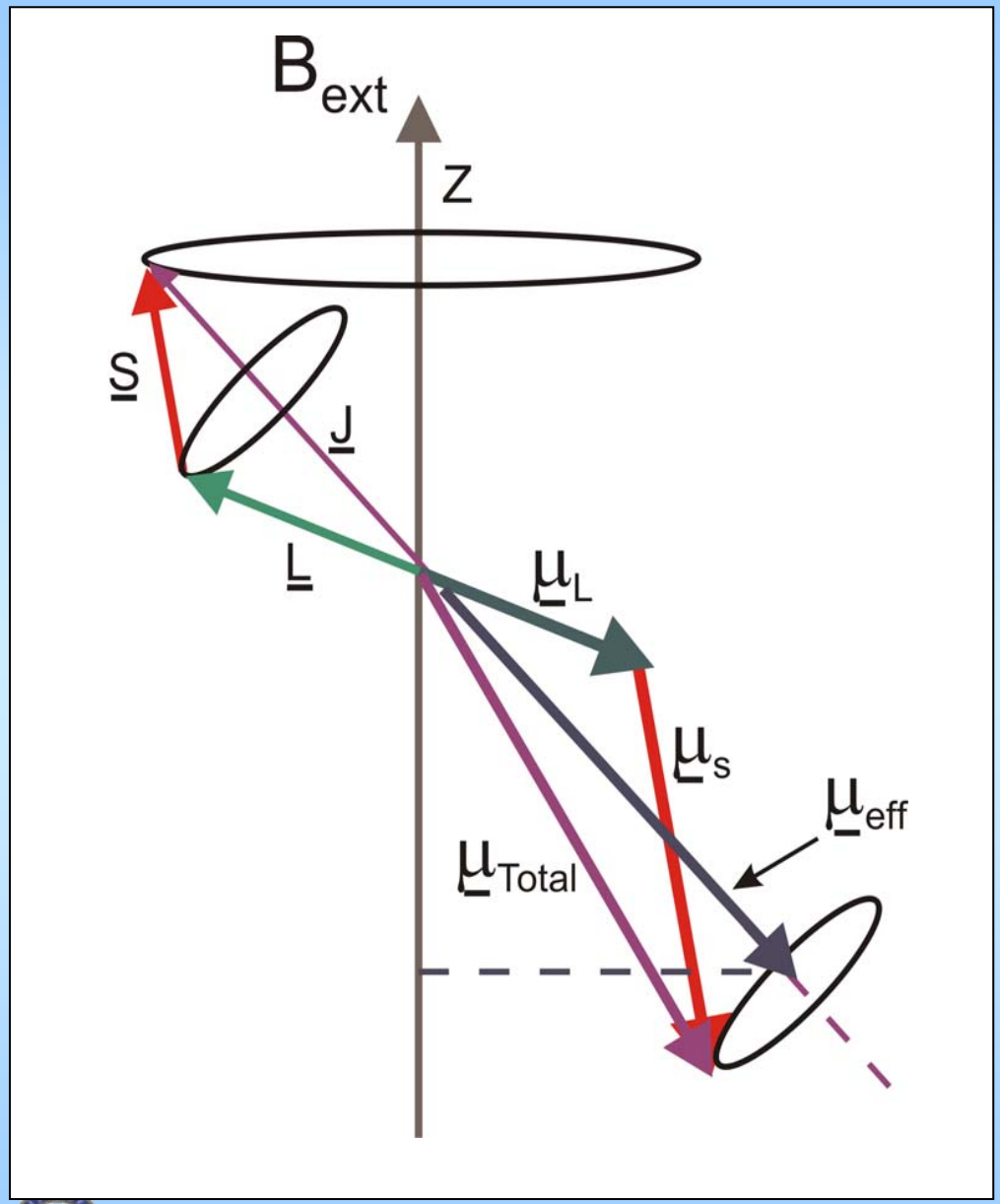


Lecture 7

- Magnetic effects on fine structure
  - Weak field
  - Strong field

- Magnetic field effects on hyperfine structure:
  - Weak field
  - Strong field

Summary of magnetic field effects on atom with spin-orbit interaction



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Perturbation Calculation of B_{ext} effect on spin-orbit level

Interaction energy

$$\hat{H}_{\mathrm{mag}} = -\underline{\mu}_{\mathrm{atom}} \cdot \underline{B}_{\mathrm{ext}}$$

Effective magnetic moment

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Perturbation Theory:
expectation value of energy

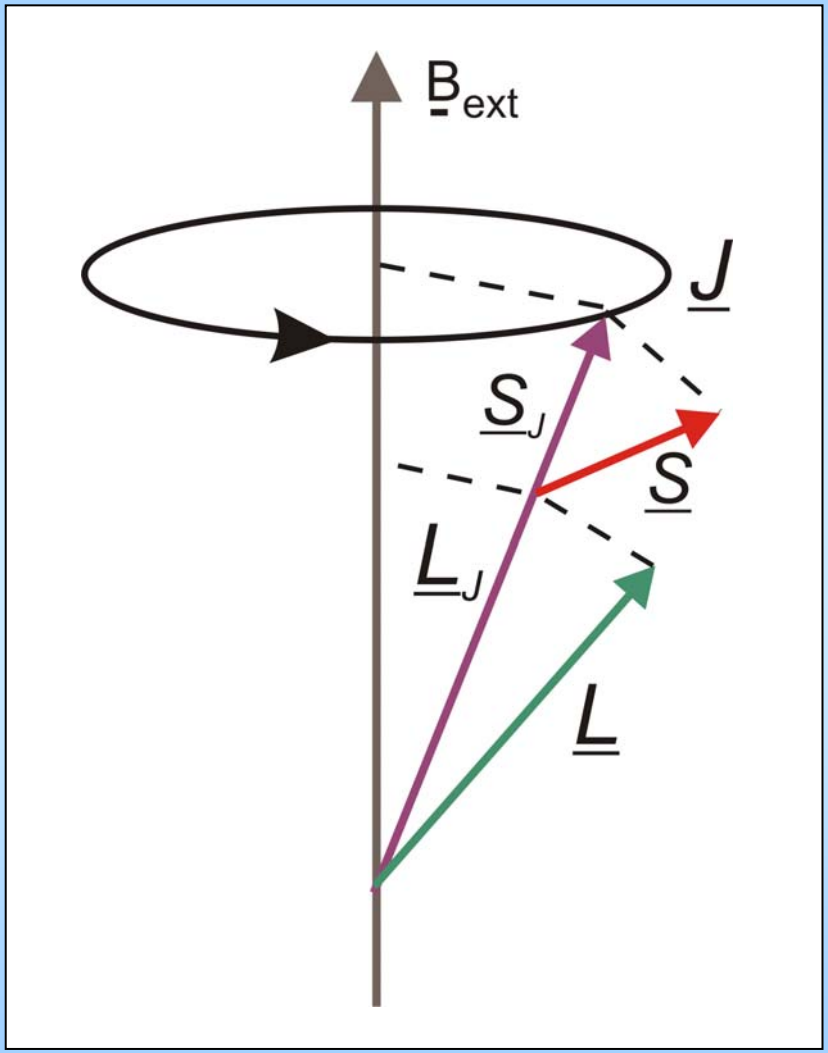
$$\Delta E_{\mathrm{AZ}} = g_J \mu_B \left\langle \underline{\hat{J}} \cdot \underline{\hat{B}}_{\mathrm{ext}} \right\rangle$$

Energy shift of M_J level

$$\Delta E_{\mathrm{AZ}} = g_J \mu_B \underline{B}_{\mathrm{ext}} M_J$$

What is g_J?

Vector Model Calculation of B_{ext} effect on spin-orbit level



Projections of $\underline{L}$ and $\underline{S}$ on $\underline{J}$ are given by

$$\frac{|\underline{L}\cdot\underline{J}|\underline{J}}{|\underline{J}|^2} = \underline{L}_J$$

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Vector Model Calculation of B_{ext} effect on spin-orbit level

$$\begin{aligned}\Delta E_{\rm AZ} &= g_L\mu_B \underline{L}_J \cdot \underline{B}_{\rm ext} + g_S\mu_B \underline{S}_J \cdot \underline{B}_{\rm ext} \\ &= g_L\mu_B \frac{|\underline{L}\cdot\underline{J}|}{|\underline{J}|^2}\underline{J}\cdot\underline{B}_{\rm ext} + g_S\mu_B \frac{|\underline{S}\cdot\underline{J}|}{|\underline{J}|^2}\underline{J}\cdot\underline{B}_{\rm ext}\end{aligned}$$

$$\Delta E_{\rm AZ} = \mu_B \frac{\left[3\underline{J}^2 - \underline{L}^2 + \underline{S}^2\right]}{2|\underline{J}|^2} J_z B_{\rm ext}$$

$$\Delta E_{\rm AZ} = \frac{[3J(J+1) - L(L+1) + S(S+1)]}{2J(J+1)} \mu_B B_{\rm ext} M_J$$

Perturbation Theory result

$$\Delta E_{\rm AZ} = g_J \mu_B \underline{B}_{\rm ext} M_J$$

Landé
g-factor

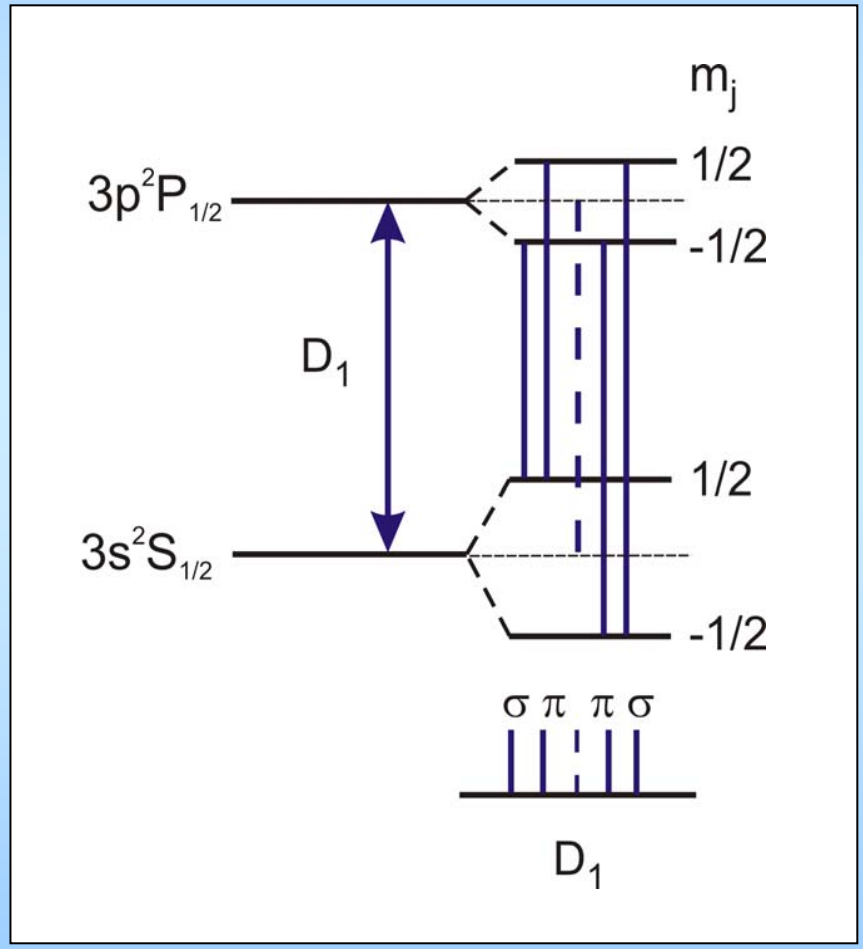
$$g_J = \frac{[3J(J+1) - L(L+1) + S(S+1)]}{2J(J+1)}$$

Anomalous Zeeman Effect:

$3s^2S_{1/2} – 3p^2P_{1/2}$ in Na

$g_J(^2P_{1/2}) = 2/3$

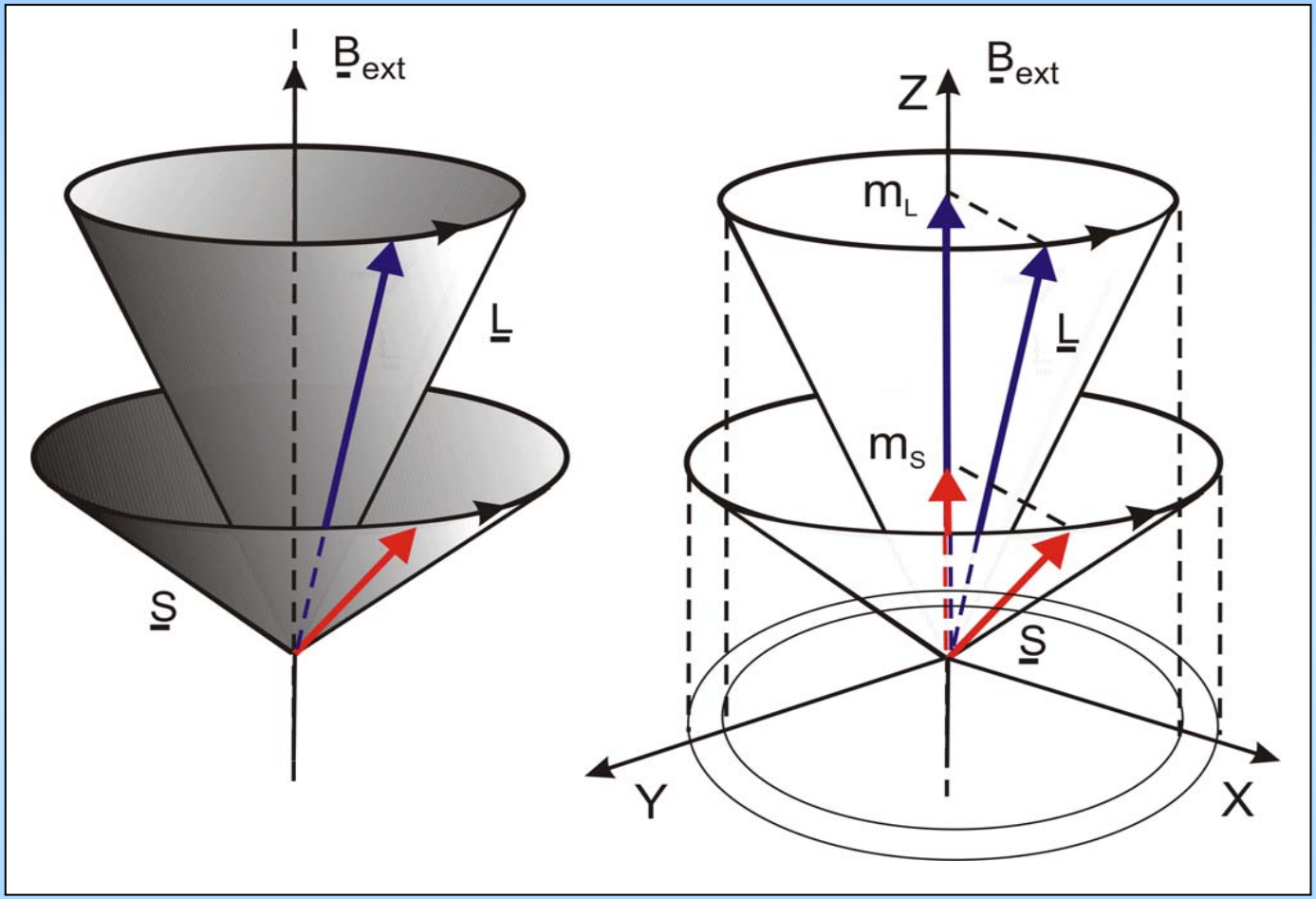
$g_J(^2S_{1/2}) = 2$



Strong field effects on atoms with spin-orbit coupling

Spin and Orbit magnetic moments couple more strongly to B_{ext} than to each other.

Strong field effect on L and S.

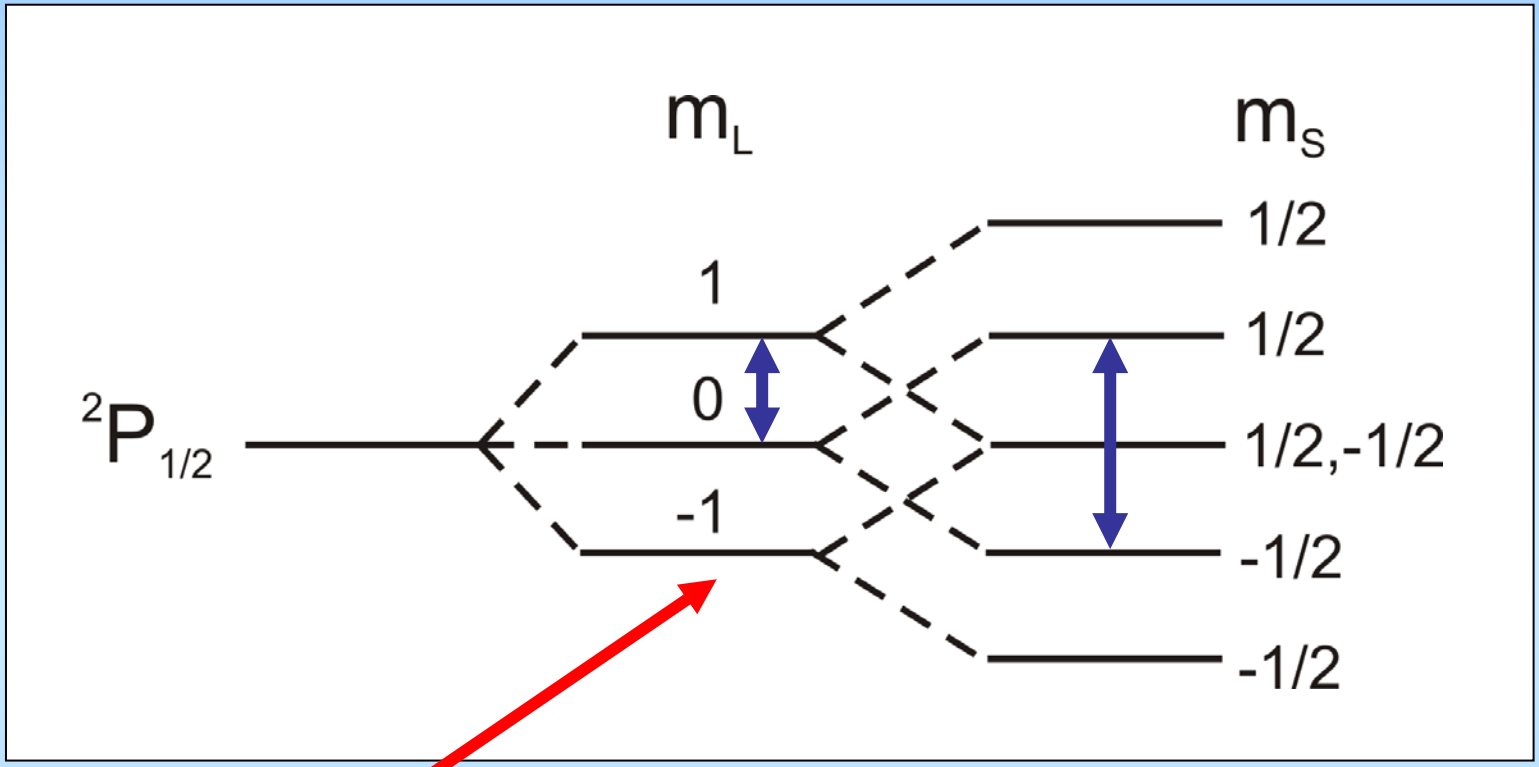


m_L and m_S are good quantum numbers

L and S precess independently around B_{ext}

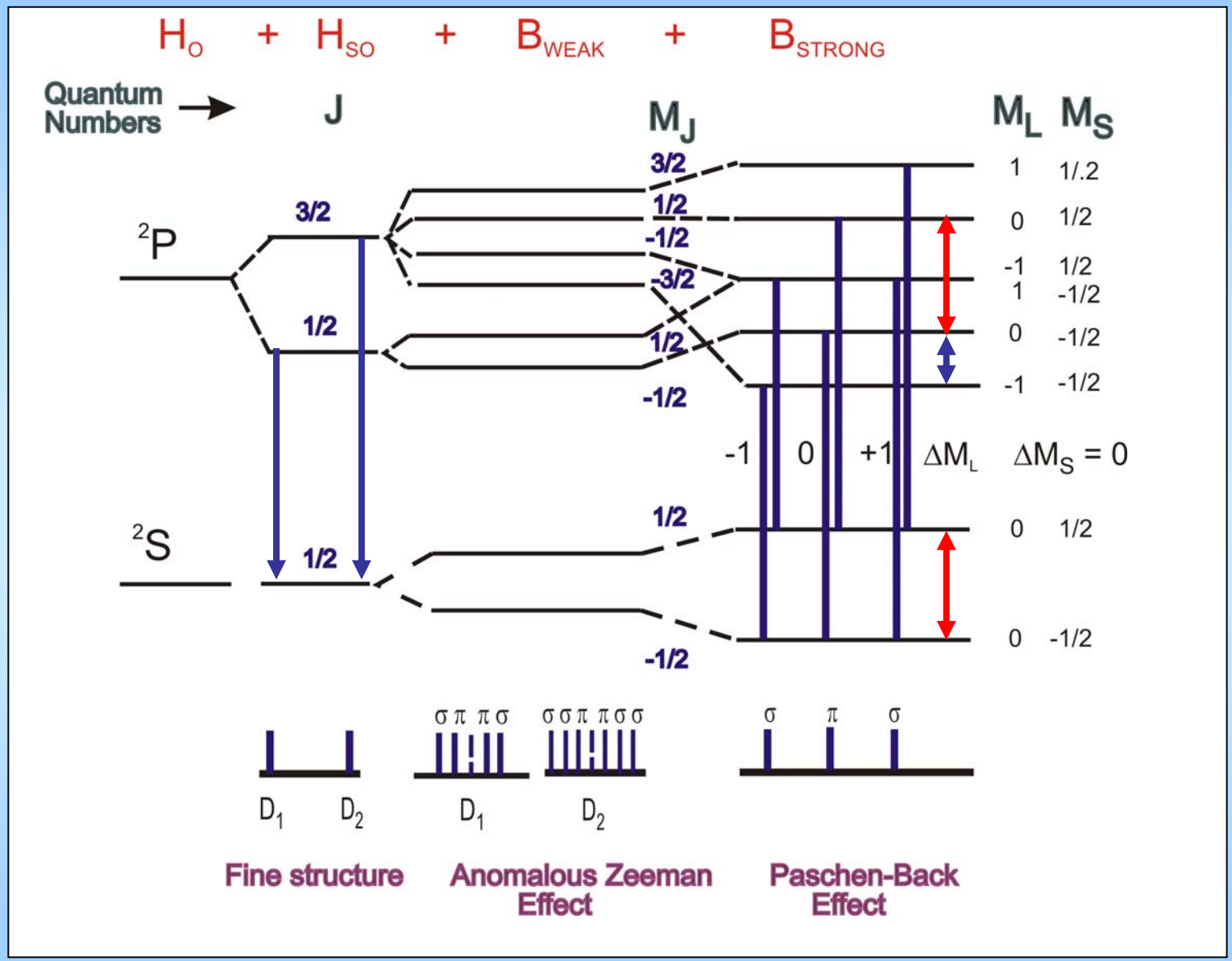
Spin-orbit coupling is relatively insignificant

Splitting of level in strong field: *Paschen-Back Effect*



N.B. Splitting like Normal Zeeman Effect

Spin splitting = 2 x Orbital
$g_S = 2 \times g_L$


H_O + H_{SO} + B_{WEAK} + B_{STRONG}
Quantum Numbers
J
M_J
M_L M_S
^2P
^2S
3/2
1/2
-1/2
-3/2
1
1/.2
0
1/2
-1
1/2
1
-1/2
0
-1/2
-1
-1/2
-1
0
+1
ΔM_L
$\Delta M_S = 0$
D_1 D_2
Fine structure
Anomalous Zeeman Effect
Paschen-Back Effect

Magnetic field effects on hyperfine structure

Hyperfine structure in Magnetic Fields

$$A_J \underline{I} \cdot \underline{J} + g_J \mu_B \underline{J} \cdot \underline{B}_{\text{ext}} - g_I \mu_N \underline{I} \cdot \underline{B}_{\text{ext}}$$

Hyperfine interaction

Electron/Field interaction

~~Nuclear spin/Field interaction~~

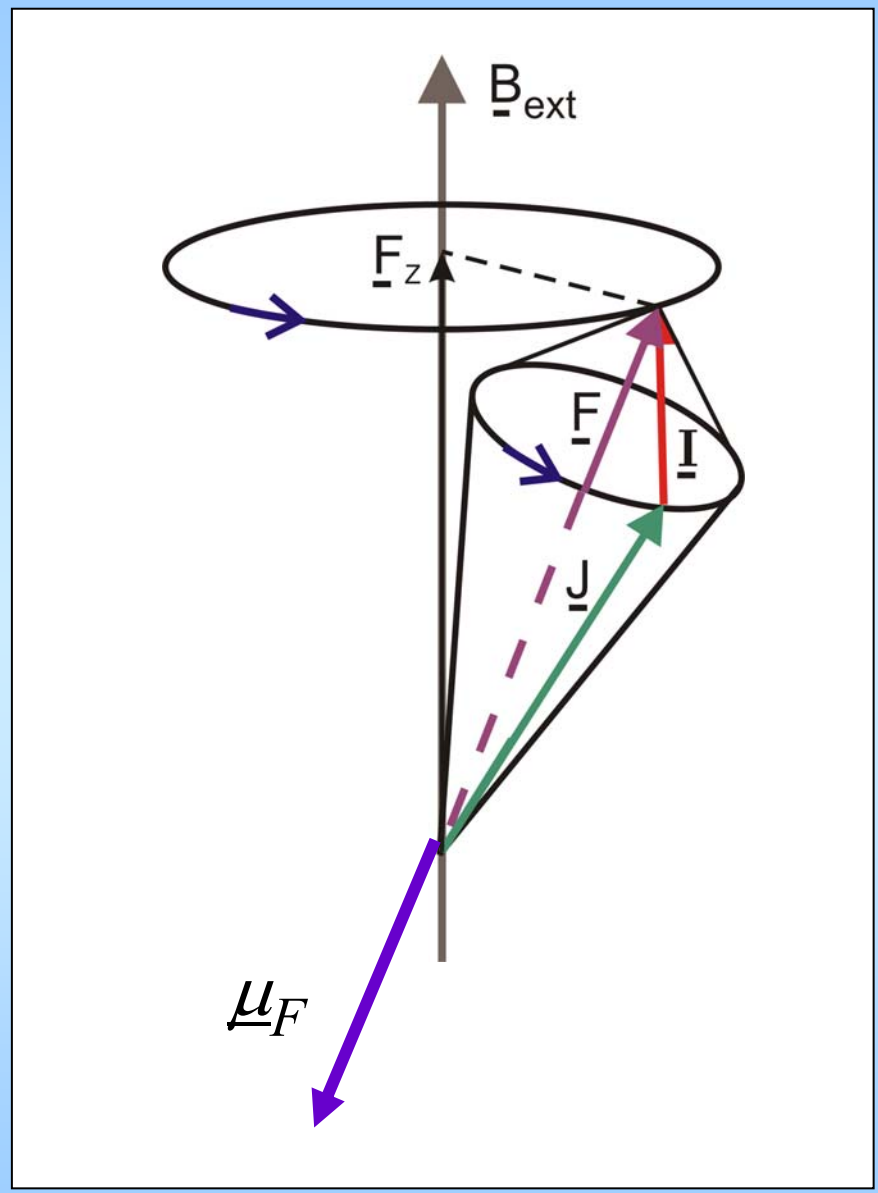
Weak field	$A\underline{I} \cdot \underline{J}$	$>>$	$g_J \mu_B \underline{J} \cdot \underline{B}_{\text{ext}}$
Strong field	$A\underline{I} \cdot \underline{J}$	$<<$	$g_J \mu_B \underline{J} \cdot \underline{B}_{\text{ext}}$

Weak field effect on hyperfine structure

I and J precess rapidly around F. F precesses slowly around B_{ext}

I, J, F and M_F are good quantum numbers

$$\underline{\mu}_F = -g_F \mu_B \underline{F}$$



$$\underline{\mu}_F = -g_F \mu_B \underline{F}$$

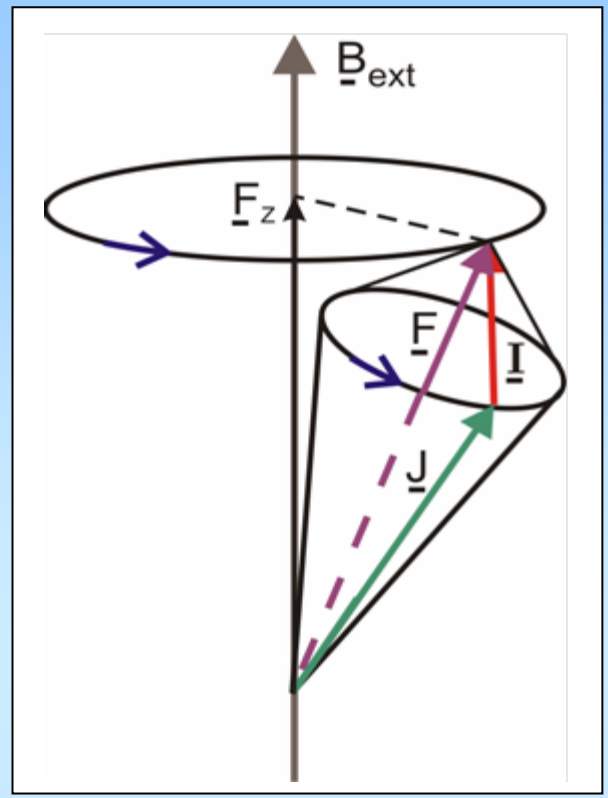
Only contribution to μ_F is component of μ_J along $\underline{F}$

$$\underline{\mu}_F = -g_J \mu_B \frac{\underline{J}.\underline{F}}{F} \times \frac{\underline{F}}{F}$$

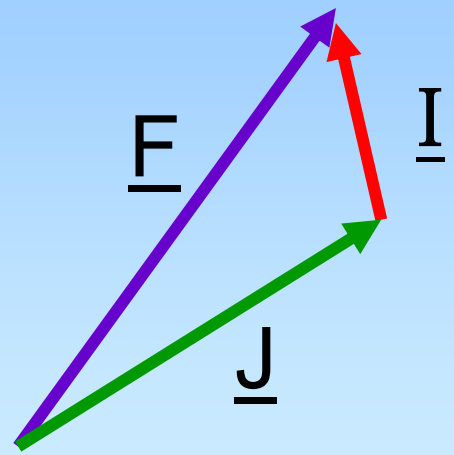
magnitude direction

$$g_F = g_J \times \frac{\underline{J}.\underline{F}}{F^2}$$

Find this using Vector Model



$$g_F = g_J \times \frac{\underline{J}.\underline{F}}{F^2}$$



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

$$\underline{I}^2 = \underline{F}^2 + \underline{J}^2 - 2\underline{J}.\underline{F}$$

$$\underline{J}.\underline{F} = \tfrac{1}{2}\{F(F+1) + J(J+1) - I(I+1)\}$$

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}$$

$$\Delta E = A_J \underline{I} \cdot \underline{J} + g_J \mu_B \underline{J} \cdot \underline{B}_{\text{ext}}$$

$$\Delta E = \frac{A_F}{2}\{F(F+1) - J(J+1) - I(I+1)\} + g_F \mu_B \underline{F} \cdot \underline{B}_{\text{ext}}$$

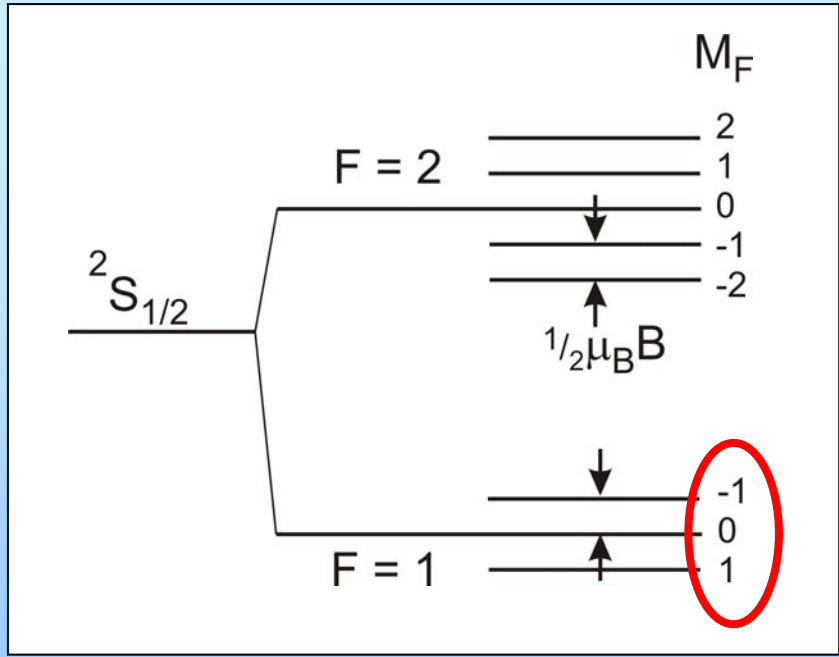
N.B. notes error eqn 207

Each hyperfine level is split by g_F term

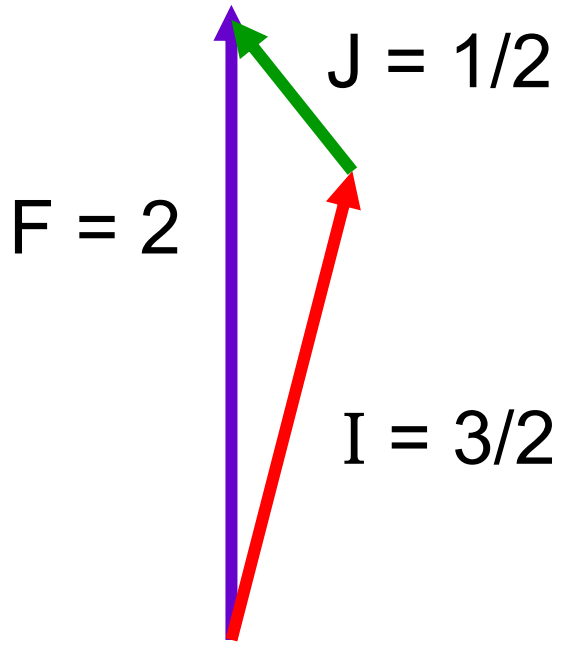
Ground level of Na:

J = 1/2 ; I = 3/2 ;
F = 1 or 2

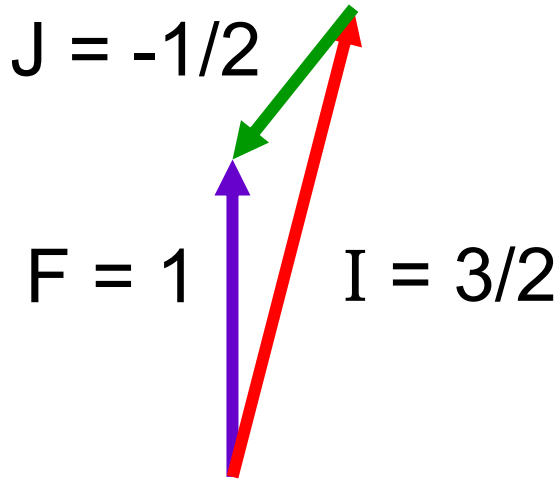
F = 2: g_F = ½ ;
F = 1: g_F = -½



Sign inversion of g_F for F = 1 and F = 2



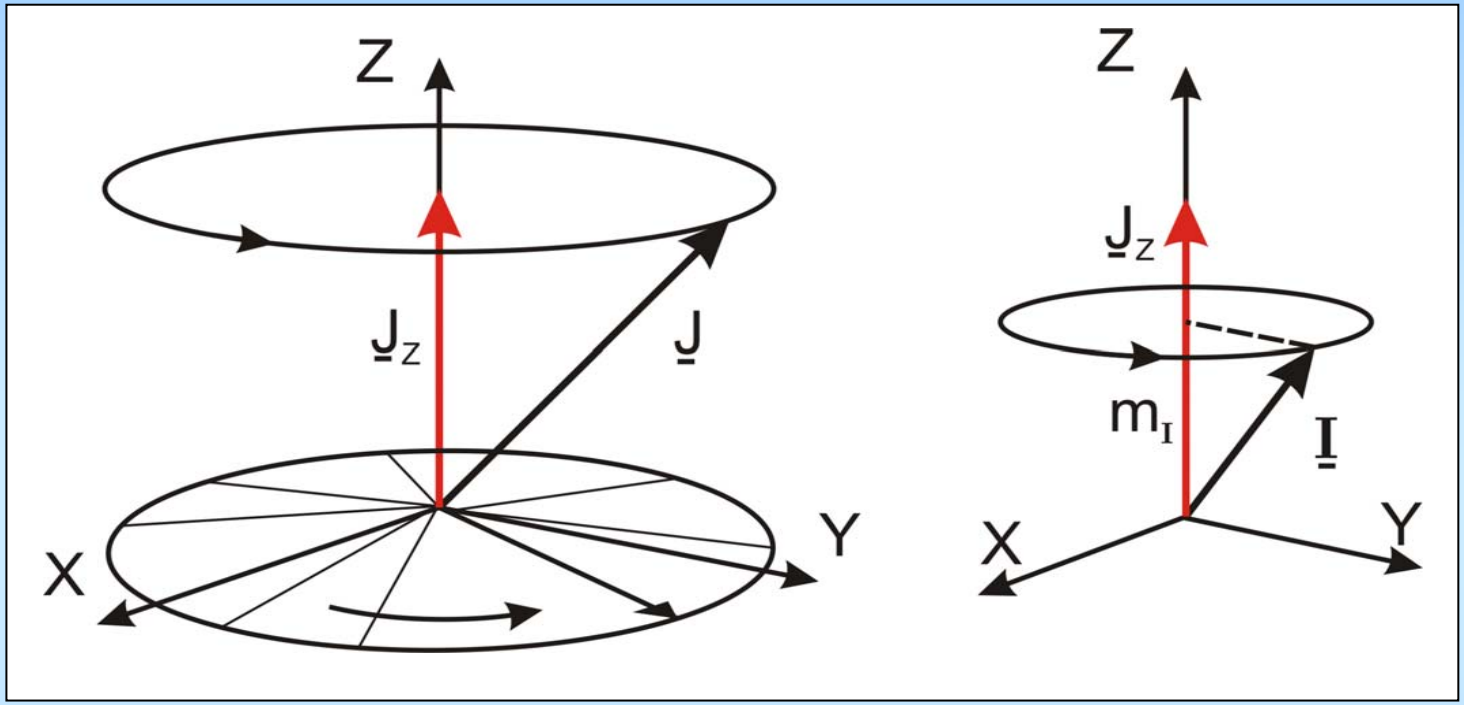
J.F positive



J.F negative

Strong field effect on hfs.

$$\Delta E = A_J \underline{I} \cdot \underline{J} + g_J \mu_B \underline{J} \cdot \underline{B}_{\text{ext}}$$



$\underline{J}$ precesses rapidly around B_{ext} (z-axis)
$\underline{I}$ tries to precess around $\underline{J}$ but can follow only the time averaged component along z-axis i.e. J_z

So $A_J \underline{I}.\underline{J}$ term $\rightarrow A_J M_I M_J$

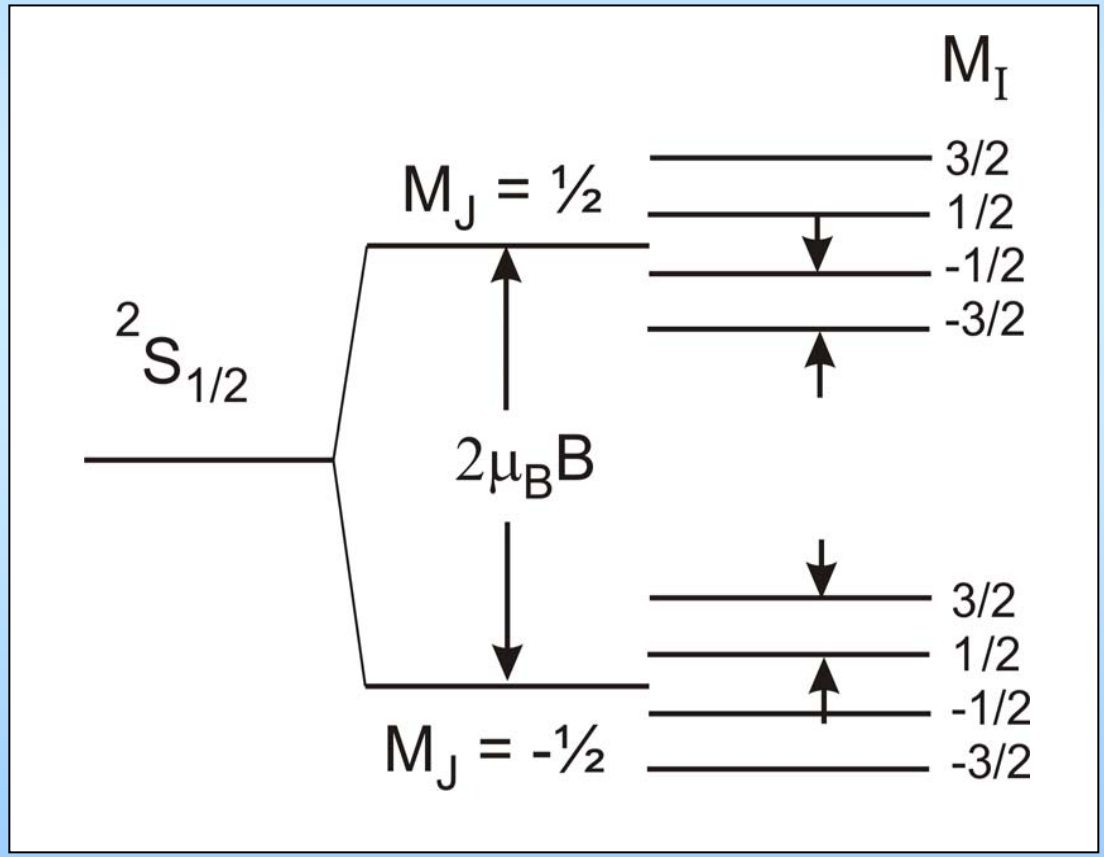
Strong field effect on hfs.

Dominant term

Energy

$$\Delta E_{\mathrm{BG}} = A_J M_I M_J + g_J \mu_B M_J B_{\mathrm{ext}}$$

Na ground state



Strong field effect on hfs.

Energy: $\Delta E = A_J \underline{I} \cdot \underline{J} + g_J \mu_B \underline{J} \cdot \underline{B}_{\text{ext}}$

$\underline{J}$ precesses around field B_{ext}

I tries to precess around J

I precesses around what it can "see" of $\underline{J}$:
The z-component of $\underline{J}$: $\underline{J}_Z$

$$\Delta E_{\text{BG}} = A_J M_I M_J + g_J \mu_B M_J B_{\text{ext}}$$

Magnetic field effects on hfs

Weak field: F, M_F are good quantum nos.
Resolve μ_J along F to get effective magnetic moment and g_F

$$\Delta E(F,M_F) = g_F \mu_B M_F B_{ext}$$

→ "Zeeman" splitting of hfs levels

Strong field: M_I and M_J are good quantum nos.
J precesses rapidly around B_{ext};
I precesses around z-component of J i.e. what it can "see" of J

$$\Delta E(M_J,M_I) = g_J \mu_B M_J B_{ext} + A_J M_I M_J$$

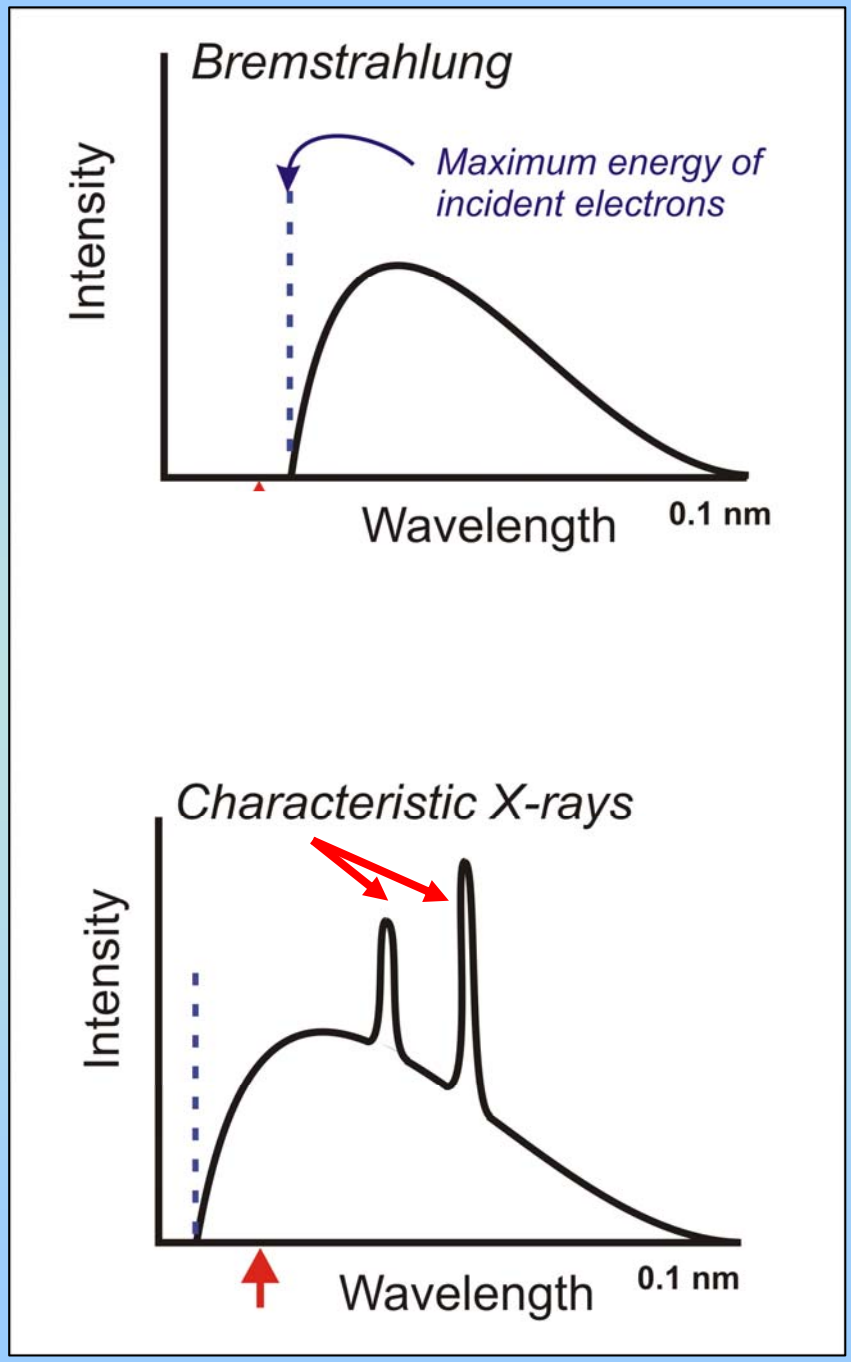
→ hfs of "Zeeman" split levels

Lecture 8

- X-rays: excitation of “inner-shell” electrons

- High resolution laser spectroscopy
  - The Doppler effect
  - Laser spectroscopy
  - “Doppler-free” spectroscopy

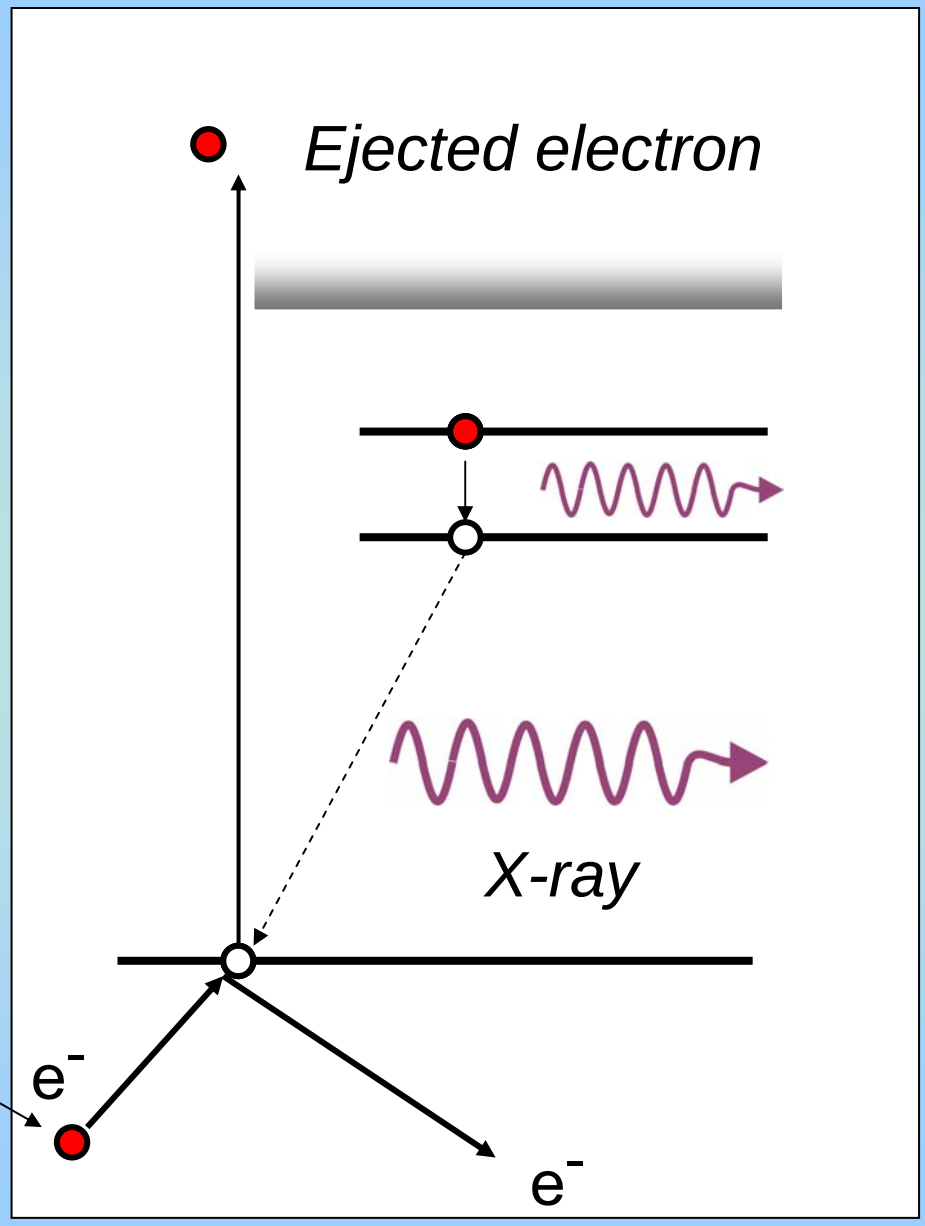
X – Ray Spectra



Characteristic X-rays

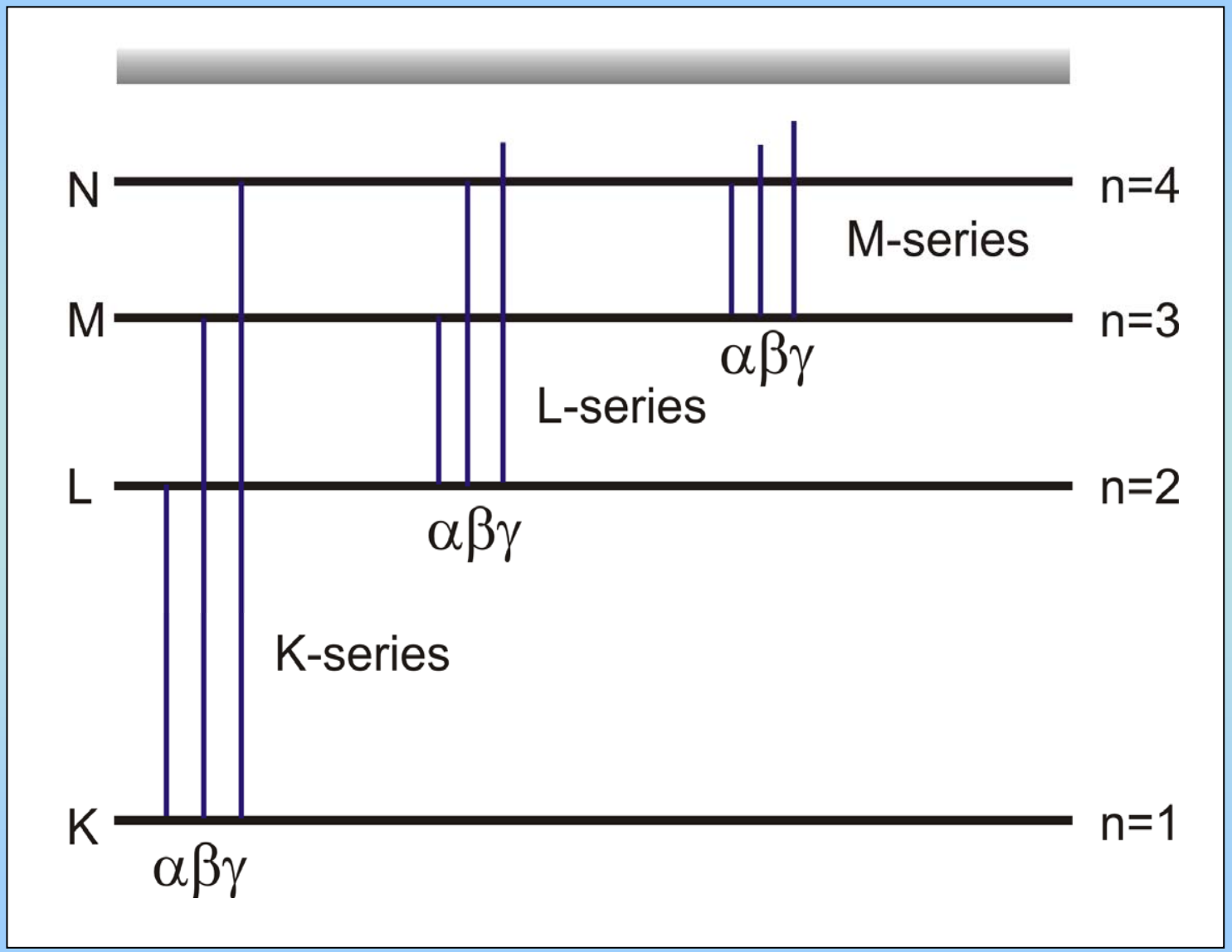
- Wavelengths fit a simple series formula
- All lines of a series appear together
  – *when excitation exceeds threshold value*
- Threshold energy just exceeds
  energy of shortest wavelength X-rays
- Above a certain energy no new series appear.

Generation of characteristic X-rays

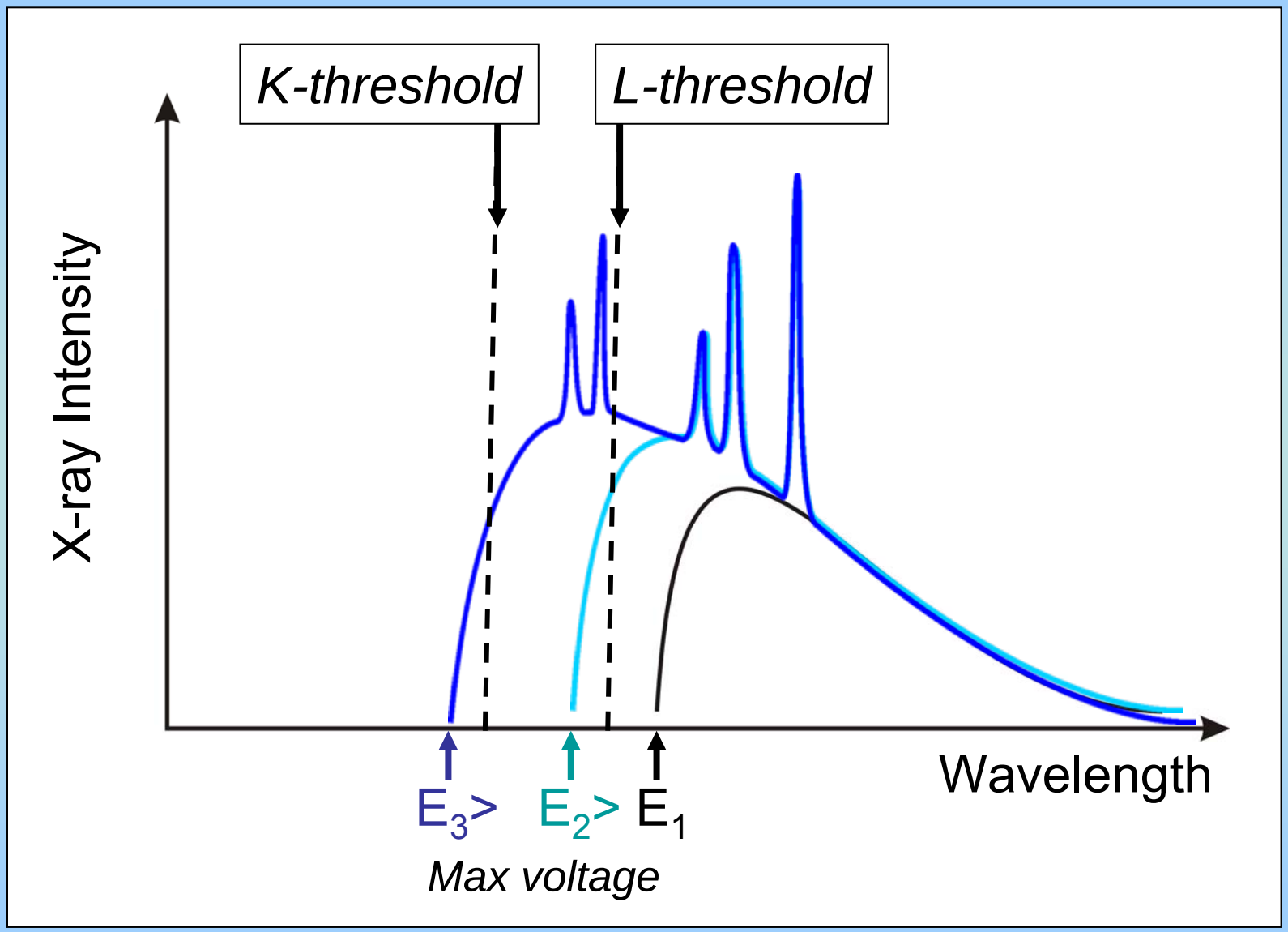


Incident high voltage electron

X-ray series



X-ray spectra for increasing electron impact energy



Binding energy for electron in hydrogen = R/n^2

Binding energy for "hydrogen-like" system = RZ^2/n^2

Screening by other electrons in inner shells:
$Z \rightarrow (Z - \sigma)$

Binding energy of inner-shell electron:

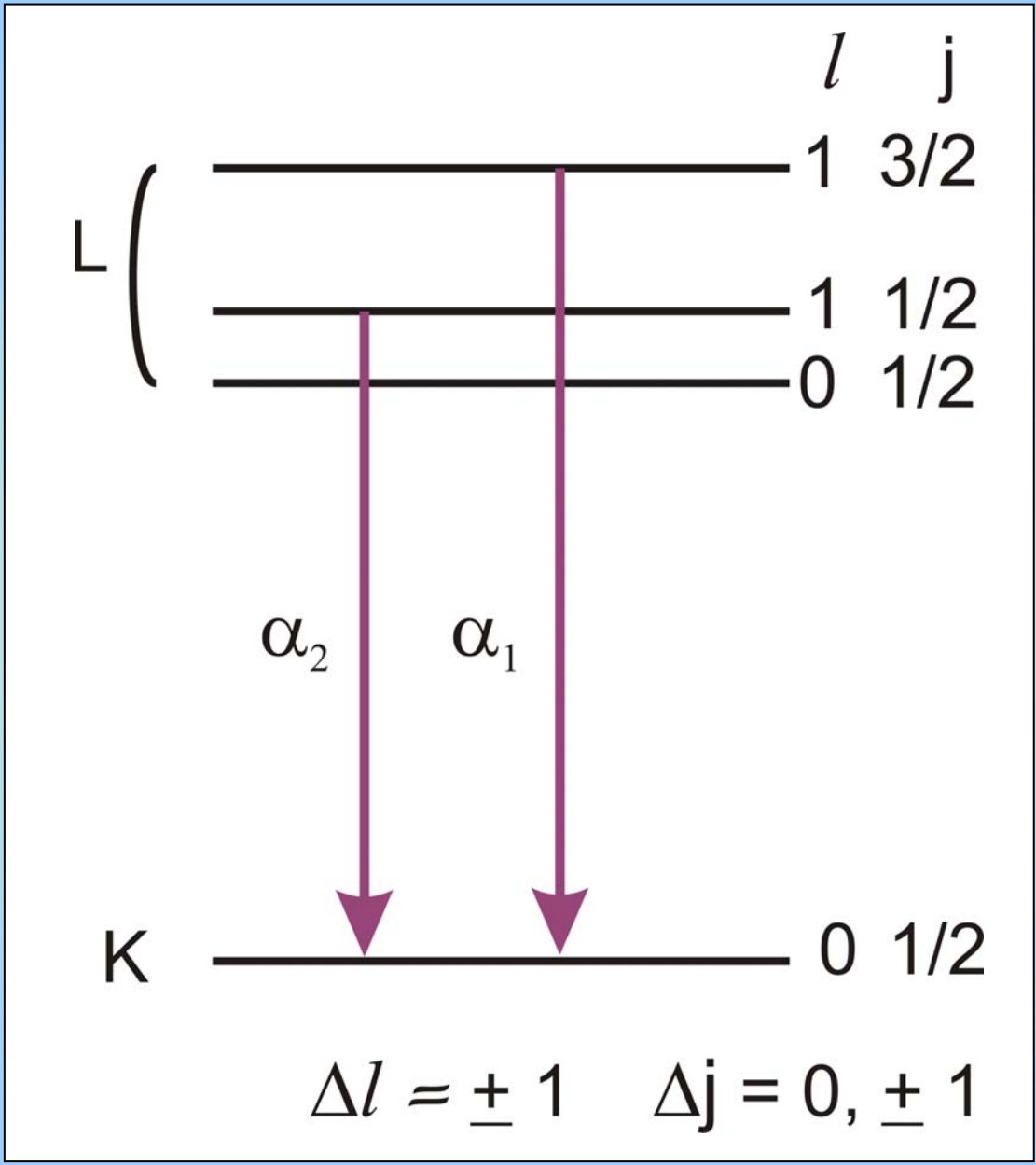
$$E_n = R(Z - \sigma)^2 / n^2$$

Transitions between inner-shells:

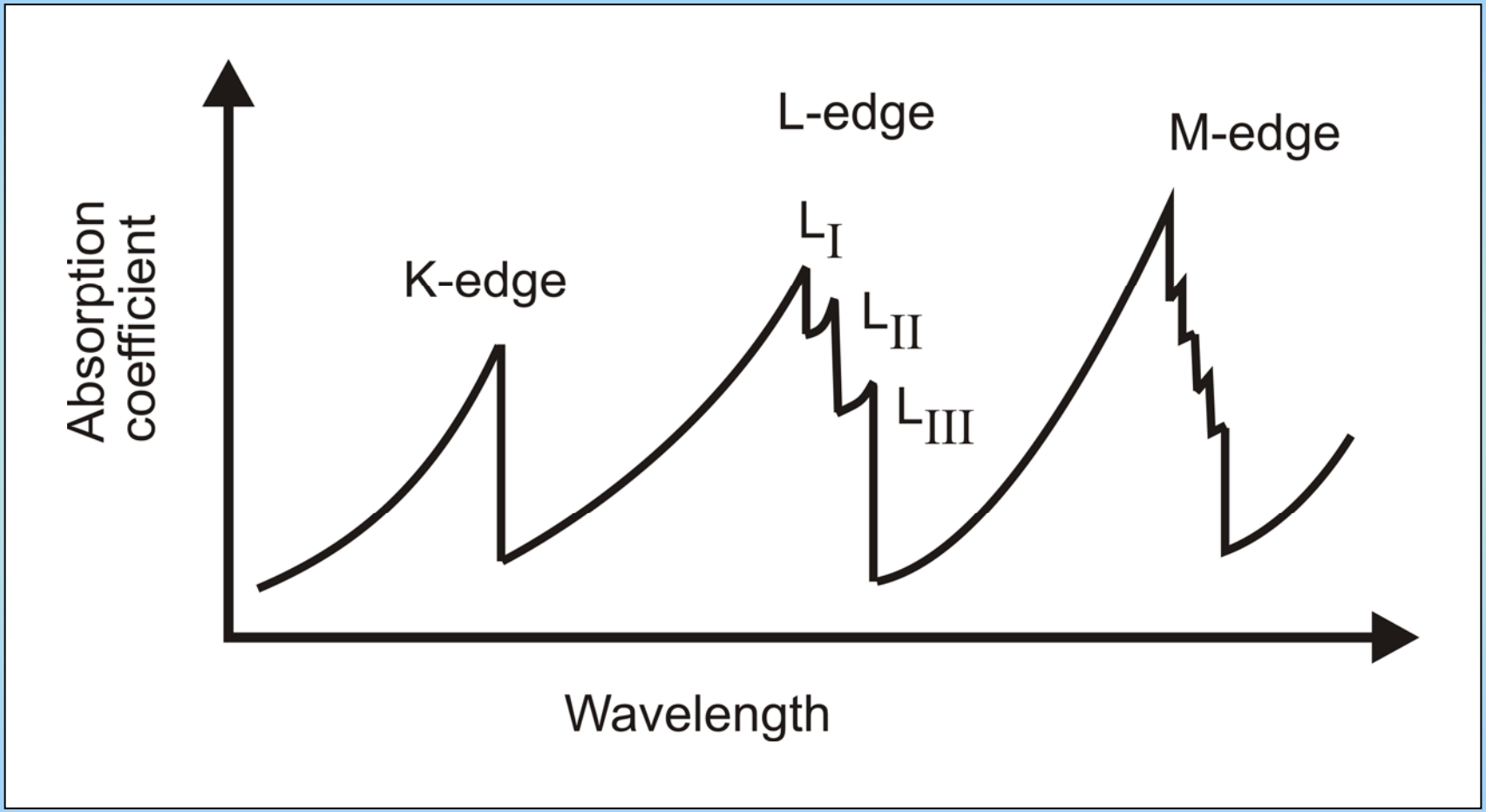
$$E_n - E_m = \bar{\nu} = R\{(Z - \sigma_i)^2 / n_i^2 - (Z - \sigma_j)^2 / n_j^2\}$$

Fine structure of X-rays

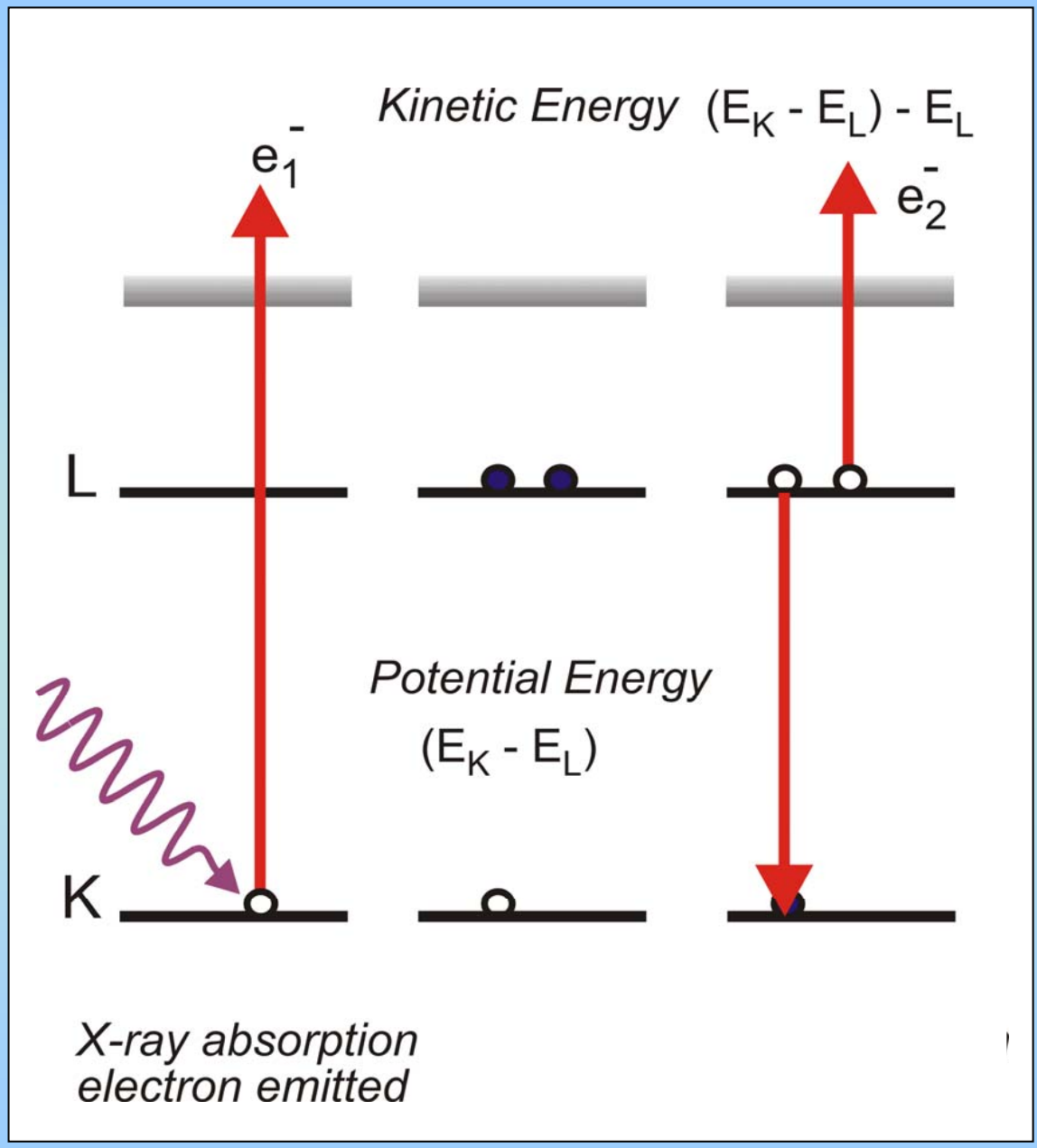
$$\Delta E_{\rm fs} = \frac{5.8 Z^4}{n^3 l(l+1)}$$



X-ray absorption spectra



Auger effect

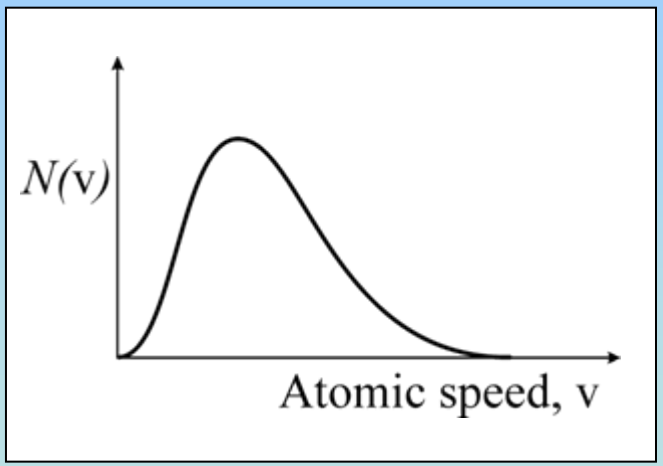


High resolution laser spectroscopy

Doppler broadening

Doppler Shift:

$$\nu = \nu_0 \left(1 \pm \frac{v}{c}\right)$$

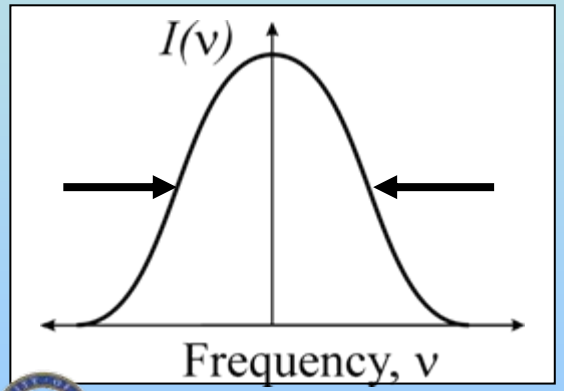


Maxwell-Boltzmann distribution of Atomic speeds

$$dN = N_0 e^{-\frac{Mv^2}{2kT}} dv$$

Distribution of Intensity

$$I(\nu) = I(\nu_0) \exp\left[-\frac{Mc^2}{2kT}\left(\frac{\nu - \nu_0}{\nu_0}\right)^2\right]$$

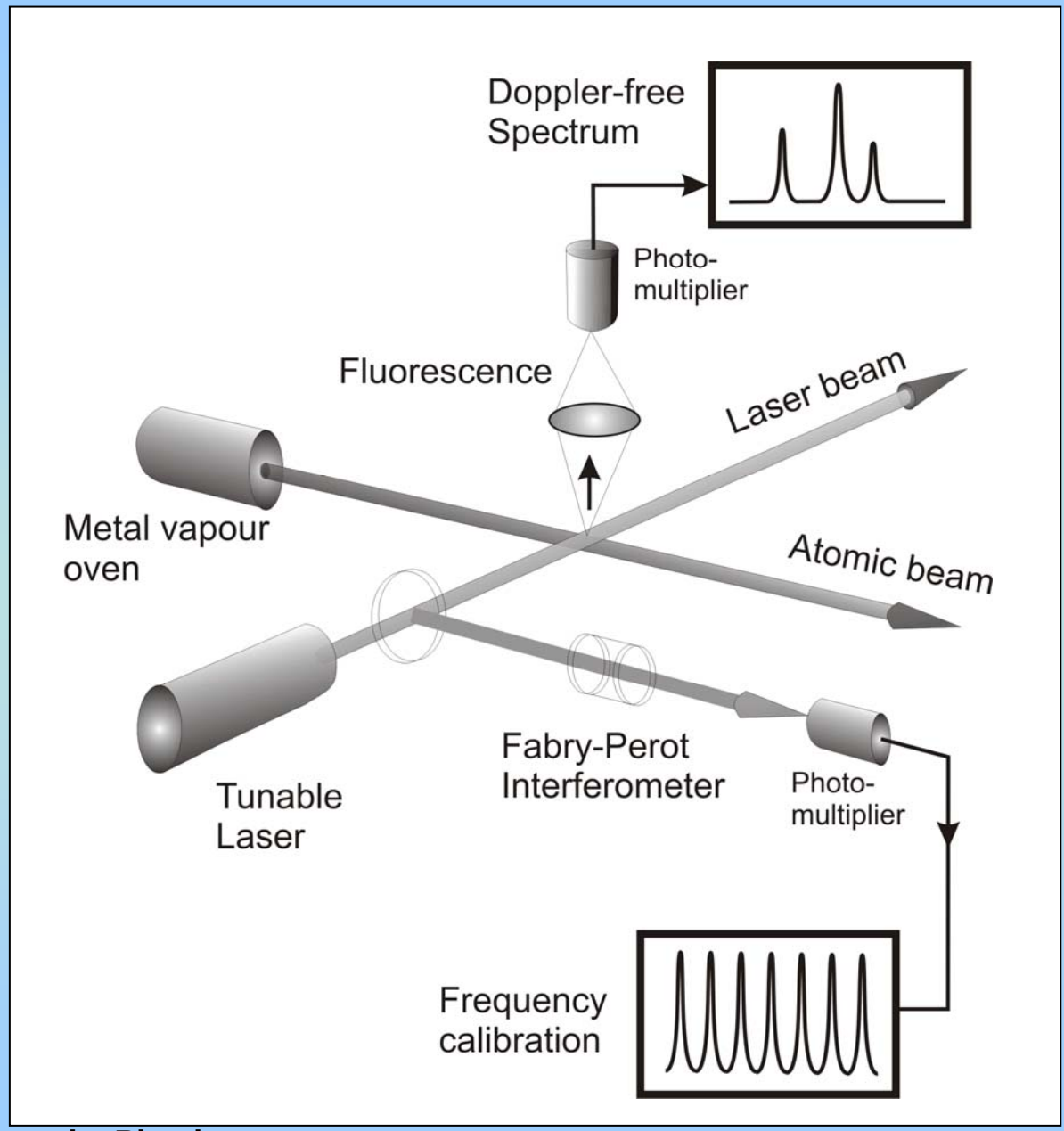


Doppler width

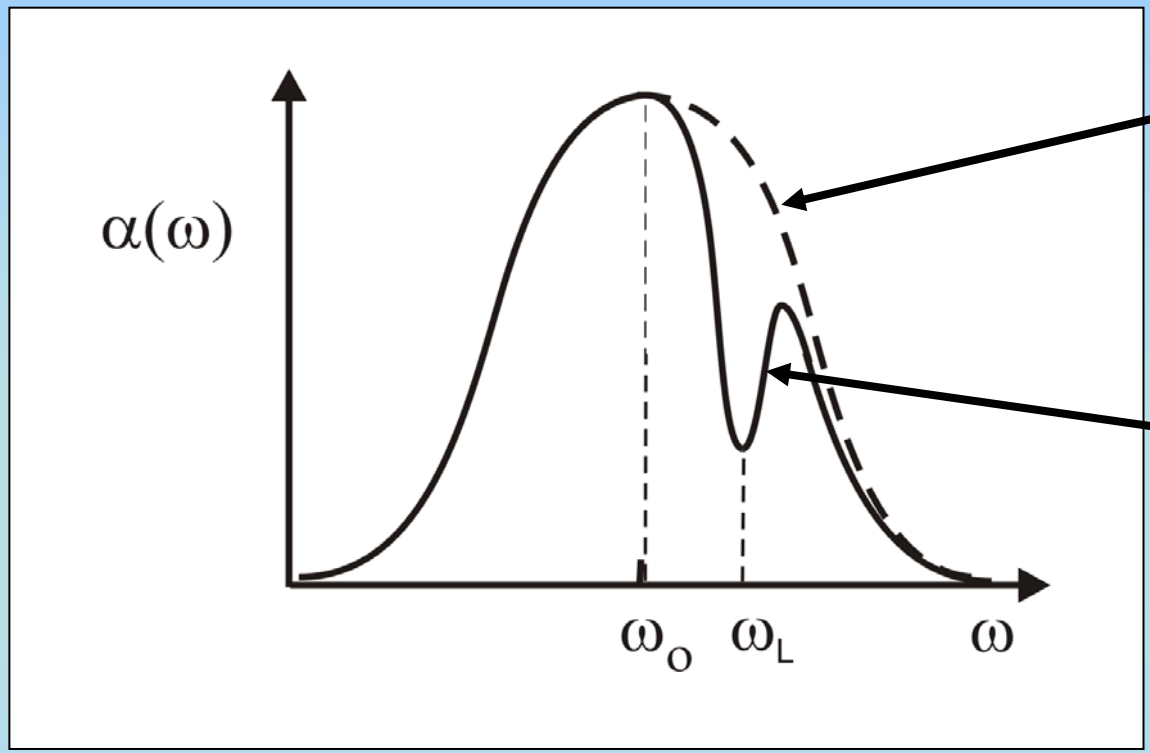
$$\Delta\nu_D = \frac{2\nu}{c}\left[\frac{2kT}{M}\log_e 2\right]^{1/2}$$

Notes error

Crossed beam Spectroscopy



Saturation effect on absorption



Absorption profile for weak probe

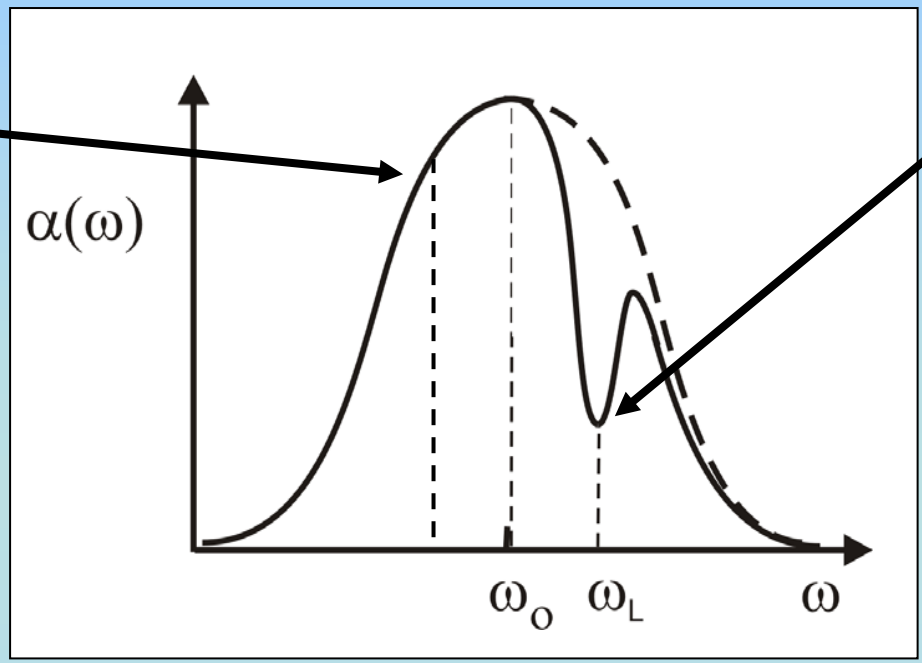
Absorption profile for weak probe – with strong pump at ω_o

Strong pump at ω_L reduces population of ground state for atoms Doppler shifted by $(\omega_L - \omega_o)$.
Hence reduced absorption for this group of atoms.

Saturation effect on absorption

Absorption of weak probe

ω_L

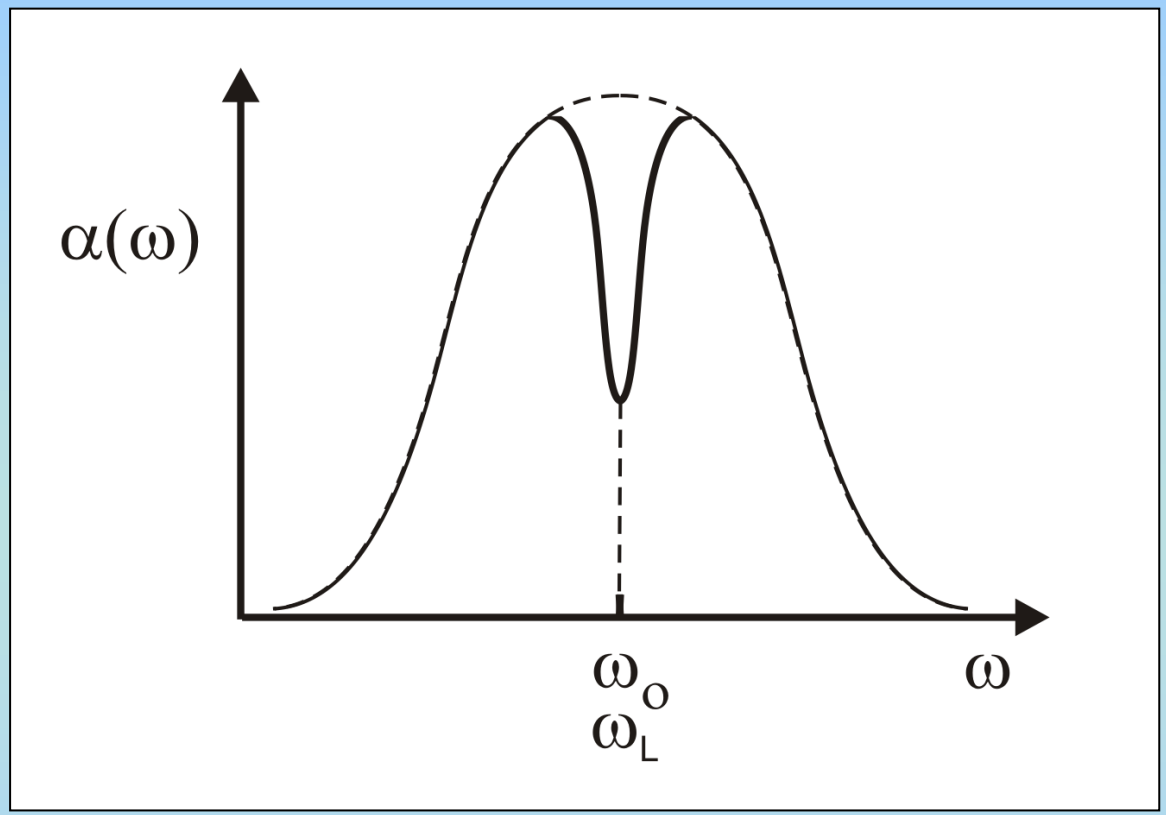


Absorption of strong pump

ω_L

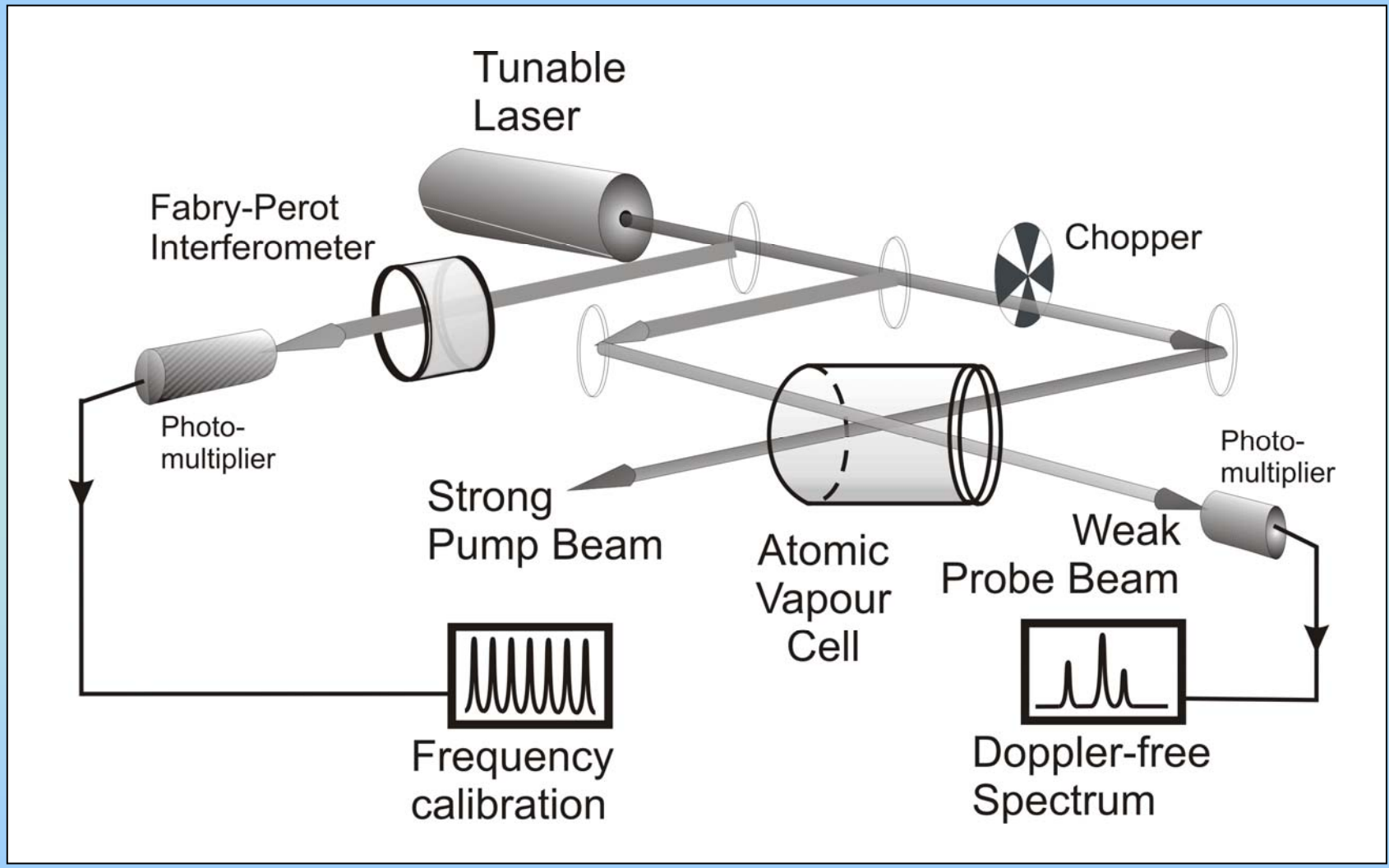
Probe and pump laser at same frequency ω_L
But propagating in opposite directions
Probe Doppler shifted down = Pump Doppler shifted up.
Hence probe and pump "see" different atoms.

Saturation of "zero velocity" group at ω_O

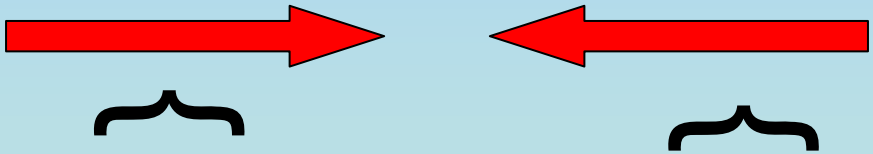


Counter-propagating pump and probe
"see" same atoms at $\omega_L = \omega_O$
i.e. atoms moving with zero velocity relative to light

Saturation spectroscopy



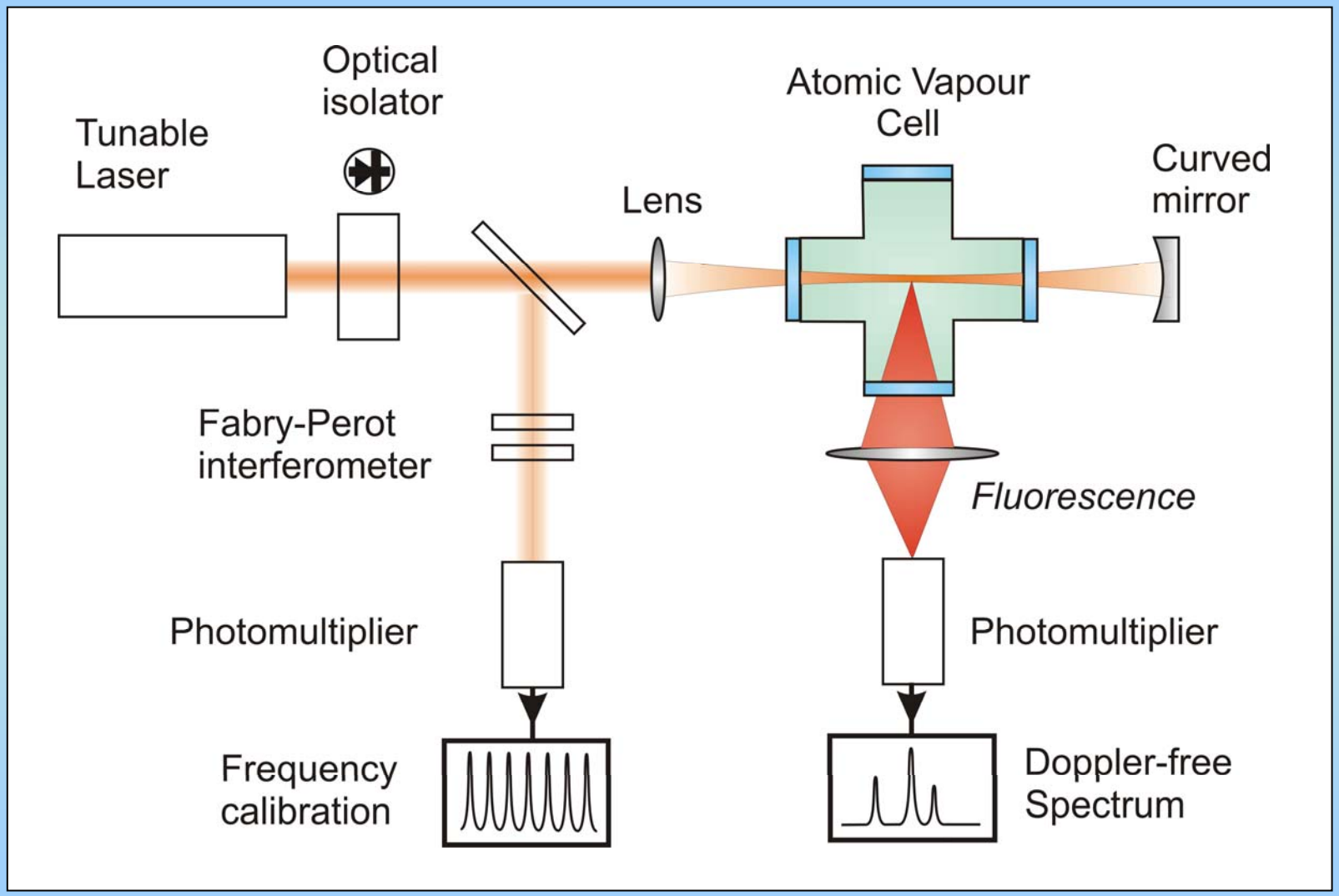
Principle of Doppler-free two-photon absorption



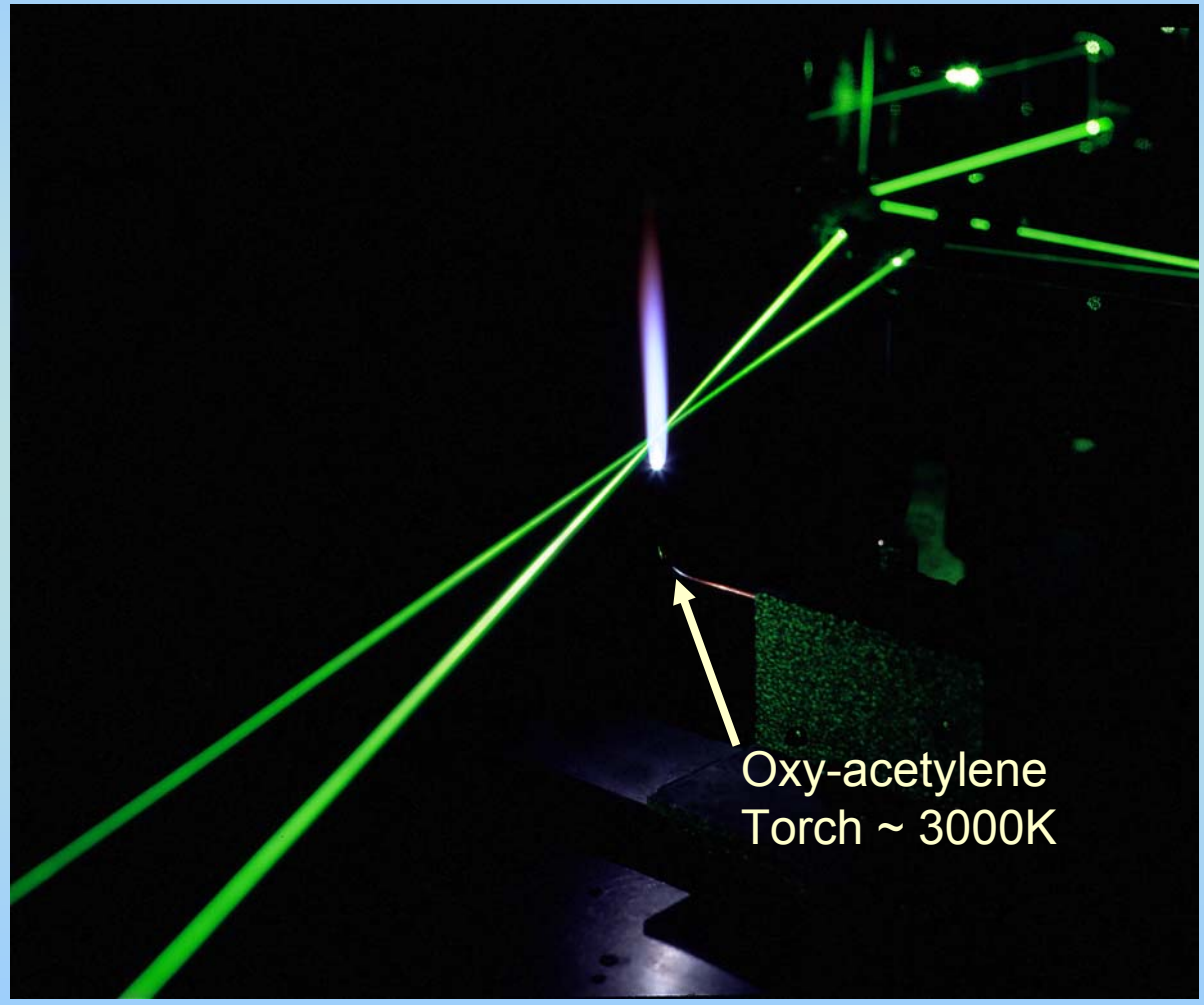
$$E = h\nu(1 + v/c) + h\nu(1 - v/c) = 2h\nu$$

Photon Doppler shifted up + Photon Doppler shifted down

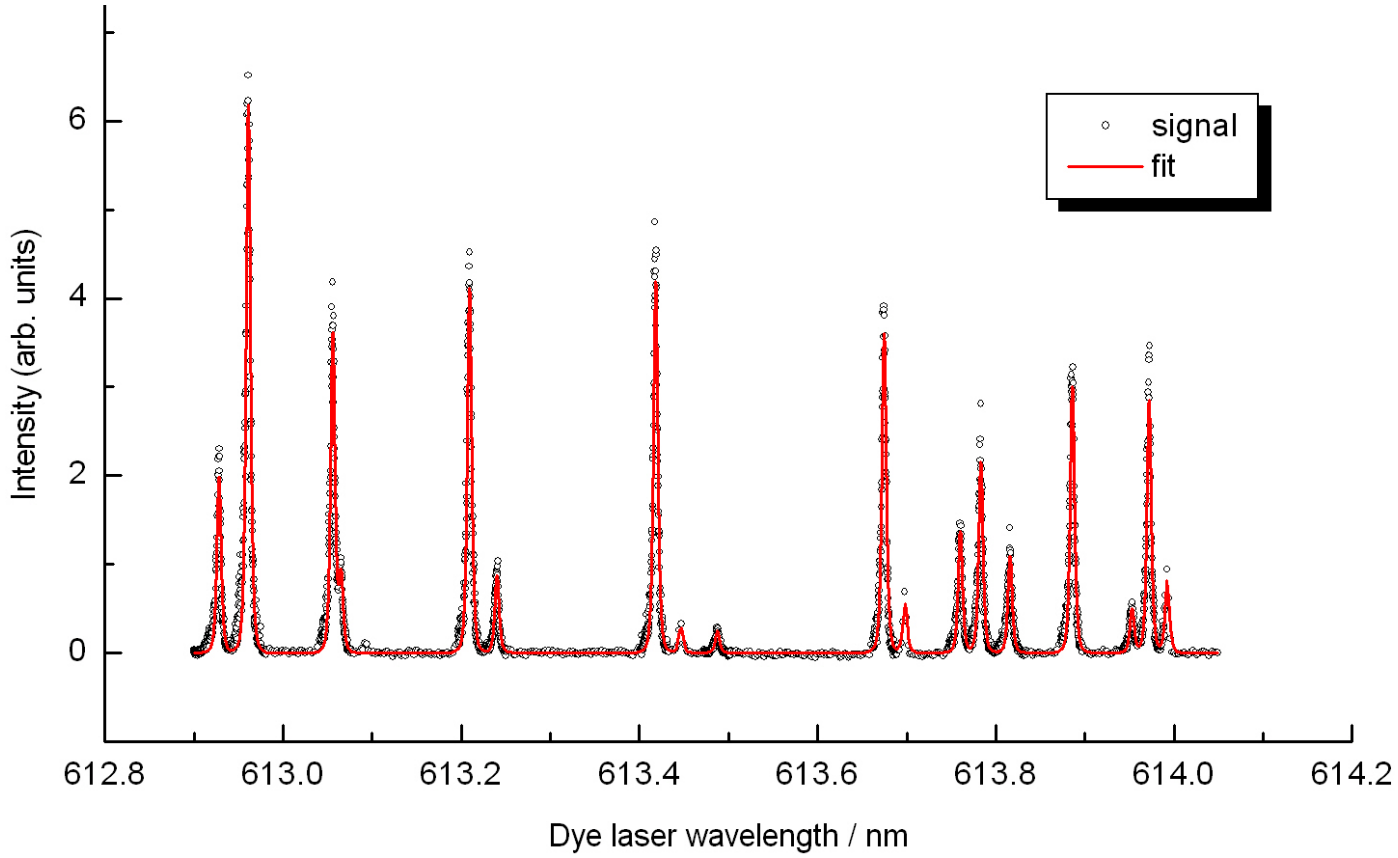
Two-photon absorption spectroscopy



Doppler-free spectroscopy of molecules in high temperature flames



Doppler-free spectrum of OH molecule in a flame



The End