

Atomic Physics

3rd year B1

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- *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

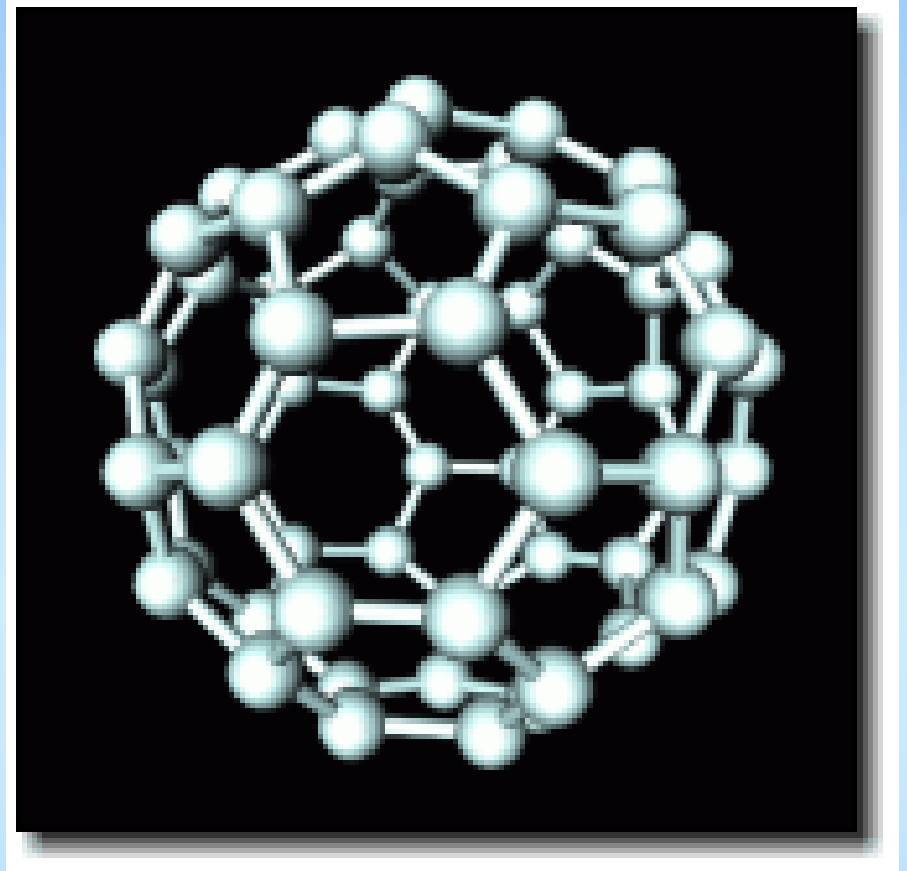


Astrophysics



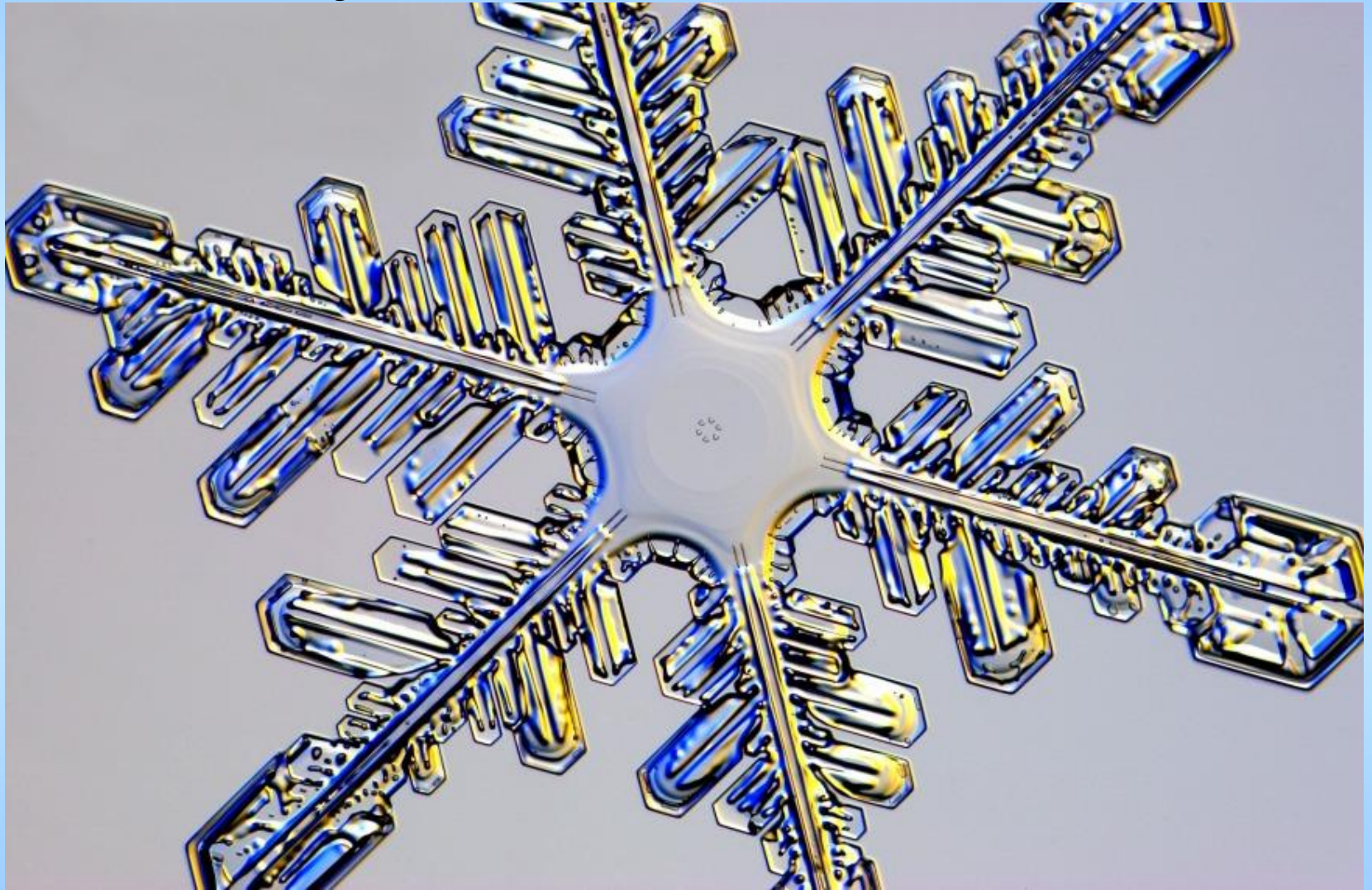
Condensed Matter

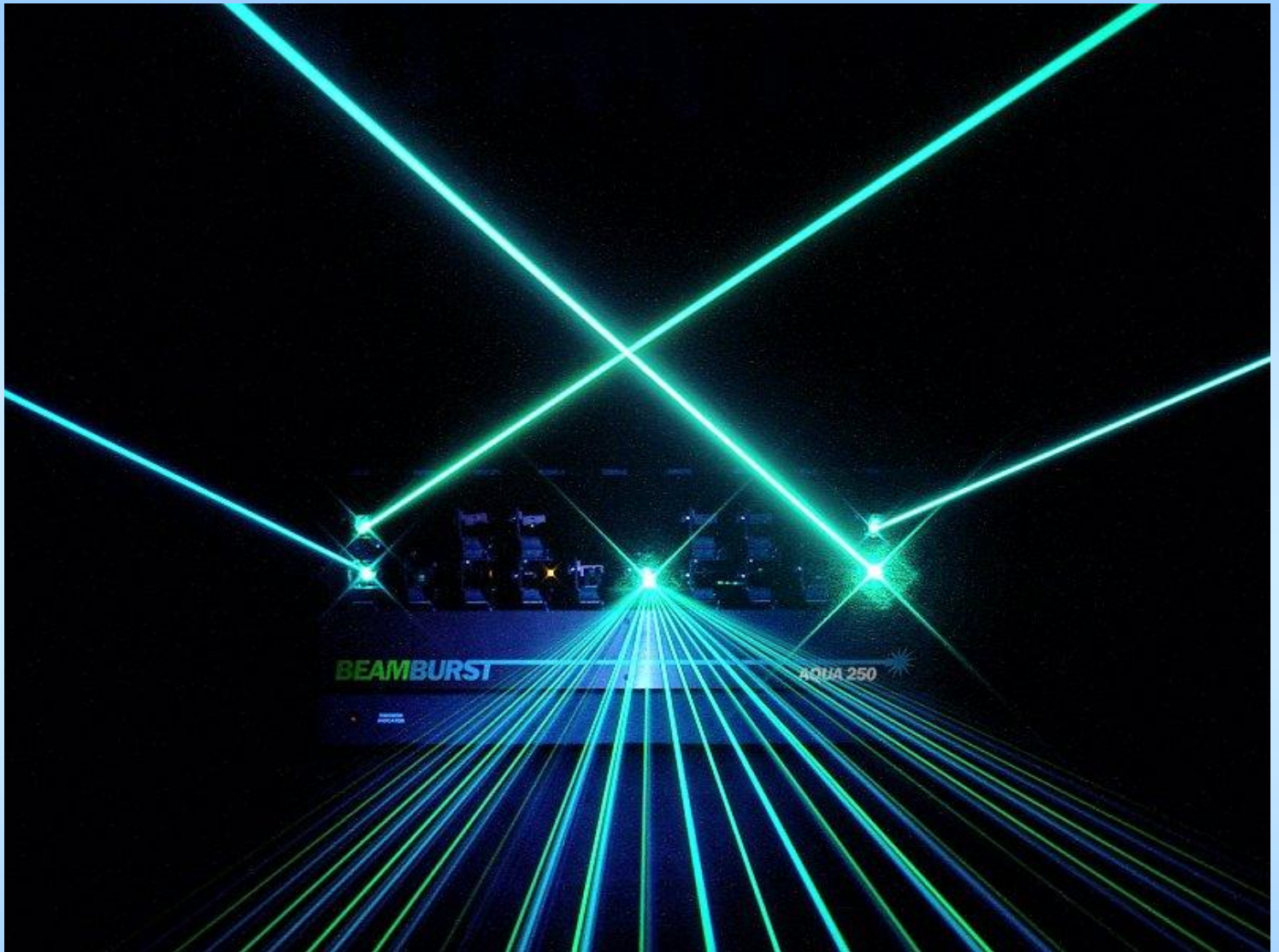
Zircon mineral crystal



C₆₀ Fullerene

Snow crystal

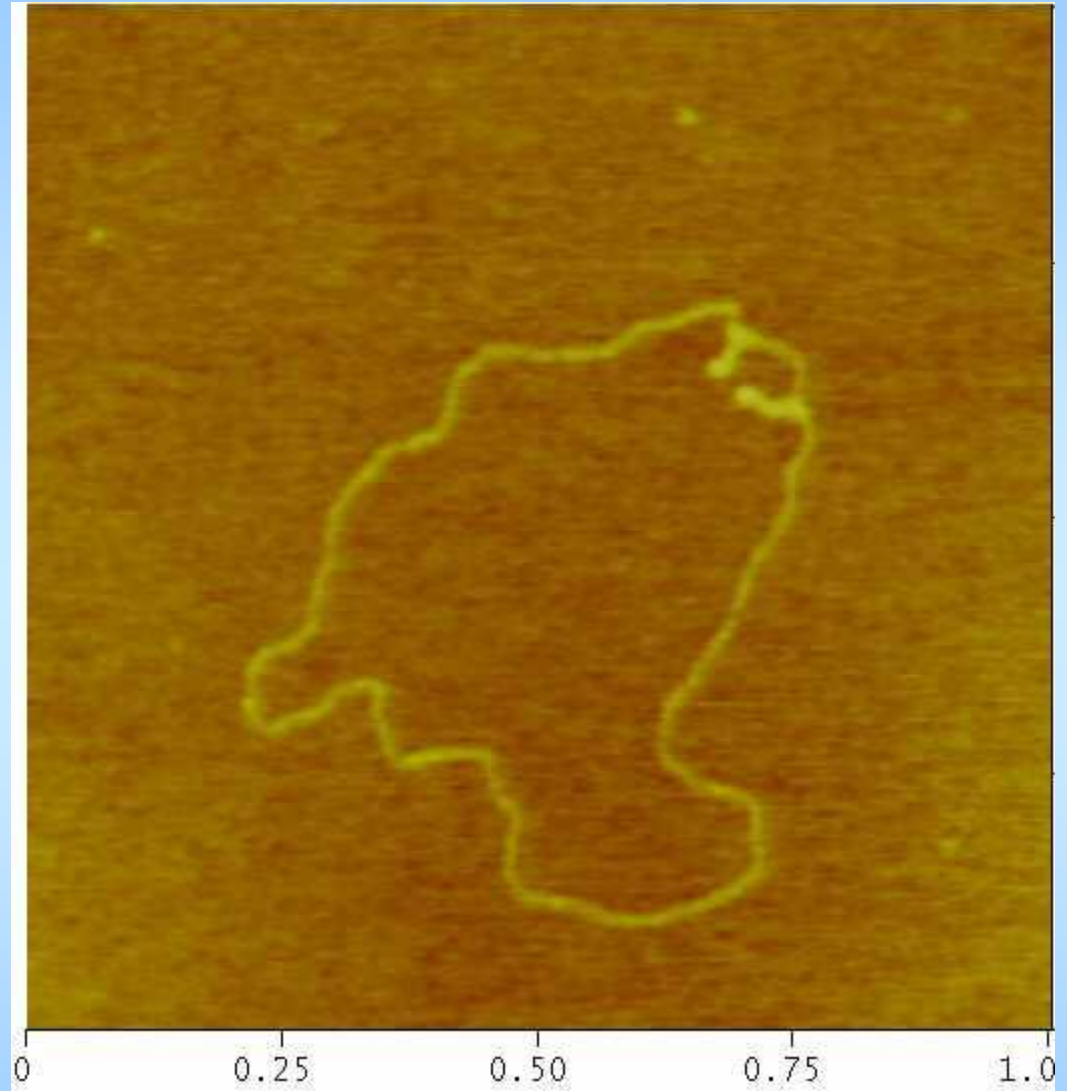




Lasers

Biology

DNA strand

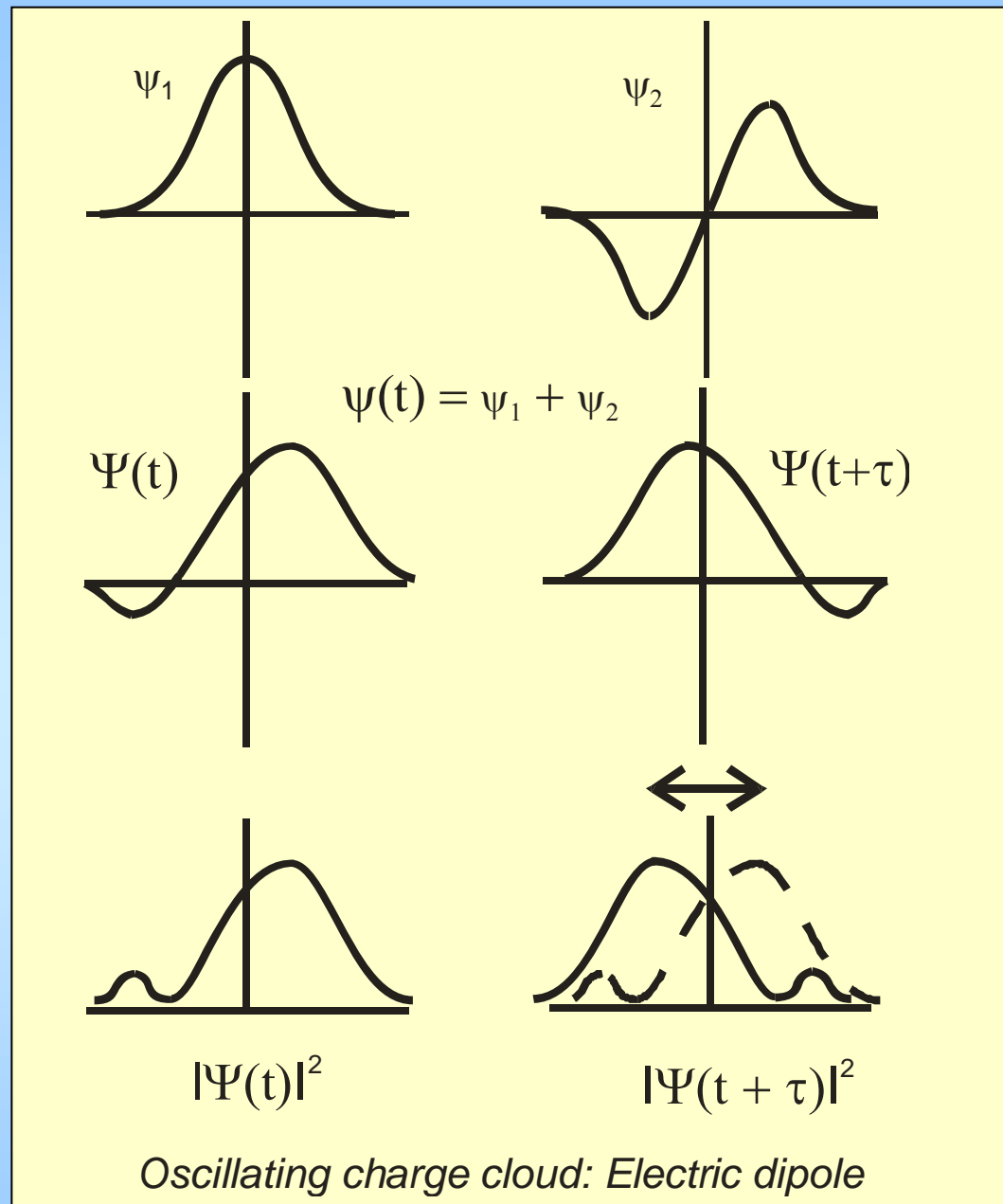


Lecture 1

- 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)

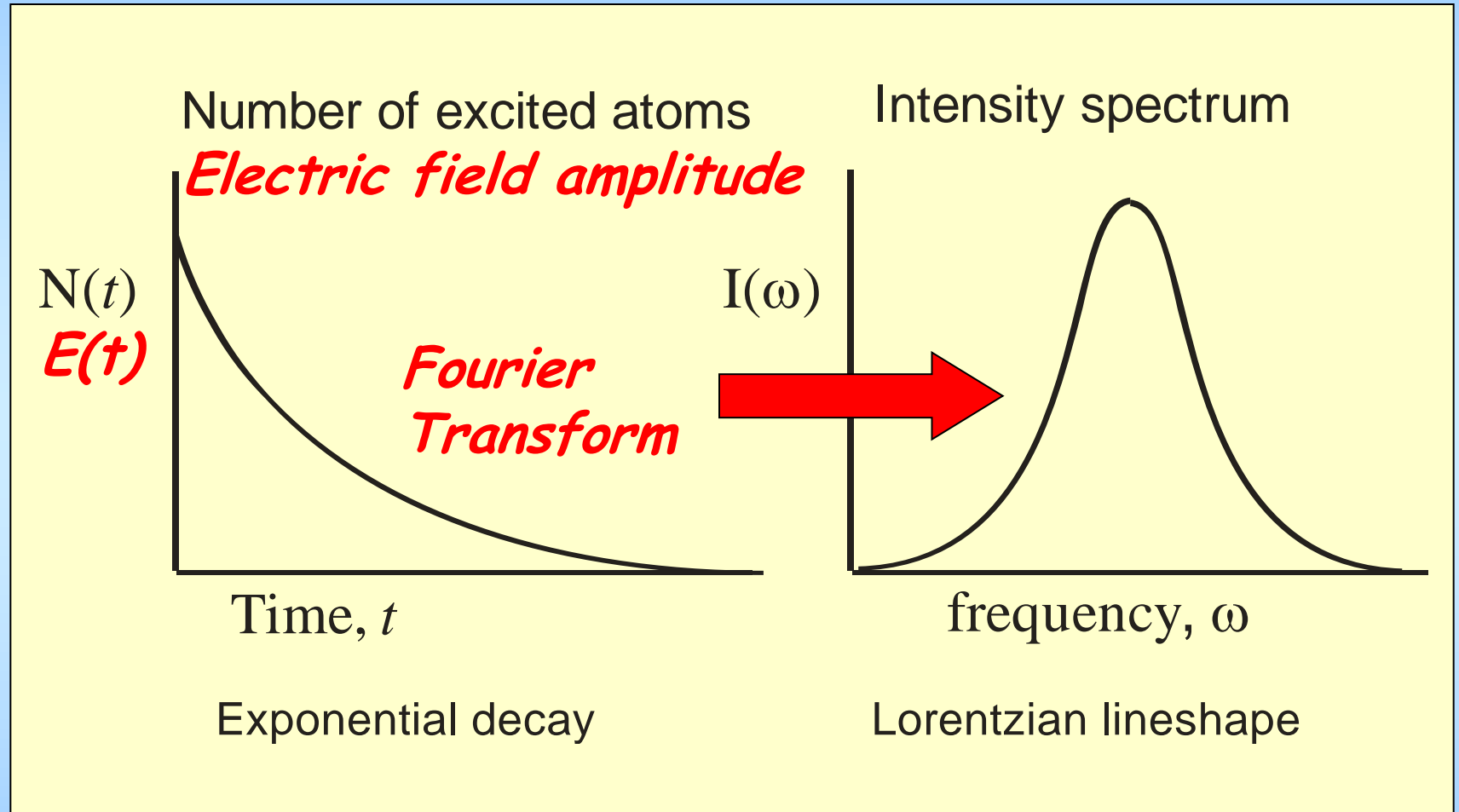
Inhomogeneous e.g.

Doppler (Atomic motion)

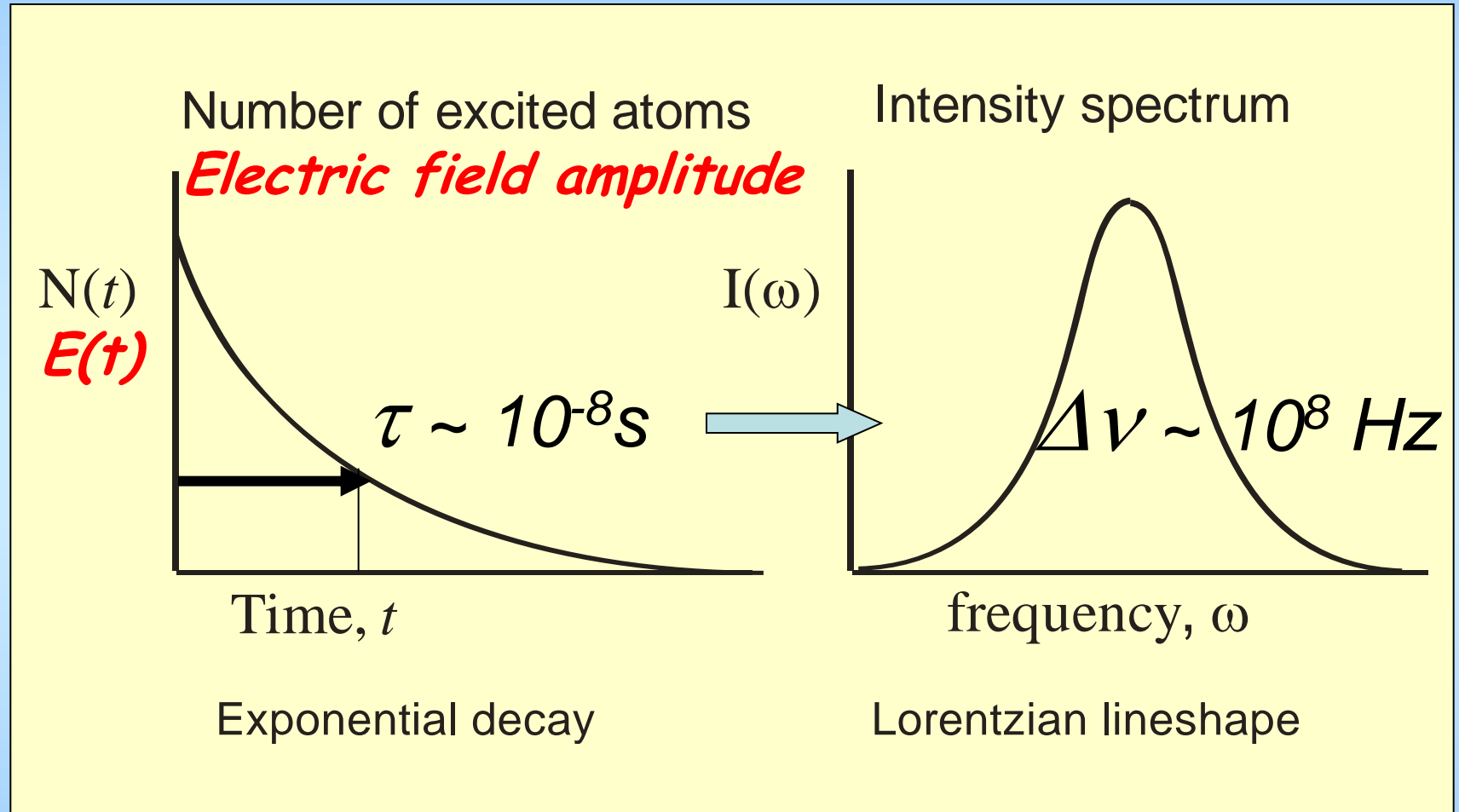
Crystal Fields



Lifetime (natural) broadening

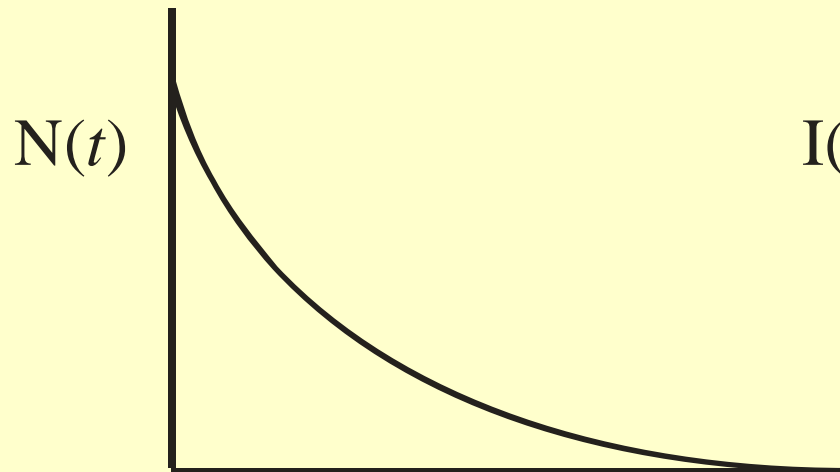


Lifetime (natural) broadening



Collision (pressure) broadening

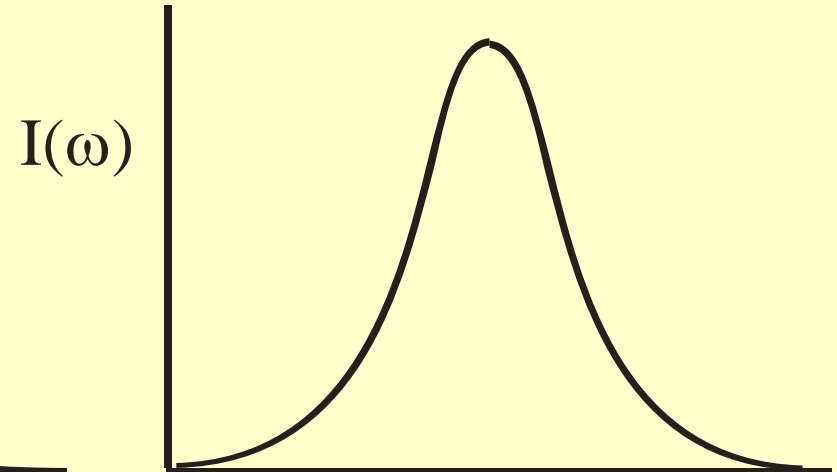
Number of uncollided atoms



Time, t

Exponential decay

Intensity spectrum

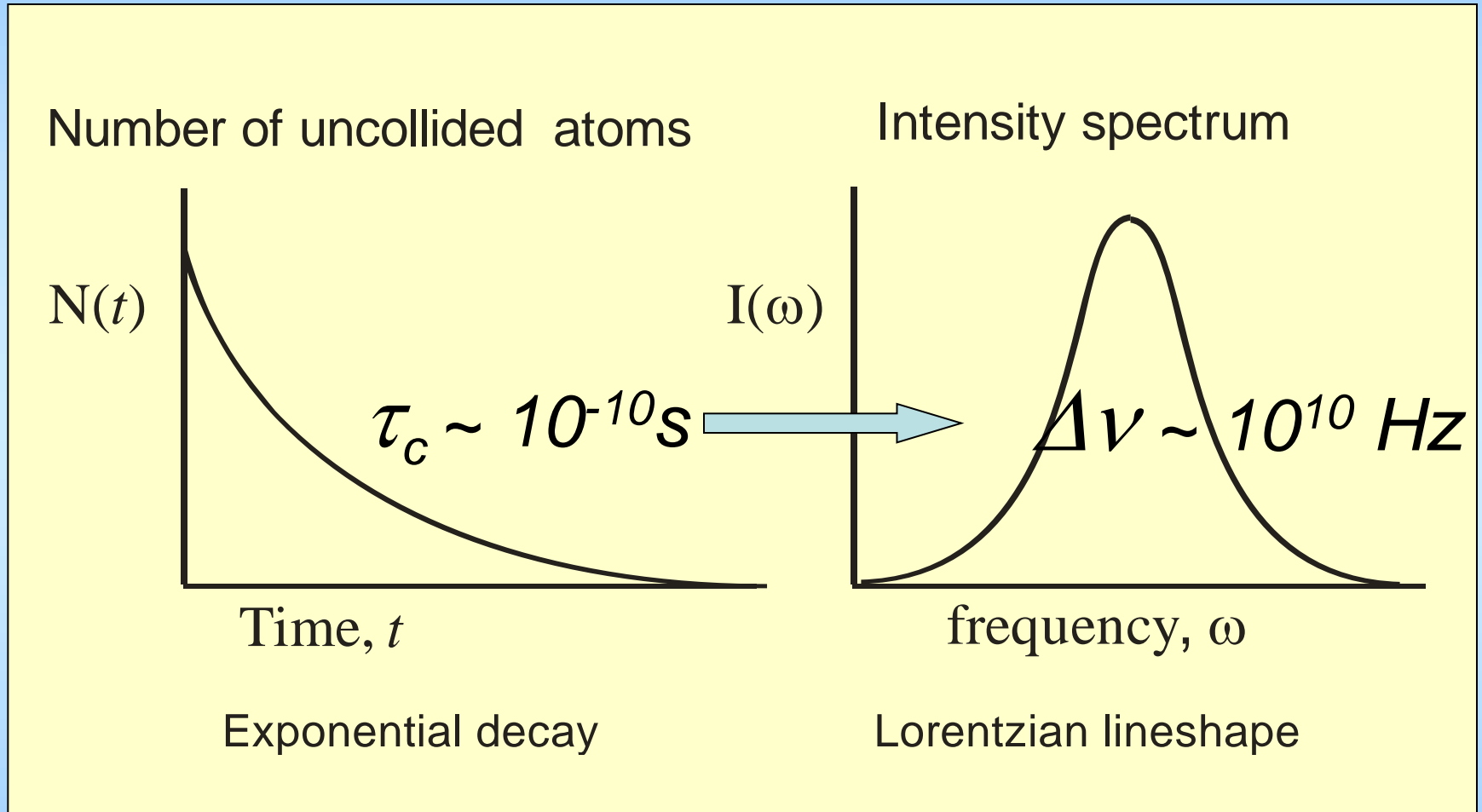


frequency, ω

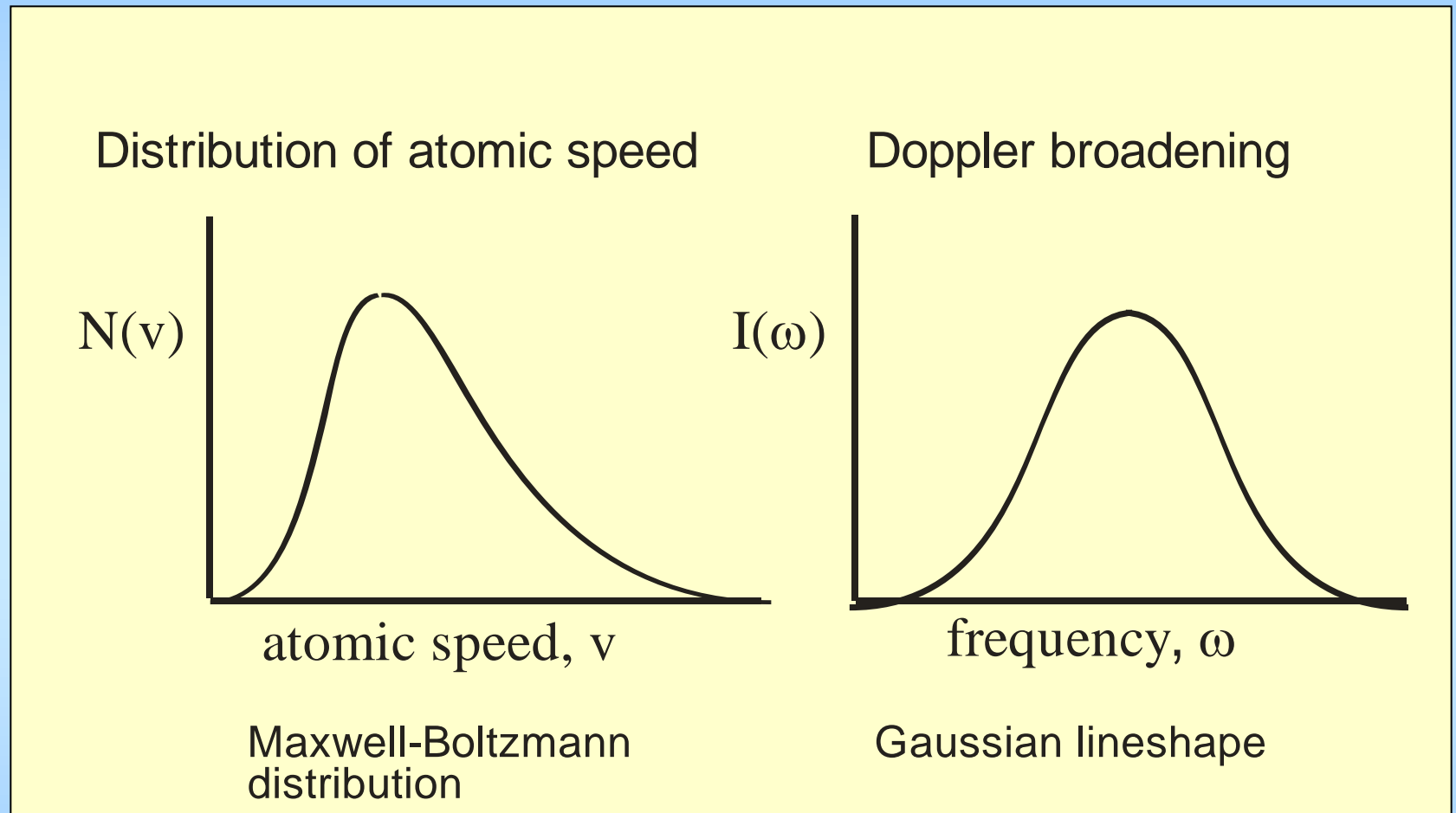
Lorentzian lineshape



Collision (pressure) broadening



Doppler (atomic motion) broadening



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



Atomic orders of magnitude

Atomic energy: $10^{-19} \text{ J} \rightarrow \sim 2 \text{ eV}$

Thermal energy: $\frac{1}{40} \text{ eV}$

Ionization energy, H: 13.6 eV

= Rydberg Constant $109,737 \text{ cm}^{-1}$

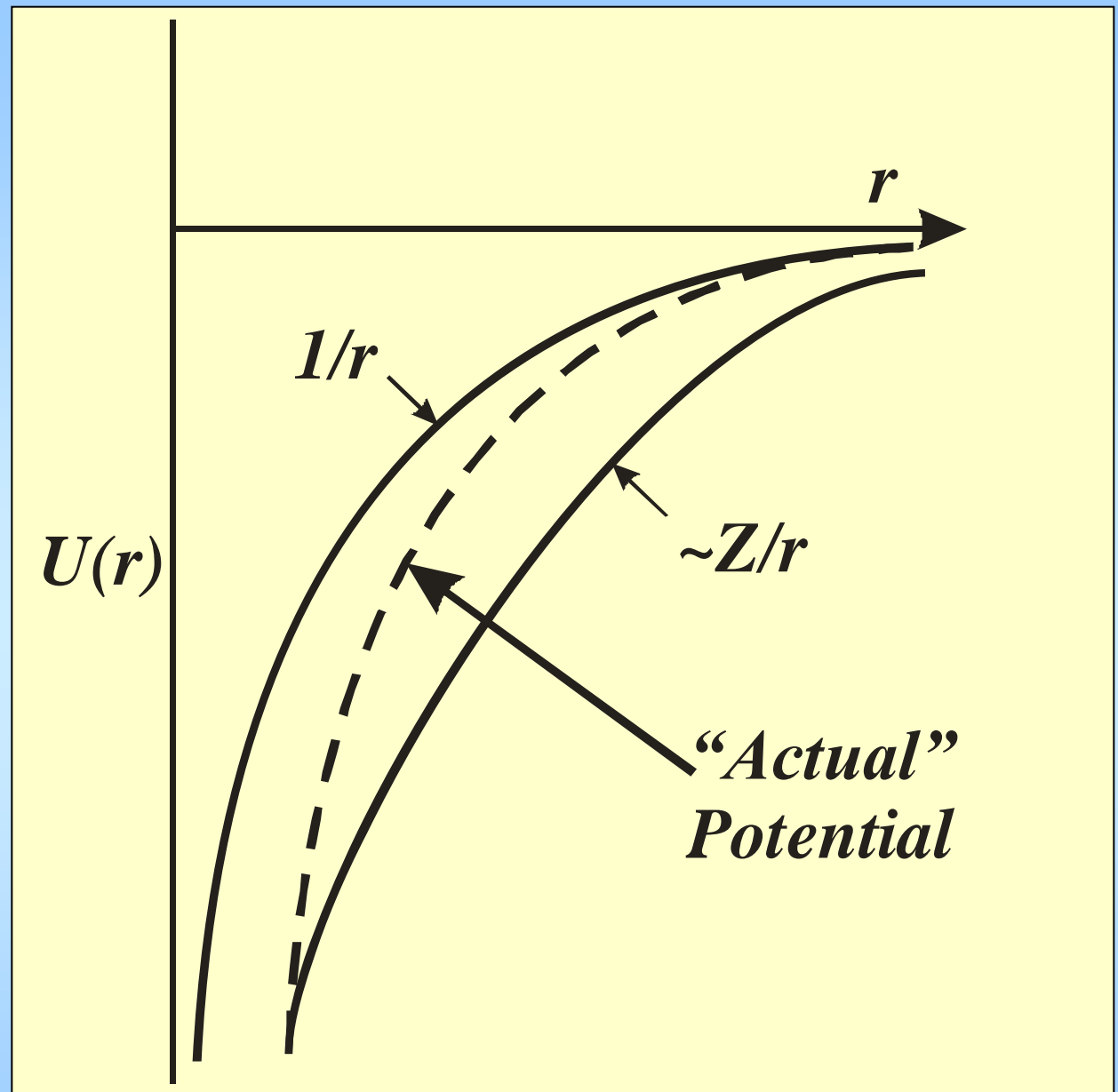
Atomic size, Bohr radius: $5.3 \times 10^{-11} \text{ m}$

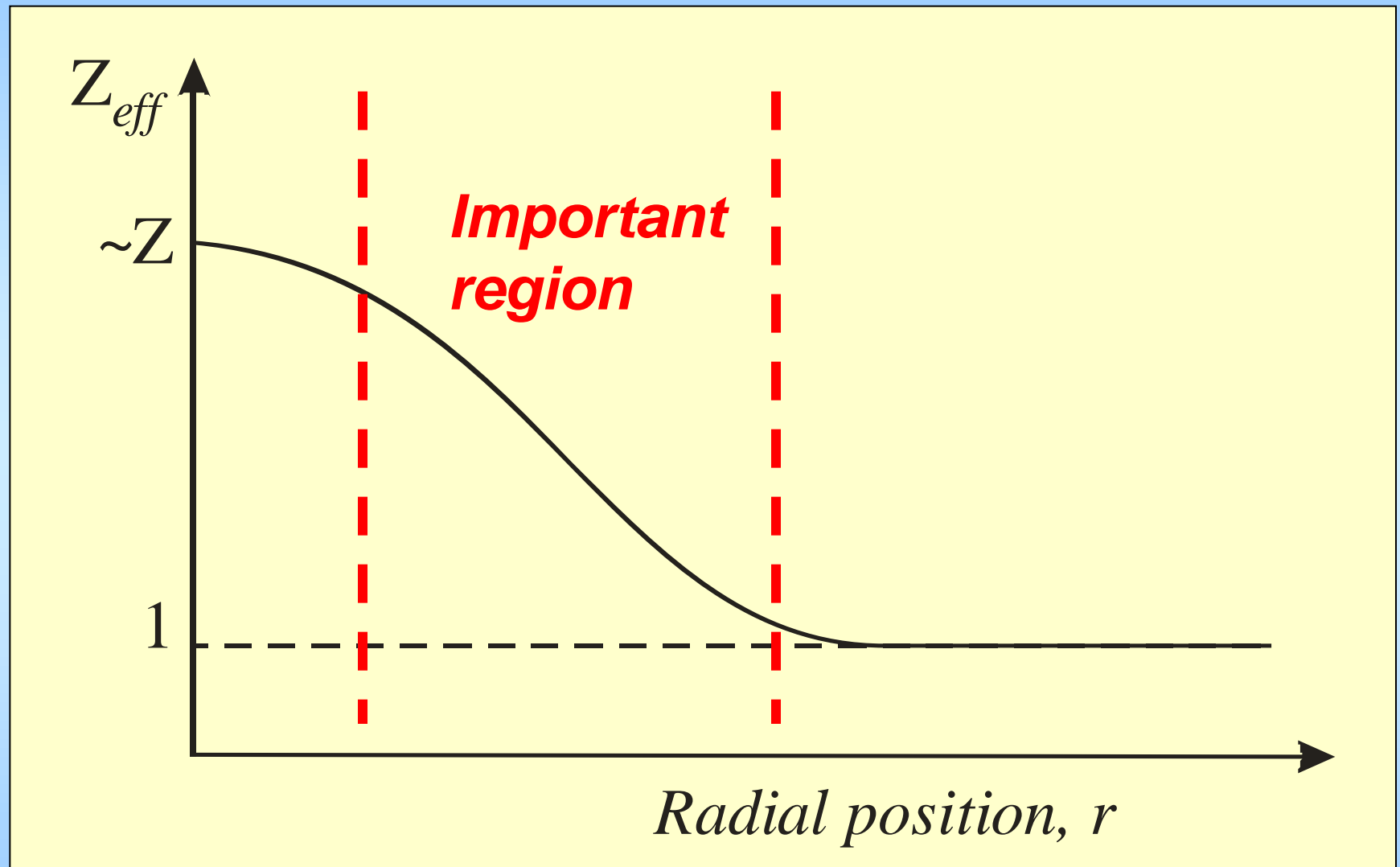
Fine structure constant, $\alpha = v/c$: $1/137$

Bohr magneton, μ_B : $9.27 \times 10^{-24} \text{ JT}^{-1}$



The Central Field





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:

$$\psi = R(r) Y_l^m(\theta, \phi) \chi(m_s)$$

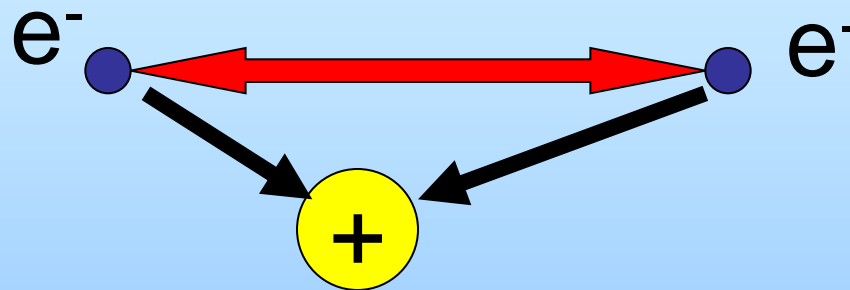
Therefore we seek a potential for multi-electron atom
that allows separation into
individual electron wave-functions of this form



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

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

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

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

\hat{H}_1 = residual electrostatic interaction

Perturbation Theory Approximation:
 $\hat{H}_1 \ll \hat{H}_0$



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*



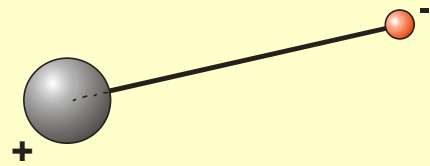
Central Field Approximation:

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

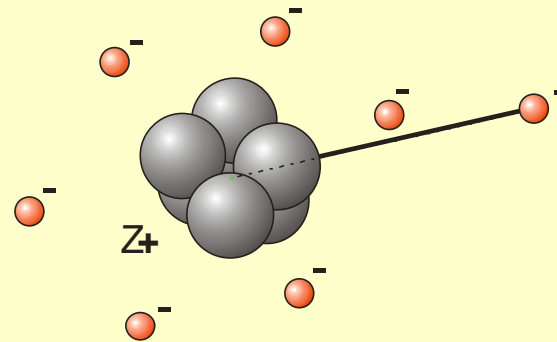
$$\text{where } \hat{H}_0 = \sum_i \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right\}$$

What form does $U(r_i)$ take?

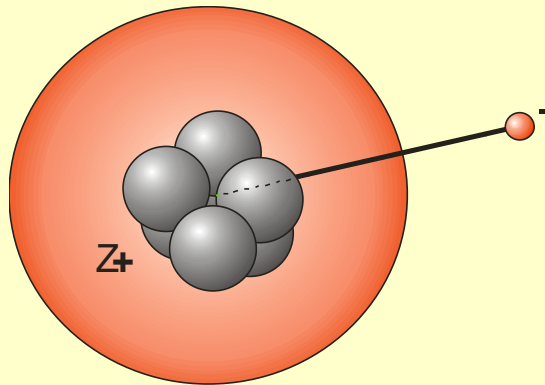




Hydrogen atom

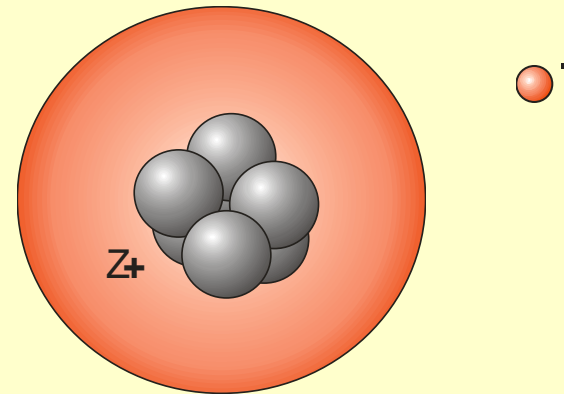


Many-electron atom



Z protons + $(Z - 1)$ electrons

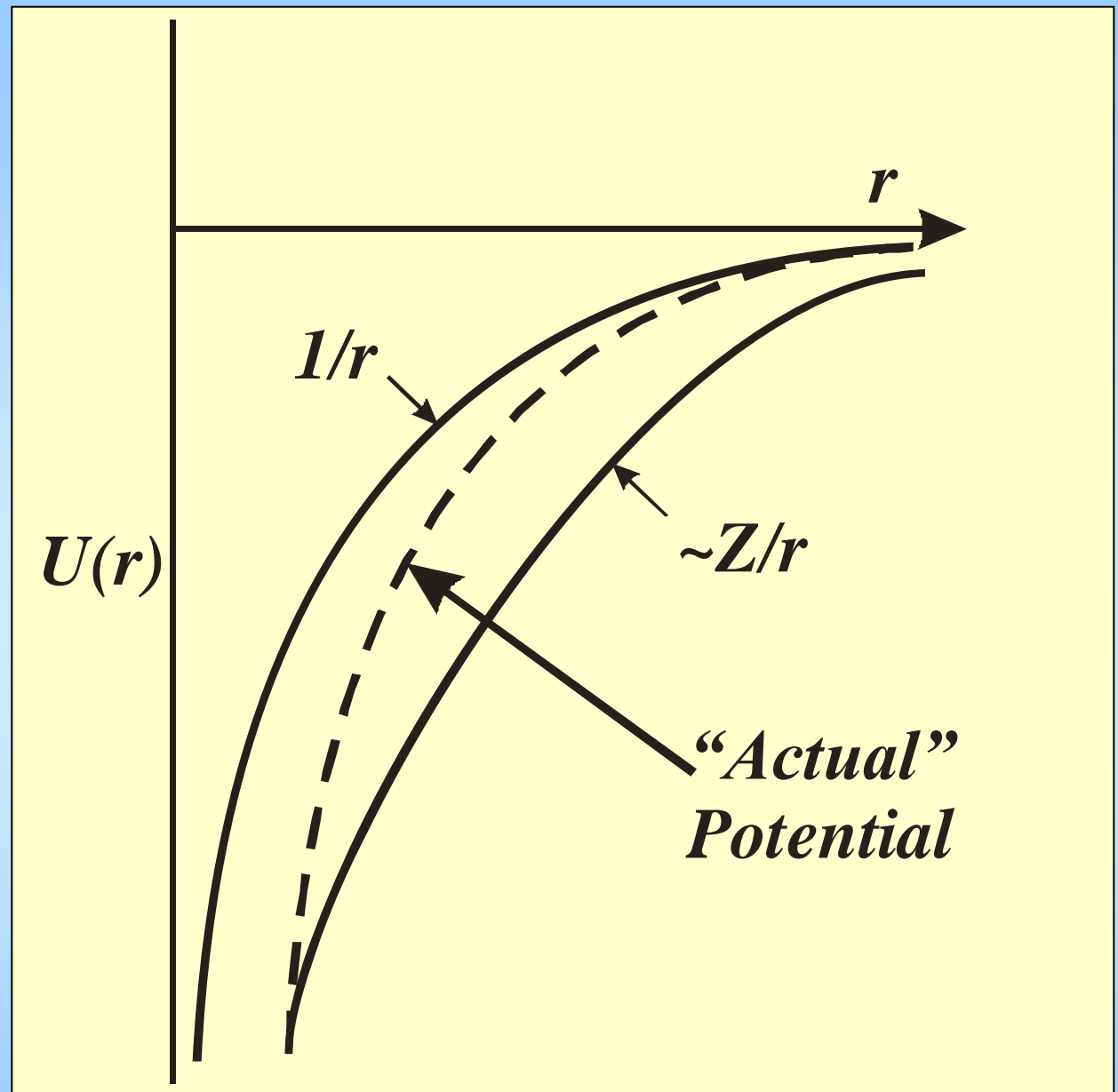
$$U(r) \sim 1/r$$

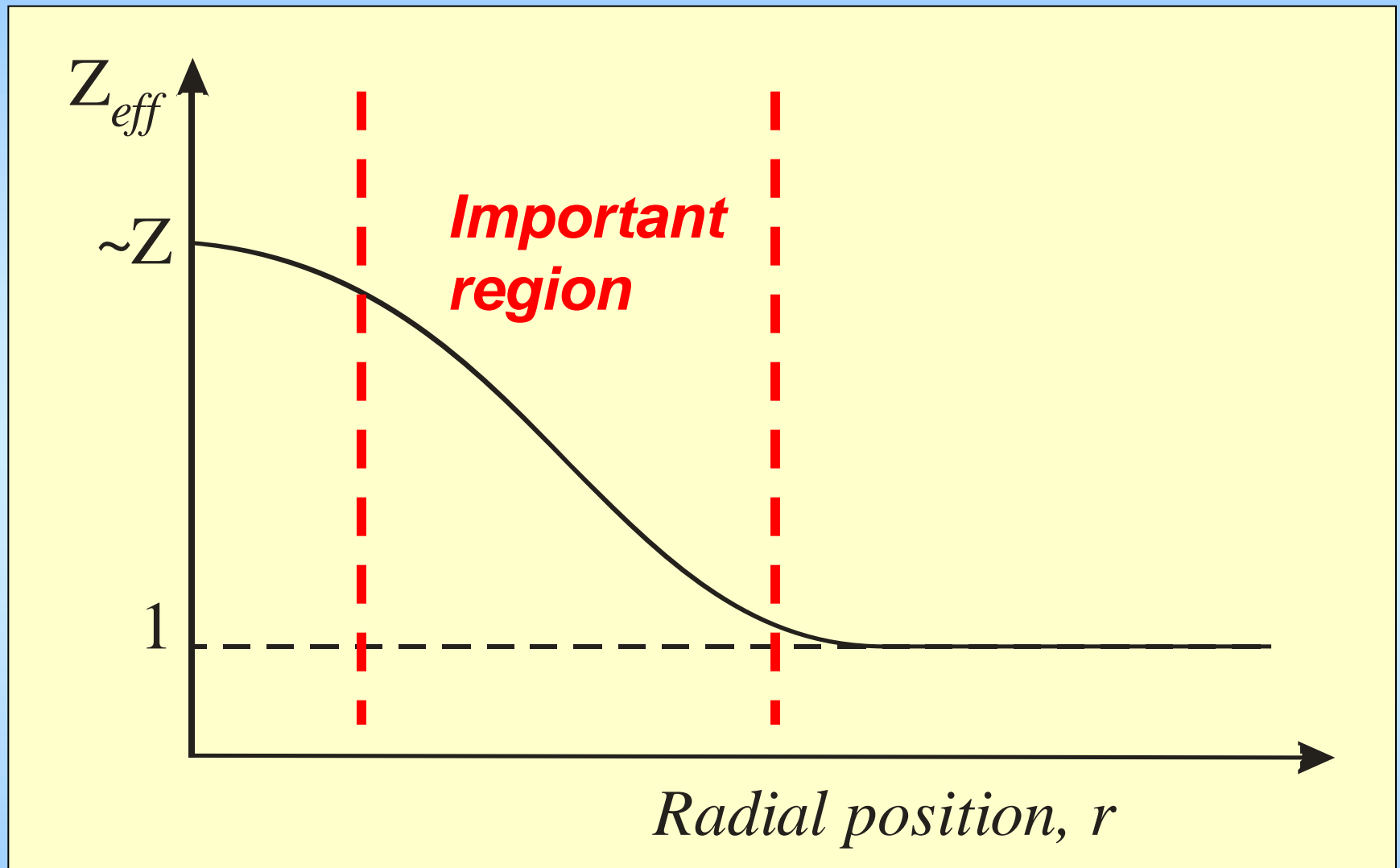


Z protons

$$U(r) \sim Z/r$$

The Central Field





Finding the Central Field

- “Guess” form of $U(r)$
- Solve Schrödinger eqn. \rightarrow 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 $U_c(r) = U(r)$

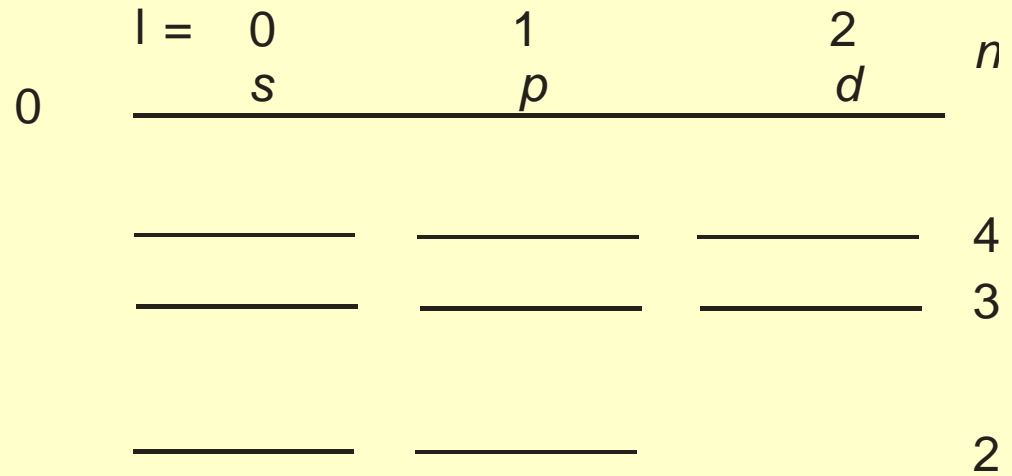


Energy eigenvalues for Hydrogen:

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



H Energy level diagram



Energy

$$E_n = \langle \psi_{n,l,m_l} | \hat{H} | \psi_{n,l,m_l} \rangle$$

$$= -\frac{Z^2 m e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

Note degeneracy in l

-13.6 eV _____

1



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

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

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

$$\hat{l}^2 Y_l^{m_l}(\theta, \phi) = l(l+1)\hbar^2 Y_l^{m_l}(\theta, \phi)$$

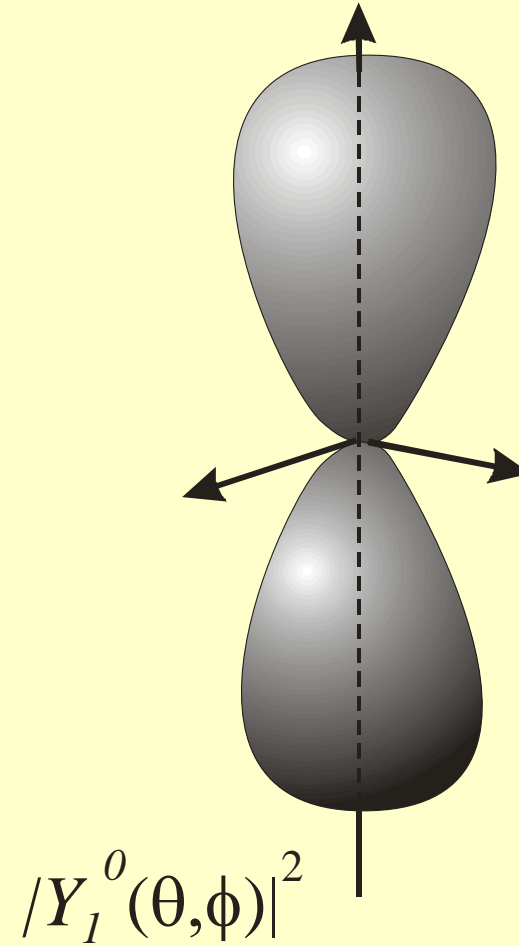
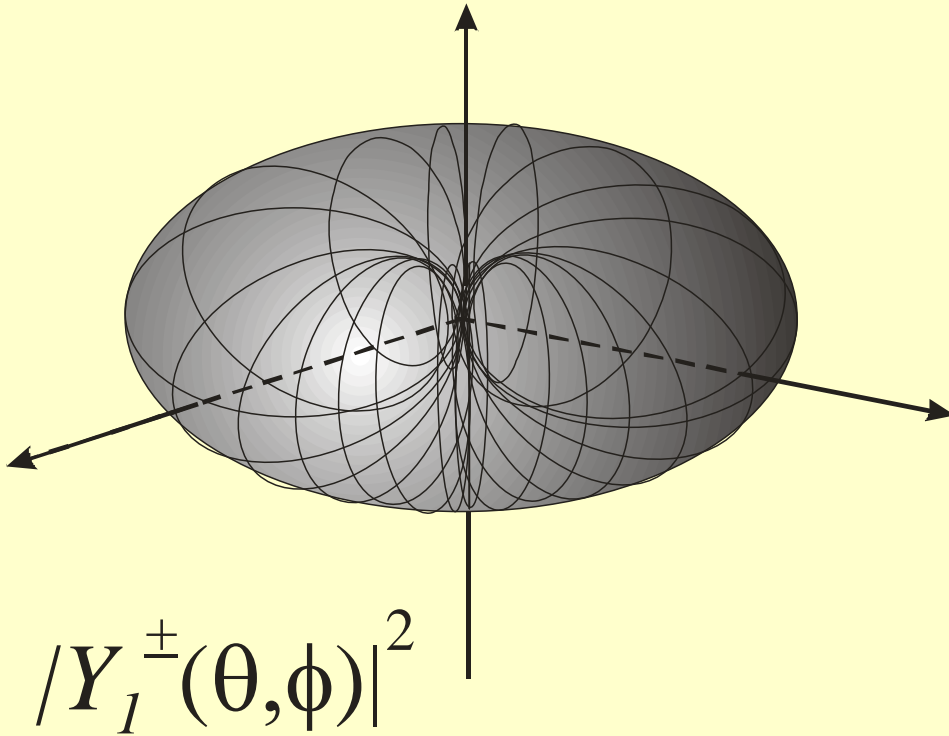
$$\hat{l}_z Y_l^{m_l}(\theta, \phi) = m_l \hbar Y_l^{m_l}(\theta, \phi)$$

Eigenvalues

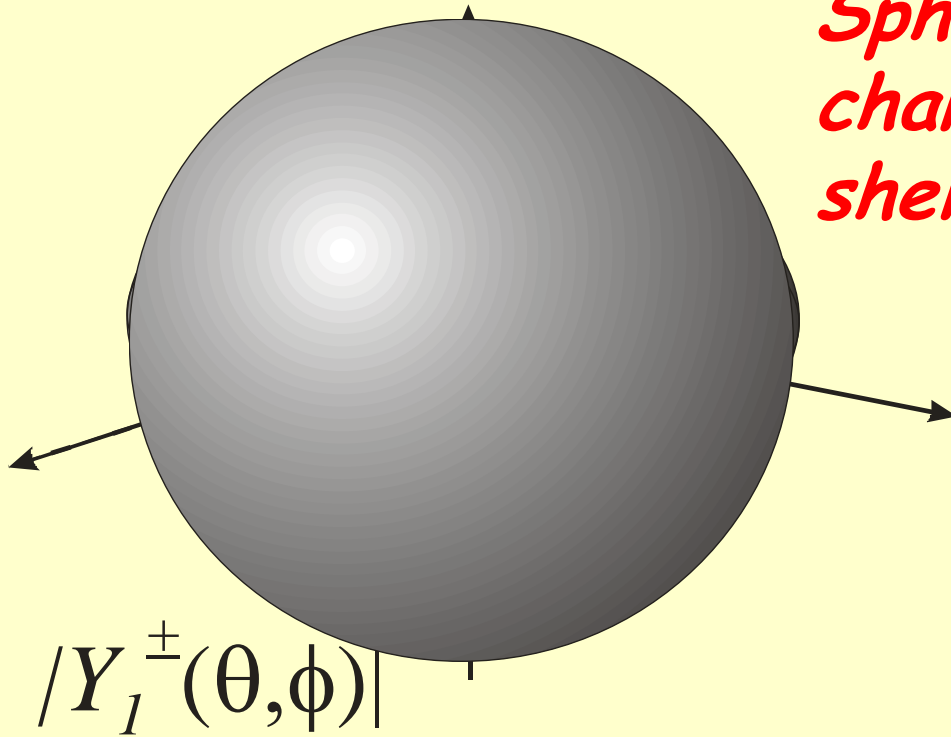
$$l = 0, 1, 2 \dots (n-1) \qquad -l \leq m_l \leq l$$



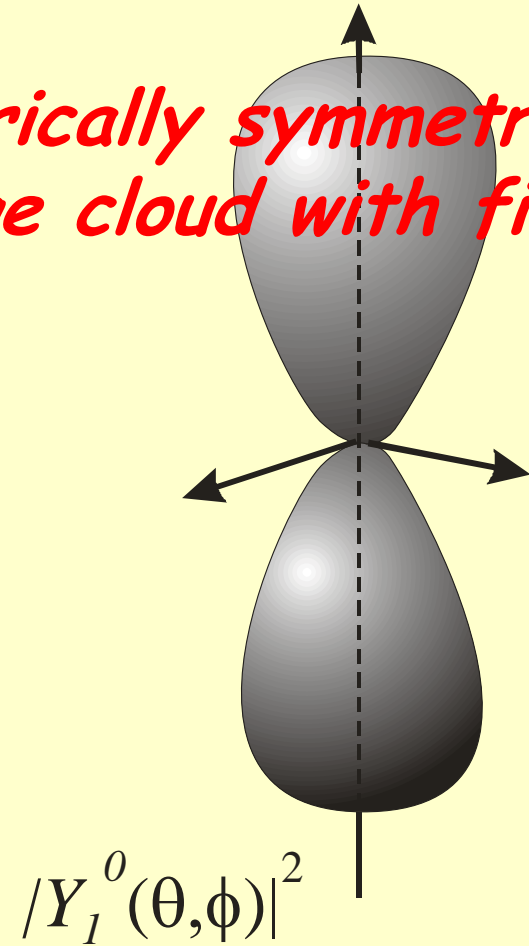
Angular momentum orbitals



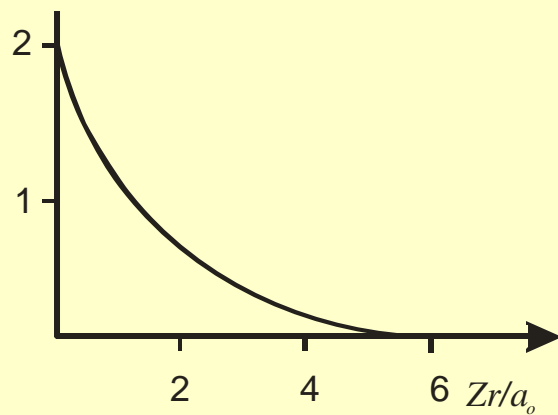
Angular momentum orbitals



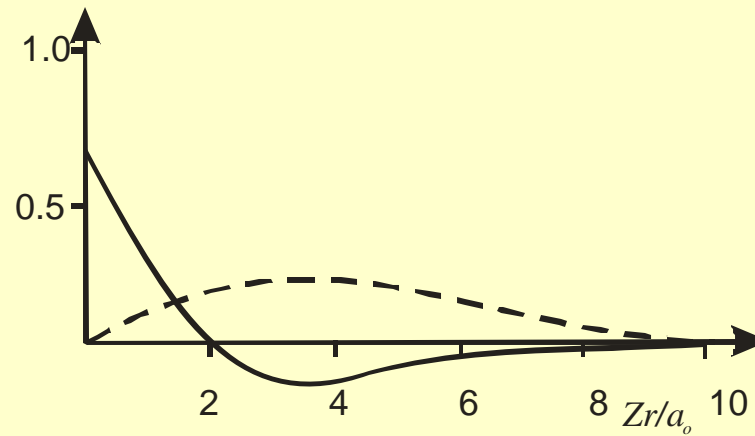
*Spherically symmetric
charge cloud with filled
shell*



Radial wavefunctions

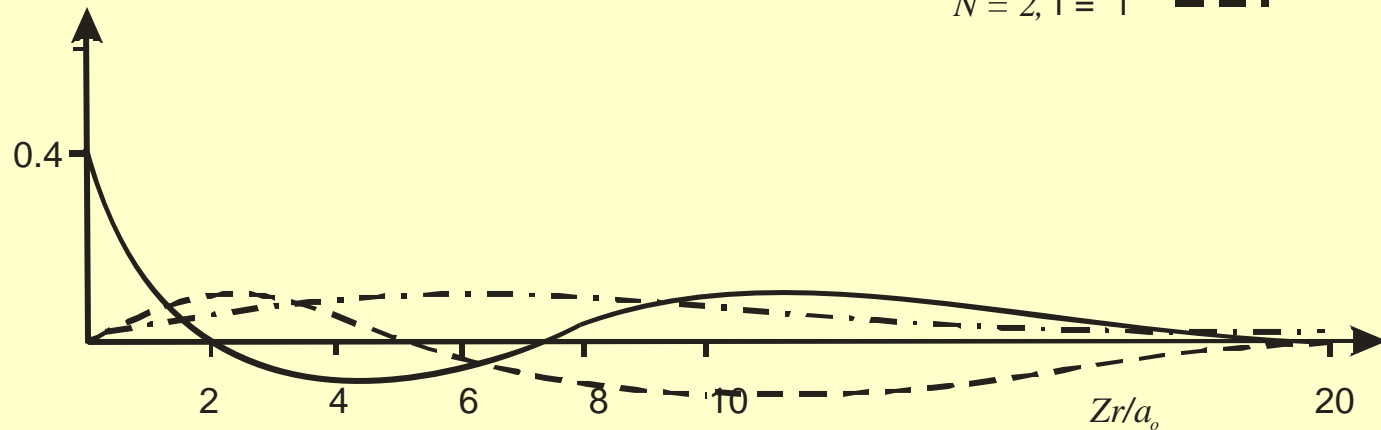


Ground state, $n = 1, l = 0$



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) $\sim n^2$
- $l = 0$ 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

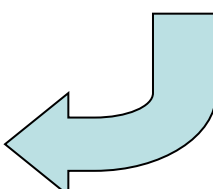


The Periodic Table

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: $4s^2$

The 3d shell now begins to fill

Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 3d 4s^2$

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: $(\dots) 4s^2 4p^6$

Xe: $(\dots\dots) 5s^2 5p^6$

Rn: $(\dots\dots\dots) 6s^2 6p^6$



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

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

etc.



H Energy level diagram

Energy:

$$E_n = \langle \psi_{n,l,m_l} | \hat{H} | \psi_{n,l,m_l} \rangle$$

$$= -\frac{Z^2 m e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

$$E_n = -\frac{R}{n^2}$$

	$l = 0$	1	2	n
0	s	p	d	
	_____	_____	_____	4
	_____	_____	_____	3
	_____	_____		2

Energy

Note degeneracy in l

-13.6 eV _____

1



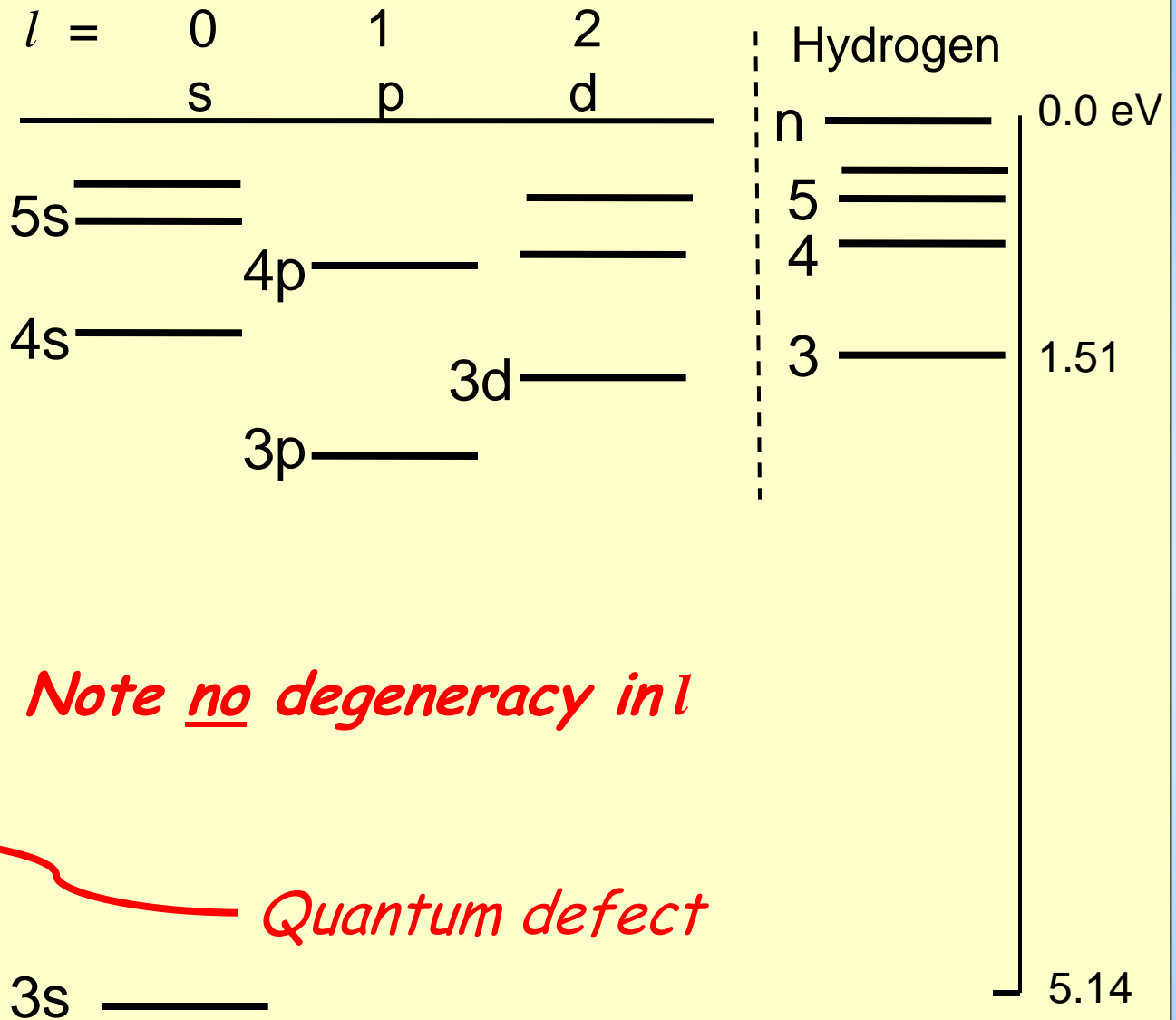
Na Energy level diagram

Energy:

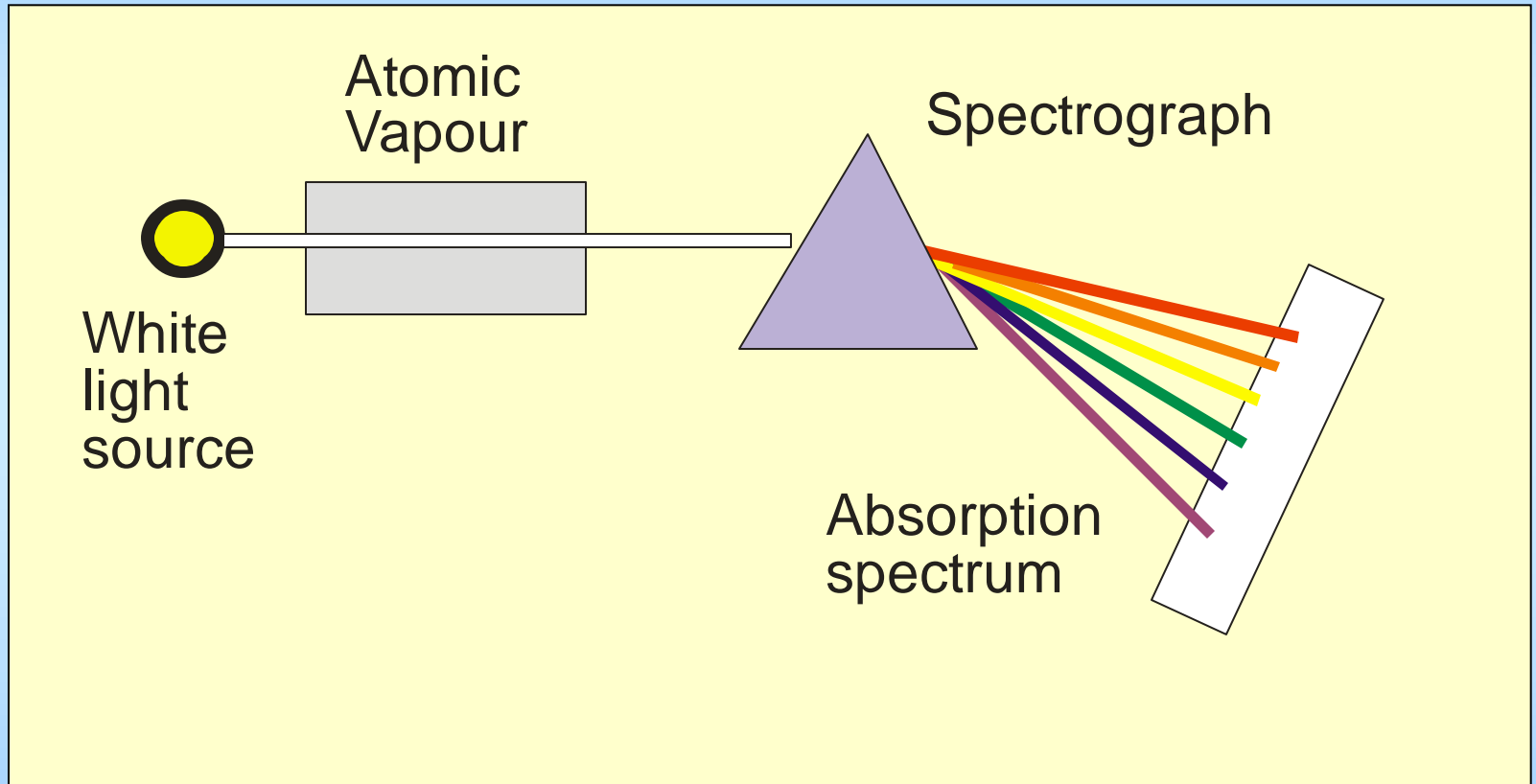
$$E_n = \frac{R}{n^{*2}}$$

$$n^* = n - \delta_l$$

Quantum defect



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: $\bar{\nu} = 1/\lambda$

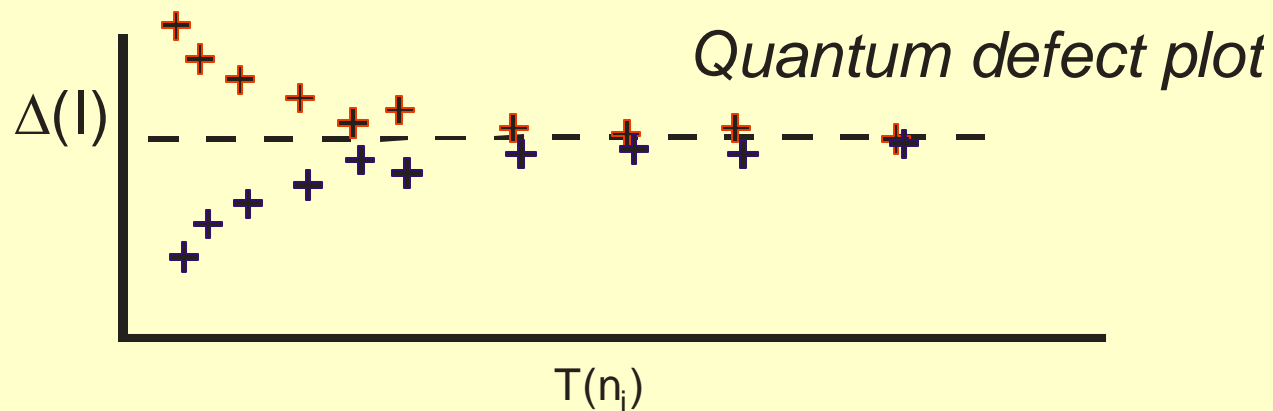
3. "Guess" ionization potential, $T(n_0)$ i.e. Series Limit

4. Calculate $T(n_i)$:

$$\bar{\nu}_i = T(n_0) - T(n_i)$$

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

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

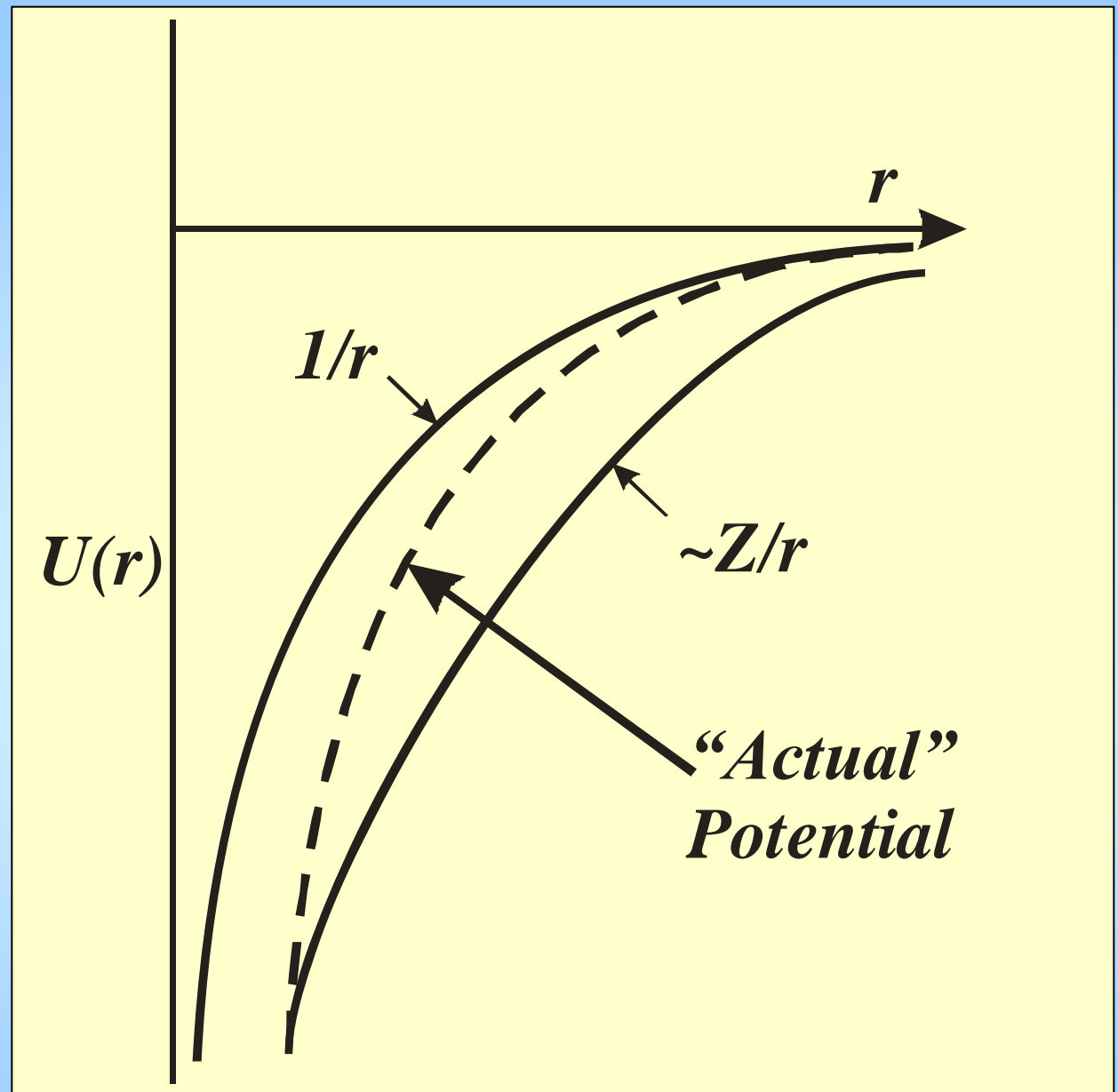


Lecture 3

- 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:

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



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:
 $-\mu \cdot B$ which is proportional to $\underline{s} \cdot \underline{l}$
- 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 $\underline{s} \cdot \underline{l}$ so have different energy:

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

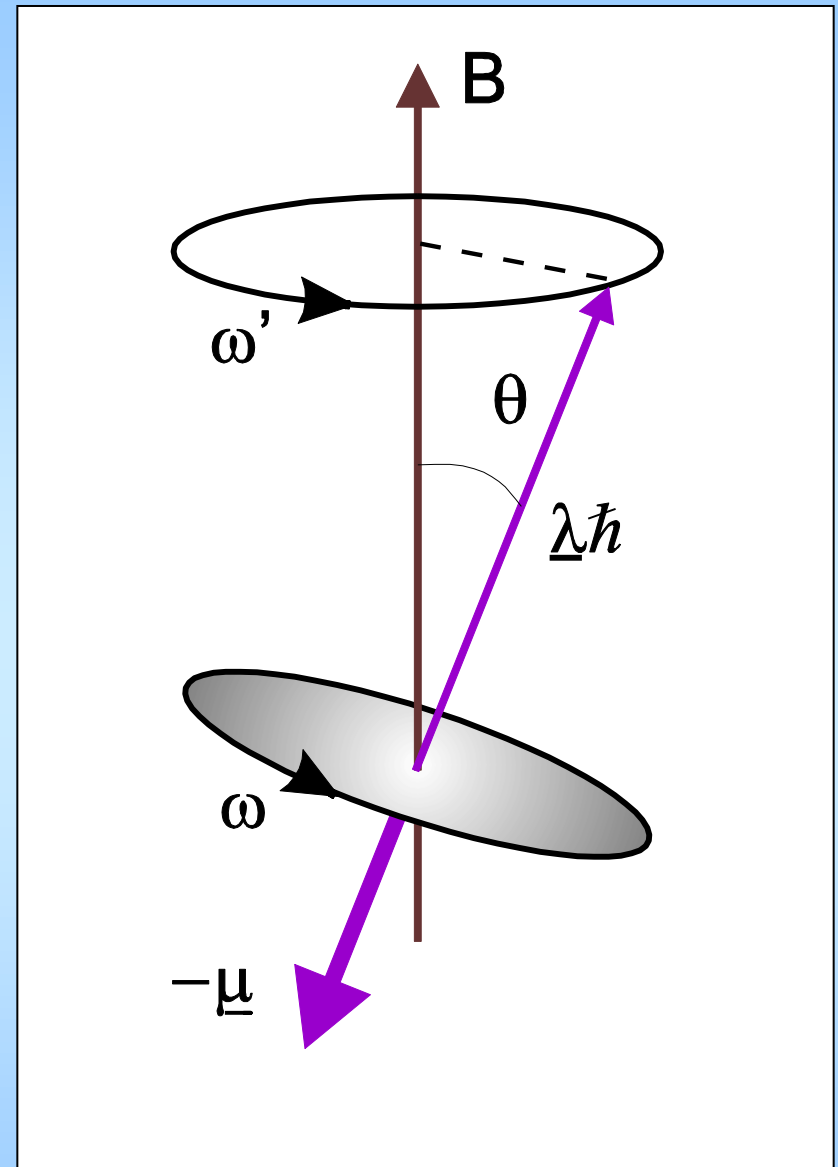


Larmor Precession

Magnetic field \mathbf{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

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



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

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

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

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

How to find $\langle \underline{\hat{s}} \cdot \underline{\hat{l}} \rangle$ 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:

$$\begin{aligned} \phi_1 &= a\psi_1 + b\psi_2 \\ \phi_2 &= b^*\psi_1 - a^*\psi_2 \end{aligned}$$



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

New
eigenvalues:

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



The Vector Model

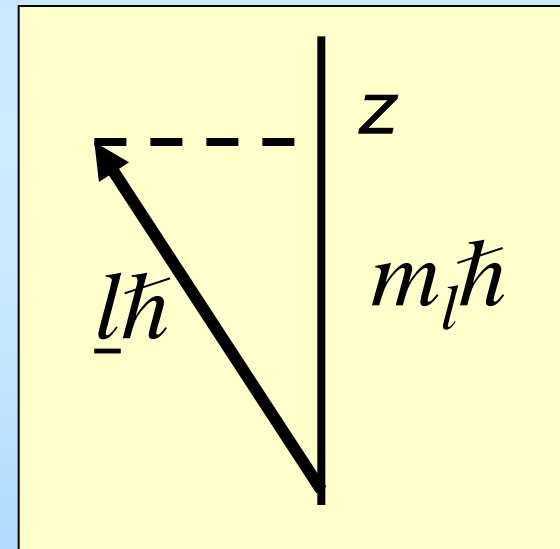
Angular momenta represented by vectors:

\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.

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

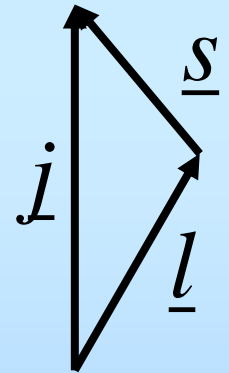
- Angular integral $\langle \underline{s} \cdot \underline{l} \rangle$ needs Degenerate Perturbation Theory

- New basis eigenfunctions:

$$\langle n, l, s, j, m_j |$$

- \underline{j} and \underline{j}_z are constants of the motion

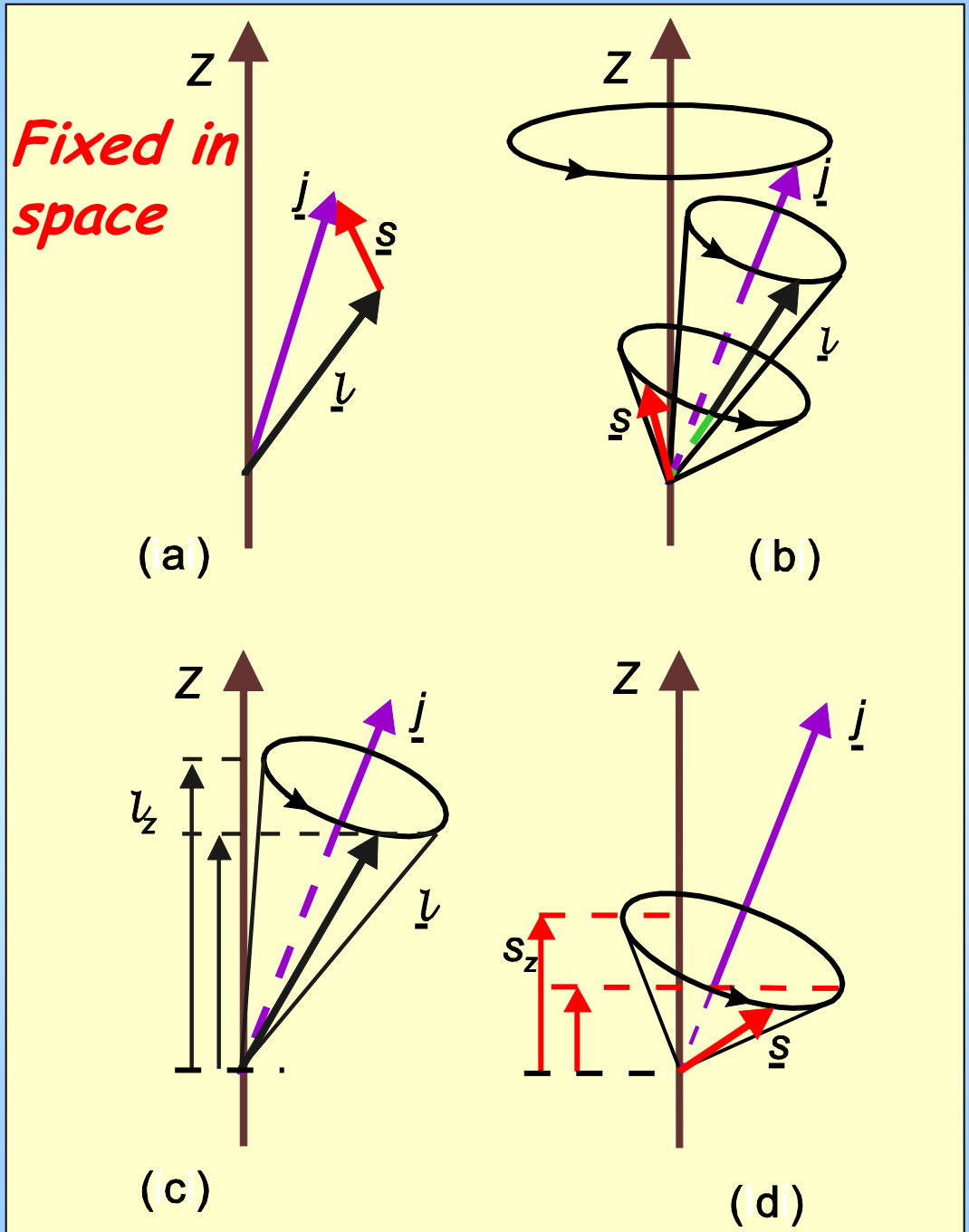
- Vector Model represents angular momenta as vectors
- These vectors can help identify constants of the motion
- These constants of the motion - represented by good quantum numbers



- (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

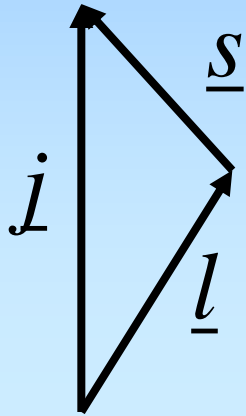
m_l and m_s are not good quantum numbers

Replace by j and m_j



Vector model defines:

$$\hat{j}^2 = (\hat{l} + \hat{s})^2 \quad \hat{j}_z = \hat{l}_z + \hat{s}_z$$



Vector triangle



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

Magnitudes

$$j(j+1)$$

$$l(l+1)$$

$$s(s+1)$$

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

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



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

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

The spin-orbit energy is:

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



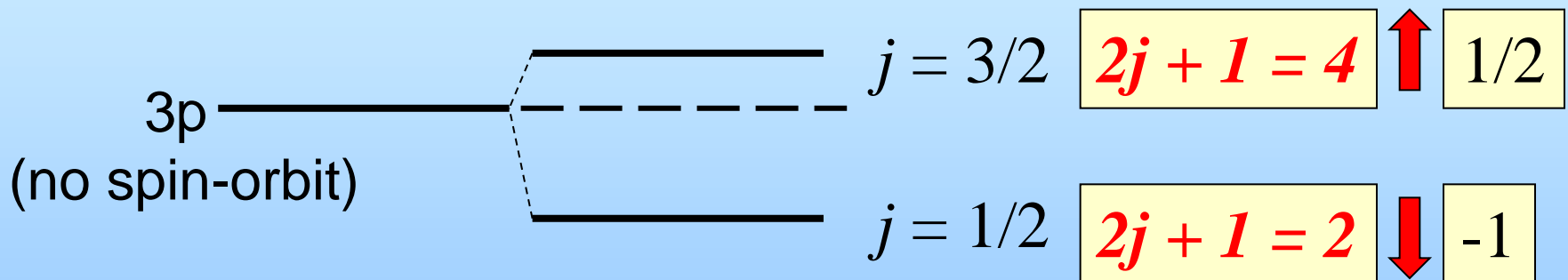
$$\Delta E = \beta_{n,l} \times (1/2) \{j(j+1) - l(l+1) - s(s+1)\}$$

Sodium

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

3p: $n = 3, l = 1, s = 1/2, -1/2, j = 1/2 \text{ or } 3/2$

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

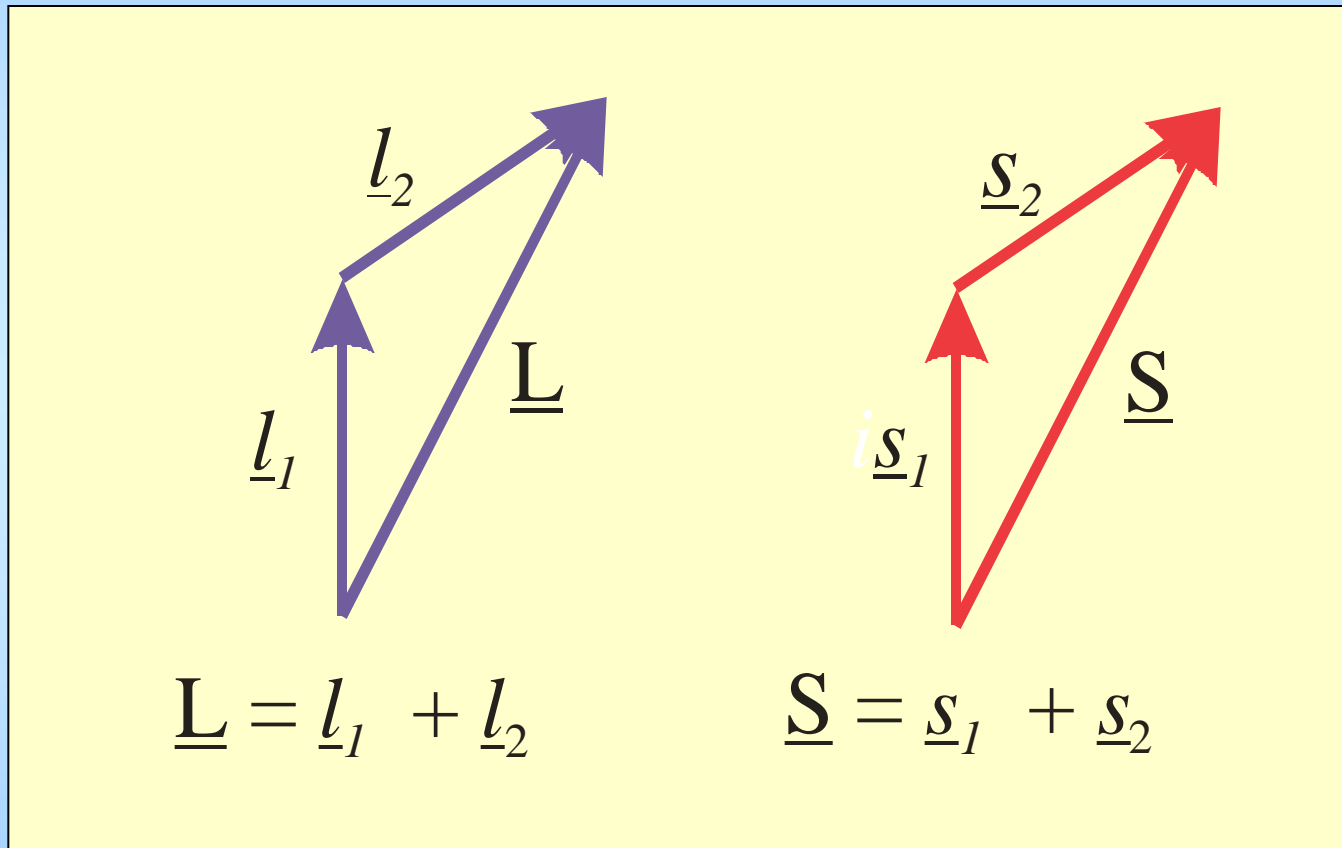


Lecture 4

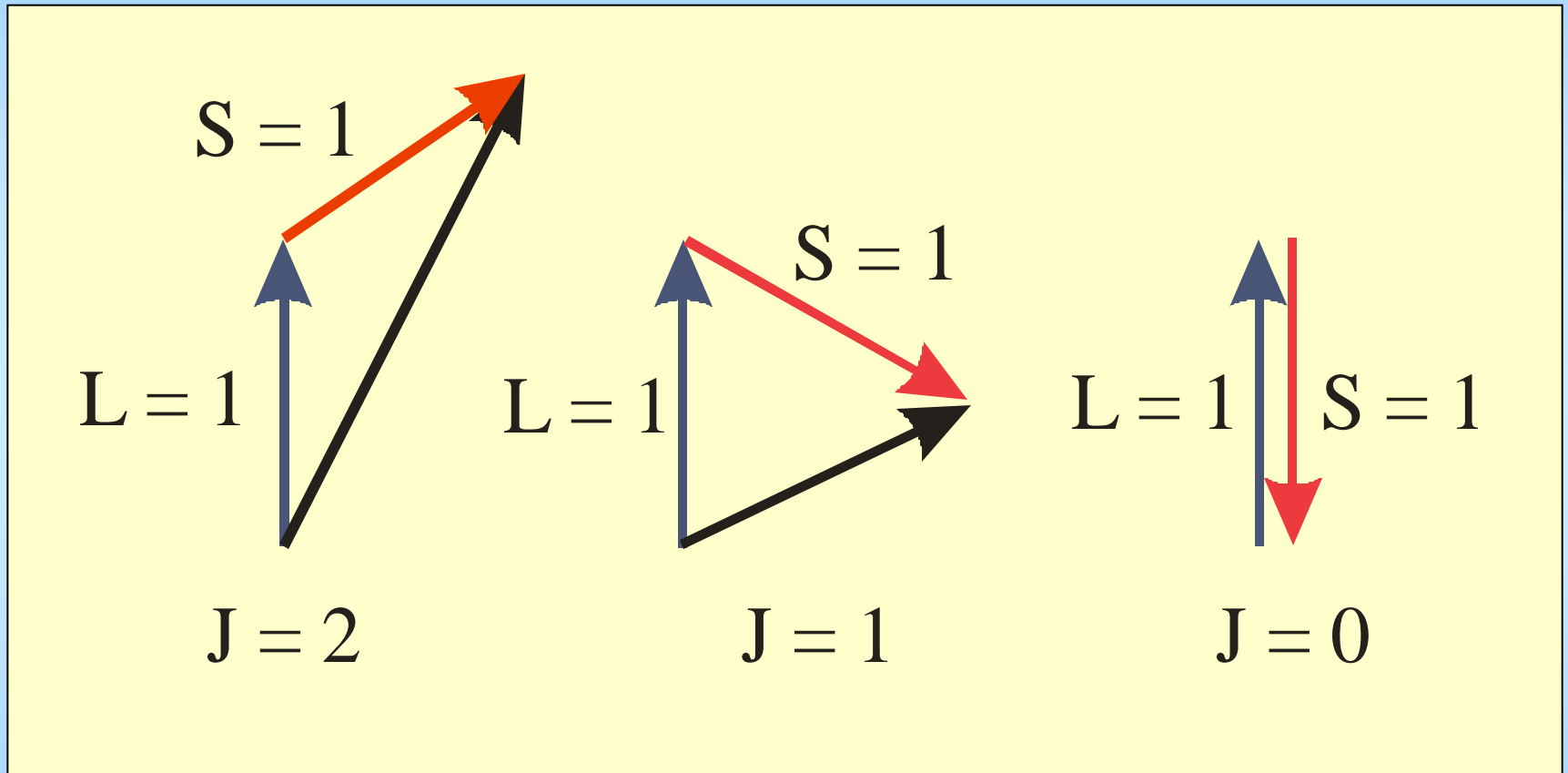
- Two-electron atoms:
the residual electrostatic interaction
- Adding angular momenta: LS-coupling
- Symmetry and indistinguishability
- Orbital effects on electrostatic interaction
- Spin-orbit effects



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

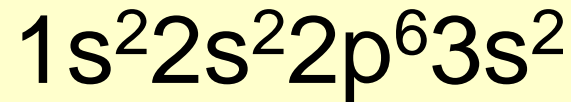


Coupling of \underline{L} and \underline{S} to form \underline{J}

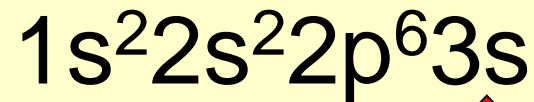


Magnesium: “typical” 2-electron atom

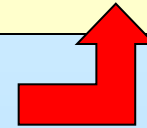
Mg Configuration:



Na Configuration:



“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:

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

?

Degenerate states



Linear combination of zero-order wave-functions

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

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

Off-diagonal matrix elements:

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

$1\uparrow$

$2\uparrow$

$3\uparrow$

$4\uparrow$



Off-diagonal matrix elements:

$$\frac{1}{2} \begin{matrix} \langle \psi_1(3s)\psi_2(4s) + \psi_1(4s)\psi_2(3s) | V | \psi_1(3s)\psi_2(4s) - \psi_1(4s)\psi_2(3s) \rangle \\ 1\uparrow \qquad \qquad \qquad 2\uparrow \qquad \qquad \qquad 3\uparrow \qquad \qquad \qquad 4\uparrow \end{matrix}$$

$$1 \times 3 = \langle \psi_1(3s)\psi_2(4s) | V | \psi_1(3s)\psi_2(4s) \rangle = J$$

$$2 \times 4 = - \langle \psi_1(4s)\psi_2(3s) | V | \psi_1(4s)\psi_2(3s) \rangle = -J$$

$$2 \times 3 = \langle \psi_1(4s)\psi_2(3s) | V | \psi_1(3s)\psi_2(4s) \rangle = K$$

$$1 \times 4 = - \langle \psi_1(3s)\psi_2(4s) | V | \psi_1(4s)\psi_2(3s) \rangle = -K$$

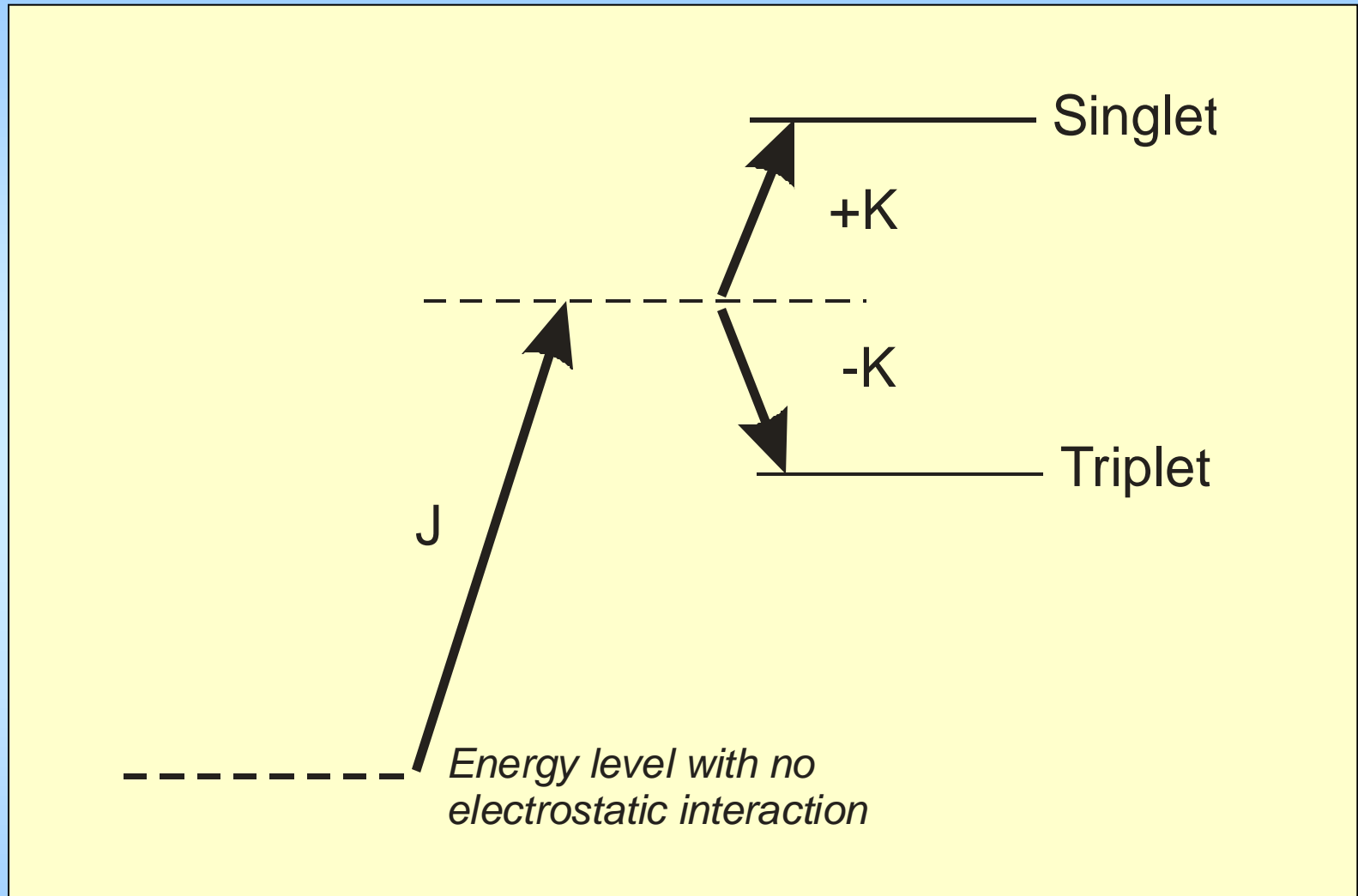
Therefore

$$\langle \phi_1 | V | \phi_2 \rangle = 0$$

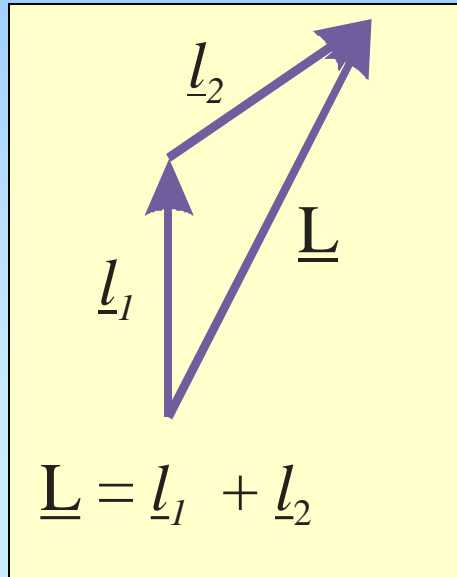
as required!



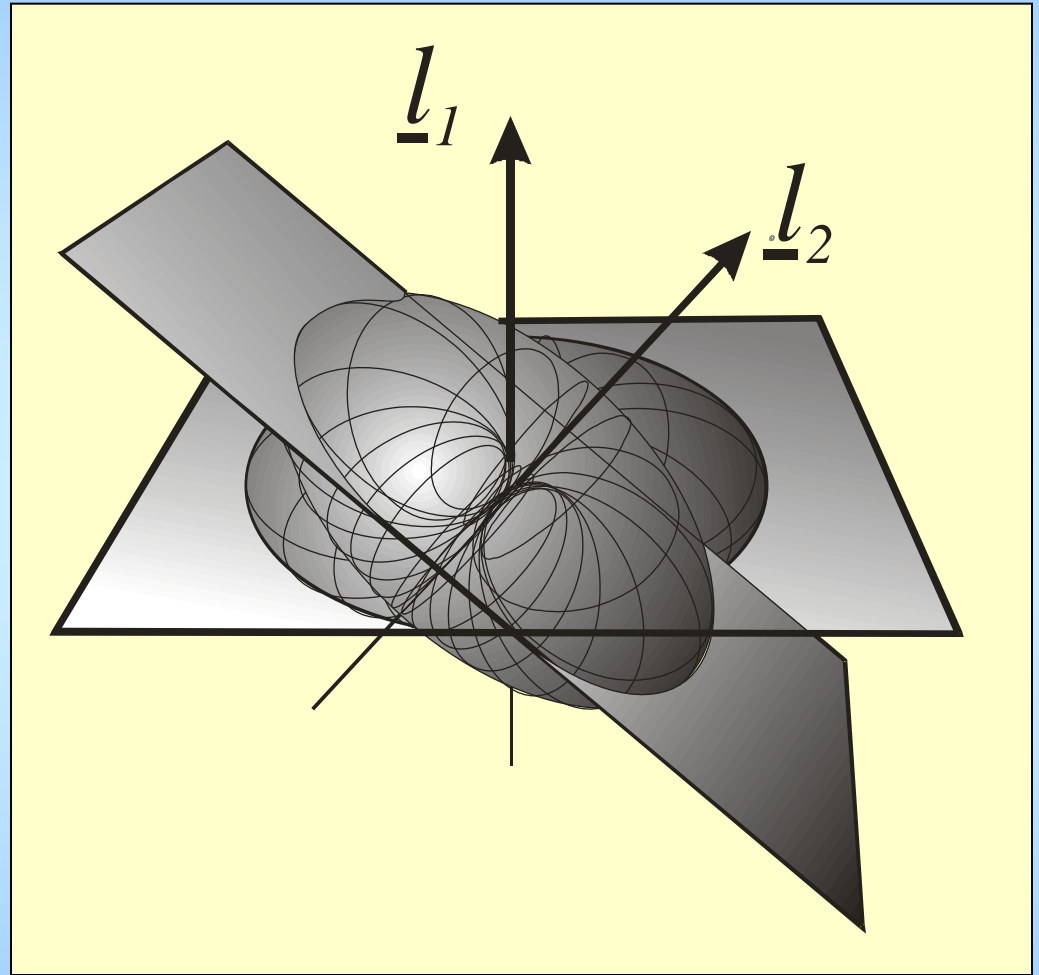
Effect of Direct and Exchange integrals



Orbital orientation effect on electrostatic interaction

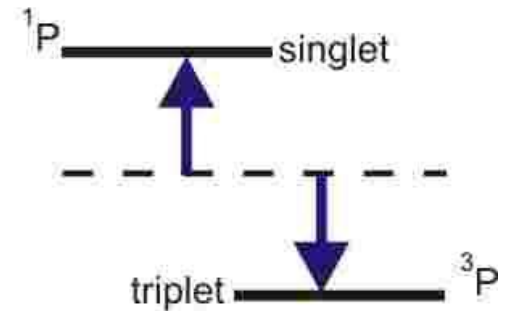


Overlap of electron wavefunctions depends on orientation of orbital angular momentum: so electrostatic interaction depends on \underline{L}

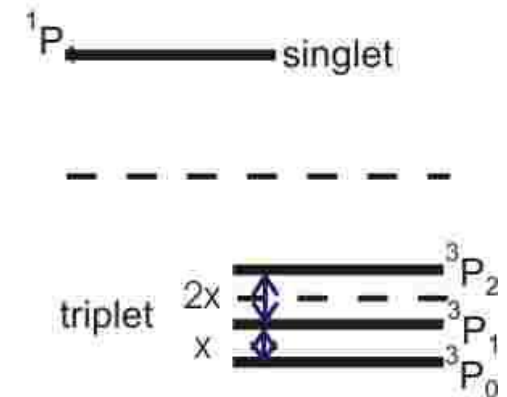
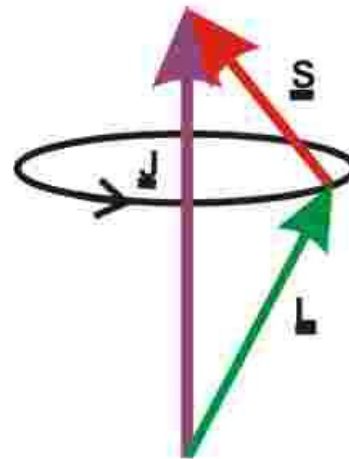


Residual Electrostatic and Spin-Orbit effects in LS-coupling

LS Coupling



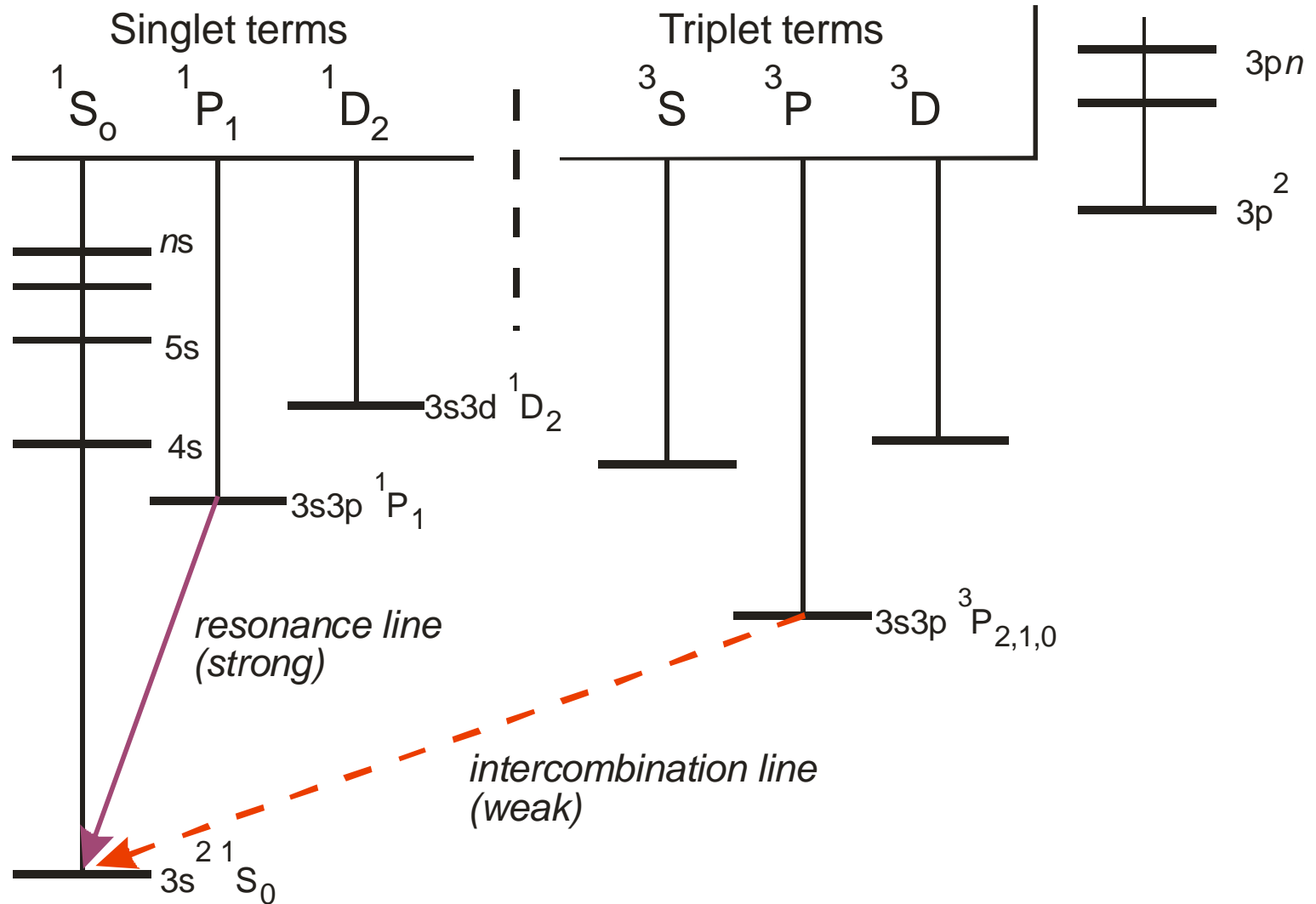
Electrostatic



Electrostatic plus Magnetic (spin-orbit)



Term diagram of Magnesium



The story so far:

Hierarchy of interactions

Central Field configuration, $n_1 l_1 n_2 l_2 \dots$ H_0
Residual Electrostatic \rightarrow Terms, $L = S, P, D \dots$ H_1
Spin-Orbit \rightarrow Level, $J = |L - S| \rightarrow L + S$ H_2

H_3 : Nuclear Effects on atomic energy

$$H_3 \ll H_2 \ll H_1 \ll H_0$$



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

Corrections

Nucleus:

- stationary Nuclear spin \rightarrow 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

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

$$\underline{\mu}_l = - g_l \mu_B \underline{l}$$

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

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

$$g_I \sim 1$$

$$\mu_N = \mu_B \times m_e/m_p \sim \mu_B / 2000$$

Perturbation energy:

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

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

Magnetic field of electrons: Orbital and Spin

Closed shells: zero contribution

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

$l > 0$, smaller contribution - neglect

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

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

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

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

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}

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

Depends on I

Depends on J

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

Nuclear spin interaction energy:

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

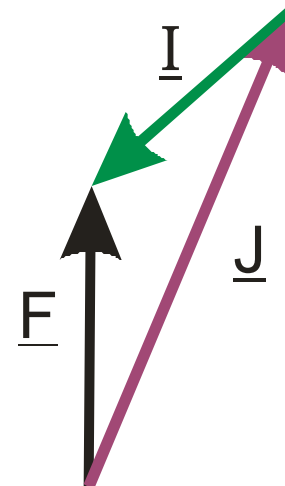
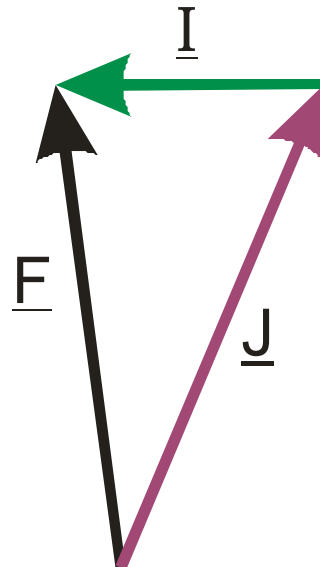
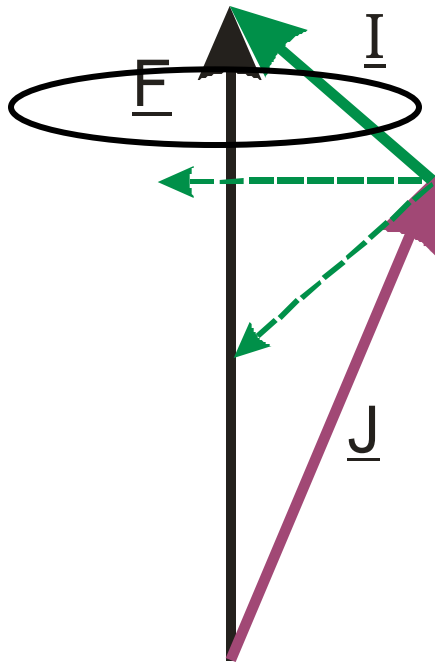
empirical

Expectation value

Vector model of nuclear interaction

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

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



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

Hyperfine structure

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

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

Hfs energy shift:

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

Hfs interval rule:

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

Finding the nuclear spin, I

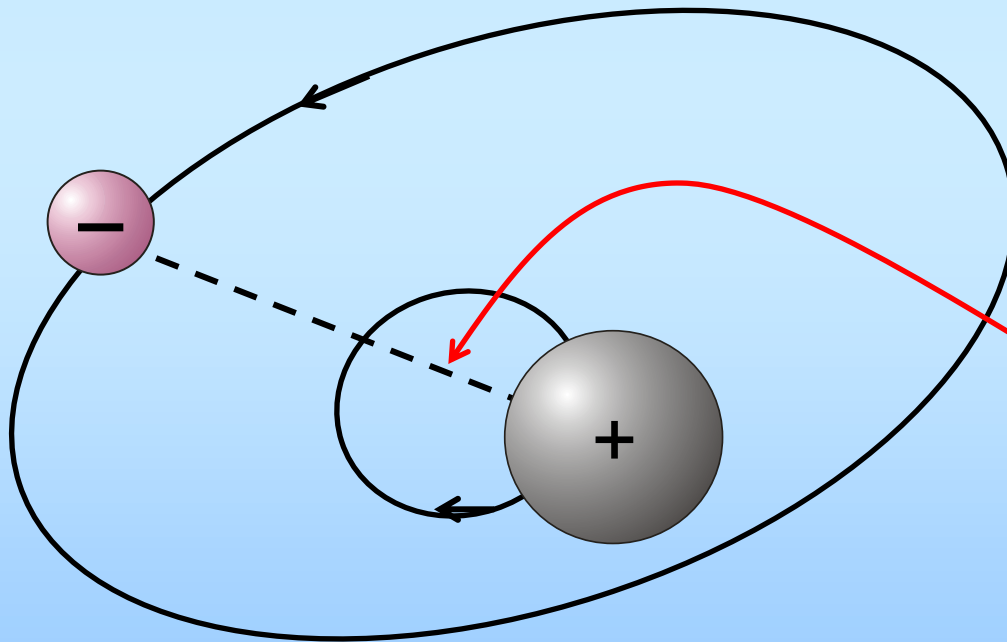
- Interval rule – finds F , then for known $J \rightarrow I$
- Number of spectral lines
 $(2I + 1)$ for $J > I$, $(2J + 1)$ for $I > J$
- Intensity
Depends on statistical weight $(2F + 1)$
finds F , then for known $J \rightarrow I$

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

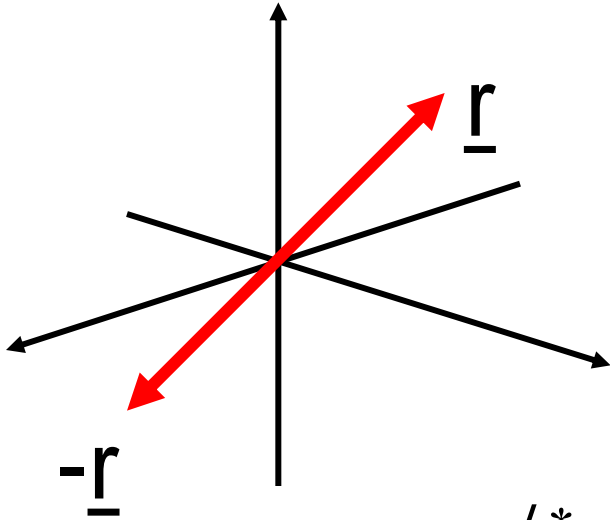


Orbiting about
centre of mass

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



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

Parity $(-1)^l$ must change

$$\Delta l = \underline{\pm} 1$$

Configuration

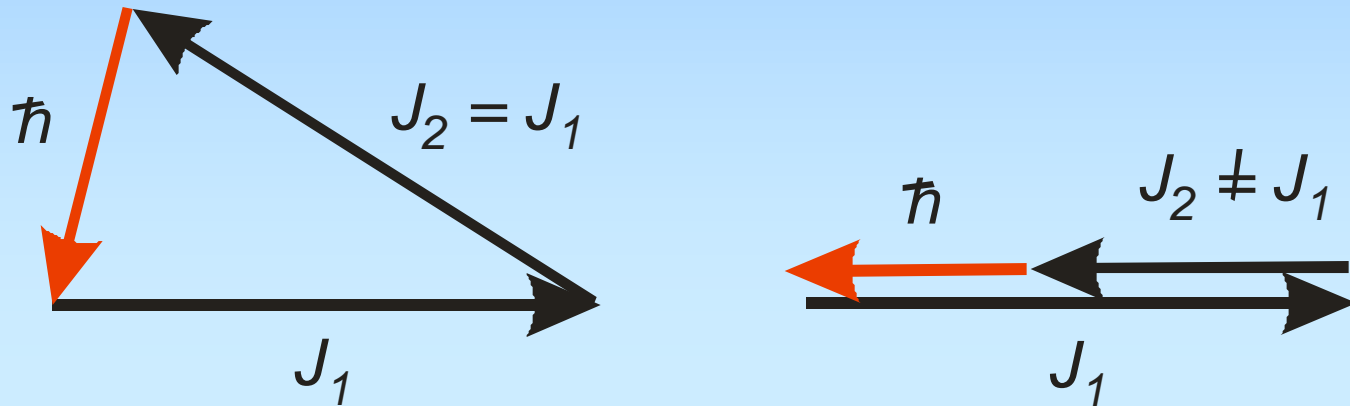
$$\begin{aligned} & \langle \psi_1(1s)\psi_2(2p) | \underline{r}_1 + \underline{r}_2 | \psi_1(3p)\psi_2(3d) \rangle \\ = & \langle \psi_1(1s) | \underline{r}_1 | \psi_1(3p) \rangle \times \langle \psi_2(2p) | \psi_2(3d) \rangle + \langle \psi_2(2p) | \underline{r}_2 | \psi_2(3d) \rangle \times \langle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

Only one electron “jumps”

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

Selection Rules:

Conservation of angular momentum



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

$$\Delta S = 0$$

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

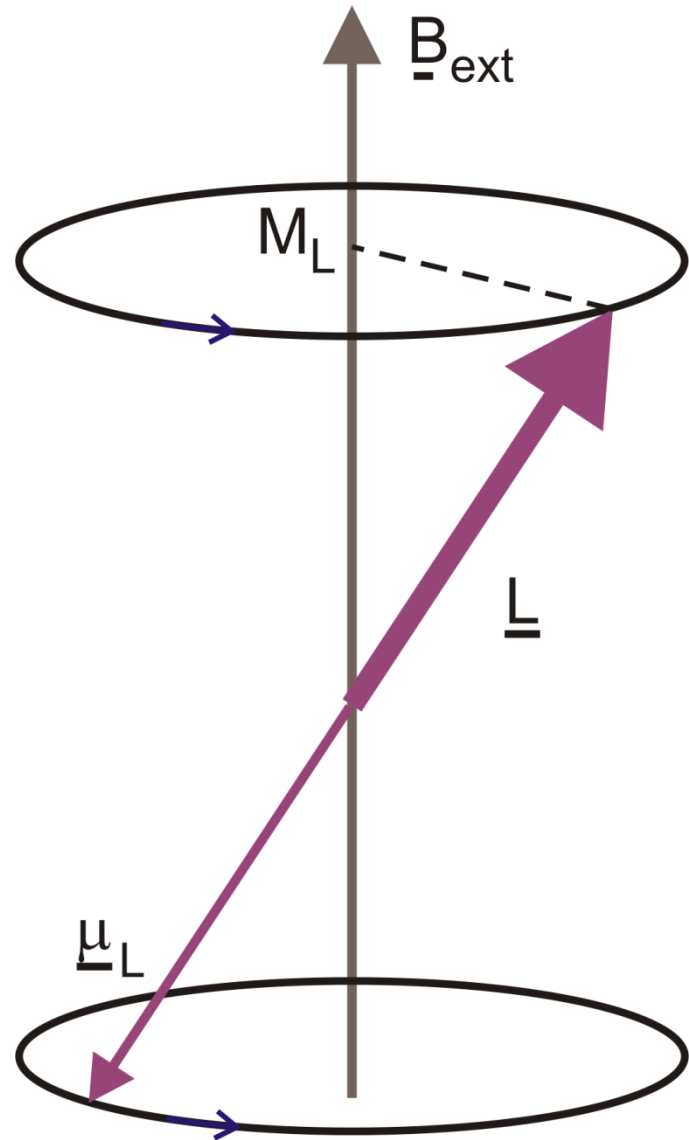
Atoms in magnetic fields



Effect of B-field on an atom with no spin

Interaction energy -
Precession energy:

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

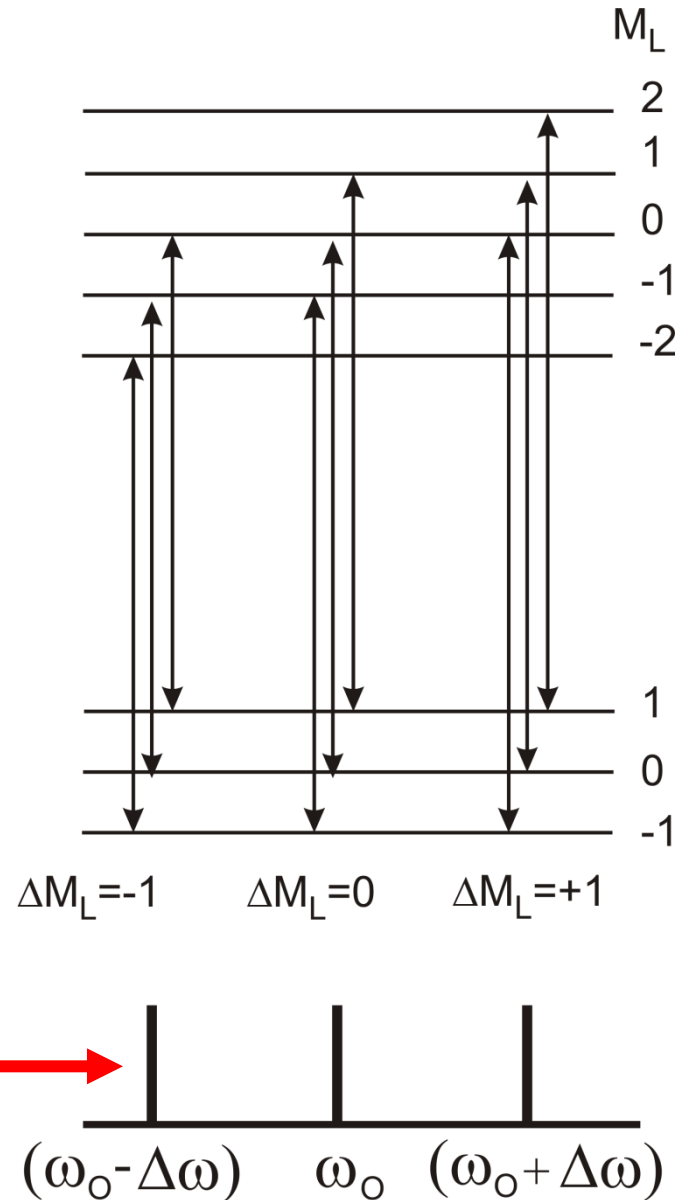


Normal Zeeman Effect

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

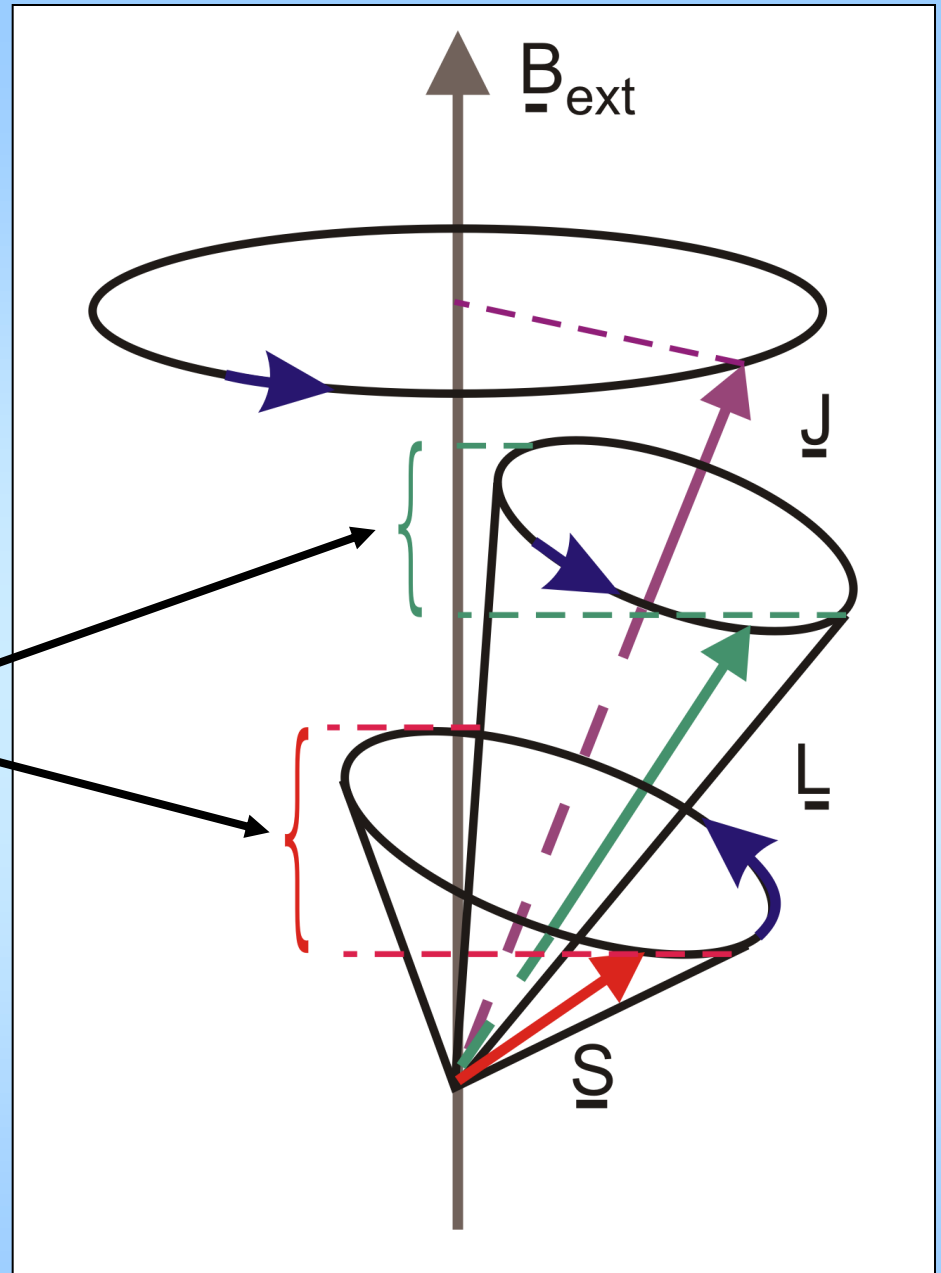
Selection rules on M_L give a spectrum of the normal Lorentz Triplet

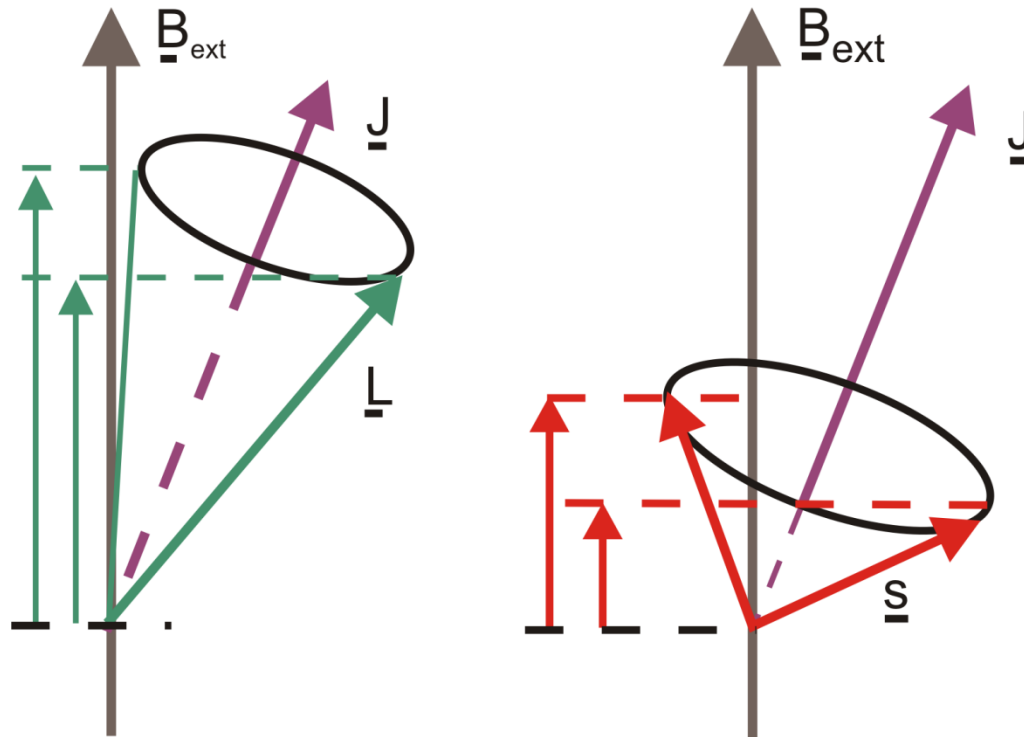
Spectrum



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

*Precession of \underline{L} and \underline{S}
around the resultant \underline{J}
leads to variation of
projections of \underline{L} and \underline{S}
on the field direction*

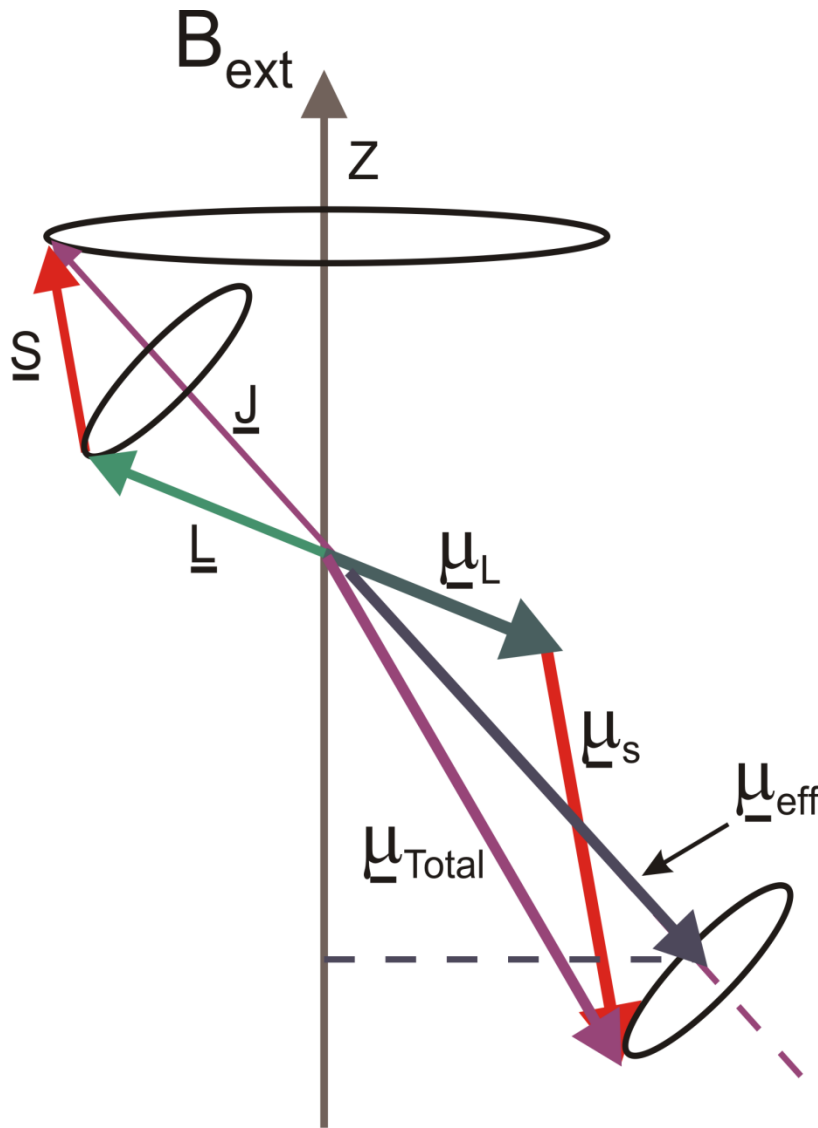




Projections of L and S on z axis vary
owing to precession around J .

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

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



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

Interaction energy

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

Effective magnetic moment

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

Perturbation Theory:
expectation value of energy

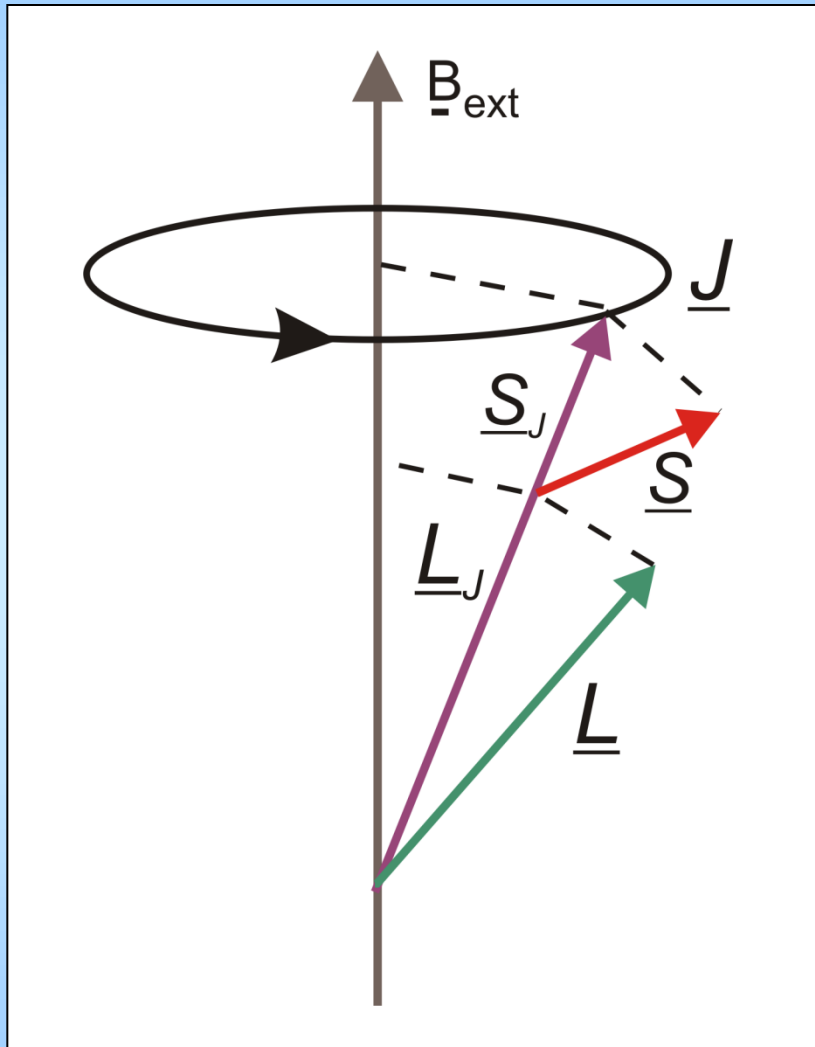
$$\Delta E_{\text{AZ}} = g_J \mu_B \langle \underline{\hat{J}} \cdot \underline{\hat{B}}_{\text{ext}} \rangle$$

Energy shift of M_J level

$$\Delta E_{\text{AZ}} = g_J \mu_B B_{\text{ext}} M_J$$



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

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

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

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

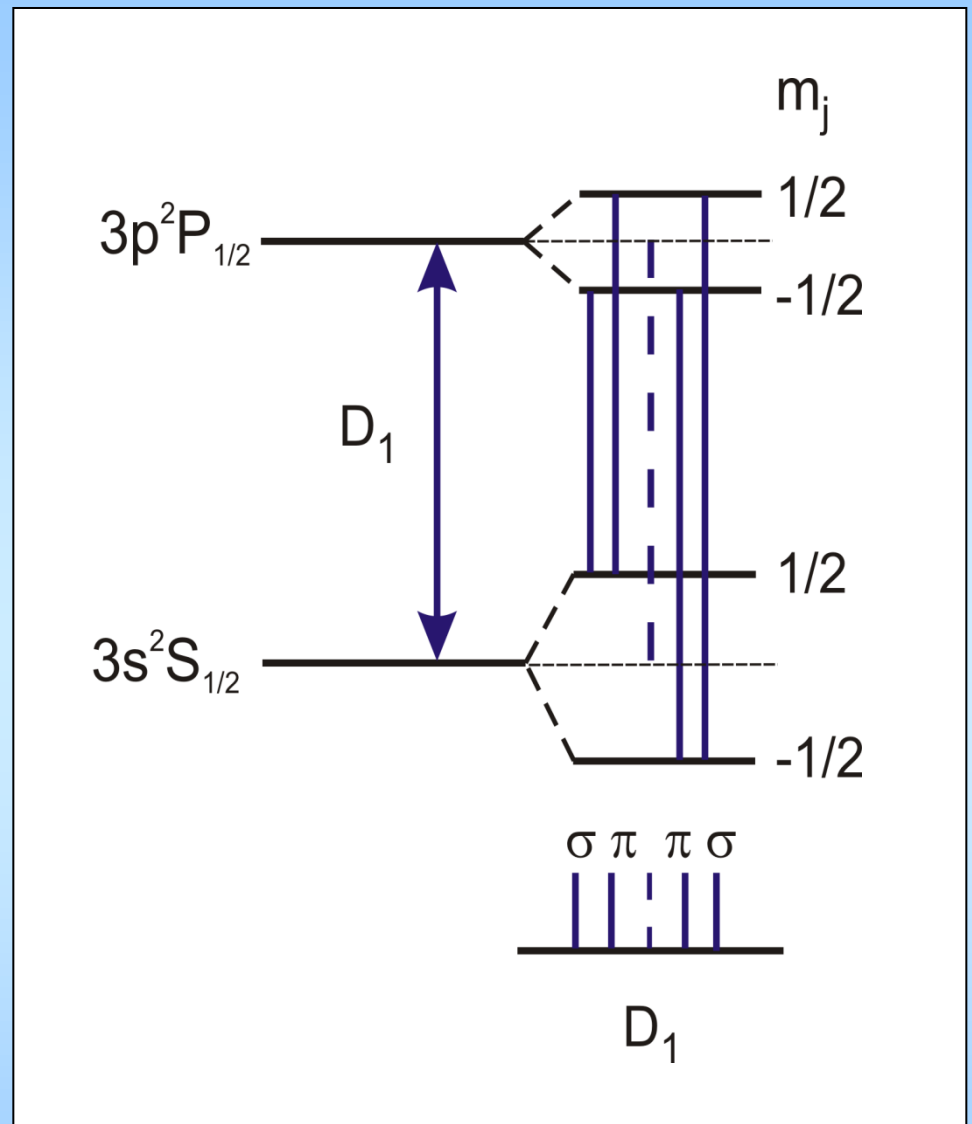
Perturbation Theory result

$$\Delta E_{\text{AZ}} = g_J \mu_B B_{\text{ext}} M_J$$

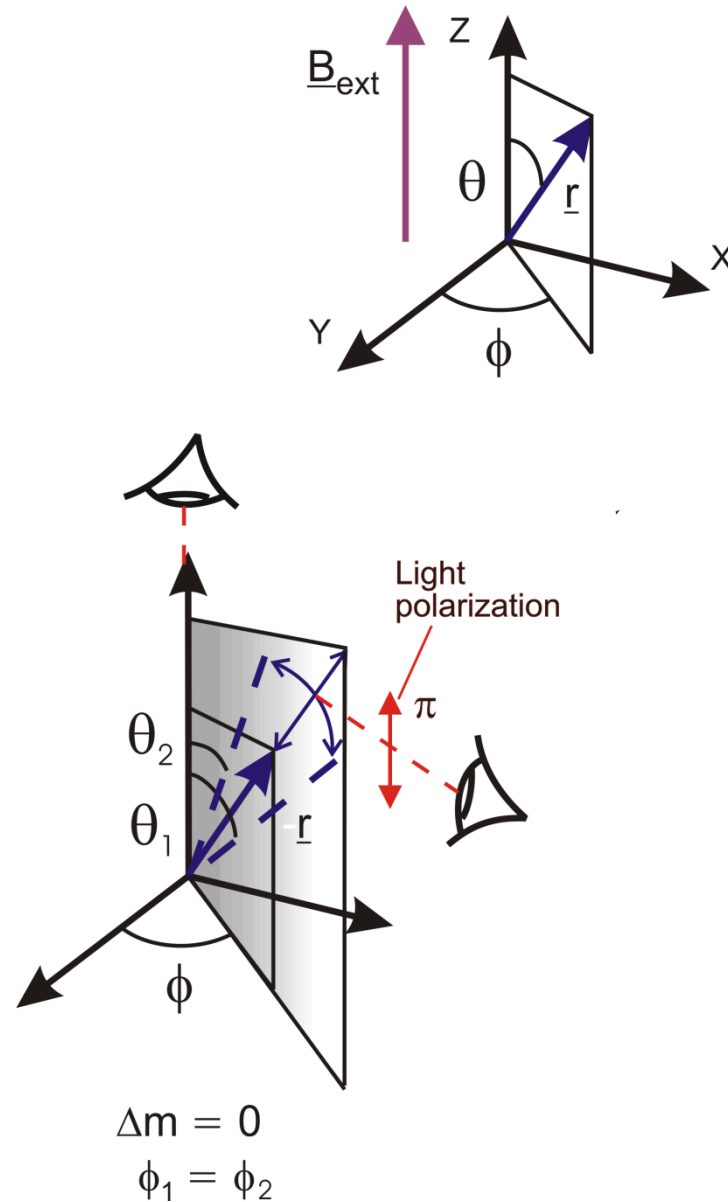


Anomalous Zeeman Effect:

$3s^2S_{1/2} - 3p^2P_{1/2}$ in Na



Polarization of Anomalous Zeeman components associated with Δm selection rules



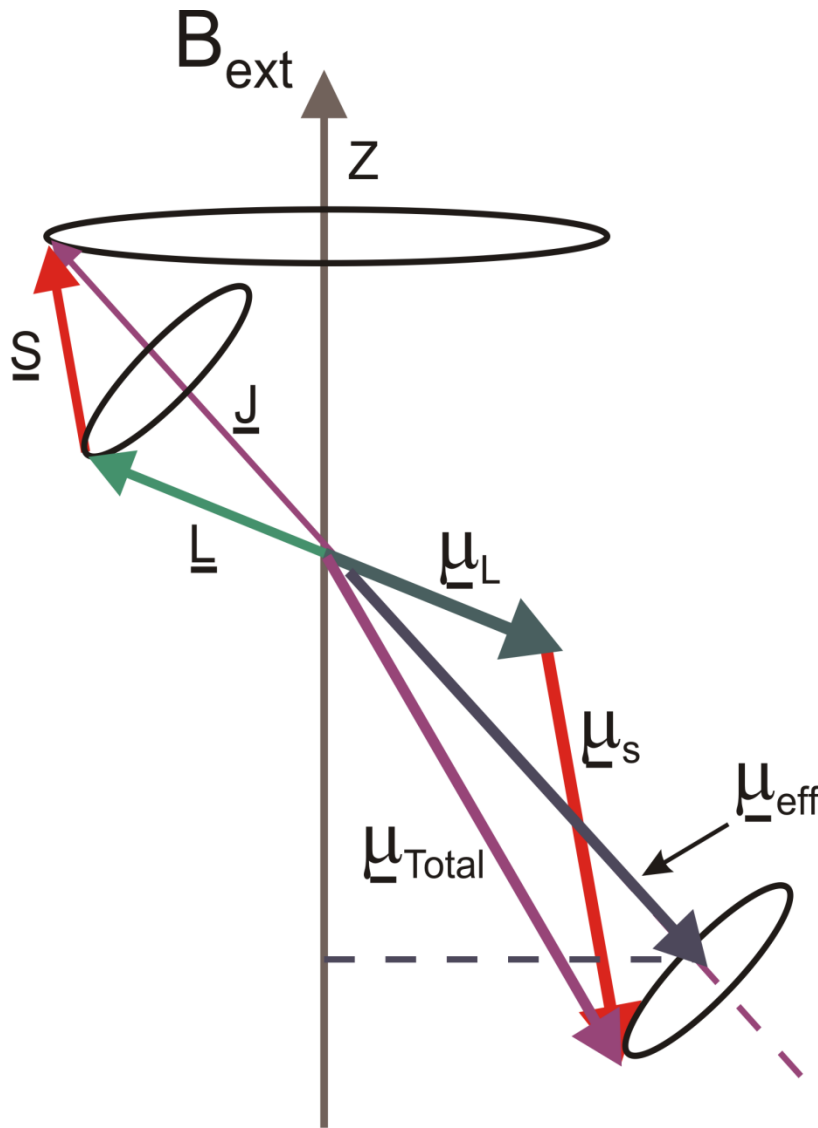
Lecture 7

- 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





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

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



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

Interaction energy

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

Effective magnetic moment

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

Perturbation Theory:
expectation value of energy

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

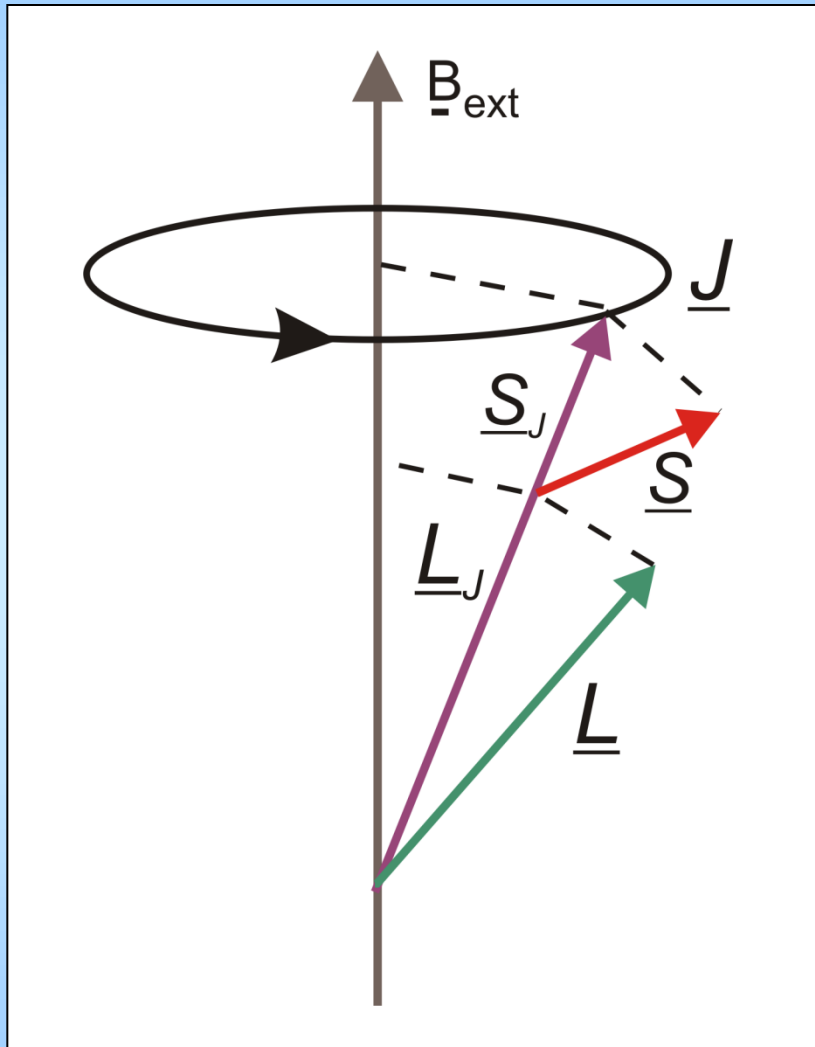
Energy shift of M_J level

$$\Delta E_{\text{AZ}} = g_J \mu_B B_{\text{ext}} M_J$$

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

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

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



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

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

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

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

Perturbation Theory result

$$\Delta E_{\text{AZ}} = g_J \mu_B B_{\text{ext}} M_J$$



Landé g-factor

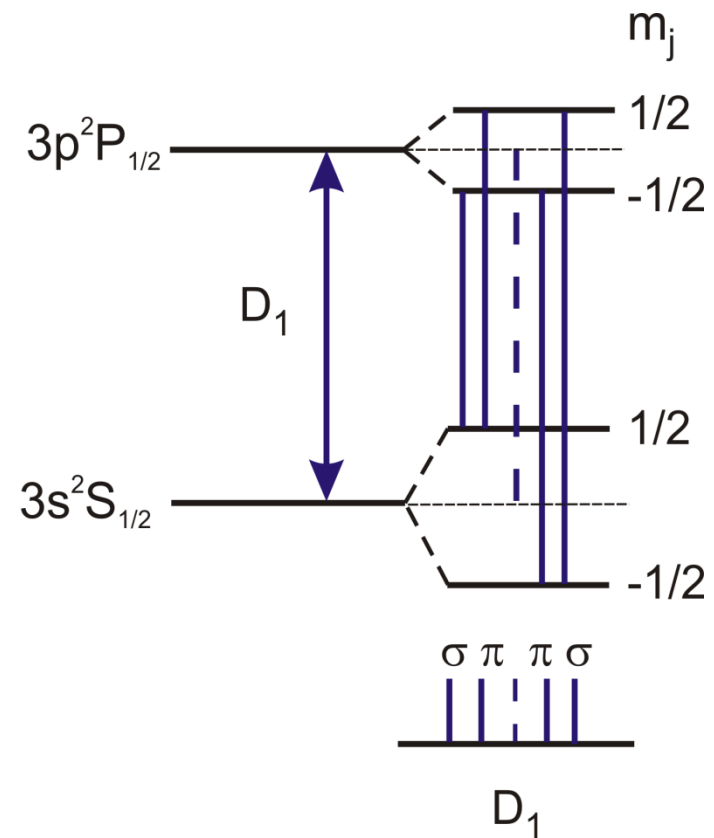
$$g_J = \frac{[3J(J + 1) - L(L + 1) + S(S + 1)]}{2J(J + 1)}$$

Anomalous Zeeman Effect:

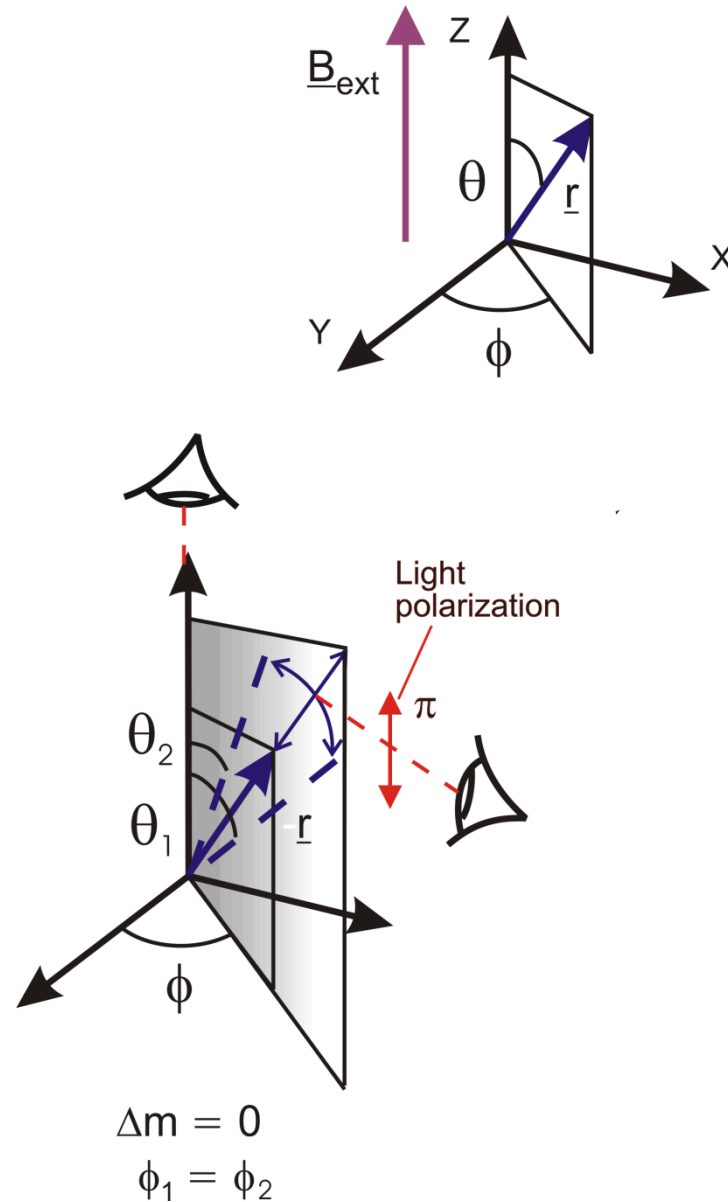
$3s^2S_{1/2} - 3p^2P_{1/2}$ in Na

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

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



Polarization of Anomalous Zeeman components associated with Δm selection rules

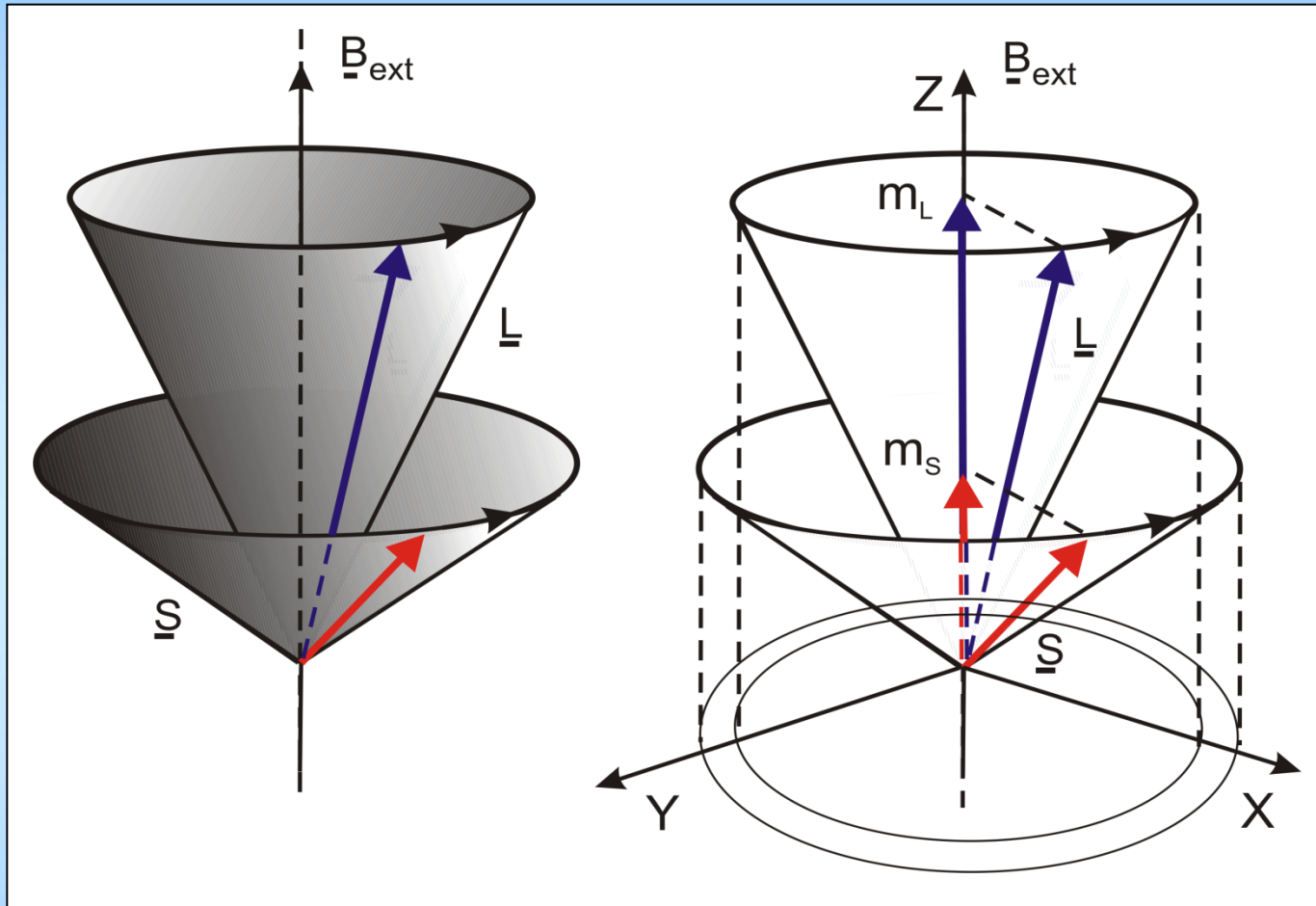


Strong field effects on atoms with spin-orbit coupling

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



Strong field effect on \underline{L} and \underline{S} .



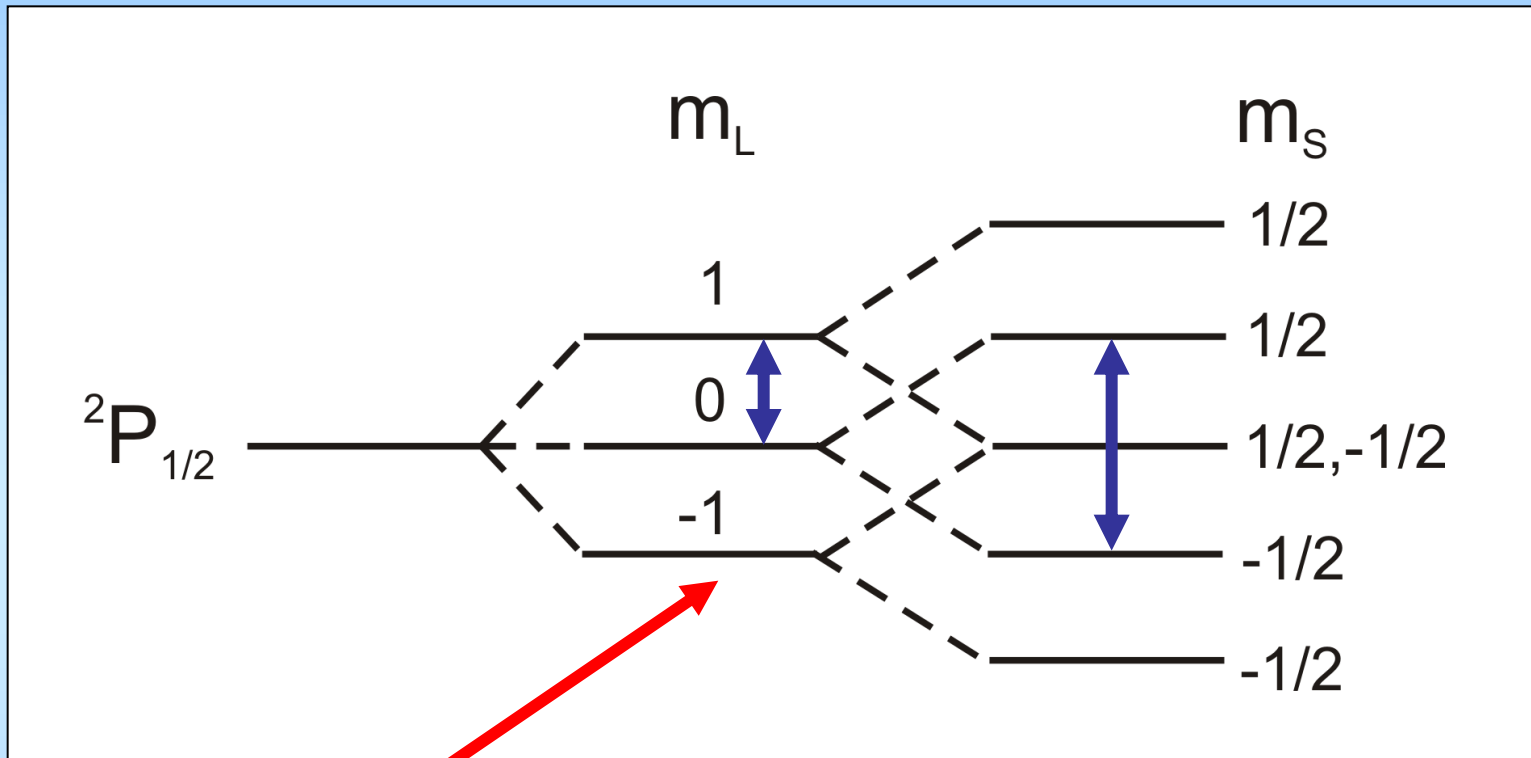
*m_L and m_S are
good quantum
numbers*

\underline{L} and \underline{S} precess independently around $\underline{B}_{\text{ext}}$

Spin-orbit coupling is relatively insignificant



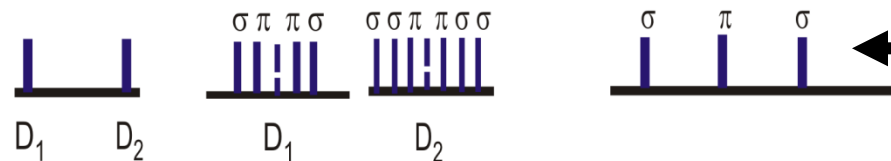
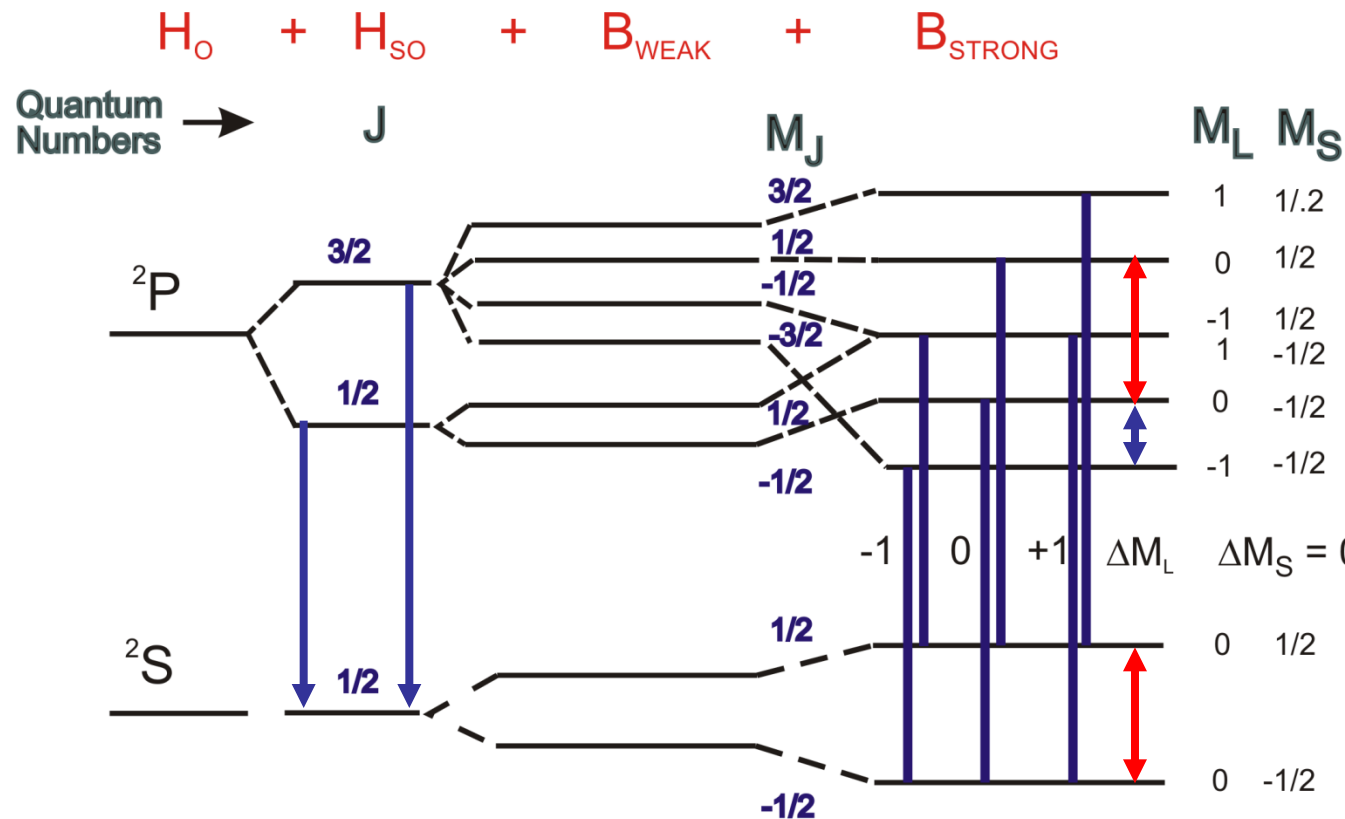
Splitting of level in strong field: *Paschen-Back Effect*



*N.B. Splitting like
Normal Zeeman Effect*

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





Fine structure

Anomalous Zeeman Effect

Paschen-Back Effect

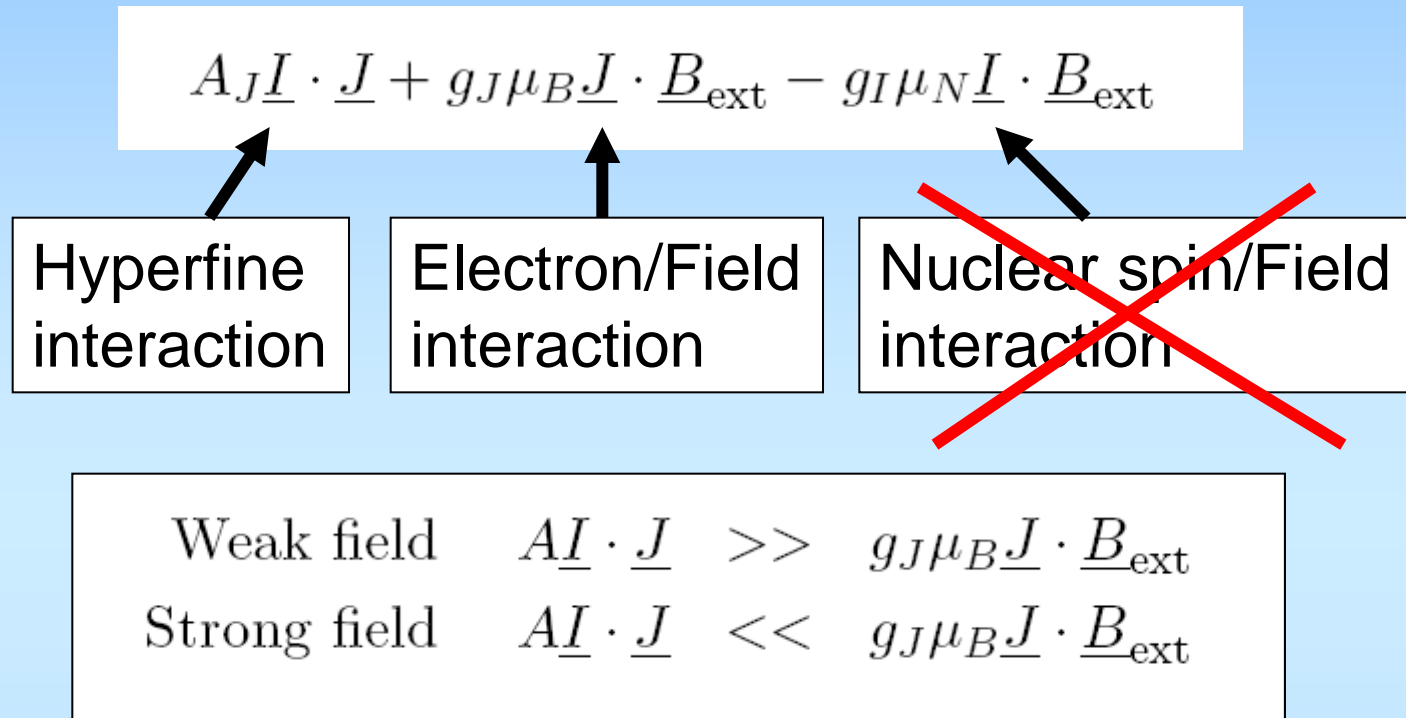
$$g_S = 2g_L$$



Magnetic field effects on hyperfine structure



Hyperfine structure in Magnetic Fields

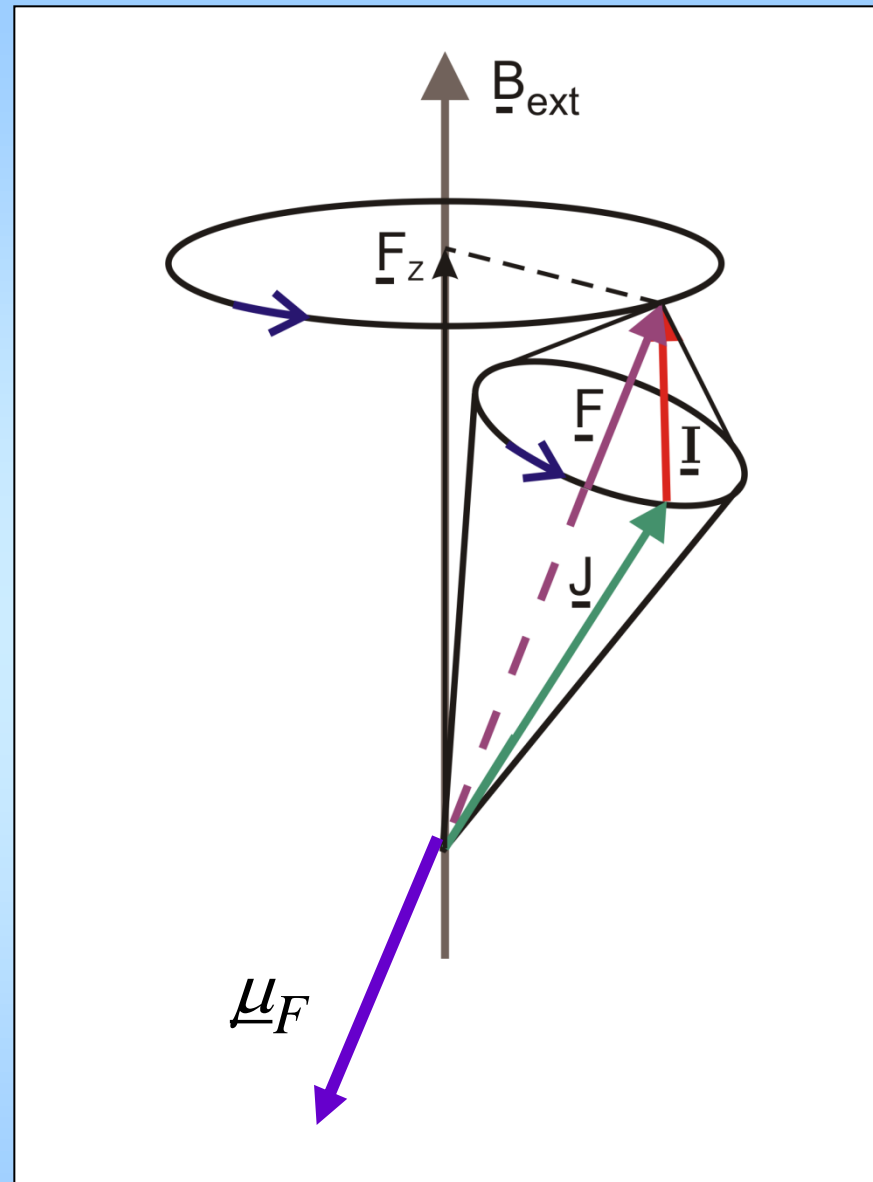


Weak field effect on hyperfine structure

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

I , J , F and M_F
are good quantum numbers

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



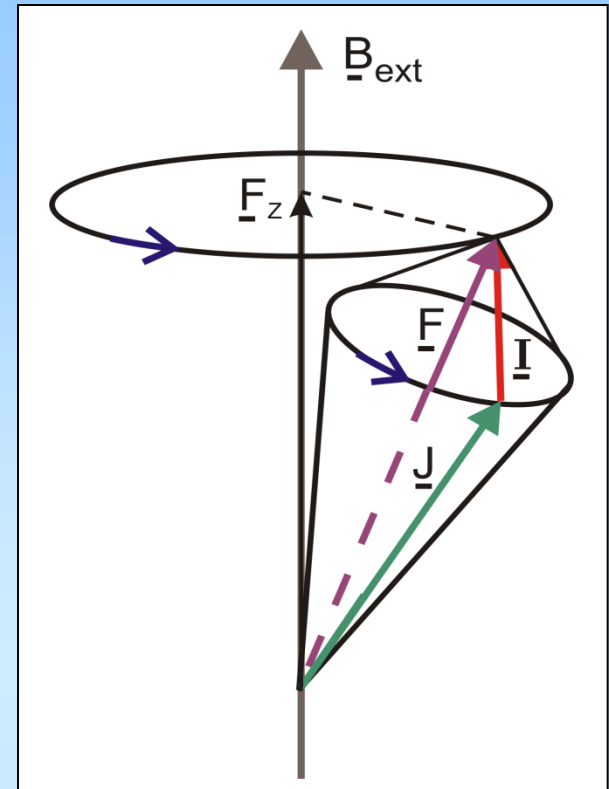
$$\underline{\mu}_F = -g_F \mu_B \underline{F}$$

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

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

magnitude direction

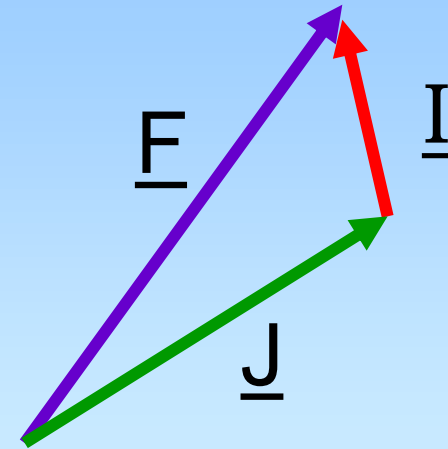
$$g_F = g_J \times \frac{\underline{J} \cdot \underline{F}}{F^2}$$



Find this using Vector Model



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



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

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

$$\underline{J} \cdot \underline{F} = \frac{1}{2}\{F(F+1) + J(J+1) - I(I+1)\}$$

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



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

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

Each hyperfine level is split by g_F term

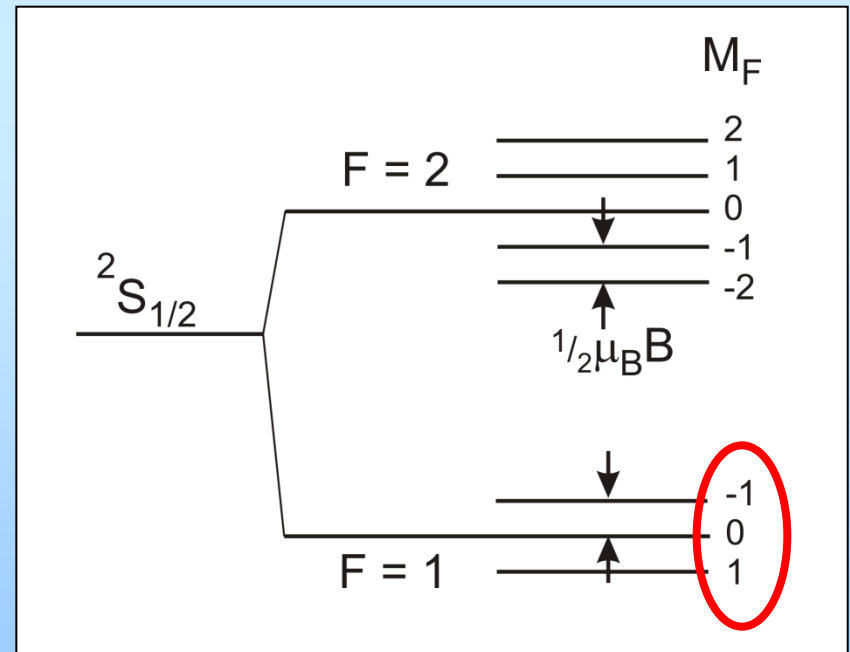
Ground level of Na:

$J = 1/2$; $I = 3/2$;

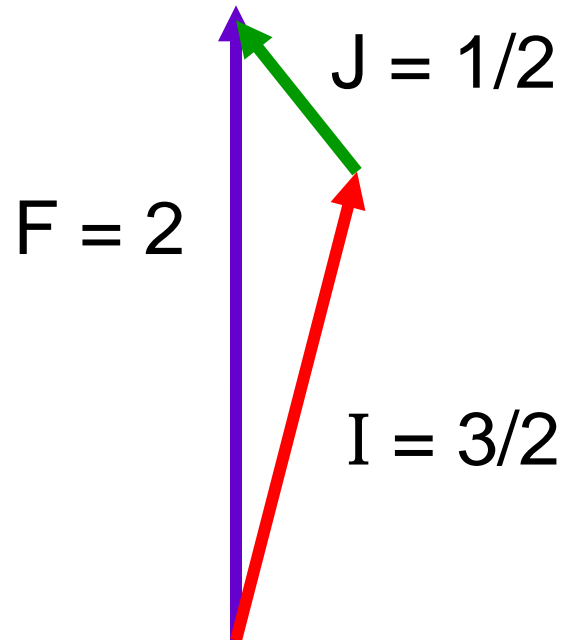
$F = 1$ or 2

$F = 2$: $g_F = 1/2$;

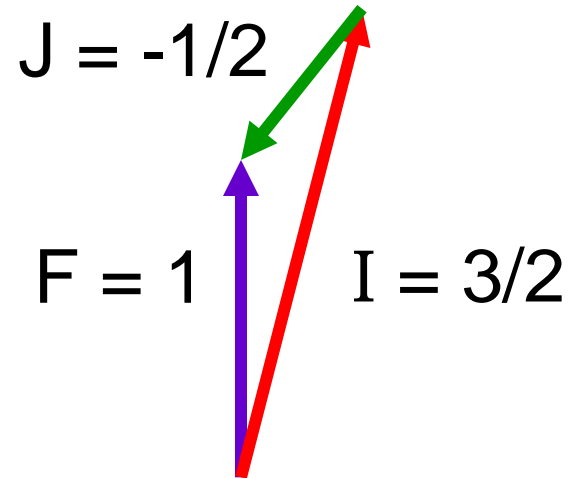
$F = 1$: $g_F = -1/2$



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



$\underline{J} \cdot \underline{F}$ positive

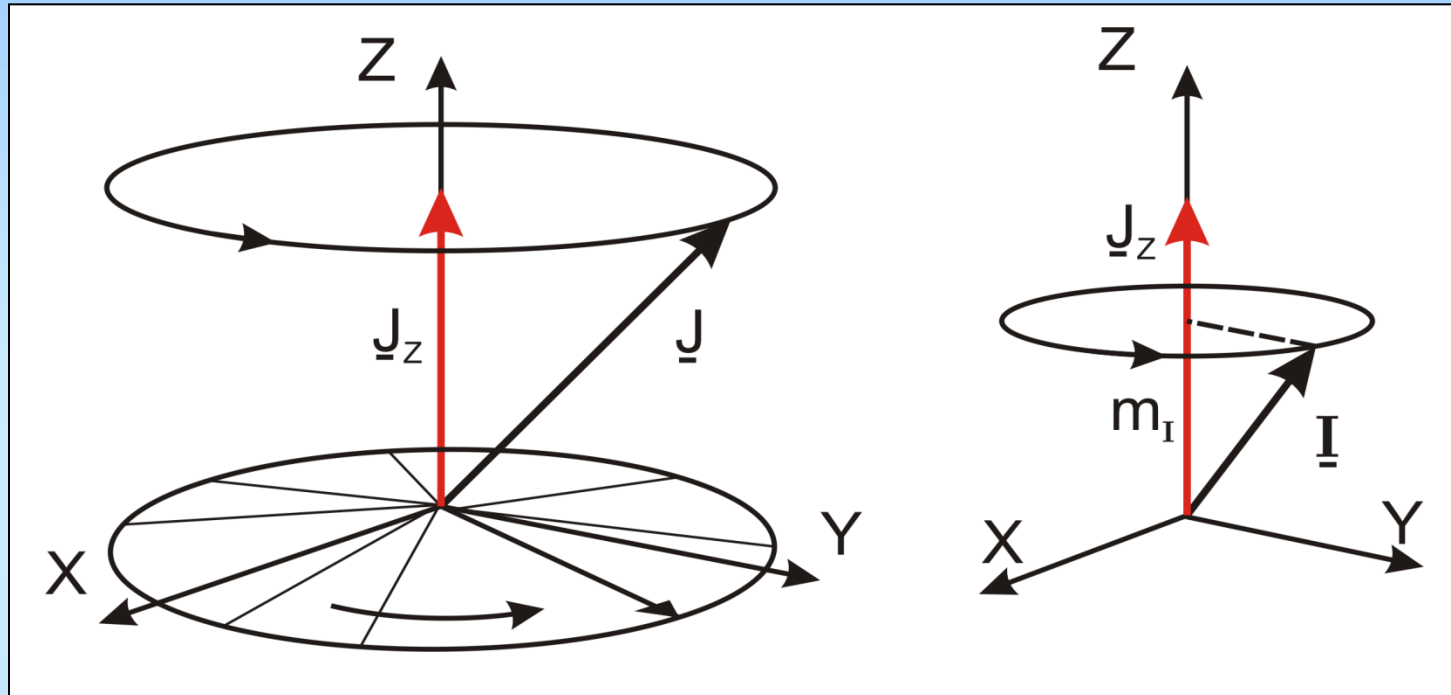


$\underline{J} \cdot \underline{F}$ negative



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. \underline{J}_z

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



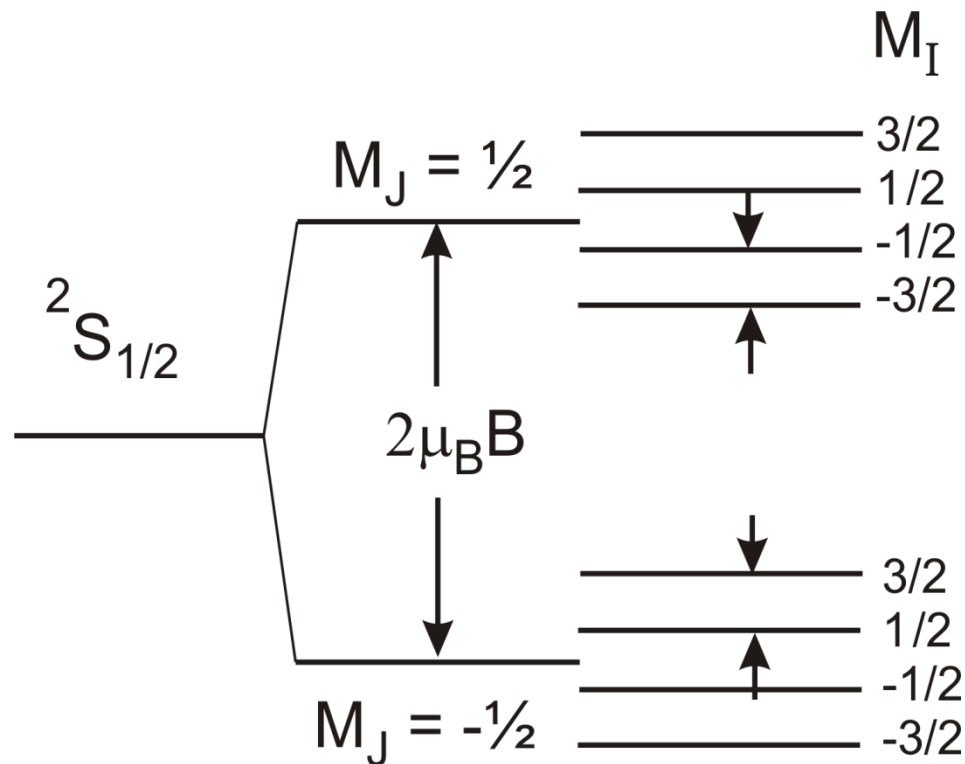
Strong field effect on hfs.

Dominant term

Energy

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

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 $\underline{B}_{\text{ext}}$

\underline{I} tries to precess around \underline{J}

\underline{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 \underline{F} to get effective magnetic moment and g_F

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

→ “Zeeman” splitting of hfs levels

Strong field: M_I and M_J are good quantum nos.

\underline{J} precesses rapidly around B_{ext} ;

\underline{I} precesses around z-component of \underline{J} i.e. what it can “see” of \underline{J}

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

• → hfs of “Zeeman” split levels

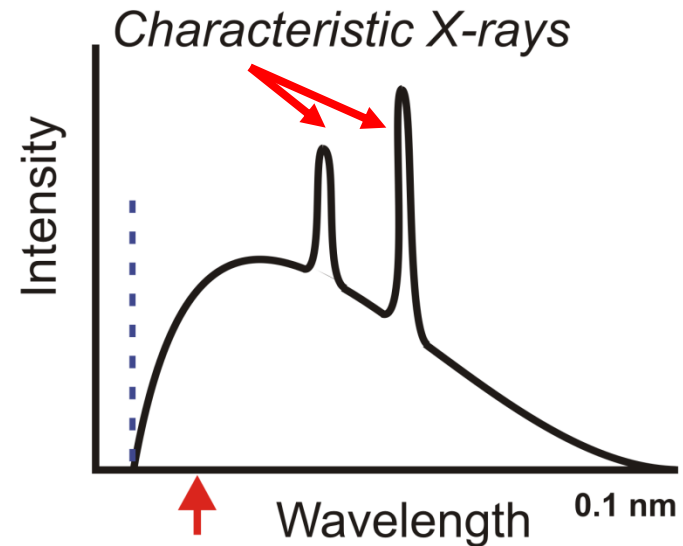
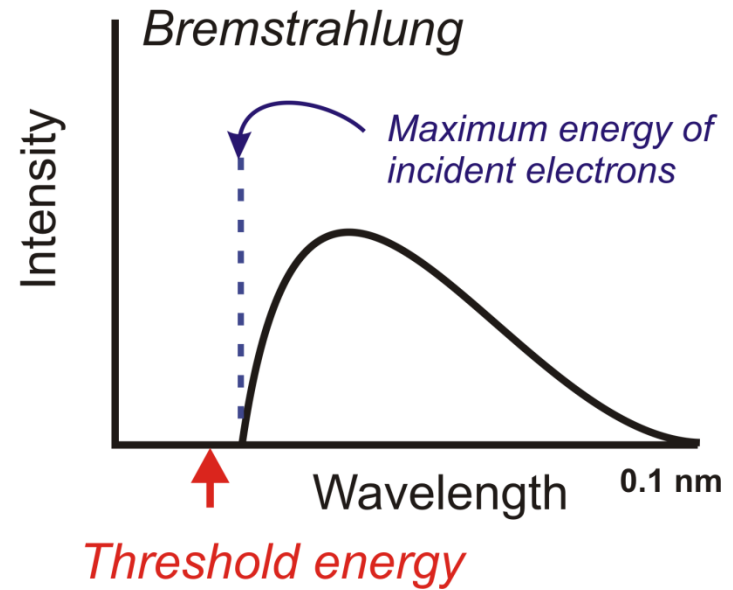


Lecture 8

- X-rays: excitation of “inner-shell” electrons
- High resolution laser spectroscopy
 - The Doppler effect
 - Laser spectroscopy
 - “Doppler-free” spectroscopy



X – Ray Spectra

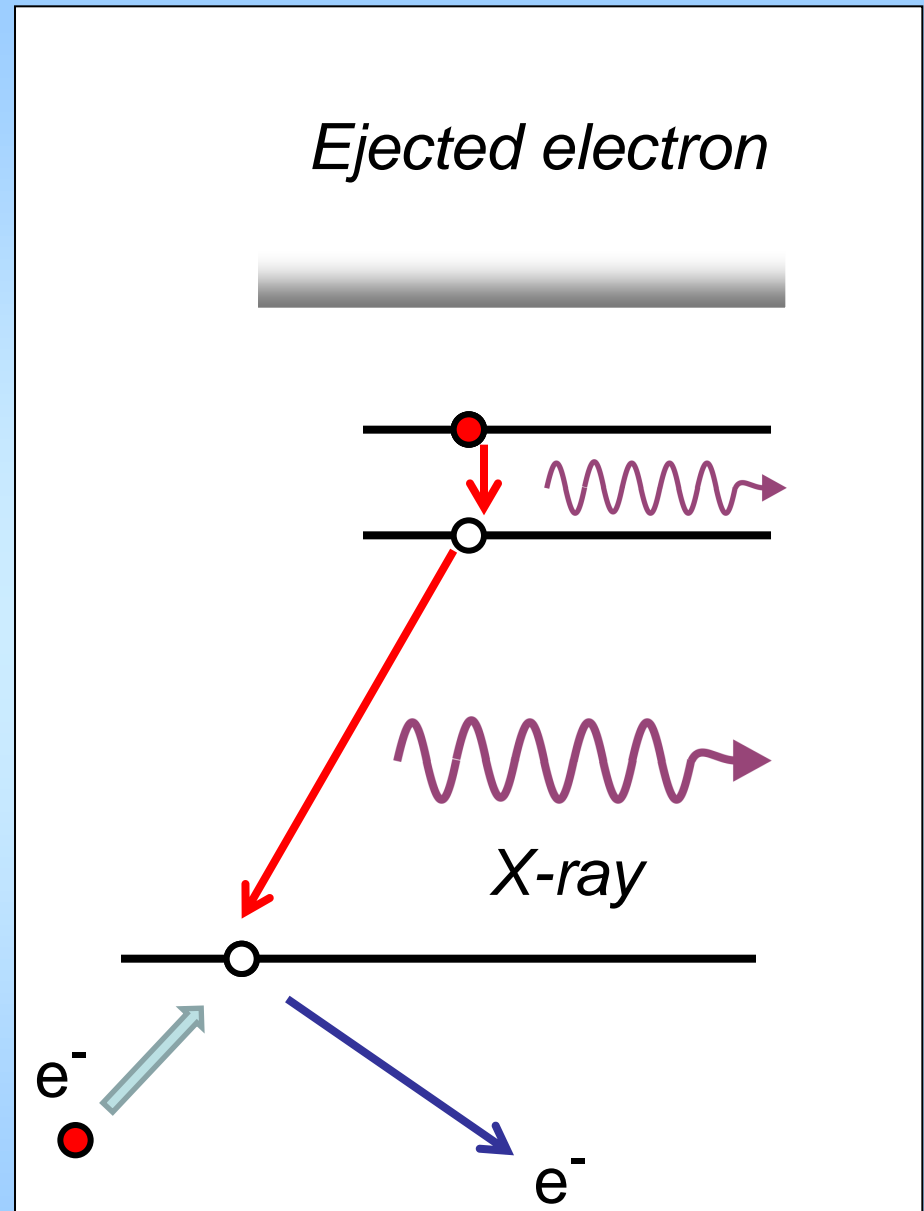


Characteristic X-rays

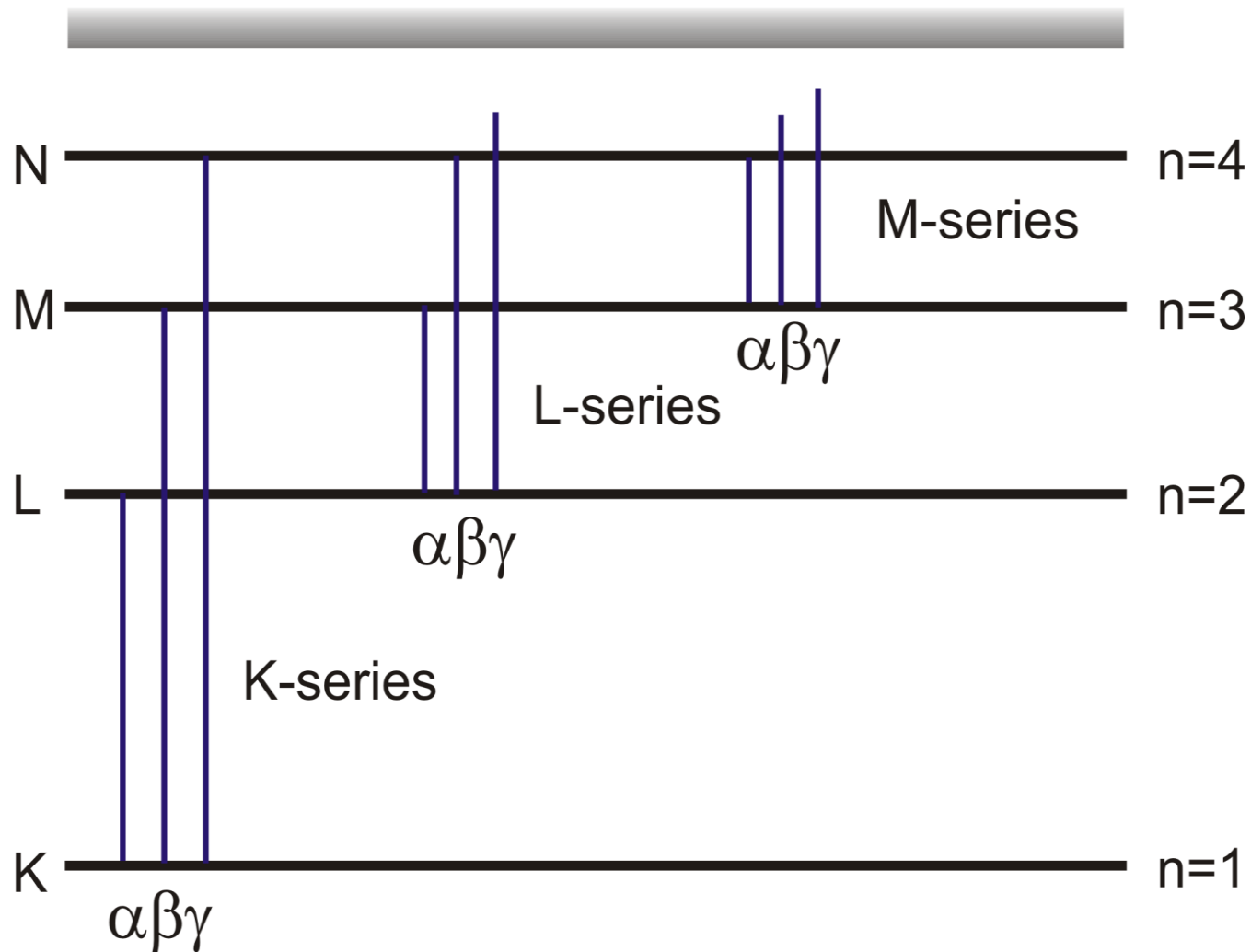
- Wavelengths fit a simple series formula
- All lines of a series appear together
 - *when excitation exceeds threshold value*
- Threshold energy just exceeds energy of shortest wavelength X-rays
- Above a certain energy no new series appear.



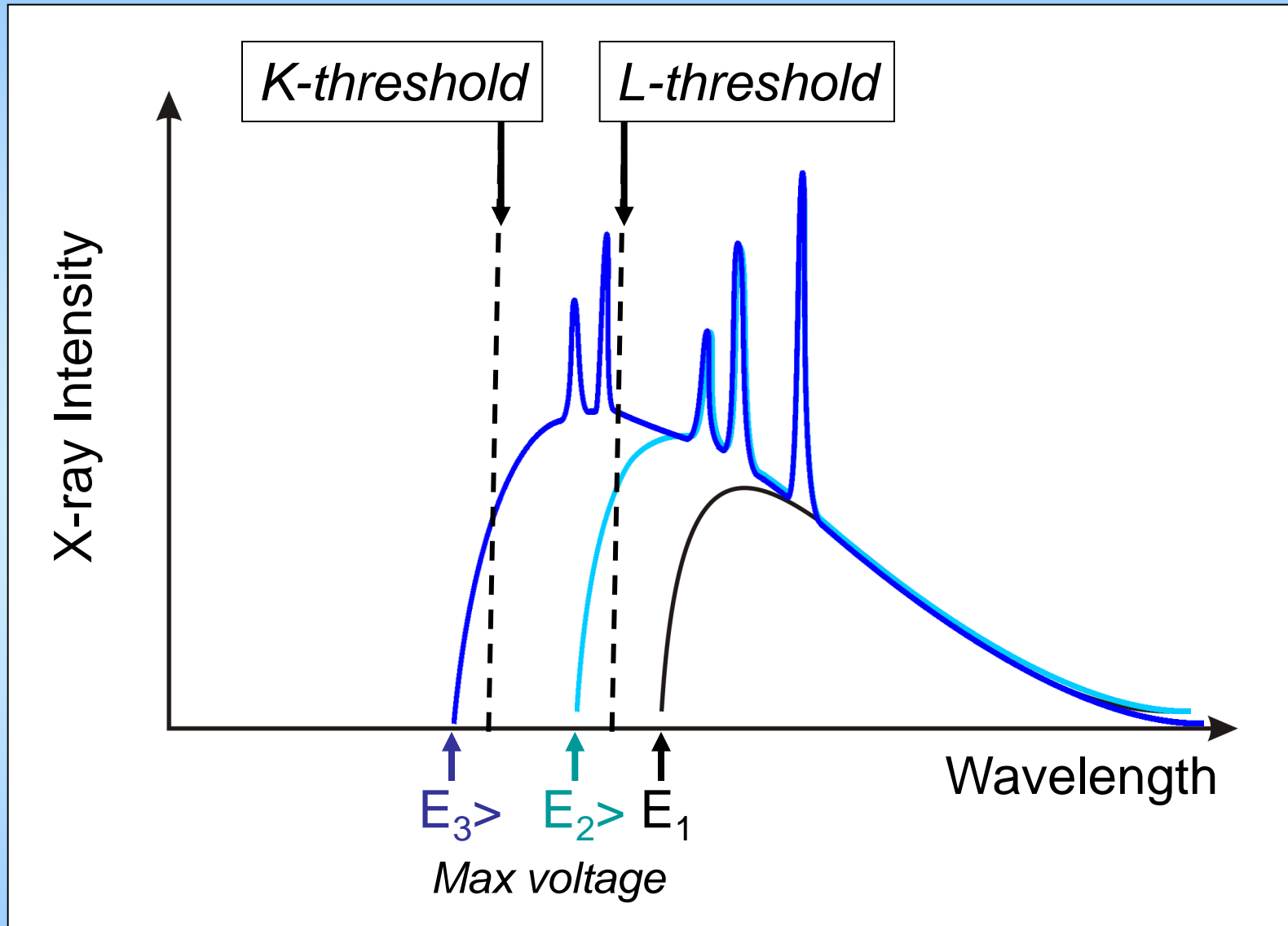
Generation of characteristic X-rays



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:

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

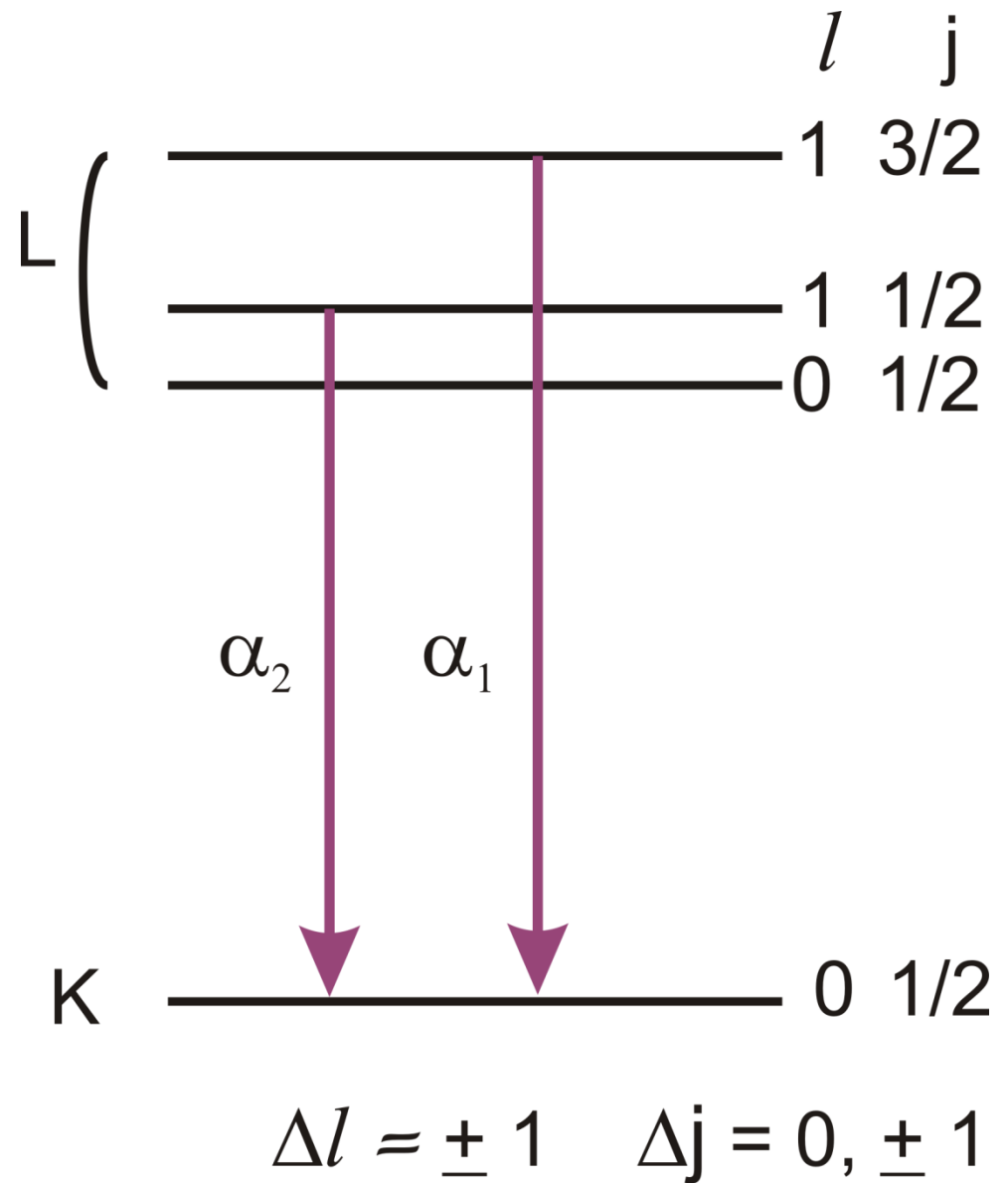
Transitions between inner-shells:

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

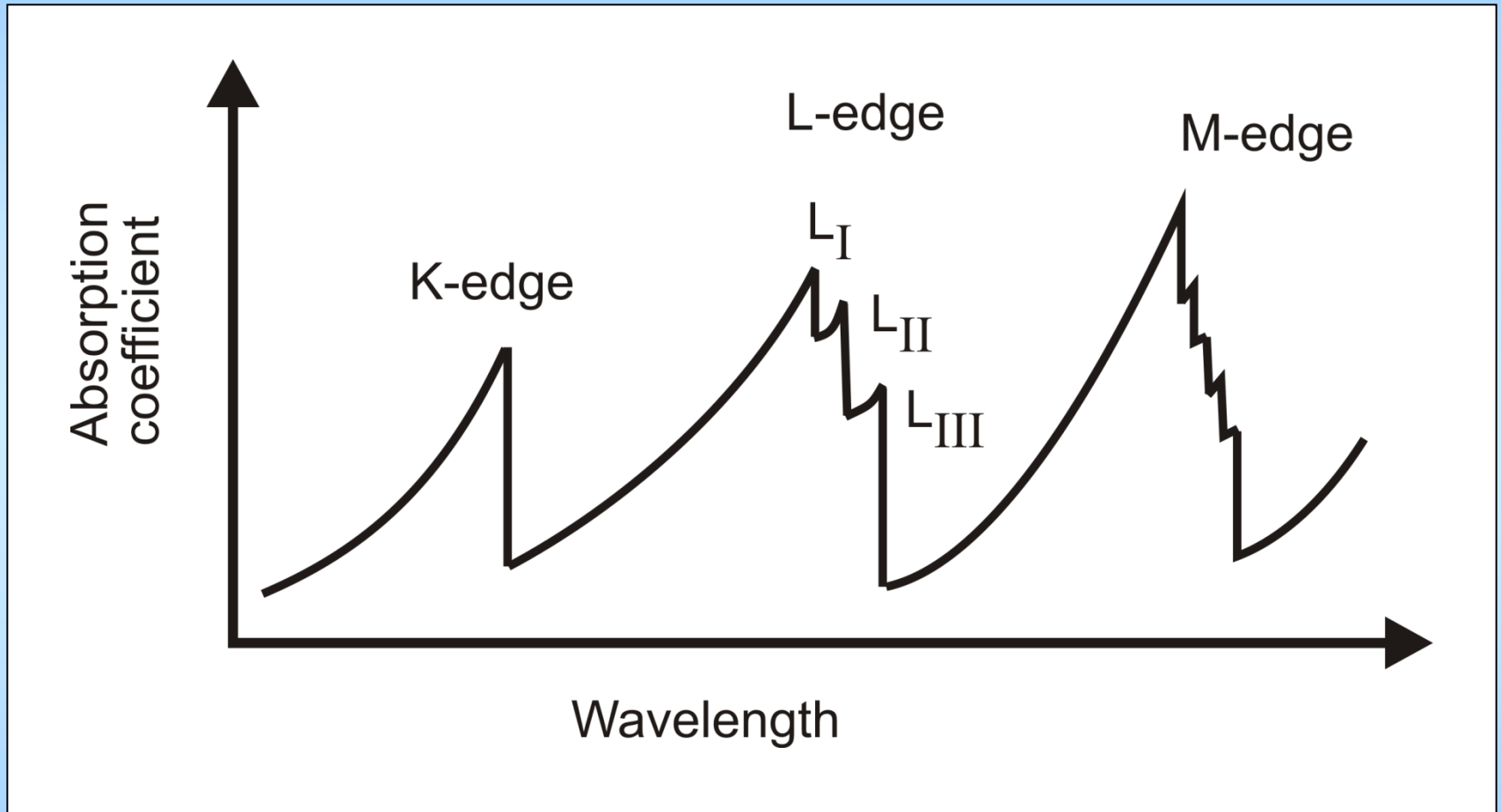


Fine structure of X-rays

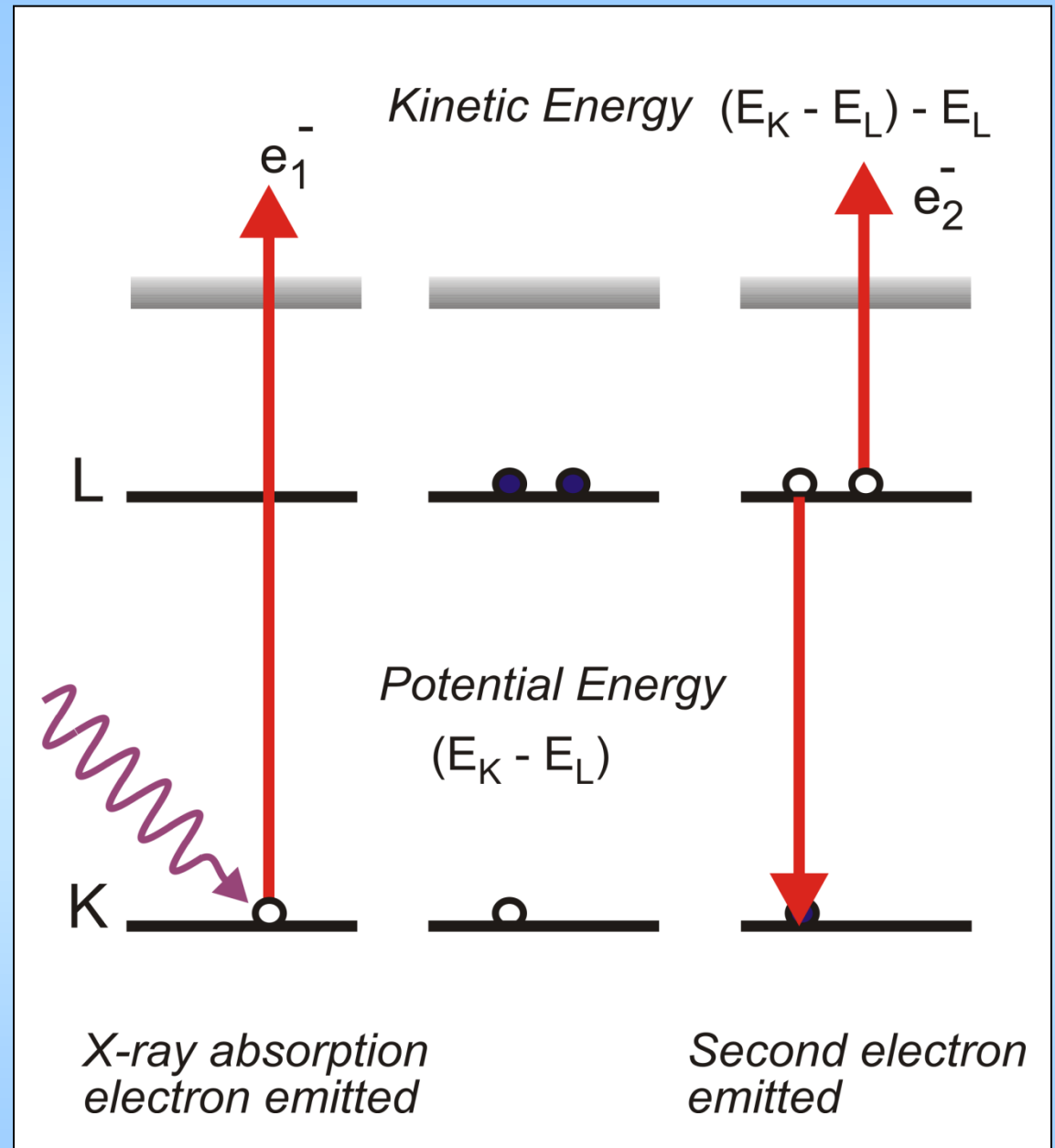
$$\Delta E_{\text{fs}} = \frac{5.8Z^4}{n^3l(l+1)}$$



X-ray absorption spectra



Auger effect



High resolution laser spectroscopy



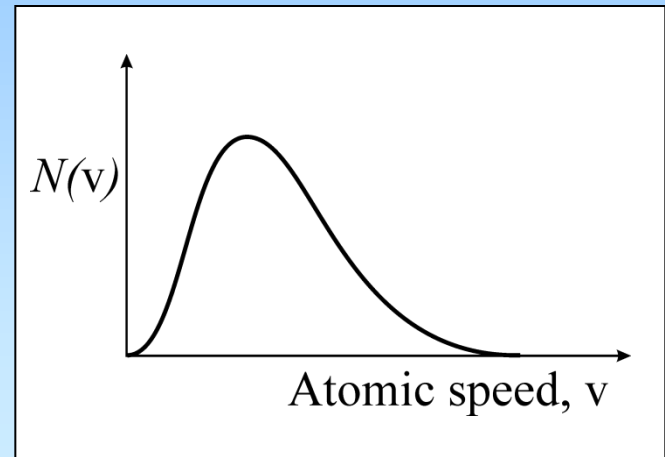
Doppler broadening

Doppler Shift:

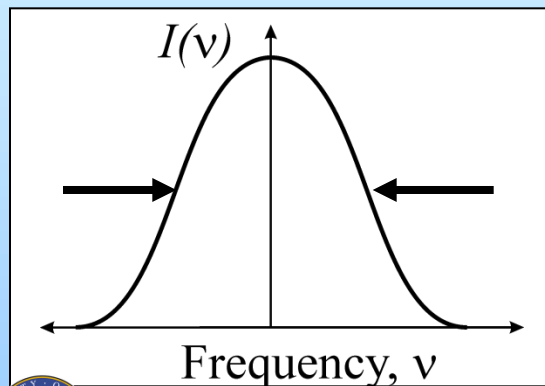
$$\nu = \nu_0 \left(1 \pm \frac{v}{c} \right)$$

Maxwell-Boltzmann distribution of Atomic speeds

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



Distribution of Intensity



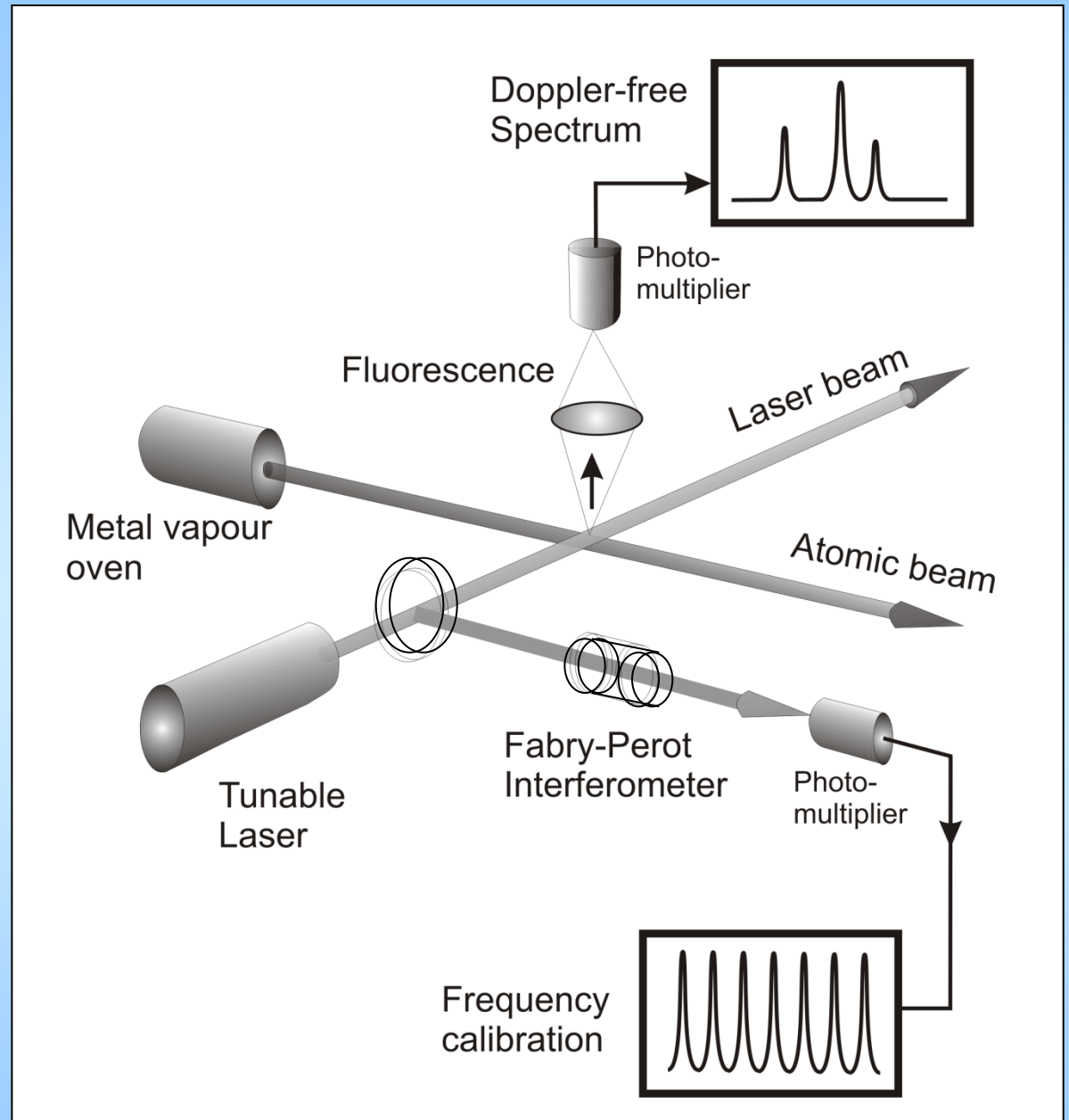
$$I(\nu) = I(\nu_0) \exp \left[-\frac{Mc^2}{2kT} \left(\frac{\nu - \nu_0}{\nu_0} \right)^2 \right]$$

Doppler width

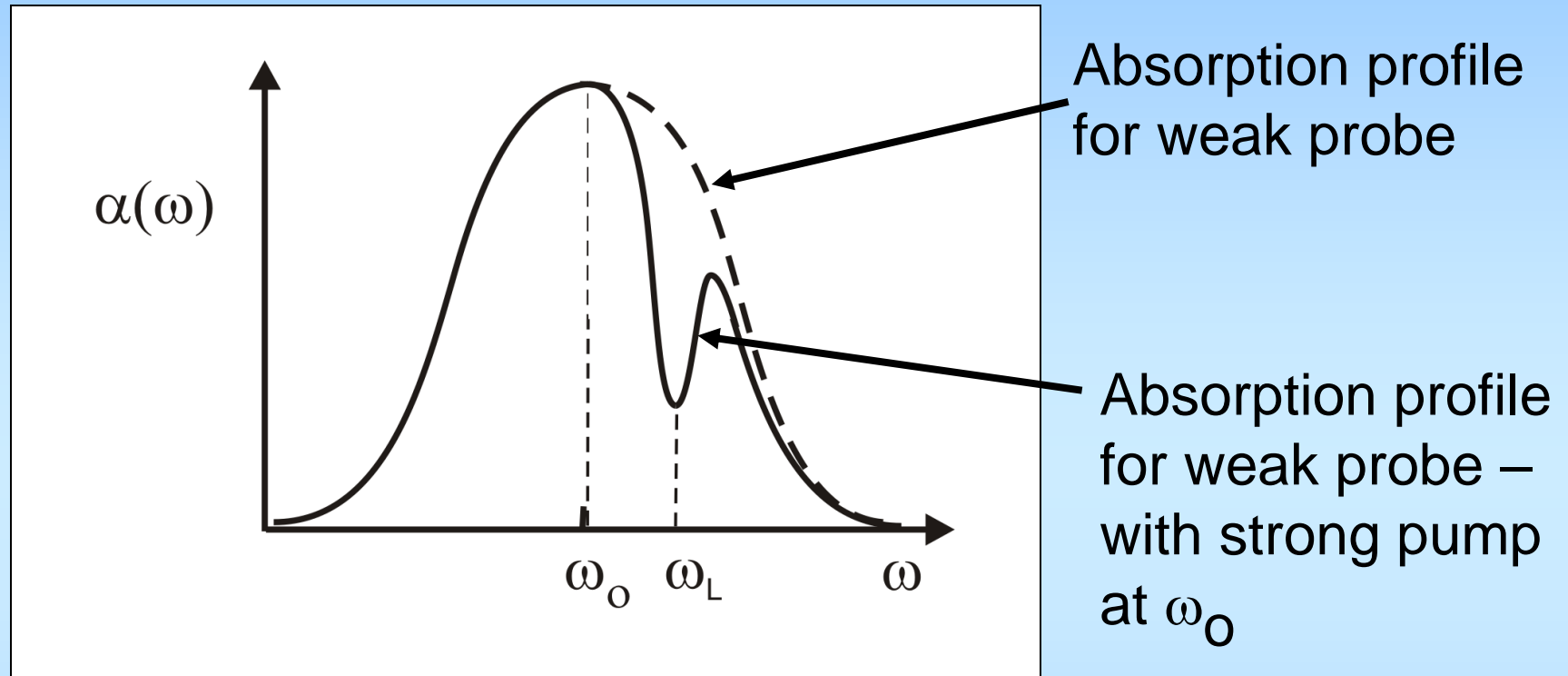
$$\Delta\nu_D = \frac{2\nu}{c} \left[\frac{2kT}{M} \log_e 2 \right]^{1/2}$$



Crossed beam Spectroscopy



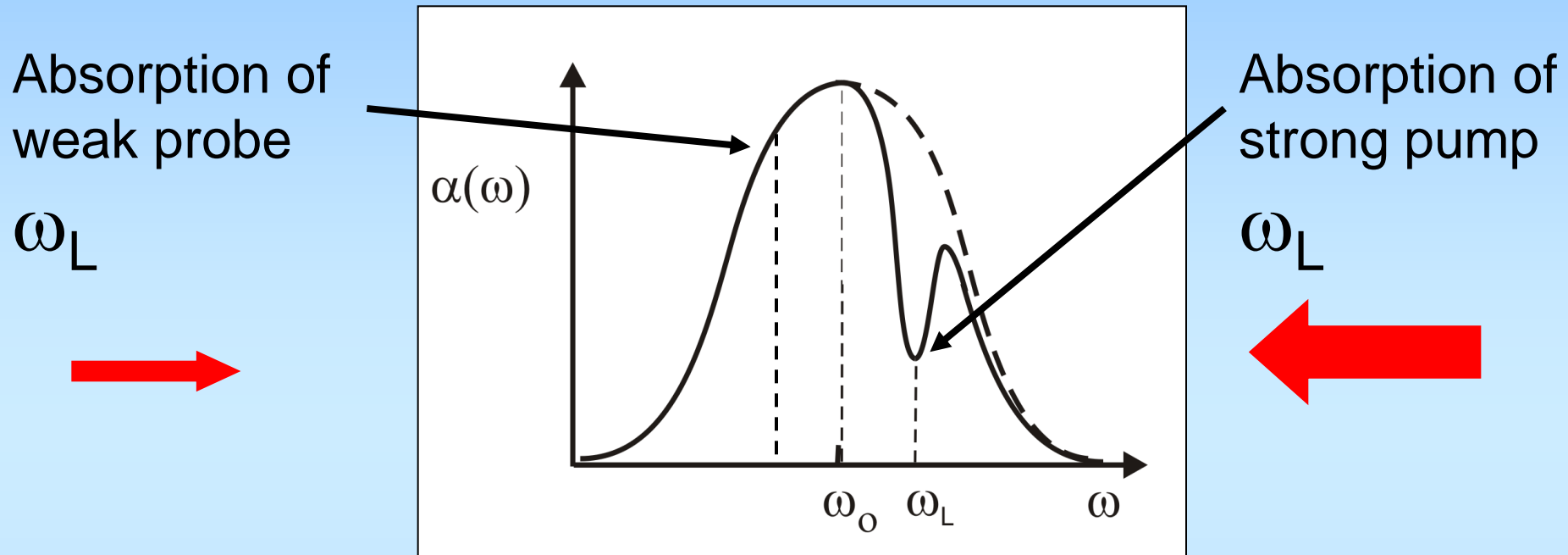
Saturation effect on absorption



Strong pump at ω_L reduces population of ground state for atoms Doppler shifted by $(\omega_L - \omega_0)$.
Hence reduced absorption for this group of atoms.



Saturation effect on absorption



Probe and pump laser at same frequency ω_L

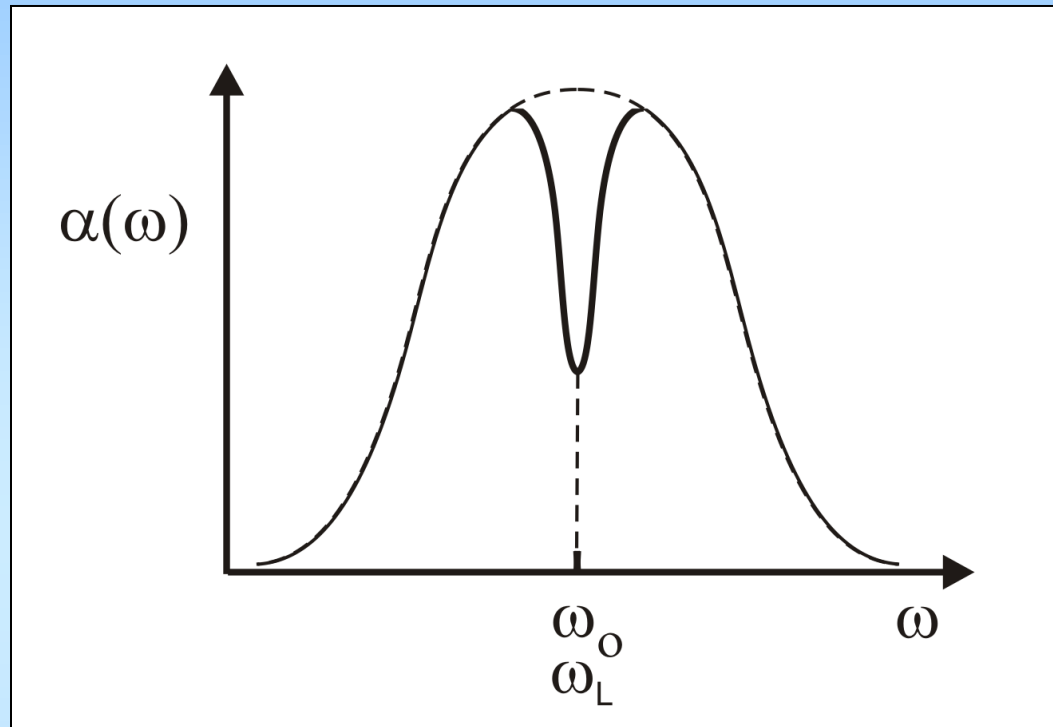
But propagating in opposite directions

Probe Doppler shifted down = Pump Doppler shifted up.

Hence probe and pump “see” different atoms.



Saturation of “zero velocity” group at ω_0



Counter-propagating pump and probe

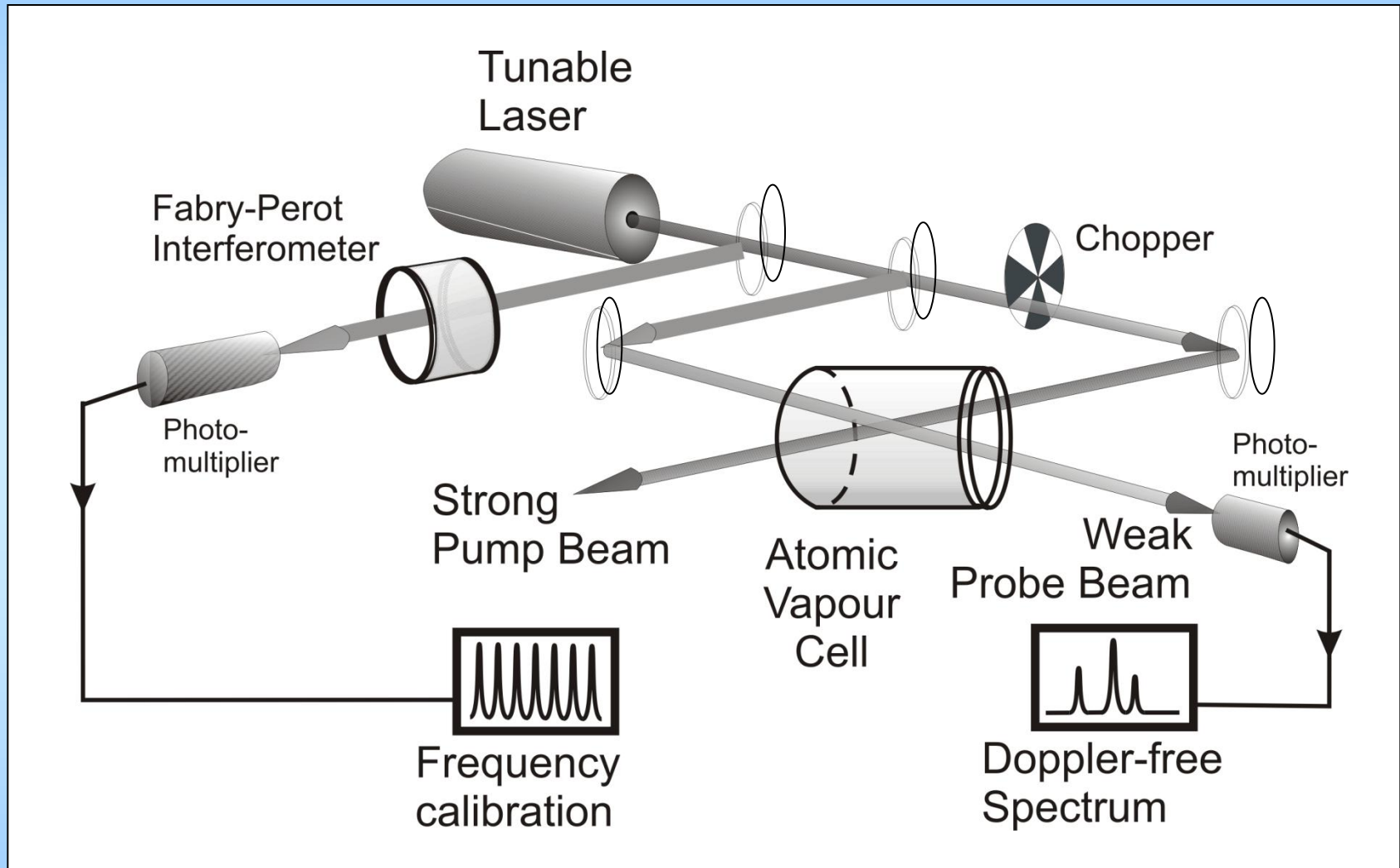
“see” same atoms at $\omega_L = \omega_0$

i.e. atoms moving with zero velocity relative to light

Probe transmission increases at ω_0



Saturation spectroscopy



Saturation spectrum of Sodium D_2 line

Doppler broadening
of hyperfine lines

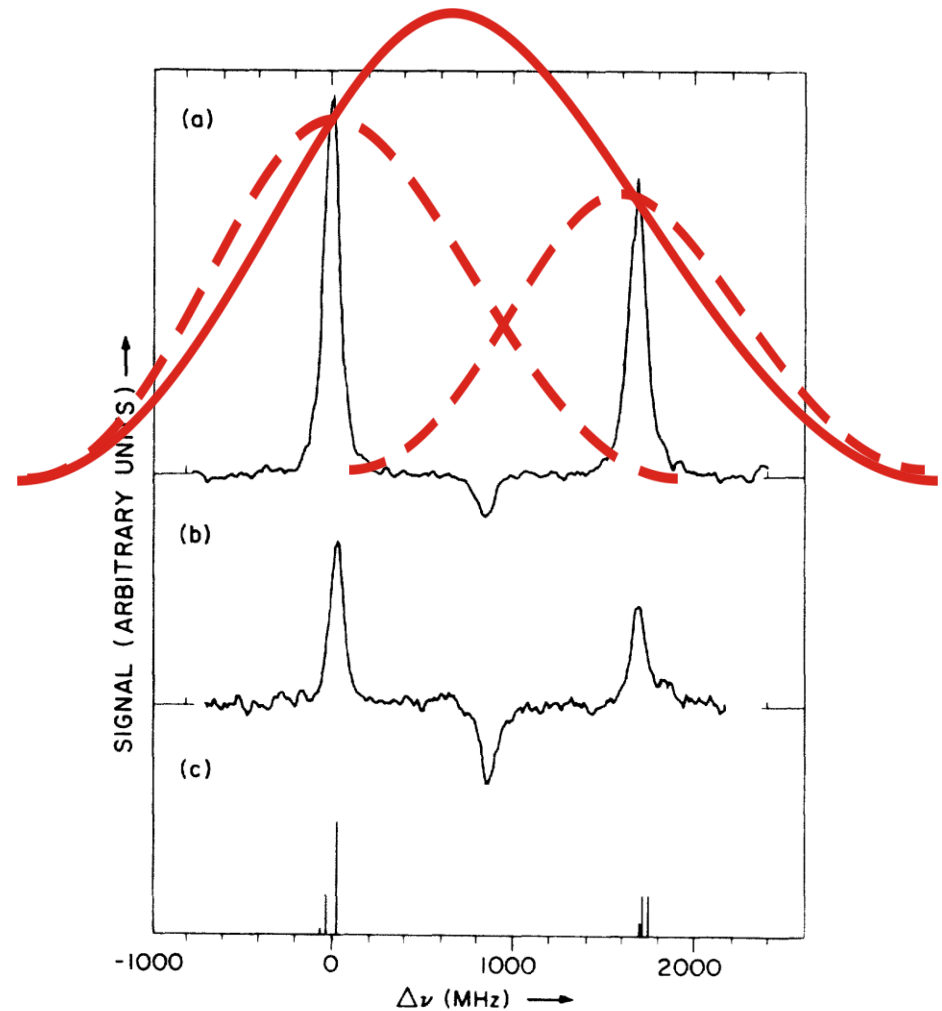
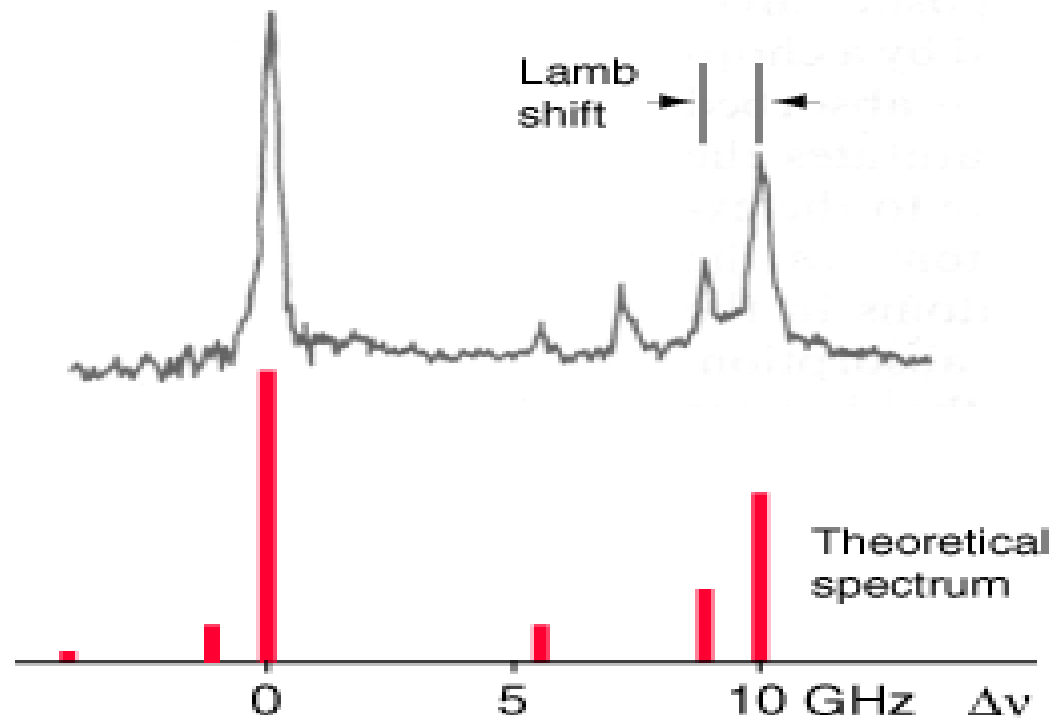


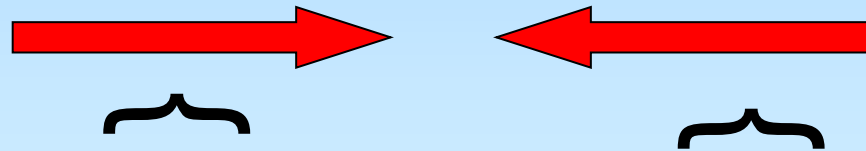
FIG. 3. (a) Saturation spectrum of the Na D_2 line without delay. (b) Like (a), but with a probe delay of 700 nsec. (c) D_2 hyperfine transitions.



Hydrogen fine structure and hyperfine structure for the $n=3 \rightarrow 2$ transition.

First saturation spectroscopy of atomic Hydrogen
T W Hansch et al 1971

Principle of Doppler-free two-photon absorption

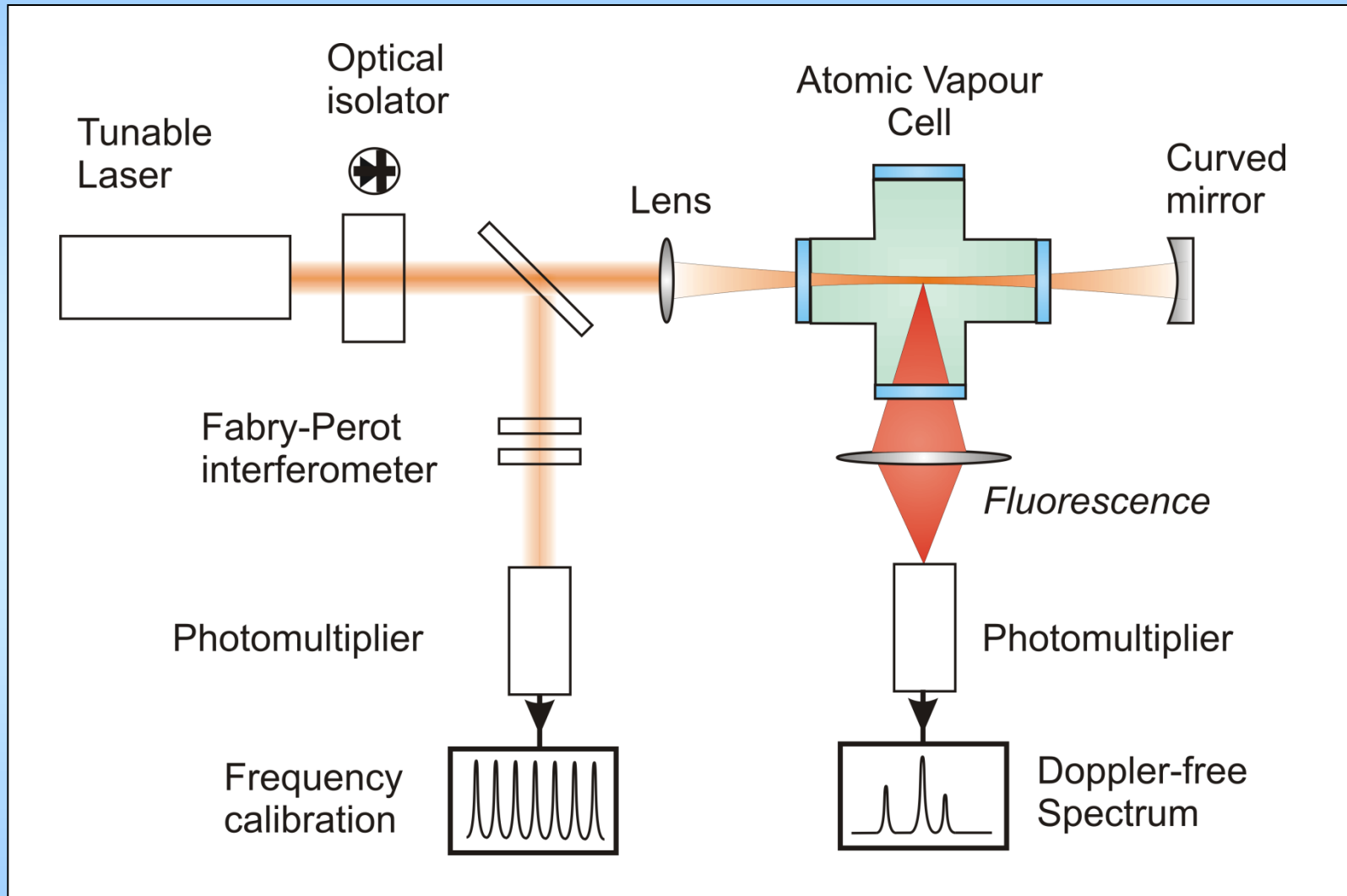


$$E = h\nu(1 + v/c) + h\nu(1 - v/c) = 2h\nu$$

Photon Doppler shifted up + Photon Doppler shifted down



Two-photon absorption spectroscopy



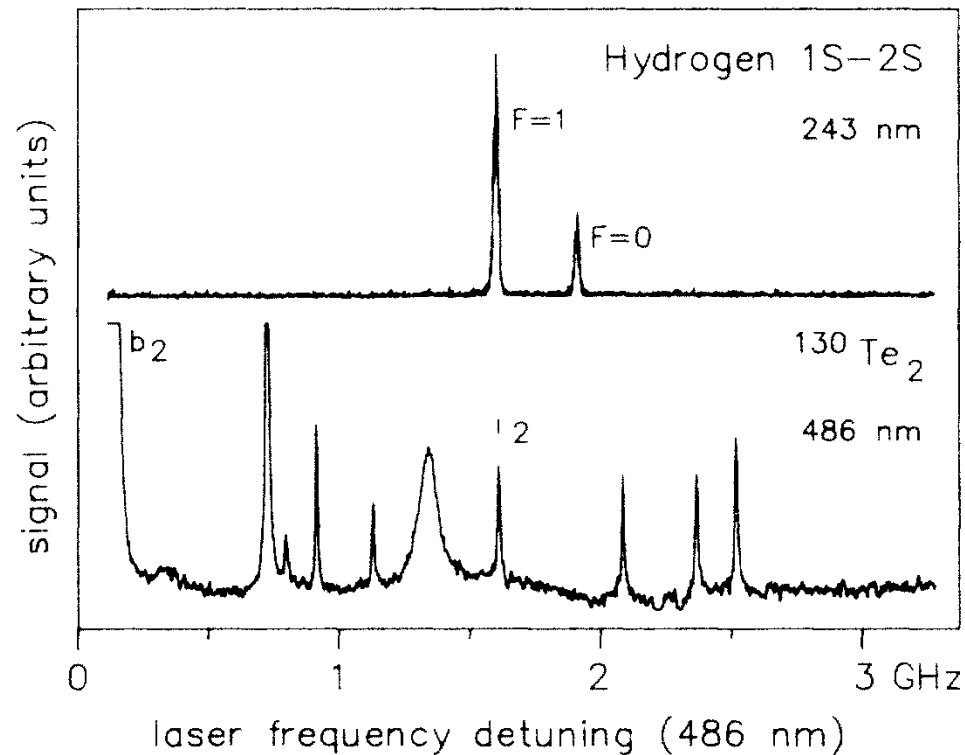
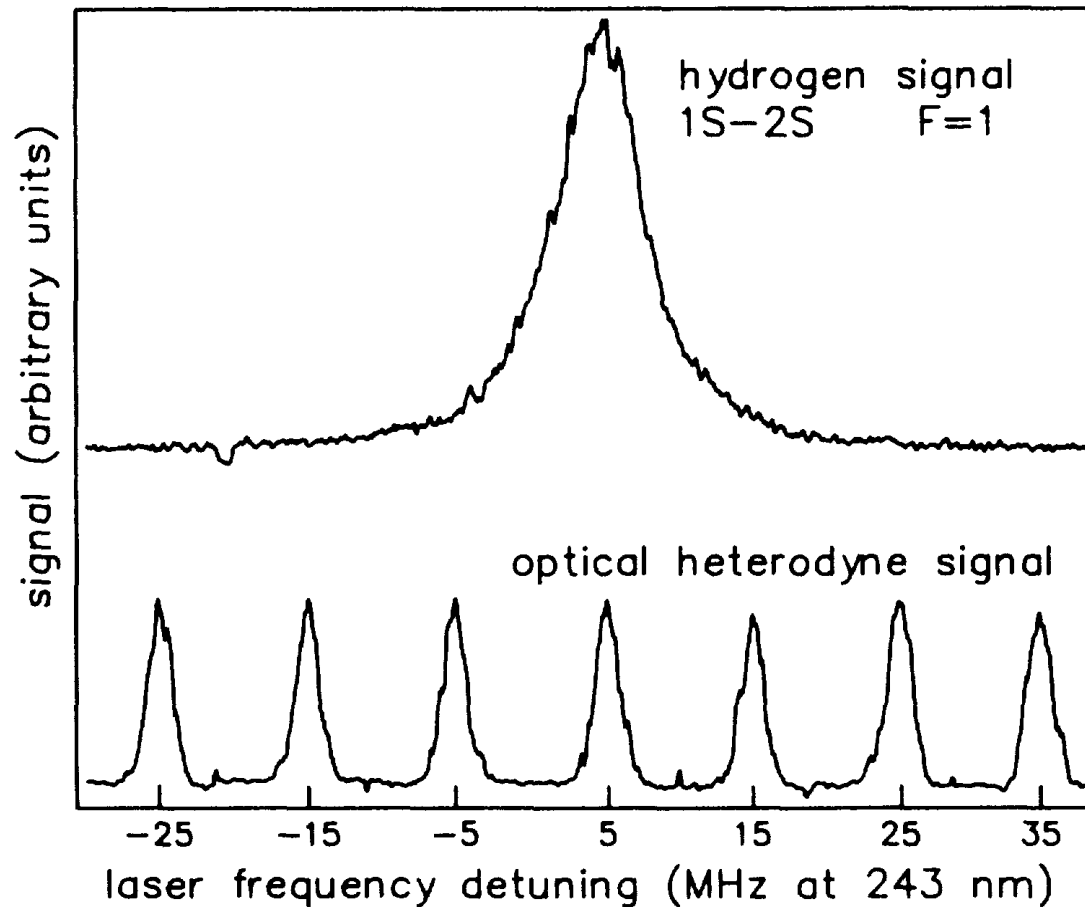
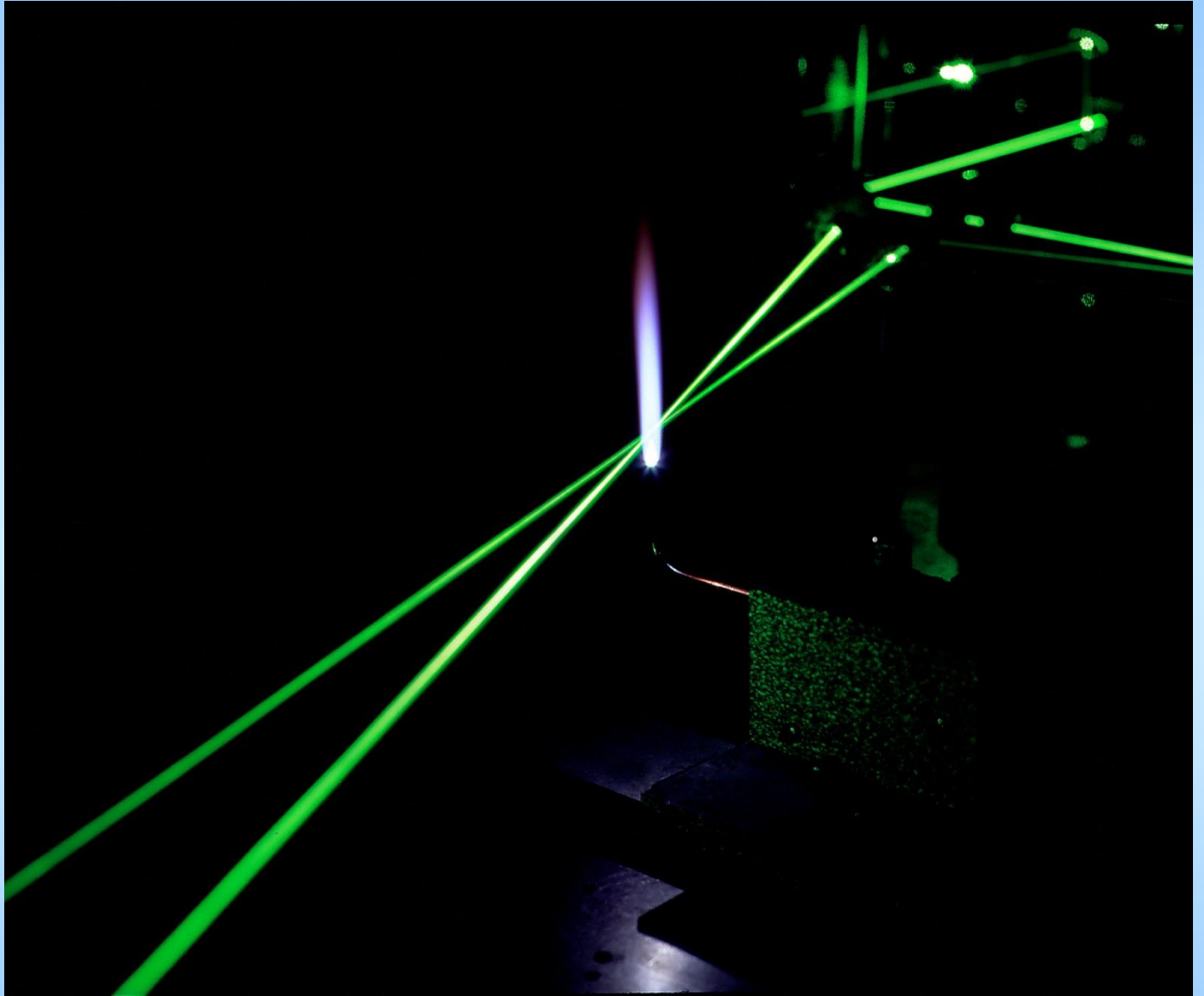


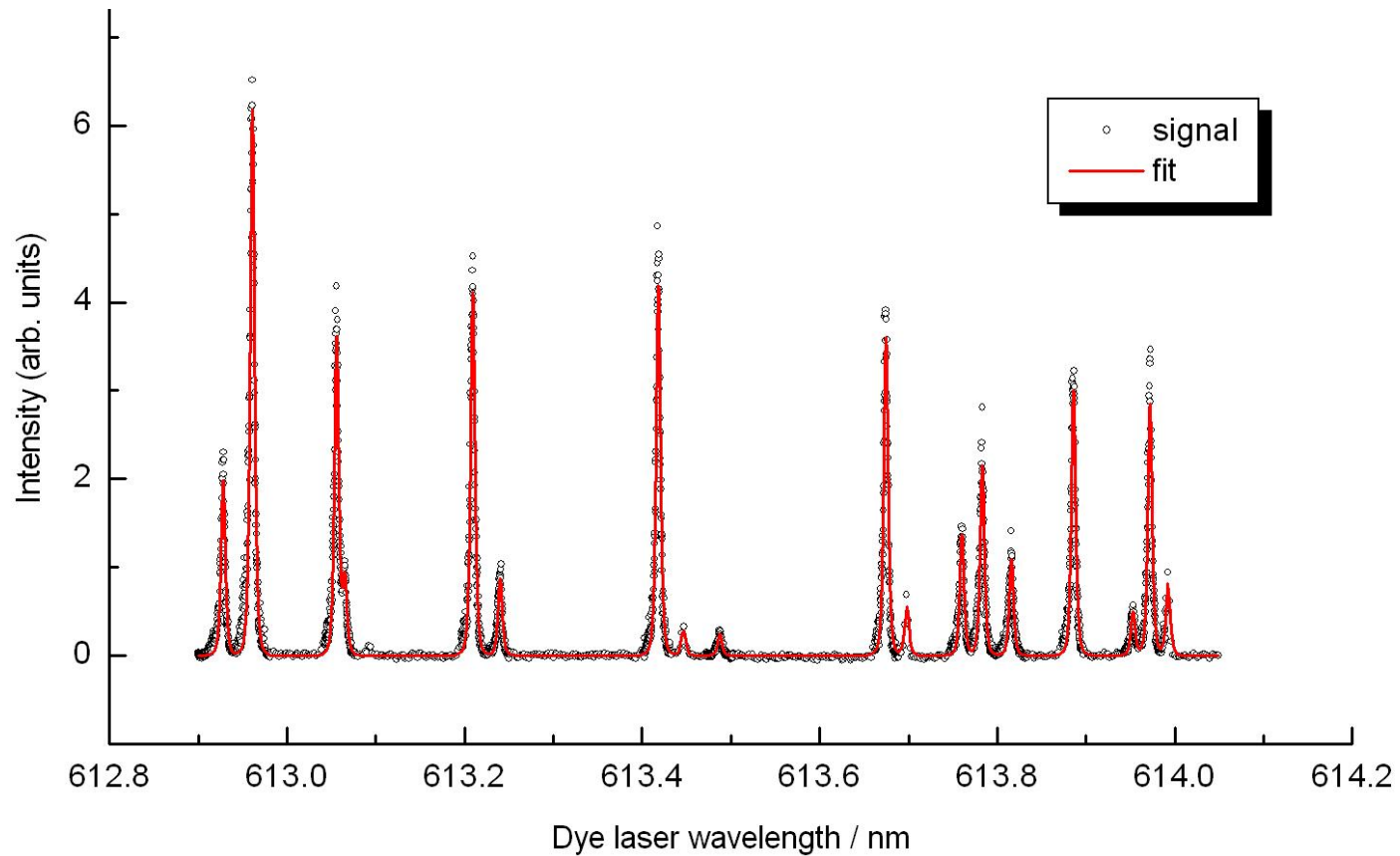
FIG. 2. Doppler-free two-photon spectrum of the hydrogen 1S-2S transition with simultaneously recorded saturation spectrum of ¹³⁰Te₂. The tellurium reference spectrum appears shifted towards lower frequencies by 60 MHz as a result of the acousto-optic modulator.



Doppler-free Two-photon spectrum of Hydrogen 1S – 2S transition
Tests QED calculation of electron interaction with proton



Doppler-free spectrum of OH molecule in a flame



THE END

