ATOMIC PHYSICS
Revision Lectures

Lecture 1	Schrödinger equation Atomic structure and notation Spin-orbit and fine structure
Lecture 2	Atoms in magnetic fields Radiation and Lasers
Lecture 3	Nuclear effects: hyperfine structure Two electron atoms X-rays

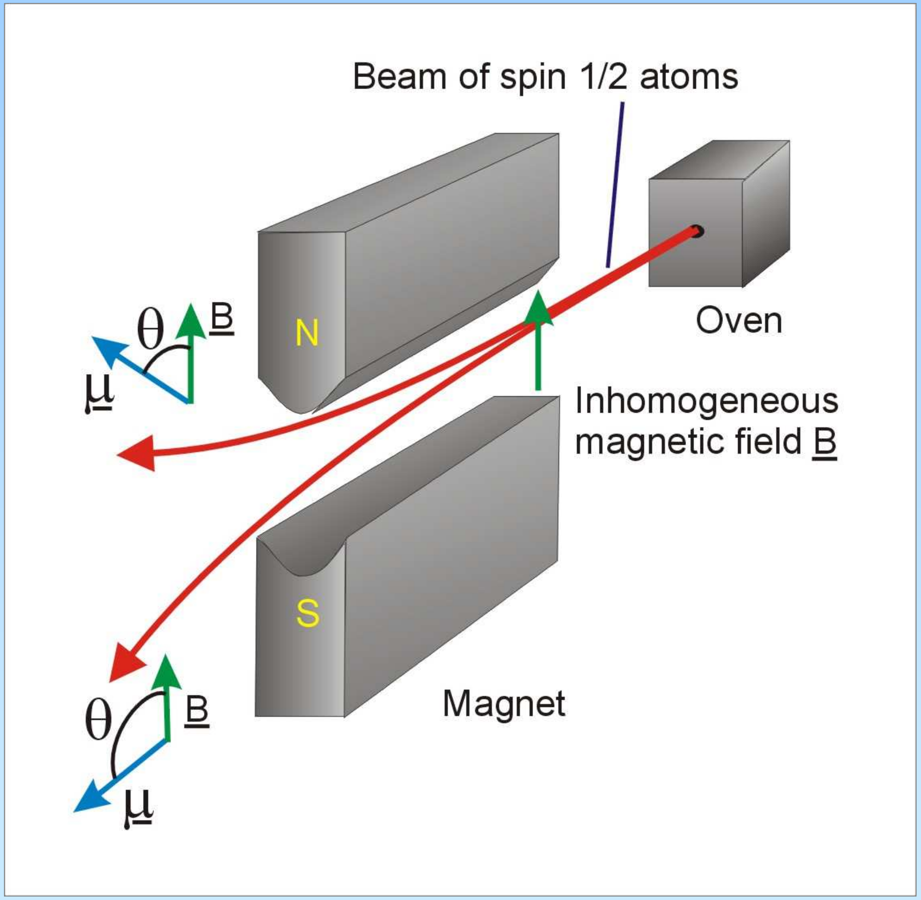
Stern Gerlach Experiment

- Demonstrates quantization of direction for interacting vectors
- A consequence of quantization of energy E
- Interaction energy for magnetic dipole $\underline{\mu}$ in field $\underline{B}$ is:

$$E = \underline{\mu}.\underline{B} = \mu.B \cos\theta$$

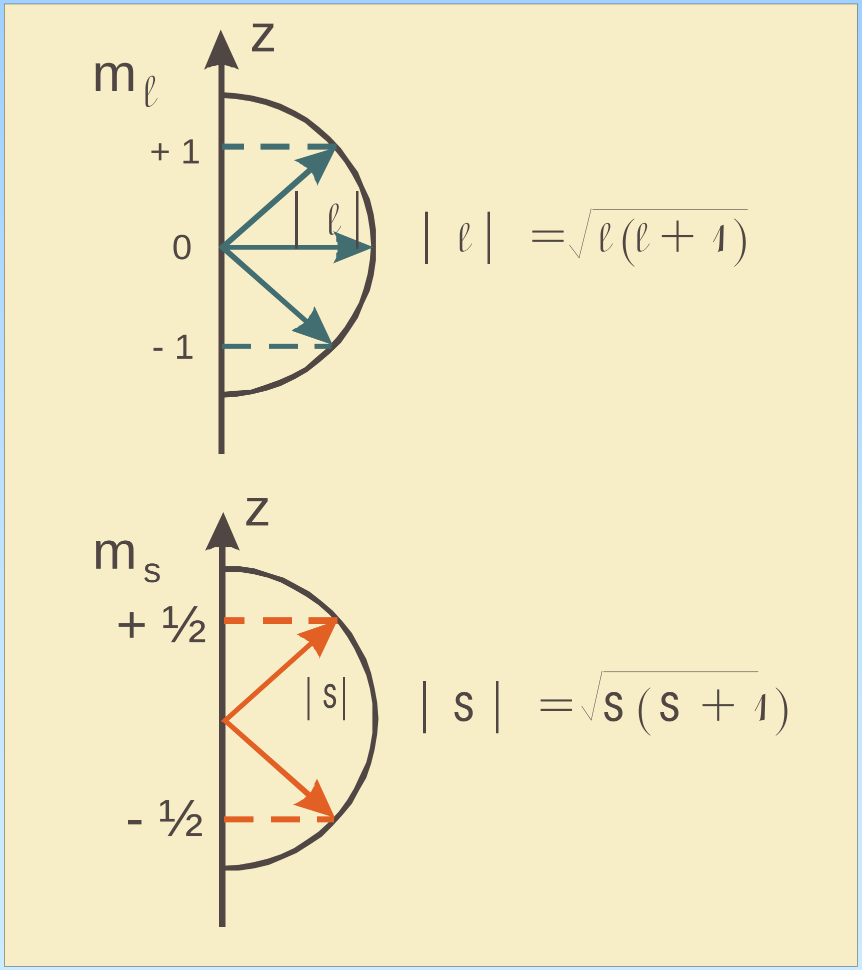
- Since μ and B are constant in time, $\cos\theta$ is quantized
- Force on atoms is:

$$\underline{F} = -\underline{\mu}.\frac{d\underline{B}}{dz}\underline{\vec{k}}$$



Directional quantization

- Direction defined by magnetic field along the z-axis
- The magnetic moment due to orbital angular momentum ℓ is m_ℓ
- The magnetic moment due to spin s is m_s
- Each orientation has different energy in field B
- In zero field the states are degenerate



The Schrödinger Equation

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right\}\psi(r,\theta,\phi) = E_n\psi(r,\theta,\phi)$$

$$\psi(r,\theta,\phi) = R(r)\Phi(\theta,\phi)$$

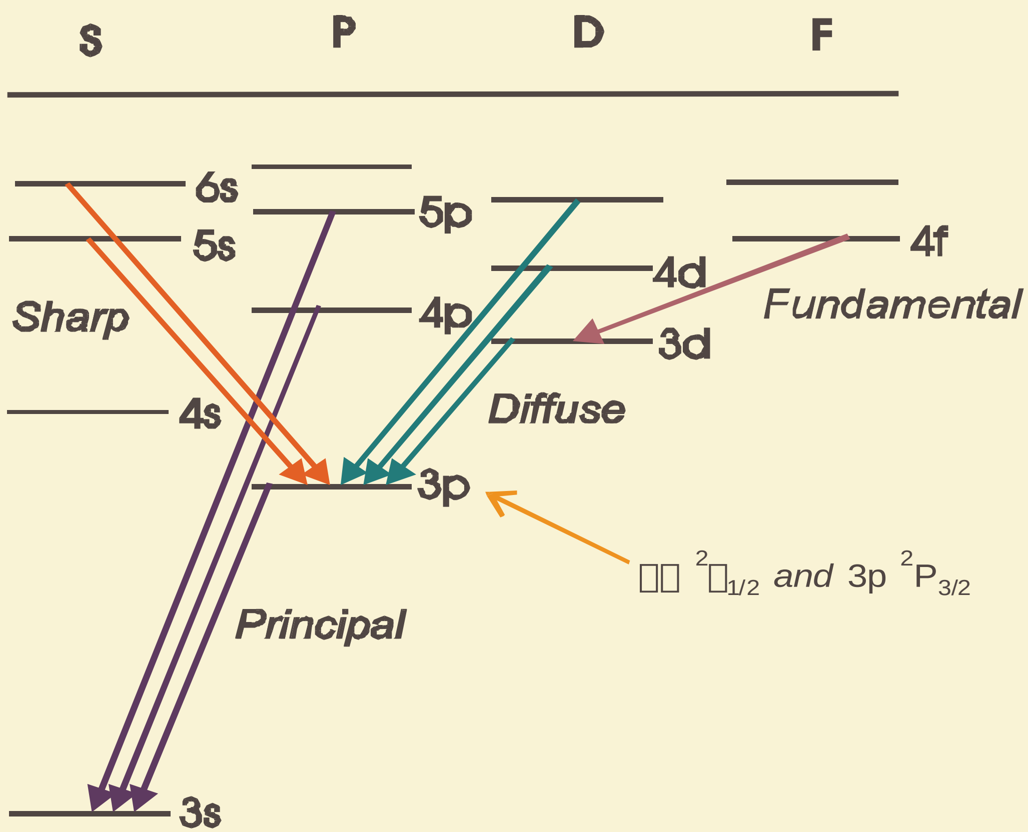
$$V(r) = \frac{Ze^2}{4\pi\varepsilon_o r} + \xi(\underline{s}.\underline{l}) + \zeta(\underline{\mu}.\underline{B}) + \left\{\frac{e^2}{4\pi\varepsilon_o r_{12}}\right\}$$

Nuclear Coulomb | **Spin-Orbit** | **External Field** | **{electron-electron interaction}**

Energy Level Diagrams

SPECTROSCOPIC NOTATION

[configuration) $^{2S+1}L_J$ eg. Na: $(1s^2 2s^2 2p^6 3s)\ 3^2S_{1/2}$



Spectroscopic Notation

- One electron atoms e.g. Na

(configuration) $^{2s+1}l_j$ $1s^2 2s^2 2p^6\ 3s\ \ {}^2S_{1/2}$

$1s^2 2s^2 2p^6\ 3p\ \ {}^2P_{1/2}\ ,\ {}^2P_{3/2}$

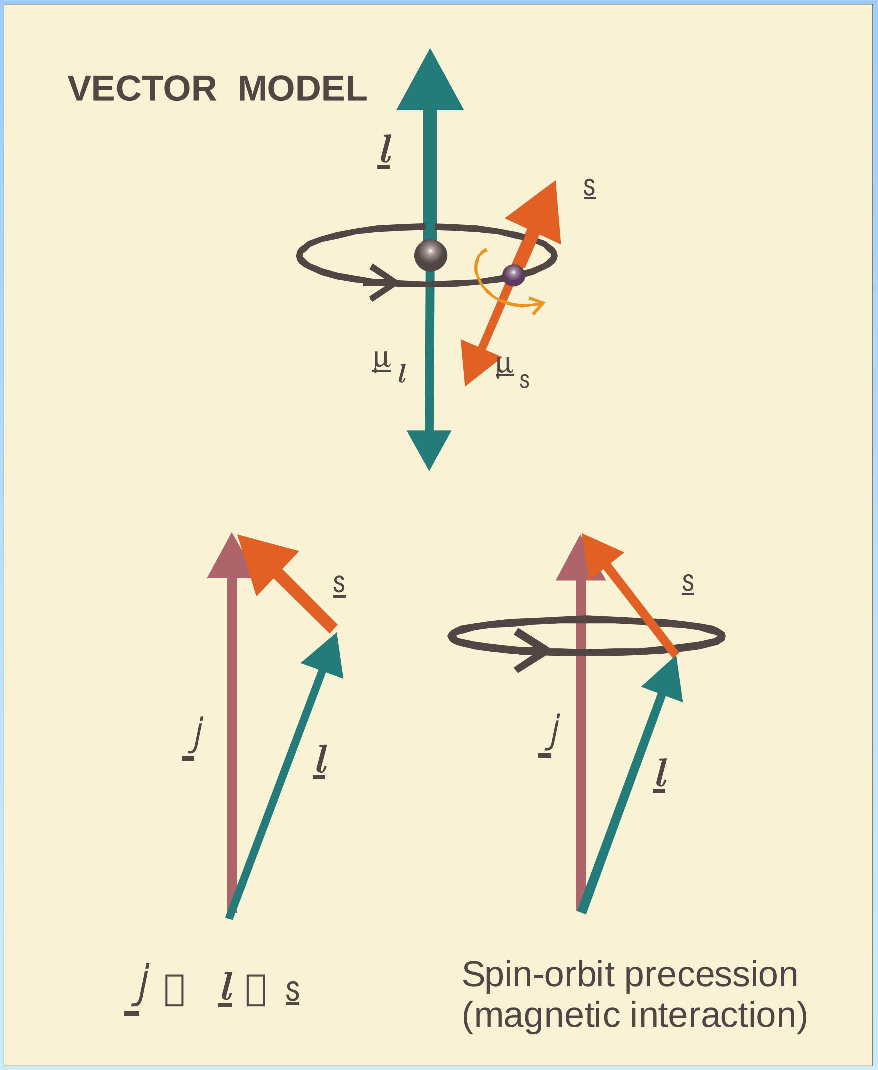
- Two electron atoms e.g. Mg

(configuration) $^{2S+1}L_J$ $1s^2 2s^2 2p^6\ 3s^2\ \ {}^1S_0$

$1s^2 2s^2 2p^6\ 3s3p\ \ {}^1P_1\ {}^3P_{2,1,0}$

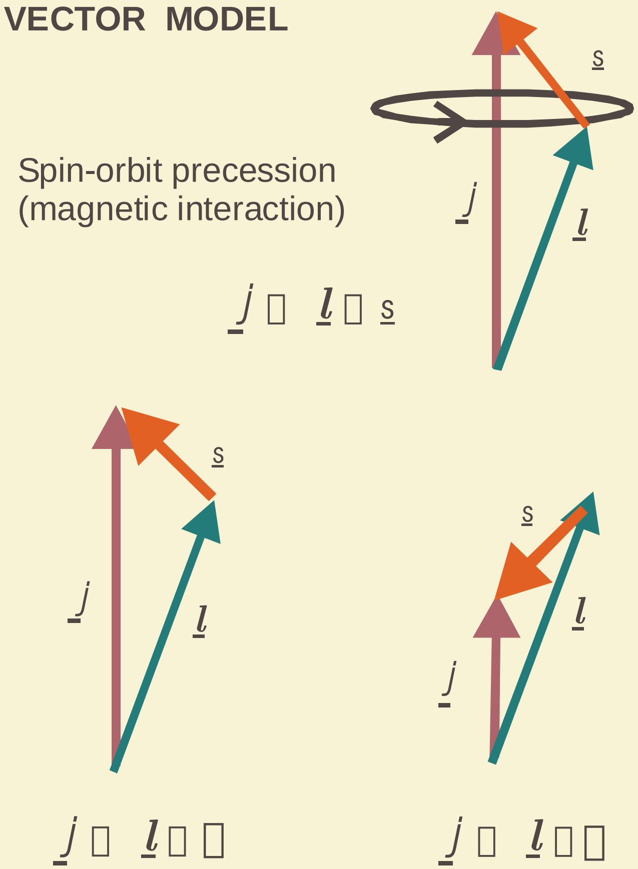
Vector Model: spin-orbit interaction

- Orbital $\underline{l}$ and spin $\underline{s}$ angular momenta give magnetic moments $\underline{m}_l$ and $\underline{m}_s$
- Orientation of $\underline{m}_l$ and $\underline{m}_s$ is quantized
- Magnetic interaction gives precessional motion
- Energy of precession shifts the energy level depending on relative orientation of $\underline{l}$ and $\underline{s}$



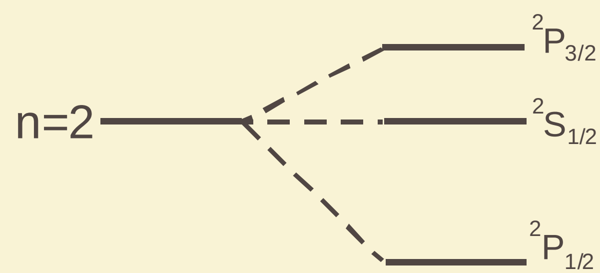
Fine structure from spin-orbit splitting in n=2 level of Hydrogen

VECTOR MODEL



For n = 2, l = 1, $^2P_{1/2}$ and $^2P_{3/2}$

Spin-orbit splitting of n=2 level in H

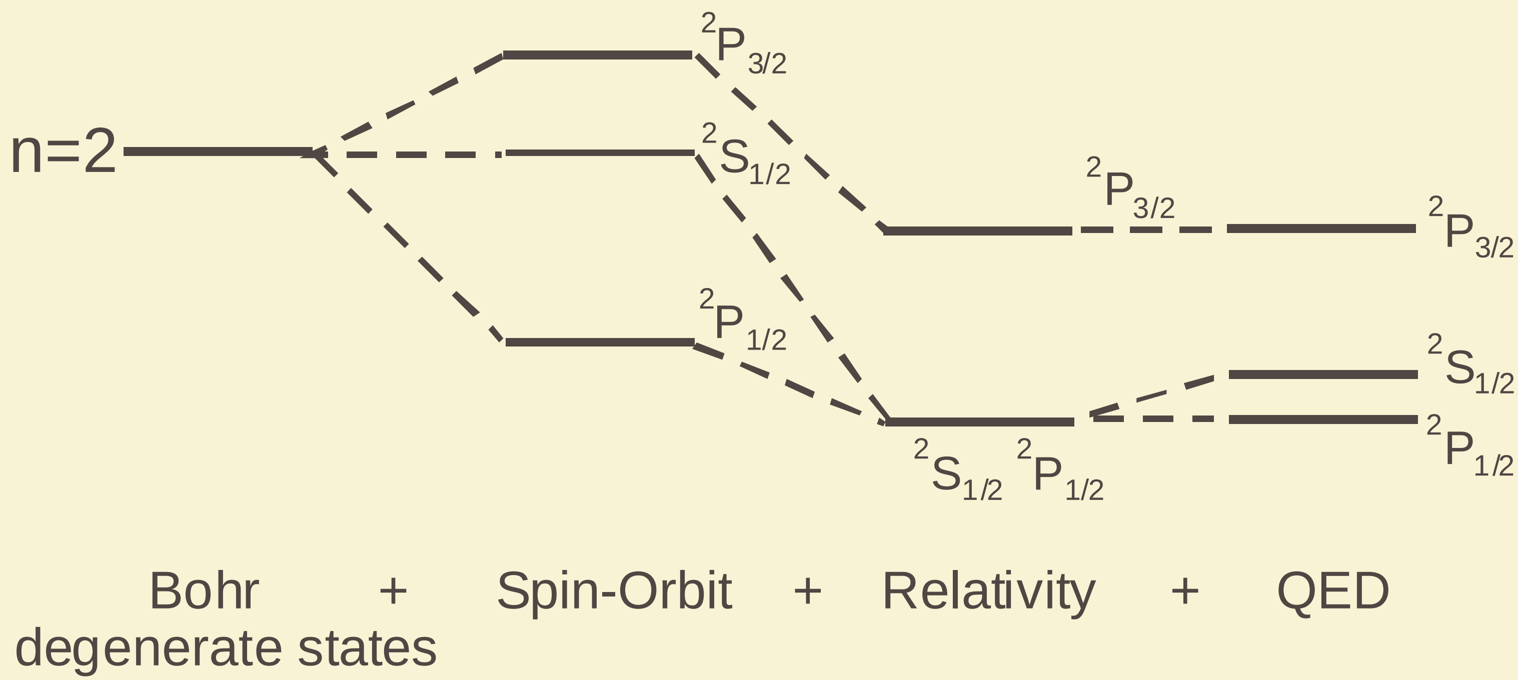


Bohr + Spin-Orbit
degenerate states

Note: only the ^2P term is split, l = 1

no splitting of ^2S as l = 0

Fine structure in n=2 level in hydrogen

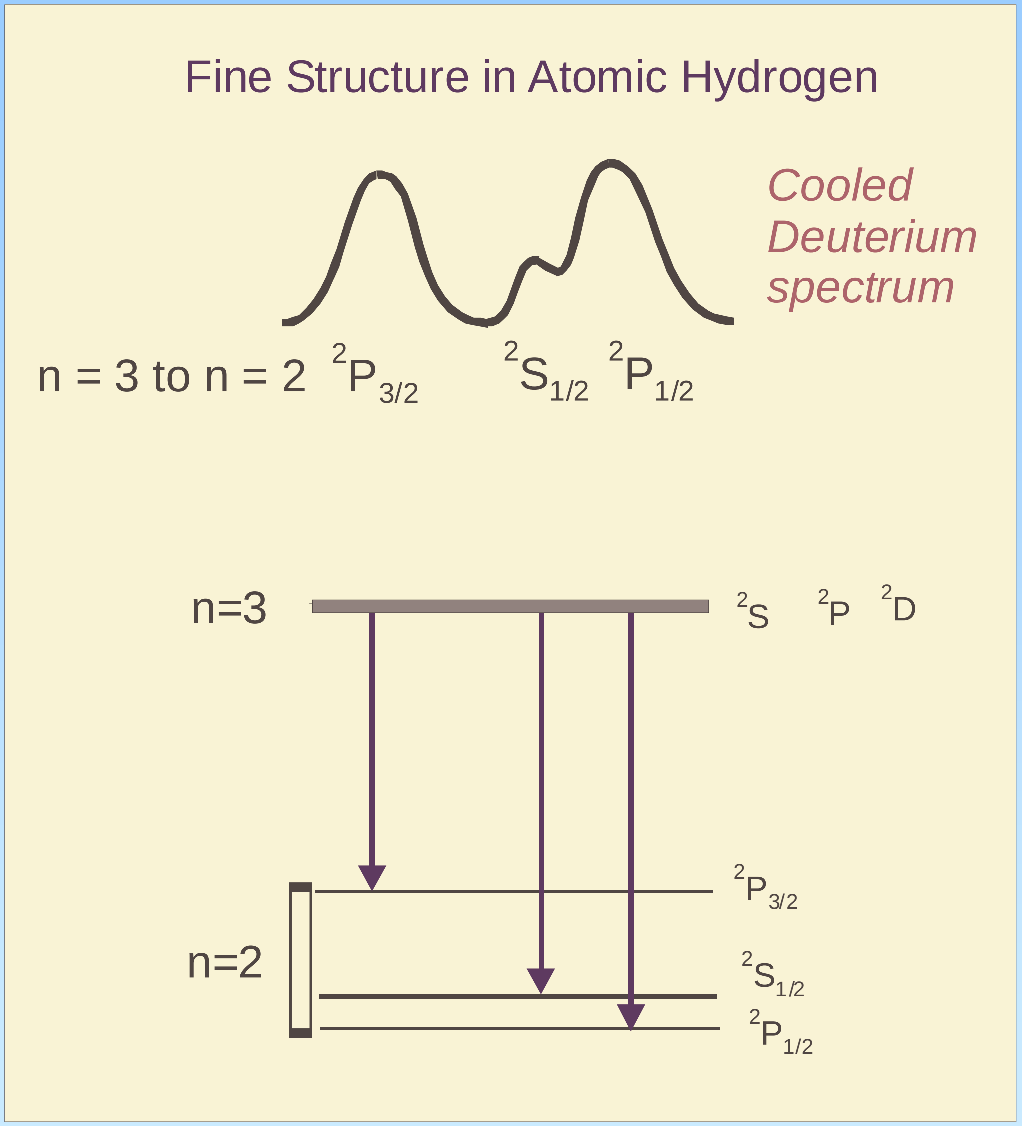


- Separation of $^2S_{1/2}$ -$^2P_{1/2}$: the Lamb shift, a QED effect, was first measured by RF spectroscopy in Hydrogen; microwave transition at 1057 MHz

- Optical measurement uses emission of Balmer α line from Deuterium gas discharge

- Spectrum formed using Fabry-Perot interferometer for high resolution.

- Shift of $^2S_{1/2}$ - $^2P_{1/2}$ is resolved



End lecture 1

- Example finals questions

(1996) A3 question 1

1. Write down the Schrödinger equation for the hydrogen atom. Use the ground state wave function $\psi_0(r) = Ae^{-br}$ (A, b are constants) to find the energy of the ground state, showing that the energy is consistent with the Bohr formula,

$$E_n = -\frac{R_\infty}{n^2}$$

where n is the principal quantum number and R_∞ is the Rydberg constant. [8]

Draw a diagram showing the fine structure of the energy levels for $n = 2$ and $n = 3$ for the hydrogen atom. Indicate on the diagram the relevant quantum numbers and the allowed radiative transitions between these levels. [6]

The separation of the $2p\,^2P_{1/2}$ and $2p\,^2P_{3/2}$ levels of hydrogen is $0{\cdot}36\,\mathrm{cm}^{-1}$ or $4{\cdot}5 \times 10^{-5}$ eV. Discuss any difficulties which might be encountered in studying this fine-structure splitting in a laboratory discharge. [6]

Positronium is the bound system of an electron and a positron. Write down the energy levels of the gross structure of this system, and explain why it might be preferred for testing the Coulomb interaction at short distances. [5]

$$\left[R_\infty = \frac{m_e e^4}{2\hbar^2 (4\pi\epsilon_0)^2} \right]$$

(1995) A3 Question 2

2. An electron with orbital angular momentum operator $\hat{\ell}\hbar$ in a central electrostatic potential $V(r)$ has a spin-orbit interaction

$$V_{\text{so}} = -\frac{e\hbar^2}{2m^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\hat{\ell}\cdot\hat{\mathbf{s}}\ ,$$

where m is the electron mass and $\hat{\mathbf{s}}\hbar$ its spin operator.

Show that, in first-order perturbation theory, the spin-orbit interaction leads to a splitting of the energy levels of an electron bound in a central potential with quantum numbers n and ℓ but does not change the mean energy of the states involved. [9]

The expectation value of $1/r^3$ for an eigenstate of the hydrogen atom with quantum numbers n and ℓ is

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

where a_0 is the Bohr radius. Find (in units of eV) the fine-structure splitting for hydrogen with $n = 2$, $\ell = 1$. Estimate the fine-structure splitting for hydrogen-like potassium with $n = 2$, $\ell = 1$ (atomic number $Z = 19$). [9]

Describe the principles and basic experimental details of one method for the measurement of fine structure in the energy levels of an atom or ion of your choice. [7]

Normal Zeeman Effect

<u>Vector Model</u>

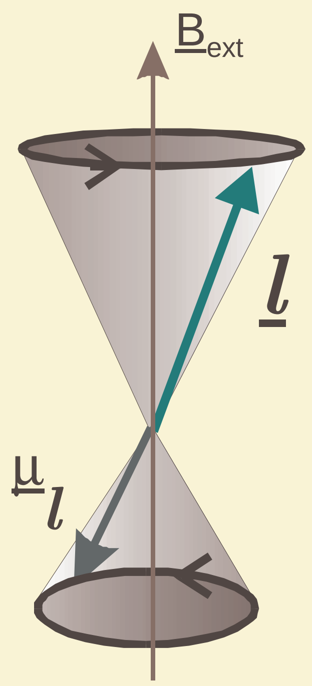
- Magnetic moment due to orbital motion

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

- Energy of precession in external field B is:

$$\Delta E_Z = \underline{\mu}.\underline{B}_l$$

Orbital magnetic moment in external magnetic field



Magnetic dipole precession

Normal Zeeman Effect

- Perturbation Energy (precession in B field)

  $\langle \Delta E_Z \rangle = \langle \underline{\mu}_B . \underline{B}_{ext} \rangle$

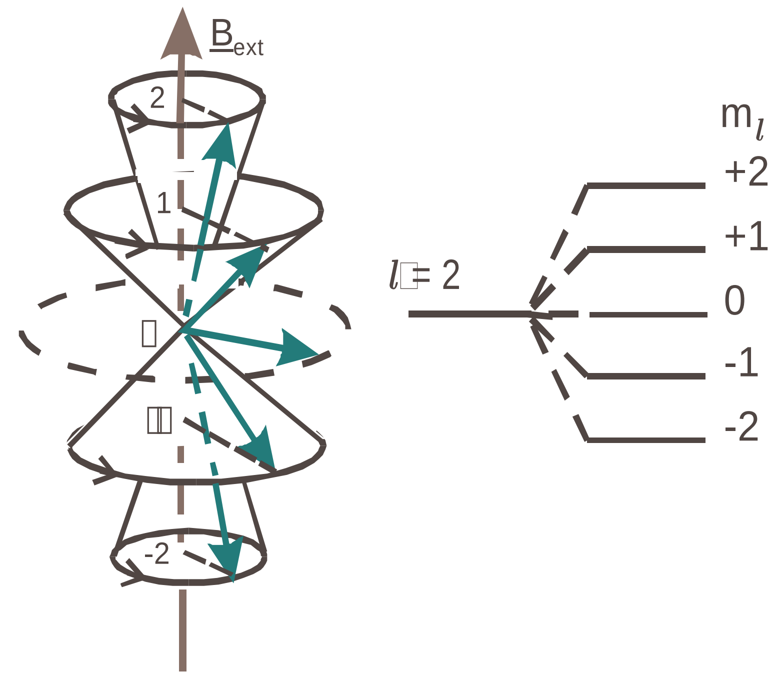
- $\langle \Delta E_Z \rangle = g_l \underline{\mu}_B . \underline{B}_{ext} m_l$

- $2l+1$ sub-levels

- Separation of levels:

  $\mu_B B_{ext}$

Orbital magnetic moment in external magnetic field



Normal Zeeman Effect

- Selection rules:

$$\Delta m_l = 0, \underline{+}1$$

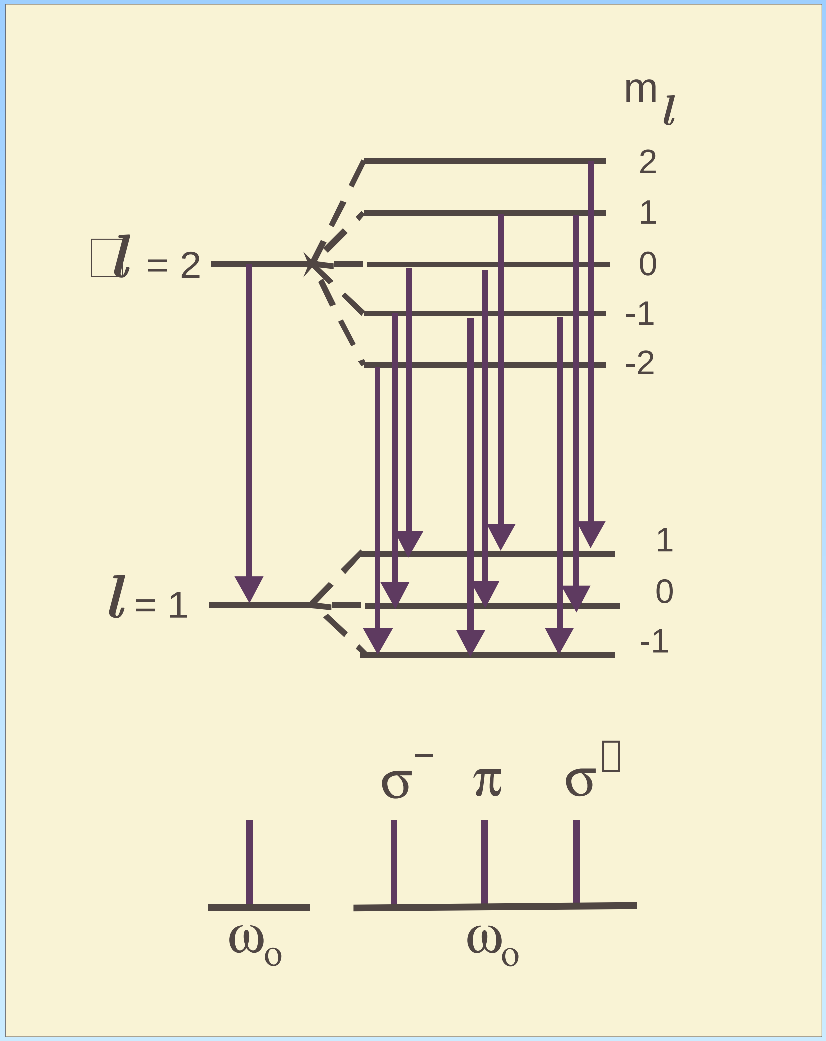
- Polarization of light:

$\Delta m_l = 0,$ π along z-axis

$\Delta m_l = \underline{+}1$ σ^+ or σ^-

σ, circular viewed along z-axis

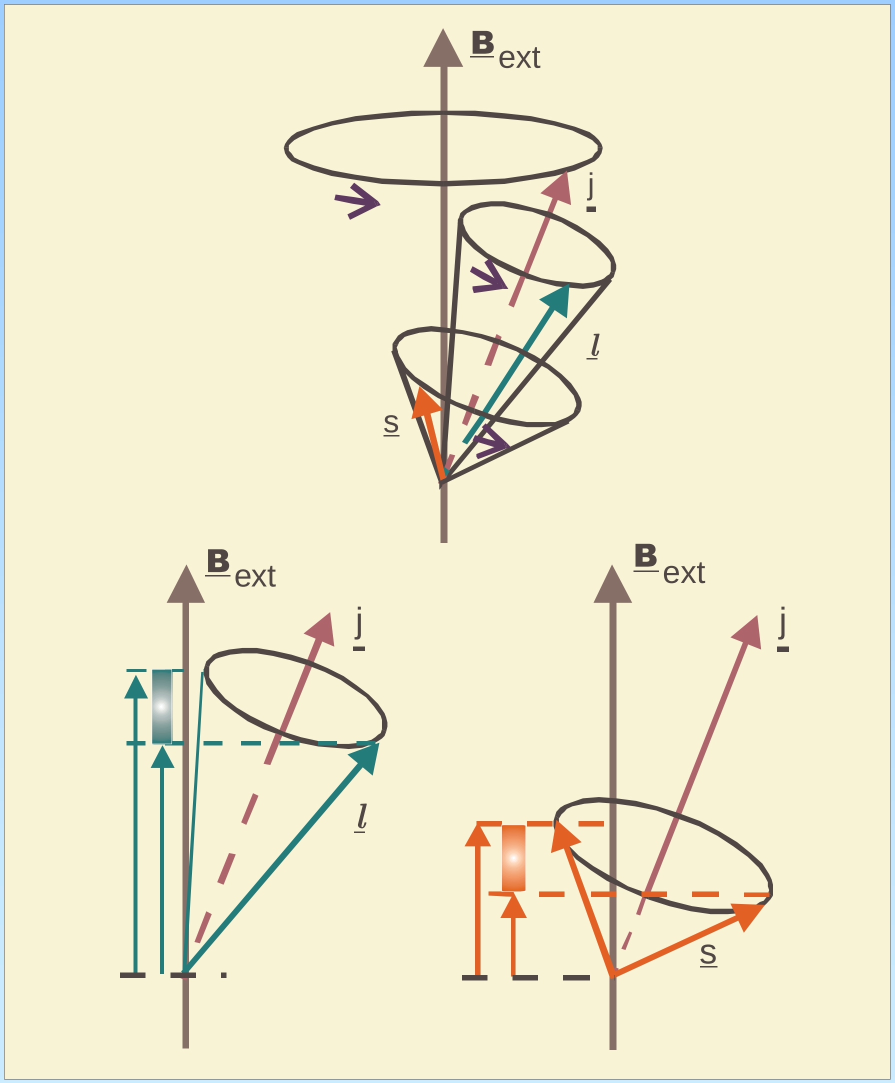
π, plane viewed along x,y-axis



Anomalous Zeeman Effect

<u>Vector Model</u>

- Spin-orbit coupled motion in external magnetic field.
- Projections of $\underline{l}$ and $\underline{s}$ on B_{ext} vary owing to precession around $\underline{j}$.
- m_l and m_s are no longer good quantum numbers



Anomalous Zeeman Effect

- Total magnetic moment $\underline{\mu}_{Total}$ precesses around effective magnetic moment $\underline{\mu}_{□□□}$

- Effective magnetic moment due to total angular momentum

$$\underline{\mu}_{□□□} = -g_{□}\mu_B\underline{□}$$

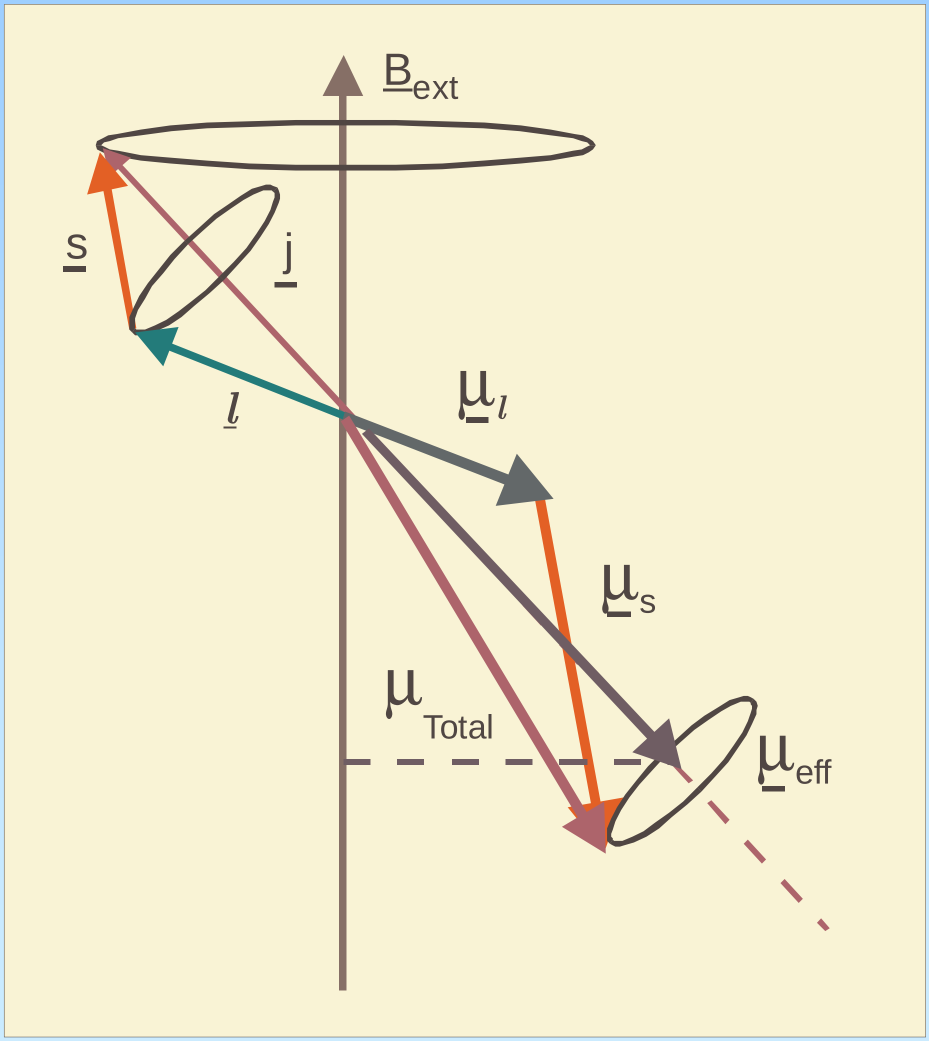
- Landé g-factor is:

$$g_j = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$$

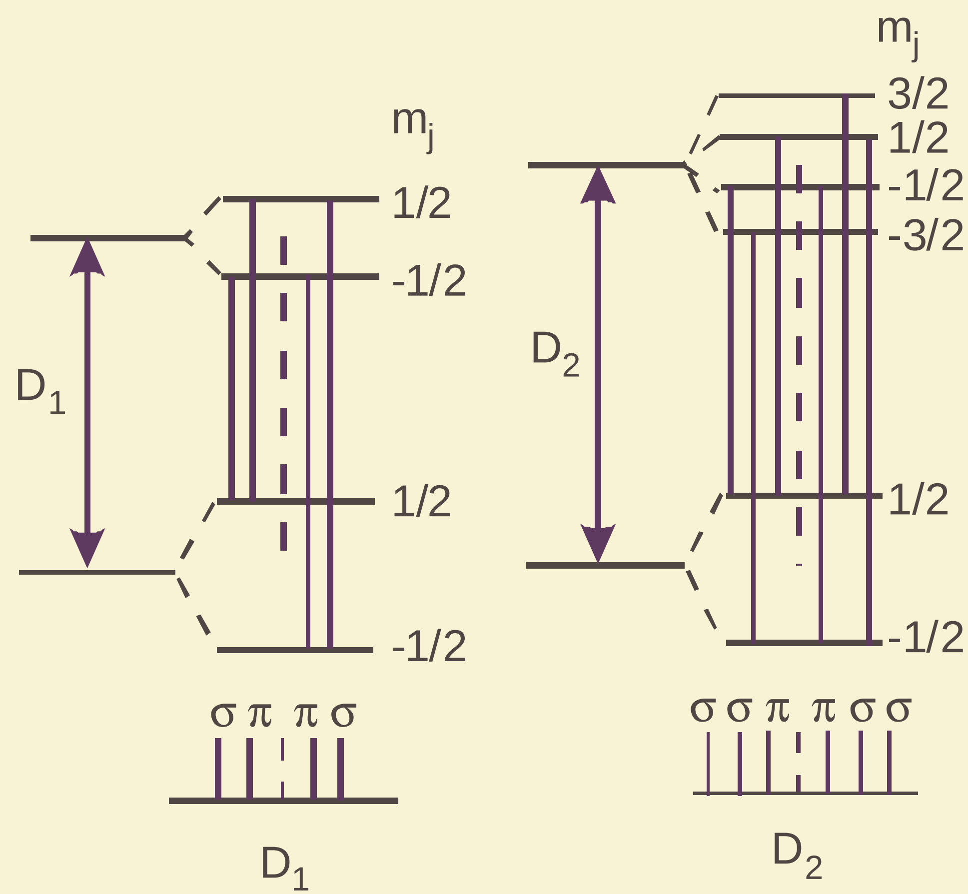
- Energy of precession in external field B is:

$$\Delta E_{AZ} = -\underline{\mu}_{□□□}.\underline{B}_{ext}$$

$$= \quad g_{□}\mu_B B_{ext} m_j$$

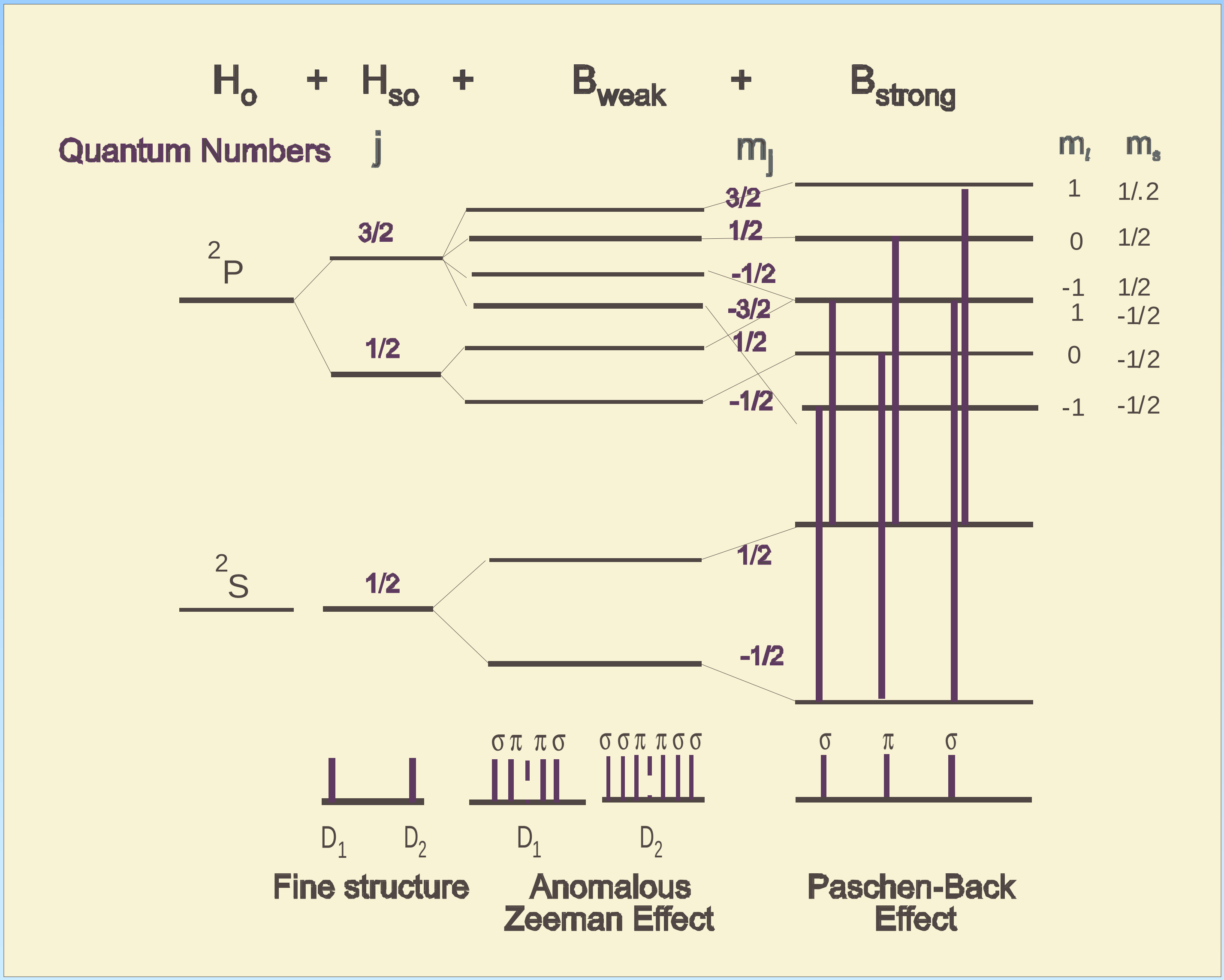


Anomalous Zeeman Effect: Na D - lines

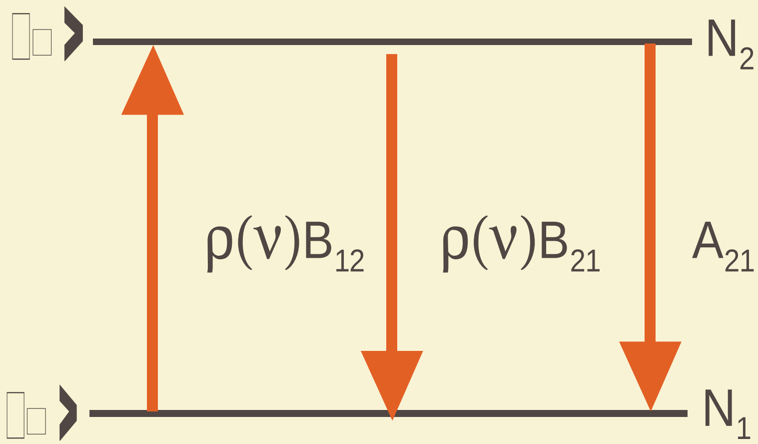


Selection rules: $\Delta m_j = 0, \pm 1$

Magnetic effects in one - electron atoms



Atomic physics of lasers



$\rho(\nu)$ Energy density of incident radiation

$\rho(\nu)B_{12}$ *Rate of stimulated absorption*

$\rho(\nu)B_{21}$ *Rate of stimulated emission*

A_{21} *Rate of spontaneous emission*

Rate equation:

$$\frac{dN_2}{dt} = B_{12}\rho(\nu)N_1 - B_{21}\rho(\nu)N_2 - AN_2$$

Steady state:

$$\frac{N_2}{N_1} = \frac{B_{12}\rho(\nu)}{A + B_{21}\rho(\nu)} = \exp\left(-\frac{h\nu}{kT}\right)$$

$$\rho(\nu) = A\frac{1}{[B_{12}\exp(h\nu/kT) - B_{21}]}$$

Planck law:

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{[\exp(h\nu/kT) - 1]}$$

Hence:

$$B_{12} = B_{21} = B$$

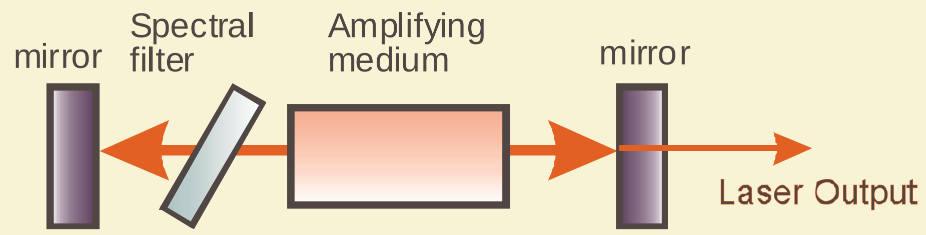
$$A = \frac{8\pi h\nu^3}{c^3}B$$

Laser operation

Rate of change of

photon number density n

$$\frac{dn}{dt} = -\frac{dN_2}{dt}$$



photon lifetime in cavity, τ_p

$$\therefore \quad \frac{dn}{dt} = (N_2 - N_1) B_{12} \rho(\nu) - \frac{n}{\tau_p}$$

and

$$\rho(\nu)\Delta\nu = n.h\nu$$

$$B_{12}\rho(\nu) = \left\{ \frac{c^3 A}{8\pi\nu^2 \Delta\nu} \right\} n = Qn$$

$$\frac{dn}{dt} = \left\{ (N_2 - N_1) Q - \frac{1}{\tau_p} \right\} n$$

$$\therefore \quad n(t) = n(0) \exp\left\{ (N_2 - N_1) Q - \frac{1}{\tau_p} \right\} t$$

Gain if $(N_2 - N_1) > \dfrac{1}{Q\tau_p}$

End lecture 2

(1998) A3 question 1

1. Discuss briefly **two** types of experimental evidence for assigning to the electron an intrinsic angular momentum of $\hbar/2$. [6]

Show that in the presence of a weak magnetic flux density B an atomic energy level described by L, S, J splits into levels displaced in energy by

$$\Delta E = \mu_{\mathrm{B}} B M_J g_J$$

and obtain an expression for g_J. [6]

An atom has a transition ${}^1\mathrm{P}_1 - {}^1\mathrm{S}_0$ which, in the presence of a weak magnetic flux density B, has three components separated by wavenumber intervals of $30\,\mathrm{m}^{-1}$. What is the value of B and the direction of the observations with respect to B? An alkali atom has a transition with wavenumber $\tilde{\nu}_0$. In the same magnetic flux density and direction of observation this transition splits into components at $\tilde{\nu} = \tilde{\nu}_0 \pm 10\,\mathrm{m}^{-1}$, $\tilde{\nu}_0 \pm 30\,\mathrm{m}^{-1}$ and $\tilde{\nu}_0 \pm 50\,\mathrm{m}^{-1}$. What are the values of S and J of the levels involved in the transition at $\tilde{\nu}_0$? Find the values of g_J and L for these levels. [7]

Describe briefly the experimental apparatus suitable for measuring such Zeeman splittings of a transition at 500 nm. [6]

Nuclear spin hyperfine structure

- Nuclear spin μ_I interacts with magnetic field B_o from total angular momentum of electron, $\underline{F}$

$$\mu_I = g_I \mu_N \underline{I}$$

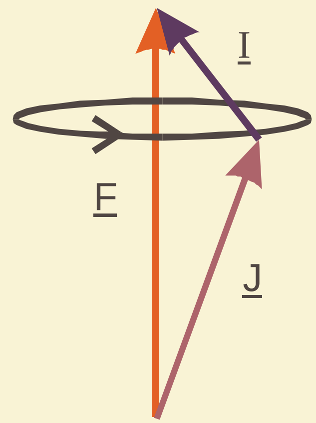
- Interaction energy:

$$H' = A_J\, \underline{I}.\underline{J}$$

- Shift in energy level:

$$\Delta E_{hfs} = \langle H' \rangle$$

Vector model of Nuclear Spin interaction



$\underline{J}$ = Total electronic angular momentum

$\underline{I}$ = Nuclear spin

$\underline{F}$ = Total atomic angular momentum

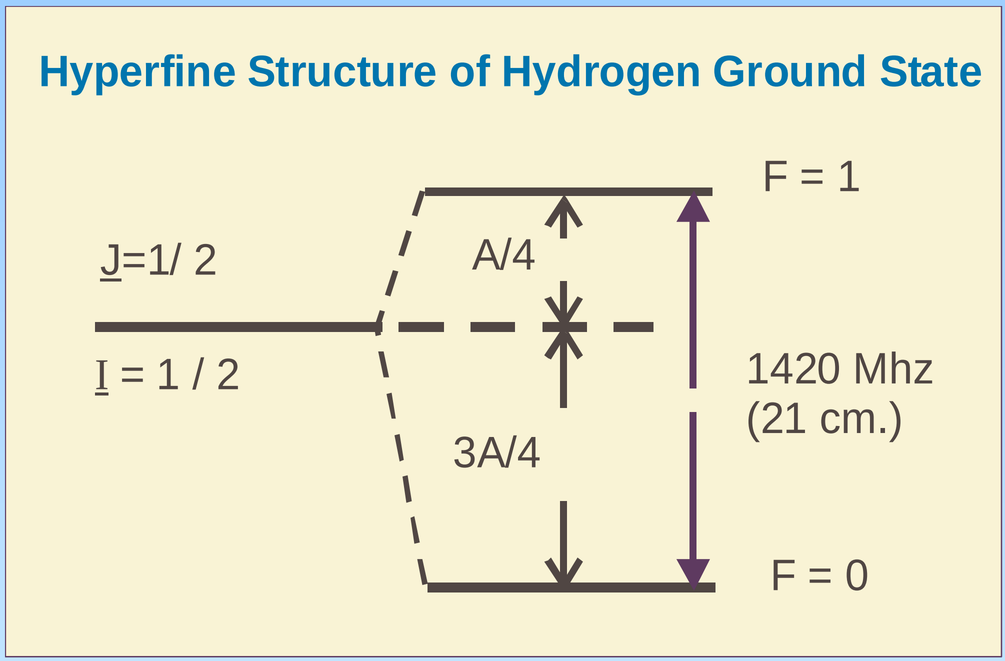
$\underline{F} = \underline{I} + \underline{J}$

$\underline{I}.\underline{J} = 1/2\,\{\underline{F}^2 - \underline{I}^2 - U^2\}$

$$\Delta E_{hfs} = (1/2)\, A_J\{F(F+1) - I(I+1) - J(J+1)\}$$

Hyperfine structure of ground state of hydrogen

- Hyperfine Energy shift:
  $\Delta E_{hfs} = A_J \, \underline{I}.\underline{J}$
- Fermi contact interaction:
  spin of nucleus with
  spin of electron
- Hyperfine interaction constant
  $A_J \rightarrow A_S$
- I = ½ , J = ½, F = 1 or 0
- $\underline{I}.\underline{J}$ = {F(F+1) – I(I+1) – J(J+1)}
  = ¼ or -¾
- Hyperfine splitting $\Delta E = A_S$



$$A_J = A_S = \tfrac{2}{3}\mu_o g_S \mu_B \left(\mu_I / I \right)_P |\psi(0)|^2$$

Determination of Nuclear Spin I from hfs spectra

- Hyperfine interval rule

$$\Delta E(F) - \Delta E(F-1) = A_J F$$

- Relative intensity in transition to level with no (or unresolved) hfs is proportional to 2F+1

- The number of hfs spectral components is

$$(2\mathrm{I}+1) \text{ for } \mathrm{I} < J$$
$$(2J+1) \text{ for } \mathrm{I} > J$$

2-electron atoms

Schrödinger equation:

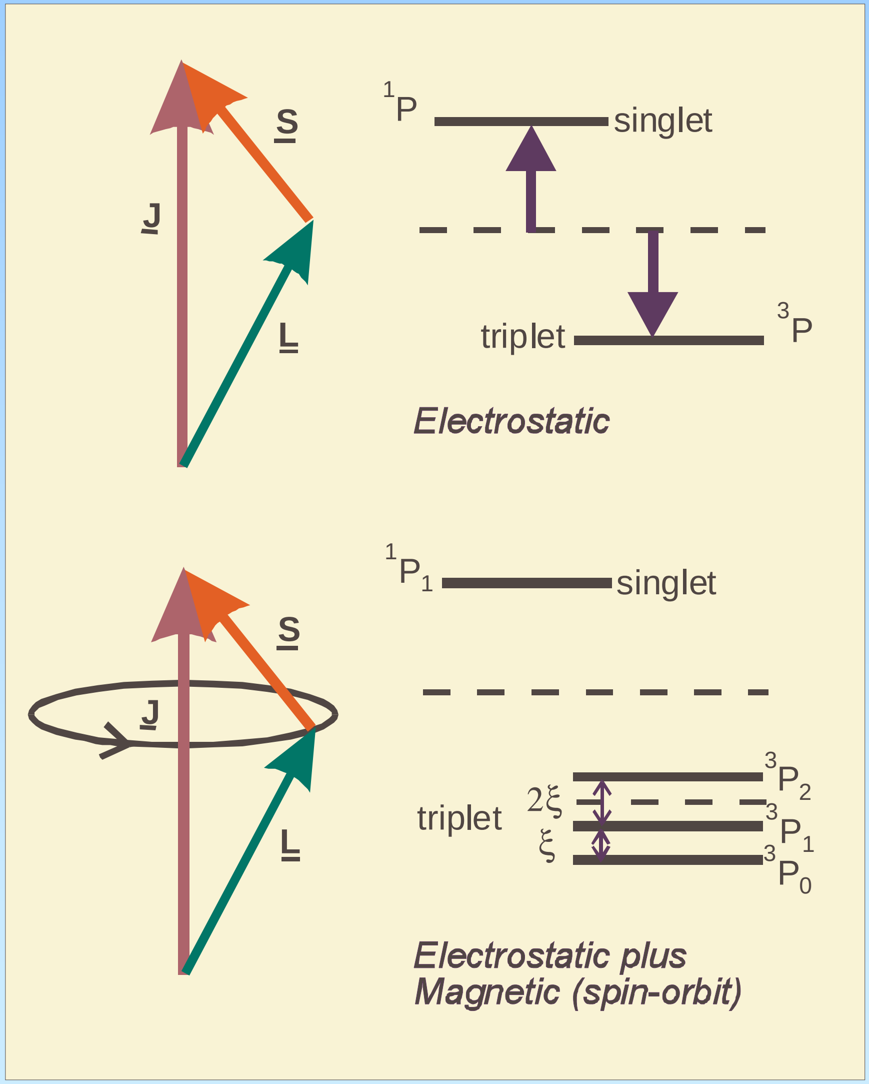
$$\left\{ -\frac{\hbar^2}{2m}\nabla_1{}^2 + \frac{\hbar^2}{2m}\nabla_2{}^2 + V(r) \right\} \psi(r,\theta,\phi) = E_n \psi(r,\theta,\phi)$$

$$V(r) = \sum_{i=1,2} \frac{Ze^2}{4\pi\varepsilon_o r_i} + \boxed{\frac{e^2}{4\pi\varepsilon_o r_{12}}} + \sum_{i=1,2} \xi_i (\underline{s}.\underline{l})$$

When <u>Electrostatic</u> interaction between electrons is the dominant perturbation $\rightarrow$ LS labelled terms

2 electron atoms: LS coupling

- **Electrostatic** interaction gives terms labelled by L and S
- $\underline{L} = \underline{l}_1 + \underline{l}_2$, $\underline{S} = \underline{s}_1 + \underline{s}_2$
- $\underline{J} = \underline{L} + \underline{S}$
- Terms are split by electrostatic interaction into Singlet and Triplet terms
- Magnetic interaction (spin-orbit) splits only triplet term



2-electron atoms: symmetry considerations

$$\Psi_{total} = \Phi(r,\theta,\phi)\chi^{\uparrow\downarrow}$$

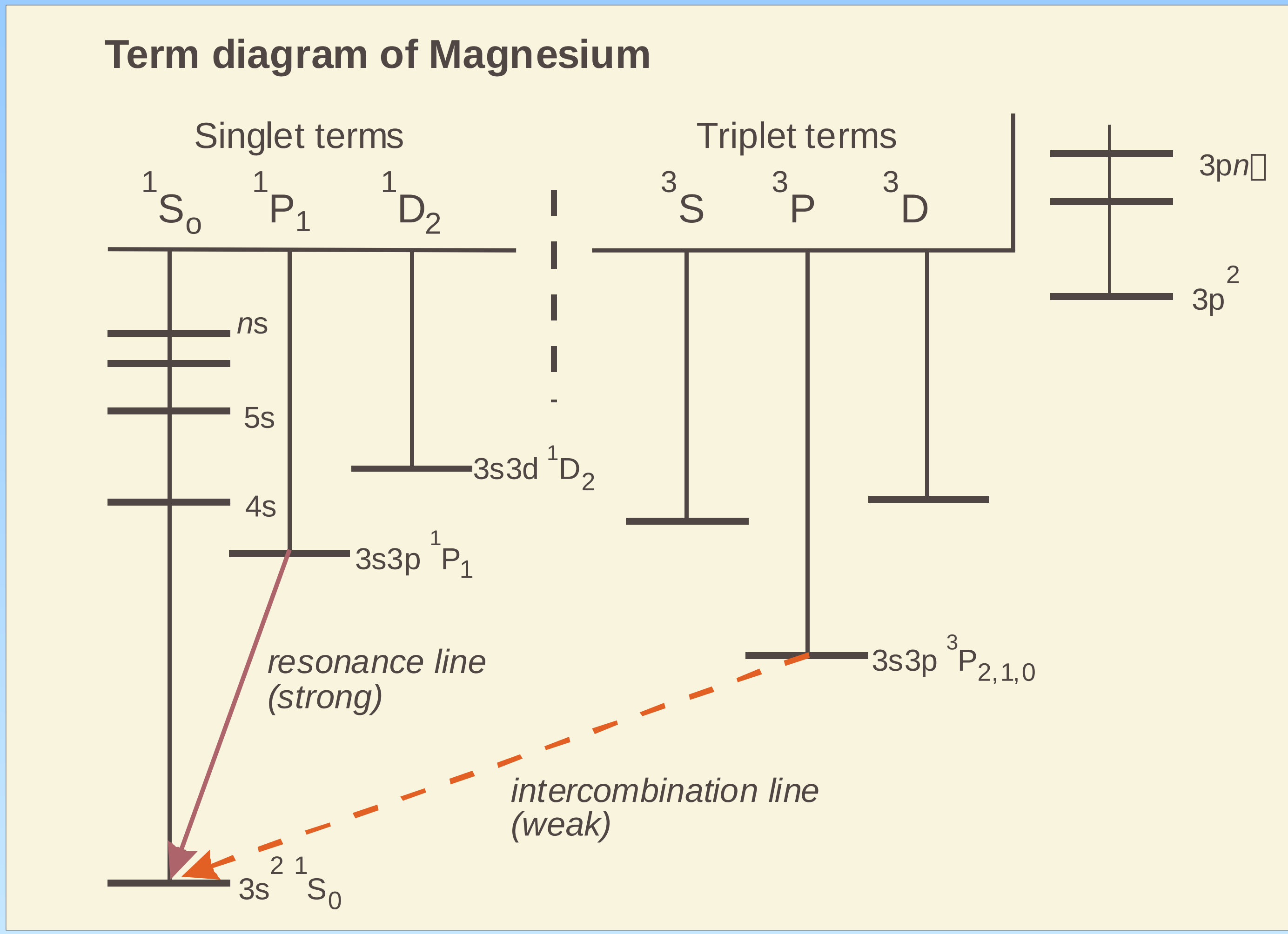
= *Antisymmetric function*

Spatial function

Spin function

- **Singlet terms** (S = 0):
  χ is antisymmetric, Φ is symmetric
  spatial overlap allowed (*Pauli Exclusion Principle*)
  increases electrostatic repulsion e^2/r_{12}

- **Triplet terms** (S = 1):
  χ is symmetric, Φ is antisymmetric
  spatial overlap forbidden (*Pauli Principle*)
  reduces electrostatic repulsion e^2/r_{12}

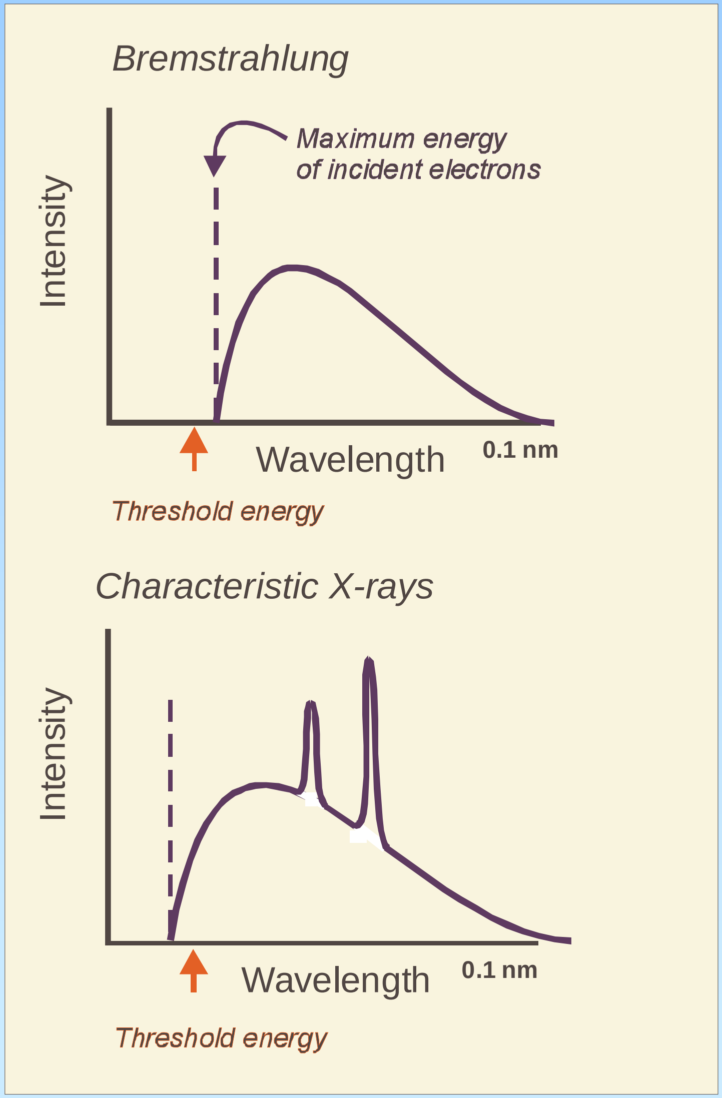


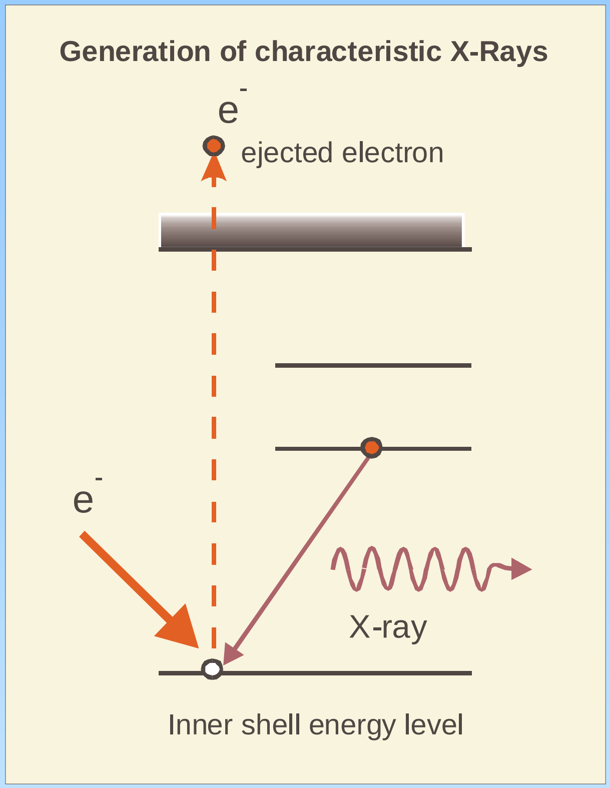
- Singlet and Triplet terms form separate systems
- Strong LS coupling:

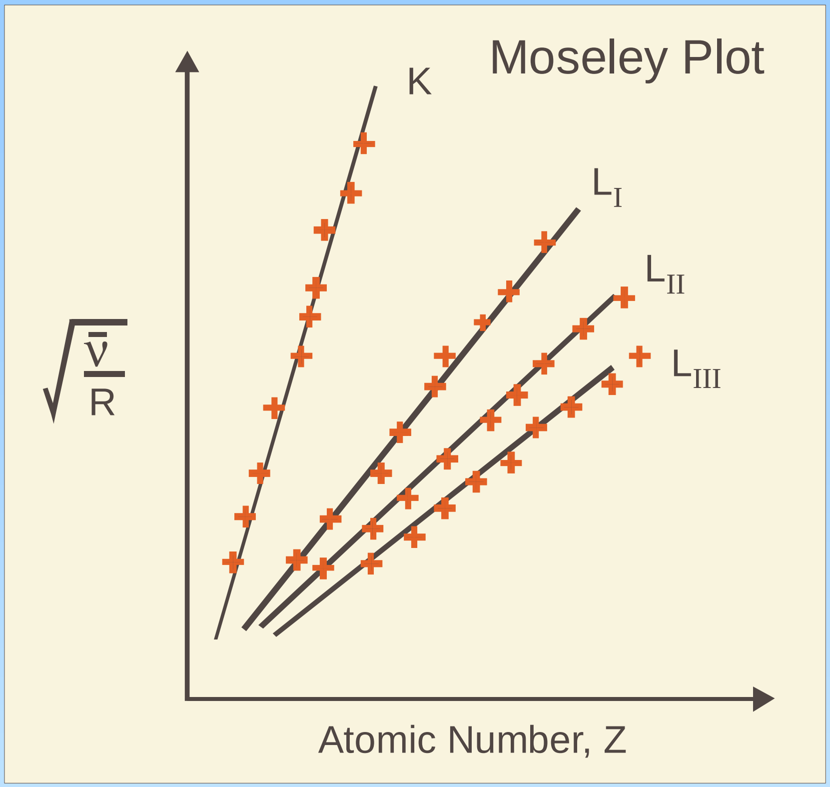
    Selection Rule $\Delta S = 0$ (weak intercombination lines)
    Singlet-Triplet splitting >> fine structure of triplet terms
    i.e Electrostatic interaction >> Magnetic (spin-orbit)
    Triplet splitting follows interval rule $\Delta E \propto J$

X-ray spectra

- Wavelengths λ fit simple formula
- All lines of series appear together
- Threshold energy for each series
- Above a certain energy no new series appear



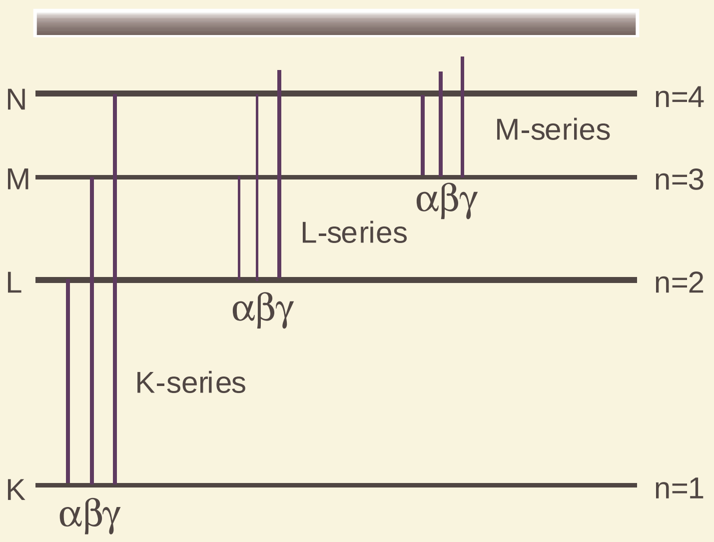




K – series: $$\bar{\nu}_K = R\left\{\frac{(Z-\sigma_K)^2}{1^2} - \frac{(Z-\sigma_i)^2}{n_i^2}\right\}$$

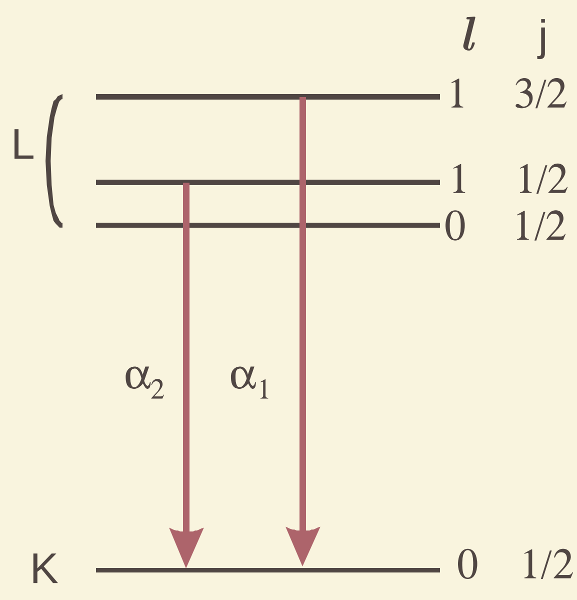
L – series: $$\bar{\nu}_L = R\left\{\frac{(Z-\sigma_L)^2}{2^2} - \frac{(Z-\sigma_i)^2}{n_i^2}\right\}$$

X-Ray Series



Fine structure of X-Rays

$\Delta l = \pm 1 \quad \Delta j = 0, \pm 1$

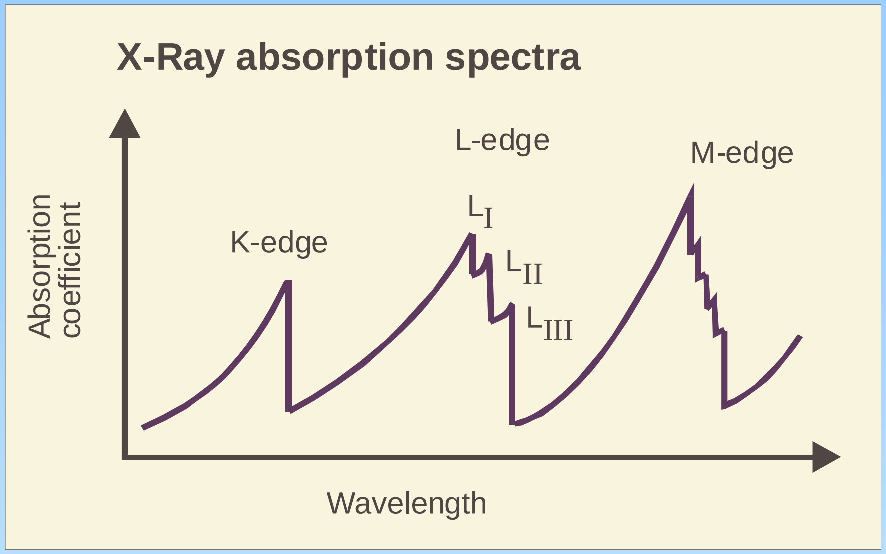


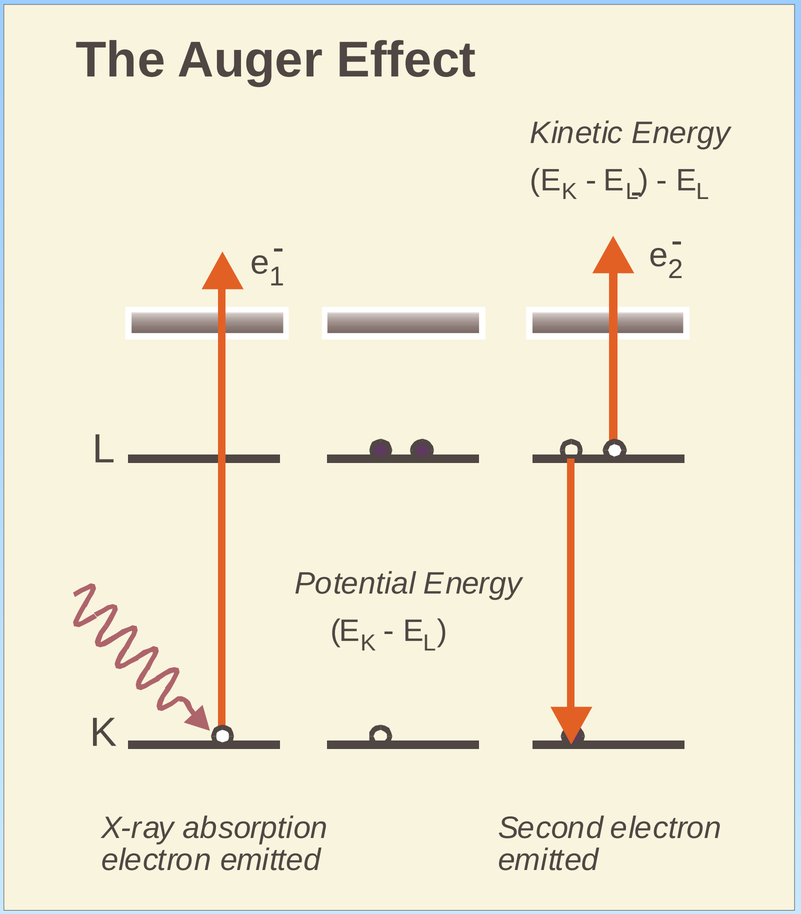
Series lines labelled by α,β, χ etc
for decreasing wavelength λ

Lines have fine structure due to
spin-orbit effect of “hole” in filled shell

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

Absorption of X-rays





- Absorption decreases below absorption edge due to effect of conservation of momentum
- Fine structure seen at edges
- Auger effect leads to emission of two electrons following X-ray absorption by inner shell electron