

Atomic and molecular physics

Revision lecture

Answer all questions

Angular momentum

$$\hat{\mathbf{J}}^2 |j, m\rangle = j(j+1) |j, m\rangle$$

$$\hat{J}_z |j, m\rangle = m |j, m\rangle$$

- Allowed values of m go from $-j$ to $+j$ in **integer steps**
- If there is no external field, energy cannot depend on the value of m – i.e. energy eigenstates are degenerate with respect to m
- Add two angular momenta: $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$
- Allowed values of j go from $|j_1 - j_2|$ to $j_1 + j_2$ in **integer steps**

Central field approximation

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

K.E. of
electron i

Coulomb attraction,
nucleus – electron i

Coulomb repulsion,
electron i – electron j

- Electron-electron repulsion term is large
- Separate it into a central part and a residual part
- First neglect the residual part – this is the central field approximation

Central field approximation

- Electrons moves independently in an effective central potential $V(r_i)$
- $V(r_i)$ contains the attraction to the nucleus and the central part of the electron-electron repulsion

$$\hat{H}_0 = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 + V(r_i) \right)$$

- Eigenfunctions separate into products of single electron functions
- Separate Schrodinger equation for each electron

$$\left(-\frac{\hbar^2}{2m_e} \nabla_i^2 + V(r_i) \right) \psi_{n,l,m_l} = E_{n,l} \psi_{n,l,m_l}.$$

- Each electron labelled by quantum numbers (n,l,m_l,m_s)
- The set of these quantum numbers is the atom configuration

Interactions left out of the central field approximation

- Residual electrostatic interaction – leads to splittings into **terms labelled by L and S**
- Relativistic effects, most importantly the spin-orbit interaction – leads to **fine-structure levels labelled by J**
- Properties of the nucleus, most importantly the magnetic moment – leads to **hyperfine structure levels labelled by F**
- Interactions with applied fields, e.g. with a magnetic field – leads to **Zeeman splitting into sub-levels labelled by M.**

Residual electrostatic interaction

- Interaction is internal to the atom – total orbital and spin angular momenta are conserved
- Define total orbital and spin angular momentum operators:

$$\hat{L} = \sum_i \hat{l}_i, \quad \hat{S} = \sum_i \hat{s}_i.$$

$$\hat{L}^2 |L, S, M_L, M_S\rangle = L(L + 1) |L, S, M_L, M_S\rangle$$

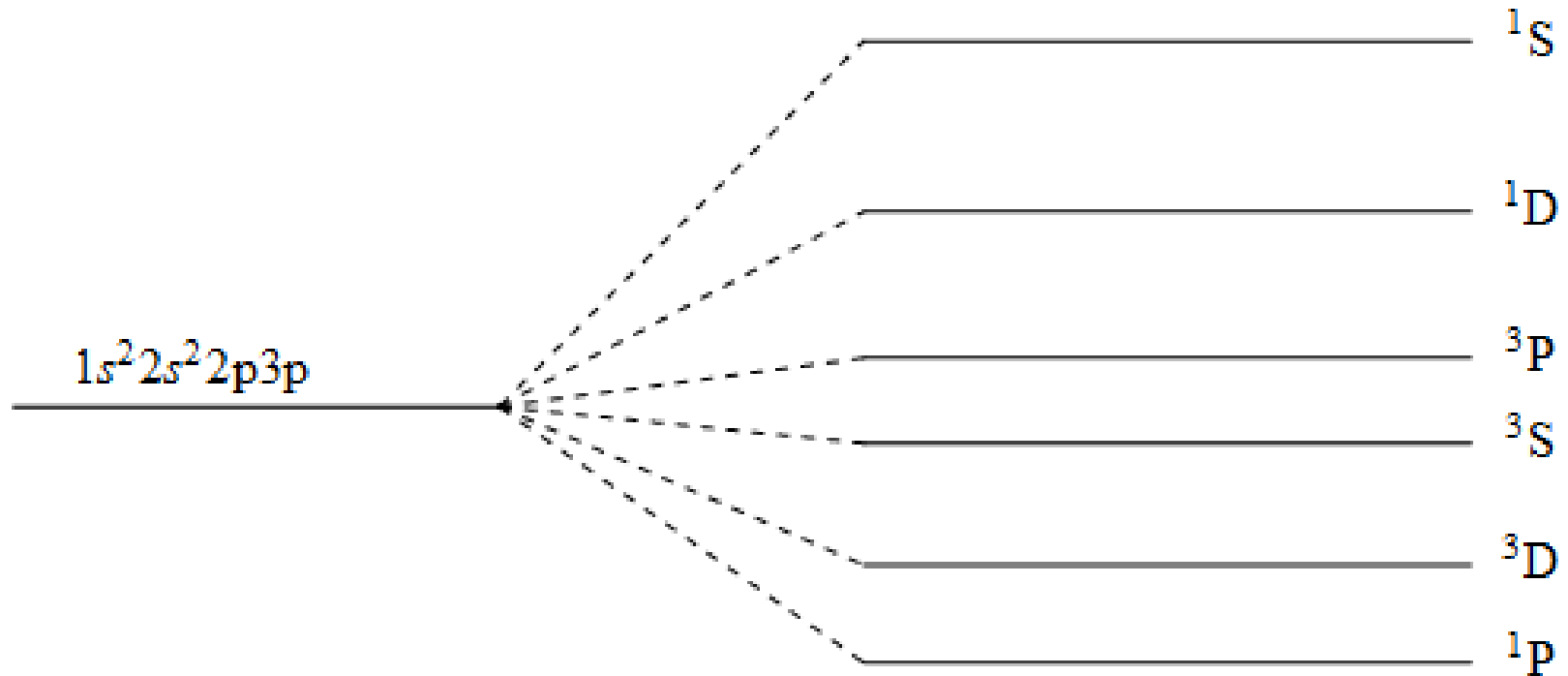
$$\hat{S}^2 |L, S, M_L, M_S\rangle = S(S + 1) |L, S, M_L, M_S\rangle$$

$$\hat{L}_z |L, S, M_L, M_S\rangle = M_L |L, S, M_L, M_S\rangle$$

$$\hat{S}_z |L, S, M_L, M_S\rangle = M_S |L, S, M_L, M_S\rangle$$

- Energies depend on the values of L and S
- Configuration splits up into terms labelled as ^{2S+1}L

Example: Carbon 2p3p configuration



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Spin-orbit interaction

- Motion of electrons through electric field produces a magnetic field
- Interaction of electron's magnetic moment with this magnetic field
- Leads to perturbation of the form: $\hat{H}_{\text{so}} = \hat{\beta}_{\text{LS}} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$
- Introduce total electronic angular momentum operator: $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$
- Term is split into levels according to the value of J

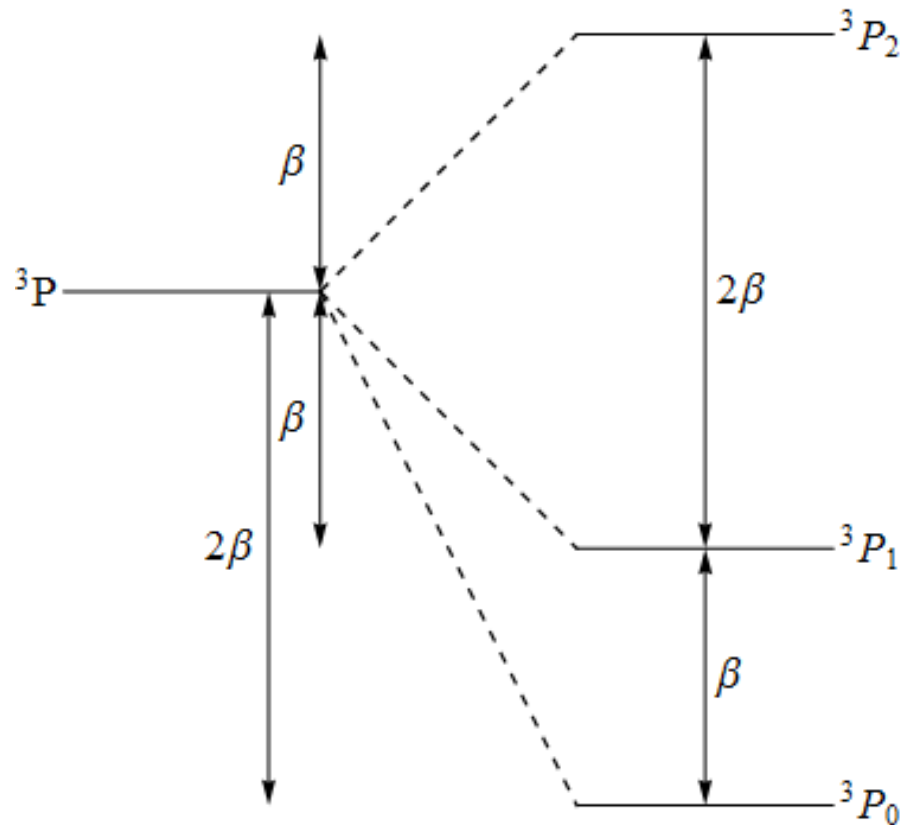
$$\Delta E_J = \frac{\beta}{2} [J(J + 1) - L(L + 1) - S(S + 1)]$$

The interval rule

$$\Delta E_J = \frac{\beta}{2} [J(J+1) - L(L+1) - S(S+1)]$$

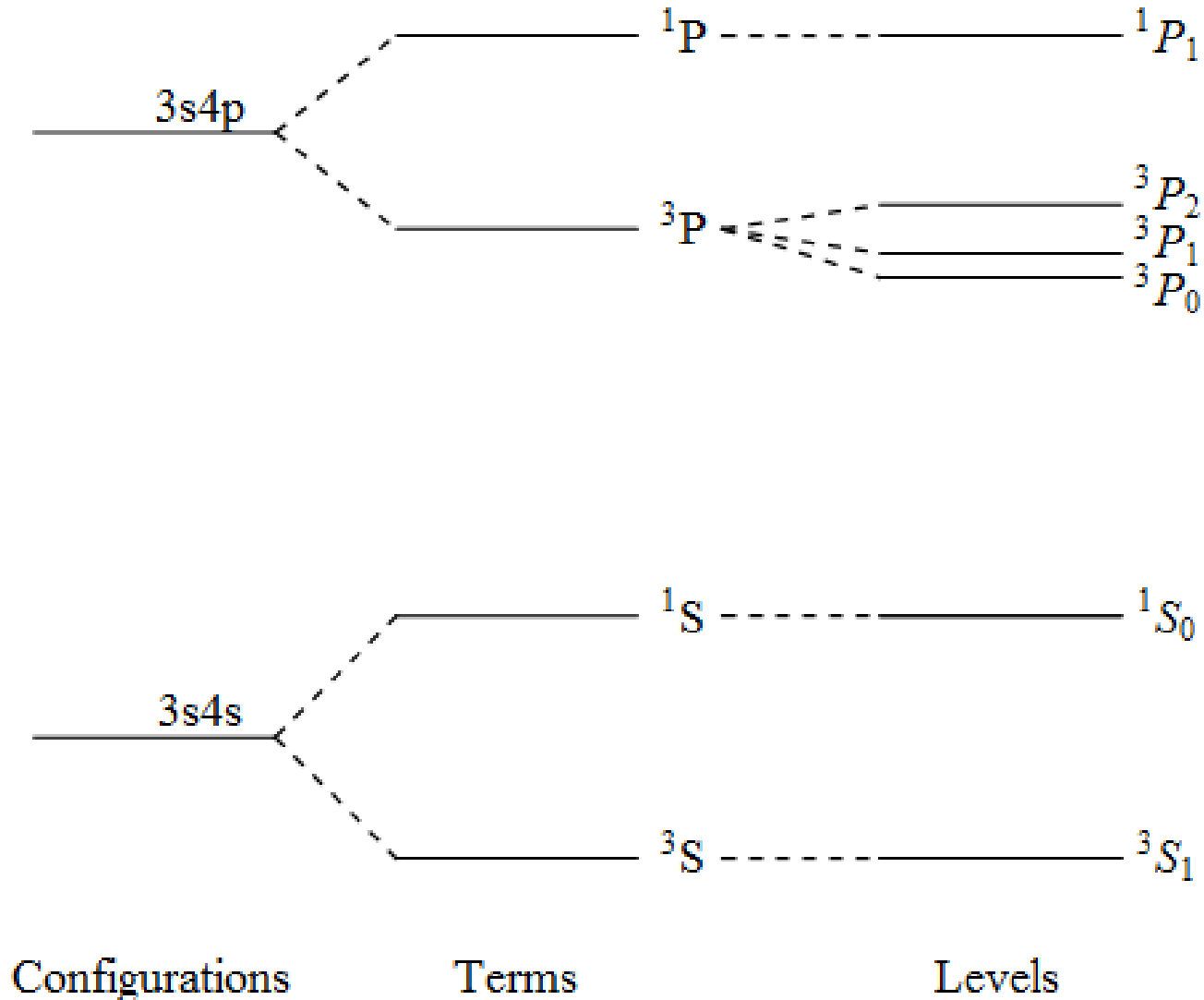
$$\Delta E_{FS} = \Delta E_J - \Delta E_{J-1} = \frac{\beta}{2} [J(J+1) - (J-1)J] = \beta J$$

Interval rule: Energy difference of adjacent levels proportional to the larger value of J



Configurations, terms, levels

Example: Magnesium



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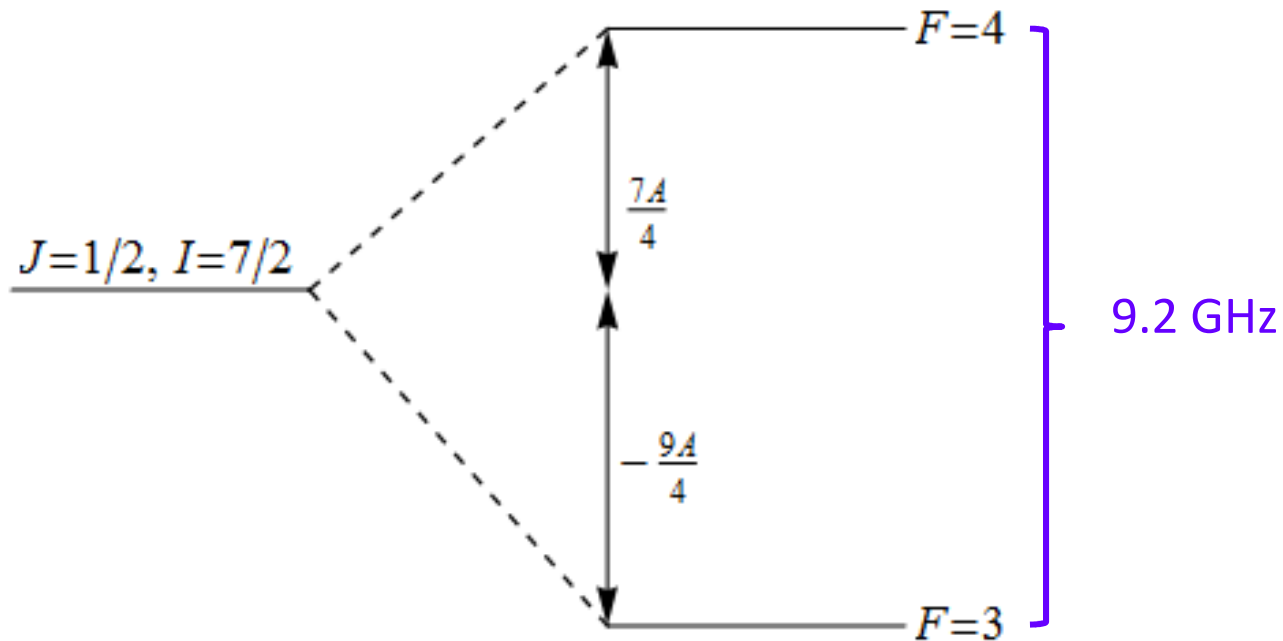
Hyperfine structure

- Due to properties of the nucleus other than its charge
- Most important is the nuclear magnetic moment $\hat{\mu}_I = g_I \mu_N \hat{I}$
- Leads to perturbation $\hat{H}_{\text{hfs}} = \hat{A}_{\text{hfs}} \hat{I} \cdot \hat{J}$
- Introduce total angular momentum operator: $\hat{F} = \hat{I} + \hat{J}$
- Splitting into hyperfine components according to the value of F

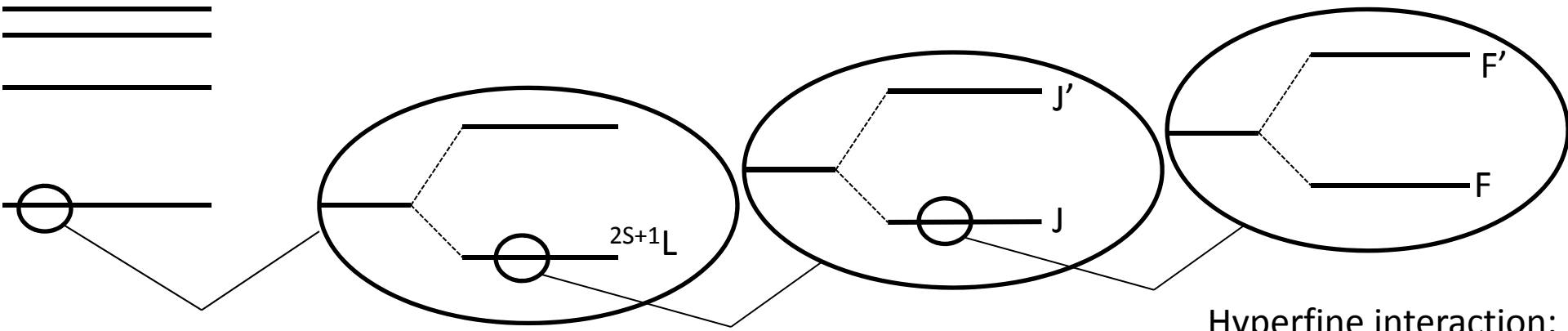
$$\Delta E_F = \frac{A}{2} [F(F + 1) - I(I + 1) - J(J + 1)]$$

Example: ground state Cs

$$\Delta E_F = \frac{A}{2} [F(F + 1) - I(I + 1) - J(J + 1)]$$



Levels of structure



Residual electrostatic:
Terms

Spin-orbit interaction:
Fine-structure levels

Hyperfine interaction:
Hyperfine levels

N.B. Schematic only – the number of levels depends on the details.

Central electrostatic:
Configurations

Interactions left out of the central field approximation

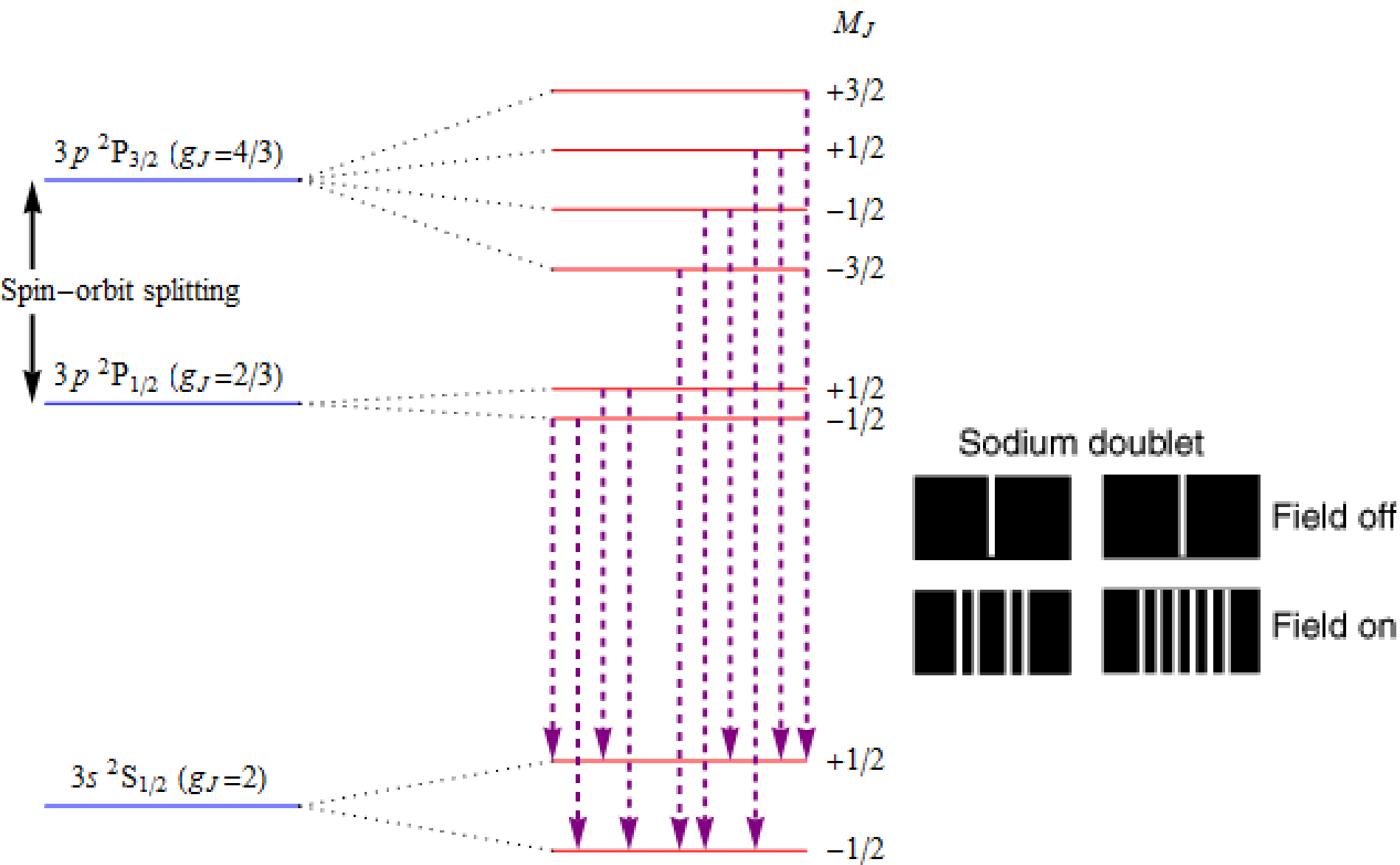
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Zeeman effect (neglecting hyperfine structure)

- Due to the interaction of the atom with an applied magnetic field
- Introduces the perturbation $\hat{H}_Z = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}$
- Magnetic moment is sum of individual moments and is proportional to total electronic angular momentum: $\hat{\boldsymbol{\mu}} = -g_J \mu_B \hat{\mathbf{J}}$
- Take magnetic field along z-axis. Then: $\hat{H}_Z = g_J \mu_B B \hat{J}_z$

$$\Delta E_Z = g_J \mu_B B M_J$$

Example: Zeeman effect in sodium



Selection rules for electric dipole transitions

Strict rules

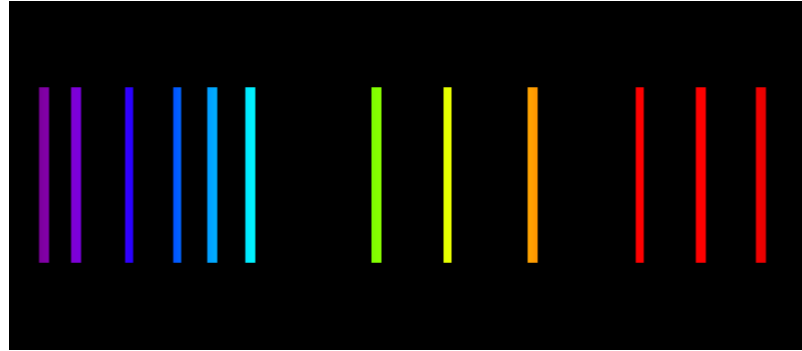
- Parity must change.
- $\Delta J=0, \pm 1$. But not $J'=0 \rightarrow J=0$.
- $\Delta M_j=0$ (parallel polarization) or ± 1 (perpendicular polarization).

Approximate rules

- $\Delta l=\pm 1$ (for the electron making the transition).
- $\Delta S=0$.
- $\Delta L=0, \pm 1$ (but 0-0 is not allowed).

Good for light atoms, not so good for heavier ones

Spectral lines



- Light emitted\absorbed when atom makes a transition → spectrum
- Broadening of spectral lines due to:
 - (1) Natural broadening – finite lifetime of transition
 - (2) Doppler broadening – random distribution of speeds (Maxwell-Boltzmann) leads to a distribution of Doppler shifts. Usually much larger than natural broadening.