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

\[ \psi_1 \quad \psi_2 \]

Oscillating charge: Electric dipole

Atomic radiation
Spectral Line Broadening

**Homogeneous** e.g.
- Lifetime (Natural)
- Collisional (Pressure)

**Inhomogeneous** e.g.
- Doppler (Atomic motion)
- Crystal Fields
Lifetime (natural) broadening

- Number of excited atoms: $N(t)$, $E(t)$
- Intensity spectrum: $I(\omega)$

- Time, $t$ (Exponential decay)
- Frequency, $\omega$ (Lorentzian lineshape)

Fourier Transform
Lifetime (natural) broadening

Number of excited atoms

Electric field amplitude

$N(t)$

$E(t)$

Time, $t$

Exponential decay

$\tau \sim 10^{-8}$s

Intensity spectrum

$I(\omega)$

Frequency, $\omega$

Lorentzian lineshape

$\Delta \nu \sim 10^8$ Hz

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Collision (pressure) broadening

Number of uncollided atoms

$N(t)$

Time, $t$

Exponential decay

Intensity spectrum

$I(\omega)$

Frequency, $\omega$

Lorentzian lineshape
Collision (pressure) broadening

Number of uncollided atoms

\[ N(t) \]

Time, \( t \)

Exponential decay

Intensity spectrum

\[ I(\omega) \]

Frequency, \( \omega \)

Lorentzian lineshape

\[ \tau_c \sim 10^{-10} \text{s} \]

\[ \Delta \nu \sim 10^{10} \text{Hz} \]
Doppler (atomic motion) broadening

Distribution of atomic speed

\[ N(v) \]

Doppler broadening

\[ I(\omega) \]

atomic speed, \( v \)

gaussian lineshape

Maxwell-Boltzmann distribution

frequency, \( \omega \)

Typical \( \Delta v \sim 10^9 \text{ Hz} \)
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: \(13.6 \text{ eV}\)

\(= \text{Rydberg Constant} \quad 109,737 \text{ cm}^{-1}\)

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

Fine structure constant, \(\alpha = \frac{v}{c} \approx 1/137\)

Bohr magneton, \(\mu_B\): \(9.27 \times 10^{-24} \text{ JT}^{-1}\)
The Central Field

U(r)

1/r

~Z/r

“Actual” Potential

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$Z_{\text{eff}}$ vs $r$ plot.

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)

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

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 \( \psi \) 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:**

\[ \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \]

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

![Diagram of electron-electron interaction](image)
Hamiltonian for Central Field Approximation

\[ \hat{H} = \hat{H}_0 + \hat{H}_1 \]

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

\[ \hat{H}_1 = \text{residual electrostatic interaction} \]

**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:

\[ \hat{H} = \hat{H}_0 + \hat{H}_1 \]

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?
$U(r) \sim \frac{1}{r}$

$U(r) \sim \frac{Z}{r}$
The Central Field

\[ U(r) \]

- \( \frac{1}{r} \)
- \( \sim \frac{Z}{r} \)
- "Actual" Potential
Radial position, $r$

$Z_{\text{eff}}$ vs. $r$

$\sim Z$

Important region

1
Finding the Central Field

• “Guess” form of U(r)
• Solve Schrödinger eqn. → Approx $\psi$.
• Use approx $\psi$ 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:

\[ E_n = \langle \psi_{n,l,m_l} | \hat{H} | \psi_{n,l,m_l} \rangle = -\frac{Z^2 \, me^4}{(4\pi \epsilon_0)^2 \, 2\hbar^2 n^2} \]
H Energy level diagram

Energy

\[ E_n = \left\langle \psi_{n,l,m_l} | \hat{H} | \psi_{n,l,m_l} \right\rangle \]
\[ = -\frac{Z^2me^4}{(4\pi\varepsilon_0)^2} \frac{1}{2\hbar^2 n^2} \]

Note degeneracy in \( l \)

-13.6 eV
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

\[ \int R_{n,l}^2(r)r^2 dr = 1 \quad \int |Y_{l}^{m_l}(\theta, \phi)|^2 d\Omega = 1 \]

\[ Y_{l}^{m_l}(\theta, \phi): \text{ Eigenfunctions of angular momentum operators} \]

\[ \hat{l}^2 Y_{l}^{m_l}(\theta, \phi) = l(l+1)\hbar^2 Y_{l}^{m_l}(\theta, \phi) \]
\[ \hat{l}_z Y_{l}^{m_l}(\theta, \phi) = m_l\hbar Y_{l}^{m_l}(\theta, \phi) \]

Eigenvalues

\[ l = 0, 1, 2... (n-1) \quad -l \leq m_l \leq l \]

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Angular momentum orbitals

\[ |Y_{1}^{\pm}(\theta,\phi)|^2 \]
Angular momentum orbitals

Spherically symmetric charge cloud with filled shell

$| Y_{1}^{\pm} (\theta, \phi) |$

$| Y_{1}^{0} (\theta, \phi) |^2$
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) \( \sim n^2 \)
- \( l = 0 \) 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

<table>
<thead>
<tr>
<th>Element</th>
<th>1s</th>
<th>2s</th>
<th>2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>1s$^2$</td>
<td>2s</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1s$^2$</td>
<td>2s$^2$</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>1s$^2$</td>
<td>2s$^2$2p</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1s$^2$</td>
<td>2s$^2$2p$^2$</td>
<td></td>
</tr>
<tr>
<td>Ne</td>
<td>1s$^2$</td>
<td>2s$^2$2p$^6$</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1s$^2$</td>
<td>2s$^2$2p$^6$</td>
<td>3s</td>
</tr>
</tbody>
</table>

Electron configuration
The Periodic Table

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1s(^2)2s(^2)2p(^6) 3s(^2)3p(^6) 4s</td>
</tr>
<tr>
<td>Ca</td>
<td>4s(^2)</td>
</tr>
<tr>
<td>Va</td>
<td>3s(^2)3p(^6) 3d(^3)4s(^2)</td>
</tr>
<tr>
<td>Cr</td>
<td>3d(^5)4s</td>
</tr>
<tr>
<td>Mn</td>
<td>3d(^5)4s(^2)</td>
</tr>
</tbody>
</table>
The Periodic Table

**Rare gases**

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1s(^2)</td>
</tr>
<tr>
<td>Ne</td>
<td>1s(^2)2s(^2)2p(^6)</td>
</tr>
<tr>
<td>Ar</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)</td>
</tr>
<tr>
<td>Kr</td>
<td>(….) 4s(^2)4p(^6)</td>
</tr>
<tr>
<td>Xe</td>
<td>(…..)5s(^2)5p(^6)</td>
</tr>
<tr>
<td>Rn</td>
<td>(…….)6s(^2)6p(^6)</td>
</tr>
</tbody>
</table>
The Periodic Table

Alkali metals

Li: $1s^22s$
Na: $1s^22s^22p^63s$
Ca: $1s^22s^22p^63s^23p^64s$
Rb: $(...) 4s^24p^65s$
Cs: $(.....)5s^25p^66s$
etc.
Absorption spectroscopy

White light source -> Atomic Vapour -> Spectrograph

Absorption spectrum
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 $\lambda$ 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 $\delta(l)$
   $$T(n_i) = R \ell(n - \delta(l))^2$$

Quantum defect plot

$\Delta(l)$

$T(n_i)$
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

\[ U(r) \]

1/r

\[ \sim Z/r \]

“Actual” Potential
Corrections to the Central Field

- Residual electrostatic interaction:

\[ \hat{H}_1 = \sum_{i > j} \frac{e^2}{4\pi \varepsilon_0 r_{ij}} - \sum_i \left\{ \frac{Ze^2}{4\pi \varepsilon_0 r_i} + U(r_i) \right\} \]

- Magnetic spin-orbit interaction:

\[ \hat{H}_2 = -\mu \cdot B_{\text{orbit}} \]
Magnetic spin-orbit interaction

- Electron moves in Electric field of nucleus, so sees a Magnetic field $B_{\text{orbit}}$
- Electron spin precesses in $B_{\text{orbit}}$ with energy:
  \[-\mu \cdot B \text{ which is proportional to } s \cdot l\]
- Different orientations of $s$ and $l$ give different total angular momentum $j = l + s$.
- Different values of $j$ give different $s \cdot l$ 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 $\mu$ causing precession of $\mu$ and the associated angular momentum vector $\lambda$

The additional angular velocity $\omega'$ changes the angular velocity and hence energy of the orbiting/spinning charge

$$\Delta E = -\mu \cdot B$$
Spin-Orbit interaction: Summary

\[
\mathbf{B} = -\frac{\mathbf{v} \times \mathbf{E}}{c^2}
\]

\[
\mathbf{B} = -\frac{1}{m c^2} \mathbf{p} \times \frac{\mathbf{E}}{|r|}
\]

\[
\mathbf{B} = \frac{1}{m c^2} \frac{|\mathbf{E}|}{|r|} \mathbf{l}
\]

\[
|\mathbf{E}| = -\frac{\partial \phi(r)}{\partial r}
\]

\[
|\mathbf{E}| = -\frac{1}{e} \frac{\partial U(r)}{\partial r}
\]

\[
\mathbf{B} = \frac{1}{e m c^2} \frac{1}{|r|} \frac{\partial U(r)}{\partial r} \mathbf{l}
\]

\[
\mathbf{B} \parallel \mathbf{l}
\]

\[
\mu_s = -g_s \frac{\mu_B}{\hbar} \hat{s}
\]

\[
\mu \parallel \hat{s}
\]

\[
-\mu_s \cdot \mathbf{B} \propto \frac{1}{r} \frac{\partial U(r)}{\partial r} \hat{s} \cdot \mathbf{l}
\]

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How to find $\langle \hat{s} \cdot \hat{l} \rangle$ using perturbation theory?

Perturbation energy

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

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

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

We need a diagonal perturbation matrix,
i.e. off-diagonal elements are zero
\[ \langle \psi_1 | \hat{H}' | \psi_2 \rangle = 0 \]
\[ \langle \phi_1 | \hat{H}' | \phi_2 \rangle = 0 \]

New wavefunctions:
\[ \phi_1 = a \psi_1 + b \psi_2 \]
\[ \phi_2 = b^* \psi_1 - a^* \psi_2 \]

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:
\( l^2, s^2 \) and \( j^2 \), and \( l, s, j \) 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:
\( l, s \) and \( j \) on z-axis
are \( m_l, m_s \) and \( m_j \).

Constants of the Motion → Good quantum numbers
Summary of Lecture 3: Spin-Orbit coupling

• Spin-Orbit energy

\[ - \mu_s \cdot B \propto \frac{1}{r} \frac{\partial U(r)}{\partial r} \hat{s} \cdot \hat{l} \]

• 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 \( \langle s \cdot l \rangle \) needs Degenerate Perturbation Theory

• New basis eigenfunctions:

\[ \langle n, l, s, j, m_j \rangle \]

• \( j \) and \( j_z \) 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 $j$
(c) Projection of $l$ on $z$ is not constant
(d) Projection of $s$ 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

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

Magnitudes

\[
j(j + 1) \quad l(l + 1) \quad s(s + 1)
\]

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

\[
\langle n, l, s, j, m_j | \hat{s} \cdot \hat{l} | n, l, s, j, m_j \rangle = \frac{1}{2} \left\{ j(j + 1) - l(l + 1) - s(s + 1) \right\} \hbar^2
\]
Using basis states: $| n, l, s, j, m_j \rangle$ to find expectation value:

The spin-orbit energy is:

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

**Sodium**

3s: \( n = 3, \ l = 0 \), no effect

3p: \( n = 3, \ l = 1 \), \( s = \frac{1}{2}, \ -\frac{1}{2} \), \( j = \frac{1}{2} \) or \( ^3/2 \)

\[ \Delta E(\frac{1}{2}) = \beta_{3p} \times (-1); \quad \Delta E(\frac{3}{2}) = \beta_{3p} \times \left( \frac{1}{2} \right) \]

3p (no spin-orbit)

\[ 2j + 1 = 4 \quad \text{and} \quad 2j + 1 = 2 \]

\[ j = 3/2 \quad \text{and} \quad j = 1/2 \]

1/2 \quad and \quad -1
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 $l_i$ and $s$ to form $L$ and $S$:

Electrostatic interaction dominates

\[ L = l_1 + l_2 \]
\[ S = s_1 + s_2 \]
Coupling of $L$ and $S$ to form $J$

$S = 1$

$L = 1$

$J = 2$

$L = 1$

$J = 1$

$L = 1$

$S = 1$

$J = 0$
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

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:

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

\[ 1\uparrow \quad 2\uparrow \quad 3\uparrow \quad 4\uparrow \]
Off-diagonal matrix elements:

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

\[ \begin{array}{cccc}
1 & 2 & 3 & 4 \\
\uparrow & \uparrow & \uparrow & \uparrow \\
1 \times 3 & = & \langle \psi_1(3s)\psi_2(4s) | V | \psi_1(3s)\psi_2(4s) \rangle & = & J \\
2 \times 4 & = & -\langle \psi_1(4s)\psi_2(3s) | V | \psi_1(4s)\psi_2(3s) \rangle & = & -J \\
2 \times 3 & = & \langle \psi_1(4s)\psi_2(3s) | V | \psi_1(3s)\psi_2(4s) \rangle & = & K \\
1 \times 4 & = & -\langle \psi_1(3s)\psi_2(4s) | V | \psi_1(4s)\psi_2(3s) \rangle & = & -K \\
\end{array} \]

Therefore \[ \langle \phi_1 | V | \phi_2 \rangle = 0 \] as required!
Effect of Direct and Exchange integrals

Energy level with no electrostatic interaction

Singlet

Triplet

+K

-K

J
Orbital orientation effect on electrostatic interaction

Overlap of electron wavefunctions depends on orientation of orbital angular momentum: so electrostatic interaction depends on $\mathbf{L}$
Residual Electrostatic and Spin-Orbit effects in LS-coupling
Term diagram of Magnesium

Singlet terms

\[ ^1S_0 \quad ^1P_1 \quad ^1D_2 \]

Triplet terms

\[ ^3S \quad ^3P \quad ^3D \]

- 3s3p \(^1P_1\)
- 3s3d \(^1D_2\)
- 3s3p \(^3P_{2,1,0}\)

resonance line (strong)
intercombination line (weak)
The story so far:  

**Hierarchy of interactions**

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

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

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

$H_3$: 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

Nucleus:
- stationary
- infinite mass
- point

 Corrections

Nuclear spin → magnetic dipole interacts with electrons

orbits centre of mass with electrons

charge spread over nuclear volume
Nuclear Spin interaction

Magnetic dipole ~ angular momentum

\[ \mu = - \gamma \lambda \hbar \]

\[ \mu_l = - g_l \mu_B l \quad \mu_s = - g_s \mu_B s \]

\[ \mu_I = - g_I \mu_N I \]

\[ g_I \approx 1 \quad \mu_N = \mu_B \times \frac{m_e}{m_P} \approx \mu_B / 2000 \]

Perturbation energy:

\[ \hat{H}_3 = - \mu_I \cdot B_{el} \]
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

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

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

$$B_{el} \sim \frac{\mu_0 \mu_B}{4\pi a_0^3} \sim 6T$$
\[ \hat{H}_3 = -\hat{\mu}_I \cdot \hat{B}_{el} \]

\[ B_{el} = (\text{scalar quantity}) \times J \]

Usually dominated by spin contribution in s-states:

Fermi “contact interaction”.
Calcuable only for Hydrogen in ground state, 1s
Coupling of $I$ and $J$

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

Depends on $I$  Depends on $J$

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

Nuclear spin interaction energy:

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

empirical  Expectation value
Vector model of nuclear interaction

\[ \mathbf{F} = \mathbf{I} + \mathbf{J} \]

\( \mathbf{I} \) and \( \mathbf{J} \) precess around \( \mathbf{F} \)

\[ \mathbf{I} \cdot \mathbf{J} = \frac{1}{2} \left\{ \mathbf{F}^2 - \mathbf{I}^2 - \mathbf{J}^2 \right\} \]
Hyperfine structure

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

Vector model result: \[ \hat{I} \cdot \hat{J} = \frac{1}{2} \left\{ F'^2 - I^2 - J^2 \right\} \]

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

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

- Orbiting about fixed nucleus, infinite mass
- Orbiting about centre of mass

reduced mass
Isotope effects

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

- Orbiting about fixed nucleus, infinite mass
- Orbiting about centre of mass

Reduction 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

Parity (-1) must change

$\Delta l = \pm 1$

N.B. Error in notes eqn (161)
Configuration

\[
\langle \psi_1(1s)\psi_2(2p)|r_1 + r_2 |\psi_1(3p)\psi_2(3d)\rangle \\
= \langle \psi_1(1s)|r_1 |\psi_1(3p)\rangle \times \langle \psi_2(2p)|\psi_2(3d)\rangle + \langle \psi_2(2p)|r_2 |\psi_2(3d)\rangle \times \langle \psi_1(1s)|\psi_1(3p)\rangle \\
= 0
\]

Only one electron "jumps"

\[
\Delta n = \text{anything} \\
\Delta l = \pm 1
\]
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:

$$\Delta E_Z = -\mu_L \cdot B_{\text{ext}}$$
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 $\mathbf{J}$.

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

\[ \mu_{\text{eff}} = gJ \mu_B J \]
Perturbation Calculation of $B_{\text{ext}}$ effect on spin-orbit level

Interaction energy
\[ \hat{H}_{\text{mag}} = -\mu_{\text{atom}} \cdot \vec{B}_{\text{ext}} \]

Effective magnetic moment
\[ \mu_{\text{eff}} = g_J \mu_B J \]

Perturbation Theory: expectation value of energy
\[ \Delta E_{AZ} = g_J \mu_B \left\langle \vec{J} \cdot \vec{B}_{\text{ext}} \right\rangle \]

Energy shift of $M_J$ level
\[ \Delta E_{AZ} = g_J \mu_B B_{\text{ext}} M_J \]
Vector Model Calculation of $B_{\text{ext}}$ effect on spin-orbit level

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

\[
\frac{|\mathbf{L} \cdot \mathbf{J}|}{|\mathbf{J}|^2} \frac{J}{J} = \mathbf{L}_J
\]

\[
\frac{|\mathbf{S} \cdot \mathbf{J}|}{|\mathbf{J}|^2} = \mathbf{S}_J
\]
Vector Model Calculation of $B_{\text{ext}}$ effect on spin-orbit level

\[
\Delta E_{AZ} = g_L \mu_B \mathbf{L} \cdot \mathbf{B}_{\text{ext}} + g_S \mu_B \mathbf{S} \cdot \mathbf{B}_{\text{ext}}
\]

\[
= g_L \mu_B \frac{|\mathbf{L} \cdot \mathbf{J}|}{|\mathbf{J}|^2} \mathbf{J} \cdot \mathbf{B}_{\text{ext}} + g_S \mu_B \frac{|\mathbf{S} \cdot \mathbf{J}|}{|\mathbf{J}|^2} \mathbf{J} \cdot \mathbf{B}_{\text{ext}}
\]

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

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

Perturbation Theory result

\[
\Delta E_{AZ} = g_J \mu_B B_{\text{ext}} M_J
\]
Anomalous Zeeman Effect:

$3s^2S_{1/2} - 3p^2P_{1/2}$ in Na
Polarization of Anomalous Zeeman components associated with $\Delta m$ 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 $\mathbf{J}$.

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

$$\mu_{\text{eff}} = g_J \mu_B J$$
Perturbation Calculation of $B_{\text{ext}}$ effect on spin-orbit level

Interaction energy
\[ \hat{H}_{\text{mag}} = -\mu_{\text{atom}} \cdot B_{\text{ext}} \]

Effective magnetic moment
\[ \mu_{\text{eff}} = g_J \mu_B J \]

Perturbation Theory:
*expectation value of energy*
\[ \Delta E_{AZ} = g_J \mu_B \left\langle \hat{J} \cdot \hat{B}_{\text{ext}} \right\rangle \]

Energy shift of $M_J$ level
\[ \Delta E_{AZ} = g_J \mu_B B_{\text{ext}} M_J \]

What is $g_J$?
Vector Model Calculation of $B_{\text{ext}}$ effect on spin-orbit level

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

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

\[ \frac{|\underline{S} \cdot \underline{J}| J}{|\underline{J}|^2} = \underline{S}_J \]
Vector Model Calculation of $B_{\text{ext}}$ effect on spin-orbit level

$$
\Delta E_{AZ} = g_L \mu_B L \cdot B_{\text{ext}} + g_S \mu_B S \cdot B_{\text{ext}} \\
= g_L \mu_B \frac{|L \cdot J|}{|J|^2} J \cdot B_{\text{ext}} + g_S \mu_B \frac{|S \cdot J|}{|J|^2} J \cdot B_{\text{ext}}
$$

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

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

Perturbation Theory result

$$
\Delta E_{AZ} = g_J \mu_B B_{\text{ext}} M_J
$$
Anomalous Zeeman Effect:

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

\[ g_J(\Sigma_{1/2}) = 2/3 \]
\[ g_J(\Sigma_{1/2}) = 2 \]
Strong field effects on atoms with spin-orbit coupling

*Spin and Orbit magnetic moments couple more strongly to $B_{\text{ext}}$ than to each other.*
Strong field effect on $L$ and $S$.

$L$ and $S$ precess independently around $B_{ext}$.

Spin-orbit coupling is relatively insignificant.

$m_L$ and $m_S$ are good quantum numbers.
Splitting of level in strong field: *Paschen-Back Effect*

N.B. Splitting like Normal Zeeman Effect

Spin splitting = 2 x Orbital

\[ g_S = 2 \times g_L \]
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Magnetic field effects on hyperfine structure
Hyperfine structure in Magnetic Fields

\[ A J I \cdot J + g_J \mu_B J \cdot B_{\text{ext}} - g_I \mu_N I \cdot B_{\text{ext}} \]

- Hyperfine interaction
- Electron/Field interaction
- Nuclear spin/Field interaction

Weak field: \[ A I \cdot J \gg g_J \mu_B J \cdot B_{\text{ext}} \]
Strong field: \[ A I \cdot J \ll g_J \mu_B J \cdot B_{\text{ext}} \]
Weak field effect on hyperfine structure

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

$I$, $J$, $F$ and $M_F$ are good quantum numbers

\[
\mu_F = -g_F \mu_B F
\]
Only contribution to $\mu_F$ is component of $\mu_J$ along $F$

\[ \mu_F = -g_J \mu_B \frac{J \cdot F}{F} \times \frac{F}{F} \]

Find this using Vector Model
\[ g_F = g_J \times \frac{J \cdot F}{F^2} \]

\[ F = I + J \]

\[ I^2 = F^2 + J^2 - 2J \cdot F \]

\[ J \cdot F = \frac{1}{2} \{ F(F+1) + J(J+1) - I(I+1) \} \]

\[ g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} \]
Each hyperfine level is split by $g_F$ term

Ground level of Na:

$J = \frac{1}{2} ; I = \frac{3}{2} ;$

$F = 1$ or $2$

$F = 2: g_F = \frac{1}{2} ;$

$F = 1: g_F = -\frac{1}{2}$

**Equation:**

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

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

N.B. notes error eqn 207
Sign inversion of $g_F$ for $F = 1$ and $F = 2$

- $I = 3/2$, $J = 1/2$, $F = 2$ (positive)
- $I = 3/2$, $J = -1/2$, $F = 1$ (negative)
Strong field effect on hfs.

\[ \Delta E = A_J \vec{I} \cdot \vec{J} + g_J \mu_B J \cdot B_{\text{ext}} \]

\( \vec{J} \) precesses rapidly around \( B_{\text{ext}} \) (z-axis)

\( \vec{I} \) tries to precess around \( \vec{J} \) but can follow only the time averaged component along z-axis i.e. \( J_z \)

So \( A_J \vec{I} \cdot \vec{J} \) term \( \rightarrow A_J M_I M_J \)
Strong field effect on hfs.

Energy

\[ \Delta E_{BG} = A_J M_I M_J + g_J \mu_B M_J B_{ext} \]

Na ground state

\[ ^2S_{1/2} \quad ^2D \]

Dominant term
Strong field effect on hfs.

Energy:

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

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

$I$ tries to precess around $J$

$I$ precesses around what it can "see" of $J$:

The z-component of $J$: $J_Z$

$$\Delta E_{BG} = A_J M_I M_J + g_J \mu_B M_J B_{\text{ext}}$$
Magnetic field effects on hfs

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

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

$\rightarrow$ “Zeeman” splitting of hfs levels

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

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

$\rightarrow$ 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

**Bremstrahlung**

- Maximum energy of incident electrons

**Characteristic X-rays**

- Intensity vs. Wavelength
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

Ejected electron

X-ray
X-ray series

N
\[ n=4 \]

M
\[ n=3 \]

L
\[ n=2 \]

K
\[ n=1 \]

K-series

L-series
\[ \alpha \beta \gamma \]

M-series
\[ \alpha \beta \gamma \]

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X-ray spectra for increasing electron impact energy

- **K-threshold**
- **L-threshold**

Max voltage
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:
$E_n - E_m = \nu = R\{(Z - \sigma_i)^2 / n_i^2 - (Z - \sigma_j)^2 / n_j^2\}$
Fine structure of X-rays

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

\[ \Delta l = \pm 1 \quad \Delta j = 0, \pm 1 \]
X-ray absorption spectra

Absorption coefficient vs. Wavelength

K-edge, L-edge, M-edge

L_I, L_{II}, L_{III}
Auger effect

Kinetic Energy \((E_K - E_L) - E_L\)

Potential Energy \((E_K - E_L)\)

X-ray absorption electron emitted
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

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

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

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

Absorption of strong pump $\omega_L$

Probe and pump laser at same frequency $\omega_L$
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 $\omega_O$

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

Tunable Laser

Fabry-Perot Interferometer

Photo-multiplier

Strong Pump Beam

Frequency calibration

Atomic Vapour Cell

Doppler-free Spectrum

Chopper

Weak Probe Beam

Photo-multiplier

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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

Diagram:
- Tunable Laser
- Optical isolator
- Lens
- Atomic Vapour Cell
- Curved mirror
- Fabry-Perot interferometer
- Photomultiplier
- Frequency calibration
- Fluorescence
- Photomultiplier
- Doppler-free Spectrum
Doppler-free spectroscopy of molecules in high temperature flames

Oxy-acetylene Torch ~ 3000K
Doppler-free spectrum of OH molecule in a flame
The End