Atoms and Nuclei
PA 322
Lecture 7

Unit 1: Recap
Unit 2: Spectrum of the Helium atom

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Lecture notes

• Available at:

http://www.star.le.ac.uk/~nrt3/322
QM description of atom

Bohr atom

Special Relativity

Schrödinger's equation

Hydrogen atom
Hydrogenic atoms

optical spectra

Periodic Table

Alkali metals

Helium

Multielectron atoms

Zeeman & Paschen-Bach Effects etc

X-ray spectra
### Terminology: Quantum Numbers

<table>
<thead>
<tr>
<th>Quantum no.</th>
<th>Name</th>
<th>Allowed values for electron</th>
<th>Amplitudes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>principal</td>
<td>any +ve integer: 1 ( \ldots ) ( \infty )</td>
<td></td>
</tr>
<tr>
<td>( l )</td>
<td>orbital angular momentum</td>
<td>( l=0, 1, \ldots n-1 )</td>
<td>( \mathbf{l} = \sqrt{l(l + 1)} \hbar )</td>
</tr>
<tr>
<td>( s )</td>
<td>spin</td>
<td>( s=1/2 )</td>
<td>( \mathbf{s} = \sqrt{s(s + 1)} \hbar )</td>
</tr>
<tr>
<td>( m_l )</td>
<td>orbital magnetic</td>
<td>( m_l = -l, \ldots +l ) (integer steps)</td>
<td>( l_z = m_l \hbar )</td>
</tr>
<tr>
<td>( m_s )</td>
<td>spin magnetic</td>
<td>( m_s = \pm s ) = ( \pm 1/2 )</td>
<td>( s_z = m_s \hbar )</td>
</tr>
<tr>
<td>( j )</td>
<td>total angular momentum</td>
<td>( j = \mid l - s \mid \ldots (l + s) ) (integer steps) ( j = l \pm 1/2 ) for single electron</td>
<td>( \mathbf{j} = \sqrt{j(j + 1)} \hbar )</td>
</tr>
<tr>
<td>( m_j )</td>
<td>total angular momentum</td>
<td>( m_j = -j, \ldots +j ) (integer steps)</td>
<td>( j_z = m_j \hbar )</td>
</tr>
</tbody>
</table>
# Terminology: shells, subshells etc.

<table>
<thead>
<tr>
<th>Concept</th>
<th>Related quantum numbers</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>shell</td>
<td>$n$</td>
<td>all levels with same $n$ belong to the same shell</td>
</tr>
<tr>
<td>sub-shell</td>
<td>$n, l$</td>
<td>all levels with the same $n, l$ belong to the same sub-shell</td>
</tr>
</tbody>
</table>

Also

**term**: configuration with specific $(n, l, s)$ split into **levels** with different $j$
Alternative notation for shells

For convenience & brevity, the shells are sometimes specified by an upper-case letter

<table>
<thead>
<tr>
<th>value of $n$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>letter code for shell</td>
<td>K</td>
<td>L</td>
<td>M</td>
<td>N</td>
<td>O</td>
<td>P</td>
<td>Q</td>
</tr>
</tbody>
</table>

Use particularly in context of X-ray spectra
(For example one might see expressions like K-shell photoelectric absorption edge... )
Terminology: notation for subshells

The configuration of the $N$ equivalent electrons in a given sub-shell is usually written as

$$nl^N$$

eg. $3p^6$

where

- $n$ is the **principal quantum number** (a positive integer, as above)
- $l$ is a letter used to specify the value of the **orbital angular momentum quantum number** (allowed values $l = 0, 1, ..., n -1$)

<table>
<thead>
<tr>
<th>value of $l$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>letter code</td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>f</td>
<td>g</td>
<td>h</td>
<td>i</td>
<td>k</td>
<td>l</td>
</tr>
</tbody>
</table>

The superscript value for $N$ is often omitted if $N = 1$. 
Terminology: notation for terms

The combination of quantum numbers for a specific configuration of optically active electron(s) can be written as a spectroscopic term symbol:

\[ \frac{2S+1}{L_J} \]

\[ 2P_{3/2} \]

e.g.

where

- \( S \) is the spin quantum number & \((2S+1)\) is the spin multiplicity (\(=2\) for a single electron \(\Rightarrow\) called ‘doublet’)
- \( L \) is the letter used to specify the value of the orbital angular momentum quantum number (in upper case)
- \( J \) is the total angular momentum quantum number
Important concepts for multi-electron atoms

- Need to work out how spin and orbital angular momenta couple together for multiple optically active electrons. Two approximation schemes are used for different situations:
  - **LS coupling**: coupling between *combined* orbital and spin angular momenta
    \[ \mathbf{L} = \sum \mathbf{l}_i; \mathbf{S} = \sum \mathbf{s}_i; \mathbf{J} = \mathbf{L} + \mathbf{S} \] (vector sums)
    - strong electron-electron interactions ‘break’ individual spin-orbit coupling
  - **j-j coupling**: strong spin-orbit coupling of individual electrons, net combined angular momenta couple
    \[ \mathbf{J} = \sum \mathbf{j}_i \]

- LS coupling dominates for low \( Z \) elements (and for low \( n \) orbitals)

Note, vectors are bold

Note, use of capitals to distinguish total from individual QNs
Helium

• Basic facts

  – Helium discovered as element late (1868) – first detected in spectrum of Sun (hence name)

  – not isolated as terrestrial element in 1895 – second lightest element

  – optical spectrum difficult to understand:
    – two distinct families of lines (but not two different elements!)
Spectrum of the Helium atom

• Context
  – atoms considered in Unit 1: hydrogen, hydrogenic species, alkali metals
  – all had *single* electron in outer shell
    • outermost electron essentially independent of inner electrons in their closed shells
    • magnetic moments from orbital and spin angular momenta in closed shells cancel out
  – but we now know helium has 1s^2 configuration, i.e. two (potentially active) electrons in outer shell
    • ⇒ more complexity ⇒ introduction to multi-electron atoms
Important concepts for helium

• Energy state for electrons in helium:

\[ E = E(n,l) + E_{so} + E_{opt.el.} \]

  binding to nucleus
(Schr. eqn.)

  spin-orbit coupling

electron interactions
(electrostatic)

• In fact, here we will mainly be concerned with the splitting of energy levels and their relative positioning.
Total spin angular momentum

- **Total** spin angular momentum in helium
  - two electrons in ground state must have $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$ (Pauli Exclusion Principle)
  - in ground configuration spins paired, i.e. anti-parallel and resultant magnetic moment is zero
  - excited states (e.g. 1s2s ...) can have spins parallel or anti-parallel
    - parallel spins: triplet states
    - anti-parallel spins: singlet states
Total spin angular momentum
(for helium)

- Must consider total spin angular momentum $S = s_1 + s_2$ (vector sum)

- Related *total* spin angular momentum *quantum number* $S$:
  - amplitude of spin vector $|S| = [S(S+1)]^{1/2} \hbar$

- In case of 2 electrons in helium possibilities are
  - $s_1 = s_2 = \frac{1}{2} \Rightarrow S = 0$ or $S = 1$

- Total spin angular momentum has $2S+1$ quantised components characterised by quantum number $m_S = -S, \ldots, +S$
  - for $S = 0$ single component ($2S+1=1$) hence *singlet* state
  - for $S = 1$ three components ($2S+1=3$) hence *triplet* state
Energy difference between singlet and triplet states

- Singlet and triplet states have different energies because the electrons in these states have different spatial distributions
  - Crudely speaking, triplet states have lower energies because electrons are “more separated”: lower probability of being in close proximity (recall electrostatic repulsion $\propto 1/r^2$)
  - Full QM treatment in terms of Coulomb and exchange integrals provides this result
Transitions in helium

• Consider transitions involving just one electron

• Absorption (usually from ground state): \(1snl \leftarrow 1s^2\) (e.g. \(1s 2p \leftarrow 1s^2\))
• Emission: \(nl n'l' \rightarrow nl n''l''\) (i.e. between arbitrary excited states)

• Selection rules: \(\Delta n = \text{any}; \Delta l = \pm 1; \Delta S = 0\)
  \(\Rightarrow\) transitions between singlet and triplet states are forbidden

• Implications:
  – absorption lines are all between singlet states (as ground state is singlet state)
  – emission lines (e.g. from discharge tube which populates various excited states): two distinct sets of lines corresponding to
    • singlet \(\leftrightarrow\) singlet states
    • triplet \(\leftrightarrow\) triplet states
Grotrian diagram for helium

Examples of allowed transitions

singlet

\[ \begin{align*}
1s^2 \\
1s^2 \\
1s2s \\
1s2p \\
1s3s \\
1s3p \\
1s3d \\
1s \end{align*} \]

triplet

\[ \begin{align*}
3s^2 \\
3s^2 \\
1s2s \\
1s2p \\
1s3s \\
1s3p \\
1s3d \\
1s \end{align*} \]
Grotrian diagram for helium

Examples of forbidden transitions
Spin-orbit coupling (revisited) for helium
(L-S coupling)

- *Orbital angular momenta* of electrons coupled as for *spin angular momenta*
- Total orbital angular momentum $L = l_1 + l_2$ (vector sum)
- For helium with one electron in 1s subshell:
  - $l_1 = 0$ and thus $L = l_2$
  - *only excited electron can (potentially) contribute to total angular momentum*
- Spin-orbit coupling in helium involves coupling of *total* spin angular momentum with *total* spin angular momentum, ie. $S$ with $L$
  - for singlet states with $S = 0$ – no spin-orbit coupling
  - for triplet states coupling to produce total angular momentum $J = L + S$
Vector sums revisited

• How do we combine the quantum numbers where the corresponding vectors are combined in a vector sum?
  – eg. sum of orbital angular momenta
    \[ L = l_1 + l_2 \]

• **Rule** is that the corresponding quantum number \( L \) can take values
  \[ L = l_1 + l_2 \ldots |l_1 - l_2| \]

• For example consider case where quantum numbers are \( l_1 = 1 \) and \( l_2 = 2 \)
  – in this case the rule gives \( L = 3, 2, 1 \)

• **Rule applies to any quantised vector sum combination**
\[ l_1 = 1 \; ; \; l_2 = 2 \]
\[ L = l_1 + l_2 \; ; \; \|l_1 - l_2\| \]
\[ \Rightarrow L = 3, 2, 1 \]

length of vector \( q \)

\[ |q| \propto \sqrt{q(q + 1)} \]
Spin-orbit coupling (revisited) for helium

• For triplet states ($S = 1$) possible values of quantum number $J$ are
  
  $J = L+1, L, L-1$  \[ \text{cf. } J = L + S, L + S-1, \ldots \mid L - S \mid \]

  and each $J$ state is $(2J+1)$-fold degenerate according to value of $m_J$
  (total angular momentum projection quantum number)

• Example: $1snp$ states
  
  – $L = 1$ ($l_1=0$ $l_2=1$)
  – $J = 2, 1, 0$
  – Term symbols: $^3P_2, ^3P_1, ^3P_0$

• Example: $1snd$ states
  
  – $L = 2$ ($l_1=0$ $l_2=2$)
  – $J = 3, 2, 1$
  – Term symbols: $^3D_3, ^3D_2, ^3D_1$

• $E_{so} = \frac{1}{2} A \left[ J(J+1)-L(L+1)-S(S+1) \right] \hbar c$  (cf. earlier version, but with much smaller constant)
Grotrian diagram for helium (full treatment)

selection rules
\( \Delta J = 0, \pm 1 \) (not 0→0)
\( \Delta S = 0; \Delta L = \pm 1 \)
Reading

• Helium atom
  – *Softley* Chapter 4: mostly sections 4.1-4.3

• Previous concepts
  – spin-orbit coupling
    • previous lectures
    • *Softley* Section 2.10