Quantum Mechanics and Atomic Physics

Lecture 23:
Multi-electron Atoms con’t/
Approximation Methods I

http://www.physics.rutgers.edu/ugrad/361

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Last time: Optical Excitations of Multi-electron Atoms

- Let’s now consider only atoms in which the outer subshell is less than half filled.

- Case I: atoms with one electron in the outermost subshell
  - Last time

- Case II: atoms with more than one electron in the outermost subshell
  - Today
Case II: Atoms with more than one outer electron

There are two ways in which $\ell_i$ and $s_i$ combine into total angular momentum

1. Most atoms observe LS coupling (also called Russel-Saunders coupling):
   \[ \vec{L}' = \ell \hat{\ell}, \quad \vec{S}' = \pm \hat{s}, \quad \vec{J}' = \vec{L}' + \vec{S}' \]
   So $\ell_i$ precess about $L'$, $s_i$ precess about $S'$ and then $L'$ and $S'$ precess about $J'$

2. Large Z-atoms ($Z \geq \sim 80$) observe jj coupling:
   \[ \vec{j}_i = \ell_i + s_i \quad \vec{J}' = \pm \vec{j}_i \]

We will restrict ourselves to LS coupling.
Example: the Carbon atom

- Carbon has 6 electrons and is $1s^2 \ 2s^2 \ 2p^2$.
- So the electrons in 2p have $\ell_1=\ell_2=1$ and $s_1=s_2=1/2$
- Let’s enumerate the possible states and determine how they are ordered in energy.

\[
\begin{align*}
L' &= |\ell_1 - \ell_2|, \ldots, (\ell_1 + \ell_2) = 0, 1, 2 \\
S' &= |s_1 - s_2|, \ldots, (s_1 + s_2) = 0, 1
\end{align*}
\]

For each $L'$ and $S'$, $J' = |L' - S'|, \ldots, (L' + S')$
Example: the Carbon atom

Do all these states exist?

- Some states don’t exist because of the generalized exclusion principle

- The energy ordering follows Hund’s Rules …
Hund’s Rules: Energy Ordering

1. **Lowest energy for maximum $S’$**
   - Parallel spins $\Rightarrow$ repulsive exchange force $\Rightarrow$ electrons apart (large $r$) $\Rightarrow$ $e-e$ energy is:
     \[
     V = \frac{1}{4\pi\varepsilon_0} \frac{(e)(-e)}{r} = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r}
     \]
   $\Rightarrow$ which is low for large $r$

2. **Lowest energy for maximum $L’$.**
   - To stay apart, they move in the same direction around the nucleus and maximize $L’$

3. **Lowest energy for minimum $J’$**
   - Usual fine structure effect, as in Hydrogen
Example

- So what is the energy ordering of the allowed states for Carbon? (see allowed states from earlier slide)

- According to Hund’s Rules:
  \[ 3P_0 \quad 3P_1 \quad 3P_2 \quad 1D_2 \quad 1S_0 \]

  - Lowest energy for maximum S’
  - Lowest energy for maximum L’
  - Lowest energy for minimum J’
Example

- An atom has two active electrons, one in 3d, the other in 4p.
- Display the energy level diagram.
  - Note, since \( n \) is different for the electrons there is no exclusion principle problem.
- First let’s determine the quantum numbers:

\[
\ell_1 = 2, \ell_2 = 1 \rightarrow L' = 1, 2, 3
\]

\[
s_1 = s_2 = 1/2 \rightarrow S' = 0, 1
\]
Follow Hund’s Rules to draw diagram

Symbol \( n \) is omitted because in this case it is not meaningful

- There is only one electron in \( n=3 \) and the other in \( n=4 \)

The fine structure energy splitting is:

\[
\Delta E_{Fs} \propto J'(J'+1) - L'(L'+1) - S'(S'+1)
\]
Lande interval rule

- Let’s define a **multiplet** as all states of the same \( L' \) and \( S' \), e.g. \(^3F\) in the previous example.

- **Within any multiplet:**
  \[
  \Delta E_{J'+1} - \Delta E_J \propto (J'+1)(J'+2) - J'(J'+1)
  \]

  \[
  = J'^2 + 3J' + 2 - J'^2 - J = 2J' + 2 = 2(J'+1)
  \]

  \[
  \Delta E_{J'+1} - \Delta E_{J'} \propto (J'+1)
  \]

- **So for the \(^3F\) multiplet, the energy spacing ratio is:**

\[
\frac{\Delta E_{F4} - \Delta E_{F3}}{\Delta E_{F3} - \Delta E_{F2}} = \frac{4}{3}
\]

**This is the Lande interval rule**
Summary of Hund’s Rules

- Fir multi-electron atoms we find that:
  - The energy ordering follows Hund’s Rules:

  - **Lowest energy for maximum S’**
    - Parallel spins ⇒ repulsive exchange force ⇒ electrons apart (large r) ⇒ low potential energy

  - **Lowest energy for maximum L’**
    - To stay apart, they move in the same direction around the nucleus and maximize L’

  - **Lowest energy for minimum J’**
    - Usual fine structure effect, as in Hydrogen

- What about if we apply a magnetic field?
What happens to a multi-electron atom in an external B field?

- Answer: analogous to what happens in Hydrogen!
- The magnetic moment is:

\[
\mu_J = \frac{\hat{M}_{tor} \cdot \hat{J}'}{J'} = -g \sqrt{J'(J'+1)} \mu_B
\]

\[
g = 1 + \frac{J'(J'+1) + S'(S'+1) - L'(L'+1)}{2J'(J'+1)}
\]
In a weak magnetic field, the energy levels split in the usual way:
\[ \Delta E = -\hat{\mu}_J \cdot \vec{B} \]

\[ \Rightarrow \Delta E = m_J \cdot g \cdot \mu_B \cdot B \]

\[ m_{J'} = -J', \ldots, J' \]

And we get magnetic substates.

And the selection rules for radiative transitions are:
- \( \Delta S' = 0 \)
- \( \Delta L' = 0, \pm 1 \)
- \( \Delta J' = 0, \pm 1 \)  Except for \( J' = 0 \rightarrow J' = 0 \)
- \( \Delta m_{J'} = 0, \pm 1 \)  But not \( 0 \rightarrow 0 \) if \( \Delta J' = 0 \)
Example

- A complex atom makes a transition from $^3D_1$ to $^3P_2$ and emits a photon of energy $E_\gamma$. If the atom is then placed in an external field $B$, describe the Zeeman Effect.

$$
^3D_1: \quad s' = 1, \quad l' = 2, \quad J' = 1
$$

$$
g = 1 + \frac{(1)(2) + (1)(2) - (2)(3)}{2(1)(2)} = \frac{1}{2}
$$

Splits into $2J'+1=3$ levels

$$
^3P_2: \quad s' = 1, \quad l' = 1, \quad J' = 2
$$

$$
g = 1 + \frac{(2)(3) + (1)(2) - (1)(2)}{2(2)(3)} = \frac{3}{2}
$$

Splits into $2J'+1=5$ levels
- Note that the magnetic moment is:

\[ \mu_J = -g \sqrt{J(J+1)} \mu_B \]

\[ ^3D_1: \quad \mu_J = -\frac{1}{2} \sqrt{1(2)} \mu_B = -\frac{1}{\sqrt{2}} \mu_B \]

\[ ^3P_2: \quad \mu_J = -\frac{3}{2} \sqrt{2(3)} \mu_B = -\frac{3\sqrt{6}}{2} \mu_B \]

- The energy splittings and radiative transitions are:
- We have $E_\gamma$ when $B=0$.
- So for $B \neq 0$, $\Delta E_\gamma = \Delta(gm_\gamma)\mu_B B$

So we get 9 photon lines, **not** equally spaced!
Strong B field

What happens if the magnetic field is strong?
- The B field destroys the coupling of $L'$ and $S'$ into $J'$
- Instead, each precess about $B$, and $J'$ is irrelevant
- This is called the Paschen-Bach Effect

\[
\mu_{\text{tot}} = -\frac{e}{2m} (\vec{L'} + 2\vec{S'}) \\
\Delta E = -\mu_{\text{tot}} \cdot \vec{B} = \frac{e}{2m} B (L_3' + 2S_3') \\
= \frac{e}{2m} B (m_L + 2m_s) = (m_L' + 2m_s) \mu_B B
Example

Let’s consider sodium D lines in a strong magnetic field $3P_{1/2} \rightarrow 3S_{1/2}$ and $3P_{3/2} \rightarrow 3S_{1/2}$

The selection rules are:

$\Delta m_s = 0 \quad \Delta m_L = 0, \pm 1$
In a strong B field

- So, in a strong magnetic field the allowed transitions correspond to

\[ \Delta(m_L + 2m_S) = -1, 0, +1 \]

- So the photon lines are

\[ \Delta E_B = -\mu_B B, 0, +\mu_B B \]

- And we get 3 equally spaced lines in the Paschen-Bach effect, i.e. the normal Zeeman Effect!
So what constitutes a “weak” or “strong” field?

Well, it depends on the atom.

- B=3T is a strong field in Lithium
- But in Sodium 3T is still weak

The transition from a weak field to a strong one is not abrupt.

- What happens to energy levels for an intermediate B field?
  - Too horrible to contemplate.
Approximation Methods

- Exact solutions to Schrodinger’s equation are possible only for mathematically simple potentials.

- However, many realistic potentials require approximations.

- This is true also for some remarkably simple ones
  - e.g. a linear potential $V(x) \propto x$

- Approximate solutions:
  - Analytic methods
    - Wentzel-Kramers-Brillouin (WKB) method (today)
  - Perturbation theory
  - Variational methods

- Numerical methods

- Note: again the emphasis is to obtain bound-state solutions
The WKB Method

- This approximation is applicable when $V$ rises sharply in the region $V > E$ so that barrier penetration is very tiny.

- The WKB assumption is:
  - Take $\Psi \sim 0$ at the classical turning points $E = V(x)$.
  - Then the oscillatory solutions for $E > V$ must be such that an integral number of half-wavelengths must fit within the turning points.

Like a standing wave of vibrating string clamped on both ends:

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Reed: Chapter 9
The WKB Method

- In general, however, $V(x)$ will not be constant and the wavelength will be a function of position. So $\lambda$ is not constant:

\[ \lambda = \frac{\hbar}{p} = \frac{\hbar}{\sqrt{2\pi k}} = \frac{\hbar}{\sqrt{2\pi m(E - V(x))}} \]

- So as $V(x)$ increases, $\lambda(x)$ increases.

- And the amplitude also increases, because as $V(x)$ increases, $K$ decreases, so speed decreases, so the particle spends more time there.
The WKB Method

- So a short distance $dx$ (so between $x$ and $x+dx$) over which the potential $V(x)$ is effectively constant will contain a number of wavelengths given by:

$$\frac{dx}{\lambda(x)} = \frac{\sqrt{2m(E-V(x))}}{h}$$

- And there must be an integral number of half wavelengths, so:

$$\int \frac{dx}{\lambda(x)} = \frac{n}{2} \Rightarrow \int \frac{\sqrt{2m(E-V(x))}}{h} \, dx = \frac{n}{2}$$

$$\Rightarrow 2\sqrt{2m} \int \sqrt{E_n-V(x)} \, dx \approx n\hbar$$
The WKB Approximation

This is the WKB approximation, for energy eigenvalues $E_n$.

One can also obtain the approximate eigenstates, but that’s beyond the scope of this course.

More next time …
Summary/Announcements

- Next time: Approximation Methods continued

- Homework 11 due on Wednesday Dec 6th.
  - \( \rightarrow \) NOTE the extended due date!

- Final exam: Wed. Dec 20th 8-11am room SEC 118
  - More details to come soon

- Next/last quiz: Monday Dec. 11th – details to come soon

- Please fill out SIRS:  [http://ctaar.rutgers.edu/sirs/current-surveys](http://ctaar.rutgers.edu/sirs/current-surveys)
  - Survey runs Monday, November 27 through Friday, December 15