Lectures 1-2: Introduction to Atomic Spectroscopy

- **Line spectra**
  - Emission spectra
  - Absorption spectra

- **Hydrogen spectrum**
  - Balmer formula
  - Bohr’s model

Types of Spectra

- **Continuous spectrum:** Produced by solids, liquids & dense gases produce - no “gaps” in wavelength of light produced:

- **Emission spectrum:** Produced by rarefied gases – emission only in narrow wavelength regions:

- **Absorption spectrum:** Gas atoms absorb the same wavelengths as they usually emit and results in an absorption line spectrum:

Emission and Absorption Spectroscopy

- **Line Spectra**
  - Electron transitions between energy levels result in emission or absorption lines.
  - Different elements produce different spectra due to differing atomic structure (discovered by Kirchhoff and Bunsen).

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td><img src="image" alt="Hydrogen Spectra" /></td>
</tr>
<tr>
<td>He</td>
<td><img src="image" alt="Helium Spectra" /></td>
</tr>
<tr>
<td>C</td>
<td><img src="image" alt="Carbon Spectra" /></td>
</tr>
</tbody>
</table>
Emission/Absorption of Radiation by Atoms

- Emission/absorption lines are due to radiative transitions:

1. Radiative (or Stimulated) absorption:
   Photon with energy \( E_\gamma = h\nu = E_2 - E_1 \) excites electron from lower energy level.

   \[ E_\gamma = h\nu \]

   Can only occur if \( E_\gamma = h\nu = E_2 - E_1 \)

2. Radiative recombination/emission:
   Electron emits photon with energy \( (h\nu' = E_2 - E_1) \) and makes transition to lower energy level.

Simplest Atomic Spectrum: Hydrogen

- In 1850s, the visible spectrum of hydrogen was found to contain strong lines at 6563, 4861 and 4340 Å.

- Lines found to fall more closely as wavelength decreases.

- Line separation converges at a particular wavelength, called the series limit.

- In 1885, Balmer found that the wavelength of lines could be written

\[ \frac{1}{\lambda} = R_H \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \]

where \( n \) is an integer \( >2 \), and \( R_H \) is the Rydberg constant.

Simplest Atomic Spectrum: Hydrogen

- If \( n = 3 \), \( \Rightarrow \)

- Called \( H_\alpha \) - first line of Balmer series.

- Other lines in Balmer series:

<table>
<thead>
<tr>
<th>Name</th>
<th>Transitions</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_\alpha )</td>
<td>3 - 2</td>
<td>6562.8</td>
</tr>
<tr>
<td>( H_\beta )</td>
<td>4 - 2</td>
<td>4861.3</td>
</tr>
<tr>
<td>( H_\gamma )</td>
<td>5 - 2</td>
<td>4340.5</td>
</tr>
</tbody>
</table>

Road to National Solar Observatory in New Mexico: “Highway 6563”
**Simplest Atomic Spectrum: Hydrogen**

- Rydberg showed that all series above could be reproduced using

\[ R_n = \frac{R_H}{n^2} \]

where \( n \) are principal quantum numbers.

- Series limit occurs when \( n_i = \infty, n_f = 1, 2, \ldots \)

- Other series of hydrogen:

<table>
<thead>
<tr>
<th>Series</th>
<th>Region</th>
<th>Quantum Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyman</td>
<td>UV</td>
<td>( n_f = 1, n_i \geq 2 )</td>
</tr>
<tr>
<td>Balmer</td>
<td>Visible/UV</td>
<td>( n_f = 2, n_i \geq 3 )</td>
</tr>
<tr>
<td>Paschen</td>
<td>IR</td>
<td>( n_f = 3, n_i \geq 4 )</td>
</tr>
<tr>
<td>Brackett</td>
<td>IR</td>
<td>( n_f = 4, n_i \geq 5 )</td>
</tr>
<tr>
<td>Pfund</td>
<td>IR</td>
<td>( n_f = 5, n_i \geq 6 )</td>
</tr>
</tbody>
</table>

**Bohr Model for Hydrogen**

- Simplest atomic system, consisting of a single electron-proton pair.

- First model put forward by Bohr in 1913. He postulated that:
  1. Electron moves in circular orbit about proton under Coulomb attraction.
  2. Only possible for electron to orbits for which angular momentum is quantised, i.e., \( L = mvr = nh \) where \( n = 1, 2, 3, \ldots \)
  3. Total energy \((K + V)\) of electron in orbit remains constant.
  4. Quantized radiation is emitted/absorbed if an electron changes orbit. The frequency emitted is \( \nu = (E_i - E_f) / h \).

**Ritz Combination Principle:** Transitions occur between terms:

\[ T_f = \frac{R_H}{n_f^2} \]

where \( T_f \) is the term value at \( n_f \).

- Transitions can occur between certain terms \( \Rightarrow \) selection rule. Selection rule for hydrogen: \( \Delta n = 1, 2, 3, \ldots \)

- Transitions between ground state and first excited state produce a resonance line.

- Grotrian diagram shows terms and the transitions.

**Bohr Model for Hydrogen**

- Consider atom consisting of a nucleus of charge \( +Ze \) and mass \( M \), and an electron on charge \(-e\) and mass \( m \). Assume \( M \gg m \) so nucleus remains at fixed position in space.

- As Coulomb force is a centripetal:

\[ L = mvr = nh \]

(1)

- And assuming angular momentum is quantised:

\[ L = n \hbar \]

(2)

- Solving for \( v \) and substituting into Eqn. 1 =>

\[ L = n \hbar \]

and

- Quantized AM has restricted the possible circular orbits of the electron.
Bohr Model for Hydrogen

- The total mechanical energy is:

- Using Eqn. 1,

- The potential energy ($V$) can be calculated from

- Total mechanical energy is therefore

- Using Eqn. 2 for $r$, 

- Therefore, quantization of AM leads to quantisation of total energy.

Bohr Model for Hydrogen

- Substituting in for constants, Eqn. 3 can be written

and Eqn. 2 can be written where $a_0 = 0.529 \ \text{Å} = \text{“Bohr radius”}$. 

- Eqn. 3 gives a theoretical energy level structure for hydrogen ($Z=1$):

- For $Z = 1$ and $n = 1$, the ground state of hydrogen is: $E_1 = -13.6 \ \text{eV}$

Correction for Motion of the Nucleus

- Spectroscopically measured $R_{M}$ does not agree exactly with theoretically derived $R_e$. 

- But, we assumed that $M>>m =>$ nucleus fixed. In reality, electron and proton move about common centre of mass. Must use electron’s reduced mass ($\mu$):

- Essential predictions of Bohr model are contained in Eqns. 3 and 4.

- As $m$ only appears in $R_e$, must replace by:

- It is found spectroscopically that $R_{M} = R_{H}$ to within three parts in 100,000.

- Therefore, different isotopes of same element have slightly different spectral lines.
Correction for Motion of the Nucleus

- Consider $^1$H (hydrogen) and $^2$H (deuterium):
  
  - Using Eqn. 4, the wavelength difference is therefore:
  
  - Called an isotope shift.
  
  - $H_p$ and $D_p$ are separated by about 1Å.
  
  - Intensity of $D$ line is proportional to fraction of $D$ in the sample.

Spectra of Hydrogen-like Atoms

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  - Using Eqn. 4, the wavelength difference is therefore:
  
  - Called an isotope shift.
  
  - $H_p$ and $D_p$ are separated by about 1Å.
  
  - Intensity of $D$ line is proportional to fraction of $D$ in the sample.

Implications of Bohr Model

- We also find that the orbital radius and velocity are quantised:
  
  - Bohr radius ($a_0$) and fine structure constant ($\alpha$) are fundamental constants:
  
  - Constants are related by
  
  - With Rydberg constant, define gross atomic characteristics of the atom.
**Exotic Atoms**

- **Positronium**
  - Electron (e) and positron (e⁺) enter a short-lived bound state, before they annihilate each other with the emission of two γ-rays (discovered in 1949).
  - Parapositronium (S=0) has a lifetime of ~1.25 x 10⁻¹⁰ s. Orthopositronium (S=1) has lifetime of ~1.4 x 10⁻¹⁰ s.
  - Energy levels proportional to reduced mass ➞ energy levels half of hydrogen.

- **Muonium**:
  - Replace proton in H atom with a µ meson (a “muon”).
  - Bound state has a lifetime of ~2.2 x 10⁻⁶ s.
  - According to Bohr’s theory (Eqn. 3), the binding energy is 13.5 eV.
  - From Eqn. 4, n = 1 to n = 2 transition produces a photon of 10.15 eV.

- **Antihydrogen**:
  - Consists of a positron bound to an antiproton - first observed in 1996 at CERN!
  - Antimatter should behave like ordinary matter according to QM.
  - Have not been investigated spectroscopically … yet.

**Failures of Bohr Model**

- Bohr model was a major step toward understanding the quantum theory of the atom - not in fact a correct description of the nature of electron orbits.

- Some of the shortcomings of the model are:
  1. Fails describe why certain spectral lines are brighter than others ➞ no mechanism for calculating transition probabilities.
  2. Violates the uncertainty principal which dictates that position and momentum cannot be simultaneously determined.

- Bohr model gives a basic conceptual model of electrons orbits and energies. The precise details can only be solved using the Schrödinger equation.

**Hydrogen Spectrum**

- Transitions actually depend on more than a single quantum number (i.e., more than n).

- Quantum mechanics leads to introduction on four quantum numbers.
  - Principal quantum number: n
  - Azimuthal quantum number: l
  - Magnetic quantum number: m_l
  - Spin quantum number: s

- Selection rules must also be modified.

<table>
<thead>
<tr>
<th>n</th>
<th>l</th>
<th>m_l</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>s</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>s</td>
</tr>
<tr>
<td>1</td>
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<td>0</td>
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<td>2</td>
<td>0</td>
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<td>2</td>
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<td>2</td>
<td>s</td>
</tr>
</tbody>
</table>

- Bohr model only valid when we approach the classical limit at large n.

- Must therefore use full quantum mechanical treatment to model electron in H atom.
### Atomic Energy Scales

<table>
<thead>
<tr>
<th>Energy scale</th>
<th>Energy (eV)</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross structure</td>
<td>1-10</td>
<td>electron-nuclear attraction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electron-electron repulsion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electron kinetic energy</td>
</tr>
<tr>
<td>Fine structure</td>
<td>0.001 - 0.01</td>
<td>Spin-orbit interaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Relativistic corrections</td>
</tr>
<tr>
<td>Hyperfine structure</td>
<td>$10^{-6} - 10^{-4}$</td>
<td>Nuclear interactions</td>
</tr>
</tbody>
</table>