Chemistry 1000 Lecture 6: Quantum mechanics and spectroscopy

Marc R. Roussel

September 7, 2018
de Broglie (matter) waves

de Broglie showed that

$$\lambda = \frac{h}{p}$$

also applies to particles for which

$$p = mv$$

**Prediction:** particles (electrons, neutrons, etc.) should diffract like light under appropriate conditions

**Modern methods based on this fact:** transmission electron microscopy, neutron diffraction
Thermal neutrons

Nuclear reactors produce a lot of “thermal” neutrons. These are neutrons which have been equilibrated to a temperature near room temperature. Typically, such neutrons travel at speeds of 2.2 km/s or so. The mass of a neutron is $1.6750 \times 10^{-27}$ kg.

\[
\therefore p = mv = (1.6750 \times 10^{-27} \text{ kg})(2.2 \times 10^3 \text{ m/s}) = 3.7 \times 10^{-24} \text{ kg m/s}
\]

\[
\therefore \lambda = \frac{h}{p} = \frac{6.62607015 \times 10^{-34} \text{ J/Hz}}{3.7 \times 10^{-24} \text{ kg m/s}} = 0.18 \text{ nm}
\]

\[\Rightarrow\text{ similar to bond lengths or to spacings between atoms in crystals}\]
<table>
<thead>
<tr>
<th>Formula</th>
<th>Applies to</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c = \lambda \nu$</td>
<td>light (or other waves)</td>
</tr>
<tr>
<td>$E = h \nu$</td>
<td>light (photons)</td>
</tr>
<tr>
<td>$p = mv$</td>
<td>ordinary particles</td>
</tr>
<tr>
<td>$p = h/\lambda$</td>
<td>both</td>
</tr>
</tbody>
</table>
Emission spectroscopy

Emission spectroscopy

Marc R. Roussel
Quantum mechanics
September 7, 2018
Line spectra can’t be explained using classical mechanics

- Rutherford’s gold foil experiment showed that the electrons move outside the positively charged nucleus. This created a big puzzle for classical physics.

- Maxwell’s equations predict that moving charges continually radiate energy.

Consequences:
- Atomic spectra should be continuous (like a rainbow).
- Atoms shouldn’t be stable: electrons should spiral down into the nucleus, collapsing the atom.

Solution: quantum mechanical Bohr atom
The Bohr atom

Hydrogenic atom: one electron circling a nucleus of atomic number $Z$
Examples: H, He$^+$, Li$^{2+}$, etc.

Assumption: circular electron orbit

Key fact: The electron has a wavelength given by $\lambda = h/p$. 
Wavelength mismatched to orbit:

Destructive interference $\implies$ no wave/particle
Wavelength matched to orbit:

\[ 2\pi r = n\lambda \quad n = 1, 2, 3, \ldots \]
The equation $2\pi r = n\lambda$ is a quantization condition. It constrains a physical observable to certain values.

$n$ is called a quantum number.
Physics background: the Coulomb force

- Electrostatic force between two charges $q_1$ and $q_2$:

$$F = \frac{q_1 q_2}{4\pi \varepsilon_0 r^2}$$

where $\varepsilon_0$ is the permittivity of free space and $r$ is the distance between the charges.

$$\varepsilon_0 = 8.854\,187\,817 \times 10^{-12} \, \text{C}^2\text{N}^{-1}\text{m}^{-2}$$

Equivalent units: C$^2$J$^{-1}$m$^{-1}$ or Fm$^{-1}$

- You may previously have seen this equation written in the form

$$F = \frac{kq_1 q_2}{r^2}$$

so the constant $k$ you had previously seen is really $\frac{1}{4\pi \varepsilon_0}$. 
The energy of an orbiting electron

- For a nucleus of charge $Ze$ separated from an electron of charge $-e$ by a distance $r$,
  \[ |F| = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \]
- From the theory of circular motion, the force required to create a circular orbit of radius $r$ is
  \[ |F| = \frac{m_e v^2}{r} \]
- Equating the two expressions and solving for $v^2$, we get
  \[ v^2 = \frac{Ze^2}{4\pi\varepsilon_0 m_e r} \] (1)
The electron’s momentum

\[ v^2 = \frac{Ze^2}{4\pi\varepsilon_0 m_e r} \]  \hspace{1cm} (1)

\[ p = mv, \] and equation (1) gives us \( v \) as a function of \( r \):

\[ v = \sqrt{\frac{Ze^2}{4\pi\varepsilon_0 m_e r}} \]

\[ \therefore p = \sqrt{\frac{Ze^2 m_e}{4\pi\varepsilon_0 r}} \]
Quantization of the orbit

\[ p = \sqrt{\frac{Ze^2 m_e}{4\pi \epsilon_0 r}} \]

- According to de Broglie, \( \lambda = \frac{h}{p} \), so
  \[ \lambda = h \sqrt{\frac{4\pi \epsilon_0 r}{Ze^2 m_e}} \]

- The quantization condition is \( 2\pi r = n\lambda \), so
  \[ 2\pi r = nh \sqrt{\frac{4\pi \epsilon_0 r}{Ze^2 m_e}} \]
  or, solving for \( r \),
  \[ r_n = \frac{n^2 h^2 \epsilon_0}{\pi Ze^2 m_e} \]
Quantization of the orbit (continued)

- Define the Bohr radius

\[
a_0 = \frac{\hbar^2\epsilon_0}{\pi e^2 m_e} = 52.917721067 \text{ pm}
\]

Therefore

\[
r_n = \frac{n^2}{Z} a_0
\]
The energy of an orbiting electron

- Equation (1) gave
  \[ v^2 = \frac{Ze^2}{4\pi\varepsilon_0 m_e r} \]
- The kinetic energy of the electron is
  \[ K = \frac{1}{2} m_e v^2 = \frac{Ze^2}{8\pi\varepsilon_0 r} \]
- The electrostatic potential energy is
  \[ U = -\frac{Ze^2}{4\pi\varepsilon_0 r} \]
- The total energy is
  \[ E = K + U = -\frac{Ze^2}{8\pi\varepsilon_0 r} \]
Quantization of the energy

Substitute \( r_n \) into the energy:

\[
E_n = \frac{-Ze^2}{8\pi\varepsilon_0 a_0 n^2}
\]

or

\[
E_n = \frac{-Z^2 e^2}{8\pi\varepsilon_0 a_0 n^2} = -\frac{Z^2}{n^2} R_H
\]

where \( R_H \) is Rydberg’s constant:

\[
R_H = \frac{e^2}{8\pi\varepsilon_0 a_0} = \frac{e^4 m_e}{8\hbar^2 \varepsilon_0} = 2.179\,872\,325 \times 10^{-18} \text{ J}
\]
Energy levels and emission spectroscopy of hydrogenic atoms

Energy levels of hydrogen

\[ E_n = -\frac{Z^2}{n^2} R_H \]

\[ h\nu = E_{\text{upper}} - E_{\text{lower}} = Z^2 R_H \left( \frac{1}{n_{\text{lower}}^2} - \frac{1}{n_{\text{upper}}^2} \right) \]
Historical note

- Historically, spectroscopic transitions were described by their wavelength.

- For a hydrogenic atom, we have

\[
\frac{hc}{\lambda} = Z^2 R_H \left( \frac{1}{n_l^2} - \frac{1}{n_u^2} \right)
\]

or

\[
\lambda = \frac{hc}{Z^2 R_H} \frac{n_u^2 n_l^2}{n_u^2 - n_l^2}
\]

- Equations like this were obtained by Balmer (1885; special case \(n_l = 2\)) and Rydberg (1888) by trial and error, before the appearance of any theory justifying them.
Quantum state terminology

The ground state of a quantum system is the lowest possible energy level. For a hydrogenic atom, this is the $n = 1$ state.

The first excited state is the next-lowest possible energy level. For a hydrogenic atom, this is $n = 2$.

The second excited state...
The Lyman series

- The emission spectrum of hydrogen (or, in general, of hydrogenic atoms) is organized into series of lines that correspond to a common $n_{\text{lower}}$.
- The Lyman series consists of the set of transitions to the ground state ($n = 1$).

**Example:** Calculate the wavelength of the longest wavelength line in the Lyman series of hydrogen.

**Answer:** 121.502 275 nm

**Note:** 122 nm is in the ultraviolet range. All the other lines in the Lyman series will also be in the ultraviolet. (Why?)

**Check at home:** The Balmer series corresponds to transitions ending at $n = 2$. Several lines in this series are in the visible range.
### Some lines in the spectrum of hydrogen

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength</th>
<th>Spectral region</th>
</tr>
</thead>
<tbody>
<tr>
<td>2→1</td>
<td>122 nm</td>
<td>UV</td>
</tr>
<tr>
<td>100→1</td>
<td>91 nm</td>
<td>UV</td>
</tr>
<tr>
<td>3→2</td>
<td>656 nm</td>
<td>red</td>
</tr>
<tr>
<td>4→2</td>
<td>486 nm</td>
<td>blue</td>
</tr>
<tr>
<td>5→2</td>
<td>434 nm</td>
<td>violet</td>
</tr>
<tr>
<td>6→2</td>
<td>410 nm</td>
<td>violet</td>
</tr>
<tr>
<td>7→2</td>
<td>397 nm</td>
<td>UV</td>
</tr>
<tr>
<td>4→3</td>
<td>1.87 μm</td>
<td>IR</td>
</tr>
<tr>
<td>100→3</td>
<td>821 nm</td>
<td>IR</td>
</tr>
</tbody>
</table>
The inverse problem

When we study the spectrum of an atom or molecule, we often want to assign the lines to particular transitions, i.e. we want to “fit” the spectrum.

Example: The emission spectrum of He\(^+\) contains an intense line at 30.3780 nm. To what transition does this line correspond? Hint: Intense lines usually involve small values of the quantum numbers.

Answer: 2 → 1

A slightly harder problem: The spectrum of He\(^+\) also has an intense line at 164.047 nm. Assign this line.

Answer: 3 → 2
Ionization

**Ionization energy**: amount of energy required to remove an electron from the ground state of an atom, molecule or ion

- In a hydrogenic atom, the ground state is \( n = 1 \).
- Ground-state energy: \( -Z^2 R_H \)
- Ionization energy: \( Z^2 R_H \)
  - Ionization energy = \( R_H = 2.179 \, 872 \, 17 \times 10^{-18} \) J for H
  - Ionization energy = \( (2)^2 R_H = 8.719 \, 489 \times 10^{-18} \) J for He\(^+\)
Successes of the Bohr theory

- Explains the stability of atoms
- Accurately predicts the emission spectra of hydrogenic atoms
Failures of the Bohr theory

- Doesn’t work for multi-electron atoms

- Incorrect treatment of angular momentum
  - Doesn’t correctly predict the splitting of emission lines in a magnetic field (Zeeman effect)

- No evidence for orbits of fixed radius
  - Such orbits are ruled out by Heisenberg’s later work (next lecture)