

Chemistry 1000 Lecture 6: Quantum mechanics and spectroscopy

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de Broglie (matter) waves

de Broglie showed that

$$\lambda = h/p$$

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

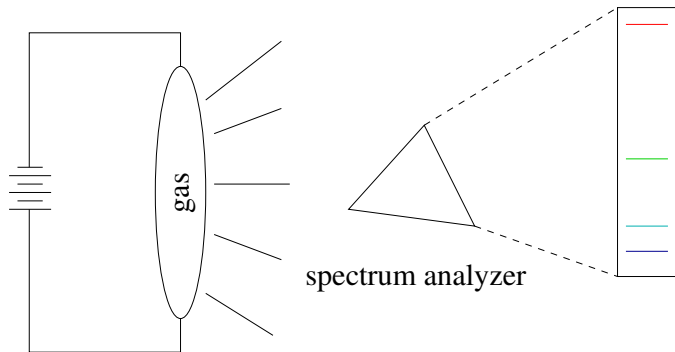
Nuclear reactors produce a lot of “thermal” neutrons. These are neutrons which have been equilibrated to a temperature near room temperature. Typically, such neutrons travel at speeds of 2.2 km/s or so. The mass of a neutron is 1.6750×10^{-27} kg.

$$\begin{aligned} \therefore p &= mv = (1.6750 \times 10^{-27} \text{ kg})(2.2 \times 10^3 \text{ m/s}) \\ &= 3.7 \times 10^{-24} \text{ kg m/s} \\ \therefore \lambda &= h/p = \frac{6.626\,070\,15 \times 10^{-34} \text{ J/Hz}}{3.7 \times 10^{-24} \text{ kg m/s}} \\ &= 0.18 \text{ nm} \end{aligned}$$

⇒ similar to bond lengths or to spacings between atoms in crystals

Formula	Applies to
$c = \lambda\nu$	light (or other waves)
$E = h\nu$	light (photons)
$p = mv$	ordinary particles
$p = h/\lambda$	both

Emission spectroscopy



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

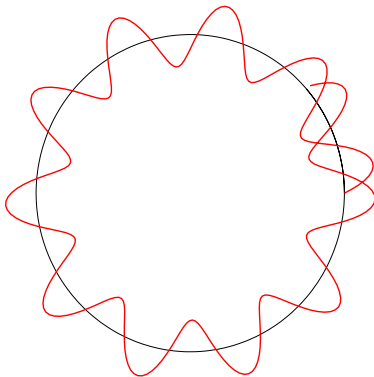
Hydrogenic atom: one electron circling a nucleus of atomic number Z

Examples: H, He⁺, Li²⁺, etc.

Assumption: circular electron orbit

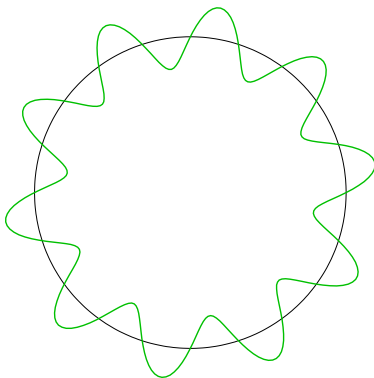
Key fact: The electron has a wavelength given by $\lambda = h/p$.

Wavelength mismatched to orbit:



Destructive interference \implies no wave/particle

Wavelength matched to orbit:



$$\implies 2\pi r = n\lambda \quad n = 1, 2, 3, \dots$$

Quantization conditions and quantum numbers

- 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 :

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}$$

where ϵ_0 is the **permittivity of free space** and r is the distance between the charges.

$$\epsilon_0 = 8.854\,187\,817 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$$

Equivalent units: $\text{C}^2\text{J}^{-1}\text{m}^{-1}$ or F m^{-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 $\frac{1}{4\pi\epsilon_0}$.

The energy of an orbiting electron

- For a nucleus of charge Ze separated from an electron of charge $-e$ by a distance r ,

$$|F| = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

- 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

$$v^2 = \frac{Ze^2}{4\pi\epsilon_0 m_e r} \quad (1)$$

The electron's momentum

$$v^2 = \frac{Ze^2}{4\pi\epsilon_0 m_e r} \quad (1)$$

- $p = mv$, and equation (1) gives us v as a function of r :

$$v = \sqrt{\frac{Ze^2}{4\pi\epsilon_0 m_e r}}$$
$$\therefore p = \sqrt{\frac{Ze^2 m_e}{4\pi\epsilon_0 r}}$$

Quantization of the orbit

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

- According to de Broglie, $\lambda = h/p$, 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

$$a_0 = \frac{h^2 \epsilon_0}{\pi e^2 m_e} = 52.917\,721\,067 \text{ pm}$$

Therefore

$$r_n = \frac{n^2}{Z} a_0$$

The energy of an orbiting electron

- Equation (1) gave

$$v^2 = \frac{Ze^2}{4\pi\epsilon_0 m_e r}$$

- The kinetic energy of the electron is

$$K = \frac{1}{2} m_e v^2 = \frac{Ze^2}{8\pi\epsilon_0 r}$$

- The electrostatic potential energy is

$$U = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

- The total energy is

$$E = K + U = \frac{-Ze^2}{8\pi\epsilon_0 r}$$

Quantization of the energy

- Substitute r_n into the energy:

$$E_n = \frac{-Ze^2}{8\pi\epsilon_0 a_0 n^2}$$

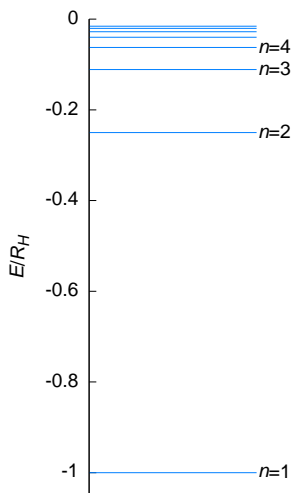
or

$$E_n = \frac{-Z^2 e^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{Z^2}{n^2} R_H$$

where R_H is Rydberg's constant:

$$R_H = \frac{e^2}{8\pi\epsilon_0 a_0} = \frac{e^4 m_e}{8h^2 \epsilon_0^2} = 2.179872325 \times 10^{-18} \text{ J}$$

Energy levels of hydrogen



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

$$\begin{aligned} h\nu &= E_{\text{upper}} - E_{\text{lower}} \\ &= Z^2 R_H \left(\frac{1}{n_{\text{lower}}^2} - \frac{1}{n_{\text{upper}}^2} \right) \end{aligned}$$

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_{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

Transition	Wavelength	Spectral region
2→1	122 nm	UV
100→1	91 nm	UV
3→2	656 nm	red
4→2	486 nm	blue
5→2	434 nm	violet
6→2	410 nm	violet
7→2	397 nm	UV
4→3	1.87 μm	IR
100→3	821 nm	IR

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: $2 \rightarrow 1$

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

Answer: $3 \rightarrow 2$

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)