Atomic spectra and structure: Bohr model of hydrogen

- Atomic structure
  - Greeks: Indivisible constituents of all matter
  - J. J. Thomson finds electron
  - Rutherford’s planetary model

- Atomic spectra
- Bohr’s quantized model
- Franck-Hertz experiment: Further evidence of quantization of atomic structure
Atomic structure – Brief history

• Greeks: Atoms determine properties of matter
  – Indivisible constituents

• J. J. Thomson discovers electron (1897)
  – Proposes plum-pudding model of atom
Atomic structure – Nuclear Atom

• Geiger-Marsden (Rutherford gold-foil) experiment (1909)
  – Demonstrates massive, positively charged nucleus

• Rutherford planetary model of atom (1911)
  – Positively charged nucleus surrounded by negative electrons
Atomic spectra

• Emission and absorption spectra
Atomic spectra – hydrogen

• Emission spectrum
  – Observe narrow emission wavelengths according to empirical formula

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

Rydberg formula

Rydberg constant

\[ R = 13.6 \text{ eV} \]

• Absorption spectrum
  – Not all lines of emission are found in absorption
Problems with planetary model

Classical treatment predicts

- Electron orbiting the nucleus undergoes constant acceleration and thus should continually emit radiation
- Electron should spiral into nucleus in approximately microseconds
- Radiation emitted should have a continuous spectrum of frequencies
Bohr model of hydrogen

- Electron orbits nucleus in circular orbit
- Electron and nucleus bound by Coulomb force

\[ F = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = \frac{m_e v^2}{r} \]

- This gives the kinetic energy

\[ K = \frac{1}{2} m_e v^2 = \frac{1}{8\pi\epsilon_0} \frac{e^2}{r} \]

- Potential energy is just Coulomb potential

\[ U = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \]

- Total energy is

\[ E = -\frac{1}{8\pi\epsilon_0} \frac{e^2}{r} \]

Classical up to this point. . .
Bohr model of hydrogen

Bohr postulates:

- Electrons can only occupy certain stationary states, in which radiation is not emitted and angular momentum is quantized
  \[ L = m_e v r = n \hbar \]
  \[ \hbar = \frac{\hbar}{2\pi} \]
- Radiation is only emitted or absorbed when the electron makes a transition from one stationary state to another.
Bohr model of hydrogen

• Solving for velocity

\[ L = m_e v r = n \hbar \quad \Rightarrow \quad v = \left( \frac{n \hbar}{m_e r} \right) \]

• Use this result in force equation

\[ F = \frac{1}{4\pi \varepsilon_0} \frac{e^2}{r^2} = \frac{m_e v^2}{r} = \frac{m_e}{r} \left( \frac{n \hbar}{m_e r} \right)^2 \]

• This can be solved for allowed radii

\[ r_n = \frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} n^2 = a_0 n^2 \]

Bohr radius

\[ a_0 \approx 0.53 \text{ Å} \]
Bohr model of hydrogen

- Allowed energy levels
  (sub $r_n$ into classical expression for total energy)

\[ E_n = -\frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2} = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{1}{n^2} = -\frac{E_1}{n^2} \]

$E_1 = 13.6 \text{ eV}$  
Same as Rydberg constant!

$n$ is called the quantum number
Emission spectra

- Photon energy given by difference between initial and final atomic energy levels

\[ E_{\text{ph}} = E_m - E_n = E_1 \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \]

\[ \nu_{\text{ph}} = \frac{E_1}{\hbar} \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \]
Absorption spectra

- Photon energy given by difference between initial and final atomic energy levels

Start in ground state at room temperature!

\[ E_{\text{ph}} = E_m - E_n = E_1 \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \]

\[ \nu_{\text{ph}} = \frac{E_1}{\hbar} \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \]
Hydrogen-like ions

- Nuclear charge now $Ze$
- Change all $e^2$ to $Ze^2$ in previous treatment
- This gives

$$r_n = \frac{a_0 n^2}{Z} \quad E_n = -E_1 \frac{Z^2}{n^2}$$

$$\nu_{ph} = \frac{E_1 Z^2}{h} \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$$
Franck-Hertz experiment – 1914

• Further evidence for Bohr model

Measured current drops every 4.9 V

Electrons experience an inelastic collision and lose 4.9 eV of energy
Limitations of Bohr model

- Cannot be applied to multi-electron atoms.
- Does not predict fine structure of atomic spectral lines.
- Does not provide a method to calculate relative intensities of spectral lines.
- Predicts the wrong value of angular momentum for the electron in the atom.
- Violates the Heisenberg uncertainty principle (although Bohr's model preceded this by more than a decade).
Summary of Bohr model

• Start with classical, circular orbits
• Angular momentum is quantized in allowed stationary states

\[ L = m_e v r = n \hbar \]

• Gives allowed radii and energy levels

\[ r_n = \frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} n^2 = a_0 n^2 \quad E_n = -\frac{E_1}{n^2} \]

• Emission and absorption of light by transitions between stationary states only
Wavelike behavior of matter

- Double slit experiment with photons
- de Broglie hypothesis
- Davisson-Germer experiment
- Diffraction and interference with larger systems: atoms, molecules
- Wave-particle duality: Wave function
Double slit experiment revisited

WAVE

• At low light levels *interference* pattern requires finite time to collect light

PARTICLE

• Photons detected *one at a time at a localized point!*
de Broglie hypothesis

• If light has both wave and particle properties, cannot matter also have wave properties?

• Special relativity implies:  \( E^2 = p^2 c^2 + (mc^2)^2 \)

• For a photon:  \( E = pc \)

• Using the Planck relation:  \( E = h\nu = \frac{hc}{\lambda} \)

\( \lambda_{dB} = \frac{h}{p} \)
de Broglie waves?

• de Broglie went beyond light and suggested this equation holds for all matter

\[ \lambda_{dB} = \frac{h}{p} \]

• de Broglie wavelength

• Why not observed in everyday life?

\[ \lambda_{cricket} = \frac{h}{mv} \]

\[ = \frac{6.626 \times 10^{-34} \text{ Js}}{(0.16 \text{ kg})(44.8 \text{ m/s})} \]

\[ = 9.2 \times 10^{-35} \text{ m} \]

\[ \lambda_{Bolt} = \frac{h}{mv} \]

\[ = \frac{6.626 \times 10^{-34} \text{ Js}}{(92 \text{ kg})(12.4 \text{ m/s})} \]

\[ = 5.8 \times 10^{-37} \text{ m} \]
de Broglie on Bohr atom

- de Broglie looked at Bohr’s atomic model like a musical instrument. Electrons guided by “pilot waves” in each orbit. Orbit circumference = integer number of wavelengths

\[
2\pi r_n = n\lambda_{dB}
\]

\[
\lambda_{dB} = \frac{\hbar}{p}
\]

\[
p_n = \frac{\hbar}{a_0 n}
\]
Analogy to optics

• When does wavelength of “matter wave” become relevant?

• Similar to diffraction in optics:

When scattering objects (of size $d$) become comparable to wavelength

<table>
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<tr>
<th>Wavelength</th>
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Momentum matters

• When does wavelength of “matter wave” become relevant?
• Similar to diffraction in optics:

When scattering objects (of size $d$) become comparable to wavelength.

Electrons with kinetic energy $K = 50$ eV

can use non-relativistic form of $K$
since $K \ll m_e c^2 = 0.511$ MeV

$$K \approx \frac{p^2}{2m} \implies p \approx \sqrt{2mK}$$

$$pc \approx \sqrt{2(0.511 \times 10^6 \text{ eV})(50) \text{ eV}}$$
$$= 7.15 \times 10^3 \text{ eV}$$

$$\lambda = \frac{hc}{pc} = \frac{1240 \text{ eV nm}}{7.15 \times 10^3 \text{ eV}}$$
$$= 0.173 \text{ nm}$$

Lattice spacing in crystals
Momentum matters

- When does wavelength of “matter wave” become relevant?
- Similar to diffraction in optics:

When scattering objects (of size $d$) become comparable to wavelength.

\[
\lambda_{dB} = \frac{h}{p}
\]

**Neutrons** with kinetic energy $K = 0.00024$ eV

- can use non-relativistic form of $K$ since $K \ll m_n c^2 = 940$ MeV

\[
K \approx \frac{p^2}{2m} \implies p \approx \sqrt{2mK}
\]

\[
p c \approx \sqrt{2mc^2K}
\]

\[
\lambda = \frac{hc}{pc} = \frac{1240 \text{ eV nm}}{672 \text{ eV}} = 1.85 \text{ nm}
\]

Nanowires
Electron diffraction: Davisson-Germer experiment (1925)

First direct demonstration of wave properties of matter

Constructive interference

\[ d \sin \theta = n\lambda \]

Nickel lattice spacing

\[ d = 0.215 \text{ nm} \]

Data and theory in good agreement!

Electrons accelerated through potential difference giving

\[ K = 54 \text{ eV} \]

\[ \lambda = \frac{h}{mv} = 0.167 \text{ nm} \]
Double slit experiment with electrons

- Two-paths around a charged wire (*Mach-Zehnder interferometer*)
- Electron microscopes used in many applications – resolution ~ 0.1 nm

Matter-wave diffraction with free-standing gratings over the years

1961
Jönssen (Cu grating)

1999
Arndt (Si₃N₄ grating)

2012
Arndt (Si₃N₄ grating)
Classical uncertainty in beam energy

• Spread in electron beam energy leads to spread in wavelength and thus diffraction pattern

• Consider diffraction grating

Constructive interference: \( d \sin \theta_n = n \lambda \)

For small angles:

\[
\theta \approx \frac{n \lambda}{d} \quad \Rightarrow \quad \frac{\Delta \theta}{\theta} \approx \frac{\Delta \lambda}{\lambda}
\]

Non-relativistic momentum:

\[
p \approx \sqrt{2mK} \quad \Rightarrow \quad \Delta p = \left| \frac{dp}{dK} \right| \Delta K = \frac{1}{2} (2mK)^{-1/2} 2m \Delta K = \frac{1}{2} p \Delta K
\]
Classical uncertainty in beam energy

- Spread in electron beam energy leads to spread in wavelength and thus diffraction pattern

- Consider diffraction grating

  Constructive interference:  \[ d \sin \theta_n = n \lambda \]

  For small angles:  \[
  \frac{\Delta \theta}{\theta} \approx \frac{\Delta \lambda}{\lambda} = \frac{\Delta p}{p} = \frac{1}{2} \frac{\Delta K}{K}
  \]

  For non-relativistic matter

  \[
  \Delta \frac{\theta}{\theta} = \frac{\Delta E_{\text{ph}}}{E_{\text{ph}}}
  \]

  For a photon (note factor of 2 difference)
Summary: Diffraction and interference of matter waves

- Interference of matter waves
  - Electrons
  - Neutrons
  - Atoms
  - Molecules
    - C60
    - Phthalocyanine
- Spread in kinetic energy of particles leads to spread in diffraction angle!

\[
\frac{\Delta \theta}{\theta} = \frac{1}{2} \frac{\Delta K}{K}
\]

\[
\frac{\Delta \theta}{\theta} = \frac{\Delta E_{\text{ph}}}{E_{\text{ph}}}
\]

de Broglie wavelength

\[
\lambda_{dB} = \frac{h}{p}
\]
Wave-particle duality

- Double slit (again)
- Superposition
- Wave function
- Probability
- Complementarity
- Uncertainty principle
Double slit interference

- Detection of a particle at point $x$ on the screen governed by interference of pathways the particle could take (Feynman)
- Two possible paths ($r_1$ or $r_2$), with equal amplitudes $A$, and phases $\phi_1$ and $\phi_2$

\[ \phi_1 = kr_1 = \frac{2\pi}{\lambda} \left( L^2 + \left( x + \frac{d}{2} \right)^2 \right)^{1/2} \]
\[ \phi_2 = kr_2 = \frac{2\pi}{\lambda} \left( L^2 + \left( x - \frac{d}{2} \right)^2 \right)^{1/2} \]
Double slit interference (Superposition)

- Particle flux (number per unit time) at a point \( x \) on the screen is given by the total amplitude squared

\[
N = |A_{\text{tot}}|^2
\]

\[
A_{\text{tot}} = A_1 + A_2 = A(e^{i\phi_1} + e^{i\phi_2})
\]

\[
N = A^2|e^{i\phi_1} + e^{i\phi_2}|^2 = 2A^2(1 + \cos(\Delta \phi))
\]

\[
\Delta \phi = \phi_1 - \phi_2 \approx \frac{2\pi xd}{\lambda L}
\]

\[
N(x) = 4A^2 \cos^2 \left( \frac{\pi xd}{\lambda L} \right)
\]
Double slit with “which-path” information

- Look to see through which slit the electron passes (put a wire loop around each slit)

- Any knowledge of “which slit” localizes the particle and destroys the superposition of possible paths – hence no interference.
Complementarity

• Wave or particle? You decide! Depends on how you look at the system...

• Wave nature of system can be observed when performing a “wave-like” experiment

• Particle nature of system is observed when performing a “particle-like” (which-path) experiment
Wave-particle duality

• Wave $\rightarrow$ wave function, e.g. a plane wave
  \[ \psi(x, t) = Ae^{i(k \cdot x - \omega t)} \]
  – Well-defined wavelength (frequency or energy) and momentum
  – Completely delocalized (no spatial or temporal information)

• Particle $\rightarrow$ trajectory
  \[ x(t) = \int_{-\infty}^{t} v(t') dt' \]
  – Well-defined position
  – Wavelength (and therefore “momentum”) undefined

In nature both wave and particle properties are present until you look!
Wave-function interpretation

• **Born interpretation**: Wave function describes probability to find “particle” in a small region about $x$ at time $t$

$$P(x)dx = |\psi(x, t)|^2 dx$$
Superposition and wavepackets

• Adding two or more plane waves gives a beat frequency and localized wavepacket

\[ \sin(k_1x) + \sin(k_2x) \]

\[ \sum_{m=1}^{10} \sin(k_m x) \]
Superposition and wavepackets

- Adding two or more plane waves gives a beat frequency and localized wavepacket
- Taken to a continuum sum -> integral
- Gaussian wavepacket

$$\psi(x) = \int_{-\infty}^{\infty} \phi(k)e^{ikx} \, dk = \int_{-\infty}^{\infty} e^{-k^2/2\Delta^2} e^{ikx} \, dk$$

$$|\phi(k)|^2$$

$$\frac{\Delta k}{\sqrt{2}}$$

$$\int_{-\infty}^{\infty} e^{-ax^2+bx} \, dx = \left(\frac{\pi}{a}\right)^{1/2} \exp\left(\frac{b^2}{4a}\right)$$
Superposition and wavepackets

- Adding two or more plane waves gives a beat frequency and localized wavepacket
- Taken to a continuum sum -> integral
- Gaussian wavepacket

$$\psi(x) = \int_{-\infty}^{\infty} \phi(k) e^{ikx} dk = \int_{-\infty}^{\infty} e^{-k^2/2\Delta k^2} e^{ikx} dk$$

$$|\phi(k)|^2 = \frac{\Delta k}{\sqrt{2}} e^{-x^2 \Delta k^2 / 2}$$

$$\Delta x = \frac{1}{\sqrt{2\Delta k}}$$
Superposition and wavepackets

- Adding two or more plane waves gives a beat frequency and localized wavepacket
- Taken to a continuum sum \(\rightarrow\) integral
- Gaussian wavepacket

\[
\Delta x \Delta k = \frac{1}{2}
\]

\[
|\phi(k)|^2
\]

\[
\frac{\Delta k}{\sqrt{2}} \quad \Delta k
\]

\[
\frac{\Delta \phi(k)}{\sqrt{2}} \quad \Delta \phi(k)
\]

\[
|\phi(k)|^2
\]

\[
p_x = \hbar k
\]

\[
\Delta x \Delta p_x = \frac{\hbar}{2}
\]

\[
\Delta x = \frac{1}{\sqrt{2} \Delta k}
\]
Heisenberg uncertainty principle

- Position and momentum are not simultaneously well-defined

\[ \Delta x \Delta p_x = \frac{\hbar}{2} \quad \text{and} \quad p = \hbar k \]

\[ \Delta x \Delta k = \frac{1}{2} \]

- Single slit or confined particle: Example – electron confined to an atom

\[ \Delta x \approx 0.5 \text{Å} \]

\[ p \approx \Delta p \approx \frac{\hbar}{\Delta x} \]

Gives nearly the same energy as the ground state energy of hydrogen!

\[ E = \frac{(pc)^2}{2mc^2} = \frac{(\hbar c)^2}{2\Delta x^2 mc^2} = 15 \text{ eV} \]
Wavicles summary

• Wave function describes de Broglie waves
  \[ \psi(x, t) = A(x, t) e^{i\phi(x,t)} \]

• Wave function describes probabilities where one will find a “particle”
  \[ P(x)\,dx = |\psi(x, t)|^2\,dx \]

• Superposition key
  – Superposition of plane waves leads to localized wavepackets
  – Measuring position collapses superposition
  – Complementarity – Can only observe wave or particle nature in a given experiment

• Heisenberg Uncertainty Relation
  \[ \Delta x \Delta p = \hbar \]