Franck-Hertz experiment: quantized energy levels in atoms (1913)

The Franck-Hertz experiment showed resonances in the electron-atom collision cross section:

\[ e^- + Hg \rightarrow e^- + Hg^+ + e^- \]

\[ e^- + Hg \rightarrow e^- + Hg^+ \]

The electrons are accelerated towards the anode flying through the mercury vapor. Some of them fly through the anode mesh, reach the detection plate D, and are detected as a current. A small potential energy difference of \(-0.5\,\text{eV}\) between D and A prevents low energy electrons with \(KE < 0.5\,\text{eV}\) to reach the detection plate. Thus, the current measured is due to all but the electrons which have close to zero KE.
Observed current as a function of anode voltage $U_a$

![Graph showing current $I$ versus anode voltage $U_a$.]

Equidistant peaks at 4.9 V, 9.8 V, 14.7 V etc. observed.

Interpretation: As voltage initially increases, more electrons reach the anode in spite of the mercury vapor. (Mercury atoms are much heavier than electrons, elastic collisions result in little energy loss.) At 4.9 V, the current suddenly drops because an inelastic collision between the electron and the Hg atom becomes possible, where the electron loses all its kinetic energy in a single collision to excite an Hg atom to a higher excited (electronic) state. Consequently, the electron does not have enough energy to reach the detector plate D and the current sharply decreases. The same repeats at 9.8 V (two inelastic collisions...
between electron and Hg atoms, 15.7 eV etc.

These resonances in the e–Hg collision cross section demonstrate the existence of a quantized energy level in Hg atoms at $q \cdot 4.9eV = 4.9eV = 8 \cdot 10^{-9} \text{J} = \frac{hc}{\lambda}$

with $\lambda = 253.7$ nm. This is indeed the strong observed mercury emission line in the UV.

Similar resonances can be observed in other atoms with (different) values of the resonant excitation energy $q$, corresponding to a different transition wavelength. The electrons in atoms have quantized energy levels, which is why atomic emission and absorption spectra have discrete lines. These lines are the fingerprint of the atoms, and some atoms (like Hg) were identified in terms of their spectra before they were isolated and otherwise characterized.
The Bohr atom (old QM) (1913)

The Rutherford model (positively charged nucleus of radius \( r \approx 10^{-15} \text{ m} \) surrounded by electron cloud of size \( r \approx 10^{-10} \text{ m} \)) explained the Rutherford scattering results, but not the stability of the atom (electrons on orbits should radiate and lose energy in \( 10^{-10} \text{ s} \)), nor the observed atomic emission spectra.

For the particularly simple case of hydrogen, Balmer had found an empirical formula that described well a group of emission lines known as the Balmer series (1985):

\[
\lambda_n = \frac{C}{\lambda_n} = R_{\infty} \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \ldots
\]

with the Rydberg constant \( R_{\infty} = 3.29 \times 10^{15} \text{ Hz} \).

\( n = 3 \) with \( \lambda_3 = \nu_m \) is called the Balmer \( \alpha \\) line, \( n = 4 \) with \( \lambda_4 = \nu_m \) the Balmer \( \beta \\) line etc.
Later different series were identified, the Lyman series in the UV with \( \frac{1}{z^2} \) replaced by \( \frac{1}{z^2} \), with the famous Lyman \( \alpha \) line at \( \lambda = 1216 \text{ Å} \), the Paschen series with \( \frac{1}{z^2} \) replaced by \( \frac{1}{3^2} \) etc. All these series can be summarized by the more general formula

\[
\nu_{nm} = \frac{C}{\lambda_{nm}} = \frac{R_\infty}{(\frac{1}{n^2} - \frac{1}{m^2})}
\]

with \( n, m \) integers and \( m \geq n \).

\( n = 1 \) Lyman series (\( m = 2 \) Lyman \( \alpha \), \( m = 3 \) Lyman \( \beta \) etc.)
\( n = 2 \) Balmer series (\( m = 3 \) Balmer \( \alpha \), \( m = 4 \) Balmer \( \beta \), ...)
\( n = 3 \) Paschen series (\( m = 4 \) Paschen \( \alpha \) etc.)

Niels Bohr could explain all of these lines by the following simple postulates that laid the foundation for quantum mechanics:
The Bohr postulates

1. Atoms have certain stable states (stationary states); light is emitted or absorbed when the atom makes a transition between stationary states.

2. If two stationary states have energies $E_2, E_1$ ($E_2 > E_1$), the light emitted in the transition $E_2 \rightarrow E_1$ has the frequency $\nu_{21} = \frac{E_2 - E_1}{h}$.

3. For circular orbits, the stationary states can be determined from a quantization condition for the angular momentum, $\nu v r = n \frac{\hbar}{2 \pi}$, $n = 1, 2, 3$, where $r$ is the classical orbit, and $v$ is the classical velocity for that orbit. The integer $n$ is called the quantum number for that orbit.

Bohr (and physics) were lucky; The Bohr postulates do reproduce the correct quantum energy levels by happenstance for a deeper reason. (Bohr correspondence principle, see
below), but for small \( n \) only "by accident."

**Bohr energy levels**

Circular orbit: centripetal force is Coulomb force

\[
\frac{f q^2}{4 \pi \varepsilon_0 r^2} = \frac{m v^2}{r} = \frac{f q^2 m r}{4 \pi \varepsilon_0}
\]

Bohr quantisation:

\[
\frac{1}{2} k \hbar^2 = (m v r)^2 = \frac{f q^2 m r}{4 \pi \varepsilon_0}
\]

\[
\Rightarrow \quad v_n = \frac{f q^2 \varepsilon_0}{m + q^2} n^2 \frac{k}{2} \quad n\text{-th Bohr orbit}
\]

\[
\frac{\hbar k}{m v n} = \frac{\hbar^2}{m} \frac{m + q^2}{4 \pi \varepsilon_0} \frac{1}{n^2} = \frac{f q^2}{4 \pi \varepsilon_0} \frac{1}{n^2}
\]

\[
\Rightarrow \quad \frac{\hbar k}{m v n} = \frac{f q^2}{4 \pi \varepsilon_0} \frac{1}{n^2} \quad n\text{-th Bohr orbital velocity}
\]

The energy is

\[
E_n = \frac{1}{2} m v_n^2 - \frac{f q^2}{4 \pi \varepsilon_0} = \frac{1}{2} m \left( \frac{f q^2}{4 \pi \varepsilon_0} \right)^2 \frac{1}{n^2} - \frac{f q^2}{4 \pi \varepsilon_0} = \frac{1}{n^2} \quad \text{Bohr energy levels}
\]

We can simplify these formulae if we define the dimensionless quantity

\[
\alpha = \frac{f q^2}{4 \pi \varepsilon_0 k} = \frac{1}{137.036}\]

**Fine structure constant**
\[ v_n = \frac{2\pi}{n} \]

\[ v_n = \frac{t}{mc^2} \]

\[ E_n = -\frac{1}{2} mc^2 \left( \frac{2\pi}{n} \right)^2 \]

Bohr energy levels for hydrogen-like atoms (one electron around a nucleus of charge $+Ze$).

Since $v \ll c$, use for $t \ll 100$, and the above non-relativistic calculation is valid.

An electron in a hydrogen atom ($t=1$) is non-relativistic, even for $n=1$.

The orbit radius increases as $n^2$, the orbit velocity decreases as $\frac{1}{n}$, the binding energy decreases as $\frac{1}{n^2}$.

The radius of the smallest stable orbit for $t=1$ is called Bohr radius $a_0 = \frac{\hbar}{e} = 0.53 \text{ Å}$.

The corresponding binding energy of the electron for the lowest stable energy state is

\[ E_1 = -\frac{1}{2} mc^2 (\frac{2\pi}{n})^2 = -\frac{3}{2} 13.6 \text{ eV} \]

\[ v_1 = \frac{t}{mc^2} \frac{1}{t} = \frac{a_0}{t} \]

Note that we have solved a non-relativistic problem.
apparently relativistic terms like \( \alpha_c \) are only introduced because we have chosen to express the results in terms of the fine structure constant \( \alpha = \frac{e^2}{4\pi\hbar c} \).

Strictly, we should have used the reduced mass \( \mu \) defined by \( \frac{1}{\mu} = \frac{1}{M} + \frac{1}{m} \) instead of the electron mass \( m \) (\( M \) is the mass of the nucleus), since we have transformed the two-body problem into an effective one-body problem. The reduced mass leads to a slight energy shift (correction on the order of \( \frac{m}{M} \)), and to slightly different transition frequencies for different isotopes. The largest difference, on the order of \( \frac{m_a}{m_h} = \frac{1}{1800} \), occurs for hydrogen and deuterium.
Hydrogen spectral lines

Emission (absorption) spectrum corresponds to transitions $E_m \rightarrow E_n$ with $m > n$ ($m < n$).

- $E = 0$
  - $13.6 \text{ ev}$
    - $\frac{16}{9}$
      - Ly$\alpha$
      - Balmer continuum limit
    - $\frac{13.6 \text{ ev}}{4}$
      - Ly$\beta$
      - Balmer series
      - $n = 3$ second excited state
    - $\frac{13.6 \text{ ev}}{1}$
      - Ly$\alpha$
      - Ly$\beta$
      - Balmer series
      - $n = 2$ first excited state
      - Ly continuum limit
      - (many closely spaced transitions)

$n$ is called the principal quantum number, labels orbit.
Transition frequencies

\[ \omega_{mn} = \frac{E_m - E_n}{\hbar} \]

Angular frequency \( \omega_{mn} \approx 2\pi \nu_{mn} \)

Transition frequency \( \nu_{mn} \)

\[ \nu_{mn} = -\frac{1}{2} \frac{mc^2}{\hbar} \left( \frac{1}{m^2} - \frac{1}{n^2} \right) = \frac{\hbar}{2mc^2} \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \quad (m > n) \]

- Matches spectroscopic (empirical) formula (\( \ell = 1 \))

\[ V = R_\infty \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \quad \text{with} \]

\[ R_\infty = \frac{mc^2}{2\hbar} = \frac{m c^2}{2\hbar} \left( \frac{e^4}{4\varepsilon_0^2 c^2} \right)^{\frac{1}{2}} = \frac{m e^4}{8\varepsilon_0^2 c^3} = 3.3 \times 10^{15} \text{ Hz} \]

Fundamental Rydberg constant

The Rydberg constant is the most accurately measured constant in physics; precision spectroscopy of hydrogen yields

\[ R = \frac{c}{\alpha} 10^{-7} = 7.31 \times 10^{15} \text{ Hz} \]

\[ \left( \frac{\alpha}{\pi} \times 10^{-12} \right) \]

Repeated measurements can be used to check experimentally if fundamental constants are really constant (in time).
Bohr correspondence principle

Calculate transition frequency for $m=n+1\rightarrow n$ for large $n$:

$$\nu_{n+1,n} = \frac{1}{h} \left( \frac{1}{n^2} - \frac{1}{(n+1)^2} \right) = \frac{1}{h} \frac{(n+1)^2 - n^2}{n^2(n+1)^2} =$$

$$= \frac{1}{h} \frac{2n+1}{n^2(n+1)^2} \approx \frac{2\nu_0}{n^3} \quad \text{to leading order in $n$}$$

Compare to electron orbit frequency (2:1)

$$f_{n+1} \approx \nu_0 = \frac{1}{2\pi m} = \frac{1}{h} \frac{1}{2\pi} \frac{mc^2}{h} \frac{1}{n^2} = \frac{mc^2}{h \cdot n^3} = \frac{2}{h^3} \nu_0$$

For large $n$ (large principal quantum number), the frequency emitted by the Bohr atom on a transition $n \rightarrow n+1$ equals the classical emission frequency by an oscillating electron.

Correspondence principle: Classical physics is contained within QM as a limiting case for large quantum number $n$.

(Same reasoning as letting $t \to 0$ to recover classical physics, number of quantze increases as $t \to 0$.)

Useful for "guessing" correct theory, but not exact principle, (e.g. there is no classical counterpart $n+2 \to n$, etc.)
Motivation for Bohr quantization condition

Compare de Broglie wavelength for Bohr-allowed momentum \( p_n \) to orbit of Bohr radius:

\[
p_n = m v_n = \frac{m v c}{\lambda_n} = \frac{\hbar}{\lambda_n} \quad \Rightarrow \quad \lambda_n = \frac{\hbar m v}{m c^2}
\]

\[
2 \pi v_n = \frac{2 \pi h}{\lambda_n} \quad \text{or} \quad \frac{m c}{\lambda_n} = \frac{n \hbar}{m c^2} = n
\]

Bohr quantization condition \( n v \psi = nh \) is equivalent to requiring that an integer number of de Broglie wavelengths fit on the classical circumference.

(Like eigenmodes on a violin string, except different boundary conditions.)

The principal quantum number \( n \) is associated with the number of de Broglie wavelengths that fit on the classical orbit.)
Generalization for elliptical orbits:

Wilson-Sommerfeld quantization condition:

\[ \oint p \, dq = n \hbar \]
for any closed orbit

(\(q\) coordinate, \(p\) momentum)

Bohr atom: \( p = mvr, \quad q = \phi \) (angle)
\[ \oint p \, dq = mvr \oint \, d\phi = 2\pi mvr = n \hbar \]

\( mvr = n \hbar \) Bohr quantization condition for circular orbit

More generally: \[ \oint p \, dq = \oint \frac{\hbar}{\lambda_d(q)} \, dq = n \hbar \]
equivalent to \[ \oint \frac{dq}{\lambda_d(q)} = n, \]
i.e. integer number of de Broglie wavelengths on closed orbit level.

If \( \lambda_d \) changes along path because momentum changes along path.

\[ \text{elliptical orbit} \]

Wilson-Sommerfeld condition describes elliptical orbits correctly (details in hydrogen spectrum).
Motivation for quantization condition

On the "wrong" orbit (slightly away from Bohr orbit), the de Broglie wave starts to interfere destructively on successive round trips = reason for "eigenmodes": Constructive interference, just as in Fermat's principle of stationary time.

Questions the Bohr model does not answer:

- How far away is "wrong" orbit?
- What about diffraction in orbit?
- Nature of transitions now, time required?
- Incorrect prediction for hydrogen ground state: \( L = 1 \) (correct answer: \( L = 0 \)).
Correct quantum mechanical description for hydrogen atom is more like three-dimensional eigenmode problem.

Compare to: oscillating metal plate, what are eigenmodes.

QMN: wavefunction $\Psi$ oscillates, $|\Psi|^2$ determines probability of finding electron in small volume $dV$ near $r$. 
Example for Wilson–Sommerfeld quantization:

Harmonic oscillator

\[ V(x) = \frac{1}{2} k x^2 \]

At constant total energy \( E \), the particle's momentum \( p \) is position-dependent:

\[ E = \frac{p^2}{2m} + \frac{1}{2} k x^2 \]

\[ \Rightarrow \quad |p(x)| = \sqrt{2m \left( E - \frac{1}{2} k x^2 \right)} \]

\[ \Rightarrow \quad \text{The de Broglie wavelength of the particle changes as it oscillates in the potential} \]

\[ \lambda_{db}(x) = \frac{\hbar}{|p(x)|} \]
Wilson–Sommerfeld quantization:

\[ \phi \rho dq = \phi \rho(x) dx = 2 \int_{-x_0}^{x_0} \sqrt{2m(E - \frac{1}{2} m w^2 x^2)} \, dx \]

\[ = 2 \sqrt{2mE} \int_{-x_0}^{x_0} dx \sqrt{1 - \frac{m w^2 x^2}{2E}} = 2 \sqrt{2mE} \int_{-x_0}^{x_0} dx \sqrt{1 - (x/x_0)^2} \]

\[ = 2 \sqrt{2mE} x_0 \int_{-1}^{1} dy \sqrt{1 - y^2} = 2 \sqrt{2mE} \frac{\pi}{2} x_0 \]

\[ = \sqrt{2mE} \pi x_0 = \sqrt{2mE} \pi \sqrt{\frac{E}{m w^2}} = 2 \pi \frac{E}{\hbar} \]

Here we have used \( E = \frac{1}{2} m w^2 x_0^2 \) as!

Thus the quantization condition \( \phi \rho dq = n \hbar \)

becomes \( 2 \pi \frac{E}{\hbar} = n \hbar \) or

\[ E_n = n \frac{1}{2\pi} \frac{E}{\hbar} = n \hbar w \]

\[ E_n = \hbar w \text{ quantized energy levels of} \]

a harmonic oscillator

according to Sommerfeld quantization.

(Almost correct: full quantum theory yields

\[ E_n = (n + \frac{1}{2}) \hbar w :) \]
The quantized energy levels of a harmonic oscillator are equidistant with step size (fundamental energy scale) \( h \).

The WS result (quantization of classical momentum \( p(x) \) or classical path \( x \)) does not yield quite the correct result because in wave mechanics the classical path exists only as an approximate concept (a limiting case). We really need to solve the "stationary oscillation problem" (eigenvalue problem).

- The Schrödinger equation is the mathematical description of the eigenvalue problem.