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

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


Figure I: Franck-Hertz apparatus. Electrons emitted from a cathode are accelerated through a mercury vapor. If the electrons lose energy in an inelastic collision, they do not reach the detector.

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 V between $D$ and $A$ prevents low-energy electrons with $\mathrm{KE}<0.5 \mathrm{eV}$ from reaching the detection plate. Thus the current measured is due to all but the electrons which have close to zero KE.

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 of its kinetic energy in a single collision to excite an Hg atom to a higher-lying (electronic) state. Consequently the electron does not have enough energy to read the detection plate $D$ and the current sharply decreases. The same repeats at 9.8 V (two inelastic collisions between electron and Hg atoms, 15.7 V etc. These resonances in the e- Hg collision cross section demonstrate the existence of a quantized energy level in Hg atoms at $q \cdot 4.9 \mathrm{~V}=4.9 \mathrm{eV}=8 \cdot 10^{-19} \mathrm{~J}=\frac{h c}{\lambda}$ with $\lambda=253.7 \mathrm{~nm}$. This is indeed the strong observed mercury emission line in the ultraviolet.


Figure II: Observed current as a function of anode voltage $U_{0}$. Equidistant peaks at 4.9 V, 9.8 V, 14.7 V, etc. observed.

Similar resonances can be observed in other atoms with different values of resonant excitation energy $q V_{0}$, 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 He which was discovered in the sun's spectrum, hence the name; helios $($ Greek $)=$ sun $)$ were identified in terms of their spectra before they were isolated and chemically characterized.

## The Bohr atom (old QM) (1913)

The Rutherford model (positively charged nucleus of radius $r \sim 10^{-15} \mathrm{~m}$ surrounded by electron cloud of size $\sim 19^{-10} \mathrm{~m}$ ) explained the Rutherford scattering results, but not the stability of the atom (electrons on orbits should radiate and lose energy in $10^{-10} \mathrm{~s}$ ), 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 (1885):

$$
\begin{equation*}
\nu_{n}=\frac{c}{\lambda_{n}}=R_{\infty}\left(\frac{1}{2^{2}}-\frac{1}{n^{2}}\right), \quad n=3,4,5, \ldots \tag{8-1}
\end{equation*}
$$

with the Rydberg constant $R_{\infty}=3.29 \cdot 10^{15} \mathrm{~Hz} ; n=3$ with $\lambda_{3}=656.3 \mathrm{~nm}$ is called the Balmer $\alpha$ line, $n=4$ with $\lambda_{4}=486.1 \mathrm{~nm}$ the Balmer $\beta$ line etc.

Later, different series were identified, the Lyman series in the UV with $\left(\frac{1}{2^{2}}\right)$ replaced by $\left(\frac{1}{1^{2}}\right)$, with the famous Lyman $\alpha$ line at $\lambda=121 \mathrm{~nm}$, the Paschen series with $\left(\frac{1}{2^{2}}\right)$ replaced by $\left(\frac{1}{3^{2}}\right)$ etc. All these series can be summarized by the more general
formula

$$
\begin{equation*}
\nu_{n m}=\frac{x}{\lambda_{n m}}=R_{\infty}\left(\frac{1}{n^{2}}-\frac{1}{m^{2}}\right) \tag{8-2}
\end{equation*}
$$

with $n, m$ integers and $m \geq n$.

$$
\begin{array}{||lcl}
\hline n=1 & \text { Lyman series } & (m=2 \text { Lyman } \alpha, m=3 \text { Lyman } \beta \text { etc. }) \\
n=2 & \text { Balmer series } & (m=3 \text { Balmer } \alpha, m=4 \text { Balmer } \beta \text { etc. }) \\
n=3 & \text { Paschen series } & (m=4 \text { Paschen } \alpha, m=5 \text { Paschen } \beta \text { etc. }) \\
\hline
\end{array}
$$

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 $E_{1}, E_{2}\left(E_{2}>E_{1}\right)$, the light emitted on the transition $E_{2} \rightarrow E_{1}$ has the frequency:

$$
\begin{equation*}
\nu_{21}=\frac{E_{2}-E_{1}}{h} \tag{8-3}
\end{equation*}
$$

3. For circular orbits, the stationary states can be determined from a quantization condition for the angular momentum, $m v r=n \hbar, n=1,2,3$, 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 QM energy levels. For large $n$ this occurs for a deeper reason (Bohr correspondence principle), but for small $n$ only "by accident."

## Bohr energy levels

- Circular orbit $\rightarrow$ centripetal force is Coulomb force:

$$
\begin{equation*}
\frac{Z q^{2}}{4 \pi \epsilon_{0} r^{2}}=\frac{m v^{2}}{r} \Longrightarrow m^{2} v^{2} r^{2}=\frac{Z q^{2}}{4 \pi \epsilon_{0}} m r \tag{8-4}
\end{equation*}
$$

- Bohr quantization:

$$
\begin{equation*}
n^{2} \hbar^{2}=(m v r)^{2}=\frac{Z q^{2}}{4 \pi \epsilon_{0}} m r \tag{8-5}
\end{equation*}
$$

- n-th Bohr orbit:

$$
\begin{equation*}
r_{n}=\frac{4 \pi \epsilon_{0}}{m Z q^{2}} n^{2} \hbar^{2} \tag{8-6}
\end{equation*}
$$

- n -th Bohr orbital velocity:

$$
\begin{equation*}
v_{n}=\frac{Z q^{2}}{4 \pi \epsilon_{0}} \frac{1}{n \hbar} \tag{8-7}
\end{equation*}
$$



Figure III: An electron of charge $-q$ on a circular orbit around a nucleus of charge $Z q$. Bohr postulated that only certain values of angular momentum correspond to stable orbits.

The energy is

$$
\begin{align*}
E_{n} & =\frac{1}{2} m v_{n}^{2}-\frac{Z q^{2}}{4 \pi \epsilon_{0} r_{n}}  \tag{8-8}\\
& =\frac{1}{2} m\left(\frac{Z q^{2}}{4 \pi \epsilon_{0}}\right)^{2} \frac{1}{n^{2} \hbar^{2}}-\frac{Z q^{2}}{4 \pi \epsilon_{0}} \frac{m Z q^{2}}{4 \pi \epsilon_{0}} \frac{1}{n^{2} \hbar^{2}}  \tag{8-9}\\
& =-\frac{1}{2} m\left(\frac{Z q^{2}}{4 \pi \epsilon_{0}}\right)^{2} \frac{1}{n^{2} \hbar^{2}} \tag{8-10}
\end{align*}
$$

We can simplify these formulae if we define the dimensionless quantity: fine structure constant.

$$
\begin{equation*}
\alpha=\frac{q^{2}}{4 \pi \epsilon_{0} \hbar c}=\frac{1}{137.036 \ldots} \tag{8-11}
\end{equation*}
$$

For hydrogen-like atoms (one electron around nucleus of charge +Zq ):

- n-th Bohr orbit:

$$
\begin{equation*}
r_{n}=\frac{\hbar}{m c Z \alpha} n^{2} \tag{8-12}
\end{equation*}
$$

- n-th Bohr orbital velocity:

$$
\begin{equation*}
v_{n}=\frac{Z \alpha c}{n} \tag{8-13}
\end{equation*}
$$

- Bohr energy levels:

$$
\begin{equation*}
E_{n}=-\frac{1}{2} m c^{2} \frac{(Z \alpha)^{2}}{n^{2}} \tag{8-14}
\end{equation*}
$$

Since $\alpha \ll 1, v \ll c$ for $Z \ll 100$, and the above non-relativistic calculation is valid. An electron in a hydrogen atom $(Z=1)$ 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 $Z=1$ is called Bohr radius.

$$
\begin{equation*}
a_{0}=\frac{\hbar}{m c \alpha}=0.53 \AA \tag{8-15}
\end{equation*}
$$

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

- $E_{1}=-\frac{1}{2} m c^{2}(Z \alpha)^{2}=-Z^{2} \cdot 13.6 \mathrm{eV}$
- $r_{1}=\frac{\hbar}{m c \alpha} \frac{1}{Z}=\frac{a_{0}}{Z}$

Note. i) We have solved a non-relativistic problem. Apparently relativistic terms like $m c^{2}$ are only introduced because we have chosen to express the results in terms of the fine structure constant $\alpha=\frac{q^{2}}{4 \pi \epsilon_{0} \hbar c}$.
ii)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 the equivalent one-body problem. The appearance of 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 fractional frequency difference, on the order of $\frac{m}{M} \approx \frac{1}{1800}$ occurs for hydrogen and deuterium.

## Hydrogen spectral lines

Emision (absorption) spectrum corresponds to transitions $E_{m} \rightarrow E_{n}$ with $m>n$ $(m<n)$.


Figure IV: Hydrogen Spectral lines. $n$ is called the principal quantum number, it labels the orbit. The spectrum consists of series that are grouped by the same lower energy level: Lyman $n=1$, Balmer $n=2$, Paschen $n=3$ ), etc.

## Transition frequencies

$$
\begin{align*}
\omega_{m n} & =\frac{E_{m}-E_{n}}{\hbar} \quad \text { angular frequency }\left(\omega_{m n}=2 \pi \nu_{m n}\right)  \tag{8-16}\\
\nu_{m n} & =\frac{E_{m}-E_{n}}{h} \quad \text { transition frequency }  \tag{8-17}\\
\frac{\nu_{m}}{\nu_{m}} & \left.=-\frac{1}{m c^{2}(Z \alpha)^{2}} \underset{\text { of Tkechnoldgga }}{ }{ }^{2}-\frac{1}{n^{2}}\right)  \tag{8-18}\\
& =\frac{Z^{2} m c^{2} \alpha^{2}}{2 h}\left(\frac{1}{n^{2}}-\frac{1}{m^{2}}\right) \quad(m>n) \tag{8-19}
\end{align*}
$$

$\rightarrow$ Matches spectroscopic (empirical) formula $(Z=1)$

The Rydberg constant is the most accurately measured constant in physics. Precision spectroscopy of hydrogen yields

$$
\begin{equation*}
R=c \cdot 10973731.568639(91) \mathrm{m}^{-11} \quad\left(\frac{\Delta R}{R} \sim 10^{-12}\right) \tag{8-23}
\end{equation*}
$$

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 $n$ :

$$
\begin{align*}
v_{n+1 \rightarrow n} & =R_{\infty}\left(\frac{1}{n^{2}}-\frac{1}{(n+1)^{2}}\right) \quad=R_{\infty} \frac{(n+1)^{2}-n^{2}}{n^{2}(n+1)^{2}}  \tag{8-24}\\
& =R_{\infty} \frac{2 n+1}{n^{2}(n+1)^{2}} \approx \frac{2 R_{\infty}}{n^{3}}  \tag{8-25}\\
& \rightarrow \text { to leading order in } n \tag{8-26}
\end{align*}
$$

Compare to electron orbit frequency ( $\mathrm{z}=1$ )

$$
\begin{equation*}
f n+1 \approx f_{n}=\frac{v_{n}}{2 \pi v_{n}}=\frac{\alpha c}{n} \frac{1}{2 \pi} \frac{m c \alpha}{\hbar} \frac{1}{n^{2}}=\frac{m c^{2} \alpha^{2}}{h \cdot n^{3}}=\frac{2}{n^{3}} R_{\infty} \tag{8-27}
\end{equation*}
$$

$\Longrightarrow$ 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 the oscillating electron.

Correspondence principle 1. Classical physics is contained within QM as a limiting case for large quantum number $n$. This is the same reasoning as letting $\hbar \rightarrow 0$ to recover classical physics, as the number of quanta increases as $\hbar \rightarrow 0$. The Bohr correspondence principle is useful for "guessing" the correct theory, but it is not an exact principle, e.g. there is no classical counterpart to the transition $n+2 \rightarrow n$ that does occur, and is allowed by QM, etc.

## Motivation for Bohr quantization condition

Compare deBroglie wavelength for Bohr-allowed momentum $\lambda_{n}$ to orbit of Bohr radius:

$$
\begin{gather*}
p_{n}=m v_{n}=\frac{m \alpha c}{n}=\frac{h}{\lambda_{n}} \rightarrow \lambda_{n}=\frac{n h}{m c \alpha}  \tag{8-28}\\
\frac{2 \pi r_{n}}{\lambda_{n}}=\frac{2 \pi \hbar}{m c \alpha} n^{2} \frac{m c \alpha}{n h}=n \tag{8-29}
\end{gather*}
$$



Figure V: The de Broglie waves on a Bohr orbit are like eigenmodes on a violin string, except that the boundary conditions are different (string closes on itself).

Bohr quantization condition $m v r=n \hbar$ is equivalent to requiring that an integer number $n$ of de Broglie waves fit on the classical circumference. 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

$$
\begin{equation*}
\oint p d q=n h \quad \rightarrow \quad \text { for any closed orbit: } q \text { coordinate, } p \text { momentum } \tag{8-30}
\end{equation*}
$$

Bohr atom: $p=m v r, q=\phi$ (angle)

$$
\begin{align*}
\oint p d q & =m v r \int_{0}^{2 \pi} d \phi=2 \pi m v r=n h  \tag{8-31}\\
m v r & =n \hbar \quad \rightarrow \quad \text { Bohr quantization condition for circular orbit. } \tag{8-32}
\end{align*}
$$

More generally,

$$
\begin{equation*}
\oint p d q=\oint \frac{h}{\lambda_{\mathrm{dB}}(q)} d q=n h \tag{8-33}
\end{equation*}
$$

equivalent to

$$
\begin{equation*}
\oint \frac{d q}{\lambda_{\mathrm{dB}}(q)}=n \tag{8-34}
\end{equation*}
$$

i.e. integer number of deBroglie wavelengths on closed orbit (even if $\lambda_{\mathrm{dB}}$ changes along path because momentum changes along path). Wilson-Sommerfeld condition


Figure VI: Wilson-Sommerfeld quantization for elliptical orbits. The condition of constructive interference on an elliptical orbit yield the correct orbits, even in the case of elliptical orbits, where the magnitude of the momentum, and thus the de Broglie wavelength, changes along the orbit.
describes elliptical orbits correctly (details in hydrogen spectrum).

## Motivation for quantization condition



Figure VII: On the "wrong" orbits the wavefunction interferes destructively on successive round trips. This is reminiscent of Fermat's principle of least time where nearby paths that result in destructive interference do not correspond to classical paths.

On the "wrong" orbit (slightly away from Bohr orbit), the deBroglie wave starts to interfere destructively on successive round trips.
$\Longrightarrow$ 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 $n \rightarrow m$, time required?
- Incorrect prediction for hydrogen ground state: $L=\hbar$ (correct answer: $L=0$ ).

Correct quantum mechanical description for hydrogen atom is more like three-dimensional eigenmode problem


Figure VIII: Oscillating metal plate: quantized modes in two dimensions.

QM. Wavefunction $\psi$ oscillates, $|\psi(\mathbf{r})|^{2} d v$ determines probability of finding electron near $\mathbf{r}$.

## Example for Wilson-Sommerfeld quantization: harmonic oscillator



Figure IX: Harmonic-oscillator potential.

At constant total energy $E$, the particle's momentum $p$ is position-dependent

$$
\begin{equation*}
E=\frac{p^{2}}{2 m}+\frac{1}{2} m \omega^{2} x^{2} \tag{8-35}
\end{equation*}
$$

- magnitude of momentum: $|p(x)|=\sqrt{2 m} \sqrt{E-\frac{1}{2} m \omega^{2} x^{2}}$
- The deBroglie wavelength of the particle changes as it oscillates in the potential.


Figure X: Position-dependent de Broglie wavelength $\lambda_{\mathrm{dB}}(x)=\frac{h}{p(x)}$. Allowed states correspond to constructive interference on successive round trips.

## Wilson-Sommerfeld quantization

$$
\begin{align*}
\oint p d q=\oint p(x) d x & =2 \int_{-x_{0}}^{x_{0}} \sqrt{2 m} \cdot \sqrt{E-\frac{1}{2} m \omega^{2} x^{2}} d x  \tag{8-36}\\
& =2 \sqrt{2 m E} \int_{-x_{0}}^{x_{0}} d x \sqrt{1-\frac{m \omega^{2}}{2 E} x^{2}}  \tag{8-37}\\
& =2 \sqrt{2 m E} \int_{-x_{0}}^{x_{0}} d x \sqrt{1-\left(\frac{x}{x_{0}}\right)^{2}}  \tag{8-38}\\
& =2 \sqrt{2 m E} x_{0} \int_{1}^{1} d y \sqrt{1-y^{2}}  \tag{8-39}\\
& =2 \sqrt{2 m E} \frac{\pi}{2} x_{0}  \tag{8-40}\\
& =\sqrt{2 m E} \pi x_{0}  \tag{8-41}\\
& =\sqrt{2 m E} \pi \sqrt{\frac{2 E}{m \omega^{2}}}=2 \pi \frac{E}{\omega} \tag{8-42}
\end{align*}
$$

Here we have used $E=\frac{1}{2} m \omega^{2} x_{0}{ }^{2}$. Thus the quantization condition $\oint p d q=n h$ becomes $2 \pi \frac{E}{\omega}=n h$ or $E_{n}=n \frac{h}{2 \pi} \omega=n \hbar \omega \Longrightarrow$ quantized energy levels of a harmonic oscillator according to Sommerfeld quantization. Almost correct: full quantum theory yields $E_{n}=\left(n+\frac{1}{2}\right) \hbar \omega$. The quantized energy levels of a harmonic oscillator are equidistant with step size (fundamental energy scale) $\hbar \omega$. The Wilson-Sommerfeld result (quantization of classical momentum $p(x)$ on classical path $x$ ) does not yield quite the correct result because in wave mechanics the classical path exist only as an approximate concept (a limiting case). We really need to solve the "stationary oscillation problem" (eigenvalue problem). The Schödinger equation is the mathematical description of the eigenvalue problem.


Figure XI: Reminder for calculating the integral 8-39 without Mathematica.

