

Bohr's model

- Based on scaling to get a distance with atomic dimensions, and then the wild guess of quantized orbital momentum: $l = n\hbar$

- Orbital radii with Bohr radius $a_0 = 0.053$ nm:

$$(1) \quad r_n = a_0 \frac{n^2}{Z} \quad \text{with} \quad a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$$

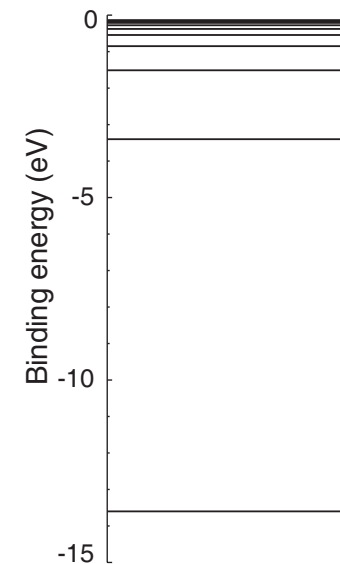
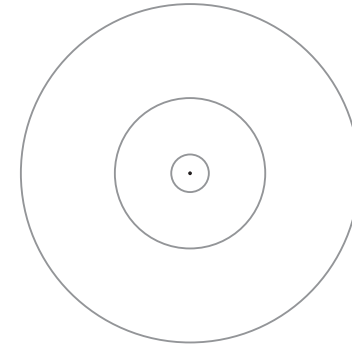
- Binding energy with $E_0 = 13.6$ eV:

$$(2) \quad E_n = -\frac{Z^2}{n^2} E_0 \quad \text{with} \quad E_0 \equiv \frac{m_e e^4}{8h^2\epsilon_0^2}$$

- Orbital velocities and fine structure constant

$$\alpha = 1/137.036:$$

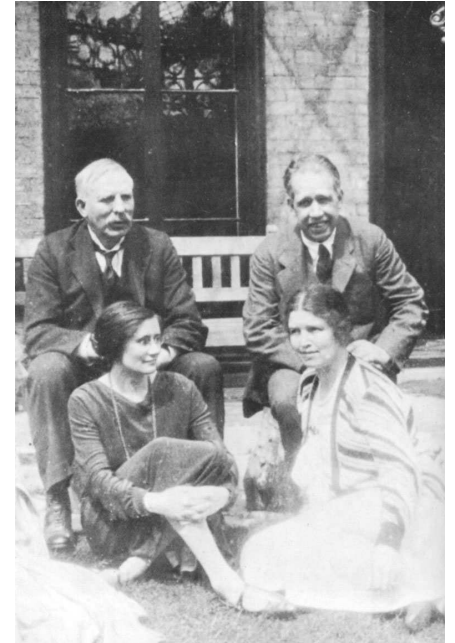
$$(3) \quad v = \frac{Z}{n} \alpha c \quad \text{with} \quad \alpha \equiv \frac{e^2}{2\epsilon_0 hc}$$



Does Bohr make sense?

- Bohr's paper is [here](#).
- Bohr developed his basic ideas while at Manchester with Rutherford April-July 1912. Started writing a paper while on his honeymoon in August 1912, before starting to teach as an Assistant Professor in Copenhagen. Finally sent a draft of his paper to Rutherford in March 1913.
- Rutherford wrote to Bohr:

There appears to me one grave difficulty in your hypothesis, which I have no doubt you fully realize, namely, how does an electron decide what frequency it is going to vibrate at when it passes from one stationary state to the other? It seems to me that you would have to assume that the electron knows beforehand where it is going to stop.



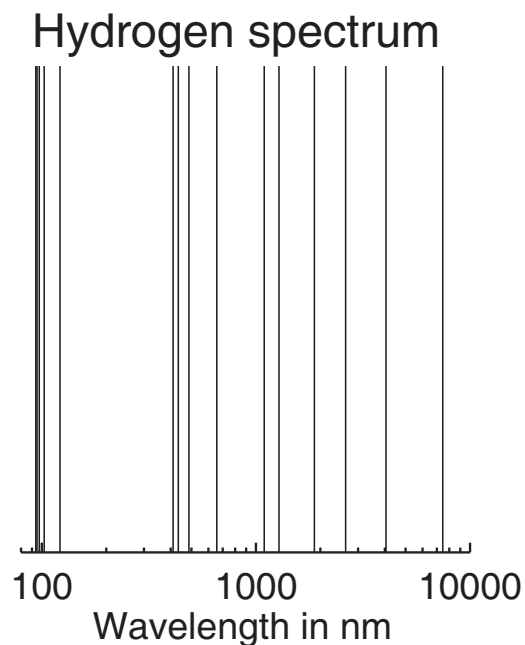
Lord and Lady Rutherford, and Niels and Margrethe Bohr (probably ca. 1930)

Nonsense or not?

- While a student in 1913, Otto Stern (Nobel Prize 1946) made a vow with Max von Laue (Nobel Prize 1914): “If this nonsense of Bohr should in the end prove to be right, we will quit physics!”—according to B. Friedrich and D. Herschbach, *Physics Today* **56** (Dec. 2003), p. 56; see their reference 3.
- Bohr’s friend H.M. Hansen points out that hydrogen atoms absorb and emit light at specific wavelengths. Back in 1885, a Swiss high school math teacher named Johan Jacob Balmer had discovered a pattern to the hydrogen spectrum:

$$(4) \quad \frac{1}{\lambda} = \text{const.} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

- Others then found similar patterns using not $1/2^2$ but $1/1^2$ (the Lyman series), $1/3^2$ (the Paschen series), $1/4^2$ (the Brackett series), and $1/5^2$ (the Pfund series).



So what would Bohr predict?

- Consider a transition from an initial state n_i to a final state n_f :

$$(5) \quad \Delta E = \frac{hc}{\lambda} = E_{n_f} - E_{n_i} = -E_0 Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = Z^2 E_0 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

or if $Z = 1$ the result

$$(6) \quad \frac{1}{\lambda} = \frac{E_0}{hc} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right).$$

Can you imagine how Bohr felt when he found this agreed with the Balmer series?

- It may have been through matching the hydrogen spectrum that Bohr found that $l = n\hbar$ rather than $l = nh$.
- The quantity $E_0/(hc)$ is also known as the Rydberg constant $R_\infty = 1.09737 \times 10^7 \text{ m}^{-1}$:

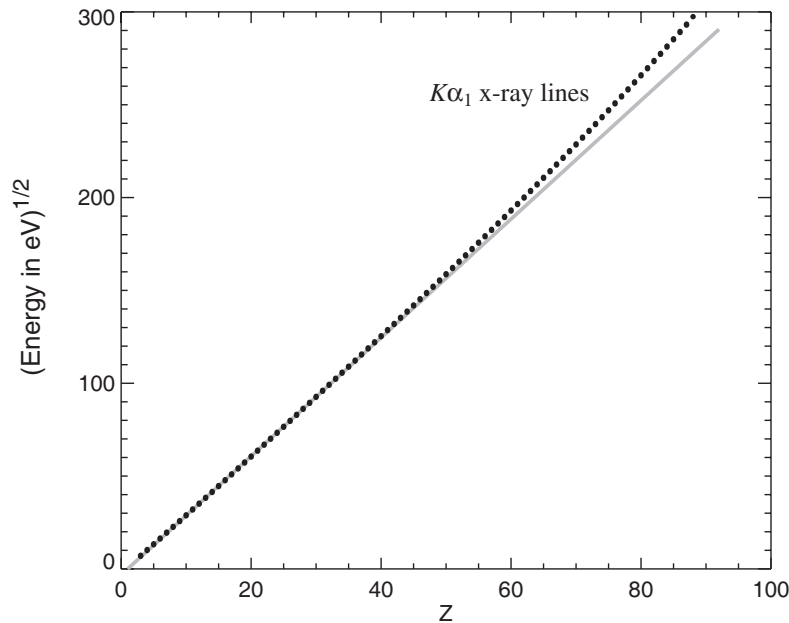
$$(7) \quad R_\infty \equiv \frac{E_0}{hc} = \frac{m_e e^4}{8h^2 \epsilon_0^2} \frac{1}{hc} = \frac{m_e e^4}{8h^3 c \epsilon_0^2}$$

Transition energies in hydrogen

$n_f:$		1	2	3	4	5
$E_f:$		-13.600 eV	-3.400 eV	-1.511 eV	-0.850 eV	-0.544 eV
$n_i:$	$E_n:$					
2	-3.400 eV	10.20 eV				
		121.6 nm				
3	-1.511 eV	12.09 eV	1.889 eV			
		102.6 nm	656.4 nm			
4	-0.850 eV	12.75 eV	2.550 eV	0.661 eV		
		97.20 nm	486.2 nm	1875. nm		
5	-0.544 eV	13.06 eV	2.856 eV	0.967 eV	0.306 eV	
		95.00 nm	434.1 nm	1282. nm	4052. nm	
∞	0 eV	13.60 eV	3.400 eV	1.511 eV	0.850 eV	0.544 eV
		91.20 nm	364.7 nm	820.5 nm	1459. nm	2279. nm

Moseley's Law

Moseley was working in Rutherford's lab, looking at the characteristic X-ray energies from different targets in x-ray tubes. He noticed that the energies of these lines seemed to follow a regular pattern of $E \propto Z^2$:



Unfortunately, Moseley left the lab in 1914 and volunteered for the army when WWI broke out in 1915. He was killed by a sniper at Gallipoli, Turkey on Aug. 10, 1915.



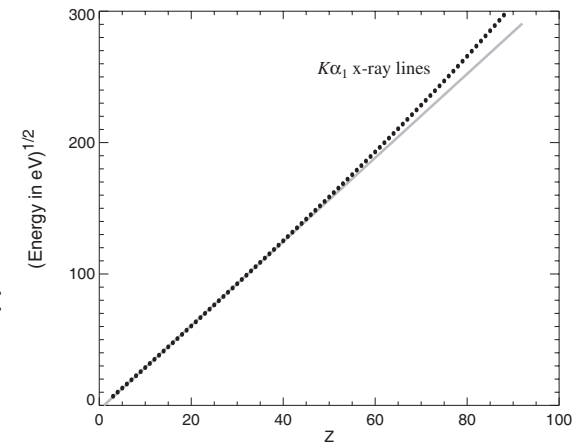
Henry Moseley (1887–1915)

Bohr and Moseley's law

- Again, Moseley had found that x-ray lines follow $E \propto Z^2$. Bohr can explain it!
- The incident electron knocks out an inner-shell electron. Another electron drops down to fill the spot. K_α lines involve $n_f = 1$ and $n_i = 2$ transitions, and assume partial screening of the nuclear charge by the other electron in the $n = 1$ orbital:

$$\begin{aligned} E_K &= (13.6 \text{ eV})(Z - 1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \\ (8) \quad &= \frac{3}{4}(13.6 \text{ eV})(Z - 1)^2 \end{aligned}$$

- This helped in pinning down the correct ordering of elements in the periodic table, and eventually led D. Coster and G. von Hevesy to discover Hafnium in 1923 while working at Bohr's Institute in Copenhagen.



K_α involves $n = 2 \rightarrow 1$

K_β involves $n = 3 \rightarrow 1$

L_α involves $n = 3 \rightarrow 2$

L_β involves $n = 4 \rightarrow 2$

and so on...

The Franck-Hertz experiment

Accelerate electrons by a varying voltage, and then run them through a gas.

Serway Fig. 4.27:

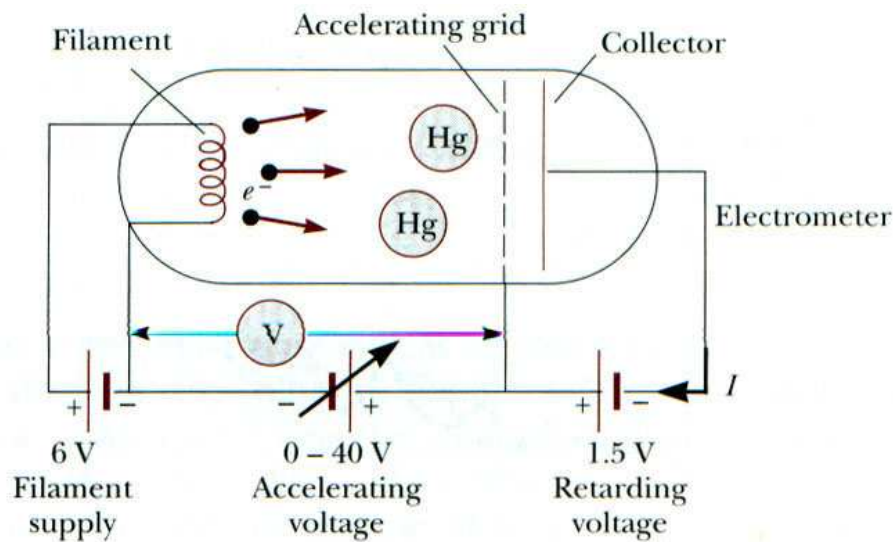


Figure 4.27 Franck–Hertz apparatus. A drop of pure mercury is sealed into an evacuated tube. The tube is heated to 185°C during measurements to provide a high-enough density of mercury to ensure many electron–atom collisions.



James Franck
(1882–1964)



Gustav Ludwig
Hertz (1887–1975)

Frank-Hertz result

Absorption of electrons seems to occur at integer multiples of a particular value (4.9 eV for Mercury vapor); inelastic energy transfer to knock gas electrons from one orbital to the next. Serway Fig. 4.28:

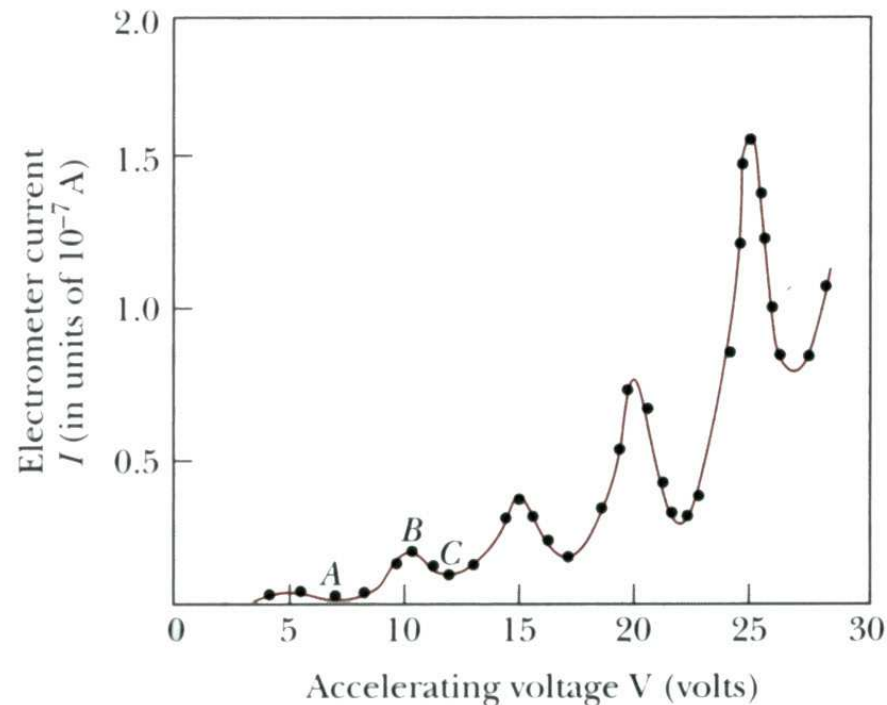


Figure 4.28 Current as a function of voltage in the Franck–Hertz experiment. To obtain these data, the filament voltage was set at 6.0 V and the tube heated to 185°C. (Data taken by Bob Rodick, Utica College, class of 1992)

Experiment done in 1913; Nobel Prize awarded in 1925.

The Bohr model: reduced mass

- One shortcoming of the original Bohr model is that it pretends that the nucleus is stationary as the electrons “orbit” it. This is only *approximately* true because $m_p \simeq 1800m_e$
- The electron and the nucleus orbit about the center of mass

$$(9) \quad r_{\text{cm}} \equiv \frac{\sum x_i m_i}{m_i} = 0 = \frac{-r_N M + r_e m_e}{M + m_e},$$

where r_N is the distance from the nucleus to the center of mass point, r_e is the distance from the center of mass point to the electron, and m_e and M are the masses of the electron and nucleus, respectively.

- This gives $r_e m_e = r_N M$ or

$$\begin{aligned} r &= r_e + r_N = r_e + r_e \frac{m_e}{M} \\ Mr &= Mr_e + m_e r_e \\ r_e &= \frac{Mr}{m_e + M}. \end{aligned}$$

Reduced mass II

- A similar procedure gives

$$(10) \quad r_N = \frac{m_e r}{m_e + M}$$

- Return to Coulomb force providing centripetal force:

$$(11) \quad \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = m_e \frac{v_e^2}{r_e} = m_e r_e \omega^2$$

where we have used $v_e = r_e \omega$ and the fact that the Coulomb force depends on the distance between the electron and the nucleus, independent of the location of the center of mass.

- Using Eq. 10, we obtain

$$(12) \quad \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = \frac{m_e M}{m_e + M} r \omega^2 = m_r r \omega^2$$

where $m_r \equiv \frac{m_e M}{m_e + M}$ is known as the *reduced mass*. Numerically,

$$(13) \quad \frac{m_e}{m_r} = \frac{m_e}{m_e M} (m_e + M) = 1 + \frac{m_e}{M} = 1 + \frac{0.511}{938} = 1.00054.$$

Reduced mass III

- If we instead have not hydrogen but deuterium (a nucleus consisting of a proton plus a neutron), we have $m_e/m_r = 1.00027$, and for tritium (two neutrons) we have $m_e/m_r = 1.00018$.
- We can also use the reduced mass to reformulate Bohr's condition for the quantization of angular momentum. We have $2\pi l = 2\pi r m v = 2\pi(m_e v_e r_e + M v_N r_N) = nh$ as the electron and nucleus rotate about the center of mass point, or

$$(14) \quad 2\pi(m_e r_e^2 \omega + M r_N^2 \omega) = nh.$$

- Using Eq. 10 for r_e and Eq. 10 for r_N , we obtain

$$(15) \quad \begin{aligned} \frac{2\pi\omega}{(m_e + M)^2} (m_e M^2 r^2 + M m_e^2 r^2) &= nh \\ 2\pi\omega r^2 \frac{m_e M}{(m_e + M)^2} (M + m_e) &= nh \\ 2\pi\omega m_r r^2 &= nh. \end{aligned}$$

Reduced mass IV

- Solving for ω and inserting this in the Coulomb-centripetal relationship of Eq. 12 gives

$$(16) \quad r = \frac{n^2}{Z} \frac{4\pi\epsilon_0 \hbar^2}{m_r e^2},$$

or, since Eq. 10 gives $r_e = (m_r/m_e)r$,

$$(17) \quad r_e = \frac{n^2}{Z} \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

- While we reproduce $r_{e,n}$, we do *not* reproduce the prior results for the *energy* of states.
- Net kinetic energy is sum of that of nucleus plus electron, or $(1/2)m_e r_e^2 \omega^2$ plus $(1/2)M r_N^2 \omega^2$.
- We note that the steps in going from Eq. 14 to Eq. 15 gave us $(m_e r_e^2 + M r_N^2) = m_r r^2$, so the kinetic energy is given by $(1/2)m_r r^2 \omega^2$.

Reduced mass V

- Using Eq. 12, we have

$$(18) \quad E_k = \frac{1}{2} m_r r^2 \omega^2 = \frac{r}{2} m_r r \omega^2 = \frac{r}{2} \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = \frac{Ze^2}{8\pi\epsilon_0 r}.$$

- Coulomb potential energy depends on the electron-nucleus separation independent of where the center of mass is, so this remains unchanged:

$$(19) \quad U = -\frac{Ze^2}{4\pi\epsilon_0 r}.$$

- The total energy of the atom is then

$$(20) \quad E = -\frac{Ze^2}{8\pi\epsilon_0 r}.$$

Reduced mass VI

- If we then use the expression of Eq. 16 for r , we obtain

$$(21) \quad E_n = -\frac{Z^2 m_r e^4}{n^2 8h^2 \epsilon_0^2},$$

which is identical for the result we had before except that m_e has been replaced by m_r . In other words,

$$(22) \quad \frac{E_n(\text{corrected})}{E_n(\text{approx.})} = \frac{m_r}{m_e}$$

or

$$(23) \quad E_n(\text{corrected}) = -\frac{Z^2}{n^2} E_0 \frac{m_r}{m_e} \simeq -\frac{Z^2}{n^2} E_0 \left(1 - \frac{m_e}{M}\right),$$

where we have used Eq. 13.

Reduced mass VII

- The energy of the n^{th} state is then reduced by a factor of $1 - 0.00054$ for hydrogen, $1 - 0.00027$ for deuterium, and $1 - 0.00018$ for tritium. Conversely, since $\lambda = hc/E$, wavelengths are increased by factors of 1.00054, 1.00027, and 1.00018, respectively.
- These shifts are small! If we consider the index of refraction n of light in atmospheric pressure air, to conserve energy we have $kn \propto (n/\lambda)$ constant so the wavelength in a medium with refractive index n is $\lambda = \lambda_0/n$. In particular, for deuterium the wavelength *increase* due to reduced mass is almost exactly equal to the wavelength *decrease* we would expect to observe with a spectrometer in air rather than in vacuum. It is by careful measurements of these sorts of wavelength shifts that Harold Urey discovered deuterium in 1932.

Mysteries of Bohr's atom

- The Bohr atom tells us a lot! Bohr gets the Nobel Prize in 1922.
 - It introduces the idea of discrete energy states and orbitals in atoms.
 - It works really well for explaining the optical spectra one-electron atoms (H, He⁺¹, Li⁺²).
 - It explains Moseley's results on characteristic X rays.
 - It explains the Franck-Hertz experiment.
 - Bohr and others (including Sommerfeld) have come up with ways to extend it to atoms with more electrons though the picture gets murkier.
- But remember Stern's comment: "If this nonsense of Bohr should in the end prove to be right, we will quit physics!"
- What is special about $l = n\hbar$? Why don't the electrons in those orbits radiate away their energy and spiral in to the nucleus in a nanosecond?
- How do electrons know to go from one radius to another, and stop there?

Matter waves: Louis de Broglie

- Switched studies from medieval history to physics.
- PhD thesis, 1924: Einstein said $E^2 = p^2 c^2 + m^4 c^4$ which for photons gives

$$E = \frac{hc}{\lambda} = pc \quad \text{or} \quad \lambda = \frac{h}{p} = \frac{h}{mv}$$

- Maybe $\lambda = h/p$ is true for matter with mass as well!
- In fact, gives a nice explanation of the Bohr model: standing waves so no radiative dissipation!

[Animation.](#)

$$2\pi r = n\lambda = n\frac{h}{p} = n\frac{h}{mv}$$

so $mv r = l = n\hbar$



Prince Louis-Victor Pierre
Raymond de Broglie (1892–
1987); Nobel Prize 1929

Is this believable?

- What's the wavelength of a Randy Johnson fastball traveling at 95 mph or 42 m/s? The mass of a baseball is 145 g, so

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{0.145 \cdot 42} = 1.1 \times 10^{-34} \text{ m}$$

which is very small. . .

- Obviously we need something lighter and faster to see this effect! How about an electron accelerated over a 50 volt potential?

$$\frac{1}{2}mv^2 = \frac{p^2}{2m} = qV$$

so $p = \sqrt{2mqV}$ giving

$$\lambda = \frac{h}{p} = \frac{hc}{c\sqrt{2mqV}} = \frac{hc}{\sqrt{2mc^2 qV}} = \frac{1240 \text{ eV} \cdot \text{nm}}{2 \cdot (511 \times 10^3 \text{ eV}) \cdot (50 \text{ eV})} = 0.17 \text{ nm.}$$

Is there a way we can see such a small wavelength?