

Modern Physics

-Bohr's atomic model-

Lecture notes by
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Atoms

- The atomic nature of matter was unambiguously stated in the works of Dalton (1803) and Avogadro (1811), followed by studies of the Brownian motion (Brown, 1827) of pollen and dust particles in water. The particular role of hydrogen was discovered by Prout (1815).
- The first atomic optical spectra, recorded in the 19th century, showed that each element possesses its own characteristic spectrum, with lines and bands. That of hydrogen (studied by Angstrom in 1853) was particularly simple and was first interpreted by Balmer (1885) and extended by Rydberg (1889). Spectra of hydrogen atoms coming from stars were collected since 1881 (Huggins).
- Following the discovery of the subatomic particles, Bohr suggested a model in 1913 connecting the well-defined observed spectral lines and the atomic structure.
- The model was based on the Rutherford atomic model (nuclei and electrons) but adding postulates which explained the quantized nature of the electron energies.
- The model was extended by Sommerfeld to elliptical orbits obtaining a better description.
- The model is unsatisfying as it still contains a definition of the orbits, not wave-functions (correct quantum mechanical treatment) and does not predict the intensity of the lines.

Spectroscopy

·Optical spectra can be observed both by emission and by absorption of light. Frequency of electromagnetic radiation ranges usually from microwave to x-rays.

·Continuous spectra are emitted by radiant solids or high-energy gases.



·Band spectra consist of groups of spectral lines close to each others, usually found in molecules



·Line spectra are typical of atoms. Absorption and emission spectra are shown here



·Typical units are wavelength in vacuum (a standard is the yellow ^{86}Kr emission line at $\lambda_{\text{vac}} = 6057.802 \text{ Ang.}$). In air or other substances the speed of light is modified (refraction index $n > 1$): $c_{\text{air}} = c/n$ ($n_{\text{air}} = 1.0002762$) so $\lambda_{\text{air}} = \lambda_{\text{vac}} / n = 6056.129 \text{ Ang}$

·A better unit is usually the frequency, that is not affected by media: $\nu = c/\lambda$. In spectroscopy it is often used the wavenumber: $\bar{\nu} = c_{\text{air}} / \lambda_{\text{air}} = c / \lambda_{\text{vac}}$ The frequency (measured in GHz) and wavenumber (cm^{-1}) are proportional to the energy $E = \nu h c$ (measured in eV).

·Some conversion factors are: $1 \text{ eV} = 2.418 \cdot 10^{14} \text{ Hz} (10^5 \text{ GHz}) = 8066 \text{ cm}^{-1}$.

Optical spectrum of Hydrogen

The emission spectrum of atomic Hydrogen shows three characteristic lines in the visible region called $H_{\alpha}, \beta, \gamma$. These are followed by a whole series of lines in the near ultraviolet region.

Balmer in 1885 found that the wavelengths could be reproduced by the simple formula:

$$\lambda = \left(\frac{n_1^2}{n_1^2 - 4} \right) G$$

Where $n_1 = 3, 4, \dots$ and G is an empirical constant.

Today the Balmer series is written for wavenumbers, Frequency or energy:

$$\nu = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right); n > 2, R_H = \frac{4}{G}$$

Here $R_H = 109677.58 \text{ cm}^{-1} = 13.6 \text{ eV}; \nu_{\infty} = \frac{R_H}{4}$

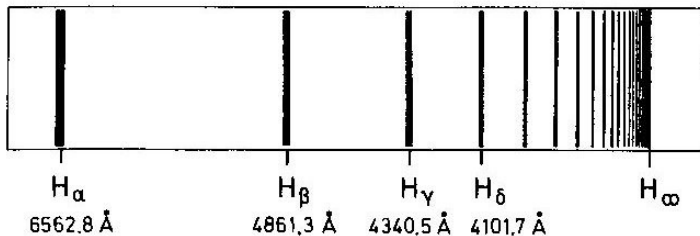
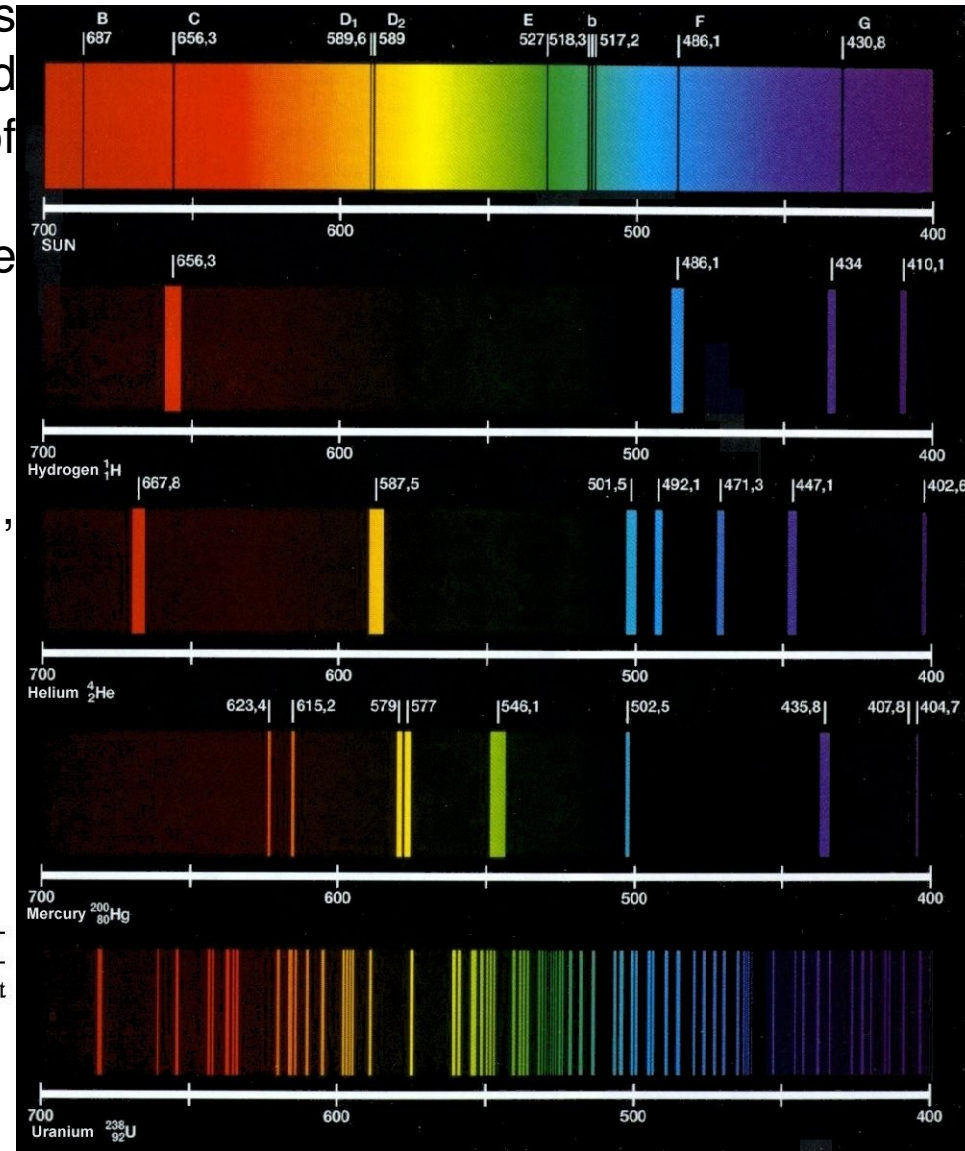


Fig. 8.3. Balmer series in the hydrogen emission spectrum. The convergence of the lines to the series limit H_{∞} is clearly seen



Spectral series in Hydrogen

While the Balmer series is perfectly explained by that simple relationship, there are other lines appearing in the ultraviolet and infrared regions: Lyman (1906, ultraviolet), Paschen (1908, infrared), Brackett (1922 far infrared).

Those series can be reproduced by introducing a second index n' , like in the Rydberg relation first written in 1889:

$$\nu = R_H \left(\frac{1}{n'^2} - \frac{1}{n^2} \right); n' < n$$

It is clear that those frequencies can be understood as differences of two terms R/n^2 , in a spectrum energy diagram.

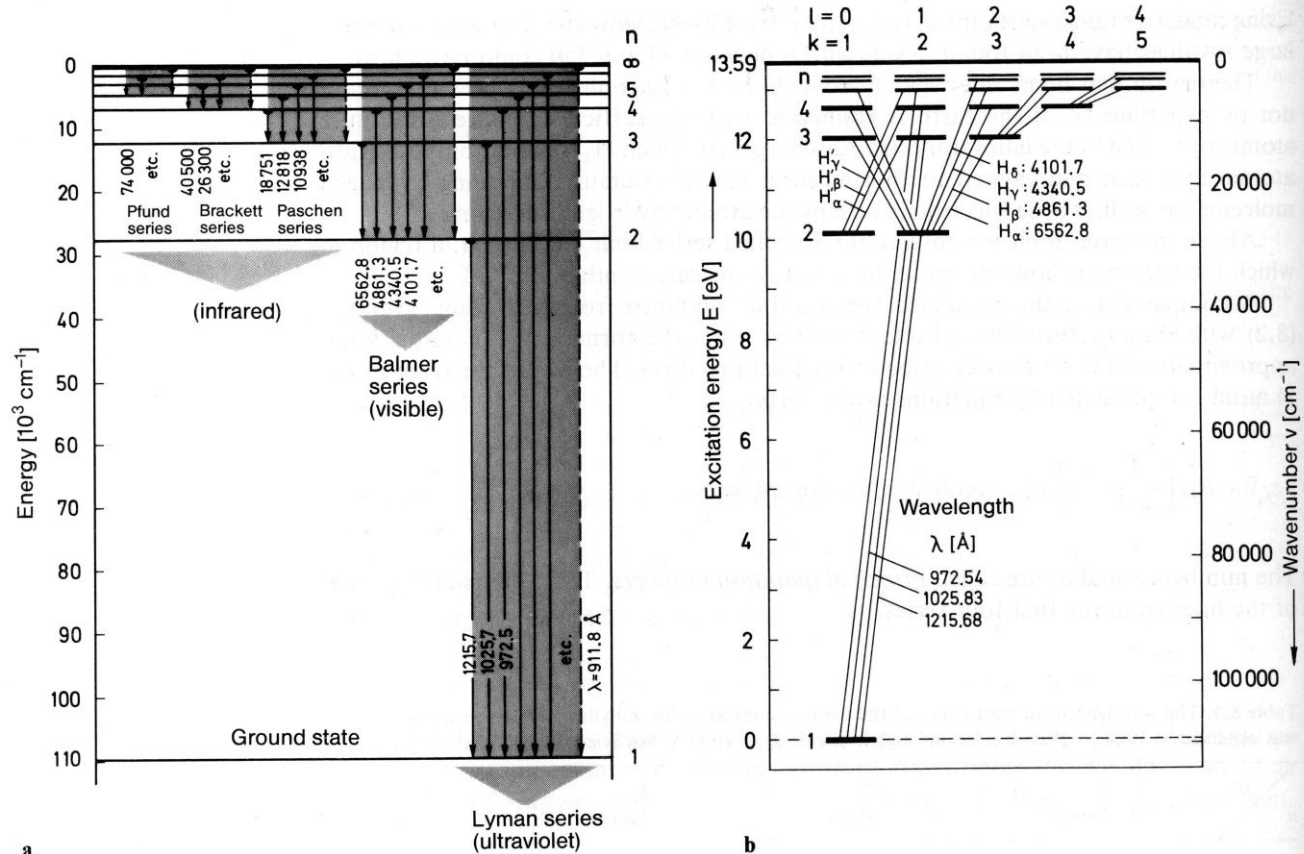


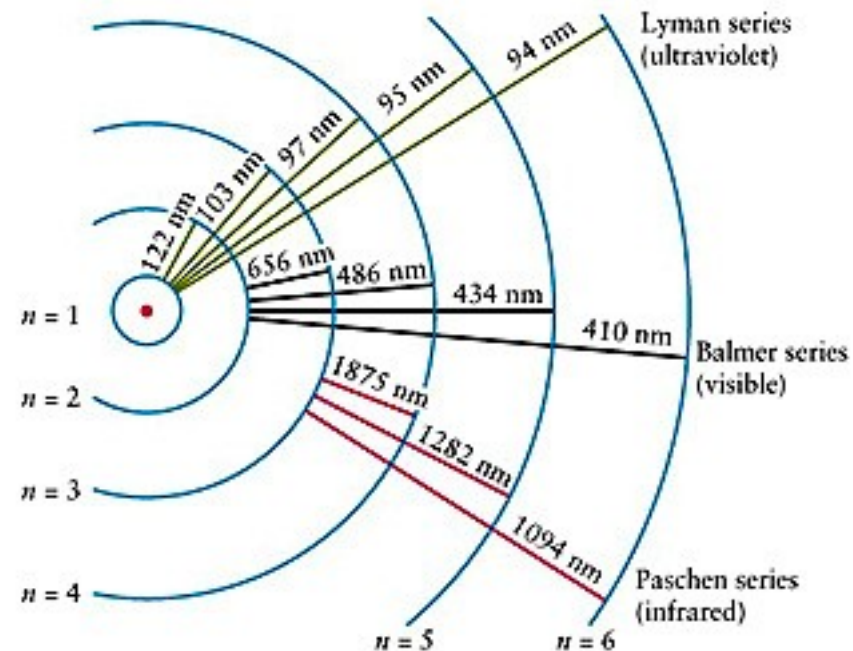
Fig. 8.4. a) Term diagram of the lines of the hydrogen spectrum and series classification. The wavelengths of the transitions are given in \AA . The energies can be given as (negative) binding energies, with the zero of energy being the ionisation limit, or they can be given as excitation energies, beginning with the ground state, so that the energy of the term n_{∞} is equal to the ionisation energy

b) This represents the lines of the hydrogen spectrum in the term scheme of *Grotrian* [Struktur der Materie VII (Springer, Berlin 1928)]. The symbols l and k appearing in the upper margin of the figure will be explained later (Sect. 8.9)

Bohr's postulates

The Bohr's simple idea was to assume the electrons moving in circular orbits around the nuclei, being in equilibrium Coulomb and centrifugal forces. The new thing with respect to the Rutherford model is to try to explain the emission and absorption of light. Classically, any orbit is possible, and the acceleration of a charge on a circular orbit would lead to radiation (in a broad range of frequencies) and final collapse of the electron into the nucleus. However, experiments show that only discrete energies are possible. Bohr tried to accomplish the task of explaining this phenomenon avoiding discrepancies with classical physics:

- 1) Only discrete Energies E_n corresponding to discrete classical orbits are allowed.
- 2) These orbits are determined by values of the angular momentum $\mathbf{l} = \mathbf{r} \times \mathbf{p} \rightarrow |\mathbf{l}| = mvr = nh/2\pi$ ($n=1,2,..$) is quantized.
- 3) The motion of electrons in these quantized orbits is radiationless and the emission (absorption) is related to spontaneous transitions between two orbits n and n' (frequency of emitted light $h\nu = E_n - E_{n'}$).



Hydrogen-like systems

The Bohr model is applied to hydrogen-like systems like He^+ , Li^{2+} . The electron moves with velocity v_n on a circular orbit n at distance r_n . There is an equilibrium between Coulomb and centrifugal forces:

$$\frac{Ze^2}{4\pi\epsilon_0 r_n^2} = \frac{m_0 v_n^2}{r_n} = m_0 r_n \omega_n^2; (v = \omega r_n)$$

The orbital angular momentum is assumed to be quantized:

$$m_0 v_n r_n = m_0 \omega_n r_n^2 = n \frac{h}{2\pi} = n \hbar$$

The possible orbital radii are thus:

$$r_n^2 = \frac{(n\hbar)^2}{m\omega} \Rightarrow (m\omega)^2 = \frac{(n\hbar)^2}{r_n^4} \Rightarrow \omega^2 = \frac{(n\hbar)^2}{(m^2 r_n^4)} \Rightarrow \frac{Ze^2}{4\pi\epsilon_0 r_n^2} = m r_n \omega^2 = \frac{(n\hbar)^2}{m r_n^3} \Rightarrow r_n = \frac{(n\hbar)^2}{m_0} \frac{4\pi\epsilon_0}{Ze^2}$$

The possible angular frequencies

$$\omega_n = \frac{1}{(4\pi\epsilon_0)^2} \frac{m_0 (Ze^2)^2}{(n\hbar)^3}$$

For $Z=1$ and $n=1$ we have 10^{16} Hz but this would correspond to the frequency of emission in a classic picture. The actual energies are instead given by the energy difference among two n and n' states.

To calculate this we sum Kinetic and Potential energies: $E = E_{\text{kin}} + E_{\text{pot}}$

The kinetic energy of the electron is simply $mv^2/2$ while the potential energy is equal to the work gained (or done) in moving the electron from infinite distance to r_n in a Coulomb field:

$$E_{\text{pot}} = \int_{\infty}^{r_n} \frac{(Ze^2)}{(4\pi\epsilon_0) r'^2} dr' = \frac{-Ze^2}{4\pi\epsilon_0 r_n}$$

Energy of emitted light

The total energy of a level n is:

$$E_n = m_0 v_n^2 / 2 - \frac{Ze^2}{4\pi\epsilon_0 r_n}$$

Where the orbital radius, frequency and velocity are:

$$r_n = \frac{(n\hbar)^2}{m_0} \frac{4\pi\epsilon_0}{Ze^2} \quad \omega_n = \frac{1}{(4\pi\epsilon_0)^2} \frac{m_0 (Ze^2)^2}{(n\hbar)^3} \Rightarrow v_n = \omega_n r_n = \frac{1}{(4\pi\epsilon_0)^2} \frac{m_0 (Ze^2)^2}{(n\hbar)^3}$$

So the energy becomes:

$$E_n = \frac{m_0}{2(4\pi\epsilon_0)^2} \frac{(Ze^2)^2}{(n\hbar)^2} - \frac{m_0}{(4\pi\epsilon_0)^2} \frac{(Ze^2)^2}{(n\hbar)^2} = \frac{-m_0}{2(4\pi\epsilon_0)^2} \frac{(Ze^2)^2}{(\hbar)^2} \frac{1}{n^2}$$

For Z=1, n=1 we have the lowest energy state: $E_1(\text{H}) = -13.59 \text{ eV} = 1 \text{ Ryd}$ (ionization energy of hydrogen). For an hydrogenic ion Z, n=1 $E_1(\text{Z}) = -Z^2 \text{ Ryd}$.

The energy of the spectral lines are then given (3rd postulate), to be compared with the Balmer series,

$$\nu = R_H \left(\frac{1}{n'^2} - \frac{1}{n^2} \right); n' < n$$

$$h\nu = E_n - E_{n'} = \frac{m_0}{2(4\pi\epsilon_0)^2} \frac{(Ze^2)^2}{(\hbar)^2} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

by the following expression:

So if we calculate the Rydberg constant

$$\Delta E(n \Rightarrow \infty) = R_\infty = 13.59 \text{ eV} = 109737.3 \text{ cm}^{-1} \quad \mu = \frac{m_0 M}{m_0 + M} \Rightarrow R_H = R_\infty \frac{1}{1 + m_0/M} = 109677.58 \text{ cm}^{-1}$$

We have a close agreement with the calculated H ionization energy. In order to have a perfect agreement we have to introduce the reduced mass which accounts for the motion of the nuclei (isotope displacement, M= 1836.15 m).

Sommerfeld's extension

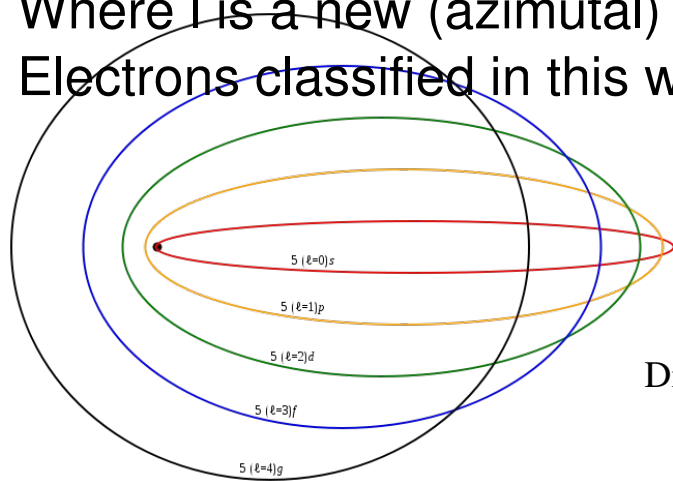
The Bohr's model is quite accurate but can not explain the details of the optical spectra. The first one observed early was that the lines of the Balmer series consist of several components: the H α line at 15233 cm⁻¹, is splitted into 3 or more components within 0.33 cm⁻¹. For heavier atoms lines are more separated and the splitting is easier to observe.

Sommerfeld extended the simple Bohr's model by including elliptical orbits for same energies, as suggested by Kepler's law in gravitation.

To distinguish circular and elliptical orbits he introduced a new quantum number. The principal q.n. n determines the major semiaxis of the ellipse, and the second would be determined by imposing that the angular momentum is a multiple k of $h/2\pi$, with $k=n, k < n$.

In a more advanced QM treatment, the angular momentum becomes $|\vec{l}| = \sqrt{l(l+1)}\hbar$ Where l is a new (azimutal) quantum number defining the “orbitals” of the Electrons classified in this way:

q.num.	$l=0$	$l=1$	$l=2$	$l=3$
name	s	p	d	f



Limits of the semiclassical models

The Bohr's model is clearly unsatisfactory because it abandons classical mechanics to allow only quantized orbits and energies, but orbits are still deterministic and follows classical laws. Moreover, no idea about calculating intensities and time evolution of the optical transitions, related to the actual dynamics of electrons.

This problem was tackled by Bohr by stating the *correspondence principle* : *every non-classical theory must yield the same results of the classical theory in the limit of high energies and high quantum numbers.*

An example of this limit can be seen by calculating the frequency of a transition between neighbouring orbits for high quantum numbers n , $\Delta n=1 \ll n$:

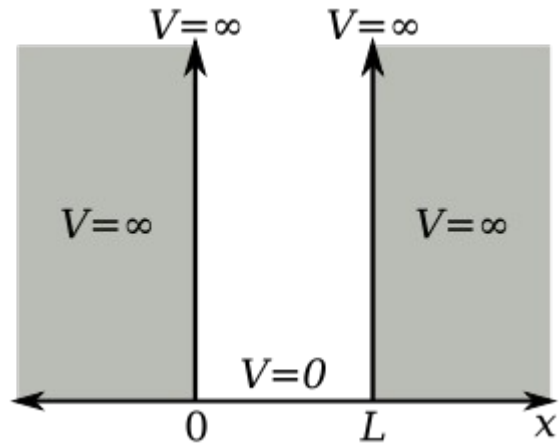
$$h \nu = E_{n+\Delta n} - E_n = \frac{m_0}{2(4\pi\epsilon_0)^2} \frac{(Ze^2)^2}{(\hbar)^2} \left(\frac{1}{n^2} - \frac{1}{(n+\Delta n)^2} \right) = R_\infty(H) Z^2 \left(\frac{1}{n^2} - \frac{1}{(n+\Delta n)^2} \right) \approx 2 \Delta n R_\infty \frac{Z^2}{n^3}$$

While according to classical physics for orbit n :

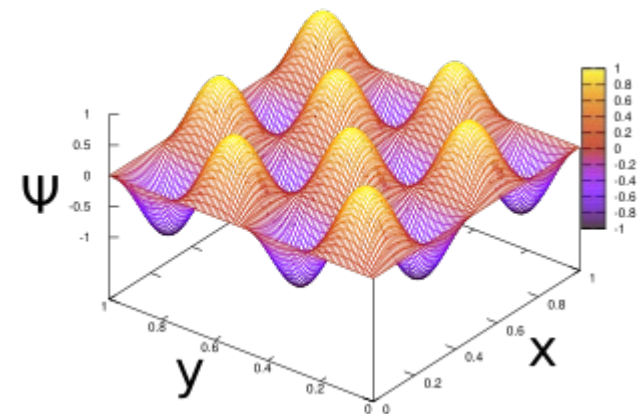
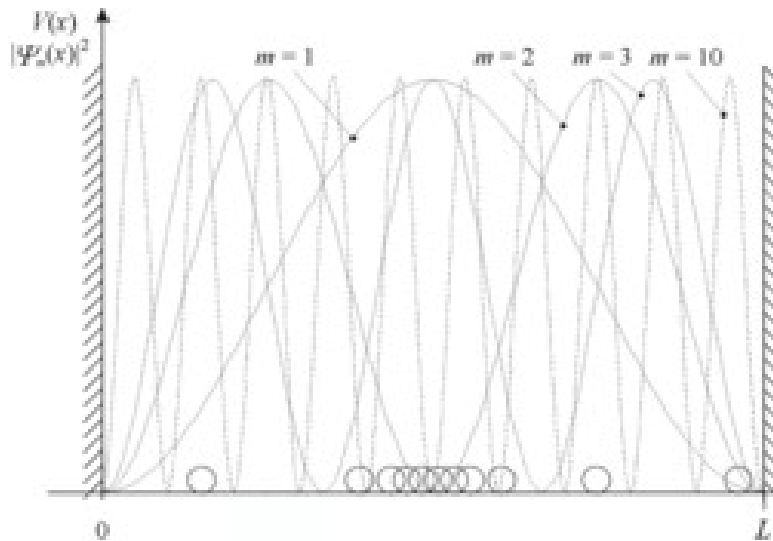
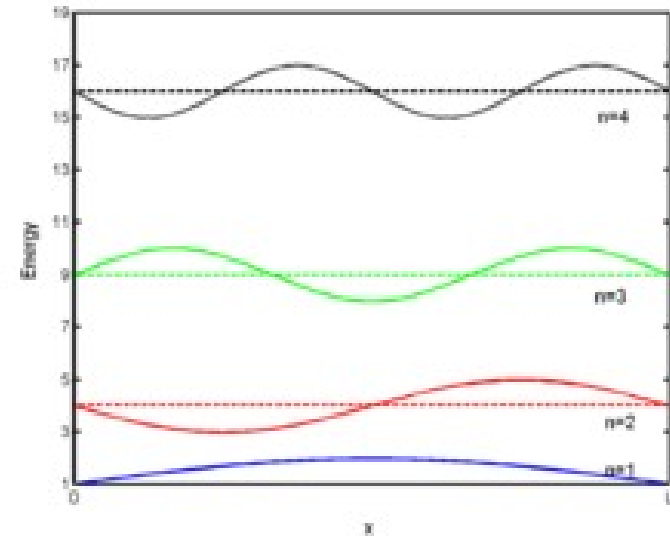
$$h \nu = \hbar \omega_n = \frac{\hbar}{(4\pi\epsilon_0)^2} \frac{m_0(Ze^2)^2}{(n\hbar)^3} = 2 R_\infty(H) \frac{Z^2}{n^3}$$

So we see that for large n the classical limit is approached. However, results of the Bohr-Sommerfeld theory were wrong increasing Z (starting from $Z=2$) and could not predict other detailed phenomena (magnetic splitting). A rigorous quantum-mechanical treatment has been necessary to proceed with atomic theory.

Background for quantum mechanics: particle in a box



Presentation and calculations at the blackboard.



Exercise: particle in a finite box.

Schroedinger' equation

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

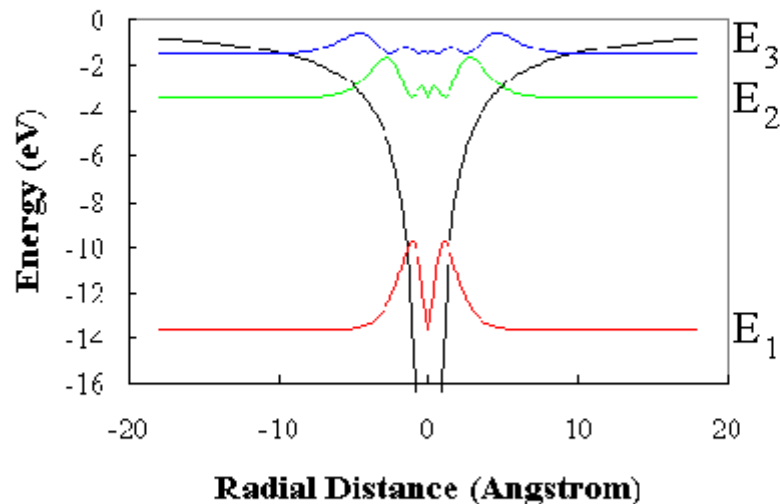
THE SCHROEDINGER EQUATION

The hydrogen atom potential and wavefunction

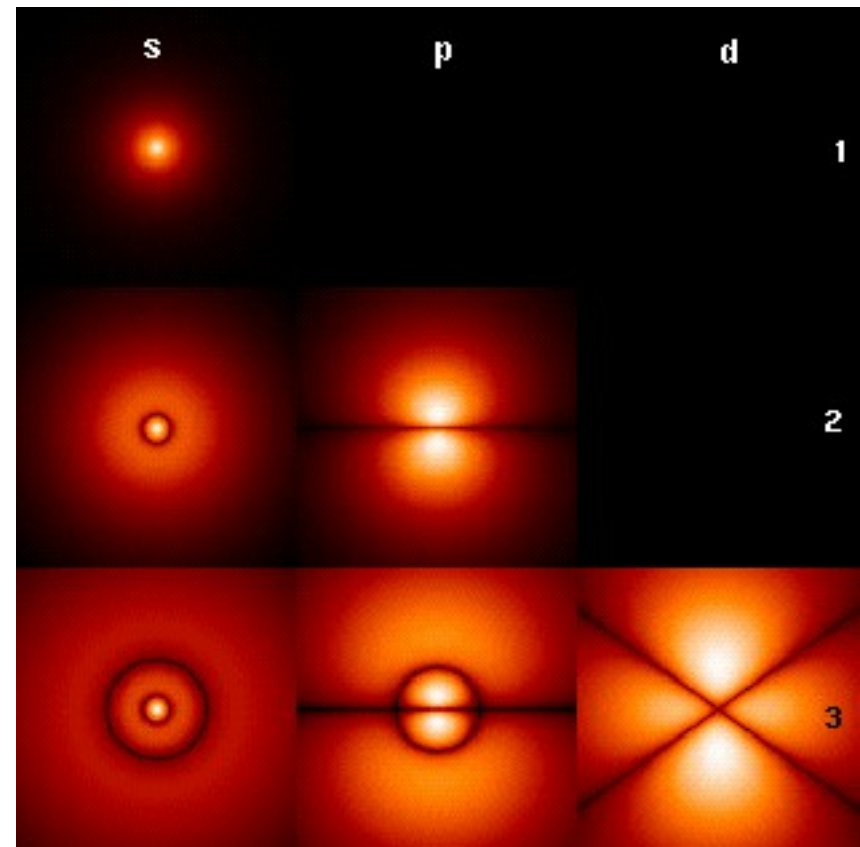
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Hydrogen wave functions

