Atomic physics and Quantum mechanics
accompanying notes

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TU Graz - Austria

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Content of this lecture

Mainly from S. M. Blinder *"Introduction to Quantum Mechanics in Chemistry, Materials Science, and Biology"*

1. Introduction: atoms and electromagnetic waves
   - Atoms and their constituents
   - Electromagnetic waves
   - Line spectra
2. Wave and Particle duality
   - Double-slit experiment
   - Light carries momentum: Compton scattering
   - Matter (Electrons) as waves
3. Bohr's atom

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- Heuristic derivation of Schrödinger equation
- Time-independent Schrödinger equation
- Interpretation of the wave function
- Summary: Schrödinger equation

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- Generalisations of the particle in a box
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9. Classification of atomic orbitals

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    - Pauli principle
    - Building-up principle
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Suggested literature I

1. S. M. Blinder, **Introduction to Quantum Mechanics in Chemistry, Materials Science, and Biology** (Elsevier, 2004)
   the lecture is essentially based on this book
2. L. van Dommelen **Fundamental Quantum Mechanics for Engineers**
3. J. E. House, **Fundamentals of Quantum Chemistry**
   some mathematical aspects are treated in more detail here
4. P. W. Atkins, **Physical Chemistry** Chap. 2
   also a good book, many details and examples, many physical aspects discussed.
5. P. A. Tipler and R. A. Llewellyn, **Moderne Physik**
   simpler treatment
6. J.J. Sakurai, **Modern Quantum Mechanics**
   High level book

Suggested literature II

7. D. Ferry **Quantum Mechanics: An Introduction for Device Physicists and Electrical Engineers**
   More advanced, special topics of interest for material physicists.
   Device physics, transport theory.
8. Applets `http://www.quantum-physics.polytechnique.fr/en/index.html`

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Atoms and their constituents

Atoms (See also Blinder, Chap. 1.1–1.2)

- Matter consists of tiny particles: the atoms (Greek *atomos* = "indivisible"), an idea going back to Leucippus and Democritus (5th century BC).
- For a long time, only indirect evidence (chemistry, kinetic theory of gases, Brownian motion, ...).

Size of an atom: $\sim 10^{-10}$ m $= 1$ Å.

But: the atom is *not* the ultimate particle of matter.

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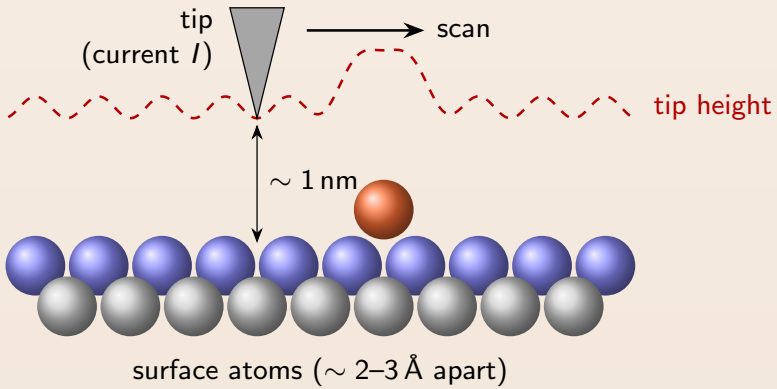
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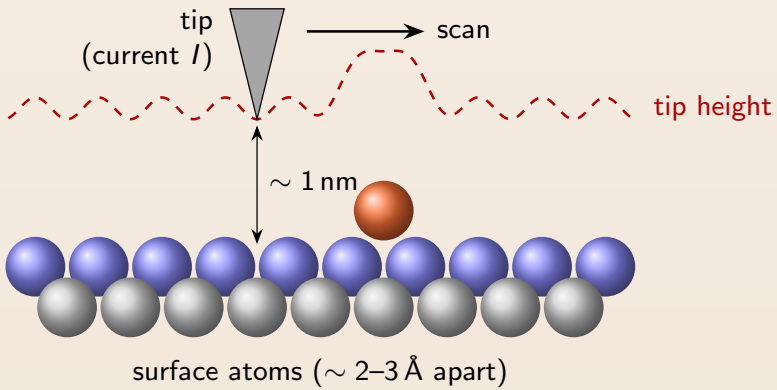


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Subatomic particles

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  Atoms emit α, β and γ radiation
  (α: helium nuclei, β: electrons, γ: high-energy electromagnetic radiation)

- Atoms are electrically neutral → they must also contain a positive charge.
  How is it distributed?

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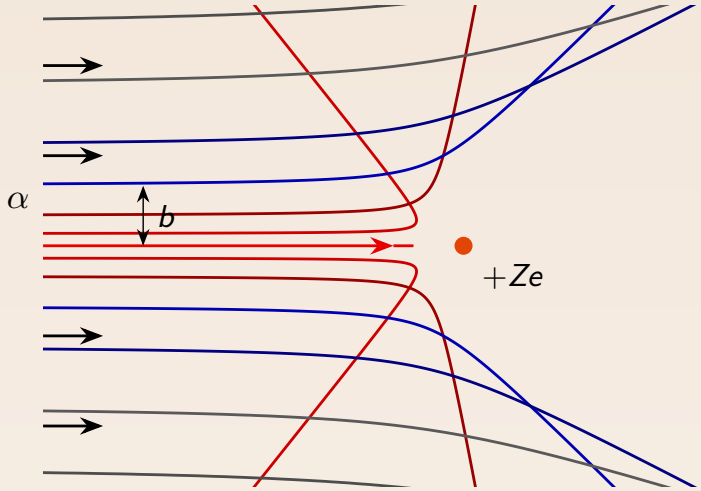
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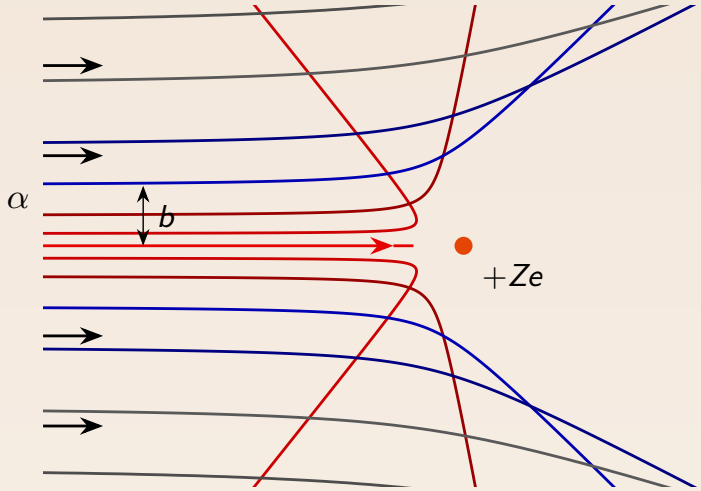
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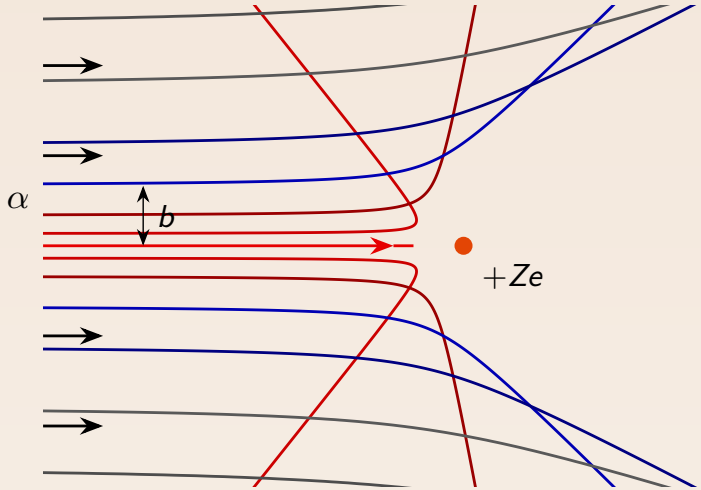
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Nuclear model: a neutral atom of atomic number Z consists of a nucleus of charge $+Ze$, containing almost the entire mass, surrounded by Z electrons of charge $-e$.

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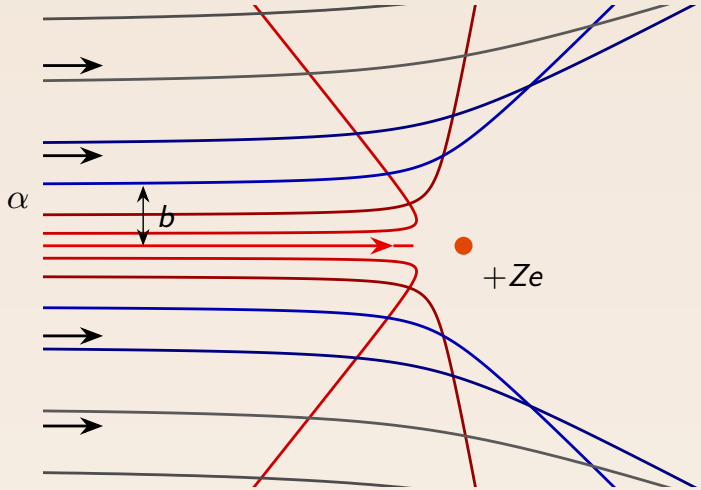
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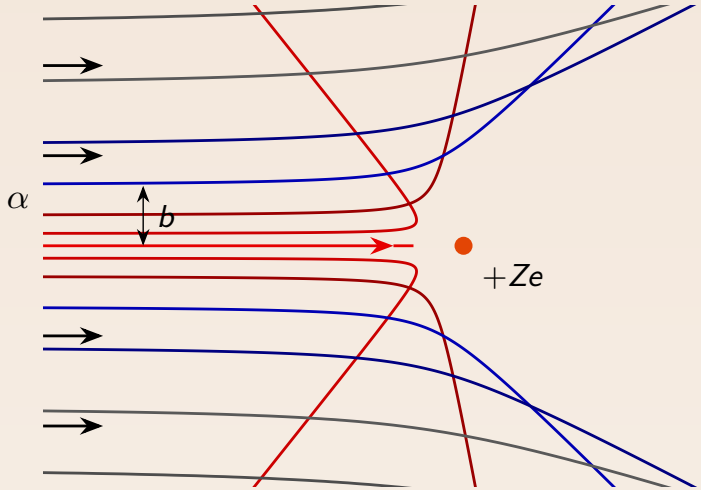
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The atomic nucleus

- 1932, J. Chadwick: the neutron (no charge, mass $\approx$ proton mass)
- a nucleus with atomic number Z and mass number A consists of Z protons and $A - Z$ neutrons
- for a given element, different isotopes exist with different A (e.g. $^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$)
- protons and neutrons themselves have a structure (quarks, Gell-Mann, 1960s) $\rightarrow$ "Standard Model" of particle physics. Not needed in atomic physics.

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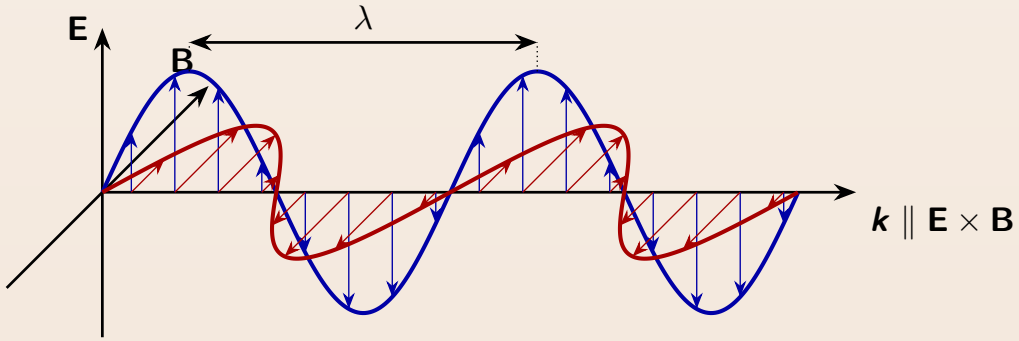
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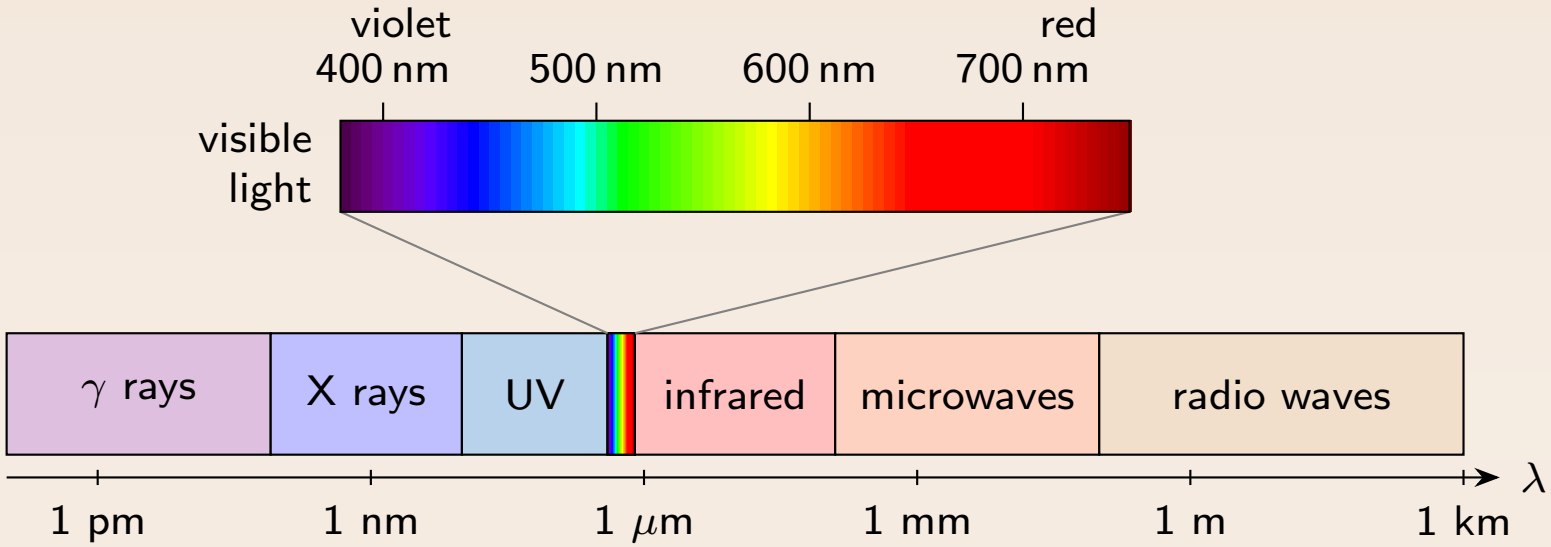
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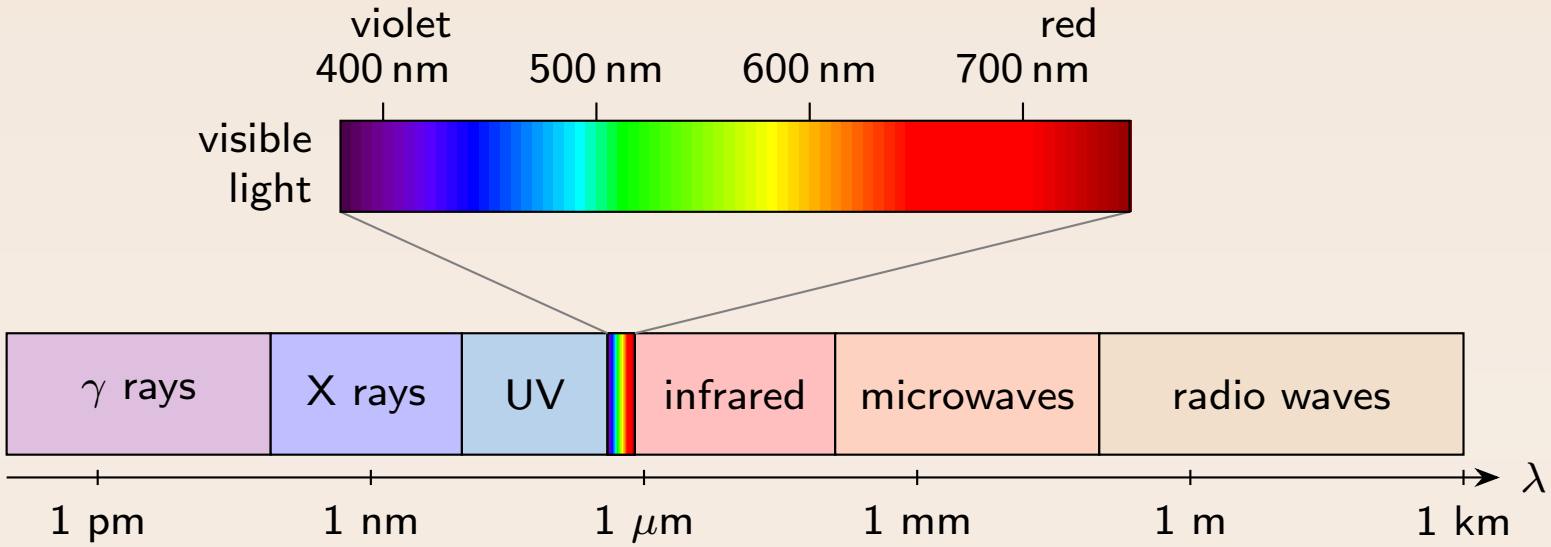
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Blackbody radiation

Thermal radiation

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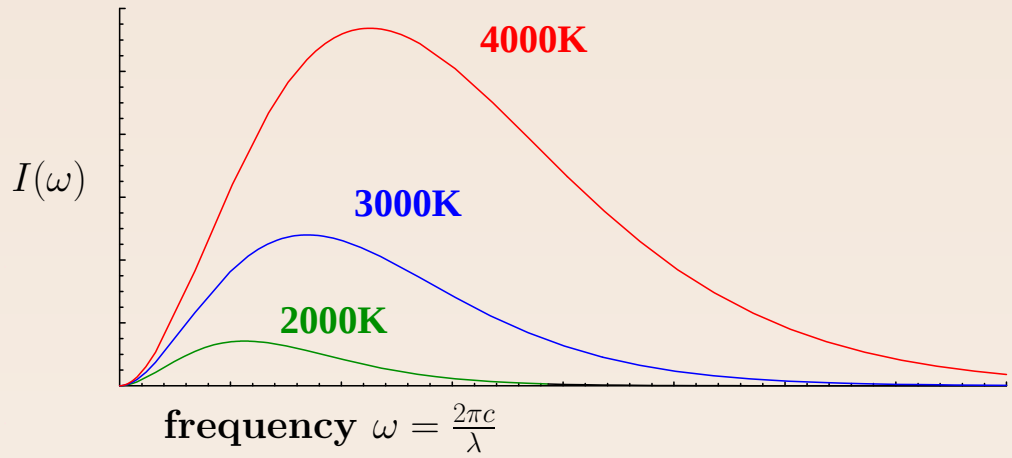
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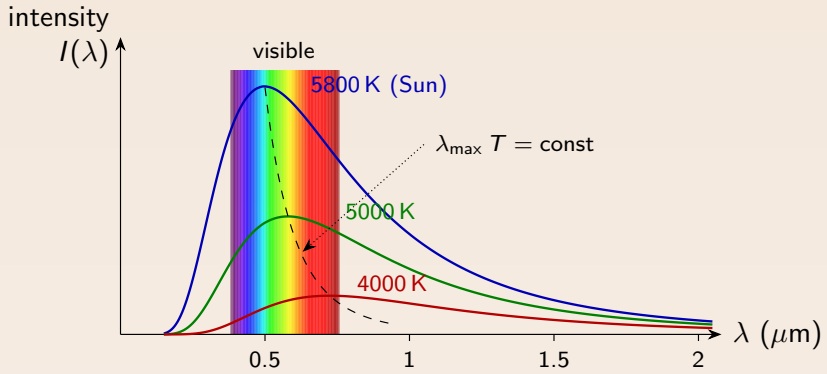
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Energy intensity $I(\omega)$ versus frequency ($\boxed{\omega = 2\pi\nu = \frac{2\pi c}{\lambda}}$) of blackbody radiation at different temperatures:

- The energy intensity $I(\omega)$ vanishes at small and large ω, there is a maximum in between.
- The frequency ω_{max} of the maximum ("color") of the distribution obeys the law (Wien's law) $\omega_{max} = \text{const.}\ T$

Wien's displacement law

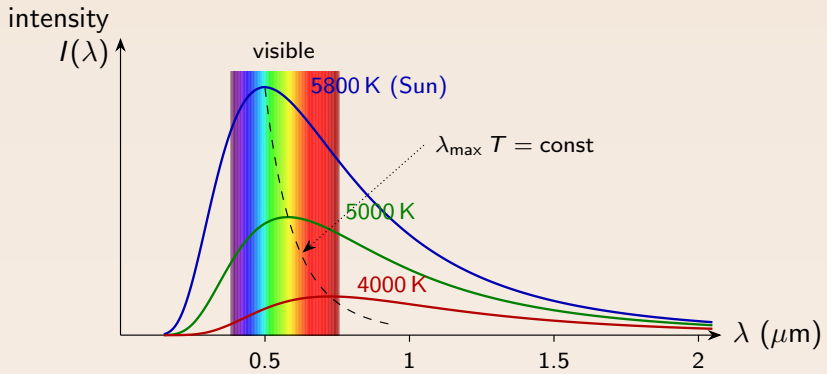


Plotted versus the wavelength, the maximum is at λ_{max} with

$$\lambda_{max}\, T = 2.898 \times 10^{-3}\,\mathrm{m\,K} \tag{2.1}$$

- room temperature ($T \approx 300\,\mathrm{K}$): $\lambda_{max} \approx 10\,\mu$m, in the infrared
- surface of the Sun ($T \approx 5800\,\mathrm{K}$): $\lambda_{max} \approx 500\,$nm, in the middle of the visible range

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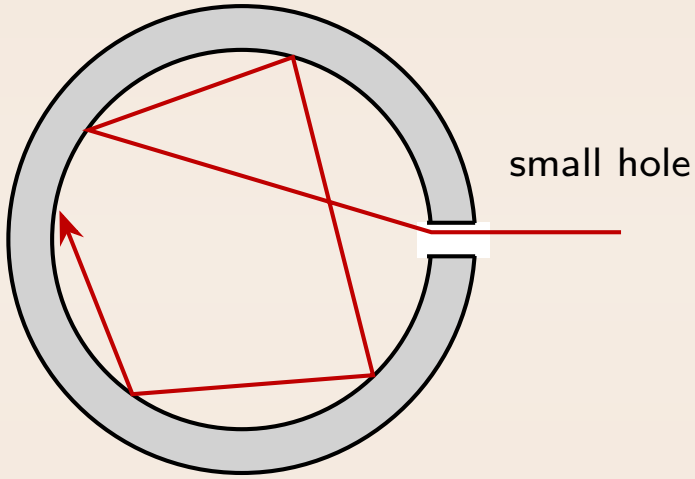
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The blackbody

An idealized description is the so-called blackbody model, which describes a perfect absorber and emitter of radiation at all wavelengths. Specifically, radiation is absorbed and has enough time to thermalize before being emitted (in contrast to "white" or a "specular" body).



Electromagnetic waves as oscillators

One single electromagnetic wave is characterised by a wavevector **k** which indicates the propagation direction and is related to the frequency and wavelength by $|\mathbf{k}| = \frac{2\pi}{\lambda} = \frac{\omega}{c}$.
In a blackbody, electromagnetic waves of all wavevectors **k** are present and distributed in equilibrium.
One can consider an electromagnetic wave with wavevector **k** as an independent oscillator ("mode").

For a given frequency ω $(= 2\pi\nu)$, there are many oscillators $\mathbf{k}$ having that frequency. Since $\omega = c\ |\mathbf{k}|$ the number (density) $n(\omega)$ of oscillators with frequency ω is proportional to the surface of a sphere with radius ω/c, i. e.

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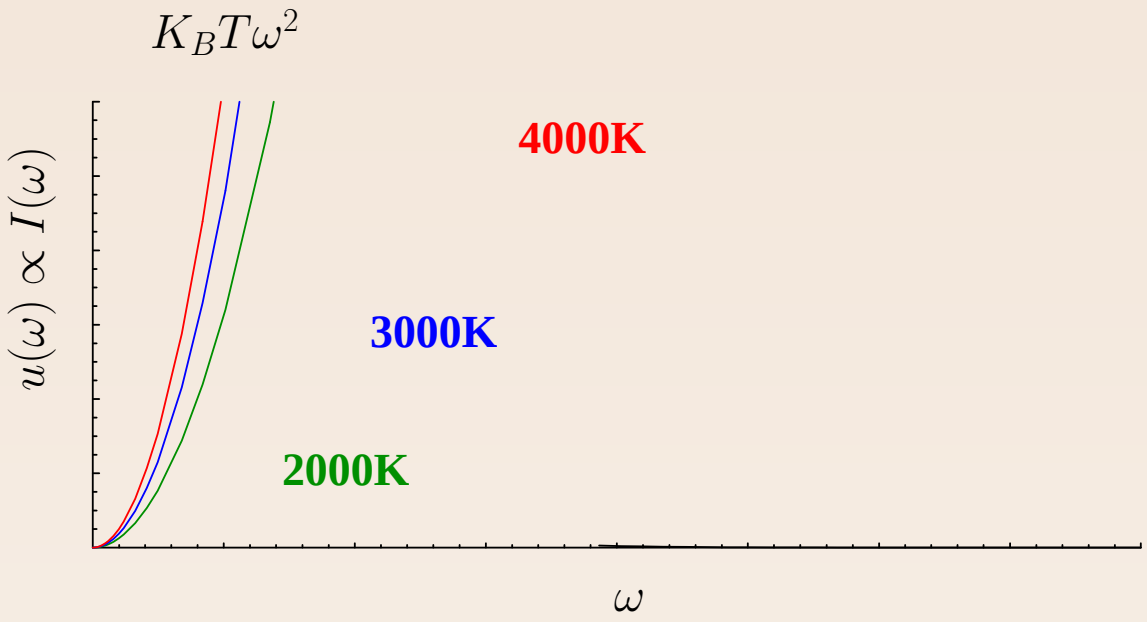
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(Rayleigh–Jeans law).

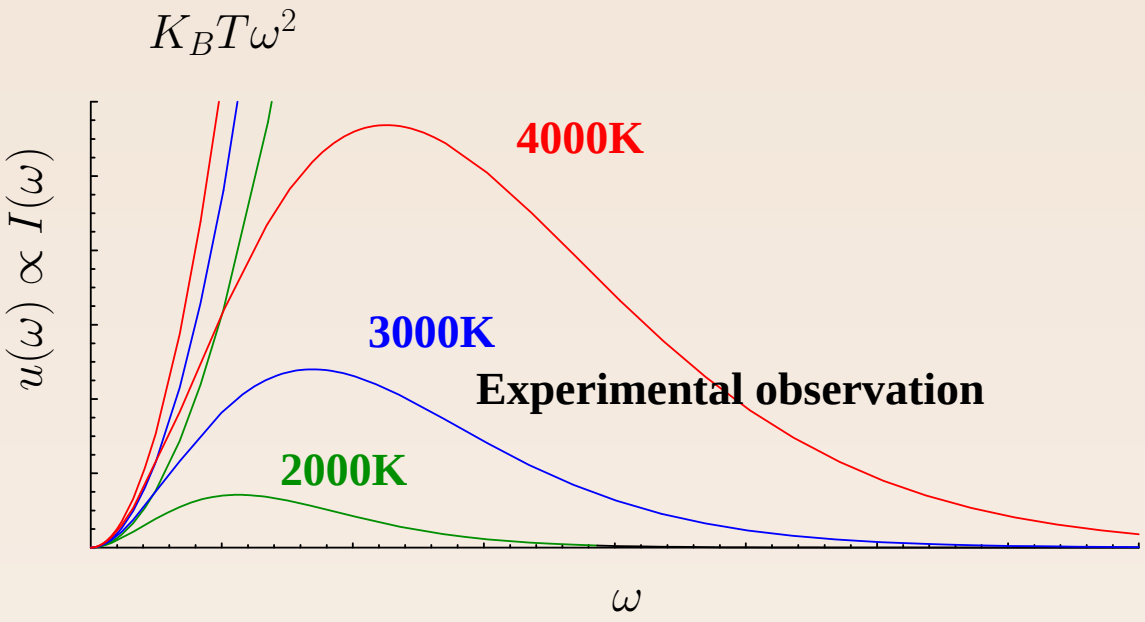


Since $I(\omega) \propto u(\omega)$, this indeed agrees with experiments at small ω, not at large ω.

At large ω, $u(\omega, T)$ must decrease again and go to zero, otherwise the total energy

$$U = \int_0^\infty u(\omega, T)\, d\omega \qquad (2.4)$$

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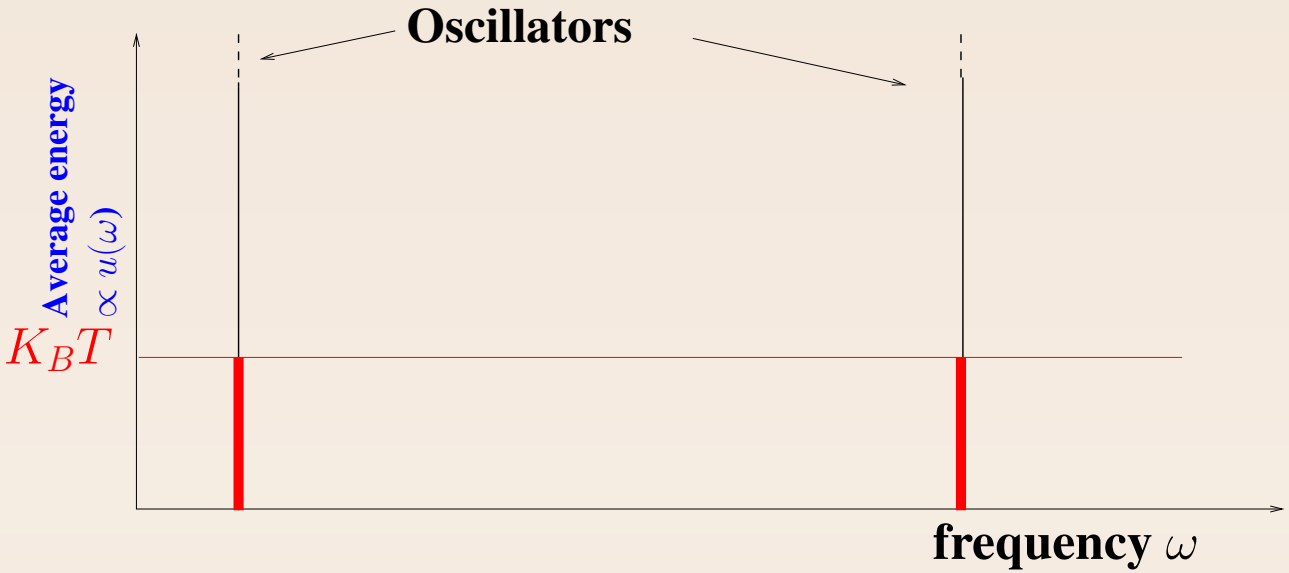
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Average energy of "oscillators"



(A) Classical behavior:

Average energy of oscillator $\langle E \rangle = K_B T$.

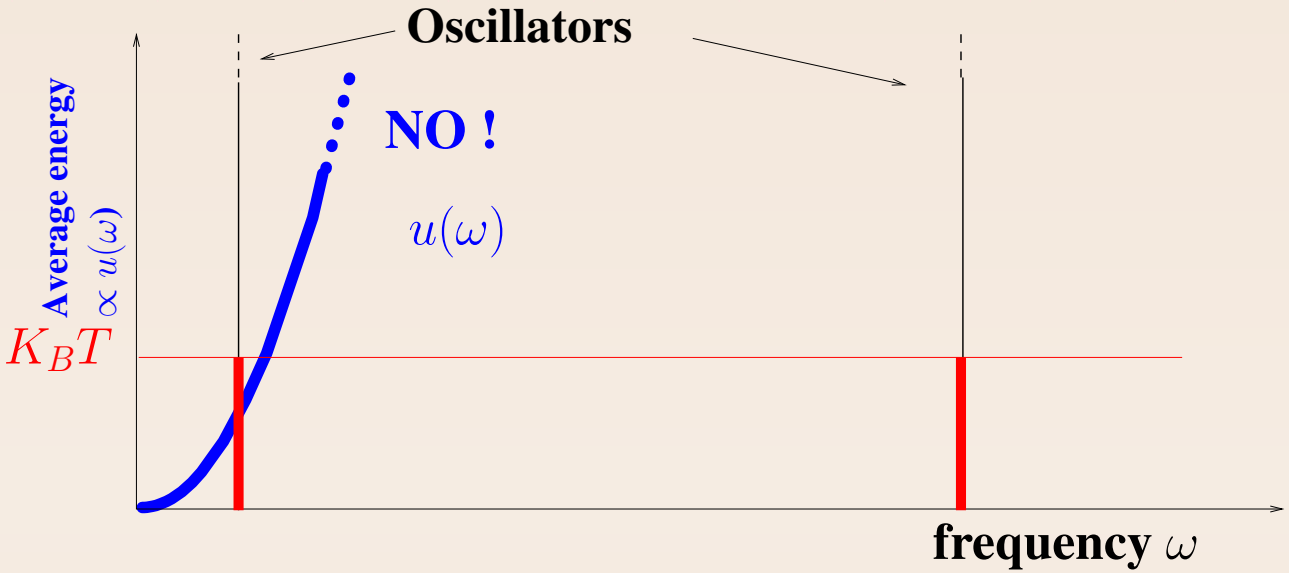
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Small ω: Like classical case: oscillator is excited up to $\langle E \rangle \approx K_B T$

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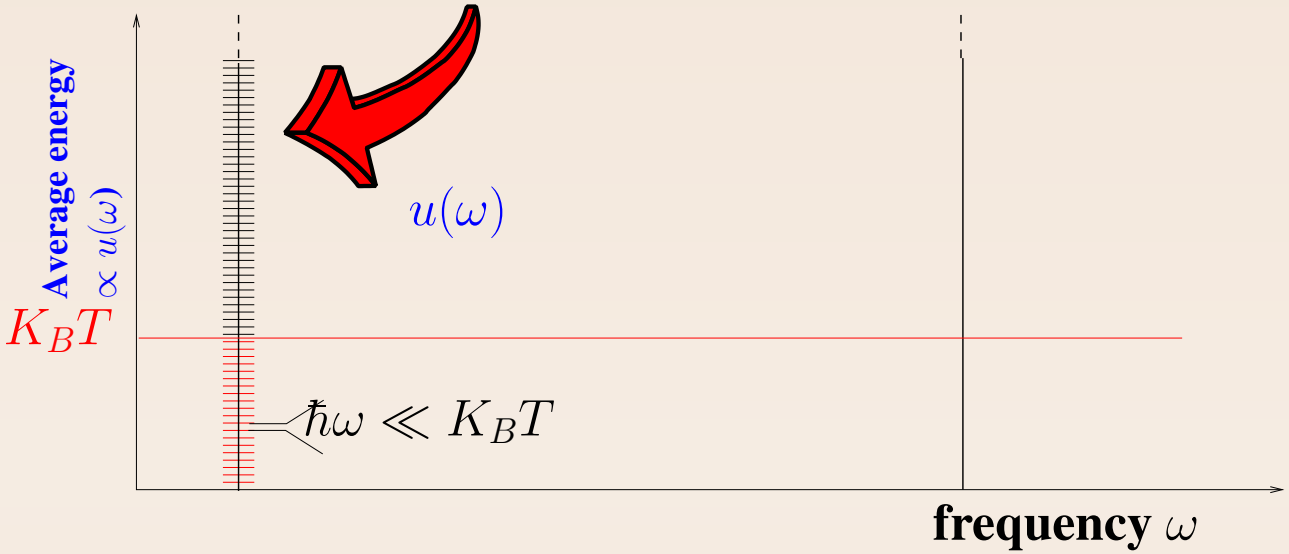
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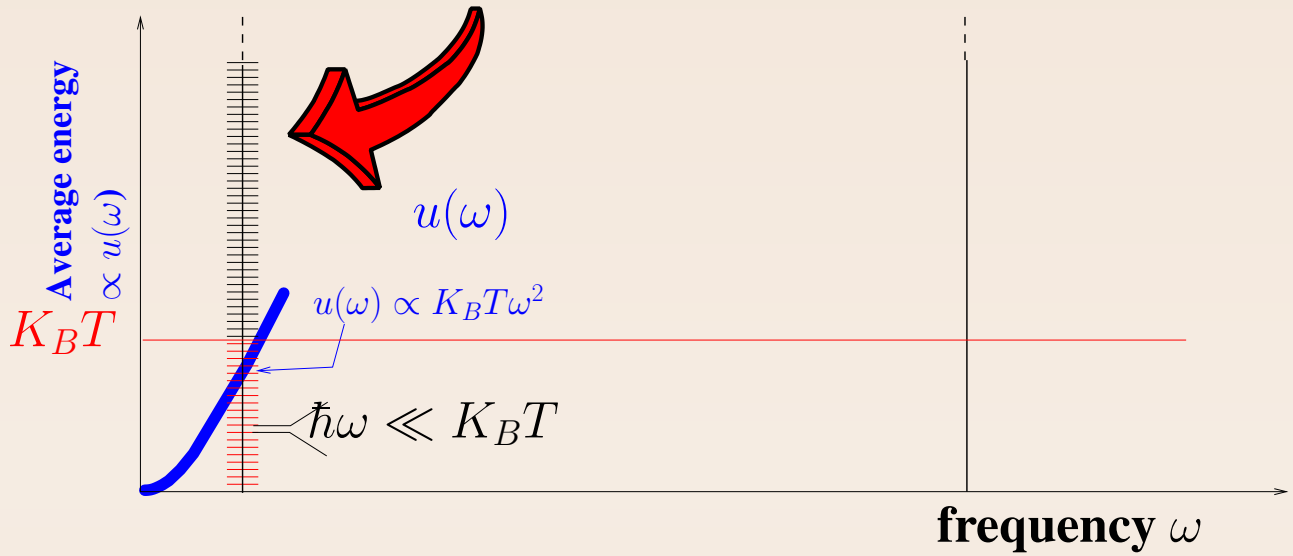
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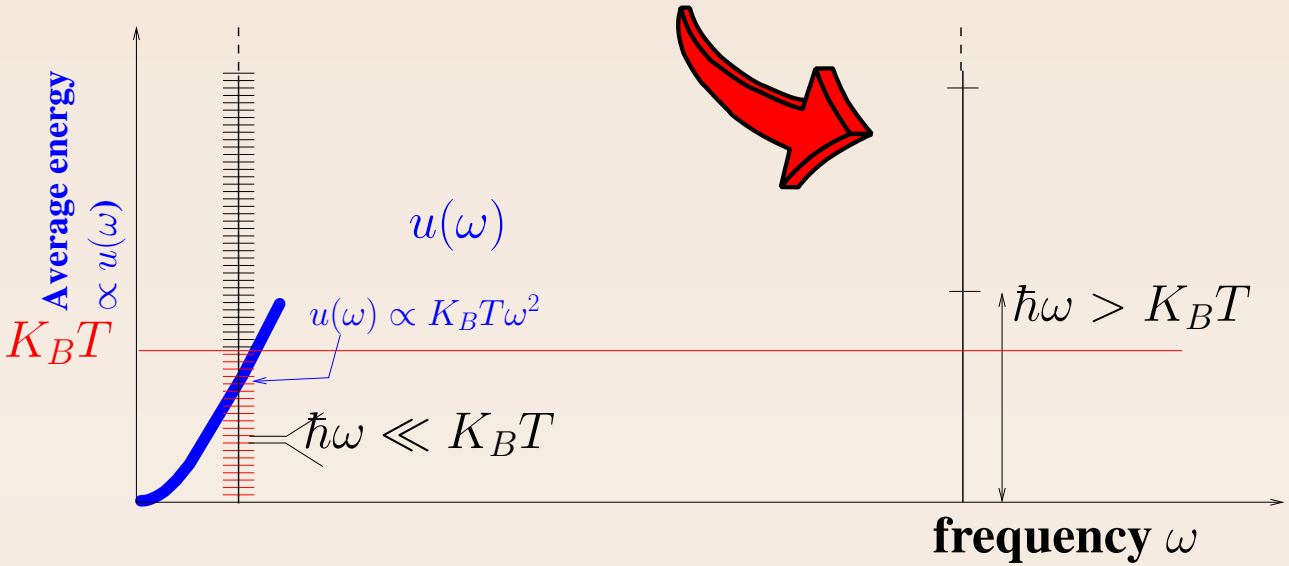


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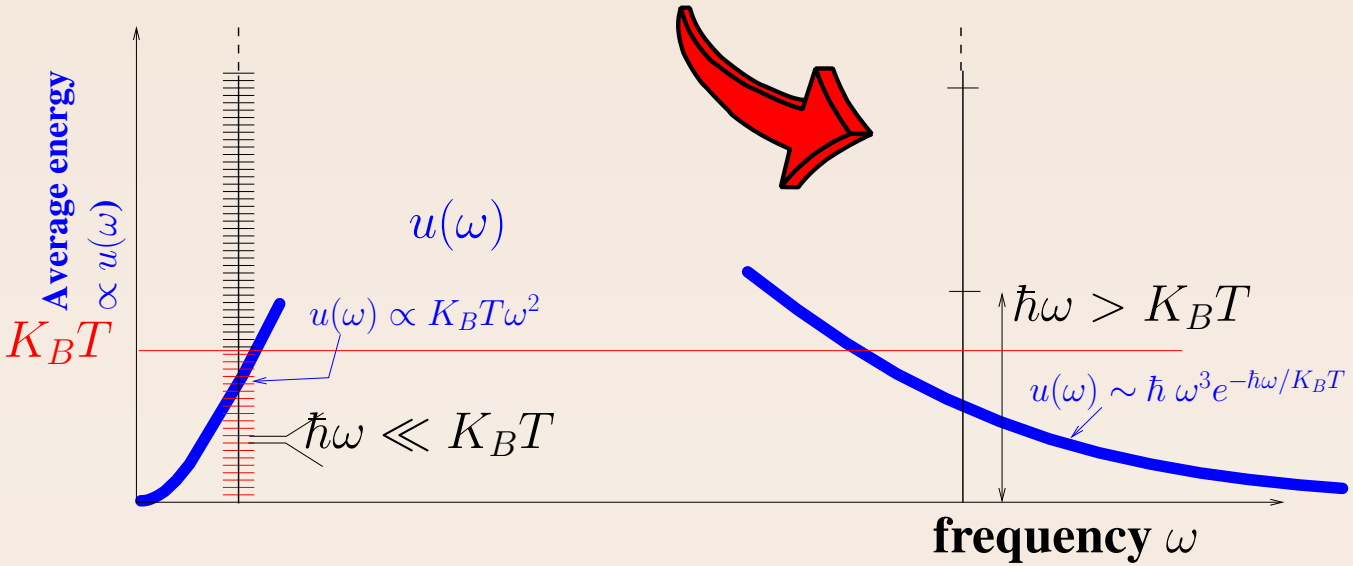


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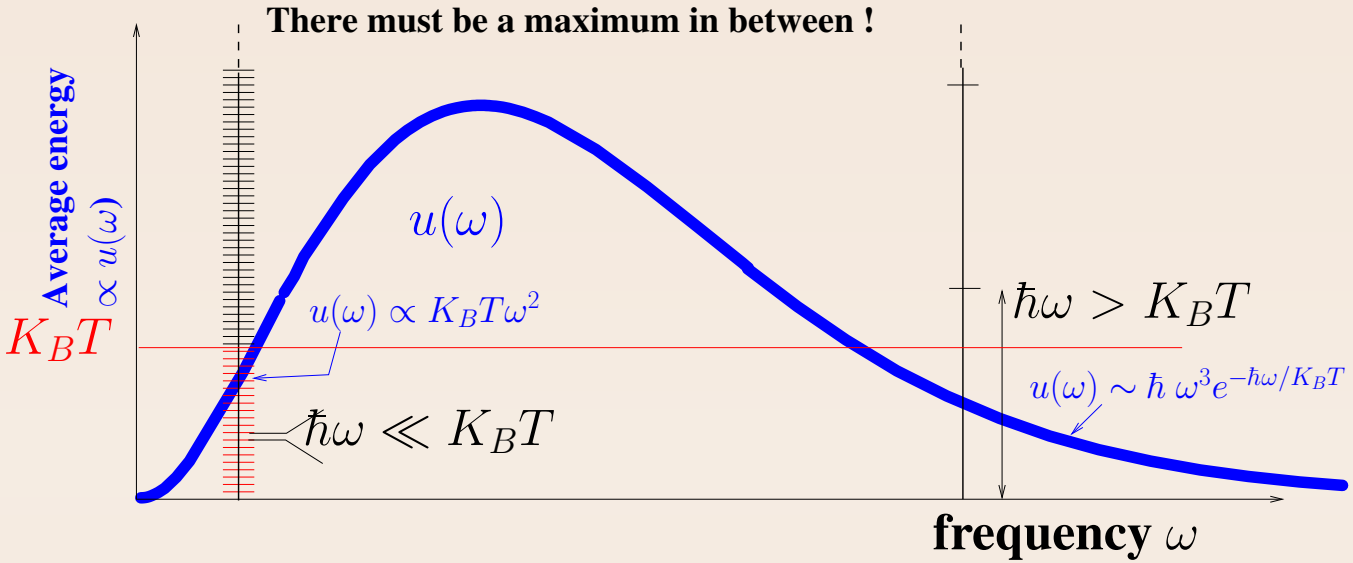
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Photoelectric effect

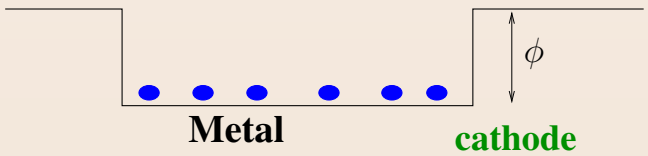
Photoelectric effect

Electrons in a metal are confined by an energy barrier (work function) ϕ.

One way to extract them is to shine light onto a metallic plate.

Light transfers an energy E_{light} to an electron.

The rest of the energy $E_{light} - \phi$ goes into the kinetic energy of the electron: $E_{kin} = E_{light} - \phi$



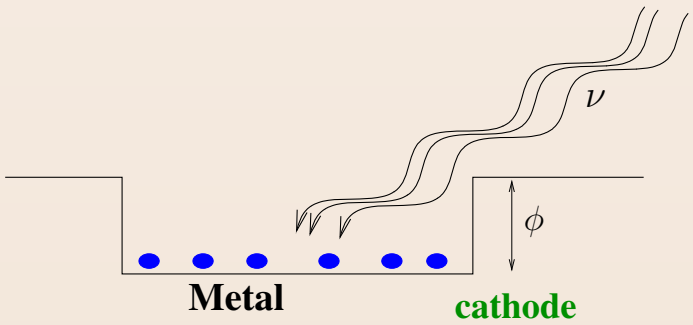
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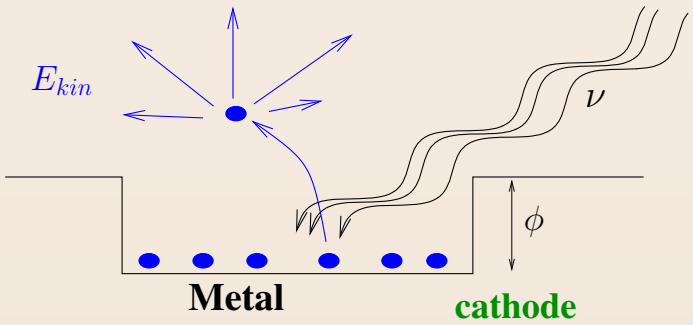
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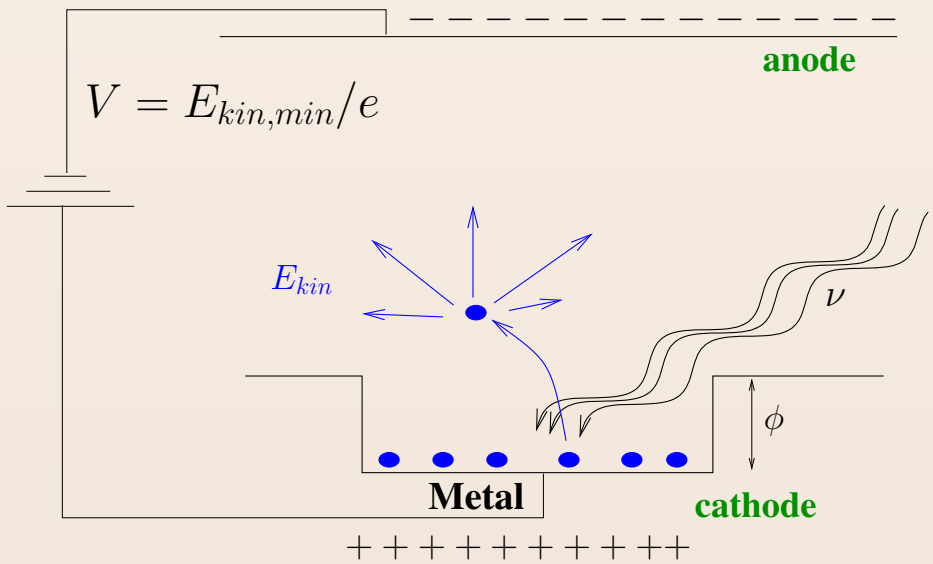
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By measuring E_{kin}, one can get E_{light}.



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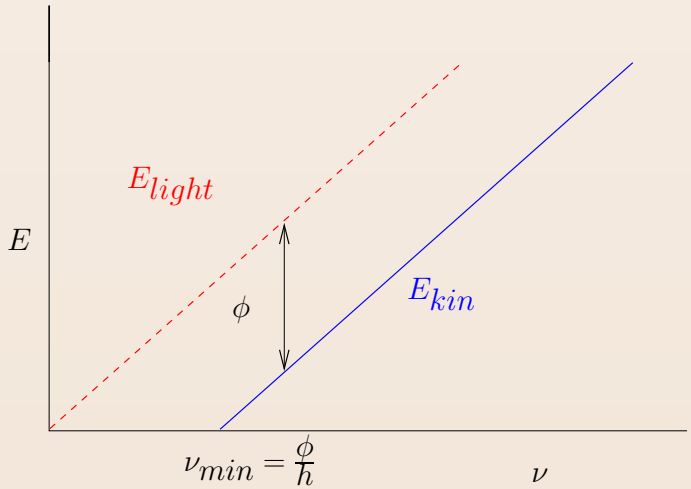
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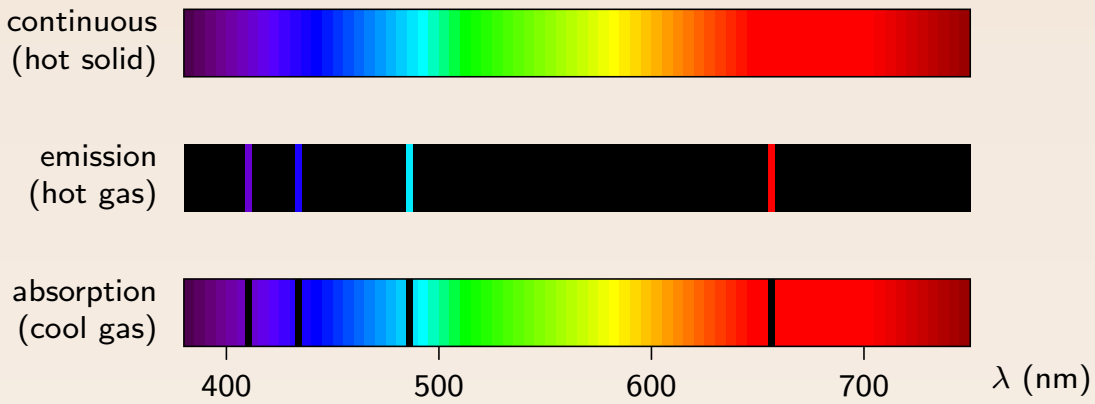
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This means that light is not a continuous object: rather, its constituents are discrete: the photons.

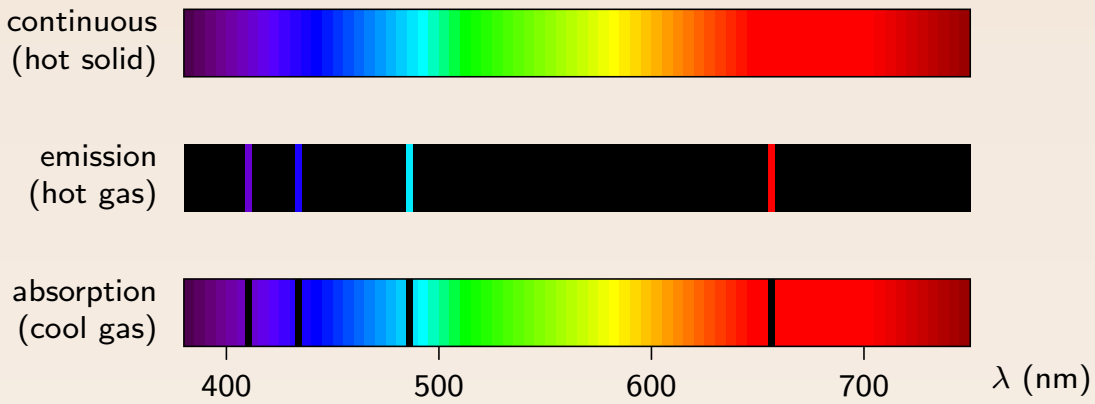
Line spectra

Continuous and line spectra



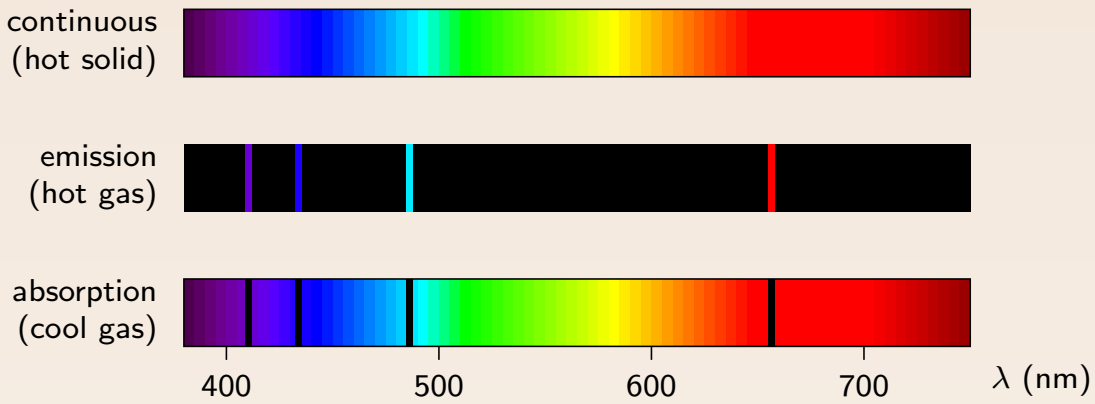
- Continuous spectrum: emitted by an incandescent solid or a gas at high pressure (e. g. blackbody radiation).
- Emission spectrum: a gas at low pressure, excited by heat or by collisions with electrons, emits light only at a series of sharp wavelengths.
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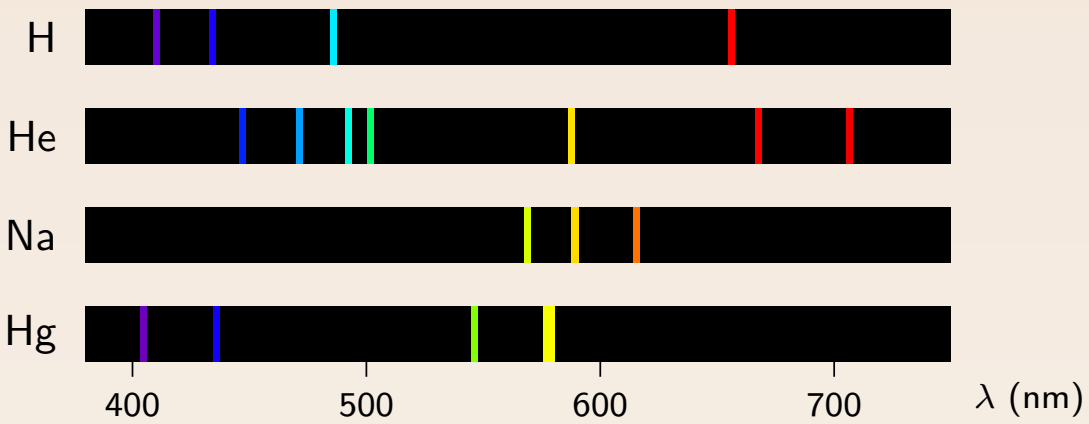
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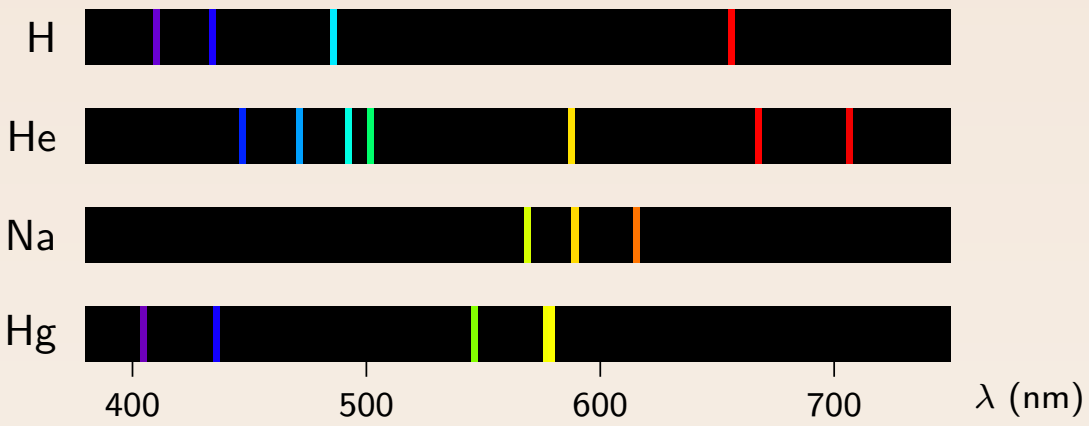
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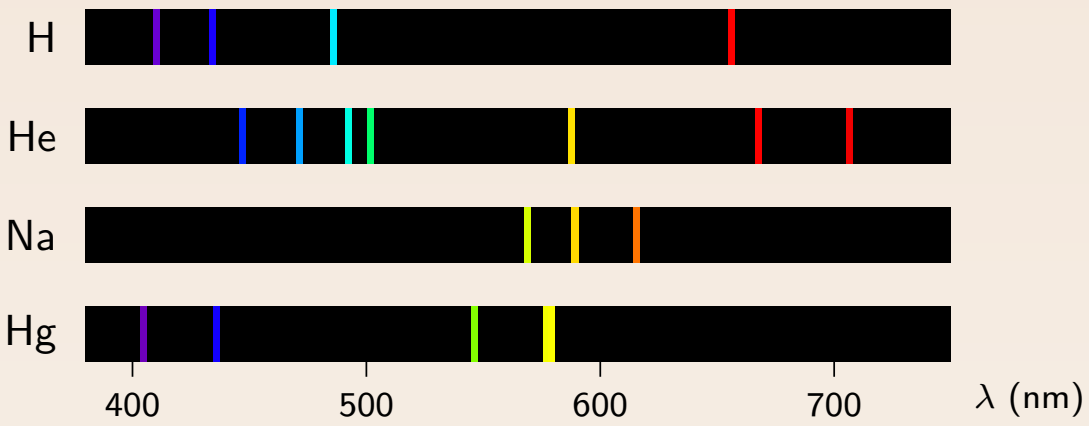
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Bohr's explanation (1913)

Bohr postulated that the energy levels of atoms take only a discrete set of values E_n, rather than a continuum as in classical mechanics.

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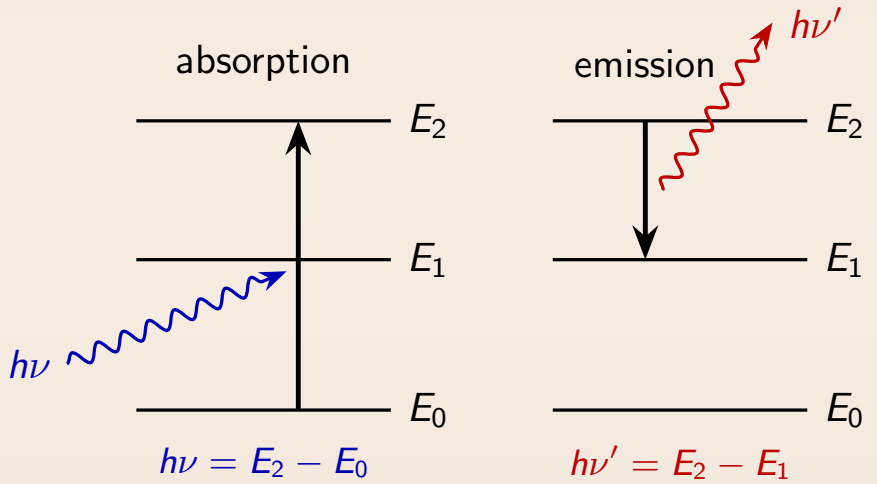
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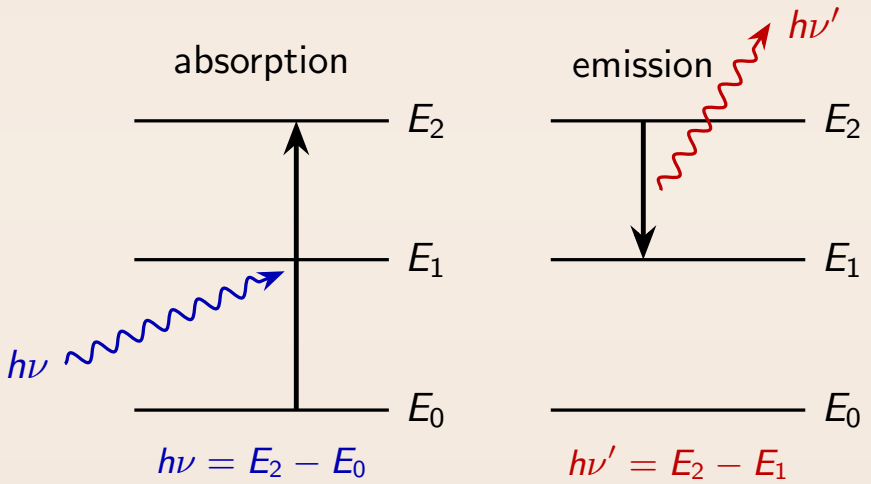
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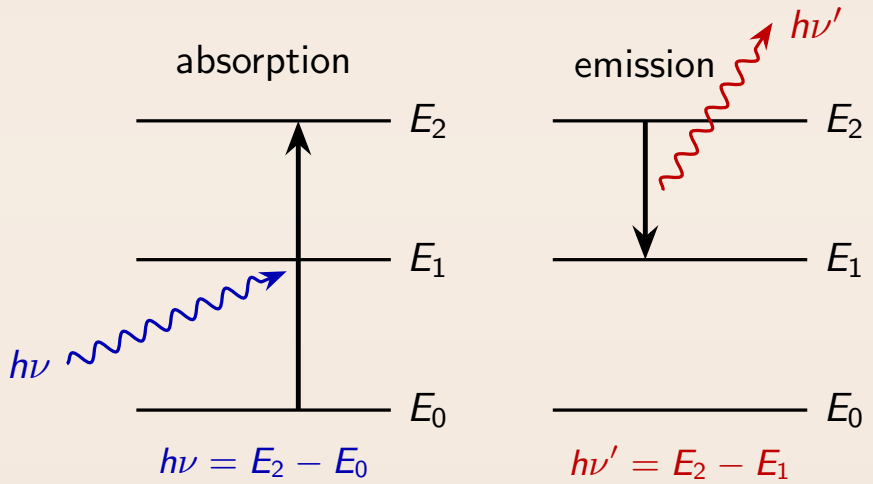
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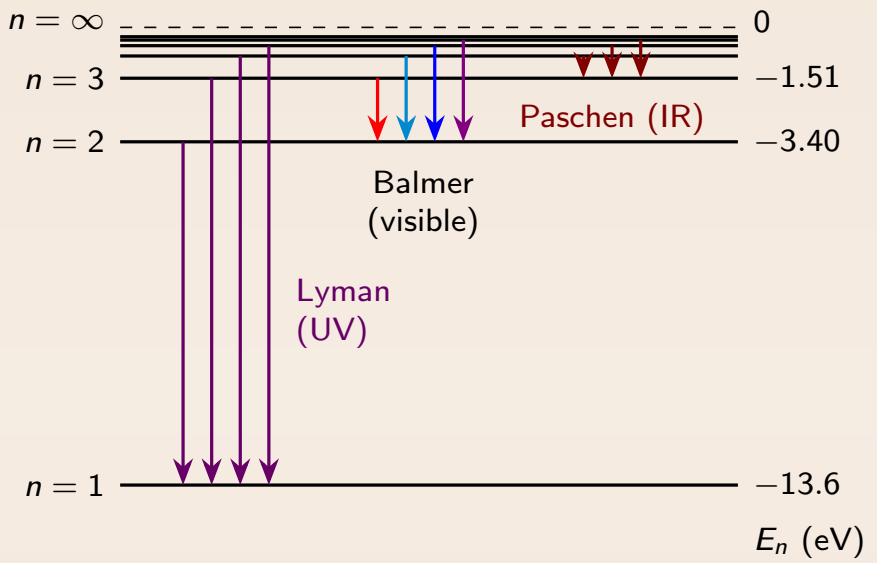
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The spectrum of hydrogen: Rydberg's formula

Rydberg (1890): all lines of atomic hydrogen are fitted by the empirical formula

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$n_1 = 1, 2, 3, \ldots, \quad n_2 > n_1.$
$\mathcal{R} = 109\,677\,\mathrm{cm}^{-1}$: Rydberg constant.



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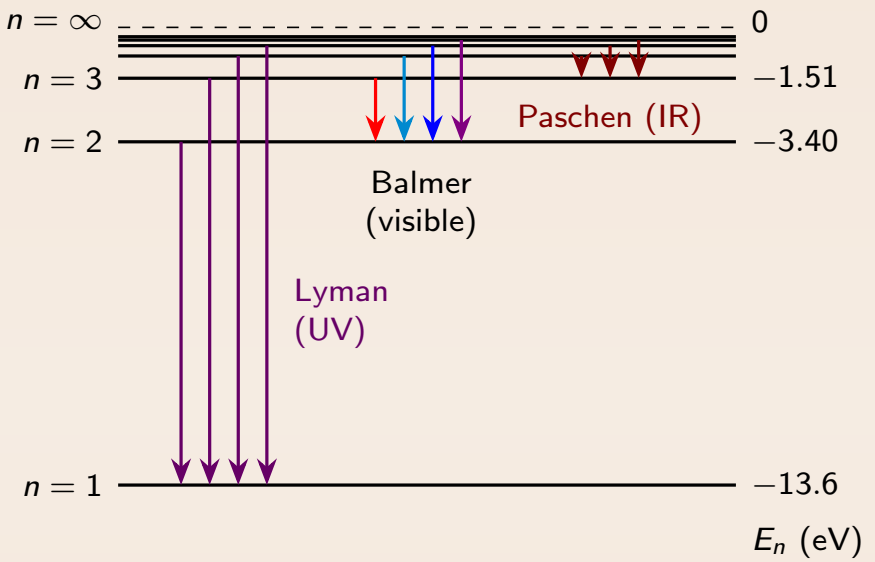
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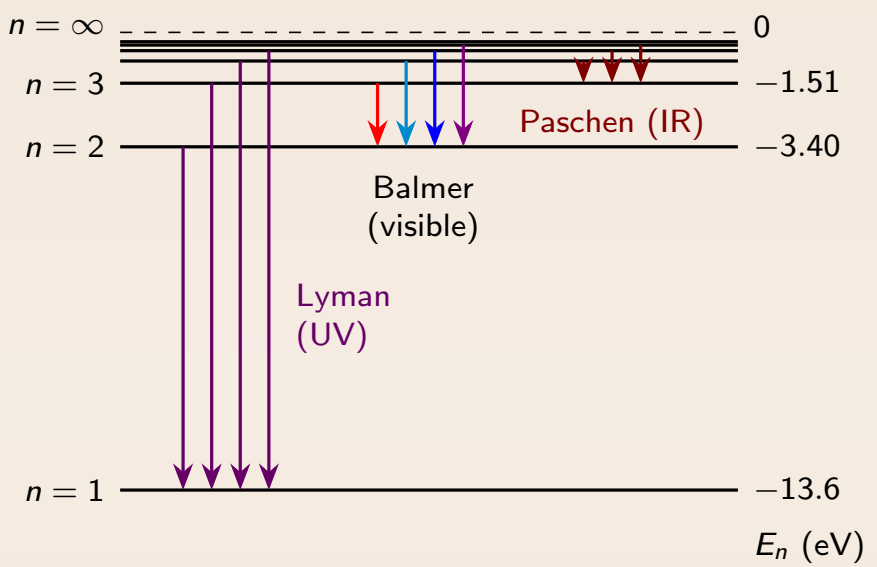
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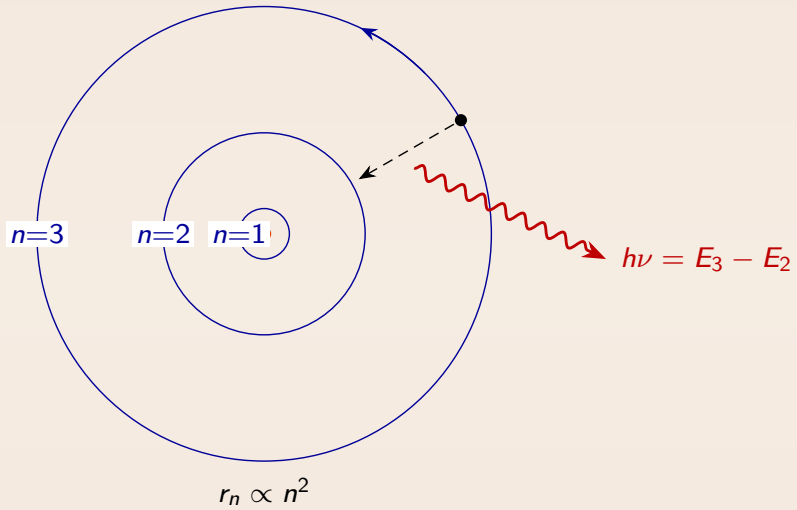


$\Rightarrow$ Comparing with (2.7) with $\nu = c/\lambda$: $E_n = -\frac{hc\mathcal{R}}{n^2} \approx -\frac{13.6\,\mathrm{eV}}{n^2}$

- No analogously simple formula has been found for any atom other than hydrogen.

Bohr's planetary model

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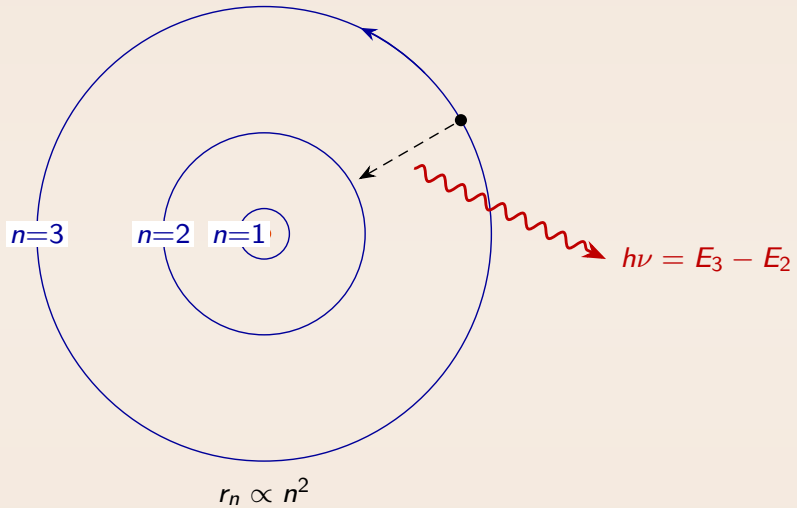
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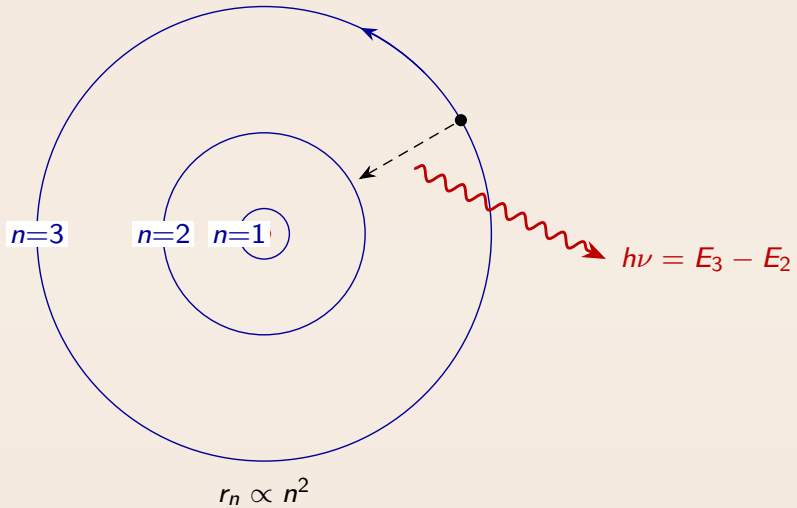
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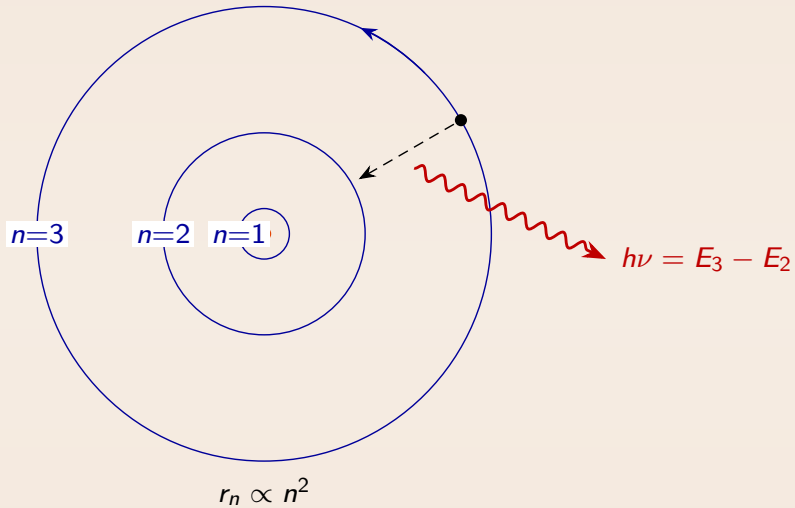
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1 Introduction: atoms and electromagnetic waves

2 Failures of classical physics

3 Wave and Particle duality
- Double-slit experiment
- Light carries momentum: Compton scattering
- Matter (Electrons) as waves

4 Bohr's atom

5 The wave function and Schrödinger equation

6 Quantum mechanics of some simple systems

7 Principles and Postulates of Quantum mechanics

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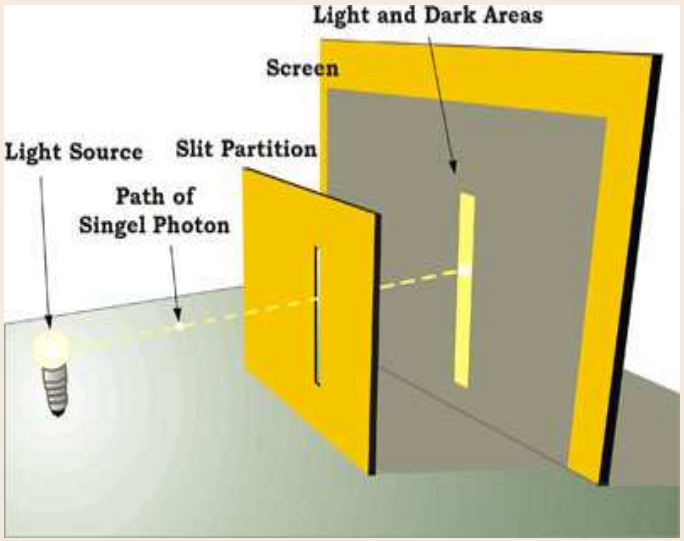
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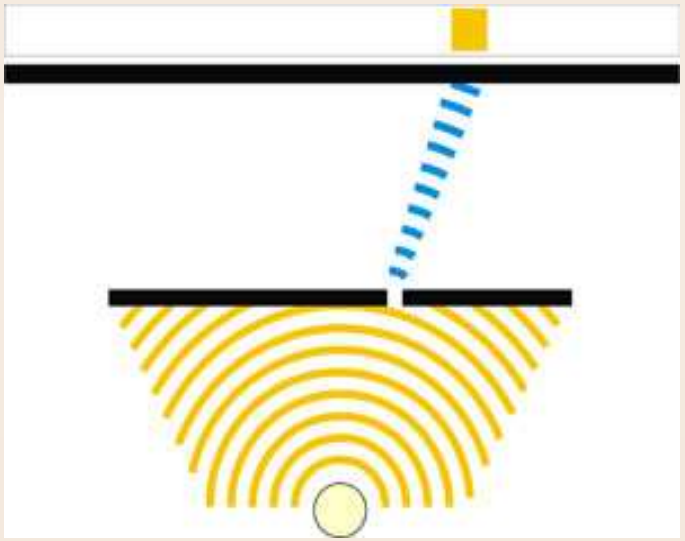
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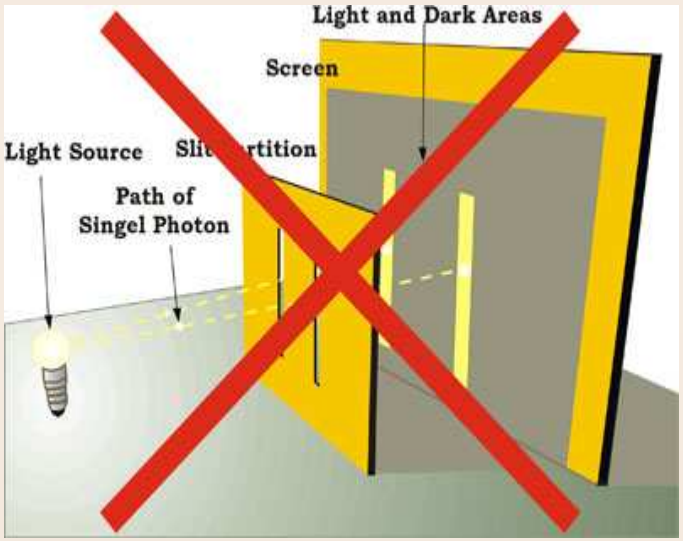


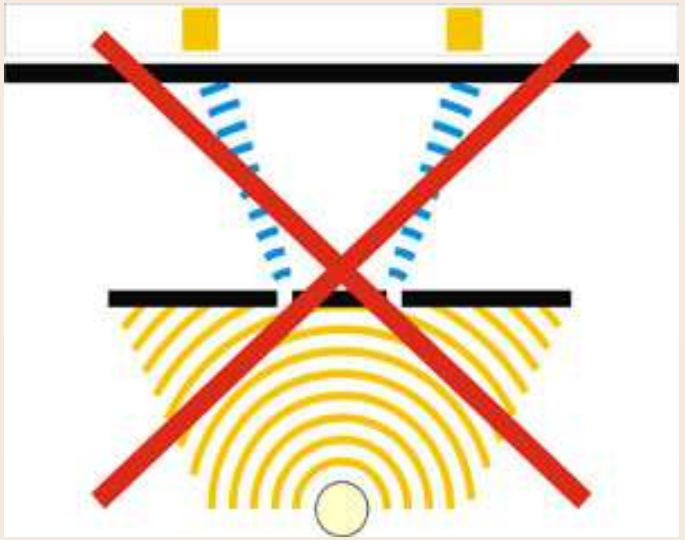


Monochromatic, coherent light is shone through a single slit

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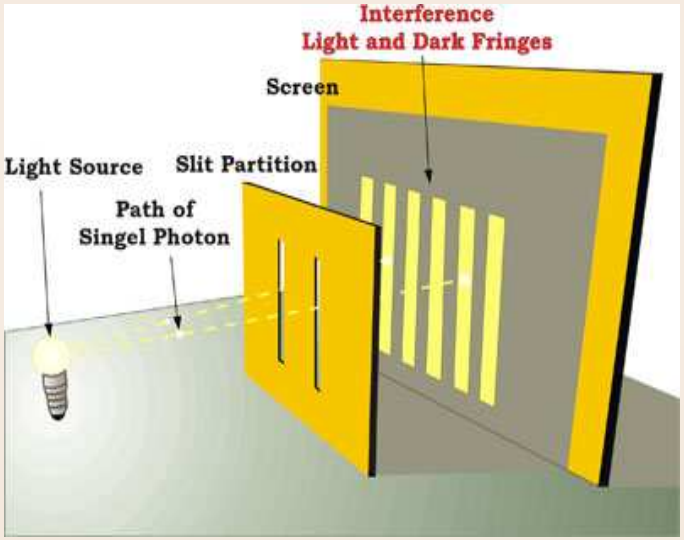


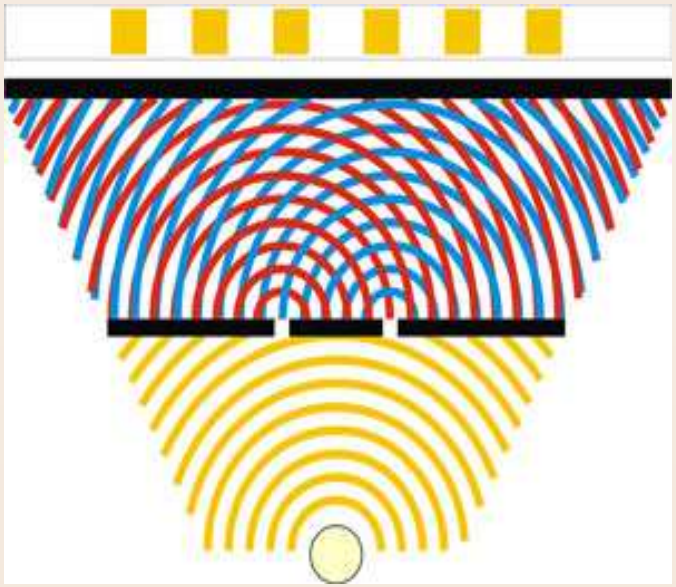
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Double slit, naive expectation

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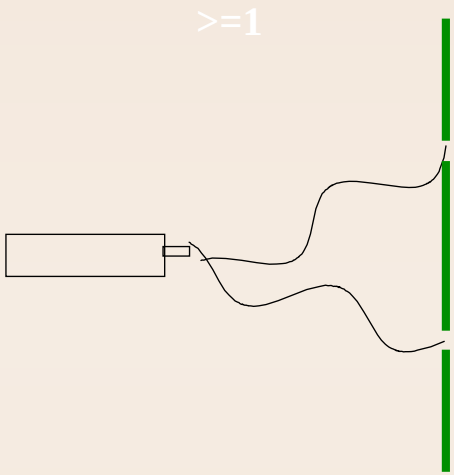




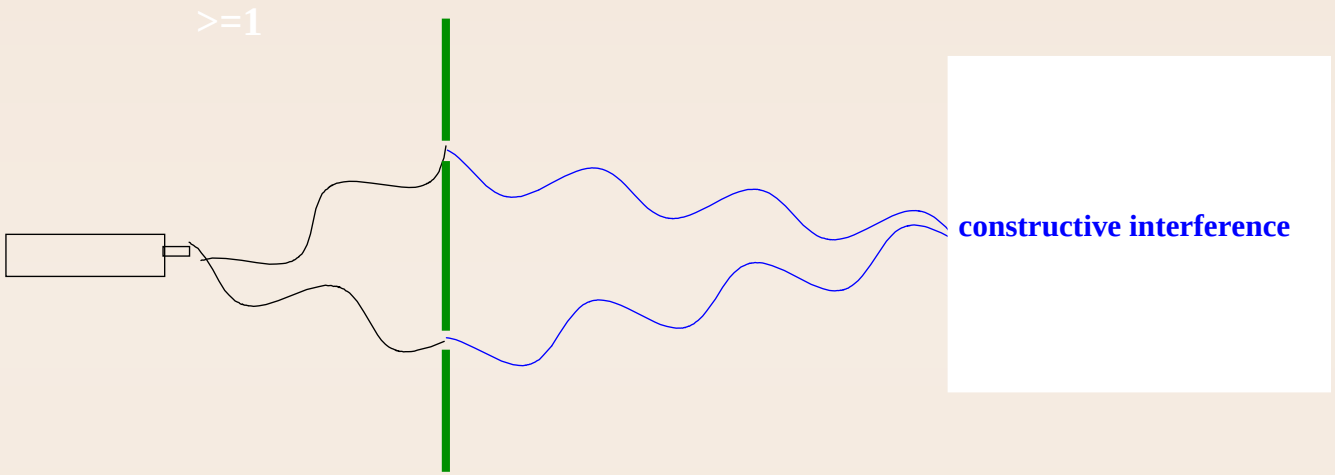
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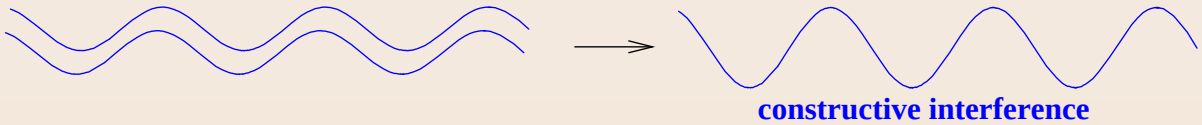
Double slit: interference pattern

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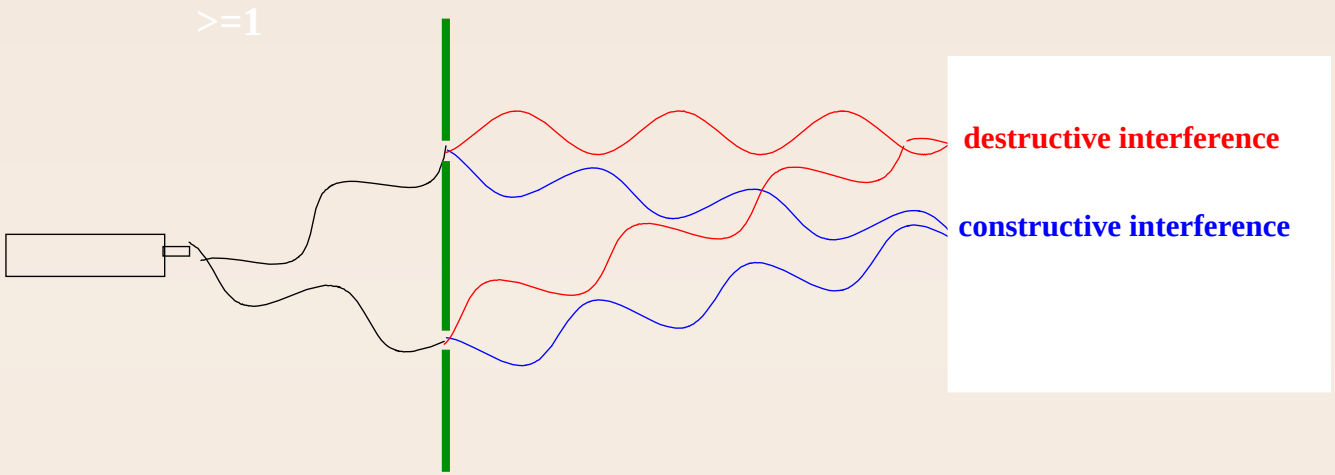


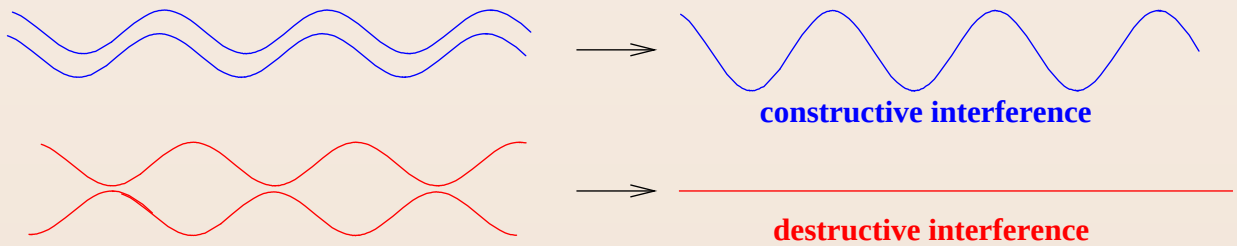
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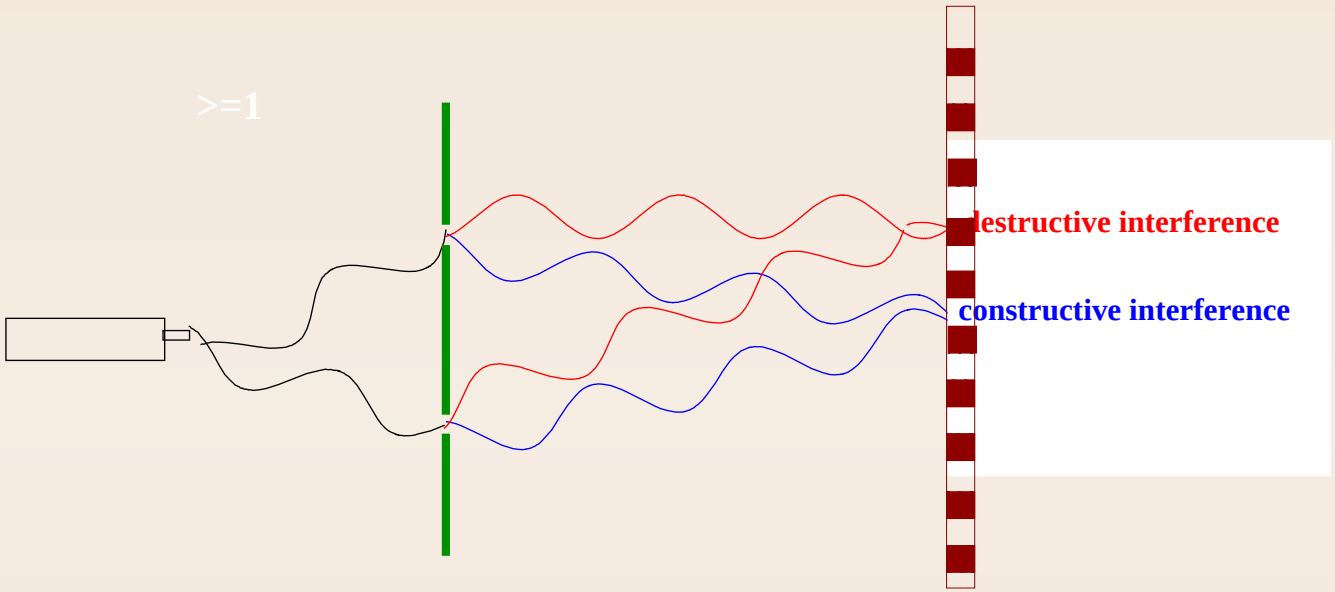


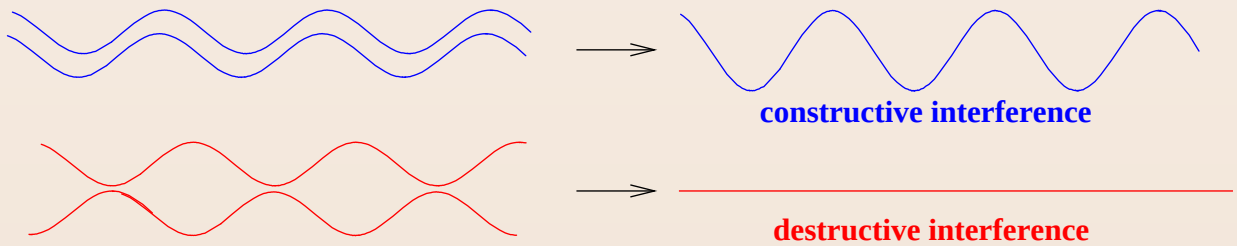
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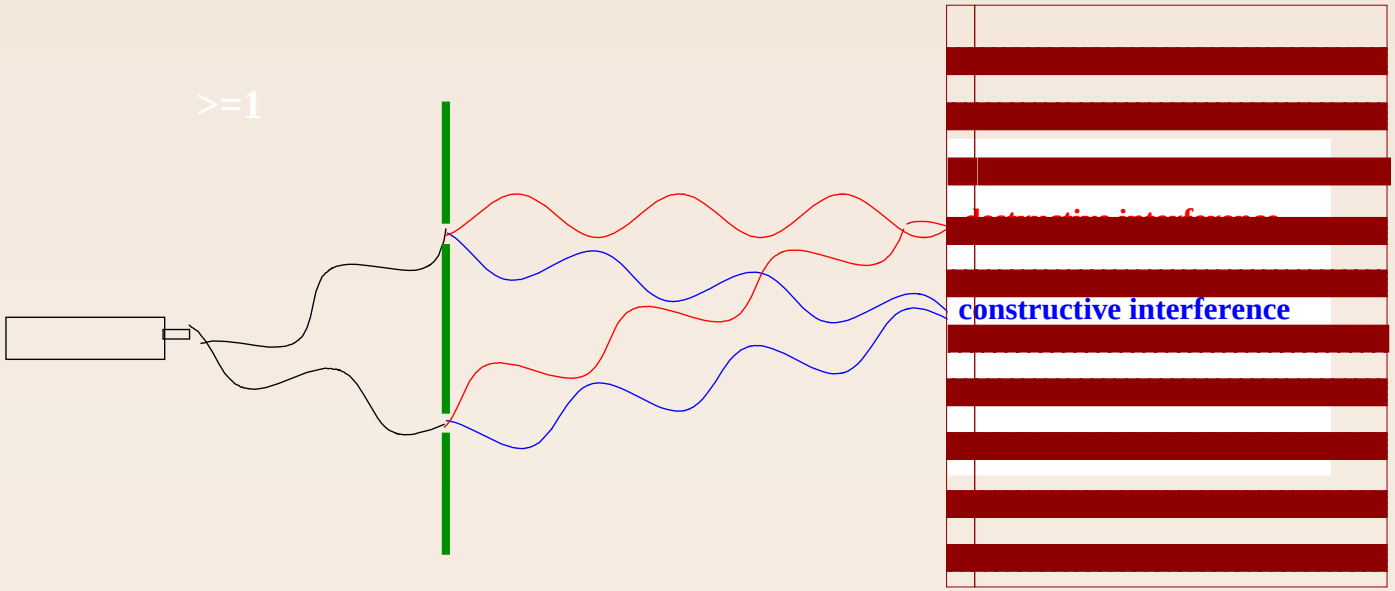


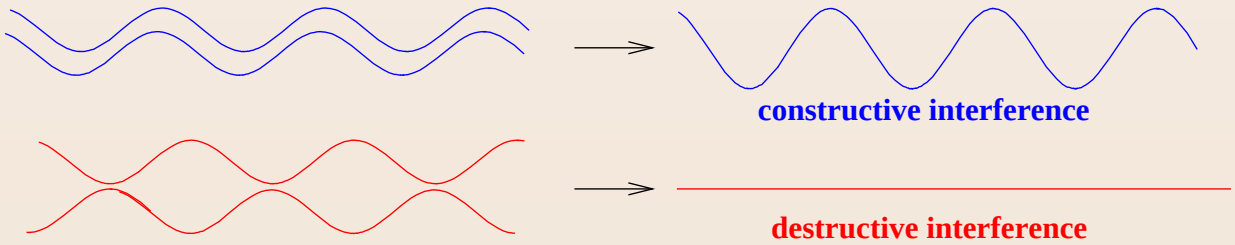
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The observation of an interference pattern proves the wave nature of light!

Amplitude and intensity of a wave

The energy density of an electromagnetic field

$$\rho = \frac{1}{2}\left(\varepsilon_0 E^2 + \frac{B^2}{\mu_0}\right) \tag{3.1}$$

depends quadratically on the fields.

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Later, Ψ will have complex values, then

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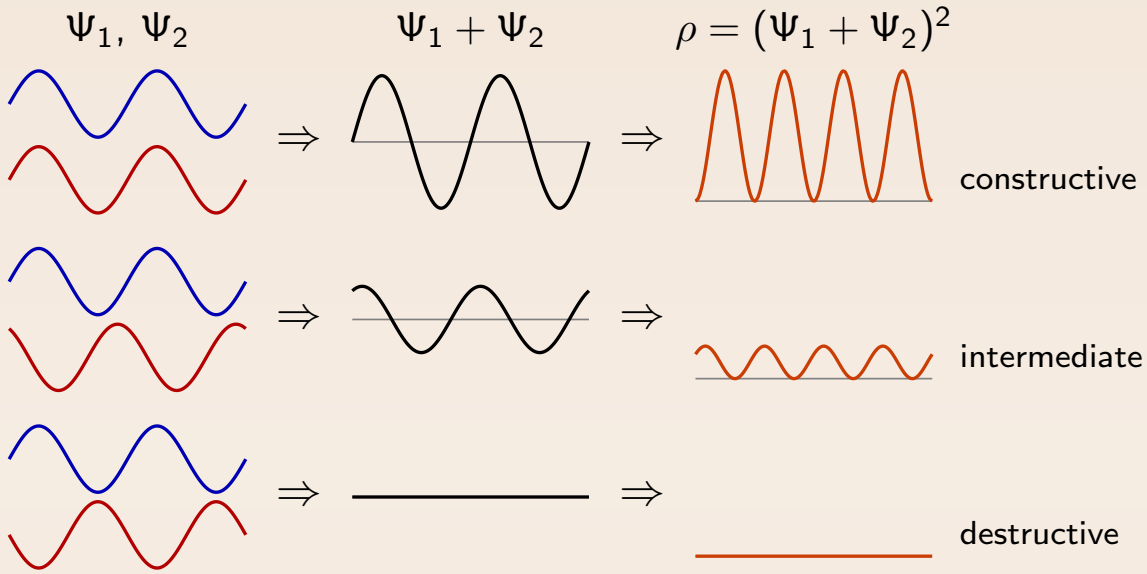
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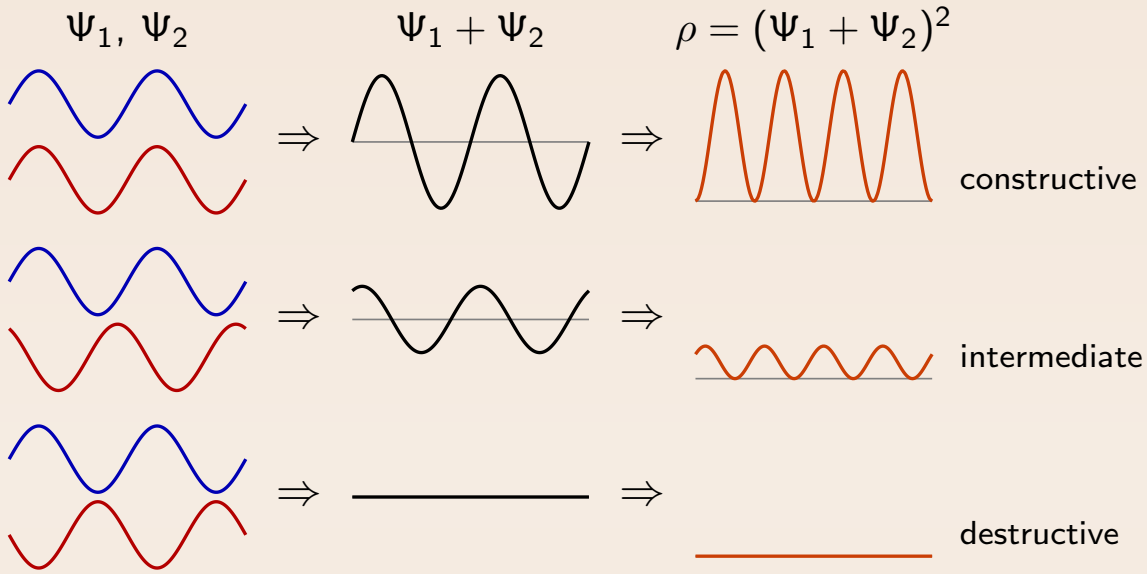
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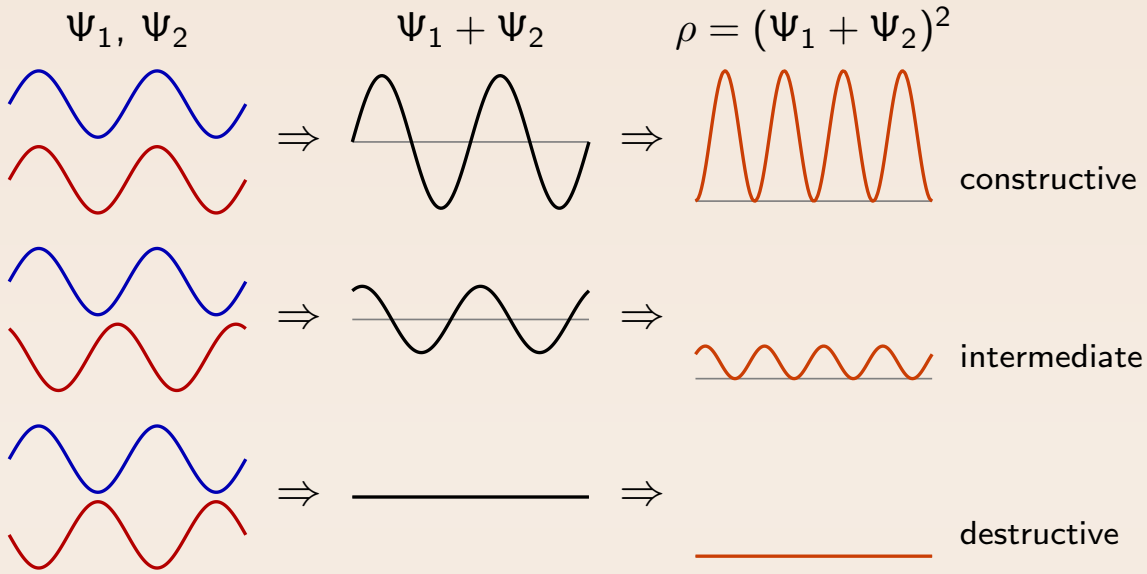
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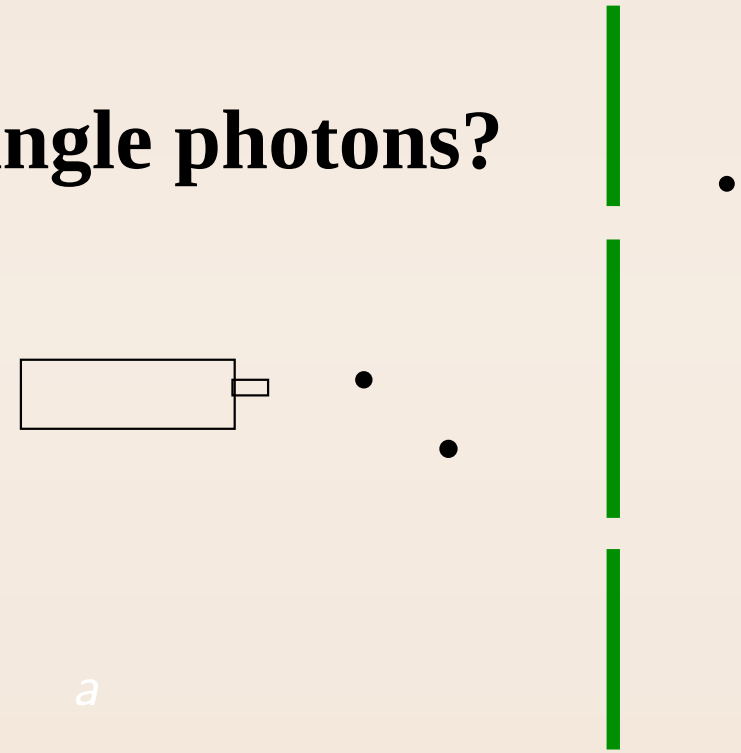
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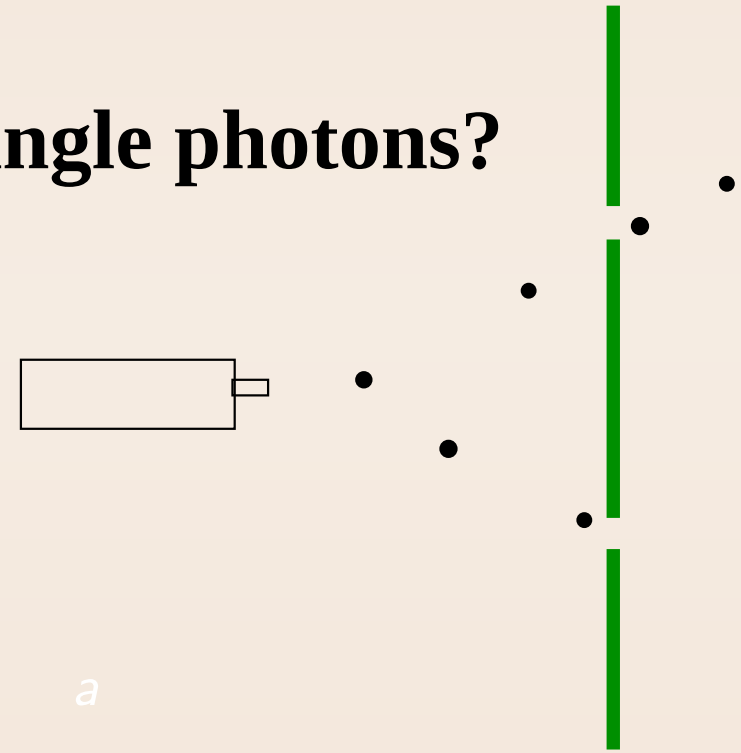
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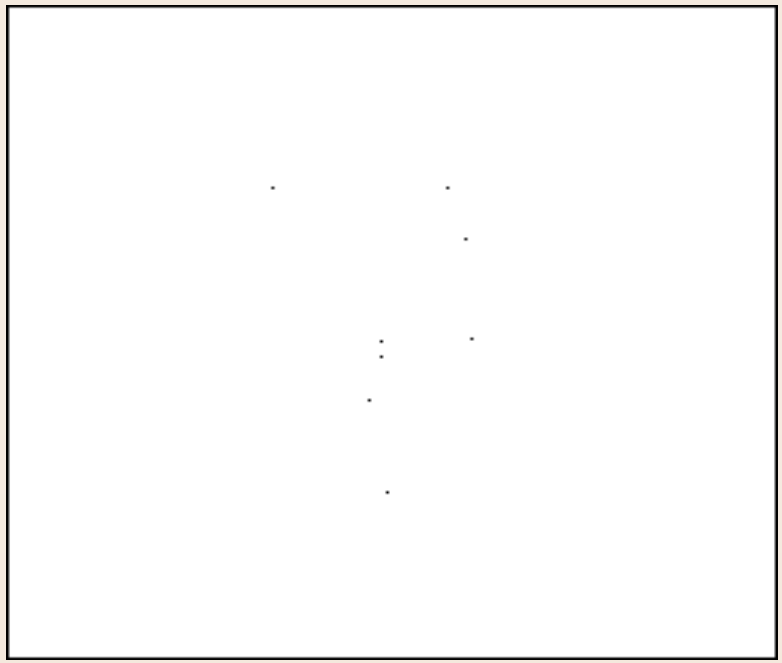
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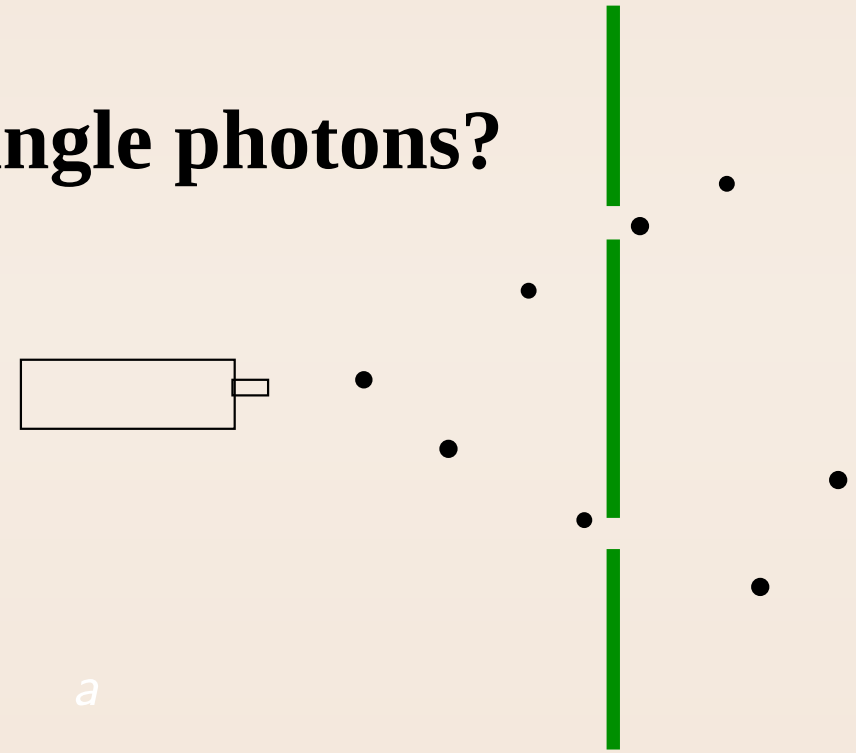
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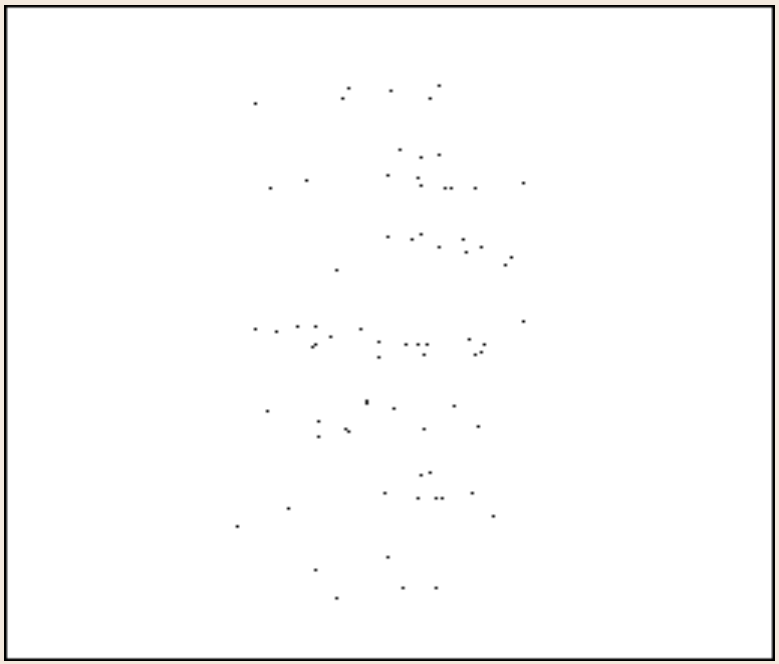




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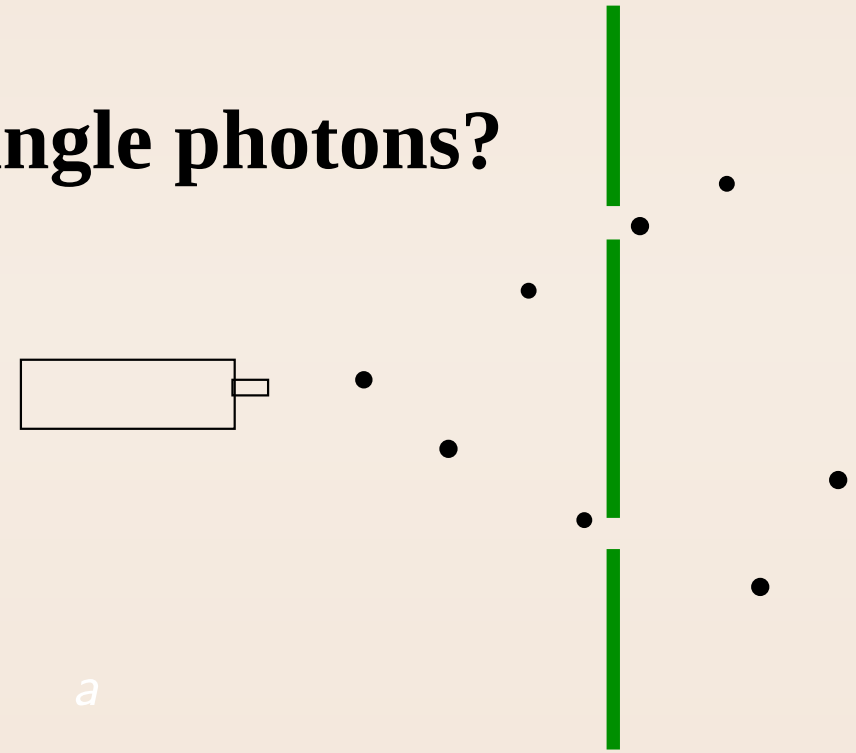
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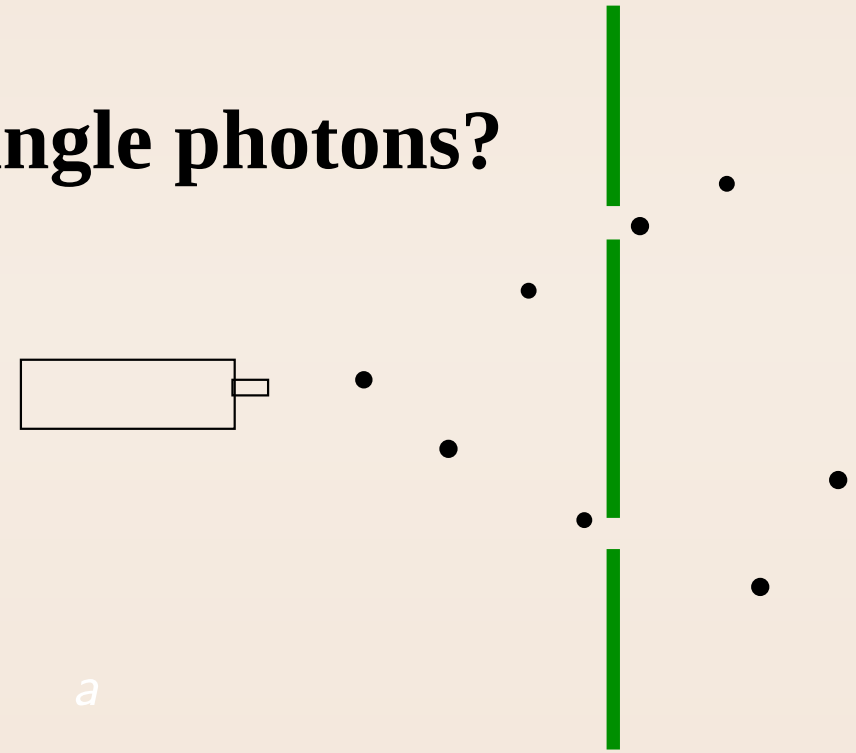
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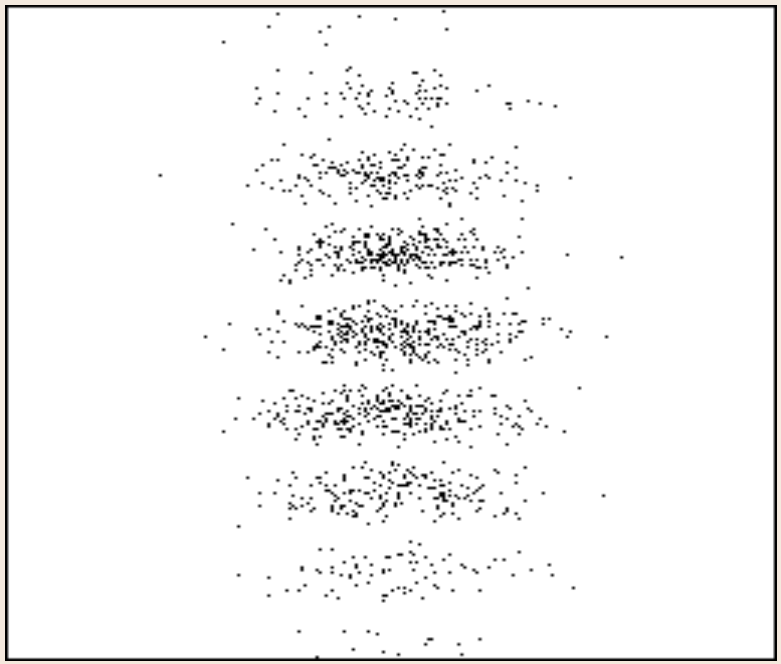




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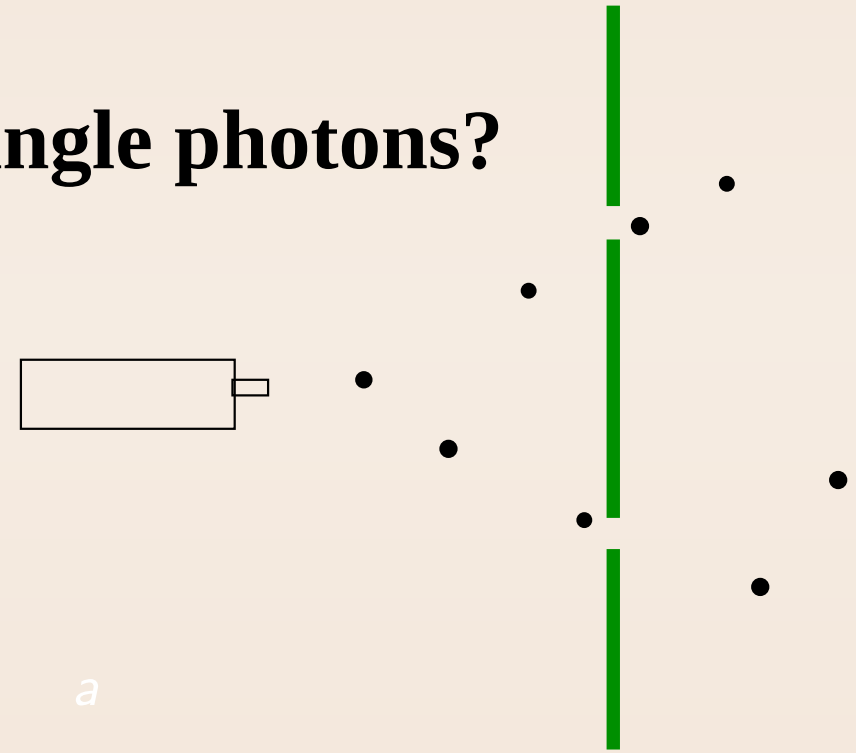
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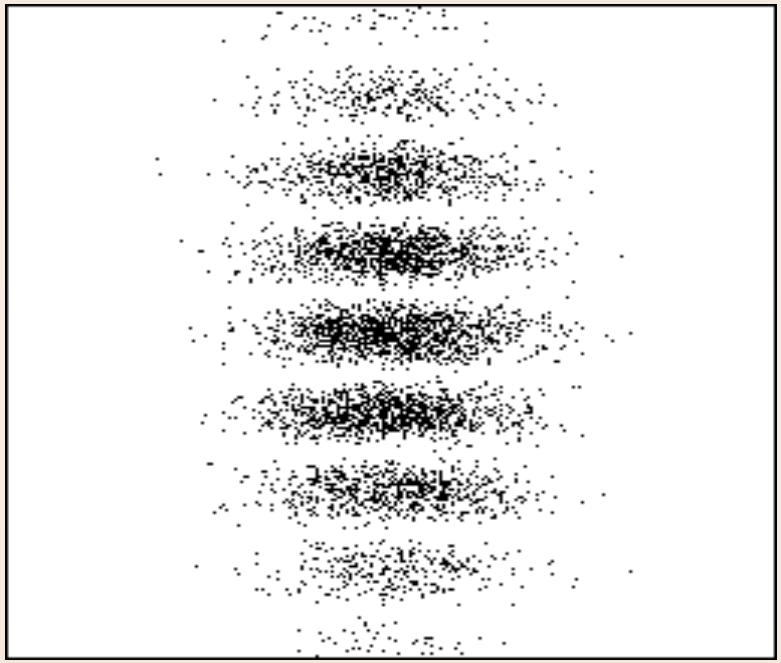




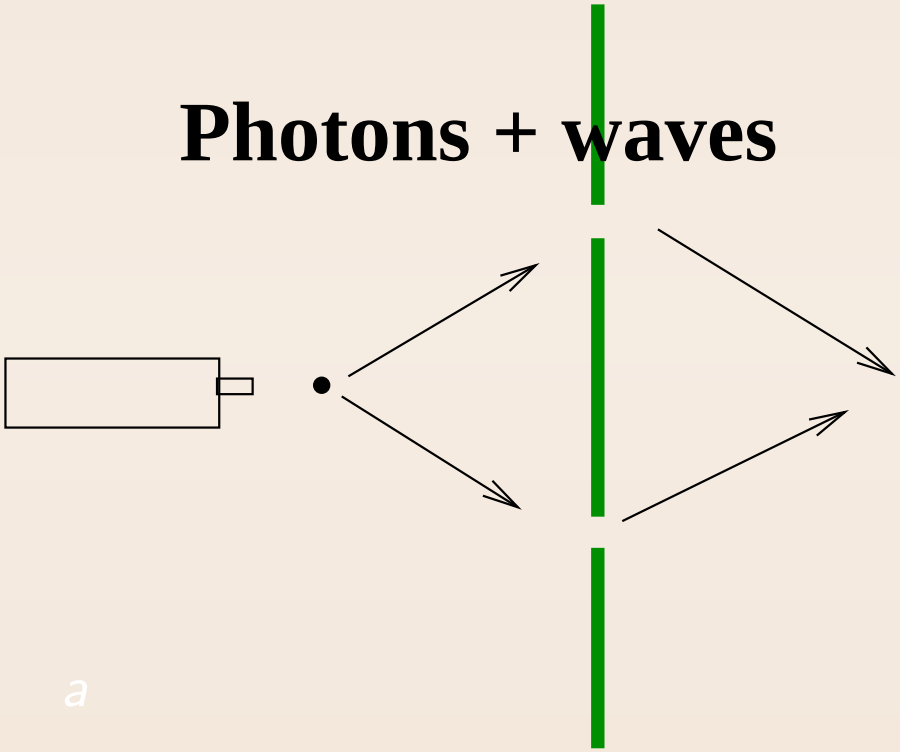
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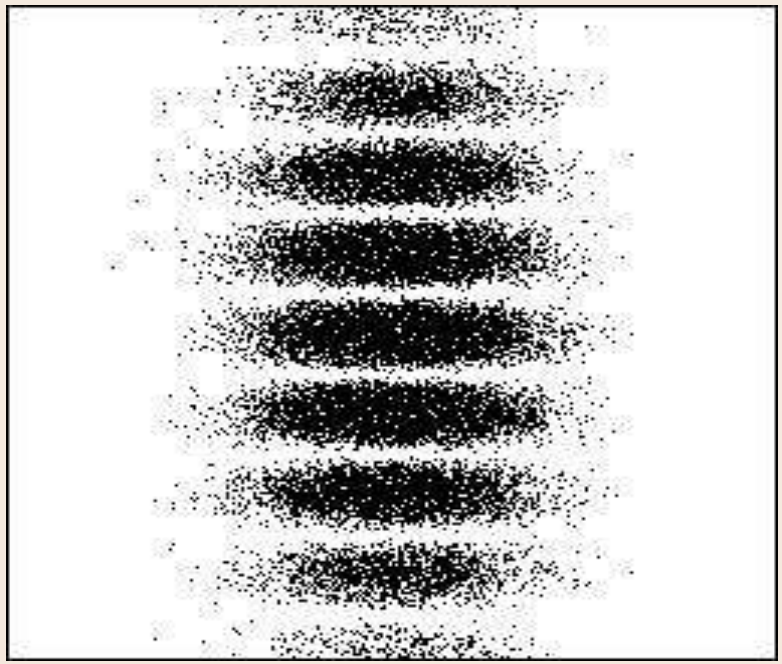
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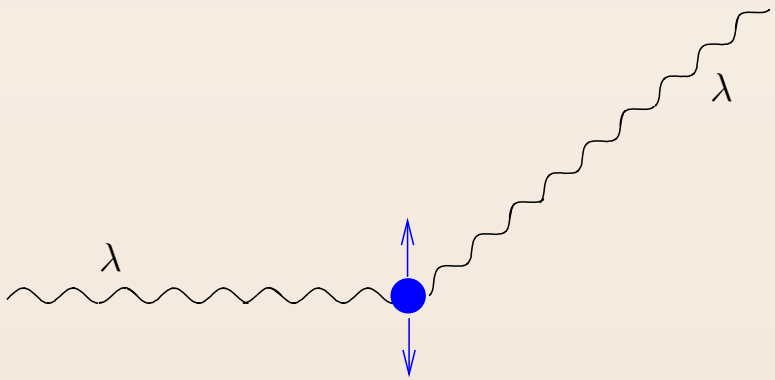
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Light carries momentum: Compton scattering

Classical view (Thomson scattering)

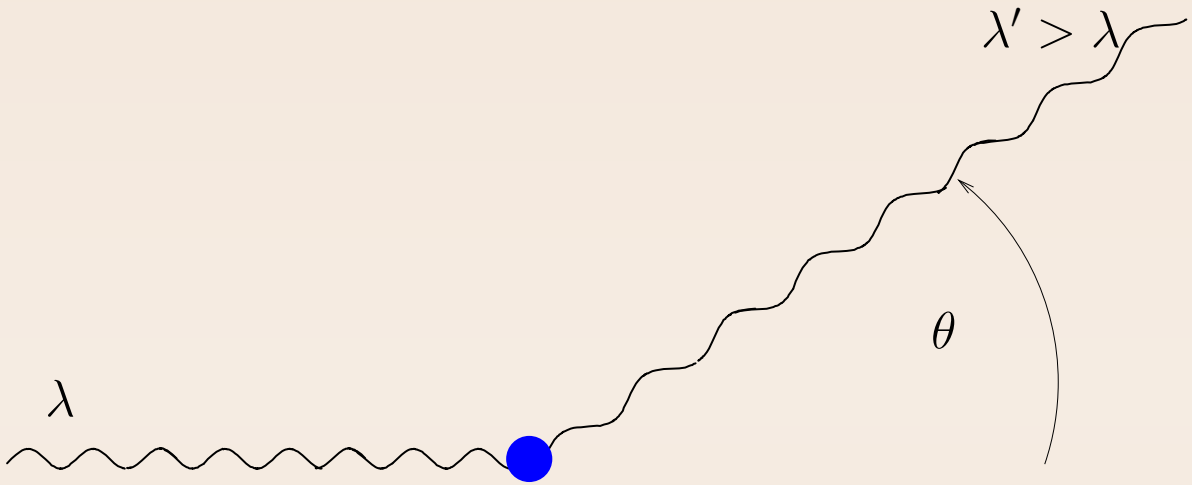
Scattering of high-energy radiation (x-rays, gamma-rays) from an electron.

The electron oscillates at the frequency of the incident wave. The electron acts as an oscillating dipole and emits radiation at the same frequency.
Wavelength of the scattered radiation remains unchanged !



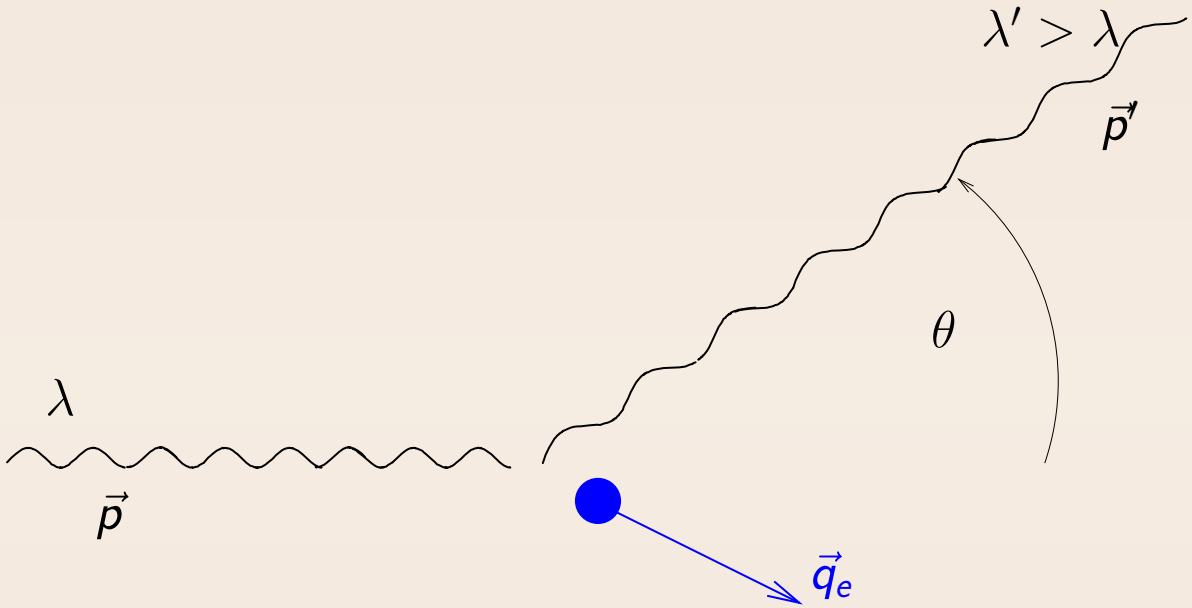
At high intensities, the electron is also pushed by the radiation and the Doppler effect must be taken into account:
light is emitted in a broader frequency range.

Experimental result (Compton scattering, 1923)



$$\lambda' - \lambda = \frac{h}{m_e c}(1 - \cos\theta) \tag{3.7}$$

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$$\vec{p} = \vec{p}' + \vec{q}_e \tag{3.6}$$

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This result can be understood if one assumes that the particles constituting electromagnetic waves (photons) have a momentum

$$|\mathbf{p}| = \frac{h}{\lambda} \tag{3.8}$$

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This is consistent with Planck's energy formula for photons and with relativity: for a particle with zero rest mass, moving with velocity c, $E = p\,c$, so that

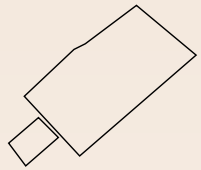
$$E = p\,c = h\nu \quad \Rightarrow \quad p = E/c = h\nu/c = h/\lambda \tag{3.9}$$

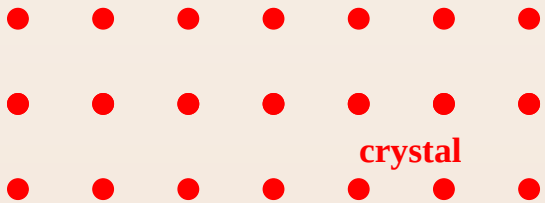
Matter (Electrons) as waves

"Double slit" experiment with crystals

examples:

Diffraction





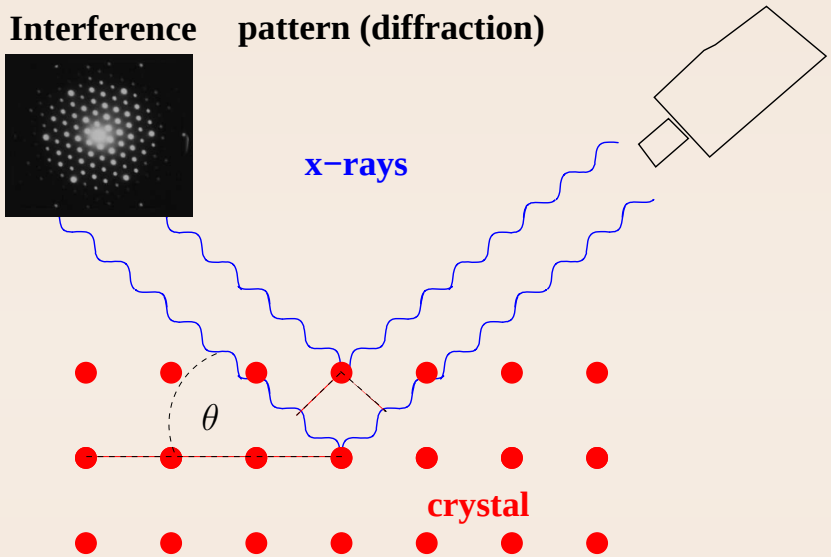
For x-rays the natural "slit" system consists of an arrangement of atoms in a crystalline structure
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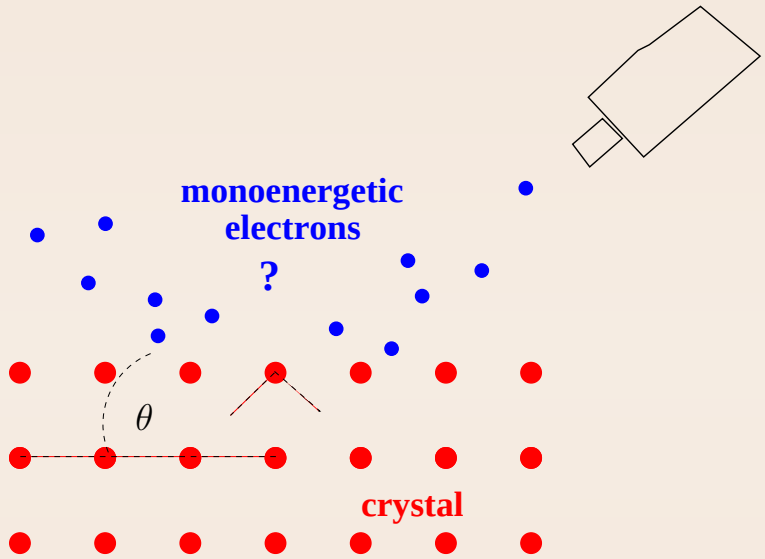
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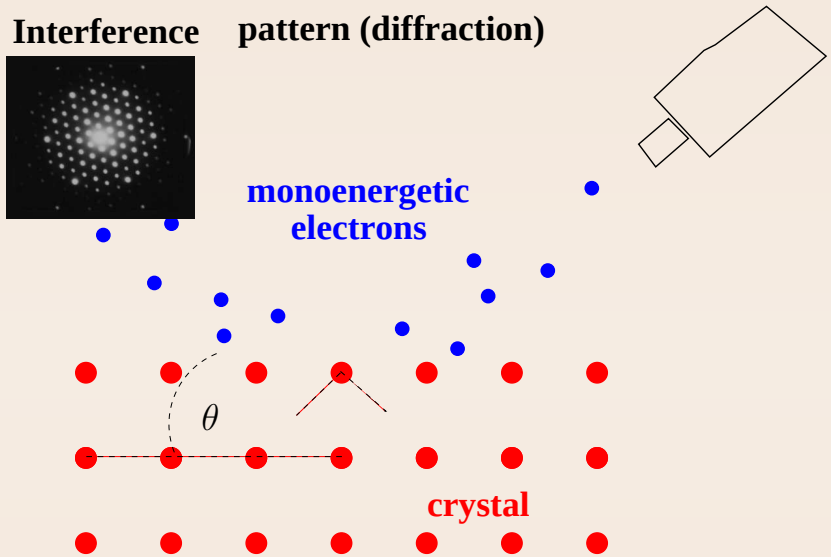
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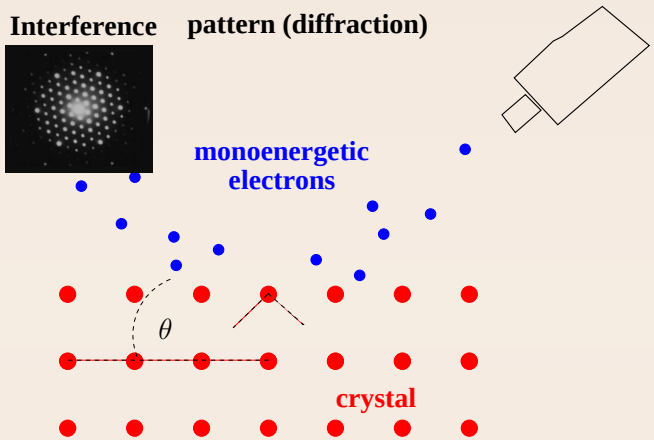
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These "matter waves" have a wavelength (cfr. (3.8))

$$\lambda = \frac{h}{p} \qquad (3.10)$$

Electrons as waves

- The double-slit experiment can also be done with electrons instead of light (technically difficult): an electron gun produces a beam of electrons with a selected velocity, focused and guided by electric and magnetic fields.

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- Example: electrons accelerated by 54 V have $\lambda = h/p \approx 0.17\,\text{nm}$, comparable to the distance between atoms.

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5 The wave function and Schrödinger equation

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7 Principles and Postulates of Quantum mechanics

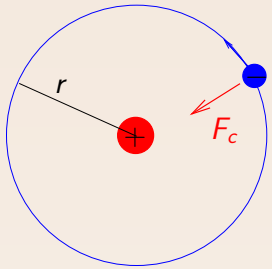
8 Angular momentum and electron spin

Bohr's atomic model (See also Blinder, Chap. 7.1–7.2)

Bohr's atomic model (1913) can be understood with the idea that electrons have a wavelength (de Broglie, 1924).
It explains:

- The very stability of electron orbits
- The discrete emission and absorption lines of atoms

Bohr Atom (Hydrogen)

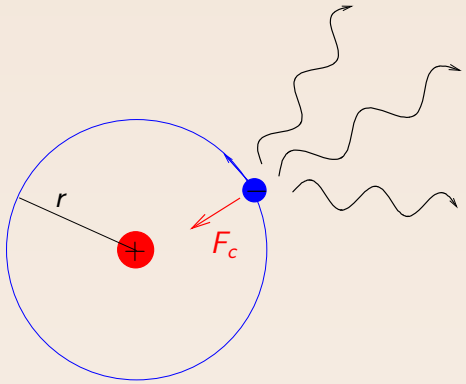


Rutherford atom:

Coulomb force provides centripetal force. For a circular orbit we have (in Gaussian cgs units; in SI units $e^2 \to e^2/(4\pi\varepsilon_0)$):

$$\frac{e^2}{r^2} = \frac{m_e v^2}{r} \tag{4.1}$$

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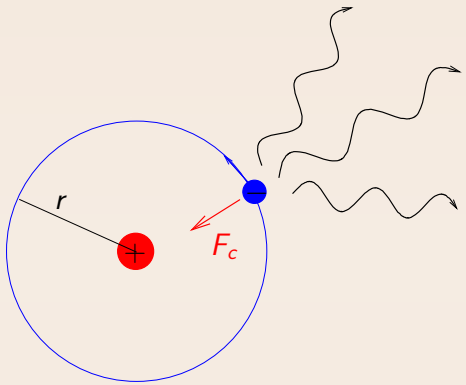
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Problem: accelerated (rotating) charges emit radiation: electron would lose energy and collapse into the nucleus!

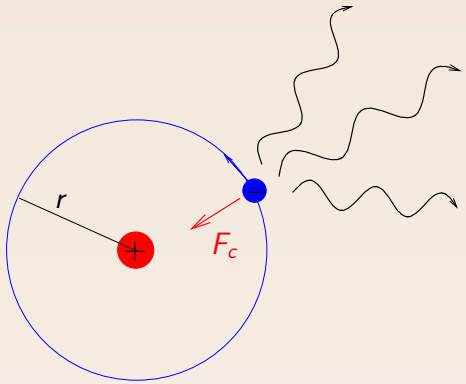
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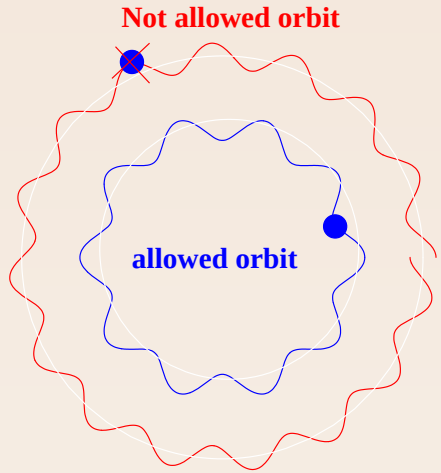


Bohr's idea of quantized orbits

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Bohr's idea of quantized orbits

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(2) Wavelength must fit an integer number of times into orbit:

$$2\pi\ r = n\ \lambda = n\ \frac{h}{m_e v} \qquad n = 1, 2, 3, \ldots \tag{4.2}$$

Here, n is an integer (quantum number) labeling the orbit.

Quantisation of orbitals

From (4.2) we obtain

$$v = \frac{n\ \hbar}{r\ m_e} \tag{4.3}$$

i. e. the angular momentum $L = m_e v r = n\hbar$ is quantized (Bohr's original postulate).

[1] By taking into account that the proton mass m_p is not infinite, one should replace the electron mass m_e with the reduced mass $m_e\ m_p/(m_e + m_p)$.

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Putting this expression back into the condition for the circular orbit (4.1), we obtain

$$\frac{e^2}{r^2} = \frac{n^2\hbar^2}{r^3 m_e} \Rightarrow \boxed{r = n^2 a_0} \tag{4.4}$$

where

$$a_0 = \frac{\hbar^2}{m_e\ e^2} \approx 0.53\,\text{Å} \tag{4.5}$$

is the Bohr radius [1]

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The energy of the orbits is given by kinetic plus potential energy (use (4.1))

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{r} = -\frac{1}{2}\frac{e^2}{r} = -\frac{1}{2}\frac{e^2}{a_0}\frac{1}{n^2} \tag{4.6}$$

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The coefficient of $-\frac{1}{n^2}$ is the Rydberg energy unit, and is given by

$$h\ c\ \mathcal{R} = \frac{1}{2}\frac{e^2}{a_0} \approx 13.6\ \mathrm{eV} \tag{4.7}$$

where $\mathcal{R}$ is the Rydberg constant.

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Explanation of line spectra (Hydrogen)

electron can gain or lose energy by jumping between these orbits.

By jumping from an orbit n_2 with higher energy to one n_1 with lower energy ($n_2 > n_1$) a photon is emitted with energy $E_{photon} = h\nu$ given by the difference of the energies of the two orbits:

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Line spectra

This is the reason why an atom can only emit photons with certain discrete frequencies. In fact, with $\nu = c/\lambda$, (4.8) is just Rydberg's formula (2.8), which correctly describes the emission line spectra of the Hydrogen atom. In a similar way, a photon can be absorbed if its energy can be given to the electron to jump between two orbits, and thus also absorption lines are discrete and are given by (4.8).

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Ionisation energy

Extracting an electron from an atom (ionisation) corresponds formally to transfer the electron to an orbit with $n = \infty$ (because then $r = \infty$). In that case, the photon energy need not be discrete because excess energy is transformed into kinetic energy of the electron. The ionisation energy is the energy to extract the electron from its ground state $n = 1$. This is given by setting $n_2 = \infty, n_1 = 1$ in (4.8):

$$E_{ionisation} = h\ c\ \mathcal{R} \approx 13.6\,\mathrm{eV} \tag{4.9}$$

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5 The wave function and Schrödinger equation
- Heuristic derivation of Schrödinger equation
- Time-independent Schrödinger equation
- Interpretation of the wave function
- Summary: Schrödinger equation

6 Quantum mechanics of some simple systems

The wave function (See also Blinder, Chap. 2.3–2.5)

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This is called the wavefunction ($\Psi(\mathbf{r}, t)$), which is a function of space $\mathbf{r}$ and time t, and is the analogue of the electric field amplitude $\mathbf{E}$ for photons.
We now want to learn how this object evolves in time. This is given by the famous Schrödinger equation.

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Heuristic derivation of Schrödinger equation

Electromagnetic plane waves

An electromagnetic wave (and in fact any elastic wave) is described by the form (Ψ plays the role of E):

$$\Psi(x,t) = \cos(kx - \omega t) = \mathrm{Re}\ e^{i(kx-\omega t)} \tag{5.1}$$

more info: (for simplicity we have taken the one-dimensional case). We will drop the Re from now on. Here,

$$k = \frac{2\pi}{\lambda}, \qquad \omega = 2\pi\nu \tag{5.2}$$

We now see that (5.1) obeys the wave equation

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i. e. the differential operators can be replaced by multiplicative factors

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but careful, it holds only for the form (5.1)!

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Introducing the Planck (2.6) and de Broglie (3.10) relations in (5.5), we observe that

$$\boxed{p = \frac{h}{\lambda} = \hbar\ k = -i\hbar\frac{\partial}{\partial x} \qquad\qquad E = \hbar\omega = i\hbar\frac{\partial}{\partial t}} \tag{5.7}$$

i. e. energy and momentum become differential operators acting on the wavefunction Ψ

Wave equation for free particles

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Let us try to find the corresponding "wave" equation for "slower" (i.e. nonrelativistic) particles. For this we use the energy-momentum relation

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See here for three dimensions:

Time-independent Schrödinger equation

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We look for solutions of (5.12) in the form

$$\Psi(\mathbf{r}, t) = \exp(-i\frac{\tilde{E}\ t}{\hbar})\ \psi(\mathbf{r}) \qquad (5.13)$$

with some constant $\tilde{E}$.

Time-independent Schrödinger equation

We look for solutions of (5.12) in the form

$$\Psi(\mathbf{r}, t) = \exp(-i\frac{\tilde{E}\ t}{\hbar})\ \psi(\mathbf{r}) \tag{5.13}$$

Let's now try to understand what $\tilde{E}$ is.
For this purpose we apply the energy operator $i\hbar\frac{\partial}{\partial t}$:

$$i\hbar\frac{\partial}{\partial t}\Psi = \tilde{E}\Psi \tag{5.14}$$

comparing with the second of (5.7), we see that
we can identify $\tilde{E}$ with the energy E itself.

Time-independent Schrödinger equation

$$\Psi(\mathbf{r},t) = \exp(-i\frac{E\ t}{\hbar})\ \psi(\mathbf{r}) \tag{5.13}$$

$$i\hbar\frac{\partial}{\partial t}\Psi = E\Psi \tag{5.14}$$

Using (5.14) in (5.12) and dividing both sides by $\exp(-i\frac{E\ t}{\hbar})$ we obtain the

time-independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{5.15}$$

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$$\boxed{\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})} \tag{5.15}$$

This is the equation for a wave function of a particle with a fixed value of the energy.
It is one of the most important equations in quantum mechanics and is used, e.g., to find atomic orbitals.

Time-independent Schrödinger equation

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$$\underbrace{\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r})\right)}_{\hat{H}}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{5.15}$$

The differential operator acting on the wavefunction is called **Hamilton operator** (or Hamiltonian). It describes the energy.

Schrödinger equation: summary of ideas

These results suggest some ideas that we are going to meet again later

Physical quantities (observables), are replaced by **differential operators**. Here we had the case of energy E and momentum $\mathbf{p}$:

$$E \to i\hbar\frac{\partial}{\partial t} = \hat{H} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r})$$
$$\mathbf{p} \to -i\hbar\boldsymbol{\nabla} \tag{5.16}$$

- (5.15) has the form of an eigenvalue equation similar to the one we encounter in linear algebra.
- The similarity is seen if we interpret $\hat{H}$ as a matrix, and $\psi(\mathbf{r})$ as a vector

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The similarity is seen if we interpret $\hat{H}$ as a matrix, and $\psi(\mathbf{r})$ as a vector.

- Indeed, the wave function $\psi(\mathbf{r})$ can be seen as a vector in an *infinite dimensional* vector space. This will be explained later

Interpretation of the wave function

Interpretation of the wave function

Analogy with electromagnetic waves:
$|E(\mathbf{r})|^2$ is proportional to the intensity, i. e. the photon density.

- $|\psi(\mathbf{r})|^2$ is the probability density of finding a particle in $\mathbf{r}$.
- probability density | what's this?
  given a small (infinitesimal) volume ΔV centered around $\mathbf{r}$,
  $p(\mathbf{r})$ is the "Probability divided by ΔV" of finding the particle in this volume.

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Normalisation

examples:

Proportional ($\propto$) means that $|\psi(\mathbf{r})|^2 = A\ \rho(\mathbf{r})$, with A some constant.

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- A can be determined by requiring that the total probability be 1, i.e. be normalized:

$$\int \rho(\mathbf{r})\, dV = 1 \qquad (5.19)$$

- Alternatively, one can use a normalized wavefunction

$$\psi_N(\mathbf{r}) = \frac{1}{\sqrt{A}}\psi(\mathbf{r}) \qquad (5.20)$$

- for which one directly gets the probability density

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Multiplying ψ by a constant

In general, two wave functions ($\psi'(\mathbf{r}) = \kappa\ \psi(\mathbf{r})$) differing by a constant κ ($\kappa \neq 0$, even a complex one), describe the same physical state.

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Insertion: functions as vectors

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Summary: Schrödinger equation

Summary of important results

The dynamics of a quantum mechanical particle is described by the Wavefunction $\Psi(\mathbf{r}, t)$

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Two wave functions differing by a (even complex) constant describe the same physical state.

- For this wave function

$$p(\mathbf{r}) = |\psi_M(\mathbf{r})|^2 \tag{5.25}$$

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Therefore, it is often convenient to choose a normalized wave function for which

$$\int |\psi_N(\mathbf{r})|^2 \, dV = 1 \tag{5.24}$$

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1 Introduction: atoms and electromagnetic waves

2 Failures of classical physics

3 Wave and Particle duality

4 Bohr's atom

5 The wave function and Schrödinger equation

6 Quantum mechanics of some simple systems
- Free particle
- Particle in a box
- Generalisations of the particle in a box
- Tunnel effect

Free particle

Free particle (See also Blinder, Chap. 3, Chap. 5.1)

We consider (5.15) for a constant potential V
((a) For the moment we could as well take $V = 0$.
(b) For simplicity we restrict to one spatial dimension.)

$$\hat{H}\,\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\,\psi(x) + V\,\psi(x) = E\,\psi(x) \qquad (6.1)$$

- This can be written in the form

$$\psi''(x) + k^2\psi(x) = 0 \quad \text{with } k^2 = \frac{2m(E-V)}{\hbar^2} \qquad (6.2)$$

- For $k^2 > 0$ we have the two linearly independent solutions

$$\psi(x) = \text{const.}\, e^{\pm i\,k\,x} \qquad (6.3)$$

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$$p\ \psi(x) = -i\hbar\frac{d}{dx}\psi(x) = \pm\hbar k\ \psi(x) \tag{6.4}$$

Free particle

Due to (6.1), the two solutions $e^{\pm i\ k\ x}$ are eigenfunctions of the Hamilton operator $\hat{H}$ with eigenvalue E and due to (6.4) they are also eigenfunctions of the momentum operator $p = -i\hbar\boldsymbol{\nabla}$ with eigenvalue $\pm\hbar k$
In quantum mechanics language we say that they have a well defined energy and momentum.
The relation between energy and momentum is correct, as
$E = \frac{\hbar^2\ k^2}{2m} + V = \frac{p^2}{2m} + V$. more details:

Particle in a box

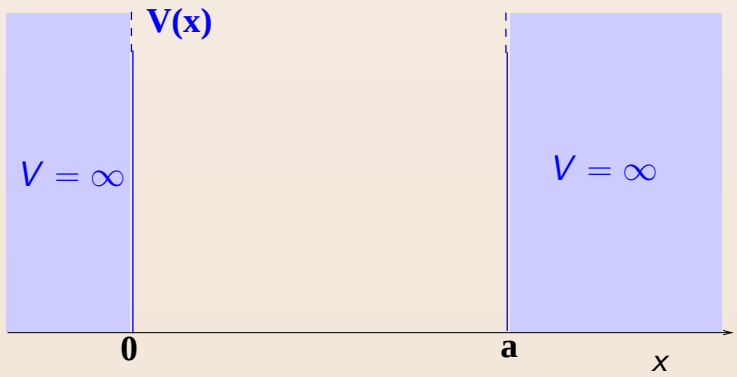
Particle in a box

The simplest quantum-mechanical problem with a non-constant potential is the so-called "Particle in a box". It describes a particle confined in a finite region.
This is achieved by taking the potential
(here we treat the one-dimensional case):

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(here we treat the one-dimensional case):

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ \infty & \text{for } x < 0 \text{ and } x > a \end{cases} \tag{6.5}$$



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$$\psi(x \to 0^+) = \psi(x \to a^-) = 0 \tag{6.6}$$

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Here comes an important result of quantum mechanics:
linear combinations of degenerate solutions are also solutions of (5.15) with the same energy. See here for details:

Particle in a box

examples:

We thus look for a suitable linear combination

$$\psi(x) = a\ e^{i\ k\ x} + b\ e^{-i\ k\ x} \tag{6.7}$$

such that $\psi(x)$ vanishes at $x = 0$.

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This is clearly the case when $a = -b$.
By taking, e. g. $a = -b = \frac{1}{2i}$ (remember, a constant factor does not change the physics), we recognise

$$\psi(x) = \sin kx \tag{6.8}$$

which is indeed a solution of (5.15) with $V = 0$ and $E = \frac{\hbar^2 k^2}{2m}$,
i. e. valid in $0 < x < a$, and vanishing at $x = 0$.

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We need to enforce the second condition, namely that $\psi(x \to a) = 0$. This gives:

$$\sin ka = 0 \tag{6.9}$$

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From trigonometry we know that this is fulfilled if ka is an integer multiple of π.
Since a is fixed, this amounts to a condition for k:

$$k = \frac{n\ \pi}{a} \quad \text{with } n = 1, 2, 3, \ldots \tag{6.10}$$

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the energy:

$$E = \frac{\hbar^2\ k^2}{2m} = \frac{\hbar^2 (n\pi)^2}{2m\ a^2} \equiv E_n \tag{6.11}$$

I. e., only discrete values of the energy are allowed. This is called energy quantisation. Allowed energies are labeled by the integer n, which is the so-called quantum number.

Uncertainty

Notice that the state with lowest energy, the ground state does not have zero energy as classically expected, but has a finite energy $E_1 = \frac{\hbar^2 \pi^2}{2m\ a^2}$. This is the so-called zero point energy.

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This comes from the fact, that a particle confined in a finite region of size $\Delta x = a$ has a nonzero kinetic energy $\Delta E \sim \Delta p^2/(2m)$, associated with a nonzero momentum Δp.

Identifying ΔE with E_1, we have

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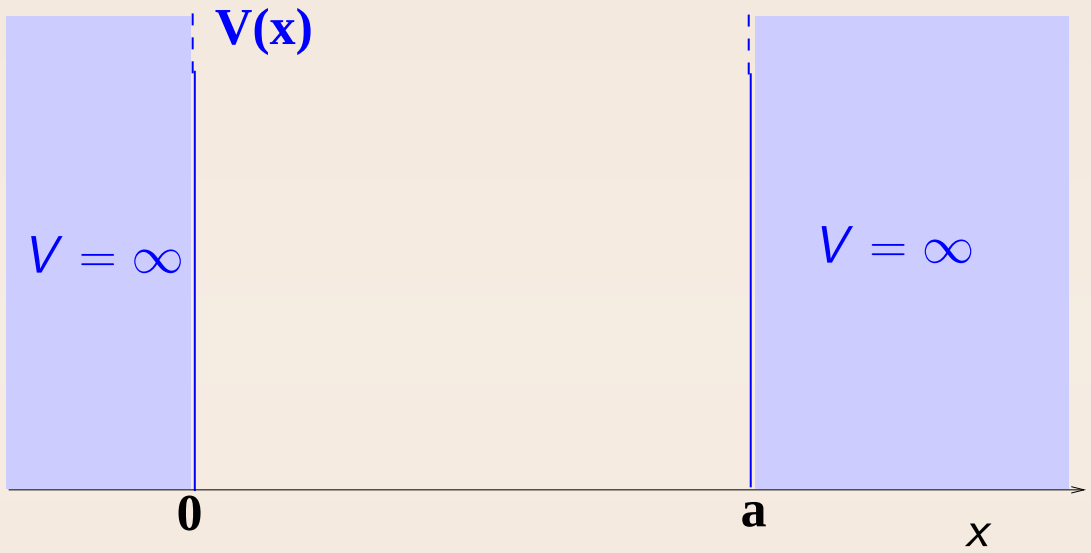
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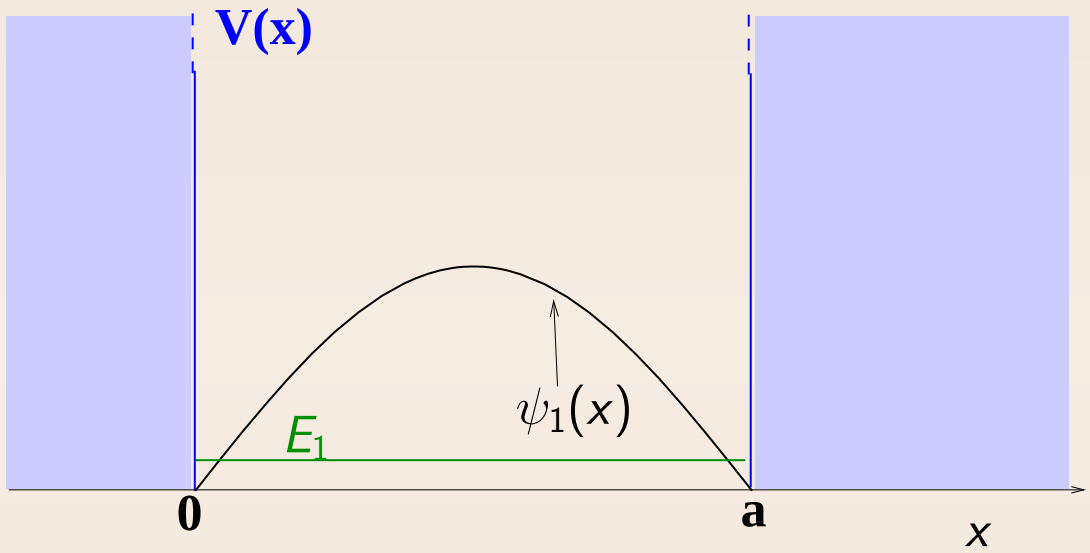
Summary: particle in a box



Summarizing, wavefunctions and corresponding energies:

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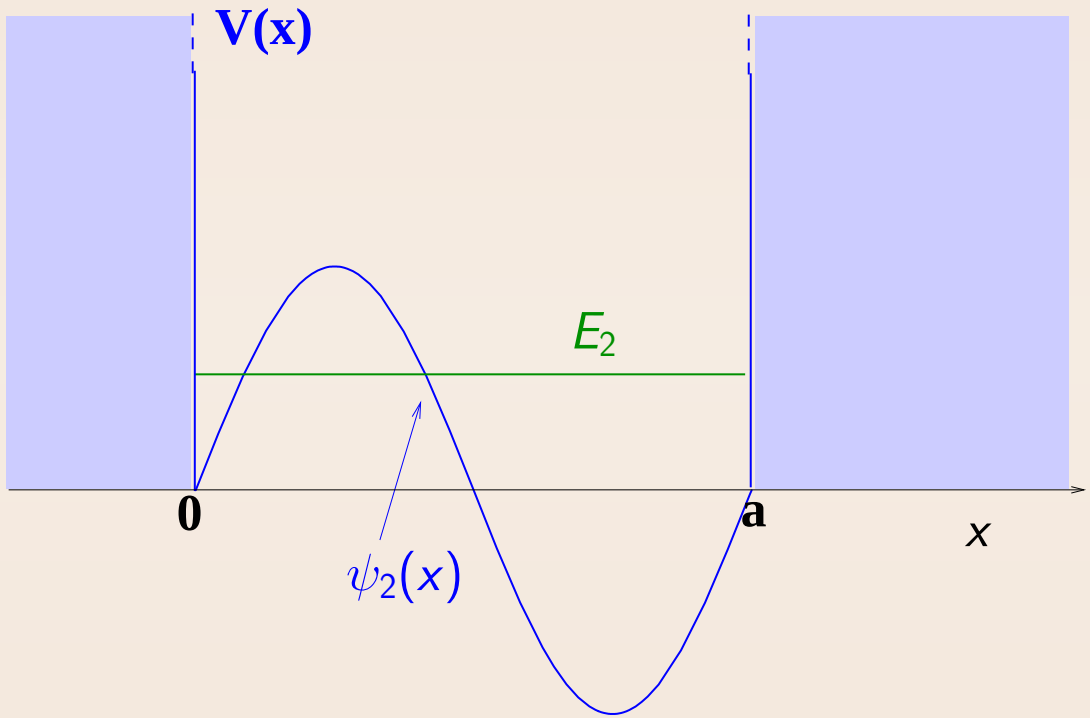
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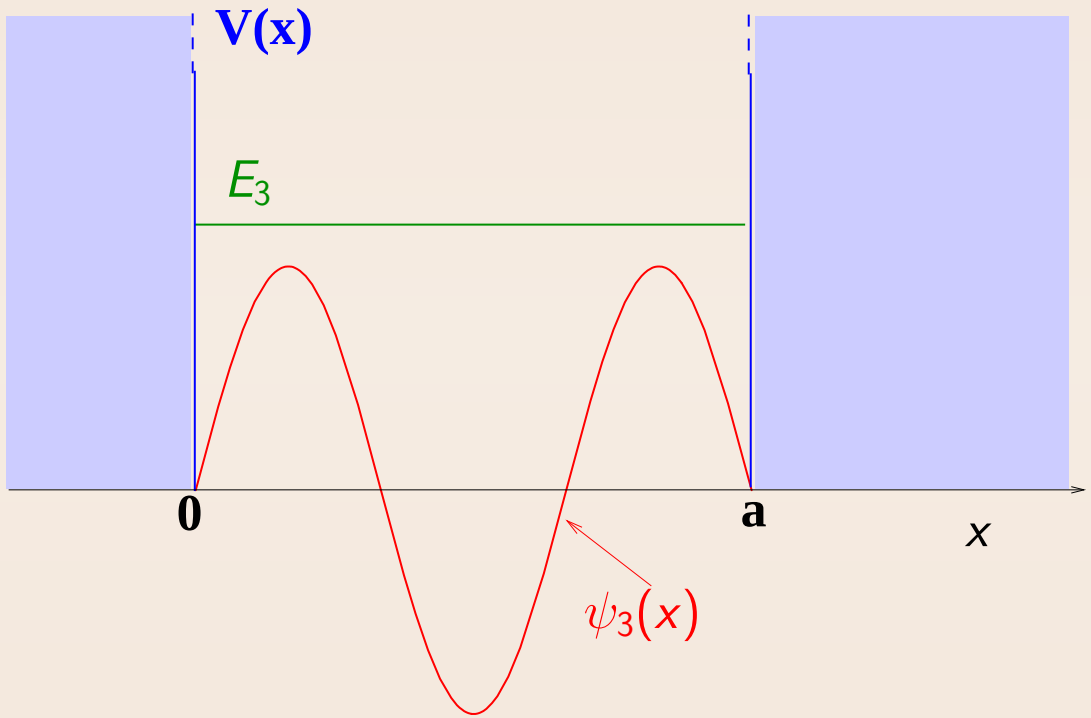
Summary: particle in a box



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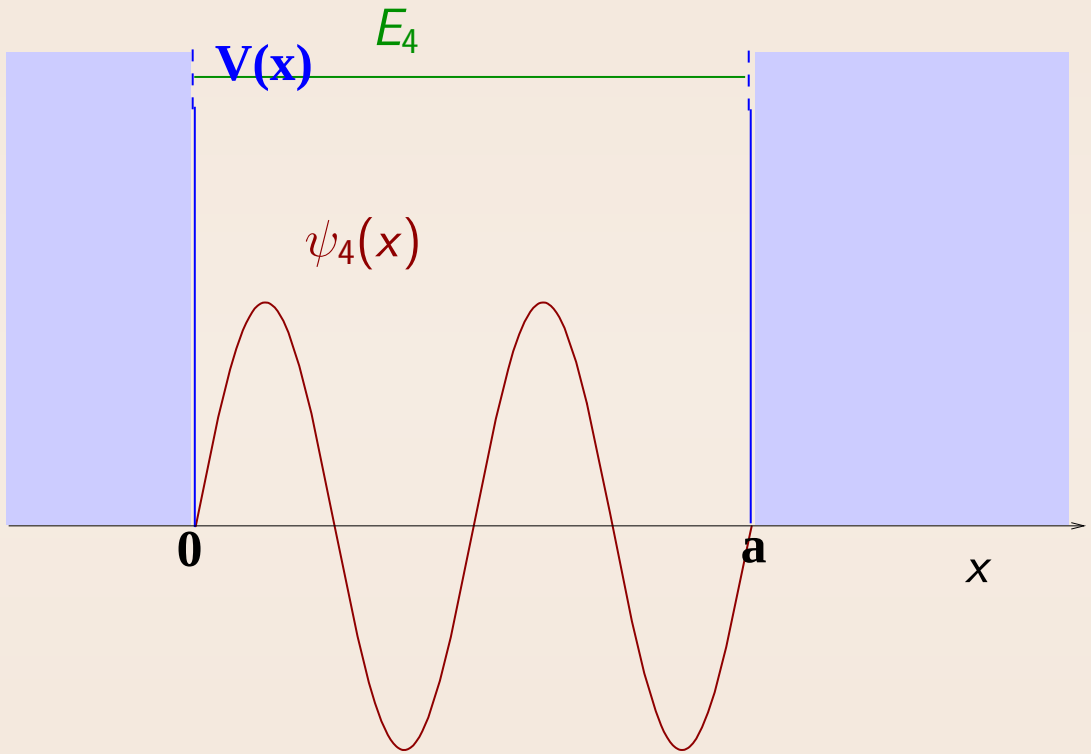
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Energy quantisation:

This particular example teaches us some important general results of quantum mechanics:

- The wavefunction of a particle confined in a finite region (so-called bound state) has only a discrete set of possible energies.
- The quantum number n gives the number of nodes of the wavefunction plus one.
- The ground state wavefunction ($n = 1$) has no nodes, the first excited state has one node, the second two, and so on.
- Two wavefunctions with different energies are orthogonal, i. e. their scalar product (see (13.4)) is zero:

$$\int_0^a \sin\frac{n\pi x}{a} \sin\frac{m\pi x}{a}\, dx = 0 \quad \text{For } n \neq m \tag{6.14}$$

Energy quantisation:

This particular example teaches us some important general results of quantum mechanics:

The wavefunction of a particle confined in a finite region (so-called bound state) has only a discrete set of possible energies.
(On the contrary, if the wavefunction is not confined, like for the free particle in Sec. 6.1, the allowed energies form a continuum.
Important examples in the real world are the energy levels of electrons in an atomic potential.)

- The minimum energy is always larger than the minimum value of the potential.
  The difference is called zero point energy.
- The ground state wavefunction has no nodes, the first excited state has one node, the second two, and so on.
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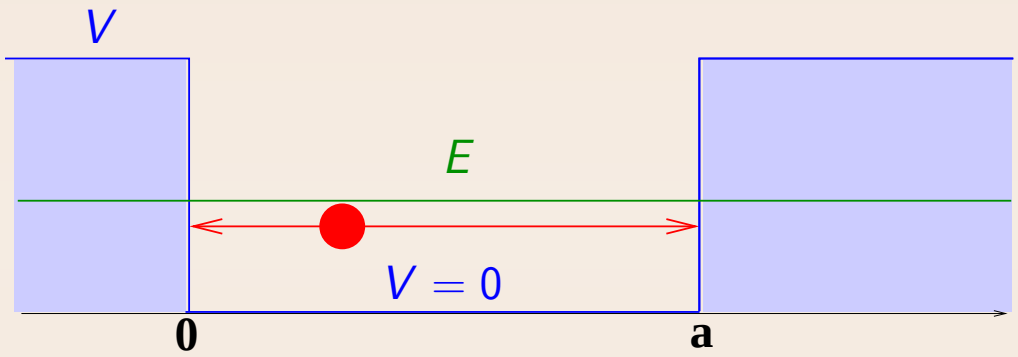
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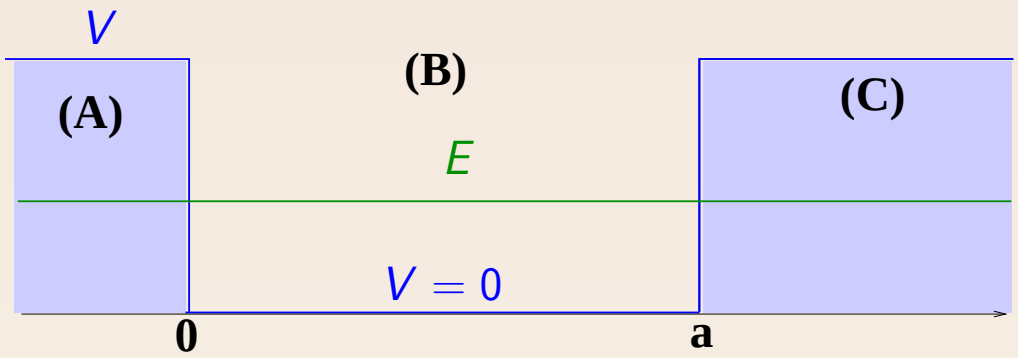
Generalisations of the particle in a box

Finite potential $V \neq \infty$, $E < V$



Classically, we expect the particle to remain confined in the "box"

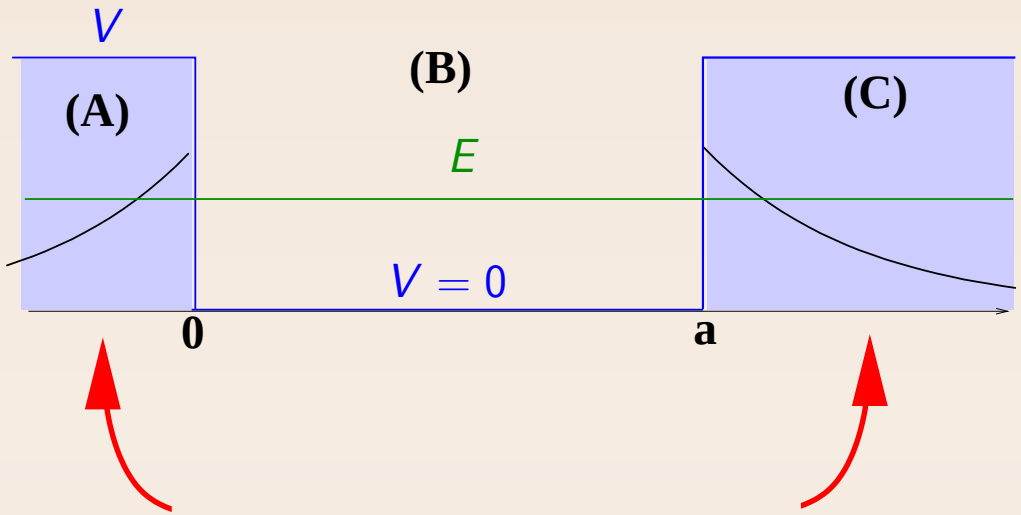
Finite potential $V \neq \infty$, $E < V$



We have to solve (6.2) separately in the three regions A,B,C:

$$\psi''(x) + k^2\psi(x) = 0 \quad \text{with } k^2 \equiv \frac{2m(E-V)}{\hbar^2} \tag{6.15}$$

Finite potential $V \neq \infty$, $E < V$



$$\psi''(x) + k^2\psi(x) = 0 \quad \text{with } k^2 \equiv \frac{2m(E-V)}{\hbar^2} \tag{6.15}$$

A+C $0 > k^2 = -q^2$.

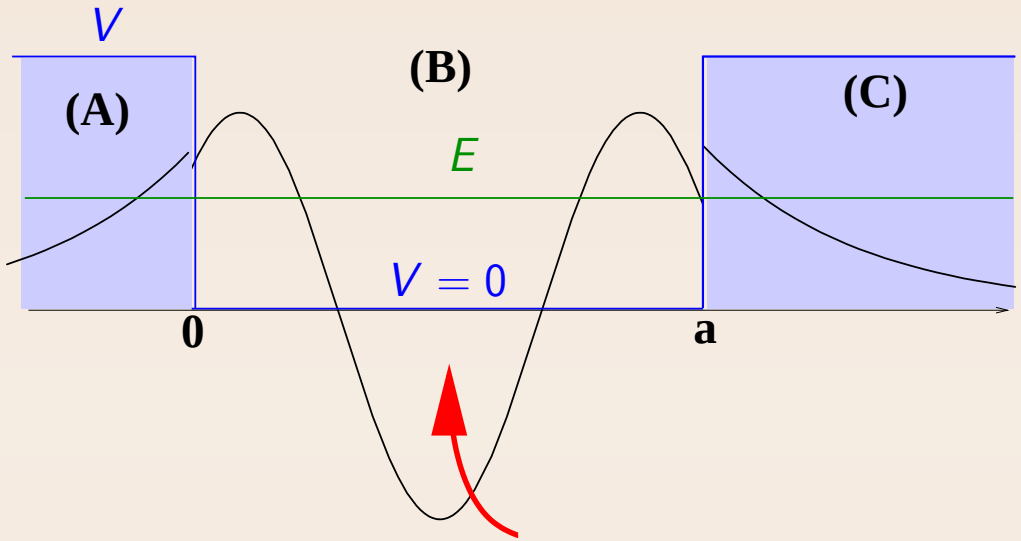
Solution in (C): $\boxed{\psi(x) = C' \ \exp(-q\ x)}$, $(q > 0)$, in (A): $\propto \exp(q\ x)$.

The wave function does not vanish in the "classically forbidden" region

there is a nonzero probability to find the particle there

exponential decay

Finite potential $V \neq \infty$, $E < V$



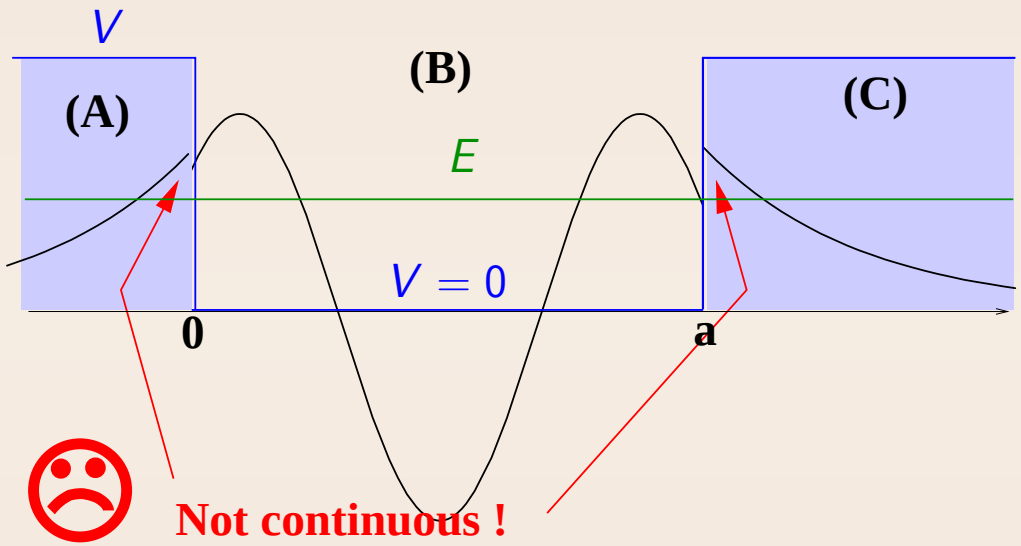
$$\psi''(x) + k^2\psi(x) = 0 \quad \text{with } k^2 \equiv \frac{2m(E-V)}{\hbar^2} \tag{6.15}$$

B $k^2 > 0$, oscillating solution as in (6.7).

Linear combination of two degenerate solutions:

$$A' \cos kx + B' \sin kx \tag{6.16}$$

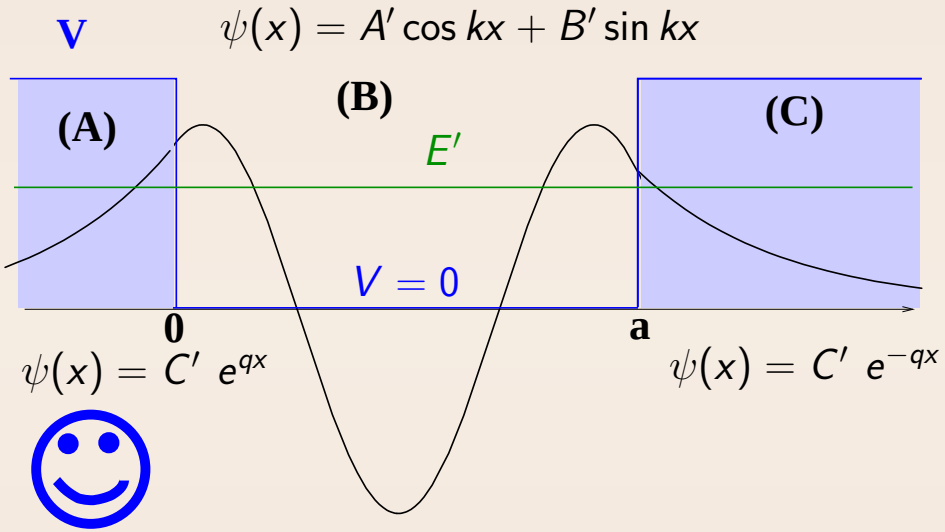
Finite potential $V \neq \infty$, $E < V$



$$\psi''(x) + k^2\psi(x) = 0 \quad \text{with } k^2 \equiv \frac{2m(E-V)}{\hbar^2} \tag{6.15}$$

However: The wave function must be continuous and differentiable!
What can we do?

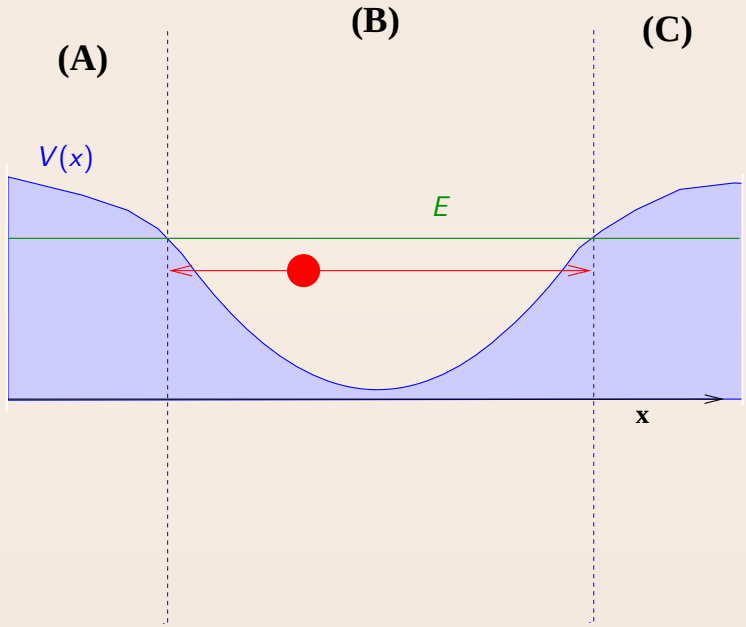
Finite potential V



This can be achieved by suitably adjusting the parameters A', B', C', but most importantly the energy E.
This results in only a discrete set of energies to be allowed:
energy quantisation

Arbitrary potential

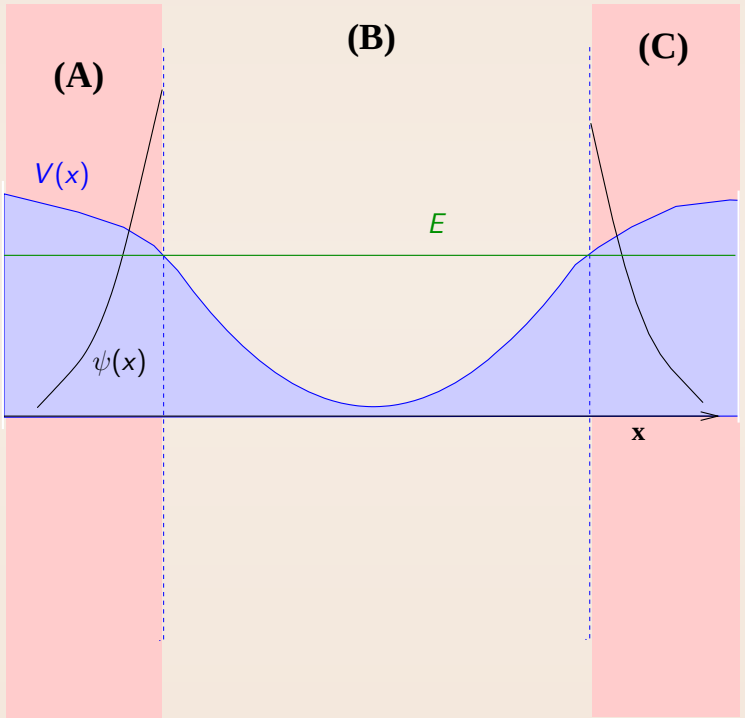
For example: harmonic oscillator



Again: the particle is classically confined in region (B)

Arbitrary potential

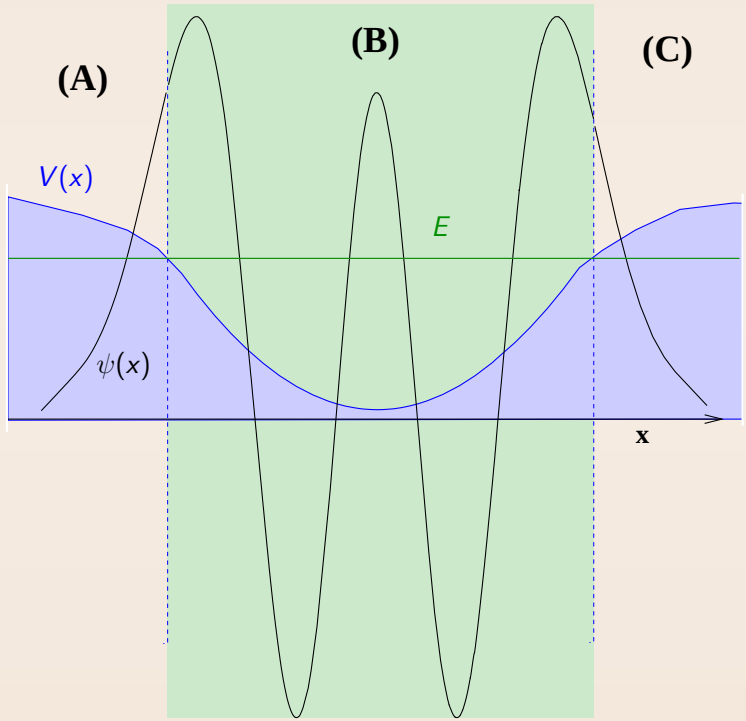
For example: harmonic oscillator



"Forbidden" region (A+C): exponential decay of $\psi(x)$

Arbitrary potential

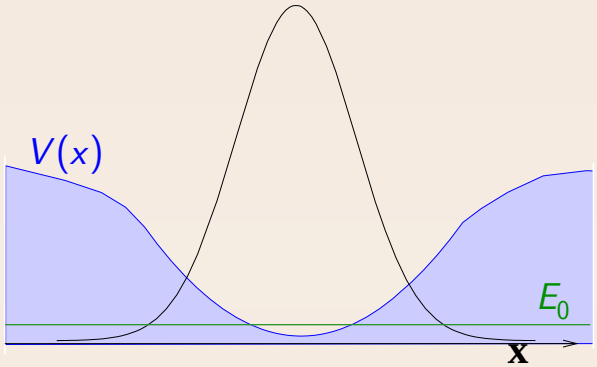
For example: harmonic oscillator



"Allowed" region (B): oscillating behavior of $\psi(x)$

Ground state and excited states

For example: harmonic oscillator



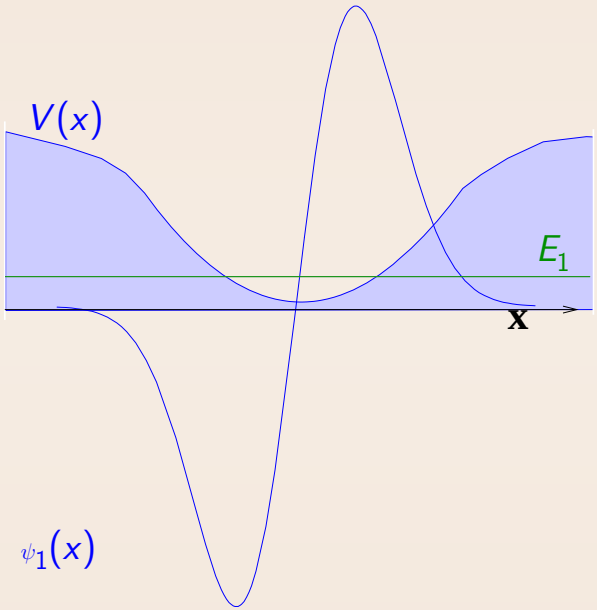
$\psi_0(x)$

State with lowest energy: ground state

no nodes

Ground state and excited states

For example: harmonic oscillator



Excited states

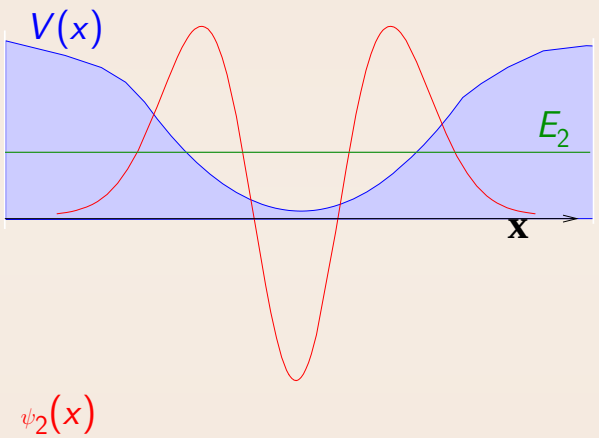
increasing number of nodes

due to orthogonality of different wavefunctions:

$$\langle \psi_n | \psi_m \rangle \equiv \int \psi_n(x)^* \psi_m(x)\, d\, x = 0 \quad (n \neq m) \qquad (6.17)$$

Ground state and excited states

For example: harmonic oscillator

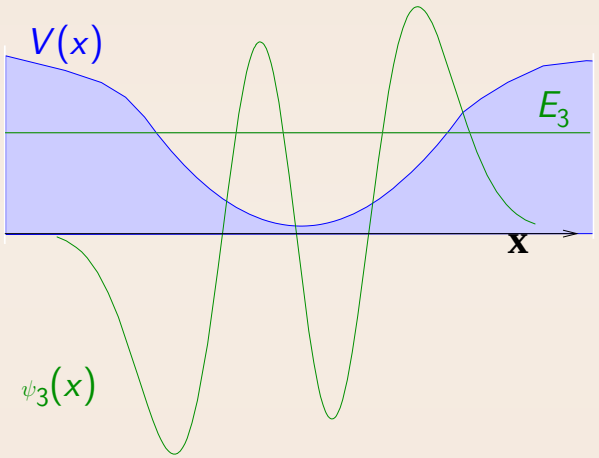


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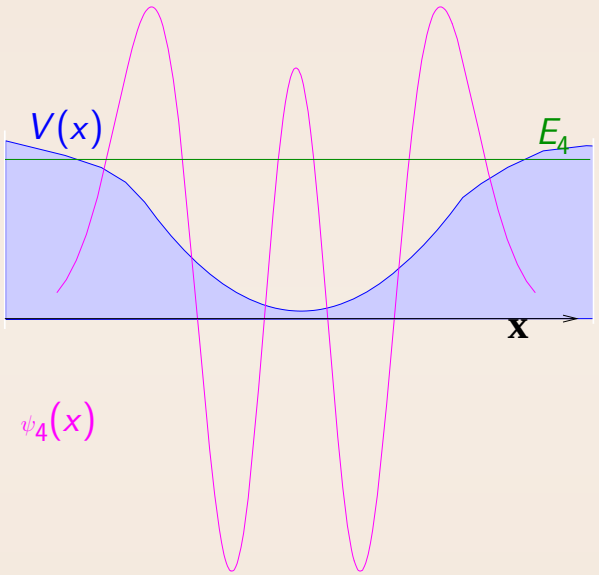


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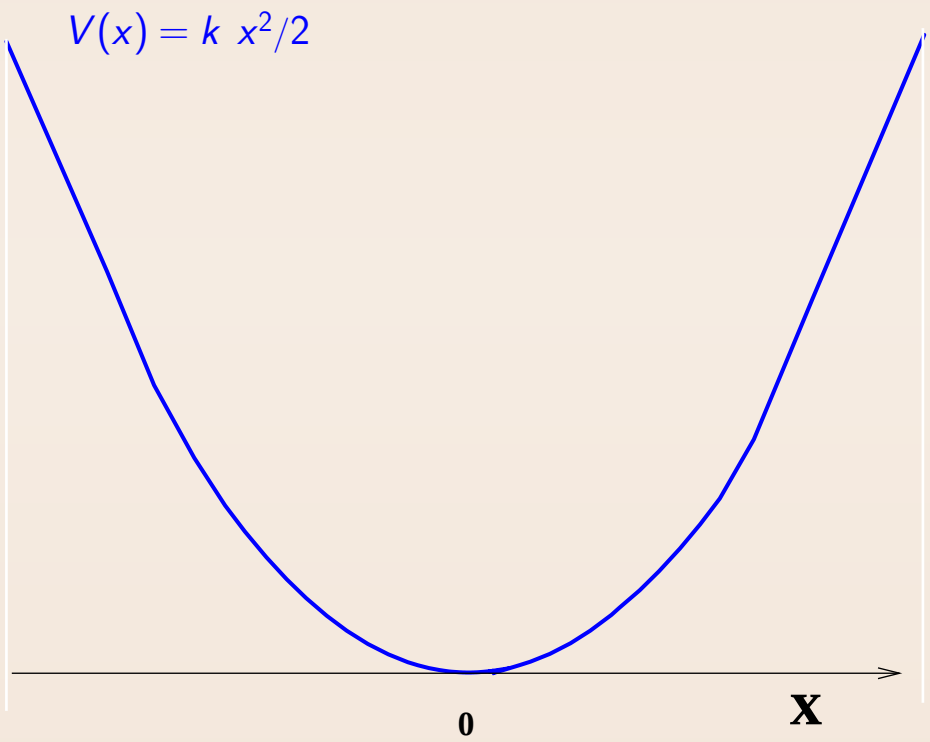


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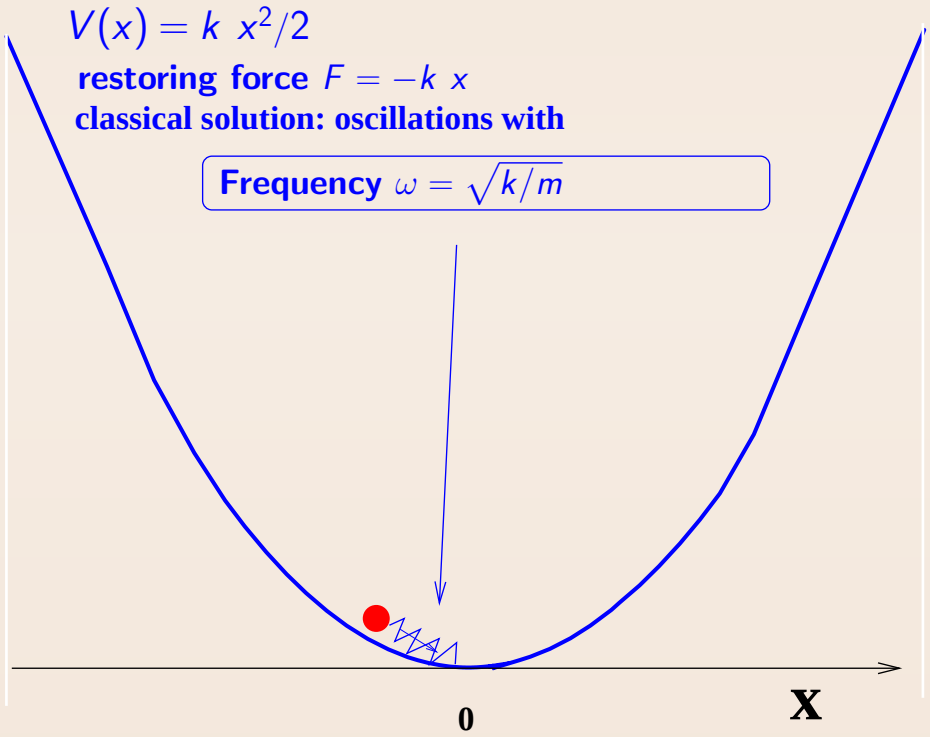
Harmonic oscillator

Why is it so interesting



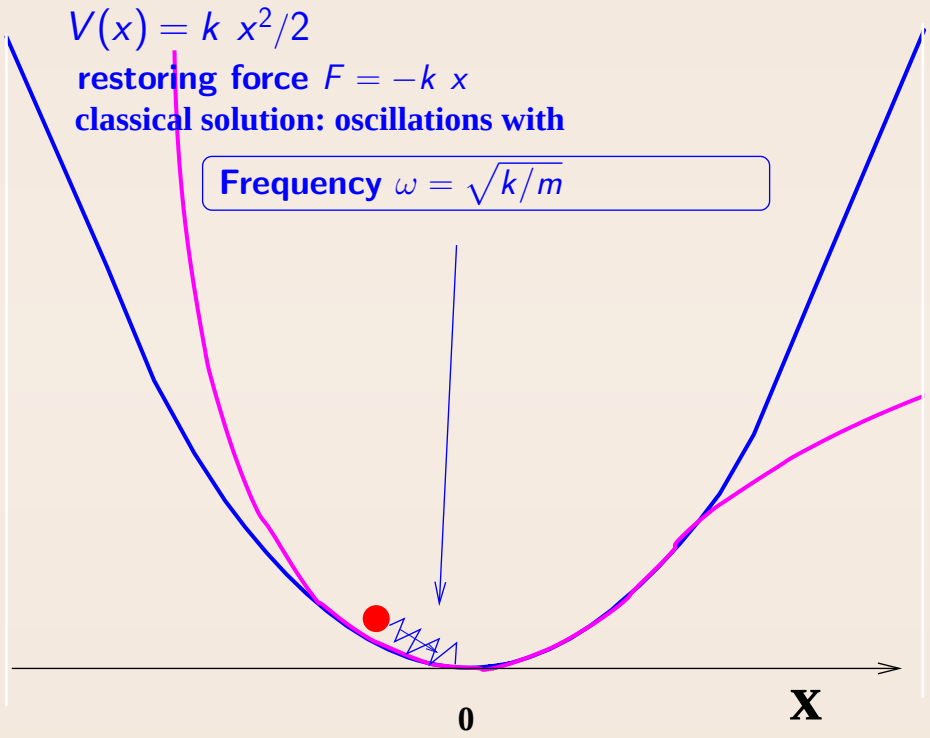
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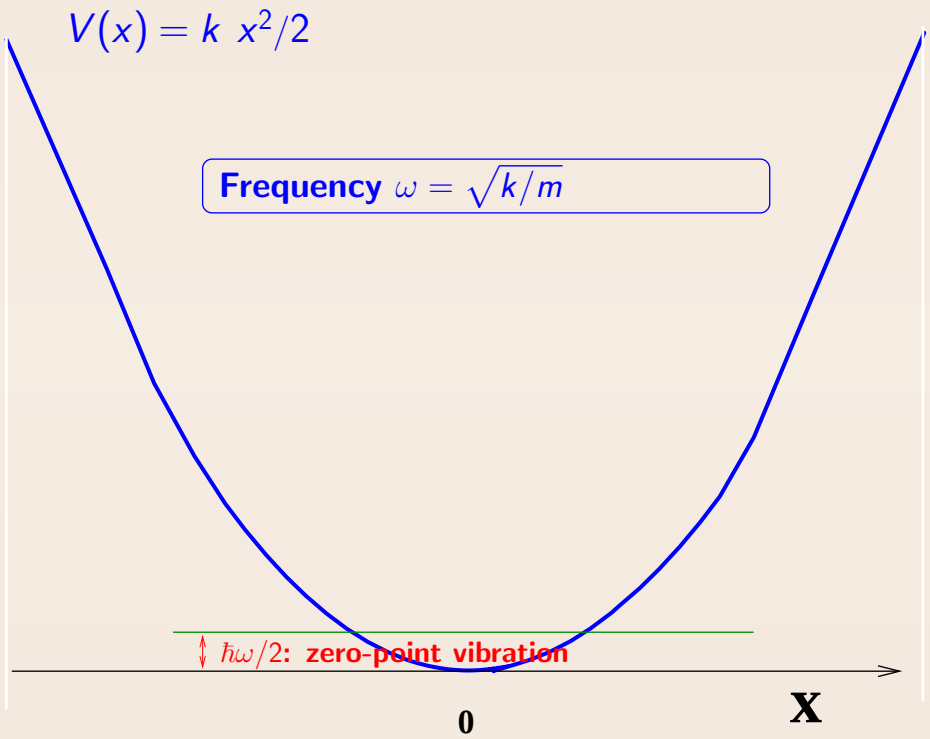


Is it a too special model?

No!: it is a good approximation for the dynamics of a particle near the minimum of a generic potential

Harmonic oscillator

Why is it so interesting

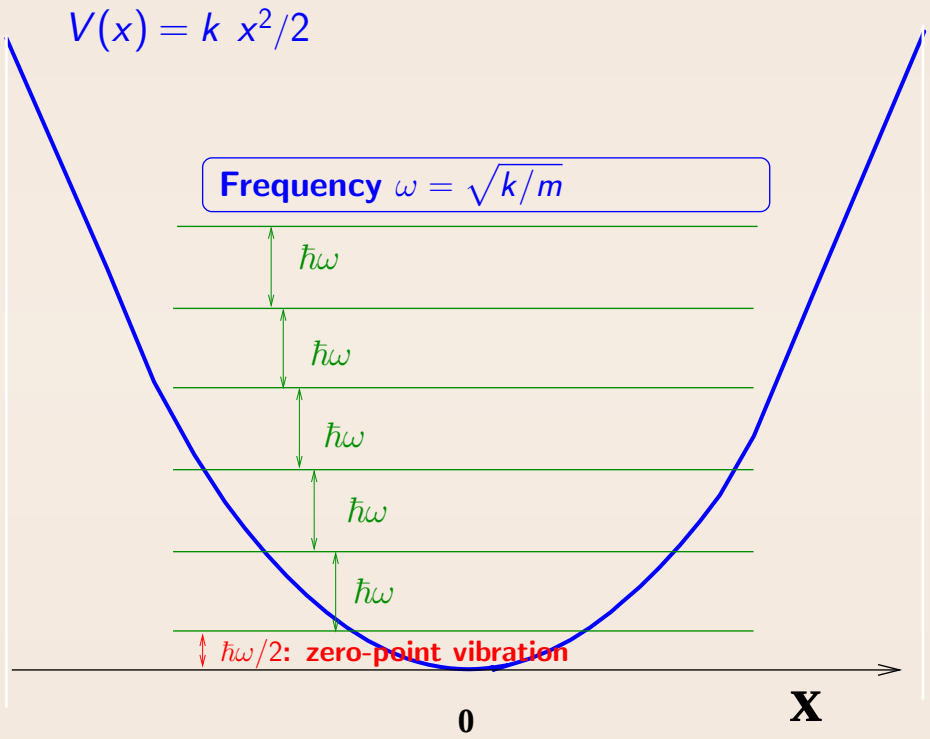


Advantage: The solution of Schrödinger equation is relatively simple:
(Even for a large number of coupled oscillators: see Phonons)

(1) Ground state energy $E_0 = \hbar\omega/2$: zero-point vibration

Harmonic oscillator

Why is it so interesting



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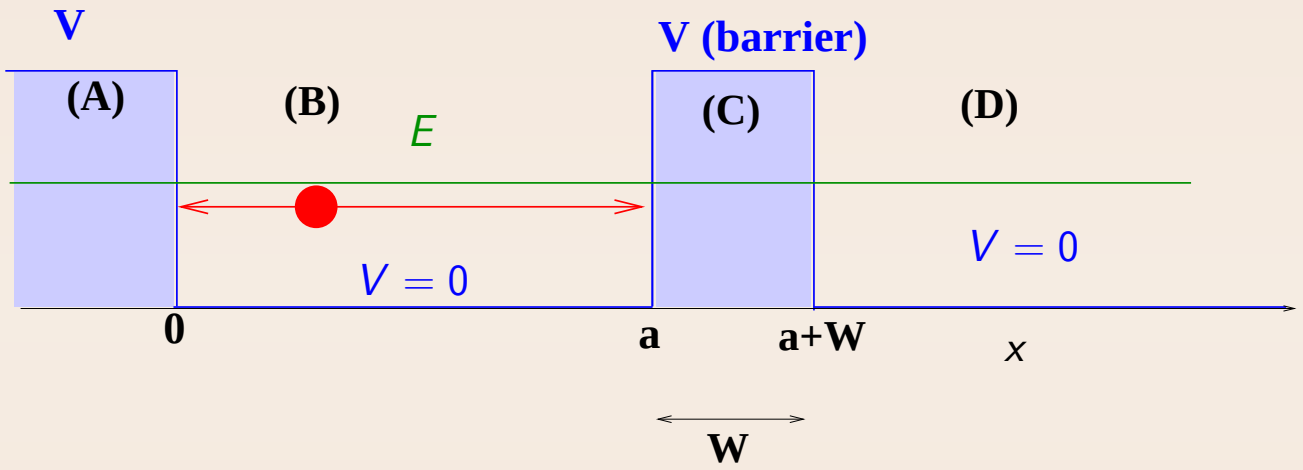
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(3) Eigenfunctions

Tunnel effect

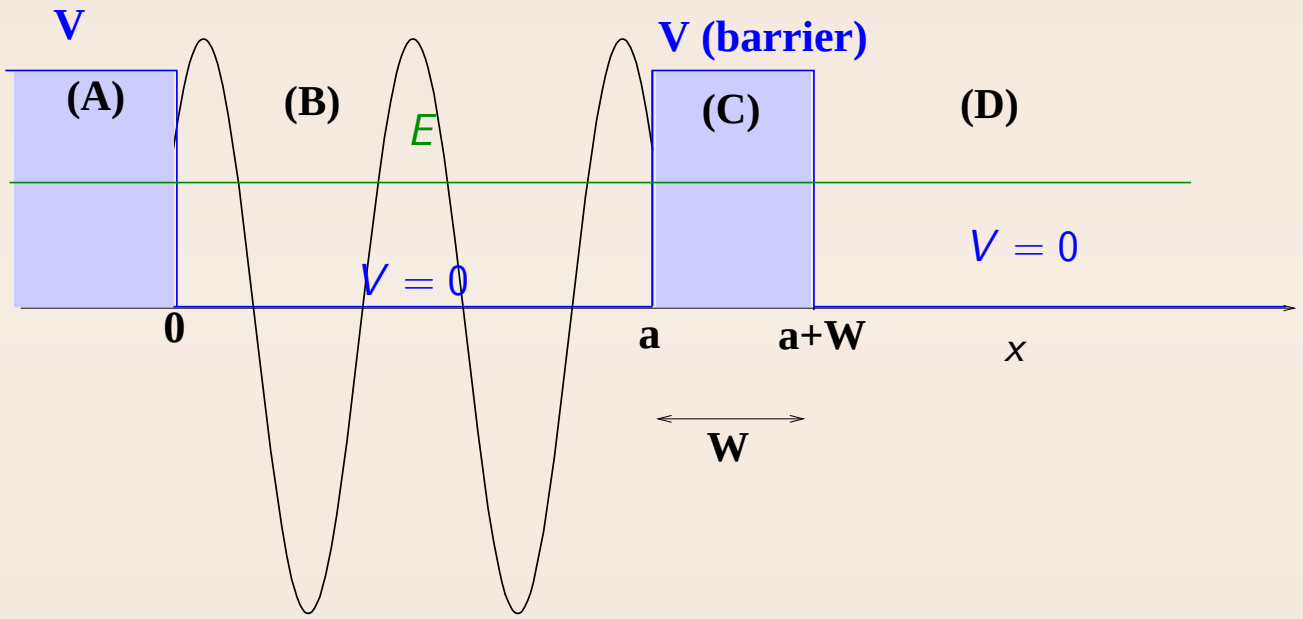
Tunneling



Classical particle would stay confined in region (B)

Quantum result:

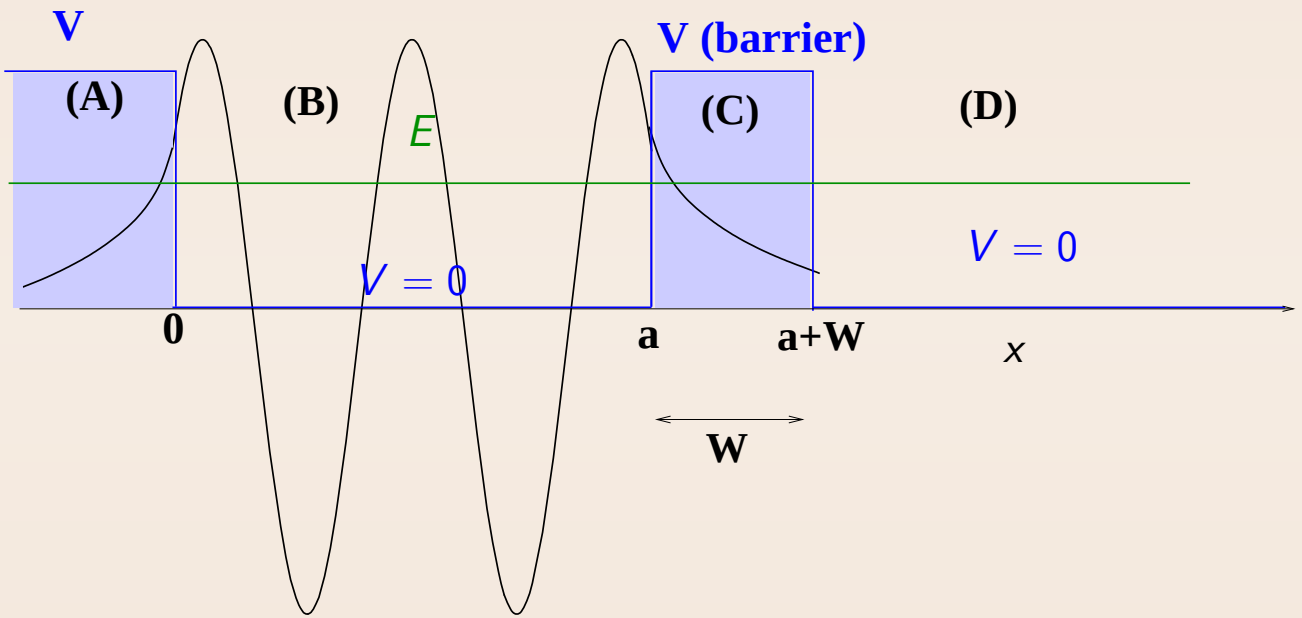
Tunneling



Quantum result:

Region B: oscillating behavior

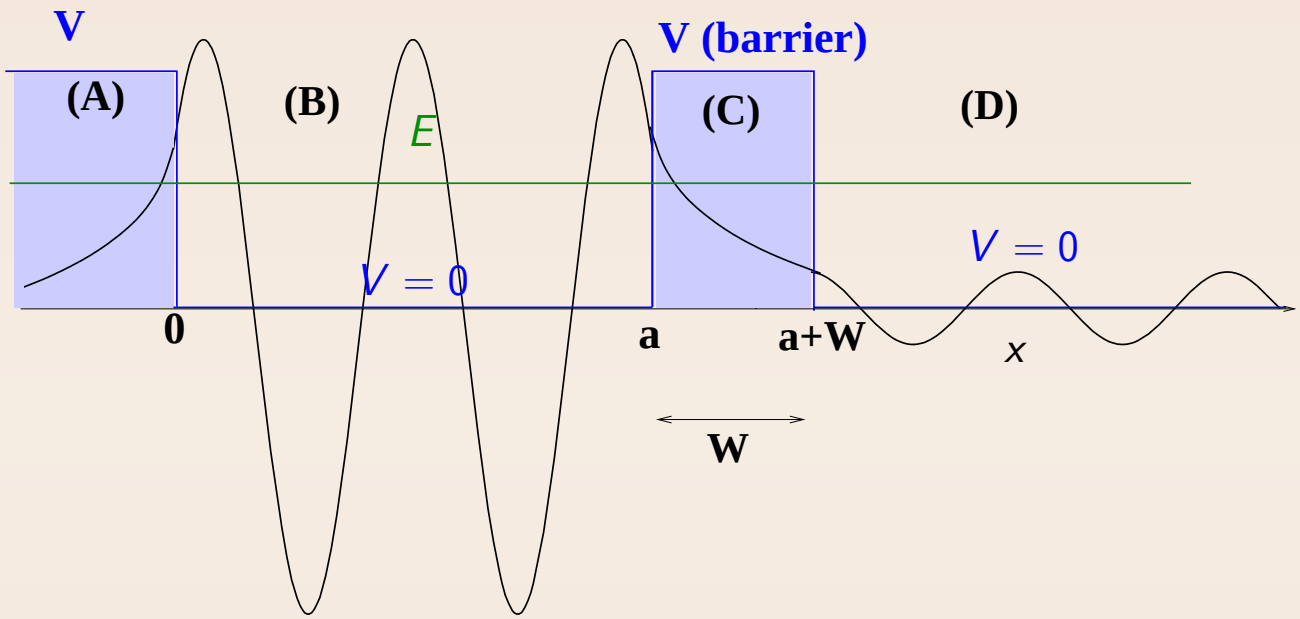
Tunneling



Quantum result:

(C): Exponential decay across the barrier

Tunneling



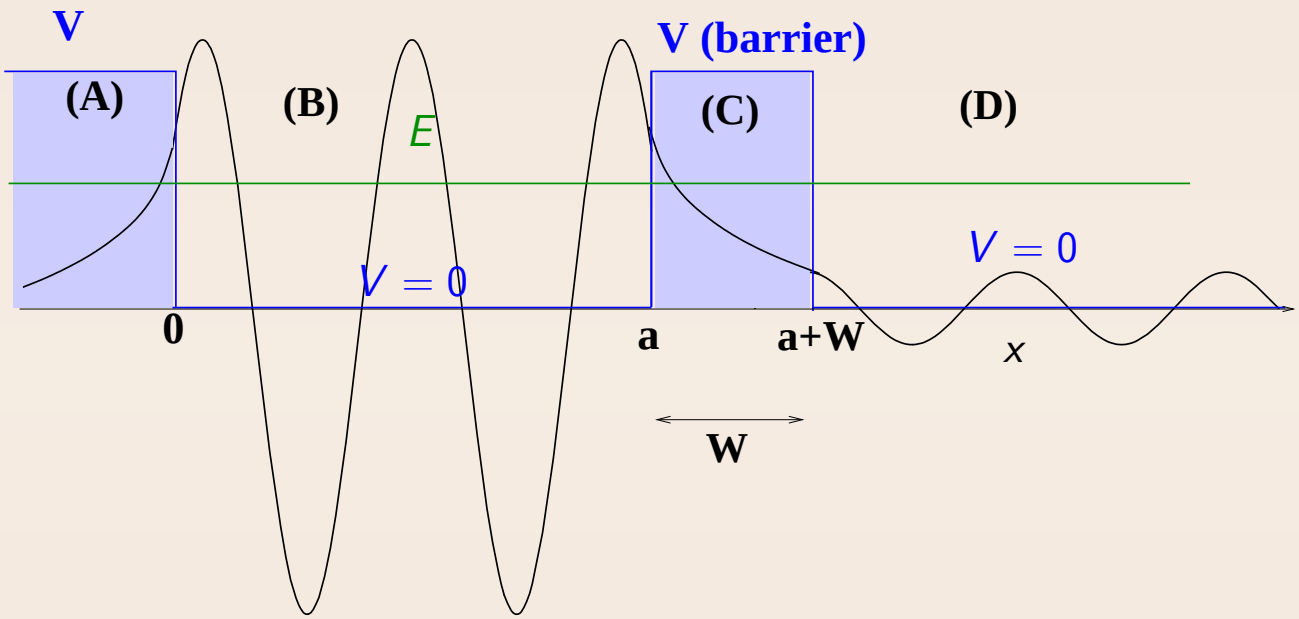
Quantum result:

(D): Again oscillating behavior, amplitude reduced by a factor

$$e^{-q\ W} = e^{-\sqrt{\frac{2m(V-E)}{\hbar^2}}W} \tag{6.18}$$

The particle tunnels through the barrier although its kinetic energy is smaller than the barrier height!

Tunneling



Quantum result:

The tunneling rate is proportional to $\left|e^{-\sqrt{\frac{2m(V-E)}{\hbar^2}}W}\right|^2$

Becomes exponentially small for increasing barrier width W, "depth" $V - E$, and mass m of the particle.

1 Introduction: atoms and electromagnetic waves

2 Failures of classical physics

3 Wave and Particle duality

4 Bohr's atom

5 The wave function and Schrödinger equation

6 Quantum mechanics of some simple systems

7 Principles and Postulates of Quantum mechanics
- Postulates of Quantum Mechanics

8 Angular momentum and electron spin

Principles and Postulates of Quantum mechanics

(See also Blinder, Chap 4.1-4.6)

Postulates of Quantum Mechanics

- The "postulates" of quantum mechanics consist in part of a summary and a formal generalisation of the ideas which we have met up to now, in the course of the years they have been put together in order to understand the meaning and to provide a description for the puzzling physical results that had been observed.
- Here, we will present these postulates together with practical examples. In these examples you will find again most of the concept introduced in the previous chapters.

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Postulate I: Wavefunction

- The state of a system (here one particle) is completely defined by a complex wavefunction, $\Psi(\mathbf{r}, t)$
  (or $\psi(\mathbf{r})$ if we stick to a fixed time t),
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- Any linear combination of wavefunctions is a possible physical state.
  (this is for example very interesting for quantum computers!)
- The wavefunction $\psi(\mathbf{r})$, represents a probability amplitude and is not directly observable.
  However $|\psi(\mathbf{r})|^2$ is proportional to the probability density of finding the particle around $\mathbf{r}$ which is directly observable.

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Examples

- In the previous section we have found the eigenfunctions $\psi_n(x)$ and energies E_n of the particle in a box (6.13).

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- In the previous section we have found the eigenfunctions $\psi_n(x)$ and energies E_n of the particle in a box (6.13).
- Now, the wavefunction $\psi(x)$ of a particle need not necessarily be one of the $\psi_n(x)$, but it can also be in a superposition, e. g.
  $\psi(x) = a\ \psi_1(x) + b\ \psi_2(x)$
  In that case it means that the energy is neither E_1 nor E_2: it is simply not sharply defined.
  (In quantum chemistry, a similar superposition of structures is called resonance.)

Postulate II: Observables and Operators

- Dynamical variables (so-called observables) are represented by Hermitian operators
  - Important observables and their operators:
    - Energy (Hamiltonian): $\hat{H}$
    - Angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$
- Above and from now on, we will use a "hat" to distinguish between operators and their values.

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    Further observables are obtained from compositions of these
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Postulate II: Observables and Operators

Insertion: Operators

About Operators:

Postulate III: Measurement

Observables and Eigenvalues

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- When trying to extract information from a state, one can only measure observables. (the wave function cannot be measured)
  So far, nothing special. In general, observables in classical physics have their counterpart in quantum mechanics.
- Postulate III: The only possible values that one can obtain are the eigenvalues of the operator corresponding to the observable.
- This means that not all classically allowed values of a physical quantity are allowed in quantum mechanics.
  The most striking example is the energy: as we have seen, for bound states only discrete values of the energy are allowed.

Postulate III: Measurement

Observables and Eigenvalues

The measurement postulate is certainly the most striking and still the most discussed in quantum mechanics.

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  So far, nothing special. In general, observables in classical physics have their counterpart in quantum mechanics.
- A new concept is that when measuring an observable, the only possible values that one can obtain are the eigenvalues of the operator corresponding to the observable.
- This means that not all classically allowed values of a physical quantity are allowed in quantum mechanics.
  The most striking example is the energy: as we have seen, for bound states only discrete values of the energy are allowed.

Postulate III: Measurement

Observables and Eigenvalues

The measurement postulate is certainly the most striking and still the most discussed in quantum mechanics.

- When trying to extract information from a state, one can only measure observables. (the wave function cannot be measured)
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Probability and Wave-function Collapse

Having specified what the possible outcome of a measurement is, we should also specify which outcome we expect to have for a given wavefunction $\psi(x)$.
Here comes the big problem:

- Unpredictable:
  - Possible results are statistically distributed
- The last important result is:
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- Assume one knows the wavefunction $\psi(x)$ with exact accuracy.
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Examples

- We have already met the uncertainty for the observable $\hat{x}$ (position): If we measure $\hat{x}$ on a particle with wave function $\psi(x)$, we cannot predict the result of the measurement even if we know $\psi(x)$ exactly! We merely know the probability density (see (5.17)) to find the particle around a certain x.
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If the observable is the position operator ($\hat{A} = \hat{x}$) we have already seen that (see, e. g. the examples here and here) its expectation value is

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Which can be written in a compact form (cf. (13.3)):

$$\langle \hat{A} \rangle = \frac{\langle \psi | \hat{A} \psi \rangle}{\langle \psi | \psi \rangle}$$

For a normalized ψ_N the denominator is 1, and can be omitted

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Solution: (we use $\hbar = 1$)

The normalized wavefunction is $\psi_1(x) = \sqrt{\frac{2}{a}} \sin kx$, with $k = \pi/a$.

Application of $\hat{p} = -i\frac{\partial}{\partial x}$ yields

$$-i\frac{\partial}{\partial x}\ \psi_1(x) = -ik\sqrt{\frac{2}{a}} \cos kx$$

then

$$\langle\psi_1|\hat{p}\ \psi_1\rangle = -ik\ \frac{2}{a}\int_0^a \sin kx\ \cos kx\ dx = 0$$

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this shows that ψ_1 is an eigenfunction of p^2 (but not of p!) with eigenvalue k^2.
Therefore one should expect the expectation value to be k^2, and indeed:

$$\langle \psi_1 | \hat{p}^2 \psi_1 \rangle = \frac{2}{a} k^2 \int_0^a \sin^2 kx \ dx = k^2$$

Further example: Heisenberg uncertainty:

Postulate IV: Time evolution

The wave function evolves according to the Schrödinger equation (5.22)

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = \hat{H}\ \Psi(\mathbf{r},t) \tag{7.1}$$

Important things to remember

- The state of a system is characterised by a wavefunction $\psi(x)$
  The wavefunction itself is not observable
- Physical quantities (observables) are represented by Hermitian operators
  (Examples: Energy $\hat{H}$, position $\hat{x}$, momentum $\hat{p}$)
- Measurement of an observable $\hat{A}$ on the system described by $\psi(x)$
  - Is unpredictable (even if one knows $\psi(x)$)
  - $\psi(x)$ is (in general) drastically modified immediately after a measurement
- The expectation (average) value of an observable $\hat{A}$ is (ψ_N is normalized)

$$\langle \hat{A} \rangle = \int \psi_N(x)^* \, \hat{A} \, \psi_N(x) \, d\,x \qquad (7.2)$$

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  (Examples: Energy $\hat{H}$, position $\hat{x}$, momentum $\hat{p}$)
- Allowed values for an observable are the eigenvalues of the corresponding operator. They can sometimes be discrete (like in the case of the energy).
- Upon measurement, the wavefunction collapses
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1 Introduction: atoms and electromagnetic waves

2 Failures of classical physics

3 Wave and Particle duality

4 Bohr's atom

5 The wave function and Schrödinger equation

6 Quantum mechanics of some simple systems

7 Principles and Postulates of Quantum mechanics

8 Angular momentum and electron spin
- First step: "particle on a ring"

Motion in a central potential (See also Blinder, Chap. 6.1–6.6)

- Our goal is to study the motion of an electron in the potential of the nucleus, which is a central potential,
  i. e. the potential $V(\mathbf{r})$ depends only on $|\mathbf{r}|$.
- In a central potential the angular momentum is a conserved quantity, i. e. it is a constant of motion. This is also true in quantum mechanics.
  As in classical mechanics, this conservation law will help us in making the problem easier.
- For a central potential it is convenient to write quantities in spherical polar coordinates, i. e. in terms of r, θ, ϕ.
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Goals of this chapter

In this chapter we will pursue the following goals

- Identify the operators associated with the angular momentum (in the same way as we identified the operators for **p** and **r**). In fact we will need only the z component L_z as well as $L^2 \equiv L_x^2 + L_y^2 + L_z^2$.
- Identify their eigenvalues. Later, we will associate them to the quantum numbers of electronic states in atoms.
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First step: “particle on a ring”

Particle moving on a ring

Consider a problem in which a particle can only move on a ring of radius R. In spherical coordinates this can be done by fixing $r = R$ and $\theta = \pi/2$, and by concentrating on the variable ϕ.

Apart from this, the potential is zero, so that the Schrödinger equation (5.15) becomes:[2]

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial s^2}\,\psi = E\,\psi \tag{8.1}$$

Here, s is the position coordinate measured along the ring, i. e. $s = R\,\phi$. Introducing $f(\phi) \equiv \psi(r = R, \theta = \pi/2, \phi)$ we can rewrite (8.1) as:

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Now, the kinetic energy of a rotating particle can be written as

$$E = \frac{L_z^2}{2I} = \frac{L_z^2}{2M\ R^2} \tag{8.3}$$

where $I = M\ R^2$ is the moment of inertia
and L_z the z-component of the angular momentum
A comparison of (8.3) with (8.2) suggests to
identify the operator $\hat{L}_z^2$ with $-\hbar^2 \frac{\partial^2}{\partial \phi^2}$ or

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \tag{8.4}$$

A more rigorous derivation can be found here:
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We now look for the eigenvalues and eigenfunctions of $\hat{L}_z$, which also give the eigenfunctions of (8.2)

Eigenvalues of $\hat{L}_z$

First of all, the function $f(\phi)$ must be single-valued. In other words, it must repeat itself, after a 2π rotation, i.e.

$$f(\phi + 2\pi) = f(\phi) \tag{8.5}$$

For the rest, the solution is very similar to the case of the particle in a box. We consider the eigenvalue problem

$$\hat{L}_z \, f = -i\hbar \frac{\partial}{\partial \phi} \, f(\phi) = L_z \, f(\phi)$$

where[3] L_z is the eigenvalue(s) we are looking for.
We already know the solutions

$$f(\phi) = e^{im\,\phi} \qquad \text{where } L_z = \hbar\, m \tag{8.6}$$

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In fact, these are much easier, as one simply requires m to be an integer.

Notice that in contrast to the particle in a box, m can also be zero, moreover negative and positive values give independent wavefunctions.

Summarizing, the eigenvalues L_z of $\hat{L}_z$ are

$$L_z = \hbar\, m \qquad m = 0, \pm 1, \pm 2, \cdots \tag{8.7}$$

i.e. L_z can only have values that are integer multiples of $\hbar$.

Notice, that the eigenfunctions (8.6) are orthogonal, as they should be (see Sec. 13.4)

$$\int_0^{2\pi} e^{-im\,\phi} e^{im'\,\phi}\, d\,\phi = 2\pi\, \delta_{m,m'}$$

From this we can also write down the normalised eigenfunctions (see (5.20)):

$$\frac{1}{\sqrt{2\pi}} e^{im\phi}$$

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$$\frac{1}{\sqrt{2\pi}} e^{im\phi}$$

The difference with respect to the particle in a box lies in the boundary conditions (8.5), which are quite different from (6.6).
In fact, these are much easier, as one simply requires m to be an integer.
Notice that in contrast to the particle in a box, m can also be zero, moreover negative and positive values give independent wavefunctions.
Summarizing, the eigenvalues L_z of $\hat{L}_z$ are

$$L_z = \hbar\, m \qquad m = 0, \pm 1, \pm 2, \cdots \tag{8.7}$$

i.e. L_z can only have values that are integer multiples of $\hbar$.
Notice, that the eigenfunctions (8.6) are orthogonal, as they should be (see Sec. 13.4)

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Notice that for the particle on a ring (8.7) is equivalent to Bohr's condition (4.2).
Indeed the circumference of the orbit is $2\pi R$, and a wave function of the form (8.6) has a wavelength $\lambda = 2\pi R/|m|$.
The problem with Bohr's picture is that, as we have seen, in quantum mechanics all coordinates have some uncertainty.
Therefore, the other two variables θ and r will also have some fluctuations.
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Second step: "particle on the surface of a sphere"

Particle on a sphere

We now make our problem a little bit more complicated and consider a particle moving on the surface of a sphere of radius R, i. e. we only fix the coordinate $r = R$.

Again there is no potential, and the Schrödinger equation (5.15) only contains the kinetic energy.

It is convenient to use the Laplace operator in spherical coordinates, which can be found in many books. We write it schematically as:

$$\nabla^2 = \nabla_r^2 + \frac{1}{r^2}\nabla_{\theta,\phi}^2 \,, \tag{8.8}$$

where we have introduced

$$\nabla_r^2 \equiv \frac{1}{r}\frac{\partial^2}{\partial\, r^2} r$$

$$\nabla_{\theta,\phi}^2 \equiv \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{8.9}$$

[For ∇_r^2 often the expression $\frac{1}{r^2}\frac{\partial}{\partial\, r} r^2 \frac{\partial}{\partial\, r}$ is used. However, this is less convenient.]

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Since the particle is confined to a sphere's surface, r is fixed, and we can neglect the ∇_r^2.
By writing the wave function as $\psi(R,\theta,\phi) = \text{const.} \times Y(\theta,\phi)$, the Schrödinger equation becomes

$$-\frac{\hbar^2}{2M\ R^2}\nabla^2_{\theta,\phi}\ Y(\theta,\phi) = E\ Y(\theta,\phi) \tag{8.10}$$

By expressing again the energy of the particle in terms of the angular momentum $\mathbf{L}$ and moment of inertia $I = M\ R^2$ as $E = \frac{\mathbf{L}^2}{2I} = \frac{\mathbf{L}^2}{2\ M\ R^2}$, we can rewrite (8.10) as

$$-\hbar^2\ \nabla^2_{\theta,\phi}\ Y(\theta,\phi) = \mathbf{L}^2\ Y(\theta,\phi) \tag{8.11}$$

Similarly to Sec. 8.1, we can thus identify the operator for the square of the angular momentum[4]

$$\hat{\mathbf{L}^2} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\nabla^2_{\theta,\phi} \tag{8.12}$$

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Eigenvalues and Eigenvectors of $\hat{\mathbf{L}}^2$

The eigenfunctions of $-\nabla^2_{\theta,\phi}$ are well known in mathematics: they are the spherical harmonics.

These have the property:

$$-\nabla^2_{\theta,\phi}\ Y_{\ell,m}(\theta,\phi) = \ell(\ell+1)\ Y_{\ell,m}(\theta,\phi)$$
$$\ell = 0, 1, \cdots, \infty \qquad m = -\ell, -\ell+1, \cdots, \ell \tag{8.13}$$

I. e. they are eigenfunctions of $-\nabla^2_{\theta,\phi}$ with eigenvalues $\ell(\ell+1)$.
Here, ℓ is a non-negative integer.
For each ℓ, there are $2\ell+1$ degenerate eigenfunctions (i. e. eigenfunctions with the same eigenvalue).
These are functions with the same ℓ but a different index m with $-\ell \le m \le \ell$
m has the same meaning as in (8.6), and indeed we have $Y_{\ell,m}(\theta,\phi) = P_{\ell,m}(\theta)e^{i\ m\ \phi}$.
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Summarizing:

the spherical harmonics are common eigenfunctions of the two operators $\hat{L}^2$ and $\hat{L}_z$, i. e. they satisfy the two eigenvalue equations:

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these operators can be written in terms of differential operators in spherical coordinates (see (8.4), (8.9))

$$\hat{\mathbf{L}}^2 = -\hbar^2 \nabla^2_{\theta,\phi} \qquad \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \tag{8.15}$$

Therefore, the kinetic term in the Hamilton operator can be written in spherical coordinates (cf. (8.8))

$$\hat{\mathbf{p}}^2 = -\hbar^2 \nabla^2 = -\hbar^2 \nabla^2_r + \frac{\hat{\mathbf{L}}^2}{r^2} \tag{8.16}$$

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Moreover, for a given allowed value of $\mathbf{L}^2 = \hbar^2\ \ell(\ell+1)$, the maximum allowed value of L_z^2 is $\hbar^2\ \ell^2$ which is smaller than $\mathbf{L}^2$ (except for $\ell = 0$).

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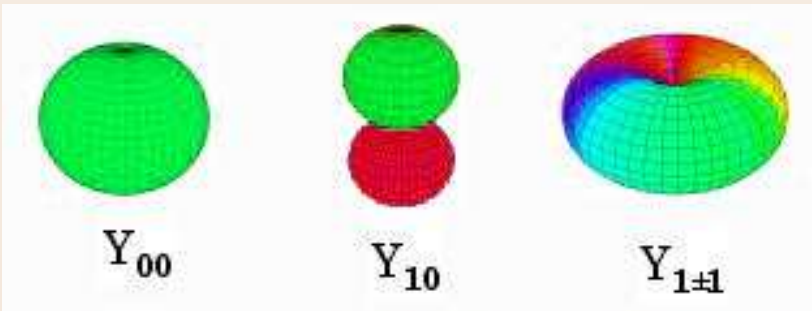
Here are the first few spherical harmonics

$Y_{0,0} = \sqrt{\frac{1}{4\pi}}$	$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos(\theta)$	$Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
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	$Y_{1,-1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\,\phi}$	$Y_{2,-1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{-i\,\phi}$
		$Y_{2,2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\,\phi}$
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\begin{array}{|c|c|c|}
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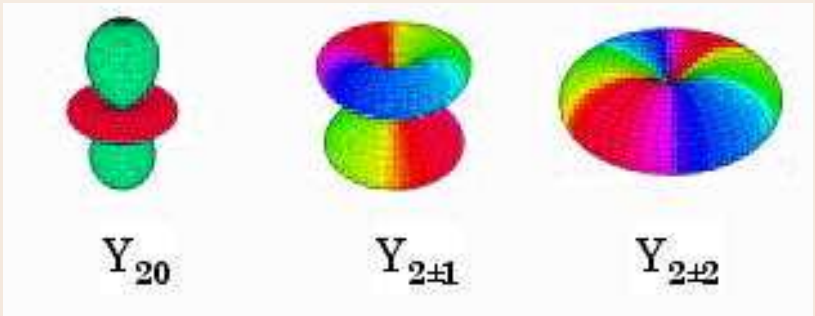


Figure: A plot of the first few spherical harmonics. The radius is proportional to $|Y_{\ell,m}|^2$, colors give $\arg(Y_{\ell,m})$, with green$= 0$, red$= \pi$.

Electron spin

Electrons, as well as protons, neutrons, quarks, etc. have an intrinsic angular momentum.

This angular momentum ($\hat{\mathbf{S}}$) is called "spin", because it can be roughly seen as an analogue of the angular momentum of a spinning rigid body.
Similarly to $\mathbf{L}$, we can classify the eigenvalues of $\hat{S}^2$ and $\hat{S}_z$ in terms of quantities s (to distinguish from ℓ) and m_s (to distinguish from m)

$$S^2 = \hbar^2\, s(s+1) \qquad S_z = \hbar m_s \qquad \text{with } m_s = -s, -s+1, \cdots, s \quad (8.18)$$

However, the important difference with ℓ is that $s = \frac{1}{2}$, i. e. it is half-integer.
From (8.18), since s is fixed, there are two possible states classified by $m_s = \pm\frac{1}{2}$,
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1 Introduction: atoms and electromagnetic waves

2 Failures of classical physics

3 Wave and Particle duality

4 Bohr's atom

5 The wave function and Schrödinger equation

6 Quantum mechanics of some simple systems

7 Principles and Postulates of Quantum mechanics

8 Angular momentum and electron spin

Atomic Units (See also Blinder, Chap. 7.1–7.7)

In this chapter, we want to study the quantum-mechanical motion of an electron in the electric field of a positive charge Ze, which, for $Z = 1$, is the Hydrogen atom.

First of all it is convenient to introduce atomic units.

This means that masses are given in units of the electron mass[5] M_e, lengths in units of the Bohr radius $a_0 = \frac{\hbar^2}{M_e\ e^2} \approx 5 \times 10^{-11} m$ (see Sec. 4), and energies in terms of the

$$\text{Hartree} = \frac{e^2}{a_0} \approx 27\ eV \tag{9.1}$$

e is the absolute value of the electron charge

Using these units makes equations much simpler, as it amounts to replacing

$$\hbar = 1 \qquad M_e = 1 \qquad e = 1 \tag{9.2}$$

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Atomic Units (See also Blinder, Chap. 7.1–7.7)

In this chapter, we want to study the quantum-mechanical motion of an electron in the electric field of a positive charge Ze, which, for $Z = 1$, is the Hydrogen atom.

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This means that masses are given in units of the electron mass[5] M_e, lengths in units of the Bohr radius $a_0 = \frac{\hbar^2}{M_e\ e^2} \approx 5 \times 10^{-11} m$ (see Sec. 4), and energies in terms of the

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Schrödinger equation and separation of variables

Schrödinger equation for the Hydrogen atom

The Schrödinger equation (5.15) for an electron in a potential $V(r)$ reads (in atomic units)

$$\left(-\frac{1}{2}\boldsymbol{\nabla}^2 + V(r)\right)\psi(r,\theta,\phi) = E\ \psi(r,\theta,\phi) \tag{9.3}$$

The potential energy for an electron in the field of a nucleus of charge $+Ze$ is given by (in Gauss/atomic units)

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where Z is the number of protons ($Z = 1$ for Hydrogen).
For convenience, however, we consider for the moment a generic central potential $V(r)$

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We take an Ansatz for the wave function in the form of separation of variables:

$$\psi(r,\theta,\phi) = R(r)\,Y_{\ell,m}(\theta,\phi) \tag{9.5}$$

where the $Y_{\ell,m}$ are the spherical harmonics defined in Sec. 8.

Use of (8.8) for the Laplace operator transforms (9.3) to details:

$$-R(r)\frac{1}{2r^2}\nabla^2_{\theta,\phi}Y_{\ell,m}(\theta,\phi) - Y_{\ell,m}(\theta,\phi)\frac{1}{2}\nabla^2_r R(r) + V(r)\; R(r)Y_{\ell,m}(\theta,\phi) =$$
$$= E\; R(r)Y_{\ell,m}(\theta,\phi) \tag{9.6}$$

The fact that $Y_{\ell,m}(\theta,\phi)$ is an eigenfunction of $-\nabla^2_{\theta,\phi}$ (i. e., of the L^2 operator see (8.13)) is a big advantage.
By using this fact in (9.6), and by dividing everywhere by $Y_{\ell,m}(\theta,\phi)$, the Schrödinger equation becomes

$$-\frac{1}{2}\nabla^2_r R(r) + \left(\frac{\ell(\ell+1)}{2\,r^2} + V(r)\right) R(r) = E\; R(r) \tag{9.7}$$

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We have, thus, managed to reduce a differential equation in three variables r, θ, ϕ into an equation in the variable r only.
This was possible because we have exploited the conservation of angular momentum.

In (9.7) we see that the part containing the angular momentum adds a repulsive contribution $L^2/(2\ r^2)$ (again, $L^2 = \ell(\ell+1)$) to the potential energy. This is the energy associated with the centrifugal force, which, of course, increases with increasing L^2.

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We will write (9.7) in a simpler form by making the transformation

$$R(r) = \frac{u(r)}{r} \tag{9.8}$$

By using the expression for ∇_r^2 ((8.9)), and multiplying by r, we finally obtain

$$-\frac{1}{2}u''(r) + \left(\frac{\ell(\ell+1)}{2\ r^2} + V(r)\right) u(r) = E\ u(r) \tag{9.9}$$

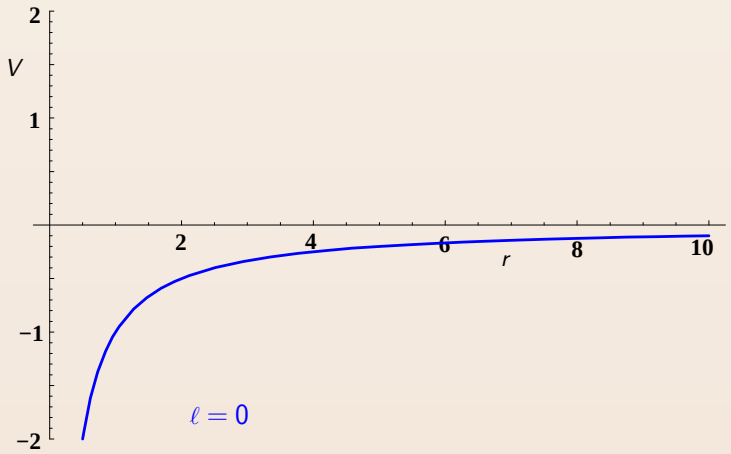
which is now identical to a Schrödinger equation for a particle moving in a one-dimensional coordinate r in an effective potential $\frac{\ell(\ell+1)}{2\ r^2} + V(r)$.
As in Sec. 6.3, we can graphically study the solutions of (9.9)

Qualitative solution

Graphical study of the Schrödinger equation

Effective potential

Let us first look at the effective potential in (9.9)
In the following discussion, we use the Coulomb potential (9.4) (with $Z = 1$), although most qualitative results will hold for similar attractive potentials.

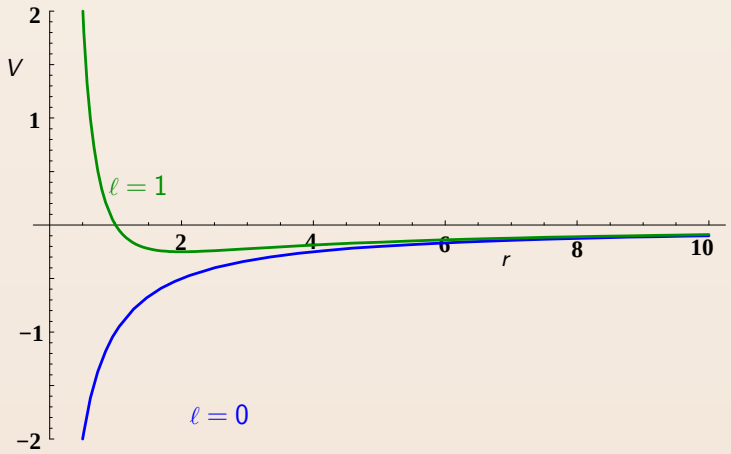


This is the effective potential for different values of ℓ.

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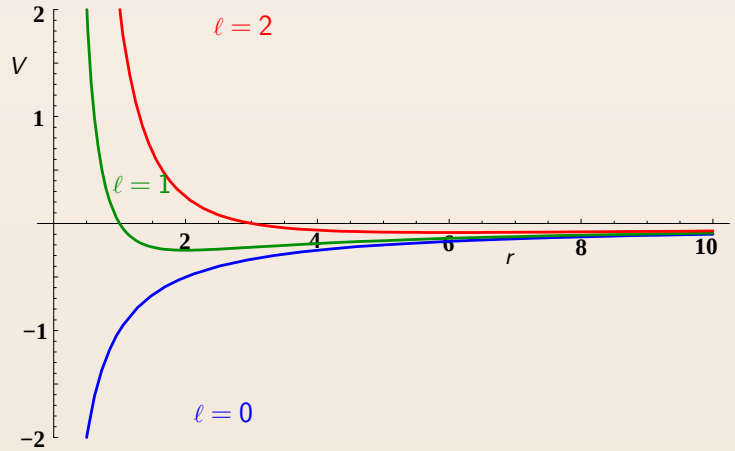


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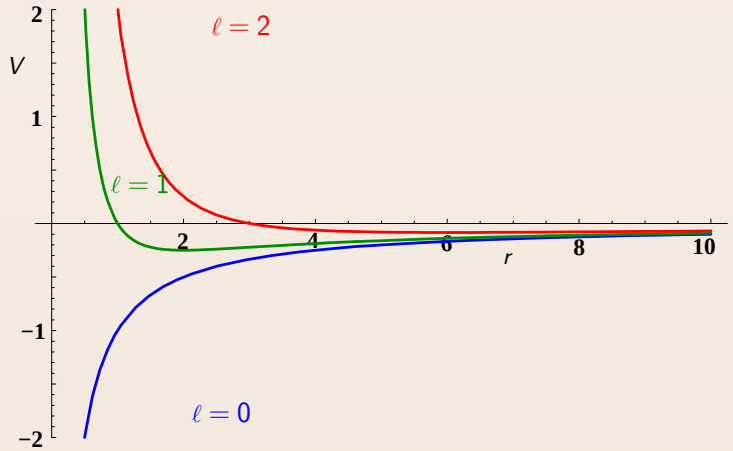


This is the effective potential for different values of ℓ.
All these potentials become 0 in the $r \to \infty$ limit, and, for $\ell > 0$, they have a minimum "bottom of the box" at some $r_{min} = \frac{\ell(\ell+1)}{Z}$

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In the following discussion, we use the Coulomb potential (9.4) (with $Z = 1$), although most qualitative results will hold for similar attractive potentials.



This is the effective potential for different values of ℓ.
We will expect that the average radius of the orbit will be proportional to r_{min}, i. e. increase with increasing ℓ and decrease with increasing Z.

Properties of the wave functions

Let us now assume that we have found the solution of (9.9) for each ℓ. We will actually do this below. Of course, we expect, as discussed qualitatively in Sec. 6.3, that (for each ℓ) there will be many solutions characterized by discrete values of the energy and with increasing number of nodes.

First of all, let us now analyze the properties of the complete wave functions (9.5), where $u(r)$ is a solution of (9.9).

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Properties of the wave functions

We rewrite (9.5) as

$$\psi(r,\theta,\phi) = \frac{u(r)}{r}\, Y_{\ell,m}(\theta,\phi) \tag{9.10}$$

We know from Sec. 8, that for each ℓ (i. e. for each L^2) there are many wave functions with different m.
Specifically, since $m = -\ell, \cdots, \ell$, there are $2\ell + 1$ of them.
The important results that we can read from (9.9) (there is no m in it) is that wave functions with the same ℓ but different m have the same energy, i. e. they are degenerate.
This important result is valid for an arbitrary central potential.
It holds for example for heavier atoms for which the potential energy is more complicated, but still central[6].

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Next we can ask the question of where is the largest probability to find the electron.
This gives us some information about the "orbit" of the particle.
We know from Sec. 5.3 ((5.17)) that the probability to find the electron in a small volume around r, θ, ϕ is proportional to $|\psi(r, \theta, \phi)|^2$, i. e.[7]

$$\rho(r, \theta, \phi) \propto \frac{u(r)^2}{r^2} \, |Y_{\ell,m}(\theta, \phi)|^2 \tag{9.11}$$

From (9.11) we can ask two questions:

1. What is the probability density $\rho_\Omega(\theta, \phi)$ that the electron is found at a certain solid angle?
   This provides information about the shape of the orbit
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[7] $u(r)$ turns out to be real

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From (9.11), the answer to question 1 is clearly

$$\rho_\Omega(\theta,\phi) \propto |Y_{\ell,m}(\theta,\phi)|^2 \tag{9.12}$$

This angular distribution is proportional to the radius of the figures 1.

Question 2 has to be better specified.

We want to know the probability density that the electron is found on the surface of a sphere of radius r.

We have, thus, to integrate $\rho(\mathbf{r})$ over the surface of this sphere, i. e.

$$\rho_r(r) \propto \int \rho(r,\theta,\phi)\; r^2\; \sin\theta\; d\theta\; d\phi =$$

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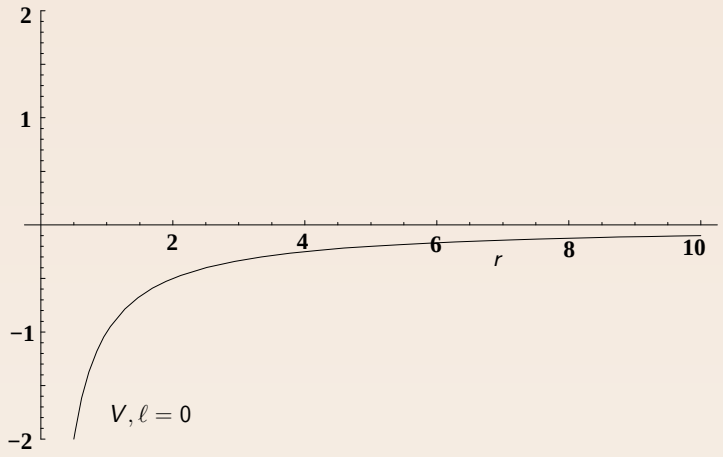
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Solution of (9.9) for $\ell = 0$



Here we show the effective potential for $\ell = 0$

We look for bound states, i. e. states with $E < 0$

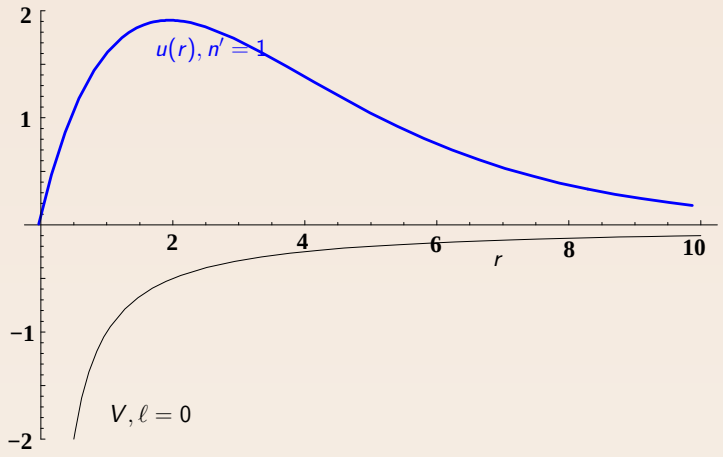
The ground-state wave function $(\ell = 0, n' = 1)$ $u(r)$, as usual, has no nodes.

All $u(r)$ must vanish for $r \to \infty$, as well as at $r = 0$, because of (9.8).

The $u(r)$ are products of a polynomial and the exponential function $\exp(-Zr/n')$

Possible values of n' are $n' = 1, 2, \cdots, \infty$

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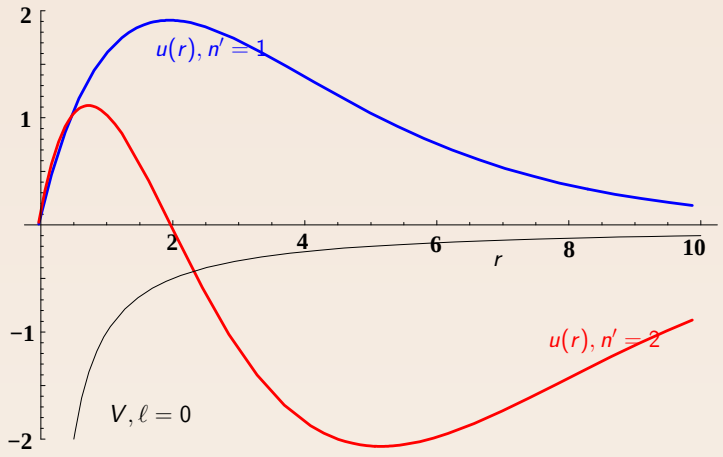
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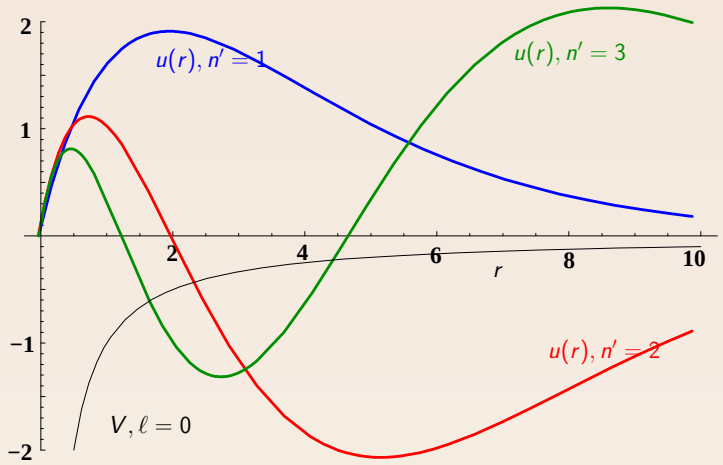
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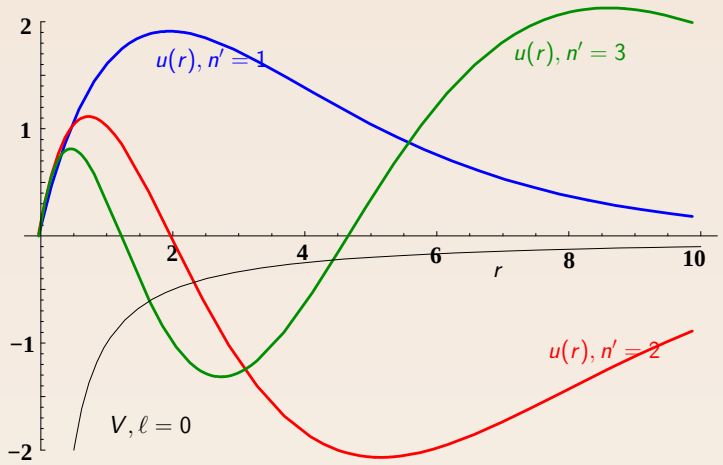
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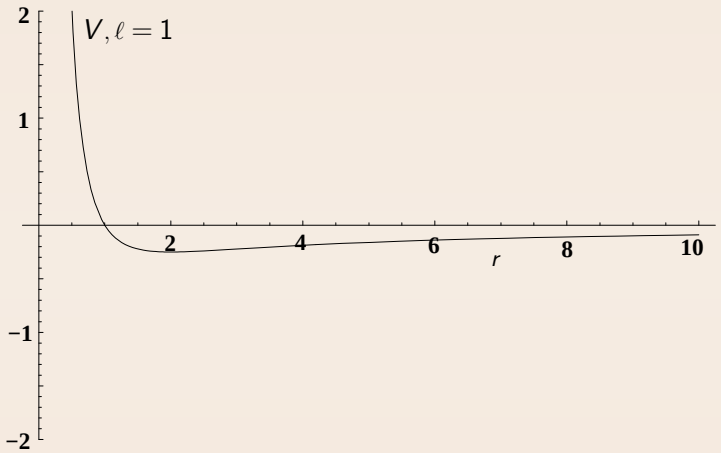
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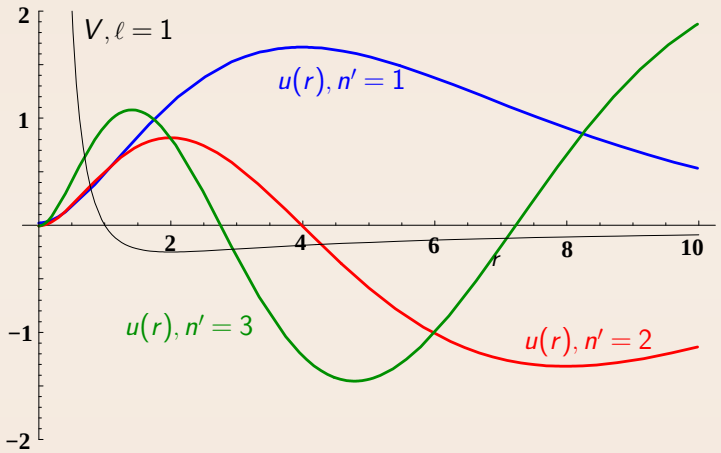
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Energies of the atomic orbitals

The energies of the Hydrogenic bound states, obtained from solving the Schrödinger equation (9.9) for the different ℓ, have a very simple expression (in Hartree, see (9.1)).

$$E_{n',\ell} = -\frac{Z^2}{2}\frac{1}{(n'+\ell)^2}$$

This suggests to introduce the principal quantum number $n = n' + \ell$, so that the energies are now independent of ℓ (and, of course, of m).

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Energies of the atomic orbitals

The energies of the Hydrogenic bound states, obtained from solving the Schrödinger equation (9.9) for the different ℓ, have a very simple expression (in Hartree, see (9.1)).

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Notice, however, that the lowest-energy state can be only attained for $\ell = 0$.

Since $n = n' + \ell$, for a given ℓ, only states with $n = \ell + 1, \cdots, \infty$ can be achieved.

Furthermore, notice that the degeneracy in (9.14) only occurs for a Coulomb potential (9.4).

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Classification of atomic orbitals

Summary: Quantum numbers

- Summarizing, the bound states (atomic orbitals) of the Hydrogen atom depend on three quantum numbers: principal (n), angular momentum (ℓ) and magnetic (m).
- The allowed values of the quantum numbers are:

$$n = 1, \cdots, \infty \qquad \ell = 0, \cdots, n-1, \qquad m = -\ell, \cdots, \ell \tag{9.15}$$

- The corresponding eigenfunctions can be written as:

$$\psi_{n,\ell,m}(r,\theta,\phi) = \frac{u_{n,\ell}(r)}{r}\, Y_{\ell,m}(\theta,\phi) \tag{9.16}$$

- The energies depend only on n:

$$E_{n,\ell} = -\frac{Z^2}{2}\frac{1}{n^2}\ (\text{Hartree}) \tag{9.17}$$

- For $n = 1$ there is only one state, for $n = 2$ there are $1 + 3 = 4$, for $n = 3$ there are $1 + 3 + 5 = 9$ states with the same energy.
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Angular momentum states

The angular momentum quantum number ℓ is conventionally designated by the following code:

$$\begin{array}{cccccc} \ell = & 0 & 1 & 2 & 3 & 4 \\ & s & p & d & f & g \end{array} \tag{9.18}$$

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s orbitals

s orbitals have $\ell = 0$ and therefore only $m = 0$.
Since $Y_{0,0} =$ constant (See (8.17)), s orbitals are spherically symmetric (see Fig. (2))

p orbitals: complex vs. real representation

- p orbitals have $\ell = 1$, and, thus there are three of them ($m = -1, 0, 1$). They have a nontrivial angular dependence, as can be seen in Fig. 1 (see also Fig. (2))
- The $m = 0$ state is also called p_z because it is oriented along z.
- The $m = \pm 1$ p orbitals are in principle complex. However, one can take two suitable linear combinations of them and obtain real orbitals. Remember that linear combinations of degenerate eigenfunctions are also eigenfunctions with the same energy. Therefore we can for example take the real orbitals p_x and p_y which have the same shape as p_z but are oriented along the x and y axes, respectively, see Fig. (2)

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- Usually, one forms the combinations $\frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1})$ and $\frac{1}{\sqrt{2}}(Y_1^1 - Y_1^{-1})$ (which are called p_{x+y} and p_{x-y} orbitals), or, equivalently, $\frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1})$ and $\frac{1}{i\sqrt{2}}(Y_1^1 - Y_1^{-1})$. These two real orbitals p_x and p_y which have the same shape as p_z but are oriented along the x and y axes, respectively, see Fig. (2)

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d orbitals

d orbitals have $\ell = 2$, and, thus, there are five of them.
As for p orbitals, one can make them real with the use of linear combinations.
In this real representation, d orbitals are termed
$d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{yz}, d_{zx}$, see Fig. (3)

Atomic orbitals in real representation

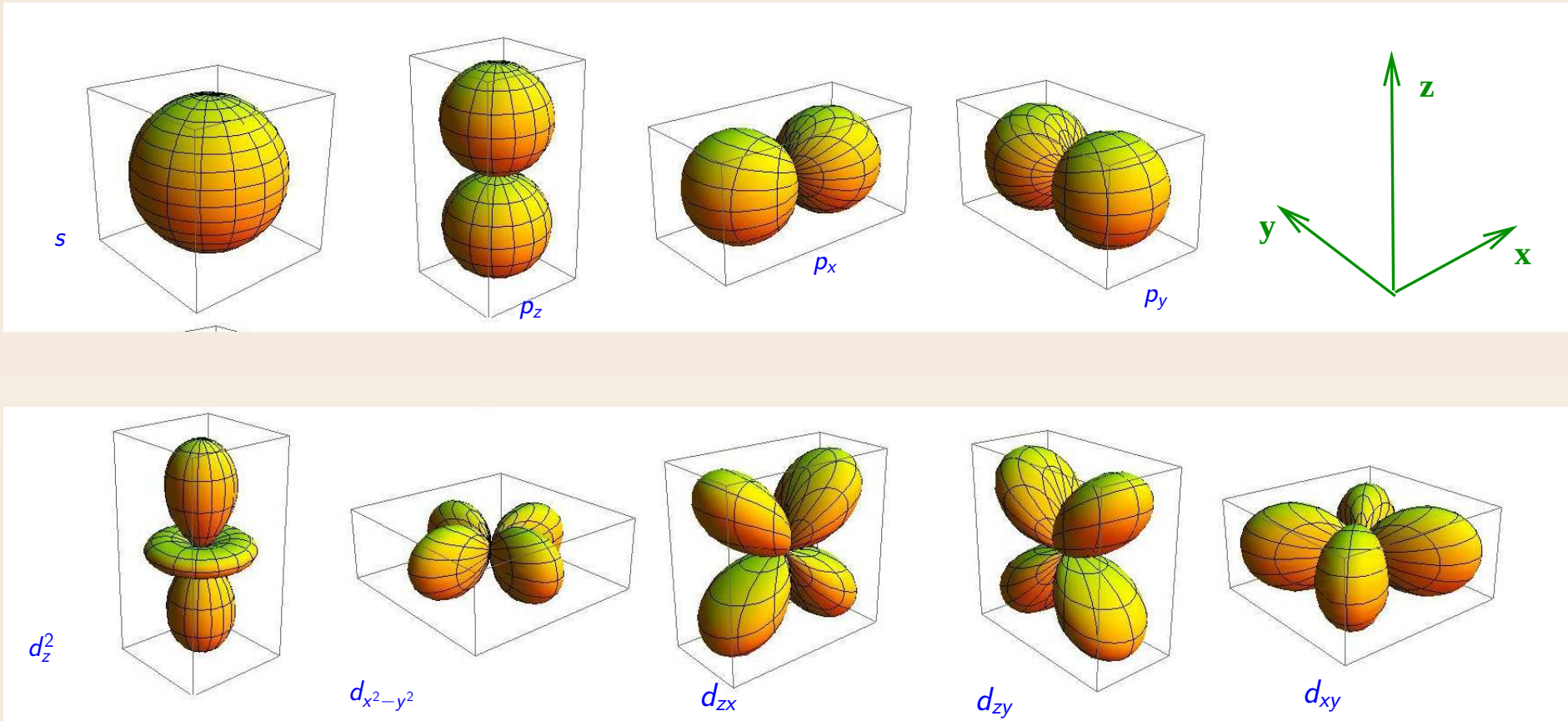


Figure: Angular dependence of atomic orbitals for $\ell = 0, 1, 2$ in real representation

Terminology of orbitals

By including the principal quantum number n, the atomic orbitals of Hydrogen are labelled in the form

$$n\,\ell_m \tag{9.19}$$

where $\ell = s, p, d, f, \cdots$, and m (not always indicated) can be either in the complex ($m = -\ell, \cdots, \ell$) or in the real representation (e.g. x, y, z). Therefore, sorted according to their energies, the first few atomic orbitals of hydrogen are:

$$\begin{array}{l} 1s \\ 2s\ 2p_x\ 2p_y\ 2p_z \\ 3s\ 3p_x\ 3p_y\ 3p_z\ 3d_{x^2-y^2}\ 3d_{z^2}\ \ 3d_{xy}\ 3d_{yz}\ 3d_{zx} \end{array} \tag{9.20}$$

where orbitals on the same row in the table have the same energy. This large degeneracy will be partially lifted in atoms with more than one electron, as we shall see in Chap. 10

1 Introduction: atoms and electromagnetic waves

2 Failures of classical physics

3 Wave and Particle duality

4 Bohr's atom

5 The wave function and Schrödinger equation

6 Quantum mechanics of some simple systems

7 Principles and Postulates of Quantum mechanics

8 Angular momentum and electron spin

Many-electron atoms (See also Blinder, Chap. 9.1–9.5)

- Heavier atoms consist of many electrons moving in the Coulomb potential of the nucleus.
- The wave function for N electrons is a very complicated function of the coordinates of all N electrons together: $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$.
- Accordingly, the Schrödinger equation becomes highly complicated because all the electrons interact with each other.
- However, in the orbital approximation we consider each electron as occupying its "own" atomic orbital.
  We can think of the individual orbitals as resembling the hydrogenic orbitals, but corresponding to nuclear charges modified by the presence of all the other electrons in the atom.
- This description is only approximate, but it is a useful model for discussing the chemical properties of atoms, and is the starting point for more sophisticated descriptions of the atomic structure.

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Pauli principle

The Pauli exclusion principle

- One restriction in adding electrons in atomic orbitals is provided by the Pauli exclusion principle.
- According to this principle, no more than two electrons may occupy any given orbital, and if two do occupy one orbital, then their spins must be opposite, i. e. one electron has spin quantum number (see Sec. 8.3) $m_s = +\frac{1}{2}$ and the other $m_s = -\frac{1}{2}$.
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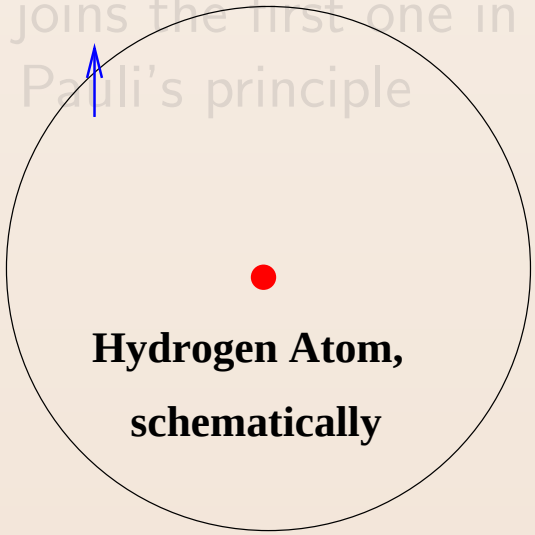
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Helium atom

- Let us start to understand these ideas by considering an atom with two electrons, i. e. the Helium atom.
- We can imagine forming the ground state of the He atom by adding the electrons in succession to the orbitals of the bare nucleus (of charge $Z = 2$), starting from the lowest levels in order to minimize the energy.
- The first electron occupies a $1s$ hydrogenic orbital, but since $Z = 2$ the orbital is closer to the nucleus than in Hydrogen.
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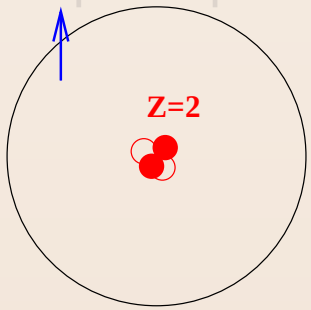
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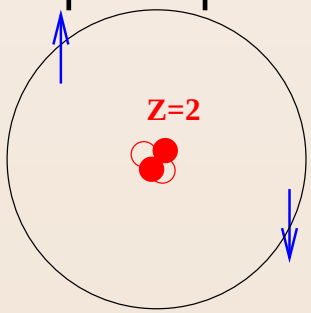
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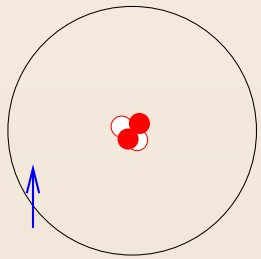
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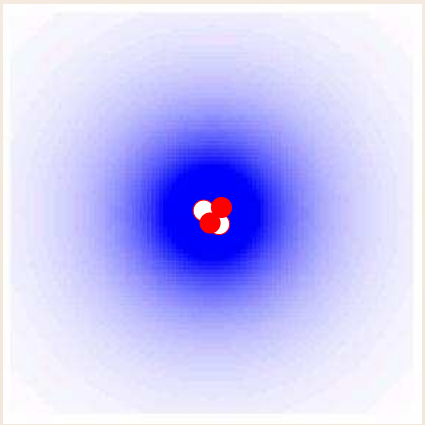
Charge screening

- In fact, the first electron does not have a well-defined orbit, but rather a certain charge distribution.
- The second electron "feels" not only the charge $+2e$ of the nucleus but also a diffuse negative charge $-e$ due to the first electron. This negative charge has a spherically symmetric distribution around the nucleus and "screens" the nuclear charge.
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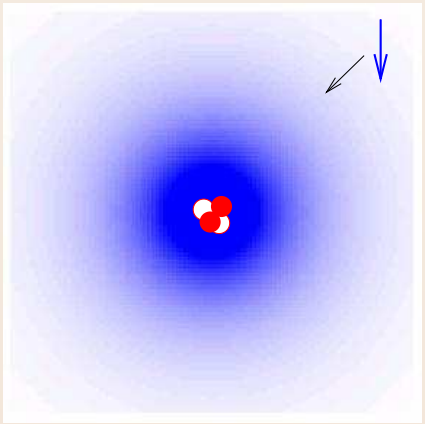
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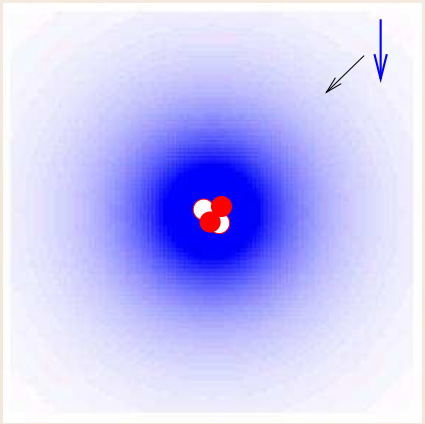
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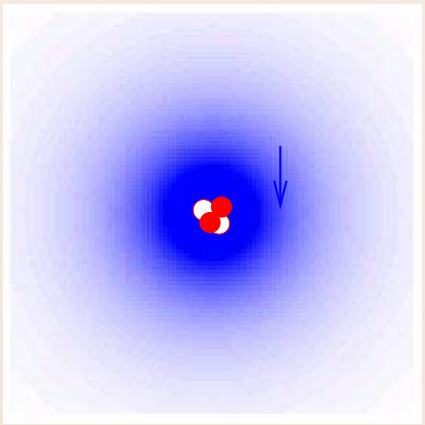
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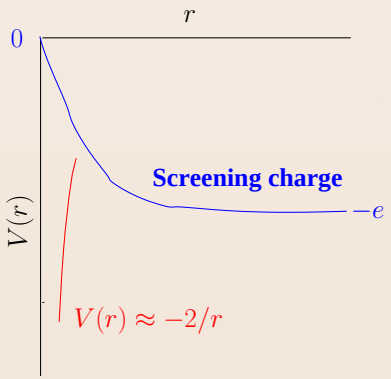
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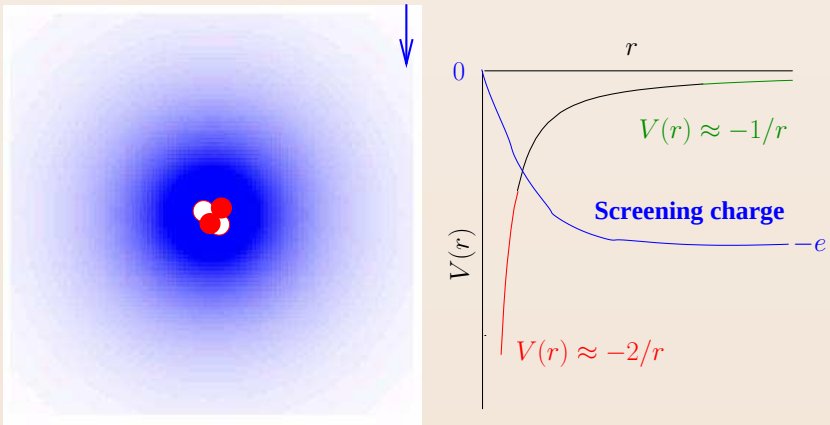
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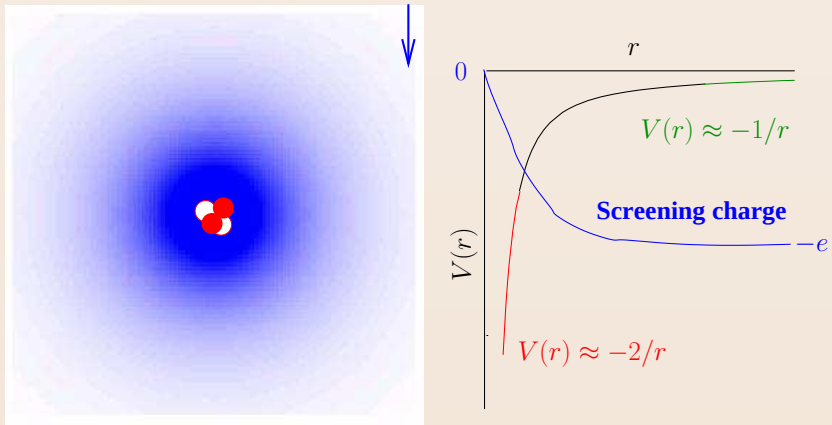
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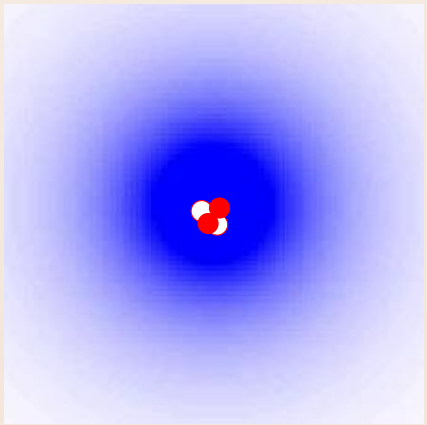
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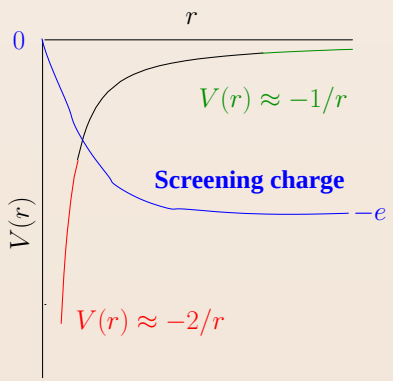
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- The "shell" of the $n = 1$ energy level "K" shell is now filled by the two electrons: A third electron is not allowed here because of Pauli principle.
- One says that the two electrons form a closed shell.
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Lithium

- Lithium, with $Z = 3$, has three electrons. The first two form a closed shell, which is nearer to the nucleus than in He, because of the larger charge.
- The third electron has to go into the next shell with $n = 2$ ("L" shell). For $n = 2$ there are two allowed values of ℓ, $\ell = 0$ and 1, i. e. one $2s$ and three $2p$ orbitals.
- However, in contrast to Hydrogen (cf.(9.20)), $2s$ and $2p$ orbitals are no longer degenerate.
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  - For this reason, an s electron experiences (on the average) less screening than a p electron (see Fig. (4))
  - Consequently, an s electron is more tightly bound, i. e. it has a lower energy, than a p electron of the same shell.
- The third electron of lithium will, therefore, occupy the $2s$ orbital. Its configuration is thus chemically denoted as
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Building-up principle

Building-up (*Aufbau*) principle

- It is easy to go on. In Be (Beryllium), with $Z = 4$ the configuration is $1s^2 2s^2$.
  Again the two electrons on the $2s$ orbital must have opposite spin.
- From $Z = 5$ one has to start putting electrons in the $2p$ orbitals.
  There are three $2p$ orbitals (Fig. (2)). Each orbital can be occupied by two electrons with opposite spin, so that we can put 6 electrons in the shell with $n = 2$ and $l = 1$.
- Hund's rule: the ground state of an atom is the one with the largest number of unpaired electrons (because it has the lowest energy).

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  The general ordering of atomic orbitals is summarized by the following scheme:

  $1s < 2s < 2p < 3s < 3p < 4s \sim 3d < 4p < 5s \sim 4d < 5p < 6s \sim 5d \sim 4f < 6p < 7s \sim 6d \sim 5f < 7p$

  Notice that the $4s$ orbital is lowered sufficiently to become comparable to $3d$. This also holds for higher orbitals.

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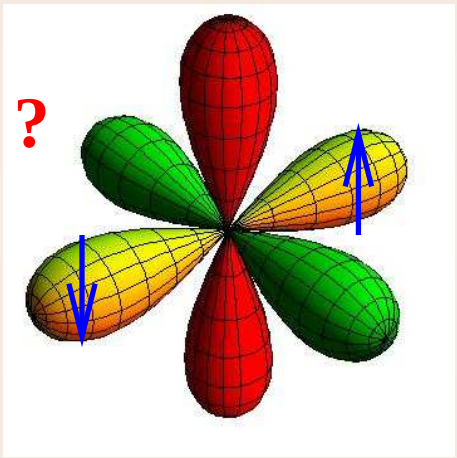
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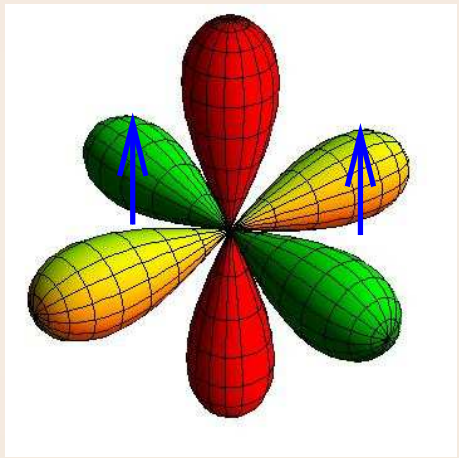
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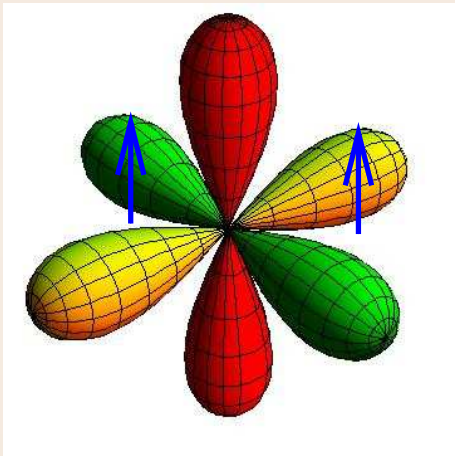
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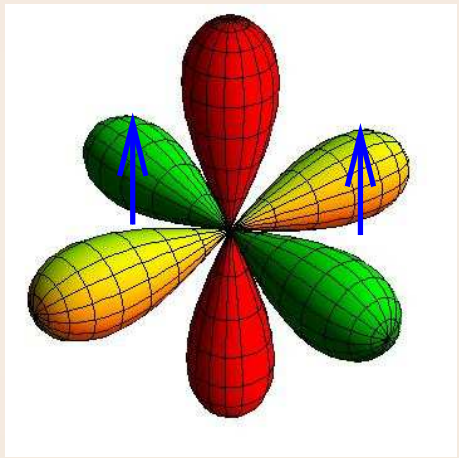
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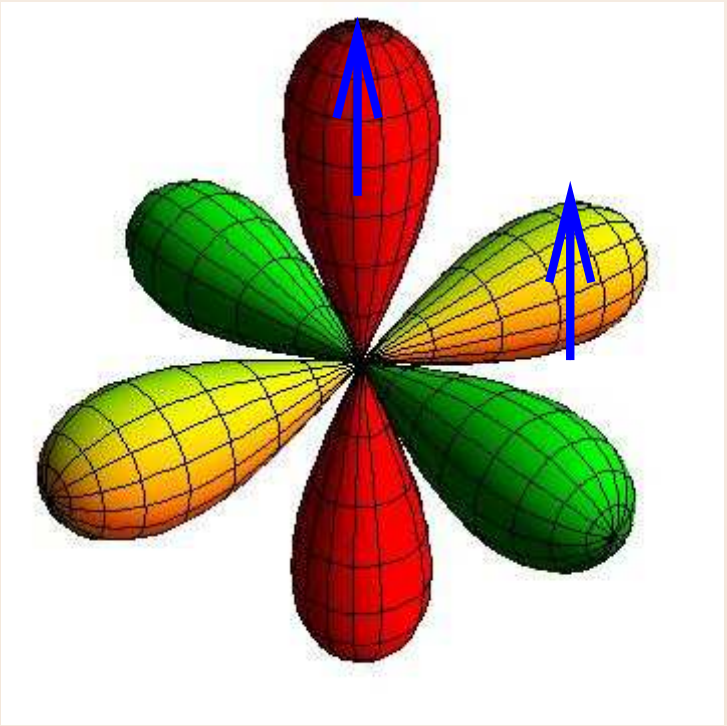
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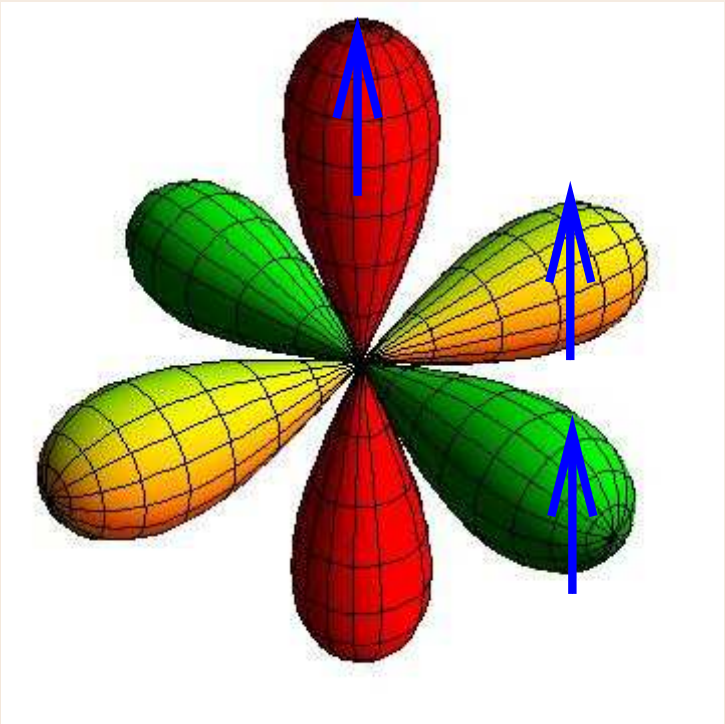
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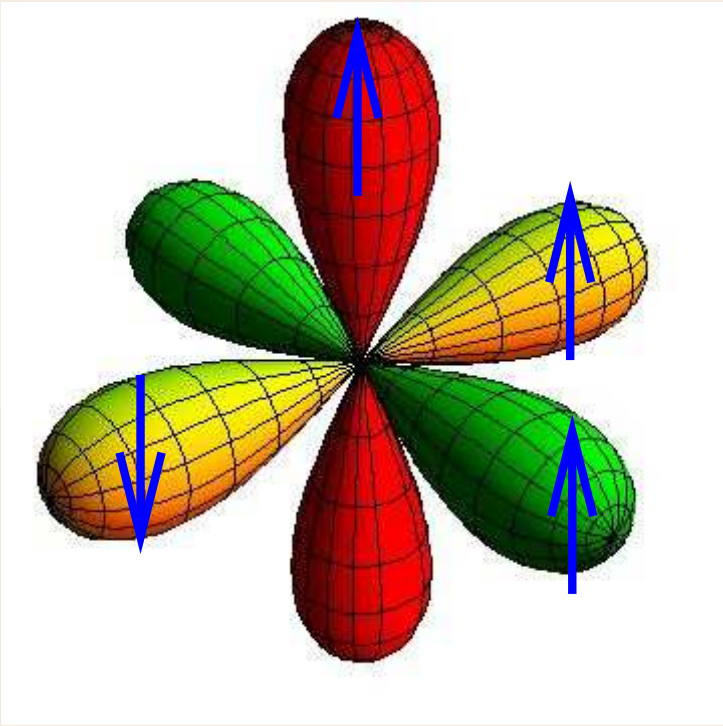
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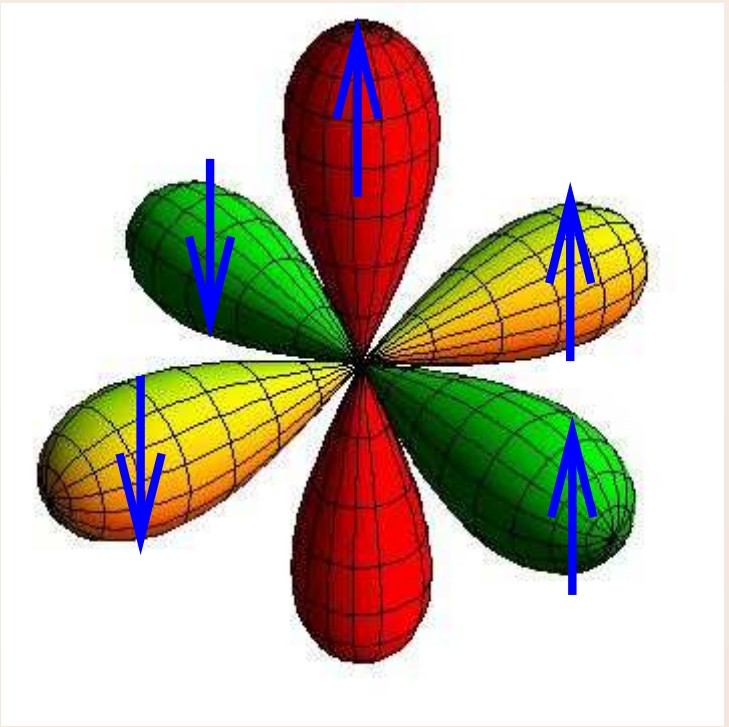
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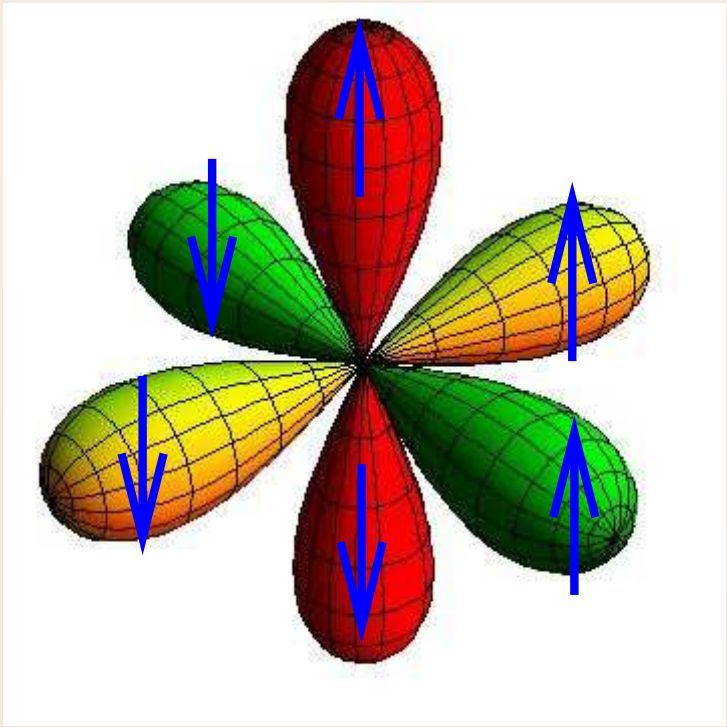
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11 Examples and exercises

12 Some details

13 Functions as (infinite-dimensional) vectors

Photoelectric effect

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The work function ϕ of a particular metal is 2.6 eV ($1\,\text{eV} = 1.6 \times 10^{-19}\,\text{J}$). What is the maximum wavelength of light which can eject an electron from that metal?

Solution:

$$\phi = h\,\nu = h\,c/\lambda \Rightarrow \lambda = h\,c/\phi =$$

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i. e. blue light: light of longer wavelength (green, red) cannot eject electrons from this metal, no matter how intense it is.

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$$\frac{6.6 \times 10^{-34}\,\mathrm{J\,s} \times 3 \times 10^{8}\,\mathrm{m/s}}{2.6 \times 1.6 \times 10^{-19}\,\mathrm{J}} \approx 4.8 \times 10^{-7}\,\mathrm{m} = 480\,\mathrm{nm}$$

i. e. blue light: light of longer wavelength (green, red) cannot eject electrons from this metal, no matter how intense it is.

Wavelength of an electron

back

Determine the kinetic energy in eV for an electron with a wavelength of 0.5 nm (a wavelength typical of X-rays).

Solution:

$$E = p^2/(2m) = h^2/(\lambda^2\ 2\ m) =$$

$$(6.6 \times 10^{-34}\,\mathrm{J\,s})^2 / \left((5 \times 10^{-10}\,\mathrm{m})^2\ 2\ \times 9.1 \times 10^{-31}\,\mathrm{kg}\right)$$

(remember $\mathrm{J} = \mathrm{kg\ m^2/s^2}$)

$$= 9.6 \times 10^{-19}\,\mathrm{J} = \frac{9.6 \times 10^{-19}}{1.6 \times 10^{-19}}\,\mathrm{eV} \approx 6\,\mathrm{eV}$$

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Properties of a wavefunction

average values, normalisation, etc.

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The ground-state wavefunction of the Hydrogen atom has the form

$$e^{-\frac{a\ r}{2}} \tag{11.1}$$

where $r = |\mathbf{r}|$ and $\mathbf{r} = (x, y, z)$.
Normalize the wavefunction.
Find the average value of the radius $< r >$ (see (B.6)).
The remaining questions are not compulsory
Find the probability $W(r_0 < r < r_0 + \Delta r_0)$ that r is found between r_0 and $r_0 + \Delta r_0$.
In the limit of small Δr_0, the probability density $P(r_0)$ for r (not for $\mathbf{r}$!) is given by

$$P(r_0)\ \Delta r_0 = W(r_0 < r < r_0 + \Delta r_0) \tag{11.2}$$

Determine $P(r_0)$ and plot it.
Determine the most probable value of r (i. e. the maximum in $P(r_0)$).

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Properties of a wavefunction

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Normalisation:

$$1 = N^2 \int (e^{-\frac{a\ r}{2}})^2\ dV = N^2 \int e^{-a\ r}\ d\ V \tag{11.3}$$

The volume element in spherical coordinates (r, θ, ϕ) is given by $dV = r^2\ d\ r\ \sin\theta\ d\ \theta\ d\phi$. The integral over the solid angle gives 4π. We thus have:

$$1 = N^2\ 4\ \pi \int_0^\infty e^{-a\ r} r^2\ dr = N^2\ 4\pi\ \frac{2}{a^3} \Rightarrow N = \sqrt{\frac{a^3}{8\pi}} \tag{11.4}$$

$$< r >= N^2\ 4\ \pi \int_0^\infty e^{-a\ r} r^2 r\ dr = \frac{3}{a} \tag{11.5}$$

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average values, normalisation, etc.

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For small Δr_0 this is obviously given by the integrand times Δr_0, so that

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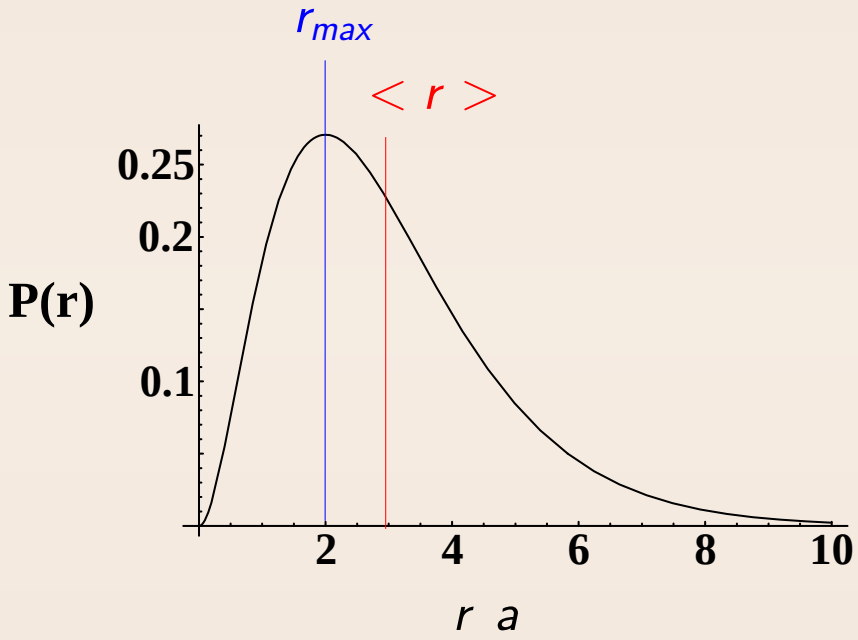
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Properties of a wavefunction

average values, normalisation, etc.



Notice that the probability density $P(\mathbf{r})$ for the coordinates $\mathbf{r} = (x, y, z)$ is given instead by $P(\mathbf{r}) = N^2 e^{-a\ r}$ (with $r = |\mathbf{r}|$) and has its maximum at the centre $\mathbf{r} = 0$.

Particle in a box: average values

back Evaluate the average value $< x >$ of the coordinate x for the ground state of the particle in a box. Evaluate its standard deviation $\Delta x \equiv \sqrt{< (x - < x >)^2 >}$.

Solution:

Ground state

$$\psi(x) = N \sin \frac{\pi}{a} x \tag{11.8}$$

Normalisation

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$$\Delta x^2 = < x^2 > - < x >^2 = a^2 \, (\frac{1}{12} - \frac{1}{2\pi^2}) \tag{11.12}$$

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Example: Heisenberg's uncertainty relation

back The wave function of a particle is given by a Gauss curve

$$\psi(x) = e^{-\frac{x^2}{2\alpha^2}}$$

Evaluate the expectation values and standard deviation of $\hat{x}$ and $\hat{p}$.

Solution: ($\hbar = 1$) We first find the norm of the wavefunction:

$$\langle\psi|\psi\rangle = \int \psi(x)^2 \, dx = \int e^{-\frac{x^2}{\alpha^2}} \, dx = \alpha\sqrt{\pi}$$

We now need the expectation values $< \hat{x} >$ and $< \hat{p} >$:
We observe, however, that both integrals vanish, since the integrands are odd functions of x:

$$\langle\psi|\hat{x}\ \psi\rangle = \int x\ \psi(x)^2 \, dx = 0$$

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We finally need $< \hat{x}^2 >$ and $< \hat{p}^2 >$:

$$< \hat{x}^2 >= \langle \psi | \hat{x}^2 \ \psi \rangle \ / < \psi | \psi >= \frac{1}{\alpha \sqrt{\pi}} \int x^2 \psi(x)^2 \ dx = \frac{\alpha^2}{2}$$

Thus, $\Delta x = \alpha/\sqrt{2}$, which is reasonable, since this is the width of the Gauss curve.

$$< \hat{p}^2 >= \langle \psi | \hat{p}^2 \ \psi \rangle \ / < \psi | \psi >= -\frac{1}{\alpha \sqrt{\pi}} \int \psi(x) \psi''(x) \ dx = \frac{1}{2\alpha^2}$$

Thus, $\Delta p = \frac{1}{\sqrt{2}\,\alpha}$

The two results combined give $\Delta x \ \Delta p = \frac{1}{2}$, or, restoring $\hbar$ by noticing that the dimensions of $\hbar$ are (length$\times$momentum):

$$\Delta x \ \Delta p = \frac{\hbar}{2} \qquad (11.13)$$

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11 Examples and exercises

12 Some details

13 Functions as (infinite-dimensional) vectors

Some useful properties of the exponential function

and complex numbers

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- i is the imaginary unit: $i^2 = -1$. Notice: in engineering notation people often use j instead.
- Useful relation: $e^{i\alpha} = \cos\alpha + i \sin\alpha$
- So that one can take the real part in (5.1): $\mathrm{Re}\ e^{i(kx-\omega t)} = \cos(kx - \omega t)$
- Differentiating just provides a multiplicative factor: $\frac{\partial}{\partial x} e^{a\,x} = a\ e^{a\,x}$

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- So that one can take the real part in (5.1): $\mathrm{Re}\ e^{i(kx-\omega t)} = \cos(kx - \omega t)$
- Differentiating just provides a multiplicative factor: $\frac{\partial}{\partial x} e^{a\,x} = a\ e^{a\,x}$

Some conventions for three dimensions

back

- Here, we use the notation that boldface objects are vectors: $\mathbf{r} = (x, y, z)$.
- Instead of $\frac{d}{dx}$ in three dimensions we have the "vector" of partial derivatives

$$\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}) \tag{12.1}$$

- In three dimensions $\frac{d^2}{dx^2}$ is replaced with

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{12.2}$$

- The three-dimensional volume integral is denoted by $\int d^3\ \mathbf{r} \cdots$, or by $\int d\ V \cdots$, both meaning $\int dx\ dy\ dz \cdots$.

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Probability density

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The Probability density can be defined in the following way:

If $\rho(x)$ is the probability density to find a particle around the position x then the probability $W(a \leq x \leq b)$ to find the particle between a and b (with $a < b$) is

$$W(a \leq x \leq b) = \int_a^b \rho(x)\, dx\,. \tag{12.3}$$

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Probability density: normalisation, average values

The probability density must be normalized, i. e. the total probability to find the particle somewhere must be 1:

$$\int \rho(\mathbf{r})\ d^3r = 1 \tag{12.5}$$

The average value (also called expectation value) $< f(\mathbf{r}) >$ of a function $f(\mathbf{r})$ (e.g. $f(\mathbf{r}) = |\mathbf{r}|$) is given by

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Solution of differential equations for free particles

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$$\psi''(x) + B\psi(x) = 0 \tag{12.7}$$

(Notice $\psi''(x)$, means "second derivative of ψ", i. e. $\frac{d^2\psi}{dx^2}$).

Try a solution of the form

$$\psi(x) = e^{ax}$$

we have

$$\frac{d}{dx}\psi(x) = a\ e^{ax} \qquad \frac{d^2}{dx^2}\psi(x) = a^2\ e^{ax}$$

Plug it into (B.7)

$$(a^2 + B)\psi(x) = 0$$

The only (nontrivial) solutions occur for $a = \pm\sqrt{-B}$.

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For $B > 0$, we conveniently write $a = \pm i\sqrt{B}$, and the two solutions are thus

$$\psi(x) = e^{i\sqrt{B}x} \qquad \psi(x) = e^{-i\sqrt{B}x} \tag{12.8}$$

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Linearity

An important property of an equation like (B.7), and, in general, of the Schrödinger equations (5.15) and (5.12), is that linear combinations of the solutions are also solutions See details

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Solution of differential equations for free particles

From exponential to sin and cos

We choose the coefficients $a_1 = \frac{1}{2}$, $a_2 = \frac{1}{2}$, we then have

$$\psi_{Ic}(x) = \frac{e^{i\sqrt{B}x} + e^{-i\sqrt{B}x}}{2} = \cos\sqrt{B}x$$

or we choose $a_1 = \frac{1}{2i}$, $a_2 = -\frac{1}{2i}$, then

$$\psi_{Ic}(x) = \frac{e^{i\sqrt{B}x} - e^{-i\sqrt{B}x}}{2i} = \sin\sqrt{B}x$$

I.e., we can replace (B.8) with

$$\psi(x) = \cos\sqrt{B}x \qquad \psi(x) = \sin\sqrt{B}x \qquad (12.9)$$

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Linear combinations are also solutions

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An important property of an equation like (B.7), and, in general, of the Schrödinger equations (5.15) and (5.12), is that they are linear and homogeneous.

As a consequence, if you find two (or more) solutions of (B.7), say $\psi_1(x)$ and $\psi_2(x)$
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Linear combinations are also solutions

We want to illustrate this fact here: we have

$$\psi_1''(x) + B\psi_1(x) = 0 \qquad \psi_2''(x) + B\psi_2(x) = 0$$

we want to prove that also

$$\psi_{lc}(x) = a_1\psi_1(x) + a_2\psi_2(x)$$

satisfies the same equation.
Proof: consider that

$$\psi_{lc}''(x) = a_1\psi_1''(x) + a_2\psi_2''(x)$$

Therefore,

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Free particle: details

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Notice: wavefunctions don't always have well defined value of energy (or momentum). For example the function $a_1\ e^{i\ k_1\ x} + a_2\ e^{i\ k_2\ x}$ with $|k_1| \neq |k_2|$ does not have a well defined energy. This function will have, however, a complicated time evolution and not just the form (5.13).

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- The solutions for negative k^2 (i. e. $E < V$) have the form

$$\psi(x) = \text{const.} e^{\pm\sqrt{-k^2}\ x} \tag{12.10}$$

these solutions are not allowed because they would imply that the wave function diverges for $x \to \infty$ or $x \to -\infty$. This form of solutions, however, will be useful for so-called bound states (see Sec. 6.3)

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Detailed proof of the form of L_z

back The angular momentum operator is given by

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} \tag{12.11}$$

The z-component

$$\hat{L}_z = \hat{x}\ \hat{p}_y - \hat{y}\ \hat{p}_x = -i\hbar(x\ \frac{\partial}{\partial y} - y\ \frac{\partial}{\partial x}) \tag{12.12}$$

We now consider an arbitrary function f in cartesian or spherical coordinates

$$\frac{\partial}{\partial \phi} f = -\frac{\partial f}{\partial x} r \sin\theta\ \sin\phi + \frac{\partial f}{\partial y} r \sin\theta\ \cos\phi = -y\frac{\partial f}{\partial x} + x\frac{\partial f}{\partial y}$$

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Laplace operator and separation of variables

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$$\left[-\frac{1}{2}\left(\underbrace{\frac{1}{r^2}\nabla^2_{\theta,\phi}+\nabla^2_r}_{\boldsymbol{\nabla}^2}\right)+V(r)\right]R(r)Y_{\ell,m}(\theta,\phi)=$$

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