Atomic physics and Quantum mechanics acompanying notes

Univ.-Prof. Dr. Enrico Arrigoni
TU Graz - Austria

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Students of the course
515.300 “Atomphysik und Quantenmechanik für ET/MB”
can access a more complete version of the lecture notes
(access password restricted)
interested people can ask me by e-mail: arrigoni@tugraz.at

PDF presentation using LaTeX and the Beamer Class
http://latex-beamer.sourceforge.net

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

- Failures of classical physics
  - Line spectra
- Wave and Particle duality
  - Double-slit experiment
  - Light carries momentum: Compton scattering
  - Matter (Electrons) as waves
- Bohr's atom

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

- Free particle
- Particle in a box
- Generalisations of the particle in a box
- Tunnel effect
- Three-dimensional box

Principles and Postulates of Quantum mechanics
- Postulates of Quantum Mechanics

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   - First step: “particle on a ring”
   - Second step: “particle on the surface of a sphere”
   - Electron spin

[illegible]

   - Qualitative solution
   - Classification of atomic orbitals

Many-electron atoms and the periodic table
   - Pauli principle
   - Building-up principle
   - Hund's rule

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Suggested literature I

1. S. M. Blinder, **Introduction to Quantum Mechanics in chemistry, Material Science, and Biology**
   see also `http://www.umich.edu/~chem461/`
   the class essentially based on this book
2. L. van Dommelen **Fundamental Quantum Mechanics for Engineers**
   notes available at `http://www.eng.fsu.edu/~dommelen/quantum`
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

Suggested literature II

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

(See also Blinder, Chap 1.1-1.2)

Blinder,Chap. 1, Pages 1-5

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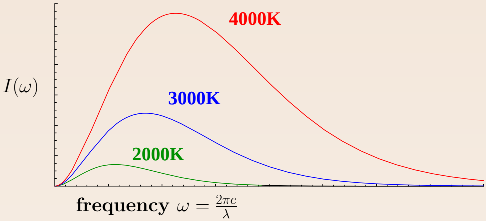
7. Principles and Postulates of Quantum mechanics

(See also Blinder, Chap 1.3-1.6)

Blackbody radiation

Blinder,Chap. 1, Pages 6-7

At high temperatures matter (for example metals) emits a continuum radiation spectrum. The “color” they emit is pretty much the same at a given temperature independent of the particular substance.



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 maximum frequency ω_{max} ("color") of the distribution obeys the law (Wien's law) $\omega_{max} = \text{const. } T$

An idealized description is the so-called blackbody model, which describes a perfect absorber and emitter of radiation.
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.

$$n(\omega) \propto \omega^2 \tag{4.1}$$

The energy equipartition law of statistical physics tells us that at temperature T each mode is excited (on average) to the same energy [illegible]

with a certain frequency ω would be given by

$$u(\omega, T) \propto K_B\, T\, \omega^2 \tag{4.2}$$

(Rayleigh hypothesis).

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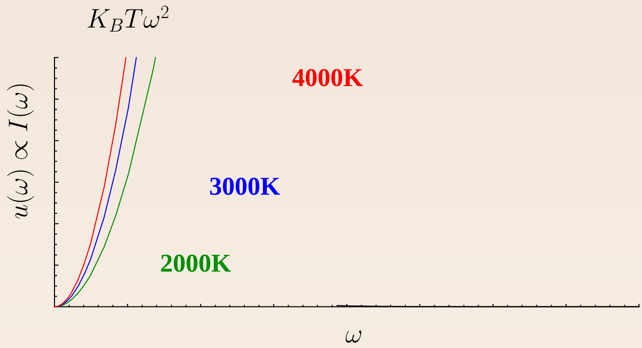
$$n(\omega) \propto \omega^2 \tag{4.1}$$

The energy equipartition law of statistical physics tells us that at temperature T each mode is excited (on average) to the same energy $K_B\ T$.
Therefore, at temperature T the energy density $u(\omega, T)$ of all oscillators with a certain frequency ω would be given by

$$u(\omega, T) \propto K_B\ T\ \omega^2 \tag{4.2}$$

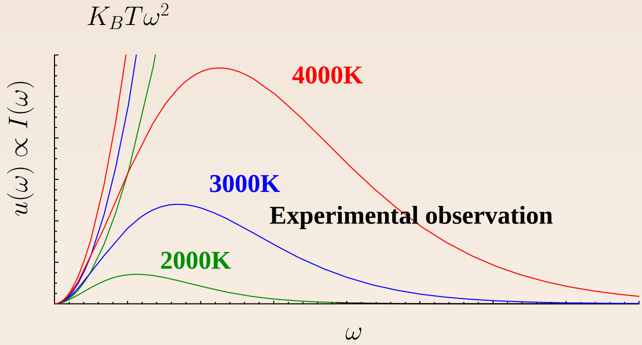
(Rayleigh hypothesis).



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

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

$$U = \int_0^\infty u(\omega, T)\, d\omega \qquad (4.3)$$



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

$$U = \int_0^\infty u(\omega, T)\ d\omega \tag{4.3}$$

would diverge !

Planck's hypothesis:

The "oscillators" (electromagnetic waves), cannot have a continuous of energies. Their energies come in "packets" (quanta) of size $h\ \nu = \hbar\omega$.
$h \approx 6.6 \times 10^{-34} Joules\ sec$ $\quad (\hbar = \frac{h}{2\pi})$ Planck's constant.

At small frequencies, as long as $K_B T \gg \hbar\omega$, this effect is irrelevant.
The effect will start to be important at $K_B T \sim \hbar\omega$: here $u(\omega, T)$ will start to decrease. And in fact Wien's empiric observation is that $u(\omega, T)$ displays a maximum at $\hbar\omega \sim K_B T$.

[illegible]

A more elaborate theoretical treatment gives the correct functional form

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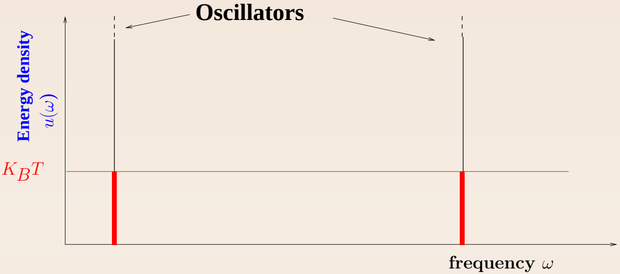
Eventually, for $K_B T \ll \hbar\omega$ the oscillators are not excited at all, their energy is vanishingly small.

A more elaborate theoretical treatment gives the correct functional form.

Average energy of “oscillators”



(A) Classical behavior:

Average energy of oscillator $< E >= K_B T$.

(B) Quantum behavior: Energy quantisation

Small ω: Like classical case: oscillator is excited up to $< E >\approx K_B T$.
$\Rightarrow \; u(\omega) \propto K_B T \omega^2$.

Large ω: first excited state ($E = 1 * \hbar\omega$) is occupied with probability

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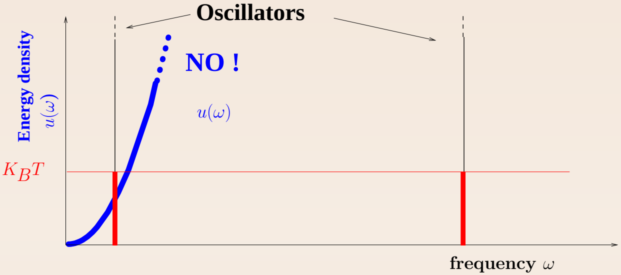

(A) Classical behavior:

Average energy of oscillator $< E >= K_B T$.

$\Rightarrow$ Distribution $u(\omega) \propto K_B T \omega^2$ at all frequencies!

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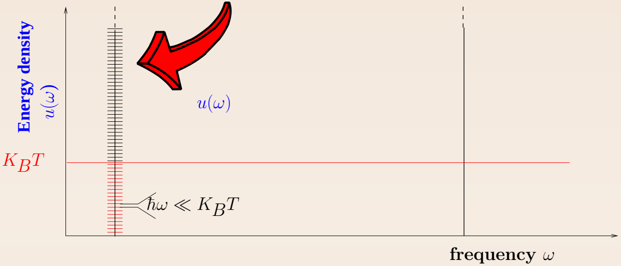

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Large ω: first excited state ($E = 1 * \hbar\omega$) is occupied with probability $e^{-\hbar\omega/K_B T}$ (Boltzmann Factor): $\Rightarrow < E > \approx \hbar\omega \; e^{-\hbar\omega/K_B T}$

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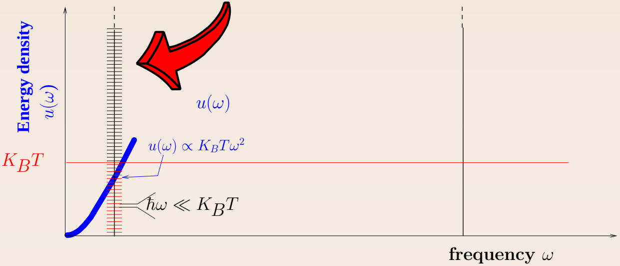

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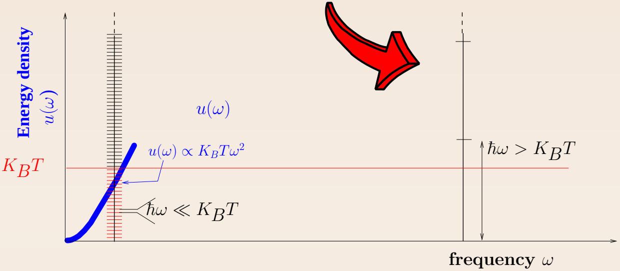

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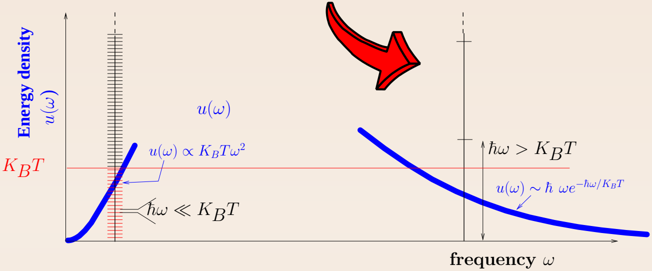

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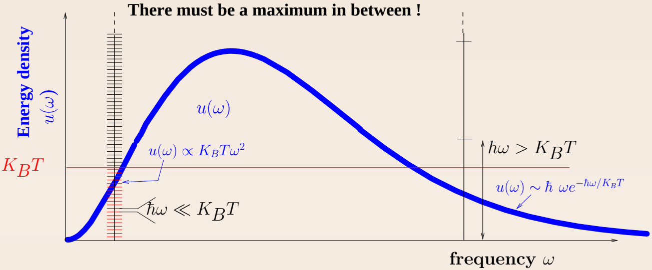

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See also [Blinder], Chap. 1, Pages 8-9

Photoelectric effect

Photoelectric effect

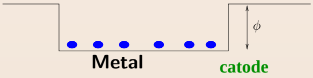
Electrons in a metal are confined by an energy barrier (work function) ϕ.

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

Light transfers an energy E_{light} to the electrons.

The rest of the energy $E_{light} - \phi$ goes into the kinetic energy of the electron $E_{kin} = \frac{1}{2} m v^2$.

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



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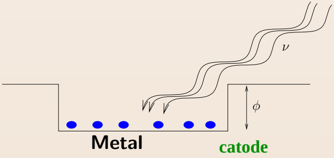

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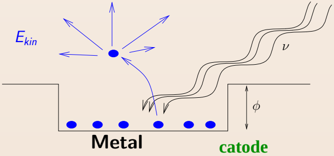

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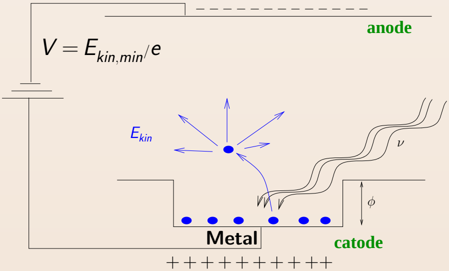

Photoelectric effect

examples:

Classicaly, we would espect the total energy transferred to an electron $E_{light} = \phi + E_{kin}$ to be proportional to the radiation intensity.

The experimental results give a different picture:
while the current (i. e. the number of electrons per second expelled from the metal) is proportional to the radiation intensity.

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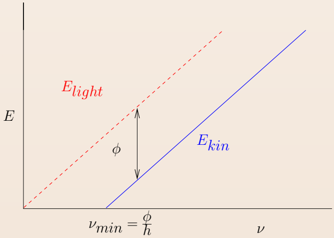
while the current (i. e. the number of electrons per second expelled from the metal) is proportional to the radiation intensity,

E_{light} is proportional to the frequency of light:

$$E_{light} = h\,\nu \tag{4.4}$$



Summary: Planck's energy quantum

The explanation of Blackbody radiation and of the Photoelectric effect are explained by Planck's idea that light carries energy only in "quanta" of size

$$E = h\nu \tag{4.5}$$

This means that light is not continuous object, but rather its constituent

Summary: Planck's energy quantum

The explanation of Blackbody radiation and of the Photoelectric effect are explained by Planck's idea that light carries energy only in "quanta" of size

$$E = h\nu \tag{4.5}$$

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

Line spectra

Blinder,Chap. 1, Pages 10-13

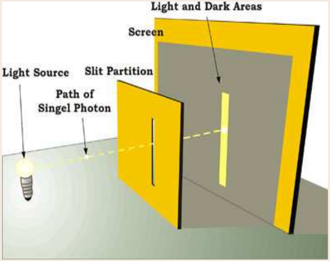
(See also Blinder, Chap 2.1-2.2)

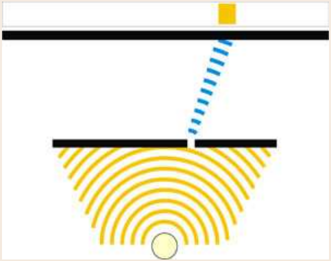
Blinder,Chap. 2, Pages 1-2

Double-slit experiment

Double-slit experiment

This experiment was done in order to distinguish whether light behaves as particle or as a wave.





a

Monochromatic, coherent light is shone through a single slit

Double-slit experiment

This experiment was done in order to distinguish whether light behaves as particle or as a wave.

[a]

Double slit, naive expectation

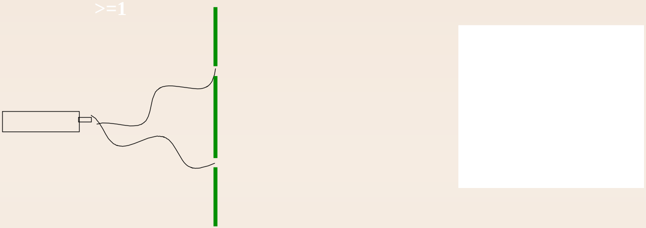
Double-slit experiment

This experiment was done in order to distinguish whether light behaves as particle or as a wave.

[a]

Double slit: interference pattern

Double-slit experiment



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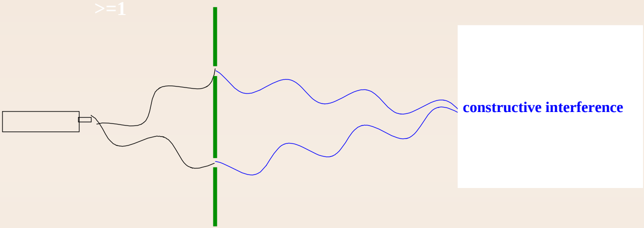

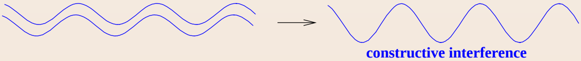

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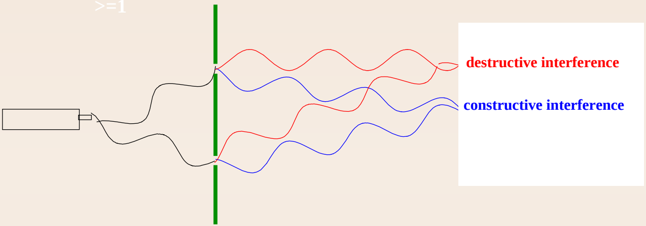

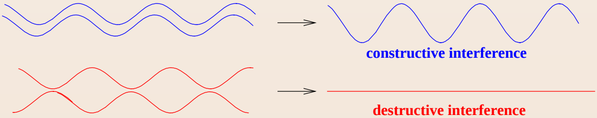

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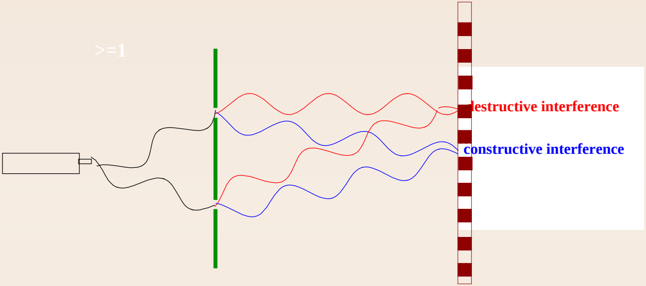

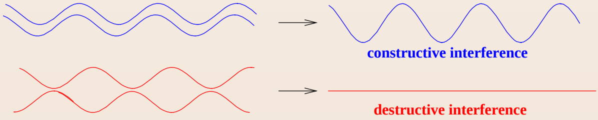

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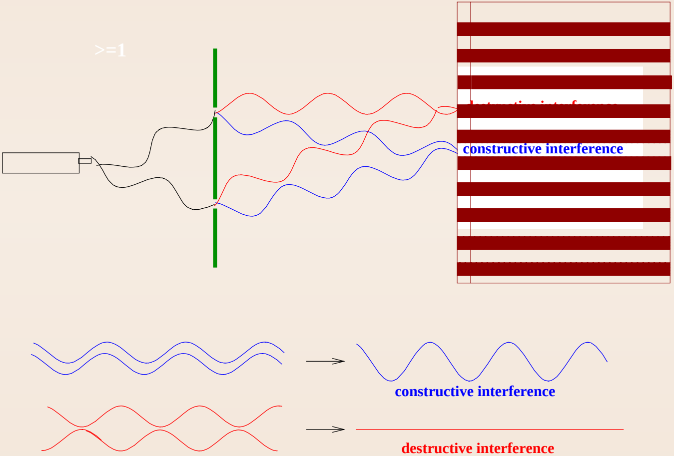
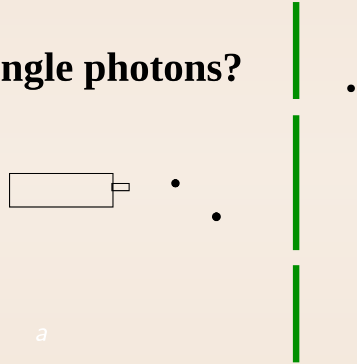


The observation of an interference pattern proves the wave nature of light!

Blinder,Chap. 2, Pages 3-5

Light: particles or waves ?



Single photons?

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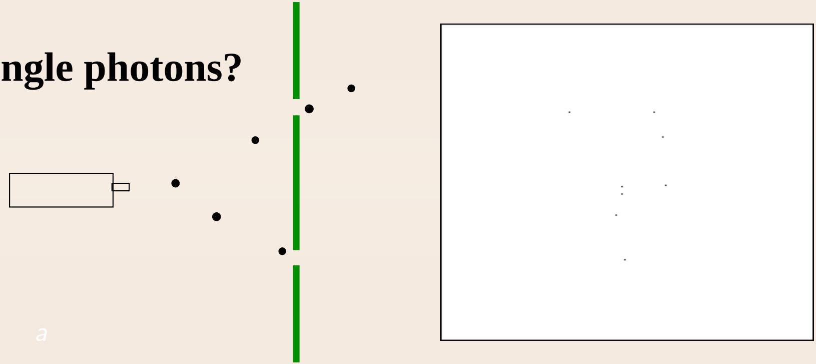

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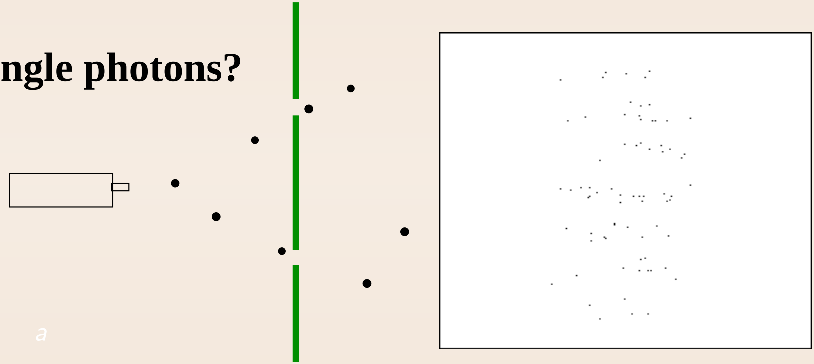

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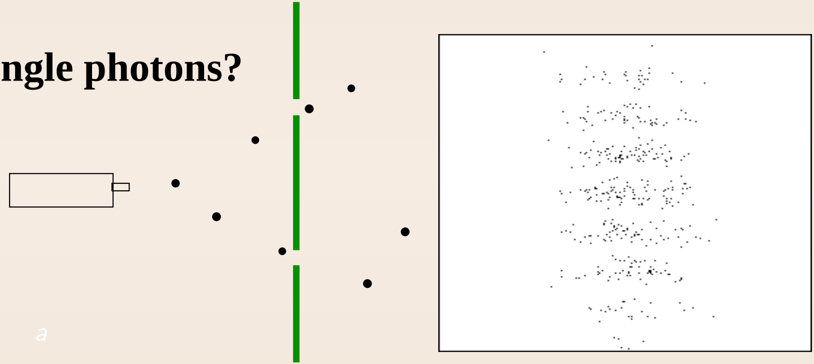

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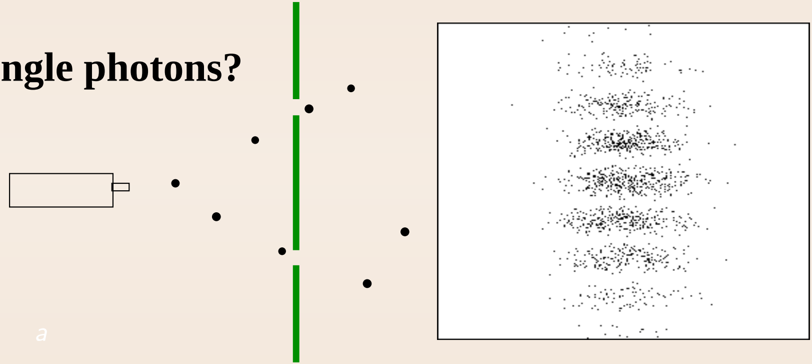

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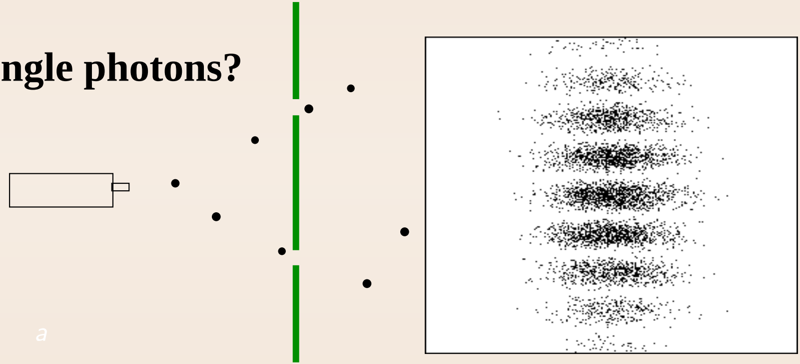

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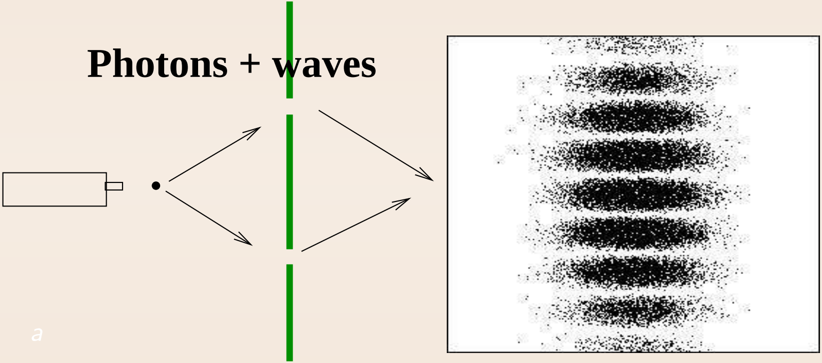

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Blinder,Chap. 2, Pages 6-6

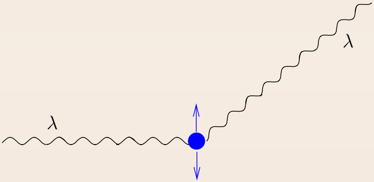
Light carries momentum: Compton scattering

See also [Blinder], Chap. 2, Pages 7-7

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

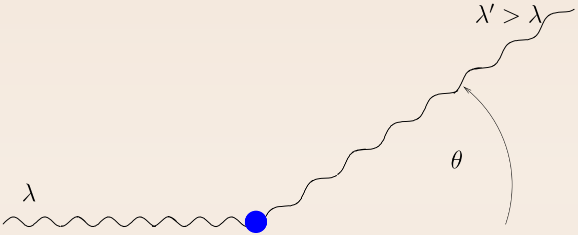
Classical view (Thomson scattering)

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



At high photon energies, the Doppler effect must be taken into account: light is emitted in a broader frequency range.

Experimental result (Compton scattering)



$$\lambda' - \lambda = \frac{h}{m_e c}(1 - \cos\theta) \tag{5.2}$$

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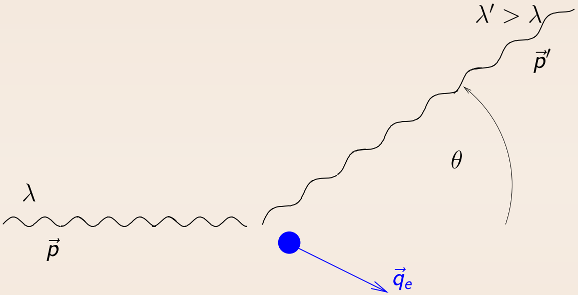

$$\vec{p} = \vec{p}' + \vec{q}_e \tag{5.1}$$

$$\lambda' - \lambda = \frac{h}{m_e c}(1 - \cos\theta) \tag{5.2}$$

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

$$\mathbf{p} = \frac{h}{\lambda} \tag{5.3}$$

and due to the kinematics part of the momentum is transferred to the electron.

This is consistent with Planck's energy formula for photons and such

$$E = mc^2 = h\nu \quad \Rightarrow \quad p = mc = E/c = h\nu/c = h/\lambda$$

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This is consistent with Planck's energy formula for photons and with relativity, assuming that photons velocity is c:

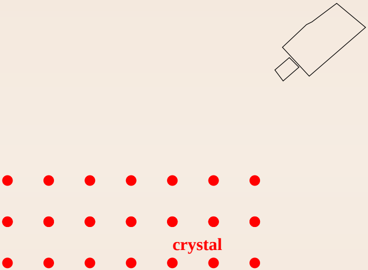
$$E = m\,c^2 = h\nu \quad \Rightarrow \; p = m\,c = E/c = h\nu/c = h/\lambda \tag{5.4}$$

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
the distance between atoms is of the order of the wavelength of *x*-rays

Surprisingly, an interference pattern was observed for electrons as well.

Based on these ideas, de Broglie suggested that matter (electrons) might

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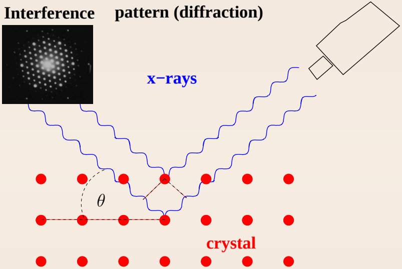

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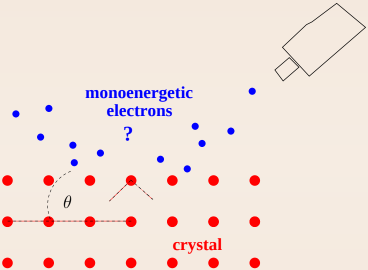

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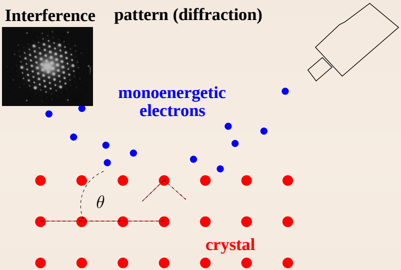

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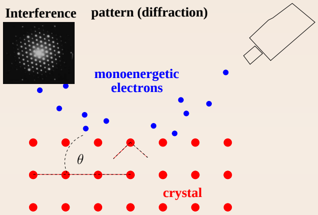

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Based on these ideas, de Broglie suggested that matter (electrons) might also behave as waves.

These "matter waves" have a wavelength (cfr. (5.3))

$$\lambda = \frac{h}{p} \tag{5.5}$$

Blinder,Chap. 2, Pages 8-9

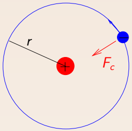
(See also Blinder, Chap 7.1-7.2)

Bohr's atomic model used the idea that electrons have a wavelength to explain:

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

See also [Blinder], Chap. 7, Pages 1-6

Bohr Atom (Hydrogen)



Rutherford atom:

Coulomb force provides centripetal force (Gauss unit system). For a circular orbit we have (in cgs units):

$$\frac{e^2}{r^2} = \frac{m_e v^2}{r} \tag{6.1}$$

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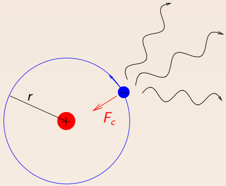

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Problem: accelerated (rotating) charges emit radiation: electron would loose energy and collapse into the nucleus!

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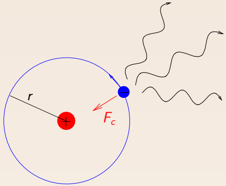

Bohr's idea of quantized orbits

(1) Electron carry (de Broglie) wavelength (5.5) $\lambda = h/p = h/vm_e$

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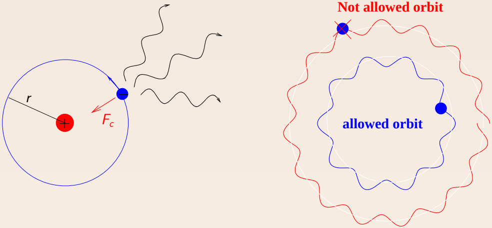

Bohr's idea of quantized orbits

(1) Electron carry (de Broglie) wavelength (5.5) $\lambda = h/p = h/vm_e$

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

$$2\pi\ r = n\ \lambda = n\ \frac{h}{vm_e} \qquad n = 1, 2, 3, \ldots \tag{6.2}$$

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

Quantisation of orbitals

From (6.2) we obtain

$$v = \frac{n\ \hbar}{r\ m_e} \tag{6.3}$$

---

[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 (6.1), we obtain

$$\frac{e^2}{r^2} = \frac{n^2 \hbar^2}{r^3 m_e} \Rightarrow \boxed{r = n^2 a_0} \tag{6.4}$$

where

$$a_0 = \frac{\hbar^2}{m_e\ e^2} \tag{6.5}$$

is the Bohr's radius[1]

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The energy of the orbits is given by kinetic plus potential energy (use (6.1))

$$E = \frac{1}{2} m_e v^2 - \frac{e^2}{r} = -\frac{1}{2}\frac{e^2}{r} = -\frac{1}{2}\frac{e^2}{a_0}\frac{1}{n^2} \tag{6.6}$$

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

$$h \; c \; \mathcal{R} = \frac{1}{2} \frac{e^2}{a_0} \approx 13.6 \; eV \tag{6.7}$$

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

---

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Explanation of line spectra (Hydrogen)

The electron can gain or loose energy by jumping between these allowed 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, (6.8) 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 (6.8).

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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 must 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 (6.8):

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

6. Quantum mechanics of some simple systems

(See also Blinder, Chap 2.3-2.5)

The goal of this chapter is to develop a description of the dynamics of quantum-mechanical particles such as electrons.

As we have learned in previous chapters, such particles behave as waves, and, thus, should be described by a similar object like electromagnetic waves.

This is called the wavefunction ($\Psi(\mathbf{r}, t)$), which is a function of space $\mathbf{r}$ and time t, and is the analogous of the electric field amplitude $\mathbf{E}$ for photons.

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We now want to learn how this object evolves in time. This is given gy the famous Schrödinger equation.

See also [Blinder], Chap. 2, Pages 9-12

Euristic 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):

$$\Psi(x,t) = \cos(kx - \omega t) = \mathrm{Re}\ e^{i(kx-\omega t)} \tag{7.1}$$

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

$$k = \frac{2\pi}{\lambda}, \qquad \omega = 2\pi\nu \tag{7.2}$$

We now see that ( ) obeys the wave equation

$$\frac{\partial^2}{\partial x^2}\Psi - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\Psi = 0 \tag{7.3}$$

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Differential operators

For the form (7.1), differential operators are particularly simple:

$$\frac{\partial}{\partial x}\Psi = i\ k\ \Psi \qquad \frac{\partial}{\partial t}\Psi = -i\ \omega\ \Psi \tag{7.4}$$

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

$$\frac{\partial}{\partial x} \to i\ k \qquad \frac{\partial}{\partial t} \to -i\ \omega \tag{7.5}$$

but careful, it holds only for the form (7.1)!

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Inserting (7.5) in (7.3), we see that the latter is satisfied provided $(-k^2 + \frac{\omega^2}{c^2})\Psi = 0$ which gives the well-known dispersion relation

$$|\omega| = c|k| \quad \to \quad \nu\lambda = c \tag{7.6}$$

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Introducing the Planck (4.5) and de Broglie (5.5) relations in (7.5), we observe that

$$\boxed{p = \frac{h}{\lambda} = \hbar\ k = -i\hbar\frac{\partial}{\partial x} \qquad\qquad E = \hbar\omega = i\hbar\frac{\partial}{\partial t}} \tag{7.7}$$

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

Wave equation for free particles

(7.3) holds for electromagnetic waves (photons). We have indeed already seen (see (5.4)) that the corresponding (7.6) is the energy-momentum relation $E/c = p$ valid for particles moving with the light velocity c.

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

$$E = \frac{p^2}{2m} \qquad (7.8)$$

Replacing ( ), and applying it to the wavefunction Ψ, we obtain

$$\underbrace{i\hbar\frac{\partial}{\partial t}}_{E}\Psi = \frac{1}{2m}\underbrace{\left(-i\hbar\frac{\partial}{\partial x}\right)^2}_{p^2}\Psi \Rightarrow i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} \qquad (7.9)$$

Which is the (time-dependent) Schrödinger equation for free particles.

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Potential

So far we have described the kinetic energy part.
To include a potential energy $V(x)$, we simply replace (7.8) with

$$E = \frac{p^2}{2m} + V(x) \tag{7.10}$$

$$i\hbar\frac{\partial\psi}{\partial t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi \tag{7.11}$$

The generalisation to three dimensions is straightforward:

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$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = \left(-\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 + V(\mathbf{r}) \right) \Psi} \tag{7.12}$$

See here for three dimensions:

Time-independent Schrödinger equation

Time-independent Schrödinger equation

We look for solutions of (7.12) in the form

$$\Psi(t, \mathbf{r}) = \exp(-i\frac{\tilde{E}\ t}{\hbar})\ \psi(\mathbf{r}) \tag{7.13}$$

with some constant $\tilde{E}$.

Time-independent Schrödinger equation

We look for solutions of (7.12) in the form

$$\Psi(t,\mathbf{r}) = \exp(-i\frac{\tilde{E}\ t}{\hbar})\ \psi(\mathbf{r}) \tag{7.13}$$

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

$$i\hbar\frac{\partial}{\partial t}\Psi = \tilde{E}\Psi \tag{7.14}$$

comparing with the second of (7.7), we see that
we can identify $\tilde{E}$ with the energy E itself.

Time-independent Schrödinger equation

$$\Psi(t,\mathbf{r}) = \exp(-i\frac{E\ t}{\hbar})\ \psi(\mathbf{r}) \tag{7.13}$$

$$i\hbar\frac{\partial}{\partial t}\Psi = E\Psi \tag{7.14}$$

Using (7.14) in (7.12) and dividing both sides by $\exp(-i\frac{E\ t}{\hbar})$ we obtain the

time-independent Schrödinger equation

$$\boxed{\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})} \tag{7.15}$$

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

Schrödinger equation: summary of ideas

These results suggest us 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 $\mathbf{p}$:

$$\begin{aligned} E &\rightarrow i\hbar\frac{\partial}{\partial t} = \hat{H} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r}) \\ \mathbf{p} &\rightarrow -i\hbar\boldsymbol{\nabla} \end{aligned} \tag{7.16}$$

- () 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 vecto

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- (7.15) 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.

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.

- Similarly, for a quantum-mechanical particle:

$$\rho(\mathbf{r}) \propto |\psi(\mathbf{r})|^2 \qquad (7.17)$$

- probability density what's this?
  given a small (infinitesimal) volume ΔV centered around $\mathbf{r}$,
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Normalisation

- Proportional ($\propto$) means that $|\psi(\mathbf{r})|^2 = A\ \rho(\mathbf{r})$, with A some constant.
- A can be determined by requiring that the total probability be 1, i. e. be normalized.

$$1 = \int \rho(\mathbf{r})\, dV = \frac{1}{A} \int |\psi(\mathbf{r})|^2\, dV \qquad (7.18)$$

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$$A = \int |\psi(\mathbf{r})|^2\, dV \qquad (7.19)$$

- Alternatively, one can use a normalized wavefunction

$$\psi_N(\mathbf{r}) = \frac{1}{\sqrt{A}} \psi(\mathbf{r}) \qquad (7.20)$$

- 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 (even a complex one), describe the same physical state.

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- In addition, both obviously have the same $\rho(\mathbf{r})$.

See also [Blinder], Chap. 2, Pages 13-14

Insertion: functions as vectors

functions as vectors:

Summary: Schrödinger equation

Summary of important results

- The dynamics of a quantum mechanical particle is described by the Wavefunction $\Psi(t, \mathbf{r})$
- Physical quantities (observables) are replaced by differential operators: $p \to -i\hbar\nabla \qquad E \to i\hbar\frac{\partial}{\partial t}$
- From the relation $E = p^2/(2m) + V(\mathbf{r})$ follows the

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\,\Psi \qquad (7.22)$$

with the Hamilton operator $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$

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(See also Blinder, Chap 3, Chap 5.1)

Free particle

See also [Blinder], Chap. 3, Pages 1-2

Free particle

- We consider (7.15) 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.)

$$\hat{H}\ \psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\ \psi(x) + V\ \psi(x) = E\ \psi(x) \tag{8.1}$$

- This can be written in the form

$$\psi''(x) + k^2\psi(x) = 0 \quad \text{with } k^2 = \frac{2m(E-V)}{\hbar^2} \tag{8.2}$$

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

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Free particle

Due to (8.1), the two solutions $e^{\pm i\ k\ x}$ are eigenfunction of the Hamilton operator $\hat{H}$ with eigenvalue E and due to (8.4) they are also eigenfunctions of the momentum operator $p = -i\hbar\boldsymbol{\nabla}$ with eigenvalue $\hbar k$
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

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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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This is achieved by taking the potential
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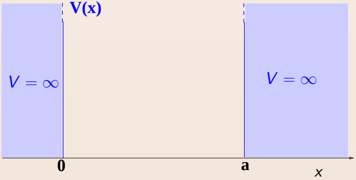
$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ \infty & \text{for } x < 0 \text{ and } x > a \end{cases} \tag{8.5}$$



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Here comes an important result of quantum mechanics: linear combinations of degenerate solutions are also solutions of (7.15) with the same energy. See here for details:

Particle in a box

examples:

We thus look for a suitable linear combination

$$\psi(x) = a\, e^{i\ k\ x} + b\, e^{-i\ k\ x} \tag{8.7}$$

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

$$\psi(x) = \sin kx \tag{8.8}$$

which is indeed a solution of (7.15) 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:

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From trigonometry we know that this is fullfilled if $ka = (integer\ *\ \pi)$ Since a is fixed, this amounts to a condition for k:

$$k = \frac{n\ \pi}{a} \quad \text{with } n \text{ integer} \tag{8.10}$$

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the energy:

$$E = \frac{\hbar^2\ k^2}{2m} = \frac{\hbar^2 (n\pi)^2}{2m\ a^2} \equiv E_n \tag{8.11}$$

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.

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

identifying ΔE with E_1, we have

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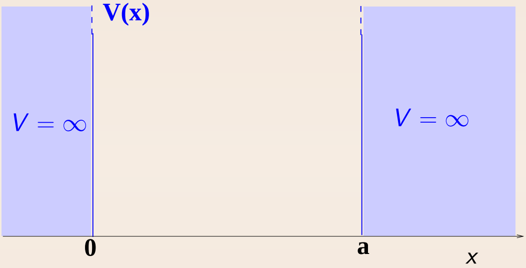
Notice that the state with lowest energy, the ground state does not have zero energy as classically expected, but has a finite energy $E_1 = \frac{\hbar^2 \pi^2}{2m\ a^2}$.
This is the so-called zero point energy.
This comes from the fact, that a particle confined in a finite region of size $\Delta x = a$ 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

$$\Delta p\ \Delta x \sim \pi \hbar \tag{8.12}$$

which is related to the well-known Heisenberg uncertainty principle

Summary: particle in a box



Summarizing, wavefunctions and corresponding energies:

$$\psi_n(x) = \sin\frac{n\ \pi}{a}x \qquad E_n = \hbar^2(n\ \pi)^2/(2m\ a^2) \qquad (n = 1, 2, \cdots) \quad (8.13)$$

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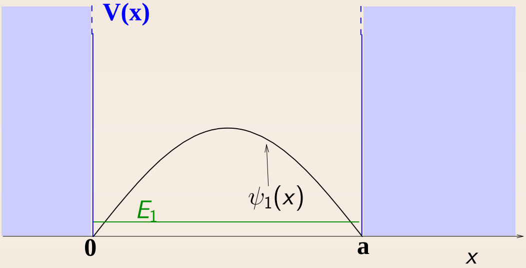

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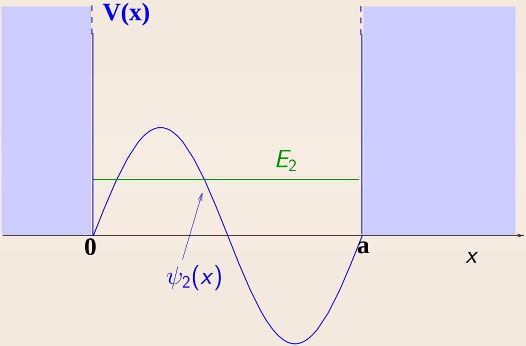

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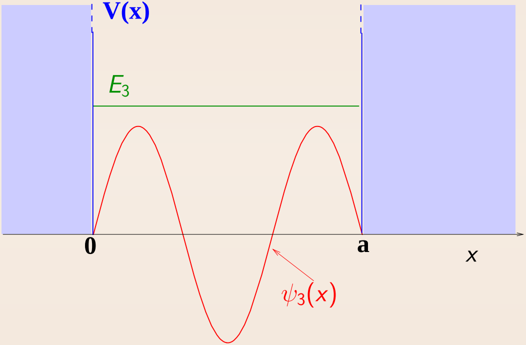

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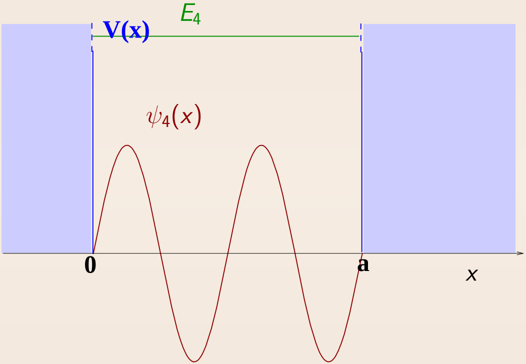

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Energy quantisation:

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 minimum energy is always larger than the minimum value of the [illegible]
- The ground state wavefunction 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 is zero:

$$\int_0^a \sin\frac{n\pi\ x}{a}\ \sin\frac{m\pi\ x}{a}\ dx = 0 \quad \text{For } n \neq m \tag{8.14}$$

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. 8.1, 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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- Two wavefunctions with different energies are orthogonal, i. e. their scalar product (see here) is zero:

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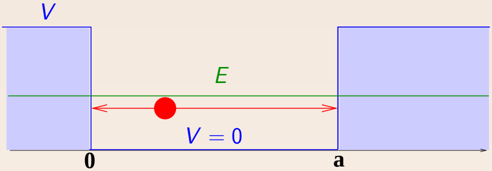
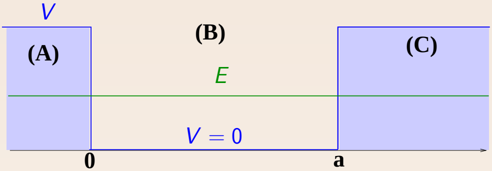
Generalisations of the particle in a box

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 (8.2) separately in the three regions A,B,C:

$$\psi''(x) + k^2\psi(x) = 0 \quad \text{with } k^2 \equiv \frac{2m(E-V)}{\hbar^2} \tag{8.15}$$

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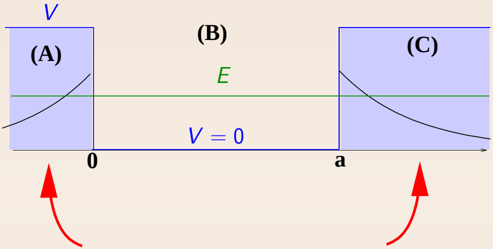


$$\psi''(x) + k^2 \psi(x) = 0 \quad \text{with } k^2 \equiv \frac{2m(E-V)}{\hbar^2} \tag{8.15}$$

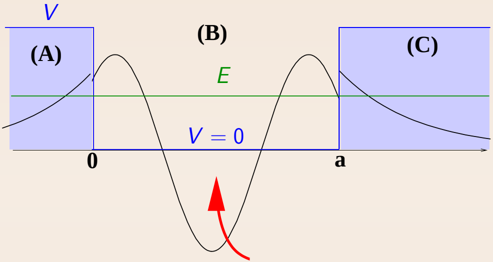
$\boxed{\text{A+C}}$ $0 > k^2 = -q^2$.

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

The wave function does not vanish in the “classically forbidden” region

there is a nonzero probability to find the particle there

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



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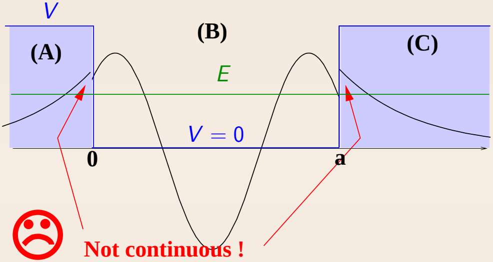
$\boxed{\text{B}}$ $k^2 > 0$, oscillating solution as in (8.7).

Linear combination of two degenerate solutions:

$$\boxed{A \;\cos kx + B \;\sin kx} \qquad (8.16)$$

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



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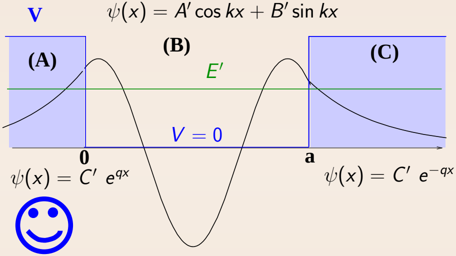
However: The wave function must be continuous and differentiable!
What can we do?

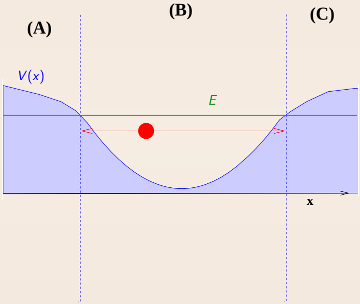
Finite potential V



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

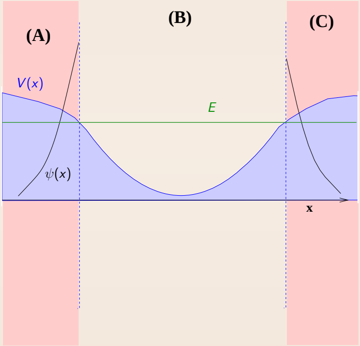
For example: harmonic oscillator



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

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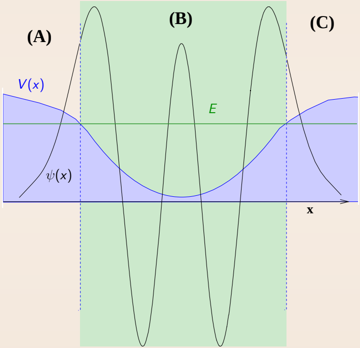
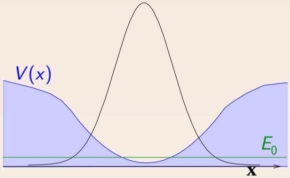


"Allowed" region (B): oscillating behavior of $\psi(x)$

Ground state and excited states

For example: harmonic oscillator

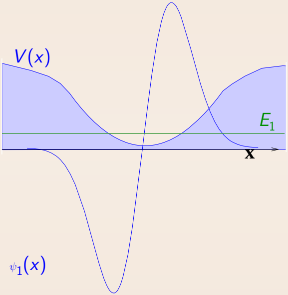


$\psi_0(x)$

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:

$$\langle\psi_n|\psi_m\rangle \equiv \int \psi_n(x)^*\psi_m(x)\ d\ x = 0 \quad (n \neq m) \tag{8.17}$$

Ground state and excited states

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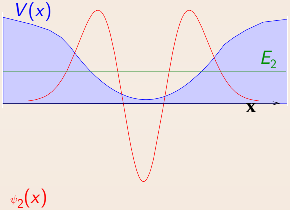

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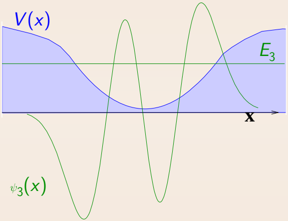

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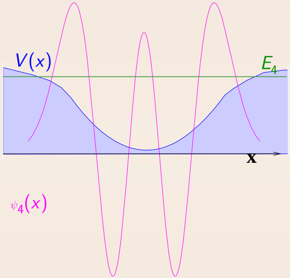

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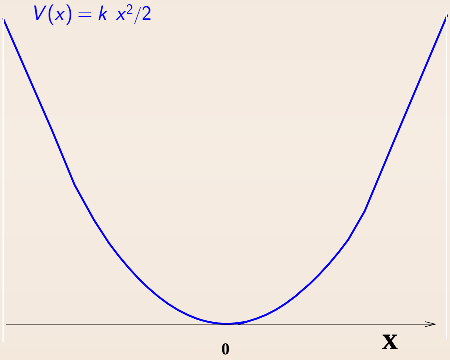
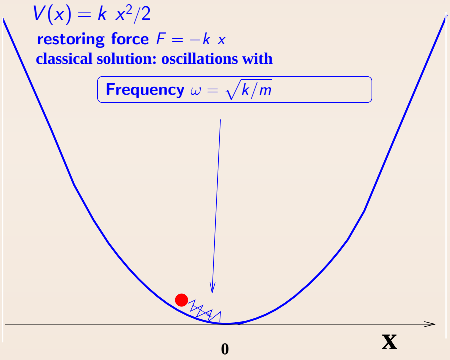
Harmonic oscillator

Why is it so interesting



Harmonic oscillator

Why is it so interesting



$V(x) = k\ x^2/2$

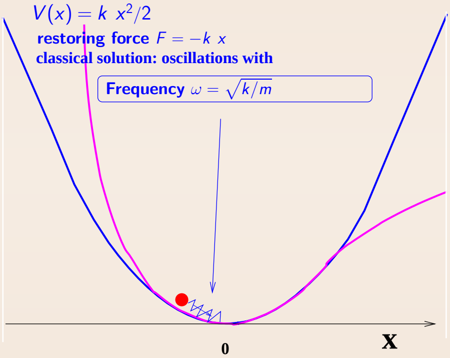
restoring force $F = -k\ x$

classical solution: oscillations with

Frequency $\omega = \sqrt{k/m}$

Harmonic oscillator

Why is it so interesting

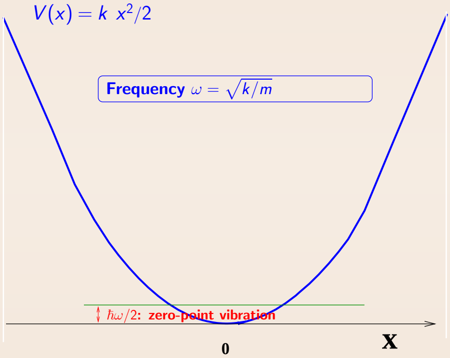


Is it a too special model?

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

Harmonic oscillator

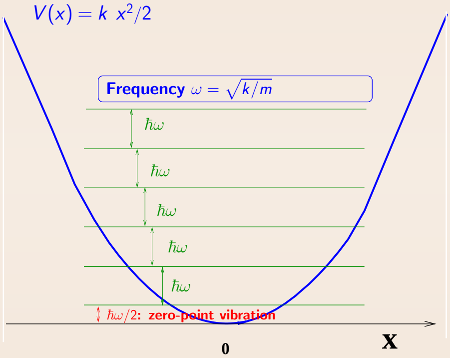
Why is it so interesting



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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(2) Equispaced energies: $E_n = \hbar\omega\ (n + \frac{1}{2})$

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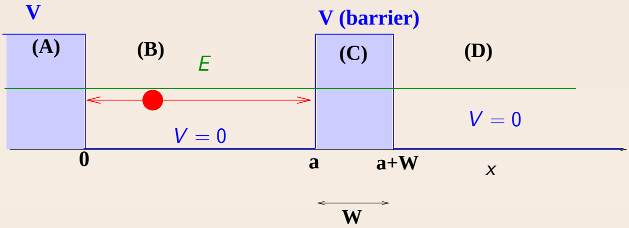
(3) Eigenfunctions

Tunnel effect

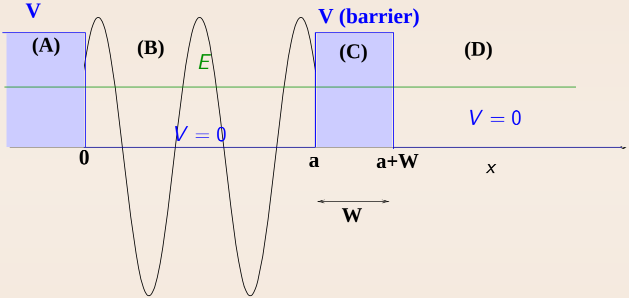
Tunneling



Classical particle would stay confined in region (B)

Quantum result:

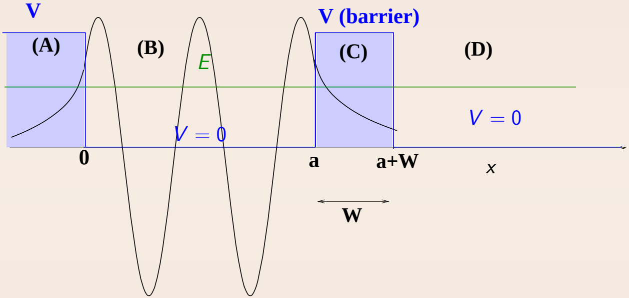
Tunneling



Quantum result:

Region B: oscillating behavior

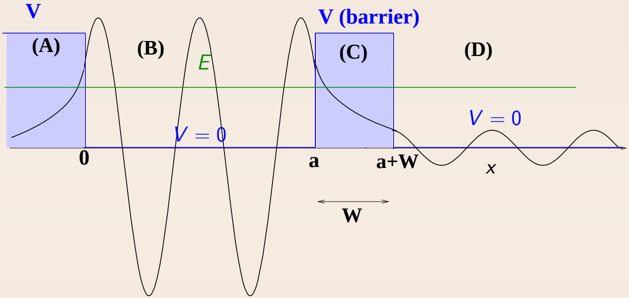
Tunneling



Quantum result:

(C): Exponential decay across the barrier

Tunneling



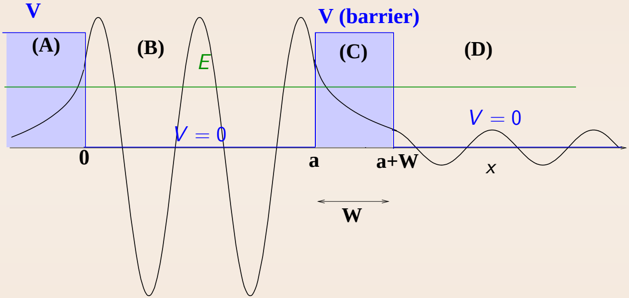
Quantum result:

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

$$e^{-q\ W} = e^{-\sqrt{\frac{2m(V-E)}{\hbar^2}}W} \tag{8.18}$$

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

Tunneling



Quantum result:

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

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

Three-dimensional box

n on the three-dimensional box is no longer in the program of

Blinder,Chap. 3, Pages 10-13

The section “Principles and Postulates of Quantum mechanics” has been changed (considerably reduced) with respect to previous versions

(See also Blinder, Chap 4.1-4.6)

Insertion: Operators

Operators:

See also [Blinder], Chap. 4, Pages 1-6

See also [Blinder], Chap. 4, Pages 9-10

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.
- These postulates have been so far been confirmed by all the experiments build up in order to verify (or falsify) their validity.
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Postulate I: Wavefunction

- The state of a system (here one particle) is completely defined by a complex wavefunction, $\Psi(t, \mathbf{r})$
  (or $\psi(\mathbf{r})$ if we stick to a fixed time t),
  which contains all the information that can be known about the system.

- 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 (8.13).
- Now, the wavefunction $\psi(x)$ of a particle must not necessary be one of the $\psi_n(x)$, but it can also be in a superposition, e. g.
  $\psi(x) = a\,\psi_1(x) + b\,\psi_2(x)$
  [illegible]

  In quantum chemistry, this is called a resonant state.

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  $\psi(x) = a\ \psi_1(x) + b\ \psi_2(x)$
  In that case it means that the energy is neither E_1 nor E_2: it is simply not sharply defined.
  In quantum chemistry, this is called a resonant state.

Postulate II: Observables and Operators

- Dynamical variables (so-called observables) are represented by Hermitian operators
- Important examples of observables are:
  - Coordinates: $\hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z})$
  - Momentum: $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, $\hat{p}_y$ [illegible], $\hat{p}_z$ ($\hat{\mathbf{p}} = -i\hbar\nabla$) [illegible]
  - Energy (Hamiltonian) $\hat{H}$.
  - Angular momentum $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$
- 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 III: Measurement

Observables and Eigenvalues

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

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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 measure even if we know $\psi(x)$ exactly! We merely know the probability density (see (7.17)) to find the particle around a certain x.

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- If one measures the energy in a resonating state $\psi(x) = a\,\psi_1(x) + b\psi_2(x)$, one can obtain as result either E_1 or E_2.

Postulate III: Measurement

Expectation Values of Measurement Results

Having learned that results of measurements have certain probabilities, we want to know something about the statistics.

A useful information that one asks in statistics is the following:
If we measure an observable many times (on different copies of the same state).

This average is termed expectation value. For a [illegible] the expectation value is represented as $\left\langle \hat{A} \right\rangle$

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Expectation Values of Measurement Results

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

$$\langle \hat{x} \rangle = \frac{\int x \; |\psi(x)|^2 \; d\, x}{\int |\psi(x)|^2 \; d\, x}$$

$$\langle \hat{A} \rangle = \frac{\int \psi(x)^* \; \hat{A} \; \psi(x) \; d\, x}{\int \psi(x)^* \; \psi(x) \; d\, x} \qquad (9.1)$$

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

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Examples

Evaluate the expectation value $\langle\psi_1|\hat{p}\ \psi_1\rangle$ where ψ_1 is the ground state of the particle in a box.

Solution:

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

Application of $\hat{p} = -i\frac{d}{dx}$ yields

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

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this shows that ψ_1 is eigenfuntion of $\hat{p}^2$ with eigenvalue k^2.

Therefore one should expect that the expectation value will be k^2, and indeed.

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Futher example: Heisenberg uncertainty:

Postulate IV: Time evolution

The wave function evolves according to the Schrödinger equation (7.22)

$$i\hbar\frac{\partial\Psi(t,\mathbf{r})}{\partial t} = \hat{H}\ \Psi(t,\mathbf{r}) \tag{9.3}$$

Important things to remember

- The state if 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 $\hat{p}$)
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- A Measurement of an observable
  - Is unpredictable (even if one knows $\psi(x)$)
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(See also Blinder, Chap 6.1-6.6)

Motion in a central potential

- Our goal ist 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.
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Goals of this chapter

In this chapter we will pursue the following goals

- Identify the operators associated to 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 (7.15) becomes:[2]

$$-\frac{\hbar^2}{2M}\frac{\partial}{\partial s^2}\,\psi = E\,\psi \tag{10.1}$$

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 (10.1) as:

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

$$E = \frac{L_z^2}{2I} = \frac{L_z^2}{2M\ R^2} \tag{10.3}$$

where $I = M\ R^2$ is the moment of inertia
and L_z the z-component of the angular momentum

A comparison of (10.3) with (10.2) suggests to
identify the operator $\hat{L}_z^2$ with $-\hbar^2 \frac{\partial^2}{\partial\phi^2}$ or

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi} \tag{10.4}$$

A more rigorous derivation can be found here:
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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.

$$f(\phi + 2\pi) = f(\phi) \tag{10.5}$$

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

$$f(\phi) = e^{im\;\phi} \qquad \text{where } L_z = \hbar \; m \tag{10.6}$$

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The difference with respect to the particle in a box lies in the boundary conditions (10.5), which are quite different from (8.6).

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

$$L_z = \hbar\ m \qquad m = 0, \pm 1, \pm 2, \cdots \tag{10.7}$$

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

Notice, that the eigenfunctions (10.6) are orthogonal, as they should be (see Sec. **??**)

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

From this we can also write down the normalised eigenfunctions (see (7.20)):

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

The difference with respect to the particle in a box lies in the boundary conditions (10.5), which are quite different from (8.6). 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

$$L_z = \hbar\ m \qquad m = 0, \pm 1, \pm 2, \cdots \tag{10.7}$$

i.e. L_z can only have values that are integer multiples of $\hbar$.
Notice, that the eigenfunctions (10.6) are orthogonal, as they should be (see Sec. **??**)

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Indeed the orbit length is $L = 2\pi R$, and a wave function of the form (10.6) has a wavelength $\lambda = L/m$.

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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 (7.15) 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:

$$\nabla^2 = \nabla_r^2 + \frac{1}{r^2}\nabla^2_{\theta,\phi}\,, \tag{10.8}$$

where we have introduced

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

$$\nabla^2_{\theta,\phi} \equiv \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{10.9}$$

[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

$$-\frac{\hbar^2}{2M\ R^2}\nabla^2_{\theta,\phi}\ Y(\theta,\phi) = E\ Y(\theta,\phi) \tag{10.10}$$

By expressing again the energy of the particle in terms of the angular momentum $\mathbf{L}$ and momentum of inertia $I = M\ R^2$ as $E = \frac{\mathbf{L}^2}{2I} = \frac{\mathbf{L}^2}{2\ M\ R^2}$, we can rewrite (10.10) as

$$-\hbar^2\ \nabla^2_{\theta,\phi}\ Y(\theta,\phi) = \mathbf{L}^2\ Y(\theta,\phi) \tag{10.11}$$

Similarly to Sec.10.1, we can thus identify the operator for the square of the angular momentum[4]

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\nabla^2_{\theta,\phi} \tag{10.12}$$

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

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

These have the property:

$$-\nabla^2_{\theta,\phi}\ Y_{\ell,m}(\theta,\phi) = \ell(\ell+1)\ Y_{\ell,m}(\theta,\phi)$$
$$\ell = 0,1,\cdots,\infty \qquad m = -\ell,-\ell+1,\cdots,\ell \tag{10.13}$$

I. e. they are eigenfunctions of $-\nabla^2_{\theta,\phi}$ with eigenvalues $\ell(\ell+1)$.
Here, ℓ a positive 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 $-\ell \leq m \leq \ell$
m has the same meaning as in (10.6), 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 polar coordinates (see (10.4), (10.9))

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Notice that, in general, the $Y_{\ell,m}$ are not eigenfunctions of L_x and/or L_y.
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 $\ell = 0$).
Since $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$, this means that $L_x^2 + L_y^2$ can never be zero, i.e. L_x and L_y always fluctuate.
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Here are the first few spherical harmonics

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\begin{array}{|l|l|l|}
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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_{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} \\
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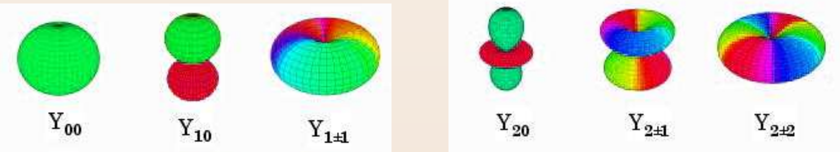

Figure: A plot of the first few spherical harmonics. The radius is proportional to $|Y_{\ell,m}|^2$, colors gives $\arg(Y_{\ell,m})$, with green$= 0$, red$= \pi$.

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 analogous to 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)

$$S^2 = \hbar^2\, s(s+1) \qquad S_z = \hbar m_s \qquad \text{with } m_s = -s, -s+1, \cdots, s \quad (10.17)$$

However, the important difference with ℓ is that $s = \frac{1}{2}$, i. e. it is half-integer.

From (10.17), since s is fixed, there are two possible states classified by $m_s = \pm\frac{1}{2}$,

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(See also Blinder, Chap 7.1-7.7)

Atomic Units

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. 6), and energies in terms of the

$$\text{Hartree } = \frac{e^2}{a_0} \approx 27 \; eV \tag{11.1}$$

e is the absolute value of the electron charge

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

$$\hbar = 1 \qquad M_e = 1 \qquad e = 1 \tag{11.2}$$

---

[5] Actually, due to the fact that the nucleus's mass is not infinite, one should use the reduced mass $\mu = M_e M_n/(M_e + M_n) \approx M_e(1 - M_e/M_n)$, where M_n is the mass of the nucleus $\approx 2000 \times M_e$. The relative difference is, thus, about 1/2000.

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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. 6), and energies in terms of the

$$\text{Hartree} \; = \frac{e^2}{a_0} \approx 27 \; eV \tag{11.1}$$

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Schrödinger equation and separation of variables

Schrödinger equation for the Hydrogen atom

The Schrödinger equation (7.15) for an electron in a potential $V(r)$ reads (in atomic units)

$$\left(-\frac{1}{2}\boldsymbol{\nabla}^2 + V(r)\right)\psi(r,\theta,\phi) = E\ \psi(r,\theta,\phi) \tag{11.3}$$

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

$$V(r) = -\frac{Z}{r} \tag{11.4}$$

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:

$$\psi(r,\theta,\phi) = R(r) Y_{\ell,m}(\theta,\phi) \qquad (11.5)$$

where the $Y_{\ell,m}$ are the spherical harmonics defined in Sec. 10.

Use of (10.8) for the Laplace operator transforms (11.3) to details:

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

$$= E\ R(r) Y_{\ell,m}(\theta,\phi) \qquad (11.6$$

The fact that $Y_{\ell,m}(\theta,\phi)$ is an eigenfunction of $-\nabla^2_{\theta,\phi}$ (i. e., of the L^2 operator see (10.13)) is a big advantage.

By using this fact in (11.6), and by dividing everywhere by $Y_{\ell,m}(\theta,\phi)$, the Schrödinger equation becomes

$$-\frac{1}{2}\nabla^2_r R(r) + \left(\frac{\ell(\ell+1)}{2\ r^2} + V(r)\right) R(r) = E\ R(r) \qquad (11.7)$$

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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 (11.7) 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 (11.7) in a simpler form by making the transformation

$$R(r) = \frac{u(r)}{r} \tag{11.8}$$

By using the expression for ∇_r^2 ((10.9)), and multiplying by r, we finally obtain

$$-\frac{1}{2}u''(r) + \left(\frac{\ell(\ell+1)}{2\ r^2} + V(r)\right) u(r) = E\ u(r) \tag{11.9}$$

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. 116, we can graphically study the solutions of (11.9)

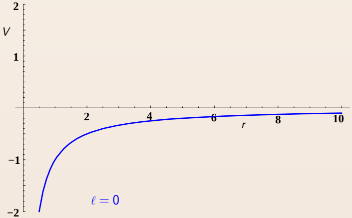
Qualitative solution

Graphical study of the Schrödinger equation

Effective potential

Let us first look at the effective potential in (11.9)

In the following discussion, we use the Coulomb potential (11.4) (with $Z = 1$), although most qualitative results will hold for similar attractive potentials.



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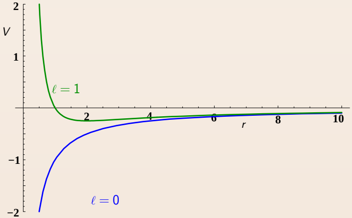

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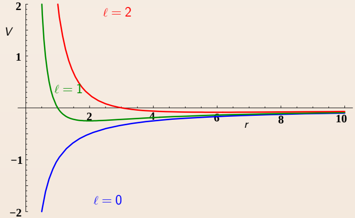

This is the effective potential for different values of ℓ.
All these potentials become 0 in the $r \to \infty$ limit, and, thus, they have a minimum "bottom of the box" at some $r_{min} = \frac{\ell(\ell+1)}{Z}$

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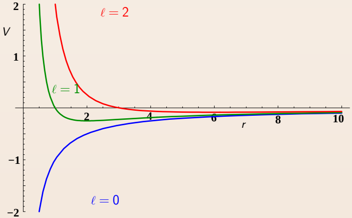

This is the effective potential for different values of ℓ.
We will expect that the average radius of the orbit will be proportional to r_{min}, i. e. increase with increasing ℓ and decrease with increasing Z

Properties of the wave functions

Let us now assume that we have found the solution of (11.9) for each ℓ. We will actually do this below. Of course, we expect, as discussed qualitatively in Sec. , 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 (11.5), where $u(r)$ is a solution of (11.9).

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First of all, let us now analyze the properties of the complete wave functions (11.5), where $u(r)$ is a solution of (11.9).

Properties of the wave functions

We rewrite (11.5) as

$$\psi(r,\theta,\phi) = \frac{u(r)}{r}\ Y_{\ell,m}(\theta,\phi) \tag{11.10}$$

We know from Sec. 10, 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 (11.9) (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 heavyer atoms for which the potential energy is more complicated, but still central[6].

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Properties of the wave functions

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. 7.3 ((7.17)) 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]

$$\rho(r, \theta, \phi) \propto \frac{u(r)^2}{r^2} \, |Y_{\ell,m}(\theta, \phi)|^2 \qquad (11.11)$$

From (11.11) 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
2. What is the probability density $\rho_r(r)$ to find the electron at a certain distance r from the nucleus?
   This provides information about the average radius of the orbit

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[7] $u(r)$ turns out to be real

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From (11.11), the answer to question 1 is clearly

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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.

$$\begin{aligned}\rho_r(r) &\propto \int \rho(r,\theta,\phi)\ r^2\ \sin\theta\ d\theta\ d\phi = \\ &\frac{u(r)^2}{r^2}\ r^2 \int |Y_{\ell,m}(\theta,\phi)|^2 \sin\theta\ d\theta\ d\phi = u(r)^2\end{aligned} \tag{11.13}$$

Where the last integral gives 1 due to the normalisation of the spherical harmonics. $u(r)^2$, thus gives the radial distribution. (see also example)

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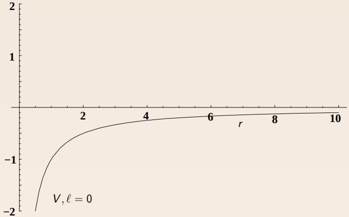
Solution of (11.9) for $\ell = 0$



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 (11.8).

The $u(r)$ are product of polynomial and the exponential function $\exp(-r/2)$

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

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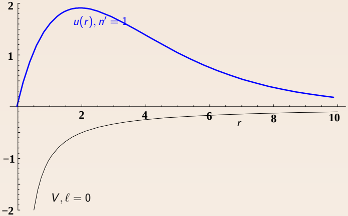

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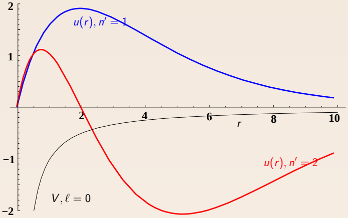

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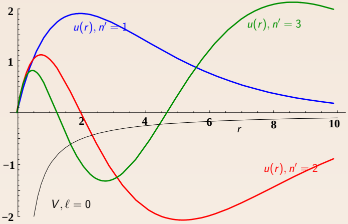

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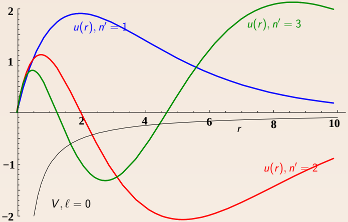

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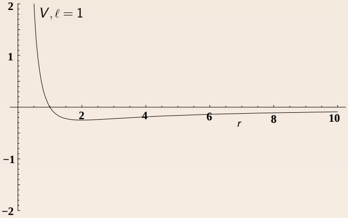

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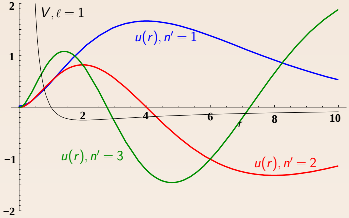

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$$E_{n',\ell} = -\frac{Z^2}{2}\frac{1}{(n'+\ell)^2}$$

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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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:

$$n = 1, \cdots, \infty \qquad \ell = 0, \cdots, n-1, \qquad m = -\ell, \cdots, \ell \tag{11.15}$$

- The corresponding eigenfunctions can be written as:

$$\psi_{n,\ell,m}(r,\theta,\phi) = \frac{u_{n,\ell}(r)}{r} \; Y_{\ell,m}(\theta,\phi) \tag{11.16}$$

- The energies depend only on n:

$$E_{n,\ell} = -\frac{Z^2}{2}\frac{1}{n^2} \text{ (Hartree)} \tag{11.17}$$

- 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.
  I. e. for a given n there are n^2 degenerate states.

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Angular momentum states

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

$$\begin{array}{cccccc} \ell = & 0 & 1 & 2 & 3 & 4 \\ & s & p & d & f & g \end{array} \tag{11.18}$$

which comes from an old classification of atomic spectral lines: sharp, principal, diffuse, fundamental.

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s orbitals

s orbitals have $\ell = 0$ and therefore only $m = 0$.
Since $Y_{0,0} =$ constant (See (10.16)), *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 combination of them and obtain real orbitals. Remember that linear combinations of degenerate eigenfunctions are also eigenfunction with the same energy. Therefore, one is free to take such linear combinations.
- [illegible] called p_{+1} and p_{-1}) orbitals one can more conveniently use the 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. ( )

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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

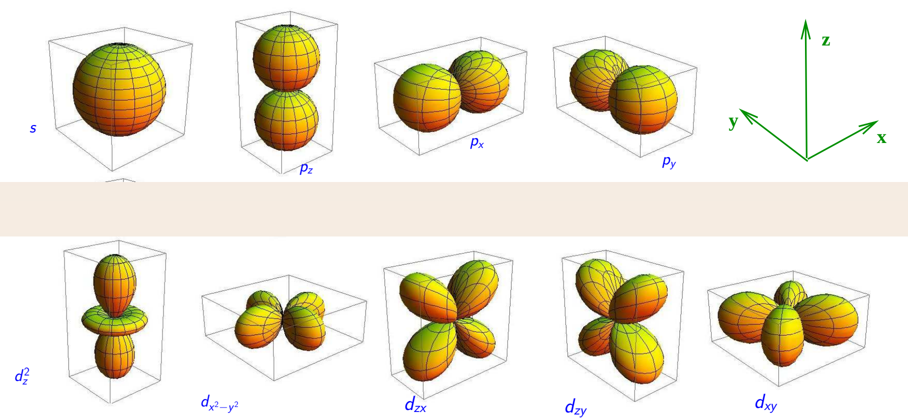

Figure: Angular dependence of atomic orbitals for $\ell = 0, 1, 2$ in real representation

Terminology of orbitals

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

$$n\ \ell_m \tag{11.19}$$

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:

$$\begin{array}{l} 1s \\ 2s\ 2p_x\ 2p_y\ 2p_z \\ 3s\ 3p_x\ 3p_y\ 3p_z\ 3d_{x^2-y^2}\ 3d_{z^2}\ \ 3d_{xy}\ 3d_{yz}\ 3d_{zx} \end{array} \tag{11.20}$$

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. 12

(See also Blinder, Chap 9.1-9.5)

Many-electron atoms

- 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. 10.3) $m_s = +\frac{1}{2}$ and the other $m_s = -\frac{1}{2}$.
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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 more close to the nucleus than in Hydrogen.
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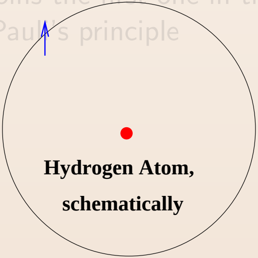

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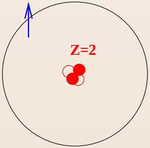

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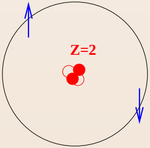
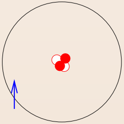


Charge screening

- 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.
- At a given distance r from the nucleus, the second electron “feels” the repulsion from the negative charge contained in a sphere of radius r, as though this charge was concentrated on the origin.



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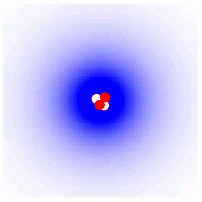

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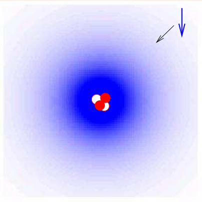

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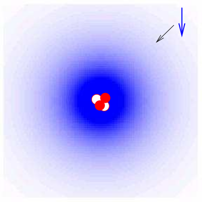
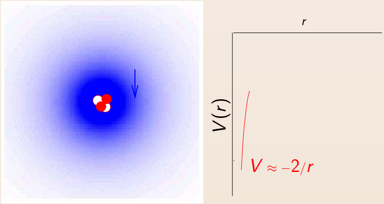


Charge screening

- Therefore, very close to the nucleus the screening effect is smaller and the electron will feel a total charge $+2e$, while far away it will be $Z = +2e - e = +e$. Accordingly, the effective screening potential seen by the second electron interpolates between $-\frac{2e}{r}$ at small distances and $-\frac{e}{r}$ at large distances.
- Notice that the situation is symmetric between the two electrons: also the first electron "sees" the nuclear charge $+2e$ screened by the second electron.



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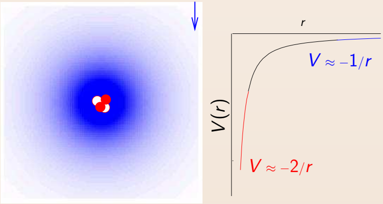

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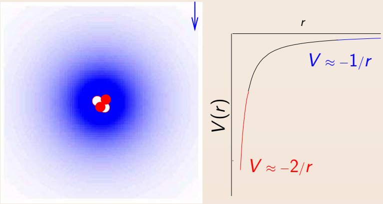

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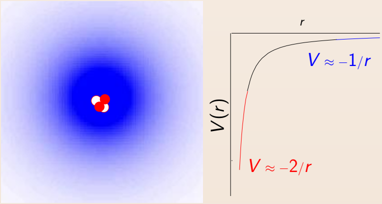

Closed shells

- The ground-state configuration of Helium ($[He]$) is denoted as $[He] = 1s^2$, i. e. 2 electrons in the $1s$ orbitals.
- 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.
  A closed shell configuration is particularly stable, i. e. it costs a lot of energy to modify it.
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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.(11.20)), 2s and 2p orbitals are no longer degenerate.
  This is due to the fact that the screened potential is not of the form $1/r$.
- Notice, however, that since the screened potential is still spherically symmetric, the degeneracy between orbitals with the same ℓ but different m remains.

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- 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.(11.20)), $2s$ and $2p$ orbitals are no longer degenerate. This is due to the fact that the screened potential is not of the form $1/r$.
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  - The wave function of 2*s* orbitals is distributed closer to the nucleus than that of 2*p* orbitals. The reason is that *p* orbitals have nodes at the origin (see Fig. (3)).
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  - 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 2*s* orbital. Its configuration is thus chemically denoted as $1s^2\ 2s$
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Building-up principle

Building-up (*Aufbau*) principle

- It is easy to go on. In Be (Brillium), 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. ([illegible])). Each orbital can be occupied by two electrons with opposite spin, so that we can put 6 electrons in total in the $2p$ orbitals.

  This is the case for atoms with Z from 5 to 10 (B,C,N,O,F,Ne).

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- The story continues, but it becomes more difficult upon reaching *d* orbitals.

  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.

  The symbol $\sim$ means that orbitals are very close in energy, and the order of occupation, depends on the occupation of other orbitals.

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Hund's rule

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- When filling the three $2p$ orbitals we have not specified in which order this is done.
- We know that all three p orbitals have the same energy, however, when putting, for example, two electrons the question remains whether it is energetically more favorable to put both in the same p orbital
- Clearly, two electrons on two different p orbitals will have experience a weaker repulsion than two electrons on the same orbital. For this reason, the second configuration is favored.
- Moreover, if both electrons have the same spin, one can guarantee that they will not meet on the same orbital.

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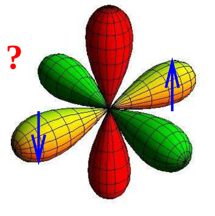

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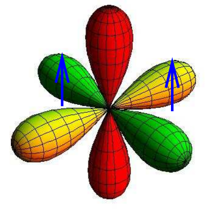

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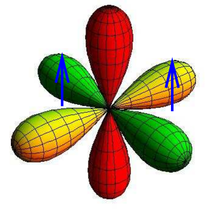

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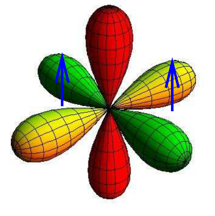

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  "An atom in its ground state adopts a configuration with the maximum number of electrons with parallel spins"
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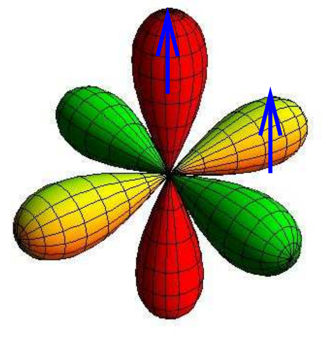

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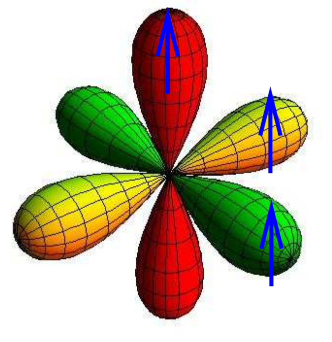

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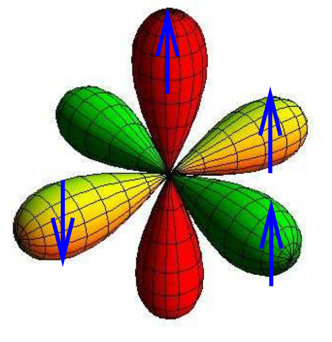

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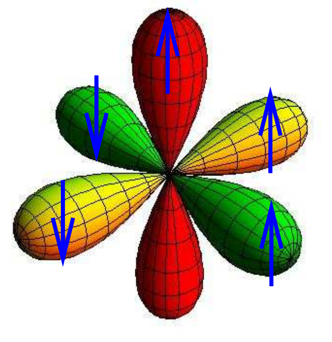

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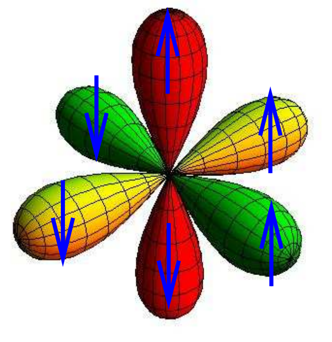

11 Examples and exercises

12 Some details

13 Functions as (infinite-dimensional) vectors

Photoelectric effect

back

The work function of a particular metal is $2.6 eV$ $(1.eV = 1.6 \times 10^{-12}\ erg)$. What maximum wavelength of light will be required to eject an electron from that metal?

Solution:

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

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

which is close to the lower (high-frequency) edge of visible spectrum.

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

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(remember $J = Kg\ m^2/s^2$)

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Properties of a wavefunction

average values, normalisation, etc.

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$$e^{-\frac{a\ r}{2}} \tag{13.1}$$

where $r = |\mathbf{r}|$ and $\mathbf{r} = (x, y, z)$.

Normalize the wavefunction.

Find the average value of the radius $< r >$ (see (14.6)).

The remaining questions are not compulsory

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$$1 = N^2 \ 4\ \pi \int_0^\infty e^{-a\ r} r^2 \, dr = N^2 \ 4\pi \ \frac{2}{a^3} \Rightarrow N = \sqrt{\frac{a^3}{8\pi}} \tag{13.4}$$

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Properties of a wavefunction

average values, normalisation, etc.

Normalisation:

$$1 = N^2 \int (e^{-\frac{a\ r}{2}})^2\ dV = N^2 \int e^{-a\ r}\ d\ V \tag{13.3}$$

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$W(r_0 < r < r_0 + \Delta r_0)$ is given by the integral (13.4) in between these limits:

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

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The most probable value is given by the maximum of $P(r_0)$, this is easily found to be $r_{max} = \frac{2}{a}$.

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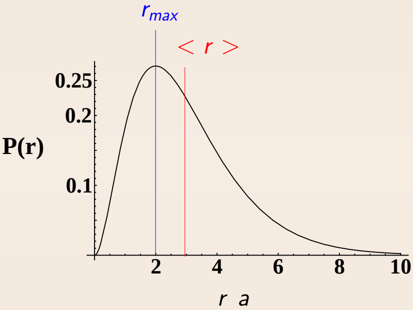

Notice that the probability density $P(\mathbf{r})$ for the coordinates $\mathbf{r} = (x, y, z)$ is given instead by $P(\mathbf{r}) = N^2 e^{-a \ r_0}$ and has its maximum at the centre $\mathbf{r} = 0$.

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

$$\psi(x) = N \; Sin \frac{\pi}{a} x \tag{13.8}$$

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$$1 = N^2 \int_0^a (Sin \frac{\pi}{a} x)^2 \; d \; x = N^2 \; \frac{a}{2} \Rightarrow N = \sqrt{\frac{2}{a}} \tag{13.9}$$

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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: We first find the norm of the wavefunction:

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

We now need the expectation values $< \hat{x} >$ and $< \hat{p} >$:
We observe, however, that both integral vanish:

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

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

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

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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 (7.1): $\mathrm{Re}\; e^{i(kx-\omega t)} = \cos(kx - \omega t)$
- Differentiating just provides a multiplicative factor: $\frac{\partial}{\partial x} e^{a\,x} = a\; e^{a\,x}$

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Some conventions for three dimensions

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- 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"

$$\nabla = (\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}) \tag{14.1}$$

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

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Probability density

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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

$$W(a \leq x \leq b) = \int_a^b \rho(x)\; dx \; . \tag{14.3}$$

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

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Solution of differential equations for free particles

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$$\psi''(x) + B\psi(x) = 0 \tag{14.7}$$

(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 (14.7)

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

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

$$\psi(x) = e^{i\sqrt{B}x} \qquad \psi(x) = e^{-i\sqrt{B}x} \tag{14.8}$$

For $B < 0$, it is more convenient to write (although this is completely equivalent to (14.8))

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Linearity

An important property of an equation like (14.7), and, in general, of the Schrödinger equations (7.15) and (7.12), is that linear combinations of the solutions are also solutions See details

This allows us to rewrite the solution (14.8) for $B > 0$ in a convenient way.

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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

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

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

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

I.e., we can replace (14.8) with

$$\psi(x) = \cos\sqrt{B}x \qquad \psi(x) = \sin\sqrt{B}x \qquad (14.9)$$

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As a consequence, if you find two (or more or less) solutions of (14.7), say $\psi_1(x)$ and $\psi_2(x)$
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$$\psi_{lc}(x) = a_1\psi_1(x) + a_2\psi_2(x)$$

(with a_1, a_2 constant coefficients) is also a solution of (14.7)

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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,

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

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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 (7.13).

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

$$\psi(x) = \text{const.}\, e^{\pm\sqrt{-k^2}\ x} \tag{14.10}$$

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Detailed proof of the form of L_z

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$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} \tag{14.11}$$

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$$\hat{L}_z = \hat{x}\ \hat{p}_y - \hat{y}\ \hat{p}_x = -i\hbar(x\ \frac{\partial}{\partial y} - y\ \frac{\partial}{\partial x}) \tag{14.12}$$

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

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Laplace operator and separation of variables

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a so-called infinite-dimensional vector space.

This treatment is very heuristic. For a more rigorous treatment, please refer to the QM Script by Evertz and von der Linden.

The main point here is that most results about vectors, scalar products, matrices, can be extended to linear vector spaces of functions.

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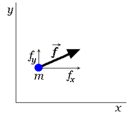
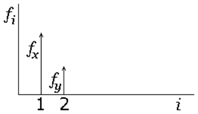
A vector **f** (which might be velocity **v**, linear momentum $\mathbf{p} = m\mathbf{v}$, force **F**, or whatever) is usually shown in physics in the form of an arrow:



However, the same vector may instead be represented as a spike diagram, by plotting the value of the components versus the component index:



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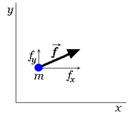

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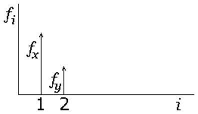

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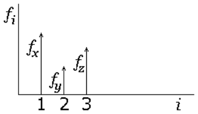
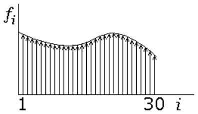
In the same way as in two dimensions, a vector in three dimensions, or, for that matter, in thirty dimensions, can be represented by a spike diagram:





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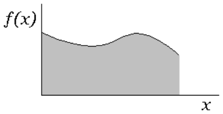
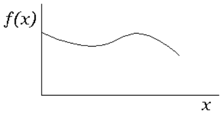
For a large number of dimensions, and in particular in the limit of infinitely many dimensions, the large values of i can be rescaled into a continuous coordinate, call it x. For example, x might be defined as i divided by the number of dimensions. In any case, the spike diagram becomes a function $f(x)$:



The spikes are usually not shown:



In this way, a function is just a vector in infinitely many dimensions.

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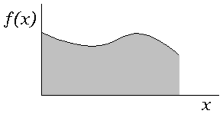

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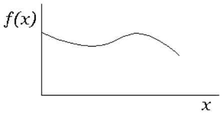

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Key Points

- ◇ Functions can be thought of as vectors with infinitely many components.
- ◇ This allows quantum mechanics do the same things with functions as you can do with vectors.

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The scalar product

The scalar product makes it possible to find the length of a vector, by multiplying the vector by itself and taking the square root. It is also used to check if two vectors are orthogonal:

The usual scalar product of two vectors **f** and **g** can be found by multiplying components with the same index *i* together and summing that:

$$\mathbf{f} \cdot \mathbf{g} \equiv f_1 g_1 + f_2 g_2 + f_3 g_3$$

Figure (4) shows multiplied components using equal colors.

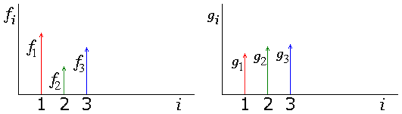

Figure:

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The scalar product

The scalar product makes it possible to find the length of a vector, by multiplying the vector by itself and taking the square root. It is also used to check if two vectors are orthogonal:

The usual scalar product of two vectors **f** and **g** can be found by multiplying components with the same index *i* together and summing that:

$$\mathbf{f} \cdot \mathbf{g} \equiv f_1 g_1 + f_2 g_2 + f_3 g_3$$

Figure (4) shows multiplied components using equal colors.

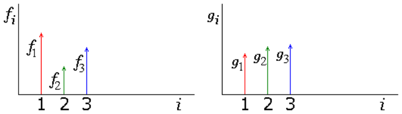

Figure:

Note the use of numeric subscripts, f_1, f_2, and f_3 rather than f_x, f_y, and f_z; it means the same thing. Numeric subscripts allow the three term sum above to be written more compactly as:

$$\mathbf{f} \cdot \mathbf{g} \equiv \sum_{\text{all } i} f_i g_i$$

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The length of a vector $\mathbf{f}$, indicated by $|\mathbf{f}|$ or simply by f, is normally computed as

$$|\mathbf{f}| = \sqrt{\mathbf{f}\cdot\mathbf{f}} = \sqrt{\sum_{\text{all } i} f_i^2}$$

However, this does not work correctly for complex vectors. Therefore, it is necessary to use a generalized "scalar product" for complex vectors, which puts a complex conjugate on the first vector:

$$\boxed{\langle\mathbf{f}|\mathbf{g}\rangle = \sum_{\text{all } i} f_i^* g_i} \tag{15.1}$$

The length of a nonzero vector is now always a positive number:

$$\boxed{|\mathbf{f}| = \sqrt{\langle\mathbf{f}|\mathbf{f}\rangle} = \sqrt{\sum_{\text{all } i} |f_i|^2}} \tag{15.2}$$

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Dirac notation:
Here, one describes vectors as so-called “bra” or “ket”:

$$\langle \mathbf{f}| \qquad |\mathbf{g}\rangle$$

bra ket

The scalar product between f and g is then represented by “attaching together” the two vectors as in

$$\langle f|g\rangle$$

Due to the complex conjugate: $\langle f|g\rangle \neq \langle g|f\rangle$

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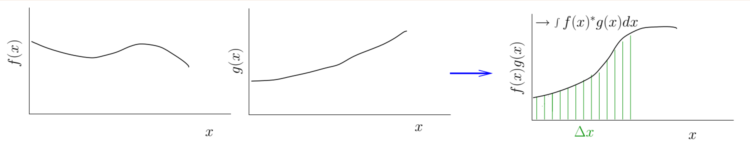
The scalar product of functions has the same form.
Since there are infinitely many x-values, one multiplies by the distance Δx:

$$\langle f|g\rangle \approx \sum_i f^*(x_i)g(x_i)\ \Delta x$$

which in the continumm limit $\Delta x \to 0$ becomes an integral:

$$\boxed{\langle f|g\rangle = \int_{\text{all } x} f^*(x)g(x)\,\mathrm{d}x} \qquad (15.3)$$



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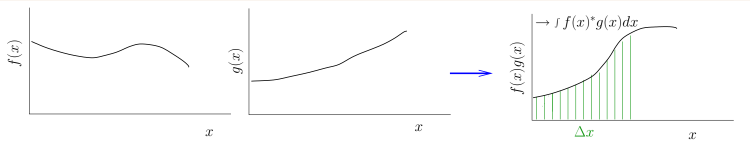

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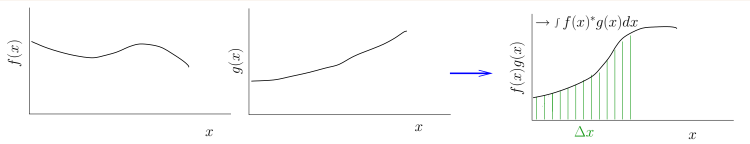

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The equivalent of the length of a vector is in case of a function called its "norm:"

$$\boxed{||f|| \equiv \sqrt{\langle f|f\rangle} = \sqrt{\int |f(x)|^2 \, \mathrm{d}x}} \tag{15.4}$$

A vector or function is called "normalized" if its length or norm is one:

$$\boxed{\langle f|f\rangle = 1 \text{ iff } f \text{ is normalized.}} \tag{15.5}$$

Two vectors, or two functions, f and g are by definition orthogonal if their scalar product is zero:

$$\boxed{\langle f|g\rangle = 0 \text{ iff } f \text{ and } g \text{ are orthogonal.}} \tag{15.6}$$

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Sets of vectors or functions that are all

- mutually orthogonal, and
- normalized

occur a lot in quantum mechanics. Such sets are called "‘orthonormal"’.

So, a set of functions or vectors $f_1, f_2, f_3, \ldots$ is orthonormal if

$$0 = \langle f_1 | f_2 \rangle = \langle f_2 | f_1 \rangle = \langle f_1 | f_3 \rangle = \langle f_3 | f_1 \rangle = \langle f_2 | f_3 \rangle = \langle f_3 | f_2 \rangle = \ldots$$

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Key Points

- ◇ To take the scalar product of vectors, (1) take complex conjugates of the components of the first vector; (2) multiply corresponding components of the two vectors together; and (3) sum these products.
- ◇ To take an scalar product of functions, (1) take the complex conjugate of the first function; (2) multiply the two functions; and (3) integrate the product function. The real difference from vectors is integration instead of summation.
- ◇ To find the length of a vector, take the scalar product of the vector with itself, and then a square root.
- ◇ To find the norm of a function, take the scalar product of the function with itself, and then a square root.
- ◇ A pair of functions, or a pair of vectors, are orthogonal if their scalar product is zero.
- ◇ A set of functions, or a set of vectors, form an orthonormal set if every one is orthogonal to all the rest, and every one is of unit norm or length.

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Operators

back

This section defines linear operators (or, more simply operators), which are a generalization of matrices.

In a finite number of dimensions, a matrix $\hat{A}$ can transform any arbitrary vector $\mathbf{v}$ into a different vector $\hat{A}\mathbf{v}$:

$$\mathbf{v} \quad \xrightarrow{\text{matrix } \hat{A}} \quad \mathbf{w} = \hat{A}\mathbf{v}$$

Similarly, an operator transforms a function into another function:

$$f(x) \quad \xrightarrow{\text{operator } \hat{A}} \quad g(x) = \hat{A}f(x)$$

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Some simple examples of operators:

$$f(x) \xrightarrow{\quad \widehat{x} \quad} g(x) = x f(x)$$

$$f(x) \xrightarrow{\quad \frac{\mathrm{d}}{\mathrm{d}x} \quad} g(x) = f'(x)$$

Note that a hat (ˆ) is often used to indicate operators, and to distinguish them from numbers;
for example, $\widehat{x}$ is the symbol for the operator that corresponds to multiplying by x.
If it is clear that something is an operator, such as $\mathrm{d}/\mathrm{d}x$, no hat will be used.
It should really be noted that the operators we are interested in in quantum mechanics are "linear" operators, i. e. such that for two functions $f(x)$ and $g(x)$ and two numbers a and b:

$$\hat{A}\ (a\ f(x) + b\ g(x)) = a\ \hat{A}\ f(x) + b\ \hat{A}\ g(x) \tag{15.7}$$

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Some simple examples of operators:

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Key Points

- ◇ Matrices turn vectors into other vectors.
- ◇ Operators turn functions into other functions.

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Eigenvalue Problems

A nonzero vector **v** is called an eigenvector of a matrix $\hat{A}$ if $\hat{A}\mathbf{v}$ is a multiple of the same vector:

$$\hat{A}\mathbf{v} = a\mathbf{v} \text{ iff } \mathbf{v} \text{ is an eigenvector of } \hat{A} \tag{15.8}$$

Similarly, a nonzero function **f** is an eigenvector (in this case it is called eigenfunction) of an operator $\hat{A}$ if $\hat{A}f(x)$ is a multiple of the same function:

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For example, e^x is an eigenfunction of the operator $\mathrm{d}/\mathrm{d}x$ with eigenvalue 1, since $\mathrm{d}e^x/\mathrm{d}x = 1e^x$.
A case that is more common in quantum mechanics:

$$\frac{\mathrm{d}}{\mathrm{d}x} e^{\mathrm{i}kx} = \mathrm{i}ke^{\mathrm{i}kx}$$

$e^{\mathrm{i}kx}$ is thus an eigenfunction of $\frac{\mathrm{d}}{\mathrm{d}x}$ with eigenvalue $\mathrm{i}k$.

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Key Points

- If a matrix turns a nonzero vector into a multiple of that vector, that vector is an eigenvector of the matrix, and the multiple is the eigenvalue.
- If an operator turns a nonzero function into a multiple of that function, that function is an eigenfunction of the operator, and the multiple is the eigenvalue.

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Hermitian Operators

Operators describing observables in quantum mechanics are of a special kind called "Hermitian".

First let us look at Hermitian conjugate $\hat{A}^\dagger$ of an operator: if $\hat{A}$ is a matrix, then $\hat{A}^\dagger$ is its transpose, complex conjugate:

$$\hat{A}^\dagger = (\hat{A}^T)^* \,. \qquad (15.10)$$

In the general case, for example for operators acting on functions the definition is:

$$\langle f|\hat{A}g\rangle = \langle \hat{A}^\dagger f|g\rangle \qquad (15.11)$$

for any vector (here in Dirac notation) $|f\rangle$ and $|g\rangle$.

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An operator for which $\hat{A} = \hat{A}^\dagger$ is called hermitian. In other words, an hermitian operator can always be flipped over to the other side if it appears in a scalar product:

$$\langle f | \hat{A} g \rangle = \langle \hat{A} f | g \rangle \text{ always iff } \hat{A} \text{ is Hermitian.} \qquad (15.12)$$

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Hermitian operators have the following additional special properties:

- They always have real eigenvalues.
- Their eigenvectors can always be chosen so that they are normalized and mutually orthogonal.
- Their eigenvectors can be chosen as a basis for the vector space. This means that *any* function can be written as some linear combination of the eigenfunctions.

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Key Points

- ◇ Hermitian operators can be flipped over to the other side in scalar products.
- ◇ Hermitian operators have only real eigenvalues.
- ◇ Hermitian operators have a complete set of orthonormal eigenfunctions (or eigenvectors) that can be used as a basis.

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Additional independent variables

In many cases, the functions involved in an scalar product may depend on more than a single variable x. For example, they might depend on the position $\mathbf{r} = (x, y, z)$ in three dimensional space.

The rule to deal with that is to ensure that the scalar product integrations are over *all* independent variables. For example, in three spatial dimensions:

$$\langle f|g\rangle = \int_{\text{all } x}\int_{\text{all } y}\int_{\text{all } z} f^*(x,y,z)g(x,y,z)\,\mathrm{d}x\mathrm{d}y\mathrm{d}z = \int f^*(\mathbf{r})g(\mathbf{r})\,\mathrm{d}^3\mathbf{r}$$

Note that the time t is a somewhat different variable from the rest, and time is *not* included in the scalar product integrations.

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