

# 1 The Photon

$c \left[ \frac{\text{m}}{\text{s}} \right]$	speed of light
$h \left[ \frac{\text{m}^2 \text{kg}}{\text{s}} \right]$	planc's constant
$e \text{ [C]}$	electorn charge
$m_e \text{ [kg]}$	electron mass
$k_B \left[ \frac{\text{m}^2 \text{kg}}{\text{s}^2 \text{K}} \right]$	bolzmann constant
$\epsilon_0 \left[ \frac{\text{F}}{\text{m}} \right]$	vacuum permittivity

$$c = 2.998 \cdot 10^8 \left[ \frac{\text{m}}{\text{s}} \right]$$

$$h = 6.626 \cdot 10^{-34} \left[ \frac{\text{m}^2 \text{kg}}{\text{s}} \right]$$

$$\hbar = \frac{h}{2\pi}$$

$$e = 1.602 \cdot 10^{-19} \text{ [C]}$$

$$m_e = 9.109 \cdot 10^{-31} \text{ [kg]}$$

$$k_B = 1.381 \cdot 10^{-23} \left[ \frac{\text{m}^2 \text{kg}}{\text{s}^2 \text{K}} \right]$$

$$\epsilon_0 = 8.854 \cdot 10^{-12} \left[ \frac{\text{F}}{\text{m}} \right]$$

$$1 \text{ [eV]} = 1.602 \cdot 10^{-19} \text{ [J]}$$

## 1.1 Photon & Electron

$\lambda \text{ [m]}, \nu \left[ \frac{1}{\text{s}} \right]$	Wavelength, Freq.
$k$	Wavenumber
$E \text{ [J]}$	Energy
$\vec{F}_c \text{ [N]}$	Coulomb Force

$$\lambda = \frac{c}{\nu} \quad \nu = \frac{c}{\lambda} \quad \omega = 2\pi\nu$$

$$k = \frac{2\pi\nu}{c}$$

$$E = h \cdot \nu = \hbar \cdot \omega$$

$$|\vec{F}_c| = \frac{Q_1 \cdot Q_2}{4\pi\epsilon_0 r^2}$$

## 1.2 Photoelectric effect

$V \text{ [V]}$	Voltage
$\phi_0 \text{ [eV]}$	Work function
$I \text{ [A]}$	Photo-current
$n \left[ \text{m}^{-3} \right]$	Volume density of electrons
$A \left[ \text{m}^2 \right]$	Area
$v \left[ \frac{\text{m}}{\text{s}} \right]$	velocity of electrons

$$h\nu - \phi_0 = \frac{1}{2}mv^2 = eV$$

$$V(\nu) = \frac{h}{e}\nu - \frac{\phi_0}{e}$$

$$I = nAve$$

## 1.3 Blackbody Radiation

$L \text{ [m]}$	length of blackbody cube	$k_i$	wave constants
$E_x$	Electric field in x-direction	$\langle E \rangle$	Average Energy
$N$	Number of states	$D$	Density of states
$u$	Blackbody radiation	$I$	Power radiated

$$E_x(x, y, z) = E_{0x} \cos(k_x x) \sin(k_y y) \sin(k_z z)$$

$$k_x = n \frac{\pi}{L} \quad k_y = m \frac{\pi}{L} \quad k_z = l \frac{\pi}{L} \quad k = \sqrt{k_x^2 + k_y^2 + k_z^2}$$

$$N(k) = \frac{1}{3\pi^2} k^3 L^3 \quad D(k) = \frac{k^2}{\pi^2}$$

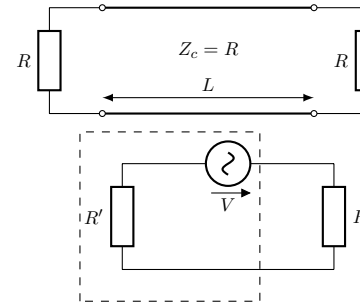
$$u(\omega) = \frac{\omega^2}{\pi^2 c^3} \cdot \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{kT}\right) - 1} d\omega \quad u(\nu) = \frac{8\pi h \nu^3}{c^3 \left( \exp\left(\frac{h\nu}{kT}\right) - 1 \right)} d\nu$$

$$I(\omega) = c \cdot u(\omega)$$

**Equipartition-Theorem:** Each degree of Freedom has an energy of  $kT$

## 1.4 Johnson-Noise

This is the noise created in a one-dimensional circuit (like a coax-cable).

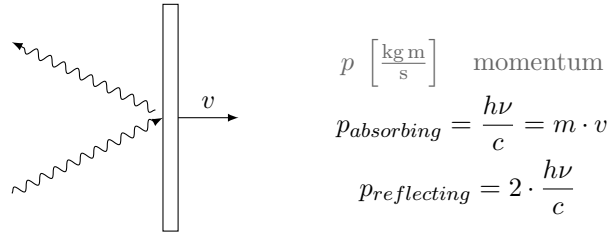


$\langle V^2 \rangle$	Noise Voltage
$\Delta\nu$	Bandwidth

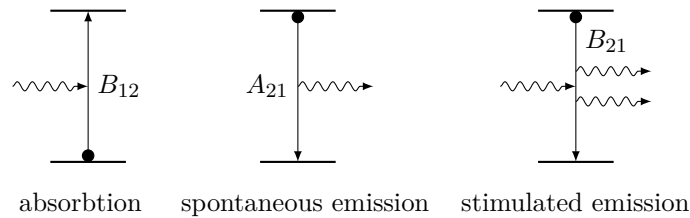
$$E = E_0 \cdot \sin(k_x \cdot x)$$

$$\langle V^2 \rangle = 4R \cdot k_B T \cdot \Delta\nu$$

## 1.5 Momentum of a photon



## 1.6 Absorption, spontaneous and stimulated emission



$n_1$  Number of electrons in the lower energy state

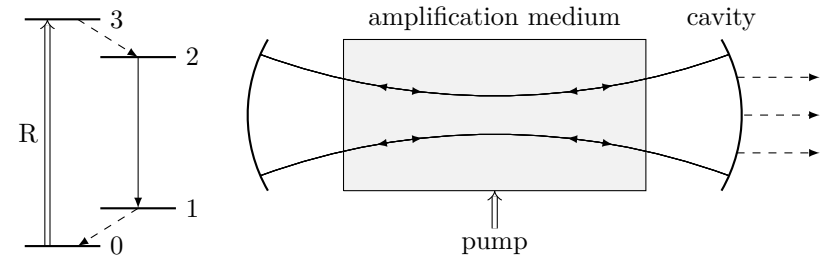
$n_2$  Number of electrons in the higher energy state

$$\frac{dn_2}{dt} = \underbrace{n_1 \cdot u(\nu) \cdot B_{12}}_{\text{absorption}} - \underbrace{n_2 \cdot u(\nu) \cdot B_{21}}_{\text{stimulated emission}} - \underbrace{n_2 \cdot A_{21}}_{\text{spontaneous emission}}$$

$$\frac{n_2}{n_1} = e^{-\frac{h\nu}{k_B T}} = \frac{u(\nu) B_{12}}{u(\nu) B_{21} + A_{21}}$$

$$B_{21} = B_{12} = B \quad A_{21} = \frac{8\pi h\nu^3}{c^3}$$

## 1.7 Laser-optical amplification



Electrons are excited from the ground state “0” to the level “3” by pumping through incoherent radiation. The electrons then fall onto a long-lived state  $n_2$  (State “2”) from level “3”. The pumping can be done either optically by shining a strong incoherent light or by passing a current. It is also assumed that the lower state is quickly emptied by a fast process with lifetime  $\tau_1$ . As a result, the population in state “2” is:

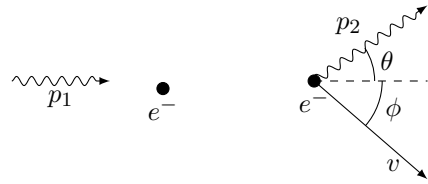
$$n_2 = \frac{R}{A_{21}} \quad \text{whereas} \quad n_1 \approx 0 \quad \text{because} \quad A_{21} < \frac{1}{\tau_1}$$

We have therefore a population inversion between the two states. The likelihood of a stimulated emission process is larger than the one of absorption. If we enclose the system in an optical cavity, we can achieve self-sustained oscillation at the frequency  $\nu$ .

## 2 Wave mechanics

	frequency	wavelength	momentum	energy
Particle		$\lambda_b = \frac{h}{p}$	$p = mv$	$E = \frac{1}{2}mv^2$
Wave	$\omega$	$\lambda = \frac{2\pi c}{\omega}$	$p = \frac{\hbar\omega}{c}$	$E = \hbar\omega$

## 2.1 Compton Scattering

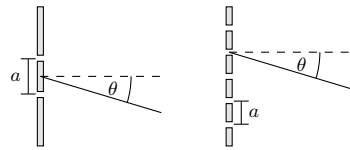


$$p_1 = \frac{h\nu_1}{c} \quad p' = \frac{h\nu_2}{c}$$

$$\nu_2 = \nu_1 - \frac{P_e^2}{2m_e h}$$

$$\lambda_2 - \lambda_1 = \frac{h}{m_e c} (1 - \cos \theta);$$

## 2.2 Double Slit and Bragg Diffraction

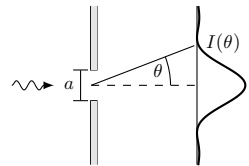


Constructive  $\sin \theta = \frac{n\lambda}{a}$

Destructive  $\sin \theta = \frac{(n + \frac{1}{2})\lambda}{a}$

$n \in \mathbb{Z}$

## 2.3 Single slit



$$I(\theta) = I_0 \frac{\sin^2 \theta}{\theta^2}$$

$$\sin \theta = \frac{\lambda}{a}$$

## 2.4 Bohr-Sommerfeld quantisation

Every single particle must satisfy the following equation. The quantized energy levels below relate to the hydrogen atom

$p$	Momentum of particle	$\int_{length} p \cdot ds = n \cdot h \quad n \in \mathbb{N}$
$E_n$	Energy of the nth state	$E_n = -\frac{Z^2}{n^2} \cdot \frac{m_e e^4}{8\epsilon_0^2 h^2} = -\frac{Z^2}{n^2} \cdot E_{ry}$
$E_{ry}$	Rydberg Energy	$r_n = \frac{n^2}{Z} \cdot \frac{2\epsilon_0 h}{m_e e^2} = \frac{n^2}{Z} \cdot a_0$
$a_0$	Bohr-radius	$E_{ry} = 13.6 \text{ [eV]}$
$Z$	Number of protons	$a_0 = 5.292 \cdot 10^{-11} \text{ [m]}$

## 3 Quantum Mechanics

### 3.1 Wave function

$$\psi(\mathbf{x}, t) : \mathbb{R}^4 \rightarrow \mathbb{C} \quad \iiint |\psi(\mathbf{x}, t)|^2 d^3 r = 1$$

$$\psi(\mathbf{x}, t) = a\psi_1(\mathbf{x}, t) + b\psi_2(\mathbf{x}, t), \quad |a|^2 + |b|^2 = 1$$

### 3.2 The Schrödinger equation

$$V(\mathbf{x}, t) \quad \text{potential} \quad \left| \quad m \quad \text{mass} \right.$$

$$i\hbar \cdot \frac{\partial \Psi}{\partial t}(\mathbf{x}, t) = -\frac{\hbar^2}{2m} \cdot \nabla^2 \Psi(\mathbf{x}, t) + V(\mathbf{x}, t) \Psi(\mathbf{x}, t)$$

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

$$\Psi = A \cdot e^{i(\mathbf{k}\mathbf{x} - \omega t)} \quad \mathbf{k} = \begin{bmatrix} k_x & k_y & k_z \end{bmatrix}, \quad \mathbf{x} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$E = \omega\hbar = \frac{\hbar^2 k^2}{2m}, \quad k^2 = |\mathbf{k}|^2$$

#### 3.2.1 Phase and Group Velocity

The phase velocity  $v_\varphi$  describes how fast the phase of the wave moves forward. The group velocity  $v_g$  describes how fast the energy is moving forward.

$$v_\varphi = \frac{\omega}{k} \quad v_g = \frac{\partial \omega}{\partial k}$$

For a particle wave, the phase velocity  $v_\varphi$  is half the group velocity  $v_g$

$$v_\varphi \cdot 2 = v_g$$

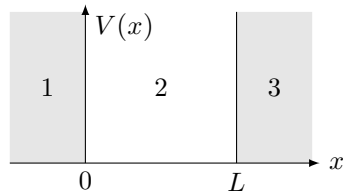
### 3.2.2 Stationary (Time independent) States

In a stationary state, the wave function is a product of a function  $\varphi(\mathbf{x})$  independent of time and a function  $\chi(t)$  independent of space.

$$\begin{aligned}\Psi_n(\mathbf{x}, t) &= \psi_n(\mathbf{x}) \cdot \chi_n(t) = \psi_n(\mathbf{x}) \cdot e^{-i \frac{E_n}{\hbar} t} \\ -\frac{\hbar^2}{2m} \nabla^2 \psi_n(\mathbf{x}) + V(\mathbf{x}) \psi_n(\mathbf{x}) &= \psi_n(\mathbf{x}) \cdot E_n \\ \iiint |\Psi|^2 d^3 \mathbf{x} &= \iiint |\psi|^2 d^3 \mathbf{x} = 1 \\ \Psi(\mathbf{x}, t) &= \sum a_n \psi_n(\mathbf{x}) \cdot e^{-i \frac{E_n}{\hbar} t} \quad \sum |a_n|^2 = 1\end{aligned}$$

Requirements: The wave function must be continuous, as well as its derivative

### 3.2.3 Example: 1D infinite potential well



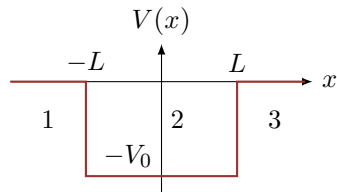
$$\begin{aligned}\Psi_1 = \Psi_3 &= 0 \\ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_2(x, t) &= E \psi_2(x, t) \\ \psi_2 &= A \sin(kx) + B \cos(kx)\end{aligned}$$

$$\text{Boundary cond.: } \psi_2(0) = \psi_2(L) = 0$$

$$\psi_{2n} = A \cdot \sin(k_n x) \quad \Psi_{2n} = A \cdot \sin(k_n x) \cdot e^{-i \frac{E_n}{\hbar} t}, \quad \text{Normalize: } A = \sqrt{\frac{2}{L}}$$

$$E_n = n^2 \cdot \frac{\hbar^2 \pi^2}{2mL} = n^2 \cdot E_0, \quad k_n = \frac{n\pi}{L}$$

### 3.2.4 Example: 1D finite potential well



The Energy  $E$  can be either bigger or smaller than 0. If  $E > 0$ , the wave function will decay exponentially in region 1 and 3. If  $E < 0$ , the wave will propagate away from the potential well.

**Inside the well:** The general solution to the rearranged Schrödinger's is:

$$\begin{aligned}-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_2(x) &= (E - V_0) \psi_2(x) \\ \psi_2(x) &= A_2 e^{ikx} + A'_2 e^{-ikx} \quad E = \frac{k^2 \hbar^2}{2m} \quad k = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}\end{aligned}$$

**Outside the well:** There are two cases, which can apply:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_1(x) = E \psi_1(x)$$

1.  $E > 0$ : **Unbound state**

$$\psi_1 = A_1 e^{ikx} + A'_1 e^{-ikx} \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

The unbound state does not make sense to be investigated, because the particle is free to be anywhere. In the following, only the unbound state is considered.

2.  $E < 0$ : **Bound state**

$$\psi_1 = B_1 e^{\delta x} + B'_1 e^{-\delta x} \quad \delta = \sqrt{-\frac{2mE}{\hbar^2}}$$

We see that as  $x \rightarrow -\infty$ , the Term  $B'_1$ , as well as  $B_3$  approaches  $\infty$ . Since the wave function cannot approach  $\infty$ ,  $B'_1 = B_3 = 0$  is a condition.

$$\psi = \begin{cases} \psi_1 = B_1 e^{\delta x} & x < -L \\ \psi_2 = A_2 e^{ikx} + A'_2 e^{-ikx} & -L < x < L \\ \psi_3 = B'_3 e^{-\delta x} & L < x \end{cases}$$

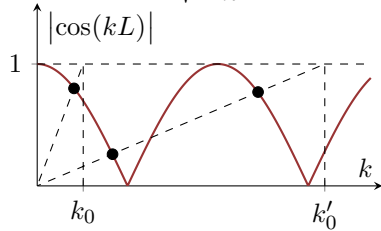
**Boundary conditions:** We require, that the wave function is continuous, as well as its spacial derivative. Therefore, we have:

$$\begin{aligned}\psi_1(-L) &= \psi_2(-L) & \psi_2(L) &= \psi_3(L) \\ \frac{\partial}{\partial x} \psi_1(-L) &= \frac{\partial}{\partial x} \psi_2(-L) & \frac{\partial}{\partial x} \psi_2(L) &= \frac{\partial}{\partial x} \psi_3(L)\end{aligned}$$

**Even solutions:** only even (cosine) components

$$|\cos(kL)| = \frac{k}{k_0}, \quad \tan(kL) > 0$$

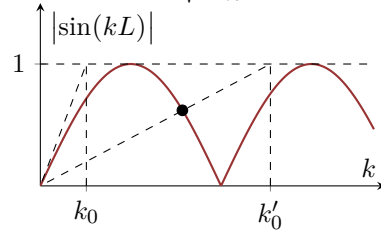
$$k_0 = \sqrt{\frac{2mV_0}{\hbar^2}}$$



**Odd solutions:** only odd (sine) components

$$|\sin(kL)| = \frac{k}{k_0}, \quad \tan(kL) > 0$$

$$k_0 = \sqrt{\frac{2mV_0}{\hbar^2}}$$



Applying the **initial conditions**, which require the wave function and its derivative to be continuous at  $x = 0$ , we get the following expression for  $A$ ,  $B$ ,  $C$ :

$$\psi_1(x=0) = \psi_2(x=0) \quad \frac{\partial}{\partial x} \psi_1(x=0) = \frac{\partial}{\partial x} \psi_2(x=0)$$

**$E > V_0$**

$$A + B = C$$

$$k_1(A - B) = k_2C$$

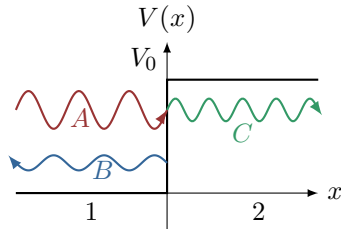
**$E < V_0$**

$$A + B = C$$

$$A = B$$

The **probability density function**  $|\psi(x,t)|^2 = |\varphi(x)|^2 = \varphi \cdot \varphi^*$  can then be computed and sketched:

### 3.3 Example: 1D potential step function



An incoming plane wave from the left hits a potential step at  $x = 0$ . In region 1, two waves are added together, one is traveling to the right and one to the left. If  $E > V_0$ , the wave is transmitted to region 2. If  $E < V_0$ , the wave decays exponentially in region 2.

In **Region 1**, the general solution to the Schrödinger equation is:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_1(x) = E\psi_1(x), \quad \psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x}, \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

In **Region 2**, there are two cases, which can apply:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_2 = (E - V_0)\psi_2(x)$$

1.  **$E > V_0$ : Transmission**

$$\psi_2 = Ce^{ik_2x}, \quad k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

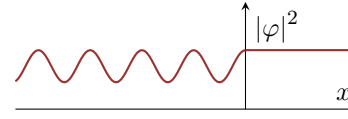
2.  **$E < V_0$ : Complete reflection**

$$\psi_2 = Ce^{\delta_2x}, \quad \delta_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

**$E > V_0$**

$$|\psi_1|^2 = A^2 + B^2 + 2AB \cos(2k_1x)$$

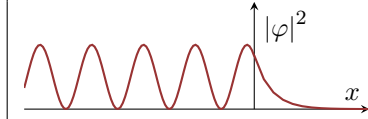
$$|\psi_2|^2 = C^2$$



**$E < V_0$**

$$|\psi_1|^2 = 2A^2 \cdot (1 - \sin(2k_1x))$$

$$|\psi_2|^2 = C^2 \cdot e^{-2\delta x}$$

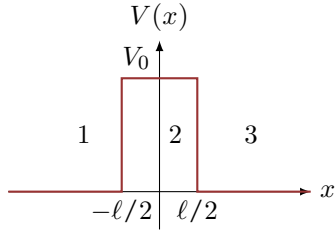


To find the **transmission coefficient**  $T$  and the **reflection coefficient**  $R$ , we normalize  $A = 1$ . Then, we can define  $B = \sqrt{R}$  and  $C = \sqrt{T}$ . Then, we can solve for  $R$  and  $T$ :

$$T = \frac{4k_1k_2}{(k_1 + k_2)^2} \quad R = \left( \frac{k_1 - k_2}{k_1 + k_2} \right)^2$$

If  $E < V_0$ , nothing is transmitted and therefore  $T = 0$  and  $R = 1$ .

### 3.3.1 Example: 1D finite potential barrier



An incoming plane wave from the left hits a potential barrier with length  $l$ . The Transmission coefficient tells, how much of the wave can continue at the other side of the barrier (quantum tunneling).

In **Region 1 and 3**, the general expression for the wave equation is the following:

$$\psi_j(x) = A_j e^{ik_j x} + A'_j e^{-ik_j x}, \quad k_j = \sqrt{\frac{2mE}{\hbar^2}}, \quad j \in \{1, 3\}$$

In **Region 2**, the expression is depending on  $V_0$ . There are two cases:

1.  $E < V_0$ :  $\varphi_2 = B_2 e^{\delta_2 x} + B'_2 e^{-\delta_2 x}$ ,  $\delta_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$
2.  $E > V_0$ :  $\varphi_2 = A_2 e^{ik_2 x} + A'_2 e^{-ik_2 x}$ ,  $k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$

Apply **boundary conditions** at  $x = -\ell/2$  and  $x = \ell/2$  in order to determine all constants. If the wave is only traveling from left to right, then  $A'_3 = 0$ .

$$\begin{aligned} \psi_1(-\ell/2) &= \psi_2(-\ell/2), & \psi_2(\ell/2) &= \psi_3(\ell/2) \\ \frac{\partial}{\partial x} \psi_1(-\ell/2) &= \frac{\partial}{\partial x} \psi_2(-\ell/2), & \frac{\partial}{\partial x} \psi_2(\ell/2) &= \frac{\partial}{\partial x} \psi_3(\ell/2) \end{aligned}$$

Then, the **transmission coefficient**  $T$  and the **reflection coefficient**  $R$  can be calculated as following:

$$R = \left( \frac{A_1}{A'_1} \right)^2, \quad T = \left( \frac{A_3}{A_1} \right)^2$$

$$T = \frac{E < V_0}{4E(V_0 - E)} \quad \left| \quad T = \frac{E > V_0}{4E(V_0 - E) + V_0^2 \sin^2(k_2 \ell)} \right.$$

If  $E > V_0$ , the transmission coefficient has a maximum. If  $k_2 \ell = n\pi \Rightarrow T = 1$  (**resonance**). The minimum of  $T$  is at:  $k_2 \ell = \pi/2 + n\pi$ .

## 4 Wave Function Space (Hilbert Space)

### 4.1 Inner Product

The inner product  $\langle \psi_1 | \psi_2 \rangle$  is defined like the scalar product for vectors. If the inner product of two wave functions is 0, those two wave functions are **orthogonal**.

$$\langle \psi_1 | \psi_2 \rangle = \int_{-\infty}^{\infty} \psi_1^*(\mathbf{x}, t) \psi_2(\mathbf{x}, t) d^3 \mathbf{x}$$

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} \psi^*(\mathbf{x}, t) \psi(\mathbf{x}, t) d^3 \mathbf{x} = \int_{-\infty}^{\infty} |\psi(\mathbf{x}, t)|^2 d^3 \mathbf{x} = 1$$

### 4.2 Fourier Transform

$$\begin{aligned} \psi(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{ipx}{\hbar}} \varphi(p) dp, & \varphi(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{ipx}{\hbar}} \psi(x) dx \\ \psi(\vec{x}) &= \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} e^{\frac{i\vec{p}\vec{x}}{\hbar}} \varphi(\vec{p}) d\vec{p}, & \varphi(\vec{p}) &= \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} e^{\frac{i\vec{p}\vec{x}}{\hbar}} \psi(\vec{x}) d\vec{x} \\ \int_{-\infty}^{\infty} \psi_1^*(x) \cdot \psi_2(x) \cdot dx &= \int_{-\infty}^{\infty} \varphi_1^*(p) \cdot \varphi_2(p) \cdot dp \end{aligned}$$

## 5 Observable Measurements, Time-dependence

Doing a measurement in quantum mechanics (observable) can be interpreted as applying an operator  $\hat{A}$  on the wave function  $\psi(\mathbf{x}, t)$ . For example, to compute the expected position  $\langle \mathbf{x} \rangle_\psi$ , we apply the operator  $\hat{\mathbf{x}} = \mathbf{x}$  to average the wave function:

$$\langle \mathbf{x} \rangle_\Psi = \iiint \Psi^*(\mathbf{x}, t) \cdot \mathbf{x} \cdot \Psi(\mathbf{x}, t) d^3 \mathbf{x} = \iiint \mathbf{x} \cdot |\Psi(\mathbf{x}, t)|^2 d^3 \mathbf{x}$$

Name	Operator
Position	$\hat{\mathbf{x}} = [\mathbf{x}]$
Momentum	$\hat{\mathbf{p}} = [-i\hbar \nabla]$
Hamiltonian	$\hat{H} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{x}) \right]$

$$\nabla = \left[ \frac{\partial}{\partial x} \quad \frac{\partial}{\partial y} \quad \frac{\partial}{\partial z} \right]^T$$

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

**Canonical commutation relation:**  $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

### 5.1 Eigenstates and Eigenvalues

An Observable has an Operator  $\hat{A}$ . a state  $u_n(x)$  is called an eigenstate the operator applied on the wave function acts like a scalar multiplication to it. Then, the measurement of the general state  $\psi(x)$  is a superposition of all the eigenstates.

$$\hat{A}u_n(x) = a_n u_n(x), \quad \int_{-\infty}^{\infty} u_n^*(x) \hat{A}u_n(x) dx = a_n$$

$$\hat{A}\psi(x) = \sum_n c_n u_n(x)$$

### 5.2 Harmonic Oscillator

A Quantum mechanical harmonic oscillator can be interpreted as the solution to the Schrödinger equation:

$$\left[ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E \psi(x), \quad V(x) = \frac{1}{2} k x^2 = \frac{m\omega^2}{2} x^2$$

To simplify the equation, we define a new length scale and energy:

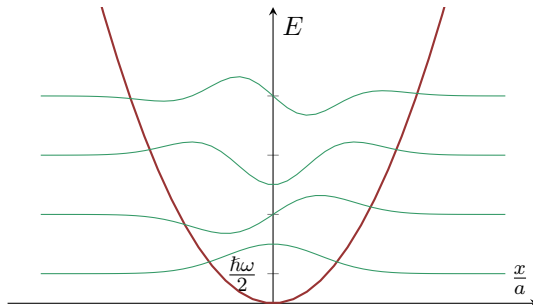
$$a = \sqrt{\frac{\hbar}{m\omega}}, \quad \tilde{x} = \frac{x}{a}, \quad \tilde{E} = \frac{E}{\hbar\omega} \Rightarrow \frac{1}{2} \left[ -\frac{\partial^2}{\partial \tilde{x}^2} + \tilde{x}^2 \right] \varphi(\tilde{x}) = \tilde{E} \varphi(\tilde{x})$$

Then, the solutions to the equation is:

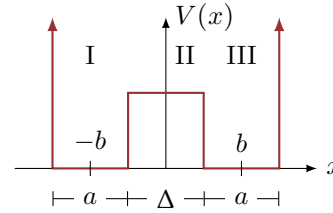
$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega, \quad \psi(\tilde{x}) = c_n H_n(\tilde{x}) e^{-\tilde{x}^2/2}, \quad H_n(\tilde{x}) = (-1)^n e^{\tilde{x}^2} \cdot \frac{\partial^n}{\partial \tilde{x}^n} e^{-\tilde{x}^2}$$

$$H_0(\tilde{x}) = 1, \quad H_1(\tilde{x}) = 2\tilde{x}, \quad H_2(\tilde{x}) = 4\tilde{x}^2 - 2, \quad H_3(\tilde{x}) = 8\tilde{x}^3 - 12\tilde{x}$$

$$\Psi_n(x) = \frac{1}{\sqrt[4]{\pi} \sqrt{2^n n!} a} \cdot H_n\left(\frac{x}{a}\right) e^{-\frac{x^2}{2a^2}}$$



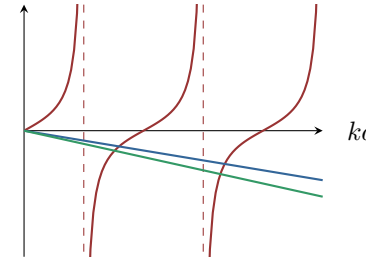
### 5.3 The coupled quantum well



This is the simplified potential of an ammonia molecule  $\text{NH}_3$ . The wave function outside the well ( $|x| > b + \frac{a}{2}$ ) is zero. There exists a symmetric, as well as an antisymmetric solution. We consider the case:  $E < V_0$

$$\psi_{\text{II}} = \begin{cases} \mu \cosh(\delta x) & \text{symmetric} \\ \mu \sinh(\delta x) & \text{antisymmetric} \end{cases} \quad k = \sqrt{\frac{2mE}{\hbar^2}}, \quad \delta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

$\tan(ka)$



$$\text{symmetric: } \varepsilon_s = \frac{1 + e^{-\delta\Delta}}{\delta a}$$

$$\text{antisymmetric: } \varepsilon_a = \frac{1 - e^{-\delta\Delta}}{\delta a}$$

$$\tan(ka) = -ka\varepsilon = -ka \frac{1 \pm e^{-\delta\Delta}}{\delta a}$$

Now, we can create a superposition of both the symmetric and the antisymmetric case:

$$\psi_{s\text{I}} = +\lambda \sin\left(k\left(b - \frac{a}{2} + x\right)\right), \quad \psi_{s\text{III}} = +\lambda \sin\left(k\left(b - \frac{a}{2} + x\right)\right)$$

$$\psi_{a\text{I}} = -\lambda \sin\left(k\left(b - \frac{a}{2} + x\right)\right), \quad \psi_{a\text{III}} = +\lambda \sin\left(k\left(b - \frac{a}{2} + x\right)\right)$$

$$\Psi_L = \frac{1}{\sqrt{2}}(\Psi_s - \Psi_a), \quad \Psi_R = \frac{1}{\sqrt{2}}(\Psi_s + \Psi_a)$$

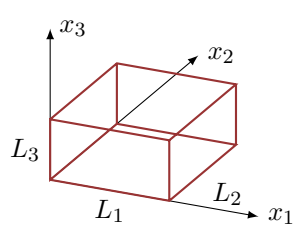
$$\Psi_L(x, t) = \frac{1}{\sqrt{2}} e^{-i\omega_s t} \left( \psi_s(x) - e^{-i(\omega_a - \omega_s)t} \psi_a(x) \right)$$

$$\omega_a = \frac{E_a}{\hbar}, \quad \omega_s = \frac{E_s}{\hbar}, \quad E_a - E_s = \frac{\hbar^2 \pi^2}{2m\delta a^2} \cdot 8e^{-\delta\Delta}$$

From the formula describing the wave equation, we can see that at  $t_0$ , the particle can only be found in region I, and after some time  $t_{1/2}$ , the particle can only be found in region III. The particle has tunneled from one side to the other. Now, we can define a period  $T$ :

$$T = \frac{2\pi\hbar}{E_a - E_s}$$

## 6 Schrödinger Equation in 3D



$$V(x_i) = \begin{cases} 0 & \text{if } 0 < x_i < L_i \\ \infty & \text{otherwise} \end{cases}$$

$$V(x, y, z) = V(x_1) + V(x_2) + V(x_3)$$

$$\psi(x_1, x_2, x_3) = \psi_1(x_1) \cdot \psi_2(x_2) \cdot \psi_3(x_3)$$

$$-\frac{\hbar^2}{2m} \left[ \frac{\psi_1''(x_1)}{\psi_1(x_1)} + \frac{\psi_2''(x_2)}{\psi_2(x_2)} + \frac{\psi_3''(x_3)}{\psi_3(x_3)} \right] + V(x_1) + V(x_2) + V(x_3) = E$$

This equation can be separated into three smaller equations for every spacial dimension  $x_i$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} \psi_i(x_i) + V(x_i) \psi_i(x_i) = E_i \psi_i(x_i)$$

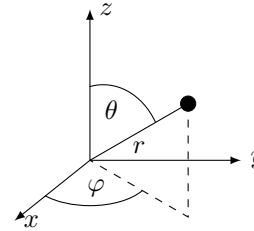
$$E_i^{(n_i)} = n_i^2 \frac{\hbar^2 \pi^2}{2m L_i^2}, \quad \psi_i^{(n_i)} = A \cdot \sin\left(\frac{\pi n_i x}{L_i}\right)$$

After normalizing, the wave function can be written as:

$$\psi(x_1, x_2, x_3) = \sqrt{\frac{8}{L_1 L_2 L_3}} \sin\left(\frac{\pi n_1 x_1}{L_1}\right) \sin\left(\frac{\pi n_2 x_2}{L_2}\right) \sin\left(\frac{\pi n_3 x_3}{L_3}\right)$$

When  $L_1 = L_2 = L_3$ , there sometimes exists multiple states (**degeneracies**) for the same energy  $E = E_1 + E_2 + E_3$ . Now, we can generate new solutions to the wave function via superposition of those states. In general, degeneracies arise from symmetries (obvious or hidden).

### 6.1 Schrödinger Equation in spherical coordinates



$$x = r \sin \theta \cos \varphi$$

$$y = r \sin \theta \sin \varphi$$

$$z = r \cos \theta$$

$$\psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r) \cdot Y_{\ell}^m(\theta, \varphi) = R_{n\ell}(r) \cdot P_{\ell}^m(\cos \theta) e^{im\varphi}$$

The angular part  $Y_{\ell}^m(\theta, \varphi)$  can be written as:

$$P_{\ell}^m(x) = (i - x^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{dx^{|m|}} P_{\ell}(x) \quad P_{\ell}(x) = \frac{1}{2^{\ell} \cdot \ell!} \frac{\partial^{\ell}}{\partial x^{\ell}} (x^2 - 1)^{\ell}$$

The solution to  $Y$  will be a **spherical harmonic**. Finally, we must apply the normalization

$$\int_0^{\infty} |R(r)|^2 r^2 dr = 1, \quad \int_{\theta=0}^{\pi} \int_{\varphi=-\pi}^{\pi} |Y_{\ell}^m(\theta, \varphi)|^2 \sin \theta d\varphi d\theta = 1$$

These solutions are the same as **spherical harmonics**. They form an **orthogonal basis**, meaning that every well-behaved function  $f(\theta, \varphi)$  can be expressed as a superposition of those harmonics.

#### 6.1.1 Hydrogen Atom

The radial part  $R_{n\ell}$  of the hydrogen atom with potential  $V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$  can be written as:

$$R_{n\ell}(r) = \frac{1}{r} \rho^{\ell+1} e^{-\rho} v(\rho), \quad \rho = \frac{r}{na_0}, \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \approx 5.29 \cdot 10^{-11} \text{ [m]}$$

$$\psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r) Y_{\ell}^m(\theta, \varphi) \quad j_{max} = (n - \ell - 1) \geq 0 \quad |m| \leq \ell$$

$v(\rho)$  is a polynomial of degree  $j_{max}$  with coefficients:  $C_{g+1} = \frac{2(g+l+1-n)}{(g+1)(g+2l+2)} C_g$ . For state  $n$ , there are  $d(n) = n^2$  different solutions (**degeneracies**). The **effective radius** is  $na_0$ . The **probability** of finding an electron between  $r$  and  $r + dr$  is:

$$p(r)dr = r^2 |R_{n\ell}(r)|^2 dr$$



### 6.1.2 Quantum Numbers

$n$  is the main quantum number,  $\ell$  is the orbital quantum number and  $m$  is the magnetic quantum number (projection of angular momentum). Chemists give the different  $\ell$ 's different names.

- $\ell = 0$ : the orbital is called an s-state ( $\max p(r)dr$  is at  $r = 0$ ).
- $\ell = 1$ : the orbital is called an p-state ( $p(r = 0)dr = 0$ ).
- $\ell = 2$ : the orbital is called an d-state.

## 7 Useful formulas

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad \int_0^{\infty} xe^{-ax^2} dx = \frac{1}{2a} \quad \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{\sqrt{\pi}}{2a^{3/2}}$$

$$\int x^n e^{cx} = e^{cx} \sum_{i=0}^n (-1)^{n-i} \frac{n!}{i! c^{n-i+1}} x^i \quad \int_0^{\infty} x^n e^{-cx} = \frac{n!}{c^{n+1}}$$

$$\text{Gaussian: } G = A \cdot e^{\frac{-x^2}{2\sigma^2}}$$

8 Periodic Table of the Elements

2.20 <b>H</b> Hydrogen 1.00784– 1.00811																				2 <b>He</b> Helium 4.002602(2)																			
3 0.98 <b>Li</b> Lithium 6.938–6.997	2s	4 1.57 <b>Be</b> Beryllium 9.0121831(5)	2s	<div><div>Zenegss</div><div>Sy</div><div>Name</div><div>saw</div></div> <div>Z = atomic number; eneg = electronegativity; ss = subshell; Sy = Symbol, Name = element name, saw = standard atomic weight</div>																		5 2.04 <b>B</b> Boron 10.806–10.821	2p	6 2.55 <b>C</b> Carbon 12.0096– 12.0116	2p	7 3.04 <b>N</b> Nitrogen 14.00643– 14.00728	2p	8 3.44 <b>O</b> Oxygen 15.99903– 15.99977	2p	9 3.98 <b>F</b> Fluorine 18.998403163(6)	2p	10 <b>Ne</b> Neon 20.1797(6)	2p						
11 0.93 <b>Na</b> Sodium 22.98976928(2)	3s	12 1.31 <b>Mg</b> Magnesium 24.304–24.307	3s																			13 1.61 <b>Al</b> Aluminium 26.9815385(7)	3p	14 1.90 <b>Si</b> Silicon 28.084–28.086	3p	15 2.19 <b>P</b> Phosphorus 30.973761998(5)	3p	16 2.58 <b>S</b> Sulphur 32.059–32.076	3p	17 3.16 <b>Cl</b> Chlorine 35.446–35.457	3p	18 <b>Ar</b> Argon 39.948(1)	3p						
19 0.82 <b>K</b> Potassium 39.0983(1)	4s	20 1.00 <b>Ca</b> Calcium 40.078(4)	4s	21 1.36 <b>Sc</b> Scandium 44.955908(5)	3d	22 1.54 <b>Ti</b> Titanium 47.867(1)	3d	23 1.63 <b>V</b> Vanadium 50.9415(1)	3d	24 1.66 3d* <b>Cr</b> Chromium 51.9961(6)	3d	25 1.55 3d <b>Mn</b> Manganese 54.938044(3)	3d	26 1.83 3d <b>Fe</b> Iron 55.845(2)	3d	27 1.88 3d <b>Co</b> Cobalt 58.933194(4)	3d	28 1.91 3d <b>Ni</b> Nickel 58.6934(4)	3d	29 1.90 3d* <b>Cu</b> Copper 63.546(3)	3d	30 1.65 3d <b>Zn</b> Zinc 65.38(2)	3d	31 1.81 4p <b>Ga</b> Gallium 69.723(1)	4p	32 2.01 4p <b>Ge</b> Germanium 72.630(8)	4p	33 2.18 4p <b>As</b> Arsenic 74.921595(6)	4p	34 2.55 4p <b>Se</b> Selenium 78.971(8)	4p	35 2.96 4p <b>Br</b> Bromine 79.901–79.907	4p	36 3.00 4p <b>Kr</b> Krypton 83.798(2)	4p				
37 0.82 <b>Rb</b> Rubidium 85.4678(3)	5s	38 0.95 <b>Sr</b> Strontium 87.62(1)	5s	39 1.22 <b>Y</b> Yttrium 88.90584(2)	4d	40 1.33 <b>Zr</b> Zirconium 91.224(2)	4d	41 1.6 4d* <b>Nb</b> Niobium 92.90637(2)	4d	42 2.16 4d* <b>Mo</b> Molybdenum 95.95(1)	4d	43 1.9 4d <b>Tc</b> Technetium (98)	4d	44 2.2 4d* <b>Ru</b> Ruthenium 101.07(2)	4d	45 2.28 4d* <b>Rh</b> Rhodium 102.90550(2)	4d	46 2.20 4d* <b>Pd</b> Palladium 106.42(1)	4d	47 1.93 4d* <b>Ag</b> Silver 107.8682(2)	4d	48 1.69 4d <b>Cd</b> Cadmium 112.414(4)	4d	49 1.78 5p <b>In</b> Indium 114.818(1)	5p	50 1.96 5p <b>Sn</b> Tin 118.710(7)	5p	51 2.05 5p <b>Sb</b> Antimony 121.760(1)	5p	52 2.1 5p <b>Te</b> Tellurium 127.60(3)	5p	53 2.66 5p <b>I</b> Iodine 126.90447(3)	5p	54 2.60 5p <b>Xe</b> Xenon 131.293(6)	5p				
55 0.79 <b>Cs</b> Cesium 132.90545196(6)	6s	56 0.89 <b>Ba</b> Barium 137.327(7)	6s	57-71 <b>*</b> Lanthanides		72 1.3 5d <b>Hf</b> Hafnium 178.49(2)	5d	73 1.5 5d <b>Ta</b> Tantalum 180.94788(2)	5d	74 2.36 5d <b>W</b> Tungsten 183.84(1)	5d	75 1.9 5d <b>Re</b> Rhenium 186.207(1)	5d	76 2.2 5d <b>Os</b> Osmium 190.23(3)	5d	77 2.20 5d <b>Ir</b> Iridium 192.217(3)	5d	78 2.28 5d* <b>Pt</b> Platinum 195.084(9)	5d	79 2.54 5d* <b>Au</b> Gold 196.966569(5)	5d	80 2.00 5d <b>Hg</b> Mercury 200.592(3)	5d	81 1.62 6p <b>Tl</b> Thallium 204.382– 204.385	6p	82 1.87 6p <b>Pb</b> Lead 207.2(1)	6p	83 2.02 6p <b>Bi</b> Bismuth 208.98040(1)	6p	84 2.0 6p <b>Po</b> Polonium (209)	6p	85 2.2 6p <b>At</b> Astatine (210)	6p	86 2.2 6p <b>Rn</b> Radon (222)	6p				
87 0.7 7s <b>Fr</b> Francium (223)	7s	88 0.9 7s <b>Ra</b> Radium (226)	7s	89-103 <b>**</b> Actinides		104 <b>Rf</b> Rutherfordium (261)	6d	105 <b>Db</b> Dubnium (268)	6d	106 <b>Sg</b> Seaborgium (269)	6d	107 <b>Bh</b> Bohrium (270)	6d	108 <b>Hs</b> Hassium (269)	6d	109 <b>Mt</b> Meitnerium (278)	6d	110 <b>Ds</b> Darmstadtium (281)	6d	111 <b>Rg</b> Roentgenium (282)	6d	112 <b>Cn</b> Copernicium (285)	6d	113 <b>Nh</b> Nihonium (286)	7p	114 <b>Fl</b> Flerovium (289)	7p	115 <b>Mc</b> Moscovium (289)	7p	116 <b>Lv</b> Livermorium (293)	7p	117 <b>Ts</b> Tennesine (294)	7p	118 <b>Og</b> Oganesson (294)	7p				
</																																							

Standard atomic weights taken from the Commission on Isotopic Abundances and Atomic Weights (ciaaw.org/atomic-weights.htm). Adapted from Ivan Griffin's L<sup>A</sup>T<sub>E</sub>X Periodic Table. © 2017 Paul Danese

An asterisk (\*) next to a subshell indicates an anomalous (Aufbau rule-breaking) ground state electron configuration.