The Photon

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

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

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

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

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

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

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

$$\epsilon_{0} = 8.854 \cdot 10^{-12} \left[\frac{\text{F}}{\text{m}} \right]$$

$$1 \text{ [eV]} = 1.602 \cdot 10^{-19} \left[\frac{\text{kg m}^{2}}{s^{2}} \right] \text{ [J]}$$

Photon & Electron

$$\begin{array}{ccc} \lambda \ [\mathrm{m}] \,, \, \nu \ \left[\frac{1}{\mathrm{s}}\right] & \text{Wavelength, Freq.} \\ k & \text{Wavenumber} \\ E \ [\mathrm{J}] & \text{Energy} \\ \vec{F_c} \ [\mathrm{N}] & \text{Coulomb Force} \end{array}$$

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

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

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

$$\left| \vec{F_c} \right| = \frac{Q_1 \cdot Q_2}{4\pi\epsilon_0 r^2}$$

Photoelectric effect

$$\begin{array}{ll} V \ [\mathrm{V}] & \mathrm{Voltage} \\ \phi_0 \ [\mathrm{eV}] & \mathrm{Work \ function} \\ I \ [\mathrm{A}] & \mathrm{Photo-current} \\ n \ [\mathrm{m}^{-3}] & \mathrm{Volume \ density \ of \ electrons} \\ A \ [\mathrm{m}^2] & \mathrm{Area} \\ v \ [\frac{\mathrm{m}}{\mathrm{s}}] & \mathrm{velocity \ of \ electrons} \end{array}$$

$$h\nu - \phi_0 = \frac{1}{2}mv^2 = eV$$
$$V(\nu) = \frac{h}{e}\nu - \frac{\phi_0}{e}$$
$$I = nAve$$

Blackbody Radiation

$$L$$
 [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 N Density of states N Blackbody radiation N Power radiated

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

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

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

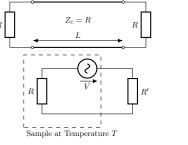
$$u(\omega) = \frac{\omega^2}{\pi^2 c^3} \cdot \frac{\hbar\omega}{\exp\left(\frac{-\hbar\omega}{kT}\right) - 1}d\omega \quad u(\nu) = \frac{8\pi\hbar\nu^3}{c^3\left(\exp\left(\frac{\hbar\nu}{kT}\right) - 1\right)}d\nu$$

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

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

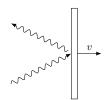
Johnson-Noise

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



$$\langle V^2 \rangle$$
 Noise Voltage
 $\Delta \nu$ Bandwidth
 $E = E_0 \cdot \sin(k_x \cdot x)$
 $\langle V^2 \rangle = 4R \cdot k_B T \cdot \Delta \nu$

Momentum of a photon



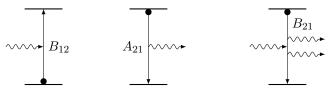
$$p \left[\frac{\log m}{s}\right] \quad \text{momentum}$$

$$p_{absorbing} = \frac{h\nu}{c} = m \cdot v$$

$$p_{reflecting} = 2 \cdot \frac{h\nu}{c}$$

$$p = \sqrt{2m_e e \Delta V}$$

1.6 Absorption, spontaneous and stimulated emission



absorbtion spontaneous emission stimulated emission

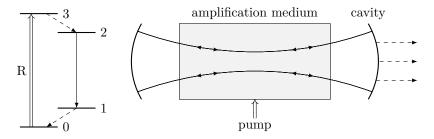
- n_1 Number of electrons in the lower energy state
- n_2 Number of electrons in the higher energy state

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

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

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

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 τ_1 . As a result, the population in state "2" is:

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

1.8 Fermi Energy of a metal

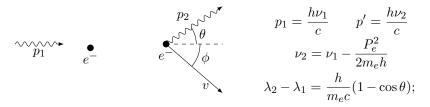
$$E_F = \frac{\hbar^2}{2m_e} \left(3n\pi^2 \right)^{2/3} \qquad n = \frac{\rho}{m} = \frac{\rho \cdot N_A}{m_{mol}}$$

Where m_e [kg] is the mass of the electron, m [kg] is the mass of an single atom of the metal, m_{mol} $\left[\frac{\text{kg}}{\text{mol}}\right]$ is the atomic weight, n $\left[\frac{1}{\text{m}^3}\right]$ is the number of atoms per unit of volume and ρ $\left[\frac{\text{kg}}{\text{m}^3}\right]$ is the density of the metal.

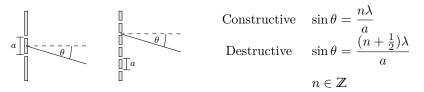
2 Wave mechanics

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

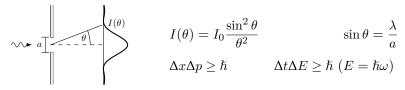
2.1 Compton Scattering



2.2 Double Slit and Bragg Diffraction



2.3 Single slit and uncertainty relation



Bohr-Sommerfeld quantisation

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

$$\int_{length} p \cdot ds = n \cdot h \qquad n \in \mathbb{N}$$

$$p \qquad \text{Momentum of particle}$$

$$E_n \qquad \text{Energy of the nth state}$$

$$E_{ry} \qquad \text{Rydberg Energy}$$

$$a_0 \qquad \text{Bohr-radius}$$

$$Z \qquad \text{Number of protons}$$

$$r_n = \frac{n^2}{Z} \cdot \frac{2\epsilon_0 h}{m_e e^2} = \frac{n^2}{Z} \cdot a_0$$

$$E_{ry} = 13.6 \text{ [eV]}$$

$$a_0 = 5.292 \cdot 10^{-11} \text{ [m]}$$

Quantum Mechanics 3

3.1Wave function

$$\psi(\boldsymbol{x},t) : \mathbb{R}^4 \to \mathbb{C} \qquad \iiint |\psi(\boldsymbol{x},t)|^2 d^3 r = 1$$
$$\psi(\boldsymbol{x},t) = a\psi_1(\boldsymbol{x},t) + b\psi_2(\boldsymbol{x},t), \qquad |a|^2 + |b|^2 = 1$$
$$P(x)dx = |\psi(x)|^2 dx \qquad P_{ab} = \int_a^b |\psi(x)|^2 dx \qquad \langle x \rangle = \int_{-\infty}^\infty x |\psi(x)|^2 dx$$

The Schrödinger equation

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

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

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

The wave function and it's derivative must be continuous where the potential V(x,t) is finite.

3.2.1Phase and Group Velocity

phase velocity v_{ω} (phase movement), group velocity v_{a} (movement of wave packet)

$$v_{\varphi} = \frac{\omega}{k}$$
 $v_g = \frac{\partial \omega}{\partial k}$ Particle wave: $v_{\varphi} \cdot 2 = v_g$

Stationary (Time independent) States

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

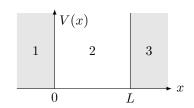
$$\Psi_n(\boldsymbol{x},t) = \psi_n(\boldsymbol{x}) \cdot \chi_n(t) = \psi_n(\boldsymbol{x}) \cdot e^{-i\frac{E_n}{\hbar}t}$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n(\boldsymbol{x}) + V(\boldsymbol{x})\psi_n(\boldsymbol{x}) = \psi_n(\boldsymbol{x}) \cdot E_n$$

$$\iiint |\Psi|^2 d^3 \boldsymbol{x} = \iiint |\psi|^2 d^3 \boldsymbol{x} = 1$$

$$\Psi(\boldsymbol{x},t) = \sum a_n \psi_n(\boldsymbol{x}) \cdot e^{-i\frac{E_n}{\hbar}t} \sum |a_n|^2 = 1$$

Example: 1D infinite potential well



$$V(x)$$

$$2$$

$$3$$

$$\Psi_{1} = \Psi_{3} = 0$$

$$-\frac{\hbar^{3}}{2m} \frac{\partial^{2}}{\partial x^{2}} \psi_{2}(x, t) = E\psi_{2}(x, t)$$

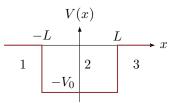
$$\psi_{2} = A \sin(kx) + B \cos(kx)$$

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

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

$$E_n = n^2 \cdot \frac{\hbar^2 \pi^2}{2mL} = n^2 \cdot E_0, \qquad k_n = \frac{n\pi}{L} \left[\frac{1}{m}\right]$$

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:

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

$$\psi_2(x) = A_2 e^{ikx} + A_2' e^{-ikx}$$
 $E = \frac{k^2 \hbar^2}{2m}$ $k = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$

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

1. E > 0:Unbound state

$$-\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2}\psi_1(x) = E\psi_1(x) \qquad \psi_1 = A_1e^{ikx} + A_1'e^{-ikx} \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

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

$$-\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2}\psi_1(x) = E\psi_1(x) \qquad \psi_1 = B_1 e^{\delta x} + B_1' e^{-\delta x} \qquad \delta = \sqrt{-\frac{2mE}{\hbar^2}}$$

We see that as $x \to -\infty$, the Term B_1' , as well as B_3 approaches ∞ . Since the wave function cannot approach ∞ , $B_1' = B_3 = 0$ is a condition.

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

$$\psi_1(-L) = \psi_2(-L) \qquad \psi_2(L) = \psi_3(L)$$
$$\frac{\partial}{\partial x}\psi_1(-L) = \frac{\partial}{\partial x}\psi_2(-L) \qquad \frac{\partial}{\partial x}\psi_2(L) = \frac{\partial}{\partial x}\psi_3(L)$$

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

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

$$|\cos(kL)|$$

$$1$$

$$k_0$$

$$k_0$$

$$k_0$$

$$k_0$$

 $\begin{array}{c} \textbf{Odd solutions: only odd (sine)} \\ \textbf{components} \end{array}$

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

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

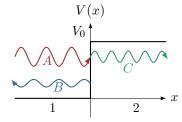
$$|\sin(kL)|$$

$$1 = \frac{1}{k_o}, \quad \tan(kL) > 0$$

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

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

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:

1. $E > V_0$: Transmission

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

2. $E < V_0$: Complete reflection

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

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

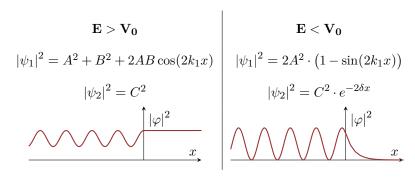
$$\psi_1(x=0) = \psi_2(x=0) \qquad \frac{\partial}{\partial x} \psi_1(x=0) = \frac{\partial}{\partial x} \psi_2(x=0)$$

$$\mathbf{E} > \mathbf{V_0} \qquad \mathbf{E} < \mathbf{V_0}$$

$$A + B = C \qquad A + B = C$$

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

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

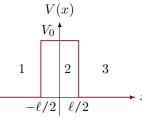


To find the **transmission coefficient** T and the **reflection coefficient** R, we normalize A=1. Then, we can define $B=\sqrt{R}$ and $C=\sqrt{T}$. Then, we can solve for R and T:

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

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:

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

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

1.
$$\mathbf{E} < \mathbf{V_0}$$
: $\varphi_2 = B_2 e^{\delta_2 x} + B_2' e^{-\delta_2 x}, \qquad \delta_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$

2.
$$\mathbf{E} > \mathbf{V_0}$$
: $\varphi_2 = A_2 e^{ik_2 x} + A_2' e^{-ik_2 x}, \qquad k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$

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 $A_3' = 0$.

$$\psi_1(-\ell/2) = \psi_2(-\ell/2), \quad \psi_2(\ell/2) = \psi_3(\ell/2)$$
$$\frac{\partial}{\partial x}\psi_1(-\ell/2) = \frac{\partial}{\partial x}\psi_2(-\ell/2), \quad \frac{\partial}{\partial x}\psi_2(\ell/2) = \frac{\partial}{\partial x}\psi_3(\ell/2)$$

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

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

$$T = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sinh^2(\delta_2 \ell)} \qquad T = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sin^2(k_2 \ell)}$$

If $\mathbf{E} > \mathbf{V_0}$, the transmission coefficient has a maximum. If $k_2 \ell = n\pi \Rightarrow T = 1$ (**resonance**). The minimum of $T\mathbf{u}$ is at: $k_2 \ell = \pi/2 + n\pi$. If $\delta_2 \ell \gg 1$, the transmission coefficient is proportional to: $T \propto e^{-2\delta_2 \ell}$

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 $\langle \psi_1 | \psi_2 \rangle = 0$, ψ_1 , ψ_2 are **orthogonal**.

$$\langle \psi_1 | \psi_2 \rangle = \int_{-\infty}^{\infty} \psi_1^*(\boldsymbol{x}, t) \psi_2(\boldsymbol{x}, t) d^3 \boldsymbol{x}$$
$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} \psi^*(\boldsymbol{x}, t) \psi(\boldsymbol{x}, t) d^3 \boldsymbol{x} = \int_{-\infty}^{\infty} \left| \psi(\boldsymbol{x}, t) \right|^2 d^3 \boldsymbol{x} = 1$$

4.2 Fourier Transform

$$\begin{split} \psi(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{ipx}{\hbar}} \varphi(p) dp, \quad \varphi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{ipx}{\hbar}} \psi(x) dx \\ \psi(\vec{\boldsymbol{x}}) &= \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} e^{\frac{i\vec{p}\vec{\boldsymbol{x}}}{\hbar}} \varphi(\vec{\boldsymbol{p}}) d\vec{\boldsymbol{p}}, \quad \varphi(\vec{\boldsymbol{p}}) = \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} e^{\frac{i\vec{p}\vec{\boldsymbol{x}}}{\hbar}} \psi(\vec{\boldsymbol{x}}) d\vec{\boldsymbol{x}} \end{split}$$

$$\int_{-\infty}^{\infty} \psi_1^*(x) \cdot \psi_2(x) \cdot dx = \int_{-\infty}^{\infty} \varphi_1^*(p) \cdot \varphi_2(p) \cdot dp$$

5 Observable Measurements, Time-dependence

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

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

Name	Operator	
Position	$\widehat{m{x}} = [m{x}]$	
Momentum	$\widehat{\boldsymbol{p}} = [-i\hbar\boldsymbol{\nabla}]$	$oldsymbol{ abla} = egin{bmatrix} rac{\partial}{\partial x} & rac{\partial}{\partial y} & rac{\partial}{\partial z} \end{bmatrix}^T$
Hamiltonian	$\widehat{H} = \left[-rac{\hbar^2}{2m} abla^2 + V(oldsymbol{x}) ight]$	$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

5.1 Canonical commutation relation

The commutators is a way of describing the effect of the order, in which multiple operators are applied.

$$\begin{aligned}
\left[\widehat{A}, \widehat{B}\right] &= \widehat{A}\widehat{B} - \widehat{B}\widehat{A}, \quad \left[\widehat{A}, \widehat{B}\right] = -\left[\widehat{B}, \widehat{A}\right], \quad \left[\widehat{A}, \widehat{A}\right] = 0 \\
\left[\widehat{A}, (\widehat{B} + \widehat{C})\right] &= \left[\widehat{A}, \widehat{B}\right] + \left[\widehat{A}, \widehat{C}\right] \\
\left[\widehat{p}_x, \widehat{p}_y\right] &= 0, \quad \left[\widehat{x}, \widehat{p}_x\right] = i\hbar, \quad \left[\widehat{z}, \widehat{p}_x\right] = \left[\widehat{z}, \widehat{p}_y\right] = 0
\end{aligned}$$

5.2 Eigenstates and Eigenvalues

An Observable has an Operator \widehat{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.

$$\widehat{A}u_n(x) = a_n u_n(x), \quad \int_{-\infty}^{\infty} u_n^*(x) \widehat{A}u_n(x) dx = a_n \quad \widehat{A}\psi(x) = \sum_n c_n u_n(x)$$

5.3 Harmonic Oscillator

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

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

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

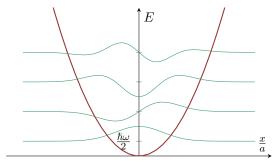
$$a = \sqrt{\frac{\hbar}{m\omega}}, \quad \tilde{x} = \frac{x}{a}, \quad \tilde{E} = \frac{E}{\hbar\omega} \Rightarrow \frac{1}{2} \left[-\frac{\partial^2}{\partial \tilde{x}^2} + \tilde{x}^2 \right] \varphi(\tilde{x}) = \tilde{E}\varphi(\tilde{x})$$

Then, the solutions to the equation is:

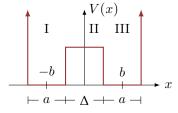
$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad \psi(\tilde{x}) = c_n H_n(\tilde{x})e^{-\tilde{x}/2}, \quad H_n(\tilde{x}) = (-1)^n e^{\tilde{x}^2} \cdot \frac{\partial^n}{\partial \tilde{x}^n} e^{-\tilde{x}^2}$$

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

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



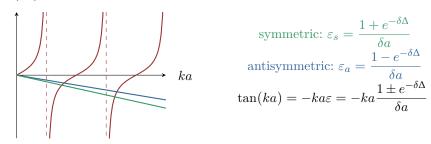
5.4 The coupled quantum well



This is the simplified potential of an ammonia molecule NH₃. 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: $E < V_0$

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

tan(ka)

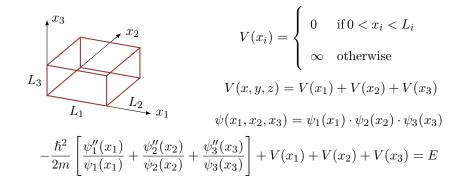


Now, we can create a superposition of both the symmetric and the antisymmetric case:

$$\begin{split} \psi_{s_{\mathrm{I}}} &= +\lambda \sin \left(k \left(b - \frac{a}{2} + x \right) \right), \quad \psi_{s_{\mathrm{III}}} = +\lambda \sin \left(k \left(b - \frac{a}{2} + x \right) \right) \\ \psi_{a_{\mathrm{I}}} &= -\lambda \sin \left(k \left(b - \frac{a}{2} + x \right) \right), \quad \psi_{a_{\mathrm{III}}} = +\lambda \sin \left(k \left(b - \frac{a}{2} + x \right) \right) \\ \Psi_{L} &= \frac{1}{\sqrt{2}} (\Psi_{s} - \Psi_{a}), \qquad \Psi_{R} = \frac{1}{\sqrt{2}} (\Psi_{s} + \Psi_{a}) \\ \Psi_{L}(x, t) &= \frac{1}{\sqrt{2}} e^{-i\omega_{s}t} \left(\psi_{s}(x) - e^{-i(\omega_{a} - \omega_{s})t} \psi_{a}(x) \right) \\ \omega_{a} &= \frac{E_{a}}{\hbar}, \quad \omega_{s} = \frac{E_{a}}{\hbar}, \quad E_{a} - E_{s} = \frac{\hbar^{2} \pi^{2}}{2m\delta a^{2}} \cdot 8e^{-\delta \Delta} \end{split}$$

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

6 Schrödinger Equation in 3D



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

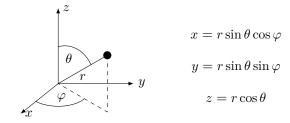
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_i^2}\psi_i(x_i) + V(x_i)\psi_i(x_i) = E_i\psi_i(x_i)$$
$$E_i^{(n_i)} = n_i^2 \frac{\hbar^2 \pi^2}{2mL_i^2}, \qquad \psi_i^{(n_1)} = A \cdot \sin\left(\frac{\pi n_i x}{L_i}\right)$$

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



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

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

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

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

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

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:

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

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

$$E = -\frac{E_{Ry}}{n^2} \approx -\frac{13.6}{n^2} \text{ [eV]}$$

 $v(\rho)$ 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 of finding an electron between r and r + dr is:

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

6.1.2 Quantum Numbers

n is the main quantum number, ℓ is the orbital quantum number and m is the magnetic quantum number (projection of angular momentum). Chemists give the different ℓ '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 Angular Momentum and Spin

$$\widehat{L}_{x} = \widehat{y}\widehat{p}_{z} - \widehat{z}\widehat{p}_{y} \qquad \widehat{L}_{y} = \widehat{z}\widehat{p}_{x} - \widehat{x}\widehat{p}_{z} \qquad \widehat{L}_{z} = \widehat{x}\widehat{p}_{y} - \widehat{y}\widehat{p}_{x} \qquad \widehat{L} = \det \begin{vmatrix} \mathbf{e}_{x} & \mathbf{e}_{y} & \mathbf{e}_{z} \\ \widehat{x} & \widehat{y} & \widehat{z} \\ \widehat{x} & \widehat{y} & \widehat{z} \\ \widehat{p}_{x} & \widehat{p}_{y} & \widehat{p}_{z} \end{vmatrix}$$

$$\widehat{L}_{x} = i\hbar \left(\sin \varphi \frac{\partial}{\partial \theta} + \frac{\cos \theta \cos \varphi}{\sin \theta} \frac{\partial}{\partial \varphi} \right), \ \widehat{L}_{y} = -i\hbar \left(\cos \varphi \frac{\partial}{\partial \theta} - \frac{\cos \theta \sin \varphi}{\sin \theta} \frac{\partial}{\partial \varphi} \right)$$

$$\widehat{L}_{z} = -i\hbar \frac{\partial}{\partial \varphi}, \quad \widehat{L}^{2} = -\hbar^{2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^{2} \theta} \frac{\partial^{2}}{\partial \varphi^{2}} \right]$$

Angular momentum operators do not commute. In order to get commutable operators, we introduce $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

$$\begin{split} \left[\widehat{L}^2,\widehat{L}_x\right] &= 0, \qquad \left[\widehat{L}^2,\widehat{L}_y\right] = 0, \qquad \left[\widehat{L}^2,\widehat{L}_z\right] = 0 \\ \widehat{L}^2Y_\ell^m(\theta,\varphi) &= \hbar^2\ell(\ell+1)Y_\ell^m(\theta,\varphi), \qquad \widehat{L}_zY_\ell^m(\theta,\varphi) = \hbar mY_\ell^m(\theta,\varphi) \end{split}$$

7.1 Ladder Operator

If a ladder operators $\widehat{L}_{\pm} = \widehat{L}_x \pm i\widehat{L}_y$ are used in the following way: Suppose, we have a wave function ψ , which is simultaneously an eigenfunction of \widehat{L}^2 and \widehat{L}_z . Then, $\widehat{L}_{\pm}\psi$ is also an eigenfunction of \widehat{L}^2 and \widehat{L}_z with the following eigenvalues:

$$\widehat{L}^2\psi = \lambda\psi, \quad \widehat{L}_z\psi = \mu\psi \qquad \widehat{L}^2(\widehat{L}_\pm\psi) = \lambda(\widehat{L}_\pm\psi), \quad \widehat{L}_z(\widehat{L}_\pm\psi) = (\mu\pm\hbar)(\widehat{L}_\pm\psi)$$

$$\widehat{L}_+Y_\ell^m = \hbar\sqrt{\ell(\ell+1) - m(m+1)}Y_\ell^{m+1} \qquad \widehat{L}_-Y_\ell^m = \hbar\sqrt{\ell(\ell+1) - m(m-1)}Y_\ell^{m-1}$$

7.2 Spin

Idea: $\ell = \frac{1}{2} \rightarrow m = \pm \frac{1}{2}$. Instead of using ℓ , we use s to describe the spin. The operators \widehat{L}_i are now called \widehat{S}_i . We define the spin as $|s, m_s\rangle$:

$$\chi_{+} = \left| \frac{1}{2}, \frac{1}{2} \right\rangle = \left| \uparrow \right\rangle, \quad \chi_{-} = \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = \left| \downarrow \right\rangle, \quad \chi = a\chi_{+} + \beta\chi_{-} = \begin{pmatrix} a \\ b \end{pmatrix}, \ |a|^{2} + |b|^{2} = 1$$

Since we have now only two eigenstates $|\uparrow\rangle$ and $|\downarrow\rangle$, we can write:

$$\widehat{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \widehat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \widehat{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \widehat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

If we separate the spin in all three directions, we can write:

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}} (|\uparrow_z\rangle + |\downarrow_z\rangle), \qquad |\downarrow_x\rangle = \frac{1}{\sqrt{2}} (|\uparrow_z\rangle - |\downarrow_z\rangle)$$

Now, we define the ladder operators in the same way as for the angular momentum:

$$\widehat{S}_{+} = \begin{pmatrix} 0 & \hbar \\ 0 & 0 \end{pmatrix} \quad \widehat{S}_{-} = \begin{pmatrix} 0 & 0 \\ \hbar & 0 \end{pmatrix} \quad \widehat{S}_{+} \mid \uparrow \rangle = \widehat{S}_{-} \mid \downarrow \rangle = 0, \ \widehat{S}_{+} \mid \downarrow \rangle = \hbar \mid \uparrow \rangle, \ \widehat{S}_{-} \mid \uparrow \rangle = \hbar \mid \downarrow \rangle$$

We can write states states in dirac notation as: $|\ell, m\rangle$. For spins, we get:

$$|1,1\rangle = |\uparrow\uparrow\rangle, \ |1,-1\rangle = |\downarrow\downarrow\rangle, \ |1,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \ |0,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

7.3 Identical Particles

When we have two particles with wave function $\varphi_a(\vec{x}_1)$ and $\varphi_b(\vec{x}_2)$, we can combine them in two different ways:

- Fermion: $\psi_{-} = \frac{1}{\sqrt{2}} \left(\varphi_a(\vec{x}_1) \varphi_b(\vec{x}_2) \varphi_b(\vec{x}_1) \varphi_a(\vec{x}_2) \right)$: symmetric (electron)
- Boson: $\psi_+ = \frac{1}{\sqrt{2}} \left(\varphi_a(\vec{x}_1) \varphi_b(\vec{x}_2) + \varphi_b(\vec{x}_1) \varphi_a(\vec{x}_2) \right)$: antisymmetric (photon)

Pauli exclusion principle: Two fermions cannot occupy the same identical state

7.3.1 Exchange Interactions

We have two particles, which have normalized and orthogonal wave functions. We have three different interactions:

1. The particles are **distinguishable**: $\psi = \psi_a(x_1)\psi_b(x_2)$

$$\left\langle (x_1 - x_2)^2 \right\rangle_{\psi} = \left\langle x^2 \right\rangle_{\psi_a} + \left\langle x^2 \right\rangle_{\psi_b} - 2 \left\langle x \right\rangle_{\psi_a} \left\langle x \right\rangle_{\psi_b}$$

2. Symmetric wave function: $\psi_{+} = \frac{1}{\sqrt{2}}(|\psi_{a}\rangle |\psi_{b}\rangle + |\psi_{b}\rangle |\psi_{a}\rangle)$

$$\left\langle (x_1 - x_2)^2 \right\rangle_{\psi} = \left\langle x^2 \right\rangle_{\psi_a} + \left\langle x^2 \right\rangle_{\psi_b} - 2 \left\langle x \right\rangle_{\psi_a} \left\langle x \right\rangle_{\psi_b} - 2 \left| \left\langle \psi_a | x | \psi_b \right\rangle \right|^2$$

3. Antisymmetric wave function: $\psi_{-} = \frac{1}{\sqrt{2}} (|\psi_a\rangle |\psi_b\rangle - |\psi_b\rangle |\psi_a\rangle)$

$$\left\langle \left(x_1 - x_2\right)^2 \right\rangle_{\psi} = \left\langle x^2 \right\rangle_{\psi_a} + \left\langle x^2 \right\rangle_{\psi_b} - 2 \left\langle x \right\rangle_{\psi_a} \left\langle x \right\rangle_{\psi_b} + 2 \left| \left\langle \psi_a | x | \psi_b \right\rangle \right|^2$$

7.4 Many Electrons: Atomic Shells

To write the wave function of an electron, we use the notation indexed by: $|n, \ell, m\rangle$.

shell n	subshell ℓ	$\max e^-$ in subshell	$\max e^-$ in shell
K	1s	2	2
L	2s	2	2+6=8
	2p	6	
M	3s	2	2+6+10=10
	3p	6	
	3d	10	

Here, the number of degeneracies per shell is displayed. Remember, we have $n \geq 1$, $0 \leq \ell < n$, $-\ell \leq m \leq \ell$, and for every different state, the electron can have either spin up or spin down. So, the number of electrons in a sub shell is the number of degeneracies.

7.5 Term Symbol

$$^{2S+1}L$$

S is the total spin quantum number, 2S+1 is the spin multiplicity, J (m) is the total angular momentum quantum number and L is the orbital quantum number in spectroscopic notation: $L=0 \to S, L=1 \to P, L=2 \to D...$

8 Quantum Statistics and Solid States

8.1 Chemical Potential

For the chemical potential μ , the flux of particles (instead of energy) is important.

$$\mu = \frac{\partial F}{\partial N}, \qquad F = U - TS$$

where F is the free energy, U is the total energy, T is the temperature, S is the entropy and N is the number of particles. In other words: Chemical Potential is the energy exchanged when a particle is added or removed.

8.2 Fermi-Dirac & Einstein Statistics

What is the probability of a given state to be occupied? And if we have multiple particles, how many electrons are in a state?

Fermions:
$$f_F(E, \mu, T) = \frac{1}{\exp\left(\frac{E-\mu}{kT}\right) + 1}$$
, Bosons: $f_B(E, \mu, T) = \frac{1}{\exp\left(\frac{E-\mu}{kT}\right) - 1}$

As the energy $E \gg \mu$, both distributions are the same: the classical Bolzmann distribution. If the electrons are far away, we do not need to consider the interaction between single particles.

8.3 Fermi-Dirac statistics of a free electron gas

The number of particles N given an energy E with temperature T=0 is:

$$N(E) = \frac{L^3}{3\pi^2} \frac{(2mE)^{\frac{3}{2}}}{\hbar^2} = \frac{4}{3}\pi k^3 \cdot \frac{1}{8} \cdot \left(\frac{L}{\pi}\right)^3 \cdot 2$$

This equation is derived by multiplying the Volume of a sphere (in the positive k sector) with radius k with the volume of a single state and the number of possible spins (2). The Density of states D(E) is given by:

$$D(E) = \frac{\partial N(E)}{\partial E} \cdot \frac{1}{V} = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \sqrt{E}$$

8.4 Bloch's Theorem

In a periodic potential, the wave equation can be written as a periodic function $u_{nk}(x)$ multiplied by a complex exponential:

$$\psi_{nk}(x) = e^{ikx} u_{nk}(x)$$

We can apply this theorem the band formation to conclude the following. As soon as we have a crystal, the electrons can be in a continuous band of energies:

$$E = E_0 - 2A\cos(ka) = E(k)$$

where A is the inter-atomic coupling. We can see that the band width is directly proportional to A.

9 Useful formulas

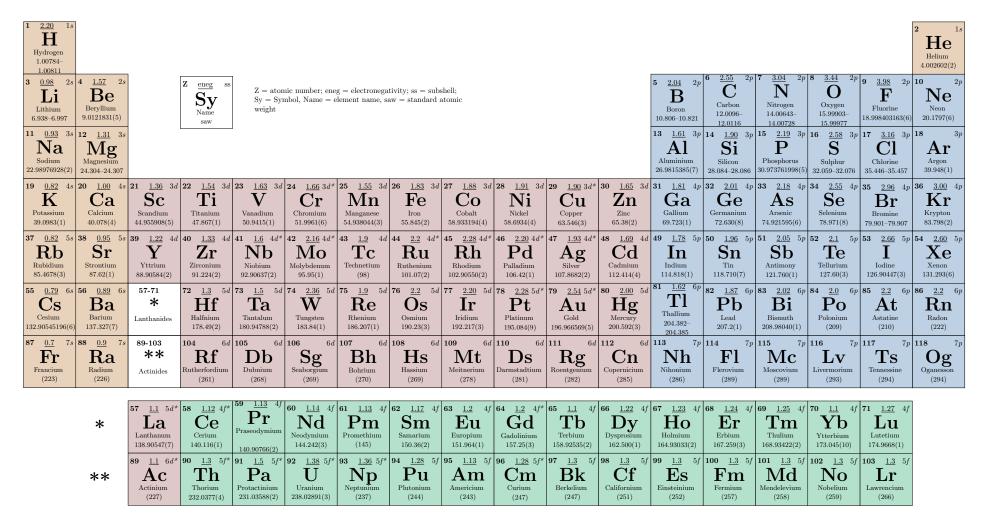
$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \qquad \int_{0}^{\infty} x e^{-ax^2} dc = \frac{1}{2a} \qquad \int_{-\infty}^{\infty} x^2 e^{-ax^2} = \frac{\sqrt{\pi}}{2a^{3/2}}$$
$$\int x^n e^{cx} = e^{cx} \sum_{i=0}^{n} (-1)^{n-i} \frac{n!}{i!c^{n-i+1}} x^i \qquad \int_{0}^{\infty} x^n e^{-cx} = \frac{n!}{c^{n+1}}$$

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

9.1 Trigonometry

$$\begin{array}{lll} \sin(2\alpha) &= 2\sin\alpha\cos\alpha & \cos(2\alpha) &= \cos^2\alpha - \sin^2\alpha \\ \sin(\alpha\pm\beta) &= \sin(\alpha)\cos(b)\pm\cos(\alpha)\sin(b) & \cos(\alpha\pm\beta) &= \cos(\alpha)\cos(b)\mp\sin(\alpha)\sin(b) \\ \sin(\alpha)\pm\sin(\beta) &= 2\sin\frac{\alpha\pm\beta}{2}\cos\frac{\alpha\mp\beta}{2} & \cos(\alpha)+\cos(\beta) &= 2\cos\frac{\alpha+\beta}{2}\cos\frac{\alpha-\beta}{2} \\ \cos(\alpha)-\cos(\beta) &= -2\sin\frac{\alpha+\beta}{2}\sin\frac{\alpha-\beta}{2} & \sin(\alpha)\sin(\beta) &= \frac{1}{2}(\cos(\alpha-\beta)-\cos(\alpha+\beta)) \\ \cos(\alpha)\cos(\beta) &= \frac{1}{2}(\cos(\alpha-\beta)+\cos(\alpha+\beta)) & \sin(\alpha)\cos(\beta) &= \frac{1}{2}(\sin(\alpha-\beta)+\sin(\alpha+\beta)) \\ \sin^2\alpha &= \frac{1}{2}\left(1-\cos2\alpha\right) & \cos^2\alpha &= \frac{1}{2}\left(1+\cos2\alpha\right) \\ \sin^3\alpha &= \frac{1}{4}\left(3\sin\alpha-\sin3\alpha\right) & \cos^3\alpha &= \frac{1}{4}\left(3\cos\alpha+\cos3\alpha\right) \\ \frac{\sin2\alpha}{\sin\alpha} &= 2\cos\alpha & \sin\alpha\cos\alpha &= \frac{1}{2}\sin2\alpha \\ c^2 &= a^2+b^2-2ab\cos\gamma & \frac{a}{\sin\alpha} &= \frac{b}{\sin\beta} &= \frac{c}{\sin\gamma} &= 2r &= \frac{u}{\pi} \end{array}$$

10 Periodic Table of the Elements



Standard atomic weights taken from the Commission on Isotopic Abundances and Atomic Weights (ciaaw.org/atomic-weights.htm). Adapted from Ivan Griffin's IsTeX Periodic Table. © 2017 Paul Danese

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