# The Photon

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

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

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

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

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

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

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

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

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

#### Photon & Electron

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

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

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

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

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

# Photoelectric effect

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

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

# **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

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

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

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

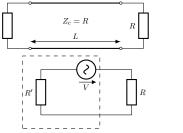
$$u(\omega) = \frac{\omega^2}{\pi^2 c^3} \cdot \frac{\hbar \omega}{\exp\left(\frac{-\hbar \omega}{kT}\right) - 1} d\omega \qquad u(\nu) = \frac{8\pi h \nu^3}{c^3 \left(\exp\left(\frac{h\nu}{kT}\right) - 1\right)} d\nu$$

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

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

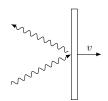
#### Johnson-Noise

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



Noise Voltage 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



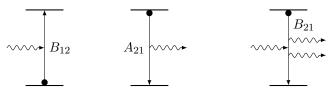
$$p \left[\frac{\log m}{s}\right] \quad \text{momentum}$$

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

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

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

## 1.6 Absorption, spontaneous and stimulated emission



absorbtion spontaneous emission stimulated emission

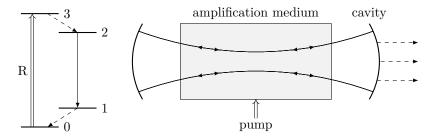
- $n_1$  Number of electrons in the lower energy state
- $n_2$  Number of electrons in the higher energy state

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

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

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

# 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:

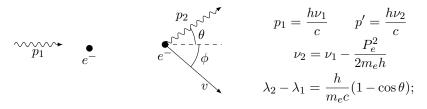
$$n_2 = \frac{R}{A_{21}}$$
 whereas  $n_1 \approx 0$  because  $A_{21} < \frac{1}{\tau_1}$ 

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

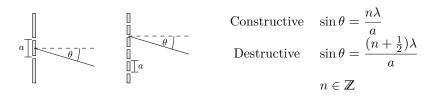
## 2 Wave mechanics

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

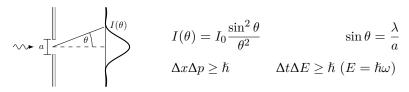
## 2.1 Compton Scattering



## 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

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

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

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

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

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

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

$$F_n = -\frac{Z^2}{n^2} \cdot \frac{m_e e^4}{8\epsilon_0^2 h^2} = -\frac{Z^2}{n^2} \cdot E_{ry}$$

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

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

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

# Quantum Mechanics

#### 3.1 Wave function

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

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

$$P(x)dx = |\psi(x)|^2 dx \qquad P_{ab} = \int_a^b |\psi(x)|^2 dx \qquad \langle x \rangle = \int_{-\infty}^\infty x |\psi(x)|^2 dx$$

#### 3.2 The Schrödinger equation

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

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

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

## 3.2.1 Phase and Group Velocity

The phase velocity  $v_{ij}$  describes how fast the phase of the wave moves forward. The group velocity  $v_q$  describes how fast the energy is moving forward.

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

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

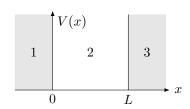
$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n(\boldsymbol{x}) + V(\boldsymbol{x})\psi_n(\boldsymbol{x}) = \psi_n(\boldsymbol{x}) \cdot E_n$$

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

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

Requirements: The wave function must be continuous, as well as it's derivative

#### 3.2.3Example: 1D infinite potential well



$$\Psi_1 = \Psi_3 = 0$$

$$-\frac{\hbar^3}{2m} \frac{\partial^2}{\partial x^2} \psi_2(x, t) = E\psi_2(x, t)$$

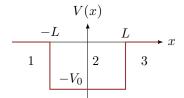
$$\psi_2 = A \sin(kx) + B \cos(kx)$$

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

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

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

## 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  $\infty$ . Since the wave function cannot approach  $\infty$ ,  $B_1' = B_3 = 0$  is a condition.

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

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

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

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

$$|\cos(kL)|$$

$$1$$

$$k_0$$

$$k_0$$

$$k_0$$

Odd solutions: only odd (sine) components

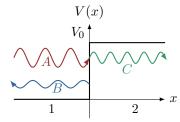
$$|\sin(kL)| = \frac{k}{k_o}, \quad \tan(kL) > 0$$

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

$$|\sin(kL)|$$

$$1 = \frac{1}{k_0} + \frac{$$

# 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:

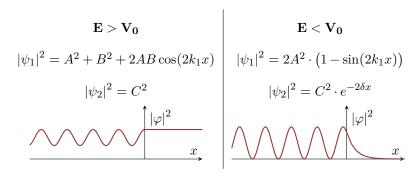
$$\psi_1(x=0) = \psi_2(x=0) \qquad \frac{\partial}{\partial x} \psi_1(x=0) = \frac{\partial}{\partial x} \psi_2(x=0)$$

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

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

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

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

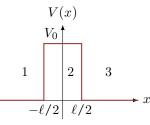


To find the **transmission coefficient** T and the **reflection coefficient** R, we normalize A=1. Then, we can define  $B=\sqrt{R}$  and  $C=\sqrt{T}$ . Then, we can solve for R and T:

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

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:  $k_2 \ell = \pi/2 + n\pi$ .

# 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  $\langle \psi_1 | \psi_2 \rangle = 0$ ,  $\psi_1$ ,  $\psi_2$  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

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{ipx}{\hbar}} \varphi(p) dp, \quad \varphi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{ipx}{\hbar}} \psi(x) dx$$

$$\psi(\vec{x}) = \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} e^{\frac{i\vec{p}\vec{x}}{\hbar}} \varphi(\vec{p}) d\vec{p}, \quad \varphi(\vec{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} e^{\frac{i\vec{p}\vec{x}}{\hbar}} \psi(\vec{x}) d\vec{x}$$

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

# 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.

$$\left[\widehat{A}, \widehat{B}\right] = \widehat{A}\widehat{B} - \widehat{B}\widehat{A}, \quad \left[\widehat{A}, \widehat{B}\right] = -\left[\widehat{B}, \widehat{A}\right], \quad \left[\widehat{A}, \widehat{A}\right] = 0$$

$$\left[\widehat{A}, (\widehat{B} + \widehat{C})\right] = \left[\widehat{A}, \widehat{B}\right] + \left[\widehat{A}, \widehat{C}\right]$$

$$\left[\widehat{p}_x, \widehat{p}_y\right] = 0, \quad \left[\widehat{x}, \widehat{p}_x\right] = i\hbar, \quad \left[\widehat{z}, \widehat{p}_x\right] = \left[\widehat{z}, \widehat{p}_y\right] = 0$$

# 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:

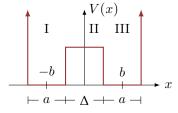
$$a = \sqrt{\frac{\hbar}{m\omega}}, \quad \tilde{x} = \frac{x}{a}, \quad \tilde{E} = \frac{E}{\hbar\omega} \Rightarrow \frac{1}{2} \left[ -\frac{\partial^2}{\partial \tilde{x}^2} + \tilde{x}^2 \right] \varphi(\tilde{x}) = \tilde{E}\varphi(\tilde{x})$$

Then, the solutions to the equation is:

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

$$H_0(\tilde{x}) = 1$$
,  $H_1(\tilde{x}) = 2\tilde{x}$ ,  $H_2(\tilde{x}) = 4\tilde{x}^2 - 2$ ,  $H_3(\tilde{x}) = 8\tilde{x}^3 - 12\tilde{x}$   
 $\Psi_n(x) = \frac{1}{\sqrt[4]{\pi}\sqrt{2^n n! a}} \cdot H_n\left(\frac{x}{a}\right) e^{-\frac{x^2}{2a^2}}$ 

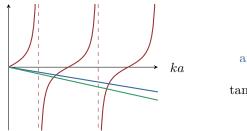
# 5.4 The coupled quantum well



This is the simplified potential of an ammonia molecule NH<sub>3</sub>. 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)



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

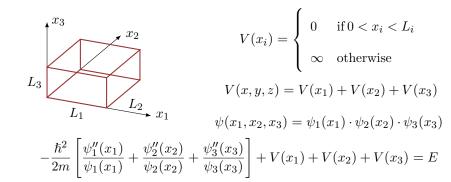
$$\tan(ka) = -ka\varepsilon = -ka\frac{1 \pm e^{-\delta \Delta}}{\delta a}$$

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

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

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  $x_i$ 

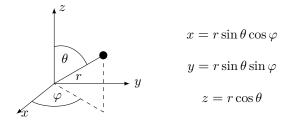
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_i^2}\psi_i(x_i) + V(x_i)\psi_i(x_i) = E_i\psi_i(x_i)$$
$$E_i^{(n_i)} = n_i^2 \frac{\hbar^2 \pi^2}{2mL_i^2}, \qquad \psi_i^{(n_1)} = A \cdot \sin\left(\frac{\pi n_i x}{L_i}\right)$$

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

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

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:

$$R_{n\ell}(r) = \frac{1}{r} \rho^{\ell+1} e^{-\rho} v(\rho), \quad \rho = \frac{r}{na_0}, \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \approx 5.29 \cdot 10^{-11} \text{ [m]}$$
  
 $\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r) Y_{\ell}^m(\theta,\varphi) \qquad j_{max} = (n-\ell-1) \ge 0 \qquad |m| \le \ell$ 

 $v(\rho)$  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,  $\ell$  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 Angular Momentum and Spin

$$\widehat{L}_{x} = \widehat{y}\widehat{p}_{z} - \widehat{z}\widehat{p}_{y} \qquad \widehat{L}_{y} = \widehat{z}\widehat{p}_{x} - \widehat{x}\widehat{p}_{z} \qquad \widehat{L}_{z} = \widehat{x}\widehat{p}_{y} - \widehat{y}\widehat{p}_{x} \qquad \widehat{L} = \det \begin{vmatrix} \mathbf{e}_{x} & \mathbf{e}_{y} & \mathbf{e}_{z} \\ \widehat{x} & \widehat{y} & \widehat{z} \\ \widehat{p}_{x} & \widehat{p}_{y} & \widehat{p}_{z} \end{vmatrix} = i\hbar\widehat{L}_{x} \qquad \left[\widehat{L}_{x},\widehat{L}_{x}\right] = i\hbar\widehat{L}_{y} \qquad \widehat{L} = \det \begin{vmatrix} \mathbf{e}_{x} & \mathbf{e}_{y} & \mathbf{e}_{z} \\ \widehat{x} & \widehat{y} & \widehat{z} \\ \widehat{p}_{x} & \widehat{p}_{y} & \widehat{p}_{z} \end{vmatrix}$$

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

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

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

$$\left[\widehat{L}^2, \widehat{L}_x\right] = 0, \qquad \left[\widehat{L}^2, \widehat{L}_y\right] = 0, \qquad \left[\widehat{L}^2, \widehat{L}_z\right] = 0$$

$$\widehat{L}^2 Y_\ell^m(\theta, \varphi) = h^2 \ell(\ell+1) Y_\ell^m(\theta, \varphi), \qquad \widehat{L}_z Y_\ell^m(\theta, \varphi) = \hbar m Y_\ell^m(\theta, \varphi)$$

# 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  $\psi$ , 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:

$$\widehat{L}^2 \psi = \lambda \psi, \quad \widehat{L}_z \psi = \mu \psi$$

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

# 7.2 Spin

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

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

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

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

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

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

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

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

This means, that the particles are closer together in the antisymmetric case than in the symmetric case. But this does not account for the spin. Because of Pauli's exclusion principle, the electrons must be in a different state, therefore they have different spin. The total angular momentum can be either  $|0,0\rangle$  or  $|1,0\rangle$ . Those are both antisymmetric wave functions. Therefore, the radial part must be symmetric, in which case, both electrons are attracted to eachother.

## 7.4 Many Electrons: Atomic Shells

Electrons with n=2 are further away from the nucleus than electrons with n=1. Therefore, those further away see a different (smaller) effective charge than those in the inner shell.

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

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

Here, the number of degeneracies per shell is displayed. Remember, we have  $n \geq 1$ ,  $0 \leq \ell \leq n$ ,  $-\ell \leq m \leq \ell$ , 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.

## 8 Useful formulas

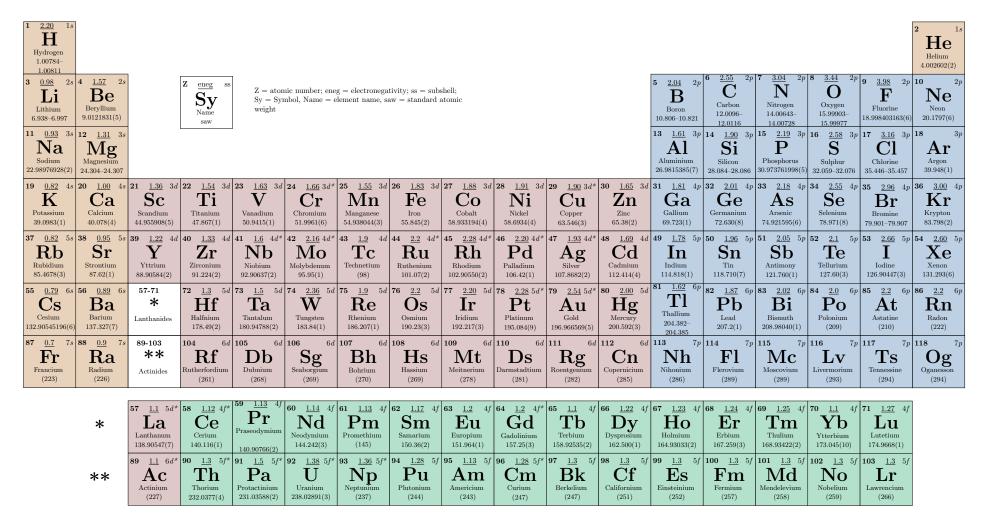
$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \qquad \int_{0}^{\infty} x e^{-ax^2} dc = \frac{1}{2a} \qquad \int_{-\infty}^{\infty} x^2 e^{-ax^2} = \frac{\sqrt{\pi}}{2a^{3/2}}$$

$$\int x^n e^{cx} = e^{cx} \sum_{i=0}^{n} (-1)^{n-i} \frac{n!}{i!c^{n-i+1}} x^i \qquad \int_{0}^{\infty} x^n e^{-cx} = \frac{n!}{c^{n+1}}$$
Gaussian:  $G = A \cdot e^{\frac{-x^2}{2\sigma^2}}$ 

## 8.1 Trigonometry

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

# 9 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.