Physik II

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HS24

1 Introduction

1.1 Blackbody spectrum

spectrum of electromagnetic radiation only dependent upon temperature. Blackbody absorbs all incident light and is at thermal equilibrium.

Rayleigh-Jeans with it's **UV-catastrophe**

$$u_{\text{RJ}}(\nu, T) = \frac{8\pi\nu^2}{c^3} kT \qquad\qquad \int_0^\infty u_{\text{RJ}}\, d\omega \to \infty$$

Planck's law (Energydensity per freq.)

$$u(\omega)d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega \qquad \text{Intensity} \quad I(\omega)d\omega = c \cdot u(\omega)d\omega$$

Derivation:

Number of permitted states $N(k) = \#$ polarisations $\cdot \dfrac{1}{2^{\#\,\text{dim}}} \cdot \dfrac{\text{total volume}}{\text{elementary volume}}$

e.g. $N_{\text{2D}}(k) = 1 \cdot \dfrac{1}{2^2} \cdot \dfrac{\pi k^2}{(\pi/L_x) \cdot (\pi/L_y)}$

e.g. $N_{\text{3D}}(k) = 2 \cdot \dfrac{1}{2^3} \cdot \dfrac{\frac{4}{3}\pi k^3}{(\pi/L_x) \cdot (\pi/L_y) \cdot (\pi/L_z)}$

Density of states: $D(k) = \dfrac{1}{\text{Vol}} \dfrac{dN(k)}{dk}$

$D(\omega)d\omega = \dots [D(k) \text{ rewritten with } \omega] \dots \cdot \dfrac{d\omega}{c}$

e.g. $D_{\text{2D}}(\omega)d\omega = \dfrac{\omega}{\pi c} \cdot \dfrac{d\omega}{c}$, $D_{\text{3D}}(\omega)d\omega = \dfrac{\omega^2}{\pi^2 c^2} \cdot \dfrac{d\omega}{c}$

Energy density (average energy per unit volume and bandwidth):

$u(\omega)d\omega = \hbar\omega \cdot p(\omega) \cdot D(\omega)d\omega = \hbar\omega \cdot \dfrac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}(\approx k_B T, h\nu << k_B T) \cdot D(\omega)d\omega$

Johnson / Nyquist noise voltage:

$V_N(\nu, T, \Delta\nu) = (\Delta V)_{\text{rms}} = \sqrt{\overline{(\Delta V)^2}}$ $\qquad \boxed{V_N = \sqrt{4Rk_B T \Delta\nu}}$

1.2 Photoelectric effect

If the energy of the absorbed photon is sufficient $h\nu > \varphi_{\text{metal}}$ (binding potential depends on surface geometry), light can cause a metallic surface to emit electrons.

$$\boxed{E_e = h\nu - \varphi} = \frac{1}{2}m_e v_e^2 = q_e V \qquad \textbf{Threshold Frequency} \quad \nu_{\text{thresh}} = \frac{\varphi}{h} \quad I \propto I_{light}$$

$$\boxed{E_{\text{Ph}} = h \cdot \nu = \frac{h \cdot c}{\lambda}} \qquad \begin{array}{ll} h: \text{Planck constant} & c: \text{speed of light} \\ \nu: \text{frequency} & \lambda: \text{wavelength} \end{array}$$

$$\boxed{p_{\text{Ph}} = \frac{E_{\text{Photon}}}{c} = \frac{h}{\lambda} = \frac{h \cdot \nu}{c}} \boxed{m_{\text{Ph}} = \frac{h \cdot \nu}{c^2}}$$

Radiation pressure: $\quad F = \dfrac{dp}{dt} = \dfrac{2h\nu}{c} \cdot \dfrac{P}{h\nu}\text{(rate of arrival)} = \dfrac{2P}{c} \qquad p = \dfrac{I}{c} = \dfrac{N'(t)E}{cA}$

1.3 Level-Laser / Einstein coefficients

Rate equation

Absorption: $B_{12}u(\nu)n_1$

Stimulated emission: $B_{21}u(\nu)n_2$

Spontaneous emission (decay): $A_{21}n_2$

$\dfrac{dn_1}{dt} = A_{21}n_2 + Bu(\nu)(n_2 - n_1)$

$\dfrac{dn_2}{dt} = -A_{21}n2 - Bu(\nu)(n_2 - n_1)$

Stationary case

$\dfrac{dn_i}{dt} = 0 \Rightarrow \dfrac{n_2}{n_1} = \dfrac{u(\nu) \cdot B_{12}}{u(\nu) \cdot B_{21} + A_{21}} \Rightarrow A_{21} = \dfrac{8\pi h\nu^3}{c^3} \cdot B \quad (kT \gg h\nu, n_1 = n_2, u(\nu) \to \infty)$

2 Wave Mechanics

2.1 Diffraction of matter waves

2.1.1 De Broglie Wavelengths

$$\lambda_e = \frac{h}{\sqrt{2mE_{kin}}} = \frac{h}{p} \quad \text{Wavelength of electron} \quad E = \sqrt{(pc)^2 + (m_0 c^2)^2}$$

2.1.2 Bragg's law

We consider electrons passing through a thin cristal.

$$\sin(\theta) = \frac{n\lambda}{d} \qquad \begin{array}{l} \theta: \text{scattering- / reflection angle} \\ \lambda: \text{wavelength of the electron} \\ d: \text{separation between the crystal planes} \\ n: \text{peak order (integer, mostly } n = 1) \end{array}$$

2.1.3 Compton scattering

Effect of an x-ray photon hitting an electron. Preserves energy and momentum.

$$\lambda_2 - \lambda_1 = \frac{h}{m_e c}(1 - \cos(\varphi)) \qquad \begin{array}{l} \lambda_1: \text{wavelength of x-ray before} \\ \lambda_2: \text{wavelength of x-ray after} \end{array}$$

φ: angle by which the x-ray photon is redirected

2.1.4 Double Slit

Constructive interference   **Destructive interference**

$$\delta = n\lambda \quad \text{with } n = 0, 1, 2, 3, \dots \qquad \delta = \frac{n\lambda}{2} \quad \text{with } n = 1, 2, 3, \dots$$

δ: path difference $\qquad \lambda$: wavelength

Path difference

$$\frac{\Delta x}{L} = \frac{\delta}{d} = \sin(\theta) \qquad \begin{array}{l} \Delta x: \text{distance from maximum} \\ L: \text{distance between wall and screen} \\ d: \text{distance between slits} \\ \theta: \text{angle from middle point on the screen} \end{array}$$

2.2 Heisenberg's uncertainty relations

$$\boxed{\Delta x \cdot \Delta p_x \geq \hbar} \qquad \begin{array}{l} \Delta x: \text{precision in space (spatial extent)} \\ \Delta p: \text{precision in momentum} \end{array}$$

$\to$ analog for y and z axis.

$$\Delta E \cdot \Delta t \geq \hbar \qquad \text{or in another form} \qquad \Delta t \cdot \Delta\omega \geq 1$$

Repetition $\qquad E_{\text{kin}} = \dfrac{p^2}{2m} \qquad \begin{array}{l} p: \text{momentum} \\ m: \text{mass} \end{array}$

2.3 Bohr-Sommerfeld Quantization

The orbit of electrons circling around an atom has to fulfil the following criteria:

$$\boxed{2\pi r = n\lambda = n\frac{\hbar}{p} = n\frac{\hbar}{m_e v}} \quad \text{or} \quad kL = n \cdot 2\pi \qquad \begin{array}{l} r: \text{radius of orbit} \\ L: \text{length of orbit} \\ k: \text{wave vector} \end{array}$$

The speed of an electron is:

$$v = \frac{e^2}{4\pi\varepsilon_0 \hbar n} \qquad \begin{array}{l} m: \text{mass of electron} \quad e: \text{electron charge} \\ v: \text{speed of the electron} \\ \varepsilon_0: \text{dielectric constant of vacuum} \end{array}$$

Derivation: Zentrifugalkraft = Coulombkraft: $\frac{m_e v^2}{r_n} = \frac{Ze^2}{4\pi\varepsilon_0 r_n^2}$

$E = T + V = \frac{1}{2}m_e v^2 - m v^2 = -\frac{1}{2}m v^2$

$$r_n = \frac{n^2}{Z}a_0, \quad n = 1, 2, 3\dots \quad \boxed{E_n = \frac{m_e e^4 Z^2}{8\varepsilon_0^2 h^2 n^2} = -13.606 eV \cdot \frac{Z^2}{n^2} = -E_R \cdot \frac{Z^2}{n^2}}$$

n quantized orbit, Z atomic number, $a_0 = 0.529 \text{Å}$ Bohrradius

3 Quantum Mechanics

3.1 Wave Function

Probability density

$$P(x, t)dx = \psi^*(x, t) \cdot \psi(x, t)dx = |\psi(x, t)|^2 dx$$

The probability density must be normalised:

$$\int_{-\infty}^\infty |\psi(x, t)|^2 \, dx = \int_{-\infty}^\infty \psi^*(x, t) \cdot \psi(x, t) \, dx = 1$$

Probability that the particle is within the interval $[a, b]$ at time t:

$$p(a, b, t) = \int_a^b |\psi(x, t)|^2 \, dx$$

3.1.1 1D Schrödinger equation

$$\boxed{i\hbar \frac{\partial\psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x, t)}{\partial x^2} + V(x, t)\psi(x, t)} \qquad \begin{array}{l} m: \text{mass of} \\ \quad \text{particle} \\ V(x, t): \text{external potential} \end{array}$$

If $V(x, t) = V(x)$ we can use this **approach**:

$$\psi(x, t) = \psi(x) \cdot T(t) \qquad \text{with} \qquad T(t) = e^{-\frac{iEt}{\hbar}}$$

which leads us to the **time-independent Schrödinger equation**

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + (E - V(x))\psi(x) = 0 \qquad E: \text{energy of the electron}$$

The wave equation $\psi(x)$ has to fulfill these **boundary-conditions**:

- $\int_{-\infty}^\infty |\psi(x)|^2 \, dx < \infty$

- $\psi_1(x_0) = \psi_2(x_0)$

- $\left(\dfrac{d\psi_1}{dx}\right)\Big|_{x_0} = \left(\dfrac{d\psi_2}{dx}\right)\Big|_{x_0}$
  except when $\lim_{\varepsilon\to\infty} V(x_0 + \varepsilon) - V(x_0 - \varepsilon) = \infty$

Time dependent solution

$$\psi_n(x, t) = \psi_n(x, 0) \cdot e^{-i\frac{E n t}{\hbar}} = \psi_n(x, 0) \cdot e^{-in^2\omega t}, \psi(x, t) = \sum_{n=1}^\infty \int \psi_n(x)^* \psi(x, 0)dx\psi_n(x, t)$$

3.1.2 Formalism

Observables

An observable is a quantity of the particle, that can be measured in an experiment. For it to be a meaningful observable, the way we calculate it, needs to yield a real number.

Operator

An operator is a mapping in function space. To every observable **A** there belongs an operator $\hat{A}$. Combining the operator with the wavefunction $\varphi(\mathbf{r},t)$ this gives us the following way to calculate the **expectation value** of an observable:

$$< A >_\varphi = \iiint \varphi^*(\mathbf{r},t) \cdot \hat{A} \cdot \varphi(\mathbf{r},t) \, \mathrm{d}\mathbf{r}$$

Standard deviation:

$$\sigma_{x,n}^2 = < x^2 >_n - < x >_n^2$$

Dirac Notation The Dirac notation is a concise way to write the inner product of two wavefunctions:

Bra: $\qquad \langle \psi_n | = \int\limits_{-\infty}^{\infty} \psi_n^*(x) \cdot [...] \, \mathrm{d}x$

Ket: $\qquad |\psi_n\rangle = \psi_n(x)$

$$\langle \psi_n | \psi_n \rangle = \int\limits_{-\infty}^{\infty} \psi_n^*(x) \cdot \psi_n(x) \, \mathrm{d}x$$

Hermitian Conjugate

The *hermitian conjugate* of an operator $\hat{A}$ is the operator $\hat{A}^\dagger$ such that:

$$\langle f | \hat{A} \cdot g \rangle = \langle \hat{A}^\dagger \cdot f | g \rangle$$

for all functions f and g.

Hermitian Operators

An operator $\hat{A}$ is called Hermitian if

$$\hat{A} = \hat{A}^\dagger$$

Now the special characteristics of a hermitian operator is, that it's *eigenvalues* **a** are all real and its *eigenfunctions* $\varphi_n(x)$ are orthogonal to each other if their eigenvalues are different. Because of these characteristics all observables are characterised by *hermitian operators*.

Eigenfuncions and Eigenvalues

An *eigenfunction* $\varphi_n(x)$ of the operator $\hat{A}$ satisfies the equation:

$$\hat{A} \cdot \varphi_n(x) = a_n \cdot \varphi_n(x), \quad a_n \in \mathbb{C}$$

Eigenfunction expansion $\psi(x)$:

$$|\psi\rangle = \sum_{n=1}^{\infty} c_n |\varphi_n\rangle$$

The allowed values are the eigenvalues a_n and the corresponding probability is given by $|c_n|^2$.

3.1.3 Uncertainty relations

Commutator

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \begin{cases} = 0 & \text{Measurement result indep. of order} \\ \neq 0 & \text{Measurement result dep. of order} \end{cases}$$

$$[\hat{A}^2, \hat{B}] = \hat{A}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{A}; \, [\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}; \, [\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C}$$

Commutator uncertainty relation

If we have two observables A, B with the standard deviations σ_A, σ_B then then the following uncertainty relation holds:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2$$

Heisenbergs uncertainty principle

$$\sigma_{x,n}^2 \cdot \sigma_{p,n}^2 \geq \frac{\hbar}{2}$$

3.1.4 Superposition principle

If $\varphi_1(x,t)$ and $\varphi_2(x,t)$ are solutions of our problem then the following is a solution as well:

$$\psi(x,t) = a_1 \cdot \varphi_1(x,t) + a_2 \cdot \varphi_2(x,t)$$

With the condition $\int\limits_{-\infty}^{\infty} |\psi|^2 \, \mathrm{d}x = 1$ we get: $\quad |a_1|^2 + |a_2|^2 = 1$

3.1.5 Finding wave function and energy levels

(with a time-independent potential $V(x)$)

1. Draw potential.

2. Define and number areas with constant potential: $V(x) = V_j$ for $x_{j-1,j} < x < x_{j,j+1}$

3. Solve the *time-independent Schrödinger equation* in every area.

4. Boundary-conditions: Are there any terms in the solution which have to be zero because otherwise $\psi(x) \to \infty$?

5. Get equations for the coefficients with the boundary-conditions

   - $u_j(x_{j,j+1}) = u_{j+1}(x_{j,j+1})$

   - $\dfrac{\mathrm{d}u_j}{\mathrm{d}x}(x_{j,j+1}) = \dfrac{\mathrm{d}u_{j+1}}{\mathrm{d}x}(x_{j,j+1}) \quad \text{except} \quad \Delta V_{j,j+1} \to \infty$

6. Determine k_n, E_n with the boundary-condition-equations.

7. Solve for prefactors with normalisation.

3.1.6 Free particle

Plane wave $\quad \Psi(x,t) = Ae^{-i(kx-\omega t)} = Ae^{-\frac{i}{\hbar}(px-Et)}$

Dispersion relation: wave packet will spread in space while propagating

v_φ=phase velocity=$\dfrac{\omega}{k}$ (point on the wave)

v_g=group velocity=$\dfrac{\partial \omega}{\partial k}$ (energy / wave front)

free matter waves: $v_\varphi = \dfrac{\hbar k}{2m} = \dfrac{1}{2}v_g$

3.1.7 The infinite potential well

Defined by the time-independent potential $V(x)$ where $V(x) = 0$ if $|x| \leq a$ and $V(x) = \infty$ if $|x| > a$.

Wave number: $\quad k_n = \dfrac{n\pi}{2a} \qquad$ with $n = 0, 1, 2, \ldots$
$\qquad\qquad\qquad\qquad$ and $2a$: width of quantum well

Energy: $\quad E_n = \dfrac{\hbar^2 k_n^2}{2m} = \dfrac{\hbar^2 \pi^2 n^2}{8ma^2} = n^2 E_1$

Solution (Ansätze):

- n odd and $|x| \leq a$: $\psi_n(x) = \dfrac{1}{\sqrt{a}} \cos(k_n x)$

- n even and $|x| \leq a$: $\psi_n(x) = \dfrac{1}{\sqrt{a}} \sin(k_n x)$

- ψ_n (n-1 nodes) alternately even and odd with respect to center of well

- $|x| > a$: $\psi_n(x) = 0$

Die zeitlich abhängige Lösung lautet:

$$\boxed{\Psi_n(x,t) = \sqrt{\frac{2}{a}} sin(\frac{n\pi}{a}x)e^{-i\frac{E_n}{\hbar}t}} \tag{3.1}$$

Randbedingung:

$$\Psi(x=0) = 0 \quad \Psi(x=a) = 0 \tag{3.2}$$

3.1.8 Potential Step

Bei einer Potentialstufe wird das Teilchen vom Potential $E_p(x) = 0$ auf ein stetiges höheres Potential $E_p(x) = E_0$ gehoben.

Die Schrödingergleichung in diesem Fall ergibt zwei Lösungen. Eine für den emittierten Teil und eine für den reflektierten Teil.

$$
\begin{array}{|l|}
\hline
E < E_0 \\
\hline
\Psi_1(x) = \overbrace{A_0 e^{ikx}}^{\text{eintretende Welle}} + \overbrace{\frac{ik+\rho}{ik-\rho} \cdot A_0 e^{-kx}}^{\text{reflektierte Welle}} \\
\hline
\Psi_2(x) = \underbrace{\frac{2ik}{ik-\rho} \cdot A_0 e^{-\rho x}}_{\text{emittierte Welle}} \\
\hline
\end{array}
\tag{3.3}
$$

$$\text{mit } k = \sqrt{\frac{2mE}{\hbar^2}} \text{ und } \rho = \sqrt{\frac{2m}{\hbar^2}(E_0 - E)} \tag{3.4}$$

$$
\begin{array}{|l|}
\hline
E > E_0 \\
\hline
\Psi_1(x) = \overbrace{A_0 e^{ipx}}^{\text{incoming wave}} + \overbrace{\frac{p-\bar{p}}{p+\bar{p}} \cdot A_0 e^{-ipx}}^{\text{reflected wave}} \\
\hline
\Psi_2(x) = \underbrace{\frac{2p}{p+\bar{p}} \cdot A_0 e^{i\bar{p}x}}_{\text{transmitted wave}} \\
\hline
\end{array}
\tag{3.5}
$$

$$\text{mit } p = \sqrt{\frac{2mE}{\hbar^2}} \text{ und } \bar{p} = \sqrt{\frac{2m}{\hbar^2}(E_0 - E)} \tag{3.6}$$

3.1.9 Tunneling

A particle in quantum mechanics can cross a potential barrier $V = V_0$ even if its energy $E < V_0$.

We look at a potential $V(x) = V_0$ if $0 \leq x \leq a$ and $V(x) = 0$ else.

We always consider a *particle flow* towards the barrier. Some of them are reflected and some of them tunnel through the barrier. We calculate them with the following approach:

- $\psi_1(x) = Ae^{ikx} + Be^{-ikx}$ (before barrier)

- $\psi_2(x) = Ce^{\kappa x} + De^{-\kappa x}$ (in the barrier)

- $\psi_3(x) = Fe^{ikx} + Ge^{-ikx}$ (after the barrier)

  (G is usually zero, since no particle wave incoming from the right)

where $k = \sqrt{\dfrac{2mE}{\hbar^2}}$ and $\kappa = \sqrt{\dfrac{2m(V_0 - E)}{\hbar^2}}$

Transmission coefficient: $T = \dfrac{|F|^2}{|A|^2}$ **Reflexion coefficient**: $R = \dfrac{|B|^2}{|A|^2}$ T+R=1

How to calculate the transmission matrix M

1. Write down the wave equation before and in the barrier with x replaced by $x - x_1$.

2. Derive both equations with respect to x.

3. Consider the point $x = x_1$ where $x - x_1 = 0$ and most of the $e^{\cdots}$ terms are equal 1.

4. Determine the matrices $M_{1,1}$ and $M_{1,2}$ which fulfill
$M_{1,1} \cdot \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} \psi \\ \frac{d\psi}{dx} \end{pmatrix}$ and $M_{1,2} \cdot \begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} \psi \\ \frac{d\psi}{dx} \end{pmatrix}$.

5. At point $x = x_1$ we have: $M_{1,1} \cdot \begin{pmatrix} A \\ B \end{pmatrix} = M_{1,2} \cdot \begin{pmatrix} C \\ D \end{pmatrix}$

6. Finally: $M = M_{1,1}{}^{-1} \cdot M_{1,2}$ and $\begin{pmatrix} A \\ B \end{pmatrix} = M \cdot \begin{pmatrix} C \\ D \end{pmatrix}$

How to calculate the propagation matrix P
Analog to the *transmission matrix* but with the same wave function evaluated at point $x - x_1$ and point $x - x_1 - L$.

You should get a matrix of the following form: $\begin{pmatrix} e^{a \cdot L} & 0 \\ 0 & e^{-a \cdot L} \end{pmatrix}$

Repetition: inverse matrix

$\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \dfrac{1}{ad - bc} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix}$

3.1.10 Scaning tunneling microscope (STM)
Total tunneling current

$I = \displaystyle\int_{\text{Surface}} j(r) \, dS$
$j(r)$: current density
r: distance from tip
    (closest point to surface)

Distance to surface (assuming a round tip)

$d(r) = d_0 + R - \sqrt{R^2 - r^2} \approx d_0 + \dfrac{r^2}{2R}$
d_0: distance at closest point to surface
R: rad. of spherical tip
r: as above

Current density

$j(r) = a \cdot e^{-\kappa d(r)} \approx a \cdot e^{-\kappa d_0 - \frac{\kappa r^2}{2R}}$
$\kappa: \to$ *previous chapter:*
"'Tunneling"'
everything else as above

Effective area   **Penetration depth**

$A_{\text{eff}} = \dfrac{2\pi R}{\kappa} \left(1 - e^{\frac{\kappa R}{2}}\right)$ $L = \dfrac{1}{\kappa}$

Resolution length

$L_{\text{res}} = \sqrt{A_{\text{eff}}} = \sqrt{2\pi R L}$

3.1.11 Harmonic Oscillator

Eigenvalues $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$

Eigenstates $\Psi_n(x) = e^{-\frac{1}{2}\lambda x^2} H_n(\eta)$ (3.7)

allg. Lösung $\Psi_n(x,t) = \Psi_n(x)e^{-i\left(n + \frac{1}{2}\right)\omega t}$

$H_n(\eta)$ sind die hermitesche Polynome mit $\eta = \sqrt{\lambda}x$. Die Aufenthaltswahrscheinlichkeit $P(x) = |\Psi_n(x,t)|^2$ der Eigenzustände des harmonischen Oszillators sind zeitunabhängig.
Die durchschnittliche Aufenthaltswarscheinlichkeit beträgt:

$$\langle \hat{x} \rangle = \int \varphi^* \cdot x \cdot \varphi \, dxdydz = \frac{a}{2} \tag{3.8}$$

Aufgeteilter Hamilton-Operator:

$$\boxed{H_{kin} + H_{pot} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m\omega^2}{2}x^2 = H} \tag{3.9}$$

3.2 Quantum Mechanics in 3D: Hydrogen Atom
3.2.1 3D Potential well and degeneracies
This models an electron confined in a 3D box of sidelength L_x, L_y, L_z with the potential:

$$V(x) = V(x) + V(y) + V(z)$$

with $V(x_i) = \begin{cases} = 0 & 0 \leq x_i \leq L_{x_i} \\ = \infty & \text{else} \end{cases}$

The Schroedinger equation is separable with the wavefunction $\Psi(x,y,z) = \Psi_1(x)\Psi_2(y)\Psi_3(z)$, where each of the $\Psi(x_i)$ is the solution to the 1D infinite quantum well. $\Psi(x,y,z) = \dfrac{\sqrt{8}}{\sqrt{L_x L_y L_z}} \sin\left(\dfrac{l\pi x}{L_x}\right) \sin\left(\dfrac{m\pi y}{L_y}\right) \sin\left(\dfrac{n\pi z}{L_z}\right)$

$E = (E_1)_l + (E_2)_m + (E_3)_n = \dfrac{\hbar^2\pi^2}{2m}\left(\dfrac{l^2}{L_x^2} + \dfrac{m^2}{L_y^2} + \dfrac{n^2}{L_z^2}\right)$

Degeneracies

Now let $L_x = L_y = L_z = L$ then we get the formula

$$E_{lmn} = \frac{\hbar^2\pi^2}{2mL^2}(l^2 + m^2 + n^2)$$

We call states degenerate, if they have the same energy. So for example the states: $\Psi_{112}, \Psi_{121}, \Psi_{211}$ all have the same energy. The *degeneracy* is here $d = 3$.

3.2.2 Hydrogen Atom
Reexpress Schrödinger equation in spherical coordinates, allows to find a solution for example for the electrical potential: $V(x,y,z) = -\dfrac{e^2}{4\pi\varepsilon_0 \sqrt{x^2 + y^2 + z^2}}$ The idea is to split the wavefunction into a radial and spherical part:

$$\Psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi)$$

This yields the equations:

Radial: $\dfrac{1}{R}\dfrac{d}{dr}\left(r^2\dfrac{dR}{dr}\right) - \dfrac{2mr^2}{\hbar^2}(V(r) - E) = l(l+1)$

Spherical: $\dfrac{1}{Y}\left(\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial Y}{\partial\theta}\right) + \dfrac{1}{\sin^2\theta}\dfrac{\partial^2 Y}{\partial\varphi^2}\right) = -l(l+1)$

The energy levels of the hydrogen atom turn out to be the rydberg energies:

$$E_n = -\frac{1}{n^2}E_{RY} = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}, \quad E_{RY} = 13.6eV$$

3.2.3 Spherical Harmonics
The solution to the spherical part are the *spherical harmonics* $Y_l^m(\theta, \varphi)$ where $l \in \mathbb{N}$ and $-l \leq m \leq l, m \in \mathbb{Z}$
l: *azimuthal quantum number*
m: *magnetic quantum number*
The spherical harmonics form an orthonormal basis.
$\langle Y_l^m | Y_j^k \rangle = \delta_{mj}\delta_{lk}$

The first spherical harmonics

- $Y_0^0(\theta, \varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}$

- $Y_1^{-1}(\theta, \varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta \, e^{-i\varphi}$

- $Y_1^0(\theta, \varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta$

- $Y_1^1(\theta, \varphi) = \frac{-1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta \, e^{i\varphi}$

3.3 Angular Momentum
3.3.1 Angular Momentum Operators

conserved for central potential $\hat{L} = \hat{r} \times \hat{p}$

- $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$

- $\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$

- $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$

- $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

- $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$

$[\hat{L}_z, \hat{x}] = i\hbar\hat{y}, \quad [\hat{L}_z, \hat{y}] = -i\hbar\hat{x}, \quad [\hat{L}_z, \hat{z}] = 0$

A very important fact is, that

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

Which means, that there exists a set of eigenfunctions $\{\varphi_n(x)\}_{n\in\mathbb{N}}$ that is an eigenbasis to both $\hat{L}^2$ and $\hat{L}_z$. It turns out, that this set of functions are again the *spherical harmonics*.

Raising and Lowering operator

Raising Operator: $\qquad \hat{L}_+ = \hat{L}_x + i\hat{L}_y$
Lowering Operator: $\qquad \hat{L}_- = \hat{L}_x - i\hat{L}_y$

Commutation: $\left[\hat{L}_z, \hat{L}_\pm\right] = \pm\hbar\hat{L}_\pm$

L-Operators in Spherical Coordinates

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \qquad \hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}.$$

3.3.2 Eigenfunctions and Eigenvalues

As stated before, the *eigenfunctions* to the *angular momentum operator* are the *spherical harmonics* $Y_m^l(\theta, \varphi)$. But there is a little difference to it. l can also take half integer values unlike in the theory of the hydrogen atom. So $l = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, ...$ but m still varies in integer steps between $m = (-l, -l+1, ..., l-1, l)$

Eigenvalues

- $\hat{L}^2 Y_l^m(\theta, \varphi) = \hbar^2 l(l+1) \cdot Y_l^m(\theta, \varphi)$

- $\hat{L}_z Y_l^m(\theta, \varphi) = \hbar m \cdot Y_l^m(\theta, \varphi)$

- $\hat{L}_z \hat{L}_\pm Y_l^m(\theta, \varphi) = \hbar(m\pm 1) \cdot \hat{L}_\pm Y_l^m(\theta, \varphi)$

- $\hat{L}_+ Y_l^m(\theta, \varphi) = \sqrt{l(l+1) - m(m+1)} Y_l^{m+1}(\theta, \varphi)$

- $\hat{L}_- Y_l^m(\theta, \varphi) = \sqrt{l(l+1) - m(m-1)} Y_l^{m-1}(\theta, \varphi)$

3.4 Spin

Intrinsic properties, result of the objects' constituents rotation around the center of mass.

3.4.1 Spin Operators

If we work with single particles that have $l = \frac{1}{2}$ we call the angular momentum operators *spin operators*, denoted by: $\quad \hat{S}^2 := \hat{L}^2, \hat{S}_z := \hat{L}_z$ when $l = \frac{1}{2}$

The eigenvalues are for

$$\hat{S}^2 : \hbar^2(s+1)s = \hbar^2(\frac{1}{2}+1)\frac{1}{2} = \frac{3\hbar^2}{4}$$

$$\hat{S}_z : \hbar \cdot m = \hbar\left(\pm\frac{1}{2}\right)$$

Relation between S_x and S_z

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

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

Example: Probability to get $\frac{\hbar}{2}$ when measuring spin up state $\chi(s) = |a\uparrow_z + b\downarrow_z\rangle$:

$$P(\uparrow_z) = |\langle\uparrow_z|\chi(s)\rangle|^2$$
$$= |\langle\uparrow_z|a\uparrow_z + b\downarrow_z\rangle|^2$$
$$= |\langle\uparrow_z|a\uparrow_z\rangle + \langle\uparrow_z|b\downarrow_z\rangle|^2$$
$$= a^2|\langle\uparrow_z|\uparrow_z\rangle|^2 + b^2 * 0 = a^2 * 1 = a^2$$

3.4.2 Spin 1/2 Theory and Pauli Matrices

There are several different notation for the possible spin states.

Dirac Notation

$|s\ m\rangle \quad$ for $s = \frac{1}{2}$ we have the two basis states $|\frac{1}{2}\ \ \frac{1}{2}\rangle, |\frac{1}{2}\ -\frac{1}{2}\rangle$

Arrow and χ notation

$$|\uparrow\rangle := \chi_+ := |\frac{1}{2}\ \ \frac{1}{2}\rangle$$

$$|\downarrow\rangle := \chi_- := |\frac{1}{2}\ -\frac{1}{2}\rangle$$

Whereby $\chi_\pm$ represent the 2 element vectors:

$$\chi_+ := \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\chi_- := \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Pauli Matrices

In this vector representation, the Spin operators are given by the Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
$$\hat{S}_x = \frac{\hbar}{2}\sigma_x \qquad \hat{S}_y = \frac{\hbar}{2}\sigma_y \qquad \hat{S}_z = \frac{\hbar}{2}\sigma_z$$

$$\hat{S}^2 = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

3.4.3 Sum of Angular Momenta

Consider two spin 1/2 particles. Each particle can have spin up and spin down giving us the 4 possible configurations: $\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$ Now consider the spin state of the two particle system, which is given by $|s\ m\rangle$:

Triplet configuration (symmetrisch):

- $|1\ \ 1\rangle = |\uparrow\uparrow\rangle$

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

- $|1\ -1\rangle = |\downarrow\downarrow\rangle$

Singlet configuration (antisymmetrisch):

- $|0\ \ 0\rangle = \frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle$

	Spin-Wellenfunktionen	
symmetrisch	$\chi_S = \chi_+(1)\chi_+(2)$	
symmetrisch	$\chi_S = \chi_-(1)\chi_-(2)$	
symmetrisch	$\chi_S = \chi_+(1)\chi_-(2) + \chi_+(2)\chi_-(1)$	
antisymmetrisch	$\chi_A = \chi_+(1)\chi_-(2) - \chi_+(2)\chi_-(1)$	(3.10)
	Bahnwellenfunktionen	
symmetrisch	$\Psi_S = \Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)$	
antisymmetrisch	$\Psi_A = \Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)$	

Clebsh Gordan

$$|j, m_j\rangle = \sum_{m_j = m_s + m_l} c_{m_s m_l m_j}^{slj} |l, m_l\rangle |s, m_s\rangle$$

3.4.4 Stern-Gerlach experiment

In the Stern-Gerlach experiment, we have a inhomogeneous magnetic field $\overrightarrow{B}$ of a strong electromagnet. Then we shoot silver atoms through the magnetic field. Because the silver atom has no net charge, the Lorenz force is no factor. The outer most valence electron gives the whole atom its spin. So depending on spin up or spin down of the electron, the beam of silver atoms is split in a spin-up and a spin-down beam.

When a magnetic moment $\overrightarrow{M}$ passes through a magnetic field $\overrightarrow{B}$, there is a potential energy equal to:

$$W = -\overrightarrow{M} \cdot \overrightarrow{B}$$

Magnetic Moment

The magnetic moment of the silver atom is given by its angular momentum:

$$\overrightarrow{M} = \mu \overrightarrow{L} \qquad \begin{array}{l} \mu\text{: gyromagnetic ratio} = \frac{e}{2m} \\ M\text{: magnetic moment} \\ L\text{: angular momentum(spin)} = m\omega r^2 \end{array}$$

Magnetic Force

Because there is a magnetic potential, the silver atom will see the force:

$$\overrightarrow{F} = \nabla(\overrightarrow{M} \cdot \overrightarrow{B})$$

3.5 Identical Particles

3.5.1 Wavefunction of two particle systems

In quantum mechanics, the solution of Schrödinger equation for the two particle system is confined to the following structure:

$$\psi_\pm(r_1, r_2) = A(\varphi_a(r_1)\varphi_b(r_2) \pm \varphi_b(r_1)\varphi_a(r_2))$$

Permutation Operator

The permutation operator exchanges the role of two particles in a wavefunction:

$$P(f(r_1, r_2)) = f(r_2, r_1)$$

The eigenvalues of the permutation operator have to be $\lambda = \pm 1$ since:

$$P^2(f(r_1, r_2)) = f(r_1, r_2) \Rightarrow P^2(f(r_1, r_2)) = \lambda^2 f(r_1, r_2) \Rightarrow \lambda = \pm 1$$

3.5.2 Fermions and Bosons

Indistinguishable Particles

Two particles are called indistinguishable, if they have the same quantum physical characteristics. This means the same:

1.	mass	$m_1 = m_2$
2.	spin	$s_1 = s_2$
3.	energy level	$n_1 = n_2$
4.	orbital angular momentum	$l_1 = l_2$
5.	overlapping wavefunctions	

The wavefunctions of identical particles must be eigenstates of the permutation operator, i.e. the permutation operator and the Hamiltonian commute.

Boson

We call a particle a *boson*, if it has integer spin $s \in \mathbb{N}$. The overall wavefunction is symmetric in the exchange of indistinguishable particles. This means:

$$P(\psi(r_1, r_2)) = \psi(r_2, r_1) = \psi(r_1, r_2)$$

Particles that are bosons: Photon

Fermion

We call a particle a *fermion*, if it has a half integer spin $s \in \mathbb{N} - \frac{1}{2}$. The overall wavefunction is anti-symmetric in the exchange of indistinguishable particles. This means:

$$P(\psi(r_1, r_2)) = \psi(r_2, r_1) = -\psi(r_1, r_2)$$

Particles that are fermions: Electron, Proton, Neutron, ...

Spacial part and spinor part of wavefunction

When we say the overall wavefunction has to be symmetric and anti-symmetric, we always have to consider the spacial $\psi(r_1, r_2)$ and the spinor part $\chi(s_1, s_2)$ of the overall wavefunction:

$$\Psi(r, s) = \psi(r) \cdot \chi(s)$$

$$\text{symmetric} \cdot \quad \text{symmetric} = \text{symmetric}$$
$$\text{symmetric} \cdot \text{anti-symmetric} = \text{anti-symmetric}$$
$$\text{anti-symmetric} \cdot \text{anti-symmetric} = \text{symmetric}$$

So if we have a pair of electrons in the singlet spin configuration s = 0 (anti-symmetric spinor), the spacial part has to be symmetric (bonding). If the electron is in the triplet configuration s = 1 (symmetric spinnor), the spacial part has to be anti-symmetric (anti-bonding).

3.5.3 Paulis Exclusion principle

Two identical *fermions* can never occupy the same state.

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\varphi_a(r_1)\varphi_b(r_2) - \varphi_b(r_1)\varphi_a(r_2)] = 0$$

3.5.4 Exchange interaction

If we look at the square distance between two particles in the three cases we get:

Distinguishable Particles: $\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$

Bosons: $\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b - 2|\langle \Psi_a |x| \Psi_b \rangle|^2$

Fermions: $\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b + 2|\langle \Psi_a |x| \Psi_b \rangle|^2$

The difference is the term $2|\langle \Psi_a |x| \Psi_b \rangle|^2$ In the case of Bosons this term makes the particles seem closer together, while it does the opposite for Fermions. We call this effect the *exchange force* because it makes Bosons appear to attract each other, while it appears to make Fermions repel each other.

3.5.5 Atoms and Bonding

Hamiltonian for an neutral atom, of atomic number Z, consisting of a heavy nucleus (electric charge Ze), surrounded by Z electrons (mass m, charge $-e$) :

$$H = \sum_{j=1}^{Z} [-\frac{\hbar^2}{2m} \nabla_j^2 - (\frac{1}{4\pi\varepsilon_0}) \frac{Ze^2}{r_j}] + \frac{1}{2} (\frac{1}{4\pi\varepsilon_0}) \sum_{i \neq k}^{Z} \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

- First term: kinetic energy plus interaction between nucleus and j[th] electron.

- Second term: repulsive interaction between electrons j and k ($j \neq k$). The factor $\frac{1}{2}$ avoids double counting.

- If one could neglect the interelectron interactions, the total wavefunction would just be composed by separate components.

$$\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z)\chi(\vec{s}_1, \vec{s}_2, \cdots, \vec{s}_Z) = \Psi(\vec{r}_1)\Psi(\vec{r}_2) \cdots \Psi(\vec{r}_Z)$$

- The SE cannot be solved exactly, except for the case $Z = 1$ (hydrogen). We must in practice use approximation methods.

Electron Configuration

$(nL_l)^{\text{\# of electrons}}$ n: Shell number
         L_l: Orbital $l = (0, 1, 2, 3, ...)$ $L_l = (s, p, d, f, ...)$

Examples:

He: $(1s)^2$
C: $(1s)^2(2s)^2(2p)^4$
Ne: $(1s)^2(2s)^2(2p)^6$
Si: $(Ne)(3s)^2(3p)^2$

Nomenclature

n	shell	subshells	# orbitals	$\frac{\#e^-}{\text{subshell}}$	$\frac{\#e^-}{\text{shell}}$
1	K	s	1	2	2
2	L	s	1	2	8
		p	3	6	
3	M	s	1	2	18
		p	3	6	
		d	5	10	
4	N	s	1	2	32
		p	3	6	
		d	5	10	
		f	7	14	

Order of filling subshells

$1s$
$2s \quad 2p$
$3s \quad 3p \quad 3d$
$4s \quad 4p \quad 4d \quad 4f$
$5s \quad 5p \quad 5d \quad 5f$
$6s \quad 6p \quad 6d$
$7s \quad 7p$
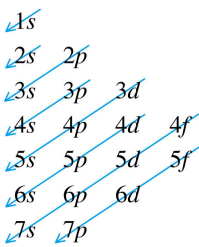
Term Symbol

- Two angular momenta j_1 and j_2 can combine into total j, such that

$$j = (j_1 + j_2), (j_1 + j_2 - 1), (j_1 + j_2 - 2), \cdots |j_1 - j_2|$$

this is because j_1, j_2 are *directional* and *quantized*.

- For multielectron atoms: we have l and s for each e^-

  L – total orbital angular momentum

  S – total spin angular momentum

  J – total angular momentum (combines L and S)

- Different combinations of angular momenta lead to different states. These states are labeled by *Term Symbols*:

$$^{2s+1}L_J$$

To determine the ground state, use *Hund's rules*

- For any filled subshell such as ns^2 or np^6 or nd^{10}, etc.

$$M_l = \sum m_l = 0 \quad ; M_s = \sum m_s = 0 \implies L = 0, S = 0, J = L + S = 0$$

i.e. to determine the term symbols we only need to consider the e^- in partially filled subshells.

- The less stable the outermost shell (the less electrons it has), the less ionization energy is required to remove the most outer electron of the atom.

Hund's rules

1. The state with the highest total spin (S) has the lowest energy.

2. For a given spin, the state with the highest total orbital angular momentum (L), consistent with overall antisymmetrization, has the lowest energy.

3. If a subshell (n, l) is no more than half filled, then the lowest energy level has $J = |L - S|$; if it is more than half filled, then $J = L + S$ has the lowest energy.

3.6 Quantum Statistics & Solid-state physics
3.6.1 Chemical Potential

We shall now consider two reservoirs in thermal contact which can exchange particles (think of salted water and fresh water). The chemical potential of the two reservoirs will be the same when there is no net flow of salt from one side to the other. The chemical potential is defined as:

$$\mu = \left(\frac{dF}{dN}\right)_{T,V}$$

F: Free Energy
N: Number of Particles
T: Temperature
V: Volume

Free Energy: $F = U - S \cdot T$

U: Internal Energy
S: Entropy of the system
T: Temperature

3.6.2 Statisticsl distributions

For the three different types of molecules we can treat there are also three different statistical distributions that estimate the number of particles at that energy:

Maxwell-Bolzmann-Statistics: $\quad n(E) = e^{\frac{-(E-\mu)}{k_B T}}$

Fermi-Dirac-Statistics: $\quad f_F(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1}$

step function which falls from 90% to 10% over an energy distance of 4kT

Bose-Einstein-Statistics: $\quad f_B(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}} - 1}$

μ is the *chemical potential* at T=0, which we call the *fermi energy* for bosons in solids.

If $(E - \mu) \gg 1$, both simplify to the classical result (Boltzmann factor), as for low occupation probability the nature of the spin can be neglected.

3.6.3 Electron Gas

The solid is treated as a cube in which we place e^- that are free to move around.

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} (\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}) \quad n_x, n_y, n_z = 1, 2, 3 \cdots$$

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin(\frac{n_x \pi}{l_x} x) \sin(\frac{n_y \pi}{l_y} y) \sin(\frac{n_z \pi}{l_z} z)$$

- Energy spacing between electronic states

$$\Delta E = \frac{\hbar^2 \pi^2}{2m}\left[\left[\frac{(n_x+1)^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right] - \left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right]\right]$$

$$= \frac{\hbar^2 \pi^2}{2ml_x^2}(2n_x+1)$$

If $l_x = l_y = l_z = 1$ cm and $n_x = n_y = n_z = (N_A)^{\frac{1}{3}}$:

$$\Delta E \approx 1 \cdot 10^{-6} \text{ eV}$$

States form essentially continuous bands.

- Electrons are fermions, i.e. only $2e^-$ to each level, and we fill from the bottom up. (If they were bosons they would all be in the lowest state.)

  The highest occupied level called *Fermi level*. We can consider the states in *k-space*.

$$k_x = n_x \frac{\pi}{l_x} \qquad k_y = n_y \frac{\pi}{l_y} \qquad k_z = n_z \frac{\pi}{l_z}$$

Each solution occupies $\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$ of k-space.

- The energy can be re-written by

$$E_{n_x,n_y,n_z} = \frac{\hbar^2 k^2}{2m} \quad \text{with} \quad \begin{cases} k^2 = k_x^2 + k_y^2 + k_z^2 \\ k_x > 0, k_y > 0, k_z > 0 \end{cases}$$

- The energy states are occupied up to k_F, the *Fermi level* (E_F: *Fermi energy*).

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}} \quad \text{and} \quad E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}}$$

- Number of states below energy E: $N(E) = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{\frac{3}{2}}$

- Number of electron states per unit energy (*density of states*):

$$\frac{1}{V}\frac{dN(E)}{dE} = D(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}}$$

The electrical conduction depends on the number of states available at E_F to carry electrical current.

3.6.4 Bloch Theorem and tight binding model

The Bloch Theorem states, that if we have a spatially periodic structure, i.e. a periodic potential $V(x+a) = V(x)$ with periodicity a, then the wavefunction is of the form:

$$\psi(x+a) = e^{iKa}\psi(x) \qquad K \in \mathbb{R}, K \text{ indep. of } x$$

Tight Binding Model Imagine a lattice of atoms separated by the distance a. In the tight binding model, we now assume, that only the potentials of the next, the current and the atom before have an influence on the electron. This gives us a periodic potential that repeats itself. Let A be the value of the potential of the previous and next atom, while E_0 is the potential at the current atom. We can then write for:

$$\psi(x) = \sum_{p=-\infty}^{\infty} c_p \varphi(x - pa)$$

$$-Ac_{p-1} + E_0 c_p - Ac_{p+1} = E \cdot c_p$$

Using the bloch theorem we find:

$$\psi(x+a) = e^{ika}\psi(x) \iff \sum_p c_{p+1}\varphi(x-pa) = e^{ika}\sum_p c_p\varphi(x-pa)$$

This leads to: $c_{p+1} = e^{ika}c_p$ and $c_{p-1} = e^{-ika}c_p$

And we get the formula for E:

$$E = E_0 - 2A\cos(ka), k \in \mathbb{R}$$

What we just found gives rise to the energy bands (width 4A) in periodic potentials.

3.6.5 Bandgaps in periodic structures

Periodic Boundary Conditions: Due to the finite size of the solid, the potential is not periodic forever. We therefore assume

$$\psi(x) = \psi(Na + x)$$

Using Bloch's theorem:

$$\psi(x) = e^{iKNa}\psi(x) \longrightarrow \begin{cases} e^{iKNa} = 1 \\ \text{OR} \\ K = \frac{2\pi s}{Na} \text{ with } s = 0, \pm 1, \pm 2, \cdots \end{cases}$$

Dirac Comb potential

- *Dirac Comb*: let $b \to 0$ and $V_0 \to \infty$

$$V(x) = \begin{cases} \alpha \sum_{j=0}^{N-1} \delta(x - ja) \\ 0 \text{ in between } \delta\text{-functions} \end{cases}$$

$$\underbrace{\cos Ka}_{\text{LHS}} = \underbrace{\cos ka + \frac{m\alpha}{\hbar^2 k}\sin ka}_{\text{RHS}}$$

If we plot RHS we notice that it goes outside the allowed range ($-1 < \text{lhs} < +1$). Therefore only certain ranges of ka and E are allowed.

- Bands and Band Gaps: Solutions of SE yield bands of allowed electronic states and gaps between-where there are no solutions. Each material will have a set of bands and electrons. We fill from the bottom up, $2e^-$ to each level in band.

3.7 Approximation Techniques: Perturbation Theory

We try to solve the system $\hat{H}\psi_n = E_n\psi_n$

The idea of perturbation theory is, to now go from a simple known system $\hat{H}^{(0)}$ and approximate the solution of a more complicated system $\hat{H}$ by in order ascending correction terms. So:

$$\hat{H} = \hat{H}^0 + \lambda\hat{H}'$$

And approximate E_n, ψ_n by power series of λ

$$\begin{cases} E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \\ \psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} \end{cases}$$

And plugging this back into the equation we get:

$$(\hat{H} = \hat{H}^0 + \lambda\hat{H}')[\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + ...] =$$

$$(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...)[\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + ...]$$

3.7.1 First order perturbation

For first order perturbation we only consider the λ terms.

correction of the energies: $E_n^{(1)} = \langle\psi_n^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle$

correction of the wavefunctions: $\psi_n^{(1)} = \sum_{m\neq n} \frac{\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle}{[E_n^{(0)} - E_m^{(0)}]}\psi_m^{(0)}$

3.7.2 second order perturbation

$$E_n^{(2)} = \sum_{m\neq n} \frac{|\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle|^2}{[E_n^{(0)} - E_m^{(0)}]} \quad \to \text{energies closer to each other are weighted more}$$

3.8 Applications of QM to semiconductor physics

3.8.1 Effective Mass approximation

When looking at the the energy-momentum diagram of Semiconductors, the energy bands are seperated by gaps, where the bands have a minimum or maximum. We call this the *band gap*. We now expand the the energy function $\varepsilon(k)$ around the minimum k_0, so:

$$\varepsilon(k) = \varepsilon_0 + \frac{\partial\varepsilon}{\partial k}(k - k_0) + \frac{1}{2}\frac{\partial^2\varepsilon}{\partial^2 k}(k - k_0)^2$$

But because we are at a minimum, $\frac{\partial\varepsilon}{\partial k}(k - k_0) = 0$. We now chose $\varepsilon_0 = 0$ and $k_0 = 0$ and we are left with the expression

$$\varepsilon(k) = \frac{1}{2}\frac{\partial^2\varepsilon}{\partial^2 k}k^2$$

We now map this onto the Free Electron case, making use of the same formal expression for the energy.

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m^*}, \quad \varepsilon(k) = \frac{1}{2}\frac{\partial^2\varepsilon}{\partial^2 k}k^2 \Rightarrow \frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2\varepsilon}{\partial^2 k}$$

We now define the mass m^* as the *effective mass* of the electron in the semiconductor. The Rydberg energy and the Bohr radius are then renormalized:

$$E_{Ry}^* = \left(\frac{m*}{m_0}\right)\left(\frac{1}{\varepsilon_r}\right)^2 E_{Ry}, \quad a_0^* = \left(\frac{m*}{m_0}\right)\varepsilon_r a_0$$

These corrections lead to a large probability of the electrons not being in the bound state at room temperature (as kT = 26meV).

3.8.2 Dopands in Semiconductors
Metals vs. insulators/semi-conductors

- Metals have partially filled bands.

- Insulators and semi-conductors have a filled band (*valence band*) separated from an empty band (*conduction band*) by the band gap E_g.

$$n = N_i \exp[-\frac{E_g}{k_B T}]$$

If $E_g > 4$ eV : insulator, else semiconductor.

- To conduct electrical current, the e^- must move in electric fields, which requires a kinetic energy. Electrons need empty states in the conduction band, otherwise they cannot move. As metals have partially filled bands, they can conduct. Filled bands are inert and cannot conduct.

Doping

In modern electronics impurities with one more/less valence e^- are added. So we have one extra electron and one extra hole. P is called a *donor*: it has an extra e^- to donate to the conduction band. Ionizing is done by removing the extra electron.

$$n_{\text{electrons}} = N_D \exp[-\frac{E_d}{k_B T}]$$

N_D: concentration of impurities. Each impurity (dopant atom) first leads to a bound state, before the band-structure follows.

3.9 Operators
3.9.1 Some Operators

$\hat{x} = x$ **(same for y,z)**
$\hat{p} = -i\hbar \frac{d}{dt}$ **momentum operator**
$\hat{H} = \frac{\hat{p}^2}{2m} + V(r) = \frac{-\hbar^2}{2m}\nabla^2 + V(r)$ **Hamiltonian**
$\hat{L} = \hat{r} \times \hat{p}$ **Angular momentum**
$[\hat{x}_x, \hat{p}_j] = i\hbar \delta_{ij}$

3.10 Repetition
3.10.1 Oscillator

$$\ddot{x} + \frac{b}{m}\dot{x} + \frac{k_F}{m}x = 0 \quad \text{or} \quad \ddot{x} + \frac{b}{m}\dot{x} + \omega_0^2 x = 0$$

$$\gamma = \frac{1}{\tau} = \frac{b}{m} \implies \text{envelope-function: } e^{-\frac{t}{2\tau}}$$

$$Q = \omega_0 \cdot \tau \qquad \omega = \sqrt{\frac{k_F}{m}}$$

3.10.2 Equation of motion

$$v = v_0 + at \qquad s = v_0 t + \frac{1}{2}at^2 \qquad v^2 = v_0^2 + 2as$$

With induction

$$F_{\text{tot}} = ma = m\ddot{x} \quad \rightarrow \quad \ddot{x} + \omega^2 x + cst = 0$$

Ansatz: $\quad x = A\cos(\omega t + \varphi_0) + x_0$

3.10.3 Centripedal force

$$F = \frac{mv^2}{r}$$

3.10.4 Energies

$$E_{\text{kin}} = \frac{1}{2}mv^2 \qquad E_{\text{pot}} = mgh \qquad E_{\text{el}} = qV$$

Potential energy of two charges (separated by a distance r)

$$E_{\text{pot}} = \frac{q_1 \cdot q_2}{4\pi\varepsilon_0 r}$$

3.11 Basics
3.11.1 Cylindrical coordinates
Conversion $x = r\cos\varphi \ y = r\sin\varphi \ z = z$

Range $r \in [a,b] \ \varphi \in [0, 2\pi] \ z \in [c,d]$

$$\iiint\limits_{\text{Vol}} 1 \, d_{\text{vol}} = \int\limits_X \int\limits_Y \int\limits_Z 1 \, dz \, dy \, dx = \int\limits_c^d \int\limits_0^{2\pi} \int\limits_a^b 1 \cdot r \, dr \, d\varphi \, dz$$

3.11.2 Spherical coordinates
Conversion $x = r\sin\theta\cos\varphi \ y = r\sin\theta\sin\varphi \ z = r\cos\theta$

Range $r \in [a,b] \ \varphi \in [0, 2\pi] \ \theta \in [0, \pi]$

$$\iiint\limits_{\text{Vol}} 1 \, d_{\text{vol}} = \int\limits_X \int\limits_Y \int\limits_Z 1 \, dz \, dy \, dx = \int\limits_a^b \int\limits_0^{2\pi} \int\limits_0^{\pi} 1 \cdot r^2 \sin\theta \, d\theta \, d\varphi \, dr$$

3.11.3 Polar coordinates
Conversion $x = r\cos\varphi \qquad y = r\sin\varphi$

Range $r \in [a,b] \qquad \varphi \in [0, 2\pi]$

$$\iint\limits_A 1 \, dA = \int\limits_X \int\limits_Y 1 \, dy \, dx = \int\limits_a^b \int\limits_0^{2\pi} 1 \cdot r \, d\varphi \, dr$$

3.11.4 Vector calculus
Gradient (with a scalar field f)

Cartesian coordinates

$$\nabla f = \frac{\partial f}{\partial x}\hat{x} + \frac{\partial f}{\partial y}\hat{y} + \frac{\partial f}{\partial z}\hat{z}$$

Cylindrical coordinates

$$\nabla f = \frac{\partial f}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial f}{\partial \varphi}\hat{\varphi} + \frac{\partial f}{\partial z}\hat{z}$$

Spherical coordinates

$$\nabla f = \frac{\partial f}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial f}{\partial \theta}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial f}{\partial \varphi}\hat{\varphi}$$

Curl $\nabla \times A = \ldots$

Cartesian coordinates

$$\ldots = \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}\right)\hat{x} + \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\hat{y} + \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right)\hat{z}$$

Laplace operator $\Delta f = \nabla^2 f = \ldots$

Cartesian coordinates $\quad \ldots = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$

Spherical coordinates

$$\ldots = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial \varphi^2}$$

3.12 Charges and Field
3.12.1 Constants and Definitions

Elementar charge	e	$+1.602 \cdot 10^{-19}$	As
Avogadro constant	N_A	$6.022140857 \cdot 10^{23}$	$\frac{1}{mol}$
Dielectric constant	ε_0	$8.854 \cdot 10^{-12}$	$\frac{As}{Vm}$
Magn. permeability	μ_0	$4\pi \cdot 10^{-7}$	$\frac{Vs}{Am}$
Mass electron	$m_{0,e}$	$9.1094 \cdot 10^{-31}$	kg
Mass proton	$m_{0,p}$	$1.6726 \cdot 10^{-27}$	kg
Speed of light	$c_{Vak.}$	$2.99792 \cdot 10^8$	$\frac{m}{s}$
Planck constant	h	$6.626'069 \cdot 10^{-34}$	Js
Planck constant	h	$4,135'667 \cdot 10^{-15}$	eV
Red. Planck constant	$\hbar$	$\frac{h}{2\pi} = 1.054'571 \cdot 10^{-34}$	Js
Red. Planck constant	$\hbar$	$\frac{h}{2\pi} = 6,582119 \cdot 10^{-16}$	eV
Boltzmann constant	k_B	$1.38 \cdot 10^{-23}$	$\frac{Ws}{K}$
Stefan-Boltzmann con.	σ	$5.67 \cdot 10^{-8}$	$\frac{W}{m^2 K^4}$