1 Optics

1.1 Geometrical Optics

Optical Path length For light to travel a distance d in a material with refractive index n, it takes a time $t = \frac{d}{v} = \frac{nd}{c}$. We call $D = n \cdot d$ the optical path length.

Fermat's Principle Light travelling between two points will follow a path whose optical path length is extremal to variations in the path

Snell's Law $n_1 \sin(\theta_1) = n_2 \sin(\theta_2)$

Paraxial Approximation Only consider rays that make a small angle with respect to some optical axis.

Single Surface Lens:

Radius of Convergence: $\frac{1}{R} = \frac{1}{n_2 - n_1}\left(\frac{n_1}{d_1} - \frac{n_2}{d_2}\right)$

Focal Length: $f = \frac{R \cdot n_2}{n_2 - n_1}$, $\frac{n_2}{f} = \frac{n_1}{s_o} + \frac{n_2}{s_i} = \frac{n_2 - n_1}{R}$

Two-Surface Lens:

Focal Length: $\frac{n_w}{s_o} + \frac{n_w}{s_i} = (n_l - n_w)\left(\frac{1}{R_1} - \frac{1}{R_2}\right)$ with n_w the refractive index of the surrounding and n_l the refractive index of the material of the lens. Further: $\frac{1}{f_w} = \frac{1}{s_o} + \frac{1}{s_i} = \left(\frac{n_l}{n_w} - 1\right)\left(\frac{1}{R_1} - \frac{1}{R_2}\right)$

Thin lens formula / lensmaker's formula: $\frac{1}{f} = \frac{1}{d_1} + \frac{1}{d_2} = \frac{1}{f_1} + \frac{1}{f_2}$

Characteristics:

a) $f > 0$: converging lens (Light is bent towards the optical axis)
b) $f < 0$: diverging lens (Light is bent away from the optial axis)
c) $d_1 = s > 0$: real object, before lens
d) $d_1 = s < 0$: virtual object, after lens
e) $d_2 = d > 0$: real image, after lens
f) $d_2 = d < 0$: virtual image, before lens

Maginfication Factor: $M = -\frac{d_2}{d_1} = \frac{h'}{h}$ where h is the hight of the object and h' is the hight of the image. If $M > 0$: image is upright, if $M < 0$: image is inverted.

Telescope $\Delta\theta' \approx \frac{f_1}{f_2}\Delta\theta$. Here, θ: incident angle, f_1: focal length lens 1, f_2: focal length lens 2, θ': angle after passing through two lenses.

Microscope Total magnification: $M = \frac{d_1 d_2}{s_1 s_2}$. Here, s_1: distance object and lens 1, s_2: distance image lens 1 and lens 2, d_1: distance image lens 1 and lens 1, d_2: distance virtual image lens 2 and lens 2. Note: d_2 is negative, thus the image is inverted.

1.2 Wave Optics

Maxwell's Equations and Wave Equations in vacuum

$$\vec{\nabla} \cdot \vec{E} = 0 \ , \ \vec{\nabla} \cdot \vec{B} = 0 \quad , \quad \vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \ , \ \vec{\nabla} \times \vec{B} = \mu_0 \varepsilon_0 \frac{\partial \vec{E}}{\partial t}$$

$$\vec{\nabla}^2 \vec{E} = \frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} \ , \ \vec{\nabla}^2 \vec{B} = \frac{1}{c^2}\frac{\partial^2 \vec{B}}{\partial t^2}$$

Superposition Principle Every linear combination of solutions to the wave equation is again a solution to the wave equation.

Huygens' Principle Every point on the "wavefront" of a wave acts as a secondary source of hemispherical waves that propagate in the "forward" direction. Here, "wavefront" means surfaces in space where the eletrical field has the same phase of oscillation.

Consider a source A at $\vec{r}_A = (x_A, y_A, z_A)$ and a detector B at $\vec{r}_B = (x_B, y_b, z_B)$ with an aperture of cross section a^2 between the two. Take C a point in the apperture. Then the spatial part of the electric field emmited from A at C is given by

$$U \propto \frac{1}{|\vec{r}_C - \vec{r}_A|} e^{ik|\vec{r}_C - \vec{r}_A|} \ , \ |\vec{r}_B - \vec{r}_C| = \sqrt{(x - x_A)^2 + (y - y_A)^2 + z_A^2}$$

Similarly we can write the electrical field at point B due to the spherical wave at C. In the end, the total electric field at B is given by

$$U \propto \int_{-a/2}^{a/2} dx \int_{-a/2}^{a/2} dy \ \frac{1}{|\vec{r}_C - \vec{r}_A| \cdot |\vec{r}_B - \vec{r}_A|} e^{ik(\vec{r}_C - \vec{r}_A) + |\vec{r}_B - \vec{r}_A|}$$

$$\begin{aligned} |\vec{r}_C - \vec{r}_A| &= \sqrt{x_A^2 + y_A^2 + z_A^2 - 2xx_A - 2yy_A + x^2 + y^2} \\ &\approx r_A - \frac{xx_A + yy_A}{r_A} + \frac{x^2 + y^2}{2r_A} \\ &\approx r_A - \frac{xx_A + yy_A}{r_A} \end{aligned}$$

where $r_A = \sqrt{x_A^2 + y_A^2 + z_A^2}$ and similarly for r_B. The first assumption made is $a \ll r_A, r_B$. The secons approximation of dropping the quadratic terms and is called **Fraunhofer approximation**.

$$U_B \propto \int_{-a/2}^{a/2} dx \int_{-a/2}^{a/2} dy \frac{e^{ik(r_A + r_B)} e^{-ik(Xx + Yy)}}{\left(r_A - \frac{xx_A - yy_A}{r_A}\right)\left(r_B - \frac{xx_B - yy_B}{r_B}\right)}$$

Where $X = \frac{x_A}{r_A} + \frac{x_B}{r_B}$ and $Y = \frac{y_A}{r_A} + \frac{y_B}{r_B}$. With third approximation, dropping the fractions in the denominator, we obtain:

$$\begin{aligned} U_B &\propto \frac{e^{ik(r_A + r_B)}}{r_A r_B} \int_{-a/2}^{a/2} dx \int_{-a/2}^{a/2} dy \ e^{-ik(Xx + Yy)} \\ &\propto \frac{a^2 e^{ik(r_A + r_B)}}{r_A + r_B} \mathrm{sinc}\left(\frac{kXa}{2}\right) \mathrm{sinc}\left(\frac{kYa}{2}\right) \end{aligned}$$

With Fermat's Principle we obtain that U is extremal if $X = 0$ and $Y = 0$. In general we can introduce a aperture function $t(x, y)$ so that

$$U_B \propto e^{ik(r_A + r_B)} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \ t(x, y) \ e^{-ik(Xx + Yy)}$$

Rayleigh Criterion Two objects are just resolved if the intensity maximum of one lines up with the intensity minimum of the other. Equivalent:

$$\frac{x_{A_2}}{r_{A_2}} = \sin(\theta_S) > \frac{\lambda}{a} \quad , \quad \theta_s = \sin^{-1}\left(\frac{\lambda}{a}\right)$$

Where the index 2 should indicate that it is the second light source, the first one is on the optical axis. θ_S is the so called **angular resolution**.

Abbé Limit In the spacial resolution of microscopes, the Abbé Limit describes the limit at which two slits in a diffraction pattern are still distinguishable.

$$d > \lambda \frac{\sqrt{s^2 + (L/2)^2}}{L}$$

where d is the distance between the two slits, s is the distance between the lense and the slits and L is the diameter of the lens.

Numerical apperture $N_A = sin(\theta_{\text{lense}}) \approx \frac{w_l}{2d_l}$ with w_l = lense width and d_l = distance object to lense

1.3 Polarization

Linear Polarization

$$\begin{aligned}\vec{E}(\vec{r},t) &= (E_x\hat{x} + E_y\hat{y})\cos(kz-\omega t)\\ &= E_0\left(\cos(\theta)\hat{x} + \sin(\theta)\hat{y}\right)e^{i(kz-\omega t)}\end{aligned}$$

Elliptical and circular Polarizations

$$\begin{aligned}\vec{E}(\vec{r},t) &= E_x\hat{x}\cos(kz-\omega t) + E_y\hat{y}\cos(kz-\omega t+\phi)\\ &= \left(E_x\hat{x} + E_y e^{i\phi}\hat{y}\right)e^{i(kz-\omega t)}\end{aligned}$$

In the case of $\phi = \pm\frac{\pi}{2}$ we have a circle. If $\phi = \frac{\pi}{2}$, we have right circular polarization and if $\phi = -\frac{\pi}{2}$ we have left circular polarization.

Birefringence A birefringent is a material that has different refraction indices for the x and y component of an electric field.

Maxwell's Equations: macroscopic version

$$\vec{\nabla}\cdot\vec{D} = 0 \;,\; \vec{\nabla}\cdot\vec{B} = 0 \;,\; \vec{\nabla}\times\vec{E} = -\frac{\partial\vec{D}}{\partial t} \;,\; \vec{\nabla}\times\vec{H} = \frac{\partial D}{\partial t}$$

$\vec{B} = \mu_0\mu_r\vec{H}$, $\vec{D} = \varepsilon_0\varepsilon_r\vec{E}$, speed of light in a material with refraction index n: $v = \frac{c}{n}$, $n = \sqrt{\mu_r\varepsilon_r}$, $\vec{k}\times\vec{B} = \omega\vec{B}$, $B = \frac{k}{\omega}E = \frac{nk_0}{\omega}E = \frac{n}{c}E$.

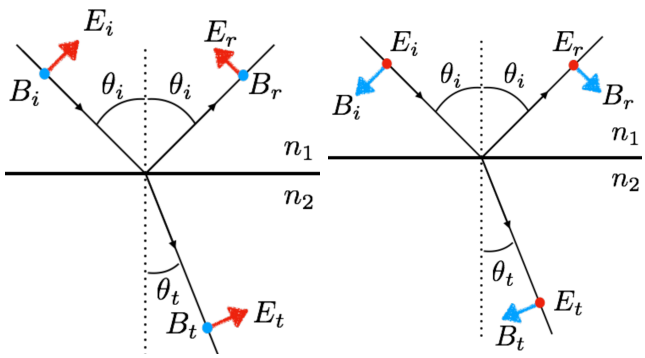

Figure 1: Left: p-polarization, Right: s-polarization

Refraction and Reflection at a surface Boundry conditions for amplitudes of plane waves across a planar interface:

$$B_{\perp 1} = B_{\perp 2} \;,\; D_{\perp 1} = D_{\perp 2} \;,\; H_{\parallel 1} = H_{\parallel 2} \;,\; E_{\parallel 1} = E_{\parallel 2}$$

With this we have: $E_i\cos(\theta_i) - E_r\cos(\theta_i) = E_t\cos(\theta_t)$ and $n_1E_i + n_1E_r = n_2E_t$.

Fresnel Equations

For p-polarization:

$$t_p = \frac{E_t}{E_i} = \frac{2n_1\cos(\theta_i)}{n_2\cos(\theta_i) + n_1\cos(\theta_t)}$$

$$r_p = \frac{E_r}{E_i} = \frac{E_r}{E_i} = \frac{n_2\cos(\theta_i) - n_1\cos(\theta_t)}{n_2\cos(\theta_i) + n_1\cos(\theta_t)} = \frac{\tan(\theta_i-\theta_t)}{\tan(\theta_i+\theta_t)}$$

For s-polarization:

$$t_s = \frac{E_t}{E_i} = \frac{2n_1\cos(\theta_i)}{n_1\cos(\theta_i) + n_2\cos(\theta_t)}$$

$$r_s = \frac{E_r}{E_i} = \frac{n_1\cos(\theta_i) - n_2\cos(\theta_t)}{n_1\cos(\theta_i) + n_2\cos(\theta_t)}$$

Brewster's Angle $r_p = 0 \Leftrightarrow \theta_i + \theta_t = \frac{\pi}{2}$. This special value of θ_i is called Brewster's angle, labeled $\theta_B = \arctan(n_2/n_1)$. For light waves incident at an angle of θ_B, no p-polarized light can be reflected. For s-polarized light, there is no incidence angle where there is no zero reflectivity.

1.4 Spectroscopy

Grating Spectrometer Phase difference between the light reflecting off of two neighboring stips:

$$\phi(\lambda) = kd\left(\sin(\theta_i) - \sin(\theta_j)\right) \quad , \; k = \frac{2\pi}{\lambda}$$

Contribution from N strips:

$$U \propto \sum_{n=0}^{N-1} e^{in\phi} = \frac{1-e^{iN\phi}}{1-e^{i\phi}} = e^{i(N-1)\phi/2}\frac{\sin\left(N\phi/2\right)}{\sin(\phi/2)}$$

$$I \propto |U|^2 \propto \frac{\sin^2\left(N\phi/2\right)}{\sin^2(\phi/2)}$$

Maxima at $\phi/2 = m\pi$ with $m \in \mathbb{Z}$. Maximal value: N^2. Yields:

$$\sin(\theta_i) - \sin(\theta_j) = \frac{2\pi m}{dk} = \frac{m\lambda}{d}$$

m is the **order of the maximum**. Condition for Minima:

$$\frac{\phi_2}{2} = \left(m + \frac{1}{N}\right)\pi$$

Combinint conditions:

$$\phi_2 - \phi_1 = \frac{2\pi}{N}$$

$$k_2 - k_1 = \frac{2\pi}{Nd\left(\sin(\theta_i) - \sin(\theta_j)\right)}$$

$$\Delta\nu = \frac{c}{Nd\left(\sin(\theta_i) - \sin(\theta_j)\right)}$$

Interferometry Consider Michelson inferometer. Beamsplitter devides input beams evenly into two parts of equal amplitude and phase and does the inverse of this on recombination. Electric field on detector:

$$U \propto \frac{1}{2}U_0e^{2ikd_1} + \frac{1}{2}U_0e^{2ikd_2} = \frac{U_0}{2}e^{2ikd_1}\left(1 + e^{2ikx}\right)$$

where U_0 is the input amplitude, d_1 and d_2 are the optical path lengths and $x = d_2 - d_1$. With this:

$$I \propto \frac{|U_0|^2}{4}\left(2 + 2\cos(2kx)\right) \propto \frac{I_0}{2}\left(1 + \cos(4\pi x/\lambda)\right)$$

The **spectral density** $S(\nu)$ of a light source: $S(\nu)d\nu$ is the power emitted by the light source between frequencies ν and $\nu + d\nu$.

$$\begin{aligned}I &\propto \int_0^\infty S(\nu)\left(1 + \cos(4\pi x/\lambda)\right)\, d\nu\\ &\propto \int_0^\infty S(\nu)\, d\nu + \int_0^\infty S(\nu)\cos(4\pi\nu x/s)\, d\nu\\ &\propto \int_0^\infty S(\nu)\, d\nu + \frac{1}{2}\int_{-\infty}^\infty S(|\nu|)e^{i4\pi\nu x/c}\, d\nu\end{aligned}$$

$$\begin{aligned}S(\nu) &\propto \int_0^\infty \left(2I(x) - I_0\right)\cos(4\pi\nu x/c)\, dx\\ &\sim \int_0^{x_{\max}} \left(2I(x) - I_0\right)\cos(4\pi\nu x/c)\, dx\\ &\sim \int_0^{x_{\max}} \cos(4\pi x\nu_0/c)\cos(4\pi x\nu/c)\, dx\\ &\sim \text{sinc}\left(\frac{2\pi(\nu-\nu_0)x_{\max}}{c}\right) + \text{sinc}\left(\frac{2\pi(\nu+\nu_0)x_{\max}}{c}\right)\end{aligned}$$

This peaks at $\nu = \pm\nu_0$. Zeros closest to the maximum at $+\nu_0$ are at

$$\nu - \nu_0 = \pm\frac{c}{2x_{\max}}$$

Thus, according to Rayleigh criterion our spectrometer resolution is

$$\frac{\Delta\nu}{\nu_0} = \frac{\lambda}{2x_{\max}} \quad \text{or} \quad \delta\nu = \frac{c}{2x_{\max}}$$

Fabry-Perot etalon Incomming light source: $A_0 e^{i(kx-\omega t)}$, t: transmission coefficient, r: reflection coefficient. Transmitted field: $A_0 \cdot t$, reflected field: $A_0 \cdot r \cdot e^{i\phi_r}$. Total field amplitude from all the paths:

$$A = A_0 t^2 e^{ikd} \sum_{n=0}^{\infty} r^{2n} e^{in\phi} = A_0 t^2 e^{ikd} \cdot \frac{1}{1 - r^2 e^{i\phi}}$$

$$\eta = \frac{|A|^2}{|A_0|^2} = \frac{t^4}{(1 - r^2 e^{i\phi})(1 - r^2 e^{-i\phi})} = \frac{t^4}{1 + r^4 - 2r^2\cos(\phi)}$$

$$= \frac{(1-R)^2}{(1-R)^2 + 2R(1-\cos(\phi))} = \frac{1}{1 + \frac{4R}{(1-R)^2}\sin^2\left(\frac{\phi}{2}\right)}$$

$$\eta = \frac{I_o}{I_i} = \frac{1}{1 + \frac{4R}{(1-R)^2}\sin^2(2\pi d/\lambda + \phi_r)}$$

with $T = t^2$, $R = r^2$ and $t^2 + r^2 = 1$. R is the reflectivity of the mirror, d the distance between the mirrors, and λ is the wavelength of the light, and ϕ_r is the phase picked up by the light when it reflects off a mirror. Wavelength resolution $\delta\nu$:

$$\frac{d\lambda}{d\nu} = \frac{d}{d\nu}\left(\frac{c}{\nu}\right) = -\frac{c}{\nu^2} \quad \Rightarrow \quad \delta\lambda = \frac{c}{\nu^2}\delta\nu$$

2 Statistical Physics

A single macrostate can be consistant with many microstates. A single microstate, however, always specifies a single macrostate. A microstate contains all the information about the macrostate, but not vice versa.

Fundamental postulate of statistical physics *"For a closed system, every microstate which satisfies the global constraint is equally likely to be occupied."* "closed system" = system that does not exchange matter with the outside but it can exchange energy, "global constraint" = system has a particular set of values for global variables such as the particle number, volume, energy, etc. Systems that fulfil this postulate are said to be in a **thermodynamic equilibrium**. Further postulates: *"Over a sufficiently long period of time, a system will sample every microstate compatible with the global constraints with equal property."*, *"The macrostate occupied in thermodynamic equilibrium is the one with the largest number of microstates."*

Variance $\Delta z = \sqrt{\langle z^2\rangle - \langle z\rangle^2}$. The factorial width $\Delta z/\langle z\rangle$ decreases as $1/\sqrt{N}$.

Ideal gas law $pV = Nk_BT = Nm\langle v_x^2\rangle$

Temperature For an isolated system with two chambers with energies U_i and numbers of particles N_i, we have:

$$\frac{1}{\Omega_1}\left(\frac{\partial\Omega_1}{\partial U_1}\right)_{N_1} = \frac{1}{\Omega_2}\left(\frac{\partial\Omega_2}{\partial U_2}\right)_{N_2} \Leftrightarrow \left(\frac{\partial}{\partial U_1}\ln(\Omega_1)\right)_{N_1} = \left(\frac{\partial}{\partial U_2}\ln(\Omega_2)\right)_{N_2}$$

$$\left(\frac{\partial\sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial\sigma_2}{\partial U_2}\right)_{N_2}$$

Where Ω_i is the number of microstates corresponding to the macrostates specified by N_i and U_i. The total number of microstates is given by $\Omega(N_1, N_2, U_1, U_2) = \Omega(N_1, U_1) \cdot \Omega(N_2, U_2)$. We define $\sigma = \ln(\Omega)$. This relation between two systems must hold, when thermodynamic equilibrium is reached. Temperature is defined as

$$\frac{1}{T} = k_B\left(\frac{\partial\sigma}{\partial U}\right)_{N,V}$$

Definitions: $\tau = k_BT$, $\beta = 1/\tau = 1/k_BT$.

Entropy $S = k_B\sigma = k_b\ln(\Omega) = -k_B\sum_s p_s\log(p_s) = \frac{\partial}{\partial T}(k_BT\ln(Z))$

Boltzmann factor and partition function Probability of finding a system in thermal equilibrium in a microstate with energy ε is proportional to $e^{-\beta\varepsilon}$, called Boltzmann factor. Absolute probability of finding the system in a microstate with energy ε

$$P(\varepsilon) = \frac{e^{-\beta\varepsilon}}{Z} \quad , \quad Z = \sum_s e^{-\beta\varepsilon_s} \quad , \quad U = \langle\varepsilon\rangle - \frac{\partial}{\partial\beta}(\ln(Z))$$

where Z is called **partition function**. U is the average energy of the system. The continuous form of the partition function is:

$$Z = \sum_{E_s}\Omega(E_s)e^{-\beta E_s} = \int_0^\infty f(E)e^{-\beta E}\,dE$$

Partition function Partition function for a single particle in $3D$:

$$Z_{sp} = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} = V\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}$$

where V = volume and h = Plank constant. For distinguishable particles: $Z_D = Z_{sp}^N$. For indistinguishable particles: $Z_I = \frac{1}{N!}Z_{sp}^N$.

Heat Capacity $\frac{1}{C} = \frac{\partial T}{\partial E} \Leftrightarrow C = \frac{\partial E}{\partial T}$

Average Energy $\langle E^k\rangle = \frac{1}{Z}\int_0^\infty E^k p(E)\,dE$

Variance $(\Delta E)^2 = \langle E^2\rangle - \langle E\rangle^2 = \frac{\partial^2\log(Z)}{\partial\beta^2}$

Equipartition Theorem *Each term in the energy that is quadratic in some coordinate contributes $k_BT/2$ to the average energy per particle.*

Gases of polyatomic molecules Internal degrees of freedom also contribute to the energy U. Each distinguishable, independent rotation axis gives one extra quadratic term to the microstate energy. Each vibration mode gives two such terms: one for the displacement, and one for the momentum.

Maxwell-Boltzmann distribution Total number of microstates with momentum magnitude between p and $p + dp$ is $g(p)dp = \frac{4\pi Vp^2dp}{h^3}$ with $g(p)$ the multiplicity function. Probability of finding a particle with momentum between p and $p + dp$ as $P(p)dp = \frac{4\pi Vp^2dp}{h^3} \cdot \frac{e^{-\beta p^2/2m}}{Z_{sp}}$. Expected number of particles in the gas with speeds between v and $v + dv$:

$$n(v)dv = 4\pi Nv^2dv\left(\frac{m}{2\pi k_BT}\right)^{3/2}e^{-mv^2/2k_BT}$$

Average speed of a particle in an ideal gas: $\langle v\rangle = \frac{\int_0^\infty vn(v)dv}{N} = \sqrt{\frac{8k_BT}{\pi m}}$. Most probable speed (maximum of distribution): $v_{max} = \sqrt{\frac{2k_BT}{m}}$. Important: speed v is the *magnitude* of the particles speed. For v_x: $\langle v_x\rangle = 0$, $\langle v_x^2\rangle = \frac{k_BT}{m}$

Blackbody Radiation A blackbody is an object that absorbs all light that hits it. In order to stay in thermal equilibrium with its surrounding, the blackbody also needs to emit light. Consider a rectangular box as a blackbody. Then the $1D$-solution to the waveequation is given as: $E(x,t) = \vec{E}_0 \sin(k_x x)e^{i\omega t}$, where $k_x = \frac{n\pi}{L_x}$ with $n = 1, 2, \dots$ and L_x the length of the box in x-direction. In $3D$:

$$\vec{E}(x,y,z,t) = \begin{pmatrix} E_{0,x}\cos(k_x x)\sin(k_y y)\sin(k_z z) \\ E_{0,y}\sin(k_x x)\cos(k_y y)\sin(k_z z) \\ E_{0,z}\sin(k_x x)\sin(k_y y)\cos(k_z z) \end{pmatrix} \cdot e^{i\omega t}$$

$\vec{k} = \left(\frac{n_x\pi}{L_x}, \frac{n_y\pi}{L_y}, \frac{n_z\pi}{L_z}\right)$, $n_x, n_y, n_z \in \mathbb{N}$, $\omega = c\cdot|\vec{k}|$, $\vec{E}_0 \cdot k = 0$. Number of modes with wavevector magnitudes between k and $k + dk$ is then given by

$$g(k)\ dk = \frac{V}{\pi^2}k^2\ dk \quad , \quad g(\nu)\ d\nu = \frac{8\pi V}{c^3}\nu^2\ d\nu$$

Rayleigh-Jeans Law Energy density of the electromagnetic field:

$$u = \frac{1}{2}\left(\varepsilon_0 E^2 + \frac{1}{\mu_0}B^2\right)$$

Each allowed mode with wavevector $\vec{k}$ and polarization $\vec{\varepsilon}$ of the EM field inside the cavity with an E-field amplitude $E_{\vec{k},\vec{\varepsilon}}$ and magnetic field amplitude $B_{\vec{k},\vec{\varepsilon}}$ has an energy

$$\varepsilon_{\vec{k},\vec{\varepsilon}} = \frac{V}{4}\left(\varepsilon_0 E_{\vec{k},\vec{\varepsilon}}^2 + \frac{1}{\mu_0}B_{\vec{k},\vec{\varepsilon}}^2\right)^2$$

Total EM energy: $\varepsilon = \sum_{\vec{k},\vec{\varepsilon}} \varepsilon_{\vec{k},\vec{\varepsilon}}$, $\langle\varepsilon_{\vec{k},\vec{\varepsilon}}\rangle = k_BT$, energy density inside the box for all modes within a cycle frequency between ν and $\nu + d\nu$ is then

$$\rho(\nu)\ d\nu = k_BT \cdot \frac{g(\nu)\ d\nu}{V} = k_BT \cdot \frac{8\pi\nu^2}{c^3}\ d\nu$$
$$\rho(\omega)\ d\omega = k_BT \cdot \frac{\omega^2}{\pi^2c^3}\ d\omega$$

Problem: if $\omega \to \infty$, then $\rho(\omega) \to \infty$.

The Planck Distribution Idea to solve ultraviolet catastrophe: only discrete values of energies are allowed. Assumption: energies are multiples of $\hbar\omega$. Then the partition function becomes:

$$Z = \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

The average energy is then:

$$\langle\varepsilon\rangle = -\frac{\partial}{\partial\beta}(\ln(Z)) = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \approx k_BT \quad (\text{if } k_bT \gg \hbar\omega)$$

Now the energy distribution (Plank distribution) is given by

$$\rho(\omega)\ d\omega = \frac{\hbar\omega^3}{\pi^2c^3}\frac{d\omega}{e^{\beta\hbar\omega} - 1}$$
$$\rho(\nu) = \frac{\langle E(\nu)\rangle g(\nu)}{V^2} \text{ (If 2D), if 1D: V}$$

Total EM energy density: (Stefan-Boltzmann Law)

$$u = \int_0^\infty \rho(\nu)\ d\nu = \frac{U}{V} = \underbrace{\frac{8\pi^5k_B^4}{15h^3c^3}}_{:=a}T^4 = aT^4$$

Emitted power per unit area of the blackbody surface

$$j(T) = \underbrace{\frac{ac}{4}}_{:=\sigma}T^4 = \sigma T^4$$

σ is called Stefan's constant.

3 Atoms

Elements ${}^A_Z G$: A is the mass of the atom, G is the symbol of the element and Z is the atomic number (number of protons).

Mass spectrometer $\vec{E} = E\vec{e}_y$, $\vec{B} = B\vec{e}_y$, $\vec{v} = v\vec{e}_z$, $\vec{F} = q\left(\vec{E} + \vec{v}\times\vec{B}\right)$. Thus $m\frac{d^2y}{dt^2} = qE \Rightarrow y = \frac{qEt^2}{2m}$ and $m\frac{d^2x}{dt^2} = -qBv \Rightarrow x = -\frac{qBvt^2}{2m}$. Since $t = l/v$ we obtain $y = \frac{m}{q}\frac{2Ex^2}{B^2l^2}$. Where l is the length of the condensator (interaction length). This is a parabola. Depending on the ratio m/q the particle will land somewhere else.

Scattering Assume we scatter atoms with radius r_1 and r_2, then they can't get closer than $r_1 + r_2$. Then the **scattering cross section** is $\sigma = \pi(r_1 + r_2)^2$. The **flux** is defines as $F = \frac{\Delta N_p}{A\Delta t}$. Rate of hitting objects is $R = F\sigma$. Using a *collection* of atoms as target: probability of two atoms lining up is small, rate of interactions is then $R = F\sigma N_A$ with N_A the number of atoms interacting with the beam. Assume atoms have a uniform density n within the volume. Probability that a single incident atom will get scattered: $P_S = n\sigma dx$. Change in number of atoms in the beam is $dN = -N\sigma n dx$. After a distance x, the number of remaining particles is $N(x) = N(0)e^{-n\sigma x}$. Number of particles over a time T through the entire cylinder is then $N(L) = N(0)e^{-\sigma nL}$, thus: $\sigma = \frac{\ln\left(\frac{N(p)}{N(L)}\right)}{nL}$.

Rutherford Scattering Shooting α particles at atom. Coulomb force acting: $\vec{F} = \frac{k}{r^2}\hat{r}$ with $k = \frac{2Ze^2}{4\pi\varepsilon_0}$ with charge electron charge e and atomic number Z. Since force is central, angular momentum needs to be conserved, resulting in $mv_0b = m\dot{\phi}r^2 \Rightarrow \frac{1}{r^2} = \frac{\dot{\phi}}{v_0b} \Rightarrow \vec{F} = \frac{k\dot{\phi}}{v_0b}\hat{r} \Rightarrow F_\perp = \frac{k\dot{\phi}}{v_0b}\sin(\phi) \Rightarrow m\dot{v}_\perp = \frac{k\dot{\phi}}{v_0b}\sin(\phi)$ Integrate this over a long period of time, t_1 long before interaction, t_2 long after interaction. At t_1: $v_\perp = 0$. At t_2: $v_\perp(t_2) = v_0\sin(\theta)$, $\phi = \phi_2 = \pi - \theta$, so: $\int_{t_1}^{t_2}\frac{dv_\perp}{dt}dt = \int_{t_1}^{t_2}\frac{k}{mv_0b}\sin(\phi)\frac{d\phi}{dt}dt$ resulting in $\int_0^{v_0\sin(\theta)} dv_\perp = \int_0^{\pi-\theta}\frac{k\sin(\phi)}{mv_0b}d\phi$ resulting in $v_0\sin(\theta) = \frac{k}{mv_0b}(1 + \cos(\theta))$ meaning $b = \frac{k}{mv_0^2}\cot\left(\frac{\theta}{2}\right)$. Now the goal is to find the distribution of particles over deflection angle. If we have a flux of particles $F = R/A$, then $dR = F\cdot 2\pi b\ db = \pi F\left(\frac{k}{mv_0^2}\right)^2\frac{\cos(\theta/2)}{\sin^3(\theta/2)}d\theta$. The differential **solid angle** is defined as $d\Omega = dA_{det}/r_{det}^2$, with dA_{det} the projection area of the detector and r_{det} the distance to the detector. $d\Omega = \sin(\theta)d\theta d\gamma$ with $d\gamma$ the azimuthal angle interval giving the size along the direction orthogonal to $d\theta$. So we obtain $dR = \frac{F}{4}\left(\frac{k}{mv_0^2}\right)^2\frac{1}{\sin^4(\theta/2)}d\Omega$.

Differential cross section: $dR = Fd\sigma \Rightarrow d\sigma = \frac{1}{4}\left(\frac{k}{mv_0^2}\right)^2\frac{1}{\sin^4(\theta/2)}d\Omega$. $d\sigma$ is called *Rutherford's differential cross section scattering formula.*

$d\dot{N} = Fd\sigma$ with dN the change in the rate of particles through some differential area $d\sigma$ and F the flux.

$b = \frac{k}{mv_0^2}\cot(\theta/2)$ for $\sim 1\text{fm} \ll b \ll r_a$

$d\Omega = 2\pi\sin(\theta)d\theta$

4 Photons and Particle-Wave Duality

The Photoelectric Effect Under some circumstances, light causes negative charges (electrons) to be ejected from a metal plate. Will not work if the plate has too much positive charge or if the frequencies of the light are too low. For each frequency of light there is a different voltage V_{max} at which electrons are ejected from the emitter plate are no longer able to reach the the collector plate. We have $E_{kin}^{max} = eV_{max}$, and $E_{max} = h\nu - \Phi$ with Φ the work function. Thus, *The energy contained in light with frequency ν can be absorbed only in multiples of $h\nu$. This quantum of light is called a photon.*

The Inverse Photoelectric Effect and X-Rays Take an energetic free electron and bring it into a metal, thereby producing a photon. The maximum frequency ν of photons emitted in this way is given by the kinetic energy $E_{kin} = eV_0$ of the electrons that hit the anode, by the relation $h\nu_{max} = eV_0 + \Phi$, where Φ is the work function. In practice $\Phi \ll eV_0$, so $\nu_{max} = eV_0/h$ and $\lambda_{min} = hc/eV_0$.

4.1 Scattering of photons with atoms

X-Ray diffraction Constructive interference occurs if the optical path length of the two paths differ by an integer multiple of the x-ray wavelength λ. This results in the **Bragg condition** $2d\sin(\theta) = n\lambda$ with d the distance between planes of atoms.

Compton Scattering Inelastic scattering, meaning, scattered light has a different energy than the incident light. Consider photons as particles with energy $E = h\nu$ and momentum $p = E/c = h\nu/c = h/\lambda$. Consider interaction of a single photon with an electron. Assume, electron initially at rest and photon moves along positive x-direction. Let θ be the deflection angle of the photon and ϕ be the deflection angle of the electron (with respect to the x-axis). Goal: study relation between θ and $\Delta\lambda$ of the photon. Conservation conditions yield: $h\nu + m_ec^2 = h\nu' + \sqrt{m_e^2c^4 + p^2c^2}$, $\frac{h\nu}{c} + 0 = \frac{h\nu'}{c}\cos(\theta) + p\cos(\phi)$ and $0 + 0 = \frac{h\nu'}{c}\sin(\theta) - p\sin(\phi)$. Thus: $p^2\cos^2(\phi) = \frac{h^2}{c^2}(\nu - \nu'\cos(\theta))^2$, $p^2\sin^2(\phi) = \frac{h^2(\nu')^2}{c^2}\sin^2(\theta) \Rightarrow p^2c^2 = h^2\left(\nu^2 - 2\nu\nu'\cos(\theta) + (\nu')^2\cos^2(\theta) + (\nu')^2\sin^2(\theta)\right) = h^2(\nu - \nu')^2 + 2h^2\nu\nu'(1 - \cos(\theta)) = \left(h(\nu - \nu') + m_ec^2\right)^2 - m_e^2c^4 = h^2(\nu - \nu')^2 + 2h(\nu - \nu')m_ec^2$. Further $h\nu\nu'(1 - \cos(\theta)) = (\nu - \nu')m_ec^2 \Rightarrow \Delta\nu = \frac{h\nu\nu'}{m_ec^2}(1 - \cos(\theta))$. Therefore: $\Delta\lambda = \frac{c\Delta\nu}{\nu\nu'} = \lambda_c(1 - \cos(\theta))$ with $\lambda_c = \frac{h}{m_ec}$ the so called **Compton wavelength**.

4.2 Matter Waves

De Broglie Wavelength $\lambda_{dB} = h/p = \frac{h}{\sqrt{2m_eE_{kin}}}$ with p the momentum of the massiv particle. Equivalent: $p = \hbar k_{dB}$. Constructive interference: $d\sin(\phi) = n\lambda_{dB}$ with d the distance between atoms, n the order of the maximum and ϕ the deflection angle.
$\langle E_{kin}\rangle = \frac{p^2}{2m} = \frac{3}{2}k_BT \Rightarrow \lambda_{dB} = \frac{h}{\sqrt{3mk_BT}}$

5 Quantum Mechanics

Heisenberg Uncertainty Principle $\Delta p_x\Delta x \geq \frac{\hbar}{2}$

5.1 Operators

Observables: observable property of a system. Observables are represented by **operators**. Suppose we have a wavefunction $\psi(x,t) = Ae^{i(kx-\omega t)}$ with $p = \hbar k$ and $E = \hbar\omega$. The **Eigenstate** is the physical state represented by the eigenfunction.

Position Oberator: $\hat{x} = x$ or $-i\hbar\frac{\partial}{\partial p}$

Momentum operator: $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ of p

Energy operator: $\hat{E} = i\hbar\frac{\partial}{\partial t}$

5.2 Operator Representation

Momentum Basis We can write wave functions $\psi(x,t)$ in the momentum basis $\phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}$ with the following relation. $\tilde{\psi}(p,t) = \frac{1}{\sqrt{2\pi\hbar}}\int\psi(x,t)e^{-ipx/\hbar}dx$. Backtransformation: $\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int\psi(p,t)e^{ipx/\hbar}dp$.

5.3 Hilbert Space and Dirac Notation

Identity operator: For a discrete basis: $\hat{I} = \sum_n|\phi_n\rangle\langle\phi_n|$, for a continuous basis: $\int|\phi(\alpha)\rangle\langle\phi(\alpha)|d\alpha = 1$. For continuous basis: $\langle\phi(\alpha)|\phi(\beta)\rangle = \delta(\alpha - \beta)$.

5.4 Quantum Measurements

If we make a measurement of the observable, we will get one eigenvalue as a result. For a discrete basis, the probability of getting the result o_n is $|\langle o_n|\psi\rangle|^2 = |c_n|^2$. After getting this result, the state of the system becomes $|o_n\rangle$. This is also called **collapse** of **projection** of $|\psi\rangle$ into $|o_n\rangle$. For a continuous basis, the probability of getting a result between $o(\alpha)$ and $o(\alpha + d\alpha)$ is $|\langle o(\alpha)|\psi\rangle|^2 d\alpha = |\psi(\alpha,t)|^2 d\alpha$

5.5 Operator Commutation

If two different operators share the same eigenstate, then particles in those states have simultanously definite values for both of those observables. Suppose we have two observables that share the same eigenstate ψ, then $\hat{O}\psi = O\psi$ and $\hat{Q}\psi = Q\psi$ with O and Q the corresponding eigenvalues. We define the **commutator** $\left[\hat{Q},\hat{O}\right] \equiv \hat{Q}\hat{O} - \hat{O}\hat{Q}$. *Two observable operators can share the same eigenstates if and only if* $\left[\hat{Q},\hat{O}\right] = \left[\hat{O},\hat{Q}\right] = 0$. The **anticommutator** is defined as $\left\{\hat{O},\hat{Q}\right\} = \hat{O}\hat{Q} + \hat{Q}\hat{O}$

Identities $\left[\hat{A},c\right] = 0$, $\left[\hat{A},\hat{A}\right] = 0$, $\left[\hat{A},\hat{B}\right] = -\left[\hat{B},\hat{A}\right]$, $\left[\hat{A},\sum_n c_n\hat{A}^n\right] = 0$, $\left[c\hat{A},\hat{B}\right] = \left[\hat{A},c\hat{B}\right] = c\left[\hat{A},\hat{B}\right]$, $\left[\hat{A},\hat{B}\pm\hat{C}\right] = \left[\hat{A},\hat{B}\right] \pm \left[\hat{A},\hat{C}\right]$, $\left[\hat{A}\hat{B},\hat{C}\right] = \hat{A}\left[\hat{B},\hat{C}\right] + \left[\hat{A},\hat{C}\right]\hat{B}$, $\left[\hat{A},\hat{B}\hat{C}\right] = \hat{B}\left[\hat{A},\hat{C}\right] + \left[\hat{A},\hat{B}\right]\hat{C}$

Important commutators $[\hat{x},\hat{p}] = i\hbar$, in 3D: $[x_i,p_j] = i\hbar\delta_{ij}$ and $[x_i,x_j] = 0$

5.6 Measurement for degenerate observables

Degeneracy is the property that an observable operator has orthonormal eigenfunctions with the same eigenstate.
Suppose we have a wavefunction $\psi(x)$ that describes a quantum state. This wavefunction can be decomposed into a basis of orthonormal eigenfunctions $\phi_n(x)$ of an observables $\hat{O}$ each with eigenvalues O_n. $\psi(x) = \sum_n a_n\phi_n(x)$ where a_n are the coefficients of the expansion.

1. The probability of a measurement of $\hat{O}$ yielding a value O_m is $P(O_m) = \sum_j |a_j|^2$ where the sum runs over all values of j such that $O_m = O_j$.
2. Immediately after a measurement resulting in O_m, the wavefunction collapses to $\psi'(x) = \frac{\sum_j a_j \phi_j(x)}{\sqrt{\sum_j |a_j|^2}}$ where again the sum runs over all values of j such that $O_m = O_j$.

Expectation value The expectation value for an observable $\hat{O}$ for a state $|\psi\rangle$ is given by $\langle\hat{O}\rangle = \langle\psi|\hat{O}|\psi\rangle = \int \overline{\psi(x,t)}\hat{O}\psi(x,t)dx$

5.7 Schrödinger Equation in 1D

Full Schrödinger equation in one spatial dimension is

$$\hat{H}\psi(x,t) = \left(\frac{\hat{p}^2}{2m} + V(\hat{x})\right)\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t)$$

With $V(\hat{x})$ the potential energy and $\hat{H}$ the hamilton operator. The time-indepentent Schrödinger equation is

$$\hat{H}\phi_E(x) = E\phi_E(x)$$

This is just the eigenvalue equation of $\hat{H}$. If $\psi(x,0) = \phi_E(x)$, then we have the following solution to the full Schrödinger equation.

$$\psi(x,t) = e^{-i\frac{E}{\hbar}t}\phi_E(x)$$

For a system in arbitrary initial states, we can always express that initial state as a superposition of energy eigenstates. We can solve the S.E. for each of them separately and so we obtain a formula for the evolution of an arbitrary state.

$$\psi(x,t) = \sum_n c_n e^{-i\frac{E_n}{\hbar}t}\phi_n(x)$$

Phase velocity $v = \frac{\omega}{k}$ velocity at which the phasefronts move.

Group velocity $v_{group} = \frac{d\omega}{dk}$ velocity of the envelope of the wavepackets.

5.8 Examples

5.8.1 Free particle in 1-D

$V(\hat{x}) = 0$, result: $\psi_E(x,t) = Ae^{i(kx-\frac{E}{\hbar}t)} + Be^{-i(kx+\frac{E}{\hbar}t)}$ with $k = \sqrt{\frac{2mE}{\hbar^2}}$

5.8.2 1-D infinite square well

$V = \begin{cases} 0 & 0 \le x \le a \\ \infty & \text{elsewhere} \end{cases}$, result: $\psi(x) = A\cos(kx) + B\sin(kx)$ with $k = \sqrt{\frac{2mE}{\hbar^2}}$

Continuity conditions on the wavefunction

1. The wavefunction $\psi(x)$ is a continuous function of x.
2. The derivative $\frac{d\psi}{dx}$ is also continuous, exept where the potential is infinite.

With the first condition we obtain for ψ between $0 \le x \le a$: $\psi(x) = \sqrt{\frac{2}{a}}\sin(k_n a)$ with $k_n = \frac{n\pi}{a}$ and $n \in \mathbb{N}$. Thus $E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}$
If we shift the coordinate system to $y = x - \frac{a}{2}$ such that it is centered at $y = 0$, we obtain

$$\psi_n(y) = \sqrt{\frac{2}{a}}\begin{cases}\cos\left(\frac{n\pi}{a}y\right) & \text{for } n = 1,3,5,\dots \text{ called } \textit{even functions} \\ -\sin\left(\frac{n\pi}{a}\right) & \text{for } n = 2,4,6,\dots \text{ called } \textit{odd functions}\end{cases}$$

Symmetry Here, in shifted hamiltonian $V(-y) = V(y)$ and kinetic energy also does not change. Define **parity operator** $\hat{\Pi}$: $\hat{\Pi}\psi(y) = \psi(-y)$. The parity operator commutes with the hamiltonian, thus $\hat{H}$ and $\hat{\Pi}$ must share a set of orthogonal eigenfunctions ϕ_π. The eigenvalues of $\hat{\Pi}$ are −1 and 1. The eigenvalues +1 corresponds to **even functions**, and the eigenvalue −1 corresponds to **odd functions**. Hence, since $\hat{H}$ and Π commute, the eigenfunctions of $\hat{H}$ can be broken up into two groups: one group with **odd parity** and one with **even parity**.

5.8.3 1-D finite square well

$V(x) = \begin{cases} 0 & |x| \le a/2 \\ V_0 & \text{elsewhere} \end{cases}$, we are looking for solutions with even parity. We can split the domain up into three regions:

Region I: $x < -a/2$, solution: $A_I e^{-\sqrt{k_0^2-k^2}x} + B_I e^{\sqrt{k_0^2-k^2}x}$ with $k_0 = \sqrt{\frac{2mV_0}{\hbar^2}}$ and $k = \sqrt{\frac{2mE}{\hbar^2}}$

Region II: $-a/2 \le x \le a/2$, solution: $A_{II}\cos(kx) + B_{II}\sin(kx)$ with the same k as above.

Region III: $x > a/2$, solution: $A_{III}e^{-\sqrt{k_0^2-k^2}x} + B_{III}e^{\sqrt{k_0^2-k^2}x}$

Different solution possibilities:

1. $E < V_0$
   (a) Even solutions: We must have $B_{II} = A_I = B_{III} = 0$ and $B_I = A_{III}$. Further restriction: $\tan(ka/2) = \frac{\sqrt{k_0^2-k^2}}{k}$. Find A_{II} by $\int_{-\infty}^{\infty}|\psi_E(x)|^2\,dx = 1$.
   (b) Odd solution We must have $A_{II} = 0$, $A_I = -B_{III}$ and $A_{III} = -B_I$. Further condition: $-\cot(ka/2) = \frac{\sqrt{k_0^2-k^2}}{k}$
2. $E > V_0$ In this case $\sqrt{k_0^2-k^2}$ is imaginary. For even parity we have the following conditions.

$$A_I e^{i\sqrt{k^2-k_0^2}a/2} + B_I e^{-i\sqrt{k^2-k_0^2}a/2} = A_{II}\cos(ka/2)$$
$$-iA_I\sqrt{k^2-k_0^2}e^{i\sqrt{k^2-k_0^2}a/2} + iB_I\sqrt{k^2-k_0^2}e^{-i\sqrt{k^2-k_0^2}a/2} = -A_{II}k\cos(ka/2)$$

   For $E > V_0$ there are no restrictions on the allowed energies! These wavefunctions are not normalizable. They are called **unbounded states**.

In fact, bound states (for which $E < V$ at $x = \pm\infty$) we have discrete energy eigenvalues. Unbound states have continuous energy eigenvalues.

5.8.4 Tunneling

$V(x) = \begin{cases} V_0 & 0 \le x \le a \\ 0 & \text{elsewhere} \end{cases}$ With $k = \sqrt{\frac{2mE}{\hbar^2}}$, $k_0 = \sqrt{\frac{2mV_0}{\hbar^2}}$ and $k' = \sqrt{k^2-k_0^2}$ wo obtain: $\phi_E = \begin{cases} A_I e^{ikx} + B_I e^{-ikx} & x < 0 \\ A_{II}e^{ik'x} + B_{II}e^{-ik'x} & 0 \le x \le a \\ A_{III}e^{ikx} + B_{III}e^{-ikx} & x > a \end{cases}$

And $\phi_E(x,t) = \phi_E(x)e^{-i\frac{E}{\hbar}t}$. Further conditions

$$A_I + B_I = A_{II} + B_{II}$$
$$A_{II}e^{ik'a} + B_{II}e^{-ik'a} = A_{III}e^{ika}$$
$$A_I k - B_I k = A_{II}k' - B_{II}k'$$
$$A_{II}k'e^{ik'a} - B_{II}k'e^{-ik'a} = A_{III}ke^{ika}$$

The transmission coefficient is $T = \left|\frac{A_{III}}{A_I}\right|^2$. In the case $E \ll V_0$ there is a non-zero probability that a particle goes through the wall.

5.8.5 Potential step

$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x > 0 \end{cases}$, General solution: Region I: $\psi(x) = A_I e^{ikx} + B_I e^{-ikx}$, Region II: $\psi(x) = A_{II} e^{\sqrt{k_0^2 - k^2}x} + B_{II} e^{-\sqrt{k_0^2 - k^2}x}$, with $k = \sqrt{\frac{2mE}{\hbar^2}}$ and $k = \sqrt{\frac{2mV_0}{\hbar^2}}$

1. $\underline{E > V_0}$: Conditions: $B_{II} = 0$ and $ikA_I - ikB_I = i\sqrt{k^2 - k_0^2}$ yield: $A_{II} = \frac{2k}{k+\sqrt{k^2-k_0^2}} A_I$ and $B_I = \frac{k-\sqrt{k^2-k_0^2}}{k+\sqrt{k^2-k_0^2}} A_I$. Thus the reflection coefficient is $|r|^2 = \left|\frac{B_I}{A_I}\right|^2$ and the transmission coefficient is $|t|^2 = \left|\frac{A_{II}}{A_I}\right|^2$
2. $\underline{E < V_0}$: Conditions: $A_{II} = 0$, $A_I + B_I = B_{II}$ and $ikA_I - ikB_I = -\sqrt{k_0^2 - k^2} B_{II}$. Thus: $B_I = -\frac{\sqrt{k_0^2-k^2}+ik}{\sqrt{k_0^2-k^2}-ik} A_I$ and $B_{II} = -\frac{2ik}{\sqrt{k_0^2-k^2}-ik} A_I$

As we can see, there is a non-zero probability to find the particle at $x > 0$.

5.8.6 Harmonic Oscillator

$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2$. The **resonance frequency** is $\omega = \sqrt{k/m}$. Hence $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$. Introduce $\hat{X} = \sqrt{\frac{m\omega}{\hbar}}\hat{x}$ and $\hat{P} = \sqrt{\frac{1}{\hbar m\omega}}\hat{p}$. Now: $\hat{H} = \frac{\hbar\omega}{2}\left(\hat{X}^2 + \hat{P}^2\right)$. If we factor this out: $\hat{H} = \frac{\hbar\omega}{2}\left(\hat{X}^2 + i\hat{X}\hat{P} - i\hat{P}\hat{X} + \hat{P}^2 - i\left(\hat{X}\hat{P} - \hat{P}\hat{X}\right)\right)$ with $-i\left(\hat{X}\hat{P} - \hat{P}\hat{X}\right) = 1$. Further define: $\hat{a} \equiv \frac{1}{\sqrt{2}}\left(\hat{X} + i\hat{P}\right)$ and $\hat{a}^\dagger \equiv \frac{1}{\sqrt{2}}\left(\hat{X} - i\hat{P}\right)$. Thus: $\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$. Important property: $\left[\hat{a}, \hat{a}^\dagger\right] = 1$. In conclusion: $c_{n-}\hat{a}|n\rangle = |n-1\rangle$ and $c_{n+}\hat{a}^\dagger|n\rangle = |n+1\rangle$. The energies of the eigenstates $|n\rangle$ are $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ and the eigenvalues of $\hat{a}^\dagger\hat{a}$ are $n = 0, 1, 2, \ldots$

Ground states $|0\rangle$ is a ground state because it has the lowest energy. For $\psi_0(x) = \langle x|0\rangle$ it has to be true that $\hat{a}\psi_0(x) = 0$. Thus we obtain: $\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}$

Excited state eigenfunctions Obtain by applying $\hat{a}^\dagger$. We find $c_{n+} = \frac{1}{\sqrt{n+1}}$ and $c_{n-} = \frac{1}{\sqrt{n}}$. Therefore: $\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$ and $\hat{a}|n\rangle = \sqrt{n}|n-1\rangle$. So in general we obtain: $\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(X) e^{-X^2/2}$ with $X = \sqrt{\frac{m\omega}{\hbar}}x$ and $H_n(X)$ are the Hermite polynomials. $\left[\hat{a}^\dagger\hat{a}, \hat{a}^\dagger\right] = \hat{a}^\dagger$, $\left[\hat{a}^\dagger\hat{a}, a\right] = -a$.

Expectation value of the harmonic oscillator We can redefine the position and momentum operators: $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}^\dagger + \hat{a})$ and $\hat{p} = i\sqrt{\frac{m\omega\hbar}{2}}(\hat{a}^\dagger - \hat{a})$. Since the eigenstates of $\hat{a}$ and $\hat{a}^\dagger$ are orthogonal, we obtain: $\langle\hat{x}\rangle = \langle n|\hat{x}|n\rangle = 0$, $\langle\hat{x}^2\rangle = \langle n|\hat{x}^2|n\rangle = \frac{\hbar}{2m\omega}(2n+1)$ and $\langle\hat{p}\rangle = \langle n|\hat{p}|n\rangle = 0$, $\langle\hat{p}^2\rangle = \langle n|\hat{p}^2|n\rangle = \frac{\hbar m\omega}{2}(2n+1)$. Further: $\Delta x = \sqrt{\langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2} = \sqrt{\frac{\hbar}{2m\omega}}\sqrt{2n+1}$ and $\Delta p = \sqrt{\langle\hat{p^2}\rangle - \langle\hat{p}\rangle^2} = \sqrt{\frac{\hbar m\omega}{2}}\sqrt{2n+1}$ Thus: $\Delta x \Delta p = \frac{\hbar}{2}(2n+1)$

Coherent states Ground state is not the only minimum uncertainty state. A coherent state is a superposition of eigenstates of the Hamiltonian. At time $t = 0$: $\psi_\alpha = |\alpha\rangle = e^{-|\alpha|^2/2}\sum_n^\infty \frac{\alpha^n}{\sqrt{n!}}\phi_n(x) = \sum_n^\infty \frac{\alpha^n}{\sqrt{n!}}|n\rangle$ with $\alpha = |\alpha|e^{i\phi}$. We can find: $\langle\hat{x}\rangle = \langle\alpha|\hat{x}|\alpha\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\alpha e^{i\omega t} + \overline{\alpha}e^{-i\omega t}\right) = \sqrt{\frac{2\hbar}{m\omega}}|\alpha|\cos(\omega t + \phi)$

5.9 Schrödinger Equation in 3D

$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$ with $\hat{H} = \frac{1}{2m}\left|\hat{\vec{p}}\right|^2 + V(\hat{\vec{r}})$ where $\hat{\vec{r}} = (\hat{x}, \hat{y}, \hat{z})$ and $\hat{\vec{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$. In the position representation: $\hat{p} = -i\hbar\nabla$. So the Schrödinger equation becomes: $i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$.

Operator commutation All operators for different cartesian coordinates commute. $[\hat{x}, \hat{p}_y] = [\hat{x}, \hat{p}_z] = 0$. <u>But</u>: $[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar$.

5.10 Symmetry

Tranformations of wavefunctions and operators in space Take wavefunction $\psi(\vec{r})$. If we act a transformation on it, we get a new wavefunction $\psi'(\vec{r})$. This transformation can be represented with an operator $\hat{Q}$: $\psi' = \hat{Q}\psi$. So if we have an operator $\hat{O}$ in the ψ basis, we can transform it into the ψ' basis: $\hat{O}' = \hat{Q}^\dagger\hat{O}\hat{Q}$.

Parity operator in $3D$ $\hat{\Pi}\psi(\vec{r}) = \psi'(\vec{r}) = \psi(-\vec{r})$. Cartesian coordinates: $\hat{\Pi}\psi(x, y, z) = \psi(-x, -y, -z)$, spherical coordinates: $\hat{\Pi}\psi(r, \theta, \phi) = \psi(r, \pi - \theta, \phi + \pi)$. Position operator: $\hat{x}' = -\hat{x}$, $\hat{y}' = -\hat{y}$, $\hat{z}' = -\hat{z}$. $\hat{\vec{r}}' = -\hat{\vec{r}}$. $\hat{\vec{p}}' = -\hat{\vec{p}}$. $\hat{\vec{L}}' = -\hat{\vec{L}}$. Thus: $\left[\hat{\Pi}, \hat{\vec{L}}\right] = 0$ and $\left[\hat{\Pi}, \hat{L}_x\right] = 0\left[\hat{\Pi}, \hat{L}_y\right] = \left[\hat{\Pi}, \hat{L}_z\right] = 0$. For spherical harmonics: $\hat{\Pi}Y_{lm} = (-1)^l Y_{lm}$

Rotation operator A rotation about the z-axis by an angle φ in position representation: $\hat{R}_z(\delta)1 - \delta\frac{\partial}{\partial\phi} = 1 - \frac{i\delta}{\hbar}\hat{L}_z$. Rotation about an arbitrary axis $\hat{n}$ is given by $\hat{R}_{\hat{n}}(\varphi) = e^{-\frac{i\varphi}{\hbar}\hat{n}\cdot\vec{L}}$

Selection rules Suppose $\hat{\Pi}^\dagger V(x)\hat{\Pi} = V(x)$, then $\left[V, \hat{\Pi}\right] = 0$ and $\left[\hat{H}, \hat{\Pi}\right] = 0$. Then the non-degenerate eigenstates $|\psi_n\rangle$ of $\hat{H}$ satisfy $\hat{\Pi}|\psi_n\rangle = \pm|\psi_n\rangle$. If $H_{i,f}(t) = \langle\phi_i|\hat{H}(t)|\phi_f\rangle = \int\phi_i(\vec{r})\hat{H}(t, \vec{r})\phi_f(\vec{r})d^3r = 0$, then the transition isn't allowed. If the integrand is odd under parity, the integral is is zero. **First selection rule**: $\langle\psi_{n'l'm'}|\hat{\vec{r}}|\psi_{nlm}\rangle = 0$ if $l + l'$ is even. $[L_z, z] = 0$, $[L_z, y] = -i\hbar x$, $[L_z, x] = i\hbar$, $[L_z, x + iy] = \hbar(x + iy)$, $[L_z, x - iy] = -\hbar(x - iy)$ Thus, selection rule will depend on polatization of light. $l' - l = \pm 1$ has to be fulfilled.

Linearly polarized light in the z direction For linearly polarized light along the z direction, transitions cannot happen unless the m quantum numbers of the initial and final state are the same.

Circularly polarized light in the plane perpendicular to the z direction For circularly polarized light, transitions are forbidden unless they are between states that defer by 1 in their m quantum number.

5.11 quantum statistical Physics

N particles with total energy E. Collection of single-particle states. g_j of these have energy ε_j. What are the number of atoms n_j with energy ε_j? If we have g_j states with the same energy, $n_j = g_j \cdot N \cdot P_j = g_j N\frac{e^{-\beta\varepsilon_j}}{Z}$. How many ways are there to put n_1 particles into g_1 states and n_2 particles into g_2 states, etc? If the number of ways to put n_j particles into g_j states is $\omega_j(n_j)$, then we have: $\Omega_{\{n_j\}} = \prod_j \omega_j(n_j)$

Fermions Each of the g_j states can only accomodate one particle. So: $\omega_j(n_j) = \frac{g_j!}{n_j!(g_j-n_j)!}$. Important: particles are indistinguishable but the states are distinguishable. So: $\Omega_{\{n_j\}} = \prod_j \frac{g_j!}{n_j!(g_j-n_j)!}$. Assume $n_j, g_j, g_j - n_j \gg 1$, then: $\ln\Omega_{\{n_j\}} = \sum_j [\ln(g_j!) - \ln(n_j!) - \ln((g_j-n_j)!)] \approx \sum_j [g_j\ln(g_j) - n_j\ln(n_j) - (g_j-n_j)\ln(g_j-n_j)]$. Constraints: $\sum_j n_j = N$ and $\sum_j n_j\varepsilon_j = E$. With lagrange multipliers we obtain: $n_j = \frac{g_j}{e^{\beta(\varepsilon_j-\mu)}+1}$ with $\beta = \frac{1}{k_B T}$ and μ the **chemical potential**. n_j is called **Fermi-Dirac Distribution**. $\mu(T=0)$ is the **Fermi energy**.

Bosons How many ways are there to devie n_j identical particles into g_j bins. $\omega_j(n_j) = \frac{(n_j+g_j-1)!}{n_j!(g_j-1)!}$, $\Omega_{\{n_j\}} = \prod_j \frac{(n_j+g_j-1)!}{n_j!(g_j-1)!}$, hence $n_j = \frac{g_j-1}{e^{\beta(\varepsilon_j-\mu)}-1} \approx \frac{g_j}{e^{\beta(\varepsilon_j-\mu)}-1}$ since we assumed $g_j \gg 1$.

Average energy in a mode with frequency ω $\langle\varepsilon\rangle = \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$, so the number of photons in that mode is just $n = \frac{\langle\varepsilon\rangle}{\hbar\omega} = \frac{1}{e^{\beta\hbar\omega}-1}$

Bose-Einstein Distribution $n_\omega = \frac{V\omega^2}{\pi^2c^3}\frac{d\omega}{e^{\beta\hbar\omega}-1} = \frac{\rho(\omega)d\omega}{\hbar\omega}\cdot V$

Classical limit $n_j \ll g_j$: $n_j \approx \frac{g_j}{e^{\beta(\varepsilon_j-\mu)}}$ With this, we already lost the information wheter it is a fermion or a boson. $N = \sum_j n_j \approx \sum_j \frac{g_j}{e^{\beta(\varepsilon_j-\mu)}} \Rightarrow \frac{1}{e^{-\beta\mu}} = \frac{N}{\sum_j g_j e^{-\beta\varepsilon_j}} = \frac{N}{Z} \Rightarrow n_j = N g_j \frac{e^{-\beta\varepsilon_j}}{Z}$ which agrees with the classical result.

6 Hydrogen

6.1 Hydrogen atom Schrödinger Equation

First few spherical harmonics:

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \;,\; Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos(\theta) \;,\; Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin(\theta)e^{\pm i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}\left(3\cos^2(\theta)-1\right) \;,\; Y_2^{\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin(\theta)\cos(\theta)e^{\pm i\phi}$$

$$Y_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2(\theta)e^{\pm 2i\phi}$$

First few radial solutions:

$$R_{10}(r) = 2\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0} \;,\; R_{20}(r) = 2\left(\frac{1}{2a_0}\right)^{3/2}\left(1-\frac{r}{2a_0}\right)e^{-r/(2a_0)}$$

$$R_{21}(r) = \frac{2}{\sqrt{3}}\left(\frac{1}{2a_0}\right)^{3/2}\left(\frac{r}{2a_0}\right)e^{-r/(2a_0)}$$

Energy $E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}$. With $E_1 = -13.6\text{eV} = -R_e$ the ground state energy.

Bohr radius $\kappa = \left(\frac{m_e e^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an}$ with $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ the Bohr radius.

Full spatial wavefunction $\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$ where n,l,m are **quantum numbers**. n is called **principle quantum number**. Energy only depends on n. $l = 0,1,2,\ldots,n-1$ and $m = -l,-l+1,\ldots,0,\ldots,l-1,l$. Number of degenerate eigenstates: n^2. n is the orbital energy level, l the shape and m the number of spatial orientations that the orbital can assume. The larger n is, the larger is E_n (because of the negative sign).

6.2 Angular Momentum

$\vec{L} = \vec{x}\times\vec{p}$, $[L_x,L_y] = i\hbar L_z$, $[L_y,L_z] = i\hbar L_x$, $[L_z,L_y] = i\hbar = L_y$, $\left[L^2,L_x\right] = 0$, $\left[L^2,L_y\right] = 0$, $\left[L^2,L_z\right] = 0$, $L^2|l,m\rangle = \hbar^2 l(l+1)|l,m\rangle$, $L_z|l,m\rangle = \hbar m|l,m\rangle$. Construct new operator: $L_\pm \equiv L_x \pm iL_y$ for which: $[L_z,L_\pm] = \pm\hbar L_\pm$ and $\left[L^2,L_\pm\right] = 0$. In general: $L_\pm|l,m\rangle = A^m_{l,\pm}|l,m\pm1\rangle$ with $A^m_{l,\pm} = \hbar\sqrt{l(l+1)-m(m\pm1)}$. Due to causality constraints we find $m_{max} = \mu$ s.t. $L_+|l,\mu\rangle = 0$ and $m_{min} = \mu'$ s.t. $L_-|l,\mu'\rangle = 0$. Also: $L_\pm L_\mp = L^2 - L_z^2 \pm \hbar L_z$ and $L^2|l,\mu\rangle = \hbar^2\mu(\mu+1)|l,\mu\rangle$ so we find $\mu = l$ and $\mu' = -l$. Possible values for l and m: $l = 0,\frac{1}{2},1,\frac{3}{2},2,\ldots$ and $m = -l,-l+1,\ldots,l-1,l$. In position representation we define the **angular momentum operator** $\vec{L} = -i\hbar(\vec{r}\times\vec{\nabla})$ where $\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{\phi}\frac{1}{r\sin(\theta)}\frac{\partial}{\partial\phi}$ Hamiltonian can be rewritten as $H = \frac{1}{2mr^2}\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + L^2\right] + V$ Thus: $H\psi = E\psi$, $L^2\psi = \hbar^2 l(l+1)\psi$, $L_z\psi = \hbar m\psi$.

6.3 Time-independent Perturbation Theory

Write Hamiltonian as $\hat{H} = \hat{H}_0 + \delta\hat{H}$ where $\hat{H}_0$ can be solved exactly and $\delta\hat{H}$ is a small perturbation, meaning: If $|\psi_n^0\rangle$ is an eigenstate of $\hat{H}_0$ s.t. $\hat{H}_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$, then the time independent S.E. can be written as $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ wher $E_n = E_n^0 + \delta E_n$, $|\delta E_n| \ll E_n^0 \;\forall n$ and $|\psi_n\rangle = |\psi_n^0\rangle + |\delta\psi_n\rangle$, $|\delta\psi_n| \ll \left|\psi_n^0\right|$. Hence $\hat{H}_0|\delta\psi_n\rangle + \delta\hat{H}|\psi_n^0\rangle = E_n^0|\delta\psi_n\rangle + \delta E_n|\psi_n^0\rangle$. Since $\left\{|\psi_n^0\rangle\right\}$ is a complete basis we can write $|\delta\psi_n\rangle = \sum_l c_l|\psi_l^0\rangle$. Thus $E_m^0 + \langle\psi_m^0|\delta\hat{H}|\psi_n^0\rangle = E_n^0 c_m + \delta E_n\langle\psi_n^0|\psi_m^0\rangle$.

If $n = m$: $\langle\psi_n^0|\delta H|\psi_n^0\rangle = \delta E_n$. This means, the correction to the energy of the eigenstate caused by the perturbation is just the expectation value of $\delta\hat{H}$ for the original eigenstate.

if $n \neq m$: $\langle\psi_m^0|\delta\hat{H}|\psi_n^0\rangle = c_m(E_n^0 - E_m^0) \;\Rightarrow\; c_m = \frac{\langle\psi_m^0|\delta\hat{H}|\psi_n^0\rangle}{E_n^0-E_m^0}$ With these coefficients we can then write $|\delta\psi_n\rangle$. Problem if $E_n^0 = E_m^0$. Could be if there is degeneracy.

6.4 Degenerate Perturbation Theory

The above problem can be resolved if $\langle\psi_m^0|\delta\hat{H}|\psi_n^0\rangle = 0$ The case if $|\psi_n^0\rangle$ and $|\psi_m^0\rangle$ were also eigenstates of $\delta\hat{H}$. Then: $\delta\hat{H}|\psi_n^0\rangle = \delta E_n|\psi_n^0\rangle$ and $\delta\hat{H}|\psi_m^0\rangle = \delta E_m|\psi_m^0\rangle$. This means, perturbed eigenstates $|\psi_n\rangle$ and $|\psi_m\rangle$ are just $|\psi_n^0\rangle$ and $|\psi_m^0\rangle$. If we have a set of N degenerate eigenstates $\left\{|\psi_{kl}^0\rangle\right\}$ of $\hat{H}_0$ with eigenenergy E_k^0, then any linear combination of these states is also an eigenstate of $\hat{H}_0$ with energy E_k. That means, $\left\{|\psi_{kl}^0\rangle\right\}$ forms a basis for a so called **N-dimensional degenerate subspace**. $\hat{p}^2 = 2m(\hat{H}_0 - \hat{V})$

6.5 Time-depentent Perturbation Theory

Suppose we can write $\hat{H} = \hat{H}_0 + \hat{H}_1(t)$ with $\hat{H}_0$ a time-independent Hamiltonian, and $\hat{H}_1(t)$ is a time-dependent perturbation. If $\hat{H}_1(t) = 0$, then $|\psi(t)\rangle = \sum_n c_n e^{-i\omega_n t}|\phi_n\rangle$ with $\omega_n = \frac{E_n}{\hbar}$ and $\{|\phi_n\rangle\}$ energy eigenstates. If $\hat{H}_1(t) \neq 0$, then $|\psi(t)\rangle = \sum_n c_n(t)e^{-i\omega_n t}|\phi_n\rangle$, such that $\frac{\partial c_m}{\partial t} = \frac{1}{i\hbar}\sum_n c_n e^{-i(\omega_n-\omega_m)t}\langle\phi_m|\hat{H}_1(t)|\phi_n\rangle$. The system cannot transition from the state j to the state n if $\langle\phi_j|H|\phi_m\rangle = 0$.
Suppose an atom encounters an electromagnetic wave. The electric field of the wave has a sinusiodal time dependence, while the atom has an electric dipole moment $\vec{p}_0$: $\vec{E} = E_0\cos(\omega t)\hat{k}$ and $\vec{p}_0 = -e\vec{r}$. Then: $\hat{H}_1(t) = -\vec{p}_0\cdot\vec{E} = eE_0\hat{\vec{r}}\cdot\hat{k}\cos(\omega t)$
If an atom starts in the state $|\phi_a\rangle$, the probability that it ends up in the state $|\phi_b\rangle$ at time t is: $P_{a\to b}(t) = |c_b(t)|^2 \approx \frac{|V_{ab}|^2}{\hbar^2}\left(\frac{t}{2}\right)^2\text{sinc}^2\left[(\omega_0-\omega)\frac{t}{2}\right]$ with $V_{ab} = \langle\phi_a|eE_0\vec{r}\cdot\hat{k}|\phi_b\rangle$ and $\omega_0 = \omega_a - \omega_b$

6.6 Zeeman Effect

$\vec{\mu}_p = \frac{g_p e}{2m_p}\vec{s}_p \ll \vec{\mu} = \frac{g_s e}{2m_e}\vec{s}$. The perturbed hamiltonian is: $\delta\hat{H} = -\vec{\mu}\cdot\vec{B}$. If the magnetic field points along the z-axis: $\delta\hat{H} = \frac{g_s eB}{2m_e}\hat{s}_z$. Spin eigenstates $|\frac{1}{2}, \pm\frac{1}{2}\rangle$ are the eigenstates of s_z, so: $\delta E_+ = \frac{g_s e\hbar B}{4m_e}$ and $\delta E_- = \frac{g_s e\hbar B}{4m_e} = -\frac{g_s}{2}\mu_B B$. In general: For any particle with magnetic moment $\vec{\mu} = g_j\frac{\mu_B}{\hbar}\vec{J}$ where $\vec{J}$ is the angular momentum operator, the energy shift is given by $\delta E = \mu_B g_j m_j B$.
For a magnetic field along the x-direction: $\delta\hat{H}_{zm} = \frac{g_s eB}{2m_e}\hat{s}_x$. Use eigenstates of $\hat{s}_x$ to calculate δE. $(|+\rangle = \frac{1}{\sqrt{2}}(1,1)$ and $|-\rangle = \frac{1}{\sqrt{2}}(1,-1))$ $\delta E_+ = \frac{g_s}{2}\mu_B B$ and $\delta E_- = -\frac{g_s}{2}\mu_B B$.

6.7 Dipole allowed transitions

- $\Delta l = \pm 1$ and $\Delta m = 0$ for linearly (π) polarized light.
- $\Delta l = \pm 1$ and $\Delta m = +1$ for right handed (σ^+) circularly polarized light.
- $\Delta l = \pm 1$ and $\Delta m = -1$ for left handed (σ^-) circularly polarized light.

6.8 Hyperfine splitting in Hydrogen

Magnetic moment of the hydrogen nucleus also generates a magnetic field which interacts with the electron spin. In classical electrodynamics, a magnetic moment $\vec{\mu}$ generates a magnetic field: $\vec{B}$ Hamiltonian of the electron: $\delta\hat{H}_{hf} = -\vec{\mu}\cdot\vec{B}$

7 Spin

Magnetic Moment $\vec{\mu} = \pi r^2 I\hat{n}$ with $\hat{n}$ the unit vector perpendicular to the plane. In Bohr model where the electron has a circular orbit $I = -e\frac{v}{2\pi r}$ thus $\vec{\mu} = -\frac{e}{2m_e}\vec{L}$. If an atom is placed into e homogeneous magnetic field along the z-direction, the force is given by $\vec{F} = -\vec{\nabla}(-\vec{\mu}\cdot\vec{B}) = \mu_z\frac{\partial B_z}{\partial z}\hat{z} \propto L_z\frac{\partial B_z}{\partial z}\hat{z}$

7.1 Spin Hypothesis

The spin is an intrinsic angular momentum of the electron. It is proportional to the magnetic moment. The spin is represented by a vector operator $\hat{\vec{s}} = \begin{pmatrix}\hat{s}_x & \hat{s}_y & \hat{s}_z\end{pmatrix}^T$. Components obey commutation relations: $[\hat{s}_x, \hat{s}_y] = i\hbar\hat{s}_z$, $[\hat{s}_y, \hat{s}_z] = i\hbar\hat{s}_x$, $[\hat{s}_x, \hat{s}_z] = -i\hbar\hat{s}_y$ and $[\hat{s}^2, \hat{s}_z] = 0$. $S^2|s, m_s\rangle = \hbar^2 s(s+1)|s, m_s\rangle$ and $S_z|s, m_s\rangle = \hbar m|s, m_s\rangle$. $s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ and $m_s = -s, -s+1, \ldots, s-1, s$. Spin 1/2 particles have only two eigenstates with $m = \pm 1/2$. In that case, there are only two eigenstates which form a basis of $\mathbb{R}^2$. $|s = \frac{1}{2}, m_s = \frac{1}{2}\rangle = \begin{pmatrix}1\\0\end{pmatrix}$ and $|s = \frac{1}{2}, m_s = -\frac{1}{2}\rangle = \begin{pmatrix}0\\1\end{pmatrix}$ So a general state can be written as $|\psi\rangle = \alpha|\frac{1}{2}, \frac{1}{2}\rangle + \beta|\frac{1}{2}, -\frac{1}{2}\rangle = \begin{pmatrix}\alpha\\\beta\end{pmatrix}$ Operators can be defined as 2×2 matrices. E.g. $\hat{s}_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} = \frac{\hbar}{2}\sigma_z$, $\hat{s}_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix} = \frac{\hbar}{2}\sigma_x$, $\hat{s}_y = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\i & 0\end{pmatrix} = \frac{\hbar}{2}\sigma_y$

7.2 Magnetic moment of spin

Total magnetic dipole moment operator $\hat{\vec{\mu}}$ of an electron is the sum of orbital and spin contributions: $\hat{\vec{\mu}} = \hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s$ with $\hat{\vec{\mu}}_l = -\frac{e}{2m_e}\hat{L} = -\frac{\mu_B}{\hbar}\hat{L}$ where $\mu_B \equiv \frac{e\hbar}{2m_e}$ is a constant called the **Bohr magneton**. $\hat{\vec{\mu}} = -g_s\frac{\mu_B}{\hbar}\hat{\vec{s}}$ with g_s the **electron g-factor**, $g_s \approx 2$. The magnetic moment of the proton and neutron are given by $\mu_{p,n} = g_{p,n}\frac{\mu_k}{\hbar}\hat{\vec{s}}$ with $\mu_k = \frac{e\hbar}{2m_p} = \mu_B\cdot\frac{m_e}{m_p}$

7.3 Spin-Orbit coupling

Consider electron at rest and proton orbiting it. Then the current is given as $I = \frac{e\cdot v}{2\pi r} = \frac{e}{2\pi r^2 m_e}L$ $(L = |\vec{L}|)$. Using Biot-savart we obtain a magnetic field $\vec{B} = \frac{e}{8\pi\varepsilon_0 c^2 r^3 m_e}\vec{L}$.

Spin-orbit interaction $\vec{L}$ and $\vec{S}$ commute. $\left[\hat{L}^2, \vec{S}\cdot\vec{L}\right] = 0$ and $\left[\hat{S}^2, \vec{S}\cdot\vec{L}\right] = 0$ but $\left[\hat{L}_z, \vec{S}\cdot\vec{L}\right] = i\hbar\left(\hat{s}_x\hat{L}_y - \hat{s}_y\hat{L}_x\right) \neq 0$ and $\left[\hat{s}_z, \vec{s}\cdot\vec{L}\right] = i\hbar\left(\hat{s}_y\hat{L}_x - \hat{s}_x\hat{L}_y\right) \neq 0$. Goal: find eigenstates that commute with $\vec{S}\cdot\vec{L}$ and $\hat{H}$. Define $\hat{A} = \hat{L}_z + \hat{S}_z \equiv \hat{J}_z$. This commutes with both $\vec{S}\cdot\vec{L}$ and $\hat{H}$. The states $|\psi_{nlm}, m_s\rangle$ are eigenstates of $\hat{J}_z$ since $\hat{J}|\psi_{nlm}, m_s\rangle = (m + m_s)|\psi_{nlm}, m_s\rangle$. Define quantum number $m_j = m + m_s$. J^2 commutes with L^2, S^2 and $\vec{S}\cdot\vec{L}$. In fact: $J^2 = (\vec{L}+\vec{S})\cdot(\vec{L}+\vec{S}) = \hat{L}^2 + \hat{S}^2 + 2\vec{S}\vec{L} \Leftrightarrow \vec{S}\cdot\vec{L} = \frac{1}{2}\left(J^2 - L^2 - S^2\right)$. Thus, simultaneous eigenstates of J^2, L^2, S^2 and J_z are also the eigenstates of $\vec{S}\cdot\vec{L}$. Let's call these $|nlj, m_j\rangle$. $J^2|nljm_j\rangle = \hbar^2 j(j+1)|nljm_j\rangle$ and $\vec{S}\cdot\vec{L}|nljm_j\rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$. Allowed values of j: for $l = 0$: $j = s = \frac{1}{2}$ and for $l > 0$: $j = l \pm \frac{1}{2}$. Now we have 5 quantum numbers n, l, m, s, m_s where m and m_s correspond to L_z and S_z which no longer commute with hamiltonian after adding the spin-orbit coupling term proportional to $\vec{S}\cdot\vec{L}$. We replace these with new quantum numbers j and m_j, corresponding to J^2 and J_z which are conserved quantities. $\langle\vec{S}\cdot\vec{L}\rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$ Unperturbed energies are $E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}$. Define $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$. Then $E_n = -\frac{1}{2}m_e c^2\alpha^2\frac{1}{n^2} = \frac{E_1}{n^2}$. Thus: $E^1_{so} = -\frac{g_s}{4}\frac{\alpha^2}{n}E_n\left[\frac{j(j+1)-l(l+1)-s(s+1)}{l(l+1/2)(l+1)}\right]$. First order correction of the kinetic energy due to relativity: $E^1_{rel} = \frac{\alpha^2}{4n^2}E_n\left(\frac{4n}{l+1/2} - 3\right)$. The **fine structure correction** is $E^1_{fs} = \frac{\alpha^2}{n}E_n\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)$. In the end, **total energies of the hydrogen atom**: $E_{nj} = E_n\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right] \approx \frac{-13.66\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right]$

8 Multiple-electron atoms

8.1 Helium

Hamiltonian for a neutral atom with atomic number Z $\hat{H} = \sum_{j=1}^{Z}\left[-\frac{\hbar^2}{2m}\nabla_j^2 - \left(\frac{1}{4\pi\varepsilon_0}\right)\frac{Ze^2}{r_j}\right] + \frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\sum_{k\neq j}^{Z}\frac{e^2}{|\vec{r}_j - \vec{r}_k|}\right)$

Hydtogen like-atoms effective Bohr-radius: a/Z and energies become $Z^2 E_n$.

Complete spatial wavefunction of the helium atom $\psi(\vec{r}_1, \vec{r}_2) = \psi_{nlm}(\vec{r})\psi_{n'l'm'}(\vec{r}_2)$

Exchange operator $\hat{X}\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$, $\hat{X}$ has eigenvalues ± 1. Eigenstates with eigenvalue $+1$ are **symmetric** and eigenstates with eigenvalue -1 are **antisymmetric**.
Construct symmetric and anti-symmetric eigenstates: $\psi^{\pm}_{ab} = (\vec{r}_1, \vec{r}_2) = A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right]$ with $A = \begin{cases}\frac{1}{\sqrt{2}} & \text{for } a \neq b\\ \frac{1}{2} & \text{for } a = b\end{cases}$

8.2 Bosons and Fermions

Spin-statistics theorem Particles whose states are symmetric under exchange have integer spin values. They are called **bosons**. Particles whose states are antisymmetric under exchange have half-integer spin value. They are called **fermions**.

Pauli exclusion principle No two identical fermions can be simultaneously in the same single-particle state.

8.3 Many electron atoms

Central field approximation Write $\hat{H}$ as $\hat{H}_c + \hat{H}_{nc}$ with $\hat{H}_c$ the spherically symmetric part of $\hat{H}$ for each electron: $\hat{H}_c = \sum_{j=1}^{Z}\left[-\frac{\hbar^2}{2m}\nabla_j^2 + U(r_j)\right] = \sum_{j=1}^{Z}\hat{H}_{cj}$ with $U(r_j)$ the central potential that is identical for each electron. $\hat{H}_{nc}$ is the rest of the Hamiltonian: $\hat{H}_{nc} = \sum_{j=1}^{Z}\left[-\frac{Ze^2}{4\pi\varepsilon_0 r_j} - U(r_j)\right] + \frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\sum_{k\neq j}^{Z}\frac{e^2}{|\vec{r}_j - \vec{r}_k|}\right)$. We have $U(r\to 0) = \frac{-Ze^2}{4\pi\varepsilon_0 r}$ and $U(r\to\infty) = \frac{-e^2}{4\pi\varepsilon_0 r}$. Energy increases with l. A lower value of n gives a lower energy.

Electron Configurations The number of single electron states if given by $2(2l+1)$

Value of l	Letter symbol	Number of single electron states
0	s	2
1	p	6
2	d	10
3	f	14
4	g	18

Total Spin: $\hat{S} = \sum_{j=1}^{N}\hat{S}_j$ with eigenvalues $\hbar^2 S(S+1)$. Total angular momenta: $\hat{L} = \sum_{j=1}^{N}\hat{L}_j$ with eigenvalues $\hbar^1 L(L+1)$. In general, since states with different L and S quantum numbers can have different energies, it's also useful to specify what they are in the form of an additional label called a term symbol, which is written as ${}^{2S+1}L$.

L-S coupling Energy depends on the value of L and S.

Spin-orbit coupling Total angular momentum $\hat{L}$ couples to the total spin $\hat{S}$ to produce a perturbation Hamiltonian: $\hat{H}_{so} = \xi\vec{L}\cdot\vec{S}$ with ξ a constant. Perturbation requires us to work with total angular momentum $\vec{J} = \vec{L} + \vec{S}$. Eigenvalues of J^2 are $\hbar^2 J(J+1)$ and the eigenvalues of J_z are $\hbar M_j$. Term symbol can be modified to specify J: ${}^{2S+1}L_J$

9 Useful Tools

Important Physics Identities

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

Approximations

(i) When $|\varepsilon| \ll 1$, $(1+\varepsilon)^\alpha \approx 1 + \alpha\varepsilon$

(ii) Stirling's Theorem: For large x: $\ln(x!) \approx x\ln(x) - x$

(iii) $\sqrt{1+x} \approx 1 + \frac{x}{2} - \frac{x^2}{8} + \frac{x^3}{16} - \frac{5x^4}{128} + \dots$

(iv) $(1+x)^{-1} = 1 - x + x^2 - \dots$ for $|x| < 1$

(v) $1 - e^x = x$ for $x \to 0$

Trigonometry

$$\sin(x) = \sum_{n=0}^{\infty}(-1)^n\frac{x^{2n+1}}{(2n+1)!} \quad , \quad \cos(x) = \sum_{n=0}^{\infty}(-1)^n\frac{x^{2n}}{(2n)!}$$
$$c^2 = a^2 + b^2 - 2ab\cos(\gamma) \quad , \quad \sin(2x) = 2\sin(x)\cos(x)$$
$$\cos(2x) = \cos^2(x) - \sin^2(x) = 1 - 2\sin^2(x) = 2\cos^2(x) - 1$$

Laplacian (Spherical and polar)

$$\Delta\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2\psi}{\partial\phi^2}$$
$$\Delta\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\frac{\partial\psi}{\partial\phi^2} \quad (2D)$$
$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{n-1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Delta_{S^{n-1}} \quad (nD)$$

Fourier Transform $\alpha \in \mathbb{R}$

$$\mathcal{F}[f(t)] = \tilde{f}(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(t)e^{-i\omega t}\,dt$$
$$\mathcal{F}^{-1}\left[\tilde{f}(\omega)\right] = f(t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\tilde{f}(\omega)e^{i\omega t}\,dt$$
$$\mathcal{F}[f(t-t_0)] = \mathcal{F}[f(t)]\cdot e^{-i\omega t_0}$$
$$\mathcal{F}f(\alpha t) = \frac{1}{|\alpha|}\tilde{f}(\omega/\alpha)$$

Derivatives

$$\frac{d}{dx}\arcsin(x) = \frac{1}{\sqrt{1-x^2}}$$

Combinatorics

Arrangement
- All n elements distinguishable: $P = n!$
- $n_1, n_2, \dots$ of total n elements, indistinguishable: $P = \frac{n!}{n_1!n_2!\dots}$

Selection
- order does not matter
  - not chosen more than once: $N = \frac{n!}{r!(n-r)!} = \binom{n}{r}$
  - chosen repetedly: $N = \binom{n+r-1}{r}$
- order matters
  - not chosen more than once: $N = \frac{n!}{(n-r)!}$
  - chosen repetedly: $N = n^r$

Probability Distribution

$$P(k) \approx \int_{k-0.5}^{k+0.5}\frac{1}{\sqrt{2\pi N\sigma^2}}\exp\left(-\frac{(x-N\mu)^2}{2N\sigma^2}\right) \approx \frac{1}{\sqrt{2\pi N\sigma^2}}\exp\left(-\frac{(k-N\mu)^2}{2N\sigma^2}\right)$$

Integrals

$$\int_{-\infty}^{\infty}e^{-ax^2\pm bx)}\,dx = \sqrt{\frac{\pi}{a}}\exp\left(\frac{b^2}{4a}\right) \quad , \quad \int_{-\infty}^{\infty}e^{-ax^2}\,dx = \sqrt{\frac{\pi}{a}}$$
$$\int_{-\infty}^{\infty}x^2e^{-ax^2}\,dx = \sqrt{\frac{\pi}{4a^3}} \quad , \quad \int_{-\infty}^{\infty}xe^{-ax^2}\,dx = 0$$
$$\int_0^{\infty}xe^{-ax^2}\,dx = \frac{1}{2a} \quad , \quad \int_0^{\infty}x^3e^{-ax^2}\,dx = \frac{1}{2a^2}$$
$$\int_0^{\infty}x^ne^{-\alpha x}\,dx = n!\alpha^{-(n+1)} \quad , \quad \int_0^{\pi}\cos(\theta)\sin(\theta)\,d\theta = 0$$
$$\int_0^{\pi}\cos^2(\theta)\sin(\theta)\,d\theta = \frac{2}{3} \quad , \quad \int_0^{\pi}\cos^3(x)\,dx = 0$$
$$\int_0^{\pi}\sin^3(x)\,dx = \frac{4}{3} \quad , \quad \int_0^{2\pi}\cos^2(x)\,dx = \pi$$
$$\int_0^{2\pi}\sin^2(x)\,dx = \pi \quad , \quad \int\frac{1}{e^x+1}\,dx = x - \log(1+e^x)$$
$$\int d\Omega = \int_0^{2\pi}d\phi\int_0^{\pi}d\theta\sin(\theta) \quad , \quad d\Omega = \sin(\theta)d\phi d\theta$$