

Introduction to Quantum Mechanics Summary

Michael Van Huffel

Quantum Mechanics Summary created by *michavan@student.ethz.ch*

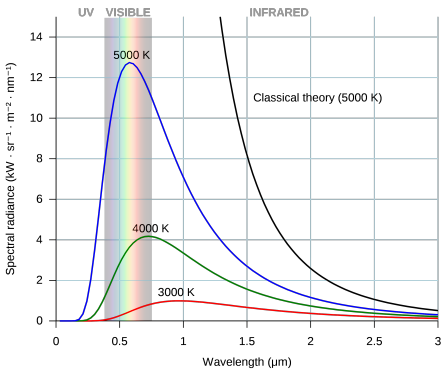
This summary has been written based on the Lecture 151-0966-00 L Introduction to Quantum Mechanics for Engineers by Prof. Dr. D. J. Norris (Spring 21s). There is no guarantee for completeness and/or correctness regarding the content of this summary. This summary is basically a modified and a more completed version of the summary of Lasse Fierz. Use it at your own discretion

Basics

Black Body Radiation and light duality:

A Black body is an ideal object that absorbes all light that hits it. \Rightarrow A Pin-hole into a cavity is a good approximation. Classical physics predict: Infinite radiation at high ν at any $T \Rightarrow$ WRONG! **Why does classical physics fail?**

- Oscillatory electrons in material emit light (electromagnetic waves)
- Only certain standing waves fit in to cavity
- Many nodes fit inside cavity at short wavelength \rightarrow high frequencies.



Note:

- The emission peak shifts to higher frequency with increasing T .
- The number of nodes per unit volume scales with $\nu^2 \Rightarrow$ at high frequencies **Infinite nodes.Finite energy = Infinite energy**
- Low frequency photon carry $k_b \cdot T$ energy
- High frequency photon cannot radiate because $E_{high\nu} = h \cdot \nu \gg k_b \cdot T$

Theorem: The Broglie Relation

An electron can act simultaneously as a particle and a wave at small lengths scales: $\lambda = \frac{h}{p} = \frac{h}{mv}$

A general wave in \mathbb{C} notation is written as: Ae^{ikx} , where $k = \frac{2\pi}{\lambda} = \frac{p}{\hbar}$.

Definitions:

Avogadro: $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$
Planck: $h = 6.626 \cdot 10^{-34} \text{ Js}$, $\hbar = \frac{h}{2\pi}$
Boltzmann: $k_b = 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$

Wavefunction Ψ represents a state (of a particle) and provides statistical information:
 $|\Psi|^2$ Is the prob. of finding the particle at place x and time t . Prob. density.
 $\int_a^b |\Psi|^2 dx$ yields probability of finding the particle between a and b . If it's 0 or ∞ it is invalid. (Unphysical)

Normalize Ψ :

Find $A \in \mathbb{C}$ so that $\int_a^b |A\Psi|^2 dx = 1$ **Note:** The wavefunction, once normalized stays that way for all t .

Expectation value of Q : $\langle \hat{Q} \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{Q} \Psi dx = \int_{-\infty}^{\infty} \hat{Q} |\Psi|^2 dx$

Theorem: Ehrenfest's theorem

Expectation values follow classical laws:

$$m \frac{d}{dt} \langle x \rangle = \langle p \rangle, \quad \frac{d}{dt} \langle p \rangle = - \langle V'(x) \rangle$$

Variance/Standard Deviation: $\sigma_Q^2 = \langle \hat{Q}^2 \rangle - \langle \hat{Q} \rangle^2, \quad \sigma_{\hat{Q}} = \sqrt{\langle \hat{Q}^2 \rangle - \langle \hat{Q} \rangle^2}$

The variance of a discrete variable j is given by $\sum_{j=0}^{\infty} (j - \langle j \rangle)^2 P(j)$, with $P(j) \rightarrow P(x)dx \Rightarrow$ probability of finding particle in $[x, x + dx]$.

Theorem: Heisenberg's uncertainty principle

Incompatible observables such as \hat{x} and \hat{p} or **energy and time** can not be measured simultaneously without uncertainty ($\Delta E = \sigma_H, \Delta t = \frac{T}{2\pi}$)

$$\left\{ \begin{array}{l} \sigma_x \sigma_p \geq \frac{\hbar}{2}, \Delta E \Delta t \leq \frac{\hbar}{2} \text{ or in general: } \sigma_A^2 \sigma_B^2 \geq (\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle)^2 \\ \sigma_H^2 \sigma_Q^2 \geq (\frac{\hbar}{2})^2 (\frac{d}{dt} \langle \hat{Q} \rangle)^2 \text{ and } \frac{d \langle Q \rangle}{dt} = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \langle \frac{\partial \hat{Q}}{\partial t} \rangle \end{array} \right.$$

Example: Rivisited Ideal Gas Law

$pV = nRT \Rightarrow pV = Nk_bT$, N = number of molecules.
 $\frac{V}{N} = \frac{k_b T}{p} \Rightarrow d = (\frac{V}{N})^{1/3}$, d = diameter of molecules.

Operators (1D):

$$\hat{x} = x \quad | \quad \hat{p} = -i\hbar \frac{\partial}{\partial x} = \frac{\hbar}{i} \frac{\partial}{\partial x} \quad | \quad \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) = \frac{\hat{p}^2}{2m} + V(x)$$

\hat{H} being the operator of the Hamiltonian = sum of potential and kinetic energy (classical mechanics). $V(x)$ is the potential energy. $F = -\nabla V(x)$
Good to know: We can allways approximate $v(x)$ as a polynomial of x . (Locally it might look like a parabola even if the potential is arbitrairy)

Theory: O.E

If $V(x) = 0 \Rightarrow$ the energy consists only of kinetic energy $\rightarrow T = \frac{1}{2m} \langle p^2 \rangle$.
The kinetic energy of a wavefunction is related to its curvature.

Schrödinger Equation:

Time dependent Schrödinger Equation(TDSE):

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

For non-time-dependent potentials $V \neq V(t)$ we can use seperation of variables ($\Psi(x, t) = \psi(x)\phi(t)$) and arrive at two parts (Attention: $\psi(x)$ must be continuous and so its first derivative as well as square integrable):

Time dependent part: $\varphi(t) = \exp(-iEt/\hbar)$ (most often the same)

Second part is the solution of the **Time Independent Schrödinger Equation (TISE)** with the coefficient c_n :

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x)\psi = E\psi \quad \text{or} \quad \hat{H}\psi = E\psi, \quad \hat{H}^2\psi = E^2\psi$$

So that in the end: $\Psi(x, t) = \psi(x)\varphi(t) = \psi(x) \exp\left(-\frac{iEt}{\hbar}\right)$

Stationary states:

Most solution to the TDSE **can't** be seperated as described above. But the general solution can **always** be written as a linear combination of our stationary solutions.:

$$\Psi_{gen}(x, t) = \sum_{n=1}^{\infty} c_n \psi_n \exp\left(-\frac{iE_n t}{\hbar}\right)$$

Procedure:
Given $V(x)$ and $\Psi(x, 0)$: \rightarrow TISE $\rightarrow \Psi(x, t) = \sum_n c_n \psi_n \varphi_n$

Before measuring the system any E_n of the ψ_n is a possible result with a probability of $|c_n|^2$. $\sum_{n=1}^{\infty} |c_n|^2 = 1 \Rightarrow$ Probabilistic measurement!
But: when measuring the same prepared system repeatedly, the following measurements will always yield the same result.

$$c_n = \int_{-\infty}^{\infty} \psi_n^*(x) \Psi_{gen}(x, 0) dx$$

Seperable solutions describe **stationary states** $\Psi(\Psi_n)$ meaning that although Ψ depends on x and t , the prob. density $|\Psi|^2$ does not $\Rightarrow |\psi(x, t)|^2 = |\Psi(x)|^2$, Expectation values of stationary states are constant in time: $\langle Q \rangle = \langle Q(x, p) \rangle$

Note:

- If $\langle x \rangle$ is time-independent $\Rightarrow \langle p \rangle = m \frac{d \langle x \rangle}{dt} = 0$
- The expectation value of \hat{H} : $\langle H \rangle$ is E , $\langle H^2 \rangle = E^2 \Rightarrow \sigma_H = 0$.
Note: if in linear combination ($\Psi = c_1 \psi_1 \varphi_1(t) + c_2 \psi_2 \varphi_2(t)$) : $\langle H \rangle = |c_1|^2 E_1 + |c_2|^2 E_2$, $\langle H^2 \rangle = |c_1|^2 E_1^2 + |c_2|^2 E_2^2$

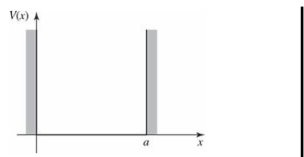
Every measurement of the total energy yields E for stationairy states.

In detail : $\langle H \rangle = \int_{n=1}^{\infty} |c_n|^2 E_n = \int \Psi^* \hat{H} \Psi dx$

Quantum mechanical systems

Infinite square well (ISW):

Infinite potential well:


$$V(x) = \begin{cases} 0, & 0 \leq x \leq a. \\ \infty, & \text{otherwise} \end{cases}$$

TISE:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E\psi \Rightarrow \psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

Characteristics of the infinite square well:

- The solution alternates between even and odd.
- $n \uparrow \Rightarrow$ more nodes, $n = 0, 1, 2, 3, \dots$
- ψ_n are mutually orthogonal $\Rightarrow \int \psi_m^* \psi_n dx = \delta_{mn}$ (not $\forall \Psi_{gen} = \sum c_n \psi_n$)
- Eigenstates are spaced as $2n + 1$ in energy
- The solutions are complete.

Completeness (for any $f(x)$ between a and b):

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right)$$

The quantized E level:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} = \frac{\hbar^2 k_n^2}{2m}, \quad k_n = \frac{n\pi}{a}$$

Note: For N non interacting bosons/fermions: $E_{0,Bosons} = \frac{N \cdot (1)^2 \pi^2 \hbar^2}{2ma^2}$, $E_{0,Fermions} = \frac{\pi^2 \hbar^2}{2ma^2} \cdot 2 \sum_{n=1}^{N/2} n^2$

Yielding for the general solution:

$$\Psi_{gen}(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) \exp\left(-i \left(\frac{n^2 \pi^2 \hbar}{2ma^2}\right) t\right)$$

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a} x\right) \Psi_{gen}(x, 0) dx$$

Example: Sin- Integral

- $\langle \psi_n | x^2 | \psi_m \rangle = \frac{1}{2} \int_0^a x^2 \left(\sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) \right) dx = (n \neq m) \frac{2a^2}{\pi^2} \left[\frac{(-1)^{n-m}}{(n-m)^2} - \frac{(-1)^{n+m}}{(n+m)^2} \right]$
- $\int_0^a x \sin\left(\frac{n\pi x}{a}\right) = \frac{a^2}{4}$

The Harmonic Oscillator (HO):

HO's apply to important particles (photons, phonons, molecular vibrations..)

$$V(x) = \frac{1}{2} m \omega^2 x^2 \Rightarrow \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2, \omega = \sqrt{\frac{k_s}{m}}$$

Note: In this case $V(x)$ is simple. An arbitrairy potential could allways locally be approximated an HO.

Total number of Quanta: total quanta $= \frac{E_{tot}}{E_{spacing}} = \frac{E_{kin} + E_{pot}}{\hbar \cdot \omega}$

After sep. of var. we arrive at various states ψ_n of which the ground state is:

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left(\frac{-m\omega}{2\hbar} x^2\right) (normalized) \Rightarrow \hat{a}_- \cdot \psi_0 = 0$$

We can ascend and descend the energy level by applying the *raising operator* \hat{a}_+ and the *lowering operator* \hat{a}_- :

$$\hat{a}_{\pm} = \frac{1}{\sqrt{2\hbar m \omega}} (\mp i \hat{p} + m \omega \hat{x}) \quad , \quad [\hat{a}_+, \hat{a}_-] = 1$$

\hat{a}_{\pm} is not a hermitian operator but $\hat{a}_+ \hat{a}_-$ is.

$$\hat{H} = \hbar \omega (\hat{a}_+ \hat{a}_- + \frac{1}{2}) = \hbar \omega (\hat{a}_- \hat{a}_+ - \frac{1}{2})$$

$\hat{H} \psi_n = E_n \psi_n \Rightarrow \psi_n$ is a solution of the TISE.
But $\hat{a}_{\pm} \psi_n$ is also a solution: $\hat{H} \hat{a}_{\pm} \psi_n = (E_n \pm \hbar \omega) \hat{a}_{\pm} \psi_n$
Per application of \hat{a}_{\pm} we rise/fall one energylevel. ($\hbar \omega$) Therefore concluding:

$$\psi_n = \frac{1}{\sqrt{n!}} \hat{a}_+^n \psi_0, \quad E_n = \langle \psi_n | \hat{H} | \psi_n \rangle = (n + \frac{1}{2}) \hbar \omega, n = 0, 1, \dots$$

or

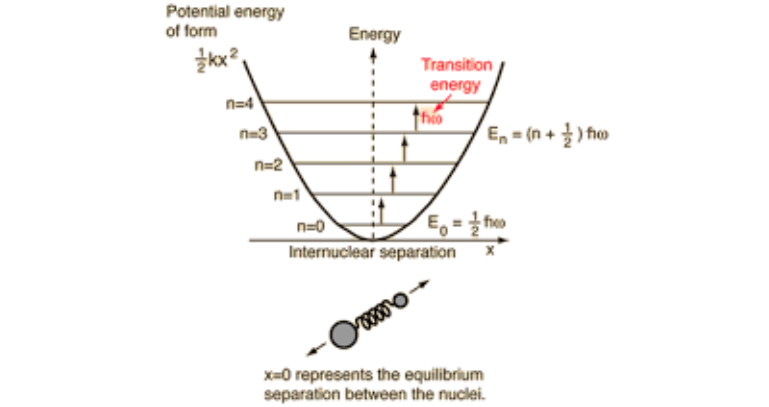
$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right) \cdot \exp\left\{\left(\frac{-m\omega}{2\hbar} x^2\right)\right\}$$

with $H_n(x) = (-1)^n \exp\{(x^2)\} \frac{d^n}{dx^n} [\exp(-x^2)]$

Note: We can't go lower in energy than the ground level $E_0 = \frac{1}{2} \hbar \omega \Rightarrow$ there-fore the oscillator is allways vibrating!

Some definitions:

- n = number of energy quanta, $n = 0, 1, 2, 3, \dots$ (starts at 0)
- $\hat{N} = \hat{a}_+ \hat{a}_-$ 'number operator', is hermitian $\langle N \rangle = n$
- $\hat{a}_- \psi_n = \sqrt{n} \psi_{n-1}, \quad \hat{a}_+ \hat{a}_- \psi_n = n \psi_n, \quad \hat{a}_+ \psi_n = \sqrt{n+1} \psi_{n+1}$
- ψ_n is even (odd) for n even (odd)
- Same characteristics as the ISW.



To be classical: $\Delta E_{n,n+1} \rightarrow 0$ and the region outside parabola are vorbidden!

Free Particle:

Note: $V(x) = 0$ everywhere, $[\hat{H}, \hat{p}] = 0$ and $\langle H \rangle = \langle K \rangle$, with $\hat{K} = \frac{\hat{p}^2}{2m}$ kinetic energy. Since $\hat{p} = \hbar \hat{k} \rightarrow \hat{K} = \frac{\hbar^2 k^2}{2m}$:

$$\langle H \rangle = \int_{-\infty}^{\infty} g^*(k, 0) \cdot \hat{K} \cdot g(k, 0) dk$$

Wavefunction:

$$\psi(x) = A \exp(ikx) + B \exp(-ikx)$$

Therefore for the wavefunction Ψ_k :

$$\Psi_k(x, t) = A \exp i \left(kx - \frac{\hbar k^2}{2m} t \right)$$

$$k = \pm \frac{\sqrt{2mE}}{\hbar} \text{ with } \begin{cases} k > 0, & \Rightarrow \text{wave travelling to the right.} \\ k < 0, & \Rightarrow \text{wave travelling to the left.} \end{cases}$$

The stationairy states of the free particle are propagating waves with wave-length $\lambda = \frac{2\pi}{|k|}$ and momentum $p = \hbar k$.

Problem: Ψ_k is not normalizable: $|A|^2 \int_{-\infty}^{\infty} \Psi_k^* \Psi_k dx = |A|^2 \infty$

For the free particle the separable solutions don't represent physically realiz-able states.

There is no free particle with a definite energy. [continuous]

The general solution is still a linear combination
(Just here an integral over the contiuous k instead of a sum):

$$\Psi_{gen}(x, t) = \int_{-\infty}^{\infty} g(k) \exp i \left(kx - \frac{\hbar k^2}{2m} t \right) dk$$

Shape function:

$$g(k, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, t) \exp(-ikx) dx$$

Note: $g(k) := g(k, 0)$.

Wave packages are normalizable but energy not always defined.

Bound and scattering states:

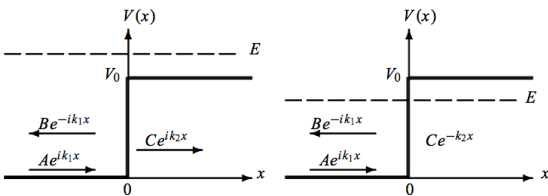
Bound particles: $V(x) > E$ The particle is trapped in the potential well.(Unless additional energy is provided)

Scattering particles $V(x < E)$ The particle can't be trapped by the poten-tial.

$$\begin{cases} E < V(-\infty) \text{ and } V(\infty) & \Rightarrow \text{bound state} \\ E > V(-\infty) \text{ or } V(\infty) & \Rightarrow \text{scattering state} \end{cases}$$

Tunneling is the phenomenon of a wavefunction leaking through a finite bar-rier. It can be quantified by the transmission coefficient T.(Prob. of particle being transmitted)

Finite step:



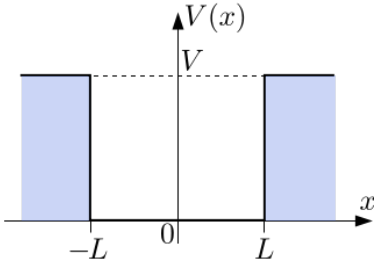
If $E > V(x = 0)$: The wave will be transmitted and reflected.

If $0 < E < V(x = 0)$ The wave will be reflected but not really transmitted (exponential decay).

For $E < 0$ there are no physical solutions.

The finite square well:

Well with finite Potential barrier

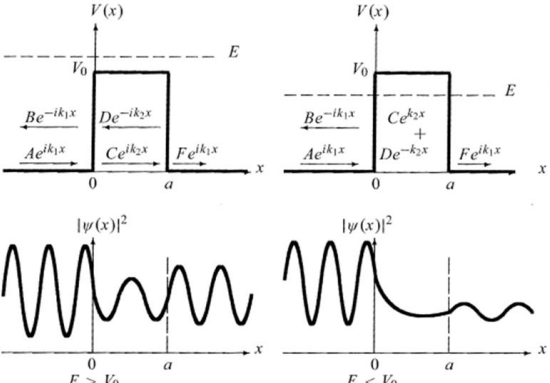


- Refl. and Transm. ($E > 0$)
- Bounded particle with penetr. into wall ($0 \leq E \leq V$)

Theory: O.E

- If a single particle approaches a potential barrier, its wavefunction is NOT always completely transmitted if it has kinetic energy above the height of the barrier.
- For any finite square well, there is always at least one bound state.
- The finite potential barrier allows only scattering states.
- If an electron has an energy E that is higher than the minimum potential energy, V_{min} , of a finite well, then the particle could be in bound state or scattering state

Finite barrier:



If $E > V(x = 0)$: Transm. and refl. as for the finite step.
If $E < V(x = 0)$: Both transm. and refl. but with an exp. decay through the barrier. Lighter particles penetrate deeper. Energy is conserved.
Tunneling: $T \approx \frac{16E(V_0 - E)}{V_0^2} \exp\left\{-\frac{4a}{h} \sqrt{2m(V_0 - E)}\right\}$

Dirac Potential:

Small **spike** barrier in the potential, not in Hilbert space. $\Rightarrow V_{barrier} = a\delta$
Dirac delta function: $\delta(x - a)$ defines a spike at position $x = a$.

$$\int_{-\infty}^{\infty} f(x)\delta(x - a)dx = f(a)$$

Formalism

Hilbert space and Dirac notation:

We imagine our wavefunctions to be n-dimensional vectors represented by n tuples in reference to an orthonormal basis **except** that they are actually infinite. We talk linear algebra.
The Hilbert space is the 'vector' space of all square-integrable (normalizable) functions. Therefore all wavefunctions of physically relizable states are in the Hilbert space.

Theorem: Dirac Notation

We define the *inner product* of two functions f(x) and g(x):

$$\langle f|g\rangle = \int_a^b f(x)^*g(x)dx, \quad \langle f|g\rangle = \langle g|f\rangle^*$$

1. Wavefunctions are represented by the 'Ket' notation: $|\Psi\rangle$
 2. 'Bra' = $\langle B| = (b_1^*, b_2^*, \dots, b_n^*)$, it is always complex conj.
 3. 'Ket' = $|A\rangle = (a_1, a_2, \dots, a_n)^T$ (Note: $\langle A| = (a_1^*, a_2^*, \dots, a_n^*)$)
 4. $\langle B|A\rangle = b_1^*a_1 + \dots + b_n^*a_n$
 5. **Normalisation:** $\langle \chi|\chi\rangle = 1$, with i.e $|\chi\rangle = A \begin{bmatrix} a_1 & a_2 & a_3 \dots \end{bmatrix}^T$.
- Operators essentially perform linear transformations on a vector.
Operators always expressed w.r.t. a basis.(usually \hat{x})

For example \hat{p} is usually defined as $-\hbar \frac{\partial}{\partial x}$ but this is **with respect to the basis \hat{x}** , in the momentum space \hat{p} would just be p.

Theory: O.E

For a general one-dimensional wavefunction $\Psi(x)$, the wavevector $|\Psi\rangle$ is infinite dimensional.

Observables:

\hat{Q} is Hermitian if: $\langle \psi|\hat{Q}\psi\rangle = \langle \hat{Q}^*\psi|\psi\rangle$

For Hermitian operators: $\langle \psi|\hat{Q}\psi\rangle = \langle \psi|\hat{Q}^*\psi\rangle = \langle \hat{Q}\psi|\psi\rangle$
Observables are represented by Hermitian operators.
Hermitian conjugate: $\langle f|\hat{Q}g\rangle = \langle \hat{Q}^\dagger f|g\rangle$
For Hermitian operators holds $\hat{Q} = \hat{Q}^\dagger$ $\hat{Q}^\dagger = (\hat{Q}^T)^*$
For **unitairy** operators: $\hat{Q}^{-1} = \hat{Q}^\dagger \equiv (\hat{Q}^T)^*$
Note: EF of a hermitian operator are dirac-orthogonal. In non relativistic QM, the observable *time* is an independent variable.

Compatibility:

- $\begin{cases} [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}, & [\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}] \\ [\hat{A}, \hat{B}^2] = [\hat{A}, \hat{B}]\hat{B} + \hat{B}[\hat{A}\hat{B}] \\ [\hat{A}\hat{B}, \hat{C}\hat{D}] = \hat{A}\hat{D}[\hat{B}, \hat{C}] + \hat{D}\hat{A}[\hat{B}, \hat{C}] \end{cases}$
- \hat{A}, \hat{B} commute. $\Leftrightarrow [\hat{A}, \hat{B}] = 0 \Leftrightarrow \hat{A}, \hat{B}$ are compatible.
- \hat{A}, \hat{B} do not commute. $\Leftrightarrow [\hat{A}, \hat{B}] \neq 0 \Leftrightarrow \hat{A}, \hat{B}$ are incompatible osservable.
- If \hat{A} and \hat{B} are compatible (osservable), they share Eigenfunctions.

Example: Some compatibility operators

$$\begin{aligned} [\hat{x}, \hat{p}] &= i\hbar, & [\hat{x}, V(x)] &= 0, & (V(x) = \sum_n a_n \hat{x}^n) \\ [\hat{Q}, \hat{Q}] &= 0, & [\hat{Q}, \hat{Q}^n] &= 0, & [\hat{a}_-, \hat{a}_+] = 1 \\ [\hat{x}, \hat{p}^2] &= 2i\hbar\hat{p}, & [\hat{x}, \hat{H}] &= \frac{1\hbar\hat{p}}{m}, & [\hat{a}_\pm, c(const)] &= 0 \end{aligned}$$

Example: Compatibility calculus

$$\begin{aligned} \left[\frac{d^2}{dx^2}, x\right] &\Rightarrow \frac{d^2}{dx^2}[xf(x)] - x\frac{d^2f(x)}{dx^2} = \frac{d}{dx}[f(x) + x\frac{df(x)}{dx}] - x\frac{d^2f(x)}{dx^2} = \\ &\frac{df(x)}{dx} + \frac{df(x)}{dx} - x\frac{d^2f(x)}{dx^2} - x\frac{d^2f(x)}{dx^2} = 2\frac{d}{dx}f(x) \rightarrow \left[\frac{d^2}{dx^2}, x\right] = 2\frac{d}{dx} \end{aligned}$$

Theory: Compatibility experiment

Given are 3 Observables $\hat{A}, \hat{B}, \hat{C}$ with $[\hat{A}, \hat{B}] = [\hat{B}, \hat{C}] = 0$ and $[\hat{A}, \hat{C}] \neq 0$.
Any inital state Ψ_{init} can be written as $|\Psi_{init}\rangle = \sum_n \tilde{c}_n |\Psi_{A,n}\rangle$ (Due to completeness), $|\Psi_{A,n}\rangle$ is A's EF
We have an initial state $|\Psi_{init}\rangle$ and measure three observables \hat{A}, \hat{B} and \hat{C} in a row.
 $\hat{A}|\Psi_{A,n}\rangle = a_n|\Psi_{A,n}\rangle, \quad \hat{B}|\Psi_{B,n}\rangle = b_n|\Psi_{B,n}\rangle, \quad \hat{C}|\Psi_{C,n}\rangle = c_n|\Psi_{C,n}\rangle$
Then during the first measurement the initial state collapses:
 $\Psi_{init} \rightarrow \begin{cases} \Psi_{A,1}(measure \ a_1), & w/ \ probability \ |\tilde{c}_1|^2 \\ \Psi_{A,2}(measure \ a_2), & w/ \ probability \ |\tilde{c}_2|^2 \end{cases}$
Second measurement is when compatibility comes into play:
Since $[\hat{A}, \hat{B}] = 0 \Rightarrow |\Psi_{A,n}\rangle = |\Psi_{B,n}\rangle$ and thus
 $\langle \Psi_{B,1}|\Psi_{A,1}\rangle = 1 \quad and \quad \langle \Psi_{B,2}|\Psi_{A,1}\rangle = 0$
 \rightarrow if $\Psi_{init} \rightarrow \Psi_{A,1}$
We know in \hat{B} we get $\begin{cases} b_1, & 1(100\%) \\ b_2, & 0(0\%) \end{cases}$ vice versa for $\Psi_{A,2}$
 \Rightarrow The second measurement is deterministic.

Given that \hat{C} and \hat{A} are incompatible, they do not share the same eigenfunctions and so the measurement of \hat{C} is probabilistic: we write EF of \hat{A} as a linear combination of EF of \hat{C} to determine probabilities. (Es: given $\rightarrow \Psi_{A,1} = k_{1a}\Psi_{C,1} + k_{1b}\Psi_{C,2}$ and $\Psi_{A,2} = k_{2a}\Psi_{C,1} - k_{2b}\Psi_{C,2}$ if Ψ_{gen} collapsed to $\Psi_{A,1}$ after \hat{A} we measure $(c_1; c_2)$ with probabilities $(k_{1a}^2; k_{1b}^2)$. Analog hold for the case when we collapsed into $\Psi_{A,2} \rightarrow \mathcal{P}(c_1; c_2) = (k_{2a}^2; k_{2b}^2)$)

Eigenfunctions and Eigenvalues:

Determinate states are states that yield the same result for measurements on equally prepared systems in the same state.
One example are stationary states for which we will in a certain state allways measure E_n .
Measurement always yields same result q, $\Rightarrow \sigma_Q = 0$.

$$\hat{Q}\Psi = q\Psi$$

Ψ is the **Eigenfunction** of \hat{Q} and q its **Eigenvalue**.

1. The TISE is an example of such an Eigenvalue equation.

2. The **EF of the momentum operator** $\hat{p} \rightarrow f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \exp\{i p x / \hbar\}$

3. Multiplying an Eigenfunction by a constant yields still an Eigenfunction. $\hat{H}\psi = E\psi$

4. The **Spectrum** of an operator are all its Eigenvalues.

5. Eigenvalues can be shared by different Eigenfunctions \Rightarrow **Degenerate spectrum**. Any linear combination of these Eigenfunctions is an Eigenfunction to the same Eigenvalue itself.

6. **Discrete spectrums** have separated Eigenvalues (\hat{H} in HO),

7. **Continuous spectrums** have continuous Eigenvalues (\hat{H} of FP) and are not normalizable.(ISW has both discrete and continuous.)

Discrete spectra:

- Real Eigenvalues

• Eigenfunctions of distinct Eigenvalues are orthogonal. (HO, ISW)

Continuous spectra: (e.g. free particle)

- Continuous Eigenvalues

• Eigenfunctions not normalizable \Rightarrow not in Hilbert space

• Linear combination must be used

The Eigenfunctions of an observable operator are complete.
Note: Measuring an observable \hat{Q} : State $\Psi(x, t) = \sum_n c_n(t) f_n(x)$, with c_n describing how much of f_n there is in Ψ . Of course $\sum_n |c_n|^2 = 1 \Rightarrow \hat{Q} f_n = q_n f_n$, $\langle \hat{Q} \rangle = \sum_n q_n |c_n|^2$

Theory: Degeneracy

Symmetry is the source of most degeneracy in Q.M. Consider \hat{H} invariant to symmetry operation \hat{Q} where $|\psi'_n\rangle = \hat{Q}|\psi_n\rangle$. Invariance says $[\hat{H}, \hat{Q}] = 0 \Rightarrow \begin{cases} \hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \\ \hat{H}|\psi'_n\rangle = E_n|\psi'_n\rangle \end{cases}$. Compatible observables share same eigenstates \rightarrow no degeneracy, they are same state.

To have degeneracy we require 2 sets of compatible observables: Let \hat{H} be invariant to at least 2 symmetry operators $\hat{Q}_1, \hat{Q}_2 \Rightarrow [\hat{H}, \hat{Q}_1] = 0, [\hat{H}, \hat{Q}_2] = 0$ but $[\hat{Q}_1, \hat{Q}_2] \neq 0 \Rightarrow \begin{cases} \hat{H}|\psi\rangle = E_n|\psi\rangle \\ \hat{Q}_1|\psi\rangle = q_n|\psi\rangle \end{cases}$. But $\hat{H}\hat{Q}_2|\psi\rangle = \hat{Q}_2\hat{H}|\psi\rangle = E_n\hat{Q}_2|\psi\rangle = E_n|\chi\rangle$. This states $|\psi\rangle, |\chi\rangle$ are distinct but with same $E_n \rightarrow$ degeneracy. **Multiple non commuting symmetry operators \Rightarrow energy degeneracy**

Theory: O.E.

- If Ψ_{gen} is an eigenstate of an operator \hat{Q} , the measurement is deterministic.

• If Ψ_{gen} is a superposition of eigenstates \Rightarrow probabilistic.

Quantum mechanics in 3 dimensions

3D - Schrödinger equation:

In 3D the hamiltonian is:

$$\hat{H} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2), \quad p_x = -i\hbar \frac{\partial}{\partial x}$$

We write $p = -i\hbar \nabla$ and therefore TISE:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi, \quad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Spherical coordinates:

In general:

$$\int |\Psi|^2 d^3r = 1$$

TISE:

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2 \psi}{\partial \varphi^2} \right) \right] + V\psi = E\psi$$

H-Atom:

Sep. of var.(again since we already split $\psi(r)\epsilon(t)$): $\psi(r, \theta, \varphi) = R(r)V(\theta, \varphi)$
The normalized spherical part is called Spherical Harmonics:

$$Y_l^{m_l}(\theta, \varphi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m_l)!}{(l+m_l)!}} e^{im_l\varphi} P_l^{m_l}(\cos \theta)$$

$\epsilon = (-1)^{m_l}$ for $m_l > 0$, $\epsilon = 1$ for $m_l \leq 0$

- For a spherically symmetric potential $V = V(r)$ the spherical part is the Spherical harmonics $Y_l^{m_l}$, which is orthogonal

• n = principle QN, l = azimuthal quantum number, m_l = magnetic quantum number

• The degeneracy of n energy level will be $2n + 1$ due to m_l .

- We could approximate the H atom as a single particle because $m_{p^+} + m_{e^-} \approx m_{e^-}$

• The ground state has no angular dependence

• Electron Electron interaction: $V(\vec{r}) = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$

• Total orbital states up to n : $\# = 2 \cdot \sum_{n=1}^n \tilde{n}^2 = 2 \cdot \sum_{l=0}^{l=n-1} 2l + 1$

	Radiale Quantenzahl	Drehimpuls- quantenzahl	Magnetische Quantenzahl
Symbol	n	l	m_l
Mögliche Werte	$n = 1, 2, 3, \dots$	$l = 0, 1, \dots, n - 1$	$m_l = -l, -l + 1, \dots, l - 1, l$
Assoziierte Polarkoordinate	r	ϑ	φ
Assoziierte physikalische Größen	Energie: $E_n = -E_R Z^2 / n^2$	Drehimpuls (Betrag): $L = \sqrt{l(l+1)}\hbar$	Drehimpuls (z-Komponente): $L_z = m_l \hbar$ Magnetischer Dipol: $m_z = -\mu_B m_l$
Merkmal in Wellenfunktion	Ist gleich der totalen Anzahl Knoten plus eins	Ist gleich der Anzahl Knotenebenen	Bestimmt die Lage der Knotenebene(n)

Theory: Normalisation/orthogonality and expectation values

- Normalisation of angular part: $\int_0^{2\pi} \int_0^\pi |Y_l^{m_l}|^2 \sin \theta \, d\theta \, d\varphi = 1$

• Orthogonality: $\int_0^{2\pi} \int_0^\pi (Y_{l_1}^{m_{l_1}})^* Y_{l_2}^{m_{l_2}} \sin \theta \, d\theta \, d\varphi = 0$

• Expectation value of r : $\langle r \rangle = \int_0^\infty \int_0^{2\pi} \int_0^\pi \Psi^* r \Psi \sin \theta \, d\theta \, d\varphi \, dr$

• Expectation value of x : $\langle x \rangle = 0$ for symmetry

• Expectation value of x^2 :

1. Ground state: $\langle x^2 \rangle \rightarrow$ use that $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3\langle (x|y|z)^2 \rangle$

2. Else: use that $x = r \cos \varphi \sin \theta$

Radial part:

$$R_{nl}(r) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \exp\left(-\frac{r}{na}\right) \left(\frac{2r}{na}\right)^l \cdot (L_{(n+l)-(2l+1)}^{2l+1}) \left(\frac{2r}{na}\right)$$

With a being the **Bohr radius**: $a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \cdot 10^{-10}m$
Final solution:

$$\Psi_{n,l,m_l}(r, \theta, \varphi) = R_{n,l}(r) Y_l^{m_l}(\theta, \varphi)$$

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2 Z}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \right] = E_1 \frac{Z^2}{n^2}, E_1 = -13.6eV$$

$$a_z = \frac{a}{Z} \Rightarrow \text{The general radius: } r_n = a_z \cdot n^2$$

E_1 is the energy of the ground state (Rhydberg energy). **Note:** For hydrogen atoms the energys depend only on $n \Rightarrow$ degeneracys, for multielectron atoms this is NOT true.

Theory: Hydrogenic Atom and Screening

1. A hydrogen atom has 1 proton and 1 electron. A hydrogenic Atom has Z protons and 1 electron \rightarrow the binding energy of a hydrogenic Atom ($E_1(z)$) will be much higher, as $Z \uparrow$. This is due to the fact that the single electron will be bound more tightly to multiple protons in nucleus of hydrogenic atom.

2. What happen when you try to solve the TISE for non Hydrogenic Atom with (A) and without (B) electron-eleton forces? Using (A) the electrons in higher orbitals now feel the repelling force eletrons sitting in inner orbitals. (es: electron in 1s and 2s repell electron in 2p orbital). The "pull" from the protons in the nucleons gets therefore reduced which leads to a higher total energy respect to (B). This effect is called screening.

Angular Momentum:

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

Example: Some compatibility operators and calcolous

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z, & [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x, & [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y \\ [\hat{L}_z, x] &= i\hbar y, & [\hat{L}_z, y] &= -i\hbar x, & [\hat{L}_z, z] &= 0 \\ [\hat{L}_z, \hat{p}_x] &= i\hbar \hat{p}_y, & [\hat{L}_z, \hat{p}_y] &= -i\hbar \hat{p}_x, & [\hat{L}_z, \hat{p}_z] &= 0 \\ [\hat{L}_z, \hat{p}_x] &= [x\hat{p}_y - y\hat{p}_x, \hat{p}_x] = [x\hat{p}_y, \hat{p}_x] = i\hbar \hat{p}_y \end{aligned}$$

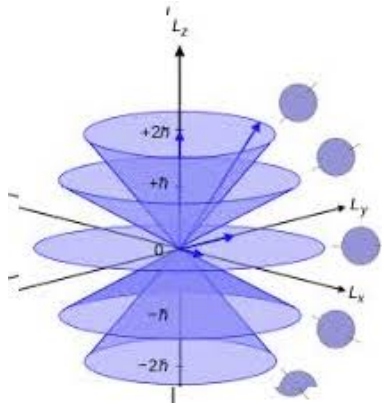
1. \hat{L}_x , \hat{L}_y and \hat{L}_z are **incompatible** \Rightarrow The can't be measured simultaneously. Their uncertainty being: $\sigma_x\sigma_y \geq \frac{\hbar}{2}|\langle L_z \rangle|$, analogous for $\sigma_x\sigma_z$ and $\sigma_y\sigma_z$.
2. Consider $\hat{L}^2 = L_x^2 + L_y^2 + L_z^2 \Rightarrow [L^2, L_i] = 0 \Rightarrow$ **they share EF** (to get EV see below).
3. Since $[\hat{L}_z, \hat{r}^2] = [\hat{L}_z, \hat{p}^2] = 0$ for spheric symmetrical potential we get $\Rightarrow [\hat{L}_{x/y}, \hat{r}^2] = [\hat{L}_{x/y}, \hat{p}^2] = 0$. So, writing $r = \sqrt{r^2}$ we get (recalling the spherically symmetric Hamiltonian previously defined): $[\hat{L}_{x/y/z}, \sqrt{r^2}] = 0$. **So all three components of \hat{L} commutes with \hat{H} .**

Note: Since $\hat{H}, \hat{L}^2, \hat{L}_z$ all commute, they are compatible observables. This implies that the energy, angular momentum squared, and projection of the angular momentum along the z-axis can be determined simultaneously.

To get the **EV of the momentum operators** we use L_{\pm} :

$$\hat{L}^2 f_l^{m_l} = \hbar^2 l(l+1) f_l^{m_l}, \quad \hat{L}_z f_l^{m_l} = \hbar m_l f_l^{m_l}$$

Diagonal and z-projection are known resulting in this appearance. (L_z defined by m_l)



$$\hat{L}_{z, \text{spherical}} = -i\hbar \frac{\partial}{\partial \varphi}$$

$$\begin{aligned} \hat{L}_{x, \text{spherical}} &= -i\hbar \left(-\sin \varphi \frac{\partial}{\partial \theta} - \cos \varphi \cot \theta \frac{\partial}{\partial \varphi} \right), \\ \hat{L}_{y, \text{spherical}} &= -i\hbar \left(+\cos \varphi \frac{\partial}{\partial \theta} - \sin \varphi \cot \theta \frac{\partial}{\partial \varphi} \right) \end{aligned}$$

Note: Z was chosen by convention.

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

The **EF of \hat{L}_z and \hat{L}^2 are the Spherical Harmonics $Y_l^{m_l}$ from the H-Atom!**

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y \pm \hbar e^{\pm i\varphi} \left(\frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \varphi} \right)$$

$$\hat{L}_+ \hat{L}_- = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \varphi^2} + i \frac{\partial}{\partial \varphi} \right)$$

Note: $\hat{L}_{\pm} |l, m_l\rangle = \sqrt{2\hbar} |l, m_l \pm 1\rangle$, if $m_l = m_{l, \text{max}} \Rightarrow \hat{L}_+ |l, m_l\rangle = 0$ Similarly for \hat{L}_- and $m_{l, \text{min}}$

The spin:

Spin of a particle is **not really a spin**. Characteristic of the part. The total angular momentum comes from the orbiting of the electron plus the AM of its spin: $L+S$

The spin has the same interactions across multiple dimensions:

$$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z, \quad [\hat{S}_y, \hat{S}_z] = i\hbar \hat{S}_x, \quad [\hat{S}_z, \hat{S}_x] = i\hbar \hat{S}_y$$

And for the EV's as before: (here $m = m_s$)

$$\hat{S}^2 |s, m\rangle = \hbar^2 s(s+1) |s, m\rangle, \quad \hat{S}_z |s, m\rangle = \hbar m |s, m\rangle \quad \text{with } |s, m\rangle = EF$$

$$\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y = \hbar \sqrt{s(s+1) - m(m \pm 1)} |s, (m \pm 1)\rangle$$

This time the EF are **NOT** $Y_l^{m_l}$. They are new EF's depending on s and m_s . We have no mathematical function for $|s, m_s\rangle$
 $s = 0, \frac{1}{2}, 1, \frac{3}{2}, m_s = -s, -(s-1), \dots, \neq 0, \dots, (s-1), s$

Theorem: Immutability of the spin

The value of s is **immutable** for any elemental particle.
For electrons $s = \frac{1}{2}$, for photons $s = 1$.
(π^- mesons: $s = 0$, baryons: $s = \frac{3}{2}$, gravitons: $s = 2 \dots$)
One fundamental difference between s and l is, that l can change for a particle but s can't.

For **electrons** there are two states: $|s, m_s\rangle = |\frac{1}{2}; \frac{1}{2}\rangle$ and $|\frac{1}{2}; -\frac{1}{2}\rangle$
Representing spin up ($\frac{1}{2}$) and spin down ($-\frac{1}{2}$) for the m_s

Theory: Spin and 3/2 basis

- For given $s \rightarrow m_s = [-s, -s+1, \dots, 0, \dots, s]$
- s is always $\frac{1}{2}$ for electrons! It is never negative!
- If we apply \hat{S}_z to a free electron, and then immediately measure \hat{S}_x on the same electron, we DO NOT always obtain the same value.
- For the basis 3/2 we have: $|s, m_s\rangle = |\frac{3}{2}; \frac{1}{2}\rangle, |\frac{3}{2}; -\frac{1}{2}\rangle, |-\frac{3}{2}; \frac{1}{2}\rangle$ and $|-\frac{3}{2}; -\frac{1}{2}\rangle$ [4 x 4 Matrix]

General state of spin: we can use a linear combination: $|\chi\rangle = a|\frac{1}{2}; \frac{1}{2}\rangle + b|\frac{1}{2}; -\frac{1}{2}\rangle$ which we can write in vector notation: $|\chi\rangle = \begin{bmatrix} a \\ b \end{bmatrix}$, therefore e.g.

spin up: $\chi_+ = |\frac{1}{2}; \frac{1}{2}\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$.

1. χ is called 'spinor'.
2. $|a|^2 + |b|^2 = 1 \Rightarrow |a|^2 =$ probability of measuring \uparrow orientation ($|b|^2$ for down).

When measuring \hat{S}_z or $\hat{S}_{x,y,z}$: $\chi \rightarrow \chi_{\pm}$ yielding either of the two respective EV's with **probability** $|c_{\text{eig}}|^2$

$$c_{\text{eig}} = \text{Eigenvector} * |\chi\rangle, \quad \sum |c_{\text{eig}}|^2 = 1$$

Example: c_{eig} probability

Given $|\chi\rangle = \begin{bmatrix} a \\ b \end{bmatrix}$ and an EV of $+\frac{\hbar}{2}$ and an EF of $\left(\frac{1/\sqrt{2}}{i/\sqrt{2}}\right) \Rightarrow c_{+\frac{\hbar}{2}} = \frac{1}{\sqrt{2}}(a - ib)$. So we get $+\frac{\hbar}{2}$ with probability $\frac{1}{2}|a - ib|^2$.

More in general, given $|\chi\rangle \rightarrow P(|\uparrow_z\rangle) = |\langle\uparrow_z|\chi\rangle|^2$

\hat{S}^2 and \hat{S}_z are **2x2 matrices** (they satisfies EV equation in their base with their EV):

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

So are \hat{S}_x and \hat{S}_y :

$$\hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \Rightarrow \hat{S}_x^2 = \hat{S}_y^2 = \hat{S}_z^2 = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Eigenfunctions in their respective base:

$$\chi_{\hat{S}^2} : \underbrace{\begin{pmatrix} 1 \\ 0 \end{pmatrix}}_{|\uparrow\rangle_{S^2}}, \underbrace{\begin{pmatrix} 0 \\ 1 \end{pmatrix}}_{|\downarrow\rangle_{S^2}}$$
$$\chi_{\hat{S}_x} : \underbrace{\begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}}_{|\uparrow\rangle_x}, \underbrace{\begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix}}_{|\downarrow\rangle_x}$$

$$\chi_{\hat{S}_z} : \underbrace{\begin{pmatrix} 1 \\ 0 \end{pmatrix}}_{|\uparrow\rangle_z}, \underbrace{\begin{pmatrix} 0 \\ 1 \end{pmatrix}}_{|\downarrow\rangle_z}$$
$$\chi_{\hat{S}_y} : \underbrace{\begin{pmatrix} 1/\sqrt{2} \\ i/\sqrt{2} \end{pmatrix}}_{|\uparrow\rangle_y}, \underbrace{\begin{pmatrix} i/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}}_{|\downarrow\rangle_y}$$

And \hat{S}_+ and \hat{S}_- :

$$\hat{S}_+ \chi_- = \hbar \chi_+, \quad \hat{S}_- \chi_+ = \hbar \chi_-, \quad \hat{S}_{\pm} \chi_{\pm} = 0$$

$$\hat{S}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \hat{S}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

\hat{S}_+ and \hat{S}_- are not hermitian and therefore not observable.

Example: Expectation value for spin matrix

Given a spin state of $|\chi\rangle$ (normalized, see subsection Hilbert space and Dirac notation) $\Rightarrow \langle \hat{S}_x \rangle = \langle \chi | \hat{S}_x | \chi \rangle$.

Example: Eigenvalue of spin

Given the spin 1/2 basis i.e. $|\frac{1}{2}; \frac{1}{2}\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and $|\frac{1}{2}; -\frac{1}{2}\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$, determine EV and EF of \hat{S}_y :

- Solve EV equation i.e $\hat{S}_y|? \rangle = \lambda|? \rangle$ and find λ
- Plug back into \hat{S}_y and find EF \Rightarrow remember that $|a|^2 + |b|^2 = 1$

Multiparticle Systems

Differences and analogy:

The following is the same in multiparticle systems:

- Ψ describes the system
- TDSE and TISE \rightarrow total energy
- $\Psi = \sum_n c_n \psi_n e^{\frac{-iE_n t}{\hbar}}$

The changes are:

- $\Psi = \Psi(\underline{r}_1, \underline{r}_2, ..., \underline{r}_n, t)$
- \hat{H} includes particle interaction!!! (through V)

left: kinetic energy, **middle:** potential energy, **right:** interaction

Probability that particle 1 is in volume 1 and part. 2 in volume 2 :

$$|\Psi(\underline{r}_1, \underline{r}_2, t)|^2 d^3r_1 d^3r_2$$

Note: Two particles in the same atom **WITH** electron interactions have never the same energy.

Two particle systems:

TISE:
$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \right) + V(\underline{r}_1, \underline{r}_2) \psi = E \psi$$

Not analytically solvable. Unless hydrogenic

- Particle interaction in form of a distance-dependent potenital (Nucleus-electron) \Rightarrow can be handled like 1-particle problem.
- Two particle problem \rightarrow division into center of mass \underline{R} and relative motion \underline{r} :

$$\underline{R} = \frac{m_1 \underline{r}_1 + m_2 \underline{r}_2}{m_1 + m_2}, \quad \underline{r} = \underline{r}_1 - \underline{r}_2, \Rightarrow \psi = \psi_R(\underline{R}) \psi_r(\underline{r})$$

- Almost no contribution from $\psi_R \Rightarrow$ 1 particle (H-Atom).
- No particle interaction \Rightarrow hydrogenic state:
- Two cases: Distinguishable (e.g. Prot. and electron) or non-distinguishable (e.g. e^- and e^-):

Distinguishable:

$$\psi(\underline{r}_1, \underline{r}_2) = \psi_a(\underline{r}_1) \psi_b(\underline{r}_2) \quad \text{or} \quad \psi_a(\underline{r}_2) \psi_b(\underline{r}_1)$$

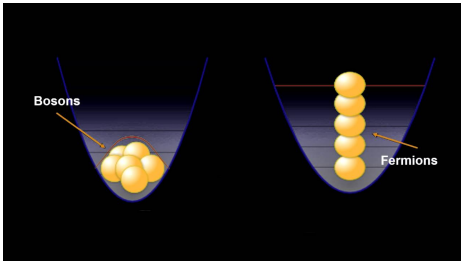
Non-distinguishable:

$$\psi_{\pm}(\underline{r}_1, \underline{r}_2) = C [\psi_a(\underline{r}_1) \psi_b(\underline{r}_2) \pm \psi_a(\underline{r}_2) \psi_b(\underline{r}_1)]$$

Note: with this superpos. we can build (a)symmetric spacial wavefunctions! For Bosons there is also an other solution for non distinguishable particle: $\psi_{Bos} = \psi_a(r_1) \psi_a(r_2)$ or $\psi_{Bos} = \psi_b(r_1) \psi_b(r_2)$

Exchange operator \hat{P} : $\hat{P} f(\underline{r}_1, \underline{r}_2) = f(\underline{r}_2, \underline{r}_1)$

- $[\hat{P}, \hat{H}] = 0$ they share EF's (ψ_{\pm}) $\Rightarrow \hat{P} \psi = \pm \psi$
- For 2 identical particle \hat{P} commute and \hat{H} too
- ψ_{\pm} is $\begin{cases} \text{symmetric,} & +1 \\ \text{antisymmetric,} & -1 \end{cases}$ with respect to exchange.
- (Anti-)symmetry **doesn't** change over time.
- ψ_{\pm} are EF's of \hat{H} and represent stationairy states.



Bosons:

- Integer spin
- Can inhabit same energy levels \Rightarrow collaps into ground-state
- Unlimited bosons can be in the ground state simultaneously.
- Symmetric $\rightarrow \psi_+$
- E.g photons, gravitons
- Non degenerate state \rightarrow if degeneracy \rightarrow linear combination

Fermions:

- Half integer spin
- Only two fermions can inhabit the same state(Pauli principle)
- Antisymmetric $\rightarrow \psi_-$
- E.g electrons, protons, neutrons

Now spin:
$$\chi(s) = \begin{cases} \uparrow\uparrow, & \text{symmetric} \Rightarrow \text{triplet (+)} \\ \downarrow\downarrow, & \text{triplet} \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow), & \text{triplet} \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow), & \text{antisymmetric} \Rightarrow \text{singlet (-)} \end{cases}$$

$$\psi_{final} = \psi_{\pm}(\underline{r}_1, \underline{r}_2) \chi(s)$$

Theorem: Symmetry requirements

The symmetry of the overall wavefunction Ψ for identical (1. bosons, 2. fermions) is (1. symmetric, 2. antiymmetric) with respect to exchange of any two particle

Boson and Fermion: **combined state** of spacial ψ_{\pm} and spin.

An electron and a photon are always distinguishable. Aall electrons in the uni-verse are indistinguishable.

Note: generally ψ_+ has less energy than ψ_- so two electrons in ground state of a H_2 molecule would rather be in the ψ_+ state.

3D infinite square well with multiple particles:

3D infinite square well neglecting electron interactions inbetween each other:

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m}$$

Where k is the absolute value of the vector $\vec{k} = (k_x, k_y, k_z)$.

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

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

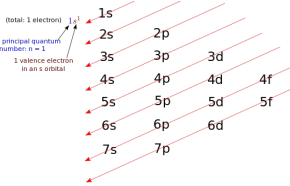
Accidental degeneracy: For the case of a cubic box in the next table are reported the first 14 "n-Energy parts". E_{14} is the first energy level where we get two different combinations of n_x, n_y, n_z that are degenerate. This is known as an accidental degeneracy". The degeneracy in this case is $1[333] + 3[115] = 4$.

	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9	E_{10}	E_{11}	E_{12}	E_{13}	E_{14}
n_x	1	1	1	1	2	1	2	1	1	1	2	2	1	3
n_y	1	1	2	1	2	2	1	3	2	3	2	3	3	1
n_z	1	2	2	3	2	3	3	4	3	4	3	4	4	5
$\sum_i n_i^2$	3	6	9	11	12	14	17	18	19	21	22	24	26	27

Note: For every column the energy level are permutation of the quantum number reported (these degeneracies come about by simply changing the quantum numbers among $n_x, n_y, n_z \rightarrow [322], [232], [223]$).

Multi-particle atoms:

$$\hat{H} = \sum_{j=1}^Z \left[-\frac{\hbar^2}{2m_j} \nabla_j^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{k \neq j}^Z \frac{e^2}{|r_j - r_k|} \right]$$



Note: For hydrogenic atoms each subshell is on the same energy level.

- Z: number of electrons
- n: number of shells (1,2,3,4)
- l: number of subshells (0=s,1=p,2=d,3=f...)
- m_l : which instance of a subshell group (e.g. which dumbbell for p)(-l,...,0,...,l)

Exceptions due to electron interaction:

- Chromium([Ar]4s¹3d⁵)
 - Copper([Ar]4s¹3d¹⁰)
 - Niobium([Kr]5s¹4d⁴)
- Molybdenum([Kr]5s¹4d⁵)
 - ...

When we still have too little information for determining the order of "filling" the atom. \Rightarrow angular momentum:

- \mathbb{L} = total orbital angular momentum,
- \mathbb{S} = total spin angular momentum,
- \mathbb{J} = total combined angular momentum,
- $M_{\mathbb{L}} = \sum m_l, \quad M_{\mathbb{S}} = \sum m_s$

Filled subshells don't contribute to the Term symbol!

Term symbol: $^{2S+1}\mathbb{L}_{\mathbb{J}}$

For two particles the way of adding angular momenta is:

- $\mathbb{L} = (l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|) \Rightarrow$ (with more l , see example), \mathbb{L} is represented by S,P,D,F.. (for 0,1,2,3...)
- $\mathbb{S} = (s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|)$
- $\mathbb{J} = (\mathbb{S} + \mathbb{L}, \mathbb{S} + \mathbb{L} - 1, \dots, |\mathbb{L} - \mathbb{S}|)$

Note: for more particles (e.g. 4 particles) $\mathbb{L} = \mathbb{L}_{12} + \mathbb{L}_{23}$ and we do all combinations possible.

Example: 4 distinguishable particles

Given are two particles with spin 1/2 and two particles with spin 1. Find \mathbb{S} :

- $\mathbb{S}_{1/2;1/2} = 0, 1$
- $\mathbb{S}_{1;1} = 0, 1, 2$
 - For $\mathbb{S}_{1/2;1/2} = 1$ and $\mathbb{S}_{1;1} = 0$ we have $\mathbb{S} = 1$
 - For $\mathbb{S}_{1/2;1/2} = 1$ and $\mathbb{S}_{1;1} = 1$ we have $\mathbb{S} = 0, 1, 2$
 - For $\mathbb{S}_{1/2;1/2} = 1$ and $\mathbb{S}_{1;1} = 2$ we have $\mathbb{S} = 1, 2, 3$
 - For $\mathbb{S}_{1/2;1/2} = 0$ and $\mathbb{S}_{1;1} = 0, 1, 2$ we have $\mathbb{S} = 0, 1, 2$ respectively

So we have the possible values of $\mathbb{S} = 0, 1, 2, 3$ with multiplicity $\mathbb{S} = 0$ (x 2), $\mathbb{S} = 1$ (x 4), $\mathbb{S} = 2$ (x 3), $\mathbb{S} = 3$ (x 1)

Example: Nitrogen Term symbols

We have $2p^3$ as valence band $\rightarrow 3p$ electrons.

- $l_1 = 1, l_2 = 1, l_3 = 1$ can combine to give $\mathbb{L} = 3, 2, 1, 0$
- $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, s_3 = \frac{1}{2}$ can combine to give $\mathbb{S} = \frac{3}{2}, \frac{1}{2}$
- For $\mathbb{J} = \mathbb{L} + \mathbb{S}$ we have 19 combinations:
 - $\mathbb{L} = 3, \mathbb{S} = \frac{3}{2} \Rightarrow \mathbb{J} = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$
 - $\mathbb{L} = 3, \mathbb{S} = \frac{1}{2} \Rightarrow \mathbb{J} = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$
 - $\mathbb{L} = 2, \mathbb{S} = \frac{3}{2} \Rightarrow \mathbb{J} = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$
 - $\mathbb{L} = 2, \mathbb{S} = \frac{1}{2} \Rightarrow \mathbb{J} = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$
 - $\mathbb{L} = 1, \mathbb{S} = \frac{3}{2} \Rightarrow \mathbb{J} = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$
 - $\mathbb{L} = 1, \mathbb{S} = \frac{1}{2} \Rightarrow \mathbb{J} = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$
 - $\mathbb{L} = 0, \mathbb{S} = \frac{3}{2} \Rightarrow \mathbb{J} = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$
 - $\mathbb{L} = 0, \mathbb{S} = \frac{1}{2} \Rightarrow \mathbb{J} = \frac{1}{2}, -\frac{1}{2}$

Note: The term-symbol also includes symmetric states which are impossible for electrons. They defy the Pauli exclusion principle.

Theorem: Hund's rule

For determining the lowest energy state (neglecting exchange symmetry):

- 1. State with largest \mathbb{S} is most stable.
- 2. States with the same $\mathbb{S} \Rightarrow$ largest \mathbb{L} is most stable.
- 3. States with the same \mathbb{S} and \mathbb{L} are most stable for:
 - smallest \mathbb{J} , subshells not more than half full (\leq)
 - largest \mathbb{J} , subshells more than half full ($>$)

Note: Singlet $\mathbb{S} = 0$, Triplet $\mathbb{S} = 1$

Solids

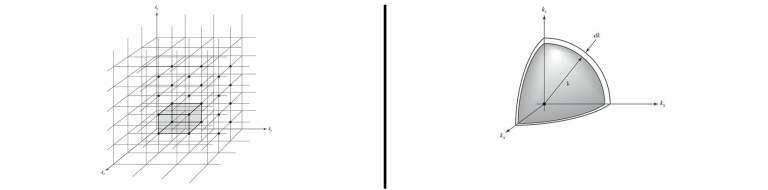
Fermi energy and solid model:

Fermi energy: The energy level of the energetically highest electron
Fermi level: The energy at which $f(E)(T > 0) = 0.5$

$$f(E) = \begin{cases} T = 0 \Rightarrow \begin{cases} 1, & \text{falls } E \leq E_F \\ 0, & \text{falls } E > E_F \end{cases} \\ T > 0 \Rightarrow \frac{1}{1 + e^{\frac{E - E_F}{k_B T}}} \end{cases}$$

Two ways to describe solids:

1. Free electron model: ignore electron-electron interactions, material is metal, $V(r) = 0$ inside box and so outside, material = box with electrons in it.
k-space:



Electronic states are filled up to k_f (right picture), $k_{x,y,z} > 0$
Every solution in the k-space occupies the same space: $\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$

Occupied volume in k-space = $\frac{1}{2}$ # of electrons * volume per electronic state

with N being the number of atoms, q their respective number of valence electrons.

Fermi energy for 1D, 2D and 3D case: plugging the equation above for

$V(x) = 0$ into $E = \frac{\hbar^2 k^2}{2m}, \hat{p} = \hbar k$ ($1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ J}$) we get:

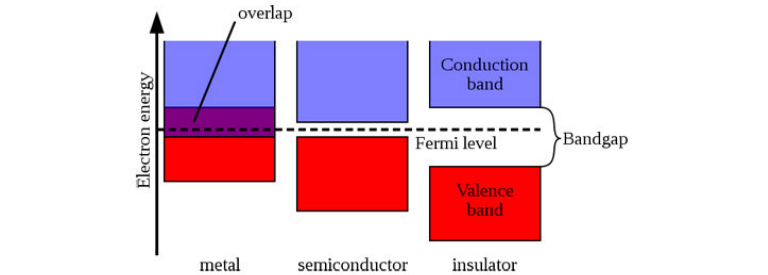
- 3D:** $\frac{1}{8} V_{\text{sphere}} = \frac{1}{2} N * q * \frac{\pi^3}{V} \Rightarrow$ where $V_{\text{sphere}} = \frac{4}{3} \pi k^3, k = \dots$
 - $E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N q}{V} \right)^{2/3}$
 - $N q = \frac{V}{3\pi^2} \left(\frac{2m E_F}{\hbar^2} \right)^{3/2}$
- 2D:** $\frac{1}{4} A_{\text{circle}} = \frac{1}{2} N * q * \frac{\pi^2}{A} \Rightarrow$ where $A_{\text{circle}} = \pi k^2, k = \dots$
 - $E_F = \frac{\hbar^2 \pi N q}{2m A}$
 - $N q = \frac{m E_F A}{\hbar^2 \pi}$

Density of states: $D(E) = \frac{dN q}{dE}$ (represents $\#e^-$ per unit energy, $\#$ of one-electron-levels)

- 3D:** $D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$
- 2D:** $D(E) = \frac{m A}{\hbar^2 \pi}$

Energy spacing: $ES = \frac{1}{D(E)}$

2. Band model: periodic $V(x)$ in atomic lattice, also bosons have Band Gaps, which only depend on atomic lattice and not on type of particle.



The Fermi energy for metals is inside a band, for semi-conductors and insulators it is in between. Semi-conductors can still conduct, the electron jumps. (E_{gap} for semi-cond. is smaller than 4eV)

Semicond. can be made more conductive with thermal and/or doping measures:

- Thermal excitation:** $n_{e^-} = N_i e^{-\frac{E_g}{k_B T}}, N_i =$ undoped carrier concentration, $n_{e^-} = \#$ free electrons per unit Volume.
Note; $\#$ photons absorbed $= n_{e^-} \cdot \text{Volume}, E_{\text{photon}} \geq E_g$
- Doping excitation:** $n_{e^-} = N_D e^{-\frac{E_d}{k_B T}}, N_d =$ Concentration of Donor atoms

Note: Dopants have low ionization energy so can release easily its extra electron or hole.

Theorem: Bloch's

For periodic potentials:

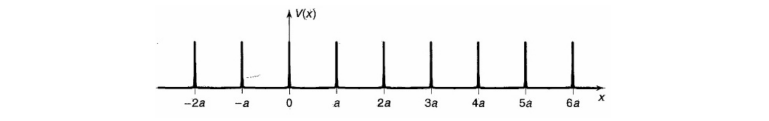
$V(x) = V(x + a) \Rightarrow \psi(x + a) = e^{i K a} \psi(x)$

Note: $|\psi(x)|^2 = |\psi(x + a)|^2 \Rightarrow |\psi|^2$ is periodic but the wavefunction is not the same for every atom in the lattice!.

Theory: O.E.

- If we add more electrons to a crystalline metallic solid, such that additional electronic states are occupied, the Fermi energy rises.
- The electronic density of states at the Fermi energy affects the ability of a solid to conduct electricity.

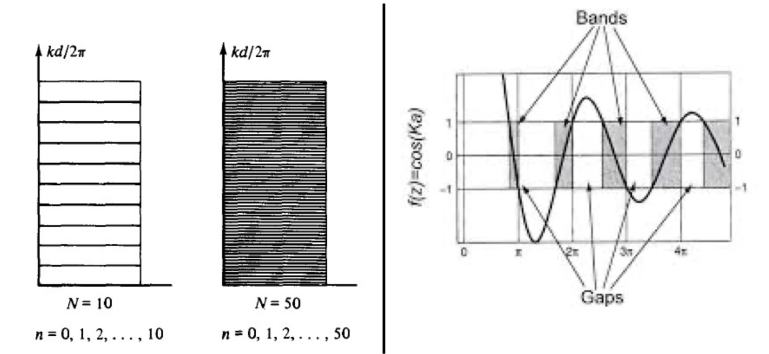
Dirac-Comb model:



The potential is of the form: $V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja)$.
Consider a one dimensionale solid of N atoms. The allowed energies for the electron are:

$$\cos(Ka) = \cos(ka) + \beta \frac{\sin(ka)}{ka}$$

where K is a real constant, a is the periodicity of the potential, $\beta = \frac{m\alpha a}{\hbar^2}$, m is the particle mass and α is the strength of the Dirac comb.



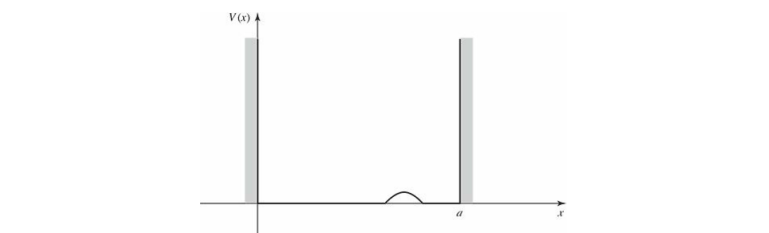
Since the LHS of the above equation is a cosine, it has to be between ± 1 . Also, the energy is proportional to k . Thus, the energy at the bottom of the lowest band will be at the point where the curve first met $f(z) = 1$.**Note:**

- For higher β , the bands exists even for larger ka (i.e) the strength of the delta function makes the band gaps arise.
- For larger ka , bands start vanishing.
- Though the bands are discrete ('n' is an integer) it has N number of solutions that makes the band forming a continuum (For very large 'N').

Approximation methods

Perturbation Theory:

Problem: perturbation in our potential:



1. $\hat{H} = \hat{H}^0 + \lambda \hat{H}'$, \hat{H}^0 being the usual potential,
2. \hat{H}' the perturbation and λ an aiding parameter.
3. $\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 \dots$, $E_n = E_n^0 + \lambda E_n^1 \dots$ (when I calculate the error correction then the total Energy is $E = E^{(0)} + E^{(1)} + \dots$ with $E^{(0)}$ from the unperturbed Hamiltonian diagonal for example).
4. ψ_n^p, E_n^p being the corrections of order p .
5. ψ_n^0 from ISW or from EV of unperturbed Hamiltonian \hat{H} (as example).

First and second order correction (can yield both to exact answer!):

- $E_n^1 = \langle \psi_n^0 | \hat{H}' | \psi_n^0 \rangle \Rightarrow \psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0$
- $E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} = \sum_{m \neq n} \frac{\langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle \langle \psi_n^0 | \hat{H}' | \psi_m^0 \rangle}{E_n^0 - E_m^0}$

If $E_m = E_n \Rightarrow$ **degeneration**: the two identical E^0 get split by perturbation.

$$\begin{cases} E_{\pm}^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right] \\ W_{ij} = \langle \psi_i^0 | \hat{H}' | \psi_j^0 \rangle, \quad \hat{H}' = \frac{\hat{H}(\lambda_0 + \partial \lambda) - \hat{H}(\lambda_0)}{\partial \lambda} = \frac{\partial \hat{H}}{\partial \lambda}, \lambda_0 = \text{unperturbed state} \end{cases}$$

Theorem: Feynman-Hellman

Suppose the Hamiltonian H is a function of λ ; let $E_n(\lambda)$ and $\psi_n(\lambda)$ be the EV and EF of $H(\lambda)$ so:

$$\frac{\partial E_n}{\partial \lambda} = \langle \psi_n | \frac{\partial H}{\partial \lambda} | \psi_n \rangle$$

Variational Principle:

Boundary for E_{ground} . Can be a boundary for first excitation too.
We choose any trial function and see (can yield to exact answer):

$$E_{ground} \leq \langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = \langle \hat{H} \rangle = \sum_{n=1}^{\infty} E_n |c_n|^2$$

Expectation value of \hat{H} is upper bound for E_{ground} . In practice we try to make $\langle \hat{H} \rangle$ as small as possible. E.g through adjustable parameters in our trial function. \Rightarrow derivation w.r.t that variable. For example for He atom, ψ_{trial} can be analog to 1s orbital $\rightarrow \Psi_{trial} = Ae^{-\alpha \cdot (r_1 + r_2)/a}$

Additions

Recap representations:

Wave representation:

States	$ \Psi\rangle = \sum_n c_n f_n\rangle$
Basis	f_n
Operations	\hat{Q} differential operators
TISE	$\hat{H}\psi_n = E_n\psi_n$
Process	solve dif. equation
output	ψ_n (eig.funct.) and E_n (eig.value)

Matrix representation:

States	$ \Psi\rangle = \sum_n c_n f_n\rangle = (c_1, c_2, \dots, c_n)^T$
Basis	f_n
Operations	matrices, elements: $\hat{H}_{ij} = \langle f_i \hat{H} f_j \rangle$
TISE	$\hat{H}\psi_n = E_n\psi_n$
Process	diagonalize \hat{H} (Eigenvalue procedure)
output	ψ_n (eig.vectors) and E_n (eig.value)

Dirac Notation:

$\langle a | b \rangle$ is a complex number while $|a\rangle\langle b|$ is a square matrix.
 $|\psi\rangle = \sum_{i=1}^n c_i |f_i\rangle = \sum_{i=1}^n |f_i\rangle \langle f_i | \psi \rangle$, $\sum_{i=1}^n |f_i\rangle \langle f_i| = \mathbb{I}$

Symmetry:

Symmetry comes for various operations:

- Translation
 - Inversion
- Rotation
 - reflection...

1. Translation:
- $$\hat{T}(a)\psi(x) = \psi'(x) = \psi(x - a)$$

It shifts by a.
 $\hat{T}(a) = \exp\left(-\frac{ia}{\hbar} \hat{p}\right) \Rightarrow$ generated by momentum.
 \hat{T} is unitairy (recall operators) $\hat{Q}'(\hat{x}, \hat{p}) = \hat{Q}(\hat{x} + a, \hat{p})$
Translation symmetry: $V(x) = V(x + a) \leftrightarrow [\hat{H}, \hat{T}] = 0$ (Linear momentum conserved!)

2. Parity:
- $$\hat{\Pi}\psi(r) = \psi(-r)$$

Inversion of coordinates
 $\hat{\Pi} = \hat{\Pi}^\dagger$ (hermitian) $\hat{\Pi}^{-1} = \hat{\Pi}$ (unitairy)
 $\hat{Q}'(\underline{r}, \hat{p}) = \hat{Q}(-\underline{r}, -\hat{p})$
Inversion symmetry: $V(\underline{r}) = V(-\underline{r}) \leftrightarrow [\hat{H}, \hat{\Pi}] = 0$
Implications: \hat{H} and $\hat{\Pi}$ share eigenstates (even states remain even and odd stay odd).
Selection rules whether photon can excite electron from ψ_{nlm} to $\psi_{n'l'm'}$

3. Rotations:
- $$\hat{R}_z(\varphi)\psi(r, \theta, \phi) = \psi'(r, \theta, \phi) = \psi(r, \theta, \phi - \varphi)$$

Here rotation around n-axis
 $\hat{R}_n(\varphi) = \exp\left(-\frac{i\varphi}{\hbar} \hat{L}_n\right) \Rightarrow$ generated by \hat{L}_n
For small rotations: $\hat{R}_n(\delta) = 1 - \frac{i\delta}{\hbar} \hat{L}_n$
Continuous rotation symmetry: \Leftrightarrow If \hat{H} is rotationally invariant $\Rightarrow \hat{V}(\vec{r}) = \hat{V}(r)$ (spherically symmetric). This implies $\Rightarrow [\hat{H}, \hat{R}_n(\varphi)] = 0$.
Implications: Since $\hat{R}_n(\delta) \approx 1 - \frac{\delta}{\hbar} \hat{L}_n \Rightarrow [\hat{H}, \hat{L}_n] = 0 \Rightarrow \frac{d}{dt} \langle \hat{L}_n \rangle = 0$.
This mean that Angular momentum conservation is a consequence of rotational invariance.
For central potential eigenstates Ψ_{nlm_l} uniquely specified by $\hat{H}, \hat{L}_n, \hat{L}^2$.
This is known as complete set of compatible observables. If only two operators, eigenstates are not uniquely specified.