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Good luck with Quantum Mechanics!
Mark

Cheatsheet
Quantum Mechanics
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Statistics: Continous Variables

Take position x as variable and $\rho(x)$ as the **probability density** in 1D. Then is $\rho(x)dx$ the probability of finding the particle between x and $x + dx$.

$\langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)dx$	Expectation value
$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$ or $\Sigma(j - \langle j \rangle)^2 P(j)$	Variance
$\sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$	Standard deviation
$\langle j \rangle = \Sigma j P(j)$	Average
$\langle j^2 \rangle \geqslant \langle j \rangle^2$	In general

The Wave Function

Schrödinger Equation (TDSE)

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

If we solve the Time Dependent Schrödinger Equation (TDSE), we obtain $\Psi(x,t)$, the particles wave function! The Kinetic energy of $\Psi(x,t)$ is related to the curvature $\left(\frac{\partial^2}{\partial x^2}\right)$

$\Psi(x,t)$: "probability amplitude", no direct physical meaning, complex function

$|\Psi(x,t)|^2$: probability density, real & non-negative

$\int_a^b |\Psi(x,t)|^2 \, dx$ = Probability of finding the particle between a and b at time t

Normalization: $\int_{-\infty}^{\infty} |C \cdot \Psi(x,t)|^2 \, dx = 1 \quad C \in \mathbb{C}$

If Ψ is normalized at $t = 0$, it stays normalized $\forall t > 0$!

Operators

Location Operator:	$\hat{x} = x = x^*$
Momentum Operator:	$\hat{p} = -i\hbar\frac{\partial}{\partial x} \quad -i = \frac{1}{i}$
Ehrenfest's Theorem:	$\langle p \rangle = m \cdot \frac{d\langle x \rangle}{dt} = m \cdot \langle v \rangle$
Remember:	$\langle p^2 \rangle = \hat{p}^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}$

All classical dynamical variables can be expressed in terms of x and p. E.g.

$$E_{kin} = \frac{1}{2}mv^2 = \frac{p^2}{2m} \qquad \vec{L} = \vec{r} \times m\vec{v} = \vec{r} \times \vec{p}$$

The quantity Q of interest is called *Observable*, $\hat{Q}$ denotes the *Operator* for Observable Q. Every observable quantity in classical mechanics is represented in quantum mechanics by a linear Hermitian operator. The expectation value of any quantity $Q(x,p)$ is given by:

$$\langle Q(x,p) \rangle = \int_{-\infty}^{\infty} \Psi^* \cdot \hat{Q}(x, -i\hbar\partial/\partial x) \cdot \Psi \, dx$$

Uncertainty Principle: $\sigma_x \cdot \sigma_p \geqslant \frac{\hbar}{2}$

De Broglie formula: $p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} = \hbar \cdot k$

Generalized Ehrenfest theorem:

$$\frac{d\langle Q \rangle}{dt} = \frac{i}{\hbar}\langle [\hat{H}, \hat{Q}] \rangle + \langle \frac{\partial \hat{Q}}{\partial t} \rangle$$

In a stationary state, where all of the expectation values do not depend on time, if $\hat{Q}$ commutes with $\hat{H}$, then $\langle Q \rangle$ is constant and it's conserved in quantity.

Time-Independent Schrödinger Equation (TISE)

Assume that V is independent of t, so one can use *separation of variables* to solve the TDSE.

$$\Psi(x,t) = \psi(x) \cdot \varphi(t) = \psi(x) \cdot \exp\left(-i\frac{Et}{\hbar}\right)$$

$\varphi(t)$ is called the **phase factor** and is obtained by plugging in the TDSE. $\psi(x)$ is obatined by solving the TISE:

$$\boxed{\textbf{TISE:} \quad \hat{H}\psi = E\psi}$$

Note: $[E - V(x)] > 0$
Where $\hat{H}$ is the Hamiltonian (total Energy) Operator:

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

$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -[E - V(x)]\frac{2m}{\hbar^2}\Psi(x,t)$
$[E - V(x)] > O$ Because, to have a physical meaningful solution we need:
$\Psi(x,t) > 0 \Rightarrow \frac{\partial^2 \Psi(x,t)}{\partial x^2} < 0$
$\Psi(x,t) < 0 \Rightarrow \frac{\partial^2 \Psi(x,t)}{\partial x^2} > 0$

Stationary States

All separable solutions $\Psi(x,t) = \psi(x)\varphi(t)$ are socalled stationary states, because the probability density does not depend on time:

$$|\Psi(x,t)|^2 = \psi^* e^{+iEt/\hbar}{}^{0} \psi e^{-iEt/\hbar}{}^{0} = |\psi(x)|^2$$

Additionally, every expectation value is constant in time:

$$\langle Q(x,p) \rangle = \int_{-\infty}^{\infty} \psi^* \cdot \hat{Q}(x, -i\hbar\partial/\partial x) \cdot \psi \, dx$$

In particular $\langle x \rangle$ is constant and hence $\langle p \rangle = 0$. The expectation value of the total energy is $\langle H \rangle = E$ and $\langle H^2 \rangle = E^2$, hence $\sigma_H = 0$. A separable solution has the property that every measurement of the total energy is certain to return $E \quad \Rightarrow \quad$ **deterministic!**

The general solution is a linear combination of separable solutions (Linear combination of the eigenstates of the hamiltonian):

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

- ψ_n tells us where the part. is when it has energy E_n
- Ψ_{gen} is not a stationary state, therefore time dependent expectation values!
- c_n is obtained by: $\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x)$
- $|c_n|^2$ is the probability that a measurement of energy returns the value E_n.
- $\sum |c_n|^2 = 1$ and $\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n$.
- $\langle H \rangle$ CAN be < 0 (For example in the ground state of the hydrogen Atom (-13.6eV)

Motion of particle with potential $V(x) = 0$:

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -k^2 \psi(x) \text{ with } k = \sqrt{\frac{2mE}{\hbar^2}} = \frac{p}{\hbar} = \frac{2\pi}{\lambda}$$

General solution (applicable for various problems)

standing wave[HO, ISW	$\psi(x) = A\sin(kx) + B\cos(kx)$	
travelling wave[FP	$\psi(x) = A \cdot e^{ikx} + B \cdot e^{-ikx}$	
Combination of both:	Finite Potential Walls	

Free Particle $\qquad\qquad V(x) = 0$

Use $\psi_k(x) = A \cdot e^{ikx}$ (k can be $\pm$), then

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

Ψ_{gen} is a <u>not</u> a lin. comb. of Ψ_k, because k is continous and Ψ_k is not normalizable, so:

$$\Psi_{gen}(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} g(k)\exp\left[i\left(kx - \frac{\hbar k^2}{2m}\right)\right]dk$$

$$\text{with } g(k) = \underbrace{\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\Psi(x,0)e^{-ikx}dx}_{\text{Shape Function}}$$

Infinite Square Well (ISW)

Infinite potential boundaries at $x = 0$ and $x = a$
$$V(x) = \begin{cases} 0 & 0 \leqslant x \leqslant a \\ \infty & \text{otherwise} \end{cases}$$

Solve $\frac{\partial^2 \psi(x)}{\partial x^2} = -k^2\psi(x)$ using standing wave ansatz!

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}}\sin(k_n x) \quad E_n = \frac{\hbar^2}{2m}k_n^2 \quad k_n = \frac{n\pi}{a}}$$
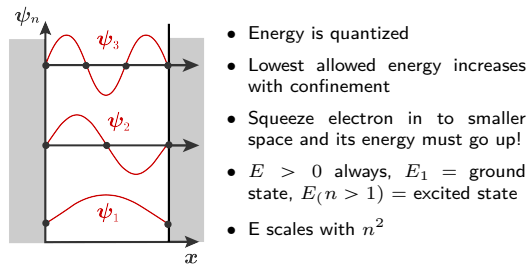
c_n's are obtained by: $c_n = \sqrt{\frac{2}{a}}\int_0^a \sin(k_n x)\Psi(x,0)\,dx$

Characteristics:

- Solutions alternate bewteen 'even' and 'odd' w.r.t the center $x = a/2$
- ψ_{n+1} has one more node than ψ_n
- Solutions are mutually orthogonal:

$$\langle \psi_m | \psi_n \rangle = \int \psi_m^* \psi_n \, dx = \delta_{mn} = \begin{cases} 0 & \text{if } m \neq n \\ 1 & \text{if } m = n \end{cases}$$

- Solutions form a complete set, s.t. for any fct. $f(x)$

$$f(x) = \Sigma c_n \psi_n(x)$$

- Energy is quantized
- Lowest allowed energy increases with confinement
- Squeeze electron in to smaller space and its energy must go up!
- $E > 0$ always, $E_1 =$ ground state, $E(n > 1) =$ excited state
- E scales with n^2

Commutators

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} = -\left[\hat{B}, \hat{A}\right]$$

$\hat{A}, \hat{B}$ commute, if $\left[\hat{A}, \hat{B}\right] = 0$.

Identities:
$$\left[\hat{A} + \hat{B}, \hat{C}\right] = \left[\hat{A}, \hat{C}\right] + \left[\hat{B}, \hat{C}\right]$$
$$\left[\hat{A}, \hat{B} \cdot \hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right]$$

Common cummutators:
$$[\hat{x}, \hat{p}] = i\hbar \quad \left[\hat{x}, f(\hat{x})\right] = 0 \quad \left[\hat{p}, f(\hat{p})\right] = 0$$
$$\left[\hat{H}, \hat{x}\right] = -\frac{\hbar^2}{m}\frac{\partial}{\partial x} = \frac{\hbar}{im}\hat{p} \quad \left[\hat{A}, C\right] = 0 \,\,\forall C \in \mathbb{C}$$

Harmonic Oscillator (HO)

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2 \quad [\hat{a}_-, \hat{a}_+] = 1 \quad i\hat{p} = \hbar\frac{\partial}{\partial x}$$

raising operator: $\hat{a}_+ = \frac{1}{\sqrt{2\hbar m\omega}}(-i\hat{p} + m\omega x)$

lowering operator: $\hat{a}_- = \frac{1}{\sqrt{2\hbar m\omega}}(i\hat{p} + m\omega x)$

This yields the Hamiltonian for the HO:

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

Solutions to TISE are obtained by solving: $\boxed{\hat{a}_-\psi_0 = 0}$

$$\Rightarrow \quad \psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{m\omega}{2\hbar}x^2\right) \quad E_0 = \frac{1}{2}\hbar\omega$$
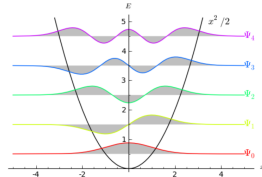
If ψ_n satisfies the TISE with Energy E_n, then

$$\hat{H}(\hat{a}_\pm\psi_n) = (E_n \pm \hbar\omega)\hat{a}_\pm\psi_n$$

satisfy the TISE with one quantum of energy more/less.

$$\boxed{\psi_n = \frac{1}{\sqrt{n!}}(\hat{a}_+)^n\psi_0 \\ E_n = \left(n + \frac{1}{2}\right)\hbar\omega}$$

Normalization constant $\frac{1}{\sqrt{n!}}$, follows directly from:

$$\hat{a}_+\psi_n = \sqrt{n+1}\psi_{n+1} \quad\quad \hat{a}_-\psi_n = \sqrt{n}\psi_{n-1}$$

- Energy is quantized (QM)
- even at 0Kelvin the H.O still vibrates and has energy = Zero Point Energy (QM)
- E_0 = Zero Point Motion
- $\langle x \rangle = 0$, because of wave-symmetry in the E-axis
- Because $V(x) \neq \infty$ particle can lay outside the potential
- At the classical turning Points (CTP): $KE = 0 \Rightarrow$ find CTP by setting: $E_n = H = V(x)$
- Energy Space increases with increased spring constant

To find the Probability $P(x)$ of the particle outside the Potential

$$P(-CTP > x > CTP) = 2\int_{|CPT|}^{\infty}|\psi_n(x)|^2 dx$$

Finite Potentials

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

- Note: If the Potential V(x) is finite, does not matter the the value, there is ALWAYS a bound state

- Note: Non-classical behavior will be *
- All the transmissions and reflections Conserve the Energy of the System

Finite Potential Step   consider incoming wavepacket

- $E > V_0$: transmitted & reflected*
- $0 < E < V_0$: reflection & penetration* into barrier
- $E < V_{min}$: no phys. solution
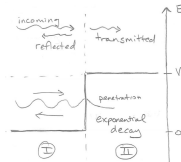
Finite Potential Well   consider incoming wavepacket

- $E > 0$: transmitted & reflected*
- $-V_0 < E < 0$: bound states with some penetration* into barrier, even if $V_0 \approx 0$, always 1 bounded State (at least)
- $E < -V_0$: no physical solution
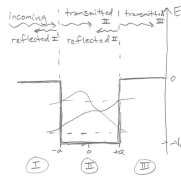
Finite Potential Barrier   consider incoming wavepacket

- $E > V_0$: transmitted & reflected*
- $0 < E < V_0$: transmitted* & reflected, exponential decay in barrier
- $E < V_0$: no physical solution
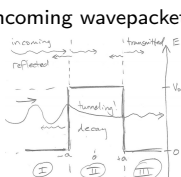
Quantum Mechanical Tunneling:

$T \equiv$ probability of particle being transmitted

$$T \approx \frac{16E(V_0-E)}{V_0^2}\exp\left[-4\frac{\sqrt{2m(V_0-E)}}{\pi}a\right]$$

Formalism and Postulates

Dirac Notation

The state of a QM System is described by $\Psi(\vec{r}, t)$. Ψ is physical if it is square integrable and normalizable! If both applies, then Ψ lives in **Hilbert-Space** $\mathcal{H}$ and can also be represented as a vector:

Dirac Notation:

$$\Psi = \sum_n c_n f_n(\vec{r}) \quad\Rightarrow\quad (c_1\ c_2 \ldots c_n)^T = |\Psi\rangle$$
$$\Psi^* = \sum_n c_n^* f_n^*(\vec{r}) \quad\Rightarrow\quad (c_1^*\ c_2^* \ldots c_n^*) = \langle\Psi|$$

Note1: $\langle\alpha\cdot\Psi| = \alpha^*\cdot\langle\Psi| \quad\quad |\beta\cdot\Psi\rangle = \beta\cdot|\Psi\rangle$

The inner product of two functions is defined as follows:

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

A set of functions f_n are ...

- ... orthonormal, if: $\langle f_m|f_n\rangle = \delta_{mn}$
- ... complete, if: $F(x) = \sum c_n f_n(x)\ \forall F \in \mathcal{H}$

Normalization: $\langle f|f\rangle = 1$
Expectation value: $\langle\hat{A}\rangle = \langle\Psi|\hat{A}|\Psi\rangle$
Neither $\langle|$ or $|\rangle$ need to be orthogonals to others.

Hermitian Operators

Requirement for an Operator to be Hermitian:

$$\boxed{\begin{array}{c} \langle f|\hat{Q}g\rangle = \langle\hat{Q}f|g\rangle \quad \forall f, g \\ or \int f^*\hat{Q}g\,d^3r = \int\hat{Q}^*f^*g\,d^3r \end{array}}$$

Observables are represented by hermitian operators! All of the physical operators we use and meassure are Hermitian(Real values). This includes:

- Note: If $\hat{A}$ and $\hat{B}$ are hermitian, $\hat{A}\hat{B}$ is only hermitian if $[\hat{A}, \hat{B}] = 0$
- $\hat{N} \equiv \hat{a}_+\hat{a}_-$ which defines Quantity of QUANTA in H.O, it includes $\hat{\Pi}$ but does not include $\hat{a}_-$ or $\hat{a}_+$ alone or S_+ or S_- or $\hat{T}_r$ or $\hat{R}_n$
- Eigenstates of a Hermitian operator are orthogonal if they have different eigenvalues.
- Eigenstates of hermitian operators form a complet set/basis in the hilbert space. You only need the eigenstates to understand what the operator does (Linear combination).
- Hermitian operators have only real eigenvalues.

Determinate States

Def: In a determinate state, every measurement of Q is certain to return the same value.
Eigenvalue Equation for hermitian Operator $\hat{Q}$:

$$\boxed{\hat{Q}\Psi = q\Psi} \quad \begin{cases} \Psi: & \text{eigenfunction of } \hat{Q} \\ q: & \text{corresponding eigenvalue} \end{cases}$$

$$\boxed{\text{Determinate states of } Q = \text{Eigenfunctions of } \hat{Q}}$$

- Measurement of Q is certain to yield q (Only if Ψ is already in the Eigenstate Ψ_q
- **Spectrum** := set of all eigenvalues
- Two or more Ψ share the same eigenvalue q $\Rightarrow$ **Degenerate State** $\Rightarrow$ For different quantum states we have the same energy level

Categories of Eigenfunctions of Hermitian Operators

Discrete Spectrum (eigenvalues are seperated)

- Eigenfunctions lie in Hilbert Space, are physically realizable states and are **complete**
- Eigenavlues are **real**
- Eigenfunctions belonging to distinct eigenvalues are **orthogonal**

Examples: Hamiltonian for the HO / ISW

Continous Spectrum (eigenvalues fill out entire range)

- Eigenfunctions are not normalizable, are not in Hilbert Space and do not represent possible physical states
- Eigenfunctions with real eigenvalues are **Dirac-orthonormalizable** and **complete** (sum → integral)

Examples: Hamiltonian for the free particle
Examples for both Discrete and Continous Spectrum:
Finite Wall, Step, Potential (where you have bound and scattering states)

- Eigenstates/functions of $f_{\hat{x}} = \delta(x - q)$ where q the eigenvalue of $\hat{x}$ is. But $\delta(x - q)$ is not in Hilbert Space because its not square-integrable!
- Eigenstates/functions of $f_{\hat{p}} = \frac{1}{\sqrt{2\pi\hbar}}exp(\frac{iqx}{\hbar})$, where q the eigenvalue of $\hat{p}$ is. They dont exist in the hilbert space either.
- Both eigenfunctions are complete! and they obey dirac orthonormality $\langle f_{q_1}|f_{q_2}\rangle = \delta(q_2 - q_1)$. Analog for $\hat{x}$.

Generalized statistical Interpretation

If you measure an Observable $Q(x, p)$ on a particle in state Ψ, you get one of the eigenvalues! The probability of getting EV q_n associated with the eigenfct. $f_n(x)$ is:

$$|c_n|^2 \quad\quad \text{where} \quad c_n = \langle f_n|\Psi\rangle$$

Upon measurement, the wave function **collapses** to the corresponding eigenstate f_n

Generealized Uncertainty Principle

For any Observables A, B:

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

Quantum Meassurement

An observable is defined by a set of orthogonal projection operators(eigenfunctions/eigenstates) in the Hilbert Space.
Note: The first meassurement is always probabilistic
Ensemble: An ensemble consists of a very large number of systems, each constructed to be a replica on the macroscopic level. You measure with ensambles

$[\hat{A}, \hat{B}] = 0$

Which means that the two operators are compatible:

- They two operators have a common eigenbasis
- They have a common set of eigenstates
- It is possible to measure both observables simultaneously with arbitrary precision
- The order of the measurements does not affect the outcome $\hat{A}\hat{B} = \hat{B}\hat{A}$

$[\hat{A}, \hat{B}] \neq 0$

- They two operators do not share common eigenbasis
- They have independent eigenstates
- It is not possible to measure both observables simultaneously with arbitrary precision
- The order of the measurements will affect the outcome $\hat{A}\hat{B} \neq \hat{B}\hat{A}$
- They always have an uncertainty principle

Quantum Mechanics in 3 Dimensions

Momentum Operator $\quad \hat{p} = -i\hbar\nabla$

Hamiltonian: $\quad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\vec{r})$

Schrödinger Equation in 3D

The TDSE in 3 Dimensions denotes as follows:

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

Solving the TDSE in 3D:
$V(\vec{r})$ is time-indep. in general, therefore we can use separable solutions:

$$\Psi_n(\vec{r},t) = \psi_n(\vec{r}) \cdot \varphi(t) = \psi_n(\vec{r}) \cdot \exp(-iE_n t/\hbar)$$

As in 1D, $\psi_n(\vec{r},t)$ is obtained by solving the TISE:

$$\hat{H}\psi_n = E_n\psi_n$$

The Laplacian ∇^2 depends on the coordinate system and $V(\vec{r})$ depends on the problem.

Cartesian Coordinates

In Cartesian coordinates the Laplacian denotes as follows:
$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$
ψ_n can be separated: $\psi_n(x,y,z) = X(x) \cdot Y(y) \cdot Z(z)$

Spherical Coordinates

In Spherical coordinates the Laplacian denotes as follows:
$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)$$
ψ_n can be separated: $\psi_n(r,\theta,\varphi) = R(r) \cdot Y(\theta,\varphi)$
Volume element: $d^3\vec{r} = r^2 \cdot \sin(\theta) \cdot dr d\theta d\varphi$

Important Examples

3D Harmonic Oscillator: $V(r) = \frac{1}{2}m\omega^2 r^2$
cartesian: $\omega^2 r^2 = \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2$
$E_n = \hbar\omega(n_x + n_y + n_z + \frac{3}{2}) \quad n_x, n_y, n_z \geq 0$
3D Infinite square well:
$\psi(x,y,z) = \left(\frac{2}{a}\right)^{\frac{3}{2}}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{a}y\right)\sin\left(\frac{n_z\pi}{a}z\right)$
$E_n = \frac{\hbar^2\pi^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z \geq 1$

Spherical Harmonics

Expectation value

$$\langle Q\rangle = \int_0^\infty\int_0^{2\pi}\int_0^\pi \Psi^* \cdot \hat{Q} \cdot \Psi \cdot r^2\sin(\theta) \cdot d\theta d\varphi dr$$

Angular Equation

$$\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\varphi^2}\right)\right) = -\ell(\ell+1)$$

Which we again solve with: $Y(\theta,\varphi) = \Theta(\theta) \cdot \Phi(\varphi)$

$$\Phi(\varphi) = \exp(i \cdot m_l \cdot \varphi) \qquad \Theta(\theta) = A \cdot P_\ell^{m_\ell}(\cos\theta)$$

$$P_\ell^{m_\ell} := \text{associated Legendre Function}$$

$$\Phi(\varphi) \overset{!}{=} \Phi(\varphi + 2\pi) \Rightarrow m_l = 0, \pm 1, \pm 2, \dots$$

The normalized angular solution are called **Spherical Harmonics $Y_\ell^{m_\ell}$** and are the same for all spherically symmetric potentials. Spherical harmonics are the stationary states or orbitals. Spherical Harmonics are orthogonal, because they are eigenstates of hermitian operators ($\hat{L}^2$ & $\hat{L}_z$):

$$\int_0^{2\pi}\int_0^\pi \left(Y_\ell^{m_\ell}\right)^* \cdot Y_\ell^{m_\ell} \cdot \sin(\theta) \cdot d\theta d\varphi = \delta_{\ell\ell'}\delta_{m_\ell m'_\ell}$$

Radial Equation

The actual shape of $V(r)$ only affects the radial part $R(r)$. Radial Equation denotes as:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right] = \ell(\ell+1)$$

Let $u(r) = r \cdot R(r)$, then radial equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2 u}{dr^2} + \underbrace{\left[V + \overbrace{\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}}^{\text{centrifugal term}}\right]}_{=V_{eff}} \cdot u = E \cdot u$$

Hydrogen(ic) Atom

Consist of a heavy, motionless nucleus with charge $Z \cdot e$ and Z protons and only one electron of charge $-e$ orbiting. **Hydrogen: $Z = 1$ Helium: $Z = 2$**
Potential: $V(r) = -\frac{Ze}{4\pi\epsilon_0 r}$

Allowed Energies: $E_n = \frac{Z^2}{n^2}E_1$

Rydberg-Energy: $E_1 = \frac{-me^4}{32\pi^2\epsilon_0^2\hbar^2} = -13.6 \ eV$

Allowed Radii: $r_n = \frac{n^2}{Z} \cdot a_0 \quad a_0 := \text{Bohr-radius}$

The energies only depend on n. Thus the energies are degenerate with degeneracy $\sum_\ell^{n-1}2(2\ell+1) = 2n^2$
The normalized Radial Equation is given by:

$$R_{n\ell}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-\ell-1)!}{2n((n+\ell)!)^3}}e^{-\rho/2}\rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho)$$

with $\rho = \frac{2r}{na_0}$

$L_{n-\ell-1}^{2\ell+1}$ is a Laguerre polynomial of degree $n - \ell - 1$

If $Z > 1 \rightarrow$ replace a_0 with $\frac{a_0}{Z}$. This leads to the State

$$\psi_{n\ell m_\ell}(r,\theta,\varphi) = R_{n\ell}(r) \cdot Y_\ell^{m_\ell}(\theta,\varphi)$$

This following constraints come out of solving the TISE. We need solutions to be physical (i.e normalizable)

n :	related to the energy	$1, 2, 3, \dots$
ℓ :	related to shape, # ang. nodes	$0, 1, 2, \dots, n-1$
m_ℓ :	related to orientation	$0, \pm 1, \dots, \pm\ell$

How did we solve H-atom problem?: 3D tise $\rightarrow$ assume separable solutions $\rightarrow$ solve radial and angular equation $\rightarrow$ assume separable solutions for angular equations $\rightarrow$ sum up.
The orbital shapes that we know from chemistry (s,p,d, etc) come from the solutions to the angular equation of the hydrogen atom.

Angular Momentum (AM) $\vec{L}$

$$\vec{L} = \vec{r} \times \vec{p} \quad L^2 = L_x^2 + L_y^2 + L_z^2 \quad \hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

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

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

In QM the Operators $\hat{L}_x, \hat{L}_y, \hat{L}_z$ don't commute!

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z \qquad \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x$$

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y \qquad \left[\hat{L}^2, \hat{L}_{x/y/z}\right] = 0$$

Since $\hat{L}^2, \hat{L}_z$ commute, they share the same eigenfunction with the following eigenvalues:

$$\hat{L}^2 \cdot f_\ell^{m_\ell} = \hbar^2\ell(\ell+1) \cdot f_\ell^{m_\ell} \qquad \hat{L}_z f_\ell^{m_\ell} = \hbar m_\ell f_\ell^{m_\ell}$$

$$\Rightarrow |\vec{L}| = \sqrt{\ell(\ell+1)}\hbar \qquad \Rightarrow L_z = m_\ell\hbar$$

These eigenvalue equations in spherical coordinates are equivalent to the angular equation for **spherical harmonics**, therefore we know the solution:
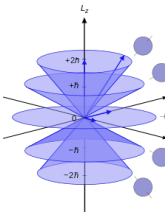
$$f_\ell^{m_\ell} = Y_\ell^{m_\ell}$$

Since $Y_\ell^{m_\ell}$ are eigenfunctions of Hermitian operators (L^2 and L_z) the $Y_\ell^{m_\ell}$ are **orthogonal**.

Visualizsation of Angular Momentum

Math tells us we have an AM-vector with

- $|\vec{L}| = \sqrt{\ell(\ell+1)}\hbar$
- projection along z-axis $|L_z| = m_\ell\hbar$ and the max. value for m_ℓ is $\pm\ell$

Since $\ell < \sqrt{\ell(\ell+1)} \forall\ell$, $\hat{L}_z$ is always smaller than $|\vec{L}|$. Therefore $\vec{L}$ can never be pointing along the z-axis. L_y and L_x can never be both determined, therefore its a cone shape! Angular momenta j_1 and j_2 are **directional = oriented** and **quantized = discrete set**

Spin

$$\hat{S}^2 f_s^{m_s} = \hbar^2 s(s+1)f_s^{m_s} \quad \hat{S}_z f_s^{m_s} = \hbar m_s f_s^{m_s}$$

$$m_s = 0, 1, \dots, \pm(s-1), \pm s$$

Spin is a fundamental conserved quantity carried by elementary particles which does not have any classical counterpart. "Quantum spin explained: Imagine a ball that is rotating, except it's not a ball and it's not rotating". Because elementary particles like electrons do not have a structural value = Volume $\rightarrow$ They are just a particle point $\rightarrow$ They do not have an axis where to rotate $\rightarrow$ it can not rotate (classic idea of rotation).

Each particle in QM has a **FIXED** value of s

Electron: $s = \frac{1}{2}$ Photons $s = 1$

Bosons: particle with integer spin
Fermions: particle with half-integer spin

$$|\vec{S}| = \hbar \cdot \sqrt{s(s+1)} = \sqrt{\frac{3}{4}}\hbar \qquad \hat{S}_z = \hbar \cdot m_s = \pm\frac{1}{2}\hbar$$

Spin & Dirac-Notation

Since the eigenstates of spin are not functions of space, it is convenient to use Dirac-Notation: $f_s^{m_s} \longrightarrow |s, m_s\rangle$

spin-up: $\quad f_{1/2}^{1/2} \rightarrow \left|\frac{1}{2}, \frac{1}{2}\right\rangle \rightarrow |\uparrow\rangle \rightarrow \left(\begin{smallmatrix}1\\0\end{smallmatrix}\right)$

spin-down: $\quad f_{1/2}^{-1/2} \rightarrow \left|\frac{1}{2}, -\frac{1}{2}\right\rangle \rightarrow |\downarrow\rangle \rightarrow \left(\begin{smallmatrix}0\\1\end{smallmatrix}\right)$

General state of χ is given by the linear combination of spin up and spin down:

$$|\chi\rangle = a|\uparrow\rangle + b|\downarrow\rangle = \left(\begin{smallmatrix}a\\b\end{smallmatrix}\right) \quad a, b \in \mathbb{C} \quad \langle\chi|\chi\rangle = 1$$

Normalizing a general spin state:

$$\langle\chi|\chi\rangle = \left(a*\ b*\right)\left(\begin{smallmatrix}a\\b\end{smallmatrix}\right) = a^* \cdot a + b^* \cdot b = 1$$

Hermitian Operators for Spin $s = \frac{1}{2}$:

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

$$\hat{S}_x \rightarrow \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{S}_y \rightarrow \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Only with basis $|\uparrow\rangle$ and $|\downarrow\rangle$. $|\uparrow\rangle$ and $|\downarrow\rangle$ are not eigenfunctions of $\hat{S}_x$ and $\hat{S}_y$ since they do not commute.

Expectation value of $\hat{S}_i$ for $|\chi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$:

$$\langle \hat{S}_i \rangle = \left\langle \chi \middle| \hat{S}_i \chi \right\rangle = (a* \, b*) \cdot \hat{S}_i \cdot \begin{pmatrix} a \\ b \end{pmatrix}$$

Eigenfunctions/-values of $\hat{S}_x$ and $\hat{S}_y$ are calculated by:

$$\hat{S}_{x/y} |?\rangle = \lambda |?\rangle \Rightarrow \det\left(\hat{S}_{x/y} - \lambda \mathbb{I} \right) = 0$$

By measuring $\hat{S}_x$ or $\hat{S}_y$ one can only obtain their eigenvalues. The probability of measuring one eigenvalue is the projection of the general spin state onto the corresponding eigenvector.
Raising/Lowering Operators for Spin:

$$\hat{S}_\pm \left| \tfrac{1}{2}, \mp\tfrac{1}{2} \right\rangle = \hbar \left| \tfrac{1}{2}, \pm\tfrac{1}{2} \right\rangle \text{ raises/lowers } S_z \text{ by } \hbar$$

$$\hat{S}_+ \rightarrow \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \hat{S}_- \rightarrow \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Two-Particle Systems

Ψ is a function of both particles: $\Psi(\vec{r}_1, \vec{r}_2, t)$
Probability that particle 1 is in $d^3\vec{r}_1$ and that particle 2 is in $d^3\vec{r}_2$

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

and

$$\hat{H} = -\underbrace{\frac{\hbar^2}{2m_1}\nabla_1^2}_{\substack{kinetic \\ particle \\ 1}} - \underbrace{\frac{\hbar^2}{2m_2}\nabla_2^2}_{\substack{kinetic \\ particle \\ 2}} + \underbrace{\hat{V}(r_1, r_2)}_{\substack{Potential \\ including \\ particle \\ interaction}}$$

Two Body Problem

Center of Mass $\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$ total Mass $M = m_1 + m_2$

relative distance $\vec{r} = \vec{r}_1 - \vec{r}_2$ reduced mass $m_r = \frac{m_1 \cdot m_2}{m_1 + m_2}$

Separates $\psi(\vec{r}_1, \vec{r}_2)$ into $\psi = \psi_R(\vec{R}) \cdot \psi_r(\vec{r})$

Distinguishability

In Quantum Mechanics, any two identical particles (eg. two electrons) are indistinguishable. Which means we have no way to tell them apart, they are exactly the same!
If particles are **distinguishable** (Proton and an electron), then

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

If particles are **indistinguishable**, then

$$\begin{cases} \psi_+(\vec{r}_1, \vec{r}_2) = C\left[\psi_a(\vec{r}_1) \cdot \psi_b(\vec{r}_2) + \psi_b(\vec{r}_1) \cdot \psi_a(\vec{r}_2)\right] \\ \psi_-(\vec{r}_1, \vec{r}_2) = C\left[\psi_a(\vec{r}_1) \cdot \psi_b(\vec{r}_2) - \psi_b(\vec{r}_1) \cdot \psi_a(\vec{r}_2)\right] \end{cases}$$

$\Rightarrow$ solution is a linear combination

Exchange symmetry

Exchange operator $\hat{P}$ $\rightarrow$ Exchanges particles (flips the particles)

$$\hat{P}f(\vec{r}_1, \vec{r}_2) = f(\vec{r}_2, \vec{r}_1) \qquad \left[\hat{P}, \hat{H}\right] = 0$$

- $\hat{H}$ and $\hat{P}$ are compatible and share the same eigenfunctions ψ_+ and ψ_-
- $\left[\hat{P}, \hat{H}\right] = 0$, $\psi_\pm$ are stationary states and therefore $\hat{P}$ is a conserved quantity.
- In $\psi_\pm$ particles are closer for ψ_+ and further away for ψ_-
- $\psi_\pm$ have different energies $\rightarrow$ exchange force / exchange interaction, which is not a real force

ψ_+ is symmetric w.r.t. exchange of particles

$$\hat{P}\psi_+ = +1\psi_+$$

ψ_- is antisymmertic w.r.t. exchange of particles

$$\hat{P}\psi_- = -1\psi_-$$

Axiom:
The symmetry of the overall wavefunction for identical

$$\left\{ \begin{array}{l} \text{bosons (integer spin)} \\ \text{fermions (half integer spin)} \end{array} \right\} \text{ is } \left\{ \begin{array}{l} \text{symmetric} \\ \text{antisymmertic} \end{array} \right\}$$

w.r.t to exchange of any two particles.

| Overall Wavefunction: $= \psi_\pm(r) \cdot \chi(s)$ |

Possible combinations of $\chi(s)$:

$$\begin{cases} \text{both spin up} & \uparrow\uparrow \\ \text{both spin down} & \downarrow\downarrow \\ \text{one up or down} & \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \text{ or } \overbrace{\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)}^{\text{antisymmetric}} \end{cases}$$

- 3 symmetric combinations (**Triplet**) $S = 1$

- 1 antisymmetric combination (**Singlet**) $S = 0$

The singlet and triplet states have different energies. The overall wavefunction for electrons (fermions) has to be antisymmetric, so there are two posibilities:

$$\psi_+ \cdot (\text{Singlet}) \qquad \psi_- \cdot (\text{Tripplet})$$

The Electron in the H_2 Atom in the ground state is:
$\psi_+ \cdot (\text{Singlet})$, As ψ_+ leads to bonding in H_2

Pauli's Exclusion Principle

Two identical <u>fermions</u> can never be in the exact same state (same n, ℓ, m_ℓ, m_s) and stil have an antisymmetric wavefunction. (if Example two electrons if $\psi_a = \psi_b$:
$\psi_-(r_1, r_2) = A[\psi_a(r_1)\psi_a(r_2) - \psi_b(r_1)\psi_b(r_2)] = 0$
ψ_a or $\psi_b = \psi^{a/b}_{\,n,l,m_l,m_s}$

At the end we get:

$$\psi_{n,l,m_l,m_s} = A \cdot R_{n\ell}(r) \cdot Y_\ell^{m_\ell}(\theta, \varphi) \cdot |s, m_s\rangle$$

Overall Wavefunction contains most of the eigenfunctions of the differents operators, we can meassure the operator into the overall wavefunction.

Atoms

$$\hat{H} = \sum_{i=1}^{Z} \underbrace{\frac{-\hbar^2}{2m}\nabla_i^2}_{E_{kin}} - \underbrace{\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_i}}_{\substack{\text{interaction} \\ \text{w. nucleus}}} + \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\underbrace{\sum_{\substack{k=1 \\ k \neq i}}^{Z}\frac{e^2}{|r_i - r_k|}}_{\substack{\text{repulsive interaction} \\ \text{between electron } i \text{ and } k}}$$

Neglecting electron interaction, each electron is in a single-particle hydrogenic orbital state Y_{n,ℓ,m_ℓ,m_s}

QN	Designates	Notation
n :	shell of orbital	$1\rightarrow K, 2\rightarrow L, 3\rightarrow M, 4\rightarrow N$
ℓ :	subshell of orbital	$0\rightarrow s, 1\rightarrow p, 2\rightarrow d, 3\rightarrow f$
m_ℓ :	orientation of orbital	
m_s :	spin state	$m_s = \pm\frac{1}{2}$

| n	shell	subshell	# orbitals	# electrons per subshell	per shell
1	K	s	1	2	$\Rightarrow 2$
2	L	s	1	2	$\Rightarrow 8$
		p	3	6	
3	M	s	1	2	$\Rightarrow 18$
		p	3	6	
		d	5	10	
4	N	s	1	2	$\Rightarrow 32$
		p	3	6	
		d	5	10	
		f	7	14	

orbitals per subshell: $2\ell + 1$, per shell: n^2
The case for one electron, the energy only depend on the main shell (n), because there is no interaction between atoms

$$E_n = \frac{-1}{n^2}\left[\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\right]$$

Where the energy only depends on the number of protons Z in the nucleus, we get n^2 degenerate states of energy which get $2n^2$ if we include spin

Filling order

Orbitals fill according to their energy increasingly.

For multielectron hydrogenic states, the energy depends not only on n (energy is **not** degenerate in a shell) because of **screening effects** and $e^- - e^-$ repulsion. The bigger ℓ the more far away from the nucleus
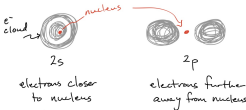
| Energy raises with ℓ in multielectron atoms |

Electronic Configuration:
Argon: $Z = 18$
$$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$$
Iron: $Z = 26$
$$[Fe] = [Ar]\,4s^2 3d^6$$
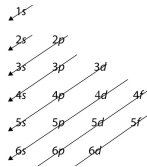
Attention: Exception for nearly (half)full subshells

Chrome: $Z = 24$ $[Cr] = [Ar]\,4s^1 3d^5$

Copper: $Z = 29$ $[Cu] = [Ar]\,4s^1 3d^{10}$

Angular Momentum in Multielectron Atoms

$$\begin{cases} L : \text{ total orbital AM} & M_L = \sum_i m_{\ell,i} \\ S : \text{ total spin AM} & M_S = \sum_i m_{s,i} \\ J : \text{ total AM} & M_J = M_L + M_S \end{cases}$$

All total AM are conserved quantities. Filled subshells never contribute to L, S, J! Unit $= [\hbar]$

| **Addition rule for AM:** $J = j_1 \oplus j_2$ |
| $J = (j_1 + j_2), \ldots, |j_1 - j_2|$ |

Term Symbols
Different combinations of AM lead to different states, which are labeled by Term Symbols. Considering an Atom with x Electrons in partially filled subshells:

$$\boxed{^{2S+1}L_J}$$

$$L = \ell_1 \oplus \ell_2 \oplus \ldots \oplus \ell_x$$

$$L = 0 \rightarrow S \qquad S = s_1 \oplus s_2 \oplus \ldots \oplus s_x$$

$$L = 1 \rightarrow P \qquad J = L \oplus S$$

$$L = 2 \rightarrow D$$

$$L = 3 \rightarrow F \qquad$$ Addition rule for AM does not care about symmetry, so not all states are antisymmetric overall as required for fermions

$$L = 4 \rightarrow G$$

To determine ground state (lowest E), we can use:

Hund's rules

① State with largest S is the most stable

② For states with same S, largest L is most stable

③ For states with same S and L:

  smallest J is most stable for subshells $\leqslant$ half full

  largest J is most stable for subshells $>$ half full
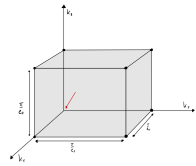
Solids

Free Electron Model

Solid is treated as a 3D-Particle in a box. Therefore its energies are given by:

$$E_{n_x,n_y,n_z} = \hbar^2/2m\,(n_x^2\pi^2/l_x^2 + n_y^2\pi^2/l_y^2 + n_z^2\pi^2/l_z^2)$$
$$= \hbar^2/2m\,(k_x^2 + k_y^2 + k_z^2) = \hbar^2/2m \cdot k^2$$

k-space

k's are the wave vectors of the wave functions. In k-space we can form an equally spaced lattice:

Each point represents a specific n_x, n_y, n_z-combination

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

The highest occupied energy level is called **Fermi-level**. The wavevector of the Fermi-level, k_F, is found by:

$$\left\{\begin{array}{c}\text{Total Volume}\\\text{of occupied}\\\text{states in k-space}\end{array}\right\} = \left\{\begin{array}{c}\text{Total number}\\\text{of electrons}\end{array}\right\} \cdot \frac{1}{2} \cdot \left\{\begin{array}{c}\text{Volume in}\\\text{k-space per}\\\text{electronic state}\end{array}\right\}$$

1D case: $\qquad k_F = Nq \cdot \frac{1}{2} \cdot \frac{\pi}{L}$

2D case: $\qquad \frac{1}{4}\left[\pi k_F^2\right] = Nq \cdot \frac{1}{2} \cdot \frac{\pi^2}{A}$

3D case: $\qquad \frac{1}{8}\left[\frac{4}{3}\pi k_F^3\right] = Nq \cdot \frac{1}{2} \cdot \frac{\pi^3}{V}$

$q :=$ # valence electrons $\qquad N :=$ # of atoms $\approx N_A$

The Fermi-Energy is determined by k_F: $E_F = \frac{\hbar^2}{2m}k_F^2$

1D: $E_F = \frac{1}{8m}\left(\hbar\pi\frac{Nq}{L}\right)^2$

2D: $E_F = \frac{\hbar^2\pi}{m}\frac{Nq}{A} = \frac{\hbar^2\pi}{m}\sigma$

3D: $E_F = \frac{\hbar^2}{2m}\left(3\pi^2\frac{Nq}{V}\right)$

In 3D the amount of atoms per volume can be calculated by: $\frac{N}{V} = \frac{N_A\rho}{M}$ The Number of $1e^-$ levels per unit energy is given by:

$$D(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E} \quad \textbf{density of energy}$$

Energy spacing at Energy E: $\Delta E = [D(E)]^{-1}$

Insulators and semi-conductors

Solid has a periodic potential: $V(x) = V(x+a)$

Bloch's Theorem: $\psi(x+a) = e^{iKa}\psi(x) \quad K \in \Re$

Where a is the lattice spacing of the solid.

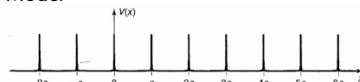$$|\psi(x+a)|^2 = |\psi(x)|^2 \Rightarrow |\psi(x)|^2 \text{ is perdiodic!}$$

Periodic boundary conditions for solid with N-Atoms:

$$\psi(x + Na) = \psi(x) \Rightarrow \psi(x) = e^{iKNa}\psi(x)$$
$$\Rightarrow e^{iKNa} = 1 \Rightarrow K = \frac{2\pi}{Na} \cdot j,\; j = 0, \pm 1, \ldots$$

Potential Models (1 dimensional)
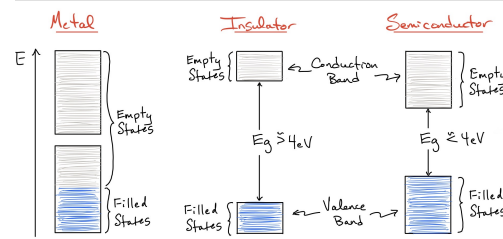
Dirac-Comb Model

Dirac-Comb Potential writes $V(x) = \alpha \sum_{j=0}^{N-1} \delta(x \pm ja)$

Solving TISE in one "cell" (ISW for $0 < x < a$) and applying Bloch's Theorem, leads to the equation:

$$\underbrace{\cos(Ka)}_{\in[-1,1]} = \underbrace{\cos(ka) + \frac{m\alpha}{\hbar k} \cdot \sin(ka)}_{\text{exceeds the range }[-1,1]}$$

For the eqution to hold, only certain ranges of ka are allowed and since $k \propto E$, only **certain ranges of Energy** are allowed $\Rightarrow$ Bands of allowed energies and Gaps:

Highest occupied band (valance-band) is filled. It's separated by a band-gap from the 1st empty band (conduction band)

- $E_g \geqslant 4eV$: Insulator
- $E_g < 4eV$: Semi-conductor

To get an Insulator/Semi-Cond. to conduct, we need to excite an electron from the VB to the CB

Thermally: $\qquad$ **Optically:**
$n_e = N_i \cdot \exp\left(\frac{-E_g}{k_B T}\right) \qquad$ if $E_p = h\nu \geqslant E_g$
only effective if $k_B T \approx E_G$ 1 Photon can excite 1 e^-

Perturbation Theory

Idea: Try to relate a more complicated problem to one we already know how to solve We can write the new Hamiltonian as:

$$\boxed{\hat{H}_{new} = \hat{H}^{(0)} + \lambda \cdot \hat{H}'}$$

$\hat{H}_{new}$ what we want
$\hat{H}^{(0)}$ what we can solve
λ Tunable parameter
$\hat{H}'$ Perturbation

We want to solve: $\qquad \hat{H}\psi_n = E_n\psi_n$

We already solved: $\qquad \hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$

Energies and wavefunctions can be written as second-oder powerseries in λ:

$$E_n = E_n^{(0)} + \lambda \cdot E_n^{(1)} + \lambda^2 \cdot E_n^{(2)}$$
$$\psi_n = \psi_n^{(0)} + \lambda \cdot \psi_n^{(1)} + \lambda^2 \cdot \psi_n^{(2)}$$

Non-Degenerate Perturbation Theory $E_n^{(0)} \neq E_m^{(0)}$

For non-degenerate eigenstates, tho following holds:
1st-Order Energy-Correction $E_n^{(1)}$ where $\psi_n^{(0)}$ is the unperturbed eigenfunction

$$E_n^{(1)} = \left\langle \psi_n^{(0)}\middle|\hat{H}'\psi_n^{(0)}\right\rangle$$

1st-Order Wavefunction-Correction $\psi_n^{(1)}$
Because $\psi_n^{(0)}$ form a complete set, we can express $\psi_n^{(1)}$ in terms of basis $\psi_m^{(0)}$:

$$\psi_n^{(1)} = \sum_{m \neq n} C_{mn}\psi_m^{(0)} \qquad C_{mn} = \frac{\langle\psi_m^{(0)}|\hat{H}'\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

Leaving out $m = n$ since $\psi_n^{(0)}$ is already included, because $\psi_n^{(1)}$ is defined:
$$\psi_n^{(1)} = \psi_n^{(0)} + \lambda \cdot \psi_n^{(1)} + \lambda^2 \cdot \psi_n^{(2)}$$

2nd-Order Energy-Correction $E_n^{(2)}$

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

Degenerate Perturbation Theory $E_n^{(0)} = E_m^{(0)}$
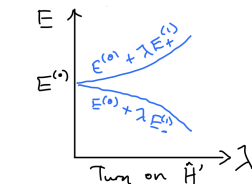
Given the degenerate unperturbed eigenstates to the same eigenvalue $\left.\begin{array}{c}\hat{H}^{(0)}\psi_a^{(0)} = E^{(0)}\psi_a^{(0)}\\\hat{H}^{(0)}\psi_b^{(0)} = E^{(0)}\psi_b^{(0)}\end{array}\right\}$ Equal energy

Any linear combination $\psi^{(0)} = \alpha\psi_a^{(0)} + \beta\psi_b^{(0)}$ is also an eigenfunction $\Rightarrow$ problem Following same linear combination one gets:
1st-Order Energy-Correction $E^{(1)}$

$$E_\pm^{(1)} = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4W_{ab}^2}\right]$$

Where $W_{ij} = \langle\psi_i^{(0)}|\hat{H}'\psi_j^{(0)}\rangle$ and $\psi_i^{(0)}$ the unperturbed, degenerate eigenstates.

Perturbation splits the degeneracy and the two states no longer have the same energy if $\lambda \neq 0$

Finding $E^{(1)}$ is equivalent to finding eigenvalues of W-matrix:
$$\begin{bmatrix}W_{aa} & W_{ab}\\W_{ba} & W_{bb}\end{bmatrix}\begin{pmatrix}\alpha\\\beta\end{pmatrix} = \mathsf{E}^{(1)}\begin{pmatrix}\alpha\\\beta\end{pmatrix}$$

Variational Principle

We pick a normalized trial function ψ_{trial}

$$\boxed{E_{gs} \leqslant \langle\psi_{trial}|\hat{H}\psi_{trial}\rangle = \langle H\rangle}$$

The expectation value of $\hat{H}$ is an upper bound for the actual ground state energy. But it relies on our choice of a good guess of ψ_{trial}
To make this method useful: We should add adjustable parameters to ψ_{trial} and use these parameters to minimize $\langle H\rangle$ and get close as possible to E_{gs}

Perturbation Theory vs Variational Principle

Perturbation Theory

- Know answer to similar problem
- Gives corrections to E_n and ψ_n
- Language to look for is:
  - Estimate to first order...
  - Consider the perturbation

Variational Principle

- No need to know anything
- Gives estimate of E_{gs}
- Language to look for is:
  - Estimate E_{gs}...
  - Use trial function...

Symmetries and Transformations

Unitary Matrix: $\hat{U}^\dagger = \hat{U}^{-1}$ where $\hat{U}^\dagger = (\hat{U}^\star)^T$

Hermitian Matrix: $\hat{U}^\dagger = \hat{U}$

Diagonalize $\hat{H}$: $\det\left(\hat{H} - E\mathbb{I}\right) = 0 \rightarrow \hat{H}_{diag} = \hat{U}\hat{H}\hat{U}^\dagger$
Where the columns of $\hat{U}$ are the eigenvectors of $\hat{H}$ described in the non-diagonalized basis.

Transfomations

To change basis, $\hat{U}$ does Unitary Transform. $\hat{U}$ operates on ket & $\hat{U}^\dagger$ operates on bra. If $\hat{U}$ is hermitian is operates on both!
$\hat{U}\,|\psi_{old}\rangle = |\psi_{new}\rangle \quad \langle\psi_{old}|\,\hat{U} = \langle\psi_{new}|$
Translation: Lin. Momentum is generator of Translat. Translation operator is unitary but not Hermitian

$$\hat{T}(a)\psi(x) = \psi(x-a) \;\Rightarrow\; \hat{T}(a) = \exp(-ia/\hbar\hat{p})$$
$$\hat{x}' = x + a \qquad\qquad \hat{p}' = \hat{p}$$

Rotation: Ang. Momentum is generator of Rot. Rotation operator is unitary but not Hermitian

$$\hat{R}_z\psi(r,\theta,\phi) = \psi(r,\theta,\phi-\varphi) \Rightarrow \hat{R}_z = \exp\left(-i\varphi\hat{L}_z/\hbar\right)$$

For central potentials (Hydrogenic atom), eigenstates are uniquely specified b $\hat{H}.\hat{L}_n, \hat{L}^2$ (neglecting spin). These are known as a complete set of compatible observables.
Inversion: Parity Operator $\hat{\Pi}$ inverts Coordinates Parity operator is unitary and Hermitian

$$\hat{\Pi}\psi(\vec{r}) = \psi(-\vec{r}) \;\Rightarrow\; \hat{\Pi}\hat{Q}(\vec{r},\vec{p}) = \hat{Q}(-\vec{r},-\vec{p})\;\forall\hat{Q}$$
$$\hat{x}' = -x \qquad\qquad \hat{p}' = -\hat{p}$$

Translation in time: Time operator $\hat{U}(t)$

$$\hat{U}(t) = \exp\left(\frac{-it}{\hbar}\hat{H}\right)$$

$\hat{H}$ is generator of translations in time

Symmetry

$$\hat{H}' = \hat{Q}^\dagger \hat{H}\hat{Q} = \hat{Q} \quad\Rightarrow\quad \left[\hat{H},\hat{Q}\right] = 0$$

$\hookrightarrow$ For Symmetry, the according operator needs to commute with the Hamiltonian! Symmertry is the source of most degeneracy in QM
Translational Sym. ($[\hat{H},\hat{T}_r] = 0$) implies:
$V(x) = V(x+a)$
$\hookrightarrow$ implies Momentum Conservation
Inversion Sym. ($[\hat{H},\hat{\Pi}] = 0$) implies: $V(\vec{r}) = V(-\vec{r})$
$\hookrightarrow$ implies Parity Conservation (states remain even/odd)
Rotational Sym. ($[\hat{H},\hat{R}_n] = 0$) implies: $V(\vec{r}) = V(r)$
$\hookrightarrow$ implies Ang. Mom. Conserv. (due to rot. invariance)
Time-translation in variance ($\frac{\partial\hat{H}}{\partial t} = 0$) implies:
$\hookrightarrow$ Energy conservation (Generalized Ehrenfest's Theorem

Degeneracy and Symmetry

Quote: Symmetry is source of most degeneracy (except accidental degeneracies) in QM

Degeneracy requires at least two sets of compatible observables, which means:
$[\hat{H},\hat{Q}_1] = 0$, $[\hat{H},\hat{Q}_2] = 0$, $[\hat{Q}_1,\hat{Q}] \neq 0$
$\rightarrow \hat{H}\,|\Psi_n\rangle = E_n\,|\Psi_n\rangle \rightarrow \hat{Q}_1\,|\Psi_n\rangle = E_n\,|\Psi_n\rangle$ with Ψ_n being eigenfunction of $\hat{H}$ and $\hat{Q}_1$.
But
$\rightarrow \hat{H}\hat{Q}_2\,|\Psi_n\rangle = \hat{Q}_2\hat{H}\,|\Psi_n\rangle = E_n\hat{Q}_2\,|\Psi_n\rangle = E_n\,|\chi\rangle \rightarrow \hat{H}\,|\chi\rangle = E_n\,|\chi\rangle$
χ being also eigenfunction of $\hat{H}$ and $\hat{Q}_2$
States $|\Psi_n\rangle, |\chi\rangle$ are distinct with same energy $E_n \Rightarrow$ Degenerate
$\Rightarrow$ Multiple non-commuting symmetry operators = Energy degeneracy

Dirac's Delta and Kronecker Delta

$$\delta(x-a) := \begin{cases} \infty & x = a \\ 0 & x \neq a \end{cases} \quad a \in [0,\infty) \quad \delta \notin \mathcal{H}$$

$$\int_0^\infty \delta(x-a)\,dx = 1 \qquad \int_0^\infty g(x)\delta(x-a)\,dx = g(a)$$

Dirac Orthonormality:
$\rightarrow \int_{-\infty}^\infty g_{x'}g_{x''} = \int_{-\infty}^\infty \delta(x-x')\delta(x-x'') = \delta(x''-x')$
$\rightarrow \langle g_{x'}|g_{x''}\rangle = \delta(x''-x')$
Kronecker orthonormality/ortholormality:
$\rightarrow \int_{-\infty}^\infty f_m f_n = \delta_{mn}$
$\rightarrow \langle f_m|f_n\rangle = \delta_{mn}$