Cheatsheet

Quantum Mechanics

Version: 18. Juli 2023

Introduction to Quantum Mechanics for Engineers

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

Harmonic Oscillator (HO)

$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$

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

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

$[\hat{a}_-, \hat{a}_+] = 1$ $\hat{p} = \hbar\frac{\partial}{\partial x}$

This yields the Hamiltonian for the HO:

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

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

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

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

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

If ψ_0 satisfies the TISE with Energy E_n, then

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

$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{m\omega}{2\hbar}x^2\right)$ $E_0 = \frac{1}{2}\hbar\omega$
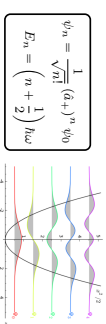
Normalization constant $\frac{1}{\sqrt{n!}}$ follows directly from:

- Energy is quantized (QM)
- even at 0Kelvin the H.O still vibrates and has energy = Zero Point Energy (QM)
- $E_0 = 0$: Zero Point Motion
- $\langle x \rangle = 0$ particle can lay outside the potential even if $V_0 \approx 0$, always 1 bounded State (at least)
- Because $V(x) \neq \infty$ particle has some wave-symmetry in the E-axis
- At the classical Turning Points (CTP): $KE = 0 \Rightarrow$ to 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

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

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

$\langle x^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$ or   Variance

$\Sigma(j - \langle j \rangle)^2 P(j)$

$\sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ Standard deviation

$\langle j \rangle = \Sigma j P(j)$ Average

$\langle j^2 \rangle \geq \langle j \rangle^2$ In general

The Wave Function

$\Psi(x, t)$:

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

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

Operators

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

$E_{kin} = \frac{1}{2}mv^2 = \frac{p^2}{2m}$

The quantity Q of interest is called *Observable*. $\hat{Q}$ denotes the *Operator* for that Observable. Every observable

Location Operator:

$\hat{x} = x = x^*$

Momentum Operator:

$\hat{p} = -i\hbar\frac{\partial}{\partial x} = -i\frac{1}{i}$

Ehrenfest's Theorem:

Remember: $\langle p \rangle = m \cdot \frac{d\langle x \rangle}{dt} = m \cdot \langle v \rangle$

$\langle p^2 \rangle = p^2 = \frac{-\hbar^2\partial^2}{\partial x^2}$

$\hat{L} = \vec{r} \times m\vec{v} = \vec{r} \times \vec{p}$

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 $\left(\frac{\partial^2}{\partial x^2}\right)$

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

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

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 is conserved in quantity.

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

Time-Independent Schrödinger Equation (TISE)

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

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

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

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

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

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:

$|\Psi(x, t)|^2 = \Psi^*\Psi = |\psi(x)|^2$

Additionally, every expectation value is constant in time:

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

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. $\Rightarrow$ **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.
- $\sum_n |c_n|^2 = 1$ and $\langle H \rangle = \sum_n |c_n|^2 E_n$.
- $\langle H \rangle$ CAN be < 0 (For example in the ground state of the hydrogen Atom -13.6eV)

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

General solution (applicable for various problems):

standing wave/no sw $\psi(x) = A\sin(kx) + B\cos(kx)$

travelling wave/pw $\psi(x) = A \cdot e^{ikx} + B \cdot e^{-ikx}$

Combination of both: Finite Potential Walls

Free Particle

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

$\boxed{V(x) = 0}$

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

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

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

$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^\infty \phi(k)e^{ikx}dx$

$\phi(k)$ Shape Function

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Finite Potential Step

consider incoming wavepacket

- $E > V_0$: transmitted & reflected*
- $0 < E < V_0$: reflection & penetration* into barrier
- $E < V_{max}$: 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

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

Quantum Mechanical Tunneling:

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

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 normalized. If both applies, then Ψ lives in **Hilbert-Space** $\mathcal{H}$ and can also be represented as a vector.

Dirac Notation:

$\Psi = \sum_n c_n\psi_n$ $\Rightarrow$ $\Psi = (c_1, c_2, \ldots, c_n)^T = |\Psi\rangle$

$\Psi^* = \sum_n c_n^*\psi_n^*$ $\Rightarrow$ $(c_1^*, c_2^* \ldots c_n^*) = \langle\Psi|$

Note1: $\langle\alpha|\Psi\rangle = \langle\alpha, \Psi\rangle$ $|\beta \cdot \Psi\rangle = \beta \cdot |\Psi\rangle$

The inner product of two functions is defined as follows:

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

A set of functions f_n are ...

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

Hermitian Operators

Requirement for an Operator to be Hermitian:

$\langle f|\hat{Q}g \rangle = \langle\hat{Q}f|g \rangle \quad \forall f, g$

$or \int f^*\hat{Q}g d^n r = \int g\hat{Q}^*f^*g d^n r$

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

- Note: If $\hat{A}$ and $\hat{B}$ are hermitian, $\hat{A}\hat{B}$ is only hermitian if $[\hat{A}, \hat{B}] = 0$
- $\hat{N} = \hat{a}_+\hat{a}_-$ which defines QUANTA of QUANTA in H.O, it includes $\hat{a}$ but does not include $\hat{a}_-$ or $\hat{a}_+$ alone or S_+ or $\hat{r}_+$ or $\hat{R}_\pm$.
- 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 $\hat{Q}$ is certain to return the same value.

Eigenvalue Equation for hermitian Operator $\hat{Q}$:

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

Determinate States of $Q = $ Eigenfunctions of $\hat{Q}$:

- Measurement of $\hat{Q}$ 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**
- Eigenvalues are **real**
- Eigenfunctions belonging to distinct eigenvalues are **orthogonal**

Examples: Hamiltonian for the HO / ISW

Contious Spectrum (eigenvalues fill out entire range)

Normalization:

$\langle f|f \rangle = 1$

Expectation value: $\langle A \rangle = \langle\Psi|\hat{A}\Psi\rangle$

Neither $|$ or $\rangle$ need to be orthogonal to others.

Dirac-orthonormalizable and complete (sum $\to$ 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)

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

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 the EV ψ_n, associated with the eigenfct. f_n (or c_n):

$|c_n|^2$ where $c_n = \langle f_n|\Psi\rangle$

$|c_n|^2 = \langle f_n|\Psi\rangle$

For continous Spectrum: $|c_n|^2 = \langle f_n|\Psi\rangle$

Upon measurement, the wave function **collapse** to the corresponding eigenstate f_n.

Generalized Uncertainity Principle

For any Observables A, B:

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

Quantum Measurement

An observable is defined by a set of orthogonal projection operators(eigenfunctions/eigenstates) in the Hilbert Space.

Note: The first measurement is always probabilistic. Ensamble: An ensamble 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 share the same 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 $\hat{A}\hat{B} = \hat{B}\hat{A}$

Infinite Square Well (ISW)

Infinite potential boundaries at $x = 0$ and $x = a$

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

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

c_n's are obtained by: $c_n = \sqrt{\frac{2}{a}}\int_0^a \sin(k_nx)\Psi(x, 0)dx$

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:

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

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

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

$\psi_n(x) = \sqrt{\frac{2}{a}}\sin(k_nx)$ $E_n = \frac{\hbar^2}{2m}k_n^2$ $k_n = \frac{n\pi}{a}$

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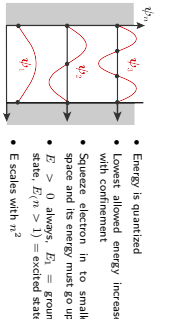
- Energy is quantized
- Lowest allowed energy increases with confinement
- Squeeze electron in to smaller space and its energy must go up!
- $E > 0$ always, $E_1 = $ ground state, $E_i(n > 1) = $ excited state
- E scales with n^2

Commutators

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

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

Identities:

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

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

Common commutators:

$[\hat{x}, \hat{p}] = i\hbar$

$[\hat{x}, \hat{f}(x)] = 0$ $[\hat{p}, \hat{f}(p)] = 0$

$[\hat{H}, \hat{x}] = \frac{\hbar^2}{m}\frac{\partial}{\partial x} = \frac{\hbar}{m}\hat{p}$ $[\hat{x}, \hat{C}] = 0 \, \forall C \in \mathbb{C}$

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

- 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 $\hat{\vec{p}} = -i\hbar\nabla$

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

Schrödinger Equation in 3D

The TDSE in 3 Dimensions denotes as:

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

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:

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

ψ_n can be separated: $\psi_n(r,\theta,\varphi) = R(r) \cdot Y(\theta,\varphi)$

Important Examples

3D Harmonic Oscillator: $V(\vec{r}) = \frac{1}{2}m\omega^2 r^2$

cartesian: $\omega^2 r^2 = \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2$

$E_n = \hbar\omega(n_x + n_y + n_z + \frac{3}{2})$

3D Infinite square well.

$$\psi(x,y,z) = \sqrt{\frac{8}{V}}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{a}y\right)\sin\left(\frac{n_z\pi}{a}z\right)$$

$$E_n = \frac{\hbar^2\pi^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z \geq 1$$

Volume element: $d^3\vec{r} = r^2\sin(\theta) \cdot dr d\theta d\varphi$

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

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

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

$$\Phi(\varphi) = \exp(i \cdot m_\ell \cdot \varphi)$$

$$\Phi(\varphi) = \Phi(\varphi + 2\pi) \Rightarrow m_\ell = 0, \pm1, \pm2, \dots$$

$$\Theta(\theta) = A \cdot P_\ell^{m_\ell}(\cos\theta)$$

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

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

$$Y_\ell^{m_\ell} = \Theta(\theta) \cdot \Phi(\varphi)$$

Radial Equation

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

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

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

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

Hydrogen(ic) Atom

Consist of a heavy, motionless nucleus with charge $Z \cdot e$ and Z protons and only one electron orbiting. Potential: $V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$ **Hydrogen:** $Z = 1$ **Helium:** $Z = 2$

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

$$\hat{L}^2 Y_\ell^{m_\ell} = \hbar^2\ell(\ell+1)Y_\ell^{m_\ell} \quad \hat{L}_z Y_\ell^{m_\ell} = \hbar m_\ell Y_\ell^{m_\ell}$$

These eigenvalue equations in spherical coordinates are equivalent to the angular equation for **spherical harmonics**, therefore we know the solution:

$$Y_\ell^{m_\ell} = Y_\ell^{m_\ell}$$

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

The energies only depend on n. Thus the energies are degenerate with degeneracy $\sum_{\ell=0}^{n-1}1 \cdot 2(2\ell+1) = 2n^2$

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 $0, \pm1, \dots, \pm\ell$

How did we solve H-atom problem?: 3D tise → assume separable solutions → solve radial and angular equations → assume separable solutions for angular equations → 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) $\vec{L}$

$$\hat{\vec{L}} = \vec{r} \times \vec{p} \quad \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

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

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

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

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

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

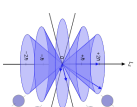$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \quad [\hat{L}^2, \hat{L}_{x/y/z}] = 0$$

Visualization 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. $\hat{L}_y$ and $\hat{L}_z$ can never be both determined, therefore its a cone shape! Angular momenta j_1 and j_2 are quantized.

Introduction to Quantum Mechanics for Engineers

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

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

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

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 $\hat{S}_z$ for $|\chi\rangle = \binom{a}{b}$:

$$\langle S_z \rangle = \langle \chi | \hat{S}_z | \chi \rangle = (a^*, b^*) \cdot \hat{S}_z \cdot \binom{a}{b}$$

Eigenfunctions/-values of $\hat{S}_z$ for $|\chi\rangle$:

$$\hat{S}_{x/y}|?\rangle^2 = \lambda|?\rangle \Rightarrow \det(\hat{S}_{x/y} - \lambda\mathbb{1}) = 0$$

Raising/Lowering Operators for Spin:

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

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

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

$$\hat{H} = -\frac{\hbar^2}{2m_1}\underbrace{\nabla_1^2}_{\substack{\text{kinetic} \\ \text{particle} \\ 1}} - \frac{\hbar^2}{2m_2}\underbrace{\nabla_2^2}_{\substack{\text{kinetic} \\ \text{particle} \\ 2}} + \underbrace{\hat{V}(\vec{r}_1, \vec{r}_2)}_{\substack{\text{Potential} \\ \text{including} \\ \text{interaction}}}$$

Two Body Problem

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

relative distance $\vec{r} = \vec{r}_1 - \vec{r}_2$

total Mass $M = m_1 + m_2$

reduced mass $m_r = \frac{m_1 m_2}{m_1+m_2}$

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

Exchange symmetry

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

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

- $\hat{H}$ and $\hat{P}$ are compatible and share the same eigenfunctions ψ_+ and ψ_-
- $[\hat{P}, \hat{H}] = 0$, ψ_+ are stationary states and therefore $\hat{P}$ is a conserved quantity.
- In ψ_+ particles are closer to ψ_+ and further away for ψ_-
- ψ_+ have different energies → 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 antisymmetric w.r.t. exchange of particles

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

Axiom:

The symmetry of the overall wavefunction for identical
$\left\{\begin{array}{l}\text{bosons (integer spin)} \\ \text{fermions (half integer spin)}\end{array}\right\}$ is $\left\{\begin{array}{l}\text{symmetric} \\ \text{antisymmetric}\end{array}\right\}$
w.r.t to exchange of any two particles

Overall Wavefunction: $\psi_\pm^{tot}(r) \cdot \chi(s)$

Possible combinations of $\chi(s)$:

both spin up $\uparrow\uparrow$

both spin down $\downarrow\downarrow$ $\left.\begin{array}{l} \\ \\ \end{array}\right\}$ symmetric

one up or down $\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$ $S = 1$

$\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$ antisymmetric

- 3 symmetric combinations (**Triplet**) $S = 1$
- 1 antisymmetric combination (**Singlet**) $S = 0$

orbitals per subshell: $2\ell+1$, per shell: n^2

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

$$\psi_+ \cdot \psi_- \text{ (Singlet)} \quad \psi_- \cdot \psi_+ \text{ (Triplet)}$$

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

Two identical fermions can never be in the exact same state (same n, ℓ, m_ℓ, m_s) and still have an antisymmetric wavefunction. (If: Example two electrons if $\psi_a = \psi_b$

$$\psi_-(\vec{r}_1, \vec{r}_2)\chi_a(\vec{r}_1, \vec{r}_2) - \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)] = 0$$

$$\psi_a \text{ or } \psi_b \Rightarrow \psi_-^{tot} = \psi_{n,\ell,m_\ell,m_s}$$

Pauli's Exclusion Principle

At the end we get:

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

Atoms

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

$$\hat{H} = \sum_{i=1}^Z\left[-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_i}\right] + \frac{1}{4\pi\varepsilon_0}\sum_{j<k}^Z\frac{e^2}{|r_j - r_k|}$$

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

QN	Designates	Notation	# orbitals	# electrons per subshell	$m_s = \pm\frac{1}{2}$	per shell
n	shell	$1, K, 2, L, 3, M, 4, N$				
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					

n	shell	ℓ	subshell	# orbitals	# electrons per subshell	per shell
1	K	0	s	1	2	$\Rightarrow 2$
2	L	1	p	3	6	$\Rightarrow 8$
3	M	2	d	5	10	$\Rightarrow 18$
4	N	3	f	7	14	$\Rightarrow 32$

All total AM are conserved quantities. Filled subshells never contribute to L, S, J!

Spin

Spin is a fundamental conserved quantity carried by elementary particles which does not have a real classical counterpart. "Quantum spin explained": Imagine a particle point → They do not have an axis where to rotate → 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

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

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

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

Since the eigenstates of spin are not functions of space, it is convenient to use Dirac-Notation:

spin-up: $f_{1/2}^{1/2} \rightarrow |\frac{1}{2}, \frac{1}{2}\rangle \rightarrow |\uparrow\rangle$

spin-down: $f_{1/2}^{-1/2} \rightarrow |\frac{1}{2}, -\frac{1}{2}\rangle \rightarrow |\downarrow\rangle$

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

$$|\chi\rangle = a|\uparrow\rangle + b|\downarrow\rangle = \binom{a}{b} \quad a, b \in \mathbb{C}$$

Normalizing a general spin state:

$$\langle\chi|\chi\rangle = (a^*, b^*) \cdot \binom{a}{b} = a^* \cdot a + b^* \cdot b = 1$$

Spin & Dirac-Notation

$$\hat{S}^2|s, m_s\rangle = \hbar^2 s(s+1)|s, m_s\rangle$$

$$\hat{S}_z|s, m_s\rangle = \hbar m_s|s, m_s\rangle$$

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 single shell) because of **screening effects** and e^--e^- repulsion. The bigger ℓ the more far away from the nucleus.

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.

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

The case for one electron, the energy only depend on the main shell (n), because there is no interaction between atoms.

Energy raises with ℓ in multielectron atoms.

Angular Momentum in Multielectron Atoms

L : total orbital AM $M_L = \sum_i m_{\ell_i}$

S : total spin AM $M_S = \sum_i m_{s_i}$

J : total AM $M_J = M_L + M_S$

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

$$J = (j_1 + j_2), \dots, |j_1 - j_2|$$

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

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.

Perturbation Theory vs Variational Mechanics for Engineers

Perturbation Theory

Variational Principle

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

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

Symmetries and Transformations

Transformations

Diagonalize $\hat{H}$: $\det(\hat{H} - EI) = 0 \rightarrow \hat{H}_{diag} = \langle \psi_i | \hat{H} | \psi_j \rangle$ Hermitian Matrix: $\hat{U}^\dagger$

Unitary Matrix: $\hat{U}$ $\det(\hat{U}) \neq 0 \rightarrow \hat{U}^{-1} = (\hat{U}^*)^T$

Where the columns of $\hat{U}$ are the eigenvectors of $\hat{H}$ described in the non-diagonalized basis.

→ For Symmetry, the according operator needs to commute with the Hamiltonian! Symmetry is the source of most degeneracy in QM

Translation: Lin. Momentum is generator of Translat. Translation operator is unitary but not Hermitian

$\hat{T}(a)\psi(x) = \psi(x-a) \Rightarrow \quad \hat{T}(a) = \exp(-ia\hat{p}/\hbar)$

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!

$\hat{U}|\psi_{old}\rangle = |\psi_{new}\rangle$ where $\langle \psi_{old}|\hat{U} = \langle\psi_{new}|$

Translation: Lin. Momentum is generator of Translat.

Inversion: Parity Operator $\hat{\Pi}$ inverts Coordinates
Parity operator is unitary and Hermitian

$\hat{\Pi}\psi(\vec{r}) = \psi(-\vec{r}) \Rightarrow \quad \hat{\Pi}\hat{Q}(\vec{r},\hat{p})\hat{\Pi}^{-1} = \hat{Q}(-\vec{r},-\hat{p}) \; \forall \hat{Q}$

$\hat{x}' = -\hat{x} \qquad \hat{p}' = -\hat{p}$

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

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

For central potentials (Hydrogenic atom), eigenstates are uniquely specified b $\hat{H}, \hat{L}_z, \hat{L}^2$ (neglecting spin). These are known as a complete set of compatible observables.

Degeneracy and Symmetry

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

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

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

Translational Sym. ($[\hat{H},\hat{T}_a] = 0$) implies:
$V(x) = V(x+a)$
→ implies Translational Momentum Conservation

Inversion Sym. ($[\hat{H},\hat{\Pi}] = 0$) implies: $V(\vec{r}) = V(-\vec{r})$
→ implies Parity Conservation (states remain even/odd)

Rotational Sym. ($[\hat{H},\hat{R}_n] = 0$) implies: $V(\vec{r}) = V(r)$
→ implies Ang. Mom. Conserv. (due to rot. invariance)

Time-translation in variance ($\frac{\partial \hat{H}}{\partial t} = 0$) implies:
→ Energy conservation (Generalized Ehrenfest's Theorem

Symmetry

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

Degeneracy requires at least two sets of compatible observables, which means:

$[\hat{H},\hat{Q}_1] = 0, [\hat{H},\hat{Q}_2] = 0, [\hat{Q}_1,\hat{Q}_2] \neq 0$

→ $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$, $\hat{Q}_1|\psi_n\rangle = E_n|\psi_n\rangle$ with ψ_n being eigenfunction of $\hat{H}$ and $\hat{Q}_1$.

But:
$\hat{H}\hat{Q}_2|\psi_n\rangle = \hat{Q}_2\hat{H}|\psi_n\rangle = E_n\hat{Q}_2|\psi_n\rangle = E_n|\chi\rangle$

$\hat{H}|\chi\rangle = E_n|\chi\rangle$

Degenerate → Multiple non-commuting symmetry operators = Energy degeneracy

Dirac's Delta and Kronecker Delta

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

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

Dirac Orthonormality:
→ $\int_{-\infty}^\infty g_x g_{x'} = \delta(x-x')\delta(x-x'') = \delta(x-x')$
→ $\langle g_{x'}|g_x\rangle = \delta(x''-x')$

Kronecker orthonormality/orthonormality:
→ $\int_{-\infty}^\infty f_m f_n = \delta_{mn}$
→ $\langle f_m|f_n\rangle = \delta_{mn}$

Symmetry

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

Proofs

Q2: $\hat{H}\Psi(x) \overset{?}{=} E\Psi(x)$
Start with: $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Apply operator: $\hat{p}\Psi(x) = \pi\Psi(x)$
Result: $\hat{p}\Psi(x)$ if $\Psi(x) = Ae^{ikx}$ and $E = \frac{\hbar^2k^2}{2m}$

Q4: $\hat{x}\Psi(x) \overset{?}{=} x\Psi(x)$
Start with: $\hat{x} = x$
Apply operator: $\hat{x}\Psi(x) = x\Psi(x)$
Result: $\hat{x}\Psi(x) = x\Psi(x)$, by definition of position operator.

Q5: $\langle E \rangle \overset{?}{=} \int_{-\infty}^\infty \Psi^*(x)\hat{H}\Psi(x)\,dx$
Start with: $\hat{H}\Psi(x) = E\Psi(x)$
Multiply by $\Psi^*(x)$, integrate: $\int_{-\infty}^\infty \Psi^*(x)|\Psi(x)|^2 dx = \langle x \rangle$
Result: $\langle x \rangle$ by definition of expectation value.

Q7: $[\hat{H},\hat{x}] \overset{?}{=} 0$
Given: $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$, $\hat{x} = x$
Evaluate: $[\hat{H},\hat{x}] = \hat{H}\hat{x} - \hat{x}\hat{H}$
Result: Non-zero (in general), as potential energy V(x) may not commute with momentum.

Q9: $\hat{H}^\dagger \overset{?}{=} \hat{H}$
Start with: $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$
Compute: $\hat{H}^\dagger$
Result: $\hat{H}^\dagger = \hat{H}$, i.e., the Hamiltonian operator is Hermitian. This ensures that the eigenvalues E are real, corresponding to observable energies.

Q10: $\frac{d\langle O\rangle}{dt} \overset{?}{=} \frac{i}{\hbar}\langle[\hat{H},\hat{O}]\rangle + \langle\frac{\partial\hat{O}}{\partial t}\rangle$
Consider: $\frac{d\langle O\rangle}{dt}$
Apply: the product rule and the time-dependent Schrödinger equation.
Calculate: $\frac{d\langle O\rangle}{dt} = \langle\frac{\partial\hat{H}}{\partial t}\hat{O}|\Psi\rangle + \langle\Psi|\hat{O}|\frac{\partial\Psi}{\partial t}\rangle + \langle\Psi|\frac{\partial\hat{O}}{\partial t}|\Psi\rangle$

Q11: $\frac{d\langle p\rangle}{dt} \overset{?}{=} -\langle\frac{dV}{dx}\rangle$
Consider: $\frac{d\langle p\rangle}{dt} = \frac{d}{dt}\langle\Psi|\hat{p}|\Psi\rangle$
Apply: the product rule and the time-dependent Schrödinger equation.
Calculate: $\frac{d\langle p\rangle}{dt} = -\langle\frac{\partial V}{\partial x}\rangle$

Q12: $E_n \overset{?}{=} \frac{\hbar^2k^2}{2m}$
Given: Boundary conditions $\psi(0) = \psi(L) = 0$, and Hamiltonian operator $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$
Result: $\frac{d\langle p\rangle}{dt} = -\langle\frac{\partial V}{\partial x}\rangle$

Q13: $\int_{-\infty}^\infty|\Psi(x)|^2 dx = 1$ Given: $\Psi(x)$ is a solution to the Schrödinger equation.
Consider: The normalization condition for probability.
Integral: $\int_{-\infty}^\infty |\Psi(x)|^2 dx = 1$
Result: The integral should be equal to 1 for the total probability to find the particle anywhere in space is 1.

Q14: $\hat{p}\Psi(x) \overset{?}{=} \pi\Psi(x)$
Given: $\Psi(x) = Ae^{ikx}$, $\hat{p} = -i\hbar\frac{\partial}{\partial x}$
Evaluate: $\hat{p}\Psi(x) = -i\hbar\frac{\partial}{\partial x}Ae^{ikx}$
Result: $\Psi(x) = Ae^{ikx}$ with $p = \hbar k$

Q15: $\langle E \rangle \overset{?}{=} \int_{-\infty}^\infty \Psi^*(x)\hat{H}\Psi(x)\,dx$
Given: $\hat{H}\Psi(x) = E\Psi(x)$
Evaluate: $\langle E \rangle = \int_{-\infty}^\infty \Psi^*(x)E\Psi(x)\,dx = E\int_{-\infty}^\infty |\Psi(x)|^2 dx$
Result: $\langle E \rangle = E$ if $\int_{-\infty}^\infty |\Psi(x)|^2 dx = 1$ (Normalization condition)

Q16: $\hat{H}^\dagger \overset{?}{=} \hat{H}$
Given: $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$
Consider: $\hat{H} = \frac{p^2}{2m} + V(x)$
Calculate: $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \hat{p}^2/2m + V(r)$
Result: $[\hat{L}^2,\hat{H}] = 0$
Therefore, total angular momentum operator $\hat{L}^2$ commutes with Hamiltonian $\hat{H}$.

Q18: $\sigma^2 \overset{?}{=} 0$
$\Rightarrow \langle(\hat{Q} - \langle Q\rangle)^2\rangle = \langle\Psi|(\hat{Q} - q)^2|\Psi\rangle = 0$
$\langle\Psi|(\hat{Q} - q)^2|\Psi\rangle$
By hermicity of $(\hat{Q} - q)$: $\langle(\hat{Q}-q)\Psi|(\hat{Q}-q)\Psi\rangle = 0$
Only true if: $(\hat{Q} - q)\Psi = 0 \Rightarrow \hat{Q}\Psi = q\Psi$

Introduction to Quantum Mechanics for Engineers

To determine the 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 $\leq$ half full
  - largest J is most stable for subshells $>$ half full

$2S+1 L_J$

$L = \ell_1 + \ell_2 \oplus \ell_3 \dots \oplus \ell_R$
$L = 0 \to S$ $S = s_1 \oplus s_2 \dots \oplus s_R$
$L = 1 \to P$ $J = L \oplus S$
$L = 2 \to D$
$L = 3 \to F$
$L = 4 \to G$

Addition rule for AM does not care about symmetry, so not all states are antisymmetric overall as required for fermions

Solids

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

$$E_{n_x,n_y,n_z} = \frac{\hbar^2}{2m}\left(\frac{n_x^2\pi^2}{L_x^2} + \frac{n_y^2\pi^2}{L_y^2} + \frac{n_z^2\pi^2}{L_z^2}\right)$$

Free Electron Model

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 combination n_x, n_y, n_z.
Each solution occupies $\frac{\pi^3}{V}$ of k-space

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

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

1D case: $k_F = N\gamma \cdot \frac{1}{2}\cdot\frac{\pi}{L}$
2D case: $\frac{1}{4}[\pi k_F^2] = N\gamma \cdot \frac{1}{2}\cdot\frac{\pi^2}{V}$
3D case: $\frac{1}{8}[\frac{4}{3}\pi k_F^3] = N\gamma \cdot \frac{1}{2}\cdot\frac{\pi^3}{V}$

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

Potential Models

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

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

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

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

1D: $E_F = \frac{1}{8m}\left(\frac{h\,N\gamma}{L}\right)^2$
2D: $E_F = \frac{h^2\pi}{2m}\cdot\frac{N\gamma}{A} = \frac{h^2\pi}{m}\cdot\sigma$
3D: $E_F = \frac{\hbar^2}{2m}\left(3\pi^2\cdot\frac{N\gamma}{V}\right)^{\frac{2}{3}}$

Insulators and semi-conductors

Solid has a periodic potential.

Bloch's Theorem

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

Where a is the lattice spacing of the solid.

Periodic boundary conditions for solid with N-Atoms:

$\psi(x + Na) = \psi(x) \Rightarrow \psi(x) = e^{iKNa}\psi(x)$
$\Rightarrow e^{iKNa} = 1 \Rightarrow K = \frac{2\pi}{Na}\cdot j, \; j = 0, \pm1,\dots$

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

$$\cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)$$
$\in [-1;1]$ exceeds the range $[-1;1]$

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

Dirac-Comb Model

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

Dirac-Comb Model

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

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

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

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

Optically: if $E_{ph} = h\nu \geq E_g$ only effective if $k_BT \approx E_G$ 1 Photon can excite 1 e^-

Perturbation Theory

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

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

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

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

Degenerate Perturbation Theory $E_n^{(0)} = E_m^{(0)}$

Given the degenerate unperturbed eigenstates to the same eigenvalue
$\hat{H}^{(0)}\psi_a^{(0)} = E^{(0)}\psi_a^{(0)}$
$\hat{H}^{(0)}\psi_b^{(0)} = E^{(0)}\psi_b^{(0)}$ } Equal energy

Any linear combination $\psi = \alpha\psi_a^{(0)} + \beta\psi_b^{(0)}$ is also an eigenfunction ⟹ problem Following same linear combination one gets:

1st-Order Energy-Correction $E^{(1)}$

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

Variational Principle

We pick a normalized trial function ψ_{trial}

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

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}. 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}

Non-Degenerate Perturbation Theory

For non-degenerate eigenstates, the following holds:

1st-Order Energy-Correction $E_n^{(1)}$ where $\psi_n^{(0)}$ is the unperturbed eigenfunction

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

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 $\psi_m^{(0)}$:

$$\psi_n^{(1)} = \sum_{m\neq n} C_{mn}\psi_m^{(0)}$$

$$C_{mn} = \frac{\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

Finding $E^{(1)}$ is equivalent to finding eigenvalues of W-matrix:

$$\begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^{(1)}\begin{pmatrix}\alpha \\ \beta\end{pmatrix}$$

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

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

We want to solve: $\hat{H}\psi_n = E_n\psi_n$
We already solved: $\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$
Energies and wavefunctions can be written as second-order powerseries in λ:

Leaving out $\psi_n^{(1)}$ because $\psi_n^{(1)}$ is already included,
$\psi_n^{(1)} = \psi_n^{(1)} + \lambda\cdot\psi_n^{(1)} + \lambda^2\cdot\psi_n^{(2)}$

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

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