Physics A - Quantum Mechanics

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Those are just the bare minimum things you need to know about Quantum Mechanics, practice many questions to learn the subject

$$E = \hbar\omega \quad \text{and} \quad p = \hbar k$$

1 Wavefunction formulation

1.1 Normalisation

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

Important: only $|\Psi|^2$ has physical significance.

$$\text{Probability density: } P(x,t)\, dx = |\Psi(x,t)|^2 dx$$

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 dx = 1$$

Finding probability of unnormalised wavefunction:

$$P = \frac{\int_a^b |\Psi|^2 dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx}$$

1.2 Travelling wave

A travelling wave represents a free particle whose momentum and energy are known precisely, but whose position is completely unknown.

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

$$\text{For a free particle: } \omega = \frac{\hbar k^2}{2m}$$

$$\Psi(\mathbf{r},t) = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} = Ae^{\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r}-Et)}$$

However, the travelling plane wave form of wavefunction is not square integrable and therefore cannot be normalised.

1.3   Momentum wavefunction

Mathematics: Fourier transform

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k)e^{i(kx-\omega t)}dk$$

This is akin to a weighted linear combination of plane waves.

For t = 0,

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k)e^{ikx}dk$$

Also,

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x)e^{-ikx}dk$$

$g(k)$ is the momentum wavefunction and $|g(k)|^2\,dk$ is the probability that a measurement of the particle's wavenumber will yield a value in the range dk at k.

$g(k)$ is the Fourier transform of $\Psi(x)$. $\Psi(x)$ is the inverse Fourier transform of $g(k)$.

Gaussian distribution:
$$f(x) = e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

with peak at $x = \mu$ and width $= \sigma$

Gaussian integral:
$$\int_{-\infty}^{+\infty} e^{-x^2}dx = \sqrt{\pi}$$

Translation in Fourier transform:
$$F^{-1}[f(k-k_0)] = e^{ika}F^{-1}[f(x)]$$

Scaling in Fourier transform:
$$F^{-1}[e^{-ck^2}] \propto e^{-\frac{x^2}{4c}}$$

Example of Gaussian wavepacket:

$$g(k) = \left(\frac{a^2}{\pi}\right)^{1/4} e^{-a^2(k-k_0)^2/2}$$

Performing Fourier Transform: use substitution to collapse exponent into a square and also completing the square when necessary.

$$\Psi(x) = \left(\frac{1}{\pi a^2}\right)^{1/4} e^{ik_0 x} e^{-\frac{x^2}{2a^2}}$$

1.4 Expectation values and uncertainty

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\Psi(x)|^2 dx$$

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 |\Psi(x)|^2 dx$$

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

For Gaussian wavepacket, $\Delta x \Delta p_x = \frac{\hbar}{2}$ (minimum uncertainty).

In general, Heisenberg's uncertainty principle:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

1.5 Time evolution of wave packet

A general wave packet can be thought of as comprising of a travelling carrier wave multiplied by an envelope.

$$\Psi(x,t) = \underbrace{e^{ik(x-v_pt)}}_{\text{Carrier}} \underbrace{f(x-v_gt)}_{\text{Envelope}}$$

where the **phase velocity**, v_p, is the rate of progression of the carrier's phase front, but its not physical:

$$\boxed{v_p = \frac{\omega}{k}}$$

and the **group velocity**, v_g, is the velocity of the wave packet/envelope:

$$\boxed{v_g = \frac{d\omega}{dk}\Big|_{k_0}}$$

Dispersion relation

$$\omega(k) = \omega(k_0) + \frac{d\omega}{dk}\Big|_{k_0} \delta k + \frac{1}{2}\frac{d^2\omega}{dk^2}\Big|_{k_0} (\delta k)^2$$

$$\delta\omega = v_g \delta k + \underbrace{\frac{1}{2}\frac{d^2\omega}{dk^2}\Big|_{k_0} (\delta k)^2}_{\text{Dispersive term}}$$

If the quadratic term is non-zero, the wave packet disperses meaning it changes shape as it propagates. In contrast, if the dispersion relation is linear, the wave packet does not spread as it propagates.

Example: Time evolution of Gaussian wave packet
The idea is to do the inverse fourier transform of $g(k)$ with the t term. Technique is to use completing the square and substitution to make it into Gaussian integral form.

1.6 Position and momentum representation of wavefunction

Momentum representation is the FT of position representation. $p = \hbar k \Rightarrow k = \frac{p}{\hbar}$ with an extra factor of $\frac{1}{\sqrt{\hbar}}$

$$\Phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x)e^{-ipx/\hbar}dx \quad [\text{FT of } \psi(x)]$$

$$\Psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Phi(p)e^{ipx/\hbar}dp \quad [\text{IFT of } \Phi(p)]$$

where $\Phi(p,t) = \frac{1}{\sqrt{\hbar}}g(\frac{p}{\hbar}, t)$

1.7 Schrodinger's Equation

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

Total energy operator (Hamiltonian): $\hat{E} = i\hbar\frac{\partial}{\partial t}$

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

Kinetic energy operator: $\frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} = -\frac{\hbar^2}{2m}\nabla^2$

The Hamiltonian is the sum of potential and kinetic energy i.e. total energy.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\mathbf{r},t)$$

More succinctly in terms of operators, the Schrodinger's equation becomes:

$$\hat{H}\Psi(\mathbf{r},t) = i\hbar\frac{\partial \Psi(x,t)}{\partial t}$$

1.8 Time-independent wave equation

Potential is a function of position only, independent of time.

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

$$\nabla^2\Psi(\mathbf{r}) = \frac{2m(E - V)}{\hbar^2}\Psi(\mathbf{r})$$

Use separation of variable to solve Schrodinger's equation.

Solution eigenfunction: $\Psi(\mathbf{r},t) = \boxed{\Psi(\mathbf{r})e^{-iEt/\hbar}}$

with corresponding eigenvalue E.

1.9 Probability current

$$\text{Continuity equation: } \nabla \cdot \mathbf{J} + \frac{\partial |\Psi|^2}{\partial t} = 0$$

Probability current:

$$\mathbf{J}(\mathbf{r}, t) = \frac{\hbar}{i} \frac{1}{2m} [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*] = Re\left[\Psi^* \frac{\hbar}{im} \nabla \Psi\right] = Re\left[\Psi^* \frac{\hat{p}}{m} \Psi\right]$$

Derivation, consider:

$$\boxed{J = -\frac{dP}{dt} = -\frac{\partial}{\partial t} \int_V \Psi \Psi^* \, dV}$$

1.10 Solving Schrodinger's equation

1. Set up potential function

2. Find k values for the different regions

$$k = \frac{\sqrt{2m(E - V)}}{\hbar}$$

3. Write down $\Psi(x)$.
   If k is real, obtain oscillatory solution:

$$\Psi(x) = \underbrace{Ae^{ikx}}_{\text{rightward}} + \underbrace{B^{-ikx}}_{\text{leftward}} = A' \sin kx + B' \cos kx$$

   If k is imaginary, obtain evanescent solution:

$$\Psi(x) = Ce^{\kappa x} + De^{-\kappa x}$$

4. Apply boundary conditions

   - Continuity of $\Psi(x)$ [otherwise get infinite momentum]
   - Continuity of $\frac{\partial \Psi(x)}{\partial x}$ [otherwise get infinite acceleration]

5. Normalisation

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1$$

6. Probability flux:

$$\boxed{J = \text{velocity} \times \text{prob} = \frac{\hbar k}{m} |A|^2}$$

$$\text{Reflection amplitude: } r = \frac{k_1 - k_2}{k_1 + k_2}$$

$$\text{Transmitted amplitude: } t = \frac{2k_1}{k_1 + k_2}$$

$$\text{Reflection probability flux: } R = \frac{J_1^-}{J_1^+} = |r|^2$$

$$\text{Transmitted probability flux: } T = \frac{J_2^+}{J_1^+} = |t|^2 \frac{\boldsymbol{k_2}}{\boldsymbol{k_1}}$$

Quantum tunnelling

$$T_1 = |t_1|^2 \frac{\kappa_2}{k_1} \quad \text{and} \quad T_2 = |t_2|^2 \frac{k_1}{\kappa_2}$$

where

$$|t_1|^2 = \left| \frac{2k_1}{k_1 + i\kappa_2} \right|^2 \text{ and } |t_2|^2 = \left| \frac{2i\kappa_2}{k_1 + i\kappa_2} \right|^2$$

$$T = T_1 T_2 e^{-2\kappa_2 a} = \boxed{\left(\frac{4k_1\kappa_2}{k_1^2 + \kappa_2^2} \right)^2 e^{-2\kappa_2 a}} \approx e^{-2\kappa_2 a}$$

On passing through the potential barrier, the wave is attenuated by a factor of $e^{-2\kappa a}$.

Infinite potential well

$$E_n - V_0 = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

where k is quantized, $k_x = \frac{\pi n}{a}$, $k_y = \frac{\pi m}{b}$, k_z ... (in the case of 3D well)

$$\Psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos(k_n x) & \text{for n odd} \\ \boxed{\sqrt{\frac{2}{a}} \sin(k_n x)} & \text{for n even} \end{cases}$$

Interpretations:

1. Allowed energy levels are discrete

2. Quantisation is a direct consequence of confinement

3. Infinite number of bound states for infinite well

4. Lowest allowed energy level is non-zero $\Rightarrow$ zero-point energy

5. The wavefunctions are the eigenfunctions of the Hamiltonian operator with the energies as the associated eigenvalues

6. The wavefunctions of different states n are orthogonal

1.11   Harmonic oscillator

At low enough energies, many systems are close to their ground state and a quadratic approximation may be sufficiently accurate to describe the behaviour of the system. (Expansion to quadratic term in Taylor series)

$$V(x) = \frac{1}{2}m\omega^2 x^2 \quad \text{or} \quad V(r) = \frac{1}{2}m\omega^2 r^2 \text{ (in 3D)}$$

$$\frac{\partial^2 \Psi(x)}{\partial x^2} + \left[\frac{2mE}{\hbar^2} - \frac{m^2\omega^2 x^2}{\hbar^2}\right]\Psi(x) = 0$$

Solving the Schrodinger's equation:

1. **Write the wave equation in dimensionless form**
   Define:
   $$q = x\sqrt{\frac{m\omega}{\hbar}} \quad \text{and} \quad \epsilon = \frac{2E}{\hbar\omega}$$

   Giving:
   $$\frac{\partial^2 \chi(q)}{\partial q^2} + \left[\epsilon - q^2\right]\chi(q) = 0$$

2. **Look at limiting form a $|q| \to \infty$**

   $$\chi(q) \propto e^{-q^2/2}$$

3. **Guess the form of solution**

   $$\chi(q) = H(q)e^{-q^2/2}$$

   Substituting back:

   $$\frac{\partial^2 H}{\partial q^2} - 2q\frac{\partial H}{\partial q} + (\epsilon - 1)H = 0 \quad \text{(Hermite's equation)}$$

   Solved using power series solution and the solution is given by Rodrigue's formula:

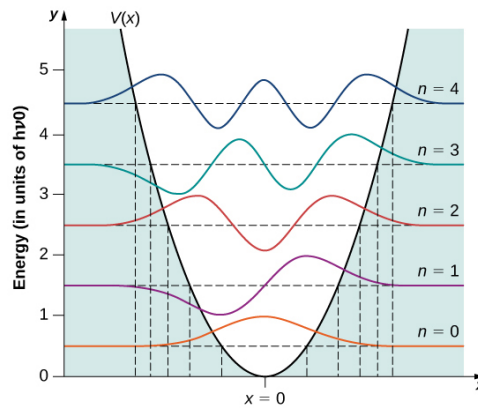 $$H_n(q) = (-1)^n e^{q^2}\frac{d^n}{dq^n}\left(e^{-q^2}\right)$$

   After substitution and observation, will realise that $n = \frac{1}{2}(\epsilon - 1)$ is an integer. Hence, we get the familiar energy levels of a SHO

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

4. **The solution**
   $$\psi_n(x) \propto H_n\left[x\frac{m\omega}{\hbar}\right]e^{-\frac{m\omega}{2\hbar}x^2}$$

5. **Drawing wavefunction**

1. Gaussian shape of ground state wavefunction, symmetry of a few excited states
2. Constant energy level separation, $\hbar\omega$
3. Leaking of wavefunction into classically forbidden region
4. Wavefunction at higher energy has higher amplitude near the edge (transition to classical limit)

1.12   Parity operator

Effect: reflect a wavefunction through the process $x \to -x$ or $\mathbf{r} \to -\mathbf{r}$
i.e. $\theta \to \pi - \theta$ and $\phi \to \phi + \pi$

$$\boxed{\hat{P}\psi_n = (-1)^{n-1}\psi_n}$$

Each allowable wavefunction is an eigenstate of the parity operator, with eigenvalue of $+1$ (even, symmetric) or -1 (odd, antisymmetric).

1.13   Correspondence principle

The correspondence principle states that quantum mechanics predicts the same observational result as classical physics in the limit of large quantum numbers (at high energies).

Extra note:

1. The kinetic energy part of the Hamiltonian can be split into radial part and angular part (similar to orbits):

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2} + \hat{V}$$

where $\hat{L} = l(l+1)\hbar^2$

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2 Some additional information

1. In a well, $\langle p_x \rangle = \langle p_y \rangle = \langle p_z \rangle = 0$ so $\langle p_x^2 \rangle = \Delta p_x^2$ etc...

2. Fewer nodes means lower energies.

3 Tripos Q & A

Q1:
(a) Explain the concept of parity in relation to potentials V(x).
(b) Explain why the ground state must be parity symmetric.

A1:
(a) Kinetic is invariant with respect to parity. For the Hamiltonian to be an eigenstate of the parity operator, $V(x) = V(-x)$.

(b) The ground state has the least energy. All the odd parity functions must have at least one node which raises the kinetic energy term. To minimise kinetic energy, there has to be no node so the ground state is parity symmetric.

4   Operator formulation

$|b\rangle$ is a ket vector. $\langle a|$ is a bra vector (dual vector).

Equivalent expressions for inner products,

$$\langle a|b\rangle = \mathbf{a}^\dagger \mathbf{b} = \int \psi^*(x)\,\phi(x)\,dx$$

If the inner product is taken between states $|\psi\rangle$ and $|\phi\rangle$, it is measuring the overlap between the 2 states. The probability of observing the system to be in state $|\psi\rangle$ given that it was in state $|\phi\rangle$ is given by:

$$\text{Overlap probability} = |\langle\psi|\phi\rangle|^2$$

$$\text{Orthonormal: } \langle a_n|b_n\rangle = \delta_{nm}$$

$$\text{Completeness relations: } \sum_n |a_n\rangle\langle a_n| = \hat{I}$$

$$\text{Vector representation: } |a\rangle = \sum_n a_n |a_n\rangle$$

$$\text{Expansion coefficient: } a_m = \langle a_m|a\rangle \text{ ,projection of } |a\rangle \text{ onto } |a_m\rangle$$

Operators can be represented as matrix

$$\text{Matrix elements of operators: } A_{nm} = \langle u_n| \hat{A} |u_m\rangle$$

Proof:
$$\hat{A}|a\rangle = \hat{I}\hat{A}\hat{I}|a\rangle = \sum_{n,m} |u_n\rangle\langle u_n| \hat{A} |u_m\rangle\langle u_m|a\rangle$$

$$\Rightarrow \hat{A}|a\rangle = \sum_{n,m} |u_n\rangle A_{nm} \langle u_m|a\rangle \quad \text{(Projection)}$$

$$\text{Adjoint: } \langle u_m| \hat{A} |u_n\rangle = \langle u_n| \hat{A}^\dagger |u_m\rangle^*$$

$$\text{Self-adjoint/Hermitian: } \hat{A}^\dagger = \hat{A}$$

$$\hat{A}|\psi\rangle = |\phi\rangle \text{ and } \langle\psi| \hat{A}^\dagger = \langle\phi|$$

All Hermitian operator can be diagonalised by unitary transformation U.

$$U\hat{A}U^\dagger = \text{diag}(\lambda_1, \lambda_2, ...)$$

Checking whether operator is Hermitian/observable

For any observable, there is an associated hermitian operator $\hat{A}$ which denotes the act of measurement.

Observable $\longleftrightarrow$ Hermitian operator.

$$\langle\phi|\,\hat{A}\,|\psi\rangle = \langle\psi|\,\hat{A}\,|\phi\rangle^*$$

$$\int_{-\infty}^{+\infty} \phi^*(x)\hat{A}\psi(x)\,dx = \left[\int_{-\infty}^{+\infty} \psi^*(x)\hat{A}\phi(x)\,dx\right]^* \quad \text{(self-adjoint)}$$

Why are observables represented by Hermitian operators: their expectation values (measured values) are always real.

Proof:
$$\langle A\rangle = \langle\psi|\,\hat{A}\,|\psi\rangle = \langle\psi|\,\hat{A}^\dagger\,|\psi\rangle^* = \langle\psi|\,\hat{A}\,|\psi\rangle^* = \langle A\rangle^*$$

$$\text{Expectation value: } \langle A\rangle = \langle\psi|\,\hat{A}\,|\psi\rangle$$
$$\text{Also: } \langle A^2\rangle = \langle\psi|\,\hat{A}^2\,|\psi\rangle$$
$$\Delta A = \sqrt{\langle A^2\rangle - \langle A\rangle^2}$$

Commutation

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

For a composite operator to be an observable, its individual parts must be observables, and they must commute.

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

$$\hat{p}\hat{x}\,|\psi\rangle = -i\hbar\frac{d}{dx}[x\psi(x)] = \text{.. by parts ..} = -i\hbar\,|\psi\rangle + \hat{x}\hat{p}\,|\psi\rangle$$

Position and momentum do not commute, they do not share eigenbasis, so it is not possible to measure position and momentum without one measurement perturbing the other (uncertainty principle).

Commute $\longleftrightarrow$ compatible: if $\hat{A}$ is known, $\hat{B}$ is known with certainty as well.

$$\text{Anti-commutator: } \hat{C} = \{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A} = \hat{C}^\dagger$$

If $\hat{A}$ and $\hat{B}$ are two non-commuting observables, we can create a composite operator (anti-commutator) that does commute, and so is an observable. We could also do it by multiplying by i.

$$\hat{C} = i[\hat{A}, \hat{B}] = \hat{C}^\dagger$$

Eigenvectors, eigenstates and eigenvalues

When an operator acts on one of its eigenvectors, the eigenvector is returned, scaled by its eigenvalue $\in \mathbb{C}$.

$$\hat{A} \ket{a_n} = a_n \ket{a_n}$$

$$\text{Operator in diagonal form: } \hat{A} = \sum_m a_m \ket{a_m} \bra{a_m}$$

Works by projecting original vector $\ket{a}$ onto the eigenvectors, scaling by the eigenvalues, and then reconstructing the result as a weighted linear combination of eigenvectors.

$$\text{Adjoint: } \hat{A}^\dagger = \sum_m a_m^* \ket{a_m} \bra{a_m}$$

1. If a system is in one of the eigenstates of an observable, the numerical value of a measurement is the eigenvalue, and this value is measured with zero uncertainty.

2. Eigenstates corresponding to different eigenvalues are **orthogonal**.

3. Degenerate eigenstates (share same eigenvalue): two eigenstates can yield the same measurement. Also, any linear combination of degenerate states is also an eigenstate.

Repeated measurements

When an observable is first measured, the wavevector collapses into the eigenstate of the value measured. Multiple repeated measurements yield the same measured value with certainty.

Born's Rule - probability of a measurement

For any general vector $\ket{\psi} = \sum_n c_n \ket{a_n}$, consider the expectation value of an operator:

$$\langle A \rangle = \bra{\psi} \hat{A} \ket{\psi} = \ldots = \sum_n a_n |c_n|^2$$

where $P_n = |c_n|^2 = |\langle a_n | \psi \rangle|^2$ is the probability of measuring the eigenvalue a_n.

Adding wavefunctions

Ensure it is normalised and factor in phase difference $e^{i\alpha}$ as well.
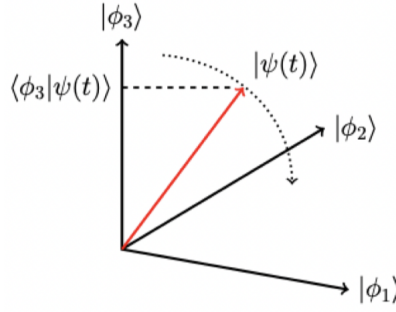
State vectors

Figure 1: A general state vector $|\psi(t)\rangle$ in terms of of the eigenstates $|\phi_n\rangle$ of some operator. The state vector moves around the vector space as time progresses (the coefficient of expansion are functions of time), but then jumps to one of the eigenstates, say $|\phi_3\rangle$ when a measurement is made. The probability of the jump is given by $|\langle\psi|\phi_n\rangle|^2$. The recorded value is the eigenvalue, say a_3. If no further measurement is taking place, the system evolves and the state vector can again start to move around the space. however, if the collapsed eigenvector is an eigenvector of the Hamiltonian operator, the state vector does not move away from it.

4.1 Heisenberg's generalised uncertainty principle

For two observables with operators $\hat{A}$ and $\hat{B}$, they have the following uncertainty relationship:
$$\Delta A \Delta B \geq \frac{1}{2}\left|\left\langle\left[\hat{A},\hat{B}\right]\right\rangle\right|$$
So, if they do not commute (cannot be made to share an eigenbasis) then we cannot know them both simultaneously.

To prove, start by considering,
$$\boxed{|\phi\rangle = \left(\hat{A}_d + i\lambda\hat{B}_d\right)|\psi\rangle}$$

where $\hat{A}_d = \hat{A} - \langle A\rangle$, is the deviation from mean value.
Then, find λ for $\langle\phi|\phi\rangle_{min}$:
$$\frac{d\langle\phi|\phi\rangle}{d\lambda} = 0 \quad \text{noting that} \quad \langle\phi|\phi\rangle_{min} \geq 0$$

Solution to minimum uncertainty state: Gaussian wavepacket.
By setting:
$$(\hat{A}_d + i\lambda\hat{B}_d)|\psi\rangle = 0$$

One might obtain a differential equation to be solved.
Example: for position and momentum:
$$\psi(x) = e^{-\frac{(x-\langle x\rangle)^2}{2\hbar\lambda}} e^{\frac{i\langle p\rangle x}{\hbar}}$$

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4.2 Harmonic oscillator - Ladder operators

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 \quad \text{and} \quad \hat{H}\left|n\right\rangle = E_n\left|n\right\rangle$$

Lowering operator:

$$\boxed{\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}}$$

$$\boxed{\hat{H}\hat{a}\left|n\right\rangle = (E - \hbar\omega)\,\hat{a}\left|n\right\rangle}$$

Raising operator:

$$\boxed{\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}}$$

$$\boxed{\hat{H}\hat{a}^\dagger\left|n\right\rangle = (E + \hbar\omega)\,\hat{a}^\dagger\left|n\right\rangle}$$

$\hat{a}^\dagger$ acts like a raising operator that raise the energy of the system by $\hbar\omega$.
$\hat{a}$ acts like a lowering operator that lowers the energy of the system by $\hbar\omega$.
Hence,

$$\hat{a}^\dagger\left|n\right\rangle \propto \left|n+1\right\rangle \quad \text{and} \quad \hat{a}\left|n\right\rangle \propto \left|n-1\right\rangle$$

Find proportionality constant by considering norm.

$$\hat{a}\left|\phi_n\right\rangle = C\left|\phi_{n-1}\right\rangle$$

$$\left\langle\phi_n\right|\hat{a}^\dagger\hat{a}\left|\phi_n\right\rangle = |C|^2\left\langle\phi_{n-1}|\phi_{n-1}\right\rangle$$

Commutation relation:

$$\boxed{[\hat{a}, \hat{a}^\dagger] = 1}$$

Number operator: corresponds to measuring the number of elementary quantum excitations, photons or phonons,
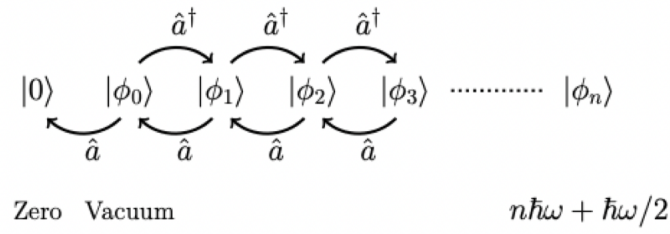
$$\hat{N} = \hat{a}^\dagger\hat{a}$$

Rewriting the Hamiltonian:

$$\boxed{\hat{H} = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)}$$

Ladder operators in action

There is a ground state where $\hat{a}\left|\phi_0\right\rangle = \left|0\right\rangle$, which acts as a means to terminate the laddering process.

With the minimum (or maximum) state known, we can generate the other states using the raising (or lowering operators):

$$\hat{a}^\dagger \qquad \hat{a}^\dagger \qquad \hat{a}^\dagger$$

$$|0\rangle \quad |\phi_0\rangle \quad |\phi_1\rangle \quad |\phi_2\rangle \quad |\phi_3\rangle \quad \cdots\cdots \quad |\phi_n\rangle$$

$$\hat{a} \qquad \hat{a} \qquad \hat{a} \qquad \hat{a}$$

Zero   Vacuum $\hspace{6cm} n\hbar\omega + \hbar\omega/2$

$$\hat{a}\,|\phi_n\rangle = \sqrt{n}\,|\phi_{n-1}\rangle$$
$$\hat{a}^\dagger\,|\phi_n\rangle = \sqrt{n+1}\,|\phi_{n+1}\rangle$$

Energy levels

$$\langle N\rangle = \langle \phi_n|\,\hat{N}\,|\phi_n\rangle = \ldots = \frac{E}{\hbar\omega} - \frac{1}{2}$$

$$\boxed{\Rightarrow E = \left(n + \frac{1}{2}\right)\hbar\omega}$$

$$\hat{H}\,|\phi_n\rangle = \left(n + \frac{1}{2}\right)\hbar\omega\,|\phi_n\rangle$$

Bringing back to wavefunction

Write $\hat{a}\,|\phi_0\rangle = |0\rangle$ in differential equation form, and solve for $\phi_0(x)$, normalising it too. Then we can generate the higher states using:

$$|\phi_n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}\,|\phi_0\rangle$$

Uncertainty

$$\Delta x \Delta p = \left(n + \frac{1}{2}\right)\hbar$$

Only the ground state is a minimum uncertainty state.

4.3 Density operators - statistical mixing

Another way of writing expectation value:

$$\langle A \rangle = \text{Tr}\left[\hat{A} \ket{\psi}\bra{\psi}\right]$$

Proof:

$$\langle A \rangle = \bra{\psi}\hat{A}\ket{\psi} = \sum_r \braket{\psi|u_r}\bra{u_r}\hat{A}\ket{\psi} = \sum_r \bra{u_r}\hat{A}\ket{\psi}\braket{\psi|u_r} = \text{Tr}\left[\hat{A}\ket{\psi}\bra{\psi}\right]$$

$$\langle A \rangle = \text{Tr}[\hat{O}\hat{A}]$$

where

$$\text{Density operator:} \quad \boxed{\hat{O} = \sum_{i=1}^{I} P_i \ket{\psi_i}\bra{\psi_i}}$$

Normalisation by $\text{Tr}[\hat{O}] = 1$ and it is self-adjoint.

Pure state $\hat{O} = \ket{\psi}\bra{\psi}$ (only one term) iff $\hat{O}^2 = \hat{O}$ (idempotent for a pure state only).

If $\hat{O}^2 \neq \hat{O}$, it is a mixed state $\hat{O} = \sum_{i=1}^{I} P_i \ket{\psi_i}\bra{\psi_i}$, with $I \geq 2$

Application: interference phenomena and entanglement.

4.4 Functions of operators

The definition of function of operators uses power series of the function, replacing the variables with the operator.

Result:

$$\boxed{F(\hat{X}) = \sum_i F(x_i) \underbrace{\ket{\psi_i}\bra{\psi_i}}_{\text{projection}}}$$

Preserve eigenvector but eigenvalue is $F(x_i)$.

Example: density operator $\hat{\rho} = \frac{1}{Z}e^{-\hat{H}/kT}$

4.5 Useful tricks for evaluating summation

$$\sum_{n=0}^{\infty} nx^n = x\frac{d}{dx}\left(\sum_{n=0}^{\infty} x^n\right)$$

$x \to e^{-a}$

$$\sum_{n=0}^{\infty} ne^{-an} = -\frac{d}{da}\left(\sum_{n=0}^{\infty} e^{-an}\right)$$

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5 Time-dependent Quantum Mechanics

Schrodinger's picture: quantum states vary with time.
Heisenberg's picture: operators change with time, not states.

Postulates of Quantum Mechanics

1. A state vector $|\psi\rangle$ represents the most complete knowledge we have about a system.

2. For every observable A, there exist a linear Hermitian operator $\hat{A}$, and the result of measurement must be one of the eigenvalues of A.

3. The probability of obtaining a_n is $\boxed{|\langle a_n|\psi\rangle|^2}$ (**Born's rule**) OR $|\langle \Psi|\Phi\rangle|^2$ where Ψ is the state it was in and Φ is the state it might be found in (overlap integral).

4. As a result of measurement, the state of the system is changed discontinuously to the corresponding eigenstate $|a_n\rangle$

5. Between measurements, the state evolve deterministically in time according to:

$$\boxed{\hat{H}|\psi\rangle = i\hbar \frac{\partial |\psi\rangle}{\partial t} = E|\Psi\rangle}$$

   This gives the phase part of any wavefunction, $e^{-iE_n t/\hbar}$.

5.1 Time-dependent state (state propagator)

If the system has a new $\hat{H}$, the original wavefunction will no longer be an energy eigenstate of the new system. To evolve it in time we have to expand it in terms of the eigenstates of the new $\hat{H}$ and evolve each individually.

To time propagate, write the state as linear combinations of energy eigenstates (i.e. eigenvectors of $\hat{H}$ or stationary states):

$$|\psi(t)\rangle = \sum_n c_n(t)|\phi_n\rangle$$

Solving the time-dependent Schrodinger's equation (integrating the first-order DE) and evolving each component of energy eigenstate with time:

$$\boxed{|\psi(t)\rangle = \sum_n c_n(0)e^{-iE_n t/\hbar}|\phi_n\rangle}$$

where $\omega_n = E_n/\hbar$ and $c_n(0) = \langle \phi_n|\psi(t=0)\rangle$.

So, overall:

$$\boxed{|\Psi(t)\rangle = |\Psi(t=0)\rangle\, e^{-iEt/\hbar}}$$

Time shift/time evolution operator

In general from $t = t_0$ to t,

$$|\psi(t)\rangle = \underbrace{e^{-i\hat{H}(t-t_0)/\hbar}}_{\hat{U}:\ \text{time shift}} |\psi(t_0)\rangle$$

Unitary operator: $\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{I}$

Ehrenfest's Theorem

Equation of motion for the expectation value of any operator:

$$\boxed{\frac{d\langle\hat{A}\rangle}{dt} = \frac{i}{\hbar}\left\langle\left[\hat{H}, \hat{A}\right]\right\rangle} + \underbrace{\langle\frac{d\hat{A}}{dt}\rangle}_{\text{zero}}$$

Proof: $\langle\hat{A}\rangle = \langle\psi(t)|\hat{A}|\psi(t)\rangle$, product rule and $\frac{d}{dt} = \frac{1}{i\hbar}\hat{H}$

Key points:

1. If operator **commutes with $\hat{H}$**, the observable is a **conserved quantity**.

2. **Stationary state:** are eigenfunctions of the Hamiltonian i.e. energy eigenstate. The probability density function is independent of time.

Time propagation

$$\langle\hat{A}\rangle = \langle\psi(t)|\hat{A}|\psi(t)\rangle = \sum_{mn} c_m^* c_n e^{i(E_m - E_n)t/\hbar} \underbrace{\langle\phi_m|\hat{A}|\phi_n\rangle}_{A_{mn}}$$

5.2   Commutation relations

The below relations can be proven by induction.

If $[\hat{A}, \hat{B}] = C \in \mathbb{C}$,

$$\left[\hat{A}, \hat{B}^l\right] = C\frac{d\hat{B}^l}{d\hat{B}}$$

$$\left[\hat{B}, \hat{A}^l\right] = -C\frac{d\hat{A}^l}{d\hat{A}}$$

In general:

$$\boxed{\left[\hat{A}, F(\hat{A}, \hat{B})\right] = C\frac{\partial F(\hat{A}, \hat{B})}{\partial\hat{B}}}$$

$$\boxed{\left[\hat{B}, F(\hat{A}, \hat{B})\right] = -C\frac{\partial F(\hat{A}, \hat{B})}{\partial\hat{A}}}$$

Other useful results:

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

5.3   Time-energy uncertainty

Combining:

$$\frac{d\langle \hat{A} \rangle}{dt} = \frac{i}{\hbar}\langle \left[\hat{H}, \hat{A}\right] \rangle \quad \text{and} \quad \Delta E \Delta A \geq \frac{1}{2}\left|\langle i\left[\hat{H}, \hat{A}\right]\rangle\right|$$

We obtain:

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

Connection between uncertainty in energy to rate of change of observable of the system.

5.4   Heisenberg's picture

Time evolution of operator:

$$\boxed{i\hbar\frac{d\hat{A}^{\hat{H}}}{dt} = \left[\hat{A}^{\hat{H}}, \hat{H}\right] = \hat{U}^{\dagger}\left[\hat{A}, \hat{H}\right]\hat{U}}$$

Proof: Start from

$$\frac{d\hat{A}^{\hat{H}}}{dt} = \frac{d}{dt}\left(\hat{U}^{\dagger}\hat{A}\hat{U}\right)$$

Time evolution of density operator

$$\text{Von-Neumann equation: } i\hbar\frac{d\hat{O}}{dt} = \left[\hat{H}, \hat{O}\right]$$

6 3D Quantum Mechanics

Orbital angular momentum

Start with classical definition of angular momentum:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

So,

$$L_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \quad \text{etc...}$$

Another form but scaled:

$$L_z = x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \quad \text{etc...}$$

Orbital angular momentum is hermitian: $\hat{\boldsymbol{L}} = \hat{\boldsymbol{L}}^\dagger$. It is an observable.

Some commutation relations

1. Position and momentum:
$$[\hat{\boldsymbol{r}}_j, \hat{\boldsymbol{p}}_k] = i\hbar\delta_{jk}$$

2. Components of angular momentum:

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

   In general,

$$\boxed{\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\,\epsilon_{ijk}\hat{L}_k}$$

   Different components of angular momentum do not commute with each other. No two components can be known precisely. Only one component of $\hat{\boldsymbol{L}}$ can be measured precisely, usually the z-component, by convention.
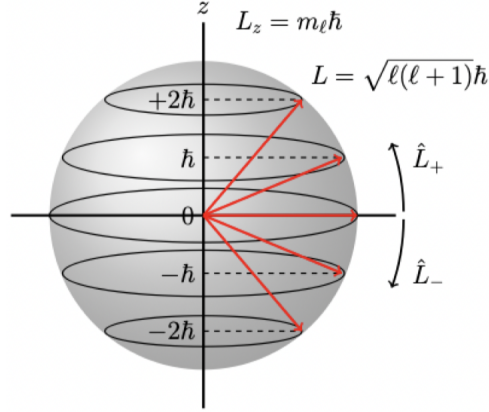
3. $\hat{L}^2$ and components of angular momentum:

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

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

   They are compatible observables, so they share the same eigenstates.

6.1 Raising and lowering operators

Ladders operators increasing/decreasing the z component of the angular momentum by $\hbar$:

$$\text{Raising operator: } \boxed{\hat{L}_+ = \hat{L}_x + i\hat{L}_y}$$

$$\text{Lowering operator: } \boxed{\hat{L}_- = \hat{L}_x - i\hat{L}_y}$$

Key results:

$$\hat{L}^2 |l, m_l\rangle = l(l+1)\hbar^2 |l, m_l\rangle$$

$$\hat{L}_z |l, m_l\rangle = m_l \hbar |l, m_l\rangle$$

$$\hat{L}_\pm |l, m_l\rangle = \hbar\sqrt{l(l+1) - m_l(m_l \pm 1)} \, |l, m_l \pm 1\rangle$$

$$m_l \in -l, -l+1, ..., -1, 0, 1, ... l-1, l$$

where l is called the orbital angular momentum quantum number.
$l = 0, 1, 2, 3, 4, ..., \boldsymbol{n-1}$ where the first 4 are called s, p, d, f, g states respectively.
n is the principle quantum number (a non-negative integer).

m_l is called the magnetic angular momentum quantum number.

Derivation

Suppose $|\phi_\alpha\rangle$ is an eigenstate of $\hat{L}_z$ having eigenvalue $\alpha\hbar$:

$$\hat{L}_z |\phi_\alpha\rangle = \alpha\hbar |\phi_\alpha\rangle$$

Now,

$$\hat{L}_z \hat{L}_\pm |\phi_\alpha\rangle = (\alpha \pm 1)\hbar \, \hat{L}_\pm |\phi_\alpha\rangle$$

$\hat{L}_\pm |\phi_\alpha\rangle$ is an eigenstate of $\hat{L}_z$ with eigenvalue $(\alpha \pm 1)\hbar$.

Since $\hat{L}^2$ and $\hat{L}_z$ commute, $|\phi_\alpha\rangle$ is also an eigenstate $\hat{L}^2$ having eigenvalue $\Lambda\hbar^2$. We will find after doing the same procedure that:

$$\hat{L}^2\hat{L}_\pm |\phi_\alpha\rangle = \Lambda\hbar^2\,\hat{L}_\pm |\phi_\alpha\rangle$$

$\hat{L}_\pm |\phi_\alpha\rangle$ is an eigenstate of $\hat{L}^2$ with eigenvalue $\Lambda\hbar^2$.

So, the ladder operators generate the eigenstates of $\hat{L}_z$ but all of them are eigenstates of $\hat{L}^2$ having the same eigenvalue $\Lambda\hbar^2$. The z-component of angular momentum changes, but the magnitude of the angular momentum does not.

Writing $\hat{L}_z$ in spherical polar form:

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

So, the eigenstate must be of the form:

$$\psi \propto e^{i\alpha\phi}$$

Since the wavefunction must be single-valued, this means $\psi(\phi+2\pi) = \psi(\phi)$ and hence $e^{2i\pi\alpha} = 1 \Rightarrow \boldsymbol{\alpha}$ **has to be integer**.

We know that $\langle\hat{L}_z^2\rangle \leq \langle\hat{L}^2\rangle$ and $\boldsymbol{\alpha^2 \leq \Lambda}$. For a given value of Λ, there is some maximum absolute value of α and α has to be symmetrical about 0.

$$\boxed{\alpha = m_l = l, l-1, l-2, ..., -l+2, -l+1, -l}$$

For a fixed angular momentum, the z-component can be increased in unit of $\hbar$ but eventually the series must terminate because the z-component cannot exceed the magnitude. Let the highest eigenstate of $\hat{L}_z$ be $|\phi_{\Lambda,l}\rangle$ such that:

$$\hat{L}_z |\phi_{\Lambda,l}\rangle = l\hbar |\phi_{\Lambda,l}\rangle \quad \text{and} \quad \hat{L}^2 |\phi_{\Lambda,l}\rangle = \Lambda\hbar^2 |\phi_{\Lambda,l}\rangle$$

Then, **terminating the series**:

$$\hat{L}_+ |\phi_{\Lambda,l}\rangle = 0 \quad \text{and} \quad \hat{L}_- |\phi_{\Lambda,-l}\rangle = 0$$

Using $\boxed{\hat{L}_-\hat{L}_+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z^2}$, we find:

$$\boxed{\Lambda = l(l+1)\hbar^2}$$

6.2 Back to wavefunction formulation

Method

In spherical polar coordinates:

$$\hat{\boldsymbol{p}} = -i\hbar\nabla = -i\hbar(\hat{\boldsymbol{e}}_r \underbrace{\frac{\partial}{\partial r}}_{\hat{p}_r} + \hat{\boldsymbol{e}}_\theta \underbrace{\frac{1}{r}\frac{\partial}{\partial \theta}}_{\hat{p}_\theta} + \hat{\boldsymbol{e}}_\phi \underbrace{\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}}_{\hat{p}_\phi})$$

Coordinate transform:
$$\begin{cases} \mathbf{e}_x = \sin\theta\cos\phi\,\mathbf{e}_r + \cos\theta\cos\phi\,\mathbf{e}_\theta - \sin\phi\,\mathbf{e}_\phi \\ \mathbf{e}_y = \sin\theta\sin\phi\,\mathbf{e}_r + \cos\theta\sin\phi\,\mathbf{e}_\theta + \cos\phi\,\mathbf{e}_\phi \\ \mathbf{e}_z = \cos\theta\,\mathbf{e}_r - \sin\theta\,\mathbf{e}_\theta \end{cases}$$

Can find similar expressions for $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$, $\hat{L}_\pm$, $\hat{L}^2$ by:

1. Transform the following canonical expression for orbital angular momentum into in spherical polar coordinates:

$$L_z = xp_y - yp_x = \dots = -i\hbar\frac{\partial}{\partial \phi}$$

2. Use the momentum operator in spherical form in previous page.

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

And note the raising and lowering operator trick.

The wavefunction

In spherical polar coordinates, the Hamiltonian takes the forms:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \underbrace{\frac{\hat{L}^2}{2mr^2}}_{\substack{\text{centrifugal}\\\text{potential}}} + V(r)$$

The wave function can be broken down into a radial and an angular part:

$$\psi_{n,l,m_l} = \underbrace{R_{n,l}(r)}_{\text{radial}}\underbrace{Y_{l,m_l}(\theta,\phi)}_{\text{angular}}$$

Note: they can be treated separately as long they each are properly normalised.

The angular part (spherical harmonics):

$$Y_{l,m_l}(\theta,\phi) = C(\sin\theta)^l e^{im_l\phi}$$

The spherical harmonics are orthogonal.

Probability density

$$\int_{dV} |\psi(r,\theta,\phi)|^2 dV = \int_{r=0}^{\infty} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} |Y_{l,m_l}|^2 |R_{n,l}|^2 r^2 \sin\theta \, d\theta \, d\phi$$

$$\boxed{P(r)dr = |R_{n,l}|^2 r^2 \, dr}$$

since

$$\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} |Y_{l,m_l}|^2 \sin\theta \, d\theta \, d\phi = 1 \quad \text{(by definition)}$$

6.3 Example 1: Diatomic molecule

For example, this rotor model is suitable for a hydrogen molecule, H_2.

$$\boxed{E_l = \frac{L^2}{2I} = \frac{l(l+1)\hbar^2}{2I} \text{ with degeneracy } 2l+1}$$

Note: $\boxed{L^2 = l(l+1)\hbar^2}$

Also, a particle exchange is equivalent to parity inversion ($\mathbf{r} \to -\mathbf{r}$) so this sends $\boxed{\theta \to \pi - \theta \text{ and } \phi \to \phi + \pi}$. This has consequences for the exchange symmetry of spherical harmonics.

Probability of state n:

$$P_n = \frac{e^{-\beta E_n}}{\sum_{n=1}^{\infty} e^{-\beta E_n}}$$

where $\beta = \frac{1}{k_B T}$.

Can find average energy:

$$\langle E \rangle = \frac{\sum_l E_l (2l+1) e^{-\frac{E_l}{k_B T}}}{\sum_l (2l+1) e^{-\frac{E_l}{k_B T}}}$$

6.4 Example 2: Hydrogen-like atom

$$\text{Coulomb potential: } V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

Energy levels:

$$E_n = -\frac{\hbar^2}{2m} \frac{Z^2}{a_0^2} \frac{1}{n^2} = \boxed{-13.6 \frac{Z^2}{n^2} eV}$$

where Bohr radius is:

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = \boxed{0.53 \text{ Å}}$$

6.5   Tripos Q & A

Q1: Find the operator for the z-component of the orbital angular momentum in spherical polar coordinates.

A1: $\hat{\boldsymbol{L}} = \mathbf{r} \times (\hat{\mathbf{p}}_r + \hat{\mathbf{p}}_\phi + \hat{\mathbf{p}}_\theta) = \mathbf{r} \times \hat{\mathbf{p}}_\phi + \mathbf{r} \times \hat{\mathbf{p}}_\theta$
$\hat{\boldsymbol{L}}_z = \hat{\boldsymbol{z}} \cdot \hat{\boldsymbol{L}} = \hat{\boldsymbol{z}} \cdot \mathbf{r} \times \hat{\mathbf{p}}_\phi = \hat{\boldsymbol{z}} \times \mathbf{r} \cdot \hat{\mathbf{p}}_\phi$

$$\hat{\boldsymbol{z}} \times \mathbf{r} = r \sin\theta \, \hat{\boldsymbol{\phi}} \quad \text{and} \quad \hat{\mathbf{p}}_\phi = -i\hbar \nabla_\phi = i\hbar \frac{1}{r \sin\theta} \hat{\boldsymbol{\phi}} \frac{\partial}{\partial \phi}$$

Q2: Explain how it is possible that the Hamiltonian is spherically symmetric, but that the eigenstate Ψ is not.

A2: Although the Hamiltonian commutes with rotations L_x, L_y and L_z, this does not mean that the rotations share an eigenbasis, as the Hamiltonian has degenerate eigenvalues.

7   Two-particle Systems

7.1   Separable and entangled states

$$|\psi_{a,b}\rangle = \psi(\mathbf{r}_a, \mathbf{r}_b, t)$$

For separable state:

$$|\psi_{a,b}\rangle = |\psi_a\rangle |\psi_b\rangle$$

$|\psi_{a,b,}\rangle$ can be written as an expansion of $M \times N$ basis vectors $|a_m\rangle |b_n\rangle$:

$$|\psi_{a,b}\rangle = \sum_m \sum_n \underbrace{a_m b_n}_{c_{mn}} |a_m\rangle |b_n\rangle$$

It is a postulate of QM that the set $\{|a_m\rangle |b_n\rangle, \forall m, n\}$ of $M \times N$ basis vectors is a complete set to describe all possible outcomes of measurements on the system.

The two measurements can be regarded as independent measurements, and the probabilities multiply together to get the probability of the composite outcome.

For entangled state:

$$|\psi\rangle = C_{1,2} |a_1\rangle |b_2\rangle + C_{2,1} |a_2\rangle |b_1\rangle$$

In general, for N subsystems:

$$|\psi\rangle = \sum_{n_1, \ldots, n_N} c_{n_1, \ldots n_N} |a_{n_1}\rangle \ldots |a_{a_N}\rangle$$

Not possible to attribute one state solely to a and a different state solely to b. Measurement on one subsystem may change the outcome of a measurement on the other.

7.2   Two particles

Hamiltonian:

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m}}_{\hat{H}_{\text{CoM}}} + \underbrace{\frac{\hat{p}_r^2}{2\mu} + \hat{V}(r)}_{\hat{H}_{\text{rotating}}}$$

where $\mu = \left(\frac{1}{m_a} + \frac{1}{m_b} \right)^{-1}$ is the reduced mass. Total energy is $E_{\text{CoM}} + E_r$.

Motion of centre of mass:

$$\frac{d\langle \hat{\mathbf{R}} \rangle}{dt} = \frac{\langle \hat{\mathbf{p}} \rangle}{m_a + m_b}$$

where $\mathbf{R} = \frac{m_a \mathbf{r}_a + m_b \mathbf{r}_b}{m_a + m_b}$.

Assume solution of the form: $\psi(\mathbf{R}, \mathbf{r}) = U(\mathbf{R}) u(\mathbf{r})$ separable into motion of centre of mass and internal motion. Upon solving the Schrodinger's equation, one gets that the
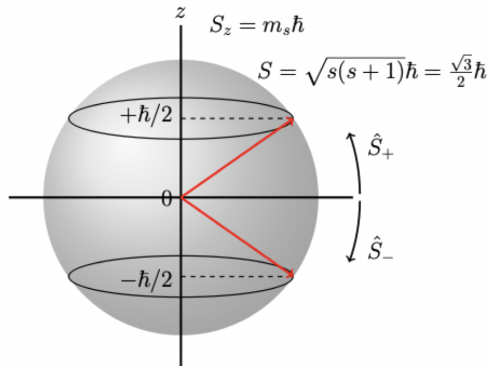
motion can be decomposed into (1) CoM frame: a free particle having mass $m_a + m_b$ (translational behaviour) and (2) internal motion: single particle of mass μ moving in central potential $V(r)$. (vibrational motion)

8 Spin

Some commutation relations

$$\left[\hat{S}_i, \hat{S}_j\right] = i\hbar\,\epsilon_{ijk}\hat{S}_k$$

8.1 Raising and lowering operators for spin

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$$

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

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

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

where $m_s = -s, -s+1, ..., s-1, s$

8.2 Components of spin

Given,

$$\hat{S}_z |\uparrow\rangle = \frac{\hbar}{2} |\uparrow\rangle \quad \text{and} \quad \hat{S}_z |\downarrow\rangle = -\frac{\hbar}{2} |\downarrow\rangle$$

Then,

$$\hat{S}_x |\uparrow\rangle = \frac{\hbar}{2} |\downarrow\rangle \quad \text{and} \quad \hat{S}_x |\downarrow\rangle = \frac{\hbar}{2} |\uparrow\rangle$$

8.3 Combining spins

$$\hat{\boldsymbol{S}} = \hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2$$

Result: 3 triplet symmetric states and 1 singlet antisymmetric state.

8.4   Total angular momentum

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}$$

$$\left[\hat{J}_i, \hat{J}_j\right] = i\hbar\,\epsilon_{ijk}\hat{J}_k$$

$$\hat{J}^2 \left|j, m_j\right\rangle = j(j+1)\hbar^2 \left|j, m_j\right\rangle$$

$$\hat{J}_z \left|j, m_j\right\rangle = m_j\hbar \left|j, m_j\right\rangle$$

$$\hat{J}_\pm = \hat{L}_\pm + \hat{S}_\pm$$

$$\hat{J}_\pm \left|j, m_j\right\rangle = \hbar\sqrt{j(j+1) - m_j(m_j \pm 1)} \left|j, m_j \pm 1\right\rangle$$

$$\hat{J}_z = \hat{L}_z + \hat{S}_z$$

$$m_j = m_l + m_s$$

$$j = \underbrace{(l+s)}_{\substack{\text{maximally}\\\text{parallel}}}, (l+s)-1, ..., |l-s|+1, \underbrace{|l-s|}_{\substack{\text{maximally}\\\text{antiparallel}}}$$

$*j$ can never be negative$*$

For each j, $m_j = -j, ..., j$

Dimensions: $\displaystyle\sum_{l-s}^{l+s}(2j+1) = (2l+1)(2s+1)$

8.5 Stern-Gerlach experiment
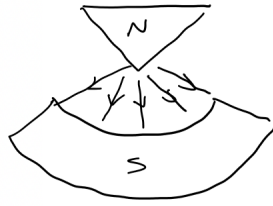
Works by passing a beam of particles through a non-uniform magnetic field. The interaction of the magnetic moment, $\boldsymbol{\mu}$ of the particle with the magnetic field exerts a force on the particle:

$$\mathbf{F} = \boldsymbol{\mu} \cdot \nabla \mathbf{B}$$

In the z-direction:

$$F_z = \mu_z \frac{\partial B_z(z)}{\partial z}$$

where

$$\boxed{\mu_z = -\mu_B m_l}$$

with $\mu_B = \frac{e\hbar}{2m_e}$ being the Bohr magneton. μ_z is quantized by m_l, hence a discrete set of forces act on a discrete set of particles exiting the apparatus. We would expect an odd number of beams $2l + 1$.

If the angular momentum is intrinsic (i.e. spin only), it is quantized by m_s and we have splitting into $2s + 1$ beams.

Past Tripos questions

1. (2019 Tripos P1 B6) **Describe the Stern-Gerlach experiment and how it could be used to demonstrate the rotation of spins in a magnetic field.**

   Second part:

   - Use a Stern-Gerlach to create a beam in which we know that all particles have the same spin.

   - This beam can be fed into a uniform field, which would cause the spin to precess

   - The output is feed into another S-G device to see if multiple beams are produced. Their relative intensities tell us how the intermediate field have rotated the spin.

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9 Indistinguishable particles

9.1 Fermions and bosons

Fermions: spin half, exchange antisymmetric. (Makes up matter).
Bosons: integer spin, exchange symmetric. (Force mediators).

Bosons obey **Bose-Einstein statistics**. Average number of bosons in a certain quantum state, j, is given by:

$$\langle n_j^b \rangle = \frac{1}{e^{(E_j - \mu)/kT} - 1}$$

Fermions obey **Fermi-Dirac statistics**. Average number of fermions in a certain quantum state, j, is given by:

$$\langle n_j^f \rangle = \frac{1}{e^{(E_j - \mu)/kT} + 1} < 1$$

Exchange operator

Effect: interchanging indices,

$$\hat{P}_{ij} \,|\zeta_i, \zeta_j\rangle = |\zeta_j, \zeta_i\rangle \ \text{ and } \ \langle\zeta_i, \zeta_j|\, \hat{P}_{ij}^\dagger = \langle\zeta_j, \zeta_i|$$

$$\hat{P}_{ij} \,|\zeta_i, \zeta_j\rangle^{s/a} = \pm |\zeta_i, \zeta_j\rangle^{s/a}$$

It is Hermitian, and thus an observable and $\hat{P}^2$ is the identity:

$$\hat{P}_{ij}^\dagger = \hat{P}_{ij} \quad \text{and} \quad \hat{P}_{ij}^\dagger \hat{P}_{ij} = \hat{I}$$

So, we know its eigenvalues are ± 1.

Time evolution
Since:

$$\langle\zeta_i, \zeta_j|\, \hat{A} \,|\zeta_i, \zeta_j\rangle = \langle\zeta_j, \zeta_i|\, \hat{A} \,|\zeta_j, \zeta_i\rangle$$

$$\langle\zeta_i, \zeta_j|\, \hat{A} \,|\zeta_i, \zeta_j\rangle = \langle\zeta_i, \zeta_j|\, \hat{P}_{ij}^\dagger \hat{A} \hat{P}_{ij} \,|\zeta_i, \zeta_j\rangle$$

$$\Rightarrow \hat{A} = \hat{P}_{ij}^\dagger \hat{A} \hat{P}_{ij}$$

$$\hat{P}_{ij} \hat{A} = \hat{A} \hat{P}_{ij}$$

$$\boxed{\left[\hat{A}, \hat{P}_{ij}\right] = 0}$$

The exchange operator any observable are compatible. Means that no experiment can distinguish one particle from another, because the particles can be swapped prior to a measurement without changing the result.

It commutes with the Hamiltonian $\Rightarrow$ if the wavefunction is exchange symmetric or antisymmetric, it remains so as it evolves $\Rightarrow$ meaning fermions do not change into bosons as time progresses or after a measurement, and vice versa.

Symmetrisation postulate

states that N identical particles are either exchange symmetric or exchange antisymmetric. States with mixed symmetry do not exist.

Pauli exclusion principle (only fermions)

Pauli exclusion principle states that no two identical fermions can be in a single particle state. In other words, two identical fermions cannot have the same set of quantum numbers.

However, bosons can share states.

9.2   Spin statistics theorem

Bosons have **integer** spin quantum numbers ($s = 0, 1, 2, 3, ...$)
Fermions have **half-odd-integer** spin quantum numbers ($s = 1/2, 3/2, 5/2, ...$)

9.3   Basis states

9.3.1   Two-particle system

Two-particle system with two energy states.
Suitable basis:

$$|\alpha_1\rangle |\alpha_2\rangle , |\alpha_1\rangle |\beta_2\rangle , |\beta_1\rangle |\alpha_2\rangle , |\beta_1\rangle |\beta_2\rangle$$

If they are identical, basis states becomes:

$$\underbrace{|\alpha\rangle |\alpha\rangle}_{\text{symmetric}} , \underbrace{|\alpha\rangle |\beta\rangle , |\beta\rangle |\alpha\rangle}_{\text{no exchange symmetry}} , \underbrace{|\beta\rangle |\beta\rangle}_{\text{symmetric}}$$

Form symmetric and antisymmetric using procedure below:

$$|s\rangle = \frac{1}{\sqrt{2}}[|\alpha\rangle |\beta\rangle + |\beta\rangle |\alpha\rangle]$$

$$|a\rangle = \frac{1}{\sqrt{2}}[|\alpha\rangle |\beta\rangle - |\beta\rangle |\alpha\rangle]$$

Inverting:

$$|\alpha\rangle |\beta\rangle = \frac{1}{\sqrt{2}}[|s\rangle + |a\rangle]$$

$$|\beta\rangle |\alpha\rangle = \frac{1}{\sqrt{2}}[|s\rangle - |a\rangle]$$

We have **3 symmetric states** and **1 antisymmetric state**.

Experimental interpretation of basis states:

1. $|\alpha\rangle |\alpha\rangle \longrightarrow 2$ bosons in low energy state

2. $|s\rangle \longrightarrow$ a boson in each of the low and high energy state, with no information about which one is which

3. $|\beta\rangle |\beta\rangle \longrightarrow$ two bosons in the high energy state

4. $|a\rangle \longrightarrow$ a fermion in each of the low and high energy states, with no information about which one is which

Calculating probabilities - Born's rule
Uncertainty about which particle is which is maximised.

9.3.2   N particles with M states

There are M^N number of such canonical basis:

$$|\zeta_1^\alpha\rangle ... |\zeta_i^r\rangle ... |\zeta_N^z\rangle$$

where i is particle and r is state.

For identical particles i.e. $|\zeta_i^r\rangle = |\zeta_j^r\rangle$, then new basis is:

$$|\zeta^\alpha\rangle ... |\zeta^r\rangle ... |\zeta^z\rangle$$

Similar to the two-particle case, when a pair of particles is swapped, we should observe the same outcome when an experiment is performed. Hence, it is necessary to symmetrise or antisymmetrise the states, depending on the type of particles involved.

Example - 3 particle in 3 states
Canonical basis:
$$|\zeta^a\rangle |\zeta^b\rangle |\zeta^c\rangle \quad a, b, c \in \{1, 2, 3\}$$

Lowest order state $|1, 1, 1\rangle$ is exchange symmetrise and correspond to finding all 3 bosons in state 1.

Next state is $|1, 1, 2\rangle$ does not have obvious exchange symmetry. We need to symmetrise it:
$$|1, 1, 2\rangle^s = \frac{1}{\sqrt{3}}[|1, 1, 2\rangle + |1, 2, 1\rangle + |2, 1, 1\rangle]$$

corresponding to an entangled state involving all 3 particle permutations where two particles in state 1 and one particle in state 2.
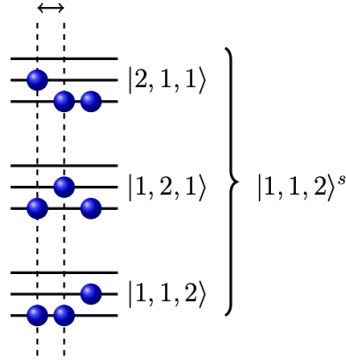
Figure 2: Symmetrisation - making bosons

Carry out the same procedure for the next unsymmetrised state e.g. $|1, 2, 2\rangle$

Only one antisymmetric state is available, $|1, 2, 3\rangle^a$:

$$|1, 2, 3\rangle^a = \frac{1}{\sqrt{3!}} [|1, 2, 3\rangle - |1, 3, 2\rangle + |2, 3, 1\rangle - |2, 1, 3\rangle + |3, 1, 2\rangle - |3, 2, 1\rangle]$$

$$= \frac{1}{\sqrt{3!}} \begin{vmatrix} |1\rangle & |2\rangle & |3\rangle \\ |1\rangle & |2\rangle & |3\rangle \\ |1\rangle & |2\rangle & |3\rangle \end{vmatrix} \quad \text{(Slater determinant)}$$
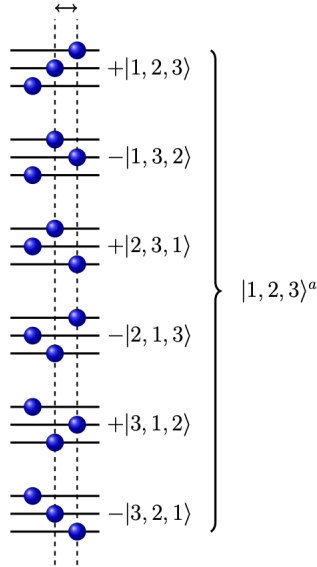
Figure 3: Antisymmetrisation - making fermions

9.4 Tripos Q&A

Q1: Describe the spin-statistics governing the behaviour of bosons and fermions.

A1: If we have a composite system of two or more identical particles occupying different states, then the fact of their indistinguishability puts constraints on the form of the wavefunction. The particle exchange operator is useful:

$$\hat{P}_{12} \ket{\psi(\mathbf{r}_1, \mathbf{r}_2)} = \ket{\psi(\mathbf{r}_2, \mathbf{r}_1)}$$

Its eigenvalues are either ± 1 and QFT tells us that:

$$\lambda = (-1)^{2s}$$

where s is the spin of the particle. So, fermions (spin-1/2) must be antisymmetric under exchange. Bosons which have integer spins are exchange symmetric.

Q2: (2015 P1 B7) 1. For a system of two identical particles, explain what constraint is placed on the overall wavefunction by considering the operation of exchanging the two particles.

2. For a system of two fermions whose wavefunction can be written as the product of a spatial part and a spin part, explain what are the possible combinations of exchange symmetries for the spatial and spin parts of the wavefunction.

3. . Explain what is meant by para-hydrogen and ortho-hydrogen.

A2: 1. Wavefunction must be symmetric or antisymmetric under particle exchange, so $|\psi|^2$ does not change.

2. For fermions, the product of the two part must be overall antisymmetric under exchange, and hence must be of the form:

- (symmetric space) $\times$ (antisymmetric spin)

- (antisymmetric space) $\times$ (symmetric spin)

3. Para is spin singlet, $s = 0$, a single state: $\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$
Ortho is spin triplet, $s = 1$, with three states: $\uparrow\uparrow$, $\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$ and $\downarrow\downarrow$.

Q3: Write down the time-dependent Schrödinger equation satisfied by the two-particle wavefunction $\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}, t)$ for two non-interacting, distinguishable particles, each of mass m, moving in some potential V, where $\boldsymbol{r_1}$ and $\boldsymbol{r_2}$ are the positions of the two particles.

A3:
$$\frac{\hbar^2}{2m}\left(\nabla_1^2\Psi + \nabla_2^2\Psi\right) + [V(\mathbf{r}_1) + V(\mathbf{r}_2)]\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Q4: Write down the possible two-particle wavefunctions for a fermion with spin $\frac{1}{2}$.

A4: Since its fermions, require overall wavefunction to be antisymmetric under particle exchange.
$$\Psi(1,2,t) = \Psi(1,2)e^{-iEt/\hbar}$$

Spatial part:

1. $\dfrac{1}{\sqrt{2}}[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)]$ (antisymmetric)

2. $\dfrac{1}{\sqrt{2}}[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)]$ (symmetric)

Spin part:

1. $|\uparrow\rangle_1 |\uparrow\rangle_1$ (symmetric)

2. $|\downarrow\rangle_1 |\downarrow\rangle_2$ (symmetric)

3. $\dfrac{1}{\sqrt{2}}[|\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2]$ (symmetric)

4. $\dfrac{1}{\sqrt{2}}[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2]$ (antisymmetric)

For the overall wavefunction to be antisymmetric. Combine antisymmetric and symmetric pair from spatial and spin part, and we have 4 such possibilities.

Which states are more likely to have lower energy in the presence of repulsion forces: **spatially antisymmetric state**.

Reason: particles are **further apart in spatially antisymmetric state**, since they can never be at the same place. Thus the addition of a short range interaction will raise the energy of the antisymmetric spatial state by less than it would raise the energy of the symmetric spatial state.

10 Matrix mechanics

Overlap integrals, level splitting/repulsion, perturbative study.

$$A_{mn} = \langle \phi_m | \hat{A} | \phi_n \rangle$$

$$\hat{A} = \sum_{mn} A_{mn} |\phi_m\rangle \langle \phi_n|$$

10.1 Two level systems

Consider a double potential well, such as an electron in the vicinity of two close atoms.

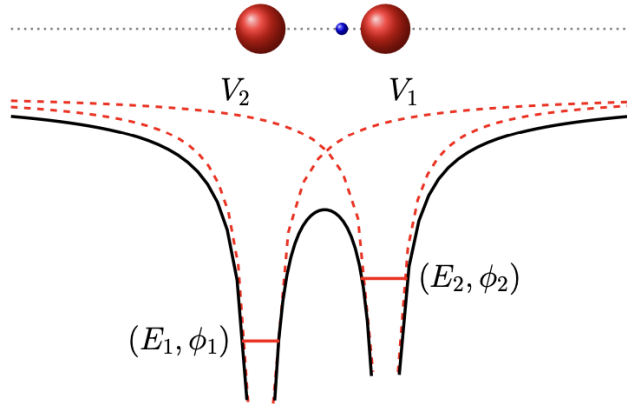V_1 is the potential due to one nucleus, and V_2 is the potential due to the other.

Figure 4: The two lowest energy states are shown

The two potential wells, when in isolation, would have Hamiltonian $\hat{H}_1$ and $\hat{H}_2$ respectively:

$$\hat{H}_1 |\phi_1\rangle = E_1 |\phi_1\rangle$$
$$\hat{H}_2 |\phi_2\rangle = E_2 |\phi_2\rangle$$

The total potential is the sum of the two potential well:

$$\hat{V} = \hat{V}_1 + \hat{V}_2$$

For the composite system having only 1 particle:

$$\hat{H} = \hat{T} + \hat{V}_1 + \hat{V}_2 \quad \text{and} \quad \hat{H} |\phi\rangle = E |\phi\rangle$$

$\hat{H}$ can be written in terms of $\hat{H}_1$ and $\hat{H}_2$:

$$\hat{H} = \hat{H}_1 + \hat{V}_2 \quad \text{and} \quad \hat{H} = \hat{H}_2 + \hat{V}_1$$

Assuming the wave function is the linear superposition of the eigenstates of the two potential wells:

$$|\phi\rangle = c_1 |\phi_1\rangle + c_2 |\phi_2\rangle$$

Then find matrix elements of $\hat{H}$:

1. Diagonal terms:

$$H_{11} = \langle \phi_1 | \hat{H}_1 + \hat{V}_2 | \phi_1 \rangle = E_1 + \langle \phi_1 | \hat{V}_2 | \phi_1 \rangle \approx E_1$$

Similarly, $H_{22} \approx E_2$. Because the wavefunction of well 1 is well-separated from the potential function of well 2 so the expectation of potential is small.

2. Off-diagonal terms (coupling potentials):

$$H_{12} = \langle \phi_1 | \hat{H} | \phi_2 \rangle = t$$
$$H_{21} = \langle \phi_2 | \hat{H} | \phi_1 \rangle = t^*$$

These are called overlap integrals because they describe the 'coupling' between the wavefunctions of the two wells.

t has the dimensions of energy and takes the form of a **coupling potential**. They appear as **off-diagonal** elements in the Hamiltonian.

Lastly, solve the eigenvector equation by setting determinant to zero:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \lambda \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\begin{vmatrix} H_{11} - \lambda & H_{12} \\ H_{21} & H_{22} - \lambda \end{vmatrix} = \begin{vmatrix} E_1 - \lambda & t \\ t^* & E_2 - \lambda \end{vmatrix} = 0$$

Solve for λ then find the corresponding eigenvectors.

Words and interpretations
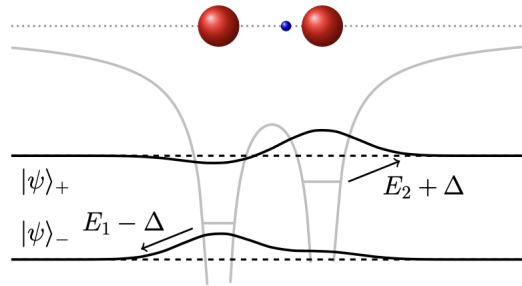
For a pair of identical potential wells,

- The original states interact and form symmetric (lower energy/bonding) and an antisymmetric states (higher energy/antibonding). The **original energy levels split**, the **degeneracy is lost**, and two new energy levels are formed. This is a characteristic feature of many interacting physical systems.

- The sharing of electrons to lower the total energy of a system is in essence the formation of a **covalent bond** between the two bound systems. For example in H_2.
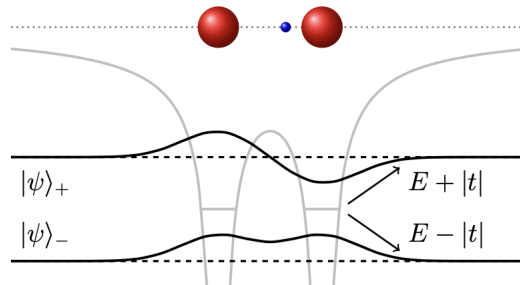
For two different potential wells and assuming weak coupling i.e. $t \ll E_2 - E_1$,

$$\frac{|t|}{E_2 - E_1} = \delta \ll 1$$

- The upper energy level shifts up and the lower energy level shifts down. This is called **level repulsion** and is a generic outcome when distinct energy eigenstates are perturbatively coupled to one another.

- $|\psi\rangle_-$ dominated by $|\phi_1\rangle$ for the energy $E_1 - \Delta$. $|\psi\rangle_+$ dominated by $|\phi_2\rangle$ for the energy $E_2 + \Delta$

$\sim$ End of Notes $\sim$