Torsten's quantum 1 summary

Foreword:
This guide is by no means a replacement of the textbook. One would study best by reading that, and summarising it themselves. But, I do ~~recom~~ recommend to read this, as certain parts are explained differently here.

If the time is there the best way to learn from my guide is to transcribe it - in full - on paper. This was ~~als~~ also originally hand-written.

I wish you all the best of luck.

Torsten van Drogenbeek

Quantum summary

1.2 minutes per point
45 points for 5.0

1 Postulates

1.1 Particles

Wave functions

quantum systems $\Psi(\vec{r},t)$

[redacted] Dirac notation $|\Psi(t)\rangle$

1.2 $i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$ ω. $\Psi \in \mathbb{C}$ $\hbar = 1.054 \cdot 10^{-34}\,J\cdot s = 6.582\cdot 10^{-16}\,eV\cdot s = \frac{h}{2\pi}$

1.3 Location is probabilistic

$|\Psi(r,t)|^2 d^3r = \Psi^*\Psi\, d^3r$, $d^3r = dx\,dy\,dz$ $\int_{-\infty}^{\infty}|\Psi|^2 d^3r = 1$

1.4 Observable in Quantum Mechanics → linear hermitian operator

Position	x	$\hat{x}$	x	$i\hbar\frac{\partial}{\partial p}$
Momentum	p	$\hat{p}$	$-i\hbar\frac{\partial}{\partial x}$	p
	Classical Mechanics	Quantum Mechanics	Operation with respect to x	Operation with respect to p

1.5 A measurement of observable $\hat{A}$ always results in 1 of its eigenvalues "a" → $\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle$

1.6 The probability P_a [redacted] for a measurement of observable $\hat{A}$ with result "a_n" is $|\langle\psi_n|\alpha\rangle|^2 = \int\psi_n(x)\alpha(x)\,dx$

1.7 The eigenfunctions of an observable operator are complete. Any function in Hilbert space can be expressed as a linear combination of them.

[redacted]

~~2 Important equations~~

2 Important equations.

around c

$$f(x) = \sum_{k=0}^{\infty} \frac{1}{k!} f^{(k)}(c)(x-c)^k \qquad [\hat{x}, \hat{p}] = i\hbar$$

$$\langle \hat{x} \rangle = \int \Psi^* x \Psi \, dx \qquad \Delta x^2 = \langle x^2 \rangle - \langle x \rangle^2 \qquad \Delta x \Delta p \geq \frac{\hbar}{2}$$

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

$$\delta(x-x_0) = \begin{cases} \infty & \text{if } x = x_0 \\ 0 & \text{if } x \neq x_0 \end{cases}$$

$$\int_{-\infty}^{\infty} \delta(x-x_0)\psi(x)dx = \psi(x_0)$$

$$\Psi(x,t) = \psi(x)\varphi(t) \qquad \varphi(t) = e^{-iE\frac{t}{\hbar}} \quad \text{"Wiggle factor"}$$

$$\Psi(x,t) = \sum \psi_n c_n \varphi(t) \qquad \sum_{n=1}^{\infty} |c_n|^2 = 1 \; , \; |c_n|^2 \text{ is probability of } \psi_n$$

Very important: exponentials

$$\sin(x) = \frac{e^{xi} - e^{-xi}}{2i} \qquad \cos(x) = \frac{e^{xi} + e^{-xi}}{2} \qquad e^{ix} = \cos(x) + i\sin(x)$$

3 Chapter 2 - Schrödinger equation mathematics

3.1 Infinite Square Well

$$V = \begin{cases} 0 & \text{if } 0 \leq x \leq a \\ \infty & \text{if otherwise} \end{cases} \rightarrow \psi \text{ is of shape } A\sin(kx) + B\cos(kx) \xrightarrow{\text{Boundary conditions}} E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

↓ Boundary conditions & normalising

$$\psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

$$c_n = \int \psi_n^*(x) f(x)\, dx. \quad f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \Psi(x,0)$$

3.2 Harmonic Oscillator

$$V(x) = \frac{1}{2}kx^2 \rightarrow \frac{1}{2m}\left[\hat{p}^2 + (m\omega x)^2\right]\psi = E\psi \qquad a_\pm \frac{1}{\sqrt{2\hbar m\omega}}\left(\mp i\hat{p} + m\omega x\right)$$

↓

$a_- \psi_0 = 0 \rightarrow \psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2}$

solve Gaussian integral

$\Rightarrow \psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}$

$\psi_n(x) = A_n (a_+)^n \psi_0 \leftarrow a_- \psi_n = A_n n \psi_{n-1}$

$a_+ \psi_n = A_{n+1}\psi_{n+1}$

$\boxed{\Rightarrow \psi_n(x) = \frac{1}{\sqrt{n!}}(a_+)^n \psi_0}$

$[\hat{a}_-, \hat{a}_+] = 1$

3.3 Free Particle

$V=0 \rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi$ $\psi = Ae^{ikx} + Be^{ikx}$. No boundary conditions.

$\Psi(x,t) = Ae^{ik(x-\frac{\hbar k}{2m}t)} + Be^{\underbrace{ik(x-\frac{\hbar k}{2m}t)}_{\gamma x \pm \omega t}}$ $k = \sqrt{\frac{2mE}{\hbar}}$ wave!

↓ This is not normalisable.

But following $\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n$,

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

can be written as a normalised function. A single $\psi(x)$ cannot be normalised, but the integral over multiple of them can.

$v = \frac{\omega}{\gamma} = \frac{\hbar k}{2m} = \sqrt{\frac{E}{2m}}$

This is weird. v, according to classical mechanics, v must be $\sqrt{\frac{2E}{m}}$. Somehow ~~$\frac{E}{2m}$ is quantum~~ $\sqrt{\frac{E}{2m}} = v_{quantum} < \sqrt{\frac{2E}{m}} = v_{classic}$.

Then follows the application of Plancherel's Theorem.

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

So, groups of wavefunctions can be described & normalised.

For groups, if a group does not change much, $\phi(k)$ is peaked around a value k_0 & the group stays defined. If a group moves and is defined, it must have a "group" velocity. So for calculating a "group" velocity, we can assume $\phi(k)$ ~~$\phi(k, k_0)$~~ peaks at $k = k_0$. In this case, terms ~~far~~ from k_0 are negligible, and $\omega(k) = \frac{\hbar k^2}{2m}$ can be taylor approximated while ignoring higher terms: $\omega(k) = \frac{\hbar k}{2m} \simeq \omega_0 + \omega_0'(k-k_0)$

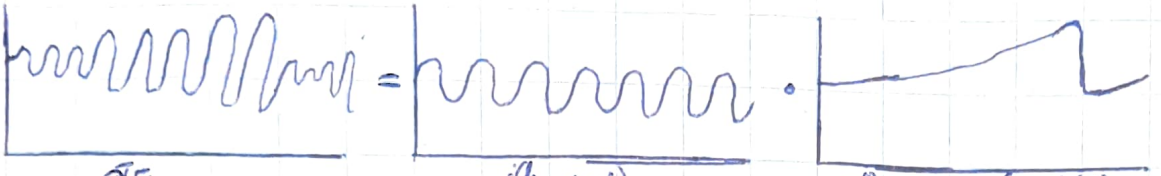
Because k peaked around k_0, $(k-k_0)^n$ goes to 0 fast as n increases. Hence, the dropped higher orders.

$\Rightarrow \Psi(x,t) \approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k_0+s) e^{i[(k_0+s)x - (\omega_0 + \omega_0' s)t]} ds$

$\Rightarrow \Psi(x,t) \approx \frac{1}{\sqrt{2\pi}} e^{i(k_0 x - \omega_0 t)} \int_{-\infty}^{\infty} \phi(k_0+s) e^{is(x-\omega_0' t)} ds$

wave 1 (sin) × wave 2 (groups)

$\Psi(x,t)$ is a combination of multiple waves! A drawing sheds more light:



$\Psi(x,t)$ $\quad$ $e^{i(kx-\omega t)}$ $\quad$ $\int_{-\infty}^{\infty}\varphi(k_0+s)e^{is(x-\omega_0' t)}\,ds$

$\omega_0 = \frac{\hbar k_0^2}{2m}$ $\quad$ $v = v_{\frac{\omega}{\gamma}} = \frac{\omega_0}{k_0} = \frac{\hbar k_0}{2m} = \sqrt{\frac{E}{km}}$ $\quad$ $v = \omega_0' = \frac{d\omega}{dk_0} = \frac{\hbar k_0}{m}$

$v = \sqrt{\frac{E}{2m}} = v_{quantum}$ $\quad$ $v = \sqrt{\frac{2E}{m}} = v_{classical}$

$v_{classical}$ is the velocity of a wave packet! The individual waves do not move as fast as the particle.

3.4 Delta Potential

For any potential V: ~~if E < V & V~~

if $E < V(-\infty)$ & $V(\infty)$, The particle is in a bound state, normalisable.
(e.g. Infinite square well, harmonic oscillator)

if $E > V(-\infty)$ or $V(\infty)$, The particle is in a scattering state - not normalisable.
(e.g. free particle)

As $V(-\infty)$ & $V(\infty)$ are usually ~~equal~~ approaching 0, $\begin{cases} E<0 \Rightarrow \text{Bound state} \\ E>0 \Rightarrow \text{Scattering state} \end{cases}$

Some $V(x)$ support Bound & scattering states

Negative delta function potential: $V(x) = -\alpha\delta(x)$

$E<0$ $\quad \frac{d^2\psi}{dx^2} = \frac{-2mE}{\hbar}\psi = \kappa^2\psi \Rightarrow \psi = Ae^{-\kappa x} + Be^{\kappa x}$ (at $x \neq 0$, $V=0$). Normalisation & Bound conditions:

$B = \sqrt{\kappa}$, ~~if~~ $\psi(x) = \sqrt{\kappa}e^{\kappa x}$ if $x < 0$, $\psi(x) = \sqrt{\kappa}e^{-\kappa x}$ if $x > 0$, ~~one can assume that~~ $\psi_0 = \sqrt{\kappa}$, assumed.

But what are the energy levels? We know $E<0$, but can we get more specific? we know $\kappa = \sqrt{\frac{-2mE}{\hbar}} \Rightarrow -\frac{\hbar^2\kappa^2}{2m} = E$. So, we need to define κ in other terms than E. κ correlates to the slope of ψ → the discontinuity of $\frac{d\psi}{dx}$. Maybe from $\frac{d\psi}{dx}$ then? Yes, as it finally involves $V(x) = -\alpha\delta(x)$ at $x=0$

Let's try. First step: Integrate both sides of schrödinger eq between ε & $-\varepsilon$ with the whole equation placed inside the limit $\lim_{\varepsilon\to 0}(\ldots)$.

$$-\frac{\hbar^2}{2m}\int_{-\varepsilon}^{\varepsilon}\frac{d^2\psi}{dx^2}dx + \int_{-\varepsilon}^{\varepsilon}V(x)\psi(x)dx = E\int_{-\varepsilon}^{\varepsilon}\psi(x)dx \qquad \int_{-\infty}^{\infty}\delta(x)\psi(x)dx = \psi(0)$$

$$-\frac{\hbar^2}{2m}\left(\frac{d\psi}{dx}\Big|_{\varepsilon} - \frac{d\psi}{dx}\Big|_{-\varepsilon}\right) \qquad -\alpha\psi_0 \qquad 0$$

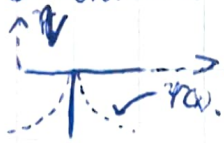
$$\Rightarrow$$

$$-\frac{\hbar^2}{2m}\cdot 2\sqrt{\tfrac{-2mE}{\hbar^2}}\cdot\sqrt{\tfrac{-2mE}{\hbar^2}} = -\alpha\sqrt{\tfrac{-2mE}{\hbar^2}} \Rightarrow \kappa = \frac{m\alpha}{\hbar^2}$$

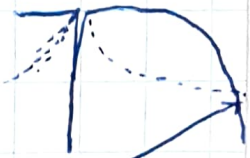
$\Rightarrow$ Exactly what we want! $E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{m^2\alpha^2}{2m\hbar^2} = \boxed{-\frac{m\alpha^2}{2\hbar^2}}$

~~$E>0$. If $x\neq 0$, free particle & $\psi = Ae^{ikx} + Be^{-ikx}$. In practice expected. Boundary conditions give $A=0$ if $x>0$ $\psi = Ae^{ikx} + Be^{-ikx}$~~

Addendum: $V(x) = -\alpha\delta$:



If however, V lowers further along:



Chance of particle appearing is nonzero!

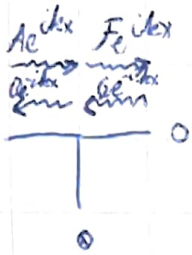
$\leftarrow V(x) < \psi(x)$

Quantum Tunneling!

$E>0$ $\psi = Ae^{ikx} + Be^{-ikx}$ if $x<0$, $Fe^{ikx} + Ge^{ikx}$ if $x>0$. Continuity at $x=0$ $\Rightarrow F+G = A+B$

Continuity of derivatives $\Rightarrow F-G = A(1+2i\beta) - B(1-2i\beta)$. $\beta = \frac{mV_0}{\hbar^2 k}$

That's it! But it is useful. Consider Physical situation!



remember, wave packets here = particles.

→ reflected & transmitted waves. For simplicity, only one wave is incident → $G=0$. Then, the boundary conditions give:

$B = \frac{i\beta}{1-i\beta} A$, $F = \frac{1}{1-i\beta} A$. Still not normalisable.

But, we can formulate Transmission & reflection coefficients: $R = \frac{|B|^2}{|A|^2}$. $T = \frac{|F|^2}{|A|^2}$

Of course, $T+R=1$ & $T = \frac{1}{1+\frac{mV_0^2}{2E\hbar^2}}$, $R = \frac{1}{1+\frac{2E\hbar^2}{mV_0^2}}$

3.5 Finite Square Well.

$$V(x) = \begin{cases} -V_0 & -a \le x \le a \\ 0 & |x| > a \end{cases}$$

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < a \\ Fe^{ikx} + Ge^{ikx} & x > a \\ Pe^{ilx} + Qe^{-ilx} = C\sin(lx) + D\cos(lx) & |x| \le a \end{cases}$$

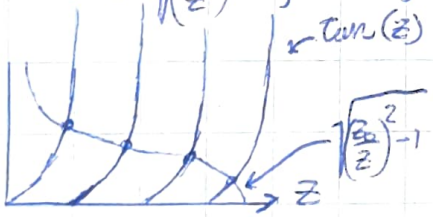
← k because $E<0$ assumed.

$$l = \frac{\sqrt{2m(E+V_0)}}{\hbar}$$

Boundary conditions → $Fe^{-ika} = D\cos(la)$, $-ikFe^{-ika} = -lD\sin(la)$

For all odd states, $C=0$.

$\Rightarrow \tan(z) = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$, $z = la$, $z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0}$. Where true? Let's plot!



⇒ Intersections are possible energy states.

⇒ If z exceeds graph ($z_0 < z$), particle exceeds well.

⇒ Crude model of bound electrons around an atom. Also a model for a solid state system.

⇒ If z exceeds graph for an atom model ⇒ Electron leaves atom. Ionisation!

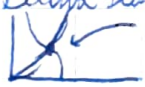
Extreme cases:

$z_0 \to \infty$, wide, deep well → Infinite Square Well.

$E_n \approx \frac{n^2\pi^2\hbar^2}{8ma^2}$

$z_0 \to 0$ shallow, narrow well. → Bound states decrease.

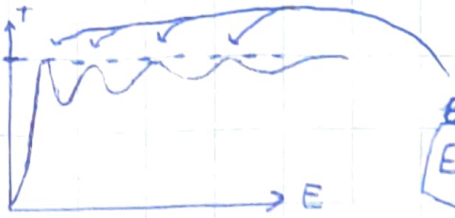
To lower limit of 1:



only one energy state. Approximately the Dirac Delta Well.

If a particle exceeds the well, it scatters. Here, $T = 1 + \frac{V_0^2}{E(E+V_0)} \sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right)$

$T = 1$ if $\frac{2a}{\hbar}\sqrt{2m(E+V_0)} = n\pi$;



$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{8ma^2}$

Energy states for the Infinite Square Well.

At these energy states, resonance occurs. This causes perfect destructive interference, which voids the reflected wave.

Following the delta well example with one incident particle, there is again transmission & reflection. But with a wide well, there will also be a wave inside the well. Its wavelength is $\lambda_{in} = \frac{2\pi}{\ell}$. $\lambda_{out} = \frac{2\pi}{k}$. In an incident wave, you can control λ_{out}. If you want resonance in the well, you have to send in a particle with a higher wavelength than resonance. As $\ell > k$, $\lambda_{out} > \lambda_{in}$.

3.6 Addendum

If $E \to 0$, bound, growth coefficient used is K. If scattered, use k.

Dirac Interpretation Harmonic Oscillator (Ladder Operators)

$\psi_n = \langle x|n\rangle \quad \langle n|m\rangle = \delta_{nm} = \begin{cases} 1, n = m \\ 0, n \neq m \end{cases}$

$a_\pm|n\rangle = |n \pm 1\rangle \quad \langle n|a_- a_-|n\rangle = \langle n|n-2\rangle = 0$

$\hat{H}|n\rangle = E_n|n\rangle \quad \hbar\omega\left(\hat{a}_\pm \hat{a}_\mp \pm \frac{1}{2}\right)|n\rangle = \hbar\omega(n+1)|n\rangle$

$|\hat{a}_+ \hat{a}_-|n\rangle = \left(n + \frac{1}{2} \mp \frac{1}{2}\right)|n\rangle$

4 Chapter 3 - Dirac Interpretation (Linear Algebra)

4.1 Dirac notation: operators written as matrices, wave functions written as vectors.

Inner product: $\langle\alpha|\beta\rangle = a_1^* b_1 + a_2^* b_2 + \dots + a_n^* b_n = \int_a^b \alpha(x)^* \beta(x) dx = \langle\beta|\alpha\rangle^*$

$\int |\psi|^2 dx = 1 = \langle\psi|\psi\rangle$. Hilbert space: all fns where $\int_{-\infty}^{\infty} |f(x)|^2 dx < \infty$. All wave functions live in Hilbert space.

If $\alpha(x)$ & $\beta(x)$ both live in Hilbert space, they must have an inner product → all wavefunctions have an inner product with all other wavefunctions. This follows from the Schwarz-Cauchy inequality: $\left|\int_a^b f(x)^* g(x) dx\right| \leq \sqrt{\int_a^b |f(x)|^2 dx \int_a^b |g(x)|^2 dx}$ $(=) |\langle\alpha|\beta\rangle|^2 \leq \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle$.

If $\langle f|f\rangle = 1$, it is normalised. If for one set of f, $\int f(x) \langle f_n | f_m \rangle = \begin{cases} 0 & \text{if } n \neq m \\ 1 & \text{if } n = m \end{cases}$, it is orthonormal. If any function f in a set f_n can be described by a linear combination of $f_n(x)$, (e.g. $f(x) = \sum_{n=1}^{\infty} c_n f_n(x)$), $f_n(x)$ is complete.

If $f_n(x)$ is complete & all f_n are orthonormal, $c_n = \langle f_n | f \rangle$

Henceforth written as n.

You can also have a complete basis: $|\alpha\rangle = \sum_n c_n |\psi_n\rangle$. The complete basis $|\alpha\rangle$ consists of the minimum set of linearly independent vectors which describe any other vector (span the space). To check if a state is in $|\alpha\rangle$, $\langle f_n | \sum_m c_m | f_m \rangle = 1 \rightarrow \sum_m c_m \delta_{nm} = 1$.

4.2 Observables

All observables in Quantum Mechanics are represented by hermitian operators by definition.

For hermitian operator $\hat{Q}$:

$\int \Psi^* \hat{Q} \Psi \, dx = \langle \Psi | \hat{Q} \Psi \rangle = \langle \hat{Q} \rangle = \langle \hat{Q} \rangle^* = \langle \hat{Q} \Psi | \Psi \rangle$, a for all $f(x)$ & $g(x)$, $\beta | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$

$\langle f | \hat{Q} g \rangle = \langle \hat{Q}^\dagger f | g \rangle \Rightarrow \hat{Q} = \hat{Q}^\dagger$. off diagonal of $\hat{Q}$ are related by complex conjugate:

$\langle \phi | \hat{Q} | \varepsilon \rangle = (\langle \varepsilon | \hat{Q} | \phi \rangle)^*$

- Determinate States

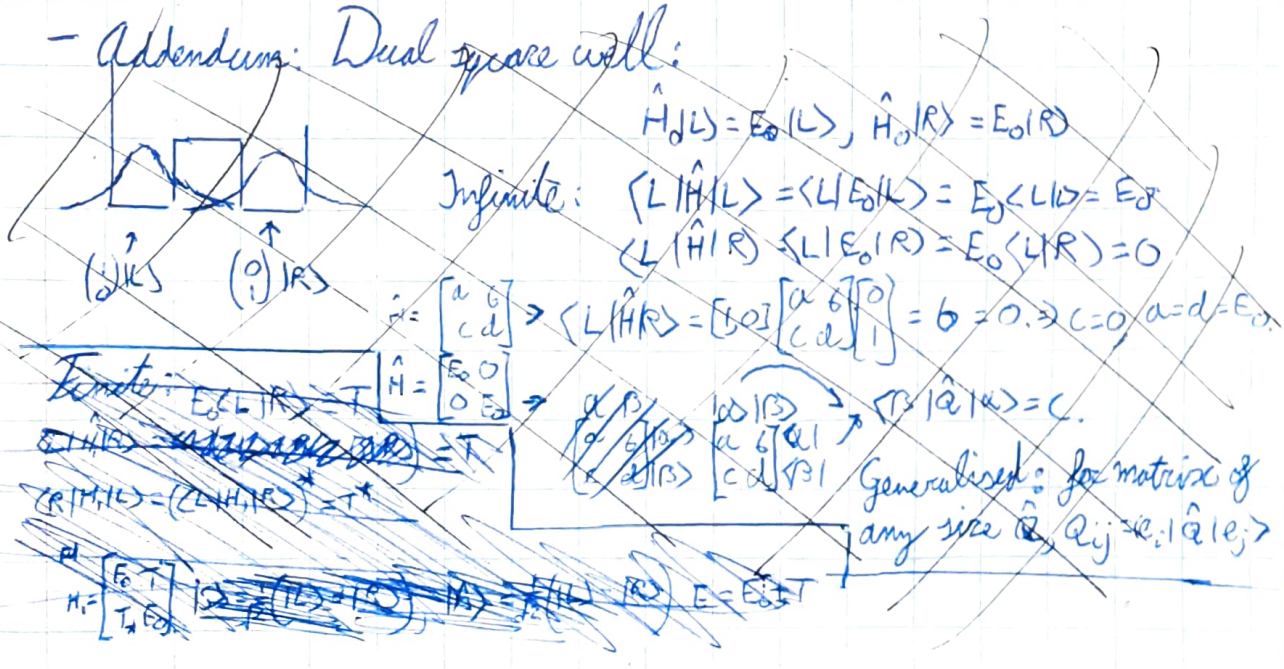
A function f with $\hat{Q} f = q$ where q on will always be the same value. (a measurement always returns the same value) is a determinate state (example, $\hat{H}$)

Determinate states are eigenfunctions of $\hat{Q}$.

$\Delta \hat{Q} = \langle (Q - \langle Q \rangle)^2 \rangle = \langle \Psi | (\hat{Q} - q)^2 \Psi \rangle = \langle (\hat{Q} - q) \Psi | (\hat{Q} - q) \Psi \rangle = 0$. 0 is not an eigenfunction.

~~$\hat{Q} f_1 = f_2 \hat{Q}$~~ If $\hat{Q} f_1 = \hat{Q} f_2 = q_{12} g$ with f_1 & f_2 ~~linearly~~ linearly independent, $\{f_1, f_2\}$ is degenerate.

- Addendum: Dual space with:



- Addendum: Dual Square Well:

Infinite potential: $\hat{H}_0|L\rangle = E_0|L\rangle$, $\hat{H}_0|R\rangle = E_0|R\rangle$

$\langle L|\hat{H}_0|L\rangle = E_0\langle L|L\rangle = E_0$.

$\langle L|\hat{H}_0|R\rangle = E_0\langle L|R\rangle = T = 0$.

$\langle L|H_0|R\rangle = [1,0]\begin{bmatrix} a & b \\ c & d \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = b = 0$

$\Rightarrow c = 0,\ a = d = E_0 \Rightarrow \hat{H}_0 = \begin{bmatrix} E_0 & 0 \\ 0 & E_0 \end{bmatrix}$

Finite Potential: $\langle L|R\rangle \neq 0$

$\langle L|H_1|L\rangle = E_0$ & $\langle L|H_1|R\rangle = E_0\langle L|R\rangle = T$.

$\hat{H}_1 = \begin{bmatrix} E_0 & T \\ T^* & E_0 \end{bmatrix}$ as $\langle R|H_1|L\rangle = \langle L|H_1|R\rangle^* = T^*$.

It is important to note that $|L\rangle$ & $|R\rangle$ are not eigenstates of $\hat{H}_1$. $\hat{H}_1|L\rangle \neq E_0|L\rangle$, $\hat{H}_1|R\rangle \neq E_0|R\rangle$. $\langle L|H|R\rangle$ is always T, but in the infinite well, it is 0. Of course, the energies don't change, so E_0 remains the same. But if $|L\rangle$ & $|R\rangle$ are not eigenstates, what are? Superpositions!

Let me define:

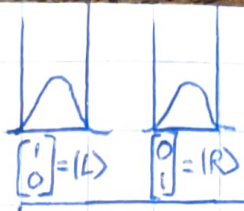
$|S\rangle = \frac{|L\rangle + |R\rangle}{\sqrt{2}}$ (Symmetric superposition vector)

$|A\rangle = \frac{|L\rangle - |R\rangle}{\sqrt{2}}$ (antisymmetric superposition vector)

$\hat{H}_1|L\rangle = E_0|L\rangle + T^*|R\rangle$, $\hat{H}_1|R\rangle = E_0|R\rangle + T|L\rangle$

$\Rightarrow \hat{H}_1|S\rangle = E_0 + T|S\rangle$

$\Rightarrow \hat{H}_1|A\rangle = E_0 - T|A\rangle$

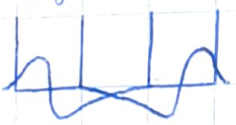


Generalised:

$\begin{bmatrix} \langle\alpha|S\rangle & \langle\alpha|R\rangle \\ \langle\beta|S\rangle & \langle\beta|R\rangle \end{bmatrix} \rightarrow \langle\alpha|\hat{Q}|\beta\rangle = b.$

$Q_{ij} = \langle e_i|\hat{Q}|e_j\rangle$

Symmetric



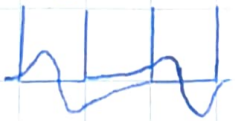
$\hat{H}_1|S\rangle = (E_0 + T)|S\rangle$

Probability for any symmetrical dual well:

$|\langle L|S\rangle|^2 = P(\text{left well}) = \frac{1}{2}$

$|\langle R|S\rangle|^2 = P(\text{right well}) = \frac{1}{2}$

antisymmetric

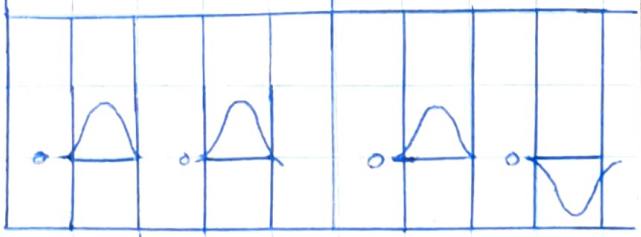


$\hat{H}_1|A\rangle = (E_0 - T)|A\rangle$

Probability for any antisymmetrical dual well:

$|\langle R|A\rangle|^2 = P(\text{right well}) = \frac{1}{2}$

$|\langle L|A\rangle|^2 = P(\text{left well}) = \frac{1}{2}$

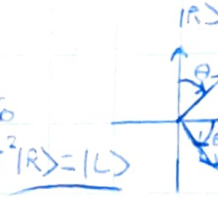


What are $|S\rangle$ & $|A\rangle$?

$\hat{T}|L\rangle = |A\rangle$, $\hat{T}|R\rangle = |S\rangle$

$\Rightarrow \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$ at $\theta = -\frac{1}{4}\pi = \begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{bmatrix}$

$\begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ 1/\sqrt{2} & -1/\sqrt{2} \end{bmatrix} = \hat{T} \Rightarrow \hat{T}$ rotates back 45°!



So $\hat{T}^2|R\rangle = |L\rangle$

4.3 Eigenfunctions of a Hermitian Operator

Sets of Determinate States of particles can be discrete (normalised) or continuous (not normalised). If it is the latter, the inner product may not exist.

- Discrete Spectra: the inner product exists & $\hat{Q}$ is hermitian.

$\Rightarrow \langle f|\hat{Q}f\rangle = \langle \hat{Q}f|f\rangle = q\langle f|f\rangle = q^*\langle f|f\rangle \Rightarrow \underline{q^* = q}$. $(\langle f|f\rangle \neq 0)$

$\Rightarrow \langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle \Rightarrow q'\langle f|g\rangle = q^*\langle f|g\rangle = q\langle f|g\rangle$. $q' = q \Rightarrow \underline{\langle f|g\rangle = 0}$

$\Rightarrow$ Eigenvalues of discrete spectra functions are real.

$\Rightarrow$ Eigenfunctions belonging to distinct eigenvalues are orthogonal

$\Rightarrow$ These properties were known in Chapter 2, but here we prove that they are simple consequences of hermitian operators.

Even in the event of degeneracy, ~~$\neq$~~ $(q = q')$, eigenfunctions are assumed orthonormal. Because of this Fourier's trick can be used for discrete spectra in general to find coefficients. (Fourier's trick is the integration of both sides of an equation, we used it in the delta potential example to find K.)

In finite space, eigenvectors of a hermitian matrix (eigenfunctions of a hermitian operator) span the space. Not the case for infinite space. (Again, this means $|\alpha\rangle = \sum_n c_n|\psi_n\rangle$

$\Rightarrow$ This also implies $\langle\hat{\alpha}\rangle = \sum_n |c_n|^2 q_n$, if you remember $\hat{Q}|m\rangle = q|m\rangle$ & $\langle\hat{Q}\rangle = \langle\psi|\hat{Q}|\psi\rangle$.

Postulate 7 applies here.

- Continuous Spectra: Eigenstates not normalisable. But, remember: the Free Particle state was normalisable for an integral of multiple wavefunctions. Similarly, a linear combination of eigenstates involving a spread in eigenfunctions is normalisable.

Orthonormality of Eigenstates can be proven by example. They are "kind of orthonormal". We call this Dirac Orthonormality.

Take $\hat{p} \to -i\hbar \frac{d}{dx} f_p(x) = p f_p(x)$. If the eigenvalues are real & we take $f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \to \langle f_{p'} | f_p \rangle = \delta(p-p')$.

($f_{p'}(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ip'x/\hbar}$)

Again, semi-orthonormal.

All eigenfunctions of a continuous spectrum can be defined. Again drawing similarities to scattering states, they are complete using an integral. For a discrete spectrum, $|a\rangle = \sum_n c_n |n\rangle$. For a continuous spectrum: $f(x) = \int C(p) f_p(x)\, dx$

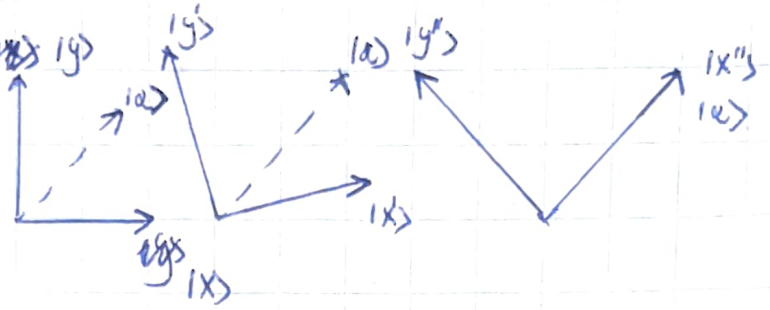
The "coefficients" $C(p)$ are obtained by multiplying both sides with $\langle f_{p'}|$, (turning $f(x)$ & $f_p(x)$ into $|f\rangle$ & $|f_p\rangle$), & Fourier's trick $\to C(p') = \langle f_{p'} | f \rangle$

The eigenfunctions of momentum $f(x)$ are sinusoidal with wavelength $\lambda = \frac{2\pi\hbar}{p} \to$ De Broglie Wavelength! Funny, because p cannot be precisely defined. This equation is relevant for wave packets with a narrow range of momenta. (Δp small.)

This all also applies to the position operator $\hat{x}$ with eigenfunction $\delta(x-y)$. It applies to all continuous spectra with real eigenvalues. Dirac Orthonormality!

- Addendum:

Changing bases:



$|\alpha\rangle = a|x\rangle + b|y\rangle$ $|\alpha\rangle = a'|x'\rangle + b'|y'\rangle$ $|\alpha\rangle = a''|x''\rangle$.

$$\begin{cases} \hat{A}|L\rangle = -a|L\rangle \\ \hat{A}|R\rangle = a|R\rangle \end{cases} \Rightarrow \hat{A} \to \begin{bmatrix} -a & 0 \\ 0 & a \end{bmatrix}, \hat{H}_0 \to \begin{bmatrix} E_0 & 0 \\ 0 & E_0 \end{bmatrix}$$

$\Rightarrow$ $\hat{A}$ & $\hat{H}_0$ share the same basis. ~~In fact, all matrices (operators) with specific eigenfunctions eigenfunctions share the same basis.~~

$\Rightarrow$ $\hat{A}$ & $\hat{H}_0$ share the same basis. In fact, all Matrices (operators) with ~~specific eigen~~ the same eigenfunctions share the same basis!

- Quantum States

Quantum States are vectors $|\alpha\rangle$. We want our definition to contain all the information we need.

E. G. $\begin{cases} \Psi(x,t) = \langle x|\alpha(t)\rangle \\ \phi(p,t) = \langle p|\alpha(t)\rangle \\ C_n(t) = \langle n|\alpha(t)\rangle \end{cases}$ with $|x\rangle$ eigenvector of $\hat{x}$ with eigenvalue x with $|p\rangle$ eigenvector of $\hat{p}$ with eigenvalue p with $|n\rangle$ eigenvector of $\hat{H}_{\text{harmonic oscillator}}$ with eigenvalue E_n

Go back to example of the harmonic oscillator: $\langle x|n\rangle = \psi_n(x)$

remember: $\Psi(x,0) = \sum_n c_n \psi_n(x) = \sum_n c_n \langle x|n\rangle = \langle x|\sum_n c_n|n\rangle$. We state: $\Psi(x,0) = \langle x|\alpha\rangle \Rightarrow |\alpha\rangle = \sum_n c_n|n\rangle$. $|0\rangle = [1\ 0\ 0\ \dots\ 0]^T$, $|1\rangle = [0\ 1\ 0\ \dots\ 0]$

$\Rightarrow \langle\alpha| = [c_0, c_1, c_2, \dots, c_n]$ $\rightarrow$ represents entire state of Harmonic oscillator

~~In~~ ge In general, $|\alpha\rangle = \begin{bmatrix} \vdots \end{bmatrix}$, contains all information on a particle in Quantum Mechanics. Not just position, momentum or energy! For example, for circular currents in ~~an inductor~~ a superposition of clockwise & counter-clockwise directions, $|I\rangle$ can be $\frac{1}{\sqrt{2}}(|CC\rangle + |CL\rangle)$

~~ca clock~~ counter clockwise ↓ clock wise ↓

also, remember $\psi_n = \langle x|\psi_n\rangle$? $|\psi_n|^2 = P_{(\text{under } \psi_n)} = |\langle x|n\rangle|^2$

this is general, $|c_n|^2 = |\langle n|\psi\rangle|^2$.

explains why in the dual space well $|\langle L|S\rangle|^2$ was equal to $P_{\text{left well}}$.

($|c_n|^2 dz = |\langle \ell_z|\psi\rangle|^2 dz$ for continuous)

Let's go back to those different bases we discussed. One might want to switch between them. For this we use a Projection operator $\hat{P}_\alpha = |\alpha\rangle\langle\alpha|$.

If with $|\alpha\rangle$ the desired basis, orthogonal to original basis $|\beta\rangle$:

$\hat{P}_\alpha |\beta\rangle = |\alpha\rangle\langle\alpha|\beta\rangle = |\alpha\rangle$.

But for a proper change in basis you need to affect all parts of the original basis equally; so we sum all changes to one operator (for discrete bases):

$\hat{I} \equiv \sum_n |e_n\rangle\langle e_n| \Rightarrow \hat{I}|\alpha\rangle = \sum_n |e_n\rangle\langle e_n|\alpha\rangle = \sum_n c_n |e_n\rangle$.

This way you can be sure that you only change the basis, not the Quantum State. We can also do this for continuous bases: $\hat{I} \equiv \int |e_z\rangle\langle e_z| dz = 1$

↑ Necessary for only basis change.

This is especially useful: consider $\int |x\rangle\langle x| dx$ & $\int |p\rangle\langle p| dp$. (both $=1$)

$\Psi(x,t) = \langle x|\alpha(t)\rangle$ & $\phi(p,t) = \langle p|\alpha(t)\rangle$ ⇔

$\langle p|\alpha\rangle = \langle p|\left(\int |x\rangle\langle x| dx\right)|\alpha\rangle = \int \langle p|x\rangle\langle x|\alpha\rangle dx = \int \langle x|p\rangle^* \Psi(x,t) dx$

$\langle x|p\rangle^* = \frac{1}{\sqrt{2\pi\hbar}} e^{-ipx/\hbar} \Rightarrow \phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{-ipx/\hbar} \Psi(x,t) dx$

Thus, we have used $\hat{I}$ to change the wavefunction from an x to a p basis.

4.4 Generalised ~~Uncertainty Principle~~ Statistical Interpretation

If you measure an observable $Q(x,p)$ on a particle in state $\Psi(x,t)$, you are certain to get one of the eigenvalues of the hermitian operator $\hat{Q}(x, -i\hbar\frac{d}{dx})$. If the spectrum of $\hat{Q}$ is discrete, the probability of getting that particular eigenvalue q_n associated with the orthonormalised eigenfunction $f_n(x)$ is $|c_n|^2$, where $c_n = \langle f_n | \Psi \rangle$

If the spectrum is continuous, with real eigenvalues z ~~& associated~~ & associated (Dirac-Orthonormalised) eigenfunctions $f_z(x)$, the probability of getting a result in range dz is $|C(z)|^2 dz$ where $C(z) = \langle f | \Psi \rangle$

Upon measurement, the wavefunction "collapses" to the corresponding eigenstate.

Probability of any continuous ~~(for example (x & p))~~ (for example x & p) value ~~between~~ of z between a & $b = \int_a^b |C(z)|^2 dz$

~~Probability Probability of any discrete value z between a & B =~~

Probability of any discrete value z between a & $b = \sum_{n_a}^{n_b} |c_n|^2$

4.5 The Uncertainty Principle

Statistics → $\Delta A^2 = \langle(\hat{A}-\langle\hat{A}\rangle)\rangle$. $\langle\Psi|\Psi\rangle = 1 \Rightarrow \Delta A^2 = \langle(\hat{A}-\langle\hat{A}\rangle)\Psi|(\hat{A}-\langle\hat{A}\rangle)\Psi\rangle$.

Define $f \equiv (\hat{A}-\langle\hat{A}\rangle)\Psi$ & $g \equiv (\hat{B}-\langle\hat{B}\rangle)\Psi$ for simplicity $\Rightarrow \Delta A^2 = \langle f|f\rangle$, $\Delta B^2 = \langle g|g\rangle$.

$\Rightarrow \Delta A^2 \Delta B^2 = \langle f|f\rangle\langle g|g\rangle$. Schwarz-Cauchy Inequality $= \langle f|f\rangle\langle g|g\rangle \geq |\langle f|g\rangle|^2$

For any complex number z: $|z|^2 = |\mathrm{Re}(z)|^2 + |\mathrm{Im}(z)|^2 \geq |\mathrm{Im}(z)|^2 = \left|\frac{1}{2i}(z-z^*)\right|^2$

$\langle f|g\rangle \in \mathbb{C} \Rightarrow |\langle f|g\rangle|^2 \geq \left|\frac{1}{2i}(\langle f|g\rangle - \langle g|f\rangle)\right|^2$. We ignore $|\mathrm{Re}(z)|^2$ because we do not like it & it is not important.

$\Rightarrow \langle f|f\rangle\langle g|g\rangle \geq \left|\frac{1}{2i}(\langle f|g\rangle - \langle g|f\rangle)\right|^2$ (Do not do this at home kids)

$(= \Delta A^2 \Delta B^2)$

So, we calculate $\langle f|g\rangle$ & $\langle g|f\rangle$.

$\langle f|g\rangle = \langle(\hat{A}-\langle\hat{A}\rangle)\Psi|(\hat{B}-\langle\hat{B}\rangle)\Psi\rangle \xrightarrow{\hat{A}\,\&\,\hat{B}\text{ are hermitian}} \langle\Psi|(\hat{A}-\langle\hat{A}\rangle)(\hat{B}-\langle\hat{B}\rangle)\Psi\rangle$

$= \langle\Psi|(\hat{A}\hat{B} - \hat{A}\langle\hat{B}\rangle - \hat{B}\langle\hat{A}\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle)\Psi\rangle = \langle\Psi|\hat{A}\hat{B}|\Psi\rangle - \langle\hat{B}\rangle\langle\Psi|\hat{A}\Psi\rangle - \langle\hat{A}\rangle\langle\Psi|\hat{B}\Psi\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle$

$= \langle\hat{A}\hat{B}\rangle - 2\langle\hat{A}\rangle\langle\hat{B}\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle = \langle\hat{A}\hat{B}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle$

Now, we can do the same calculation for $\langle g|f\rangle$. But because f & g are arbitrary and weighted the same, we can just flip them. $\langle g|f\rangle = \langle\hat{B}\hat{A}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle$.

(Flipping has a fancy word: Cyclic permutation of the indices)

Thus: $\Delta A^2 \Delta B^2 \geq \left|\frac{1}{2i}(\langle\hat{A}\hat{B}\rangle - \langle\hat{B}\hat{A}\rangle)\right|^2 = \left|\frac{1}{2i}[\hat{A},\hat{B}]\right|^2$. In case $[\hat{x},\hat{p}] = i\hbar$, $\boxed{\Delta x \Delta p \geq \frac{\hbar}{2}}$

(In fact: if $\Delta x^2 \Delta p^2 = \frac{\hbar}{2}$, Ψ is a gaussian!)

The uncertainty principle is merely a consequence of the schwarz-cauchy inequality! Where does this come from? Let me define $|\gamma\rangle \equiv |\beta\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\alpha|\alpha\rangle}|\alpha\rangle$.

Then $\langle\gamma| = \langle\beta| - \frac{\langle\alpha|\beta\rangle}{\langle\alpha|\alpha\rangle}\langle\alpha|$ & $\langle\gamma|\gamma\rangle = \langle\beta|\beta\rangle - \frac{|\langle\alpha|\beta\rangle|^2}{\langle\alpha|\alpha\rangle}$. The only prerequisite is that α & β live in Hilbert space. As a quantum state's inner product with itself must be greater or equal to 0, $\langle\beta|\beta\rangle \geq \frac{|\langle\alpha|\beta\rangle|^2}{\langle\alpha|\alpha\rangle}$.

Thus we formulate $\langle\beta|\beta\rangle\langle\alpha|\alpha\rangle \geq |\langle\alpha|\beta\rangle|^2$. That brings us to a conclusion! the uncertainty principle $\sigma_x \sigma_p \geq \frac{\hbar}{2}$ is a mathematical necessity of the framework of Quantum mechanics (Hermitian operators, Orthonormality & completeness)!

- Time-Energy Uncertainty Principle.

$\Delta E\,\Delta t \geq \frac{\hbar}{t}$. We can derive a time & energy uncertainty principle as well. T is not an observable however, so this is not a standard uncertainty principle. Δt is defined as the amount of time for a substantial change in a system. So $\Delta t \Delta E$ is the amount of time for a change of size ΔE in energy.

Start with $\frac{d\langle\hat{Q}\rangle}{dt} = \frac{d}{dt}\langle\Psi|\hat{Q}\Psi\rangle = \langle\frac{\hat{H}\Psi}{dt}|\hat{Q}\Psi\rangle + \langle\Psi|\frac{d\hat{Q}}{dt}\Psi\rangle + \langle\Psi|\hat{Q}\frac{d}{dt}\Psi\rangle$.

Then if $\frac{\partial\Psi}{\partial t} = \hat{H}\Psi \Rightarrow \frac{d\Psi}{dt} = \frac{\hat{H}\Psi}{i\hbar} \Rightarrow \frac{d\langle\hat{Q}\rangle}{dt} = \langle\frac{\hat{H}\Psi}{i\hbar}|\hat{Q}\Psi\rangle + \langle\frac{d\hat{Q}}{dt}\rangle + \langle\Psi|\frac{\hat{Q}\hat{H}}{i\hbar}\Psi\rangle$

~~$\Rightarrow \frac{d\langle\hat{Q}\rangle}{dt} = \frac{1}{i\hbar}\langle\Psi|\hat{H}\hat{Q}\Psi\rangle + \frac{1}{i\hbar}\langle\Psi|\hat{Q}\hat{H}\Psi\rangle + \langle\frac{d\hat{Q}}{dt}\rangle$~~

$\Rightarrow \frac{d\langle\hat{Q}\rangle}{dt} = \frac{1}{i\hbar}\langle\Psi|\hat{H}\hat{Q}\Psi\rangle - \frac{1}{i\hbar}\langle\Psi|\hat{Q}\hat{H}\Psi\rangle + \langle\frac{d\hat{Q}}{dt}\rangle = \frac{d\langle\hat{Q}\rangle}{dt} = \frac{\frac{1}{i\hbar}}{\hbar}[\hat{H},\hat{Q}] + \langle\frac{d\hat{Q}}{dt}\rangle$

~~$\frac{d\langle\hat{Q}\rangle}{dt}\frac{d\langle\hat{Q}\rangle}{dt} \geq \frac{2}{\hbar}\Delta Q\,\Delta H + \frac{d\langle\hat{Q}\rangle}{dt}$~~. Assume $\frac{d\hat{Q}}{dt} = 0$, $\boxed{\Delta Q\,\Delta H \geq \frac{\hbar}{2}\frac{d\langle\hat{Q}\rangle}{dt}}$.

To get $\Delta E\Delta t$, $\Delta H = \Delta E$ & $\Delta t = \frac{\Delta Q}{\frac{d\langle\hat{Q}\rangle}{dt}} \Rightarrow \boxed{\Delta E\,\Delta t \geq \frac{\hbar}{2}}$

Evidently the uncertainty principle is a necessity of the mathematical framework of Quantum Mechanics, but it being nonzero is a consequence of operators not commuting. Its severity is proportional to the commutation relation of the two relevant operators.

5 Chapter 7: Expanding in Three Dimensions

5.1 Framework

For an expansion into three dimensions change x into $r \to dx$ into dr, $\frac{d^2}{dx^2}$ into ∇^2. Now, so far we have always worked in Cartesian coordinates, which is unimportant when working in only one dimension. But in more dimensions, other coordinate systems become important. Let me write down a few:

Polar, 2D: $\begin{cases} x = r\cos\theta \\ y = r\sin\theta \end{cases}$ Cylindrical, 3D: $\begin{cases} x = r\cos\theta \\ y = r\sin\theta \\ z = z \end{cases}$ Spherical, 3D: $\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases}$

Polar, 2D: $\begin{cases} x = r\cos\phi \\ y = r\sin\phi \end{cases}$ Cylindrical, 3D: $\begin{cases} x = r\cos\phi \\ y = r\sin\phi \\ z = z \end{cases}$ Spherical, 3D: $\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases}$

For now, we will use spherical coordinates as an example. Substituting into ∇^2:

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

We would like to find possible solutions for $\Psi(r,\theta,\phi)$. Again try to find separable solutions. Substitute our new ∇^2 & $\Psi(r,\theta,\phi) = R(r)Y(\theta\phi)$ into the time-independent Schrödinger Equation and you'll find something of the shape $\alpha(r) + \frac{1}{Y(\theta,\phi)}\beta(\theta\phi) = 0$. This means $\alpha(r)$ & $\frac{\beta(\theta,\phi)}{Y(\theta,\phi)}$ are constant. We define this constant as $\alpha(r) = \ell(\ell+1)$ & $\frac{\beta(\theta,\phi)}{Y(\theta,\phi)} = -\ell(\ell+1)$. The latter one particularly interests us, as it allows us to further separate. Define $Y(\theta,\phi) \equiv \Theta(\theta)\Phi(\phi)$ and substitute again. This brings us again to an equation of form $\gamma(\theta) + \varepsilon(\phi) = 0$. This time we use constant m^2, with $\gamma(\theta) = m^2$ & $\varepsilon(\phi) = -m^2$. Φ can be defined by $\varepsilon(\phi) = -m^2 \Rightarrow \Phi(\phi) = e^{im\phi}$. $\Theta(\theta)$ too, but it is a little more complex: $\Theta(\theta) = AP_\ell^m(\cos\theta)$ where P_ℓ^m is the associated Legendre function:

$$P_\ell^m(x) \equiv (-1)^m(1-x^2)^{m/2}\left(\frac{d}{dx}\right)^{m+\ell}\frac{(x^2-1)^\ell}{2^\ell\ell!}. \quad m \in \mathbb{Z}^+,\ \ell \in \mathbb{Z}^+$$

We can also define $Y_\ell^m(\theta,\phi)$, the normalized angular wave functions, or spherical harmonics:

$$Y_\ell^m(\theta,\phi) = \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}e^{im\phi}P_\ell^m(\cos\theta).$$

Notice how $\frac{d}{dV}\frac{Y_l^m(\theta,\varphi)}{dV} = 0$? That's right, the angular part of the wave function is the same for all potentials! Only the radial equation depends on it: define $u(r) = rR(r)$ & ~~substitute $u(r)$ for Ψ in the~~ rewrite: you get $-\frac{\hbar}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$. This is identical to the one-dimensional Schrodinger Equation, with two key differences: $\Psi \Rightarrow u$, $V \Rightarrow V_{eff} = V + \frac{\hbar}{2m}\frac{l(l+1)}{r^2}$. It is called the radial equation. The second term of the effective potential is called the centrifugal term, it tends to push the particle outward.

One more note: normalising $u(r)$ is done by the equation $\int_0^\infty |u|^2 dr = 1$. This is, of course, because r cannot be negative. Also, just to write it, the radial Hamiltonian is $\hat{H}_r = -\frac{\hbar}{2m}\frac{d^2}{dr^2} + V + \frac{\hbar}{2m}\frac{l(l+1)}{r^2}$.

Let's do a very important example: The Hydrogen Atom! $V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$. Substitute this and clean it up by $k \equiv \frac{\sqrt{-2m_e E}}{\hbar}$, $\rho \equiv kr$, $\rho_0 \equiv \frac{m_e e^2}{2\pi\varepsilon_0\hbar^2 k}$.

That gets us: $\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u$. We'll derive the wavefunction in parts. Taking $\frac{d^2u}{d\rho^2} = u \Rightarrow u = Ae^{-\rho} + Be^{\rho} \Rightarrow u = Ae^{-\rho}$ due to boundary conditions. Taking $\frac{d^2u}{d\rho^2} \approx -\frac{\rho_0}{\rho}u$. ~~$\Rightarrow u = \rho(\rho\ln(\rho) - \rho)$~~. Problem! This is unsolvable! Solution: Ignore it for now. We get the term $V(\rho)$ out of it. Lastly, $\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u$, which produces $u(\rho) = C\rho^{l+1} + D\rho^{-l} = C\rho^{l+1}$ due to boundary conditions. So, $u(\rho) = \rho^{l+1}\cdot e^{-\rho}\cdot v(\rho)$. The radial equation becomes:

$\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0$ which gets us back to the problem of $v(\rho)$. We assume its solution is a power series: $v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j$. Substituting this into the radial equation gets us a new equation: $c_{j+1} = \left\{\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}\right\}c_j$. For $u(\rho)$ to be normalisable, when $\rho^j \to \infty$, $c_j \to 0$. So, somewhere $c_{j+1} = 0$. This is at $2(j+l+1) - \rho_0 = 0 \Rightarrow n \equiv j+1+l \Rightarrow \rho_0 = 2n \Rightarrow$ ~~$\rho_0 = 2n = \frac{m_e e^2}{2\pi\varepsilon_0\hbar^2}\cdot\frac{\hbar}{\sqrt{-2m_e E}} \Rightarrow E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}$~~ $(n \in \mathbb{N})$

So we calculate the allowed energies E_n, the most important result of Quantum Mechanics!

This is the case, because it was known but unexplainable before Quantum Mechanics were incepted in 1926 by the invention of the Schrödinger Equation!

Back to the math. $\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r) Y_l^m(\theta,\phi)$ with $E_n = -\left[\frac{E_0}{2\pi}\left(\frac{e^2}{(1\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}$.
Another funny explanation of Quantum mechanics is $\frac{1}{\alpha} = \frac{1}{\frac{1}{137}n} = a \equiv$ Bohr radius.

With this you can calculate $E_1 = -13.6eV$, the ground state energy, or otherwise known as the binding energy. $E_2 = -\frac{13.6}{4}eV = 3.40eV$, the first excited states.
$\Psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a}} e^{-r/a}$

$\nu(\rho)$ is nice as a power series, but we can also write it as a polynomial:
$\nu(\rho) = L_{n-l-1}^{2l+1}(2\rho) = \frac{e^{\rho}}{\rho^{2l+1}e^{\rho}} \frac{(-1)^{2l+1}}{(n+l)!}\left(\frac{d}{d(2\rho)}\right)^{2l+1}\left(e^{2\rho}\left(\frac{d}{d(2\rho)}\right)^{n+l}\left(e^{-\rho}(2\rho)^{n+l}\right)\right)$.

This turns $\Psi_{nlm}(r,\theta,\phi)$ into a rather unappealing equation:
$$\left[\sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n(n+l)!}}e^{-r/na}\left(\frac{2r}{na}\right)^l\left[\frac{(-1)^{2l+1}}{(n+l)!}\left(\frac{d}{d(\frac{2r}{na})}\right)^{2l+1}\left(e^{2r/na}\left(\frac{d}{d(2r/na)}\right)^{n+l}\left(e^{-2r/na}\left(\frac{2r}{na}\right)^{n+l}\right)\right)\right]\right]$$
$$\cdot\left[\sqrt{\frac{2l+1}{\pi}\frac{(l-m)!}{(l+m)!}}e^{im\phi}\cdot\left[(-1)^m(1-\cos^2\theta)^{\frac{m}{2}}\left(\frac{d}{d(\cos\theta)}\right)^{m+l}\frac{(\cos^2\theta-1)^l}{2^l\,l!}\right]\right] = \Psi_{nlm}(r,\theta,\phi)$$

This is more simply written as $\sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n(n+l)!}}e^{-\frac{r}{na}}\left(\frac{2r}{na}\right)^l\left[L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)\right]Y_l^m(\theta,\phi) = \Psi_{nlm}^{(r,\theta,\phi)}$.

It is a beast, but it is one of the only solvable realistic quantum systems, and with that a beautifully accessible consequence of quantum mechanics!

One last note - $\int \Psi_{nlm}^* \Psi_{n'l'm'} r^2 dr\, d\Omega = \delta_{nn'}\delta_{mm'}\delta_{ll'}$. all Ψ_{nlm} are mutually orthogonal!

5.1 Addendum: Spectral Lines

Perturbations in a Hydrogen atom's stationary state can result in that stationary state changing. This can also change its energy level. In the case of this energy lowering a photon is emitted of energy $E_\gamma = E_i - E_f = -13.6\,eV\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = h\nu = \frac{hc}{\lambda}$.

Photons emitted by specific perturbations have determined wavelengths:

$$\lambda = \left(R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)\right)^{-1}, \text{ where } R = \frac{m_e}{4\pi c h^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 1.097 \cdot 10^7\, m^{-1}$$

These wavelengths are the spectral lines we observe!

5.2 Angular Momentum

~~in $L^{2l+1}_{n(l)\,n-l-1}$, Y^m_l, n is related to the energy levels ($E_n = \frac{E_1}{n^2}$)~~

In L^{2l+1}_{n-l-1}, Y^m_l, n is related to the energy levels ($E_n = \frac{E_1}{n^2}$), whereas l and m are related to the orbital angular momentum, the other fundamentally conserved energy quantity. How does that work in Quantum Mechanics? Let me write the classical equation: $L = r \times p$

$\Rightarrow L = [yp_z - zp_y,\ zp_x - xp_z,\ xp_y - yp_x]$. (Also written as $[L_x, L_y, L_z]$). We want to know the allowed energies and states of the angular momentum. In other words, we want the eigenstates & eigenfunctions.

The first thing we should consider is that for two operators that commute, the eigenfunctions are shared. So let's see if, for example, $[L_x, L_y] = 0$. $[L_x, L_y] = [yp_z - zp_y, zp_x - xp_z] = [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z]$

$[L_x, L_y] = i\hbar L_z$, which of course means $[L_x, L_z] = i\hbar L_y$ & $[L_y, L_z] = i\hbar L_x$.

Terror and Despair! None commute. But we have an ace up our sleeve:
$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. Let's see $[\hat{L}^2, \hat{L}_x]$! $[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2, \hat{L}_x] + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x]$
$= \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_z[\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z$
$= \hat{L}_y(-i\hbar\hat{L}_z) + (-i\hbar\hat{L}_z)\hat{L}_y + \hat{L}_z(i\hbar\hat{L}_y) + (i\hbar\hat{L}_y)\hat{L}_z$
$= 0$!
which means $[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = [\hat{L}^2, \vec{\hat{L}}] = 0$.
e.g. $\hat{L}^2 f = \lambda f$ & $\hat{L}_x f = \mu f$, $\hat{L}^2 g = \xi g$ & $\hat{L}_y g = \gamma g$, $\hat{L}^2 d = \zeta d$, $\hat{L}_z d = \eta d$

For now, we choose to work with $\hat{L}_z$. I'll switch to the variables λ, μ, f [redacted] to match the book: [redacted] $\hat{L}^2 f = \lambda f$ & [redacted] $\hat{L}_z f = \mu f$.

[redacted]

Now, the eigenvalue μ is proportional to the [redacted] size of $\hat{L}_z$ within $\hat{L}^2$. Because of this, it has to be greater or equal to 0. But also μ cannot exceed $\hat{L}^2$'s eigenvalue, λ. So it is bounded, and I suspect quantized. So, I'll try our good friend ladder operators first!

Let me define: $\hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y$ for $\hat{L}_z$. $[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm$, $[\hat{L}^2, \hat{L}_\pm] = 0$
[redacted] Is $\hat{L}_\pm f$ an eigenfunction of $\hat{L}^2$ (and $\hat{L}_z$)?
$\Rightarrow \hat{L}^2(\hat{L}_\pm f) = \hat{L}_\pm(\hat{L}^2 f) = \hat{L}_\pm(\lambda f) = \lambda(\hat{L}_\pm f)$ $\Rightarrow$ yes! [redacted]
$\hat{L}_z(\hat{L}_\pm f) = (\hat{L}_z\hat{L}_\pm - \hat{L}_\pm\hat{L}_z)f + \hat{L}_\pm\hat{L}_z f = [\hat{L}_z, \hat{L}_\pm]f + \hat{L}_\pm\hat{L}_z f = \pm\hbar\hat{L}_\pm f + \hat{L}_\pm(\mu f)$
$= (\mu \pm \hbar)(\hat{L}_\pm f)$ $\Rightarrow$ yes, but with eigenvalue $\mu \pm \hbar$ $\Rightarrow$ raising & lowering

We go back to the concept of bounds. Let me define $(L_+)^n f_0 = f_{top}$

$L_-^n f_{top} = f_0$. Both f_0 & f_{top} have to be 0 to honor the bounds.

Begin with the top: $L_+ f_{top} = 0$. $L_z f_{top} = \hbar l f_{top}$, $L^2 f_{top} = \lambda f_{top}$

We'll need $L_\pm L_\mp = (L_x \pm iL_y)(L_x \mp iL_y) = L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x)$

$= L^2 - L_z^2 \mp i(i\hbar L_z) \Rightarrow L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$

Substitute this into $L^2 f_{top} = \lambda f_{top}$ and we can use $L_+ f_{top} = 0$!

$\Rightarrow L_- L_+ f_{top} + L_z^2 f_{top} + \hbar L_z f_{top} = \lambda f_{top}$

$\Rightarrow L_z^2 f_{top} + \hbar L_z f_{top} = \lambda f_{top} \Rightarrow \mu^2 f_{top} + \mu\hbar f_{top} = \lambda f_{top}$

$\Rightarrow \mu^2 + \mu\hbar = \lambda$. Define $\mu \equiv \hbar l \Rightarrow \lambda = \hbar^2 l(l+1)$.

This is the eigenvalue of L^2 expressed in the top eigenvalue of L_z.

For the bottom rung: $L_- f_0 = 0$, $L^2 f_0 = \lambda f_0$, $L_z f_0 = \bar{l}\hbar f_0$

$\Rightarrow L_+ L_- f_0 + L_z^2 f_0 - \hbar L_z = \bar{l}\hbar f_0 \Rightarrow \bar{l}^2\hbar^2 f_0 - \bar{l}\hbar^2 f_0 = \lambda f_0$

$\Rightarrow \hbar^2 \bar{l}(\bar{l}-1) = \lambda$

To figure out the relation between l & $\bar{l}$, equate the two definitions for λ: $\hbar^2 \bar{l}(\bar{l}-1) = \hbar^2 l(l+1) \Rightarrow \bar{l}(\bar{l}-1) = l(l+1) \Rightarrow \bar{l} = l$ or $\bar{l} = l+1$

Remember, eigenvalues are $l\hbar$ for the highest rung, $-l\hbar$ or $l\hbar + \hbar$ for the lowest rung. Of course, $l\hbar > \bar{l}\hbar$, so the eigenvalue of the bottom rung is $-l\hbar$. Remember the n at the top of the page? Now it's useful: $l = n + \bar{l} \Rightarrow l = n - l \Rightarrow l = \frac{n}{2}$ where $n \in \mathbb{Z}^+ \Rightarrow l$ is a half-integer.

Now, for the eigenfunctions: $\hat{L}^2 Y_\ell^m = \hbar^2 \ell(\ell+1) Y_\ell^m$; $\hat{L}_z Y_\ell^m = \hbar m Y_\ell^m$

where m: $-\ell, -\ell+1, \ldots, 0, \ldots \ell-1, \ell$; $\ell = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$

The Plan: rewrite $\hat{L}_z$ & $\hat{L}_\pm$ in spherical coordinates & substitute to express $\hat{L}^2$ into spherical coordinates. Use that to calculate the eigenfunctions:

$$\hat{L} = \vec{r} \times \hat{P} = \vec{r} \times -i\hbar \vec{\nabla} = -i\hbar(\vec{r} \times \vec{\nabla}).$$

$$\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

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

Resolve $\hat{\theta}$ & $\hat{\phi}$ into cartesian components:

$\hat{\theta} = (\cos\theta\cos\phi)\hat{i} + (\cos\theta\sin\phi)\hat{j} - (\sin\theta)\hat{k}$, $\hat{\phi} = -(\sin\phi)\hat{i} + (\cos\phi)\hat{j}$

$\Rightarrow$

$$\left.\begin{aligned} \hat{L}_x &= -i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} - \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right) \\ \hat{L}_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right) \\ \hat{L}_z &= -i\hbar\frac{\partial}{\partial\phi} \end{aligned}\right\}$$ Observe why we picked $\hat{L}_z$ at the start - it's easier here.

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

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

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

which finally brings us:

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y_\ell^m = \hbar^2\ell(\ell+1)Y_\ell^m$$

$\hat{L}_z f_\ell^m = \hbar m f_\ell^m$ is easy: just substitute $\hat{L}_z$! We have two equations now!

$$\begin{cases} -i\hbar\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] f_\ell^m = \hbar^2 \ell(\ell+1) f_\ell^m \\ -i\hbar\frac{\partial}{\partial\phi} f_\ell^m = \hbar m f_\ell^m \end{cases}$$

You should recognise these equations if you did the math - I wrote them a little simpler:

$$\begin{cases} \frac{\Theta(\theta,\phi)}{Y(\theta,\phi)}\cdot Y\sin^2\theta = -\ell(\ell+1)\cdot Y\sin^2\theta \\ \Xi(\phi) = -m^2 \end{cases}$$

We already solved this system on page 18! They lead to $Y_\ell^m(\theta\phi)$. It shouldn't be a surprise then, to learn that $f_\ell^m = Y_\ell^m(\theta,\phi)$

To recap:
The eigenfunctions of angular momentum operators $\hat{L}^2$ & $\hat{L}_z$ are the spherical harmonics $Y_\ell^m(\theta,\phi)$. Their eigenvalues at $\hat{L}^2$ are $\hbar^2\ell(\ell+1)$. Their eigenvalues at $\hat{L}_z$ are $\hbar m$.

Addendum: Dirac Notation

Eigenfunctions & eigenstates. We can also write that in dirac notation:

~~$\hat{L}_z|\ell m_\ell\rangle = \hbar m$~~ ~~$\hat{L}_z|1\ 1\rangle$~~ $\hat{L}_z|\ell m_\ell\rangle = \hbar m_\ell|\ell m_\ell\rangle$ ($Y_\ell^m = |\ell m_\ell\rangle$)

1D → $\hat{L}_z|0\ 0\rangle = 0|0\ 0\rangle = 0$ easy.

3D

Addendum: Dirac Notation

Eigenfunctions & Eigenstates are also writeable in Dirac Notation:

$\hat{L}_z|\ell m_\ell\rangle = \hbar m_\ell |\ell m_\ell\rangle$, $Y_\ell^{m_\ell} = |\ell m_\ell\rangle$. 1D: $\hat{L}_z|00\rangle = 0|00\rangle = 0$. Easy.

3D: $\begin{cases} \hat{L}_z|1\,-1\rangle = -\hbar|1\,-1\rangle \\ \hat{L}_z|1\,0\rangle = 0|1\,0\rangle \\ \hat{L}_z|1\,+1\rangle = \hbar|1\,+1\rangle \end{cases}$ $|1\,-1\rangle = \begin{pmatrix}0\\1\\0\end{pmatrix}$, $|1\,0\rangle = \begin{bmatrix}0\\1\\0\end{bmatrix}$, $|1\,+1\rangle = \begin{bmatrix}1\\0\\0\end{bmatrix}$

↳ Chosen because easy & orthogonal.

$\hat{L}_x \Rightarrow \frac{\hbar}{\sqrt{2}}\begin{bmatrix}0&1&0\\1&0&1\\0&1&0\end{bmatrix}$ $\hat{L}_y \Rightarrow \frac{\hbar}{\sqrt{2}}\begin{bmatrix}0&-i&0\\i&0&-i\\0&i&0\end{bmatrix}$ $\hat{L}_z \Rightarrow \hbar\begin{bmatrix}1&0&0\\0&0&0\\0&0&-1\end{bmatrix}$

In Z-basis

Similarly $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \Rightarrow \hat{L}_+ \to \frac{\hbar}{\sqrt{2}}\begin{bmatrix}0&1&0\\0&0&1\\0&0&0\end{bmatrix}$, $\hat{L}_- \to \frac{\hbar}{\sqrt{2}}\begin{bmatrix}0&0&0\\1&0&0\\0&1&0\end{bmatrix}$

$\begin{matrix}\langle 1\,1| \\ \langle 1\,0| \\ \langle 1\,-1|\end{matrix}\begin{bmatrix}0&1&0\\1&0&1\\0&1&0\end{bmatrix}$ $\begin{matrix}|1\,1\rangle & |1\,0\rangle & |1\,-1\rangle\end{matrix}$ $\Rightarrow \langle 1\,0|\hat{L}_x|1\,1\rangle = \int_0^{2\pi}\int_0^{\pi} (Y_1^0)^* \hat{L}_x (Y_1^1)\, d\Omega$ $\quad (d\Omega = r^2\sin\theta\, d\phi\, d\theta)$

5.3 Spin

"Here be Monsters" - Geoffrey Rush

5.2 discussed orbital angular momentum, associated with the motion of the center of mass. But that's not the only sort of angular momentum. There is also spin: $S = I\omega$. It starts similar:

$[S_x, S_y] = i\hbar S_z$ $[S_y, S_z] = i\hbar S_x$ $[S_z, S_x] = i\hbar S_y$.

$S^2|s\,m\rangle = \hbar^2 s(s+1)|s\,m\rangle$ $S_z|s\,m\rangle = \hbar m|s\,m\rangle$

$S_\pm|s\,m\rangle = \hbar\sqrt{s(s+1) - m(m\pm1)}\,|s\,(m+1)\rangle$, $S_\pm \equiv S_x \pm iS_y$

$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$; $m = -s, -s+1, \ldots, s-1, s$. But that's where it ends.

$|s\,m\rangle \neq \chi_s^m$. S is called the spin of a particle, every type has a particular spin:

particle	S
π mesons	0
electrons	1/2
Photons	1
Baryons	3/2
gravitons	2

keeps going ↓

l can change when perturbed, but S is fixed!

Well do the spin 1/2 example, relevant for electrons, protons & neutrons:

- Spin 1/2:

Spin 1/2 has two eigenstates: $|\frac{1}{2}\,\frac{1}{2}\rangle$ & $|\frac{1}{2}(-\frac{1}{2})\rangle$, a spin up (↑) & spin down (↓). Also noted as $|\uparrow\rangle$ & $|\downarrow\rangle$ or $|+\rangle$ & $|-\rangle$.

A general state of a spin 1/2 particle can be represented by a 2x1 matrix, also known as a spinor.

$\chi = \begin{bmatrix} a \\ b \end{bmatrix} = a\chi_+ + b\chi_-$, where $\chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ represents spin up & $\chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$ represents spin down.

$\Rightarrow S^2, S_1, S_2, S_x, S_y$ are all 2x2 matrices. Let's define them!

$S^2|s\,m\rangle = \hbar^2 s(s+1)|s\,m\rangle$. $s = \frac{1}{2}$ & $m = -\frac{1}{2}$ V $\frac{1}{2}$ for spin 1/2.

$\Rightarrow S^2\chi_+ = \hbar\frac{3}{4}\chi_+$ & $S^2\chi_- = \hbar\frac{3}{4}\chi_-$.

$S^2 \to \begin{bmatrix} a & b \\ c & d \end{bmatrix} \Rightarrow \begin{bmatrix} a & b \\ c & d \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \hbar\frac{3}{4}\begin{bmatrix} 1 \\ 0 \end{bmatrix} \Rightarrow \begin{bmatrix} a \\ c \end{bmatrix} = \begin{bmatrix} \hbar 3/4 \\ 0 \end{bmatrix} \Rightarrow a = \hbar 3/4$ & $c = 0$

$\begin{bmatrix} \hbar & b \\ 0 & d \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \hbar\frac{3}{4}\begin{bmatrix} 0 \\ 1 \end{bmatrix} \Rightarrow \begin{bmatrix} b \\ d \end{bmatrix} = \begin{bmatrix} 0 \\ 3\hbar/4 \end{bmatrix} \Rightarrow b = 0$ & $d = \hbar\frac{3}{4}$

$\Rightarrow S^2 \to \frac{3\hbar}{4}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$. Similarly, $S_z \to \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

The ladder operators work as usual: $S_+\chi_- = \hbar\chi_+$, $S_-\chi_+ = \hbar\chi_-$, $S_-\chi_- = 0$, $S_+\chi_+ = 0$

which lead to: $S_+ \Rightarrow \hbar\begin{bmatrix}0&1\\0&0\end{bmatrix}$, $S_- \Rightarrow \hbar\begin{bmatrix}0&0\\1&0\end{bmatrix}$. As $S_\pm = S_x \pm iS_y$, we can state

$S_x = \frac{1}{2}(S_+ + S_-) \Rightarrow \frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}$, $S_y = \frac{1}{2i}(S_+ - S_-) \Rightarrow \frac{\hbar}{2}\begin{bmatrix}0&-i\\i&0\end{bmatrix}$. $S_z \Rightarrow \frac{\hbar}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}$.

Tidier, one writes $S = \frac{\hbar}{2}\sigma$, with $\sigma_x = \begin{bmatrix}0&1\\1&0\end{bmatrix}$, $\sigma_y = \begin{bmatrix}0&-i\\i&0\end{bmatrix}$, $\sigma_z = \begin{bmatrix}1&0\\0&-1\end{bmatrix}$ The Pauli Spin Matrices

Probabilities can also be calculated: $\chi = a\chi_+ + b\chi_-$. $P_{(+)} = |a|^2$, $P_{(-)} = |b|^2$.
So, it follows: $|a|^2 + |b|^2 = 1$ (normalising)

What are possibilities S_x? First, eigenvalues: $D\begin{bmatrix}a-\lambda & b\\ c & d-\lambda\end{bmatrix} = 0$
$\Rightarrow (a-\lambda)(d-\lambda) = bc$. For S_x, $\lambda^2 = \frac{\hbar^2}{4} \Rightarrow \lambda = \frac{\hbar}{2}$ v. $-\frac{\hbar}{2}$.

Then, eigenspinors: $S_x\chi_x = \pm\frac{\hbar}{2}\chi_x \Rightarrow \begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}\alpha\\\beta\end{bmatrix} = \pm\begin{bmatrix}\alpha\\\beta\end{bmatrix} \Rightarrow \begin{bmatrix}\beta\\\alpha\end{bmatrix} = \pm\begin{bmatrix}\alpha\\\beta\end{bmatrix}$
$|\alpha|^2 + |\beta|^2 = 1 \Rightarrow \alpha = \frac{1}{\sqrt{2}} \Rightarrow \alpha = \pm\beta \Rightarrow \chi_+^{(x)} = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\end{bmatrix}$ $\chi_-^{(x)} = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\-1\end{bmatrix}$ where

where $\begin{bmatrix}a\\b\end{bmatrix} = \frac{a+b}{\sqrt{2}}\chi_+^{(x)} + \frac{a-b}{\sqrt{2}}\chi_-^{(x)} = \chi$

$\Rightarrow P_{(+)}^x = \frac{|a+b|^2}{2}$, $P_{(-)}^x = \frac{|a-b|^2}{2}$

- Addendum: Electron in a magnetic field:
$\mu = \gamma S$ $\quad H = -\mu\cdot B$ $\quad \hat{H} = -\gamma B\cdot\hat{S} = \omega\hat{S}_z$

5.4 Baryons; particles made of particles
Otherwise known as composite states.
Particles $|s_1 m_1\rangle$ & $|s_2 m_2\rangle$ form composite state $|s_1 s_2 m_1 m_2\rangle$.
$S^{(1)^2}|s_1 s_2 m_1 m_2\rangle = s_1(s_1+1)\hbar^2|s_1 s_2 m_1 m_2\rangle$, $S^{(2)^2}|s_1 s_2 m_1 m_2\rangle = s_2(s_2+1)\hbar^2|s_1 s_2 m_1 m_2\rangle$
$S_z^{(1)}|s_1 s_2 m_1 m_2\rangle = m_1\hbar|s_1 s_2 m_1 m_1\rangle$, $S_z^{(2)}|s_1 s_2 m_1 m_2\rangle = m_2\hbar|s_1 s_2 m_1 m_2\rangle$

But what is the total angular momentum? $S = S^{(1)} = S^{(2)}$

$S_z \Rightarrow S_z^{(1)} |s_1 s_2 m_1 m_2\rangle + S_z^{(2)} |s_1 s_2 m_1 m_2\rangle = (m_1 + m_2)\hbar\, |s_1 s_2 m_1 m_2\rangle$

$S^2 \Rightarrow \left(S_1(S_1+1)\hbar^2 + S_2(S_2+1)\hbar^2\right) |s_1 s_2 m_1 m_2\rangle$ $\Rightarrow$ Not so easy.

Let's do an example again. I like Hydrogen.

Hydrogen's possible composite states:

$|\uparrow\uparrow\rangle = |\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\rangle \; m = 1$

$|\uparrow\downarrow\rangle = |\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\rangle \; m = 0$ → weird. Let's try $S_- |\uparrow\uparrow\rangle$

$|\downarrow\uparrow\rangle = |\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\rangle \; m = 0$ ↗

$|\downarrow\downarrow\rangle = |\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\rangle \; m = -1$

$$S_- |\uparrow\uparrow\rangle = \left((S_-|\uparrow\rangle)|\uparrow\rangle + |\uparrow\rangle(S_-|\uparrow\rangle)\right) = \hbar\left(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle\right)$$

$\Rightarrow$ middle state is

$$|1\,0\rangle = \frac{1}{\sqrt{2}}\left(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle\right)$$

There is also an orthogonal state $|0\,0\rangle = \frac{|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle}{\sqrt{2}}$. This state, in contrast to the other ~~two~~ three, has net 0 spin. For this, prove $S^2|1\,1\rangle = 2\hbar^2|1\,1\rangle$, $S^2|1\,0\rangle = 2\hbar^2|1\,0\rangle$, $S^2|1\,{-1}\rangle = 2\hbar^2|1\,{-1}\rangle$, $S^2|0\,0\rangle = 0|0\,0\rangle$. It's true, ~~check~~

You can combine spins as in baryons to get net spins. Hydrogen has net 1 or 0 spin. In this case, $S = (s_1+s_2), (s_1+s_2-1), \ldots, |s_1 - s_2|$.

Concluding: $|S\,m\rangle = \sum_{m_1+m_2=m} C^{s_1 s_2 S}_{m_1 m_2 m} |s_1 s_2 m_1 m_2\rangle$ (Clebsch-Gordan Coefficients)

Baryon state $S\,m$

Addendum: how to read Clebsch-Gordan Coefficients

$S = 2 \otimes 0$

2×1 Table → two particles, one $S=2$, one $S=1 \otimes 0$

Column: 3 / 0 / $\frac{1}{5}$ / $\frac{3}{5}$ / $\frac{1}{5}$

$$|S_{tot}\, m_{tot}\rangle = \sqrt{P_\alpha}\,|2, S_{1\max}\rangle|1, S_{2\min}\rangle + \sqrt{P_\beta}\,|2, S_{1\mathrm{mid}}\rangle|1, S_{2\mathrm{mid}}\rangle + \sqrt{P_\gamma}\,|2, S_{1\min}\rangle|1, S_{2\max}\rangle$$

Notice that for a combination of $|S_{1a}\, m_{1a}\rangle|S_{2a}, S_{2b}\rangle$,
$|S_1 m_1\rangle|S_2, m_2\rangle$, $S_1 + S_2 = S_{tot}$, $m_1 + m_2 = m_{tot}$ for all spin combinations.

So any total spin state can be divided into that total spin split between multiple particles, where Clebsch-Gordan then gives the probabilities.

It also works in reverse:

$$|S_1 S_2 m_1 m_2\rangle = \sum_S {}^{S_1 S_2 S}_{m_1 m_2 m}\, |S\, m\rangle \qquad m = m_1 + m_2$$

in $\frac{3}{2} \times 1$ table

row				
$\frac{1}{2}$	0	$\frac{3}{5}$	$\frac{1}{15}$	$-\frac{1}{3}$

$S_1\ S_2\ \ m_1\ m_2$

$$\left|\tfrac{3}{2}\,1\ \tfrac{1}{2}\,0\right\rangle = \sqrt{|P_\alpha|}\left|S_1+S_2\,1,\ m_{tot}\right\rangle^{m_1+m_2=1} + \sqrt{|P_\beta|}\left|S_1+S_2\,0,\ m_{tot}\right\rangle^{m_1+m_2=0} + \sqrt{|P_\gamma|}\left|S_1+S_2\,{-1},\ m_1+1,\ m_2\right\rangle$$

6 Chapter 5: Identical Particles

6.1 Two-Particle-Systems.

Two particles $\Rightarrow \Psi(r_1, r_2, t) \Rightarrow \hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar}{2m_1}\nabla_2^2 + V(r_1, r_2, t)$

$\int |\Psi(r_1, r_2, t)|^2 d^3r_1 d^3r_2 = 1$,

$\Psi(r_1, r_2) e^{iEt/\hbar} = \Psi(r_1, r_2, t)$

$-\frac{\hbar}{2m_1}\nabla_1^2\Psi - \frac{\hbar}{2m_2}\nabla_2^2\Psi + V\Psi = E\Psi$. Simple expansion.

This is done by reducing to one-particle problems

But what is V in terms of V_1 & V_2? Two cases can be easily solved:

No interaction: $V(r_1, r_2) = V_1(r_1) + V_2(r_2) \Rightarrow \Psi(r_1, r_2) = \Psi_a(r_1)\Psi_b(r_2)$ (solved by)

$\Rightarrow$ Substituting this into the Schrödinger Equation gives rise to a system of equations:

$$\begin{cases} -\frac{\hbar^2}{2m_1}\nabla_1^2\Psi_a(r_1) + V_1(r_1)\Psi_a(r_1) = E_a\Psi_a(r_1) \\ -\frac{\hbar^2}{2m_2}\nabla_2^2\Psi_b(r_2) + V_2(r_2)\Psi_b(r_2) = E_b\Psi_b(r_2) \end{cases}$$

Where $E = E_a + E_b$ & $\Psi(r_1, r_2, t) = \Psi_a(r_1, t)\Psi_b(r_2, t)$

Remember $\Psi = \sum \psi_n c_n \varphi(t)$, so $\Psi(r_1, r_2, t) = \alpha$

$\Psi(r_1, r_2, t) = \alpha\Psi_a(r_1, t)\Psi_b(r_2, t) + \beta\Psi_c(r_1, t)\Psi_d(r_2, t)$

with probabilities $|\alpha|^2$ & $|\beta|^2 \Rightarrow |\alpha|^2 + |\beta|^2 = 1$.

Consider: Measure particle at 1 in this state and get state Ψ_a. This enforces a ~~measurement of~~ particle 2 being in state Ψ_b, collapsing its wavefunction. It doesn't matter how far 1 & 2 are apart $\Rightarrow$ Measuring particle 1 will collapse the wavefunction of particle 2 as well.

$\Rightarrow$ Quantum Entanglement!

Central potentials:

Think - hydrogen atom: $V(r_1 r_2) \to V(|r_1 - r_2|)$

~~Usually~~ usually more complex: Coulomb attraction of two helium electrons + ~~repulsion~~ repulsion $\Rightarrow$ $V(r_1, r_2) = \frac{1}{4\pi\varepsilon_0}\left(-\frac{2e^2}{|r_1|} - \frac{2e^2}{|r_2|} + \frac{e^2}{|r_1 - r_2|}\right)$

the equation $\Psi(r_1 r_2) = \psi_a(r_1)\psi_b(r_2)$ suggests we know particle 1 is in state a, and 2 in state b. Truth is, we don't. The particles are identical, and indistinguishable. There will always be ~~an electron~~ a particle in state 1, and one in state 2, but they could switch and we would be none the wiser.

Of course, that is only the case for particles of the same type - a proton and an electron are of course not identical or indistinguishable. The point is, that two electrons are.

So we define $\Psi_\pm$ to reflect that: $\Psi_\pm(r_1 r_1) = A[\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2)]$

This means we allow two types of particles: fermions, Ψ_- & bosons, Ψ_+.

$\Psi_+(r_1 r_2) = \Psi_+(r_2 r_1) \Rightarrow$ Bosons are symmetric under interchange. Also integer spin

$\Psi_-(r_1 r_2) = -\Psi_-(r_2 r_1) \Rightarrow$ fermions are not symmetric under interchange. ~~Also half integer~~

↳ fermions also have half-integer spin.

Fun fact, this is true. Only Fermions & Bosons have been found, no other particles.

Another interesting thing: $\psi_a = \psi_b \Rightarrow \Psi_-(r_1 r_2) = A(\psi_a\psi_a - \psi_a\psi_a) = 0$.

$\Rightarrow$ No two fermions can occupy the same state! "Pauli Exclusion Principle"

~~$\Rightarrow$ also, $\Psi_\pm = \psi\chi \Rightarrow$ including spin. Pretty generic $\hat{P}|12\rangle = \pm|21\rangle \Rightarrow$~~

6.2 Exchange forces

Consider $\langle \Delta x^2 \rangle$ for 2 indistinguishable fermions, 2 indistinguishable bosons & 2 distinguishable particles: $\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle + 2\langle x_1 \cdot x_2 \rangle$.

For 2 distinguishable particles: $\langle \Delta x^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$ $\int x \psi_a^*(x) \psi_b(x) dx$

For 2 indistinguishable particles: $\langle \Delta x^2 \rangle_\pm = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \pm \int x \psi_a^* \psi_b \, dx$

The difference lies in the last term: $\pm \int x \psi_a^*(x) \psi_b(x) dx$. This physically results in the idea that fermions, where the extra term is subtracted, lie closer together than distinguishable particles, whereas the bosons lie further apart. This physically manifests as a repulsion and attraction force, while it is not a force at all. This is called the exchange force.

6.3 Spin

A complete quantum state of an electron includes both its position wave function, and its spin. Written as $\psi(\vec{r}) \chi \Rightarrow \psi(\vec{r}_1, \vec{r}_2) \chi(1,2)$ for composite states.

~~Spin also has to~~

6.4 Generalised symmetrisation principle

$\hat{\mathcal{P}} |1,2\rangle = |2,1\rangle$, for wave $\hat{\mathcal{P}}$ $\hat{\mathcal{P}} \psi(\vec{r}_1, \vec{r}_2) \chi(1,2) = \psi(\vec{r}_2, \vec{r}_1) \chi_{sym} \cdot \chi(2,1)$

$\hat{\mathcal{P}} \Rightarrow$ Exchange operator.

1.0 for identical particles the state is required to satisfy $\hat{\mathcal{P}} |1,2\rangle = \pm |2,1\rangle$.

6.5 Atoms

For a neutral atom with atomic number Z, consisting of a heavy nucleus & electric charge Z_e, surrounded by Z electrons (mass m_e & elem. charge $-e$), $\hat{H}$:

$$\hat{H} = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \frac{1}{4\pi\varepsilon_0} \frac{Z_e e^2}{r_j} \right\} + \frac{1}{2} \left(\frac{1}{4\pi\varepsilon_0} \right) \sum_{j \neq k}^{Z} \frac{e^2}{|\vec{r}_j - \vec{r}_k|}, \quad \hat{H}\psi = E\psi.$$

Only solved for $Z = 1$.

Nomenclature for the periodic table:
Horizontal rows correspond to filling out each shell.
An atomic state is noted as $n l^{(N)}$
with: n = number of shell, l specifying orbital angular momentum & N ~~specifies~~ specifying the amount of electrons in the state.

l's denominated as: $s, p, d, f, g, h, i, k, l$ for $l = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9$.

Or you can also write according to Hund's rules.

$^{2S+1}L_J$ where S is the total spin, J is the total spin + orbital & L is the letter for total orbital angular momentum, the letter associated with l, capitalised.

6.6 Solids

Solids can be modelled as an electron gas, basically a 3D infinite square well.
Here, the allowed energies are: $E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m}$.

This model works really well for conductors.

For the electron gas model, each state can be imagined as in a grid in k-space. Here, each state occupies a volume $k_x k_y k_z = \frac{\pi^3}{V}$. Assume a spherical model with radius k_F, then: $\frac{1}{8}\left(\frac{4}{3}\pi k_F^3\right) = \frac{N_e}{2}\left(\frac{\pi^3}{V}\right)$. $k_F = (3\rho\pi^2)^{1/3}$, $\rho \equiv \frac{N_e}{V}$.

$E_{n_x n_y n_z} = \frac{\hbar^2 k^2}{2m} \Rightarrow E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m}(3\rho\pi^2)^{2/3}$ (Energy of the highest energy electron)

6.7 Periodic potentials: $V(x+a) = V(x)$.

Bloch's theorem: for periodic potentials, $\psi(x+a) = e^{ika}\psi(x)$ for constant k. To make this mathematically true, wrap x axis in a circle after N periods. Then: $\psi(x+Na) = \psi(x)$. A simple example is the dirac comb: $V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja)$. Imposing boundary conditions: $\cos(Nka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)$. Simplify to: $f(z) = \cos(z) + \frac{m\alpha}{\hbar^2 k}\sin(z)$. Plotting $f(z)$ gives a graph that sometimes exceeds $|1|$. But $f(z) = \cos(Nqa)$, which can never exceed $|1|$. As the allowed energies are at the points where the equality holds, points with $|f(z)| > 1$ are forbidden energies. Thus we have bands of allowed energies, and gaps of forbidden energies in solids!

7 Chapter 7: Afterword / Intermission: What quantum mechanics means.

A question might be posed: Is the wavefunction & probabilities really physically accurate, or can the state of a particle be known exactly before a measurement?

Einstein, Podolsky & Rosen: It can! Quantum mechanics is missing a hidden variable λ. Because of the EPR Paradox:

A pion, spin zero, decays into $e^- + e^+$. Conservation of momentum & angular momentum exists in the singlet configuration: $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ & The electron & positron

flying off in opposite directions. Wait until this distance is great. Measure the electron: Spin up! Then the positron has spin down. But now we know the positron's state, ~~so its wavefunction must collapse so its state~~ so its wavefunction collapses! Now we instantaneously collapsed that wavefunction, and the influence moved faster than light. Breaks causality!

Conclusion: Hidden variables! The positron & electron had predefined spins, and no information was transfered at all.

In 1964, ~~This is proven to~~ This is proven to be untrue by Bell.

The first he did was propose to calculate the average product of measurements of differently oriented measurement devices, expressed in the vectors of these ~~see~~ orientations:

$P(\vec{a},\vec{b}) = -\vec{a}\cdot\vec{b}$.

$\vec{a}$

The state of the particle measured at a

Then state that ~~$P(\vec{a},\vec{b})$~~ is not also dependent on $\vec{b}$. If this state λ is dependent ~~on λ, then $P(\vec{a},\lambda) = \pm 1$. & similarly, $P(\vec{b},\lambda) = \pm 1$.~~

~~on λ, then~~ on λ, then $A(\vec{a},\lambda) = \pm 1$ & $B(\vec{b},\lambda) = \pm 1$.

$P(\vec{a},\vec{b}) = \int \rho(\lambda) A(\vec{a},\lambda) B(\vec{b},\lambda) d\lambda$, $\rho(\lambda)$ - Probability density λ.

Take case of aligned detectors: $A(\vec{a},\lambda) = -B(\vec{a},\lambda)$.

and insert arbitrary vector $\vec{c}$:

$P(\vec{a},\vec{b}) - P(\vec{a},\vec{c}) = -\int \rho(\lambda)\left[A(\vec{a},\lambda)A(\vec{b},\lambda) - A(\vec{a},\lambda)A(\vec{c},\lambda)\right] d\lambda$

$P(\vec{a},\vec{b}) - P(\vec{a},\vec{c}) = -\int \rho(\lambda)\left[-A(\vec{b},\lambda)A(\vec{c},\lambda)\right] A(\vec{a},\lambda) A(\vec{b},\lambda) d\lambda$

$|P(\vec{a},\vec{b}) - P(\vec{a},\vec{c})| \leq$ ~~$1 + P(\vec{b},\vec{c})$~~ $\int \rho(\lambda)\left[1 - A(\vec{b},\lambda)A(\vec{c},\lambda)\right] d\lambda$

$|P(\vec{a},\vec{b}) - P(\vec{a},\vec{c})| \leq 1 + P(\vec{b},\vec{c})$ → Does not hold with $P(\vec{a},\vec{b}) = -\vec{a}\cdot\vec{b}$.

~~So Bell p~~

So Bell proved that Quantum Mechanics cannot have hidden variables, and nature is indeed probabilistic. But what about our old friend, the EPR Paradox?

Consider: can the collapse of the wavefunction be measured, transferring information? No. Causality is not broken, as entanglement is ~~no~~ in this regard similar to a shadow.

Let me discuss one final topic: The no-cloning theorem.
The uncertainty principle is physically enforced by a measurement being destructive: If you measure a system's position, you can't measure its momentum because the position measurement changed the system. But Why, then, can't you clone a system and measure its momentum & position separately? The answer is simple: you can't make clones.

Before I state why, let me know why this is even more important:
You can't measure one particle's wavefunction being ~~collapsed~~ collapsed, but if you clone it, you can: If a wavefunction is collapsed, and cloned millions of times, all measurements of the clones will return the same value. If the wavefunction is not collapsed, measurements of the clones will return an array of values. This can be noticed, and as ~~such~~ such breaks causality. So ~~ok~~ this shouldn't be possible!

Let Let me show why it's not possible: |ψ⟩

Here's how it would work: $|\psi\rangle|\chi\rangle \to |\psi\rangle|\psi\rangle$. It works for states ψ_1 & ψ_2: $|\psi_1\rangle|\chi\rangle \to |\psi_1\rangle|\psi_1\rangle$ & $|\psi_2\rangle|\chi\rangle \to |\psi_2\rangle|\psi_2\rangle$. Then, it also works for a linear combination of them: $|\psi_3\rangle = \alpha|\psi_1\rangle + \beta|\psi_2\rangle \Rightarrow$

$\Rightarrow |\psi_3\rangle|\chi\rangle \Rightarrow |\psi_3\rangle|\psi_3\rangle = \alpha^2|\psi_1\rangle|\psi_1\rangle + \beta^2|\psi_2\rangle|\psi_2\rangle + \alpha\beta[|\psi_1\rangle|\psi_2\rangle + |\psi_2\rangle|\psi_1\rangle]$.

But try the math: $|\psi_3\rangle|\chi\rangle = \alpha|\psi_1\rangle|\chi\rangle + \beta|\psi_2\rangle|\chi\rangle \Rightarrow \alpha|\psi_1\rangle|\psi_1\rangle + \beta|\psi_2\rangle|\psi_2\rangle$. It doesn't clone it perfectly. In fact, it only clones spin up & spin down, but not any ~~of combination of the two~~ superposition of the two. What it actually produces, is an entangled state where all clones are either spin up or spin down. So whether or not the state was initially collapsed, ~~all clones~~ all clones would produce the same result when measured. That's why it's useless to use clone the particles: it changes nothing.

The End