The laws of motion in QM.

Classical mechanics:

All we need is x and p. All energies:

E_p
E_k
L (angular momentum)

$\left.\right\} f(x,p)$ functions of x, p

But x and p are particular numbers at particular moment in time t.
So, what can we say about the future?
Then we can think what rate of change will be:

$$\boxed{\frac{d^2x}{dt^2}m = F = -\frac{dV}{dx}}$$

potential

Second Newton's law

We see the rate is actually determined by acceleration. Once the forces are known this acceleration is unique.

$$x = x_0 + \frac{dx}{dt}t$$
$$V = U_0 + \frac{dV}{dt}t = V_0 + \frac{d^2x}{dt^2}t$$

x_0, V_0 initial conditions

We are free to choose:

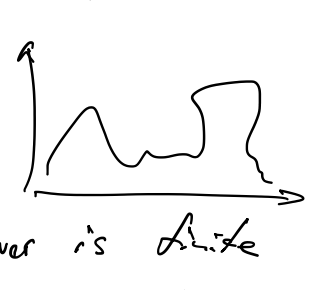
$$\left\{\begin{matrix} x \\ \frac{dx}{dt} \to p \end{matrix}\right.$$

but accelaration $\frac{d^2x}{dt^2}$ not up to us to decide

That is direct result of math:
if rate is given by second order differential equation, the initial conditions comes from 0 and 1'st order.
All higher derivatives are slaves to applied force F = ma.

Quantum mechanics

In QM we assign particle position as $\psi(x) \rightsquigarrow$ any function



It literally can be any function as long as the answer is finite over all space, i.e. $\psi \to 0$ at infinity.

So, what it can tell us?
Depends what you want to know.

1) Ok, now we would like to know, where is the particle exactly.

$$P(x) = |\psi(x)|^2$$

probability density

$\rightsquigarrow$ even if ψ is complex P is real

2) What is the particle momentum?
This is just math recipe:

Remember $\psi(x) = e^{ikx}$?

$$\psi(x) = \sum A_p \frac{e^{ipx/\hbar}}{\sqrt{L}}$$

a b L

$$A_p = \int \frac{e^{-\frac{ipx}{\hbar}}}{\sqrt{L}} \cdot \psi(x)\,dx$$

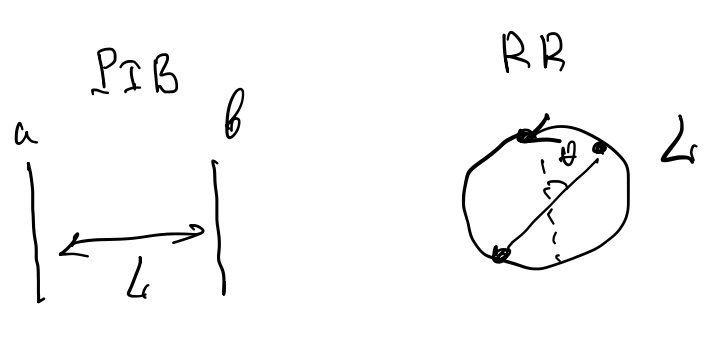
$\sim$ complex conjugate

The probability to obtain momentum:

$$P(p) = |A_p|^2$$

But who told us $\psi(x) = \sum A_p \frac{e^{\frac{ipx}{\hbar}}}{\sqrt{L}}$

Fourier did as in closed system it has to be periodical.

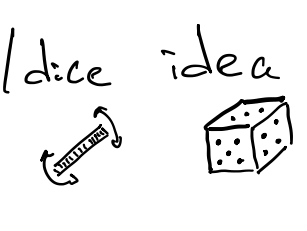


QM tells you here (postulate):

a) $|A_p|^2$ is probability to get value p when you measure momentum

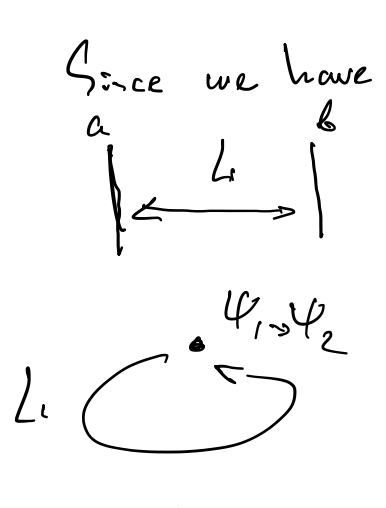
b) Once you measure p the state goes from $\psi(x) = \sum \psi_p$ to ψ_p.

Coin/dice idea



c) p is not every arbitrary number

Since we have boundary or circle:



$$p_n = \frac{2\pi\hbar}{L}n$$

$\psi_1 = \psi_2$ p is quantized

3) Most difficult is to answer what particle energy is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi_E(x) = E\psi(x)$$

$$\psi(x) = \sum A_E \psi_E(x)$$

While momentum is defined by kinetic energy

Momentum defined once and for all:

$$\psi = \sum A_p \left(e^{\frac{ipx}{\hbar}}\right)\frac{1}{\sqrt{L}}$$

the E states will be determined by:
$V(x) \to$ external potential
In fact, SE is energy conservation law:

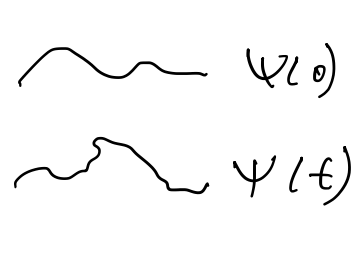
$$\hat{E}_k + \hat{E}_p = \hat{H}$$

We have to solve it for every possible potential

Let's introduce time:

$\psi(x)$, while $x(t)$ and $p(t)$

$\psi(x,t)$



Time-dependent Schrödinger equation:

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

from this equation follows everything

Now the question is:
If we know $\psi(x,0)$, what it will be in future, i.e. $\psi(x,t)$
But this is first order differential equation, hence $\psi(x,0)$ our initial condition that determines the future.

Classical	QM
$x, \frac{\partial x}{\partial t}$	$\psi(x,0)$

Knowing $\psi(x,0)$ and $V(x)$ we can predict its future state

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i presented in equation of motion
Remember in EM $E = E_0 e^{i(\omega t - \bar{k}\bar{r})}$
we always took Re part at the end.
$\psi(x,t)$ is complex, both parts are important.

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \underbrace{-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi(x,t)}_{\text{almost SE, only with } \psi(x,t)}$$

How we are able to calculate future, while given only present?

We will not be able to solve it for every possible $\psi(x)$, but we can take special case:

$$\psi(x,t) = F(t)\psi(x)$$

not always working!

Let's go back to SE:

$$i\hbar\psi(x)\frac{dF(t)}{dt} = \underbrace{F(t)\left[-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x)\right]}_{F(t)(\hat{H}\psi)}$$

Let's devide by $F(t)\psi(x)$:

$$\underbrace{i\hbar\frac{1}{F(t)}\frac{dF(t)}{dt}}_{f(t)} = \underbrace{\frac{1}{\psi(x)}(\hat{H}\psi)}_{f(x)}$$

The only way this functions are equal if they are constants!

$$i\hbar\frac{1}{F(t)}\frac{dF(t)}{dt} = \frac{1}{\psi(x)}(\hat{H}\psi) = E$$

$$\left\{\begin{matrix} i\hbar\frac{dF}{dt} = FE \\ \hat{H}\psi = E\psi \quad \text{(static SE)} \end{matrix}\right.$$

$$i\hbar\frac{dF(t)}{dt} = EF(t) \Rightarrow F(t) = F(0)e^{-\frac{iEt}{\hbar}}$$

What does it mean?

1) If $\psi(x,t) = F(t)\psi(x) \Rightarrow F(t)$ must be exp function

2) We can pick any E, as long as static SE is satisfied.

These E are states of definite energy

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$$

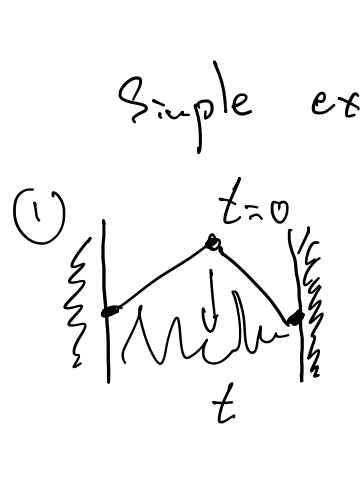
$\rightsquigarrow \psi_E(x)$

$$\Downarrow$$

$$\psi(x,t) = F(t)\psi(x) = e^{-\frac{iEt}{\hbar}}\psi_E(x)$$

If we start at $\psi_E(x)$, the future is only phase $e^{-i\frac{Et}{\hbar}}\psi_E(x)$

Simple example will be PIB:

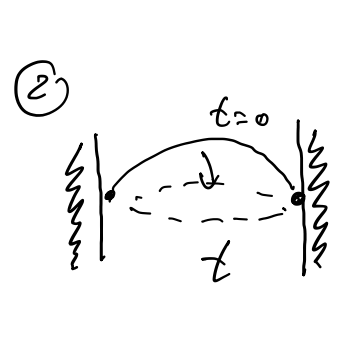


I have no idea!

$\psi(x,0) \to$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2}$$

wave equation for the string



$$\psi(x,t) = A\sin\frac{\pi x}{L} \cdot \cos\frac{\pi x v t}{L}$$

static time evolution

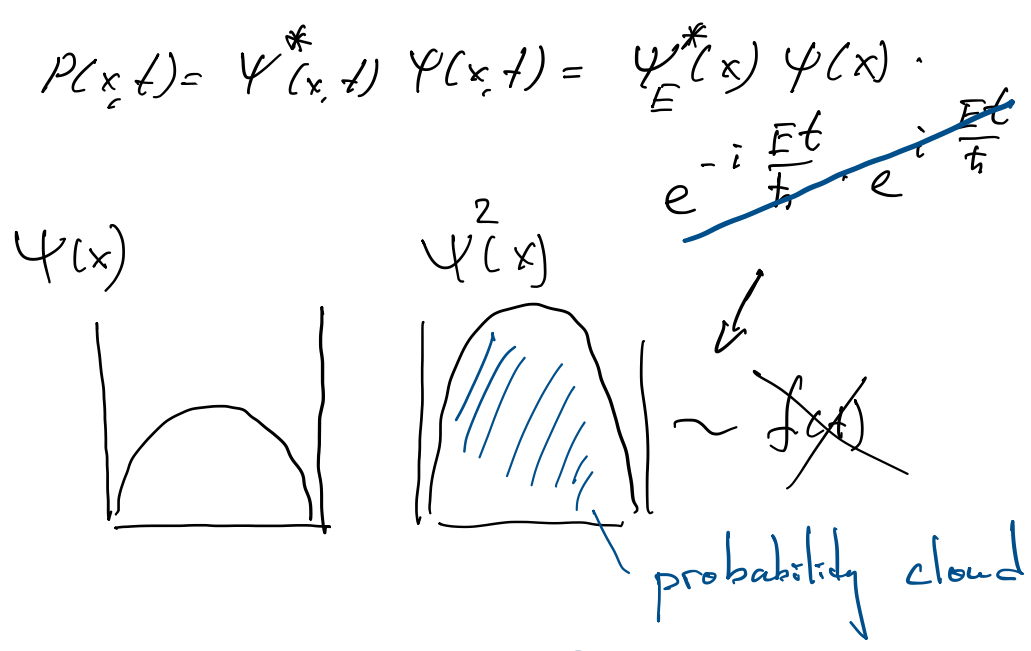
$$A = \sqrt{\frac{2}{L}}$$

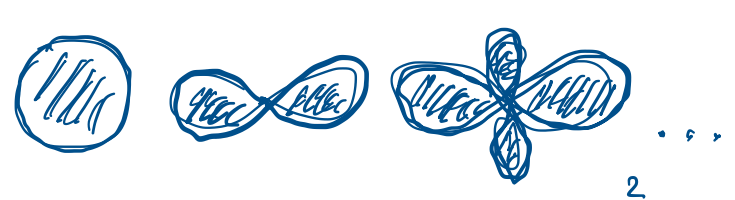
But again, every periodic function can be

$$\psi = \sum \psi_n(x) \quad \text{(Fourier)}$$

But what are probabilities to determine x, p?
Amazing thing, nothing will depend on t!

$$P(x,t) = \psi^*(x,t)\psi(x,t) = \psi_E^*(x)\psi(x) \cdot \cancel{e^{-i\frac{Et}{\hbar}} e^{i\frac{Et}{\hbar}}}$$





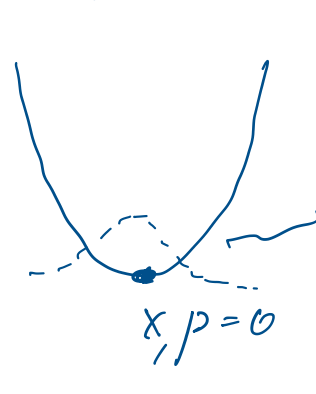
$$V(r) = -\frac{ze^2}{\sqrt{x^2+y^2+z^2}}$$

These are stationary states. We can stay there forever. The only thing we will need is to change $V(x,t)$!

Why if we make E = 0 and B = 0 hydrogen atom still goes from $|e\rangle \to |g\rangle$?

Spontaneous emission

E and B, same as x and p!
The state of definite E is not the state of definite B.



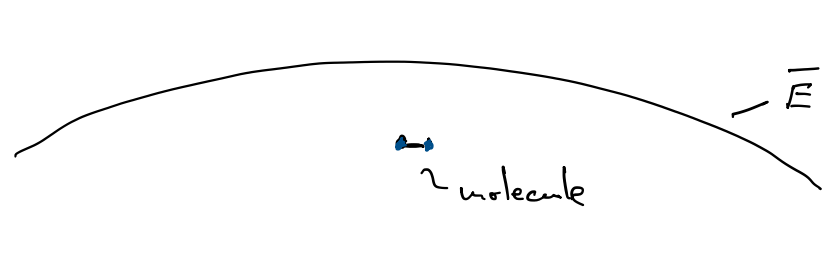
We are not allowed to sit here

E, B $\sim$ theory of nothing

We cannot switch them off, because of quantum fluctuations of the vacuum.

We can introduce external perturbation as:

$$\bar{E} = \bar{E}_0\cos(\bar{k}\bar{r} - \omega t) \text{ or } \bar{B} = \bar{B}_0\cos(\bar{k}\bar{r} - \omega t)$$



$$\left\{\begin{matrix} \bar{E} = \bar{E}_0\cos\omega t \\ \bar{B} = \bar{B}_0\cos\omega t \end{matrix}\right.$$

$d_m \ll \lambda$ - dipole approximation

In case of electric field:

$$\hat{H} = -\bar{\mu}\bar{E}(t)$$

In case of magnetic field:

$$\hat{H} = -\bar{m}\bar{B}(t) = -\frac{qg}{2m}\hat{I}\bar{B}(t)$$

$\hat{I}$ - spin angular momentum

$$\Downarrow$$

$$\hat{H} = \hat{H}^0 + \hat{H}_E^1 + \hat{H}_B^1$$

0 - field is off
1 - field is on

Let's take only one case:
- continuous wave
- weak

$$\varphi_n(x,t) = e^{\frac{iEt}{\hbar}}\varphi_n(x,0)$$

$$\psi(t) = \sum_n c_n(t)\varphi_n(t)$$

$\sim$ superposition of all normal modes

$$\boxed{i\hbar\dot{\psi}(t) = \hat{H}\psi(t)}$$

Our previous equation

$$i\hbar\frac{\partial}{\partial t}\sum c_n(t)\varphi_n(t) = \hat{H}\sum c_n(t)\varphi_n(t)$$

$$i\hbar\sum\left[\frac{\partial c_n(t)}{\partial t}\varphi_n(t) + c_n(t)\frac{\partial\varphi_n(t)}{\partial t}\right] = \sum c_n(t)\left(\hat{H}^0 + \hat{H}'(t)\right)\varphi_n(t)$$

$$i\hbar\sum\left[\frac{\partial c_n(t)}{\partial t}\varphi_n(t) - \frac{iE_n}{\hbar}c_n(t)\varphi_n(t)\right] = \sum c_n(t)\left(E_n + \hat{H}'(t)\right)\varphi_n(t)$$

$$i\hbar\sum\frac{\partial c_n(t)}{\partial t}\varphi_n(t) + \cancel{\sum E_n c_n(t)\varphi_n(t)} = \sum c_n(t)\left[\cancel{E_n} + \hat{H}'(t)\right]\varphi_n(t)$$

$$i\hbar\sum\frac{\partial c_n(t)}{\partial t}\varphi_n(t) = \sum c_n(t)\hat{H}^{(1)}(t)\varphi_n(t)$$

Let's multiply both sides by φ_f^* and integrate over space:

1) left side:

$$i\hbar\int\varphi_f^*(t)\sum\frac{\partial c_n(t)}{\partial t}\varphi_n(t)\,dx = i\hbar\sum\frac{\partial c_n(t)}{\partial t}\int\varphi_f^*(t)\varphi_n(t)\,dx =$$

δ_{nf} (orthonormality)

$$= i\hbar\frac{\partial c_f(t)}{\partial t}$$

2) right side:

$$\int\varphi_f^*(t)\sum c_n(t)\hat{H}^{(1)}(t)\varphi_n(t)\,dx = \sum c_n(t)\int\varphi_f^*(t)\hat{H}^{(1)}(t)\varphi_n(t)\,dx$$

$$\Downarrow$$

$$\boxed{i\hbar\frac{\partial c_f(t)}{\partial t} = \sum c_n(t)\int\varphi_f^*(t)\hat{H}^{(1)}(t)\varphi_n(t)\,dx}$$

Let's take $\hat{H}^{(1)}(t) = \hat{V}\cos\omega t$

$$\Downarrow$$

$$\hat{H}^{(1)} = \hat{V}\frac{1}{2}\left[e^{i\omega t} + e^{-i\omega t}\right]$$

$$\hat{V} = -q\bar{r}\cdot\bar{E}_0 \quad \text{electric}$$

$$\hat{V} = -\frac{qg}{2m}\hat{I}\bar{B}_0 \quad \text{magnetic}$$

$$i\hbar\frac{\partial c_f(t)}{\partial t} = \sum_n c_n(t)\int\varphi_f^*(t)\frac{1}{2}\hat{V}\left(e^{i\omega t} + e^{-i\omega t}\right)\varphi_n(t)\,dx =$$

$$\varphi_f^*(t) = e^{i\frac{E_f t}{\hbar}}\varphi_f(0)$$

$$\varphi_n(t) = e^{-i\frac{E_n t}{\hbar}}\varphi_n(0)$$

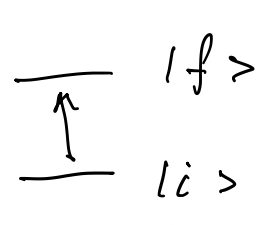
$$= \sum_n c_n(t)\int e^{i\frac{E_f t}{\hbar}}\varphi_f(0)\frac{1}{2}\hat{V}\left(e^{i\omega t} + e^{-i\omega t}\right)e^{-i\frac{E_n t}{\hbar}}\varphi_n(0)\,dx =$$

$$= \sum c_n(t)\int\varphi_f^*(0)\frac{1}{2}\hat{V}\varphi_n(0)\left[e^{-i(E_f - E_n - \hbar\omega)t/\hbar} + e^{-i(E_f - E_n + \hbar\omega)t/\hbar}\right]dx$$

$$E_f - E_n = \pm\hbar\omega \quad \text{- resonance!}$$

Now we need to assume transitions only between normal states.

$i \to f$



The molecule starts at start i, so $c_n(0) = 0$ at $t = 0$, if $n \neq i$

$$\int\varphi_f^*(0)\hat{V}\varphi_n(0)\,dx = V_{fn}$$

$$\Downarrow$$

$$i\hbar\frac{\partial c_f(t)}{\partial t} = \frac{1}{2}V_{if}\left(e^{-i(E_f - E_i - \hbar\omega)\frac{t}{\hbar}} + e^{-i(E_f - E_i + \hbar\omega)\frac{t}{\hbar}}\right)c_i(t)$$

Next, important assumption:

$$c_i(t) \approx 1 \text{ and } c_n(t) \ll c_i(t) \text{ if } n \neq i$$

This is linear response assumption and not always true. It means we creat only small population at f

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Integrating over time:

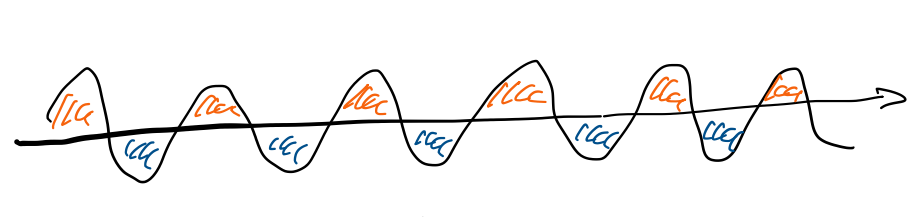
$$c_f(T) = \frac{V_{fi}}{2i\hbar}\int_0^T\left[e^{-i(E_f - E_i - \hbar\omega)\frac{t}{\hbar}} + e^{-i(E_f - E_i + \hbar\omega)\frac{t}{\hbar}}\right]dt$$

Probability at $T \to \infty$

$$\boxed{P_{fi} = |c_f(T)|^2 = \frac{|V_{fi}|^2}{4\hbar^2}\lim_{T\to\infty}\int_0^T\left[e^{-i(E_f - E_i - \hbar\omega)\frac{t}{\hbar}} + e^{-i(E_f - E_i + \hbar\omega)\frac{t}{\hbar}}\right]dt}$$

Fermi Golden Rule

If $E_f - E_i \neq \pm\hbar\omega$ the function oscillates very rapidly:



Overall integral is zero.

Fermi Golden Rule

1) Selection rules driven by:

$$|V_{if}|^2 = \left|\int\varphi_f^* V\varphi_i\,dx\right|^2$$

For electric field:

$$|V_{fi}|^2 = \left|\int\varphi_f^*\hat{\mu}\bar{E}_0\varphi_i\,dx\right|^2 = \left(\bar{E}_0\cdot\bar{\mu}_{fi}\right)^2$$

dipole matrix element have to be ≠ 0

For magnetic field:

$$|V_{fi}|^2 = \left|\int\varphi_f^*\hat{m}\bar{B}_0\varphi_i\,dx\right|^2 = \left|\frac{q\cdot g}{2m}B_0\cdot I_{fi}\right|^2$$

2) It has to be resonance:

$$E_f - E_i = \pm\hbar\omega$$

The potential now is:

$$V = \frac{1}{2}kx^2 + \mu E(t) = \frac{1}{2}kx^2 + Aex\cos\omega t$$

One can hit it hard by amplitud A, but smart thing to do is to find resonance

$$c_f \sim \int e^{-i(\Delta E - \hbar\omega)\frac{t}{\hbar}} + e^{-i(\Delta E + \hbar\omega)\frac{t}{\hbar}}\,dt$$

$$\sim \frac{1}{\Delta E^2 - (\hbar\omega)^2}$$

assuming no absorption