The laws of motion in QM.

Classical mechanics:

All we need is x and p. All energies:

$$\left.\begin{array}{l} E_p \\ E_k \\ \bar{L} \text{ (angular momentum)} \end{array}\right\} f(x,p)$$

functions of x, p

But x and p are particular numbers at particular time. What can we say about the future? That means the rate of change:

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

Second Newton's law

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

$$\left.\begin{array}{l} x = x_0 + \frac{dx}{dt}t \\ V = V_0 + \frac{dV}{dt}t = V_0 + \frac{d^2x}{dt^2}t \end{array}\right\} x_0, V_0$$

initial conditions

We are free to give particle any position $\left.\begin{array}{l} x \\ p \end{array}\right\}$, but we cannot pick $\frac{\partial^2 x}{\partial t^2}$

That is direct result of math:

if rate is given by second order equation the initial conditions are 0 and 1st orders.

Quantum mechanics

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

It literally can be any function as long as answer is finite in 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 the particle exactly is.

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

$\rightarrow$ probability density

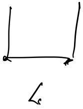
$\rightsquigarrow$ even if it is complex P is real

2) What will be particle momentum?

This is just math recipe!

We suppose to write:

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



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

$\sim$ complex conjugate

The probability to obtain momentum p is

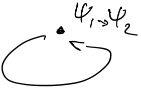
$$P(p) = |A_p|^2$$

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

↙

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

Since you go a circle $p_n = \frac{2\pi\hbar}{L} n$



$\psi_1 = \psi_2$

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

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

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

While momentum is defined by kinetic energy the E states will be determined by

$V(x) \longrightarrow$ external potential.

In fact SE is energy conservation law:

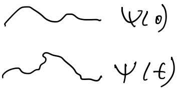
$$E_k + E_p = \hat{H}$$

We have to solve it for every possible potential.

Let's introduce time:

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

$\psi(x,t)$



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

from this equation follows everything.

The real question, knowing $\Psi(x,0)$ tell me what is $\Psi(x,t)$.

But this is first order equation in time, meaning mathematically: initial $\Psi(x,0)$ determines the future.

Classical QM

$x, \frac{\partial x}{\partial t}$ $\Psi(x) \rightsquigarrow x$ Knowing $\Psi(x,0)$ math gives future

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i here shows the equation is real complex.

Remember to EM $E=E_0 e^{i(\omega t-\vec{k}\vec{r})}$

we always took Re part at the end.

He it is complex, both parts are important.

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

How we can calculate future, while given the 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:

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

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

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

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

$$\begin{cases} i\hbar\dfrac{dF(t)}{dt} = EF \\ (H\psi) = E\psi \quad \text{(static SE)} \end{cases}$$

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

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.

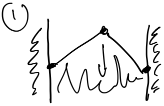
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x) \rightarrow \psi_E(x)$$

$$\Downarrow$$

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

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

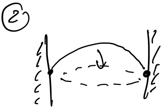
①



I have no idea!

$$\psi(x,0) \longrightarrow \frac{\partial^2\psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2}$$

②



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

↓

normal mode

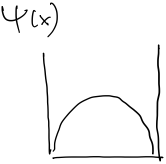
Simple example will be PIB

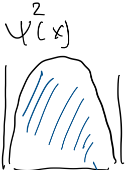
But again, every periodic function can be written as $\sum \psi_n(x)$

But what are probabilities to determine x, p?

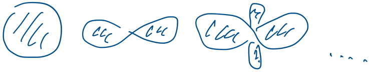
Amazing thing, nothing will depend on t!

$$P(x,t) = \psi^*(x,t)\,\psi(x,t) = \psi_E^*(x)\,\psi(x)\cdot\cancelto{1}{\left|e^{-i\frac{Et}{\hbar}}\right|^2}$$





$\sim \cancel{f(t)}$

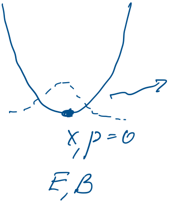


this are stationary states. We can stay there forever. The only thing we will need is to change $V(x,t)\ \underset{0}{\nabla}$.

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

E and B are same as x and p

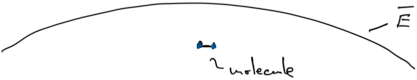
We never can switch them off because of quantum fluctuations of the vacuum.



we are not allowed to sit here

We can introduce external perturbation as:

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



$$\begin{cases} \bar{E} = \bar{E}_0 \cos \omega t \\ \bar{B} = \bar{B}_0 \cos \omega t \end{cases} \qquad d_m \ll \lambda \quad \text{– dipole approximation}$$

In case of electric field:

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

In case of magnetic field:

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

$\hat{I}$ - spin angular momentum

$$\Downarrow$$

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}_{E} + \hat{H}^{(1)}_{B}$$

Let's take only one case:

- continuous wave
- weak

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

$$\Psi(t) = \sum_n c_n(t)\varphi_n(t)$$ ~ superposition of all normal modes

$$\boxed{i\hbar\dot{\Psi}(t) = \hat{H}\Psi(t)}$$ our previous equation

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

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

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

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

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

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

1) left side:

$$i\hbar\int\varphi_f^*(t)\sum\frac{\partial c_n(t)}{\partial t}\varphi_n(t)\,dx = i\hbar\sum\frac{\partial c_n(t)}{\partial t}\underbrace{\int\varphi_f^*(t)\varphi_n(t)\,dx}_{\delta_{nf}\ \text{(orthonormality)}} =$$

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

2) right side:

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

$$\Downarrow$$

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

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

$$\Downarrow$$

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

$$\Downarrow \qquad \hat{V} = -q\bar{r}\cdot\bar{E}_0 \qquad\qquad \hat{V} = -\frac{qg}{2m}\hat{I}\bar{B}_0$$

electric magnetic

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

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

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

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

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

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

Now, we need to assume transitions only between two normal states:

$i \to f$ $\qquad c_n(0)=0$ if $n \neq i$

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

$$\Downarrow$$

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

Assuming only $c_i(t)=1$

(linear response approximation normalization)

Integrating over time:

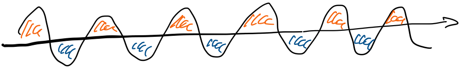
$$c_f(T) = \frac{V_{fi}}{2i\hbar}\int_0^T \left[e^{-i(E_f-E_i-\hbar\omega)\frac{t}{\hbar}} + e^{-i(E_f-E_i+\hbar\omega)\frac{t}{\hbar}}\right]dt$$

Probability at $T \to \infty$

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

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 (light)

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

dipole matrix element have to be ≠ 0

For magnetic field:

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

2) It has to be resonance:

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

The potential now

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

A can be large, but $\Psi(x)$ will be influenced by resonce:

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

$$\sim \frac{1}{\Delta E^2 - (\hbar\omega)^2}$$ assuming no absorption

https://www.desmos.com/calculator/c3u5vyvmhh