

In Wave Mechanics, we have $\Psi(x,t)$ as the QM state function. Its time evolution is determined by the TDSE:

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

We can also describe wave mechanics in Momentum space. Then the state function is $\Phi(k,t)$, and the TDSE is

$$i\hbar \frac{\partial \Phi(k,t)}{\partial t} = \hat{H} \Phi(k,t)$$

All of Wave Mechanics can be translated to momentum space. For example

	<u>x-space</u>	<u>p-space</u>
wavefunction @ $t=0$	$\Psi(x)$	$\Phi(k)$
wavefunction @ $t>0$	$\Psi(x,t)$	$\Phi(k,t)$
\hat{x}	multiply by x	$-i\hbar \frac{d}{dp}$
\hat{p}	$-i\hbar \frac{d}{dx}$	multiply by p
\hat{H}	$\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$	$\frac{p^2}{2m} + V(-i\hbar \frac{d}{dp})$
TDSE	$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$	$i\hbar \frac{\partial \Phi}{\partial t} = \hat{H} \Phi$

(2)

$\psi(x)$ & $\phi(k)$ are two types of QM amplitudes

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

$$|\phi(k)|^2 dk = P(k) dk$$

x & p are continuous observables, so these amplitudes are continuous functions. Their equations of motion are partial differential equations, and the operators are differential operators.

In QM, we also have discrete observables, like the energies of bound states. We use discrete amplitudes to calculate their probabilities:

$$|a_n|^2 = P(E_n)$$

The $\{a_n\}$ contain the same information as $\psi(x)$ & $\phi(k)$. For example, if we know the $\{a_n\}$, we know what $\psi(x)$ is also:

$$\psi(x) = \sum_n a_n Q_n$$

So the $\{a_n\}$ describe the system just as well as $\psi(x)$. Can we write all of QM in terms of the $\{a_n\}$??

Answer: Yes.

For example, how do the $\{a_n\}$ evolve in time?
Answer: each a_n gets a phase factor of $e^{-i\omega_n t}$.

We know this from wave mechanics:

$$\Psi(x,t) = \sum_n a_n \phi_n e^{-i\omega_n t} = \sum_n a_n(t) \phi_n$$

$$\text{where } a_n(t) \equiv a_n e^{-i\omega_n t}$$

So if our initial state is a column vector in energy space:

$$\text{initial state} \sim \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix}$$

then the state evolves in time as

$$\text{state at time } t \sim \begin{pmatrix} a_1 e^{-i\omega_1 t} \\ a_2 e^{-i\omega_2 t} \\ a_3 e^{-i\omega_3 t} \\ \vdots \end{pmatrix}$$

In the energy basis,

Each component evolves independently of the other components. This is why we like the energy basis.

We would like to find an equation of motion which describes the time evolution of the $\{a_n\}$,

just like its $\frac{\partial \Psi}{\partial t} = \hat{H} \Psi$ describes the time evolution of $\Psi(x,t)$. We can write down the $\{a_n(t)\}$ individually as

$$a_1(t) = a_1 e^{-i\omega_1 t}$$

$$a_2(t) = a_2 e^{-i\omega_2 t}$$

$$a_3(t) = a_3 e^{-i\omega_3 t}$$

Each of these equations is the solution of a first-order differential equation:

~~$i\hbar \frac{da_1(t)}{dt} = E_1 a_1(t)$~~

Solu $i\hbar \frac{da_1(t)}{dt} = E_1 a_1(t) \Rightarrow a_1(t) = a_1 e^{-iE_1 t/\hbar} = a_1 e^{-i\omega_1 t}$

$i\hbar \frac{da_2(t)}{dt} = E_2 a_2(t) \Rightarrow a_2(t) = a_2 e^{-iE_2 t/\hbar} = a_2 e^{-i\omega_2 t}$

\vdots

We can write all these equations at once using matrix notation.

$$i\hbar \begin{pmatrix} \frac{da_1(t)}{dt} \\ \frac{da_2(t)}{dt} \\ \frac{da_3(t)}{dt} \\ \vdots \end{pmatrix} = \begin{pmatrix} E_1 & 0 & 0 & \dots \\ 0 & E_2 & 0 & \dots \\ 0 & 0 & E_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1(t) \\ a_2(t) \\ a_3(t) \\ \vdots \end{pmatrix}$$

or

$$i\hbar \frac{d}{dt} \begin{pmatrix} a_1(t) \\ a_2(t) \\ a_3(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} E_1 & 0 & 0 & \dots \\ 0 & E_2 & 0 & \dots \\ 0 & 0 & E_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1(t) \\ a_2(t) \\ a_3(t) \\ \vdots \end{pmatrix}$$

This is the Quantum Mechanical Equation of Motion in the energy basis. ~~It is the Schrödinger Equation for the $\{a_n\}$.~~ It is the Schrödinger Equation for the $\{a_n\}$. The matrix $\begin{pmatrix} E_1 & 0 & 0 & \dots \\ 0 & E_2 & 0 & \dots \\ 0 & 0 & E_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$ is the Hamiltonian in the energy basis.

For continuous variables like x & p , QM predicts an amplitude function ($\Psi(x,t)$ or $\Phi(k,t)$) and the ^{time} evolution is a partial differential Eq.

For a discrete variable, like E_n for bound states, QM predicts discrete amplitudes like $\{a_n\}$, and the evolution is a matrix ~~matrix~~ equation. Heisenberg, Born, Jordan were the first to write a quantum mechanical equations using matrices, so we call it Heisenberg's Matrix Mechanics.

Continuous Variables (x, p) \rightarrow Partial Diff. Eqs. \rightarrow Schrodinger's Wave Mechan
Discrete Variables (E_n) \rightarrow Matrix Equations \rightarrow Heisenberg's Matrix Mechanics

The QM equation of motion in the energy basis is

$$i\hbar \frac{d}{dt} \begin{pmatrix} a_1(t) \\ a_2(t) \\ a_3(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} E_1 & 0 & 0 & \dots \\ 0 & E_2 & 0 & \dots \\ 0 & 0 & E_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1(t) \\ a_2(t) \\ a_3(t) \\ \vdots \end{pmatrix}$$

This is the Time-Dependent Schrödinger Eq in the energy basis (for bound states).

It looks similar to our usual TISE:

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

Since $\Psi(x,t)$ becomes $\begin{pmatrix} a_1(t) \\ a_2(t) \\ a_3(t) \\ \vdots \end{pmatrix}$ in the energy basis,

the correspondence is exact if we identify the matrix as the Hamiltonian.

- In a continuous basis like position space or momentum space, the QM amplitudes are continuous functions, and the operators are differential. $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$, for example.
- In a discrete basis, like energy for bound states, the QM amplitudes are discrete, and the operators are Matrices.

In the energy basis, the Hamiltonian is a diagonal matrix. This reflects the fact that each amplitude evolves independently of the others:

$$a_n(t) = a_n(t \rightarrow 0) e^{-iE_n t / \hbar}, \quad E_n = \hbar \omega_n$$

~~We can write the TDSE more compactly using Dirac notation.~~

We can write ^{a general} the TDSE independent of any particular basis using Dirac Notation. It is

$$i\hbar \frac{d}{dt} |\psi\rangle = \hat{H} |\psi\rangle \leftarrow \text{"Generalized Schrödinger Eq."}$$

~~What does~~

or "the QM Equation of Motion" ^{Eq.?}

What does it mean to write $\frac{d}{dt} |\psi\rangle$? What is the time derivative of a ket vector? We can see by making the ~~expr~~ expression less abstract, and more concrete, by projecting it into a particular basis. For example, let's project into the x -basis; by multiplying by $\langle x|$:

$$\langle x | \frac{d}{dt} |\psi\rangle = ?$$

The bra vector $\langle x|$ does not change in time, so we can move the derivative outside

$$\langle x | \frac{d}{dt} |\psi\rangle = \frac{d}{dt} \underbrace{\langle x | \psi\rangle}_{\psi(x)} = \frac{d}{dt} \psi(x) \stackrel{?}{=} 0 \text{ ???!}$$

This should not equal zero, because the ket vector $|\psi\rangle$

We need to indicate that $|\psi\rangle$ is changing in time

We will use either $|\psi(t)\rangle$ or $|\psi\rangle_t$

(remember, this is a label, not a function!!)

$$\therefore \langle x | \frac{d}{dt} |\psi\rangle_t = \frac{d}{dt} \langle x | \psi\rangle_t = \frac{d}{dt} \psi(x,t) \approx \frac{\partial}{\partial t} \psi(x,t)$$

should now be a partial derivative

Let's Project the Generalized TDSE into the energy basis:

$$i\hbar \frac{d}{dt} |\psi\rangle_t = \hat{H} |\psi\rangle_t \quad \text{Generalized TDSE.}$$

Project into energy basis by multiplying both sides by $\langle n |$.

$$\langle n | i\hbar \frac{d}{dt} |\psi\rangle_t = \langle n | \hat{H} |\psi\rangle_t \quad \langle n |$$

since $\langle n |$ does not depend on time.

$$i\hbar \frac{d}{dt} \langle n | \psi\rangle_t = \langle n | \hat{H} |\psi\rangle_t$$

$$i\hbar \frac{d}{dt} a_n(t) = \langle n | \hat{H} |\psi\rangle_t$$

What is this thing? Insert the identity operator to find out.

$$= \langle n | \hat{H} \left(\sum_m |m\rangle \langle m| \right) |\psi\rangle_t$$

$$= \sum_m \langle n | \hat{H} |m\rangle \langle m | \psi\rangle_t$$

$$= \sum_m E_m \langle n | m\rangle a_m(t)$$

$$i\hbar \frac{d}{dt} a_n(t) = E_n a_n(t)$$

By projecting it $i\hbar \frac{d}{dt} |\psi\rangle_t = \hat{H} |\psi\rangle_t$ into the energy basis, we recover the ~~generalized~~ correct equation of motion for the $\{a_n\}$.

Suppose we choose to use a complete, discrete basis, which is not energy. ~~For example, imagine that we think of position (x) as being discretized~~

Let $\{|i\rangle\}$ be a complete basis which is discrete, but it is not energy. Let's project the GTDSE into the $\{|i\rangle\}$ basis: (let the eigenvalues be called λ_i)

$$i\hbar \frac{d}{dt} |\psi\rangle_t = \hat{H} |\psi\rangle_t$$

Multiply from the left with $\langle i|$:

$$i\hbar \frac{d}{dt} \langle i|\psi\rangle_t = \langle i|\hat{H}|\psi\rangle_t$$

Let's call the overlap $\langle i|\psi\rangle_t \equiv c_i(t)$ (because it's just a complex number).

$$i\hbar \frac{d}{dt} c_i(t) = \langle i|\hat{H}|\psi\rangle_t$$

Insert the identity operator: $\hat{I} = \sum_j |j\rangle\langle j|$

$$= \langle i|\hat{H}(\sum_j |j\rangle\langle j|)|\psi\rangle_t$$

$$= \sum_j \langle i|\hat{H}|j\rangle \underbrace{\langle j|\psi\rangle_t}_{c_j(t)}$$

$$= \sum_j \langle i|\hat{H}|j\rangle c_j(t)$$

By the way, what is the physical interpretation of $c_j(t)$? Well, since $c_j(t) \equiv \langle j|\psi\rangle_t$, it is the amplitude to measure the eigenvalue λ_j corresponding to state $|j\rangle$.

$$|j(t)\rangle = P(\lambda_j)$$

Since $|j\rangle$ is not an energy eigenstate, we cannot do $\hat{H}|j\rangle = E_j|j\rangle$!! Wrong!

So we can go no further. But we can rename things. We call ~~$\langle i | \hat{H} | j \rangle$~~ $\langle i | \hat{H} | j \rangle$ the "matrix element of \hat{H} in the $|i\rangle$ basis"

$$\langle i | \hat{H} | j \rangle \equiv H_{ij} = \text{some complex number} \\ = \text{"Matrix Element of } \hat{H}$$

Then $i\hbar \frac{d}{dt} c_j(t) = \sum_j H_{ij} c_j(t)$

is the QM equation of motion in this basis.

In pure matrix notation we have

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_1(t) \\ c_2(t) \\ c_3(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} & H_{13} & \dots \\ H_{21} & H_{22} & H_{23} & \dots \\ H_{31} & H_{32} & H_{33} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \\ c_3(t) \\ \vdots \end{pmatrix}$$

So In the energy basis, the Hamiltonian is a diagonal matrix, and the amplitudes $\{c_n\}$ evolve in time independently of each other.

If we use a discrete basis which is not the energy basis, the Hamiltonian is not diagonal, and the time evolution of the amplitudes $\{c_j\}$ depends on all of the other amplitudes through the H_{ij} matrix.

P. AMRAN

In a discrete basis, ~~which is not the case~~ the TDSE looks like

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_1(t) \\ c_2(t) \\ c_3(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} & H_{13} & \dots \\ H_{21} & H_{22} & H_{23} & \dots \\ H_{31} & H_{32} & H_{33} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \\ c_3(t) \\ \vdots \end{pmatrix}$$

The $\{c_i(t)\}$ are the amplitudes to measure the eigenvalue λ_i associated with state $|i\rangle$:

$$c_i(t) = \langle i | \psi \rangle_t$$

$$|c_i(t)|^2 = P(\lambda_i)$$

If the observable for these states is called Λ , then if we measure Λ , we get a value λ_i with probability $|c_i(t)|^2$. After the measurement, the state of the system is

$$\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} \leftarrow \begin{array}{l} \text{the } i\text{th} \\ \text{position, corresponds} \\ \text{to measurement} \\ \lambda_i. \end{array}$$

The measurement of Λ has collapsed the wavefunction into an eigenstate of Λ .

The ~~base~~ state then evolves in time according to the matrix version of the TDSE.

Because it's annoying to write these column vectors & matrices, we often use summation notation:

$$i\hbar \frac{d}{dt} c_i(t) = \sum_j H_{ij} c_j(t)$$

TDSE in matrix form using summation notation

$$= H_{11} c_1(t) + H_{12} c_2(t) + H_{13} c_3(t) + \dots$$

This says exactly the same thing as

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_1(t) \\ c_2(t) \\ c_3(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} & H_{13} & \dots \\ H_{21} & H_{22} & H_{23} & \dots \\ H_{31} & H_{32} & H_{33} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \\ c_3(t) \\ c_4(t) \end{pmatrix}$$

Recall that the Matrix elements H_{ij} are defined by

$$H_{ij} \equiv \langle i | \hat{H} | j \rangle \text{ in the } \{|i\rangle\} \text{ basis.}$$

To completely define the Hamiltonian for any discrete system in a discrete basis, we have to know all of the H_{ij} .

If we have a bound-state system, like the particle-in-the-box or the Harmonic Oscillator, we can use "Matrix Mechanics" to describe the time evolution of the system in the discrete energy eigenstates (stationary states).

In that case,

$$H_{nm} = \langle n | \hat{H} | m \rangle = E_m \langle n | m \rangle = E_m \delta_{nm}$$

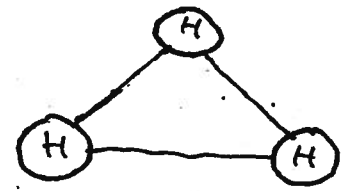
∴ The Hamiltonian Matrix is diagonal in the energy basis: $H_{nm} = E_m \delta_{nm}$ or

$$\hat{H} = \begin{pmatrix} E_1 & 0 & 0 & \dots \\ 0 & E_2 & 0 & \dots \\ 0 & 0 & E_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

If we choose to use a discrete basis, which is not the energy basis, then the Hamiltonian in general is not diagonal: $H_{ij} \neq \delta_{ij}$

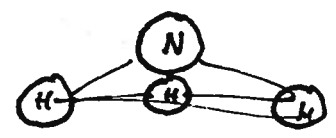
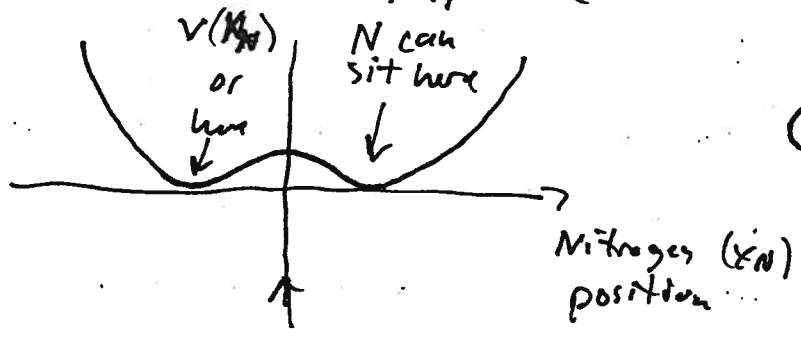
Ex Ammonia Molecule (NH_3)

The three Hydrogens in Ammonia looks like:



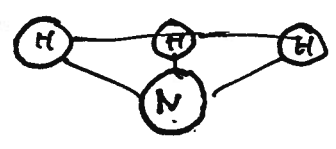
They form a triangle. The Nitrogen molecule can rest on the top of the triangle, or the bottom.

The Nitrogen sees a potential which looks roughly like



stable view

or



The position of the Nitrogen atom is a continuous variable. However, due to the shape of NH_3 , to a good approximation we can pretend that the N atom can take only 2 discrete positions, above and below the 3 hydrogens. So this is a discrete, two-state system.

First state: $|up\rangle \leftarrow$ N atom up

second state: $|down\rangle \leftarrow$ N atom down.

We can write down the TDSE in Matrix Mechanics form for this system:

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}$$

In this notation, $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ stands for an ammonia molecule with Nitrogen up:

and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ stand for nitrogen down

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \sim |up\rangle, \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix} \sim |down\rangle$$

The Matrix Equations can ^{also} be written explicitly as

$$i\hbar \frac{dc_1(t)}{dt} = H_{11} c_1(t) + H_{12} c_2(t)$$

$$i\hbar \frac{dc_2(t)}{dt} = H_{21} c_1(t) + H_{22} c_2(t)$$

Given an initial condition for $c_1(t=0)$ & $c_2(t=0)$, and given the Hamiltonian Matrix, we can solve for $c_1(t)$ & $c_2(t)$.