

* Lecture 8 *

ANDREA AIELLO
SS2017 FAU-ERLANGEN LP-1)
IK-1

- The energy operator -

In classical mechanics the energy of a particle is:

$$E = K + V \leftarrow \text{potential energy}$$

↑
kinetic energy

where

$$K = \frac{1}{2} m \vec{v}^2 = \frac{\vec{p}^2}{2m}$$

$$V = V(\underline{r})$$

↑ position vector of the particle

In Quantum Mechanics:

$$\underline{r} \rightarrow \hat{\underline{r}} = (\hat{x}, \hat{y}, \hat{z})$$

$$\underline{p} \rightarrow \hat{\underline{p}} = -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

Therefore

$$K \rightarrow \frac{\hat{\underline{p}}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2$$

$$V \rightarrow V(\hat{\underline{r}})$$

Now we understand the meaning of the Schrödinger equation for a free particle:

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}, t)$$

$$= \frac{\hat{P}^2}{2m} \psi(\mathbf{r}, t)$$

The energy operator

$$\frac{\hat{P}^2}{2m} + V(\hat{r}) \equiv \hat{H}$$

is called the HAMILTONIAN OF THE SYSTEM and is denoted with the letter \hat{H} .

For systems more general than a single particle

$$\psi(\mathbf{r}, t) \rightarrow \psi(q, t)$$

but the Sch. eq. remains the same:

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$$

where \hat{H} now is the Hamiltonian for the system.

For a single particle \hat{H} has ALWAYS the form:

$$\hat{H} = \frac{\hat{P}^2}{2m} + V(\mathbf{r})$$

For a free-particle

The "0" denotes free particle

$$\hat{H}_0 = \frac{\hat{p}^2}{2m}$$

and $[\hat{H}_0, \hat{p}] = 0 \Rightarrow \hat{H}_0$ and \hat{p} have the same eigen functions. We know that

$$\hat{p} \phi(r, p') = p' \phi(r, p')$$

where

$$\phi(r, p') = \frac{1}{(2\pi\hbar)^{3/2}} \exp\left(\frac{i}{\hbar} p' \cdot r\right)$$

Therefore

$$\begin{aligned} \hat{p}_i^2 \phi(r, p') &= \hat{p}_i (\hat{p}_i \phi(r, p')) \\ &= \hat{p}_i (p'_i \phi(r, p')) \\ &= p_i'^2 \phi(r, p') \Rightarrow \end{aligned}$$

$$\begin{aligned} \Rightarrow \hat{H}_0 \phi(r, p') &= \frac{p' \cdot p'}{2m} \phi(r, p') \\ &= \frac{p_x'^2 + p_y'^2 + p_z'^2}{2m} \phi(r, p') \end{aligned}$$

Homework: calculate a) $[\hat{H}, \hat{p}]$ and d) $[\hat{H}, \hat{E}]$ when

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r}) \text{ for any } V(\hat{r}) \in \mathbb{R}$$

In some cases, when the particle is interacting with another system, it is possible to describe a single part by a TIME-DEPENDENT Hamiltonian

$$\hat{H} = \hat{H}(r, t)$$

This is the case, e.g., of an atom interacting with an electromagnetic wave.

For the moment, we consider only TIME-INDEPENDENT Hamiltonians of the form:

$$\hat{H} = \hat{H}(r)$$

In this case:

$$i\hbar \frac{\partial \psi(r, t)}{\partial t} = \hat{H}(r) \psi(r, t) \quad (1.4)$$

can be solved separating the variables:

$$\psi(r, t) = u(r) T(t) \Rightarrow$$

$$\Rightarrow \left. \begin{aligned} i\hbar \frac{\partial \psi}{\partial t} &= i\hbar u \frac{\partial T}{\partial t} \\ \hat{H}(r) \psi &= T(t) (\hat{H}u)(r) \end{aligned} \right\} \Rightarrow$$

The function $u(r)$ is usually denoted as: STATIONARY STATE

L8-5)

$$\Rightarrow (1.4) \text{ becomes: } i\hbar u(\underline{r}) \frac{\partial T}{\partial t}(t) = T(t) (\hat{H}u)(\underline{r})$$

We divide both sides by $\Psi(\underline{r}, t) = u(\underline{r})T(t)$; to obtain:

$$i\hbar \frac{1}{T(t)} \frac{\partial T}{\partial t}(t) = \frac{1}{u(\underline{r})} (\hat{H}u)(\underline{r})$$

function of t

function of \underline{r}

So, if

$$f(t) = g(\underline{r})$$

the only possibility is that they are both constant. Let "E" denote this constant:

$$(1.5a) \quad \left\{ \begin{array}{l} i\hbar \frac{\partial T(t)}{\partial t} = E T(t) \end{array} \right.$$

Two independent equations

$$(1.5b) \quad \left\{ \begin{array}{l} \hat{H}(\underline{r}) u(\underline{r}) = E u(\underline{r}) \end{array} \right.$$

\equiv Time-independent Schrödinger equation

It looks like an eigenvalue equation, which can be solved (hopefully!) when $\hat{H}(\underline{r})$ is known.

Suppose to know the eigen functions $\Psi_n(r)$ and the eigenvalues E_n of $\hat{H}(r)$:

$$(1.6) \quad \boxed{\hat{H}\Psi_n = E_n\Psi_n}$$

(We suppose that they are discrete. For a free-particle this is not true).
Then the time evolution of the state n :

$$\Psi_n(r) \rightarrow \Psi_n(r,t)$$

is governed by (1.5Q) with $E = E_n$:

$$i\hbar \frac{\partial T}{\partial t} = E_n T$$

whose solution is:

$$T(t) = T(0) \exp\left(-\frac{i}{\hbar} E_n t\right)$$

But if $\Psi(r,0) = U(r)T(0) = \Psi_n(r) \Rightarrow T(0) = 1$

and

$$\boxed{\Psi_n(r,t) = \exp\left(-\frac{i}{\hbar} E_n t\right) \Psi_n(r)} \quad (2.6)$$

These eigenvalues and eigenfunctions exists if \hat{H} is Hermitian. Now we show that this is the case.

- Proof that $\hat{H} = \hat{H}^\dagger$ -

We start from $i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$

and $\int \psi^* \psi dq = 1 \Rightarrow$

$$\Rightarrow \frac{d}{dt} \left(\int \psi^* \psi dq \right) = 0$$

$$\Leftrightarrow \int \left(\frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \right) dq = 0$$

$$\Leftrightarrow \int \left[\left(\frac{1}{i\hbar} \hat{H}\psi \right)^* \psi + \psi^* \left(\frac{1}{i\hbar} \hat{H}\psi \right) \right] dq = 0$$

$$\Leftrightarrow \int \psi (\hat{H}^* \psi) dq - \int \psi^* (\hat{H}\psi) dq = 0$$

$$\Leftrightarrow \int \psi^* (\hat{H}^\dagger \psi) dq - \int \psi^* (\hat{H}\psi) dq = 0$$

$$\Leftrightarrow \int \psi^* (\hat{H}^\dagger - \hat{H}) \psi dq = 0$$

← This must be true
for any $\psi \Rightarrow$

$$\Rightarrow \hat{H}^\dagger = \hat{H}$$

c.v.d

Now, since $\hat{H} = \hat{H}^\dagger$ the eigenfunctions are orthogonal (1.8) and complete. This implies that at $t=0$ we can write:

$$\Psi(q, 0) = \sum_n a_n \Psi_n(q)$$

where $a_n = \int \Psi_n^*(q) \Psi(q, 0) dq$

Since for $t > 0$ $\Psi_n(q) \rightarrow \Psi_n(q) \exp\left(-\frac{i}{\hbar} E_n t\right) \Rightarrow$

$$\Rightarrow \Psi(q, t) = \sum_n a_n \Psi_n(q) \exp\left(-\frac{i}{\hbar} E_n t\right) \quad (1.8)$$

- Theorem -

If a physical quantity f is CONSERVED, that is its value does not change with time, the corresponding operator \hat{f} commutes with \hat{H} .

- Proof -

Let \hat{f} such that has mean value $\langle \hat{f} \rangle_\Psi$ when the system is prepared in the state Ψ , and let $\frac{d\hat{f}}{dt} \equiv \dot{\hat{f}}$ the time-derivative of such operator. Then $\dot{\hat{f}}$ is DEFINED as the quantity such that:

$$\langle \dot{\hat{f}} \rangle_\Psi \equiv \frac{d}{dt} \langle \hat{f} \rangle_\Psi \quad \forall \Psi \quad (2.8)$$

← This is a definition

By definition:

$$\begin{aligned} \frac{d}{dt} \langle \hat{f} \rangle_{\psi} &= \frac{d}{dt} \int \psi^*(q, t) \hat{f}(t) \psi(q, t) dq \\ &= \int \frac{\partial \psi^*}{\partial t} (\hat{f} \psi) dq + \int \psi^* \left(\hat{f} \frac{\partial \psi}{\partial t} \right) dq + \int \psi^* \left(\frac{\partial \hat{f}}{\partial t} \psi \right) dq \end{aligned}$$

but $\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar} \hat{H} \psi \Rightarrow$

$$\begin{aligned} \Rightarrow \frac{d}{dt} \langle \hat{f} \rangle_{\psi} &= \frac{1}{i\hbar} \int (\hat{H}^* \psi^*) (\hat{f} \psi) dq \\ &\quad + \frac{1}{i\hbar} \int \psi^* (\hat{f} \hat{H} \psi) dq + \int \psi^* \frac{\partial \hat{f}}{\partial t} \psi dq \\ &= -\frac{1}{i\hbar} \int \left[\psi^* (\hat{H}^* \hat{f} \psi) - (\hat{f} \hat{H} \psi) \right] dq + \int \psi^* \frac{\partial \hat{f}}{\partial t} \psi dq \\ &= \int \psi^* \left\{ \frac{1}{i\hbar} [\hat{f}, \hat{H}] + \frac{\partial \hat{f}}{\partial t} \right\} \psi dq \quad (1.9) \end{aligned}$$

On the other hand, by definition:

$$\langle \dot{\hat{f}} \rangle_{\psi} = \int \psi^* \frac{d\hat{f}}{dt} \psi dq \quad (2.9)$$

Imposing (1.9) = (2.9) we find: (to be valid $\forall \psi$)

$$\boxed{\frac{d\hat{f}}{dt} = \frac{1}{i\hbar} [\hat{f}, \hat{H}] + \frac{\partial \hat{f}}{\partial t}} \quad (3.9)$$

The last term

(8-10)

$$\frac{\partial \hat{f}}{\partial t}$$

is non-zero only if \hat{f} has an explicit time-dependence. If this is not the case, as in the case of conserved observables, we have:

$$\frac{d\hat{f}}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{f}] = 0 \Rightarrow [\hat{H}, \hat{f}] = 0 \quad \underline{\underline{\text{c.v.d}}}$$

If $\frac{\partial \hat{f}}{\partial t} = 0$, then its mean value with respect to the energy eigenfunctions ψ_n is time independent because:

$$\frac{d}{dt} \int \psi_n^*(q, t) \hat{f} \psi_n(q, t) dq$$
$$= \frac{d}{dt} \int \psi_n^*(q) e^{\frac{i}{\hbar} E_n t} \hat{f} \psi_n(q) e^{\frac{i}{\hbar} E_n t} dq$$

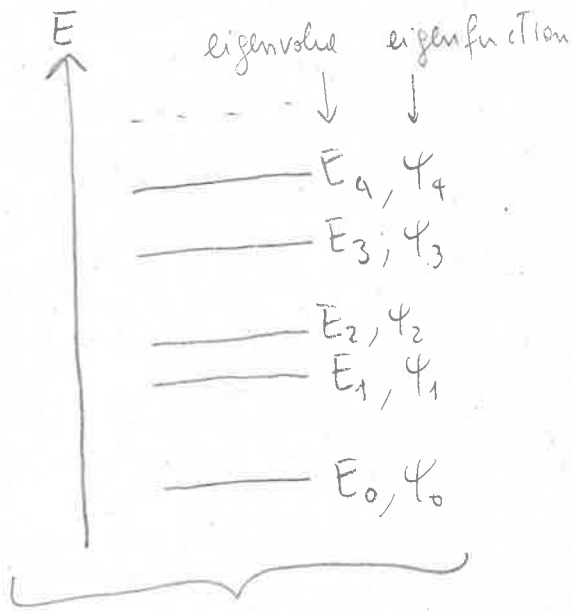
↑
Their product = 1

$$= \frac{d}{dt} \int \psi_n^*(q) \hat{f} \psi_n(q) dq = 0$$

Torgon:

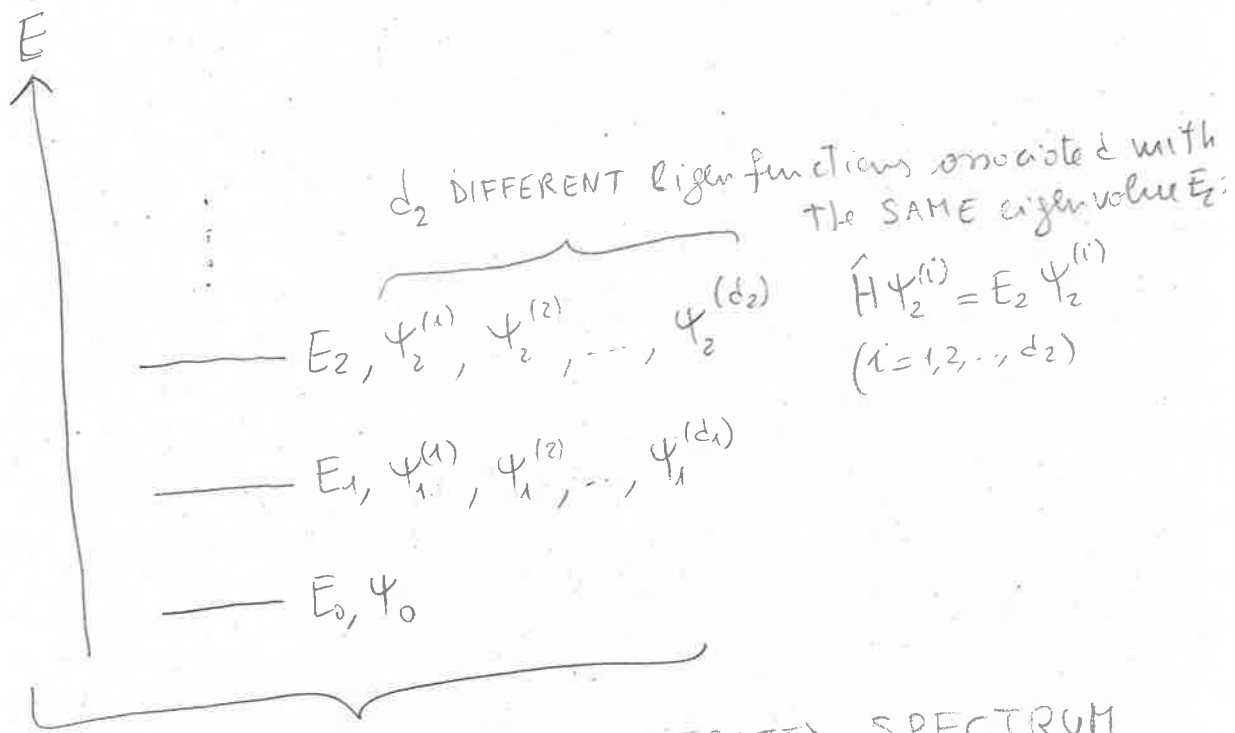
SPECTRUM of \hat{H} = set of all eigenvalues of \hat{H}

A typical DISCRETE spectrum looks like:



SIMPLE (OR NON DEGENERATE) SPECTRUM

In the case of degenerate eigenvalues we have:



NON-SIMPLE (OR DEGENERATE) SPECTRUM

When does a degenerate spectrum occur? (8-12)

When there are two (or more) CONSERVED observables, say f and g , that are INCOMPATIBLE (that is, their associated Hermitian operators \hat{f} and \hat{g} do not commute: $[\hat{f}, \hat{g}] \neq 0$, as, e.g., $[\hat{x}, \hat{p}] = i\hbar$), but commute with \hat{H} (because, by hypothesis, they are conserved):

$$\hat{f}, \hat{g}: [\hat{f}, \hat{g}] \neq 0 \quad \text{and} \quad [\hat{f}, \hat{H}] = 0 = [\hat{g}, \hat{H}]$$

Let $\hat{g}u_n = g_n u_n$ and $\hat{f}v_m = f_m v_m$ and $\hat{H}\psi = E\psi$

Choose ψ such that $\hat{f}\psi = f\psi$, so f has a determined value. I can do because $[\hat{H}, \hat{f}] = 0$.

$$\hat{H}(\hat{f}\psi) = \hat{f}(\hat{H}\psi) = E(\hat{f}\psi)$$

So $\hat{f}\psi$ is an ^{synonymous of eigenfunction} eigenstate of \hat{H} with eigenvalue E

However, also $\hat{H}(\hat{g}\psi) = \hat{g}(\hat{H}\psi) = E(\hat{g}\psi)$ is an eigenstate of \hat{H} associated with the SAME eigenvalue E .

So, if $\hat{f}\psi \neq \lambda \hat{g}\psi$, then \hat{H} has at least 2 eigenstates,
 \uparrow
 c-number

ψ and $\hat{g}\psi$ ($\hat{f}\psi = f_n\psi \in \psi$ by hypothesis) associated with the same eigenvalue E .

However, if it were

$$\hat{f}\psi = \lambda \hat{g}\psi \quad \text{and} \quad \hat{f}\psi = f\psi$$

Then we would have $f\psi = \lambda(\hat{g}\psi) \Leftrightarrow$

$$\Leftrightarrow \hat{g}\psi = \left(\frac{f}{\lambda}\right)\psi \equiv g\psi$$

So ψ would also be eigenstate of \hat{g} . But this cannot be true in general because $[\hat{f}, \hat{g}] \neq 0$.

Note: There can exist common eigenstates of non commuting operators. These eigenstates span a subspace where $[\hat{f}, \hat{g}] = 0$. In this subspace you can measure simultaneously \hat{f} and \hat{g} with a determined value.

Example let $F = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix}$; $G = \begin{bmatrix} 0 & x & 0 \\ x & 0 & 0 \\ 0 & 0 & y \end{bmatrix}$

Then $[F, G] = \begin{bmatrix} 0 & (a-b)x & 0 \\ -(a-b)x & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \neq 0$ eigenvalues = (-x, x, y)

$\hookrightarrow [F, G] = 0$ in this 1-dimensional subspace.

The eigenvectors of F or G are, respectively,

$$\underline{v}_n = \left\{ \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \right\}; \quad \underline{u}_n = \left\{ \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \right\} \quad \text{so} \quad \underline{v}_3 = \underline{u}_3$$

So, if \hat{f} and \hat{g} have some non-common eigenstates (and it must be so because $[\hat{f}, \hat{g}] \neq 0$) then \hat{H} has degenerate eigenvalues.

Let $\{\psi_n^{(1)}, \psi_n^{(2)}, \dots, \psi_n^{(d_n)}\}$ a set of d_n eigenfunctions associated with the same eigenvalue E_n . Then,

ANY linear combination

$$\psi = \sum_{i=1}^{d_n} c_i \psi_n^{(i)}$$

is associated with E_n because

$$\hat{H}\psi = \sum_i c_i \hat{H}\psi_n^{(i)} = E_n \sum_i c_i \psi_n^{(i)}$$

So, I can always choose d_n linear combinations

$$\phi_{ni} = \sum_{j=1}^{d_n} c_{ij} \psi_n^{(j)} \quad (i=1, 2, \dots, d_n)$$

such that:

$$\int \phi_{ni}^* \phi_{nj} dq = \delta_{ij}$$

HOMEWORK - Prove that there are infinitely many different sets $\{\phi_{n1}, \phi_{n2}, \dots, \phi_{nd_n}\}$ of orthogonal wavefunctions associated to E_n by showing that $C > D$, where

C = number of independent coefficients of the linear transformation generating the set $\{\phi_{n1}, \dots, \phi_{nd_n}\}$ from the set $\{\psi_n^{(1)}, \dots, \psi_n^{(d_n)}\}$

D = number of conditions of normalization and orthogonality satisfied by the set $\{\phi_{n1}, \dots, \phi_{nd_n}\}$

- Matrices and unitary operators -

Let $\hat{H}\psi_n = E_n \psi_n$ and ψ arbitraryThen $\psi(t) = \sum_n a_n(t) \psi_n$. Let f be an observable.

$$\langle \hat{f} \rangle_\psi \stackrel{\text{def.}}{=} \int \psi^* (\hat{f} \psi) d\varrho$$

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

$$\omega_n \equiv \frac{E_n}{\hbar}$$

$$= \int \left(\sum_n a_n \psi_n \right)^* \hat{f} \left(\sum_m a_m \psi_m \right) d\varrho$$

$$= \sum_{n,m} a_n^* a_m \int \psi_n^* (\hat{f} \psi_m) d\varrho$$

$$\equiv f_{nm} \leftarrow \text{matrix element}$$

$$= \sum_{n,m} a_n^*(t) f_{nm} a_m(t)$$

$$= \sum_{n,m} a_n^*(0) f_{nm} a_m(0) e^{i\omega_{nm} t}$$

$$\omega_{nm} \equiv \frac{E_n - E_m}{\hbar}$$

$$\equiv \text{Transition frequency between level } n \text{ and } m$$
By definition, the operator \hat{f} is such that:

$$\langle \hat{f} \rangle_\psi = \frac{d}{dt} \langle \hat{f} \rangle_\psi$$

$$= \frac{d}{dt} \sum_{n,m} a_n^*(0) f_{nm} a_m(0) e^{i\omega_{nm} t}$$

$$= i \sum_{n,m} \omega_{nm} a_n^*(0) f_{nm} a_m(0) e^{i\omega_{nm} t}$$

However, by def:

$$\langle \hat{f} \rangle_{\psi} = \sum_n a_n^*(0) \dot{f}_{nm} a_m(0) e^{i\omega_{nm}t} \Rightarrow$$

$$\Rightarrow \boxed{\dot{f}_{nm} = i\omega_{nm} f_{nm}}$$

It is easy to see that for a generic operator \hat{f} :

$$(\hat{f}^\dagger)_{nm} = (f_{mn})^*$$

because

$$\begin{aligned} (\hat{f}^\dagger)_{nm} &\equiv \int \psi_n^* (\hat{f}^\dagger \psi_m) dq \\ &= \int \psi_m (\hat{f}^* \psi_n^*) dq = \left(\int \psi_m^* (\hat{f} \psi_n) dq \right)^* \\ &= (f_{mn})^* \end{aligned}$$

The Schrödinger equation

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi} \quad (1.9)$$

can also be written in matrix form

$$\text{Let } \hat{f}: \hat{f} \phi_n = f_n \phi_n \Rightarrow \psi(q, t) = \sum_n a_n(t) \phi_n(q)$$

Multiply 1.9 by $\phi_n^*(q)$ and integrate.

$$\begin{aligned} i\hbar \underbrace{\frac{d}{dt} \int \phi_n^*(q) \psi dq}_{= a_n(t) \text{ by def}} &= \underbrace{\int \phi_n^*(q) \hat{H} \psi dq}_{= \int \phi_n^* \hat{H} (\sum_m a_m(t) \phi_m) dq} \\ &= \sum_m a_m(t) H_{nm} \quad ; \quad H_{nm} \equiv \int \phi_n^* \hat{H} \phi_m dq \end{aligned}$$

Therefore we get:

$$\boxed{i\hbar \frac{d}{dt} a_n(t) = \sum_m H_{nm} a_m(t)} \quad (1.3)$$

If \hat{H} does not depend on t (isolated system) this is a first-order differential linear system w/o solution is trivial for finite dimension N :

let $H = [H_{nm}]$ a $N \times N$

and U a unitary matrix such that: (U is time-indep.)

$$U H U^\dagger = D = \text{diag}(E_1, E_2, \dots, E_N)$$

If $|a\rangle = (a_1, a_2, \dots, a_N)$ we rewrite (1.3) as:

$i\hbar \frac{d}{dt} |a\rangle = H |a\rangle$ multiply from left by U :

$$\begin{aligned} i\hbar \frac{d}{dt} (U|a\rangle) &= U H |a\rangle \quad \text{identity matrix} \\ &= U H I |a\rangle \\ &= (U H U^\dagger) U |a\rangle \end{aligned}$$

$$\text{Let } |b\rangle \equiv U |a\rangle \Rightarrow$$

$$\Rightarrow \boxed{i\hbar \frac{d}{dt} |b\rangle = D |b\rangle} \Leftrightarrow i\hbar \frac{d}{dt} b_n = \lambda_n b_n \Rightarrow b_n(t) = b_n(0) e^{-\frac{i}{\hbar} \lambda_n t}$$

Or, equivalently:

$$|b(t)\rangle = e^{-iDt/\hbar} |b(0)\rangle$$

but $|a(t)\rangle = U^\dagger |b(t)\rangle \Rightarrow$

$$\Rightarrow \underbrace{U^\dagger |b(t)\rangle}_{= |a(t)\rangle} = \underbrace{\left(U^\dagger e^{-iDt/\hbar} U \right)}_{= \exp(-iHt/\hbar)} \underbrace{U^\dagger |b(0)\rangle}_{\equiv |a_0\rangle}$$

because $U^\dagger e^{-iDt/\hbar} U = U^\dagger \sum_k \left(\frac{-it}{\hbar} \right)^k \frac{D^k}{k!} U$

$$= \sum_k \left(\frac{-it}{\hbar} \right)^k \frac{(U^\dagger D U)^k}{k!} = e^{-iHt/\hbar}$$

Therefore:

$|a(t)\rangle = \exp\left(-iHt/\hbar\right) |a_0\rangle$

There are some systems for which it is not important to know the spatial dependence of the state,