4.3 The Schrödinger equation

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

① How to get $\hat{H}$:

Start from classical Hamilton function $H(\vec{x}_i, \vec{p}_j) = T(\vec{p}_j) + V(\vec{x}_i)$ ← usually
$(i, j = 1, \ldots, N$ for N particles$)$

Replace $x \mapsto \hat{X}$, $p \mapsto \hat{P}$

Examples:

(i) Harmonic oscillator in 1d:

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

$$\mapsto \hat{H} = \frac{\hat{P}^2}{2m} + \frac{m}{2}\omega^2 \hat{X}^2$$

In 3d:

$$\hat{H} = \frac{\hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2}{2m} + \frac{m}{2}\omega^2 \left(\hat{X}^2 + \hat{Y}^2 + \hat{Z}^2\right)$$

(ii) Particle subject to a constant force f:

$$H(x,p) = \frac{p^2}{2m} - f x \qquad \mapsto \hat{H} = \frac{\hat{P}^2}{2m} - f\hat{X}$$

(iii) Charged particle in an electromagnetic field in 3d:

$$H(\vec{r}, \vec{p}) = \frac{\left(\vec{p} - \frac{q}{c}\vec{A}(\vec{r}, t)\right)^2}{2m} + q\phi(\vec{r}, t)$$

$$\mapsto \hat{H} = \frac{1}{2m}\Big[\hat{\vec{P}}\cdot\hat{\vec{P}} - \frac{q}{c}\hat{\vec{P}}\cdot\hat{\vec{A}}(\hat{X},\hat{Y},\hat{Z},t) - \frac{q}{c}\hat{\vec{A}}(\hat{X},\hat{Y},\hat{Z},t)\cdot\hat{\vec{P}}$$
$$+ \frac{q^2}{c^2}\hat{\vec{A}}(\ldots)\cdot\hat{\vec{A}}(\ldots)\Big] + q\phi(\hat{X},\hat{Y},\hat{Z};t)$$

Symmetrize PA terms since $[\hat{P}_i, \hat{A}_j] \neq 0$ $(\hat{\vec{A}}$ depends on $\hat{X}, \hat{Y}, \hat{Z})$

② General approach to the solution:

Let's first assume that $H(\vec{x},\vec{p})$ has no explicit time dependence.

Then solve $i\hbar|\dot{\psi}\rangle = \hat{H}|\psi\rangle$

by first solving the eigenvalue problem for $\hat{H}$:

$$\hat{H}|E\rangle = E|E\rangle$$

The we expand

$$|\psi(t)\rangle = \sum\!\!\!\!\!\!\int_E |E\rangle\underbrace{\langle E|\psi(t)\rangle}_{a_E(t)} \equiv \sum\!\!\!\!\!\!\int_E a_E(t)|E\rangle$$

Insert into S-Eq:

$$\sum\!\!\!\!\!\!\int_E i\hbar\frac{da_E(t)}{dt}|E\rangle = \sum\!\!\!\!\!\!\int_E a_E(t)\,E\,|E\rangle$$

Project on $\langle E'|$ and use $\langle E|E'\rangle = \delta(E,E')$ (Kronecker δ for discrete E, Dirac-δ for continuous E)

Use $\delta(E,E')$ to kill $\sum\!\!\!\!\!\!\int_E$:

$$i\hbar\,\dot{a}_E(t) = E\,a_E(t) \Rightarrow \boxed{a_E(t) = a_E(0)e^{-iEt/\hbar}}$$

$$\left(a_E(0) = \langle E|\psi(0)\rangle\right)$$

$$\Rightarrow |\psi(t)\rangle = \sum\!\!\!\!\!\!\int_E a_E(t)|E\rangle = \sum\!\!\!\!\!\!\int_E |E\rangle\langle E|\psi(0)\rangle e^{-iEt/\hbar}$$

or
$$\boxed{\begin{gathered}|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle \\ \text{with } \hat{U}(t) = \sum\!\!\!\!\!\!\int_E |E\rangle\langle E|e^{-iEt/\hbar}\end{gathered}}$$

If the eigenstates E are degenerate:

$$\boxed{\hat{U}(t) = \sum\!\!\!\!\!\!\int_E e^{-iEt/\hbar}\sum_{\alpha=1}^{d_E}|E,\alpha\rangle\langle E,\alpha|}$$

(d_E = degeneracy of eigenvalue E)

The normal modes $|E(t)\rangle \equiv |E\rangle e^{-iEt/\hbar}$

are called stationary states: For any time-independent observable $\hat{\Omega}$, the probability distribution $P(\omega)$ is time-independent in such states:

$$P(\omega,t) = |\langle\omega|E(t)\rangle|^2 = |\langle\omega|E\rangle e^{-iEt/\hbar}|^2 = |\langle\omega|E\rangle|^2$$
$$= P(\omega, t=0)$$

We can also write $\boxed{\hat{\mathcal{U}}(t) = e^{-i\hat{H}t/\hbar}}$ (if $\hat{H}$ does not depend on time explicitly:

$$e^{-i\hat{H}t/\hbar} = e^{-i\hat{H}t/\hbar} \sum\!\!\!\!\!\!\int_E |E\rangle\langle E|$$
$$= \sum\!\!\!\!\!\!\int_E \left(e^{-i\hat{H}t/\hbar}|E\rangle\right)\langle E| = \sum\!\!\!\!\!\!\int_E \left(\sum_{n=0}^{\infty} \frac{(-i\hat{H}t/\hbar)^n}{n!}|E\rangle\right)\langle E|$$
$$= \sum\!\!\!\!\!\!\int_E \left(\underbrace{\sum_{n=0}^{\infty} \frac{(-iEt/\hbar)^n}{n!}}_{e^{-iEt/\hbar}}|E\rangle\right)\langle E| = \sum\!\!\!\!\!\!\int_E |E\rangle\langle E| e^{-iEt/\hbar} \checkmark$$

This expression is very useful. Since $\hat{H} = \hat{H}^+$, $\hat{\mathcal{U}}^+(t) = \hat{\mathcal{U}}^{-1}(t)$ is unitary $\rightarrow$ "unitary time evolution"

$\Rightarrow$ Time evolution of $|\psi(t)\rangle$ = rotation of $|\psi\rangle$ in Hilbert space.

such that $\langle\psi(t)|\psi(t)\rangle = \langle\psi(0)|\hat{\mathcal{U}}^+(t)\hat{\mathcal{U}}(t)|\psi(0)\rangle$
$= \langle\psi(0)|\psi(0)\rangle$ is time-independent.

If instead of the fixed basis $|E\rangle$ with use rotating basis vectors $|E(t)\rangle = \hat{\mathcal{U}}(t)|E\rangle = e^{-iEt/\hbar}|E\rangle$, then

$$|\psi(t)\rangle = \sum\!\!\!\!\!\!\int_E a_E(0)\, e^{-iEt/\hbar}|E\rangle = \sum\!\!\!\!\!\!\int_E a_E(0)|E(t)\rangle$$

has time independent components, i.e. it appears frozen

Instead, the operators $\hat{\Omega}$ would now become time dependent:

$$\langle\varphi(t)|\hat{\Omega}|\psi(t)\rangle = \langle\varphi(0)|\hat{\mathcal{U}}^{+}(t)\,\hat{\Omega}\,\hat{\mathcal{U}}(t)|\psi(0)\rangle$$

$$= \langle\varphi(0)|\hat{\Omega}(t)|\psi(0)\rangle$$

Instead of the Schrödinger eq. of motion for $|\psi(t)\rangle$ this view results in a <u>Heisenberg equation of motion</u> for $\hat{\Omega}(t)$ $\longrightarrow$ "Heisenberg picture"

The view where $|\psi(t)\rangle$ obeys the S-Eq. is called "Schrödinger picture"

Other pictures are possible, too, and in some cases useful – see chapter 18.

What if $\hat{H} = \hat{H}(t)$ depends explicitly on t?

Let's look at the evolution $|\psi(t)\rangle = \hat{\mathcal{U}}(t)|\psi(0)\rangle$ over time t, by dividing t into N $(N\to\infty)$ pieces of length $\Delta = \frac{t}{N}$ $(\Delta\to 0)$.

$$\Rightarrow \quad |\psi(\Delta)\rangle = |\psi(0)\rangle + \Delta \left.\frac{d|\psi\rangle}{dt}\right|_{t=0} + O(\Delta^2)$$

As $N\to\infty$, $\Delta\to 0$, we can ignore the terms of $O(\Delta^2)$.

$$= |\psi(0)\rangle - \frac{i}{\hbar}\Delta\hat{H}(0)|\psi(0)\rangle$$

$$= \left(1 - \frac{i}{\hbar}\hat{H}(0)\Delta\right)|\psi(0)\rangle \approx e^{-i\hat{H}(0)\Delta/\hbar}|\psi(0)\rangle$$

where the last approximation is again accurate to $O(\Delta)$ and becomes exact in the limit $\Delta\to 0$.

Also, if we replace $\hat{H}(0)$ by $\hat{H}(\Delta)$ or $\hat{H}(\frac{\Delta}{2})$, the difference is of order Δ, so in $(1 - \frac{i\Delta}{2}\hat{H})$ the difference is only of order Δ^2 and thus negligible.

Repeating this procedure to get from time Δ to time 2Δ etc. we get

$$\boxed{|\psi(t) = \prod_{n=0}^{N-1} e^{-i\Delta \hat{H}(n\Delta)/\hbar} |\psi(0)\rangle}$$

$$\neq e^{-\frac{i}{\hbar}\Delta \sum_{n=0}^{N-1} \hat{H}(n\Delta)} |\psi(0)\rangle$$

$$\left(\underset{N\to\infty}{\overset{\Delta\to 0}{\longrightarrow}} e^{-i/\hbar \int_0^t dt' \hat{H}(t')} |\psi(0)\rangle \right)$$

The step labelled by $\neq$ is not allowed since $[\hat{H}(t_1), \hat{H}(t_2)] \neq 0$ in general. The correct result is the box. One denotes its limit as $N\to\infty$, $\Delta\to 0$ by the so-called time-ordered integral

$$\boxed{\hat{T} e^{-i/\hbar \int_0^t dt' \hat{H}(t')} \equiv \lim_{N\to\infty} \prod_{n=0}^{\infty} e^{-\frac{i}{\hbar}\hat{H}(\frac{n}{N}t)\frac{t}{N}}} \equiv \hat{\mathcal{U}}(t,0)$$

On the r.h.s. the factors are ordered by time argument of $\hat{H}$.

Note that, as a product of unitary operators, $\hat{\mathcal{U}}(t)$ is still unitary. It satisfies

$$\hat{\mathcal{U}}(t_3,t_2)\hat{\mathcal{U}}(t_2,t_1) = \hat{\mathcal{U}}(t_3,t_1)$$

$$\hat{\mathcal{U}}^{+}(t_2,t_1) = \hat{\mathcal{U}}^{-1}(t_2,t_1) = \hat{\mathcal{U}}(t_1,t_2)$$