Time evolution of a quantum system

$t=0$ $\quad |\psi(t=0)\rangle \xrightarrow[\text{time-evolution operator}]{\hat{U}(t)} |\psi(t)\rangle = \hat{U}(t)\,|\psi(t=0)\rangle$

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar}$$

where $\hat{H}$ is Hamiltonian, the energy operator

Shrodinger equation: $\boxed{i\hbar \frac{\partial}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle}$

$\hat{H} = \hat{H}^{+}$ — Hermitian operator

~~eigen-values~~ — ~~energy~~ ~~state~~

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}\,|\psi(0)\rangle$$

Time evolution is the easiest to predict for eigenstates of $\hat{H}$

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

here $|E\rangle$ is an eigenstate corresponding to the energy eigenvalue E

When we talk about "energy levels" of an atom or ~~the~~ molecule or any other quantum system, that is what we usually mean.

That is also what a lot of people calculate for, for example, complex molecules to figure out there structure.

$|E\rangle$ are often referred to as "stationary" states, since their time evolution is trivial (a time-dependent phase factor)

Indeed, if $|\psi(t=0)\rangle = |E\rangle$

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(t=0)\rangle = \left(\hat{\mathbb{1}} + \left(-\frac{it}{\hbar}\right)\hat{H} + \frac{1}{2!}\left(-\frac{it}{\hbar}\right)^2\hat{H}^2 + \ldots\right)|E\rangle$$

$$= \left(1 + \left(-\frac{itE}{\hbar}\right) + \frac{1}{2!}\left(-\frac{itE}{\hbar}\right)^2 + \ldots\right)|E\rangle = e^{-itE/\hbar}|E\rangle$$

Thus, the ~~those~~ expectation value of any operator in such a stationary state does not change in time

$$\langle\hat{A}(t)\rangle = \langle\psi(t)|\hat{A}|\psi(t)\rangle = \cancel{e^{itE/\hbar}}\langle E|\hat{A}|E\rangle\cancel{e^{-itE/\hbar}} =$$

$$= \langle E|\hat{A}|E\rangle = \langle\hat{A}(t=0)\rangle$$

It is not the case in general, even if an operator does not have an explicite time dependence.

Indeed, for any state the shrodinger equation predicts:

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

and for the bra vector

$$-i\hbar\frac{d}{dt}\langle\psi(t)| = \langle\psi(t)|\hat{H}^+ = \langle\psi(t)|\hat{H} \qquad (\hat{H} = \hat{H}^+)$$

Thus $\frac{d}{dt}\langle\hat{A}(t)\rangle = \frac{d}{dt}\langle\psi(t)|\hat{A}|\psi(t)\rangle =$

$$= \left(\frac{d}{dt}\langle\psi(t)|\right)\hat{A}|\psi(t)\rangle + \langle\psi(t)|\frac{d\hat{A}}{dt}|\psi(t)\rangle + \langle\psi(t)|\hat{A}\left(\frac{d}{dt}|\psi\rangle\right)$$

If $\hat{A} \neq \hat{A}(t)$, this term disappears

$$\frac{d}{dt}\langle \hat{A}(t)\rangle = \left(\frac{d}{dt}\langle\psi(t)|\right)\hat{A}|\psi(t)\rangle + \langle\psi(t)|\hat{A}\left(\frac{d}{dt}|\psi(t)\rangle\right) =$$

$$= -\frac{1}{i\hbar}\langle\psi(t)|\hat{H}\hat{A}|\psi(t)\rangle + \frac{1}{i\hbar}\langle\psi(t)|\hat{A}\hat{H}|\psi(t)\rangle =$$

$$= \frac{i}{\hbar}\langle\psi(t)|\hat{H}\hat{A}-\hat{A}\hat{H}|\psi(t)\rangle = \frac{i}{\hbar}\langle\psi(t)|[\hat{H},\hat{A}]|\psi(t)\rangle$$

So if $\hat{A}$ and $\hat{H}$ commute, the expectation values of $\hat{A}$ will be constant in time for any state — constants of motion

Two-level system (with two energy levels)

E_2

E_1

$$\hat{H}|1\rangle = E_1|1\rangle$$
$$\hat{H}|2\rangle = E_2|2\rangle$$

If $|\psi(t=0)\rangle = |1\rangle \longrightarrow |\psi(t)\rangle = e^{-iE_1t/\hbar}|1\rangle$

$|\psi(t=0)\rangle = |2\rangle \longrightarrow |\psi(t)\rangle = e^{-iE_2t/\hbar}|2\rangle$

If $|\psi(t=0)\rangle = \frac{1}{\sqrt{2}}(|1\rangle+|2\rangle)$ then

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(e^{-iE_1t/\hbar}|1\rangle + e^{-iE_2t/\hbar}|2\rangle\right)$$

What is the probability to find the system in the same state $\frac{1}{\sqrt{2}}(|1\rangle+|2\rangle)$ as time goes by?

$$P_{1+2} = \left|\langle \text{target state} | \text{system state}\rangle\right|^2 =$$

$$= \frac{1}{4}\left|\left(\langle 1| + \langle 2|\right)\left(e^{-iE_1t/\hbar}|1\rangle + e^{-iE_2t/\hbar}|2\rangle\right)\right|^2 =$$

$$= \frac{1}{4}\left|e^{-iE_1t/\hbar} + e^{-iE_2t/\hbar}\right|^2 = \frac{1}{4}\overbrace{\left|e^{\frac{-i(E_2+E_1)t}{2\hbar}}\right|^2}^{=1} \times$$

$$\times\left|\underbrace{e^{-i(E_2-E_1)t/2\hbar}}_{e^{-i\varphi}} + \underbrace{e^{i(E_2-E_1)t/2\hbar}}_{e^{i\varphi}}\right|^2$$

$$= \left| \frac{e^{i(E_2-E_1)t/2\hbar} + e^{-i(E_2-E_1)t/2\hbar}}{2} \right|^2 = \cos^2\left(\frac{(E_2-E_1)t}{2\hbar}\right)$$

Going through similar steps, we can find the probability of finding system in state $\frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$

$$P_{1-2} = \frac{1}{4}\left|(\langle 1| - \langle 2|)(e^{-iE_1t/\hbar}|1\rangle + e^{-iE_2t/\hbar}|2\rangle)\right|^2 =$$

$$= \frac{1}{4}\left| e^{-iE_1t/\hbar} - e^{-iE_2t/\hbar}\right|^2 = \sin^2\left(\frac{(E_2-E_1)t}{2\hbar}\right)$$

At the same time $P_{1,2}$ (the probability of finding the system in a state $|1\rangle$ or $|2\rangle$ stays the same

$$P_{1,2} = \left|\frac{1}{\sqrt{2}}\langle 1,2|(e^{-iE_1t/\hbar}|1\rangle + e^{-iE_2t/\hbar}|2\rangle)\right|^2 =$$

$$= \frac{1}{2}\left| e^{-iE_{1,2}t/\hbar}\right|^2 = \frac{1}{2}$$

We can say that the populations of the levels 1 and 2 stay constant, while the system ~~evolves~~ evolves from $\frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$ to $\frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$ in time with frequency $\omega = \frac{E_2 - E_1}{2\hbar}$