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- We have built up most of the formalism we need to analyze QM systems. To now, we have focused mostly on spin 1/2 systems and spin eigenstates. This is because spin has no classical analog and spin 1/2 helps introduce QM formalism in a way that is analytically tractable.
- As we shift to study a wider variety of phenomenon, we will find that the energetics of the system are truly important. This becomes obvious as soon as we try to study the dynamics of a QM system. (i.e. how the system evolves in time). The dynamics of a QM system is governed by the Schrödinger Equation (postulate 6)

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

where $H(t)$ is the energy operator (Hamiltonian)

Energy Eigenstates

The Hamiltonian is an observable.

So, It is a square, Hermitian matrix

remember? ⟹ that has real eigenvalues.

It's eigenvalues are the energy of the various energy eigenstates.

We can setup the usual eigenvalue problem where E_n is the eigenvalue & $|E_n\rangle$ is the eigenstate.

$$\boxed{H|E_n\rangle = E_n|E_n\rangle}$$

Some call this the time ind. Schrödinger eqn. It does not describe the dynamics so we will call it the "energy eigenvalue eqn."

Because H is a Hermitian operator the energy eigenstates form a complete, orthonormal basis,

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$$|\psi(t)\rangle = \sum_n c_n(t)\,|E_n\rangle \Leftarrow \text{complete}$$

$$\langle E_m | E_n \rangle = \delta_{nm} \Leftarrow \text{orthonormal}$$

Time Evolution for Time Independent Hamiltonian

As we want to study the dynamics, $|\psi(t)\rangle$, we can actually generate a general solution for any nondegenerate, time independent Hamiltonian.

We will come to this later, but it means each eigenstate has a unique energy. (Not all QM systems have this property!)

Let's start with

$$|\psi(t)\rangle = \sum_n c_n(t)\,|E_n\rangle$$

and pop it into the S.E.

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

So we get,

$$i\hbar \frac{d}{dt}\left(\sum_n c_n(t)\,|E_n\rangle\right) = H \sum_n c_n(t)\,|E_n\rangle$$

$$i\hbar \sum_n \frac{dc_n(t)}{dt}|E_n\rangle = \sum_n c_n(t)\,E_n|E_n\rangle$$

this is as far as we can go and this is (in principle) a sum over many states.

we can make use of the orthonormality condition $\langle E_m|E_n\rangle = \delta_{mn}$

$$\langle E_m|\, i\hbar \sum_n \frac{dc_n(t)}{dt}|E_n\rangle = \langle E_m|\sum_n c_n(t) E_n\,|E_n\rangle$$

$$i\hbar \sum_n \frac{dc_n(t)}{dt}\underbrace{\langle E_m|E_n\rangle}_{\delta_{mn}} = \sum_n c_n(t)\,E_n\underbrace{\langle E_m|E_n\rangle}_{\delta_{mn}}$$

these collapse the sum to a single term. where $n=m$.

$$i\hbar \frac{dc_m(t)}{dt} = c_m(t)\,E_m$$

or

$$\boxed{\frac{dc_m(t)}{dt} = -i\frac{E_m}{\hbar}\,c_m(t)}$$

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The power in this expression is that it holds for all nondegenerate, time ind. Hamiltonians!

We solved Differential Equations like this before.

$$C_m(t) = C_m(t=0)\, \underbrace{e^{-i\frac{E_m}{\hbar}t}}_{\text{oscillatory solutions!}}$$

$$e^{i\omega t} = \cos(\omega t) + i\sin(\omega t)$$

So in general,

$$\boxed{|\psi(t)\rangle = \sum_n c_n e^{-i\frac{E_n t}{\hbar}} |E_n\rangle}$$

* if you know your energy eigenstates were generated from a time independent, nondeg. Hamiltonian, then you know how any state vector will evolve in time.

Stationary States

Let's assume a QM system starts of in a particular energy eigenstate.

$$|\psi(t=0)\rangle = |E_0\rangle$$

after a time t, the state vector will evolve,

$$|\psi(t)\rangle = c_0 e^{-iE_0t/\hbar} |E_0\rangle$$

Note: $c_0 = 1$ for this ket to be normalized for all time,

$$\langle\psi(t)|\psi(t)\rangle = \langle E_0| c_0^* \underbrace{e^{+iE_0t/\hbar} \quad c_0 e^{-iE_0t/\hbar}}_{1} |E_0\rangle$$

$$= c_0^* c_0 \langle E_0|E_0\rangle = 1 \qquad |c_0|^2 = 1 \qquad c_0 = 1$$

$$|\psi(t)\rangle = e^{-\frac{iE_0t}{\hbar}} |E_0\rangle \Leftarrow$$ so this state changes its overall phase.

That does not affect measurements!

The observable A has an eigenvalue

a_j and eigenstate $|a_j\rangle$.

The probability of measuring $|\psi(t)\rangle$ in $|a_j\rangle$ is time independent!

$$P_{a_j} = |\langle a_j|\psi(t)\rangle|^2$$

$$= |\langle a_j| e^{-iE_0t/\hbar} |E_0\rangle|^2$$

$$= \langle a_j| e^{-iE_0t/\hbar} |E_0\rangle \langle E_0| e^{+iE_0t/\hbar} |a_j\rangle$$

$$= \underbrace{e^{-iE_0t/\hbar} \, e^{+iE_0t/\hbar}}_{1} \langle a_j|E_0\rangle\langle E_0|a_j\rangle$$

$$P_{a_j} = |\langle a_j|E_0\rangle|^2$$

This is energy eigenstates are stationary states

Because energy eigenstates are stationary states the probability to measure a given energy is time independent.

Consider

$$|\psi(0)\rangle = c_0|E_0\rangle + c_1|E_1\rangle$$

$$|\psi(t)\rangle = c_0 e^{-iE_0t/\hbar}|E_0\rangle + c_1 e^{-iE_1t/\hbar}|E_1\rangle$$ 8

$$P_{E_0} = |\langle E_0|\psi(t)\rangle|^2$$

$$P_{E_0} = \Big|\langle E_0|c_0 e^{-iE_0t/\hbar}|E_0\rangle + \underbrace{\langle E_0|c_1 e^{-iE_1t/\hbar}|E_1\rangle}_{\text{orthogonal, }\underline{\underline{0}}}\Big|^2$$

$$P_{E_0} = |\langle E_0|c_0 e^{-iE_0t/\hbar}|E_0\rangle|^2$$

$$P_{E_0} = c_0^2 \qquad \text{Same for } P_{E_1} = c_1^2$$

This result holds for any operator that commutes with H. B/c energy eigenstates would be eigenstates of that operator.

if $[H,\hat{O}] = 0$ then

$P_{\hat{O}_0}$ is time independent b/c $|E_0\rangle$ is an eigenstate of $\hat{O}$.

If the operator doesn't commute $[H,A] \neq 0$ then eigenstates of A are superpositions of the energy eigenstates, $|E_n\rangle$.

Assume $|a_0\rangle$ is an eigenstate of A w/ 9
eigenvalue a_0.

$$|a_0\rangle = \alpha_0|E_0\rangle + \alpha_1|E_1\rangle$$

The probability of measuring a_0 for the state, $|\psi(t)\rangle = c_0 e^{-iE_0t/\hbar}|E_0\rangle + c_1 e^{-iE_1t/\hbar}|E_1\rangle$

is,

$$P_{a_0} = |\langle a_0|\psi(t)\rangle|^2$$

$$= \left|\left[\alpha_0^*\langle E_0| + \alpha_1^*\langle E_1|\right]\left[c_0 e^{-iE_0t/\hbar}|E_0\rangle + c_1 e^{-iE_1t/\hbar}|E_1\rangle\right]\right|^2$$

orthogonality helps alot! $\langle E_0|E_1\rangle = \langle E_1|E_0\rangle = 0$

$$P_{a_0} = \left|\alpha_0^* c_0 e^{-iE_0t/\hbar} + \alpha_1^* c_1 e^{-iE_1t/\hbar}\right|^2$$

we can factor out the first phase,

$$P_{a_0} = \underbrace{\left|e^{-iE_0t/\hbar}\right|^2}_{1}\left|\alpha_0^* c_0 + \alpha_1^* c_1 e^{-i(E_1-E_0)t/\hbar}\right|^2$$

$$P_{a_0} = |\alpha_0|^2|c_0|^2 + |\alpha_1|^2|c_1|^2 + 2\mathrm{Re}\left(\alpha_0 c_0^* \alpha_1^* c_1 e^{-i(E_1-E_0)t/\hbar}\right)$$

So b/c $[H, A] \neq 0$, P_{a_0} is time dependent. 10

and frequency of oscillation depends on the energy difference $\Rightarrow \omega_{10} = \dfrac{E_1 - E_0}{\hbar}$

Let's end with an example that illustrates all these ideas.

Example: Problem 3.14 in McIntyre

A system starts out in

$$|\psi(0)\rangle = c\,(3|a_1\rangle + 4|a_2\rangle)$$

$|a_i\rangle$ are normalized eigenstates of A with eigenvalues a_i.

In the $|a_i\rangle$ basis the Hamiltonian is represented by,

$$H \doteq E_0 \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$$

1. What energies are possible and what are there probabilities?
2. What is $\langle A \rangle$?

Solution: 11

1. First observe that H is not diagonal in the $|a_i\rangle$ basis. So H & A do not commute. So we have to diagonalize H.

$$\det(H - \mathbb{I}\lambda) = \begin{vmatrix} 2E_0 - \lambda & E_0 \\ E_0 & 2E_0 - \lambda \end{vmatrix}$$

$$= (2E_0 - \lambda)^2 - E_0^2 = 0$$

$$(2E_0 - \lambda)^2 = E_0^2$$

$$2E_0 - \lambda = \pm E_0$$

$$\lambda = 2E_0 \mp E_0$$

$\lambda_1 = E_0$

$\lambda_2 = 3E_0$

these are the possible

So,

$$\boxed{\begin{aligned} &H|\lambda_1\rangle = E_0|\lambda_1\rangle \\ \text{and } &H|\lambda_2\rangle = 3E_0|\lambda_2\rangle \end{aligned}}$$

possible energy measurements

We need to find $|\lambda_1\rangle$ & $|\lambda_2\rangle$

B/c the probabilities depend on

$$|\langle \lambda_1 | \psi(t) \rangle|^2 \quad \& \quad |\langle \lambda_2 | \psi(t) \rangle|^2$$ (12)

$\underline{\lambda_1 = E_0}$: $\qquad |\lambda_1\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$

$H|\lambda_1\rangle = E_0 |\lambda_1\rangle$ means,

$$\cancel{E_0}\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \cancel{E_0}\begin{pmatrix} a \\ b \end{pmatrix}$$

$$\left.\begin{aligned} 2a + b &= a \\ 1a + 2b &= b \end{aligned}\right\} \rightarrow \quad \begin{aligned} b &= -a \\ a &= -b \end{aligned}$$

normalize

$$\langle \lambda_1 | \lambda_1 \rangle = |a|^2 + |b|^2 = 1$$

$$a = \frac{1}{\sqrt{2}} \quad b = -\frac{1}{\sqrt{2}}$$

$$\boxed{|\lambda_1\rangle = \frac{1}{\sqrt{2}}|a_1\rangle - \frac{1}{\sqrt{2}}|a_2\rangle \doteq \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}}$$

* Remember we are in the $|a_i\rangle$ basis

$\underline{\lambda_2 = 3E_0}$:

$$H|\lambda_2\rangle = 3E_0|\lambda_2\rangle \qquad |\lambda_2\rangle = \begin{pmatrix} c \\ d \end{pmatrix}$$

$$\cancel{E_0}\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}\begin{pmatrix} c \\ d \end{pmatrix} = 3\cancel{E_0}\begin{pmatrix} c \\ d \end{pmatrix}$$

$$\left.\begin{aligned} 2c + d &= 3c \\ c + 2d &= 3d \end{aligned}\right\} \quad \begin{aligned} d &= c \\ c &= d \end{aligned}$$

Normalize,

$$\langle \lambda_2 | \lambda_2 \rangle = |c|^2 + |d|^2 = 1$$

$$c = \frac{1}{\sqrt{2}} \qquad d = \frac{1}{\sqrt{2}}$$

we probably could have guessed this since $\langle \lambda_1 | \lambda_2 \rangle = 0$

$$\boxed{|\lambda_2\rangle = \frac{1}{\sqrt{2}}|a_1\rangle + \frac{1}{\sqrt{2}}|a_2\rangle \doteq \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}}$$

OK with $|\lambda_1\rangle$ & $|\lambda_2\rangle$ we can determine $|a_1\rangle$ & $|a_2\rangle$ in the energy basis which we need for time evolution!

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

relies on the energy basis!

$$|\lambda_1\rangle = \frac{1}{\sqrt{2}}|a_1\rangle - \frac{1}{\sqrt{2}}|a_2\rangle$$

$$|\lambda_2\rangle = \frac{1}{\sqrt{2}}|a_1\rangle + \frac{1}{\sqrt{2}}|a_2\rangle$$

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$$|\lambda_1\rangle + |\lambda_2\rangle = \frac{2}{\sqrt{2}}|a_1\rangle$$

$$\boxed{|a_1\rangle = \frac{1}{\sqrt{2}}|\lambda_1\rangle + \frac{1}{\sqrt{2}}|\lambda_2\rangle}$$

$$|\lambda_2\rangle - |\lambda_1\rangle = \frac{2}{\sqrt{2}}|a_2\rangle$$

$$\boxed{|a_2\rangle = -\frac{1}{\sqrt{2}}|\lambda_1\rangle + \frac{1}{\sqrt{2}}|\lambda_2\rangle}$$

We can rewrite $|\psi(0)\rangle$ in the energy basis now,

$$|\psi(0)\rangle = C\left(3|a_1\rangle + 4|a_2\rangle\right)$$

$$= C\left(3\left(\frac{1}{\sqrt{2}}|\lambda_1\rangle + \frac{1}{\sqrt{2}}|\lambda_2\rangle\right) + 4\left(-\frac{1}{\sqrt{2}}|\lambda_1\rangle + \frac{1}{\sqrt{2}}|\lambda_2\rangle\right)\right)$$

$$|\psi(0)\rangle = C\left(-\frac{1}{\sqrt{2}}|\lambda_1\rangle + \frac{7}{\sqrt{2}}|\lambda_2\rangle\right)$$

let's normalize $|\psi(0)\rangle$,

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$$\langle\psi|\psi\rangle = c^2\left(\frac{1}{2}+\frac{49}{2}\right) = c^2 25 = 1$$

$$c^2 = \frac{1}{25} \qquad c = \pm\frac{1}{5}$$

overall phase doesn't matter choose $+1/2$

$$|\psi(0)\rangle = -\frac{1}{5\sqrt{2}}|\lambda_1\rangle + \frac{7}{5\sqrt{2}}|\lambda_2\rangle$$

From S.E.,

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar}|E_n\rangle$$

$$\boxed{|\psi(t)\rangle = -\frac{1}{5\sqrt{2}}e^{-iE_0 t/\hbar}|\lambda_1\rangle + \frac{7}{5\sqrt{2}}e^{-i3E_0 t/\hbar}|\lambda_2\rangle}$$

Finally we can find the probabilities,

$$\langle\lambda_1|\psi(t)\rangle = \left|\frac{1}{5\sqrt{2}}\right|^2 = \frac{1}{50}$$

$$\langle\lambda_2|\psi(t)\rangle = \left|\frac{7}{5\sqrt{2}}\right|^9 = \frac{49}{50}$$

Solution: $\langle A \rangle = ?$ (16)

(2)

$$\langle A \rangle = \langle \psi(t) | A | \psi(t) \rangle$$

We have to rewrite $|\psi(t)\rangle$ in the $|a_i\rangle$ basis <u>with</u> time dependence!

$$|\psi(t)\rangle = -\frac{1}{5\sqrt{2}} e^{-iE_0 t/\hbar} |\lambda_1\rangle + \frac{7}{5\sqrt{2}} e^{-i3E_0 t/\hbar} |\lambda_2\rangle$$

with,

$$|\lambda_1\rangle = \frac{1}{\sqrt{2}}|a_1\rangle - \frac{1}{\sqrt{2}}|a_2\rangle$$

$$|\lambda_2\rangle = \frac{1}{\sqrt{2}}|a_1\rangle + \frac{1}{\sqrt{2}}|a_2\rangle$$

So in the $|a_i\rangle$ basis,

$$|\psi(t)\rangle = -\frac{1}{5\sqrt{2}} e^{-iE_0 t/\hbar}\left(\frac{1}{\sqrt{2}}|a_1\rangle - \frac{1}{\sqrt{2}}|a_2\rangle\right)$$

$$+ \frac{7}{5\sqrt{2}} e^{-i3E_0 t/\hbar}\left(\frac{1}{\sqrt{2}}|a_1\rangle + \frac{1}{\sqrt{2}}|a_2\rangle\right)$$

$$= \Big(\underbrace{-\frac{1}{10} e^{-iE_0 t/\hbar} + \frac{7}{10} e^{-i3E_0 t/\hbar}}_{c_1(t)}\Big)|a_1\rangle$$

$$+\Big(\underbrace{-\frac{1}{10}e^{-E_0t/\hbar}+\frac{7}{10}e^{-i3E_0t/\hbar}}_{c_2(t)}\Big)|a_2\rangle$$

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$$|\psi(t)\rangle = c_1(t)|a_1\rangle + c_2(t)|a_2\rangle$$

now,

$$\langle A\rangle = \langle\psi|A|\psi\rangle$$

exploit orthogonality $\langle a_1|a_2\rangle = 0$!

$$= \left(c_1^*\langle a_1| + c_2^*\langle a_2|\right) A \left(c_1|a_1\rangle + c_2|a_2\rangle\right)$$

$$= \left(c_1^*\langle a_1| + c_2^*\langle a_2|\right)\left(a_1c_1|a_1\rangle + a_2c_2|a_2\rangle\right)$$

$$= |c_1|^2a_1 + |c_2|^2a_2$$

$$\langle A\rangle = a_1|c_1(t)|^2 + a_2|c_2(t)|^2$$

yuck.