Time dependent Schrödinger eqn.

Thus far we have concentrated almost exclusively on energy eigenstates, in which the time dependence is a trivial $e^{-iEt/\hbar}$, and the probability density $|\psi(\vec{x},t)|^2$ is a $f(\vec{x})$ only.

Of course this is a theoretical abstraction, almost everything we deal with has time dependent probabilities in practice. These include resonance decays, transition rates, emission & absorption of radiation, transient responses etc. All these phenomena can be treated using the time dependent Schrödinger equation, with a suitable choice for $\mathcal{H}$ and the Hilbert space.

the TDSE (for a mass point in a potential) is

normally $V(\vec{x})$, sometimes $V(\vec{x},t)$

$$i\hbar\dot{\psi}(\vec{x},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t) + V\psi(\vec{x},t) \equiv \mathcal{H}_{op}\psi(\vec{x},t)$$

before we go into the details of solving this, let's consider the more general aspects.

If we know $\psi(\vec{x},0)$, does this specify the subsequent wfn completely? Yes (excluding singularities):

$$\psi(\vec{x},\delta t) = \psi(\vec{x},0) + \delta t\,\dot{\psi}(\vec{x},0) + \tfrac{1}{2}(\delta t)^2\ddot{\psi}(\vec{x},0) + \ldots \tfrac{1}{n!}(\delta t)^n\psi^{(n)}(\vec{x},0)$$

need these

and the time derivatives are exactly what the Schrödinger equation gives us

$$\dot{\psi}(\vec{x},0) = -\frac{i}{\hbar}\mathcal{H}_{op}\,\psi(\vec{x},0)$$

$$\overset{o(n)}{\psi}(\vec{x},0) = \left(-\frac{i}{\hbar}\mathcal{H}_{op}\right)^n \psi(\vec{x},0)$$

so

$$\psi(\vec{x},t) = \sum_{n=0}^{\infty} \frac{1}{n!}(\delta t)^n \underbrace{\overset{o(n)}{\psi}(\vec{x},0)}_{\left(-\frac{i}{\hbar}\mathcal{H}_{op}\right)^n \psi(\vec{x},0)}$$

$$= \underbrace{\sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{i}{\hbar}\mathcal{H}_{op}\,\delta t\right)^n}\ \psi(\vec{x},0)$$

or for finite interval, "δt" $\to t$, $\quad \psi(\vec{x},t) = \underbrace{e^{-\frac{i}{\hbar}\mathcal{H}_{op}t}}\ \psi(\vec{x},0)$

$\underline{U(t,0)}$ $\quad$ <u>time translation operator</u>

n.b. recall $\quad U(\vec{a}) = e^{+\frac{i}{\hbar}\vec{P}_{op}\cdot\vec{a}}$ was the spatial translation operator,

$$U(\vec{\delta a}) \approx 1 + \frac{i}{\hbar}\underbrace{\vec{P}_{op}}\cdot\vec{\delta a}$$

↳ "generator of space translations"

similarly $\quad U(\delta t) \approx 1 - \frac{i}{\hbar}\underbrace{\mathcal{H}_{op}}\,\delta t$

↳ ∴ <u>the Hamiltonian is the generator of time translations</u>

n.b. <u>why different signs?</u>

$U(a^\mu) = e^{-\frac{i}{\hbar}P_\mu a^\mu}$

↳ Lorentz metric

For energy eigenstates $\mathcal{H}_{op}$ is diagonal, and the full time dependence is

$$\underline{\psi_E(\vec{x},t)} = e^{-\frac{i}{\hbar}\mathcal{H}_{op}t}\,\psi_E(\vec{x},0) = \underline{e^{-\frac{i}{\hbar}Et}\,\psi_E(\vec{x},0)}$$

which we already know.

for simple, finite-dimensional systems we can calculate the full $U(t,0)$ directly, and obtain the time evolution of an arbitrary initial state.

As a simple example, $\mathcal{H} = gS_z$ on a spin-1/2 system
$S_z = \frac{1}{2}\hbar\sigma_z$,

$$\mathcal{H} = \tfrac{1}{2}g\hbar\sigma_z \qquad \begin{bmatrix} |\uparrow\rangle \\ |\downarrow\rangle \end{bmatrix}$$

$\underset{\sim}{2}$ Hilbert space basis states

$$U(t,0) = e^{-\frac{i}{\hbar}\cdot\frac{1}{2}g\hbar\sigma_z t} = \sum_{n=0}^{\infty} \frac{1}{n!}(-igt/2)^n\sigma_z^n$$

$\sigma_z = \begin{bmatrix} 1 & \\ & -1 \end{bmatrix}$

$\sigma_z^2 = \begin{bmatrix} 1 & \\ & 1 \end{bmatrix} = I$

$$\therefore \sigma_z^{\text{even}} = I,\ \sigma_z^{\text{odd}} = \sigma_z \longrightarrow U = \Big\{\sum_{n\ \text{even}} \frac{1}{n!}(-igt/2)^n\Big\} I + \Big\{\sum_{n\ \text{odd}} \frac{1}{n!}(-igt/2)^n\Big\}\sigma_z$$

$$= \cos(gt/2)\,I - i\sin(gt/2)\,\sigma_z$$

$$U(t,0) = \begin{bmatrix} e^{-igt/2} & 0 \\ 0 & e^{+igt/2} \end{bmatrix} = e^{-iE_n t/\hbar}$$

for each eigenstate ($|\uparrow\rangle$ & $|\downarrow\rangle$ here)

This trivial time dependence of energy eigenstates is one way to find the general result: you can project a general initial state onto orthonormal energy eigenstates

$$|\psi(0)\rangle = \sum_n a_n(0)\,|n\rangle \qquad a_n(0) = \langle n|\psi(0)\rangle = \int dx\, \psi_n^*(x)\psi(x,0)$$

and the subsequent time evolution is

$$|\psi(t)\rangle = \sum_n \underbrace{a_n(0)\, e^{-iE_n t/\hbar}}_{\equiv a_n(t)}\, |n\rangle .$$

The time dependence of an expected value of an operator $\mathcal{O}$ is then

$$\underline{\langle\psi(t)|\mathcal{O}|\psi(t)\rangle} = \sum_{nn'} \langle n|\mathcal{O}|n'\rangle a_n^*(t)\, a_{n'}(t)$$

$$= \sum_{nn'} \underbrace{\langle n|\mathcal{O}|n'\rangle}_{\text{operator matrix elements between energy eigenstates.}} e^{i(E_n - E_{n'})t/\hbar}\, a_n^*(0)\, a_{n'}(0)$$

<u>if the operator is diagonal on energy eigenstates</u>
(e.g. $\mathcal{H}$), more generally, $[\mathcal{O},\mathcal{H}]=0$, we find

$$\underbrace{\langle\mathcal{O}\rangle(t)}_{\text{I may use this shorthand.}} = \langle\psi(t)|\mathcal{O}|\psi(t)\rangle = \sum_{nn'} \underbrace{\langle n|\mathcal{O}|n'\rangle}_{\propto \langle n|\mathcal{O}|n\rangle\delta_{nn'}} \cdot e^{i(E_n - E_{n'})t/\hbar}\, a_n^*(0)\, a_{n'}(0)$$

$$= \underline{\sum_n \langle n|\mathcal{O}|n\rangle\, |a_n(0)|^2} \quad \underline{\text{indep. of } t}$$

An e.g.

An initially spin-up particle $\swarrow(s = 1/2)$ is placed in a magnetic field pointing in the $\hat{x}$-direction. How does the spin precess in time?

(= what is $\langle \vec{S} \rangle(t)$?)

$$\mathcal{H} = -\vec{\mu} \cdot \vec{B}$$

$$\underbrace{= -\mu_B g B \sigma_x / 2}_{}$$

if you recall our prev. discussion of spins, $\vec{\mu} = \underbrace{\frac{e\hbar}{2mc}}_{\mu_B} \cdot \underbrace{g}_{\substack{\text{gyromag. ratio} \\ (\approx 2 \text{ for } e^-)}} \cdot \vec{\sigma}/2$

Pauli matrices $\vec{\sigma} = \sigma_x \hat{x} + \sigma_y \hat{y} + \sigma_z \hat{z}$

(Spin operator is really $\vec{S} = \frac{1}{2}\hbar\vec{\sigma}$, but typically the $\hbar$ is grouped with $\frac{e}{2mc}$ to make μ_B)

$\mu_B = 5.788 \cdot 10^{-5}$ [eV T^{-1}]
Bohr magneton

for $g = 2$, $\mathcal{H} = -\mu_B B \sigma_x$.

To find the time dependence of the expected spin vector, we first solve for the time evolution of the wavefunction (state vector), & then take the matrix element.

$$U(t,0) = e^{-\frac{i}{\hbar}\mathcal{H}_{op} t} = e^{+\frac{i}{\hbar}\mu_B B t \sigma_x}$$

$$= \underbrace{\left\{ \sum_{n \text{ even}} \frac{1}{n!}\left(i \frac{\mu_B B t}{\hbar}\right)^n \right\}}_{\cos\left(\frac{\mu_B B t}{\hbar}\right)} \cdot I + \underbrace{\left\{ \sum_{n \text{ odd}} \frac{1}{n!}\left(i \frac{\mu_B B t}{\hbar}\right)^n \right\}}_{i\sin\left(\frac{\mu_B B t}{\hbar}\right)} \cdot \sigma_x$$

$$U(t,0) = \begin{bmatrix} c & is \\ is & c \end{bmatrix}$$

$$|\psi(0)\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \text{(spin-up)}$$

So,

$$|\psi(t)\rangle = \begin{bmatrix} e & is \\ is & e \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} e \\ is \end{bmatrix} = e|\uparrow\rangle + is|\downarrow\rangle$$

$$\langle\psi(t)| = \begin{bmatrix} e & -is \end{bmatrix}$$

what is the expected spin vector? We work it out component by component: $\vec{S} = \frac{1}{2}\vec{\sigma}$ (drop the $\hbar$),

$$\langle S_z\rangle(t) = \langle\psi(t)|S_z|\psi(t)\rangle = \begin{bmatrix} e & -is \end{bmatrix}\begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}\begin{bmatrix} e \\ is \end{bmatrix}$$

$$= \frac{1}{2}\left(e^2 - s^2\right) = \frac{1}{2}e_2$$

$$\langle S_x\rangle(t) = \begin{bmatrix} e & -is \end{bmatrix}\begin{bmatrix} 0 & 1/2 \\ 1/2 & 0 \end{bmatrix}\begin{bmatrix} e \\ is \end{bmatrix} = 0$$

$$\langle S_y\rangle(t) = \begin{bmatrix} e & -is \end{bmatrix}\begin{bmatrix} & -i/2 \\ i/2 & \end{bmatrix}\begin{bmatrix} e \\ is \end{bmatrix} = es = \frac{1}{2}s_2$$

$$\underline{\langle\vec{S}\rangle(t) = \frac{1}{2}\left[\cos\left(\frac{2\mu_B B}{\hbar}t\right)\hat{z} + \sin\left(\frac{2\mu_B B}{\hbar}t\right)\hat{y}\right]}$$

$\therefore$ with a $\vec{B}$ field applied along $\hat{x}$, the initial spin vector $\langle\vec{S}\rangle(0) = \frac{1}{2}\hat{z}$ rotates about the $\hat{x}$ axis, with angular frequency

$$\underline{\omega = \frac{2\mu_B B}{\hbar}}$$ "Larmor precession"

$1\,\text{eV} = 1.60 \cdot 10^{-12}$ erg

How large is this?

e.g. an electron, $\hbar \sim 10^{-27}$ erg·sec,

$$B = 1 \text{ gauss} = 10^{-4}\,\text{T}$$

$$\omega \sim \frac{2 \cdot \quad \cdot 10^{-4}}{10^{-27}} \cdot 6 \cdot 10^{-5} \; \frac{[\cancel{T}]\,[\text{eV} \cdot \cancel{T^{-1}}]}{[\text{erg} \cdot \text{sec}]} \sim \frac{10^{-8}}{10^{-27}} \frac{[\text{eV}]}{[\text{erg} \cdot \text{sec}]}$$

$$\sim \frac{2 \cdot 10^{-20} \text{ erg}}{10^{-27} \text{ erg sec}} \sim 2 \cdot 10^{7} \text{ sec}^{-1}$$

$$\nu = \frac{\omega}{2\pi} \sim 3 \cdot 10^{6} \text{ sec}^{-1} = 3\,\text{MHz}.$$

radio frequencies.

Choice of picture.

(An amusing trick & important simplification in evaluating the time dependence of matrix elements.

We just evaluated the expected spin $\langle \vec{s} \rangle (t)$ as a function of time, using the formula

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

where the time evolution operator is

$$U(t,0) = e^{-\frac{i}{\hbar} \mathcal{H}_{op} t}$$

(note it's unitary since $\mathcal{H}$ is hermitian,

$U^{+} = e^{+\frac{i}{\hbar}\mathcal{H}^{+} t} = e^{+\frac{i}{\hbar}\mathcal{H} t} = U^{-1}$)

$\therefore \langle \psi(t) | \psi(t) \rangle = \langle \psi(0) | U^{+} U | \psi(0) \rangle = \langle \psi(0) | \psi(0) \rangle$, norm is const.

This approach, with $\underline{|\psi(t)\rangle = U(t,0)\,|\psi(0)\rangle}$,
is called the Schrödinger picture.

States and wavefunctions however are not directly observable.
Only expected values (≡ matrix elements) are.
Thus, although

$$\langle\psi|\mathcal{O}|\psi\rangle(t) = \langle\psi(0)|\underbrace{U^\dagger(t,0)\,\mathcal{O}\,U(t,0)}_{\mathcal{O}(t)\ \text{(Heisenberg picture)}}\overbrace{|\psi(0)\rangle}^{|\psi(t)\rangle\ \text{(Schrödinger picture)}}$$

or

is certainly true, we cannot
really say that the time evolution op.
U is only applied to the state vector $|\psi(0)\rangle$.
We could instead say that the states $|\psi(0)\rangle$ (wfns.) never change
with time, and that instead it is the operators that are changing,

$$\underline{\mathcal{O}(t) = U^\dagger(t)\;\mathcal{O}\;U(t)}$$

this defines the Heisenberg picture, which is often much more
useful than the Schrödinger picture for calculating "real" (actual) matrix
elements.

Let's apply this to our previous problem, $|\psi(0)\rangle = \begin{bmatrix}1\\0\end{bmatrix}$, $\mathcal{H} = -\mu_B B\sigma_x$,
find $\langle\vec{S}\rangle(t)$.

(I'll just solve for $\langle S_z\rangle(t)$.)

$$|\psi(0)\rangle = \begin{bmatrix}1\\0\end{bmatrix} \quad \underline{\text{fixed}} \text{ in the Heisenberg picture.}$$

However, the operator $S_z(t)$ that measures the z-component of spin changes with time :

$$S_z(t) = U^\dagger(t,0)\, S_z(0)\, U(t,0)$$

$$= e^{+\frac{i}{\hbar}\mathcal{H}_{op} t}\, S_z(0)\, e^{-\frac{i}{\hbar}\mathcal{H}_{op} t} \qquad \mathcal{H}_{op} = -\mu_B B \sigma_x$$

oops is this such a good idea?

Yes, if $\mathcal{H}_{op}$ is relatively simple, due to the nested commutator identity

$$e^{A} B e^{-A} = B + [A,B] + \frac{1}{2!}[A,[A,B]] + \ldots$$

$$+ \frac{1}{n!}\underbrace{[A,[A,[A,\ldots[A,B]\ldots]}_{n \text{ occurrences of } A} .$$

$$\left(\sum_{n=0}^{\infty}\right)$$

In our case $A = -\dfrac{i\mu_B B t}{\hbar}\sigma_x$, $(\equiv c\sigma_x)$

$$B = S_z(0) = \frac{1}{2}\sigma_z$$

so $$S_z(t) = S_z(0) + c\left[\sigma_x, \frac{\sigma_z}{2}\right] + \frac{1}{2!}c^2\left[\sigma_x,\left[\sigma_x,\frac{\sigma_z}{2}\right]\right]$$

$$+ \frac{1}{3!}c^3\left[\sigma_x,\left[\sigma_x,\left[\sigma_x,\frac{\sigma_z}{2}\right]\right]\right] + \ldots$$

the commutators are all given by $[\sigma_i,\sigma_j] = 2i\epsilon_{ijk}\sigma_k$ $\qquad (\sigma_i\sigma_j = \delta_{ij} + i\epsilon_{ijk}\sigma_k)$

$$[\sigma_x,\sigma_z] = 2i\epsilon_{13k}\sigma_k = -2i\sigma_y$$

$$[\sigma_x,[\sigma_x,\underset{\sim}{\sigma_z}]] = [\sigma_x, 2i\sigma_y] = +2^2\underset{\sim}{\sigma_z} \qquad \text{so it repeats!}$$

$$\text{n.b.}\left[2ic = +\frac{2\mu_B B}{\hbar}t\right]$$

$$S_z(t) = \frac{1}{2}\sigma_z - 2c\,\frac{1}{2}\sigma_y + \frac{1}{2!}2c^2\,\frac{1}{2}\sigma_z - 2c^3\frac{1}{3!}\frac{1}{2}\sigma_y + \frac{1}{4!}2c^4\frac{1}{2}\sigma_z + \ldots$$

$$= \frac{1}{2}\sigma_z\left(1 - \frac{1}{2!}\left(\frac{2\mu_B Bt}{\hbar}\right)^2 + \frac{1}{4!}\left(\frac{2\mu_B Bt}{\hbar}\right)^4 - \ldots\right)$$

$$-\frac{1}{2}\sigma_y\left(\left(\frac{2\mu_B Bt}{\hbar}\right) - \frac{1}{3!}\left(\frac{2\mu_B Bt}{\hbar}\right)^3 + \ldots\right)$$

$$\underline{S_z(t) = \frac{1}{2}\sigma_z\cos(\omega t) - \frac{1}{2}\sigma_y\sin(\omega t)} \qquad \omega \equiv \frac{2\mu_B B}{\hbar}$$

So,

$$\underline{\langle S_z\rangle(t)} = \underbrace{[1\ 0]}_{\text{fixed}}\cdot\frac{1}{2}\sigma_z\cos(\omega t)\cdot\begin{bmatrix}1\\0\end{bmatrix} = \underline{\frac{1}{2}\cos(\omega t)}$$

" "

$$\langle\psi(0)|\,S_z(t)\,|\psi(0)\rangle$$

Although this problem looks harder in the Heisenberg picture, there are examples that can only be done this way (to my knowledge).

n.b. one may use the Heisenberg picture operator equs. of motion

$$\mathcal{O}(t) = U^\dagger(t)\,\mathcal{O}\,U(t)$$

$$U(t) \to e^{-\frac{i}{\hbar}\mathcal{H}_{op}t}$$

in the limit $t\to 0$ to derive a convenient operator DE for $\mathcal{O}(t)$,

$$\underline{-i\hbar\,\dot{\mathcal{O}}(t) = [\mathcal{H}_{op}, \mathcal{O}(t)]}$$

which is analogous to the Schrödinger DE

$$\underline{i\hbar\dot{\psi} = \mathcal{H}\psi}$$