Lecture #10: The Time-Dependent Schrödinger Equation

Last time:

$$\left.\begin{aligned}\hat{\tilde{x}} &= \left[\frac{\mu\omega}{\hbar}\right]^{1/2}\hat{x}\\ \hat{\tilde{p}} &= \left[\hbar\mu\omega\right]^{-1/2}\hat{p}\end{aligned}\right\}\ \text{dimensionless variables}$$

$\hat{\mathbf{a}} = 2^{-1/2}\left(i\hat{\tilde{p}} + \hat{\tilde{x}}\right)$ annihilation operator

$\widehat{\mathbf{a}^\dagger} = 2^{-1/2}\left(-i\hat{\tilde{p}} + \hat{\tilde{x}}\right)$ creation operator

$\hat{\tilde{x}} = 2^{-1/2}\left(\hat{\mathbf{a}}^\dagger + \hat{\mathbf{a}}\right)$

$\hat{\tilde{p}} = 2^{-1/2} i\left(\hat{\mathbf{a}}^\dagger - \hat{\mathbf{a}}\right)$

$$\hat{x} = \left(\frac{\hbar}{2\mu\omega}\right)^{1/2}\left(\hat{\mathbf{a}}^\dagger + \hat{\mathbf{a}}\right),\ \hat{x}^n = \left(\frac{\hbar}{2\mu\omega}\right)^{n/2}\left(\hat{\mathbf{a}}^\dagger + \hat{\mathbf{a}}\right)^n$$

$$\hat{p} = \left(\frac{\hbar\mu\omega}{2}\right)^{1/2} i\left(\hat{\mathbf{a}}^\dagger - \hat{\mathbf{a}}\right)\ \hat{p}^n = \left(\frac{\hbar\mu\omega}{2}\right)^{n/2} i^n\left(\hat{\mathbf{a}}^\dagger - \hat{\mathbf{a}}\right)^n$$

$$\boxed{\begin{aligned}\hat{\mathbf{a}}\psi_v &= [v]^{1/2}\psi_{v-1}\\ \hat{\mathbf{a}}^\dagger\psi_v &= [v+1]^{1/2}\psi_{v+1}\end{aligned}}$$

, e.g. $\hat{\mathbf{a}}^3\psi_v = \left[v(v-1)(v-2)\right]^{1/2}\psi_{v-3}$

, e.g. $\widehat{\mathbf{a}^\dagger}^{10}\psi_v = \left[(v+10)\ldots(v+1)\right]^{1/2}\psi_{v+10}$

$\hat{N} = \hat{\mathrm{a}}^\dagger\hat{\mathrm{a}}, \qquad \hat{N}\psi_v = v\psi_v$

$\psi_v = [v!]^{-1/2}(\mathrm{a}^\dagger)\psi_0, \quad \psi_0$ is a known Gaussian

Operator algebra, to combine terms like $\hat{\mathbf{a}}^\dagger\hat{\mathbf{a}}\hat{\mathbf{a}}$, $\hat{\mathbf{a}}\hat{\mathbf{a}}^\dagger\hat{\mathbf{a}}$, $\hat{\mathbf{a}}\hat{\mathbf{a}}\hat{\mathbf{a}}^\dagger$, is based on $\left[\hat{\mathbf{a}},\hat{\mathbf{a}}^\dagger\right] = 1$.

What is so great about $\hat{\mathbf{a}},\hat{\mathbf{a}}^\dagger$?
It is born with its *selection rule* and the *values* of all integrals attached!

$$\int dx\psi_v^\star(\hat{\mathbf{a}}^\dagger)^m(\hat{\mathbf{a}})^n\psi_{\underbrace{v+n-m}_{v_i}} = \left[\underbrace{(v+n-m)(v+n-m-1)\ldots(v-m+1)}_{n\text{ terms}}\underbrace{(v-m+1)\ldots(v-1)(v)}_{m\text{ terms}}\right]^{1/2}$$

ψ_{v_f}

$$(\hat{\mathbf{a}}^\dagger)^m(\hat{\mathbf{a}})^n \rightarrow v_f - v_i = m - n$$

Suppose you want $\int dx\psi_{v+2}^*\hat{\mathbf{O}}\mathbf{p}\psi_v \neq 0$? Then $\hat{\mathbf{O}}\mathbf{p}$ could be $\hat{\mathbf{a}}^{\dagger 2}$ or $\hat{\mathbf{a}}^{\dagger 3}\hat{\mathbf{a}}$ (in any order).

Suppose you have $\hat{p}^3$ and want the $\psi_{v+3}\hat{p}^3\psi_v$ integral? Only a total of 3 multiplicative $\hat{\mathbf{a}}$ or $\hat{\mathbf{a}}^\dagger$ factors are possible in $\hat{p}^3$, thus you only keep the $\hat{\mathbf{a}}^{\dagger 3}$ term.
Recall: semi-classical method based on $p_{\text{classical}}(x) = [2\mu(E - V(x))]^{1/2}$

* node spacing
* amplitude envelope of $\psi(x)$
* quantization condition

The REAL Schrödinger Equation is the Time Dependent Schrödinger Equation (TDSE).

The ordinary time-independent Schrödinger Equation, $\hat{H}\psi = E\psi$, is a special case.

Eigenstates do not move, but they *encode* motion.

TDSE: $\boxed{\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi}{\partial t}}$

We usually use Ψ for solutions of TDSE and ψ for solutions of the ordinary SE.

Suppose we have a complete set of solutions of ordinary SE

$$\hat{H}\psi_n = E_n\psi_n \qquad \left(\hat{H} \text{ is independent of time}\right),$$

then

$$\boxed{\Psi_n(x,t) = e^{-iE_nt/\hbar}\psi_n(x)}$$

satisfies the TDSE.

$$i\hbar\frac{\partial\Psi}{\partial t} = (i\hbar)\left(\frac{-i}{\hbar}\right)E_n e^{-iE_nt/\hbar}\psi_n(x)$$

$$= E_n \underbrace{e^{-iE_nt/\hbar}\psi_n}_{\text{this is } \Psi_n(x,t)}$$

$$= E_n\Psi_n(x,t)$$

$$\hat{H}\Psi(x,t) = \underbrace{\hat{H}}\,\psi_n e^{-iE_nt/\hbar} = E_n\psi_n e^{-iE_nt/\hbar}$$

does not operate on $e^{-iE_nt/\hbar}$

Thus it is evident that, for $\hat{H}$ independent of t, if $\psi_n(x)$ is a *solution of the SE*, then $\Psi_n(x,t) = e^{-iE_n t/\hbar}\psi_n(x)$ is a *solution of the TDSE*.

The TDSE is the truth, the whole truth, and nothing but the truth of Quantum Mechanics. However, we will use the TDSE in 5.61 only occasionally.

Here are some very important properties of solutions of the TDSE.

1) The probability density $|\Psi^*(x,t)\Psi(x,t)|$, exhibits motion only if the $\Psi(x,t)$ contains a linear combination of eigenstates that belong to *at least two* energy eigenvalues, $E_1 \neq E_2$.

$$\Psi(x,t) = c_1 e^{-iE_1 t/\hbar}\psi_1 + c_2 e^{-iE_2 t/\hbar}\psi_2$$

$$\begin{aligned}\Psi^*(x,t)\Psi(x,t) = &|c_1|^2|\psi_1|^2 + |c_2|^2|\psi_2|^2 \\ &+ c_1^* c_2 e^{-i(E_2-E_1)t/\hbar}\psi_1^*\psi_2 \\ &+ c_1 c_2^* e^{+i(E_2-E_1)t/\hbar}\psi_1\psi_2^*\end{aligned}$$

The first two terms are independent of t. The second two terms are oscillatory. The second two terms can be re-expressed as

$$2\,\mathrm{Re}\left[c_1^* c_2 e^{-i(E_2-E_1)t/\hbar}\psi_1^*\psi_2\right]$$

Re means "the real part." If C is a complex number

$$\mathrm{Re}\,C = \frac{1}{2}\left(C + C^*\right)$$

and in the above $\Psi\cdot\Psi$ equation, the fourth term is the complex conjugate of the third term (see McQuarrie, Chapter A) and

$$\omega_{12} = \frac{E_1}{\hbar} - \frac{E_2}{\hbar}.$$

For the special case that $c_1^* = c_2 = 2^{-1/2}$ and ψ_1 and ψ_2 are real

$$\Psi^*(x,t)\Psi(x,t) = \underbrace{\frac{1}{2}\psi_1^2 + \frac{1}{2}\psi_2^2}_{\text{static}} + \left(\cos\omega_{12}t\right)\underbrace{\psi_1\psi_2}_{\substack{\text{regions of} \\ +\text{ and } - \\ \text{amplitude}}}.$$

It is clear that the only way we get motion is from a $\Psi(x,t)$ that *contains at least two eigenfunctions of* $\hat{H}$ that belong to two *different* energy eigenvalues. The TDSE is the only way we make contact with the familiar world of moving objects.

There are several easily computed observable dynamical properties that we can use to gain insight into the ways in which Quantum Mechanics encodes motion and to discover what are the Quantum Mechanical laws for motion.

2) If we integrate $\Psi^*(x,t)\Psi(x,t)$ over x, we have a simple normalization integral. Since probability is conserved, the normalization integral should *not* be (and is not) time-dependent, no matter how many ψ_i are present in Ψ. For the two-state superposition state

$$\int dx \Psi^*(x,t)\Psi(x,t) = |c_1|^2 + |c_2|^2 \,!$$

Probability is conserved (and orthogonality simplifies matters).

The $c_1^* c_2 \psi_1^* \psi_2$ terms go away because ψ_1 is orthogonal to ψ_2. The $|\psi_1|^2$ and $|\psi_2|^2$ terms become 1 because the ψ_i are normalized to 1.

3) Expectation values of $\hat{x}$ and $\hat{p}$. Here is an example where the integrals $x_{v,v'}$ and $p_{v,v'}$ become important.

$$\begin{aligned}
\langle \hat{x} \rangle_t &= \int dx \Psi^*(x,t)\hat{x}\Psi(x,t) \\
&= |c_1|^2 \int dx \psi_1^* \hat{x} \psi_1 + |c_2|^2 \int dx \psi_2^* \hat{x} \psi_2 \\
&\quad + c_1^* c_2 e^{-i\omega_{21}t} \int dx \psi_1^* \hat{x} \psi_2 \\
&\quad + c_1 c_2^* e^{+i\omega_{21}t} \int dx \psi_1 \hat{x} \psi_2^* \\
&= \underbrace{|c_1|^2 x_{11} + |c_2|^2 x_{22}}_{\text{stationary}} + \underbrace{2\,\mathrm{Re}\left(c_1^* c_2 e^{-i\omega_{21}t} x_{12}\right)}_{\text{motion}}
\end{aligned}$$

x_{ij} notation

Note that, *for a harmonic oscillator*, $x_{11} = 0$, $x_{22} = 0$ and $x_{12} \neq 0$ *only if* $v_2 = v_1 \pm 1$.

For a particle in a box, you can use symmetry to decide whether x_{11}, x_{22}, and x_{12} are zero. It often helps to shift the box so that it goes from $-a/2 < x < a/2$ (symmetric) rather than $0 < x < a$. For all PIB, $x_{11} = x_{22} = x_{\text{center of box}}$, but $x_{12} = 0$ if both quantum numbers are even or both are odd. WHY? The only case where $\langle x \rangle_t$ is time-dependent for PIB is when Ψ contains at least one even-n and one odd-n eigenstate. We also saw this for the wave equation.

What about $\langle \hat{p} \rangle_t$? It is possible to show (you should show this) that whenever $\langle \hat{x} \rangle_t$ is time-dependent, so too is $\langle \hat{p} \rangle_t$ and

$$m\frac{d\langle x\rangle_t}{dt}=\langle p\rangle_t,$$

which is one of Newton's laws. The motion of the center of any wavepacket is governed by **Ehrenfest's Theorem**

$$\frac{d\langle\vec{r}\rangle_t}{dt}=\frac{1}{m}\langle\vec{p}\rangle_t \qquad (\vec{r},\vec{p} \text{ are 3-D vectors})$$

and

$$\frac{d\langle\vec{p}\rangle_t}{dt}=-\langle\nabla V(\vec{r})\rangle_t$$

These two equations express **both** of Newton's Laws.

4) Another useful measure of dynamics is the "survival probability",

$$P(t)=\left|\int dx\Psi^*(x,t)\Psi(x,0)\right|^2,$$

which provides a measure of how rapidly a time-dependent state departs from (and returns to) the $t = 0$ form of itself. For the two-component state

$$\Psi(x,t)=c_1\psi_1e^{-iE_1t/\hbar}+c_2\psi_2e^{-iE_2t/\hbar}$$
$$\Psi(x,0)=c_1\psi_1+c_2\psi_2$$
$$\int dx\Psi^*(x,t)\Psi(x,0)=|c_1|^2e^{iE_1t/\hbar}+|c_2|^2e^{iE_2t/\hbar}$$

square this to get $P(t)$

$$P(t)=|c_1|^4+|c_2|^4+|c_1|^2|c_2|^2\left[e^{i\omega_{21}t}+e^{-i\omega_{21}t}\right]$$
$$=|c_1|^4+|c_2|^4+2|c_1|^2|c_2|^2\cos\omega_{21}t$$

For $|c_1|=|c_2|$

$$P(t)=\frac{1}{2}\left[1+\cos\omega_{21}t\right],$$

which oscillates between 1 and 0. Is it ever possible (at some t) for $P(t) < 0$?

5) Recurrence

Whenever you have a model system where the energy levels (or energy level differences) are an integer multiple of a common factor, as for

(i) particle in a box, $E_n = E_1\, n^2$

(ii) harmonic oscillator, $E_{v+n} - E_v = \hbar\omega n$

(iii) rigid rotor, $E_J = hcBJ(J+1)$, thus $E_{J+1} - E_J = 2hcB[J+1]$

you get perfect, 100% recurrences at a series of times that are integer multiples of

$$t_{\text{grand recurrence}} = \frac{h}{E_1} \quad \text{or} \quad \frac{h}{\hbar\omega} \quad \text{or} \quad \frac{h}{2hcB}$$

Why? Because, at these special times, every $e^{i\omega_{jk}t}$ phase factor is +1. Interesting things also occur at $t_{gr}/2$.
Recurrence is a very useful experimental signature and can be a basis for very clever experimental manipulations of dynamics.

Next Lecture: we will examine some time evolving $\Psi(x,t)$ "wavepackets" in PIB and HO potentials in order to gain an intuitive understanding of how what is familiar in classical mechanics appears in quantum mechanical systems.

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