FURTHER QUANTUM MECHANICS

Review of QM Concepts

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Lecture 1: QM Concepts

Quantum Mechanics is based on three new concepts, none of which have simple correlates in classical physics:

- The state, or ket $|\psi\rangle$;
- The probability amplitude, or amplitude $\langle\phi|\,\psi\rangle$.
- The operator $\hat{A}$;

Combining the last two we obtain the final concept which derives from these:

- The matrix element $\langle\phi|\hat{A}|\psi\rangle$.

The ket $|\psi\rangle$.

The ket is the complete quantum state of the system, from which we can diagnose all its properties at a given time.

By contrast: **the complete Classical State**

The complete dynamical state of a *classical* system of particles consists of the positions and momenta of all its particles (a point in *phase space*); or some other set of variables equivalent to these. (Obviously this is not a complete description — we would need to add something about what particles were at each of the specified positions. But it is a complete set of dynamical information.)

Consider the planet Mercury, viewed as a point mass orbiting an fixed attractive centre. We could specify its current position $\mathbf{r}$, relative to a defined coordinate system, and its current momentum $\mathbf{p}$, or velocity $\mathbf{v}$ — a total of 6 variables. Or we could give the standard set of orbital elements: (see http://ssd.jpl.nasa.gov/?ephemerides)

a	Semi-major axis	Ω	Longitude of Ascending Node
e	Eccentricity	ω	Argument of Perihelion
i	Inclination	t_p	Time of Perihelion Passage

The ket $|\psi\rangle$.

But this example is dynamically equivalent (same force law) to Hydrogen. The complete quantum state for Hydrogen $|n, \ell, m\rangle$ is specified by just *three* numbers:

- n Principal quantum number ($E_n = -R/n^2$.)
- ℓ Angular Momentum quantum number ($L^2 = \ell(\ell+1)\hbar^2$)
- m Azimuthal quantum number ($L_z = m\hbar$).

In fact these specify an orbit shape and inclination but none of the parameters in left-hand column.

The ket specifies the state less completely than the classical state.

But QM is right. So we should perhaps say

The classical state over-specifies the state.

and if we recall the uncertainty principle this is obvious.

But there is a choice about which if any of the classical variables are defined by the ket . . .

The amplitude $\langle \phi | \psi \rangle$.

Instead of the $|n, \ell, m\rangle$ states we could choose other complete sets of kets:

$|\mathbf{x}\rangle$: the particle is at $\mathbf{x}$ (but momentum is quite unknown);

$|\mathbf{p}\rangle$: the particle has momentum $\mathbf{p}$ (but position is quite unknown);

$|\mathbf{a}(t)\rangle$: a moving wave-packet ket, with a range of positions around $\mathbf{a}$ and a range of momenta around $m\dot{\mathbf{a}}$;

...

These specify some things *more* precisely than the $|n, \ell, m\rangle$ kets, and some things less precisely. So the kets overlap in some sense.

$\langle \phi | \psi \rangle$ denotes the probability amplitude that a particle whose state is the ket $|\psi\rangle$ is found to be in the ket $|\phi\rangle$.

Aside on Probability and Probability Amplitude:

Probability (and probability density) are classical concepts. In all cases they are used to answer incompletely specified problems — ignorance of some aspect of the system — *epistemic* probability.

Probability amplitude is a new concept invented for QM: a complex number whose square is a a probability (or probability density). Why?

Linearity of ket space — amplitudes can add or cancel — interference, waves. You need this to be able to make all the various kets of the previous page (how else can you combine different complete sets of information and make some information more precise and some less precise?).

So the desire to permit wave-like phenomena, like interference, has the effect that the primary quantity of the theory is not directly accessible. — measurable things tend to involve squaring something.

The operator $\hat{A}$:

Having introduced linearity, so that kets are elements of a linear vector space (i.e. we can add them and multiply by numbers) then it follows that we can have linear operators, and these turn out to represent observables. Given an operator $\hat{A}$ we can find eigenkets

$$\hat{A}\,|a\rangle = a\,|a\rangle\,.$$

Hermitian operators play a special role because then several special things happen:

a is real

Eigenkets belonging to different eigenvalues are orthogonal $\langle b|\,a\rangle = 0$.

The set of eigenkets is complete: $\sum_a |a\rangle\,\langle a| = 1$.

Eigenkets of $\hat{A}$ represent states in which the observable A has the value a.

The Measurement Postulate:

If we measure the observable A on a state $|\psi\rangle$ then:

(i) The result is one of the eigenvalues of A, a_n

(ii) with probability $|\,\langle a_n|\,\psi\rangle\,|^2$.

(iii) After the measurement the state is $|a_n\rangle$.

The first two parts simply follow from our definition of amplitude and interpretation of eigenkets. So the measurement postulate defines the complete probability distribution of possible outcomes $P(a_n)$. The expectation value of the distribution is, as for any other probability distribution, $\sum_a a\,P(a)$ and it's easy to show this is equal to $\langle\psi|\,\hat{A}\,|\psi\rangle$.

The last part here is the *collapse of the wavefunction* and is a *big deal.* No other part of QM has occasioned so much (or such bad-tempered) dispute. This is the *measurement problem.* P&P's take note.

The Matrix Element $\langle m|\,\hat{A}\,|n\rangle$:
Consider finding the expectation of A in a superposition state $|\psi\rangle = \sum_{n=1}^{3} c_n\,|n\rangle$.
(The basis $|n\rangle$ is unrelated to A; e.g. A is position and the basis states are energy eigenstates).
Then clearly we just substitute into both bra and ket:

$$\langle\psi|\,\hat{A}\,|\psi\rangle = \sum_{m=1}^{3}\sum_{n=1}^{3} c_m^*\,\langle m|\,\hat{A}\,|n\rangle\,c_n$$

which we can conveniently write in a matrix and vector notation:

$$\langle\psi|\,\hat{A}\,|\psi\rangle = \mathbf{c}^\dagger\mathbf{A}\mathbf{c} = \begin{pmatrix} c_1^* & c_2^* & c_3^* \end{pmatrix}\begin{pmatrix} A_{11} & A_{12} & A_{12} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

where $A_{mn} = \langle m|\,\hat{A}\,|n\rangle$. It's called a matrix element because it's an element of a matrix! The matrix is the representative of the operator $\hat{A}$ in this basis.
The vector $\mathbf{c}$ is the representative of the ket ψ in the basis $|n\rangle$. It's elements are $c_n = \langle n|\,\psi\rangle$.
(But the restriction to just three states is just for this example — it's an infinite vector unless we have a reason to focus on just a subset of states.)

Dynamics:
States evolve in time — so kets evolve in time:

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

where H is the Hamiltonian operator (the energy expressed as a function of position and momentum).
This *looks* really simple if H does not depend on time: compare

$$\frac{df}{dt} + Kf = 0 \quad \rightarrow \quad f(t) = f(0)\exp(-Kt).$$

Can we do the same here? Well we need to make the operator come before the ket:

$$|\psi(t)\rangle = \exp\left[-\frac{\mathrm{i}Ht}{\hbar}\right]|\psi(0)\rangle$$

and we need to know how to take the exponential of an operator — use the series expansion:

$$\exp\left[-\frac{\mathrm{i}Ht}{\hbar}\right] = \sum_{n=0}^{\infty}\left(\frac{-\mathrm{i}t}{\hbar}\right)^n\frac{H^n}{n!}$$

Since powers of H are well defined, and we can add kets together, this isn't mathematical nonsense! And in fact it solves the Schrodinger equation — and is the usual solution!

It looks particularly simple when we expand the ket at $t = 0$ in terms of the eigenkets of H:

$$|\psi(0)\rangle = \sum_i c_i |E_i\rangle \qquad \text{where} \quad H|E_i\rangle = E_i|E_i\rangle .$$

(These are time-independent kets. Sometimes time-dependent energy eigenkets are used, but I will always be explicit if I use them.) Then

$$\exp\left[-\frac{\mathrm{i}Ht}{\hbar}\right]|E_i\rangle = \sum_{n=0}^{\infty}\left(\frac{-\mathrm{i}t}{\hbar}\right)^n \frac{H^n}{n!}|E_i\rangle = \sum_{n=0}^{\infty}\left(\frac{-\mathrm{i}t}{\hbar}\right)^n \frac{E_i^n}{n!}|E_i\rangle = \exp(-\mathrm{i}E_i t/\hbar)|E_i\rangle .$$

So that our superposition state is just a sum of these

$$\boxed{|\psi(t)\rangle = \sum_i c_i \exp(-\mathrm{i}E_i t/\hbar)|E_i\rangle .}$$

The operator $U(t) = \exp(-\mathrm{i}Ht/\hbar)$ is called the *time development operator* or the *propagator* because it propagates the ket forward in time from 0 to t. It is also *unitary*: $U^\dagger = U^{-1}$ which has the important consequence that the normalisation is conserved:

$$\langle\psi(t)|\psi(t)\rangle = \langle\psi(0)|U^\dagger U|\psi(0)\rangle = \langle\psi(0)|\psi(0)\rangle .$$

Example: Particle in a box We consider a box of width a, from 0 to a. Then the eigenfunctions and eigenvalues are easily found:

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad u_n(x) = \langle x|n\rangle = \sqrt{\frac{2}{a}}\sin\left[\frac{n\pi x}{a}\right] .$$

(You may have see a version of this with a different definition of a, and symmetry about $x = 0$; this version has the nice property that we have a single formula for all the eigenfunctions).

To see wavepackets based on this see: (linked from FQM webpage)
http://www.physics.ox.ac.uk/users/palmerc/tdse_Applet.htm

Correspondence Principle: One implication of this follows from the time-dependence that we get in expectation values:

$$\frac{dE_n}{dn} \to h\nu_{\text{class}}(E_n) \qquad \text{at large } n$$

where ν_{class} is the classical orbit frequency as a function of energy.

Commutators

One of the most striking non-classical features of QM is the non-commutation of operators representing classical variables. What does it mean?

$[\hat{A}, \hat{B}] = 0$: There is a really powerful theorem, which we will use repeatedly, which states that if two operators commute then there exists a complete set of mutual eigenkets $|a, b\rangle$:

$$\hat{A}\,|a, b\rangle = a\,|a, b\rangle$$
$$\hat{B}\,|a, b\rangle = b\,|a, b\rangle.$$

This also implies that the observables A and B can be measured compatibly.
(There is a slight wrinkle concerning degeneracy).

$[\hat{H}, \hat{A}] = 0$: In the case of operators commuting with the Hamiltonian then there is a further consequence: for any state $|\psi(t)\rangle$, the expectation value of A is independent of time

$$\frac{d}{dt}\langle\psi(t)|\,\hat{A}\,|\psi(t)\rangle = 0$$

and in a borrowing of classical terminology A is often referred to as a constant of the motion.

Note that this is true for all $\hat{A}$ commuting with $\hat{H}$ even if they don't commute with each other. $[\hat{H}, \hat{L}_i] = 0$ for all components of $\hat{\mathbf{L}}$, so all are constants of the motion.

Commutators

(Finally there are commutators of the form $[a, \hat{B}] = c\,a$ for some real number c. This implies that a is a ladder operator: but it can't be a classical observable! That's because if $\hat{A}$ and $\hat{B}$ are Hermitian then $[\hat{A}, \hat{B}]$ is anti-Hermitian: that is, a Hermitian operator multipled by i. The absence of an i on the RHS means that a is neither Hermitian nor anti-Hermitian.)

Scaling the Hamiltonian

The harmonic oscillator Hamiltonian in the x-representation contains three constants:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \quad \text{involves} \quad \hbar,\ m,\ \omega.$$

This means we can devise a system of units specially adapted for the oscillator:

Constant	Dimensions
m	$[M]$
ω	$[T^{-1}]$
$\hbar$	$[ML^2T^{-1}]$

Thus m has dimensions of mass, ω^{-1} of time and $\sqrt{\hbar/m\omega}$ of length, and in these units the unit of energy is $\hbar\omega$.

We now switch to these units — we define $x = \sqrt{\frac{\hbar}{m\omega}}\,\mathsf{x}$ $\qquad E = \hbar\omega\mathsf{E}$ which gives the time-independent Schrodinger equation as

$$\frac{\hbar^2}{2m}\,\frac{m\omega}{\hbar}\frac{d^2\psi}{d\mathsf{x}^2} + \frac{1}{2}m\omega^2\frac{\hbar}{m\omega}\mathsf{x}^2\psi = \hbar\omega\mathsf{E}\psi.$$

$\hbar\omega$ cancels throughout to leave $\qquad -\dfrac{d^2\psi}{d\mathsf{x}^2} + \mathsf{x}^2\psi = 2\mathsf{E}\psi$

which is the underlying equation stripped of constants.

In these units the eigenvalues are just $\mathsf{E}_n = n + \frac{1}{2}$,

the ground state wavefunction is $\psi_0(\mathsf{x}) = \dfrac{e^{-\mathsf{x}^2/2}}{\pi^{1/4}}$

and the creation operator is $a^\dagger = \dfrac{1}{\sqrt{2}}\,(\mathsf{x} - \mathrm{i}\mathsf{p})$ where $\mathsf{p} = -\mathrm{i}(d/d\mathsf{x})$.

We can always recover the wavefuction in standard units by replacing x with $\sqrt{m\omega/\hbar}\,x$ and multiplying the wavefuntion by $(m\omega/\hbar)^{1/4}$ because ψ has dimensions of $[L]^{-1/2}$:

$$\psi(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\exp\left(-m\omega x^2/2\hbar\right).$$