CHM 502 - Module 1 - The Postulates of Quantum Mechanics

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We begin by reviewing the main concepts of quantum mechanics that you should have seen in prior coursework, using the framework of the postulates (with various asides along the way). We'll touch on, in particular:

- wavefunctions, and their various representations

- Hermitian operators

- quantum observables, expectation values, and measurement

- collapse of the wavefunction, non-commuting operators, and uncertainty

- the time-dependent Schrödinger equation

If you need more review of any of these topics as we get started, some excellent resources are (a) Griffiths "Introduction to Quantum Mechanics," (b) McQuarrie's "Quantum Chemistry," and/or (c) my lecture notes from my undergraduate quantum course, CHM 305, which can be found here.

1   Wavefunctions

The wavefunction, $\Psi(x, y, z, t)$, describes all observable physical quantities of a quantum system, including its state at time t.

The wavefunction must be normalizeable, or square-integrable, e.g.

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi(x, y, z, t)|^2 \, dx \, dy \, dz = 1 \tag{1}$$

because $|\Psi(x, y, z, t)|^2$ represents a spatial probability distribution.

The system's wavefunction will evolve in time according to the time-dependent Schrödinger equation (TDSE):

$$\hat{H}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(x, y, z)\Psi = i\hbar\frac{\partial}{\partial t}\Psi \tag{2}$$

where $V(x, y, z)$ is the potential energy landscape the system is exploring.

In order to be a valid solution to the TDSE, Ψ must be a continuous and smooth function of x, y, z. In other words, we must be able to evaluate two spatial derivatives of Ψ, as $\nabla^2\Psi$ appears in the differential equation above. *Note:* the only exception to this rule is when $V(x, y, z)$ itself is non-differentiable, in which case Ψ may exhibit some weird kinks.

1.1 Wavefunction representation in a continuous basis

It is also useful to recall how to work with expansions in continuous basis sets. Let's consider a wavefunction expanded in the basis of position eigenstates $\{|x\rangle\}$:

$$|\Psi\rangle = \int_{-\infty}^{\infty} \psi(x) |x\rangle \ dx \tag{3}$$

Here you can think of $\psi(x)$ as the continuous analog of the discrete expansion coefficients c_i that we saw in Section 1.2. In essence, $\psi(x)$ is the distribution that gives the weighting of each component position eigenstate.

Aside: What does a position eigenstate $|x_0\rangle$ look like? It must have well-defined position. Let's use a Dirac delta function: an infinitely narrow peak centered at x_0 that nevertheless remains properly normalized. The Dirac delta can be defined in various ways, most commonly as a Lorentzian or Gaussian in the limit where the linewidth approaches zero:

$$\delta(x - x_0) = \lim_{\epsilon \to 0} \frac{1}{\pi} \frac{\epsilon}{(x - x_0)^2 + \epsilon^2} \tag{4}$$

$$= \lim_{\epsilon \to 0} \frac{1}{\epsilon\sqrt{\pi}} \exp^{-(x-x_0)^2/\epsilon^2} \tag{5}$$

Either way, we have

$$\delta(x - x_0) = \begin{cases} +\infty, \ x = x_0 \\ 0, \ x \neq x_0 \end{cases} \tag{6}$$

but constrained such that the distribution remains normalized:

$$\int_{-\infty}^{\infty} \delta(x - x_0) dx = 1 \tag{7}$$

How do we go back and forth between the wavefunction's ket representation, $|\Psi\rangle$ and its position representation $\psi(x)$? We consider a projection of $|\Psi\rangle$ with each position eigenstate:

$$\langle x_0 | \Psi \rangle = \langle x_0 | \int dx \ |x\rangle \psi(x) = \int dx \ \langle x_0 | x \rangle \psi(x) \tag{8}$$

$$= \int dx \ \delta(x - x_0) \psi(x) \tag{9}$$

$$= \psi(x_0) \tag{10}$$

where we used the following:

- The position eigenstates form an orthonormal set so $\langle x_0 | x \rangle = \delta(x - x_0)$. You can also think of $\delta(x - x_0)$ as the explicit position representation of $|x\rangle$ given by $\langle x_0 | x \rangle$, just as $\psi(x_0)$ is the position representation of $|\Psi\rangle$ given by $\langle x_0 | \Psi \rangle$.

- The Dirac delta function has the unusual property that integrated against a function:

$$\int_{-\infty}^{\infty} dx \, f(x) \, \delta(x - x_0) = f(x_0) \tag{11}$$

Therefore integrating $\psi(x)$ against $\delta(x - x_0)$ plucks out the value of $\psi(x)$ at $x = x_0$.

We need not limit ourselves to the position representation. We can also consider an expansion in momentum eigenstates:

$$|\Psi\rangle = \int_{-\infty}^{\infty} \tilde{\psi}(p) \, |p\rangle \, dp \tag{12}$$

Here, we'll again find that $\tilde{\psi}(p)$ represents the distribution of weightings the momentum eigenstates in $|\Psi\rangle$. The momentum eigenstates will also be sharply peaked distributions in *momentum space*, and obey $\langle p_0|p\rangle = \delta(p - p_0)$.

What does the *position space representation* of these momentum eigenstates look like? Recall that sinusoidal traveling waves have well-defined momenta - you may have seen this in previous coursework covering the behavior of the quantum mechanical free particle.

A typical quantum wave traveling through free space looks like:

$$\Psi(x,t) = Ae^{i(k_0 x - \omega_0 t)} \equiv \psi(x) \cdot \phi(t) = Ae^{ik_0 x} \cdot e^{-i\omega_0 t} \tag{13}$$

Aside: A quick reminder that complex exponentials, which pop up all over quantum mechanics, are simply a mathematically convenient notation for working with sinusoids. You can switch back and forth between complex exponentials and sines and cosines using Euler's relations:

$$e^{ix} \equiv \cos(x) + i\sin(x) \tag{14}$$

$$\cos(x) = \mathrm{Re}\left[e^{ix}\right] = \frac{1}{2}\left[e^{ix} + e^{-ix}\right] \tag{15}$$

$$\sin(x) = \mathrm{Im}\left[e^{ix}\right] = \frac{1}{2i}\left[e^{ix} - e^{-ix}\right] \tag{16}$$

The spatial component of our wave is

$$\psi(x) = Ae^{ik_0 x} \tag{17}$$

Here k_0 is the wavevector, defined as $k_0 = 2\pi/\lambda_0$. We can use the deBroglie relation ($\lambda = h/p$) to connect to momentum. So $k_0 = 2\pi p_0/h = p_0/\hbar$. So in terms of momentum:

$$\psi(x) = Ae^{ip_0 x/\hbar} \tag{18}$$

Here p_0 is a constant that is well-defined, while x is a variable that runs over all space. Our sinusoidal traveling wave is therefore completely delocalized spatially, but would be highly localized in its momentum space representation.

The $\psi(x)$ position space representation of a wavefunction and its momentum space representation, which we'll call $\tilde{\psi}(p)$, are closely related by a Fourier transform. We can move back and forth between them using:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dp\, e^{ipx/\hbar}\, \tilde{\psi}(p) \tag{19}$$

$$\tilde{\psi}(p) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar}\, \psi(x) \tag{20}$$

So let's confirm: what is the momentum space representation of a wavefunction with only a single momentum component p_0? Starting from the position space representation:

$$\psi(x) = e^{ip_0 x/\hbar} \tag{21}$$

We evaluate:

$$\tilde{\psi}(p) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar}\psi(x) \tag{22}$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar}e^{ip_0 x/\hbar} \tag{23}$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{-i(p-p_0)x/\hbar} \tag{24}$$

$$= \begin{cases} +\infty, \ p = p_0 \\ 0, \ p \neq p_0 \end{cases} \qquad \propto \delta(p - p_0) \quad \checkmark \tag{25}$$

So indeed, we recover the fact that a position-space sinusoid is represented as a delta function in momentum space, because x and p are conjugate variables related by the Fourier transform. We also see a manifestation of the uncertainty principle here, in that our total certainty in p yields a total uncertainty in x. For a wave (either quantum mechanical or classical!), the two quantities are incomptible and cannot be known simultaneously with perfect precision.

1.2 Wavefunction representation in a discrete basis

We can work with the wavefunction as a continuous function in position space (or momentum space) and time, but it is often much more compact and convenient to represent it as a vector in state space. For instance, we can think about the Dirac notation representations of "*kets*" $|\Psi\rangle$ and "*bras*" $\langle\Psi|$ as column and row vectors, respectively.

We can describe an arbitrary ket $|\Psi\rangle$ as a discrete expansion of some relevant basis set that spans state space:

$$|\Psi\rangle = \sum_{i=1}^{\infty} c_i \,|u_i\rangle = c_1 \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{bmatrix} + c_2 \begin{bmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{bmatrix} + \cdots = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} \tag{26}$$

The bra $\langle\Psi|$ is a dual vector constructed from the complex conjugate transpose (or "adjoint") of the corresponding ket $|\Psi\rangle$:

$$\langle\Psi| = |\Psi\rangle^{\dagger} = \begin{bmatrix} c_1^* & c_2^* & c_3^* & \dots \end{bmatrix} = \sum_i c_i^* \,\langle u_i| \tag{27}$$

It is most convenient to work with orthonormal basis sets. Let's assume that $\{|u_i\rangle\}$ is an orthonormal basis set, meaning that:

$$\langle u_i|u_j\rangle = \delta_{ij} = \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases} \tag{28}$$

where δ_{ij} is the Kronecker delta.

We can find the expansion coefficients $\{c_i\}$ of $|\Psi\rangle$ by evaluating the projection, or inner product, of each $\{|u_i\rangle\}\}$ basis vector with $|\Psi\rangle$:

$$\langle u_j|\Psi\rangle = \langle u_j| \sum_i c_i |u_i\rangle = \sum_i c_i \langle u_j|u_i\rangle = \sum_i c_i \delta_{ij} = c_j \tag{29}$$

We can therefore write:

$$|\Psi\rangle = \sum_i |u_i\rangle c_i = \sum_i |u_i\rangle \langle u_i|\Psi\rangle = \left[\sum_i |u_i\rangle \langle u_i|\right] |\Psi\rangle \tag{30}$$

Here $|u_i\rangle \langle u_i|$ is an outer product that when applied to returns $|\Psi\rangle$ returns a vector in state space oriented along $|u_i\rangle$ whose magnitude captures the weighting of $|u_i\rangle$ in $|\Psi\rangle$. We can think of $|u_i\rangle \langle u_i|$ as a "projection operator." We can also see from Eqn. 30 that we must have:

$$\sum_i |u_i\rangle \langle u_i| = \hat{I} \tag{31}$$

where $\hat{I}$ is the identity matrix. This arises from the completeness of our basis set and will prove very useful.

2 Operators

The physical observable quantities of quantum system – quantities like a particle's position x, momentum p, or energy E – are represented by Hermitian operators, denoted with hats ($\hat{x}$, $\hat{p}$, $\hat{H}$).

We measure a physical observable of our system by applying an operator $\hat{A}$ to our system's wavefunction: $\hat{A}|\psi\rangle$. We should already be familiar with what various relevant operators look like:

$$\hat{x}|\psi\rangle = x|\psi\rangle \tag{32}$$

$$\hat{p}|\psi\rangle = -i\hbar \frac{\partial}{\partial x}|\psi\rangle \tag{33}$$

$$\hat{H}|\psi\rangle = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]|\psi\rangle \tag{34}$$

In Dirac notation, we think of operators as matrices. In particular, using our definition of the identity matrix from Eqn. 31:

$$\hat{A} = \left[\sum_i |u_i\rangle \langle u_i|\right] \hat{A} \left[\sum_j |u_j\rangle \langle u_j|\right] \tag{35}$$

$$= \sum_{i,j} |u_i\rangle \langle u_i|\hat{A}|u_j\rangle \langle u_j| \tag{36}$$

$$= \sum_{ij} |u_i\rangle A_{ij} \langle u_j| \quad \text{where} \quad A_{ij} \equiv \langle u_i|\hat{A}|u_j\rangle \tag{37}$$

We think of A_{ij} (which is just a number) as a matrix element of the $\hat{A}$ matrix represented in the $\{|u_i\rangle\}$ basis. The A_{ij} element gets pulled out by projection of matrix $\hat{A}$ with row vector $\langle u_i|$ and column vector $|u_j\rangle$:

$$A_{ij} = \begin{bmatrix} 0 \cdots 1 \cdots 0 \end{bmatrix} \begin{bmatrix} \ddots & \vdots & \cdot^{\cdot^{\cdot}} \\ \cdots & A_{ij} & \cdots \\ \cdot^{\cdot^{\cdot}} & \vdots & \ddots \end{bmatrix} \begin{bmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{bmatrix} \tag{38}$$

Like matrices, quantum operators have eigenvectors and eigenvalues. If the $\hat{A}|\psi\rangle$ operation returns a wavefunction that is proportional to $|\psi\rangle$:

$$\hat{A}|\psi\rangle = \lambda|\psi\rangle \tag{39}$$

then $|\psi\rangle$ is an *eigenstate* (or *eigenvector* or *eigenfunction*) of $\hat{A}$, with *eigenvalue* λ.

2.1 Solving matrix eigenvalue problems

Let's quickly review how we find the eigenvalues and eigenvectors of a matrix using linear algebra. An eigenvector $\{|u\rangle$ and its corresponding eigenvalue $\{\lambda\}$ must obey:

$$\hat{A}|u\rangle = \lambda|u\rangle \tag{40}$$

$$\rightarrow \quad \left[\hat{A} - \lambda \cdot \hat{I}\right] \cdot |u\rangle = 0 \tag{41}$$

$$\equiv \hat{B}|u\rangle = 0 \tag{42}$$

If $\hat{B}|u\rangle = 0$, then the inverse $\hat{B}^{-1}$ must not exist. Suppose we assume that $\hat{B}^{-1}$ exists. Then:

$$\hat{B}^{-1}\hat{B}|u\rangle = \hat{I}|u\rangle = |u\rangle \tag{43}$$

$$= \hat{B}^{-1} \cdot 0 = 0 \tag{44}$$

$$\rightarrow \quad |u\rangle = 0 \quad \text{regardless of what } |u\rangle \text{ was initially} \tag{45}$$

We have reached a logical inconsistency and therefore our assumption that $\hat{B}$ has an inverse must be false. Hence, $\hat{B}$ must be non-invertible if $\hat{B}|u\rangle = 0$ for $|u\rangle \neq 0$.

Linear algebra tells us that a non-invertible matrix has the convenient property that its determinant is equal to zero:

$$\det \hat{B} = \det\left[\hat{A} - \lambda \cdot \hat{I}\right] = 0 \tag{46}$$

We can use this fact to find the set of eigenvalues $\{\lambda\}$ of $\hat{A}$.

Let's take a look at the explicit solutions for a 2×2 system, which we'll use throughout this course for our treatment of 2-level systems:

$$\hat{A} = \begin{bmatrix} a & b \\ c & d \end{bmatrix} \quad \rightarrow \quad \hat{A} - \lambda\hat{I} = \begin{bmatrix} a - \lambda & b \\ c & d - \lambda \end{bmatrix} \tag{47}$$

$$\det\left[\hat{A} - \lambda\hat{I}\right] = (a - \lambda)(d - \lambda) - bc = 0 \tag{48}$$

$$\lambda_{\pm} = \frac{(a + d) \pm \sqrt{(a + d)^2 - 4(ad - bc)}}{2} \tag{49}$$

Using these two eigenvalues, we then find the corresponding eigenvectors by solving

$$\begin{bmatrix} a - \lambda_\pm & b \\ c & d - \lambda_\pm \end{bmatrix} \begin{bmatrix} u_{\pm,1} \\ u_{\pm,2} \end{bmatrix} = 0 \tag{50}$$

to find the components of each eigenvector $|u_\pm\rangle$.

A quick note: it is important to distinguish between non-degenerate and degenerate eigenvalues. If $\lambda_+ = \lambda_- = \lambda$, then $|u_+\rangle$ and $|u_-\rangle$ form a 2-D vector space:

$$\hat{A}|u_+\rangle = \lambda|u_+\rangle, \quad \hat{A}|u_-\rangle = \lambda|u_-\rangle \tag{51}$$

$$\rightarrow \quad \hat{A}\left[c_+|u_+\rangle + c_-|u_-\rangle\right] = \lambda\left[c_+|u_+\rangle + c_-|u_-\rangle\right] \tag{52}$$

Therefore any linear combination of $|u_+\rangle$ and $|u_-\rangle$ will also be an eigenvector of $\hat{A}$ with eigenvalue λ. The choice of the $|u_\pm\rangle$ basis vectors are not unique.

2.2   Quantum operators are Hermitian

All valid quantum operators have the property that they are *Hermitian*. Hermitian operators are self-adjoint, which is to say that they are their own complex-conjugate transpose:

$$\hat{A}^\dagger = \hat{A} \tag{53}$$

$$A_{ij} = A_{ji}^* \tag{54}$$

Aside: Let's take this opportunity to quickly recall how we work with operators and adjoints within Dirac notation.

First, a trick for quickly evaluating expressions in Dirac notation:

(i) anything enclosed by $|\quad\rangle$ is a ket (regardless of how many terms are inside!)

(ii) anything enclosed by $\langle\quad|$ is a bra

(iii) anything enclosed by $|\quad|$ is a matrix or operator (e.g. $|\psi\rangle\langle\phi|$)

(iv) anything enclosed by $\langle\quad\rangle$ is just a number (e.g. $\langle\phi|\hat{A}|\psi\rangle$)

In order to take the adjoint of an expression, we:

(i) replace any number by its complex conjugate

(ii) replace any ket by its corresponding bra (and vice versa)

(iii) replace any operator by its adjoint

(iv) and finally ***reverse the order of the entire expression***

By way of some examples:

$$|\psi\rangle^\dagger = \langle\psi| \tag{55}$$

$$\lambda^\dagger = \lambda^* \tag{56}$$

$$\left[\lambda_1 |\psi_1\rangle + \lambda_2 |\psi_2\rangle\right]^\dagger = \langle\psi_1| \lambda_1^* + \langle\psi_2| \lambda_2^* \tag{57}$$

$$\left[\hat{A}^\dagger\right]^\dagger = \hat{A} \tag{58}$$

$$\left[\hat{A} + \hat{B}\right]^\dagger = \hat{A}^\dagger + \hat{B}^\dagger \tag{59}$$

$$\left[\hat{A}\hat{B}\right]^\dagger = \hat{B}^\dagger \hat{A}^\dagger \tag{60}$$

$$\left[\hat{A} |\psi\rangle\right]^\dagger = \langle\psi| \hat{A}^\dagger \tag{61}$$

$$\langle\psi|\hat{A}|\phi\rangle^\dagger = \langle\phi|\hat{A}|\psi\rangle \tag{62}$$

Hermitian operators have two nice properties:

The eigenvalues of Hermitian operators are real. This makes sense because the eigenvalues returned by operators represent real, observable physical quantities. We can easily prove that this is the case:

$$\hat{A} |u\rangle = \lambda |u\rangle \quad \rightarrow \quad \langle u|\hat{A}|u\rangle = \lambda \tag{63}$$

$$\langle u|\hat{A}|u\rangle^\dagger = \langle u|\hat{A}^\dagger|u\rangle = \lambda^* \tag{64}$$

$$= \langle u|\hat{A}|u\rangle = \lambda \tag{65}$$

$$\rightarrow \quad \lambda = \lambda^* \quad \rightarrow \quad \boxed{\lambda \text{ real}} \tag{66}$$

Eigenvectors of the same operator with different eigenvalues are orthogonal and form a handy basis set. Let's quickly prove this:

$$①\quad \hat{A} |u_1\rangle = \lambda_1 |u_1\rangle \quad \rightarrow \quad \langle u_2|\hat{A}|u_1\rangle = \langle u_2|\lambda_1|u_1\rangle = \lambda_1 \langle u_2|u_1\rangle \tag{67}$$

$$②\quad \hat{A} |u_2\rangle = \lambda_2 |u_2\rangle \quad \rightarrow \quad \langle u_1|\hat{A}|u_2\rangle = \langle u_1|\lambda_2|u_2\rangle = \lambda_2 \langle u_1|u_2\rangle \tag{68}$$

$$③\quad \text{take the adjoint of } ② : \langle u_1|\hat{A}|u_2\rangle^\dagger = \langle u_2|\hat{A}^\dagger|u_1\rangle = \langle u_2|\hat{A}|u_1\rangle = ① \tag{69}$$

$$= [\lambda_2 \langle u_1|u_2\rangle]^\dagger = \lambda_2 \langle u_2|u_1\rangle \tag{70}$$

$$① - ③ = (\lambda_1 - \lambda_2) \langle u_2|u_1\rangle = 0 \tag{71}$$

$$\rightarrow \quad \langle u_2|u_1\rangle = 0 \text{ if } \lambda_1 \neq \lambda_2 \quad \checkmark \tag{72}$$

Note that if $\lambda_1 = \lambda_2$, then we can always choose a set of orthogonal vectors to span their degenerate subspace, but the choice of these vectors is not unique.

3   Quantum Measurement

Say our system has wavefunction $|\psi(t)\rangle$ and we measure some observable $\hat{A}$ at time t. The outcome of this measurement must be one of the eigenvalues of $\hat{A}$.

Say that $\hat{A}$ has eigenvalues $\{\lambda_i\}$ and eigenvectors $|u_i\rangle$. We can think about an expansion of our wavefunction in the $|u_i\rangle$ basis, then:

$$|\psi\rangle = \sum_i c_i |u_i\rangle \tag{73}$$

Assuming our λ_i eigenvalues are non-degenerate, the probability that we measure eigenvalue λ_i after we apply $\hat{A}$ to $|\psi\rangle$ is given by:

$$\Pr\left[\lambda_i\right] = |c_i|^2 = |\langle u_i|\psi\rangle|^2 \tag{74}$$

If eigenvalue λ_i *is* degenerate with degeneracy m, then instead we have:

$$\Pr\left[\lambda_i\right] = \sum_{\alpha=1}^{m} |\langle u_i^\alpha|\psi\rangle|^2 \tag{75}$$

This probability picture is why wavefunctions must be normalized, since the probabilities of each possible outcome must add up to 1:

$$\sum_{i=1}^{\infty} |c_i|^2 = 1 \tag{76}$$

3.1   Expectation values

Quantum measurement of a superposition state will stochastically return discrete eigenvalues. But we can learn something about the distribution of possible results by calculate the expected value of a particular observable. The expected value is equivalent to the average quantity you would measure if you repeated the measurement many times on an identically prepared system.

For an operator $\hat{A}$ with eigenvalues λ_i and eigenvectors $|u_i\rangle$:

$$\langle \hat{A}\rangle = \sum_i \lambda_i \cdot \Pr\left[\lambda_i\right] = \sum_i \lambda_i |\langle u_i|\psi\rangle|^2 \tag{77}$$

$$= \sum_i \lambda_i \langle\psi|u_i\rangle\langle u_i|\psi\rangle \tag{78}$$

$$= \sum_i \langle\psi|u_i\rangle \lambda_i \langle u_i|\psi\rangle \tag{79}$$

$$= \langle\psi|\left[\sum_i |u_i\rangle \lambda_i \langle u_i|\right]|\psi\rangle \equiv \langle\psi|\hat{A}|\psi\rangle \tag{80}$$

where we've essentially constructed the $\hat{A}$ operator diagonalized in its own basis of eigenvectors.

Note that we've also assumed here that $|\psi\rangle$ is normalized. If not, we'd need to re-scale the expectation value of $\hat{A}$:

$$\langle \hat{A}\rangle = \frac{\langle\psi|\hat{A}|\psi\rangle}{\langle\psi|\psi\rangle} \tag{81}$$

4 Wavefunction Collapse and Uncertainty

If we make a measurement and record the outcome λ_i, we collapse the state of the system to lie in the vector space associated with that eigenvalue. In particular:

(i) if the measured eigenvalue λ_i is non-degenerate, then $|\psi\rangle \to |u_i\rangle$

(ii) if λ_i has degeneracy m then $|\psi\rangle \to \sum_{\alpha=1}^{m} c_\alpha |u_i^\alpha\rangle$

Suppose instead that we make two subsequent measurements using two different operators, e.g. $\hat{B}\hat{A}|\psi\rangle$. It matters whether the operator that acts first ($\hat{A}$) collapses the wavefunction into an eigenvector of the second operator. It therefore matters whether the two operators share a common set of eigenvectors, which can be determined by examining whether or not $\hat{A}$ and $\hat{B}$ commute.

Two operators $\hat{A}$ and $\hat{B}$ are said to commute if

$$\left[\hat{A}\hat{B} - \hat{B}\hat{A}\right]|\psi\rangle \equiv \left[\hat{A}, \hat{B}\right]|\psi\rangle = 0 \tag{82}$$

Various pairs of operators commute, e.g.:

$$\hat{p} \qquad \text{and} \qquad \hat{KE} = \frac{\hat{p}^2}{2m} \tag{83}$$

$$\hat{x} \qquad \text{and} \qquad \hat{V}(x) = \frac{1}{2}kx^2 \tag{84}$$

Various pairs of operators do not commute including, famously, $\hat{x}$ and $\hat{p}$:

$$[\hat{x}, \hat{p}]|\psi\rangle = x \cdot -i\hbar\frac{\partial}{\partial x}|\psi\rangle + i\hbar\frac{\partial}{\partial x}[x|\psi\rangle] \tag{85}$$

$$= +i\hbar|\psi\rangle \tag{86}$$

$$\to \quad \boxed{[\hat{x}, \hat{p}] = +i\hbar} \tag{87}$$

4.1 Commuting operators have common eigenvectors

If two operators commute, then their eigenvectors are closely related. Let's prove this. Say we have $\hat{A}|u\rangle = \lambda|u\rangle$. Now consider a second operator $\hat{B}$, which commutes with $\hat{A}$:

$$\hat{A}\left[\hat{B}|u\rangle\right] = \hat{B}\hat{A}|u\rangle = \hat{B}\left[\lambda|u\rangle\right] = \lambda\left[\hat{B}|u\rangle\right] \tag{88}$$

Therefore, $\hat{B}|u\rangle$ is an eigenvector of $\hat{A}$ with eigenvalue λ.

If λ is a non-degenerate eigenvalue of $\hat{A}$, then we must have $\hat{B}|u\rangle \propto |u\rangle$, and we have therefore shown that $|u\rangle$ is an eigenvector of $\hat{B}$ as well as an eigenvector of $\hat{A}$.

Things are always slightly more complicated if we have degenerate eigenvalues. If λ is a degenerate eigenvalue of $\hat{A}$ with degeneracy m and a corresponding set of m eigenvectors $|u_\alpha\rangle$, then measurement with $\hat{B}$ must give us:

$$\hat{B}|u\rangle = \sum_{\alpha=1}^{m} c_\alpha |u_\alpha\rangle \tag{89}$$

Another way to say this is that if $\hat{A}$ and $\hat{B}$ commute, then $\hat{B}$ is block diagonal in the basis of $\hat{A}$ eigenstates. We can prove this:

$$\hat{A}\,|u_i\rangle = \lambda_i\,|u_i\rangle\,;\quad \hat{A}\,|u_j\rangle = \lambda_j\,|u_j\rangle \tag{90}$$

$$\langle u_i|\hat{B}\hat{A}|u_j\rangle = \lambda_j\,\langle u_i|\hat{B}|u_j\rangle \tag{91}$$

$$-\,\langle u_i|\hat{A}\hat{B}|u_j\rangle = \lambda_i^*\,\langle u_i|\hat{B}|u_j\rangle \tag{92}$$

$$0 = (\lambda_j - \lambda_i^*)\,\langle u_i|\hat{B}|u_j\rangle \tag{93}$$

And therefore we must have

$$\langle u_i|\hat{B}|u_j\rangle = B_{ij} = 0 \quad\text{for}\quad \lambda_j \neq \lambda_i^* \tag{94}$$

And we've proved that the off-diagonal elements of $\hat{B}$ are zero in the $\hat{A}$ basis, except when two eigenvalues of $\hat{A}$ are degenerate, in which case $\hat{B}$ will be block diagonal.

4.2 Non-commuting operators yield uncertainty in measurement

Measurement uncertainty is minimized when you prepare your wavefunction in an eigenstate of the operator you are making a measurement with. In this case, you have perfect certainty about what you'll expect to measure – the corresponding eigenvalue. You can only make perfect measurements of two separate observables if your state is an eigenfunction of both observables. And we now know this is only the case if your two observables commute.

Let's quickly illustrate how our certainties get scrambled if two operators don't commute. Imagine we have two non-commuting operators with two separate sets of eigenstates, each of which form a complete basis:

$$\hat{A}\,|\phi_n\rangle = a_n\,|\phi_n\rangle$$
$$\hat{B}\,|\psi_n\rangle = b_n\,|\psi_n\rangle$$

Because $\{|\psi_n\rangle\}$ and $\{|\phi_n\rangle\}$ both form complete basis sets, we can express any one of these wavefunctions from either group in terms of the other:

$$|\psi_n\rangle = \sum_m c_{mn}\,|\phi_m\rangle \tag{95}$$

$$|\phi_n\rangle = \sum_m d_{mn}\,|\psi_m\rangle \tag{96}$$

where we would need to find appropriate c_{mn} and d_{mn} coefficients.

Now let's think about what might happen if we make some measurements:

- Imagine we prepare the system in the $|\phi_1\rangle$ eigenstate of $\hat{A}$. If we measure $\hat{A}\,|\phi_1\rangle$, we will measure eigenvalue a_1 with perfect certainty and leave our system unchanged in $|\phi_1\rangle$.

- Now we take $|\phi_1\rangle$ and make a measurement with $\hat{B}$. We will only measure eigenvalues of $\hat{B}$. To determine the probability of each outcome we need to re-express our wavefunction in terms of the eigenfunctions of $\hat{B}$:

$$\hat{B}\,|\phi_1\rangle = \hat{B}\sum_m d_{m1}\,|\psi_m\rangle \tag{97}$$

We measure the b_n eigenvalue of $\hat{B}$ with probability $|d_{n1}|^2$. In doing so, we collapse the wavefunction and leave it in $|\psi_n\rangle$. Note that there is now (potentially great) uncertainty in our measurement outcome.

- Finally, we can return to measure our $|\psi_n\rangle$ system with $\hat{A}$, after completing measurement with $\hat{B}$. To say anything sensible about the outcome of the measurement with $\hat{A}$, we need to re-express our wavefunction in terms of the eigenfunctions of $\hat{A}$:

$$\hat{A}\,|\psi_n\rangle = \hat{A}\sum_m c_{mn}\,|\phi_m\rangle \tag{98}$$

We will therefore measure the a_n eigenvalue of $\hat{A}$ with probability $|d_{n1}|^2$. In doing so, we collapse the wavefunction and leave it in the $|\phi_n\rangle$ state. Again, there's uncertainty here because our last two measurements were made with non-commuting operators.

If we have a system with degenerate eigenvalues, it turns out that we can construct a *complete set of commuting observables* (CSCO) and use quantum measurement to prepare a well-defined state. For instance, imagine a case where $\hat{A}$ and $\hat{B}$ commute, and where $\hat{B}$ has non-degenerate eigenvalues in a degenerate subspace of $\hat{A}$. By applying $\hat{A}$ and then $\hat{B}$ to the system, we can uniquely define the final state after the measurements are complete:

$$|\psi\rangle = \sum_{i=1}^{\infty} c_i\,|a_i\rangle \quad \xrightarrow[\text{with result }\alpha]{\text{apply }\hat{A}} \quad |\psi_A\rangle = \sum_{i=1}^{m_\alpha} c_i^\alpha\,|a_i^\alpha\rangle \quad \xrightarrow[\text{with result }\beta]{\text{apply }\hat{B}} \quad |\psi_{AB}\rangle = |b_j\rangle \tag{99}$$

We essentially design a CSCO to filter our wavefunction into ever smaller subspaces, until it is uniquely defined.

Some final takeaways:

- Commuting operators are *compatible* because there is no uncertainty in a chain of measurements $\hat{B}\hat{A}$ provided that $\left[\hat{A}, \hat{B}\right] = 0$. $\hat{A}$ leaves the system in a state where it still has a well-defined eigenvalue when measured with $\hat{B}$. This means that we can make measurements with $\hat{A}$ and $\hat{B}$ simultaneously with perfect precision.

- Non-commuting operators, on the other hand, are *incompatible*, because applying $\hat{B}$ after $\hat{A}$ destroys our knowledge of the state the system was left in after the first measurement. This is a manifestation of the uncertainty principle - we cannot know the precise values of incompatible observables simultaneously.

4.3 The uncertainty principle

For completeness, let's write down Heisenberg's uncertainty principle. Any two quantum operators $\hat{A}$ and $\hat{B}$ must obey:

$$\sigma_A^2 \sigma_B^2 \geq -\frac{1}{4}\left| \langle\psi|\,\hat{A}, \hat{B}\,|\psi\rangle \right|^2 \tag{100}$$

where σ^2 represent the variance of making a measurement of $|\psi\rangle$ with a given operator, e.g.

$$\sigma_A^2 = \langle A^2 \rangle - \langle A \rangle^2 \tag{101}$$

5 The Time-Dependent Schrödinger Equation

Wavefunctions evolve according to the time-dependent Schrödinger equation (TDSE):

$$\hat{H} \ket{\Psi(t)} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(x,y,z) \right] \ket{\Psi(t)} = i\hbar \frac{\partial}{\partial t} \ket{\Psi(t)} \qquad \text{(TDSE)} \qquad (102)$$

$$= E \ket{\Psi(t)} \text{ only if } \ket{\Psi(t)} \text{ is an eigenstate of } \hat{H} \qquad \text{(TISE)} \qquad (103)$$

For conservative systems, we have $\hat{H} \neq \hat{H}(t)$. Let's assume that we have already solved the time-independent Schrödinger equation (TISE), $\hat{H} \ket{\phi_i} = E_i \ket{\phi_i}$, for our set of energy eigenstates $\{\ket{\phi_i}\}$ and corresponding energy eigenvalues $\{E_i\}$.

We can express an arbitrary time-dependent wavefunction $\ket{\Psi(t)}$ in this convenient energy eigenstate basis as:

$$\ket{\Psi(t)} = \sum_i c_i(t) \ket{\phi_i} \qquad (104)$$

We find $c_j(t)$ by plugging our wavefunction into the TSDE $i\hbar \ket{\dot{\Psi}} = \hat{H} \ket{\Psi}$ and projecting with $\bra{\phi_j}$:

$$\bra{\phi_j} i\hbar \frac{\partial}{\partial t} \sum_i c_i(t) \ket{\phi_i} = \bra{\phi_j} \hat{H} \sum_i c_i(t) \ket{\phi_i} = \bra{\phi_j} \sum_i E_i c_i(t) \ket{\phi_i} \qquad (105)$$

Since $\{\ket{\phi_i}\}$ are an orthogonal set, projection with $\bra{\phi_j}$ pulls out just the jth term of the sums:

$$i\hbar \frac{\partial}{\partial t} c_j(t) = E_j c_j(t) \qquad (106)$$

$$\rightarrow \quad \frac{d\,[c_j(t)]}{c_j(t)} = \frac{1}{i\hbar} E_j dt \qquad (107)$$

$$\ln\,[c_j(t)] - \ln\,[c_j(0)] = \frac{1}{i\hbar} E_j t \qquad (108)$$

$$\rightarrow \quad c_j(t) = c_j(0) \cdot e^{-iE_j t/\hbar} \qquad (109)$$

$$\rightarrow \quad \boxed{\ket{\Psi(t)} = \sum_i c_i(0) \ket{\phi_i} e^{-iE_i t/\hbar}} \qquad (110)$$

If we initialize our system in an energy eigenstate with $\ket{\Psi(t=0)} = \ket{\phi_k}$ then

$$\ket{\Psi(t)} = \ket{\phi_k} e^{-iE_k t/\hbar} \qquad (111)$$

The state is therefore modulated in time by a complex sinusoidal oscillation, which oscillates at a frequency closely related to the energy of that eigenstate $\omega_k = E_k/\hbar$.

Note that energy eigenstates feature spatial probability distributions and expectation values that are *independent* of time:

$$\braket{\Psi(t)|\Psi(t)} = \bra{\phi_k} e^{+iE_k t/\hbar} \cdot e^{-iE_k t/\hbar} \ket{\phi_k} = \braket{\phi_k|\phi_k} = 1 \neq f(t) \qquad (112)$$

$$\bra{\Psi(t)}\hat{A}\ket{\Psi(t)} = \bra{\phi_k} e^{+iE_k t/\hbar} \cdot \hat{A} \cdot e^{-iE_k t/\hbar} \ket{\phi_k} = \bra{\phi_k}\hat{A}\ket{\phi_k} = \braket{\hat{A}} \neq \braket{\hat{A}(t)} \qquad (113)$$

Hence why we often refer to energy eigenstates as "stationary states."

This behavior illustrates why it is convenient to work in the basis of energy eigenstates: their time-dependence is simple and often cancels out. Superpositions of energy eigenstates become more complicated as the time dependence won't neatly disappear. This leads to interesting behavior which we will explore in the coming lectures.