The Postulates of QM

- Why postulates?
  - Clarifies assumptions
  - Closely tied with measurement anyway

- QM is based on 6 postulates

- Postulates can’t be proven; validity has been tested by experiments
  - Do the postulates “make sense”?

- No violation of the postulates has been found in the ~70 years since their formulation.
  - Both Planck and Einstein spent their lives trying to find something wrong with Q. M.
  - String Theory may supercede it but for chemists it works very, very well.
1st postulate: meaning of (WF) $\Psi(x,t)$

Postulate 1: The state of a quantum mechanical system is completely specified by a wave function $\Psi(x,t)$. The probability that a particle will be found at time $t$ in a spatial interval of width $dx$ centered at $x_0$ is given by

$$P(x_0,t_0) = \Psi^*(x_0,t_0)\Psi(x_0,t_0)dx$$
Properties of $\Psi(x,t)$

- What is knowable about system is contained in $\Psi(x,t)$
- Tie to physical reality is $\Psi^*(x_0,t_0)\Psi(x_0,t_0)$
- Magnitude of $|\Psi(x,t)|$ always > 0
- Two $\Psi(x,t)$ differing only by phase $e^{i\theta}$ are not distinguishable
- Link to probability means that

$$\int_{-\infty}^{\infty} P(x,t) \, dx = \int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t) \, dx = 1$$

This is the normalization condition.
Conditions on $\Psi(x,t)$

$\Psi(x,t)$ must be single valued

Otherwise two different probabilities for same x
More conditions on $\Psi(x,t)$

$\Psi(x,t)$ must be continuous. Otherwise $\frac{d^2\psi(x)}{dx^2}$ doesn’t exist.

WF must be a good function, well behaved and vanish at infinity (to be square integrable).
2nd postulate relates observables and operators

Postulate 2: For every measurable property of the system in classical mechanics such as position, momentum and energy, there exists a corresponding operator in quantum mechanics.

Properly combining the operator and the wave function will enable you to compute average values, that then may be compared with the average value of the experimentally measured quantities.

The outcome of a single experiment will be quite different from that of the average outcome.
Some frequently used operators

<table>
<thead>
<tr>
<th>Observable</th>
<th>Operator</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Momentum:</td>
<td>$-i\hbar \frac{\partial}{\partial x}$</td>
<td>$\hat{p}_x$</td>
</tr>
<tr>
<td>Kinetic Energy:</td>
<td>$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$</td>
<td>$\hat{E}_{kinetic} = \hat{T} = \frac{1}{2m}(\hat{p}_x)\hat{p}_x$</td>
</tr>
<tr>
<td>Position:</td>
<td>$x$</td>
<td>$\hat{x}$</td>
</tr>
<tr>
<td>Potential Energy:</td>
<td>$V(x)$</td>
<td>$\hat{E}_{potential} = \hat{V}$</td>
</tr>
<tr>
<td>Total Energy</td>
<td>$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$</td>
<td>$\hat{H} = \hat{T} + \hat{V}$</td>
</tr>
</tbody>
</table>
### Some other operators

<table>
<thead>
<tr>
<th>Observable</th>
<th>Operator</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>((\hat{x} - \langle x \rangle)^2)</td>
<td>(\hat{\sigma}_x^2)</td>
</tr>
<tr>
<td>Variance</td>
<td>((\hat{x} - \langle x \rangle)^2)</td>
<td>(\hat{\sigma}_x^2)</td>
</tr>
<tr>
<td>Momentum</td>
<td>((\hat{p} - \langle p \rangle)^2)</td>
<td>(\hat{\sigma}_p^2)</td>
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</table>
Postulate 3: In any single measurement of the observable of interest at the moment (eg. X or P) the only values that you can measure are ones contained in the set of the possible values of that observable (ie. The set of all eigenvalues of that operator.)

Example: Total energy of a hydrogen atom: You can only measure energies which are eigenvalues of the Hamiltonian for the hydrogen atom system.
Postulate 4: The system is in a state described by $\Psi(x,t)$. The individual values of the observable $a$ (e.g. $X$, $P$, $E$, $V$) are obtained by measuring many identically prepared systems once. The average value (also called expectation value) of $a$, $\langle a \rangle$ is given by

$$\langle a \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x,t) \hat{A} \Psi(x,t) \, dx}{\int_{-\infty}^{\infty} \Psi^*(x,t) \Psi(x,t) \, dx}$$
\( \Psi(x, t) \) either is or is not an eigenfunction of \( \hat{A} \). Assume it is.

\( \Psi(x, t) \) normalized EF of \( \hat{A} \), \( \phi_j(x, t) \) with eigenvalue \( a_j \)

Then \( \hat{A} \phi_j(x, t) = a_j \phi_j(x, t) \)

\[
\langle a \rangle = \int_{-\infty}^{\infty} \phi_j^*(x, t) \hat{A} \phi_j(x, t) dx = a_j \int_{-\infty}^{\infty} \phi_j^*(x, t) \phi_j(x, t) dx
\]

\( \langle a \rangle = a_j \)

Every measurement gives the same result, \( a_j \)
Wave Function is **Not an Eigenfunction** of the observable of interest

We write the wave function in terms of the eigenfunctions of the observable of interest, $A$, (e.g. $A = X, P, H$ etc.). We expand the wave function as a linear sum of the eigenfunctions of $A$. This implies that the set of functions of any operator are complete. They are thought to be complete.

\[
\hat{A}\phi_n(x) = a_n\phi_n(x)
\]

\[
\Psi(x,t) = \sum_n b_n(t)\phi_n(x)
\]

\[
\hat{A}\Psi(x,t) = \sum_n b_n(t)a_n\phi_n(x)
\]
The eigenfunctions of $A$ are orthonormal.
The wave function is normalized.

\[ \int_{x} \phi_{m}^{*}(x) \phi_{n}(x) dx = \delta_{m,n} \]

\[ 1 = \int_{x} \Psi^{*}(x,t) \Psi(x,t) dx = \int_{x} \left\{ \sum_{m} b_{m}(t) \phi_{m}(x) \right\}^{*} \left\{ \sum_{n} b_{n}(t) \phi_{n}(x) \right\} dx \]

\[ 1 = \left\{ \sum_{m,n} b_{m}^{*}(t) b_{n}(t) \int_{x} \phi_{m}^{*}(x) \phi_{n}(x) dx \right\} = \sum_{m,n} b_{m}^{*}(t) b_{n}(t) \delta_{m,n} \]

\[ 1 = \sum_{m} b_{m}^{*}(t) b_{m}(t) = \sum_{m} P_{m}(t) \]

The meaning of $P_{m}(t)$

These are the probabilities of measuring the mth eigenvalue of $A$: $a_{m}$
Using the properties of The expansion write out the expectation value.

\[
\int \phi_m^*(x) \Psi(x, t) dx = \sum_n b_n(t) \int \phi_n^*(x) \phi_n(x) dx = \sum_n b_n(t) \delta_{n,m}
\]
\[
= b_m(t)
\]

\[
\int \Psi^*(x, t) \phi_m(x) dx = b_m^*(t)
\]

\[
\langle a \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx}{\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx}
\]

\[
1 = \int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx
\]

\[
\langle a \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) = \sum_n b_n(t) a_n \int \Psi^*(x, t) \phi_n(x) dx
\]
\[
= \sum_n b_n(t) a_n b_n^*(t) = \sum_n p_n(t) a_n
\]
Probabilities and Averages

From our discussion on measurement: If we have the probability of measuring each possible value, what is the average?

\[ \langle a(t) \rangle = \sum_m a_m P_m(t) \]

This must be what we should obtain for the average.

What is the average of \( A^2 \)?

\[ \langle a^2(t) \rangle = \sum_m a_m^2 P_m(t) \]

Let’s convince ourselves that Postulate 4 gives us these results using the fundamental definitions on the previous slides.
In this case......

Expectation value given by

\[ \langle a \rangle = \int \Psi^* (x,t) \hat{A} \Psi (x,t) \, dx \]

\[ = \int \left( \sum_{m=1}^{\infty} b_m^* \phi_m^* (x,t) \right) \left( \sum_{n=1}^{\infty} a_n b_n \phi_n (x,t) \right) \, dx \]

\[ = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} b_m^* b_n a_n \int \phi_m^* (x,t) \phi_n (x,t) \, dx \]

Because EF are orthogonal, only nonzero terms in sum are for \( m = n \).
The expectation value is a weighted average of the different possible eigenvalues.

What will be observed in individual experiment?

The measurement process in any experimental system (QM or otherwise) is inherently probabilistic! There is no way to predict the outcome of an individual experiment if the WF is not an EF.
First measurement on a system is probabilistic, but second is deterministic!

**Copenhagen interpretation:** Appears that measurement has converted WF to a single EF.
5th Postulate:
The wave function evolves in time following a time-dependent Schrödinger Like Equation of Motion:

\[ i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{H} \Psi(x,t) \]

Solutions to time independent Schrödinger equation come from the Eigenfunctions of the Hamiltonian (energy) operator.

\[ \Psi(x,t) = e^{-i\omega t} \psi_n(x) \]

Plug this solution into the Schrödinger equation to generate the time independent wave equation:

\[ i\hbar \frac{\partial \psi_n(x) e^{-i\omega t}}{\partial t} = \hat{H} \psi_n(x) e^{-i\omega t} \]

\[ i\hbar \psi_n(x) e^{+i\omega t} \frac{\partial e^{-i\omega t}}{\partial t} = \hat{H} \psi_n(x) \]

\[ \hbar \omega_n \psi_n(x) = \hat{H} \psi_n(x) \]

\[ \hat{H} \Psi_n(x,t) = E_n \psi_n(x) \]

\[ \hbar \omega_n = E_n \]
Compare Measurement Predictions with QM Rules

• The formula for computing expectation values of any classical object are the same as that used for Quantum Mechanics.
• The “collapse of the wave function” is what happens when we do measurements anyway.
• Let’s do Matrix Mechanics on Classical Objects.