

Chapter 3. The Quantum Mechanical Postulates

Postulates 1: A quantum state is completely specified by a wave function, which is the solution of the Schrödinger equation.

Born's interpretation: The probability of finding the system between x and $x+dx$ is proportional to $|\Psi(x)|^2 dx$.

As a result, a wavefunction must be

- i. normalized, $\int |\Psi|^2 dx = \int \Psi^* \Psi dx = 1$
- ii. single valued,
- iii. finite,
- iv. continuous in zeroth and first derivatives.

Generalization:

3D: $\Psi^*(x, y, z)\Psi(x, y, z)dxdydz$

2 particles: $\Psi^*(\mathbf{r}_1, \mathbf{r}_2)\Psi(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2$, where $\mathbf{r} = (x, y, z)$

Ψ is the probability amplitude, and $|\Psi|^2$ is the probability density.

Postulate 2: Every observable has a corresponding quantum operator. Measuring an observable is equivalent to applying the operator on a wave function.

All quantum operators are Hermitian

$$\int \psi^* [\hat{O}\phi] dx = \int [(\hat{O}\psi)]^* \phi dx$$

whose eigenvalues are always real and eigenfunctions are complete and orthonormal:

$$\int \Psi_n^* \Psi_m dx = \delta_{nm}$$

where the Kroenecker delta is defined as

$$\delta_{nm} = \begin{cases} 1, & \text{if } n = m \\ 0, & \text{if } n \neq m \end{cases}$$

Postulate 3: Each measurement only yields an eigenvalue as the observable.

Postulate 4: For many measurements, the average observable is given by the expectation value:

$$\langle a \rangle = \frac{\int \Psi^* \hat{A} \Psi dx}{\int \Psi^* \Psi dx}$$

If Ψ is an eigenstate ($\Psi = \Psi_n, \hat{A}\Psi_n = a_n\Psi_n$), then $\langle a \rangle$ is simply a_n :

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi dx = \int \Psi_n^* a_n \Psi_n dx = a_n \int \Psi_n^* \Psi_n dx = a_n$$

what if Ψ is not an eigenstate?

$$\Psi(x) = \sum_n b_n \Psi_n \quad (\text{completeness})$$

Superposition principle

$$\begin{aligned} \langle a \rangle &= \int \left(\sum_n b_n \Psi_n \right)^* \hat{A} \left(\sum_m b_m \Psi_m \right) d\tau \\ &= \int \left(\sum_n b_n \Psi_n \right)^* \left(\sum_m b_m a_m \Psi_m \right) d\tau && (\int \Psi_n^* \Psi_m d\tau = \delta_{nm}) \\ &= \sum_n \sum_m b_n^* b_m a_m \int \Psi_n^* \Psi_m d\tau \\ &= \sum_n |b_n|^2 a_n \end{aligned}$$

- i. Each measurement always yields one of the eigenvalues,
- ii. The chance for a particular eigenvalue (a_n) to appear in a measurement is given by $|b_n|^2$.
- iii. Average value of many measurements is given by $\langle a \rangle$.

Interestingly, the precise state of the system is unknown until the measurement, which collapses the system to an eigenstate.

Example: an electron in a molecule (e.g., H_2) is described by a molecular orbital, which is a superposition of atomic orbitals:

$$\Phi^{MO} = \sum_n c_n \Psi_n^{AO} = c_1 1s_1 + c_2 1s_2$$

Same as double slit.