

Chem. 540
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Postulates of Quantum Mechanics

1. *Wavefunction*

The state of a system is described by a vector in a Hilbert space. The state of a system can be fully specified by its wavefunction in position space, $\Psi(\mathbf{r};t)$, or by its wavefunction in momentum space, $\tilde{\Psi}(\mathbf{p};t)$ etc.

The probability of finding the particle within a volume $d\mathbf{r}$ around point \mathbf{r} is equal to $|\Psi(\mathbf{r})|^2 d\mathbf{r}$.

In order for the probability of finding the particle anywhere to be equal to unity, we require wavefunctions to be normalized:

$$\int d\mathbf{r} |\Psi(\mathbf{r})|^2 = 1.$$

Hilbert space is a vector space (over complex-valued vectors) of up to infinite dimension, which is complete, and in which the inner product $\mathbf{u}^* \cdot \mathbf{v}$ is finite.

2. Operators

States are transformed by linear operators:

$$\hat{A}(\alpha \Psi_1 + \beta \Psi_2) = \alpha \hat{A} \Psi_1 + \beta \hat{A} \Psi_2 .$$

The commutator of two operators \hat{A}, \hat{B} is defined as

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} .$$

If the commutator of two operators is equal to zero we say that the operators commute. This is not always the case.

To every physical observable corresponds a Hermitian operator. An operator \hat{A} is called Hermitian if

$$\int d\mathbf{r} \Psi_1^*(\mathbf{r}) \hat{A} \Psi_2(\mathbf{r}) = \left\{ \int d\mathbf{r} \Psi_2^*(\mathbf{r}) \hat{A} \Psi_1(\mathbf{r}) \right\}^*$$

for any two wavefunctions Ψ_1, Ψ_2 .

3. Uncertainty principle

The momentum operator is a vector with components $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$, etc.

Therefore the operators for position and momentum satisfy the commutation relation

$$[\hat{x}, \hat{p}_x] = \hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar .$$

This implies that it is not possible to determine simultaneously the position and momentum of a particle to precision better than Planck's constant:

$$\Delta p_x \Delta x \geq \hbar / 2 .$$

4. *Measurement*

A given physical observable can take only certain values, which are the eigenvalues of the corresponding quantum mechanical operator.

Eigenvalue equation: $\hat{A}\Phi_n = A_n\Phi_n$

The eigenstates of a hermitian operator form a complete set; i.e., if $\{\Phi_n\}$ are all the eigenstates of an operator \hat{A} , then any other state in the same space can be expanded uniquely in terms of $\{\Phi_n\}$, i.e.,

$$\Psi = \sum_n c_n \Phi_n$$

where c_n are complex numbers.

The eigenvalues A_n of hermitian operators are real valued, and the eigenstates Φ_n are mutually orthogonal. Orthogonality is a condition on the “overlap integral” between two functions,

$$S_{nm} \equiv \int d\mathbf{r} \Phi_n^*(\mathbf{r})\Phi_m(\mathbf{r}).$$

If this overlap is zero, we say that the states Φ_n, Φ_m are orthogonal to each other. In other words, the eigenstates of hermitian operators satisfy the relation

$$\int d\mathbf{r} \Phi_n^*(\mathbf{r})\Phi_m(\mathbf{r}) = \delta_{nm},$$

where δ_{nm} is the Kronecker delta:

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

This postulate states that when the wavefunction Ψ is an eigenfunction of the operator \hat{A} corresponding to the observable of interest, the determination of A always yields one result, the corresponding eigenvalue A_n of \hat{A} . Note that the state of the system changes to Φ_n as a result of this measurement. When Ψ is not an eigenfunction of \hat{A} , a single measurement of A yields a single result which is one of the eigenvalues of \hat{A} ; the probability that a particular eigenvalue A_n is measured is equal to $|c_n|^2$, where c_n is the coefficient of the eigenfunction Φ_n in the expansion of the wavefunction Ψ .

5. *Time evolution*

The time evolution of states satisfies the linear partial differential equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = \hat{H} \Psi(t)$$

where \hat{H} is the operator that corresponds to the energy of the system. Thus, usually (in Cartesian coordinates, assuming no magnetic fields are present) \hat{H} has the form

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}.$$

\hat{H} is called the Hamiltonian operator, and the differential equation is called the time-dependent Schrödinger equation.