POSTULATES OF QUANTUM MECHANICS

- **Quantum-mechanical states**

  - In the coordinate representation, the state of a quantum-mechanical system is described by the wave function $\psi(q,t) = \psi(q_1,\ldots,q_f,t)$ (in Dirac's notation, ket $|\psi\rangle$ or $|\psi(t)\rangle$; f is the number of degrees of freedom). In the case of a single particle moving along the x axis, we would write $\psi = \psi(x,t)$. In the case of an unconstrained motion of a single particle in three dimensions, described by the radius vector $\mathbf{r}$ or the three Cartesian coordinates x, y, and z, we would write $\psi = \psi(\mathbf{r},t) \equiv \psi(x,y,z,t)$. In the case of an unconstrained motion of N particles in three dimensions, described by the radii vectors $\mathbf{r}_i$ or the Cartesian coordinates x_i, y_i, and z_i, with $i = 1,\ldots,N$, we would write $\psi = \psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t) \equiv \psi(x_1,y_1,z_1,\ldots,x_N,y_N,z_N,t)$. Other choices of coordinates $q_1,\ldots,q_f$ can be used, particularly when there are constraints ($f < 3N$). We require that the wave function $\psi(q,t)$ is bounded, continuous, single-valued, and has continuous first derivatives. The wave function $\psi(q,t)$ (or ket $|\psi\rangle$) contains *all* information that can be determined about the state of a system of interest.

  - Bound states are characterized by the condition

$$||\psi|| = \langle\psi|\psi\rangle^{\frac{1}{2}} = \left(\int_\Gamma \psi^*(q,t)\psi(q,t)d\tau\right)^{\frac{1}{2}} < \infty$$

    (Γ is the corresponding configuration space). The physically meaningful wave functions describing bound states should be normalized to unity, so that

$$||\psi|| = 1.$$

    For the normalized wave functions, the expression

$$P(q,t) = |\psi(q,t)|^2$$

    has a meaning of the position probability density.

- **Operators representing dynamical variables**

  - Each dynamical variable $F = F(q, p, t)$ $[q \equiv (q_1, \ldots, q_f)$, $p \equiv (p_1, \ldots, p_f)]$ is represented by a linear self-adjoint operator $\hat{F}$ defined in the Hilbert space $L^2(\Gamma)$ (for our purposes, self-adjoint = Hermitian, but strictly speaking these are not identical terms; $L^2(\Gamma)$ is a space of square-integrable functions and, strictly speaking, one should define $\hat{F}$ in a suitable subspace of $L^2(\Gamma)$ which defines the domain of $\hat{F}$). Normally, we define the operator $\hat{F}$ as follows,

  $$\hat{F} = F(\hat{q}_1, \ldots, \hat{q}_f, \hat{p}_1, \ldots, \hat{p}_f, t), \tag{1}$$

  where $\hat{q}_1, \ldots, \hat{q}_f$ and $\hat{p}_1, \ldots, \hat{p}_f$ are the operators representing the coordinates and momenta, respectively. If there is a choice between several forms of the operator $\hat{F}$ that result from Eq. (1), we choose the form that guarantees that the resulting operator $\hat{F}$ is self-adjoint. In particular, the operator $\hat{F}$ has to satisfy the condition

  $$\begin{aligned} \langle \phi | \hat{F} \psi \rangle &\equiv \int_\Gamma \phi^*(q, t) \, [\hat{F} \, \psi(q, t)] \, d\tau \\ &= \int_\Gamma [\hat{F} \, \phi(q, t)]^* \, \psi(q, t) \, d\tau \equiv \langle \hat{F} \phi | \psi \rangle. \end{aligned}$$

  - In the coordinate representation, the coordinate and momentum operators, $\hat{q}_l$ and $\hat{p}_l$, respectively, $(l = 1, \ldots, f)$ are defined as follows,

  $$\hat{q}_l \phi(q) = q_l \phi(q),$$

  $$\hat{p}_l \phi(q) = -i\hbar \frac{\partial}{\partial q_l} \phi(q),$$

  where $\phi(q)$ is a function of coordinates $q_1, \ldots, q_f$.

- **Interpretation of quantum-mechanical calculations**

  - The only possible result of a single precise measurement of the dynamical variable F is a real number λ_μ that belongs to a spectrum of the corresponding operator $\hat{F}$. The spectrum of self-adjoint operator $\hat{F}$ can be discrete or continuous and, in general, is a subset of real numbers. We can write the equation

  $$\hat{F} | f_\mu \rangle = \lambda_\mu | f_\mu \rangle, \tag{2}$$

  where ket $| f_\mu \rangle$ corresponds to function $f_\mu(q)$, which is associated with λ_μ from the spectrum of $\hat{F}$. Each λ_μ is interpreted as a value of F in the quantum state described by $|f_\mu\rangle$. In the case of the discrete part of the spectrum of $\hat{F}$, describing bound states (which corresponds to the values of λ_μ belonging to a point spectrum of $\hat{F}$), Eq. (2) describes the well-known eigenvalue problem for the self-adjoint operator $\hat{F}$. The resulting λ_μ values are the eigenvalues of $\hat{F}$ and $|f_\mu\rangle$ are the corresponding eigenstates, which can be made orthonormal, so that $\langle f_\mu|f_\nu\rangle = \delta_{\mu\nu}$ ($\delta_{\mu\nu}$ is the Kronecker delta). In the continuous (scattering) case, the resulting λ_μ values belong to a continuous part of the spectrum of $\hat{F}$ and we can view λ_μ as a continuous function of the label μ. Although the corresponding states $|f_\mu\rangle$ no longer belong to the $L^2(\Gamma)$ space, they can be normalized using the Dirac delta function, so that $\langle f_\mu|f_\nu\rangle = \delta(\mu - \nu)$ ($\delta(\mu - \nu)$ is the Dirac delta function).

- The probability that in the quantum state described by $|\psi\rangle$ the dynamical variable F (observable) equals to one of the eigenvalues λ_μ [discrete case; we designate this probability by $P(F = \lambda_\mu)$] or the probability that the value of the observable F belongs to an interval $[\lambda_\mu, \lambda_\mu + d\lambda_\mu]$ (continuous case; we designate this probability by $P(F \in [\lambda_\mu, \lambda_\mu + d\lambda_\mu])$), is proportional to $|c_\mu|^2$, where

$$c_\mu = \langle f_\mu|\psi\rangle \equiv \int_\Gamma f_\mu^*(q)\, \psi(q, t)\, d\tau.$$

are the coefficients defining the expansion

$$|\psi\rangle = \mathcal{S}_\mu c_\mu |f_\mu\rangle$$

($\mathcal{S}_\mu = \sum_\mu$ in the discrete case and $\mathcal{S}_\mu = \int d\mu$ in the continuous case). For the normalized states $|\psi\rangle$ ($||\psi|| = 1$), we have

$$P(F = \lambda_\mu) = |c_\mu|^2$$

in the discrete case, and

$$P(F \in [\lambda_\mu, \lambda_\mu + d\lambda_\mu]) = |c_\mu|^2\, d\mu$$

in the continuous case.

- The expectation (mean) value of the observable F in the quantum state described by the normalized ket $|\psi\rangle$, which is defined as

$$\langle \hat{F}\rangle = \sum_\mu \lambda_\mu P(F = \lambda_\mu) = \sum_\mu \lambda_\mu |c_\mu|^2$$

in the discrete case, and as

$$\langle \hat{F} \rangle = \int \lambda_\mu P(F \in [\lambda_\mu, \lambda_\mu + d\lambda_\mu]) = \int \lambda_\mu |c_\mu|^2 d\mu$$

in the continuous case, is calculated using the formula

$$\langle \hat{F} \rangle = \langle \psi | \hat{F} | \psi \rangle = \int_\Gamma \psi^*(q,t) \hat{F} \psi(q,t)\, d\tau.$$

If the wave function ψ is not normalized to unity, we use

$$\langle \hat{F} \rangle = \frac{\langle \psi | \hat{F} \psi \rangle}{\langle \psi | \psi \rangle} \equiv \frac{\int_\Gamma \psi^*(q,t)\, \hat{F}\, \psi(q,t)\, d\tau}{\int_\Gamma \psi^*(q,t)\, \psi(q,t)\, d\tau}\,.$$

- **Time evolution of quantum-mechanical systems**

  - The time evolution of quantum-mechanical systems is described by the equation of motion called (in the Schrödinger picture) the time-dependent Schrödinger equation,

    $$i\hbar \frac{\partial}{\partial t} \psi(q,t) = \hat{H} \psi(q,t),$$

    where

    $$\hat{H} = H(\hat{q}_1, \ldots, \hat{q}_f, \hat{p}_1, \ldots, \hat{p}_f, t)$$

    is an operator representing the Hamiltonian of the system (a quantum-mechanical operator representing the Hamilton function). Alternatively, we can write,

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

  - When $\frac{\partial H}{\partial t} = 0$, the most general solution of the Schrödinger equation can be given the form

    $$\psi(q', t') = i \int_\Gamma G(q', t'; q, t) \psi(q,t) d\tau,$$

    where the spectral representation of Green's function $G(q', t'; q, t)$ is

    $$G(q', t'; q, t) = -i \mathcal{S}_\mu u_\mu(q') u_\mu^*(q) e^{-iE_\mu(t'-t)/\hbar},$$

    where $u_\mu(q)$ and E_μ are, respectively, the eigenfunctions and the eigenvalues of the Hamiltonian (including solutions corresponding to a continuous part of the spectrum of $\hat{H}$, if there is any). Alternatively, the wave function $\psi(q,t)$ at coordinates q and time t can be given the form

$$\psi(q,t) = \mathcal{S}_\mu c_\mu(t)\, u_\mu(q),$$

where the time-dependent coefficients $c_\mu(t)$ can be calculated as follows:

$$c_\mu(t) = e^{-iE_\mu(t-t_0)/\hbar}\, c_\mu(t_0),$$

with

$$c_\mu(t_0) = \int_\Gamma u_\mu^*(q)\, \psi(q,t_0)\, d\tau$$

determined from the information about the initial form of the wave function $\psi(q,t_0)$ for all values of the coordinates $q_1,\ldots,q_f$ at some fixed time t_0. In particular, if the initial state at t_0 is defined as

$$\psi(q,t_0) = u_m(q)$$

(at time $t = t_0$, the wave function ψ is one of the normalized eigenfunctions of the Hamiltonian corresponding to a discrete state $|u_m\rangle$), we can write $c_m(t_0) = 1$ and $c_\mu(t_0) = 0$ for $\mu \neq m$, so that

$$\psi(q,t) = e^{-iE_m(t-t_0)/\hbar}\, u_m(q). \tag{3}$$

The solutions of the time-dependent Schrödinger equation described by Eq. (3) are sometimes referred to as the stationary solutions, since in this case the probability density,

$$P(q,t) = |\psi(q,t)|^2 = \psi^*(q,t)\,\psi(q,t) = u_m^*(q)\, u_m(q) = |u_m(q)|^2,$$

does not depend on time. The eigenvalue or eigenvalue-like equation for the Hamiltonian,

$$\hat{H} u_\mu(q) = E_\mu u_\mu(q),$$

which is used to determine $u_\mu(q)$ and E_μ in the discrete case and $u_\mu(q)$ in the continuous (i.e. scattering) case is often referred to as the time-independent Schrödinger equation.