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.

TIME EVOLUTION OF QUANTUM-MECHANICAL SYSTEMS

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

$$\psi = \psi(\underbrace{q_1, \ldots, q_f}_{q}, t) \equiv \psi(q, t)$$

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

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

If $\frac{\partial H}{\partial t} = 0$, then among the solutions of the Schrödinger equation we can find

$$\psi(q,t) = e^{-iE(t-t_0)/\hbar}\, u(q),$$

where

$$\hat{H} u = E u \,.$$

These special solutions are stationary,

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

does not depend on time

$$\frac{\partial P}{\partial t} = 0 .$$

GENERAL SOLUTION

We will assume that $\frac{\partial H}{\partial t} = 0$.

✓ $\psi(q,t) = \sum_\mu c_\mu(t)\, u_\mu(q)$

✓ $|\psi(t)\rangle = \sum_\mu c_\mu(t)\, |u_\mu\rangle$

where

$$\hat{H}|u_\mu\rangle = E_\mu |u_\mu\rangle$$ ✓

$(u_\mu = u_\mu(q))$

$\sim dq_1 \ldots dq_f$

✓ $c_\mu(t) = \langle u_\mu | \psi(t)\rangle$

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

$$\text{lhs} = i\hbar \frac{\partial \psi}{\partial t}$$

$$= i\hbar \frac{\partial}{\partial t} \sum_\mu c_\mu(t)\, u_\mu(q)$$

$$\text{lhs} = i\hbar \sum_\mu \frac{d c_\mu(t)}{dt} u_\mu(q)$$

$$\text{rhs} = \hat{H}\psi(q,t)$$

$$= \hat{H} \sum_\mu c_\mu(t) u_\mu(q)$$

$$= \sum_\mu c_\mu(t) \hat{H} u_\mu(q)$$

$$= \sum_\mu c_\mu(t) E_\mu u_\mu(q)$$

$$\text{lhs} = \text{rhs}$$

linearly independent

$$i\hbar \sum_\mu \frac{d c_\mu(t)}{dt} u_\mu(q) = \sum_\mu c_\mu(t) E_\mu u_\mu(q)$$

At $u_\mu(q)$:

$$i\hbar \frac{dc_\mu(t)}{dt} = E_\mu c_\mu(t)$$

Solution:

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

$$c_\mu(t_0) = \langle u_\mu | \psi(t_0)\rangle$$

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

$\sim dq_1' \ldots dq_f'$

$$\psi(q,t) = S_\mu\, c_\mu(t)\, u_\mu(q)$$

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

$\psi(q', t_0) \rightarrow$ initial ψ

$$\psi(q,t) = S_\mu \left(\int_\Gamma u_\mu^*(q')\, \psi(q', t_0)\, d\tau' \right) \times e^{-iE_\mu (t-t_0)/\hbar}$$

$u_\mu(q)$

$$= \int_\Gamma \left[S_\mu\, u_\mu^*(q')\, u_\mu(q)\, e^{-iE_\mu (t-t_0)/\hbar} \right] \times \psi(q', t_0)\, d\tau'$$

$$\psi(\overset{q'}{q}, \overset{t'}{t}) = i \int_\Gamma G(\overset{q'}{q}, \overset{t'}{t}; \overset{q}{q'}, \overset{t}{t_0})\, \psi(\overset{q}{q'}, \overset{t}{t_0})\, d\tau'$$

$$G(q,t;q',t_0) = -i\, S_\mu\, u_\mu^*(\overset{q}{q'})\, u_\mu(\overset{q'}{q}) \times e^{-iE_\mu (\underset{t'}{t} - \underset{t}{t_0})/\hbar}$$

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

kernel

$$G(q',t';q,t) = -i\sum_\mu u_\mu(q')\,u_\mu^*(q) \times e^{-iE_\mu(t'-t)/\hbar}$$ ✓✓

G → Green's function (propagator)

Let us check this by looking at $\psi(q,t) \rightarrow \psi(q',t)$. $t'=t$

We anticipate the following result:

✓ $$G(q',t;q,t) = -i\delta(q-q')$$

$$i\int_{\Gamma} G(q',t;q,t)\,\psi(q,t)\,dq$$

$$= i(-i)\int_{\Gamma} \delta(q-q')\,\psi(q,t)\,dq$$

$$= \psi(q',t)$$

Verification:

$$G(q',t;q,t) = -i\sum_{\mu} u_{\mu}(q')\,u_{\mu}^{*}(q) \times \underbrace{e^{-iE_{\mu}\underbrace{(t-t)}_{=0}/\hbar}}_{1}$$

$$= -i\sum_{\mu} u_{\mu}(q')\,u_{\mu}^{*}(q)$$

closure

$$= -i\,\delta(q-q')$$

COMMUTATORS AND SIMULTANEOUS VARIABLES

Conditions under which several observables can have well-defined values in the same state $|\varphi\rangle$.

F has a well-defined value λ_μ if $|\varphi\rangle = |f_\mu\rangle$,

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

$$\lambda_\mu = \langle f_\mu|\hat{F}|f_\mu\rangle \quad (\||f_\mu\|=1)$$

If $|f_\mu\rangle$ is an eigenfunction of several operators,

$$\hat{F}_1 |f_\mu\rangle = \lambda_\mu^{(1)} |f_\mu\rangle,$$

$$\hat{F}_2 |f_\mu\rangle = \lambda_\mu^{(2)} |f_\mu\rangle, \ldots,$$

then $F_1, F_2, \ldots$ have well defined values $(\lambda_\mu^{(1)}, \lambda_\mu^{(2)}, \ldots)$.

Example:

$$u_{\vec{k}}(\vec{r}) = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}\cdot\vec{r}}$$

$$\hat{\vec{p}}\, u_{\vec{k}}(\vec{r}) = (\hbar \vec{k})\, u_{\vec{k}}(\vec{r})$$

Momentum is known precisely and so is kinetic energy,

$$\hat{T} u_{\vec{k}} = \frac{\hat{\vec{p}}^{\,2}}{2m} u_{\vec{k}}$$

$$= \left(\frac{(\hbar \vec{k})^2}{2m} \right) u_{\vec{k}} ,$$

but L^2 and L_z are not,

$$\hat{L}_z u_{\vec{k}}(\vec{r}) = (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) u_{\vec{k}}(\vec{r})$$

$$= [x(\hbar k_y) - y(\hbar k_x)] u_{\vec{k}}(\vec{r})$$

$\neq$ number times $u_{\vec{k}}(\vec{r})$

Conditions that allow us to state which observables can have well-defined values in the same state.

Definition: F_1 and F_2 have well-defined values iff all $|\psi_n\rangle$s are eigenstates of $\hat{F}_1$ and $\hat{F}_2$

Theorem: Two observables F_1 and F_2 have well-defined values in the same state iff $[\hat{F}_1, \hat{F}_2] = 0$.

Proof:

$\longrightarrow$ (F_1 and F_2 have well-defined values $\Rightarrow [\hat{F}_1, \hat{F}_2] = 0$)

$$-\hat{F}_2 \Big/ \ \hat{F}_1 |f_\mu\rangle = \lambda_\mu^{(1)} |f_\mu\rangle$$

$$+\hat{F}_1 \Big/ \ \hat{F}_2 |f_\mu\rangle = \lambda_\mu^{(2)} |f_\mu\rangle$$

$$(\hat{F}_1\hat{F}_2 - \hat{F}_2\hat{F}_1)|f_\mu\rangle$$

$$= \lambda_\mu^{(2)} \hat{F}_1 |f_\mu\rangle - \lambda_\mu^{(1)} \hat{F}_2 |f_\mu\rangle$$

$$= \lambda_\mu^{(2)} \lambda_\mu^{(1)} |f_\mu\rangle$$

$$- \lambda_\mu^{(1)} \lambda_2^{(2)} |f_\mu\rangle$$

$$= 0$$

$$(\hat{F}_1 \hat{F}_2 - \hat{F}_2 \hat{F}_1) |f_\mu\rangle$$

$$= [\hat{F}_1, \hat{F}_2] |f_\mu\rangle = 0$$

$$[\hat{F}_1, \hat{F}_2] |f_\mu\rangle = 0 \quad \forall \mu$$

$|\varphi\rangle \in \mathcal{H}$ (arbitrary $|\varphi\rangle$)

$$|\varphi\rangle = \sum_\mu c_\mu |f_\mu\rangle$$

$$[\hat{F}_1, \hat{F}_2]|\varphi\rangle$$

$$= \sum_\mu c_\mu \underbrace{[\hat{F}_1, \hat{F}_2]|f_\mu\rangle}_{0}$$

$$= 0$$

$$[\hat{F}_1, \hat{F}_2] = 0$$

$\therefore$

$\longleftarrow$ $\left([\hat{F}_1, \hat{F}_2] = 0 \Rightarrow \hat{F}_1 \text{ and } \hat{F}_2 \text{ share eigenstates (all)}\right)$

$$[\hat{F}_1, \hat{F}_2] = 0$$

Let $\{|f_\mu\rangle\}$ be the complete and orthonormal set of eigenstates of $\hat{F}_1$:

$$\hat{F}_2 \,/\, \hat{F}_1 |f_\mu\rangle = \lambda_\mu^{(1)} |f_\mu\rangle .$$

$$[\hat{F}_1, \hat{F}_2] = 0 \qquad \underbrace{\hat{F}_2 \hat{F}_1}_{\hat{F}_1 \hat{F}_2} |f_\mu\rangle = \lambda_\mu^{(1)} \hat{F}_2 |f_\mu\rangle$$

$$\hat{F}_1 \left(\hat{F}_2 |f_\mu\rangle\right) = \lambda_\mu^{(1)} \left(\hat{F}_2 |f_\mu\rangle\right)$$

$\hat{F}_2 |f_\mu\rangle$ is an eigenstate of $\hat{F}_1$ corresponding to $\lambda_\mu^{(1)}$.

Two possibilities:

- $\lambda_\mu^{(1)}$ is nondegenerate,

— $\lambda_\mu^{(1)}$ is degenerate.

When $\lambda_\mu^{(1)}$ is nondegenerate,

$$\hat{F}_2|f_\mu\rangle \sim |f_\mu\rangle \checkmark$$

We can state that there exists $\lambda_\mu^{(2)}$ such that

$$\hat{F}_2|f_\mu\rangle = \lambda_\mu^{(2)}|f_\mu\rangle,$$

i.e., $|f_\mu\rangle$ is an eigenstate of $\hat{F}_2$.

When $\lambda_\mu^{(1)}$ is degenerate,

$$\hat{F}_1|f_{\mu p}\rangle = \lambda_\mu^{(1)}|f_{\mu p}\rangle,$$

$$\underbrace{\{ |f_{\mu p}\rangle, \ p = 1, \ldots, n_\mu \}}_{\text{eigenstate of } \hat{E}_1 \text{ corr. to } \lambda_\mu^{(1)}} \quad \text{(eigen-space)}$$

degeneracy

$$\hat{F}_2 |f_{\mu p}\rangle = \sum_{q=1}^{n_\mu} a_{qp} |f_{\mu q}\rangle$$

We can always transform $|f_{\mu q}\rangle$s among themselves such that matrix $|a_{qp}|_{p,q=1}^{n_\mu}$ is diagonal, i.e.,

$$\hat{F}_2 |f_{\mu p}\rangle = \lambda_\mu^{(2)} |f_{\mu p}\rangle.$$

Again, $|f_{\mu p}\rangle$ is an eigenstate of $\hat{F}_2$.

We assumed that $[\hat{F}_1, \hat{F}_2] = 0$ and proved that eigenstates $|f_n\rangle$ of $\hat{F}_1$ are also the eigenstates of $\hat{F}_2$.

$\because$