Postulates of quantum mechanics

Cohen-Tannoudji et al. ch. 3, slightly different form Levine ch. 7.8.

1. The state of a physical system is described by a well-behaved function of the coordinates and time, $\Psi(\underline{q}, t)$. The function contains all the information that can be known about the system. If the function is normalized,

$$\int \Psi^* \Psi d\underline{q} = 1,$$

   then $\Psi^*(\underline{q}, t)\Psi(\underline{q}, t)dq$ gives the probability of finding the system in the volume element $d\underline{q}$ around $\underline{q}$.

   Note: $\Psi^*\Psi$ is the probability density, probability per unit volume.

2. To every physical property B there corresponds a linear Hermitian operator $\hat{B}$. This operator is obtained by taking the classical expression of the property in terms of coordinates, momenta and time, $B = B(\underline{q}, \underline{p}, t)$ and replacing each p by $-i\hbar$ times the derivative wrt corresponding q, e.g.,

$$p_x \longrightarrow -i\hbar\partial/\partial x.$$

   Example: The angular momentum $\vec{\hat{L}} = \vec{r} \times \vec{\hat{p}}$.
   $l_x = yp_z - zp_y \quad \Rightarrow \hat{L}_x = -i\hbar(y\partial/\partial z - z\partial/\partial y).$

3. The only values of the property B which can be observed are the eigenvalues of the corresponding operator $\hat{B}$, $\hat{B}g_i = b_i g_i$. Assuming Ψ is normalized, the probability of observing the value b_i is given by

$$\left| \int g_i^* \Psi d\underline{q} \right|^2 .$$

If b_i is a degenerate eigenvalue with several eigenfunctions g_{id}, the probability of observing it is the sum

$$\sum_d \left| \int g_{id}^* \Psi d\underline{q} \right|^2 .$$

This probability can be understood physically. Since all the eigenfunctions of $\hat{B}$ form a basis for the space of functions with the same boundary conditions, we may write

$$\Psi = \sum_i c_i g_i \ .$$

c_i may be found by

$$\int g_j^* \Psi d\underline{q} = \sum_i c_i \int g_j^* g_i d\underline{q} = \sum_i \delta_{ij} c_i = c_j .$$

The probability of observing the value b_i is therefore $|c_i|^2$.

It can be shown that the average of $\hat{B}$ is $\int \Psi^* \hat{B} \Psi d\underline{q}$:

$$\int \Psi^* \hat{B} \Psi d\underline{q} = \sum_{ij} c_i^* c_j \int g_i^* \hat{B} g_j d\underline{q} = \sum_{ij} c_i^* c_j b_j \int g_i^* g_j d\underline{q} =$$

$$= \sum_i |c_i|^2 b_i = \sum_i P(b_i) b_i = \overline{B}.$$

If Ψ is an eigenfunction of $\hat{B}$, measuring B will yield the corresponding eigenvalue with probability 1.

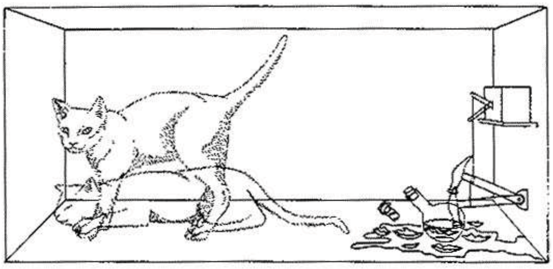
Note: If $\hat{B}$ and g_i are time independent, the expansion is $\Psi(\underline{q}, t) = \sum_i c_i(t) g_i(\underline{q})$. The average and probabilities may depend on time.

4. If the Hamiltonian $\hat{H}$ is the operator corresponding to the energy, $\Psi(\underline{q}, t)$ obeys the time dependent Schrödinger equation

$$\hat{H}\left(\underline{q}, -i\hbar\frac{\partial}{\partial \underline{q}}, t\right)\Psi(\underline{q}, t) = -\frac{\hbar}{i}\frac{\partial}{\partial t}\Psi(\underline{q}, t).$$

5. Reduction (or collapse) of the wave function: If the observation of B gave the value b_k, the wf immediately after the observation is g_k. This may be regarded as selecting one of the components of $\Psi = \sum_i c_i g_i$. Note that the collapse is a dramatic change of the wf. A subsequent measurement of B, taken before the wf had time to evolve, will yield the same b_k. However, if an observation of another operator, which does not commute with $\hat{B}$, is interposed between the two measurements of B, results of the last measurement will change. This is not due to any interaction; it shows the deep statistical character of quantum mechanics.

This statistical character was not universally accepted, and Einstein said that "God does not play dice". It was suggested that this character results from summation over deeper inner variables, called "hidden variables", in a manner similar to statistical mechanics. Bell showed in 1964 that certain experiments can determine the existence of hidden variables, assuming some basic properties. Such experiments were carried out by Aspect in 1980 and showed that hidden variables are incompatible with such assumptions. For more details see Levine Section 7.9, or the book by Moiseyev.



Eigenfunctions of some physical operators:

Momentum: $p_x \to -i\hbar\partial/\partial x$, ef $\exp(ikx/\hbar)$, ev k.

Angular momentum: operators $\hat{L}^2$, $\hat{L}_z$, common ef Y_{lm}, ev $\hbar^2 l(l+1)$ and $m\hbar$ respectively.

Spatial coordinates: operator $\hat{x}$, multiplies function by x. The ef $g_a(x)$ corresponds to finding the particle at point a:

$$xg_a(x) = ag_a(x).$$

$g_a(x)$ must vanish for all $x \neq a$, $g_a(a) \neq 0$, $\int_{-\infty}^{\infty} g(x)^2 dx = 1$. Obviously, the function must be infinite at a. This is the $\delta(x-a)$ function. It may be defined as the derivative of the step or Heaviside function, given by

$H(x < 0) = 0; \quad H(x > 0) = 1.$
Then $\delta(x) = dH(x)/dx$, or $\delta(x-a) = dH(x-a)/dx$.

A useful property of $\delta(x-a)$:

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)dx = f(x)H(x-a)|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} H(x-a)f'(x)dx =$$

$$= f(\infty) - \int_{a}^{\infty} f'(x)dx = f(\infty) - f(\infty) + f(a) = f(a).$$

Stationary states

Assume the potential V does not depend on time. This does not mean that observations of a physical property will give the same value every time. A state will have a well-defined energy (giving the same value in all measurements) if the state function $\Psi(\underline{q}, t)$ is an eigenfunction of the energy operator $\hat{H}$. Ψ always satisfies the Schrödinger equation, therefore

$$\begin{aligned}\hat{H}\Psi(\underline{q}, t) &= -\frac{\hbar}{i}\frac{\partial}{\partial t}\Psi(\underline{q}, t) \\ \hat{H}\Psi(\underline{q}, t) &= E\Psi(\underline{q}, t).\end{aligned}$$

Equating the rhs of the two equations and dividing by $(-\hbar/i)\Psi$ leads to

$$-\frac{i}{\hbar}E = \frac{\partial \ln \Psi(\underline{q}, t)}{\partial t}.$$

Integration gives

$$\ln \Psi(\underline{q}, t) = -\frac{i}{\hbar}Et + A(\underline{q}),$$

where $A(\underline{q})$ is an arbitrary integration constant. Taking the exponential form gives

$$\Psi(\underline{q}, t) = \psi(\underline{q}) \exp\left(-\frac{i}{\hbar}Et\right),$$

where $\psi = \exp(A)$. Substituting in one of the equations we started from (above) gives

$$\hat{H}\psi(\underline{q}) = E\psi(\underline{q}),$$

the time-independent Schrödinger equation.

Stationary states are thus characterized by a wave function which is a product of coordinate- and time-dependent functions. The time factor is $e^{-i/\hbar Et}$, and $\psi(q)$ is obtained by solving the time-independent Schrödinger equation.

For a system in a stationary state, an operator $\hat{O}$ which does not depend explicitly on time will have a time independent expectation value:

$$\int \Psi^* \hat{O} \Psi dq = \int \psi(q) e^{i/\hbar Et} \hat{O} \psi(q) e^{-i/\hbar Et} dq = \int \psi(q) \hat{O} \psi(q) dq.$$

The manipulations above are made possible because $\hat{O}$ is time independent.

If $\hat{O}$ commutes with the Hamiltonian, there exists a complete set of common eigenfunctions, and the observable corresponding to $\hat{O}$ is well defined (constant of motion). Such operators (symmetry operators) facilitate the classification, treatment and understanding of the energy levels of physical systems, and we shall always look for them when approaching new systems. A well known example – the $\hat{L}^2$ and $\hat{L}_z$ operators for one-electron atoms, leading to level classification by the quantum number l, m.