

Quantum Mechanics

In the short space of an appendix it is not possible to develop quantum mechanics. However, it is possible to review some of the key concepts that are used in the textbook[†] and at the Web site.

In the Schrödinger description of quantum mechanics a physical system such as an atom or even a photon is described by a wavefunction ψ . The wavefunction depends on the variables describing the degrees of freedom of the system and on time. Thus for a particle moving in one dimension, the wavefunction is $\psi(x, t)$; for a particle moving in three dimensions, it is $\psi(\mathbf{r}, t)$; for a two-particle system in three dimensions, it is $\psi(\mathbf{r}_1, \mathbf{r}_2, t)$; and so on. In the Dirac notation an abstract state vector $|\psi(t)\rangle$ is introduced and is projected onto the appropriate space, according to the identification $\psi(x, t) = \langle x|\psi(t)\rangle$, $\psi(\mathbf{r}, t) = \langle \mathbf{r}|\psi(t)\rangle$, and so on. As will be seen shortly, $\psi(x, t)$ is a complex function (i.e., it has real and imaginary parts). The wavefunction contains all the information that may be obtained about a physical system. Unfortunately, it is now possible to write down the exact wavefunctions only for very simple systems.

According to Born's interpretation of the wavefunction, if a measurement of the position of a particle is made at time t (in the one-dimensional case), the relative probability of finding the particle between x and $x + dx$ is given by $dP = |\psi(x, t)|^2 dx$, where the square of the absolute value of ψ is taken. When possible, it is useful to normalize the probability density so that

$$\langle \psi(t)|\psi(t)\rangle \equiv \int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 1. \quad (\text{WC.1})$$

This states that the particle must be found somewhere, with probability 1.

The wavefunction for a particle in one dimension satisfies the Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = i\hbar \frac{\partial \psi}{\partial t}. \quad (\text{WC.2})$$

Here m is the mass of the particle, $\hbar = h/2\pi = 1.0545887 \times 10^{-34}$ Js, $i = \sqrt{-1}$, and $V(x)$ is the potential energy influencing the particle's motion as it moves through space. In general, the wavefunction will be a complex function of its arguments. The Schrödinger equation is linear in ψ . Thus, if $\psi_1(x, t)$ and $\psi_2(x, t)$ are solutions, the

[†]The material on this home page is supplemental to *The Physics and Chemistry of Materials* by Joel I. Gersten and Frederick W. Smith. Cross-references to material herein are prefixed by a "W"; cross-references to material in the textbook appear without the "W."

superposition $\psi = c_1\psi_1 + c_2\psi_2$ is also a solution. This means that both constructive and destructive interference are possible for matter waves, just as for light waves.

In quantum mechanics physical quantities are represented by operators. Examples include the position, x , the momentum, $p_x = -i\hbar\partial/\partial x$, and the energy (or Hamiltonian), $H = p_x^2/2m + V(x)$, which is the sum of the kinetic energy and the potential energy operators. If a number of measurements of a physical quantity are made and the results averaged, one obtains the expectation value of the quantity. The expectation value of any physical operator, Q , is given in quantum mechanics by

$$\langle Q \rangle = \langle \psi(t) | Q | \psi(t) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) Q \psi(x, t) dx. \quad (\text{WC.3})$$

To guarantee that the expectation value always be a real number, it is necessary for Q to be a Hermitian operator. A Hermitian operator is one for which the following identity holds for any two functions f and g :

$$\langle f | Qg \rangle = \langle Qf | g \rangle = \int_{-\infty}^{\infty} f^*(x) Qg(x) dx = \int_{-\infty}^{\infty} (Qf(x))^* g(x) dx. \quad (\text{WC.4})$$

The operators x , p_x , and H are examples of Hermitian operators, as is the set of orbital angular momentum operators:

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x. \quad (\text{WC.5})$$

If a measurement is made of a physical variable Q , the result will be one of the eigenvalues q_i of the operator Q , and the act of measurement will reset the wavefunction to the corresponding eigenfunction of that operator, $|q_i\rangle$. The eigenvalues and eigenfunctions are defined through the relation

$$Q|q_i\rangle = q_i|q_i\rangle. \quad (\text{WC.6})$$

The eigenvalues of a Hermitian operator may be shown to be real numbers. Their eigenfunctions may be chosen so that they form an orthogonal set, that is,

$$\langle q_i | q_j \rangle = \int \phi_{q_i}^*(x) \phi_{q_j}(x) dx = \delta_{i,j}. \quad (\text{WC.7})$$

It is customary to normalize the eigenfunctions as well, when possible. For example, the eigenfunctions of the momentum operator p_x are the plane waves $\phi_k(x) = \exp(ikx)$. They are not normalizable since it is equally probable to find the particle anywhere on the infinite domain $-\infty < x < \infty$. The corresponding momentum eigenvalue is $\hbar k$.

It is assumed that the eigenfunctions of any physical operator form a complete set (i.e., that the wavefunction may be expanded in terms of them). Thus

$$|\psi(t)\rangle = \sum_n c_n(t) |q_n\rangle. \quad (\text{WC.8})$$

If a measurement of Q is made, the probability of finding the eigenvalue q_n is given by $|c_n|^2$. Obviously, $\sum |c_n|^2 = 1$.

A necessary and sufficient condition for a set of operators $\{Q_i\}$ to be observable simultaneously is that they commute with each other (i.e., $[Q_i, Q_j] = Q_i Q_j - Q_j Q_i = 0$). Examples of sets of commuting operators are $\{Q_1, Q_2, Q_3\} = \{x, y, z\}$, or $\{Q_1, Q_2, Q_3\} = \{p_x, p_y, p_z\}$, or $\{Q_1, Q_2\} = \{L^2, L_z\}$, where $L^2 = L_x^2 + L_y^2 + L_z^2$. Noncommuting operators may not be measured simultaneously to arbitrary accuracy. Examples include $\{Q_1, Q_2\} = \{x, p_x\}$, since $[x, p_x] = i\hbar$, or $\{Q_1, Q_2, Q_3\} = \{L_x, L_y, L_z\}$ [see Eq. (WC.22)]. When operators fail to commute, successive measurements of the respective physical variables interfere with each other. Thus measurement of x affects the outcome of a measurement of p_x . The result is summarized by the *Heisenberg uncertainty principle*, which states that the product of the uncertainties in these variables obeys the inequality $\Delta x \Delta p_x \geq \hbar/2$.

Stationary states of the Schrödinger equation are the analogs of standing waves in classical wave physics. They are solutions that may be expressed in factored form [i.e., $\psi(x, t) = \phi(x) \exp(-iEt/\hbar)$]. Such a state has a time-independent probability density, $|\phi(x)|^2$ and an energy E . Insertion of this expression into Eq. (WC.2) results in the time-independent Schrödinger equation,

$$H\phi(x) = E\phi(x), \quad (\text{WC.9})$$

which shows that $\phi(x)$ is an eigenfunction of H with energy eigenvalue E .

Examples of common quantum-mechanical systems include the one-dimensional infinite square well, the simple harmonic oscillator, and the hydrogen atom. For the one-dimensional infinite square well, the potential energy operator is given by $V(x) = 0$ for $0 < x < a$ and $V(x) = \infty$ otherwise. The energy eigenfunctions are (see Table 11.5)

$$\phi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}, \quad (\text{WC.10})$$

where $n = 1, 2, 3, \dots$. The energy eigenvalues are

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{a} \right)^2. \quad (\text{WC.11})$$

For the simple harmonic oscillator with frequency ω , the time-independent Schrödinger equation is given by

$$H\phi_n(x) = -\frac{\hbar^2}{2m} \frac{\partial^2 \phi_n(x)}{\partial x^2} + \frac{m\omega^2 x^2}{2} \phi_n(x) = E_n \phi_n(x). \quad (\text{WC.12})$$

The energy eigenvalues are given by

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega, \quad (\text{WC.13})$$

where $n = 0, 1, 2, \dots$. The eigenfunctions may be expressed as products of Gaussians multiplied by Hermite polynomials:

$$\phi_n(x) = \frac{1}{2^{n/2} \sqrt{n!}} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar} \right) H_n \left(\sqrt{\frac{m\omega}{\hbar}} x \right). \quad (\text{WC.14})$$

The first few Hermite polynomials are $H_0(x) = 1$, $H_1(x) = 2x$, and $H_2(x) = 4x^2 - 2$.

The Schrödinger equation for the hydrogen atom is

$$-\frac{\hbar^2}{2m}\nabla^2\phi_{nlm}(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0 r}\phi_{nlm}(\mathbf{r}) = E_n\phi_{nlm}(\mathbf{r}). \quad (\text{WC.15})$$

The energy eigenvalues for the bound states are

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_1 n^2}, \quad (\text{WC.16})$$

where the first Bohr radius is given by $a_1 = 4\pi\epsilon_0\hbar^2/me^2$ and $n = 1, 2, 3, \dots$. The bound-state wavefunctions are of the form

$$\phi_{nlm}(\mathbf{r}) = N_{nlm}R_{nl}(r)Y_{lm}(\theta, \phi), \quad (\text{WC.17})$$

where $Y_{lm}(\theta, \phi)$ is a spherical harmonic (see the next paragraph). The quantum number l assume the values $0, 1, 2, \dots, n-1$. The m quantum numbers take on the values $-l, -l+1, \dots, l-1, l$. The ground state, with the quantum numbers $(n, l, m) = (1, 0, 0)$, is

$$\phi_{100}(\mathbf{r}) = \sqrt{\frac{1}{\pi a_1^3}} \exp\left(-\frac{r}{a_1}\right). \quad (\text{WC.18})$$

The hydrogen atom also possesses a continuum of states for $E > 0$, which describe the Coulomb scattering of an electron from a proton.

The spherical harmonics are simultaneous eigenstates of the angular momentum operators L^2 and L_z , that is,

$$L^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi), \quad (\text{WC.19})$$

$$L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi), \quad (\text{WC.20})$$

where θ and ϕ are spherical polar coordinates. The first few spherical harmonics are

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}, \quad Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta, \quad (\text{WC.21})$$

$$Y_{11} = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}, \quad Y_{1-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi}.$$

The angular momentum commutation relations are

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y. \quad (\text{WC.22})$$

The spin of the electron is incorporated by writing the wavefunction as a two-component column vector. The upper and lower elements are the probability amplitudes for the electron having spin up or spin down, respectively. The operators for spin angular momentum are written in terms of the Pauli spin matrices:

$$S_x = \frac{\hbar}{2}\sigma_x, \quad S_y = \frac{\hbar}{2}\sigma_y, \quad S_z = \frac{\hbar}{2}\sigma_z, \quad (\text{WC.23})$$

where the Pauli spin matrices are given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (\text{WC.24})$$

The S_x , S_y , and S_z matrices obey the angular momentum commutation rules given in Eq. (WC.22).

Tunneling through a barrier is one of the dramatic quantum-mechanical effects. Consider a potential barrier given by $V(x) = V_0$ for $0 < x < a$ and $V(x) = 0$ otherwise. Let a particle approach it with energy $E < V_0$. The particle is able to tunnel through the barrier with some finite probability. The transmission probability is given by

$$T = \frac{1}{1 + V_0^2 \sinh^2 qa/4E(V_0 - E)}, \quad (\text{WC.25})$$

where $q = \sqrt{2m(V_0 - E)}/\hbar$.

Time-independent perturbation theory is used to calculate the effect of a small interaction term added to the Hamiltonian. Let $H = H_0 + \lambda V$ and $H_0 \phi_n = E_n^0 \phi_n$ define the unperturbed eigenvalues and eigenfunctions. The quantity λ is a small parameter. Assume that the eigenvalues are nondegenerate (i.e., no two values of E_n^0 coincide). Then an approximate expression for the eigenvalues of $H \phi_n = E_n \phi_n$ is

$$E_n = E_n^0 + \lambda \langle \phi_n^0 | V | \phi_n^0 \rangle + \lambda^2 \sum_j \frac{|\langle \phi_j^0 | V | \phi_n^0 \rangle|^2}{E_n^0 - E_j^0} + \dots, \quad (\text{WC.26})$$

where the term $j = n$ is excluded from the sum.

The case in which there is degeneracy is usually handled by matrix techniques. A finite set of eigenfunctions is chosen and the matrix elements of H are formed:

$$H_{jn} = \langle \phi_j^0 | H | \phi_n^0 \rangle. \quad (\text{WC.27})$$

The eigenvalues and eigenvectors of the Hamiltonian matrix are computed. An example of this is provided by the two-level system in which the unperturbed states are labeled $|1\rangle$ and $|2\rangle$. The Hamiltonian matrix is

$$H = \begin{pmatrix} E_1 & V_{12} \\ V_{21} & E_2 \end{pmatrix}, \quad (\text{WC.28})$$

where $V_{21} = V_{12}^*$. The eigenvalues are obtained as solutions of the secular equation

$$\begin{vmatrix} E_1 - E & V_{12} \\ V_{21} & E_2 - E \end{vmatrix} = (E_1 - E)(E_2 - E) - |V_{12}|^2 = 0 \quad (\text{WC.29})$$

and are given by

$$E_{\pm} = \frac{E_1 + E_2}{2} \pm \sqrt{\left(\frac{E_1 - E_2}{2}\right)^2 + |V_{12}|^2}. \quad (\text{WC.30})$$

The variation principle permits one to obtain an approximate solution to the Schrödinger equation and an upper bound on the energy of the ground state of a system. An arbitrary function $F(x)$ is chosen and the expectation value of the Hamiltonian is computed using this function:

$$E[F(x)] = \frac{\langle F|H|F \rangle}{\langle F|F \rangle}. \quad (\text{WC.31})$$

Then it may be shown that the ground-state energy obeys the inequality $E_0 \leq E[F(x)]$. The function $F(x)$ depends on a set of parameters, $\{\alpha_i\}$. The parameters are varied to obtain the minimum value of $E[F(x)]$. The more parameters the function contains, the more accurately $F(x)$ will approximate the ground-state wavefunction and the closer $E[F(x)]$ will be to the ground-state energy.

In some problems there is a discrete state that is degenerate with a continuum of states. Assuming that the system starts in the discrete state, one calculates the transition rate, Γ , to the final continuum of states. Again, take the Hamiltonian to be of the form $H = H_0 + \lambda V$. The initial state satisfies $H_0|i\rangle = E_i|i\rangle$ and the final state satisfies $H_0|f\rangle = E_f|f\rangle$. The Fermi golden rule states that

$$\Gamma = \frac{2\pi}{\hbar} \sum_f |\langle f|\lambda V|i\rangle|^2 \delta(E_f - E_i). \quad (\text{WC.32})$$

In treating systems with more than one particle, the symmetry of the wavefunction under interchange is important. For identical particles with half-integer spin, such as electrons, protons, neutrons, and ^3He , the wavefunction changes sign if any two particles have their positions (and spins) interchanged, that is,

$$\psi(1, \dots, i, \dots, j, \dots, N) = -\psi(1, \dots, j, \dots, i, \dots, N). \quad (\text{WC.33})$$

The particles are said to obey Fermi–Dirac statistics. For identical particles with integer spin, such as photons or ^4He , the wavefunction is symmetric under interchange:

$$\psi(1, \dots, i, \dots, j, \dots, N) = \psi(1, \dots, j, \dots, i, \dots, N). \quad (\text{WC.34})$$

Such particles obey Bose–Einstein statistics.