# 6

# Further Interpretation of the Wave Function

Consider a quantum-mechanical system with a Hamiltonian that has a discrete spectrum only, with allowed energies, $E_n$, and eigenfunctions, $\psi_n$. In general, the state of this quantum system can be specified by a wave function

$$\Psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}), e^{-\frac{i}{\hbar}E_n t} \tag{1}$$

describing a system for which the energy is not uniquely specified. If it is a single particle,

$$< \Psi, \Psi >= 1 = \sum_n c_n^* c_n < \psi_n, \psi_n > + \sum_{n \neq m} c_n^* c_m < \psi_n, \psi_m > e^{\frac{i}{\hbar}(E_n - E_m)t}. \tag{2}$$

Because $< \psi_n, \psi_m >= 0$ for $n \neq m$,

$$< \Psi, \Psi >= \sum_n |c_n|^2. \tag{3}$$

Similarly,

$$< E >=< \Psi, H\Psi >= \sum_n |c_n|^2 E_n, \tag{4}$$

$$< E^k >=< \Psi, H^k \Psi >= \sum_n |c_n|^2 E_n^k. \tag{5}$$

It is natural to interpret $|c_n|^2$ as $P(E_n)$, the probability the particle be found in the state with energy $E_n$. Without a coupling of our system to an outside field, that is, without an outside perturbation, these $P(E_n)$ are independent of the time.

K. T. Hecht, *Quantum Mechanics*

# A Application 1: Tunneling through a Barrier

As a simplest application, consider the $NH_3$ molecule system, where the motion of the N-atom relative to the $H_3$ plane is governed by the double-minimum potential of problem 7. The lowest-energy eigenfunction was an even function of $x$; the first excited state, at an excitation energy, $\Delta E$, above the ground state (see Fig. 6.1), has an eigenfunction that is an odd function of $x$, but otherwise almost identical with the lowest-energy eigenfunction (see Fig. 6.2). If we actually make a measurement of the position of the N-atom when the $x$-vibrational motion is not excited, we will find the N-atom either above the $H_3$ plane, $x > 0$, or below it, $x < 0$. Suppose at $t = 0$ we make a measurement telling us the N-atom is above the $H_3$ plane. Then,

$$\Psi(x, t = 0) = \frac{1}{\sqrt{2}}\left(\psi_{0,\text{even}} + \psi_{0,\text{odd}}\right) = \psi_{\text{Right}}. \tag{6}$$

Note $\sum_n |c_n|^2 = 1$. At any later time,

$$\begin{aligned}\Psi(x, t) &= \frac{1}{\sqrt{2}}\left(\psi_{0,\text{even}} e^{-\frac{i}{\hbar}E_{0,\text{even}}t} + \psi_{0,\text{odd}} e^{-\frac{i}{\hbar}E_{0,\text{odd}}t}\right) \\ &= \frac{1}{\sqrt{2}} e^{-\frac{i}{\hbar}E_{0,\text{even}}t}\left(\psi_{0,\text{even}} + \psi_{0,\text{odd}} e^{-\frac{i}{\hbar}\Delta E t}\right).\end{aligned} \tag{7}$$

In particular, when

$$t = \frac{\hbar\pi}{\Delta E}, \tag{8}$$

$$\Psi(x, t) = \frac{1}{\sqrt{2}} e^{-\frac{i}{\hbar}E_{0,\text{even}}t}(\psi_{0,\text{even}} - \psi_{0,\text{odd}}), \qquad |\Psi(x, t)| = |\psi_{\text{Left}}|. \tag{9}$$

In this time, therefore, the N-atom has tunneled from the right potential minimum through the barrier to the left potential minimum. In twice this time, we will again find the N-atom in the right minimum. The N-atom tunnels back and forth through the potential barrier with a frequency given by

$$\nu_{\text{tunneling}} = \frac{\Delta E}{2\pi\hbar}. \tag{10}$$

From the solution of problem 7, $\Delta E$ is proportional to the Gamow factor, $e^{-G}$, with $G = 2a\sqrt{[2\mu(V_0 - E)/\hbar^2]}$ for the square well barrier of width $2a$. For a more general $V(x)$, this would be replaced by

$$G = \int_{-a}^{+a} dx \sqrt{[2\mu(V(x) - E)/\hbar^2]},$$

as will be shown in Chapter 37, where the Gamow factor, $e^{-G}$, is the most crucial part for the probability of tunneling through the barrier.

We end with a parenthetic remark: In the above discussion, we have used another result of problem 7. The lowest-state eigenfunction for our symmetric potential, with $V(-x) = V(x)$, is an even function of $x$. This result seems to be universally

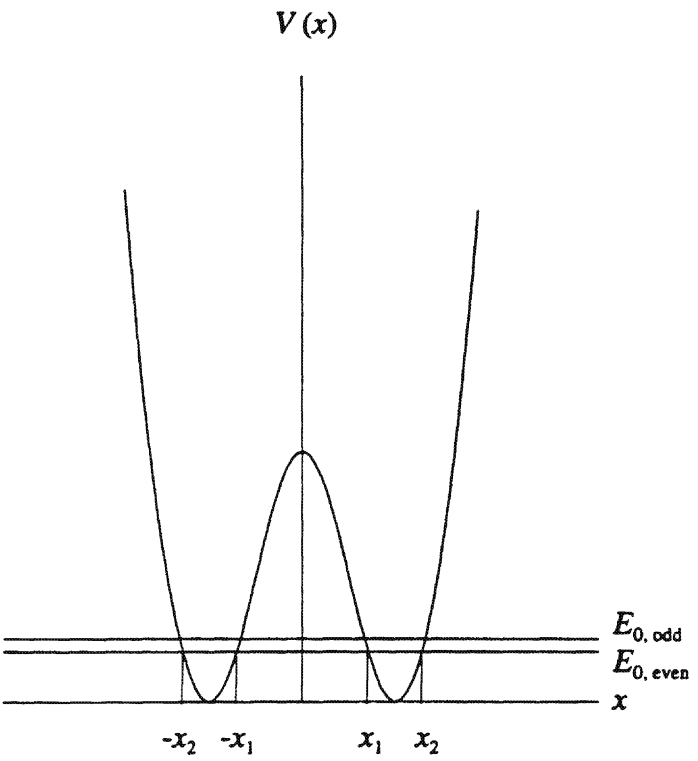


FIGURE 6.1. The ground-state doublet of the $NH_3$ double minimum potential.

true for symmetric potentials, which can be understood in terms of the curvature of the eigenfunctions. For two similar eigenfunctions of opposite parity, the function of odd parity must have a node in the center at $x = 0$ and must therefore have a somewhat greater curvature to "fit" into the potential, leading to a greater positive value of the expectation value of the kinetic energy. It is, however, not completely clear this property could be negated by the expectation value of the potential energy for a "pathological" potential perhaps having a large contribution to $< V >$ from the region near $x = 0$. In fact, the double minimum potential of this section, in which the central potential barrier is sufficiently infinite, is such a "pathological" case for which the ground state wave function is a degenerate doublet of an even and odd function. The ground-state wave function is no longer a pure even function of $x$.

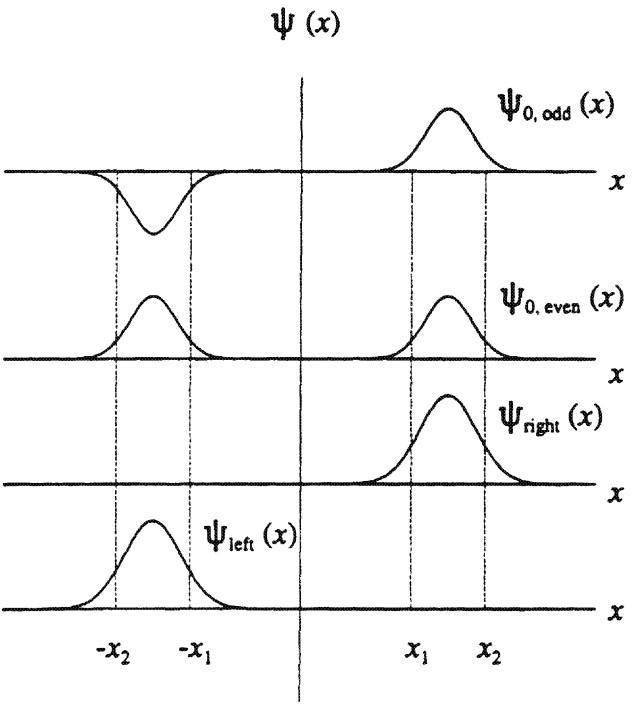


FIGURE 6.2. The eigenfunctions $\psi_{0,\text{odd}}$ and $\psi_{0,\text{even}}$ of the ground state doublet and $\psi_{\text{right/left}} = \sqrt{\frac{1}{2}}(\psi_{0,\text{even}} \pm \psi_{0,\text{odd}})$.

## B Application 2: Time-dependence of a general oscillator $< q >$

The probability amplitudes $c_n$ can tell us the quantum mechanical expectation value of any operator, O, through

$$< O >= \sum_{n,m} c_n^* c_m < \psi_n, O\psi_m > e^{\frac{i}{\hbar}(E_n - E_m)t}. \tag{11}$$

As a particular example, let $O = q$, the physical displacement coordinate of the 1-D harmonic oscillator. The two-index quantities $(q)_{nm} =< \psi_n, q\psi_m >$ for the harmonic oscillator were nonzero only for $m = n \pm 1$ (see Chapter 5). Thus,

$$< q > = \sqrt{\frac{\hbar}{m\omega_0}}\langle x\rangle = \sqrt{\frac{\hbar}{2m\omega_0}}\sum_n \left[c_n^* c_{n-1}\sqrt{n}e^{i\omega_0 t} + c_n^* c_{n+1}\sqrt{n+1}e^{-i\omega_0 t}\right]$$

$$= \sum_n \sqrt{\frac{\hbar n}{2m\omega_0}}\left[c_n^* c_{n-1}e^{i\omega_0 t} + c_{n-1}^* c_n e^{-i\omega_0 t}\right]$$

$$= \sum_n \sqrt{\frac{\hbar n}{2m\omega_0}} \left[ 2\mathcal{R}eal(c_n^* c_{n-1}) \cos\omega_0 t - 2\mathcal{I}m(c_n^* c_{n-1}) \sin\omega_0 t \right]$$

$$= \sum_n \sqrt{\frac{\hbar n}{2m\omega_0}} A_n \cos(\omega_0 t + \phi_n), \tag{12}$$

where we have defined $2c_n^* c_{n-1} \equiv A_n e^{i\phi_n}$. If we use $< q >$ to describe the quantum-mechanical motion of the simple 1-D harmonic oscillator, the result is very similar to the classical motion.

# C Matrix Representations

For the expectation value, $< O >$, of eq. (11), it is tempting to interpret the two-index quantity, $O_{nm} \equiv < \psi_n, O\psi_m >$, as the $nm^{th}$ matrix element of an infinite-dimensional matrix. (The set of numbers, $O_{nm}$, contain all experimentally observable information about the dynamical quantity represented by the operator, $O$.) To prove $O_{nm}$ is a matrix, all laws of matrix algebra must be satisfied:

1) multiplication by a scalar (a complex number or "c-number"), $\lambda O$:

$$< \psi_n, \lambda O \psi_m > = \lambda O_{nm}. \tag{13}$$

2) addition of two matrices, $O_1 + O_2$:

$$< \psi_n, (O_1 + O_2)\psi_m > = (O_1)_{nm} + (O_2)_{nm}. \tag{14}$$

3) matrix multiplication, $O_2 O_1$:

$$< \psi_n, O_2 O_1 \psi_m > = ? \tag{15}$$

To prove the law of matrix-multiplication, the new function obtained by acting with $O_1$ on $\psi_m$ can be expanded in terms of the $\psi_k$ in a generalized Fourier series

$$O_1 \psi_m = \sum_k c_k \psi_k, \qquad \text{with} \quad c_k = < \psi_k, O_1 \psi_m > = (O_1)_{km}, \tag{16}$$

so

$$< \psi_n, O_2 O_1 \psi_m > = \sum_k < \psi_n, O_2 \psi_k > < \psi_k, O_1 \psi_m >, \tag{17}$$

or

$$(O_2 O_1)_{nm} = \sum_k (O_2)_{nk} (O_1)_{km}. \tag{18}$$

This relation is the familiar law of matrix multiplication. The matrix elements,

$$O_{nm} = < \psi_n, O\psi_m > = \int dx \psi_n^*(x) O \psi_m(x),$$

were introduced here with the concept of the Schrödinger wave equation and the use of the energy eigenfunctions of this wave equation. Heisenberg first introduced

such matrix elements of dynamical quantities entirely without the concept of a wave equation or a wave function.

## D Heisenberg Matrix Mechanics

We are therefore now at a stage where we can make a short historical remark about the Heisenberg derivation of the laws of quantum mechanics. Heisenberg did not think in terms of a wave equation or in terms of a wave function. He started by thinking about the laws of classical dynamics for a periodic (or more generally a multiple-periodic or quasiperiodic system) in terms of a Fourier analysis of the classical generalized coordinates, $q$. For a simple periodic system,

$$q(t) = \sum_n q_n e^{in\omega t}, \quad \text{with} \quad \omega = 2\pi\nu, \tag{19}$$

where $q_n$ is the Fourier amplitude for the $n^{th}$ overtone of the classical fundamental $\omega$. (For a multiple-periodic system, $n\omega$ would be replaced by $n_1\omega_1 + n_2\omega_2 + \cdots + n_f\omega_f$, and the sum would be over $f$ overtone indices, and the Fourier coefficients would depend on $f$ integers, $q_{\vec{n}} = q_{n_1 n_2 \cdots n_f}$.)

Now, Heisenberg reasoned: Because the $n^{th}$ overtone has to be replaced by a two-index quantity, via the Bohr frequency relation,

$$n\omega \quad \rightarrow \quad \frac{E_n - E_m}{\hbar} = \omega_{nm} \qquad \text{Bohr}, \tag{20}$$

the Fourier coefficient $q_n$ should also be replaced by a two-index quantity

$$q_n \quad \rightarrow \quad q_{nm} \qquad \text{Heisenberg matrix}. \tag{21}$$

Moreover, these $q_{nm}$ are the only observable (physically meaningful) quantities. In addition, because matrices do not commute, the quantum mechanically meaningful $p$ and $q$ matrices do not commute. In particular, Heisenberg introduced the Planck constant into his matrix algebra with the simple *assumption*

$$\sum_k (p_{nk}q_{km} - q_{nk}p_{km}) = \frac{\hbar}{i}\delta_{nm}. \tag{22}$$

In the limit, $\hbar \rightarrow 0$, $p$ and $q$ do commute as they should in the classical limit, when $\hbar$ becomes too small to matter. The genius of the Heisenberg approach is contained in this *Heisenberg relation*, which we have already met in Section 3G in the framework of the Schrödinger approach.

Using the $p, q$ matrix commutation relation, the relation between $H(p, q)$ and E, and the commutators $[p, H(p, q)]$ and $[q, H(p, q)]$, which follow from eq. (22), Heisenberg found the allowed energy values and the matrix elements of $p$ and $q$ via matrix algebra for the 1-D harmonic oscillator and other simple dynamical systems, *without* the use of a wave equation. The equivalence between the Heisenberg $q_{nm}$ and the Schrödinger $< \psi_n, q\psi_m >$ was demonstrated by Schrödinger in 1926. (Wolfgang Pauli in an unpublished letter to P. Jordan is reputed to have shown

this equivalence even earlier). In these lectures, we shall give the Heisenberg derivation for the energy eigenvalues, $E_n$, and the matrix elements $q_{nm}$ and $p_{nm}$ of the simple harmonic oscillator in Chapter 19 after we have gained some facility in the calculation of matrix elements of dynamical quantities by both Schrödinger and algebraic (Heisenberg) techniques.