4

Schrödinger Theory: The Existence of Discrete Energy Levels

A The Time-Independent Schrödinger Equation

The Schrödinger equation for a single particle moving under the influence of a time-independent conservative force

$$-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = H\Psi \tag{1}$$

can be converted to the time-independent equation for the function $\psi(x, y, z)$ by assuming

$$\Psi = f(t)\psi(x, y, z), \tag{2}$$

with

$$-\frac{1}{f}\left\{\frac{\hbar}{i}\frac{df}{dt}\right\} = \frac{1}{\psi}\left\{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right\} = \frac{1}{\psi}(H\psi) = \text{const}, \tag{3}$$

where we have converted a function of the time only on the left-hand side of the equation into a function of x, y, z only on the right-hand side. Because this must hold for all values of t and all x, y, z, the left-hand side and the right-hand side must be equal to a constant. We have separated the equation. The physical significance of the constant can be seen to be the energy, E.

$$f(t) = \exp(-\frac{i}{\hbar}Et) \tag{4}$$

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and

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi. \tag{5}$$

For a 1-D problem, in particular,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi = 0. \tag{6}$$

In this chapter, we shall show the Schrödinger equation, eq. (5), for potentials V, for which the classical motion would be restricted to a bound region of space, will lead to allowed (square-integrable) solutions, the so-called characteristic functions, or "eigenfunctions," of the equation only for certain discrete allowed energies, the so-called "eigenvalues" or characteristic values of the energies.

B The Simple, Attractive Square Well

The 1-D Schrödinger equation, eq. (6), has particularly simple solutions in regions $a < x < b$, where $V(x)$ can be replaced by a constant, with simple sinusoidal solutions for regions with $E > V$ and simple exponentials for regions with $E < V$. The simplest 1-D problem is that of a single, attractive square well of width $2a$, with

$$V(x) = 0 \quad \text{for} \quad -a \le x \le +a, \qquad V(x) = +V_0 \quad \text{for} \quad |x| > a, \tag{7}$$

(see Fig. 4.1). The Schrödinger equation becomes

$$\begin{aligned} &\frac{d^2\psi}{dx^2} + k^2\psi(x) = 0, \quad \text{with } k^2 = \frac{2mE}{\hbar^2} \quad \text{for } -a \le x \le +a, \\ &\frac{d^2\psi}{dx^2} - \kappa^2\psi(x) = 0, \quad \text{with } \kappa^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad \text{for } |x| \ge a. \end{aligned} \tag{8}$$

In order to have square-integrable solutions, the $\psi(x)$ must be restricted to exponentially decaying solutions outside the potential well; i.e.,

$$\psi(x) = Ce^{-\kappa x} \quad \text{for } x > +a, \qquad \psi(x) = De^{+\kappa x} \quad \text{for } x < -a. \tag{9}$$

In the interior, for $-a \le x \le +a$, the most general solution is

$$\psi(x) = A\cos kx + B\sin kx.$$

(For the moment, we have not made use of the symmetry of the potential.) In order to have solutions with sensible probability densities, both the probability density and the probability density currents must be continuous functions of x. This solution can be ensured by requiring the continuity of both $\psi(x)$ and its first derivative at the discontinuities of the potential at $x = \pm a$. The continuity of $\psi(x)$ and its first derivative at $x = +a$ leads to the boundary conditions

$$A\cos ka + B\sin ka = Ce^{-\kappa a}, \tag{10}$$

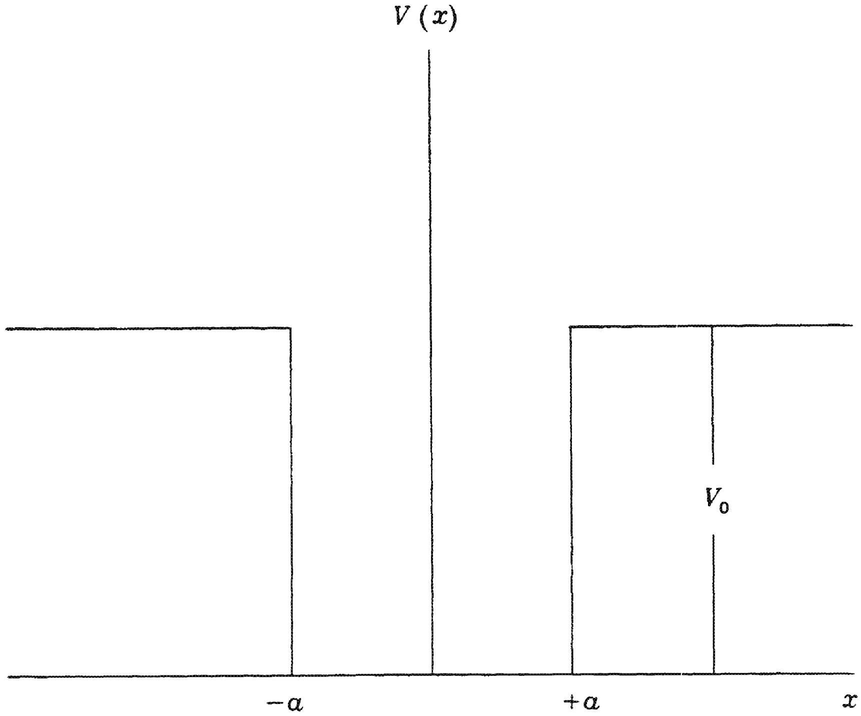

FIGURE 4.1. The attractive square well potential.

$$-Ak\sin ka + Bk\cos ka = -\kappa C e^{-\kappa a}, \tag{11}$$

and at $x = -a$, we are led to the boundary conditions

$$A\cos ka - B\sin ka = De^{-\kappa a}, \tag{12}$$

$$Ak\sin ka + Bk\cos ka = \kappa De^{-\kappa a}. \tag{13}$$

Eliminating the constant C from eqs. (10) and (11) and the constant D from eqs. (12) and (13), we are led to the further restriction

$$AB = 0,$$

with the two possible solutions:

$$B = 0, \quad D = C, \qquad \text{or} \qquad A = 0, \quad D = -C. \tag{14}$$

We see the solutions are either even or odd functions of x. This could have been seen at once from the space-reflection symmetry of our potential, $V(-x) = V(x)$. Because the Schrödinger equation is invariant under the 1-D space-inversion operation, $x \to -x$, our solutions must have good parity; see Section I of Chapter 3. The $\psi(x)$ must be either even or odd functions of x; either $\cos kx$ or $\sin kx$ functions in the region $|x| < a$. It would have been sufficient to apply the boundary conditions at $x = +a$. The boundary conditions at $x = -a$ follow from symmetry. The two boundary conditions at $x = +a$, however, are consistent only if

$$\begin{aligned} k \tan ka &= +\kappa, \qquad \text{for even } \psi(x), \\ k \cot ka &= -\kappa, \qquad \text{for odd } \psi(x). \end{aligned} \tag{15}$$

Because k and κ are functions of the energy E, these relations are transcendental equations with solutions only for very specific values of E, the discrete allowed values of the energy. To solve the transcendental equations, it will be convenient to introduce dimensionless coordinates z and z_0,

$$z = ka = \sqrt{\frac{2mEa^2}{\hbar^2}}, \quad \text{and} \quad z_0 = \sqrt{\frac{2mV_0a^2}{\hbar^2}}, \tag{16}$$

transforming eq. (15) into

$$\begin{aligned} z \tan z &= +\sqrt{(z_0^2 - z^2)} \qquad \text{for even } \psi(x), \\ z \cot z &= -\sqrt{(z_0^2 - z^2)} \qquad \text{for odd } \psi(x). \end{aligned} \tag{17}$$

These two relations are plotted in Fig. 4.2. The solutions $z(E)$ at the intersections of the curves $z \tan z$ with $+\sqrt{(z_0^2 - z^2)}$ and the curves $z \cot z$ with $-\sqrt{(z_0^2 - z^2)}$ give the allowed values of E. Fig. 4.2 for the case $z_0 = 4$ shows a potential with this depth has three bound states, two with solutions of even parity and only one with a solution of odd parity. Note also, only one even bound state exists if $z_0 < \pi/2$, but at least this one bound state always exists, even in the limit of a shallow potential well, with $V_0 \to 0$. Note, also, in the limit of an infinitely deep well, as $V_0 \to \infty$, the solutions are

$$\begin{aligned} &z \to (2N + 1)\frac{\pi}{2}, \quad N = 0, 1, 2, \ldots, \qquad \text{for even } \psi \\ &z \to 2N\frac{\pi}{2}, \quad N = 1, 2, \ldots, \qquad \text{for odd } \psi \end{aligned} \tag{18}$$

or

$$z_n = n\frac{\pi}{2}, \quad \text{thus,} \quad E_n = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \quad \text{with} \quad n = 1, 2, \ldots. \tag{19}$$

Note, in the case, $V_0 \to \infty$, the wave functions are exactly 0 in the region $|x| > a$, and the interior solutions obey $\psi(\pm a) = 0$. In this case, the derivatives of the wave function are discontinuous at $x = \pm a$. Both the probability density and the probability density current, however, have the value zero at the boundaries and are therefore still continuous at the boundaries.

Note, also, so far we have considered only bound states with $E < V_0$. For $E > V_0$, the solutions of the Schrödinger equation are oscillatory for all values of x, from $-\infty \to +\infty$. Merely, a change of wavelength ("index of refraction") occurs as the wave traverses the region of the potential well. Because they reach from $x = -\infty$ to $x = +\infty$, the wave functions are no longer square integrable. They still have, however, a sensible probability interpretation. The amplitudes of

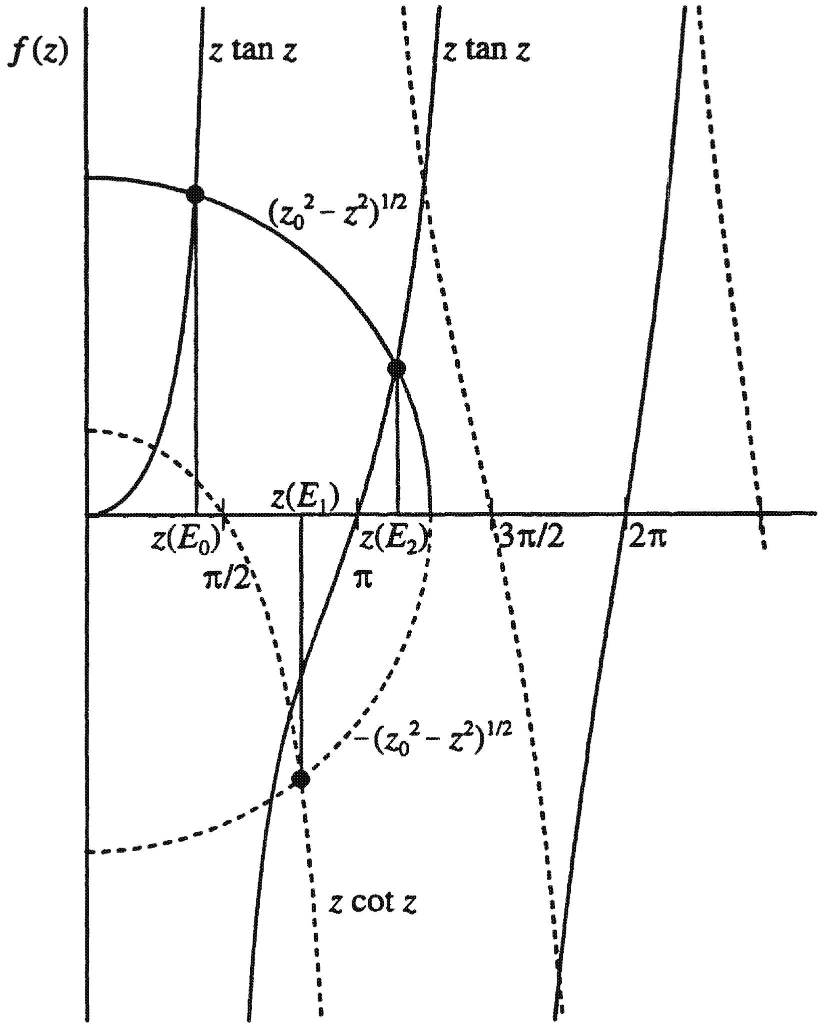

FIGURE 4.2. The transcendental eqs. (17) for the case $z_0 = 4$. Solid lines for even $\psi(x)$. Dashed lines for odd $\psi(x)$.

the sinusoidal waves give the strengths of the probability density current and can therefore be determined from the experimental flux of particles. Note, however, $\vec{S}$ is zero for real $\psi(x)$. The physics of the problem dictates we use complex solutions of the type

$$e^{i(\pm kx - Et)}$$

for particles moving in the $\pm x$ direction. The amplitude of the wave $Ae^{i(k_0 x - Et)}$, for $x < -a$, with $k_0 = [2m(E - V_0)/\hbar^2]^{1/2}$, is determined by the flux of particles from a source at $x = -\infty$. These particles can be reflected or transmitted by the potential step, leading to a reflected wave, $Be^{(-ik_0x-iEt)}$ in the region, $x < -a$, and a transmitted wave $Ce^{i(k_0x-Et)}$ in the region $x > +a$. This is a 1-D scattering problem. Scattering of particles by square wells will be treated in Part V of these lectures. For the moment, we content ourselves with noting that all energies for $E > V_0$ are possible. In this energy regime, we therefore have a continuum of allowed energies.

As a final remark, we note the solutions of the simple square well above can also be used to solve a slightly different square well problem with

$$\begin{aligned} &V(x) = \infty, \quad \text{for } x < 0, \qquad V(x) = 0, \quad \text{for } 0 < x \le a, \\ &V(x) = V_0 \quad \text{for } x > a; \end{aligned} \tag{20}$$

i.e., the left potential has been replaced by a very high (∞) potential step. Therefore, $\psi(x) = 0$ for $x < 0$. This can therefore also be used for a 3-D spherically symmetric square well leading to a 1-D Schrödinger equation of the above type, where x is replaced by the radial coordinate, r. (Note, the region $r < 0$ is excluded by the fictitious infinite potential for $r < 0$.) Because the boundary condition at $r = 0$ is $\psi(r = 0) = 0$, only the odd solutions of the above potential will be allowed (see the dashed curves of Fig. 4.2). We see a bound state exists for this problem, only if

$$z_0 > \frac{\pi}{2}, \qquad \text{or} \quad V_0 a^2 > \frac{\hbar^2}{2m}\frac{\pi^2}{4}. \tag{21}$$

If the sinusoidal radial wave function starting with the value 0 at $r = 0$ does not have enough curvature in the potential well region to have at least a first maximum for $r < a$, it will reach the barrier at $r = a$ with a positive slope that cannot fit onto a negative (decaying) exponential in the region $r > a$ without a discontinuity in slope and, hence, a discontinuity in the probability density current. If the potential well is not deep enough or wide enough, no bound state will exist. The potential of eq. (20) is a reasonably good approximation for the effective potential between neutron and proton in the deuteron. [Note that the mass in eq. (21) must be replaced by the reduced mass of this 2-body problem.] The deuteron has only a single bound state in its 2-particle spin triplet ($S = 1$) state. Moreover, the binding energy of this state, of 2.22 MeV (with $E = V_0 - 2.22$ MeV) is small compared with the expected value of V_0. The deuteron is therefore a barely bound system with

$$V_0 a^2 \approx \frac{\hbar^2}{2\mu}\frac{\pi^2}{4}.$$

The deuteron has no bound states with 2-particle spin $S = 0$. The potential must therefore be spin dependent. The $S = 0$ potential just misses having a bound state. This property makes itself felt in a large scattering cross section for $E - V_0 \approx 0$, a low-energy resonance. For a detailed discussion of proton–neutron scattering and the bound or nearly bound states of the deuteron, see Chapter 44.

Problems 7–8: Square Well Problems

More complicated square well problems can often be used to gain qualitative solutions for more sophisticated problems. The following two problems can be used to illustrate some interesting physics.

7. The double-minimum potential problem. The square well double-minimum potential, shown in (c) of Fig. P7, can be used as a rough approximation for the potential governing the motion of the N atom relative to the H_3 plane, one of the vibrational degrees of freedom of the ammonia molecule, NH_3 (the degree of freedom responsible for the transition used in the NH_3 MASER, the historical forerunner of all LASERS and MASERS).

$$V = V_0 \quad \text{for } |x| < a \qquad \text{Region II},$$

$$V = 0 \quad \text{for } a < |x| < b \qquad \text{Regions I, III},$$

$$V = \infty \quad \text{for } |x| > b \qquad \text{Regions IV}.$$

The mass, μ, is the reduced mass for the N–H_3 pair:

$$\mu = \frac{3m_H m_N}{(3m_H + m_N)}.$$

Exploit $V(x)$ is an even function of x, so the solutions, $\psi(x)$, must be either even or odd functions of x. It is therefore sufficient to find acceptable solutions for $x \geq 0$ and continue these appropriately into the region, $x < 0$. Find the transcendental equations from which the eigenvalues of E, corresponding to both the even and odd eigenfunctions, can be found for the states with $E < V_0$. Show graphically how the solutions can be found. Show, in particular, that for $E \ll V_0$, the solutions follow from

$$k_n(b - a) = n\pi - \Delta\phi, \quad \text{with } \Delta\phi \ll 1, \quad k_n^2 = \frac{2\mu}{\hbar^2} E_n,$$

with slightly different $\Delta\phi$ for the eigenvalues associated with the even and odd solutions, so the eigenvalues of E occur in nearly degenerate pairs, when $E \ll V_0$.

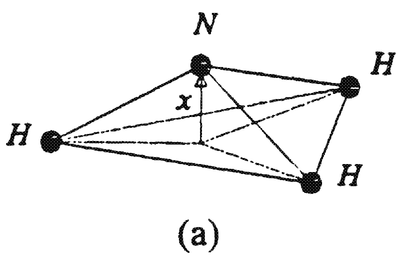

FIGURE P7. (a) The NH_3 inversion coordinate, x.

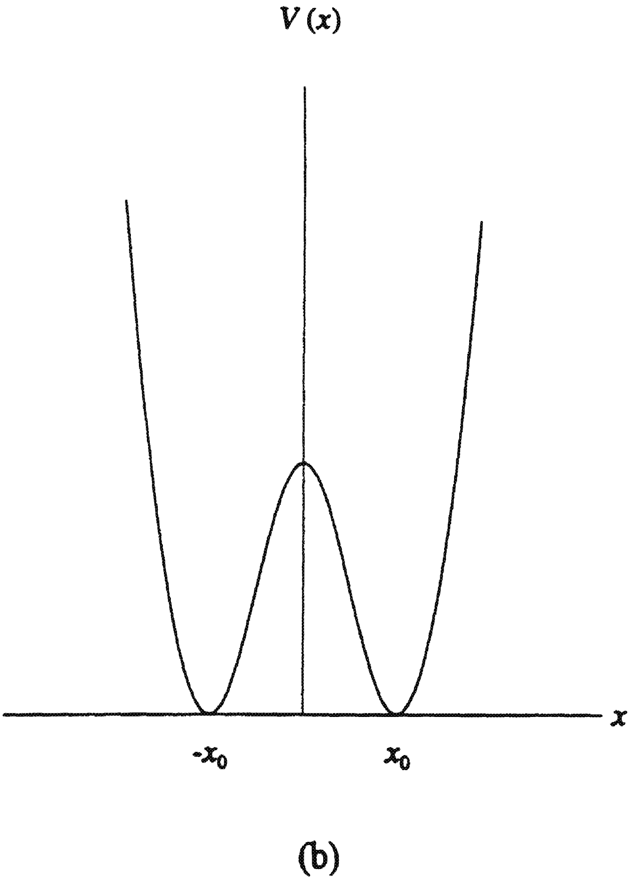

FIGURE P7. (b) Realistic $V(x)$.

Show, in this case, the splitting, ΔE_n, of the nearly degenerate pair is given by

$$\Delta E_n = (E_n^{\text{odd}} - E_n^{\text{even}}) = \frac{\hbar^3 n^2 \pi^2 \sqrt{8}}{(b-a)^3 \sqrt{\mu^3 (V_0 - E_n)}} e^{-\frac{2a}{\hbar}\sqrt{2\mu(V_0 - E_n)}},$$

where

$$E_n \approx \frac{n^2 \pi^2 \hbar^2}{2\mu(b-a)^2}.$$

Retain only dominant terms in all expansions of $\Delta\phi$ and in powers of E_n / V_0. Hints: The even (odd) solutions in the central region, II, are of the form $\cosh \kappa x$, ($\sinh \kappa x$), where $\kappa^2 = 2\mu(V_0 - E)/\hbar^2$. All solutions are of the form $\sin[k(x-b)]$ in region III.

8. Virtually bound states. Assume the potential, $V(r)$, shown in (a) of the Fig. P8, which is an effective potential for the motion of an α-particle relative to a heavy nucleus, can be approximated by the simpler square well potential of (b). Find solutions, $\psi(r)$, for this square well problem for energies, $E > 0$. The boundary condition at $r = 0$ is $\psi(r = 0) = 0$. Note, all energies, $E > 0$, lead to acceptable oscillatory solutions in region III.

Show, in general, for arbitrary positive energies, E,

$$\left|\frac{\psi_{\rm III}}{\psi_{\rm I}}\right|^2 \text{ is of order } e^G, \qquad \text{with } G = \frac{2(b-a)}{\hbar}\sqrt{2\mu(V_{\rm I} - E)}.$$

For $|\psi_{\rm I}|$ and $|\psi_{\rm III}|$, take the amplitudes of the oscillatory functions in regions I and III.

Show, however, the ratio

$$\left|\frac{\psi_{\rm III}}{\psi_{\rm I}}\right|^2 \text{ can be of order } e^{-G}$$

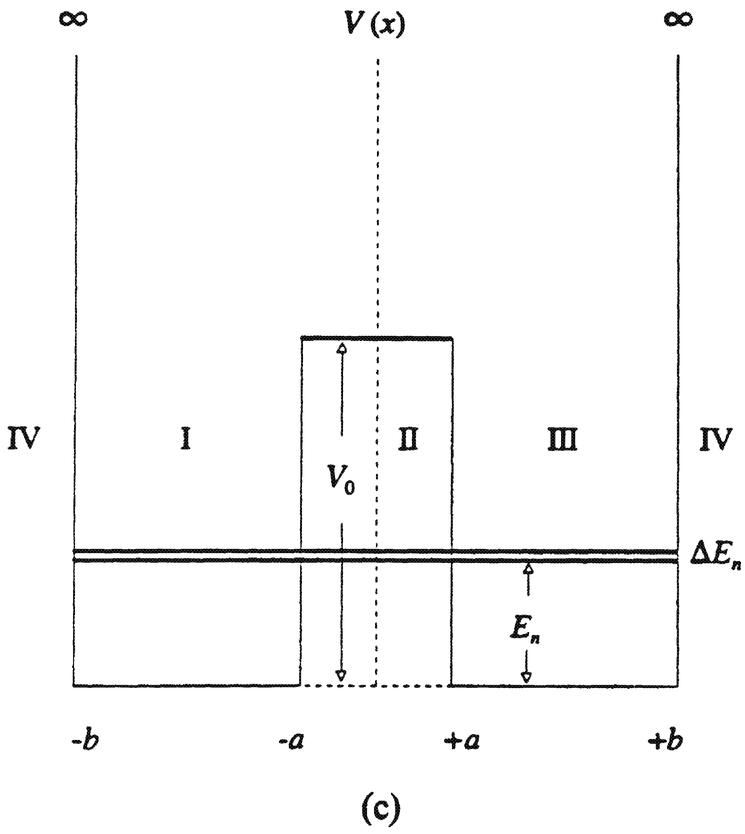

FIGURE P7. (c) Square well analogue.

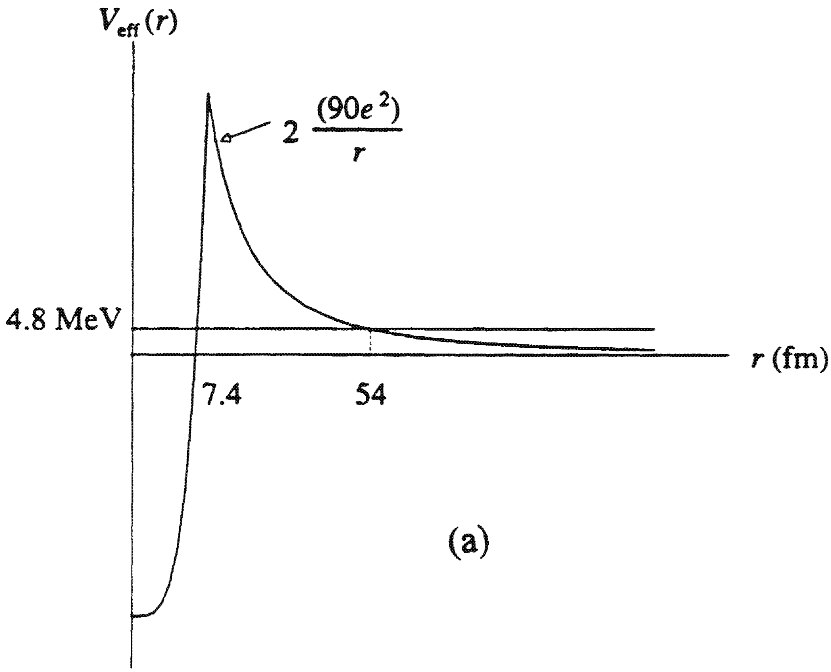

FIGURE P8. (a) Realistic $V_{\text{eff.}}(r)$ for the α-^{234}Th motion.

for certain, specific values of $E = \bar{E}$. The factor e^{-G} is known as the Gamow penetrability factor. Find the transcendental equation from which these values of $\bar{E}$ can be determined graphically in terms of the parameters, μ, a, b, V_0, V_1. Show also, for each such solution, $\bar{E}$, a range of energies exists, ΔE, about $\bar{E}$, for which

$$\left| \frac{\psi_{\text{III}}}{\psi_{\text{I}}} \right|^2 \approx e^{-G},$$

and show

$$\Delta E \approx 4\frac{(V_1 - \bar{E})}{(V_1 + V_0)} \sqrt{\frac{\hbar^2(\bar{E} + V_0)}{2\mu a^2}} \frac{1}{\cos\sqrt{2\mu a^2(\bar{E} + V_0)/\hbar^2}} e^{-G}.$$

Note: A realistic estimate of e^G in a heavy nucleus, e.g., ^{238}U, would be $e^G \approx 10^{38}$.

C The Periodic Square Well Potential

Another interesting case in which a square well approximation may shed considerable light on an important physical problem is that of an N-fold periodic potential. For very large N, this leads to a basic problem in condensed matter physics, the motion of an electron in a crystalline lattice with N lattice points. For very small

N, such as $N = 2$ or $N = 3$, examples of motions in an N-fold periodic potential may be found in the hindered internal rotation of one atomic unit relative to another in a molecule. A symmetrical X_2Y_4 molecule, such as ethylene, C_2H_4, e.g., has one degree of freedom, ϕ, which describes the highly hindered rotational motion of one essentially rigid CH_2 unit relative to the other on a circle in a plane perpendicular to the C – C symmetry axis, as shown in Fig. 4.3. The wave equation separates approximately, so the hindered internal rotation can be described by the one degree of freedom Schrödinger equation

$$-\frac{\hbar^2}{2I}\frac{d^2\psi}{d\phi^2} + V(\phi)\psi(\phi) = E\psi(\phi), \tag{22}$$

with $I = I_1 I_2/(I_1 + I_2)$, and $I_1 = I_2 = 2m_Y r_Y^2$. The potential, $V(\phi)$, could be approximated by a purely sinusoidal potential,

$$V(\phi) = \tfrac{1}{2}V_0(1 - \cos 2\phi),$$

or, on the other hand, by a square well potential with potential valleys of $V = 0$ and widths $2a$ centered at $\phi = 0$ and at $\phi = \pi$, and potential barriers of constant heights of V_0 and widths w centered at $\phi = \frac{1}{2}\pi$ and at $\phi = \frac{3}{2}\pi$, where $4a + 2w = 2\pi r_Y$.

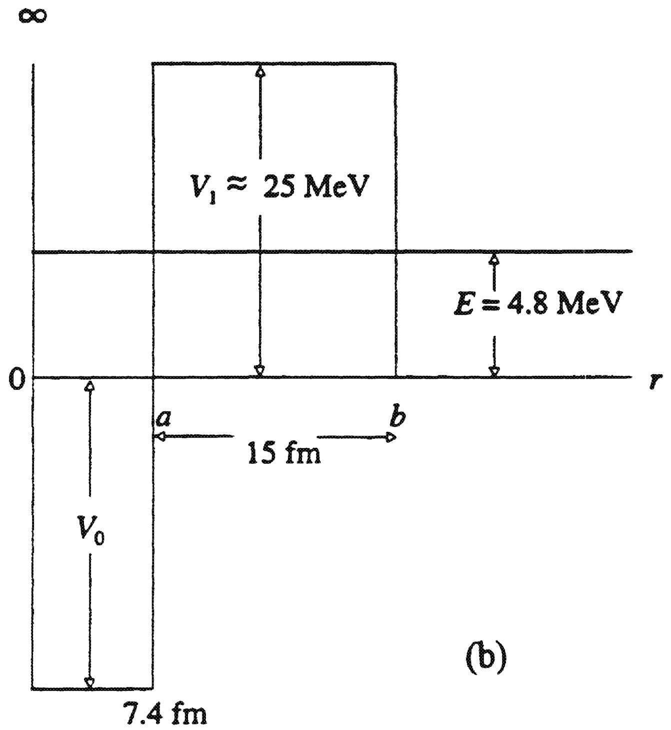

FIGURE P8. (b) Square well analogue.

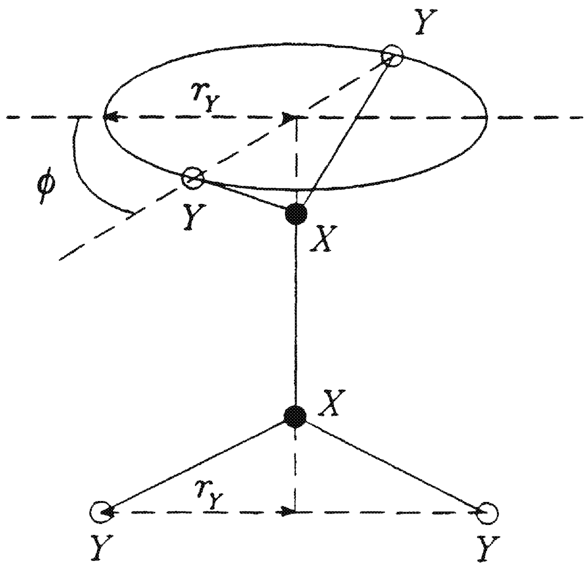

FIGURE 4.3. The X_2Y_4 molecule and its internal rotational coordinate, ϕ.

The true hindering potential is probably somewhere between these two extremes. The square well approximation leads to the easiest solution; yet it contains the essential physics of the problem. A symmetrical X_2Y_6 molecule such as C_2H_6 (ethane) leads to a similar Schrödinger equation with 3-fold periodicity, i.e., with $N = 3$. The symmetrical CH_3NO_2 molecule furnishes an example with $N = 6$-fold periodicity. Here, the C–N bond furnishes the symmetry axis for both the CH_3 and NO_2 units of the molecule. In these examples, the $(N + 1)^{\text{st}}$ site of the potential is truly the same point in 3-D space as the first site. In the condensed matter problem with N lattice sites, one usually takes periodic boundary conditions by assuming the $(N + 1)^{\text{st}}$ site is equivalent to the first site, in the limit $N \to \infty$.

In the square well approximation for the periodic potential, we assume

$$\begin{aligned} &V = 0 \qquad \text{for } (2m - 1)a + mw < x < (2m + 1)a + mw; \\ &V = +V_0 \qquad \text{for } (2m + 1)a + mw < x < (2m + 1)a + (m + 1)w; \\ &m = 0, 1, \ldots, N. \end{aligned} \tag{23}$$

We see the m^{th} potential valley is centered at $x = 2ma + mw$, and the m^{th} potential barrier is centered at $x = (2m + 1)a + (m + \frac{1}{2}w)$; see Fig. 4.4. For the moment, we shall seek only solutions for $E < V_0$. (For the hindered internal rotation problems, we can expect the barrier heights, V_0, to be very large compared with the energies of interest.) For this case, we define

$$k^2 = \frac{2\mu E}{\hbar^2}, \qquad \kappa^2 = \frac{2\mu(V_0 - E)}{\hbar^2},$$

where μ is an effective mass for the problem. We expect the following solutions. In the m^{th} valley centered at $x = 2ma + mw$:

$$\psi(x) = C_m \cos k[x - m(2a + w)] + D_m \sin k[x - m(2a + w)];$$

under the m^{th} potential hill, centered at $x = (2m + 1)a + (m + \frac{1}{2}w)$:

$$\psi(x) = A_m \cosh \kappa\Big(x - [(2m + 1)a + (m + \tfrac{1}{2}w)]\Big)$$

$$+B_m \sinh \kappa\Big(x - [(2m + 1)a + (m + \tfrac{1}{2})w]\Big).$$

The potential is invariant under reflections in the planes centered at $x = 2ma+mw$ and at $x = (2m+1)a+(m+\frac{1}{2}w)$. We might thus be tempted to assume our solutions are either even or odd under these reflection operations and that either $A_m = 0$ or $B_m = 0$, and, similarly, either $C_m = 0$ or $D_m = 0$. These assumptions would be good if all allowed energies were nondegenerate. We shall find, however, most of the allowed energy values are doubly degenerate, with two allowed solutions. We therefore retain the above linear combinations of even and odd functions. To ensure the continuity of the probability density and the probability density currents at the discontinuities of the potential, we shall again require the continuity of the wave functions and their first derivatives at the boundaries between the potential hills and valleys. With the solution under the $(m - 1)^{\text{st}}$ potential hill given by

$$\psi(x) = A_{m-1} \cosh \kappa\Big(x - [(2m - 1)a + (m - \tfrac{1}{2})w]\Big)$$

$$+B_{m-1} \sinh \kappa\Big(x - [(2m - 1)a + (m - \tfrac{1}{2})w]\Big),$$

the continuity of ψ and its first derivative at the left boundary of the m^{th} valley, i.e., at $x = (2m - 1)a + mw$, leads to

$$A_{m-1} \cosh \kappa \tfrac{w}{2} + B_{m-1} \sinh \kappa \tfrac{w}{2} = C_m \cos ka - D_m \sin ka; \tag{24}$$

$$\kappa\big(A_{m-1} \sinh \kappa \tfrac{w}{2} + B_{m-1} \cosh \kappa \tfrac{w}{2}\big) = k\big(C_m \sin ka + D_m \cos ka\big). \tag{25}$$

The continuity of ψ and its first derivative at the right boundary of the m^{th} valley, at $x = (2m + 1)a + mw$, leads to

$$C_m \cos ka + D_m \sin ka = A_m \cosh \kappa \tfrac{w}{2} - B_m \sinh \kappa \tfrac{w}{2}, \tag{26}$$

$$k\big(-C_m \sin ka + D_m \cos ka\big) = \kappa\big(-A_m \sinh \kappa \tfrac{w}{2} + B_m \cosh \kappa \tfrac{w}{2}\big). \tag{27}$$

Solving eqs. (24) and (25) for C_m and D_m and substituting into eqs. (26) and (27) leads to the relation

$$\begin{pmatrix} A_m \\ B_m \end{pmatrix} = \mathbf{M} \begin{pmatrix} A_{m-1} \\ B_{m-1} \end{pmatrix}, \tag{28}$$

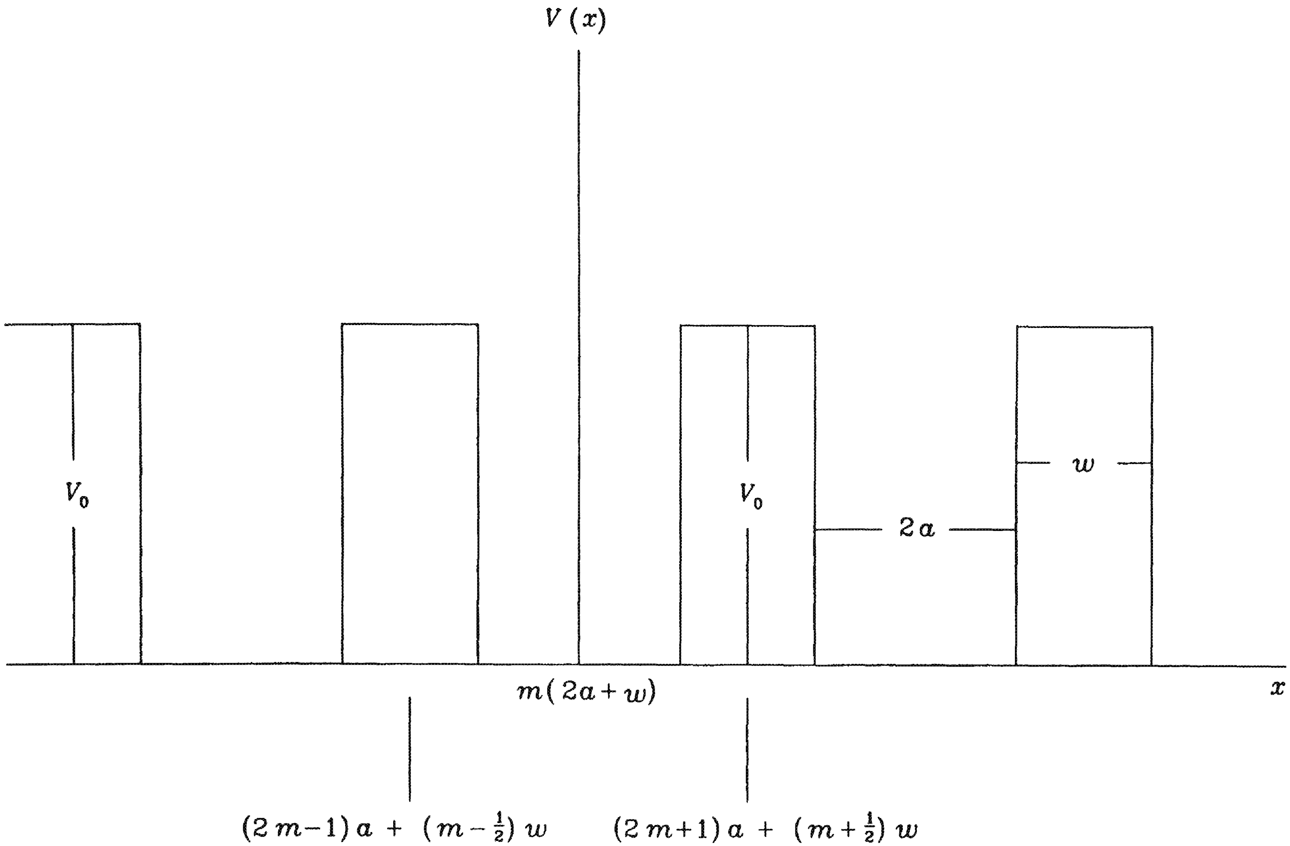

FIGURE 4.4. The periodic square well potential with barrier height, V_0, width, w, and potential valleys of width, $2a$, with $V = 0$.

where the 2×2 matrix, $\mathbf{M}$, is given by

$$\mathbf{M} = \cos 2ka \begin{pmatrix} P & Q+\gamma \\ Q-\gamma & P \end{pmatrix}, \tag{29}$$

with

$$\begin{aligned} P &= \cosh \kappa w + \tfrac{1}{2}\Big(\frac{\kappa}{k} - \frac{k}{\kappa}\Big) \tan 2ka \sinh \kappa w \\ &= \tfrac{1}{2}e^{\kappa w}\Big[1 + \tfrac{1}{2}\big(\frac{\kappa}{k} - \frac{k}{\kappa}\big) \tan 2ka\Big] + \tfrac{1}{2}e^{-\kappa w}\Big[1 - \tfrac{1}{2}\big(\frac{\kappa}{k} - \frac{k}{\kappa}\big) \tan 2ka\Big], \\ Q &= \sinh \kappa w + \tfrac{1}{2}\Big(\frac{\kappa}{k} - \frac{k}{\kappa}\Big) \tan 2ka \cosh \kappa w \\ &= \tfrac{1}{2}e^{\kappa w}\Big[1 + \tfrac{1}{2}\big(\frac{\kappa}{k} - \frac{k}{\kappa}\big) \tan 2ka\Big] - \tfrac{1}{2}e^{-\kappa w}\Big[1 - \tfrac{1}{2}\big(\frac{\kappa}{k} - \frac{k}{\kappa}\big) \tan 2ka\Big], \\ \gamma &= \tfrac{1}{2}\big(\frac{\kappa}{k} + \frac{k}{\kappa}\big) \tan 2ka. \end{aligned} \tag{30}$$

The continuity of the probability density and the probability density current require

$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = \mathbf{M}^N \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \pm \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}. \tag{31}$$

In particular, the *wave function* is not single valued for the case of the minus sign in the $\pm$ above. The probability density and the probability density current, however, are single valued. Also, the wave function would diverge as $e^{pN\kappa w}$ as $x \to pN(2a+w)$ in the above, or as $\phi \to pN(2\pi)$ in the wave function of eq. (22), as $p \to \infty$; unless the coefficients of the $e^{+\kappa w}$ terms of P and Q above are precisely equal to zero, or at most of order $e^{-\kappa w}$. We are thus led to the requirement

$$\tfrac{1}{2}\big(\frac{\kappa}{k} - \frac{k}{\kappa}\big) \tan 2ka = -1 + 2\beta e^{-\kappa w}, \tag{32}$$

where the new parameter, β, may, like k and κ, in general, also be a function of the energy E. Eq. (32) will thus lead to a transcendental equation for the determination of the allowed values of the energy, E, where the parameter, β, must also be fixed to satisfy eq. (31). It will be instructive to examine first the case of high potential barriers, $V_0 \gg E$. This case will actually be of interest for the problems of internal hindered rotations in most molecules. In the limit $V_0 \to \infty$, we have a problem with N-potential wells with infinitely high walls. In that case we saw [eq. (19)] $ka = \frac{1}{2}n\pi$. For the N-fold periodic square well with large V_0, we shall therefore try

$$2ka = n\pi + 2(\Delta k)a, \tag{33}$$

where $(\Delta k)a$ are small quantities, dependent on the integer n. Terms of second order in these small quantities will be negligible. Thus,

$$\cos 2ka \approx (-1)^n, \qquad \tan 2ka \approx 2(\Delta k)a = -2\frac{1}{\big(\frac{\kappa}{k} - \frac{k}{\kappa}\big)}(1 - 2\beta e^{-\kappa w}). \tag{34}$$

In the high barrier approximation, we have

$$e^{-\kappa w} \ll \frac{k}{\kappa} \ll 1.$$

With $\beta \approx$ order(1), we might thus expect the $\beta e^{-\kappa w}$ term to be negligible and obtain an energy shift, given by $(\Delta k)a \approx (-k/\kappa)$, of the $2N$-fold degenerate zeroth-order energy of $E_n^{(0)} = (\hbar^2 n^2 \pi^2/8\mu a^2)$. [The factor 2 in the degeneracy factor, $2N$, comes from the $\pm$ sign in the boundary condition of eq. (31).] Even though the splitting of the $2N$-fold degenerate levels with $E \ll V_0$ will be smaller than the above shifts by a factor of $e^{-\kappa w}$, this splitting is of primary interest. We will therefore retain this factor in eq. (34). In the high barrier limit, $e^{-\kappa w} \ll (k/\kappa) \ll 1$, the 2×2 matrix $\mathbf{M}$ reduces to

$$\mathbf{M} = (-1)^n \begin{pmatrix} \beta & \beta - 1 \\ \beta + 1 & \beta \end{pmatrix}. \tag{35}$$

For $N = 2$, the matrix needed for eq. (31) is

$$\mathbf{M}^2 = \begin{pmatrix} (2\beta^2 - 1) & 2\beta(\beta - 1) \\ 2\beta(\beta + 1) & (2\beta^2 - 1) \end{pmatrix}. \tag{36}$$

Eq. (31) then has allowed solutions for

$$\begin{aligned}
&\beta = +1, \quad \text{with} \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \quad \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 4 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = +1\begin{pmatrix} 0 \\ 1 \end{pmatrix},\\
&\beta = -1, \quad \text{with} \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = \begin{pmatrix} 1 & 4 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = +1\begin{pmatrix} 1 \\ 0 \end{pmatrix},\\
&\beta = 0, \quad \text{with} \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = -1\begin{pmatrix} A_0 \\ B_0 \end{pmatrix},\\
&\qquad \text{where now} \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ or } \begin{pmatrix} 0 \\ 1 \end{pmatrix}.
\end{aligned} \tag{37}$$

For $N = 2$, three solutions exist for the allowed energies: two of them corresponding to $\beta = +1$ and $\beta = -1$ with but a single eigenfunction, corresponding to nondegenerate energy eigenvalues; and one with $\beta = 0$ with two independent solutions (which could be any linear combination of the above solutions), corresponding to a double degeneracy of this energy level. Expanding eq. (34) in powers of (k/κ), but retaining the dominant energy splitting term, we obtain for $N = 2$

$$E_n = \frac{\hbar^2}{2\mu a^2}\left(\frac{n^2\pi^2}{4} - n\pi\frac{k_n}{\kappa_n} + \begin{matrix} +2n\pi(k_n/\kappa_n)e^{-\kappa_n w} \\ 0 \\ -2n\pi(k_n/\kappa_n)e^{-\kappa_n w} \end{matrix} \right), \tag{38}$$

where we can approximate (k_n/κ_n) by $\sqrt{(E_n^{(0)}/V_0)}$, but will retain the $E_n^{(0)}$ term in the exponential factor,

$$e^{-\kappa_n w} \approx e^{-[2\mu(V_0 - E_n^{(0)})w^2/\hbar^2]^{\frac{1}{2}}},$$

because of the sensitivity of the exponential factor on its exponent.

Next, for the three-fold periodic potential with $N = 3$, we have

$$\mathbf{M}^3 = (-1)^n \begin{pmatrix} \beta(4\beta^2 - 3) & (4\beta^2 - 1)(\beta - 1) \\ (4\beta^2 - 1)(\beta + 1) & \beta(4\beta^2 - 3) \end{pmatrix}. \tag{39}$$

The boundary condition of eq. (31) is satisfied for $\beta = +1$ and $\beta = -1$, with nondegenerate solutions

$$\begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{respectively,}$$

and for $\beta = +\frac{1}{2}$ and $\beta = -\frac{1}{2}$, where both of these lead to doubly degenerate levels with a linear combination of the above two solutions. The energy $E_n^{(0)}$ is thus split into four levels, a highest and a lowest nondegenerate level and two intermediate doubly degenerate levels.

At this stage, it should be mentioned that the splittings of the ground-state $n = 0$ internal rotation energies in the molecules, C_2H_4 and C_2H_6, are too small to be observable. The factors, $e^{-\kappa_0 w}$, are too small to be observable in these molecules. In the methyl alcohol molecule, CH_3OH, however, the splittings of the $n = 0$ and higher levels are observable and have been studied extensively by microwave spectroscopy. In this molecule, the internal rotation degree of freedom is strongly coupled with the rotational degrees of freedom of the whole molecule. Since this molecule is an asymmetric rotator, (see Chapter 15), the combined rotation–internal rotation spectrum is very complicated.

For the case of general N, it will be convenient to introduce the new parameter α, via

$$\beta = \cos\alpha.$$

In terms of this new parameter, we have

$$\mathbf{M}^N = (-1)^{nN} \begin{pmatrix} \cos N\alpha & \frac{\sin N\alpha}{\sin\alpha}(\cos\alpha - 1) \\ \frac{\sin N\alpha}{\sin\alpha}(\cos\alpha + 1) & \cos N\alpha \end{pmatrix}. \tag{40}$$

Eqs. (36) and (39) show this is satisfied for $N = 2$ and $N = 3$. Also,

$$\begin{pmatrix} \cos(N-1)\alpha & \frac{\sin(N-1)\alpha}{\sin\alpha}(\cos\alpha - 1) \\ \frac{\sin(N-1)\alpha}{\sin\alpha}(\cos\alpha + 1) & \cos(N-1)\alpha \end{pmatrix} \begin{pmatrix} \cos\alpha & (\cos\alpha - 1) \\ (\cos\alpha + 1) & \cos\alpha \end{pmatrix}$$
$$= \begin{pmatrix} \cos N\alpha & \frac{\sin N\alpha}{\sin\alpha}(\cos\alpha - 1) \\ \frac{\sin N\alpha}{\sin\alpha}(\cos\alpha + 1) & \cos N\alpha \end{pmatrix}, \tag{41}$$

so that the relation (40) is proved by induction. In this general case, two nondegenerate levels again exist, with $\alpha = 0$, and $\alpha = \pi$, and now $(N - 1)$ doubly degenerate levels with

$$\alpha = \frac{\ell\pi}{N}; \qquad \ell = 1, 2, \ldots, (N-1).$$

The energies for the case $E_n^{(0)} \ll V_0$ are given by

$$E_n = \frac{\hbar^2}{2\mu a^2}\left(\frac{n^2\pi^2}{4} - n\pi\sqrt{\frac{E_n^{(0)}}{V_0}}\left[1 - 2\cos\frac{\ell\pi}{N} e^{-[2\mu(V_0 - E_n^{(0)})w^2/\hbar^2]^{\frac{1}{2}}}\right]\right)$$

$$\ell = 0, 1, \ldots, N. \tag{42}$$

For very large N in a crystalline lattice, therefore, we have a set of $(N + 1)$ finely spaced, discrete, allowed energy values, centered about a slightly downward-shifted $E_n^{(0)}$. In the limit, $N \to \infty$, this becomes a continuous narrow band of allowed energies of bandwidth

$$\Delta E = \frac{\hbar^2}{ma^2} n^2 \pi^2 \sqrt{\frac{\hbar^2}{2ma^2 V_0}} e^{-[2m(V_0 - E_n^{(0)})w^2/\hbar^2]^{\frac{1}{2}}}, \tag{43}$$

where we have set $\mu = m$, the electron mass. These continuous bands of allowed energies are separated by energy gaps of order $(E_{n+1}^{(0)} - E_n^{(0)})$. As $E_n^{(0)}$ approaches V_0, the bandwidths become larger and the gaps smaller. Of course, as $E_n^{(0)} \to V_0$, our high V_0 approximations are no longer valid. The bandwidth and gap structure, however, survives even into the region $E > V_0$. (For details, see, e.g., C. Kittel, *Introduction to Solid State Physics*, New York: John Wiley, 1956.) In a real solid, we must of course also deal with a 3-D structure. It is therefore perhaps interesting to note that in a cooler ring of some modern generation heavy ion accelerators we may approximate a truly 1-D crystal of cold (hence, nearly monoenergetic) heavy ions. In the limit of temperature, $T \to 0$, these form a 1-D crystal of equally spaced monoenergetic heavy ions. Here, indeed, the $(N + 1)^{\text{st}}$ ion *is* the 1^{st} ion, and the periodic boundary condition of eq. (31) is no longer an approximation. Although the square well solution has all of the qualitative features found with a more realistic potential, an approximate solution for a more realistic $V(x)$ can be found through the WKB approximation to be treated in Chapters 36 and 37 (see, in particular, problem 55).

D The Existence of Discrete Energy Levels: General $V(x)$

For a $V(x)$ that is such that $V \to \infty$ for both large positive and large negative values of x, the existence of a discrete set of allowed energy levels follows in a general way from the requirement that the solutions be square-integrable, i.e.,

$$\int_{-\infty}^{+\infty} \psi^* \psi \, dx = \text{finite}, \tag{44}$$

and that ψ and $\frac{d\psi}{dx}$ be continuous. For the type of potential function shown in Fig. 4.5, with an arbitrary E, but $E > V_{min.}$, we have in region I, with $E > V(x)$, between the left and right classical turning points,

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi = 0. \tag{45}$$

In region I, therefore, the solutions are oscillatory, but with a variable (x-dependent) wavelength because $k(x) = \frac{2\pi}{\lambda}$; i.e., the curvature is always toward the x-axis. In

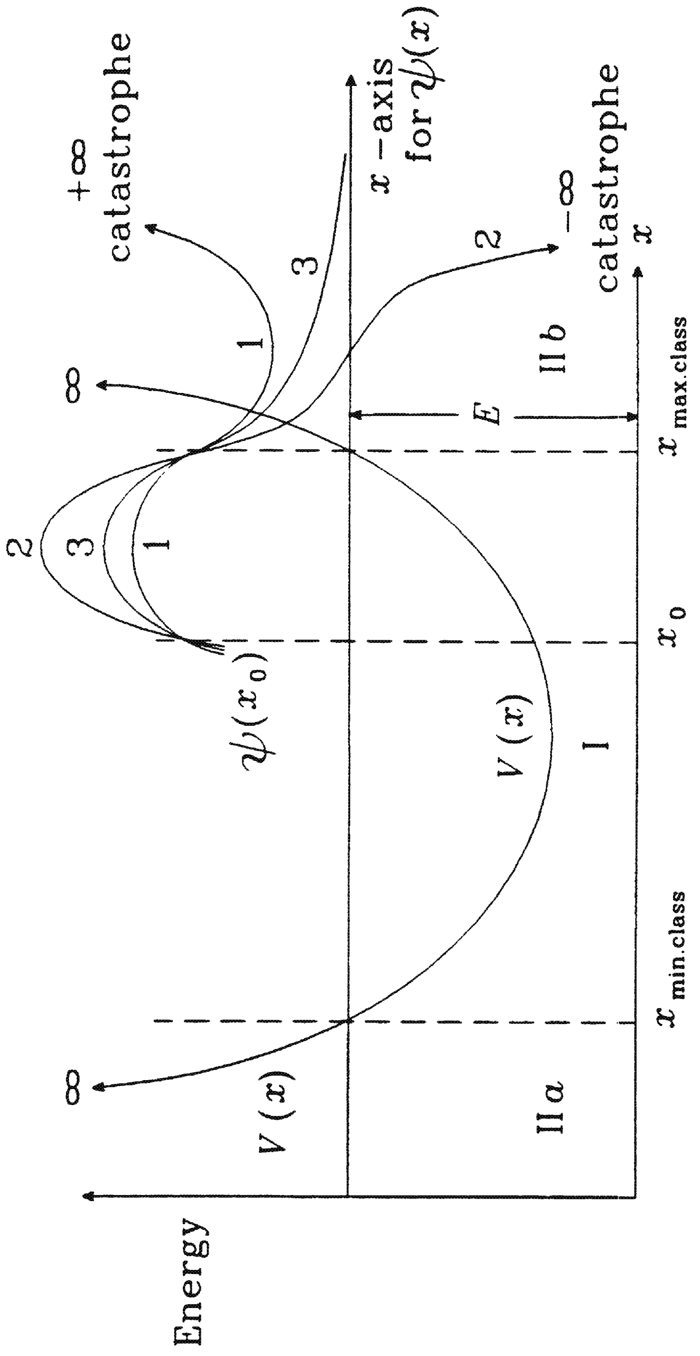

FIGURE 4.5. Solutions, $\psi(x)$, for three different initial conditions at x_0.

regions II, conversely, for $x > x_{\text{max.class.}}$, or for $x < x_{\text{min.class.}}$, the Schrödinger equation has the form

$$\frac{d^2\psi}{dx^2} - \kappa^2(x)\psi = 0, \tag{46}$$

because $E < V(x)$. In regions II, therefore, the curvature is always away from the axis. To find a solution, start with some assumed initial value for $\psi(x_0)$ and $\frac{d\psi}{dx}|_{x_0}$. The equation then gives us the value of $\psi(x)$ and $\frac{d\psi}{dx}$ at the neighboring points. We could numerically determine the solution, say, from some x_0 in the classically allowed region to the right boundary, where the solution changes from one with curvature toward the axis to one with curvature away from the axis. For the solution, labeled 1, in Fig. 4.5, e.g., the curvature away from the axis will be such that $\psi(x)$ never reaches negative values. The function and its derivative will thus both get larger and larger as x reaches further away from the classically allowed values of x; and both $\psi(x)$ and $\frac{d\psi}{dx}$ will go to $+\infty$ as $x \to +\infty$. This is a catastrophe. Such a function is surely not square-integrable. We can, however, start the process over again. Starting with the same $\psi(x_0)$ at x_0, we can adjust the first derivative at x_0, as in the curve, labeled 2. Now, as we reach the right classical turning point, the curvature away from the axis can be made less; perhaps we have chosen a derivative at x_0 such that now the solution in the classically forbidden region, IIa, reaches the value 0 and thereafter curves away from the axis becoming more and more negative along with its first derivative, so now both $\psi \to -\infty$ and $\frac{d\psi}{dx} \to -\infty$ as $x \to +\infty$. Again, we have a catastrophe. This solution cannot be square-integrable. We can, however, continue to adjust the first derivative at x_0 until it is just right, so both $\psi(x)$ and $\frac{d\psi}{dx} \to 0$ together as we penetrate into the classically forbidden region, $x \to +\infty$, as shown in the solution, labeled 3 in Fig. 4.5. This solution will have only a small probability the particle will be found in the classically forbidden region. This solution can now be continued from x_0 to more negative values of x, but because we have no further freedom of "fixing" the first derivative at x_0, when the solution reaches the left turning point, it will undoubtedly curve away from the axis such that either both $\psi(x)$ and $\frac{d\psi}{dx} \to +\infty$ or both $\to -\infty$ as $x \to -\infty$. Again, a catastrophe: a nonsquare-integrable solution. For arbitrary values of E, therefore, we will not get an allowed (square-integrable) solution. We can now, however, further adjust the energy E such that once we have fixed the proper behavior as $x \to +\infty$ we will also have both $\psi(x)$ and $\frac{d\psi}{dx} \to 0$ as $x \to -\infty$. This unique situation can only occur for a discrete set of values of E, the allowed values of E: $E_0, E_1, E_2, \ldots, E_n, \ldots$. This situation exists for a $V(x)$, which $\to +\infty$ for both $x \to \pm\infty$.

In Fig. 4.6, we show a potential function that for $E > \bar{V} = V_\infty$ has only a left classically forbidden region. For such a $V(x)$, for $E > \bar{V}$, we can always fix the solution such that both $\psi(x)$ and $\frac{d\psi}{dx}$ together $\to 0$ as $x \to -\infty$. For such a potential, all values of $E > \bar{V}$ are allowed. As $x \to +\infty$, the solution remains oscillatory. The $\psi(x)$ is not square integrable, but the solution has a sensible probability interpretation. It now corresponds to a particle with finite kinetic energy coming in from $+\infty$ being reflected near $x = 0$ and going back out to $+\infty$. This

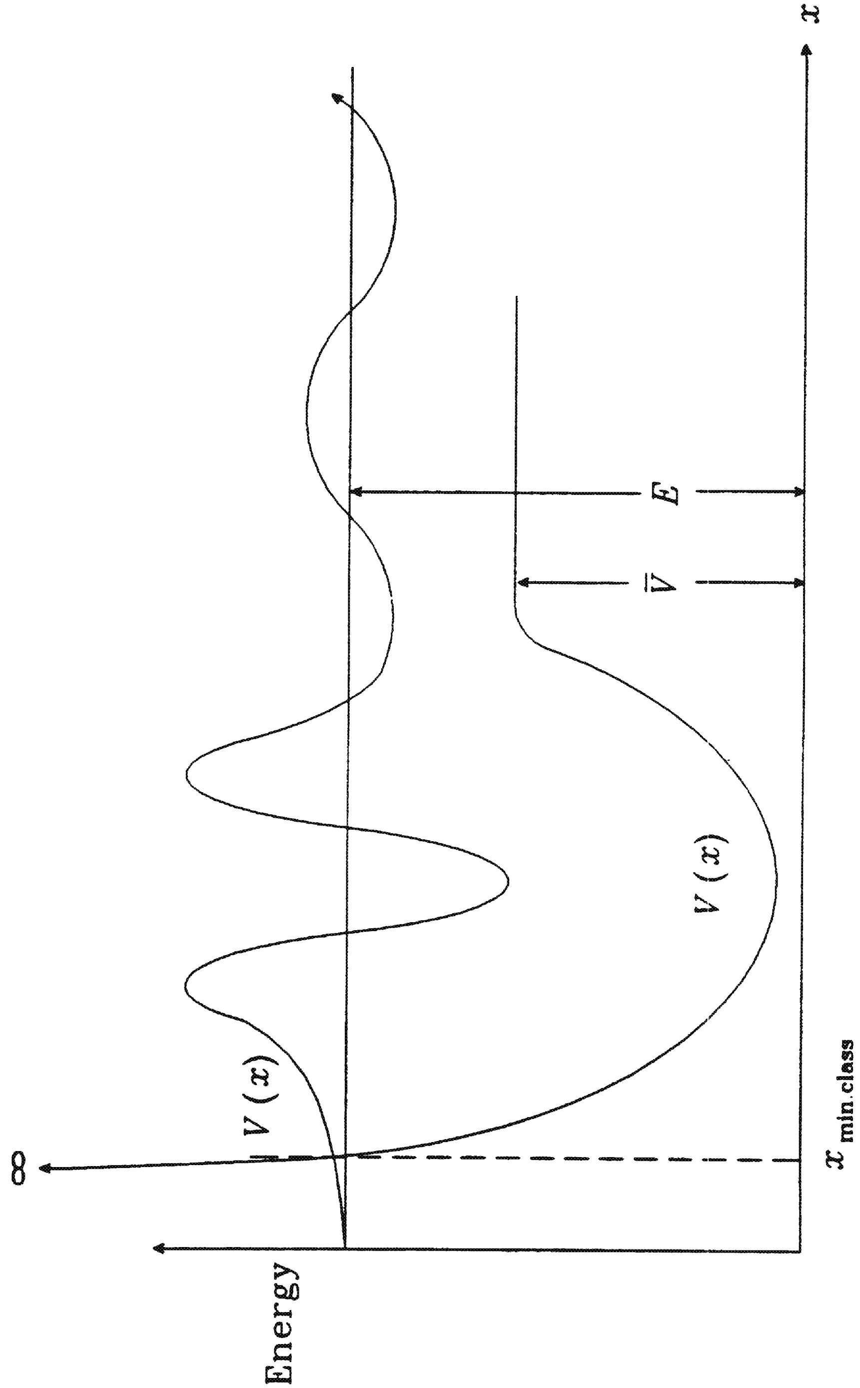

FIGURE 4.6. $V(x)$ with a continuous spectrum for $E > \bar{V} = V_\infty$.

is a scattering problem, associated with the continuum of allowed energies. The wave function is now normalized to describe a definite flux (value of $\vec{S}$). Because the solution $\psi(x)$ again has a sensible probability interpretation for values of x as $x \to +\infty$ for all values of $E > \bar{V}$, all values of $E > \bar{V}$ are allowed leading to a continuum of allowed energies.

Finally, in Fig. 4.7, another potential is shown, of the type perhaps describing the motion of an α-particle relative to a heavy nucleus. For $E > \bar{V} = V_{\infty}$, we again have an energy continuum; for values of $\bar{V} < E < V_{\text{barrier}}$ and arbitrary values of E, however, we would expect a much greater probability the particle be in region III, outside the barrier. Now, certain states will exist, with a narrow width (narrow range ΔE) about a discrete E for which the probability of finding the particle in region I rather than in region III is overwhelmingly large. These states are the virtually bound states. They are, however, part of the energy continuum and have a finite (perhaps very small) probability the particle will tunnel through the barrier and stream out to $+\infty$ (see problem 8).

E The Energy Eigenvalue Problem: General

For potentials with a discrete spectrum of allowed energy values (as in Fig. 4.5), the Schrödinger equation leads to the allowed solutions

$$H\psi_n(x) = E_n\psi_n(x), \tag{47}$$

with allowed energy values, E_n, the so-called eigenvalues, or characteristic values of E.

1. If the Hamiltonian operator is hermitian, $H = H^{\dagger}$, the E_n are real.

$$\begin{aligned} &< \psi_n, H\psi_n >= E_n < \psi_n, \psi_n >= E_n \\ &=< (H^{\dagger}\psi_n), \psi_n >=< (H\psi_n), \psi_n >=< \psi_n, H\psi_n >^*= E_n^*. \end{aligned} \tag{48}$$

2. The orthogonality of the eigenfunctions, ψ_n, follows from

$$H\psi_n = E_n\psi_n, \tag{49}$$

and

$$H\psi_m^* = E_m\psi_m^*. \tag{50}$$

By multiplying the first of these equations by ψ_m^*, the second by ψ_n, and subtracting, we get

$$< \psi_m, H\psi_n > - < \psi_n, H\psi_m >^* \quad = \quad (E_n - E_m) < \psi_m, \psi_n > . \tag{51}$$

The left-hand side of this equation is zero via the hermiticity of H, so

$$(E_n - E_m) < \psi_m, \psi_n > \quad = \quad 0. \tag{52}$$

Thus, with $E_n \neq E_m$, $< \psi_m, \psi_n >= 0$. The eigenfunctions are orthogonal to each other.

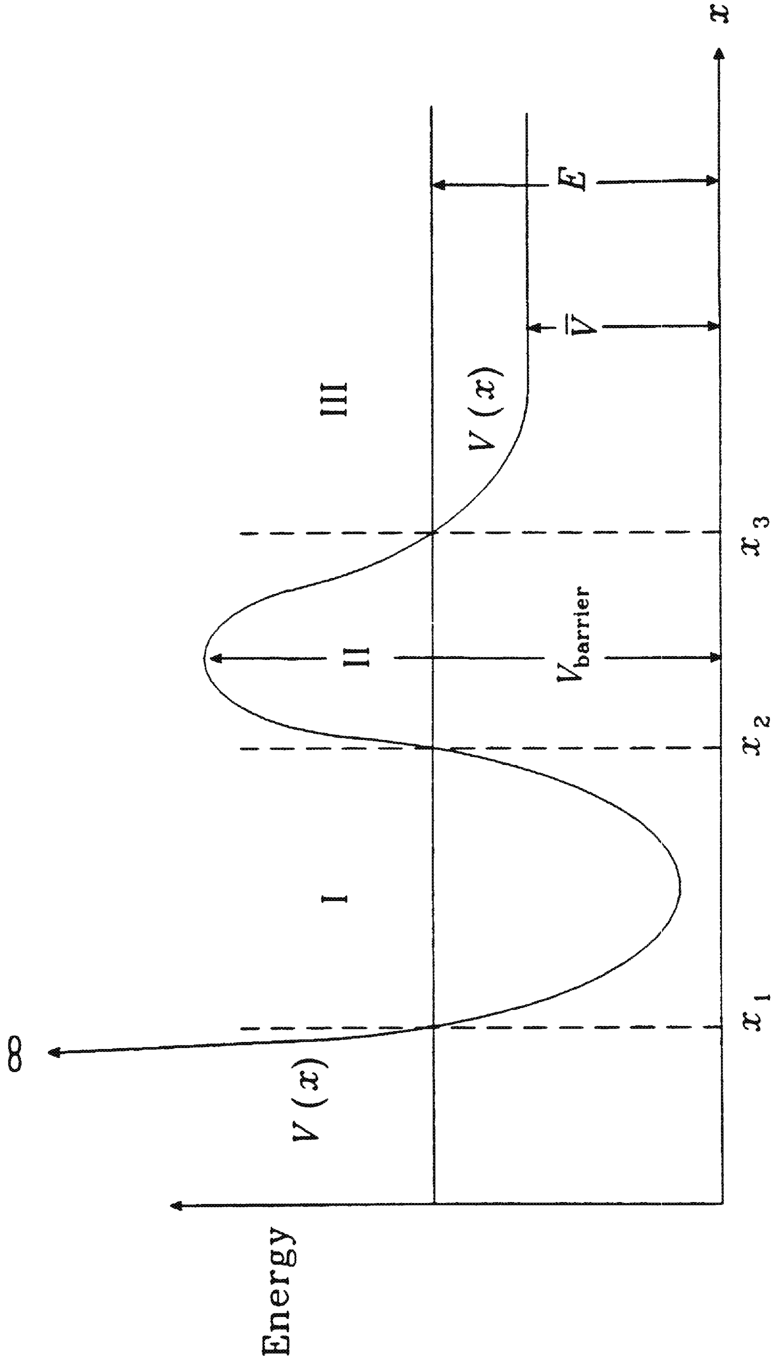

FIGURE 4.7. $V(x)$ with possible virtually bound states for $\bar{V} < E < V_{\text{barrier}}$.

F A Specific Example: The One-Dimensional Harmonic Oscillator

The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dq^2}\psi(q) + \frac{m\omega_0^2}{2}q^2\psi(q) = E\psi(q). \tag{53}$$

As a first step in the solution, it will be convenient to introduce a dimensionless coordinate x; i.e., to define appropriately scaled coordinates. Thus, the physical displacement, q, will be transformed into a dimensionless coordinate, x, where the "yardstick" for q can be obtained from the value of the potential energy which must be proportional to the basic energy scale of the problem, $m\omega_0^2 q^2 = \text{const.}(\hbar\omega_0)$, so a natural yardstick for q is $\sqrt{\hbar/m\omega_0}$:

$$q = \sqrt{\frac{\hbar}{m\omega_0}}x. \tag{54}$$

Similarly,

$$p = \sqrt{\hbar m\omega_0}\,p_x, \qquad p_x = \frac{1}{i}\frac{d}{dx}, \tag{55}$$

$$E = \hbar\omega_0\epsilon, \tag{56}$$

and the wave equation becomes

$$-\frac{1}{2}\frac{d^2}{dx^2}\psi(x) + \frac{1}{2}x^2\psi(x) = \epsilon\psi(x). \tag{57}$$

The equation has a singular point only at $x = \pm\infty$. The first step is to find the asymptotic form of the solution at $\pm\infty$. The $\epsilon\psi(x)$ term of eq. (57) is negligible compared with the $x^2\psi(x)$ term as $x \to \pm\infty$. Because

$$\frac{d^2}{dx^2}\left(e^{-\frac{x^2}{2}}\right) = (x^2-1)e^{-\frac{x^2}{2}} \to x^2 e^{-\frac{x^2}{2}} \quad \text{as } x \to \pm\infty,$$

$$\psi(x) \to e^{-\frac{x^2}{2}} \quad \text{as } x \to \pm\infty. \tag{58}$$

(The second possible solution with a + exponential is ruled out by the boundary condition.) We transform the solution into

$$\psi(x) = u(x)e^{-\frac{x^2}{2}}, \tag{59}$$

$$\frac{d^2u}{dx^2} - 2x\frac{du}{dx} + (2\epsilon - 1)u(x) = 0. \tag{60}$$

For $u(x)$, try a series solution

$$u(x) = \sum_{k=0} a_k x^k, \tag{61}$$

where

$$\sum_{k=2} a_k k(k-1)x^{k-2} = \sum_{k=0} (2k+1-2\epsilon)a_k x^k. \tag{62}$$

Changing the dummy summation index on the left-hand side from $k \to (k+2)$ and equating coefficients of the k^{th} term leads to the two-term recursion relation

$$\frac{a_{k+2}}{a_k} = \frac{2k+1-2\epsilon}{(k+2)(k+1)}. \tag{63}$$

To examine the behavior of this infinite series at large values of x, look at the asymptotic form as $k \to \infty$. This form is

$$\frac{a_{k+2}}{a_k} \to \frac{2}{k} \tag{64}$$

or

$$a_{2m} \to \frac{1}{m!}, \tag{65}$$

so we would have

$$u(x) \to e^{+x^2}. \tag{66}$$

Thus, for general values of ϵ, $\psi(x) \to \infty$, we do not have a square-integrable solution. For the special value

$$2\epsilon = (2n+1), \tag{67}$$

the infinite series of eq. (61) can terminate at the n^{th} term. If n is an even integer and $a_0 \neq 0$, the recursion formula of eq. (63) yields $a_{n+2} = 0$, and, therefore, $a_m = 0$ with $m = n+2k$. If n is an even integer, and if we had $a_1 \neq 0$, however, all a_m with odd integers m would survive up to $m \to \infty$, and the infinite series would again diverge as e^{+x^2}. If n is an even integer, we must therefore have $a_1 = 0$. Similarly, if n is an odd integer, we must have $a_0 = 0$. The series therefore terminates

$$\begin{array}{llll} \text{with} \quad \text{n} = \text{even}, & a_0 \neq 0, & a_1 = 0, & a_{n+2} = 0, \\ \text{with} \quad \text{n} = \text{odd}, & a_1 \neq 0, & a_0 = 0, & a_{n+2} = 0. \end{array} \tag{68}$$

For these cases, the wave functions of eqs. (59) and (61) are square-integrable and lead to the discrete set of allowed energy eigenvalues

$$2\epsilon = (2n+1); \qquad E = \hbar\omega_0(n+\frac{1}{2}). \tag{69}$$

To find the coefficients of the polynomial of degree n, invert the recursion relation:

$$\frac{a_{k-2}}{a_k} = -\frac{k(k-1)}{2(n-k+2)}, \tag{70}$$

leading to

$$\frac{a_{n-2j}}{a_n} = (-1)^j \frac{n(n-1)\cdots(n-2j+2)(n-2j+1)}{2^j 2\cdot 4\cdots(2j-2)2j}$$

$$= (-1)^j \frac{n!}{(n-2j)!2^{2j}j!}. \tag{71}$$

With $a_n = 2^n$, this solution is the standard Hermite polynomial, $H_n(x)$,

$$H_n(x) = \sum_{j=0}^{[\frac{n}{2}]} (-1)^j \frac{2^{n-2j}n!}{j!(n-2j)!} x^{n-2j}. \tag{72}$$

The Hermite polynomial can be defined in three ways:
1. Through the regular solutions of the differential equation:

$$H_n''(x) - 2xH_n'(x) + 2nH_n(x) = 0. \tag{73}$$

2. Through a generating function, where the parameter, s, may be an arbitrary complex number:

$$e^{-s^2+2sx} = \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} s^n. \tag{74}$$

3. Through a differential relation, or a Rodrigues-type formula:

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n}(e^{-x^2}). \tag{75}$$

Thus,

$$E_n = \hbar\omega_0(n + \tfrac{1}{2}), \qquad \psi_n(x) = N_n H_n(x) e^{-\frac{x^2}{2}}. \tag{76}$$

The normalization constant, N_n, can be evaluated most simply through the Rodrigues-type formula

$$\begin{aligned} |N_n|^2 \int_{-\infty}^{\infty} dx H_n^2(x) e^{-x^2} &= |N_n|^2 \int_{-\infty}^{\infty} dx H_n(x)(-1)^n \frac{d^n}{dx^n}(e^{-x^2}) \\ = |N_n|^2 \int_{-\infty}^{\infty} dx (e^{-x^2})(\frac{d^n}{dx^n} H_n(x)) &= |N_n|^2 \int_{-\infty}^{\infty} dx e^{-x^2} n! a_n \\ &= |N_n|^2 \sqrt{\pi} n! 2^n = 1. \end{aligned} \tag{77}$$

Here, we have integrated by parts n times and have used the fact that the integrated parts, to be evaluated at $\pm\infty$, are all dominated by the factor e^{-x^2}. Choosing N_n to be real

$$N_n = \sqrt{\frac{1}{n!2^n\sqrt{\pi}}}. \tag{78}$$

Final note: Sometimes it is necessary to normalize the wave function in real, physical space, i.e., with

$$\int_{-\infty}^{\infty} dq\, \psi^* \psi = 1. \tag{79}$$

Then,

$$N_n = \sqrt{\frac{1}{n!2^n} \sqrt{\frac{m\omega_0}{\hbar\pi}}}. \tag{80}$$