C343: Physical Chemistry Lab II

4 and 5 March 2021

4. Tunneling Splitting in Ammonia

1. Compute the potential energy profile for the ammonia inversion process using an ab initio method for example MP2/6-31G**. Fit the energy profile to a one-dimensional potential energy function, $V(x) = a + bx^2 + cx^4$, where a, b, and c are the parameters. Plot the potential energy profiles obtained from the ab initio calculations and the fit and comment on the quality of the fit. Report the fitted parameters and the barrier for the inversion.

2. Calculate the first few eigenfunctions and eigenvalues for the harmonic oscillator using numerov method. You can do this by either writing a program or using a spreadsheet. Show the plot of the eigenfunctions and report the eigenvalues.

3. Using numerov method calculate the first few eigenstates for the double-well potential representing ammonia inversion. You should be able to see the tunneling splitting. Show the plot of the eigenfunctions, report the eigenvalues, and comment on the observations.

number of the *i*th normal mode. Each v_i takes on the values 0, 1, 2, ... independently of the values of the other vibrational quantum numbers. A linear molecule with n atoms has $3n - 5$ normal modes; a nonlinear molecule has $3n - 6$ normal modes.

To calculate the reduced mass μ in (4.59), one needs the masses of isotopic species. Some relative isotopic masses are listed in Table A.3 in the Appendix.

EXAMPLE

The strongest infrared band of $^{12}C^{16}O$ occurs at $\tilde{\nu} = 2143 \text{ cm}^{-1}$. Find the force constant of $^{12}C^{16}O$. State any approximation made.

The strongest infrared band corresponds to the $v = 0 \rightarrow 1$ transition. We approximate the molecular vibration as that of a harmonic oscillator. From (4.61), the equilibrium molecular vibrational frequency is approximately

$$\nu_e \approx \nu_{\text{light}} = \tilde{\nu}c = (2143 \text{ cm}^{-1})(2.9979 \times 10^{10} \text{ cm/s}) = 6.424 \times 10^{13} \text{ s}^{-1}$$

To relate k to ν_e in (4.59), we need the reduced mass $\mu = m_1 m_2/(m_1 + m_2)$. One mole of ^{12}C has a mass of 12 g and contains Avogadro's number of atoms. Hence the mass of one atom of ^{12}C is $(12 \text{ g})/(6.02214 \times 10^{23})$. The reduced mass and force constant are

$$\mu = \frac{12(15.9949) \text{ g}}{27.9949} \frac{1}{6.02214 \times 10^{23}} = 1.1385 \times 10^{-23} \text{ g}$$

$$k = 4\pi^2 \nu_e^2 \mu = 4\pi^2 (6.424 \times 10^{13} \text{ s}^{-1})^2 (1.1385 \times 10^{-26} \text{ kg}) = 1855 \text{ N/m}$$

EXERCISE   (a) Find the approximate zero-point energy of $^{12}C^{16}O$. (*Answer:* 2.1×10^{-20} J.) (b) Estimate ν_e of $^{13}C^{16}O$. (*Answer:* $6.28 \times 10^{13} \text{ s}^{-1}$.)

4.4 Numerical Solution of the One-Dimensional Time-Independent Schrödinger Equation

The Numerov Method

We solved the Schrödinger equation exactly for the particle in a box and the harmonic oscillator. For many potential-energy functions $V(x)$, the one-particle, one-dimensional Schrödinger equation cannot be solved exactly. This section presents a numerical method (the **Numerov method**) for computer solution of the one-particle, one-dimensional Schrödinger equation that allows one to get accurate bound-state eigenvalues and eigenfunctions for an arbitrary $V(x)$.

To solve the Schrödinger equation numerically, we deal with a portion of the x axis that includes the classically allowed region and that extends somewhat into the classically forbidden region at each end of the classically allowed region. We divide this portion of the x axis into small intervals, each of length s (**Fig. 4.7**). The points x_0 and x_{max} are the endpoints of this portion, and x_n is the endpoint of the nth interval. Let ψ_{n-1}, ψ_n, and ψ_{n+1} denote the values of ψ at the points $x_n - s, x_n$, and $x_n + s$, respectively (these are the endpoints of adjacent intervals)

$$\psi_{n-1} \equiv \psi(x_n - s), \quad \psi_n \equiv \psi(x_n), \quad \psi_{n+1} \equiv \psi(x_n + s) \tag{4.65}$$

Don't be confused by the notation. The subscripts $n - 1, n$, and $n + 1$ do not label different states but rather indicate values of one particular wave function ψ at points on the x axis separated by the interval s. The n subscript means ψ is evaluated at the point x_n. We write the Schrödinger equation $-(\hbar^2/2m)\psi'' + V\psi = E\psi$ as

$$\psi'' = G\psi, \quad \text{where } G \equiv m\hbar^{-2}[2V(x) - 2E] \tag{4.66}$$
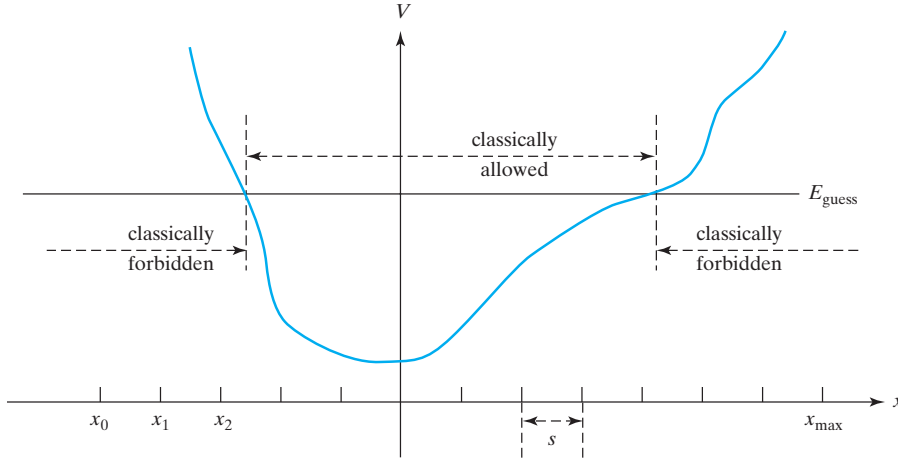
By expanding $\psi(x_n + s)$ and $\psi(x_n - s)$ in Taylor series involving powers of s, add-
ing these two expansions to eliminate odd powers of s, using the Schrödinger equation to
express ψ'' and $\psi^{(iv)}$ in terms of ψ, and neglecting terms in s^6 and higher powers of s (an
approximation that will be accurate if s is small), one finds that (Prob. 4.43)

$$\psi_{n+1} \approx \frac{2\psi_n - \psi_{n-1} + 5G_n\psi_n s^2/6 + G_{n-1}\psi_{n-1}s^2/12}{1 - G_{n+1}s^2/12} \tag{4.67}$$

where $G_n \equiv G(x_n) \equiv m\hbar^{-2}[2V(x_n) - 2E]$ [Eqs. (4.66) and (4.65)]. Equation (4.67)
allows us to calculate ψ_{n+1}, the value of ψ at point $x_n + s$, if we know ψ_n and ψ_{n-1}, the
values of ψ at the preceding two points x_n and $x_n - s$.

How do we use (4.67) to solve the Schrödinger equation? We first guess a value E_{guess}
for an energy eigenvalue. We start at a point x_0 well into the left-hand classically forbidden
region (Fig. 4.7), where ψ will be very small, and we approximate ψ as zero at this point:
$\psi_0 \equiv \psi(x_0) = 0$. Also, we pick a point x_{max} well into the right-hand classically forbidden
region, where ψ will be very small and we shall demand that $\psi(x_{\text{max}}) = 0$. We pick a
small value for the interval s between successive points, and we take ψ at $x_0 + s$ as some
small number, say, 0.0001: $\psi_1 \equiv \psi(x_1) \equiv \psi(x_0 + s) = 0.0001$. The value of ψ_1 will not
make any difference in the eigenvalues found. If 0.001 were used instead of 0.0001 for ψ_1,
Eq. (4.67) shows that this would simply multiply all values of ψ at subsequent points by 10
(Prob. 4.41). This would not affect the eigenvalues [see the example after Eq. (3.14)]. The
wave function can be normalized after each eigenvalue is found.

Having chosen values for ψ_0 and ψ_1, we then use (4.67) with $n = 1$ to calculate
$\psi_2 \equiv \psi(x_2) \equiv \psi(x_1 + s)$, where the G values are calculated using E_{guess}. Next, (4.67)
with $n = 2$ gives ψ_3; and so on. We continue until we reach x_{max}. If E_{guess} is not equal to
or very close to an eigenvalue, ψ will not be quadratically integrable and $|\psi(x_{\text{max}})|$ will
be very large. If $\psi(x_{\text{max}})$ is not found to be close to zero, we start again at x_0 and repeat
the process using a new E_{guess}. The process is repeated until we find an E_{guess} that makes
$\psi(x_{\text{max}})$ very close to zero. E_{guess} is then essentially equal to an eigenvalue. The systematic
way to locate the eigenvalues is to count the nodes in the ψ produced by E_{guess}. Recall
(Section 4.2) that in a one-dimensional problem, the number of interior nodes is 0 for the
ground state, 1 for the first excited state, and so on. Let $E_1, E_2, E_3, \ldots$ denote the energies
of the ground state, the first excited state, the second excited state, and so on, respectively.
If ψ_{guess} contains no nodes between x_0 and x_{max}, then E_{guess} is less than or equal to E_1; if
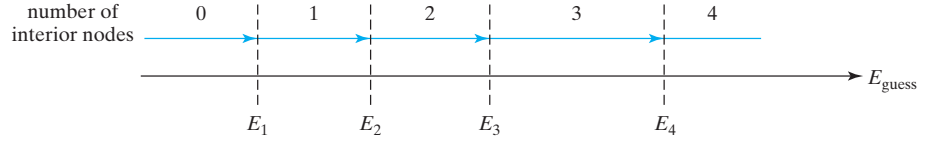
ψ_{guess} contains one interior node, then E_{guess} is between E_1 and E_2 (**Fig. 4.8**). Examples are given later.

Dimensionless Variables

The Numerov method requires that we guess values of E. What should be the order of magnitude of our guesses: 10^{-20} J, 10^{-15} J, ... ? To answer this question, we reformulate the Schrödinger equation using dimensionless variables, taking the harmonic oscillator as the example.

The harmonic oscillator has $V = \frac{1}{2}kx^2$, and the harmonic-oscillator Schrödinger equation contains the three constants k, m, and $\hbar$. We seek to find a dimensionless reduced energy E_r and a dimensionless reduced x coordinate x_r that are defined by

$$E_r \equiv E/A, \quad x_r \equiv x/B \tag{4.68}$$

where the constant A is a combination of k, m, and $\hbar$ that has dimensions of energy, and B is a combination with dimensions of length. The dimensions of energy are mass $\times$ length^2 $\times$ time^{-2}, which we write as

$$[E] = ML^2T^{-2} \tag{4.69}$$

where the brackets around E denote its dimensions, and M, L, and T stand for the dimensions mass, length, and time, respectively. The equation $V = \frac{1}{2}kx^2$ shows that k has dimensions of energy $\times$ length^{-2}, and (4.69) gives $[k] = MT^{-2}$. The dimensions of $\hbar$ are energy $\times$ time. Thus

$$[m] = M, \quad [k] = MT^{-2}, \quad [\hbar] = ML^2T^{-1} \tag{4.70}$$

The dimensions of A and B in (4.68) are energy and length, respectively, so

$$[A] = ML^2T^{-2}, \quad [B] = L \tag{4.71}$$

Let $A = m^a k^b \hbar^c$, where a, b, and c are powers that are determined by the requirement that the dimensions of A must be ML^2T^{-2}. We have

$$[A] = [m^a k^b \hbar^c] = M^a(MT^{-2})^b(ML^2T^{-1})^c = M^{a+b+c}L^{2c}T^{-2b-c} \tag{4.72}$$

Equating the exponents of each of M, L, and T in (4.71) and (4.72), we have

$$a + b + c = 1, \quad 2c = 2, \quad -2b - c = -2$$

Solving these equations, we get $c = 1$, $b = \frac{1}{2}$, $a = -\frac{1}{2}$. Therefore,

$$A = m^{-1/2}k^{1/2}\hbar \tag{4.73}$$

Let $B = m^d k^e \hbar^f$. The same dimensional-analysis procedure that gave (4.73) gives (Prob. 4.44)

$$B = m^{-1/4}k^{-1/4}\hbar^{1/2} \tag{4.74}$$

From (4.68), (4.73), and (4.74), the reduced variables for the harmonic oscillator are

$$E_r = E/m^{-1/2}k^{1/2}\hbar, \quad x_r = x/m^{-1/4}k^{-1/4}\hbar^{1/2} \tag{4.75}$$

Using $k^{1/2} = 2\pi\nu m^{1/2}$ [Eq. (4.23)] to eliminate k from (4.75) and recalling the definition $\alpha \equiv 2\pi\nu m/\hbar$ [Eq. (4.31)], we have the alternative expressions

$$E_r = E/h\nu, \quad x_r = \alpha^{1/2}x \tag{4.76}$$

Similar to the equation $E_r \equiv E/A$ [Eq. (4.68)], we define the reduced potential energy function V_r as

$$V_r \equiv V/A \tag{4.77}$$

Since $|\psi(x)|^2\, dx$ is a probability, and probabilities are dimensionless, the normalized $\psi(x)$ must have the dimensions of length$^{-1/2}$. We therefore define a reduced normalized wave function ψ_r that is dimensionless. From (4.71), B has dimensions of length, so $B^{-1/2}$ has units of length$^{-1/2}$. Therefore,

$$\psi_r = \psi/B^{-1/2} \tag{4.78}$$

ψ_r satisfies $\int_{-\infty}^{\infty} |\psi_r|^2\, dx_r = 1$; this follows from (4.68), (4.78), and $\int_{-\infty}^{\infty} |\psi|^2\, dx = 1$.

We now rewrite the Schrödinger equation in terms of the reduced variables x_r, ψ_r, V_r, and E_r. We have

$$\frac{d^2\psi}{dx^2} = \frac{d^2}{dx^2}B^{-1/2}\psi_r = B^{-1/2}\frac{d}{dx}\frac{d\psi_r}{dx} = B^{-1/2}\frac{d}{dx}\frac{d\psi_r}{dx_r}\frac{dx_r}{dx} = B^{-1/2}\frac{d(d\psi_r/dx_r)}{dx_r}\frac{dx_r}{dx}\frac{dx_r}{dx}$$

$$\frac{d^2\psi}{dx^2} = B^{-5/2}\frac{d^2\psi_r}{dx_r^2} \tag{4.79}$$

since $dx_r/dx = B^{-1}$ [Eq. (4.68)]. Substitution of (4.68), (4.77), and (4.79) into the Schrödinger equation $-(\hbar^2/2m)(d^2\psi/dx^2) + V\psi = E\psi$ gives

$$-\frac{\hbar^2}{2m}B^{-5/2}\frac{d^2\psi_r}{dx_r^2} + AV_rB^{-1/2}\psi_r = AE_rB^{-1/2}\psi_r$$

$$-\frac{\hbar^2}{2m}\frac{1}{AB^2}\frac{d^2\psi_r}{dx_r^2} + V_r\psi_r = E_r\psi_r \tag{4.80}$$

From (4.73) and (4.74), we get $AB^2 = \hbar^2/m$, so $\hbar^2/mAB^2 = 1$ for the harmonic oscillator.

More generally, let V contain a single parameter c that is not dimensionless. For example, we might have $V = cx^4$ or $V = cx^2(1 + 0.05m^{1/2}c^{1/2}\hbar^{-1}x^2)$. (Note that $m^{1/2}c^{1/2}\hbar^{-1}x^2$ is dimensionless, as it must be, since 1 is dimensionless.) The quantity AB^2 in (4.80) must have the form $AB^2 = \hbar^r m^s c^t$, where r, s, and t are certain powers. Since the term $V_r\psi_r$ in (4.80) is dimensionless, the first term is dimensionless. Therefore, $\hbar^2/mAB^2$ is dimensionless and AB^2 has the same dimensions as $\hbar^2/m$; so $r = 2$, $s = -1$, and $t = 0$. With $AB^2 = \hbar^2/m$, Eq. (4.80) gives as the dimensionless Schrödinger equation

$$\frac{d^2\psi_r}{dx_r^2} = (2V_r - 2E_r)\psi_r \tag{4.81}$$

$$\psi_r'' = G_r\psi_r, \quad \text{where} \quad G_r \equiv 2V_r - 2E_r \tag{4.82}$$

For the harmonic oscillator, $V_r \equiv V/A = \frac{1}{2}kx^2/m^{-1/2}k^{1/2}\hbar = \frac{1}{2}x_r^2$ [Eqs. (4.73) and (4.75)]:

$$V_r = \tfrac{1}{2}x_r^2 \tag{4.83}$$

Having reduced the harmonic-oscillator Schrödinger equation to the form (4.81) involving only dimensionless quantities, we can expect that the lowest energy eigenvalues will be of the order of magnitude 1.

The reduced harmonic-oscillator Schrödinger equation (4.82) has the same form as (4.66), so we can use the Numerov formula (4.67) with ψ, G, and s replaced by ψ_r, G_r, and s_r, respectively, where, similar to (4.68), $s_r \equiv s/B$.

Once numerical values of the reduced energy E_r have been found, the energies E are found from (4.75) or (4.76).

Choice of $x_{r,0}$, $x_{r,\max}$, and s_r

We now need to choose initial and final values of x_r and the value of the interval s_r between adjacent points. Suppose we want to find all the harmonic-oscillator eigenvalues and eigenfunctions with $E_r \leq 5$. We start the solution in the left-hand classically forbidden region, so we first locate the classically forbidden regions for $E_r = 5$. The boundaries between the classically allowed and forbidden regions are where $E_r = V_r$. From (4.83), $V_r = \frac{1}{2}x_r^2$. Thus $E_r = V_r$ becomes $5 = \frac{1}{2}x_r^2$ and the classically allowed region for $E_r = 5$ is from $x_r = -(10)^{1/2} = -3.16$ to $+3.16$. For $E_r < 5$, the classically allowed region is smaller. We want to start the solution at a point well into the left-hand classically forbidden region, where ψ is very small, and we want to end the solution well into the right-hand classically forbidden region. The left-hand classically forbidden region ends at $x_r = -3.16$ for $E_r = 5$, and a reasonable choice is to start at $x_r = -5$. [Starting too far into the classically forbidden region can sometimes lead to trouble (see the following), so some trial-and-error might be needed in picking the starting point.] Since V is symmetrical, we shall end the solution at $x_r = 5$.

For reasonable accuracy, one usually needs a minimum of 100 points, so we shall take $s_r = 0.1$ to give us 100 points. As is evident from the derivation of the Numerov method, s_r must be small. A reasonable rule might be to have s_r no greater than 0.1.

> If, as is often true, $V \to \infty$ as $x \to \pm\infty$, then starting too far into the classically forbidden region can make the denominator $1 - G_{n+1}s^2/12$ in the Numerov formula (4.67) negative. We have $G_r = 2V_r - 2E_r$, and if we start at a point x_0 where V_r is extremely large, G_r at that point might be large enough to make the Numerov denominator negative. The method will then fail to work. We are taking ψ_0 as zero and ψ_1 as a positive number. The Numerov formula (4.67) shows that if the denominator is negative, then ψ_2 will be negative, and we will have produced a spurious node in ψ between x_1 and x_2. To avoid this problem, we can decrease either the step size s_r or $x_{r,\max} - x_{r,0}$ (see Prob. 4.46).

Computer Program for the Numerov Method

Table 4.1 contains a C++ computer program that applies the Numerov method to the harmonic-oscillator Schrödinger equation. The fifth and sixth lines declare variables as either integers or double precision. m is the number of intervals between $x_{r,0}$ and $x_{r,\max}$ and equals $(x_{r,\max} - x_{r,0})/s$. cout and cin provide for output to the computer screen and input to the variables of the program. Note the colon at the end of line 13 and the semicolons after most other lines. The three lines beginning with g[0]=, g[1]=, and g[i+1]= contain two times the potential-energy function. These lines must be modified if the problem is not the harmonic oscillator. If there is a node between two successive values of x_r, then the ψ_r values at these two points will have opposite signs (see Prob. 4.45) and the statement nn=nn+1 will increase the nodes counter nn by 1.

You can download a free C++ compiler and integrated development environment—see the Wikipedia article, List of Compilers. Even simpler, you can enter and run C++ programs online without downloading anything. The website ideone.com provides this service (after you register) for C++ and other languages. However, at this site, you must enter your complete input into the input area before running the program, since the website does not accept input once the program begins; each input number is separated from its neighbors by a space.

TABLE 4.1 **C++ Program for Numerov Solution of the One-Dimensional Schrödinger Equation**

```cpp
#include <iostream>
#include <math.h>
using namespace std;
int main() {
    int m, i, nn;
    double x[1000], g[1000], p[1000], E, s, ss;
    cout << "Enter initial xr ";
    cin>>x[0];
    cout << "Enter the increment sr ";
    cin>>s;
    cout << "Enter the number of intervals m ";
    cin>>m;
    label1:
    cout << "Enter the reduced energy Er (enter 1e10 to quit) ";
    cin>>E;
    if (E > 1e9) {
        cout << "Quitting";
        return 0;
    }
    nn=0; p[0]=0;
    p[1]=0.0001;
    x[1]=x[0]+s;
    g[0]=x[0]*x[0]-2*E;
    g[1]=x[1]*x[1]-2*E;
    ss=s*s/12;
    for (i=1; i<=m-1; i=i+1) {
        x[i+1]=x[i]+s;
        g[i+1]=x[i+1]*x[i+1]-2*E;
        p[i+1]=(-p[i-1]+2*p[i]+10*g[i]*p[i]*ss+g[i-1]*p[i-1]*ss)/(1-g[i+1]*ss);
        if(p[i+1]*p[i]<0)
            nn=nn+1;
    }
    cout << " Er = " << E << " Nodes = " << nn << " Psir(xm) = " << p[m] << endl;
    goto label1;
}
```

For example, suppose we want the harmonic-oscillator ground-state energy. The program of Table 4.1, with $s_r = 0.1$, $x_{r,0} = -5$, and m $= 100$ gives the following results. The guess $E_r = 0$ gives a wave function with zero nodes, nn $= 0$, telling us (Fig. 4.8) that the ground-state energy $E_{r,1}$ is above 0. (Also, the wave function at the rightmost point is found to be 9.94×10^6, very far from 0.) If we now guess 0.9 for E_r, we get a function with one

node, so (Fig. 4.8) 0.9 is between $E_{r,1}$ and $E_{r,2}$. Hence the ground state E_r is between 0 and 0.9. Averaging these, we try 0.45. This value gives a function with no nodes, and so 0.45 is below $E_{r,1}$. Averaging 0.45 and 0.9, we get 0.675, which is found to give one node and so is too high. Averaging 0.675 and 0.45, we try 0.5625, which gives one node and is too high. We next try 0.50625, and so on. The program's results show that as we get closer to the true $E_{r,1}$, $\psi_r(5)$ comes closer to zero.

Use of a Spreadsheet to Solve the One-Dimensional Schrödinger Equation

An alternative to a Numerov-method computer program is a spreadsheet.

The following directions for the Excel 2010 spreadsheet apply the Numerov method to solve the harmonic-oscillator Schrödinger equation. (Other versions of Excel can be used with modified directions.)

The columns in the spreadsheet are labeled A, B, C, . . . and the rows are labeled 1, 2, 3, . . . (see Fig. 4.9 later in this section). A cell's location is specified by its row and column. For example, the cell at the upper left is cell A1. To enter something into a cell, you first **select** that cell, either by moving the mouse pointer over the desired cell and then clicking the (left) mouse button, or by using the arrow keys to move from the currently selected cell (which has a heavy outline) to the desired cell. After a cell has been selected, type the entry for that cell and press Enter or one of the four arrow keys.

To begin, enter a title in cell A1. Then enter Er = in cell A3. We shall enter our guesses for E_r in cell B3. We shall look first for the ground-state (lowest) eigenvalue, pretending that we don't know the answer. The minimum value of $V(x)$ for the harmonic oscillator is zero, so E_r cannot be negative. We shall take zero as our initial guess for E_r, so enter 0 in cell B3. Enter sr= in cell C3.

Enter 0.1 (the s_r value chosen earlier) in cell D3. Enter xr in cell A5, Gr in cell B5, and psir in cell C5. (These entries are labels for the data columns that we shall construct.) Enter −5 (the starting value for x_r) in cell A7. Enter =A7+$D$3 in cell A8. The equal sign at the beginning of the entry tells the spreadsheet that a **formula** is being entered. This formula tells the spreadsheet to add the numbers in cells A7 and D3. The reason for the $ signs in D3 will be explained shortly. When you type a formula, you will see it displayed in the formula bar above the spreadsheet. When you press Enter, the value −4.9 is displayed in cell A8. This is the sum of cells A7 and D3. (If you see a different value in A8 or get an error message, you probably mistyped the formula. To correct the formula, select cell A8 and click in the formula displayed in the formula bar to make the correction.)

Select cell A8 and then click the Home tab and in the Clipboard group click the Copy icon. This copies the contents of cell A8 to a storage area called the Clipboard. Then in the Editing group click the Find & Select icon and choose Go To. In the Go To box, enter A9:A107 under Reference: and click OK. This selects cells A9 through A107. Then in the Clipboard group click the Paste icon. This pastes the cell A8 formula (which was stored on the Clipboard) into each of cells A9 through A107. To see how this works, click on cell A9. You will see the formula =A8+$D$3 in the formula bar. Note that when the cell A8 formula =A7+$D$3 was copied one cell down to cell A9, the A7 in the formula was changed to A8. However, the $ signs prevented cell D3 in the formula from being changed when it was copied. In a spreadsheet formula, a cell address without $ signs is called a **relative** reference, whereas a cell address with $ signs is called an **absolute** reference. When a relative reference is copied to the next row in a column, the row number is increased by one; when it is copied two rows below the original row, the row number is increased by two; and so on. Click in some of the other cells in column A to see their formulas. The net result of this copy-and-paste procedure is to fill

the column-A cells with numbers from −5 to 5 in increments of 0.1. (Spreadsheets have faster ways to accomplish this than using Copy and Paste.)

We next fill in the G_r column. From Eqs. (4.82) and (4.83), $G_r = x_r^2 - 2E_r$ for the harmonic oscillator. We therefore enter =A7^2−2*$B$3 in cell B7 (which will contain the value of G_r at $x_r = -5$). Cell A7 contains the $x_r = -5$ value, and the ^ symbol denotes exponentiation. The * denotes multiplication. Cell B3 contains the E_r value. Next, the rest of the G_r values are calculated. Select cell B7. Then click Copy in the Clipboard group. Now select cells B8 through B107 by using Find & Select as before. Then click Paste in the Clipboard group. This fills the cells with the appropriate G_r values. (Click on cell B8 or B9 and see how its formula compares with that of B7.)

We now go to the ψ_r values. Enter 0 in cell C7. Cell C7 contains the value of ψ_r at $x_r = -5$. Since this point is well into the classically forbidden region, ψ_r will be very small here, and we can approximate it as zero. Cell C8 contains the value of ψ_r at $x_r = -4.9$. This value will be very small, and we can enter any small number in C8 without affecting the eigenvalues. Enter 1E-4 in cell C8 (where E denotes the power of 10). Now that we have values in cells C7 and C8 for ψ_r at the first two points −5.0 and −4.9 [points x_{n-1} and x_n in (4.67)], we use (4.67) to calculate ψ_r at $x_r = -4.8$ (point x_{n+1}). Therefore, enter the Eq. (4.67) formula

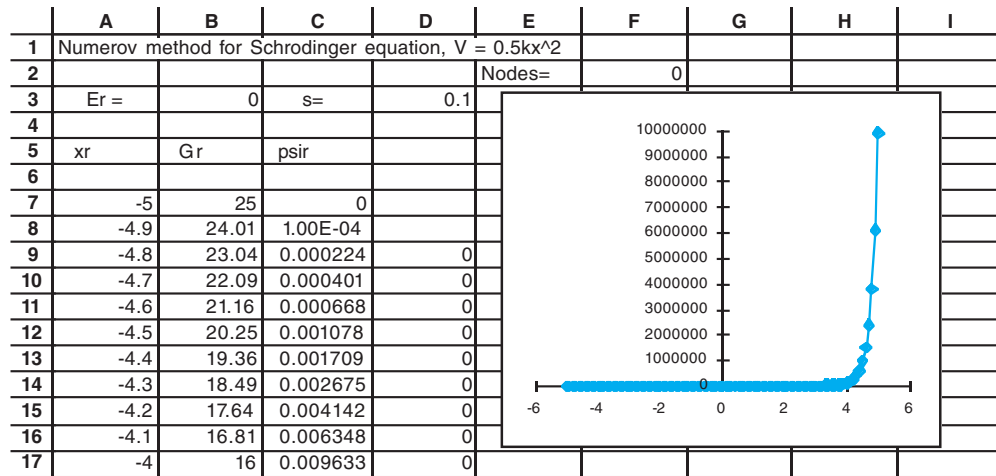=(2*C8-C7+5*B8*C8*$D$3^2/6+B7*C7*$D$3^2/12)/(1-B9*$D$3^2/12)

in cell C9. After the Enter key is pressed, the value 0.000224 for ψ_r at $x_r = -4.8$ appears in cell C9. Select cell C9. Click Copy. Select C10 through C107. Click Paste. Cells C10 through C107 will now be filled with their appropriate ψ_r values. As a further check that you entered the C9 formula correctly, verify that cell C10 contains 0.000401.

Since the number of nodes tells us which eigenvalues our energy guess is between (Fig. 4.8), we want to count and display the number of nodes in ψ_r. To do this, enter into cell D9 the formula = IF(C9*C8<0,1,0). This formula enters the number 1 into D9 if C9 times C8 is negative and enters 0 into D9 if C9 times C8 is not negative. If there is a node between the x_r values in A8 and A9, then the ψ_r values in C8 and C9 will have opposite signs, and the value 1 will be entered into D9. Use Copy and Paste to copy the cell D9 formula into cells D10 through D107. Enter nodes = into cell E2. Enter =SUM(D9:D107) into F2. This formula gives the sum of the values in D9 through D107 and thus gives the number of interior nodes in ψ_r.

Next, we graph ψ_r versus x_r. Select cells A7 through A107 and C7 through C107 by clicking Find & Select, clicking Go To, typing A7:A107,C7:C107 in the Reference box, and clicking OK. Then click the Insert tab and in the Chart group click the Scatter icon and then click the chart showing smoothed lines with markers (Scatter with Smooth Lines and Markers). On the chart that appears, right-click Series1 and choose Delete. Right-click the horizontal grid line at 4×10^6 and choose Delete. The spreadsheet will look like **Fig. 4.9**.

Since $x_r = 5$ is well into the right-hand classically forbidden region, ψ_r should be very close to zero at this point. However, the graph shows that for our choice $E_r = 0$, the wave function ψ_r is very large at $x_r = 5$. Therefore, $E_r = 0$ does not give a well-behaved ψ_r, and we must try a different E_r. Cell F2 has a zero, so this ψ_r has no nodes. Therefore (Fig. 4.8), the guess $E_r = 0$ is less than the true ground-state energy. Let us try $E_r = 2$. Select cell B3 and enter 2 into it. After you press Enter, the spreadsheet will recalculate every column B and column C cell whose value depends on E_r (all column B and C cells except C7 and C8 change) and will then replot the graph. The graph for $E_r = 2$ goes to a very large positive ψ_r value at $x_r = 5$. Also, cell F2 tells us that ψ_r for $E_r = 2$ contains two nodes. These are not readily visible on the graph, but the column-C data show that ψ_r changes sign between the x_r values −0.4 and −0.3 and between 1.2 and 1.3. We are

FIGURE 4.9 Spreadsheet for Numerov-method solution of the harmonic oscillator.

	A	B	C	D	E	F	G	H	I
1	Numerov method for Schrodinger equation, V = 0.5kx^2								
2					Nodes=	0			
3	Er =	0	s=	0.1					
4									
5	xr	Gr	psir						
6									
7	-5	25	0						
8	-4.9	24.01	1.00E-04						
9	-4.8	23.04	0.000224	0					
10	-4.7	22.09	0.000401	0					
11	-4.6	21.16	0.000668	0					
12	-4.5	20.25	0.001078	0					
13	-4.4	19.36	0.001709	0					
14	-4.3	18.49	0.002675	0					
15	-4.2	17.64	0.004142	0					
16	-4.1	16.81	0.006348	0					
17	-4	16	0.009633	0					

looking for the ground-state eigenfunction, which does not contain a node, or rather, in our approximation, will contain nodes at -5 and 5. The presence of the two interior nodes shows (Fig. 4.8) that the value 2 for E_r is not only too high for the ground state, but is higher than E_r for the first excited state (whose wave function contains one interior node). We therefore need to try a lower value of E_r.

Before doing so, let us change the graph scale so as to make the nodes more visible. Double click on the y axis of the graph. In the Format Axis dialog box that appears, click Axis Options at the left and click Fixed next to Minimum and Maximum. Replace the original numbers in the Minimum and Maximum boxes with -10 and 10, respectively. Then click Close. The graph will be redrawn with -10 and 10 as the minimum and maximum y-axis values, making the two nodes easily visible.

We now change E_r to a smaller value, say 1.2. Enter 1.2 in cell B3. We get a ψ_r that goes to a large negative value on the right and that has only one node. The presence of one node tells us that we are now below the energy of the second-lowest state and above the ground-state energy (see Fig. 4.8). We have bracketed the ground-state energy to lie between 0 and 1.2. Let us average these two numbers and try 0.6 as the energy. When we enter 0.6 into cell B3, we get a function with one node, so we are still above the ground-state energy. Since the maximum on the graph is now off scale, it's a good idea to change the graph scale and reset the y maximum and minimum values to 25 and -25.

We have found the lowest eigenvalue to be between 0 and 0.6. Averaging these values, we enter 0.3 into B3. This gives a function that has no nodes, so 0.3 is below the ground-state reduced energy, and E_r is between 0.3 and 0.6. Averaging these, we enter 0.45 into B3. We get a function that has no nodes, so we are still below the correct eigenvalue. However, if we rescale the y axis suitably (taking, for example, -15 and 30 as the minimum and maximum values), we see a function that for values of x_r less than 0.2 resembles closely what we expect for the ground state, so we are getting warm. The eigenvalue is now known to be between 0.45 and 0.60. Averaging these, we enter 0.525 into B3. We get a function with one node, so we are too high. Averaging 0.45 and 0.525, we try 0.4875, which we find to be too low.

Continuing in this manner, we get the successive values 0.50625 (too high), 0.496875 (too low), . . . , 0.4999995943548 (low), 0.4999996301176 (high). Thus we have found

0.4999996 as the lowest eigenvalue. Since $E_r = E/h\nu$, we should have gotten 0.5. The slight error is due to the approximations of the Numerov method.

Suppose we want the second-lowest eigenvalue. We previously found this eigenvalue to be below 2.0, so it lies between 0.5 and 2.0. Averaging these numbers, we enter 1.25 into B3. We get a function that has the desired one node but that goes to a large negative value at the right, rather than returning to the x axis at the right. Therefore, 1.25 is too low (Fig. 4.8). Averaging 1.25 and 2.0, we next try 1.625. This gives a function with two nodes, so we are too high. Continuing, we get the successive values 1.4375 (low), 1.53125 (high), 1.484375 (low), 1.5078125 (high), and so on.

To test the accuracy of the eigenvalues found, we can repeat the calculation with s_r half as large and see if the new eigenvalues differ significantly from those found with the larger s_r. Also, we can start further into the classically forbidden region.

Finding eigenvalues as we have done by trial and error is instructive and fun the first few times, but if you have a lot of eigenvalues to find, you can use a faster method. Most spreadsheets have a built-in program that can adjust the value in one cell so as to yield a desired value in a second cell. This tool is called the Solver in Excel. Click the Data tab. In the Analysis group (at the right), see if there is an icon for Solver. (If the Solver icon is missing, click the File tab and click Options at the left. In the Excel Options box, click Add-Ins at the left. In the Manage box select Excel Add-Ins at the bottom and click the Go button. In the Add-Ins box check Solver Add-In and click OK. After a while, the Solver icon will appear in the Analysis group.) To see how the Solver works, enter 0 into cell B3. Click the Solver icon. The Solver Parameters box opens. The ψ_r value at $x_r = 5$ is in cell C107, and we want to make this value zero. Therefore, in the Set Objective box of the Solver, enter $C$107. Next to To: click on Value of and enter 0. We want to adjust the energy so as to satisfy the boundary condition at $x_r = 5$, so click in the By Changing Variable Cells box and enter $B$3. Select the Solver Method as GRG Nonlinear. Then click on Solve. When Solver declares it has found a solution, select Accept Solver solution to close the Solver box. The solution found by Excel has 0.500002 in cell B3 (the formula bar will show the full value if you select cell B3). Cell C107 will have the value -6.38. Since this value is not close to the desired value of 0, click the Solver icon and then click Solve, thereby re-running Solver starting from the 0.500002 value. This time Solver gives 0.4999996089, similar to the value found by hand, and C107 has the value -3.66×10^{-9}. (The Solver uses either the quasi-Newton or the conjugate-gradient method, both of which are discussed in Section 15.10.)

To find higher eigenvalues using the Solver, start with a value in B3 that is well above the previously found eigenvalue. If the program converges to the previous eigenvalue, start with a still-higher value in B3. You can check which eigenvalue you have found by counting the nodes in the wave function. If the Solver fails to find the desired eigenvalue, use trial and error to find an approximate value and then use the Solver starting from the approximate eigenvalue.

The wave function we have found is unnormalized. The normalization constant is given by Eq. (3.93) as $N = \left[\int_{-\infty}^{\infty} |\psi_r|^2 \, dx_r \right]^{-1/2}$. We have $\int_{-\infty}^{\infty} |\psi_r|^2 \, dx_r \approx \int_{-5}^{5} \psi_r^2 \, dx_r \approx \sum_{i=1}^{100} \psi_{r,i}^2 s_r$, where the $\psi_{r,i}$ values are in column B. Enter npsir in E5. In cell D109, enter the formula = SUMSQ(C8:C107)*$D$3. The SUMSQ function adds the squares of a series of numbers. Enter = C7/$D$109^0.5 in E7. Copy and paste E7 into E8 through E107. Column E will contain the normalized ψ_r values if E_{guess} is equal to an eigenvalue.

Excel is widely used to do statistical and scientific calculations, but studies of Excel 2007 and its predecessors found many significant errors [B. D. McCullough and D. A. Heiser, *Comput. Statist. Data Anal.*, **52,** 4570 (2008)]. For example, McCullough and Heiser state: "It has been noted that Excel Solver has a marked tendency to stop at a point that is not a solution and declare that it has found a solution." Therefore one should

always verify the correctness of the Solver's solution. A study of Excel 2010 found that many of the errors present in earlier versions of Excel were fixed, but some problems remain [G. Mélard, "On the Accuracy of Statistical Procedures in Excel 2010," available at homepages.ulb.ac.be/~gmelard/rech/gmelard_csda24.pdf]. Mélard noted that "The conclusion is that Microsoft did not make an attempt to fix all the errors in Excel, and this point needs to be made strongly." Mélard found that the Solver yielded results with zero significant-figure accuracy in a substantial fraction of test cases.

Use of Mathcad to Solve the One-Dimensional Schrödinger Equation

Several programs classified as *computer algebra systems* do a wide variety of mathematical procedures, including symbolic integration and differentiation, numerical integration, algebraic manipulations, solving systems of equations, graphing, and matrix computations. Examples of such computer algebra systems are Maple, *Mathematica*, MATLAB, Mathcad, and LiveMath Maker. The Numerov procedure can be performed using these programs. One nice feature of Mathcad is its ability to produce animations ("movies"). With Mathcad one can create a movie showing how ψ_r changes as E_r goes through an eigenvalue.

Summary of Numerov-Method Steps

Problems 4.30–4.38 apply the Numerov method to several other one-dimensional problems. In solving these problems, you need to (a) find combinations of the constants in the problem that will give a dimensionless reduced energy and length [Eq. (4.68)]; (b) convert the Schrödinger equation to dimensionless form and find what $G_r(x_r)$ in (4.82) is; (c) decide on a maximum E_r value, below which you will find all eigenvalues; (d) locate the boundaries between the classically allowed and forbidden regions for this maximum E_r value and choose $x_{r,0}$ and $x_{r,\max}$ values in the classically forbidden regions (for the particle in a box with infinitely high walls, use $x_0 = 0$ and $x_{\max} = l$); and (e) decide on a value for the interval s_r.

Summary

The one-dimensional harmonic oscillator has $V = \frac{1}{2}kx^2$. Its stationary-state energies are $E = (v + \frac{1}{2})h\nu$, where the vibrational frequency is $\nu = (1/2\pi)(k/m)^{1/2}$ and the quantum number v is $v = 0, 1, 2, \ldots$. The eigenfunctions are even or odd functions and are given by (4.47). An even function satisfies $f(-x) = f(x)$. An odd function satisfies $f(-x) = -f(x)$. If f is even, then $\int_{-a}^{a} f(x)\,dx = 2\int_{0}^{a} f(x)\,dx$. If f is odd, then $\int_{-a}^{a} f(x)\,dx = 0$. The vibrational energy of a diatomic molecule can be roughly approximated by the harmonic-oscillator energies with $\nu = (1/2\pi)(k/\mu)^{1/2}$, where the reduced mass is $\mu = m_1 m_2/(m_1 + m_2)$.

The Numerov method is a numerical method that allows one to find bound-state energies and wave functions for the one-particle, one-dimensional Schrödinger equation.

Problems

Sec.	4.1	4.2	4.3	4.4	general
Probs.	4.1–4.3	4.4–4.23	4.24–4.29	4.30–4.48	4.49–4.53

4.1 Provided certain conditions are met, we can expand the function $f(x)$ in an infinite power series about the point $x = a$:

$$f(x) = \sum_{n=0}^{\infty} c_n (x - a)^n \tag{4.84}$$