Solving the Time-Independent Schrödinger Equation*

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Abstract

Approaches for numerically solving the time-independent Schrödinger equation in one dimension are discussed. Possible simulation projects include solving the TISE for various potentials, testing the validity of stationary state perturbation theory, and developing a simple model of covalent bonding. Some background on numerical techniques for integrating differential equations is provided.

Keywords: quantum mechanics, Schrödinger equation, stationary states, covalent bonding, shooting method, ordinary differential equations, Euler method, Runge-Kutta method

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I. MODULE OVERVIEW

This module discusses the solution of the time-independent Schrödinger equation (TISE) in one dimension using the "shooting" method (sometimes also called the "wag the dog" method). Solving the TISE is one of the central problems in quantum mechanics, and courses in quantum physics typically devote considerable time to developing solutions in analytically tractable cases (e.g., square wells, the harmonic oscillator). The ability to determine the stationary state wavefunctions and energy eigenvalues numerically allows exploration of much wider class of potentials, however, and allows the development of deeper intuition regarding the properties of these systems.

II. WHAT YOU WILL NEED

The minimal physics background required will include quantum mechanics at the level of a typical sophomore-level course on modern physics, specifically the basic properties of wavefunctions and exposure to the time-independent Schrödinger equation. An upper-level course in quantum mechanics will allow a richer exploration of problems with the tools developed here.

On the mathematical side, facility with differential and integral calculus is essential, as is a basic familiarity with ordinary differential equations. Students who have passed through a sophomore-level modern physics course should have the necessary background.

The computing resources needed are actually minimal, as the "size" of the computational problem is rather modest. The natural framework for scientific computing is a high-level language like Fortran, C or C++, and this is an excellent project for students to sharpen their programming skills. However, the needed calculations can be done using Matlab or Mathematica, or even with a spreadsheet such as Excel. Some facility for generating plots will also be useful, for example Excel or `gnuplot`.

III. QUANTUM MECHANICS BACKGROUND

The central problem of quantum mechanics is to find solutions to the Schrödinger equation, which determines the time evolutions of the wavefunction for a system [1]. For a single non-relativistic particle in one dimension this takes the form

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,t)}{\partial t}, \tag{3.1}$$

where m is the particle mass and $V(x)$ is the potential energy, here assumed to be independent of the time t. Given an initial wavefunction $\Psi(x,0)$, the Schrödinger equation determines Ψ for all later (and earlier) times.

The physical meaning of Ψ is that it gives the probability density for finding the particle at different locations, if its position is measured. Specifically, the probability dP to find the particle in a small range from x to $x+dx$ at time t is given by

$$dP=|\Psi(x,t)|^2dx. \tag{3.2}$$

The probability to find the particle in some finite interval in x, say between $x=a$ and $x=b$, is then the sum of the probabilities for each infinitesimal interval between a and b:

$$P=\int_a^b|\Psi(x,t)|^2dx. \tag{3.3}$$

A critical requirement for the consistency of the framework is that the total probability to find the particle *somewhere* be unity; hence we must require that

$$\int_{-\infty}^{\infty}|\Psi(x,t)|^2dx=1. \tag{3.4}$$

Wavefunctions that satisfy this condition are said to be "normalized." An important feature of the time evolution defind by the Schrödinger equation is that if the wavefunction is normalized at one time, then it will be normalized for all other times as well.

The physical importance of the normalization requirement cannot be over-emphasized; it is this condition that puts the "quantum" in quantum mechanics. Wavefunctions that do not satisfy this fall into two classes: functions for which the normalization integral is finite but not equal to one; and functions for which the normalization integral is infinite. Given a function in the first class, we can easily produce a normalized wavefunction. Assume that we have found a solution of the Schrödinger equation Ψ for which

$$\int_{-\infty}^{\infty}|\Psi(x,t)|^2dx=A, \tag{3.5}$$

with A a finite number. Then the rescaled wavefunction

$$\Psi'(x,t)=\frac{1}{\sqrt{A}}\Psi(x,t) \tag{3.6}$$

will be properly normalized, i.e., will satisfy

$$\int_{-\infty}^{\infty} |\Psi'(x,t)|^2 dx = 1. \tag{3.7}$$

Note that because the Schrödinger equation is *linear* in the wavefunction, the rescaled wavefunction remains a solution.

Functions for which the normalization integral is infinite, on the other hand, cannot be normalized at all. Such wavefunctions are simply unacceptable for describing real physical systems, and must be discarded despite being solutions to the Schrödinger equation [3].

The problem of finding solutions to the Schrödinger equation is often approached using the technique of *separation of variables.* Here one begins by writing

$$\Psi(x,t) = \psi(x)\varphi(t). \tag{3.8}$$

Substitution into the Schrödinger equation then results in a pair of ordinary differential equations:

$$i\hbar \frac{\partial \varphi(t)}{\partial t} = E\varphi(t) \tag{3.9}$$

and

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x), \tag{3.10}$$

where E is a constant to be determined [4]. The solution to eq. (3.9) is elementary:

$$\varphi(t) = Ae^{-iEt/\hbar} \tag{3.11}$$

where A is a constant that can be set to one. Notice that $\varphi(t)$ plays no role in the normalization integral – as a pure phase, it disappears in the modulus squared of Ψ [5].

Eq. (3.10) is known as the "time-independent Schrödinger equation" (TISE), and solving it is a central problem in quantum theory. It has the form of an "eigenvalue" equation,

$$\hat{H}\psi = E\psi, \tag{3.12}$$

where $\hat{H}$ is the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{3.13}$$

and E is the eigenvalue. It should be emphasized that the TISE determines both ψ and E, that is, we find that each solution ψ works only with some particular value of E. We can label the solutions by an index n, so that each function ψ_n has a corresponding eigenvalue E_n. We must also be sure that our wavefunctions are normalizable; this means that ψ itself must be normalizable. It is convenient to normalize the ψ_n so that

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = 1. \tag{3.14}$$

The wavefunction $\Psi(x,t) = \psi(x)\varphi(t)$ is then properly normalized as well.

Wavefunctions of the assumed form $\Psi(x,t) = \psi(x)\varphi(t)$ are not the most general solutions to the Schrödinger equation; however, general solutions can be built as linear combinations of the product solutions:

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}, \tag{3.15}$$

where the c_n are constants. These can be determined from the initial conditions: given $\Psi(x,0)$, we calculate

$$c_n = \int_{-\infty}^{\infty} \psi_n^*(x)\Psi(x,0). \tag{3.16}$$

Eq. (3.15) then gives the full solution at any other time.

IV. SOLVING THE TIME-INDEPENDENT SCHRÖDINGER EQUATION

To avoid the complications associated with non-normalizable states, we focus on the bound state problem. A characteristic feature of such quantum systems is that the eigenvalues E_n are *discrete*, or "quantized." To see why this occurs, we can consider solving the TISE in the following way. This approach will also form the basis of our numerical method.

We consider a potential $V(x)$ which is zero outside of some characteristic range $|x| > a$ and negative for $|x| < a$. The bound state wavefunctions will have energies less than zero and will be confined roughly to the region of the potential well. There will be some "leaking" of the wavefunction outside of the well (into the classically forbidden region), but outside the well the wavefunction typically decays exponentially to zero. Inside the well (i.e., in the classically allowed region) we generically obtain oscillating solutions for ψ_n.

Now, the exponential decay outside the well is the result of the normalization condition (3.14). In these regions there is a growing solution to the TISE in addition to the decaying one, and the general solution is a linear combination of the two. However, for the wavefunction to be normalized it must (at a minimum) go to zero for large values of $|x|$. Hence the growing solution must be discarded for physically acceptable solutions.

For simplicity, consider first potentials that are even functions of x: $V(-x) = V(x)$. In this case the solutions to the TISE can be chosen to have definite parity, that is, to be even or odd functions of x:

$$\psi_n(-x) = \pm\psi_n(x). \tag{4.1}$$

Let's start by looking for an even solution. Begin at the middle of the box and choose a value for $\psi(0)$. (It doesn't matter what value we choose here – we must eventually normalize the wavefunction anyway.) An even solution will also have $\psi'(0) \equiv d\psi/dx|_{x=0} = 0$. Now, the TISE is a second-order differential equation that allows us to integrate forward in x, given the "initial" values $\psi(0)$ and $\psi'(0)$. Of course, to do this we need a value for E to use in the integration. Let's just guess something to start with.

Now imagine integrating forward in x until we exit the well. Since the general solution outside the well contains a growing piece, we expect that the solution we obtain will typically be growing there, hence not physically acceptable. Let's assume the solution diverges towards positive values of ψ as x gets large. Now try again with a different value of E. This will probably also diverge. Only for specific values of E will the solution arrive at the edge of the well with just the right shape corresponding to the decaying solution only, hence normalizable, hence physically acceptable. The general result will be that only particular values of E are allowed, so the energy levels are quantized.

This also suggests a way to determine the solutions numerically. We start at the center of the well with a specified ψ and $\psi' = 0$, guess a value of E and integrate forward past the edge of the well. If the solution is diverging there, change E and try again. As we vary E, the solution will typically diverge either towards positive or negative values of ψ; it is in between these cases that an acceptable solution is found, one that diverges in neither direction but continues to asymptote towards zero as $x \to \infty$ (see fig. 1). So we can find allowed values of E by bracketing them in this way. For the odd solutions we start instead with $\psi = 0$ and some arbitrary value for ψ' at the center.

This is commonly known as the "shooting" method, or sometimes the "wag the dog" method. Refinements of the basic idea are possible, and I discuss some of these below.

To implement this in detail, we need to address two basic problems: (1) how to perform the numerical integration; and (2) how to bracket and zero in on the allowed values of E.

The first is addressed by working on a discrete grid of points in x and treating the TISE as a *difference* equation, replacing the derivatives by finite differences. An overview of this

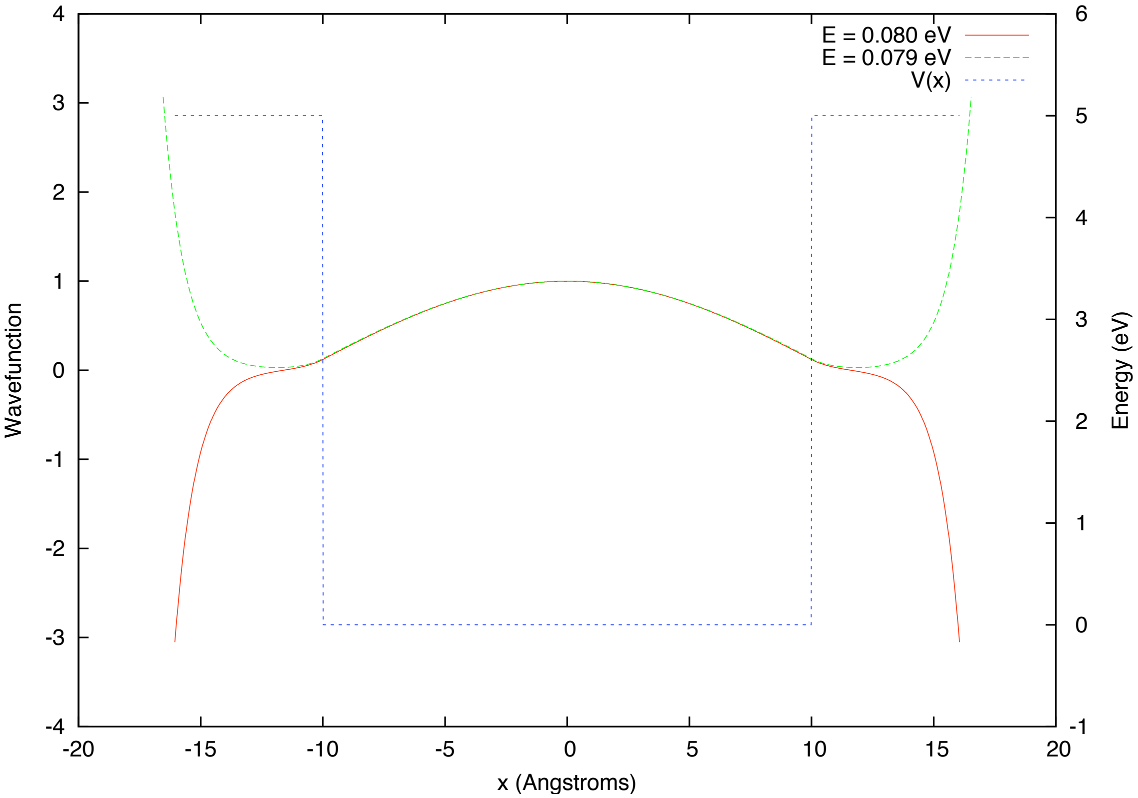

FIG. 1: Two trial solutions bracketing an even-parity energy eigenvalue, for a finite square well of depth 5 eV and width 20 Å.

approach is given in the appendix, but the simplest method, given a differential equation of the form

$$\frac{d\phi}{dx} = f(\phi, x), \tag{4.2}$$

would be to write

$$\frac{\phi(x+\epsilon) - \phi(x)}{\epsilon} \approx f(\phi, x), \tag{4.3}$$

where ϵ is the spacing between grid points. We then have

$$\phi(x+\epsilon) = \phi(x) + \epsilon f(\phi, x). \tag{4.4}$$

Given the value of ϕ at x, this allows us to take a step forward to $x+\epsilon$. The new value of ϕ then furnishes the basis for another step forward, and so on. Hence given one initial value (at $x = 0$, say) we can calculate ϕ for other values of x. The approach should be accurate as long as ϵ is sufficiently small so that

$$\frac{\phi(x+\epsilon) - \phi(x)}{\epsilon} \tag{4.5}$$

well approximates the true derivative $d\phi/dx$. Of course, this expression becomes the exact derivative in the limit $\epsilon \to 0$ [6].

This simple scheme is known as Euler's method, and is not very accurate. Much more sophisticated techniques are available, some of which are discussed in the appendix. They are all based on the same fundamental idea, however, that of discretizing the domain and approximating derivatives with finite differences.

The second problem is essentially that of finding the zeroes of some quantity, here ψ at a point $x_{\max}$ well outside the potential well. Let us call this $\psi_+ \equiv \lim_{x \to x_{\max}} \psi(x)$. This should be regarded as a function of E,

$$\psi_+ = \psi_+(E) \tag{4.6}$$

and we wish to find the values of E for which this vanishes, i.e., to effectively solve

$$\psi_+(E) = 0 \tag{4.7}$$

for E.

The simplest approach to this problem is just to start with a guess for E that is guaranteed to be less than the solution [7], then increase E in small steps until ψ_+ changes sign. This indicates that we have passed through a solution – the wavefunction went from diverging in one direction to diverging in the other. When this happens we back up to the previous value of E and halve the step size. Eventually when the relative difference between two successive values of E drops below some specified tolerance, we declare the solution reached. This approach is known as the "bisection" method, and it is reliable although rather slow. More sophisticated approaches, which typically converge to the answer more rapidly, include the "Newton-Raphson" and "secant" methods. The interested reader should consult a text on numerical methods to learn about these [2].

V. SIMULATION PROJECTS

1. **Infinite Square Well**

   Write a program to solve for the stationary states of the infinite square well potential. In this case the boundary conditions require the wavefunction to simply vanish at the edge of the well. As discussed above, your code should start at the center with either $\psi(0)$ or $\psi'(0)$ set to zero, depending on the assumed parity of the solution. The initial value of the other variable may be arbitrarily taken to be one; if desired, the wavefunctions can be normalized after the fact. Now integrate the TISE out to the edge of the box. Change the energy by some small amount until the sign of ψ changes at the edge of the well; when this occurs, go back to the previous energy and halve the step size. Once the relative change in the energy $|E_{\mathrm{new}} - E_{\mathrm{old}}|/E_{\mathrm{old}}$ falls below some threshold, the calculation is complete.

You can use arbitrary units, e.g., setting $\hbar^2/2m = 4/\pi^2$; this makes the exact energy eigenvalues the simple $E_n = n^2$. Alternatively, you can assume the particle is an electron, say, and use some convenient units such as eV and Å.

If desired, the computed wavefunctions can be normalized according to eq. (3.14). Use Simpson's rule or the trapezoid rule to evaluate the integral of ψ^2, and then rescale all values of ψ by the square root of the result. Compare the eigenvalues and wavefunctions to the known exact results.

2. **Finite Square Well**

Write a program to solve for the stationary states of a finite square well potential. This works as above except that you now need to integrate past the edge of the box out to some conveniently chosen maximum value of x, or until the absolute value of the wavefunction exceeds some specified threshold. (For a "wrong" choice of E the solution will be exponentially growing in the classically forbidden region. We only need to notice this fact.) Again, vary E until the sign of ψ_+ changes, then back up and halve the step size. Quit when the relative change in the energy drops below a specified tolerance.

If desired, the computed wavefunctions can be normalized according to eq. (3.14). Use Simpson's rule or the trapezoid rule to evaluate the integral of ψ^2, and then rescale all values of ψ by the square root of this integral.

Note that as the energy nears the top of the well, the wavefunction penetrates more and more into the classically forbidden region. Be sure that your code is integrating far enough into this region to give good results.

3. **Other Potentials**

   (a) **Harmonic Oscillator**

   Use your program to determine the eigenvalues and wavefunctions for an electron in a harmonic oscillator potential, $V = (1/2)m\omega^2 x^2$. Use eV and Å as above, and choose ω such that

   $$m\omega^2 = 1 \text{ eV}/\text{Å}^2, \tag{5.1}$$

   or some other convenient value. Note that as you get higher in the spectrum of states, the range in x over which the wavefunctions are substantially nonzero increases. Be sure that the code is integrating far enough past the classical turning points to give good results.

   (b) **Anharmonic Oscillator**

   Study the eigenvalues and wavefunctions for an anharmonic oscillator, with

   $$V = Ax^2 + Bx^4.$$

   (c) **Linear Potential**

   Study the eigenvalues and wavefunctions for the linear potential

   $$V(x) = A|x|.$$

4. **Infinite Square Well with Perturbation**

   Determine the effect on the eigenvalues and wavefunctions of adding a small rectangular bump to the center of the infinite square well. Can you understand qualitatively why the energies change as they do? Compare to the results of stationary state perturbation theory for this problem.

5. **Orthogonality** For any of the potential problems you solve, verify that eigenfunctions corresponding to different eigenvalues are *orthogonal*, that is,

   $$\int_{-\infty}^{\infty} \psi_n(x)\psi_{n'}(x)dx = 0$$

   for $n \neq n'$. You will need to use Simpson's rule, the trapezoid rule, or any other convenient algorithm for numerical integration.

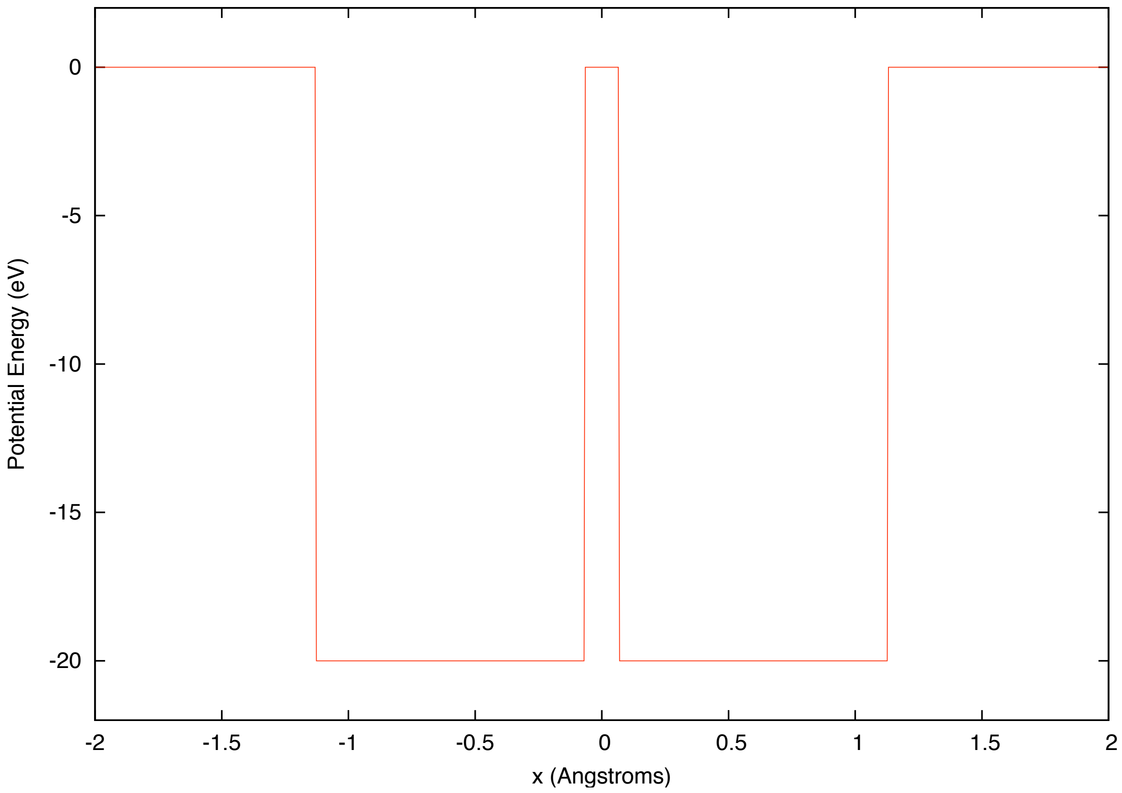

FIG. 2: Potential for hydrogen molecule model (energy scale approximate).

6. Model for Covalent Bonding

We can use the program to build a very simple of an H_2^+ molecule, i.e., singly ionized H_2, or a bound state of two protons and one electron. This model is really something of a joke and must not be taken seriously; however, it does exhibit the basic mechanism behind covalent bonding.

First, let's model an H atom as a one-dimensional object using a finite square well in place of the actual Coulomb potential. To match the usual conventions for the Coulomb potential ($V = 0$ at large distances), the potential energy should be shifted so that $E = 0$ is the top of the well, and its bottom is at $E = -V_0$ where V_0 is a positive constant. The basic properties of the H atom we wish to reproduce are its size, roughly the Bohr radius, $a_0 \approx 0.53$ Å, and the ground state energy, -13.6 eV. Set the well width to $2a_0$ and use your program to determine V_0 such that the ground state energy is -13.6 eV.

Next, model the potential experienced by the electron in the H_2^+ molecule using two of these wells side by side, with centers separated by the known bond length, $B = 1.2$ Å. The basic setup is shown in fig. 2. Now use the code to determine the energies of the ground and first excited states for this double well potential. The result represents the kinetic and potential energy of the electron, including the "Coulomb" energy arising from its interaction with the protons. The total energy of the system is obtained by adding in the Coulomb energy of the protons themselves, estimated as

$$V_{pp} \approx \frac{e^2}{4\pi\epsilon_0 r}$$

with $r = B$. (We assume the protons are sufficiently heavy, compared to the electron, that they are effectively at rest and so have no appreciable kinetic energy.)

Now, based on your results, is the ground state of the system bound? That is, does it form a stable molecule? What about the first excited state? Can you understand the results based on the shape of the wavefunction in each case?

VI. ELABORATIONS

The approach presented above is useful when the potential is symmetric, so that the wavefunctions have definite parity. For nonsymmetric potentials another approach is needed. In addition, intergration *into* the classically forbidden regions is likely to be rather unstable – even if we know the exact eigenvalue, so that the unwanted growing solution should be absent, round-off error and other numerical inaccuracies will inevitably re-introduce it. For both these reasons, it is useful to consider an approach in which we integrate in from the wings, rather than out from the center.

The basic idea is essentially unchanged. We integrate in from both ends, and at a convenient matching point x_0 we require that the two integrations meet with the same value and slope, just the continuity conditions we impose in analytical problems of this sort. We adjust E until they join smoothly.

This approach works for any potential, since it makes no assumption about the symmetry properties of the wavefunctions. It is also more stable, since in the inward integration the unwanted solutions tend to be *suppressed* rather than enhanced. The main problem is determining the starting conditions for the inward integrations. I shall here discuss two approaches to this.

The first is to simply assume that somewhere outside the well of interest there is an infinite square well, i.e., the potential gets extremely large. If we start the integrations at these points then the proper boundary condition is $\psi = 0$. The derivative ψ' can be set arbitrarily, since the wavefunction will need to be normalized at the end anyway. The unphysical walls should have a minimal effect on the results so long as they are far enough into the classically forbidden region that the true wavefunction will have decayed essentially to zero there. In practice this can be checked by repeating the calculations with the walls in different places; if the results are unchanged (to within the desired tolerance), then they may be accepted.

The second approach is to choose some starting points well outside the potential well, pick an arbitrary (small) value for ψ at these points, and then determine the derivative approximately from the Schrödinger equation. In the region outside, the wavefunction decays exponentially,

$$\psi \sim e^{-\kappa x} \tag{6.1}$$

(for $x > 0$), where

$$\kappa \equiv \sqrt{\frac{2m}{\hbar}\,(V - E)}, \tag{6.2}$$

with V the potential at this point. Hence

$$\frac{d\psi}{dx} \approx -\kappa\psi, \tag{6.3}$$

and this furnishes an approximate starting value for the derivative. Now the integration can proceed and the solutions matched at an intermediate point.

In either case the matching is conveniently carried out in the following way. Since the wavefunctions are not normalized, we can easily make ψ itself agree between the two solutions by rescaling one of them. We then have to match the derivatives. A simple way to accomplish both needs simultaneously is to match the logarithmic derivatives at the intermediate point. If ψ_L and ψ_R are the solutions integrated inward from the left and right, respectively, then we require that

$$\left[\frac{\psi_L'}{\psi_L} - \frac{\psi_R'}{\psi_R}\right]_{x=x_0} = 0. \tag{6.4}$$

This then becomes the quantity that the code attempts to zero by adjusting E.

Interested readers may wish to repeat some of the ealier exercises using these techniques.

Appendix A: Numerical Solution of Ordinary Differential Equations

In this section I discuss the basics of solving ordinary differential equations on a computer. A disclaimer is perhaps in order. This is actually a large and technical area, and I can afford to touch only on the most basic aspects here. Knowledgeable readers may in fact find certain aspects of the presentation to be scandalously slipshod and incomplete. In response I can only say that my goal is to give a basic overview that illustrates most of the relevant issues. My hope is that this orientation will be sufficient to help guide interested students in further inquiry, should they choose to pursue it. Additional details may be found in standard texts, for example, refs. [2].

1. Basic Concepts

An ordinary differential equation (ODE) is an equation satisfied by a function of a single independent variable, involving derivatives of that function. The *order* of the ODE is the order of the highest derivative that occurs; thus

$$\frac{d^3y}{dx^3} + a(x)\frac{d^2y}{dx^2} + b(x)\frac{dy}{dx} + c(x)y + d(x) = 0, \tag{A1}$$

where a, b, c and d are specified functions, is a third-order ODE for the function $y(x)$. We may also consider a system of ODEs that determines a set of functions, each of the same independent variable. Typically each function appears in more than one of the equations, so that they are *coupled.* Any equation involving only one of the functions can be solved independently of the others.

To determine a unique solution to an n-th order ODE, it is necessary to further provide n independent "boundary conditions," or known values of the function and/or its derivatives for some value(s) of the independent variable. Often this takes the form of specifying the function and $n - 1$ of its derivatives at some common reference value of x; this is known as the "initial value problem." (For convenience we often choose this reference point to be $x = 0$, if possible.) The canonical example would be the solution to Newton's second law of motion, a second-order ODE. A unique solution is determined by specifying the position and velocity at some reference time. There are other possibilities as well for the specification of boundary values, but in this module I shall focus on the initial value problem.

As a first step, note that an ODE of any order can always be reduced to a coupled system of first-order ODEs. The basic point may be appreciated by considering Newton's second law in one dimension,

$$\frac{d^2y}{dt^2} = f(y), \tag{A2}$$

where $f = F/m$ with F the net force and m the mass. This is a second-order ODE, but by introducing the velocity $v = dy/dt$ we can re-write it as a pair first-order equations:

$$\frac{dy}{dt} = v \tag{A3}$$

$$\frac{dv}{dt} = f(y). \tag{A4}$$

The idea is easy to generalize and we leave this to the reader. In general, an n-th order equation will reduce to a set of n first-order equations. It is therefore sufficient to consider a set of coupled first-order ODEs. These equations will have the general form

$$\frac{dy_i}{dx} = f_i(x, y_1, \ldots, y_n) \qquad i = 1, \ldots, n, \tag{A5}$$

where the y_i are the functions to be determined and the f_i are given. A full solution to these also requires the specification of boundary conditions on the functions y_i. As discussed above, we will here consider only the initial value problem. Starting values for all the y_i are thus specified at some common x, which we take to be $x = 0$ for convenience. The system of equations (A5) then determines the y_i for any other value of x.

Our basic approach to finding approximate solutions will be to advance in x in small steps of size ϵ, treating eqs. (A5) as a set of *difference* equations. We thus evaluate the solution at a discrete set of x values, $x_n = n\epsilon$, where $n = 0, 1, 2, \ldots$. The differential equations are re-written by replacing differentials dx and dy with differences Δx and Δy. The result is a set of algebraic equations for the change in the functions y_i in each "step" of size $\Delta x \equiv \epsilon$.

As an example, consider Newton's second law as presented in eqs. (A4). The simplest approach would be to approximate these as

$$\frac{\Delta y}{\epsilon} = v \tag{A6}$$

$$\frac{\Delta v}{\epsilon} = f(y), \tag{A7}$$

whence

$$\Delta y = y(t+\epsilon) - y(t) = \epsilon v \tag{A8}$$

and

$$\Delta v = v(t+\epsilon) - v(t) = \epsilon f(y). \tag{A9}$$

Given values for y and v at time t, we can then obtain these quantities at the next step:

$$y(t+\epsilon) \;=\; y(t) + \epsilon v \tag{A10}$$

$$v(t+\epsilon) \;=\; v(t) + \epsilon f(y). \tag{A11}$$

The new values then allow us to take the next step, and so on. Since by assumption we have the starting values for y and v at $t = 0$, we can step along and calculate y and v for any t. If ϵ is small enough then the differences will approximate the differentials reasonably well, and the resulting solution can be made as accurate as desired.

This approach, in which we approximate the original derivatives as

$$\frac{dy}{dx} \approx \frac{y(x+\epsilon) - y(x)}{\epsilon}, \tag{A12}$$

is known as Euler's method. It is the simplest approach to solving ODEs numerically, although it is not especially accurate. To quantify the accuracy, let's imagine we know the full solution $y(x)$ for all x. We can then Taylor expand around a point x to obtain

$$y(x+\epsilon) = y(x) + \epsilon y'(x) + \mathcal{O}(\epsilon^2), \tag{A13}$$

where $y' = dy/dx$ as usual. We thus see that Euler's method is equivalent to neglecting terms of order ϵ^2 (and higher) in the true answer. In principle this error can be made as small as we like, however, by making ϵ sufficiently small [8].

However, the smaller we make ϵ, the more steps we need to take to obtain the solution at some fixed x of interest. For simplicity, say we need y at $x = 1$. The number of steps needed is then $N = 1/\epsilon$. If the error in each step is $\mathcal{O}(\epsilon^2)$ then the total error in reaching $x = 1$ is $N\mathcal{O}(\epsilon^2)$ or $\mathcal{O}(\epsilon)$. Hence to make the solution twice as accurate we will need to halve the step size ϵ, leading to twice as much computational work. The work involved is a single evaluation of the function f at each step.

While conceptually simple, Euler's method is not recommended for practical applications due to its poor accuracy. In addition to the extra computational work required, the need to take many steps to achieve high accuracy can magnify the effect of "roundoff error" in the computations. The basic issue here is that real numbers are represented discretely on a computer, which means that only a finite subset of all the reals actually "exist" on the computer. For example, say we use a computer on which a `float` is 4 bytes, or 32 bits. Each bit can be 0 or 1, so there are $2^{32} \approx 4.3 \times 10^9$ possible different configurations of these bits. Thus the computer can at most represent this many different `float`s from among the infinity of real numbers. The result is that a float on the computer generally is slightly different than its "true" value – most of the "true" values are simply not representable. Even if we do start with values that are represented exactly on the computer, when we operate on them – multiply them together, for example – the exact result is generally not represented. Thus a small error, called "roundoff error," is unavoidably introduced [9].

Often this roundoff error can be thought of as a sort of random error – it's just as likely to be positive as negative – so that it grows like $\sqrt{N}$ for N calculations. In unfavorable cases the situation may well be worse, however, and in very unfavorable situations this error may quickly come to dominate a calculation. We will see an example of this below.

2. More Accurate Techniques

We would like to develop algorithms for solving our ODEs that have better accuracy than Euler's method, i.e., with overall errors that are $\mathcal{O}(\epsilon^n)$ with $n > 1$. Such an algorithm will result in a more rapid increase in accuracy with decreasing step size, leading to greater overall accuracy for a fixed amount of computational work.

The invocation of the Taylor series above may suggest some ideas. For example, let us include the next term in the expansion,

$$y(x+\epsilon) = y(x) + \epsilon y'(x) + \frac{1}{2}\epsilon^2 y''(x) + \ldots . \tag{A14}$$

Since $y'(x) = f(x, y)$ is a known function, we can calculate the second derivative in the ϵ^2 term:

$$\begin{aligned} y''(x) &= \frac{df}{dx} \\ &= \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y}\frac{dy}{dx} \\ &= \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y} f. \end{aligned}$$

So we could step y using

$$y(x+\epsilon) = y(x) + \epsilon y'(x) + \frac{1}{2}\epsilon^2 \left[\frac{\partial f}{\partial x} + f\frac{\partial f}{\partial y}\right], \tag{A15}$$

which is correct to $\mathcal{O}(\epsilon^3)$. The overall error in taking n steps would then be $\mathcal{O}(\epsilon^2)$. This approach is most useful when f is sufficiently simple that its derivatives can be readily computed.

As another example, consider that Euler's method amounts to approximating the derivative dy/dx by the "forward" difference:

$$\frac{dy}{dx} \approx \frac{y(x+\epsilon) - y(x)}{\epsilon}. \tag{A16}$$

There is no reason to suppose this is any more accurate than the "backwards" difference

$$\frac{dy}{dx} \approx \frac{y(x) - y(x-\epsilon)}{\epsilon}, \tag{A17}$$

but consider using the average of these, the "symmetric" difference. In this case we would have

$$\begin{aligned} \frac{dy}{dx} &\approx \frac{1}{2}\left[\frac{y(x+\epsilon) - y(x)}{\epsilon} + \frac{y(x) - y(x-\epsilon)}{\epsilon}\right] \\ &= \frac{y(x+\epsilon) - y(x-\epsilon)}{2\epsilon}, \end{aligned} \tag{A18}$$

resulting in

$$y(x+\epsilon) = y(x-\epsilon) + 2\epsilon f(x,y). \tag{A19}$$

At first glance this looks about as good as Euler, but if we insert the Taylor expansions for $y(x+\epsilon)$ and $y(x-\epsilon)$ we find that all the $\mathcal{O}(\epsilon^2)$ terms on the right hand side of eq. (A19) actually cancel; hence this formula is accurate to $\mathcal{O}(\epsilon^3)$, as is eq. (A15). We might even be tempted to use it in preference to eq. (A15), since it does not require us to take additional derivatives of f. However, this approximation has a problem, which you can explore in one of the exercises. Do not use it to solve a real problem!

3. The Runge-Kutta Algorithm

A very useful algorithm is known as the Runge-Kutta approach. It is stable and can be made quite accurate, although it is not always the most efficient algorithm (i.e., the fastest for a given accuracy). We shall derive here the second-order version of the RK algorithm, and then simply present the more accurate fourth-order version.

We begin by observing that the basic Euler method,

$$y(x+\epsilon) = y(x) + \epsilon f(x,y), \tag{A20}$$

assumes the entire change in y over the step is obtained from the derivative at the *beginning* of the step. (In fact, if the derivative is constant over the step, or in other words if y is a linear function of x, then Euler's method is exact.) A better result might be obtained if we use eq. (A20) to take a "trial" step to the midpoint of the interval $(x + \epsilon/2)$, and then take the full step from x to $x + \epsilon/2$ using the midpoint values. This corresponds to using the (approximate) *average* derivative over the interval in Euler's method.

Specifically, we take for the trial step:

$$y(x+\epsilon/2) = y(x) + (\epsilon/2) f(x,y), \tag{A21}$$

and then step from x to $x + \epsilon$ using the midpoint values of both x and y:

$$y(x+\epsilon) = y(x) + \epsilon f(x+\epsilon/2, y(x+\epsilon/2)). \tag{A22}$$

This algorithm is more conventionally expressed by defining the quantities

$$\begin{aligned} k_1 &= \epsilon f(x,y) && \text{(A23)} \\ k_2 &= \epsilon f(x+\epsilon/2, y(x) + k_1/2), && \text{(A24)} \end{aligned}$$

and then stepping as

$$y(x+\epsilon) = y(x) + k_2 + \mathcal{O}(\epsilon^3). \tag{A25}$$

As indicated, the second order dependence on ϵ cancels (again, substitute the full Taylor expansions into the given formulas to demonstrate this) so that the algorithm is accurate to $\mathcal{O}(\epsilon^3)$. The full error in taking n steps will then be $\mathcal{O}(\epsilon^2)$, and hence this is known as the second-order Runge-Kutta algorithm.

More accurate versions of this are possible, in which we take various partial steps across the interval and combine them so that error terms of higher and higher order are cancelled. The most popular version is probably the standard fourth-order algorithm, which is as follows:

$$\begin{aligned} k_1 &= \epsilon f(x,y) && \text{(A26)} \\ k_2 &= \epsilon f(x+\epsilon/2, y(x) + k_1/2) && \text{(A27)} \\ k_3 &= \epsilon f(x+\epsilon/2, y(x) + k_2/2) && \text{(A28)} \\ k_4 &= \epsilon f(x+\epsilon, y(x) + k_3) && \text{(A29)} \\ y(x+\epsilon) &= y(x) + \frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} + \mathcal{O}(\epsilon^5). && \text{(A30)} \end{aligned}$$

It is a straightforward if somewhat tedious exercise to verify that all error terms through $\mathcal{O}(\epsilon^4)$ cancel in eq. (A30).

4. Exercises

1. Consider the equation
$$\frac{dy}{dx} = -xy$$
with initial condition $y(0) = 1$, which has the exact solution $y = \exp(-x^2/2)$. Study the numerical integration of this using the methods described above. In particular, verify that the errors (difference between numerical and exact solutions) decrease according to the expected power of ϵ.

2. Generalize one or more of the schemes presented here to solve a system of two coupled ODEs, and apply it to solve Newton's second law for the simple harmonic oscillator (with $m = 1$):
$$\begin{aligned}\frac{dx}{dt} &= v \\ \frac{dv}{dt} &= -\omega^2 x.\end{aligned}$$
A useful criterion for accuracy is the degree to which a known integral of the motion, for example, the energy, is conserved in the evolution. Study the constancy of $2E = v^2 + \omega^2 x^2$ for the various algorithms and choices for ϵ.

3. Another common test of accuracy is to integrate backwards to the original starting point, using the ending x, y as the initial condition. The difference between the resulting value for y and the original initial condition then gives a measure of the overall accuracy of the result. Apply this test to the example from problem 1, for the various algorithms discussed above.

4. Study the approximation given in eq. (A19), by using it to solve the equation
$$\frac{dy}{dx} = -y,$$
with the initial condition $y(0) = 1$. This equation has the exact solution
$$y = e^{-x},$$

of course. To start the calculation off we need both $y(0)$ and $y(\epsilon)$; you can use eq. (A15) to obtain $y(\epsilon)$. Eq. (A19) can then be used to generate the solution for other values of x. Does this give a reasonable approximation to the exact answer? If not, can you determine why?

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[1] For additional details on background, see a standard introductory text on quantum mechanics, e.g., D.J. Griffiths, *Introduction to Quantum Mechanics*, 2nd ed. (Prentice Hall, 2005); R.L. Liboff, *Introductory Quantum Mechanics*, 4th ed. (Addison Wesley, 2003).

[2] For example, S.E. Koonin, *Computational Physics* (Benjamin/Cummings, 1985); T. Pang, *An Introduction to Computational Physics* (Cambridge University Press, 2006); L.D. Fosdick, E.R. Jessup, C.J.C. Schauble, and G. Domik, *Introduction to High-Performance Scientific Computing* (MIT Press, 1996).

[3] There is an important case where non-normalizable wavefunctions are useful despite their unphysicality: plane wave solutions for a free particle ($V = 0$), corresponding to a particle with a definite momentum. In this case the lack of normalizability is connected to the failure of such states to properly respect the uncertainty principle: a particle with a definite p would have $\Delta p = 0$ and hence $\Delta x = \infty$. However, normalizable states *can* be constructed as linear superpositions of these plane waves, and, indeed, if sufficient care is exercised, the plane waves themselves can often be used directly to obtain physical results (e.g., transition and reflection probabilities for potential scattering).

[4] E can be shown to be a real number, assuming V is real.

[5] By the same token φ disappears from the probability integral, eq. (3.2). Hence for particles described by wavefunctions of the form (3.8), all probabilities are independent of t. Such states are called "stationary states," and are static in the sense that their physical properties do not change in time. A *superposition* of stationary states with different values of E will produce time-dependent probabilities, however.

[6] To apply this scheme to a second-order differential equation such as the TISE, we must first re-write it as a pair of first-order equations for ψ and ψ':

$$\frac{d\psi}{dx} = \psi'$$

and

$$\frac{d\psi'}{dx} = \frac{2m}{\hbar^2}\left(V(x) - E\right)\psi.$$

Then two initial conditions allow us to step both quantities forward in x. See the appendix for a more detailed discussion of this point.

[7] For the problem at hand, this initial guess could be the minimum of the potential energy, since it can be shown that the lowest eigenvalue of the TISE is always greater than this.

[8] In practice things are not so simple. On a computer, where real numbers are represented in a discrete fashion, problems will arise if ϵ is made too small. The precise nature of the problem will depend on the details of our scheme, and a detailed discussion of these issues would take us too far afield. For the moment just keep in mind that ϵ cannot be made too small in practice.

[9] This is called "roundoff error" because it can be thought of as arising from rounding the results of calculations from their true mathematical values to values that are actually represented on the computer.

Glossary

bisecion method	Simple search-based approach to root finding. The basic idea is to change the independent variable until the function changes sign, then back up and halve the step size. Reliable, albeit slow.
bound state	A quantum state in which the wavefunction is nonzero (apart from exponentially small contributions) only in some finite region; represents a particle that is localized in that region.
covalent bond	Chemical bond in which atoms effectively "share" electrons.
Euler method	Simple method of integrating an ODE based on approximating differentials by differences. Not recommended for practical use due to poor accuracy.
Hamiltonian	In quantum theory, the operator corresponding to the total energy of a system.
Newton-Raphson	Root-finding algorithm, more efficient than bisection but requiring the computation of the derivative of the function.
normalization	Requirement applied to wavefunctions; physical content is that the probability of finding the particle somewhere should be unity.
ordinary differential equation	An equation for a function of one independent variable, involving derivatives of that function.
round-off error	Error in floating-point computations on a computer introduced due to the discrete representation of real numbers.
Runge-Kutta	A numerical integration algorithm.
Schrödinger equation	The central equation of quantum theory, which determines the time development of the wavefunction.

secant method	A root-finding algorithm, faster than simple bisection and without the need to compute derivatives, as in Newton-Raphson.
separation of variables	Technique for separating a partial differential equation into ordinary differential equations. The basic assumption is a product form for the solutions.
shooting method	Technique for solving boundary value problems in which the solution is integrated from one side of the domain to the other and adjusted until the appropriate boundary conditions are satisfied.
wavefunction	The entity that describes the quantum state of a system. Its modulus squared gives the probability density for position.