Lab 8

Schrödinger's Equation

Derivations

Here is the time-dependent Schrödinger equation which governs the way a quantum wave function changes with time in a one-dimensional potential well $V(x)$:[1]

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi \tag{8.1}$$

Note that except for the presence of the imaginary unit i, this is very much like the diffusion equation. In fact, a good way to solve it is with the Crank-Nicolson algorithm. Not only is this algorithm stable for Schrödinger's equation, but it has another important property: it conserves probability. This is very important. If the algorithm you use does not have this property, then as ψ for a single particle is advanced in time you have (after a while) 3/4 of a particle, then 1/2, etc.

The Schrödinger equation usually describes the behavior of very tiny things on very short timescales, so SI quantities like kilograms, meters, and Joules are essentially infinite in quantum mechanics. Instead, we'll use a system of units called atomic units. In this system, lengths are measured in units of a_0 (the Bohr radius, $a_0 = 5.29 \times 10^{-11}$), masses are measured in units of the electron mass m_e, energies are measured in units of E_0 ($E_0 = \alpha^2 mc^2 \approx 27$ eV), and time is measured in units of t_0 ($t_0 = 24.2$ attoseconds). These base units are chosen so that the constants $\hbar$ and m both have the numerical value of 1 (e.g. $m = 1m_e$ for an electron).

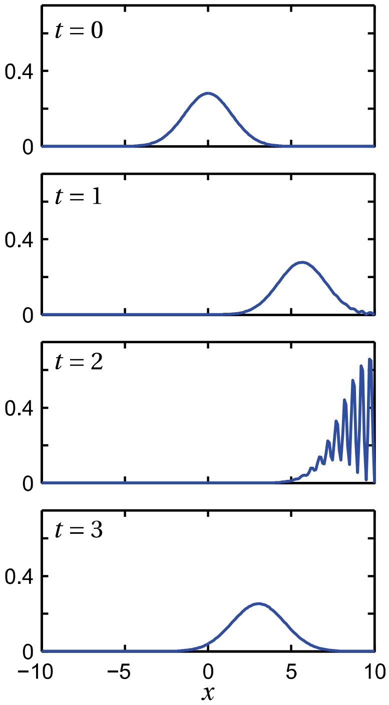

Figure 8.1 The probability density $|\psi(x)|^2$ of a particle in a box that initially moves to the right and then interferes with itself as it reflects from an infinite potential (Problem 8.2(a)).

P8.1 Use paper and pencil to derive a Crank-Nicolson algorithm to solve the Schrödinger equation. It will probably be helpful to use the material in Lab 7 as a guide (beginning with Eq. (7.15)). Make sure the $V(x)\psi$ term enters the algorithm correctly.

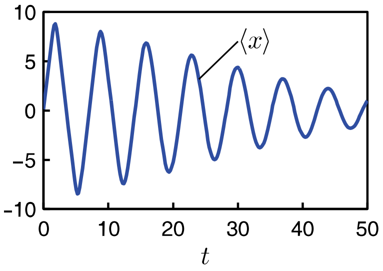

Figure 8.2 The expectation position $\langle x\rangle$ for the particle in Fig. 8.1 as time progresses and the packet spreads out (Problem 8.2(c)).

Particle in a box

Let's use this algorithm for solving Schrödinger's equation to study the evolution of a particle in a box with

$$V(x) = \begin{cases} 0 & \text{if } -L < x < L \\ +\infty & \text{otherwise} \end{cases} \tag{8.2}$$

[1] N. Asmar, *Partial Differential Equations and Boundary Value Problems* (Prentice Hall, New Jersey, 2000), p. 470-506.

The infinite potential at the box edges is imposed by forcing the wave function to be zero at these points:

$$\psi(-L) = 0 \quad ; \quad \psi(L) = 0 \tag{8.3}$$

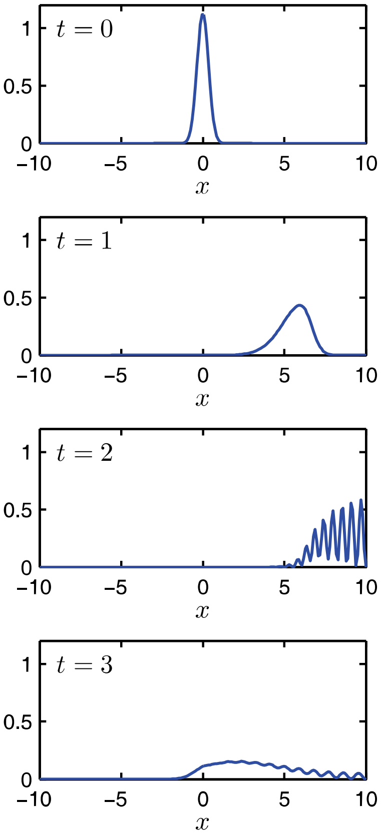

Figure 8.3 The probability density $|\psi(x)|^2$ of a particle that is initially more localized quickly spreads (Problem 8.2(d)).

P8.2 Modify one of your programs from Lab 7 to implement the Crank-Nicolson algorithm derived above for the case of a particle in a box with $L = 10$. Note we are doing quantum mechanics and the imaginary parts matter now. When assigning complex variables in NumPy, you use the engineering complex number j, like this:

```
a = 1.0 + 0.5j
```

When you allocate your arrays, you'll need to specify up-front that they will hold complex values, like this:

```
A = np.zeros((N,N),dtype=np.complex_)
B = np.zeros_like(A,dtype=np.complex_)
```

(a) Write a script to solve the time-dependent Schrödinger equation using Crank-Nicolson. We find that a cell-edge grid is easiest, but you can also do cell-center with ghost points if you like. Start with a localized wave packet of width σ and momentum p:

$$\psi(x,0) = \frac{1}{\sqrt{\sigma\sqrt{\pi}}} e^{ipx/\hbar} e^{-x^2/(2\sigma^2)} \tag{8.4}$$

with $p = 2\pi$ and $\sigma = 2$. This initial condition does not exactly satisfy the boundary conditions, but it is very close. Check to see how far off it is at the boundary, and decide how the sizes of L and σ must compare in to use this initial condition.

Run the script with $N = 200$ and watch the particle (wave packet) bounce back and forth in the well. Plot the real part of ψ as an animation to visualize the spatial oscillation of the wave packet, then plot an animation of $\psi^*\psi$ so that you can visualize the probability distribution of the particle. Try switching the sign of p and see what happens.

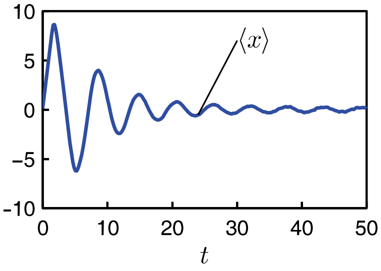

Figure 8.4 The expectation position of the particle in Fig. 8.3 as time progresses.

(b) Verify by doing a numerical integral that $\psi(x,0)$ in the formula given above is properly normalized. Then run the script and check that the wave packet stays properly normalized, even though the wave function is bouncing and spreading within the well. If you are on a cell-edge grid you should do the integrals with NumPy's `trapz` rather than `sum`.

(c) Run the script and verify by numerical integration that the expectation value of the particle position

$$\langle x \rangle = \int_{-L}^{L} \psi^*(x,t)\; x\, \psi(x,t)\, dx \tag{8.5}$$

is correct for a bouncing particle. Plot $\langle x\rangle(t)$ to see the bouncing behavior. Run long enough that the wave packet spreading modifies the bouncing to something more like a harmonic oscillator. (Note: you will only see bouncing-particle behavior until the wave packet spreads enough to start filling the entire well.)

(d) You may be annoyed that the particle spreads out so much in time. Try to fix this problem by narrowing the wave packet (decrease the value of σ) so the particle is more localized. Run the script and explain what you see in terms of quantum mechanics.

Tunneling

Now we will allow the pulse to collide with a with a non-infinite potential barrier of height V_0 and width $\Delta x = 0.02L$, and study what happens. Classically, the answer is simple: if the particle has a kinetic energy less than V_0 it will be unable to get over the barrier, but if its kinetic energy is greater than V_0 it will slow down as it passes over the barrier, then resume its normal speed in the region beyond the barrier. (Think of a ball rolling over a bump on a frictionless track.) Can the particle get past a barrier that is higher than its kinetic energy in quantum mechanics? The answer is yes, and this effect is called tunneling.

To see how the classical picture is modified in quantum mechanics we must first compute the energy of our pulse so we can compare it to the height of the barrier. The quantum mechanical formula for the expectation value of the energy is

$$\langle E\rangle = \int_{-\infty}^{\infty} \psi^* H\psi \, dx \tag{8.6}$$

where ψ^* is the complex conjugate of ψ and where

$$H\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi(x) \tag{8.7}$$

In our case the initial wave function $\psi(x,0)$ given by Eq. (8.4) is essentially zero at the location of the potential barrier, so we may take $V(x) = 0$ in the integral when we compute the initial energy. Performing the integral, we find

$$\langle E\rangle = \frac{p^2}{2m} + \frac{\hbar^2}{4m\sigma^2} \tag{8.8}$$

Since this is a conservative system, the energy should remain constant throughout the propagation.

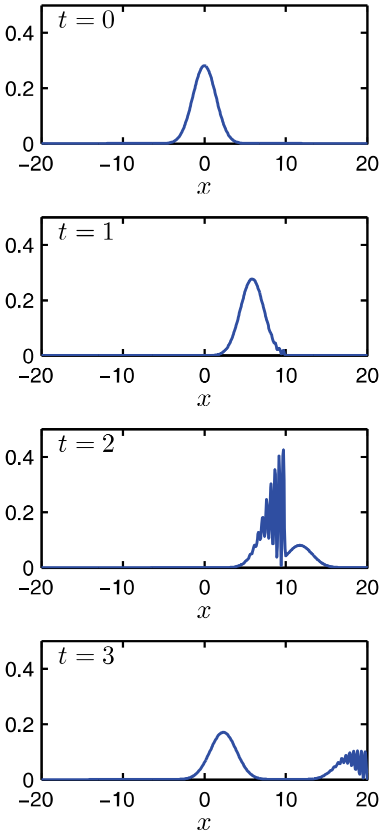

Figure 8.5 The probability distribution $|\psi(x)|^2$ for a particle incident on a narrow potential barrier located just before $x = 10$ with $V_0 > \langle E\rangle$. Part of the wave tunnels through the barrier and part interferes with itself as it is reflected.

P8.3 (a) Modify your script from Problem 8.2 so that it uses a computing region that goes from $-2L$ to $3L$ and a potential

$$V(x) = \begin{cases} 0 & \text{if } -2L < x < 0.98L \\ V_0 & \text{if } 0.98L \leq x \leq L \\ 0 & \text{if } L < x < 3L \\ \\ +\infty & \text{otherwise} \end{cases} \tag{8.9}$$

so that we have a square potential hill $V(x) = V_0$ between $x = 0.98L$ and $x = L$ and $V = 0$ everywhere else in the well.

Note: Since $V(x)$ was just zero in the last problem, this is the first time to check if your $V(x)$ terms in Crank-Nicolson are right. If you see strange behavior, you might want to look at these terms in your code.

(b) Run your script several times, varying the height V_0 from less than your pulse energy to more than your pulse energy. Overlay a plot of $V(x)/V_0$ on your plot of $|\psi|^2$ and look at the behavior of ψ in the barrier region.

You should do several experiments with your code. (1) Try making the barrier height both higher than your initial energy and lower than your initial energy. Explain to your TA how the quantum behavior differs from classical behavior. You should find that even when the barrier is low enough that a classical particle could get over it, some particles still come back. (2) Experiment with the width of your barrier and see what its effect is on how many particles tunnel through. As part of this experiment, figure out a way to calculate what fraction of the particles make it through the barrier.