30

Confined Electronic Wave Packets ⊙

30.1 PROBLEM: A CONFINED ELECTRON

An electron is initially confined to a one-dimensional region of space the size of an atom. Your **problem** is to determine how long in time the electron remains confined. This is different from the problem of a particle confined to a box considered in Chapter 10, *Quantum Eigenvalues; Zero-Finding and Matching.* There we had a time-independent situation in which we had to solve for the spatial wave function; here we have a time-dependent problem in which we know the wave function at time zero, and even though that state is not in an eigenstate or stationary state of the Hamiltonian, we wish to determine it for all future times.

30.2 MODEL: TIME-DEPENDENT SCHRÖDINGER EQUATION

We use a wave function (or wave packet) $\psi(x,t)$ that is a function of the position x and time t to describe a localized electron. We assume that the electron is initially localized around $x = 5$, and model this by a Gaussian wave function multiplying a plane wave:

$$\psi(x, t = 0) = \exp\left[-\frac{1}{2}\left(\frac{x - 5.0}{\sigma_0}\right)^2\right] e^{ik_0 x}. \tag{30.1}$$

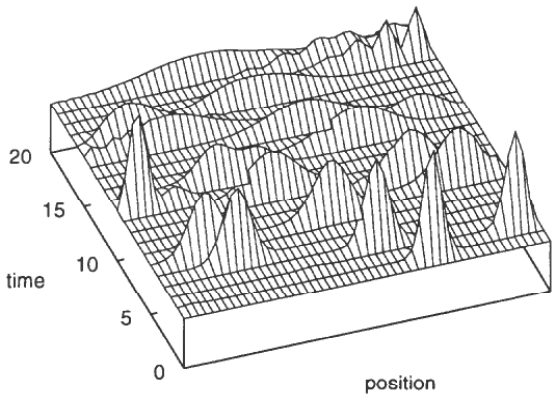

Fig. 30.1 The position as a function of time of a localized electron confined to a square well. The electron is initially on the right with a Gaussian wave packet. In time, the wave packet spreads out and collides with the walls.

The behavior of this wave packet as a function of time, when placed in a square well, is shown in Fig. 30.1. The behavior, when placed in an harmonic oscillator potential, is shown in Fig. 30.2.

As you may verify by applying the momentum operator $\tilde{p} = id/dx$, the wave packet (30.1) does not correspond to an electron with a definite momentum (that is, it is not an eigenstate of $\tilde{p}$).[1] However, if the width σ_0 of the Gaussian is made very large, the electron gets spread over a sufficiently large region of space to consider the wave packet as a plane wave of momentum k_0 with a slowly varying amplitude.

The time and space evolution of a quantum particle is described by the time-dependent Schrödinger equation (here in one dimension):

$$i\frac{\partial\psi(x,t)}{\partial t} = \tilde{H}\psi(x,t). \tag{30.2}$$

Here $\tilde{H}$ is the Hamiltonian operator:

$$\tilde{H} = -\frac{1}{2m}\frac{\partial^2}{\partial x^2} + V(x), \tag{30.3}$$

where we have set $2m = 1$ to keep the equations simple, and use a partial x derivative because ψ is also a function of t.

An important aspect of quantum mechanics is that the wave function is

[1]We use natural units in which $\hbar = 1$, so there is no difference between momentum and wave numbers [L 96, Appendix A.1].

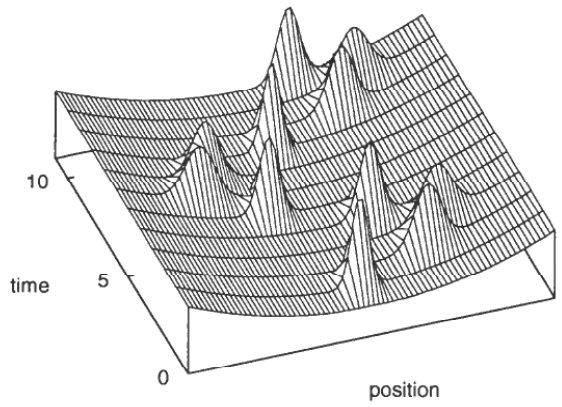

Fig. 30.2 The probability density as a function of time for an electron confined to a 1-D harmonic oscillator potential well. The electron's initial localization is described by the Gaussian wave packet (30.1). Because the wave packet is an eigenfunction of the potential, it does not break up on collision but instead returns to its original form.

complex (because it is not directly observable, this is not a problem). Even though many computer languages can handle complex functions, we will find it advantageous to decompose the wave function into its real and imaginary parts:

$$\psi(x,t) = R(x,t) + iI(x,t). \tag{30.4}$$

Substitution of (30.4) into Schrödinger equation (30.2) produces the coupled PDEs:

$$\frac{\partial R(x,t)}{\partial t} = +\tilde{H}I(x,t) = -\frac{1}{2m}\frac{\partial^2 I(x,t)}{\partial x^2} + V(x)I(x,t), \tag{30.5}$$

$$\frac{\partial I(x,t)}{\partial t} = -\tilde{H}R(x,t) = +\frac{1}{2m}\frac{\partial^2 R(x,t)}{\partial x^2} + V(x)R(x,t), \tag{30.6}$$

where the Hamiltonian operator $\tilde{H}$ is assumed real.

30.3 METHOD, NUMERIC: FINITE DIFFERENCE

The time-dependent Schrödinger equation can be solved with both implicit and explicit methods. An *implicit* method [Gold 67] converts the PDEs into a very large set of simultaneous linear equations involving the wave function evaluated at each grid point, and then solves these linear equations by matrix inversion for each time. This can cause problems when the matrices get very large. For our project, we modify the *explicit* method described by [Ask 77] and [Viss 91]. This is an iterative scheme that avoids the inversion of large

matrices.

There are some challenges in solving the Schrödinger equation. First, we need an algorithm that converges and is stable, the usual concerns. Second, we need an algorithm that ensures, at least to some order, that probability is conserved with time; otherwise the electron will fade away right before our eyes. A good solution to the probability problem is to determine the real and imaginary parts of the wave function at slightly different or "staggered" times. Explicitly, the real part R is determined at times $0, \Delta t, \ldots$, and the imaginary part I at $\frac{1}{2}\Delta t$, $\frac{3}{2}\Delta t$, and so forth. The algorithm is based on (what else) the Taylor expansions of R and I:

$$R(x, t + \tfrac{1}{2}\Delta t) \simeq R(x, t - \tfrac{1}{2}\Delta t) \qquad (30.7)$$
$$-2\left\{\alpha\left[I(x + \Delta x, t) + I(x - \Delta x, t)\right] - 2\left[\alpha + V(x)\Delta t\right] I(x, t)\right\},$$
$$I(x, t + \tfrac{1}{2}\Delta t) \simeq I(x, t - \tfrac{1}{2}\Delta t) \qquad (30.8)$$
$$+2\left\{\alpha\left[R(x + \Delta x, t) + R(x - \Delta x, t)\right] - 2\left[\alpha + V(x)\Delta t\right] R(x, t)\right\},$$
$$\alpha = \frac{\Delta t}{2(\Delta x)^2}. \qquad (30.9)$$

In discrete form, these equations become our algorithm:

$$R_i^{n+1} = R_i^n - 2\left\{\alpha\left[I_{i+1}^n + I_{i-1}^n\right] - 2\left[\alpha + V_i\Delta t\right] I_i^n\right\}, \qquad (30.10)$$
$$I_i^{n+1} = I_i^n + 2\left\{\alpha\left[R_{i+1}^n + R_{i-1}^n\right] - 2\left[\alpha + V_i\Delta t\right] R_i^n\right\}, \qquad (30.11)$$

where the superscript n indicates the time $t = n\Delta t$ and the subscript i, the position $x = i\Delta x$.

In order to conserve probability to a higher level of precision, the probability density ρ is defined in terms of the wave function evaluated at three different times:

$$\rho(t) = \begin{cases} R^2(t) + I(t + \frac{\Delta t}{2})I(t - \frac{\Delta t}{2}), & \text{for integer } t, \\ I^2(t) + R(t + \frac{\Delta t}{2})R(t - \frac{\Delta t}{2}), & \text{for half-integer } t. \end{cases} \qquad (30.12)$$

While this definition of ρ may seem strange, it reduces to the usual one for $\Delta t \to 0$, and so can be viewed as part of the art of numerical analysis. You will verify, if you do as told, that with this definition, the integral of the probability over all space is approximately constant from one time to the next:

$$\sum_x \rho(x, t + \tfrac{1}{2}\Delta t) \simeq \sum_x \rho(x, t). \qquad (30.13)$$

We refer the reader to [Koon 86] and [Viss 91] for details on the stability of the algorithm and on the behavior of the evolution matrix $\exp(iH\Delta t)$.

30.4 IMPLEMENTATION: WAVE PACKET IN WELL, SQWELL.F

On the diskette and the Web you will find a program that solves for the motion of the wave packet (30.1) inside the infinite potential well:

$$V(x) = \begin{cases} \infty, & \text{for } x < 0, \\ 0, & \text{for } 0 \le x \le 15, \\ \infty, & \text{for } x > 15. \end{cases} \tag{30.14}$$

1. Define arrays `R(751,2)` and `I(751,2)` for the real and imaginary parts of the wave function, and `Rho(751)` for the probability density. The first subscript refers to the x position on the grid and the second to the present and future times.
2. Use the values $\sigma_0 = 0.5$, $\Delta x = 0.02$, $k_0 = 17\pi$, and $\Delta t = \frac{1}{2}\Delta x^2$.
3. Use equation (30.1) for the initial wave packet to define `R(j,1)` for all j at $t = 0$, and `I(j,1)` at $t = \frac{1}{2}\Delta t$.
4. Set `Rho(1)=Rho(751)` $= 0.0$ because the wave function must vanish at the infinitely high well walls.
5. Increment time by $\frac{1}{2}\Delta t$. Use (30.10) to compute `R(j,2)` in terms of `R(j,1)`, and (30.11) to compute `I(j,2)` in terms of `I(j,1)`.
6. Repeat the steps through all of space; that is, for i=2–750.
7. Throughout all of space, replace the present wave packet (second index equal to 1) by the future wave packet (second index 2).
8. Repeat the time stepping many times, ultimately ~5000, but do not let your program run that long until you are sure it is working properly.

30.5 ASSESSMENT: VISUALIZATION, AND ANIMATION

1. Output the probability density `Rho` on a coarse grid, say, about every fifth grid point. For crude animation, output the entire space behavior after every 200 time steps.
2. Make a 3-D plot of probability versus position versus time. This should look like Fig. 30.1 or Fig. 30.2.
3. Make a movie showing the wave function as a function of time.
4. Check how well probability is conserved for early and late times. Determine the integral of the probability over all of space, $\int_0^\infty dx\rho(x)$, and see if it changes with time (its explicit value doesn't matter because that's just normalization).

5. What might be a good explanation of why collisions with the walls cause the wave packet to broaden and break up? (*Hint:* The collisions do not appear so disruptive when a Gaussian wave packet is confined within a harmonic oscillator potential well.)

30.6 EXPLORATION: 1-D HARMONIC OSCILLATOR

Modify the sample program to describe the motion of a Gaussian wave packet in the harmonic oscillator potential:

$$V(x) = \tfrac{1}{2}x^2 \quad (-\infty \le x \le \infty). \tag{30.15}$$

Take the initial momentum of the wave packet as $k_0 = 3\pi$ and the time and space steps as $\Delta x = 0.02$ and $\Delta t = \frac{1}{4}\Delta x^2$. Note that the wave packet appears to breathe, yet returns to it initial shape!

30.7 IMPLEMENTATION: WAVE PACKET IN HARMONIC WELL, HARMOS.F

30.8 PROBLEM: TWO-DIMENSIONAL CONFINEMENT

Consider now an electron moving in 2-D space as shown in Fig. 30.3. This adds another degree of freedom to the problem, which means that we must solve the 2-D time-dependent Schrödinger equation:

$$i\frac{\partial \psi(x,y,t)}{\partial t} = \tilde{H}\psi(x,y,t), \tag{30.16}$$

$$i\frac{\partial \psi(x,y,t)}{\partial t} = -\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2}\right) + V(x,y)\psi, \tag{30.17}$$

where we have chosen units in which $2m = \hbar = 1$. To be more specific, have the electron move in an infinitely long tube with a parabolic cross section:

$$V(x,y) = 0.9x^2, \quad (-9.0 \le x \le 9.0), \quad (0 \le y \le 18.0). \tag{30.18}$$

Assume that the electron's initial localization is described by a Gaussian wave packet in two dimensions:

$$\psi(x,y,t=0) = e^{ik_{0x}x}e^{ik_{0y}y}\exp\left[-\frac{(x-x_0)^2}{2\sigma_0^2}\right]\exp\left[-\frac{(y-y_0)^2}{2\sigma_0^2}\right]. \tag{30.19}$$

We show the tube potential and the wave packet in Fig. 30.3.

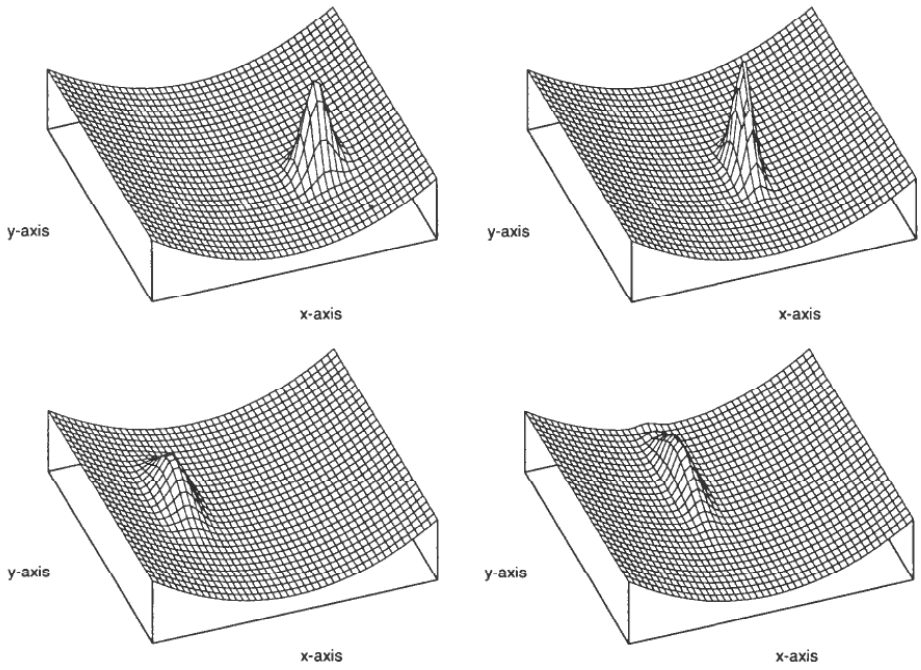

Fig. 30.3 The probability density as a function of x and y of an electron confined to a 2-D parabolic "tube." The electron's initial localization is described by a Gaussian wave packet in both the x and y directions. The times are 100, 300, 500, and 750.

30.9 METHOD: NUMERICAL

One way to develop an algorithm for solving the time-dependent Schrödinger equation in two dimensions is to extend the 1-D algorithm. Rather than do that, we apply quantum theory directly to obtain a more powerful algorithm. First we note that equation (30.17) can be integrated in a formal sense [L 96, p.4] to obtain the operator solution:

$$\psi(x,y,t) = U(t)\psi(x,y,t=0) = e^{-i\tilde{H}t}\psi(x,y,t=0). \tag{30.20}$$

From this formal solution we deduce that a wave packet can be moved ahead by a time Δt with the action of the time evolution operator:

$$\psi(t+\Delta t) = U(\Delta t)\psi(t), \tag{30.21}$$

$$U(\Delta t) = e^{-i\tilde{H}\Delta t}. \tag{30.22}$$

If the operator U were known exactly, it would provide the exact advance of the solution by one time step:

$$\psi_{i,j}^{n+1} = U(\Delta t)\psi_{i,j}^{n}, \tag{30.23}$$

where the superscripts denote time and the subscripts denote the two spatial variables,

$$\psi_{i,j}^{n} \stackrel{\text{def}}{=} \psi(i\Delta x, j\Delta y, n\Delta t). \tag{30.24}$$

Likewise, the inverse of the time evolution operator moves the solution back one time step:

$$\psi^{n-1} = U^{-1}(\Delta t)\psi^{n} = e^{+i\tilde{H}\Delta t}\psi^{n}. \tag{30.25}$$

While it would be nice to have an algorithm based on a direct application of (30.23), the references show that the resulting algorithm is not stable. That being so, we base our algorithm on an indirect application [Ask 77], namely, the relation between the difference in ψ^{n+1} (30.23) and ψ^{n-1} (30.25):

$$\psi^{n+1} = \psi^{n-1} + [e^{-i\tilde{H}\Delta t} - e^{i\tilde{H}\Delta t}]\psi^{n}, \tag{30.26}$$

where the difference in sign of the exponents is to be noted. The algorithm derives from combining the $O(\Delta x^2)$ expression for the second derivative obtained from the Taylor expansion,

$$\frac{\partial^2\psi}{\partial x^2} \simeq -\frac{1}{2}\left[\psi_{i+1,j}^{n} + \psi_{i-1,j}^{n} - 2\psi_{i,j}^{n}\right], \tag{30.27}$$

with the corresponding-order expansion of the evolution equation (30.26). When the resulting expression for the second derivative is substituted into

the 2-D time-dependent Schrödinger equation, there results[2]

$$\begin{aligned}\psi_{i,j}^{n+1} &= \psi_{i,j}^{n-1} - 2i\left[(4\alpha + \Delta t V_{i,j})\,\psi_{i,j}^{n}\right. \\ &\quad \left. -\alpha\left(\psi_{i+1,j}^{n} + \psi_{i-1,j}^{n} + \psi_{i,j+1}^{n} + \psi_{i,j-1}^{n}\right)\right], \qquad (30.28)\\ \alpha &= \frac{\Delta t}{2(\Delta x)^2}. \qquad (30.29)\end{aligned}$$

We convert these complex equations into coupled real equations by substituting the real and imaginary parts of the wave function, $\psi = R + iI$, into (30.28):

$$\begin{aligned}R_{i,j}^{n+1} &= R_{i,j}^{n-1} + 2\times \qquad (30.30)\\ &\quad \left[(4\alpha + \Delta t V_{i,j})\,I_{i,j}^{n} - \alpha\left(I_{i+1,j}^{n} + I_{i-1,j}^{n} + I_{i,j+1}^{n} + I_{i,j-1}^{n}\right)\right],\\ I_{i,j}^{n+1} &= I_{i,j}^{n-1} - 2\times \qquad (30.31)\\ &\quad \left[(4\alpha + \Delta t V_{i,j})\,R_{i,j}^{n} + \alpha\left(R_{i+1,j}^{n} + R_{i-1,j}^{n} + R_{i,j+1}^{n} + R_{i,j-1}^{n}\right)\right].\end{aligned}$$

This is the basic algorithm we use to integrate the 2-D Schrödinger equation. To determine the probability, we generalize [Viss 91] the expression used for one-dimension to:

$$\rho(t) = \begin{cases} R^2(t) + I(t + \frac{1}{2}\Delta t)I(t - \frac{1}{2}\Delta t), & \text{for integer time,} \\ R(t + \frac{1}{2}\Delta t)R(t - \frac{1}{2}\Delta t) + I^2(t), & \text{for half-integer time.} \end{cases} \qquad (30.32)$$

Although probability is not conserved exactly with this algorithm, the error is two orders higher than that in the wave function, and this is usually quite satisfactory. If it is not satisfactory, then we need to use smaller steps.

30.10 EXPLORATION: 2-D HARMONIC OSCILLATOR

Determine the motion of a 2-D Gaussian wave packet within the 2-D harmonic oscillator potential:

$$V(x,y) = 0.3(x^2 + y^2), \quad (-9.0 \le x \le 9.0), \quad (-9.0 \le y \le 9.0). \qquad (30.33)$$

Center the initial wave packet at $(x,y) = (3.0, -3)$ with momentum $(k_{0x}, k_{0y}) = (3.0, 1.5)$.

[2]For reference sake, note that the constants in the equation change as the dimension of the equation change; that is, there will be different constants for the 3-D equation, and therefore our constants are different from the references!

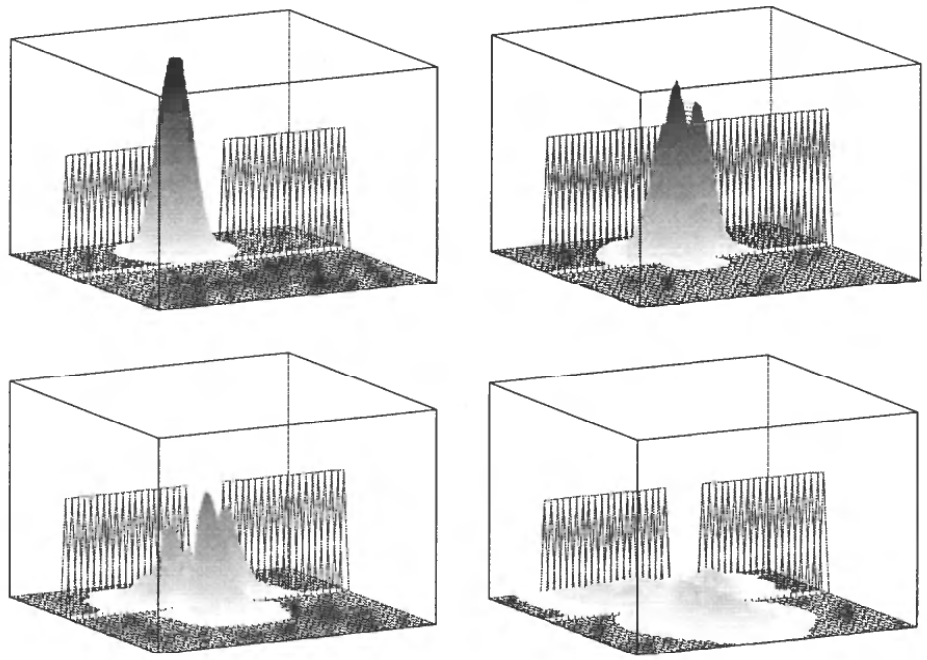

Fig. 30.4 The probability density as a function of position and time for an electron incident upon and passing through a slit.

30.11 EXPLORATION: SINGLE-SLIT DIFFRACTION, SLIT.F

Young's single-slit experiment has a wave passing through a small slit, which causes the emerging wavelets to interfere with each other. In quantum mechanics, where we represent a particle by a wave packet, this means that an interference pattern should be formed when a particle passes through a small slit. Consider a Gaussian wave packet of initial width 3 incident on a slit of width 5, as shown in Fig. 30.4.