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Chapter 2

Solutions to the One-Dimensional Schrödinger Equation

2.1 Separation of Variables

The solution of partial differential equations is notoriously difficult. When it can be applied, the method of *separation of variables* is effective. With this method a partial differential equation in n variables is reduced to n ordinary differential equations, for which there is a large literature on the methods of solution. We have already referred to this for the one-dimensional Schrödinger Equation. Let us now apply it a little more systematically.

We suppose that we can represent the function of two dimensions as a product of two one-dimensional functions:

$$\Psi(x,t) = \psi(x)f(t) \tag{2.1}$$

By direct substitution into the Schrödinger Equation :

$$-\frac{\hbar^2}{2m}f(t)\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)f(t) = i\hbar\psi(x)\frac{df}{dt} \tag{2.2}$$

Except for isolated points where one of the functions vanishes, we are free to divide through this equation by the product $\psi(x)f(t)$, to obtain:

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = i\hbar\frac{1}{f(t)}\frac{df}{dt} \tag{2.3}$$

The lhs depends only on x and the rhs depends only on t. Since these are independent variables, I can choose one of them to be anything I want without affecting the other. The only way the above equation can be consistent with this is for the lhs and the rhs to be constant, independent of x or t. Thus:

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+V(x)=E \tag{2.4}$$

$$i\hbar\frac{1}{f(t)}\frac{df}{dt}=E \tag{2.5}$$

where, by virtue of our discussion of operators, I have used E to represent the constant, since we have decided to interpret the lhs of the S.E. as the Hamiltonian, which in classical physics is the energy of a particle. Note that this separation depended on the fact that the potential was time independent.

Rewriting the equations as ordinary D.E.'s:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x) \tag{2.6}$$

$$\frac{df}{dt}=-i\frac{E}{\hbar}f(t) \tag{2.7}$$

The solution of the second equation is trivial:

$$f(t)=Ce^{-i\frac{E}{\hbar}t} \tag{2.8}$$

Since we must eventually normalize the entire wave-function $\psi(x)g(t)$, we might as well set $C=1$, and throw the overall normalization constant into the solution for ψ. Thus, we have:

$$\Psi(x,t)=\psi(x)e^{-i\frac{E}{\hbar}t} \tag{2.9}$$

As you might expect, solutions obtained by separation of variables are only a fraction (infinitesimal) of the totality of solutions. However, there are an infinite number of them, and it will be possible to construct an infinite variety of new solutions by linear combinations of the separated solutions.

2.1.1 Properties of the separated solutions

The separation constant, E, is real

Suppose the separation constant is complex, i.e.:

$$E=E_0+i\Gamma \tag{2.10}$$

The solution for f is:

$$f(t) = e^{-i\frac{E}{t\hbar}t} = e^{\frac{\Gamma}{\hbar}t}e^{-i\frac{E_0}{\hbar}t} \tag{2.11}$$

The probability distribution for this solution is:

$$P(x,t) = e^{\frac{2\Gamma}{\hbar}t}|\psi(x)|^2 \tag{2.12}$$

The probability integrated over all space is:

$$\int_{-\infty}^{\infty} P(x,t)\,dx = e^{\frac{2\Gamma}{\hbar}t}\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = Ce^{\frac{2\Gamma}{\hbar}t} \tag{2.13}$$

If we normalize the wave-function at $t = 0$, $C = 1$, and:

$$\int_{-\infty}^{\infty} P(x,t)\,dx = e^{\frac{2\Gamma}{\hbar}t} \tag{2.14}$$

The probability is not constant in time, unless $\Gamma = 0$. Unless the total probability of finding the particle anywhere in space changes with time, the separation constant E is real.

Separated solutions are stationary states

With E real, a separated solution represents a state with a stationary probability distribution, $P(x,t) = \psi(x)^*\psi(x) = P(x)$. For any dynamical variable constructed from coordinates and momenta:

$$\langle Q(x,p,t)\rangle = \int \Psi^* Q(x, \frac{\hbar}{i}\frac{\partial}{\partial x})\Psi\,dx = \int \psi^* Q(x, \frac{\hbar}{i}\frac{d}{dx})\psi\,dx = \langle Q\rangle \tag{2.15}$$

The expectation value is independent of time. It follows that the expectation value $\langle x\rangle$ for the position is constant, so $\langle p\rangle = 0$. Therefore, a separated state is called a *stationary state.*

The stationary state has a definite energy

Since in operator form, the separated Schrödinger Equation is:

$$\frac{p^2}{2m}\psi + V\psi = E\psi$$

It follows that:

$$E = \frac{\langle p^2\rangle}{2m} + \langle V\rangle \tag{2.16}$$

again verifying that E is the energy of the state associated with the separation constant, E.

Writing the equation for $\Psi(x,t)$ in terms of the Hamiltonian:

$$\mathcal{H}\Psi = \left[\frac{p^2}{2m} + V(x)\right]\Psi = E\Psi \tag{2.17}$$

it is obvious that:

$$\langle \mathcal{H} \rangle = \int \Psi^* \mathcal{H} \Psi dx = E \int \psi^* \psi \, dx = E \tag{2.18}$$

We can apply the Hamiltonian again to both sides of the S.E. to obtain:

$$\mathcal{H}\mathcal{H}\Psi = \mathcal{H}^2\Psi = E\mathcal{H}\Psi = E^2\Psi \tag{2.19}$$

From this it follows that:

$$\langle \mathcal{H}^2 \rangle = E^2 \tag{2.20}$$

so that:

$$\sigma^2_{\mathcal{H}} = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = 0 \tag{2.21}$$

A system in a stationary state has a definite energy, and a measurement of energy will always yield the value, E.

Wave function for stationary states can be chosen to be real

Our only requirement on $\psi(x)$ beyond that it satisfies the separated S.E. is that it be normalizable. In this section we show that We can always take it to be a real function if we want to. Suppose we happen to obtain a complex solution ψ, where the real and imaginary parts are linearly independent (a complex solution $A\psi(x)$ where $\psi(x)$ is real but A is complex is not of interest). Writing $\psi = \psi_r + i\psi_i$ substituting in the the Schrödinger Equation , it is easy to show that ψ_r and ψ_i separately satisfy the Schrödinger Equation . This follows from the reality of the operators in the Schrödinger Equation . The complex solution really consists of two independent real solutions for the same choice of E. This proves that we can always choose the stationary wave-functions to be a real linear combination of the two independent solutions. For a real wave-function:

$$P(x,t) = \psi(x)^2 \tag{2.22}$$

This doesn't mean that we will always use the real form.

Parity of the stationary states for symmetric potentials

Another useful property of stationary solutions is obtained when the potential is an even function of x, i.e. $V(x) = V(-x)$. If we change variables x to $-x$ in the separated Schrödinger Equation :

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(-x)}{dx^2} + V(-x)\psi(-x) = E\psi(-x) \tag{2.23}$$

Using the fact that V is even:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(-x)}{dx^2} + V(x)\psi(-x) = E\psi(-x) \tag{2.24}$$

so it follows that for such potentials, if $\psi(x)$ is a solution then so is $\psi(-x)$. If the solution $\psi(x)$, that we obtained has no particular symmetry around $x = 0$ then $\psi(-x) \neq \psi(x)$, i.e. by changing x to $-x$ we obtain a second independent solution. We can now combine those linearly to obtain two new functions:

$$\psi_1(x) = \psi(x) + \psi(-x), \qquad \psi_2(x) = \psi(x) - \psi(-x) \tag{2.25}$$

Clearly, ψ_1 is an even function and ψ_2 is an odd function of x. Thus, it follows that when V is an even function of x, the stationary solution can always be taken as even or odd. This property is called parity. Even functions have parity of 1, and odd functions have parity of -1. Classifying wave-functions in this way is frequently very useful. It is apparent that choosing your coordinate system to match the symmetry of the potential is a wise idea.

Orthogonality of the Stationary State Solutions

There is another important property of the stationary solutions. Consider the equations for two different energies:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_i}{dx^2} + V(x)\psi_i = E_i\psi_i \tag{2.26}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_j^*}{dx^2} + V(x)\psi_j^* = E_j\psi_j^* \tag{2.27}$$

Multiplying the first by ψ_j^* and the second by ψ_i and subtracting the two equations, we get:

$$-\frac{\hbar^2}{2m}\left[\psi_j^*\frac{d^2\psi_i}{dx^2} - \psi_i\frac{d^2\psi_j^*}{dx^2}\right] = (E_i - E_j)\psi_j^*\psi_i \tag{2.28}$$

We can rewrite the lhs as:

$$-\frac{\hbar^2}{2m}\frac{d}{dx}\left[\psi_j^*\frac{d\psi_i}{dx}-\psi_i\frac{d\psi_j^*}{dx}\right]=(E_i-E_j)\psi_j^*\psi_i \tag{2.29}$$

Integrating over all space:

$$-\frac{\hbar^2}{2m}\left[\psi_j^*\frac{d\psi_i}{dx}-\psi_i\frac{d\psi_j^*}{dx}\right]_{-\infty}^{\infty}=(E_i-E_j)\int_{-\infty}^{\infty}\psi_j^*\psi_i\,dx \tag{2.30}$$

Since we assume that our wave-functions are normalizable they must vanish at infinity, so the lhs vanishes:

$$0=(E_i-E_j)\int_{-\infty}^{\infty}\psi_j^*\psi_i\,dx \tag{2.31}$$

If E_i and E_j are different energies, it follows that:

$$\int_{-\infty}^{\infty}\psi_j^*(x)\psi_i(x)\,dx=0 \tag{2.32}$$

Functions satisfying this condition are *orthogonal.* We can combine this result with the normalization requirement to write:

$$\int_{-\infty}^{\infty}\psi_j^*(x)\psi_i(x)\,dx=\delta_{ij} \tag{2.33}$$

where δ_{ij} is the Kronecker delta symbol.

For a given E the second order differential equation for $\psi(x)$ has two independent solutions. With more degrees of freedom (e.g. a particle in three dimensions, multiple particles, particles with spin) there can be even more wave-functions with the same energy. In quantum mechanics independent solutions with the same energy are said to be *degenerate.* The above argument tells us nothing about the orthogonality of degenerate solutions.

In one dimension, if V is an even function, we can take the solutions to be even and odd, which are necessarily orthogonal. This procedure won't help us when $V(x)$ has no special symmetry. The following argument is more complicated than necessary for the one dimensional problem, but it has the advantage that it is easily generalized to more complicated situations. Suppose $\psi_a(x)$ and $\psi_b(x)$ are two independent normalizable but non-orthogonal solutions for the same energy. If one of the solutions is not normalizable, we would have to discard it as unphysical and this would remove the degeneracy for the energy, E. If neither solution is normalizable, then E is not a physically possible value of the energy. Now let us assume that both solutions are physical and normalized. Since linear combinations of the two solutions are also solutions, we are free to let $\psi_1 = \psi_a$ be taken as one solution. We can construct a second orthogonal solution as follows:

$$\psi_2 = A(c\psi_a + \psi_b) \tag{2.34}$$

where A and c are constants. We shall see that c can be chosen to orthogonalize ψ_1 and ψ_2 and A can be chosen to normalize ψ_2. For orthogonality, we require that:

$$0 = \int \psi_1^* \psi_2 \, dx = A\left(c\int \psi_a^*\psi_a \, dx + \int \psi_a^*\psi_b \, dx\right) = A\left(c + \int \psi_a^*\psi_b \, dx\right) \tag{2.35}$$

The orthogonality condition is satisfied by choosing:

$$c = -\int \psi_a^*\psi_b \, dx \tag{2.36}$$

If we choose the stationary state wave-functions to be real, then c is real. To normalize ψ_2:

$$\begin{aligned} \int \psi_2^*\psi_2 \, dx &= |A|^2 \int [c^*\psi_a^* + \psi_b^*][c\psi_a + \psi_b] \, dx \\ &= |A|^2 \left[|c|^2 + 1 + c^*\int \psi_a^*\psi_b \, dx + c\int \psi_b^*\psi_a \, dx\right] \\ &= |A|^2 \left[|c|^2 + 1 - 2|c|^2\right] = |A|^2(1 - |c|^2) \end{aligned} \tag{2.37}$$

Since $\int |\psi_2|^2 \, dx \geq 0$, $|c| \leq 1$. Moreover, $|c| \neq 1$. Proof: Suppose $|c| = 1$, Then $\int |\psi_2|^2 \, dx = 0$. Since $|\psi_2|^2 \geq 0$, the integral can vanish only if $\psi_2 \equiv 0$. In that case $c\psi_a + \psi_b = 0$ so that ψ_a and ψ_b would not be linearly independent, contrary to our original assumption.

We are free to choose A to be real, obtaining:

$$A = \frac{1}{\sqrt{1 - |c|^2}} \tag{2.38}$$

We have demonstrated that all normalizable stationary state solutions can be chosen to be orthogonal and normalized.

2.1.2 Linear Combinations of Separated Solutions

Since the time dependent Schrödinger Equation is homogeneous, arbitrary linear combinations of the stationary state solutions (with their time dependent factor included) are also solutions. Suppose we label the stationary state solutions with a counting index n, writing the solution as $\psi_n(x)e^{-iE_nt}$. Then the linear combination:

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-i\frac{E_n}{\hbar}t} \tag{2.39}$$

where c_n can be any complex number, is also a solution. It can be shown that the stationary state solutions of the Schrödinger Equation form a *complete set* of functions, which means that any solution can be expressed as a linear sum of the stationary state solutions.

Normalization of the Linear Combination

The constants used in constructing a wave-function as a linear sum of stationary state solutions are subject to the normalization requirement:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = 1 \tag{2.40}$$

The normalization condition can be carried out at $t = 0$, giving us:

$$1 = \sum_i \sum_j \int_{-\infty}^{\infty} c_i^* c_j \psi_i^*(x) \psi_j(x) \, dx = \sum_i \sum_j c_i^* c_j \int_{-\infty}^{\infty} \psi_i^*(x)\psi_j(x) \, dx \tag{2.41}$$

This doubly infinite sum looks pretty messy, but if we remember that the states are orthogonal, the normalization condition has the simple form:

$$1 = \sum_i \sum_j c_i^* c_j \delta_{ij} = \sum_i |c_i|^2 \tag{2.42}$$

Example:

Suppose we make a combination that is 60% state 1, 30% state 2 and 10% state 3:

$$\Psi(x,t) = c(.6\psi_1 e^{-i\frac{E_1}{\hbar}t} + 0.3\psi_2 e^{-i\frac{E_2}{\hbar}t} + 0.1\psi_3 e^{-i\frac{E_3}{\hbar}t})$$

Here, $c_1 = c, \ c_2 = 0.5c, \ c_3 = 0.1c$. The normalization condition is:

$$1 = |c|^2(.36 + .09 + 0.01) = 0.46|c|^2$$

$$|c|^2 = \frac{1}{0.46} = 0.2.174, \qquad c = 1.474$$

$$\Psi(x,t) = .885\psi_1 e^{-i\frac{E_1}{\hbar}t} + 0.442\psi_2 e^{-i\frac{E_2}{\hbar}t} + 0.147\psi_3 e^{-i\frac{E_3}{\hbar}t})$$

Expectation values for a linear combination

Write the linear combination as:

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-i\frac{E_n}{\hbar}t} = \sum_n \alpha_n(t)\psi_n(x) \tag{2.43}$$

where the quantity:

$$\alpha_i \equiv c_n e^{-i\frac{E_n}{\hbar}t}$$

does not depend on x. The expectation value of any physical operator $\mathcal{O}(\S, \surd)$ is:

$$\langle \mathcal{O} \rangle = \int \left(\sum_i \alpha_i^* \psi_i \right) \left(\mathcal{O} \sum_j \alpha_j \psi \right) dx = \sum_{ij} \alpha_i^* \alpha_j \int \psi_i \mathcal{O} \psi_j \, dx \tag{2.44}$$

Suppose we replace $\mathcal{O}$ with the energy operator, $E = p^2/2m + V$. From the separated Schrödinger Equation itself:

$$\left(p^2/2m + V \right) \psi_i = E_i \psi_i$$

so by substitution into Eq. 2.44

$$\langle E \rangle = \sum_{ij} \alpha_i^* \alpha_j \int \psi_i E_j \psi_j \, dx \sum_{ij} \alpha_i^* \alpha_j E_j \int \psi_i \psi_j \, dx = \sum_{ij} \alpha_i^* \alpha_j E \delta_{ij} = \sum_i |\alpha_i|^2 E_i$$

$$\langle E \rangle = \sum_i |c_i|^2 E_i \tag{2.45}$$

You are asked in one of the problems to explain why a measurement of the energy of system described as a mixture of stationary states must yield one of the stationary state energies. Since this is true, we write:

$$\langle E \rangle = \sum_i P_i E_i$$

where $P_i = |c_i|^2$ is evidently the probability of measuring the energy E_i. The probabilities add to 1, $\sum_i P_i = 1$. Using the previous example for a linear combination, the probabilities for measuring E_1, E_2 and E_3 are .783, 0.195 and 0.022. Although 10% of the wave function is made of the the third state, there is only a 2% chance of measuring the energy associated with the third state.

As another useful exercise, you can try calculating the general form for the expectation values, $\langle x \rangle$ and $\langle p \rangle$.

2.2 The Infinite Square Well

Perhaps the simplest approximation (or model) to a binding potential is the infinite square well. In this potential the particle is bounded between two hard walls, and is otherwise free inside. A particle near the bottom of a deep physically real potential will not behave very differently from one in an infinitely deep well. The potential is given by:

$$V(x) = \begin{cases} 0 & \text{if } -\frac{a}{2} \leq x \leq \frac{a}{2}; \\ \infty & \text{otherwise.} \end{cases} \tag{2.46}$$

Classically, a particle would bounce back and forth, reflecting elastically off the walls. For the S.E. we require that the wave function be 0 in the region of infinite potential. We require that the wave function be everywhere continuous. If the function were not continuous it would not be possible to assign a unique probability distribution to the point of discontinuity. The continuity requirement means that the solutions must vanish at the walls of the potential ($x = \pm a/2$). The infinite potential well is therefore a problem of a free particle subject to a boundary condition. The boundary condition has a profound effect on the solution.

Solutions that satisfy boundary conditions

Inside the well:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{2.47}$$

Defining $k^2 = \frac{2mE}{\hbar^2}$:

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \tag{2.48}$$

We must distinguish the solutions for $k = 0$ from those for $k^2 > 0$. For both cases, the equation has two independent solutions:

$$\psi = \begin{cases} c_1 \cos(kx) + c_2 \sin(kx) & \text{if } k^2 > 0; \\ c_1 + c_2 x & \text{if } k = 0. \end{cases} \tag{2.49}$$

The condition that the wave function vanish at $x = \pm a/2$ rules out $k = 0$, since the corresponding solution is a straight line. For $k \neq 0$, the boundary conditions are satisfied by:

$$0 = \begin{cases} c_1 \cos(ka/2) - c_2 \sin(ka/2) & ; \\ c_1 \cos(ka/2) + c_2 \sin(ka/2) & . \end{cases} \tag{2.50}$$

Solving for c_1 and c_2:

$$c_1 \cos(ka/2) = 0 \qquad c_2 \sin(ka/2) = 0 \tag{2.51}$$

Either the coefficients are 0 or the trig functions are 0. To obtain non-zero coefficients only special discrete values of k are possible. If:

$$ka/2 = \pi/2, 3\pi/2, \cdots \tag{2.52}$$

then c_1 can be anything while $c_2 = 0$. If:

$$ka/2 = \pi, 2\pi, 3\pi, \cdots \tag{2.53}$$

then c_2 can be anything and $c_1 = 0$. For any other choice of k there is no solution.

Thus the solutions are:

$$\psi = \begin{cases} c_1 \cos(n\pi x/a), & \text{for } n = 1, 3, 5, \cdots; \\ c_2 \sin(n\pi x/a), & \text{for } \; n = 2, 4, 6, \cdots. \end{cases} \tag{2.54}$$

For both sets, $k = n\pi/a$. As advertised, we were able to express the separated solutions as real functions.

Normalization of the solutions

The stationary state wave functions are easily normalized.

For odd n:

$$\int_{-\infty}^{\infty} \psi_n^* \psi_n \, dx = \int_{-a/2}^{a/2} \cos^2(n\pi x/a) \, dx = \frac{1}{2} \int_{-a/2}^{a/2} \left(1 + \cos(2n\pi x/a)\right) \, dx = \frac{a}{2} \tag{2.55}$$

For even n:

$$\int_{-a/2}^{a/2} \sin^2(n\pi x/a) \, dx = \frac{1}{2} \int_{-a/2}^{a/2} \left(1 - \sin(2n\pi x/a)\right) \, dx = \frac{a}{2} \tag{2.56}$$

so that the sine and cosine solutions have the same normalization constant, namely $\sqrt{2/a}$. The normalized stationary state wave functions are:

$$\psi = \begin{cases} \sqrt{\frac{2}{a}} \cos(n\pi x/a), & \text{for } n = 1, 3, 5, \cdots; \\ \sqrt{\frac{2}{a}} \sin(n\pi x/a), & \text{for } \; n = 2, 4, 6, \cdots. \end{cases} \tag{2.57}$$

Explicit Demonstration of Orthogonality

Consider the functions $\sin(n\pi x/a)$ and $\cos(m\pi x/a)$, for which n is even and m is odd:

$$\int_{-a/2}^{a/2} \sin(n\pi x/a)\cos(m\pi x/a)\,dx = \frac{1}{2}\int_{-a/2}^{a/2} \left[\sin\left((n+m)\pi x/a\right) + \sin\left((n-m)\pi x/a\right)\right] dx$$

$$= -\frac{1}{2}\left[\frac{\cos\left((n+m)\pi x/a\right)}{(n+m)\pi/a} + \frac{\cos\left((n-m)\pi x/a\right)}{(n-m)\pi/a}\right]_{-a/2}^{a/2} = 0$$

Next consider two different even functions, $\sin(n\pi x/a)$ and $\sin(m\pi x/a)$, $n \neq m$. For this case $n-m$ and $n+m$ are even integers. Then:

$$\int_{-a/2}^{a/2} \sin(n\pi x/a)\sin(m\pi x/a)\,dx = \frac{1}{2}\int_{-a/2}^{a/2} \left[\cos\left((n-m)\pi x/a\right) - \cos\left((n+m)\pi x/a\right)\right] dx$$

$$= \frac{1}{2}\left[\frac{\sin\left((n-m)\pi x/a\right)}{(n-m)\pi/a} - \frac{\sin\left((n+m)\pi x/a\right)}{(n+m)\pi/a}\right]_{-a/2}^{a/2}$$

$$= \frac{1}{2}\left[\frac{2\sin\left((n-m)\pi/2\right)}{(n-m)\pi/a} - \frac{2\sin\left((n+m)\pi/2\right)}{(n+m)\pi/a}\right]$$

Since both $n-m$ and $n+m$ are even non-zero integers, this is zero. The same method can be used to show that the cosine functions are orthogonal to each other.

Allowed energies

Although there are an infinite number of solutions, the possible values of k are limited to discrete values:

$$k = k_n = \frac{n\pi}{a}, \qquad n = 1, 2, \cdots \tag{2.58}$$

Since k is defined in terms of the energy, it follows that only discrete values of energy are possible:

$$E = E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2\pi^2}{2ma^2}n^2, \qquad n = 1, 2, \cdots \tag{2.59}$$

In the above derivation we noted that $k = 0$ is not allowed. The particle cannot exist inside the infinite well with 0 energy.

Note that the wave function for the lowest energy state, or ground-state, $n = 1$, has no zeros (not counting the boundary points). The $n = 2$ state has one zero, at the center of the well, the $n = 3$ state has two zeros, and so on. This is characteristic of quantum states. The smoother the wave function the lower the energy. We can understand this by recalling that the kinetic energy is $p^2/2m$, and that p is the derivative operator. The more wiggles in the wave function, the larger the value of $\langle p^2 \rangle$.

By choosing the coordinate system to take advantage of the symmetry of the potential, the solutions automatically have well-defined parity. Solutions corresponding to E_n with n odd have even parity, and solutions with n even have odd parity. Finally, there is only one solution for each possible energy. The stationary states are not degenerate.

General solution as a linear sum of stationary states

A completely general solution can be formed from the linear combination:

$$\Psi(x,t) = \sum_{n=1}^{\infty} a_n \sin(2n\pi x/a) e^{-i(E_n/\hbar)t} + \sum_{m=1}^{\infty} b_m \cos((2m+1)\pi x/a) e^{-i(E_m/\hbar)t} \tag{2.60}$$

At any given time this is the Fourier expansion of a function in the interval $-a/2 \leq x \leq a/2$. In the theory of Fourier analysis, it is proved that all well-behaved functions, with a period of a can be represented by such a series. Since every term in the series vanishes at $x = \pm a/2$, the class of functions that can be represented in this way is limited to functions which satisfy the infinite well B.C. If the wave-function is known to have even parity, the infinite series will contain only the cosine terms. If the wave-function is known to be odd, the series will contain only the sine terms.

Effect of shifting the origin of x

Griffiths solves the problem by shifting the origin so that the walls are at $x = 0$ and $x = a$. This simplifies the algebra to some extent. This shift corresponds to defining a new coordinate, $x' = x + a/2$, or $x = x' - a/2$. We could express the preceding solutions in terms of x', and obtain Griffith's results. We can simply note, however, that the solutions are still sines and cosines. Since $\cos(0) = 1$, and $\sin(0) = 0$ only sine functions are allowed. The stationary states are now expressed more compactly as:

$$\psi_n = \sqrt{\frac{2}{a}} \sin(n\pi x/a), \qquad n = 1, 2, 3 \cdots \tag{2.61}$$

and the allowed energies are still the same:

$$E_n = \frac{\hbar^2\pi^2}{2ma^2}n^2, \qquad n = 1, 2, \cdots \tag{2.62}$$

Relative to $x = a/2$, the parity of the functions alternate in n. A general solution is given by:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i\frac{E_n}{\hbar}t} \tag{2.63}$$

Provided we know Ψ at $t = 0$, the coefficients c_n are easily obtained, using what Griffiths calls Fourier's trick. Multiply both sides by one of the states, ψ_j and integrate over x, obtaining:

$$\int_0^a \Psi(x,0)\psi_j(x)\,dx = \sum_n c_n \int_0^a \psi_j(x)\psi_n(x)\,dx = \sum_n c_n \delta_{nj} = c_j \tag{2.64}$$

$$c_j = \sqrt{\frac{2}{a}} \int_0^a \Psi(x,0)\sin(j\pi x/a)\,dx \tag{2.65}$$

The proof that any function satisfying the boundary conditions can be represented by such a series is carried out in the theory of Fourier analysis. The property is called *completeness* of the set of functions. If the state $\Psi(x,t)$ is normalized then the coefficients will satisfy the condition:

$$\sum_{n=1}^{\infty} |c_n|^2 = 1 \tag{2.66}$$

2.2.1 Example

Here is an example that doesn't quite satisfy the B.C. Suppose we start with an initial wave function that gives a uniform probability:

$$\Psi(x,0) = \frac{1}{\sqrt{a}} \tag{2.67}$$

so that:

$$P(x,0) = \frac{1}{a}, \qquad \int_0^a P(x,0)\,dx = 1$$

A major defect in the function is that because of the singularities at the end points the expectation values of momentum and energy are undefined.

Nevertheless, we can forge ahead and use Eq. 2.65 to calculate the Fourier coefficients:

$$c_n = \frac{1}{\sqrt{a}}\sqrt{\frac{2}{a}}\int_0^a \sin(n\pi x/a)\,dx \tag{2.68}$$

$$c_n = \frac{\sqrt{2}}{a}\int_0^a \sin(n\pi x/a)\,dx = -\frac{\sqrt{2}}{a}\frac{a}{n\pi}\left[\cos(n\pi x/a)\right]_0^a \tag{2.69}$$

$$c_n = \frac{\sqrt{2}}{n\pi}[1-\cos(n\pi)] = \frac{\sqrt{2}}{n\pi}[1-(-1)^n] \tag{2.70}$$

The coefficients vanish for even values of n. We expect this since the wavefunction has even parity around $x = a/2$. For odd values,

$$c_n = \frac{2\sqrt{2}}{\pi n} \tag{2.71}$$

(a side remark: the relation, $\sum |c_n|^2 = 1$, tells us that $\sum \frac{1}{n^2} = \frac{\pi^2}{8}$) The coefficients decrease very slowly, $c_{n+1}/c_n = n/(n+1)$, so it takes many terms to get a decent representation of this wave function. Moreover, the series can never get things quite right at $x = 0$ and $x = a$. These are singular points, and excluded from the Fourier statement of completeness. The wave function can be written as:

$$\Psi(x,t) = \frac{2\sqrt{2}}{\pi}\frac{\sqrt{2}}{a}\sum_{n\ \mathrm{odd}}\frac{1}{n}\sin(\frac{n\pi x}{a})e^{-\frac{E_n t}{\hbar}} = \frac{4}{\pi a}\sum_{n\ \mathrm{odd}}\frac{1}{n}\sin(\frac{n\pi x}{a})e^{-\frac{E_n t}{\hbar}} \tag{2.72}$$

Using the general result of Eq. 2.45 the expectation value of the energy is:

$$\langle E\rangle = \sum |c_n|^2 E_n$$

Using our results for c_n and the energies of the square well:

$$|c_n|^2 E_n = \frac{8}{\pi^2 n^2}\frac{\hbar^2\pi^2 n^2}{2ma^2} = \frac{4\hbar^2}{ma^2}$$

$$\langle E\rangle = \frac{4N\hbar^2}{ma^2} \tag{2.73}$$

where N is the number of terms in the sum. The more terms we include the higher the expectation value of the energy. We must cut off the infinite sum to avoid having an infinite energy. For an electron in a space of atomic dimensions, $a = 10^{-10}$ m, for 64 terms $E \approx 2000$ eV. For comparison, the binding energy of the hydrogen atom is only 13 eV and the electron's kinetic energy is comparable to the binding energy.

Plots of the probability distributions for summations over 2, 4, 8, 16, 32, and 64 terms are shown in Figures 2.1 and 2.2. The horizontal scale is in units of u=x/a and the vertical scale shows $P(u) = |\psi(u)|^2 = aP(x)$. If we choose the expansion with 64 terms as the exact initial state wave function, the time development of the probability distribution is illustrated in Figures 2.3 and 2.4. In these figures the unit of time is:

$$\Delta t = \frac{2ma^2}{\pi^2\hbar} \tag{2.74}$$

For an electron in a well of atomic size, $a = 10^{-10}$ m, $\Delta t \approx 1.6 \times 10^{-17}$ s.

From these figures one might infer that after the initial time the electron tends to avoid the edge regions. One can see the onset of this tendency by looking at even earlier times, as shown in Figures 2.5 and 2.6

A physically acceptable approximation to the square function might be:

$$\Psi(x,0) = N(1 - e^{-\alpha x})(1 - e^{\alpha(x-a)})$$

in the limit $\alpha a >> 1$. Oddly enough, this function can be normalized, and expectation values of x, p and p^2 can be calculated, in terms of elementary integrals. Moreover, the coefficients of the Fourier expansion can also be obtained in terms of elementary integrals. The integrals are elementary, but numerous.

2.3 The Harmonic Oscillator

The harmonic oscillator potential is one of the most important problems in physics. This is not simply because it is soluble in terms of familiar functions with simple properties, but also because it is usually the first approximation when a particle is bound to a finite region in space. In the neighborhood of a potential minimum, an analytic potential can be represented by a Taylor series:

$$V(x) = V(x_0) + \left[\frac{dV}{dx}\right]_{x_0}(x - x_0) + \frac{1}{2}\left[\frac{d^2V}{dx^2}\right]_{x_0}(x - x_0)^2 + \cdots \tag{2.75}$$

If x_0 is a point where the potential is minimum, then the second term vanishes. Since a potential is always arbitrary within a constant, we can ignore the first term. If we denote the value of the second derivative at $x = x_0$ by the symbol k:

$$V(x) = \frac{1}{2}k(x - x_0)^2 + c_2(x - x_0)^3 + \tag{2.76}$$

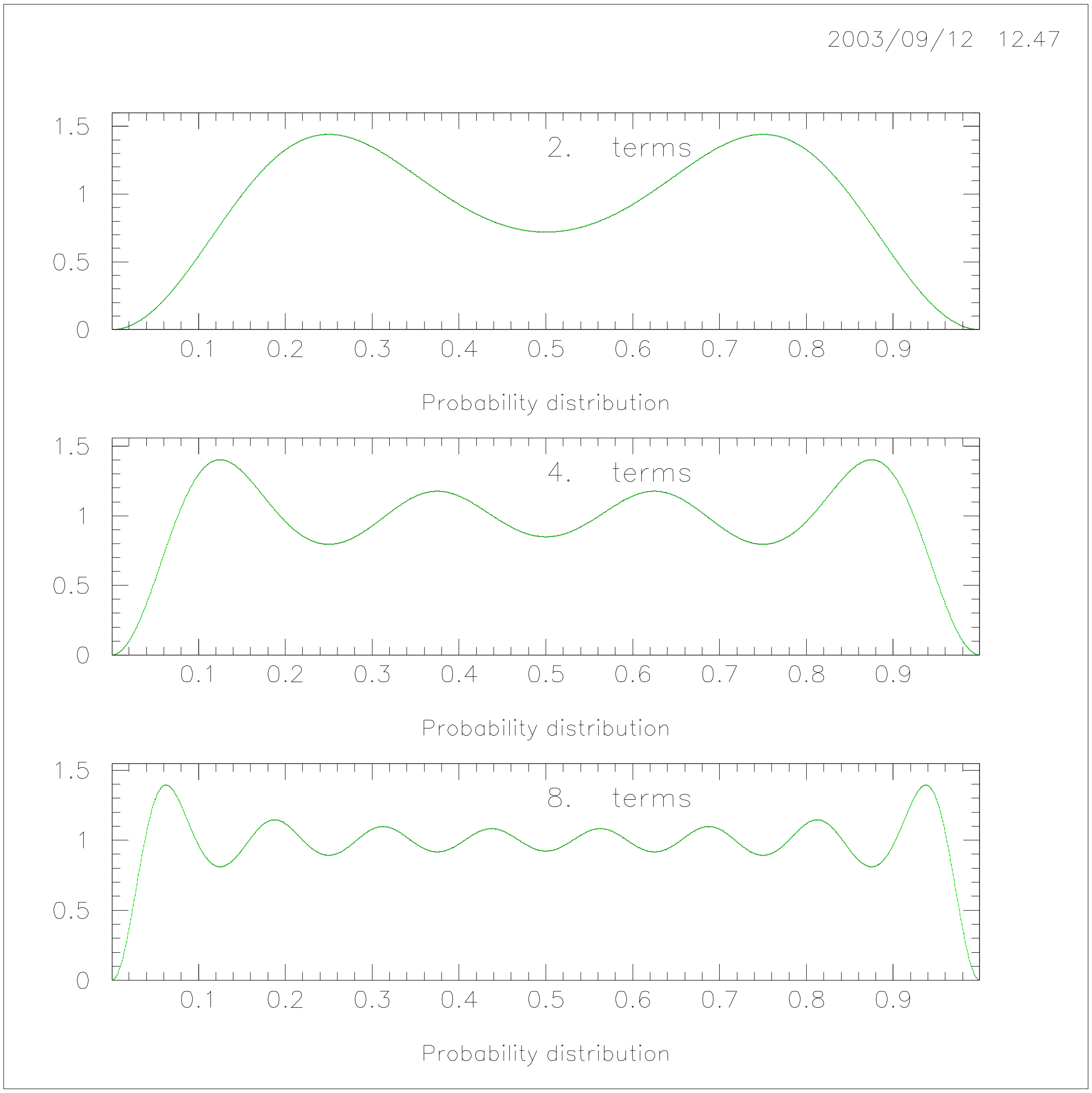

Figure 2.1: Approximation to a square wave for 2, 4 and 8 terms.

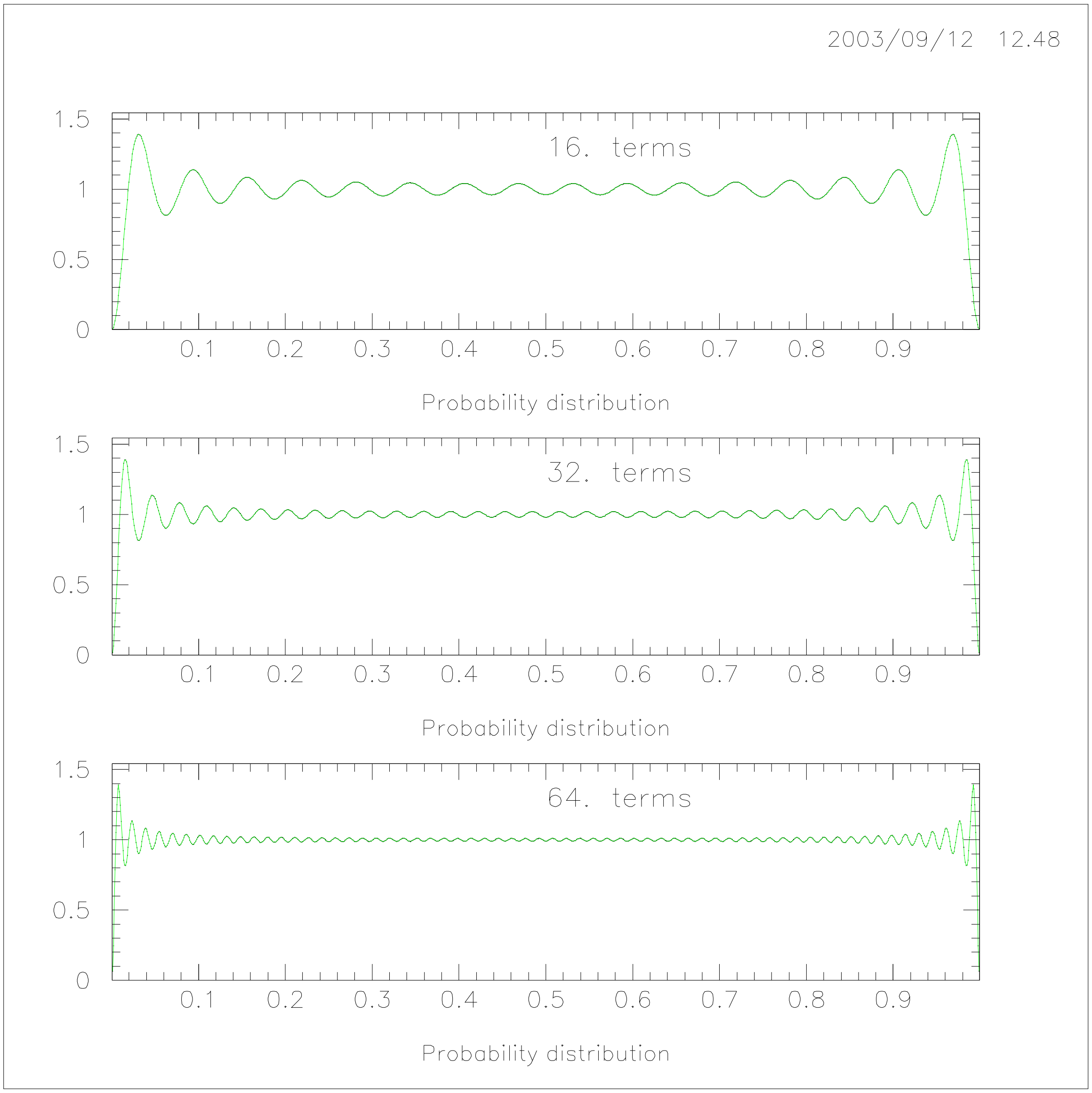

Figure 2.2: Approximation to a square wave for 16, 32 and 64 terms.

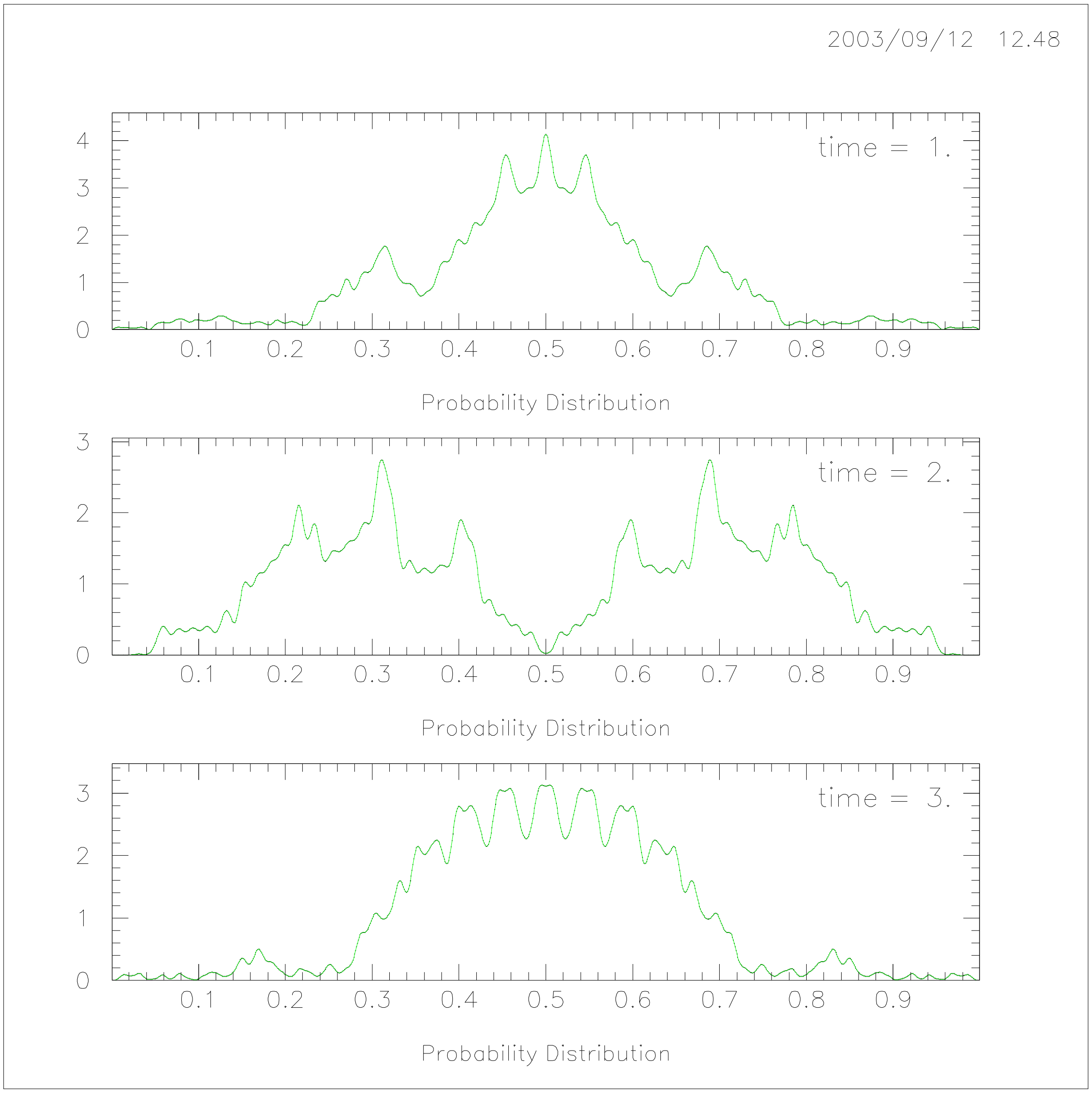

Figure 2.3: Time development for the 64 term solution, t=1,2, 3 in units of $\frac{2ma^2}{\pi^2\hbar}$

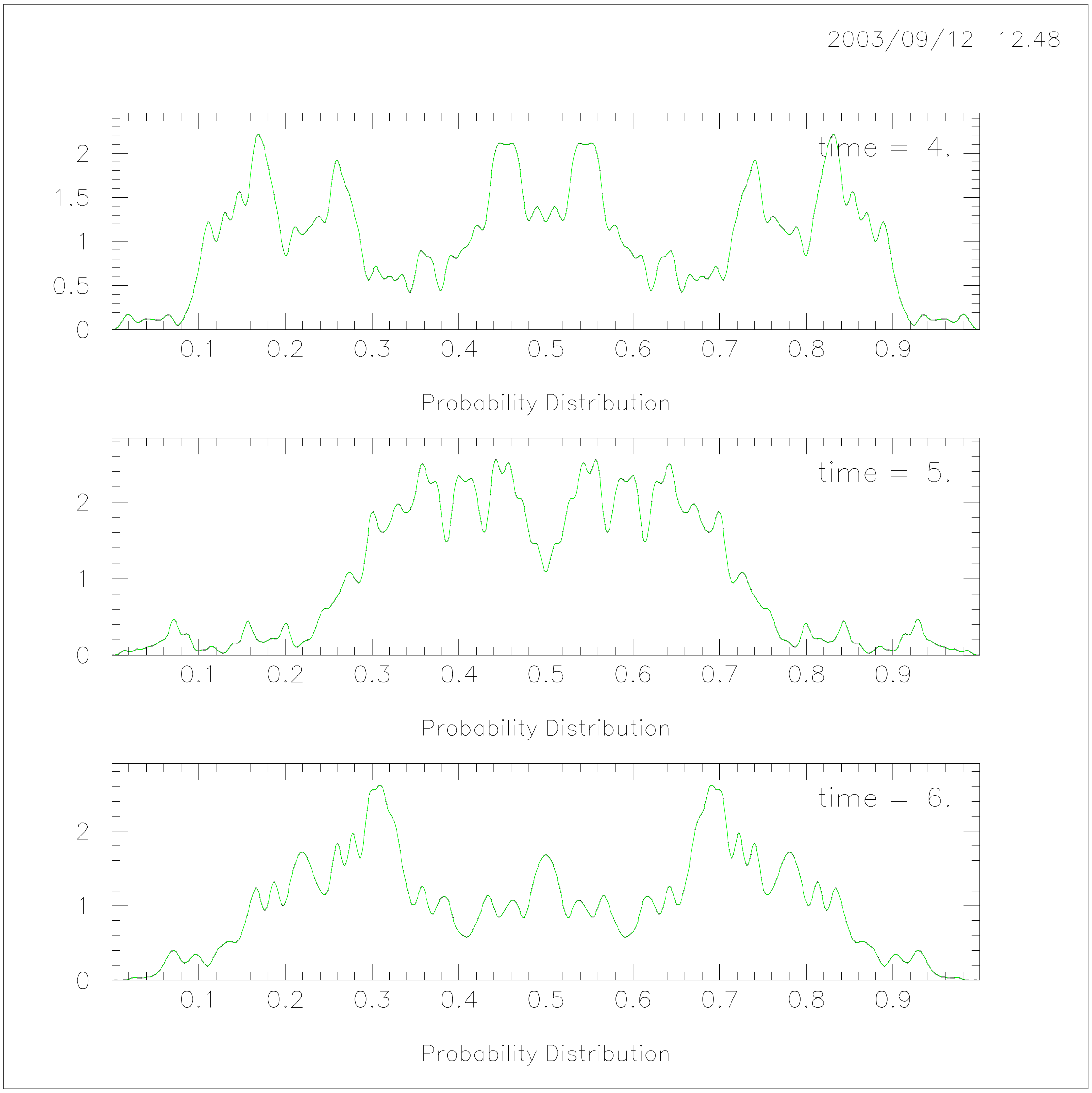

Figure 2.4: Time development for the 64 term solution, t=4,5, 6 in units of $\frac{2ma^2}{\pi^2\hbar}$

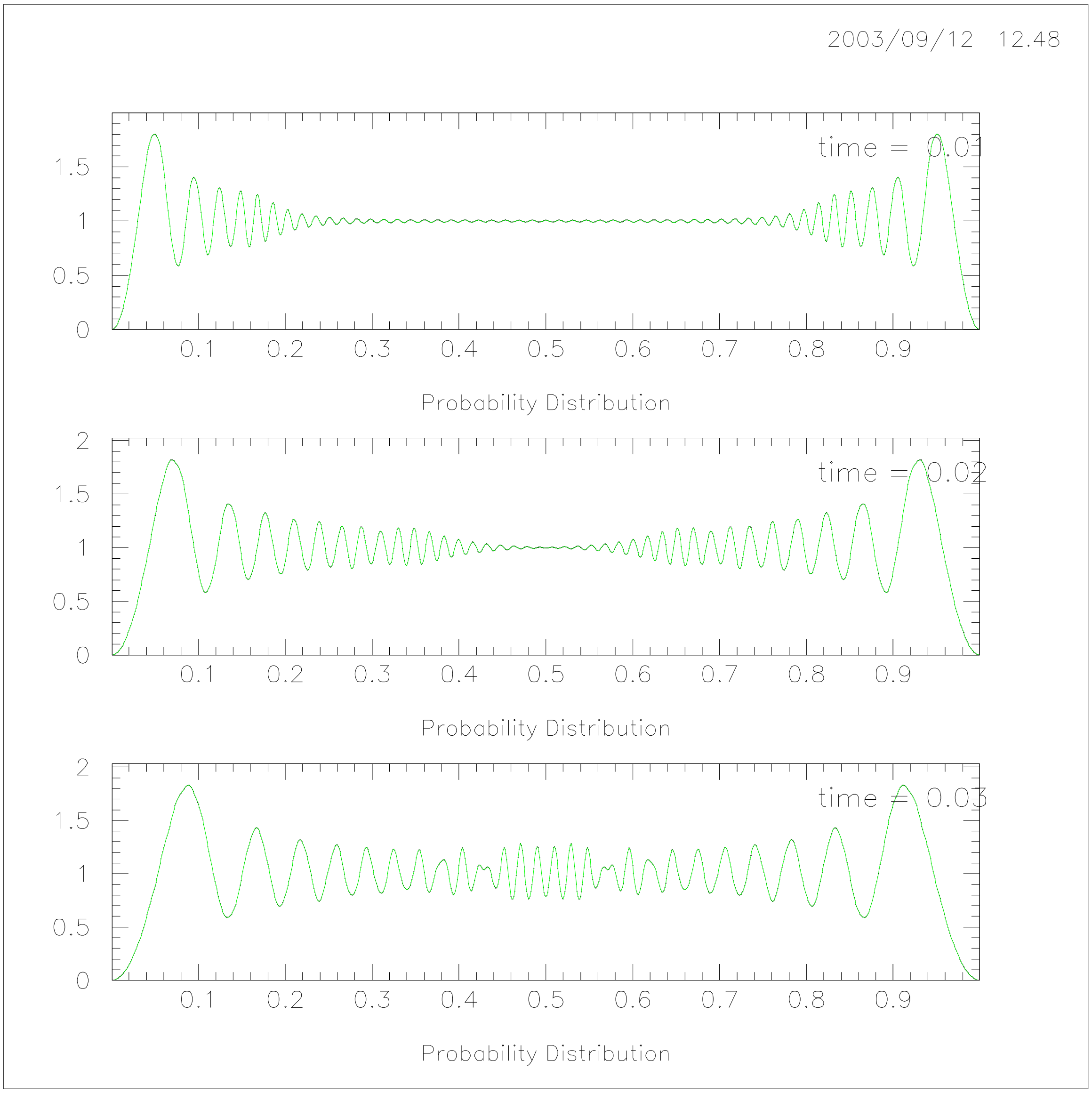

Figure 2.5: Early time development for the 64 term solution, t=.01,.02, .03 in units of $\frac{2ma^2}{\pi^2\hbar}$

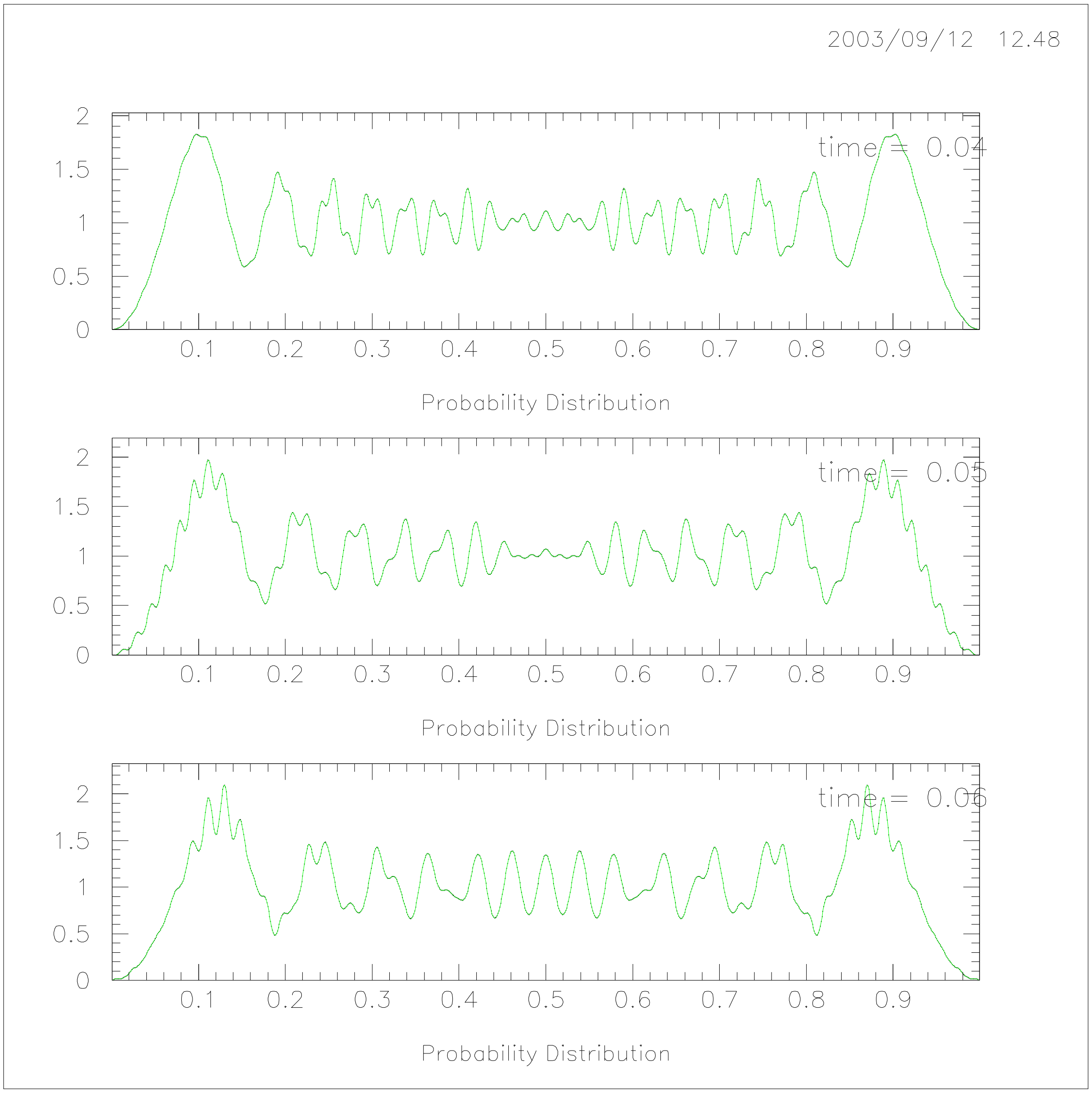

Figure 2.6: Early time development for the 64 term solution, t=.04,.05, .06 in units of $\frac{2ma^2}{\pi^2\hbar}$

Unless the second derivative is 0, there is always some region in the neighborhood of x_0 in which the harmonic oscillator terms dominates the rest of the terms in the series. The infinite square well is an example of a potential that does not meet this requirement. Practically any real potential will satisfy it. In classical mechanics this feature motivates the study of *small motions*, i.e. the behavior of systems where the amplitude of motion about an equilibrium point is small enough that the higher order terms in the Taylor expansion can be ignored.

The separated S.E. that accompanies this potential is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+\frac{1}{2}kx^2\psi(x)=E\psi(x) \tag{2.77}$$

Since the potential rises to infinity for both positive and negative values of x, all the states of a particle will be bound states. Moreover, since $V_{min}=0$, the energies $E>0$.

Just as for the classical oscillator it is convenient to define a constant ω such that $k=m\omega^2$. In classical mechanics ω is the angular frequency of the oscillator:

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}-\frac{m\omega^2}{2}x^2\psi(x)+E\psi(x)=0 \tag{2.78}$$

We then divide through by $\hbar\omega.2$ to obtain:

$$\frac{\hbar}{m\omega}\frac{d^2\psi(x)}{dx^2}-\frac{m\omega}{\hbar}x^2\psi(x)+\frac{2E}{\hbar\omega}\psi(x)=0 \tag{2.79}$$

Expressing E in units of $\hbar\omega$ by defining $K=\frac{E}{\hbar\omega}$:

$$\frac{\hbar}{m\omega}\frac{d^2\psi(x)}{dx^2}+(2K-\frac{m\omega}{\hbar}x^2)\psi(x)=0 \tag{2.80}$$

Solution by conversion to a dimensionless equation

The standard solution to the harmonic oscillator is obtained in terms of a dimensionless variable:

$$\xi=\sqrt{\frac{m\omega}{\hbar}}x \tag{2.81}$$

$$\frac{d\psi}{dx}=\frac{d\psi}{d\xi}\sqrt{\frac{m\omega}{\hbar}}$$

$$\frac{d^2\psi}{dx^2}=\frac{m\omega}{\hbar}\frac{d^2\psi}{d\xi^2}$$

By substitution:

$$\frac{d^2\psi}{d\xi^2} + (2K - \xi^2)\psi(\xi) = 0 \tag{2.82}$$

To solve this we first examine the behavior for $\xi^2 >> K$:

$$\frac{d^2\psi(\xi)}{d\xi^2} = \xi^2\psi(u) \tag{2.83}$$

The solutions of this equation are:

$$e^{\pm\xi^2/2} \tag{2.84}$$

Only the solution with the negative sign is physically possible. This choice is a Gaussian function. Let us try to find the solution with this asymptotic behavior by defining a new function, $f(\xi)$:

$$\psi(\xi) = f(\xi)e^{-\xi^2/2} \tag{2.85}$$

where $f(\xi)$ does not need to vanish as $\xi^2 \to \infty$. All we require is that $f(\xi)e^{-\xi^2/2} \to 0$ as $\xi^2 \to \infty$. In terms of f, the derivatives of $\psi(\xi)$ are:

$$\frac{d\psi}{du} = (f' - \xi f)e^{-\xi^2/2} \tag{2.86}$$

$$\frac{d^2\psi}{d\xi^2} = -(f' - \xi f)\xi e^{-\xi^2/2} + (f'' - \xi f' + (\xi^2 - 1)f)e^{-\xi^2/2} \tag{2.87}$$

$$= \left(f'' - 2\xi f' + (\xi^2 - 1)f\right)e^{-\xi^2/2} \tag{2.88}$$

Substituting this expression for $\frac{d^2\psi}{d\xi^2}$ into the D.E. we obtain a differential equation for $f(\xi)$:

$$\left(f'' - 2\xi f' + (\xi^2 - 1)f + (2K - \xi^2)f\right)e^{-\xi^2/2} = 0 \tag{2.89}$$

so that:

$$f'' - 2\xi f' + (2K - 1)f = 0 \tag{2.90}$$

We will try to solve this equation in the form of an infinite series:

$$f = \sum_{j=0} c_j\xi^j \tag{2.91}$$

$$f' = \sum_{j=1} jc_j\xi^{j-1} \tag{2.92}$$

$$\xi f' = \sum_{j=1} j c_j \xi^j = \sum_{j=0} j c_j \xi^j \tag{2.93}$$

$$f'' = \sum_{j=2} j(j-1) c_j \xi^{j-2} = \sum_{j=0} (j+1)(j+2) c_{j+2} \xi^j \tag{2.94}$$

By substitution into the D.E.:

$$\sum_{j=0} [c_{j+2}(j+1)(j+2)\xi^j - 2jc_j\xi^j + (2K-1)c_j\xi^j] = 0 \tag{2.95}$$

For this solution to be valid for all ξ, the coefficient of every power of ξ must vanish. This means that:

$$c_{j+2} = c_j \frac{1 - 2K + 2j}{(j+1)(j+2)} \tag{2.96}$$

Provided we specify two constants, c_0 and c_1, all the remaining coefficients in the series are determined by this recursion relation. These two arbitrary constants are what we expect for the solution of a second order differential equation. One of them multiplies a function represented as an infinite series of odd powers of ξ and the other an infinite series of even powers of ξ. These two series provide two linearly independent solutions.

Of course, an infinite series is not useful if it doesn't converge. We can check convergence using the ratio test, comparing two successive terms, s_n and s_{n+2} in the series:

$$\frac{s_{n+2}}{s_n} = \frac{(1 - 2K + 2n)\xi^2}{(n+1)(n+2)}$$

For $n >> K$ and $n >> 1$:

$$\frac{s_{n+2}}{s_n} \rightarrow \frac{2n\xi^2}{n^2} = \frac{2\xi^2}{n}$$

For any finite value of ξ:

$$\lim_{n \to \infty} \frac{s_{n+2}}{s_n} = 0$$

According to the ratio test both the even and odd infinite series converge for any finite value of ξ.

What is the behavior of the solutions as $\xi \rightarrow \infty$. The ratio of the coefficients of successive terms in either series for large j is:

$$\frac{c_{j+2}}{c_j} \rightarrow \frac{2j}{(j+1)(j+2)} \rightarrow \frac{2}{j} \tag{2.97}$$

But this is just the relation for the series expansion of the function, e^{ξ^2}, which diverges as $\xi \to \infty$. Asymptotically both solutions for $f(\xi)$ diverge at infinity like e^{ξ^2}. Since these solutions are multiplied by $e^{-\xi^2/2}$ to obtain $\psi(x)$, we see that both of the independent solutions for ψ diverge like $e^{\xi^2/2}$. Thus, there seem to be no normalizable solutions to the harmonic oscillator potential. But, wait a minute! Notice that if any constant c_{j+2} should vanish, all the higher order constants will also vanish, and the infinite sum will become a polynomial of order j, $P_j(\xi)$. Then:

$$\psi(\xi) = P_j(\xi)e^{-\xi^2/2}, \qquad \lim \xi^2 \to \infty\psi(\xi) = 0$$

By examining the recursion relation, we see that $c_{n+2} = 0$ if $K = n+1/2$, reducing the infinite series to a polynomial of order n. If n is even, the even solution is:

$$f_e = c_0 + c_2\xi^2 + c_4\xi^4 + \cdots + c_n\xi^n$$

but the odd series that starts with $c_1\xi$ does not terminate. For this case we must set $c_1 = 0$. Similarly, if we choose an odd value for n:

$$f_o = c_1\xi + c_3\xi^3 + c_5\xi^5 + \cdots + c_n\xi^n$$

but the even solution does not terminate so we must set $c_0 = 0$. Other choices for K will not permit a normalizable solution.

The parameter K was defined as $E/(\hbar\omega)$, so the allowed values of energy are:

$$E = (n + 1/2)\hbar\omega, \qquad n = 0, 1, 2, \cdots \tag{2.98}$$

These are the allowed energies for the quantum mechanical solution to the harmonic oscillator potential. Unlike the n^2 behavior of the energy levels for the square well, the energy levels for the harmonic oscillator are evenly spaced, separated by steps of $\Delta E = \hbar\omega$. For even values of n the solutions are even functions of ξ and for odd values they are odd functions of ξ. The polynomials for different values of n are orthogonal. The lowest possible energy is $E_0 = \frac{1}{2}\hbar\omega$, which is therefore the ground state energy of the harmonic oscillator. Consistent with the uncertainty principle, the oscillator cannot be in a state of 0 energy, for which the expectation values of both the momentum and position would be identically 0.

Solutions for f:

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x \tag{2.99}$$

$$\psi = f(\xi)e^{-\frac{m\omega}{2\hbar}x^2} \tag{2.100}$$

Setting $K = n + 1/2$

$$c_{j+2} = -2c_j \frac{n-j}{(j+1)(j+2)}, \qquad j \leq n \tag{2.101}$$

$$\frac{c_{j+2}}{c_j} = -2\frac{n-j}{(j+1)(j+2)} \tag{2.102}$$

- n=0: $f = 1, \qquad \psi = c_0 e^{-\frac{m\omega x^2}{2\hbar}}$
- n=1: $f = c_1\xi, \qquad \psi = c_1 x e^{-\frac{m\omega x^2}{2\hbar}}$
- n=2; $f = c_0(1 - 2\xi^2), \qquad \psi = c_0(1 - \frac{2m\omega}{\hbar}x^2)e^{-\frac{m\omega x^2}{2\hbar}}$
- n=3: $f = c_1\xi(1 - \frac{2}{3}\xi^2), \qquad \psi = c_1 x(1 - \frac{2m\omega}{3\hbar}x^2)e^{-\frac{m\omega x^2}{2\hbar}}$

The ground-state wave function is:

$$\psi_0 = c_0 e^{-\frac{m\omega x^2}{2\hbar}} \tag{2.103}$$

The probability distribution is:

$$P(x) = \psi^*\psi = |c_0|^2 e^{-\frac{m\omega x^2}{\hbar}} \tag{2.104}$$

This is a Gaussian with a standard deviation for the probability distribution of x given by:

$$\sigma_x^2 = \frac{\hbar}{2m\omega} \tag{2.105}$$

To normalize the distribution:

$$|c_0|^2 = \frac{1}{\sqrt{2\pi\sigma_x^2}} = \sqrt{\frac{m\omega}{\pi\hbar}} \tag{2.106}$$

For this state, both $\langle x \rangle$ and $\langle p \rangle$ are zero. After calculating $\langle x^2 \rangle$ and $\langle p^2 \rangle$ one can show that:

$$\sigma_x \sigma_p = \hbar/2 \tag{2.107}$$

The higher the oscillator frequency (the greater the oscillator strength), the less the uncertainty in position for the ground state and the greater the uncertainty in momentum.

As polynomials in ξ, the solutions are known as the Hermite polynomials. The advantage of writing the solution in terms of $H_n(\xi)$ is that the functions have been thoroughly studied and there are many useful formulas relating them. Traditionally, the Hermite polynomials are normalized so that the coefficient of the highest power is 2^n. This convention, of course, precedes the invention of quantum mechanics. The stationary states are:

$$\psi_n(x) = A_n H_n(\xi) e^{-\frac{m\omega}{2\hbar}x^2} \tag{2.108}$$

At this point we have solved the harmonic oscillator problem in terms of a complete set of orthogonal states. Any physical state can be represented as linear combination of these states. Using the usual procedures one can calculate the expectation value of any physical observable.

2.3.1 Solution of the H.O. using ladder operators

In operator form the Schrödinger Equation is:

$$\left(\frac{p_x^2}{2m} + \frac{m\omega^2}{2}x^2\right)\psi = E\psi \tag{2.109}$$

where I use p_x to indicate explicitly that the momentum operator is a derivative with respect to x. The equation can be shortened to:

$$H\psi = E\psi \tag{2.110}$$

where:

$$H \equiv \left(\frac{p_x}{\sqrt{2m}}\right)^2 + \left(\sqrt{\frac{m}{2}}\omega x\right)^2 \tag{2.111}$$

If we treat this operator equation like ordinary Algieba we can factor the lhs into:

$$H = \left(\frac{p_x}{\sqrt{2m}} - i\sqrt{\frac{m}{2}}\omega x\right)\left(\frac{p_x}{\sqrt{2m}} + i\sqrt{\frac{m}{2}}\omega x\right) \tag{2.112}$$

However, since $p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$ is a derivative operator that acts on x as well as on any function to the right, this algebra isn't right. Nevertheless, something very interesting happens if we push ahead with this idea. Define the two operators, a_+ and a_-, by:

$$a_\pm = \frac{p_x}{\sqrt{2m}} \pm i\sqrt{\frac{m}{2}}\,\omega x \tag{2.113}$$

The products of the two operators are:

$$a_-a_+ = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 - i\frac{\omega}{2}(xp_x - p_x x) = H - i\frac{\omega}{2}(xp_x - p_x x) = H - \frac{i\omega}{2}[x, p_x]$$

and:

$$a_+a_- = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 + i\frac{\omega}{2}(xp_x - p_xx) = H + \frac{i\omega}{2}[x, p_x]$$

where the symbol $[x, p] \equiv xp - px$ is called the *commutator* of the two operators. For ordinary algebraic quantities the commutator is 0, but it need not be for operators. For any function $f(x)$:

$$[x, p_x]f(x) = (xp_x - p_xx)f(x) = \frac{\hbar}{i}\left(x\frac{df}{dx} - \frac{d(xf)}{dx}\right) = \frac{\hbar}{i}\left(x\frac{df}{dx} - x\frac{df}{dx} - f\right)$$
$$= i\hbar f \tag{2.114}$$

Since the function $f(x)$ is arbitrary, we can write:

$$[x, p_x] = i\hbar \tag{2.115}$$

The commutator of x and p_x is fundamental to the algebra of quantum mechanics. It is easy to extend the result to three dimensions:

$$\begin{cases} [x, p_x] = [y, p_y] = [z, p_z] = i\hbar; \\ [x, p_y] = [x, p_z] = [y, p_x] = [y, p_z] = [z, p_x] = [z, p_y] = 0. \end{cases} \tag{2.116}$$

Using the commutation relation:

$$a_-a_+ = H + \frac{\hbar\omega}{2} \tag{2.117}$$

Similarly, we can show that:

$$a_+a_- = H - \frac{\hbar\omega}{2} \tag{2.118}$$

so that:

$$[a_-, a_+] = \hbar\omega \tag{2.119}$$

Now suppose there is some energy E for which there is a stationary state ψ_E such that $H\psi_E = E\psi_E$. Operating on this state with a_-a_+:

$$a_-a_+\psi_E = E\psi_E + \frac{1}{2}\hbar\omega\psi_E = (E + \frac{1}{2}\hbar\omega)\psi_E \tag{2.120}$$

Applying a_+ to both sides of this equation:

$$a_+a_-a_+\psi_E = (E + \frac{1}{2}\hbar\omega)a_+\psi_E \tag{2.121}$$

Now, $a_+\psi_E$ is itself some function of x, call it $f(x)$:.

$$a_+a_-f(x) = (E + \frac{1}{2}\hbar\omega)f(x) \tag{2.122}$$

or:

$$(H - \frac{\hbar\omega}{2})f(x) = (E + \frac{1}{2}\hbar\omega)f(x) \tag{2.123}$$

so that:

$$Hf(x) = (E + \hbar\omega)f(x) \tag{2.124}$$

We see that $f(x)$ is a stationary state solution to the Schrödinger Equation for the energy $E' = E + \hbar\omega$:

$$f(x) = a_+\psi_E = \alpha\psi_{E+\hbar\omega} \tag{2.125}$$

where α is some constant that may depend on E, and $\psi_{E+\hbar\omega}$ is the solution of the Schrödinger Equation for $E' = E + \bar{\omega}$.

By the same process we can show that:

$$a_-\psi_E = \beta\psi_{E-\hbar\omega} \tag{2.126}$$

where β is another constant that may depend on E. The operators a_+ and a_- allow us to start from the stationary state solution for any energy, E, and work our way up and down from there obtaining solutions for higher and lower energies ad infinitum. For this reason, they are called *ladder operators*. After each ladder operation we would need to normalize the result by adjusting the proportionality constants.

But it looks like we can start from a valid stationary state and continue the lowering process to negative energies. Since the potential is everywhere positive, a negative energy implies imaginary momentum, which is non-physical. To prevent this, there must be a lowest energy, $E_0 \geq 0$, for which:

$$a_-\psi_0 = 0 \tag{2.127}$$

But:

$$H\psi_0 = (a_+a_- + \frac{1}{2}\hbar\omega)\psi_0 = E_0\psi_0 \tag{2.128}$$

Using the condition that $a_-\psi_0 = 0$:

$$\frac{1}{2}\hbar\omega\psi_0 = E_0\psi_0 \tag{2.129}$$

so:

$$E_0 = \frac{1}{2}\hbar\omega \tag{2.130}$$

Using only an algebraic argument we have deduced the ground state energy of the harmonic oscillator. Once we find the ground state wave function we can apply the raising operator to obtain successively higher energy states, separated by $\Delta E = \hbar\omega$. No other energies are possible. If there were a state at some energy not in this sequence we could apply the lowering operator indefinitely to reach negative energies.

To get the ground state, we need only solve the first order differential equation:

$$a_-\psi_0 = 0 \tag{2.131}$$

Using the definition of a_- from Eq. 2.113:

$$(\frac{p_x}{\sqrt{2m}} - i\sqrt{\frac{m}{2}}\omega x)\psi_0 = 0 \tag{2.132}$$

Multiplying through by $\sqrt{2m}$ and setting $p_x = -i\hbar\frac{d}{dx}$, this reduces to:

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar}x\psi_0 \tag{2.133}$$

After dividing by ψ_0, we get:

$$\frac{d\ln(\psi_0)}{dx} = -\frac{m\omega}{\hbar}x \tag{2.134}$$

Integrating this first order differential equation:

$$\ln(\psi_0) = \alpha - \frac{m\omega}{2\hbar}x^2 \tag{2.135}$$

so that:

$$\psi_0 = Ae^{-\frac{m\omega x^2}{2\hbar}} \tag{2.136}$$

Example

The ground state wave function is $\psi_0 = Ae^{-\alpha x^2}$, where $\alpha = m\omega/(2\hbar)$. Applying the raising operator:

$$\psi_1 = C\left(\frac{p_x}{\sqrt{2m}} + i\sqrt{\frac{m\omega^2}{2}}x\right)\psi_0 \tag{2.137}$$

$$\psi_1 = C\frac{\hbar}{i\sqrt{2m}}\frac{d\psi_0}{dx} + iC\sqrt{\frac{m\omega^2}{2}}x\psi_0 \tag{2.138}$$

$$\psi_1 = C\frac{\hbar}{i\sqrt{2m}}(-2\alpha x)\psi_0 + iC\sqrt{\frac{m\omega^2}{2}}x\psi_0 = iC\left(\frac{2\hbar\alpha}{\sqrt{2m}} + \sqrt{\frac{m\omega^2}{2}}\right)x\psi_0 \tag{2.139}$$

$$\psi_1 = c_1 x e^{-\alpha x^2} \tag{2.140}$$

We can get the normalization constant c_1 from a general formula (see the problems) or by setting $\int_{-\infty}^{\infty} |\psi_1(x)|^2\, dx = 1$.

2.4 Free Particle

A solution to the Schrödinger Equation for a free particle is more difficult than one might at first expect. The separated equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{2.141}$$

Since $V = 0$, we know that $E > 0$, we can define a positive constant k^2 as:

$$2mE/\hbar^2 = \frac{p^2}{\hbar^2} = k^2, \qquad p = \hbar k, \qquad E = \frac{\hbar^2 k^2}{2m}$$

The Schrödinger Equation becomes:

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \tag{2.142}$$

For a single choice of E, the solutions are $\sin(kx)$ and $\cos(kx)$. which are not normalizable. A free particle with a unique energy is not a possibility.

Let us imagine that the particle is in a square well, and consider the limit as the walls get so far apart that we can ignore them. For the square well, we used the boundary condition that the wave function should vanish at the walls. However, if the walls are going to recede to infinity, this boundary condition is no longer relevant. Therefore we will keep both the sine and cosine functions associated with a particular energy and expand a free particle wave function as a linear sum of solutions with different energies. The solutions are limited to sines and cosines with discrete values of $k_n = n\pi x/a$.

From Fourier analysis any periodic function defined in the range, $-a \leq x \leq a$, can be represented by the series:

$$f(x) = \bar{f} + \sum_{n=1}^{\infty}\left[a_n \sin(n\pi x/a) + b_n \cos(n\pi x/a)\right] \tag{2.143}$$

where $\bar{f}$ is the average value of $f(x)$, and:

$$a_n = \frac{1}{a}\int_{-a}^{a} f(x)\ \sin(n\pi x/a)\,dx$$

$$b_n = \frac{1}{a}\int_{-a}^{a} f(x)\ \cos(n\pi x/a)\,dx$$

Using the exponential representation for the sine and cosine functions:

$$\sin(n\pi x/a) = \frac{e^{i\frac{n\pi}{a}x} - e^{-i\frac{n\pi}{a}x}}{2i} \tag{2.144}$$

and:

$$\cos(n\pi x/a) = \frac{e^{i\frac{n\pi}{a}x} + e^{-i\frac{n\pi}{a}x}}{2} \tag{2.145}$$

$$f(x) = \bar{f} + \sum_{n=1}^{\infty}\frac{1}{2}\left[(b_n - ia_n)e^{i\frac{n\pi}{a}x} + (b_n + ia_n)e^{-i\frac{n\pi}{a}x}\right]$$

$$f(x) = \bar{f} + \frac{1}{2}\sum_{m=1}^{\infty}(b_m - ia_m)e^{i\frac{n\pi}{a}x}\frac{1}{2} + \sum_{m=-\infty}^{-1}(b_{-m} + ia_{-m})e^{i\frac{m\pi}{a}x}$$

$$= \sum_{m=-\infty}^{\infty} c_m e^{i\frac{m\pi}{a}x} \tag{2.146}$$

where for $m > 0$:

$$c_m = \frac{b_m - ia_m}{2} = \frac{1}{2a}\int_{-a}^{a}\left[\cos(\frac{m\pi x}{a}) - i\sin(m\pi xa)\right]\ f(x)\,dx$$

$$= \frac{1}{2a}\int_{-a}^{a} e^{-i\frac{m\pi}{a}x}\,f(x)\,dx$$

and for $m < 0$,

$$c_m = \frac{b_{-m} + ia_{-m}}{2} = \frac{1}{2a}\int_{-a}^{a}\left[\cos(-\frac{m\pi x}{a}) + i\sin(-\frac{m\pi x}{a})\right]\ f(x)\,dx$$

$$= \frac{1}{2a}\int_{-a}^{a}\left[\cos(\frac{m\pi x}{a}) - i\sin(\frac{m\pi x}{a})\right]\ f(x)\,dx = \frac{1}{2a}\int_{-a}^{a} e^{-i\frac{m\pi}{a}x}\,f(x)\,dx$$

The formulas for c_m for both the positive and negative integers can be combined into:

$$c_m = \frac{1}{2a}\int_{-a}^{a} e^{-i\frac{m\pi}{a}x}\ f(x)\,dx \tag{2.147}$$

Notice that the $m = 0$ term accounts for $\bar{f}$, since:

$$c_0 = \frac{1}{2a}\int_{-a}^{a} f(x)\,dx = \bar{f}$$

If the function $f(x)$ is complex ($f(x) = g(x) + ih(x)$) where $g(x)$ and $h(x)$ are real functions, we can write a separate Fourier series of the form of Eq. 2.143 for g and h. When we combine these into an equation for $f(x)$, we will get a result that looks just like eqn. 2.143, but the coefficients a_n and b_n will be complex numbers. The above analysis therefore works equally well for real and complex functions.

For a free particle we want the limit as $a \to \infty$. We begin by observing that successive values of $n\pi/a$ are separated by π/a, which goes to 0 as $a \to \infty$. Let us denote:

$$k_n = n\pi/a, \qquad \Delta k = \pi/a \tag{2.148}$$

If we imagine the values of k_n lying on a k axis, we see that as $a \to \infty$, the points get more and more crowded with the interval between each one diminishing to 0. Thus as we let the walls go to infinity the values of k become continuously distributed. We can write the spacing in k as:

$$\Delta k \equiv \frac{\pi}{a} \to 0 \tag{2.149}$$

We can re-express the Fourier sum by defining $c(k_n) = c_n$ and inserting $1 = a\Delta k/\pi$:

$$f(x) = \sum_{k_n=-\infty}^{\infty} c(k_n)e^{ik_nx}\left(\frac{a}{\pi}\right)\Delta k \tag{2.150}$$

Next, define $b(k) = \frac{a}{\pi}c(k)$:

$$f(x) = \sum_{k_n=-\infty}^{\infty} b(k_n)e^{ik_nx}\Delta k \tag{2.151}$$

where:

$$b(k_n) = \frac{a}{\pi}c_n = \frac{1}{2\pi}\int_{-a}^{a} f(x)e^{-ik_nx}\,dx$$

In the limit of $\Delta k \to 0$, the sum goes over into an integral:

$$f(x) \to \int_{-\infty}^{\infty} b(k)e^{ikx}\,dk \tag{2.152}$$

and:

$$b(k) \to \frac{1}{2\pi}\int_{-\infty}^{\infty} f(x)e^{-ikx}\,dx$$

We can make this symmetrical by defining:

$$F(k) = \sqrt{2\pi}b(k) \tag{2.153}$$

so that:

$$f(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} F(k)e^{ikx}\;dk \tag{2.154}$$

and:

$$F(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(x)e^{-ikx}\,dx$$

Equations 2.154 and 2.4 are the generalizations of the Fourier series from a finite region in x to the entire x axis. Equations 2.154 can still be thought of as a linear sum of states of different energies E_i where the energies have become continuously distributed. The function $F(k)$ plays the role of the linear expansion coefficients, and is called the *Fourier transform* of the function $f(x)$. Since the relationship between the two functions is symmetrical, they are usually called the Fourier transform of each other.

In the discrete linear sums previously used we learned that the n^{th} component is to be multiplied by $e^{-iE_nt/\hbar}$. This time dependence carries over to the integral form so that for each component $\phi(k)$ we must multiply by $e^{iE(k)t/\hbar}$ to get the solution for $t > 0$. Using:

$$E = \frac{k^2\hbar^2}{2m} > 0$$

and defining:

$$\omega = E/\hbar \tag{2.155}$$

the general time-dependent solution for the free-particle is:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \phi(k)e^{ikx}e^{-i\omega t}\;dk \tag{2.156}$$

One can show by direct substitution that $\Psi(x,t)$ defined in equation 2.156 satisfies the time-dependent Schrödinger Equation for any choice of $\phi(k)$. For a particular choice of the initial wave function:

$$\phi(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \Psi(x,0)e^{-ikx}\,dx \tag{2.157}$$

We can equally well write the Fourier transforms explicitly in terms of x, p and E:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(p) e^{\frac{i}{\hbar}(px - Et)} \, dk \tag{2.158}$$

$$\phi(p) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-i\frac{p}{\hbar}x} \, dx \tag{2.159}$$

Example: A Gaussian wave packet

Consider the following normalized wave-function:

$$\psi(x) = \left(\frac{1}{2\pi\sigma_x^2}\right)^{1/4} e^{-\frac{x^2}{4\sigma_x^2}} = \alpha e^{-\beta^2 x^2} \tag{2.160}$$

where:

$$\alpha \equiv \left(\frac{1}{2\pi\sigma_x^2}\right)^{1/4}, \qquad \beta^2 \equiv \frac{1}{4\sigma_x^2} \tag{2.161}$$

This represents a wave packet with $\langle x \rangle = 0$ and a standard deviation of σ_x. The Fourier transform is:

$$\phi(k) = \frac{\alpha}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{(-\beta^2 x^2 - ikx)} \, dx \tag{2.162}$$

Completing the square in the exponential:

$$\phi(k) = \frac{\alpha}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e{-}[\beta x - ik/(2\beta)]^2 e^{-k^2/(4\beta^2)} dx \tag{2.163}$$

$$= \frac{\alpha}{\sqrt{2\pi}} e^{-k^2/(4\beta^2)} \int_{-\infty}^{\infty} e^{-[\beta x - ik/(2\beta)]^2} dx \tag{2.164}$$

Letting $u = \beta x - ik/(2\beta)$:

$$\phi(k) = \frac{\alpha}{\sqrt{2\pi}} e^{-k^2/(4\beta^2)} \int_{-\infty}^{\infty} e^{-u^2} du/\beta = \frac{\alpha}{\beta\sqrt{2\pi}} e^{-k^2/(4\beta^2)} \sqrt{\pi} \tag{2.165}$$

$$= \frac{\alpha}{\beta\sqrt{2}} e^{-\frac{k^2}{4\beta^2}} \tag{2.166}$$

Substituting in the definition of α:

$$\phi(k) = \left(\frac{1}{2\pi\sigma_x^2}\right)^{1/4} \frac{1}{\beta\sqrt{2}} e^{-\frac{k^2}{4\beta^2}} \tag{2.167}$$

Expressing σ_x in terms of β:

$$\phi(k) = \left(\frac{2\beta^2}{\pi}\right)^{1/4} \frac{1}{\beta\sqrt{2}} e^{-\frac{k^2}{4\beta^2}} = \left(\frac{1}{2\pi\beta^2}\right)^{1/4} e^{-\frac{k^2}{4\beta^2}} \tag{2.168}$$

This is exactly the same form that we started with for $\psi(x)$. The square of the distribution $|\phi(k)|^2$ is normalized over the region of k running from $-\infty$ to ∞, so it probably is not too difficult to imagine that it is the probability distribution for values of k. In fact the function plays the same role as the c_n's did in the infinite square well problem. The probability distribution is a Gaussian function with standard deviation $\sigma_k = \beta = 1/(2\sigma_x)$. Thus:

$$\sigma_k \sigma_x = \frac{1}{2} \tag{2.169}$$

If we use $p = \hbar k$, we obtain:

$$\sigma_p \sigma_x = \frac{\hbar}{2} \tag{2.170}$$

which is the minimum value allowed by the Heisenberg uncertainty principle.

For this wave-function $\langle x \rangle = 0$, and $\langle p \rangle = 0$. We can put the particle into uniform motion by modifying $\phi(k)$ to shift the centroid to a non-zero value:

$$\phi(k) = \left(\frac{2\beta^2}{\pi}\right)^{1/4} \frac{1}{\beta\sqrt{2}} e^{-\frac{(k-k_0)^2}{4\beta^2}} = \left(\frac{1}{2\pi\beta^2}\right)^{1/4} e^{-\frac{(k-k_0)^2}{4\beta^2}} \tag{2.171}$$

We can now use this as the transform of the wave-function to obtain at $t = 0$:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx}\, dk = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{2\pi\beta^2}\right)^{1/4} \int_{-\infty}^{\infty} e^{-\frac{(k-k_0)^2}{4\beta^2}} e^{ikx}\, dk \tag{2.172}$$

Now let $\kappa = k - k_0$, so that:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx}\, dk = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{2\pi\beta^2}\right)^{1/4} \int_{-\infty}^{\infty} e^{-\frac{\kappa^2}{4\beta^2}} e^{i(\kappa+k_0)x}\, d\kappa \tag{2.173}$$

Now let $\kappa = k - k_0$, so that:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx}\, dk = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{2\pi\beta^2}\right)^{1/4} e^{ik_0x} \int_{-\infty}^{\infty} e^{-\frac{\kappa^2}{4\beta^2}} e^{i\kappa x}\, d\kappa \tag{2.174}$$

Again, using the trick of completing the square in the exponential:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{2\pi\beta^2}\right)^{1/4} e^{ik_0x} \int_{-\infty}^{\infty} e^{-(\frac{\kappa}{2\beta} - i\beta x)^2}\ d\kappa\ e^{-\beta^2x^2} \tag{2.175}$$

Substituting $u = \frac{\kappa}{2\beta} - i\beta x$:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{2\pi\beta^2}\right)^{1/4} e^{ik_0x}\ 2\beta\ e^{-\beta^2x^2} \int_{-\infty}^{\infty} e^{-u^2}\ du \tag{2.176}$$

The integral is $\sqrt{\pi}$. Collecting the terms:

$$\psi(x) = \left(\frac{2\beta^2}{\pi}\right)^{1/4} e^{ik_0x}\ e^{-\beta^2x^2} \tag{2.177}$$

Using the definition $2\beta^2 \equiv \frac{1}{2\sigma_x^2}$:

$$\psi(x) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/4} e^{ik_0x}\ e^{-x^2/(4\sigma^2)} \tag{2.178}$$

which is the same as before except for the additional term involving k_0.

The solution for $\Psi(x,t)$ requires still more work, using the form:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx-\omega t)}\ dk \tag{2.179}$$

where ω is a function of k:

$$\omega \equiv \frac{E}{\hbar} = \frac{p^2}{2m\hbar} = \frac{\hbar k^2}{2m} \tag{2.180}$$

2.4.1 Group Velocity

Another problem that we noticed with the single energy wave solutions of the free particle equation was that their phase velocity was half of the particle velocity. Now that we have a solution in terms of a wave packet, it is time to ask how this wave-packet moves in space. If the packet consists of waves spread over a small enough region of k or momentum space, the packet will not spread out so rapidly in time that it quickly becomes meaningless to say it represents a localized particle. We assume that the the function $\phi(k)$ peaks fairly sharply around the value k_0. We then expand $\omega(k)$ in a first order Taylor series around $k = k_0$:

$$\omega = \omega_0 + \left[\frac{d\omega}{dk}\right]_{k_0} (k - k_0) = \omega_0 + \omega'(k - k_0) \tag{2.181}$$

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx-\omega_0 t-\omega'(k-k_0)t)}\ dk \tag{2.182}$$

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} e^{-i\omega_0 t} \int_{-\infty}^{\infty} \phi(k) e^{i(kx-\omega'(k-k_0)t)}\ dk \tag{2.183}$$

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} e^{-i\omega_0 t} \int_{-\infty}^{\infty} \phi(k) e^{ik(x-\omega' t)} e^{ik_0\omega' t}\ dk \tag{2.184}$$

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} e^{-i(\omega_0 - k_0\omega')t} \int_{-\infty}^{\infty} \phi(k) e^{i(k(x-\omega' t)}\ dk \tag{2.185}$$

$$= e^{-i(\omega_0 - k_0\omega')t} F(x-\omega' t) \tag{2.186}$$

The probability distribution is:

$$|\Psi(x,t)|^2 = |F(x-\omega' t)|^2 \tag{2.187}$$

To the degree of validity of our linear approximation for the dependence of frequency on k, we see that the wave packet is constant in time except that it moves with velocity, ω', along the x axis. This analysis holds for any wave-packet that maintains its shape over time. The derivative, ω' is called the group velocity:

$$v_g = \left[\frac{d\omega}{dk}\right]_{k_0} \tag{2.188}$$

For the free-particle solution to the Schrödinger Equation :

$$\omega = \frac{\hbar k^2}{2m}, \qquad v_g = \hbar k_0/m \tag{2.189}$$

Associating the value k_0 with a deBroglie wave, we see that $v_g = p_0/m$. The group velocity is the classical velocity for the central wave number in the wave-packet.

2.5 Scattering

2.5.1 Distinction between scattering and bound states

We have examined the one-dimensional S.E. for particles bound in a finite region of space, and we have developed the solution for a free particle. We now turn to a study of more general potentials, for which it may be possible to find both bound state and unbound states (resembling the free particle solutions discussed above).

An example of a one-dimensional potential that could support both types of states is shown in Fig. 2.7. In classical mechanics a particle with energy

$E < 0$ is bound to a region around the orgin inside the well. For $0 \leq E < V_m$ the particle is bound if it is inside the well and free but restricted to either positive or negative values of x if it is outside the well. In quantum mechanics the particle is bound only if $E < 0$ if $V \to 0$ as $x \to \pm\infty$. For $E > 0$ the solutions are called scattering states.

Real-life potentials usually go to 0 at infinity. In this case, a particle with positive energy can move from some far distance into the region where the potential is noticeable, respond to it in some way, and then proceed on to infinity carrying the scars of the interaction. This process is called scattering, and the states representing it are called scattering states. In three dimensions we imagine a beam of particles impinging on a target. The interaction results in waves emerging in all directions from the target. In one dimension, the picture is like a light beam incident normally on a window. Part of the light is reflected and part is transmitted and we describe the process in terms of transmission and reflection coefficients.

For scattering problems we assume that the potential is 0 at infinity. In fact, we usually assume that it exists only in a finite region, and can be ignored everywhere outside this region. Thus, if $E > 0$ we should use free particle solutions of the S.E. outside the region of the potential. Although we know that a free particle cannot be represented by a wave of a single energy and momentum, it is convenient to represent scattering in terms of such waves. We can imagine that the waves describe a continuous stream of particles moving in the x direction. Then the probability of finding a particular particle in some finite region is 0, but the probability of finding some particle is $\rho\, dx$, where ρ is the density of particles in the beam. For a wave-function representing a beam of particles we generally normalize the wave function so that $|\Psi|^2 = \rho$.

In this regard it is interesting to note with this normalization the particle flux is equal to the probability current:

$$J = \frac{i\hbar}{2m}\left[\Psi\frac{\partial\Psi^*}{\partial x} - \Psi^*\frac{\partial\Psi}{\partial x}\right]$$

For $\Psi = \sqrt{\rho}e^{i(kx-\omega t}$:

$$J = \rho\frac{\hbar k}{m} = \rho\frac{p}{m} = \rho v$$

which is just the number of particles per second crossing any point on the x axis. Generally, a measurement would be in the form of the ratio of final amplitude to initial amplitude, so that the normalization drops out anyway.

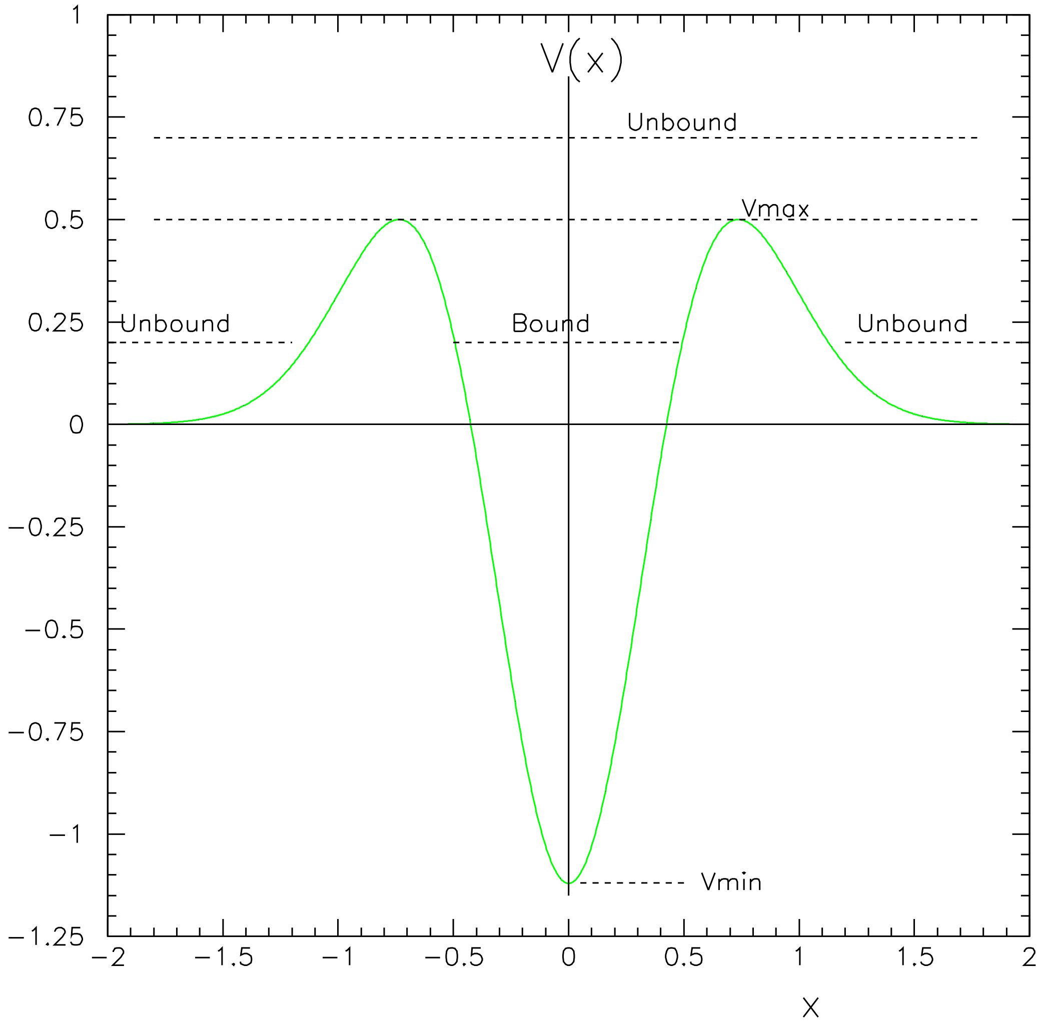

Figure 2.7: A potential that classically has both bound and unbound states. Particles with energy E, $V_{min} \leq E < 0.$ are bound to a region around the origin. If $0 \leq E < V_{max}$ the particles are bound if they are inside the well and free (but restricted to be either on the right side or the left side of the potential barrier) if they are outside the well. If $E \geq V_{max}$ the particles are free and can be anywhere. Quantum mechanically, particles with $V_{min} < E < 0.$ are bound, while particles with $E > 0$ are unbound.

2.5.2 The Dirac Delta function

Dirac invented a very useful function for dealing with quantum problems. The Dirac Delta function is defined by the following properties:

$$\delta(x - x_0) = 0, \qquad x \neq x_0 \tag{2.190}$$

$$\int_a^b f(x)\delta(x - x_0)\,dx = f(x_0), \qquad a < x_0 < b \tag{2.191}$$

From this integral property we see that the units of the function are the inverse of the units of its argument.

The function has an important property:

$$\delta(a(x - x_0)) = \frac{1}{|a|}\delta(x - x_0) \tag{2.192}$$

Proof: Let $a > 0$. Substitute $u = ax$, so that:

$$\int f(x)\delta(a(x - x_0))\,dx = \frac{1}{a}\int f(\frac{u}{a})\delta(u - u_0)\ du \tag{2.193}$$

$$= \frac{1}{a}f(\frac{u_0}{a}) = \frac{1}{a}f(x_0) = \frac{1}{a}\int f(x)\delta(x - x_0)\,dx \tag{2.194}$$

Let $a < 0$ and substitute $b = -a = |a|$:

$$I = \int {x_1}^{x_2} f(x)\delta(a(x - x_0))\,dx = \int_{x_1}^{x_2} f(x)\delta(-b(x - x_0))\,dx \tag{2.195}$$

Let $u = -b(x - x_0)$ so that $dx = -du/b$. The limits on u are such that $u_1 > 0$ and $u_2 < 0$. Then:

$$I = -\frac{1}{b}\int_{u_1}^{u_2} f(u)\delta(u)\ du = \frac{1}{b}\int_{u_2}^{u_1} f(u)\delta(u)\ du = \frac{1}{b}f(u)|_{u=0} \tag{2.196}$$

When $u = 0$, $x = x_0$ so:

$$I = \frac{1}{b}f(x_0) = \frac{1}{|a|}f(x_0) \tag{2.197}$$

Corollary:

$$\delta(x - x_0) = \delta(x_0 - x) \tag{2.198}$$

Mathematicians have proved that the delta function is a valid concept. It is not actually a function, but is what mathematicians call a distribution.

2.5.3 Negative delta function potential

We shall try using the delta function itself as a potential in the Schrödinger Equation :

$$V(x) = -a\delta(x) \tag{2.199}$$

We can think of this as an approximation to a potential confined to a small region in space. The force will act over this entire region, but we imagine thinking of the region as shrinking to a point, and letting the potential become infinite to compensate for this approximation.

Since $\delta(x)$ has units of $1/L$, a must have units of energy times length, $E \cdot L$.

Bound state

Since the potential reaches negative, the theorem that $E > V_{min}$ does not restrict the solutions to positive energies. Let us see if we can find solutions with negative energy (bound states). We could think of these as the bound states in a potential well whose width has shrunk to 0:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - a\delta(x)\psi = E\psi \tag{2.200}$$

$$\frac{d^2\psi}{dx^2} + \frac{2ma}{\hbar^2}\delta(x)\psi = -\frac{2mE}{\hbar^2}\psi \tag{2.201}$$

With $C < 0$, we can define a positive parameter $\kappa^2 = -\frac{2mE}{\hbar^2}$ so that:

$$\frac{d^2\psi}{dx^2} + \frac{2ma}{\hbar^2}\delta(x)\psi = \kappa^2\psi \tag{2.202}$$

The δ function is 0 everywhere except at a single point, so except at $x = 0$ we have:

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi \tag{2.203}$$

The solution of this equation is:

$$\psi = Ae^{\kappa x} + Be^{-\kappa x} \tag{2.204}$$

For the wave function to vanish at $x \to \pm\infty$, we must use:

$$\psi = Ae^{\kappa x}, \qquad x < 0 \tag{2.205}$$

$$\psi = Be^{-\kappa x}, \qquad x > 0 \tag{2.206}$$

For the wave function to be continuous at $x = 0$, $A = B$. To normalize the solution:

$$1 = |A|^2 \left(\int_{-\infty}^{0} e^{2\kappa x} dx + \int_{0}^{\infty} e^{-2\kappa x} dx \right) = 2|A|^2 \int_{0}^{\infty} e^{-2\kappa x} dx = |A|^2/\kappa \tag{2.207}$$

so:

$$A = \sqrt{\kappa} \tag{2.208}$$

Our solution has a discontinuity in the derivative at the origin. The δ function specifies the magnitude of that discontinuity. To determine it we integrate the Schrödinger Equation over a very small interval that encloses the origin:

$$\int_{-\epsilon}^{\epsilon} \frac{d^2\psi}{dx^2}\, dx + \frac{2ma}{\hbar^2} \int_{-\epsilon}^{\epsilon} \delta(x)\psi\, dx = \kappa^2 \int_{-\epsilon}^{\epsilon} \psi\, dx \tag{2.209}$$

Integrating this equation:

$$\left[\frac{d\psi}{dx}\right]_{-\epsilon}^{\epsilon} + \frac{2ma}{\hbar^2}\psi(0) = 2\epsilon\kappa^2\psi(0) \tag{2.210}$$

In the limit of $\epsilon \to 0$:

$$\left[\frac{d\psi}{dx}\right]_{-\epsilon}^{\epsilon} = -\frac{2ma}{\hbar^2}\psi(0) \tag{2.211}$$

The discontinuity in the derivative at the origin is therefore:

$$\left(\frac{d\psi}{dx}\right)_{+} - \left(\frac{d\psi}{dx}\right)_{-} = -\frac{2ma}{\hbar^2}\psi(0) \tag{2.212}$$

This condition is satisfied when:

$$-\kappa - \kappa = -\frac{2ma}{\hbar^2} \tag{2.213}$$

$$\kappa = \sqrt{-2mE}\hbar = \frac{ma}{\hbar^2} \tag{2.214}$$

No matter what its strength the delta function potential has one and only one bound state. The value of this single bound energy depends on the strength of the potential:

$$E = -\frac{ma^2}{2\hbar^2} \tag{2.215}$$

Scattering states

For a wave moving to the right, the solutions are:

$$\Psi = e^{i(kx-\omega t)} \tag{2.216}$$

and for a wave moving to the left, the solution is:

$$\Psi = e^{i(-kx-\omega t)} = e^{-i(kx+\omega t)} \tag{2.217}$$

If particles are incident from the left, there can be reflected waves moving to the left, but on the right side there can only be transmitted waves moving to the right:

$$\Psi = Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)}, \qquad x < 0 \tag{2.218}$$

$$\Psi = Ce^{i(kx-\omega t)}, \qquad x > 0 \tag{2.219}$$

The matching conditions at $x = 0$ yield:

$$A + B = C, \qquad ikC - (ikA - ikB) = -\frac{2ma}{\hbar^2}C \tag{2.220}$$

Substituting from the first, $B = C - A$, into the second:

$$ikC - ikA + ik(C - A) = -\frac{2ma}{\hbar^2}C \tag{2.221}$$

$$\frac{C}{A} = \frac{1}{1 - i\frac{ma}{\hbar^2 k}} \tag{2.222}$$

and:

$$\frac{B}{A} = \frac{C}{A} - 1 = -\frac{1}{1 + i\frac{\hbar^2 k}{ma}} \tag{2.223}$$

Since the probability distribution is proportional to the square of the wave function, we can define the transmission probability as:

$$T = |C/A|^2 = \frac{1}{1 + \frac{m^2a^2}{\hbar^4k^2}} \tag{2.224}$$

For large k the transmission approaches 1, and as k goes to 0, the transmission goes to 0. The reflected probability is given by:

$$R = |B/A|^2 = \frac{\frac{m^2a^2}{\hbar^4k^2}}{1 + \frac{m^2a^2}{\hbar^4k^2}} \tag{2.225}$$

We see that $T + R = 1$.

2.5.4 Positive delta function potential

If the potential is positive, the delta function presents a barrier to the incoming wave. With the positive delta function the minimum potential energy is 0 and there are no negative energy solutions(bound states).

For positive energies, we use the same technique as above for the scattering problem. This time the matching conditions at $x = 0$ yield:

$$A + B = C, \qquad A - B = C(1 - \frac{2ma}{i\hbar^2 k}) \tag{2.226}$$

The only change is that we have changed the sign of a. Thus, T and R, which depend on a^2 are unchanged. The scattering from a negative and a positive delta function potential is identical.

2.6 The Finite Square Well

A good approximation to the force between a neutron and a nucleus is given by:

$$V(r) = \begin{cases} -V_0, & r \le a; \\ 0, & r > a. \end{cases} \tag{2.227}$$

Because of its sharp edges and flat bottom this potential is called a *finite square well.* Its one-dimensional version is:

$$V(x) = -V_0, \qquad -a < x < a, \qquad V = 0 \ \text{ elsewhere} \tag{2.228}$$

We can solve this problem by solving the free-particle problem with separate coefficients in the three regions, $x < -a$, $-a < x < a$, and $x > a$. We match the solutions and their derivatives at the boundaries separating the three regions to get the final solution.

2.6.1 Bound States

For $-V_0 < E < 0$, we require that the wave-function vanish at infinity. Outside the well, where $V = 0$:

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = \kappa^2\psi \tag{2.229}$$

where:

$$\kappa^2 = -\frac{2mE}{\hbar^2} \tag{2.230}$$

the solutions are the same as for the delta function potential:

$$\psi(x) = Ae^{\kappa x}, \qquad x < -a \tag{2.231}$$

$$\psi(x) = Be^{-\kappa x}, \qquad x > a \tag{2.232}$$

Inside the well, where $E > V_0$:

$$\frac{d^2\psi}{dx^2} = -\frac{2m(E+V_0)}{\hbar^2}\psi = -k^2\psi \tag{2.233}$$

where:

$$k^2 = \frac{2m(V_0+E)}{\hbar^2} = \frac{2mV_0}{\hbar^2} - \kappa^2 \tag{2.234}$$

and the solutions are sines and cosines:

$$\psi(x) = C\sin(kx) + D\cos(kx). \qquad -a < x < a \tag{2.235}$$

Since the potential is even in x we know that we can write the solutions as even and odd functions. For the even functions, $A = B$, and $C = 0$. For the odd functions, $B = -A$ and $D = 0$. As usual the wave function must be continuous at the edge of the well, and since the well is finite the derivative must also be continuous. Imposing these conditions at $x = a$, the even functions give us:

$$Be^{-\kappa a} = D\cos ka \tag{2.236}$$

$$-\kappa Be^{-\kappa a} = -kD\sin(ka) \tag{2.237}$$

while the odd functions give:

$$Be^{-\kappa a} = C\sin ka \tag{2.238}$$

$$-\kappa Be^{-\kappa a} = kC\cos(ka) \tag{2.239}$$

Two linear homogeneous equations in two unknowns can be solved only for certain values of the coefficients of the unknowns. By taking the ratios of the two equations in each pair, we see that:

$$k\tan(ka) = \kappa, \qquad \text{even solutions} \tag{2.240}$$

and:

$$k\cot(ka) = -\kappa, \qquad \text{odd solutions} \tag{2.241}$$

From Eqn. 2.234 :

$$\frac{\kappa^2}{k^2} = \frac{2mV_0}{\hbar^2k^2} - 1 \tag{2.242}$$

and two conditions can be written in terms of k as:

$$\tan(ka) = \sqrt{\frac{2mV_0}{\hbar^2 k^2} - 1} = \sqrt{\frac{V_0}{V_0 + E} - 1} \tag{2.243}$$

and:

$$\tan(ka) = -\frac{k}{\kappa} = \frac{-1}{\sqrt{\frac{V_0}{V_0+E} - 1}} \tag{2.244}$$

Note that:

$$\frac{V_0}{V_0 + E} > 1, \quad \text{since} E < 0 \tag{2.245}$$

These two conditions can be written more compactly by defining:

$$z^2 \equiv k^2 a^2 = \frac{2ma^2(V_0 + E)}{\hbar^2}, \qquad z_0^2 \equiv (2ma^2 V_0)/(\hbar^2) \tag{2.246}$$

$$\frac{z_0^2}{z^2} = \frac{V_0}{V_0 + E}$$

By substitution:

$$\tan(z) = \sqrt{(z_0/z)^2 - 1}, \qquad \text{even solutions} \tag{2.247}$$

$$\tan(z) = -\frac{1}{\sqrt{(z_0/z)^2 - 1}} \qquad \text{odd solutions} \tag{2.248}$$

Eqns. 2.247 and 2.248 for z are transcendental and must be solved numerically. These solutions for $z = ka$ specify the allowed values of:

$$E = \frac{\hbar^2 k^2}{2m} - V_0.$$

The solutions for a series of values of z_0 are illustrated graphically in Figs. 2.8 - 2.14

We obtain solutions only if $z < z_0$, No matter how small z_0 there will be at least one even solution. There is no odd solution unless $z_0 > \pi/2$. The total number of solutions is given by

$$N = \text{Int}(2z_0/\pi) + 1$$

where $\text{Int}(x)$ is the integer part of x.

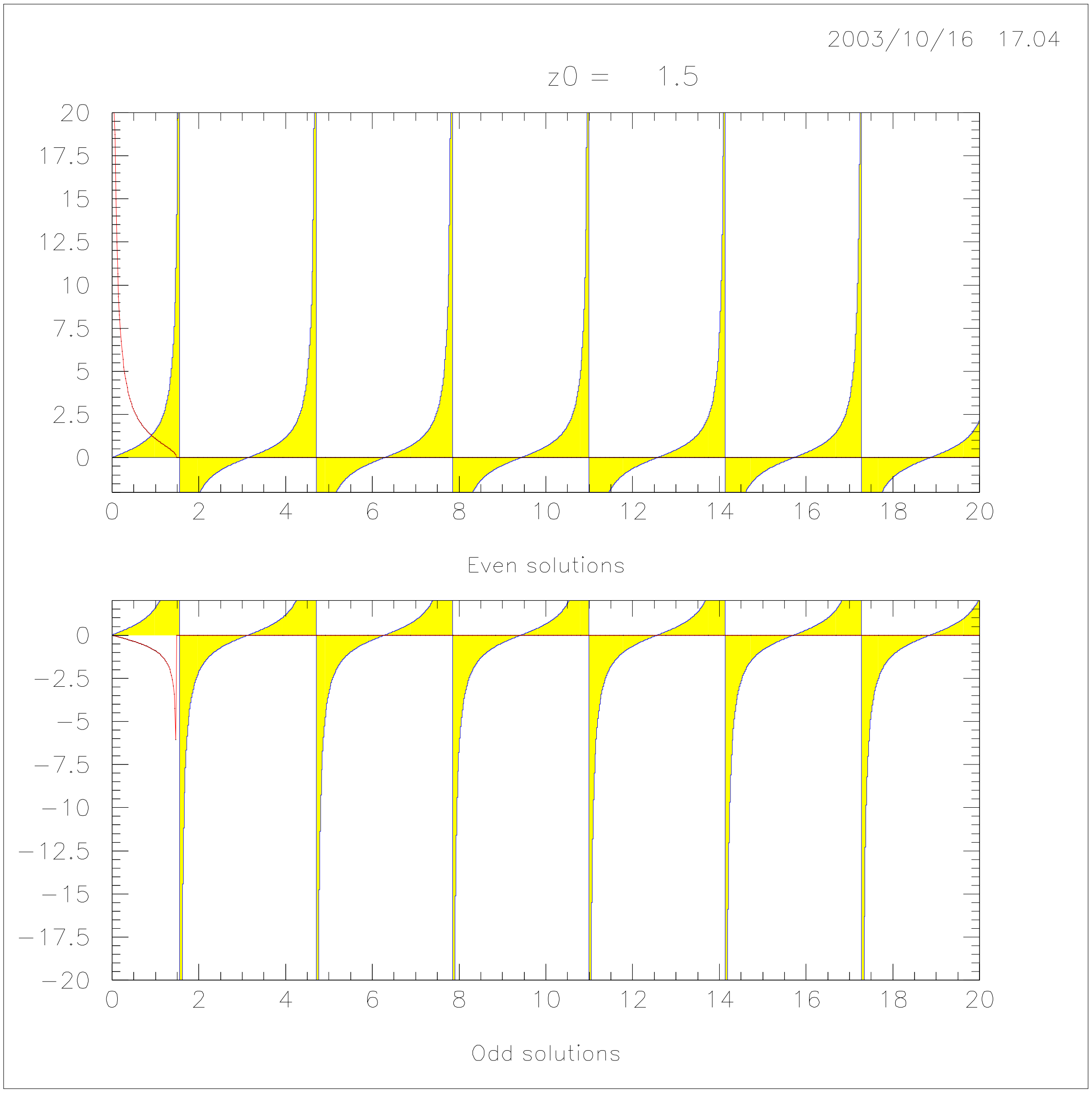

Figure 2.8: Bound states for finite square well ($z_0 = 1.5$).

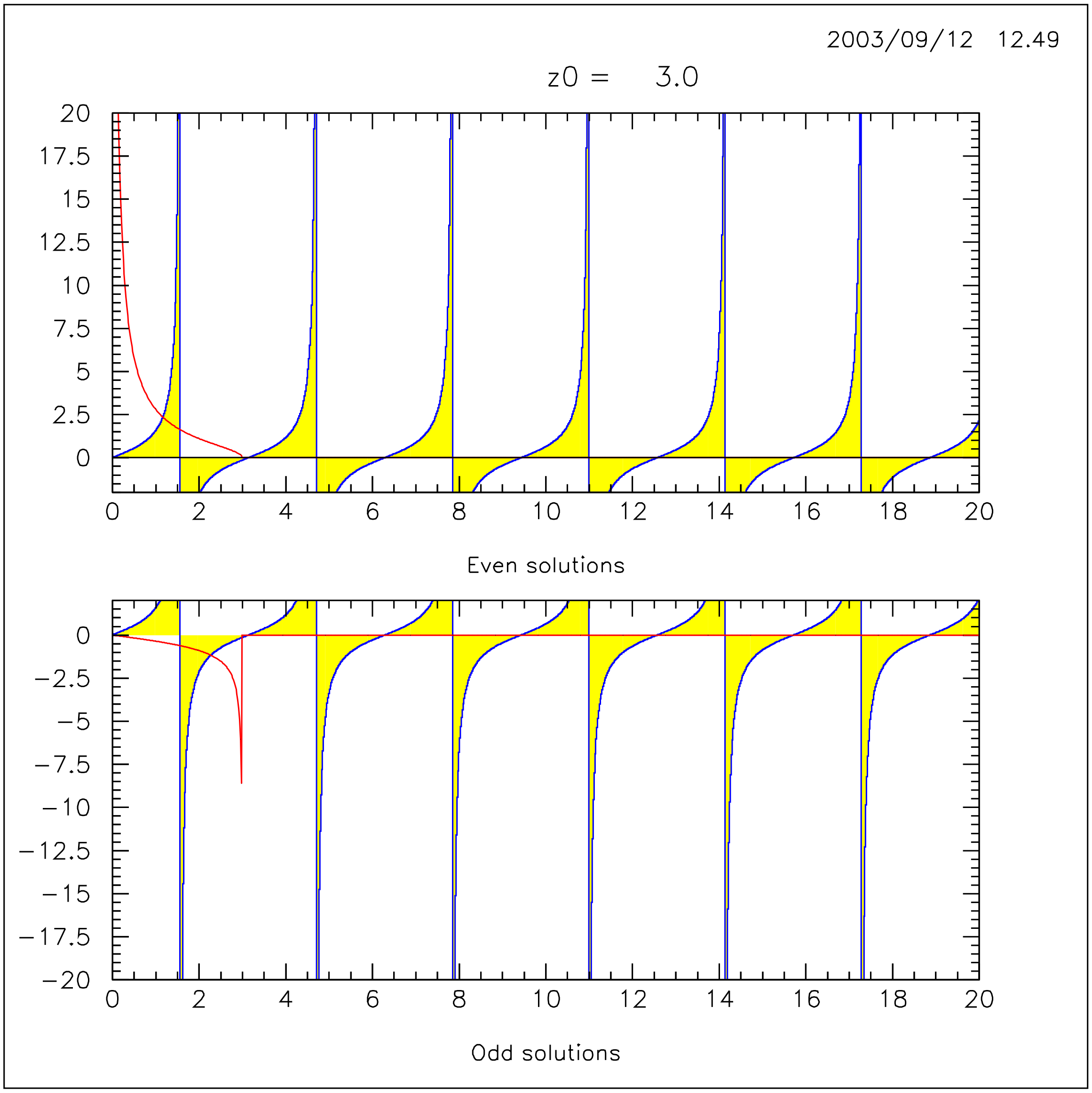

Figure 2.9: Bound states for finite square well ($z_0 = 3.0$).

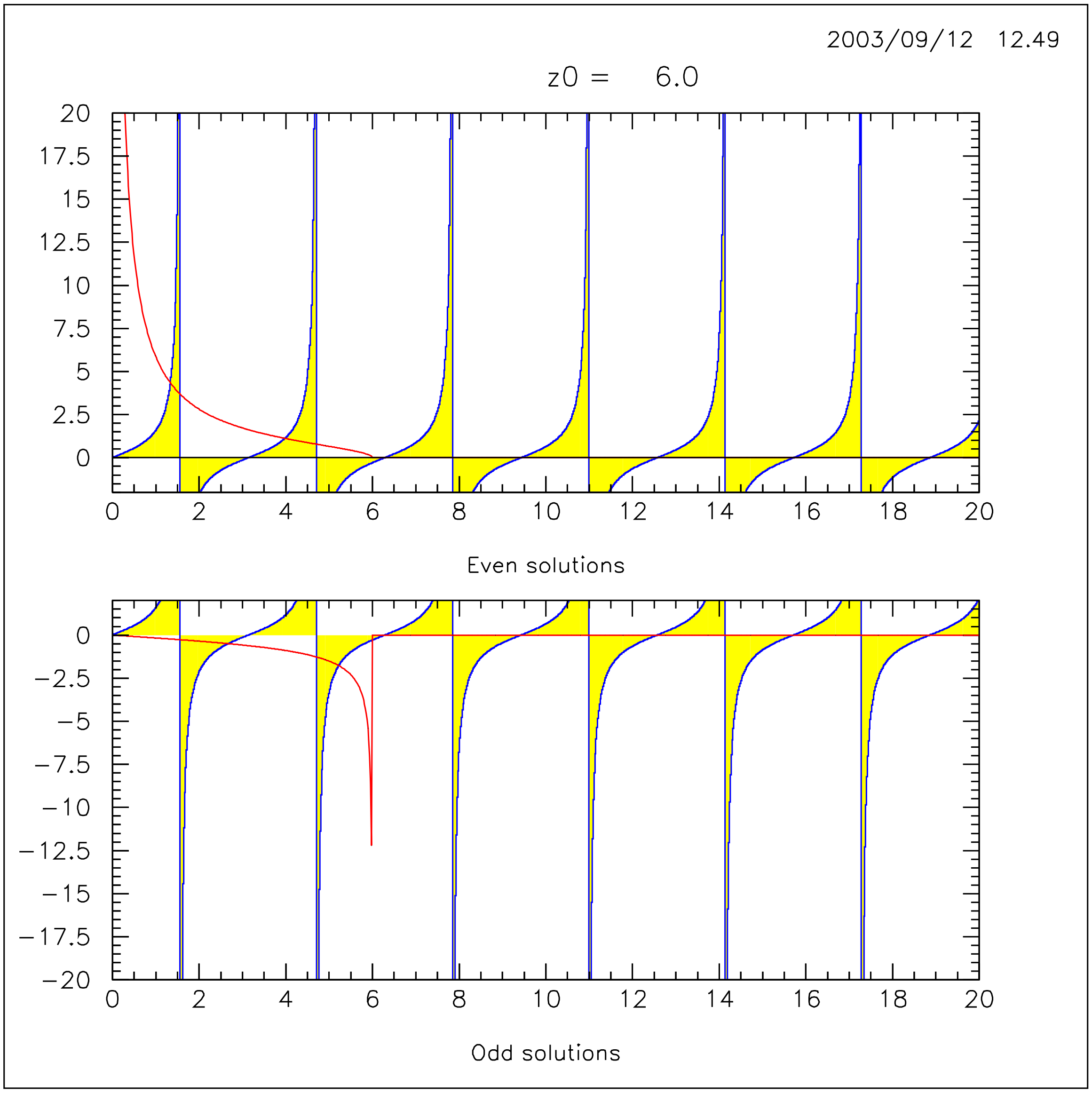

Figure 2.10: Bound states for finite square well ($z_0 = 6.0$).

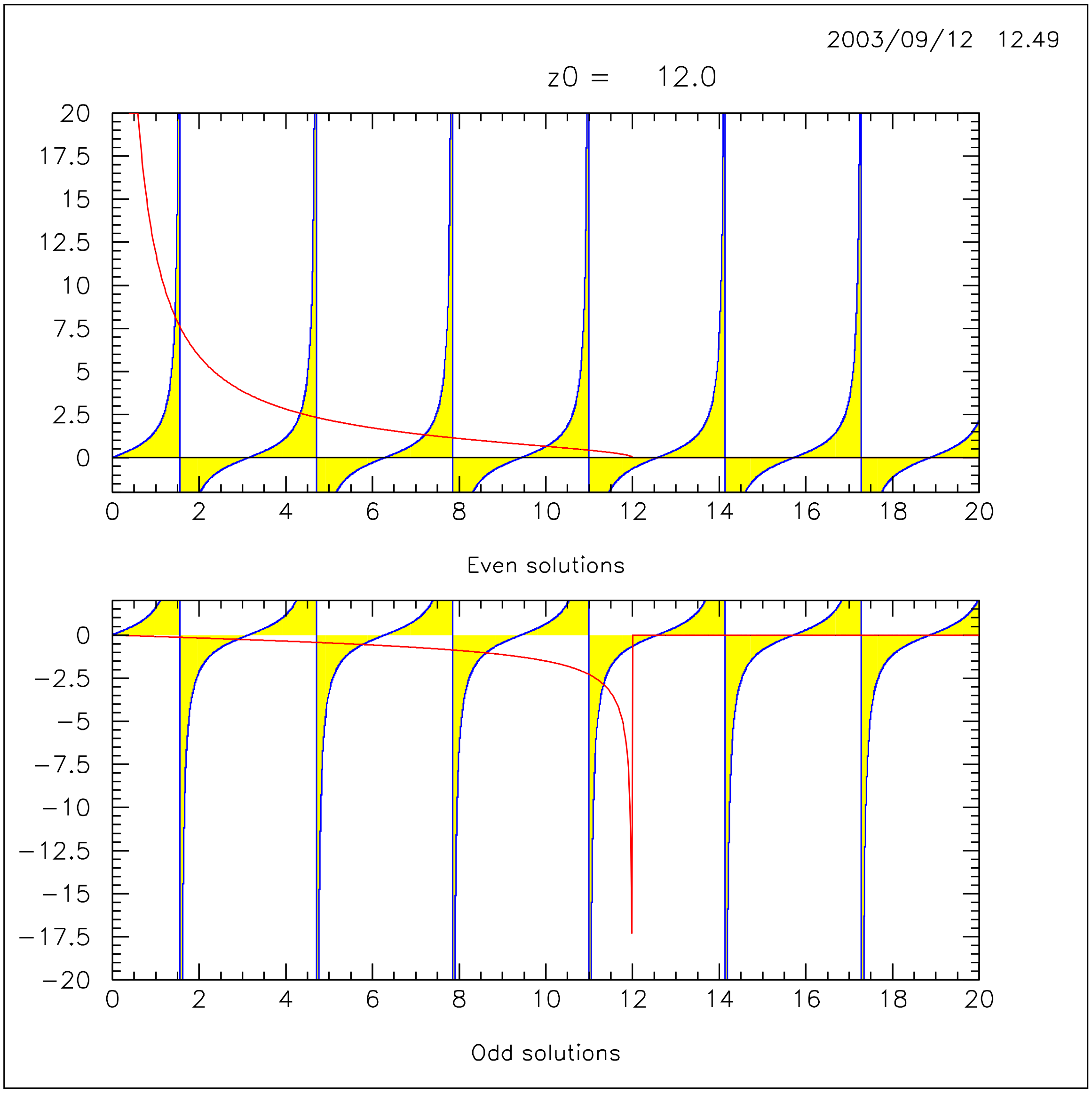

Figure 2.11: Bound states for finite square well ($z_0 = 12.0$).

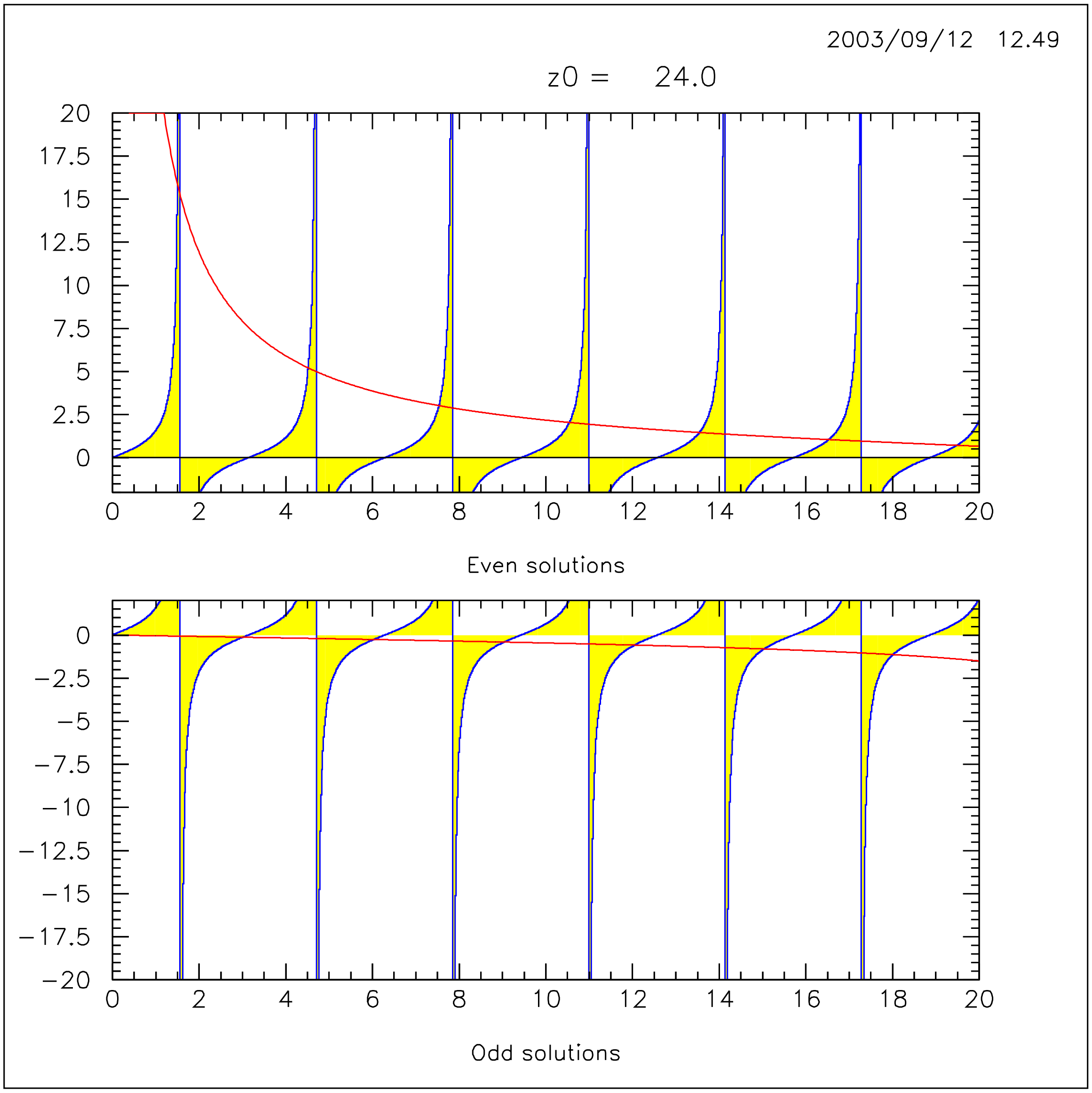

Figure 2.12: Bound states for finite square well ($z_0 = 24.0$).

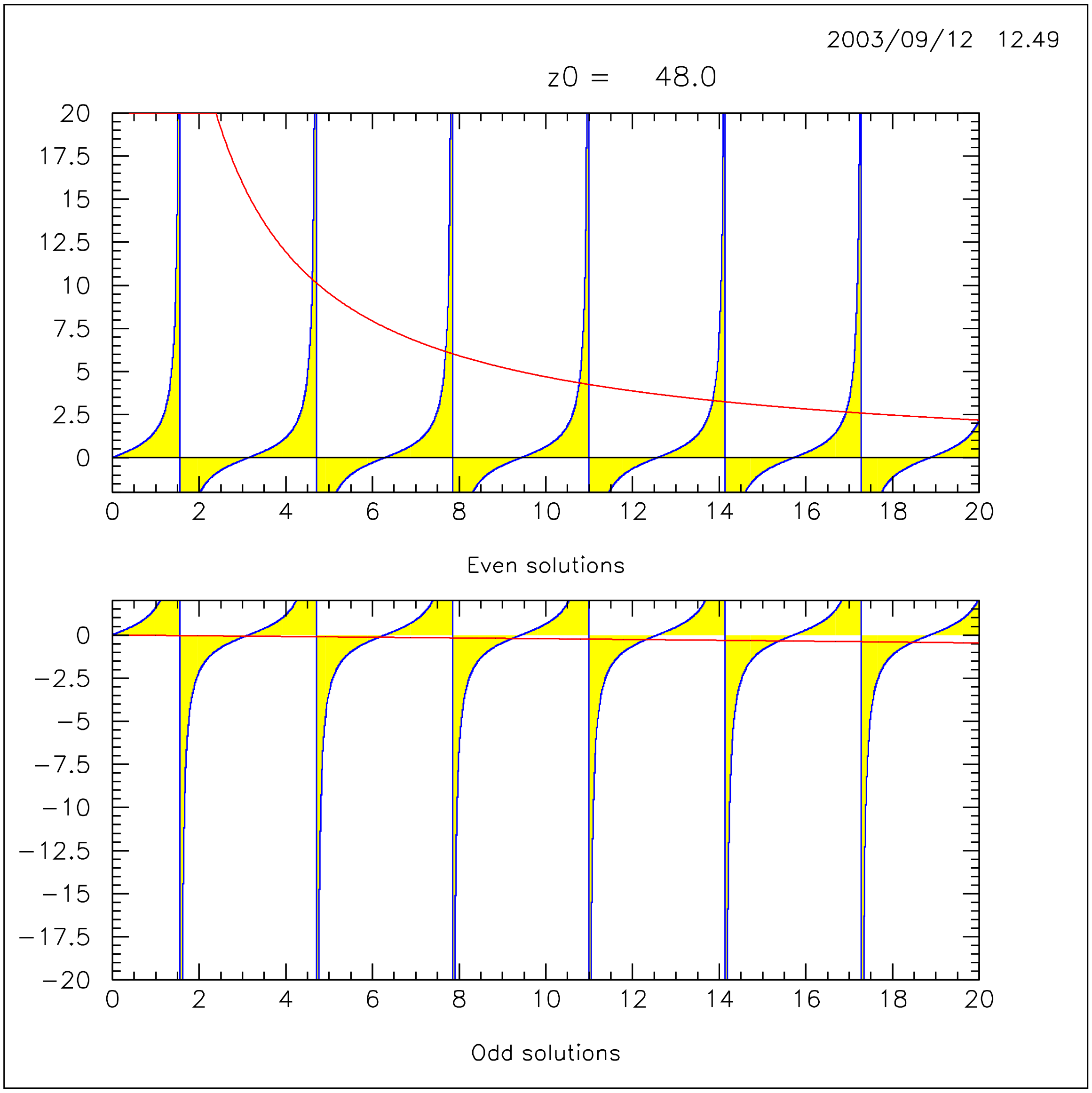

Figure 2.13: Bound states for finite square well ($z_0 = 48.0$).

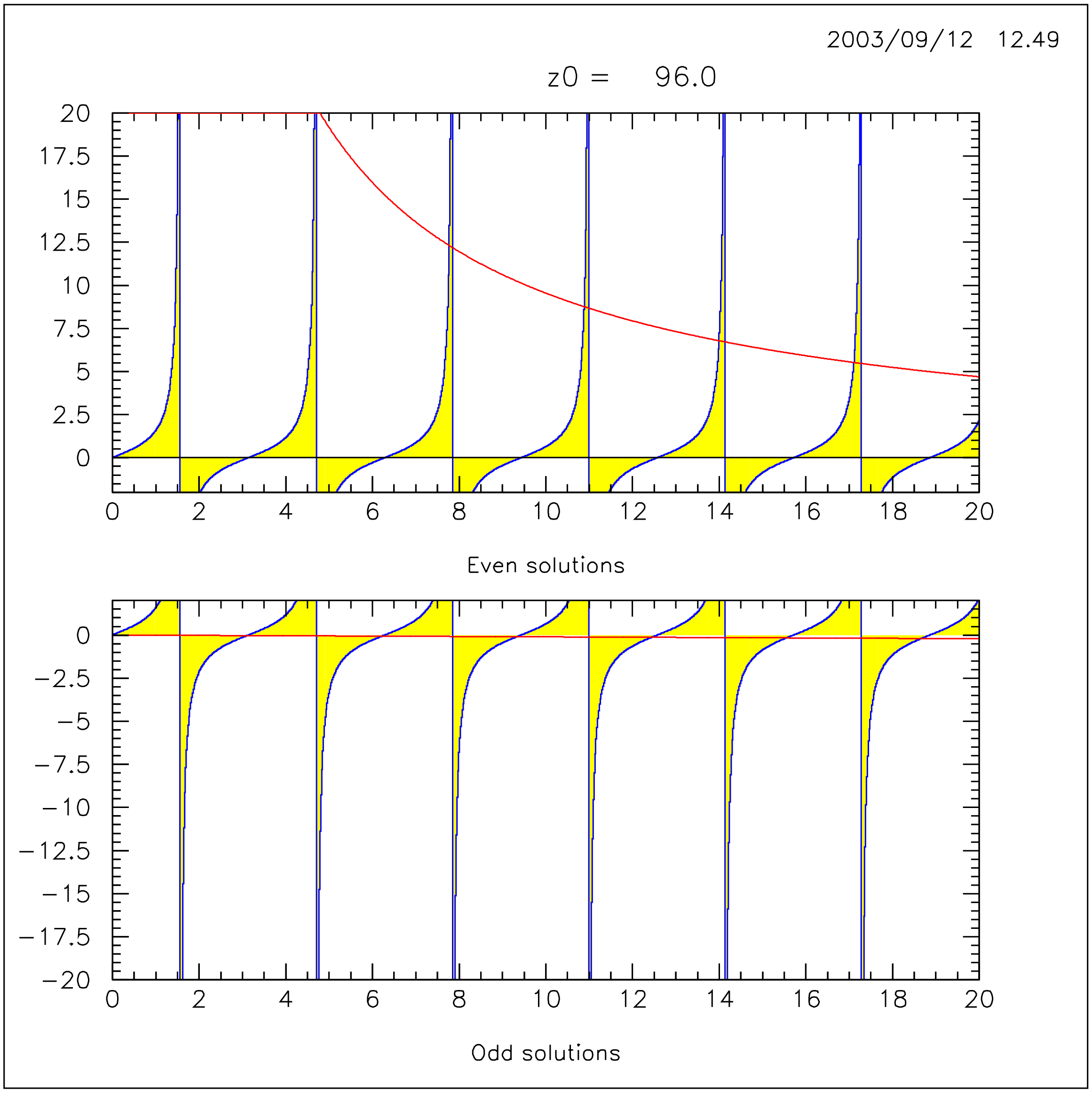

Figure 2.14: Bound states for finite square well ($z_0 = 96.0$).

For a **wide, deep well**, we can find many values of k for which $z_0 >> z$. For the even wave functions the solutions of the transcendental equation occur where $\tan(z)$ is very large so that:

$$z \approx (n - 1/2)\pi, \qquad n = 1, 2 \cdots \qquad \text{even wave} - \text{functions}$$

For the odd wave functions the solutions of the transcendental equation occur where $\tan(z)$ is close to 0 so that:

$$z \approx n\pi, \qquad n = 1, 2 \cdots \qquad \text{odd wave} - \text{functions}$$

We can summarize these solutions in one equation,

$$z \approx l\pi/2, \qquad l = 1, 2 \cdots$$

Inserting the definition of z:

$$z^2 = \frac{2ma^2(V_0 + E)}{\hbar^2} \approx l^2\pi^2/4$$

$$V_0 + E \approx \frac{l^2\hbar^2\pi^2}{8ma^2}$$

$$E \approx -V_0 + \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \qquad n = 1, 2, 3, \cdots \tag{2.249}$$

where odd values of n are associated with the even solutions and even values of n are associated with the odd solutions. The values of these energies relative to the bottom of the well are the energies associated with the infinite square well of width $2a$. The approximation that $z_0 >> z$ breaks down as $E_n \to 0$.

2.6.2 Scattering States

We can solve the equations for positive energies, using states outside the well corresponding to left-moving and right-moving waves, just as we did for the delta function potential. Inside the well, the wave function is a linear combination of sine and cosine functions. Matching the wave function and its derivative at $x = \pm a$, we can solve for the transmission and reflection coefficients.

$$\Psi = Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)} = (Ae^{ikx} + Be^{-ikx})e^{-i\omega t}, \qquad x < -a \tag{2.250}$$

Since the wave function in all three regions will have a common factor of $e^{-i\omega t}$, we can drop that term from the matching conditions and work with:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \qquad x < -a \tag{2.251}$$

$$\psi(x) = C\sin(\kappa x) + D\cos(\kappa x), \qquad -a < x < a \tag{2.252}$$

$$\psi(x) = Fe^{ikx}, \qquad x > a \tag{2.253}$$

For continuity of the wave function and its derivative at $x = \pm a$:

$$Ae^{-ika} + Be^{ika} = -C\sin(\kappa a) + D\cos(\kappa a) \tag{2.254}$$

$$Fe^{ika} = C\sin(\kappa a) + D\cos(\kappa a) \tag{2.255}$$

$$ikAe^{-ika} - ikBe^{ika} = \kappa[C\cos(\kappa a) + D\sin(\kappa a)] \tag{2.256}$$

$$ikFe^{ika} = \kappa[C\cos(\kappa a) - D\sin(\kappa a)] \tag{2.257}$$

Our goal is to solve for B and F in terms of A. We can simplify the arithmetic by defining some constants:

$$\alpha = \sin(\kappa a), \qquad \beta = \cos(\kappa a), \qquad \gamma = e^{ika}, \qquad r = \frac{\kappa}{ik} \tag{2.258}$$

$$-\gamma^2 Be - \alpha\gamma C + \beta\gamma D = A$$

$$\alpha C + \beta D + \gamma F = 0$$

$$\gamma^2 B - r\gamma[\beta C + \alpha D] = A$$

$$r\beta C - r\alpha D - \gamma F = 0$$

$$\begin{pmatrix} -\gamma^2 & -\alpha\gamma & \beta\gamma & 0 \\ 0 & \alpha & \beta & \gamma \\ \gamma^2 & -r\gamma\beta & -r\gamma\alpha & 0 \\ 0 & r\beta & -r\alpha & -\gamma \end{pmatrix} \begin{pmatrix} B \\ C \\ D \\ F \end{pmatrix} = A \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

If we denote the matrix by M, the desired solution is obtained by inverting it to obtain:

$$\begin{pmatrix} B \\ C \\ D \\ F \end{pmatrix} = AM^{-1} \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

The inverse matrix is:

$$M^{-1} =$$

$$\begin{pmatrix} \frac{r\cos(2\kappa a)-r^2\sin(2\kappa a)}{2\gamma^2 X_1} & r\frac{1}{2\gamma X_1} & -\frac{\sin(2\kappa a)+r\cos(2\kappa a)}{2\gamma^2 X_1} & -\frac{r}{2\gamma X_1} \\ -\frac{1}{2\gamma X_3} & \frac{1}{2X_3} & -\frac{1}{2\gamma X_3} & \frac{1}{2X_3} \\ -\frac{1}{2\gamma X_2} & -\frac{1}{2X_2} & -\frac{1}{2\gamma X_2} & -\frac{1}{2X_2} \\ \frac{r}{2\gamma^2 X_1} & \frac{r^2\sin(1\kappa a)-r\cos(2\kappa a)}{2\gamma X_1} & \frac{r}{2g^2 X_1} & \frac{r\cos(2\kappa a)+\sin(2\kappa a)}{2\gamma X_1} \end{pmatrix} \tag{2.259}$$

where:

$$X_1 \equiv \frac{1}{2}(r^2-1)\sin(2\kappa a) - r\cos(2\kappa a)$$

$$X_2 = r\sin(\kappa a) - \cos(\kappa a)$$

$$X_3 = r\cos(\kappa a) + \sin(\kappa a)$$

From this we obtain:

$$B/A = M^{-1}_{11} + M^{-1}_{13}$$

$$B/A = -e^{-2ika}\frac{(r^2+1)\sin(2\kappa a)}{(r^2-1)\sin(2\kappa a) - 2r\cos(2\kappa a)}$$

Replacing r with its definition from eqns. 2.258:

$$B/A = -e^{-2ika}\frac{(\kappa^2-k^2)\sin(2\kappa a)}{(\kappa^2+k^2)\sin(2\kappa a) + 2i\kappa k\cos(2\kappa a)} \tag{2.260}$$

The reflection coefficient is:

$$R = |B/A|^2 = \frac{(\kappa^2-k^2)^2\sin^2(2\kappa a)}{(\kappa^2+k^2)^2\sin^2(2\kappa a) + 4\kappa^2 k^2\cos^2(2\kappa a)} \tag{2.261}$$

For the transmitted wave:

$$\begin{aligned} F/A &= M^{-1}_{41} + M^{-1}_{43} \\ &= \frac{r}{g^2 X_1} = 2g^{-2}\frac{r}{(r^2-1)\sin(2\kappa a) - 2r\cos(2\kappa a)} \\ &= -e^{-2ika}\frac{2\kappa k}{2\kappa k\cos(2\kappa a) + i(k^2+\kappa^2)\sin(2\kappa a)} \end{aligned} \tag{2.262}$$

The transmission coefficient is:

$$T = |F/A|^2$$

$$T^{-1} = \cos^2(2\kappa a) + \frac{(k^2+\kappa^2)^2}{4\kappa^2 k^2}\sin^2(2\kappa a)$$

$$= 1 + \frac{(k^2 + \kappa^2)^2 - 4\kappa^2 k^2}{4\kappa^2 k^2} \sin^2(2\kappa a)$$

$$= 1 + \frac{(k^2 - \kappa^2)^2}{4\kappa^2 k^2} \sin^2(2\kappa a) \geq 1 \qquad (2.263)$$

If:

$$2\kappa a = \frac{2a}{\hbar}\sqrt{2m(E_n + V_0)} = n\pi \qquad (2.264)$$

$T = 1$, and the wave passes through the interaction region as if it weren't there. This is the condition for an integer number of half-wave lengths to fit inside the potential well. It is the same condition that we obtained for the stationary states of an infinite square well. For perfect transmission:

$$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2} \qquad (2.265)$$

which are the conditions for the stationary states of the infinite square well. This effect has been observed for the scattering of low energy electrons (≈ 0.7 eV) by rare gas atoms, and is known as the *Ramsauer effect.*