

As  $\delta z$  is an as yet undefined small step length along the  $z$ -axis, and as it only appears in equation (3.14) with the factor 2, then this finite-difference representation of the second derivative can be simplified slightly by substituting  $\delta z$  for  $2\delta z$ , i.e.

$$\frac{d^2 f}{dz^2} \approx \frac{f(z + \delta z) - 2f(z) + f(z - \delta z)}{(\delta z)^2} \quad (3.15)$$

### 3.4 Discretised Schrödinger equation

The time-independent Schrödinger equation may now be reformulated as a *difference equation*, in which the functions are expressed using discrete samples over a number of spatial points rather than as continuous analytical expressions.

As a starting point, consider a general, but simple (constant-mass) form for the time-independent Schrödinger equation, the analytical solutions of which have been extensively studied in the previous chapter:

$$-\frac{\hbar^2}{2m^*} \frac{\partial^2}{\partial z^2} \psi(z) + V(z)\psi(z) = E\psi(z) \quad (3.16)$$

where the one-dimensional potential  $V(z)$  will remain undefined and again  $\psi(z)$  is the wave function representing the particle of interest *while under the effective mass and envelope function approximations*.

Using the finite-difference form for the second derivative in the original Schrödinger equation and taking the step length  $\delta z$  as sufficiently small that the approximation is good, i.e. drop the ‘ $\approx$ ’ in favour of ‘=’, then:

$$-\frac{\hbar^2}{2m^*} \left[ \frac{\psi(z + \delta z) - 2\psi(z) + \psi(z - \delta z)}{(\delta z)^2} \right] + V(z)\psi(z) = E\psi(z) \quad (3.17)$$

This can be rearranged so that each sample of  $\psi(z)$  appears in the sequence:

$$a\psi(z - \delta z) + b(z)\psi(z) + c\psi(z + \delta z) = E\psi(z), \quad (3.18)$$

where

$$a = c = -\frac{\hbar^2}{2m^*(\delta z)^2} \quad \text{and} \quad b(z) = \frac{\hbar^2}{m^*(\delta z)^2} + V(z) \quad (3.19)$$

This equation describes how the wave function at point  $z$  is related to its value at neighbouring points, in terms of the potential, the mass and the energy of the state. It is important to note that this is a completely general equation, which can be applied to *any* one-dimensional confining potential. The following sections describe methods to solve this difference equation to find  $\psi(z)$  and  $E$ .

### 3.5 Shooting method

The discretised Schrödinger equation (equation (3.18)) can be written as:

$$\psi(z + \delta z) = \frac{1}{c}[E - b(z)]\psi(z) - \frac{a}{c}\psi(z - \delta z) \quad (3.20)$$

Since  $a = c$  (for constant effective mass), this can be simplified to obtain:

$$\psi(z + \delta z) = \frac{1}{c}[E - b(z)]\psi(z) - \psi(z - \delta z) \quad (3.21)$$

Equation (3.21) implies that if the wave function is known at the two points  $z - \delta z$  and  $z$ , then the value of the wave function at  $z + \delta z$  can be calculated for any energy  $E$ . This iterative equation forms the basis of a standard method of solving differential equations numerically, and is known as the *shooting method* [4].

Using two known values of the wave function  $\psi(z - \delta z)$  and  $\psi(z)$ , a third value, i.e.  $\psi(z + \delta z)$ , can be predicted. Using this new point  $\psi(z + \delta z)$ , together with  $\psi(z)$ , and by making the transformation  $z + \delta z \rightarrow z$ , a fourth point,  $\psi(z + 2\delta z)$ , can be calculated, and so on. Hence the complete wave function can be deduced for any particular energy. The solutions for stationary states have wave functions which satisfy the standard boundary conditions, i.e.

$$\psi(z) \rightarrow 0 \quad \text{and} \quad \frac{\partial}{\partial z}\psi(z) \rightarrow 0, \quad \text{as } z \rightarrow \pm\infty \quad (3.22)$$

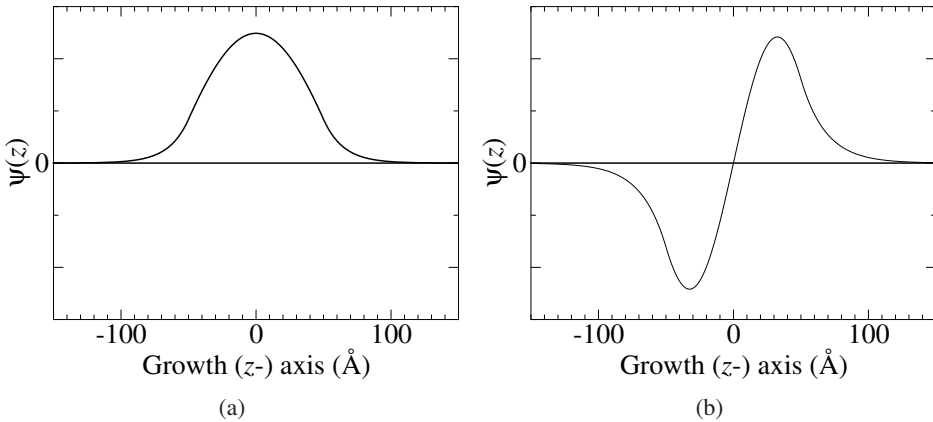


Figure 3.3: Wave functions for the (a) even-parity ground state and (b) odd-parity first excited state in a symmetrical quantum well

The first two values of the wave function necessary to start off the procedure *can* be deduced by using simple symmetry arguments, namely that if the potential  $V(z)$  is symmetric, then the eigenstates must be either symmetric (even parity) or anti-symmetric (odd parity). If the state of interest has odd parity, e.g. the first excited state of a symmetric quantum well, as illustrated in Fig. 3.3(b), then the wave function at the centre of the well (call this the origin  $z = 0$  for now) must be zero. Correspondingly, a small displacement along the growth ( $z$ -)direction must yield a finite value for the wave function. The actual magnitude is not relevant since the energy eigenvalues of the linear Schrödinger equation

are unchanged if the wave function is scaled by any given number. Hence in this case, the following starting conditions could be chosen:

$$\psi(0) = 0, \quad \psi(\delta z) = 1 \quad (3.23)$$

Given this, it remains to find the eigenvalue energy  $E$ . As stated above, the value of  $E$  corresponding to a stationary state, or more specifically in this case a confined state within a well potential, is that value which produces a wave function conforming to the standard boundary conditions. As  $E$  is an unknown in equation (3.21), then  $\psi$  is really a function of both position  $z$  and energy  $E$ , since given the starting conditions a wave function can be generated for any  $E$ —although it will not always tend to zero at infinity and be a stationary state. Thus the wave function should be written as  $\psi(z, E)$ , in which case solutions are sought to the equation:

$$\psi(\infty, E) = 0 \quad (3.24)$$

which can be found by using standard techniques such as the Newton–Raphson iteration (Section 3.2).

If the eigenstate of interest has even parity, e.g. the ground state of a symmetric quantum well, as shown in Fig. 3.3(a), then new starting conditions must be deduced. In particular, as the value of the wave function at the origin is non-zero, then  $\psi(0) = 1$  can be chosen. In addition, as the wave function is symmetric then  $\psi(-\delta z) = \psi(+\delta z)$ . Substituting both of these expressions into equation (3.21) then gives:

$$\psi(+\delta z) = \frac{1}{c}[E - b(0)] \times 1 - \psi(+\delta z) \quad (3.25)$$

$$\therefore \psi(+\delta z) = \frac{m^*(\delta z)^2}{\hbar^2} [V(0) - E] + 1 \quad (3.26)$$

### 3.6 Generalised initial conditions

While such initial (starting) conditions for symmetric potentials are very useful, they are restrictive in that there are many systems that do not have symmetric potentials, perhaps the most obvious being the quantum well with an electric field applied (see Section 2.10). To deduce more general starting conditions for the iterative equation (equation (3.21)), note that at the moment particles are always confined by potential barriers at the edges of the system. Hence, as stated above many times, all wave functions satisfy the standard boundary conditions:

$$\psi(z) \rightarrow 0 \quad \text{and} \quad \frac{\partial}{\partial z} \psi(z) \rightarrow 0, \quad \text{as } z \rightarrow \pm\infty \quad (3.27)$$

In addition, learning from the analytical solutions of the previous chapter, the wave function decays exponentially into the end barriers (see Fig. 3.4). The decay constant  $\kappa$  is also given by:

$$\kappa = \frac{\sqrt{2m^*(V - E)}}{\hbar} \quad (3.28)$$

Hence, upon choosing the first value of the wave function  $\psi(z - \delta z) = 1$ ,

$$\psi(z - \delta z) = \psi(z) \exp(-\kappa|\delta z|) \quad (3.29)$$

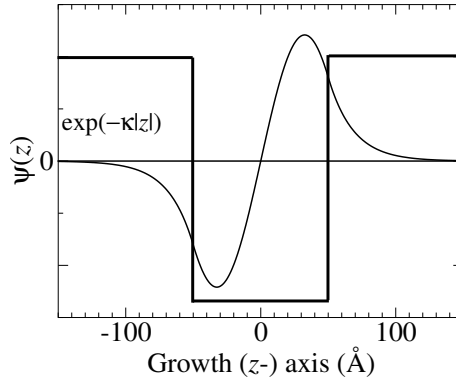


Figure 3.4: Exponential decay of the wave function into the end barrier

Therefore, given the starting value  $\psi(z - \delta z)$ , the next value  $\psi(z)$  can be calculated, thus implementing the boundary condition of exponential growth.

In practice, however, these boundary conditions *can* be unreliable, not because of the starting conditions they impose, but because of the boundary conditions that must be sought at the other end of the potential structure. The mathematics implies that energies must be sought for which  $\psi$  tends to zero; however, the original choice of  $\psi = 1$  at the start of the potential structure immediately implies an asymmetry. Generally this asymmetry is very small, but not always. In order to correct this asymmetry, the (at first sight bizarre) starting conditions are chosen as:

$$\psi(z - \delta z) = 0 \quad \text{and} \quad \psi(z) = 1 \quad (3.30)$$

Such starting conditions for the shooting method solution of the Schrödinger equation are important because of their generality. They are applicable to all potential profiles, whether symmetric or not, whether the outer barrier is flat or not, and whether the eigenstate of interest is symmetric, anti-symmetric or without definite parity.

These conditions can be partially justified mathematically. As multiplying an eigenstate (wave function  $\psi$ ) by a constant does not affect the eigenvalue (the energy  $E$ ), if the first wave function point,  $\psi(z - \delta z)$ , was taken as a small but finite value (say,  $\delta\psi$ ), then the second starting point,  $\psi(z)$ , could be given any value larger than  $\delta\psi$  (say,  $N\delta\psi$ ), where  $N$  is a large number, while still giving exponential growth and without changing the energy eigenvalue. The third value of the wave function simply follows from the shooting equation (equation (3.21)) as follows:

$$\psi(z + \delta z) = \left\{ \frac{2m^*}{\hbar^2} (\delta z)^2 [V(z) - E] + 2 \right\} N\delta\psi - \delta\psi \quad (3.31)$$

$$\therefore \psi(z + \delta z) = \left( \left\{ \frac{2m^*}{\hbar^2} (\delta z)^2 [V(z) - E] + 2 \right\} N - 1 \right) \delta\psi \quad (3.32)$$

These new starting conditions of 0 and 1 merely represent the limit of large  $N$ .

While the above only offers partial justification, full vindication will be given by the results of the convergence tests in the following sections.

### 3.7 Practical implementation of the shooting method

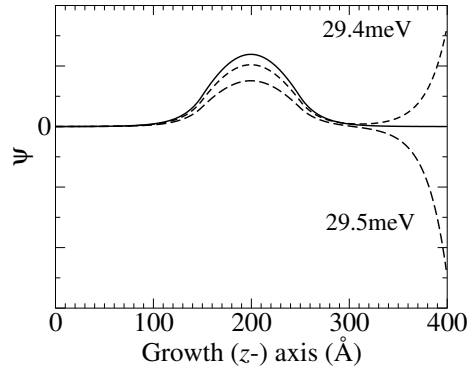


Figure 3.5: Numerically obtained wave functions above and below the true solution at  $E = 29.43$  meV, for an electron in a  $150 \text{ \AA}$   $\text{Ga}_{0.8}\text{Al}_{0.2}\text{As}/100 \text{ \AA}$   $\text{GaAs}/150 \text{ \AA}$   $\text{Ga}_{0.8}\text{Al}_{0.2}\text{As}$  single quantum well

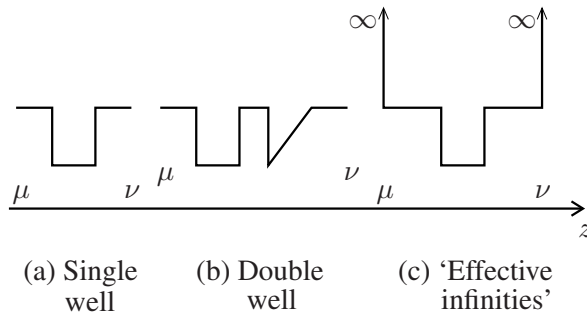


Figure 3.6: Schematic illustration of the extent of the potential  $V(z)$ , where  $\mu < z < \nu$

A two-stage search method may be used to locate the solutions of equation (3.21). First, the range of energies under consideration is divided coarsely into a set of discrete cells. In many cases, the states of interest are those that lie between the minimum and maximum values of the confining potential (i.e. the bound states). The size of each energy cell,  $\delta E$ , is selected to be smaller than the minimum energy spacing between states.

The sign of  $\psi(z \rightarrow \infty)$  is computed at the maximum and minimum energy of each cell, and a sign change indicates that a solution lies within that range. Figure 3.5 illustrates a true solution at  $E = 29.43$  meV, which satisfies the boundary condition at  $z \rightarrow \infty$ , and two incorrect solutions at energies slightly above and below the correct value. The wave functions

that correspond to the incorrect solutions are shown to diverge in opposite directions. Having detected the existence of a solution within a given cell, a Newton–Raphson iteration is then used to converge on the true solution to the desired precision.

In practice, the wave function iteration is begun a finite distance to the left of the first well in the potential and is halted a finite distance to the right of the last well (see Fig. 3.6). The potential, which can be merely a list of numbers specifying  $V(z)$  at regular intervals along the  $z$ -axis, defines the step length, the extent of the wave functions, and the effective infinities. The latter are the points by which the wave function is considered to have converged towards zero at both limits of the potential profile. Seeking solutions based on this criterion is, in effect, equivalent to applying infinite potentials a sufficient distance into the outer barriers of the finite structure, as shown in Fig. 3.6(c). The positions of these effective infinities,  $\mu$  and  $\nu$ , which are the lower and upper limits of the  $z$ -domain, should be chosen to be of sufficient extent so as not to affect the eigenvalues. Defining this mathematically:

$$\lim_{\mu \rightarrow -\infty} E = E_n \quad \text{and} \quad \lim_{\nu \rightarrow +\infty} E = E_n \quad (3.33)$$

where  $E_n$  are the set of true eigenenergies.

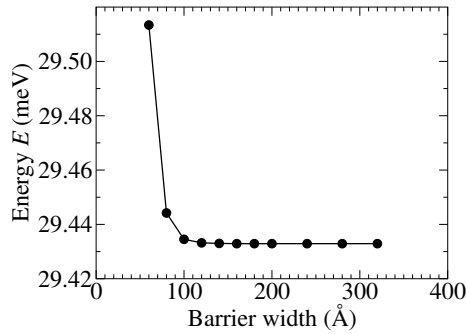


Figure 3.7: Effect of barrier width (effective infinities,  $\mu$  and  $\nu$ ) on energy

In Fig. 3.7 the left- and right-hand barriers are varied in thickness to illustrate the effect on the solution for the energy produced by this numerical method, for the single quantum well as discussed above. Clearly, the energy converges to a constant, which is the true stationary state—in this case, the ground state  $E_1$ . Thus if the energy is the only motivation for the calculation, any barrier width beyond, say, 150 Å will suffice. Note, however, that this can vary depending on the barrier height, well width and carrier effective mass.

If the wave function is also desired, e.g. to be used as an input for calculating another property, such as the exciton binding energy or an electron–phonon scattering rate, then greater care has to be taken. While very large outer barrier layers can be chosen to ensure convergence of the eigenenergy, this can have a detrimental effect on the wave function, as can be seen in Fig. 3.8. At too narrow a barrier width, e.g. the 60 Å case, although the energy may be returned to within 1 meV, the wave function does not satisfy the second of the standard boundary conditions, i.e.  $\psi' = 0$ . With a 200 Å barrier, which corresponds to

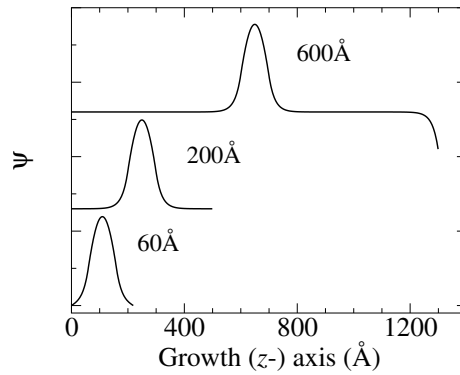


Figure 3.8: Effect of barrier width (effective infinities,  $\mu$  and  $\nu$ ) on the solution to the wave function

just after the energy has converged, the wave function is as expected and satisfies both the standard boundary conditions—this represents the optimal barrier width. However, at very large barrier widths, such as 600 Å as illustrated, the wave function is beginning to diverge, and, as stated above, although the energy obtained from such a solution is reliable, the wave function cannot be used to calculate other properties.

The energy  $E$  can always be obtained to far higher accuracy than would be required for comparison of, say, electron confinement energies with photoluminescence data. Computer codes typically assign 16-figure accuracy to a double-precision number, and the shooting method can be used to determine  $E$  to 12 of these, for example. However, even at this high accuracy the wave function at the end of an iteration, i.e. the value of  $\psi(\infty, E) = \psi(\nu, E)$ , cannot be made equal to zero for large barrier widths, simply because  $E$  cannot be stored to enough significant figures. If 32-figure accuracy could be used in the computing, then the wave function could be returned realistically for larger barrier widths.

The wave functions obtained from this numerical method are not normalised, i.e. they do not satisfy:

$$\int_{\text{all space}} \psi^*(z)\psi(z) \, dz = 1 \quad (3.34)$$

This can easily be achieved with the following transformation:

$$\psi(z) \rightarrow \frac{\psi(z)}{\sqrt{\int_{\text{all space}} \psi^*(z)\psi(z) \, dz}} \quad (3.35)$$

This numerical solution to a still simplistic Schrödinger equation is of use as it enables comparison with a number of curved potentials that have analytical solutions, such as the parabolic and the Pöschl–Teller potentials.