Single and Double δ-Function Potential

Single δ-Function Potential

$V(x) = -V_0 \delta(x)$ $\quad V_0 > 0$ attractive potential

The Schrodinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}u(x) - V_0\delta(x)u(x) = Eu(x)$$

$$\Rightarrow \frac{d^2}{dx^2}u(x) + \frac{2mE}{\hbar^2}u(x) = -\frac{2mV_0}{\hbar^2}\delta(x) = -\lambda\delta(x)$$

$$\lambda \equiv \frac{2mV_0}{\hbar^2}$$

$E<0$ $\quad \frac{d^2u}{dx^2} - \kappa^2 u(x) = 0$ for $x \neq 0$

$$\kappa^2 = \frac{2m|E|}{\hbar^2}$$

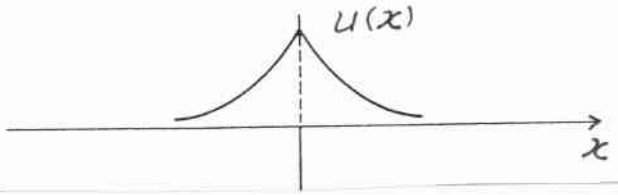
$u(x) = Ae^{-\kappa x} + A'e^{\kappa x}$ for $x>0$

$A' = 0$ required by normalization condition

$u(x) = Be^{\kappa x} + B'e^{-\kappa x}$ for $x<0$

$B' = 0$ required by normalization condition

The wave function must be continuous at $x=0 \Rightarrow A = B$



The derivative of the wave function has a discontinuity at $x=0$

$$\left(\frac{du}{dx}\right)_{x=0^+} - \left(\frac{du}{dx}\right)_{x=0^-} = -\lambda u(0)$$

$$-\kappa A - \kappa a = -\lambda A$$

$$\Rightarrow \kappa = \frac{\lambda}{2} \Rightarrow \frac{\lambda^2}{4} = \frac{2m|E|}{\hbar^2}$$

$$\Rightarrow \text{only at } |E| = \frac{\hbar^2\lambda^2}{8m} \text{ there exists solution}$$

Normalization $|A|^2 \left[\int_0^\infty e^{-2\kappa x} dx + \int_{-\infty}^0 e^{2\kappa x} dx \right] = 1$

$\Rightarrow |A|^2 \frac{1}{2\kappa} \cdot 2 = 1 \Rightarrow |A|^2 = \kappa$

$\Rightarrow A = \sqrt{\kappa}$

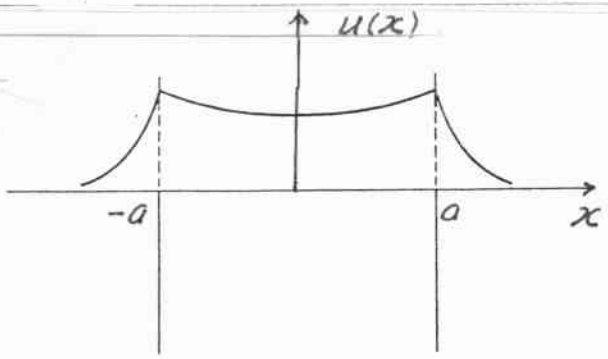
Double δ - Function Potential

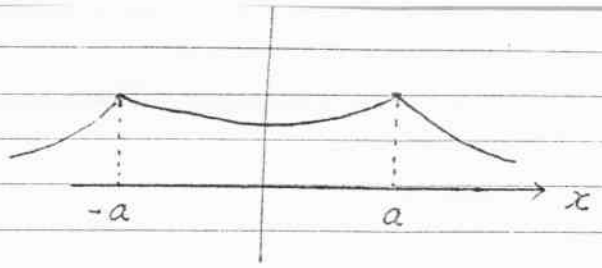
$V(x) = -V_0 \delta(x+a) - V_0 \delta(x-a)$

$V(-x) = V(x)$, the potential is symmetric under $x \to -x$.
The solution should be either even or odd
We shall discuss the case: $E < 0$

Even solution.
We are looking for the eigenvalue of the problem, we may leave the overall normalization to be open.

$u(x) = e^{-\kappa x}$ for $x > a$ ($e^{\kappa x}$ term is absent due to normalization requirement)
$u(x) = A \cosh \kappa x$ for $a > x > -a$ (originally, it is a linear combination of $e^{\kappa x}$ and $e^{-\kappa x}$, even solution requirement makes it possible to write it as $\cosh \kappa x$)
$u(x) = e^{\kappa x}$ for $x < -a$ (from even solution requirement)





Wave function is continuous at $x = a$

$$e^{-\kappa a} = A \cosh \kappa a$$

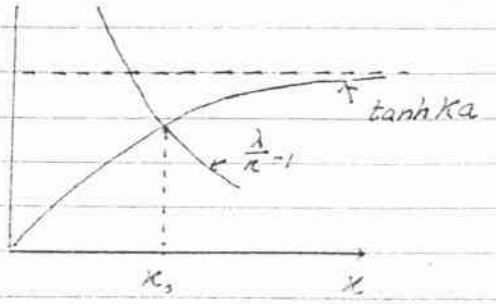
Derivative of the wave function has a discontinuity at $x = a$

$$-\kappa e^{-\kappa a} - \kappa A \sinh \kappa a = -\lambda e^{-\kappa a} \qquad \lambda = \frac{2mV_0}{\hbar^2}$$

$\downarrow$ $u(a)$

Due to symmetry requirement, the boundary condition at $x = -a$ will give no new result.

$$\Rightarrow \quad \tanh \kappa a = \frac{\lambda}{\kappa} - 1 \quad \text{eigenvalue equation}$$



$$\kappa = \sqrt{\frac{2m|E|}{\hbar^2}}$$

$\kappa_0 \rightarrow$ eigenvalue of energy

Discussion

$\tanh \kappa a > 0 \qquad \frac{\lambda}{\kappa_0} - 1 > 0 \Rightarrow \lambda > \kappa_0$

$\tanh \kappa a < 1 \qquad \frac{\lambda}{\kappa_0} - 1 < 1 \Rightarrow \frac{\lambda}{2} < \kappa_0$

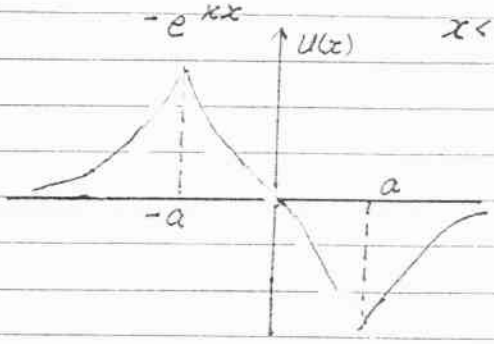
$\Rightarrow \quad \lambda > \kappa_0 > \frac{\lambda}{2}$ $\qquad \kappa = \frac{\lambda}{2}$ for single δ function

Energy of the double well is a larger negative number than that of a single δ function potential with the same strength

In real world, an electron bound to two nuclei seperated by a small distance (similar to a double δ-function potential) will have lower energy than bound to a single nuclei (similar to a single δ-function potential)

Odd solution

$$U(x) = \begin{cases} e^{-\kappa x} & x > a \\ A \sinh \kappa x & a > x > -a \\ -e^{\kappa x} & x < -a \end{cases}$$



Boundary condition at $x = a$

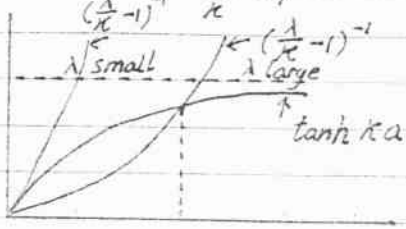
$$A \sinh \kappa a = e^{-\kappa a}$$

$$-\kappa e^{-\kappa a} - \kappa a \cosh \kappa a = -\lambda e^{-\kappa a}$$

$$\Rightarrow \quad \coth \kappa a = \frac{\lambda}{\kappa} - 1 \quad \Rightarrow \quad \tanh \kappa a = \frac{1}{(\frac{\lambda}{\kappa} - 1)}$$

$$\tanh \kappa a > 0 \quad \Rightarrow \quad \frac{\lambda}{\kappa} - 1 > 0 \quad \Rightarrow \quad \frac{\lambda}{\kappa} > 1 \quad \Rightarrow \quad \lambda > \kappa$$

$$\tanh \kappa a < 1 \quad \Rightarrow \quad \frac{1}{\frac{\lambda}{\kappa} - 1} < 1 \quad \Rightarrow \quad 1 < \frac{\lambda}{\kappa} - 1 \quad \Rightarrow \quad \kappa < \frac{\lambda}{2}$$



⇒ The odd solution, if there is a bound state, is less strongly bound than the even solution.
The wave function, which has to go through zero, is forced to be steep because the wells, and thus can only accommodate to a less rapidly falling exponential
Depending on the size of λ, there may or may not exist an odd bound state.

Supplement 4-C

Periodic Potentials

Metals generally have a crystalline structure; that is, the ions are arranged in a way that exhibits a spatial periodicity. In our one-dimensional discussion of this topic, we will see that this periodicity has two effects on the motion of the free electrons in the metal. One is that for a perfect *lattice*—that is, for ions spaced equally—the *electron propagates without reflection*; the other is that there are restrictions on the energies allowed for the electrons; that is, *there are allowed and forbidden energy "bands."*

We begin with a discussion of the consequences of perfect periodicity.

The periodicity will be built into the potential, for which we require that

$$V(x + a) = V(x) \tag{4C-1}$$

Since the kinetic energy term $-(\hbar^2/2m)(d^2/dx^2)$ is unaltered by the change $x \to x + a$, the whole *Hamiltonian is invariant under displacements by a*. For the case of zero potential, when the solution corresponding to a given energy $E = \hbar^2k^2/2m$ is

$$\psi(x) = e^{ikx} \tag{4C-2}$$

the displacement yields

$$\psi(x + a) = e^{ik(x+a)} = e^{ika}\psi(x) \tag{4C-3}$$

that is, the original solution multiplied by a phase factor, so that

$$|\psi(x + a)|^2 = |\psi(x)|^2 \tag{4C-4}$$

The observables will therefore be the same at x as at $x + a$; that is, we cannot tell whether we are at x or at $x + a$. In our example we shall also insist that $\psi(x)$ and $\psi(x + a)$ differ only by a phase factor, which need not, however, be of the form e^{ika}.

We digress briefly to discuss this requirement more formally. The invariance of the Hamiltonian under a displacement $x \to x + a$ can be treated formally as follows. Let D_a be an operator whose rule of operation is that

$$D_a f(x) = f(x + a) \tag{4C-5}$$

The invariance implies that

$$[H, D_a] = 0 \tag{4C-6}$$

We can find the eigenvalues of this operator by noting that

$$D_a\psi(x) = \lambda_a\psi(x) \tag{4C-7}$$

together with

$$D_{-a}D_a f(x) = D_aD_{-a} f(x) = f(x) \tag{4C-8}$$

implies that $\lambda_a\lambda_{-a} = 1$. This then implies that λ_a must be of the form e^{iqa}. Here q must be real, because if q had an imaginary part, a succession of displacements by a would make the wave function larger and larger with each displacement in one or the other direction.

Consider now a simultaneous eigenfunction of H and D_a, and define

$$u(x) = e^{-iqx}\psi(x) \tag{4C-9}$$

Then, using the fact that $\lambda_a = e^{iqa}$, we get

$$D_a u(x) = e^{-iq(x+a)}D_a\psi(x) = e^{-iq(x+a)}e^{iqa}\psi(x) = e^{-iqx}\psi(x) = u(x) \tag{4C-10}$$

This means that $u(x)$ is a periodic function obeying $u(x + a) = u(x)$. The upshot is that a function which is a simultaneous eigenfunction of H and D_a must be of the form

$$\psi(x) = e^{iqx}u(x) \tag{4C-11}$$

with $u(x)$ periodic. This result is known as *Bloch's Theorem.*

For a free particle $q = k$, the wave number corresponds to the energy E. More generally, the relation between q and k is more complicated. In any case, it is clear that (4C-4) holds, so that the net flux is unchanged as we go from x to $x + a$, and by extension to $x + na$. This means that an electron propagates without a change in flux.

Let us consider a series of ions in a line, with their centers located at $x = na$. To avoid having to deal with *end effects*, we assume that there are N ions placed on a very large ring, so that $n = 1$ and $n = N + 1$ are the same site. We will assume that the most loosely bound electrons—the ones that are viewed as "free"—are still sufficiently strongly bound to the ions that their wave functions do not overlap more than one or two nearest neighbors. We may now ask: What is the effect of this overlap on the energies of the electrons?

To answer this question, we consider first a classical analogy. We represent the electrons at the different sites by simple harmonic oscillators, all oscillating with the same angular frequency ω. In the absence of any coupling between the oscillators, we have the equation of motion

$$\frac{d^2x_n}{dt^2} = -\omega^2 x_n \qquad (n = 0, 1, 2, \ldots) \tag{4C-12}$$

If the harmonic oscillators are coupled to their nearest neighbors, then the equation is changed to

$$\frac{d^2x_n}{dt^2} = -\omega^2 x_n - K[(x_n - x_{n-1}) + (x_n - x_{n+1})] \tag{4C-13}$$

To solve this we write down a trial solution

$$x_n = A_n \cos \Omega t \tag{4C-14}$$

When this is substituted into (4C-13), we get

$$(\omega^2 - \Omega^2)A_n = -K(2A_n - A_{n-1} - A_{n+1}) \tag{4C-15}$$

This is known as a *difference equation*. We solve it by a trial solution. Let us assume that

$$A_n = L^n \tag{4C-16}$$

The identification of the sites at $n = 1$ and $N + 1$ implies $A_1 = A_{N+1}$ so that $L^N = 1$. This means that

$$L = e^{2\pi ir/N} \qquad r = 0, 1, 2, \ldots, (N - 1) \tag{4C-17}$$

The equation for the frequency Ω now yields

$$\omega^2 - \Omega^2 = -2K\left(1 - \cos\frac{2\pi r}{N}\right) = -4K \sin^2\frac{\pi r}{N}$$

The result

$$\Omega^2 = \omega^2 + 4K \sin^2\frac{\pi r}{N} \tag{4C-18}$$

shows that the frequencies, which, without coupling are all ω—that is, are *N-fold degenerate* (which corresponds to all the pendulums moving together)—are now spread over a range from ω to $\sqrt{\omega^2 + 4K}$. For large N there are many such frequencies, and they can be said to form a *band*. If we think of electrons as undergoing harmonic oscillations about their central locations, we can translate the above into a statement that in the absence of neighbors, all electron energies are degenerate, and the interaction with neighboring atoms spreads the energy values. We can, of course, have several fundamental frequencies ω_1, ω_2, . . . , and different couplings to their neighbors, with strengths K_1, K_2, . . . , which will then give rise to several bands that may or may not overlap.

The spreading of the frequencies is the same effect as the spreading of the energy levels of the most loosely bound electrons. For atoms far apart, with spacing larger than the exponential fall-off of the wave functions, all the energies are the same so that we have an N-fold degenerate single energy. Because the atoms are not so far apart, there is some coupling between nearest neighbors, and the energy levels spread. The classical analogy is suggestive, but not exact, since for the quantum case levels are pushed up as well as down, whereas all the frequencies above, lie above ω. Later we solve the Kronig-Penney model in which the potential takes the form

$$V(x) = \frac{\hbar^2}{2m}\frac{\lambda}{a}\sum_{-\infty}^{\infty}\delta(x - na) \tag{4C-19}$$

The solution can be shown to lead to a condition on q, which reads

$$\cos qa = \cos ka + \frac{1}{2}\lambda\frac{\sin ka}{ka} \tag{4C-20}$$

As can be seen from Figure (4C-1), this clearly shows the energy band structure.

THE KRONIG-PENNEY MODEL

To simplify the algebra, we will take a series of repulsive delta-function potentials,

$$V(x) = \frac{\hbar^2}{2m}\frac{\lambda}{a}\sum_{n=-\infty}^{\infty}\delta(x - na) \tag{4C-21}$$

Away from the points $x = na$, the solution will be that of the free-particle equation—that is, some linear combination of sin kx and cos kx (we deal with real functions for simplicity). Let us assume that in the region R_n defined by $(n - 1)\,a \leq x \leq na$, we have

$$\psi(x) = A_n \sin k(x - na) + B_n \cos k(x - na) \tag{4C-22}$$

and in the region R_{n+1} defined by $na \leq x \leq (n + 1)\,a$ we have

$$\psi(x) = A_{n+1} \sin k[x - (n + 1)\,a] + B_{n+1} \cos k[x - (n + 1)\,a] \tag{4C-23}$$

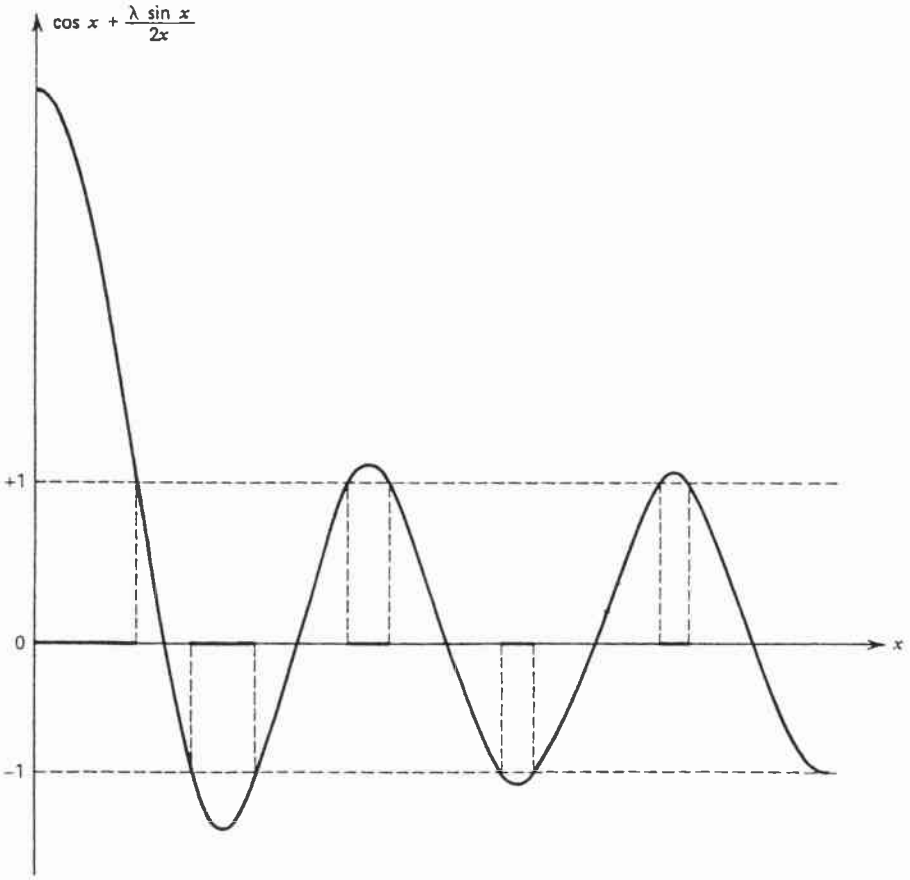


Figure 4C-1 Plot of $\cos x + (\lambda/2)(\sin x/x)$ as a function of x. The horizontal lines represent the bounds ± 1. The regions of x for which the curve lines outside the strip are forbidden.

Continuity of the wave function implies that ($x = na$)

$$-A_{n+1} \sin ka + B_{n+1} \cos ka = B_n \tag{4C-24}$$

and the discontinuity condition (4-68) here reads

$$kA_{n+1} \cos ka + kB_{n+1} \sin ka - kA_n = \frac{\lambda}{a} B_n \tag{4C-25}$$

A little manipulation yields

$$\begin{aligned} A_{n+1} &= A_n \cos ka + (g \cos ka - \sin ka) B_n \\ B_{n+1} &= (g \sin ka + \cos ka) B_n + A_n \sin ka \end{aligned} \tag{4C-26}$$

where $g = \lambda/ka$.

The requirement from Bloch's theorem that

$$\psi(x + a) = e^{iq(x+a)} u(x + a) = e^{iq(x+a)} u(x) = e^{iqa} \psi(x) \tag{4C-27}$$

implies that the wave functions in the adjacent regions R_n and R_{n+1} are related, since the wave function in (4C-22) may be written as

$$\psi(x) = A_n \sin[k((x+a)-(n+1)a] + B_n \cos k[k((x+a)-(n+1)a]$$

which is identical to that in (4C-23), provided

$$\begin{aligned} A_{n+1} &= e^{iqa} A_n \\ B_{n+1} &= e^{iqa} B_n \end{aligned} \tag{4C-28}$$

When this is inserted into the (4C-26), that is, into the conditions that the wave equation obeys the Schrödinger equation with the delta function potential, we get

$$\begin{aligned} A_n(e^{iqa} - \cos ka) &= B_n(g \cos ka - \sin ka) \\ B_n(e^{iqa} - (g \sin ka + \cos ka)) &= A_n \sin ka \end{aligned} \tag{4C-29}$$

This leads to the condition

$$(e^{iqa} - \cos ka)(e^{iqa} - (g \sin ka + \cos ka)) = \sin ka(g \cos ka - \sin ka) \tag{4C-30}$$

This may be rewritten in the form

$$e^{2iqa} - 2(\cos ka + \frac{g}{2} \sin ka)e^{iqa} + 1 = 0 \tag{4C-31}$$

This quadratic equation can be solved, and both real and imaginary parts lead to the condition

$$\cos qa = \cos ka + \frac{\lambda}{2} \frac{\sin ka}{ka} \tag{4C-32}$$

This is a very interesting result, because the left side is always bounded by 1; that is, there are restrictions on the possible ranges of the energy $E = \hbar^2 k^2/2m$ that depend on the parameters of our "crystal." Figure 4C-1 shows a plot of the function $\cos x + \lambda \sin x/2x$ as a function of $x = ka$. The horizontal line represents the bounds on $\cos qa$, and the regions of x, for which the curve lies outside the strip, are forbidden regions. Thus there are *allowed energy bands* separated by regions that are forbidden. Note that the onset of a forbidden band corresponds to the condition

$$qa = n\pi \qquad n = \pm 1, \pm 2, \pm 3, \ldots \tag{4C-33}$$

This, however, is just the condition for Bragg reflection with normal incidence. The existence of energy gaps can be understood qualitatively. In first approximation the electrons are free, except that there will be Bragg reflection when the waves reflected from successive atoms differ in phase by an integral number of 2π—that is, when (4C-33) is satisfied. These reflections give rise to standing waves, with even and odd waves of the form $\cos \pi x/a$ and $\sin \pi x/a$, respectively. The energy levels corresponding to these standing waves are degenerate. Once the attractive interaction between the electrons and the positively charged ions at $x = ma$ (m integer) is taken into account, the even states, peaked in between, will move up in energy. Thus the energy degeneracy is split at $q = n\pi/a$, and this leads to energy gaps, as shown in Fig. 4C-1.

The Kronig-Penney model has some relevance to the theory of metals, insulators, and semiconductors if we take into account the fact (to be studied later) that energy levels

occupied by electrons cannot accept more electrons. Thus a metal may have an energy band partially filled. If an external field is applied, the electrons are accelerated, and if there are momentum states available to them, the electrons will occupy the momentum states under the influence of the electric field. Insulators have completely filled bands, and an electric field cannot accelerate electrons, since there are no neighboring empty states. If the electric field is strong enough, the electrons can "jump" across a forbidden energy gap and go into an empty allowed energy band. This corresponds to the breakdown of an insulator. The semiconductor is an insulator with a very narrow forbidden gap. There, small changes of conditions, such as a rise in temperature, can produce the "jump" and the insulator becomes a conductor.

The band structure is of great relevance in solid state physics. Fig. 4C-2 shows three situations that can arise when energy levels are filled with electrons. We shall learn in Chapter 13 that only two electrons are allowed per energy level. In case (*a*) the electrons fill all the energy levels below the edge of the energy gap. The application of a weak electric field will have no effect on the material. The electrons near the top of the filled band cannot be accelerated. There are no levels with higher energy available to them. Materials in which this occurs are *insulators*; that is, they do not carry currents when electric fields are applied. In case (*b*) the energy levels are only partly filled. In this case the application of an electric field accelerates the electrons at the top of the stack of levels. These electrons have empty energy levels to move into, and they would accelerate indefinitely in a perfect lattice, as stated in the previous section. What keeps them from doing that is *dissipation*. The lattice is not perfect for two reasons: one is the presence of impurities, which destroys the perfect periodicity; the other is the effect of thermal agitation on the position of the ions forming the lattice, which has the same effect of destroying perfect periodicity. Materials in which the energy levels below the gaps are only partially filled are *conductors*.

The width of the gaps in the energy spectrum depends on the materials. For some insulators the gaps are quite narrow. When this happens, then at finite temperatures T, there is a calculable probability that some of the electrons are excited to the bottom of the set of energy levels above the gap. (To good approximation the probability is proportional to the Boltzmann factor $e^{-E/kT}$). These electrons can be accelerated as in a conductor, so that the application of an electric field will give rise to a current. The current is augmented by another effect: the energy levels that had been occupied by the electrons promoted to the higher energy band (called the *conduction band*) are now empty. They provide vacancies into which electrons in the lower band (called the *valence band*) can be accelerated into,

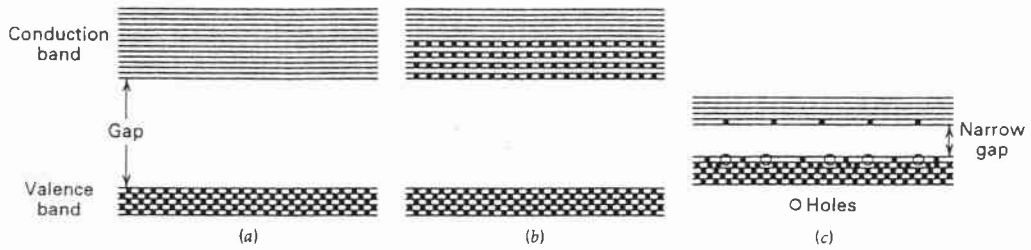


Figure 4C-2 Occupation of levels in the lowest two energy bands, separated by a gap. (*a*) Insulator has a completely filled band. Electrons cannot be accelerated into a nearby energy level. (*b*) Conductor has a half-filled band, allowing electrons to be accelerated into nearby energy levels. (*c*) In a semiconductor, thermal effects promote some electrons into a second band. These electrons can conduct electricity. The electrons leave behind them *holes* that act as positively charged particles and also conduct electricity.

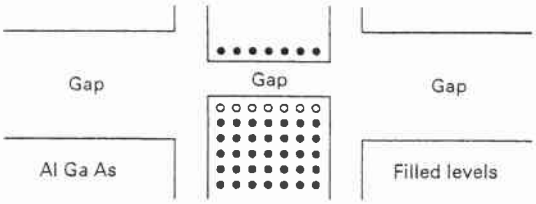


Figure 4C-3 Schematic picture of electrons and holes trapped in a well created by adjacent semiconductors with a wider gap. An example of such a heterostructure is provided by a layer of GaAs sandwiched between two layers of AlGaAs.

when an electric field is applied. These vacancies, called *holes*, propagate in the direction opposite to that of the electrons and thus add to the electric current. This is the situation shown in Fig. 4C-2(*c*).

The technology of making very thin layers of compounds of materials has improved in recent decades to such an extent that it is possible to create the analog of the infinite wells discussed in Chapter 3. Consider a "sandwich" created by two materials. The outer one has a larger energy gap than the inner one, as shown in Fig. 4C-3. The midpoints of the gaps must coincide[1] (for equilibrium reasons). The result is that both electrons and holes in the interior semiconductor cannot move out of the region between the outer semiconductors, because there are no energy levels that they can move to. Such confined regions may occur in one, two, or three dimensions. In the last case we deal with *quantum dots*. The study of the behavior of electrons in such confined regions is a very active field of research in the study of materials.

In summary, one-dimensional problems give us a very important glimpse into the physics of quantum systems in the real world of three dimensions.

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[1]A brief, semiquantitative discussion of this material may be found in *Modern Physics* by J. Bernstein, P. M. Fishbane, and S. Gasiorowicz (Prentice Hall, 2000). See also Chapter 44 in *Physics for Scientists and Engineers*, (2nd Edition) by P. M. Fishbane, S. Gasiorowicz and S. T. Thornton (Prentice Hall, 1996). There are, of course, many textbooks on semiconductors, which discuss the many devices that use *bandgap engineering* in great quantitative detail. See in particular L. Solymar and D. Walsh, *Lectures on the Electrical Properties of Materials*, Oxford University Press, New York (1998).

One-dimensional potentials: potential step

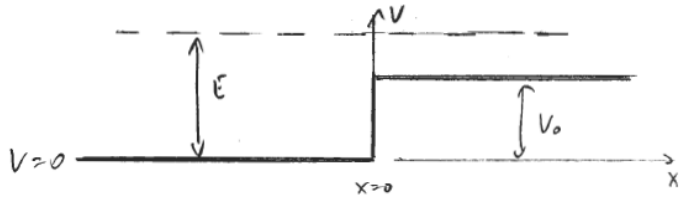

Figure I: Potential step of height V_0. The particle is incident from the left with energy E.

We analyze a time independent situation where a current of particles with a well-defined energy is incident on the barrier. The time-independent SE is

$$\hat{H}u(x) = Eu(x) \tag{15-1}$$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2}(x) + V(x)u(x) = Eu(x) \tag{15-2}$$

$$\frac{d^2u}{dx^2} = -\frac{2m}{\hbar^2}[E - V(x)]u(x) \tag{15-3}$$

Qualitative features of solutions for regions of constant V_1:

If $E - V_1 > 0$, the solutions are of the form $e^{\pm ik_1 x}$ with $\frac{\hbar^2 k^2}{2m} = E - V_1$, k_1 real.

Interpretation. $\frac{\hbar^2 k^2}{2m}$ is the KE of the particle with total energy E in a region of potential V_1, the $e^{\pm ikx}$ wavefunctions correspond to particles traveling left / right.

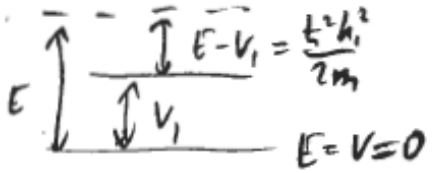

Figure II: In a region where the particle energy is greater than the (constant) potential, the solutions of the SE are plane waves $e^{\pm ikx}$, where $E - V_1 = \hbar^2 k^2/2m$ is the kinetic energy of the particle in that region.

If $E - V_1 < 0$, the solutions are of the form $e^{\pm \kappa_1 x}$ with $\frac{\hbar^2 {\kappa_1}^2}{2m} = V_1 - E$, κ_1 real. These are damped exponentials with a decay length constant κ_1 (decay length ${\kappa_1}^{-1}$), where $\frac{\hbar^2 {\kappa_1}^2}{2m} = V_1 - E$ represents the "missing" kinetic energy of the particle As $E \to V$, the decay length ${\kappa_1}^{-1}$ becomes longer and longer.

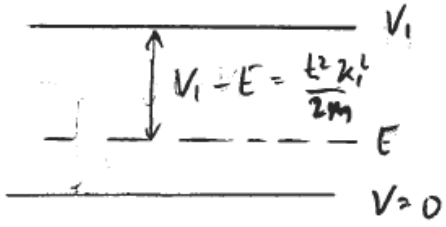

Figure III: In a region where the particle energy is less than the (constant) potential, the solutions of the SE are exponentially growing or decaying functions, $e^{\pm\kappa x}$, where $V_1 - E = \hbar^2\kappa^2/2m$ is the "missing kinetic energy" of the particle in that region.

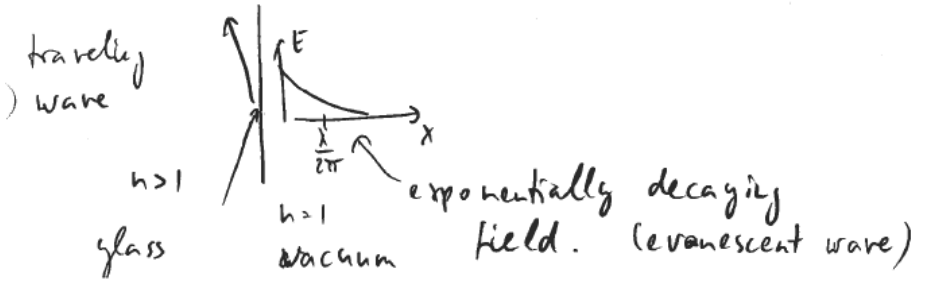

Figure IV: When a light wave experiences total internal reflection on a glass-vacuum interface, an evanescent (non-traveling, exponentially decaying wave) builds up inside the vacuum. The closer we are to the critical angle for total internal reflection, the longer the decay length of the evanescent wave. This phenomenon is analogous to a particle entering a classically forbidden region with $V_1 > E$. The less forbidden the region, the longer the decay length.

Note. There is a non-zero probability to find the particle with energy E in a "classically forbidden region" with $E < V_1$. The less the region is forbidden (the smaller $V_1 - E$), the further the particle penetrates into the forbidden region (the longer the decay length ${\kappa_1}^{-1}$). The phenomenon is similar to total internal reflection inside glass at a glass-vacuum interface.

The light field has non-zero amplitude in the "forbidden region". How do we know? Approach with a second prism. The evanescent (decaying) field existing in the vacuum is converted back into a traveling wave in the second prism.

Similarly, **a particle can tunnel through a potential barrier** even if its energy is insufficient to surpass it.

Back to potential step Assume $E > V_0$: define

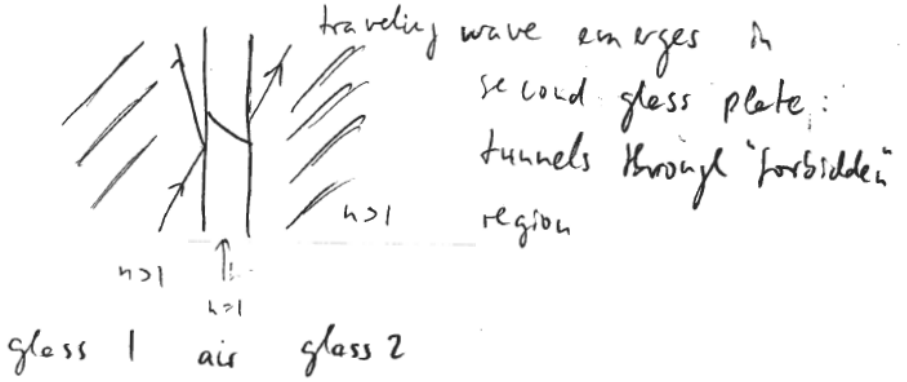

Figure V: The light field "tunneling" through the forbidden region can be detected as it emerges on the other side in a second prism.

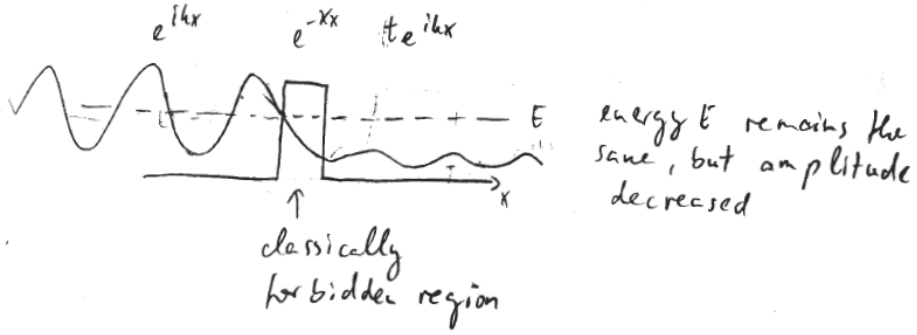

Figure VI: As a particle tunnels through a barrier and emerges from the other side, the energy E and the Broglie wavelength $2\pi/k$ remain the same. The amplitude of the emerging wave is smaller than that of the incident wave.

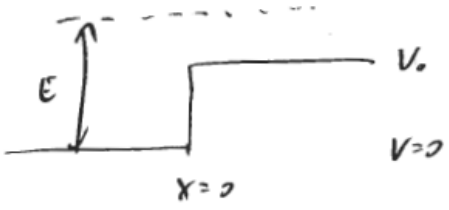

Figure VII: Potential step

$$\frac{\hbar^2 k^2}{2m} = E \qquad \text{(KE in region } x < 0\text{)} \qquad (15\text{-}4)$$

$$\frac{\hbar^2 q^2}{2m} = E - V_0 \qquad \text{(KE in region } x > 0\text{)} \qquad (15\text{-}5)$$

The most general solution is

$$Ae^{ikx} + Be^{-ikx} \qquad \text{in the region } x < 0 \tag{15-6}$$

$$Ce^{iqx} + De^{-iqx} \qquad \text{in the region } x > 0 \tag{15-7}$$

If we choose as the initial condition a particle incident from the left ($A \neq 0$), then the particle can be transmitted to the RHS ($C \neq 0$), or, as we shall see, partially reflected by the barrier in spite of $E > V_0$ ($B \neq 0$). However, if no particle is incident from the right then $D = 0$.

Calculate the particle current (or flux)

In region $x < 0$:

$$j_< = \frac{\hbar}{2im}\left(u^*\frac{du}{dx} - \left(\frac{du^*}{dx}\right)u\right) \tag{15-8}$$

$$= \frac{\hbar}{2im}\left[\left(A^*e^{-ikx} + B^*e^{ikx}\right)\left(ikAe^{ikx} - ikBe^{-ikx}\right) - \text{ c.c.}\right] \tag{15-9}$$

$$= \frac{\hbar k}{2m}\left[|A|^2 + AB^*e^{2ikx} - A^*Be^{-2ikx} - |B|^2 - \text{ c.c.}\right] \tag{15-10}$$

$$= \frac{\hbar k}{m}\left[|A|^2 - |B|^2\right] \quad \rightarrow \quad \text{net current for } x < 0 \tag{15-11}$$

We define the reflection amplitude $r = \frac{B}{A}$, and the reflection coefficient as $R = |r|^2 = \left|\frac{B}{A}\right|^2$.

For $x > 0$:

$$j_> = \frac{\hbar q}{m}|C|^2 \tag{15-12}$$

Continuity of wavefunction at $x = 0$:

$$\psi(x \rightarrow 0) = A + B = \psi(x \leftarrow 0) = C \tag{15-13}$$

In spite of the potential step, the derivative of the wavefunction must also be continuous:

$$\left(\frac{du}{dx}\right)_{x=\epsilon} - \left(\frac{du}{dx}\right)_{x=-\epsilon} = \int_{-\epsilon}^{\epsilon} dx \frac{d}{dx}\left(\frac{du}{dx}\right) \tag{15-14}$$

$$= -\frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon} dx[E - V(x)]u(x) = 0 \tag{15-15}$$

For future applications, we note that if the potential contains a delta function term $\lambda\delta(x - a)$, with some magnitude of the delta function λ, then the same calculation

gives

$$\left(\frac{du}{dx}\right)_{x=a+\epsilon} - \left(\frac{du}{dx}\right)_{x==a-\epsilon} = \frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon} dx\lambda\delta(x-a)u(\lambda) \tag{15-16}$$

$$= \frac{2m}{\hbar^2}\lambda u(a) \tag{15-17}$$

To summarize, we have the following rules:

Rule 1. The wavefunction u(x) is always continuous

Rule 2. The first spatial derivative of the wavefunction $\frac{du}{dx}$ is continuous if the potential does not contain δ-function like terms. (It may contain potential steps).

Rule 2.1. if the potential contains a term $\lambda\delta(x-a)$, the the first derivative $\frac{du}{dx}$ is discontinuous at $x = a$ amnd satisfies the relation

$$\left(\frac{du}{dx}\right)_{x=a+\epsilon} - \left(\frac{du}{dx}\right)_{x=a-\epsilon} = \frac{2m}{\hbar^2}\lambda u(a) \tag{15-18}$$

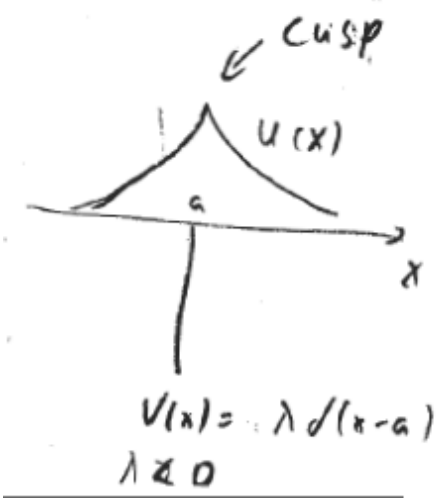

Figure VIII: A discontinuity in the slope of the wavefunction occurs at a delta function potential. The difference in wavefunction slopes is proportional to the strength of the δ potential, and to the value of the wavefunction at the cusp.

Continuity of ψ:	$A + B = C$	(15-19)
Continuity of ψ':	$ik(A - B) = iqC$	(15-20)

Solve for B, C in terms of A

$$C = A + B = \frac{k}{q}(A - B) \tag{15-21}$$

$$A\left(1 - \frac{k}{q}\right) = -B\left(1 + \frac{k}{q}\right) \tag{15-22}$$

$$A\frac{q-k}{q} = -B\frac{q+k}{q} \tag{15-23}$$

$$B = \frac{k-q}{k+q}A \tag{15-24}$$

$$C = A + B = A + \frac{k-q}{k+q}A = \frac{2}{k+q}A \tag{15-25}$$

Reflection amplitude
$$r = \frac{B}{A} = \frac{k-q}{k+q} \tag{15-26}$$

Transmission amplitude
$$t = \frac{C}{A} = \frac{2k}{k+q} \tag{15-27}$$

Reflection coefficient
$$|r|^2 = \left|\frac{B}{A}\right|^2 = \left(\frac{k-q}{k+q}\right)^2 \tag{15-28}$$

Transmission coefficient
$$|t|^2 = \left|\frac{C}{A}\right|^2 = \frac{4k^2}{(k+q)^2} \tag{15-29}$$

Reflection current
$$j_{\leftarrow} = \frac{\hbar k}{m}|B|^2 = \frac{\hbar k}{m}\left(\frac{k-q}{k+q}\right)^2|A|^2 \tag{15-30}$$

Transmission current
$$j_{\rightarrow, x>0} = \frac{\hbar q}{m}|C|^2 = \frac{\hbar k}{m}\frac{4kq}{(k+q)^2}^2|A|^2 \tag{15-31}$$

Net current for $x < 0$
$$j_< = \frac{\hbar k}{m}(|A|^2 - |B|^2) = \frac{\hbar k}{m}|A|^2\frac{4kq}{(k+q)^2} \tag{15-32}$$

Net current for $x > 0$
$$j_> = \frac{\hbar q}{m}|C|^2 = \frac{\hbar k}{m}\frac{4kq}{(k+q)^2}|A|^2 \tag{15-33}$$

The current obeys the continuity equation (see problem set)

$$\frac{\partial j}{\partial x} + \frac{\partial}{\partial t}|\psi|^2 = 0 \tag{15-34}$$

Here we are considering stationary states, $\frac{\partial}{\partial t}|\psi|^2 = 0$ (no change of probability density in time), $\Longrightarrow j = \text{const}$, current is continuous across the potential step,

$$j_< = j_>, \tag{15-35}$$

or

$$j_{\text{inc}} = j_{\rightarrow,x<0} = \frac{\hbar k}{m}|A|^2 = j_{\text{refl}} + j_{\text{trans}} \tag{15-36}$$

$$= j_{\leftarrow,x<0} + j_{\rightarrow,x>0} \tag{15-37}$$

$$= \frac{\hbar k}{m}|B|^2 + \frac{\hbar q}{m}|C|^2. \tag{15-38}$$

Note. $|r|^2 + |t|^2 \neq 1$ because the particle velocity is different for $x > 0$ from that for $x < 0$.

Discussion of results

In contrast to classical mechanics, there is some reflection at the potential step even though the energy of the particle is sufficient to surpass it. This is familiar from optics, where a step-like change in the index of refraction (e.g., air-glass interface) leads to partial reflection. The particle reflection is a consequence of the matching of the wavefunction and its derivative at the boundary. Again, this is similar to optics where the matching of th electromagnetic fields at the boundary results in a reflected field.

Note. For a very smooth change of potential (or refractive index in optics) there is not reflection. What is smooth? A change over many wavelengths. Changes of the potential over a distance l short compared to a wavelength $\lambda = \frac{2\pi}{k}$ result in reflection. Slow changes of potential over many λ do not result in reflection if particle energy exceeds barrier height.

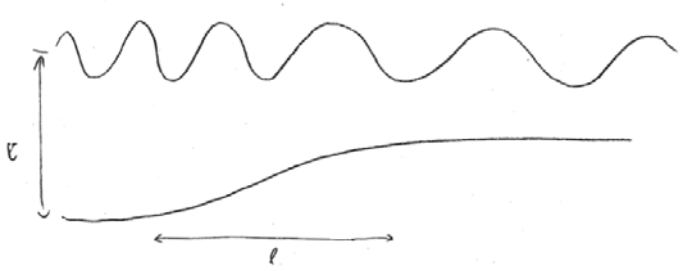

Figure IX: A potential that varies smoothly over many de Broglie wavelengths does not produce partial reflection if the particle energy is sufficient to surpass it.

Intermediate region $l \sim \lambda$: we expect resonance phenomena (non-monotonic changes of reflection probability with particle energy). For the potential step, the

reflection probability

$$|r|^2 \to 0 \qquad \text{for } k \to q \qquad (E \gg V_1), \text{and} \tag{15-39}$$

$$|r|^2 \to 1 \qquad \text{for } q \to 0 \qquad (E \gg V_1), \text{as expected.} \tag{15-40}$$

$$\tag{15-41}$$

Interestingly, the reflection probability can be written as

$$|r|^2 = \left(\frac{\sqrt{E} - \sqrt{E - V_1}}{\sqrt{E} + \sqrt{E - V_1}} \right)^2 \tag{15-42}$$

i.e. it does not depend explicitly on $\hbar$. However, the reflection is still inherenetly non-classical in that the potential needs to change abruptly compared to the particle's de Broglie wavelength, that depends on $\hbar$.

Solution for $E < V_0$: We define

$$\frac{\hbar^2 k^2}{2m} = E \qquad \text{(KE for } x < 0) \tag{15-43}$$

$$\frac{\hbar^2 \kappa^2}{2m} = V_0 - E \qquad \text{(“missing KE to surpass barrier”)} \tag{15-44}$$

Most general solution

$$Ae^{ikx} + Be^{-ikx} \qquad \text{for } x < 0 \tag{15-45}$$

$$Ce^{-\kappa x} + De^{\kappa x} \qquad \text{for } x > 0 \tag{15-46}$$

The $e^{+\kappa x}$ term is not normalizable, $D = 0$

We can go through the same procedure as before using the continuity of $\psi_1 \psi'$ at $x = 0$, or use the previous calculation if we set $q \to i\kappa$ ($Ce^{iqx} \to Ce^{-\kappa x}$ then). Consequently,

$$|r|^2 = \left| \frac{B}{A} \right|^2 = \left| \frac{k - i\kappa}{k + iq} \right|^2 = \frac{k^2 + \kappa^2}{k^2 + \kappa^2} = 1 \tag{15-47}$$

$$|t|^2 = \left| \frac{C}{A} \right|^2 = \left| \frac{2k}{k + i\kappa} \right|^2 = \frac{4k^2 + \kappa^2}{k^2 + \kappa^2} \neq 0 \tag{15-48}$$

$$\tag{15-49}$$

A part of the wave penetrates the barrier, which is why the 'transmission' amplitude does not vanish. Note, however, that there is no associated particle current: Since Ce^{-kx} does not have a spatially varying phase, the particle current

$$j = \frac{\hbar}{2im} \left(\psi^* \frac{\partial \psi}{\partial x} - \text{ c.c.} \right) \tag{15-50}$$

vanishes for $x > 0$,

$$j_< = \frac{\hbar k}{m}(|A|^2 - |B|^2) = 0 \tag{15-51}$$

$$j_> = 0 \tag{15-52}$$

The net current is zer0 in steady-state because all particles are reflected.

Note. The reflected wave has an energy-dependent phase shift

$$r = \frac{B}{A} = \frac{k - i\kappa}{k + i\kappa} \tag{15-53}$$

$$= \frac{(k - i\kappa)^2}{k^2 + \kappa^2} \tag{15-54}$$

$$= \frac{k^2 - \kappa^2 - 2ik\kappa}{k^2 + \kappa^2} \tag{15-55}$$

$$= e^{i\phi} \tag{15-56}$$

with $\tan\phi = -\frac{2k\kappa}{k^2 - \kappa^2}$

The phase shift of the wave is important in 3D scattering problems.

Can we localize the particle in the forbidden region?

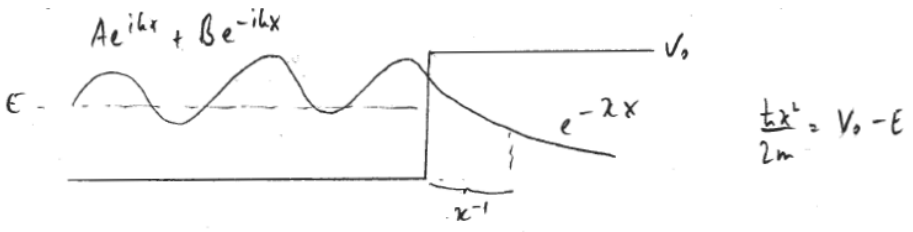

Figure X: The wavefunction for $E < V_0$ protrudes into the forbidden region $x > 0$. Can the particle be observed there?

To be sure that we have measured the particle inside the barrier, and not outside, we must measure its position at least with accuracy $\Delta x \approx \kappa^{-1}$. Then according to Heisenberg uncertainty, a momentum kick exceeding $\Delta p \geq \frac{\hbar}{\Delta x} \sim \hbar\kappa$ will be transferred onto the particle.

How much energy do we transfer?

$$\Delta E = E(p + \Delta p) - E(p) \tag{15-57}$$

$$= \frac{(p + \Delta p)^2}{2m} - \frac{p^2}{2m} \tag{15-58}$$

$$= \frac{p\Delta p}{m} + \frac{(\Delta p)^2}{2m} \tag{15-59}$$

$$p = \hbar k \tag{15-60}$$

$p\Delta p$ can be positive or negative, $(\Delta p)^2$ is always positive. the transferred energy is on average

$$\langle \Delta E \rangle = \frac{(\Delta p)^2}{2m} = \frac{\hbar^2}{2m(\Delta x)^2} = \frac{\hbar^2 \kappa^2}{2m} = V_0 - E \tag{15-61}$$

According to Heisenberg uncertainty, the measurement that localizes the particle inside the barrier transfers enough energy to allow the particle to be legitimately there.

Rule. A positive KE $E - V_1 > 0$ corresponds to a spatially oscillating wavefunction $e^{\pm ikx}$ with rate constant k (oscillation period $\lambda = \frac{2\pi}{k}$). A negative ("missing") KE $E - V_1 < 0$ corresponds to a spatially decaying or growing wavefunction $e^{\pm}\kappa x$ with decay rate constant κ (decay length κ^{-1}).

The "missing" KE is associated with the size of the region (κ^{-1}) that the particle occupies in the classically forbidden space.

The potential barrier: tunneling

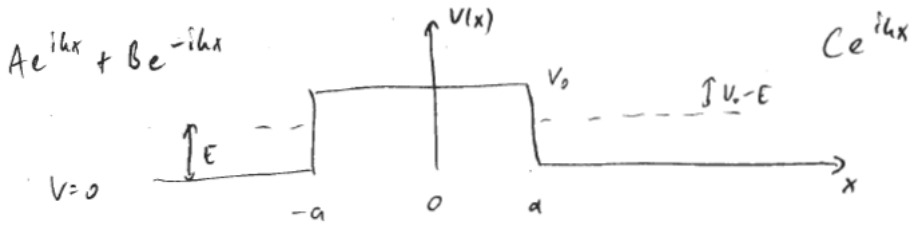

Figure I: Tunneling through a potential barrier.

Assume $E < V_0$ (classically particle is reflected). Outside barrier solutions to the SE are

$$u(x) = Ae^{ikx} + Be^{-ikx} \qquad \text{for } x < -a, \tag{16-1}$$

$$u(x) = Ce^{ikx} \qquad \text{for } x > a, \tag{16-2}$$

$$\tag{16-3}$$

where we have omitted the term De^{-ikx} that corresponds to an incident waveform the right. Inside the barrier the SE is

$$\frac{d^2u}{dx^2}(x) = +\frac{2m}{\hbar}(V_0 - E)u(x) = \kappa^2 u(x) \tag{16-4}$$

with $\kappa^2 = \frac{2m}{\hbar^2}(V_o - E)$. As before, κ is the decay constant in the classically forbidden region (κ^{-1} is the decay length) that is associated with the "missing" KE necessary to surpass the barrier classically, $\frac{\hbar^2\kappa^2}{2m} = V_0 - E$. Consequently inside the barrier

$$u(x) = Ee^{-\kappa x} + Fe^{\kappa x}, \text{for } |x| \leq a \tag{16-5}$$

As before, we need to match the solution $u(x)$ and its derivative $u'(x)$ at the boundaries.

- At $x = -a$:

$$Ae^{-ika} + Be^{ika} = Ee^{+\kappa a} + Fe^{-\kappa a} \qquad \text{for } u \tag{16-6}$$

$$+ikAe^{-ika} - ikBe^{ika} = +\kappa Ee^{+\kappa a} + \kappa Fe^{-\kappa a} \qquad \text{for } u' \tag{16-7}$$

- At $x = a$:

$$Ce^{ika} = Ee^{-\kappa a} + Fe^{\kappa a} \qquad \text{for } u \tag{16-8}$$

$$ikAe^{ika} = -\kappa Ee^{-\kappa a} + \kappa Fe^{\kappa a} \qquad \text{for } u' \tag{16-9}$$

We are interested in the reflection amplitude $r = \frac{B}{A}$ (or the reflection probability $|r|^2 = \left|\frac{B}{A}\right|^2$) and the transmission amplitude $t = \frac{C}{A}$ (or transmission probability $|t|^2 = \left|\frac{C}{A}\right|^2$) from the barrier. Remember that $|A|^2$ determines the incident current, and is a free parameter. It is useful to divide the equation for u' by the equation for u (or alternatively, match $\frac{1}{u(x)}\frac{du}{dx} = \frac{d}{dx}(\ln u(x))$ directly. Then we write

- At $x = -a$:

$$\frac{+ikAe^{-ika} - ikBe^{+ika}}{Ae^{-ika} + Be^{ika}} = \frac{-\kappa Ee^{\kappa a} + \kappa Fe^{-\kappa a}}{Ee^{\kappa a} + Fe^{-\kappa a}} \tag{16-10}$$

- At $x = a$:

$$ik = \frac{+ikCe^{ika}}{Ce^{ika}} = \frac{-\kappa Ee^{-\kappa a} + \kappa Fe^{\kappa a}}{Ee^{-\kappa a} + Fe^{\kappa a}} \tag{16-11}$$

(matching of $\frac{d}{dx}(\ln u(x)) = \frac{1}{u(x)}\frac{du}{dx}$ at boundaries).

Now we proceed to eliminate E, F (Eq. 16-11):

$$ikEe^{-\kappa a} + ikFe^{\kappa a} = -\kappa Ee^{-\kappa a} + \kappa Fe^{\kappa a} \tag{16-12}$$

$$(\kappa + ik)Ee^{-\kappa a} = (\kappa - ik)Fe^{\kappa a} \tag{16-13}$$

$$E = \frac{\kappa - ik}{\kappa + ik}Fe^{2\kappa a} \tag{16-14}$$

Substitute into Eq. 16-10:

$$\text{RHS} = \frac{-\kappa\frac{\kappa - ik}{\kappa + ik}Fe^{3\kappa a} + \kappa Fe^{-\kappa a}}{\frac{\kappa - ik}{\kappa + ik}Fe^{3\kappa a} + Fe^{-\kappa a}} \tag{16-15}$$

$$= \frac{-\kappa(\kappa - ik)e^{+2\kappa a} + \kappa(\kappa + ik)e^{-2\kappa a}}{(\kappa - ik)e^{2\kappa a} + (\kappa + ik)e^{-2\kappa a}} \tag{16-16}$$

$$= \frac{-\kappa^2(e^{2\kappa a} - e^{-2\kappa a}) + ik\kappa(e^{2\kappa a} + e^{-2\kappa a})}{\kappa(e^{2\kappa a} + e^{-2\kappa a}) - ik(e^{2\kappa a} - e^{-2\kappa a})} \tag{16-17}$$

$$= -\frac{\kappa^2 \sinh(2\pi a) + ik\kappa\cosh(2\kappa a)}{\kappa\cosh(2\kappa a) - ik\sinh(2\kappa a)} \tag{16-18}$$

Consequently, Eq. 16-10

$$\left[+ikAe^{-ika} - ikBe^{ika}\right]\left[\kappa\cosh(2\kappa a) - ik\sinh(2\kappa a)\right] \tag{16-19}$$

$$= \left[Ae^{-ika} + Be^{ika}\right]\left[-\kappa^2\sinh(2\kappa a) + ik\kappa\cosh(2\kappa a)\right] \tag{16-20}$$

$$= Ae^{-ika}(+ik\kappa\cosh(2\kappa a) + k^2\sinh(2\kappa a) + \kappa^2\sinh(2\kappa a) - ik\kappa\cosh(2\kappa a)) \tag{16-21}$$

$$= Be^{ika}(+ik\kappa\cosh(2\kappa a) + k^2\sinh(2\kappa a) - \kappa^2\sinh(2\kappa a) + ik\kappa\cosh(2\kappa a)) \tag{16-22}$$

$$Ae^{-ika}\left[(k^2+\kappa^2)\sinh(2\kappa a)\right] = Be^{ika}\left[2ik\kappa\cosh(2\kappa a) + (k^2-\kappa^2)\sinh(2\kappa a)\right] \tag{16-23}$$

$$r = \frac{B}{A} \tag{16-24}$$

$$= e^{-2ika}\frac{(k^2+\kappa^2)\sinh(2\kappa a)}{2ik\kappa\cosh(2\kappa a) + (k^2-\kappa^2)\sinh(2\kappa a)} \tag{16-25}$$

reflection amplitude from barrier.

To calculate the transmission amplitude $\frac{C}{A}$, we use the continuity of u at $x = a$:

$$Ce^{ika} = Ee^{-\kappa a} + Fe^{+\kappa a} \tag{16-26}$$

$$= \frac{\kappa - ik}{\kappa + ik}Fe^{\kappa a} + Fe^{\kappa a} \tag{16-27}$$

$$= \frac{2\kappa}{\kappa + ik}Fe^{\kappa a} \tag{16-28}$$

We find F from the continuity of u at $x = -a$:

$$\text{RHS} = Ee^{\kappa a} + Fe^{-\kappa a} \tag{16-29}$$

$$= \frac{\kappa - ik}{\kappa + ik} Fe^{3\kappa a} + Fe^{-\kappa a} \tag{16-30}$$

$$= Fe^{\kappa a}\left[\frac{\kappa - ik}{\kappa + ik} e^{2\kappa a} + \frac{\kappa + ik}{\kappa + ik} e^{-2\kappa a}\right] \tag{16-31}$$

$$= Fe^{\kappa a} \frac{2\kappa \cosh(2\kappa a) - 2ik \sinh(2\kappa a)}{\kappa + ik} \tag{16-32}$$

$$\text{RHS} = Ae^{-ika} + Be^{ika} \tag{16-33}$$

$$= Ae^{-ika} + Ae^{-ika} \frac{(k^2 + \kappa^2)\sinh(2\kappa a)}{2ik\kappa \cosh(2\kappa a) + (k^2 - \kappa^2)\sinh(2\kappa a)} \tag{16-34}$$

$$= Ae^{-ika}\left[1 + \frac{(k^2 + \kappa^2)\sinh(2\kappa a)}{2ik\kappa \cosh(2\kappa a) + (k^2 - \kappa^2)\sinh(2\kappa a)}\right] \tag{16-35}$$

$$= Ae^{-ika} \frac{2ik\kappa \cosh(2\kappa a) + 2k^2 \sinh(2\kappa a)}{2ik\kappa \cosh(2\kappa a) + (k^2 - \kappa^2)\sinh(2\kappa a)}. \tag{16-36}$$

Then,

$$\frac{C}{A} = \frac{2\kappa}{A} \frac{F}{\kappa + ik} e^{\kappa a - ika} \tag{16-37}$$

$$= \frac{2\kappa}{A} \frac{Ae^{-2ika}}{2\kappa \cosh(2\kappa a) - 2ik \sinh(2\kappa a)} \frac{(2ik\kappa \cosh(2\kappa a) + 2k^2 \sinh(2\kappa a)}{2ik\kappa \cosh(2\kappa a) + (k^2 - \kappa^2)\sinh(2\kappa a)} \tag{16-38}$$

$$= 2\kappa e^{-2ika} ik \frac{1}{2ik\kappa \cosh(2\kappa a) + (k^2 - \kappa^2)\sinh(2\kappa a)} \tag{16-39}$$

$$= \frac{C}{A} \tag{16-40}$$

$$= e^{-2ika} \frac{2k\kappa}{2k\kappa \cosh(2\kappa a) - i(k^2 - \kappa^2)\sinh(2\kappa a)} \tag{16-41}$$

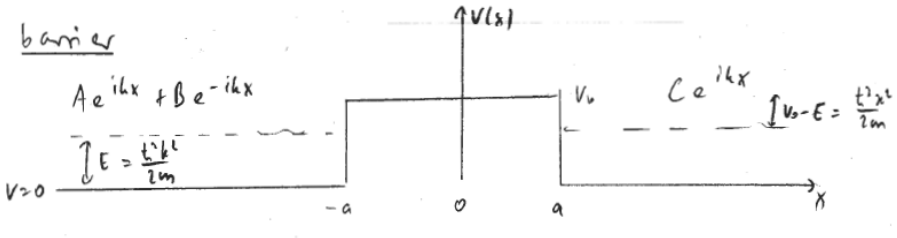

Figure II: Tunneling through the potential barrier.

Consequently, we have the **results for the barrier**

- $\frac{\hbar^2 k^2}{2m} = E$
- $\frac{\hbar^2 \kappa^2}{2m} = V_0 - E$
- $r = \frac{B}{A} = e^{-2ika} \frac{-i(k^2+\kappa^2)\sinh(2\kappa a)}{2k\kappa\cosh(2\kappa a) - i(k^2-\kappa^2)\sinh(2\kappa a)}$
- $t = \frac{C}{A} = e^{-2ika} \frac{2k\kappa}{2k\kappa\cosh(2\kappa a) - i(k^2-\kappa^2)\sinh(2\kappa a)}$

Since the energy and particle velocity are the same on both sides of the barrier, here we have $|r|^2 + |t|^2 = 1$.

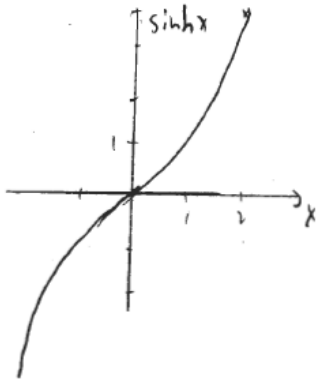

Figure III: The sinh function.

Let us look at $|t|^2$

$$|t|^2 = \frac{(2k\kappa)^2}{(2k\kappa)^2 + (k^2+\kappa^2)^2 \sinh^2(2\kappa a)} \tag{16-42}$$

where we have used $\cosh^2(x) = 1 + \sinh^2(x)$. Since, sinh is a monotonically increasing function, and $\kappa = \frac{2m}{\hbar^2}\sqrt{V_0 - E}$, the transmission is monotonically decreasing with barrier height V_0.

In the limit of small transmission, $\kappa a \gg 1$ (barrier width large compared to decay length κ^{-1}), we have $\sinh(2\kappa a) \approx \left(\frac{1}{2}e^{2\kappa a}\right)^2 = \frac{1}{4}e^{4\kappa a}$ and $|t|^2 \to \left(\frac{4k\kappa}{k^2+\kappa^2}\right)^2 e^{-4\kappa a}$. In this limit the tunneling probability falls off exponentially with barrier thickness (in units of decay length κ^{-1}).

$\rightarrow$ This exponential dependence explains the extremely wide variation in, e.g., lifetimes of unstable nuclei (μs to 10^9 years, corresponding to a variation by a factor of 10^{22}).

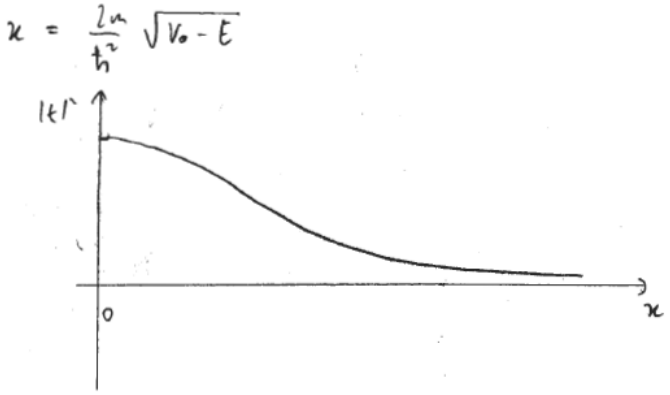

Figure IV: The transmission through the barrier as a function of decay wavevector κ.

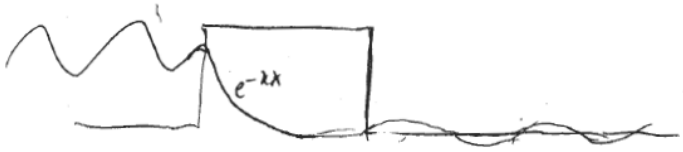

Figure V: In the limit of large barrier height or width, the transmission falls off exponentially because the wavefunction inside the barrier is dominated by the exponentially decaying term.

Potential well: resonance phenomena

We first consider scattering ($E > 0$)

$$x \leq -a : \qquad Ae^{ikx} + B^{-ikx} \tag{16-43}$$

$$-a \leq x \leq a : \qquad Ee^{+iqx} + Fe^{-iqx} \tag{16-44}$$

$$x \geq a : \qquad Ce^{ikx} \tag{16-45}$$

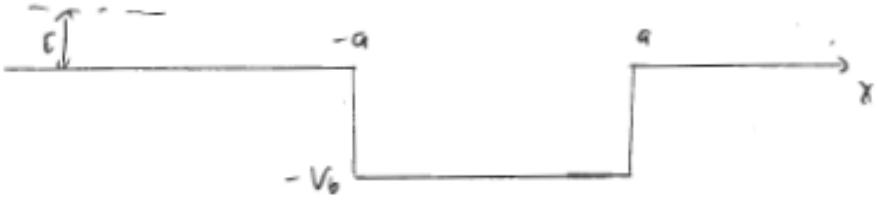

Figure VI: The potential well.

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

Instead of going through the calculation again, we note that these equations are equivalent to those of the potential barrier (for $E < V_0$) if we replace $\kappa \to -iq$. Consequently, we obtain

$$r = ie^{-2ika}\frac{(q^2 - k^2)\sin(2qa)}{2kq\cos(2qa) - i(q^2 + k^2)\sin(2qa)} \tag{16-46}$$

$$t = e^{-2ika}\frac{2kq}{2kq\cos(2qa) - i(q^2 + k^2)\sin(2qa)} \tag{16-47}$$

For the potential well, in contrast to tunneling through the barrier, the reflection and transmission oscillate as a function of parameter $2qa$, i.e. as a function of number of de Broglie wavelengths $\frac{2\pi}{q}$ inside the well of size a. In particular, for values

$$2q_n a = n\pi \quad \to \quad n \text{ integer} \tag{16-48}$$

$$q_n = \frac{n\pi}{2a} \tag{16-49}$$

$$\lambda_n = \frac{2\pi}{q} = \frac{4a}{n} \tag{16-50}$$

the reflection goes to zero because of destructive interference between the waves reflected at $-a$ and $+a$. This corresponds to the resonance condition for a Fabry-Perot resonator in optics. the phenomenon persists in 3D, and for electrons scattering off noble gas atoms is called a Ramsaner-Townsend resonance. A very similar phenomenon has been observed in collision of ultracold atoms, where the effective depth of the interatomic potential V_0 can be tuned with a magnetic field, there (and in nuclear collisions) it is called a Feshbach resonance).

Bound states in attractive δ-potential

What happens for negative energies $-V_0 < E < 0$ in the potential well?

We expect discrete bound states, at least if potential is sufficiently deep. Particularly simple mathematically is a limiting case where we shrink the size of the potential, simultaneously making it deeper, such that the product of depth and width is constant.

Let $V_0 \to \infty$, $\tilde{a} \to 0$ such that $\tilde{a} \cdot V_0 = \text{const} = \lambda > 0$. We then obtain the attractive delta potential $V(x) = -\lambda\delta(x)$. We are interested in bound states: $E < 0$

- Define

$$\frac{\hbar^2\kappa^2}{2m} = 0 - E = -E = |E|, \quad \kappa > 0 \tag{16-51}$$

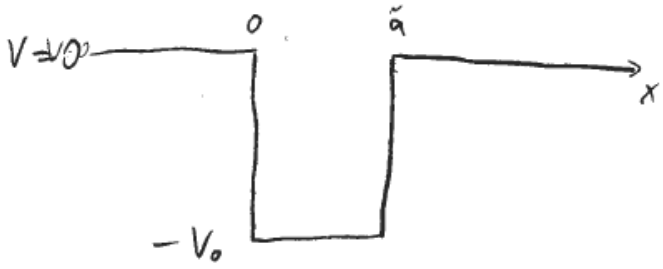

Figure VII: If the potential well is sufficiently deep or wide, it can support bound states with discrete energies $-V_0 < E < 0$.

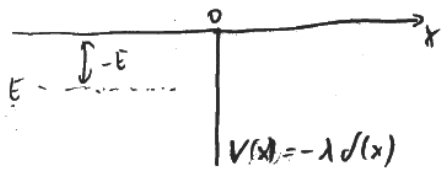

Figure VIII: Attactive delta potential.

- Solutions for $x < 0$:

$$Ae^{\kappa x} + \underbrace{\cancel{Be^{-\kappa x}}}_{\text{diverges for } x \to -\infty} \tag{16-52}$$

- Solutions for $x > 0$:

$$\cancel{Ce^{\kappa x}} + De^{-\kappa x} \tag{16-53}$$

- Continuity of wavefunction at $x = 0$:

$$A = D \tag{16-54}$$

- Derivative obeys (Lecture XV)

$$u'(\epsilon) - u'(-\epsilon) = -\frac{2m}{\hbar^2}\lambda u(0) \tag{16-55}$$

$$\kappa D - \kappa A = -\frac{2m}{\hbar^2}\lambda A \tag{16-56}$$

$$-2\kappa = -\frac{2m}{\hbar^2}\lambda \tag{16-57}$$

$$\boxed{\kappa_1 = \frac{m}{\hbar^2}\lambda} \tag{16-58}$$

$$E_1 = -\frac{\hbar^2\kappa^2}{2m} = -\frac{\hbar^2 m^2}{2m\hbar^4}\lambda^2 = -\frac{m}{2\hbar^2}\lambda^2 \tag{16-59}$$

→ **Binding energy for attractive δ-function.** The δ potential supports

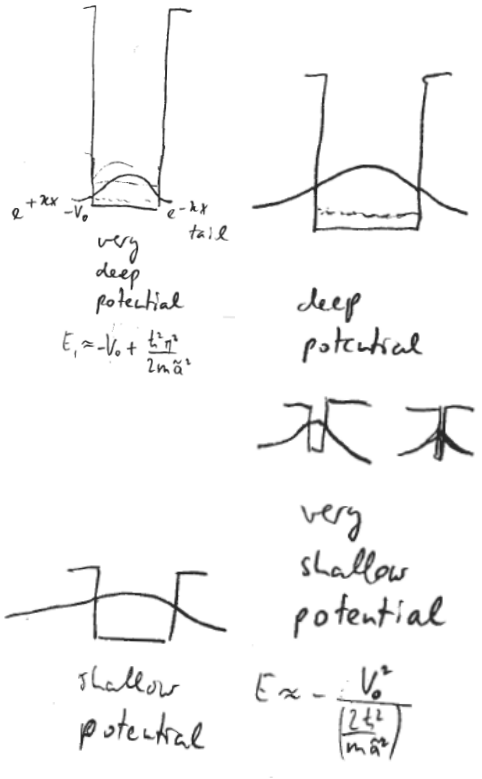

Figure IX: Comparison of bound states as the potential evolves from a very deep to a very shallow potential. In the very deep potential, like in the infinite well, the wave function oscillates sinusoidally inside the well, and decays exponentially in the forbidden region. In the very shallow potential, the wavefunction is is mostly located in the "forbidden" region outside the well.

exactly one bound state of energy $E = -\frac{m\lambda^2}{2\hbar^2}$. For a finite-size well, this result corresponds to the limiting case of a weak potential that supports only one bound state ($V_0 \ll \frac{2\hbar^2}{m\tilde{a}^2}$) with energy $E = -\frac{m\tilde{a}^2}{2\hbar^2}V_0^2$.

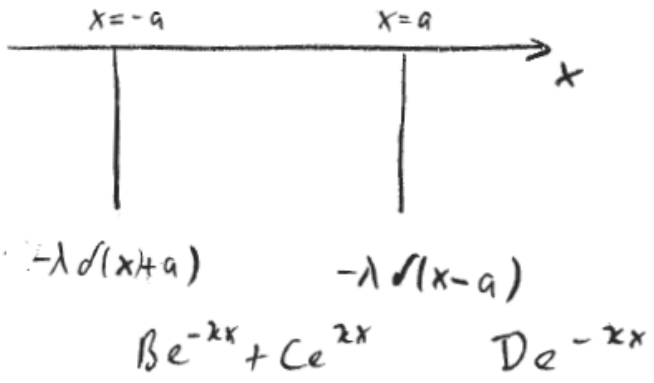

Figure X: Solutions in different regions.

Two attractive δ-potentials

We could proceed as before, or simplify slightly by making use of the fact that the potential is symmetric $x \to -x$, and therefore we expect solutions of definite parity. The even solution in the middle region is $2B\cosh(\kappa x)$, and $A = D$, which eliminates two parameters.

- Continuity of u:

$$2B\cosh(\kappa a) = Ae^{-\kappa a} \tag{16-60}$$

- Derivative:

$$-\kappa Ae^{-\kappa a} - \kappa 2B\sinh(\kappa a) = -\frac{2m}{\hbar^2}\lambda Ae^{-\kappa a} \tag{16-61}$$

$$\left(\frac{2m}{\hbar^2}\lambda - \kappa\right) Ae^{-\kappa a} = 2\kappa B\sinh(\kappa a) \tag{16-62}$$

$$\left(\frac{2m}{\hbar^2}\lambda - \kappa\right) 2B\cosh(\kappa a) = 2\kappa B\sinh(\kappa a) \tag{16-63}$$

$$\frac{2ma}{\hbar^2\kappa a}\lambda - 1 = \tanh(\kappa a) \tag{16-64}$$

There is always exactly one solution of the eigenvalue equation (16-64) for even parity. From the figure we see that for the bound state $\kappa a < \frac{2ma\lambda}{\hbar^2}$, which is where the function $\frac{2ma\lambda}{\hbar^2}\frac{1}{\kappa a} - 1$ intersects zero. On the other hand, since $\tanh(x) \leq 1$, we need $\frac{2ma\lambda}{\hbar^2}\frac{1}{\kappa a} - 1 < 1$, or $\kappa > \frac{m}{\hbar^2}\lambda$. Larger κ means larger magnitude of binding energy $E = -\frac{\hbar^2\kappa^2}{2m}$. We have $\frac{m}{\hbar^2}\lambda < \kappa < \frac{2m}{\hbar^2}\lambda$ If we compare this to the binding-energy in single δ-potential, $\kappa_1 = \frac{m}{\hbar^2}\lambda$ we see that the particle is more strongly bound in the double-well potential.

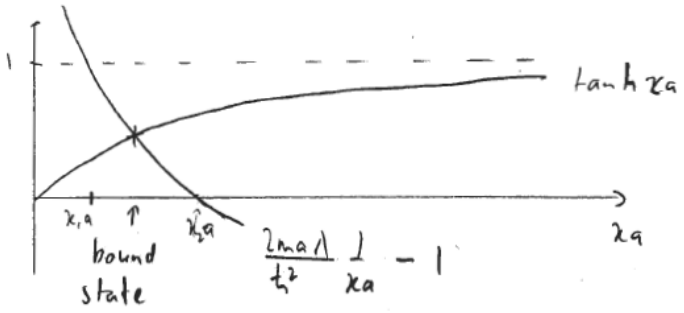

Figure XI: Graphic solution of the eigenvalue equation 16-64.

Reason. Given the discontinuity in slope due to the potential, it is possible to choose a steeper wavefunction (larger $\kappa \rightarrow$ larger binding energy) when the two δ-functions are close. Variation of binding energy with well separation a: As we decrease a, the

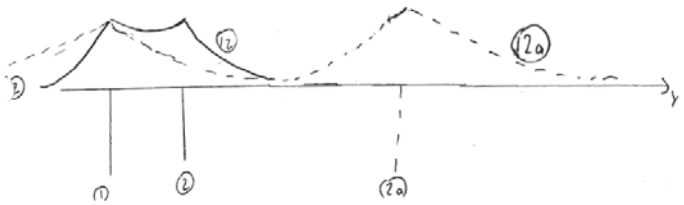

Figure XII: Comparison of the wavefunction for two different well spacings. If the wells are close, for the same wavefunction discontinuity at each δ function the wavefunction outside the two wells can decay faster (larger κ), resulting in larger binding energy $|E| = \hbar^2\kappa^2/2m$.

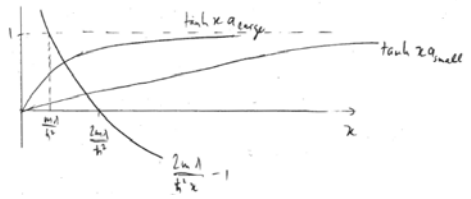

Figure XIII: Graphic comparison of the binding energies for large and small separation $2a$ between the binding sites.

binding energy increases from the value given by $\kappa = \frac{m\lambda}{\hbar^2}$ (binding energy of a single well attained at $a \rightarrow \infty$) towards the value $\kappa = \frac{2m\lambda}{\hbar^2}$, attained as $a \rightarrow 0$. Thus the binding energy quadruples. the possibility of the wavefunction in a double-well system to change so as to decrease the kinetic (and possibly potential) energy is at the origin of chemical bonds in molecules.

For the single δ-potential we have exactly one bound state (symmetric state), for the double δ-potential we always have one symmetric bound state, and we may have (depending on the potential strength) also an antisymmetric bound state. For the finite-size potential well we may have several (but always a finite number) of bound states.

Bound states in potential well

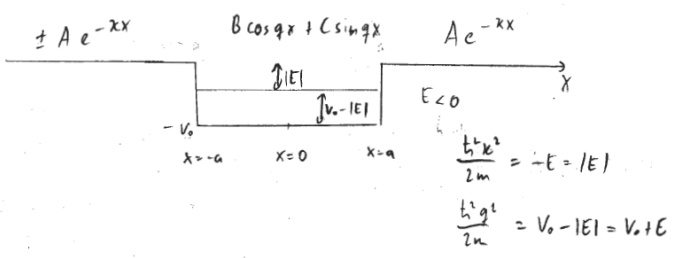

Figure I: Solutions in different regions for bound states in a potential well.

Here, instead of writing the solutions as exponentials, $\tilde{B}e^{iqx} + \tilde{C}e^{-iqx}$, we have already written them in a form that reflects the symmetry of the potential. We match $\frac{1}{u}\frac{du}{dx}$ at $x = a$:

- For even solutions: $C = 0$

$$\frac{-q\sin(qa)}{\cos(qa)} = \frac{-\kappa e^{-\kappa a}}{e^{-\kappa a}} \tag{17-1}$$

$$\kappa = q\tan(qa) \tag{17-2}$$

- For odd solutions: $D = 0$

$$\frac{q\cos(qa)}{\sin(qa)} = -\kappa \tag{17-3}$$

$$\kappa = -q\cot(qa) \tag{17-4}$$

Even solutions

Let us introduce $y = qa$, $\lambda = \frac{2m}{\hbar^2} V_0 a^2$

$$\kappa a = \sqrt{\frac{2ma^2}{\hbar^2}|E|} \tag{17-5}$$

$$= \sqrt{\frac{2ma^2}{\hbar^2}V_0 - \frac{2ma^2}{\hbar^2}(V_0 - |E|)} \tag{17-6}$$

$$= \sqrt{\lambda - q^2a^2} \tag{17-7}$$

$$= \sqrt{\lambda - y^2} \tag{17-8}$$

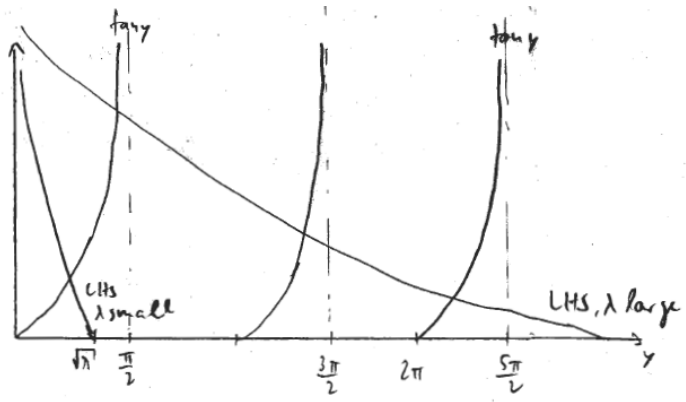

Figure II: Graphic solution of the eigenvalue equation (17-2) for symmetric bound states.

There is always at least one solution, more if $\lambda = \frac{2m}{\hbar^2} V_0 a^2$ is larger (potential deeper and/or wider). For $\lambda \gg 1$, the lowest energy solutions are approximately located at $y = qa = \left(n + \frac{1}{2}\right)\pi$, or $V_0 - |E_n| = \frac{\hbar^2 {q_n}^2}{2m} = \frac{\hbar^2\pi^2}{2ma^2}\left(n + \frac{1}{2}\right)^2$, similar to infinite well.

The existence of at least one bound state is typical of 1D problems, but not of 3D problems that behave more like odd solutions.

Odd solutions

$$\frac{\sqrt{\lambda - y}}{y} = -\cot(y) = \tan\left(\frac{\pi}{2} + y\right) \tag{17-9}$$

The looks similar to the previous plot, but with shifted RHS. For large λ, the solutions are $q_n a = n\sigma$. For small λ, a solution exists only if $\sqrt{\lambda - \left(\frac{\pi}{2}\right)^2} \geq 0$ or $\frac{2mV_0a^2}{\hbar^2} \geq \frac{\pi^2}{4}$.

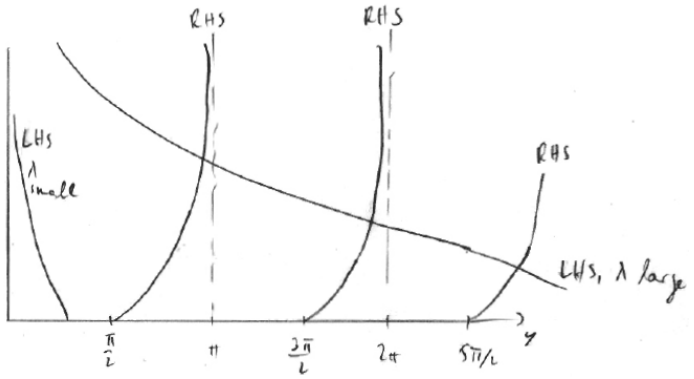

Figure III: Graphic solution of the eigenvalue equation (17-4) for antisymmetric bound states.

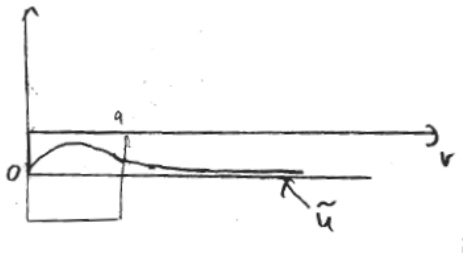

Figure IV: Graphic construction of an odd-state solution, or of a solution in 3D, where the wavefunction must vanish at the origin.

Condition for the existence of odd solutions. In 3D, we will require that a (modified) wavefunction vanishes at the origin, therefore the solutions will look like odd-parity solutions. (It is as if the wavefunction were continued at $-r$.)

Odd solutions do not always exist because the wavefunction needs to bend around sufficiently to match a decaying exponential, this requires high KE.

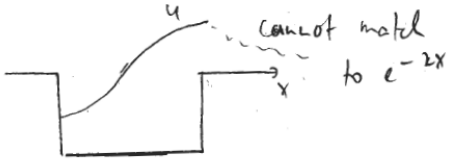

Figure V: If the well is not deep enough, the odd solution cannot bend down sufficiently to match (with continuous slope) a decaying exponential at the edge of the well.

Three Dimensional Problems

Schrodinger Equation in Three Dimension.

A. In Cartesian coordinates

Key concepts

Seperation of Variable

Degeneray $\leftrightarrow$ symmetry

Remarks

Remember the examination problem (two dimensional problem

Free Particle

Particle in a Box

Harmonic Oscillator

Exercise

Schrodinger Equation in Three Dimension.

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

$\psi(x,y,z,t)$ = wave function.

$|\psi(x,y,z,t)|^2\,dx\,dy\,dz$ = probability of finding the "electron" in the volume element between x and $x+dx$, y and $y+dy$, z and $z+dz$ at time t

$= |\psi|^2 d^3r = |\psi|^2 dV$

In more compact notation, it can be written as

$$-\frac{\hbar^2}{2m}\cdot\nabla^2\psi(\vec{r},t)+V(\vec{r},t)\psi(\vec{r},t)=i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)$$

$$\Rightarrow \quad H\psi=i\hbar\frac{\partial\psi}{\partial t}$$

$$H=-\frac{\hbar^2}{2m}\nabla^2+V$$

For $V(\vec{r},t)=V(\vec{r})$ time independent potential, the problem can be solved by the method of seperation of variable

$$\psi(\vec{r},t)=u(\vec{r})\,e^{-iEt/\hbar}$$

with $u(\vec{r})$ satisfies the time-independent Schrodinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)u(x,y,z)+V(x,y,z)\,u(x,y,z)$$
$$=E\,u(x,y,z)$$

If $V(x,y,z)=V_1(x)+V_2(y)+V_3(z)$, then

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)u(x,y,z)+\left(V_1(x)+V_2(y)+V_3(z)\right)$$
$$u(x,y,z)=E\,u(x,y,z)$$

Ansatz: $u(x,y,z)=X(x)Y(y)Z(z)$

Substitute into the above equation

$$-\frac{\hbar^2}{2m}YZ\frac{d^2}{dx^2}X-\frac{\hbar^2}{2m}XZ\frac{d^2}{dy^2}Y-\frac{\hbar^2}{2m}XY\frac{d^2}{dz^2}Z$$

$$+ V_1(x)\,X\,Y\,Z + V_2(y)\,X\,Y\,Z + V_3(z)\,X\,Y\,Z = E\,X\,Y\,Z$$

Divide through by $X\,Y\,Z$ and rearrange

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2}{dx^2}X + V_1(x) = \frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2}{dy^2}Y + \frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2}{dz^2}Z - V_2(y) - V_3(z) + E$$

LHS is function of x only
RHS is function of y, z only

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2}{dx^2}X + V_1(x) = E_x$$

$$+\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y + \frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2}{dz^2}Z - V_2(y) - V_3(z) + E = E_x$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y + V_2(y) = \frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2}{dz^2} - V_3(z) + E - E_x$$

LHS is function of y only
RHS is function of z alone

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2}{dy^2}Y + V_2(y) = E_y$$

and $$-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2}{dz^2} + V_3(z) = E - E_x - E_y = E_z$$

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X(x) + V_1(x)X(x) = E_x X(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}Y(y) + V_2(y)Y(y) = E_y X(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}Z(z) + V_3(z)Z(z) = E_z Z(z)$$

with $E = E_x + E_y + E_z$

The problem is reduced to solve three one dimensional Schrodinger equations.

Example: three dimensional infinite well problem

$$V_1(x) = \begin{cases} 0 & \text{for } 0 < x < L_1 \\ \infty & \text{for } x > L_1,\ x < 0 \end{cases}$$

$$V_2(y) = \begin{cases} 0 & \text{for } 0 < y < L_2 \\ \infty & \text{for } y > L_2,\ y < 0 \end{cases}$$

$$V_3(z) = \begin{cases} 0 & \text{for } 0 < z < L_3 \\ \infty & \text{for } z > L_3,\ z < 0 \end{cases}$$

$$X(x) = A_1 \sin kx + B \cos kx \quad \text{in} \quad 0 < x < L_1$$

$$\frac{\hbar^2 k^2}{2m} = E_x$$

$$= 0 \quad \text{in} \quad x < 0,\ x > L_1$$

Boundary condition $X(0) = 0 \Rightarrow B = 0$

$X(L_1) = 0 \Rightarrow k_n L_1 = n\pi$

$$\Rightarrow k_n = \frac{n_x \pi}{L_1} \qquad n_x = \text{integers}$$

$$\Rightarrow X(x) = A_n \sin \frac{n_x \pi}{L_1} x \quad \text{with } n_x = \text{integrals}$$

in $0 < x < L_1$

Normalization $|A_n|^2 \int_0^{L_1} \sin^2 \frac{n_x \pi}{L_1} x \, dx = 1.$

$$A_n = \sqrt{\frac{2}{L_1}}$$

$$E_{x,n_x} = \frac{\hbar^2 n_x^2 \pi^2}{2m L_1^2}$$

The same method can be used to solve the y, z equation

$$\Rightarrow U_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{2^3}{L_1 L_2 L_3}} \sin \frac{n_x \pi x}{L_1} \sin \frac{n_y \pi y}{L_2} \sin \frac{n_z \pi z}{L_3}$$

$$\Rightarrow \psi_{n_x, n_y, n_z}(x, y, z; t) = U_{n_x, n_y, n_z}(x, y, z)\, e^{-i \frac{E}{\hbar} t}$$

$$E = E_{n_x} + E_{n_y} + E_{n_z} = \frac{\hbar^2 \pi^2 n_x^2}{2m L_1^2} + \frac{\hbar^2 \pi^2 n_y^2}{2m L_2^2} + \frac{\hbar^2 \pi^2 n_z^2}{2m L_3^2}$$

Degeneracy : different (number) wave functions with same energy

↓ linear independent

Example : for the case $L_1 = L_2 = L_3 = L$

$$E = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

Clearly, $n_x = 2$, $n_y = 1$, $n_z = 1$, $n_x = 1$, $n_y = 2$, $n_z = 1$ and $n_x = 1$, $n_y = 1$, $n_z = 2$ will have the

⇒ these three states are said to be degenerate.
the number of degeneracy = 3.

- This is an important concept that we shall encount often
- From this example, it can be seen the concept of degeneracy is closely related to symmetry.

6

Three-Dimensional Problems

6.1 Introduction

In this chapter we examine how to solve the Schrödinger equation for spinless particles moving in three-dimensional potentials. We carry out this study in two different coordinate systems: the Cartesian system and the spherical system.

First, working within the context of Cartesian coordinates, we study the motion of a particle in different potentials: the free particle, a particle in a (three-dimensional) rectangular potential, and a particle in a harmonic oscillator potential. This study is going to be a simple generalization of the one-dimensional problems presented in Chapter 4. Unlike the one-dimensional case, three-dimensional problems often exhibit degeneracy, which occurs whenever the potential displays symmetry.

Second, using spherical coordinates, we describe the motion of a particle in spherically symmetric potentials. After presenting a general treatment, we consider several applications ranging from the free particle and the isotropic harmonic oscillator to the hydrogen atom. We conclude the chapter by calculating the energy levels of a hydrogen atom when placed in a constant magnetic field; this gives rise to the Zeeman effect.

6.2 3D Problems in Cartesian Coordinates

We examine here how to extend Schrödinger's theory of one-dimensional problems (Chapter 4) to three dimensions.

6.2.1 General Treatment: Separation of Variables

The time-dependent Schrödinger equation for a spinless particle of mass m moving under the influence of a three-dimensional potential is

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi(x,y,z,t)+\hat{V}(x,y,z,t)\Psi(x,y,z)=i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t}, \tag{6.1}$$

where $\vec{\nabla}^2$ is the Laplacian, $\vec{\nabla}^2=\partial^2/\partial x^2+\partial^2/\partial y^2+\partial^2/\partial z^2$. As seen in Chapter 4, the wave function of a particle moving in a time-independent potential can be written as a product of

spatial and time components:

$$\Psi(x, y, z, t) = \psi(x, y, z)e^{-iEt/\hbar}, \tag{6.2}$$

where $\psi(x, y, z)$ is solution to the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(x, y, z) + \hat{V}(x, y, z)\psi(x, y, z) = E\psi(x, y, z), \tag{6.3}$$

which is of the form $\hat{H}\psi = E\psi$.

This partial differential equation is generally difficult to solve. But, for those cases where the potential $\hat{V}(x, y, z)$ separates into the sum of three independent, one-dimensional terms (which should not be confused with a vector)

$$V(x, y, z) = V_x(x) + V_y(y) + V_z(z), \tag{6.4}$$

we can solve (6.3) by means of the technique of *separation of variables*. This technique consists of separating the three-dimensional Schrödinger equation (6.3) into three independent one-dimensional Schrödinger equations. Let us examine how to achieve this. Note that (6.3), in conjunction with (6.4), can be written as

$$\left[\hat{H}_x + \hat{H}_y + \hat{H}_z\right]\psi(x, y, z) = E\psi(x, y, z), \tag{6.5}$$

where $\hat{H}_x$ is given by

$$\hat{H}_x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_x(x); \tag{6.6}$$

the expressions for $\hat{H}_y$ and $\hat{H}_z$ are analogous.

As $\hat{V}(x, y, z)$ separates into three independent terms, we can also write $\psi(x, y, z)$ as a product of three functions of a single variable each:

$$\psi(x, y, z) = X(x)Y(y)Z(z). \tag{6.7}$$

Substituting (6.7) into (6.5) and dividing by $X(x)Y(y)Z(z)$, we obtain

$$\left[-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} + V_x(x)\right] + \left[-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} + V_y(y)\right] + \left[-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2} + V_z(z)\right] = E. \tag{6.8}$$

Since each expression in the square brackets depends on only one of the variables x, y, z, and since the sum of these three expressions is equal to a constant, E, each separate expression must then be equal to a constant such that the sum of these three constants is equal to E. For instance, the x-dependent expression is given by

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_x(x)\right]X(x) = E_xX(x). \tag{6.9}$$

Similar equations hold for the y and z coordinates, with

$$E_x + E_y + E_z = E. \tag{6.10}$$

The separation of variables technique consists in essence of reducing the three-dimensional Schrödinger equation (6.3) into three separate one-dimensional equations (6.9).

6.2.2 The Free Particle

In the simple case of a free particle, the Schrödinger equation (6.3) reduces to three equations similar to (6.9) with $V_x = 0$, $V_y = 0$ and $V_z = 0$. The x-equation can be obtained from (6.9):

$$\frac{d^2X(x)}{dx^2} = -k_x^2 X(x), \tag{6.11}$$

where $k_x^2 = 2mE_x/\hbar^2$, and hence $E_x = \hbar^2 k_x^2/2m$. As shown in Chapter 4, the normalized solutions to (6.11) are plane waves

$$X(x) = \frac{1}{\sqrt{2\pi}} e^{ik_x x}. \tag{6.12}$$

Thus, the solution to the three-dimensional Schrödinger equation (6.3) is given by

$$\psi_{\vec{k}}(x, y, z) = (2\pi)^{-3/2} e^{ik_x x} e^{ik_y y} e^{ik_z z} = (2\pi)^{-3/2} e^{i\vec{k}\cdot\vec{r}}, \tag{6.13}$$

where $\vec{k}$ and $\vec{r}$ are the wave and position vectors of the particle, respectively. As for the total energy E, it is equal to the sum of the eigenvalues of the three one-dimensional equations (6.11):

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2}{2m}\vec{k}^2. \tag{6.14}$$

Note that, since the energy (6.14) depends only on the magnitude of $\vec{k}$, all different orientations of $\vec{k}$ (obtained by varying k_x, k_y, k_z) subject to the condition

$$|\vec{k}| = \sqrt{k_x^2 + k_y^2 + k_z^2} = constant, \tag{6.15}$$

generate different eigenfunctions (6.13) without a change in the energy. As the total number of orientations of $\vec{k}$ which preserve its magnitude is infinite, the energy of a free particle is *infinitely degenerate*.

Note that the solutions to the time-dependent Schrödinger equation (6.1) are obtained by substituting (6.13) into (6.2):

$$\Psi_{\vec{k}}(\vec{r}, t) = \psi(\vec{r}) e^{-i\omega t} = (2\pi)^{-3/2} e^{i(\vec{k}\cdot\vec{r} - \omega t)}, \tag{6.16}$$

where $\omega = E/\hbar$; this represents a propagating wave with wave vector $\vec{k}$. The orthonormality condition of this wave function is expressed by

$$\int \Psi^*_{\vec{k}'}(\vec{r}, t)\Psi_{\vec{k}}(\vec{r}, t)\, d^3r = \int \psi^*_{\vec{k}'}(\vec{r})\psi_{\vec{k}}(\vec{r})\, d^3r = (2\pi)^{-3} \int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} d^3r = \delta(\vec{k} - \vec{k}'), \tag{6.17}$$

which can be written in Dirac's notation as

$$\langle \Psi_{\vec{k}'}(t) | \Psi_{\vec{k}}(t) \rangle = \langle \psi_{\vec{k}'} | \psi_{\vec{k}} \rangle = \delta(\vec{k} - \vec{k}'). \tag{6.18}$$

The free particle can be represented, as seen in Chapter 3, by a wave packet (a superposition of wave functions corresponding to the various wave vectors):

$$\Psi(\vec{r}, t) = (2\pi)^{-3/2} \int A(\vec{k}, t)\Psi_{\vec{k}}(\vec{k}, t)\, d^3k = (2\pi)^{-3/2} \int A(\vec{k}, t) e^{i(\vec{k}\cdot\vec{r} - \omega t)} d^3k, \tag{6.19}$$

where $A(\vec{k}, t)$ is the Fourier transform of $\Psi(\vec{r}, t)$

$$A(\vec{k}, t) = (2\pi)^{-3/2} \int \Psi(\vec{r}, t) e^{-i(\vec{k}\cdot\vec{r}-\omega t)} d^3r. \tag{6.20}$$

As seen in Chapters 1 and 4, the position of the particle can be represented classically by the center of the wave packet.

6.2.3 The Box Potential

We are going to begin with the rectangular box potential, which has no symmetry, and then consider the cubic potential, which displays a great deal of symmetry, since the xyz axes are equivalent.

6.2.3.1 The Rectangular Box Potential

Consider first the case of a spinless particle of mass m confined in a *rectangular* box of sides L_x, L_y, L_z:

$$V(x, y, z) = \begin{cases} 0 & 0 < x < L_x,\ 0 < y < L_y,\ 0 < z < L_z \\ \infty & \text{elsewhere,} \end{cases} \tag{6.21}$$

which can be written as $V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$, with

$$V_x(x) = \begin{cases} 0 & 0 < x < L_x \\ \infty & \text{elsewhere;} \end{cases} \tag{6.22}$$

the potentials $V_y(y)$ and $V_z(z)$ have similar forms.

The wave function $\psi(x, y, z)$ must vanish at the walls of the box. We have seen in Chapter 4 that the solutions for this potential are of the form

$$X(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x\pi}{L_x}x\right), \qquad n_x = 1, 2, 3, \ldots, \tag{6.23}$$

and the corresponding energy eigenvalues are

$$E_{n_x} = \frac{\hbar^2\pi^2}{2mL_x^2} n_x^2. \tag{6.24}$$

From these expressions we can write the normalized three-dimensional eigenfunctions and their corresponding energies:

$$\boxed{\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x\pi}{L_x}x\right) \sin\left(\frac{n_y\pi}{L_y}y\right) \sin\left(\frac{n_z\pi}{L_z}z\right),} \tag{6.25}$$

$$\boxed{E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right).} \tag{6.26}$$

Table 6.1 Energy levels and their degeneracies for the cubic potential $E_1 = \pi^2\hbar^2/(2mL^2)$.

$E_{n_x n_y n_z}/E_1$	(n_x, n_y, n_z)	g_n
3	(111)	1
6	(211), (121), (112)	3
9	(221), (212), (122)	3
11	(311), (131), (113)	3
12	(222)	1
14	(321), (312), (231), (213), (132), (123)	6

6.2.3.2 The Cubic Potential

For the simpler case of a *cubic* box of side L, the energy expression can be inferred from (6.26) by substituting $L_x = L_y = L_z = L$:

$$\boxed{E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2), \qquad n_x, n_y, n_z = 1, 2, 3, \ldots.} \tag{6.27}$$

The ground state corresponds to $n_x = n_y = n_z = 1$; its energy is given by

$$E_{111} = \frac{3\pi^2\hbar^2}{2mL^2} = 3E_1, \tag{6.28}$$

where, as shown in Chapter 4, $E_1 = \pi^2\hbar^2/(2mL^2)$ is the zero-point energy of a particle in a one-dimensional box. Thus, the zero-point energy for a particle in a three-dimensional box is three times that in a one-dimensional box. The factor 3 can be viewed as originating from the fact that we are confining the particle symmetrically in all three dimensions.

The first excited state has three possible sets of quantum numbers $(n_x, n_y, n_z) = (2, 1, 1)$, $(1, 2, 1)$, $(1, 1, 2)$ corresponding to three different states $\psi_{211}(x, y, z)$, $\psi_{121}(x, y, z)$, $\psi_{112}(x, y, z)$, where

$$\psi_{211}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{2\pi}{L}x\right) \sin\left(\frac{\pi}{L}y\right) \sin\left(\frac{\pi}{L}z\right); \tag{6.29}$$

the expressions for $\psi_{121}(x, y, z)$ and $\psi_{112}(x, y, z)$ can be inferred from $\psi_{211}(x, y, z)$. Notice that all three states have the same energy:

$$E_{211} = E_{121} = E_{112} = 6\frac{\pi^2\hbar^2}{2mL^2} = 6E_1. \tag{6.30}$$

The first excited state is thus threefold *degenerate*.

Degeneracy occurs only when there is a symmetry in the problem. For the present case of a particle in a cubic box, there is a great deal of symmetry, since all three dimensions are equivalent. Note that for the rectangular box, there is no degeneracy since the three dimensions are not equivalent. Moreover, degeneracy did not exist when we treated one-dimensional problems in Chapter 4, for they give rise to only one quantum number.

The second excited state also has three different states, hence it is threefold degenerate; its energy is equal to $9E_1$: $E_{221} = E_{212} = E_{122} = 9E_1$.

The energy spectrum is shown in Table 6.1, where every nth level is characterized by its energy, its quantum numbers, and its degeneracy g_n.

6.2.4 The Harmonic Oscillator

We are going to begin with the anisotropic oscillator, which displays no symmetry, then consider the isotropic oscillator where the xyz axes are all equivalent.

6.2.4.1 The Anisotropic Oscillator

Consider a particle of mass m moving in a three-dimensional anisotropic oscillator potential

$$\hat{V}(\hat{x},\hat{y},\hat{z}) = \frac{1}{2}m\omega_x^2\hat{X}^2 + \frac{1}{2}m\omega_y^2\hat{Y}^2 + \frac{1}{2}m\omega_z^2\hat{Z}^2. \tag{6.31}$$

Its Schrödinger equation separates into three equations similar to (6.9):

$$-\frac{\hbar^2}{2m}\frac{d^2X(x)}{dx^2} + \frac{1}{2}m\omega_x x^2 X(x) = E_x X(x), \tag{6.32}$$

with similar equations for $Y(y)$ and $Z(z)$. The eigenenergies corresponding to the potential (6.31) can be expressed as

$$\boxed{E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z} = \left(n_x + \frac{1}{2}\right)\hbar\omega_x + \left(n_y + \frac{1}{2}\right)\hbar\omega_y + \left(n_z + \frac{1}{2}\right)\hbar\omega_z,} \tag{6.33}$$

with $n_x, n_y, n_z = 0, 1, 2, 3, \ldots$. The corresponding stationary states are

$$\psi_{n_x n_y n_z}(x,y,z) = X_{n_x}(x)Y_{n_y}(y)Z_{n_z}(z), \tag{6.34}$$

where $X_{n_x}(x)$, $Y_{n_y}(y)$, and $Z_{n_z}(z)$ are one-dimensional harmonic oscillator wave functions. These states are not degenerate, because the potential (6.31) has no symmetry (it is anisotropic).

6.2.4.2 The Isotropic Harmonic Oscillator

Consider now an *isotropic* harmonic oscillator potential. Its energy eigenvalues can be inferred from (6.33) by substituting $\omega_x = \omega_y = \omega_z = \omega$,

$$\boxed{E_{n_x n_y n_z} = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega.} \tag{6.35}$$

Since the energy depends on the sum of n_x, n_y, n_z, any set of quantum numbers having the same sum will represent states of equal energy.

The ground state, whose energy is $E_{000} = 3\hbar\omega/2$, is not degenerate. The first excited state is threefold degenerate, since there are three different states, ψ_{100}, ψ_{010}, ψ_{001}, that correspond to the same energy $5\hbar\omega/2$. The second excited state is sixfold degenerate; its energy is $7\hbar\omega/2$.

In general, we can show that the degeneracy g_n of the nth excited state, which is equal to the number of ways the nonnegative integers n_x, n_y, n_z may be chosen to total to n, is given by

$$\boxed{g_n = \frac{1}{2}(n+1)(n+2),} \tag{6.36}$$

where $n = n_x + n_y + n_z$; Table. 6.2 displays the first few energy levels along with their degeneracies.

Table 6.2 Energy levels and their degeneracies for an isotropic harmonic oscillator.

n	$2E_n/(\hbar\omega)$	$(n_x n_y n_z)$	g_n
0	3	(000)	1
1	5	(100), (010), (001)	3
2	7	(200), (020), (002)	6
		(110), (101), (011)	
3	9	(300), (030), (003)	10
		(210), (201), (021)	
		(120), (102), (012)	
		(111)	

Example 6.1 (Degeneracy of a harmonic oscillator)
Show how to obtain the degeneracy relation (6.36) for a harmonic oscillator.

Solution
For a fixed value of n, the degeneracy g_n is given by the number of ways of choosing n_x, n_y and n_z so that $n = n_x + n_y + n_z$.

For a fixed value of n_x, the number of ways of choosing n_y and n_z so that $n_y + n_z = n - n_x$ is given by $(n - n_x + 1)$; this can be shown as follows. For a given value of n_x, the various permissible values of (n_y, n_z) are given by $(n_y, n_z) = (0, n-n_x), (1, n-n_x-1), (2, n-n_x-2), (3, n-n_x-3), \ldots, (n-n_x-3, 3), (n-n_x-2, 2), (n-n_x-1, 1)$ and $(n-n_x, 0)$. In all, there are $(n-n_x+1)$ sets of (n_y, n_z) so that $n_y + n_z = n - n_x$. Now, since the values of n_x can vary from 0 to n, the degeneracy is then given by

$$g_n = \sum_{n_x=0}^{n} (n - n_x + 1) = (n+1)\sum_{n_x=0}^{n} 1 - \sum_{n_x=0}^{n} n_x = (n+1)^2 - \frac{1}{2}n(n+1) = \frac{1}{2}(n+1)(n+2). \tag{6.37}$$

A more primitive way of calculating this series is to use Gauss's method: simply write the series $\sum_{n_x=0}^{n}(n - n_x + 1)$ in the following two equivalent forms:

$$g_n = (n+1) + n + (n-1) + (n-2) + \cdots + 4 + 3 + 2 + 1, \tag{6.38}$$

$$g_n = 1 + 2 + 3 + 4 + \cdots + (n-2) + (n-1) + n + (n+1). \tag{6.39}$$

Since both of these two series contain $(n + 1)$ terms each, a term by term addition of these relations yields

$$\begin{aligned} 2g_n &= (n+2) + (n+2) + (n+2) + \cdots + (n+2) + (n+2) + (n+2) \\ &= (n+1)(n+2), \end{aligned} \tag{6.40}$$

hence $g_n = \frac{1}{2}(n + 1)(n + 2)$.

19. Calculate the possible energy values of a particle in the potential given by $V(x) = \infty$ if $x \leq 0$, and $V(x) = \dfrac{m\omega^2}{2} x^2$ if $x > 0$.

20. A system described by the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \frac{m}{2} (\omega_1^2 x^2 + \omega_2^2 y^2 + \omega_3^2 z^2) \tag{20a}$$

is called an "anisotropic harmonic oscillator".

Determine the possible energies of this system, and, for the isotropic case ($\omega_1 = \omega_2 = \omega_3 = \omega$), calculate the degeneracy of the level E_n.

19. Since the particle cannot penetrate into the range $x < 0$, the eigenfunctions of the corresponding Schrödinger equation have to vanish for $x = 0$. On the other hand, in the range $x > 0$, these eigenfunctions are the same as those of the harmonic oscillator. Hence the odd wavefunctions of the oscillator, with $n = 2k+1$, which vanish at $x = 0$, are the solutions of this problem. Therefore

$$E_k = \hbar\omega(2k+\tfrac{3}{2}), \quad k = 0, 1, 2, \ldots$$

20. Since $V(x, y, z) = V_1(x)+V_2(y)+V_3(z)$, this problem reduces to the problem of three independent harmonic oscillators of frequencies $\omega_1, \omega_2, \omega_3$, along the axes x, y, z respectively (see problem 1). Therefore

$$E_{n_1n_2n_3} = \hbar\omega_1(n_1+\tfrac{1}{2})+\hbar\omega_2(n_2+\tfrac{1}{2})+\hbar\omega_3(n_3+\tfrac{1}{2}), \tag{20.1}$$

$$\psi_{n_1n_2n_3}(x, y, z) = \left(\frac{m^3\omega_1\omega_2\omega_3}{\hbar^3\pi^3}\right)^{1/4}\left(\frac{2^{-(n_1+n_2+n_3)}}{n_1!n_2!n_3!}\right)^{1/2}\times$$

$$\times H_{n_1}(\xi_1)\,H_{n_2}(\xi_2)\,H_{n_3}(\xi_3)\exp\left[-\frac{1}{2}(\xi_1^2+\xi_2^2+\xi_3^2)\right], \tag{20.2}$$

where

$$\xi_1 = \left(\frac{m\omega_1}{\hbar}\right)^{1/2}x, \quad \xi_2 = \left(\frac{m\omega_2}{\hbar}\right)^{1/2}y, \quad \xi_3 = \left(\frac{m\omega_3}{\hbar}\right)^{1/2}z$$

and $n_1, n_2, n_3 = 0, 1, 2, \ldots$.

If the ratios of the eigenfrequencies are irrational, the energy levels are non-degenerate, otherwise they may be degenerate. The ground state E_{000} is always non-degenerate.

For the isotropic harmonic oscillator

$$E_n = \hbar\omega(n+\tfrac{3}{2}), \quad \text{where} \quad n = n_1+n_2+n_3\,. \tag{20.3}$$

In this case all the energy levels with the exception of E_0 are degenerate. To calculate the degeneracy of the level of energy E_n, consider for the moment a particular value of the quantum number n_1. n_2 can then have any of the values $0, 1, \ldots, n-n_1$, and the sum $n = n_1+n_2+n_3$ for given n and n_1 can be obtained in $n-n_1+1$ ways. Since $n_1 = 0, 1, 2, \ldots, n$, the degeneracy of E_n will be

$$\sum_{n_1=0}^{n}(n-n_1+1) = \tfrac{1}{2}(n+1)(n+2). \tag{20.4}$$