

# The Postulates

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In its beginnings, quantum mechanics was approached in two completely different ways. Schrödinger, reasoning that electronic motions could be treated as waves, developed wave mechanics. This utilized the great body of information from classical physics and applied it to electronic and orbital motions. The stationary states that an electron or molecule might have were analogous to standing waves set up by applying appropriate boundary conditions. Heisenberg, independently and slightly earlier, had used the properties of matrices to get the same results. This approach looked very different at first, but was later shown to be equivalent to the Schrödinger approach.

The approach that most books take is to start with a motivation for the need for quantum mechanics. At the turn of the the twentieth century experimental evidence had accumulated which suggested a breakdown of classical physics. Examples included black body radiation, line spectra of atoms, photoelectric effect, Compton effect, etc. We will not concern ourselves with these experiments or what classical mechanics failed to explain about them or for that matter how quantum mechanics was able to circumvent these inconsistencies. The premise is that you are aware of the essence of these experimental findings. If you are not, then you will find excellent discussions in most Modern Physics textbooks, both modern (Krane, Singh, Beiser etc.) and not-so-modern (Leighton or Richtmeyer, Kennard, and Cooper are two classic ones).

The formulation of quantum mechanics we pursue is a postulatory approach within the Schrödinger method. This treats quantum mechanics as a new subject with its own set of postulates analogous to the way in which Euclid's geometry is formulated. The basic ideas are introduced as postulates and these postulates are justified, in part, by the fact that the results that one gets agree with experiments. This approach is similar to that followed in classical thermodynamics.

The postulates of any theory are a set of fundamental statements that the student is asked to believe and draw conclusions from. These conclusions are then tested by experiment and if they are confirmed, the belief in the postulate is justified. The postulates can not be explained in terms of fundamental concepts or else the more fundamental concepts would be used as postulates. For this reason the student should not allow himself to try and “understand” the postulates. A second point that should be kept in mind is that the ease with which a postulate may be made to appear reasonable depends on how readily it may be related to everyday experience. In quantum mechanics, the postulates are about atomic and molecular properties, and these are, in general, quite far removed from every day experience. Consequently, the postulates, may, also, in this sense be “difficult to understand.” The main point to keep in mind is that postulates are justified by their ability to predict and correlate experimental facts and by their general applicability.

With this background in mind we introduce the basic postulates of quantum theory. The five postulates usher in the concepts of wave function, operator, measurement, expectation value, and the time dependent Schrödinger equation. Note that the exact wording of the postulates will depend on the source.

# 1 The wavefunction

**Postulate 1** A state of a dynamical system of  $N$  particles is described as fully as possible by a function  $\Psi(q_1, q_2, \dots, q_{3N}, t)$  such that the quantity  $\Psi^*\Psi d\tau$  is proportional to the probability of finding  $q_1$  between  $q_1$  and  $q_1 + dq_1$ ,  $q_2$  between  $q_2$  and  $q_2 + dq_2$ ,  $\dots$ ,  $q_{3N}$  between  $q_{3N}$  and  $q_{3N} + dq_{3N}$  at a specific time  $t$ .

In less succinct form, this postulate says that all the information about the properties of a system is contained in a function  $\Psi$  (usually called a wave function) which is a function only of the coordinates and time. Note that  $\Psi$  may be complex. If the wave function includes the time explicitly, it is called a time-dependent wave function. If the observable properties of a system do not change with time, a system is said to be in a stationary state.

The second part of the postulate gives a physical interpretation of the  $\Psi$  function. This interpretation is easiest to visualize for a system containing a single particle constrained to move in one dimension. The quantity  $\Psi^*\Psi dx$  is then just the probability of finding the particle between  $x$  and  $x + dx$  at a given time. Because of this probabilistic interpretation for the wave function and in order for it to be in accord with physical reality, it is subject to certain restrictions. These restrictions are the following.

1. The function should be SQUARE INTEGRABLE or in other words  $\int_{-\infty}^{\infty} \psi^*\psi dx$  is finite. For most situations this can be interpreted to mean that the function is everywhere FINITE and that  $\Psi$  will go to zero at  $\pm\infty$ . A special case of this requirement is that, like any probability distribution, the probability of finding the system in all space must be unity, or mathematically

$$\int_{-\infty}^{\infty} \psi^*\psi dx = 1.$$

A function for which this is true is said to be normalized. A solution,  $\psi$ , of the Schrödinger equation may not be normalized to begin with but a constant can always be determined such that  $\psi' = N\psi$  is normalized. This is because the Hamiltonian is a linear operator, which implies that if  $\psi$  is an eigenfunction then so is  $N\psi$ . The constant  $N$  is called the normalization constant and is given by

$$N = \frac{1}{\sqrt{\int_{-\infty}^{\infty} \psi^*\psi dx}}.$$

2. The function should be CONTINUOUS.
3. The function should be SINGLE VALUED.

We reiterate that the conditions laid out above arise from the fact that  $\psi$  supports a probabilistic description.

# 2 Operator

**Postulate 2** For every observable property of a system there exists a corresponding linear Hermitian operator, and the physical properties of the observable can be inferred from the mathematical properties of its associated operator.

An operator is nothing more than a symbol that tells one to do something to what follows that symbol. Thus in the expression  $\sqrt{2}$ , the  $\sqrt{\quad}$  is an operator telling one to take the square root of what follows, in this case 2. Likewise, in the expression

$$\frac{d}{dx}(x^2 + 5x + 1)$$

the operator is  $\frac{d}{dx}$  and one has to take derivative with respect to  $x$  of what follows, that is,  $x^2 + 5x + 1$ . In general, operators will be represented with a caret (hat) over it, that is,  $\hat{P}$  or  $\hat{\alpha}$ .

An operator can be a vector or complex quantity. If an operator is a vector, one usually thinks of it in terms of its components. An example of a vector operator is “del.”

$$\nabla = \frac{\partial}{\partial x} \mathbf{i} + \frac{\partial}{\partial y} \mathbf{j} + \frac{\partial}{\partial z} \mathbf{k}$$

If an operator is complex, the complex conjugate is formed by replacing  $i$  by  $-i$  wherever it occurs. Thus if  $\hat{P} = i \frac{d}{dx}$ ,  $\hat{P}^* = -i \frac{d}{dx}$ .

In quantum mechanics only linear operators are used. An operator is linear if it is true that

$$\hat{P}(f + g) = \hat{P}f + \hat{P}g$$

or

$$\hat{P}af = a\hat{P}f$$

where  $a$  is a constant. An example of a linear operator is  $\frac{d}{dx}$  whereas the operator  $\sqrt{\quad}$  is not.

When dealing with operators one must be careful of the order of operations. Thus if  $\hat{P} = \left(\frac{\partial}{\partial x}\right)_{yz}$  and  $\hat{Q} = \left(\frac{\partial}{\partial y}\right)_{zz}$  then

$$\hat{P}\hat{Q} = \left| \frac{\partial}{\partial x} \left( \frac{\partial}{\partial y} \right)_{xz} \right|_{yz} = \frac{\partial^2}{\partial x \partial y}.$$

By convention, one always begins with the operator on the right and works outward to the left. Like matrix multiplication operations are not necessarily commutative. Thus we may have

$$\hat{P}\hat{Q} \neq \hat{Q}\hat{P}.$$

The quantity  $\hat{P}\hat{Q} - \hat{Q}\hat{P}$  is called the commutator of  $\hat{P}$  and  $\hat{Q}$  and is notated  $[\hat{P}, \hat{Q}]$ . It is zero if  $\hat{P}$  and  $\hat{Q}$  commute and non-zero otherwise.

The concept of a Hermitian operator is also introduced in this postulate. An operator is  $\hat{\alpha}$  is Hermitian if

$$\int \psi_i^* \hat{\alpha} \psi_j d\tau = \int (\hat{\alpha} \psi_i)^* \psi_j d\tau$$

where  $\psi_i$  and  $\psi_j$  are arbitrary normalizable functions. Hermitian operators have real eigenvalues.

How does one get the operators for a given observable? A rigorous way to do this is to relate the commutator of two operators to a classical quantity called the Poisson bracket, but here we will follow the prescription given below. First, the classical expression for the observable of interest is written in terms of coordinates, momenta, and time. Next, the time and coordinates are left just as they are while the momenta,  $p_x$  say, in Cartesian coordinates, is replaced by the operator  $-i\hbar \frac{\partial}{\partial x}$ . As an example, let us construct the quantum mechanical operator for the kinetic energy  $T$ . The classical kinetic energy of a particle in Cartesian coordinates is

$$T = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

Using the prescription given above, and being careful of the order of the operations, this becomes

$$\hat{T} = \frac{1}{2m} \left[ \left( -i\hbar \frac{\partial}{\partial x} \right) \left( -i\hbar \frac{\partial}{\partial x} \right) + \left( -i\hbar \frac{\partial}{\partial y} \right) \left( -i\hbar \frac{\partial}{\partial y} \right) + \left( -i\hbar \frac{\partial}{\partial z} \right) \left( -i\hbar \frac{\partial}{\partial z} \right) \right]$$

or

$$\hat{T} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \nabla^2$$

Perhaps the most important operator that will concern us is the operator connected with the total energy  $E$  of a system. The classical expression for the total energy is Hamilton's function, and the corresponding operator is called the Hamiltonian. The expression for the Hamiltonian for a single particle system is

$$\hat{H} = \hat{T} + \hat{V}$$

But  $\hat{T}$  is given above and  $\hat{V}$  is only a function of the coordinates, that according to our prescription remains the same.

### 3 Measurement

**Postulate 3** Suppose that  $\hat{\alpha}$  is an operator corresponding to an observable and that there is a set of identical systems in state  $\Psi_s$ . Suppose further that  $\Psi_s$  is an eigenfunction of  $\hat{\alpha}$ . That is  $\hat{\alpha}\Psi_s = a_s\Psi_s$ , where  $a_s$  is a number. Then, a series of measurements of the quantity corresponding to  $\hat{\alpha}$  on different members of the set, will always yield the result  $a_s$ . It is only when  $\Psi_s$  and  $\hat{\alpha}$  satisfy this condition that an experiment will give the same result on each measurement.

An equation of the type

$$\hat{\alpha}(q_i)f(q_i) = af(q_i)$$

where  $\hat{\alpha}(q_i)$  is an operator, and  $f(q_i)$  is a function, both involving variable  $q_i$ , and  $a$  is a constant, is called an eigenvalue equation. When such an equation holds,  $f(q_i)$  is called an eigenfunction of the operator  $\hat{\alpha}(q_i)$  and  $a$  is called the eigenvalue.

Eigenvalue equations are of great importance in the mathematical formalism of quantum mechanics. In quantum mechanics,  $\hat{\alpha}$  is often a differential operator and, therefore, the eigenvalue equation is a differential equation. The principal mathematical problem of quantum mechanics is to find the solution  $f$  and the eigenvalues  $a$  of these eigenvalue equations.

To give an example of an eigenvalue equation, suppose that the operator of interest is  $\hat{\alpha} = d^2/dx^2$ . We seek to find functions  $f(x)$  such that  $\hat{\alpha}$  operates on  $f(x)$ ,  $f(x)$  again results, multiplied by a constant. There are a number of functions with this property,  $\sin kx$ ,  $\cos kx$ , and  $\exp(\pm kx)$  are some examples. If we were to choose  $\sin(kx)$  we would find that the eigenvalue is  $-k^2$ .

A physical observable like position, energy, dipole moment, etc. when measured necessarily should give real results. Because Hermitian operators have real eigenvalues quantum mechanical operators which represent physical observables are Hermitian.

### 4 Expectation value

**Postulate 4** Given an operator  $\hat{\alpha}$  and a set of identical systems characterized by a function  $\Psi_s$  that is not an eigenfunction of  $\hat{\alpha}$ , a series of measurements of the property corresponding to  $\hat{\alpha}$  on different members of the set will not give the same result but will always be one of the eigenvalues of the observable. A distribution results, the average of which is

$$\langle \alpha \rangle = \frac{\int \Psi_s^* \hat{\alpha} \Psi_s d\tau}{\int \Psi_s^* \Psi_s d\tau}$$

The expectation formula implies, for example, that, if we are told that the state of a one-dimensional system is specified by a given wave function  $\psi$ , then we can compute the average value of the momentum  $\hat{p}_x$  of the particle for this state by evaluating

$$\langle p_x \rangle = \frac{\int \psi^* \left( -i\hbar \frac{\partial}{\partial x} \right) \psi dx}{\int \psi^* \psi dx}$$

Note that, since  $\psi$  is a function of  $t$ ,  $\langle \alpha \rangle$  is in general also a function of  $t$ , even though the dynamical variable  $\hat{\alpha}$  may not depend on  $t$  explicitly.

The following three general implications of the expectation postulate are very important:

1. Because operators associated with dynamical variables are linear, a substitution of  $c\psi$  for  $\psi$  does not affect the expectation value.
2. If the dynamical variable  $\hat{\alpha}$  is a function of position only, then the expectation may be rewritten as

$$\langle f(x) \rangle = \frac{\int f(x)\psi^*\psi d\tau}{\int \psi^*\psi d\tau}.$$

On the other hand, if the operator  $\hat{\alpha}$  involves differentiation, it is of course not possible to rearrange the factors in the integrand in the numerator.

3. If the state specified by a wave function  $\psi$  that is an eigenvalue of the observable  $\hat{\alpha}$  then the expectation value is the same as the eigenvalue.

## 5 Schrödinger equation

**Postulate 5** The evolution of a state vector  $\Psi(q, t)$  in time is given by the relation

$$i\hbar \frac{d\Psi}{dt} = \hat{H}\Psi$$

where  $\hat{H}$  is the Hamiltonian operator for the system.

This equation is called the *time dependent Schrödinger equation*. This is the central equation of nonrelativistic quantum mechanics.

When the potential does not depend on the time, the Schrödinger equation admits stationary state solutions of the form

$$\Psi(\mathbf{r}, t) = \psi_E(\mathbf{r}) \exp(-iEt/\hbar)$$

where  $E$  is a constant and where  $\psi_E(\mathbf{r})$  satisfies the time independent Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi_E(\mathbf{r}) = E\psi_E(\mathbf{r})$$

or

$$\hat{H}\psi_E(\mathbf{r}) = E\psi(\mathbf{r}).$$

This is achieved by a straightforward application of the separation of variables procedure outlined in one of the appendices. The significance of the constant  $E$  is seen by recognizing that  $E$  is the expectation value of the total energy  $\hat{H} = \hat{T} + \hat{V}$ . Indeed by using the expectation value and the stationary state solution, we have

$$\langle E \rangle = \int \Psi^* \hat{H} \Psi d\tau$$

We shall find that only certain values of  $E$  are compatible with normalizable solutions. These values are called the energy eigenvalues and the corresponding solutions  $\psi_E$  are the eigenfunctions of the total energy or Hamiltonian operator  $\hat{H}$ .

The set of all eigenvalues of the Hamiltonian is called the energy spectrum. It may consist of discrete values or a continuous range or both. In general the discrete eigenvalues are associated with bound state and the continuum with scattering states.

## 6 Properties of the Wave Function

The physical interpretation of the wave function in terms of a probability implied that a function needs to satisfy some conditions, which were laid out in the previous chapter, before it is an acceptable wave function. We will now look at some more properties of the solutions to the Schrödinger equation. For simplicity we will restrict our attention to one-dimensional spatial problems, although most results are applicable to higher dimensional problems.

The wavefunction is the solution of the eigenvalue equation

$$\mathcal{H}\psi(x) = E\psi(x), \quad (1)$$

where  $\mathcal{H}$  is the Hamiltonian operator and has the form

$$\mathcal{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x).$$

Over and above the conditions laid out in chapter 1 we will now show that, for finite potentials, the first derivative of the wavefunction,  $\frac{d\psi}{dx}$  should also be single valued and continuous. To this end we rewrite the Schrödinger equation in the form

$$\frac{d^2\psi}{dx^2} = \frac{2m(V - E)}{\hbar^2} \psi. \quad (2)$$

A discontinuity in  $\frac{d\psi}{dx}$  would mean that the LHS of this expression would become infinite, which for finite  $V$  is unacceptable.

We will analyze the one-dimensional Schrödinger equation in slightly greater detail, which will allow us to draw some other general conclusions about the wavefunction. Consider a potential of the form given in the figure below.

We will consider four different regions and will focus our attention on the Schrödinger equation written in the form given in eq. 2.

### 6.1 $E < V_{\min}$

In this region  $V - E$  is always positive, so that the second derivative of the wavefunction, which represents the concavity, has the same sign as the wavefunction. This may be a good time to step aside and remind ourselves some simple things about how one sketches functions from a knowledge of the derivatives.

The derivative of a function  $y = f(x)$ , is the rate at which  $y$  changes with respect to  $x$ . It defines the slope of the function's graph at  $x$  and provides an estimate of how much  $y$  changes when  $x$  is changed by a small amount. If a function has a derivative over an interval, then it is continuous over the interval and its graph over the interval is unbroken. Even more information about the graph of a differentiable function can be obtained from a knowledge of where the derivative is positive, negative, and zero. Suppose that over an interval a function  $y = f(x)$  has derivative at every point  $x$ , then  $f$  increases in the interval if  $f'(x) > 0$  and decreases if  $f'(x) < 0$ . Moreover, if  $f'$  changes continuously from positive to negative as we move from left to right through a point  $c$ , then the value of  $f$  at  $c$  is a local maximum of  $f$ . But, a horizontal tangent does not imply a maximum or a minimum. Take the function  $y = x^3$  which crosses the horizontal tangent at  $x = 0$  but keeps on rising. If you look at the function closely, however, we find that the portions of the curves in the region  $(-\infty, 0)$  and  $(0, \infty)$  turn in different ways. To the left of the origin the curve turns to the right, while to the right of the origin it turns to the left. In other words, the left portion "bends downward" while the right portion "bends upward." More rigorously we would say that the curve is concave down on the interval  $(-\infty, 0)$  and concave up on  $(0, \infty)$ . The direction of concavity is determined by the sign of  $f''$  being

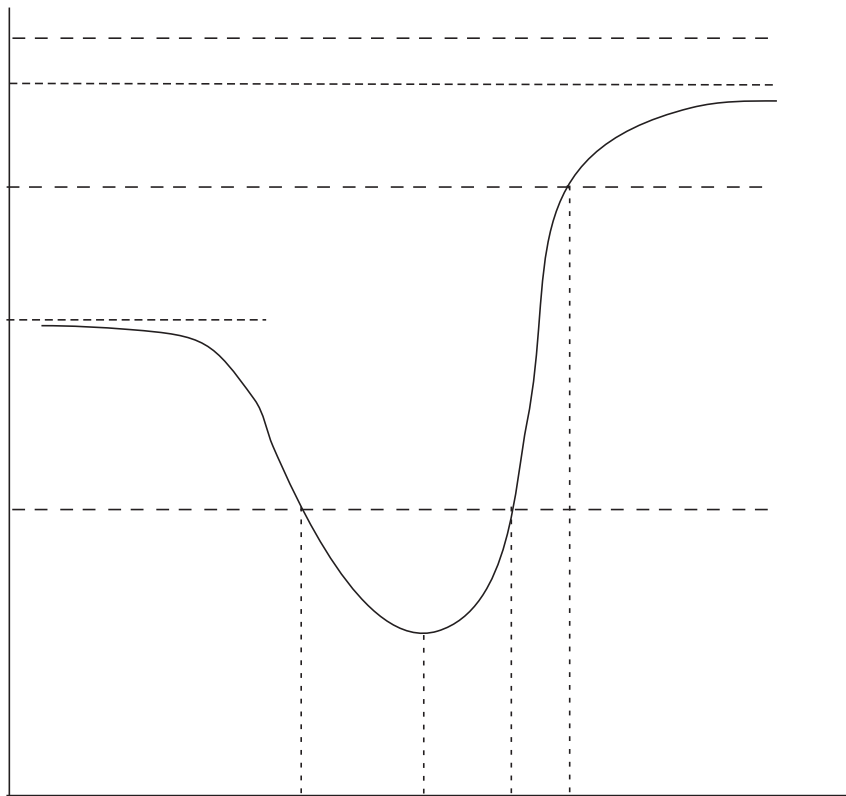


Figure 1: A typical one-dimensional potential showing a minimum at  $x_0$ . The potential has two classical turning points at  $x_1$  and  $x_2$  when the  $V_{\min} < E < V_-$  and a turning point  $x_3$  when  $V_- < E < V_+$ .

concave down if  $f'' < 0$  and concave up if  $f'' > 0$ . A point on the curve where the concavity changes from up to down or vice versa is called a point of inflection,  $f'' = 0$ .

Coming back to the problem at hand, from the discussion in the last paragraph we now know that in this case the function will be concave upwards when  $\psi > 0$  and concave downwards when  $\psi < 0$  as is represented in Fig. 2. Since  $V - E$  is positive for all  $x$ , it is clear that a

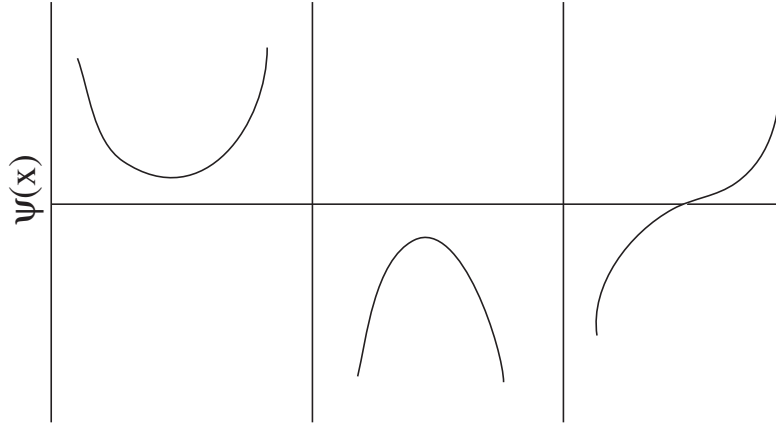


Figure 2: The curvature of the wavefunction when the energy is below  $V_{\min}$  is of the same sign as the wavefunction and is hence concave upwards if  $\psi$  is  $> 0$  and concave downwards if  $\psi$  is  $< 0$ .

solution which remains finite everywhere cannot be found. In fact,  $|\psi(x)|$  grows without limit as  $x \rightarrow +\infty$  or/and as  $x \rightarrow -\infty$ . The best we could do is to select from among the two linearly independent solutions a function which approaches the  $x$ -axis asymptotically either on the left or on the right, but then this solution will necessarily ‘blow up’ on the other side. We conclude therefore that there is no acceptable solution of the Schrödinger equation when  $E < V(x)$  for all  $x$ . Classically also this is not possible since this would correspond to negative kinetic energy.

## 6.2 $V_{\min} < E < V_-$

This region can be broken up into three parts: left of the classical turning point  $x_1$ , between the two turning points, and to the right of the turning point  $x_2$ . The classical turning points are those points at which  $E = V$ , that is points where the kinetic energy becomes zero. Classically at these points the particle would stop and turn around and no classical motion is possible to the left of  $x_1$  and to the right of  $x_2$ . In the first and the third parts,  $V - E > 0$ , and hence the curvature of the wavefunction is similar to that in region 0 and is represented by Fig. 2. This implies that we cannot have oscillatory solutions in these two parts. Between the two turning points  $V - E < 0$  and hence the curvature is opposite to the sign of the wavefunction. In this case, the function is concave downwards when  $\psi > 0$  and concave upwards when  $\psi < 0$ . The curvature in this region is represented in Fig. 3. Thus in this part the wavefunction will exhibit oscillatory behavior. For some values of the energy, say  $E'$ , the oscillatory solution between the two turning points will connect smoothly with the asymptotic solutions to the left of  $x_1$  and to the right of  $x_2$  as in the middle part of Fig. 4. For values of the energy either greater or lesser than  $E'$  the solutions diverge to  $+\infty$  or  $-\infty$  when  $x \rightarrow \infty$ . It is important to realise that this smooth connection to give physically acceptable solutions called eigenfunctions only happens for some values of energy, which are called the eigenvalues. The number of such energies for which reasonable solutions exist will depend on the characteristics of the potential. Finally, we observe that we have obtained a fundamental result: the quantization of the bound-state energies, the determination of which appears in Schrödinger’s mechanics as an eigenvalue problem.



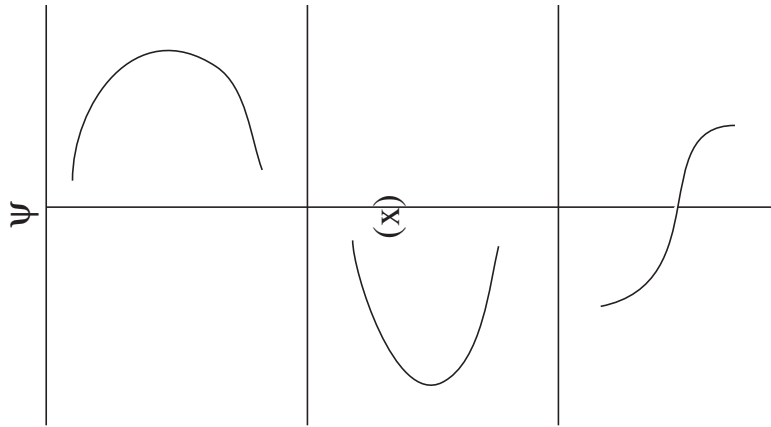


Figure 3: The curvature of the wavefunction when  $V - E < 0$  as is the case between the two turning points in region 1

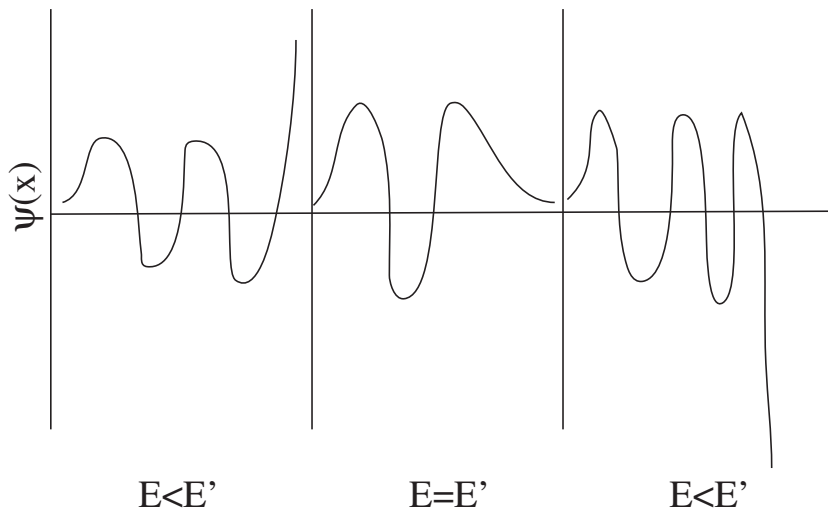


Figure 4: For values of the energy greater or less than the eigenvalue  $E'$  the solutions of the Schrödinger equation give physically unreasonable results. Note that there may be a number of  $E$ 's for which physically acceptable results are obtained

### 6.3 $V_- < E < V_+$

In this energy range we note there is only one classical turning point, at  $x = x_3$ . No classical motion is allowed for  $x > x_3$  or else it would be reflected at  $x_3$ . The classical particle is unbound since it can move in an infinite region of the  $x$ -axis. Quantum mechanically, we see that for  $x < x_3$  there are two linearly independent solutions (since we are solving a second order differential equation) both of which are oscillatory (reasons evident by looking at Fig. 3), one corresponding to the particle moving to the left and the other to it moving to the right. For values of  $x > x_3$  also there will be two solutions, one which tends to zero as  $x \rightarrow \infty$  and the other which is unbounded as  $x$  approaches  $\infty$ . Obviously the only physically acceptable solution is the former. The continuity conditions of  $\psi$  and  $d\psi/dx$  at  $x_3$  yields two conditions which determine a unique linear combination of the two independent oscillatory solutions in the region  $x < x_3$ . It is important to note that in this region 'smooth matching' at  $x = x_3$  is possible for every energy. We conclude that in this interval the allowed energies form a continuum.

### 6.4 $E > V_+$

In this region there are no classical turning points because  $V - E$  is negative for all values of  $x$ . For reasons discussed with regard to Fig. 3 we expect the solutions to be oscillatory. There are two linearly independent solutions corresponding to the two directions that the particle could be moving for every value of the energy. Thus in this region the energy values are continuous and doubly degenerate.

### 6.5 Infinite Potential Energy

So far our discussions have been restricted to the case where the potential energy was finite. We would like to look finally at the situation when the potential energy becomes infinite. Indeed, because a particle cannot have infinite potential energy, it cannot penetrate into a region of space where  $V = \infty$ . We focus our attention on the Schrödinger equation written in the form given in eq. 1. Both  $E$  and  $\psi$  on the RHS are finite while the LHS has one term that is infinite. This equality can only hold when  $\psi$  is identically zero, which implies that the wavefunction goes to zero when the potential becomes infinite. We also note that since  $V$  exhibits a second order discontinuity (infinite jump) across the border,  $d^2\psi/dx^2$  will also exhibit this discontinuity, so that  $d\psi/dx$  will be discontinuous there.

One last thing that we will look at is the relation that exists between the energy of a state and the number of nodes. Even without carrying out detailed calculations, it is often possible to make general conclusions concerning the ordering of the states by considering their nodal structure. We consider a one-dimensional potential, one-particle system with the Hamiltonian

$$\hat{\mathcal{H}} = -\frac{1}{2M} \frac{d^2}{dx^2} + V(x),$$

where  $M = m/\hbar^2$  and  $V(x)$  is some function of  $x$  depending only upon the spatial coordinates. If the potential supports the existence of bound states we can show that:

- i) The ground state wavefunction does not change sign (has no nodes)
- ii) The bound state with  $n$  sign changes has a lower energy than the state with  $n + 1$  sign changes.

Consider first the functions  $\psi_0$  and  $\psi_1$ , which are the eigenstates of  $\hat{\mathcal{H}}$ , with zero and one node respectively and energies  $E_0$  and  $E_1$  respectively. Let the boundaries of the system be  $a$  and  $b$  and let  $\psi_1$  undergo a zero-crossing at  $c$ . Consider the region  $a < x < c$  so that both  $\psi_0$  and  $\psi_1$  are positive. From the eigenvalue equation we then have

$$E_0 = V + \frac{1}{\psi_0} \hat{\mathcal{T}} \psi_0$$

$$E_1 = V + \frac{1}{\psi_1} \hat{\mathcal{T}} \psi_1$$

Taking the difference of these two expressions we get

$$E_1 - E_0 = \frac{1}{\psi_1} \hat{\mathcal{T}} \psi_1 - \frac{1}{\psi_0} \hat{\mathcal{T}} \psi_0 = \frac{1}{\psi_0 \psi_1} (\psi_0 \hat{\mathcal{T}} \psi_1 - \psi_1 \hat{\mathcal{T}} \psi_0)$$

The Hermiticity of  $\hat{\mathcal{T}}$  implies that the term in parenthesis is zero (the integrand is generally not zero). To estimate the sign of  $E_1 - E_0$ , multiply by  $\psi_1 \psi_0$ , then integrate from  $a$  to  $c$ . We then obtain

$$E_1 - E_0 = \frac{B}{A}$$

where

$$B = \int_a^c dx \psi_0 \hat{\mathcal{T}} \psi_1 - \int_a^c dx \psi_1 \hat{\mathcal{T}} \psi_0$$

$$A = \int_a^c dx \psi_1 \psi_0$$

Consider the first term in  $B$ . Integrating this by parts we get

$$\begin{aligned} \int_a^c dx \psi_0 \hat{\mathcal{T}} \psi_1 &= -\frac{1}{2M} \int_a^c dx \psi_0 \frac{\partial^2 \psi_1}{\partial x^2} \\ &= \frac{1}{2M} \int_a^c dx \frac{\partial \psi_0}{\partial x} \frac{\partial \psi_1}{\partial x} - \frac{1}{2M} \psi_0 \frac{\partial \psi_1}{\partial x} \Big|_a^c \\ &= -\frac{1}{2M} \int_a^c dx \psi_1 \frac{\partial^2 \psi_0}{\partial x^2} + \frac{1}{2M} \left( \psi_1 \frac{\partial \psi_0}{\partial x} - \psi_0 \frac{\partial \psi_1}{\partial x} \right)_a^c \end{aligned}$$

Combining these results we obtain

$$E_1 - E_0 = \frac{1}{2A} \left[ \psi_1 \left( \frac{\partial \psi_0}{\partial x} \right) - \psi_0 \left( \frac{\partial \psi_1}{\partial x} \right) \right]_a^c.$$

Because

$$\begin{aligned} \psi_1(c) &= 0 \\ \psi_0(c) &> 0 \\ \left( \frac{\partial \psi_1}{\partial x} \right)_{x=c} &< 0 \\ A = \int_a^c dx \psi_1^* \psi_0 &> 0 \end{aligned}$$

we obtain

$$E_1 - E_0 = -\frac{1}{2A} \psi_0(c) \left( \frac{\partial \psi_1}{\partial x} \right)_{x=c} > 0,$$

that is,

$$E_1 - E_0 > 0.$$

Thus the nodeless wavefunction has a lower energy than the wavefunction with one node. A similar proof shows that  $\psi_0$  has a lower energy than any wavefunction with more than one node. Hence the ground state of the system has no nodal points.

Similarly, the above proof can be applied to the comparison of  $E_n$  and  $E_{n+1}$ , that is, the energies for wavefunctions having  $n$  and  $n+1$  nodes, respectively. The result is that

$$E_{n+1} > E_n$$

and hence the eigenstates of a system have energies increasing in the same sequence as the number of nodes.