Bound States in d=1

In this section we will discuss a number of properties of bound states, concentrating on $d = 1$, but many properties hold for other dimensions, including $d = 3$.

Schrödinger Equation Let us start with the Hamiltonian

$$H = \frac{PP}{2m} + V(X)$$

Our state is $|\Psi(0)>=|\Psi>$ at $t = 0$. For $|\Psi(t)>$, we have

$$|\Psi(t)>= U(t,0)|\Psi(0)>,$$

where

$$U(t,0) = \exp(-i\frac{Ht}{\hbar})$$

(Note that we are back in the Schrödinger picture, where all the time dependence is carried by the states.) The derivative of $U(t,0)$ is

$$i\hbar\partial_t U(t,0) = HU(t,0)$$

Using this to get the derivative of $|\Psi(t)>$, we have

$$i\hbar\partial_t U(t,0)|\Psi>= HU(t,0)|\Psi>= H|\Psi(t)>,$$

so taking the matrix element with $< x|$, we have

$$i\hbar\partial_t < x|\Psi(t)>=< x|H|\Psi(t)>= (-\frac{\hbar^2}{2m}\partial_x^2 + V(x)) < x|\Psi(t)> \tag{1}$$

We can now leave Dirac notation for the present, and set $< x|\Psi(t)>= \Psi(x,t)$. Eq.(1) now reads

$$i\hbar\partial_t\Psi(x,t) = (-\frac{\hbar^2}{2m}\partial_x^2 + V(x))\Psi(x,t) \tag{2}$$

We are looking for bound states or normalized energy eigenstates which satisfy

$$H|\Psi>= E|\Psi>, \quad <\Psi|\Psi>= 1$$

For an energy eigenstate, we have

$$< x|\Psi(t)>=< x|U(t,0)|\Psi>= \exp(-i\frac{Et}{\hbar}) < x|\Psi>,$$

or in wave function language,

$$\Psi(x,t) = \exp(-i\frac{Et}{\hbar})\Psi(x)$$

and pulling off the factor $\exp(-i\frac{Et}{\hbar})$ from every term, the Schrödinger equation becomes

$$(-\frac{\hbar^2}{2m}\partial_x^2 + V(x))\Psi(x) = E\Psi(x)$$

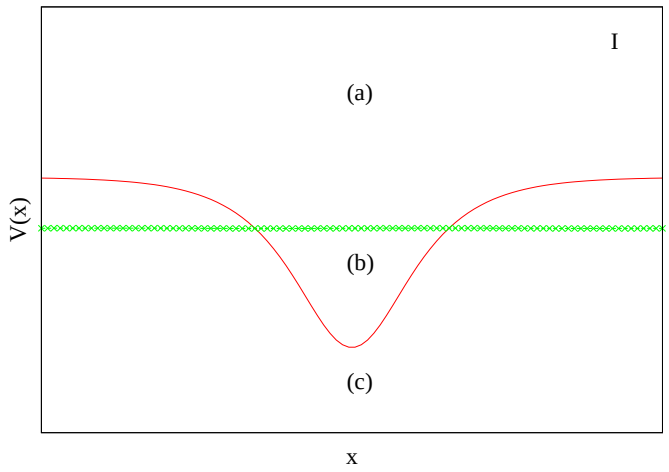
Classical Motions Much insight into the solutions of the Schrödinger equation can be obtained by first looking at the classical motion in a given potential $V(x)$. We will consider three general classes of potential;

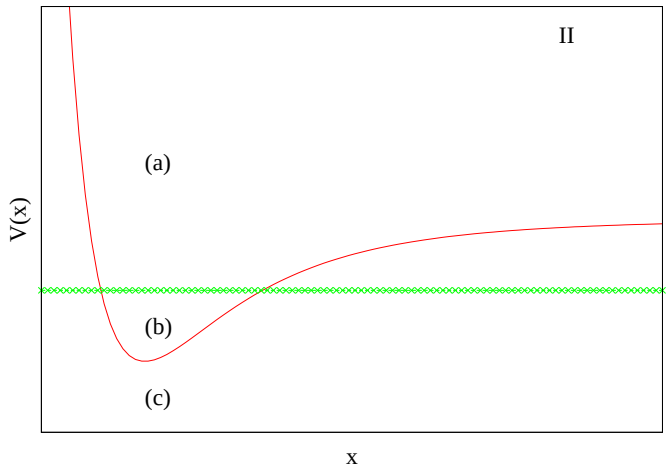
I $V(x) \to 0$, as $|x| \to \infty$.

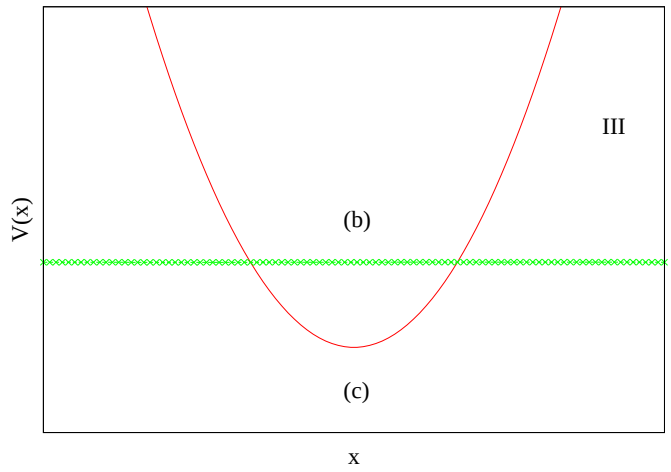
II $V(x) \to 0$ as $x \to \infty$, $V(x) \to \infty$ as $\to -\infty$.

III $V(x) \to \infty$ as $|x| \to \infty$.

Simple examples of these three types are shown in the next three plots.







In these plots, the potential is shown in red, and a constant energy line is shown in green. The regions marked (a),(b), and (c) are defined as follows

(a) $E > V$ for at least one of $x \to \infty$. $x \to -\infty$.

(b) $E > V$ for a finite range of x values. $E < V$ as $|x| \to \infty$.

(c) $E < V$ for all x.

Now consider the possible classical motions of the particle in (a),(b),(c). We write the classical Hamiltonian

$$H_{cl} = \frac{p^2}{2m} + V(x) = E$$

and solve for the kinetic energy,

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

Now, as far as classical motion is concerned, the particle can never be in region (c). That would correspond to a negative kinetic energy. The particle is allowed in classical motion to be in that part of region (b), where the kinetic energy is positive. In the plots, the green line is always in region (b). Here the classical motion involves going back and forth between two points, called *turning points* where the kinetic energy vanishes. Finally in region (a), the particle again has positive kinetic energy, and will either approach the potential from infinity or escape to infinity as time goes on. As we will see, region (b) is the only one where quantum bound states can occur.

Behaviors of Schrödinger equation Let us write the Schrödinger equation for an energy eigenstate. We have

$$(-\frac{\hbar^2\partial_x^2}{2m} + V(x))\Psi(x) = E\Psi(x).$$

Denoting $\partial_x^2\Psi$ as Ψ'', we re-arrange the equation to

$$\Psi'' = -\frac{2m}{\hbar^2}(E - V(x))\Psi(x)$$

We see that the sign of $E-V(x)$ which is classically the kinetic energy, plays an important role in determining the sign of Ψ''. Let us classify the different cases that can occur. The two broad classes are $E > V$ and $E < V$.

$E > V$: If $E > V$ and $\Psi > 0$, we have $\Psi'' < 0$, so Ψ is turning downward toward $\Psi = 0$ as x increases. If $E < V$ and $\Psi < 0$ we have $\Psi'' > 0$, and Ψ is being turned upward toward $\Psi = 0$. So for $E > V$, the general behavior is oscillatory. The trigonometric functions $\sin(\alpha x)$ and $\cos(\alpha x)$ are simple examples of this behavior.

$E < V$: If $E < V$ and $\Psi > 0$, we have $\Psi'' > 0$, so Ψ is turning upward away from $\Psi = 0$. If $E < V$ and $\Psi < 0$ we have $\Psi'' < 0$, and Ψ is being turned downward away from $\Psi = 0$. So for $E < V$, the general behavior is exponential . The functions $\exp(\alpha x)$ and $\exp(-\alpha x)$ are simple examples of this behavior.

Now suppose we are looking for a bound state of the system. The wave function must fall off as $|x| \to \infty$ fast enough so that $< \Psi|\Psi >= 1$ is possible. This immediately rules out region (a), since in region (a), the wave function oscillates in at least one of the directions $|x| \to \infty$, so it does not fall off fast enough for normalizability. We can also rule out region (c). In region (c) the sign of $E - V$ is always negative, so the wave function is always headed away from the $\Psi = 0$ axis as x increases. Imagine the wave function is damped as $x \to -\infty$. Now as x increases, the wave function is always turning away from the axis, so if $\Psi > 0$, Ψ is always increasing and inevitably will explode as $x \to +\infty$. We are left with region (b). Classically any energy in region (b) is allowed. But in quantum mechanics, only certain energies are possible for physical states. We again imagine starting at large negative x and choose the solution that is damped as $x \to -\infty$. If $\Psi > 0$ it will continue to increase as x increases, but does not do so for all x. As x enters the region where $E > V$ and classical motion is possible, the wave function starts to turn back toward the axis. At an eigenvalue of H, the wave function will turn over just enough to match onto a decaying exponential, resulting in a normalizable wave function. It is clear that this cannot happen for an arbitrary energy. This is ultimately the reason bound state energies are discrete in quantum mechanics or "quantized."

A Certain Expected Value always exceeds E_0 Suppose our system does have a lowest bound state with energy E_0. We form the ration

$$\frac{< \Psi|H|\Psi >}{< \Psi|\Psi >}$$

where $|\Psi>$ corresponds to *any* normalizable state vector or wave function. We claim that

$$\frac{<\Psi|H|\Psi>}{<\Psi|\Psi>} \geq E_0.$$

This result is intuitively obvious, and we show it as follows. We expect the eigenstates of H form an complete set of states. Here we must include all bound states and all continuum states. We will assume for simplicity that the bound states have negative energy, and the continuum starts at zero energy. Then we can write a formula for the identity as follows:

$$I = \sum_b |E_b><E_b| + \int_0^\infty dE_c |E_c><E_c|,$$

where the $|E_c>$ are non-normalizable states satisfying $H|E_c>=E_c|E_c>$. (The normalization of the $|E_c$ involves Dirac delta functions and will be discussed in a later section.) Now consider the expression $<\Psi|H|\Psi>$ for an arbitrary normalizable state $|\Psi>$. We sandwich the identity just to the right of H. This gives

$$<\Psi|H|\Psi> = <\Psi|H\left(\sum_b |E_b><E_b| + \int_0^\infty dE_c|E_c><E_c|\right)|\Psi>$$

Letting H act and writing the matrix elements, we have

$$<\Psi|H|\Psi> = \left(\sum_b E_b <\Psi|E_b><E_b|\Psi> + \int_0^\infty dE_c E_c <\Psi|E_c><E_c\Psi>\right).$$

Now pull out a factor of E_0 from every term, and write

$$\frac{E_b}{E_0} = 1 + \frac{E_b - E_0}{E_0},$$

and likewise for E_c/E_0. We now have

$$<\Psi|H|\Psi> = E_0\left(\sum_b (1+\frac{E_b-E_0}{E_0})|<\Psi|E_b>|^2 + \int_0^\infty dE_c(1+\frac{E_c-E_0}{E_0})|<\Psi|E_c>|^2\right).$$

In this formula the "1" terms just add up to $E_0<\Psi|\Psi>$, so altogether we have

$$\frac{<\Psi|H|\Psi>}{<\Psi|\Psi>} = E_0 + \frac{1}{<\Psi|\Psi>}\left(\sum_b (\frac{E_b-E_0}{E_0})|<\Psi|E_b>|^2 + \int_0^\infty dE_c(\frac{E_c-E_0}{E_0})|<\Psi|E_c>|^2\right).$$

The terms which add onto E_0 are all either positive or zero, so we have our result

$$\frac{<\Psi|H|\Psi>}{<\Psi|\Psi>} \geq E_0 \tag{3}$$

Nothing in this argument really depended on the system being one dimensional, and in fact the result Eq.(3) is generally true.

The Ground State Wave Function Has No Zeroes Let us return to a one dimensional system. We will assume that at least one bound state exists. Our goal in this section is to show that the wave function for the lowest energy bound state cannot have zeroes, i.e. it must be of the same sign (say positive) for all x. We start from the expression

$$< \Psi|H|\Psi >= \int_{-\infty}^{\infty} dx \Psi^*(x) \left(-\frac{\hbar^2}{2m}\partial_x^2 + V(x) \right) \Psi(x)$$

Let us integrate the kinetic energy operator term by parts. This gives

$$\int_{-\infty}^{\infty} dx \Psi^*(x)(-\frac{\hbar^2}{2m}\partial_x^2)\Psi(x) = \int_{-\infty}^{\infty} dx \frac{\hbar^2}{2m}|\partial_x \Psi(x)|^2.$$

The "surface" terms from $x = \pm\infty$ vanish since $\Psi(x)$ is assumed to be normalizable. We now have

$$\frac{< \Psi|H|\Psi >}{< \Psi|\Psi >} = \frac{\int_{-\infty}^{\infty} dx (\frac{\hbar^2}{2m}|\partial_x \Psi(x)|^2 + V(x)|\Psi|^2)}{\int_{-\infty}^{\infty} dx |\Psi(x)|^2} \tag{4}$$

Let us now assume that we have an eigenstate of H satisfying

$$H|\Psi >= E|\Psi >,$$

and further that the wave function $\Psi(x)$ has a linear zero at $x = x_0$. We will show that $|\Psi >$ cannot be the ground state of the system. We will do this by constructing another wave function Ψ' which satisfies

$$\frac{< \Psi'|H|\Psi' >}{< \Psi'|\Psi' >} < E.$$

This shows that $|\Psi >$ is not the ground state, since if it were, according to Eq.(3) any other state would need to *increase* the ratio of expected values. We construct $\Psi'(x)$ as follows. First we flip over the wave function for $x > x_0$. This gives a function which has one sign (say positive) for all x. The "flipped" wave function is not quite acceptable however, since if $\Psi(x) \sim C(x_0 - x)$ near x_0, the flipped wave function will be $\sim C|x_0 - x|$. This is unacceptable right at x_0 since it has a discontinuous derivative. We solve that problem by smoothing the function near $x = x_0$. An acceptable smoothing would be to replace $C|x_0 - x|$ by $C\sqrt{(x_0 - x)^2 + \epsilon^2}$ where ϵ is very small. So $\Psi'(x)$ is constructed by first flipping $\Psi(x)$ beyond x_0 and then smoothing it near $x = x_0$ so there is no discontinuity in the derivative at x_0. As can be seen by examining $C\sqrt{(x_0 - x)^2 + \epsilon^2}$, $\Psi'(x)$ will have a *smaller* magnitude for its derivative than $\Psi(x)$ in a small region right near x_0. But this will lower the term in $|\partial_x \Psi|^2$ in Eq.(4). In other words, the wave function $\Psi'(x)$ has a slightly lower kinetic energy expected value than $\Psi(x)$. This means that the numerator in Eq.(4) has decreased. It is easy to see that flipping followed by smoothing near x_0 results in the normalization integral in the denominator of Eq.(4) *increasing*. The net result is that if we substitute Ψ' into Eq.(4), the result is *smaller*

than E, so this means that E was not the ground state energy and $\Psi(x)$ was not the ground state wave function. This argument rules out an eigenstate with a wave function that crosses the axis being the lowest state. Here we have assumed the zero was linear, but higher order zeroes can also be ruled out. The general pattern in $d = 1$ is that the lowest bound state has no zeroes, the first excited bound state has one zero,etc. Much of this discussion carries over to higher dimensions. In higher dimensions, zeroes lie on surfaces not points, but still for many systems, the lowest state wave function has no zeroes.

Variational Principle Suppose $|\Psi>$ is an eigenstate of the Hamiltonian, satisfying

$$H|\Psi>= E|\Psi>$$

The variational principle states that

$$\frac{<\Psi|H|\Psi>}{<\Psi|\Psi>}$$

is *stationary* against small changes in the state vector. To state this more precisely, let us consider a varied state vector,

$$|\Psi'>\equiv |\Psi> +|\delta\Psi>,$$

where $|\delta\Psi>$ is "small" in the following sense:

$$<\delta\Psi|\delta\Psi> << <\Psi|\Psi> .$$

This means that the vector $|\delta\Psi>$ has a much smaller length than $|\Psi>$, where length is meant in the Hilbert space sense.

Now, let us substitute $|\Psi'>$ into our expresssion. The goal is to show that as long as we keep only terms *linear* in small quantities, the result is the same as using $|\Psi>$. Proceeding, we form

$$\frac{<\Psi'|H|\Psi'>}{<\Psi'|\Psi'>} = \frac{(<\Psi|+<\delta\Psi|)H(|\Psi>+|\delta\Psi>)}{(<\Psi|+<\delta\Psi|)\cdot(|\Psi>+|\delta\Psi>)}.$$

Next, we use the fact that $|\Psi>$ is an eigenstate of H. Our expression becomes,

$$\frac{<\Psi'|H|\Psi'>}{<\Psi'|\Psi'>} = \frac{E(<\Psi|\Psi>+<\delta\Psi|\Psi>+<\delta\Psi|\Psi>)+<\delta\Psi|H|\delta\Psi>)}{<\Psi|\Psi>+<\delta\Psi|\Psi>+<\delta\Psi|\Psi>+<\delta\Psi|\delta\Psi>)}.$$

We note that if we drop terms quadratic in $\delta\Psi$ in numerator and denominator, the result is E, or in other words the expression is *stationary* to linear order in $\delta\Psi$. We have then

$$\frac{<\Psi'|H|\Psi'>}{<\Psi'|\Psi'>} = E + O(\delta\Psi)^2$$

If it is the ground state of the system that is being considered then the expression is not merely stationary, but is a minimum. This is used in practice to search for a good approximation to the ground state energy and wave function. The trial wave function may depend on several parameters. The expected value of H in the trial state divided by its norm will then be a function of these parameters. Searching for the minimum in the parameter space brings the system closer and closer to the ground state.