

## 2. Approximation Methods

Physicists have a dirty secret: we're not very good at solving equations. More precisely, humans aren't very good at solving equations. We know this because we have computers and they're much better at solving things than we are.

We usually do a good job of hiding this secret when teaching physics. In quantum physics we start with examples like the harmonic oscillator or the hydrogen atom and then proudly demonstrate how clever we all are by solving the Schrödinger equation exactly. But there are very very few examples where we can write down the solution in closed form. For the vast majority of problems, the answer is something complicated that isn't captured by some simple mathematical formula. For these problems we need to develop different tools.

You already met one of these tools in an earlier course: it's called *perturbation theory* and it's useful whenever the problem we want to solve is, in some sense, close to one that we've already solved. This works for a surprisingly large number of problems. Indeed, one of the arts of theoretical physics is making everything look like a coupled harmonic oscillator so that you can use perturbation theory. But there are also many problems for which perturbation theory fails dismally and we need to find another approach. In general, there's no panacea, no universal solution to all problems in quantum mechanics. Instead, the best we can hope for is to build a collection of tools. Then, whenever we're faced with a new problem we can root around in our toolbox, hoping to find a method that works. The purpose of this chapter is to stock up your toolbox.

### 2.1 The Variational Method

The *variational method* provides a simple way to place an upper bound on the ground state energy of any quantum system and is particularly useful when trying to demonstrate that bound states exist. In some cases, it can also be used to estimate higher energy levels too.

#### 2.1.1 An Upper Bound on the Ground State

We start with a quantum system with Hamiltonian  $H$ . We will assume that  $H$  has a discrete spectrum

$$H|n\rangle = E_n|n\rangle \quad n = 0, 1, \dots$$

with the energy eigenvalues ordered such that  $E_n \leq E_{n+1}$ . The simplest application of the variational method places an upper bound on the value of the ground state energy  $E_0$ .

**Theorem:** Consider an arbitrary state  $|\psi\rangle$ . The expected value of the energy obeys the inequality

$$\langle E \rangle = \langle \psi | H | \psi \rangle \geq E_0$$

**Proof:** The proposed claim is, hopefully, intuitive and the proof is straightforward. We expand  $|\psi\rangle = \sum_n a_n |n\rangle$  with  $\sum_n |a_n|^2 = 1$  to ensure that  $\langle \psi | \psi \rangle = 1$ . Then

$$\begin{aligned} \langle E \rangle &= \sum_{n,m=0}^{\infty} a_m^* a_n \langle m | H | n \rangle = \sum_{n,m=0}^{\infty} a_m^* a_n E_n \delta_{mn} \\ &= \sum_{n=0}^{\infty} |a_n|^2 E_n = E_0 \sum_{n=0}^{\infty} |a_n|^2 + \sum_{n=0}^{\infty} |a_n|^2 (E_n - E_0) \geq E_0 \end{aligned}$$

In the case of a non-degenerate ground state, we have equality only if  $a_0 = 1$  which implies  $a_n = 0$  for all  $n \neq 0$ .  $\square$

Now consider a family of states,  $|\psi(\alpha)\rangle$ , depending on some number of parameters  $\alpha_i$ . If we like, we can relax our assumption that the states are normalised and define

$$E(\alpha) = \frac{\langle \psi(\alpha) | H | \psi(\alpha) \rangle}{\langle \psi(\alpha) | \psi(\alpha) \rangle}$$

This is sometimes called the *Rayleigh-Ritz quotient*. We still have

$$E(\alpha) \geq E_0 \quad \text{for all } \alpha$$

The most stringent bound on the ground state energy comes from the minimum value of  $E(\alpha)$  over the range of  $\alpha$ . This, of course, obeys

$$\left. \frac{\partial E}{\partial \alpha_i} \right|_{\alpha=\alpha_*} = 0$$

giving us the upper bound  $E_0 \leq E(\alpha_*)$ . This is the essence of the variational method.

The variational method does not tell us how far above the ground state  $E(\alpha_*)$  lies. It would be much better if we could also get a lower bound for  $E_0$  so that we can say for sure that ground state energy sits within a particular range. However, for particles moving in a general potential  $V(\mathbf{x})$ , the only lower bound that is known is  $E_0 > \min V(\mathbf{x})$ . Since we're often interested in potentials like  $V(\mathbf{x}) \sim -1/r$ , which have no lower bound this is not particularly useful.

Despite these limitations, when used cleverly by choosing a set of states  $|\psi(\alpha)\rangle$  which are likely to be fairly close to the ground state, the variational method can give remarkably accurate results.

### An Example: A Quartic Potential

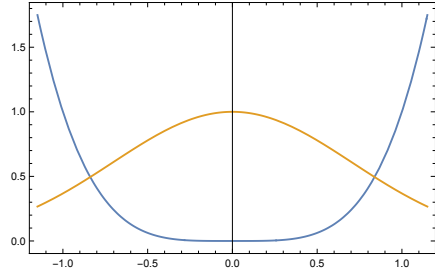
Consider a particle moving in one-dimension in a quartic potential. The Hamiltonian, written in units where everything is set to one, is

$$H = -\frac{d^2}{dx^2} + x^4$$

Unlike the harmonic oscillator, this problem does not have a simple solution. Nonetheless, it is easy to solve numerically where one finds

$$E_0 \approx 1.06$$

Let's see how close we get with the variational method. We need to cook up a trial wavefunction which we think might look something like the true ground state. The potential is shown on the right and, on general grounds, the ground state wavefunction should have support where the potential is smallest; an example is shown in orange. All we need to do is write down a function which has vaguely this shape. We will take



**Figure 20:**

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

where the factor in front ensures that this wavefunction is normalised. You can check that this isn't an eigenstate of the Hamiltonian. But it does have the expected crude features of the ground state: e.g. it goes up in the middle and has no nodes. (Indeed, it's actually the ground state of the harmonic oscillator). The expected energy is

$$E(\alpha) = \sqrt{\frac{\alpha}{\pi}} \int dx (\alpha - \alpha^2 x^2 + x^4) e^{-\alpha x^2/2} = \frac{\alpha}{2} + \frac{3}{4\alpha^2}$$

The minimum value occurs at  $\alpha_\star^3 = 3$ , giving

$$E(\alpha_\star) \approx 1.08$$

We see that our guess does pretty well, getting within 2% of the true value. You can try other trial wavefunctions which have the same basic shape and see how they do.

## How Accurate is the Variational Method?

Formally, we can see why a clever application of the variational method will give a good estimate of the ground state energy. Suppose that the trial wavefunction which minimizes the energy differs from the true ground state by

$$|\psi(\alpha_*)\rangle = \frac{1}{\sqrt{1+\epsilon^2}} (|0\rangle + \epsilon|\phi\rangle)$$

where  $|\phi\rangle$  is a normalised state, orthogonal to the ground state,  $\langle 0|\phi\rangle = 0$ , and  $\epsilon$  is assumed to be small. Then our guess at the energy is

$$E(\alpha_*) = \frac{1}{1+\epsilon^2} [\langle 0|H|0\rangle + \epsilon(\langle 0|H|\phi\rangle + \langle \phi|H|0\rangle) + \epsilon^2\langle \phi|H|\phi\rangle]$$

Importantly the terms linear in  $\epsilon$  vanish. This is because  $\langle \phi|H|0\rangle = E_0\langle \phi|0\rangle = 0$ . We can then expand the remaining terms as

$$E(\alpha_*) = E_0 + \epsilon^2 (\langle \phi|H|\phi\rangle - E_0) + \mathcal{O}(\epsilon^2)$$

This means that if the difference from the true ground state is  $\mathcal{O}(\epsilon)$ , then the difference from the ground state energy is  $\mathcal{O}(\epsilon^2)$ . This is the reason that the variational method often does quite well.

Nonetheless, one flaw with the variational method is that unless someone tells us the true answer, we have no way of telling how good our approximation is. Or, in the language above, we have no way of estimating the size of  $\epsilon$ . Despite this, we will see below that there are some useful things we can do with it.

### 2.1.2 An Example: The Helium Atom

One important application of quantum mechanics is to explain the structure of atoms. Here we will look at two simple approaches to understand an atom with two electrons. This atom is helium.

The Hamiltonian for two electrons, each of charge  $-e$ , orbiting a nucleus of charge  $Ze$  is

$$H = \frac{\mathbf{p}_1^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_1} + \frac{\mathbf{p}_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_2} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \quad (2.1)$$

For helium,  $Z = 2$  but, for reasons that will become clear, we will leave it arbitrary and only set it to  $Z = 2$  at the end of the calculation.

If we ignore the final term, then this Hamiltonian is easy to solve: it simply consists of two independent copies of the hydrogen atom. The eigenstates would be

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \psi_{n_1, l_1, m_1}(\mathbf{x}_1) \psi_{n_2, l_2, m_2}(\mathbf{x}_2)$$

where  $\psi_{n, l, m}(r)$  are the usual energy eigenstates of the hydrogen atom. We should remember that the electrons are fermions so we can't put them in the same state. However, electrons also have a spin degree of freedom which we have neglected above. This means that two electrons can have the same spatial wavefunction as long as one is spin up and the other spin down.

Ignoring the interaction term between electrons gives the energy

$$E = -Z^2 \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) Ry \quad (2.2)$$

where  $Ry$  is the *Rydberg constant*, given by

$$Ry = \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \approx 13.6 \text{ eV}$$

Setting  $Z = 2$  and  $n_1 = n_2 = 1$ , this very naive approach suggests that the ground state of helium has energy  $E_0 = -8 Ry \approx -109 \text{ eV}$ . The true ground state of helium turns out to have energy

$$E_0 \approx -79.0 \text{ eV} \quad (2.3)$$

Our task is to find a method to take into account the final, interaction term between electrons in (2.1) and so get closer to the true result (2.3). Here we try two alternatives.

### Perturbation Theory

Our first approach is to treat the Coulomb energy between two electrons as a perturbation on the original problem. Before proceeding, there is a question that we should always ask in perturbation theory: what is the small, dimensionless parameter that ensures that the additional term is smaller than the original terms?

For us, we need a reason to justify why the last term in the Hamiltonian (2.1) is likely to be smaller than the other two potential terms. All are due to the Coulomb force, so come with a factor of  $e^2/4\pi\epsilon_0$ . But the interactions with the nucleus also come with a factor of  $Z$ . This is absent in the electron-electron interaction. This, then, is what we hang our hopes on: the perturbative expansion will be an expansion in  $1/Z$ . Of course, ultimately we will set  $1/Z = 1/2$  which is not a terribly small number. This might give us concern that perturbation theory will not be very accurate for this problem.

We now place each electron in the usual hydrogen ground state  $\psi_{1,0,0}(\mathbf{x})$ , adapted to general  $Z$

$$\psi_{1,0,0}(\mathbf{x}) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0} \quad (2.4)$$

where  $a_0$  is the Bohr radius, defined as

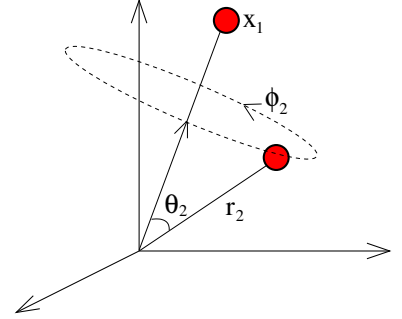
$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 5 \times 10^{-11} \text{ m}$$

To leading order, the shift of the ground state energy is given by the standard result of first order perturbation theory,

$$\Delta E = \frac{e^2}{4\pi\epsilon_0} \int d^3x_1 d^3x_2 \frac{|\psi_{1,0,0}(\mathbf{x}_1)|^2 |\psi_{1,0,0}(\mathbf{x}_2)|^2}{|\mathbf{x}_1 - \mathbf{x}_2|}$$

We need to compute this integral.

The trick is to pick the right coordinate system. We will work in spherical polar coordinates for both particles. However, we will choose the  $z$  axis for the second particle to lie along the direction  $\mathbf{x}_1$  set by the first particle. The advantage of this choice is that the angle  $\theta$  between the two particles coincides with the polar angle  $\theta_2$  for the second particle. In particular, the separation between the two particles can be written as



**Figure 21:**

$$|\mathbf{x}_1 - \mathbf{x}_2| = \sqrt{(\mathbf{x}_1 - \mathbf{x}_2)^2} = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}$$

In these coordinates, it is simple to do the integration over the angular variables for the first particle, and over  $\phi_2$  for the second. The shift in the energy then becomes

$$\begin{aligned} \Delta E &= \frac{8\pi^2 e^2}{4\pi\epsilon_0} \left( \frac{Z^3}{\pi a_0^3} \right)^2 \int dr_1 r_1^2 e^{-2Zr_1/a_0} \int dr_2 r_2^2 e^{-2Zr_2/a_0} \\ &\quad \times \int_{-1}^{+1} d(\cos \theta_2) \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} \\ &= -\frac{2\pi e^2}{\epsilon_0} \left( \frac{Z^3}{\pi a_0^3} \right)^2 \int dr_1 r_1^2 e^{-2Zr_1/a_0} \int dr_2 r_2^2 e^{-2Zr_2/a_0} \frac{\sqrt{(r_1 - r_2)^2} - \sqrt{(r_1 + r_2)^2}}{r_1 r_2} \\ &= -\frac{2\pi e^2}{\epsilon_0} \left( \frac{Z^3}{\pi a_0^3} \right)^2 \int dr_1 r_1^2 e^{-2Zr_1/a_0} \int dr_2 r_2^2 e^{-2Zr_2/a_0} \frac{|r_1 - r_2| - |r_1 + r_2|}{r_1 r_2} \end{aligned}$$

Those modulus signs are a little odd, but easily dealt with. Because the integral is symmetric in  $r_1$  and  $r_2$ , the regime  $r_1 > r_2$  must give the same result as the regime  $r_1 < r_2$ . We can then focus on one of these regimes — say  $r_1 > r_2$  where  $|r_1 - r_2| = |r_1 + r_2| = -2r_2$  — and just double our result. We have

$$\begin{aligned}\Delta E &= \frac{8\pi e^2}{\epsilon_0} \left( \frac{Z^3}{\pi a_0^3} \right)^2 \int_{r_2}^{\infty} dr_1 r_1 e^{-2Zr_1/a_0} \int_0^{\infty} dr_2 r_2^2 e^{-2Zr_2/a_0} \\ &= \frac{8\pi e^2}{\epsilon_0} \left( \frac{Z^3}{\pi a_0^3} \right)^2 \int_0^{\infty} dr_2 r_2^2 \left( \frac{a_0 r_2}{2Z} + \frac{a_0^2}{4Z^2} \right) e^{-4Zr_2/a_0} \\ &= \frac{5}{8} \frac{Ze^2}{4\pi\epsilon_0 a_0} = \frac{5Z}{4} Ry\end{aligned}$$

Using first order perturbation, we find that the ground state energy of helium is

$$E_0 \approx E + \Delta E = \left( -2Z^2 + \frac{5Z}{4} \right) Ry \approx -74.8 \text{ eV}$$

This is much closer to the correct value of  $E_0 \approx -79 \text{ eV}$ . In fact, given that our perturbative expansion parameter is  $1/Z = 1/2$ , it's much better than we might have anticipated.

## The Variational Method

We'll now try again, this time using the variational method. For our trial wavefunction we pick  $\Psi(\mathbf{x}_1, \mathbf{x}_2) = \psi(\mathbf{x}_1)\psi(\mathbf{x}_2)$  where

$$\psi(\mathbf{x}; \alpha) = \sqrt{\frac{\alpha^3}{\pi a_0^3}} e^{-\alpha r/a_0} \quad (2.5)$$

This is almost the same as the hydrogen ground state (2.4) that we worked with above. The only difference is that we've replaced the atomic number  $Z$  with a general parameter  $\alpha$  that we will allow to vary. We can tell immediately that this approach must do at least as well at estimating the ground state energy because setting  $\alpha = Z$  reproduces the results of first order perturbation theory.

The expectation of the energy using our trial wavefunction is

$$E(\alpha) = \int d^3x_1 d^3x_2 \psi^*(\mathbf{x}_1)\psi^*(\mathbf{x}_2) H\psi(\mathbf{x}_1)\psi(\mathbf{x}_2)$$

with  $H$  the differential operator given in (2.1). Now we have to evaluate all terms in the Hamiltonian afresh. However, there is a trick we can use. We know that (2.5) is the ground state of the Hamiltonian

$$H_\alpha = \frac{\mathbf{p}^2}{2m} - \frac{\alpha e^2}{4\pi\epsilon_0} \frac{1}{r}$$

where we've replaced  $Z$  by  $\alpha$  in the second term. With this observation, we write the helium Hamiltonian (2.1) as

$$H = H_\alpha(\mathbf{p}_1, \mathbf{r}_1) + H_\alpha(\mathbf{p}_2, \mathbf{r}_2) + \frac{e^2}{4\pi\epsilon_0} \left[ (\alpha - Z) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \right]$$

Written in this way, the expected energy becomes

$$E(\alpha) = -2\alpha^2 Ry + \frac{e^2}{4\pi\epsilon_0} \left[ 2(\alpha - Z) \int d^3x \frac{|\psi(\mathbf{x})|^2}{r} + \int d^3x_1 d^3x_2 \frac{|\psi(\mathbf{x}_1)|^2 |\psi(\mathbf{x}_2)|^2}{|\mathbf{x}_1 - \mathbf{x}_2|} \right]$$

Here, the first term comes from the fact that our trial wavefunction is the ground state of  $H_\alpha$  with ground state energy given by (2.2). We still need to compute the integrals in the second and third term. But both of these are straightforward. The first is

$$\int d^3x \frac{|\psi(\mathbf{x})|^2}{r} = 4\pi \frac{\alpha^3}{\pi a_0^3} \int dr r e^{-2\alpha r/a_0} = \frac{\alpha}{a_0}$$

Meanwhile, the final integral is the same as we computed in our perturbative calculation. It is

$$\int d^3x_1 d^3x_2 \frac{|\psi(\mathbf{x}_1)|^2 |\psi(\mathbf{x}_2)|^2}{|\mathbf{x}_1 - \mathbf{x}_2|} = \frac{5\alpha}{8a_0}$$

Putting this together, we have

$$E(\alpha) = \left( -2\alpha^2 + 4(\alpha - Z)\alpha + \frac{5}{4}\alpha \right) Ry$$

This is minimized for  $\alpha_\star = Z - 5/16$ . The minimum value of the energy is then

$$E(\alpha_\star) = -2 \left( Z - \frac{5}{16} \right)^2 Ry \approx -77.5 eV \quad (2.6)$$

We see that this is somewhat closer to the true value of  $E_0 \approx -79.0 eV$ .

There's one last bit of physics hidden in this calculation. The optimum trial wavefunction that we ended up using was that of an electron orbiting a nucleus with charge  $(Z - 5/16)e$ , rather than charge  $Ze$ . This has a nice interpretation: the charge of the nucleus is screened by the presence of the other electron.

### 2.1.3 Do Bound States Exist?

There is one kind of question where variational methods can give a definitive answer. This is the question of the existence of bound states.

Consider a particle moving in a localised potential  $V(\mathbf{x})$ , such that  $V(\mathbf{x}) \rightarrow 0$  as  $x \rightarrow \infty$ . A bound state is an energy eigenstate with  $E < 0$ . For some potentials, there exist an infinite number of bound states; the Coulomb potential  $V = 1/r$  in three dimensions is a familiar example. For other potentials there will be only a finite number. And for some potentials there will be none. How can we tell what properties a given potential has?

Clearly the variational method can be used to prove the existence of a bound state. All we need to do is exhibit a trial wavefunction which has  $E < 0$ . This then ensures that the true ground state also has  $E_0 < 0$ .

### An Example: The Hydrogen Anion

A hydrogen anion  $H^-$  consists of a single proton, with two electrons in its orbit. But does a bound state of two electrons and a proton exist?

The Hamiltonian for  $H^-$  is the same as that for helium, (2.1), but now with  $Z = 1$ . This means that we can import all the calculations of the previous section. In particular, our variational method gives a minimum energy (2.6) which is negative when we set  $Z = 1$ . This tells us that a bound state of two electrons and a proton does indeed exist.

### An Example: The Yukawa Potential

The Yukawa potential in three-dimensions takes the form

$$V(r) = -A \frac{e^{-\lambda r}}{r} \quad (2.7)$$

For  $A > 0$ , this is an attractive potential. Note that if we set  $\lambda = 0$ , this coincides with the Coulomb force. However, for  $\lambda \neq 0$  the Yukawa force drops off much more quickly.

The Yukawa potential arises in a number of different places in physics. Here are two examples:

- In a metal, electric charge is *screened*. This was described in Section 7.7 of the lecture notes on [Electromagnetism](#). This causes the Coulomb potential to be replaced by the Yukawa potential.
- The strong nuclear force between a proton and a neutron is complicated. However, at suitably large distances it is well approximated by the Yukawa potential, with  $r$  the relative separation of the proton and neutron. Indeed, this is the context in which Yukawa first suggested his potential. Thus the question of whether (2.7) admits a bound state is the question of whether a proton and neutron can bind together.

A spoiler: the hydrogen atom has stable isotope known as deuterium. Its nucleus, known as the deuteron, consists of a proton and neutron. Thus, experiment tells us that a bound state must exist. We'd like to understand this theoretically, if only to be sure that the experiments aren't wrong!

The Hamiltonian is

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

In the context of deuterium,  $r$  is the distance between the proton and neutron so  $m$  should really be interpreted as the reduced mass  $m = m_p m_n / (m_p + m_n) \approx m_p/2$ . We will work with a familiar trial wavefunction,

$$\psi(\mathbf{x}; \alpha) = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r}$$

This is the ground state of the hydrogen atom. The factor in front ensures that the wavefunction is normalised:  $\int d^3x |\psi|^2 = 1$ . A short calculation shows that the expected energy is

$$E(\alpha) = \frac{\hbar^2 \alpha^2}{2m} - \frac{4A\alpha^3}{(\lambda + 2\alpha)^2}$$

It's easy to check that there is a value of  $\alpha$  for which  $E(\alpha) < 0$  whenever

$$\lambda < \frac{Am}{\hbar^2}$$

This guarantees that the Yukawa potential has a bound state when the parameters lie within this regime. We cannot, however, infer the converse: this method doesn't tell us whether there is a bound state when  $\lambda > Am/\hbar^2$ .

It turns out that for  $\lambda$  suitably large, bound states do cease to exist. The simple variational method above gets this qualitative bit of physics right, but it does not do so well in estimating the bound. Numerical results tell us that there should be a bound state whenever  $\lambda \lesssim 2.4Am/\hbar$ .

## Bound States and The Virial Theorem

There is a connection between these ideas and the virial theorem. Let's first remind ourselves what the virial theorem is in this context. Suppose that we have a particle in  $d$  dimensions, moving in the potential

$$V(\mathbf{x}) = Ar^n \tag{2.8}$$

This means that the potential scales as  $V(\lambda\mathbf{x}) = \lambda^n V(\mathbf{x})$ . We will assume that there is a normalised ground state with wavefunction  $\psi_0(\mathbf{x})$ .

The ground state energy is

$$E_0 = \int d^d \mathbf{x} \frac{\hbar^2}{2m} |\nabla \psi_0(\mathbf{x})|^2 + V(\mathbf{x}) |\psi_0(\mathbf{x})|^2 \equiv \langle T \rangle_0 + \langle V \rangle_0$$

Now consider the trial wavefunction  $\psi(\mathbf{x}) = \alpha^{d/2} \psi_0(\alpha \mathbf{x})$ , where the prefactor ensures that  $\psi(\mathbf{x})$  continues to be normalised. From the scaling property of the potential (2.8), it is simple to show that

$$E(\alpha) = \alpha^2 \langle T \rangle_0 + \alpha^{-n} \langle V \rangle_0$$

The minimum of  $E(\alpha)$  is at

$$\frac{dE}{d\alpha} = 2\alpha \langle T \rangle_0 - n\alpha^{-n+1} \langle V \rangle_0 = 0$$

But this minimum must sit at  $\alpha = 1$  since, by construction, this is the true ground state. We learn that for the homogeneous potentials (2.8), we have

$$2\langle T \rangle_0 = n\langle V \rangle_0 \tag{2.9}$$

This is the *virial theorem*.

Let's now apply this to our question of bound states. Here are some examples:

- $V \sim -1/r$ : This is the Coulomb potential. The virial theorem tells us that  $E_0 = \langle T \rangle_0 + \langle V \rangle_0 = -\langle T \rangle_0 < 0$ . In other words, we proved what we already know: the Coulomb potential has bound states.

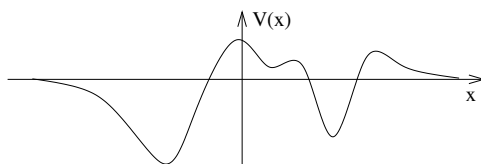
There's a subtlety here. Nowhere in our argument of the virial theorem did we state that the potential (2.8) has  $A < 0$ . Our conclusion above would seem to hold for  $A > 0$ , yet this is clearly wrong: the repulsive potential  $V \sim +1/r$  has no bound states. What did we miss? Well, we assumed right at the beginning of the argument that the ground state  $\psi_0$  was normalisable. For repulsive potentials like  $V \sim 1/r$  this is not true: all states are asymptotically plane waves of the form  $e^{i\mathbf{k}\cdot\mathbf{x}}$ . The virial theorem is not valid for repulsive potentials of this kind.

- $V \sim -1/r^3$ : Now the virial theorem tells us that  $E_0 = \frac{1}{3}\langle T \rangle_0 > 0$ . This is actually a contradiction! In a potential like  $V \sim 1/r^3$ , any state with  $E > 0$  is non-normalisable since it mixes with the asymptotic plane waves. It must be that this potential has no localised states.

This result might seem surprising. Any potential  $V \sim -r^n$  with  $n \leq -3$  descends steeply at the origin and you might think that this makes it efficient at trapping particles there. The trouble is that it is too efficient. The kinetic energy of the particle is not sufficient to hold it up at some finite distance, and the particle falls towards the origin. Such potentials have no bound states.

## Bound States in One Dimension

There is an exact and rather pretty result that holds for particles moving in one-dimension. Consider a particle moving in a potential  $V(x)$  such that  $V(x) = 0$  for  $|x| > L$ . However, when  $|x| < L$ , the potential can do anything you like: it can be positive or negative, oscillate wildly or behave very calmly.



**Figure 22:** Does a bound state exist?

**Theorem:** A bound state exists whenever  $\int dx V(x) < 0$ . In other words, a bound state exists whenever the potential is "mostly attractive".

**Proof:** We use the Gaussian variational ansatz

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

Then we find

$$E(\alpha) = \frac{\hbar^2 \alpha}{4m} + \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} dx V(x) e^{-\alpha x^2}$$

where the  $\hbar^2 \alpha / 4m$  term comes from the kinetic energy. The trick is to look at the function

$$\frac{E(\alpha)}{\sqrt{\alpha}} = \frac{\hbar^2 \sqrt{\alpha}}{4m} + \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx V(x) e^{-\alpha x^2}$$

This is a continuous function of  $\alpha$ . In the limit  $\alpha \rightarrow 0$ , we have

$$\frac{E(\alpha)}{\sqrt{\alpha}} \rightarrow \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx V(x)$$

If  $\int dx V(x) < 0$  then  $\lim_{\alpha \rightarrow 0} E(\alpha)/\sqrt{\alpha} < 0$  and, by continuity, there must be some small  $\alpha > 0$  for which  $E(\alpha) < 0$ . This ensures that a bound state exists.  $\square$

Once again, the converse to this statement does not hold. There are potentials with  $\int dx V(x) > 0$  which do admit bound states.

You may wonder if we can extend this result to higher dimensions. It turns out that there is an analogous statement in two dimensions<sup>4</sup>. However, in three dimensions or higher there is no such statement. In that case, if the potential is suitably shallow there are no bound states.

### 2.1.4 An Upper Bound on Excited States

So far, we've focussed only on approximating the energy of the ground state. Can we also use the variational method to give a bound on the energy of excited states?

This is rather more tricky. We can make progress if we know the ground state  $|0\rangle$  exactly. In this case, we construct a trial wavefunction  $|\psi(\alpha)\rangle$  that is orthogonal to the ground state,

$$\langle\psi(\alpha)|0\rangle = 0 \quad \text{for all } \alpha \quad (2.10)$$

Now we can simply rerun our arguments of Section 2.1.1. The minimum of  $E(\alpha) = \langle\psi(\alpha)|H|\psi(\alpha)\rangle$  provides an upper bound on the energy  $E_1$  of the first excited state.

In principle, we could then repeat this argument. Working with a trial wavefunction that is orthogonal to both  $|0\rangle$  and  $|1\rangle$  will provide an upper bound on the energy  $E_2$  of the second excited state.

In practice, this approach is not much use. Usually, if we're working with the variational method then it's because we don't have an exact expression for the ground state, making it difficult to construct a trial wavefunction obeying (2.10). If all we have is an approximation to the ground state, this is no good at all in providing a bound for excited states.

There is, however, one situation where we can make progress: this is if our Hamiltonian has some symmetry or, equivalently, some other conserved quantity. If we know the quantum number of the ground state under this symmetry then we can guarantee (2.10) by constructing our trial wavefunction to have a different quantum number.

### An Example: Parity and the Quartic Potential

For a simple example of this, let's return to the quartic potential of Section 2.1.1. The Hamiltonian is

$$H = -\frac{d^2}{dx^2} + x^4$$

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<sup>4</sup>More details can be found in the paper by Barry Simon, “*The bound state of weakly coupled Schrödinger operators in one and two dimensions*”, Ann. Phys. 97, 2 (1976), which you can [download here](#).

This Hamiltonian is invariant under parity, mapping  $x \rightarrow -x$ . The true ground state must be even under parity. We can therefore construct a class of trial wavefunctions for the first excited state which are odd under parity. An obvious choice is

$$\psi(x; \alpha) = \left( \frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\alpha x^2/2}$$

Churning through some algebra, one finds that the minimum energy using this wavefunction is

$$E(\alpha_*) \approx 3.85$$

The true value is  $E_1 \approx 3.80$ .