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

$$H|n\rangle = E_n|n\rangle \qquad n = 0, 1, \ldots$$

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

$$\langle E \rangle = \sum_{n,m=0}^{\infty} a_m^\star a_n \langle m | H | n \rangle = \sum_{n,m=0}^{\infty} a_m^\star a_n E_n \delta_{mn}$$

$$= \sum_{n=0}^{\infty} |a_n|^2 E_n = E_0 \sum_{n=0}^{\infty} |a_n|^2 + \sum_{n=0}^{\infty} |a_n|^2 (E_n - E_0) \geq E_0$$

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

Now consider a family of states, $|\psi(\alpha)\rangle$, depending on some number of parameters α_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 α. This, of course, obeys

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

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

The variational method does not tell us how far above the ground state $E(\alpha_\star)$ 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 a have 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
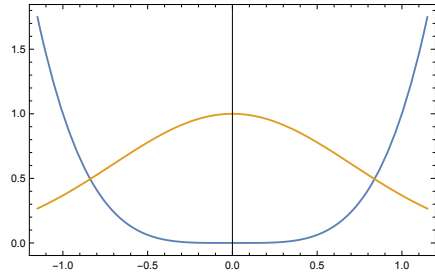

Figure 1:

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

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

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

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

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

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

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

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

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

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 ϵ. 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

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

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

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

where Ry is the *Rydberg constant*, given by

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

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

$$E_0 \approx -79.0 \ eV \tag{2.3}$$

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

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

where a_0 is the Bohr radius, defined as

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

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 θ between the two particles coincides with the polar angle θ_2 for the second particle. In particular, the separation between the two particles particles can be written as
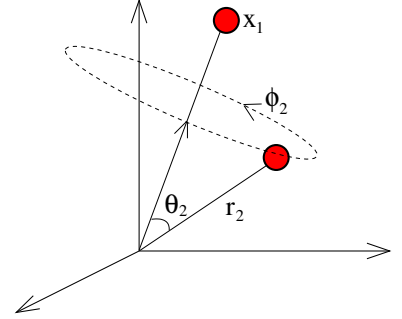

Figure 2:

$$|\mathbf{x_1} - \mathbf{x_2}| = \sqrt{(\mathbf{x_1} - \mathbf{x_2})^2} = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}$$

In these coordinates, it is simple to do the integration over the angular variables for the first particle, and over ϕ_2 for the second. The shift in the energy then becomes

$$\Delta E = \frac{8\pi^2 e^2}{4\pi\epsilon_0} \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int dr_1\, r_1^2 e^{-2Zr_1/a_0} \int dr_2\, r_2^2 e^{-2Zr_2/a_0}$$

$$\times \int_{-1}^{+1} d(\cos\theta_2)\, \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}$$

$$= -\frac{2\pi e^2}{\epsilon_0} \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int dr_1\, r_1^2 e^{-2Zr_1/a_0} \int dr_2\, r_2^2 e^{-2Zr_2/a_0}\, \frac{\sqrt{(r_1 - r_2)^2} - \sqrt{(r_1 + r_2)^2}}{r_1 r_2}$$

$$= -\frac{2\pi e^2}{\epsilon_0} \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int dr_1\, r_1^2 e^{-2Zr_1/a_0} \int dr_2\, r_2^2 e^{-2Zr_2/a_0}\, \frac{|r_1 - r_2| - |r_1 + r_2|}{r_1 r_2}$$

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

$$\Delta E = \frac{8\pi e^2}{\epsilon_0} \left(\frac{Z^3}{\pi a_0^3} \right)^2 \int_{r_2}^{\infty} dr_1 \, r_1 \, e^{-2Zr_1/a_0} \int_0^{\infty} dr_2 \, r_2^2 \, e^{-2Zr_2/a_0}$$

$$= \frac{8\pi e^2}{\epsilon_0} \left(\frac{Z^3}{\pi a_0^3} \right)^2 \int_0^{\infty} dr_2 \, r_2^2 \left(\frac{a_0 r_2}{2Z} + \frac{a_0^2}{4Z^2} \right) e^{-4Zr_2/a_0}$$

$$= \frac{5}{8} \frac{Ze^2}{4\pi\epsilon_0 a_0} = \frac{5Z}{4} Ry$$

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

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

This is much closer to the correct value of $E_0 \approx -79 \ eV$. 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

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

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 α 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

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

with H the differential operator given in (2.1). Now we have to evaluate all terms in the Hamiltonian afresh. However, there is 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 α 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_α 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

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

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 $V(\mathbf{x}) \to 0$ as $x \to \infty$. 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

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

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 α 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 λ 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 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 ψ_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.
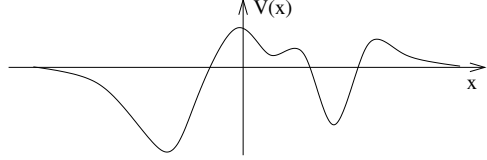

Figure 3: Does a bound state exist?

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 α. In the limit $\alpha \to 0$, we have

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

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

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[1]. 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,

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

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

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

---

[1]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 $x \to -x$. 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

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

The true value is $E_1 \approx 3.80$.

2.2 WKB

The WKB approximation is a method for solving the one-dimensional Schrödinger equation. The approximation is valid in situations where the potential changes slowly compared to the de Broglie wavelength $\lambda = 2\pi\hbar/p$ of the particle. The basic idea is that the wavefunction will be approximately that of a free particle, but with an amplitude and phase that vary to compensate the changes in the potential.

The method is named after the physicists Wentzel, Kramers and Brillouin. It is sometimes called the WKBJ approximation, with Harold Jeffreys' name tagged on the end to recognise the fact that he discovered before any of the other three. The main applications of the method are in estimating bound state energies and computing tunnelling rates.

2.2.1 The Semi-Classical Expansion

Before we jump into the quantum problem, let's build some classical intuition. Suppose that a one-dimensional potential $V(x)$ takes the form shown on the left-hand figure below. A classical particle with energy E will oscillate backwards and forwards, with momentum given by

$$p(x) \equiv \hbar k(x) \equiv \Big(2m\,(E - V(x))\Big)^{1/2} \tag{2.11}$$

Clearly, the particle only exists in the regions where $E \geq V(x)$. At the points where $E = V(x)$, it turns around and goes back the other way.
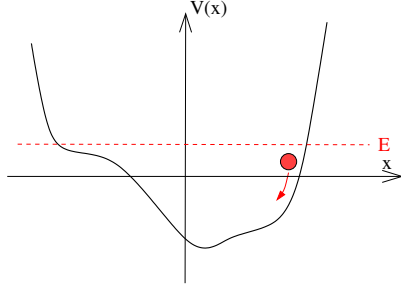
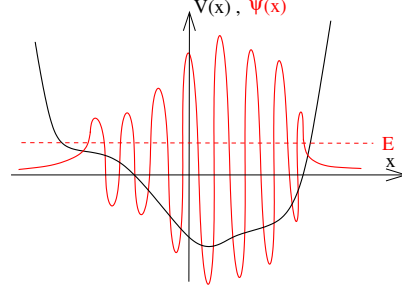**Figure 4:** The classical state.

Figure 5: The quantum state.

Now let's think about a quantum particle. Suppose that the potential varies slowly. This means that if we zoom into some part of the figure then the potential will be approximately constant. We may imagine that in this part of the potential, we can approximate the wavefunction by the plane wave $\psi(x) \sim e^{ip(x)\,x}$. However, the wavefunction also spreads beyond the region where the classical particle can reach. Here $E < V(x)$ and so, taken at face value, (2.11) tells us that $p(x)$ becomes purely imaginary. This means that the ansatz $\psi(x) \sim e^{ip(x)\,x}$ will lead to an exponentially decaying tail of the wavefunction (at least if we pick the minus sign correctly). But that's exactly what we expect the wavefunction to do in this region.

These ideas form the basis of the WKB approximation. Our goal now is to place them on a more systematic footing. To this end, consider the one-dimensional time-independent Schrödinger equation

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

It will prove useful to write this as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - V(x)\right)\psi = 0$$

Motivated by our discussion above, we will look for solutions of the form

$$\psi(x) = e^{iW(x)/\hbar}$$

Plugging this ansatz into the Schrödinger equation leaves us with the differential equation

$$i\hbar\frac{d^2W}{dx^2} - \left(\frac{dW}{dx}\right)^2 + p(x)^2 = 0 \tag{2.12}$$

where we the classical momentum $p(x)$ defined in (2.11) makes an appearance.

The plane wave solutions arise when $W(x) = \hbar k x$, in which case the second derivative in (2.12) vanishes. Here we'll look for solutions where this second derivative is merely small, meaning

$$\hbar \left| \frac{d^2 W}{dx^2} \right| \ll \left| \frac{dW}{dx} \right|^2 \tag{2.13}$$

We refer to this as the *semi-classical* limit.

Roughly speaking, (2.13) can be thought of as the $\hbar \to 0$ limit. Indeed, mathematically, it makes sense to attempt to solve (2.12) using a power series in $\hbar$. As physicists, this should makes us squirm a little as $\hbar$ is dimensionful, and so can't be "small". But we'll first solve the problem and then get a better understanding of when the solution is valid. For these purposes, we treat $p(x)$ as the background potential which we will take to be $\mathcal{O}(\hbar^0)$. We expand our solution as

$$W(x) = W_0(x) + \hbar W_1(x) + \hbar^2 W_2(x) + \dots$$

Plugging this ansatz into (2.12) gives

$$\left[-W_0'(x)^2 + p(x)^2 \right] + \hbar \left[iW_0''(x) - 2W_0'(x)W_1'(x) \right] + \mathcal{O}(\hbar^2) = 0$$

We see that we can now hope to solve these equations order by order in $\hbar$. The first is straightforward,

$$W_0'(x) = \pm p(x) \quad \Rightarrow \quad W_0(x) = \pm \int^x dx' \; p(x')$$

This is actually something that arises also in classical mechanics: it is the *Hamilton-Jacobi function*. More details can be found in Sections 4.7 and 4.8 of the lecture notes on Classical Dynamics.

At $\mathcal{O}(\hbar)$, we have

$$W_1'(x) = \frac{i}{2} \frac{W_0''(x)}{W_0'(x)} = \frac{i}{2} \frac{p'(x)}{p(x)} \quad \Rightarrow \quad W_1(x) = \frac{i}{2} \log p(x) + c$$

for some constant c. Putting these together gives us the WKB approximation to the wavefunction,

$$\psi(x) \approx \frac{A}{\sqrt{p(x)}} \exp\left(\pm \frac{i}{\hbar} \int^x dx' \; p(x') \right) \tag{2.14}$$

The probability of finding a particle at x is, of course, $|\psi(x)|^2 \sim 1/p(x)$. This is intuitive: the probability of finding a particle in some region point should be proportional to how long it spends there which, in turn, is inversely proportional to its momentum.

Validity of WKB

Before moving on, let's try to get a better feeling for the validity of the WKB approximation. To leading order, our requirement (2.13) reads

$$\hbar \left| \frac{dp}{dx} \right| \ll |p(x)|^2 \quad \Rightarrow \quad \frac{1}{2\pi} \frac{d\lambda}{dx} \ll 1$$

where $\lambda = 2\pi\hbar/p$ is the de Broglie wavelength. This is the statement that the de Broglie wavelength of the particle does not change considerably over distances comparable to its wavelength.

Alternatively, we can phrase this as a condition on the potential. Using (2.11), we have

$$\lambda(x) \left| \frac{dV}{dx} \right| \ll 4\pi \times \frac{|p(x)|^2}{2m}$$

which roughly says that the change of the potential energy over a de Broglie wavelength should be much less than the kinetic energy (with the factor of 4π giving an order of magnitude in leniency.)

The Need for a Matching Condition

Let's take a slowly varying potential. We want to find a solution to the Schrödinger equation with some energy E.

The WKB approximation does provides a solution in regions where $E \gg V(x)$ and, correspondingly, $p(x)$ is real. This is the case in the middle of the potential, where the wavefunction oscillates. The WKB approximation also provides a solutions when $E \ll V(x)$, where $p(x)$ is imaginary. This is the case to the far left and far right, where the wavefunction suffers either exponential decay or growth

$$\psi(x) \approx \frac{A}{2m(V(x) - E))^{1/4}} \exp\left(\pm \frac{1}{\hbar} \int^x dx' \ \sqrt{2m(V(x') - E)} \right)$$

The choice of $\pm$ is typically fixed by normalisability requirements.

But what happens in the region near $E = V(x)$? Here the WKB approximation is never valid and the putative wavefunction (2.14) diverges because $p(x) = 0$. What to do?

The point x_0 where $p(x_0) = 0$ is the classical turning point. The key idea that makes the WKB approximation work is *matching*. This means that we use the WKB approximation where it is valid. But in the neighbourhood of any turning point we will instead find a different solution. This will then be matched onto our WKB solution.

So what is the Schrödinger equation that we want to solve in the vicinity of x_0? We expand the potential energy, keeping only the linear term

$$V(x) \approx E + C(x - x_0) + \dots$$

The Schrödinger equation is then

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + C(x - x_0)\psi = 0 \tag{2.15}$$

We will solve this Schrödinger equation exactly, and then match this solution to the WKB wavefunction (2.14) to the left and right.

2.2.2 A Linear Potential and the Airy Function

The problem of the Schrödinger equation for a linear potential is interesting in its own right. For example, this describes a particle in a constant gravitational field with x the distance above the Earth. (In this case, we would place a hard wall — corresponding to the surface of the Earth — at $x = 0$ by requiring that $\psi(0) = 0$.) Another example involves *quarkonium*, a bound state of a heavy quark and anti-quark. Due to confinement of QCD, these experience a linearly growing potential between them.

For a linear potential $V(x) = Cx$, with C constant, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + Cx\psi = E\psi \tag{2.16}$$

Before proceeding, it's best rescale our variables to absorb all the factors floating around. Define the dimensionless position

$$u = \left(\frac{2mC}{\hbar^2}\right)^{1/3}(x - E/C) \tag{2.17}$$

Then the Schrödinger equation (2.16) becomes

$$\frac{d^2\psi}{du^2} - u\psi = 0 \tag{2.18}$$

This is known as the *Airy equation*. The solution is the *Airy function*, $\psi(u) = \mathrm{Ai}(u)$, which is defined by the somewhat strange looking integral

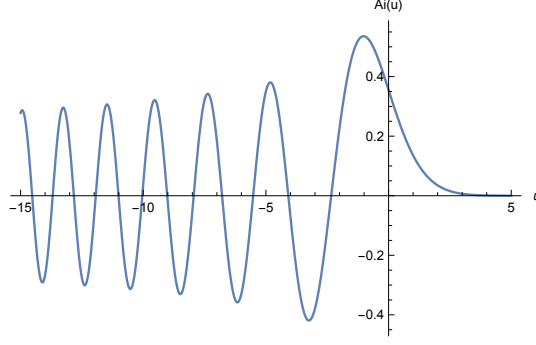$$\mathrm{Ai}(u) = \frac{1}{\pi}\int_0^\infty dt \ \cos\left(\frac{t^3}{3} + ut\right)$$

Figure 6: The Airy function.

To check this, note that

$$\left(\frac{d^2}{du^2} - u\right) \mathrm{Ai}(u) = -\frac{1}{\pi} \int_0^\infty dt \ (t^2 + u) \cos\left(\frac{t^3}{3} + ut\right)$$
$$= -\frac{1}{\pi} \int_0^\infty dt \ \frac{d}{dt} \sin\left(\frac{t^3}{3} + ut\right)$$

The lower limit of the integral clearly vanishes. The upper limit is more tricky. Heuristically, it vanishes as $\sin t^3$ oscillates more and more quickly as $t \to \infty$. More care is needed to make a rigorous argument.

A plot of the Airy function is shown in Figure 6. It has the nice property that it oscillates for $u < 0$, but decays exponentially for $u > 0$. Indeed, it can be shown that the asymptotic behaviour is given by

$$\mathrm{Ai}(u) \sim \frac{1}{2} \left(\frac{1}{\pi\sqrt{u}}\right)^{1/2} \exp\left(-\frac{2}{3}u^{3/2}\right) \qquad u \gg 0 \tag{2.19}$$

and

$$\mathrm{Ai}(u) \sim \left(\frac{1}{\pi\sqrt{-u}}\right)^{1/2} \cos\left(\frac{2}{3}u\sqrt{-u} + \frac{\pi}{4}\right) \qquad u \ll 0 \tag{2.20}$$

This kind of behaviour is what we would expect physically. Tracing through our definitions above, the region $u < 0$ corresponds to $E > V(x)$ and the wavefunction oscillates. Meanwhile, $u > 0$ corresponds to $E < V(x)$ and the wavefunction dies quickly.

The Airy equation (2.18) is a second order differential equation and so must have a second solution. This is known as $\mathrm{Bi}(u)$. It has the property that it diverges as $x \to \infty$, so does not qualify as a good wavefunction in our problem.

An Aside: Quarkonium

Take a quark and anti-quark and separate them. The quarks generate a field which is associated to the strong nuclear force and is sometimes called the *chromoelectric* field. Just like in Maxwell theory, this field gives rise to a force between the two quarks.

Classically the force between two quarks scales as $V \sim 1/r$, just like the Coulomb force. However, quantum fluctuations of the chromoelectric field dramatically change this behaviour and the chromoelectric field forms a collimated flux tube linking the quarks. A numerical simulation of this effect is shown on the right[2]. The upshot of this is that the potential between two quarks changes from being $V \sim 1/r$ to the form

Figure 7:

$$V = Cr \qquad (2.21)$$

This means that, in sharp contrast to other forces, it gets harder and harder to separate quarks. This behaviour is known as *confinement*. The coefficient C is referred to as the *string tension*.

We won't explain here why the potential takes the linear form (2.21). (In fact, you won't find a simple explanation of that anywhere! It's closely related to the Clay millenium prize problem on Yang-Mills theory. A large part of the lecture notes on Gauge Theory is devoted to an intuitive understanding of how confinement comes about.) Instead we'll just look at the spectrum of states that arises when two quarks experience a linear potential. These states are called *quarkonium*. The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) - \frac{l(l+1)}{r^2}\psi(r)\right) + Cr\psi(r) = E\psi(r)$$

There is an interesting story about how this spectrum depends on the angular momentum l but, for now, we look at the $l = 0$ sector. Defining $\chi = r\psi$ and the dimensionless coordinate $u = (2mC/\hbar^2)^{1/3}(r - E/C)$ as in (2.17), we see that this once again reduces to the Airy equation, with solutions given by $\chi(u) = \mathrm{Ai}(u)$

So far there is no quantisation of the allowed energy E. This comes from the requirement that $\chi(r = 0)$. In other words,

$$\mathrm{Ai}\left(-\left(\frac{2m}{\hbar^2 C^2}\right)^{1/3} E\right) = 0$$

---

[2]This is part of a set of animations of QCD, the theory of the strong force. You can see them at Derek Leinweber's webpage. They're pretty!
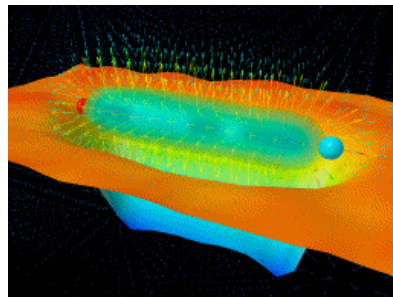
The zeros of the Airy function $\mathrm{Ai}(y)$ can be computed numerically. The first few occur at $y = -y_\star$, with

$$y_\star = 2.34, \ 4.09, \ 5.52, \ 6.79, \ 7.94, \ 9.02, \ \ldots$$

The first few energy levels are then $E = (\hbar^2 C^2/2m)^{1/3} y_\star$.

An Application: Matching the WKB Solution

For us, the main purpose in introducing the Airy function is to put it to work in the WKB approximation. The Airy function solves the Schrödinger equation (2.15) in the vicinity of the turning point x_0 where, comparing to (2.16), we see that we should set $x_0 = E/C$. The asymptotic behaviour (2.19) and (2.20) is exactly what we need to match onto the WKB solution (2.14).

Let's see how this works. First consider $u \ll 0$, corresponding to $x \ll x_0$. Here $E > V(x)$ and we have the oscillatory solution. We want to rewrite this in terms of our original variables. In this region, $V(x) \approx E + C(x - x_0)$, so we can justifiably replace

$$|u| = \left(\frac{2mC}{\hbar^2}\right)^{1/3} (x_0 - x) = \left(\frac{2m}{\hbar^2 C^2}\right)^{1/3} (E - V(x))$$

where we've used our definition of $p(x)$ given in (2.11). In these variables, the asymptotic form of the Airy function (2.20) is given by

$$\mathrm{Ai}(x) \sim \left(\frac{(2mC\hbar)^{1/3}}{\pi \sqrt{2m(E - V(x))}}\right)^{1/2} \cos\left(\frac{1}{\hbar} \int_{x_0}^{x} dx' \ \sqrt{2m(E - V(x'))} + \frac{\pi}{4}\right) \quad (2.22)$$

This takes the same oscillatory form as the WKB solution (2.14). The two solutions can be patched together simply by picking an appropriate normalisation factor and phase for the WKB solution.

Similarly, in the region $u \gg 0$, the exponentially decaying form of the Airy function (2.19) can be written as

$$\mathrm{Ai}(x) \sim \frac{1}{2} \left(\frac{(2mC\hbar)^{1/3}}{\pi \sqrt{2m(V(x) - E)|}}\right)^{1/2} \exp\left(-\frac{1}{\hbar} \int_{x_0}^{x} dx' \ \sqrt{2m((V(x') - E)}\right) \quad (2.23)$$

This too has the same form as the exponentially decaying WKB solution (2.14).

This, then, is how we piece together solutions. In regions where $E > V(x)$, the WKB approximation gives oscillating solutions. In regimes where $E < V(x)$, it gives exponentially decaying solutions. The Airy function interpolates between these two regimes. The following examples describes this method in practice.

2.2.3 Bound State Spectrum

As an example of this matching, let's return to the potential shown on the right. Our goal is to compute the spectrum of bound states. We first split the potential into three regions where the WKB approximation can be trusted:
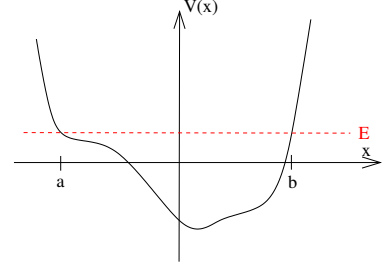

Figure 8:

$$\begin{array}{lc} \text{Region 1} & x \ll a \\ \text{Region 2} & a \ll x \ll b \\ \text{Region 3} & x \gg b \end{array}$$

We'll start in the left-most Region 1. Here the WKB approximation tells us that the solution dies exponentially as

$$\psi_1(x) \approx \frac{A}{2m(V(x) - E))^{1/4}} \exp\left(-\int_x^a dx' \sqrt{2m(V(x') - E)}\right)$$

As we approach $x = a$, the potential takes the linear form $V(x) \approx E + V'(a)(x - a)$ and this coincides with the asymptotic form (2.19) of the Airy function $\text{Ai}(-u)$. We then follow this Airy function through to Region 2 where the asymptotic form (2.22) tells us that we have

$$\psi_2(x) \approx \frac{2A}{2m(V(x) - E))^{1/4}} \cos\left(\frac{1}{\hbar}\int_a^x dx' \sqrt{2m(E - V(x'))} - \frac{\pi}{4}\right) \qquad (2.24)$$

Note the minus sign in the phase shift $-\pi/4$. This arises because we're working with $\text{Ai}(-u)$. The Airy function takes this form close to $x = a$ where $V(x)$ is linear. But, as we saw above, we can now extend this solution throughout Region 2 where it coincides with the WKB approximation.

We now repeat this procedure to match Regions 2 an 3. When $x \gg b$, the WKB approximation tells us that the wavefunction is

$$\psi_3(x) \approx \frac{A'}{2m(V(x) - E))^{1/4}} \exp\left(-\int_b^x dx' \sqrt{2m(V(x) - E)}\right)$$

Matching to the Airy function across the turning point $x = b$, we have

$$\psi_2(x) \approx \frac{2A'}{2m(V(x) - E))^{1/4}} \cos\left(\frac{1}{\hbar}\int_b^x dx' \sqrt{2m(E - V(x'))} + \frac{\pi}{4}\right) \qquad (2.25)$$

We're left with two expressions (2.24) and (2.25) for the wavefunction in Region 2. Clearly these must agree. Equating the two tells us that $|A| = |A'|$, but they may differ

by a sign, since this can be compensated by the cos function. Insisting that the two cos functions agree, up to sign, gives us the condition

$$\frac{1}{\hbar} \int_a^x dx' \ \sqrt{2m(E - V(x'))} - \frac{\pi}{4} = \frac{1}{\hbar} \int_b^x dx' \ \sqrt{2m(E - V(x'))} + \frac{\pi}{4} + n\pi$$

for some integer n. Rearranging gives

$$\int_a^b dx' \ \sqrt{2m(E - V(x'))} = \left(n + \frac{1}{2}\right) \hbar\pi \qquad (2.26)$$

To complete this expression, we should recall what we mean by a and b. For a given energy E, these are the extreme values of the classical trajectory where $p(x) = 0$. In other words, we can write $a = x_{\min}$ and $b = x_{\max}$. If we write our final expression in terms of the momentum $p(x)$, it takes the simple form

$$\int_{x_{\min}}^{x_{\max}} dx' \ p(x') = \left(n + \frac{1}{2}\right) \hbar\pi \qquad (2.27)$$

An Example: The Harmonic Oscillator

To illustrate this, let's look at an example that we all known and love: the harmonic oscillator with $V(x) = m^2\omega^2 x^2$. The quantisation condition (2.26) becomes

$$\int_{x_{\min}}^{x^{\max}} dx \ \sqrt{2m(E - m^2\omega^2 x^2)} = \frac{2mE}{m\omega} \frac{\pi}{2} = \left(n + \frac{1}{2}\right) \hbar\pi \quad \Rightarrow \quad E = \left(n + \frac{1}{2}\right) \hbar\omega$$

This, of course, is the exact spectrum of the harmonic oscillator. I should confess that this is something of a fluke. In general, we will not get the exact answer. For most potentials, the accuracy of the answer improves as n increases. This is because the high n are high energy states. These have large momentum and, hence, small de Broglie wavelength, which is where the WKB approximation works best.

2.2.4 Bohr-Sommerfeld Quantisation

The WKB approximation underlies an important piece of history from the pre-Schrödinger era of quantum mechanics. We can rewrite the quantisation condition (2.27) as

$$\oint dx \ p(x) = \left(n + \frac{1}{2}\right) 2\pi\hbar$$

where $\oint$ means that we take a closed path in phase space which, in this one-dimensional example, is from $x_{\min}$ to $x_{\max}$ and back again. This gives the extra factor of 2 on the right-hand side. You may recognise the left-hand-side as the adiabatic invariant from the Classical Dynamics lectures. This is a sensible object to quantise as it doesn't change if we slowly vary the parameters of the system.

In the old days of quantum mechanics, Bohr and Sommerfeld introduced an ad-hoc method of quantisation. They suggested that one should impose the condition

$$\oint dx\, p(x) = 2\pi n\hbar$$

with n an integer. They didn't include the factor of $1/2$. They made this guess because it turns out to correctly describe the spectrum of the hydrogen atom. This too is something of a fluke! But it was an important fluke that laid the groundwork for the full development of quantum mechanics. The WKB approximation provides an a-posteriori justification of the Bohr-Sommerfeld quantisation rule, laced with some irony: they guessed the wrong approximate quantisation rule which, for the system they were interested in, just happened to give the correct answer!

More generally, "Bohr-Sommerfeld quantisation" means packaging up a $2d$-dimensional phase space of the system into small parcels of volume $(2\pi\hbar)^d$ and assigning a quantum state to each. It is, at best, a crude approximation to the correct quantisation treatment.

2.2.5 Tunnelling out of a Trap

For our final application of the WKB approximation, we look at the problem of tunnelling out of a trap. This kind of problem was first introduced by Gammow as a model for alpa decay.

Consider the potential shown in the figure, with functional form

$$V(x) = \begin{cases} -V_0 & x < R \\ +\alpha/x & x > R \end{cases}$$

Figure 9:

We'll think of this as a one-dimensional problem; it is not difficult to generalise to to a three-dimensions. Here R is the be thought of as the size of the nucleus; V_0 is models the nuclear binding energy, while outside the nucleus the particle feels a Coulomb repulsion. If we take the particle to have charge q (for an alpha particle, this is $q = 2e$) and the nucleus that remains to have charge Ze, we should have

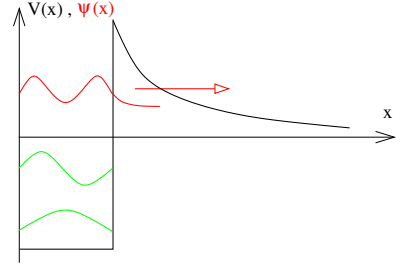$$\alpha = \frac{Zqe}{4\pi\epsilon_0} \tag{2.28}$$

Any state with $E < 0$ is bound and cannot leave the trap. (These are shown in green in the figure.) But those with $0 < E < \alpha/R$ are bound only classically; quantum mechanics allows them to tunnel through the barrier and escape to infinity. We would like to calculate the rate at which this happens.

In the region $x < R$, the wavefunction has the form

$$\psi_{\text{inside}}(x) = A e^{ikx} \qquad \text{with } E = \frac{\hbar^2 k^2}{2m}$$

After tunnelling, the particle emerges at distance $x = x_\star$ defined by $E = \alpha/x_\star$. For $x > x_\star$, the wavefunction again oscillates, with a form given by the WKB approximation (2.14), However, the amplitude of this wavefunction differs from the value A. The ratio of these two amplitudes determines the tunnelling rate.

To compute this, we patch the two wavefunctions together using the exponentially decaying WKB solution in the region $R < x < x_\star$. This gives

$$\psi(x_\star) = \psi(R) \, e^{-S/\hbar}$$

where the exponent is given by the integral

$$S = \int_R^{x_\star} dx' \sqrt{2m \left(\frac{\alpha}{x'} - E\right)} \tag{2.29}$$

This integral is particularly simple to compute in the limit $R \to 0$ where it is given by

$$S = \sqrt{\frac{2m}{E}} \pi \alpha = \frac{2\pi\alpha}{\hbar v}$$

where, in the second equality, we've set the energy of the particle equal to its classical kinetic energy: $E = \frac{1}{2}mv^2$.

The transmission probability T is then given by

$$T = \frac{|\psi(x_\star)|^2}{|\psi(R)|^2} = e^{-2S/\hbar} \tag{2.30}$$

This already contains some interesting information. In particular, recalling the definition of α in (2.28), we see that the larger the charge of the nucleus, the less likely the decay.

Usually we discuss the decay of atomic nuclei in terms of lifetimes. We can compute this by adding some simple (semi)-classical ideas to the above analysis. Inside the trap, the particle is bouncing backwards and forwards with velocity

$$v_0 = \sqrt{\frac{2(E + V_0)}{m}}$$

This means that the particle hits the barrier with frequency $\nu = v_0/R$. The decay rate is then $\Gamma = \nu e^{-\gamma}$ and the lifetime is

$$\tau = \frac{Rm}{\sqrt{2(E + V_0)}} e^{\gamma}$$

We didn't really treat the dependence on R correctly above. We set $R = 0$ when evaluating the exponent in (2.29), but retained it in the pre-factor. A better treatment does not change the qualitative results.

One Last Thing...

It is not difficult to extend this to a general potential $V(x)$ as shown in the figure. In all cases, the transmission probability has an exponential fall-off of the form $T \sim e^{-2S/\hbar}$ where S is given by

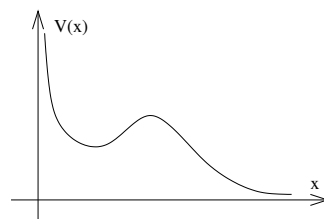$$S = \int_{x_0}^{x_1} dx' \ \sqrt{2m(V(x) - E)} \qquad (2.31)$$

Figure 10:

where the positions x_0 and x_1 are the classical values where $V(x) = E$, so that the integral is performed only over the forbidden region of the potential.

There is a lovely interpretation of this result that has its heart in the path integral formulation of quantum mechanics. Consider the a classical system with the potential $-V(x)$ rather than $+V(x)$. In other words, we turn the potential upside down. The action for such a system is

$$S[x(t)] = \int_{t_0}^{t_1} dt \ \frac{1}{2} m \dot{x}^2 + V(x)$$

In this auxiliary system, there is a classical solution, $x_{cl}(t)$ which bounces between the two turning points, so $x_{cl}(t_0) = x_0$ and $x_{cl}(t_1) = x_1$. It turns out that the exponent (2.31) is precisely the value of the action evaluated on this solution

$$S = S[x_{cl}(t)]$$

This result essentially follows from the discussion of Hamilton-Jacobi theory in the Classical Dynamics lecture notes.

2.3 Changing Hamiltonians, Fast and Slow

You learned in the previous course how to set-up perturbation theory when the Hamiltonian $H(t)$ changes with time. There are, however, two extreme situations where life is somewhat easier. This is when the changes to the Hamiltonian are either very fast, or very slow.

2.3.1 The Sudden Approximation

We start with the fast case. We consider the situation where the system starts with some Hamiltonian H_0, but then very quickly changes to another Hamiltonian H. This occurs over a small timescale τ.

Of course "very quickly" is relative. We require that the time τ is much smaller than any characteristic time scale of the original system. These time scales are set by the energy splitting, so we must have

$$\tau \ll \frac{\hbar}{\Delta E}$$

If these conditions are obeyed, the physics is very intuitive. The system originally sits in some state $|\psi\rangle$. But the change happens so quickly that the state does not have a chance to respond. After time τ, the system still sits in the same state $|\psi\rangle$. The only difference is that the time dynamics is now governed by H rather than H_0.

An Example: Tritium

Tritium, ^3H, is an isotope of hydrogen whose nucleus contains a single proton and two neutrons. It is unstable with a half-life of around 12 years. It suffers beta decay to helium, emitting an electron and anti-neutrino in the process

$$^3H \rightarrow {}^3He^+ + e^- + \bar{\nu}_e$$
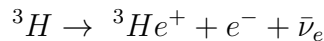
The electron is emitted with a fairly wide range of energies, whose mean is $E \sim 5.6~keV$. Since the mass of the electron is $mc^2 \approx 511~keV$, the electron departs with a speed given by $E = \frac{1}{2}mv^2$ (we could use the relativistic formula $E = m\gamma c^2$ but it doesn't affect the answer too much). This is $v \approx 0.15\,c$. The time taken to leave the atom is then $\tau \approx a_0/v \approx 10^{-19}~s$ where $a_0 \approx 5 \times 10^{-11}~m$ is the Bohr radius.

We'll initially take the electron in the tritium atom to sit in its ground state. The first excited state has energy difference $\Delta E = \frac{3}{4}E_0 \approx 10~eV$, corresponding to a time scale $\hbar/\Delta E \approx 6.5 \times 10^{-17}~s$. We therefore find $\tau \ll \hbar/\Delta E$ by almost two orders of magnitude. This justifies our use of the sudden approximation.

The electron ground state of the tritium atom is the same as that of hydrogen, namely

$$\psi_0 = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0} \quad \text{with } Z = 1$$

After the beta decay, the electron remains in this same state, but this is no longer an energy eigenstate. Indeed, the ground state of helium takes the same functional form, but with $Z = 2$. The probability that the electron sits in the ground state of helium is given by the overlap

$$P = \left| \int d^3x \; \psi_0^\star(\mathbf{x}; Z = 1) \, \psi_0(\mathbf{x}; Z = 2) \right|^2 = \frac{8^3}{3^6} \approx 0.7$$

We see that 70% of the time the electron remains in the ground state. The rest of the time it sits in some excited state, and subsequently decays down to the ground state.

2.3.2 An Example: Quantum Quench of a Harmonic Oscillator

There are a number of experimental situation where one deliberately make a rapid change to the Hamiltonian. This forces the system away from equilibrium, with the goal of opening a window on interesting dynamics. In this situation, the process of the sudden change of the Hamiltonian is called a *quantum quench*.

As usual, the harmonic oscillator provides a particularly simple example. Suppose that we start with the Hamiltonian

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}\omega_0^2 x^2 = \hbar\omega_0 \left(a_0^\dagger a_0 + \frac{1}{2} \right)$$

where

$$a_0 = \frac{1}{\sqrt{2m\omega_0}}(m\omega_0 x + ip)$$

Then, on a time scale $\tau \ll \hbar/\omega_0$, we change the frequency of the oscillator so that the Hamiltonian becomes

$$H = \frac{p^2}{2m} + \frac{1}{2}\omega^2 x^2 = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right)$$

Clearly the wavefunctions for energy eigenstates are closely related since the change in frequency can be compensated by rescaling x. However, here we would like to answer different questions: if we originally sit in the ground state of H_0, which state of H do we end up in?

A little bit of algebra shows that we can write the new annihilation operator as

$$a = \frac{1}{\sqrt{2m\omega}}(m\omega x + ip) = \frac{1}{2}\left(\sqrt{\frac{\omega}{\omega_0}} + \sqrt{\frac{\omega_0}{\omega}}\right)a_0 + \frac{1}{2}\left(\sqrt{\frac{\omega}{\omega_0}} - \sqrt{\frac{\omega_0}{\omega}}\right)a_0^\dagger$$

Let's denote the ground state of H_0 by $|\emptyset\rangle$. It obeys $a_0|\emptyset\rangle = 0$. In terms of our new creation and annihilation operators, this state satisfies $(\omega + \omega_0)a|\emptyset\rangle = (\omega - \omega_0)a^\dagger|\emptyset\rangle$. Expanded in terms of the eigenstates $|n\rangle$, $n = 0, 1, \ldots$ of H, we find that it involves the whole slew of parity-even excited states

$$|\emptyset\rangle = \sum_{n=0}^{\infty} \alpha_{2n}|2n\rangle \quad \text{with} \quad \alpha_{2n+2} = \sqrt{\frac{2n+1}{2n+2}}\left(\frac{\omega - \omega_0}{\omega + \omega_0}\right)\alpha_{2n}$$

We can also address more detailed questions about the dynamics. Suppose that the quench takes place at time $t = 0$. Working in the Heisenberg picture, we know that

$$\langle\emptyset|x^2(0)|\emptyset\rangle = \frac{\hbar}{2m\omega_0} \quad \text{and} \quad \langle\emptyset|p^2(0)|\emptyset\rangle = \frac{\hbar m\omega}{2}$$

The position operator now evolves, governed by the new Hamiltonian H,

$$x(t) = x(0)\cos(\omega t) + \frac{p(0)}{m\omega}\sin(\omega t)$$

With a little bit of algebra we find that, for $t_2 > t_1$, the positions are correlated as

$$\langle\emptyset|x(t_2)x(t_1)|\emptyset\rangle = \frac{\hbar}{2m\omega}\left[e^{-i\omega(t_2-t_1)} + \frac{(\omega^2 - \omega_0^2)\cos(\omega(t_2+t_1)) + (\omega - \omega_0)^2\cos(\omega(t_2-t_1))}{2\omega\omega_0}\right]$$

The first term is the evolution of an energy eigenstate; this is what we would get if no quench took place. The other terms are due to the quench. The surprise is the existence of the term that depends on $(t_1 + t_2)$. This is not time translationally invariant, even though both times are measured after $t = 0$. This means that the state carries a memory of the traumatic event that happened during the quench.

2.3.3 The Adiabatic Approximation

We now turn to the opposite limit, when the Hamiltonian changes very slowly. Here "slow" is again relative to the energy splitting $\hbar/\Delta E$, as we will see below.

Consider a Hamiltonian $H(\lambda)$ which depends on some number of parameters λ^i. For simplicity, we will assume that H has a discrete spectrum. We write these states as

$$H|n(\lambda)\rangle = E_n(\lambda)|n(\lambda)\rangle \tag{2.32}$$

Let's place ourselves in one of these energy eigenstates. Now vary the parameters λ^i. The *adiabatic theorem* states that if λ^i are changed suitably slowly, then the system will cling to the energy eigenstate $|n(\lambda(t))\rangle$ that we started off in.

To see this, we want to solve the time-dependent Schrödinger equation

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = H|\psi(t)\rangle$$

We expand the solution in a basis of instantaneous energy eigenstates,

$$|\psi(t)\rangle = \sum_m a_m(t) \, e^{i\xi_m(t)} \, |m(\lambda(t))\rangle \tag{2.33}$$

Here $a_m(t)$ are coefficients that we wish to determine, while $\xi_m(t)$ is the usual energy-dependent phase factor

$$\xi_m(t) = -\frac{1}{\hbar} \int_0^t dt' \, E_m(t')$$

To proceed, we substitute our ansatz (2.33) into the Schrödinger equation to find

$$\sum_m \left[\dot{a}_m \, e^{i\xi_m} |m(\lambda)\rangle + a_m \, e^{i\xi_m} \frac{\partial}{\partial \lambda^i} |m(\lambda)\rangle \dot{\lambda}^i \right] = 0$$

where we've cancelled the two terms which depend on E_n. Taking the inner product with $\langle n(\lambda)|$ gives

$$\dot{a}_n = -\sum_m a_m e^{i(\xi_m - \xi_n)} \langle n(\lambda)| \frac{\partial}{\partial \lambda^i} |m(\lambda)\rangle \, \dot{\lambda}^i$$

$$= i a_n \, \mathcal{A}_i(\lambda) \, \dot{\lambda}^i - \sum_{m \neq n} a_m e^{i(\xi_m - \xi_n)} \langle n(\lambda)| \frac{\partial}{\partial \lambda^i} |m(\lambda)\rangle \, \dot{\lambda}^i \tag{2.34}$$

In the second line, we've singled out the $m = n$ term and defined

$$\mathcal{A}_i(\lambda) = -i\langle n| \frac{\partial}{\partial \lambda^i} |n\rangle \tag{2.35}$$

This is called the *Berry connection*. It plays a very important role in many aspects of theoretical physics, and we'll see some examples in Section 2.3.4.

First, we need to deal with the second term in (2.34). We will argue that this is small. To see this, we return to our original definition (2.32) and differentiate with respect to λ,

$$\frac{\partial H}{\partial \lambda^i} |m\rangle + H \frac{\partial}{\partial \lambda^i} |m\rangle = \frac{\partial E_m}{\partial \lambda^i} |m\rangle + E_m \frac{\partial}{\partial \lambda^i} |m\rangle$$

Now take the inner product with $\langle n|$ where $n \neq m$ to find

$$(E_m - E_n)\langle n| \frac{\partial}{\partial \lambda^i} |m\rangle = \langle n| \frac{\partial H}{\partial \lambda^i} |m\rangle$$

This means that the second term in (2.34) is proportional to

$$\langle n|\frac{\partial}{\partial \lambda^i}|m\rangle \, \dot{\lambda}^i = \langle n|\frac{\partial H}{\partial \lambda^i}|m\rangle \, \frac{\dot{\lambda}^i}{E_m - E_n} \tag{2.36}$$

The adiabatic theorem holds when the change of parameters $\dot{\lambda}^i$ is much smaller than the splitting of energy levels $E_m - E_n$. In this limit, we can ignore this term. From (2.34), we're then left with

$$\dot{a}_n = ia_n \mathcal{A}_i \dot{\lambda}$$

This is easily solved to give

$$a_n = C_n \exp\left(i \int_0^t dt' \, \mathcal{A}_i(\lambda(t')) \, \dot{\lambda}^i\right) \tag{2.37}$$

where C_n are constants.

This is the *adiabatic theorem*. If we start at time $t = 0$ with $a_m = \delta_{mn}$, so the system is in a definite energy eigenstate $|n\rangle$, then the system remains in the state $|n(\lambda)\rangle$ as we vary λ. This is true as long as $\hbar\dot{\lambda}^i \ll \Delta E$, so that we can drop the term (2.36). In particular, this means that when we vary the parameters λ, we should be careful to avoid *level crossing*, where another state becomes degenerate with the $|n(\lambda)\rangle$ that we're sitting in. In this case, we will have $E_m = E_n$ for some $|m\rangle$ and all bets are off: when the states separate again, there's no simple way to tell which linear combinations of the state we now sit in.

However, level crossings are rare in quantum mechanics. In general, you have to tune three parameters to specific values in order to get two states to have the same energy. This follows by thinking about the a general Hermitian 2×2 matrix which can be viewed as the Hamiltonian for the two states of interest. The general Hermitian 2×2 matrix depends on 4 parameters, but its eigenvalues only coincide if it is proportional to the identity matrix. This means that three of those parameters have to be set to zero.

2.3.4 Berry Phase

There is a surprise hiding in the details of the adiabatic theorem. As we vary the parameters λ, the phase of the state $|n(\lambda)\rangle$ changes but there are two contributions, rather than one. The first is the usual "$e^{-iEt/\hbar}$" phase that we expect for an energy eigenstate; this is shown explicitly in our original ansatz (2.33). But there is also a second contribution to the phase, shown in (2.37).

To highlight the distinction between these two contributions, suppose that we vary the parameters λ but, finally we put them back to their starting values. This means that we trace out a closed path C in the space of parameters. The second contribution (2.37) can now be written as

$$e^{i\gamma} = \exp\left(i \oint_C d\lambda^i \, \mathcal{A}_i(\lambda) \right) \tag{2.38}$$

In contrast to the energy-dependent phase, this does not depend on the time taken to make the journey in parameter space. Instead, it depends only on the path path we take through parameter space.

Although the extra contribution (2.38) was correctly included in many calculations over the decades, its general status was only appreciated by Michael Berry in 1984. It is known as the *Berry phase*. It plays an important role in many of the more subtle applications that are related to topology, such as the quantum Hall effect and topological insulators.

There is some very pretty geometry underlying the Berry phase. We can start to get a feel for this by looking a little more closely at the Berry connection (2.35). This is an example of a kind of object that you've seen before: it is like the gauge potential in electromagnetism! Let's explore this analogy a little further.

In the relativistic form of electromagnetism, we have a gauge potential $A_\mu(x)$ where $\mu = 0, 1, 2, 3$ and x are coordinates over Minkowski spacetime. There is a redundancy in the description of the gauge potential: all physics remains invariant under the gauge transformation

$$A_\mu \rightarrow A'_\mu = A_\mu + \partial_\mu \omega \tag{2.39}$$

for any function $\omega(x)$. In our course on Electromagnetism, we were learned that if we want to extract the physical information contained in A_μ, we should compute the field strength

$$F_{\mu\nu} = \frac{\partial A_\mu}{\partial x^\nu} - \frac{\partial A_\nu}{\partial x^\mu}$$

This contains the electric and magnetic fields. It is invariant under gauge transformations.

Now let's compare this to the Berry connection $\mathcal{A}_i(\lambda)$. Of course, this no longer depends on the coordinates of Minkowski space; instead it depends on the parameters λ^i. The number of these parameters is arbitrary; let's suppose that we have d of them. This means that $i = 1, \ldots, d$. In the language of differential geometry $\mathcal{A}_i(\lambda)$ is said to be a one-form over the space of parameters, while $A_\mu(x)$ is said to be a one-form over Minkowski space.

There is also a redundancy in the information contained in the Berry connection $\mathcal{A}_i(\lambda)$. This follows from the arbitrary choice we made in fixing the phase of the reference states $|n(\lambda)\rangle$. We could just as happily have chosen a different set of reference states which differ by a phase. Moreover, we could pick a different phase for every choice of parameters λ,

$$|n'(\lambda)\rangle = e^{i\omega(\lambda)} |n(\lambda)\rangle$$

for any function $\omega(\lambda)$. If we compute the Berry connection arising from this new choice, we have

$$\mathcal{A}_i' = -i\langle n'|\frac{\partial}{\partial \lambda^i}|n'\rangle = \mathcal{A}_i + \frac{\partial \omega}{\partial \lambda^i} \tag{2.40}$$

This takes the same form as the gauge transformation (2.39).

Following the analogy with electromagnetism, we might expect that the physical information in the Berry connection can be found in the gauge invariant field strength which, mathematically, is known as the *curvature* of the connection,

$$\mathcal{F}_{ij}(\lambda) = \frac{\partial \mathcal{A}_i}{\partial \lambda^j} - \frac{\partial \mathcal{A}_j}{\partial \lambda^i}$$

It's certainly true that $\mathcal{F}$ contains some physical information about our quantum system, but it's not the only gauge invariant quantity of interest. In the present context, the most natural thing to compute is the Berry phase (2.38). Importantly, this too is independent of the arbitrariness arising from the gauge transformation (2.40). This is because $\oint \partial_i \omega \, d\lambda^i = 0$. Indeed, we've already seen this same expression in the context of electromagnetism: it is the Aharonov-Bohm phase that we also met in the lectures on Solid State Physics.

In fact, it's possible to write the Berry phase in terms of the field strength using the higher-dimensional version of Stokes' theorem

$$e^{i\gamma} = \exp\left(-i \oint_C \mathcal{A}_i(\lambda) \, d\lambda^i\right) = \exp\left(-i \int_S \mathcal{F}_{ij} \, dS^{ij}\right) \tag{2.41}$$

where S is a two-dimensional surface in the parameter space bounded by the path C.

2.3.5 An Example: A Spin in a Magnetic Field

The standard example of the Berry phase is very simple. It is a spin, with a Hilbert space consisting of just two states. The spin is placed in a magnetic field $\mathbf{B}$. We met the Hamiltonian in this system when we discussed particles in a magnetic field in the lectures on Solid State Physics: it is

$$H = -\mathbf{B} \cdot \boldsymbol{\sigma} + B$$

where $\boldsymbol{\sigma}$ are the triplet of Pauli vectors. We've set the magnetic moment of the particle to unity for convenience, and we've also added the constant offset $B = |\mathbf{B}|$ to this Hamiltonian to ensure that the ground state always has vanishing energy. This is so that the phase $e^{-iEt/\hbar}$ will vanish for the ground state and we can focus on the Berry phase that we care about.

The Hamiltonian has two eigenvalues: 0 and $+2B$. We denote the ground state as $|\downarrow\rangle$ and the excited state as $|\uparrow\rangle$,

$$H|\downarrow\rangle = 0 \quad \text{and} \quad H|\uparrow\rangle = 2B|\uparrow\rangle$$

Note that these two states are non-degenerate as long as $\mathbf{B} \neq 0$.

We are going to treat the magnetic field as the parameters, so that $\lambda^i \equiv B^i$ in this example. Be warned: this means that things are about to get confusing because we'll be talking about Berry connections $\mathcal{A}_i$ and curvatures $\mathcal{F}_{ij}$ over the space of magnetic fields. (As opposed to electromagnetism where we talk about magnetic fields over actual space).

The specific form of $|\uparrow\rangle$ and $|\downarrow\rangle$ will depend on the orientation of $\mathbf{B}$. To provide more explicit forms for these states, we write the magnetic field $\mathbf{B}$ in spherical polar coordinates

$$\mathbf{B} = \begin{pmatrix} B\sin\theta\cos\phi \\ B\sin\theta\sin\phi \\ B\cos\theta \end{pmatrix}$$

with $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi)$ The Hamiltonian then reads

$$H = -B\begin{pmatrix} \cos\theta - 1 & e^{-i\phi}\sin\theta \\ e^{+i\phi}\sin\theta & -\cos\theta - 1 \end{pmatrix}$$

In these coordinates, two normalised eigenstates are given by

$$|\downarrow\rangle = \begin{pmatrix} e^{-i\phi}\sin\theta/2 \\ -\cos\theta/2 \end{pmatrix} \quad \text{and} \quad |\uparrow\rangle = \begin{pmatrix} e^{-i\phi}\cos\theta/2 \\ \sin\theta/2 \end{pmatrix}$$

These states play the role of our $|n(\lambda)\rangle$ that we had in our general derivation. Note, however, that they are not well defined for all values of $\mathbf{B}$. When we have $\theta = \pi$, the angular coordinate ϕ is not well defined. This means that $|\downarrow\rangle$ and $|\uparrow\rangle$ don't have well defined phases. This kind of behaviour is typical of systems with non-trivial Berry phase.

We can easily compute the Berry phase arising from these states (staying away from $\theta = \pi$ to be on the safe side). We have

$$\mathcal{A}_\theta = -i\langle\downarrow|\frac{\partial}{\partial\theta}|\downarrow\rangle = 0 \quad \text{and} \quad \mathcal{A}_\phi = -i\langle\downarrow|\frac{\partial}{\partial\phi}|\downarrow\rangle = -\sin^2\left(\frac{\theta}{2}\right)$$

The resulting Berry curvature in polar coordinates is

$$\mathcal{F}_{\theta\phi} = \frac{\partial\mathcal{A}_\phi}{\partial\theta} - \frac{\partial\mathcal{A}_\theta}{\partial\phi} = -\sin\theta$$

This is simpler if we translate it back to cartesian coordinates where the rotational symmetry is more manifest. It becomes

$$\mathcal{F}_{ij}(\mathbf{B}) = -\epsilon_{ijk}\frac{B^k}{2|\mathbf{B}|^3}$$

But this is interesting. It is a magnetic monopole. Except now it's not a magnetic monopole of electromagnetism. Instead it is, rather confusingly, a magnetic monopole in the space of magnetic fields.

Note that the magnetic monopole sits at the point $\mathbf{B} = 0$ where the two energy levels coincide. Here, the field strength is singular. This is the point where we can no longer trust the Berry phase computation. Nonetheless, it is the presence of this level crossing and the resulting singularity which is dominating the physics of the Berry phase.

The magnetic monopole has charge $g = -1/2$, meaning that the integral of the Berry curvature over any two-sphere $\mathbf{S}^2$ which surrounds the origin is

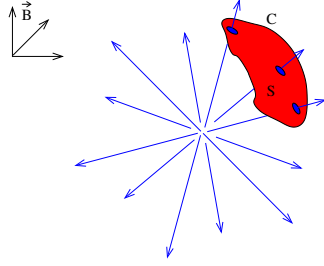$$\int_{\mathbf{S}^2} \mathcal{F}_{ij}\, dS^{ij} = 4\pi g = -2\pi \tag{2.42}$$
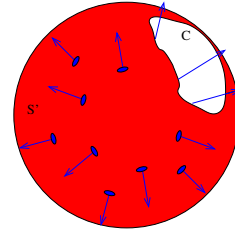
Figure 11: Integrating over S...

Figure 12: ...or over S'.

Using this, we can easily compute the Berry phase for any path C that we choose to take in the space of magnetic fields $\mathbf{B}$. We only insist that the path C avoids the origin. Suppose that the surface S, bounded by C, makes a solid angle Ω. Then, using the form (2.41) of the Berry phase, we have

$$e^{i\gamma} = \exp\left(-i\int_S \mathcal{F}_{ij}\, dS^{ij}\right) = \exp\left(\frac{i\Omega}{2}\right) \tag{2.43}$$

Note, however, that there is an ambiguity in this computation. We could choose to form S as shown in the left hand figure. But we could equally well choose the surface S' to go around the back of the sphere, as shown in the right-hand figure. In this case, the solid angle formed by S' is $\Omega' = 4\pi - \Omega$. Computing the Berry phase using S' gives

$$e^{i\gamma'} = \exp\left(-i\int_{S'} \mathcal{F}_{ij}\, dS^{ij}\right) = \exp\left(\frac{-i(4\pi - \Omega)}{2}\right) = e^{i\gamma} \tag{2.44}$$

where the difference in sign in the second equality comes because the surface now has opposite orientation. So, happily, the two computations agree. Note, however, that this agreement requires that the charge of the monopole in (2.42) is $2g \in \mathbf{Z}$.

The discussion above is a repeat of Dirac's argument for the quantisation of magnetic charge; this can also be found in the lectures on Solid State Physics and the lectures on Gauge Theory (where you'll even find the same figures!). Dirac's quantisation argument extends to a general Berry curvature $\mathcal{F}_{ij}$ with an arbitrary number of parameters: the integral of the curvature over any closed surface must be quantised in units of 2π,

$$\int \mathcal{F}_{ij}\, dS^{ij} = 2\pi C \tag{2.45}$$

The integer $C \in \mathbf{Z}$ is called the *Chern number*.

You can read more about extensions of the Berry phase and its applications in the lectures on the Quantum Hall Effect.

2.3.6 The Born-Oppenheimer Approximation

"I couldn't find any mistake - did you really do this alone?"

Oppenheimer to his research supervisor Max Born

The Born-Oppenhemier approximation is an approach to solving quantum mechanical problems in which there is a hierarchy of scales. The standard example is the a bunch of nuclei, each with position $\mathbf{R}_\alpha$ mass M_α and charge $Z_\alpha e$, interacting with a bunch of electrons, each with position $\mathbf{r}_i$, mass m and charge $-e$. The Hamiltonian is

$$H = \sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + \sum_i \frac{\hbar^2}{2m}\nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(\sum_{i,j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\alpha,i}\frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} - \sum_{i,\alpha}\frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}\right)$$

This simple Hamiltonian is believed to describe much of what we see around us in the world, so much so that some condensed matter physicists will refer to this, only half-jokingly, as the "theory of everything". Of course, the information about any complex system is deeply hidden within this equation, and the art of physics is finding approximation schemes, or emergent organising principles, to extract this information.

The hierarchy of scales in the Hamiltonian above arises because of the mass difference between the nuclei and the electrons. Recall that the proton-to-electron mass ratio is $m_p/m_e \approx 1836$. This means that the nuclei are cumbersome and slow, while the electrons are nimble and quick. Relatedly, the nuclei wavefunctions are much more localised than the electron wavefunctions. This motivates us to first fix the positions of the nuclei and look at the electron Hamiltonian, and only later solve for the nuclei dynamics. This is the essence of the *Born-Oppenheimer approximation*.

To this end, we write

$$H = H_{\text{nucl}} + H_{\text{el}}$$

where

$$H_{\text{nucl}} = \sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + \frac{e^2}{4\pi\epsilon_0}\sum_{\alpha,i}\frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}$$

and

$$H_{\text{el}} = \sum_i \frac{\hbar^2}{2m}\nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(\sum_{i,j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,\alpha}\frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}\right)$$

We then solve for the eigenstates of H_e, where the nuclei positions $\mathbf{R}$ are viewed as parameters which, as in the adiabatic approximation, will subsequently vary slowly.

The only difference with our previous discussion is that the time evolution of $\mathbf{R}$ is determined by the dynamics of the system, rather than under the control of some experimenter.

For fixed $\mathbf{R}$, the instantaneous electron wavefunctions are

$$H_{\text{el}}\,\phi_n(\mathbf{r};\mathbf{R}) = \epsilon_n(\mathbf{R})\,\phi_n(\mathbf{r};\mathbf{R})$$

In what follows, we will assume that the energy levels are non-degenerate. (There is an interesting generalisation if there is a degeneracy which we will not discuss in these lectures.) We then make the ansatz for the wavefunction of the full system

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_n \Phi_n(\mathbf{R})\phi_n(\mathbf{r};\mathbf{R})$$

We'd like to write down an *effective Hamiltonian* which governs the nuclei wavefunctions $\Phi_n(\mathbf{R})$. This is straightforward. The wavefunction Ψ obeys

$$(H_{\text{nucl}} + H_{\text{el}})\Psi = E\Psi$$

Switching to bra-ket notation for the electron eigenstates, we can write this as

$$\sum_n \langle\phi_m|H_{\text{nucl}}\Phi_n|\phi_n\rangle + \epsilon_m(\mathbf{R})\Phi_m = E\Phi_m \tag{2.46}$$

Now H_{nucl} contains the kinetic term $\nabla_{\mathbf{R}}^2$, and this acts both on the nuclei wavefunction Φ_n, but also on the electron wavefunction $\phi_n(\mathbf{r};\mathbf{R})$ where the nuclei positions sit as parameters. We have

$$\langle\phi_m|\nabla_{\mathbf{R}}^2\Phi_n|\phi_n\rangle = \sum_k \Big(\delta_{mk}\nabla_{\mathbf{R}} + \langle\phi_m|\nabla_{\mathbf{R}}|\phi_k\rangle\Big)\Big(\delta_{kn}\nabla_{\mathbf{R}} + \langle\phi_k|\nabla_{\mathbf{R}}|\phi_n\rangle\Big)\Phi_n$$

We now argue that, as in Section 2.3.3, the off-diagonal terms are small. The same analysis as in (2.36) shows that they can be written as

$$\sum_{k\neq n}\langle\phi_n|\nabla_{\mathbf{R}}|\phi_k\rangle\langle\phi_k|\nabla_{\mathbf{R}}|\phi_n\rangle = \sum_{k\neq n}\left|\frac{\langle\phi_n|(\nabla_{\mathbf{R}}H_{\text{el}})|\phi_k\rangle}{\epsilon_n - \epsilon_k}\right|^2$$

In the spirit of the adiabatic approximation, these can be neglected as long as the motion of the nuclei is smaller than the splitting of the electron energy levels. In this limit, we get a simple effective Hamiltonian for the nuclei (2.46). The Hamiltonian depends on the state $|\phi_n\rangle$ that the electrons sit in, and is given by

$$H_n^{\text{eff}} = \sum_\alpha \frac{\hbar^2}{2M_\alpha}\left(\nabla_\alpha - i\boldsymbol{\mathcal{A}}_{n,\alpha}\right)^2 + \frac{e^2}{4\pi\epsilon_0}\sum_{\alpha,i}\frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} + \epsilon_n(\mathbf{R})$$

We see that the electron energy level $\epsilon_n(\mathbf{R})$ acts as an effective potential for the nuclei. Perhaps more surprisingly, the Berry connection

$$\mathcal{A}_{n,\alpha} = -i\langle\phi_n|\nabla_{\mathbf{R}_\alpha}|\phi_n\rangle$$

also makes an appearance, now acting as an effective magnetic field in which the nuclei $\mathbf{R}_\alpha$ moves.

The idea of the Born-Oppenheimer approximation is that we can first solve for the fast-moving degrees of freedom, to find an effective action for the slow-moving degrees of freedom. We sometimes say that we have "*integrated out*" the electron degrees of freedom, language which really comes from the path integral formulation of quantum mechanics. This is a very powerful idea, and one which becomes increasingly important as we progress in theoretical physics. Indeed, this simple idea underpins the *Wilsonian renormalisation group* which we will meet in later courses.

2.3.7 An Example: Molecules

The Born-Oppenheimer approximation plays a key role in chemistry (and, therefore, in life in general). This is because it provides quantitative insight into the formation of covalent bonds, in which its energetically preferable for nuclei to stick together because the gain in energy from sharing an electron beats their mutual Coulomb repulsion.

The simplest example is the formation of the hydrogen molecule H_2^-, consisting of two protons and a single electron. If we fix the proton separation to $\mathbf{R}$, then the resulting Hamiltonian for the electrons is

$$H_{\mathrm{el}} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r} + \frac{1}{|\mathbf{r} - \mathbf{R}|}\right]$$

To proceed, we will combine the Born-Oppenheimer approximation with the variational method that we met in Section 2.1. Our ultimate goal is simply to show that a bound state exists. For this, the effective potential energy is much more important than the Berry connection. We will consider two possible ansatz for the electron ground state

$$\phi_\pm(\mathbf{r}) = A_\pm\Big(\psi_0(\mathbf{r}) \pm \psi_0(\mathbf{r} - \mathbf{R})\Big)$$

where

$$\psi_0 = \sqrt{\frac{1}{\pi a_0^3}}e^{-r/a_0}$$

is the ground state wavefunction of hydrogen, which has energy $E_0 = -e^2/8\pi\epsilon_0 a_0$.
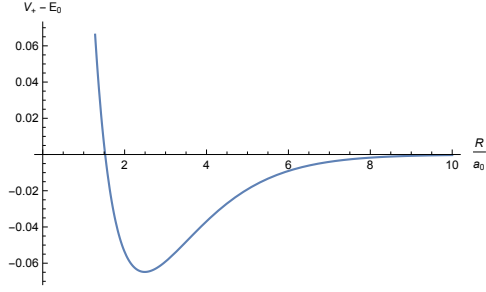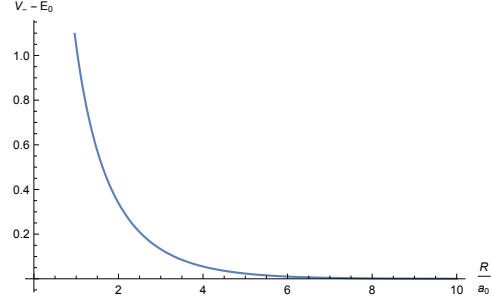
Figure 13: The potential for Ψ_+

Figure 14: The potential for Ψ_-

Although ψ_0 is normalised, the full wavefunction $\phi_\pm$ is not. The normalisation condition gives

$$A_\pm^2 = \frac{1}{2}\left[1 \pm \int d^3r \; \psi_0(\mathbf{r})\psi_0(\mathbf{r} - \mathbf{R})\right]^{-1}$$

This is the first of several, rather tedious integrals that we have in store. They can all be done using the kind of techniques that we introduced in Section 2.1.2 when discussing helium. Here I'll simply state the answers. It turns out that

$$u(R) = \int d^3r \; \psi_0(\mathbf{r})\psi_0(\mathbf{r} - \mathbf{R}) = \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right)e^{-R/a_0}$$

Moreover, we'll also need

$$v(R) = \int d^3r \; \frac{\psi_0(\mathbf{r})\psi_0(\mathbf{r} - \mathbf{R})}{r} = \frac{1}{a_0}\left(1 + \frac{R}{a_0}\right)e^{-R/a_0}$$

$$w(R) = \int d^3r \; \frac{\psi_0(\mathbf{r})^2}{|\mathbf{r} - \mathbf{R}|} = \frac{1}{R} - \frac{1}{R}\left(1 + \frac{R}{a_0}\right)e^{-2R/a_0}$$

The expected energy in the state $\Psi_\pm(\mathbf{r})$ can be calculated to be

$$\epsilon_\pm(R) = \langle\phi_\pm|H_{\text{el}}|\phi_\pm\rangle = E_0 - 2A_\pm^2\Big(w(R) \pm v(R)\Big)$$

This means that the nuclei experience an effective potential energy given by

$$V_\pm^{\text{eff}}(\mathbf{R}) = \frac{e^2}{4\pi\epsilon_0 R} + \epsilon_\pm(R) = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R} - \frac{w(R) \pm v(R)}{1 \pm u(R)}\right) + E_0$$

This makes sense: as $R \to \infty$, we get $V_{\text{eff}} \to E_0$, which is the energy of a hydrogen atom. Above, we have sketched the effective potential $V_\pm^{\text{eff}} - E_0$ for the two wavefunctions $\phi_\pm$. We see that the state ϕ_+ gives rise to a minimum below zero. This is the indicating the existence of a molecular bound state. In contrast, there is no such bound state for ϕ_-. This difference is primarily due to the fact that ϕ_+ varies more slowly and so costs less kinetic energy.