8.06 Spring 2016 Lecture Notes

1. Approximate methods for time-independent Hamiltonians

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Often we can't solve the Schrödinger equation exactly. This is in fact almost always the case. For example, consider the van der Waals force between two Hydrogen atoms. What happens then? Do we give up?

Of course not! We use *approximate methods.* The guiding philosophy is

- Reduce real system to toy model that can be exactly solved.
- "Solve" actual Schrödinger equation in some (hopefully controlled) approximation.

Our strategy will depend on how our real system is close to our toy system. If the difference is small (meaning not very much energy) we use perturbation theory. If we are dealing with a Hamiltonian changing slowly in time we use the adiabatic approximation and for a Hamiltonian varying slowly in space we use WKB. We can also consider perturbations that are localized in space, which leads to the framework of scattering.

1 Time-independent perturbation theory

1.1 Non-degenerate case

1.1.1 Setup

Suppose

$$H = H_0 + \delta H,$$

where H_0 has a known eigenspectrum

$$H_0|n^0\rangle = E_n^0|n^0\rangle \qquad n = 0, 1, 2, \ldots,$$

and δH is a "small" perturbation. We can make this precise by saying that $\|\delta H\| = O(\lambda)$, and λ is a small dimensionless number (say around 0.01). (Here the norm of a Hermitian matrix is defined to be the largest absolute value of its eigenvalues.) Some examples are:

- Relativistic effects: $\lambda \sim v/c$.
- spin-orbit coupling: $\lambda \sim \alpha \approx 1/137$.
- weak E or B field

We will solve for $|n\rangle$ and E_n order by order in λ; i.e.

$$\begin{aligned} |n\rangle &= |n^0\rangle + |\delta n\rangle = \underbrace{|n^0\rangle}_{O(\lambda^0)} + \underbrace{|n^1\rangle}_{O(\lambda^1)} + \underbrace{|n^2\rangle}_{O(\lambda^2)} + \ldots \\ E_n &= E_n^0 + \delta E_n = \underbrace{E_n^0}_{O(\lambda^0)} + \underbrace{E_n^1}_{O(\lambda^1)} + \underbrace{E_n^2}_{O(\lambda^2)} + \ldots \end{aligned}$$

The definition of $|n^k\rangle$ is the $O(\lambda^k)$ piece of $|n\rangle$. Formally $|n^k\rangle = k!\frac{\partial^k}{\partial\lambda^k}|n\rangle|_{\lambda=0}$ and $E_n^k = k!\frac{\partial^k}{\partial\lambda^k}E_n|_{\lambda=0}$. While we know the energies and eigenstates of H_0, we may not know so much about δH. However, we will need to assume that at least we know its matrix elements in the unperturbed eigenbasis. Denote these by

$$\delta H_{mn} \equiv \langle m^0|\delta H|n^0\rangle.$$

Today we will consider the non-degenerate case; i.e. when $E_m^0 \neq E_n^0$ for $m \neq n$. Next time we will consider the degenerate case. Your antennae should be going up at this: the difference between $E_m^0 \neq E_n^0$ and $E_m^0 = E_n^0$ can be arbitrarily small, so how can they really lead to different physical theories? In fact, we will see that for non-degenerate perturbation theory to make sense, the energy levels need to be not only different, but also far enough apart, in a sense that we will make precise later.

Difference from Griffiths We will work in a basis where $\langle n^0|\delta n\rangle = 0$. Equivalently $\langle n^0|n^k\rangle = 0$ for all $k > 0$. Since $|n^0\rangle$ is normalized, this means that

$$\langle n|n\rangle = \langle n^0|n^0\rangle + \langle\delta n|\delta n\rangle = 1 + \langle\delta n|\delta n\rangle \geq 1.$$

Of course $|n\rangle$ is still a valid eigenvector even it is not a unit vector. But if we want a unit vector, we will need to take

$$|n\rangle_{\text{norm}} = \frac{|n^0\rangle + |\delta n\rangle}{\sqrt{1 + \langle\delta n|\delta n\rangle}}.$$

This convention is used in Sakurai.

As a result of this convention

$$\langle n^0|n\rangle = 1 \tag{1}$$

$$\langle m^0|n\rangle = \langle m^0|\delta n\rangle \qquad \text{for } m \neq n \tag{2}$$

1.1.2 Perturbative solutions

We want to solve the eigenvalue equation

$$H|n\rangle = E_n|n\rangle. \tag{3}$$

Instead of expanding every term, we will make choices that will be justified in hindsight:

$$(H_0 + \delta H)|n\rangle = E_n(|n^0\rangle + |\delta n\rangle) \tag{4}$$

Thus we avoid for now expanding $|n\rangle$ on the LHS and E_n on the RHS. Now left-multiply (4) by $\langle n^0|$ and use $\langle n^0|H_0 = \langle n_0|E_n^0$ and $\langle n^0|n\rangle = 1$ to obtain

$$\langle n_0|\delta H|n\rangle = E_n - E_n^0. \tag{5}$$

What if we instead left-multiply by $\langle m^0|$ for some $m \neq n$? Then we obtain (using $\langle m^0|n^0\rangle = 0$)

$$\langle m^0|\delta H|n\rangle = (E_n - E_m^0)\langle m^0|\delta n\rangle. \tag{6}$$

So far everything is still exact, but further progress will require approximation. We now solve (5) and (6) order by order in λ.

Replacing the $|n\rangle$ in (5) with $|n_0\rangle + O(\lambda)$ we obtain

$$\boxed{E_n = E_n^0 + \langle n^0|\delta H|n^0\rangle + O(\lambda^2)}. \tag{7}$$

This is the *first-order energy shift*. It will soon become an old friend.

Performing the same substitution in a rearranged version of (6) yields

$$\langle m^0|\delta n\rangle = \frac{\langle m^0|\delta H|n\rangle}{E_n - E_m^0} = \frac{\langle m^0|\delta H|n^0\rangle + O(\lambda^2)}{E_n^0 - E_m^0 + O(\lambda)} \tag{8}$$

Repeating for all values of $m \neq n$ (recall that $\langle n^0|\delta n\rangle = 0$ by fiat) we obtain

$$|\delta n\rangle = \sum_{m\neq n} |m^0\rangle \frac{\langle m^0|\delta H|n^0\rangle)}{E_n^0 - E_m^0} + O(\lambda^2) \tag{9}$$

This yields the *first-order shift in the wavefunction*. We need to be a little careful here. Clearly we are using the non-degenerate condition here by assuming that $E_n^0 - E_m^0 \neq 0$ for $n \neq m$. But we have actually used a robust version of this assumption

On to second order!

$$\begin{aligned}
E_n &= E_n^0 + \langle n^0|\delta H|n\rangle && \text{exact} && \text{(10a)}\\
&= E_n^0 + \langle n^0|\delta H|n^0\rangle + \langle n^0|\delta H|\delta n\rangle && \text{still exact} && \text{(10b)}\\
&= E_n^0 + \delta H_{nn} + \langle n^0|\delta H \sum_{m\neq n} |m^0\rangle \frac{\langle m^0|\delta H|n\rangle + O(\lambda^2)}{E_n - E_m^0} && \text{using (9)} && \text{(10c)}\\
&= E_n^0 + \delta H_{nn} + \sum_{m\neq n} \frac{|\delta H_{mn}|^2}{E_n^0 - E_m^0} + O(\lambda^3) && && \text{(10d)}
\end{aligned}$$

We will generally not need the second-order shift in the wavefunction, but it can be computed to be

$$|n^2\rangle = \sum_{k\neq n}\sum_{l\neq n} \frac{|k^0\rangle \delta H_{k,l}\delta H_{l,n}}{(E_n^0 - E_k^0)(E_n^0 - E_l^0)} - \sum_{k\neq n} \frac{|k^0\rangle \delta H_{n,n}\delta H_{k,n}}{(E_n^0 - E_k^0)^2}. \tag{11}$$

For higher-order corrections, Sakurai is the best reference. For 8.06, we will never go beyond second order in energy or first order in wavefunction, although below we will see that (11) is relevant to degenerate perturbation theory.

To summarize, we have

$$\begin{aligned}
E_n^0 &= E_n^0 \\
E_n^1 &= \delta H_{nn} \\
E_n^2 &= \sum_{m\neq n} \frac{|\delta H_{mn}|^2}{E_n^0 - E_m^0} \\
|n^0\rangle &= |n^0\rangle \\
|n^1\rangle &= \sum_{m\neq n} |m^0\rangle \frac{\langle m^0|\delta H|n^0\rangle}{E_n^0 - E_m^0}
\end{aligned}$$

What about normalization? We should multiply by $(1 + \langle \delta n|\delta n\rangle)^{-1/2} = 1 - \frac{1}{2}\langle n^1|n^1\rangle + O(\lambda^4)$ so this affects only $|n^2\rangle$ and not $|n^1\rangle$.

1.1.3 Energy shifts of the ground state

The first-order energy shift can of course be either positive or negative; e.g. suppose $\delta H = \pm\lambda I$. But there is one thing we can always say about it: it always *overstates* the true ground-state energy of the perturbed system. Here is the proof. The first-order estimate of the ground-state energy is

$$E_0^0 + E_0^1 = \langle 0^0|H_0|0^0\rangle + \langle 0^0|\delta H|0^0\rangle = \langle 0^0|H|0^0\rangle \geq \langle 0|H|0\rangle = E_0.$$

The second equality is from the identity $H = H_0 + \delta H$ and the inequality is the variational principle: $\langle\psi|H|\psi\rangle \geq \langle 0|H|0\rangle$ for all unit vectors $|\psi\rangle$.

In this case, we would hope that the second-order term E_0^2 would improve things by being negative. And this is indeed the case.

$$E_0^2 = \sum_{m\neq 0} \frac{|\delta H_{m0}|^2}{E_0^0 - E_m^0}.$$

Every term in the sum is ≤ 0 so we always have $E_0^2 \leq 0$.

More generally at 2nd order we observe "level repulsion." The n'th energy level is pushed up by levels with $m < n$ and pushed down by levels with $m > n$ (assuming that $E_0 < E_1 < \ldots$).

1.1.4 Range of validity and a two-state example

As we go to higher orders of perturbation theory, we multiply by entries of δH (e.g. δH_{mn}) and divide by *differences* of eigenvalues of H_0, e.g. $E_n^0 - E_m^0$. So the perturbation has to be small w.r.t the level spacing. See diagram on blackboard plotting $E(\lambda)$ as a function of λ.

Here's probably the simplest possible example.

$$H = \begin{pmatrix} E_0^0 & \lambda \\ \lambda & E_1^0 \end{pmatrix} = \underbrace{\begin{pmatrix} E_0^0 & 0 \\ 0 & E_1^0 \end{pmatrix}}_{H_0} + \underbrace{\begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix}}_{\delta H}.$$

Let's write $E_0^0, E_1^0 = \bar{E} \pm \Delta$ so that $H_0 = \bar{E} + \Delta\sigma_z$. The first-order shifts are $\delta H_{00} = \delta H_{11} = 0$. The second-order shifts are

$$E_0^2 = \frac{|\delta H_{01}|^2}{E_0^0 - E_1^0} = -\frac{\lambda^2}{2\Delta}$$

$$E_1^2 = \frac{|\delta H_{01}|^2}{E_1^0 - E_0^0} = \frac{\lambda^2}{2\Delta}$$

Of course this problem can be solved directly more easily, as you will explore on your pset. There you will find that the energy levels are (exactly)

$$E_0, E_1 = \bar{E} \pm \sqrt{\lambda^2 + \Delta^2}$$

In the $|\Delta| \gg |\lambda|$ limit this can be written as

$$\bar{E} \pm \Delta\sqrt{1 + \left(\frac{\lambda}{\Delta}\right)^2},$$

while in the $|\lambda| \gg |\Delta|$ limit we can write this as

$$\bar{E} \pm \lambda\sqrt{1 + \left(\frac{\Delta}{\lambda}\right)^2}.$$

The splitting in energy levels is 2Δ for $\lambda = 0$ and then has a $O(\lambda^2)$ term for small λ and finally becomes approximately linear in λ for large λ. This type of behavior is called an "avoided crossing" because of the fact that generically Hamiltonians tend to have non-degenerate eigenvalues. See figure drawn in lecture.

1.1.5 Anharmonic oscillator

$$H = \underbrace{\frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}}_{H_0} + \underbrace{\lambda x^4}_{\delta H}. \tag{12}$$

How does the ground-state energy change? The unperturbed ground-state energy is $E_0^0 = \frac{1}{2}\hbar\omega$. Using $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger)$ we can calculate

$$\begin{aligned} E_0^1 &= \lambda\langle 0| \left(\sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger)\right)^4 |0\rangle \\ &= \lambda\frac{\hbar^2}{4m^2\omega^2} \left|(a + a^\dagger)^2|0\rangle\right|^2 \\ &= \lambda\frac{\hbar^2}{4m^2\omega^2} \left|(a + a^\dagger)|1\rangle\right|^2 \\ &= \lambda\frac{\hbar^2}{4m^2\omega^2} \left||0\rangle + \sqrt{2}|2\rangle\right|^2 \\ &= \frac{3}{4}\lambda\frac{\hbar^2}{m^2\omega^2} \end{aligned}$$

Here is an alternate derivation using integrals. This one is hairier, so let's set $\hbar = m = \omega = 1$. We will use $\langle x|0\rangle = Ne^{-x^2/2}$, for some normalization N. Then we can compute

$$E_0^1 = \lambda\langle 0|x^4|0\rangle = \lambda\frac{\int_{-\infty}^{\infty} dx e^{-x^2} x^4}{\int_{-\infty}^{\infty} dx e^{-x^2}}.$$

Here our job becomes easier if we introduce a parameter.

$$\begin{aligned}
\int dx\, e^{-ax^2} &= \sqrt{\frac{\pi}{a}} \\
\frac{d}{da}\int dx\, e^{-ax^2} &= \int dx\,(-x^2)e^{-ax^2} = -\frac{1}{2}\frac{\sqrt{\pi}}{a^{3/2}} \\
\frac{d^2}{da^2}\int dx\, e^{-ax^2} &= \int dx\, x^4 e^{-ax^2} = \left(-\frac{1}{2}\right)\left(-\frac{3}{2}\right)\frac{\sqrt{\pi}}{a^{5/2}}
\end{aligned}$$

Thus $\langle x^4\rangle = 3/4$.

Moral of the story: Gaussian integrals involve some beautiful tricks that you should learn. But raising and lowering operators are easier.

1.2 Degenerate perturbation theory

1.2.1 Overview

The first-order corrections to the wavefunction and the second-order corrections to the energy all have factors of $E_n^0 - E_m^0$ in the denominator. So when two energy levels become equal, these give nonsense answers. But in fact, even the first-order energy shift will be wrong in this case. Let us revisit the case of two-level systems. Suppose that $E_0^0 = E_1^1$. For simplicity, assume $E_0^0 = E_1^1 = 0$ so the overall Hamiltonian is

$$H = \delta H = \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix}.$$

The eigenvalues are $\pm\lambda$, which is first order in δH. But the diagonal elements of δH are zero, so (7) would say that the first-order energy shifts are zero. To summarize, the first-order energy shift is wrong, and the second-order energy shift and first-order wavefunction shift are infinite. The situation looks grim.

There is one point in the above paragraph where I pulled a fast one. The reference to "diagonal elements" refers to the eigenbasis of H_0. In the above example, this is labeled $|0^0\rangle$ and $|1^0\rangle$, which we took to be $|\uparrow\rangle$ and $|\downarrow\rangle$ respectively. But since H_0 has degenerate eigenvalues, the corresponding eigenvectors are not unique. We can make a unitary change of basis within the degenerate eigenspace and obtain new eigenvectors. In that example, we could take

$$|0^0\rangle = \frac{|\uparrow\rangle - |\downarrow\rangle}{\sqrt{2}} \qquad \text{and} \qquad |1^0\rangle = \frac{|\uparrow\rangle + |\downarrow\rangle}{\sqrt{2}}$$

so that the matrix for δH would be diagonal in the $\{|0^0\rangle, |1^0\rangle\}$ basis. In this case the first-order energy shift is exactly correct and the second-order energy shift is zero.

General rule for degeneracy in H_0. For a general Hamiltonian where H_0 has degenerate eigenvalues, the strategy is:

1. Choose an eigenbasis $\{|n^0\rangle\}$ for H_0 where $\delta H_{mn} = 0$ for each $m \neq n$ with $E^0_m = E^0_n$. This is called a "good basis."
2. Apply non-degenerate perturbation theory to handle the remaining off-diagonal terms in δH (which now will only be nonzero when $E^0_m \neq E^0_n$).

Why is this possible? By the spectral theorem, we can write H_0 as

$$H_0 = \sum_i E^0_i \Pi_i, \tag{13}$$

where Π_i is a projection operator supported on the space of E^0_i-eigenvectors. Call this space V_i. We will think of H_0 as block diagonal with blocks corresponding to the subspaces $V_1, V_2, \ldots$.

We can write $\delta H = \sum_{i,j} \Pi_i \delta H \Pi_j$. The diagonal blocks are the components of the form $\Pi_i \delta H \Pi_i$. These are the blocks we would like to diagonalize. Since each $\Pi_i \delta H \Pi_i$ is a Hermitian matrix we can write

$$\Pi_i \, \delta H \, \Pi_i = \sum_{a=1}^{\dim V_i} \Delta_{i,a} |i,a\rangle\langle i,a| \tag{14}$$

where $\Delta_{i,a}$ are the eigenvalues of $\Pi_i \delta H \Pi_i$ (when considered an operator on V_i) and $\{|i,a\rangle\}_{a=1,\ldots,\dim V_i}$ forms an orthonormal basis for V_i. Since each $|i,a\rangle \in V_i$, we also have $H_0|i,a\rangle = E^0_i|i,a\rangle$. Now the first-order energy shifts are given by the $\Delta_{i,a}$ and the second-order energy shifts and first-order wavefunction corrections involve off-diagonal elements of δH between eigenvectors of H_0 with different eigenvalues. *If* this fully breaks the degeneracy of H_0, then we can follow the lines of the non-degenerate case. We first introduce a little more notation: let n stand for the pair (i,a), denote $|n\rangle^{\text{rotated}} = |i,a\rangle$ and let $\delta H^{\text{rotated}}$ denote δH in the $\{|n\rangle^{\text{rotated}}\}$ basis.

$$E_n = E^0_n + \delta H^{\text{rotated}}_{nn} + \sum_{m: E^0_m \neq E^0_n} \frac{|\delta H^{\text{rotated}}_{mn}|^2}{E^0_n - E^0_m} + O(\lambda^3) \tag{15}$$

The above equations work in many cases, including all the examples on problems sets or exams that you will encounter. However, it may be that the diagonal elements of δH do not fully break the degeneracy. In this case, higher-order corrections may encounter new degeneracies which may require new changes of basis[1]. In the next section we will describe systematically what to do in this case.

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[1] Here is an example. Take $\lambda \ll \Delta$ and let

$$H = \begin{pmatrix} 0 & 0 & \lambda \\ 0 & 0 & \lambda \\ \lambda & \lambda & \Delta \end{pmatrix}.$$

Graphically, H_0 might look something like

$$H_0 = \left(\begin{array}{cc|ccc|c} E_1^0 & & & & & \\ & E_1^0 & & & & \\ \hline & & E_2^0 & & & \\ & & & E_2^0 & & \\ & & & & E_2^0 & \\ \hline & & & & & E_3^0 \end{array}\right) \tag{16}$$

We can write δH in this basis and generically it could have every matrix element nonzero, e.g.

$$\delta H = \left(\begin{array}{cc|ccc|c} * & * & * & * & * & * \\ * & * & * & * & * & * \\ \hline * & * & * & * & * & * \\ * & * & * & * & * & * \\ * & * & * & * & * & * \\ \hline * & * & * & * & * & * \end{array}\right) \tag{17}$$

By choosing a new basis for each block, H_0 stays the same and δH takes on the form

$$\delta H^{\text{rotated}} = \left(\begin{array}{cc|ccc|c} * & 0 & * & * & * & * \\ 0 & * & * & * & * & * \\ \hline * & * & * & 0 & 0 & * \\ * & * & 0 & * & 0 & * \\ * & * & 0 & 0 & * & * \\ \hline * & * & * & * & * & * \end{array}\right) \tag{18}$$

There are still off-diagonal terms but only between different eigenvalues of H_0.

Why is it reasonable to ask that we find a new basis in this way? After all, the whole point of perturbation theory was that it was too hard to diagonalize $H_0 + \delta H$. However, now we only need to diagonalize δH *in each block* of degenerate eigenvalues. Typically these will be much lower dimension than the overall space.

1.2.2 First-order wavefunction correction - degenerate case

Note: This section is included for completeness, but contains material that goes beyond lecture and will not appear on any problem sets or exams.

What about the perturbed wavefunction $|n\rangle$? The zeroth order wavefunction should be $|n^0\rangle^{\text{rotated}}$. It is tempting to state that the first-order correction to $|n\rangle = |i, a\rangle$ is

$$|n^1\rangle \overset{?}{=} \sum_{m:E_m^0 \neq E_n^0} |m^0\rangle^{\text{rotated}} \frac{\delta H_{mn}^{\text{rotated}}}{E_n^0 - E_m^0} = \sum_{j \neq i} \sum_{b=1}^{\dim V_j} |j, b\rangle^{\text{rotated}} \frac{\delta H_{jb,ia}^{\text{rotated}}}{E_i^0 - E_j^0} \tag{19}$$

but this is only part of the story (the $\overset{?}{=}$ is a warning that this equation is not quite correct). (19) does indeed describe the contribution to $|i,a\rangle$ from states $|j,a^0\rangle^{\text{rotated}}$ with $i \neq j$, but there are also contributions within the same block, i.e. from states with $j = i$. This can be thought of as representing the need to *further rotate* our rotated basis to account for degeneracies that arise at higher order in perturbation theory.

Another way to think about that is that if we go to second order in perturbation theory, we get the contribution (following (11)):

$$|n^2\rangle \overset{?}{=} |i,a^2\rangle \overset{?}{=} \sum_{(j,b)\neq(i,a)} \sum_{(k,c)\neq(i,a)} \frac{|j,b\rangle^{\text{rotated}} \delta H^{\text{rot}}_{jb,kc} \delta H^{\text{rot}}_{kc,ia}}{(E_{ia}-E_{jb})(E_{ia}-E_{kc})} - \sum_{(j,b)\neq(i,a)} \frac{|j,b\rangle^{\text{rotated}} \delta H^{\text{rot}}_{ia,ia} \delta H^{\text{rot}}_{jb,ia}}{(E_{ia}-E_{jb})^2} \tag{20}$$

Is this really a second-order (i.e. $O(\lambda^2)$) correction? First look at the second term. Because we have rotated into a block-diagonal basis $\delta H_{jb,ia}$ is zero unless $i \neq j$. Thus the denominator is $O(1)$ and the numerator is $O(\lambda^2)$, and the second term gives a $O(\lambda^2)$ correction. What about the first term? Now the block-diagonal constraint means that only the $i \neq k \neq j$ terms survive, and again the numerator is $O(\lambda^2)$. However, it is legal to have $i = j$ (as long as $a \neq b$. In this case, the energy splitting between i,a and i,b is $O(\lambda)$. Thus, this term contributes $O(\frac{\lambda^2}{\lambda}) = O(\lambda)$. In other words, it is a first-order contribution, despite appearing in the expansions of the second-order term. (For similar reasons, (20) gives only part of the true second-order contribution, for which we need to go to third order.) We conclude that the true first-order correction to the wavefunction is

$$|i,a^1\rangle = \sum_{j\neq i} \sum_{b=1}^{\dim V_j} |j,b\rangle^{\text{rotated}} \frac{\delta H^{\text{rotated}}_{jb,ia}}{E^0_i - E^0_j} + \sum_{b\neq a} \sum_{j\neq i} \sum_{c=1}^{\dim V_j} \frac{|i,b\rangle^{\text{rotated}} \delta H^{\text{rot}}_{ib,jc} \delta H^{\text{rot}}_{jc,ia}}{(\delta H^{\text{rot}}_{ia} - \delta H^0_{ib})(E^0_i - E^0_j)} \tag{21}$$

1.2.3 Hydrogen preview

An important application of degenerate perturbation theory is to the spectrum of hydrogen. Here

$$H_0 = \frac{p^2}{2m_e} - \frac{e^2}{r}.$$

The eigenbasis can be taken to be $|n,l,m,m_s\rangle$ where n is the principle quantum number, l denote total orbital angular momentum, m its z-component and m_s the z-component of the electron spin. Another valid basis is $|n,l,j,m_j\rangle$ where j denotes the total overall angular momentum (i.e. corresponding to the operator $\vec{J}^2$ where $\vec{J} = \vec{L} + \vec{S}$) and m_j its z component.

In both cases, the eigenvalues of H_0 depend only on n and all the other degrees of freedom are degenerate. Indeed

$$E^0_{nlmm_s} = -\frac{1}{n^2}\frac{m_e e^4}{2\hbar^2} \approx -\frac{13.6\text{eV}}{n^2}.$$

Next week we will discuss a number of corrections to this that are smaller by factors of either $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$ (the fine structure constant) or $\frac{m_e}{m_p} \approx \frac{1}{1800}$. (Indeed even $\frac{m_e e^2}{\hbar^2}$ can be written as $m_e c^2 \alpha^2$, where $m_e c^2$ is the energy scale from the energy from the rest mass of the electron. And this of course is smaller by a factor of roughly $\frac{m_e}{m_p}$ than the mass of the entire atom. We ignore these larger energies in what follows because they are not relevant to experiments in which the electron or proton are not created or destroyed.) The contributions to the energy of hydrogen are summarized as follows.

We mention here also the "spectroscopic notation" convention, which is used for the coupled basis. The state $|n,l,j,m_j\rangle$ is written as nL_j where "L" is a letter that expresses the orbital angular momentum according to the rule:

what	where discussed	magnitude
0th order	8.04/8.05	$E_n^0 \sim \frac{m_e e^4}{\hbar^2} \sim m_e c^2 \alpha^2$
fine structure	8.05	$E_{\text{fs}} \sim m_e c^2 \alpha^4$
Lamb shift	QFT	$E_{\text{Lamb}} \sim m_e c^2 \alpha^5$
hyperfine structure	8.05	$E_{\text{hf}} \sim m_e c^2 \alpha^4 \frac{m_e}{m_p}$
proton radius	pset	$\sim m_e c^2 \alpha^3 \left(\frac{m_e}{m_p}\right)^2$
Zeeman effect	Griffiths	depends on $\vec{B}$ field
Stark effect	pset	depends on $\vec{E}$ field

Table 1: Contributions to the hydrogen energy levels.

$L =$	S	P	D	F	G	...
$l =$	0	1	2	3	4	...

Some examples are

nL_j	n	l	j
$1S_{1/2}$	1	0	1/2
$2S_{1/2}$	2	0	1/2
$2P_{1/2}$	2	1	1/2
$2P_{3/2}$	2	1	3/2

1.2.4 Two-spin example

Let's see how these ideas work with a simple example. Consider two spin-1/2 particles with Hamiltonian

$$H_0 = \frac{E_0}{\hbar^2} \vec{S}_1 \cdot \vec{S}_2 = \frac{E_0}{\hbar^2} (S_x \otimes S_x + S_y \otimes S_y + S_z \otimes S_z).$$

To diagonalize this, define $\vec{J} = \vec{S}_1 + \vec{S}_2$ and observe that $\vec{J}^2 = \vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1 \cdot \vec{S}_2$. Thus

$$H_0 = \frac{E_0}{\hbar^2} \frac{\vec{J}^2 - \vec{S}_1^2 - \vec{S}_2^2}{2} = E_0 \left(\frac{\vec{J}^2}{2\hbar^2} - \frac{3}{4} \right).$$

The eigenvalues of $\vec{J}^2$ are 0 (degeneracy 1) and $2\hbar^2$ (degeneracy 3); these correspond to total spin 0 and 1 respectively. Thus spectrum of H_0 is $-\frac{3}{4}E_0$ (with degeneracy 1) and $\frac{1}{4}E_0$ (with degeneracy 3).

Case 1 Now suppose we add a perturbation

$$\delta H = \frac{\Delta}{\hbar}(S_{z,1} + S_{z,2}) = \frac{\Delta}{\hbar} J_z.$$

(This might arise from applying a magnetic field in the $\hat{z}$ direction.) We need to choose a good basis. Fortunately, δH and H_0 commute and the coupled basis $|j, m\rangle$ (with $j = 0, 1$ and $-j \leq m \leq j$) works. In this basis we have

$$\begin{aligned} H_0|j,m\rangle &= E_0 \left(\frac{j(j+1)}{2} - \frac{3}{4} \right) |j,m\rangle \\ \delta H|j,m\rangle &= \Delta m |j,m\rangle \end{aligned}$$

[Draw energy level diagram of this.]

This was too easy! When everything commutes, this is what it looks like. Of course, we could have chosen a more foolish eigenbasis of H_0. Any eigenbasis would to include the singlet $|0,0\rangle = \frac{|+\rangle\otimes|-\rangle - |-\rangle\otimes|+\rangle}{\sqrt{2}}$, but it could be completed with any additional three orthonormal states in the triple space. If we chose these to be anything other than $|1,1\rangle, |1,0\rangle, |1,-1\rangle$, then even first-order perturbation theory would give the wrong answer. (Working this out is an exercise left to the reader.)

Case 2 Let us try a slightly more interesting perturbation.

$$\delta H = \frac{\Delta}{\hbar}(S_{z,1} - S_{z,2}).$$

This could arise from applying a magnetic field to positronium. We calculate its matrix elements in the coupled basis as follows:

$$\begin{aligned} \delta H|1,1\rangle &= \delta H|+\rangle \otimes |+\rangle = 0 \\ \delta H|1,-1\rangle &= \delta H|-\rangle \otimes |-\rangle = 0 \\ \delta H|1,0\rangle &= \delta H \frac{|+\rangle \otimes |-\rangle + |-\rangle \otimes |+\rangle}{\sqrt{2}} = \Delta \frac{|+\rangle \otimes |-\rangle - |-\rangle \otimes |+\rangle}{\sqrt{2}} = \Delta|0,0\rangle \end{aligned}$$

Since δH is Hermitian we know also that $\delta H|0,0\rangle = \Delta|1,0\rangle$.

Thus, in the coupled basis we have

$$H_0 = \begin{array}{c} \\ 1,1 \\ 1,0 \\ 1,-1 \\ 0,0 \end{array} \!\!\begin{array}{c} \begin{array}{cccc} 1,1 & 1,0 & 1,-1 & 0,0 \end{array} \\ \begin{pmatrix} \frac{E_0}{4} & 0 & 0 & 0 \\ 0 & \frac{E_0}{4} & 0 & 0 \\ 0 & 0 & \frac{E_0}{4} & 0 \\ 0 & 0 & 0 & \frac{-3}{4}E_0 \end{pmatrix} \end{array} \quad \text{and} \quad \delta H = \begin{array}{c} \\ 1,1 \\ 1,0 \\ 1,-1 \\ 0,0 \end{array} \!\!\begin{array}{c} \begin{array}{cccc} 1,1 & 1,0 & 1,-1 & 0,0 \end{array} \\ \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \Delta \\ 0 & 0 & 0 & 0 \\ 0 & \Delta & 0 & 0 \end{pmatrix} \end{array} \tag{22}$$

First-order perturbation theory (correctly) gives us zero energy shift to first order in Δ. The second-order shifts are

$$\begin{aligned} E^2_{(1,0)} &= \frac{|\delta H_{(1,0),(0,0)}|^2}{E^0_{(1,0)} - E^0_{(0,0)}} = \frac{\Delta^2}{E_0} \\ E^2_{(0,0)} &= \frac{|\delta H_{(0,0),(1,0)}|^2}{E^0_{(0,0)} - E^0_{(1,0)}} = \frac{\Delta^2}{-E_0}, \end{aligned}$$

where we have used the fact that $E_0 = E^0_{j=1} - E^0_{j=0}$.

2 The Hydrogen spectrum

See Section 1.2.3 for an overview.

2.1 Fine structure

The term "fine structure" refers to three different contributions to the energy that are $O(m_e c^2 \alpha^4)$, compared with the $O(m_e c^2 \alpha^2)$ zeroth order contribution: relativistic corrections, spin-orbit coupling and the Darwin term. The contributions all arise from the Dirac equation for a particle with charge q and mass m:

$$H_{\text{Dirac}} = c\vec{\alpha} \cdot (\vec{p} - \frac{q}{c}\vec{A}) + \beta mc^2 + q\phi,$$

where $\vec{A}, \phi$ are the vector and scalar potentials of the EM field, and $\vec{\alpha}$ and β are given by

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} = \sigma_x \otimes \vec{\sigma} \qquad \text{and} \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} = \sigma_z \otimes I.$$

The Hilbert space here is the space of well-behaved functions from $\mathbb{R}^3 \to \mathbb{C}$ as well as a four-dimensional discrete space. Why four dimensions? Two are to account for spin, and another two are to allow a particle to be either an electron or positron. While the Dirac equation was originally motivated by the need to properly account for the fine structure of hydrogen and to unify quantum mechanics with special relativity, it as a bonus generated the prediction of antimatter.

We will not further explore the Dirac equation in 8.06, but at this point we should observe its symmetry under *collective* rotation. That is, if R is a 3×3 rotation matrix and we replace $(\sigma_1, \sigma_2, \sigma_3)$ with $(\sum_i R_{i1}\sigma_i, \sum_i R_{i2}\sigma_i, \sum_i R_{i3}\sigma_i)$ and (p_1, p_2, p_3) with $(\sum_i R_{i1}p_i, \sum_i R_{i2}p_i, \sum_i R_{i3}p_i)$ (and similarly transform $\vec{A}, \phi$) , then H^{Dirac} is unchanged.

This means that H^{Dirac} commutes with the collective rotation operators $\vec{J} = \vec{L} + \vec{S}$, although not necessarily the individual rotations $\vec{L}$ and $\vec{S}$. As a result, a good basis for the Dirac-equation version of hydrogen is likely to be $|n, l, j, m_j\rangle$ (since the Hamiltonian should be block-diagonal in n, j and independent of m_j) instead of the alternative $|n, l, m_l, m_s\rangle$. After much calculation we will see this fact confirmed.

2.1.1 Relativistic correction

Let's first do some back-of-the-envelope estimates of how important relativity is to the hydrogen atom. The unperturbed ground-state wavefunction is

$$\psi_{100}(\vec{r}) = \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}}, \qquad a_0 = \frac{\hbar^2}{me^2} = \frac{1}{\alpha}\frac{\hbar}{mc}.$$

We can then estimate

$$\begin{aligned} p &\approx \frac{\hbar}{a_0} = \alpha mc \\ v &\approx \frac{p}{m} = \alpha c \end{aligned}$$

Thus the electron velocity is ≈ 1/137 the speed of light. This is non-relativistic, but still fast enough that relativistic corrections will be non-negligible. Let's compute them!

$$
\begin{aligned}
\text{KE} &= \sqrt{m^2c^4 + \vec{p}^2c^2} - mc^2 \\
&= \underbrace{\frac{\vec{p}^2}{2m}}_{\text{usual term}} \underbrace{-\frac{\vec{p}^4}{8m^3c^2}}_{\delta H_{\text{rel}}}
\end{aligned}
$$

The first-order contribution to the energy is

$$
\begin{aligned}
E^1_{nlj} &= \langle n,l,j|\delta H_{\text{rel}}|n,l,j\rangle \qquad\qquad \text{independent of } m_j \\
&= \langle n,l,j| - \frac{\vec{p}^4}{8m^3c^2}|n,l,j\rangle \\
&= \text{calculation omitted, see textbooks} \\
&= -\frac{\alpha^4 mc^2}{8n^4}\left(\frac{4n}{l+\frac{1}{2}} - 3\right)
\end{aligned}
$$

One key feature of this calculation is that the answer indeed scales as $\alpha^4 mc^2$ (since $\frac{p^4}{m^3c^2} \sim \frac{(\alpha mc)^4}{m^3c^2} = \alpha^4 mc^2$) which is smaller than E^0_n by a factor of α^2. Also note that the answer depends on l but not j. This is not surprising since spin never appeared. But it is inconsistent with the prediction from the Dirac equation that the energy should depend instead on j. To get there we will need to consider additional terms.

2.1.2 Spin-orbit coupling

See Lecture 23 of the 2015 8.05 notes (or Griffiths) for more detail. The general formula for the energy of a dipole in a magnetic field is $\delta H = -\vec{\mu}\cdot\vec{B}$. For an electron, the dipole moment is

$$
\vec{\mu}_e = -\underbrace{\mu_B}_{\frac{e\hbar}{2mc}}\underbrace{g_e}_{2}\frac{\vec{S}}{\hbar} = -\frac{e}{mc}\vec{S}.
$$

Compute the $\vec{B}$ field from the proton in the rest frame of the electron, which see the proton orbiting it. If $\vec{r}$ is the vector pointing from the proton to the electron, then the magnetic field strength is

$$
\vec{B} = -\frac{\vec{v}}{c}\times\frac{e\vec{r}}{r^3} = \frac{e}{c}\frac{\vec{v}\times\vec{r}}{r^3} = \frac{e}{mc}\frac{\vec{L}}{r^3}
$$

(In both cases, the "mass" is technically the reduced mass $\frac{m_e+m_p}{m_e m_p}$ which we can approximate with $m \approx m_e$.) Putting this together we get a semi-classical estimate of δH:

$$
\delta H^{\text{semi-classical}} = \frac{e^2}{m^2c^2r^3}\vec{S}\cdot\vec{L}.
$$

This is close, but not quite, the true answer that can be obtained from the Dirac equation, which is exactly half the semi-classical estimate.

$$
\delta H^{\text{Dirac}} = \frac{e^2}{2m^2c^2r^3}\vec{S}\cdot\vec{L}.
$$

Now we compute the first-order correction to the energies. We will use the facts that

$$
\langle nlj|\vec{S}\cdot\vec{L}|nlj\rangle = \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - \frac{3}{4}\right) \tag{23a}
$$

$$
\langle nlj|\frac{1}{r^3}|nlj\rangle = \frac{1}{n^3 l(l+\frac{1}{2})(l+1)a_0^3} \qquad \text{(see Griffiths problem 6.35(c))} \tag{23b}
$$

Now we can calculate:

$$\begin{aligned}
E^1_{nlj,\mathrm{SO}} &= \frac{e^2}{2m^2c^2}\langle nlj|\frac{\vec{S}\cdot\vec{L}}{r^3}|nlj\rangle \\
&= \frac{\alpha^4 mc^2}{4n^4}\left(\frac{n(j(j+1)-l(l+1)-\frac{3}{4})}{l(l+\frac{1}{2})(l+1)}\right)
\end{aligned}$$

While the exact form of this equation is a bit hairy, we can see that its order of magnitude is $\sim \alpha^4 mc^2$, which is comparable to the relativistic correction. Also note that now there is a j and l dependence, because spin is part of the picture as well.

2.1.3 Fine structure

Combining the relativistic and spin-orbit coupling leads to a miraculous cancelation

$$E^1_{nlj,\mathrm{FS}} = E^1_{nlj,\mathrm{rel}} + E^1_{nlj,\mathrm{SO}} = \frac{\alpha^4 mc^2}{8n^4}\left(3 - \frac{4n}{j+\frac{1}{2}}\right). \tag{24}$$

This derivation used the fact that $j = l \pm 1/2$ and can be proved to hold separately for each case $j = l+1/2$ and $j = l-1/2$. An additional complication is that the above formulas for the relativistic and spin-orbit corrections were not quite right when $l = 0$ (e.g. the spin-orbit coupling should really be zero then, and p^4 is not a Hermitian operator for $l = 0$); additionally, there is a *third* correction of order $\alpha^4 mc^2$ called the *Darwin shift*, due to the fact that the electron is delocalized across a distance given by its Compton wavelength (which is $\sim \alpha a_0$). However, this term affects only the $l = 0$ term and, together with the correct $l = 0$ versions of the spin-orbit and relativistic couplings, ends up giving precisely the formula in (24).

To summarize, while the previous calculations had limited validity, (24) is exactly correct for all values of n and j. It can also be derived directly from the Dirac equation. We reassuringly find that it depends only on n and j and not on other quantum numbers.

Draw a diagram showing the $n = 2$ states of hydrogen. The zeroth order energy is $-\frac{\alpha^2 mc^2}{8}$. The fine structure then contributes energy $-5\frac{\alpha^4 mc^2}{8}$ to the $2S_{1/2}$ and $2P_{1/2}$ states and energy $-\frac{\alpha^4 mc^2}{8}$ to the $2P_{3/2}$ states. Are the $2S_{1/2}$ and $2P_{1/2}$ states degenerate? It turns out that the *Lamb shift* leads to a further splitting of these two levels, of order $\alpha^3 \ln(1/\alpha) 5mc^2$. The Lamb shift comes from the interaction of the electron with the electromagnetic field (since even a harmonic oscillator in the ground state has nonzero expectation value for observables like $\hat{x}^2$) and a precise derivation of the Lamb shift requires QED.

2.2 Hyperfine splitting

This was covered in 8.05, but I want to review the derivation and briefly justify one point that we previously did not have the tools for.

The electron and proton are both magnetic dipoles and thus contribute to the Hamiltonian a term

$$\delta H_{\mathrm{HF}} = -\vec{\mu}_e \cdot \vec{B}_{\text{proton dipole}},$$

where the $\vec{B}$ field coming from the dipole moment of the proton is

$$\vec{B}_{\text{proton dipole}} = \frac{1}{r^3}\left(3(\vec{\mu}_p\cdot\hat{r})\hat{r} - \vec{\mu}_p\right) + \frac{8\pi}{3}\vec{\mu}_p\delta^{(3)}(\vec{r}). \tag{25}$$

The first term has the property that $\langle\psi|\text{first term}|\psi\rangle = 0$ if $|\psi\rangle$ is an $l = 0$ state (because the rotational invariance of $|\psi\rangle$ means we can replace $\hat{r}_i\hat{r}_j$ with its average over rotations, which is $\frac{1}{3}\delta_{ij}$). This was discussed in 8.05, but now first-order perturbation theory lets us rigorously justify that this means that the first term contributes zero to the energy of $l = 0$ states at first order in perturbation theory.

The second term is called the "contact term" because of the presence of the delta function. Again we can use perturbation theory to obtain that the first-order correction to the wavefunction $|\psi_{\text{spatial}}\rangle \otimes |\psi_{\text{spin}}\rangle$ is

$$\begin{aligned} E^1_{\text{HF}} &= -\langle\psi_{\text{spatial}}| \otimes \langle\psi_{\text{spin}}| \left(\frac{8\pi}{3}\vec{\mu}_e \cdot \vec{\mu}_p \delta^{(3)}(\vec{r})\right) |\psi_{\text{spatial}}\rangle \otimes |\psi_{\text{spin}}\rangle \\ &= \frac{g_e g_p}{m_e m_p}\frac{2\pi e^2}{3c^2}\langle\psi_{\text{spin}}|\vec{S}_e \cdot \vec{S}_p|\psi_{\text{spin}}\rangle\langle\psi_{\text{spatial}}|\delta^{(3)}(\vec{r})|\psi_{\text{spatial}}\rangle \end{aligned}$$

We now should pause to consider good bases. In fact, treating the spatial and spin wavefunctions as a tensor product was already an assumption that cannot always be justified, since the fine structure wants a basis where j (involving both spatial and electron-spin degrees of freedom) is well-defined. However for the $n = 1$ state of hydrogen, we always have $l = 0$ and $j = 1/2$. Thus $|\psi_{\text{spatial}}\rangle = |1, 0, 0\rangle$ and we obtain a factor of $\frac{1}{\pi a_0^3}$ from the $\langle\psi_{\text{spatial}}|\delta^{(3)}(\vec{r})|\psi_{\text{spatial}}\rangle$ term.

For the electron and nuclear spins, we have so far a degenerate Hamiltonian. Thus we will choose a basis for the spin space that diagonalizes the hyperfine splitting. The eigenvalues of $\vec{S}_e \cdot \vec{S}_p$ are $\frac{\hbar^2}{4}$ with degeneracy 3 (the triplet states) and $-\frac{3}{4}\hbar^2$ (the singlet state). Thus we find that the hyperfine splitting is

$$\begin{aligned} \Delta E^{\text{HF}}_{1,0,0} &= E^1_{1,0,0,\text{triplet}} - E^1_{1,0,0,\text{singlet}} \\ &= \frac{2}{3}g_e g_p \frac{m_e}{m_p}\alpha^4 m_e c^2 = 5.9 \cdot 10^{-6}\text{eV} \end{aligned}$$

The wavelength $\lambda = \frac{hc}{\Delta E}$ is 21cm, and radiation at this wavelength plays a central role in radio astronomy.

2.3 Zeeman effect

We have so far considered internal magnetic fields, but what happens when we apply an *external* magnetic field? Then the contribution to energy from the interaction of this field with the electron orbital angular momentum and spin angular momentum is

$$\begin{aligned} \delta H_{\text{Zeeman}} &= -(\underbrace{\vec{\mu}_L}_{-\mu_B\frac{\vec{L}}{\hbar}} + \underbrace{\vec{\mu}_S}_{-2\mu_B\frac{\vec{S}}{\hbar}}) \cdot \underbrace{\vec{B}_{\text{ext}}}_{(0,0,B)} \\ &= \frac{\mu_B B}{\hbar}(L_z + 2S_z) \\ &= \frac{eB}{2mc}(L_z + 2S_z) \qquad\qquad \text{using } \mu_B = \frac{\hbar e}{2mc} \end{aligned}$$

Because $\vec{L}$ and $\vec{S}$ are multiplied by different g-factors (1 and ≈ 2 respectively), we do *not* simply end up with something that depends on $\vec{J}$. As a result, the states $|n, l, j, m_j\rangle$ that were good for the fine structure do not diagonalize δH_{Zeeman}. One basis that would diagonalize the Zeeman Hamiltonian is $|n, l, m_l, m_s\rangle$. However, if we use this, then the fine structure is no longer diagonal! This is a fundamental problem: δH_{FS} and δH_{Zeeman} do not commute, and thus there is no basis that simultaneously diagonalizes them.

To solve this problem we will use perturbation theory. But which Hamiltonian is the base Hamiltonian and which is the perturbation will depend on how strong the magnetic field is.

2.3.1 Strong-field Zeeman

If $E_{\text{Zeeman}} \gg E_{\text{FS}}$ then we treat $H_0 + \delta H_{\text{Zeeman}}$ as the base Hamiltonian, use the $|n, l, m_l, m_s\rangle$ basis and treat δH_{FS} as the perturbation. In this case the energy is

$$E_{n,l,m_l,m_s} = \underbrace{E_n^0}_{-\frac{\alpha^2 m_e c^2}{2n^2}} + \mu_B B(m_l + 2m_S) + E_{\text{FS}}^1 + \dots \tag{26}$$

To compute the fine-structure contribution we need to evaluate things like $\langle \vec{L} \cdot \vec{S} \rangle$ and $\langle p^4 \rangle$ with respect to the states $|n, l, m_l, m_s\rangle$. We will not fully carry out this calculation. One example is the spin-orbit coupling which is proportional to

$$\langle \vec{L} \cdot \vec{S} \rangle = \langle L_x \rangle \langle S_x \rangle + \langle L_y \rangle \langle S_y \rangle + \langle L_z \rangle \langle S_z \rangle = \langle L_z \rangle \langle S_z \rangle = \hbar^2 m_l m_s.$$

Here we have used the fact that if a state $|\psi\rangle$ satisfies $J_z|\psi\rangle = \lambda|\psi\rangle$ (for any operators J_x, J_y, J_z with the appropriate commutation relations for angular momentum) then

$$\langle \psi | J_x | \psi \rangle = \langle \psi | \frac{J_y J_z - J_z J_y}{i\hbar} | \psi \rangle = \langle \psi | \frac{J_y \lambda - \lambda J_y}{i\hbar} | \psi \rangle = 0$$

and similarly $\langle \psi | J_x | \psi \rangle = 0$.

After some (omitted) calculations we arrive at

$$E_{n,l,m_l,m_s}^{\text{FS}} = \begin{cases} \frac{\alpha^4 m_e c^2}{2n^3} \left(\frac{3}{4n} - 1 \right) & \text{if } l = 0 \\ \frac{\alpha^4 m_e c^2}{2n^3} \left(\frac{3}{4n} - \frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right) & \text{otherwise} \end{cases} \tag{27}$$

The field strength needed for this is not unreasonable. Since the fine-structure splitting between $j = 1/2$ and $j = 3/2$ is $5.7 \cdot 10^{-5}$eV and $\mu_B = 5.8 \cdot 10^{-5}$eV/T, we need a field of about one Tesla, which is large but achievable. This strong-field case is sometimes called the Paschen-Back effect.

2.3.2 Weak-field Zeeman effect

Now we write

$$H = \underbrace{H_0 + \delta H_{\text{FS}}}_{H_0^{\text{Zee}}} + \delta H_{\text{Zee}}. \tag{28}$$

As we've seen before, the eigenbasis of H_0^{Zee} is $|n, l, j, m_j\rangle$, so the first-order energy shift when we add a magnetic field is

$$\begin{aligned} E_{n,l,j,m_j}^{\text{Zee}} &= \frac{\mu_B B}{\hbar} \langle n, l, j, m_j | L_z + 2S_z | n, l, j, m_j \rangle \\ &= \frac{\mu_B B}{\hbar} \langle n, l, j, m_j | J_z + S_z | n, l, j, m_j \rangle \\ &= \mu_B B m_j + \frac{\mu_B B}{\hbar} \langle n, l, j, m_j | S_z | n, l, j, m_j \rangle \end{aligned}$$

How do we evaluate this $\vec{S}_z$ term? One method is described in Griffiths, and involves an argument about the Heisenberg-picture time average of $\vec{S}$ under the fine-structure Hamiltonian. A more direct method is to use Clebsch-Gordan coefficients. Indeed

$$|j = l \pm \frac{1}{2}, m_j\rangle = \pm\sqrt{\frac{l \pm m_j + \frac{1}{2}}{2l+1}}|m_l = m_j - \frac{1}{2}, m_s = \frac{1}{2}\rangle + \sqrt{\frac{l \mp m_j + \frac{1}{2}}{2l+1}}|m_l = m_j + \frac{1}{2}, m_s = -\frac{1}{2}\rangle \tag{29}$$

so if $\Pr[\pm]$ denotes the probability of obtaining outcome $\pm\hbar/2$ when measuring the spin, then we have

$$\begin{aligned}\langle S_z\rangle &= \frac{\hbar}{2}(\Pr[+] - \Pr[-]) \\ &= \frac{\hbar}{2}\frac{1}{2l+1}\left(\left(l \pm m_j + \frac{1}{2}\right) - \left(l \mp m_j + \frac{1}{2}\right)\right) \\ &= \pm\frac{\hbar m_j}{2l+1}\end{aligned}$$

We conclude that

$$E^{\text{Zee}}_{n,l,j,m_j} = \frac{e\hbar B}{2m_e c} m_j \underbrace{\left(1 \pm \frac{1}{2l+1}\right)}_{g_J}.$$

The term in braces is called the Landé g-factor, after Alfred Landé, who discovered it in 1921. We see throughout the spectrum of the hydrogen atom many of the precursors of modern quantum theory.

3 WKB

3.1 Introduction to WKB

Perturbation theory covers the case when δH_{mn} is small relative to $|E^0_m - E^0_n|$. The Wentzel-Kramers-Brillouin (WKB) approximation covers a different limit, when quantum systems are in some ways approximately classical. For this reason, it is an example of a *semi-classical* approximation. It will result in powers not of δH but of $\hbar$, and thus becomes exact in the "classical" limit $\hbar \to 0$.

We begin with some exact manipulations of the Schrödinger equation. For a spin-0 mass-m particle in 3-d, define

$$\begin{aligned}\rho(\vec{x}, t) &= |\psi(\vec{x}, t)|^2 && \text{probability density} \\ \vec{J}(\vec{x}, t) &= \frac{\hbar}{m}\,\text{Im}(\psi^*\vec{\nabla}\psi) && \text{probability flux}\end{aligned}$$

The flux $\vec{J}$ has units of probability / area x time and can be seen to be related to momentum as follows:

$$\begin{aligned}\vec{J}(\vec{x}, t) &= \frac{\hbar}{m}\,\text{Im}\left(\psi^*\frac{i}{\hbar}\vec{p}\psi\right) \\ &= \frac{1}{m}\,\text{Re}\left(\psi^*\vec{p}\psi\right)\end{aligned}$$

Thus, if we integrate over all $\vec{x}$, we obtain

$$\int d^3x\vec{J} = \int d^3x\frac{1}{m}\,\text{Re}\left(\psi^*\vec{p}\psi\right) = \text{Re}\,\frac{\langle\vec{p}\rangle_t}{m} = \frac{\langle\vec{p}\rangle_t}{m}.$$

One can show (using the Schrödinger equation) the *conservation equation*

$$\boxed{\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0}. \tag{30}$$

We can also re-express the wavefunction using ρ as

$$\boxed{\psi(\vec{x}, t) = \sqrt{\rho(\vec{x}, t)} e^{i\frac{S(\vec{x},t)}{\hbar}}} \tag{31}$$

with $S(\vec{x}, t)$ *real* so that the exponent contributes a pure phase. What does it mean physically? In terms of ρ, S we can compute

$$\begin{aligned}
\vec{\nabla}\psi &= \frac{1}{2}\frac{\vec{\nabla}\rho}{\sqrt{\rho}} e^{iS/\hbar} + i\frac{\vec{\nabla}S}{\hbar}\psi \\
\psi^* \vec{\nabla}\psi &= \underbrace{\frac{1}{2}\vec{\nabla}\rho}_{\text{real}} + \underbrace{\frac{i}{\hbar}\rho\vec{\nabla}S}_{\text{imaginary}} \\
\vec{J}(\vec{x}, t) &= \frac{\hbar}{m}\,\mathrm{Im}(\psi^*\vec{\nabla}\psi) = \frac{\hbar}{m}\frac{\rho}{\hbar}\vec{\nabla}S
\end{aligned}$$

Thus we obtain a physical interpretation for the phase.

$$\vec{J}(\vec{x}, t) = \rho\frac{\vec{\nabla}S}{m}. \tag{32}$$

Namely its gradient relates to the probability flux. If $\vec{J} = \rho$"$\vec{v}$" then $\vec{\nabla}S \approx \vec{p}$. These equivalences are pretty loose, but we will build on this intuition as we proceed. For now, observe that for a free particle, they indeed give the right idea:

$$\psi_{\text{free}}(\vec{x}, t) \sim e^{-\frac{i\vec{p}\cdot\vec{x}}{\hbar} - \frac{iEt}{\hbar}}.$$

So $S = \vec{p}\cdot\vec{x} - Et$ and we have $\vec{\nabla}S = \vec{p}$ exactly. We also have $\vec{\nabla}^2 S = 0$, and it will turn out later that this quantity will measure how "non-plane-wave-like" our wavefunction is.

Schrödinger equation for a general 1-D potential Consider a region where $V(x) \leq E$ (called "classically allowed"). Then

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} &= (E - V(x))\psi(x) \\
-\hbar^2\frac{d^2\psi}{dx^2} &= \underbrace{2m(E - V(x))}_{p^2(x)}\psi(x)
\end{aligned}$$

We can interpret $p(x)$ as a classical momentum. The solution of this corresponds (roughly) to oscillations with period $\lambda(x) \equiv \frac{2\pi\hbar}{p(x)}$, which is the De Broglie wavelength corresponding to momentum $p(x)$.

What if $V(x) > E$? These are called "classically forbidden." Then we get

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

corresponding to solutions that exponentially decay at rate $\kappa(x)$.

The claims of "oscillating with period $\lambda(x)$" or "decaying at rate $\kappa(x)$" are only rigorous when $p(x)$ or $\kappa(x)$ are independent of x. But we will see how they can be good approximations even when $p(x)$ or $\kappa(x)$ are merely slowly varying with x.

Let's write $\psi(x) = \exp(iS(x)/\hbar)$, for some S with units of angular momentum. Since S can be complex, this is without loss of generality.

Substituting (in the classically allowed region) we get

$$\begin{aligned}
p^2(x)e^{\frac{iS(x)}{\hbar}} &= -\hbar^2 \frac{d^2}{dx^2} e^{\frac{iS(x)}{\hbar}} \\
&= -\hbar^2 \frac{d}{dx}\left(i\frac{S'(x)}{\hbar} e^{\frac{iS(x)}{\hbar}}\right) \\
&= -\hbar^2 \left(i\frac{S''(x)}{\hbar} - \frac{(S'(x))^2}{\hbar^2}\right) e^{\frac{iS(x)}{\hbar}}
\end{aligned}$$

The $e^{\frac{iS(x)}{\hbar}}$ terms drop out and we obtain

$$\boxed{(S')^2 - i\hbar S'' = p^2(x)} \tag{33}$$

So far this is exact. But if the potential is slowly varying, then $p(x)$ is slowly varying, and the $-i\hbar S''$ term will be small. What does "slowly varying" mean? The wavelength $\lambda(x) = \frac{2\pi\hbar}{p(x)}$ should be small relative to the variation of $p(x)$. In the classical limit $\hbar \to 0$ we have $\lambda(x) \to 0$. Thus it makes sense to expand around this limit in powers of $\hbar$, in a way analogous to our perturbation-theory strategy of expanding in terms of the perturbation. Thus we write

$$S(x) = \underbrace{S_0(x) + \hbar S_1(x)}_{\text{WKB approximation}} + \hbar^2 S_2(x) + \dots$$

and will take only the first two terms to be the WKB approximation.

Let us now substitute $S(x) = S_0(x) + \hbar S_1(x)$ into (33). We obtain

$$\begin{aligned}
(S_0' + \hbar S_1')^2 - i\hbar S_0'' - i\hbar^2 S_1'' &= p^2(x) \\
(S_0')^2 + 2\hbar S_0' S_1' - i\hbar S_0'' + \hbar^2((S_1')^2 - iS_1'') &= p^2(x)
\end{aligned}$$

We want to equate powers of $\hbar$. Treat $\hbar$ here as a former parameter, and we obtain

$$(S_0')^2 = p^2(x) \qquad \text{at } O(\hbar^0) \tag{34a}$$

$$2S_0' S_1' - iS_0'' = 0 \qquad \text{at } O(\hbar^1) \tag{34b}$$

From (34a), we obtain $S_0' = \pm p(x)$, which we can solve to obtain

$$S_0(x) = \pm \int_{x_0}^{x} p(x')dx',$$

where x_0 is arbitrary. Substituting $S_0' = \pm p(x), S_0'' = \pm p'(x)$ into (34b) we find

$$S_1' = \frac{i}{2}\frac{p'(x)}{p(x)} = \frac{i}{2}\frac{d}{dx}\ln p(x).$$

This has solution

$$\boxed{S_1(x) = \frac{i}{2}\ln p(x) + C} \tag{35}$$

Substituting into our equation for $\psi(x)$ we get

$$\psi(x) = e^{iS(x)/\hbar} \approx e^{\frac{i}{\hbar}(S_0+\hbar S_1)} = \exp\left(\pm\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'\right)\exp\left(-\frac{1}{2}\ln p(x) + C\right)$$

Thus in the classically allowed regions we have the solution

$$\boxed{\psi(x) = \frac{A}{\sqrt{p(x)}}\exp\left(\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'\right) + \frac{B}{\sqrt{p(x)}}\exp\left(-\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'\right)} \tag{36}$$

with $p(x) = \sqrt{2m(V - E(x))}$. The solution in the classically forbidden regions is the same but with $p(x) = i\kappa(x)$. This corresponds to

$$\boxed{\psi(x) = \frac{C}{\sqrt{\kappa(x)}}\exp\left(\frac{1}{\hbar}\int_{x_0}^{x} \kappa(x')dx'\right) + \frac{D}{\sqrt{\kappa(x)}}\exp\left(-\frac{1}{\hbar}\int_{x_0}^{x} \kappa(x')dx'\right)} \tag{37}$$

3.2 Validity of WKB

Let's just look at the first part of the classically allowed solution: $\psi(x) = \frac{A}{\sqrt{p(x)}}\exp\left(\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'\right)$. The probability density $\rho(x) = |\psi(x)|^2 = \frac{|A|^2}{p(x)} = \frac{|A|^2}{mv(x)}$, where $v(x)$ can be thought of as a classical velocity. This makes sense because it says that the particle spends less time in regions where it is moving faster.

Another check is to look at the probability current: $J = \frac{\hbar}{m}\operatorname{Im}\left(\psi^*\frac{\partial}{\partial x}\psi\right)$. We calculate

$$\begin{aligned}
\psi' &= -\frac{1}{2}\frac{p'(x)}{p(x)}\psi + \frac{i}{\hbar}p(x)\psi \\
\psi^*\psi' &= -\frac{1}{2}\frac{p'(x)}{p(x)}|\psi|^2 + i\frac{p(x)}{\hbar}|\psi|^2 \\
J &= \frac{\hbar}{m}\frac{p(x)}{\hbar}\rho = \rho\frac{p(x)}{m} = \rho v(x).
\end{aligned}$$

Next, let's look at the first discarded term. Our approximation assumed that $|\hbar^2(S_1')^2| \ll |\hbar S_0' S_1'|$, or equivalently, $|\hbar S_1'| \ll |S_0'|$. In terms of $p(x)$ this condition states that

$$\left|\hbar\frac{p'}{p}\right| \ll |p| \quad\Longleftrightarrow\quad 1 \gg \left|\hbar\frac{p'}{p^2}\right| = \left|\partial_x\frac{\hbar}{p}\right| = |\partial_x\lambda(x)|. \tag{38}$$

In other words, the de Broglie wavelength should be slowly varying. How slowly? Return to $1 \gg \left|\hbar\frac{p'}{p^2}\right|$. Rearranging, we obtain

$$|p| \gg \frac{\hbar}{|p|}|p'| = \lambda(x)\left|\frac{dp}{dx}\right|.$$

In other words, the change of p over a de Broglie wavelength should be $\ll |p|$.

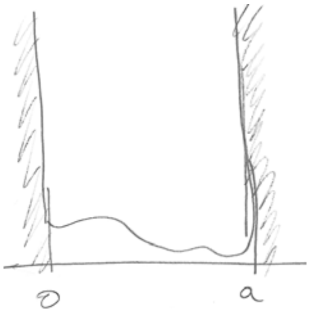


Figure 1: Example of a potential $V(x)$ that is finite only in the interval $0 < x < a$.

We can relate this back to the potential energy.

$$\begin{aligned}
p^2 &= 2m(E - V) \\
|2pp'| &= 2m|V'| \\
\hbar|p'| &= m\frac{\hbar}{p}|V'| = m\lambda(x)|V'| \\
\hbar|p'| &\ll |p|^2 && \text{from (38)} \\
m\lambda(x)|V'| &\ll |p|^2 \\
\lambda(x)|V'| &\ll \frac{|p|^2}{m}
\end{aligned}$$

The change of potential energy over one wavelength should be $\ll$ the kinetic energy.

3.3 Bohr-Sommerfeld quantization

The WKB approximation can be used to generalize the old idea that quantum "orbits" should have action (integral of $p\,dx$) that is an integer multiple of $h = 2\pi\hbar$. This idea is part of what is called "old quantum mechanics" because it predates the modern (ca. 1925) formulation in terms of the Schrödinger equation.

We illustrate this with an example. Consider a potential $V(x)$ such that $V(x) = \infty$ for $x \leq 0$ or $x \geq a$ and $V(x)$ is finite for $0 < x < a$. This is depicted in Fig. 1.

Assume that $E > V(x)$ for all $0 < x < a$. Then the solution has the form

$$\begin{aligned}
\psi(x) &= \frac{1}{\sqrt{p(x)}}\left(A\exp\left(\frac{i}{\hbar}\int_0^x p(x')dx'\right) + B\exp\left(-\frac{i}{\hbar}\int_0^x p(x')dx'\right)\right) \\
&= \frac{1}{\sqrt{p(x)}}\left(Ae^{i\phi(x)} + Be^{-i\phi(x)}\right) && \phi(x) = \frac{1}{\hbar}\int_0^x p(x')dx' \\
&= \frac{1}{\sqrt{p(x)}}\left(C\cos(\phi(x)) + D\sin(\phi(x))\right)
\end{aligned}$$

From the boundary condition $\psi(0) = 0$ and the fact that $\phi(0) = 0$ we obtain $C = 0$. From the condition $\psi(a) = 0$ we find that $\phi(a) = n\pi$. Plugging in the definition of $\phi(x)$ we find the quantization condition:

$$\frac{1}{\hbar}\int_0^a dx\sqrt{2m(E_n - V(x))} = n\pi, \tag{39}$$

where we have defined E_n to be the n^{th} energy level.

As a sanity check, if $V(x) = 0$ then (39) yields

$$\frac{1}{\hbar} a \sqrt{2mE_n} = n\pi \qquad \Rightarrow \qquad E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}. \tag{40}$$

What if we have “soft” walls? For this we need to connect the oscillating solutions in the allowed regions with the decaying solutions in the forbidden regions. This is achieved by the connection formulae.

To see the need for this, let’s examine the integral of $p(x)$ over the classically allowed region of a harmonic oscillator.

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2.$$

The energy levels are of course $E_n = \hbar\omega(n + 1/2)$. The turning points are given by solution to the equation $\frac{1}{2} m\omega^2 x^2 = \hbar\omega(n + 1/2)$. These are

$$x = \pm l\sqrt{2n+1} \qquad l \equiv \sqrt{\frac{\hbar}{m\omega}}. \tag{41}$$

Let’s see what happens when we integrate $p(x)/\hbar$ between these turning points. We obtain

$$\begin{aligned}
\frac{1}{\hbar} \int_{-l\sqrt{2n+1}}^{l\sqrt{2n+1}} p(x)dx &= \frac{1}{\hbar} \int_{-l\sqrt{2n+1}}^{l\sqrt{2n+1}} \sqrt{2m(\hbar\omega(n+1/2) - \frac{1}{2} m\omega^2 x^2)} dx \\
&= \int_{-l\sqrt{2n+1}}^{l\sqrt{2n+1}} \frac{1}{l} \sqrt{2n+1 - \frac{x^2}{l^2}} dx \\
&= (2n+1) \int_{-1}^{1} \sqrt{1-u^2} du \qquad\qquad \text{defining } u \equiv l\sqrt{2n+1} \\
&= \pi(n+1/2).
\end{aligned}$$

There is an extra factor of $\pi/2$ relative to what happens with hard walls. We will see below why this is.

Before continuing, we can see that the WKB approximation does give a pretty accurate picture of the harmonic oscillator. In the forbidden region ($|x| > l$) they describe the wavefunction as exponentially decaying. Specifically suppose that $|x| \gg l$ so that $\kappa(x) = \sqrt{2m(V(x) - E_n)} \approx \sqrt{2mV(x)} = m\omega|x|$. Integrating this we get

$$\psi(x) \propto \exp(-\frac{m\omega}{\hbar} \frac{x^2}{2}) = e^{-\frac{x^2}{2l^2}}, \tag{42}$$

which gives the correct rate of exponential decay.

In the classically allowed region WKB also correctly predicts the number of oscillations of the wavefunction. But how can WKB predict the $\pi(n + 1/2)$ result we found above?

3.4 Connection formulae

When $E = V(a)$ then we say that a is a “turning point”. Turning points separate allowed from forbidden regions, and therefore oscillating from decaying solutions. However, near a turning point, the WKB approximation breaks down. So if we want to glue together oscillating and decaying solutions, we cannot just match boundary conditions at the border. Something nontrivial will happen at the turning point, which could involve reflection/transmission as well as phase shifts.

There are two approaches to this, both difficult. One that we will not explore is to use complex analysis and analytically continue the wavefunction to complex-valued x. In this way we can avoid going near a: x goes up to $a-\epsilon$ along the real line, then follows a half-circle in the complex plane to $a+\epsilon$ and then continues along the real line.

Instead we will follow Griffiths and use Airy functions. Near a turning point, we can approximate $V(x) = V(a) + (a-x)V'(a) + \ldots$. To simplify notation shift the origin and the overall energy level so that $a = 0$ and $E = V(0) = 0$. In the vicinity of the turning point, the Schrödinger equation looks like

$$-\frac{\hbar^2}{2m}\psi''(x) + xV'(0)\psi(x) = 0 \tag{43}$$

$$\psi''(x) = \underbrace{\frac{2mV'(0)}{\hbar^2}}_{\alpha^3} x\psi(x). \tag{44}$$

We define α in this way so that when we change coordinates to $z = \alpha x$ then z is dimensionless and we obtain the dimensionless equation

$$\psi''(z) = z\psi(z). \tag{45}$$

This is a second-order differential equation and thus has a two-dimensional space of solutions. These are called the Airy function $Ai(z)$ and the Airy function of the second kind $Bi(z)$. There are exact expressions for these that are somewhat unilluminating (see Griffiths or wikipedia for details), but what will be more useful are the asymptotic formulas. These are oscillatory for $z < 0$ and exponentially decaying or growing for $z > 0$. Specifically:

	$Ai(z)$	$Bi(z)$
$z \ll 0$	$\frac{1}{\sqrt{\pi}(-z)^{1/4}} \sin\left(\frac{2}{3}(-z)^{3/2} + \frac{\pi}{4}\right)$	$\frac{1}{\sqrt{\pi}(-z)^{1/4}} \cos\left(\frac{2}{3}(-z)^{3/2} + \frac{\pi}{4}\right)$
$z \gg 0$	$\frac{e^{-\frac{2}{3}z^{\frac{3}{2}}}}{2\sqrt{\pi}z^{1/4}}$	$\frac{e^{\frac{2}{3}z^{\frac{3}{2}}}}{\sqrt{\pi}z^{1/4}}$

We can then match up the Airy function near the turning point with the decaying and oscillating solutions that are valid far from the turning point. This yield connection formulas. The high-level picture is that in the classically allowed region we have two oscillating solutions, near the turning point we have two Airy functions as solutions and in the forbidden region we have two exponentially decaying/growing solutions. At each boundary we have two constraints given by continuity of $\psi(x)$ and $\psi'(x)$. These give the following connection formulae:

Allowed on the left, forbidden on the right Consider the turning point depicted in Fig. 2(a). Then we find

$$\frac{2A}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_x^a p(x')dx' + \frac{\pi}{4}\right) + \frac{B}{\sqrt{p(x)}} \cos\left(\frac{1}{\hbar}\int_x^a p(x')dx' + \frac{\pi}{4}\right) \qquad x \ll a \tag{46a}$$

$$\Longleftrightarrow \frac{A}{\sqrt{\kappa(x)}} \exp\left(-\frac{1}{\hbar}\int_a^x \kappa(x')dx'\right) + \frac{B}{\sqrt{\kappa(x)}} \exp\left(\frac{1}{\hbar}\int_a^x \kappa(x')dx'\right) \qquad x \gg a \tag{46b}$$

A few words of caution. If $B \neq 0$ then in the $x \gg a$ we might be tempted to neglect the A term. But this will give a bad error in the $x \ll a$ region.

Conversely if $|B| \ll |A|$, then we have to be careful about neglecting it in the $x \gg a$ region because it can become dominant for large x.

(a) (b)

Figure 2: Turning points. In (a) the classically allowed region is on the left and the classically forbidden region is on the right. In (b) the classically allowed region is on the right and the classically forbidden region is on the left.

Allowed on the right, forbidden on the left Suppose the turning point is at $x = b$, as depicted in Fig. 2(b). Now the connection formula is

$$\frac{A}{\sqrt{\kappa(x)}} \exp\left(-\frac{1}{\hbar}\int_x^b \kappa(x')dx'\right) + \frac{B}{\sqrt{\kappa(x)}} \exp\left(\frac{1}{\hbar}\int_x^b \kappa(x')dx'\right) \qquad x \ll b \tag{47a}$$

$$\Longleftrightarrow \frac{2A}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_b^x p(x')dx' + \frac{\pi}{4}\right) + \frac{B}{\sqrt{p(x)}} \cos\left(\frac{1}{\hbar}\int_b^x p(x')dx' + \frac{\pi}{4}\right) \qquad x \gg b \tag{47b}$$

Application to harmonic oscillator Applying these to the harmonic oscillator predicts that (calculation omitted - see Griffiths)

$$\int_{-x_0}^{x_0} p(x)dx = (n - 1/2)\pi,$$

where $\pm x_0$ are the turning points. Here we take $n = 1, 2, 3, \ldots$, which is why it matches what we observed above (where $n = 0, 1, 2, \ldots$ is from the conventional way to label the harmonic oscillator energy levels). To summarize, the Bohr-Sommerfeld quantization condition for $\frac{1}{\hbar}\int_a^b p(x)dx$ (where $[a, b]$ is the classically allowed region) is

two hard walls	$n\pi$
one hard wall, one soft wall	$(n - 1/4)\pi$
two soft walls	$(n - 1/2)\pi$

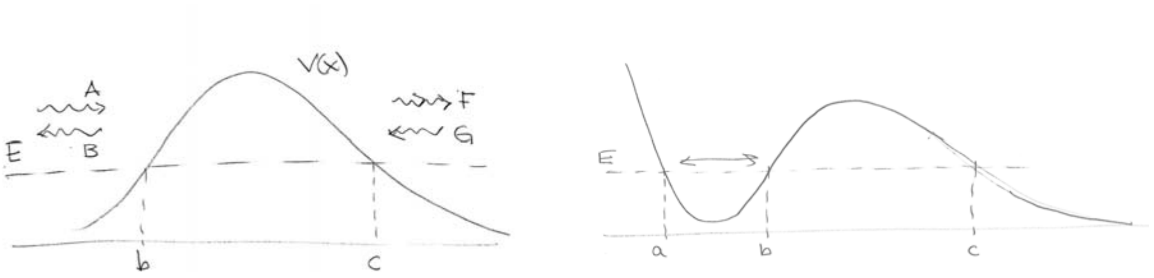
3.5 Tunneling

We can also use WKB to estimate the rate at which a particle will "tunnel" through a classically forbidden region, as depicted in Fig. 3(a). This is useful for modeling phenomena such as radioactive decay.

The transmission probability is

$$T = \frac{|F|^2}{|A|^2} \approx \exp\left[-\frac{2}{\hbar}\int_b^c \kappa(x)dx\right].$$

This approximation is valid if the barrier is broad and high.



(a) (b)

Figure 3: (a) Tunneling through a classically forbidden region. (b) A particle localized in the region $a < x < b$ will eventually tunnel into the region $x > c$.

How do we get a lifetime from this? Suppose that the particle is localized in the region $a < x < b$ in Fig. 3(b). Then we can approximate

$$\text{lifetime} = \frac{1}{\text{tunnel prob per unit time}} \simeq \frac{1}{T \cdot \#\text{ hits per unit time}} = \frac{1}{T\frac{1}{\tau}} = \frac{\tau}{T}$$

where τ is the period of oscillation within the region $a < x < b$. This can be approximated by

$$\tau = 2\int_a^b \frac{dx}{v(x)} = 2\int_a^b m\frac{dx}{p(x)}.$$

Putting this together we can approximate the lifetime as

$$\text{lifetime} \approx 2\int_a^b m\frac{dx}{p(x)} \cdot \exp\left[\frac{2}{\hbar}\int_b^c \kappa(x)dx\right].$$

The fact that lifetime scales exponentially with barrier height explains the vast differences we see in alpha decay. The halflife at which ^{238}U decays to ^{234}Th is 4.5 billion years while the halflife for the decay of ^{214}Po to ^{210}Tl is 0.164ms; see Fig. 4 for the full decay chain. This difference is due to the difference in barrier height relative to the energy of the ejected alpha particle.

$$ {}^{238}_{92}\mathrm{U} \xrightarrow[4{,}468\times10^{9}\ \mathrm{y}]{\alpha} {}^{234}_{90}\mathrm{Th} \xrightarrow[24{,}1\ \mathrm{d}]{\beta^-} {}^{234\mathrm{m}}_{91}\mathrm{Pa} \left\{ \begin{array}{c} \xrightarrow[1{,}17\ min]{0{,}16\%} {}^{234}_{91}Pa \xrightarrow[6{,}7\ h]{\beta^-} \\ \xrightarrow[1{,}17\ min]{99{,}84\%\beta^-} \end{array} \right\} {}^{234}_{92}\mathrm{U} \xrightarrow[2{,}445\times10^{5}\ \mathrm{y}]{\alpha} {}^{230}_{90}\mathrm{Th} \xrightarrow[7{,}7\times10^{4}\ \mathrm{y}]{\alpha} {}^{226}_{88}\mathrm{Ra} \xrightarrow[1600\ \mathrm{y}]{\alpha} {}^{222}_{86}\mathrm{Rn} $$

$$ {}^{222}_{86}\mathrm{Rn} \xrightarrow[3{,}8235\ \mathrm{d}]{\alpha} {}^{218}_{84}\mathrm{Po} \xrightarrow[3{,}05\ \mathrm{min}]{\alpha} {}^{214}_{82}\mathrm{Pb} \xrightarrow[26{,}8\ \mathrm{min}]{\beta^-} {}^{214}_{83}\mathrm{Bi} \xrightarrow[19{,}9\ \mathrm{min}]{\beta^-} {}^{214}_{84}\mathrm{Po} \xrightarrow[164.3\ \mu\mathrm{s}]{\alpha} {}^{210}_{82}\mathrm{Pb} \xrightarrow[22{,}26\ \mathrm{y}]{\beta^-} {}^{210}_{83}\mathrm{Bi} \xrightarrow[5{,}013\ \mathrm{d}]{\beta^-} {}^{210}_{84}\mathrm{Po} \xrightarrow[138{,}38\ \mathrm{d}]{\alpha} {}^{206}_{82}\mathrm{Pb} $$

Figure 4: Decay chain of ^{238}U. From wikipedia article on Uranium-238.

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