

Approximate methods. Time-independent perturbation theory
Variational principles. Semiclassical approximation.

There exist only a handful of problems in quantum mechanics which can be solved exactly. More often one is faced with a potential or a Hamiltonian for which exact methods are unavailable and approximate solutions must be found. Here we review three approximate methods each of which has its own strengths and weaknesses.

- (i) Perturbation theory: useful when the Hamiltonian can be written as an exactly solvable piece plus 'small' correction;
- (ii) Variational method: in the standard form helps to determine ground state properties in a complex system. The major drawback is lack of control over the accuracy (which often is remarkably good!). Can be re-formulated to deal with excited states, but quickly becomes inaccurate.
- (iii) Semiclassical approximation: deals with slowly-varying potentials.

Time-independent perturbation theory

In perturbation theory one considers corrections to energy eigenstates and eigenvalues which originate from 'small' terms, let's denote them \hat{V} , added to the exactly solvable Hamiltonian \hat{H}_0 :

$$\hat{H} = \hat{H}_0 + \hat{V} .$$

The conditions for naming \hat{V} 'small' will be quantified below. Let $E_n^{(0)}$ and $\psi_n^{(0)}$ be eigenenergies and the corresponding eigenstates of \hat{H}_0 :

$$\hat{H}_0|\psi_n^{(0)}\rangle = E_n|\psi_n^{(0)}\rangle , \quad n = 0, 1, 2, 3, \dots .$$

The goal is to determine corrections to $\psi_n^{(0)}$ and $E_n^{(0)}$ which take us closer and closer to the exact eigenstates ψ_n with exact eigenenergies E_n under the assumption that \hat{V} is small. Since \hat{V} is a matrix and has a dimension of energy the notion of small can not be attached to it directly without comparing matrix elements of \hat{V} to some energy scale. To avoid this complication we introduce an auxiliary quantity λ , replace \hat{V} with $\lambda\hat{V}$, and pretend that $\lambda \rightarrow 0$ is a small parameter. At the end of the calculation we set $\lambda = 1$. In essence, we simplify the bookkeeping of collecting terms which are proportional to the same power of \hat{V} terms. So, we start solving the eigenvalue equation

$$[\hat{H}_0 + \lambda\hat{V}]|\psi_n\rangle = E_n|\psi_n\rangle ,$$

by assuming the existence of expansions

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots + \lambda^k E_n^{(k)} + \dots , \\ \psi_n &= Z_n \left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots + \lambda^k \psi_n^{(k)} + \dots \right) , \end{aligned} \quad (1)$$

where the global normalization factor has to be established at the end of the calculation (this allows one to demand that the wavefunction correction is orthogonal to the un-perturbed state). Plugging these expansions back to the eigenvalue equation we get

$$[\hat{H}_0 + \lambda\hat{V}] \left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \right) = \left[E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \right] \left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \right) .$$

The rest of the theory requires that we express both the l.h.s and the r.h.s. of this equation as power series expansions in λ and then equate expressions in front of each λ^k , i.e. we match Taylor

series expansions about the $\lambda = 0$ point. This is why this procedure is called the 'perturbation theory'. Now the l.h.s is

$$\hat{H}_0\psi_n^{(0)} + \lambda \left(\hat{H}_0\psi_n^{(1)} + \hat{V}\psi_n^{(0)} \right) + \lambda^2 \left(\hat{H}_0\psi_n^{(2)} + \hat{V}\psi_n^{(1)} \right) + \dots + \lambda^k \left(\hat{H}_0\psi_n^{(k)} + \hat{V}\psi_n^{(k-1)} \right) + \dots ,$$

and the r.h.s. is

$$E_n^{(0)}\psi_n^{(0)} + \lambda \left(E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \right) + \lambda^2 \left(E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)} \right) + \dots + \lambda^k \sum_{m=0}^k E_n^{(m)}\psi_n^{(k-m)} + \dots .$$

Matching power series we get a set of coupled equations which admit an easy step-by-step solution. The first equation is

$$\hat{H}_0\psi_n^{(1)} + \hat{V}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} . \quad (2)$$

We project it on the $\psi_l^{(0)}$ state to replace operators with numbers and matrix elements. For $l = n$ we obtain

$$\hat{V}_{nn}\psi_n^{(0)} = E_n^{(1)}\psi_n^{(0)} \quad \longrightarrow \quad E_n^{(1)} = \hat{V}_{nn} . \quad (3)$$

which immediately solves for the lowest, or first, order correction to the energy eigenvalue. It is nothing but the average of the perturbation term over the unperturbed state. For $l \neq n$ we obtain

$$E_l^{(0)}\langle\psi_l^{(0)}|\psi_n^{(1)}\rangle + \hat{V}_{ln} = E_n^{(0)}\langle\psi_l^{(0)}|\psi_n^{(1)}\rangle \quad \longrightarrow \quad \langle\psi_l^{(0)}|\psi_n^{(1)}\rangle = -\frac{\hat{V}_{ln}}{E_l^{(0)} - E_n^{(0)}} . \quad (4)$$

which solves for the lowest-order correction to the wavefunction

$$\psi_n^{(1)} = -\sum_{l \neq n} \psi_l^{(0)} \frac{\hat{V}_{ln}}{E_l^{(0)} - E_n^{(0)}} . \quad (5)$$

We immediately see that an admixture of states with $l \neq n$ is small as long as $|\hat{V}_{ln}/(E_l^{(0)} - E_n^{(0)})| \ll 1$, and the sum over l converges fast enough. Thus is a major condition which justifies the use of the perturbation theory.

This wonderful conspiracy that one only needs to know wavefunction corrections up to $\psi_n^{(k-1)}$ to find $E_n^{(k)}$ which is then used to determine $\psi_n^{(k)}$ persists in higher orders, making the whole scheme slightly increasing in complexity for larger k , but still easily manageable. Consider now second-order corrections. Projecting

$$\hat{H}_0\psi_n^{(2)} + \hat{V}\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)} , \quad (6)$$

onto the state $\psi_l^{(0)}$ with $l = n$ we get the second order correction to energy as

$$\langle\psi_n^{(0)}|\hat{V}|\psi_n^{(1)}\rangle = E_n^{(2)} , \quad \longrightarrow \quad E_n^{(2)} = -\sum_{l \neq n} \frac{\hat{V}_{nl}\hat{V}_{ln}}{E_l^{(0)} - E_n^{(0)}} . \quad (7)$$

Note that $\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$ as well as $\langle\psi_n^{(0)}|\psi_n^{(k)}\rangle = 0$ for any k by construction, see Eq. (1). Since for Hermitian operators $\hat{V}_{nl} = \hat{V}_{ln}^*$ we can write the answer in the form which makes it clear that the second-order correction to the ground state is always negative

$$E_n^{(2)} = -\sum_{l \neq n} \frac{|\hat{V}_{ln}|^2}{E_l^{(0)} - E_n^{(0)}} , \quad (8)$$

because for $n = 0$ all denominators are positive. This result has numerous important implications in physics. For example, if the ground state of \hat{H}_0 is degenerate and matrix elements of \hat{V} are zero between all ground states (say by symmetry) then the the best state is the one which admits larger matrix elements between the ground state manifold and excited states. Second-order perturbation theory for energy is also behind many effective interactions such as the VdW force between neutral atoms without dipole moments, or any force mediated by an exchange of an intermediate particle for that matter. Below I also discuss how it leads to the notion of effective Hamiltonian under appropriate conditions; after all nearly everything in physics is an effective description at the relevant energy scale.

By projecting (6) on $\psi_l^{(0)}$ with $l \neq n$ we find the second-order correction to the wavefunction

$$\langle \psi_l^{(0)} | \psi_n^{(2)} \rangle = - \frac{\langle \psi_l^{(0)} | \hat{V} | \psi_n^{(1)} \rangle - E_n^{(1)} \langle \psi_l^{(0)} | \psi_n^{(1)} \rangle}{E_l^{(0)} - E_n^{(0)}}. \quad (9)$$

What is left is to plug in here expressions for $\psi_n^{(1)}$ and $E_n^{(1)}$:

$$\psi_n^{(2)} = \sum_{l \neq n} \psi_l^{(0)} \left(\sum_{k \neq n} \frac{\hat{V}_{lk} \hat{V}_{kn}}{(E_l^{(0)} - E_n^{(0)})(E_k^{(0)} - E_n^{(0)})} - \frac{\hat{V}_{ln} \hat{V}_{nn}}{(E_l^{(0)} - E_n^{(0)})^2} \right). \quad (10)$$

Since

$$E_n^{(k)} = \langle \psi_n^{(0)} | \hat{V} | \psi_n^{(k-1)} \rangle,$$

holds for any k , it does not cost us anything to write the next-order correction to energy

$$E_n^{(3)} = \sum_{l, k \neq n} \frac{\hat{V}_{nl} \hat{V}_{lk} \hat{V}_{kn}}{(E_l^{(0)} - E_n^{(0)})(E_k^{(0)} - E_n^{(0)})} - \sum_{l \neq n} \frac{\hat{V}_{nn} |\hat{V}_{nl}|^2}{(E_l^{(0)} - E_n^{(0)})^2}. \quad (11)$$

We will stop here since the protocol is clear. Let us now turn to examples of how it works.

Take a fake problem when the potential is represented by two harmonic oscillator terms

$$U(x) = U_0(x) + V(x) = \frac{1}{2}m\omega^2 x^2 + \frac{1}{2}m\nu^2 x^2,$$

with $\nu \ll \omega$. The exact solution is, of course, readily obtained by introducing $\Omega = (\omega^2 + \nu^2)^{1/2}$ which also can be Taylor expanded as

$$\Omega = \omega \left(1 + \frac{\nu^2}{2\omega^2} - \frac{\nu^4}{8\omega^4} + \dots \right).$$

The exact energies are

$$E_n = \Omega \left(n + \frac{1}{2} \right).$$

In perturbation theory we have

$$E_n^{(1)} = \langle n | \frac{1}{2}m\nu^2 x^2 | n \rangle = \frac{m\nu^2 \langle n | x^2 | n \rangle}{2} = \frac{m\nu^2 (2n+1)}{4m\omega} = \omega \left(n + \frac{1}{2} \right) \frac{\nu^2}{2\omega^2},$$

exactly as expected from exact E_0 with Ω expanded in a series.

Doing the check for the wavefunction is also straightforward conceptually but more messy:

$$\psi_n^{(1)} = - \sum_{l \neq n} \psi_l^{(0)} \frac{\langle l | m \nu^2 x^2 / 2 | n \rangle}{\omega(l-n)} = - \frac{\nu^2}{4\omega^2} \sum_{l \neq n} \psi_l^{(0)} \frac{\langle l | [(\hat{a}) + (\hat{a})^\dagger]^2 | n \rangle}{l-n}.$$

Substituting here

$$\langle l | [(\hat{a}) + (\hat{a})^\dagger]^2 | n \rangle = (2n+1)\delta_{l,n} + \sqrt{(n+1)(n+2)}\delta_{l,n+2} + \sqrt{n(n-1)}\delta_{l,n-2}$$

we get

$$\psi_n^{(1)} = \frac{\nu^2}{8\omega^2} \left(-\sqrt{(n+1)(n+2)} \psi_{n+2}^{(0)} + \sqrt{n(n-1)} \psi_{n-2}^{(0)} \right),$$

(the second term is present only if $n-2 \geq 0$). To compare this expression with exact solution we have to take $\psi_n^{(0)}(\sqrt{m\Omega}x)$ and differentiate it with respect to Ω

$$\psi_n^{(1)} = \delta\Omega \frac{d}{d\Omega} \psi_n^{(0)}(\sqrt{m\Omega}x) \Big|_{\Omega=\omega} = \frac{\nu^2}{2\omega} \frac{d}{d\omega} \psi_n^{(0)}(\sqrt{m\omega}x).$$

It is convenient to use $y = \sqrt{m\omega}x$ at this point

$$\psi_n^{(1)} = \frac{\nu^2}{2\omega^2} \left(\frac{m\omega}{\pi} \right)^{1/4} \frac{1}{\sqrt{2^n n!}} \left[\frac{1}{4} H_n(y) + \frac{y}{2} H_n'(y) - \frac{y^2}{2} H_n(y) \right] e^{-y^2/2}.$$

The rest is lengthy algebra of manipulating with Hermite polynomials using

$$H_n'(y) = 2yH_n(y) - H_{n+1}(y)$$

to write square brackets as

$$[\dots] = \frac{1}{2} \left[\frac{1}{2} H_n - yH_{n+1} + y^2 H_n \right],$$

and then applying

$$yH_n = nH_{n-1} + \frac{1}{2}H_{n+1},$$

couple of times to get rid of the powers of y in front of polynomials

$$\begin{aligned} [\dots] &= \frac{1}{2} \left[\frac{1}{2} H_n - yH_{n+1} + y(nH_{n-1} + \frac{1}{2}H_{n+1}) \right] = \frac{1}{4} \left[H_n - yH_{n+1} + 2nyH_{n-1} \right] = \\ &= \frac{1}{4} \left[H_n - ((n+1)H_n + \frac{1}{2}H_{n+2}) + 2n((n-1)H_{n-2} + \frac{1}{2}H_n) \right] = -\frac{1}{8}H_{n+2} + \frac{n(n-1)}{2}H_{n-2}. \end{aligned}$$

The final step is to attach the proper normalization factors to Hermite polynomials to obtain $\psi_{n+2}^{(0)}$ and $\psi_{n-2}^{(0)}$

$$\begin{aligned} &\frac{1}{\sqrt{2^n n!}} \left[\frac{n(n-1)}{2} H_{n-2} - \frac{1}{8} H_{n+2} \right] \equiv \\ &\frac{\sqrt{n(n-1)}}{4} \frac{1}{\sqrt{2^{n-2}(n-2)!}} H_{n-2} - \frac{\sqrt{(n+1)(n+2)}}{4} \frac{1}{\sqrt{2^{n+2}(n+2)!}} H_{n+2}. \end{aligned}$$

This leads to

$$\psi_n^{(1)} = \frac{\nu^2}{8\omega^2} \left(\sqrt{(n)(n-1)} \psi_{n-2}^{(0)} - \sqrt{(n+1)(n+2)} \psi_{n+2}^{(0)} \right),$$

which matches the result of the perturbation theory precisely.

Problem 35. Shifted harmonic oscillator by perturbation theory

Consider a harmonic oscillator accompanied by a constant force f which is considered to be small

$$V(x) = \frac{1}{2}m\omega^2x^2 - fx.$$

a). Show that this system can be solved exactly by using a shifted coordinate

$$y = x - \frac{f}{m\omega^2},$$

and write exact expressions for energy eigenvalues and eigenfunctions.

b). Use perturbation theory (by considering the force term as a perturbation) to calculate $E_n^{(1)}$, $E_n^{(2)}$, and $\psi_n^{(1)}$. Compare your answers with the exact expression and demonstrate match when exact expressions are expanded in powers of f .

Problem 36. Anharmonic oscillator₁.

Evaluate the effect of a small anharmonic term of the form

$$V_{anh} = -\epsilon x^3,$$

on the spectrum of harmonic oscillator with mass m and frequency ω .

a). Start by showing that

$$\langle k|x^3|n\rangle = \left(\frac{1}{2m\omega}\right)^{3/2} \left[\sqrt{(n+1)(n+2)(n+3)}\delta_{k,n+3} + 3(n+1)^{3/2}\delta_{k,n+1} + 3n^{3/2}\delta_{k,n-1} + \sqrt{n(n-1)(n-2)}\delta_{k,n-3} \right].$$

b). Calculate the first-order energy shift $E_n^{(1)}$ in perturbation theory in V_{anh} .

c). Calculate the second-order energy shift $E_n^{(2)}$.

Degenerate perturbation theory. Effective Hamiltonians.

We observe that the perturbation theory fails when denominators in expressions for $E_n^{(k)}$ and $\psi_n^{(k)}$ are either zero, or comparable to the mixing matrix element, i.e. when $|E_l^{(0)} - E_n^{(0)}| \lesssim |\hat{V}_{ln}|$. Often this is a sign that the perturbation theory has to be abandoned altogether. However, there are important cases when the condition of validity of the perturbation theory is violated only for two, or several, say N , isolated levels which happen to be near degenerate. Let's denote the corresponding N -dimensional Hilbert space by ν_A while the rest of the Hilbert space is ν_B

In this case we proceed as follows:

- Account for the diagonal matrix elements of \hat{V}_{nn} in the renormalized spectrum $\epsilon_n = E_n^{(0)} + E_n^{(1)}$. Formally, they are exact energy eigenstates of the Hamiltonian $\hat{H}'_0 = \hat{H}_0 + \hat{D}$, where $\hat{D}_{nm} = \hat{V}_{nn}\delta_{nm}$. I thus suggest that we *always* transfer diagonal matrix elements of \hat{V} to \hat{H}_0 and consider the rest as perturbation $\hat{V}' = \hat{V} - \hat{D}$. By construction $\hat{V}'_{nn} = 0$. At this point we check again whether conditions for the validity of the perturbation theory are violated for \hat{V}' and the spectrum $\{\epsilon_n\}$ to identify the troubled group of states ν_A , if any.

- Suppose that we do have a group of N states for which the perturbation theory cannot be applied directly.

We split the matrix $\hat{V}'_{kk'}$ into two matrixes $\hat{A}_{kk'}$ and $\hat{B}_{kk'}$ such that \hat{B} does not have non-zero matrix elements between states which *both* belong to ν_A , while \hat{A} has non-zero matrix elements *only* between the states in the ν_A subspace. This is illustrated in the figure which explains which matrix elements are assigned to \hat{A} and \hat{B} . By definition, the perturbation theory can be applied for \hat{B} . We thus proceed as usual and calculate corrections to energy levels and wavefunctions for all levels. The final result must be regarded as an approximate solution for the energy spectrum and eigenstates of $\hat{H}'_0 + \hat{B}$. Let us denote them as $\{\tilde{\epsilon}_n\}$ and $\{\tilde{\psi}_n\}$.

$$\hat{V}' = \begin{pmatrix} 0 & a & b & c \\ a^* & 0 & e & f \\ b^* & e^* & 0 & g \\ c^* & f^* & g^* & 0 \end{pmatrix} = \hat{A} + \hat{B}$$

$$\hat{A} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & e & 0 \\ 0 & e^* & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad \hat{B} = \begin{pmatrix} 0 & a & b & c \\ a^* & 0 & 0 & f \\ b^* & 0 & 0 & g \\ c^* & f^* & g^* & 0 \end{pmatrix}$$

ν_A subspace

- We now account for the effects of matrix \hat{A} and new matrix elements generated in the near-degenerate subspace ν_A . In some cases we have non-zero \hat{A} from the very outset and in the leading approximation it is possible to skip the previous step completely and proceed with the diagonalization of the Hamiltonian matrix

$$\hat{H}_{nm}^{(A)} = \epsilon_n \delta_{nm} + \hat{A}_{nm}, \quad \psi_n, \psi_m \in \nu_A,$$

in the ν_A subspace. For the two-level example shown in the figure we readily find

$$E_{\pm} = \frac{\epsilon_2 + \epsilon_3}{2} \pm \sqrt{\frac{(\epsilon_2 - \epsilon_3)^2}{4} + |A_{23}|^2},$$

i.e. we deal with this problem exactly the same way as with any other finite-dimensional space.

One immediate improvement would be to use corrected spectrum $\tilde{\epsilon}_n$ instead of ϵ_n . However, to be consistent we must also account for corrections to the matrix \hat{A} introduced by the change of basis states from ψ_n to $\tilde{\psi}_n$ and new matrix elements generated from higher orders in \hat{B} . This is especially important in cases when \hat{A} is small, or even zero! This brings us to the notion of effective Hamiltonian in the selected energy subspace ν_A . Needless to say that effective Hamiltonians and theories are found in physics all over the place. More precisely, all we do in physics is effective Hamiltonians and models which emerge after high-energy modes are 'absorbed' into effective constants and potentials. Here I will discuss how things are done at the level of the lowest-order perturbation theory (first for the wavefunction).

We have

$$\tilde{\psi}_n = Z_n \left(\psi_n^{(0)} - \sum_{l \neq \nu_A} \psi_l^{(0)} \frac{\hat{B}_{ln}}{\epsilon_l - \epsilon_n} \right) \equiv Z_n \left(\psi_n^{(0)} - \sum_{l \neq \nu_A} \psi_l^{(0)} C_{ln} \right), \quad (12)$$

with Z -factors close to unity because

$$Z_n = \left(1 + \sum_{l \neq \nu_A} |C_{ln}|^2 \right)^{-1/2} \longrightarrow Z_n \approx 1 - \frac{1}{2} \sum_{l \neq \nu_A} |C_{ln}|^2.$$

Now

$$\hat{A}_{mn} = \langle \tilde{\psi}_m | \hat{A} | \tilde{\psi}_n \rangle = Z_m Z_n \hat{A}_{mn} \approx \hat{A}_{mn}.$$

I will not keep terms proportional to AB^2 here, though it is possible at a little cost (see below for normalized and orthogonal functions).

Given new wavefunctions we also find that the \hat{B} matrix in the ν_A subspace now has non-zero matrix elements. They may be small, i.e. proportional to \hat{B}^2 , but given near degeneracy of energy levels in ν_A their effect on these levels may be strong and even non-perturbative. These matrix elements are (keeping only terms $\propto \hat{B}^2$):

$$\begin{aligned} \hat{A}'_{m \neq n} &= \left\langle \psi_m^{(0)} - \sum_{l \neq \nu_A} \psi_l^{(0)} C_{lm} \left| \hat{B} \right| \psi_n^{(0)} - \sum_{l \neq \nu_A} \psi_l^{(0)} C_{ln} \right\rangle = - \sum_{l \neq \nu_A} [C_{lm}^* \hat{B}_{ln} + \hat{B}_{ml} C_{ln}] = \\ &= -2 \sum_{l \neq \nu_A} \hat{B}_{ml} \hat{B}_{ln} \frac{\epsilon_l - (\epsilon_n + \epsilon_m)/2}{(\epsilon_l - \epsilon_m)(\epsilon_l - \epsilon_n)} \end{aligned}$$

Finally, we have to account for contributions coming from $[\hat{H}'_0]_{n \neq m}$. If we naively use wavefunctions (12) we will get a meaningless expression because it will *not* be invariant under the choice of where the energy is counted from. This is because the overlap

$$\langle \tilde{\psi}_m | \tilde{\psi}_n \rangle \approx O_{mn} = \sum_{l \neq \nu_A} C_{lm}^* C_{ln} \neq 0,$$

is non-zero. By small rotation of states (again, keeping only the leading small terms)

$$e_m = \psi_m^{(0)} - \frac{1}{2} \sum_n O_{nm} \psi_n^{(0)} - \sum_{l \neq \nu_A} C_{lm} \psi_l^{(0)},$$

we fix orthogonality (and normalization!) to leading order. Now

$$\begin{aligned} \hat{A}''_{m \neq n} &= [\hat{H}'_0]_{n \neq m} = \left\langle \psi_m^{(0)} - \sum_{l \neq \nu_A} \psi_l^{(0)} C_{lm} - \frac{1}{2} \sum_k O_{km} \psi_k^{(0)} \left| \hat{H}'_0 \right| \psi_n^{(0)} - \sum_{l \neq \nu_A} \psi_l^{(0)} C_{ln} - \frac{1}{2} \sum_i O_{in} \psi_i^{(0)} \right\rangle = \\ &= \sum_{l \neq \nu_A} C_{lm}^* C_{ln} \left[\epsilon_l - \frac{1}{2} (\epsilon_m + \epsilon_n) \right] = \sum_{l \neq \nu_A} B_{ml} B_{ln} \frac{\epsilon_l - (\epsilon_m + \epsilon_n)/2}{(\epsilon_l - \epsilon_n)(\epsilon_l - \epsilon_m)} \equiv -\frac{1}{2} \hat{A}'_{m \neq n}. \end{aligned}$$

Combining all pieces together we finally get

$$\hat{H}_{mn}^{(eff)} = \tilde{\epsilon}_n \delta_{nm} + \left[\hat{A} + \hat{A}' + \hat{A}'' \right]_{m \neq n} = \tilde{\epsilon}_n \delta_{nm} + \hat{A}_{mn} - \sum_{l \neq \nu_A} \hat{B}_{ml} \hat{B}_{ln} \frac{\epsilon_l - (\epsilon_n + \epsilon_m)/2}{(\epsilon_l - \epsilon_m)(\epsilon_l - \epsilon_n)} (1 - \delta_{nm}) .$$

Establishing an effective Hamiltonian for the N -dimensional subspace is important when $|\epsilon_l - \epsilon_n| \gg |\epsilon_n - \epsilon_m|$, for all $l \neq \nu_A$ and $n, m \in \nu_A$, i.e. when near degenerate states are separated by large energy gaps from the rest of the spectrum. In this case we can use a simplified expression

$$\hat{H}_{nm}^{(eff)} = \tilde{\epsilon}_n \delta_{nm} + \hat{A}_{mn} - \sum_{l \neq \nu_A} \frac{\hat{B}_{ml} \hat{B}_{ln}}{\epsilon_l - \epsilon_A} (1 - \delta_{nm}) ,$$

where $\epsilon_A = N^{-1} \sum_{n \in \nu_A} \epsilon_n$ is the 'central' energy of the ν_A subspace. This completes our derivation. Notice that for exact degeneracy of ϵ_n levels and zero \hat{A} -matrix, an arbitrary small mixing of levels generated by \hat{A}' -matrix is a non-perturbative effect.

Problem 37. Degenerate perturbation theory.

Go back to the Three-Level Problem (# 26), i.e.

$$\hat{H} = \begin{pmatrix} 0 & 0 & \Delta \\ 0 & 0 & \Delta \\ \Delta & \Delta & U \end{pmatrix} ,$$

(it is exactly the same Problem; I simply re-ordered the matrix for transparency) and address it now in the limit of large $U \gg \Delta$ using degenerate perturbation theory and the effective Hamiltonian approach. At the end compare your final result to the result of exact calculation from Problem 34.

Problem 38. Perturbation theory for the two level system.

Well, we already know the exact solution for the two level system. Now try to reproduce known results by considering the case of large bias, or small mixing, $\Delta/\xi \ll 1$, and applying the perturbation theory in Δ .

- a). Calculate the second order corrections to energies $E_{1,2} = \pm\xi$. Compare with the exact result at the same level of accuracy.
- b). Calculate the first order corrections to the energy wavefunctions. Compare with the exact result at the same level of accuracy.

Variational principle

Consider the quantity

$$J[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} ,$$

which can be constructed for any state. The fancy name for it is 'functional' because it converts an input in the form of a function into an output which is a number. Next we expand ψ in the

energy basis

$$\psi(x) = \sum_n c_n \psi_n, \quad \hat{H}\psi_n = E_n \psi_n,$$

and write $J[\psi]$ as

$$J = \frac{\sum_n E_n |c_n|^2}{\sum_n |c_n|^2} \geq \frac{E_0 \sum_n |c_n|^2}{\sum_n |c_n|^2} = E_0.$$

The inequality follows from the fact that $E_n \geq E_0$ for all n . Thus J is minimized when $\psi = \psi_0$ in which case $J = E_0$. However any other choice will yield something larger. A good choice of wavefunction will result in an answer which is closer to the exact value. The protocol then is to make a variational guess of ψ containing one or more parameters $\{\alpha_i\}$, calculate $J(\{\alpha_i\})$, and minimize J with respect to this parameter set. For example, consider the standard harmonic oscillator Hamiltonian for which the ground state energy is $E_0 = \omega/2$. Of course, the actual ground state wavefunction is a Gaussian, but suppose we don't know this and choose instead

$$\psi(x) = N(a^2 - x^2)^2 \quad \text{for } |x| \leq a \quad \text{and zero otherwise.}$$

First, choose N to normalize the wavefunction

$$1 = \int_{-a}^a dx |\psi(x)|^2 = N^2 \int_{-a}^a dx (a^2 - x^2)^4 = N^2 a^9 \frac{256}{315} \quad \rightarrow \quad N = \sqrt{\frac{315}{256a^9}}.$$

Then

$$\langle \psi | x^2 | \psi \rangle = N^2 \int_{-a}^a dx x^2 (a^2 - x^2)^4 = N^2 a^{11} \frac{256}{3465} = \frac{315}{3465} a^2 = \frac{a^2}{11}.$$

Also

$$\langle \psi | -\frac{d^2}{dx^2} | \psi \rangle = \langle \psi' | \psi' \rangle = N^2 \int_{-a}^a dx [4x(a^2 - x^2)]^2 = N^2 a^7 \frac{256}{105} = \frac{3}{a^2}.$$

Hence

$$J = \frac{3}{2ma^2} + \frac{m\omega^2 a^2}{22} \quad \rightarrow \quad \frac{dJ}{da} = -\frac{3}{ma^3} + \frac{m\omega^2 a}{11} = 0 \quad \rightarrow \quad a^2 = \frac{\sqrt{33}}{m\omega}.$$

Substituting this back to J we finally get

$$E_{min} = \frac{3\omega}{2\sqrt{33}} + \frac{\sqrt{33}\omega}{22} = \frac{\omega}{2} \left(2\sqrt{\frac{3}{11}} \right) = 1.044 \frac{\omega}{2},$$

which is only 4% above the true ground state despite the crude guess for the wave function.

Today, the whole machinery is developed for variational calculations of many-body ground states with the trial states containing hundreds and even thousands of variational parameters. At this level of complexity, the evaluation and minimization of J is done by computers (in the multi-dimensional Hilbert space of particle coordinates, J is often simulated by Monte Carlo). The most recent advance came from quantum information science when Vidal and Verstraete introduced matrix product and tensor network states. In quantum chemistry calculations people can do 200 electrons and calculate energies with relative accuracy of about 0.1%, a remarkable achievement. But even this is not enough because 0.1% on 1 keV energy is about 10000 K—not sufficient to make reliable predictions for chemical reaction rates at room temperature. Still ...

We have discussed the variational principle for the ground state. Can it be generalized to excited states? The answer is yes. First, the trivial way. Sometimes the symmetry of the ground and excited states is different, say one is even and the other is odd. By taking variational states which respect different symmetries we obtain a standard variational principle for the ground states *in each of the different symmetry sectors*. This works because expansion coefficients c_n are non-zero only in the same-symmetry sector; the rest of the proof is exactly as before with E_0 being replaced with the lowest energy in a given symmetry sector. This observation can be carried out also at the level of conserved quantum numbers: for example, if the total momentum is conserved, then taking trial states with different total momentum we have a variational principle in this momentum sector. Same for the conserved total angular momentum, or magnetization component on the symmetry axis, etc. etc.

An idea of using trial states orthogonal to the variational ground state (in the same symmetry, or conserved quantum number sector) in attempt to determine the first excited level might work in practice for the lowest excited state, though, strictly speaking, it is not based on a solid mathematical foundation because of an unknown contribution from an admixture of the exact ground state.

There is, however, an extension of the variational principle which works for any energy level, in principle. Consider quantity, called 'local energy', defined by

$$E(x) = \frac{\psi^*(x)\hat{H}\psi(x)}{|\psi(x)|^2} .$$

For an arbitrary state it is a function of x , but whenever $\psi(x)$ coincides with one of the energy eigenstates it becomes a constant (!). This immediately suggests that a functional looking at local fluctuations of $E(x)$ about its average (averaging can be done using $|\psi|^2$):

$$J_{loc} = \left\langle (E(x) - \langle E(x) \rangle)^2 \right\rangle = \langle E^2(x) \rangle - \langle E(x) \rangle^2 ,$$

which is non-negative by construction, reaches a minimum value of $J_{loc} = 0$ when the trial state is hitting one of the eigenstates. Not only we have a general variational principle, but also some measure of estimating the accuracy by monitoring how close is the minimum value of J_{loc} to zero. Once the best state is determined (by minimization of J_{loc} with respect to variational parameters) one proceeds with the calculation of energy using the standard expression for J .

Problem 39. Anharmonic oscillator₂.

Consider a harmonic oscillator with additional ϵx^4 term

$$V(x) = \frac{1}{2}m\omega^2x^2 + \epsilon x^4 .$$

a). Use the variational principle with a Gaussian trial wavefunction

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

in order to estimate the ground state energy E_0 .

b). Evaluate your variational answer for E_0 analytically in the limit of vanishing ϵ .

c). Use first-order perturbation theory in order to calculate E_0 , and compare with the result found

in b).

Problem 40. Quartic potential.

Use Gaussian trial wavefunction to estimate the ground state energy for the quartic potential $V(x) = gx^4$ (save time by paying attention to the previous problem :) Show that your answer is

$$E_{min} = \left(\frac{3}{4}\right)^{4/3} \left(\frac{g}{m^2}\right)^{1/3} .$$

Compare this to the 'exact' answer $0.668(g/m^2)^{1/3}$.

The semiclassical approximation

This method paves the road connecting QM with the classical mechanics. It is also a useful tool for obtaining accurate results under circumstances when the potential is relatively smooth. It was developed by Wentzel, Kramers, and Brillouin, giving it the 'WKB' name. Well, some actually call it LG=Liouville-Green method by arguing that borrowing math. tools for solving math. equation when it happens to be relevant for physics does not qualify for name giving, some add another letter to the end, WKBJ with J=Jeffreys, some call it 'eikonal approximation', etc. I will generically call it the semiclassical approximation. The idea here is to write the wavefunction as

$$\psi(x) = A(x) e^{iB(x)/\hbar} ,$$

where $A(x)$, $B(x)$ are real functions. Now demand that the form satisfy the time independent Schrödinger Equation . In preparation for that, compute

$$\begin{aligned} \frac{d\psi}{dx} &= A' e^{iB(x)/\hbar} + \frac{i}{\hbar} AB' e^{iB(x)/\hbar} , \\ \frac{d^2\psi}{dx^2} &= A'' e^{iB(x)/\hbar} + \frac{2i}{\hbar} A'B' e^{iB(x)/\hbar} + \frac{i}{\hbar} AB'' e^{iB(x)/\hbar} + \frac{i^2}{\hbar^2} A(B')^2 e^{iB(x)/\hbar} . \end{aligned}$$

We then have

$$\left[-\frac{\hbar^2}{2m} \left(A''(x) + \frac{2i}{\hbar} A'(x)B'(x) + \frac{i}{\hbar} A(x)B''(x) + \frac{i^2}{\hbar^2} A(x)(B'(x))^2 \right) + (V(x) - E)A(x) \right] = 0 ,$$

let us consider the limit of $\hbar \rightarrow 0$, which is formally the same as assuming that higher-order derivative of the wavefunction amplitude is small, and start solving the Schrödinger Equation approximately by dealing separately with different powers of \hbar in the above expression. In the leading approximation we find

$$A'' = 0 , \quad \text{neglect this derivative ,}$$

$$2A'B' + AB'' = 0 ,$$

$$A(B')^2 + 2m(V(x) - E)A = 0 \quad \longrightarrow \quad B' = \pm \sqrt{2m(E - V(x))} \quad \longrightarrow \quad B = \pm \int_{x_0}^x \sqrt{2m(E - V(x))} dx .$$

The usual way of writing the last expression is

$$B(x) = \pm \int_{x_0}^x p(x) dx, \quad \text{where } p(x) = \sqrt{2m(E - V(x))},$$

where $p(x)$ is called the semiclassical momentum; correspondingly, $v(x) = p(x)/m$ is called the semiclassical velocity. If $E - V(x)$ is negative, i.e. we are dealing with the classically forbidden region, the value of $p(x)$ becomes purely imaginary, $p(x) = i\kappa(x)$, where $\kappa(x) = \sqrt{2m(V(x) - E)}$. I will also call $\kappa(x)$ a semiclassical momentum in the forbidden region.

Knowing $B(x)$ we solve for $A(x)$ using the second equation

$$\frac{d \ln A}{dx} = -\frac{1}{2} \frac{d \ln B'}{dx} \quad \rightarrow \quad A(x) = \frac{C}{\sqrt{p(x)}}.$$

This completes the derivation of the semiclassical approximation for the wavefunction

$$\psi(x) \approx \frac{C}{\sqrt{p(x)}} \exp \left\{ \pm \frac{i}{\hbar} \int_{x_0}^x p(x) dx \right\}. \quad (13)$$

There is also good physical reasoning for this functional form. We know that a particle moving in a constant potential is described by a plane wave Ce^{ipx} with $p = \sqrt{2m(E - V)}$. If potential is smooth, i.e. does not change much on the scale of the particle wavelength then locally the plane wave description should be also valid, but with locally defined momentum $p(x)$ adjusted to the current value of the potential. The only problem with the replacement

$$px \quad \rightarrow \quad \int^x \sqrt{2m(E - V(x))} dx,$$

is that if we do not do something with the wave amplitude then the current density $j = |C|^2 p(x)/m$ will decrease while for smooth potentials we do not expect any reflections (with exponentially good accuracy), i.e. the current density should remain constant. This leads to

$$C \quad \rightarrow \quad C(x) \propto p(x)^{-1/2}.$$

We can now explicitly check under what conditions it is possible to neglect the second derivative of A . To this end require that

$$A''(x) \ll \frac{A(x)(B'(x))^2}{\hbar^2},$$

If L is the length scale over which the $A(x)$ function changes substantially then $A'' \sim A/L^2$ leading to

$$L(x) \gg \frac{\hbar}{p(x)} = \frac{\lambda(x)}{2\pi}, \quad (14)$$

i.e. the amplitude has to change a little (in relative terms) over the particle wavelength.

We can not consider the theory of the semiclassical approximation complete until we discuss the matching conditions. The problem is that in the vicinity of points where $E = V(x)$ called the classical 'turning points', the semiclassical momentum goes to zero. This invalidates condition (14) leaving us with an incomplete description because even if we can use (13) in different regions in space, to the left and to the right of the turning point, we do not know yet how to match them to establish a common state and find the energy quantization condition. The only exception from

this is the case of a stepwise change in $V(x)$ at point x_0 — then the semiclassical approximation may be valid all the way to point x_0 from both sides and the matching conditions are standard, i.e. continuity of $\psi(x)$ and its derivative.

One of the many equivalent solutions for the generic turning point is as follows. In the vicinity of the turning point a we can write $V(x) - E = V(x) - V(a) \approx f(x - a)$ and try to solve the Schrödinger Equation equation (let's assume that f is positive)

$$\left[-\frac{1}{2m} \frac{d^2}{dx^2} + f(x - a) \right] \psi(x) = 0 .$$

we have to do it only once (!) because in terms of the dimensionless variable $z = (2mf)^{1/3}(x - a)$ we have a universal (system independent) equation

$$\left[\frac{d^2}{dz^2} - z \right] \psi = 0 .$$

Its solutions are special (Airy) functions $Ai(z)$ and $Bi(z)$. What is crucial for our semiclassical theory is their asymptotic form for large positive and negative z :

$$Ai(z) \longrightarrow \lim_{z \rightarrow \infty} \frac{1}{2\sqrt{\pi}z^{1/4}} e^{-(2/3)z^{3/2}} ,$$

$$Bi(z) \longrightarrow \lim_{z \rightarrow \infty} \frac{1}{\sqrt{\pi}z^{1/4}} e^{(2/3)z^{3/2}} ,$$

$$Ai(-z) \longrightarrow \lim_{z \rightarrow \infty} \frac{1}{\sqrt{\pi}z^{1/4}} \cos\left(\frac{2}{3}z^{3/2} - \frac{\pi}{4}\right) ,$$

$$Bi(-z) \longrightarrow \lim_{z \rightarrow \infty} -\frac{1}{\sqrt{\pi}z^{1/4}} \sin\left(\frac{2}{3}z^{3/2} - \frac{\pi}{4}\right) ,$$

These are exact relations across the turning point.

Now, if we look at the semiclassical solutions in the same asymptotic regions we find that

$$\int_x^a p(x)dx = \sqrt{2mf} \int_x^a \sqrt{a-x} dx = \sqrt{2mf} \frac{2}{3}(a-x)^{3/2} = \frac{2}{3}(-z)^{3/2} , \text{ for } -z > 0 ,$$

and

$$\int_a^x p(x)dx = \sqrt{2mf} \int_a^x \sqrt{(x-a)} dx = \sqrt{2mf} \frac{2}{3}(x-a)^{3/2} = \frac{2}{3}z^{3/2} , \text{ for } z > 0 .$$

This allows us to write the general solution to the left of the turning point as

$$\psi(-z) \longrightarrow \lim_{z \rightarrow \infty} \frac{1}{\sqrt{\pi}z^{1/4}} \left[\alpha \cos\left(\frac{2}{3}z^{3/2} - \frac{\pi}{4}\right) - \beta \sin\left(\frac{2}{3}z^{3/2} - \frac{\pi}{4}\right) \right] ,$$

with arbitrary α and β , and to the right of the turning point as

$$\psi(z) \longrightarrow \lim_{z \rightarrow \infty} \frac{1}{\sqrt{\pi}z^{1/4}} \left[\gamma e^{-(2/3)z^{3/2}} + \delta e^{(2/3)z^{3/2}} \right] ,$$

with arbitrary γ and δ . All what is left is to notice that our expression to the left can be re-written identically as

$$\psi(-z) = \alpha Ai(-z) + \beta Bi(-z) ,$$

and to the right as

$$\psi(-z) = 2\gamma Ai(z) + \delta Bi(z) .$$

To agree with the exact solution we must then have $\gamma = \alpha/2$ and $\delta = \beta$. These are our matching conditions across the turning point. To summarize:

$$\begin{aligned} \psi_{x < a} &= \frac{\alpha}{\sqrt{p(x)}} \cos \left(\int_x^a p(x) dx - \frac{\pi}{4} \right) - \frac{\beta}{\sqrt{p(x)}} \sin \left(\int_x^a p(x) dx - \frac{\pi}{4} \right) \longleftrightarrow \\ \psi_{a < x} &= \frac{\alpha/2}{\sqrt{\kappa(x)}} \exp \left(- \int_a^x \kappa(x) dx \right) + \frac{\beta}{\sqrt{\kappa(x)}} \exp \left(\int_a^x \kappa(x) dx \right) . \end{aligned}$$

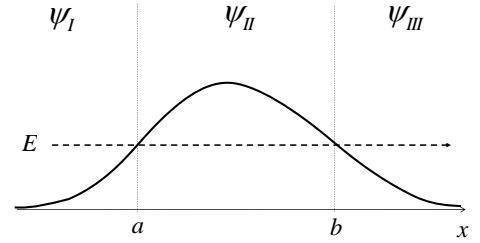
Note, that in this matching rule the integrals are always increasing as we move *away* from the turning point. We do not need to do anything to obtain matching conditions when the classically forbidden region is to the left of the turning point $x = b$, i.e. when $f < 0$. Simply notice that if we change $z \rightarrow -z$ we will get the same problem with $f \rightarrow -f$. Thus

$$\begin{aligned} \psi_{b < x} &= \frac{\alpha}{\sqrt{p(x)}} \cos \left(\int_b^x p(x) dx - \frac{\pi}{4} \right) - \frac{\beta}{\sqrt{p(x)}} \sin \left(\int_b^x p(x) dx - \frac{\pi}{4} \right) \longleftrightarrow \\ \psi_{x < b} &= \frac{\alpha/2}{\sqrt{\kappa(x)}} \exp \left(- \int_x^b \kappa(x) dx \right) + \frac{\beta}{\sqrt{\kappa(x)}} \exp \left(\int_x^b \kappa(x) dx \right) . \end{aligned}$$

Again, the integrals are all increasing as we move away from the turning point. With this, the semiclassical approximation is complete and can be used as a tool to establish interesting results under rather generic conditions when exact solutions are not available.

Consider particle transmission through the large smooth barrier shown to the left. For the reflection/transmission setup in region III we require that there is only an outgoing wave

$$\begin{aligned} \psi_{III} &= \frac{\delta}{\sqrt{p(x)}} e^{i \int_b^x p(x) dx - i\pi/4} = \\ &= \frac{\delta}{\sqrt{p(x)}} \left[\cos \left(\int_b^x p(x) dx - \frac{\pi}{4} \right) + i \sin \left(\int_b^x p(x) dx - \frac{\pi}{4} \right) \right] \end{aligned}$$



In the second region, the wavefunction is a superposition of increasing and decreasing exponentials

$$\psi_{x < b} = \frac{\delta/2}{\sqrt{\kappa(x)}} \exp \left(- \int_x^b \kappa(x) dx \right) + \frac{-i\delta}{\sqrt{\kappa(x)}} \exp \left(\int_x^b \kappa(x) dx \right) . \quad (15)$$

We immediately fix the amplitudes in this expression using matching conditions; in a way it even looks easier than 'continuity of ψ and its derivative' because we can work our way from right to

left in a unique way and build the solution, i.e. no need for solving a set of linear equations for free coefficients. We rewrite (15) identically as

$$\psi_{x < b} = \frac{e^{-C} \delta / 2}{\sqrt{\kappa(x)}} \exp\left(\int_a^x \kappa(x) dx\right) + \frac{-i e^C \delta}{\sqrt{\kappa(x)}} \exp\left(-\int_a^x \kappa(x) dx\right). \quad (16)$$

but now we count all integrals from point $x = a$ to prepare for applying the matching conditions for the second point. Here

$$C = \int_a^b \kappa(x) dx,$$

is the semiclassical action for the underbarrier motion. According to the conditions of validity, the length of the underbarrier passage has to be much longer than the typical wavelength $2\pi\hbar/\kappa(x)$, i.e. the value of C is large. Applying the second matching condition we get

$$\psi_{x < a} = -\frac{e^{-C} \delta / 2}{\sqrt{p(x)}} \sin\left(\int_x^a p(x) dx - \frac{\pi}{4}\right) + \frac{-2i e^C \delta}{\sqrt{p(x)}} \cos\left(\int_x^a p(x) dx - \frac{\pi}{4}\right). \quad (17)$$

We can write it as

$$\psi_{x < a} = \frac{\alpha}{\sqrt{p(x)}} \exp\left(-i \int_x^a p(x) dx + i \frac{\pi}{4}\right) + \frac{\beta}{\sqrt{p(x)}} \exp\left(i \int_x^a p(x) dx - i \frac{\pi}{4}\right). \quad (18)$$

with

$$\alpha = -i\delta (e^C + e^{-C}/4), \quad \beta = -i\delta (e^C - e^{-C}/4).$$

Assuming that the potential goes to zero on both sides of the barrier as $|x| \rightarrow \infty$ we have the current density of incoming/reflected/transmitted particles being proportional to $|\alpha|^2$, $|\beta|^2$, and $|\delta|^2$, respectively. This leads to the transmission coefficient

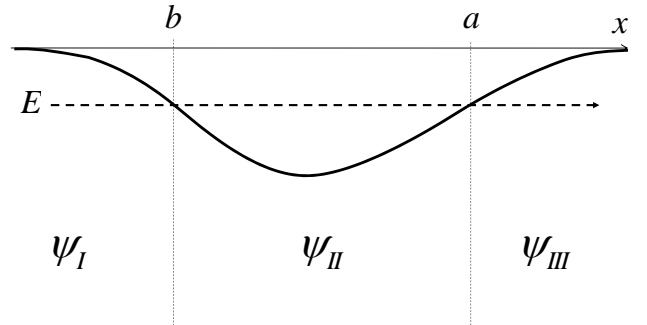
$$T = \frac{1}{(e^C + e^{-C}/4)^2} \approx e^{-2C} = \exp\left\{-2 \int_a^b \kappa(x) dx\right\},$$

which is exponentially small, but non-zero. The final answer is remarkably compact despite being valid for smooth potentials of arbitrary shape!

The other powerful application of the method is the semiclassical quantization rule. We consider now a smooth potential well shown to the left and work our solution from the right to the left. In region III we have a decaying exponential

$$\psi_{III} = \frac{\delta}{\sqrt{\kappa(x)}} \exp\left\{-\int_a^x \kappa(x) dx\right\}.$$

Using matching conditions we write the solution in the well, in region II, as



$$\psi_{II} = \frac{2\delta}{\sqrt{p(x)}} \cos\left(\int_x^a p(x)dx - \frac{\pi}{4}\right) \equiv \frac{2\delta}{\sqrt{p(x)}} \cos\left(C - \int_b^x p(x)dx + \frac{\pi}{4}\right) \equiv \frac{2\delta}{\sqrt{p(x)}} \cos\left(\int_b^x p(x)dx - \frac{\pi}{4} - C\right),$$

where

$$C = \int_b^a p(x)dx - \frac{\pi}{2}.$$

On the other hand we may start with

$$\psi_I = \frac{\alpha}{\sqrt{\kappa(x)}} \exp\left\{-\int_x^b \kappa(x)dx\right\},$$

and use matching conditions to obtain

$$\psi_{II} = \frac{2\alpha}{\sqrt{p(x)}} \cos\left(\int_b^x p(x)dx - \frac{\pi}{4}\right).$$

The two expressions for region II are consistent with each other only if $\alpha = \pm\delta$ and $C = \pi n$ (odd values of n correspond to $\alpha = -\delta$). This leads to the famous Bohr-Sommerfeld quantization rule

$$\int_b^a p(x)dx = \pi\left(n + \frac{1}{2}\right).$$

Again, its power is that it applies to an arbitrary smooth potential with large enough separation between the turning points, i.e. for high excited levels. Though formally it is not supposed to work accurately for the ground state, typically it does, and extremely well! It is a conspiracy of Nature that Bohr-Sommerfeld rule happens to be exact for the harmonic oscillator. Indeed,

$$p(x) = \sqrt{2m(E - V(x))} = m\omega\sqrt{x_0^2 - x^2}, \quad x_0 = \sqrt{\frac{2E}{m\omega^2}}.$$

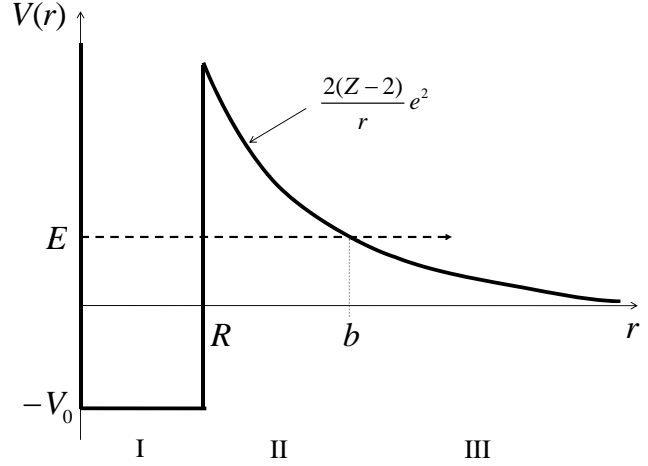
Next

$$\int_{-x_0}^{x_0} m\omega\sqrt{x_0^2 - x^2} dx = m\omega x_0^2 \int_{-1}^1 \sqrt{1 - s^2} ds = \frac{\pi E}{\omega} = \pi\left(n + \frac{1}{2}\right).$$

If a smooth and deep potential near the minimum is well approximated by a parabola (an exception would be a minimum with zero second derivative) then the semiclassical formula will describe the lowest energy levels perfectly well.

The last application in this chapter will be the α -particle decay rate in nuclear physics. We will ignore many details of what happens inside the nucleus thus our answer is not expected to be accurate down to the number in front of the exponential factor which is determined by the alpha particle moving in the Coulomb potential barrier.

The simplified model is depicted to the left where α -particle in the parent nucleus is considered as being trapped in the potential well created by the remaining protons and neutrons (forming the so-called daughter nucleus). This potential well is mostly of strong-force origin. The radius of the well is the radius of the nucleus $R \sim r_0 A^{1/3}$ where $r_0 = 1.2$ fm and A the atomic mass number. On the other hand, once outside this well the α -particle experiences the repulsive Coulomb interaction with the positively charged $Z - 2$ daughter nucleus. Thus our model is a potential of the form



$$V(r) = \begin{cases} -V_0 & r < R \\ \frac{2(Z-2)e^2}{r} & r > R \end{cases}$$

Later on we will see that motion in the three-dimensional potential well with the orbital momentum $L = 0$ can be reduced to the study of radial motion $r \in (0, \infty)$ which is (i) one-dimensional, and (ii) described by the one-dimensional Schrödinger Equation with $r \in (0, \infty)$. Indeed, the radial part of the Laplace operator is given by

$$\Delta_r = \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr}.$$

The Schrödinger Equation for the spherically symmetric $L = 0$ wavefunction written as $\psi(r) = u(r)/r$ is then

$$\left[-\frac{1}{2m} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + V(r) \right] \frac{u(r)}{r} = E \frac{u(r)}{r}.$$

After performing the differentiation

$$\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \frac{u(r)}{r} = \frac{1}{r^2} \frac{d}{dr} (ru' - u) = \frac{u''}{r},$$

we arrive at

$$\left[-\frac{1}{2m} \frac{d^2}{dr^2} + V(r) \right] u(r) = E u(r).$$

So, the semiclassical analysis will be applied to $u(r)$. The last remark is that m in this calculation is the reduced mass, but since α -particle is much lighter than the relatively heavy daughter nucleus we have $m \approx m_\alpha$.

In three regions we have (N is the normalization constant)

$$u_I = N \sin kr \qquad k = \sqrt{2m(E + V_0)},$$

$$u_{II} = N \frac{A}{\sqrt{\kappa(r)}} \exp \left\{ \int_R^r \kappa(r) dr \right\} + N \frac{B}{\sqrt{\kappa(r)}} \exp \left\{ - \int_R^r \kappa(r) dr \right\}, \quad \kappa(r) = \sqrt{2m \left(\frac{2(Z-2)e^2}{r} - E \right)},$$

$$u_{III} = N \frac{D}{\sqrt{p(r)}} \exp \left\{ i \int_b^r p(r) dr - i \frac{\pi}{4} \right\} \quad p(r) = \sqrt{2m \left(E - \frac{2(Z-2)e^2}{r} \right)} .$$

We may now proceed with the solution using matching conditions from left to the right. I will present the derivation in two different ways, one will be based on calculating the particle flux out of the well using u_{III} . The other will be based on the imaginary part (!) of the energy level in the well.

Matching conditions at $r = R$ lead to (they are standard and *not* semiclassical because of the potential jump)

$$\begin{aligned} \sin kR &= \frac{A+B}{\sqrt{\kappa(R)}} , & k \cos kR &= \sqrt{\kappa(R)}(A-B) , \\ A &= \frac{\sqrt{\kappa(R)}}{2} \left(\sin kR + \frac{k}{\kappa(R)} \cos kR \right) , & B &= \frac{\sqrt{\kappa(R)}}{2} \left(\sin kR - \frac{k}{\kappa(R)} \cos kR \right) \end{aligned}$$

Next, we rewrite u_{II} identically as

$$u_{II} = \frac{Ae^C}{\sqrt{\kappa(r)}} \exp \left\{ - \int_r^b \kappa(r) dr \right\} + \frac{Be^{-C}}{\sqrt{\kappa(r)}} \exp \left\{ \int_r^b \kappa(r) dr \right\} ,$$

and proceed with obtaining u_{III} using matching conditions at the turning point $x = b$ (below we use the same notation for the under-the-barrier integral $C = \int_R^b \kappa(x) dx$)

$$\begin{aligned} u_{III} &= \frac{2Ae^C}{\sqrt{p(r)}} \cos \left(\int_b^r p(r) dr - \frac{\pi}{4} \right) - \frac{Be^{-C}}{\sqrt{p(r)}} \sin \left(\int_b^r p(r) dr - \frac{\pi}{4} \right) \equiv \\ &= \frac{Ae^C + iBe^{-C}/2}{\sqrt{p(r)}} \exp \left(i \int_b^r p(r) dr - i \frac{\pi}{4} \right) + \frac{Ae^C - iBe^{-C}/2}{\sqrt{p(r)}} \exp \left(-i \int_b^r p(r) dr + i \frac{\pi}{4} \right) . \end{aligned}$$

To ensure that we have only an outgoing wave we require that

$$A = \frac{i}{2} Be^{-2C} .$$

This leads to

$$\tan kR + \frac{k}{\kappa(R)} = \frac{ie^{-2C}}{2} \left(\tan kR - \frac{k}{\kappa(R)} \right) . \quad (19)$$

and

$$D = Ae^C + iBe^{-C}/2 = iBe^{-C} = i \frac{\sqrt{\kappa(R)}}{2} \cos(kR) \left(\tan kR - \frac{k}{\kappa(R)} \right) e^{-C} .$$

We notice that Eq. (19) depends on energy only and thus is supposed to give us the energy spectrum, but we know that (i) any positive energy is allowed, and (ii) this equation is complex and thus its solutions will also be complex. What is going on here? The proper answer is that the boundary condition with an outgoing wave leads to the non-Hermitian energy operator (recall that the Sturm-Liouville theory of second-order differential operators leads to Hermitian operators only with the canonical boundary conditions). The outgoing wave is *not* one of them. The whole setup then has to be understood as a physically appealing situation when the *dynamic* solution of the Schrödinger Equation with initial condition corresponding to the particle localized on the E_n

eigenstate of the potential well, starts leaking out of the well at $t > 0$. After some relatively short transient time the wavefunction will establish a quasi-static profile over large distances $r \gg b$ with the outgoing wave. At this point the flux can be calculated in the vicinity of the well without even bothering about properties of the wavefront. Over a much-much longer time scale the amplitude of the quasi-static profile will actually slowly decay to zero.

Since e^{-2C} is an exponentially small parameter, we compute everything by keeping only the leading non-vanishing terms in this small parameter. Then, Eq. (19) solves as

$$k = k_n + \frac{ie^{-2C}}{R} \epsilon, \quad \text{where} \quad \tan k_n R = -k_n/\kappa(R). \quad (20)$$

The value of k_n is the same as one would obtain from the exact quantization rule for the non-decaying potential well with Coulomb potential at $r > R$ being replaced with the constant $2(Z-2)e^2/R$, i.e. $E_n = k_n^2/2m - V_0$ is the exact energy level in the non-decaying well. For deep wells $k_n/\kappa(R) \ll 1$ and

$$k_n \approx \frac{\pi n}{R} \left(1 - \frac{1}{R\kappa(R)} \right).$$

To find the correction we write

$$\tan kR \approx \tan k_n R + \frac{ie^{-2C}\epsilon}{\cos^2 k_n R} = -\frac{k_n}{\kappa(R)} + i\frac{1}{\cos^2(k_n R)} e^{-2C}\epsilon,$$

and substitute this expression to Eq. (19) to get

$$\epsilon = -\frac{k_n \cos^2(k_n R)}{\kappa(R)}.$$

The value of the exponentially small coefficient D is determined by the leading term

$$D \approx -i\frac{k_n}{\sqrt{\kappa(R)}} \cos(kR) e^{-C}.$$

An energy calculated as $E = k^2/2m - V_0$ contains then a small complex part

$$E = E_n - i\frac{k_n^2 \cos^2(k_n R)}{mR\kappa(R)} e^{-2C}.$$

The time evolution of the state which is mostly localized in the well will then contain a decaying exponential part

$$|\psi(x)e^{-iEt}|^2 = |\psi(x)|^2 \exp \left\{ -\frac{2k_n^2 \cos^2(k_n R) e^{-2C}}{mR\kappa(R)} t \right\}.$$

This determines the decay rate

$$\Gamma = \frac{2k_n^2 \cos^2(k_n R)}{mR\kappa(R)} e^{-2C}.$$

One may also proceed the other way and calculate the rate from the particle flux (below $p = \sqrt{2mE}$)

$$\Gamma = 4\pi r^2 \frac{1}{2im} \left(\frac{u^*(r)}{r} \frac{d}{dr} \frac{u(r)}{r} - \frac{u(r)}{r} \frac{d}{dr} \frac{u^*(r)}{r} \right) = 4\pi |ND|^2 \frac{p}{pm} =$$

$$\frac{4\pi N^2 k_n^2 \cos^2(kR)}{m\kappa(R)} e^{-2C} .$$

To complete the derivation we need to normalize the wave function in the well to unity. By assuming that it is dominated by the inter-well part (which is the case within the semiclassical approximation) we have

$$N^2 4\pi \int_0^R \sin^2 k_n r dr = 2\pi N^2 = 1 \quad \longrightarrow \quad N^2 = \frac{1}{2\pi R} .$$

With this the result for the decay rate is

$$\Gamma = \frac{2k_n^2 \cos^2(kR)}{mR\kappa(R)} e^{-2C} \equiv \frac{k_n}{mR} \frac{2k_n\kappa(R)}{k_n^2 + \kappa^2(R)} e^{-2C} ,$$

in perfect agreement with the 'imaginary energy' way of doing it. The interpretation of this expression is 'transmission through the barrier' times an 'attempt rate for escaping = number of attempts per second to hit the wall' $\sim v/R = k_n/mR$.

To complete our theory we have to evaluate C for the Coulomb potential when $E = 2(Z - 2)e^2/b$:

$$2C = 2 \int_R^b \sqrt{4m(Z - 2)e^2(1/r - 1/b)} dr = 4\sqrt{m(Z - 2)e^2b} \int_{R/b}^1 \sqrt{\frac{1-r}{r}} dr =$$

$$4(Z - 2)e^2 \sqrt{\frac{2m}{E}} \left[\frac{\pi}{2} - \sin^{-1} \sqrt{\frac{R}{b}} - \sqrt{\frac{R}{b}} \left(1 - \frac{R}{b} \right) \right] .$$

Since typical values for R and b are such that $R/b \ll 1$ we may write it approximately as

$$2C \approx 2\pi(Z - 2)e^2 \sqrt{\frac{2m}{E}} .$$

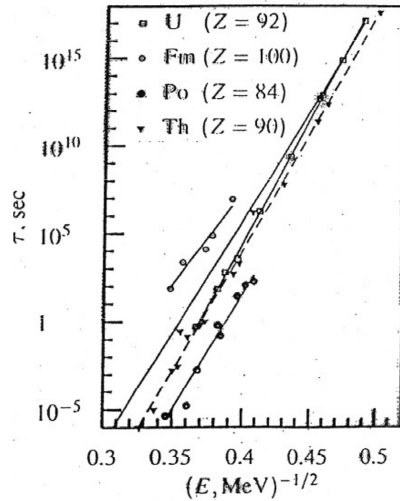
Exponential dependence of the decay rate on energy is remarkable: using isotopes of the same element one can change the decay rate by ~ 24 orders of magnitude (!) by changing E roughly by a factor of 2.5 To the left you see the table of thorium $Z = 90$ isotopes with their α -decay lifetimes which range from less than a fraction of a microsecond to fifteen billion years.

	Mass number	τ	E_α (MeV)
Th	232	1.4×10^{10} yr	4.01
	230	7.7×10^4 yr	4.69
	229	7.34×10^3 yr	4.85
	228	1.91 yr	5.42
	227	18.7 day	6.04
	226	31 min	6.34
	225	8 min	6.48
	224	1.04 s	7.17
	223	0.66 s	7.29
	222	2.9 ms	7.98
	221	1.68 ms	8.15
	220	10 μ s	8.79
	219	1.05 μ s	9.34
	218	0.11 μ s	9.67

A convenient way to check this formula is to plot the logarithm of the decay time $\tau = \Gamma^{-1}$

$$\ln \tau = \ln \left(\frac{mR\kappa(R)}{2k_n^2 \cos^2(kR)} \right) + 2\pi(Z-2)e^2 \sqrt{\frac{2m}{E}},$$

as a function of inverse square-root of energy which is shown here for different elements and their isotopes.



Problem 41. cosh-potential by semiclassical approximation

Apply the Bohr-Sommerfeld quantization rule to calculate the bound state energies of the potential

$$V(x) = -\frac{V_0}{\cosh^2(x/a)}.$$

a). Show that your results can be written in the form

$$E_n = -\left(\sqrt{V_0} - \left[n + \frac{1}{2} \right] \sqrt{\frac{1}{2ma^2}} \right)^2.$$

Hint: You might use the integral

$$\int_0^A \sqrt{A^2 - u^2} \frac{du}{1 + u^2} = \frac{\pi}{2} \left(\sqrt{1 + A^2} - 1 \right) .$$

b). If $V_0 \gg 1/2ma^2$, show that your result approximates the harmonic oscillator behavior at the bottom of the well.

Problem 42. Exactly solvable α -decay problem

Consider a particle of mass m trapped at time $t = 0$ in the potential well

$$V(r) = \begin{cases} -V_0 & r < R \\ +V_1 & R < r < b \\ 0 & b < r \end{cases} ,$$

with positive V_0 and V_1 .

a). Formulate the form of the solution in all three regions with the outgoing wave for the outside region. Specify all relations between momenta in different regions and energy.

b). Solve for the unknown coefficients in terms of introduced momenta; check that your eigenvalue equation has the form equivalent to

$$\frac{\kappa + ik}{\kappa - ik} = e^{2C} \frac{\kappa \sin k_1 R + k_1 \cos k_1 R}{\kappa \sin k_1 R - k_1 \cos k_1 R} .$$

c). Assuming that $e^{-C} \ll 1$ where $C = \kappa(b - R)$ show that this leads to the quantization rule

$$\tan k_1 R = -\frac{k_1}{\kappa} .$$

d). In the high barrier limit $k_n/\kappa \ll 1$ show that this leads to a decay rate

$$\Gamma \approx \frac{k_n}{mR} \frac{8kk_n}{\kappa^2} e^{-2C} .$$

e). Compare the result in part **d)** with the result

$$\Gamma \sim \frac{v}{R} e^{-2C} ,$$

expected from the semiclassical approximation.

Problem 43. Potential with an angle by two methods

Given one-dimensional potential $V(x) = f|x|$ with $f > 0$, find approximate values for the two lowest levels by

a). the semiclassical approximation method and

b). the variational method, using a Gaussian trial function with one variable parameter and minimizing $\langle \hat{H} \rangle$ with respect to it.