II. Non-degenerate PT

A. Perturbation series

\[ H = H_0 + \delta H \]

Non degenerate \(\Rightarrow\) 3 orthonormal basis \(\{|\psi^{(n)}\}\)

\[ \langle \psi^{(n)} | H_0 | \psi^{(n)} \rangle = E^{(n)} \]

\[ E^{(n)} \neq E^{(m)} \text{ if } n \neq m \]

(1) Now we want to find \(E_{\text{pert}}\) of

\[ H|\psi^{(n)}\rangle = E^{(n)} |\psi^{(n)}\rangle + \delta |\psi^{(n)}\rangle \]

\[ E^{(n)} = E^{(n)} + \delta E^{(n)} + \delta^2 E^{(n)} + \cdots \]

Solve \(\delta E^{(n)}\) iteratively

\[ (H_0 + \delta H)|\psi^{(n)}\rangle = E^{(n)} |\psi^{(n)}\rangle + \delta |\psi^{(n)}\rangle + \delta^2 |\psi^{(n)}\rangle + \cdots \]
\[ \psi(0) : H_0 |n(0)\rangle + H_1 |n(0)\rangle = E_0 |n(0)\rangle + E_1 |n(0)\rangle \]

1. To find \( E_n \) : take inner product with \( |n(0)\rangle \)

\[ \langle n(0) | H_0 | n(0) \rangle = E_n - \langle n(0) | H_1 | n(0) \rangle \]

\[ E_n = \langle n(0) | H_0 | n(0) \rangle \]

Simple but very very important.

2. To find \( |n(0)\rangle \) : take inner product with \( |n(0)\rangle \)

\[ \langle n(0) | H_0 | n(0) \rangle + \langle n(0) | H_1 | n(0) \rangle \]

\[ = E_n \langle n(0) | n(0) \rangle + E_1 \langle n(0) | n(0) \rangle \]

\[ = (E_n - E_1) \langle n(0) | n(0) \rangle \]

\[ \sum_{n} \langle n | n(0) \rangle | n(0) \rangle = \sum_{n} \frac{\langle n | n(0) \rangle | n(0) \rangle}{E_n - E_1} \]

3. In general, we have

\[ |n\rangle = |n(0)\rangle + \sum_{n} \frac{\langle n | n(0) \rangle | n(0) \rangle}{E_n - E(0)} \]

\[ \text{How to deal with this?} \]

\[ \text{We will have to choose} \]

\[ \text{a normalization for } |n\rangle \]
Choice #1: $\langle \eta^{(m)} | \eta^{(m)} \rangle = 1$

$\eta^{(m)} | \eta^{(m)} \rangle = 0$

$\xi = 0$

Choice #2: $| \eta \rangle = 2 \frac{1}{2} | \eta \rangle$

$\langle \eta | \eta \rangle = 1 = 2 \langle \eta | \eta \rangle \Rightarrow 2 = (\langle \eta | \eta \rangle)^2$

$\langle \eta | \eta \rangle = (\langle \eta^{(m)} | \eta^{(m)} \rangle + \xi \langle \eta^{(m)} | \eta^{(m)} \rangle \langle \eta^{(m)} | \eta^{(m)} \rangle + \xi^2 \langle \eta^{(m)} | \eta^{(m)} \rangle + \ldots)$

$= 1 + \xi^2 \langle \eta^{(m)} | \eta^{(m)} \rangle + \ldots$

$1 + O(\xi^3)$

So at this order, choices #1, 2 are the same.
C. Second order PT

$\mathcal{O}(\alpha^2)$:

$$H_0 |\psi^{(0)}\rangle \rightarrow H_0 |\psi^{(0)}\rangle = e^{\alpha |\psi^{(0)}\rangle} \rightarrow e^{\alpha |\psi^{(0)}\rangle} \rightarrow E_0^{(0)} |\psi^{(0)}\rangle - E_0^{(0)} |\psi^{(0)}\rangle$$

(i) Energy shift: take inner product with $C_n^{(0)}$

$$\langle n^{(0)} | H_0 - E_0^{(0)} | n^{(0)} \rangle = 0$$

$$E_0^{(2)} = \langle n^{(0)} | H_0 | n^{(0)} \rangle - E_0^{(0)} \langle n^{(0)} | n^{(0)} \rangle$$

(ii) State: take inner product with $C_n^{(1)}$, summation

$$E_0^{(2)} \langle n^{(0)} | n^{(0)} \rangle + \langle n^{(0)} | H_0 | n^{(0)} \rangle = E_0^{(2)} \langle n^{(0)} | n^{(0)} \rangle$$

$$E_0^{(2)} = \langle n^{(0)} | n^{(0)} \rangle = \langle n^{(0)} | H_0 | n^{(0)} \rangle - E_0^{(0)} \langle n^{(0)} | n^{(0)} \rangle$$

$$E_0^{(2)}$$

$$= \sum_{n,m} \frac{\langle n^{(0)} | H_0 | m^{(0)} \rangle \langle m^{(0)} | H_0 | n^{(0)} \rangle}{(E_0^{(0)} - E_0^{(0)}) (E_0^{(0)} - E_0^{(0)2})}$$
\[ |n^{(0)}\rangle = \sum_{m,n} \frac{\langle m^{(0)}|H|n^{(0)}\rangle |m^{(0)}\rangle |n^{(0)}\rangle}{(E_n^{(0)} - E_m^{(0)})^2} \]

\[ = \sum_{m,n} \frac{\langle m^{(0)}|H_2|n^{(0)}\rangle \langle r^{(0)}|H_1|l^{(0)}\rangle}{(E_n^{(0)} - E_m^{(0)})^2} \]

(1) Wavefunction renormalization (Baym)

\[ Z_n = \langle n | \langle n |^{-\frac{1}{2}} \]

\[ = 1 - \frac{1}{2} \sum_{m,n} \frac{|\langle m^{(0)}|H_2|n^{(0)}\rangle|^2}{(E_n^{(0)} - E_m^{(0)})^2} \]

\[ = \frac{2}{\partial E_n} \left( E_n^{(0)} + \langle n^{(0)}|H_1|l^{(0)}\rangle \right) + \epsilon \sum_{m,n} \frac{|\langle m^{(0)}|H_2|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \]

\[ Z_n = \frac{2}{\partial E_n} \left( E_n^{(0)} + \langle n^{(0)}|H_1|l^{(0)}\rangle \right) \]

\[ \mu \text{th element, } E_n \text{ fixed.} \]

Due to all orders in \( \epsilon \).
D. Example

\[ H_0 = -\frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 \]

\[ H_0 = i \hbar \frac{\partial}{\partial x} \]

\[ E_n^{(0)} = \hbar \omega n \left( \frac{\omega}{2\hbar} \right) \text{ ; } n \geq 0 \]

\[ a = \left( \frac{\mu^2}{2\hbar} \right)^{1/2} x + \frac{i}{(2\mu \hbar)^{1/2}} \hbar \text{ ; } [a, a^\dagger] = 1 \]

\[ a|0\rangle = 0 \text{ ; } a^\dagger |n\rangle = \sqrt{n} |n-1\rangle \text{ ; } a |n\rangle = \sqrt{n} |n-1\rangle \]

\[ E_n^{(i)} = \left( \frac{\hbar \omega}{2m} \right)^{1/2} \sqrt{n} |n\rangle |n\rangle \text{ ; } n = 0, 1, 2, \ldots \]

Note: \[ \int dx |V(x)|^2 q(x) = 0 \]

\[ E_{\text{even}} = \sum_n \left\{ \left| \frac{\omega_{n}^{(i)}(\text{even}) |n\rangle |n\rangle \right|^2 \frac{1}{n!} \right\} = \frac{\hbar \omega^2}{2m} \]

\[ E_{\text{odd}} = \frac{\hbar \omega^2}{2m} \left[ \frac{n}{n+1} + \frac{n+1}{n} \right] = \frac{\hbar \omega^2}{2m} \]

Exact solution:

\[ V = \frac{1}{2} m \omega^2 x^2 + \frac{1}{2} m \omega^2 x^2 + \frac{1}{2} \frac{-\hbar \omega^2}{2m} x^2 \]

\[ \frac{1}{2} m \omega^2 (x + \frac{\hbar \omega}{m \omega})^2 = \frac{\hbar \omega^2}{2m} \]

same energy, \[ n = \frac{\hbar \omega}{m \omega} x = \frac{\hbar \omega}{m \omega} \]
III. Closely spaced energy levels

In non-degenerate T IPT, higher orders in \( \xi \) involve higher orders of expressions like

\[
\frac{<\mu \xi | H_{\text{def}} | \nu \xi>}{E_{\mu \xi} - E_{\nu \xi}} \quad (\ast)
\]

(a) If this is not small, the perturbation series will not converge and low orders (the orders we can calculate) do not provide a good approximation.

(b) If the spectrum is degenerate, then \((\ast)\) diverges for some \( \xi \).

This includes fairly standard examples:

- non-rel. Coulomb Hamiltonian energies \( E_n = \frac{1}{2n^2} \) for \( n^2 \) states

- 3d spherically symmetric \( \text{SHO} \)

\[ H = \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \]
A First order degenerate PT

Typically we are handed some orthonormal basis

$$|\psi_{n}\rangle = \alpha_n |\omega_n\rangle$$

$$H_{0}|\psi_{n}\rangle = E_n |\psi_{n}\rangle$$

Let $$H = H_0 + H_{ij}$$, how do we expect the spectrum to behave? 

Let us assume $$H_{ij}$$ is not degenerate.

The energy eigenstates will be

$$|\psi_{n}\rangle \sim |\psi_{n}\rangle^{(0)} + \epsilon |\psi_{n}\rangle^{(1)} + ...$$

There is no reason for this to be $$= |\psi_{n}\rangle$$ for some fixed $$\epsilon$$.

Instead,

$$|\psi_{n}\rangle \sim |\psi_{n}\rangle^{(0)} + \epsilon_{\alpha n} |\psi_{n}\rangle^{(\alpha)}$$

If we try to find $$|\psi_{n}\rangle$$ by starting with $$|\psi_{n}\rangle^{(0)}$$, the change will not in general be small.
Example spin-½ particle

\[ H = \sum_{i} \alpha_i + \mathbf{p}^2 \]

\[ H_0 = \frac{p^2}{2m} \]

\[ \psi_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \psi_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \]

\[ E_1 = \gamma + \epsilon \]

\[ E_2 = \gamma - \epsilon \]

Suppose any orthonormal vectors are a basis of energy eigenvectors.

If we attempt to perturb around, say

\[ \psi_+ = (1) \]

\[ \psi_- = (0) \]

then the difference between \( \psi_+ \) and \( \psi_- \) is finite as \( \epsilon \to 0 \).
(3) Procedure:

We are given the basis \( \{ \{1, j = \alpha \} \} \).

We want to find

\[ \{ i, j = \alpha \} = \{ i, j = \alpha \}^0 + 2 \{ i, j = \alpha \}^0 \]

as before:

\[ (H_0 - E_0^0 ) \{ i, j = \alpha \} = \{ i, j = \alpha \}^0 \]

\( O(\varepsilon^2) \) : automatically solved

\[ \begin{align*}
(2c_{\alpha}) & (H_0 - E_0^0 ) \{ i, j = \alpha \} = (E_0^0 - H_0 ) \{ i, j = \alpha \}^0 \\
& (2c_{\alpha}) \\
& (H_0 - E_0^0 ) \{ i, j = \alpha \} = (E_0^0 - H_0 ) \{ i, j = \alpha \}^0 \\
& (2c_{\alpha}) \\
& (H_0 - E_0^0 ) \{ i, j = \alpha \} = (E_0^0 - H_0 ) \{ i, j = \alpha \}^0 \\
\end{align*} \]

(4) Finding \( E_0^1 \)

\[ \vec{A} = \sum_{\alpha} \{ i, j = \alpha \} \{ i, j = \alpha \}^0 \]

\[ \{ i, j = \alpha \} = \sum_{\alpha} \{ i, j = \alpha \} \{ i, j = \alpha \}^0 \]

Take inner product with \( \{ i, \{ j = \beta \} \} \) LHS of \((*)\) vanishes:

\[ \sum_{\alpha} \{ i, \{ j = \beta \} \} H_0 \{ i, j = \alpha \} \{ i, j = \alpha \}^0 = E_0^0 \{ i, \{ j = \beta \} \} \{ i, j = \alpha \}^0 \]

\[ (H_0)_{\alpha, \alpha} U(\alpha)_{\alpha} = E_0^0 U(\alpha)_{\alpha} \]

\( \{ i, j = \alpha \} \) is an eigenstate of \( H_0 \) in the subspace \( \{ i, j = \beta \} \)

\( E_0^1 \) is an eigenvector.
In general, we can write \( H \) in block form:

\[
\begin{pmatrix}
  H_{11} & H_{12} & H_{13} \\
  H_{21} & H_{22} & H_{23} \\
  H_{31} & H_{32} & H_{33}
\end{pmatrix}
\]

where \( H \) is a \( d \times d \) dimensional matrix.

At first order in \( \epsilon \), we diagonalize \( H \); the eigenvalues are the first order shifts \( E_{\alpha} \).

(b) Finding \( \langle \lambda | \gamma \rangle \)

1. Take inner product of (1) with \( \psi_{\alpha}^{\dagger} \) from (1):

\[
\langle \psi_{\alpha} | H | \gamma \rangle = \langle \psi_{\alpha} | H_{\alpha \beta} | \gamma \rangle
\]

2. Use \( \psi_{\alpha}^{\dagger} | \psi_{\alpha} \rangle = 0 \) and (3):

\[
\langle \psi_{\alpha} | H | \gamma \rangle = \langle \psi_{\alpha} | H_{\alpha \beta} | \gamma \rangle = \langle \psi_{\alpha} | H | \gamma \rangle
\]

3. Use (4) and (5):

\[
\langle \psi_{\alpha} | H | \gamma \rangle = \frac{\langle \psi_{\alpha} | H_{\alpha \beta} | \gamma \rangle}{E_{\alpha} - E_{\beta}}
\]

4. Use (6):

\[
\langle 0 | H | \gamma \rangle = \frac{\langle 0 | H_{\alpha \beta} | \gamma \rangle}{E_{\alpha} - E_{\beta}}
\]
We can choose our basis such that \\
\langle \psi_{jm} | \psi_{jm'} \rangle = \delta_{mn} \delta_{m'm}.

\[ L_{jm} = \sum \langle \psi_{jm} | \psi_{jm'} \rangle (\epsilon_{jm'} - \epsilon_{jm}) \]

If we set \( C = 0 \), \( \langle \psi_{jm} L_{jm} \psi_{jm'} \rangle = \delta_{mn} \delta_{m'm} \)

\[ \langle \psi_{jm} \rangle = \sum \langle \psi_{jm} | \psi_{jm'} \rangle \frac{(\epsilon_{jm'}) - (\epsilon_{jm})}{\epsilon_{jm'} - \epsilon_{jm}} \]

\[ \langle \psi_{jm} | \psi_{jm'} \rangle \]

\[ \langle \psi_{jm} | \psi_{jm'} \rangle \frac{(\epsilon_{jm'}) - (\epsilon_{jm})}{\epsilon_{jm'} - \epsilon_{jm}} \]

\[ \langle \psi_{jm} | \psi_{jm'} \rangle \frac{(\epsilon_{jm'}) - (\epsilon_{jm})}{\epsilon_{jm'} - \epsilon_{jm}} \]

(3) Example: Stark effect

Hydrogen atom in constant electric field (ignore spin)

\[ E = E_z = q = E_z \]

For \( n = 1 \):

\[ E_1 = \langle 1 | E_z | 1 \rangle \]

\[ = \int d^3r \left| \psi(r) \right|^2 \epsilon \cos \theta \]

\[ = \epsilon \]

\[ = 0 \quad \text{(deduce from 'parity selection rule')} \]

\[ \text{(must go to 2nd order M.E...)} \]
\[ n = 2 \text{ states have a degeneracy:} \]
\[ 2S \text{ has } 2 \not= 0 \]
\[ 2P \quad l=1, m_s = \pm 1, 0 \]
\[ \sum \text{ 4 states} \]

We want to diagonalize \( H = eEz \) in this subspace.

- Parity selection rules

\[ \Pi: \psi_{(x,y,z)} \rightarrow \psi_{(-x,-y,-z)} \]  
\[ \Pi^2 = 1; \quad \Pi x \Pi y = -\Pi y \Pi x \]

Coulomb problem: \( [H, \Pi] = 0 \Rightarrow \text{diagonalize both} \]

New \( \psi_{\pm m} = e^{\pm \frac{\pi m}{\cos \theta}} \psi_\theta \)

\[ \Pi: (\theta, \phi) \rightarrow (\theta, \pi + \phi) \Rightarrow \psi_\theta \rightarrow (-1)^m \psi_{-m} \]
\[ \langle \psi_{m'} | \Pi | \psi_{m''} \rangle = (-1)^{m'+m} \]
\[ \Pi^2 = 0 \text{ unless } l = 0 \text{ or } l = \pm 2 \]

\[ \text{Parity selection rule:} \]

Pathway only \( \langle 2S | 2, 2P, m_\sigma \rangle \) survives
Angular momentum selection rule:

\[ z \propto \cos \theta \]

\[ \langle w | \hat{L}_z | z \rangle \propto \sum_{\ell} e^{i\ell \theta} \langle \ell, m | z \rangle = 0 \]

But we know that already.

\[ \langle \ell, m | z \rangle \]

Still degenerate at 1st order.

For the rest, must diagonalize:

\[
\begin{pmatrix}
0 & \langle 2\ell | \hat{E} \hat{z} | 2\ell, m, 0 \rangle \\
\langle 2\ell, m | \hat{E} \hat{z} | 2\ell \rangle & 0
\end{pmatrix}
\]

\[ \langle 2\ell | \hat{E} \hat{z} | 2\ell, m, 0 \rangle = 0 \]

No other dimensionful \( \theta \)!

\[ -3E_0 \]

\[ \begin{pmatrix}
0 & -3E_0 \\
-3E_0 & 0
\end{pmatrix} \]

Has eigenvectors:

\[ \psi_+ = \frac{1}{\sqrt{2}} (1, 1) \]

\[ E^+ = 3E_0 \]

\[ E^- = -3E_0 \]
(a) Higher order

- Let us assume degeneracy is completely split at first order (if not, the story is a bit complicated)

Locally diagonalized the Hamiltonian

\[ H_0 + \begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix} \]

Exactly, this Hamiltonian is nondegenerate (by definition). Now we confront \( H_1 \) as our unperturbed Hamiltonian and

\[ H_1 = \begin{pmatrix} 0 & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & 0 & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & 0 \end{pmatrix} \]

can be treated as a perturbation.
B. Nearly degenerate states

\[ E \uparrow \quad (\mathbf{D}) \]
\[ \quad \longrightarrow \quad \mathbf{V} \]
\[ \mathbf{E} \mathbf{M} \quad \mathbf{E} \mathbf{M} \quad \mathbf{E} \mathbf{M} \quad \mathbf{E} \mathbf{M} \quad \mathbf{E} \mathbf{M} \quad \mathbf{E} \mathbf{M} \]

\[ \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \]

\[ \text{assume } E_{\mathbf{D}} - E_{\mathbf{M}} \ll \langle H_2 \rangle \]

\[ H_3 = \begin{pmatrix} E_{\mathbf{D}} & E_{\mathbf{M}} \\ E_{\mathbf{M}} & E_{\mathbf{D}} \end{pmatrix} \]

\[ \text{assume matrix elements are smaller than gap between typical states not in nearly-degenerate subspace.} \]

\[ \begin{pmatrix} E_{\mathbf{D}} & 0 \\ 0 & E_{\mathbf{M}} \end{pmatrix} \rightarrow \begin{pmatrix} 0 & E_{\mathbf{M}} \\ E_{\mathbf{D}} & 0 \end{pmatrix} \]

\[ V_1 \quad V_2 \]

\[ \text{diagonalize these } V, \quad \text{using standard perturbation theory.} \]
To diagonalize $V_z$, we need merely work in the subspace $D_z$ of nearly-degenerate eigenstates of $H_0$.

Call the eigenstates of $H_0$ living in $D_z$

$$|\tilde{k}\tilde{l}\tilde{m}\cdots\tilde{d}\rangle$$

with eigenvalues $E_\tilde{k}$ of $H_0$.

Call the remaining eigenstates of $H_0$

$$|\tilde{k}'\tilde{l}'\tilde{m}'\cdots\tilde{d}'\rangle$$

with eigenvalues $E_{\tilde{k}'}$ of $H_0$.

Now $V_z$ appears in perturbation theory through expressions of the form

$$\frac{\langle \tilde{k}'|V_z|\tilde{k}\rangle}{E_{\tilde{k}'} - E_{\tilde{k}}}$$

which are (hopefully) not large.
Example:

Take $S_2$ to be 2-dimensional. We must then diagonalize:

$$
\begin{pmatrix}
E_1 & \psi \\
\psi^* & E_2
\end{pmatrix}
$$

Eigenvalue equation:

$$(E_i - \bar{v})(E_i - \bar{v}) = \mu_i^2 = 0$$

$$\bar{v} = \frac{1}{2}(E_i + E_2) \pm \sqrt{(E_i + E_2)^2 - 4E_iE_2 + 4\mu_i^2}$$

Exercise: read pp. 237-241 of Boyum (will have notes available)
Non-perturbative methods

I. Introduction

If energies are large compared to the scale of perturbations, they may work very badly.

Furthermore, there are cases where there is no obvious split

\[ H = H_0 + \varepsilon H' \]

Nevertheless, we can estimate the energy of the ground state.
II. The variational method.

(1) The basic point

- Given a state $|\psi\rangle$,

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

Now insert $|\psi\rangle = \sum_n \alpha_n |n\rangle$ as eigenstates of $H$.

$$\langle E \rangle = \sum_n \frac{\langle \psi | H | n \rangle}{\langle \psi | \psi \rangle} = \sum_n E_n \frac{\langle n | \psi \rangle^2}{\langle \psi | \psi \rangle}$$

$$\geq E_0 \frac{\langle \psi | \psi \rangle}{\langle \psi | \psi \rangle} = E_0$$

Therefore we try to choose a state $|\psi\rangle$ to minimize $\langle E \rangle$.

- This technique is used when we cannot write $H = H_{\text{ex}} + H_{\text{int}}$ where $H_{\text{ex}}$ and $H_{\text{int}}$ are exactly solvable. Instead, we use physical intuition to choose a "trial family of "trial states" $|\psi_\alpha\rangle$ where $\alpha$ are some parameters, and minimize $\langle E \rangle$ by varying $\alpha$. 
(2) Examples - we will demonstrate and test this method on potentials for which we secretly know the answers.

(a) Infinite square well

\[ V(x) = \begin{cases} 0 & |x| \leq L \\ \infty & |x| > L \end{cases} \]

\[ \psi(x) = \frac{1}{\sqrt{2L}} \cos \left( \frac{n\pi x}{2L} \right) \quad E_n = \frac{n^2 \pi^2}{8L^2} \]

- Let us say we were ignorant of the precise solution. We know:

  (a) Wavefunction should vanish for \( x \geq L \)

  (b) Wavefunction should have no other nodes.

\[ \begin{array}{c}
\text{guess} \quad 1x^2 - 1x^2 \\
\langle E \rangle = \frac{(4m_1)(2m_1)}{2\hbar^2} \left( \frac{\pi^2}{4m_1 L^2} \right)
\end{array} \]

\[ \frac{d\langle E \rangle}{d\alpha} \Rightarrow \text{solution which is } \text{a minimum when } \alpha = \frac{\pi}{2}, 2.37 \]

\[ \langle E \rangle = \left( \frac{5\hbar^2}{m_1 L^2} \right) E_0 \approx 1.000298 E_0 \]

\[ \text{7% to accuracy} \]
\[ \psi(x) = A_i \left[ \left( \frac{2E_i}{\hbar^2} \right)^{1/3} (x - E_i) \right] \]

where \( \psi''(x) = 0 \) at even \( n \) nodes

\[ \psi'(x) = 0 \] at odd \( n \) nodes

\[ E_0 = \frac{h^2}{8m} \left( \frac{m^2R^2}{h^2} \right)^{1/3} \]

This involves a special function which might scare people.

Let us try a nice trial wave function. It should die off rapidly at infinity and have no nodes.

\[ \phi(x) = \text{gaussian} \quad \psi(x) = (\frac{1}{\sqrt{2\pi}})^{1/2} e^{-ax^2} \]
\[ \langle E \rangle = \int d^3x \, \psi^*(x) \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{e^2}{4\pi \epsilon_0 r} \right) \psi \]

\[ = \frac{\hbar^2}{{2m}} \left( \frac{\partial}{\partial r} \right)^2 \]

\[ \frac{\partial}{\partial r} \langle E \rangle_m \bigg|_{r=\infty} = 0 \]

\[ \Rightarrow \alpha = \left( \frac{\hbar^2}{2m} \right)^{\frac{1}{2}} \]

\[ \langle E \rangle = \frac{1}{\hbar^2} \left[ \frac{1}{r^2} + \frac{1}{r^3} \right] \left( \frac{8 \frac{\epsilon_0}{m}}{\hbar^2} \right)^{\frac{1}{2}} \]

\[ 0.813 \quad \text{compare to } 0.8086 \]

(3) Why does this work so well?

Let \( \langle \psi \rangle = \langle E_0 \rangle + \langle \delta \psi \rangle \)

\[ \langle \delta \psi \rangle = \alpha \langle E_0 \rangle + \langle \delta \psi \rangle \quad \text{and choose} \]

\[ \langle \delta \psi \rangle = \alpha \langle E_0 \rangle + \langle \delta \psi \rangle \quad \text{so} \quad \langle \delta \psi \rangle_1 \langle E_0 \rangle = 0 \]

\[ \langle E \rangle = \frac{12 \alpha^2 \langle E_0 \rangle + \delta^2 \langle \psi_{11} | 1 | \psi_{11} \rangle}{1 + \alpha^2 \langle E_0 \rangle + \delta^2 \langle \psi_{11} | 1 | \psi_{11} \rangle} \]

\[ = \langle E_0 \rangle + \frac{\delta^2}{1 + \alpha^2 \langle E_0 \rangle} \left( \langle \psi_{11} | 1 | \psi_{11} \rangle - \langle E_0 \psi_{11} | 1 | E_0 \psi_{11} \rangle \right) \]

\[ \approx 0(\epsilon^2) \text{ for } 0(\epsilon) \text{ match in total wave function.} \]
(a) Back to helium:

\[ \psi = \left( \frac{1}{\sqrt{a_0^3}} \right)^{1/2} e^{-\frac{r}{a_0}} \left( \frac{1}{3} \right)^{1/2} \left( \frac{1}{3} \right)^{-1/2} \]

Next we want to choose Z as our variational parameter.

\[ E[Z] = -2 \left( \frac{\text{int}}{2Z^2} \right) \left( 4Z^2 - \frac{2}{\text{int}} \right) \]

\[ \text{minimum of } Z = \frac{27}{16} \]

\[ E = -77.5 \text{ eV} \]

which is a marked improvement over previous solution.
C. Interpretation

\[ \psi(x) \sim e^{\frac{-i}{\hbar} \int_{x_0}^{x} \left( \frac{p^2}{2m} + V(x') \right) dx'} \]

\[ \psi(x_\alpha) = e^{\frac{-i}{\hbar} \int_{x_0}^{x_\alpha} \left( \frac{p^2}{2m} - \mu(x') \right) dx'} \]

\[ \psi(x_\alpha) \sim \frac{1}{\sqrt{2\hbar}} \text{ for } \mu(x) \text{ as } V(x) \text{ and } \psi(x) \text{ as } \phi(x) \]

D. Tunneling

\[ \psi(x) \sim \frac{1}{\sqrt{2\hbar}} e^{-\frac{i}{\hbar} \int_{x_0}^{x} \left( \frac{p^2}{2m} - \mu(x') \right) dx'} \]

\[ \psi(x_\alpha) \sim \frac{1}{\sqrt{2\hbar}} e^{\frac{-i}{\hbar} \int_{x_0}^{x_\alpha} \left( \frac{p^2}{2m} - \mu(x') \right) dx'} \]

\[ \psi(x_\alpha) = e^{\frac{-i}{\hbar} \int_{x_0}^{x_\alpha} \left( \frac{p^2}{2m} - \mu(x') \right) dx'} \]

The approximate tunneling occurs if \( E < \mu \) and the case \( p \to 0 \).

\[ \psi(x) \sim \frac{1}{\sqrt{2\hbar}} \text{ for } V(x) \text{ as } \mu(x) \text{ and } \psi(x) \text{ as } \phi(x) \]

\[ \psi(x_\alpha) \sim \frac{1}{\sqrt{2\hbar}} e^{\frac{-i}{\hbar} \int_{x_0}^{x_\alpha} \left( \frac{p^2}{2m} - \mu(x') \right) dx'} \]

\[ \psi(x_\alpha) = e^{\frac{-i}{\hbar} \int_{x_0}^{x_\alpha} \left( \frac{p^2}{2m} - \mu(x') \right) dx'} \]
III. The WKB approximation

A. Short-wavelength limit

If \( \psi(x) \) varies rapidly enough, \( V(x) \) can be treated as constant.

\[
\psi(x) \sim A(x) e^{\frac{2i}{\hbar} \int V(x) \, dx}
\]

We need the wavelength to change very little over the course of 1 wavelength:

\[
\frac{\Delta \lambda}{\lambda} \ll 1 \Rightarrow \frac{\lambda \Delta \lambda}{\hbar} \ll 1
\]

\[
\Delta \lambda = \frac{\hbar}{pc} \ll \frac{\hbar}{2\pi \lambda(E-V_0)}
\]

\[
\Delta \lambda \ll \frac{\hbar}{2\pi \sqrt{2mV}} \ll 1
\]

This is a slight dodgy as \( E, \mu \), are dimensionful we need to talk about dimensionless numbers (e.g. ratios of dimensionful quantities) to talk about "small" or "large".
& Systematic expansion

\( \psi(\omega) = e^{i\phi(\omega)} = e^{-\frac{1}{2} \nabla^2 \varphi + \frac{2\omega}{c} (E-VG) \varphi} \), \( \psi = 0 \)

\( \nabla \psi = i \frac{\nabla \phi}{\hbar} e^{i\phi} \)

\( \nabla^2 \psi = i \frac{\nabla^2 \phi}{\hbar^2} e^{i\phi} - \frac{i}{\hbar^2} (\nabla \phi)^2 \)

\( (\nabla \phi)^2 = 2m(E-VG) + \frac{\hbar^2}{\hbar^2} (\nabla \phi)^2 \)

Now let \( \psi = \psi_0 + \psi_1 + \psi_2 + \cdots \)

and solve order by order assuming \( \hbar \to 0 \), etc.

\( \nabla \psi_0 = \sqrt{2m(E-VG)} \) = \( \varphi(x) \)

\( \psi_0 = \int_{-\infty}^{x} dx' \sqrt{2m(E-VG)} \approx \int_{-\infty}^{x} dx' \varphi(x') \)

\( 2\partial \psi_0 \partial \psi_1 + \cdots \chi_{\omega} \nabla \psi_0 \)

\( \nabla \psi_1 = \frac{\hbar^2}{2m} \nabla^2 \varphi_0 \)

\( \psi_1 = \frac{\hbar^2}{2m} \ln(p\varphi) + \frac{1}{2m} (\ln(p\varphi))^2 \)

\( \psi(x) \sim \frac{1}{p\varphi} \sum \varphi(x') \)

\( \psi(x) \sim \left( \frac{p\varphi}{p\varphi} \right)^{\frac{1}{2}} \right \}

\( \psi(\omega) \sim \left( \frac{p\varphi}{p\varphi} \right)^{\frac{1}{2}} \right \}

\( \psi(\omega) \sim \left( \frac{p\varphi}{p\varphi} \right)^{\frac{1}{2}} \right \} \)
C. Interpretation

a) Phase factor - energy eigenvalue
\[ \psi(x,t) = e^{i\int \mathcal{L} dx} \]

- Interpretation: Feynman path integral

Recall:
\[ \psi(x,t) = \int Dx(t)e^{i\frac{\mathcal{L}}{\hbar}} \]

(Asymptotic) "small-\( t \) limit": exponential oscillates very rapidly

\[ \frac{\partial}{\partial x(t)} = 0 \]

But these are just the classical equations of motion.

\[ \sum_{\text{causal solutions}} A(x(t))e^{i\int \mathcal{L} dx(t)} \]
(b) Prefactor

Probability of particle being in interval \( [x, x+\delta x] \),
\[
\left( \frac{dx}{u(x)} \right) = \frac{1}{\hbar 0}\text{ for natural probability amplitude.}
\]

(c) Aside: Stationary phase approximation

Consider \( I = \int dx \ e^{i f(x)} \quad \alpha \gg 1 \)

\[
f(x) = \alpha f_n(x) + \frac{1}{2} \alpha^2 g_n(x) + \frac{1}{6} \alpha^3 \theta(x - x_0) + \ldots.
\]

\[
\implies I \approx \alpha f_n(x) e^{i E_n \alpha}.\]

\[\int f_n(x) dx \text{ correction to integrand}\]

\[
\approx I = \frac{1}{\alpha^2 \hbar} \int dy \ e^{i \left( \alpha y + \frac{1}{2} \alpha^2 g_n(y) + \ldots \right)}
\]

\[
\times \left( \frac{\alpha}{\hbar} \right)^\frac{1}{2} e^{i \alpha f_n(y)} (1 + O(\alpha^2), \ldots)
\]
Bound state problems

(3) The basic issue

\[ V(x) \]

\[ \psi(x) = \frac{1}{k(x)} e^{-\int_{x_0}^{x} dx' k(x')} \]

Region I

\[ x < x_0 \]

(approximative)

(Will hold)

\[ d_0 = \int_{x_0}^{x} dx \sqrt{2m(E - V(x))} \]

\[ \frac{d}{dx} \left( \frac{2mE - V(x)}{4k(x)} \right) \]

should die out as \( x \to -\infty \)

\( \Rightarrow \) pick (2) sign for \( x_0 \) fixed

Region II

\[ x \gg x_0 \]

Region III

\[ x < x_0 \]

Typically: match to region

I, III - fixers \( \beta \)

\( \Psi \) square well.
For $x \to \pm \infty$ WKB approximation fails.

For $x \to x_{A,B}$ there are 2 methods for dealing with this.

1. Wavefunctions near turning points

   Expand $V(x)$ near $x = x_B$

   $V(x) \approx V(x_B) + (x - x_B) V_1 + (x - x_B)^2 V_2 + \cdots$

   where $V(x_B) = E$

   $\text{ISE: } \frac{-\hbar^2}{2m} \psi'' + \left[ (x - x_B) V_1 - (x - x_B)^2 V_2 \right] \psi = 0$

   The quadratic term is small if $|x - x_B| \ll \frac{V_1}{V_2}$

   Now

   $\frac{-\hbar^2}{2m} \psi''(x) + (x - x_B) V_1 \psi(x) = 0$

   has an exact solution: 

   Let $\psi(x) \equiv L(y)$

   $-\frac{\hbar^2}{2mL^2} \frac{d^2}{dy^2} \psi(y) - \frac{2mL^3}{\hbar^2} y \psi(y) = 0$

   $\Rightarrow \left[ -\frac{\hbar^2}{2mL^2} + \frac{2mL^3}{\hbar^2} y \right] \psi(y) = 0$

   $L = \left( \frac{\hbar^2}{2mL^3} \right)^{1/2}$
How do we solve this? (E. Lundell, Lifschitz, App. b)

Let \( \psi = \int_{C} z(t)e^{gt} dt \)

\( \psi \) is independent of contour as long as asymptotic shaded region is fixed.

\[
-\nabla^{2} \psi + g \psi = \int_{C} -\epsilon \frac{\partial z(t)}{\partial t} e^{gt} + 2\epsilon \frac{\partial^{2} z(t)}{\partial t^{2}} e^{gt} = \int_{C} e^{gt} (2\epsilon \frac{\partial z(t)}{\partial t} + \epsilon^{2} \frac{\partial^{2} z(t)}{\partial t^{2}}) \Rightarrow z(t) = e^{-\frac{1}{2}gt}
\]

now we need to choose \( C \) such that this integral converges. For large \( t \), the \( t^{3} \) term dominates

\( \Rightarrow \text{Re}(t^{3}) > 0 \)

Furthermore, we want \( \psi \to 0 \) as \( t \to \infty \)

\( \Rightarrow \) do not asymptote to region (2)
\[ \int_0^\infty \cos \left( \frac{1}{2} u^2 - uv \right) du = A_1(x) \]

- Now note first that for large enough \( y \), one could use the \( \text{WKB} \) approximation on \( A_1(y) \).

- Furthermore, by choosing \( C \) such that \( A_1(y) \) does not blow up as \( y \to \infty \), we have chosen our solution such that \( \psi \sim e^{-\frac{1}{\hbar} x^2} \).

For \( y \gg 1 \): \( A_1(y) \approx \frac{1}{2y} e^{-\frac{1}{2} y^2} \) (use \( \text{WKB} \) approximation)

\[ g = \left( \frac{2\sqrt{\hbar}}{m} \right)^{\frac{1}{3}} (x-y) \]

which matches the WKB approximation.

\[ \psi(x) \approx A_1 \frac{1}{\sqrt{\hbar}} e^{\frac{1}{2} x^2} \]

\text{Exercise: } when \( \Delta \) what \( (x-y) \) is the \( \text{WKB} \) approximation compatible with linear approximation for \( U(x) \)?

\text{Note that this is valid under...}
For $x \in \mathbb{R}$, we can use the stationary phase approximation

$$
\psi = \frac{c_1}{i \pi} \cos \left( \frac{1}{i \hbar} \int_x^{x_0} p(x) \, dx + \frac{\pi}{4} \right)
$$

we have fixed $A, B$ (up to a phase factor)

exercise: show this is a true stationary phase approximation.

Similarly, we can expand $V$ near $x = x_0$, and do the same thing.

$$
\psi = \frac{c_2}{i \pi} \cos \left( \frac{1}{i \hbar} \int_{x_0}^{x} p(x) \, dx + \frac{\pi}{4} \right)
$$

These two must match — up to a factor of $\frac{c_1}{c_2} \exp \left( \frac{-i \pi}{4} \right)$

$$
\frac{1}{i \hbar} \int_x^{x_0} p(x') \, dx' - \frac{\pi}{4} = -\frac{1}{i \hbar} \int_{x_0}^{x} p(x') + \frac{\pi}{4} + 2 \pi n
$$

$$
\frac{1}{i \hbar} \int_{x_0}^{x} p(x') \, dx' = (2n + \frac{1}{2}) \pi
$$

Bohr-Sommerfeld quantization rule.
Example: consider a p-orbital in the potential $V = k|x|$

\[ \int p(x) \, dx = (\pi + \frac{3}{2})n^2 \]

\[ U(x) = \begin{cases} 
0 & \text{if } |x| < \alpha \\
V_0 & \text{if } |x| = \alpha \\
\infty & \text{if } |x| > \alpha 
\end{cases} \]

$k_x = E_{k_x}$ \quad $k_y = E_{k_y}$

$p(x) = \sqrt{2m(E - k_x \alpha^2)}$

\[ \int E_{k_x} \, dx \sqrt{2m(E - k_x \alpha^2)} = \left( \frac{n^2 \pi^2}{2} \right) \alpha^2 \]

\[ \int_0^{2\pi} E_{k_x} \, dy \sqrt{2m(E - k_x \alpha^2)} = \left( \frac{n^2 \pi^2}{2} \right) \alpha^2 \]

\[ E = \left( \frac{k^2}{2m} \right) \left( \frac{n^2 \pi^2}{2} \right) \alpha^2 \]

\[ c = \int_0^1 d\gamma \left[ (1 - \gamma)^2 \right] = \frac{3}{2} \]

\[ E = \left( \frac{3k^2}{4m} \right) \left( \frac{n^2 \pi^2}{2} \right) \]
Example 2: \[ V(x) = \lambda x^4 \]

\[ E_n = \frac{N_n x}{m \lambda^2} \left[ \frac{\mu + \nu}{\mu} \right]^{\nu / 2} \]

some integral

\[ E_{n(\text{num})} \approx \frac{E_n}{(\text{numeral})} \]

\[ E_{(''')} \approx \frac{E_n}{(''')} \]

continues to improve!

Barrier penetration

---

The story is slightly different:

Here we want to fix, whereas to \( R \) is completely okay.

Even if moving work on \( L \) is \( I \).
To work this out, we can use connection formula:

\[ \frac{1}{\mu} \cos \left( \int_{x_0}^{x} p(x') \, dx' \right) \quad \Rightarrow \quad \frac{1}{\mu(x)} e^{-\int_{x_0}^{x} k(x') \, dx'} \]

\[ \int_{\text{Im}(\mu(x) - E)} \]

Similarly we could look for contours

\[ \mu \Rightarrow \int_{c} e^{\frac{1}{\mu} + \mu} \]

such that solution is given by exponentially \( \exp \frac{1}{\mu} \). 

\[ \frac{1}{\mu} \sin \left( \int_{x_0}^{x} p(x') \, dx' \right) \quad \Rightarrow \quad \frac{1}{\mu(x)} e^{\int_{x_0}^{x} k(x') \, dx'} \]

Similarly for

\[ \frac{1}{\mu} e^{\int_{x_0}^{x} k(x) \, dx} \quad \Rightarrow \quad \frac{1}{\mu(x)} e^{\int_{x_0}^{x} k(x') \, dx'} \]

Linear combinations give us

\[ \frac{1}{\mu(x)} e^{\int_{x_0}^{x} p(x') \, dx'} \quad \Rightarrow \quad A e^{-\int_{x_0}^{x} k(x') \, dx'} + B e^{\int_{x_0}^{x} k(x) \, dx} \]
\[ T = \frac{\psi_{n_{1}}^{*} \psi_{n_{2}}}{|\psi_{n_{1}}^{*} \psi_{n_{2}}|} = \frac{1}{\hat{\rho}_{n_{1}} \hat{\rho}_{n_{2}}} \frac{E_{2}^{2}}{A_{1}^{2}} \]

\[ = \frac{4}{(2\theta + \theta_{t})^{2}} \]

\[ \Theta_{11} = \frac{1}{\theta^{2}} \cdot e^{-2\int_{0}^{b} k(x) dx} \]
Ex: alpha decay as He^4 nucleus makes large step

\[ \nu = \frac{1}{m} \sqrt{2m(E_{\text{fin}})} \]

Killing energy:
\[ \frac{2m\nu^2}{\hbar^2} - \frac{2m\nu^2}{\hbar^2} = \text{seemingly} \]

Tunneling rate:
\[ R_0 = \frac{2m(E_{\text{fin}})}{2m\nu^2} e^{-2\varphi} \quad \text{with } \varphi = \int_{x_0}^{x_1} \frac{dx}{\sqrt{2m(E_{\text{fin}})}} \]

Proof of long path and \( x \), given particle \( x_0 \) and \( x_1 \).