Chapter 6: Time-Independent Perturbation Theory

Most problems cannot be solved exactly. We need approximations. Perturbation theory is one of the approximations.

First we will study the non-degenerate case.

Suppose we have a problem that we can solve such as the square well or the harmonic oscillator. We will use the notation of Ch. 3:

\[ H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad \rightarrow \quad H^0 |\psi_n^0 \rangle = E_n^0 |\psi_n^0 \rangle \]

\[ \langle \psi_n^0 |\psi_m^0 \rangle = \delta_{nm} \]
Adding a tiny perturbation to the square well already renders the problem not exactly solvable:

\[ H \psi_n = E_n \psi_n \]

However, common sense indicates that the solutions cannot be too different from the solutions of the perfect square well. Thus, we apply perturbation theory:

\[ H = H^0 + \lambda H' \]

The little bump, \( \lambda \) could be the bump's height, but for the math it is an auxiliary number that will be made 1 at the end.
We will assume that we can expand the exact results in powers of $\lambda$, which basically controls the order of the expansion:

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots \quad E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$$

$$(H^0 + \lambda H')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots]$$

$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots]$$

Collecting the same powers left and right:

$$H^0 \psi_n^0 + \lambda(H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2(H^0 \psi_n^2 + H' \psi_n^1) + \cdots$$

$$= E_n^0 \psi_n^0 + \lambda(E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2(E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \cdots$$
Since $\lambda$ is arbitrary and simply controls the power expansion, now we make equal the terms with the same power:

\[ H^0 \psi_n^0 = E_n^0 \psi_n^0 \]

\[ H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \]

\[ H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 \]

... etcetera ...

Perturbation theory can lead to very accurate results! Example quantum electrodynamics, the most accurate theory of all.
6.1.2 First-Order Theory:

Take the first order expression

\[ H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \]

and construct the inner product with \( \psi_n^0 \)

\[ \langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle \]

From Chapter 3, remember notation: \( \langle \hat{Q} \rangle = \int \Psi^* \hat{Q} \Psi \, dx = \langle \Psi | \hat{Q} \Psi \rangle \)

\[ \langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle \]

Because \( H^0 \) is Hermitian: \( \langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle \)
\[ \langle \psi_n^0 | H^0 | \psi_n^1 \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle \]

From last line, previous page, these two terms are equal

\[ E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle \]

**Example 6.1:**

Consider, as usual ☺, the 1D infinite square well.

The solutions are \[ \psi_n^0(x) = \sqrt{\frac{2}{a}} \sin \left( \frac{n\pi}{a} x \right) \]
This is the exact solution of course: all levels are shifted uniformly. Higher order corrections vanish.

\[ E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0 \]

This is reasonable but not the exact solution. Higher order corrections will improve the accuracy (in HW19 you will be solving this integral).

\[ E_n^1 = \frac{2V_0}{a} \int_0^{a/2} \sin^2 \left( \frac{n\pi}{a} x \right) \, dx = \frac{V_0}{2} \]
We have found the correction to the energies. Now let us address the wave functions. Start again with:

\[ H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \]

Rearranging:

\[ (H^0 - E_n^0) \psi_n^1 = -(H' - E_n^1) \psi_n^0 \]

Expanding in a complete basis:

\[ \psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0 \]

\[ \sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n^1) \psi_n^0 \]
Inner product:

\[
\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle.
\]

\[\delta_{lm}\]

0 if \(n\) and \(l\) are different

\[
(E_l^0 - E_n^0) c_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle
\]

Rearranging and switching “l” with “m”:

\[
c_m^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}
\]

\[
\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0
\]

No divergences since we are assuming that the level “n” is non-degenerate
6.1.3 Second-Order Energies:

We use a formula we derived a few pages before:

\[ H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 \]

Again, we take the inner product with \( \psi_n^0 \) and arrive to:

\[ \langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle \]

Again, we use the hermiticity of the unperturbed \( H^0 \):

\[ \langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle \]

The first term on each side cancels.
We are left with a formula for the quantity we need:

\[
E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle
\]

Moreover, we already expanded in a complete basis before:

\[
\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0
\]

Then:

\[
\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0
\]

Also, we already deduced the wave function first-order correction:

\[
\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0
\]
Putting all together:

\[ E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_m^0 \rangle}{E_n^0 - E_m^0} \]

\[ E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \]

We use Hermitian

\[ \langle \Psi | \hat{Q} \Psi \rangle = \langle \hat{Q} \Psi | \Psi \rangle \]

and \[ \langle g | f \rangle = \langle f | g \rangle^* \]

from chapter 3.

Usually the derivation of formulas stops here, although in principle we can follow the same steps at any order.