Chapter 7: Time-Independent Perturbation Theory

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

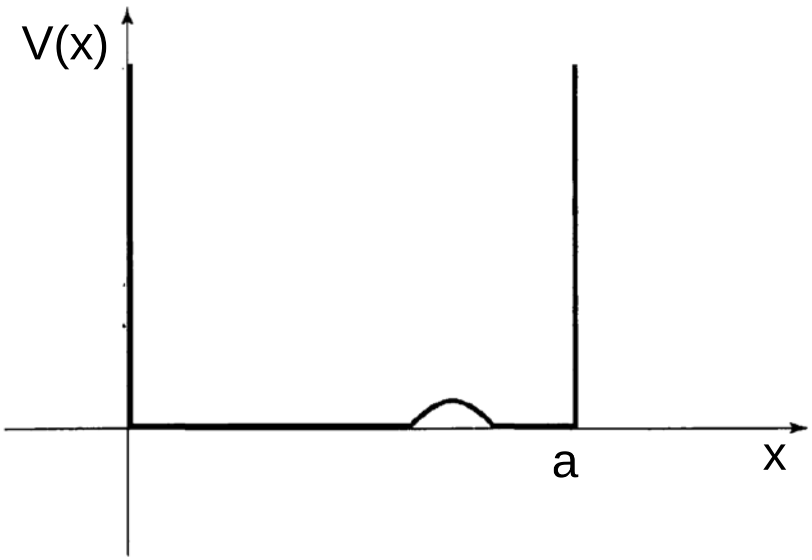
First we will study the non-degenerate case.
For example: the 1s level of H.
Counterexample: the 2p levels of H which have degeneracy 3.

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

$$H^0\psi_n^0 = E_n^0\psi_n^0 \longrightarrow H^0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$$

$$\langle\psi_n^0|\psi_m^0\rangle = \delta_{nm}$$

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:

$$H = H^0 + \lambda H'$$

Original perfect square well. (H^0)

The little bump. λ could be the bump's height, but for the math it is an auxiliary number that will be made 1 at the end. ($\lambda H'$)

We will assume that we can expand the exact results in powers of λ, which basically controls the order of the expansion:

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

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

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 λ is arbitrary and simply controls the power expansion, now we make equal the terms with the same power:

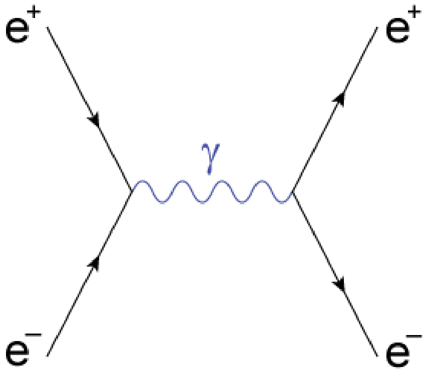
$$H^0\psi_n^0 = E_n^0\psi_n^0$$

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$$

… etcetera …

Perturbation theory can lead to very accurate results! Example quantum electrodynamics, the most accurate theory of all.



7.1.2 First-Order Theory:

Consider 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 ψ_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

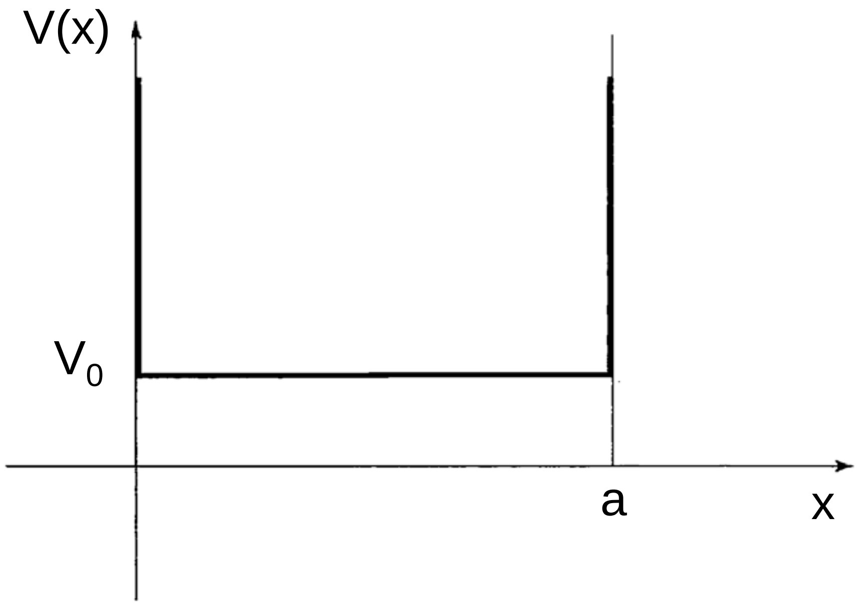
Normalized to 1

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

Example 7.1:

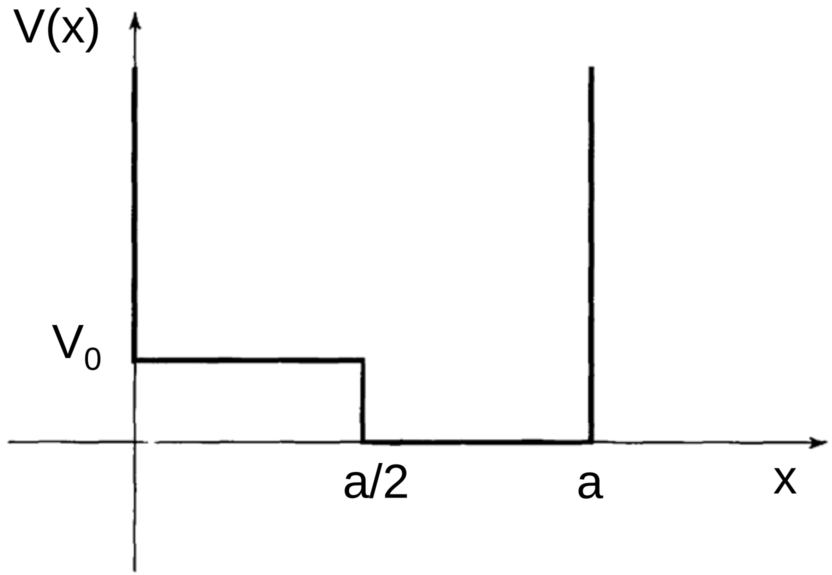
Consider, as usual ☺, the 1D infinite square well.

The exact solutions are $\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$



$$E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0$$

This is the exact solution of course: all levels are shifted uniformly. Higher order corrections vanish.



$$E_n^1 = \frac{2V_0}{a} \int_0^{a/2} \sin^2\left(\frac{n\pi}{a}x\right) dx = \frac{V_0}{2}$$

This is reasonable but not the exact solution. Higher order corrections will improve the accuracy (in HW6 you will be solving this integral).

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:

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

Note: Consider adding $\alpha\psi_n^0$. $(H^0 - E_n^0)\alpha\psi_n^0 = 0$ on the left. $(H' - E_n^1)\alpha\psi_n^0 = 0$ cancels also by taking inner product with $\langle\psi_n^0|$ and using $E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle$

$$\sum_{m\neq n}(E_m^0 - E_n^0)c_m^{(n)}\psi_m^0 = -(H' - E_n^1)\psi_n^0$$

Inner product:

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

$\langle\psi_l^0|\psi_m^0\rangle$: δ_{lm}

$\langle\psi_l^0|\psi_n^0\rangle$: 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 replacing "l" by "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

7.1.3 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 ψ_n^0 and arrive to:

$$\langle\psi_n^0|H^0\psi_n^2\rangle + \langle\psi_n^0|H'\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle + E_n^1\langle\psi_n^0|\psi_n^1\rangle + E_n^2\underbrace{\langle\psi_n^0|\psi_n^0\rangle}$$

Normalized to 1. Note that E_n^2 is what we want.

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 are equal and they cancel.

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, expanding in a complete basis as 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:

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

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

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.

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