

# TIME-INDEPENDENT PERTURBATION THEORY

[φ 15, HF.1, GF]

## Motivation

Up to now, we have only studied systems which can be solved exactly, i.e.

the Schrödinger equation has an exact analytical solution. Unfortunately, this is possible for only a few systems, most of which we have discussed already.

For those cases that cannot be solved exactly, we need good approximation methods in order to find good approximate solutions. In the coming weeks we will look at some of the methods used to reduce complex problems to simpler problems which can be solved analytically (or numerically).

## General formulation

In many situations, the Hamiltonian  $H$  of a system differs only slightly from that of an exactly solvable system,  $H_0$ :

$$H = H_0 + V.$$

The term  $V$  is the perturbation from the exactly solvable system. We assume that  $V$  has no time-dependence [that would require time-dependent pert. theory.]

Furthermore we assume that we know the eigenvalues  $E_n^0$  and eigenstates  $|n\rangle$  of the unperturbed system,

$$H_0|n\rangle = E_n^0|n\rangle, \quad (1)$$

and want to find eigenvalues and eigenstates of the perturbed Hamiltonian  $H = H_0 + \lambda V$ :

$$H|\psi_n\rangle = E_n|\psi_n\rangle. \quad (2)$$

Here,  $\lambda \in \mathbb{R}$  is included as a book-keeping device: if  $\lambda=0$  we have only  $H_0$ , if  $\lambda=1$  we have the true Hamiltonian  $H$ .

### NON-DEGENERATE PERTURBATION THEORY

If we lower  $\lambda$  from 1 to 0,  $E_n$  and  $|\psi_n\rangle$  should gradually approach the unperturbed solutions  $E_n^0$  and  $|n\rangle$ . We therefore write  $E_n$  and  $|\psi_n\rangle$  as power series in  $\lambda$ :

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (3)$$

$$|\psi_n\rangle = |n\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots, \quad (4)$$

where  $E_n^{(1)}$  and  $|n^{(1)}\rangle$  are the first-order corrections to the  $n^{\text{th}}$  eigenvalue and eigenstate, respectively. We have here assumed non-degenerate states, meaning that each eigenvalue has only one eigenstate. We will make the necessary modifications for degenerate states later.

# Analogy - "Perturbation theory" for polynomials

To get a glimpse of the arguments used when deriving the expressions for perturbation theory, consider the polynomial

$$x^2 + \lambda x - c = 0. \quad (*)$$

This equation has solutions

$$x = -\frac{\lambda}{2} \pm \frac{1}{2}\sqrt{\lambda^2 + 4c}.$$

Pretend that we didn't know or remember the formula. If  $\lambda$  is a small parameter, we have

$$x^2 - c = 0 \Rightarrow x = \pm \sqrt{c},$$

We now try to improve upon this solution by using the ansatz

$$x = x_0 + \lambda x_1 + \lambda^2 x_2 + \dots,$$

and insert it into (\*).

We then get

$$\begin{aligned} & x_0^2 + 2\lambda x_0 x_1 + \lambda^2 x_1^2 + 2\lambda^2 x_0 x_2 + \dots \\ & + \lambda [x_0 + \lambda x_1 + \lambda^2 x_2 + \dots] - c = 0 \\ = & \lambda^0 [x_0^2 - c] + \lambda [2x_0 x_1 + x_0] \\ & + \lambda^2 [x_1^2 + 2x_0 x_2 + x_1] + \dots = 0. \end{aligned}$$

By assumption  $x_n$  are independent of  $\lambda$ . Therefore, if the above equation should hold for any  $\lambda$ , it has to be satisfied term-by-term for each power of  $\lambda$  separately:

$$\lambda^0: x_0^2 - c = 0 \Rightarrow x_0 = \pm \sqrt{c}$$

$$\lambda^1: 2x_0 x_1 + x_0 = 0 \rightarrow x_1 = -\frac{1}{2}$$

$$\lambda^2: x_1^2 + 2x_0 x_2 + x_1 = 0 \Rightarrow x_2 = \pm \frac{1}{8\sqrt{c}}$$

:

Hence, we have

$$x \approx \pm \sqrt{c} - \frac{\lambda}{2} \pm \frac{\lambda^2}{8\sqrt{c}} + \dots$$

which is in fact the Taylor expansion of the exact solution to second order in  $\lambda$ .

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where  $E_n^{(1)}$  and  $|n^{(1)}\rangle$  are the first-order corrections to the  $n$ 'th eigenvalue and eigenstate, respectively. We have here assumed non-degenerate states, meaning that each eigenvalue has only one eigenstate. We will make the necessary modifications for degenerate states later.

We now insert the expansions (3) and (4) into the exact eigenvalue problem:

$$\begin{aligned} H|\psi_n\rangle &= E_n|\psi_n\rangle \\ \Rightarrow (H_0 + \lambda V)\left[|n\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \dots\right] &= \left(E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots\right)\left[|n\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \dots\right] \end{aligned}$$

This equation must hold for all  $\lambda$ , which means that it must hold for each order in  $\lambda$  separately. Collecting like powers of  $\lambda$ , we get the equations

$$\lambda^0: H_0|n\rangle = E_n^0|n\rangle,$$

$$\lambda^1: H_0|n^{(1)}\rangle + V|n\rangle = E_n^0|n^{(1)}\rangle + E_n^{(1)}|n\rangle, \quad (5)$$

$$\lambda^2: H_0|n^{(2)}\rangle + V|n^{(1)}\rangle = E_n^0|n^{(2)}\rangle + E_n^{(1)}|n^{(1)}\rangle + E_n^{(2)}|n\rangle, \quad (6)$$

etc.

The  $\lambda^0$  equation is already satisfied by assumption.

### First order theory

Multiplying (5) by  $\langle n|$  from the left, we get

$$\langle n|H_0 - E_n^0|n^{(1)}\rangle + \langle n|V|n\rangle - \langle n|E_n^{(1)}|n\rangle = 0.$$

Here  $\langle n|E_n^{(1)}|n\rangle = E_n^{(1)}$ , and

$$\langle n|H_0|n^{(1)}\rangle = \langle n^{(1)}|H_0|n\rangle^* = \langle n^{(1)}|E_n^0|n\rangle^* = \langle n|E_n^0|n^{(1)}\rangle.$$

$$\Rightarrow \langle n|H_0 - E_n^0|n^{(1)}\rangle = 0.$$

Hence, we find

$$\underline{E_n^{(1)} = \langle n | V | n \rangle},$$

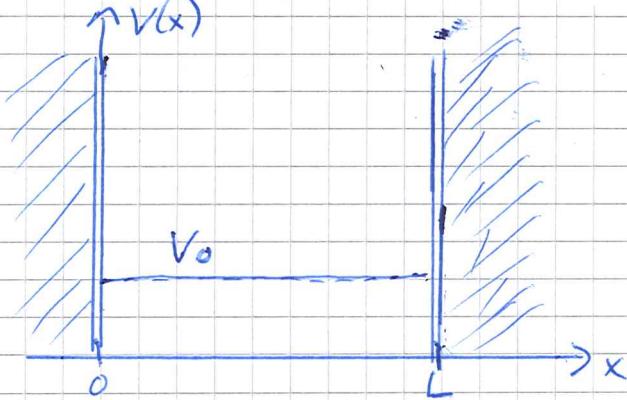
the lowest order energy correction is the expectation value of the perturbation, in the unperturbed state.

Example - Infinite square well:

Unperturbed wavefunctions are

$$\psi_n^0(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x.$$

What is the first order correction to the energies if  $V(x) \rightarrow V(x) + V_0$ , with  $V_0$  const?



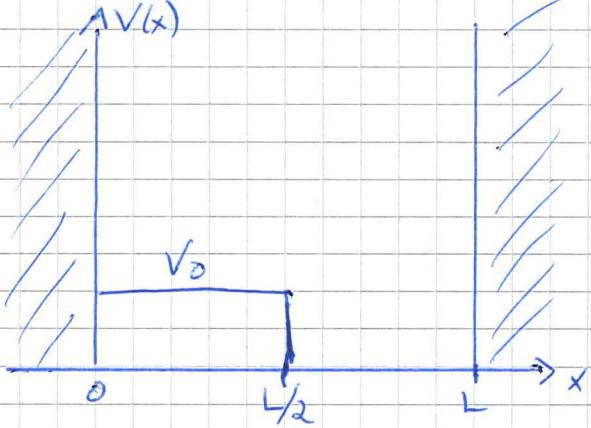
We get

$$E_n^{(1)} = \langle n | V_0 | n \rangle = V_0 \langle n | n \rangle = V_0.$$

$$\Rightarrow E_n \approx E_n^0 + V_0;$$

makes sense! This is also the exact result.

What if we have  $V(x) \Rightarrow V(x) + V_0 \Theta\left(\frac{L}{2} - x\right)$ ?



$$\Rightarrow E_n^{(1)} = \langle n | V_0 \Theta\left(\frac{L}{2} - x\right) | n \rangle$$

$$= \frac{2V_0}{L} \int_0^{\frac{L}{2}} dx \sin^2 \frac{n\pi}{L} x = \frac{V_0}{2},$$

every energy is lifted by  $\frac{V_0}{2}$ . (Probably)  
not the exact result.

In order to find the first order correction  $\langle n^{(1)} \rangle$ , we multiply (5) by  $\langle m |$ ,  $m \neq n$ , from the left, resulting in

$$\langle m | H_0 - E_n^0 | n^{(1)} \rangle = - \langle m | V | n \rangle \quad (m \neq n).$$

Again we use

$$\begin{aligned} \langle m | H_0 - E_n^0 | n^{(1)} \rangle &= \langle n^{(1)} | H_0 - E_n^0 | m \rangle^* = \langle n^{(1)} | E_m^0 - E_n^0 | m \rangle^* \\ &= \langle m | E_m^0 - E_n^0 | n^{(1)} \rangle = (E_m^0 - E_n^0) \langle m | n^{(1)} \rangle \end{aligned}$$

which when inserted into the above equation results in

$$\langle m | n^{(1)} \rangle = \frac{\langle m | V | n \rangle}{E_n^0 - E_m^0}.$$

Since the unperturbed vectors constitute a complete set, we can write

$$|n^{(1)}\rangle = \sum_m |m\rangle \langle m|n^{(0)}\rangle.$$

Inserting the expression for  $\langle m|n^{(1)}\rangle$ , we get

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

Note that  $n=m$  is excluded from the sum.

We see that the first-order term in general may contain contributions along all the unperturbed vectors  $|m\rangle \neq |n\rangle$  — the perturbation causes a "rotation" of state number  $n$ , "mixing" in contributions along  $|m\rangle \neq |n\rangle$ . The degree of mixing or coupling is determined by the ratio between  $\langle m|V|n\rangle$  and  $E_n^0 - E_m^0$ .

The above equation is fine as long as the unperturbed states are non-degenerate — that ensures  $E_n^0 - E_m^0 \neq 0$  for  $m \neq n$ . However, if another unperturbed state has the same energy as the unperturbed state  $|n\rangle$ , we would need degenerate perturbation theory.

Finally, we note that many of the matrix elements  $\langle m|V|n\rangle$  may be zero, so that the sum is restricted.

## Second-order energies

In order to find the second-order corrections to the energies, we multiply (6) by  $\langle n |$  from the left:

$$\underbrace{\langle n | H_0 - E_n^0 | n^{(1)} \rangle}_{=0} + \langle n | V | n^{(1)} \rangle - \overline{E_n^{(1)}} \underbrace{\langle n | n^{(1)} \rangle}_{=0} - E_n^{(2)} \langle n | n \rangle = 0$$

$$\Rightarrow E_n^{(2)} = \langle n | V | n^{(1)} \rangle$$

Inserting the first-order result  $|n^{(1)}\rangle$ , we get

$$E_n^{(2)} = \langle n | V \left( \sum_{m \neq n} \frac{\langle m | V | n \rangle}{E_n^0 - E_m^0} \right) | m \rangle$$

$$= \sum_{m \neq n} \frac{\langle n | V | m \rangle \langle m | V | n \rangle}{E_n^0 - E_m^0}$$

Using  $\langle n | V | m \rangle = \langle m | V | n \rangle^*$ , we get

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m | V | n \rangle|^2}{E_n^0 - E_m^0}$$

We could continue, calculating  $|n^{(2)}\rangle$ ,  $E_n^{(3)}$  etc, but will stop here. To summarize:  
The solution of the eigenvalue problem

$$(H_0 + \lambda V) |\psi_n\rangle = E_n |\psi_n\rangle$$

is

$$|\psi_n\rangle = |n\rangle + \sum_{m \neq n} \frac{\langle m | V | n \rangle}{E_n^0 - E_m^0} |m\rangle + \mathcal{O}(\lambda^2)$$

$$E_n = E_n^0 + \langle n | \lambda V | n \rangle + \sum_{m \neq n} \frac{|\langle m | \lambda V | n \rangle|^2}{E_n^0 - E_m^0} + \mathcal{O}(\lambda^3)$$

## EXAMPLE - Perturbed harmonic oscillator

Consider a harmonic oscillator which is perturbed by a force  $F$  in the positive  $x$ -direction. The system Hamiltonian is then

$$H = H_0 + V$$

with unperturbed Hamiltonian

$$H_0 = \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

and perturbation

$$V = -x F.$$

We'll now calculate the corrections to the energies and eigenstates.

First-order correction:

$$\begin{aligned} E_n^{(1)} &= \langle n | V | n \rangle = \langle n | -F \hat{x} | n \rangle \\ &= -F \sqrt{\frac{\hbar}{2m\omega}} \langle n | a + a^\dagger | n \rangle = 0. \end{aligned}$$

Here we have used  $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger)$  and  $a|n\rangle = \sqrt{n}|n-1\rangle$ ,  $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$ ,

which gives

$$\langle k | \hat{x} | n \rangle = \sqrt{\frac{\hbar}{2m\omega}} \left[ \sqrt{n} \delta_{k,n-1} + \sqrt{n+1} \delta_{k,n+1} \right].$$

The second order correction to the energy is

$$\begin{aligned} E_n^{(2)} &= \sum_{k \neq n} \frac{|\langle k | -F\hat{x}|n \rangle|^2}{E_n^0 - E_k^0} \\ &= F^2 \frac{\hbar}{2m\omega} \sum_{k \neq n} \frac{\left[ \sqrt{n} \delta_{k,n-1} + \sqrt{n+1} \delta_{k,n+1} \right]^2}{\hbar\omega [n-k]} \\ &= \frac{F^2}{2m\omega^2} \left[ \frac{n}{n-(n-1)} + \frac{n+1}{n-(n+1)} \right] \\ &= -\frac{F^2}{2m\omega^2}. \end{aligned}$$

In this case only two  $k$ 's contributed to the correction — we were lucky!

The state vector to first order is

$$\begin{aligned}
 |\psi_n\rangle &= |n\rangle + \sum_{k \neq n} \frac{\langle k| - F \hat{x}|n\rangle}{E_n^0 - E_k^0} |k\rangle \\
 &= |n\rangle - F \sqrt{\frac{\hbar}{2m\omega}} \left[ \frac{\sqrt{n}}{\hbar\omega} |n-1\rangle - \frac{\sqrt{n+1}}{\hbar\omega} |n+1\rangle \right] \\
 &= |n\rangle - \frac{F}{\hbar m \omega^2} \sqrt{\frac{\hbar m \omega}{2}} (a - a^\dagger) |n\rangle.
 \end{aligned}$$

We now use

$$\hat{p}_x = -i \sqrt{\frac{\hbar m \omega}{2}} (a - a^\dagger)$$

and define

$$x_0 \equiv \frac{F}{m \omega^2},$$

Check units:

$$\begin{aligned}
 [x_0] &= \left[ \frac{F}{m \omega^2} \right] = \frac{\text{kg m/s}^2}{\text{kg/s}^2} \\
 &= \text{m} \quad \text{OK.}
 \end{aligned}$$

resulting in

$$|\psi_n\rangle = \left( 1 - i \frac{\hat{p}_x x_0}{\hbar} \right) |n\rangle,$$

or, in position space;

$$\psi_n(x) = \langle x | \psi_n \rangle = \left( 1 - x_0 \frac{d}{dx} \right) \psi_n^0(x).$$

For this example we are actually able to determine how well perturbation theory works by looking at the exact solution.

## Exact solutions

We can find the exact solutions by rewriting the Hamiltonian:

$$\begin{aligned} H &= H_0 + V = \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 x^2 - Fx \\ &= \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 \left( x - \frac{F}{m\omega^2} \right)^2 - \frac{F^2}{2m\omega^2}, \end{aligned}$$

where we have completed the square.

If we now use

$$x_0 = \frac{F}{m\omega^2},$$

we get

$$H = \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 (x - x_0)^2 - \frac{F^2}{2m\omega^2}.$$

The Hamiltonian describes a harmonic oscillator with equilibrium position at  $x=x_0$  instead of at  $x=0$ . The energy levels are therefore directly given by

$$E_n(F) = \hbar\omega \left( n + \frac{1}{2} \right) - \frac{F^2}{2m\omega^2} \equiv E_n^0 - \frac{F^2}{2m\omega^2},$$

with eigenfunctions

$$\psi_n(x) = \psi_n^0(x - x_0),$$

We therefore realize that our second approximation for the energy is actually the exact solution:

$$E_n = E_n^0 + E_n^{(1)} + E_n^{(2)}$$

The correction due to the force is  $\mathcal{O}(F^2)$  in both cases.

If we Taylor expand the wavefunction around  $x$ , we get

$$\begin{aligned}\psi_n(x) &= \psi_n^0(x - x_0) \\ &= \psi_n^0(x) - x_0 \frac{d}{dx} \psi_n^0(x) + \\ &= \sum_{k=0}^{\infty} \frac{1}{k!} \left(-x_0 \frac{d}{dx}\right)^k \psi_n^0(x) \\ &= e^{-x_0 \frac{d}{dx}} \psi_n^0(x),\end{aligned}$$

which corresponds to the state vector

$$|\psi_n\rangle = e^{-\frac{i\hat{p}_x x_0}{\hbar}} |n\rangle.$$

Our perturbation result corresponds to the two lowest order terms in this expansion.