# Phys 506 lecture 14: Rayleigh-Schrodinger perturbation theory

## 1 Introduction to nondegenerate perturbation theory

We start with the exact energy eigenvalue problem, given by $\hat{H}|n\rangle = E_n|n\rangle$. But, perhaps this problem is too difficult to solve. Then, if $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{H}_0$ can be solved exactly, but $\hat{H}$ cannot and $\hat{V}$ is in some sense "small," then I can try to find how $\hat{V}$ perturbs $\hat{H}_0$ to arrive at $\hat{H}$.

The unperturbed problem is $\hat{H}_0|n\rangle_0 = E_n^0|n\rangle_0$, whose exact solution we know by assumption. Furthermore, we assume the system is nondegenerate, so we have $E_n^0 \neq E_m^0$ unless $m = n$. This is known to be the case for all one-dimensional problems on the infinite one-dimensional spatial domain via the so-called node theorem.

We want to find $E_n$ and $|n\rangle$ as a power series in $\hat{V}$. We start with what we know, which is

$$\left(\hat{H}_0 + \hat{V}\right)|n\rangle = \left(E_n^0 + \Delta E_n\right)|n\rangle, \quad \text{with} \quad E_n = E_n^0 + \Delta E_n.$$

We then re-arrange this expression to

$$\left(E_n^0 - \hat{H}_0\right)|n\rangle = \left(\hat{V} - \Delta E_n\right)|n\rangle.$$

We want to somehow "invert" this, in the sense that we wish to multiply by the inverse of the operator on the far left to obtain the perturbed state $|n\rangle$. Unfortunately, that operator cannot be inverted, because it can involve a divide by zero.

Let us examine how to work with nontraditional operators such as $\frac{1}{E_n^0 - \hat{H}_0}$. This operator can be best expressed in terms of the eigenbasis of $\hat{H}_0$ as

$$\frac{1}{E_n^0 - \hat{H}_0} \underbrace{\sum_m |m\rangle_{00}\langle m|}_{\text{complete set of states}=\mathbb{I}}$$

by a multiply by one. But, $\hat{H}_0|m\rangle_0 = E_m^0|m\rangle_0$, so

$$\frac{1}{E_n^0 - \hat{H}_0}\sum_m |m\rangle_{00}\langle m| = \sum_m \frac{1}{E_n^0 - E_m^0}|m\rangle_{00}\langle m|$$

becomes singular for the one term in the sum, where $m = n$.

## 2 Projection oeprators

We deal with this by introducing projection operators.

Define $\hat{P}_n = |n\rangle_{00}\langle n|$ and $\hat{Q}_n = \mathbb{I} - \hat{P}_n = \sum_{m\neq n} |m\rangle_{00}\langle m|$.

Let us first note some properties of projection operators:

$$\hat{P}_n + \hat{Q}_n = \mathbb{I}$$

$$\hat{P}_n^2 = \hat{P}_n \quad \text{check} \quad \hat{P}_n^2 = |n\rangle_{00} \underbrace{\langle n \mid n\rangle_{00}}_{1} \langle n| = |n\rangle_{00}\langle n| = \hat{P}_n$$

$$\hat{Q}_n^2 = \hat{Q}_n \quad \text{check} \quad \hat{Q}_n^2 = \left(1 - \hat{P}_n\right)^2 = 1 - \hat{P}_n - \hat{P}_n + \hat{P}_n^2 = 1 - \hat{P}_n - \hat{P}_n + \hat{P}_n = 1 - \hat{P}_n = \hat{Q}_n$$

$$\hat{P}_n\hat{Q}_n = 0 \quad \text{check} \quad \hat{P}_n\hat{Q}_n = |n\rangle_{00}\langle n| \sum_{m+n} |m\rangle_{00}\langle m|, \quad \text{but } {}_0\langle n|m\rangle_0 = 0 \text{ if } m \neq n, \quad \text{so} \quad \hat{Q}_n\hat{P}_n = 0$$

and then $\left[\hat{P}_n, \hat{Q}_n\right] = 0$.

How do projection operators act on an arbitrary operator? We determine this by representing the operator in the energy eigenbasis of $\hat{H}_0$, where we can immediately apply the projection operators:

$$\hat{O} = \sum_{mm'} O_{mm'} |m\rangle_{00} \left\langle m'\right|$$

$$\hat{P}_n\hat{O} = \sum_{m'} O_{nm'} |n\rangle_{00} \left\langle m'\right|, \quad \hat{P}_n\hat{O}\hat{P}_n = O_{nn} |n\rangle_{00}\langle n|$$

$$\hat{Q}_n\hat{O} = \sum_{m\neq n} \sum_{m'} O_{mm'} |m\rangle_{00}\langle m'|$$

$$\hat{Q}_n\hat{O}\hat{Q}_n = \sum_{m\neq n} \sum_{m'\neq n} O_{mm'} |m\rangle_{00}\langle m'|, \text{ and so on}$$

$$\hat{Q}_n\hat{O}\hat{P}_n = \sum_{m\neq} O_{mn} |m\rangle_{00}\langle n|, \text{ etc.}$$

In words, we say $\hat{P}_n$ projects parallel to $|n\rangle_0$ and $\hat{Q}_n$ projects perpendicular to $|n\rangle_0$.

Claim: $\left[\hat{P}_n, \hat{H}_0\right] = 0$.

Proof:

$$\hat{P}_n\hat{H}_0 = |n\rangle_{00}\langle n|\hat{H}_0 = E_n^0 |n\rangle_{00}\langle n|$$

$$\hat{H}_0\hat{P}_n = \hat{H}_0|n\rangle_{00}\langle n| = E_n^0 |n\rangle_{00}\langle n|$$

$$\text{so } \hat{P}_n\hat{H}_0 - \hat{H}_0\hat{P}_n = 0.$$

Since $\hat{Q}_n = 1 - \hat{P}_n$ we have $\left[\hat{Q}_n, \hat{H}_0\right] = \left[1 - \hat{P}_n, \hat{H}_0\right] = 0$ as well.

## 3 Formalism to generate the series

Now examine the original equation

$$(E_n^0 - \hat{H}_0)|n\rangle = (\hat{V} - \Delta E_n)|n\rangle.$$

Then

$$\hat{Q}_n|n\rangle = \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(\hat{V} - \Delta E_n\right)|n\rangle.$$

Check:

$$\hat{Q}_n|n\rangle = \sum_{m\neq n}|m\rangle_{00}\langle m|n\rangle,$$

$$\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \Delta E_n)|n\rangle = \sum_{m\neq n}|m\rangle_{00}\langle m|\frac{\hat{V} - \Delta E_n}{E_n^0 - E_m^0}|n\rangle.$$

But,

$$\sum_{m\neq n}|m\rangle_{00}\langle m|(E_n^0 - \hat{H}_0)|n\rangle = \sum_{m\neq n}|m\rangle_{00}\langle m|(\hat{V} - \Delta E_n)|n\rangle,$$

from our first equations above. Hence,

$$\text{LHS} = \sum_{m\neq n}\left(E_n^0 - E_m^0\right)|m\rangle_{00}\langle m|n\rangle = \sum_{m\neq n}|m\rangle_{00}\langle m|(\hat{V} - \Delta E_n)|n\rangle$$

since each coefficient of $|m\rangle_0$ must be equal and $E_n^0 - E_m^0 \neq 0$, we then have

$$\sum_{m\neq n}|m\rangle_{00}\langle m|n\rangle = \sum_{m\neq n}|m\rangle_{00}\langle m|\frac{\hat{V} - \Delta E_n}{E_n^0 - E_m^0}|n\rangle$$

as claimed.

But $|n\rangle = \left(\hat{P}_n + \hat{Q}_n\right)|n\rangle$ and $\hat{P}_n|n\rangle = |n\rangle_{00}\langle n|n\rangle$, So

$$|n\rangle = |n\rangle_{00}\langle n|n\rangle + \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \Delta E_n\rangle|n\rangle$$

We move the rightmost term to the left hand side to get

$$\left[\mathbb{I} - \frac{\hat{Q}_n}{E_n^0 - \hat{H}}(\hat{V} - \Delta E_n)\right]|n\rangle = |n\rangle_{00}\langle n|n\rangle.$$

Now, we can multiply by the inverse operator, because it never vanishes (which is where we use the fact that $\hat{V}$ is small), so we have

$$|n\rangle = {}_0\langle n|n\rangle\left[\mathbb{I} - \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(\hat{V} - \Delta E_n\right)\right]^{-1}|n\rangle_0.$$

As a convention we choose ${}_0\langle n|n\rangle = 1$ and normalize the true wavefunction $|n\rangle$ only at the end. This simplifies many places in the calculation, but one needs to remember that $\langle n|n\rangle \neq 1$ now.

$$\text{so } \boxed{|n\rangle = [\mathbb{I} - \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \Delta E_n)]^{-1}|n\rangle_0.}$$

## 4 Examining the first few terms in the expansion

By expanding the inverse operator as a geometric series, we generate the perturbation theory expansion. This gives us

$$\begin{aligned}|n\rangle =&|n\rangle_0 + \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(\hat{V} - \underbrace{\Delta E_n}_{\text{drop}}\right)|n\rangle_0 + \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(\hat{V} - \Delta E_n\right)\frac{\hat{Q}}{E_n^0 - \hat{H}_0}\left(\hat{V} - \underbrace{\Delta E_n}_{\text{drop}}\right)|n\rangle_0\\ &+ \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(\hat{V} - \Delta E_n\right)\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(\hat{V} - \Delta E_n\right)\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(\hat{V} - \underbrace{\Delta E_n}_{\text{drop}}\right)|n\rangle_0 + \cdots\end{aligned}$$

We can always drop the last $\Delta E_n$ term since

$$\Delta E_n = \text{ number} \quad \text{and} \quad \hat{Q}_n \Delta E_n |n\rangle_0 = 0 \text{ always.}$$

To perform the perturbation theory expansion, we write

$$\begin{aligned}|n\rangle &= \sum_{m=0}^{\infty} |n\rangle^{(m)}, \quad \text{with} \quad |n\rangle^{(0)} = |n\rangle_0 \quad \text{and the index denotes the powers of } \hat{V} \quad \text{in the expression}\\ E_n &= \sum_{m=0}^{\infty} E_n^{(m)} \quad E_n^{(0)} = E_n^0\\ \Delta E_n &= \sum_{m=1}^{\infty} E_n^{(m)}\end{aligned}$$

We need to know the results up to $E_n^{(m)}$ in order to find $|n\rangle^{(m+1)}$.

The first few terms in the expansion are then

$$\begin{aligned}|n\rangle^{(0)} &= |n\rangle_0\\ |n\rangle^{(1)} &= \frac{\hat{Q}_n}{\hat{E}_n^0 - \hat{H}_0}\hat{V}|n\rangle_0, \quad |n\rangle^{(2)} = \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(\hat{V} - E_n^{(1)}\right)\frac{\hat{Q}_n}{E_n^0 - H_0}\hat{V}|n\rangle_0,\\ (n\rangle^{(3)} &= \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(-E_n^{(2)}\right)\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\hat{V}|n\rangle_0 + \frac{\hat{Q}_n}{E_n^0 - H_0}\left(\hat{V} - E_n^{(1)}\right)\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\left(\hat{V} - E_n^{(0)}\right)\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\hat{V}|n\rangle_0,\end{aligned}$$

and so on.

How do we find $E_n^{(m)}$ ? Note that we have

$$\begin{aligned}\left(E_n^0 - \hat{H}_0\right)|n\rangle &= \left(\hat{V} - \Delta E_n\right)|n\rangle \quad \text{multiply by } {}_0\langle n|\\ {}_0\langle n|(E_n^0 - \hat{H}_0)|n\rangle &= {}_0\langle n|(\hat{V} - \Delta E_n)|n\rangle, \quad \text{which gives us}\\ \Delta E_n &= \frac{{}_0\langle n|\hat{V}|n\rangle}{{}_0\langle n|n\rangle} = {}_0\langle n|\hat{V}|n,\rangle, \quad \text{since } {}_0\langle n|n\rangle = 1.\end{aligned}$$

So $\sum_{m=1}^{\infty} E_n^{(m)} = \sum_{m=0}^{\infty}\langle n|\hat{V}|n\rangle^{(m)}$. By matching powers of $\hat{V}$, we get

$$\boxed{E_n^{(m)} = {}_0\langle n|\hat{V}|n\rangle^{(m-1)}}$$

So, we work out the first few orders:

$$E_n^{(1)} = {}_0\langle n|\hat{V}|n\rangle_0 = \boxed{V_{nn}}$$
$$|n\rangle^{(1)} = \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\hat{V}|n\rangle_0 = \sum_{m\neq n}\frac{V_{mn}}{E_n^0 - E_m^0}|m\rangle_0.$$

For $m = 2$ and 3, we have

$$E_n^{(2)} = \sum_{m\neq n}\frac{V_{nm}V_{mn}}{E_n^0 - E_m^0} = \sum_{m\neq n}\frac{|V_{nm}|^2}{E_n^0 - E_m^0} = \boxed{\sum_m{}'\frac{|V_{nm}|^2}{E_n^0 - E_m^0}}\text{ prime } \Rightarrow m \neq n$$
$$|n\rangle^{(2)} = \frac{\hat{Q}_n\left(\hat{V} - E_n^{(1)}\right)}{E_n^0 - \hat{H}_0}\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\hat{V}|n\rangle_0$$
$$= \sum_{m\neq n}\sum_{m'\neq n}|m'\rangle_0\frac{(V_{m'm} - E_n^{(1)}\delta_{mm\prime})}{E_n^0 - E_{m'}^0}\frac{V_{mn}}{E_n^0 - E_m^0}, \quad E_n^{(1)} = V_{nn}$$
$$E_n^{(3)} = \sum_{m\neq n}\sum_{m'\neq n}\frac{V_{nm'}V_{m'm}V_{mn}}{\left(E_n^0 - E_{m'}^0\right)\left(E_n^0 - E_m^0\right)} - V_{nn}\sum_{m\neq n}\frac{|V_{nm}|^2}{\left(E_n^0 - E_m^0\right)^2}$$
$$= \boxed{\sum_m{}'\sum_{m'}{}''\frac{V_{nm'}V_{m'm}V_{mn}}{\left(E_n^0 - E_{m'}^0\right)\left(E_n^0 - E_m^0\right)} - V_{nn}\sum_m{}'\frac{|V_{nm}|^2}{\left(E_n^0 - E_m^0\right)^2}}$$

This process can be continued to arbitrary order (on the HW you will examine through 4th order.)