Notes for Lecture 3

Time independent perturbation – non-degenerate case

The perturbation theory is essential. Here, we consider the most basic case.

Just like in any general perturbation theory, including that of classical mechanics, one begins the perturbation theory by recognizing which term is easy to solve and which term is difficult to solve and small. If such an identification is possible, then the perturbation theory gives a systematic way to solve the problem.

3.1 TISE

We start with the time-independent Schrödinger equation (TISE). It reads

$$\hat{H}\,|E\rangle \;=\; E\,|E\rangle \tag{3.1}$$

where E is the energy eigenvalue. So, the TISE is simply the eigenvalue equation for the Hamiltonian.

The TISE is the most meaningful when $\hat{H}$ is conserved, i.e. when time is homogeneous, i.e. $\hat{H}$ is not explicitly dependent on time. Let us consider an energy eigenstate with energy E: $|E,t\rangle$. As any physical state must, this state satisfies the (time-dependent) Schrödinger equation, Eq. 1.15. However, we already know how this state must evolve in time, since we know that the time evolution operator (starting from $t = 0$, by an arbitrary choice of the origin of time) is given by $\hat{\mathcal{U}}(t) = \exp\left(-i\hat{H}t/\hbar\right)$ (Eq. 1.22) for any real value of t when time is homogeneous. Then, it follows that an

energy eigenstate with energy E can be simply written down as

$$|E,t\rangle \;=\; \exp\left(-i\frac{Et}{\hbar}\right)|E\rangle \tag{3.2}$$

where we assumed that the state $|E\rangle$ is the $t = 0$ state. Then, the Schrödinger equation, $\hat{H}\,|E,t\rangle = i\hbar\frac{d}{dt}\,|E,t\rangle$ becomes the TISE, if we plug in $\exp\left(-i\frac{Et}{\hbar}\right)|E\rangle$, effecting the time-differentiation, and then dividing out $\exp\left(-i\frac{Et}{\hbar}\right)$ from both sides.

While the above TISE form is nice, since the notation is so obvious, it is not the only way that the TISE can be written. In fact, another common way that you see is

$$\hat{H}\,|\psi\rangle \;=\; E\,|\psi\rangle \tag{3.3}$$

Here, we will be concerned with the case when the energy is bounded from below and the energy spectrum is discrete. In this case, an energy eigenstate can simply be referred to as $|n\rangle$, and the energy eigenvalue can be subscripted. So, we get

$$\hat{H}\,|n\rangle \;=\; E_n\,|n\rangle \qquad\qquad n = 0,1,2,...;\ \text{discrete energy spectrum} \tag{3.4}$$

We assume that $E_n \geq E_{n-1}$. Thus, the ground state is $|0\rangle$. This is the form of TISE that we will work for a while, as we do the perturbation theory.

3.2 Basic setup for perturbation

Suppose that

$$\hat{H} \;=\; \hat{H}_0 + \hat{H}_1 \tag{3.5}$$

where $\hat{H}_0$ is a simple/easy Hamiltonian and $\hat{H}_1$ is a difficult and small Hamiltonian. What we mean by $\hat{H}_0$ being easy is that we assume that $\hat{H}_0$ has already been solved completely

$$\hat{H}_0\left|n^{(0)}\right\rangle \;=\; E_n^{(0)}\left|n^{(0)}\right\rangle \tag{3.6}$$

where the meaning of the superscript $^{(0)}$ will become clear shortly. What do we mean by $\hat{H}_1$ being small? It means that

$$\hat{H}_1 \propto \delta, \quad |\delta| \ll 1 \qquad\qquad \delta \text{ is small, } \textit{dimensionless} \tag{3.7}$$

What could be such a parameter δ? It can be the ratio of the energy scale parameters of $\hat{H}_1$ and $\hat{H}_0$. Or, the inverse ratio of the length scale parameters. Regardless, there must be such a δ for the perturbation theory to be applicable.

Now, strange as it may sound, this does not mean that such a parameter is easy to identify, before you do a problem! However, *it will become clear as you obtain the perturbation solution.* If it does not, then it probably means that something went wrong – or the perturbation assumption was wrong! In a real research problem, this can happen quite easily if the researcher is not very careful! We will discuss some more about δ near the end of this LN.

The perturbation theory is basically a Taylor expansion theory on δ. Symbolically, a problem to solve can be represented as an equation L = R (see the box below), where both L and R contain unknowns variables to solve for[1]. Assuming that the problem can be expanded in series of δ, and assuming that δ can be an arbitrary small number, one transforms the equation to

$$L_0 + L_1\delta + L_2\delta^2 + ... \;=\; R_0 + R_1\delta + R_2\delta^2 + ... \tag{3.8}$$

Since we assume that this equality is valid for any δ, all coefficients must be equal, $L_j = R_j$, which means that the left hand side and the right hand side must be equal *term by term*!

$$L_j\delta^j \;=\; R_j\delta^j \tag{3.9}$$

If this sounds too obvious, I do not blame you! But, please remember this fact, forever! **In the perturbative solution of** L = R, **the left hand side and the right hand side must be equal term by term for each order of δ.**

The real trick of the perturbation method is that R is a collection of small terms and L is a collection of easy terms. With that, an iterative procedure is possible, and this is what makes the perturbation method so useful in general, not just in QM[2].

I present the general perturbation procedure in the box below. Then, we will learn why this procedure works, *while* we carry it out for the current problem. Near

[1] L and R can be multi-dimensional. I.e., one can have a set of equations to solve. This is indeed what will happen for the current problem as we shall see below: we will have to deal with two coupled equations involving two unknowns, E_n and $|n\rangle$.

[2] A more elementary explanation about the perturbation theory is given in `https://griffin.ucsc.edu/ph105-11/Lecture%2B?action=AttachFile&do=get&target=A01-Perturbation.pdf`.

the end of this LN, I will discuss some more about the formal theory aspect of this procedure.

Procedure for *any* perturbation theory

First of all, divide your equation into two parts. The left hand side (L) should collect easy terms. The right hand side (R) should collect difficult and small terms. Your equation to solve is L = R.

1. Start from the "current best solution" you got: this is by definition "the solution up to the j-th order (in δ) correction." The zero-th order solution, i.e. the solution for L = 0, starts this whole procedure.

2. Plug that solution into R. This turns R into a "source term" without any unknown variables. Let us denote this source term as R_{j+1}. The subscript means that this source term is correct up to the $(j+1)$-th order, with the additional order coming from the very fact that R is a collection of small terms $\propto \delta$.

3. Solve your equation $\mathrm{L} = \mathrm{R}_{j+1}$, an approximate equation where the unknowns appear only in L.

4. The solution will contain the $(j+1)$-th order correction *and* possibly higher order corrections. **You can keep only the $(j+1)$-th order correction, which is the only new information you get at this step.** Any lower order corrections are ones you knew already in step 1. Any higher order corrections are invalid, since they are incomplete. This is due to the approximate nature of $\mathrm{L} = \mathrm{R}_{j+1}$.

5. Now you have obtained the "solution correct up to the $(j+1)$-th order correction." Go to the first step, and repeat, if you would like a higher order correction; otherwise, stop.

So, now we come back to our problem at hand. The equation to solve is $\hat{H}|n\rangle = \hat{H}_0|n\rangle + \hat{H}_1|n\rangle = E_n|n\rangle$. In other words, $\hat{H}_0|n\rangle + \hat{H}_1|n\rangle = E_n^{(0)}|n\rangle + \Delta_n|n\rangle$ where

$$\Delta_n \equiv E_n - E_n^{(0)} \tag{3.10}$$

The eigenvalue equation can thus be rewritten as

$$\left(E_n^{(0)} - \hat{H}_0\right)|n\rangle \;=\; \left(\hat{H}_1 - \Delta_n\right)|n\rangle \tag{3.11}$$

The above form is just what we wanted – the left hand side (L) is a collection of easy terms and the right hand side (R) is a collection of difficult and small terms.

There is apparently a problem, though, as we set out to apply the above procedure. The number of unknowns in this equation is two, not one: the unknowns are Δ_n and $|n\rangle$. When R is approximated as R_{j+1}, it seems that all we can solve for using the equation $\mathrm{L} = \mathrm{R}_{j+1}$ is only $|n\rangle$. How can we obtain Δ_n? The answer is in the above equation, itself, actually. By multiplying $\langle n^{(0)}|$ from the left, we get $\langle n^{(0)}|\left(E_n^{(0)} - \hat{H}_0\right)|n\rangle = \langle n^{(0)}|\left(\hat{H}_1 - \Delta_n\right)|n\rangle$. Now, the left hand side of this equation clearly vanishes. Why? Because $\langle n^{(0)}|\left(E_n^{(0)} - \hat{H}_0\right) = \left[\left(E_n^{(0)} - \hat{H}_0\right)|n^{(0)}\rangle\right]^\dagger = 0$ using Eq. 3.6. Therefore, we conclude $\langle n^{(0)}|\left(\hat{H}_1 - \Delta_n\right)|n\rangle = 0$, which answers our question "how can we obtain Δ_n?":

$$\Delta_n \;=\; \left\langle n^{(0)}\left|\hat{H}_1\right|n\right\rangle \qquad \text{if we take the convention } \left\langle n^{(0)}\middle|n\right\rangle = 1 \tag{3.12}$$

These two equations are the machines through which the perturbation solutions can be churned out. That is, they together represent the symbolic equation $\mathrm{L} = \mathrm{R}$ to solve (see footnote 1) for two unknowns Δ_n and $|n\rangle$. The normalization convention just employed is a common one, which will be discussed further below.

Now we come to the point where we need to specify what we mean by the **non-degenerate perturbation theory**. It means[3]

$$E_n^{(0)} \neq E_m^{(0)} \qquad \text{for any } m \neq n \tag{3.13}$$

3.3 Solutions

Let us run the perturbation machine! You are the operator of this fine machine, and your job is to collect terms that have the same order of δ. In one loop of the perturbation procedure to compute the $(j+1)$-th order correction, your attention is focused laser sharp on those terms of $(j+1)$-th order only.

The solutions for $|n\rangle$ and Δ_n can be written formally as

$$|n\rangle = \left|n^{(0)}\right\rangle + \left|n^{(1)}\right\rangle + \left|n^{(2)}\right\rangle + \left|n^{(3)}\right\rangle + ... \tag{3.14}$$

$$\Delta_n = E_n^{(1)} + E_n^{(2)} + E_n^{(3)} + ... \tag{3.15}$$

where the superscript means the order in δ, i.e. $|n^{(j)}\rangle, E_n^{(j)} \propto \delta^j$. And, of course, remember the fundamental assumption $\hat{H}_1 \propto \delta$ (Eq. 3.7).

Zeroth order: Eq. 3.11 without the RHS: $E_n^{(0)}$ and $|n^{(0)}\rangle$ is the solution.

First order correction: Eq. 3.12 with $|n\rangle = |n^{(0)}\rangle$ on the RHS gives an approximate equation $\Delta_n = \left\langle n^{(0)} \left| \hat{H}_1 \right| n^{(0)} \right\rangle$. Notice that there are no unknowns on the right hand side, which is a "source term." We can solve for Δ_n. But, here we must concentrate only on the first order part of it. $\Delta_n = E_n^{(1)} + E_n^{(2)} + ... = \left\langle n^{(0)} \left| \hat{H}_1 \right| n^{(0)} \right\rangle$. There is only one first order term on the left hand side, and similarly on the right hand side.

$$E_n^{(1)} = \left\langle n^{(0)} \left| \hat{H}_1 \right| n^{(0)} \right\rangle \tag{3.16}$$

So, now we have $E_n^{(0)}$, $|n^{(0)}\rangle$, and $E_n^{(1)}$, as part of our approximate solutions. We pay our attention to the other equation in our machinery: Eq. 3.11. We like to turn the right hand side of it into a source term, by plugging in the approximate solutions that we have obtained *so far*. In particular, our task is to extract all terms linear in δ from the right hand side, since we are going for the first order correction. Can we do it? Yes! Since, $\hat{H}_1 - \Delta_n = \hat{H}_1 - E_n^{(1)} - E_n^{(2)} - ...$ is of first order or higher in δ, it is sufficient to plug in $|n^{(0)}\rangle$ for $|n\rangle$ to calculate the first order terms. Also, for the first order calculation, $E_n^{(2)}$ and higher are totally unnecessary to keep. So, the first order terms extracted from the right hand side become $\left(\hat{H}_1 - E_n^{(1)}\right)|n^{(0)}\rangle$. Now, we need to do the same for the left hand side, with $|n\rangle = |n^{(0)}\rangle + |n^{(1)}\rangle + ...$ The first order term for the left hand side is $\left(E_n^{(0)} - \hat{H}_0\right)|n^{(1)}\rangle$, since $E_n^{(0)} - \hat{H}_0$ is of order δ^0, being

independent of $\hat{H}_1$.

$$\begin{aligned}
\left(E_n^{(0)} - \hat{H}_0\right)\left|n^{(1)}\right\rangle &= \left(\hat{H}_1 - E_n^{(1)}\right)\left|n^{(0)}\right\rangle \\
&= \sum_m \left|m^{(0)}\right\rangle\left\langle m^{(0)}\right|\left(\hat{H}_1 - E_n^{(1)}\right)\left|n^{(0)}\right\rangle && \text{resolution of identity inserted} \\
&= \sum_{m\neq n} \left|m^{(0)}\right\rangle\left\langle m^{(0)}\right|\left(\hat{H}_1 - E_n^{(1)}\right)\left|n^{(0)}\right\rangle && m = n \text{ term vanishes (Eq. 3.16)} \\
&= \sum_{m\neq n} \left|m^{(0)}\right\rangle\left\langle m^{(0)}\right|\hat{H}_1\left|n^{(0)}\right\rangle && \text{orthogonality due to Hermitian } \hat{H}_0
\end{aligned}$$

Thus, multiplying $1/(E_n^{(0)} - \hat{H}_0)$ from the left, and noting that $|m^{(0)}\rangle$ is an eigenstate of this operator, we get

$$\left|n^{(1)}\right\rangle = \sum_{m\neq n} \frac{\left|m^{(0)}\right\rangle\left\langle m^{(0)}\right|\hat{H}_1\left|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \tag{3.17}$$

Second order correction: We like to extract the second order correction on the left hand side of Eq. 3.12. Since $\hat{H}_1$ is of order δ by assumption, this means that we plug in the solution that we just got for $|n^{(1)}\rangle$ on the RHS for $|n\rangle$, we will get $E_n^{(2)}$. The result is

$$E_n^{(2)} = \sum_{m\neq n} \frac{\left|\left\langle m^{(0)}\right|\hat{H}_1\left|n^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}} \tag{3.18}$$

This iterative method can go on indefinitely, but the results we obtained so far are already golden, and we stop here.

For a more general perturbative solution, instead of writing down increasingly complex formula for higher order corrections, let us write down the recursion relation for the correction terms. These relations are suitable for numerical computations. You are invited to derive these expressions yourself (only the second expression should require some real efforts).

$$E_n^{(j+1)} = \left\langle n^{(0)}\right|\hat{H}_1\left|n^{(j)}\right\rangle \tag{3.19}$$

$$\left|n^{(j+1)}\right\rangle = \frac{1}{E_n^{(0)} - \hat{H}_0}\left(\hat{H}_1\left|n^{(j)}\right\rangle - \sum_{l=0}^{j} E_n^{(j+1-l)}\left|n^{(l)}\right\rangle\right) \tag{3.20}$$

It is easy to verify that the quantity in the parenthesis of the last equation has no $|n^{(0)}\rangle$ component at any order (using the equation just above it), which must be true given what we proved just above Eq. 3.12. This means that any $|n^{(j)}\rangle$ for $j > 0$ has no overlap with $|n^{(0)}\rangle$. This means that in view of the expansion, Eq. 3.14

$$\left\langle n^{(0)} \middle| n \right\rangle = 1 \tag{3.21}$$

which is the convention already mentioned in Eq. 3.12. **Notice that this necessarily means that $\langle n | n \rangle \neq 1$. *After* the perturbation solution is obtained, however, the eigenstate must be normalized before calculating physical quantities using it.**

3.4 Key results

The most practical result out of all our efforts here is the following formula for the energy eigenvalue correct up to the second order. One major goal of this course is that you would become so familiar with this formula so that you can remember it as easily as you would remember Newton's second law! **This formula is that important!**

$$E_n \approx E_n^{(0)} + \left\langle n^{(0)} \middle| \hat{H}_1 \middle| n^{(0)} \right\rangle + \sum_{m \neq n} \frac{\left| \langle m^{(0)} | \hat{H}_1 | n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} \tag{3.22}$$

Other than this formula, another simple result worth trying to put on top of your mind stack may be Eq. 3.20: $E_n^{(j+1)} = \left\langle n^{(0)} \middle| \hat{H}_1 \middle| n^{(j)} \right\rangle$. This simple formula is a reminder of two important points. (1) The sequence in which we obtain perturbative solutions is: $E_n^{(1)} \to |n^{(1)}\rangle \to E_n^{(2)} \to |n^{(2)}\rangle \to ...$ (2) It is possible to remember the formula for $|n^{(1)}\rangle$ (Eq. 3.17) from this simple formula and the expression for $E_n^{(2)}$.

Let us discuss the physics of our solution up to the second order. The first order term is reasonable, since up to first order the expectation value of energy *must be* $E_n^{(0)} + \left\langle n^{(0)} \middle| \hat{H}_1 \middle| n^{(0)} \right\rangle$. The proof is left for your exercise. The second order term is more complicated. One thing that it indicates is very important to notice. If you take $n = 0$ (ground state), then you can see that the second order correction is negative, assuming that not all of the matrix elements of $\hat{H}_1$ vanish. This means that the ground state energy is pushed *down* by the second order correction. This is different from the first order correction, which can go either way. The pushing down

effect of the second order correction is the consequence of what is generally called **quantum level repulsion**: if two quantum levels are mixed/hybridized, then the result is that their energy values "push apart," namely the lower energy gets even lower and the higher energy gets even higher. The ground state level is pushed down by all higher energy levels, which is why the above second order correction is negative for the ground state.

[*Optional reading, recommended to everyone*] The second order energy correction is often referred to in terms of **virtual processes.** In the Feynman picture of QM, a process in which a particle in state $|n^{(0)}\rangle$ virtually transitions/hops to $|m^{(0)}\rangle$, stays there ("propagates") a bit, and then virtually hops back to $|n^{(0)}\rangle$ is responsible for this second order term. The two occurrences of the matrix elements of $\hat{H}_1$ in the numerator correspond to the two virtual hopping process, while the term $1/(E_n^{(0)} - E_m^{(0)})$ corresponds to the intermediate propagation:

$$E_n^{(2)} = \sum_{m \neq n} \left\langle n^{(0)} \right| \hat{H}_1 \left| m^{(0)} \right\rangle \frac{1}{E_n^{(0)} - E_m^{(0)}} \left\langle m^{(0)} \right| \hat{H}_1 \left| n^{(0)} \right\rangle$$

A virtual transition means a transition process in which the final state or the initial state is not a physically measured state, but a transient/virtual state that transitions into another state, physical or virtual. In contrast, a real transition is a transition event in which the initial state and the final state are real in the sense that they are both measured.

3.5 Perturbation parameter

What is the perturbation parameter δ for the current theory? There is no general sharp answer to this question. Here, we will discuss a general vague answer, leaving the actual determination of the perturbation parameter to each individual problem.

It is important to note that the ultimate criterion to determine that the perturbation theory works is that the perturbation theory, Eqs. 3.14, 3.15 converge. If successive terms remain large, then this will not occur!

In view of our solution up to the second order, Eq. 3.22, one can say the following. The general structure is that the first order $\sim h_1$ and the second order term $\sim h_1^2/\text{UELS}$, where h_1 refers to the matrix element of $\hat{H}_1$. Where UELS stands for "unperturbed energy level spacing." Here, we assume that the summation in the second order term is dominated by a few terms that correspond to m close to n. Thus, it follows that the ratio of the second order term to the first order term $\sim h_1/\text{UELS}$, a dimensionless parameter which corresponds to the general rough answer for what the perturbation

parameter is.

$$\text{Perturbation parameter } \delta \sim \frac{\text{Matrix element of } \hat{H}_1}{\text{Unperturbed energy level spacing near } E_n} \tag{3.23}$$

For any specific problem, the parameter δ will turn out to be a ratio of a certain parameter in $\hat{H}_1$ and another parameter in $\hat{H}_0$.

3.6 δ and λ

One often sees the symbol λ in the literature in discussing the perturbation theory. Indeed, it is a standard symbol, for the *small* perturbation parameter.

However, in some discussions, it is often "cranked up to be" 1, after the perturbation theory is done. However, 1 is clearly not a small number. What is happening? The answer is that in those cases, λ **is used as a stand-in mathematical device for keeping track of smallness of terms**. λ is not a real perturbation parameter in those cases (including our textbook). In those discussions, one writes

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... \\ |n\rangle &= \left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + ... \\ \hat{H} &= \hat{H}_0 + \lambda \hat{H}_1 \end{aligned}$$

From this point of view, the perturbation theory comes down to simply matching coefficients of λ, in the two "master equations:"

$$\begin{aligned} \left(E_n^{(0)} - \hat{H}_0\right)\left(\sum_{j=0}^{\infty} \lambda^j \left|n^{(j)}\right\rangle\right) &= \left(\lambda \hat{H}_1 - \sum_{j=1}^{\infty} \lambda^j E_n^{(j)}\right)\left(\sum_{j=0}^{\infty} \lambda^j \left|n^{(j)}\right\rangle\right) \\ \sum_{j=1}^{\infty} \lambda^j E_n^{(j)} &= \left\langle n^{(0)}\right| \lambda \hat{H}_1 \left|\left(\sum_{j=0}^{\infty} \lambda^j \left|n^{(j)}\right\rangle\right)\right. \end{aligned}$$

Unfortunately, the fact that λ is used as a fake stand-in for the real perturbation parameter is not communicated well in elementary texts, in my opinion.

This is why in my note I am using δ for the real perturbation parameter. If it is not confusing to you, I actually recommend using λ for the *real* perturbation parameter. A stand-in parameter, if necessary, can be given a symbol different from λ, then. However, since the notation $^{(j)}$ already carries information on the smallness order, a fake stand-in is arguably mostly redundant, with its only real usefulness being helping to remember that $\hat{H}_1$ is of the first order.

Of course, the real physics is that the perturbation method works only when correction terms become smaller and smaller as the order increases. So, it remains a mandatory task for the practitioner of the perturbation method to always identify the real perturbation parameter that is dimensionless and small, regardless of symbols used or not used.