Notes for Lecture 5

Degenerate perturbation examples, symmetry

Now that we have fully established the theory of time independent perturbation, we learn some key examples for the degenerate perturbation. This leads naturally to the discussion of symmetry.

5.1 Examples of degenerate perturbation

Particle in 1D

We imagine a circular one dimensional world, in which a particle lives. Let the radius be R, and the angular position along the circle be θ. The free particle Hamiltonian is simply given by

$$\hat{H}_0 = \frac{\hat{L}_\theta^2}{2mR^2} \qquad \hat{L}_\theta \doteq -i\hbar\frac{\partial}{\partial\theta} \quad (\theta \text{ representation}) \tag{5.1}$$

The energy eigenstate can be written as the simultaneous eigenstate of $\hat{L}_\theta$, and thus we get

$$\langle\,\theta\,|\,n\rangle = \frac{1}{\sqrt{2\pi}}\exp(in\theta) \qquad n \text{ is an integer} \tag{5.2}$$

$$\hat{H}_0\,|n\rangle = E_n\,|n\rangle \qquad E_n = \frac{n^2\hbar^2}{2mR^2} \tag{5.3}$$

The reason why n must be an integer is because the wave function must be single valued.

Now, let us consider a perturbing potential

$$V(\theta) = -V_0 \exp\left(-\frac{\theta^2}{\Delta^2}\right) \qquad V_0 > 0, \quad \Delta \ll \pi \tag{5.4}$$

This is an attractive potential localized on one point of a circle. Localized, since the angular range $\sim 2\Delta$ (the standard deviation for the above function of θ is given by $\sigma_\theta = \Delta/\sqrt{2}$) is assumed much smaller than the full angle of a circle. We shall assume that V_0 is small, in the sense that $V_0/\Delta E_n = 2V_0 mR^2/((2|n|+1)\hbar^2) \ll 1$. However, no matter how small V_0 is, the energy level for any finite integer n defines a degenerate perturbation theory, since $E_n = E_{-n}$.

So, let us ask, what is the zeroth order eigenstate and the first order energy correction for $n \neq 0$?

To answer this, we need to build a 2×2 matrix for a given n. This is what we called "sub-matrix" in the discussion above. We will denote it as $\hat{W}$. It reads, using $|n\rangle$ and $|-n\rangle$ as the basis,

$$\hat{W} \doteq \begin{pmatrix} E_n + \left\langle n \left| \hat{V} \right| n \right\rangle & \left\langle n \left| \hat{V} \right| -n \right\rangle \\ \left\langle -n \left| \hat{V} \right| n \right\rangle & E_n + \left\langle -n \left| \hat{V} \right| -n \right\rangle \end{pmatrix} \tag{5.5}$$

Note that

$$\begin{aligned}
\left\langle n \left| \hat{V} \right| n \right\rangle = \left\langle -n \left| \hat{V} \right| -n \right\rangle &= -V_0 \int_{-\pi}^{\pi} d\theta \, \frac{1}{2\pi} \exp\left(-\frac{\theta^2}{\Delta^2}\right) \\
&= -\frac{V_0 \Delta}{2\pi} \int_{-\pi/\Delta}^{\pi/\Delta} d\xi \, \exp(-\xi^2) \qquad \xi \equiv \theta/\Delta \\
&\approx -\frac{V_0 \Delta}{2\pi} \int_{-\infty}^{\infty} d\xi \, \exp(-\xi^2) \\
&= -\frac{V_0 \Delta}{2\sqrt{\pi}} \\
&\equiv -\eta \\
\left\langle n \left| \hat{V} \right| -n \right\rangle = \left\langle -n \left| \hat{V} \right| n \right\rangle^* &= -V_0 \int_{-\pi}^{\pi} d\theta \, \frac{1}{2\pi} \exp\left(-\frac{\theta^2}{\Delta^2} + 2in\theta\right) \\
&\approx -\frac{V_0 \Delta}{2\pi} \int_{-\infty}^{\infty} d\xi \, \exp\left(-\xi^2 + 2in\Delta\xi\right) \\
&= -\frac{V_0 \Delta}{2\pi} \int_{-\infty}^{\infty} d\xi \, \exp\left[-(\xi - in\Delta)^2\right] \exp\left(-n^2\Delta^2\right) \\
&= -\frac{V_0 \Delta}{2\sqrt{\pi}} \exp\left(-n^2\Delta^2\right) \\
&\equiv -\varepsilon_n
\end{aligned}$$

Therefore, the W matrix becomes

$$\hat{W} \doteq \begin{pmatrix} E_n - \eta & -\varepsilon_n \\ -\varepsilon_n & E_n - \eta \end{pmatrix} \tag{5.6}$$

The eigenvalues and the corresponding eigenvectors are

$$E\pm = E_n - \eta \pm \varepsilon_n \tag{5.7}$$

$$|n, \pm\rangle = \frac{1}{\sqrt{2}} \left(|n\rangle \mp |-n\rangle \right) \tag{5.8}$$

Note that, as advertised, the energy eigenvalues include the zeroth order value (E_n) and the first order corrections ($-\eta \pm \varepsilon_n$), while $|n, \pm\rangle$ are now "good zero order states."

Some things to note.

1. **Here is very important physics. Due to the degenerate perturbation, the off-diagonal element gives the *first order* contribution in energy.** This is quite different from the non-degenerate case where the off-diagonal element gives only the second order contribution, at the most. **For this reason, the degenerate perturbation is more important than the non-degenerate perturbation.** To summarize this effect, one can say that the **energy level repulsion is much stronger when two levels are degenerate.**

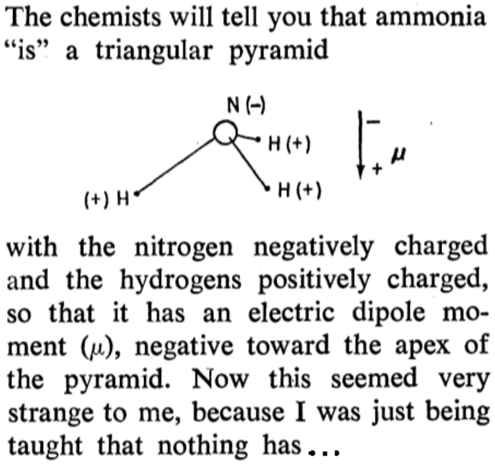
2. The lower energy state $|n, -\rangle$ with energy E_- corresponds to a symmetric sum of the two states. Since each state is a plane wave state, it follows that $\langle \theta | n, - \rangle = \frac{1}{\sqrt{\pi}} \cos(n\theta)$ and $\langle \theta | n, + \rangle = \frac{i}{\sqrt{\pi}} \sin(n\theta)$. As discussed next, these are θ-parity eigenstates. Now a physics question: why is the cosine solution lower in energy? It is because the probability is high near $\theta = 0$ where the attractive potential is strong. Both solutions have the same kinetic energy (as they are degenerate under $\hat{H}_0$. It is the potential energy that makes the difference.

3. **Good zero order states are parity eigenstates for $\theta \to -\theta$.** This problem is reminiscent of HW 2.4. The free particle Hamiltonian $\hat{H}_0$ is highly symmetric: it has the translational symmetry in angle (i.e. rotation) and the parity symmetry in angle ($\theta \to -\theta$). So, the energy eigenfunction can be taken either as plane waves in angle (as we did above), or as sine and cosine functions in θ. What we found above is that, if we include the perturbation, then the parity eigenstates (sine, cosine) are good eigenstates, while the plane waves are not. Why? It is because the perturbation has the θ-parity symmetry, but not the θ-translational symmetry. **If both $\hat{H}_0$ and $\hat{H}_1$ respects a certain symmetry, then it**

is generally a very good idea[1] to look for good eigenstates that are eigenstates of that symmetry operation (or equivalently, its generator, if applicable).

Maser, Chemical bonding, etc.

Consider an ammonia molecule NH_3, as presented in Fig. 5.1. Is this really how an ammonia molecule looks like? The answer is actually no. Why? The N ion at the top does not stay there forever. Due to the quantum tunneling mechanism, there is a finite chance that the N ion will will tunnel through the plane of hydrogen.



The chemists will tell you that ammonia "is" a triangular pyramid

with the nitrogen negatively charged and the hydrogens positively charged, so that it has an electric dipole moment (μ), negative toward the apex of the pyramid. Now this seemed very strange to me, because I was just being taught that nothing has...

Figure 5.1: A diagram of an ammonia molecule and some texts surrounding it, taken from a ground-breaking article of P. W. Anderson, *More is different*, Science **177** 4047 (1972). Words after "nothing has" have been omitted. Read the original article to find out the omitted text.

So, let us think about two configurations. One like shown in this figure, and the other where the N ion has appeared below the plane of hydrogen. It is clear that the two configurations involved here are degenerate in energy. And, from the above reasoning, it is clear that neither of them is a stationary state. In another words, they would be stationary states, only if the tunneling barrier is so high that there is no chance for us to observe that one state transitions to the other state. But, tunnel it does. We know it because this is the tunneling that is responsible for an oscillation at 24.0 GHz, and this oscillation is what has been utilized for the building of the so-called MASER (with M = microwave), a precursor of the now omni-present laser.

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[1] The only reason why this is stated as a "very good idea," not a must-do, is because there may be a *better* common symmetry to consider.

Let us focus our attention to the two states, $|A\rangle$ and $|B\rangle$, where A means N above the plane of hydrogen and B means N below the plane of hydrogen. We assume that they are orthogonal to each other[2] Since our physical argument here makes it clear that $|A\rangle$ and $|B\rangle$ are "coupled" as the system evolves in time, it follows that the Hamilton representation with these two states as the basis states cannot be diagonal. Thus, we must have

$$\hat{H} \doteq \begin{pmatrix} E_0 & t \\ t & E_0 \end{pmatrix} \tag{5.9}$$

in the $|A\rangle$, $|B\rangle$ basis, where E_0 is the energy of either state and t is the matrix element between these two states. Note that we have taken the liberty to take t to be real, which amounts to assuming that the wave functions for both A and B are real[3]. Indeed, we shall see, later in the course, that the probability for the transition between these two states is proportional to t^2, and so the above Hamiltonian representation models exactly the kind of physics that we discussed above. With the standard form of wave functions, *t will turn out to be negative ($t < 0$).*

Now, we have a simple question. What are the eigenstates and the eigenvalues of $\hat{H}$? The answer is (as you will see from HW 2.1)

$$|s\rangle = \frac{|A\rangle + |B\rangle}{\sqrt{2}} \qquad E_s = E_0 + t \tag{5.10}$$

$$|a\rangle = \frac{|A\rangle - |B\rangle}{\sqrt{2}} \qquad E_a = E_0 - t \tag{5.11}$$

Here, the letter s means the "symmetric" sum, while a means the "anti-symmetric" sum.

Note that this problem is a two state problem, just as the Larmor precession problem is a two state problem. Just as in the Larmor precession problem, a general spin state will have a time dependence that is given by ΔE, the energy level difference, here the oscillation frequency is given by $\Delta E/\hbar = 2t/\hbar$, which is the frequency of the MASER. Here is a simple exercise for you. Here, in this problem, if you prepare a state $|A\rangle$, then the state will bob up and down with frequency $2t/\hbar$. What state in the Larmor precession problem will correspond to this state?

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[2] If a quantum chemist calculates the state as shown in Fig. 5.1 to get $\langle \vec{x} | A \rangle$ and then reflect this wave function to get $\langle \vec{x} | B \rangle$, then these two wave functions will *not* be orthogonal to each other. The value $\langle A | B \rangle$ will be small, but not zero. However, it is possible to find a small number ϵ ($\approx -\langle A | B \rangle /2$) such that $\langle A' | B' \rangle = 0$ where $|A'\rangle = |A\rangle + \epsilon |B\rangle$ and $|B'\rangle = |B\rangle + \epsilon |A\rangle$. We can normalize $|A'\rangle$ and $|B'\rangle$, and then re-name them as $|A\rangle$ and $|B\rangle$, which are now orthonormal.

[3] This is always possible to do, if there is a "time-reversal symmetry." So this is OK to do for the current problem.

Note that the solution $|s\rangle$ is the even parity state with respect to the reflection on the hydrogen plane, and $|a\rangle$ is the odd parity state. If t is somehow turned off, then the two states are degenerate. Any small tunneling probability will however split the degeneracy as shown above.

Notice that this example and the previous example are mathematically equivalent as far as the 2×2 sub-matrix of the Hamiltonian is concerned. What we have discovered is that a two state problem provides an essential description of a very interesting aspect of the ammonia molecule. Thus, a two state problem is not just for spin 1/2's. Its application is indeed wide. The same exact math is applicable to covalent bonding (as in a H_2 molecule) or resonating valence bond in a benzene molecule. Also, a very similar mechanism[4] is responsible for the energy gap opening between the valence band and the conduction band in a crystal, like in silicone!

Notice that there is an energy lowering that occurs in this simple problem due to the off-diagonal element. Qualitatively, this type of lowering is mainly responsible for the binding energy of the so-called "covalent bonding" in H_2, Si crystal, graphite, graphene, etc.

Book example

Please read the textbook example, Example T6.2 (T means textbook) for the degenerate perturbation theory. Prove to yourself that

$$\left\langle n_x, n_y, n_z \left| \hat{H}' \right| n_x, n_y, n_z \right\rangle = \frac{V_0}{4} \tag{5.12}$$

for *any* values of n_x, n_y, n_z.

5.2 Symmetry—the art of physics

We have been discussing symmetry and conservation a little bit. In the next lecture, we will consider them in some more depth, so that everyone can be much more sure about them.

Here, let us remind ourselves what it actually means when we say "the system is invariant under such and such symmetry operation."

Physically, this means that when we transform our experimental set up in a certain way we would get exactly the same results if we apply the same initial conditions. I.e.,

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[4] A complex 2×2 matrix is necessary for this physics, even in the simplest model.

it means that the physical law is symmetric, i.e. remains the same upon such a transformation. Here, the transformation might mean a rotation, for example. Please read more extensive discussion about symmetry in `https://griffin.ucsc.edu/ph105-11/Lecture%2B?action=AttachFile&do=get&target=L09-Sym-Cons%2B.pdf`. The general discussion of symmetry and conservation, as presented there, applies both to classical mechanics and quantum mechanics.

In classical mechanics, a symmetry means that the Lagrangian or the Hamiltonian is invariant under that symmetry operation. It is the same in QM, as well. If we say that "the system is invariant under rotation" (or the space is isotropic) then it means that the Hamiltonian is exactly the same when expressed in the original coordinate system or in any rotated coordinate system.

We will make our discussion on this point mathematically very sharp in the next lecture.