

# Chapter 1

## Time independent perturbation theory

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The kind of problems that we solve by exact methods are far and few. As we edge beyond the hydrogen atom, and enter into the world of helium, lithium and the bigger atoms and then enter the world of molecules, the situation becomes so complicated that we have to resort to approximate methods. These are of different kinds. Today we are going to look at one of the simplest approaches that provide approximate solutions. This technique is called the time independent perturbation theory.

In time independent perturbation theory, we know there is some Hamiltonian  $\hat{\mathcal{H}}_0$  which is large and whose solution is well known, i.e. the eigenstates and eigenenergies are all established. Let's denote the eigenstates of  $\hat{\mathcal{H}}_0$  as  $|\psi_n^{(0)}\rangle$ , with a zero in the superscript. We label the eigenvalues as  $E_n^{(0)}$ :

$$\hat{\mathcal{H}}_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle. \quad (1.1)$$

Therefore this is a well known system and becomes the starting point for the approximate approach.

If the Hamiltonian now includes a small perturbative term,  $\hat{\mathcal{H}}_p$ , the overall Hamiltonian changes to

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_p. \quad (1.2)$$

What do we mean by small? For now, we can say that change in energy due to  $\hat{\mathcal{H}}_p$  is much smaller than the energy eigenvalue  $E_n^{(0)}$  itself. How do we find the eigenstates of the perturbed  $\hat{\mathcal{H}}$ ? Our approach is to put a small parameter, a

scalar  $\lambda$ , next to  $\hat{\mathcal{H}}_p$

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_o + \lambda \hat{\mathcal{H}}_p, \quad (1.3)$$

such that if  $\lambda$  equals zero, we get the exact Hamiltonian. If  $\lambda$  equals one, we have turned on the full perturbation. For  $0 < \lambda < 1$ , we have mild to strong perturbation. This parameter  $\lambda$  will also help keep track of the order of the problem, as we shortly demonstrate.

The eigenstates of the unperturbed Hamiltonian,  $\hat{\mathcal{H}}_o$ , are  $|\psi_n^{(0)}\rangle$ . With  $\lambda > 0$  the eigenstates will change. So in addition to the unperturbed wavefunction, we have some undetermined correction. Suppose these corrections are  $|\psi_n^{(1)}\rangle$ ,  $|\psi_n^{(2)}\rangle$  and so on, and each correction is multiplied by a successively increasing order of  $\lambda$ :

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots \quad (1.4)$$

Eq.(1.4) is now the eigenstate of the fully perturbed Hamiltonian  $\hat{\mathcal{H}}$ . In this formalism  $|\psi_n^{(0)}\rangle$  is the original eigenstate,  $|\psi_n^{(1)}\rangle$  is the first order term,  $|\psi_n^{(2)}\rangle$  is the second order term and henceforth. Likewise, the energy eigenvalues of the Hamiltonian will also be different from  $E_n^0$ . The new energy eigenvalues will include a zero'th order term,  $E_n^{(0)}$ , which is the unperturbed energy plus higher order terms, in exactly an analogous,

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (1.5)$$

All of these terms are identified with our parameter  $\lambda$ .

## 1.1 First order correction to the energy

The first task is to find the first order correction to the energy  $E_n^{(1)}$ . The equation we like to solve is the time independent Schrodinger equation,

$$\hat{\mathcal{H}} |\psi_n\rangle = E_n |\psi_n\rangle \quad (1.6)$$

given the Hamiltonian Eq.(1.3),

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_o + \lambda \hat{\mathcal{H}}_p. \quad (1.7)$$

Let's expand  $|\psi_n\rangle$  and  $E_n$  in terms of their approximations, picking from Eq.(1.4) and Eq.(1.5), we obtain,

$$\begin{aligned} & \left( \hat{\mathcal{H}}_o + \lambda \hat{\mathcal{H}}_p \right) \left( |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots \right) \\ & = \left( E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \right) \left( |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots \right), \end{aligned}$$

while we assume that all eigenstates of the unperturbed Hamiltonian are nondegenerate. This means there is only one eigenstate corresponding to one eigenvalue. This simplifies the problem, especially when we are tackling it for the very first time. We expand and collect the terms with same order of  $\lambda$ , on both sides of the equation, yielding

$$\begin{aligned} \hat{\mathcal{H}}_0 \left| \psi_n^{(0)} \right\rangle + \lambda \left( \hat{\mathcal{H}}_0 \left| \psi_n^{(1)} \right\rangle + \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right) + \lambda^2 \left( \hat{\mathcal{H}}_0 \left| \psi_n^{(2)} \right\rangle + \hat{\mathcal{H}}_p \left| \psi_n^{(1)} \right\rangle \right) + \dots \\ = E_n^{(0)} \left| \psi_n^{(0)} \right\rangle + \lambda \left( E_n^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(1)} \left| \psi_n^{(0)} \right\rangle \right) \\ + \lambda^2 \left( E_n^{(0)} \left| \psi_n^{(2)} \right\rangle + E_n^{(1)} \left| \psi_n^{(1)} \right\rangle + E_n^{(2)} \left| \psi_n^{(0)} \right\rangle \right) + \dots \end{aligned}$$

In the first stage, let's collect all the terms that are independent of  $\lambda$ , yielding

$$\hat{\mathcal{H}}_0 \left| \psi_n^{(0)} \right\rangle = E_n^{(0)} \left| \psi_n^{(0)} \right\rangle \quad (1.8)$$

Ah! That's no surprise! This is something we already know, that is  $E_n^{(0)}$  is the unperturbed eigenvalue and  $\left| \psi_n^{(0)} \right\rangle$  is the unperturbed eigenfunction of the unperturbed  $\hat{\mathcal{H}}_0$ .

In the second stage, let's collect all terms in first order,

$$\hat{\mathcal{H}}_0 \left| \psi_n^{(1)} \right\rangle + \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle = E_n^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(1)} \left| \psi_n^{(0)} \right\rangle \quad (1.9)$$

and likewise to second order, we have

$$\hat{\mathcal{H}}_0 \left| \psi_n^{(2)} \right\rangle + \hat{\mathcal{H}}_p \left| \psi_n^{(1)} \right\rangle = E_n^{(0)} \left| \psi_n^{(2)} \right\rangle + E_n^{(1)} \left| \psi_n^{(1)} \right\rangle + E_n^{(2)} \left| \psi_n^{(0)} \right\rangle \quad (1.10)$$

If you project Eq.(1.9) onto  $\left| \psi_n^{(0)} \right\rangle$ , we obtain

$$\left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_0 \left| \psi_n^{(1)} \right\rangle + \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right\rangle = E_n^{(0)} \left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(1)} \left\langle \psi_n^{(0)} \left| \psi_n^{(0)} \right\rangle \right\rangle. \quad (1.11)$$

We observe the terms one by one. Since  $\hat{\mathcal{H}}_0$  is a hermitian operator, it can act on the bra to its left in the very first term to give  $E_n^{(0)}$ , resulting in the cancellations,

$$\cancel{E_n^{(0)} \left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right\rangle} + \left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right\rangle = \cancel{E_n^{(0)} \left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right\rangle} + E_n^{(1)} \left\langle \psi_n^{(0)} \left| \psi_n^{(0)} \right\rangle \right\rangle, \quad (1.12)$$

after which we are left with

$$\left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right\rangle = E_n^{(1)} \left\langle \psi_n^{(0)} \left| \psi_n^{(0)} \right\rangle \right\rangle, \quad (1.13)$$

and since  $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$  is equal to one, we finally obtain

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{\mathcal{H}}_p | \psi_n^{(0)} \rangle, \quad (1.14)$$

which is the first order correction to energy. This correction to energy equals the expectation value of the perturbative Hamiltonian considering the unperturbed eigenstate. This appears a simple prescription and often very easy to remember and straightforward to apply to real scenarios. Here is an interim summary.

Find  $|\psi_n^{(0)}\rangle$  the unperturbed eigenstate of the original Hamiltonian,  $\hat{\mathcal{H}}_0$ . There will be  $N$  such eigenstates, for the nondegenerate  $N$  dimensional system. Let's look at the  $n$ 'th state, one of those states and find the expectation value of the perturbative Hamiltonian in that particular state. The energy of  $n$ 'th eigenstate  $E_n$  is then approximately equal to the unperturbed energy  $E_n^{(0)}$  plus the correction term  $E_n^{(1)}$  (put  $\lambda = 1$ ):

$$E_n \cong E_n^{(0)} + E_n^{(1)}. \quad (1.15)$$

At the moment, the role of  $\lambda$  is just for bookkeeping purposes and for comparing terms on both sides of the equation. In the end,  $\lambda$  slips the scene. We are now in a position to calculate how the perturbation corrects the wavefunction correction.

## 1.2 First order correction to the eigenstates

Next, we are interested in the first order correction to the eigenstate. Assuming that  $\lambda = 1$ , the new eigenstate  $|\psi_n\rangle$  would approximately be equal to the unperturbed state,  $|\psi_n^{(0)}\rangle$  plus the first order correction,  $|\psi_n^{(1)}\rangle$ ,

$$|\psi_n\rangle \cong |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle. \quad (1.16)$$

To begin with, all we know are the  $|\psi_n^{(0)}\rangle$ , which form the eigenstates of  $\hat{\mathcal{H}}_0$ , and hence form a complete basis of the nondegenerate system. We can expand the correction term  $|\psi_n^{(1)}\rangle$  in the basis,  $|\psi_m^{(0)}\rangle$  within the same Hilbert space,

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} C_{mn}^{(1)} |\psi_m^{(0)}\rangle, \quad (1.17)$$

with the as yet unknown complex coefficient  $C_{mn}^{(1)}$ . In order to make progress, we assume that the state,  $|\psi_n^{(1)}\rangle$  does not include any amount of  $|\psi_n^{(0)}\rangle$  which translates to eliminating one term from the finite sum, hence the restraint  $m \neq n$  inside Eq.(1.17). There are two ways in which we can describe this exclusion. If

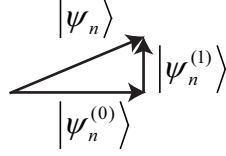


Figure 1.1: Pictorial representation of the perturbation altering the unperturbed state. The diagram cannot be taken literally because quantum states do not live in the Euclidean space and it's unjust to show states in this manner, but the diagram is a useful pedagogical aid.

there is no perturbation, then the set of states

$$\left\{ \left| \psi_1^{(0)} \right\rangle, \left| \psi_2^{(0)} \right\rangle, \left| \psi_3^{(0)} \right\rangle \dots \left| \psi_N^{(0)} \right\rangle \right\} \quad (1.18)$$

forms a basis in which any state can be represented. If I fetch some state inside this manifold,  $\left| \psi_n^{(0)} \right\rangle$  which is an eigenstate of unperturbed Hamiltonian, a correction term  $\left| \psi_n^{(1)} \right\rangle$  must be added to it. The correction should be orthogonal to the unperturbed state (See Figure 1.1). The reason is simple. If  $\left| \psi_n^{(1)} \right\rangle$  were not orthogonal to  $\left| \psi_n^{(0)} \right\rangle$ , it will add to or subtract from the length of  $\left| \psi_n^{(0)} \right\rangle$ , resulting in loss of normalization which is physically unrealizable.

The argument can also be seen to hold mathematically. The correction can be written as superposition of all the unperturbed states,

$$\left| \psi_n^{(1)} \right\rangle = \sum_{\text{all } m} C_{mn}^{(1)} \left| \psi_m^{(0)} \right\rangle \quad (1.19)$$

The coefficient  $C_{mn}^{(1)}$ , is found as the inner product

$$C_{mn}^{(1)} = \left\langle \psi_m^{(0)} \left| \psi_n^{(1)} \right\rangle. \quad (1.20)$$

Suppose the state after correction is

$$\left| \psi_n \right\rangle = \left| \psi_n^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle + O(\lambda^2). \quad (1.21)$$

The overlap of this state with itself must also be equal to 1, while  $\left\langle \psi_n^{(0)} \left| \psi_n^{(0)} \right\rangle = 1$  as well. The inner product of the corrected state, therefore can be computed as,

$$\begin{aligned} \langle \psi_n | \psi_n \rangle = 1 &= \left( \left\langle \psi_n^{(0)} \right| + \lambda \left\langle \psi_n^{(1)} \right| \right) \left( \left| \psi_n^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle \right) + O(\lambda^2) \\ &= \left\langle \psi_n^{(0)} \left| \psi_n^{(0)} \right\rangle + \lambda \left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right\rangle + \lambda \left\langle \psi_n^{(1)} \left| \psi_n^{(0)} \right\rangle + O(\lambda^2) \right. \\ &= 1 + \lambda \left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right\rangle + \lambda \left\langle \psi_n^{(1)} \left| \psi_n^{(0)} \right\rangle + O(\lambda^2). \end{aligned} \quad (1.22)$$

Since  $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle^*$ , the middle term can be replaced by the real number, yielding

$$2\lambda \Re \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + O(\lambda^2) = 0. \quad (1.23)$$

This must hold true for all choices of  $\lambda$ . Therefore  $2\lambda \Re \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle$  must be equal to 0 implying that  $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle$  can at best be purely imaginary,

$$\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = ia, \quad a \in \Re. \quad (1.24)$$

Now it is legitimate to write,

$$|\psi^{(1)}\rangle = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle |\psi_n^{(0)}\rangle + \sum_{m \neq n} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle |\psi_m^{(0)}\rangle, \quad (1.25)$$

where I have partitioned the sum into two sectors; one is the projection onto the eigenstate with basis state of the same index and second, is the projection onto all the other basis states with different indices. Therefore, the state Eq.(1.21) after perturbation is

$$\begin{aligned} |\psi_n\rangle &= |\psi_n^{(0)}\rangle + |\psi_n^1\rangle + O(\lambda^2) \\ &= |\psi_n^{(0)}\rangle + \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle |\psi_n^{(0)}\rangle + \sum_{m \neq n} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle |\psi_m^{(0)}\rangle + O(\lambda^2) \\ &= \left(1 + ia + O(\lambda^2)\right) |\psi_n^{(0)}\rangle + \sum_{m \neq n} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle |\psi_m^{(0)}\rangle \end{aligned} \quad (1.26)$$

$$= e^{ia\lambda} |\psi_n^{(0)}\rangle + \sum_{m \neq n} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle |\psi_m^{(0)}\rangle, \quad (1.27)$$

where Eq.(1.26) uses Eq.(1.24). Since this must be true for any real value of  $a$  including  $a = 0$ , we can write

$$|\psi_n\rangle \cong |\psi_n^{(0)}\rangle + \sum_{m \neq n} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle |\psi_m^{(0)}\rangle. \quad (1.28)$$

which upon comparison with Eq.(1.16) immediately shows

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle |\psi_m^{(0)}\rangle, \quad (1.29)$$

excluding the  $m = n$  term from the sum. The non-overlap assumption therefore means that the correction term is orthogonal living in subspace orthogonal to the unperturbed wavefunction. The overlaps  $\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$  are the coefficients  $C_{mn}^{(1)}$ .

Let's once again consider the Eq.(1.9), which I rewrite here,

$$\hat{\mathcal{H}}_0 \left| \psi_n^{(1)} \right\rangle + \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle = E_n^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(1)} \left| \psi_n^{(0)} \right\rangle \quad (1.30)$$

which upon projection onto  $\left| \psi_m^{(0)} \right\rangle$  gives,

$$\left\langle \psi_m^{(0)} \left| \hat{\mathcal{H}}_0 \left| \psi_n^{(1)} \right\rangle + \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right\rangle = E_n^{(0)} \left\langle \psi_m^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(1)} \left\langle \psi_m^{(0)} \left| \psi_n^{(0)} \right\rangle \right\rangle \quad (1.31)$$

where the last term cancels out since  $m \neq n$  indicating orthogonal eigenstates of the unperturbed Hamiltonian. The first term  $\left\langle \psi_m^{(0)} \left| \hat{\mathcal{H}}_0 \left| \psi_n^{(1)} \right\rangle \right\rangle$  can be written as  $E_m^{(0)} \left\langle \psi_m^{(0)} \left| \psi_n^{(1)} \right\rangle$ .

$$E_m^{(0)} \left\langle \psi_m^{(0)} \left| \psi_n^{(1)} \right\rangle + \left\langle \psi_m^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right\rangle = E_n^{(0)} \left\langle \psi_m^{(0)} \left| \psi_n^{(1)} \right\rangle \right. \quad (1.32)$$

and rearranging,

$$\left\langle \psi_m^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right\rangle = E_n^{(0)} \left\langle \psi_m^{(0)} \left| \psi_n^{(1)} \right\rangle - E_m^{(0)} \left\langle \psi_m^{(0)} \left| \psi_n^{(1)} \right\rangle \right\rangle \quad (1.33)$$

$$\left\langle \psi_m^{(0)} \left| \psi_n^{(1)} \right\rangle = \frac{\left\langle \psi_m^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right\rangle}{E_n^{(0)} - E_m^{(0)}}, \quad m \neq n \quad (1.34)$$

which is precisely the inner product we are seeking for in Eq.(1.29). Therefore if we insert Eq.(1.34) into Eq.(1.29), we finally obtain the first order correction to the eigenstate, .

$$\left| \psi_n^{(1)} \right\rangle = \sum_{m \neq n} \left[ \frac{\left\langle \psi_m^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right\rangle}{E_n^{(0)} - E_m^{(0)}} \right] \left| \psi_m^{(0)} \right\rangle. \quad (1.35)$$

Note that  $\left\langle \psi_m^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle \right\rangle$  is not an expectation value, but a matrix element of  $\hat{\mathcal{H}}_p$ , between  $\left| \psi_m^{(0)} \right\rangle$  and  $\left| \psi_n^{(0)} \right\rangle$ . All in all, Eq.(1.35) is the first order correction to the eigenstate. What does the correction term to  $n$ 'th state look like? Its a sum over all the unperturbed eigenstates of the original Hamiltonian,  $\left| \psi_m^{(0)} \right\rangle$ , excluding the  $n$ 'th state weighted by a coefficient with each term! This coefficient is simply a matrix element of the perturbative Hamiltonian. Also remember to divide by the difference in energy between the  $n^{\text{th}}$  state and  $m^{\text{th}}$  state. We notice that the coefficients are indexed by  $m$  and  $n$ ,  $\hat{\mathcal{H}}_{p,mn}$ . We can write the matrix in the basis of unperturbed eigenstates, picking up the element in that matrix at the  $m$ 'th row and  $n$ 'th column and weighing the unperturbed state with that element.

Luckily, this formula applies to a nondegenerate system so the values of  $E_n^{(0)}$  and  $E_m^{(0)}$  are unequal, otherwise you run into trouble as the denominator will blow

up. Degenerate states are different eigenstates which possess the same energy. For degenerate perturbation theory, this procedure needs further adjustment as we describe shortly. Let's now go to the next level of approximation and perform a second order correction to the energy; after all, this approximation may be required in some important cases.

### 1.3 Second order correction to the energy

The mechanism by which we compute and update perturbed energies may now be very clear. Let's give the process another shot, attempting to calculate the second order correction. We start with Eq.(1.10), which is the second order balance,

$$\hat{\mathcal{H}}_0 \left| \psi_n^{(2)} \right\rangle + \hat{\mathcal{H}}_p \left| \psi_n^{(1)} \right\rangle = E_n^{(0)} \left| \psi_n^{(2)} \right\rangle + E_n^{(1)} \left| \psi_n^{(1)} \right\rangle + E_n^{(2)} \left| \psi_n^{(0)} \right\rangle \quad (1.36)$$

let's project this onto the unperturbed state with an identical index  $n$  i.e,  $\left| \psi_n^{(0)} \right\rangle$ , resulting in

$$\left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_0 \left| \psi_n^{(2)} \right\rangle + \left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(1)} \right\rangle = E_n^{(0)} \left\langle \psi_n^{(0)} \left| \psi_n^{(2)} \right\rangle + E_n^{(1)} \left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(2)} \left\langle \psi_n^{(0)} \left| \psi_n^{(0)} \right\rangle. \right. \right. \quad (1.37)$$

The inner product  $\left\langle \psi_n^{(0)} \left| \psi_n^{(0)} \right\rangle = 1$  and furthermore, canceling the first term on either side of the equation, leaves us with

$$\left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(1)} \right\rangle = E_n^{(1)} \left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(2)} \quad (1.38)$$

but according to our previous argument  $\left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right\rangle = 0$ , finally yielding

$$E_n^{(2)} = \left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(1)} \right\rangle \quad (1.39)$$

Compare this with the first order correction term,  $\left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle$  given in Eq.(1.14). The first order correction to energy is a sandwich of  $\hat{\mathcal{H}}_p$  between  $\left| \psi_n^{(0)} \right\rangle$  and itself while the second order correction to energy is a sandwich between  $\left| \psi_n^{(0)} \right\rangle$  and  $\left| \psi_n^{(1)} \right\rangle$ . The latter state  $\left| \psi_n^{(1)} \right\rangle$  is something we have already determined in Eq.(1.35), and can be recursively inserted in to Eq.(1.39), resulting in

$$E_n^{(2)} = \left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_p \left( \sum_{m \neq n} \frac{\left\langle \psi_m^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} \left| \psi_m^{(0)} \right\rangle \right) \right. \right. \quad (1.40)$$



Correction	Formula	Where
First order correction to energy, $E_n^{(1)}$	$\langle \psi_n^{(0)}   \hat{\mathcal{H}}_p   \psi_n^{(0)} \rangle$	Eq.(1.14)
Second order correction to energy, $E_n^{(2)}$	$\sum_{m \neq n} \frac{ \langle \psi_m^{(0)}   \hat{\mathcal{H}}_p   \psi_n^{(0)} \rangle ^2}{E_n^{(0)} - E_m^{(0)}}$	Eq.(1.42)
First order correction to wavefunction, $ \psi_n^{(1)}\rangle$	$\sum_{m \neq n} \left[ \frac{\langle \psi_m^{(0)}   \hat{\mathcal{H}}_p   \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \right]  \psi_m^{(0)}\rangle$	Eq. (1.35)

The variable  $m$  in the sum is different from  $n$ , so we can take it outside the summation. Moreover since,  $\langle \psi_m^{(0)} | \hat{\mathcal{H}}_p | \psi_n^{(0)} \rangle$  is just a scalar so we can move it anywhere we like,

$$E_n^{(2)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{\mathcal{H}}_p | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | \hat{\mathcal{H}}_p | \psi_m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad (1.41)$$

$$= \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | \hat{\mathcal{H}}_p | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad (1.42)$$

which is the desired correction, to correct up to second order. In most cases we don't need to go beyond the second order correction in energy and seldom do we need to find the second order correction to the wavefunction. We are now in a good starting position to apply the time independent perturbation analysis to some interesting physical problems. Of course, the method has wide application in all fields, and is our first ammunition to attack complex problems of solving Hamiltonians which defy a simple and exact solution. A rapid glance summary is provided next.

## 1.4 Some applications of nondegenerate perturbation

### 1.4.1 Electron trapped inside an infinite well and subject to an electric field

Suppose we have an electron inside infinite well (of length  $L$ ) and we subject it to an electric field. Without the field, everything is really simple and is all well-

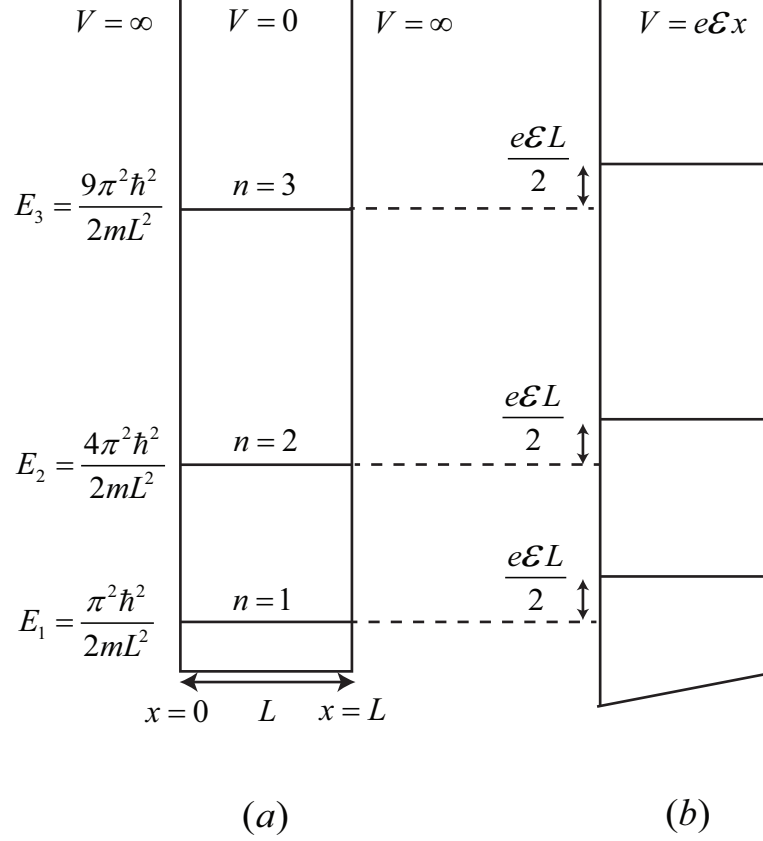


Figure 1.2: (a) Unperturbed and (b) tilted potential wells and some of the lowest energy states.

known. The unperturbed Hamiltonian for the electron inside the well is

$$\hat{\mathcal{H}}_o = \frac{\hat{p}^2}{2m}, \quad (1.43)$$

where  $p$  is momentum and  $m$  is the mass of electron. The  $n$ 'th unperturbed eigenenergy is,

$$E_n^{(0)} = \frac{n^2 \pi^2 \hbar^2}{2mL^2}. \quad (1.44)$$

The eigenstates in position basis are

$$\psi_n^{(0)}(x) = \langle x | \psi_n^{(0)} \rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \quad (1.45)$$

That is all as far as the unperturbed solution to the Hamiltonian is concerned.

The electric field is our perturbation. A relevant scenario could be of an electron trapped inside the junction between two semiconductors, confined to move in one dimension, and on top of it, one applies an electric field to the junction. Consider an electric field  $\vec{\mathcal{E}}$  is applied from left to right leading to higher potential energy (for the electron) towards the right. This tilts the floor of the well, as shown in Figure 1.2 (b). There is still zero probability for finding the electron outside the well because of the impenetrably high walls. How does the sloped floor change the energy eigenvalues? The potential energy  $V$  is charge of the electron  $-e$  times  $\mathcal{E}$  times distance  $x$ , ensuring that as  $x$  increases,  $V(x)$  also increases

$$V(x) = e\mathcal{E}x. \quad (1.46)$$

The energy is the eigenvalue of perturbed Hamiltonian  $\hat{\mathcal{H}}_p$ , therefore

$$\hat{\mathcal{H}}_p = e\mathcal{E}\hat{x}. \quad (1.47)$$

As  $x$  increases the potential energy increases. Consequently, the height of potential energy on the right edge is,  $e\mathcal{E}L$  above the potential energy on the left edge.<sup>1</sup> We want to find the first order correction to the energy due to the presence of tilted potential at the bottom. This correction is simply the expectation value of the perturbation Hamiltonian calculated using the unperturbed wavefunctions, Eq.(1.14),

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \left| \hat{\mathcal{H}}_p \right| \psi_n^{(0)} \right\rangle. \quad (1.49)$$

Using the completeness relation for the pure states of the position,

$$\hat{\mathbf{1}} = \int_{-\infty}^{\infty} dx |x\rangle \langle x|. \quad (1.50)$$

this correction becomes

$$E_n^{(1)} = \int_{x=0}^{\infty} \int_{x'=0}^{\infty} dx dx' \left\langle \psi_n^{(0)} \left| x \right\rangle \langle x | \hat{\mathcal{H}}_p | x' \rangle \langle x' | \psi_n^{(0)} \right\rangle \quad (1.51)$$

$x$  and  $x'$  being independent running variable. Let's see what the middle term looks like:

$$\langle x | \hat{\mathcal{H}}_p | x' \rangle = e\mathcal{E} \langle x | \hat{x} | x' \rangle = e\mathcal{E}x \langle x | x' \rangle = e\mathcal{E}x\delta(x - x'), \quad (1.52)$$

---

<sup>1</sup>Let's impose a condition that the raise in potential energy is less than the lowest unperturbed state ( $n = 1$ ),

$$\frac{\pi^2 \hbar^2}{2mL^2} > e\mathcal{E}L. \quad (1.48)$$

resulting in,

$$\begin{aligned}
 E_n^{(1)} &= \int_{x=0}^{\infty} \int_{x'=0}^{\infty} dx dx' \psi_n^{*(0)}(x') \psi_n^{(0)}(x) \langle x | \hat{\mathcal{H}}_p | x' \rangle \\
 &= \int_{x=0}^{\infty} \int_{x'=0}^{\infty} dx dx' \psi_n^{*(0)}(x') \psi_n^{(0)}(x) e\mathcal{E}x\delta(x-x') \\
 &= \frac{2}{L}(e\mathcal{E}) \int_{x=0}^L dx x \sin^2\left(\frac{n\pi x}{L}\right) \\
 &= \frac{e\mathcal{E}L}{2}.
 \end{aligned}$$

This result is independent of  $n$ , indicating that each one of the levels will shift upward by an identical amount  $e\mathcal{E}L/2$ . The total energy spectrum will shift wholesale! The spacing between levels will however not change. If there are many electrons and those electrons are making transition inside tilted infinite well, the spectrum of emitted radiation will remain unchanged. Next, we determine the

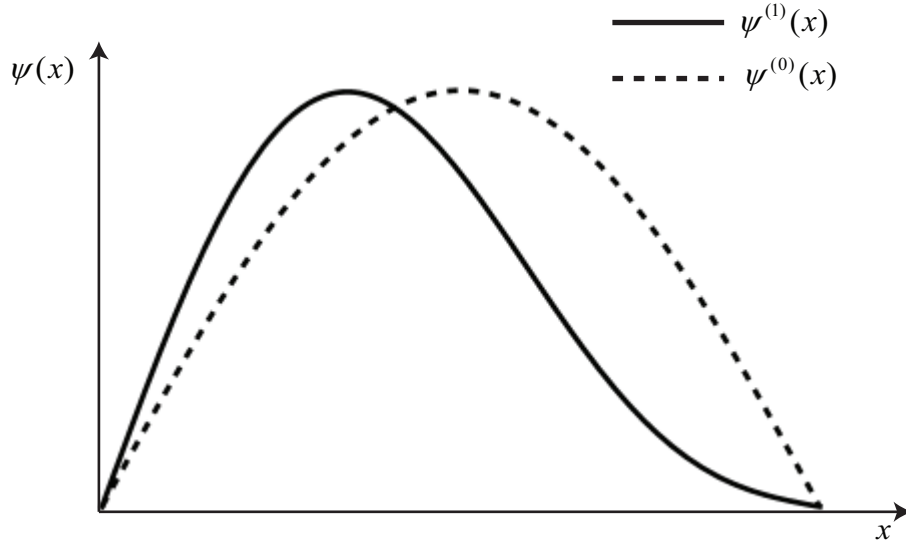


Figure 1.3: In tilted potential well the electron would prefer to occupy the position of lower potential. The solid curve shows the unperturbed ground state wavefunction. The dashed curves show the perturbed states, resulting in superposition of ground state and first excited state.

corrections to the eigenstates  $|\psi_n^{(0)}\rangle$ . The correction by virtue of Eq.(1.35) is

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} \left[ \frac{\langle \psi_m^{(0)} | \hat{\mathcal{H}}_p | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \right] |\psi_m^{(0)}\rangle, \quad (1.53)$$

for which we need the unperturbed wavefunction,

$$\langle x | \psi_m^{(0)} \rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{m\pi x}{L}\right) \quad (1.54)$$

the denominator

$$E_n^{(0)} - E_m^{(0)} = \frac{\hbar^2 \pi^2}{2m' L^2} (n^2 - m^2) \quad (1.55)$$

where we have now used primed  $m'$  to denote the mass. The required matrix element is

$$\begin{aligned} \langle \psi_m^{(0)} | \hat{\mathcal{H}}_p | \psi_n^{(0)} \rangle &= \frac{2e\mathcal{E}}{L} \int \int dx' dx \sin\left(\frac{m\pi x'}{L}\right) \sin\left(\frac{n\pi x}{L}\right) \langle x' | \hat{x} | x' \rangle \\ &= \frac{2e\mathcal{E}}{L} \int_0^L dx x \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) \\ &= -\frac{e\mathcal{E}}{L} \int_0^L dx x \left( \cos\left(\frac{(m+n)\pi x}{L}\right) - \cos\left(\frac{(m-n)\pi x}{L}\right) \right) \end{aligned} \quad (1.56)$$

Let's evaluate the first integral,

$$\begin{aligned} &\left( \int_0^L dx x \cos\left(\frac{(m+n)\pi x}{L}\right) \right) = \\ &= \frac{Lx}{(m+n)\pi} \sin\left(\frac{(m+n)\pi x}{L}\right) \Big|_0^L - \frac{L}{(m+n)\pi} \int_0^L dx \sin\left(\frac{(m+n)\pi x}{L}\right) \\ &= \left( \frac{L}{(m+n)\pi} \right)^2 \cos\left(\frac{(m+n)\pi x}{L}\right) \Big|_0^L \\ &= \left( \frac{L}{(m+n)\pi} \right)^2 \left( \cos((m+n)\pi) - 1 \right) \\ &= \left( \frac{L}{(m+n)\pi} \right)^2 \left( (-1)^{(m+n)} - 1 \right), \end{aligned} \quad (1.57)$$

while for the second integral,

$$\int_0^L dx x \cos\left(\frac{(m-n)\pi x}{L}\right) = \left( \frac{L}{(m-n)\pi} \right)^2 \left( (-1)^{(m-n)} - 1 \right). \quad (1.58)$$

Stringing these results together, we obtain for the integral Eq.(1.56), the following form

$$\begin{aligned}
& \langle \psi_m^{(0)} | \hat{\mathcal{H}}_p | \psi_n^{(0)} \rangle \\
&= -\frac{e\mathcal{E}}{L} \left( \frac{L}{\pi} \right)^2 \left( \frac{1}{(m+n)^2} \left( (-1)^{(m+n)} - 1 \right) - \frac{1}{(m-n)^2} \left( (-1)^{(m-n)} - 1 \right) \right) \\
&= -\frac{e\mathcal{E}L}{\pi^2} \frac{1}{(m+n)^2(m-n)^2} \\
&\quad \left( (m-n)^2 \left( (-1)^{(m+n)} - 1 \right) - (m+n)^2 \left( (-1)^{(m-n)} - 1 \right) \right) \\
&= -\frac{e\mathcal{E}L}{\pi^2} \frac{1}{(m^2-n^2)^2} \\
&\quad \left( \cancel{m^2 \left( (-1)^{(m+n)} - (-1)^{(m-n)} \right)} + \cancel{n^2 \left( (-1)^{(m+n)} - (-1)^{(m-n)} \right)} \right. \\
&\quad \left. - 2mn \left( (-1)^{(m+n)} + (-1)^{(m-n)} - 2 \right) \right) \\
&= \frac{e\mathcal{E}L}{\pi^2} \frac{1}{(m^2-n^2)^2} 2mn \left( (-1)^{(m+n)} + (-1)^{(m-n)} - 2 \right) \\
&= \begin{cases} -\frac{8e\mathcal{E}Lmn}{\pi^2(m^2-n^2)^2} & ; m+n \text{ is odd} \\ 0 & ; m+n \text{ is even} \end{cases} \tag{1.59}
\end{aligned}$$

Inserting the expression into Eq.(1.53), the correction to the  $n$ 'th eigenstates becomes

$$\left| \psi_n^{(1)} \right\rangle = \frac{16e\mathcal{E}L^3m'n}{\pi^4\hbar^2} \sum_{\substack{m \neq n \\ (m+n) \text{ is odd}}} \frac{m}{(m^2-n^2)^3} \left| \psi_m^{(0)} \right\rangle \tag{1.60}$$

For computing correction to the ground state,  $n = 1$ , we obtain

$$\left| \psi_1^{(1)} \right\rangle = \frac{16e\mathcal{E}L^3m'}{\pi^4\hbar^2} \sum_{\substack{m \neq 1 \\ m=2,4,6\dots}} \frac{m}{(m^2-1)^3} \left| \psi_m^{(0)} \right\rangle \tag{1.61}$$

The coefficients  $m/(m^2-1)^3$  decreases rapidly as  $m$  goes up. Therefore, taking only  $m = 2$ , will give

$$\left| \psi_1^{(1)} \right\rangle = \frac{32e\mathcal{E}L^3m'}{27\pi^4\hbar^2} \left| \psi_2^{(0)} \right\rangle, \tag{1.62}$$

resulting in the corrected ground state,

$$\langle x | \psi_1 \rangle \cong \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) + \frac{32e\mathcal{E}L^3m'}{27\pi^4\hbar^2} \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) \tag{1.63}$$

which is correct up to a normalization factor and shows intermixing of some fraction of the first excited state's wavefunction into the ground state polynomial. The corrected wavefunction for some imagined values of the electric field  $\mathcal{E}$ , and length  $L$  are shown in Figure 1.3

### 1.4.2 A harmonic oscillator inside an electric field

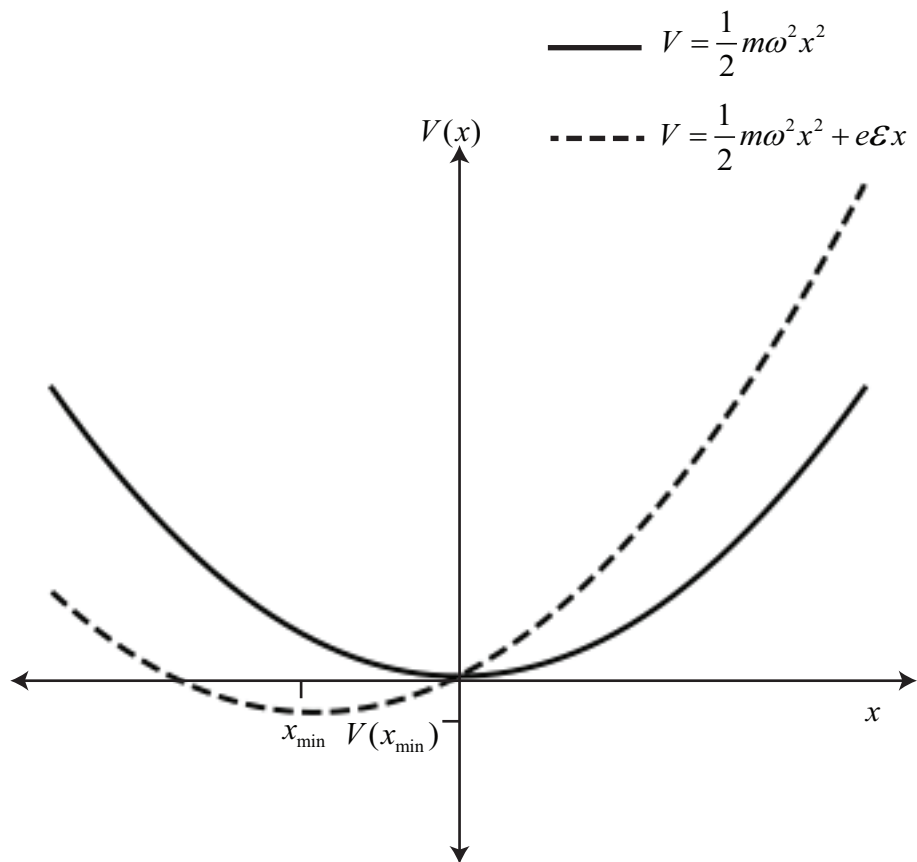


Figure 1.4: Harmonic oscillator inside an electric field. The solid (dashed) curve shows the unperturbed (perturbed) potential energy function.

As another example of the application of the time independent perturbation theory, consider a harmonic oscillator placed inside an electric field  $\mathcal{E}$ . An electron acts like a harmonic oscillator inside a parabolic potential and over and above sees the electric field too. The curve in Figure 1.4 for the Harmonic oscillator which is given by

$$V(x) = \frac{1}{2}m\omega^2x^2. \quad (1.64)$$

The potential energy is minimum at  $x = 0$ . The Hamiltonian corresponding to this system is of the form,

$$\hat{\mathcal{H}} = \hbar\omega \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right). \quad (1.65)$$

We impose an electric field once again acting toward the right, producing the perturbative Hamiltonian given in Eq.(1.47),

$$\hat{\mathcal{H}}_p = e\mathcal{E}\hat{x}. \quad (1.66)$$

What are the perturbed energies and eigenstates? The perturbed energies? Beginning with the unperturbed scenario, the eigenstates are just the number (Fock) states, while the energies are

$$E_n^{(0)} = \hbar\omega \left( n + \frac{1}{2} \right), \quad (1.67)$$

where  $n$  is a quantum number going from 0 to  $\infty$ . The first order correction to the energy is quite straightforward to compute,

$$E_n^{(1)} = \langle n | \hat{\mathcal{H}}_p | m \rangle = e\mathcal{E} \langle n | \hat{x} | m \rangle \quad (1.68)$$

and since  $\hat{x}$  can be written in terms of raising and lowering operators,

$$E_n^{(1)} = e\mathcal{E} \sqrt{\frac{\hbar}{2m\omega}} \langle n | \left( \hat{a} + \hat{a}^\dagger \right) | m \rangle = 0. \quad (1.69)$$

Lo and behold, the energies do not change but this is only true up to first order. It is, thus, instructive to investigate the second order correction to the energy, which goes as,

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| \langle \psi_m^{(0)} | \hat{\mathcal{H}}_p | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} = e^2 \mathcal{E}^2 \sum_{m \neq n} \frac{|\langle m | \hat{x} | n \rangle|^2}{\hbar\omega (n - m)} \quad (1.70)$$

Once again, replacing  $\hat{x}$  by the combination of raising and lowering operators, we obtain

$$E_n^{(2)} = \frac{e^2 \mathcal{E}^2}{\hbar\omega} \frac{\hbar}{2m\omega} \sum_{m \neq n} \frac{\left| \langle m | \left( \hat{a} + \hat{a}^\dagger \right) | n \rangle \right|^2}{(n - m)} = \frac{e^2 \mathcal{E}^2}{2m\omega^2} \sum_{m \neq n} \frac{\left| \langle m | \left( \hat{a} + \hat{a}^\dagger \right) | n \rangle \right|^2}{(n - m)} \quad (1.71)$$



When the lowering operator acts on  $|n\rangle$ , we get  $\sqrt{n}|n-1\rangle$ , while the raising operator acting on  $|n\rangle$  produces  $\sqrt{n+1}|n+1\rangle$ . As we take the square of these terms, we obtain

$$\begin{aligned}
E_n^{(2)} &= \frac{e^2\mathcal{E}^2}{2m\omega^2} \sum_{m \neq n} \frac{|\sqrt{n}\langle m|n-1\rangle + \sqrt{n+1}\langle m|n+1\rangle|^2}{\binom{n-m}{}} \\
&= \frac{e^2\mathcal{E}^2}{2m\omega^2} \sum_{m \neq n} \frac{|\sqrt{n}\delta_{m,n-1} + \sqrt{n+1}\delta_{m,n+1}|^2}{\binom{n-m}{}} \\
&= \frac{e^2\mathcal{E}^2}{2m\omega^2} \sum_{m \neq n} \frac{\left(n\delta_{m,n-1}^2 + (n+1)\delta_{m,n+1}^2\right)}{\binom{n-m}{}} \\
&\quad + \frac{e^2\mathcal{E}^2}{2m\omega^2} \sum_{m \neq n} \frac{\cancel{\sqrt{n}\sqrt{n+1}\delta_{m,n-1}\delta_{m,n+1}} + \cancel{\sqrt{n+1}\sqrt{n}\delta_{m,n+1}\delta_{m,n-1}}}{\binom{n-m}{}},
\end{aligned}$$

where in the third step, we employ the property that the product of  $\delta_{m,n-1}$  and  $\delta_{m,n+1}$  is zero, and the square of delta function is equal to the delta function itself.

$$E_n^{(2)} = \frac{e^2\mathcal{E}^2}{2m\omega^2} \sum_{m \neq n} \frac{\left(n\delta_{m,n-1} + (n+1)\delta_{m,n+1}\right)}{\binom{n-m}{}} \quad (1.72)$$

The first term is non-zero when  $m$  equals  $n-1$ . So all terms in the sum besides  $m = n-1$  vanish. Similarly for the second term that contains  $\delta_{m,n+1}$ , there is only one value of  $m = n+1$  which renders only this very term to be non-zero, while all other terms in the sum vanish. Putting this all together, we obtain for the correction,

$$E_n^{(2)} = \frac{e^2\mathcal{E}^2}{2m\omega^2} \left(n - (n+1)\right) = -\frac{e^2\mathcal{E}^2}{2m\omega^2} \quad (1.73)$$

This is the correction to the energy and it is negative! Since the correction has  $\mathcal{E}^2$ , the direction of the electric field does not matter; the energies are always reduced. Furthermore, we obtain the same correction no matter which number state we are talking about.

Figure 1.4 shows our unperturbed potential a smooth parabola with a minimum at  $x = 0$ . When we apply an electric field the potential will clearly shift downwards and depart from its nice parabolic feature, attaining a modified form

$$V(x) = \frac{1}{2}m\omega^2x^2 + e\mathcal{E}x. \quad (1.74)$$

What is the  $-e\mathcal{E}x$  term going to do? First it translates the potential energy along the axis. Secondly, it changes the form from parabolic to parabolic plus linear. Let's find the minimum of this function through the derivative

$$\frac{dV}{dx} = m\omega^2x + e\mathcal{E} = 0 \quad (1.75)$$

$$x_{min} = -\frac{e\mathcal{E}}{m\omega^2}, \quad (1.76)$$

which shows a translation towards the negative axis which is completely understandable as the electron would tend to spend more time to the left rather than the right, in a region of lower energy. Next we find the minimum value of potential energy. If we put  $x_{min}$  value into  $V(x)$ , we obtain

$$V(x_{min}) = \frac{1}{2}m\omega^2x_{min}^2 + e\mathcal{E}x_{min} \quad (1.77)$$

$$= \frac{1}{2}m\omega^2\left(\frac{e\mathcal{E}}{m\omega^2}\right)^2 - e\mathcal{E}\left(\frac{e\mathcal{E}}{m\omega^2}\right) = -\left(\frac{e^2\mathcal{E}^2}{2m\omega^2}\right) \quad (1.78)$$

indicating the amount by which the potential energy (non-parabolic) curve shifts downwards. Figure 1.4 compares the unperturbed and perturbed potentials and the eigenenergy landscape. Since the potential is no longer parabolic, the eigenstates will not be the nice Hermite polynomials that we derived earlier for a bare harmonic oscillator.

## 1.5 Time independent degenerate perturbation theory

In nondegenerate perturbation theory which was the subject of previous sections, all the eigenvalues are unique. However, degenerate perturbation theory deals with  $\hat{\mathcal{H}}_o$  possessing at least two identical eigenvalues. For example, consider  $\hat{\mathcal{H}}_o$  with the following set of eigenvalues called the spectrum,

$$\hat{\mathcal{H}}_o = \{E_1, E_2, \dots, E_{n+1} = E_{n+2} = E_{n+3}, \dots, E_N\} \quad (1.79)$$

In this spectrum three eigenstates  $\{|\psi_{n,1}^{(0)}\rangle, |\psi_{n,2}^{(0)}\rangle, |\psi_{n,3}^{(0)}\rangle\}$  have the same eigenvalue and hence are degenerate. The degenerate eigenstates can always be constructed

to become orthogonal and there are infinite variety of ways in which one can do that. For example, suppose you have a two-dimensional degenerate subspace in which there are two basis eigenvectors

$$\left\{ \left| \psi_{n,1}^{(0)} \right\rangle, \left| \psi_{n,2}^{(0)} \right\rangle \right\} \quad (1.80)$$

which are orthogonal to one another. It is well nigh possible that one choose another basis which is still orthonormal. For example I can create an equal superposition of states,

$$\left| \psi_{n,+}^{(0)} \right\rangle = \frac{1}{\sqrt{2}} \left( \left| \psi_{n,1}^{(0)} \right\rangle + \left| \psi_{n,2}^{(0)} \right\rangle \right), \quad \text{and} \quad (1.81)$$

$$\left| \psi_{n,-}^{(0)} \right\rangle = \frac{1}{\sqrt{2}} \left( \left| \psi_{n,1}^{(0)} \right\rangle - \left| \psi_{n,2}^{(0)} \right\rangle \right) \quad (1.82)$$

which forms another legitimate choice for the basis set for the unperturbed degenerate subspace. The conundrum therefore is: which of the eigenstates do I choose as my unperturbed eigenbasis. Technically I can choose from a large variety of orthonormal basis but I need to choose one. The first order correction to the eigenstate is Eq.(1.16)

$$\left| \psi_n \right\rangle \cong \left| \psi_n^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle, \quad (1.83)$$

in the nondegenerate perturbation theory. The correction will of course depend on what you start off with. For the degenerate I will write the corresponding corrected eigenstate to first order

$$\left| \psi_n \right\rangle = \sum_{i=1}^N C_i \left| \psi_{n,i}^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle, \quad (1.84)$$

where the first term is the sum over the  $i$  unperturbed degenerate eigenstates, with some unknown coefficients  $C_i$  and the second term is the first order correction weighted with some  $\lambda$  real. I am suppressing the  $i$  in first order correction of eigenstate to make life a bit easier. I take the overlap of the corrected eigenstate with anyone of the basis states exclusively, in the unperturbed degenerate subspace,

$$\left\langle \psi_{n,j}^{(0)} \left| \psi_n \right\rangle = \sum_{i=1}^N C_i \left\langle \psi_{n,j}^{(0)} \left| \psi_{n,i}^{(0)} \right\rangle + \lambda \left\langle \psi_{n,j}^{(0)} \left| \psi_n^{(1)} \right\rangle, \quad (1.85)$$

where  $j \in [1, 2 \dots N]$  is an index in the degenerate subspace. The Schrodinger equation in the degenerate subspace becomes

$$\left( \hat{\mathcal{H}}_0 + \lambda \hat{\mathcal{H}}_p \right) \left( \sum_{i=1}^N C_i \left| \psi_{n,i}^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle \right) = \left( E_n^{(0)} + \lambda E_n^{(1)} \right) \left( \sum_{i=1}^N C_i \left| \psi_{n,i}^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle \right). \quad (1.86)$$

Let's first collect the terms up to zeroth order in  $\lambda$ ,

$$\hat{\mathcal{H}}_0 \sum_{i=1}^N C_i \left| \psi_{n,i}^{(0)} \right\rangle = E_n^{(0)} \sum_{i=1}^N C_i \left| \psi_{n,i}^{(0)} \right\rangle \quad (1.87)$$

that would just be unperturbed time independent Schrodinger equation which in plain words, mean that  $\hat{\mathcal{H}}_0$  acting on some combination of degenerate basis vectors equals the unperturbed energy and the same state. Clearly  $\sum_{i=1}^N C_i \left| \psi_{n,i}^{(0)} \right\rangle$  is an eigenstate of  $\hat{\mathcal{H}}_0$  but we don't know the  $C_i$ 's at the moment unless of course we diagonalize  $\hat{\mathcal{H}}_0$ .

For the first order correction, we extract from Eq.(1.86),

$$\hat{\mathcal{H}}_0 \left| \psi_n^{(1)} \right\rangle + \hat{\mathcal{H}}_p \sum_{i=1}^N C_i \left| \psi_{n,i}^{(0)} \right\rangle = E_n^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(1)} \sum_{i=1}^N C_i \left| \psi_{n,i}^{(0)} \right\rangle. \quad (1.88)$$

Note that while in the nondegenerate case there was no need for summation  $\sum C_i$  because  $i$  was just a single index. In the degenerate case, the degenerate subspace has dimensionality  $N$ . Let's project Eq.(1.88) on to an eigenstate of the degenerate unperturbed Hamiltonian  $\left| \psi_{n,j}^{(0)} \right\rangle$ , with some  $j$ . The  $i$  can be moved around allowing  $C_i$  to be pulled out, finally giving the equation,

$$\left\langle \psi_{n,j}^{(0)} \left| \hat{\mathcal{H}}_0 \left| \psi_n^{(1)} \right\rangle + \sum_{i=1}^N C_i \left\langle \psi_{n,j}^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_{n,i}^{(0)} \right\rangle = E_n^{(0)} \left\langle \psi_{n,j}^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(1)} \sum_{i=1}^N C_i \left\langle \psi_{n,j}^{(0)} \left| \psi_{n,i}^{(0)} \right\rangle. \quad (1.89)$$

Since  $\hat{\mathcal{H}}_0$  is a hermitian operator, it can act from the left on an eigenstate giving back the eigenvalue  $E_n^{(0)}$  and the state. That's the first term above. Using similar argument that predicate that the first order correction must be in a space that is orthonormal to the unperturbed states, leads to the following fortuitous cancellations,

$$\cancel{E_n^{(0)} \left\langle \psi_{n,j}^{(0)} \left| \psi_n^{(1)} \right\rangle} + \sum_{i=1}^N C_i \left\langle \psi_{n,j}^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_{n,i}^{(0)} \right\rangle = \cancel{E_n^{(0)} \left\langle \psi_{n,j}^{(0)} \left| \psi_n^{(1)} \right\rangle} + \sum_{i=1}^N C_i E_n^{(1)} \left\langle \psi_{n,j}^{(0)} \left| \psi_{n,i}^{(0)} \right\rangle \quad (1.90)$$

and we are left with the statement

$$\sum_{i=1}^N C_i \left\langle \psi_{n,j}^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_{n,i}^{(0)} \right\rangle = \sum_{i=1}^N C_i E_n^{(1)} \left\langle \psi_{n,j}^{(0)} \left| \psi_{n,i}^{(0)} \right\rangle. \quad (1.91)$$

Since the inner product  $\left\langle \psi_{n,j}^{(0)} \left| \psi_{n,i}^{(0)} \right\rangle$  is of unperturbed eigenstates in the degenerate subspace, the product will be the Kronecker delta

$$\sum_{i=1}^N C_i \left\langle \psi_{n,j}^{(0)} \left| \hat{\mathcal{H}}_p \left| \psi_{n,i}^{(0)} \right\rangle = E_n^{(1)} \sum_{i=1}^N C_i \delta_{i,j}. \quad (1.92)$$

On the L.H.S, the perturbative Hamiltonian is sandwiched between two basis states inside the degenerate subspace, indexed by  $i$  and  $j$ . This is really a scalar matrix element, often denoted by  $\langle \psi_{n,j}^{(0)} | \hat{\mathcal{H}}_p | \psi_{n,i}^{(0)} \rangle$ , which can also be written in shorthand way as  $(\hat{\mathcal{H}}_p)_{j,i}$ , indicating which element located in the  $j^{\text{th}}$  row and  $i^{\text{th}}$  column of the matrix representation in the original choice of the unperturbed eigenbasis. We express eq.(1.92) as the matrix equation

$$\sum_{i=1}^N (\hat{\mathcal{H}}_p)_{j,i} C_i = E_n^{(1)} \sum_{i=1}^N C_i \delta_{i,j}, \quad (1.93)$$

which primarily shows the  $j^{\text{th}}$  row in the matrix  $\hat{\mathcal{H}}_p$  being multiplied with a column vector comprising all the  $C$ 's. The size of  $(\hat{\mathcal{H}}_p)_{j,i}$  is  $N \times N$ . From our basic understanding of the quantum algebraic functions when we write this matrix, we are essentially talking about two things: a choice of basis and a particular ordering in which we choose to write the basis. The matrix can be written as

$$\hat{\mathcal{H}}_p = \begin{array}{c} \langle 1| \\ \langle 2| \\ \langle 3| \\ \vdots \\ \langle N| \end{array} \begin{array}{ccccc} |1\rangle & |2\rangle & |3\rangle & \dots & |N\rangle \\ \left( \begin{array}{ccccc} \langle 1|\hat{\mathcal{H}}_p|1\rangle & \langle 1|\hat{\mathcal{H}}_p|2\rangle & \langle 1|\hat{\mathcal{H}}_p|3\rangle & \dots & \langle 1|\hat{\mathcal{H}}_p|N\rangle \\ \langle 2|\hat{\mathcal{H}}_p|1\rangle & \langle 2|\hat{\mathcal{H}}_p|2\rangle & \langle 2|\hat{\mathcal{H}}_p|3\rangle & \dots & \langle 2|\hat{\mathcal{H}}_p|N\rangle \\ \langle 3|\hat{\mathcal{H}}_p|1\rangle & \langle 3|\hat{\mathcal{H}}_p|2\rangle & \langle 3|\hat{\mathcal{H}}_p|3\rangle & \dots & \langle 3|\hat{\mathcal{H}}_p|N\rangle \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \langle N|\hat{\mathcal{H}}_p|1\rangle & \langle N|\hat{\mathcal{H}}_p|2\rangle & \langle N|\hat{\mathcal{H}}_p|3\rangle & \dots & \langle N|\hat{\mathcal{H}}_p|N\rangle \end{array} \right) \end{array}.$$

If you like to remember which order to use, write these small bras and kets next to the rows and columns respectively Here the states  $\{|1\rangle, |2\rangle, \dots, |N\rangle\}$  are the unperturbed eigenstates in the degenerate subspace and are expressed in the usual fashion,

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad \dots, \quad |N\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix}.$$

Moreover, we can represent the  $C_i$ 's as a column vector,

$$\mathbf{C} = \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \\ C_N \end{pmatrix}. \quad (1.94)$$

Therefore expressing Eq.(1.93) in matrix form, we obtain the amenable form

$$\begin{pmatrix} \langle 1|\hat{\mathcal{H}}_p|1\rangle & \dots & \langle 1|\hat{\mathcal{H}}_p|i\rangle & \dots & \langle 1|\hat{\mathcal{H}}_p|N\rangle \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \langle j|\hat{\mathcal{H}}_p|1\rangle & \dots & \langle j|\hat{\mathcal{H}}_p|i\rangle & \dots & \langle j|\hat{\mathcal{H}}_p|N\rangle \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \langle N|\hat{\mathcal{H}}_p|1\rangle & \dots & \langle N|\hat{\mathcal{H}}_p|i\rangle & \dots & \langle N|\hat{\mathcal{H}}_p|N\rangle \end{pmatrix} \begin{pmatrix} C_1 \\ \vdots \\ C_i \\ \vdots \\ C_N \end{pmatrix} = E_n^{(1)} \begin{pmatrix} C_1 \\ \vdots \\ C_i \\ \vdots \\ C_N \end{pmatrix} \quad (1.95)$$

allowing us to find the eigenvalue  $E_n^{(1)}$  and the vector  $\mathbf{C}$  which is the set of coefficients that are required to completely settle the superposition needed for determining the first order correction. This converts the problem of finding energy corrections to a problem in diagonalizing  $\hat{\mathcal{H}}_p$  in the degenerate subspace. This is kind of cute! You want to find perturbation to the energy, you don't know which energy eigenstate you want to find perturbation to. As you solve the problem, find the perturbation to the energy and automatically obtain corrected eigenstates which are linear superposition of the unperturbed eigenstates:

$$|\psi_n^{(0)}\rangle = \sum_i C_i |\psi_{n,i}^{(0)}\rangle. \quad (1.96)$$

This rather circuitous argument is clarified through some applications, as is always the case in the subject of quantum mechanics.

## 1.6 Some applications of time independent degenerate perturbation

### 1.6.1 Single ion anisotropy

In many magnetic system such as molecular magnets which is rendered magnetic by the presence of a suitable transition metal ion, the background Hamiltonian is

$m_s$	$E_n^{(0)}$	$ \psi_n^{(0)}\rangle$
1	$D$	$ 1, 1\rangle$
0	0	$ 1, 0\rangle$
-1	$D$	$ 1, -1\rangle$

Table 1.1: Eigenstates and eigenenergies of unperturbed Hamiltonian for the application 1.6.1.

of the form

$$\hat{\mathcal{H}}_o = D \frac{\hat{S}_z^2}{\hbar^2}, \quad (1.97)$$

where  $D$  is some scalar constant. Consider a spin  $s = 1$  which has this Hamiltonian has three eigenstates

$$|1, 1\rangle, |1, 0\rangle, |1, -1\rangle, \quad (1.98)$$

and has respectively, the eigenvalues

$$\{D, 0, D\}. \quad (1.99)$$

where the states are written in the usual notation  $|s, m_s\rangle$ . Two eigenvalues of  $\hat{\mathcal{H}}_o$  the first and the third, are just the same so they form a degenerate subspace spanned by  $|1, 1\rangle$  and  $|1, -1\rangle$ . In the absence of perturbation there are two states with the same energy  $D$  and one state with lower energy 0. See Table 1.6.1 the unperturbed Hamiltonian in matrix form is,

$$\hat{\mathcal{H}}_o = D \frac{\hat{S}_z^2}{\hbar^2} = \begin{pmatrix} D & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & D \end{pmatrix}, \quad (1.100)$$

which being expressed in its eigenbasis is clearly diagonal. Now suppose that a perturbation is switched on, that is smaller than  $\hat{\mathcal{H}}_o$ ,

$$\hat{\mathcal{H}}_p = C \left( \frac{\hat{S}_x^2 - \hat{S}_y^2}{\hbar^2} \right), \quad (1.101)$$

under the constraint that  $C \ll D$ . This is a useful problem because it treats both degenerate and nondegenerate systems in one go. We intend to find the correction

to unperturbed energies and we also need to determine which combination of unperturbed states to use, for which we are calculating the perturbed energies. We need to write the perturbed Hamiltonian in a particular basis. We choose the unperturbed set of states given in Eq.(1.98). This results in,

$$\hat{\mathcal{H}}_p = \frac{C}{\hbar^2} \times \begin{array}{c} |1,1\rangle \\ |1,0\rangle \\ |1,-1\rangle \end{array} \begin{array}{ccc} |1,1\rangle & |1,0\rangle & |1,-1\rangle \\ \left( \begin{array}{ccc} \langle 1,1|(\hat{S}_x^2 - \hat{S}_y^2)|1,1\rangle & \langle 1,1|(\hat{S}_x^2 - \hat{S}_y^2)|1,0\rangle & \langle 1,1|(\hat{S}_x^2 - \hat{S}_y^2)|1,-1\rangle \\ \langle 1,0|(\hat{S}_x^2 - \hat{S}_y^2)|1,1\rangle & \langle 1,0|(\hat{S}_x^2 - \hat{S}_y^2)|1,0\rangle & \langle 1,0|(\hat{S}_x^2 - \hat{S}_y^2)|1,-1\rangle \\ \langle 1,-1|(\hat{S}_x^2 - \hat{S}_y^2)|1,1\rangle & \langle 1,-1|(\hat{S}_x^2 - \hat{S}_y^2)|1,0\rangle & \langle 1,-1|(\hat{S}_x^2 - \hat{S}_y^2)|1,-1\rangle \end{array} \right); \end{array} \quad (1.102)$$

where for your convenience, we have demarcated the rows and column with properly ordered bras and kets. Given the prescription in the (Chapter on Angular momentum) we know that in the eigenbasis (1.98) of  $\hat{S}_z$ , the operators  $\hat{S}_x$  and  $\hat{S}_y$  for the  $s = 1$  system are,

$$\hat{S}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad \hat{S}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad (1.103)$$

which results in the perturbative Hamiltonian

$$\hat{\mathcal{H}}_p = \frac{C}{\hbar^2} (\hat{S}_x^2 - \hat{S}_y^2) = C \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}. \quad (1.104)$$

Is  $\hat{\mathcal{H}}_p$  diagonal in the basis of  $\hat{\mathcal{H}}_o$ ? No, it's not. Therefore when you switch on the perturbation the eigenstates in Eq.(1.98) are no longer eigenstates of the unperturbed Hamiltonian. To consider the perturbed energy, we need to diagonalize the matrix. In fact, the perturbative Hamiltonian matrix, Eq.(1.104), can be broken down into two parts. One is the nondegenerate part comprising just the middle



element  $\langle 1, 0 | \hat{\mathcal{H}}_p | 1, 0 \rangle = 0$ ,

$$\hat{\mathcal{H}}_p = \begin{array}{c} |1, 1\rangle |1, 0\rangle |1, -1\rangle \\ \langle 1, 1| \\ \langle 1, 0| \\ \langle 1, -1| \end{array} \begin{pmatrix} 0 & 0 & C \\ 0 & 0 & 0 \\ C & 0 & 0 \end{pmatrix}. \quad (1.105)$$

with  $|1, 0\rangle$  being the approximate eigenstate. Second, we isolate out the colored elements shown on diagonal edges of the matrix

$$\hat{\mathcal{H}}_p = \begin{array}{c} |1, 1\rangle |1, 0\rangle |1, -1\rangle \\ \langle 1, 1| \\ \langle 1, 0| \\ \langle 1, -1| \end{array} \begin{pmatrix} 0 & 0 & C \\ 0 & 0 & 0 \\ C & 0 & 0 \end{pmatrix} \quad (1.106)$$

yielding the degenerate block matrix

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (1.107)$$

which is the Pauli  $\sigma_x$  matrix whose eigenstates are

$$|+\rangle = \frac{1}{\sqrt{2}}(|1, 1\rangle + |1, -1\rangle) \quad (1.108)$$

$$|-\rangle = \frac{1}{\sqrt{2}}(|1, 1\rangle - |1, -1\rangle) \quad (1.109)$$

with eigenvalues  $\pm D$ . This would result in the perturbed eigenenergies  $C + D$  and  $C - D$  for  $|+\rangle$  and  $|-\rangle$  and merely 0 for  $|1, 0\rangle$ . The fanning of energies is shown in Figure 1.5, plotted as the strength of the perturbation  $C$  is increased. Note that the energy of  $|1, 0\rangle$  state remains constant even in the presence of perturbation.

### 1.6.2 A coupled 2D harmonic oscillator

For the two dimensional uncoupled harmonic oscillator the Hamiltonian is

$$\hat{\mathcal{H}}_o = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2\hat{y}^2 \quad (1.110)$$

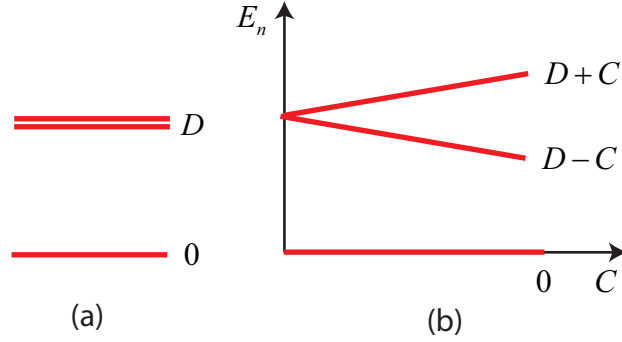


Figure 1.5: (a) Two degenerate eigenvalues  $D$  and nondegenerate eigenvalue  $0$ . (b) Perturbation  $C$  lifts degeneracy giving eigenvalues  $D + C$  and  $D - C$ . Increasing the perturbation  $C$  causes further fanning of degenerate energies. However  $C \ll D$  for degenerate theory to work.

The energy eigenstates are  $|n_x n_y\rangle$  where  $n_x$  is the quantum number energy level along  $x$  and  $n_y$  is the quantum number for energy level along  $y$ , where  $n_x, n_y \in \{0, 1, 2, \dots\}$ . When  $n_x = 0$  and  $n_y = 0$  the energy eigenvalue is

$$E_{0,0}^{(0)} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{2} = \hbar\omega \quad (1.111)$$

in the eigenstate  $|n_x = 0, n_y = 0\rangle$  is nondegenerate. As  $n_x, n_y$  increase the degeneracy increases, for example the eigenvalues

$$E_{1,0}^{(0)} = E_{0,1}^{(0)} = 2\hbar\omega; \quad \text{being 2-fold degenerate} \quad (1.112)$$

$$E_{1,1}^{(0)} = E_{2,0}^{(0)} = E_{0,2}^{(0)} = 3\hbar\omega; \quad \text{being 3 fold degenerate} \quad (1.113)$$

In general, when  $n_x = n$  and  $n_y = m$ , the eigenvalue is

$$E_{n,m}^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega + \left(m + \frac{1}{2}\right)\hbar\omega = \left(n + m + 1\right)\hbar\omega. \quad (1.114)$$

The gist of the problem is the addition of coupling between the two directions. This adds the perturbation

$$\hat{\mathcal{H}}_p = C\hat{x}\hat{y}. \quad (1.115)$$

and we seek to find the correction to energies Eq.(1.114) and the energy eigenstates  $|n_x, n_y\rangle$ . Starting for the ground state, which is nondegenerate we need to evaluate the matrix element

$$E_{0,0}^{(1)} = \langle 0, 0 | \hat{\mathcal{H}}_p | 0, 0 \rangle = C \langle 0, 0 | \hat{x}\hat{y} | 0, 0 \rangle. \quad (1.116)$$

For the unperturbed harmonic oscillator, the eigenfunctions are Hermite polynomials,

$$\langle x|0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} \quad (1.117)$$

$$\langle x|1\rangle = \left(\frac{4}{\pi}\left(\frac{m\omega}{\hbar}\right)^3\right)^{1/4} x e^{-\frac{m\omega x^2}{2\hbar}}, \text{ etc.} \quad (1.118)$$

In two dimensions we can write the ground state as

$$\langle x|0\rangle \otimes \langle y|0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-\frac{m\omega(x^2+y^2)}{2\hbar}} \quad (1.119)$$

Let's first find the first order energy correction thus

$$E_{0,0}^{(1)} = C \int \int \int \int dx' dx'' dy' dy'' \langle 0|x''\rangle \langle 0|y''\rangle \langle x''| \langle y''| (\hat{x}\hat{y}) |x'\rangle |y'\rangle \langle x'|0\rangle \langle y'|0\rangle \quad (1.120)$$

Inserting Eq.(1.119) in Eq.(1.120)

$$E_{0,0}^{(1)} = C \int \int \int \int dx' dx'' dy' dy'' \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-\frac{m\omega(x''^2+y''^2)}{2\hbar}} \langle x''|x'\rangle \langle y''|y'\rangle x' y' \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-\frac{m\omega(x'^2+y'^2)}{2\hbar}} \quad (1.121)$$

Due to the orthonormality of position states we get

$$E_{0,0}^{(1)} = \int \int dx' dy' C \left(\frac{m\omega}{\pi\hbar}\right) (x' y') e^{-\frac{m\omega(x'^2+y'^2)}{\hbar}} \quad (1.122)$$

$$= C \left(\frac{m\omega}{\pi\hbar}\right) \left(\int dx' x' e^{-\frac{m\omega x'^2}{\hbar}}\right) \left(\int dy' y' e^{-\frac{m\omega y'^2}{\hbar}}\right) = 0, \quad (1.123)$$

Therefore we find the first order correction for the ground state energy is zero.

For first degenerate state which is 2-fold degenerate we need to find four matrix elements

$$\hat{\mathcal{H}}_p = C \times \begin{array}{c} \langle 1,0| \\ \langle 0,1| \end{array} \begin{array}{cc} |1,0\rangle & |0,1\rangle \\ \left( \begin{array}{cc} \langle 1,0|\hat{x}\hat{y}|1,0\rangle & \langle 1,0|\hat{x}\hat{y}|0,1\rangle \\ \langle 0,1|\hat{x}\hat{y}|1,0\rangle & \langle 0,1|\hat{x}\hat{y}|0,1\rangle \end{array} \right) \end{array} \quad (1.124)$$

The matrix elements can be calculated using the concept that integral of odd function over all of space is zero

$$\langle 1, 0 | \hat{x} \hat{y} | 1, 0 \rangle = C A \int \int dx dy (x y) x^2 e^{-\frac{m\omega x'^2}{\hbar}} e^{-\frac{m\omega y'^2}{\hbar}} = 0 \quad (1.125)$$

$$\langle 1, 0 | \hat{x} \hat{y} | 0, 1 \rangle = C B \int \int dx dy (x y) x y e^{-\frac{m\omega x'^2}{\hbar}} e^{-\frac{m\omega y'^2}{\hbar}} \quad (1.126)$$

$$\langle 0, 1 | \hat{x} \hat{y} | 1, 0 \rangle = C B \int \int dx dy (x y) x y e^{-\frac{m\omega x'^2}{\hbar}} e^{-\frac{m\omega y'^2}{\hbar}} \quad (1.127)$$

$$\langle 0, 1 | \hat{x} \hat{y} | 0, 1 \rangle = C A \int \int dx dy (x y) y^2 e^{-\frac{m\omega x'^2}{\hbar}} e^{-\frac{m\omega y'^2}{\hbar}} = 0, \quad (1.128)$$

where  $A$  and  $B$  are some constants. Here, we do not bother about the constant  $A$  in the first and last integrals that computes to zero anyway. The elements Eqs.(1.126) and (1.127) are identical. We now show the explicit calculation for Eq.(1.126), which automatically yields an expression for  $B$  as well,

$$\begin{aligned} & \langle 1, 0 | \hat{x} \hat{y} | 0, 1 \rangle \\ &= C \int \int \int \int dx' dx'' dy' dy'' \langle 1 | x'' \rangle \langle 0 | y'' \rangle \langle x'' | \langle y'' | \hat{x} \hat{y} | x' \rangle | y' \rangle \langle x' | 0 \rangle \langle y' | 1 \rangle \\ &= C \int \int \int \int dx' dx'' dy' dy'' (x' y') \langle x'' | x' \rangle \langle y'' | y' \rangle \\ & \quad \left( \frac{4}{\pi} \left( \frac{m\omega}{\hbar} \right)^3 \right)^{1/2} (x'' y'') e^{-\frac{m\omega x''^2}{2\hbar}} e^{-\frac{m\omega y''^2}{2\hbar}} \left( \frac{m\omega}{\pi\hbar} \right)^{1/2} e^{-\frac{m\omega y'^2}{2\hbar}} e^{-\frac{m\omega x'^2}{2\hbar}} \\ &= C \left( \frac{2}{\pi} \right) \left( \frac{m\omega}{\hbar} \right)^2 \int \int dx dy (x^2 y^2) e^{-\frac{m\omega x^2}{\hbar}} e^{-\frac{m\omega y^2}{\hbar}} \\ &= C \left( \frac{2}{\pi} \right) \left( \frac{m\omega}{\hbar} \right)^2 \left( \int dx x^2 e^{-\frac{m\omega x^2}{\hbar}} \right) \left( \int dy y^2 e^{-\frac{m\omega y^2}{\hbar}} \right). \end{aligned}$$

Finally using the standard integral,

$$\int_{-\infty}^{\infty} dx x^2 e^{-ax^2} = \frac{1}{2a} \sqrt{\frac{\pi}{a}}, \quad (1.129)$$

we obtain

$$\langle 1, 0 | \hat{x} \hat{y} | 0, 1 \rangle = C \frac{\hbar}{2m\omega} \quad (1.130)$$

Repeating this process for (1.127), we obtain an identical value resulting in

$$\hat{\mathcal{H}}_p = C \frac{\hbar}{2m\omega} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (1.131)$$

which provides an energy shift of

$$2\hbar\omega \pm C \frac{\hbar}{2m\omega} \quad (1.132)$$

for the eigenstates

$$\frac{|0, 1\rangle \pm |1, 0\rangle}{\sqrt{2}}, \quad (1.133)$$

yielding the energies for the coupled 2D harmonic oscillator.