Approximate Methods: I. Perturbation Theory

So far in the previous all chapters, we have discussed those Hamiltonians which are exactly solvable. By exactly solvable, we mean its energy eigenstates and eigenvalues can be obtained. But unfortunately, apart from few simple potentials, most of the potentials, especially many-particle interactions that you will learn in QM-II, are not solvable. For that we have to invent some approximation schemes. In this chapter, we will learn some of the approximation methods.

I. Time-Independent Perturbation Theory

The general idea of the perturbation theory is that suppose we have a Hamiltonian H which is not fully solvable. What we do here is to try to solve the maximum part of the Hamiltonian that is possible to solve and then we will try to approximate the remaining part as best as we can. Let us split the Hamiltonian H into solvable (H_0) & perturbation (H') parts:

$$H = H_0 + H' . \qquad ----(1)$$

- It is not at all clear from what we said above that for the perturbation method to work, the energy of the perturbation part $E' = \langle H' \rangle$ has to be smaller than the unperturbed energy $E_0 = \langle H_0 \rangle$. This is just a limitation arising from how we are setting up the perturbation method that we will discuss in details.

- It is clear from the above discussion that the perturbation term H' is our choice, which can be a part of the Hamiltonian that we are unable to solve, and/or an external term arising when we are probing the system with light, magnetic field, electric field, pressure etc to make a measurement. For the method to work $\langle H' \rangle < \langle H_0 \rangle$ as we will see more below.

⊛ So our ultimate goal is to find the eigenstates $|\psi_n\rangle$ & eigenvalues E_n of the full Hamiltonian H,

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

with 'n' being some generic quantum number of $|\psi_n\rangle$.

But according to our setup above, we have the exact eigenstates and eigenvalues of H_0 only:

$$H_0|\psi_m^{(0)}\rangle = E_m^{(0)}|\psi_m^{(0)}\rangle, \quad --- \quad (3).$$

with 'm' being some generic quantum number of $|\psi_m^{(0)}\rangle$ and not necessarily the same quantum number 'n' of $|\psi_n\rangle$.

- So our goal is now clear: We already know $E_m^{(0)}$ & $|\psi_m^{(0)}\rangle$ and we want to find out E_n & $|\psi_n\rangle$. Since we cannot solve Eq (2) exactly, we cannot determine E_n & $|\psi_n\rangle$ exactly. Since we already know $E_m^{(0)}$ & $|\psi_m^{(0)}\rangle$, we want to take advantage of it and try to express $|\psi_n\rangle$ in terms of $|\psi_m^{(0)}\rangle$ and hence E_n in terms of $E_n^{(0)}$ in this approximation method.

How do we do that?

Well! We have encountered this scenarios before and we learned a coupled of apparently different but equivalent techniques. Let us visit them first and discuss their difficulties.

(a) Since $|\psi_n^{(0)}\rangle$ form a Hilbert space, so we can expand $|\psi_n\rangle$ in this Hilbert space as $|\psi_n\rangle = \sum_m \langle\psi_m^{(0)}|\psi_n\rangle\, |\psi_m^{(0)}\rangle$, where $\langle\psi_m^{(0)}|\psi_n\rangle$ are the complex coefficients. This procedure is exact if we can evaluate all the coefficients $\langle\psi_m^{(0)}|\psi_n\rangle$ exactly. That's very hard. Then one can try some approximate methods. (People do that in many ways. For example, one approximate method people do is to minimize the energy of the full Hamiltonian $E_n = \langle\psi_n|H|\psi_n\rangle$ with respect to the coefficients $\langle\psi_m^{(0)}|\psi_n\rangle$ and this works for the ground state pretty well. This is an application of the approximate method called the variational method that we will learn in QM-II.)

(b) Another approach would be to think of $|\psi_m^{(0)}\rangle$ and $|\psi_n\rangle$ to be related to each other by some $M\times N$ matrix, 'S', where M, N are the Hilbert space dimension of $|\psi_m^{(0)}\rangle$ & $|\psi_n\rangle$, as, $|\psi_n\rangle = S\,|\psi_m^{(0)}\rangle$. For $N=M$, and due to the fact that both $|\psi_m^{(0)}\rangle$ & $|\psi_n\rangle$ are normalized, the matrix 'S' can be identified as a unitary matrix and this procedure is the unitary transformation: $|\psi_n\rangle = \sum_m U_{mn}\, |\psi_m^{(0)}\rangle$. Clearly, we can identify the components of V as $U_{mn} = \langle \psi_m^{(0)} | \psi_n \rangle$ and hence both procedures are the same with same difficulties of computing all terms.

(Then we know that any unitary operator can be written as an exponential of some Hermitian generator operator, such as $e^{i\hat{A}a}$, where $\hat{A}$ is the Hermitian (generator) operator (e.g. $\hat{H}$, $\hat{p}$, $\hat{L}$ etc) and 'a' is the corresponding domain variable (t, x, θ etc). Then we will have the interpretation that $|\psi_n\rangle$ are the unitarily evolved states from the $|\psi_m^{(0)}\rangle$ states and due to the unitary evolution the inner product of both states will be preserved. Clearly one can do that, and since $|\psi_n\rangle$ are the states of a Hamiltonian which has extra component H' compared to $|\psi_n^{(0)}\rangle$, so, one can actually think of $|\psi_n\rangle$ states evolved from $|\psi_n^{(0)}\rangle$ states by the H'-operator. Since the corresponding domain variable is time (t), so the interpretation of this procedure will be the H' term is turned on at some time t_0 before which the states were $|\psi_n^{(0)}\rangle$ and then at some latter time $t > t_0$, we obtain $|\psi_m\rangle$ state by an evolution or time translation by the unitary operator $e^{iH'(t-t_0)}$. This procedure is called the time-dependent perturbation theory which also we will learn in QM-II.)

(e) However we can substitute $|\Psi_n\rangle$ in the above form in H

$$E_n = \langle \Psi_n | H | \Psi_n \rangle = E_0 + \sum_{m,\ell} V^*_{nm} V_{\ell n} \langle \Psi_m^{(0)} | H' | \Psi_\ell^{(0)} \rangle \quad \text{--- (4)}$$

Then, we say, we will compute the first few largest energy matrix elements and ignore the rest. But the trouble is that from eq(4), we don't have any knowledge of which matrix elements has the highest contributions and which one has lower contributions. There is no expansion parameter and there is no way to organise the matrix elements from higher values to lower values.

The perturbation theory allows us to organize these terms.

(i) To do so, we introduce a parameter 'λ' in eq (1) as

$$H = H_0 + \lambda H' \quad \text{---} \quad (5)$$

and, needless to say, we will eventually set $\lambda = 1$. (we will see that it won't be necessary and λ will drop out).

(ii) Note that $(1, \lambda, \lambda^2, \lambda^3, \cdots)$ gives a linear basis function of a vector space and we can expand a function in this basis set. So, we take an expansion of $|\Psi_n\rangle$ as

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

$$= \sum_k \lambda^k |\psi_n^{(k)}\rangle, \qquad \text{------} \quad (6)$$

in which $\psi_n^{(0)}$ is known and the rest of the expansion coefficient $\psi_n^{(k)}$ we have to evaluate. clearly, there are infinite number of coefficient. This is where the smallness of H' will rescue us with computing the first few terms will suffice a good result for ψ_n and also E_n.

(i) + (ii) : As a consequence of eq (5) & (6), we will show that the we can organize the terms in powers of λ as

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \cdots, \quad (7).$$

where $E_n^{(0)}$ is the unperturbed, n^{th} eigenenergy of H_0, and $E_n^{(k)}$ are the k^{th} correction terms, which depends on H' and also H_0. We will evaluate below each perturbation terms $\psi_n^{(k)}$ & $E_n^{(k)}$ and show that indeed the perturbation energies are now sorted as

$$E_n^{(0)} \gg E_n^{(1)} \gg E_n^{(2)} \gg \cdots$$

as long as as long as $H' \ll H_0$.

Before doing that, let us discuss an important and hidden <u>assumption</u> that lies in (6) and in eq (7):

• One may interpret the above two expansions as Taylor expansions. Note that the full Hamiltonian H is now a function of λ : $H(\lambda) = H_0 + \lambda H'$. So, both the energy eigenvalues $E_n(\lambda)$ & the eigenstates $\langle\lambda|\psi_n\rangle = \psi_n(\lambda)$ are now λ-dependent. So, we do a Taylor expansion

$$\psi_n(\lambda) = \psi_n(\lambda=0) + \lambda \left.\frac{\partial \psi_n}{\partial \lambda}\right|_{\lambda=0} + \lambda^2 \left.\frac{\partial^2 \psi_n}{\partial \lambda^2}\right|_{\lambda=0} + \cdots$$

$$= \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots$$

And $$E_n(\lambda) = E_n(\lambda=0) + \lambda \left.\frac{\partial E_n}{\partial \lambda}\right|_{\lambda=0} + \lambda^2 \left.\frac{\partial^2 E_n}{\partial \lambda^2}\right|_{\lambda=0} + \cdots$$

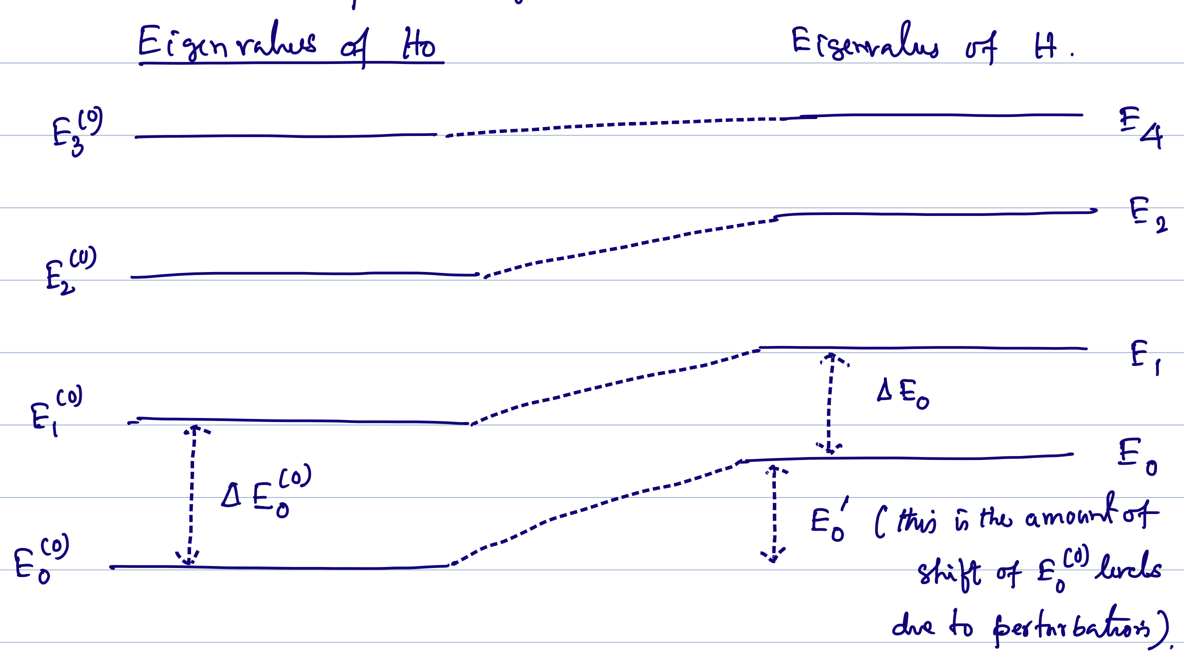
$$= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots.$$

It makes now perfect sense that $\psi_n^{(0)}$ & $E_n^{(0)}$ are the eigenstates and eigenvalues of H when $\lambda=0$, i.e., of H_0.

The advantage of this procedure, as we will see below, is that we can arrange the coefficients of $\lambda^{(k)}$, coming from both $E_n(\lambda)$ & $\psi_n(\lambda)$ expansions, and obtain the expansion coefficients in a systematic fashion.

One of the key and hidden assumptions of the perturbation theory is that, here we assume the quantum numbers in $|\psi_n\rangle$ & $|\psi_m^{(0)}\rangle$ remain the same, i.e. $n = m$. Both Hilbert spaces have same dim. So, whatever the quantum numbers we have obtained for H_0 (either by selecting the normalizable states, and or via angular momentum, number operator or any conserved operator) which quantize the energy eigenvalues and separate different energy eigenvalues by a gap $\Delta E_n^{(0)} = E_{n+1}^{(0)} - E_n^{(0)}$, the full Hamiltonian H also has the same quantum number. This is possible only when the perturbation term $E_n' = \langle H' \rangle$ only shifts each energy levels $E_n^{(0)}$ by small amount, but does not close its energy level spacing $\Delta E_n^{(0)}$.

Let us see that pictorically.



In the above schematic plot, we have the energy levels of $H^{(0)}$ have finite gap $\Delta E_n^{(0)}$. The perturbation term E_n' is assumed not to give same energy shifts to the corresponding $E_n^{(0)}$ levels, but it should not produce any level inversion in E_n. It's not clear yet why E_n' should be small, but we will now see that E_n' contains infinite numbers of matrix elements that is impossible to calculate. We will only calculate few leading order in λ terms and hope the rest is negligible. This approximation hence works better as long as H' is small compared to H_0.

(What happens when $E_n^{(0)}$ states have degeneracy? We have to treat it differently).

⊛ Normalization: We only know so far that $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$ are orthogonalized. We know nothing yet about the other coefficients $\langle \psi_n^{(k)} | \psi_n^{(\ell)} \rangle = ?$ for $k, \ell \neq 0$. On the other hand, we want $|\psi_n\rangle$ to be orthonormalized as well. What does it imply?

$$\langle \psi_n | \psi_n \rangle = 1 = \sum_{k,\ell} \underbrace{\lambda^k}_{= \lambda^k \text{ since } \lambda \text{ is chosen to be real}} \lambda^\ell \langle \psi_n^{(k)} | \psi_n^{(\ell)} \rangle$$

$$= \underbrace{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle}_{k=\ell=0} + \lambda \Big[\underbrace{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle}_{k=0,\ \ell=1} + \underbrace{\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle}_{\ell=1,\ k=0} \Big]$$

$$+ \lambda^2 \Big[\underbrace{\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle}_{k=0,\ \ell=2} + \underbrace{\langle \psi_n^{(2)} | \psi_n^{(0)} \rangle}_{k=2,\ \ell=0} + \underbrace{\langle \psi_n^{(1)} | \psi_n^{(1)} \rangle}_{k=\ell=1} \Big]$$

$$+ O(\lambda^3)$$

$$= 1 + \lambda \underbrace{\Big[\quad \Big]}_{=0} + \lambda^2 \underbrace{\Big[\quad \Big]}_{=0} + O(\lambda^3) \qquad \text{—(8)}$$

Now, we see that the L.H.S is 1, and on R.H.S the first term is 1. Since $\lambda \neq 0$, all the coefficients in the expansion on R.H.S must be identically zero. Hence we get a condition that

- $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle = 2\,\mathrm{Re}\big[\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle \big] = 0.$
- $\mathrm{Im} \langle \psi_n^{(k)} | \psi_n^{(\ell)} \rangle$ is undetermined but we won't need it.

$$\boxed{\Rightarrow \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle = 2\,\mathrm{Re}\big[\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle \big] = 0 \quad \text{— (9a)}}$$

- From the 2nd term in eq (5), $2\,\mathrm{Re}\left[\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle\right] = -\langle\psi_n^{(1)}|\psi_n^{(1)}\rangle$

$$\boxed{\Rightarrow \langle\psi_n^{(0)}|\psi_n^{(2)}\rangle + \langle\psi_n^{(2)}|\psi_n^{(0)}\rangle = -\langle\psi_n^{(1)}|\psi_n^{(1)}\rangle \quad \text{---}(9b)}$$

- Similarly, setting the coefficient of λ^p term, we get.

$$\boxed{\begin{aligned}\langle\psi_n^{(0)}|\psi_n^{(p)}\rangle + \langle\psi_n^{(p)}|\psi_n^{(0)}\rangle &= -\Big[\langle\psi_n^{(p-1)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(p-2)}|\psi_n^{(2)}\rangle + \cdots \\ &\quad + \langle\psi_n^{(2)}|\psi_n^{(p-2)}\rangle + \langle\psi_n^{(1)}|\psi_n^{(p-1)}\rangle\Big]. \\ &\qquad \text{— }(9c).\end{aligned}}$$

⊛ Energy:

$$H|\psi_n\rangle = E_n|\psi_n\rangle \Rightarrow (H+H_0)\sum_k \lambda^k |\psi_n^{(k)}\rangle = \sum_\ell \lambda^\ell E_n^{(0)} \sum_k \lambda^k |\psi_n^{(k)}\rangle$$

$$\Rightarrow (H_0 + \lambda H')\sum_k \lambda^k |\psi_n^{(k)}\rangle = \sum_{k,\ell} \lambda^{k+\ell} E_n^{(\ell)} |\psi_n^{(k)}\rangle$$

$$\Rightarrow \sum_k \left(\lambda^k H_0 + \lambda^{k+1} H'\right)|\psi_n^{(k)}\rangle = \sum_{k,\ell} \lambda^{k+\ell} E_n^{(\ell)} |\psi_n^{(k)}\rangle$$

- $\lambda = 0$ Coefficient: $H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$

- $\lambda = 1$ Coefficient: $H_0|\psi_n^{(1)}\rangle + H'|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle$

- $\lambda = 2$ coefficient: $H_0|\psi_n^{(2)}\rangle + H'|\psi_n^{(1)}\rangle = E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\psi_n^{(0)}\rangle$

⋮

- Multiply $\langle\psi_n^{(0)}|$ from left on the above three equations:

$E_n^{(0)}\langle\psi_n^{(0)}|$

$$\Rightarrow (\lambda = 1 \text{ coeff}) \quad \cancel{\langle\psi_n^{(0)}|H_0|\psi_n^{(1)}\rangle} + \langle\psi_n^{(0)}|H'|\psi_n^{(0)}\rangle = \cancel{E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle} + E_n^{(1)}$$

So, we get $\boxed{E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle}$ ---(10a) .

$\Rightarrow$ ($\lambda = 2$ coeff) : $E_n^{(0)} \cancel{\langle \psi_n^{(0)}} | \psi_n^{(2)} \rangle + \langle \psi_n^{(0)} | H' | \psi_n^{(1)} \rangle$

$$= E_n^{(0)} \cancel{\langle \psi_n^{(0)}} | \psi_n^{(2)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(2)}$$

$\Rightarrow$ $\boxed{E_n^{(2)} = \langle \psi_n^{(0)} | (H' - E_n) | \psi_n^{(1)} \rangle \quad \text{---(10b)}}$

$\Rightarrow$ Proceeding similarly for $\lambda = 3$ coefficient we get

$$\boxed{\begin{aligned} E_n^{(3)} = {} & \langle \psi_n^{(1)} | (H' - E_n^{(1)}) | \psi_n^{(1)} \rangle \\ & - 2 E_n^{(2)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle \quad \text{---(10c)} \end{aligned}}$$

(*) Wavefunction:

Here one can choose different approach to proceed and they are pretty much of equal difficulties. We take Bransden book's approach. Remember that although we could have expanded $|\psi\rangle$ in the Hilbert space of $|\psi_n^{(0)}\rangle$ to begin with, but we did not do that in the perturbation theory, because we wanted a series in the powers of λ, which is the essence of the perturbation theory. But now we can expand each coefficients $\psi_n^{(k)}$ in the Hilbert space of $\psi_n^{(k)}$.

$$a_{nm}^{(1)} = \langle \psi_n^{(1)} | \psi_m^{(0)} \rangle.$$

$$|\psi_n^{(1)}\rangle = \sum_m a_{nm}^{(1)} |\psi_m^{(0)}\rangle \qquad \text{---- (11 a)}$$

$$|\psi_n^{(2)}\rangle = \sum_m a_{nm}^{(2)} |\psi_m^{(0)}\rangle \qquad \text{---- (11 b)}$$

and so on.

Although, it may not be obvious from eqs(11), that this expansion leads to the unitary transformation $|\psi_n\rangle = \sum_m U_{nm} |\psi_n^{(0)}\rangle$ that we discussed above, but this can be established easily:

$$|\psi_n\rangle = \psi_n^{(0)} + \lambda \sum_m a_{nm}^{(1)} |\psi_m^{(0)}\rangle + \lambda^2 \sum_m a_{nm}^{(2)} |\psi_m^{(0)}\rangle + \cdots$$

$$= \sum_m \left[\frac{1}{N} \delta_{nm} + \lambda^1 a_{nm}^{(1)} + \lambda^2 a_{nm}^{(2)} + \cdots\right] |\psi_m^{(0)}\rangle$$

$$= \sum_m \underbrace{\left(\sum_k \lambda^k a_{nm}^{(k)}\right)}_{U_{nm} = \langle \psi_n | \psi_m^{(0)} \rangle} |\psi_m^{(0)}\rangle, \quad \text{where } a_{nm}^{(0)} = \frac{1}{N} \delta_{nm}$$

So, what we essentially did is to expand all coefficients U_{nm} in the same vector space of $(1, \lambda, \lambda^2, \cdots)$.

• So, we substitute eq (11a) in the $\lambda = 1$ coefficient:

$$H_0 |\psi_n^{(1)}\rangle + H' |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(1)}\rangle + E_n^{(1)} |\psi_n^{(0)}\rangle$$

$$\Rightarrow \left(H_0 - E_n^{(0)}\right) \sum_k a_{nk}^{(1)} |\psi_k^{(0)}\rangle = -\left(H' - E_n^{(1)}\right) |\psi_n^{(0)}\rangle.$$

Multiply $\langle \psi_m^{(0)}|$ from left to get

$$\left(E_m^{(0)} - E_n^{(0)}\right) a_{nm}^{(1)} = -\underbrace{\langle \psi_m^{(0)} | H' | \psi_n^{(0)}\rangle}_{H'_{mn}} + E_n^{(1)} \delta_{nm}$$

For $n = m$, $\quad E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)}\rangle$ which was eq (10a).

For $n \neq m$,

$$\boxed{a_{nm}^{(1)} = \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}}} \quad --- \quad (11c)$$

for $n \neq m$.

Now, we see from eq (11c) that a sufficient condition for the applicability of the perturbation theory is that $a_{mn}^{(1)} << 1$, which means $\left|\frac{H'_{mn}}{E_m^{(0)} - E_n^{(0)}}\right| \leq 1$ as we prescribed above also.

$\Rightarrow$ So substituting for $a_{mn}^{(1)}$ we get

$$\boxed{|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{H'_{mn}}{E_m^{(0)} - E_n^{(0)}} |\psi_m^{(0)}\rangle} \quad \text{--- (11d)}.$$

⊛ Proceeding similarly and equating the λ^2-coefficient on both sides, we get a very long expression for the 2nd order correction:

$$a_{mn}^{(2)} = \frac{1}{E_m^{(0)} - E_n^{(0)}} \sum_{l\neq m\neq n} \frac{H'_{ml} H'_{ln}}{E_m^{(0)} - E_l^{(0)}} - \frac{H'_{mm} H'_{nm}}{(E_m^{(0)} - E_n^{(0)})^2} - a_{mm}^{(1)} \frac{H'_{nm}}{E_m^{(0)} - E_n^{(0)}}$$

for $m \neq n$. --- (11f)

The coefficients gets larger and larger for the wave function as we go to higher and higher terms.

⊛ And substituting eq (11c) in eq (10b) for $E_n^{(1)}$ we get

$$E_n^{(2)} = \langle \psi_n^{(0)} | H' - E_n^{(1)} | \psi_n^{(1)} \rangle$$

$$= \sum_{m\neq n} a_{mn}^{(1)} \left[\underbrace{\langle \psi_n^{(0)} | H' | \psi_m^{(0)} \rangle}_{H'_{nm}} - E_n^{(1)} \underbrace{\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle}_{=0} \right]$$

$$= \sum_{m\neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} \quad \text{--- (11h)}$$

⊛ Summary of results:

$$E_n = E_n^{(0)} + H'_{nn} + \sum_{m\neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} + \cdots \quad (12a)$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \sum_{m\neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle + \cdots \quad (12b)$$

where $H'_{mn} = \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle$.

⊛ Examples:

<u>Ex 1</u> Let us consider an anharmonic oscillator in 1D:

$$H = \underbrace{\frac{p^2}{2m} + \frac{1}{2}kx^2}_{H_0} + \underbrace{Ax^3 + Bx^4}_{H'} \quad \text{--- (1)}$$

In this case, we will clearly consider upto x^2 term as unperturbed Hamiltonian H_0 since it exactly solvable, and the rest as perturbation. Here we will not bother too much with the limiting values of A, B for the perturbation theory to be valid, but rather calculate upto 2nd order term as a practice of the method we learned above.

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \Rightarrow E_n = \left(n+\frac{1}{2}\right)\hbar\omega \quad , \quad n = 0, 1, 2, \cdots$$

with $\omega = \sqrt{k/m}$ --- (2)

$$\psi_n(x) = \langle x|n\rangle = N_n H_n(\alpha x) e^{-\alpha x^2/2} \quad \text{--- (3)}$$

- For all the perturbation energy corrections, we need to evaluate the matrix elements of H' as $\langle n|H'|m\rangle = A\langle n|x^3|m\rangle + B\langle n|x^4|m\rangle$. To evaluate these matrix elements it is easier to use the ladder operator formalism: $\hat{x} = \underbrace{\sqrt{\frac{\hbar}{2m\omega}}}_{\beta}\left(\hat{a}^+ + a\right)$

- Recall $\hat{a}^+ |n\rangle = \sqrt{n+1}\,|n+1\rangle$ & $a|n\rangle = \sqrt{n}\,|n-1\rangle$ & $a|0\rangle = 0$.

Since a^+, a do not commute, we should try to evaluate it rather than using the formula for the quartic expansion.

$$(a^+ + a)^2 = (a^+)^2 + a^2 + a^+ a + a a^+ \qquad \because [a, a^+] = 1$$

$$= (a^+)^2 + a^2 + 2a^+ a + 1 \qquad -(4)$$

$$(a^+ + a)^3 = \left((a^+)^2 + a^2 + 2a^+ a + 1\right)(a^+ + a)$$

$$= (a^+)^3 + (a^+)^2 a + a^2 a^+ + a^3 + 2a^+ a a^+ + 2a^+ a^2 + a^+ + a.$$

$$= (a^+)^3 + a^3 + 3(a^+)^2 a + 3a^+ a^2 + 3(a^+ + a) \qquad -(5)$$

- $a^2 a^+ = a a a^+$
$= a + a a^+ a$
$= 2a + a^+ a^2$

- $a^3 a^+ = a(a^2 a^+)$
$= a(2a + a^+ a^2)$
$= 3a^2 + a^+ a^3.$

$$(a^+ + a)^4 = (a^+ + a)^3 (a^+ + a)$$

$$= (a^+)^4 + (a^+)^3 a + a^3 a^+ + a^4 + 3(a^+)^2 a a^+ + 3(a^+)^2 a^2$$

$$+ 3a^+ a^2 a^+ + 3a^+ a^3 + 3(a^+)^2 + 3(a^+ + a)^2$$

$$= (a^+)^4 + a^4 + a^{+3} a + (3a^2 + a^+ a^3) + 3(a^+)^2(1 + a^+ a) + 3(a^+)^2 a^2$$

$$+ 3a^+(2a + a^+ a^2) + 3a^+ a^3 + 3(a^+)^2 + 3\left[(a^+)^2 + a^2 + 2a^+ a + 1\right]$$

$$= (a^+)^4 + a^4 + 4(a^+)^3 a + 4a^+ a^3 + 6a^{+2} a^2 + 6a^{+2} + 6a^2 + 12a^+ a + 3 \qquad -(6)$$

(Notice that in the above expressions, we have always ordered the operators such that 'a' always appears on the right. This has no particular reason, its mainly done often to benefit the calculation as a on the right always annihilate the ground state. We do not have to do it otherwise).

- Now, $$(a^{\dagger}+a)^3|m\rangle = \sqrt{(m+1)(m+2)(m+3)}\,|m+3\rangle + \sqrt{m(m-1)(m-2)}\,|m-3\rangle$$
$$+\,3\sqrt{m\,m\,(m+1)}\,|m+1\rangle + 3\sqrt{m(m-1)(m-1)}\,|m-1\rangle$$
$$+\,3\sqrt{m+1}\,|m+1\rangle + 3\sqrt{m}\,|m-1\rangle. \qquad -(7)$$

and, $$(a^{\dagger}+a)^4|m\rangle = \sqrt{(m+1)(m+2)(m+3)(m+4)}\,|m+4\rangle + \sqrt{m(m-1)(m-2)(m-3)}\,|m-4\rangle$$
$$+\,4\sqrt{m\,m\,(m+1)(m+2)}\,|m+2\rangle + 4\sqrt{m(m-1)(m-2)(m-2)}\,|m-2\rangle$$
$$+\,6\sqrt{m(m-1)(m-1)m}\,|m\rangle + 6\sqrt{(m+1)(m+2)}\,|m+2\rangle$$
$$+\,6\sqrt{m(m-1)}\,|m-2\rangle + 12\sqrt{m\,m}\,|m\rangle + 3|m\rangle. \qquad -(8)$$

We notice that there is no $|m\rangle$ term on the R.H.S of $x^3|m\rangle = (a^{\dagger}+a)^3|m\rangle$ term. Therefore, $\langle m|x^3|m\rangle = 0$, which means the expectation values of x^3 in any eigenstate of S.H.O is zero. This is however expected because S.H.O states have definite parity and x^3 is an odd function in space. So, its expectation value is zero. So, first order perturbation correction is zero.

Now we are ready to compute all the perturbation terms.

- 1st order energy correction:

$$E_n^{(1)} = \langle n|H'|n\rangle = A\underbrace{\langle n|x^3|n\rangle}_{=0 \text{ as just discussed.}} + B\langle n|x^4|n\rangle.$$
$$= B\langle n|x^4|n\rangle.$$
$$= B\beta^4\left[6n(n-1) + 12n + 3\right] \qquad (\text{only } |n\rangle \text{ state contributes})$$
$$= 6B\beta^4(2n^2+2n+1). \qquad -(9).$$

- 2nd order energy correction

$$E_n^{(2)} = \sum_{m \neq n} \frac{|H'_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\begin{aligned} H'_{nm} &= \langle n | A x^3 + B x^4 | m \rangle \\ &= A \beta^3 \langle n | (a^\dagger + a)^3 | m \rangle + B \beta^4 \langle n | (a^\dagger + a)^4 | m \rangle \\ &= A \beta^2 \sqrt{(m+1)(m+2)(m+3)} \langle n | m+3 \rangle + \cdots \\ &\quad + B \beta^4 \sqrt{m(m+1)(m+2)(m+3)} \underbrace{\langle n | m+4 \rangle}_{\delta_{n,m+4}} + \cdots \end{aligned}$$

And $E_n^{(0)} - E_m^{(0)} = (n-m)\hbar\omega$.

With a lengthy calculation one obtains (H.W.)

$$\begin{aligned} E_n^{(2)} &= -\frac{15}{4} \frac{A^2}{\hbar\omega} \left(\frac{\hbar}{m\omega}\right)^3 \left(n^2 + n + \frac{11}{30}\right) \\ &\quad - \frac{1}{8} \frac{B^2}{\hbar\omega} \left(\frac{\hbar}{m\omega}\right)^4 (34n^3 + 51n^2 + 59n + 21) \end{aligned} \quad \text{— (10).}$$

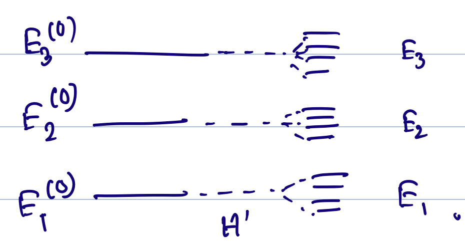
- Proceeding similarly, one can calculate the correction to eigenfunction as

$$|n\rangle' = |n\rangle + \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} |m\rangle + \cdots \quad \text{— (11).}$$

Degenerate Perturbation Theory

The above perturbation theory does not hold if the n^{th} unperturbed state $|\psi_n^{(0)}\rangle$ is α-fold degenerate. Because, for a degenerate case, the degenerate eigenfunctions are <u>not</u> uniquely determined, or a better and correct way to say, any linear combination of the α-fold degenerate states is also an eigenstate of the Hamiltonian. We actually have to incorporate this fact into our calculation now. In fact, what we will find is that the perturbation can lift the degeneracy fully or partially in the 'H_0' state, and hence the $E_n^{(0)}$ level splits into $E_n^{(0)} + E_{n,\gamma}^{(1)} + \cdots$, where $\gamma = 1, 2, \ldots \alpha$.

Let us say n^{th} energy level of H_0 is α-fold degenerate. (One can have multiple energy levels being differently degenerate, but remaining faithful to the core approximation of the perturbation theory that the perturbed energy splitting is less than the energy separation in $E_n^{(0)}$ between its nearest levels. Pictorically, this means.



So, we can only focus on a given n^{th} state's α-fold degeneracy.)

- $$H_0 |\psi_{n,r}^{(0)}\rangle = E_n^{(0)} |\psi_{n,r}^{(0)}\rangle \quad \text{---} (1)$$

where $r = 1, 2, \cdots, \alpha$ runs over all degenerate states. Although, all the degenerate eigenstates need not be orthogonal among themselves, but they are linearly independent and we can orthogonalized them. Therefore, without loosing generality, can assume $|\psi_{n,r}^{(0)}\rangle$ are orthonormalized states

$$\langle \psi_{n,r}^{(0)} | \psi_{n,s}^{(0)} \rangle = \delta_{r,s}\, ; \; r,s = 1, 2, \cdots, \alpha. \quad \text{--} (2).$$

- Since any linear combinations of $|\psi_{n,r}^{(0)}\rangle$ is also an eigenstate of eq(1), so, one <u>cannot</u> just consider a r^{th} state seperately and expand in the vector space of λ^k, because in the perturbed states, different degenerate levels can mix. Therefore, we have to start with a mix state or linear superposition of all unperturbed degenerate states:

$$|\chi_{n,r}^{(0)}\rangle = \sum_{s=1}^{\alpha} c_{r,s} |\psi_{ns}^{(0)}\rangle \;, \; r = 1, 2, \cdots \alpha \quad \text{--} (3).$$

where $c_{r,s}$ are the complex coefficients defined in the usual way. ($c_{r,s}$ also carries the 'n' index, but for simplicity we have not included it).

- Now we assume $|\Psi_{n,r}\rangle$ are the desired eigenstates of the full Hamiltonian $H = H_0 + \lambda H'$, as

$$(H_0 + \lambda H')\,|\Psi_{n,r}\rangle = E_{n,r}\,|\Psi_{n,r}\rangle \quad \text{---}(4)$$

with eigenvalues $E_{n,r}$ which carries the index 'r' now, since they may no longer be degenerate.

- Then we expand $|\Psi_{n,r}\rangle$ and $E_{n,r}$ in powers of λ as

$$|\Psi_{n,r}\rangle = \underbrace{|\chi_{n,r}^{(0)}\rangle}_{\text{different from no-degenerate case.}} + \lambda\,|\Psi_{n,r}^{(1)}\rangle + \lambda^2\,|\Psi_{n,r}^{(2)}\rangle + \cdots \quad (5)$$

$$E_{n,r} = \underbrace{E_n^{(0)}}_{\text{does not carry any r-index, since they are deg.}} + \lambda\, E_{n,r}^{(1)} + \lambda^2\, E_{n,r}^{(2)} + \cdots \quad (6)$$

- Substituting eqs (5), (6) in eq (4) and equating the coeff of λ,

$$H_0\,|\Psi_{n,r}^{(1)}\rangle + H'\,|\chi_{n,r}^{(0)}\rangle = E_n^{(0)}\,|\Psi_{n,r}^{(1)}\rangle + E_{n,r}^{(1)}\,|\chi_{n,r}^{(0)}\rangle \quad \text{---}(7)$$

- As in the non-degenerate case, we expand $|\Psi_{n,r}^{(1)}\rangle$ in the Hilbert space of $|\Psi_n^{(0)}\rangle$ (note, the N-dim Hibert space of $|\Psi_n^{(0)}\rangle$ consist of α-degenerate states and $N-\alpha$ non-degenerate states. So need to sum over both n & r indices) as

$$|\psi_{n,r}^{(1)}\rangle = \sum_{m\neq n}^{N-\alpha} \sum_{s=1}^{\alpha} a^{(1)}_{nm,rs} \, |\psi^{(0)}_{m,s}\rangle \quad \text{--- (8)}$$

(n states)

- Substituting eq(8) in eq(7) and with little bit of straightforward algebra we get

$$\sum_m \sum_s a^{(1)}_{nm,rs} \left(E_m^{(0)} - E_n^{(0)}\right) |\psi^{(0)}_{m,s}\rangle$$

$$+ \sum_s c_{rs} \left(H' - E^{(1)}_{nr}\right) |\psi^{(0)}_{n,s}\rangle = 0. \quad \text{--- (9)}$$

Multiplying with $\langle \psi^{(0)}_{n,t}|$ from the left, and defining the matrix element:

$$H'_{nn,ts} \equiv \langle \psi^{(0)}_{n,t} | H' | \psi^{(0)}_{n,s}\rangle. \quad \text{--- (10)}$$

and, since $|\psi^{(0)}_{n,r}\rangle$ states are orthogonal, we have $\langle \psi^{(0)}_{n,t} | \psi^{(0)}_{m,s}\rangle = 0$ when $m \neq n$ and $E_m^{(0)} = E_n^{(0)}$ when $m = n$, we get from eq(9):

$$\boxed{\sum_{s=1}^{\alpha} c_{rs}\left(H'_{nn,ts} - E^{(1)}_{nr}\,\delta_{ts}\right) = 0} \; ; \; t = 1, 2, \ldots \alpha$$

— (11).

This is the master equation we have to solve to obtain all the 1st order energy splittings $E^{(1)}_{nr}$ for the n^{th} level. Eq(11) gives a linear, homogeneous system of equations for the α unknown coefficients $c_{n,r}$, where $r = 1, 2, \ldots \alpha$. Bringing the $E^{(1)}_{n,r}\,\delta_{ts}$ to the right hand side, we can view eq (11) as an eigenvalue equation of $\alpha \times \alpha$ matrix $H'_{nn,ts}$ for a given value of n, with $E^{(1)}_{n,r}$ being its eigenvalues and $c_{r,s}$ are the components of the eigenvector. We know the solution of a eigenvalue problem is defined by the secular equation:

$$\boxed{\det\left[H'_{nn,ts} - E^{(1)}_{n,r}\,\delta_{t,s}\right] = 0} \quad \cdots (12)$$

[One should rather read it as a $\alpha \times \alpha$ matrix $\overleftrightarrow{H}'_{nn}$ whose t,s component is $H'_{nn,ts}$, and δ_{ts} as a t,s component of $\alpha \times \alpha$ unit matrix $\mathbb{I}$. $\Rightarrow \det\left[\overleftrightarrow{H}_{nn} - E^{(1)}_{n,r}\,\mathbb{I}\right] = 0$.]

- After solving eq (12) for $E^{(1)}_{n,r}$ for the rth eigenvalue of $\overleftrightarrow{H}_{nn}$, and then obtaining its eigenvector $c_{r,s}$ from eq (11), we obtain the unperturbed eigenstate in eq (3).
- Going back to eq (9), and equating the coefficient of λ on both sides for $m \neq n$, we can obtain the coefficients $a^{(1)}_{mn,rs}$ in a same way as before. This gives a slightly longer procedure and we will not do that here. Typically one computes the correction to the wavefunctions for the degenerate case numerically, and in many cases the corrections are small.

(*) That is all about the degenerate perturbation theory in terms for general α-fold degenerate case. For a simple $\alpha=2$ fold degenerate case, one can proceed into few more steps and obtain analytical expressions for $E^{(1)}_{n,r}$.

* Doubly degenerate ($\alpha=2$) case. *

Let us consider a doubly degenerate case for n^{th} eigenvalue $E_n^{(0)}$ and eigenvector $\psi_{n,1}^{(0)}$, $\psi_{n,2}^{(0)}$. For notational simplicity we will drop the subscript 'n' and only carry the subscript for $r, s, t = 1, 2$.

From eq (11) we get

$$\begin{pmatrix} H'_{11} - E_r^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_r^{(1)} \end{pmatrix} \begin{pmatrix} c_{r1} \\ c_{r2} \end{pmatrix} = 0 \quad \text{-- (13)}$$

Here, $\quad H'_{s,t} = \langle \psi_s^{(0)} | H' | \psi_t^{(0)} \rangle, \quad s,t = 1,2.$

[Eq(13) can also be written in the typical eigenvalue equation format as

$$\begin{pmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{pmatrix} \begin{pmatrix} c_{r1} \\ c_{r2} \end{pmatrix} = E_r^{(1)} \begin{pmatrix} c_{r1} \\ c_{r2} \end{pmatrix} \quad \text{--(14)}$$

for the r^{th} eigenvalue with $r = 1, 2$.]

The secular equation of eq (13) is then

$$\det \begin{vmatrix} H'_{11} - E_r^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_r^{(2)} \end{vmatrix} = 0. \quad --- (15).$$

Solving eq (15) we can obtain the two eigenvalues and then from eq (16) we can get the eigenvectors as done in Bransden book.

There is a nice structure that underlies in eq (14) that we can exploit to obtain the results easily. Lets define a matrix

$M = \begin{pmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{pmatrix}$. Since the eigenvalue of M, i.e., $E_r^{(1)}$ is real so, M is Hermitian. This gives H'_{11}, H'_{22} are real and $H'_{12} = H'^{*}_{21}$

We can then express the 2x2 generic Hermitian matrix in terms of three Pauli matrices $\sigma_x, \sigma_y, \sigma_z$ as

$$M = m_0 \mathbb{I}_{2\times 2} + m_z \sigma_z + m_x \sigma_x + m_y \sigma_y, \quad --- (16)$$

where

$$\left. \begin{aligned} m_0 &= \frac{H'_{11} + H'_{22}}{2}, \quad m_z = \frac{H'_{11} - H'_{22}}{2} \\ m_x &= \mathrm{Re}\, H'_{12} = \mathrm{Re}\, H'_{12} \\ m_y &= -\mathrm{Im}\, H'_{12} = \mathrm{Im}\, H'_{21} \end{aligned} \right\} - (17).$$

Since m_0 term appears in the diagonal part, this appears in all eigenvalues. So, let's only focus on the remaining terms in eq (16) as $P = m_z\sigma_z + m_x\sigma_x + m_y\sigma_y = \sum_\mu m_\mu \sigma_\mu$, $\mu = x, y, z$.

Since we learned from angular momentum chapter that $\sigma_x, \sigma_y, \sigma_z$ are the generators of rotation for spin-1/2 object (although here there is no real spin, but mathematically the algebra works) and $[\sigma_\mu, \sigma_\nu] = 2i\epsilon_{\mu\nu\xi}\sigma_\xi$, so we can define the eigenstates of σ_z & σ^2 as the basis for this Hamiltonian. Now, $\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = \mathbb{I}_{2\times2}$, so, the eigenfunctions of P are also the eigenfunctions of P^2.

Let see that

$$P^2 = \left(\sum_\mu m_\mu \sigma_\mu\right)\left(\sum_\nu m_\nu \sigma_\nu\right)$$

$$= \sum_{\mu\nu} m_\mu m_\nu \sigma_\mu \sigma_\nu$$

Levi civita

$$= \sum_{\mu\nu} m_\mu m_\nu \left(\delta_{\mu\nu} + \underbrace{\sum_\xi \epsilon_{\mu\nu\xi}\sigma_\xi}_{=0}\right)$$

$=0$ since $\epsilon_{\mu\nu\xi}$ is antisymmetric and there is a summation over $\mu\nu\xi$.

$$= \sum_\mu m_\mu^2 = m_x^2 + m_y^2 + m_z^2 = p^2 \quad -(18)$$

where p is the eigenvalue of P matrix. Then the eigenvalue of M matrix, i.e., $E^{(c)}_{\gamma=1,2}$ is then

$$E^{(c)}_\gamma = m_0 \pm p \quad , \text{ for } \gamma = 1, 2.$$

$$\Rightarrow \boxed{\begin{aligned} E^{(c)}_{1,2} &= m_0 \pm \sqrt{m_x^2 + m_y^2 + m_z^2} \\ &= m_0 + (-1)^\gamma p \end{aligned}} \quad -(19)$$

- Eigenvectors of $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ are $\varphi_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\varphi_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ with the eigenvalues of ± 1. One can explicitly check that $\sigma_\pm = \sigma_x \pm i\sigma_y$ gives the raising & lower operator between the two states φ_1 & φ_2.

We can obtain the eigenstates of M in this basis as $\chi_r^{(0)} = c_{r_1}\varphi_1 + c_{r_2}\varphi_2$ for the two eigenvalues $E_{1,2}^{(1)}$ and obtain the coefficients c_{r_1} & c_{r_2} to be

$$\left.\begin{aligned} c_{r_1} &= \frac{1}{\sqrt{2}}\left[1 - (-1)^r \frac{m_z}{\beta}\right], \\ c_{r_2} &= \frac{1}{\sqrt{2}} \operatorname{sgn}(m_x)\left[1 + (-1)^r \frac{m_z}{\beta}\right] \end{aligned}\right\} \quad — (20)$$

which do not depend on m_0.

Examples of degenerate Perturbation theory

1. Fine structure of Hydrogen Atom.

The hydrogen Atom Hamiltonian we have studied in the previous chapter is

$$H_0 = \frac{p^2}{2m} + V(r) \quad - \quad (21)$$

where $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$

Now we want to study three different perturbation terms separately:

$$H_1' = -\frac{p^4}{8m^3c^2} \quad -- \quad (22a)$$

$$H_2' = \frac{1}{2m^2c^2}\left(\frac{1}{r}\frac{dV}{dr}\right)\vec{L}\cdot\vec{S} \quad --- \quad (22b)$$

$$H_3' = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\delta(\vec{r}) \quad -- \quad (22c).$$

The first term (H_1') arise from the relativistic correction to the Schrödinger equation. The second term (H_2') gives the spin-orbit coupling term. The third term (H_3') gives a onsite $(r=0)$ correction from the nucleus, called the Darwin term.

- $\underline{H_0}$: We have already solved H_0 with its eigenvalues E_n, depends on the principle quantum number obtained by selecting the normalizable solutions in the radial direction, and the eigenstates have three quantum numbers n, l, m, where l, m are related to the eigenvalues of L^2 & L_z. So we have

$$H_0 \psi_{nlm}^{(0)} = E_n^{(0)} \psi_{nlm}^{(0)} \quad \text{---} (23)$$

where ψ_{nlm} are orthonormalized as

$$\langle \psi_{nlm}^{(0)} | \psi_{n'l'm'}^{(0)} \rangle = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

$$= \int r\,dr \sin\theta \, d\theta \, d\phi \; \psi_{nlm}^{(0)*} \psi_{n'l'm'}^{(0)}$$

$$= \int r\,dr \; R_{nl}^{*}(r) R_{n'l'}(r) \int \sin\theta \, d\theta \, d\phi \; Y_{lm}(\theta,\phi) Y_{l'm'}(\theta,\phi) \quad \text{---} (24).$$

- Since ψ_{nlm} states have l, m quantum numbers degenerate we need to use degenerate perturbation theory. There are two degeneracy indices l, m which we combine in the single index 't' & 's' as used in the general derivation.

(*) $\langle H_1' \rangle$: Let us calculate the first order perturbation correction of

$$H_1' = -\frac{1}{8m^3c^2} p^4 = -\frac{1}{2mc^2} T^2 \qquad \text{where } T = K.E = \frac{p^2}{2m}.$$

$$= -\frac{1}{2mc^2}\left(H_0 - V(r)\right)^2$$

$$= -\frac{1}{2mc^2}\left[H_0^2 - 2H_0 V(r) + V(r)^2\right] \quad \text{--- (25)}.$$

which only depends on 'r', like the central field potential. Therefore, the perturbation term will be diagonal in the degenerate variable l, m.

From the degenerate perturbation theory we have from eq(1)

$$\sum_{s=1}^{\alpha} c_{rs}\left(H'_{nn,ts} - E^{(1)}_{nr}\,\delta_{ts}\right) = 0 \;; \quad r, s, t = 1, 2, \cdots (lm).$$

where $H'_{1nn,ts} = H'_{1,nn,tt}$ (diagonal).

$$= H'_{1,nn\,(lm)} = \langle nlm | H_1' | nlm \rangle$$

And since $\langle H_1' \rangle$ matrix elements are diagonal, so, its eigenvalues are simply the diagonal components only, i.e.,

$$E^{(1)}_{1,nlm} = \langle nlm | H_1' | nlm \rangle$$

$$= -\frac{1}{2mc^2}\left[\langle nlm | \left[H_0^2 - 2H_0 V(r) + (V(r))^2\right] | nlm \rangle\right].$$

$$= -\frac{1}{2mc^2}\left[\left(E_n^{(0)}\right)^2 + 2E_n^{(0)}\frac{Ze^2}{4\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle_{nlm} + \left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle_{nlm}\right]$$

— (26)

(H-W) Using virial theorem or another method (See Problem 7·6 of Bransden book) we can evaluate the two matrix elements as

$$\left.\begin{aligned} \left\langle \frac{1}{r} \right\rangle_{n\ell m} &= \frac{Z}{a_0 n^2} \\ \left\langle \frac{1}{r^2} \right\rangle_{n\ell m} &= \frac{Z^2}{a_0^2 n^2 (\ell + \frac{1}{2})} \end{aligned}\right\} \quad -(27).$$

↑ depends on ℓ

- substituting eq (27) in (26) we obtain the final result

$$E^{(1)}_{1, n\ell m} = - E_n^{(0)} \frac{(Z\alpha)^2}{n^2} \left[\frac{3}{4} - \frac{n}{\ell + 1/2} \right] \quad -(28).$$

where $\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx 1/137$ = fine structure constant.

We notice that the relativistic correction lifts the orbital angular momentum 'ℓ' degeneracy of the atomic orbitals.

(*) H_2' : Next we consider the spin-orbit coupling perturbation term $H_2' = \xi(r)\,\vec{L}\cdot\vec{S}$, where $\xi(r)$ = SOC strength

$$= \frac{1}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}$$

$$= \frac{1}{2m^2c^2}\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r^3} \quad \text{---} (29)$$

- Two things to notice before we proceed further. (i) The perturbation includes spin of the electron $s = 1/2$ and we now have to include the spin basis in the overall eigenbasis of $\psi^{(0)}_{nlm}$. (ii) The orbital angular momentum $\vec{L}^2$ & L_z are no longer commute with H_0 and hence (l, m_l) are not good quantum number. So, does the $\vec{S}^2$ & S_z and hence s, m_s are not good quantum numbers.
- But the total angular momentum $\vec{J} = \vec{L} + \vec{S}$ will be provide a good quantum number j, m_j. To see that lets expand $\vec{J}^2$ as

$$\vec{J}^2 = (\vec{L}+\vec{S})^2 = \vec{L}^2 + \vec{S}^2 + \vec{L}\cdot\vec{S} + \vec{S}\cdot\vec{L}$$

$$= \vec{L}^2 + \vec{S}^2 + 2\vec{L}\cdot\vec{S} \quad \text{, since } \vec{L} \text{ \& } \vec{S} \text{ commute.}$$

So, $\vec{L}\cdot\vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$ --- (30)

Since J^2, $\vec{L}^2$, $\vec{S}^2$ commute with themselves, as we saw in the chapter of angular momentum (think of $\vec{L}_1 = \vec{L}, \vec{L}_2 = \vec{S}$) so, we can use the total angular momentum basis of

$$|j\, m_j; l_1 l_2\rangle \equiv |j\, m_j\, l\, s\rangle \quad \text{---} (30).$$

where j ranges from $|l-s|$ to $l+s$, and $m_j = -j, -j+1, \cdots j-1, j$.

- We expand $|j\, m_j\, l s\rangle$ in the direct product state of $|l m_l\rangle |s m_s\rangle$ with the coefficients called Clebsch-Gordon coefficient.

$$|j\, m_j\, l\, s\rangle = \sum_{m_l m_s} C^{j\, l s}_{m_j\, m_l m_s} |l m_l\rangle |s m_s\rangle \quad --- (31)$$

(Sometimes we write $|\Psi_{l m_l s m_s}\rangle$, and sometimes $|l m_l s m_s\rangle$, both are however the same).

(We have not included the principle quantum number 'n' in this basis. Because it is there on both sides. The principle quantum corresponds to $R_{nl}(r)$ & $|j\, m_j\, l s\rangle \equiv \Psi_{j m_l l s}(\theta,\phi)$, and they decouple since these coordinates are separable. We will now call the unperturbed state of H_0 as: $|n j m_j l s\rangle = |n l\rangle |j m_j l s\rangle$.

$$\langle r, \theta \phi \,|\, \Psi^{(0)}_{n j m_j l s}\rangle = R^{(0)}_{nl}(r)\, Y^{(0)}_{j m_j l s}(\theta,\phi) \quad --- (32).$$

- Since again j, m_j, l, s quantum numbers do not appear in the energy $E_n^{(0)}$, so, we have to use degenerate perturbation theory. Following the same procedure as for H_1', we can show that the matrix elements of $\langle H_2'\rangle_{n j m_j l s}$ are diagonal and hence gives the eigenvalues $E^{(1)}_{2, n j m_j l s}$:

$$E^{(2)}_{2, n j m_j l s} = \langle \Psi^{(0)}_{n j m_j l s} \,|\, H_2' \,|\, \Psi^{(0)}_{n j m_j l s}\rangle$$

$$= \langle R_{nl}^{(0)} | \xi(r) | R_{nl}^{(0)} \rangle \langle \psi_{jm_jls}^{(0)} | \vec{L}\cdot\vec{S} | \psi_{jm_jls} \rangle \quad \text{--- (33)}$$

$$\langle R_{nl}^{(0)} | \xi(r) | R_{nl}^{(0)} \rangle = \frac{1}{2m^2c^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\left\langle \frac{1}{r^3}\right\rangle_{jm_jls}$$

$$= \frac{1}{2m^2c^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\frac{Z^3}{a_0^3 n^3 l(l+\frac{1}{2})(l+1)} \quad \text{--- (34a)}$$

(Again see Problem 7.16 of Bransden book).

$$\langle \psi_{jm_jls}^{(0)} | \tfrac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2) | \psi_{jm_jls}^{(0)} \rangle = \frac{1}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]\hbar^2 \quad \text{--- (34b)}$$

- For $l=0$, the SOC term vanishes.
- For $l \neq 0$, we can now write the 1st order perturbed energy

$$E_{2,nljm_jls}^{(1)} = -E_n^{(0)} \frac{(Z\alpha)^2}{2nl(l+\frac{1}{2})(l+1)} \times \begin{cases} l & \text{for } j = l + 1/2. \\ -l+1 & \text{for } j = l - 1/2. \end{cases} \quad \text{--- (35)}$$

⊛ Darwin term $\quad H_3' = \underbrace{\frac{\pi \hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)}_{A} \delta(\vec{r}) \qquad \text{--- (36)}.$

(No orbital & spin angular momentum, so lets go back to our simpler basis of $\psi^{(0)}_{n\ell m}$ here).

- H_3' only acts at the origin $\vec{r}=0$. All wavefunction $R_{n\ell}(r)$ vanishes at $\vec{r}=0$ for $\ell \neq 0$, except for $\ell = 0$ state. Therefore we only have to consider the $\ell=0$ & $m=0$ case. clearly, the matrix element $\langle H_3' \rangle$ will be diagonal and hence we have

$$\left.\begin{aligned} E^{(3)}_{3,n00} &= \langle \psi^{(0)}_{n00} \,|\, A\,\delta(\vec{r}) \,|\, \psi^{(0)}_{n00} \rangle \\ &= A \,|\psi^{(0)}_{n00}(0)|^2 \\ &= -E_n^{(0)} \frac{(Z\alpha)^2}{n} \qquad \text{for } \ell = 0. \\ &= 0 \qquad \text{for } \ell \neq 0. \end{aligned}\right\} \text{--(37)}$$

* Combine all three perturbations: Fine structure splitting.

$$E^{(1)}_{nj m_j \ell s} = E^{(1)}_{1,n\ell m} + E^{(1)}_{2,njm_j\ell s} + E^{(1)}_{3,n00}$$

not needed.

$$= -E_n^{(0)} \frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) \qquad \text{--- (38)}.$$

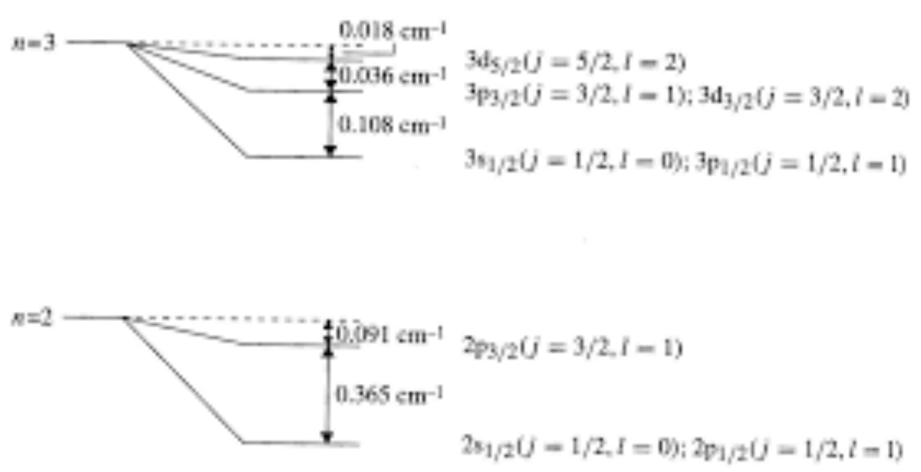
- Interestingly, 1st two perturbations depend on ℓ, but the total contribution depends on only j.

Recall the relation between n, l from the previous chapter and then $j = |l-s|$ to $(l+s)$. Using them we can obtain the allowed values of $j = 1/2, 3/2, \ldots, n - 1/2$.

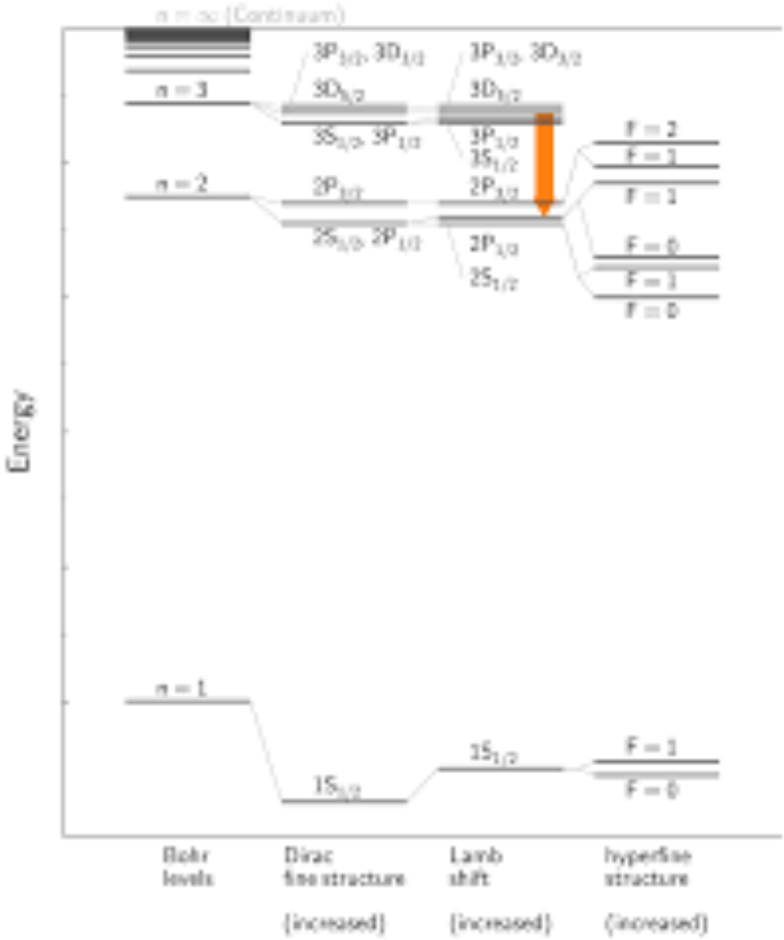
- Then the total energy levels of Hydrogen atom upto 1st order relativistic correction:

$$E_{nj} = E_n^{(0)} + E_{nj}^{(1)} \qquad \text{— (39).}$$

(Solving the Dirac equation of relativistic quantum mechanics one obtains the energy levels which are close to eq (39).)



This splitting is called fine structure splitting with the values of j due to relativistic corrections. The splitting is proportional to α^2, where α = Fine structure constant. There are more corrections, called Lamb shift, Hyperfine splittings.



n = ∞ (Continuum)
n = 3
n = 2
n = 1
Energy
3P3/2, 3D3/2
3D5/2
3S1/2, 3P1/2
2P3/2
2S1/2, 2P1/2
1S1/2
F = 2
F = 1
F = 1
F = 0
F = 1
F = 0
F = 1
F = 0
Bohr
levels
Dirac
fine structure
(increased)
Lamb
shift
(increased)
hyperfine
structure
(increased)

Ex 2: Stark effect: (Bransden chap 12)

In the angular momentum chapter, we discussed the splitting of an energy levels due to applied magnetic field which allign the spins and hence spin degeneracy is lost. This is called Zeeman effect.

Now we will study via perturbation theory how the energy levels of an Hydrogen atom split due to applied electric field. Electric field acting on the charge of the electron, rather than on the spin, the effect will be different than the Zeeman term and the corresponding splitting is called the Stark effect.

Without loosing generality we apply the electric field along the z direction, then the perturbation term is

$$H' = e E z \quad --- \quad (40)$$

We are interested to find the energy spitting of the ground state ($n=1, \ell = m = 0$), and the first excited state ($n=2, \ell=1, m=-1,0,1$).

- <u>Ground State $\psi_{100}^{(0)}$</u> is non-degenerate. So using non-degenerate perturbation theory, we write the 1st order correction:

$$E_{100}^{(1)} = \langle \psi_{100}^{(0)} | H' | \psi_{100}^{(0)} \rangle$$
$$= eE \langle \psi_{100}^{(0)} | z | \psi_{100}^{(0)} \rangle \quad \text{--- (41)}$$
$$= 0$$ since Hydrogen atom solutions have definite parity.

For the same reason actually all diagonal matrix elements $\langle \psi_{nlm}^{(0)} | z | \psi_{nlm}^{(0)} \rangle = 0$.

The 2nd order perturbation term involves off-diagonal transition from the ground state to the excited state:

$$E_{100}^{(2)} = \sum_{n \neq 1} \sum_{\substack{l \neq 0 \\ m \neq 0}} \frac{|\langle nlm | H' | 100 \rangle|^2}{E_1^{(0)} - E_{nlm}^{(0)}} \quad \text{--- (42)}$$

Since the energy differences $(E_1^{(0)} - E_{nlm}^{(0)})$ with $n \geq 2$ are always negative, and $E_{100}^{(1)} = 0$, the ground state energy is always lowered by the interaction with electric field. The 2nd order stark effect in eq (42) is very small, $\sim -2.5 \times 10^{-6}$ eV for the Hydrogen atom and hence negligible.

* <u>Excited States</u>: Lets consider $n=2$ as an example. This has $(l=0, m=0)$ & $(l=1, m=0,\pm1)$, <u>degenerate</u> multiplets which are denoted by $\psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1}$ states. Therefore, we need to consider now the degenerate perturbation theory. We need to calculate the matrix elements of $\langle n\, l'm' | H' | n\, l\, m\rangle$, for $n=2$, (l,m) are the four degenerate indices (r,s,t). Clearly, for $l'=l$, $m'=m$, the matrix elements vanish due to the well defined parity of the states while $H' = -eEz$ is odd under parity.

The other matrix element that survives are for $l' = l\pm1$, $m'=m$, due to the selection rule (section 11.4 of Bransden book). Therefore, the only two matrix element that survived are between the 2s (200) to 2p (210) states. We denote 2s & 2p state as ψ_1 & ψ_2 and then $H'_{12} = \langle \psi_1 | H' | \psi_2\rangle = +eE\langle 200|z|210\rangle$ and so on. This matrix element can be calculated as

$$H'_{12} = eE\int \psi^*_{200}(r,\theta,\phi)\,(r\cos\theta)\,\psi_{210}(r,\theta,\phi)\, r^2 dr\sin\theta\, d\theta\, d\phi$$

$$= eE\int R^*_{20}(r)\,R_{21}(r)\,r^3 dr \int Y^*_{00}(\theta,\phi)\,Y_{10}(\theta,\phi)\sin\theta\cos\theta\, d\theta\, d\phi$$

$$= eE\frac{3a_0}{Z} \quad \text{after substituting } R_{nl} \text{ \& } Y_{lm}. \quad (\text{H.W}) \qquad ---(43).$$

$H'_{21} = H_{12}$, $H_{11} = H_{22} = 0$. Therefore, the eigenvalue equation we have is

$$\underbrace{\begin{pmatrix} 0 & H'_{12} \\ H'_{12} & 0 \end{pmatrix}}_{M \,=\, H'_{12}\,\sigma_x} \begin{pmatrix} c_{r1} \\ c_{r2} \end{pmatrix} = E_r^{(1)} \begin{pmatrix} c_{r1} \\ c_{r2} \end{pmatrix}$$

So, we just have to look for the eigenvalue/eigenvectors of the Pauli matrix σ_x. The eigenvalue is

$$E^{(1)}_{1,2} = \pm |H_{12}| = \pm eE \frac{3a_0}{Z}. \qquad -(44)$$

eigenvectors are $\begin{pmatrix} c_{11} \\ c_{12} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$; $\begin{pmatrix} c_{21} \\ c_{22} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$.

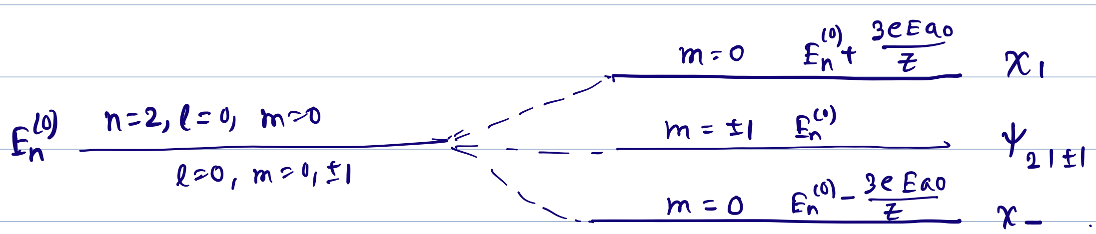
These two eigenvalues gives the wavefunctions of

$$\chi_{r=1} = c_{11}\psi_1 + c_{12}\psi_2 \quad , \text{where } \psi_1 = \psi_{200},\ \psi_2 = \psi_{210}$$

$$= \frac{1}{\sqrt{2}}\left(\psi_{200} + \psi_{210}\right) \qquad \text{Bonding state}$$

$$\chi_{r=2} = \frac{1}{\sqrt{2}}\left(\psi_{200} - \psi_{210}\right) \qquad \text{Antibonding state}$$

$-(45)$



SPIN: If we consider spin, there will be a further shift, not a splitting by the electric field for the ground and excited states. This can be evaluated using the Wigner-Eckart theorem.

$$Z = \frac{\langle \vec{J}\cdot\hat{z}\rangle}{j(j+1)\hbar^2} J_z = \frac{\langle J_z\rangle}{j(j+1)\hbar^2} J_z$$

$$\Rightarrow \langle Z\rangle = \frac{\langle J_z\rangle^2}{j(j+1)\hbar^2} = \frac{m_j^2\hbar^2}{j(j+1)\hbar^2} \quad \cdots \quad (46)$$

For, $l=0$, $s=1/2$, $m_s=m_l=\pm 1/2$, we get

$$\langle Z\rangle = \frac{(1/2)^4\hbar^2}{1/2(1/2+1)\hbar^2} = \frac{1}{3}.$$

So. $\langle H'\rangle = eE\langle z\rangle = \frac{1}{3}eE.$

Therefore, due to spin, the energy levels get shifted via an applied electric field, but get splitted by a magnetic field.