

# Time independent perturbation theory: Obtaining approximate solutions to perturbed problems.

Suppose we have solved the time independent Schrodinger equation :

$$H^o \psi_n^o = E_n^o \psi_n^o$$

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What we have solved for

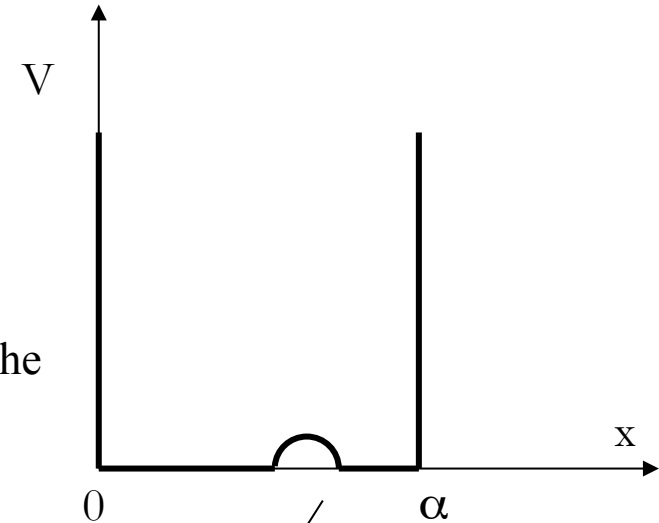
obtaining a complete set of orthonormal eigenfunctions  $\psi_n^o$ ,

$\langle \psi_n^o | \psi_m^o \rangle = \delta_{nm}$  and the corresponding eigenvalues  $E_n^o$ .

Let's perturb the potential slightly, by putting a little bump in the bottom of the well:

We would like to find  $H\psi_n = E_n\psi_n$

What we would like to find



Small perturbation

# Methodology

## Step 1

We initially write the new Hamiltonian as a sum of 2 terms:

$$H = H^o + \lambda V$$

## Step 2

Then we write  $\psi_n$  and  $E_n$  as a power series in  $\lambda$ .

$$\psi_n = \psi_n^o + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots$$

$$E_n = E_n^o + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

Note: The corrections to the wavefunction are perpendicular to it since they must correspond to really new contributions to it. Thus:

$$(\psi_n^o, \psi_n^1) = (\psi_n^o, \psi_n^2) = \dots = 0$$

1st , 2nd, 3rd order corrections.....

### Step 3

Substituting in  $(H^0 + V)\psi_n = E_n\psi_n$  we have:

$$(H^0 + \lambda V)\left[\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots\right] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)\left[\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots\right]$$

Collecting powers of  $\lambda$ :

$$H^0\psi_n^0 + \lambda(H^0\psi_n^1 + V\psi_n^0) + \lambda^2(H^0\psi_n^2 + V\psi_n^1) + \dots$$

$$= E_n^0\psi_n^0 + \lambda(E_n^0\psi_n^1 + E_n^1\psi_n^0) + \lambda^2(E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0) + \dots$$

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0th order in  $\lambda$ :  $H^0\psi_n^0 = E_n^0\psi_n^0$

1st order in  $\lambda$ :  $H^0\psi_n^1 + V\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$

2nd order in  $\lambda$ :  $H^0\psi_n^2 + V\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$

# First order theory

$$H^o \psi_n^1 + V \psi_n^o = E_n^o \psi_n^1 + E_n^1 \psi_n^o$$

Taking the inner product with  $\psi_n^o$ , that is multiplying with  $(\psi_n^o)^*$  and integrating:

$$\langle \psi_n^o | H^o \psi_n^1 \rangle + \langle \psi_n^o | V \psi_n^o \rangle = E_n^o \langle \psi_n^o | \psi_n^1 \rangle + E_n^1 \langle \psi_n^o | \psi_n^o \rangle$$

Step 4

But  $H^o$  is Hermitian:

$$\langle \psi_n^o | H^o \psi_n^1 \rangle = \langle H^o \psi_n^o | \psi_n^1 \rangle = \langle E_n^o \psi_n^o | \psi_n^1 \rangle = E_n^o \langle \psi_n^o | \psi_n^1 \rangle$$

$$\text{Also: } \langle \psi_n^o | \psi_n^o \rangle = 1$$

$$E_n^1 = \langle \psi_n^o | V \psi_n^o \rangle$$

Thus: the first order correction to the energy is the expectation value of the perturbation in the unperturbed state

# First order correction to the wavefunction

$$\text{1st order in } \lambda: H^o \psi_n^1 + V \psi_n^o = E_n^o \psi_n^1 + E_n^1 \psi_n^o \rightarrow (H^o - E_n^o) \psi_n^1 = -(V - E_n^1) \psi_n^o$$

$$\text{Let: } \psi_n^1 = \sum_{m \neq n} c_m^n \psi_m^o$$

Use the usual fact that a wavefunction can be expressed using the superposition principle, where  $c_n$ , is how much of  $\psi_m$  is contained in  $\psi_n$ .

$$\sum_{m \neq n} (E_m^o - E_n^o) c_m^n \psi_m^o = -(V - E_n^1) \psi_n^o \quad \text{Taking the product with } \psi_l^o$$

$$\rightarrow \sum_{m \neq n} (E_m^o - E_n^o) c_m^n \langle \psi_l^o | \psi_m^o \rangle = -\langle \psi_l^o | V | \psi_n^o \rangle + E_n^1 \langle \psi_l^o | \psi_n^o \rangle$$

$$\rightarrow (E_l^o - E_n^o) c_l^n = -\langle \psi_l^o | V | \psi_n^o \rangle \quad \text{or} \quad c_l^n = \frac{\langle \psi_l^o | V | \psi_n^o \rangle}{(E_n^o - E_l^o)}$$

$$\therefore \psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^o | V | \psi_n^o \rangle}{(E_n^o - E_m^o)} \psi_m^o$$

Does this hold if the energy spectrum is degenerate?

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## Second order correction to the energy

- From the second order perturbative equation:

$$2nd \text{ order in } \lambda: H^o \psi_n^2 + V \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^o$$

- Multiply with  $\psi_n^0$  and get

$$\left( \psi_n^0, H^o \psi_n^2 \right) + \left( \psi_n^0, V \psi_n^1 \right) = \underbrace{E_n^0 \left( \psi_n^0, \psi_n^2 \right)}_{= \left( \psi_n^0, H^o \psi_n^2 \right)} + E_n^1 \underbrace{\left( \psi_n^0, \psi_n^1 \right)}_{=0} + E_n^2$$

- From the above you get

$$E_n^2 = \left( \psi_n^0, V \psi_n^1 \right)$$

## Second order correction to the energy

- Using  $\psi_n^1 = \sum_{m \neq n} c_m^n \psi_m^0$  we have

$$\begin{aligned} E_n^2 &= (\psi_n^0, V \psi_n^1) = \left( \psi_n^0, V \sum_{m \neq n} c_{nm}^1 \psi_m^0 \right) = \sum_{m \neq n} c_{nm}^1 (\psi_n^0, V \psi_m^0) \\ &= \sum_{m \neq n} c_{nm}^1 V_{nm} = \sum_{m \neq n} \frac{V_{mn}}{E_n^0 - E_m^0} V_{nm} \\ \Rightarrow E_n^2 &= \sum_{m \neq n} \frac{|V_{nm}|^2}{E_n^0 - E_m^0} \end{aligned}$$

# Notes and Remarks

- The perturbation method is valid when the Hamiltonian can be split in two parts: the unperturbed  $H^0$  which is solvable and a small perturbation  $V$ .
- We may be led to believe that a perturbation expansion always exists for a sufficiently weak perturbation. Unfortunately, this is not necessarily the case.



# Perturbation and Degenerate States

- It is clear that the series

$$E_n - E_n^o = \lambda \langle \psi_n^o | V \psi_n^o \rangle + \lambda^2 \sum_{m \neq n} \frac{|\langle \psi_n^o | V \psi_m^o \rangle|^2}{E_n^o - E_m^o} + \dots$$

will converge if the term

$$\frac{|\langle \psi_n^o | V \psi_m^o \rangle|}{E_n^o - E_m^o}$$

is sufficiently small.

# Notes and Remarks

- When we have two energy levels that are connected with the perturbed potential tend to repel each other.

$$E_n - E_n^o = \lambda \langle \psi_n^0 | V \psi_n^o \rangle + \lambda^2 \sum_{m \neq n} \frac{|\langle \psi_n^0 | V \psi_m^o \rangle|^2}{E_n^o - E_m^o} + \dots$$

- This is a special case of the **no-level-crossing theorem** which states that a pair of energy levels connected by perturbation do not cross as the strength of the perturbation is varied.
- The second order energy shift for the ground state is always negative. The lower state tends to get lower as a result of mixing.

# Perturbation and Degenerate States

- Consider now the case where one or more states of the unperturbed Hamiltonian  $H^0$  are degenerate. Let's consider that the energy of such a state is  $E^{(0)}$  and that  $\psi^{(0)}_n$  ( $n=1, 2, 3, \dots, N$ ) the corresponding **degenerate states**.
- Applying the theory of the non-degenerate states we would have two problems:
- A) For the first correction in energy:  $E^{(1)} = \langle \psi^0 | V \psi^0 \rangle$  which state of the  $\psi^{(0)}_n$  are we going to use?

# Perturbation and Degenerate States

- B) For the first correction in the wavefunction:

$$\psi_n^{(1)} = \sum_m \frac{\langle \psi_n^0 | V \psi_m^0 \rangle}{E_n^0 - E_m^0} \psi_m^{(0)}$$

The denominator is zero. So the only case that it would give a physically acceptable result is if

$$\langle \psi_n^0 | V \psi_m^0 \rangle = 0 \quad (n \neq m)$$

Where now the states belong in the degeneracy subspace. But now we reached the answer!

# Perturbation and Degenerate States

- The theory of the non-degenerate states can be applied in the degenerate case **if and only if** the degenerate states have been chosen in such a way that :

$$\langle \psi_n^0 | V \psi_m^0 \rangle = 0 \quad (n \neq m)$$

- In a matrix language it means that the non-diagonal elements of the perturbation  $V$  matrix to be zero in the degeneracy subspace. The problem reduces to a problem of a matrix diagonalization!

# Perturbation and Degenerate States

- Given that the degenerate states  $\psi^{(0)}_n$  have been chosen arbitrarily the corresponding perturbation matrix is:

$$V = \begin{pmatrix} V_{11} & \cdot & \cdot & V_{1N} \\ \cdot & \cdot & \cdot & \cdot \\ V_{N1} & \cdot & \cdot & V_{NN} \end{pmatrix}$$

- We know that a Hermitian matrix can be always diagonalized with a proper choice of basis. This means that we can choose a new set of states  $\hat{\psi}_n^0$  with respect to which the matrix will take the form:

$$V = \begin{pmatrix} \epsilon_1 & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \epsilon_N \end{pmatrix}$$

# Perturbation and Degenerate States

- The relation of the new basis  $\psi_n$  to the old  $\psi^{(0)}_n$  will be given by the solution of the solution of the eigenvalues:

$$\begin{pmatrix} V_{11} & \cdot & \cdot & V_{1N} \\ \cdot & \cdot & \cdot & \cdot \\ V_{N1} & \cdot & \cdot & V_{NN} \end{pmatrix} \begin{pmatrix} c_1 \\ \cdot \\ c_N \end{pmatrix} = \epsilon \begin{pmatrix} c_1 \\ \cdot \\ c_N \end{pmatrix}$$

- From the above we will take the eigenvalues of the energy as roots of the characteristic equation:

$$\det(V - \epsilon I) = \det \begin{pmatrix} V_{11} - \epsilon & \cdot & \cdot & V_{1N} \\ V_{21} & V_{22} - \epsilon & \cdot & V_{2N} \\ \cdot & \cdot & \cdot & \cdot \\ V_{N1} & \cdot & \cdot & V_{NN} - \epsilon \end{pmatrix}$$

# Perturbation and Degenerate States

- For each eigenvalue we calculate the relevant eigenvector  $(c_1, \dots, c_N)$  and the relation of the new basis to the old is given by:

$$\hat{\psi}_n^{(0)} = c_{n1} \psi_1^{(0)} + c_{n2} \psi_2^{(0)} + \dots + c_{nN} \psi_N^{(0)}$$

- **The components of the eigenvectors of the perturbation matrix  $V$  are simultaneously the coefficients of the linear combination that relates the new base to the old one!**
- And what is the next step? We just apply the theory of the non-degenerate states!



# Perturbation and Degenerate States

- For each of the new eigenfunctions  $\hat{\psi}_n^{(0)}$  we get the first order correction as follows:

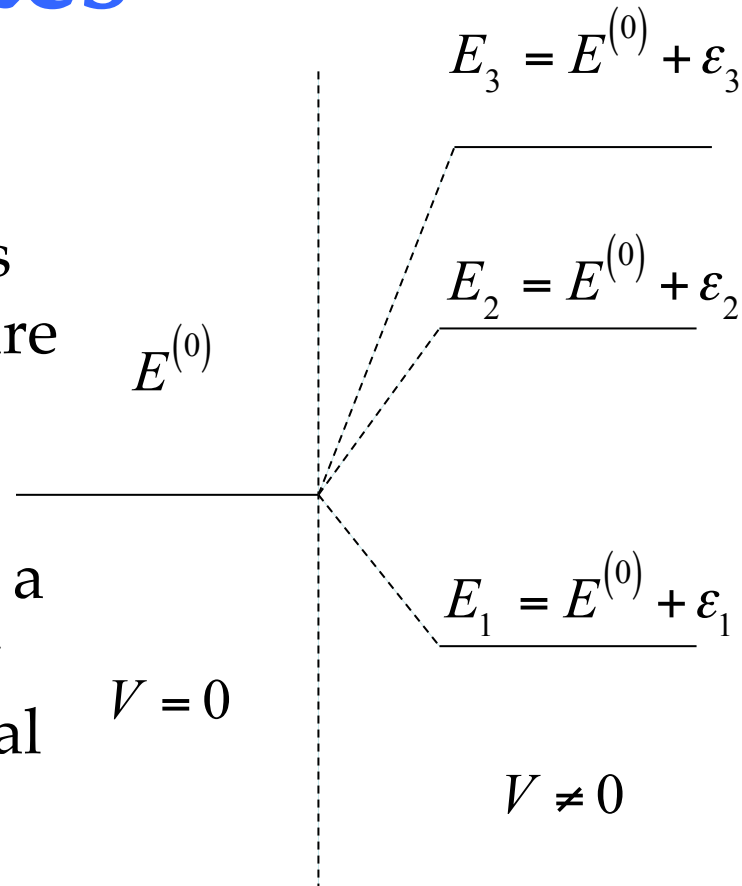
$$E_n^{(1)} = \left( \hat{\psi}_n^{(0)}, V \hat{\psi}_n^{(0)} \right) = \widehat{V}_{nn} = \varepsilon_n$$

- **If the matrix eigenvalues are different then the number of first order corrections will be equal to the degeneracy order, that means equal to  $N$ .**
- This means that the initially degenerate level  $E^{(0)}$  will be split in  $N$  separate levels with energies:

$$E_n = E^{(0)} + \varepsilon_n, \quad n = 1, \dots, N$$

# Perturbation and Degenerate States

- Perturbation lifts the degeneracy. This lifting is complete if all the eigenvalues of the perturbation matrix  $V$  are different and partial in the opposite case.
- Degeneracy and its lifting has a direct relation with symmetry and its breaking. E.g. rotational symmetry of Coulomb force imposes a degeneracy which can be broken by applying a magnetic field (Zeeman Effect)



# The Method of Variations

- This method is applicable in cases where the perturbation method is either completely non applicable or it gives very bad results. The starting point of this method is the following obvious mathematical statement:
- “The average value of a statistical quantity is always larger or at least equal to its smallest value”. Which in quantum mechanics means:
- “The average value of a quantum mechanical quantity is always larger or at least equal to its smallest eigenvalue” so:

# The Method of Variations

- “The average value of the energy of a quantum system a statistical quantity is always larger or at least equal to the energy of its ground state”.

$$\langle E \rangle = (\psi, H\psi) \geq E_0$$

- The “hard core” of this method is the following: We know that the ground state eigenfunction has no nodes (like a Gaussian) and bears the full symmetry of the problem.
- This idea reduces strongly the size of the set of all the possible candidate functions for the ground state. We need one more step.

# The Method of Variations

- We get a set of parameters  $\lambda_1, \lambda_2, \dots, \lambda_n$ , on which the eigenfunction may depend and we seek for which values of these parameters the average energy becomes minimum. Assume that we have a single parameter and thus we can write  $\psi = \psi(x, \lambda)$ . Then the average value of the energy is a function of  $\lambda$ .

$$\bar{E} = \langle E(\lambda) \rangle = \langle \psi(\lambda) | H | \psi(\lambda) \rangle = \int \psi^*(\lambda) (H \psi^*(\lambda)) dx$$

- The value of  $\lambda$  which minimizes the average energy is given by:

$$d\bar{E} / d\lambda = 0 \Rightarrow \lambda = \lambda_0$$

$$E_{\min} = \bar{E}(\lambda_0)$$

<http://fac.ksu.edu.sa/vlmpesis>