

CHAPTER 5: STATIONARY PERTURBATION THEORY

(From Cohen-Tannoudji, Chapter XI)

A. DESCRIPTION OF THE METHOD

Approximation methods to obtain analytical solution of eigenvalue problems.

1. Statement of the problem

We consider a time-independent perturbation

$$\hat{H} = \hat{H}_0 + W \quad (5.1)$$

of the time-independent Hamiltonian \hat{H}_0 , whose eigenvalues and eigenvectors are known and which captures the essential physics, by an additional term

$$W = \lambda \hat{W} \quad (5.2)$$

$$\lambda \ll 1 \quad (5.3)$$

We assume that the eigenvalues and eigenstates of \hat{H}_0 are known and that the unperturbed energies form a discrete spectrum E_p^0 with eigenvectors $|\varphi_p^i\rangle$ (where the index i refers to degeneracy):

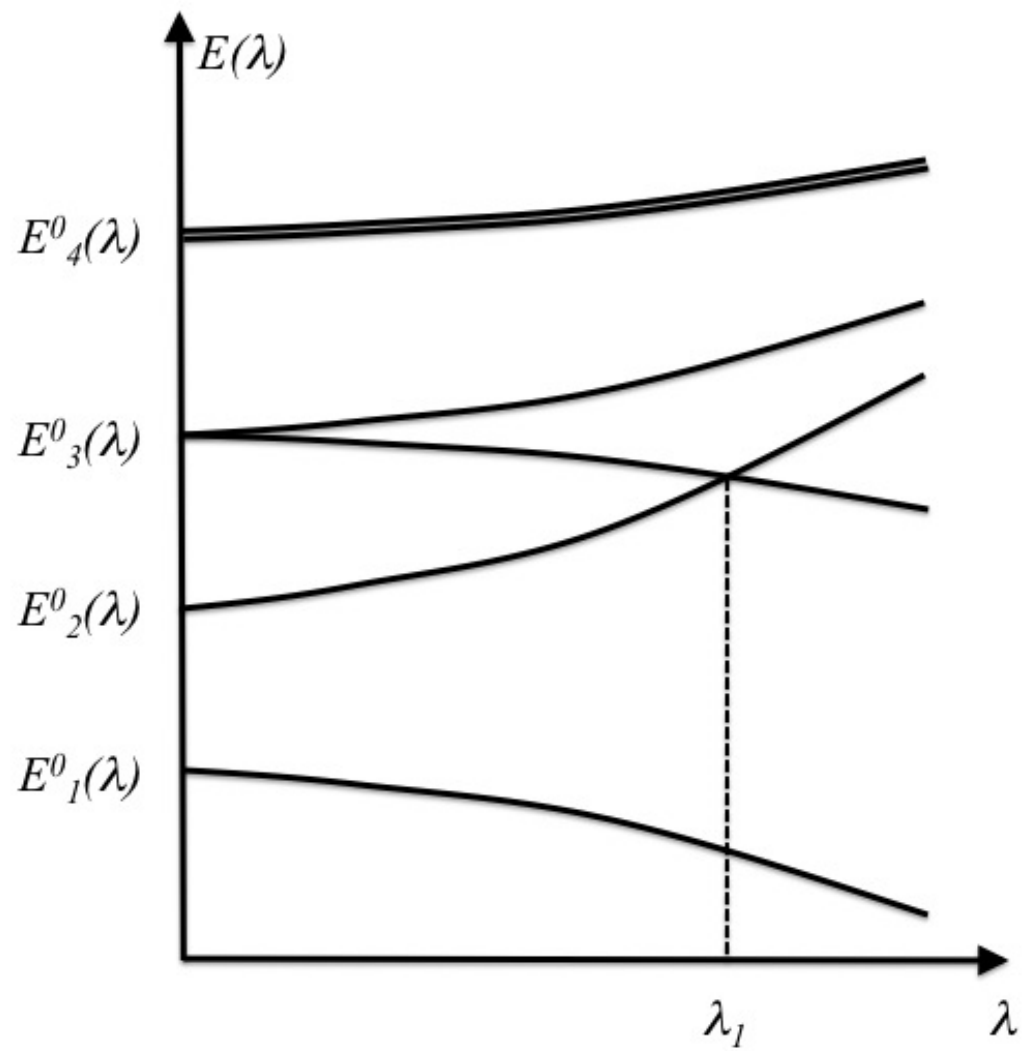
$$\hat{H}_0|\varphi_p^i\rangle = E_p^0|\varphi_p^i\rangle \quad (5.4)$$

where

$$\langle\varphi_p^i|\varphi_{p'}^{i'}\rangle = \delta_{pp'}\delta_{ii'} \quad (5.5)$$

$$\sum_p \sum_i |\varphi_p^i\rangle\langle\varphi_p^i| = \hat{1} \quad (5.6)$$

i.e. the states $|\varphi_p^i\rangle$ form a basis.



We seek an approximative solution of the full Hamiltonian $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{W}$

$$\hat{H}(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle \quad (5.7)$$

where the eigenvalue and eigenvector can be expanded in terms of λ

$$E(\lambda) = \varepsilon_0 + \lambda\varepsilon_1 + \dots + \lambda^q\varepsilon_q + \dots \quad (5.8)$$

$$|\psi(\lambda)\rangle = |0\rangle + \lambda|1\rangle + \dots + \lambda^q|q\rangle + \dots \quad (5.9)$$

Inserting these into the eigenvalue equation yields

$$(\hat{H}_0 + \lambda\hat{W}) \left[\sum_{q=0}^{\infty} \lambda^q |q\rangle \right] = \left[\sum_{q'=0}^{\infty} \lambda^{q'} \varepsilon_{q'} \right] \left[\sum_{q=0}^{\infty} \lambda^q |q\rangle \right] \quad (5.10)$$

As this equation must hold for any (small) value of λ , it must hold for each power of λ separately, giving the equations for various orders of the perturbation:

0th-order: is just the eigenvalue equation of the unperturbed Hamiltonian, $\varepsilon_0 = E_n^0$

$$\hat{H}_0|0\rangle = \varepsilon_0|0\rangle \quad (5.11)$$

1st order:

$$(\hat{H}_0 - \varepsilon_0)|1\rangle + (\hat{W} - \varepsilon_1)|0\rangle = 0 \quad (5.12)$$

2nd order

$$(\hat{H}_0 - \varepsilon_0)|2\rangle + (\hat{W} - \varepsilon_1)|1\rangle - \varepsilon_2|0\rangle = 0 \quad (5.13)$$

q-th order

$$(\hat{H}_0 - \varepsilon_0)|q\rangle + (\hat{W} - \varepsilon_1)|q-1\rangle - \varepsilon_2|q-2\rangle \dots - \varepsilon_q|0\rangle = 0 \quad (5.14)$$

We shall write $|\psi(\lambda)\rangle$ to be normalized and its phase will be chosen s.t. $\langle 0|\psi(\lambda)\rangle \in \mathbb{R}$.
 For 0th order we have

$$\langle 0|0\rangle = 1 \quad (5.15)$$

and to the 1st order we get

$$\langle \psi(\lambda)|\psi(\lambda)\rangle = [\langle 0| + \lambda\langle 1|] [|0\rangle + \lambda|1\rangle] + \mathcal{O}(\lambda^2) \quad (5.16)$$

$$= \langle 0|0\rangle + \lambda[\langle 1|0\rangle + \langle 0|1\rangle] + \mathcal{O}(\lambda^2) \quad (5.17)$$

Since both $\langle 0|0\rangle = 1$ and $\langle \psi(\lambda)|\psi(\lambda)\rangle = 1$ we get to the 1st order

$$\begin{aligned} \lambda[\langle 1|0\rangle + \langle 0|1\rangle] &= 0 \\ \Rightarrow \langle 0|1\rangle = \langle 1|0\rangle &= 0 \end{aligned} \quad (5.18)$$

For the 2nd order we get

$$\begin{aligned}\langle \psi(\lambda) | \psi(\lambda) \rangle &= \langle 0|0 \rangle + \lambda [\langle 1|0 \rangle + \langle 0|1 \rangle] \\ &\quad + \lambda^2 [\langle 2|0 \rangle + \langle 0|2 \rangle + \langle 1|1 \rangle] + \mathcal{O}(\lambda^3)\end{aligned}\tag{5.19}$$

$$\Rightarrow \langle 0|2 \rangle = \langle 2|0 \rangle = -\frac{1}{2} \langle 1|1 \rangle\tag{5.20}$$

and eventually for q-th order we have

$$\langle 0|q \rangle = \langle q|0 \rangle = -\frac{1}{2} [\langle q-1|1 \rangle + \langle q-2|2 \rangle + \dots + \langle 2|q-2 \rangle + \langle 1|q-1 \rangle]\tag{5.21}$$

B. PERTURBATION OF A NON-DEGENERATE LEVEL

We will try to answer how a nondegenerate eigenvalue and eigenvector of the unperturbed Hamiltonian \hat{H}_0

$$\begin{aligned}\varepsilon_0 &= E_n^0 \\ |0\rangle &= |\phi_n\rangle\end{aligned}$$

are modified by introducing the perturbation W .

We will be seeking the eigenvalue $E_n(\lambda)$ of the full Hamiltonian $\hat{H}(\lambda)$ which when $\lambda \rightarrow 0$ approaches E_n^0 of \hat{H}_0 .

We will assume that λ is small enough for this eigenvalue to remain non-degenerate.

1. First-order corrections

a. ENERGY CORRECTION

Taking the 1st order equation we found above, and projecting onto $|\varphi_n\rangle$ gives

$$\langle\varphi_n|(\hat{H}_0 - \varepsilon_0)|1\rangle + \langle\varphi_n|(\hat{W} - \varepsilon_1)|0\rangle = 0 \quad (5.22)$$

and since $|\varphi_n\rangle = |0\rangle$ is the eigenvector of \hat{H}_0 with the eigenvalue $\varepsilon_0 = E_n^0$, we obtain the first order correction to the energy

$$\varepsilon_1 = \langle\varphi_n|\hat{W}|0\rangle = \langle\varphi_n|\hat{W}|\varphi_n\rangle \quad (5.23)$$

and the 1st order perturbative expression for the energy eigenvalue of the perturbed system in the form (recall, $W = \lambda\hat{W}$)

$$E_n(\lambda) = E_n^0 + \langle\varphi_n|W|\varphi_n\rangle + O(\lambda^2)$$

b. EIGENVECTOR CORRECTION

To find the first-order correction to the eigenvector, we must project the first-order equation above onto all the vectors of the $\{|\varphi_p^i\rangle\}$ basis other than $|\varphi_n\rangle$

$$\langle\varphi_p^i|(\hat{H}_0 - E_n^0)|1\rangle + \langle\varphi_p^i|(\hat{W} - \varepsilon_1)|\varphi_n\rangle = 0 \quad (p \neq n) \quad (5.24)$$

Since the eigenvectors of \hat{H}_0 associated with different eigenvalues are orthogonal $\varepsilon_1\langle\varphi_p^i|\varphi_n\rangle = 0$ and $\langle\varphi_p^i|\hat{H}_0 = \langle\varphi_p^i|E_p^0$, we get

$$(E_p^0 - E_n^0)\langle\varphi_p^i|1\rangle + \langle\varphi_p^i|\hat{W}|\varphi_n\rangle = 0 \quad (5.25)$$

and

$$\langle\varphi_p^i|1\rangle = \frac{1}{E_n^0 - E_p^0}\langle\varphi_p^i|\hat{W}|\varphi_n\rangle \quad (p \neq n) \quad (5.26)$$

and, since $\langle \varphi_n | 1 \rangle = \langle 0 | 1 \rangle = 0$, the first order correction to the eigenvector can be written as

$$|1\rangle = \sum_{p \neq n} \sum_i \frac{\langle \varphi_p^i | \hat{W} | \varphi_n \rangle}{E_n^0 - E_p^0} |\varphi_p^i\rangle \quad (5.27)$$

The expression for the eigenvector of the perturbed Hamiltonian to the first-order is thus

$$|\psi_n(\lambda)\rangle = |\varphi_n\rangle + \sum_{p \neq n} \sum_i \frac{\langle \varphi_p^i | W | \varphi_n \rangle}{E_n^0 - E_p^0} |\varphi_p^i\rangle + O(\lambda^2) \quad (5.28)$$

The perturbation W mixes the state $|\phi_n\rangle$ with the other eigenstates of \hat{H}_0 .

2. Second-order corrections

a. ENERGY CORRECTION

We proceed in a way similar to the previous case. We project the 2nd order equation obtained above onto $|\varphi_n\rangle$

$$\langle\varphi_n|(\hat{H}_0 - E_n^0)|2\rangle + \langle\varphi_n|(\hat{W} - \varepsilon_1)|1\rangle - \varepsilon_2\langle\varphi_n|\varphi_n\rangle = 0 \quad (5.29)$$

Since $|\varphi_n\rangle = |0\rangle$ is the eigenvector of \hat{H}_0 with the eigenvalue $\varepsilon_0 = E_n^0$, the first term is zero and the second order correction becomes

$$\varepsilon_2 = \langle\varphi_n|\hat{W}|1\rangle \quad (5.30)$$

With the expression for $|1\rangle$ obtained above we can write the second order correction to the energy eigenvalue as

$$\varepsilon_2 = \sum_{p \neq n} \sum_i \frac{|\langle \varphi_p^i | \hat{W} | \varphi_n \rangle|^2}{E_n^0 - E_p^0} \quad (5.31)$$

The 2nd order expression for the energy eigenvalue of the perturbed system becomes

$$E_n(\lambda) = E_n^0 + \langle \varphi_n | W | \varphi_n \rangle + \sum_{p \neq n} \sum_i \frac{|\langle \varphi_p^i | W | \varphi_n \rangle|^2}{E_n^0 - E_p^0} + O(\lambda^3) \quad (5.32)$$

b. EIGENVECTOR CORRECTION

The eigenvector corrections $|2\rangle$ can be obtained by projecting the equation

$$\left(\hat{H}_0 - \varepsilon_0\right)|2\rangle + \left(\hat{W} - \varepsilon_1\right)|1\rangle - \varepsilon_2|0\rangle = 0 \quad (5.33)$$

onto the set of basis vectors $|\phi_p^i\rangle$ different from $|\phi_n\rangle$ and by using the condition

$$\langle 0|2\rangle = \langle 2|0\rangle = -\frac{1}{2}\langle 1|1\rangle \quad (5.34)$$

c. UPPER LIMIT OF ε_2

What is the error involved in the 1st order perturbation theory?

Consider

$$\varepsilon_2 = \sum_{p \neq n} \sum_i \frac{|\langle \varphi_p^i | \hat{W} | \varphi_n \rangle|^2}{E_n^0 - E_p^0} \quad (5.35)$$

and let the absolute value of difference of E_n^0 being studied and that of the nearest level E_p^0 be

$$\left| E_n^0 - E_p^0 \right| \geq \Delta E \quad (5.36)$$

then an upper limit for the absolute value of ε_2 is

$$|\varepsilon_2| \leq \frac{1}{\Delta E} \sum_{p \neq n} \sum_i \left| \langle \varphi_p^i | \hat{W} | \varphi_n \rangle \right|^2 \quad (5.37)$$

$$|\varepsilon_2| \leq \frac{1}{\Delta E} \sum_{p \neq n} \sum_i \left| \langle \varphi_p^i | \hat{W} | \varphi_n \rangle \right|^2 \quad (5.38)$$

$$= \frac{1}{\Delta E} \sum_{p \neq n} \sum_i \langle \varphi_n | \hat{W} | \varphi_p^i \rangle \langle \varphi_p^i | \hat{W} | \varphi_n \rangle \quad (5.39)$$

$$= \frac{1}{\Delta E} \langle \varphi_n | \hat{W} \left[\sum_{p \neq n} \sum_i |\varphi_p^i \rangle \langle \varphi_p^i| \right] \hat{W} | \varphi_n \rangle \quad (5.40)$$

Taking into account the completeness relation

$$|\varphi_n \rangle \langle \varphi_n| + \sum_{p \neq n} \sum_i |\varphi_p^i \rangle \langle \varphi_p^i| = \hat{1} \quad (5.41)$$

allows us to rewrite the inequality as

$$|\varepsilon_2| \leq \frac{1}{\Delta E} \langle \varphi_n | \hat{W} [\hat{1} - |\varphi_n\rangle\langle\varphi_n|] \hat{W} | \varphi_n \rangle \quad (5.42)$$

$$\leq \frac{1}{\Delta E} \left[\langle \varphi_n | \hat{W}^2 | \varphi_n \rangle - \left(\langle \varphi_n | \hat{W} | \varphi_n \rangle \right)^2 \right] = \frac{1}{\Delta E} (\Delta \hat{W})^2 \quad (5.43)$$

An upper limit for the 2nd order term in $E_n(\lambda) = \varepsilon_0 + \lambda\varepsilon_1 + \lambda^2\varepsilon_2 + \dots$ is then

$$\left| \lambda^2 \varepsilon_2 \right| \leq \frac{1}{\Delta E} (\Delta W)^2 \quad (5.44)$$

This indicates the order of magnitude of the error committed by taking only the 1st order correction into account.

C. PERTURBATION OF A DEGENERATE STATE

Assume that the level E_n^0 to be g_n -fold degenerate, and \mathcal{E}_n^0 be the corresponding g_n -fold dimensional eigenspace of \hat{H}_0 .

Now the choice

$$\epsilon_0 = E_n^0 \quad (5.45)$$

is not sufficient to determine $|0\rangle$ since the equation $\hat{H}_0|0\rangle = \epsilon_0|0\rangle$ can be satisfied by any linear combination of vectors in \mathcal{E}_n^0 .

To determine $|0\rangle$ and ϵ_1 we project the 1st order equation

$$(\hat{H}_0 - \epsilon_0)|1\rangle + (\hat{W} - \epsilon_1)|0\rangle = 0 \quad (5.46)$$

onto the g_n basis vectors $|\phi_n^i\rangle$:

since $\hat{H}_0|\phi_n^i\rangle = \epsilon_0|\phi_n^i\rangle$ for all $|\phi_n^i\rangle$ we obtain the g_n relations:

$$\langle\phi_n^i|\hat{W}|0\rangle = \epsilon_1\langle\phi_n^i|0\rangle \quad (5.47)$$

Now using the completeness relation

$$\sum_p \sum_{i'} \langle\phi_n^i|\hat{W}|\phi_p^{i'}\rangle \langle\phi_p^{i'}|0\rangle = \epsilon_1\langle\phi_n^i|0\rangle \quad (5.48)$$

where $\langle\phi_p^{i'}|0\rangle = 0$ for all $p \neq n$.

Taking into account only the terms where $p = n$ we get

$$\sum_{i'=1}^{g_n} \langle \varphi_n^i | \hat{W} | \varphi_n^{i'} \rangle \langle \varphi_n^{i'} | 0 \rangle = \varepsilon_1 \langle \varphi_n^i | 0 \rangle \quad (5.49)$$

where the $g_n \times g_n$ matrix

$$\hat{W}^{(n)} = \langle \varphi_n^i | \hat{W} | \varphi_n^{i'} \rangle \quad (5.50)$$

is the restriction of \hat{W} to the eigenspace \mathcal{E}_n^0 .

We can rewrite the equation

$$\sum_{i'=1}^{g_n} \langle \varphi_n^i | \hat{W} | \varphi_n^{i'} \rangle \langle \varphi_n^{i'} | 0 \rangle = \varepsilon_1 \langle \varphi_n^i | 0 \rangle \quad (5.51)$$

into a vector equation

$$\hat{W}^{(n)} |0\rangle = \varepsilon_1 |0\rangle \quad (5.52)$$

To calculate the eigenvalues (to the 1st order) and the eigenstates (to the 0th order) of the Hamiltonian corresponding to a degenerate unperturbed state E_n^0 , we have to diagonalize the matrix $W^{(n)}$, which represents the perturbation \hat{W} inside the eigenspace \mathcal{E}_n^0 associated with the eigenvalue E_n^0 .

The first order effect of the perturbation is given by the various roots of the characteristic equation of $W^{(n)}$, $\epsilon_1^j (j = 1, 2, \dots, f_n^{(1)})$.

Since $W^{(n)}$ is self-adjoint, its eigenvalues are real numbers and their degrees of degeneracy sum to g_n .

Each eigenvalue introduces a different energy correction, i.e. under $W = \lambda \hat{W}$, the degenerate levels split to the 1st order into $f_n^{(1)}$ distinct sublevels

$$E_{n,j}(\lambda) = E_n^0 + \lambda \epsilon_1^j \quad j = 1, 2, \dots, f_n^{(1)} \leq g_n \quad (5.53)$$

We shall now choose an eigenvalue ϵ_1^j of $W^{(n)}$:

- if it is non-degenerate, the corresponding vector $|0\rangle$ is completely determined, i.e. there exists a single eigenvalue $E(\lambda)$ of $\hat{H}(\lambda)$ which is

$$E_n^0 + \lambda \epsilon_1^j \quad (5.54)$$

and is non-degenerate;

- if it is q -fold degenerate, the equation

$$W^{(n)}|0\rangle = \epsilon_1^j|0\rangle \quad (5.55)$$

indicates only that $|0\rangle$ belongs to the corresponding q -dimensional subspace $\mathcal{F}_j^{(1)}$.