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):

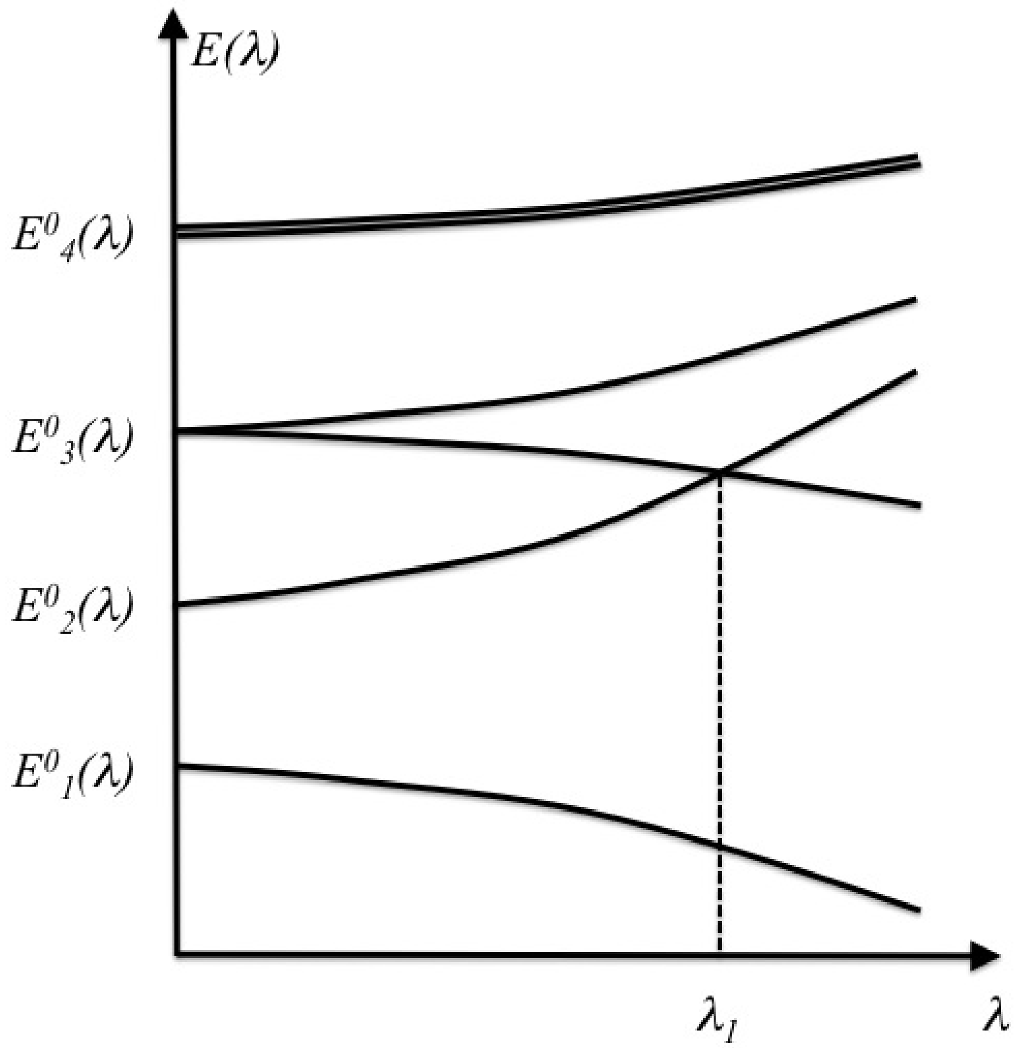
$$\hat{H}_0|\varphi_p^i\rangle = E_p^0|\varphi_p^i\rangle \tag{5.4}$$

where

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

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

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



$E(\lambda)$
$E^0{}_4(\lambda)$
$E^0{}_3(\lambda)$
$E^0{}_2(\lambda)$
$E^0{}_1(\lambda)$
λ_1
λ

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

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

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

$$E(\lambda) = \varepsilon_0 + \lambda\varepsilon_1 + \ldots + \lambda^q\varepsilon_q + \ldots \tag{5.8}$$

$$|\psi(\lambda)\rangle = |0\rangle + \lambda|1\rangle + \ldots + \lambda^q|q\rangle + \ldots \tag{5.9}$$

Inserting these into the eigenvalue equation yields

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

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, $\varepsilon_0 = E_n^0$

$$\hat{H}_0|0\rangle = \varepsilon_0|0\rangle \tag{5.11}$$

1st order:

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

2nd order

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

q-th order

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

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

$$\langle 0|0\rangle = 1 \tag{5.15}$$

and to the 1st order we get

$$\begin{aligned}\langle\psi(\lambda)|\psi(\lambda)\rangle &= [\langle 0| + \lambda\langle 1|]\,[|0\rangle + \lambda|1\rangle] + O\left(\lambda^2\right) &(5.16)\\ &= \langle 0|0\rangle + \lambda\,[\langle 1|0\rangle + \langle 0|1\rangle] + O\left(\lambda^2\right) &(5.17)\end{aligned}$$

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

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

For the 2nd order we get

$$\langle\psi(\lambda)|\psi(\lambda)\rangle = \langle 0|0\rangle + \lambda\left[\langle 1|0\rangle + \langle 0|1\rangle\right] + \lambda^2\left[\langle 2|0\rangle + \langle 0|2\rangle + \langle 1|1\rangle\right] + O\left(\lambda^3\right) \quad (5.19)$$

$$\Rightarrow \langle 0|2\rangle = \langle 2|0\rangle = -\frac{1}{2}\langle 1|1\rangle \quad (5.20)$$

and eventually for q-th order we have

$$\langle 0|q\rangle = \langle q|0\rangle = -\frac{1}{2}\left[\langle q-1|1\rangle + \langle q-2|2\rangle + \ldots + \langle 2|q-2\rangle + \langle 1|q-1\rangle\right] \quad (5.21)$$

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 $\lambda \to 0$ 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

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

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

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

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

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

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 $\left\{|\varphi_p^i\rangle\right\}$ basis other than $|\varphi_n\rangle$

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

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

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

and

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

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

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

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

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

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 $|\varphi_n\rangle$

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

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

$$\varepsilon_2 = \langle\varphi_n|\hat{W}|1\rangle \tag{5.30}$$

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

$$\varepsilon_2 = \sum_{p\neq n}\sum_{i}\frac{\left|\langle\varphi_p^i|\hat{W}|\varphi_n\rangle\right|^2}{E_n^0 - E_p^0} \tag{5.31}$$

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

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

b. EIGENVECTOR CORRECTION

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

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

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

$$\langle 0|2\rangle = \langle 2|0\rangle = -\frac{1}{2}\langle 1|1\rangle \tag{5.34}$$

c. UPPER LIMIT OF ε_2

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

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

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

$$\left|E_n^0 - E_p^0\right| \geq \Delta E \tag{5.36}$$

then an upper limit for the absolute value of ϵ_2 is

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

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

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

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

Taking into account the completeness relation

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

allows us to rewrite the inequality as

$$|\varepsilon_2| \leq \frac{1}{\Delta E}\langle\varphi_n|\hat{W}\left[\hat{1} - |\varphi_n\rangle\langle\varphi_n|\right]\hat{W}|\varphi_n\rangle \tag{5.42}$$

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

An upper limit for the 2nd order term in $E_n(\lambda) = \epsilon_0 + \lambda\epsilon_1 + \lambda^2\epsilon_2 + \ldots$ is then

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

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

$$\varepsilon_0 = E_n^0 \tag{5.45}$$

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

$$\left(\hat{H}_0 - \varepsilon_0\right)|1\rangle + \left(\hat{W} - \varepsilon_1\right)|0\rangle \quad = \quad 0 \tag{5.46}$$

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:

$$\langle\varphi_n^i|\hat{W}|0\rangle \quad = \quad \varepsilon_1\langle\varphi_n^i|0\rangle \tag{5.47}$$

Now using the completeness relation

$$\sum_p \sum_{i'} \langle\varphi_n^i|\hat{W}|\varphi_p^{i'}\rangle\langle\varphi_p^{i'}|0\rangle \quad = \quad \varepsilon_1\langle\varphi_n^i|0\rangle \tag{5.48}$$

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

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

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

where the $g_n \times g_n$ matrix

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

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

We can rewrite the equation

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

into a vector equation

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

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 $W^{(n)}$, $\epsilon_1^j (j = 1, 2, \ldots, f_n^{(1)})$.

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

$$E_{n,j}(\lambda) = E_n^0 + \lambda \varepsilon_1^j \qquad j = 1, 2, \ldots, f_n^{(1)} \leq g_n \tag{5.53}$$

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

$$E_n^0 + \lambda \varepsilon_1^j \tag{5.54}$$

and is non-degenerate;

- if it is q-fold degenerate, the equation

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

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