Notes of Quantum Mechanics

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Preface

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Chapter 1

Stationary perturbation theory

In real problems, the Hamiltonian are not that easy to solve analytically. In general, the equation is too complicated for us to be able to find its solutions in an analytic form.

There exists, however, **approximation methods** that enable us to obtain analytically approximate solutions of the basic eigenequation in certain cases. This technique is known as **stationary perturbation theory**.

In studying a phenomenon or a physical system, one begins by isolating the principal effects that are responsible for the main features of this phenomenon or this system. Once understood, one tries to explain the finer details by taking into account less important effects that were neglected in the first approximation. It is in treating these secondary effects that one commonly uses perturbation theory.

There is also another approximation method called the **variational method**.

1.1 Description of the method

1.1.1 Statement of the problem

Perturbation theory is applicable when the Hamiltonian H of the system being studied can be put in the form

$$\text{Hamiltonian of the system} \qquad H(\lambda) = H_0 + \underbrace{\lambda \hat{W}}_{W}, \quad \text{with} \quad \lambda \ll 1\,, \tag{1.1}$$

where the spectrum of H_0 is known, and where W is **much smaller** than H_0. This means that the matrix elements of W are much smaller than those of H_0. The operator H_0 is time-independent and is knwon as **unperturbed Hamiltonian**, while W is called the **perturbation**. When W is time-independent, we say we are dealing a *stationary perturbation*.

The problem then is to find the modifications produced in the enery levels of the system and its stationary states by the influence of W. Perturbation theory consists of expanding the eigenpairs of H in power of λ with a finite number of terms.

We assume the spectrum of H_0 is discrete, where eiganvalue E_p^0 and eigenstate $|\varphi_p^i\rangle$. We therefore have:

$$\text{Spectrum of } H_0 \qquad H_0|\varphi_p^i\rangle = E_p^0|\varphi_p^i\rangle, \quad \text{with} \quad \begin{array}{c}\langle\varphi_p^i|\varphi_p^i\rangle = \delta_{pp'}\delta_{ii'} \\ \displaystyle\sum_p \sum_i |\varphi_p^i\rangle\langle\varphi_p^i| = 1\end{array}\,. \tag{1.2}$$

Figure **??** represents possible forms of the variations of the eigenvalues $E(\lambda)$ of (1.1) with respect to λ. For a given value of λ, these vectors form a basis of the state space of $H(\lambda)$. The operator may have several degeneracies, as in E_3^0 and E_4^0. The perturbation is able to remove some degeneracies as for E_3^0.

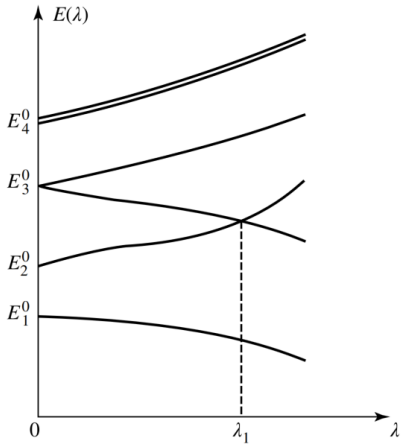

Figure 1.1 Variation of $E(\lambda)$ with respect to λ. For $\lambda = 0$, we obtain the spectrum of H_0. We see the two-fold of E_3^0 and E_4^0 where perturbation removes the degeneracy of E_3^0 but not that of E_4^0. Additional two-fold degeneracy appears at $\lambda = \lambda_1$.

1.1.2 Approximate solution of $H(\lambda)$

Lets define the eigenequation for the Hermitian operator $H(\lambda)$:

$$\text{Eigenequation of } H(\lambda) \qquad H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle\,. \tag{1.3}$$

We assume that $E(\lambda)$ and $|\psi(\lambda)\rangle$ can be expanded in powers of λ in the form:

$$E(\lambda) = \sum_{q=1}^{\infty} \lambda^q \varepsilon_q, \quad \text{and} \quad |\psi(\lambda)\rangle = \sum_{q=1}^{\infty} \lambda^q |q\rangle. \tag{1.4}$$

Substituting the above along with (1.1) in the eigenequation (1.3) yields

$$(H_0 + \lambda W) \left[\sum_{q=1}^{q} \lambda^q |q\rangle\right] = \left[\sum_{q'=1}^{q'} \lambda^{q'} \varepsilon_q\right] \left[\sum_{q=1}^{\infty} \lambda^q |q\rangle\right].$$

Equating the terms of the same power q:

$$\begin{aligned}
\text{0th-order}: &\quad H_0|0\rangle = \varepsilon_0|0\rangle && (1.5)\\
\text{1st-order}: &\quad (H_0 - \varepsilon_0)|1\rangle = (W - \varepsilon_1)|0\rangle = 0 && (1.6)\\
\text{2nd-order}: &\quad (H_0 - \varepsilon_0)|2\rangle + (W - \varepsilon_1)|1\rangle - \varepsilon_2|0\rangle = 0 && (1.7)\\
&\vdots\\
\text{qth-order}: &\quad (H_0 - \varepsilon_0)|q\rangle + (W - \varepsilon_1)|q-1\rangle - \varepsilon_2|q-2\rangle - \cdots - \varepsilon_q|0\rangle = 0 && (1.8)
\end{aligned}$$

We can choose the norm of $|\psi(\lambda)\rangle$ and its phase: we require it to be normalized, we choose its phase such that the scalar product $\langle 0|\psi(\lambda)\rangle$ is real. To 0th-order, this implies that the vector $|0\rangle$ must be normalized:

$$\langle 0|0\rangle = 1. \tag{1.9}$$

Its phase remain arbitrary, we will choose it after. To 1st order, the square of the nomro of $|\psi(\lambda)\rangle$ is written

$$\begin{aligned}
\langle\psi(\lambda)|\psi(\lambda)\rangle &= [\langle 0| + \lambda\langle 1|][|0\rangle + \lambda|1\rangle] + O(\lambda^2) && (1.10)\\
&= \langle 0|0\rangle + \lambda[\langle 1|0\rangle + \langle 0|1\rangle] + O(\lambda^2) && (1.11)\\
&= 1 + \lambda[\langle 1|0\rangle + \langle 0|1\rangle] + O(\lambda^2) = 1. && (1.12)
\end{aligned}$$

The choice of phase indicates that the scalar product $\langle 0|1\rangle$ is real since λ is real. Therefore,

$$\langle 0|1\rangle = \langle 1|0\rangle = 0. \tag{1.13}$$

Anologously,

$$\langle 0|2\rangle = \langle 2|0\rangle = -\frac{1}{2}\langle 1|1\rangle, \tag{1.14}$$

and in general:

$$\langle 0|q\rangle = \langle q|0\rangle = -\frac{1}{2}[\langle q-1|1\rangle + \langle q-2|2\rangle + \cdots + \langle 2|q-2\rangle + \langle 1|q-1\rangle]. \tag{1.15}$$

When we confine to second order in λ, the perturbation equations and the conditions, from above,

Second-order in λ

Equations	Conditions
$H_0\|0\rangle = \varepsilon_0\|0\rangle$	$\langle 0\|0\rangle = 1$
$(H_0 - \varepsilon_0)\|1\rangle = (W - \varepsilon_1)\|0\rangle = 0$	$\langle 0\|1\rangle = \langle 1\|0\rangle = 0$
$(H_0 - \varepsilon_0)\|2\rangle + (W - \varepsilon_1)\|1\rangle - \varepsilon_2\|0\rangle = 0$	$\langle 0\|2\rangle = \langle 2\|0\rangle = -\frac{1}{2}\langle 1\|1\rangle$

. (1.16)

From them, we now that $|0\rangle$ is an eigenvector of H_0 with eigenvalue ε_0, with the particular value E_n^0. Consider the set of eigenstates of $H(\lambda)$ corresponding to the various eigenvalues $E(\lambda)$ that approach E_n^0 when $\lambda \to 0$. They span a vector subspace whose dimension clearly cannot vary discontinuously when λ varies in the vecinity of zero. This dimension is consequently equal to the degeneracy g_n of E_n^0. We now consider the case of non-degenerae, and degenerate levels of H_0.

1.2 Perturbation of a non-degenerate case

Let be a non-denegerate eigenvalue E_n^0 of H_0, which is associated with the unique eigenvector $|\varphi_n\rangle$. We want to determine the modifications in this unperturbed energy in the corresponding statinary state produces by W.

For the eigenvalues of $H(\lambda)$ that approaches E_n^0 when $\lambda \to 0$ we ave

$$\varepsilon_0 = E_n^0 \Longrightarrow |0\rangle = |\varphi_n\rangle. \tag{1.17}$$

Thus, when $\lambda \to 0$ we again find the unperturbed state $|\varphi_n\rangle$ with the same phase. We call $E_n(\lambda)$ the eigenvalue of $H(\lambda)$ which when $\lambda \to 0$, approaches the eigenvalue E_n^0 of H_0, with eigenvector $|\psi_n(\lambda)\rangle$. We now compute the expansion of $E_n(\lambda)$ and $|\psi_n(\lambda)\rangle$ in powers of λ.

1.2.1 First-order corrections

We will determine the eigenvalue ε_1 and the eigenvector $|1\rangle$.

Energy correction

Projecting the first-order equation from (1.16) onto $|\varphi_n\rangle$ yields

$$\langle\varphi_n|(H_0-\varepsilon_0)|1\rangle + \langle\varphi_n|(W-\varepsilon_1)|0\rangle = \cancelto{0}{\langle\varphi_n|(\varepsilon_0-\varepsilon_0)|1\rangle} + \langle\varphi_n|(W-\varepsilon_1)|0\rangle = 0. \tag{1.18}$$

Considering equation (1.17), we have that:

$$\varepsilon_1 = \langle\varphi_n|W|0\rangle = \langle\varphi_n|W|\varphi_n\rangle. \tag{1.19}$$

The eigenvalue $E_n(\lambda)$ of H which corresponds to E_n^0 can be written, to first order in the perturbation as:

$$\text{First-order eigenvalue of } H \qquad E_n(\lambda) = E_n^0 + \langle\varphi_n|W|\varphi_n\rangle + O(\lambda^2)\,. \tag{1.20}$$

The first-order correction to a non-degenerate energy E_n^0 is simply equal to the averae value of the perturbation term W in the unperturbed state $|\varphi_n\rangle$.

Eigenvector correction

To exhaust all the information of the first-order perturbation equation (1.16), we must project it onto all the vectors of the $\{|\varphi_p^i\rangle\}$ basis other than $|\varphi_n\rangle$. Using (1.17):

$$\langle\varphi_p^i|(H_0-E_n^0)|1\rangle + \langle\varphi_p^i|(W-\cancelto{0}{\varepsilon_1})|\varphi_n\rangle = 0, \quad p \neq n \qquad \text{Orthogonality}$$
$$(E_p^0 - E_n^0)\langle\varphi_p^i|1\rangle + \langle\varphi_p^i|W|\varphi_n\rangle =$$

THe index i is for any possible degeneration in the energies E_p^0 other than E_n^0. This expression gives the coefficients of the desired expansion of the vector $|1\rangle$ on all the unperturbed basis states, except $|\varphi_n\rangle$:

$$\langle\varphi_p^i\rangle = \frac{1}{E_n^0 - E_p^0}\langle\varphi_p^i|W|\varphi_n\rangle, \quad p \neq n. \tag{1.21}$$

The las coefficient which we lack, $\langle\varphi_n|1\rangle = \langle 0|1\rangle$, is zero by the second condition of (1.16). We therefore know the vector $|1\rangle$ since we know its expansion on the $\{|\varphi_p^i\rangle\}$ basis:

$$|1\rangle = \sum_{p\neq n}\sum_i \frac{\langle\varphi_p^i|W|\varphi_n\rangle}{E_n^0 - E_p^0}|\varphi_p^i\rangle. \tag{1.22}$$

Thus, to first order in the perturbation, the eigenvector $|\varphi_n(\lambda)\rangle$ of H corresponding to the unperturbed state $|\varphi_n\rangle$ can be written as:

First-order eigenvector of H

$$|\psi_n(\lambda)\rangle = |\varphi_n\rangle + \sum_{p\neq n}\sum_i \frac{\langle\varphi_p^i|W|\varphi_n\rangle}{E_n^0 - E_p^0} + O(\lambda^2)\,. \tag{1.23}$$

It is a linear combination of all unperturbed states other than $|\varphi_n\rangle$: the perturbation W is said to produce a mixing of the state $|\varphi_n\rangle$ with the other iegenstates of H_0. The contribution of a given state $|\varphi_p^i\rangle$ is zero if the perturbation has no matrix element between $|\varphi_n\rangle$ and $|\varphi_p^i\rangle$.

First-order correction constraint

The first order correction of the state vector is small only if the non-diagonal matrix elements of W are much smaller than the corresponding unperturbed energy differences.

1.2.2 Second-order corrections

The process is analogous to the first-order, with the use of the second equation in (1.16).

Energy correction

We project second equation of (1.16) onto the vector $|\varphi_n\rangle$, using the conditions:

$$\langle\varphi_n|\cancelto{0}{(H_0 - E_n^0)}|2\rangle + \langle\varphi_n|(W - \cancelto{0}{\varepsilon_1})|1\rangle - \varepsilon_2\langle\varphi_n|\varphi_n\rangle = 0 \Longrightarrow \varepsilon_2 = \langle\varphi_n|W|1\rangle.$$

(0 Orthogonality; 0 Orhtogonality)

Using the expression for $|1\rangle$ from the first-order section, we have that:

$$\varepsilon_2 = \sum_{p\neq n}\sum_i \frac{|\langle\varphi_p^i|W|\varphi_n\rangle|^2}{E_n^0 - E_p^0}. \tag{1.24}$$

This enables us to write the energy $E_n(\lambda)$ to second order in the perturbation in the form:

Second-order eigenvalue of H

$$E_n(\lambda) = E_n^0 + \langle\varphi_n|W|\varphi_n\rangle + \sum_{p\neq n}\sum_i \frac{|\langle\varphi_p^i|W|\varphi_n\rangle|^2}{E_n^0 - E_p^0} + O(\lambda^3)\,. \tag{1.25}$$

To second-order, the closer the state $|\varphi_p^i\rangle$ to $|\varphi_n\rangle$, and th estronger the coupling $|\langle\varphi_p^i|W|\varphi_n\rangle|$, the more these two levels repel each other.

Eigenvector correction

By projecting the second equation (1.16) onto the set of basis vectors $|\varphi_p^i\rangle$ different from $|\varphi_n\rangle$, and by using conditions we can obtain the expression for the ket $|2\rangle$ and therefore the eigenvector to second order. It is not present in CT nor FG.

In general, we retain one more term in the energy expansion than in that of the eigenvector. This is because when projecting the second-order equation onto $|\varphi_n\rangle$, one makes the first term go to zero, which gives ε_q in terms of the corrections of order $q-1, q-2, \cdots$ of the eigenvector.

Upper limit of ε_2

If we limit the energy expansion to first order in λ, we can obtain an approximate idea of the error involver by evaluating the second-order term. We denote by $\Delta E =$ the absolute value of the difference between the energy E_n^0 of the level being studied and that of the closest level. We have:

$$\Delta E \leq |E_n^0 - E_p^0|, \quad \forall n. \tag{1.26}$$

This gives us an upper limit for the absolute value of ε_2:

$$\begin{aligned}
|\varepsilon_2| \leq & \frac{1}{\Delta E} \sum_{p\neq n} \sum_i |\langle \varphi_p^i | W | \varphi_n \rangle|^2 \\
= & \frac{1}{\Delta E} \sum_{p\neq n} \sum_i \langle \varphi_n | W | \varphi_p^i \rangle \langle \varphi_p^i | W | \varphi_n \rangle \\
= & \frac{1}{\Delta E} \langle \varphi_n | W \left[\sum_{p\neq n} \sum_i |\varphi_p^i\rangle\langle\varphi_p^i| \right] W | \varphi_n \rangle \\
\overset{(a)}{=} & \frac{1}{\Delta E} \langle \varphi_n | W \big[1 - |\varphi_n\rangle\langle\varphi_n| \big] W | \varphi_n \rangle \\
= & \frac{1}{\Delta E} \left[\langle \varphi_n | W^2 | \varphi_n \rangle - (\langle \varphi_n | W | \varphi_n \rangle)^2 \right]
\end{aligned}$$

In (a), we have used the fact that inside the brakets, we have the projector onto the basis $\{|\varphi_p^i\rangle\}$ minus a single elements $|\varphi_n\rangle$.

Finally, we multiply both sides by λ^2 to obtain an upper limit for the second-order term in the expansin of $E_n(\lambda)$, in the form:

$$\text{Upper limit for second-order term in } E_n(\lambda) \qquad \boxed{|\lambda^2 \varepsilon_2| \leq \frac{1}{\Delta E} (\Delta W)^2}. \tag{1.27}$$

This indicates the order of magnitude of the error on the energy resulting from taking only the first-order correction into account.

1.3 Perturbation of a degenerate level

Now assume that the level E_n^0 whose perturbatino we want to study is g_n-degenerate, with $\mathscr{E}_n^0$ the eigen-subspace of H_0. In this case, the choice $\varepsilon_0 = E_n^0$ does not suffice to determine the vector $|0\rangle$, since the 0th-order equation (1.16) can be satisfied by any linear combinarion of the g_n vectors $|\varphi_n^i\rangle$.

Under the action of W, the level E_n^0 generally gives rise to several distinct **sublevels** $f_n \in [0, g_n]$. If $f_n < g_n$, some of these sublevels are degenerate, since the total number of orthogonal eigenvectors of H associated with the f_n sublevels is always equal to g_n.

To determine ε_1 and $|0\rangle$, we project 1st-order equation (1.16) onto the g_n basis vectors $|\varphi_n^i\rangle$. Since these are eigenvectors of H_0 with eigenvalue $\varepsilon_0 = E_n^0$, we obtain

$$\varepsilon_1\langle\varphi_n^i|0\rangle = \langle\varphi_n^i|W|0\rangle = \sum_p \sum_{i'} \langle\varphi_n^i|W|\varphi_p^{i'}\rangle\langle\varphi_p^{i'}|0\rangle \overset{(a)}{=} \sum_{i'=1}^{g_n} \langle\varphi_n^i|W|\varphi_n^{i'}\rangle\langle\varphi_n^{i'}|0\rangle.$$

In (a), the vector $|0\rangle$ belongs to the eigensubspace with E_n^0, is orthogonal to all the basis vectors $|\varphi_p^{i'}\rangle,\ p \neq n$; it only produces a single term for $p = n$.

We arrange the g_n^2 numbers $\langle\varphi_n^i|W|\varphi_n^{i'}\rangle$ (n fixed, $i, i' = 1, \cdots, g_n$) in a $g_n \times g_n$ matrix of row index i and collumn index i'. This matrix is denoted by W^n and is the part which corresponds to $\mathscr{E}_n^0$. The column vector of elements $\langle\varphi_n^i|0\rangle$ is an eigenvector of W^n with the eigenvalue ε_1.

This equation can also be transformed into a vector equation inside $\mathscr{E}_n^0$. The equivalent vector equation is then:

$$\text{Eigenequation of } W^{(n)} \text{ (in } \mathscr{E}_n^0) \qquad \boxed{W^{(n)}|0\rangle = \varepsilon_1|0\rangle}\,. \tag{1.28}$$

To calculate the eigenvalues (to first order) and the eigenstates (to zeroth order) of the Hamiltonian corresponding to a degenerate uperturbed state E_n^0, diagonalize the matrix W^n, which represents the perturbation W inside the eigensubspace $\mathscr{E}_n^0$ associated with E_n^0.

Let $\varepsilon_1^j,\ j = 1, \cdots, f_n^{(1)}$ be the various distinct roots of the characteristic equation of $W^{(n)}$. Since $W^{(n)}$ is Hermitian, its eigenvalues are all real, and the sum of their degree of degeneracy is equal to g_n ($f_n^{(1)} \leq g_n$). Each eigenvalue introduces a different energy correction. Therefore, under W, the degeneracy level splits, to first order, into $f_n^{(1)}$ distintc sublevels, whose energies can be written as:

$$\text{First-order eigenvalue of } W^{(n)} \qquad \boxed{E_{n,j}(\lambda) = E_n^0 + \lambda\varepsilon_j^i, \quad j = 1, \cdots, f_n^{(1)} \leq g_n}\,. \tag{1.29}$$

If $f_n^{(1)} = g_n$, we say that, to first order, W completely removes the degeneracy of the level E_n^0. When $f_n^{(1)} < g_n$, the degeneracy, to first order, is only partially removed (or not at all if $f_n^{(1)} = 1$).

We now choose ε_1^j of $W^{(n)}$. If it is non-degenerate, the corresponding $|0\rangle$ is uniquely determined by (1.28). There then exist a single eigenvalue $E(\lambda)$ of $H(\lambda)$ which is equal to $E_n^0 + \lambda\varepsilon_1^j$, to first order, and this eigenvalue is non-degenerate. On the other hand, if ε_1^j is q-degenerate, (1.28) indicates that only that $|0\rangle$ belongs to the corresponding q-dimensional subspace $\mathcal{F}_j^{(1)}$.

This property of ε_1^j can reflect two different situations:

- There is only one exact energy $E(\lambda)$ that is equal, to first order, to $E_n^0 + \lambda\varepsilon_1^j$, and that this energy is q-degenerate. A q-dimensional eigensubspace then corresponds to the eigenvalue $E(\lambda)$, so that the degeneracy of the approximate eigenvalues will never be removes, to any order of λ.

  This often arises when H_0 and W possess common symmetry properties. The degeneracy then remains to all order in the perturbation theory.

- Several different energies $E(\lambda)$ are equal, to first order, to $E_n^0 + \lambda\varepsilon_1^j$. The subspace $\mathcal{F}_j^{(1)}$ obtained to first order is only the direct sum of the limits, for $\lambda \to 0$, of several eigensubspaces associated with these various energies $E(\lambda)$. That is, all the eigenvectors of $H(\lambda)$ corresponding to these energies

certainly approach kets of $\mathcal{F}_j^{(1)}$, but, inversely, a particular ket of $\mathcal{F}_j^{(1)}$ is not necessarily the limits $|0\rangle$ of an eigenket of $H(\lambda)$. Going to higher order terms allows one, not only to improve the accuracy of the energies, but also to determine the zeroth-order kets $|0\rangle$.

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