Chapter 6, Time-independent perturbation Theory

1. Nondegenerate perturbation theory

To solve $H\Psi = E\Psi$

but $H = H^0 + H'$

suppose we know how to solve H^0, and H' is small,

we want to obtain approximate solution of $H\Psi = E\Psi$

Let $H = H^0 + \lambda H'$

Assume we know

$$H^0 \varphi_n^0 = E_n^0 \varphi_n^0$$

Write $H\varphi_n = E_n \varphi_n$

Expand
$$\varphi_n = \varphi_n^0 + \lambda \varphi_n^1 + \lambda^2 \varphi_n^2 + \cdots$$
$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$$

plug in

$$(H^0 + \lambda H')(\varphi_n^0 + \lambda \varphi_n^1 + \lambda^2 \varphi_n^2 + \cdots)$$
$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)(\varphi_n^0 + \lambda \varphi_n^1 + \lambda^2 \varphi_n^2 + \cdots)$$

collecting terms of different orders in λ

λ^0
$$H^0 \varphi_n^0 = E_n^0 \varphi_n^0 \qquad (1)$$

λ^1
$$H^0 \varphi_n^1 + H' \varphi_n^0 = E_n^0 \varphi_n^1 + E_n^1 \varphi_n^0 \qquad (2)$$

λ^2
$$H^0 \varphi_n^2 + H' \varphi_n^1 = E_n^0 \varphi_n^2 + E_n^1 \varphi_n^1 + E_n^2 \varphi_n^0 \qquad (3)$$

Note that $\{\varphi_n^\circ\}$ orthonormal

and that it is not degenerate.

From (2), take $\langle \varphi_n^\circ |$ on both sides

$$\underbrace{\langle \varphi_n^\circ | H^\circ | \varphi_n^1 \rangle}_{E_n^\circ \langle \varphi_n^\circ | \varphi_n^1 \rangle} + \langle \varphi_n^\circ | H' | \varphi_n^\circ \rangle = E_n^\circ \langle \varphi_n^\circ | \varphi_n^1 \rangle + E_n^1$$

cancell

Thus
$$\boxed{E_n^1 = \langle \varphi_n^\circ | H' | \varphi_n^\circ \rangle} \qquad (4)$$

1st order perturbation to the energy E_n°

Note: To calculate 1st order correction to energy, we need only φ_n°.

From (2), we solve

$$(H^\circ - E_n^\circ)\varphi_n^1 = -(H' - E_n^1)\varphi_n^\circ$$

Note that we can expand φ_n^1 in the basis of $\{\varphi_n^\circ\}$

$$\varphi_n^1 = \sum_{m \neq n} c_m \varphi_m^\circ$$

$m = n$ is excluded

$$(H^\circ - E_n^\circ) \sum_{m \neq n} c_m \varphi_m^\circ = -(H' - E_n^1)\varphi_n^\circ$$

Take $\langle \varphi_m^\circ |$ from the left $(m \neq n)$

$$(E_m^\circ - E_n^\circ) c_m = -\langle \varphi_m^\circ | H' | \varphi_n^\circ \rangle$$

$$c_m = \frac{\langle \varphi_m^\circ | H' | \varphi_n^\circ \rangle}{E_n^\circ - E_m^\circ}$$

or
$$\boxed{\varphi_n^1 = \sum_{m \neq n} \frac{|\varphi_m^\circ\rangle \langle \varphi_m^\circ | H' | \varphi_n^\circ \rangle}{E_n^\circ - E_m^\circ}} \qquad (5)$$

1st order correction to the wavefunction

2nd-order correction of energy.

From Eq. (3)

$$\cancel{\langle \varphi_n^0 | H^0 | \varphi_n^2 \rangle} + \langle \varphi_n^0 | H' | \varphi_n^1 \rangle = \cancel{E_n^0 \langle \varphi_n^0 | \varphi_n^2 \rangle} + E_n^1 \underbrace{\langle \varphi_n^0 | \varphi_n^1 \rangle}_{0} + E_n^2$$

Since $\quad |\varphi_n^1\rangle = \sum_{m \neq n} c_m |\varphi_m^0\rangle$

Note that $\quad \langle \varphi_n^0 | \varphi_n^1 \rangle = 0$ from the eq. above

Thus

$$E_n^2 = \langle \varphi_n^0 | H' | \varphi_n^1 \rangle$$

$$= \langle \varphi_n^0 | H' | \sum_{m \neq n} \frac{|\varphi_m^0\rangle \langle \varphi_m^0 | H' | \varphi_n^0 \rangle}{E_n^0 - E_m^0} \rangle$$

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \varphi_m^0 | H' | \varphi_n^0 \rangle|^2}{E_n^0 - E_m^0}} \qquad (6)$$

↑

2nd order correction to energy

General comments:

(1) No need to go to E_n^2 if E_n^1 is not zero. In other words, you need to calculate only the first nonzero term.

(2) The calculation of E_n^2 is not trivial since you need to sum over <u>all</u> the states (except $m=n$) in the Hilbert space.

(3) Many matrix elements need to be evaluated.

2. Degenerate perturbation Theory

For simplicity, consider the case that H^0 has two-fold degeneracy.

$$H^\circ \varphi_1^\circ = E^\circ \varphi_1^\circ$$

$$H^\circ \varphi_2^\circ = E^\circ \varphi_2^\circ$$

We can assume $\langle \varphi_1^\circ | \varphi_2^\circ \rangle = 0$

We look for solutions

$$H \Psi = E \Psi$$

where $H = H^\circ + H'$

We will look for

$$\Psi = a \varphi_1^\circ + b \varphi_2^\circ + \cdots$$

but neglecting the other terms that are not degenerate with E°.

From $(H^\circ + H')(a\varphi_1^\circ + b\varphi_2^\circ) = E\,(a\varphi_1^\circ + b\varphi_2^\circ)$

$$a\, H^\circ\varphi_1^\circ + b\, H^\circ\varphi_2^\circ + a\, H'\varphi_1^\circ + b\, H'\varphi_2^\circ = aE\,\varphi_1^\circ + bE\,\varphi_2^\circ$$

$\langle \varphi_1^\circ |$ $\quad a E^\circ + b E^\circ \underbrace{\langle \varphi_1^\circ | \varphi_2^\circ \rangle}_{0} + a\, H'_{11} + b\, H'_{12} = aE + bE\,\cancel{\langle \varphi_1^\circ | \varphi_2^\circ \rangle}_{0}$

or

$$a(E^\circ - E) + a\, H'_{11} + b\, H'_{12} = 0 \qquad (7)$$

$\langle \varphi_2^0 |$ $\quad b E^0 + a H'_{21} + b H'_{22} = E b \quad (8)$

Solve (7) and (8)

$$\begin{pmatrix} E^0 + H'_{11} - E & H'_{12} \\ H'_{21} & E^0 + H'_{22} - E \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0$$

This is an eigenvalue equation which can be solved by diagonalization.

We can write

$$E = E^0 + E'$$

then the eq. for E' is

$$\det \begin{pmatrix} H'_{11} - E^1 & H'_{12} \\ H'_{21} & H'_{22} - E^1 \end{pmatrix} = 0$$

Note $H'_{ij} = H_{ji}$ since H' is Hermitian

We can generalize to n-fold degenerate systems.

The first-order wavefunctions are obtained by solving a and b.

Applications and examples:— procedure

(1) Identify H^0 and H'

(2) solve eigenstates of H^0 needed

(3) calculate the matrix elements
→ use symmetry conditions

(4) ~~Ba~~ finish the calulation.