Chapter 41 Perturbation theory: time independent case

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41.1 Perturbation theory-nondegenerate case

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1$$

where $\hat{H}_0$ is an unperturbed Hamiltonian and $\hat{H}_1$ is the perturbation.

Approximate solution of the $\hat{H}(\lambda)$ eigenvalue equation (non-degenerate case):

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

We assume that

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + ...$$

We get

$$(\hat{H}_0 + \lambda\hat{H}_1)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + ...)$$

$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + ...)$$

For the 0-th order terms in λ,

$$(\hat{H}_0 - E_n^{(0)})|\psi_n^{(0)}\rangle = 0,$$

For the 1st-order terms in λ,

$$(\hat{H}_0 - E_n^{(0)})|\psi_n^{(1)}\rangle + (\hat{H}_1 - E_n^{(1)})|\psi_n^{(0)}\rangle = 0, \quad (1)$$

For the 2nd-order terms in λ,

$$(\hat{H}_0 - E_n^{(0)})|\psi_n^{(2)}\rangle + (\hat{H}_1 - E_n^{(1)})|\psi_n^{(1)}\rangle - E_n^{(2)}|\psi_n^{(0)}\rangle = 0, \quad (2)$$

For the 3rd-order terms in λ,

$$(\hat{H}_0 - E_n^{(0)})\left|\psi_n^{(3)}\right\rangle + (\hat{H}_1 - E_n^{(1)})\left|\psi_n^{(2)}\right\rangle - E_n^{(2)}\left|\psi_n^{(1)}\right\rangle - E_n^{(3)}\left|\psi_n^{(0)}\right\rangle = 0$$

((**Mathematica**))

Perturbation (theory : case nondegenerate)

```
eq1 = (H0 + λ H1) (Sum[λ^q ψn[q], {q, 0, 10}]) - (Sum[λ^q En[q], {q, 0, 10}]) ((Sum[λ^q ψn[q], {q, 0, 10}])); eq2 = Expand[eq1, λ];
eq1 = Table[{n, Coefficient[eq2, λ, n]}, {n, 0, 4}] // Simplify;
eq1 // TableForm
0  (H0 - En[0]) ψn[0]
1  H1 ψn[0] - En[1] ψn[0] + (H0 - En[0]) ψn[1]
2  -En[2] ψn[0] + H1 ψn[1] - En[1] ψn[1] + H0 ψn[2] - En[0] ψn[2]
3  -En[3] ψn[0] - En[2] ψn[1] + H1 ψn[2] - En[1] ψn[2] + H0 ψn[3] - En[0] ψn[3]
4  -En[4] ψn[0] - En[3] ψn[1] - En[2] ψn[2] + H1 ψn[3] - En[1] ψn[3] + H0 ψn[4] - En[0] ψn[4]
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41.2 The first-order energy shift

$\left|\psi_n^{(0)}\right\rangle$ forms the complete set. We star with Eq.(1) and take the inner product with $\left\langle\psi_n^{(0)}\right|$

$$\left\langle\psi_n^{(0)}\right|(\hat{H}_0 - E_n^{(0)})\left|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^{(0)}\right|(\hat{H}_1 - E_n^{(1)})\left|\psi_n^{(0)}\right\rangle = 0$$

or

$$E_n^{(1)} = \left\langle\psi_n^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle$$

The first-order correction of Eq.(1) with $\left\langle\psi_k^{(0)}\right|$ for $k \neq n$.

$$\left\langle\psi_k^{(0)}\right|\hat{H}_0 - E_n^{(0)}\left|\psi_n^{(1)}\right\rangle + \left\langle\psi_k^{(0)}\right|\hat{H}_1 - E_n^{(1)}\left|\psi_n^{(0)}\right\rangle = 0$$

or

$$(E_k^{(0)} - E_n^{(0)})\left\langle\psi_k^{(0)}\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_k^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle = 0 \text{ for } k \neq n.$$

or

$$\left\langle\psi_k^{(0)}\middle|\psi_n^{(1)}\right\rangle = \frac{\left\langle\psi_k^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle}{(E_n^{(0)} - E_k^{(0)})}$$

If we use the basis states $\left|\psi_k^{(0)}\right\rangle$ to express $\left|\psi_n^{(1)}\right\rangle$ as

$$\left|\psi_n^{(1)}\right\rangle = \sum_k \left|\psi_k^{(0)}\right\rangle\left\langle\psi_k^{(0)}\middle|\psi_n^{(1)}\right\rangle \qquad \text{(closure relation)}$$

or

$$\left|\psi_n^{(1)}\right\rangle = \left|\psi_n^{(0)}\right\rangle\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle + \sum_{k\neq n}\left|\psi_k^{(0)}\right\rangle\left\langle\psi_k^{(0)}\middle|\psi_n^{(1)}\right\rangle$$

What about $\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle$?

Normalization:

$$1 = \left\langle\psi_n\middle|\psi_n\right\rangle = \left\langle\psi_n^{(0)}\middle|\psi_n^{(0)}\right\rangle + \lambda\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle + \lambda\left\langle\psi_n^{(1)}\middle|\psi_n^{(0)}\right\rangle +$$

$$+\lambda^2(\left\langle\psi_n^{(2)}\middle|\psi_n^{(0)}\right\rangle + \left\langle\psi_n^{(1)}\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^{(0)}\middle|\psi_n^{(2)}\right\rangle) + ...$$

Since $\left\langle\psi_n^{(0)}\middle|\psi_n^{(0)}\right\rangle = 1$, through first order in λ, we must have

$$\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^{(1)}\middle|\psi_n^{(0)}\right\rangle = 0$$

or

$$\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle^* = 2\,\mathrm{Re}[\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle] = 0$$

or

$$\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle = ia \quad (a\text{: real})$$

which means that

$$\left|\psi_n^{(1)}\right\rangle = ia\left|\psi_n^{(0)}\right\rangle + \left|\varphi_n^{(1)}\right\rangle$$

where

$$\left\langle\psi_n^{(0)}\middle|\varphi_n^{(1)}\right\rangle = ia$$

Then

$$\left|\psi_n\right\rangle = \left|\psi_n^{(0)}\right\rangle + ia\lambda\left|\psi_n^{(0)}\right\rangle + \lambda\left|\varphi_n^{(1)}\right\rangle + ...$$
$$= (1 + ia\lambda)\left|\psi_n^{(0)}\right\rangle + \lambda\left|\varphi_n^{(1)}\right\rangle + ...$$
$$= e^{ia\lambda}\left|\psi_n^{(0)}\right\rangle + \lambda\left|\varphi_n^{(1)}\right\rangle + ...$$

where we use

$$e^{ia\lambda} = 1 + ia\lambda + ... \cong 1 + ia\lambda \qquad \text{for } |a\lambda| << 1.$$

We assume that $a = 0$:

$$\left\langle\psi_n^{(0)}\middle|\varphi_n^{(1)}\right\rangle = 0$$

Then we have

$$\left|\psi_n^{(1)}\right\rangle = \left|\varphi_n^{(1)}\right\rangle$$

or

$$\left|\psi_n^{(1)}\right\rangle = \sum_{k\neq n}\left|\psi_k^{(0)}\right\rangle\left\langle\psi_k^{(0)}\middle|\psi_n^{(1)}\right\rangle = \sum_{k\neq n}\left|\psi_k^{(0)}\right\rangle\frac{\left\langle\psi_k^{(0)}\middle|\hat{H}_1\middle|\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_k^{(0)}}$$

In summary

$$E_n = E_n^{(0)} + \lambda\left\langle\psi_n^{(0)}\middle|\hat{H}_1\middle|\psi_n^{(0)}\right\rangle$$

$$\left|\psi_n\right\rangle = \left|\psi_n^{(0)}\right\rangle + \lambda\sum_{k\neq n}\left|\psi_k^{(0)}\right\rangle\frac{\left\langle\psi_k^{(0)}\middle|\hat{H}_1\middle|\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_k^{(0)}}$$

41.3 The second-order energy shift

We take the inner product of Eq.(2) with the bra $\left\langle\psi_n^{(0)}\right|$

$$\left\langle\psi_n^{(0)}\middle|\hat{H}_0 - E_n^{(0)}\middle|\psi_n^{(2)}\right\rangle + \left\langle\psi_n^{(0)}\middle|\hat{H}_1 - E_n^{(1)}\middle|\psi_n^{(1)}\right\rangle - E_n^{(2)} = 0$$

or

$$
\begin{aligned}
E_n^{(2)} &= \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(1)} \rangle \\
&= \langle \psi_n^{(0)} | \hat{H}_1 \sum_{k\neq n} | \psi_k^{(0)} \rangle \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} \\
&= \sum_{k\neq n} \frac{\langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} \\
&= \sum_{k\neq n} \frac{\left| \langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \right|^2}{(E_n^{(0)} - E_k^{(0)})}
\end{aligned}
$$

In summary

$$
E_n^{(2)} = \sum_{k\neq n} \frac{\left| \langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} = \sum_{k\neq n} \frac{\langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}
$$

The first-order correction of Eq.(2) with $\langle \psi_k^{(0)} |$ for $k \neq n$.

$$
\langle \psi_k^{(0)} | (\hat{H}_0 - E_n^{(0)}) | \psi_n^{(2)} \rangle + \langle \psi_k^{(0)} | (\hat{H}_1 - E_n^{(1)}) | \psi_n^{(1)} \rangle - E_n^{(2)} \langle \psi_k^{(0)} | \psi_n^{(0)} \rangle = 0
$$

$$
\langle \psi_k^{(0)} | \psi_n^{(2)} \rangle = -\frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(1)} \rangle}{E_k^{(0)} - E_n^{(0)}}
$$

$$
| \psi_n^{(2)} \rangle = \sum_{k\neq n} | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \psi_n^{(2)} \rangle = -\sum_{k\neq n} | \psi_k^{(0)} \rangle \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(1)} \rangle}{E_k^{(0)} - E_n^{(0)}}
$$

$$
| \psi_n^{(1)} \rangle = \sum_{l\neq n} | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | \psi_n^{(1)} \rangle = \sum_{l\neq n} | \psi_l^{(0)} \rangle \frac{\langle \psi_l^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_l^{(0)}}
$$

Thus we have

$$
| \psi_n^{(2)} \rangle = \sum_{l\neq n} \sum_{k\neq n} | \psi_k^{(0)} \rangle \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})}
$$

41.4 Example-1: simple harmonics

$$\hat{H}_0 = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega_0{}^2\hat{x}^2, \qquad \hat{H}_1 = \frac{1}{2}\varepsilon m\omega_0{}^2\hat{x}^2 = \frac{\varepsilon}{4}\hbar\omega_0(\hat{a}+\hat{a}^+)^2$$

$$\hat{H}_0|n\rangle = E_n{}^{(0)}|n\rangle$$

with

$$E_n{}^{(0)} = (n+\frac{1}{2})\hbar\omega_0$$

$$\hat{H}_1|n\rangle = \frac{1}{4}\varepsilon\hbar\omega_0[\sqrt{n(n-1)}|n-2\rangle + (2n+1)|n\rangle + \sqrt{(n+1)(n+2)}|n+2\rangle]$$

$$\langle n+2|\hat{H}_1|n\rangle = \frac{1}{4}\varepsilon\hbar\omega_0\sqrt{(n+1)(n+2)}$$

$$\langle n|\hat{H}_1|n\rangle = \frac{1}{2}\varepsilon\hbar\omega_0(n+\frac{1}{2})$$

$$\langle n-2|\hat{H}_1|n\rangle = \frac{1}{4}\varepsilon\hbar\omega_0\sqrt{n(n-1)}$$

Then

$$E_n = E_n{}^{(0)} + \langle n|\hat{H}_1|n\rangle + \sum_{k\neq n}\frac{\left|\langle n|\hat{H}_1|k\rangle\right|^2}{E_n{}^{(0)} - E_k{}^{(0)}} + ...$$

or

$$E_n = E_n{}^{(0)} + \langle n|\hat{H}_1|n\rangle + \frac{\left|\langle n|\hat{H}_1|n-2\rangle\right|^2}{E_n{}^{(0)} - E_{n-2}{}^{(0)}} + \frac{\left|\langle n|\hat{H}_1|n+2\rangle\right|^2}{E_n{}^{(0)} - E_{n+2}{}^{(0)}}$$

or

$$E_n = E_n{}^{(0)} + \frac{1}{2}\varepsilon\hbar\omega_0(n+\frac{1}{2}) + \frac{\varepsilon^2\hbar\omega_0}{32}[n(n-1)-(n+1)(n+2)]$$

or

$$E_n = \hbar\omega_0(n+\frac{1}{2})(1+\frac{1}{2}\varepsilon - \frac{1}{8}\varepsilon^2 + ...)$$

((**Note**))

$$\hat{\pi}|n\rangle = (-1)^n |n\rangle$$

Since

$$\hat{\pi}\hat{x}\hat{\pi} = -\hat{x} \text{: odd parity}$$

$$\hat{\pi}\hat{x}^2\hat{\pi} = \hat{\pi}\hat{x}\hat{\pi}\hat{\pi}\hat{x}\hat{\pi} = \hat{x}^2 \text{: even parity}$$

Here

$$\hat{\pi}^2 = 1, \qquad \hat{\pi}^+ = \hat{\pi}$$

$\langle n|\hat{x}^2|m\rangle \neq 0$ for both n and m being odd and for both n and m being even.

When n is fixed, m should be $m = n$ and $m = n \pm 2$.

((**Note**)) Exact solution

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega_0{}^2(1+\varepsilon)\hat{x}^2$$

Then we have

$$E_n = \hbar\omega_0\sqrt{1+\varepsilon}(n+\frac{1}{2}) = E_n{}^{(0)}\sqrt{1+\varepsilon}$$
$$= E_n{}^{(0)}(1+\frac{1}{2}\varepsilon - \frac{1}{8}\varepsilon^2 + \frac{1}{16}\varepsilon^3 - \frac{5}{128}\varepsilon^4 + \frac{7}{256}\varepsilon^5 + ...)$$

41.5 Example-2: anharmonic oscillator

We calculate the eigenstates of the anharmonic oscillator whose Hamiltonian is given by

$$\hat{H}_0 = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega_0{}^2\hat{x}^2,$$

$$\hat{H}_1 = K\hat{x}^4 = \frac{K}{4\beta^4}(\hat{a} + \hat{a}^+)^4$$

$$\hat{H}_0|n\rangle = E_n{}^{(0)}|n\rangle$$

with

$$E_n^{(0)} = (n+\frac{1}{2})\hbar\omega_0$$

$$\hat{H}_1|n\rangle = \frac{K}{4\beta^4}[\sqrt{n(n-1)(n-2)(n-3}|n-4\rangle + 2(2n-1)\sqrt{n(n-1)}|n-2\rangle$$
$$+3(1+2n+2n^2)|n\rangle + (6+4n)\sqrt{(n+2)(n+1)}|n+2\rangle$$
$$+\sqrt{(n+4)(n+3)(n+2)(n+1)}|n+4\rangle]$$

$$E_n = E_n^{(0)} + \langle n|\hat{H}_1|n\rangle + \sum_{k\neq n}\frac{|\langle n|\hat{H}_1|k\rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

or

$$E_n = E_n^{(0)} + \langle n|\hat{H}_1|n\rangle + \sum_{k\neq n}\frac{|\langle k|\hat{H}_1|n\rangle|^2}{\hbar\omega_0(n-k)}$$

$$= E_n^{(0)} + \langle n|\hat{H}_1|n\rangle$$
$$+\frac{1}{\hbar\omega_0}\left[\frac{|\langle n-4|\hat{H}_1|n\rangle|^2}{[n-(n-4)]} + \frac{|\langle n-2|\hat{H}_1|n\rangle|^2}{[n-(n-2)]} + \frac{|\langle n+2|\hat{H}_1|n\rangle|^2}{[n-(n+2)]} + \frac{|\langle n+4|\hat{H}_1|n\rangle|^2}{[n-(n+4)]}\right]$$

$$= E_n^{(0)} + \langle n|\hat{H}_1|n\rangle$$
$$+\frac{1}{\hbar\omega_0}\left[\frac{|\langle n-4|\hat{H}_1|n\rangle|^2}{4} + \frac{|\langle n-2|\hat{H}_1|n\rangle|^2}{2} - \frac{|\langle n+2|\hat{H}_1|n\rangle|^2}{2} - \frac{|\langle n+4|\hat{H}_1|n\rangle|^2}{4}\right]$$

where

$$\langle n|\hat{H}_1|n\rangle = \frac{K}{4\beta^4}(6n^2+6n+3)$$

$$|\langle n-4|\hat{H}_1|n\rangle|^2 = (\frac{K}{4\beta^4})^2 n(n-1)(n-2)(n-3)$$

$$|\langle n-2|\hat{H}_1|n\rangle|^2 = (\frac{K}{4\beta^4})^2[4(2n-1)^2 n(n-1)]$$

$$\left|\langle n+2|\hat{H}_1|n\rangle\right|^2 = (\frac{K}{4\beta^4})^2(6+4n)^2(n+2)(n+1)$$

$$\left|\langle n-4|\hat{H}_1|n\rangle\right|^2 = (\frac{K}{4\beta^4})^2(n+1)(n+2)(n+3)(n+4)$$

41.6 Formulation of perturbation (non-degenerate case)

$$\hat{H}_0\left|\psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\psi_n^{(0)}\right\rangle$$

$$|\psi_n\rangle = \left|\psi_n^{(0)}\right\rangle + |\Phi\rangle$$

with

$$|\Phi\rangle = \lambda\left|\psi_n^{(1)}\right\rangle + \lambda^2\left|\psi_n^{(2)}\right\rangle + ...$$

and

$$\left\langle\psi_n^{(0)}\middle|\Phi\right\rangle = 0$$

((**Note-1**))
Normalization of $|\psi_n\rangle = \left|\psi_n^{(0)}\right\rangle + |\Phi\rangle$:

$$\begin{aligned}\langle\psi_n|\psi_n\rangle &= (\left\langle\psi_n^{(0)}\right| + \langle\Phi|)(\left|\psi_n^{(0)}\right\rangle + |\Phi\rangle) \\ &= \left\langle\psi_n^{(0)}\middle|\psi_n^{(0)}\right\rangle + \left\langle\psi_n^{(0)}\middle|\Phi\right\rangle + \left\langle\Phi\middle|\psi_n^{(0)}\right\rangle + \langle\Phi|\Phi\rangle \\ &= 1 + \langle\Phi|\Phi\rangle\end{aligned}$$

((**Note-2**))

What does $\left\langle\psi_n^{(0)}\middle|\Phi\right\rangle = 0$ mean?

This means that we choose all eigenstate corrections $\left|\psi_n^{(k)}\right\rangle$ for k>0 to be orthogonal to $\left|\psi_n^{(0)}\right\rangle$.

or

$$\langle \psi_n^{(0)} | \psi_n^{(k)} \rangle = \delta_{k,0}$$

Then the normalization

$$\langle \psi_n^{(0)} | \psi_n \rangle = 1$$

holds to all orders in λ. Obviously, with these choices the perturbed state $|\psi_n\rangle$ is generally not normalized to unity.

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + ...$$

$$\begin{aligned}
\langle \psi_n | \psi_n \rangle = & \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \lambda (\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle) \\
& + \lambda^2 (\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle) \\
& + \lambda^3 (\langle \psi_n^{(0)} | \psi_n^{(3)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(2)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(3)} | \psi_n^{(0)} \rangle) \\
& + \lambda^4 (\langle \psi_n^{(0)} | \psi_n^{(4)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(3)} \rangle + \langle \psi_n^{(2)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(3)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(4)} | \psi_n^{(0)} \rangle) + .. \\
& = 1 + \lambda^2 \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \lambda^4 \langle \psi_n^{(2)} | \psi_n^{(2)} \rangle + \lambda^6 \langle \psi_n^{(3)} | \psi_n^{(3)} \rangle + ...
\end{aligned}$$

Schrödinger equation

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle$$

with

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

or

$$(\hat{H}_0 + \hat{H}_1) |\psi_n\rangle = E_n |\psi_n\rangle$$

Here we define the projection operator given by

$$\hat{M} = |\psi_n^{(0)}\rangle \langle \psi_n^{(0)}|$$

where

$$\hat{M} |\psi_n^{(0)}\rangle = |\psi_n^{(0)}\rangle$$

$\hat{M}$ satisfies $\hat{M}^2 = \hat{M}$

((Note))
$\hat{M}$ is the Hermitian operator.

$$\hat{M}^+ = (\left|\psi_n{}^{(0)}\right\rangle\left\langle\psi_n{}^{(0)}\right|)^+ = \left|\psi_n{}^{(0)}\right\rangle\left\langle\psi_n{}^{(0)}\right| = \hat{M}$$

$$\hat{M}\left|\psi_n{}^{(0)}\right\rangle = \left|\psi_n{}^{(0)}\right\rangle$$

or

$$\left\langle\psi_n{}^{(0)}\right|\hat{M}^+ = \left\langle\psi_n{}^{(0)}\right|$$

or

$$\left\langle\psi_n{}^{(0)}\right|\hat{M} = \left\langle\psi_n{}^{(0)}\right|$$

We introduce

$$\hat{P} = \hat{1} - \hat{M},$$

which is the complementary projection operator.

((Theorem-1))

$$\hat{P}\left|\psi_n{}^{(0)}\right\rangle = 0$$

$$\hat{P}\left|\Phi\right\rangle = \left|\Phi\right\rangle$$

((Proof))

$$\hat{P}\left|\psi_n{}^{(0)}\right\rangle = (\hat{1} - \left|\psi_n{}^{(0)}\right\rangle\left\langle\psi_n{}^{(0)}\right|)\left|\left|\psi_n{}^{(0)}\right\rangle\right\rangle = 0$$

$$\hat{P}\left|\Phi\right\rangle = (\hat{1} - \left|\psi_n{}^{(0)}\right\rangle\left\langle\psi_n{}^{(0)}\right|)\left|\Phi\right\rangle = \left|\Phi\right\rangle$$

((Theorem-2))

$$[\hat{P}, \hat{H}_0] = 0$$

((**Proof**))

$$\hat{P}\hat{H}_0 - \hat{H}_0\hat{P} = (\hat{1} - |\psi_n{}^{(0)}\rangle\langle\psi_n{}^{(0)}|)\hat{H}_0 - \hat{H}_0(\hat{1} - |\psi_n{}^{(0)}\rangle\langle\psi_n{}^{(0)}|)$$

$$= (\hat{H}_0 - E_n{}^{(0)}|\psi_n{}^{(0)}\rangle\langle\psi_n{}^{(0)}| - \hat{H}_0 + E_n{}^{(0)}|\psi_n{}^{(0)}\rangle\langle\psi_n{}^{(0)}| = 0$$

((Theorem-3))

$$[\hat{M}, \hat{H}_0] = 0$$

((**Proof**))

$$\hat{M}\hat{H}_0 - \hat{H}_0\hat{M} = (\hat{1} - \hat{P})\hat{H}_0 - \hat{H}_0(\hat{1} - \hat{P}) = 0$$

41.7 Schrödinger equation

Now we discuss the Schrödinger equation,

$$(\hat{H}_0 + \hat{H}_1)|\psi_n\rangle = E_n|\psi_n\rangle$$

$$(\hat{H}_0 + \hat{H}_1)(|\psi_n{}^{(0)}\rangle + |\Phi\rangle) = E_n(|\psi_n{}^{(0)}\rangle + |\Phi\rangle)$$

or

$$E_n|\psi_n{}^{(0)}\rangle + E_n|\Phi\rangle = (\hat{H}_0 + \hat{H}_1)|\psi_n{}^{(0)}\rangle + (\hat{H}_0 + \hat{H}_1)|\Phi\rangle)$$

or

$$E_n|\psi_n{}^{(0)}\rangle + E_n|\Phi\rangle = E_n{}^{(0)}|\psi_n{}^{(0)}\rangle + \hat{H}_0|\Phi\rangle + \hat{H}_1|\psi_n\rangle$$

or

$$(E_n - \hat{H}_0)|\Phi\rangle = \hat{H}_1|\psi_n\rangle - (E_n - E_n{}^{(0)})|\psi_n{}^{(0)}\rangle$$

Projecting on both sides with $\hat{P}$

$$\hat{P}(E_n - \hat{H}_0)|\Phi\rangle = \hat{P}\hat{H}_1|\psi_n\rangle - (E_n - E_n{}^{(0)})\hat{P}|\psi_n{}^{(0)}\rangle$$

$$(E_n - \hat{H}_0)\hat{P}|\Phi\rangle = \hat{P}\hat{H}_1|\psi_n\rangle$$

or

$$(E_n - \hat{H}_0)|\Phi\rangle = \hat{P}\hat{H}_1|\psi_n\rangle$$

or

$$|\Phi\rangle = (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n\rangle$$

Thus we get the final form

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n\rangle$$

We solve this by iteration

$$\begin{aligned}
|\psi_n\rangle &= |\psi_n^{(0)}\rangle + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(|\psi_n^{(0)}\rangle + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n\rangle) \\
&= |\psi_n^{(0)}\rangle + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n^{(0)}\rangle \\
&\quad + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n^{(0)}\rangle + \\
&\quad + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n^{(0)}\rangle + \\
&\quad + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n^{(0)}\rangle + \ldots
\end{aligned}$$

41.8 Brillouin-Wigner perturbation expansion

What is the energy shift due to the perturbation?

$$(E_n - \hat{H}_0)|\psi_n\rangle = \hat{H}_1|\psi_n\rangle$$

Projecting on both sides with $\hat{M}$

$$\hat{M}(E_n - \hat{H}_0)|\psi_n\rangle = \hat{M}\hat{H}_1|\psi_n\rangle$$

or

$$(E_n - \hat{H}_0)\hat{M}|\psi_n\rangle = \hat{M}\hat{H}_1|\psi_n\rangle$$

or

$$(E_n - \hat{H}_0)|\psi_n^{(0)}\rangle = \hat{M}\hat{H}_1|\psi_n\rangle$$

Multiplying on both sides with $\langle\psi_n^{(0)}|$

$$\left\langle \psi_n^{(0)} \middle| (E_n - \hat{H}_0) \middle| \psi_n^{(0)} \right\rangle = \psi_n^{(0)} \hat{M}\hat{H}_1 \left| \psi_n^{(0)} \right\rangle$$

or

The energy shift is

$$E_n - E_n^{(0)} = \left\langle \psi_n^{(0)} \middle| \hat{M}\hat{H}_1 \middle| \psi_n^{(0)} \right\rangle = \left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle$$

or

$$\begin{aligned} E_n - E_n^{(0)} &= \left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle + \left\langle \psi_n^{(0)} \middle| \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 \middle| \psi_n^{(0)} \right\rangle \\ &\quad + \left\langle \psi_n^{(0)} \middle| \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 \middle| \psi_n^{(0)} \right\rangle + \\ &\quad + \left\langle \psi_n^{(0)} \middle| \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 \middle| \psi_n^{(0)} \right\rangle + \end{aligned}$$

The first-order energy shift:

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle$$

The second-order energy shift:

$$\begin{aligned} E_n^{(2)} &= \left\langle \psi_n^{(0)} \middle| \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 \middle| \psi_n^{(0)} \right\rangle \\ &= \sum_{k \neq n} \left\langle \psi_n^{(0)} \middle| \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} \middle| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle \\ &= \sum_{k \neq n} \frac{\left| \left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_k^{(0)} \right\rangle \right|^2}{E_n - E_k^{(0)}} \end{aligned}$$

When $E_n \to E_n^{(0)}$, we get a “Rayleigh-Schrödinger series of conventional perturbation theory.”

$$E_n^{(2)} = \sum_{k \neq n} \frac{\left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_k^{(0)}}$$

The third order of the energy shift:

$$E_n^{(3)} = \left\langle \psi_n^{(0)} \middle| \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle$$

$$= \sum_{k \neq n. l \neq n} \left\langle \psi_n^{(0)} \middle| \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} \middle| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} \middle| \psi_l^{(0)} \right\rangle \left\langle \psi_l^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle$$

$$= \sum_{k \neq n. l \neq n} \frac{\left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \hat{H}_1 \middle| \psi_l^{(0)} \right\rangle \left\langle \psi_l^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle}{(E_n - E_k^{(0)})(E_n - E_l^{(0)})}$$

or

$$E_n^{(3)} \approx \sum_{k \neq n. l \neq n} \frac{\left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \hat{H}_1 \middle| \psi_l^{(0)} \right\rangle \left\langle \psi_l^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})}$$

where $E_n \to E_n^{(0)}$.

The fourth-order of the energy shift

$$E_n^{(4)} \approx \sum_{\substack{k \neq n. l \neq n \\ m \neq n}} \frac{\left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \hat{H}_1 \middle| \psi_l^{(0)} \right\rangle \left\langle \psi_l^{(0)} \middle| \hat{H}_1 \middle| \psi_m^{(0)} \right\rangle \left\langle \psi_m^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})(E_n^{(0)} - E_m^{(0)})}$$

where $E_n \to E_n^{(0)}$.

41.9 Wavefunctions

Next we discuss the wave function to the high order.

The first order of wave function:

$$\left| \psi_n^{(1)} \right\rangle = (E_n - \hat{H}_0)^{-1} \hat{P} \hat{H}_1 \left| \psi_n^{(0)} \right\rangle$$

$$= \sum_{k \neq n} (E_n - \hat{H}_0)^{-1} \hat{P} \left| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle$$

$$= \sum_{k \neq n} \frac{\left| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle}{(E_n - E_k^{(0)})}$$

or

$$\left| \psi_n^{(1)} \right\rangle \approx \sum_{k \neq n} \frac{\left| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle}{(E_n^{(0)} - E_k^{(0)})}$$

where $E_n \to E_n^{(0)}$.

The second order of the wave function:

$$\left|\psi_n^{(2)}\right\rangle = (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1\left|\psi_n^{(0)}\right\rangle$$
$$= \sum_{k\neq n, l\neq n}(E_n - \hat{H}_0)^{-1}\hat{P}\left|\psi_k^{(0)}\right\rangle\left\langle\psi_k^{(0)}\right|\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\left|\psi_l^{(0)}\right\rangle\left\langle\psi_l^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\langle$$
$$= \sum_{k\neq n, l\neq n}\frac{\left|\psi_k^{(0)}\right\rangle\left\langle\psi_k^{(0)}\right|\hat{H}_1\left|\psi_l^{(0)}\right\rangle\left\langle\psi_l^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})}$$

where $E_n \to E_n^{(0)}$.

The third order of the wave function:

$$\left|\psi_n^{(3)}\right\rangle \approx \sum_{\substack{k\neq n, l\neq n\\ m\neq n}}\frac{\left|\psi_k^{(0)}\right\rangle\left\langle\psi_k^{(0)}\right|\hat{H}_1\left|\psi_l^{(0)}\right\rangle\left\langle\psi_l^{(0)}\right|\hat{H}_1\left|\psi_m^{(0)}\right\rangle\left\langle\psi_m^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})(E_n^{(0)} - E_m^{(0)})}$$

The fourth order of the wave function:

$$\left|\psi_n^{(4)}\right\rangle \approx \sum_{\substack{k\neq n, l\neq n\\ m\neq n}}\frac{\left|\psi_k^{(0)}\right\rangle\left\langle\psi_k^{(0)}\right|\hat{H}_1\left|\psi_l^{(0)}\right\rangle\left\langle\psi_l^{(0)}\right|\hat{H}_1\left|\psi_m^{(0)}\right\rangle\left\langle\psi_m^{(0)}\right|\hat{H}_1\left|\psi_p^{(0)}\right\rangle\left\langle\psi_p^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_p^{(0)})}$$

41.10 Degenerate case-1

with the energy $E_{n\eta}^{(1)}$

Here is the procedure of calculation for the perturbation with degeneracy. We have now g-degenerate states with

$$\hat{H}_0\left|\varphi_{n,\mu}^{(0)}\right\rangle = E_n^{(0)}\left|\varphi_{n,\mu}^{(0)}\right\rangle$$

with

$$\left|\varphi_{n,\mu}^{(0)}\right\rangle \qquad (\mu = 1, 2, 3, ..., g)$$

New Hamiltonian H is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \qquad (\hat{H}_1 \text{ is the perturbation}).$$

(1) Calculate

$$\hat{H}_1\left|\varphi_{n,\mu}{}^{(0)}\right\rangle$$

(i) For example, we have

$$\hat{H}_1\left|\varphi_{n,\mu}{}^{(0)}\right\rangle = \varepsilon_\mu\left|\varphi_{n,\mu}{}^{(0)}\right\rangle$$

where ε_μ are different for different μ. The perturbed energy is given by $E_n^{(0)} + \varepsilon_\mu$

(ii) The second case

$$\hat{H}_1\left|\varphi_{n,1}{}^{(0)}\right\rangle = A_{11}\left|\varphi_{n,1}{}^{(0)}\right\rangle + A_{12}\left|\varphi_{n,2}{}^{(0)}\right\rangle$$

$$\hat{H}_1\left|\varphi_{n,2}{}^{(0)}\right\rangle = A_{21}\left|\varphi_{n,1}{}^{(0)}\right\rangle + A_{22}\left|\varphi_{n,2}{}^{(0)}\right\rangle$$

$$\hat{H}_1\left|\varphi_{n,\mu}{}^{(0)}\right\rangle = \varepsilon_\mu\left|\varphi_{n,\mu}{}^{(0)}\right\rangle \qquad \text{with } \mu = 3,4,..., g.$$

We consider only the case

$$\hat{H}_1\left|\varphi_{n,1}{}^{(0)}\right\rangle = A_{11}\left|\varphi_{n,1}{}^{(0)}\right\rangle + A_{12}\left|\varphi_{n,2}{}^{(0)}\right\rangle$$

$$\hat{H}_1\left|\varphi_{n,2}{}^{(0)}\right\rangle = A_{21}\left|\varphi_{n,1}{}^{(0)}\right\rangle + A_{22}\left|\varphi_{n,2}{}^{(0)}\right\rangle$$

$$\hat{H}_1 = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}$$

The Unitary matrix

$$\hat{U} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix}$$

$$\left|\psi_{n,1}{}^{(0)}\right\rangle = \hat{U}\left|\varphi_{n,1}{}^{(0)}\right\rangle = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} U_{11} \\ U_{21} \end{pmatrix}$$

$$\left|\psi_{n,2}{}^{(0)}\right\rangle = \hat{U}\left|\varphi_{n,2}{}^{(0)}\right\rangle = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} U_{12} \\ U_{22} \end{pmatrix}$$

For $\lambda = \varepsilon_1$,

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\begin{pmatrix} U_{11} \\ U_{21} \end{pmatrix} = \varepsilon_1 \begin{pmatrix} U_{11} \\ U_{21} \end{pmatrix}$$

For $\lambda = \varepsilon_2$,

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\begin{pmatrix} U_{21} \\ U_{22} \end{pmatrix} = \varepsilon_2 \begin{pmatrix} U_{21} \\ U_{22} \end{pmatrix}$$

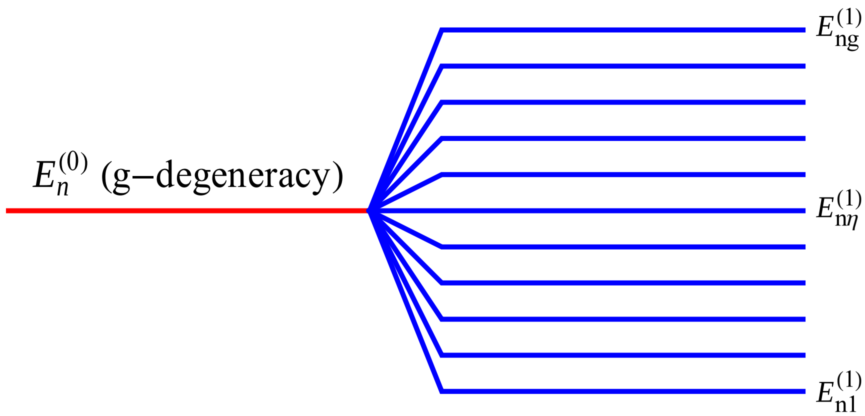
41.11 Degenerate case-II

We have now g-degenerate states with

$$\hat{H}_0 \left| \varphi_{n,\mu}{}^{(0)} \right\rangle = E_n{}^{(0)} \left| \varphi_{n,\mu}{}^{(0)} \right\rangle$$

with

$$\left| \varphi_{n,\mu}{}^{(0)} \right\rangle \qquad (\mu = 1, 2, 3, ..., g)$$



((Eigenvalue problem))
We now calculate the matrix elements

$$\left\langle \varphi_{n,\mu}{}^{(0)} \right| \hat{H}_1 \left| \varphi_{n,\nu}{}^{(0)} \right\rangle$$

Then we solve the eigenvalue problem

$$\sum_{\nu=1}^{g} [\left\langle \varphi_{n,\mu}{}^{(0)} \right| \hat{H}_1 \left| \varphi_{n,\nu}{}^{(0)} \right\rangle - E_{n\eta}{}^{(1)} \delta_{ij}] \left\langle \varphi_{n,\mu}{}^{(0)} \middle| \psi_{n\eta}{}^{(0)} \right\rangle = 0$$

where $\eta = 1, 2, ..., g$, and $\mu = 1, 2, ..., g$

or

$$\begin{pmatrix} H_{11}-E_{n\eta}^{(1)} & H_{12} & H_{13} & . & . & . & H_{1g} \\ H_{21} & H_{22}-E_{n\eta}^{(1)} & H_{23} & . & . & . & H_{2g} \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ H_{g1} & H_{g2} & H_{g3} & . & . & . & H_{gg}-E_{n\eta}^{(1)} \end{pmatrix} \begin{pmatrix} \langle \varphi_{n,1}^{(0)} | \psi_{n\eta}^{(0)} \rangle \\ \langle \varphi_{n,2}^{(0)} | \psi_{n\eta}^{(0)} \rangle \\ . \\ . \\ . \\ . \\ \langle \varphi_{n,g}^{(0)} | \psi_{n\eta}^{(0)} \rangle \end{pmatrix} = 0$$

for the eigenvalue $E_{n\eta}^{(1)}$. The Unitary transformation:

$$|\psi_{n\eta}^{(0)}\rangle = \hat{U}|\varphi_{n\eta}^{(0)}\rangle$$

where

$$\hat{U} = \begin{pmatrix} U_{11} & U_{12} & . & . & U_{1g} \\ U_{21} & U_{22} & . & . & . \\ . & . & . & . & . \\ . & . & . & . & . \\ U_{g1} & U_{g2} & . & . & U_{gg} \end{pmatrix}$$

$$|\varphi_{n1}^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ . \\ . \\ . \\ 0 \end{pmatrix}, \quad |\varphi_{n2}^{(0)}\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ . \\ . \\ . \\ 0 \end{pmatrix}, \ldots\ldots\ldots\ldots\ldots\ldots, \quad |\varphi_{ng}^{(0)}\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ . \\ . \\ . \\ 1 \end{pmatrix}$$

Then we have the resultant energy as

$$E_n^{(0)} + E_{n\eta}^{(1)} \qquad (\eta = 1, 2, 3, ..., g).$$

$$\left|\psi_{n\eta}{}^{(0)}\right\rangle = \begin{pmatrix} U_{\eta 1} \\ U_{\eta 1} \\ . \\ . \\ . \\ . \\ . \\ U_{\eta g} \end{pmatrix},$$

41.12 Example

Consider the so-called spin Hamiltonian:

$$\hat{H} = \frac{a}{\hbar^2}\hat{S}_z{}^2 + \frac{b}{\hbar^2}(\hat{S}_x{}^2 - \hat{S}_y{}^2) = \hat{H}_0 + \hat{H}_1$$

for a system of spin $S = 1$, where $0 \leq b << a$. Such a Hamiltonian obtains for a spin-1 ion located in a crystal with rhombic symmetry. Find the eigenvalues of this Hamiltonian using degenerate perturbation theory [Amit Goswami, Chapter 18, p.394 Problem((8))

Eigenvalue of $\hat{H}_0$

$$\hat{H}_0 = \frac{a}{\hbar^2}\hat{S}_z{}^2\left|1,m\right\rangle = am^2\left|1,m\right\rangle$$

$\left|1,m\right\rangle$ (m = 1, 0, -1) is the eigenket of $\hat{H}_0$:

$\left|1,\pm 1\right\rangle$ is the eigenket of $\hat{H}_0$ with energy a (degenerate)

$\left|1,0\right\rangle$ is the eigenket of $\hat{H}_0$ with energy 0 (nondegenerate)

Now we calculate $\hat{H}_1\left|1,m\right\rangle = \frac{b}{\hbar^2}(\hat{S}_x{}^2 - \hat{S}_y{}^2)\left|1,m\right\rangle$

$$S_x = \hbar\begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix}, \quad S_y = \hbar\begin{pmatrix} 0 & -\frac{i}{\sqrt{2}} & 0 \\ \frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} \\ 0 & \frac{i}{\sqrt{2}} & 0 \end{pmatrix}, \quad S_z = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The Hamiltonian H is expressed by

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = \begin{pmatrix} a & 0 & b \\ 0 & 0 & 0 \\ b & 0 & a \end{pmatrix}$$

(1) Exact solution

We use the Mathematica to solve the eigenvalue problem.

Eigenvlaue $\varepsilon_1 = a + b$

Eigenket:

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle + |1,-1\rangle)$$

Eigenvlaue $\varepsilon_2 = a - b$

Eigenket $|\psi_2\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle - |1,-1\rangle)$

Eigenvalue $\varepsilon_3 = 0$

Eigenket $|\psi_3\rangle = |1,0\rangle$

((**Mathematica**))

```
Clear["Global`*"];

exp_ * := exp /. {Complex[re_, im_] :→ Complex[re, -im]};

H = (a 0 b
     0 0 0
     b 0 a);

eq1 = Eigensystem[H]
```

{{0, a − b, a + b}, {{0, 1, 0}, {−1, 0, 1}, {1, 0, 1}}}

```
ψ1 = Normalize[eq1[[2, 1]]]
```

{0, 1, 0}

```
ψ2 = Normalize[eq1[[2, 2]]]
```

$\left\{-\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right\}$

```
ψ3 = Normalize[eq1[[2, 3]]]
```

$\left\{\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right\}$

```
{ψ1*. ψ2, ψ2*. ψ3,  ψ3*. ψ1}
```

{0, 0, 0}

---

(2) Perturbation method

$$\hat{H}_1 = \begin{pmatrix} 0 & 0 & b \\ 0 & 0 & 0 \\ b & 0 & 0 \end{pmatrix}$$

$$\hat{H}_1 |1,1\rangle = b|1,-1\rangle$$

$$\hat{H}_1 |1,-1\rangle = b|1,1\rangle$$

Matrix of $\hat{H}_1$ of the basis of $|1,1\rangle$ and $|1,-1\rangle$ is

$$\hat{H}_{11} = \begin{pmatrix} 0 & b \\ b & 0 \end{pmatrix}$$

We use the Mathematica to solve the eigenvalue problem.

$\varepsilon_1' = b$ (or $\varepsilon_1 = a + b$)

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle + |1,-1\rangle)$$

and

$\varepsilon_1' = -b$ (or $\varepsilon_2 = a - b$)

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle - |1,-1\rangle)$$

((**Mathematica**))

```
Clear["Global`*"];

exp_* := exp /. {Complex[re_, im_] :> Complex[re, -im]};

H11 = (0 b
       b 0);

eq1 = Eigensystem[H11]

{{-b, b}, {{-1, 1}, {1, 1}}}

ψ1 = Normalize[eq1[[2, 1]]]

{-1/√2, 1/√2}

ψ2 = Normalize[eq1[[2, 2]]]

{1/√2, 1/√2}

{ψ1*. ψ2}

{0}
```

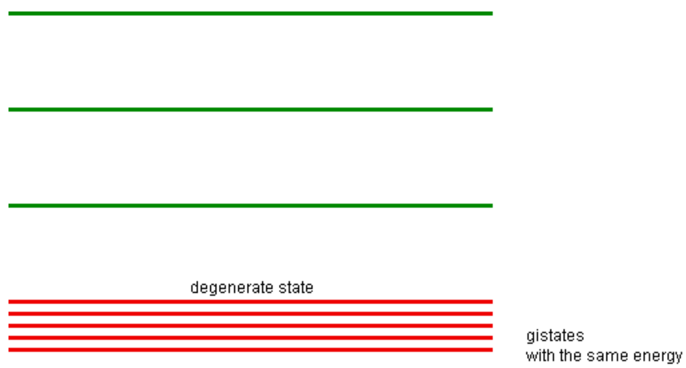
41.13 Perturbation theory-degenerate case

The first-order correction to the eigenstate and, consequently, the second-order shift in the energy involves the quantity diverges, if there exists states other than $|\psi_n^{(0)}\rangle$ with energy $E_n^{(0)}$, that is, if there is degeneracy.

or

$$E_n = E_n^{(0)} + \lambda \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle + \sum_{k \neq n} \frac{\langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})}$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda \sum_{k \neq n} |\psi_k^{(0)}\rangle \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})}$$



Suppose that there are g-states with

$$|\varphi_{n\mu}^{(0)}\rangle \; (i = 1, 2, 3, ..., g)$$

all with the same energy

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + ...$$

where

$$|\psi_{n\nu}^{(0)}\rangle = \hat{U} |\varphi_{n,\nu}^{(0)}\rangle$$

and

$\hat{U}$ is a unitary operator.

$$\langle \varphi_{n\nu}^{(0)} | \psi_n^{(1)} \rangle = 0 , \qquad \langle \varphi_{n\nu}^{(0)} | \psi_n^{(2)} \rangle = 0 ,....$$

We need to determine the unitary operator and eigenvalue $E_{n\eta}^{(0)}$

Eigenvalue problem

$$(\hat{H}_0 + \lambda \hat{H}_1)(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + ...)$$

$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + ...)$$

For the 0-th order terms in λ,

$$(\hat{H}_0 - E_n^{(0)})|\psi_n^{(0)}\rangle = 0\,, \qquad (1)$$

For the 1st-order terms in λ,

$$(\hat{H}_0 - E_n^{(0)})|\psi_n^{(1)}\rangle + (\hat{H}_1 - E_n^{(1)})|\psi_n^{(0)}\rangle = 0\,, \qquad (2)$$

For the 2nd-order terms in λ,

$$(\hat{H}_0 - E_n^{(0)})|\psi_n^{(2)}\rangle + (\hat{H}_1 - E_n^{(1)})|\psi_n^{(1)}\rangle - E_n^{(2)}|\psi_n^{(0)}\rangle = 0\,, \qquad (3)$$

For the 3rd-order terms in λ,

$$(\hat{H}_0 - E_n^{(0)})|\psi_n^{(3)}\rangle + (\hat{H}_1 - E_n^{(1)})|\psi_n^{(2)}\rangle - E_n^{(2)}|\psi_n^{(1)}\rangle - E_n^{(3)}|\psi_n^{(0)}\rangle = 0$$

Here we assume that

$$\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0\,,\ \langle\psi_n^{(0)}|\psi_n^{(2)}\rangle = 0\,,\ ....$$

We take the inner product of Eq.(2) with each of the g bra vectors $\langle\varphi_{n,\mu}^{(0)}|$ (μ = 1, 2, ...,g)

$$\langle\varphi_{n,\mu}^{(0)}|(\hat{H}_0 - E_n^{(0)})|\psi_n^{(1)}\rangle + \langle\varphi_{n,\mu}^{(0)}|(\hat{H}_1 - E_n^{(1)})|\psi_n^{(0)}\rangle = 0\,, \qquad (2)$$

or

$$\langle\varphi_{n,\mu}^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle = E_n^{(1)}\langle\varphi_{n,\mu}^{(0)}|\psi_n^{(0)}\rangle$$

$$\sum_{\nu=1}^{g}\langle\varphi_{n,\mu}^{(0)}|\hat{H}_1|\varphi_{n,\nu}^{(0)}\rangle\langle\varphi_{n,\nu}^{(0)}|\psi_n^{(0)}\rangle = E_n^{(1)}\sum_{\nu=1}^{g}\langle\varphi_{n,\mu}^{(0)}|\varphi_{n,\nu}^{(0)}\rangle\langle\varphi_{n,\nu}^{(0)}|\psi_n^{(0)}\rangle$$

or

$$\sum_{\nu=1}^{g}[\langle\varphi_{n,\mu}^{(0)}|\hat{H}_1|\varphi_{n,\nu}^{(0)}\rangle - E_n^{(1)}\delta_{\mu\nu}]\langle\varphi_{n,\mu}^{(0)}|\psi_n^{(0)}\rangle = 0$$

(Eigenvalue problem)

$E_n{}^{(1)} = E_{n\eta}{}^{(1)}$ (η = 1,2,,…,g) and $\left|\psi_n^{(0)}\right\rangle = \left|\psi_{n\eta}^{(0)}\right\rangle$,

$$\sum_{\nu=1}^{g} [\left\langle \varphi_{n,\mu}{}^{(0)} \right| \hat{H}_1 \left| \varphi_{n,\nu}{}^{(0)} \right\rangle - E_{n\eta}{}^{(1)} \delta_{ij}] \left\langle \varphi_{n,\mu}{}^{(0)} \middle| \psi_{n\eta}{}^{(0)} \right\rangle = 0$$

where η = 1, 2, ..., g, and μ = 1, 2, ..., g

or

$$\begin{pmatrix} H_{11} - E_{n\eta}{}^{(1)} & H_{12} & H_{13} & . & . & . & H_{1g} \\ H_{21} & H_{22} - E_{n\eta}{}^{(1)} & H_{23} & . & . & . & H_{2g} \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ H_{g1} & H_{g2} & H_{g3} & . & . & . & H_{gg} - E_{n\eta}{}^{(1)} \end{pmatrix} \begin{pmatrix} \left\langle \varphi_{n,1}{}^{(0)} \middle| \psi_{n\eta}{}^{(0)} \right\rangle \\ \left\langle \varphi_{n,2}{}^{(0)} \middle| \psi_{n\eta}{}^{(0)} \right\rangle \\ . \\ . \\ . \\ . \\ \left\langle \varphi_{n,g}{}^{(0)} \middle| \psi_{n\eta}{}^{(0)} \right\rangle \end{pmatrix} = 0$$

Unitary transformation

$$\left|\psi_{n\eta}{}^{(0)}\right\rangle = \hat{U}\left|\varphi_{n\eta}{}^{(0)}\right\rangle$$

$$\hat{H}_1\left|\psi_{n\eta}^{(0)}\right\rangle = E_{n\eta}^{(1)}\left|\psi_{n\eta}^{(0)}\right\rangle$$

where

$$\hat{U} = \begin{pmatrix} U_{11} & U_{12} & . & . & U_{1g} \\ U_{21} & U_{22} & . & . & . \\ . & . & . & . & . \\ . & . & . & . & . \\ U_{g1} & U_{g2} & . & . & U_{gg} \end{pmatrix}$$

$$|\varphi_{n1}^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ . \\ . \\ . \\ 0 \end{pmatrix}, \qquad |\varphi_{n2}^{(0)}\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ . \\ . \\ . \\ 0 \end{pmatrix}, \qquad ...., \quad |\varphi_{ng}^{(0)}\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ . \\ . \\ . \\ 1 \end{pmatrix}$$

Then we have

$$|\psi_{n\eta}^{(0)}\rangle = \begin{pmatrix} U_{1\eta} \\ U_{2\eta} \\ . \\ . \\ . \\ . \\ . \\ U_{g\eta} \end{pmatrix}, \text{ with the energy } E_{n\eta}^{(1)}$$

The eigenvalue problem is described by

$$\begin{pmatrix} H_{11} - E_{n\eta}^{(1)} & H_{12} & H_{13} & . & . & . & H_{1g} \\ H_{21} & H_{22} - E_{n\eta}^{(1)} & H_{23} & . & . & . & H_{2g} \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ H_{g1} & H_{g2} & H_{g3} & . & . & . & H_{gg} - E_{n\eta}^{(1)} \end{pmatrix} \begin{pmatrix} U_{1\eta} \\ U_{2\eta} \\ \\ \\ \\ \\ U_{g\eta} \end{pmatrix} = 0$$

43.12 Second-order perturbation:

$$(\hat{H}_0 - E_n^{(0)})|\psi_n^{(2)}\rangle + (\hat{H}_1 - E_n^{(1)})|\psi_n^{(1)}\rangle - E_n^{(2)}|\psi_n^{(0)}\rangle = 0$$

$\langle \varphi_{n,\mu}{}^{(0)} | \times$

$$\langle \varphi_{n,\mu}{}^{(0)} | (\hat{H}_0 - E_n{}^{(0)}) | \psi_n{}^{(2)} \rangle + \langle \varphi_{n,\mu}{}^{(0)} | (\hat{H}_1 - E_n{}^{(1)}) | \psi_n{}^{(1)} \rangle - E_n{}^{(2)} \langle \varphi_{n,\mu}{}^{(0)} | \psi_n{}^{(0)} \rangle = 0$$

$$\langle \varphi_{n,\mu}{}^{(0)} | (\hat{H}_1 - E_n{}^{(1)}) | \psi_n{}^{(1)} \rangle - E_n{}^{(2)} \langle \varphi_{n,\mu}{}^{(0)} | \psi_n{}^{(0)} \rangle = 0$$

or

$$\langle \varphi_{n,\mu}{}^{(0)} | \hat{H}_1 | \psi_n{}^{(1)} \rangle - E_n{}^{(1)} \langle \varphi_{n,\mu}{}^{(0)} | \psi_n{}^{(1)} \rangle - E_n{}^{(2)} \langle \varphi_{n,\mu}{}^{(0)} | \psi_n{}^{(0)} \rangle = 0 \qquad (1)$$

Here we use

$$|\psi_n{}^{(1)}\rangle = \sum_{k \neq n} \frac{|\psi_k{}^{(0)}\rangle \langle \psi_k{}^{(0)} | \hat{H}_1 | \psi_n{}^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}$$

which is obtained from the perturbation theory for the non-degenerate case.

Note that

$$\langle \psi_k{}^{(0)} | \hat{H}_1 | \psi_n{}^{(0)} \rangle = \sum_{\nu=1}^{g} \langle \psi_k{}^{(0)} | \hat{H}_1 | \varphi_{n,\nu}{}^{(0)} \rangle \langle \varphi_{n,\nu}{}^{(0)} | \psi_n{}^{(0)} \rangle$$

and

$$\langle \varphi_{n,\nu}{}^{(0)} | \psi_n{}^{(1)} \rangle = 0$$

From Eq.(1),

$$\sum_{\nu=1}^{g} \sum_{k \neq n} \frac{\langle \varphi_{n,\mu}{}^{(0)} | \hat{H}_1 | \psi_k{}^{(0)} \rangle \langle \psi_k{}^{(0)} | \hat{H}_1 | \varphi_{n,\nu}{}^{(0)} \rangle \langle \varphi_{n,\nu}{}^{(0)} | \psi_n{}^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} = E_n{}^{(2)} \langle \varphi_{n,\mu}{}^{(0)} | \psi_n{}^{(0)} \rangle$$

We define the following operator

$$\hat{\Lambda} = \sum_{k \neq n} \frac{\hat{H}_1 |\psi_k{}^{(0)}\rangle \langle \psi_k{}^{(0)} | \hat{H}_1}{E_n^{(0)} - E_k^{(0)}}$$

Then we have

$$\sum_{\nu=1}^{g} \langle \varphi_{n,\mu}{}^{(0)} | \hat{\Lambda} | \varphi_{n,\nu}{}^{(0)} \rangle \langle \varphi_{n,\nu}{}^{(0)} | \psi_n{}^{(0)} \rangle = E_n{}^{(2)} \langle \varphi_{n,\mu}{}^{(0)} | \psi_n{}^{(0)} \rangle$$

$$\begin{pmatrix} \Lambda_{11}-E_{n\eta}^{(2)} & \Lambda_{12} & \Lambda_{13} & . & . & . & \Lambda_{1g} \\ \Lambda_{21} & \Lambda_{22}-E_{n\eta}^{(2)} & \Lambda_{23} & . & . & . & \Lambda_{2g} \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ H_{g1} & \Lambda_{g2} & \Lambda_{g3} & . & . & . & \Lambda_{gg}-E_{n\eta}^{(2)} \end{pmatrix} \begin{pmatrix} U_{1\eta} \\ U_{2\eta} \\ \\ \\ \\ \\ U_{g\eta} \end{pmatrix} = 0$$

This is a tricky problem because the degeneracy between the first and the second state is not removed in first order. See also Gottfried 1966, 397, Problem 1.) This problem is from Schiff 1968, 295, Problem 4. A system that has three unperturbed states can be represented by the pertrurbed Hamiltonian matrix

$$\begin{pmatrix} E_1 & 0 & a \\ 0 & E_1 & b \\ a^* & b^* & E_2 \end{pmatrix}$$

where $E_2>E_1$. The quantities a and b are to be regarded as perturbations that are of the same order and are small compared with E_2-E_1. Use the second-order nondegenerate perturbation theory to calculate the perturbed eigenvalues. (Is this procedure correct?) Then diagonalize the matrix to find the exact eigenvalues. Finally, use the second-order degenerate perturbation theory. Compare the three results obtained.

((Exact solution))

$$H = \begin{pmatrix} E_1 & 0 & a \\ 0 & E_1 & b \\ a^* & b^* & E_2 \end{pmatrix}$$

Det[H - λI] = 0

$$\lambda = E_1,$$

$$\lambda = \frac{E_1+E_2}{2} \pm \frac{1}{2}\sqrt{(E_2-E_1)^2 + 4(|a|^2+|b|^2)}$$

$$= \frac{E_1+E_2}{2} \pm \frac{1}{2}(E_2-E_1)[1+\frac{4(|a|^2+|b|^2)}{(E_2-E_1)^2}]^{1/2}$$

When $|a| << E_2 - E_1, |b| << E_2 - E_1$,

$$= \frac{E_1 + E_2}{2} \pm [\frac{E_2 - E_1}{2} + \frac{(|a|^2 + |b|^2)}{(E_2 - E_1)}]$$

or

$$\lambda = E_1 - \frac{|a|^2 + |b|^2}{E_2 - E_1}$$

$$\lambda = E_2 + \frac{|a|^2 + |b|^2}{E_2 - E_1}$$

((Perturbation theory))

$$H_0 = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{pmatrix}, \qquad H_1 = \begin{pmatrix} 0 & 0 & a \\ 0 & 0 & b \\ a^* & b^* & 0 \end{pmatrix}$$

$$\hat{H}_0 |\phi_\alpha\rangle = E_1 |\phi_\alpha\rangle$$

$$\hat{H}_0 |\phi_\beta\rangle = E_1 |\phi_\beta\rangle$$

$$\hat{H}_0 |\phi_\gamma\rangle = E_2 |\phi_\gamma\rangle$$

$|\phi_\gamma\rangle$ is the eigenket of $\hat{H}_0$ with the energy E_2. Since this state is nondegenerate, we can apply the perturbation theory (non-degenerate case) to calculate the energy

The resulting energy is

$$E_\gamma = E_2 + \langle\phi_3|\hat{H}_1|\phi_3\rangle + \frac{|\langle\phi_3|\hat{H}_1|\phi_3\rangle|^2}{E_2 - E_1} + \frac{|\langle\phi_2|\hat{H}_1|\phi_3\rangle|^2}{E_2 - E_1} = E_2 + \frac{|a|^2 + |b|^2}{E_2 - E_1}$$

$$\hat{H}_1 |\phi_\alpha\rangle = a^* |\phi_\gamma\rangle$$

$$\hat{H}_1 |\phi_\beta\rangle = b^* |\phi_\gamma\rangle$$

$$\hat{H}_1 |\phi_\gamma\rangle = a |\phi_\alpha\rangle + b |\phi_\beta\rangle$$

$|\phi_\alpha\rangle$ and $|\phi_\beta\rangle$ are degenerate.

This is the degenerate case.

First order:

The matrix element of $\hat{H}_1$ in the basis of $\left|\phi_\alpha\right\rangle$ and $\left|\phi_\beta\right\rangle$ is equal to zero. So we need to calculate the second order

$$\sum_{\nu=1}^{g}\left\langle \varphi_{n,\mu}{}^{(0)}\middle|\hat{\Lambda}\middle|\varphi_{n,\nu}{}^{(0)}\right\rangle\left\langle \varphi_{n,\nu}{}^{(0)}\middle|\psi_n{}^{(0)}\right\rangle = E_n{}^{(2)}\left\langle \varphi_{n,\mu}{}^{(0)}\middle|\psi_n{}^{(0)}\right\rangle$$

$$\hat{\Lambda} = \sum_{k\neq n}\frac{\hat{H}_1\left|\psi_k{}^{(0)}\right\rangle\left\langle\psi_k{}^{(0)}\right|\hat{H}_1}{E_n{}^{(0)} - E_k{}^{(0)}} = \frac{\hat{H}_1\left|\phi_\gamma\right\rangle\left\langle\phi_\gamma\right|\hat{H}_1}{E_1 - E_2}$$

The matrix element

$$\Lambda = \begin{pmatrix} \dfrac{\left\langle\phi_\alpha\middle|\hat{H}_1\middle|\phi_\gamma\right\rangle\left\langle\phi_\gamma\middle|\hat{H}_1\middle|\phi_\alpha\right\rangle}{E_1 - E_2} & \dfrac{\left\langle\phi_\alpha\middle|\hat{H}_1\middle|\phi_\gamma\right\rangle\left\langle\phi_\gamma\middle|\hat{H}_1\middle|\phi_\beta\right\rangle}{E_1 - E_2} \\ \dfrac{\left\langle\phi_\beta\middle|\hat{H}_1\middle|\phi_\gamma\right\rangle\left\langle\phi_\gamma\middle|\hat{H}_1\middle|\phi_\alpha\right\rangle}{E_1 - E_2} & \dfrac{\left\langle\phi_\beta\middle|\hat{H}_1\middle|\phi_\gamma\right\rangle\left\langle\phi_\gamma\middle|\hat{H}_1\middle|\phi_\alpha\right\rangle}{E_1 - E_2} \end{pmatrix} = \begin{pmatrix} \dfrac{|a|^2}{E_1 - E_2} & \dfrac{ab^*}{E_1 - E_2} \\ \dfrac{a^*b}{E_1 - E_2} & \dfrac{|b|^2}{E_1 - E_2} \end{pmatrix}$$

Det[Λ-λI] = 0.

$$\begin{vmatrix} \dfrac{|a|^2}{E_1 - E_2} - \lambda & \dfrac{ab^*}{E_1 - E_2} \\ \dfrac{a^*b}{E_1 - E_2} & \dfrac{|b|^2}{E_1 - E_2} - \lambda \end{vmatrix} = 0$$

$$\left(\frac{|a|^2}{E_2 - E_1} + \lambda\right)\left(\frac{|b|^2}{E_2 - E_1} + \lambda\right) - \frac{|a|^2|b|^2}{(E_1 - E_2)^2} = 0$$

or

$$\lambda\left[\lambda + \frac{|a|^2 + |b|^2}{E_2 - E_1}\right] = 0$$

Then we have

$$\lambda = 0 \text{ and } \lambda = -\frac{|a|^2 + |b|^2}{E_2 - E_1}$$

The final result is

$$\widetilde{E}_a = E_1$$

$$\widetilde{E}_\beta = E_1 - \frac{|a|^2 + |b|^2}{E_2 - E_1}$$

$$\widetilde{E}_\gamma = E_2 + \frac{|a|^2 + |b|^2}{E_2 - E_1}$$

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APPENDIX

Matrix elememt of the simple harmonics for the perturbation calculation

$$\beta = \sqrt{\frac{m\omega_0}{\hbar}}$$

annihilation and creation operators

$$\hat{a} = \frac{\beta}{\sqrt{2}}(\hat{x} + i\frac{\hat{p}}{m\omega_0})$$

$$\hat{a}^+ = \frac{\beta}{\sqrt{2}}(\hat{x} - i\frac{\hat{p}}{m\omega_0})$$

$$[\hat{a}, \hat{a}^+] = 1$$

$$\hat{N} = \hat{a}^+\hat{a}$$

$$\hat{H} = \hbar\omega_0(\hat{N} + \frac{1}{2})$$

$$\hat{a} \mid n >= \sqrt{n} \mid n-1 >$$

$$\hat{a}^+ \mid n >= \sqrt{n+1} \mid n+1 >$$

$$\hat{N} \mid n >= n \mid n >$$

$$\mid n >= \frac{1}{\sqrt{n!}}(\hat{a}^+)^n \mid 0 >$$

$$[\hat{N}, \hat{a}] = -\hat{a}$$

$$[\hat{N}, \hat{a}^+] = \hat{a}^+$$

The parity operator

$$\hat{\pi} \mid n >= (-1)^n \mid n >$$

$$\hat{x} = \frac{1}{\sqrt{2}\beta}(\hat{a}^+ + \hat{a})$$

$$\hat{p} = \frac{m\omega_0}{i}(\frac{\hat{a} - \hat{a}^+}{\sqrt{2}\beta})$$

$$\hat{x}|n\rangle = \frac{1}{\sqrt{2}\beta}(\sqrt{n}|n-1\rangle + \sqrt{n+1}|n+1\rangle)$$

$$\hat{x}^2|n\rangle = \frac{1}{2\beta^2}(\sqrt{n(n-1)}|n-2\rangle + (2n+1)|n\rangle + \sqrt{(n+1)(n+2)}|n+2\rangle)$$

$$\hat{x}^3|n\rangle = \frac{1}{2\sqrt{2}\beta^3}(\sqrt{n(n-1)(n-2)}|n-3\rangle + 3n^{3/2}|n-1\rangle + 3(n+1)^{3/2}|n+1\rangle$$
$$+ \sqrt{(n+1)(n+2)(n+3)}|n+3\rangle)$$

$$\hat{x}^4|n\rangle = \frac{1}{4\beta^4}(\sqrt{n(n-1)(n-2)(n-3)}|n-4\rangle + 2\sqrt{(n-1)n}(2n-1)|n-2\rangle$$
$$+3(2n^2+2n+1)|n\rangle + (6+4n)\sqrt{(n+1)(n+2)}|n+2\rangle$$
$$+\sqrt{(n+1)(n+2)(n+3)(n+4)}|n+4\rangle)$$

$$\hat{x}^5|n\rangle = \frac{1}{4\sqrt{2}\beta^5}(\sqrt{n(n-1)(n-2)(n-3)(n-4)}|n-5\rangle$$
$$+5(n-1)\sqrt{(n-2)(n-1)n}|n-3\rangle$$
$$+5(2n^2+1)\sqrt{n}|n-1\rangle + 5(2n^2+4n+3)\sqrt{n+1}|n+1\rangle$$
$$+5(n+2)\sqrt{(n+1)(n+2)(n+3)}|n+3\rangle$$
$$+\sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)}|n+5\rangle)$$