Time-independent Perturbation Theory

Nondegenerate case

Reyleigh-Schrodinger perturbation theory

Definition

- Hamiltonian is $H = H_0 + H'$
- Define two projection operator

$$P_n = |n^0\rangle\langle n^0|,\ Q_n = I - P_n$$

- Unperturbed state $|n^0\rangle$ and energy E_n^0

$$H_0|n^0\rangle = E_n^0|n^0\rangle$$

- Perturbed state $|n\rangle$ and energy E_n

$$H|n\rangle = E_n|n\rangle$$
$$|n\rangle = |n^0\rangle + |n^1\rangle + |n^2\rangle + \dots$$
$$E_n = E_n^0 + E_n^1 + E_n^2 + \dots$$

Deduction

By definition, we have

$$(H_0 + H')|n\rangle = E_n|n\rangle = \left(E_n^0 + E_n\right)|n\rangle$$
$$\left(E_n^0 - H_0\right)|n\rangle = (H' - E_n)|n\rangle \tag{1}$$

Applying Q_n on both sides of Eq.(1), we get

$$\left(E_n^0 - H_0\right)Q_n|n\rangle = Q_n(H' - E_n)|n\rangle$$
$$Q_n|n\rangle = \frac{Q_n(H' - E_n)}{E_n^0 - H_0}|n\rangle$$

Therefore, we can express the $|n\rangle$ as

$$|n\rangle = P_n|n\rangle + Q_n|n\rangle = |n^0\rangle\langle n^0|n\rangle + \frac{Q_n(H' - E_n)}{E_n^0 - H_0}|n\rangle$$

Considering $|n^0\rangle$ is the leading order contribution of $|n\rangle$, we can set $\langle n^0|n\rangle = 1$ to get

$$|n\rangle = |n^0\rangle + \frac{Q_n(H' - E_n)}{E_n^0 - H_0}|n\rangle \tag{2}$$

Besides, add a bra $\langle n^0|$ to both sides of Eq.(1), we get

$$\left\langle n^0\middle|\left(E_n^0 - H_0\right)\middle|n\right\rangle = 0 = \langle n^0|(H' - E_n)|n\rangle$$
$$E_n = \frac{\langle n^0|H'|n\rangle}{\langle n^0|n\rangle} = \langle n^0|H'|n\rangle \tag{3}$$

With Eq.(2) and Eq.(3) and the initial condition $E_n^1 = \langle n^0|H'|n^0\rangle$, we can get E_n^i and $|n^i\rangle$ order by order.

- First order

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

$$|n^0\rangle + |n^1\rangle = |n^0\rangle + \frac{Q_n\left(H' - E_n^1\right)}{E_n^0 - H_0}|n^0\rangle$$

considering $Q_n E_n^1|n^0\rangle = E_n^1 Q_n|n^0\rangle = 0$, we have

$$|n^1\rangle = \frac{Q_n H'}{E_n^0 - H_0}|n^0\rangle = \sum_{k\neq n}\frac{\langle k^0|H'|n^0\rangle}{E_n^0 - E_k^0}|k^0\rangle$$

- Second order

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

$$E_n^2 = \langle n^0|H'|n^1\rangle = \sum_{k\neq n}\frac{|\langle k^0|H'|n^0\rangle|^2}{E_n^0 - E_k^0}$$

$$|n^0\rangle + |n^1\rangle + |n^2\rangle = |n^0\rangle + \frac{Q_n(H' - E_n)}{E_n^0 - H_0}\left(|n^0\rangle + |n^1\rangle\right)$$

$$|n^2\rangle = \frac{Q_n\left(H' - E_n^1\right)}{E_n^0 - H_0}|n^1\rangle - \frac{Q_n E_n^2}{E_n^0 - H_0}|n^0\rangle = \frac{Q_n\left(H' - E_n^1\right)}{E_n^0 - H_0}|n^1\rangle$$

$$|n^2\rangle = \frac{Q_n H'}{E_n^0 - H_0}|n^1\rangle - \frac{Q_n E_n^1}{E_n^0 - H_0}|n^1\rangle$$

$$= \frac{Q_n H'}{E_n^0 - H_0}\frac{Q_n H'}{E_n^0 - H_0}|n^0\rangle - \frac{Q_n}{E_n^0 - H_0}\langle n^0|H'|n^0\rangle\frac{Q_n H'}{E_n^0 - H_0}|n^0\rangle$$

Another simple way

By definition we have

$$(H_0 + H')\left(|n^0\rangle + |n^1\rangle + |n^2\rangle + \ldots\right) = \left(E_n^0 + E_n^1 + E_n^2 + \ldots\right)\left(|n^0\rangle + |n^1\rangle + |n^2\rangle + \ldots\right) \quad (4)$$

Then rearrange it order by order to get

$$\begin{aligned}&\left(H_0|n^0\rangle - E_n^0|n^0\rangle\right) + \left(H_0|n^1\rangle + H'|n^0\rangle - E_n^0|n^1\rangle - E_n^1|n^0\rangle\right)\\ &+\left(H_0|n^2\rangle + H'|n^1\rangle - E_n^0|n^2\rangle - E_n^1|n^1\rangle - E_n^2|n^0\rangle\right) + \ldots = 0\end{aligned}$$

The equation above should have zero at each order, so we have

$$H_0|n^0\rangle - E_n^0|n^0\rangle = 0 \quad \text{(i)}$$

$$H_0|n^1\rangle + H'|n^0\rangle - E_n^0|n^1\rangle - E_n^1|n^0\rangle = 0 \quad \text{(ii)}$$

$$\ldots$$

Apply $\langle n^0|$ to (ii) to get

$$E_n^0 + \langle n^0|H'|n^0\rangle - E_n^0 - E_n^1 = 0$$
$$E_n^1 = \langle n^0|H'|n^0\rangle$$

Expand $|n^1\rangle$ as $|n^1\rangle = \sum_{k\neq n} \langle k^0|n^1\rangle|k^0\rangle$ because $\langle n^0|n^1\rangle = 0$, then apply $\langle k^0|$ to get

$$\langle k^0|H_0|n^1\rangle + \langle k^0|H'|n^0\rangle - E_n^0\langle k^0|n^1\rangle = 0$$
$$\left(E_k^0 - E_n^0\right)\langle k^0|n^1\rangle + \langle k^0|H'|n^0\rangle = 0$$
$$\langle k^0|n^1\rangle = \frac{\langle k^0|H'|n^0\rangle}{E_n^0 - E_k^0}$$
$$|n^1\rangle = \sum_{k\neq n} \frac{\langle k^0|H'|n^0\rangle}{E_n^0 - E_k^0}|k^0\rangle$$

Brillouin-Wigner perturbation theory

[The main difference compared with RSPT is that BWPT keeps E_n without expanding it.]

Definition

- Hamiltonian is $H = H_0 + H'$
- Define two projection operator

$$P_n = |n^0\rangle\langle n^0|,\ Q_n = I - P_n$$

- Unperturbed state $|n^0\rangle$ and perturbed state $|n\rangle$

Deduction

By definition we have

$$(H_0 + H')|n\rangle = E_n|n\rangle$$
$$(E_n - H_0)|n\rangle = H'|n\rangle$$

Apply Q_n on both sides, we get

$$(E_n - H_0)Q_n|n\rangle = Q_n H'|n\rangle$$
$$Q_n|n\rangle = \frac{Q_n}{E_n - H_0}H'|n\rangle$$

By definition, we have

$$|n\rangle = P_n|n\rangle + Q_n|n\rangle = |n^0\rangle\langle n^0|n\rangle + \frac{Q_n}{E_n - H_0}H'|n\rangle = |n^0\rangle + \frac{Q_n}{E_n - H_0}H'|n\rangle$$

here we used approximation $\langle n^0|n\rangle = 1$.

Then, we can iterate to get

$$|n\rangle = |n^0\rangle + \frac{Q_n}{E_n - H_0} H'|n^0\rangle + \frac{Q_n}{E_n - H_0} H' \frac{Q_n}{E_n - H_0} H'|n^0\rangle \ + \ ...$$

For energy corrections, we have

$$E_n = E_n\langle n^0|n\rangle = \langle n^0|H|n\rangle = \langle n^0|H_0|n\rangle + \langle n^0|H'|n\rangle$$
$$E_n - E_n^0 = \langle n^0|H'|n\rangle$$

For the first and the second order correction, we have

$$E_n^1 = \langle n^0|H'|n^0\rangle$$
$$E_n^2 = \langle n^0|H'|n^1\rangle = \sum_{k\neq n} \frac{|\langle k^0|H'|n^0\rangle|^2}{E_n^0 - E_k^0}$$

Degenerate case

Reyleigh-Schrodinger perturbation theory

In general, we just want to split the degenerated states (by rearranging the degenerate unperturbed states) and go back to the non-degenerate case that we are familiar with. So, the following discussion will give the zero-th order state and first order energy corrections.

We still have the expansion as Eq.(4), and we want to use (ii) as well. But considering degeneracy, we need to choose what is the proper $|n^0\rangle$ because we have many choices now.
Suppose we have $H_0|n_i^0\rangle = E_n^0|n_i^0\rangle, i = 1, 2, 3, \ \dots, s$, so it is s-fold degeneracy. Suppose the rearranged state we want is $|n^0\rangle$, and $|n^0\rangle = \sum_{i=1}^{s} \langle n_i^0|n^0\rangle|n_i^0\rangle = \sum_{i=1}^{s} C_{n,i}^0|n_i^0\rangle$. Then we put $|n^0\rangle$ into (ii) to get

$$\sum_{i=1}^{s} C_{n,i}^0 \cdot H'|n_i^0\rangle - E_n^1 \sum_{i=1}^{s} C_{n,i}^0|n_i^0\rangle = \left(E_n^0 - H_0\right)|n^1\rangle$$

Apply $\langle n_j^0|$ to the equation above,

$$\sum_{i=1}^{s} C_{n,i}^0 \cdot \langle n_j^0|H'|n_i^0\rangle - E_n^1 C_{n,j}^0 = \langle n_j^0|E_n^0 - H_0|n^1\rangle = 0$$

Then, in the original basis ($\left\{|n_i^0\rangle\right\}$ before rearrangement), we have

$$\begin{pmatrix} H'_{11} - E_n^1 & H'_{12} & \dots & H'_{1s} \\ H'_{21} & H'_{22} - E_n^1 & & \\ \dots & & \dots & \dots \\ H'_{s1} & H'_{s2} & \dots & H'_{ss} - E_n^1 \end{pmatrix} \begin{pmatrix} C_{n,1}^0 \\ C_{n,2}^0 \\ \dots \\ C_{n,s}^0 \end{pmatrix} = 0$$

Then the trace of the left matrix (which is $H - E_n I$) is zero, and the eigenvalues are E_{nm}^1 with

$m = 1, 2, 3 \dots s$, there are s different first order energy corrections, the corresponding eigenvectors are zero-th order state corrections.

Brillouin-Wigner perturbation theory

Definition

- Hamiltonian is $H = H_0 + H'$
- Define two projection operator

$$P = |n_i^0\rangle\langle n_i^0|,\ Q = I - P$$

in which $|n_i^0\rangle$ are degenerate states $H_0\left|n_i^0\right\rangle = E_n^0\left|n_i^0\right\rangle$.

Deduction

With the projection operator, we can separate the basis into two groups, then

$$H = \begin{pmatrix} H^{PP} & H^{PQ} \\ H^{QP} & H^{QQ} \end{pmatrix} = \begin{pmatrix} H_0^{PP} & 0 \\ 0 & H_0^{QQ} \end{pmatrix} + \begin{pmatrix} H'^{PP} & H^{PQ} \\ H^{QP} & H'^{QQ} \end{pmatrix}$$

in which $H_0^{PP} = E_n^0 I$.
By definition, we have

$$(H_0 + H')|n\rangle = E_n|n\rangle$$

project both sides by P to get

$$P(H_0 + H')(P + Q)|n\rangle = E_n P|n\rangle$$
$$\left(H_0^{PP} + H'^{PP}\right)P|n\rangle + H^{PQ}Q|n\rangle = E_n P|n\rangle$$

project both sides by Q to get

$$Q(H_0 + H')(P + Q)|n\rangle = E_n Q|n\rangle$$
$$H^{QP}P|n\rangle + \left(H_0^{QQ} + H'^{QQ}\right)Q|n\rangle = E_n Q|n\rangle$$

here we used $P^2 = P$ and $Q^2 = Q$.
Solve to eliminate all Q space states

$$\left(E_n - H_0^{QQ} - H'^{QQ}\right)Q|n\rangle = H^{QP}P|n\rangle$$
$$Q|n\rangle = \frac{H^{QP}}{E_n - H_0^{QQ} - H'^{QQ}}P|n\rangle$$

then go back to the equation above to get

$$\left(H_0^{PP} + H'^{PP}\right)P|n\rangle + H^{PQ}\frac{H^{QP}}{E_n - H_0^{QQ} - H'^{QQ}}P|n\rangle = E_n P|n\rangle$$
$$\left(H^{PP} + H^{PQ}\frac{1}{E_n - H_0^{QQ} - H'^{QQ}}H^{QP}\right)P|n\rangle = E_n P|n\rangle$$

If we define the effective Hamiltonian as

$$H_{eff} = H^{PP} + H^{PQ} \frac{1}{E_n - H_0^{QQ} - H'^{QQ}} H^{QP}$$

Then we have the effective Schrodinger equation as

$$(H_0 + H')|n\rangle = E_n|n\rangle \Longrightarrow H_{eff}\left(P|n\rangle\right) = E_n\left(P|n\rangle\right)$$

move all to the LHS to get

$$(H_{eff} - E_n)\left(P|n\rangle\right) = 0$$

And one thing need to notice is that the matrix blocks above is actually a abbreviation as

$$H_0^{PP} \equiv \begin{pmatrix} H_0^{PP} & 0 \\ 0 & 0 \end{pmatrix}$$

So, our H_{eff} looks like

$$H_{eff} - E_n = \begin{pmatrix} H^{PP} & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & H^{PQ} \\ 0 & 0 \end{pmatrix} \begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} 0 & 0 \\ H^{QP} & 0 \end{pmatrix} - \begin{pmatrix} E_n I & 0 \\ 0 & E_n I \end{pmatrix}$$

To solve the first order energy corrections and zero-th order state corrections, we can ignore the second term to get

$$\begin{pmatrix} H^{PP} - E_n I & 0 \\ 0 & -E_n I \end{pmatrix} \begin{pmatrix} P|n\rangle \\ 0 \end{pmatrix} = 0$$

$$\left(H^{PP} - E_n I\right)\left(P|n\rangle\right) = 0$$

So, the first order energy corrections are just the eigenvalues of $\det\left(H^{PP} - E_n I\right) = 0$, the corresponding eigenvectors are the zero-th order state corrections. Then the degenerate states are splited out, it goes back to our familiar situation.