Rayleigh Schrodinger Perturbation theory (non-degenerate case)

$$H = H_0 + V$$

Assume H_0 is simple enough to solve the eigenvalue problem exactly

$$H_0 |\psi_n^0\rangle = E_n^0 |\psi_n^0\rangle \quad \text{all } n$$

$$E_n \neq E_m \quad n \neq m$$

(the last line is what is meant by non degenerate. We also assume that V is small in the sense that the solution of the exact eigenvalue problem

$$H |\psi_n\rangle = E_n |\psi_n\rangle$$

can be expressed in a

series in powers of the potential. In order to keep track of powers of the potential we replace H by

$$H = H_0 + \lambda V$$

so powers of λ = powers of V (at the end of the calculation λ will be set to 1)

We assume

$$|\psi_n\rangle = |\psi_n^0\rangle + \sum_{m=1}^{\infty} \lambda^m |\psi_n^m\rangle$$

$$E_n = E_n^0 + \sum_{m=1}^{\infty} \lambda^m |E_n^m\rangle$$

where

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

Using these expansions in the eigenvalue equation gives

$$(H_0 + \lambda V) \sum_{m=0}^{\infty} \lambda^m |\psi_n^m\rangle =$$

$$\sum_{k=0}^{\infty} \sum_{\ell=0}^{\infty} \lambda^{k+\ell} |\psi_n^k\rangle E_n^\ell$$

We expand this as follows

$$H_0 \sum_{m=0}^{\infty} \lambda^m |\psi_n^m\rangle + V \sum_{m=0}^{\infty} \lambda^{m+1} |\psi_n^m\rangle$$

$$= \sum_{k=0}^{\infty} \sum_{\ell=0}^{\infty} \lambda^{k+\ell} |\psi_n^k\rangle E_n^\ell$$

In the second term on the left let $m' = m+1$ $\quad 1 \leq m' < \infty$

In the term on the right let $m = k+\ell$ $\quad \ell = m-k$ where $0 \leq m < \infty$, $\quad 0 \leq k \leq m$. With these changes the eigenvalue equation becomes

$$H_0 \sum_{m=0}^{\infty} \lambda^m |\psi_n^m\rangle + V \sum_{m'=1}^{\infty} \lambda^{m'} |\psi_n^{m'-1}\rangle =$$

$$\sum_{m=0}^{\infty} \lambda^m \sum_{k=0}^{m} |\psi_n^k\rangle E_n^{m-k}$$

set common power of λ =

(equivalently differential $\frac{d^m}{d\lambda^m}$ and set $\lambda=0$) to

get

$m=0$

$$\boxed{H_0 |\psi_n^0\rangle = E_n^0 |\psi_n^0\rangle}$$

$m>0$

$$\boxed{H_0 |\psi_n^m\rangle + V |\psi_n^{m-1}\rangle = \sum_{k=0}^{m} |\psi_n^k\rangle E_n^{m-k}}$$

The first equation is the unperturbed equation which we assume is solved.

we would like to treat the second equation by induction — to do this we express $|\psi_n^m\rangle$ and E_n^m in terms of quantiti $E_n^k, |\psi_n^k\rangle$ with $k<m$

$$\boxed{H_0|\psi_n^m\rangle - E_n^0|\psi_n^m\rangle - E_n^m|\psi_n^0\rangle = -V|\psi_n^{m-1}\rangle + \sum_{k=1}^{m-1}|\psi_n^k\rangle E_n^{m-k}}$$

This equation has 2 unknown quantities on the left. — If we replace

$$|\psi_n^m\rangle \text{ by } |\psi_n^m\rangle + \eta|\psi_n^0\rangle$$

it is still a solution

since

$$(H_0 - E_n^0)(|\psi_n^m\rangle + \eta|\psi_n^0\rangle) = (H_0 - E_n^0)|\psi_n^m\rangle$$

and $|\psi_n^m\rangle$ only appears on the left.

to remove this ambiguity we choose $|\psi_n^m\rangle$ to be orthogonal to $|\psi_n^0\rangle$

$$\boxed{\langle\psi_n^0|\psi_n^m\rangle = 0 \quad m \neq 0}$$

(choice)

For this choice

$$|\psi_n\rangle = |\psi_n^0\rangle + |\chi\rangle$$

where $\langle\chi|\psi_n^0\rangle = 0$ which means

$$\langle\psi_n|\psi_n\rangle = \langle\psi_n^0|\psi_n^0\rangle + \langle\chi|\chi\rangle$$

This means that $|\psi_n^0\rangle$ and $|\psi_n\rangle$ cannot both be normalized to unity unless the difference $|\chi\rangle = |\psi_n\rangle - |\psi_n^0\rangle$ is 0.

To proceed we make the following 2 choices

$$\boxed{\begin{array}{lll} (1) & \langle \psi_n^0 | \psi_n^m \rangle = 0 & m \neq 0 \\ (2) & \langle \psi_k^0 | \psi_n^0 \rangle = 1 & \text{all } k \end{array}}$$

These conditions can be used to express $|\psi_n^m\rangle$ and E_n^m in terms of $|\psi_n^k\rangle$ and E_n^k for $k<m$

① To calculate E_n^m multiply on the left by $\langle \psi_n^0 |$.

Because $\underbrace{\langle \psi_n^0 | (H_0 - E_n^0)}_{0} | \psi_n^m \rangle =$

the unknown $|\psi_n^m\rangle$ is eliminated from the equation and

$$-E_n^m \underbrace{\langle \psi_n^0 | \psi_n^0 \rangle}_{\text{1 normalization assumption}} = -E_n^m =$$

$$-\langle \psi_n^0 | V | \psi_n^{m-1} \rangle + \sum_{k=1}^{m-1} \underbrace{\langle \psi_n^0 | \psi_n^k \rangle}_{\text{0 by orthogonality assumption}} E_n^{m-k}$$

$$= -\langle \psi_n^0 | V | \psi_n^{m-1} \rangle$$

Therefore

$$\boxed{E_n^m = \langle \psi_n^0 | V | \psi_n^{m-1} \rangle}$$

This expresses E_n^m in terms of $|\psi_n^k\rangle$ with $k < m$

(2) The next step is to calculate $|\psi_n^m\rangle$

This first step is to multiply by $\langle\psi_k^0|$ $k \neq n$. This gives

$$\langle\psi_k^0|(H_0 - E_n^0)|\psi_n^m\rangle - E_n^m \underbrace{\langle\psi_k^0|\psi_n^0\rangle}_{0 \quad k\neq n}$$

$$= -\langle\psi_k^0|V|\psi_n^{m-1}\rangle + \sum_{\ell=1}^{m-1}\langle\psi_k^0|\psi_n^\ell\rangle E_n^{m-\ell}$$

or

$$(E_n^0 - E_k^0)\langle\psi_k^0|\psi_n^m\rangle =$$

$$\langle\psi_k^0|V|\psi_n^{m-1}\rangle - \sum_{\ell=1}^{m-1}\langle\psi_k^0|\psi_n^\ell\rangle E_n^{m-\ell}$$

since $E_n^0 - E_k^0 \neq 0$ for $k \neq n$ (non degeneracy assumption) we can divide by $E_n^0 - E_m^0$

$$\langle\psi_k^0|\psi_n^m\rangle = \frac{\langle\psi_k^0|V|\psi_n^{m-1} - \sum_{\ell=1}^{m-1}\langle\psi_k^0|\psi_n^\ell\rangle E_n^{m-\ell}}{E_n^0 - E_m^0}$$

using completeness of the unperturbed eigenstates and the condition $\langle\psi_n^0|\psi_n^m\rangle = 0$ for $m \neq n$

$$\boxed{\begin{aligned} |\psi_n^m\rangle &= \sum_{k=0}^{\infty} |\psi_k^0\rangle\langle\psi_k^0|\psi_n^m\rangle = \\ &\sum_{k\neq n} |\psi_k^0\rangle\langle\psi_k^0|\psi_n^m\rangle = \\ &\sum_{k\neq n} |\psi_k^0\rangle \left\{ \frac{\langle\psi_k^0|V|\psi_n^{m-1}\rangle - \sum_{\ell=1}^{m-1} \langle\psi_k^0|\psi_n^\ell\rangle E_n^{m-\ell}}{E_n^0 - E_k^0} \right\} \end{aligned}}$$

where the denominator is not 0 because n is excluded from the sum.

Comments

* when V is small usually it is only necessary to consider corrections involving the

lowest non zero power of V

case m=1

$$\boxed{\begin{aligned} E_1^n &= \langle \psi_n^0 | V | \psi_n^0 \rangle \\ |\psi_n^1\rangle &= \sum_{m \neq n} |\psi_m^0\rangle \frac{\langle \psi_m^0 | V | \psi_n^0 \rangle}{E_n^0 - E_m^0} \end{aligned}}$$

comments

(1) in many cases

$\langle \psi_n^0 | V | \psi_n^0 \rangle = 0$

so it may be necessary to go to second order in V.

(2) while the wave function is formally an infinite expansion, often all but a finite number of the $\langle \psi_m^0 | V | \psi_n^0 \rangle = 0$

case $m = 2$

$$E_n^2 = \langle \psi_n^0 | V | \psi_n^1 \rangle =$$

$$\sum_{m \neq n} \frac{\langle \psi_n^0 | V | \psi_m^0 \rangle \langle \psi_m^0 | V | \psi_n^0 \rangle}{E_n^0 - E_m^0} =$$

$$\sum_{m \neq n} \frac{|\langle \psi_n^0 | V | \psi_m^0 \rangle|^2}{E_n^0 - E_m^0}$$

$$|\psi_n^2\rangle = \sum_{m \neq n} |\psi_m^0\rangle \times$$

$$\left[\frac{\langle \psi_m^0 | V | \psi_n^1 \rangle - \langle \psi_m^0 | \psi_n^1 \rangle E_n^1}{E_n^0 - E_m^0} \right] =$$

$$\sum_{\substack{m \neq n \\ k \neq n}} \left[\frac{\langle \psi_m^0 | V | \psi_k^0 \rangle \langle \psi_k^0 | V | \psi_n^0 \rangle}{(E_n^0 - E_m^0)(E_n^0 - E_k^0)} \right]$$

$$- \sum_{m \neq n} \frac{\langle \psi_m^0 | V | \psi_n^0 \rangle \langle \psi_n^0 | V | \psi_n^0 \rangle}{(E_n^0 - E_m^0)^2}$$

remarks — if E_n^0 is the ground state energy $E_n^2 \leq 0$

examples

Anharmonic Oscillator

$$H_0 = \frac{1}{2}(p^2 + q^2) \qquad [q,p] = i$$

$$q = \frac{1}{\sqrt{2}}(a + a^\dagger) \qquad p = \frac{i}{\sqrt{2}}(a^\dagger - a)$$

$$a = \frac{1}{\sqrt{2}}(q + ip) \qquad a^\dagger = \frac{1}{\sqrt{2}}(q - ip)$$

$$[a, a^\dagger] = \frac{1}{2}[q + ip, q - ip]$$

$$= \frac{1}{2}(i[p\,q] - i[q,p])$$

$$= \frac{1}{2}(1 + 1) = 1$$

$$\frac{1}{2}(p^2 + q^2) = \frac{1}{2}\Big(-\frac{1}{2}(a^\dagger a^\dagger + a^\dagger a - a a^\dagger - aa)$$

$$+ \frac{1}{2}(a^\dagger a^\dagger + a a^\dagger + a^\dagger a + aa)\Big)$$

$$= \frac{1}{4}(2a^\dagger a + 2 a a^\dagger)$$

$$= \frac{1}{2}(a^\dagger a + a^\dagger a - a^\dagger a + a a^\dagger)$$

$$= a^\dagger a + \frac{1}{2}[a, a^\dagger]$$

$$= a^\dagger a + \frac{1}{2}$$

$$H = H_0 + V$$

$$H_0 = a^+ a + \frac{1}{2} = \frac{1}{2}(p^2 + q^2)$$

$$V = \lambda q^4 = \frac{\lambda}{4}(a + a^+)^4$$

$$E_n^1 = \langle n | V | n \rangle$$

$$\frac{1}{2}(a + a^+)^2 | n \rangle$$

$$\frac{1}{2}(a + a^+)\left(|n+1\rangle \sqrt{n+1} + |n-1\rangle \sqrt{n} \right) =$$

$$\frac{1}{2}\left(|n\rangle (n+1) \quad |n+2\rangle \sqrt{(n+1)(n+2)} \right.$$
$$\left. + |n\rangle n + |n-2\rangle \sqrt{n(n-1)} \right)$$

$$E_n^1 = \lambda \frac{1}{4}\left((2n+1)^2 + (n+1)(n+2) + n(n-1) \right)$$

$$\frac{\lambda}{4}(6n^2 + 6n + 3)$$

$$\boxed{E = \left(n + \frac{1}{2}\right) + \frac{\lambda}{4}(6n^2 + 6n + 3) + O(\lambda^2)}$$

example 2

$$H_0 = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}$$

$$V = \eta \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$E_1^0 = E_1 \qquad \psi_1^0 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$E_2^0 = E_2 \qquad \psi_2^0 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

$$E_3^0 = E_3 \qquad \psi_3^0 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$E_1^1 = (1\ 0\ 0)\,\eta \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 0$$

$$E_2^1 = (0\ 1\ 0)\,\eta \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0$$

$$E_3^1 = (0\ 0\ 1)\,\eta \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \eta$$

we can calculate the second order correction to E_1 and E_2

$$\Delta E_1^2 = \frac{|\langle \psi_1^0 | V | \psi_2^0 \rangle|^2}{E_1^0 - E_2^0} + \frac{|\langle \psi_1^0 | V | \psi_3^0 \rangle|^2}{E_1^0 - E_3^0}$$

$$= \eta^2 \frac{\left| (1\ 0\ 0) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \right|^2}{E_1 - E_2} + \eta^2 \frac{\left| (1\ 0\ 0) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \right|^2}{E_1 - E_3}$$

$$= \frac{\eta^2}{E_1 - E_2} + 0$$

similarly

$$\Delta E_2^2 = \frac{|\langle \psi_2^0 | V | \psi_1^0 \rangle|^2}{E_2^0 - E_1^0} + \frac{|\langle \psi_2^0 | V | \psi_3^0 \rangle|^2}{E_2 - E_3} =$$

$$\eta^2 \frac{\left| (0\ 1\ 0) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \right|^2}{E_2 - E_1} + \eta^2 \frac{\left| (0\ 1\ 0) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \right|^2}{E_2 - E_3}$$

$$= \frac{\eta^2}{E_2 - E_1} + 0$$

Typically if H_0 is solvable it is generally simple. This often occurs when there is a symmetry that commutes with H_0. Then

if

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

$$H_0 S |\psi_n^0\rangle = S H_0 |\psi_n^0\rangle = E_n^0 S |\psi_n^0\rangle$$

this means that if

$$|\psi_n^0\rangle \neq S |\psi_n^0\rangle$$

then the states $|\psi_n^0\rangle$ and $S|\psi_n^0\rangle$ have identical eigenvalues and non degenerate perturbation theory is not applicable.

To treat the degenerate case assume H_0 has N states with eigenvalue E^0. We can relable the states so

$$E_n^0 = E^0 \qquad n \leq N$$
$$E_n^0 \neq E^0 \qquad n > N$$

We can also choose $|\psi_n^0\rangle$ for $n \leq N$ to be orthogonal

Let $$P_N = \sum_{n=1}^{N} |\psi_n^0\rangle\langle\psi_n^0|$$

Then $$P_N = P_N^{\dagger} = P_N^2$$

so P_N is an orthogonal projection. Define

$$H_N = P_N H P_N$$

H_N is an $N \times N$ Hermitian matrix. It has the form

$$P_N H P_N = E\delta_{nm} + V_{mn}$$

where

$$V_{mn} = \langle \varphi^0_m | V | \varphi^0_n \rangle \qquad m, n \leq N$$

since this matrix is not diagonal due to the non diagonal potential term it can be diagonalized

$$P_N H P_N | \tilde{\varphi}_n \rangle = \tilde{E}_n | \hat{\varphi}_n \rangle \qquad n = 1 \cdots N$$

normally this is enough to determine the effect of V - in this case this goes beyond first order

To go further we define

$$Q = I - P \qquad P \cdot Q = 0$$

$$Q^2 = Q^+ = Q$$

$$H = PHP + QHQ + QHP + PHQ$$

$$H = (Q+P)(H_0 + V)(Q+P) =$$

$$= PHP + QHP + PHQ + QHQ$$

since $[H_0, Q] = [H_0 P] = 0$

$$= PHP + QH_0Q + QVP + PVQ + QVQ$$

In this case we define a new $\tilde{H}_0$ by

$$\tilde{H}_0 = PHP + QH_0Q$$

The eigenstates and eigenvalues of $\tilde{H}_0$ are known

$$\tilde{E}_n^0 = \begin{cases} \tilde{E}_n & n \leq N \\ E_n^0 & n > N \end{cases}$$

$$\tilde{\psi}_n^0 = \begin{cases} \tilde{\psi}_n & n \leq N \\ \psi_n^0 & n > N \end{cases}$$

$$\tilde{V} = QVP + PVQ + QVQ$$

Then we can proceed using non degenerate perturbation theory with this new decomposition - in this case there are no additional first order corrections to the previously degenerate states since

$$\underbrace{\langle \tilde{\psi}_n | (\underline{\underline{Q}} VP + PV\underline{\underline{Q}} + \underline{\underline{Q}} V \underline{\underline{Q}}) | \tilde{\psi}_n \rangle}_{P|\tilde{\psi}_n\rangle = |\tilde{\psi}_n\rangle} = 0$$

for $n \leq N$.