Perturbation theory

Stationary perturbation methods

Let us suppose that

- we have solved completely the problem
$$H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle.$$
The basis $\{|n^{(0)}\rangle\}$ is now complete.
- the states $|n^{(0)}\rangle$ are non degenerate.
- we want to solve the problem
$$(H_0+\lambda V)|n\rangle_\lambda = E_n^{(\lambda)}|n\rangle_\lambda.$$
Usualy the index λ is dropped off.

When we denote
$$\Delta_n \equiv E_n - E_n^{(0)},$$
the eigenvalue equation to be solved takes the form
$$(E_n^{(0)}-H_0)|n\rangle = (\lambda V - \Delta_n)|n\rangle.$$

Note Because the expression $(E_n^{(0)}-H_0)^{-1}|n^{(0)}\rangle$ is undefined the operator $(E_n^{(0)}-H_0)^{-1}$ is not well defined. So, in the equation above we cannot invert the operator $(E_n^{(0)}-H_0)$.
Now
$$\langle n^{(0)}|\lambda V-\Delta_n|n\rangle = \langle n^{(0)}|E_n^{(0)}-H_0|n\rangle,$$
so in the state $(\lambda V-\Delta_n)|n\rangle$ there is no component along the state $|n^{(0)}\rangle$.
We define a projection operator as
$$\phi_n = 1-|n^{(0)}\rangle\langle n^{(0)}| = \sum_{k\neq n}|k^{(0)}\rangle\langle k^{(0)}|.$$
Now
$$\frac{1}{E_n^{(0)}-H_0}\phi_n = \sum_{k\neq n}\frac{1}{E_n^{(0)}-E_k^{(0)}}|k^{(0)}\rangle\langle k^{(0)}|$$
and
$$(\lambda V-\Delta_n)|n\rangle = \phi_n(\lambda V-\Delta_n)|n\rangle.$$
Since in the limit $\lambda\to 0$ we must have
$$|n\rangle \to |n^{(0)}\rangle,$$
the formal solution is of the form
$$|n\rangle = c_n(\lambda)|n^{(0)}\rangle + \frac{1}{E_n^{(0)}-H_0}\phi_n(\lambda V-\Delta_n)|n\rangle,$$
where
$$\lim_{\lambda\to 0} c_n(\lambda) = 1$$
and
$$c_n(\lambda) = \langle n^{(0)}|n\rangle.$$
Diverting from the normal procedure we normalize
$$\langle n^{(0)}|n\rangle = c_n(\lambda) = 1.$$

We write
$$\begin{aligned}|n\rangle &= |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots\\ \Delta_n &= \lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \cdots.\end{aligned}$$
Because
$$\langle n^{(0)}|\lambda V-\Delta_n|n\rangle = 0,$$
we have, on the other hand
$$\Delta_n = \lambda\langle n^{(0)}|V|n\rangle.$$
Thus we get
$$\begin{aligned}&\lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \cdots\\ &\quad= \lambda\langle n^{(0)}|V|n^{(0)}\rangle + \lambda^2\langle n^{(0)}|V|n^{(1)}\rangle + \cdots.\end{aligned}$$
Equalizing the coefficients of the powers of the parameter λ we get
$$\begin{array}{lcll}\mathcal{O}(\lambda^1): & \Delta_n^{(1)} &=& \langle n^{(0)}|V|n^{(0)}\rangle\\ \mathcal{O}(\lambda^2): & \Delta_n^{(2)} &=& \langle n^{(0)}|V|n^{(1)}\rangle\\ \vdots & \vdots & & \\ \mathcal{O}(\lambda^N): & \Delta_n^{(N)} &=& \langle n^{(0)}|V|n^{(N-1)}\rangle\\ \vdots & \vdots & & \end{array}.$$
We substitute into the expression
$$|n\rangle = |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)}-H_0}(\lambda V-\Delta_n)|n\rangle$$
for the state vector the power series of the state vector and the energy correction and we get
$$\begin{aligned}&|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots\\ &\quad= |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)}-H_0}(\lambda V - \lambda\Delta_n^{(1)} - \lambda^2\Delta_n^{(2)} - \cdots)\\ &\quad\quad\times(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \cdots).\end{aligned}$$
Equalizing the coefficients of the linear λ-terms we get in the first order
$$\begin{aligned}&\mathcal{O}(\lambda):\ |n^{(1)}\rangle\\ &\quad= \frac{\phi_n}{E_n^{(0)}-H_0}V|n^{(0)}\rangle - \frac{\Delta_n^{(1)}}{E_n^{(0)}-H_0}\phi_n|n^{(0)}\rangle\\ &\quad= \frac{\phi_n}{E_n^{(0)}-H_0}V|n^{(0)}\rangle,\end{aligned}$$
because
$$\phi_n\Delta_n^{(1)}|n^{(0)}\rangle = 0.$$
We substitute $|n^{(1)}\rangle$ into the expression
$$\Delta_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle,$$
so
$$\Delta_n^{(2)} = \langle n^{(0)}|V\frac{\phi_n}{E_n^{(0)}-H_0}V|n^{(0)}\rangle.$$

We substitute this further into the power series of the state vectors and we get for the coeffients of λ^2 the condition

$$\mathcal{O}(\lambda^2): \ |n^{(2)}\rangle = \frac{\phi_n}{E_n^{(0)} - H_0} V \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle - \frac{\phi_n}{E_n^{(0)} - H_0} \langle n^{(0)}|V|n^{(0)}\rangle \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle.$$

Likewise we could continue to higher powers of the parameter λ. This method is known as the *Rayleigh-Schrödinger perturbation theory.*

The explicit expression for the second order energy correction will be

$$\begin{aligned}\Delta_n^{(2)} &= \langle n^{(0)}|V \frac{\phi_n}{E_n^{(0)} - H_0} V|n^{(0)}\rangle \\ &= \sum_{k,l} \langle n^{(0)}|V|k^{(0)}\rangle\langle k^{(0)}|\frac{\phi_n}{E_n^{(0)} - H_0}|l^{(0)}\rangle\langle l^{(0)}|V|n^{(0)}\rangle \\ &= \sum_{k,l\neq n} V_{nk} \frac{\langle k^{(0)}|l^{(0)}\rangle}{E_n^{(0)} - E_l^{(0)}} V_{ln} \\ &= \sum_{k\neq n} \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}}.\end{aligned}$$

Thus, up to the second order we have

$$\begin{aligned}\Delta_n &\equiv E_n - E_n^{(0)} \\ &= \lambda V_{nn} + \lambda^2 \sum_{k\neq n} \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} + \cdots.\end{aligned}$$

Correspondingly, up to the second order the state vector is

$$\begin{aligned}|n\rangle = |n^{(0)}\rangle &+ \lambda \sum_{k\neq n} |k^{(0)}\rangle \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \\ &+ \lambda^2 \sum_{k\neq n} |k^{(0)}\rangle \left(\sum_{l\neq n} \frac{V_{kl}V_{ln}}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})} - \frac{V_{nn}V_{kn}}{(E_n^{(0)} - E_k^{(0)})^2} \right) \\ &+ \cdots.\end{aligned}$$

We see that the perturbation *mixes* in also other states (than $|n^{(0)}\rangle$).

We see that

- in the 1st order we need only the matrix element V_{nn}.
- in the 2nd order the energy levels i and j repel each other. Namely, if $E_i^{(0)} < E_j^{(0)}$, then the contributions of one of these states to the energy corrections of the other are

$$\begin{aligned}\Delta_i^{(2)} &= \frac{|V_{ij}|^2}{E_i^{(0)} - E_j^{(0)}} < 0 \\ \Delta_j^{(2)} &= \frac{|V_{ij}|^2}{E_j^{(0)} - E_i^{(0)}} > 0\end{aligned}$$

  and the energy levels move apart from each other.

Perturbation expansions converge if $|V_{ij}/(E_i^{(0)} - E_j^{(0)})|$ is "small". In general, no exact convergence criterion is known.

The state $|n\rangle$ is not normalized. We define the normalized state

$$|n\rangle_N = Z_n^{1/2}|n\rangle,$$

so that

$$\langle n^{(0)}|n\rangle_N = Z_n^{1/2}\langle n^{(0)}|n\rangle = Z_n^{1/2}.$$

Thus the normalization factor Z_n is the probablility for the perturbed state to be in the unperturbed state.

The normalization condition

$${}_N\langle n|n\rangle_N = Z_n\langle n|n\rangle = 1$$

gives us

$$\begin{aligned}Z_n^{-1} &= \langle n|n\rangle = (\langle n^{(0)}| + \lambda\langle n^{(1)}| + \lambda^2\langle n^{(2)}| + \cdots) \\ &\quad \times(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots) \\ &= 1 + \lambda^2\langle n^{(1)}|n^{(1)}\rangle + \mathcal{O}(\lambda^3) \\ &= 1 + \lambda^2 \sum_{k\neq n} \frac{|V_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2} + \mathcal{O}(\lambda^3).\end{aligned}$$

Up to the order λ^2 the probability for the perturbed state to lie in the unperturbed state is thus

$$Z_n \approx 1 - \lambda^2 \sum_{k\neq n} \frac{|V_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2}.$$

The latter term can be interpreted as the probability for the "leakage" of the system from the state $|n^{(0)}\rangle$ to other states.

Example The quadratic Stark effect.

We consider hydrogen like atoms, i.e. atoms with one electron outside a closed shell, under external uniform electric field parallel to the positive z-axis. Now

$$H_0 = \frac{\boldsymbol{p}^2}{2m} + V_0(r) \text{ and } V = -e|\boldsymbol{E}|z.$$

We suppose that the eigenstates of H_0 are non degenerate (not valid for hydrogen). The energy shift due to the external field is

$$\Delta_k = -e|\boldsymbol{E}|z_{kk} + e^2|\boldsymbol{E}|^2 \sum_{j\neq k} \frac{|z_{kj}|^2}{E_k^{(0)} - E_j^{(0)}} + \cdots,$$

where

$$z_{kj} = \langle k^{(0)}|z|j^{(0)}\rangle.$$

Since we assumed the states $|k^{(0)}\rangle$ to be non degenerate they are eigenstates of the parity. So, according to the parity selection rule the matrix element of z_{kk} vanishes. Indeces k and j are collective indeces standing for the quantum number triplet (n, l, m). According to the Wigner-Eckart theorem we have

$$\begin{aligned}z_{kj} &= \langle n', l'm'|z|n, lm\rangle \\ &= \langle l1; m0|l1; l'm'\rangle \frac{\langle n'l'\|T^{(1)}\|nl\rangle}{\sqrt{2l+1}},\end{aligned}$$

where we have written the operator z as the spherical tensor

$$T_0^{(1)} = z.$$

In order to satisfy $z_{kj} \neq 0$ we must have

- $m' = m$ and
- $l' = l-1, l, l+1$. From these $l' = l$ is not suitable due to the parity selection rule.

So we get

$$\langle n', l'm'|z|n, lm\rangle = 0 \text{ unless } \begin{cases} l' = l \pm 1 \\ m' = m \end{cases}.$$

We define the polarizability α so that

$$\Delta = -\frac{1}{2}\alpha|\boldsymbol{E}|^2.$$

As a special case we consider the ground state $|0^{(0)}\rangle = |1,00\rangle$ of hydrogen atom which is non degenerate when we ignore the spin. The perturbation expansion gives

$$\alpha = -2e^2 \sum_{k\neq 0}^{\infty} \frac{|\langle k^{(0)}|z|1,00\rangle|^2}{E_0^{(0)} - E_k^{(0)}},$$

where the summing must be extended also over the continuum states.
Let us suppose that

$$E_0^{(0)} - E_k^{(0)} \approx \text{constant},$$

so that

$$\begin{aligned}\sum_{k\neq 0} |\langle k^{(0)}|z|1,00\rangle|^2 &= \sum_{\text{all } k\text{'s}} |\langle k^{(0)}|z|1,00\rangle|^2 \\ &= \langle 1,00|z^2|1,00\rangle.\end{aligned}$$

In the spherically symmetric ground state we obviously have

$$\langle z^2\rangle = \langle x^2\rangle = \langle y^2\rangle = \frac{1}{3}\langle r^2\rangle.$$

Using the explicit wave functions we get

$$\langle z^2\rangle = a_0^2.$$

Now

$$-E_0^{(0)} + E_k^{(0)} \geq -E_0^{(0)} + E_1^{(0)} = \frac{e^2}{2a_0}\left[1 - \frac{1}{4}\right],$$

so

$$\alpha < 2e^2 a_0^2 \frac{8a_0}{3e^2} = \frac{16a_0^3}{3} \approx 5.3a_0^3.$$

The exact summation gives

$$\alpha = \frac{9a_0^3}{2} = 4.5a_0^3.$$

Degeneracy
Let's suppose that the energy state $E_D^{(0)}$ is g-foldly degenerated:

$$H_0|m^{(0)}\rangle = E_D^{(0)}|m^{(0)}\rangle,\ \forall|m^{(0)}\rangle \in D,\ \dim D = g.$$

We want to solve the problem

$$(H_0 + \lambda V)|l\rangle = E_l|l\rangle$$

with the boundary condition

$$\lim_{\lambda\to 0}|l\rangle \to \sum_{m\in D}\langle m^{(0)}|l^{(0)}\rangle|m^{(0)}\rangle,$$

i.e. we are looking for corrections to the degenerated states. With the help of the energy correction we have to solve

$$(E_D^{(0)} - H_0)|l\rangle = (\lambda V - \Delta_l)|l\rangle.$$

We write again

$$\begin{aligned}|l\rangle &= |l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \lambda^2|l^{(2)}\rangle + \cdots \\ \Delta_l &= \lambda\Delta_l^{(1)} + \lambda^2\Delta_l^{(2)} + \cdots,\end{aligned}$$

so we get

$$\begin{aligned}&(E_D^{(0)} - H_0)(|l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \lambda^2|l^{(2)}\rangle + \cdots) \\ &= (\lambda V - \lambda\Delta_l^{(1)} - \lambda^2\Delta_l^{(2)} - \cdots) \\ &\quad\times(|l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \lambda^2|l^{(2)}\rangle + \cdots).\end{aligned}$$

Equalizing the coefficients of the powers of λ we get in the first order

$$\begin{aligned}&(E_D^{(0)} - H_0)|l^{(1)}\rangle \\ &= (V - \Delta_l^{(1)})|l^{(0)}\rangle \\ &= (V - \Delta_l^{(1)})\left[\sum_{m\in D}|m^{(0)}\rangle\langle m^{(0)}|l^{(0)}\rangle\right].\end{aligned}$$

Taking the scalar product with the vector $\langle m'^{(0)}|$ and recalling that

$$\langle m'^{(0)}|(E_D^{(0)} - H_0) = 0,$$

we end up with the simultaneous eigenvalue equations

$$\sum_m V_{m'm}\langle m^{(0)}|l^{(0)}\rangle = \Delta_l^{(1)}\langle m'^{(0)}|l^{(0)}\rangle.$$

The energy corrections $\Delta_l^{(1)}$ are obtained as eigenvalues. From the equation

$$(E_D^{(0)} - H_0)|l^{(1)}\rangle = (\lambda V - \Delta_l)|l^{(0)}\rangle$$

we also see that

$$\langle m^{(0)}|V - \Delta_l^{(1)}|l^{(0)}\rangle = 0\ \forall|m^{(0)}\rangle \in D.$$

Thus the vector $(V - \Delta_l^{(1)})|l^{(0)}\rangle$ has no components in the subspace D. Defining a projection operator as

$$\phi_D = 1 - \sum_{m\in D}^{g}|m^{(0)}\rangle\langle m^{(0)}| = \sum_{k\notin D}|k^{(0)}\rangle\langle k^{(0)}|$$

we can write

$$(V-\Delta_l^{(1)})|l^{(0)}\rangle = \phi_D(V-\Delta_l^{(1)})|l^{(0)}\rangle = \phi_D V|l^{(0)}\rangle.$$

We get the equation

$$(E_D^{(0)}-H_0)|l^{(1)}\rangle = \phi_D(\lambda V-\Delta_l)|l^{(0)}\rangle,$$

where now the operator $(E_D^{(0)}-H_0)$ can be inverted:

$$\begin{aligned}|l^{(1)}\rangle &= \frac{\phi_D}{E_D^{(0)}-H_0}V|l^{(0)}\rangle \\ &= \sum_{k\notin D}\frac{|k^{(0)}\rangle V_{kl}}{E_D^{(0)}-E_k^{(0)}}.\end{aligned}$$

When we again normalize

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

we get from the equation

$$(E_D^{(0)}-H_0)|l\rangle = (\lambda V-\Delta_l)|l\rangle$$

for the energy shift

$$\Delta_l = \lambda\langle l^{(0)}|V|l\rangle.$$

We substitute the power series and get

$$\begin{aligned}&\lambda\langle l^{(0)}|V(|l^{(0)}\rangle+\lambda|l^{(1)}\rangle+\lambda^2|l^{(2)}\rangle+\cdots) \\ &\quad= \lambda\Delta_l^{(1)}+\lambda^2\Delta_l^{(2)}+\cdots.\end{aligned}$$

The second order energy correction is now

$$\begin{aligned}\Delta_l^{(2)} &= \langle l^{(0)}|V|l^{(1)}\rangle = \langle l^{(0)}|V\frac{\phi_D}{E_D^{(0)}-H_0}V|l^{(0)}\rangle \\ &= \sum_{k\notin D}\frac{|V_{kl}|^2}{E_D^{(0)}-E_k^{(0)}}.\end{aligned}$$

Thus the perturbation calculation in a degenerate system proceeds as follows:

1° Identify the degenerated eigenstates. We suppose that their count is g. Construct the $g\times g$-perturbation matrix V.

2° Diagonalize the perturbation matrix.

3° The resulting eigenvalues are first order corrections for the energy shifts. The corresponding eigenvectors are those zeroth order eigenvectors to which the corrected eigenvectors approach when $\lambda\to 0$.

4° Evaluate higher order corrections using non degenerate perturbation methods but omit in the summations all contributions coming from the degenerated state vectors of the space D.

Example The Stark efect in the hydrogen atom. The hydrogen 2s $(n=2, l=0, m=0)$ and 2p $(n=2, l=1, m=-1,0,1)$ states are degenerate. Their energy is

$$E_D^{(0)} = -e^2/8a_0.$$

We put the atom in external electric field parallel to the z-axis:

$$V = -ez|\boldsymbol{E}|.$$

Now z is the $q=0$ component of a spherical tensor:

$$z = T_0^{(1)}.$$

According to the parity selection rule the operator V now has nonzero matrix elements only between states with $l=0$ and $l=1$, and due to the m-selection rule all states must have the same m:

$$V = \begin{array}{c} \\ 2s \\ 2p,0 \\ 2p,1 \\ 2p,-1\end{array}\begin{array}{c}\begin{array}{cccc}2s & 2p,0 & 2p,1 & 2p,-1\end{array}\\ \left(\begin{array}{cccc}0 & \times & 0 & 0\\ \times & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{array}\right)\end{array}.$$

The nonzero matrix elements are

$$\langle 2s|V|2p, m=0\rangle = \langle 2p, m=0|V|2s\rangle = 3ea_0|\boldsymbol{E}|.$$

The eigenvalues of the perturbation matrix are

$$\Delta_\pm^{(1)} = \pm 3ea_0|\boldsymbol{E}|$$

and the eigenvectors

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|2s, m=0\rangle \pm |2p, m=0\rangle).$$

Note The energy shift is a linear function of the electric field. The states $|\pm\rangle$ are not parity eigenstates so it is perfectly possible that they have permanent electric dipole moment $\langle z\rangle \neq 0$.

Nearly degenerated states

Let the states $m\in D$ to be almost degenerate. We write

$$V = V_1 + V_2,$$

where

$$\begin{aligned}V_1 &= \sum_{m\in D}\sum_{m'\in D}|m^{(0)}\rangle\langle m^{(0)}|V|m'^{(0)}\rangle\langle m'^{(0)}| \\ V_2 &= V - V_1.\end{aligned}$$

We proceed so that

1. we diagonalize the Hamiltonian H_0+V_1 exactly in the basis $\{|m^{(0)}\rangle\}$ and
2. handle the term V_2 like in an ordinary non degenerate perturbation theory. This is possible since

$$\langle m'^{(0)}|V_2|m^{(0)}\rangle = 0 \quad \forall m, m'\in D.$$

Example Weak periodic potential.
Now

$$H_0 = \frac{p^2}{2m}$$

and for the perturbation

$$V(x) = V(x+a).$$

We denote the unperturbed eigenstates by the wave vector:

$$H_0|k\rangle = \frac{\hbar^2 k^2}{2m}|k\rangle,$$

so that

$$E_k^{(0)} = \frac{\hbar^2 k^2}{2m}.$$

We impose the periodic boundary conditions

$$\langle x'|k\rangle = \psi_k(x') = \langle x'+L|k\rangle = \psi_k(x'+L),$$

for the wave function and get

$$\psi_k(x') = \frac{1}{\sqrt{L}}e^{ikx'},\ k = \frac{2\pi}{L}n, n \in I.$$

Because the potential V is periodic it can be represented as the Fourier series

$$V(x) = \sum_{n=-\infty}^{\infty} e^{inKx}V_n,$$

where

$$K = 2\pi/a$$

is the *reciprocal lattice vector*. The only nonzero matrix elements are now

$$\langle k+nK|V|k\rangle = V_n,$$

because

$$\begin{aligned}\langle k'|V|k\rangle &= \frac{1}{L}\sum_n V_n \int dx' e^{-ik'x'}e^{inKx'}e^{inkx'} \\ &= \sum_n V_n \delta_{k+nK,k'}.\end{aligned}$$

So the potential couples states

$$|k\rangle, |k+K\rangle, \ldots, |k+nK\rangle, \ldots.$$

The corresponding energy denominators are

$$E_k^{(0)} - E_{k+nK}^{(0)}.$$

In general

$$E_k^{(0)} \neq E_{k+nK}^{(0)}$$

except when

$$k \approx -\frac{nK}{2}.$$

We suppose that the condition

$$k \neq -\frac{nK}{2}$$

holds safely. The first order state vectors are then

$$|k^{(1)}\rangle = |k\rangle + \sum_{n\neq 0}|k+nK\rangle\frac{V_n}{E_k^{(0)} - E_{k+nK}^{(0)}},$$

and the wave functions

$$\psi_k^{(1)}(x') = \frac{1}{\sqrt{L}}e^{ikx'} + \sum_{n\neq 0}\frac{1}{\sqrt{L}}e^{i(k+nK)x'}\frac{V_n}{E_k^{(0)} - E_{k+nK}^{(0)}}.$$

Correspondingly the energy up to the second order is

$$E_k^{(2)} = E_k^{(0)} + V_0 + \sum_{n\neq 0}\frac{|V_n|^2}{E_k^{(0)} - E_{k+nK}^{(0)}}.$$

Let us suppose now that

$$k \approx -\frac{nK}{2}.$$

We diagonalize the Hamiltonian in the basis

$$\{|k\rangle, |k+nK\rangle\},$$

i.e. we diagonalize the matrix

$$\begin{array}{c} \\ |k\rangle \\ |k+nK\rangle \end{array}\begin{array}{c} \begin{array}{cc} |k\rangle & \quad |k+nK\rangle \end{array} \\ \begin{pmatrix} E_k^{(0)} + V_0 & V_n^* \\ V_n & E_k^{(0)} + V_0 \end{pmatrix} \end{array}.$$

Its eigenvalues are

$$\begin{aligned}E_{k\pm} = V_0 &+ \frac{E_k^{(0)} + E_{k+nK}^{(0)}}{2} \\ &\pm\sqrt{\left(\frac{E_k^{(0)} - E_{k+nK}^{(0)}}{2}\right)^2 + |V_n|^2}.\end{aligned}$$

When $|E_k^{(0)} - E_{k+nK}^{(0)}| \gg |V_n|$, it reduces to two solutions

$$\begin{aligned}E_{k+} &= E_k^{(0)} + V_0 \\ E_{k-} &= E_{k+nK}^{(0)} + V_0,\end{aligned}$$

which are first order corrected energies. In the limiting case we get

$$\lim_{k\to -nK/2} E_{k\pm} = E_{nK/2}^{(0)} + V_0 \pm |V_n|.$$

Brillouin-Wigner perturbation theory
We start with the Schrödinger equation

$$(E_n - H_0)|n\rangle = \lambda V|n\rangle,$$

and take on both sides the scalar product with the state $|m^{(0)}\rangle$, and get

$$(E_n - E_m^{(0)})\langle m^{(0)}|n\rangle = \lambda\langle m^{(0)}|V|n\rangle.$$

We correct the state $|n^{(0)}\rangle$. We write the corrected state $|n\rangle$ in the form

$$\begin{aligned}|n\rangle &= \sum_m |m^{(0)}\rangle\langle m^{(0)}|n\rangle = |n^{(0)}\rangle\langle n^{(0)}|n\rangle + \phi_n|n\rangle \\ &= |n^{(0)}\rangle + \sum_{m\neq n}|m^{(0)}\rangle\langle m^{(0)}|n\rangle,\end{aligned}$$

which has been normalized, like before,

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

We substitute into this the scalar products

$$\langle m^{(0)}|n\rangle = \frac{\lambda\langle m^{(0)}|V|n\rangle}{E_n - E_m^{(0)}},$$

and end up with the fundamental equation of the *Brillouin-Wigner method*

$$|n\rangle = |n^{(0)}\rangle + \sum_{m\neq n} |m^{(0)}\rangle \frac{\lambda}{E_n - E_m^{(0)}} \langle m^{(0)}|V|n\rangle.$$

Iteration gives us the series

$$\begin{aligned}
|n\rangle &= |n^{(0)}\rangle + \lambda \sum_{m\neq n} |m^{(0)}\rangle \frac{1}{E_n - E_m^{(0)}} \langle m^{(0)}|V|n^{(0)}\rangle \\
&\quad + \lambda^2 \sum_{m\neq n} \sum_{l\neq n} |l^{(0)}\rangle \frac{1}{E_n - E_l^{(0)}} \langle l^{(0)}|V|m^{(0)}\rangle \\
&\qquad \times \frac{1}{E_n - E_m^{(0)}} \langle m^{(0)}|V|n^{(0)}\rangle \\
&\quad + \lambda^3 \sum_{m\neq n} \sum_{l\neq n} \sum_{k\neq n} |k^{(0)}\rangle \frac{1}{E_n - E_k^{(0)}} \langle k^{(0)}|V|l^{(0)}\rangle \\
&\qquad \times \frac{1}{E_n - E_l^{(0)}} \langle l^{(0)}|V|m^{(0)}\rangle \frac{1}{E_n - E_m^{(0)}} \langle m^{(0)}|V|n^{(0)}\rangle \\
&\quad + \cdots .
\end{aligned}$$

Note This is not a power series of the parameter λ because the energy denominators

$$E_n - E_m^{(0)} = E_n^{(0)} - E_m^{(0)} + \Delta_n$$

depend also on the parameter λ according to the equation

$$\Delta_n = \lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \cdots$$