Perturbation theory

Very few quantum mechanics problems can be solved analytically (exactly).
Typically, perturbation theory is implemented in such a way that Hamiltonian consist on two parts: H_0 which we can solve analytically and the V part that is considered as a small "perturbation".
We will consider several different cases:
Hamiltonian does not depend on time and the energy eigenvalues are non-degenerate
Hamiltonian does not depend on time but the eigenvalues are degenerate
The H_0 does not depend on time while V does
Whole Hamiltonian is time-dependent

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 find the approximate eigenkets of

$$(H_0 + V)|n\rangle = E_n|n\rangle.$$

in which V represents the "unknown" perturbation part and is, in general, just part of the whole potential.
The problem can be re-formulated with the aid of continuous parameter λ

$$(H_0 + \lambda V)|n\rangle_\lambda = E_n^{(\lambda)}|n\rangle_\lambda.$$

Now $\lambda \to 0$: unperturbed system
and $\lambda \to 1$: full perturbation
It is evident that eigenkets are λ dependent but we always take the $\lambda \to 1$ limit in the end and thus we can drop the index from now on.
The idea is then to expand the final eigenkets in powers of λ
Perturbation method is effective if first few terms converge, this is often the case in QED.
In QCD problems arise more often.
With $\lambda \neq 0$ we expect $E_n \neq E_n^{(0)}$ and 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
$$\langle n^{(0)}|\lambda V - \Delta_n|n\rangle = \langle n^{(0)}|E_n^{(0)} - H_0|n\rangle = 0,$$
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
$$\frac{1}{E_n^{(0)} - H_0}\phi_n = \sum_{k\neq n} \frac{1}{E_n^{(0)} - E_k^{(0)}}|k^{(0)}\rangle\langle k^{(0)}|$$
is well defined (non-degenerate case) and
$$(\lambda V - \Delta_n)|n\rangle = \phi_n(\lambda V - \Delta_n)|n\rangle.$$
We can relax here a bit and write
$$\begin{aligned}\frac{1}{E_n^{(0)} - H_0}\phi_n &= \phi_n\frac{1}{E_n^{(0)} - H_0} = \frac{\phi_n}{E_n^{(0)} - H_0} \\ &= \left(\phi_n\frac{1}{E_n^{(0)} - H_0}\phi_n\right)\end{aligned}$$
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
$$\langle n^{(0)}|n\rangle = c_n(\lambda) = 1.$$
for every λ.
This only affects the overall normalization which can be fixed in the end.
Remembering
$$\langle n^{(0)}|\lambda V - \Delta_n|n\rangle = 0,$$

we get

$$\Delta_n = \lambda\langle n^{(0)}|V|n\rangle \qquad (*)$$

Thus, we have two coupled equations

$$\begin{aligned}
|n\rangle &= |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)} - H_0}(\lambda V - \Delta_n)|n\rangle \\
\Delta_n &= \lambda\langle n^{(0)}|V|n\rangle
\end{aligned}$$

which we want to expand in powers of λ.
Explicitely

$$\begin{aligned}
|n\rangle &= |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots \\
\Delta_n &= \lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \cdots.
\end{aligned}$$

Inserting these into (*),
we get

$$\begin{aligned}
&\lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \cdots \\
&\qquad = \lambda\langle n^{(0)}|V|n^{(0)}\rangle + \lambda^2\langle n^{(0)}|V|n^{(1)}\rangle + \cdots.
\end{aligned}$$

Equalizing the coefficients of the powers of the parameter λ we get

$$\begin{array}{rcl}
\mathcal{O}(\lambda^1): \quad \Delta_n^{(1)} &=& \langle n^{(0)}|V|n^{(0)}\rangle \\
\mathcal{O}(\lambda^2): \quad \Delta_n^{(2)} &=& \langle n^{(0)}|V|n^{(1)}\rangle \\
\vdots \qquad\qquad \vdots & & \\
\mathcal{O}(\lambda^N): \quad \Delta_n^{(N)} &=& \langle n^{(0)}|V|n^{(N-1)}\rangle \\
\vdots \qquad\qquad \vdots & &
\end{array}.$$

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

$$\begin{aligned}
&|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots \\
&\qquad = |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)} - H_0}(\lambda V - \lambda\Delta_n^{(1)} - \lambda^2\Delta_n^{(2)} - \cdots) \\
&\qquad\quad \times(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \cdots).
\end{aligned}$$

Equalizing the coefficients of the linear λ-terms we get in the first order

$$\begin{aligned}
&\mathcal{O}(\lambda): \ |n^{(1)}\rangle \\
&\qquad = \frac{\phi_n}{E_n^{(0)} - H_0}V|n^{(0)}\rangle - \frac{\phi_n\Delta_n^{(1)}}{E_n^{(0)} - H_0}|n^{(0)}\rangle \\
&\qquad = \frac{\phi_n}{E_n^{(0)} - H_0}V|n^{(0)}\rangle,
\end{aligned}$$

because

$$\begin{aligned}
\phi_n \Delta_n^{(1)} |n^{(0)}\rangle &= \Delta_n^{(1)} \phi_n |n^{(0)}\rangle \\
&= \Delta_n^{(1)} \sum_{k \neq n} |k^{(0)}\rangle\langle k^{(0)}|n^{(0)}\rangle = 0
\end{aligned}$$

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

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

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

$$|n\rangle = |n^{(0)}\rangle + \lambda \sum_{k \neq n} |k^{(0)}\rangle \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}$$

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

Note Again the matrix elements are taken with respect to the unpertubed energy eigenkets.
We see that the perturbet eigenket $|n\rangle$ takes contribution from other unperturbed eigenkets as well ($|k^{(0)}\rangle$:s)
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.
Furthermore, we see that different orders in the expansion are orhogonal with respect to the $|n^{(0)}\rangle$ state, for example

$$
|n^{(1)}\rangle = \frac{\phi_n}{E_n^{(0)}-H_0} V|n^{(0)}\rangle = \sum_{k\neq n} \frac{V_{kn}}{E_n^{(0)}-E_k^{(0)}} |k^{(0)}\rangle
$$

and so clearly

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

and similarly to the higher orders.
We will need

$$
\langle n^{(1)}|n^{(1)}\rangle = \sum_{k\neq n} \frac{|V_{kn}|^2}{(E_n^{(0)}-E_k^{(0)})^2}
$$

Normalization
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 (i.e. we ignore spin, obviously this is not valid for hydrogen atom in states $n \neq 1$).
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

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

Now since,

1) we assumed the states $|k^{(0)}\rangle$ to be non degenerate they are eigenstates of the parity (remember earlier theorem)
2) position operator z is odd under parity,
$\rightarrow$ only states with opposite parity can be connected
$\rightarrow$ the matrix element of z_{kk} vanishes
$\rightarrow$ there is no linear Stark effect, instead, the effect is quadratic in $|\mathbf{E}|$
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 $l' = l-1, l, l+1.$
$l' = l$ is not suitable due to the parity sel. rule.
Reminder:

$$\langle \alpha', j'm'|T_q^{(k)}|\alpha, jm\rangle = \langle jk; mq|jk; j'm'\rangle \frac{\langle \alpha' j'\|T^{(k)}\|\alpha j\rangle}{\sqrt{2j+1}},$$

$m = m_1 + m_2$ and $|j_1 - j_2| < j < j_1 + j_2$ in

$$\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle$$

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

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

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

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

Time-independent Hamiltonian, degenerate case

If the unperturbed energy eigenkets are degenerate, previous perturbation theory will fail since
in the limit $\lambda \to 0$ $\quad |n\rangle \to |n^{(0)}\rangle$ is not well defined (several possible $|n^{(0)}\rangle$)
and so $\frac{1}{E_n^{(0)} - H_0}|k^{(0)}\rangle$ may diverge
Actually any linear combination of (the degenerate) unperturbed kets has the same energy eigenvalue
Thus we need to label the degenerate energy eigenkets by some other observable A:

$$H_0|n_1^{(0)}\rangle = E_n^{(0)}|n_1^{(0)}\rangle \quad ; \quad H_0|n_2^{(0)}\rangle = E_n^{(0)}|n_2^{(0)}\rangle \ldots$$

and then we can "rename" them as $|k^{(0)}\rangle$
Luckily, we are allowed to choose our base set of unperturbed kets so that the eigenkets become unique.
This is done by using as base kets the linear combinations of the degenerate unperturbed kets that diagonalize H in the subspace spanned by the unperturbed kets.
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

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

because $\{|m^{(0)}\rangle\}, \{|l^{(0)}\rangle\}$ span the same subspace. Notice $H|l^{(0)}\rangle = E_D^{(0)}|l^{(0)}\rangle$
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

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

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

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

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

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

This is an eigenvalue equation from which energy corrections $\Delta_l^{(1)}$ are obtained as eigenvalues.
Note There are g independent equations and by solving $\Delta_l^{(1)}$ we get the $\langle m^{(0)}|l^{(0)}\rangle$:s up to a normalization constant. The resulting eigenvectors are the ones that diagonalize the perturbation in the subspace D.

The first order E-shift is given by the diagonal matrix elements

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

From the equation

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

we also see that

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

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

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

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

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

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:

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

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

$$\Delta_{\pm}^{(1)} = \pm 3 e a_0 |\boldsymbol{E}|$$

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 $\langle z\rangle \neq 0$.
In reality, the $n > 1$ energy levels are not degenerate. $2p_{3/2}$ and $2p_{1/2}$ are separated due to the spin orbit force and $2s_{1/2}$ and $2p_{1/2}$ due to the Lamb shift. However, as long as the matrix elements of the perturbation are much larger than these effects, our aproach yields reasonable results.

Nearly degenerated states
If some of the energy eigenvalues are close to each other (more generally $V_{nm}/(E_n^{(0)} - E_m^{(0)})$ is small) in the system, then the perturbation series may converge uncomfortably slowly. For such systems, we can apply a special version of perturbation theory. Namely,
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
(electron in a one dimensional lattice).
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 $\delta_{x,y} = 1/2\pi \int_0^{2\pi} \mathrm{e}^{i(x-y)\phi} \mathrm{d}\phi$

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

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

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

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

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

This method is sometimes referred as weak binding approximation.

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

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

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

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

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

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

Iteration gives us the series

$$\begin{aligned}|n\rangle = |n^{(0)}\rangle &+ \lambda\sum_{m\neq n}|m^{(0)}\rangle\frac{1}{E_n - E^{(0)}_m}\langle m^{(0)}|V|n^{(0)}\rangle \\ &+ \lambda^2\sum_{m\neq n}\sum_{l\neq n}|l^{(0)}\rangle\frac{1}{E_n - E^{(0)}_l}\langle l^{(0)}|V|m^{(0)}\rangle \\ &\times\frac{1}{E_n - E^{(0)}_m}\langle m^{(0)}|V|n^{(0)}\rangle \\ &+ \lambda^3\sum_{m\neq n}\sum_{l\neq n}\sum_{k\neq n}|k^{(0)}\rangle\frac{1}{E_n - E^{(0)}_k}\langle k^{(0)}|V|l^{(0)}\rangle \\ &\times\frac{1}{E_n - E^{(0)}_l}\langle l^{(0)}|V|m^{(0)}\rangle\frac{1}{E_n - E^{(0)}_m}\langle m^{(0)}|V|n^{(0)}\rangle \\ &+\cdots.\end{aligned}$$

Note The perturbed energy eigenvalues enter the denominator.
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

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

In general this series expansion is more complicated to evaluate than the Rayleigh-Scrödinger perturbation series.
However, this method may lead to more accurate solution faster than the R-S series.

Variational method
Perturbative methods rest on the assumption that we know the exact solutions to a problem similar to the one we are considering, i.e. that the unperturbed energy eigenkets with corresponding eigenvalues are known.
If above is not true, then perturbative expansion is useless.
Variational method can be useful in this case for estimating the ground state (in special cases excited states too).
Let us define "a trial ground state" $|\overline{O}\rangle$ with a ground state energy

$$\overline{H} = \frac{\langle\overline{O}|H|\overline{O}\rangle}{\langle\overline{O}|\overline{O}\rangle}$$

Our goal is to find a form for the $|\overline{O}\rangle$ so that it would imitate the true ground state as good as possible.
First, let us prove a theorem

$$\overline{H} \geq E_0$$

which states that we can find an upper boundary for the true groud state by considering various $|\overline{O}\rangle$
Proof. $|\overline{O}\rangle$ can be written

$$|\overline{O}\rangle = \sum_k |k\rangle\langle k|\overline{O}\rangle$$

in which $|k\rangle$ is an exact energy eigenket.
Thus

$$\begin{aligned}
\overline{H} &= \frac{\sum\limits_{k=0} E_k|\langle k|\overline{O}\rangle|^2}{\sum\limits_{k=0} |\langle k|\overline{O}\rangle|^2} \\
&= \frac{\sum\limits_{k=0}(E_k - E_0 + E_0)|\langle k|\overline{O}\rangle|^2}{\sum\limits_{k=0} |\langle k|\overline{O}\rangle|^2}
\end{aligned}$$

$$= \frac{\displaystyle\sum_{k=1}(E_k - E_0)|\langle k|\overline{O}\rangle|^2}{\displaystyle\sum_{k=0} |\langle k|\overline{O}\rangle|^2} + E_0 \geq E_0$$

Unfortunately, the theorem does not say how far $\overline{H}$ is from the true groud state E_0.
It is obvious, though, that whenever $\overline{H}$ is stationary in the variation

$$|\overline{O}\rangle \rightarrow |\overline{O}\rangle + \delta|\overline{O}\rangle$$

i.e. when $\delta\overline{H} = 0$, then $|\overline{O}\rangle$ coincide* with the true ground state. (the error in our ground state is of the order $(\delta|\overline{O}\rangle)^2$)
We must make a good guess for the functional form of the ground state wave function $\Psi_0 = \Psi_0(\lambda)$ and fix possible free parameters by variational principle.
In practise the procedure goes

- guess $|\overline{O}\rangle = |\text{something}\rangle$
- $\Psi = \langle x|\overline{O}\rangle = f(x, \lambda, ...)$
- Calculate $\overline{H}$ from

$$\overline{H} = \frac{\displaystyle\int \Psi^*(\frac{-\hbar^2}{2m}\nabla^2 + V)\Psi \mathrm{d}x}{\displaystyle\int \Psi^*\Psi \mathrm{d}x}$$

- Variate $\overline{H}$, i.e. calculate the derivatives

$$\frac{\partial \overline{H}}{\partial \lambda_i} = 0 \quad \forall i$$

- "Re-calculate" $\overline{H}$ with the best values.