Consider the Hamiltonian
\[ \hat{H} = \hat{H}_0 + \hat{V}(\mathbf{r}) \]  
and we wish to solve the Schrödinger Equation:
\[ \hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \]

Assume a finite linear basis set expansion of 2 states:
\[ \Phi(\mathbf{r}) = c_1\phi_1^0(\mathbf{r}) + c_2\phi_2^0(\mathbf{r}) \]

where
\[ \hat{H}_0\phi_i^0(\mathbf{r}) = E_i^0\phi_i^0(\mathbf{r}) \]

The best estimate for the energy is
\[ \left( \begin{array}{cc} E_1^0 + V_{11} & V_{12} \\ V_{21} & E_2^0 + V_{22} \end{array} \right) \left( \begin{array}{c} c_1 \\ c_2 \end{array} \right) = E \left( \begin{array}{c} c_1 \\ c_2 \end{array} \right) \]

Therefore:
\[ \left| \begin{array}{cc} E_1^0 + V_{11} - E & V_{12} \\ V_{21} & E_2^0 + V_{22} - E \end{array} \right| = 0 \]

And the Energy is
\[ E_{1,2} = \frac{E_2^0 + V_{22} + E_1^0 + V_{11}}{2} + \sqrt{\left( \frac{E_2^0 + V_{22} - E_1^0 - V_{11}}{2} \right)^2 + |V_{12}|^2} \]
If \( E_0^0 + V_{22} - E_1^0 - V_{11} \gg |V_{12}| \), then to 2nd order in \( |V_{12}| \),

\[
E_1 \approx E_{01}^0 + V_{11} + \frac{|V_{12}|^2}{E_{11} - E_{22}}
\]
and

\[
E_2 \approx E_{02}^0 + V_{22} + \frac{|V_{12}|^2}{E_{22} - E_{11}}
\]

Likewise, the corresponding wave functions for these energies to first order in \( |V_{12}| \) are,

\[
\begin{pmatrix}
c_1^- \\
c_2^-
\end{pmatrix} = \frac{1}{V_{12}} \begin{pmatrix}
E_{11} - E_{22} \\
E_{11} + V_{11} - E_{22}
\end{pmatrix}
\]
and

\[
\begin{pmatrix}
c_1^+ \\
c_2^+
\end{pmatrix} = \frac{1}{V_{22}} \begin{pmatrix}
E_{11} - E_{22} \\
E_{22} + V_{22} - E_{11}
\end{pmatrix}
\]

If all the \( V \)'s are small compared to the energies, then

(a) to **first order** in \( V \),

\[
E_1^{(1)} = E_1^0 + V_{11}
\]
and

\[
E_2^{(1)} = E_2^0 + V_{22}
\]

and the corresponding wave functions are

\[
\Phi_1(x) \approx \phi_1(x)
\]
and

\[
\Phi_2(x) \approx \phi_2(x)
\]
(b) and to second order in $V$,

$$E_{1}^{(2)} = E_{1}^{0} + V_{11} + \frac{|V_{12}|^2}{E_{1}^{0} - E_{2}^{0}}$$

and

$$E_{2}^{(2)} = E_{2}^{0} + V_{22} + \frac{|V_{12}|^2}{E_{2}^{0} - E_{1}^{0}}$$

with wave functions

$$\Phi_{1}(x) \approx \phi_{1}(x) + \frac{V_{12}}{E_{1}^{0} - E_{2}^{0}} \phi_{2}(x)$$

and

$$\Phi_{2}(x) \approx \phi_{2}(x) + \frac{V_{21}}{E_{2}^{0} - E_{1}^{0}} \phi_{1}(x)$$

Note these expansions assume that $E_{2}^{0} \neq E_{1}^{0}$.

What if $E_{2}^{0} = E_{1}^{0}$? or What if $E_{2}^{0} \approx E_{1}^{0}$?
Now assume a finite linear basis set expansion of with 3 states:

$$\Phi(r) = c_1 \phi_1^0(r) + c_2 \phi_2^0(r) + c_3 \phi_3^0(r)$$

where

$$\hat{H}_0 \phi_i^0(r) = E_i^0 \phi_i^0(r)$$

The best estimate for the energy is

$$\begin{pmatrix} E_1^0 + V_{11} & V_{12} & V_{13} \\ V_{21} & E_2^0 + V_{22} & V_{23} \\ V_{31} & V_{32} & E_3^0 + V_{33} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

Therefore:

$$\begin{vmatrix} E_1^0 + V_{11} - E & V_{12} & V_{13} \\ V_{21} & E_2^0 + V_{22} - E & V_{23} \\ V_{31} & V_{32} & E_3^0 + V_{33} - E \end{vmatrix} = 0$$
Expanding the determinant, we have

\[
0 = (E_1 + V_{11} - E)(E_2 + V_{22} - E)(E_3 + V_{33} - E) \\
- (E_1 + V_{11} - E)V_{23}V_{32} \\
- (E_2 + V_{22} - E)V_{31}V_{13} \\
- (E_3 + V_{33} - E)V_{21}V_{12} \\
+ V_{12}V_{23}V_{31} + V_{13}V_{32}V_{12}
\]

To first order in \( V \), need only the first line so that

\[
0 \approx (E_1 + V_{11} - E)(E_2 + V_{22} - E)(E_3 + V_{33} - E)
\]

and we find

\[
E_1^{(1)} \approx E_1^0 + V_{11}
\]

and

\[
E_2^{(1)} \approx E_2^0 + V_{22}
\]

and

\[
E_3^{(1)} \approx E_3^0 + V_{33}
\]
To second order in $V$ one needs the first 4 lines so that

\[
0 \approx (E_1 + V_{11} - E)(E_2 + V_{22} - E)(E_3 + V_{33} - E)
- (E_1 + V_{11} - E)V_{23}V_{32}
- (E_2 + V_{22} - E)V_{31}V_{13}
- (E_3 + V_{33} - E)V_{21}V_{12}
\]

so that

\[
E^{(2)}_1 \approx E_0^1 + V_{11} + \frac{|V_{12}|^2}{E_1^0 - E_2^0} + \frac{|V_{13}|^2}{E_1^0 - E_3^0}
\]

and

\[
E^{(2)}_2 \approx E_0^2 + V_{22} + \frac{|V_{12}|^2}{E_2^0 - E_1^0} + \frac{|V_{23}|^2}{E_2^0 - E_3^0}
\]

and

\[
E^{(2)}_3 \approx E_0^3 + V_{33} + \frac{|V_{13}|^2}{E_3^0 - E_1^0} + \frac{|V_{23}|^2}{E_3^0 - E_2^0}
\]

In general,

\[
E^{(2)}_n \approx E_0^n + V_{nn} + \sum_{p \neq n} \frac{|V_{np}|^2}{E_n^0 - E_p^0} \quad \text{provided} \quad E_n^0 \neq E_p^0
\]

and

\[
|\Phi_n\rangle \approx |\phi_n\rangle + \sum_{p \neq n} \frac{V_{pn}}{E_n^0 - E_p^0} |\phi_p\rangle \quad \text{provided} \quad E_n^0 \neq E_p^0
\]

This is known as **non-degenerate perturbation theory**.