It's important to choose good initial states, which transform smoothly into the perturbed states.

Fig. 8.4. (a) Good, (b) poor choices of a degenerate-basis linear combination for a perturbation leading to the wavefunctions shown in the middle.

(Remember any linear combination of degenerate eigenstates is also an eigenstate.)
Write the wavefns. as a sum over a finite number of unperturbed states. Then the first order energies are obtained by solving the secular equations

\[
\begin{pmatrix}
\mathcal{H}_{11} - E^{(1)} & \mathcal{H}_{12} & \cdots & \mathcal{H}_{1N} \\
\mathcal{H}_{21} & \mathcal{H}_{22} - E^{(1)} & \cdots & \mathcal{H}_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
\mathcal{H}_{N1} & \mathcal{H}_{N2} & \cdots & \mathcal{H}_{NN} - E^{(1)}
\end{pmatrix} = 0
\]

Note that this is the same result as we obtained from a variational treatment of a trial function of the same form. This indicates that it's not restricted to the degenerate case.

We can find the first-order wavefns. \+ 2nd order energy corrections as before, but the sum must be taken over the unperturbed states that do not form part of the degenerate set.

Again, we're familiar with this formalism for a 2-state system:

\[
\begin{align*}
\text{Energy} & \quad \alpha \\
\text{Increasing } \beta &
\end{align*}
\]
**AN EXAMPLE OF DEGENERATE PERTURBATION THEORY:**

**THE NEARLY FREE ELECTRON MODEL.**

**Reminder:** Free Electrons, $V = 0$

$$\psi_k(x) \propto e^{ikx}$$

$$E_k = \frac{k^2 k^2}{2m}$$

Note that:

- the states $+k, -k$ are degenerate
- there are no "band gaps" i.e. every energy value is allowed

In the nearly free electron method we apply a weak, periodic potential to the electron gas (e.g. an array of $s$-functions or a cosine potential) to represent the electron-ion interaction. This causes band gaps in the energy spectrum and changes in the electronic effective mass!

Let's take $P^{(0)} = \frac{p^2}{2m}$ and impose periodic

BCs, $\psi_k(x+L) = \psi_k(x)$, where $L = Na$ is the size of our crystal. Then

$$\psi_k^{(0)}(x) = \frac{1}{\sqrt{L}} e^{ikx} ; \quad E_k^{(0)} = \frac{k^2 k^2}{2m} ; \quad k = n \frac{2\pi}{Na} \quad n = 0, 1, 2, \ldots, \infty$$

So the zeroth order problem is solved and we know all the eigenstates and eneriges.
Now apply a 1-D periodic potential,

\[ V = \varphi^{(1)} = -2U_0 \cos G x \quad \text{where} \quad G = \frac{2\pi}{a} \]

To do degenerate perturbation theory, we need the matrix elements \( \langle k_i | \varphi^{(1)} | k_j \rangle = \Phi_{ij} \)

\[ \Phi_{ij} = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} e^{ik_i x} (-2U_0 \cos G x) e^{ik_j x} \, dx \]

\[ = 0 \quad \text{unless} \quad k_i - k_j = \pm G \]

\[ = -U_0 \delta_{ij} \quad k_i - k_j = \pm G \]

i.e. \( \Phi_{ij} = -U_0 \delta(k_i - k_j, \pm G) \)

so each state mixes with only two other states - those with \( k \) values \( k + G \), and \( k - G \)

When \( k = \frac{G}{2} \)

\( |k = \frac{G}{2} \rangle \) can mix with \( |k = \frac{3G}{2} \rangle \) and \( |k = -\frac{G}{2} \rangle \)

We'll focus on the interaction between states \( k = \pm \frac{G}{2} \) which are degenerate (since \( E_k = \frac{1}{2} k^2 \)).
The two unperturbed plane waves are degenerate, with energy, 
\[ E^0 \equiv \frac{k^2 k^2}{2m} = \frac{k^2 G^2}{8m} \]

so \[ \mu_{11} = \mu_{22} = \frac{k^2 G^2}{8m} \]

The off-diagonal matrix elements coupling the two plane waves are
\[ \mu_{12} = \mu_{21} = -U_0 \]

So we have to solve
\[
\begin{vmatrix}
\frac{k^2 G^2}{8m} - E & -U_0 \\
-U_0 & \frac{k^2 G^2}{8m} - E
\end{vmatrix} = 0
\]

\[
\Rightarrow E = \frac{k^2 G^2}{8m} \pm U_0
\]

The states are no longer degenerate!

Also the eigenstates are given by
\[
\frac{1}{\sqrt{2}} \left( |1k_1\rangle \pm |1k_2\rangle \right) = \frac{1}{\sqrt{2L}} \left( e^{ikx} \pm e^{-ikx} \right)
\]

\[
= \sqrt{\frac{2}{L}} \cos kx \text{ or } i\sqrt{\frac{2}{L}} \sin kx
\]

The eigenstates are now standing waves with the lower energy, \( \cos kx \) having high probability density in the attractive region of the potential, and the higher energy, \( \sin kx \) having high probability in the repulsive region.