In fact we've already seen examples of perturbation theory in 2-state systems (MO theory/coupled quantum wells).

\[ \Phi_{11}^{0} = \lambda_1, \quad \Phi_{22}^{0} = \lambda_2, \quad \Phi_{12}^{0} = \Phi_{21}^{0} = 0 \]

\[ \Phi_{11}^{1} = \Phi_{22}^{1} = 0; \quad \Phi_{21}^{1} = \Phi_{12}^{1} = \epsilon \]

Then

\[ \left| \lambda - \epsilon \right| \gg \left| \epsilon \right| \Rightarrow E = \frac{1}{2} \left( \lambda_1 + \lambda_2 \right) \pm \sqrt{\left( \lambda_1 - \lambda_2 \right)^2 + 4 \epsilon^2} \]

\[ = \lambda \pm \epsilon \quad \text{if} \quad \lambda_1 = \lambda_2 \]

Fig. 8.1. The effect of a perturbation on (a) a non-degenerate system, (b) a degenerate system.
Consider a perturbation that's small compared to the separation of the levels, i.e. $\epsilon \ll \Delta E$.

**Fig. 8.2. Unperturbed energies $(E_1, E_2)$, exact perturbed energies $(E_{\pm}, E_0)$, and the perturbation approximation for $\epsilon/\Delta E \ll 1$.**

If $\frac{\epsilon}{\Delta E} \ll 1$, we can expand the energy expression:

$$E_{\pm} = \frac{1}{2}(\lambda_1 + \lambda_2) \pm \frac{1}{2}(\lambda_1 - \lambda_2) \left\{ 1 + \frac{2 \epsilon^2}{\Delta E^2} + \ldots \right\}$$

i.e. $E_+ \approx \lambda_1 - \frac{\epsilon^2}{\Delta E}$; $E_- \approx \lambda_2 + \frac{\epsilon^2}{\Delta E}$

i.e. energy corrections $\frac{\epsilon^2}{\Delta E}$ are a reasonable approximation when the perturbation is weak and the energy separation is large.
Suppose we've solved \( \Psi_n^{(0)} = E_n \Psi_n^{(0)} \) \( n = 0, 1, 2, \ldots \)
and have a complete set of solutions.

Suppose also that the true \( \Psi \) is close to \( \Psi^{(0)} \),
so we may write
\[
\begin{align*}
\Psi &= \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \cdots \\
\Psi &= \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \cdots \\
E &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots
\end{align*}
\]
\( \lambda \) is the order of magnitude of the perturbation.

Inserting equations \( \ast \) into \( \lambda \Psi = E \Psi \), and collecting like terms in \( \lambda \) \( \Rightarrow \) (details in Handout)

First-order energy correction
\[
E_n^{(1)} = \langle n \rvert \Psi^{(1)} \lvert n \rangle = \sum_k \begin{pmatrix} \Psi_{kn}^{(1)} \\ E_n - E_k \end{pmatrix}
\]

First-order wavefunction,
\[
\Psi_n = \Psi_n^{(0)} + \sum_k \begin{pmatrix} \Psi_{kn}^{(1)} \\ E_n - E_k \end{pmatrix}
\]

Second-order energy correction,
\[
E_n^{(2)} = \sum_k \sum_k \begin{pmatrix} \Psi_{kn}^{(2)} \\ E_n - E_k \end{pmatrix}
\]

Note:
- \( \Psi_{nn}^{(1)} \) is kind of an average of the 1st order perturbation over the state.
- The wavefunction is perturbed by mixing the other states into the one of interest.
- This formalism won't work if \( E_n = E_k \)!
- \( E_n^{(2)} \) includes an average of the 2nd order perturbation over the 0th order wavefunctions plus an average of the 1st order perturbation over the perturbed wavefunctions!
A rough estimate of the 2nd-order energy through the Closure Approximation.

Approximate $E_n - E_0$ by $\Delta E$. Then

$$E_0^{(2)} \approx \mu_{oo}^{(2)} - \frac{1}{\Delta E} \sum_n \mu_{on}^{(1)} \mu_{no}^{(1)}$$

---

**Fig. 8.3.** The basis of the closure approximation.

Extend the sum to include $n = 0$

$$E_0^{(2)} \approx \mu_{oo}^{(2)} - \frac{1}{\Delta E} \left\{ \sum_n \mu_{on}^{(1)} \mu_{no}^{(1)} - \mu_{oo}^{(1)} \mu_{oo}^{(1)} \right\}$$

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

so

$$E_0^{(2)} \approx \mu_{oo}^{(2)} - \frac{1}{\Delta E} \left\{ \langle 0 | \mu^{(n)^2} | 0 \rangle - \langle 0 | \mu^{(n)} | 0 \rangle^2 \right\}$$

let $\Delta E^2 = \langle 0 | \mu^{(n)^2} | 0 \rangle - \langle 0 | \mu^{(n)} | 0 \rangle^2$ mean square deviation of the perturbation

$$\Rightarrow E_0^{(2)} \approx \mu_{oo}^{(2)} - \frac{\Delta E^2}{\Delta E}$$