

Let's find 2nd correction to Energy

$$(\hat{H}_0 + \lambda \hat{H}_1) (\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \underline{O(\lambda^3)}) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \underline{O(\lambda^3)}) (\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \underline{O(\lambda^3)})$$

We will worry only about  $\lambda^2$  terms:  
 lower order (0) and (1) we already did and  
 $\lambda^3$  is not our concern.

$$\lambda^2 \times (\hat{H}_0 |\Psi_n^{(2)}\rangle + \hat{H}_1 |\Psi_n^{(1)}\rangle) = \lambda^2 \times (E_n^{(0)} |\Psi_n^{(2)}\rangle + E_n^{(1)} |\Psi_n^{(1)}\rangle + E_n^{(2)} |\Psi_n^{(0)}\rangle)$$

Our goal to find  $E_n^{(2)}$ , so we will  
 calculate  $\langle \Psi_n^{(0)} | * \rangle$

$$\langle \Psi_n^{(0)} | \hat{H}_0 | \Psi_n^{(2)} \rangle + \langle \Psi_n^{(0)} | \hat{H}_1 | \Psi_n^{(1)} \rangle = E_n^{(0)} \langle \Psi_n^{(0)} | \Psi_n^{(2)} \rangle + E_n^{(1)} \langle \Psi_n^{(0)} | \Psi_n^{(1)} \rangle + E_n^{(2)} \langle \Psi_n^{(0)} | \Psi_n^{(0)} \rangle$$

$$E_n^{(2)} = \langle \Psi_n^{(0)} | \hat{H}_1 | \Psi_n^{(1)} \rangle$$

since  $|\Psi_n^{(1)}\rangle = \sum_{k \neq n} c_{kn} |\Psi_k^{(0)}\rangle$   
 and  $\langle \Psi_n^{(0)} | \Psi_k^{(0)} \rangle = 0$

$$\begin{aligned}
 E_n^{(2)} &= \langle \Psi_n^{(1)} | H_1 | \Psi_n^{(1)} \rangle = \\
 &= \langle \Psi_n^{(1)} | H_1 | \left( \sum_{k \neq n} c_{kn} | \Psi_k^{(1)} \rangle \right) \rangle = \\
 &= \langle \Psi_n^{(1)} | H_1 | \left( \sum_{k \neq n} \frac{\langle \Psi_k^{(1)} | H_1 | \Psi_n^{(1)} \rangle}{E_n^{(1)} - E_k^{(1)}} | \Psi_k^{(1)} \rangle \right) \rangle =
 \end{aligned}$$

just a number

$$= \sum_{k \neq n} \frac{\langle \Psi_n^{(1)} | H_1 | \Psi_k^{(1)} \rangle \cdot \langle \Psi_k^{(1)} | H_1 | \Psi_n^{(1)} \rangle}{E_n^{(1)} - E_k^{(1)}}$$

note  $\langle \Psi_n | H | \Psi_k \rangle = (\langle \Psi_k | H | \Psi_n \rangle)^*$   
 since  $H$  is Hermitian

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \Psi_n^{(1)} | H_1 | \Psi_k^{(1)} \rangle|^2}{E_n^{(1)} - E_k^{(1)}}$$

Note:  
 $E_{\text{ground}}^{(2)} \leq 0$   
always!  
 since  $E_g < E_n$