10. Apply linear variation procedure ~~to~~ using orthonormal basis set to non-degenerate perturbation theory. Derive first order and second order correction to energy.

$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(0)} + \hat{\mathcal{H}}'$ $\qquad \phi = \sum a_i \psi_i^{(0)}$

This leads to the secular determinant,

Show how!

$$\begin{vmatrix} H_{11}' - (E - E_1^0) & H_{12}' & H_{13}' & \cdots \\ H_{21}' & H_{22}' - (E - E_2^0) & H_{23}' & \cdots \\ H_{31}' & H_{32}' & H_{33}' - (E - E_3^0) & \cdots \\ - & - & - & - \\ - & - & - & - \end{vmatrix} = 0$$

The corrected energy for the ground state $= E_1$.
This will be closer to E_1^0 than to any other zeroth order level. Therefore, we make the approximations: $E_1 - E_k^0 \gg H_{kk}'$ for $k \neq 1$.
Further, neglect all off-diagonal elements other than those in the first row and first column:

$$\begin{vmatrix} H_{11} - \Delta E_1 & H_{12}' & H_{13}' & \cdots \\ H_{21}' & E_2^0 - E_1^0 & 0 & \cdots \\ H_{31}' & 0 & E_3^0 - E_1^0 & \cdots \\ \cdots & \cdots & \cdots & \\ \cdots & \cdots & \cdots & \end{vmatrix} = 0$$

Substracting appropriate multiples of the second and ~~higher~~ lower ~~for~~ rows from the first row (row transformations) we can solve for ΔE_1:

$$\begin{vmatrix} H'_{11} - \Delta E_1 - \dfrac{H'_{21} H'_{12}}{E_2^0 - E_1^0} - \dfrac{H'_{31} H'_{13}}{E_3^0 - E_1^0} \cdots & 0 & 0 & \cdots \\ H'_{21} & E_2^0 - E_1^0 & 0 & \cdots \\ H'_{31} & 0 & E_3^0 - E_1^0 & \cdots \\ \cdots & \cdots & \cdots & \\ \cdots & \cdots & \cdots & \end{vmatrix} = 0$$

$$\therefore \Delta E_1 = \underbrace{H'_{11}}_{\text{First order}} - \underbrace{\sum_{i=2}^{n} |H_{1i}|^2 / (E_i^0 - E_1^0)}_{\text{Second order}}$$

Q Generalise this result to the k^{th} energy level.

Suggest a way to obtain higher order corrections.