Rayleigh-Schrödinger PT with nondiagonal 0^{th} order

$\{\phi_k\}$ arbitrary ONS: $\langle \phi_k | \phi_L \rangle = \delta_{kL}$

but

$$\hat{H}^0 \phi_k \neq E_k^0 \phi_k^0$$

$$\hat{H}^0 \psi_0^0 = E_0^0 \psi_0^0 \quad \text{(ground state)}$$

↑ is known, but

$$\hat{H}^0 \psi_k^0 = E_k^0 \psi_k^0 \quad k > 0 \quad \text{(excited states)}$$

are unknown.

Expand

$$\psi_0^0 = \sum_k \phi_k c_k$$

$$\sum_k \hat{H}^0 | \phi_k \rangle c_k = E_0^0 \sum_k c_k | \phi_k \rangle$$

$/ \langle \phi_L |$

$$\sum_k \underbrace{\langle \phi_L | H^0 | \phi_k \rangle}_{H^0_{Lk}} c_k = E_0^0 c_L$$

— remains unsolved.

1st order:

$$\hat{H}^0 \Psi^1 + \hat{W} \Psi^0 = E^0 \Psi^1 - E^1 \Psi^0$$

$$= E^0 \Psi^1 \quad \text{if } E^1 = 0$$

↑ always can be achieved

$$\left(\hat{H}^0 - E^0\right) \Psi^1 = -\hat{W} \Psi_0^0$$

Expand

$$\Psi^1 = \sum_k c_k^1 \phi_k \quad \text{but: } \langle \phi_k | \psi_0^0 \rangle = 0$$

(instead of in $\{\psi_k^0\}$)

(e.g.: $\phi_k = (1 - |\psi_0^0\rangle\langle\psi_0^0|)\,\phi_k^0$)

Then

$$\sum_k \left(\hat{H}^0 - E^0\right) |\phi_k\rangle c_k^1 = -\hat{W} |\psi_0^0\rangle \Big/ \langle \phi_L |$$

$$\sum_k \underbrace{\langle \phi_L | \hat{H}^0 - E^0 | \phi_k \rangle}_{K_{Lk}} c_k^1 = \underbrace{-\langle \phi_L | \hat{W} | \psi_0^0 \rangle}_{b_L}$$

$$\underline{\underline{K}}\, \underline{c}^1 = \underline{b}$$

a linear equation system for $\underline{c}^1$.

$$\underline{\underline{G}} = \underline{\underline{K}}^{-1}$$

$$\underline{C}^1 = \underline{\underline{K}}^{-1} b = \underline{\underline{G}}\, \underline{b}$$

$$C_K^1 = \sum_L G_{KL} b_L = -\sum_L G_{KL} \langle \phi_L | w | \psi_0^0 \rangle$$

So

$$\psi^1 = -\sum_{KL} |\phi_K\rangle G_{KL} \langle \phi_L | \hat{w} | \psi_0^0 \rangle$$

The 2nd order energy:

$$E^2 = \langle \psi_0^0 | \hat{w} | \psi^1 \rangle$$

$$= -\sum_{KL} \langle \psi_0^0 | w | \phi_K \rangle G_{KL} \langle \phi_L | \hat{w} | \psi_0^0 \rangle$$

$$= \langle \psi_0^0 | w \hat{Q} w | \psi_0^0 \rangle \quad \text{again,}$$

but:

$$\hat{Q} = -\sum_{KL} |\phi_K\rangle G_{KL} \langle \phi_L |$$

non-diagonal