

1 The PNO++ Approach

The regular PNO density can be written as,

$$\mathbf{D}^{ij} = \frac{2}{1 + \delta_{ij}} (\mathbf{T}^{ij} \tilde{\mathbf{T}}^{ij\dagger} + \mathbf{T}^{ij\dagger} \tilde{\mathbf{T}}^{ij}) \quad (1)$$

where,

$$\tilde{\mathbf{T}}^{ij} = 2\mathbf{T}^{ij} - \mathbf{T}^{ij\dagger} \quad (2)$$

$$T_{ab}^{ij} = \frac{\langle ab | i j \rangle}{f_{ii} + f_{jj} - \epsilon_a - \epsilon_b} \quad (3)$$

In the PNO++ approach, we create a perturbation specific density for each ij pair. For a given perturbation A, the PNO++ density is constructed by replacing the ground state T_{ab}^{ij} amplitudes by perturbed amplitudes $T(A)_{ab}^{ij}$,

$$\mathbf{D}(A)^{ij} = \frac{2}{1 + \delta_{ij}} (\mathbf{T}(A)^{ij} \tilde{\mathbf{T}}(A)^{ij\dagger} + \mathbf{T}(A)^{ij\dagger} \tilde{\mathbf{T}}(A)^{ij}) \quad (4)$$

The leading order contribution to these perturbed amplitudes come from \bar{A} which is nothing but the similarity transformed perturbation operator A , $e^{-T} \hat{A} e^T$. So, we choose the following form of the $T(A)_{ab}^{ij}$ amplitudes,

$$T(A)_{ab}^{ij} = \frac{\bar{A}_{ab}^{ij}}{f_{ii} + f_{jj} - \epsilon_a - \epsilon_b} \quad (5)$$

where,

$$\bar{A}_{ab}^{ij} = P_{ij}^{ab} \left[\sum_e t_{eb}^{ij} [A_e^a - t_a^m A_e^m] - \sum_m t_{ab}^{mj} [A_i^m - t_e^i A_e^m] \right] \quad (6)$$

$$P_{ij}^{ab} f_{ij}^{ab} = f_{ij}^{ab} + f_{ji}^{ba}. \quad (7)$$

Some other points:

- For length gauge optical rotation calculations, one can choose either the electric dipole or the angular momentum operator as the perturbation. However in my experience, the electric dipole operator gives better results for all the molecules.
- I have sent you the graphs of the $(H_2)_4$ system but similar behavior can be seen for other $(H_2)_n$ systems as well.

- Instead of the occupation threshold, T_2 ratios are plotted on the X-axis because the eigen-spectrum of the PNO and PNO++ densities are quite different.
- All the calculations were done at 589 nm with aug-cc-pVDZ basis set.