NOCI-MP2: corrects a NOCI reference for dynamic correlation (Shane Yost)

- NOCI has no well-defined occupied or virtual space!

$$\begin{bmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = \begin{bmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} E$$

- Expand energy to 2nd order, overlap to first order

$$H_{AB} = H_{AB}^{(0+1)} + \tfrac{1}{2}\left\{ \left\langle \Phi_A^{(0)} \middle| H_B^{(1)} \middle| \Phi_B^{(1)} \right\rangle + \left\langle \Phi_B^{(0)} \middle| H_A^{(1)} \middle| \Phi_A^{(1)} \right\rangle \right\}$$

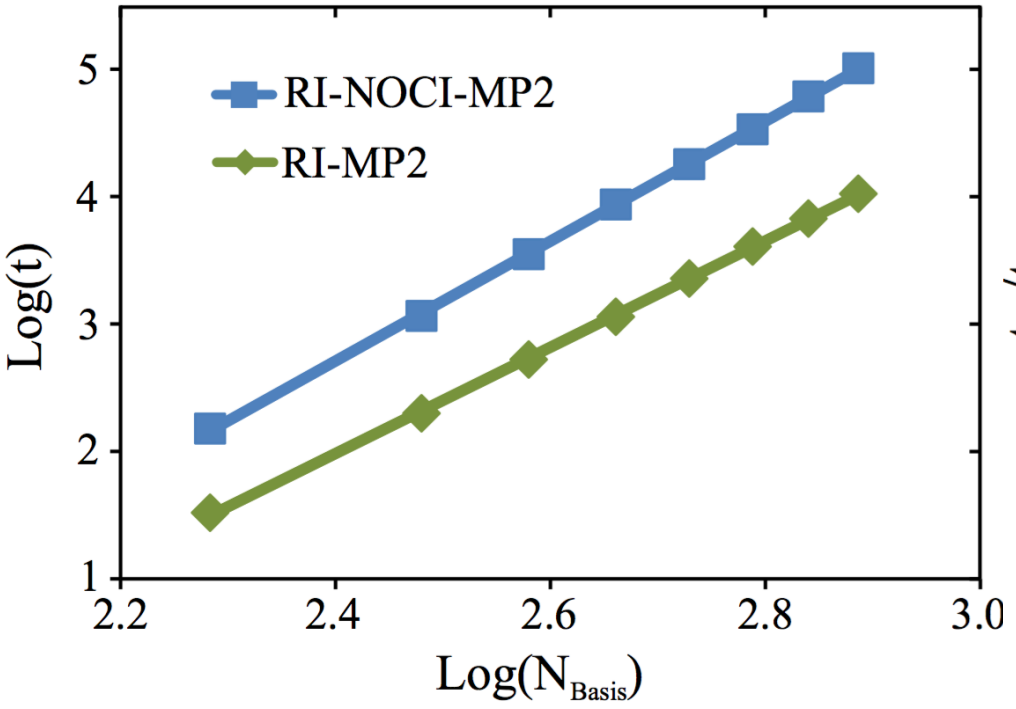
$$S_{AB} = S_{AB}^{(0)} + \tfrac{1}{2}\left\{ \left\langle \Phi_A^{(0)} \middle| \Phi_B^{(1)} \right\rangle + \left\langle \Phi_B^{(0)} \middle| \Phi_A^{(1)} \right\rangle \right\}$$

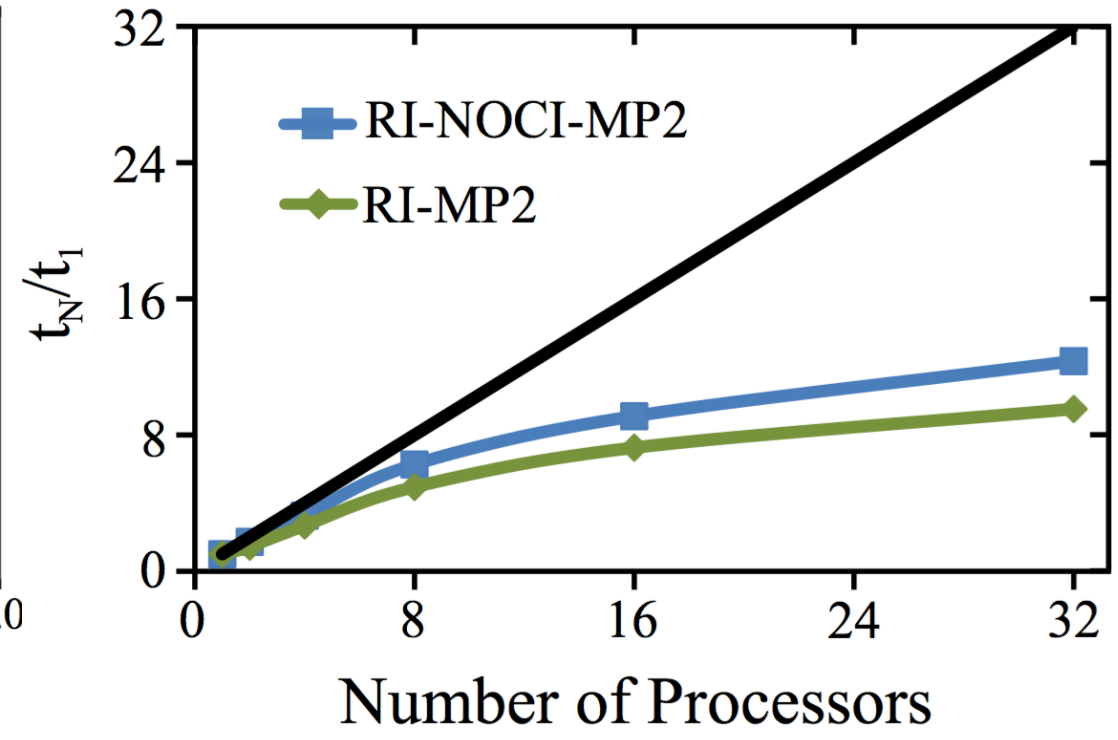
- Modify off-diagonal H_{AB} to be size-consistent.

P.Y. Ayala & H.B. Schlegel, JCP 108, 7560 (1998)
S.R. Yost, T. Kowalczyk, T. Van Voorhis, JCP 139, 174104 (2013)
S.R. Yost, MHG, JCP 145, 054105 (2016)

Efficient RI-based implementation (Shane Yost)

- Scaling can be made identical with RI-MP2.
- Pre-factor is about 10 times larger for off-diagonal H_{AB}
- Our code is moderately parallel per matrix element
- It is also embarrassingly parallel across multiple H_{AB}





Application to di-diamantane ethane.

synthesized by Schreiner, stable at RT, r_{CC} = 1.65 Å

- Use 6 NOCI states (RHF, $\sigma^2 \rightarrow \sigma^{*2}$, 2 $\sigma \rightarrow \sigma^*$, 2UHF)
- Find 67 kcal/mol of binding energy at NOCI-MP2 level
- With 30 kcal/mol of side-chain relaxation with stretching!