Workshop of ESNT

Explicitly Correlated N-Electron Valence State Perturbation Theory (NEVPT2-F12)

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Born-Oppenheimer Approximation

- Nonrelativistic Hamiltonian

$$H = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A}\nabla_A^2 - \sum_{A,i}\frac{Z_A}{r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}\frac{1}{r_{ij}}$$

$$= \quad T_e(\vec{r}) + \quad T_N(\vec{R}) + \quad V_{Ne}(\vec{r},\vec{R}) + V_{NN}(\vec{R}) + V_{ee}(\vec{r})$$

- Electronic Hamiltonian and Schrödinger equation

$$H_{ele} = T_e(\vec{r}) + V_{Ne}(\vec{r},\vec{R}) + V_{NN}(\vec{R}) + V_{ee}(\vec{r})$$

$$H_{ele}\Psi(\vec{r},\vec{R}) = E_{ele}\Psi(\vec{r},\vec{R})$$

Hartree-Fock (HF) approximation

- Slater Determinant (HF wavefunction)

$$\Psi_{HF} = \Phi = \frac{1}{\sqrt{N!}} \begin{bmatrix} \varphi_1(\overrightarrow{r_1}) & \cdots & \varphi_N(\overrightarrow{r_1}) \\ \vdots & \ddots & \vdots \\ \varphi_1(\overrightarrow{r_N}) & \cdots & \varphi_N(\overrightarrow{r_N}) \end{bmatrix}$$

$$= |\varphi_1 \varphi_2 \cdots \varphi_N\rangle$$

- Variational theorem

$$E_{ele} = \langle \Psi | H_{ele} | \Psi \rangle$$

- Hartree-Fock approximation

$$E_{HF} = \sum_i \left\langle \varphi_i \middle| -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{A,i} \frac{Z_A}{r_{Ai}} \middle| \varphi_i \right\rangle + \sum_{i>j} \langle \varphi_i \varphi_j | \varphi_i \varphi_j \rangle - \langle \varphi_i \varphi_j | \varphi_j \varphi_i \rangle + C$$

Single-reference methods

- Perturbation theory (PT)
  - Size-consistent
  - Not variational
- Configuration interaction (CI)
  - Variational
  - Not Size-consistent
- Coupled Cluster (CC)
  - Size-consistent
  - Not variational
  - CCSD(T) “Golden Standard”

Multi-configurational methods

- MC self-consistent-field (MCSCF) wave function

$$\Psi_{MCSCF} = \sum_{I}^{CI} C_I \Phi_I$$

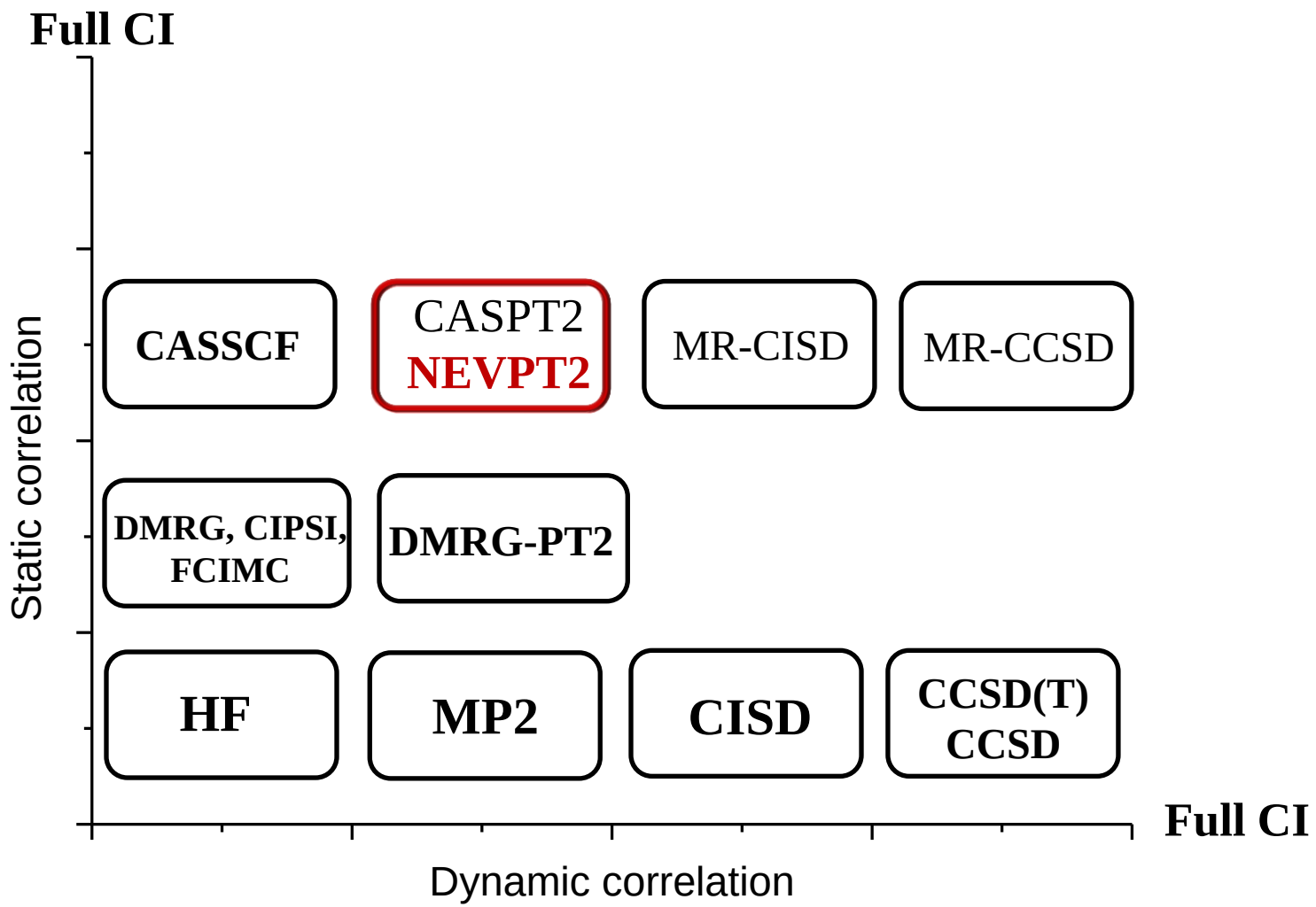
- Advantages
  - Qualitative correct bond-breaking curve
  - Open-shell low spin states
  - Degenerate states

- Disadvantages
  - Not a black-box methods
  - Dynamic correlation is absent

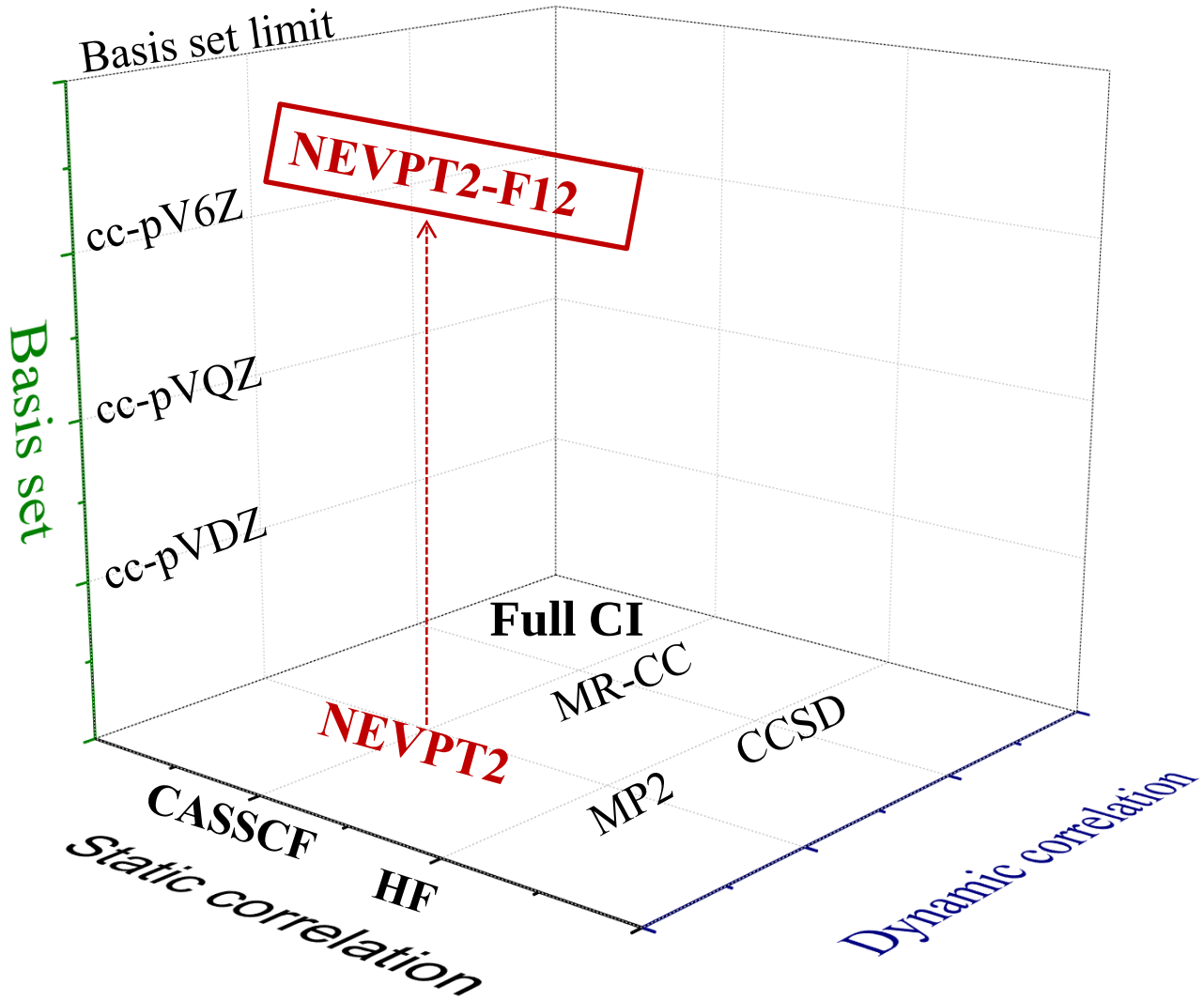
Multi-reference (MR) methods

- MR Perturbation methods (MRPT)
  - Complete Active Space 2nd-order Perturbation Theory (CASPT2)
  - 2nd-order N-Electron Valence state Perturbation Theory (NEVPT2)
- MR Configuration interaction (MRCI)
  - Uncontracted MRCI
  - (Semi-)Internally contracted MRCI
  - Strongly contracted MRCI
- MR Coupled Cluster theory (MRCC)
  - Hilbert Space MRCC
  - Fock Space MRCC

SR & MR methods



CBS-Full CI


Basis set limit
NEVPT2-F12
cc-pV6Z
cc-pVQZ
cc-pVDZ
Basis set
Full CI
MR-CC
NEVPT2
CCSD
MP2
CASSCF
HF
Static correlation
Dynamic correlation

Most widely used MRPT methods

- CASPT2
  - First successful MRPT method
  - Size consistent problem
  - Intruder state
- ***NEVPT2***
  - Size consistent
  - Intruder state free
  - No inter subspace interactions
  - Energy invariance under the unitary transformation within each space (internal space/active space/ virtual space)

$$E^{PT} = -\sum_{k} \frac{\langle 0|H|k\rangle\langle k|H|0\rangle}{E_k - E_0}$$

Andersson, K.; Malmqvist, P. A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K., ***JCP.* 1990,** *94* (14), 5483-5488.
Angeli, C.; Cimiraglia, R.; Evangelisti, S.; Leininger, T.; Malrieu, J. P., ***JCP.* 2001,** *114* (23), 10252-10264.

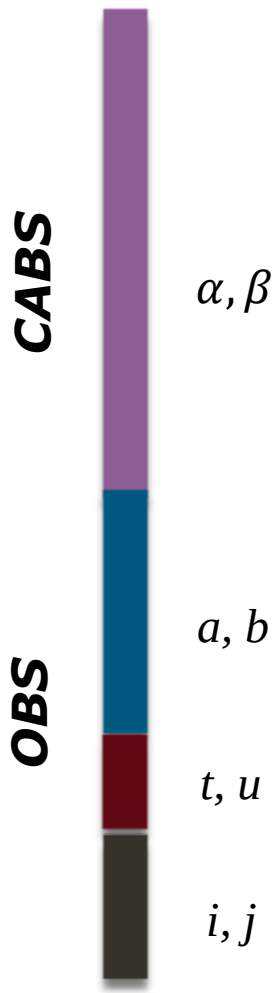
Open questions about NEVPT2

- The prohibitive cost for systems with large active space.
  - Malrieu's group
  - Chan's and Reiher's group
  - Alavi's group
  - ……..
- The high computational cost for very large systems with moderate active space.
  - DLPNO-NEVPT2

- How to achieve basis set limit.
  - NEVPT2-F12
  - Linear scaling NEVPT2-F12

NEVPT2-F12

Symbols



- $i, j, k, l,$ Inactive MOs
- t, u, v, w Active MOs
- a, b, c, d External MOs
- p, q, r, s arbitrary OBS
- $\alpha, \beta, \gamma, \delta$ Complete auxiliary orbitals

Recap of NEVPT2

- 0th-order WFN and Hamiltonian

$$E_p^q = a_{q\uparrow}^+ a_{p\uparrow} + a_{q\downarrow}^+ a_{p\downarrow}$$

$$|0\rangle = \sum_I C_I |\Phi_I\rangle$$

$$H_0 = \sum_{k,l} H_l^{(k)} = \sum_{k,l} P_l^{(k)} H^{Dyall} P_l^{(k)} + P_{CAS} H^{Dyall} P_{CAS}$$

$$H^{Dyall} = \sum_{ij} F_{ij} E_i^j + \sum_{ab} F_{ab} E_a^b + \sum_{tu} F_{tu} E_u^t + \frac{1}{2} \sum_{tuvw} (tv|uw)(E_v^t E_w^u - \delta_v^u E_w^t) + C$$

- Hylleraas functional of NEVPT2

$$Hyl = \langle 1|H_0 - E_0|1\rangle + 2\langle 1|H|0\rangle$$

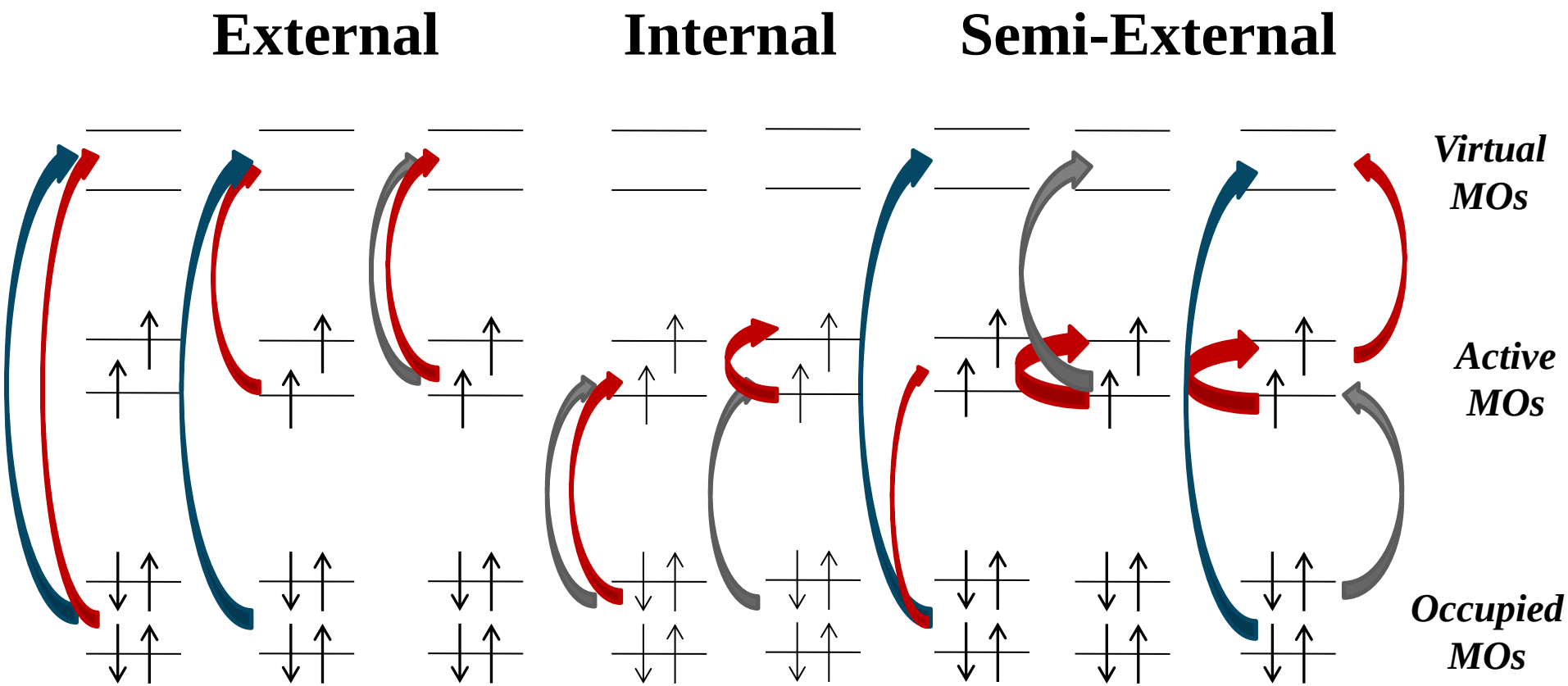
Insert $|1\rangle = \sum_I C_I^{(1)} |\Psi_I\rangle$ into $\delta(Hyl) = |H_0 - E_0|1\rangle + |H^{BO}|0\rangle = 0$

$$\boldsymbol{R = \sum_I \langle \Psi_K | E_0 - H_0 | \Psi_I \rangle C_I^{(1)} - \langle \Psi_K | H_v | 0 \rangle}$$

K. G. Dyall, ***J. Chem. Phys.*** **102**, 4909 (1995).

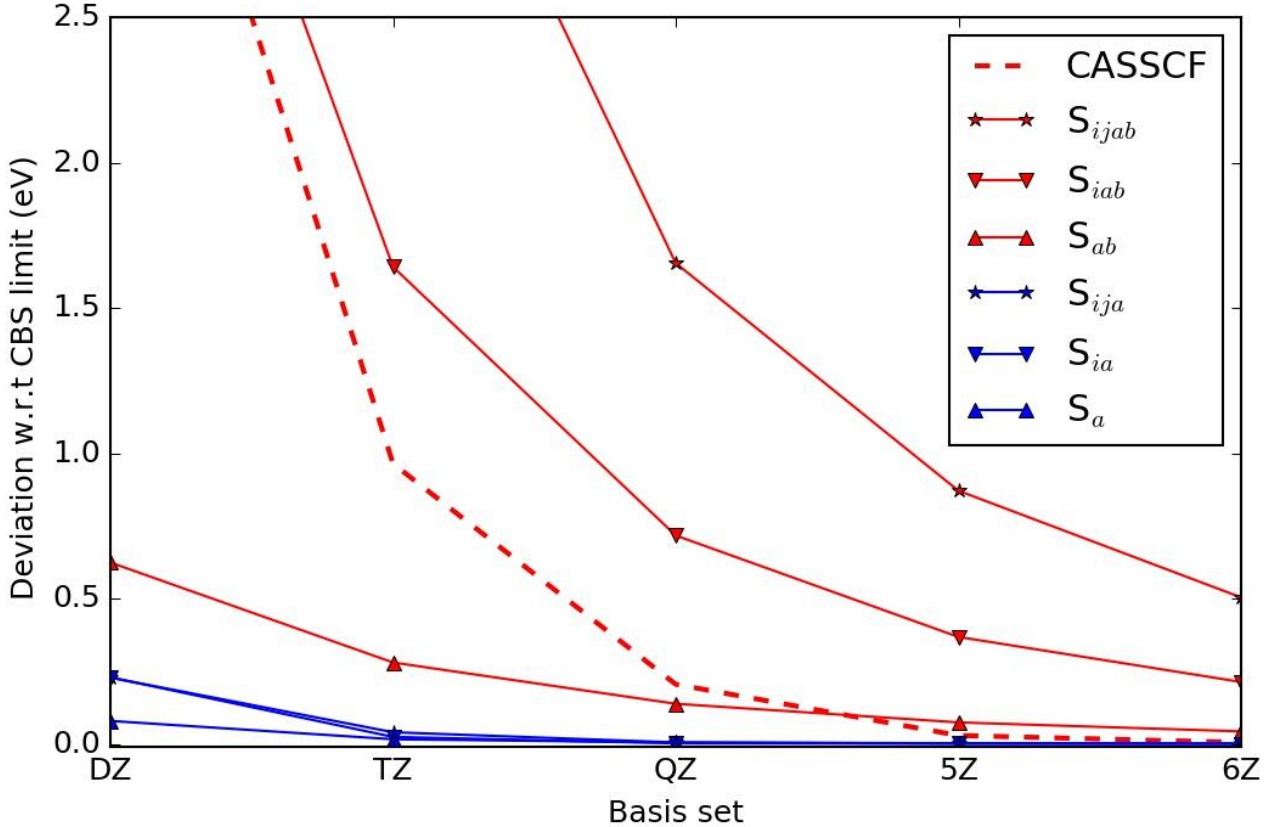
C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger *et al.*, ***J. Chem. Phys.*** **114**, 10252 (2001).

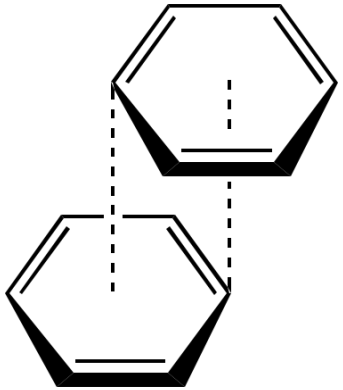
1st-order wave functions



$E_i^a E_j^b \lvert 0\rangle$	$E_i^a E_t^b \lvert 0\rangle$	$E_t^a E_u^b \lvert 0\rangle$	$E_i^t E_j^u \lvert 0\rangle$	$E_i^u E_t^v \lvert 0\rangle$	$E_i^a E_j^t \lvert 0\rangle$	$E_u^a E_v^t \lvert 0\rangle$	$E_i^a E_u^t \lvert 0\rangle + E_i^t E_u^a \lvert 0\rangle$
S_{ijab}	S_{iab}	S_{ab}	S_{ij}	S_i	S_{ija}	S_a	S_{ia}

Basis set convergence of NEVPT2





CASSCF(12,12)

cc-pV6Z result still has very large error w.r.t CBS limit, 0.767 eV !

Development of MR-F12 methods

- MRCI-R12 by Gdanitz
- MR-MP2-F12 by Tenno
- CASPT2-F12 & MRCI-F12 by Werner
- The $[2]R_{12}$ and SF-$[2]R_{12}$ by Valeev
- The Brillouin-Wigner CC-F12 by Noga
- Mk-MRPT2-F12 by Haunschild
- The ic-MRCCSD by Köhn

NEVPT2-F12 not yet implemented !

General equations of NEVPT2-F12

For the simplest subspace $S_{ij,ab}$, its F12 equations are exactly the same as MP2-F12.

$$\left| 1^{S^{(0)}_{ij,ab}} \right\rangle = \frac{1}{2} E^{ab}_{ij} |0\rangle T^{ij}_{ab} + \frac{1}{2} E^{\alpha\beta}_{ij} |0\rangle W^{kl}_{\alpha\beta} T^{ij}_{kl} \quad \left(W^{kl}_{\alpha\beta} = \langle \alpha\beta | Q_{12} \hat{f}_{12} | kl \rangle\right)$$

$$\left| \tilde{\Phi}^{S^{(0)}_{ij,ab}} \right\rangle = {}^{2}/_{6} \left(E^{ab}_{ij} + W^{kl}_{\alpha\beta} E^{\alpha\beta}_{ij}\right)|0\rangle + {}^{1}/_{6} \left(E^{ba}_{ij} + W^{lk}_{\alpha\beta} E^{\beta\alpha}_{ij}\right)|0\rangle$$

$$R = \sum_{I} \langle \Psi_K | E_0 - H_0 | \Psi_I \rangle C^{(1)}_I - \langle \Psi_K | H_v | 0 \rangle$$

$$R^{ij}_{ab} = (ia|jb) + (\varepsilon_a + \varepsilon_b) T^{ij}_{ab} - (\varepsilon_i + \varepsilon_j) T^{ij}_{ab} + C^{kl}_{ab} T^{ij}_{kl}$$

$$R^{ij}_{kl} = V^{kl}_{ij} + \qquad B^{kl}_{ij} T^{ij}_{kl} - (\varepsilon_i + \varepsilon_j) X^{kl}_{ij} T^{ij}_{kl} + C^{ab}_{ij} T^{kl}_{ab}$$

$$E^{S^{(0)}_{ij,ab}} = \left(2T^{ij}_{ab} - T^{ji}_{ab}\right)\left\{(ia|jb) + R^{ij}_{ab}\right\} + \left(2T^{ij}_{kl} - T^{ji}_{kl}\right)\left\{V^{kl}_{ij} + R^{ij}_{kl}\right\}$$

$$V^{kl}_{ij} = (i\alpha|j\beta) W^{ij}_{\alpha\beta}, B^{kl}_{ij} = W^{lk}_{\alpha\beta} (\varepsilon_\alpha + \varepsilon_\beta) W^{ij}_{\alpha\beta}, X^{kl}_{ij} = W^{lk}_{\alpha\beta} W^{ij}_{\alpha\beta}, C^{ab}_{ij} = f_{a\gamma} W^{ij}_{\gamma b} + f_{b\gamma} W^{ij}_{\gamma a}$$

Fixed amplitudes ansatz

- Fixed amplitudes ansatz

$$T_{kl}^{ij} = \frac{3}{8}\delta_{ik}\delta_{jl} + \frac{1}{8}\delta_{il}\delta_{jk}$$

  - Based on wave function cusp conditions
  - Unitary invariant
  - Size-consistent
  - Only diagonal elements of intermediates are needed
- Energy expression

$$\begin{aligned} E_{Total}^{s_{ij,ab}^{(0)}} &= (\tilde{T}_{0\,ab}^{\;\;ij} - \frac{\tilde{R}_{ab}^{ij}}{\Delta_{ijab}})(ia|jb) + \tilde{T}_{kl}^{ij}\left[V_{ij}^{kl} + R_{kl}^{ij}\right] \\ &= E_{NEVPT}^{s_{ij,ab}^{(0)}} - T_{ab}^{ij} C_{ab}^{kl} \tilde{T}_{kl}^{ij} + \tilde{T}_{kl}^{ij}\left[V_{ij}^{kl} + R_{kl}^{ij}\right] \\ &= E_{NEVPT}^{s_{ij,ab}^{(0)}} + E_{F12}^{s_{ij,ab}^{(0)}} \end{aligned}$$

S. Ten-no, ***J. Chem. Phys.*** **121**, 117 (2004).
C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, ***Chem. Rev.*** **112**, 4 (2012).

1st-order WFN for NEVPT2-F12

Subspace	$\lvert 1_{NEVPT2}\rangle$	$\lvert 1_{NEVPT2-F12}\rangle$
$S^{(0)}_{ij,ab}$	$\frac{1}{2}E^a_i E^b_j \lvert 0\rangle T^{ij}_{ab}$	$\frac{1}{2}W^{kl}_{\alpha\beta}E^\alpha_i E^\beta_j \lvert 0\rangle T^{ij}_{kl}$
$S^{(-1)}_{i,ab}$	$E^a_i E^b_t \lvert 0\rangle T^{it}_{ab}$	$W^{ju}_{\alpha\beta}E^\alpha_i E^\beta_t \lvert 0\rangle T^{it}_{ju}$
$S^{(-2)}_{ab}$	$E^a_t E^b_u \lvert 0\rangle T^{tu}_{ab}$	$W^{vw}_{\alpha\beta}E^\alpha_t E^\beta_u \lvert 0\rangle T^{tu}_{vw}$
$S^{(1)}_{ij,a}$	$E^a_i E^t_j \lvert 0\rangle T^{ij}_{at}$	$W^{kl}_{\alpha t}E^\alpha_i E^t_j \lvert 0\rangle T^{ij}_{kl}$
$S^{(0)}_{i,a}$	$E^a_i E^t_u \lvert 0\rangle T^{iu}_{at} + E^t_i E^a_u \lvert 0\rangle T^{iu}_{ta}$	$W^{jv}_{\alpha t}(E^\alpha_i E^t_u - \langle 0\lvert E^t_u\rvert 0\rangle E^\alpha_i)\lvert 0\rangle T^{iu}_{jv} + W^{jv}_{t\alpha}\left(E^t_i E^\alpha_u + \frac{1}{2}\langle 0\lvert E^t_u\rvert 0\rangle E^\alpha_i\right)\lvert 0\rangle T^{iu}_{jv}$
$S^{(-1)}_{a}$	$E^a_u E^t_v \lvert 0\rangle T^{uv}_{at}$	$W^{wx}_{\alpha t}\left(E^\alpha_u E^t_v - \sum_{xy}\frac{\langle 0\lvert E^t_v E^x_u\rvert 0\rangle}{\langle 0\lvert E^x_y\rvert 0\rangle}E^\alpha_y\right)\lvert 0\rangle T^{uv}_{wx}$

For $S^{(0)}_{i,a}$ and $S^{(-1)}_{a}$ subspaces, the single excitations must be projected out.

Y. Guo, K. Sivalingam, E. F. Valeev, and F. Neese, ***J. Chem. Phys.*** **147**, 064110 (2017).

Equation of $S_{i,ab}$ subspace

$$R = \sum_I \langle \tilde{\Psi}_K | E_0 - H_0 | \Psi_I \rangle C_I^{(1)} - \langle \tilde{\Psi}_K | H_v | 0 \rangle$$

$$R_{ab}^{it} = (ia|ub)\Gamma_u^t + (\varepsilon_a + \varepsilon_b) T_{ab}^{iu} \Gamma_u^t + T_{ab}^{iu} K_u^t - \varepsilon_i T_{ab}^{iu} \Gamma_u^t + T_{ju}^{it} C_{jv}^{ab} \Gamma_v^u$$

$$R_{ju}^{it} = V_{it}^{jv} \Gamma_u^v + T_{ju}^{it} B_{it}^{jv} \Gamma_u^v + T_{ju}^{it} X_{it}^{jv} K_u^v - \varepsilon_i T_{ju}^{it} X_{it}^{jv} \Gamma_u^v + C_{jv}^{ab} T_{ab}^{it} \Gamma_v^u$$

$$\begin{aligned}
E_{Total}^{S_{i,ab}^{(-1)}} &= \tilde{T}_{ab}^{it} \Gamma_u^t (ia|ub) + \tilde{T}_{ju}^{it} \Gamma_u^t \left[V_{it}^{ju} + R_{ju}^{it} \right] \\
&= (\tilde{T}_{0\,ab}^{\;\;it} - S_{\bar{t}}^{t} \frac{\tilde{R}_{ab}^{i\bar{t}}}{\Delta_{i\bar{t}ab}}) \Gamma_u^t (ia|ub) + \tilde{T}_{ju}^{it} \Gamma_u^t \left[V_{it}^{ju} + R_{ju}^{it} \right] \\
&= E_{NEVPT}^{S_{i,ab}^{(-1)}} - T_{ab}^{it} \Gamma_u^t C_{ab}^{ju} \tilde{T}_{ju}^{it} + \tilde{T}_{ju}^{it} \Gamma_u^t \left[V_{it}^{ju} + R_{ju}^{it} \right] \\
&= E_{NEVPT}^{S_{i,ab}^{(-1)}} + E_{F12}^{S_{i,ab}^{(-1)}}
\end{aligned}$$

Y. Guo, K. Sivalingam, E. F. Valeev, and F. Neese, ***J. Chem. Phys.*** **147**, 064110 (2017).

Semi-external subspace S_a

$$R = \sum_I \langle \Psi_K | E_0 - H_0 | \Psi_I \rangle C_I^{(1)} - \langle \Psi_K | H_v | 0 \rangle$$

$$R_{at}^{uv} = (wa|xy)\Gamma_{tuv}^{wxy} + F'_{wa}\Gamma'^{w}_{tuv} + \varepsilon_a T_{aw}^{xy}\Gamma_{tuv}^{wxy} + T_{aw}^{xy}K_{tuv}^{wxy} + T_{xy}^{uv}\Gamma_{tuv}^{wxy}W_{aw}^{xy}$$

$$R_{xy}^{uv} = W_{\alpha w}^{xy}(\alpha u|tv)\tilde{\Gamma}_{tuv}^{wxy} + \varepsilon_\alpha W_{\alpha t}^{uv}W_{\alpha w}^{xy}\tilde{\Gamma}_{tuv}^{wxy}T_{xy}^{uv} + W_{\alpha w}^{xy}W_{\alpha t}^{uv}\tilde{K}_{tuv}^{wxy}T_{xy}^{uv} + W_{aw}^{xy}\tilde{\Gamma}_{tuv}^{wxy}T_{at}^{uv}$$

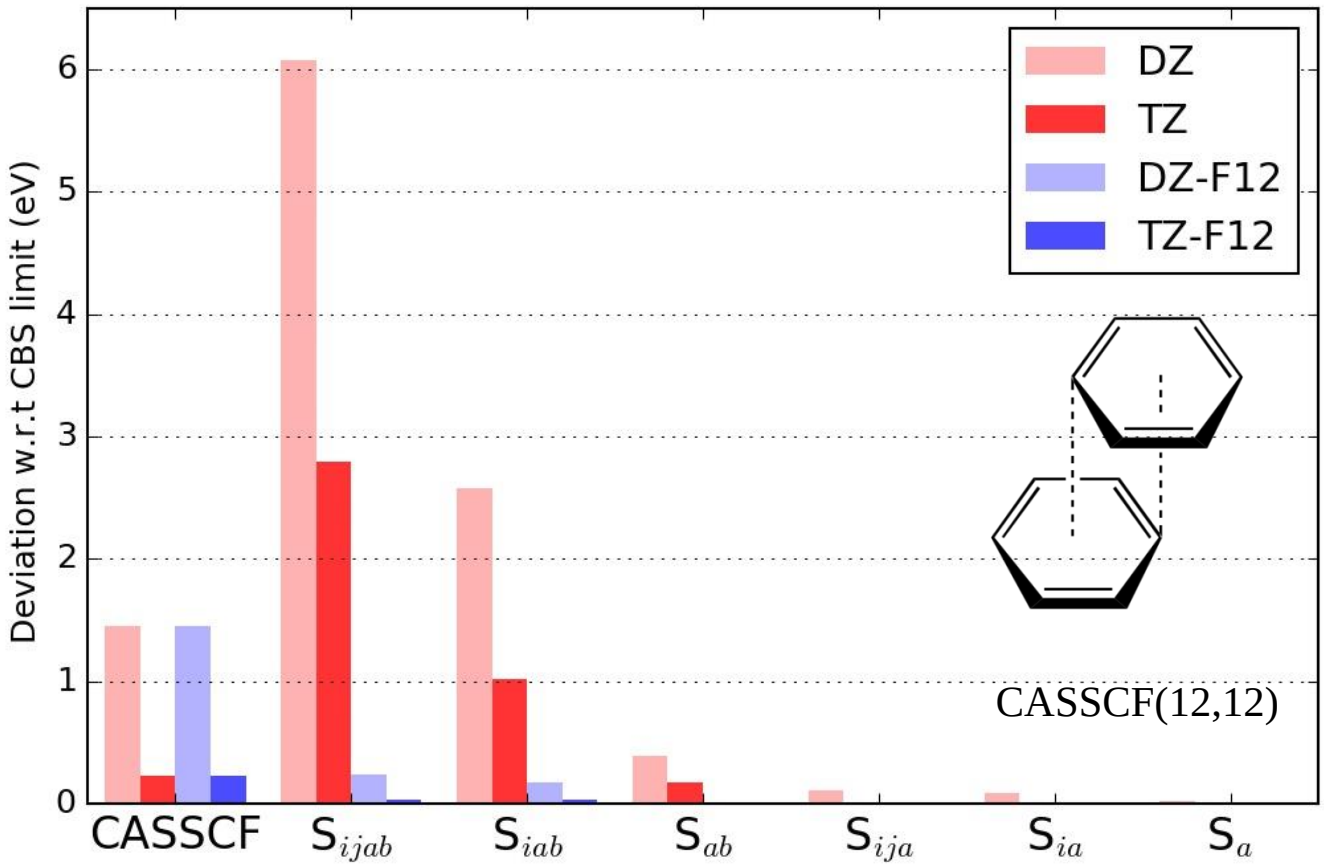
$$E_{Total}^{S_a^{(-1)}} = E_{NEVPT}^{S_a^{(-1)}} + T_{ta}^{uv}\left[T_{xy}^{uv}\Gamma_{tuv}^{wxy}W_{aw}^{xy}\right] + T_{xy}^{uv}\left[W_{\alpha w}^{xy}\tilde{\Gamma}_{tuv}^{wxy}(t\alpha|uv) + R_{xy}^{uv}\right]$$
$$= E_{NEVPT}^{S_a^{(-1)}} + E_{F12}^{S_a^{(-1)}}$$

$$\tilde{\Gamma}_{tuv}^{wxy} = \Gamma_{tuv}^{wxy} - \sum_{zz'}\Gamma_{tu}^{vz}\Gamma_{wx}^{yz'}(\Gamma^{-1})_z^{z'} = \langle 0 | E_w^y E_u^x E_v^t | 0 \rangle - \sum_{zz'}\Gamma_{tu}^{vz}\Gamma_{wx}^{yz'}(\Gamma^{-1})_z^{z'}$$

$$\tilde{K}_{tuv}^{wxy} = A_{tuv}^{wxy} - \sum_{zz'} B_{tu}^{vz}\Gamma_{wx}^{yz'}(\Gamma^{-1})_z^{z'} - \sum_{zz'}\Gamma_{tu}^{vz}C_{wx}^{yz'}(\Gamma^{-1})_z^{z'} + \sum_{\substack{z_1 z_2 \\ z_3 z_4}} D_{z_4}^{z_3}\Gamma_{tu}^{vz_1}\Gamma_{wx}^{yz_2}(\Gamma^{-1})_{z_1}^{z_3}(\Gamma^{-1})_{z_2}^{z_4}$$

C. Angeli, R. Cimiraglia, and J.-P. Malrieu, ***J. Chem. Phys.*** **117**, 9138 (2002).
Y. Guo, K. Sivalingam, E. F. Valeev, and F. Neese, ***J. Chem. Phys.*** **147**, 064110 (2017).

Accuracy of NEVPT2-F12



With F12 correction, CASSCF is less accurate than correlation energies.

$[2]_s$ Correction for CASSCF

- Brillouin condition:

$$\langle 0|\hat{E}_i^a H|0\rangle = 0, \qquad \langle 0|\hat{E}_t^a H|0\rangle = 0 \ (a \in vir)$$

$$\langle 0|\hat{E}_i^\alpha H|0\rangle = 0, \qquad \langle 0|\hat{E}_t^\alpha H|0\rangle = 0 \ (\alpha \in CBS)$$

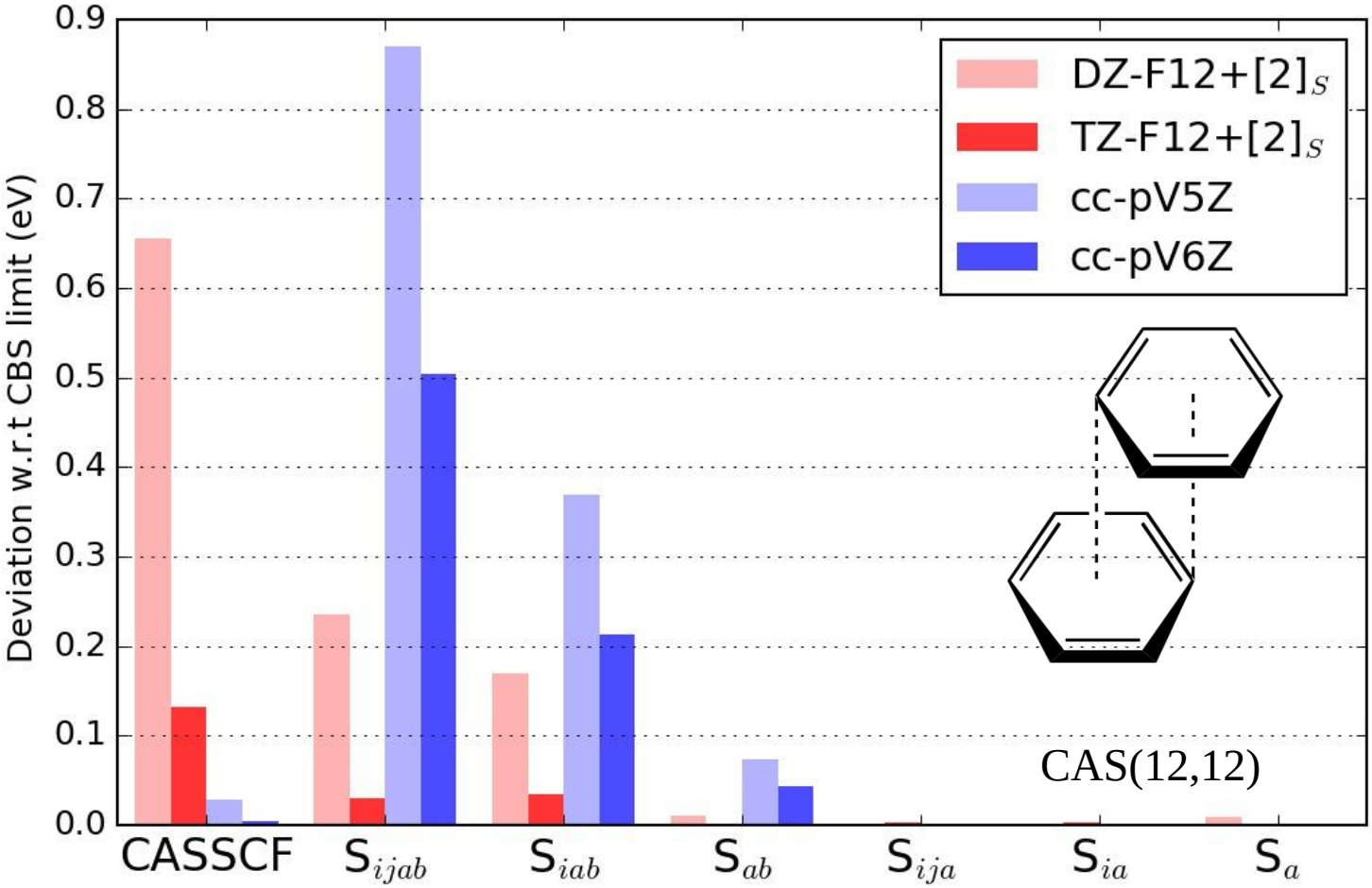
- Perturbative correction to CASSCF

$$R_\alpha^i = \left\langle 0\middle|\hat{E}_p^\alpha (H_0 - E_{CASSCF})\hat{E}_q^\beta\middle|0\right\rangle T_q^\beta + \langle 0|\hat{E}_p^\alpha H|0\rangle$$

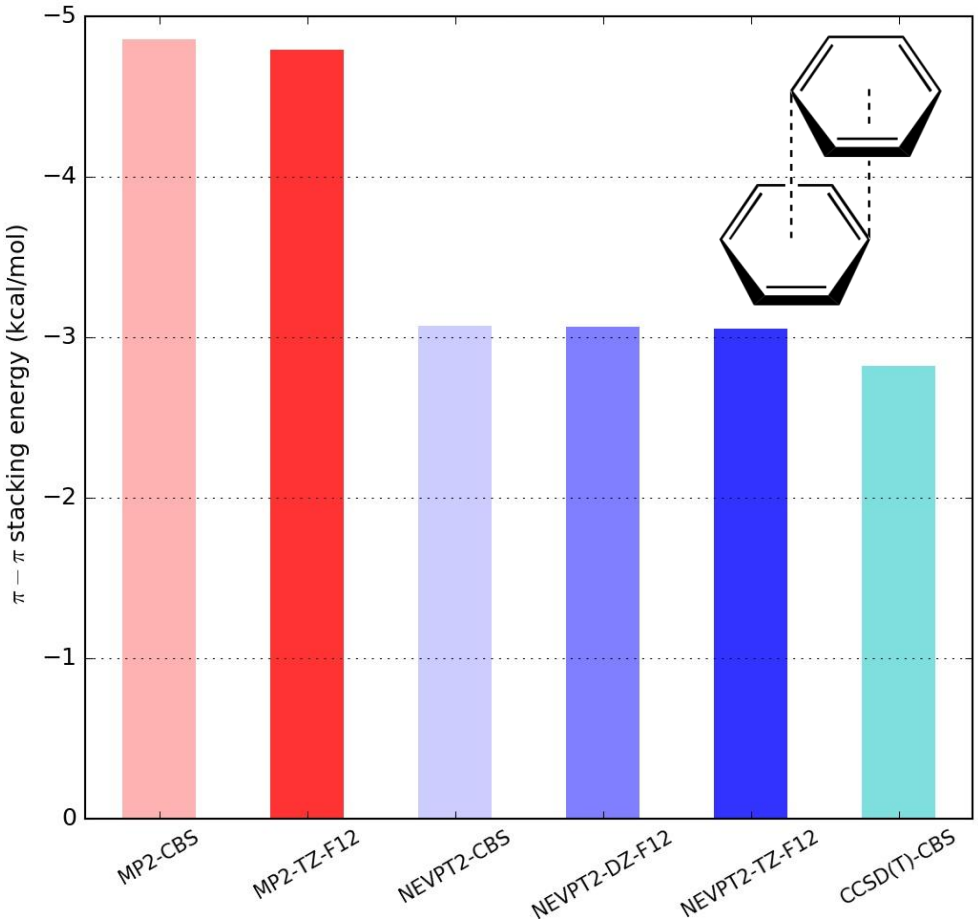
$$E_{[2]s} = \sum T_\alpha^p \langle 0|H\hat{E}_p^\alpha|0\rangle \qquad (p \in occ, act)$$

L. Kong, and E. F. Valeev, ***J. Chem. Phys.*** **133**, 174126 (2010).

Absolute Energy



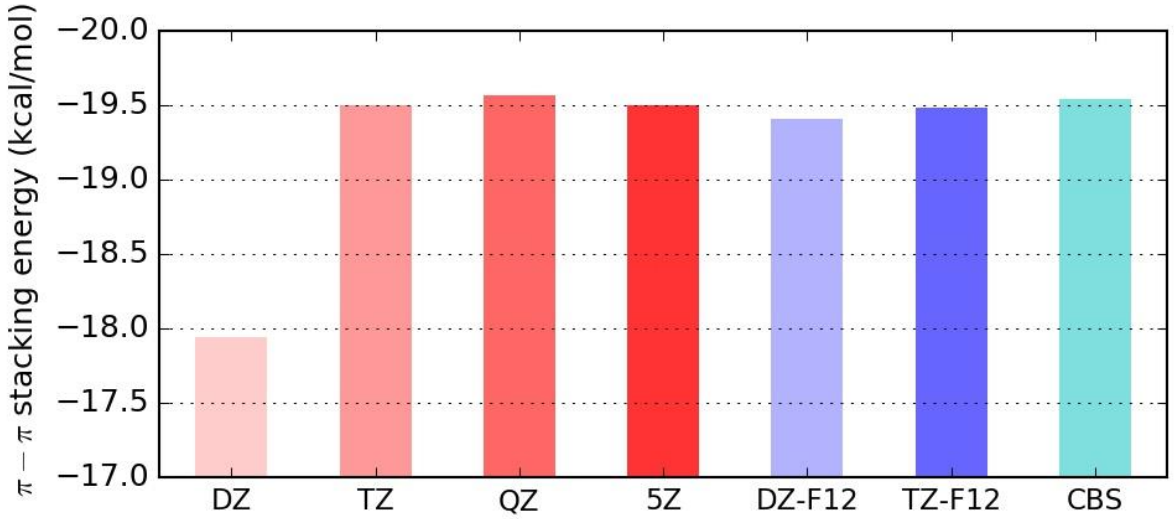
Relative energy

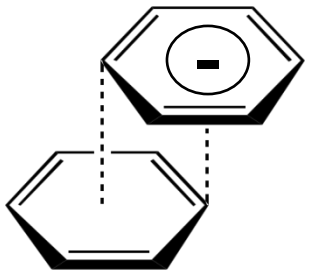


CAS(12,12)/NEVPT2 can reproduce very accurate interaction energy!

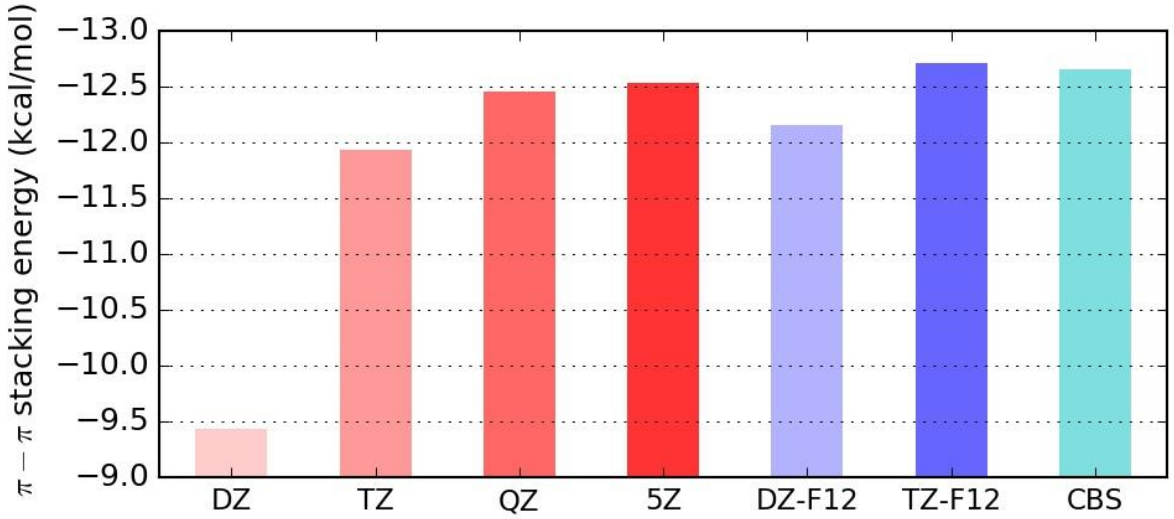
Rezác, J., Riley, K.E., Hobza, P., ***J. Chem. Theory Comput***. (2011)

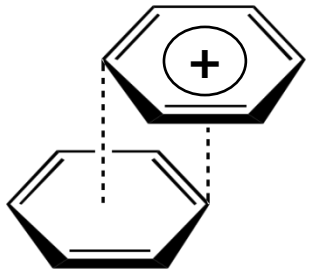
Relative energy





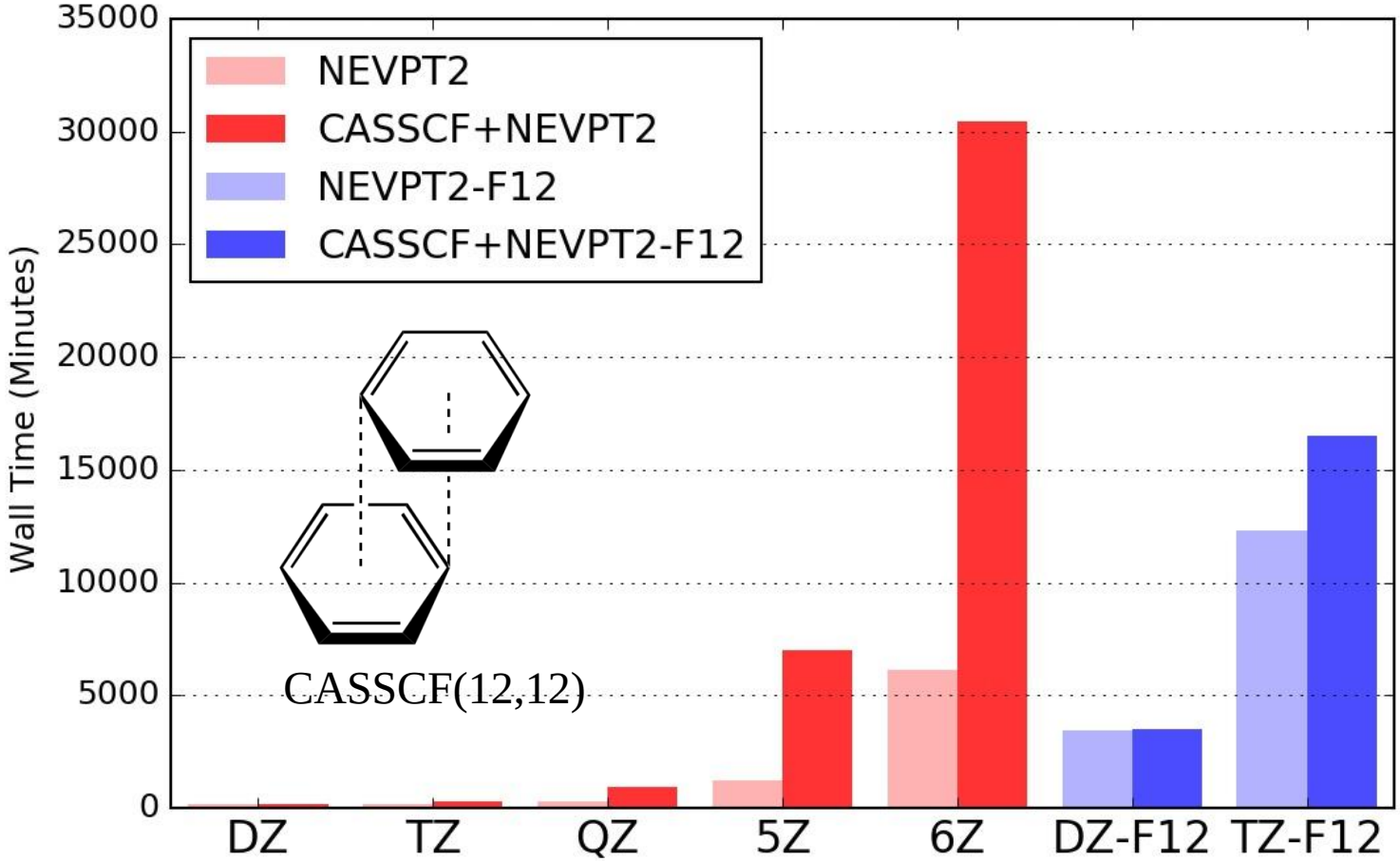
CAS(13,12)/NEVPT2





CAS(11,12)/NEVPT2

Bottleneck of NEVPT2-F12

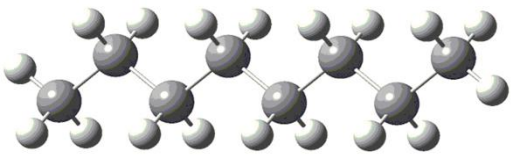


Domain based local pair natural orbital (DLPNO)-NEVPT2-F12

Introduction to DLPNO

$$E^{cor} = \sum_{ijab} [2(ia|jb) - (ib|ja)]\tau_{ij}^{ab}$$

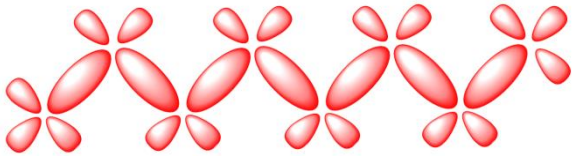
Molecule

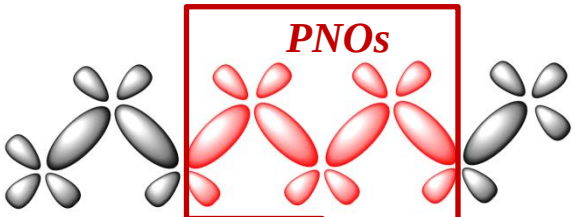


Truncation of occupied space (Pre-screen)

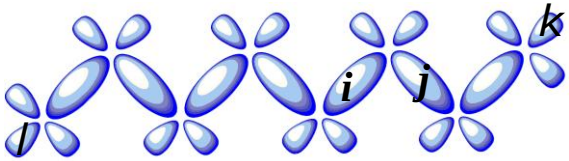
Truncation of virtual space (PNO)

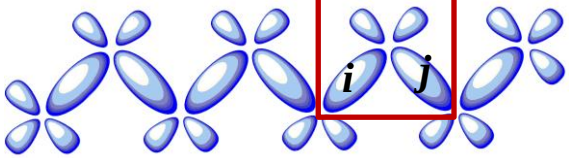
Virtual MOs





Occupied LMOs





DLPNO-NEVPT2 algorithm

Perform CASSCF calculation, localize occupied MOs, and construct PAOs

Use differential overlap integrals (DOI) to construct ‘Sparse-maps’

Dipole-integral based SC-NEVPT2 for pre-screen

Estimate energy contributions from pre-screening pairs

Construct RI integrals $(ia|K),(ta|K),(it|K),(tt,K)$ using ‘Sparse-map’

Loop over 8 subspaces

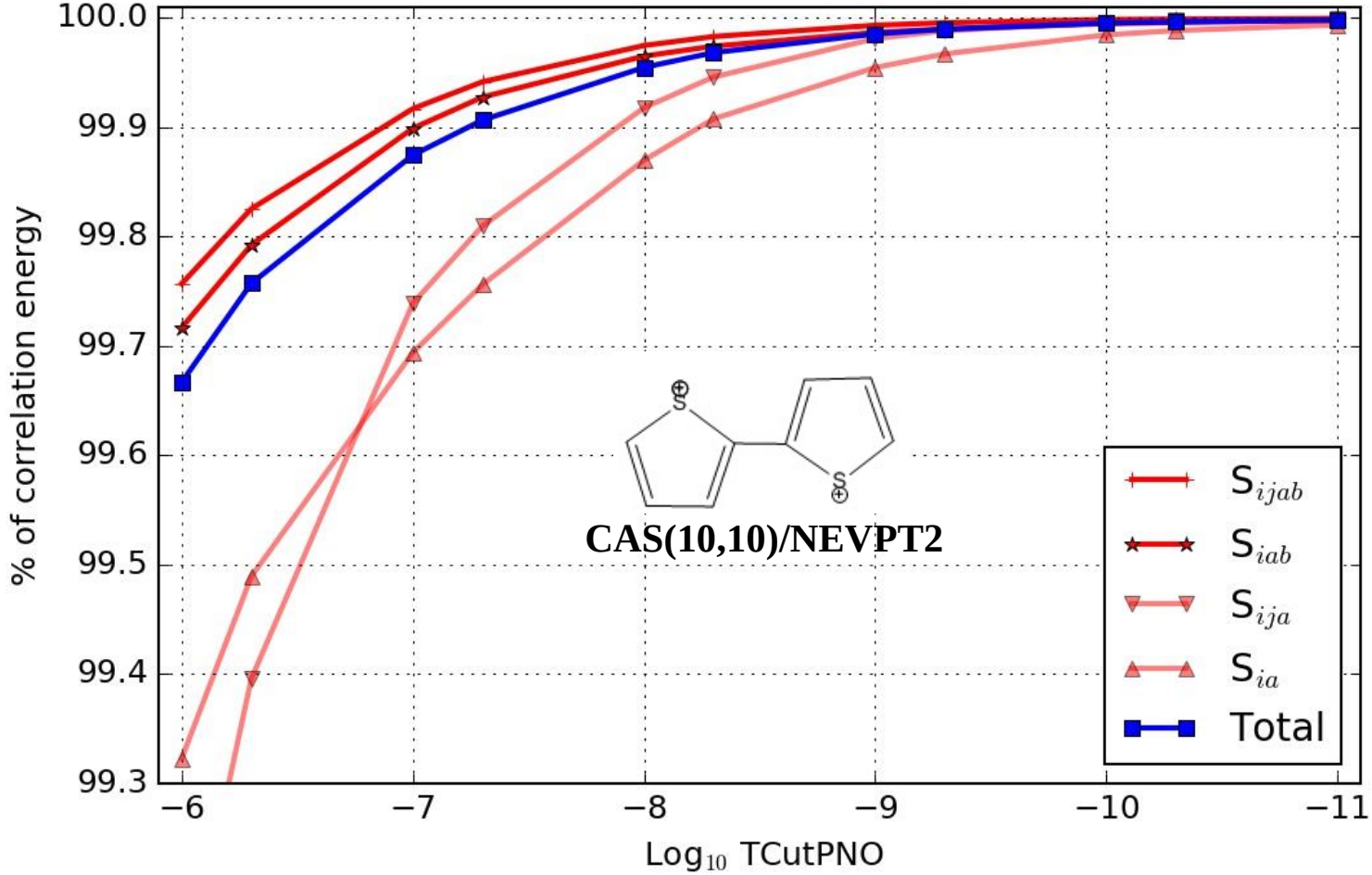
Truncate PAOs to PNOs, estimate the truncation error

Solve FIC-NEVPT2 residual equations iteratively

Calculate total correlation energy

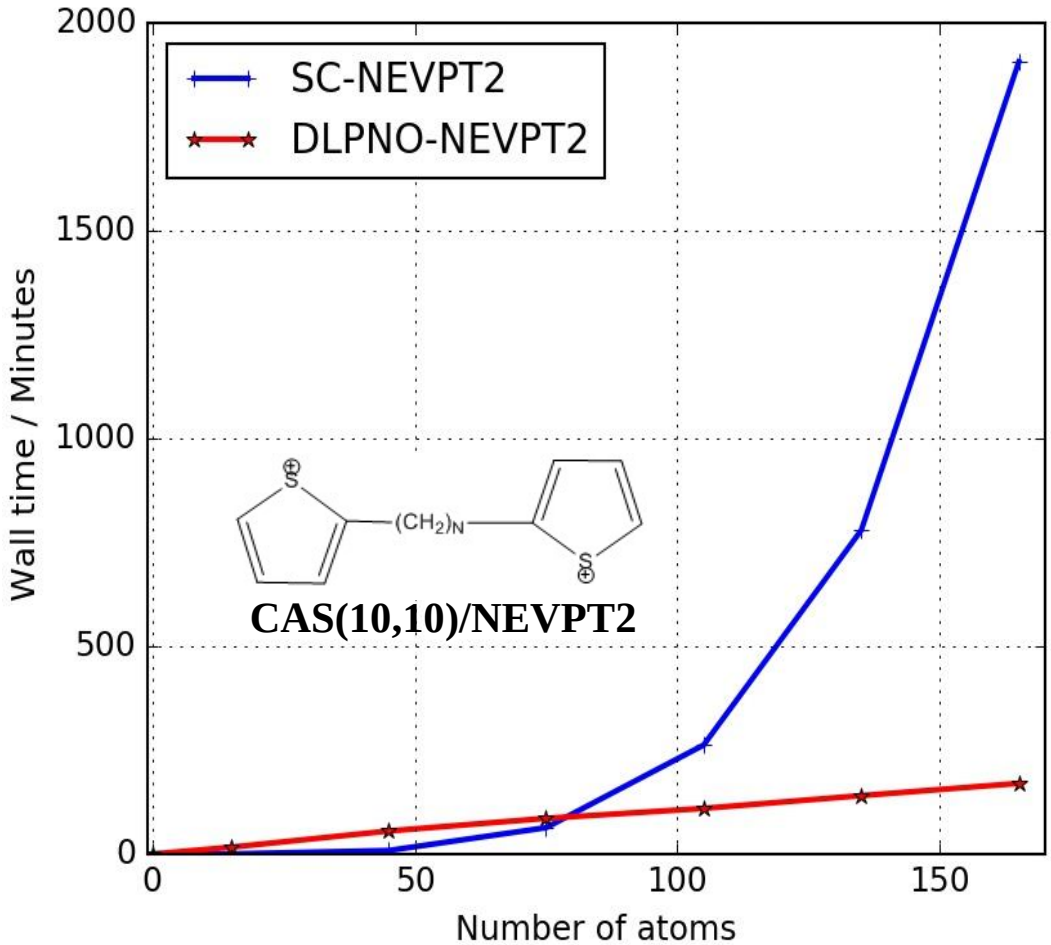
Y. Guo, K. Sivalingam, E. F. Valeev, and F. Neese, ***J. Chem. Phys.*** **144**, 094111 (2016).

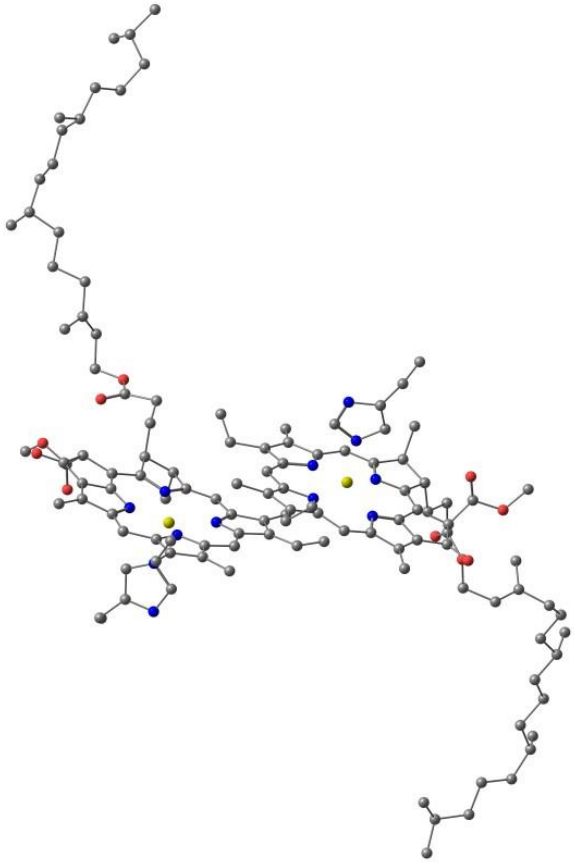
Accuracy of DLPNO-NEVPT2



Y. Guo, K. Sivalingam, E. F. Valeev, and F. Neese, ***J. Chem. Phys.* 144**, 094111 (2016).

Scaling behavior

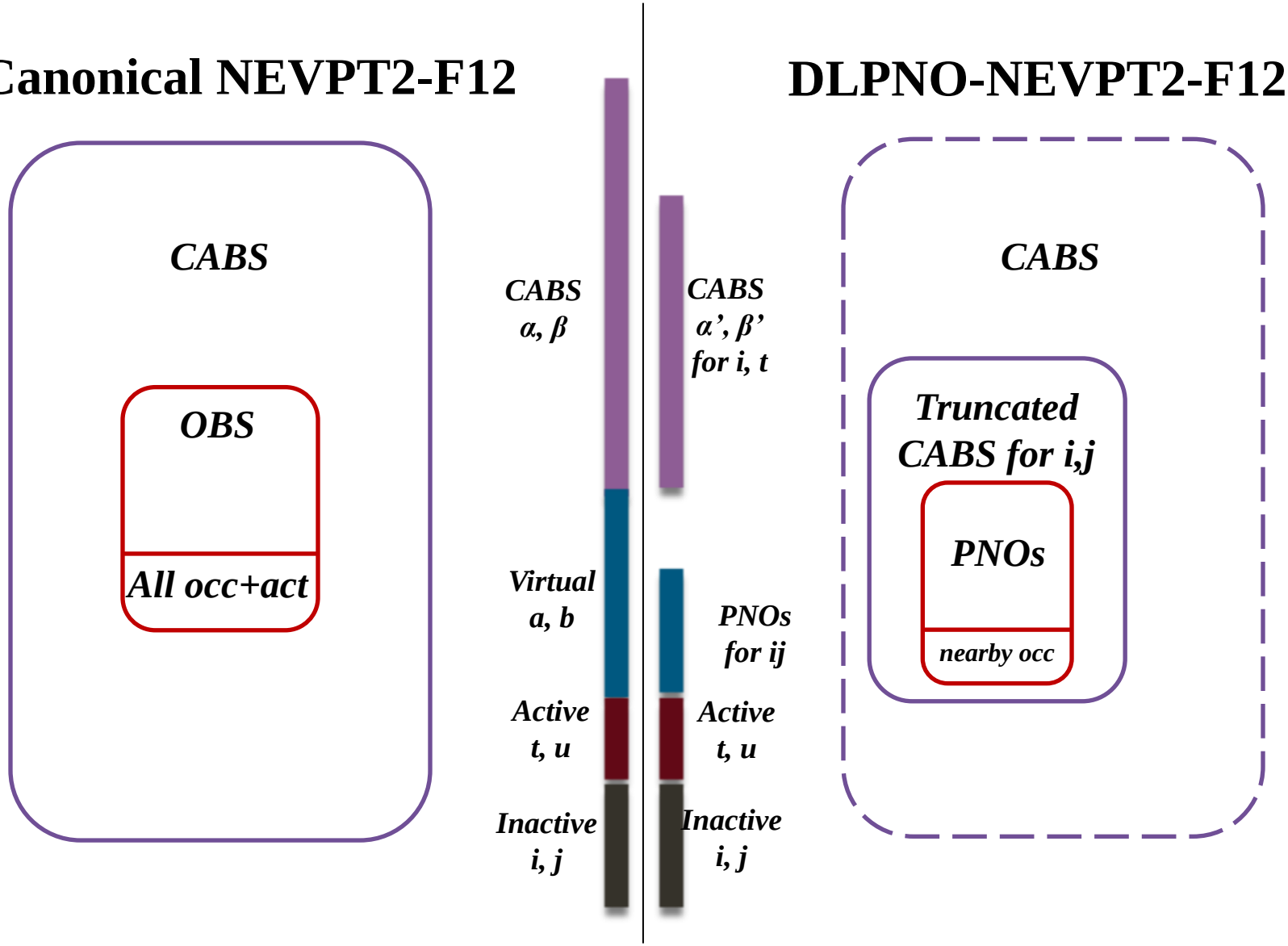




5426 basis functions
62 hours

Y. Guo, K. Sivalingam, E. F. Valeev, and F. Neese, ***J. Chem. Phys.* 144**, 094111 (2016).

Basic idea of DLPNO-NEVPT2-F12



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Equations of $S_{i,ab}$

- Canonical MO residual expressions

$$R_{ab}^{it} = (ia|ub)\Gamma_u^t + (\varepsilon_a + \varepsilon_b)T_{ab}^{iu}\Gamma_u^t + T_{ab}^{iu}K_u^t - \varepsilon_i T_{ab}^{iu}\Gamma_u^t + T_{ju}^{it}C_{jv}^{ab}\Gamma_v^u$$

$$R_{ju}^{it} = V_{it}^{jv}\Gamma_u^v + \quad T_{ju}^{it}B_{it}^{jv}\Gamma_u^v + T_{ju}^{it}X_{it}^{jv}K_u^v - \varepsilon_i T_{ju}^{it}X_{it}^{jv}\Gamma_u^v + C_{jv}^{ab}T_{ab}^{it}\Gamma_v^u$$

NEVPT2 residuals are never solved in practice.

- Localized occupied MO residual expressions

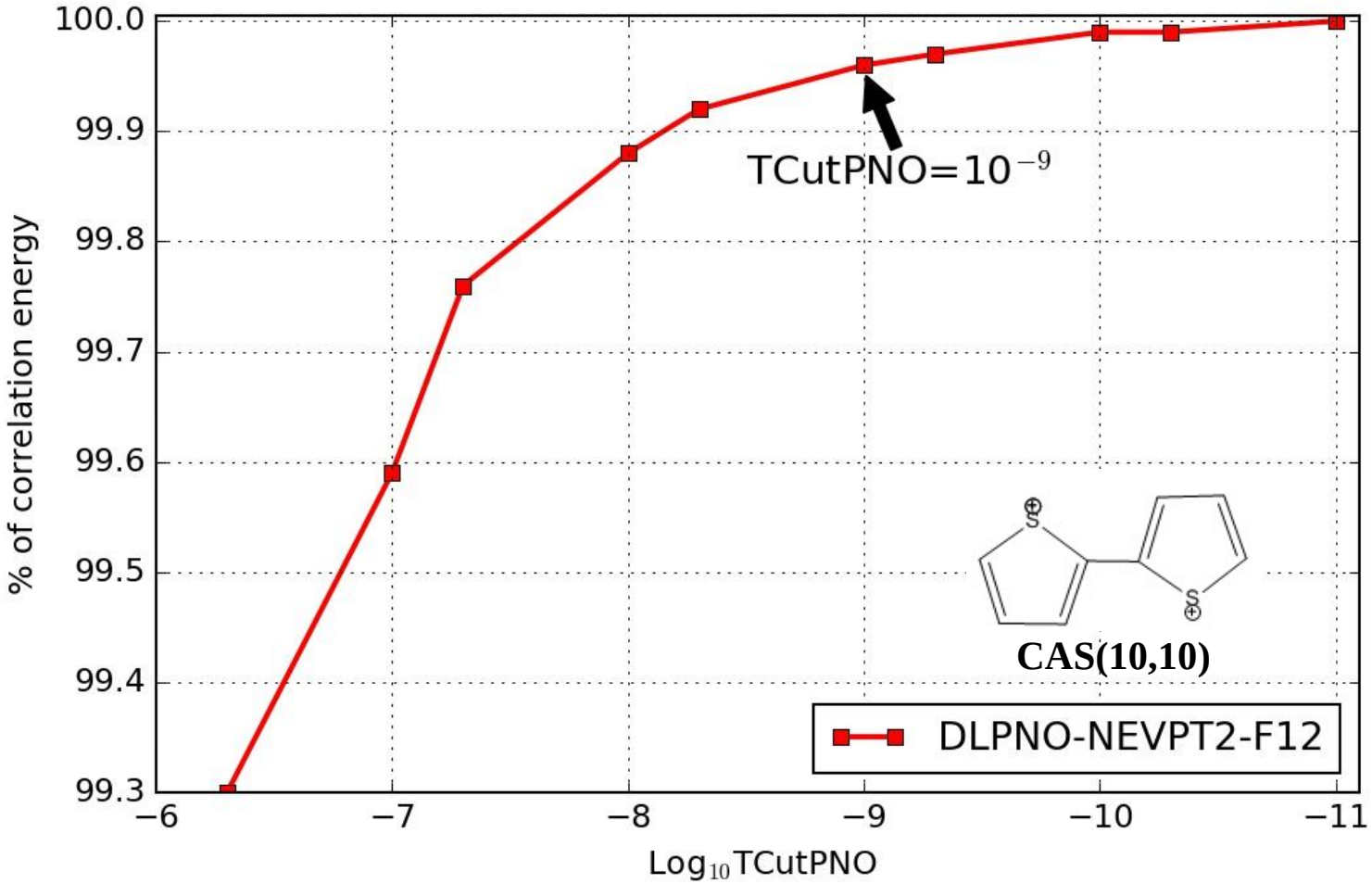
$$R_{ab}^{it} = (ia|ub)\Gamma_u^t + (\varepsilon_a + \varepsilon_b)T_{ab}^{iu}\Gamma_u^t + T_{ab}^{iu}K_u^t - \boldsymbol{F_{ik}T_{ab}^{ku}}\Gamma_u^t + T_{ju}^{it}C_{jv}^{ab}\Gamma_v^u$$

$$R_{ju}^{it} = V_{it}^{jv}\Gamma_u^v + \quad T_{ju}^{it}B_{it}^{jv}\Gamma_u^v + T_{ju}^{it}X_{it}^{jv}K_u^v - T_{ju}^{it}\boldsymbol{F_{ik}X_{kt}^{jv}}\Gamma_u^v + C_{jv}^{ab}T_{ab}^{it}\Gamma_v^u$$

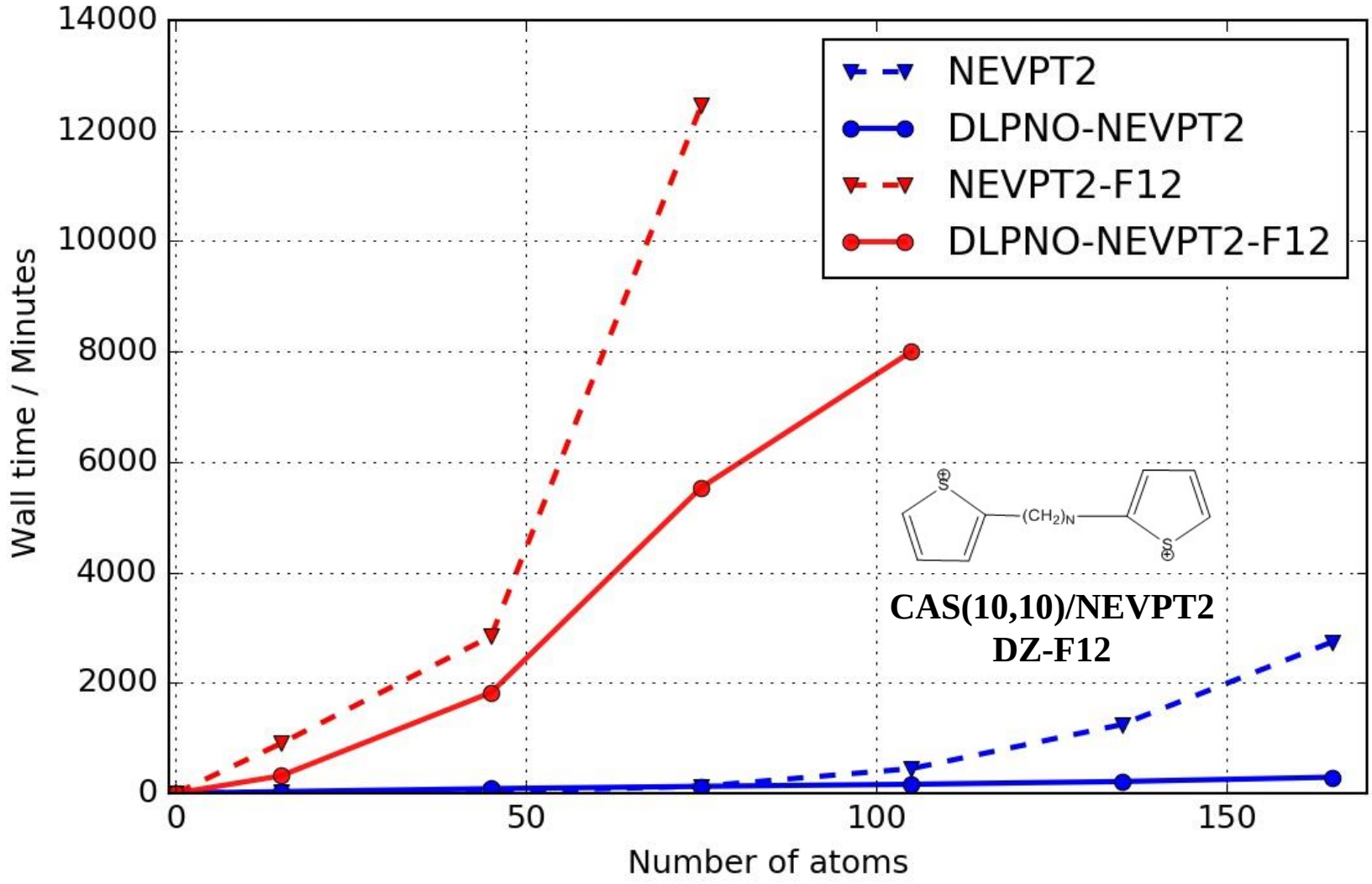
NEVPT2 residuals have to be solved iteratively.

F. Pavošević, P. Pinski, C. Riplinger, F. Neese *et al.*, ***J. Chem. Phys.*** **144**, 144109 (2016).

Accuracy


100.0
99.9
99.8
99.7
99.6
99.5
99.4
99.3
% of correlation energy
−6
−7
−8
−9
−10
−11
Log10TCutPNO
TCutPNO=10−9
CAS(10,10)
DLPNO-NEVPT2-F12

Scaling behavior



Conclusion and outlook

- Conclusion
  - NEVPT2-F12 method is developed for the first time.
  - Accurate CBS limit NEVPT2 results can be calculated with double-ζ basis.
  - Linear scaling version of NEVPT2-F12 (DLPNO-NEVPT2-F12) is developed.
- Outlook
  - NEVPT2 Algorithms based on large active space 0th-order wave function are undergoing.

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- Kantharuban Sivalingam
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- Prof. Edward Valeev
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Thank you for your attention!