

# Exploring pair natural orbitals for linear scaling MP2

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# Goals

- ▶ **Chemical accuracy** (1 kcal/mol) in relative energy for reactions and molecular clusters involving **large molecules**<sup>1</sup>
  - ▶ 99.9% of the canonical correlation energy required
- ▶ To develop an **explicitly correlated local coupled-cluster method** PNO-LCCSD(T)-F12
  - ▶ Exploit the short-range nature of weak electron correlation
  - ▶ Base model: **CCSD(T)-F12** → CCSD(T)/CBS
  - ▶ Starting from: second-order Møller–Plesset perturbation theory (**MP2**)
- ▶ Black box, efficient (minimize redundancies)
- ▶ **Linear scaling**
  - ▶ Cost (CPU time and resource usage) with the molecular size
  - ▶ Speedup with the number of CPU cores

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<sup>1</sup>Up to 200 atoms and 8000 of basis functions

# Outline

Introduction

Benchmark system

Local treatment of electron correlation

- Localization of occupied orbitals

- Domain approximations

- Pair approximations

Technical aspects

Further benchmark results

## Introduction

### Benchmark system

### Local treatment of electron correlation

- Localization of occupied orbitals

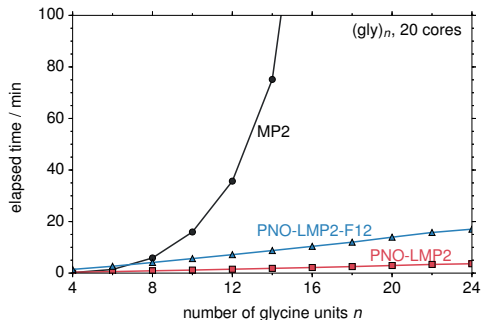
- Domain approximations

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### Technical aspects

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# Scalability problem in electron correlation methods



## Scaling in CPU time

- ▶ MP2  $O(N_{\text{el}}^5)$
- ▶ CCSD(T)  $O(N_{\text{el}}^7)$
- ▶ Local MP2  
 $\sim O(N_{\text{el}})$

## Scaling in storage requirements

- ▶ 2-electron integrals:  $O(N_{\text{AO}}^4)$  scaling
- ▶ ~ 1000 basis functions (20–30 atoms with reliable basis sets) to fill a 1 TB hard drive
- ▶ Integral-direct methods introduce redundancies

# Domain approximations

MP2 pair energy from  $|\Phi_{ij}^{ab}\rangle$

$$E_{ij} \sim \sum_{ab} [2(ai|bj) - (aj|bi)] (ai|bj)$$

$i, j$  – occupied orbitals;  $a, b$  – virtual orbitals

## Exponential decay of the integrals

If orbitals are local

$$(ai|bj) = \langle ab|r_{12}^{-1}|ij\rangle = \int \underbrace{\phi_a(\mathbf{r}_1)\phi_i(\mathbf{r}_1)}_{\rho_{ai}(\mathbf{r}_1)} r_{12}^{-1} \underbrace{\phi_b(\mathbf{r}_2)\phi_j(\mathbf{r}_2)}_{\rho_{bj}(\mathbf{r}_2)} d\mathbf{r}_1 d\mathbf{r}_2$$

We only need to consider excitations to external orbitals close to either  $i$  or  $j$

# Pair approximations

## MP2 pair energy

$$E_{ij} \sim \sum_{ab} [2(ai|bj) - (aj|bi)] (ai|bj)$$

$i, j$  – occupied orbitals;  $a, b$  – virtual orbitals

## For distant pairs $ij$

- ▶  $a$  close to  $i$ ,  $b$  close to  $j$ ,  $(aj|bi) \approx 0$
- ▶  $(ai|bj) = \int \rho_{ai}(\mathbf{r}_1) r_{12}^{-1} \rho_{bj}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$ , approximate with a multipole expansion
- ▶ Effective charge  $\int \rho_{ai}(\mathbf{r}) d\mathbf{r} = \langle a|i \rangle = 0$
- ▶  $(ai|bj)$  decays as  $R_{ij}^{-3}$ , pair energy as  $R_{ij}^{-6}$

## Explicit correlation: F12 methods

- ▶ Correlation energy **converges very slowly with the basis set size** due to the wave function cusp at  $r_{12} = 0$
- ▶ The wave function cusps cannot be represented by expansions of Slater determinants
- ▶ Explicit correlation treatments introduce terms in the wave function that **depend explicitly on  $r_{12}$**  (Hylleraas 1928, Kutzelnigg 1985, Kutzelnigg and Klopper 1990)
- ▶ Modern F12 methods (Ten-no 2004, Manby, Noga, Tew, Valeev, Werner...)

$$F_{12}(r_{12}) = -\frac{1}{\gamma}e^{-\gamma r_{12}} \approx -\frac{1}{\gamma} \sum_{i=1}^6 c_i e^{-\alpha_i r_{12}^2}$$



## Local MP2-F12 method

$$\Psi^{(1)} = \sum_{ij} \left[ \sum_{a,b \in [ij]} |\Phi_{ij}^{ab}\rangle T_{ab}^{ij} + \sum_{\alpha\beta}^{\text{complete}} |\Phi_{ij}^{\alpha\beta}\rangle T_{\alpha\beta}^{ij} \right]$$

$$T_{\alpha\beta}^{ij} = \frac{3}{8} \langle \alpha\beta | \hat{Q}_{12}^{ij} F_{12} | ij \rangle + \frac{1}{8} \langle \alpha\beta | \hat{Q}_{12}^{ij} F_{12} | ji \rangle$$

$$\begin{aligned} \hat{Q}_{12}^{ij} = & 1 + \sum_{m,n \in [ij]_{\text{LMO}}} |mn\rangle \langle mn| - \sum_{a,b \in [ij]} |ab\rangle \langle ab| \\ & - \sum_{m \in [ij]_{\text{LMO}}} \sum_{\alpha \in [ij]_{\text{RI}}} (|m\alpha\rangle \langle m\alpha| + \underbrace{|\alpha m\rangle \langle \alpha m|}_{\text{yields } \langle ij | r_{12}^{-1} | \alpha m \rangle \langle \alpha m | F_{12} | ij \rangle \text{ in } E^{(2)}}) \end{aligned}$$

- If F12 is combined with local methods, the domain error is reduced by an order of magnitude

# PNO-LCCSD(T)-F12 methods

- ▶ Pair natural orbitals (PNOs) minimize the necessary domain size for a given accuracy (Meyer 1971, 1973; Neese et al. 2009)

## Problems in large systems

- ▶ Very large number of PNOs, non-orthogonal between pairs
- ▶ Difficult integral transformations and complicated logic

## Solutions: Local density fitting, projections, etc

- ▶ **DLPNO-CCSD(T)-F12** (Orca): Riplinger, Neese, Valeev, et al.
- ▶ **PNO-CCSD(T)[F12]** (Turbomole): Schmitz, Hättig, Tew
- ▶ Our work: Parallel **PNO-LCCSD(T)-F12** (Molpro)

# Role of many-body perturbation theory

## Domain approximations

- ▶ Provides a guess of pair density matrices from which natural orbitals are made

## Pair approximations

- ▶ Provides pair selection criteria and approximate distant pair energies
- ▶ Provides a hierarchy of the terms in the CCSD equations

## Perturbative triples correction

- ▶ Significantly improve the accuracy of the CCSD method

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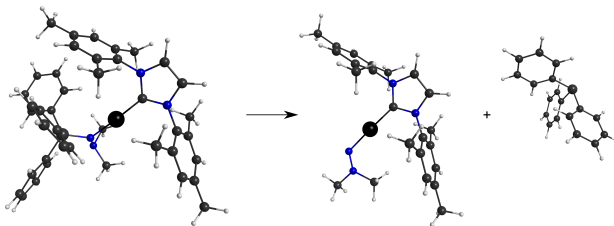
- Domain approximations

- Pair approximations

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# AuAmin reaction

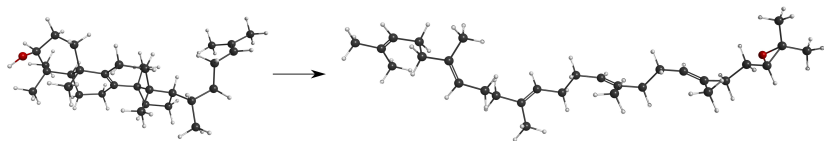


- ▶ “AuAmin” is a gold(I)-aminonitrene complex which plays an important role in catalytic reactions<sup>2</sup>
- ▶ Experimental dissociation energy:  $47.0 \pm 2.6 \text{ kcal mol}^{-1}$
- ▶ HF/VTZ-F12 + CABS:  $22.0 \text{ kcal mol}^{-1}$
- ▶ LMP2:  $57.2 \text{ kcal mol}^{-1}$ ; LMP2-F12:  $60.3 \text{ kcal mol}^{-1}$
- ▶ LCCSD(T)-F12:  $47.5 \text{ kcal mol}^{-1}$

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<sup>2</sup>Fedorov et al., ChemPhysChem, 11, 1002, (2010)

# Isomer4 reaction



- ▶ Most difficult reaction of the ISOL24 benchmark set<sup>3</sup>

$E_r$ (kcal/mol)	local	canonical
HF + CABS:	18.7	18.7
LMP2-F12:	79.8	79.8
SCS-LMP2-F12:	65.0	64.7
LCCSD(T)-F12:	67.9	?

- ▶ The accuracy of local methods has been established by studying the convergence with respect to **all** local approximations

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<sup>3</sup>Huenerbein et al., PCCP 12, 6940 (2010)

# Error cancellation

## Extensivity of the error

- ▶ Errors in absolute energies are extensive for quantum chemistry methods, and **grow with the molecule size**
- ▶ We rely on **systematic error compensations** when computing relative energies

**Avoid “random” error cancellations as much as possible, e.g.,**

- ▶ Basis-set errors and the intrinsic error of the method
- ▶ Errors from pair approximations and domain approximations

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# Orbital localization

Localized molecular orbitals are obtained from the canonical molecular orbitals (CMOs) by a unitary transformation

$$|i\rangle = \sum_k^{\text{val}} |\phi_k^{\text{can}}\rangle U_{ki}^{\text{loc}}$$

## Foster and Boys (FB) localization

Minimize the sum of the orbital variances:

$$P^{\text{fb}} = \sum_p^{x,y,z} \sum_i^{\text{val}} \langle i | (\hat{p} - \langle i | \hat{p} | i \rangle)^2 | i \rangle$$

# Orbital localization

## Pipek–Mezey (PM) localization

Maximize the sum of squared Mulliken partial charges on atoms:

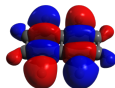
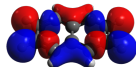
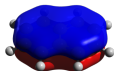
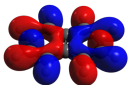
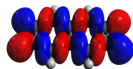
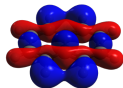
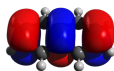
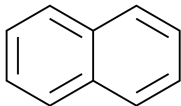
$$P^{\text{PM}} = \sum_A^{\text{atoms}} \sum_i^{\text{val}} q_{iA}^2$$

$$q_{iA} = 2 \sum_{\mu \in A} L_{\mu i} \sum_{\nu} S_{\mu\nu} L_{\nu i}$$

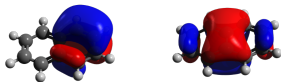
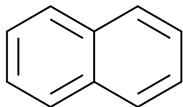
## Intrinsic bond orbitals (IBOs)

Create a molecule-intrinsic minimal basis of polarized AOs and compute  $q_{iA}$  for PM localization

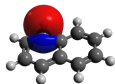
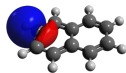
# Canonical orbitals



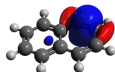
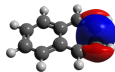
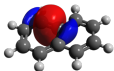
# Local orbitals (IBO)



5  $\pi$ -orbitals



8 C—H bonds



11 C—C bonds

# Projected atomic orbitals

## PAOs (Pulay 1983)

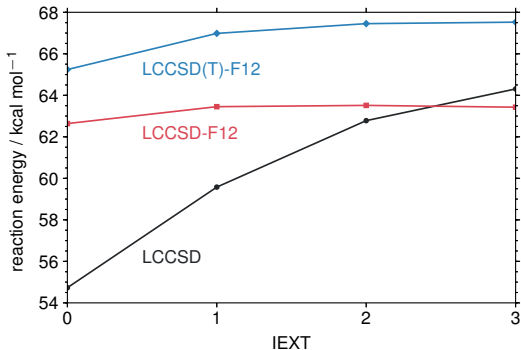
Project the atomic orbitals against the occupied subspace

$$|r\rangle = \hat{P} |r^{AO}\rangle$$

$$\hat{P} = 1 - \sum_m^{\text{occ}} |m\rangle \langle m|$$

- ▶ Centered on atoms but possess tails
- ▶ Nonorthogonal and forms a redundant set
- ▶ Domain truncation based on **distance** and **connectivity** criteria
- ▶ Pair domain:  $[ij]_{\text{PAO}} = [i]_{\text{PAO}} \cup [j]_{\text{PAO}}$
- ▶ 500–800 orbitals per pair needed for chemical accuracy

# Effect of PAO domain sizes on reaction energies



- ▶ F12 correction strongly reduces the domain error
- ▶ Domain errors re-introduced by (T) which is not explicitly correlated

# Pair natural orbitals

## Pair natural orbitals (PNOs)

Obtained by diagonalizing (approximate MP2) external pair density matrices:

$$[\mathbf{D}^{ij}]_{ab} = \frac{1}{1 + \delta_{ij}} [\tilde{\mathbf{T}}^{ij\dagger} \mathbf{T}^{ij} + \tilde{\mathbf{T}}^{ij} \mathbf{T}^{ij\dagger}]_{ab}, \quad \tilde{\mathbf{T}}^{ij} = 2\mathbf{T}^{ij} - \mathbf{T}^{ji}$$

$$[\mathbf{Q}^{ij\dagger} \mathbf{D}^{ij} \mathbf{Q}^{ij}]_{rs} = n_r^{ij} \delta_{rs}$$

- ▶ **Pair-specific**, but typically only **50–80 orbitals** per pair are needed for chemical accuracy
- ▶ Domains selection based on **occupation number**:  $n_a^{ij} \geq T_{\text{PNO}}$

# Orbital specific virtuals

- ▶ Orbital specific virtuals (OSVs) are PNOs for diagonal pairs
- ▶ Pair domain:  $[ij]_{\text{osv}} = [i]_{\text{osv}} \cup [j]_{\text{osv}}$
- ▶ 200–300 orbitals per pair needed for chemical accuracy
- ▶ Domain per pair: PNO < OSV < PAO
- ▶ Total number of orbitals: PAO < OSV < PNO

## Stepwise transformations

- ▶ PAO→OSV→PNO leads to successively smaller domains and linear scaling
- ▶ The use of OSVs reduces the storage and communication cost of the orbital transformation matrices



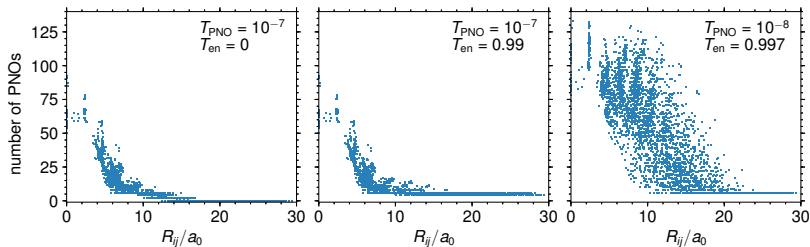
# Semi-canonical approximations

## LMP2 amplitude equations

$$\begin{aligned} R_{ab}^{ij} = & (ai|bj) + (\varepsilon_a^{ij} + \varepsilon_b^{ij} - f_{ii} - f_{jj})T_{ab}^{ij} \\ & + \underbrace{\sum_{c \in [ij], c \neq a, b} (f_{ac}T_{cb}^{ij} + T_{ac}^{ij}f_{cb})}_{\text{0 with pseudocanonical PNOs}} - \underbrace{\sum_{k \in [ij]_{\text{LMO}}, k \neq i, j} (f_{ik}\bar{T}_{ab}^{kj} + \bar{T}_{ab}^{ik}f_{kj})}_{\text{ignored with semi-canonical approx.}} \\ = & 0 \quad (\forall i, j; a, b \in [ij]) \end{aligned}$$

- ▶ Usually provide > 95% of the LMP2 electron correlation energy
- ▶ Sensitive to the orbital localization method
- ▶ Provide sufficiently good amplitudes for making PNOs

# PNO domain size as a function of $R_{ij}$



## Energy threshold

- ▶  $E_{ij}^{\text{PNO(SC)}} \geq T_{\text{en}} \cdot E_{ij}^{\text{OSV(SC)}}$
- ▶ Improves the accuracy for more distant pairs at a rather small added cost

# Domain corrections

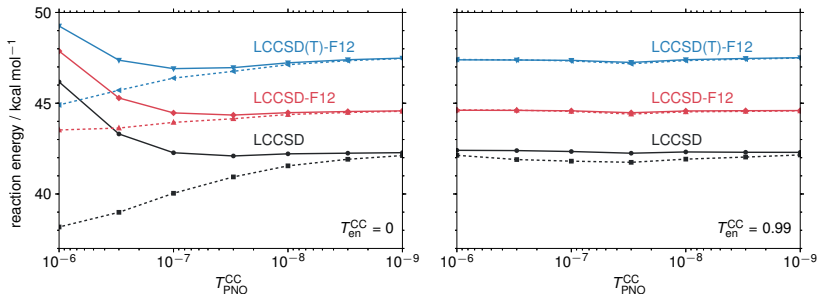
- ▶ The size of PNO domains strongly affects the computational cost in LCCSD.

## MP2 domain correction

$$E_{\text{LCCSD-F12}}(\text{large}) \approx E_{\text{LCCSD-F12}}(\text{small}) - E_{\text{LMP2-F12}}(\text{small}) \\ + E_{\text{LMP2-F12}}(\text{large})$$

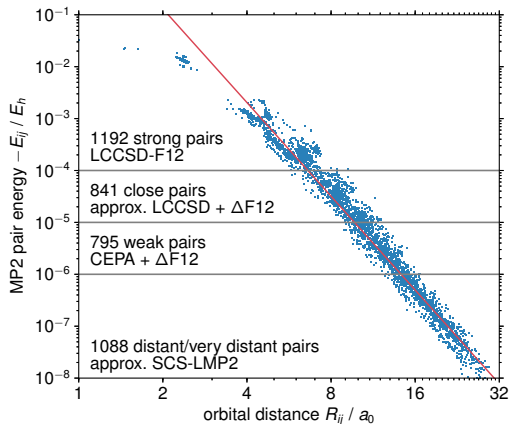
This approach improves the convergence with respect to the PNO domain size.

# Effect of PNO domain sizes on reaction energies



- For the “AuAmin” reaction, the domain errors in PNO-LCCSD(T)-F12 calculations can be reduced to less than 0.5 kcal mol<sup>-1</sup>.

# $R_{ij}^{-6}$ decay of pair energies



For distant pairs  $ij$ ,  $E_{ij} \sim \left[ \underbrace{2(ai|bj) - (aj|bi)}_{\approx 0} \right] \underbrace{(ai|bj)}_{\text{dipole-dipole interaction, } \sim R_{ij}^{-3}}$

# Approximations for close and weak pairs

## Close-pair approximation

- ▶ Neglect slowly decaying terms in the LCCSD amplitude equations which cancel at long-range
- ▶ Truncation of summations over occupied indices according to the decay properties of individual terms (exponential or  $R^{-6}$ ) and the order in MPPT

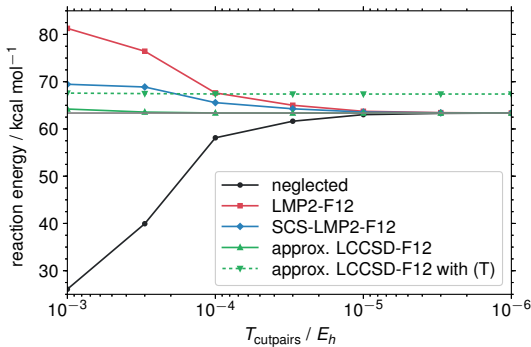
## Weak approximation

- ▶ Neglect all non-linear terms (CEPA)

## Distant pairs

- ▶ Iterative PNO-LMP2 with multipole approximation

# Effect of pair approximations on reaction energies



- ▶ "Isomer4" reaction
- ▶ Large long-range effects, strongly overestimated by LMP2
- ▶ Approximate LCCSD is very accurate

## (T) correction

$$R_{abc}^{ijk} = (\epsilon_a^{ijk} + \epsilon_b^{ijk} + \epsilon_c^{ijk} - f_{ij} - f_{jj} - f_{kk}) T_{abc}^{ijk} + W_{abc}^{ijk} - Z_{abc}^{ijk} = 0$$

$$W_{abc}^{ijk} = \hat{P}_{abc}^{ijk} \left[ \sum_d (ia|bd) \bar{T}_{dc}^{jk} - \sum_l (ia|jl) \bar{T}_{bc}^{lk} \right]$$

$$Z_{abc}^{ijk} = \underbrace{\sum_{l \neq k} f_{kl} \bar{T}_{abc}^{ijl} + \sum_{l \neq j} f_{jl} \bar{T}_{abc}^{ilk} + \sum_{l \neq i} f_{il} \bar{T}_{abc}^{ljk}}_{\text{ignored in (T0) approximation}} + \ddots$$

0 with pseudocanonical orbitals

## Triple-list truncation

- ▶ Include only triples  $ijk$  where at least one of the pairs  $ij$ ,  $ik$ ,  $jk$  is strong



# Domain approximation in the (T) treatment

## Triples natural orbitals

- ▶ Similar to PNOs, but the external density matrices are approximated (Riplinger et al. 2013)

$$\mathbf{D}^{ijk} = \frac{1}{3}(\mathbf{D}^{ij} + \mathbf{D}^{ik} + \mathbf{D}^{jk})$$

- ▶ (T0) domain correction

$$E^{(T)}(\text{large}) \approx E^{(T)}(\text{small}) - E^{(T0)}(\text{small}) + E^{(T0)}(\text{large})$$

- ▶ Typically 80–100 TNOs needed for (T0) and 30–50 TNOs for the iterative (T)

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# Robust local density fitting<sup>4</sup>

## Integral transformation

$$(A|\mu i) = \sum_{\nu} (A|\mu \nu) L_{\nu i}, \quad (A|ri) = \sum_{\mu} (A|\mu i) P_{\mu r}.$$

## Fitting and assembly

Density fitting: Whitten 1973, Dunlap 1977

$$\underbrace{\int \rho_{ri}(\mathbf{r}_1) r_{12}^{-1} \rho_{sj}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}_{(ri|sj)} \approx \sum_{A \in [ij]_{\text{fit}}} d_{ri}^A \underbrace{\int \phi_A(\mathbf{r}_1) r_{12}^{-1} \rho_{sj}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}_{(A|sj)}$$

$$(ri|B) \approx \sum_{A \in [ij]_{\text{fit}}} d_{ri}^A \underbrace{\int \phi_A(\mathbf{r}_1) r_{12}^{-1} \phi_B(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}_{(A|B)}$$

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<sup>4</sup> $i, j$ : occupied orbitals;  $r, s$ : PAOs

# Parallelization in LMP2

## Fundamental Strategy

- ▶ **Dynamic** task distribution in integral transformation
  - ▶ Store all integrals in distributed memory
- ▶ **Static** pair distribution in CCSD iterations
  - ▶ Keep a copy of required amplitudes in local memory
  - ▶ Load integrals to local memory before the iterations
  - ▶ Synchronize the amplitudes after each iteration

## 2-Electron integrals

- ▶ Evaluate and transform (to MOs/PAOs) 2, 3-index integrals
  - ▶ Parallelize over fitting basis
- ▶ Assembly and transform (to PNOs) 4-index integrals
  - ▶ Parallelize over pairs of LMOs
  - ▶ Algorithms to reduce duplicated communication/computation

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# Comparison with canonical CCSD(T)-F12 results

## Friedrich and Hänchen test set<sup>5</sup>

- ▶ 55 reactions of medium-sized molecules
- ▶ RMS error from canonical CCSD(T)-F12: 0.18 kcal mol<sup>-1</sup> (default); 0.09 kcal mol<sup>-1</sup> (large domains), using cc-pVTZ-F12 basis

## S22 test set<sup>6</sup> of weak intermolecular interaction

- ▶ Binding energy of molecular dimers up to 30 atoms
- ▶ F12-scaled triples necessary to reduce the basis-set errors in (T)
- ▶ RMS error from the best available CCSD(T)/CBS estimations: 0.22 kcal mol<sup>-1</sup> (default), 0.06 kcal mol<sup>-1</sup> (large domains), using aug-cc-pVTZ basis

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<sup>5</sup>Friedrich and Hänchen, JCTC, 9, 5381 (2013)

<sup>6</sup>Jurečka et al., PCCP, 8, 1985 (2006)

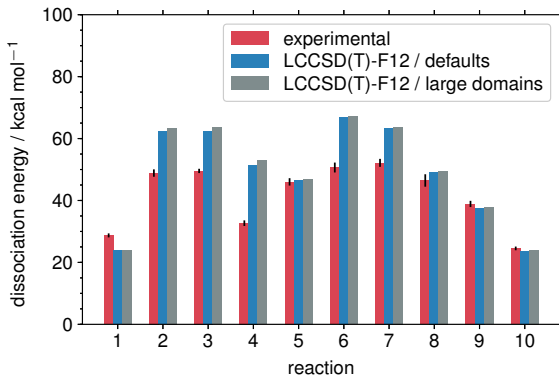
## Benzene dimer (counterpoise corrected)

Method	Canonical	Local	
		default	large domains
HF	5.36	5.36 (0.00)	5.36 (0.00)
MP2	-4.70	-4.46 (0.24)	-4.63 (0.07)
MP2-F12	-4.95	-4.88 (0.07)	-4.95 (0.00)
CCSD-F12	-1.12	-1.06 (0.06)	-1.12 (0.00)
CCSD(T)-F12	-2.50	-2.27 (0.23)	-2.43 (0.07)
CCSD(T*)-F12	-2.63	-2.47 (0.26)	-2.56 (0.07)
S22B <sup>7</sup>		-2.65	

- ▶ Domain errors are largely eliminated with the F12 treatment, but reintroduced in (T)

<sup>7</sup>Marshall, Burns, and Sherrill, JCP, 135, 194102 (2011)

## WCCR10 test set<sup>8</sup>



- ▶ Dissociation of transition metal complexes of 42–174 atoms
- ▶ Large theory–experiment discrepancies

<sup>8</sup>Weymuth et al., JCTC, 10, 3092 (2014)



# Theory-experiment discrepancies

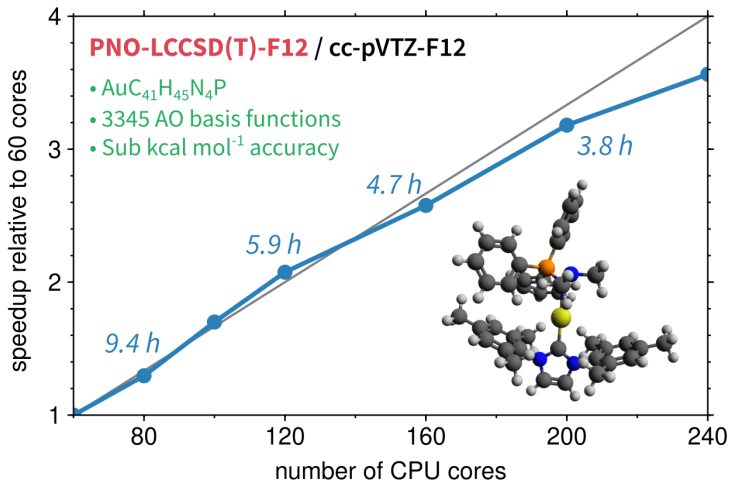
## Electronic structure theory

- ▶ Local errors, basis-set convergence
- ▶ Breakdown of the CCSD(T) model
- ▶ Structure optimization

## “Experiment”

- ▶ Uncertain dissociation product
- ▶ Multiple conformation of the molecule
- ▶ Kinetic model in post-processing protocol

# Scaling with the number of processors



- ▶ Canonical DF-HF: 1.7 h with 20 cores
- ▶ PNO-LMP2: < 5 min with 80 cores

# Summary

- ▶ An efficient parallel PNO-LCCSD(T)-F12 method has been implemented
- ▶ All approximations can be well controlled and converged, so that errors become negligible
- ▶ F12 terms strongly reduce basis set and domain errors
- ▶ PNO-LCCSD(T)-F12 needs only 10% more computational power than PNO-LCCSD(T)
- ▶ Open-shell methods are under development

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Dr. Christoph Köppl

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