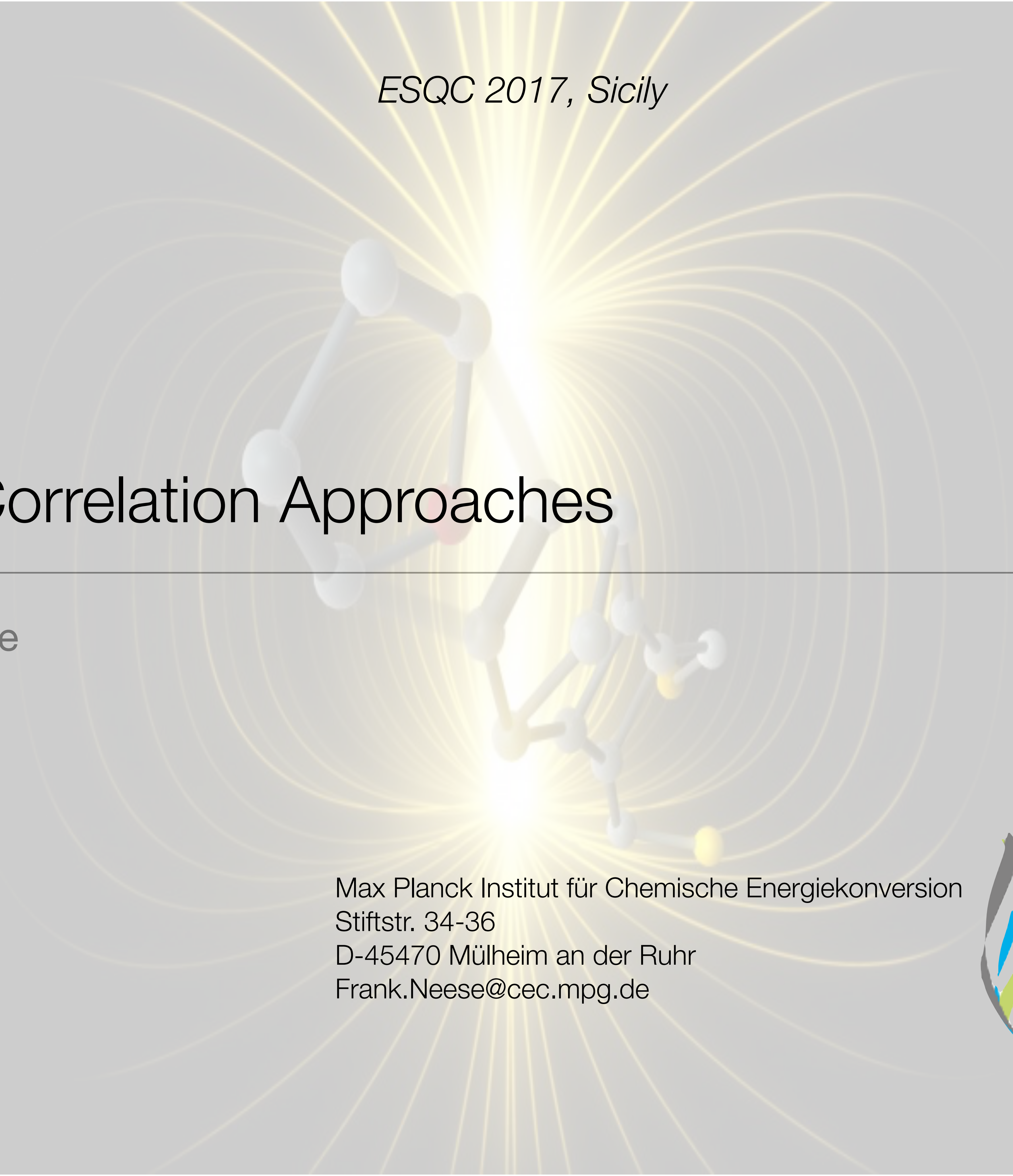
ESQC 2017, Sicily



Local Correlation Approaches

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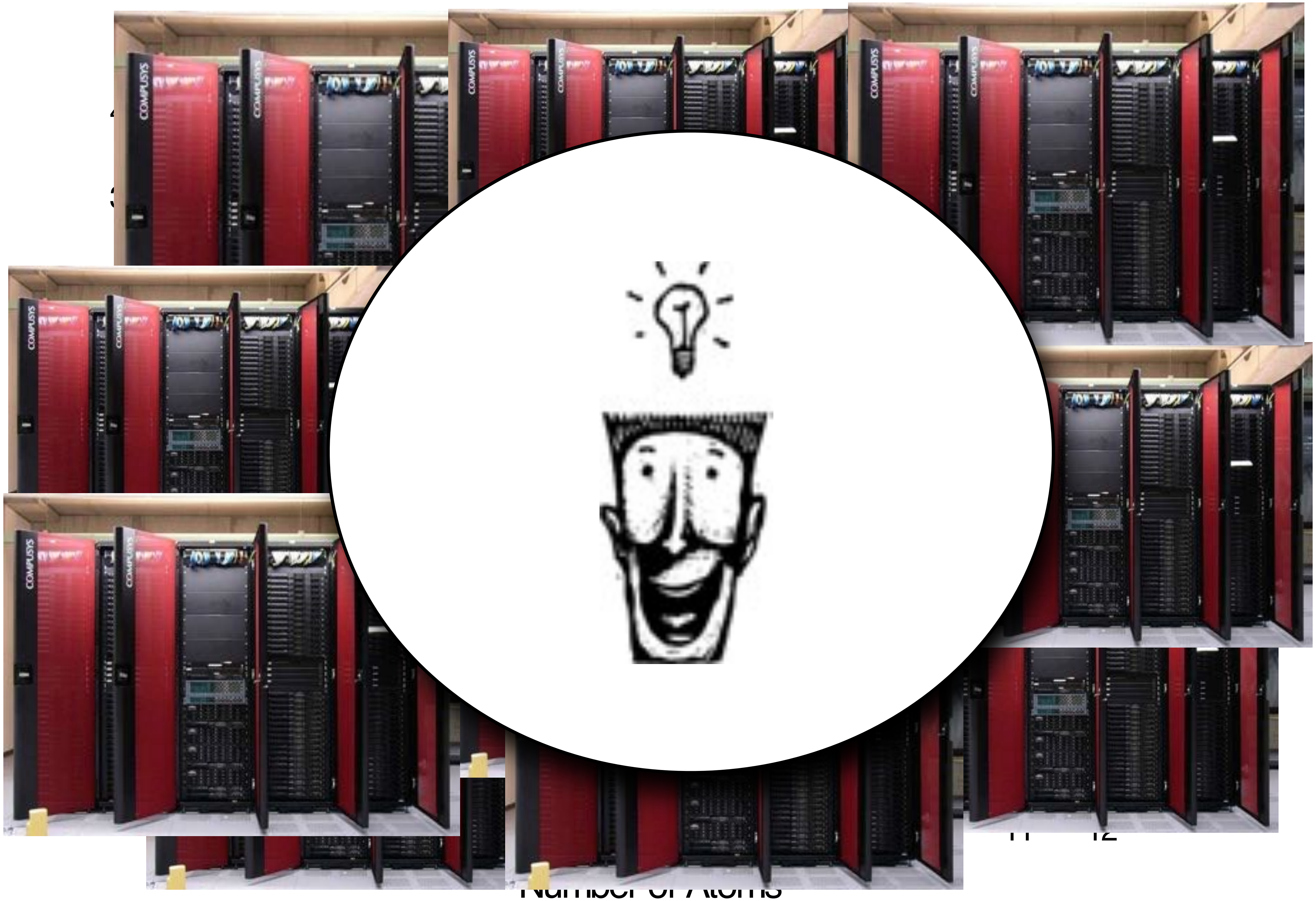
Problem with Wavefunction Methods



Early Local Correlation Approaches

The idea of local correlation is almost as old as correlation theory itself and has been suggested long before even Hartree-Fock calculation on medium sized molecules were feasible

O Sinanoglu *Adv. Chem. Phys.*, **1964**, 6,315
RK Nesbet, *Adv. Chem. Phys.*, **1965**, 9, 321

it took almost 20 years before it was taken up again. An important paper is from Cullen and Zerner (received no attention, perhaps because it was in a semi-empirical context)

JM Cullen, MC Zerner *J. Chem. Phys.*, **1982**, 77, 4088

Followed by the pioneering work of Pulay and Saebo (CISD, MP4)

P Pulay, *Chem. Phys. Lett.* **1983,** 100, 151.; S Saebo, P Pulay, *Chem. Phys. Lett.* **1985,** 113 13.
P Pulay, S Saebø, *Theor. Chim. Acta* **1986** 69, 357.; S Saebo, P Pulay, *J. Chem. Phys.* **1987,** 87 914.

And the early coupled cluster work (mostly CCD)

RJ Bartlett, GD Purvis, *Int. J. Quantum Chem*. 14, 561 **1978** WD Laidig, GD Purvis III, RJ Bartlett, *Int. J. Quantum Chem., Symp.* 16, 561 **1982**. WD Laidig, GD Purvis III RJ Bartlett, *Chem. Phys. Lett.* 97, 209 **1983**; WD Laidig, GD Purvis III RJ Bartlett, *J. Phys. Chem.* 89, 2161 **1985**; W Förner, J Ladik, P Otto, J Čížek, *Chem. Phys.* 97, 251 **1985** W Förner, *Chem. Phys.* 114, 21 **1987** M Takahashi J Paldus, *Phys. Rev. B* 31, 5121 **1985**

… given the hard- and software limitation at the time real applications were not feasible

Importance of Accuracy Goals

- ✓ preserve - *as much as possible* - the accuracy of wave function based approaches.
- ✓ Reduce the unfavorable scaling with system size - *ideally to linear*

HOWEVER

- ➡ **The error that we introduce by exploiting the locality must not spoil the intrinsic accuracy of the method!**
- ➡ Example: large molecule E_c **~10 Eh=6270** kcal/mol
- ➡ Chemical accuracy is ~1 kcal/mol
- ➡ **The target accuracy MUST be 99.9 to 99.99% of E_c**
- ➡ **Error cancellation is NOT better than ~1 order of magnitude**

Principles of Local Correlation Theory

Pretty much all local correlation methods:

$$E_{corr} = \sum_{Chunks\ K=1}^{N_K} \delta E_K \approx \sum_{Chunks\ K'=1}^{N'_K < N_K} \delta E_K^{(approx)}$$

Approximation 1

Approximation 2

where „chunks“ =

- **Fragments**
- **Atoms**
- **Atom Pairs**
- **Orbitals**
- **Orbital Pairs**
- **…**

Approximation 1: Correlation Energy ‚Chunks’

Decomposition of the Exact Correlation Energy

Start from the Schrödinger equation $\hat{H}_{BO}\Psi = E\Psi$

Insert the full CI expansion

$$\hat{H}_{BO}(\Phi_{HF} + \sum_{ia} C_a^i \Phi_i^a + (\tfrac{1}{2!})^2 \sum_{ijab} C_{ab}^{ij} \Phi_{ij}^{ab} + \ldots) = E(C_0 \Phi_{HF} + \sum_{ia} C_a^i \Phi_i^a + (\tfrac{1}{2!})^2 \sum_{ijab} C_{ab}^{ij} \Phi_{ij}^{ab} + \ldots)$$

Multiply with the HF function from the left:

$$\underbrace{\left\langle \Phi_{HF} \mid \hat{H}_{BO} \mid \Phi_{HF} \right\rangle}_{E_{HF}} + \sum_{ia} C_i^a \underbrace{\left\langle \Phi_{HF} \mid \hat{H}_{BO} \mid \Phi_i^a \right\rangle}_{F_{ia} \quad \text{=0 (Brillouin)}} + \tfrac{1}{4} \sum_{ijab} C_{ij}^{ab} \underbrace{\left\langle \Phi_{HF} \mid \hat{H}_{BO} \mid \Phi_{ij}^{ab} \right\rangle}_{\langle ij \| ab \rangle}$$

$$= E\left(\underbrace{\left\langle \Phi_{HF} \mid \Phi_{HF} \right\rangle}_{1} + \sum_{ia} C_i^a \underbrace{\left\langle \Phi_{HF} \mid \Phi_i^a \right\rangle}_{0} + \tfrac{1}{4} \sum_{ijab} C_{ij}^{ab} \underbrace{\left\langle \Phi_{HF} \mid \Phi_{ij}^{ab} \right\rangle}_{0} \right)$$

Thus:

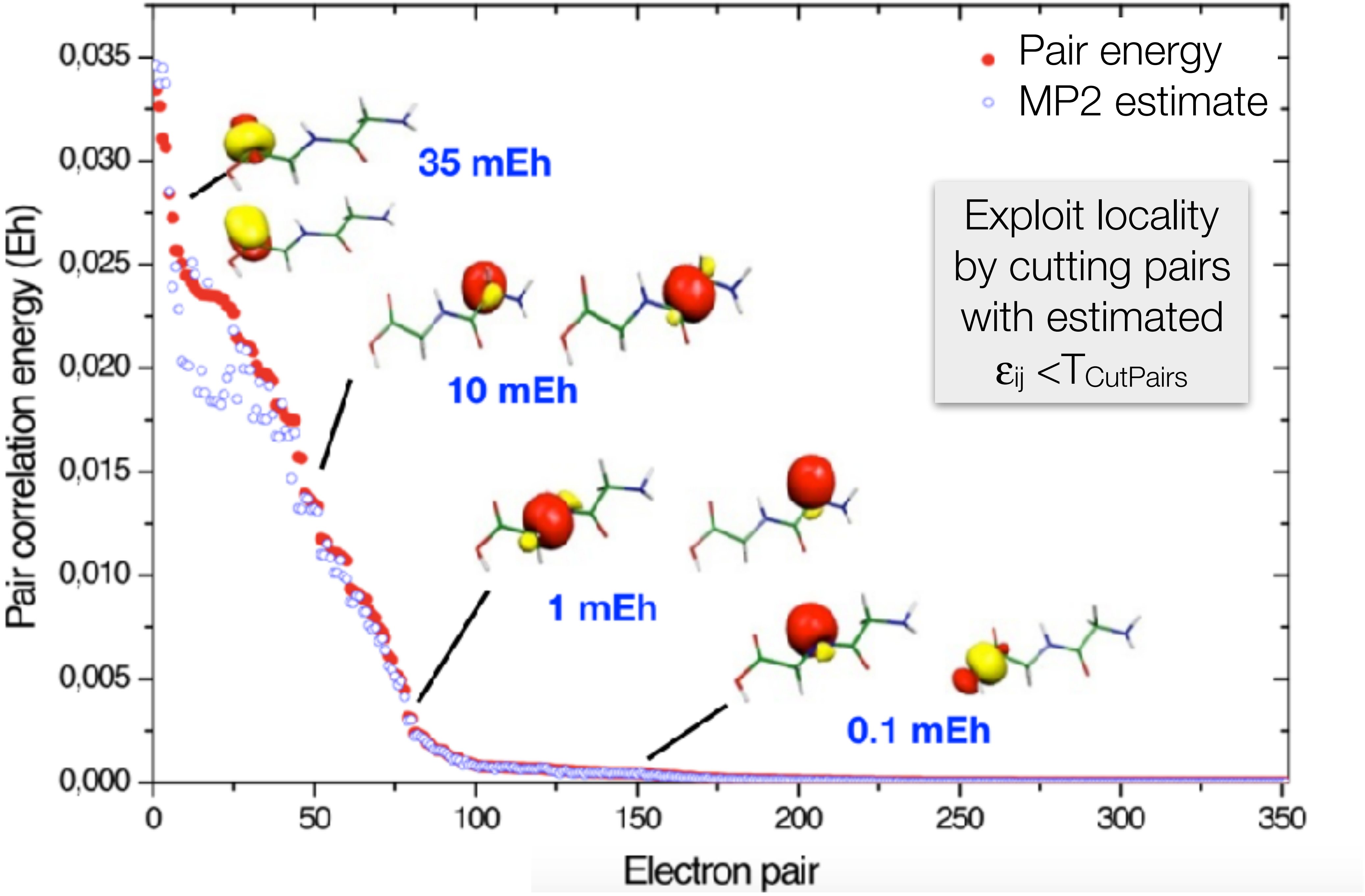
$$\boxed{\tfrac{1}{4} \sum_{ijab} C_{ab}^{ij} \left\langle ij \,\|\, ab \right\rangle = \tfrac{1}{2} \sum_{ij} \varepsilon_{ij} = E_{corr}}$$

(Nesbet‘s theorem)

If we know the precise values of the double excitation coefficients we know the <u>EXACT</u> correlation energy! It is a sum of PAIR CORRELATION ENERGIES

Approximation 1: Pair Approximation

$$E_{corr} = \frac{1}{4}\sum_{ijab} C_{ab}^{ij}\left\langle ij \,||\, ab \right\rangle = \frac{1}{2}\sum_{ij}\varepsilon_{ij}$$



Exploit locality by cutting pairs with estimated $\varepsilon_{ij} < T_{CutPairs}$

FN, Wennmohs, F.; Hansen, A. **2009**, *J. Chem. Phys.* 130, 114108

The Leading Term of Electron Correlation

Coulomb **Exchange**

$$\varepsilon_{ij}^{MP2} = -\sum_{ab} \frac{4(ia\,|\,jb)(ia\,|\,jb) - 2(ia\,|\,jb)(ib\,|\,ja)}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

Assumptions:

- Occupied orbitals are localized
- Orbital energies in the denominator can be replaced by diagonal Fock matrix elements (**semi-canonical approximation**)
- Drop the exchange part for the long range behavior (*it falls off exponentially*)

$$\varepsilon_{ij}^{SC-MP2} \approx -4\sum_{ab} \frac{(ia\,|\,jb)^2}{\varepsilon_a + \varepsilon_b - F_{ii} - F_{jj}}$$

Analysis:

- For non-zero contributions, orbitals i and a and j and b must be „close“
- If the charge distributions $\rho_{ia}(\mathbf{r})=i(\mathbf{r})a(\mathbf{r})$ and $\rho_{jb}(\mathbf{r})=j(\mathbf{r})b(\mathbf{r})$ are well separated, we can make a **multipole expansion.**

Bipolar Expansion

Use the bipolar expansion in real spherical harmonics:

$$(ia\,|\,jb) \approx \sum_{l_a} \sum_{l_b} \sum_{m=l_<}^{l_>} d^m_{l_a l_b} \frac{Q^{ia}_{l_a m} Q^{jb}_{l_b m}}{\color{red}{R^{l_a+l_b+1}}}$$

$$\left(d^m_{l_a l_b} = \frac{4\pi}{(2l_a+1)(2l_b+1)} \frac{(-1)^{l_a m}(l_a+l_b)!}{\sqrt{(l_a+m)(l_b+m)(l_b-m)(l_b-m)}} \right)$$

Distance between the center of the charge distributions

$$Q^{ia}_{lm} = \int r^l S_{lm}(\theta,\phi)\rho_{ia}(\mathbf{r})\,d\mathbf{r}$$

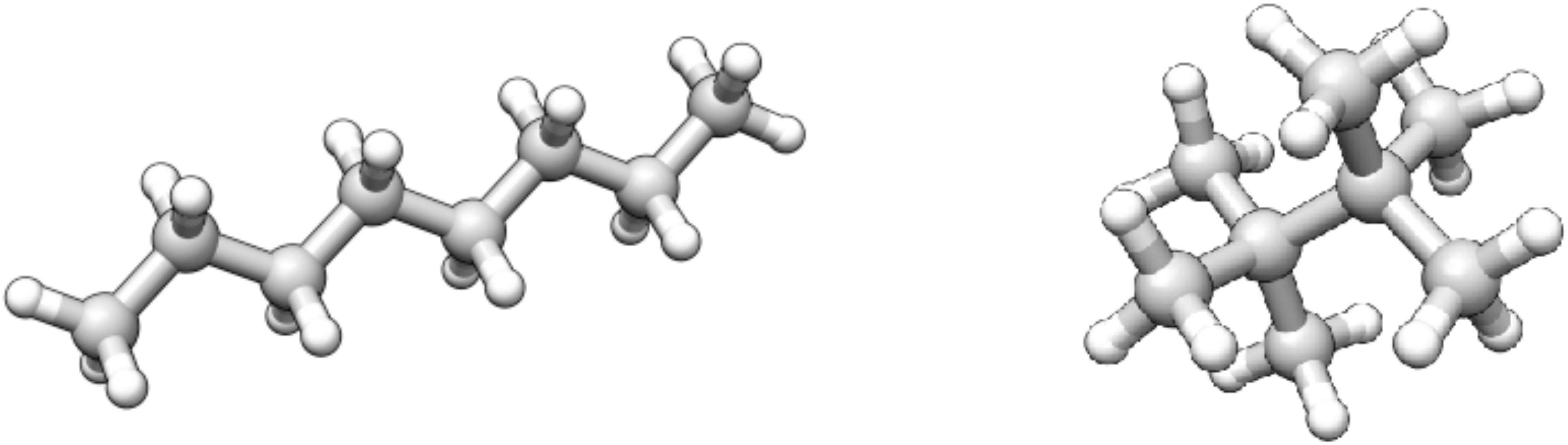
Multipole moments of the charge distributions

Since occupied and virtual orbitals are orthogonal, they have **no monopole**.
➡ the leading term is the **dipole-dipole-interaction**

$$(ia\,|\,jb) \propto R^{-3} \quad \Rightarrow \varepsilon^{SC-MP2}_{ij} \propto \color{red}{R^{-6}}$$

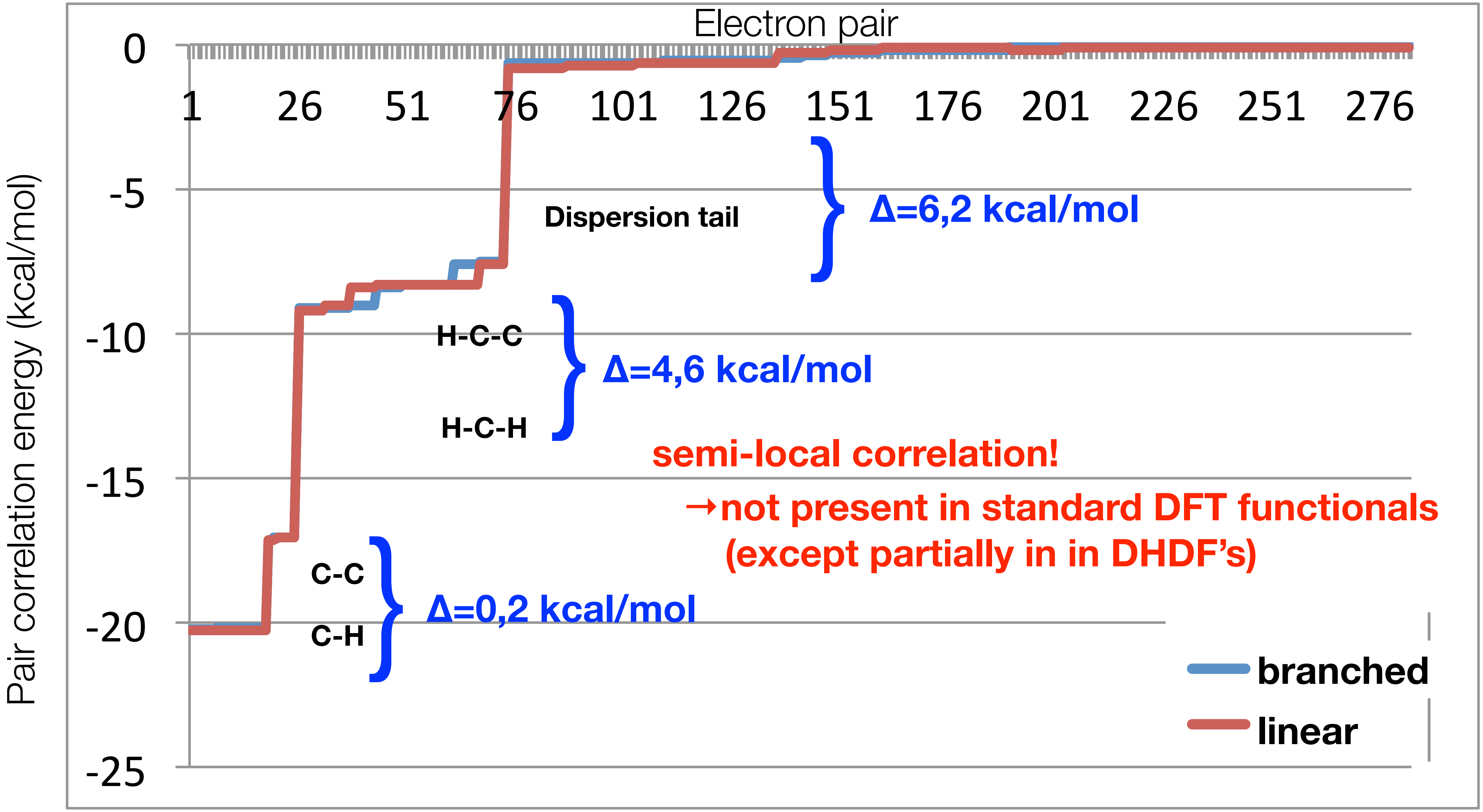
This is the **pure dispersion (induced dipole-induced dipole) interaction**.

Chemically Speaking: How Local is the Correlation?



ΔE	=	+1.9±0.5	kcal/mol	Exp.
		-11.4	kcal/mol	HF
		-0,4	kcal/mol	CCSD
		-8.4	kcal/mol	B3LYP
		-9.9	kcal/mol	BLYP

Semi-Local Correlation Effects



Δ=6,2 kcal/mol

Δ=4,6 kcal/mol

Δ=0,2 kcal/mol

semi-local correlation!

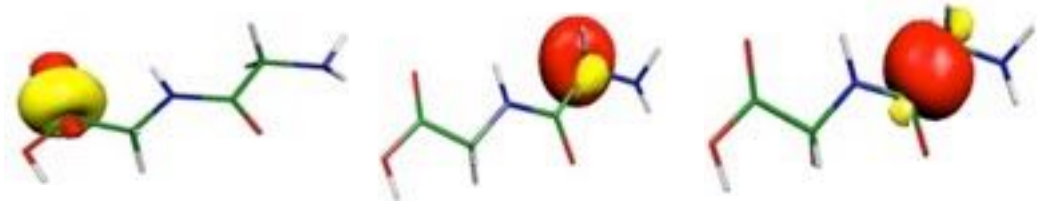
→not present in standard DFT functionals (except partially in in DHDF's)

- **We really need to capture both: semi-local and dispersion effects**
- **Correlation is not quite as local as we'd like it to be!**

Approximation 2: Limited Excitation Spaces

Approximation 2: Virtual Space Truncation

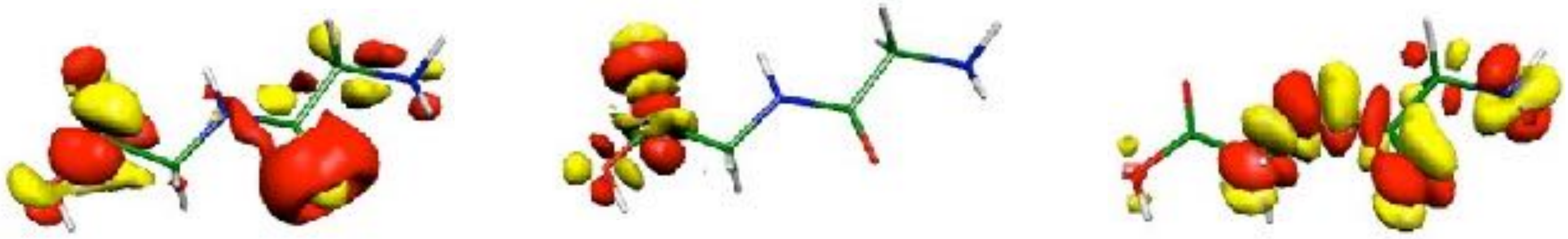
- ✓ The **occupied (internal) orbitals** localize nicely (mostly, that is)



  - ➡ *Significant MO coefficients extend over only a few atoms (1-5)*

- ✓ Pair correlation energies based on localized internal orbitals show locality with the expected R^{-6} decay

- ✓ The **virtual (external) orbitals** are problematic



  - ➡ *„Chaotic“, delocalized nature*
  - ➡ *‚Building higher and higher towers with smaller and smaller stones*
  - ➡ *Truncation schemes based on canonical MOs are unlikely to be highly successful*

Local Excitation Spaces

Let us go back to our analysis of the leading correlation term

$$\varepsilon_{ij}^{SC-MP2} \approx -4\sum_{ab} \frac{(ia\,|\,jb)^2}{\varepsilon_a + \varepsilon_b - F_{ii} - F_{jj}}$$

In order for this term to be significant

orbital a must be close to i AND orbital b must be close to j

in mathematical terms

The orbital pair ia and jb must have a significant *differential overlap*

Consequence: We can focus on local excitations and neglect long range charge transfer

However: A local representation of the virtual space is necessary

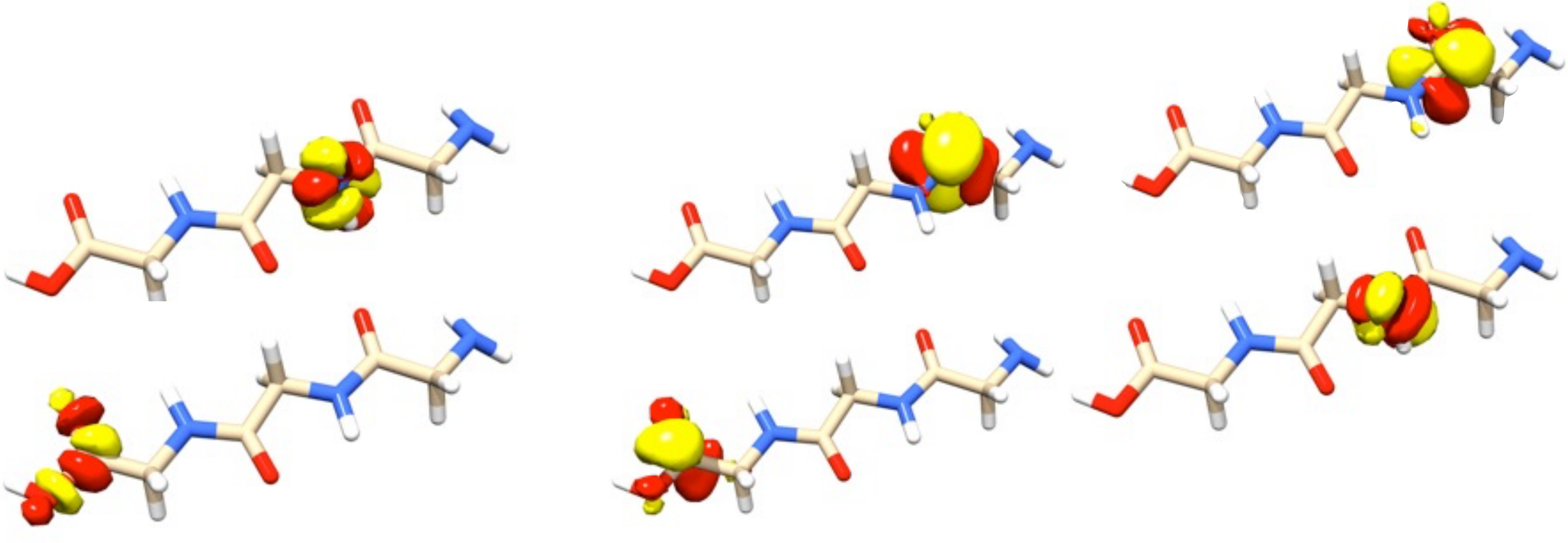
BUT: Standard localization schemes do not work well (but see Jörgensen et al)

- in particular for large basis sets the virtual orbitals do not localize well since the orthogonality constraint leads to highly oscillatory behavior
- Most researchers: Choose a non-orthogonal, local representation

Projected Atomic Orbitals

Projected atomic orbitals, PAOs, Pulay, P. *CPL*, **1983**, 100, 151

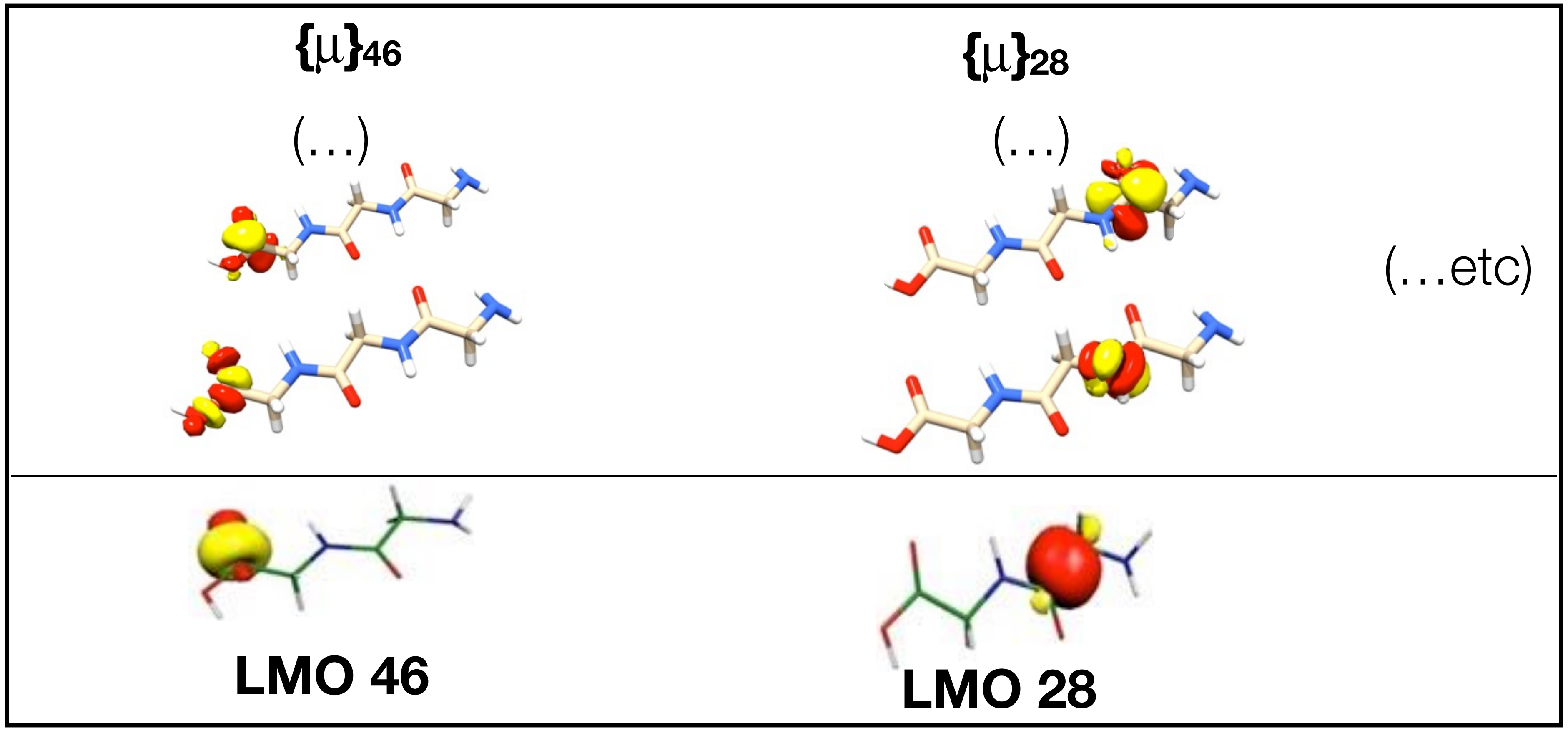
$$\left|\tilde{\mu}\right\rangle = \left(1 - \sum_i \left|i\right\rangle\left\langle i\right|\right)\left|\mu\right\rangle$$



- PAO’s are local close to the ‚parent‘ atom (but have significant tails)
- PAO’s span the virtual space and are orthogonal to the occupied space
- PAO’s are non-orthogonal and linearly dependent

Domains and Pair Domains

A **domain** $\{\mu\}_i$ is a set of PAOs chosen for a given internal LMO according to some prescription (Mostly heuristic - most researchers use connectivity and distance criteria)



A **pair domain** $\{\mu\}_{ii}$ is the union of the individual orbital domains

$$\{\mu\}_{ij} = \{\mu\}_i \cup \{\mu\}_j$$

Orthonormal Localized Virtual Orbitals

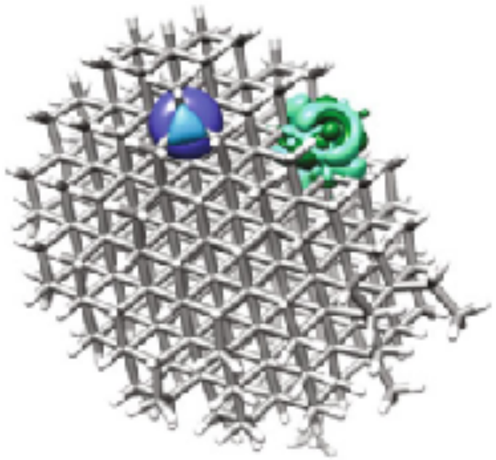
IM Hoyvik, K Kristensen, T Kjaergaard, P Jörgensen *Theo. Chem. Acc.*, **2014**, 133, 1417

- Careful comparison of PAOs and standard localized virtual MOs
- Suggested localization functional

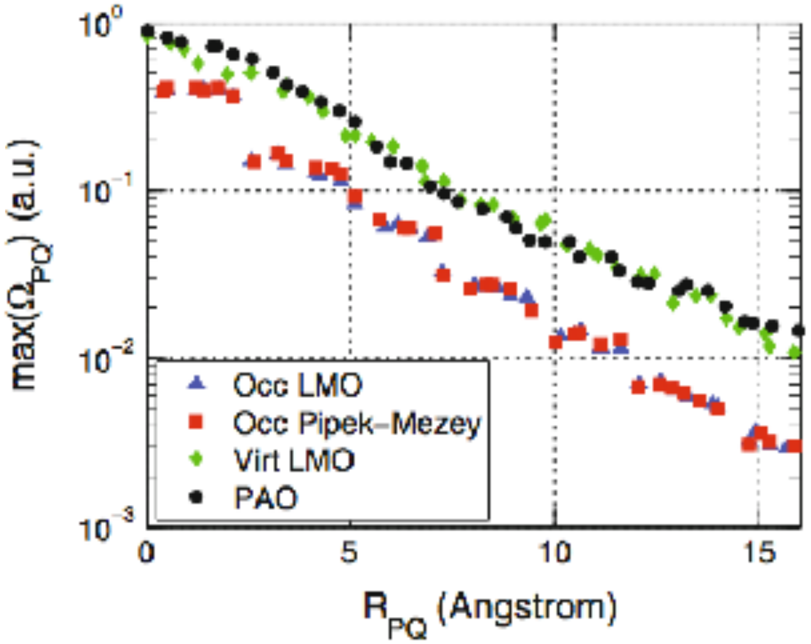
$$L = \sum_i \left| \left\langle \psi_i \,\middle|\, (\mathbf{r} - \mathbf{R}_i)^4 \,\middle|\, \psi_i \right\rangle \right|^2 \qquad \mathbf{R}_i = \left\langle \psi_i \,\middle|\, \mathbf{r} \,\middle|\, \psi_i \right\rangle$$

Fourth ‚central moment‘ (emphasizes the LMO tail region)

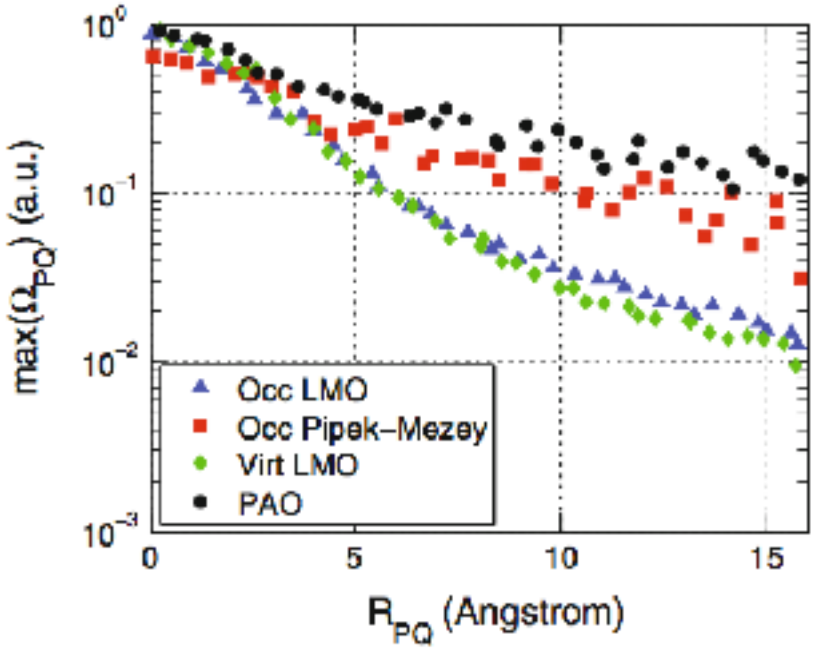
Center of gravity of MO i

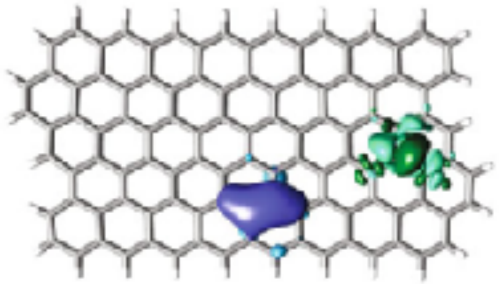


Diamond (localized)



Graphene (delocalized)





it seems possible to generate orthonormal virtual molecular orbitals that are as good or better than PAOs

Types of Local Correlation Approaches

Methods to exploit the locality of electron correlation fall into two broad categories:

1) „Piecewise“ Local Approaches (Stoll, Piecuch, Kallay, Li, Jörgensen, Friedrich, ...)

- ✓ Locality is used by dividing the molecule into subsystems (molecular fragments, orbital groups, ...).
- ✓ Small calculations are carried out on one, two, three ... subsystems at the time and
- ✓ Results are combined to estimate the total correlation energy

2) „Direct“ Local Approaches (Pulay, Werner/Schütz, FN, ...)

- ✓ Locality is used in the algorithm to avoid the computation of terms that are near zero or factors that are unity.
- ✓ Some kind of localized representation of the virtual space is required

‚Piecewise‘ Local Correlation Schemes

The Divide-Expand-Consolidate (DEC) Approach

- ✓ Jörgensen and co-workers proposed a variant of an incremental scheme that is called Divide-Expand-Consolidate (DEC)

- ✓ Linear scaling and massively parallel

- Localize occupied and virtual HF orbitals separately using standard algorithms.
- Assign localized orbitals to ***atomic sites*****:**

$$\psi_i, \psi_j \Rightarrow P, Q$$

$$\psi_a, \psi_b \Rightarrow \bar{P}, \bar{Q}$$

Hence, each atom has a set of (orthonormal) occupied and virtual orbitals assigned to it.

- Expansion of the correlation energy:

$$E_C = \sum_P E_P + \sum_{P<Q} \Delta E_{PQ} \quad \begin{cases} E_P = \frac{1}{2} \sum_{i<j\in P} \sum_{ab} (t_{ab}^{ij} + t_a^i t_b^j) \langle ij \,||\, ab \rangle \\ \Delta E_{PQ} = \frac{1}{2} \sum_{i\in P,Q,\, j\in Q,P} \sum_{ab} (t_{ab}^{ij} + t_a^i t_b^j) \langle ij \,||\, ab \rangle - E_P - E_Q \end{cases}$$

still exact!

M Ziolkowski, B Jansik, T Kjaergaard, P Jörgensen *J. Chem. Phys.*, **2010**, 133, 014107; K Kristensen, M Ziolkowski, B Jansik, T Kjaergaard, P Jörgensen J. Chem. Theo. Comp., **2011**, 7, 1677

The DEC family of methods

- Local approximations

$$E_P \approx \frac{1}{2}\sum_{i<j\in P}\ \sum_{a,b\in\bar{P}}\left(t_{ab}^{ij}+t_a^i t_b^j\right)\left\langle ij\,||\,ab\right\rangle$$

This is a 0th approximation. Solve the CC equations just using these MOs. This would be missing a lot of pair-pair coupling contributions. Hence need to refine

- Expansion and consolidation step

Add spatially close orbitals k and c to the local space of P (Three distance thresholds ***R_t****) and recalculate E_p until convergence is reached to a pre-specified accuracy threshold* ***FOT***

$$E_P \approx \frac{1}{2}\sum_{i<j\in P+k\in B_P}\ \sum_{a,b\in\bar{P}+c\in B_{\bar{P}}}\left(t_{ab}^{ij}+t_a^i t_b^j\right)\left\langle ij\,||\,ab\right\rangle$$

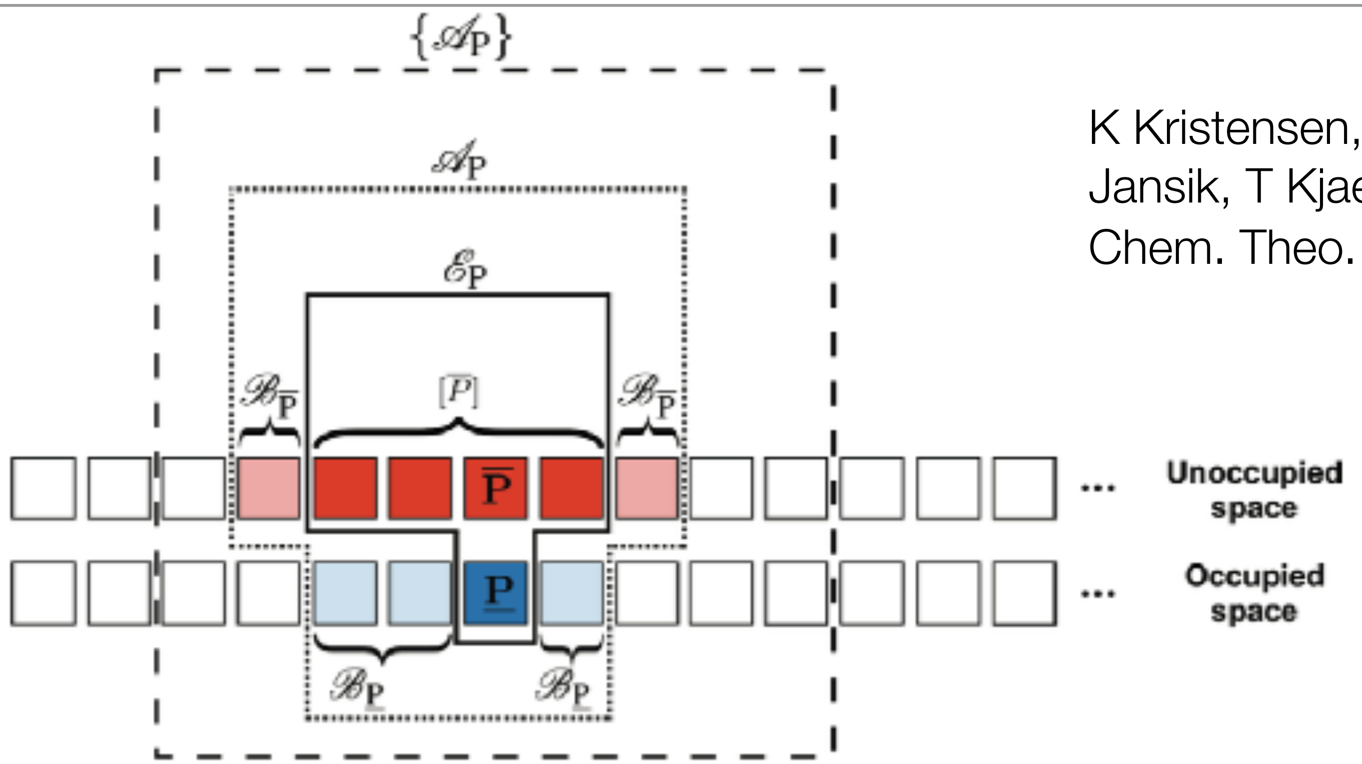
- Orbital truncation step

Truncate the AO contributions to the occupied and virtual MOs according to a completeness relation with ***threshold*** *δ. The truncated MOs are fitted to be as similar to the original, untruncated MOs*

- Pair neglect step

Neglect pair increments according to another distance threshold ***R_{crit}***

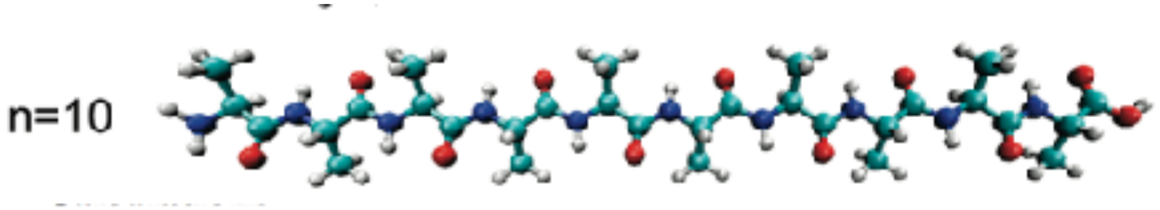
The Divide Expand Consolidate (DEC) Approach

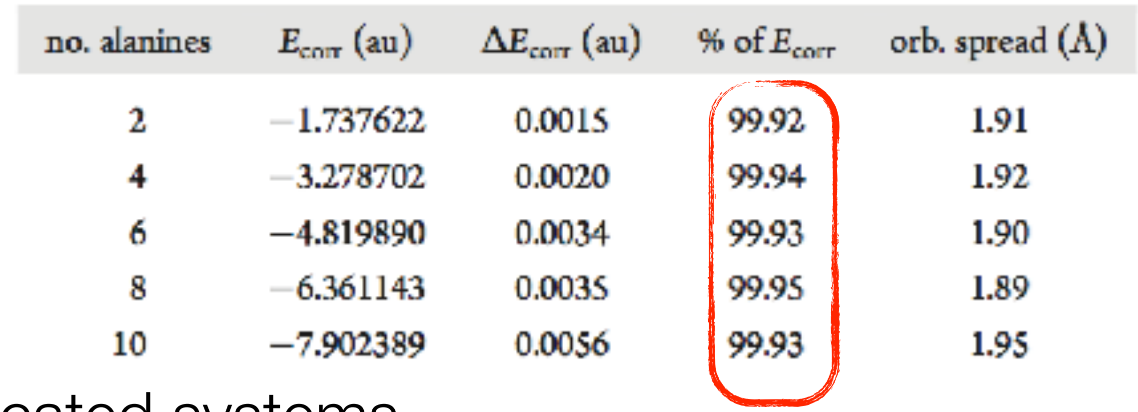


K Kristensen, M Ziolkowski, B Jansik, T Kjaergaard, P Jörgensen J. Chem. Theo. Comp., **2011**, 7, 1677

Nice features of DEC

- Can drive existing canonical CC programs for the site calculations
- ‚Embarassingly well parallelizable‘
- Accuracy essentially controlled by FOT. High accuracy reachable





no. alanines	E_{corr} (au)	ΔE_{corr} (au)	% of E_{corr}	orb. spread (Å)
2	−1.737622	0.0015	99.92	1.91
4	−3.278702	0.0020	99.94	1.92
6	−4.819890	0.0034	99.93	1.90
8	−6.361143	0.0035	99.95	1.89
10	−7.902389	0.0056	99.93	1.95

Not yet reported for DEC:

- Statistical error analysis for chemical test sets
- Chemical applications on electronically more complicated systems
- Calculations with large and diffuse basis sets

The Cluster in Molecules (CIM) Approach

The Cluster in Molecules (CIM) approach was proposed by Li et al. and adopted by Piecuch et al. and Kallay et al.

Let us start from the (orbital invariant) coupled cluster energy expression

$$E_C = \sum_{ia} t_a^i f_{ia} + \tfrac{1}{4}\sum_{ijab}\left(t_{ab}^{ij} + t_a^i t_b^j\right)\left\langle ij \,||\, ab\right\rangle$$

and re-write it in terms of single-occupied orbital increments:

$$E_C = \sum_{i} \delta E_i \qquad \delta E_i = \sum_{a} t_a^i f_{ia} + \tfrac{1}{4}\sum_{jab}\left(t_{ab}^{ij} + t_a^i t_b^j\right)\left\langle ij \,||\, ab\right\rangle$$

let the occupied orbital be localized.

Replace: $\psi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i}\mu(\mathbf{r}) \rightarrow \psi_i(\mathbf{r}) \approx \sum_{\mu\in\{i\}} c_{\mu i}\mu(\mathbf{r})$

{i} is the orbital domain of localized MO i and contains the AOs of all atoms to ensure a population of at least 1.98 when summed. Threshold τ Very small: 1-3 atoms!

S Li, J Ma, Y Jiang *J. Comp. Chem.*, **2002**, 23, 237; S Li, W Li, J Ma *Chin. J. Chem.*, **2003**, 21, 1422; S Li, J Shen, W Li, Y Jiang *J. Chem. Phys*, **2006**, 125, 074109

The Cluster in Molecules (CIM) Approach

Now use the off-diagonal Fock matrix elements $F_{ij} > \zeta_1$ to select orbitals j interacting with i

➡ **Environment [i]=[i, j_{1i}, j_{2i},…,j_{Ni}]**

Associated with the primary environment are the AOs that are the union of the AO domains of the orbitals in the environment

➡ **AO domain $[\mu]_i$**

Finally, the virtual space for the domain of orbital i is spanned by the PAO's belonging to the atoms that compose the AO domains

➡ **PAO domain $[\tilde{\mu}]_i$**

After orthogonalization, removal of linear dependencies and cutting small AO contributions, there is a set of orthonormal virtual orbitals that belong to the domain of i

(the actual algorithms are more involved than this, but the essence is just this)

W Li, P Piecuch, JR Gour, S Li *j Chem. Phys*, **2009**, 131, 114109

Implementation of CIM

Since the described algorithm has selected as subset of occupied orbitals, and a subset of virtual orbitals that are all orthonormal and a subset of atomic orbitals one can simply drive an existing correlation code using the subsystem information as input

- ➡ Reduces one large CC problem to N_{occ} smaller coupled cluster calculations
- ➡ Highly efficient parallelization since no communication is required
- ➡ Can take full advantage of sophisticated canonical programs that have been developed (e.g. completely renormalized CC methods)
- ➡ Reasonably simple implementation since no new coupled cluster routines for non-orthogonal orbitals need to be written

However:

- ◉ CIM or DEC will only be as efficient as the most expensive subsystem CC calculation. If this is getting out of hand (e.g. >500 orbitals) the algorithm will fail
- ◉ There is a significant amount of redundant computation since the various domains have overlapping orbitals and atoms and hence, many intergrals are computed multiple times

An Integral-Direct Linear-Scaling Second-Order Møller–Plesset Approach

Péter R. Nagy*, **Gyula Samu**, and **Mihály Kállay***
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Budapest University of Technology and Economics, P.O. Box 91, Budapest H-1521, Hungary

J. Chem. Theory Comput., Article ASAP
DOI: 10.1021/acs.jctc.6b00732
Publication Date (Web): September 12, 2016

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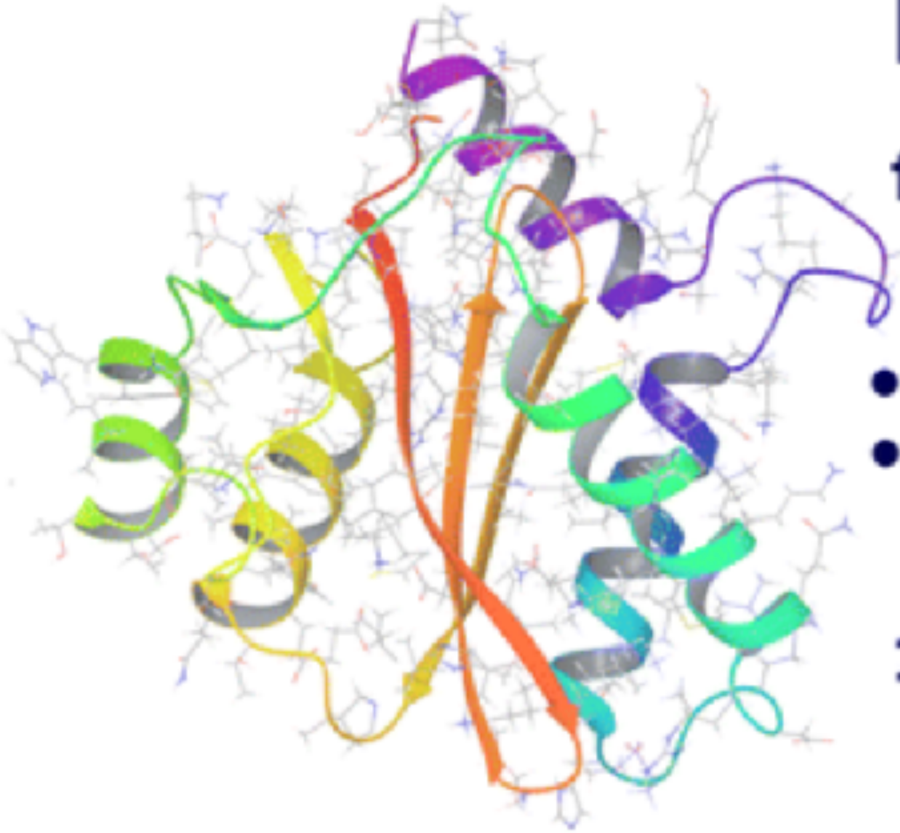


Local MP2

for HIV-1 integrase

- **2380 atoms**
- **22621 atomic orbitals**

12 h on a workstation

Direct Local Correlation Schemes

A Treatment on Sparsity

Formal Treatment of Sparsity

… Local correlation approaches lead to complicated book-keeping problems since subspaces of a large number of function spaces must be organized *(occupied MOs, electron pairs, PAOs, fit functions, atomic orbitals, atoms, …)*

… So far, developers have each addressed the problem individually by developing complicated software solutions that are difficult to understand and maintain

… exploitation of sparsity to the point of reaching linear scaling creates a **complex circular interdependencies** that are easy to get lost in

… recently, an attempt was made to provide a **formal (and programming) framework** for exploiting sparsity in quantum chemistry in a systematic manner

SparseMap formalism

P Pinski, C Riplinger, E Valeev, FN, *J Chem Phys.* **2015,** 143, 034108

Multiplicative *vs* Additive Sparsity

Consider two sets of functions $\{f\}$ and $\{g\}$

We differentiate *two different types of sparsity*

Additive

$$f_i = \sum_k x_{ki} g_k$$

e.g. $|i\rangle = \sum_\mu c^L_{\mu i} |\mu\rangle$

Multiplicative

$$\int f_i(\mathbf{r}) g_k(\mathbf{r})\, d\mathbf{r}$$

e.g. $(i\tilde{\mu}\,|\,K)$

Sparse List: $L_i(f \rightarrow g)$ for which $|\, x_{ki} \,| > \varepsilon$

Sparse Map: $\mathbf{L}(f \rightarrow g) = \{L_1, L_2, \ldots, L_M\}$ (collection of lists for all i)

Pretty obvious sparsity criterion for additive sparsity, but what about multiplicative sparsity?

P Pinski, C Riplinger, E Valeev, FN, *J Chem Phys.* **2015,** 143, 034108

Multiplicative Sparsity

A great way to implement multiplicative sparsity would be the Schwartz Integral:

$$SPI_{ik} \equiv \sqrt{(fg \mid fg)} = \sqrt{\int \int \frac{f_i(\mathbf{r}_1) g_k(\mathbf{r}_1) f_i(\mathbf{r}_2) g_k(\mathbf{r}_2)}{\left| \mathbf{r}_1 - \mathbf{r}_2 \right|} d\mathbf{r}_1 \, d\mathbf{r}_2}$$

✓ Positive semi-definite

✓ Used as an upper bound for ERI's

✓ Easy to compute for AO's

✗ Hard to *efficiently* compute for MOs and related quantities

Want a simple substitute for the SPI to implement multiplicative sparsity

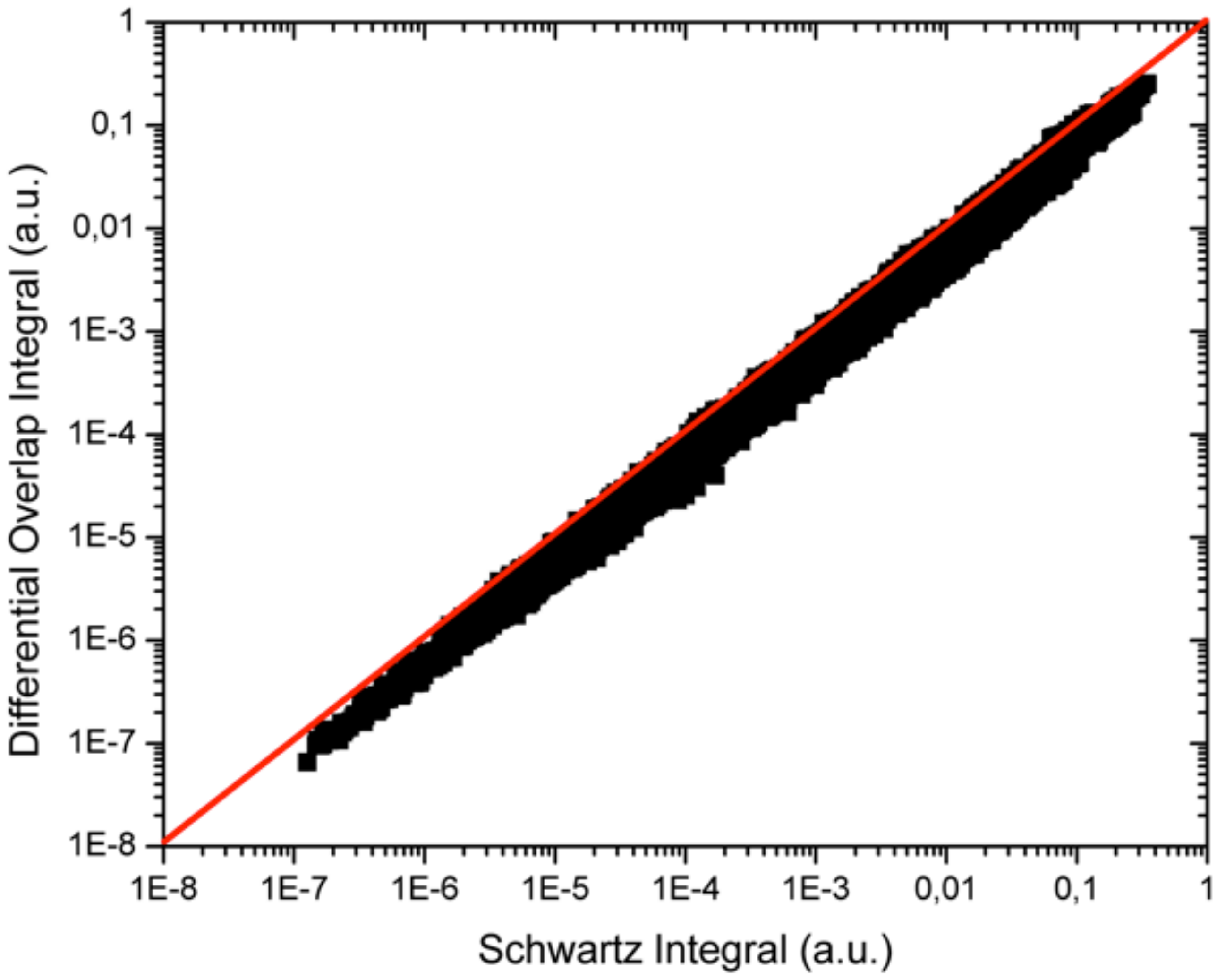
P Pinski, C Riplinger, E Valeev, FN, *J Chem Phys.* **2015,** 143, 034108

The Differential Overlap Integral (DOI)

New proposal: Use the ***Differential Overlap Integral***

$$DOI_{ik} = \sqrt{\int |f_i(\mathbf{r})|^2 \, |g_k(\mathbf{r})|^2 \, d\mathbf{r}}$$

to implement multiplicative sparsity



- ✓ Excellent estimate for the SPI
- ✓ Easy to compute efficiently in linear scaling for any set of functions

P Pinski, C Riplinger, E Valeev, FN,
J Chem Phys. **2015,** 143, 034108

Implementing Sparsity:‚*Linked Index Principle*‘

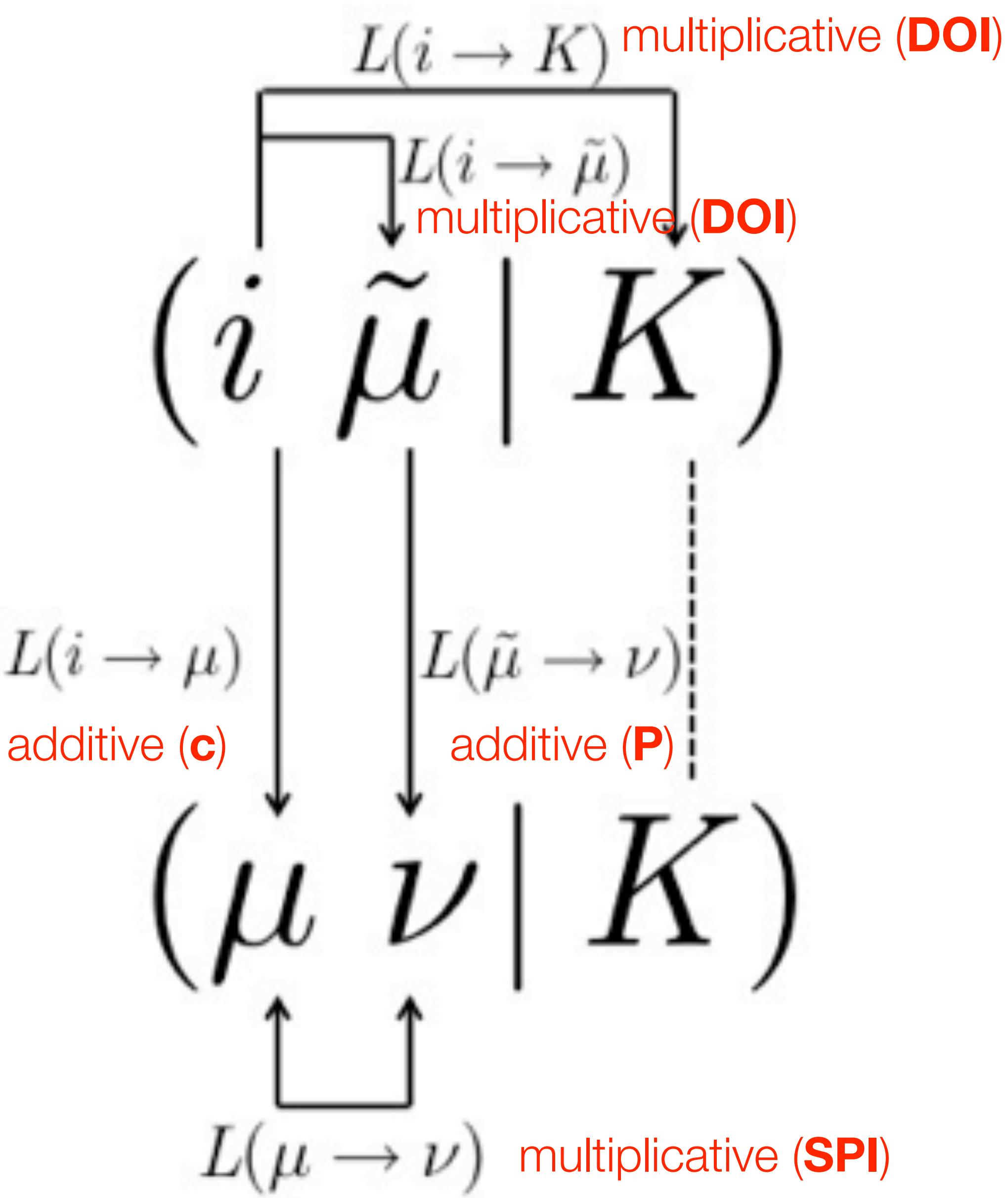
In order to reach linear scaling there MUST be an uninterrupted path of sparsity relationships that connects each index of a given object (integral, amplitude) to each other index)

Example: Three-Index Integral transformation

$$(i\tilde{\mu}\,|\,K)=\sum_{\mu\nu}c^{L}_{\mu i}\tilde{P}_{\nu\tilde{\mu}}(\mu\nu\,|\,K)$$

Chain of sparsity relationships exist

Linear scaling is possible



P Pinski, C Riplinger, E Valeev, FN, *J Chem Phys.* **2015,** 143, 034108

Working with Sparsity:‚Sparse Map‘ Operations

In order to *actually* (not just formally) take advantage of sparsity one needs to define ***operations on sparse maps***. Consider $\mathbf{L}(f \rightarrow g)$

Inversion:

$$\mathbf{L}(g \rightarrow f) = \mathbf{L}^{-1}(f \rightarrow g)$$

Contraction:

$$\mathbf{L}(f \rightarrow \nu) \rightarrow \mathbf{L}(f \rightarrow \nu_S) \qquad \mathbf{L}(f \rightarrow \nu) \rightarrow \mathbf{L}(f \rightarrow \nu_A)$$

shells

atoms

Union & Dissection:

$\mathbf{L}_1(f \rightarrow g)$ $\mathbf{L}_2(f \rightarrow g)$

$$\mathbf{L}_3 = \mathbf{L}_1 \cup \mathbf{L}_2 \qquad \mathbf{L}_3 = \mathbf{L}_1 \cap \mathbf{L}_2$$

Chaining

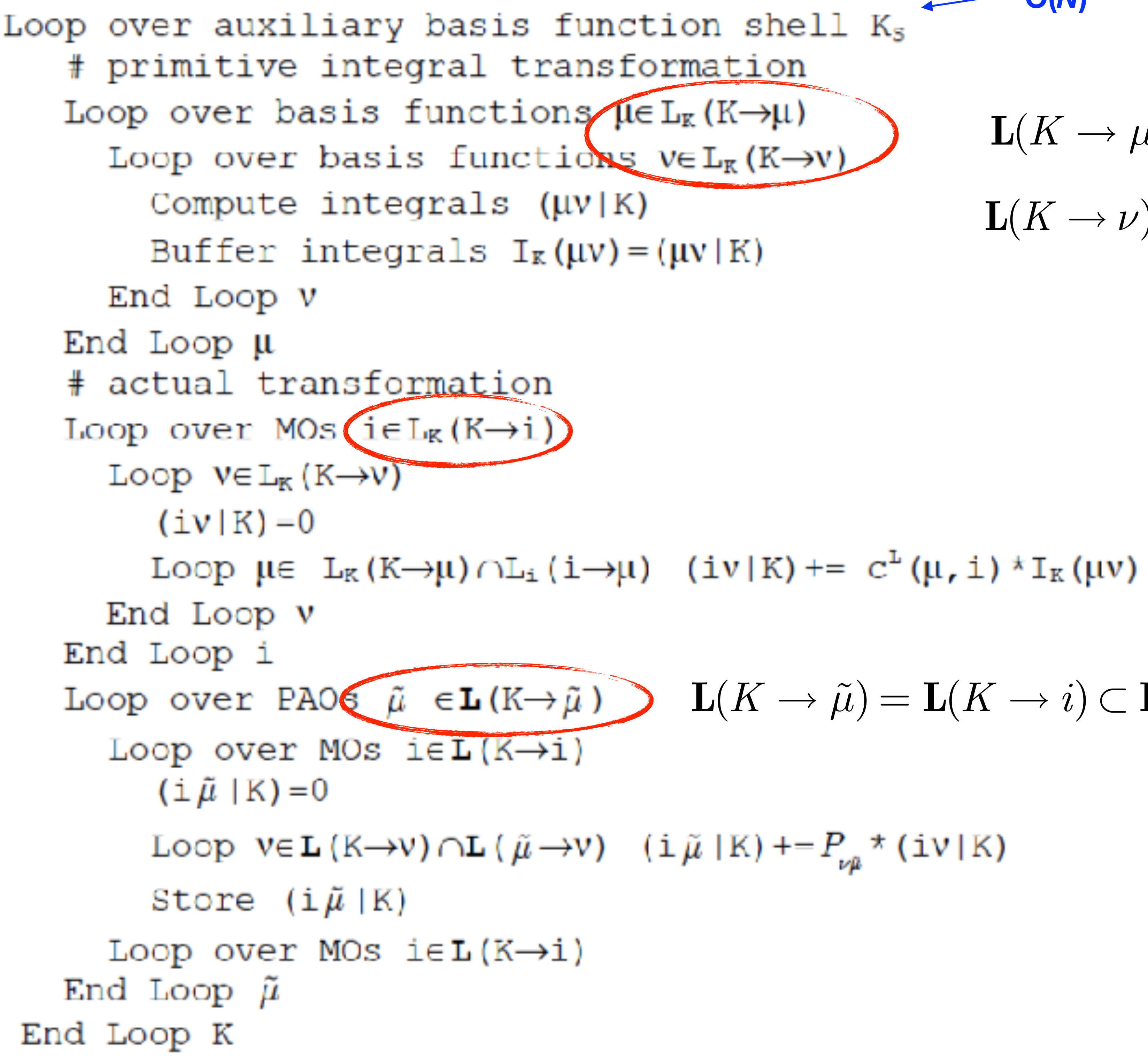
$\mathbf{L}_1(f \rightarrow g)$ $\mathbf{L}_2(g \rightarrow h)$

$$\mathbf{L}_3(f \rightarrow h) = \mathbf{L}_1(f \rightarrow g) \subset \mathbf{L}_2(g \rightarrow h)$$

We have developed a C++ object library that implements sparse map operations

$$(i\tilde{\mu} \mid K) = \sum_{\mu\nu} c^{L}_{\mu i} \tilde{P}_{\nu\tilde{\mu}} (\mu\nu \mid K)$$

Example 2: Linear Scaling 3-Index Transformation



```
Loop over auxiliary basis function shell $K_S$
  # primitive integral transformation
  Loop over basis functions $\mu \in L_K(K \to \mu)$
    Loop over basis functions $\nu \in L_K(K \to \nu)$
      Compute integrals $(\mu\nu|K)$
      Buffer integrals $I_K(\mu\nu) = (\mu\nu|K)$
    End Loop $\nu$
  End Loop $\mu$
  # actual transformation
  Loop over MOs $i \in L_K(K \to i)$
    Loop $\nu \in L_K(K \to \nu)$
      $(i\nu|K) = 0$
      Loop $\mu \in L_K(K \to \mu) \cap L_i(i \to \mu)$  $(i\nu|K)$ += $c^L(\mu,i) * I_K(\mu\nu)$
    End Loop $\nu$
  End Loop i
  Loop over PAOs $\tilde{\mu} \in \mathbf{L}(K \to \tilde{\mu})$
    Loop over MOs $i \in \mathbf{L}(K \to i)$
      $(i\tilde{\mu}|K) = 0$
      Loop $\nu \in \mathbf{L}(K \to \nu) \cap \mathbf{L}(\tilde{\mu} \to \nu)$  $(i\tilde{\mu}|K)$ += $P_{\nu\tilde{\mu}} * (i\nu|K)$
      Store $(i\tilde{\mu}|K)$
    Loop over MOs $i \in \mathbf{L}(K \to i)$
  End Loop $\tilde{\mu}$
End Loop K
```

O(*N*)

$$\mathbf{L}(K \to i) = \mathbf{L}^{-1}(i \to K)$$

$$\mathbf{L}(K \to \mu) = \mathbf{L}(K \to i) \subset \mathbf{L}(i \to \mu)$$

$$\mathbf{L}(K \to \nu) = \mathbf{L}(K \to i) \subset \mathbf{L}(i \to \tilde{\mu}) \subset \mathbf{L}(\tilde{\mu} \to \nu)$$

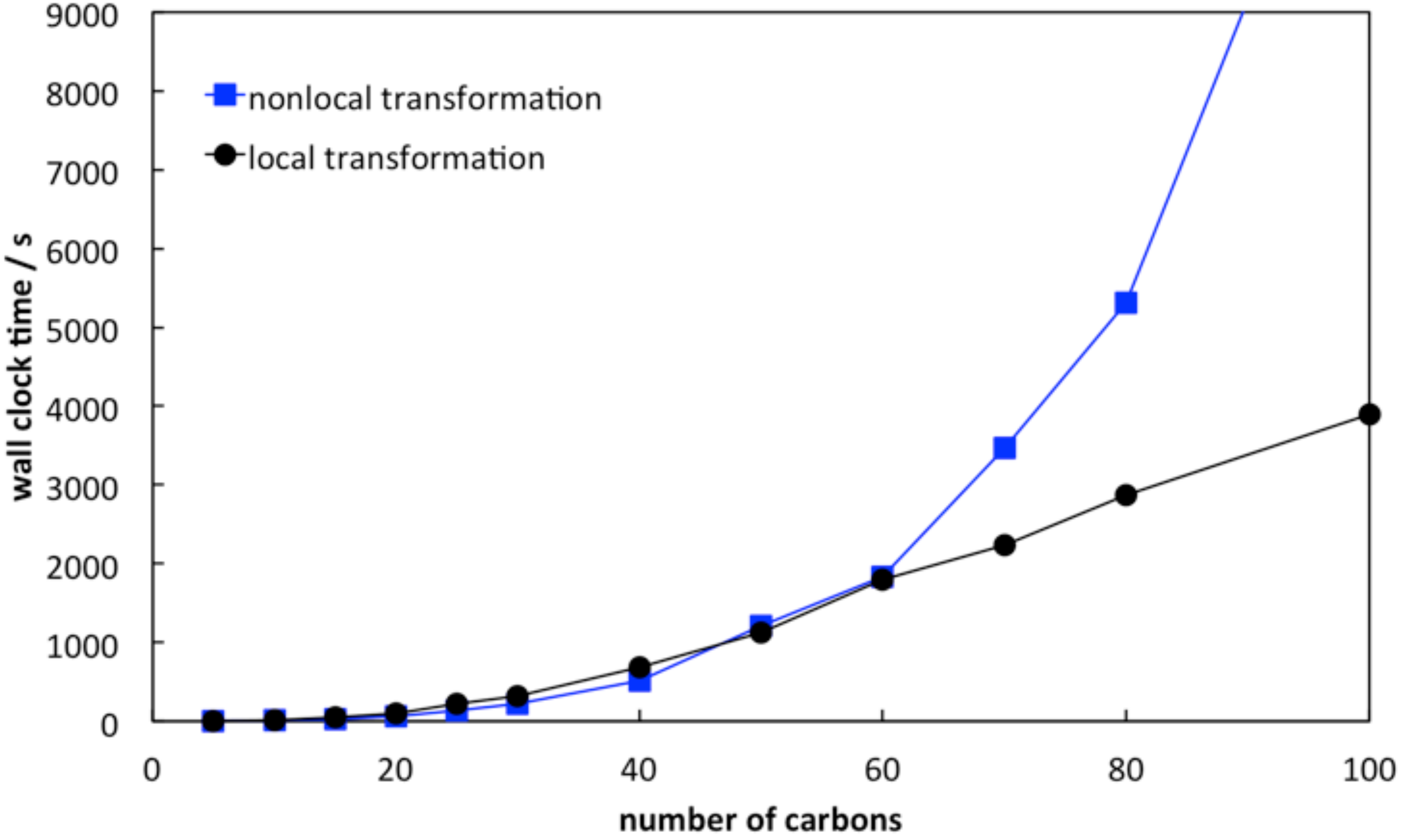
$$\mathbf{L}(K \to \tilde{\mu}) = \mathbf{L}(K \to i) \subset \mathbf{L}(i \to \tilde{\mu})$$

All O(0) operations on the current auxiliary shell

P Pinski, C Riplinger, E Valeev, FN, *J Chem Phys.* **2015,** 143, 034108

Linear Scaling 3-Index Transformation Performance

Linear carbon chains:



- Next to no overhead compared to dens transformation that heavily uses BLAS
- Linear scaling sets in around 40 carbon atoms

P Pinski, C Riplinger, E Valeev, FN, *J Chem Phys.* **2015,** 143, 034108

Projected Atomic Orbitals and Correlation Domains

Local MP2 Theory

Two complications relative to canonical MP2:

- At first sight the use of **non-orthogonal orbitals** appears to be „nightmare“ of added complexity. However, the PAO’s remain orthogonal to the occupied space and there are never more than two PAOs in any excited determinant

- In the local representation the **Fock matrix is no longer diagonal** and hence the usual Möller Plesset expansion does not apply.

Pulay and Saebo suggested to use the **Hylleraas functional** instead

$$E^{(2)} = \min(2\left\langle \Psi^{(1)} \mid H \mid \Psi^{(0)} \right\rangle + \left\langle \Psi^{(1)} \mid H_0 - E_0 \mid \Psi^{(1)} \right\rangle)$$

it readily leads to an orbital invariant formulation of MP2

$$\Psi = \Psi^{(0)} + \Psi^{(1)} = \Psi_{HF} + \tfrac{1}{4}\sum_{ijab} C_{ab}^{ij} \Phi_{ij}^{ab}$$

$$H = H_0 + V \qquad H_0 = F, \quad V = H - H_0$$

P. Pulay, and S. Saebø, *Theor. Chim. Acta* 69, 357 (**1986**).

Local MP2 Theory

$$\left\langle \Psi^{(1)} \mid H \mid \Psi^{(0)} \right\rangle = \tfrac{1}{4} \sum_{ijab} C_{ab}^{ij} \left\langle ij \,\|\, ab \right\rangle$$

$$\left\langle \Psi^{(1)} \mid H_{0} - E_{0} \mid \Psi^{(1)} \right\rangle = \tfrac{1}{8} \sum_{ijabc} C_{ab}^{ij} F_{cb} C_{ac}^{ij} - \tfrac{1}{8} \sum_{ijkab} C_{ab}^{ij} F_{jk} C_{ab}^{ik}$$

Minimization w.r.t. the coefficients C leads to the linear equation system:

$$R_{ab}^{ij} = \left\langle ij \,\|\, ab \right\rangle + \sum_{c} (C_{ac}^{ij} F_{cb} + F_{ac} C_{cb}^{ij}) - \sum_{k} (C_{ab}^{ik} F_{kj} + F_{ik} C_{ab}^{kj}) = 0$$

Which immediately leads back to canonical MP2 if the Fock operator is diagonal.

If now the virtual orbitals are replaced by non-orthogonal PAO’s, only a slight complication arises. The first order wave function is:

$$\Psi^{(1)} = \tfrac{1}{4} \sum_{ij\tilde{\mu}\tilde{\nu}} C_{\tilde{\mu}\tilde{\nu}}^{ij} \Phi_{ij}^{\tilde{\mu}\tilde{\nu}}$$

Local MP2 Theory

The residual becomes:

$$R^{ij}_{\tilde{\mu}\tilde{\nu}} = \left\langle ij \,||\, \tilde{\mu}\tilde{\nu} \right\rangle + \sum_{c} \left(F_{\tilde{\mu}\tilde{\kappa}} C^{ij}_{\tilde{\kappa}\tilde{\tau}} \tilde{S}_{\tilde{\tau}\tilde{\nu}} + \tilde{S}_{\tilde{\mu}\tilde{\kappa}} C^{ij}_{\tilde{\kappa}\tilde{\tau}} F_{\tilde{\tau}\tilde{\nu}} \right) - \sum_{k} \left(F_{ik} \tilde{S}_{\tilde{\mu}\tilde{\kappa}} C^{kj}_{\tilde{\kappa}\tilde{\tau}} \tilde{S}_{\tilde{\tau}\tilde{\nu}} + F_{kj} \tilde{S}_{\tilde{\mu}\tilde{\kappa}} C^{ik}_{\tilde{\kappa}\tilde{\tau}} \tilde{S}_{\tilde{\tau}\tilde{\nu}} \right) = 0$$

or:

$$\mathbf{R}^{ij} = \mathbf{K}^{ij} + \left(\mathbf{F}\mathbf{C}^{ij}\tilde{\mathbf{S}} + \tilde{\mathbf{S}}\mathbf{C}^{ij}\mathbf{F} \right) - \sum_{k} \left(f_{ik} \tilde{\mathbf{S}}\mathbf{C}^{kj}\tilde{\mathbf{S}} + f_{kj} \tilde{\mathbf{S}}\mathbf{C}^{ik}\tilde{\mathbf{S}} \right) = 0$$

With the PAO overlap matrix $\tilde{S}_{\tilde{\mu}\tilde{\nu}} = \left\langle \tilde{\mu} \,|\, \tilde{\nu} \right\rangle$

So far: **no approximation!**

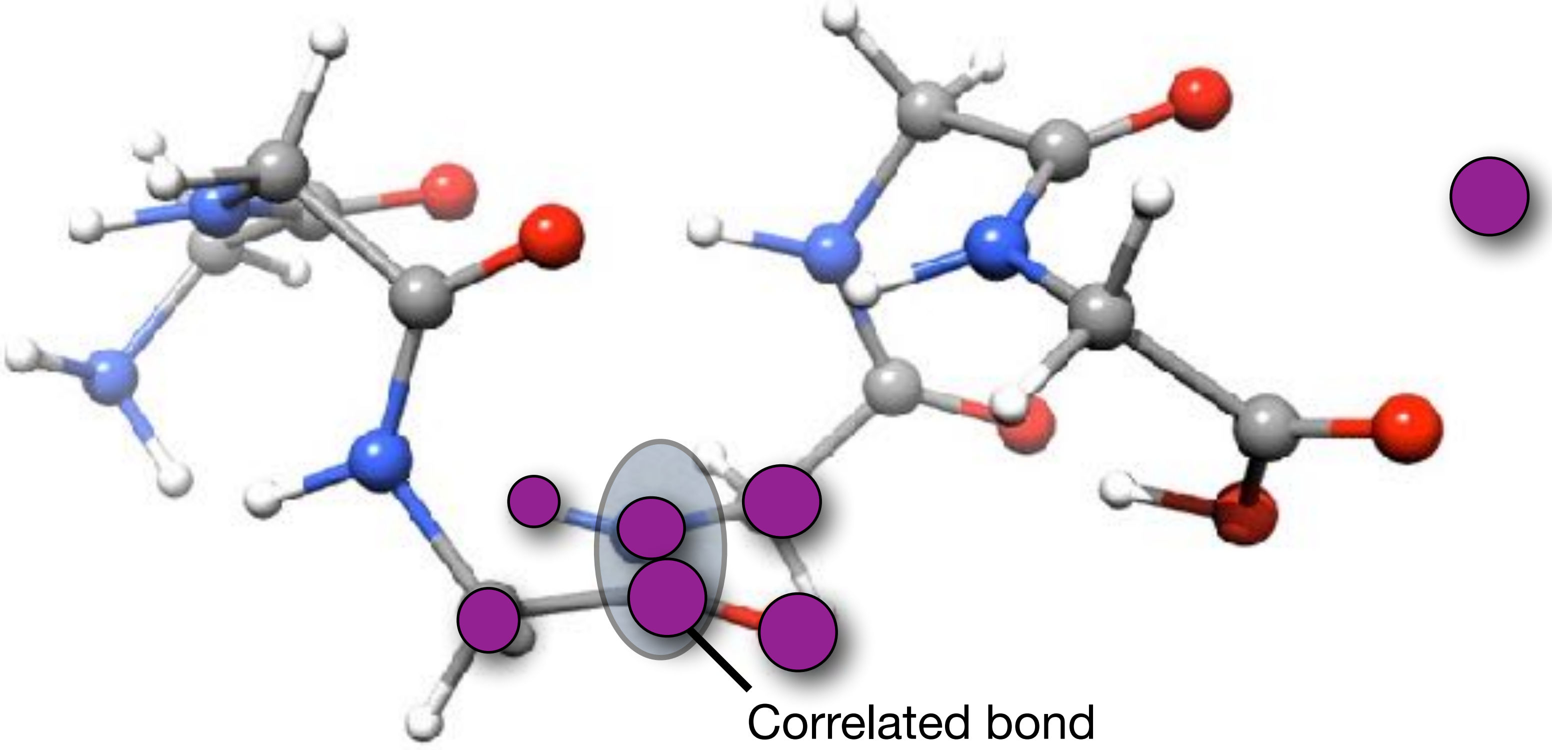
These equations represent a more complicated and ill-conditioned way to do MP2!

- Owing to the linear dependencies in the PAO set, the equations are singular.
- Removing the singularities by diagonalizing of the PAO overlap matrix and dropping the eigenvectors corresponding to zero eigenvalues leads back to canonical MP2

➡ **Introduce correlation domains for each electron pair ij**

Local MP2 Theory

- In the local treatment, only a subset of PAOs are included for each electron pair (ij), e.g. those PAOs that are „**spatially close**“ to (ij)
- In the early days of correlation theory this was done using heuristic connectivity arguments and analyzing the MO coefficients of occupied local orbitals (i) and (j).
- **Pair domains** are constructed as the union of **orbital domains**
- Correlation domains contained typical 2-5 atoms



PAO’s of these atoms define the domain

Correlated bond

J. W. Boughton and P. Pulay, *J. Comput. Chem.* 14, 736 **1993**.

Local MP2 Theory

Using the domains, the residual becomes

$$\mathbf{R}^{ij} = \mathbf{K}^{ij} + (\mathbf{F}^{(ij)}\mathbf{C}^{ij}\tilde{\mathbf{S}}^{(ij,ij)} + \tilde{\mathbf{S}}^{(ij,ij)}\mathbf{C}^{ij}\mathbf{F}^{(ij)}) - \sum_{k}(f_{ik}\tilde{\mathbf{S}}^{(ij,jk)}\mathbf{C}^{kj}\tilde{\mathbf{S}}^{(kj,ij)} + f_{kj}\tilde{\mathbf{S}}^{(ij,ik)}\mathbf{C}^{ik}\tilde{\mathbf{S}}^{(ik,ij)}) = 0$$

Where all matrices are now local:

$$\left.\begin{aligned} R^{ij}_{\tilde{\mu}\tilde{\nu}} &\longrightarrow R^{ij}_{\tilde{\mu}\in\{ij\},\tilde{\nu}\in\{ij\}} \\ K^{ij}_{\tilde{\mu}\tilde{\nu}} &\longrightarrow K^{ij}_{\tilde{\mu}\in\{ij\},\tilde{\nu}\in\{ij\}} \\ F^{(ij)}_{\tilde{\mu}\tilde{\nu}} &\longrightarrow F_{\tilde{\mu}\in\{ij\},\tilde{\nu}\in\{ij\}} \\ \tilde{S}^{(ij,kl)}_{\tilde{\mu}\tilde{\nu}} &\longrightarrow \tilde{S}_{\tilde{\mu}\in\{ij\},\tilde{\nu}\in\{kl\}} \end{aligned}\right\}$$

✓ Sub-matrices can either be stored or constructed on the fly

Two more steps are necessary to reach linear scaling

1. **Discard weakly interacting electron pairs:**
   In almost all local treatments done by *distance criteria* (R_{ij}=distance between orbital centroids)
2. **Discard small terms in the sum over k** by analyzing f_{ik},f_{jk}
   Threshold F_{Cut}~10^{-5} Eh

Amplitude Update

After the domains have been formed, it is advantageous to diagonalize the **local overlap matrix**

$$\tilde{S}^{(ij)}_{\tilde{\mu}\tilde{\nu}} = \left\langle \tilde{\mu} \mid \tilde{\nu} \right\rangle$$

and discard eigenvalues smaller than a threshold (i.e. 10^{-8}). This gives a set of **non-redundant**, locally orthonormal PAO's

$$\tilde{\mu}' = \sum_{\tilde{\mu} \in \{ij\}} s_{\tilde{\mu}\tilde{\mu}'} \tilde{\mu}$$

Furthermore, one can diagonalize the Fock matrix over this local set to arrive at a set of local **quasi-canonical PAO's** $\tilde{\mu}''$ with energies $\varepsilon_{\tilde{\mu}''}$

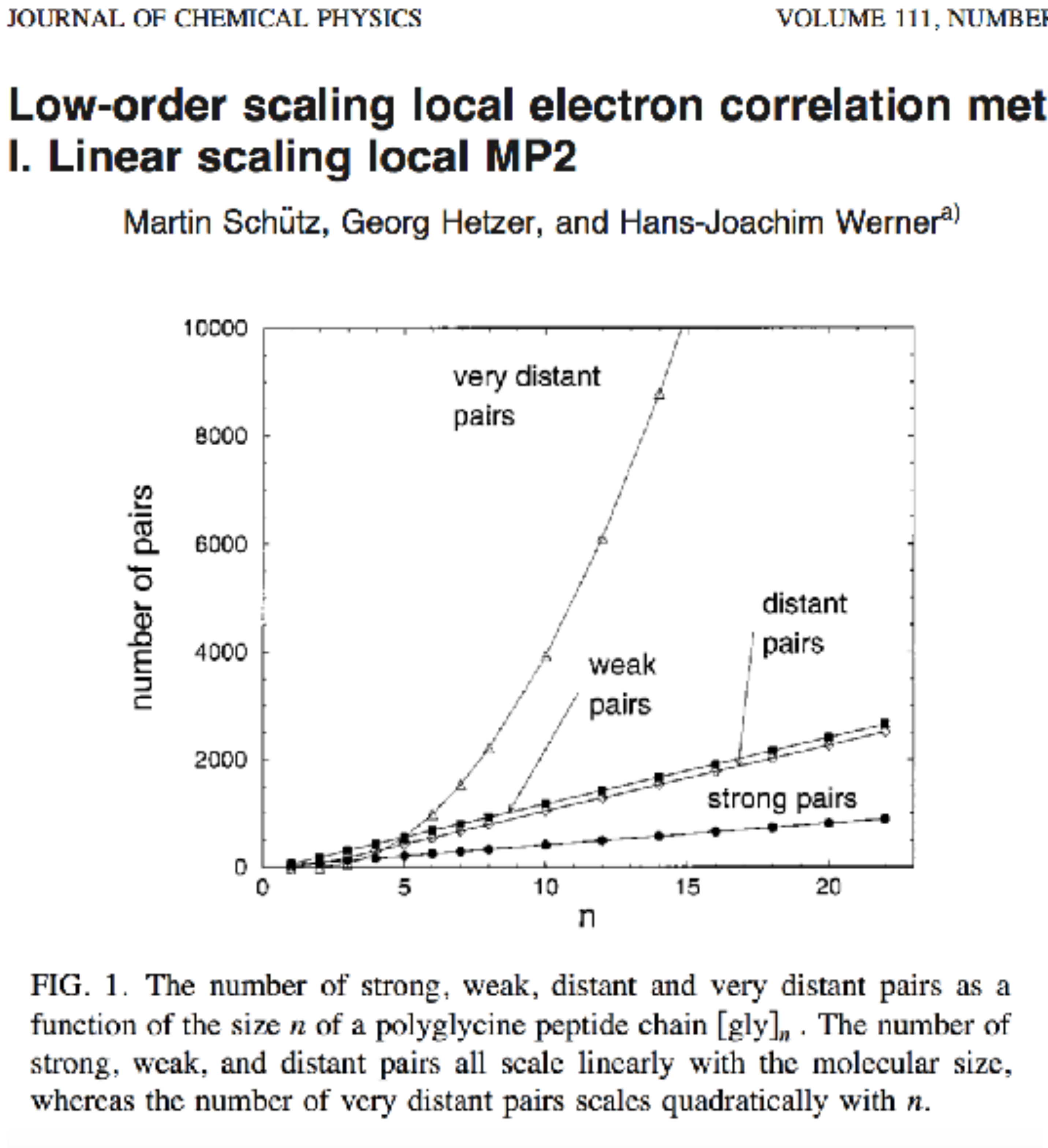
We assume this done (and drop the primes). The **initial guess** to the amplitudes is:

$$C^{ij}_{\tilde{\mu}\tilde{\nu}}(guess) = -\frac{(i\tilde{\mu} \mid j\tilde{\nu})}{\varepsilon_{\tilde{\mu}} + \varepsilon_{\tilde{\nu}} - f_{ii} - f_{jj}} \quad (\tilde{\mu}\tilde{\nu} \in \{ij\})$$

And in each iteration **update** the amplitudes according to:

$$C^{ij}_{\tilde{\mu}\tilde{\nu}} \leftarrow C^{ij}_{\tilde{\mu}\tilde{\nu}} - \frac{R^{ij}_{\tilde{\mu}\tilde{\nu}}}{\varepsilon_{\tilde{\mu}} + \varepsilon_{\tilde{\nu}} - f_{ii} - f_{jj}} \quad (\tilde{\mu}\tilde{\nu} \in \{ij\})$$

PAO based Local Correlation Treatments



JOURNAL OF CHEMICAL PHYSICS VOLUME 111, NUMBER 13 1 OCTOBER 1999

Low-order scaling local electron correlation methods. I. Linear scaling local MP2

Martin Schütz, Georg Hetzer, and Hans-Joachim Werner[a)]

FIG. 1. The number of strong, weak, distant and very distant pairs as a function of the size *n* of a polyglycine peptide chain $[\mathrm{gly}]_n$. The number of strong, weak, and distant pairs all scale linearly with the molecular size, whereas the number of very distant pairs scales quadratically with *n*.

Hierarchical treatment of electron pairs, multipole approximations, careful thresholding lead to efficient, linear scaling algorithms

Problems with PAO based treatments

NJ Russ, TD Crawford J. Chem. Phys., **2004**, 121, 691

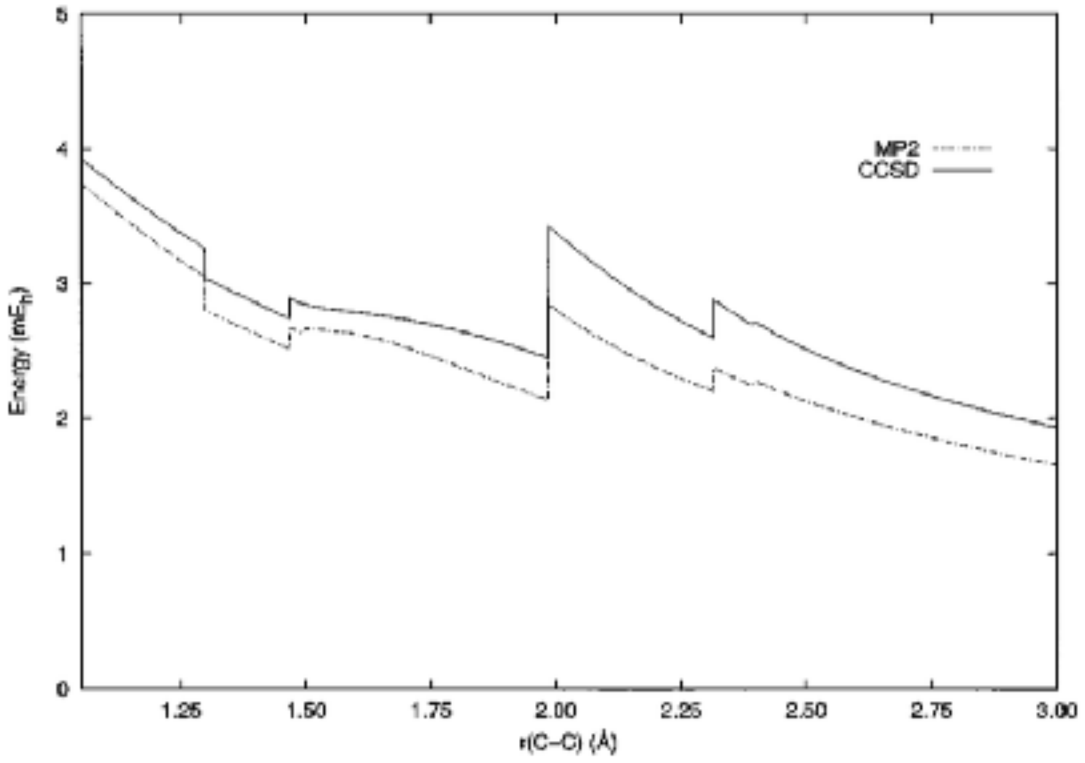


FIG. 7. LMP2 and LCCSD localization errors (in mE_h) for singlet ketene dissociation, where the four discontinuities discussed in the text are clearly visible.

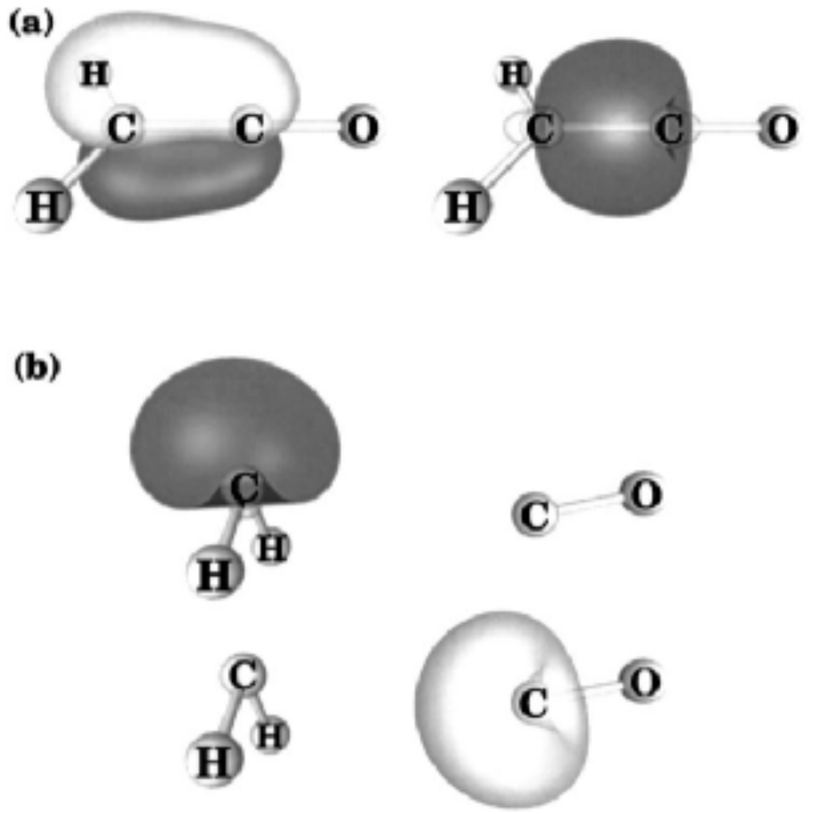


FIG. 8. Contour plots of the relevant Pipek–Mezey localized orbitals for singlet ketene: (a) The π and σ bonding orbitals near the equilibrium geometry and (b) the corresponding lone-pair dissociated MOs of singlet methylene and carbon monoxide.

- ➡ Discontinuous potential energy surfaces due to small and changing domains along the PES
- ➡ Reply:

THE JOURNAL OF CHEMICAL PHYSICS **125**, 184110 (2006)

Calculation of smooth potential energy surfaces using local electron correlation methods

Ricardo A. Mata and Hans-Joachim Werner[a]

Improvements of Local MP2

1. **RI/DF Approximation of K^{ij}**
   HJ Werner, F Manby, PJ Knowles, *J. Chem. Phys.* **2003**, 118, 8149
2. **Pseudospectral construction of K^{ij}**
   RB Murphy, MD Beachy, RA Friesner, MN Ringnalda *J. Chem. Phys.*, **1995**, 103, 1481
3. **Laplace Transformation**
   A Wilson, J. Almlöf Theoret. Chim. Acta, **1997**, 95, 49

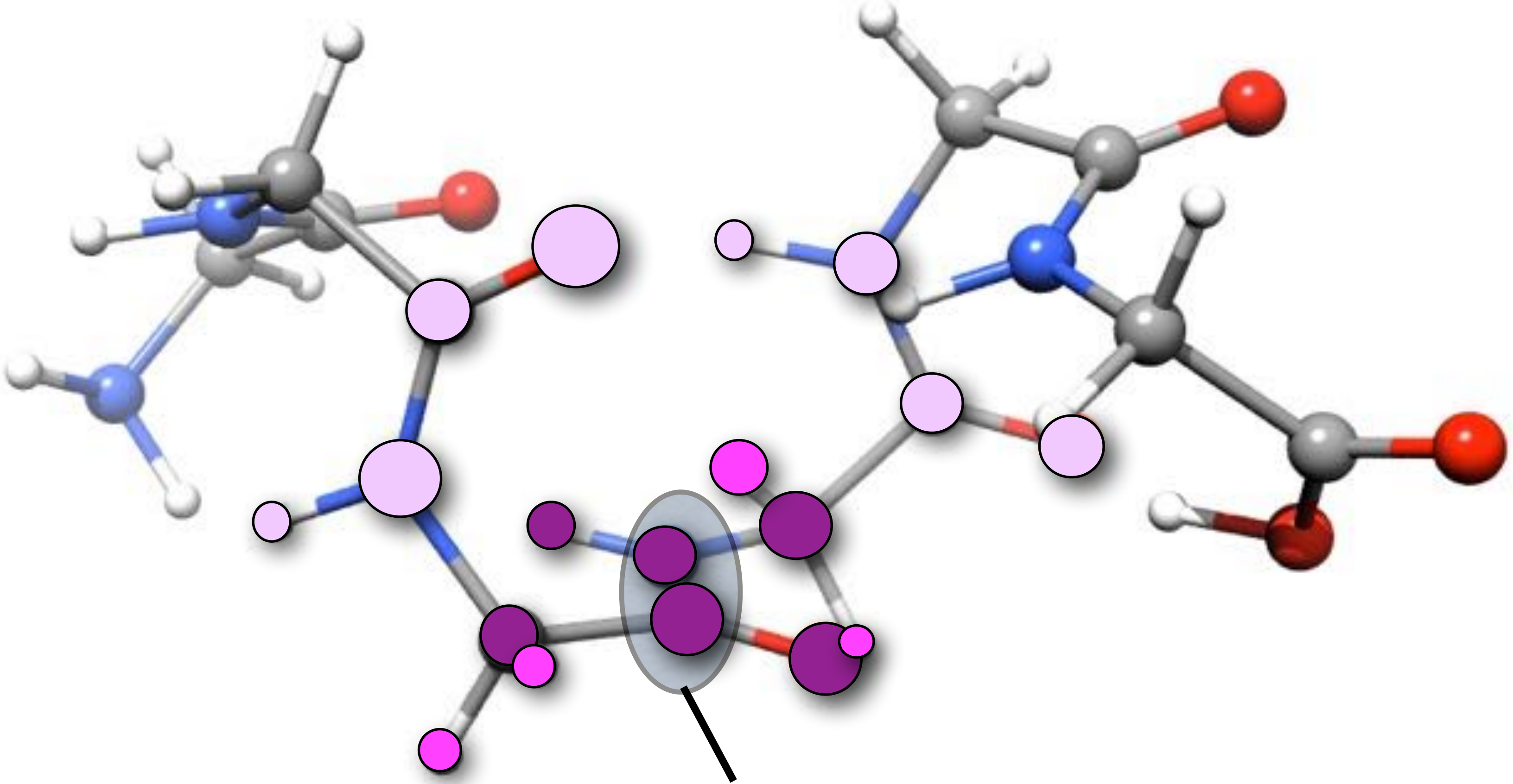
…

➡ Endless possibilities for performance improvements and minor tweaks

In either PAO based or CIM based procedures the correlation energy recovered depends critically on the PAO domains.

… how large do they have to be in order to lead to an accurate result?

How Large do Domains have to be?



Correlated bond

T_{DO}=0.1 98.4% E_{corr} N^{av}_{PAO}=115

T_{DO}=0.01 99.7% E_{corr} N^{av}_{PAO}=588

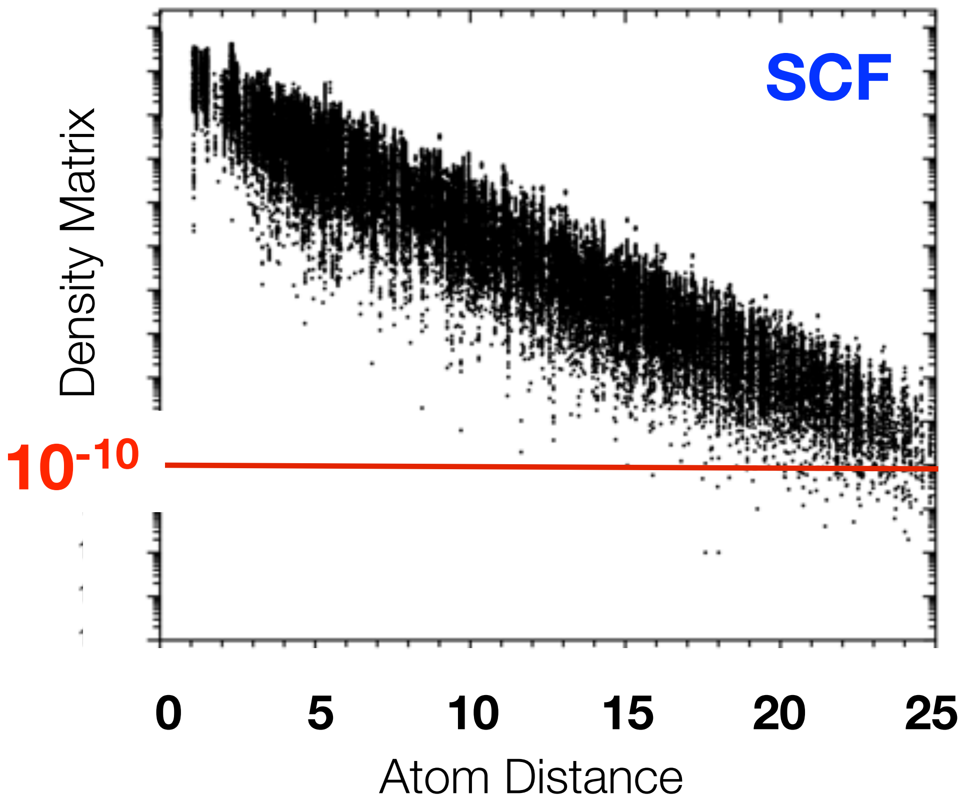
T_{DO}=0.001 99.9% E_{corr} N^{av}_{PAO}=935

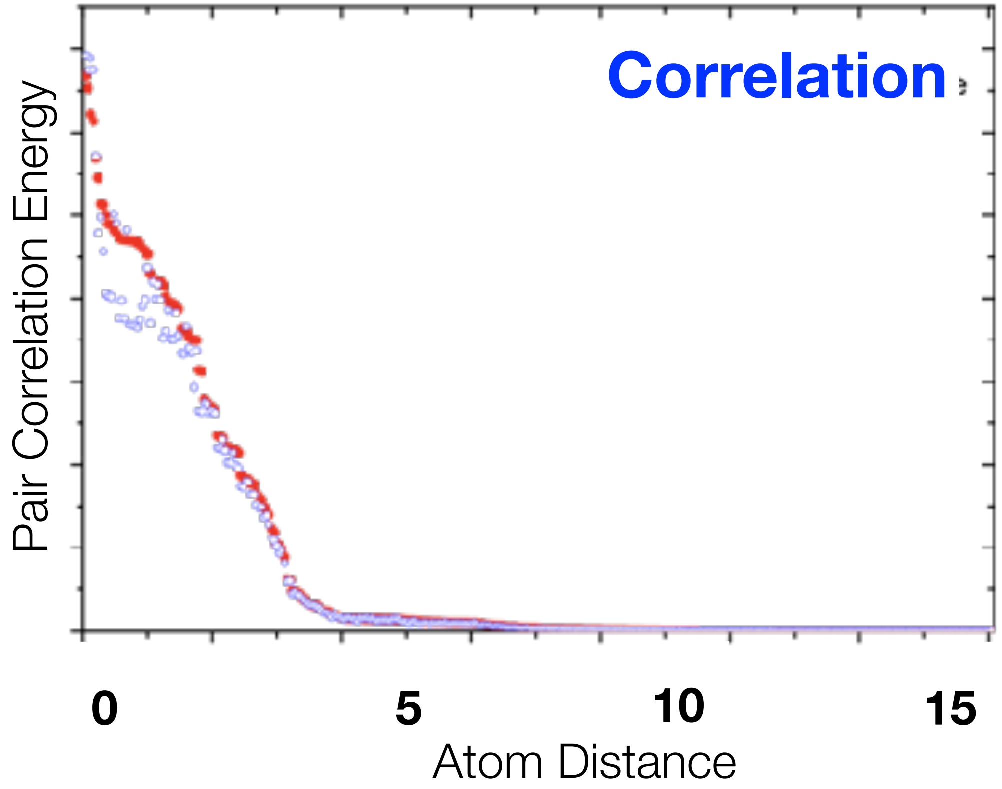
- At the domain size one reaches target accuracy the average number of PAOs per domain is too large for the calculation to be efficient or even doable
- There are important correlation effects that are not *that* local

Virtual Space Compaction: Pair Natural orbitals

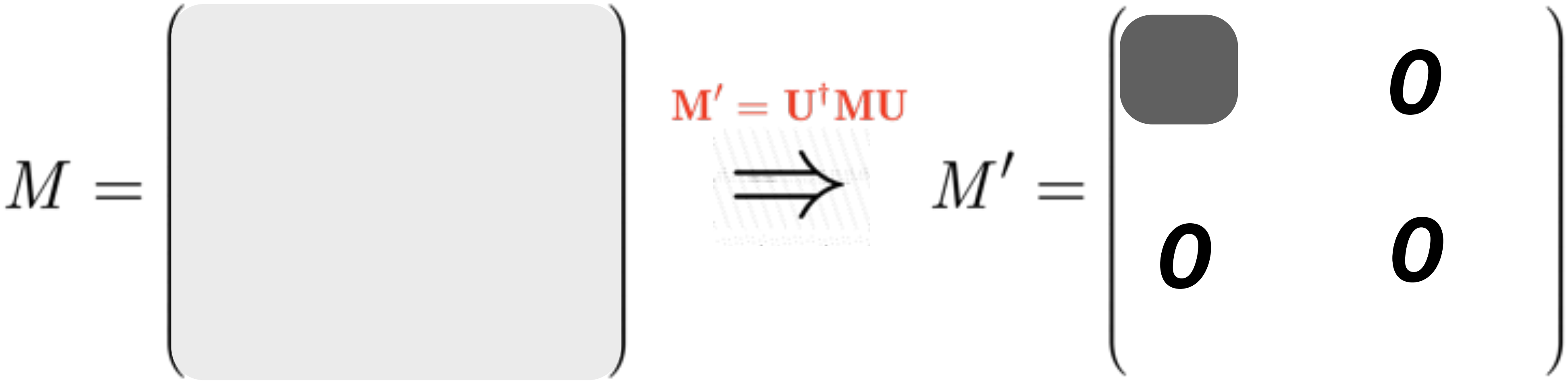
Saving Time in Electronic Structure Calculations

Exploit Sparsity!





Compress Data!



$$M' = U^{\dagger}MU$$

PHYSICAL REVIEW VOLUME 97, NUMBER 6 MARCH 15, 1955

Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction*

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(Received July 8, 1954)

in the *k*-space, i.e., the charge- and bond-order matrix, is *Hermitean*, and it is therefore possible to find a unitary matrix **U** which transforms this matrix to diagonal form with the eigenvalues $n_{kk}=n_k$:

$$\mathbf{U}^\dagger\gamma\mathbf{U}=\mathbf{n}=\text{diagonal matrix.} \tag{72}$$

We have further, in matrix form, $\gamma=\mathbf{UnU}^\dagger$, and, if we introduce a new set of spin-orbitals χ_k by the matrix relation $\chi=\psi\mathbf{U}$, or

$$\chi_k=\sum_\alpha\psi_\alpha U_{\alpha k}, \tag{73}$$

we may rewrite the density matrix in the form

$$\gamma(\mathbf{x}_1'|\mathbf{x}_1)=\sum_k n_k\chi_k^*(\mathbf{x}_1')\chi_k(\mathbf{x}_1). \tag{74}$$

This form is characterized by the fact that all bond orders are vanishing, and the new spin-orbitals χ_k will therefore be called the *natural spin-orbitals* associated

4. NATURAL SPIN-ORBITALS AND THE CONVERGENCE PROBLEM IN THE METHOD OF CONFIGURATIONAL INTERACTION

Its convergence properties may now be understood from the relations (63), (64), and (74). In the limiting case, when exactly N natural spin-orbitals are fully occupied and the relation $\gamma^2=\gamma$ is fulfilled, the natural expansion (80) is reduced to a *single* Slater determinant. In considering the convergence, this is of course the most favorable case. However, if only a finite number of the occupation numbers n_k in (74) are essentially different from zero, the natural expansion (80) will be reduced to a sum of determinants over all ordered configurations associated with these essentially occurring spin-orbitals, i.e., to a sum of comparatively few terms. The introduction of natural spin-orbitals seems therefore to provide a simple solution of the convergence problem, previously discussed by Slater.[17]

Note added in proof.—It is desirable to have also a more exact mathematical measure for the rapidity of convergence of the two configurational interaction series (66) and (80). We note that, according to (60) and (63), the charge order $\gamma(k)$ gives the probability for the ordinary spin-orbital ψ_k to occur in the expansion of the total wave function Ψ. If only M of the numbers $\gamma(k)$, $k=1, 2, 3, \cdots$, are essentially different from zero, then the number of essential terms in (66) is given by the corresponding number of possible configurations: $M!/N!(M-N)!$. In using this procedure, however, it is necessary to evaluate the individual quantities $\gamma(k)$ and to distinguish between essential and unessential charge orders.

A still simpler measure of convergence may be constructed by observing that the charge orders always lie between 0 and 1 and that, in the limiting cases $\gamma(k)=0$ and $\gamma(k)=1$, the corresponding spin-orbital ψ_k occurs in none or in all of the terms in (66), respectively, without contributing to the slowing down of the convergence of the series. The eventual slowness of the convergence of (66) depends instead on the possibility for an electron to be distributed over two or more spin-orbitals, giving charge orders of an intermediate order of magnitude, $0<\gamma(k)<1$. The rapidity of convergence of (66) may therefore be measured by the smallness of the quantity

$$\vartheta=(1/N)\Sigma_k\{1-\gamma(k)\}\gamma(k)=1-(1/N)\Sigma_k\{\gamma(k)\}^2,$$

which fulfills the inequality of $0\leqq\vartheta<1$. In considering different basic sets $\psi_1, \psi_2, \psi_3, \cdots$ for the description of the same total wave function Ψ, it is clear that the natural spin-orbitals χ_k are characterized by having the *smallest* ϑ *value possible.* According to (72), we have $\boldsymbol{\gamma}=\mathbf{UnU}^\dagger$ and $\boldsymbol{\gamma}^2=\mathbf{Un}^2\mathbf{U}^\dagger$, leading to $\mathrm{Tr}(\boldsymbol{\gamma}^2)=\mathrm{Tr}(\mathbf{n}^2)$ and

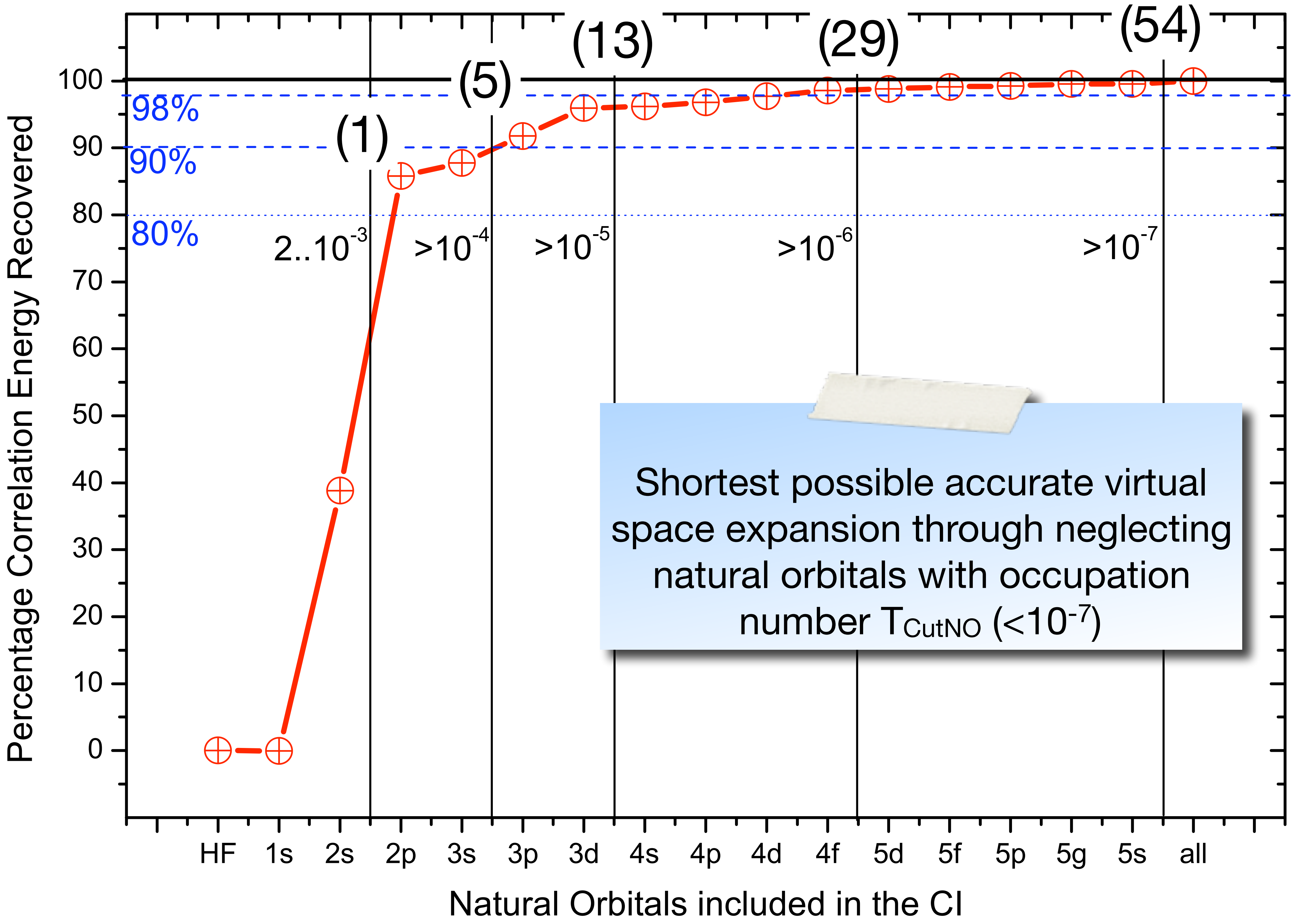
$$\Sigma_k\gamma_k^2=\Sigma_k n_k^2-\sum_{l\neq k}|\gamma_{kl}|^2\leq\Sigma_k n_k^2,$$

with the final result

$$1-(1/N)\ \Sigma_k n_k^2\leq 1-(1/N)\ \Sigma_k\gamma_k^2,$$

which proves our theorem. This means that the natural spin-orbitals are distinguished not only by having vanishing bond orders but also by giving the smallest number of essential charge orders possible. By investigating the quantity ϑ, one can therefore easily estimate how much improvement one can expect in the convergence of a given configurational interaction series by introducing the natural spin-orbitals.

Most Compact Expansion: Natural Orbitals



Shortest possible accurate virtual space expansion through neglecting natural orbitals with occupation number T_{CutNO} ($<10^{-7}$)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 45, NUMBER 5 1 SEPTEMBER 1966

Pseudonatural Orbitals as a Basis for the Superposition of Configurations. I. He_2^+

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AND
M. Krauss
National Bureau of Standards, Washington, D. C.

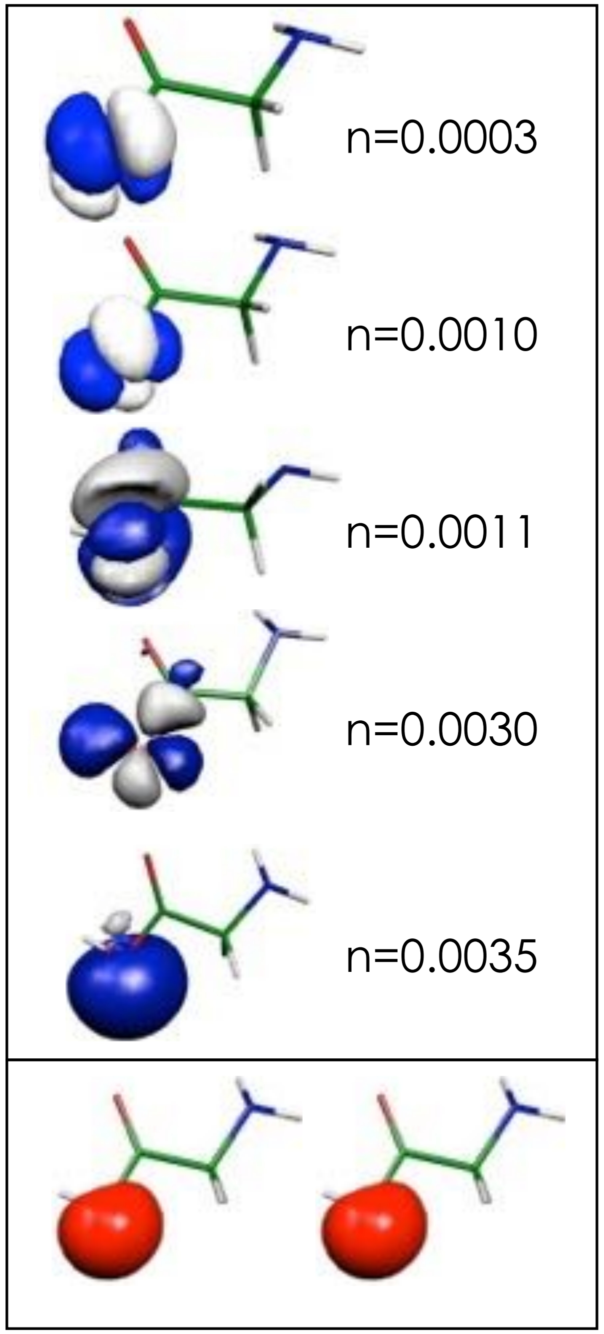
(Received 1 December 1965)

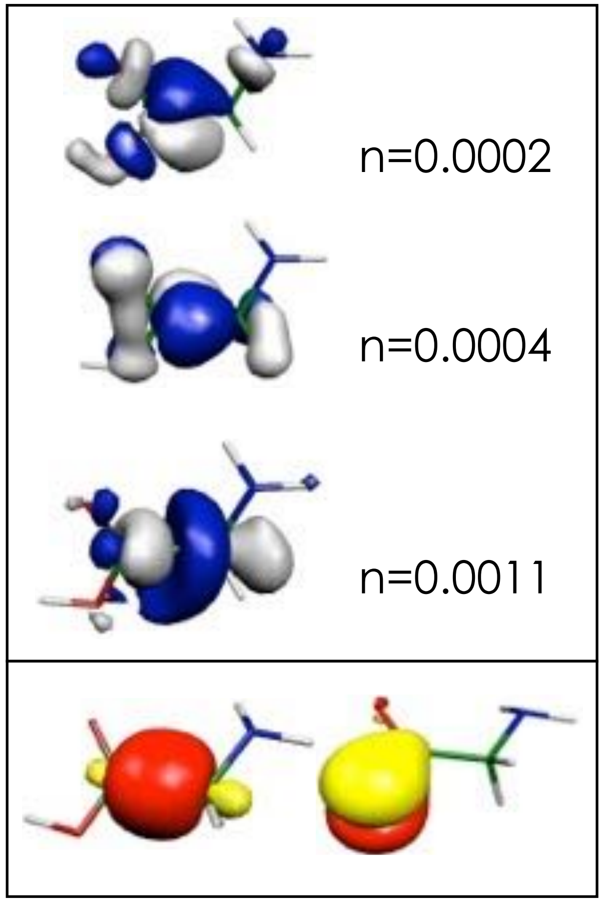
The use of pseudonatural orbitals (PNO) is proposed to improve the rate of convergence in the superposition of configurations (SOC). Natural orbitals are determined for selected electron pairs in the Hartree–Fock field of the $n-2$ electron core and are then used as the basis for the total SOC calculation. Since these natural orbitals are not natural for the n-electron system they are considered false or pseudonatural orbitals when used in the n-electron problem.

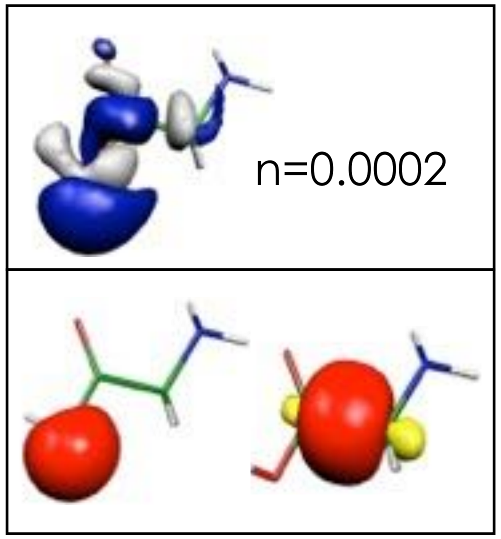
The PNO basis has been applied to He_2^+ and H_3 to test the convergence. Complete results are reported here only for He_2^+. The PNO's are quite successful in speeding up the convergence of the SOC and rendering the calculation of correlation energy quite practical in general. Gaussian-type orbitals (GTO) are used throughout and were not a serious impediment to obtaining quantitative accuracy. In fact the large number of unoccupied Hartree–Fock orbitals consequent upon the use of a GTO basis permit a straightforward determination of the PNO orbitals.

Pair Natural Orbitals (PNOs)

- Small number of significant PNOs per electron pair
- Vanishing (0-5) PNOs for weak pairs
- Located in the same region of space as the internal pair but as delocalized as necessary
- Orthonormal within one pair, non-orthogonal between pairs







FN; Wennmohs, F.; Hansen, A. *J. Chem. Phys.* **2009**, 130, 114108

Approximate PNO Construction

Problem:

- Have to know the pair amplitudes to make the pair densities and hence the PNOs!
- Fortunately, approximate NOs and exact NOs typically behave similarly

Easiest approach: Use the MP2 amplitudes

$$T^{ij}_{ab} = -\frac{K^{ij}_{ab}}{\varepsilon_a - \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

$$\mathbf{D}^{ij} = \frac{1+\delta_{ij}}{N}\left(\tilde{\mathbf{T}}^{ij-}\mathbf{T}^{ij} + \tilde{\mathbf{T}}^{ij}\mathbf{T}^{ij+}\right) \qquad \tilde{\mathbf{T}}^{ij} = \frac{1}{1+\delta_{ij}}\left(4\mathbf{T}^{ij} - 2\mathbf{T}^{ij-}\right) \qquad \boxed{N = 1 + \left\langle \tilde{\mathbf{T}}^{ij} \middle| \mathbf{T}^{ij} \right\rangle}$$

Normalization subject to debate, presently dropped

The PNOs are obtained as the eigenfunctions of the virtual pair density

$$\mathbf{D}^{ij}\mathbf{d}^{ij} = \mathbf{n}^{ij}\mathbf{d}^{ij} \qquad \left|\bar{a}^{ij}\right\rangle = \sum_{a} d^{ij}_{a\bar{a}}\left|a\right\rangle \qquad \left|a\right\rangle = \sum_{\bar{a}^{ij}} d^{ij}_{\bar{a}a}\left|\bar{a}^{ij}\right\rangle$$

PNOs with occupation numbers below $\mathbf{T}_{\mathbf{CutPNO}}$ are neglected

Refined approach: Construct pair specific orbitals which lead to nearly diagonal intra-pair (IEPA) CI matrices (Meyer):

$$\mathbf{G}^{ii} = \mathbf{F} + \mathbf{K}^{ii} - \mathbf{J}^{ii}$$

$$\mathbf{G}^{ij} = \mathbf{F} + \mathbf{K}^{ii} + \mathbf{K}^{jj} - \tfrac{1}{2}\mathbf{J}^{ii} - \tfrac{1}{2}\mathbf{J}^{jj}$$

Domain Based Local Pair Natural Orbital Coupled Cluster Theory

The DLPNO-CCSD Approach

The DLPNO approach to CCSD follows as a natural extension to MP2 (although historically, DLPNO-CCSD was much earlier than DLPNO-MP2)

The **cluster operator** is written in the PNO basis:

$$T_1 + T_2 = \sum_{ia} t^{i}_{\tilde{a}_i} a^{+}_{\tilde{a}_i} a_i + \tfrac{1}{4} \sum_{ijab} t^{ij}_{\tilde{a}_{ij}\tilde{b}_{ij}} a^{+}_{\tilde{b}_{ij}} a^{+}_{\tilde{a}_{ij}} a_j a_i$$

- *PNO's for doubles are made from DLPNO-MP2 and cut with* `TCutPNO`
- *PNO's for singles are identical to the PNOs of the diagonal pairs and cut with* `0.01TCutPNO`

The **PNOs** are expanded in large PAO domains (using `TCutDO`) for domain construction and `TCutMKN` for aux-domain construction)

$$\left|\tilde{a}_{ij}\right\rangle = \sum_{\tilde{\mu}\in\{ij\}} d^{ij}_{\tilde{\mu}\tilde{a}} \left|\tilde{\mu}\right\rangle$$

PNO based Correlation Equations

PNO-CI Wavefunction:

$$\Psi = \Psi_{HF} + \sum_{ia} t_a^i \Psi_i^a + \sum_{i\leq j} \sum_{\tilde{a}_{ij}\tilde{b}_{ij}} \tilde{T}^{ij}_{\tilde{a}_{ij}\tilde{b}_{ij}} \Psi_{ij}^{\tilde{a}_{ij}\tilde{b}_{ij}}$$

$$\bar{\mathbf{T}}^{ij} = \mathbf{d}^{ij+}\mathbf{T}^{ij}\mathbf{d}^{ij}$$

very compact Linear, scaling number of doubles amplitudes (reduction > factor > ***10⁷****)*

PNO-CI Doubles Residual:

$$\begin{aligned}\sigma^{ij}_{\tilde{a}\tilde{b}} = {} & K^{ij}_{\tilde{a}\tilde{b}} + \mathbf{K}(\bar{\mathbf{T}}^{ij})_{\tilde{a}\tilde{b}} + (\mathbf{d}^{ij+}\mathbf{F}\mathbf{d}^{ij}\bar{\mathbf{T}}^{ij} + \bar{\mathbf{T}}^{ij}\mathbf{d}^{ij+}\mathbf{F}\mathbf{d}^{ij})_{\tilde{a}\tilde{b}} \\ & - \sum_k \left(F_{jk}'(\mathbf{S}^{ij,ik}\bar{\mathbf{T}}^{ik}\mathbf{S}^{ij,ik+})_{\tilde{a}\tilde{b}} + F_{ik}'(\mathbf{S}^{ij,kj}\bar{\mathbf{T}}^{kj}\mathbf{S}^{ij,kj+})_{\tilde{a}\tilde{b}}\right) + \sum_{kl}(ik|jl)(\mathbf{S}^{ij,kl}\mathbf{T}^{kl}\mathbf{S}^{ij,kl+})_{\tilde{a}\tilde{b}} \\ & + \sum_k \left\{\mathbf{S}^{ij,ik}(2\bar{\mathbf{T}}^{ik} - \bar{\mathbf{T}}^{ik+})(\mathbf{K}^{kj} - \tfrac{1}{2}\mathbf{J}^{kj})\mathbf{d}^{ij} + \mathbf{d}^{ij+}(\mathbf{K}^{ik} - \tfrac{1}{2}\mathbf{J}^{ik})(2\mathbf{T}^{kj} - \mathbf{T}^{kj+})\mathbf{S}^{ij,kj+}\right\}_{\tilde{a}\tilde{b}} \\ & - \sum_k \left\{\tfrac{1}{2}\mathbf{S}^{ij,ik}\mathbf{T}^{ik+}\mathbf{J}^{jk+}\mathbf{d}^{ij} + \tfrac{1}{2}\mathbf{d}^{ij+}\mathbf{J}^{ik}\mathbf{T}^{kj+}\mathbf{S}^{kj,ij} + \mathbf{d}^{ij+}\mathbf{J}^{jk}\mathbf{T}^{ik}\mathbf{S}^{ik,ij} + \mathbf{S}^{ij,kj}\mathbf{T}^{kj}\mathbf{J}^{ik+}\mathbf{d}^{ij}\right\}_{\tilde{a}\tilde{b}}\end{aligned}$$

$$S^{ij,kl}_{\tilde{a},\tilde{b}} = \left\langle \tilde{a}^{ij} \middle| \tilde{b}^{kl} \right\rangle = (\mathbf{d}^{ij+}\mathbf{d}^{kl})_{\tilde{a}\tilde{b}}$$

Meyer, W.; IJQC, **1971**, 5, 341; FN, Wennmohs, F.; Hansen, A. **2009**, *J. Chem. Phys.* 130, 114108

Natural Triple Excitations

Our suggestion: **Natural triples orbitals** (TNO's)

- ✓ Three-pair density: $\mathbf{D}^{ijk} = \frac{1}{3}(\mathbf{D}^{ij} + \mathbf{D}^{ik} + \mathbf{D}^{jk})$

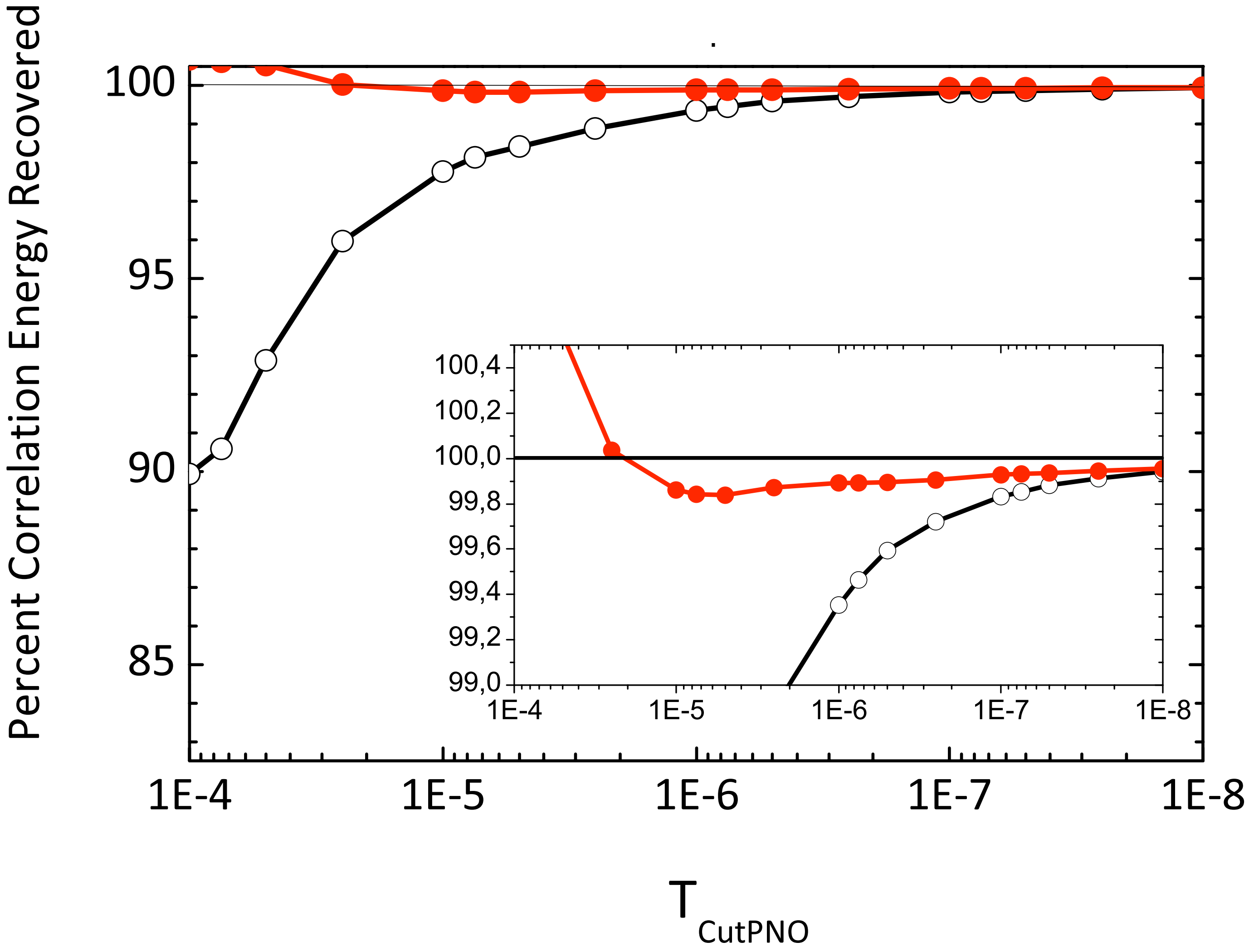
  (The operator $\hat{D}^{ijk} = \sum_{\bar{a}_{ij}} |\bar{a}_{ij}\rangle\langle\bar{a}_{ij}| + \sum_{\bar{a}_{ik}} |\bar{a}_{ik}\rangle\langle\bar{a}_{ik}| + \sum_{\bar{a}_{jk}} |\bar{a}_{jk}\rangle\langle\bar{a}_{jk}|$ *projects onto the joint PNO space of the three pairs)*
- ✓ Formation of the three pair density in the **PAO basis** is linear scaling:
- ✓ Eigenfunctions: $\mathbf{D}^{ijk}\mathbf{x}^{ijk} = n^{ijk}\mathbf{x}^{ijk}$ (cut-off below a given n^{ijk}(min) just as for PNOs)
- ✓ Recanonicalize: $\mathbf{x}^{ijk+}\mathbf{F}\mathbf{x}^{ijk}$
- ✓ Amplitudes are projected into the TNO basis: $T^{ij;TNO}_{\tilde{a}_{ijk},\tilde{b}_{ijk}} = S^{ijk,ij}_{\tilde{a}_{ijk},\tilde{c}_{ij}} T^{ij;PNO}_{\tilde{c}_{ij},\tilde{d}_{ij}} S^{ijk,ij}_{\tilde{b}_{ijk},\tilde{d}_{ij}}$

➡ Integrals over TNOs must be generated for each triple
(bookkeeping complicated but linear scaling) *avoiding projection*

➡ *Linear scaling implementation achieved (Dr. Christoph Riplinger)*

Riplinger, Sandhöfer, Hansen, FN, JCP, **2013**,139(13):134101

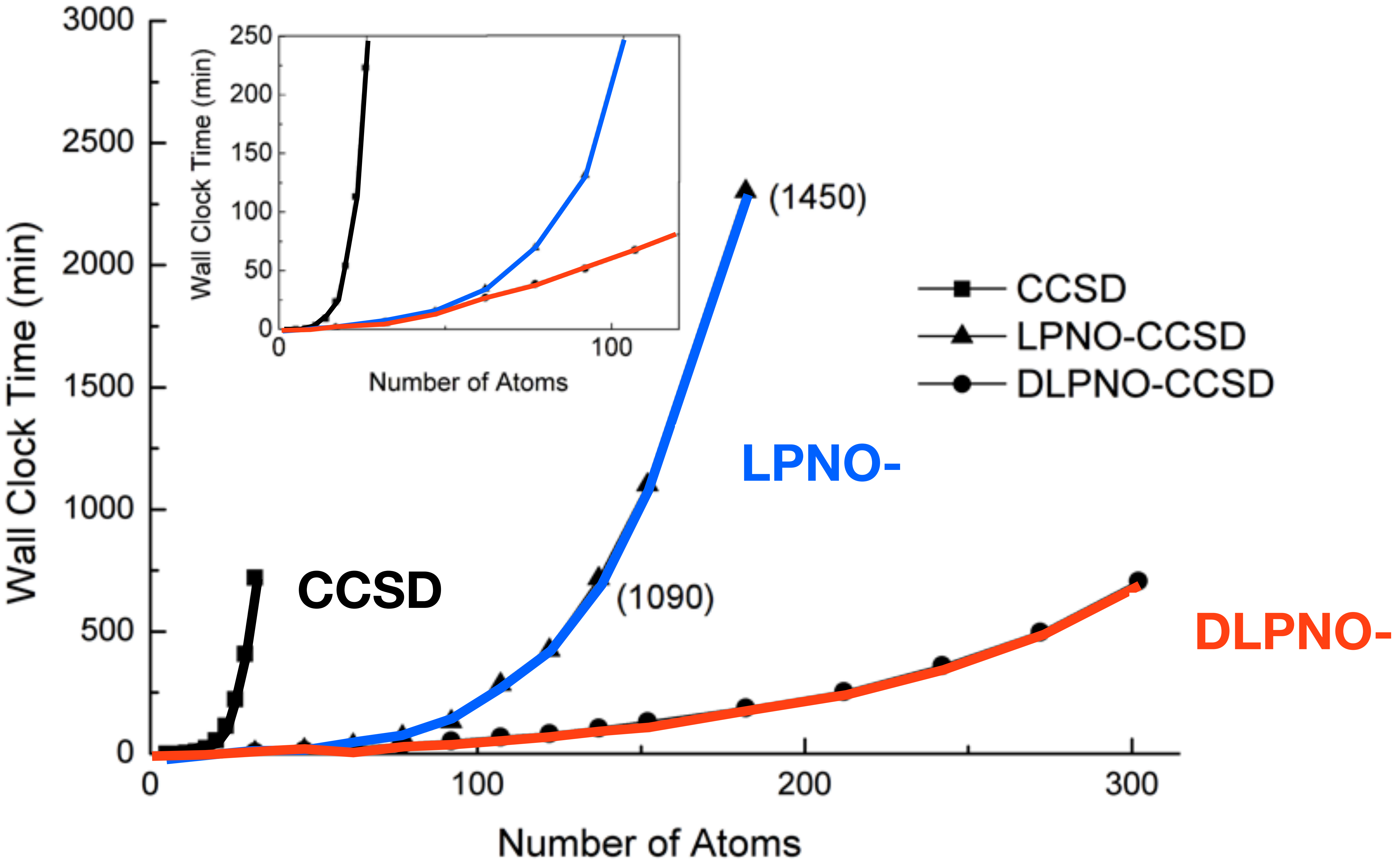
Convergence of DLPNO-CCSD(T)



- ✓ Typically 99.8-99.9% of the canonical correlation energy
- ✓ Energetics of the canonical counterpart methods is reproduced to a few tenth of kcal/mol. Maximum achievable accuracy ~0.1 kcal/mol of the canonical result.
- ✓ The methods are robust and completely black box in character

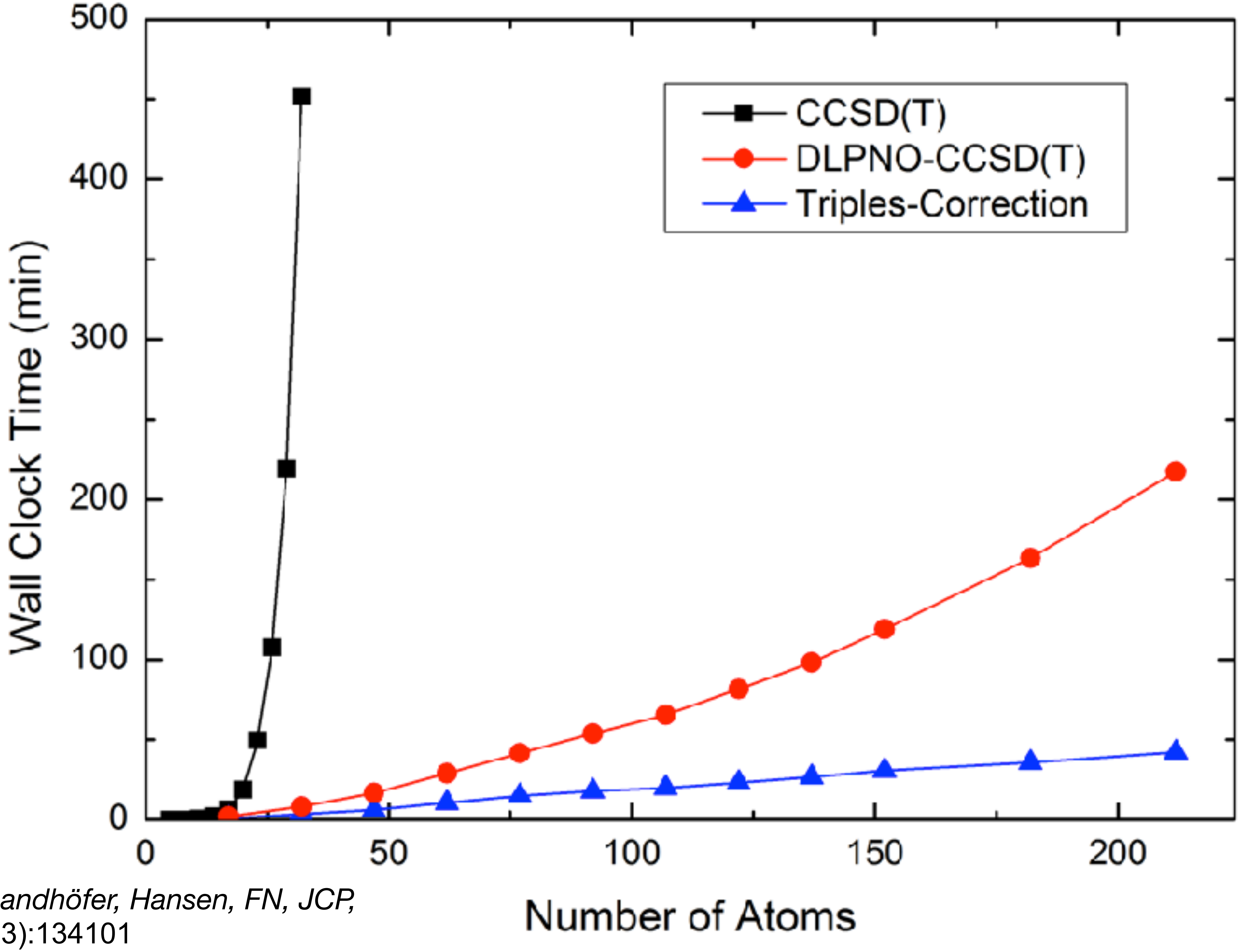
Riplinger, C. FN *J. Chem. Phys*, **2013**, 138, 034106; FN; A. Hansen, D.G. Liakos,, *J. Chem. Phys.*, **2009** 131, 064103

Scaling of LPNO-CCSD



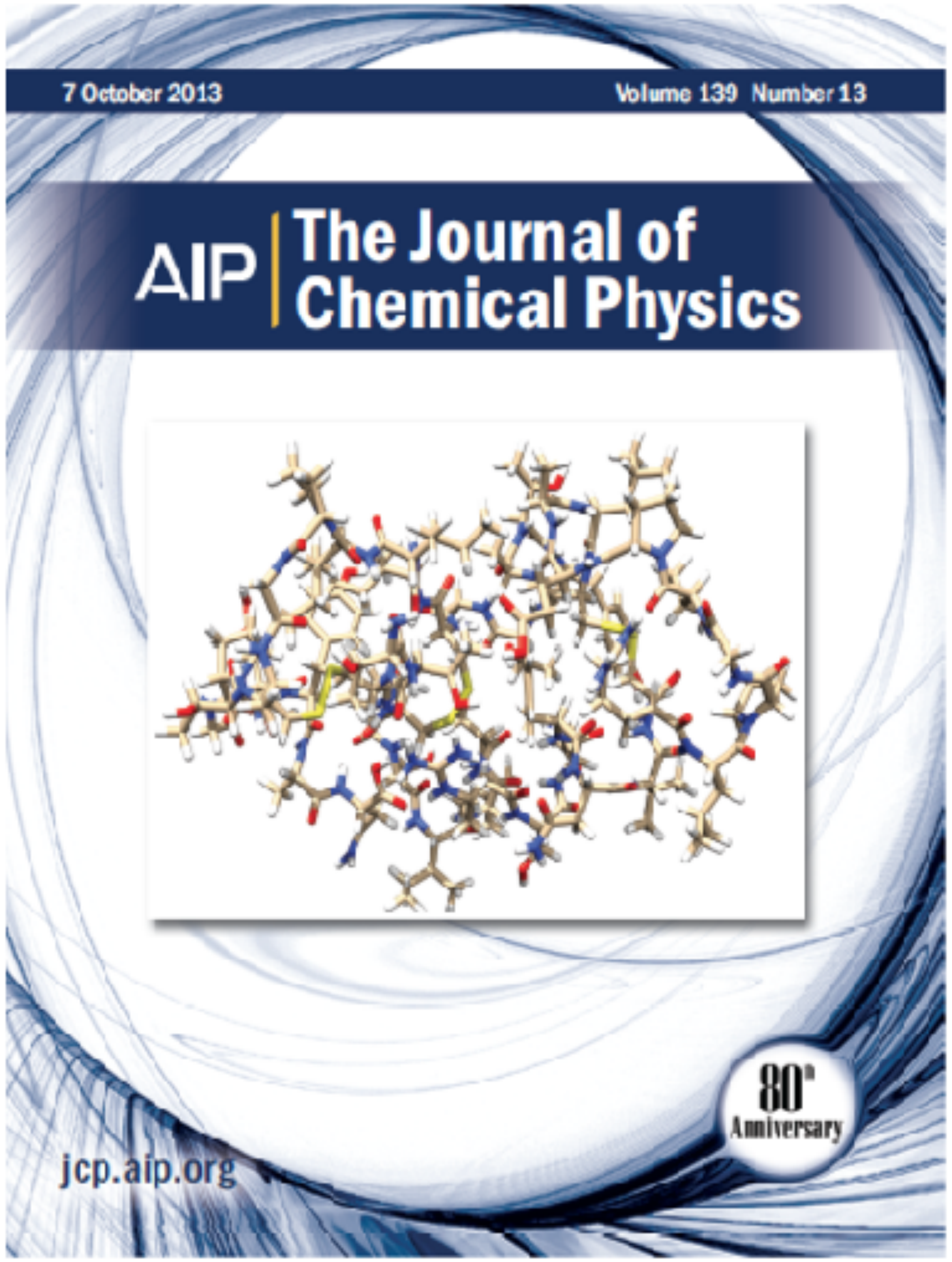
Riplinger, C. FN *J. Chem. Phys*, **2013**, 138, 034106

Scaling of DLPNO-CCSD(T)



Riplinger, Sandhöfer, Hansen, FN, JCP,
2013,139(13):134101

CCSD(T) Calculations on Entire Proteins

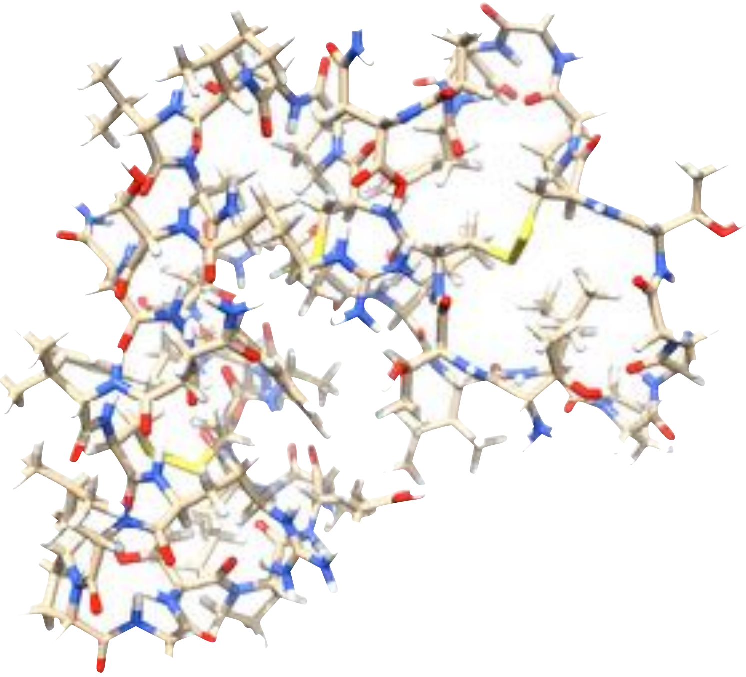


Crambin

644 atoms
def2-SV(P)/6187 basis functions

Canonical computation time
~5 Million Years

DLPNO-CCSD(T)
~3 weeks/1 Core

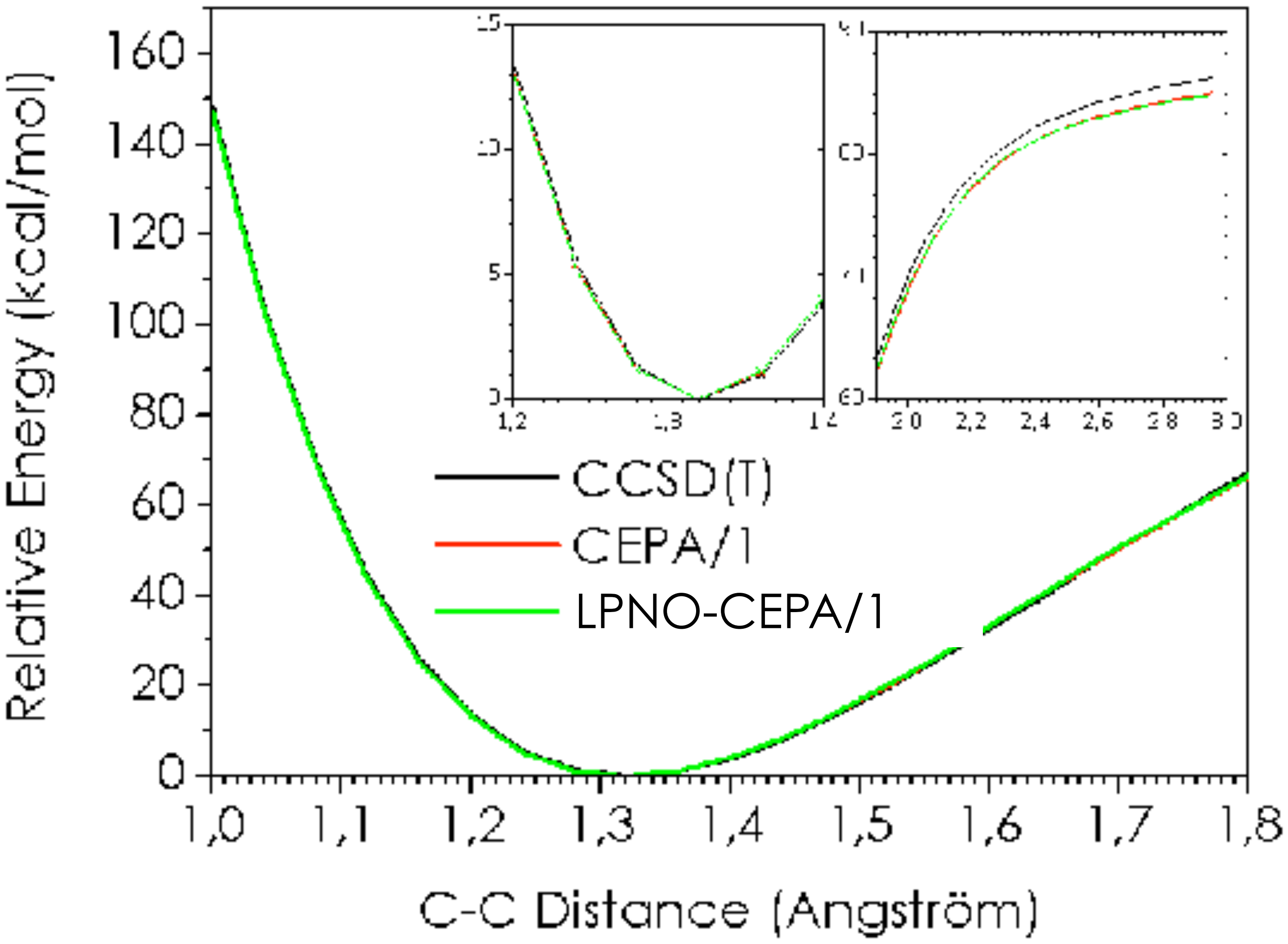


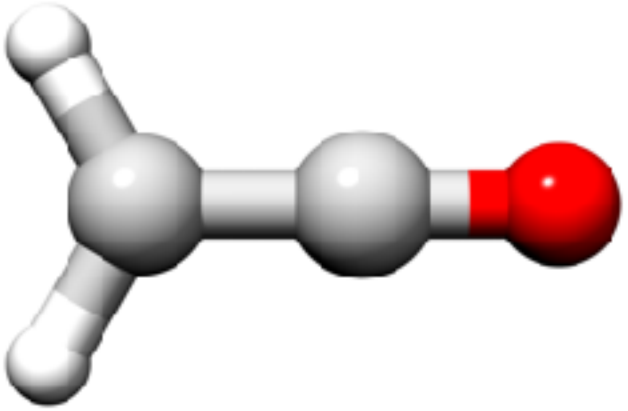
Riplinger, Sandhöfer, Hansen, FN, JCP, **2013**,139(13):134101

http://www.physicstoday.org/daily_edition/physics_update/coupled_cluster_theory_tackles_a_protein

DLPNO Potential Energy Surfaces

Relaxed PES using default settings



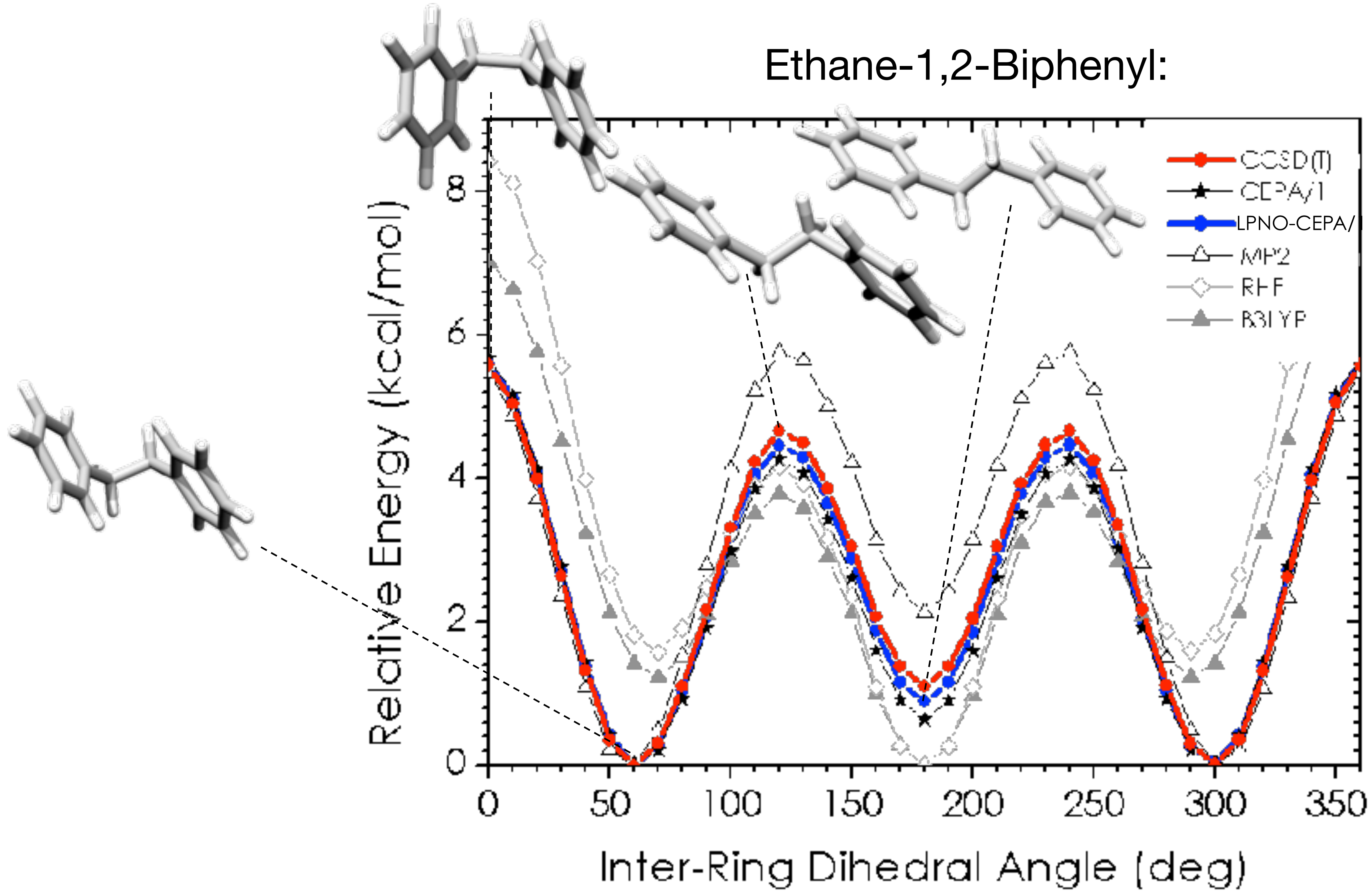


Russ, NJ; Crawford, T.D. *J. Chem. Phys.*, **2004**, 121, 691

No sign of artifacts anywhere. Agreement of CCSD(T), CEPA/1 and L-RI-PNO-CEPA/1 is excellent

DLPNO Potential Energy Surfaces

Ethane-1,2-Biphenyl:

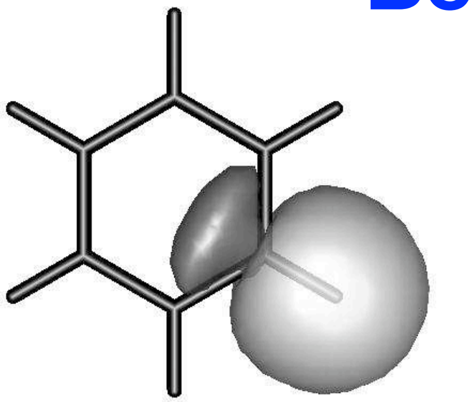


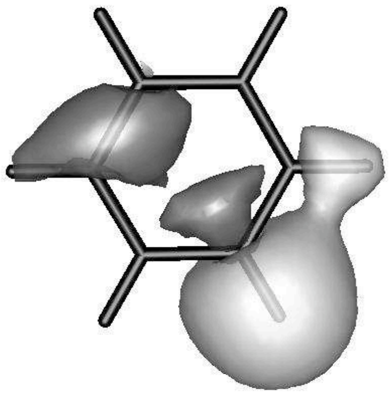
Structures from a PBE-D/TZVP relaxed surface scan; other calculations at the optimized geometries with SV(P)

Riplinger, C. FN *J. Chem. Phys*, **2013**, 138, 034106

(In)sensitivity to the Nature of the Localized Orbitals

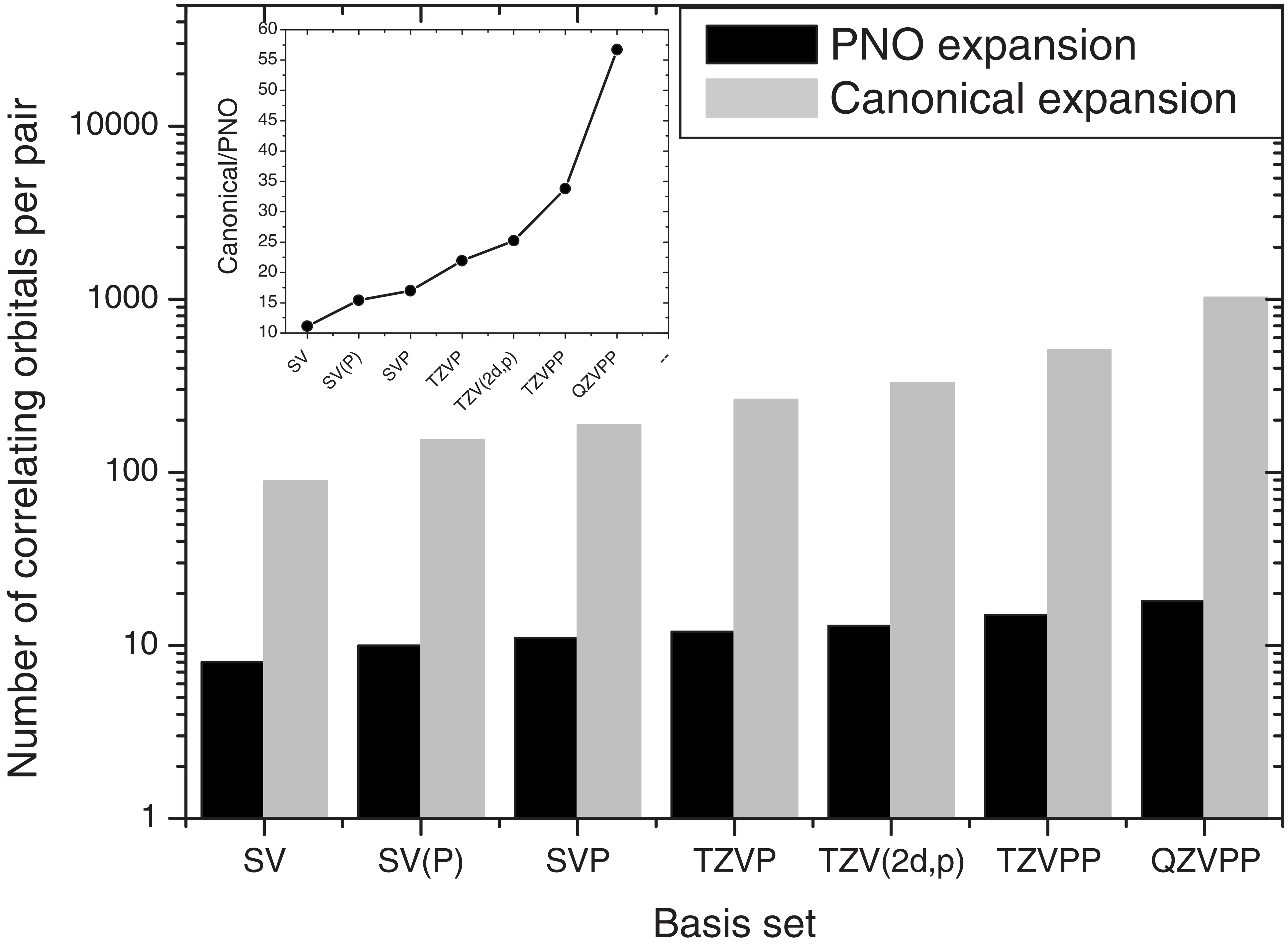
Benzene/aug-cc-pVDZ


Foster-Boys


Pipek-Mezey

		E_{tot} [Eh]	E_{tot} (LPNO-CEPA/1)-E_{tot}(CEPA/1) [kcal/mol]	
Method	Molecule	Foster-Boys	Foster-Boys	Pipek-Mezey
LPNO-CEPA/1	benzene	-231.555559	0.51	0.53
(cc-pVDZ)	octahedran	-463.079091	1.46	1.49
LPNO-CEPA/1	benzene	-231.586412	0.53	0.47
(aug-cc-pVDZ)	octahedran	-463.145835	1.63	1.79

Basis Set Dependence of DLPNO Methods



$$N_{PNO} \propto \sqrt{N_{bas}}$$

FN, Wennmohs, F.; Hansen, A. **2009**, *J. Chem. Phys.* 130, 114108

DLPNO-CCSD(T): Summary

(1) **(relative) Simplicity**. Only one critical cut-off (T_{CutPNO}); local approximations only ‚boost‘ efficiency. T_{CutPNO} can be use to control the absolute desired accuracy

(2) **No real-space cut-offs** and **no fragmentation** necessary

(3) **No redundant integral generation** or amplitude optimizations

(4) **No *reliance* on sparsity** (e.g. not linear scaling ‚by construction‘)

(5) Correlation space for each electron pair is optimal: a) very small for weak pairs, b) as delocalized as necessary

(6) **Excellent behavior with basis set size**

(7) Only local method with **proven accuracy** (better than 1 kcal/mol) and **proven efficiency** (approaching SCF/DFT times) for real life applications.

(8) **Very weak or no dependence on the localization method**. Well localized internal space not even required

(9) **Very smooth error**; no kinks and jumps in PESs

(10) **Black box character**

Canonical:
! cc-pVTZ CCSD
LPNO:
! cc-pVTZ cc-pVTZ/C DLPNO-CCSD(T)