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Local Correlation Approaches

Frank Neese

MAX-PLANCK-GESELLSCHAFT

MPI für Kohlenforschung

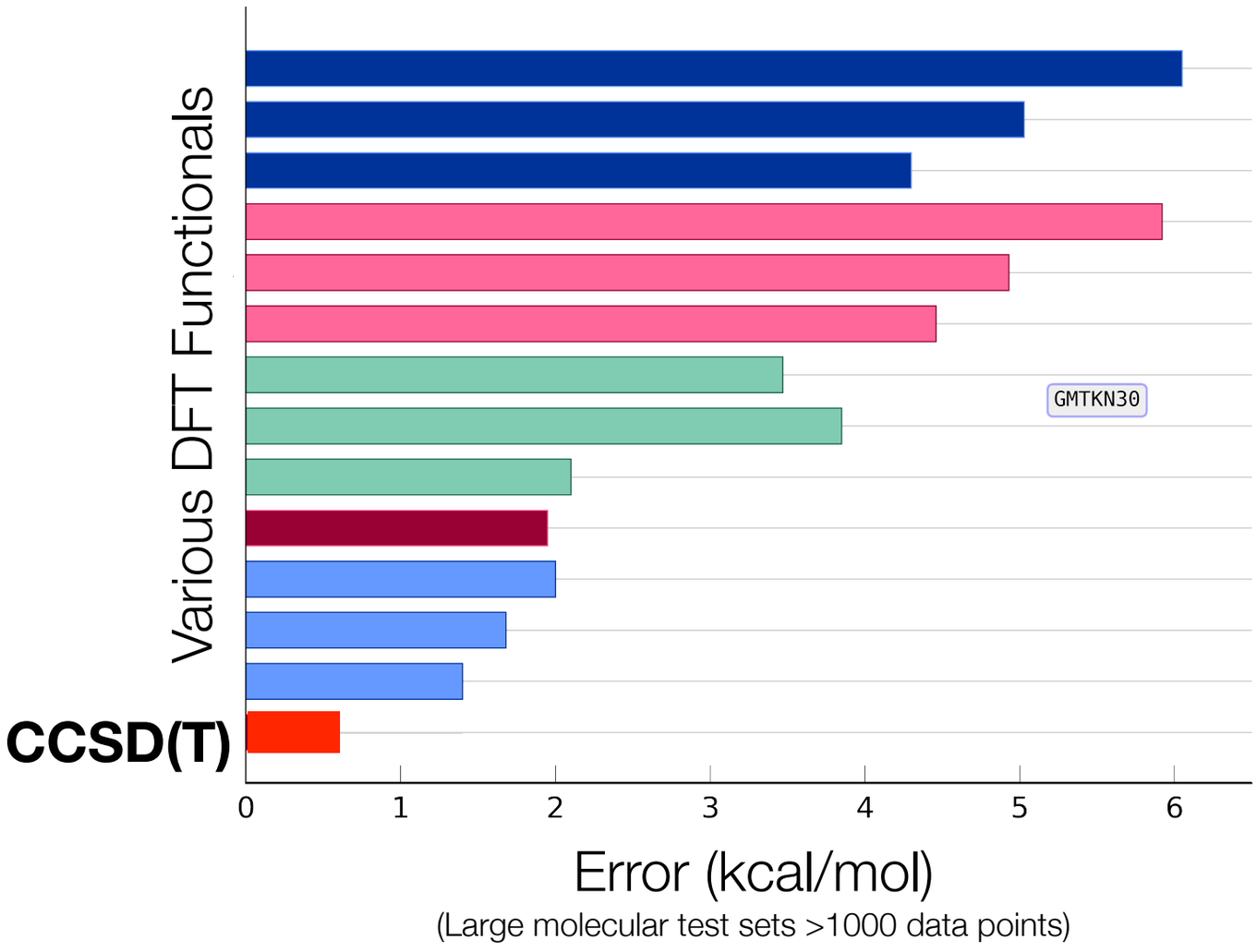
Kaiser-Wilhelm Platz 1

45470 Mülheim an der Ruhr

Goals of Quantum Chemical Method Development

- ✓ To be able to calculate ‚things' (energies, properties) that could not be calculated before or on systems that were not accessible before
- ✓ To develop a better (more accurate, more elegant, more compact, more transparent, …) theory for a known property.
- ✓ Develop new approximations to known equations
- ✓ …
- ✓ **To obtain the same number faster than before** ← We/Thu
- ✓ **To obtain an approximate number faster (and in ‚improved scaling') than before**

Accuracy: Wavefunction vs DFT Methods



- Wavefunction based methods are *the only systematic* route towards *accurate* quantum chemistry
- *Only* wavefunction based methods converge towards the exact energy and all properties *simultaneously*
- *Only* correlated wavefunction based methods can handle complicated bonding situations (like multiplets)

Latest: Liakos, D. G.; Guo, Y.; Neese, F. Comprehensive Benchmark Results for the Domain Based Local Pair Natural Orbital Coupled Cluster Method (DLPNO-CCSD(T)) for Closed- and Open-Shell Systems. *J. Phys. Chem. A* **2020**, *124* (1), 90-100

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

Local Correlation: Importance of Accuracy Goals

The idea of local correlation methods is:

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

HOWEVER

- ➡ **One will only get wave function based ab initio quality, if the error that we introduce by exploiting the locality is not spoiling the intrinsic accuracy of the method!**

- ➡ Example: In a large molecule the correlation energy is **~10 Eh=6270** kcal/mol

- ➡ Chemical accuracy is ~1 kcal/mol

- ➡ **The target accuracy MUST be 99.9 to 99.99% of E_c to preserve the features of the methods**
- ➡ **Error cancellation in local approximations is NOT better than about 1 order of magnitude**

Principles of Local Correlation Theory

Pretty much all local correlation methods:

Approximation 1

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

Approximation 2

where „chunks“ =

Fragments, **Atoms**, **Atom Pairs**, **Orbitals**, **Orbital Pairs**, ..

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*

Decomposition of the Exact Correlation Energy

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

Insert the full CI expansion

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

Multiply with the HF function from the left:

$$\underbrace{\langle \Phi_{HF} \mid \hat{H}_{BO} \mid \Phi_{HF} \rangle}_{E_{HF}} + \sum_{ia} C_i^a \underbrace{\langle \Phi_{HF} \mid \hat{H}_{BO} \mid \Phi_i^a \rangle}_{F_{ia}} + \tfrac{1}{4} \sum_{ijab} C_{ij}^{ab} \underbrace{\langle \Phi_{HF} \mid \hat{H}_{BO} \mid \Phi_{ij}^{ab} \rangle}_{\langle ij||ab \rangle}$$

=0 (Brillouin)

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

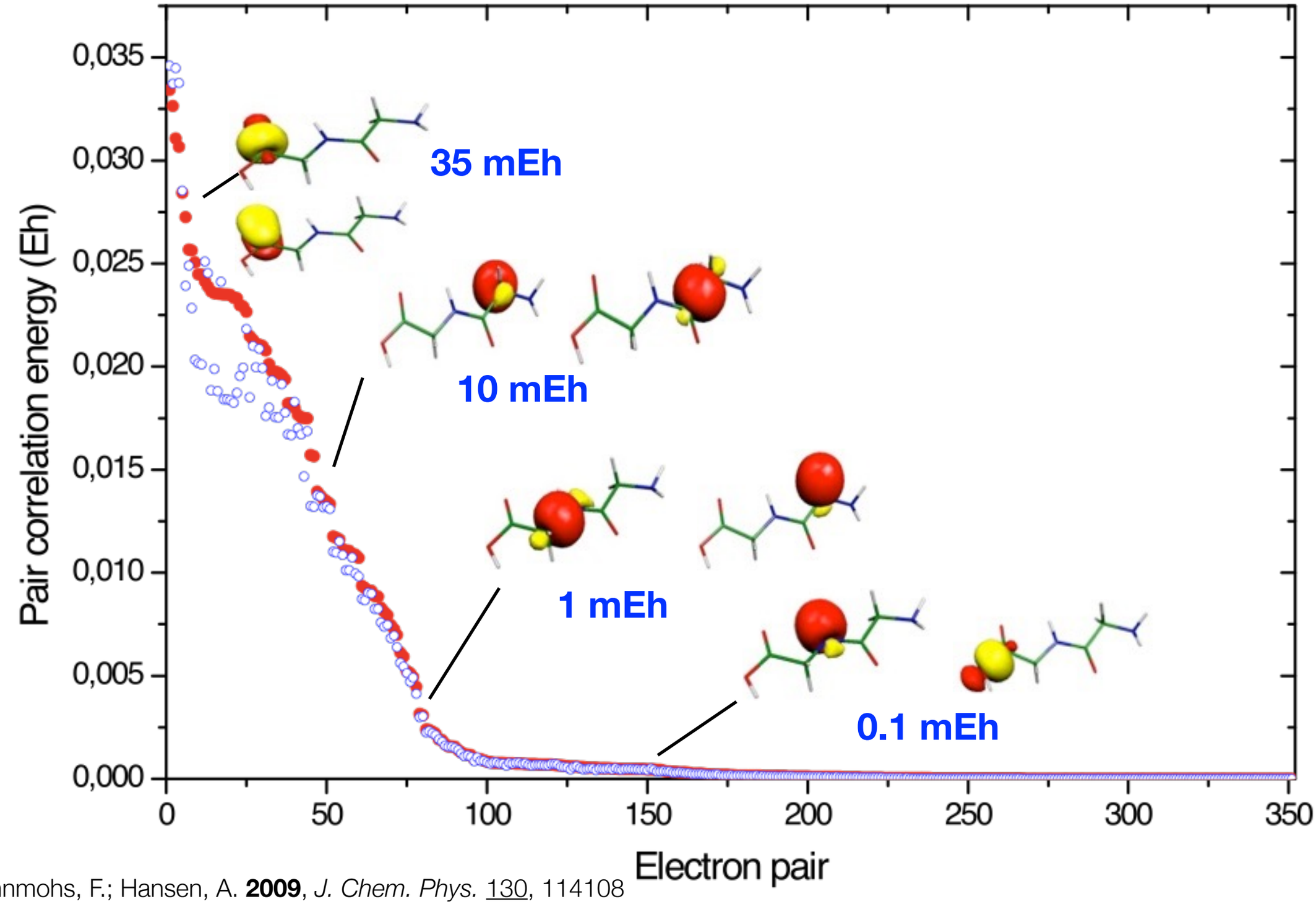
Thus:

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

(**Nesbet's theorem**)

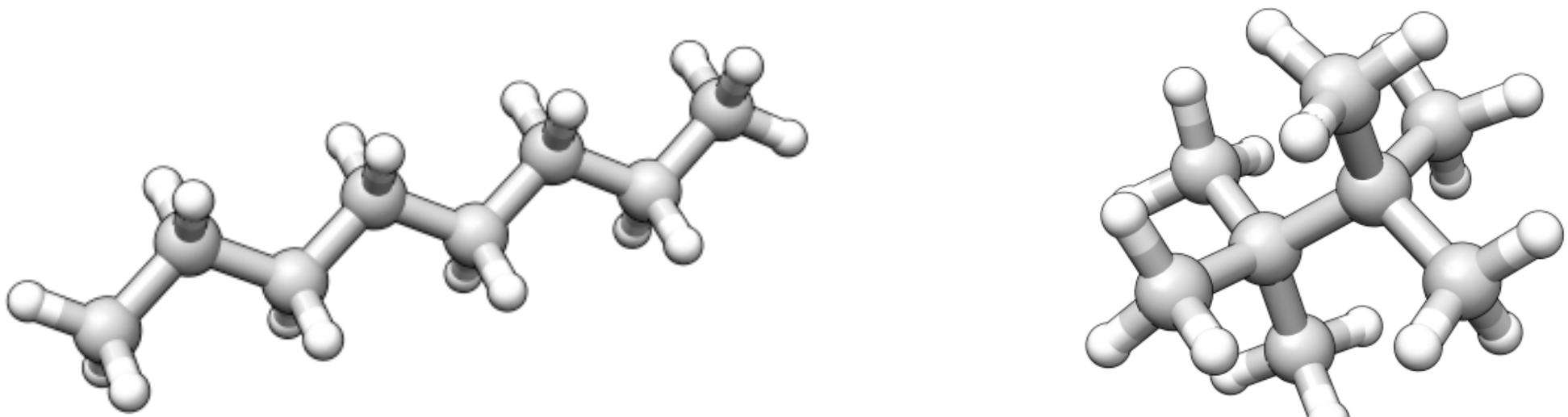
If we know the precise values of the double excitation coefficients we know the <u>EXACT</u> correlation energy! It is a sum of PAIR CORRELATION ENERGIES

Approximation 1: Locality of Pair Correlation Energies



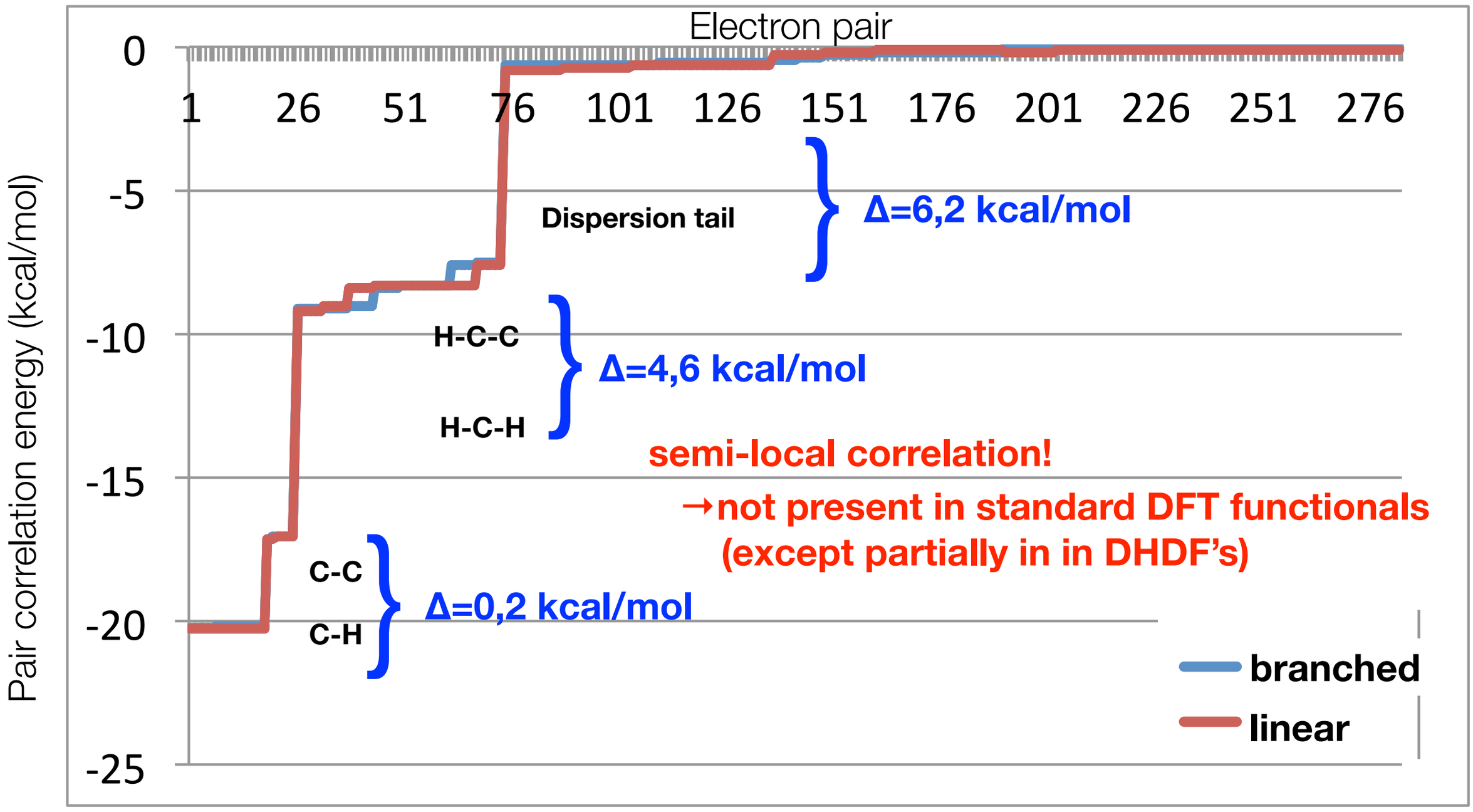
FN, Wennmohs, F.; Hansen, A. **2009**, *J. Chem. Phys.* 130, 114108

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



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

Local MP2 Theory

Orbital Invariant Reformulation of MP2 Theory

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

$$E^{(PT2)} = min\left[2\langle\Psi^{(0)}|\hat{H}|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|\hat{H}^{(0)} - E_0|\Psi^{(1)}\rangle\right]$$

it readily leads to an orbital invariant formulation of MP2

Full Hamiltonian: $\hat{H} = \hat{H}^{(0)} + \hat{V} \;\leftrightarrow\; \hat{V} = \hat{H} - \hat{H}^{(0)}$

0th order Hamiltonian: $\hat{H}^{(0)} = \hat{F}$

Fock operator: $\hat{F} = \hat{h} + \sum_j (jj|\,\boxdot\boxdot) - (j\,\boxdot\,|j\,\boxdot)$

that is a placeholder for an actual label
once the Fock operator acts on something

0th order wavefunction: $|\Psi^{(0)}\rangle = |\psi_0 \ldots \psi_i \ldots \psi_n|$

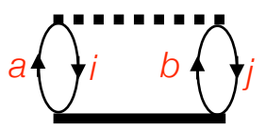
1st order wavefunction: $|\Psi^{(1)}\rangle = \frac{1}{4}\sum_{ijab} t_{ab}^{ij}|\Phi_{ij}^{ab}\rangle$

Brillouin Theorem: $\langle a|\hat{F}|i\rangle = \langle\Psi^{(0)}|\hat{H}|\Phi_i^a\rangle = 0$

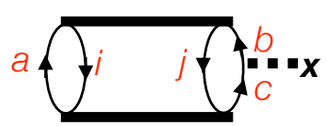
P. Pulay, and S. Saebø, *Theor. Chim. Acta* 69, 357 (**1986**).

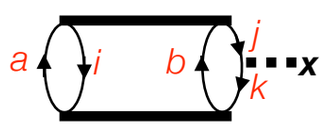
Evaluation of the Hylleraas Functional

$$\langle \Psi^{(0)} | \hat{H} | \Psi^{(1)} \rangle = \frac{1}{4} \sum_{ijab} t_{ab}^{ij} \langle ij||ab \rangle$$



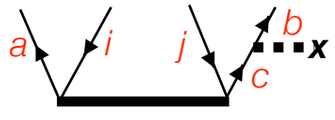
$$\langle \Psi^{(1)} | \hat{H}^{(0)} - E_0 | \Psi^{(1)} \rangle = \frac{1}{8} P_{a/b}^{+} \sum_{ijabc} t_{ab}^{ij} F_{bc} t_{ac}^{ij} - \frac{1}{8} P_{i/j}^{+} \sum_{ijkab} t_{ab}^{ij} F_{jk} t_{ab}^{ik}$$

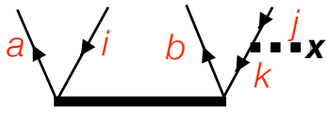




Minimize with respect to the amplitudes:

$$\mathrm{R}_{ab}^{ij} = \langle ij||ab \rangle + \sum_{c} \left(t_{ac}^{ij} F_{cb} + F_{ac} t_{cb}^{ij} \right) - \sum_{k} \left(t_{ab}^{ik} F_{kj} + F_{ik} t_{ab}^{kj} \right) = 0$$





Check the canonical case: $F_{pq} = \delta_{pq} \varepsilon_p \qquad \Delta_{ab}^{ij} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$

$$t_{ab}^{ij} = -\frac{\langle ij||ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \quad \checkmark \qquad E^{(PT2)} = -\frac{1}{4} \sum_{ijab} \frac{\langle ij||ab \rangle \langle ij||ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \quad \checkmark$$

Solving the Hylleraas-MP2 Linear Equations

For a non-diagonal Fock matrix we really have to solve the linear equations. It must be done iteratively due to the large number of doubles amplitudes.

The key step is the evaluation of the residual:

$$\mathrm{R}_{ab}^{ij} = \langle ij||ab\rangle + \sum_{c}\left(t_{ac}^{ij}F_{cb} + F_{ac}t_{cb}^{ij}\right) - \sum_{k}\left(t_{ab}^{ik}F_{kj} + F_{ik}t_{ab}^{kj}\right)$$

For trial amplitudes **t**. From this we can update the amplitudes for the next iteration

$$t_{ab}^{ij} \rightarrow t_{ab}^{ij} - \mathrm{R}_{ij}^{ab}/\Delta_{ab}^{ij}$$

This usually converges in about 10'ish iterations.

- ➡ Convergence accelerators (DIIS, Pople, Conjugate gradient, ...) usually applied
- ➡ NOTE: NO approximation here. This gives the exact MP2 energy!

Introducing Local Approximations

The next step is to introduce the local approximations one after the other.

➡ Organize everything in terms of electron pairs:

$$\langle ij||ab\rangle = \left(\boldsymbol{K}^{ij}\right)_{ab} - \left(\boldsymbol{K}^{ij}\right)_{ba}$$

$$\mathrm{R}_{ab}^{ij} \rightarrow \left(\boldsymbol{R}^{ij}\right)_{ab}$$

Process electrons pairs sequentially and separately

$$\mathbf{R}^{ij} = \mathbf{K}^{ij} - \mathbf{K}^{ji} + \boldsymbol{t}^{ij}\overline{\boldsymbol{F}} + \overline{\boldsymbol{F}}\boldsymbol{t}^{ij} - \sum_{k}\left(\boldsymbol{t}^{ik}F_{kj} + F_{ik}\boldsymbol{t}^{kj}\right)$$

Approximation 1: Eliminate negligible electron pairs to go from O(N^2) or O(N) pairs

➡ Some schemes use the value of $|F_{ij}|$ to eliminate ij pairs. This is not rigorous.

➡ Better: Use a multipole expansion to estimate pair correlation energies

The Leading Term of Electron Correlation

$$\varepsilon_{ij}^{MP2} = -\sum_{ab} \frac{\overbrace{4(ia \mid jb)(ia \mid jb)}^{\textbf{Coulomb}} - \overbrace{2(ia \mid jb)(ib \mid ja)}^{\textbf{Exchange}}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

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*)

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

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:

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

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

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**

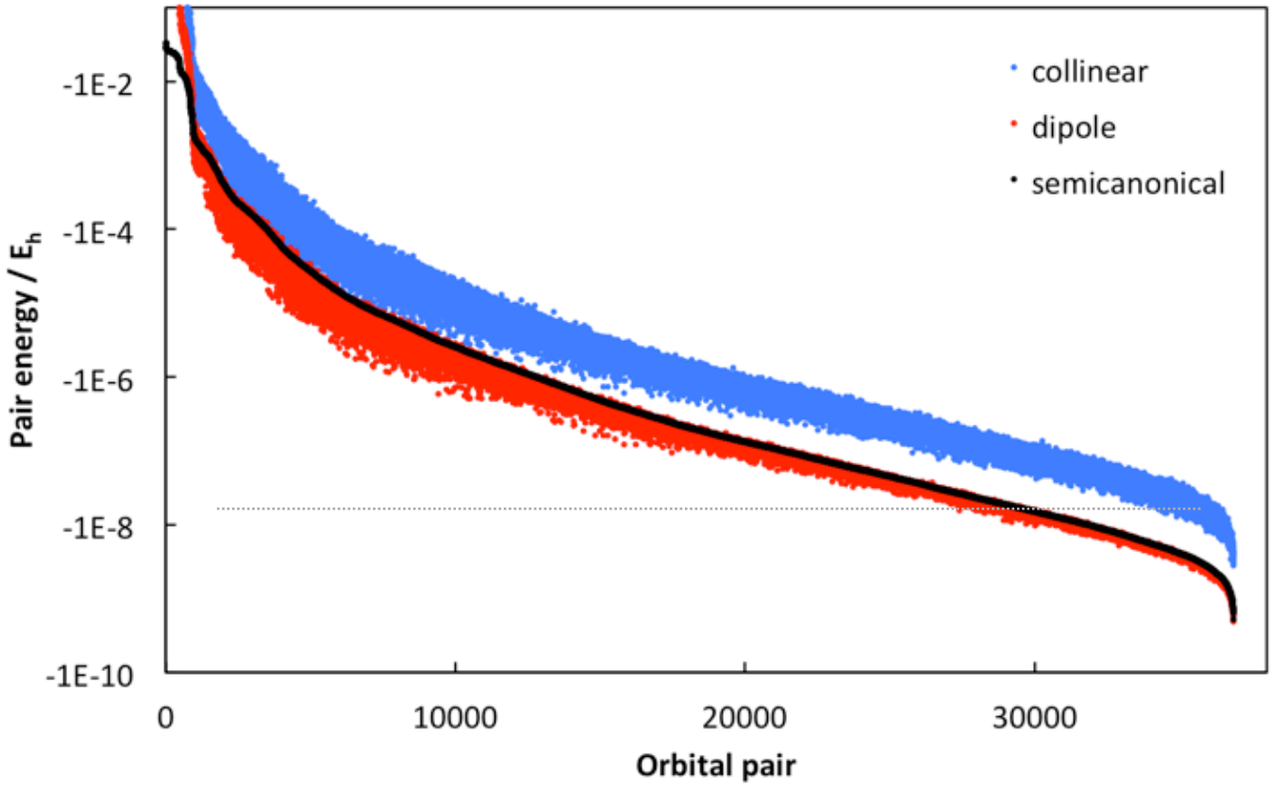
$$(ia \mid jb) \propto R^{-3} \quad \Rightarrow \varepsilon^{SC-MP2}_{ij} \propto R^{-6}$$

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

Multipole Based Pair Prescreening

Dipole approximation to the pair-correlation energy: $\boldsymbol{R}_i = \langle i|\boldsymbol{r}|i\rangle \qquad \boldsymbol{R}_{ij} = \boldsymbol{R}_j - \boldsymbol{R}_j$

$$\varepsilon_{ij}^{(DIP)} = -\frac{4}{R_{ij}^6}\sum_{ab}\frac{\left[\langle i|\boldsymbol{r}|a\rangle\langle j|\boldsymbol{r}|b\rangle - 3\big(\langle i|\boldsymbol{r}|a\rangle\boldsymbol{R}_{ij}\big)\big(\langle j|\boldsymbol{r}|b\rangle\boldsymbol{R}_{ij}\big)\right]^2}{\varepsilon_a + \varepsilon_b - F_{ii} - F_{jj}}$$



- Drop pairs below a (conservative) selection threshold→linear scaling (ij)
- Correction for dropped pairs

$$\Delta E_{\mathrm{Pre}} = \sum_{ij(dropped)} \varepsilon_{ij}^{DIP}$$

(this is actually very small relative to the residual error of the method)

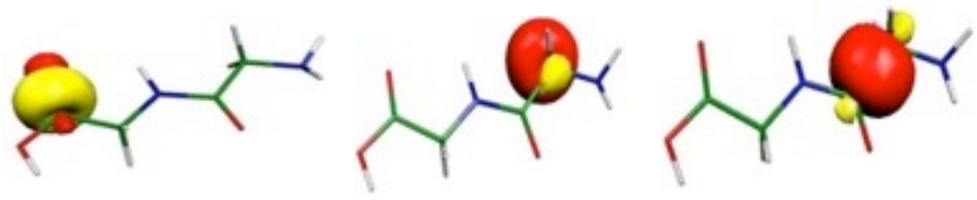
Hetzer, G.; Pulay, P.; Werner, HJ *Chem. Phys. Lett.*, **1998**, 290, 143

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

Local Excitation Spaces

Approximation 2: Local Excitation Spaces

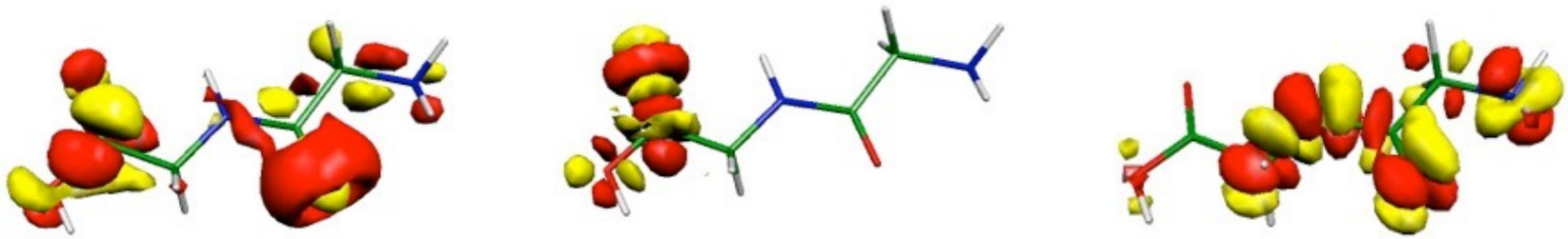
✓ The **occupied (internal) orbitals** localize nicely (mostly, that is)



➡ *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

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

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

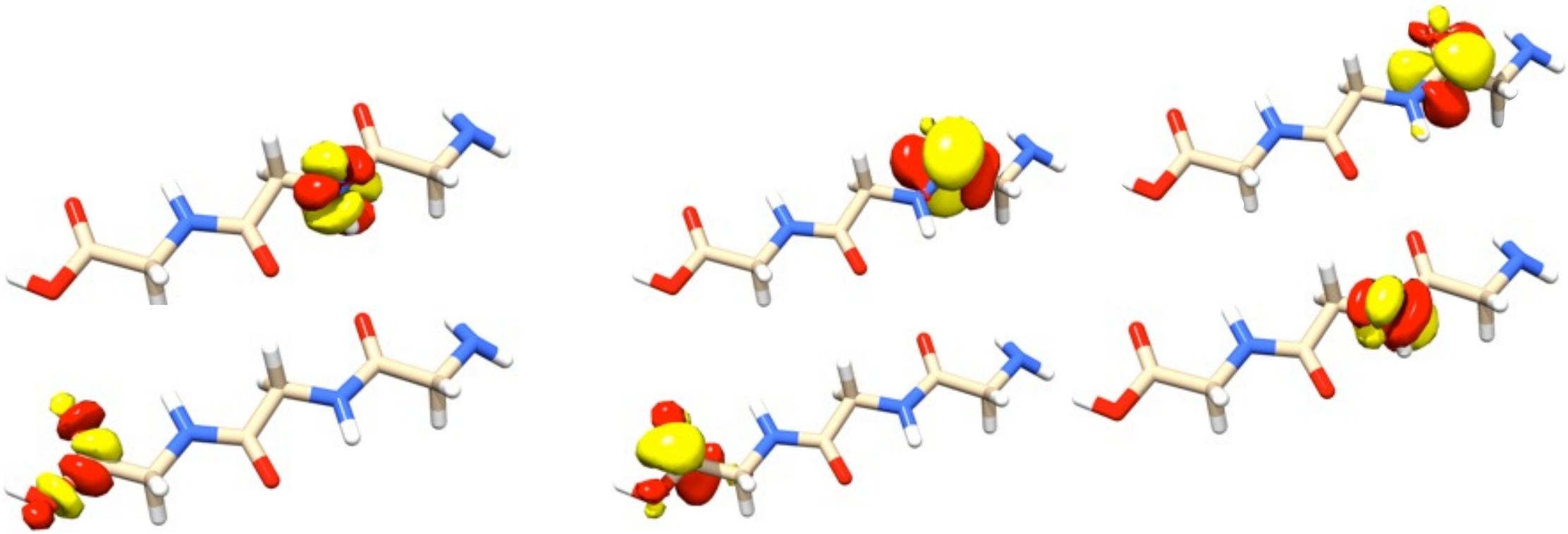
BUT: Standard localization schemes do not work well (but see Jörgensen et al)

- 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

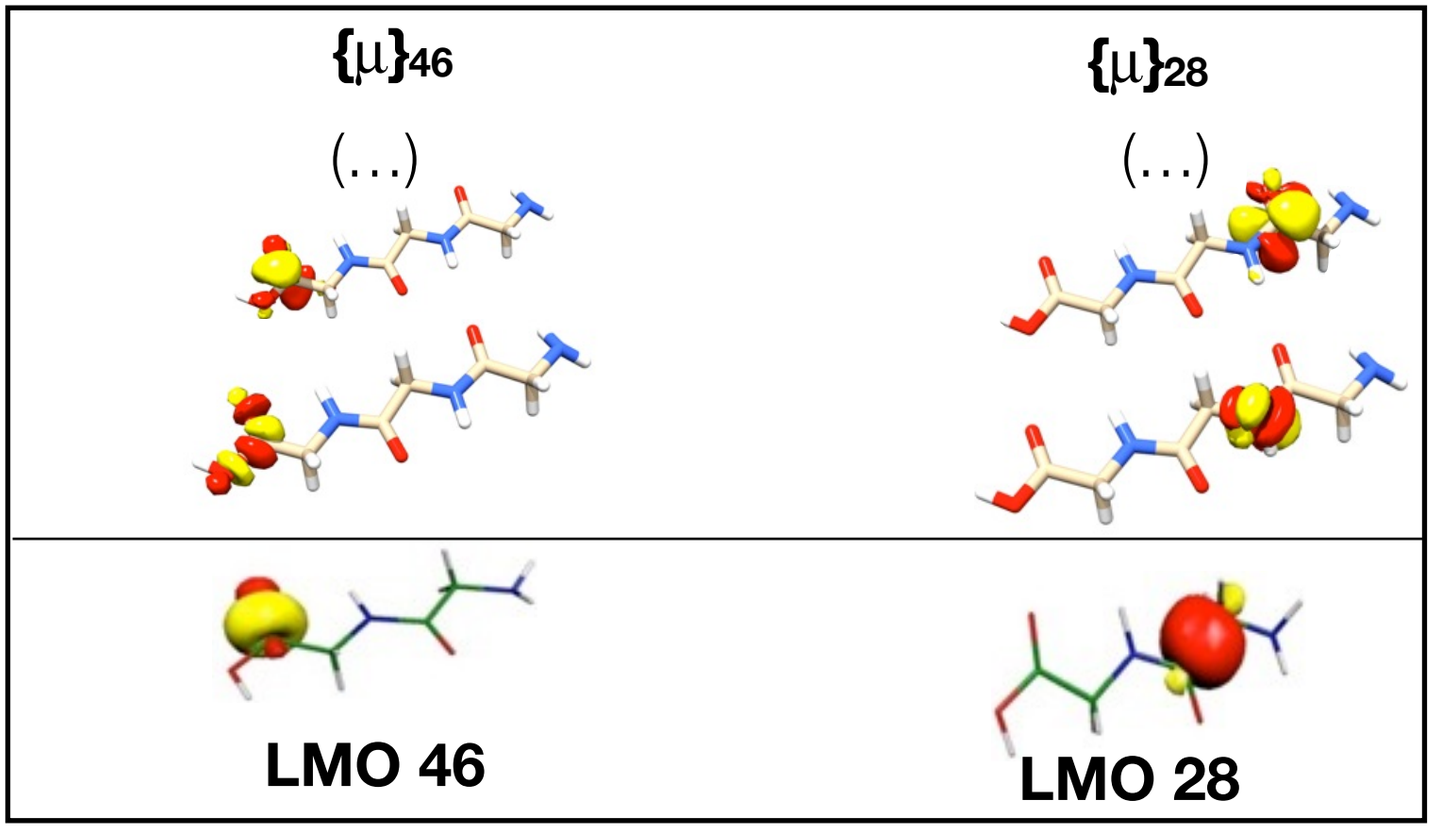
$$\left|\tilde{\mu}\right\rangle = (1 - \sum\nolimits_i \left|i\right\rangle\left\langle i\right|)\left|\mu\right\rangle$$

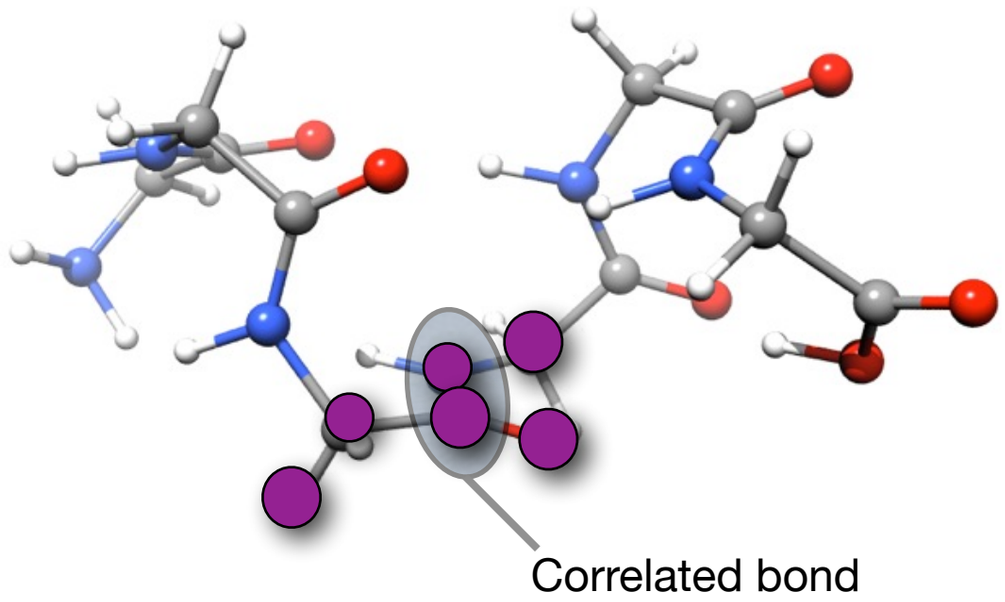


- PAO’s are local close to the ‚parent‘ atom (but have significant tails)
- PAO’s span the virtual space and are orthogonal to the occupied space
- PAO’s are non-orthogonal and linearly dependent

PAO's, Domains and Pair Domains

A **domain** $\{\mu\}_i$ is a set of PAOs chosen for a given internal LMO according to some prescription





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

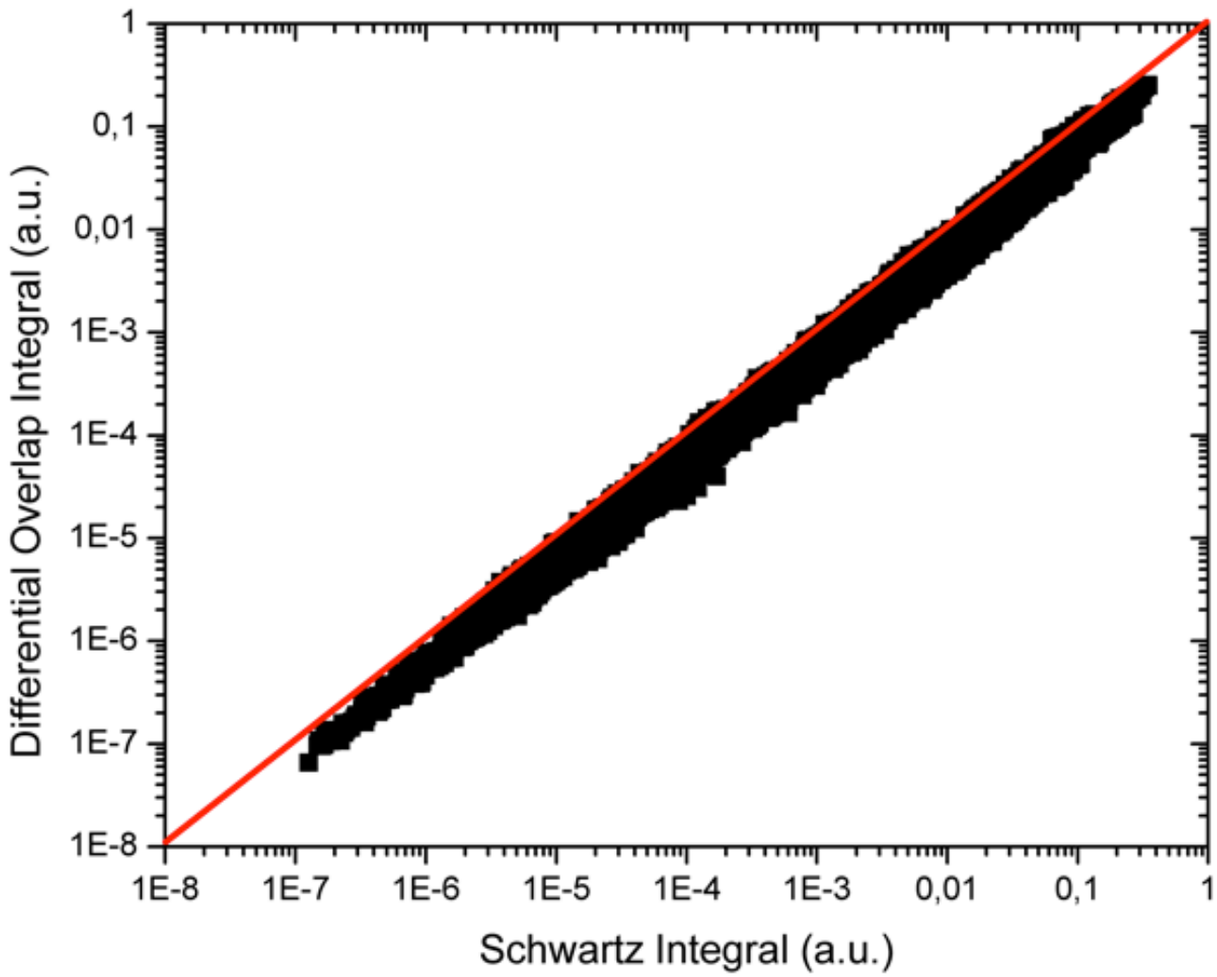
A **pair domain** $\{\mu\}_{ij}$ is the union of the individual orbital domains

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

Domain Construction

Our proposal: ***Differential Overlap Integral***

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



✓ PAOs that have a DOI above threshold with the LMO in question are added to the domain (then atom completed)

- Actual spatial extent of the virtual space is taken into account
- Excellent approximation to the the Schwartz screening integrals
- Easy to compute efficiently in linear scaling for any set of functions

Pinski, P.; Riplinger, C.; Valeev, E. F.; Neese, F. *J. Chem. Phys.* **2015**, *143*.

Using Local Excitation Spaces into MP2

Next we need to insert the local excitation spaces into the residual:

$$\mathrm{R}_{ab}^{ij} = \langle ij||ab\rangle + \sum_{c}\left(t_{ac}^{ij}F_{cb} + F_{ac}t_{cb}^{ij}\right) - \sum_{k}\left(t_{ab}^{ik}F_{kj} + F_{ik}t_{ab}^{kj}\right)$$

Hence: $t_{ab}^{ij} \rightarrow t_{\tilde{\mu}\tilde{\nu}}^{ij} \qquad \left(\boldsymbol{K}^{ij}\right)_{ab} \rightarrow \left(\boldsymbol{K}^{ij}\right)_{\tilde{\mu}\tilde{\nu}} \qquad F_{ab} \rightarrow F_{\tilde{\mu}\tilde{\nu}}$

PROBLEMS:

- The PAO's are not orthogonal
- The local excitation spaces have different dimensions

$$\mathbf{R}^{ij} = \mathbf{K}^{ij} - \mathbf{K}^{ji} + \boldsymbol{t}^{ij}\overline{\boldsymbol{F}}\tilde{\boldsymbol{S}}^{(ij,ij)} + \tilde{\boldsymbol{S}}^{(ij,ij)}\overline{\boldsymbol{F}}\boldsymbol{t}^{ij} - \sum_{k}\left(\tilde{\boldsymbol{S}}^{(ij,ik)}\boldsymbol{t}^{ik}\tilde{\boldsymbol{S}}^{(ik,ij)}F_{kj} + F_{ik}\tilde{\boldsymbol{S}}^{(ij,ikj)}\boldsymbol{t}^{kj}\tilde{\boldsymbol{S}}^{(kj,ij)}\right)$$

Overlap Projector: $\left(\tilde{\boldsymbol{S}}^{(ij,kl)}\right)_{\tilde{\mu}\tilde{\nu}} = \langle\tilde{\mu}_{\in\{ij\}}|\tilde{\nu}_{\in\{kl\}}\rangle$

Some Notes

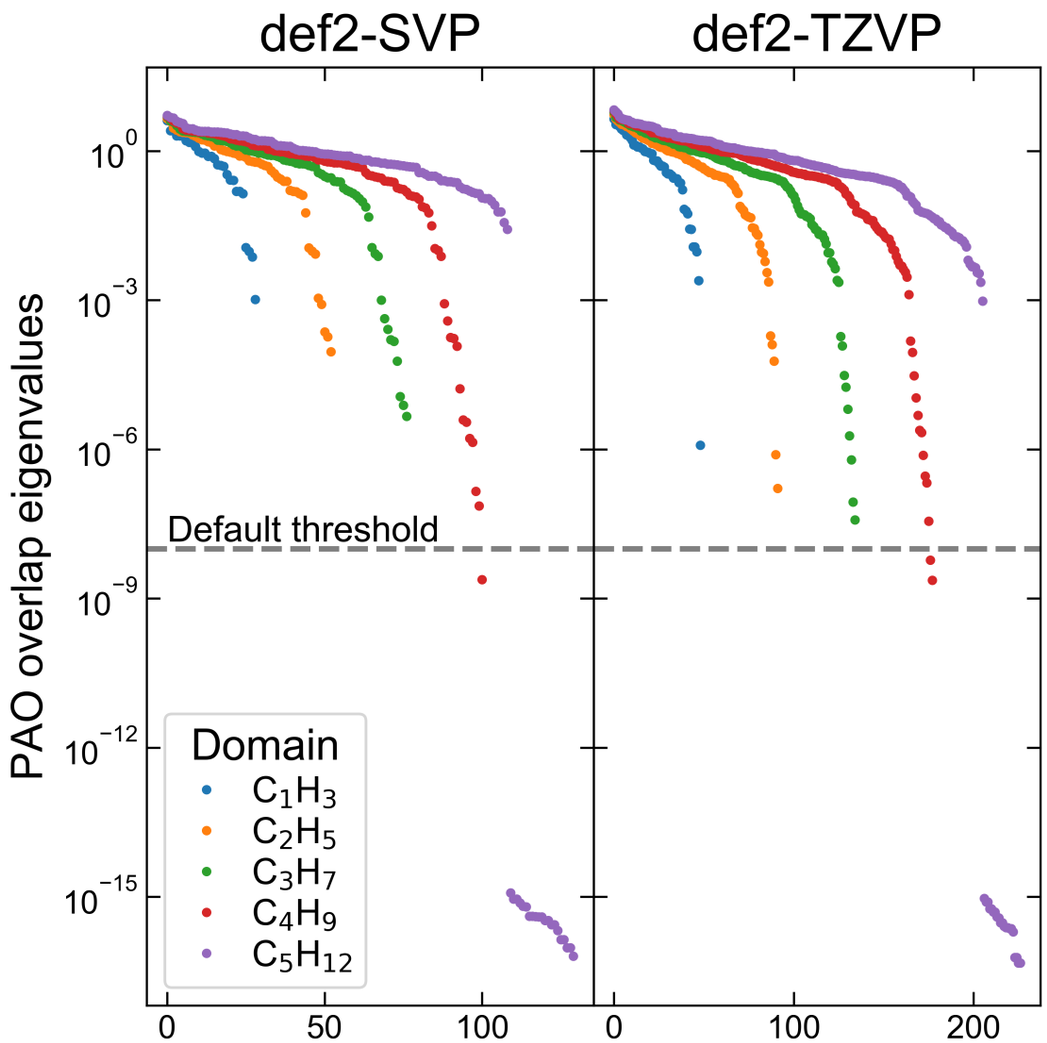
- ✓ The overlap projector takes care of the non-orthogonality of the PAO's.
- ✓ If no pairs are dropped and all PAO's are in all pair domains, the equations are still exact

- ✓ The full PAO overlap matrix is linearly dependent by construction
- ✓ Local Overlap projectors MAY be linearly dependent.
- ➡ Linear dependencies MUST be removed

Properties of the PAO's in Domains

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

- Not normalized
- Guaranteed to be linearly dependent (spans the virtual space only and has full AO dimension)
- Somewhat local



$\left\{\tilde{\mu}_i\right\}$

- Now normalized but still not orthogonal and linearly dependent
- Diagonalize PAO overlap in a given domain and discard eigenvectors to eigenvalues $<10^{-8}$ (smallest possible to retain numerical stability)
- Diagonalize the Fock operator in the non-redundant space to get to normalized, non-redundant, quasi-canonical PAO's

Linear Scaling Local MP2 Theory

Using the domains, the residual becomes

$$\mathbf{R}^{ij} = \mathbf{K}^{ij} - \mathbf{K}^{ji} + \boldsymbol{t}^{ij}\overline{\boldsymbol{F}}\tilde{\boldsymbol{S}}^{(ij,ij)} + \tilde{\boldsymbol{S}}^{(ij,ij)}\overline{\boldsymbol{F}}\boldsymbol{t}^{ij} - \sum_{k}\left(\tilde{\boldsymbol{S}}^{(ij,ik)}\boldsymbol{t}^{ik}\tilde{\boldsymbol{S}}^{(ik,ij)}F_{kj} + F_{ik}\tilde{\boldsymbol{S}}^{(ij,ikj)}\boldsymbol{t}^{kj}\tilde{\boldsymbol{S}}^{(kj,ij)}\tilde{\boldsymbol{S}}\right)$$

Where all matrices are now local (size of order O(1)):

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

- ✓ Sub-matrices can either be stored or constructed on the fly
- ✓ All matrix multiplications are order O(1)

Linear scaling

1. **Discard weakly interacting electron pairs:**

   Pair pre-screening → linear scaling number of pairs ij

2. **Discard small terms in the sum over k** by analyzing f_{ik}, f_{jk}

   Threshold F_{Cut}~10^{-5} Eh

Volume 100, number 2 CHEMICAL PHYSICS LETTERS 2 September 1983

LOCALIZABILITY OF DYNAMIC ELECTRON CORRELATION

Peter PULAY
Department of Chemistry, University of Arkansas, Fayetteville, Arizona 72701, USA

Volume 113, number 1 CHEMICAL PHYSICS LETTERS 4 January 1985

LOCAL CONFIGURATION INTERACTION: AN EFFICIENT APPROACH FOR LARGER MOLECULES

Svein SÆBØ and Peter PULAY
Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA

Received 22 October 1984; in final form 7 November 1984

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)]

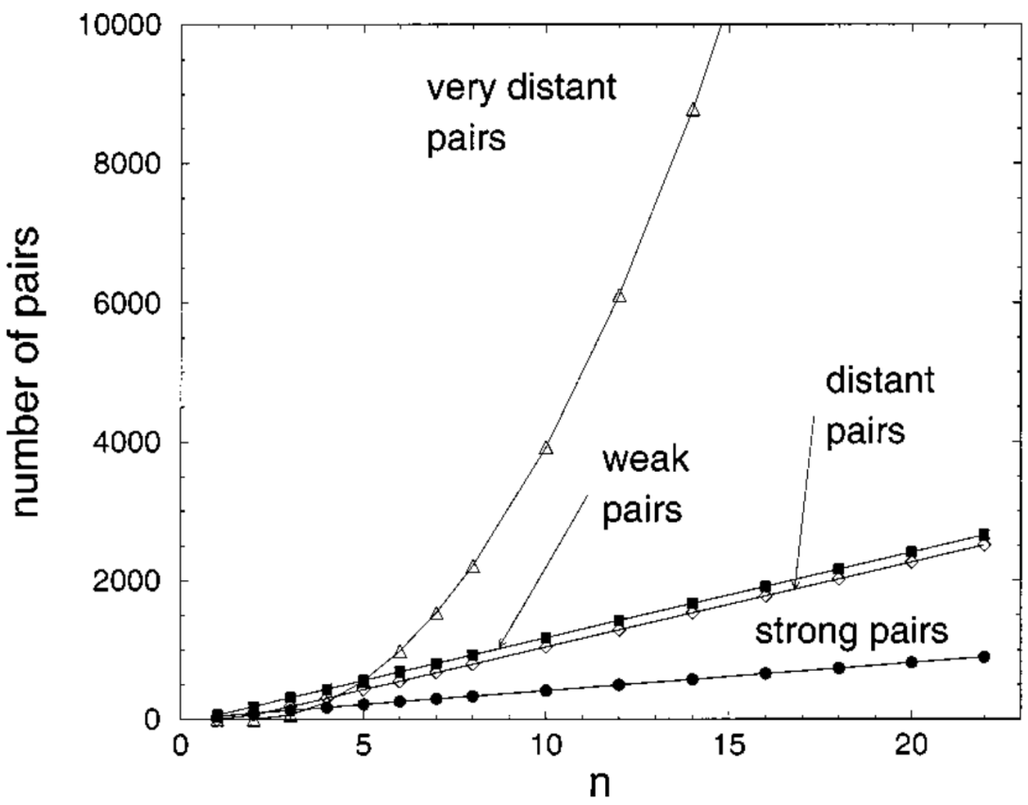


FIG. 1. The number of strong, weak, distant and very distant pairs as a function of the size n of a polyglycine peptide chain $[\mathrm{gly}]_n$. The number of strong, weak, and distant pairs all scale linearly with the molecular size, whereas the number of very distant pairs scales quadratically with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

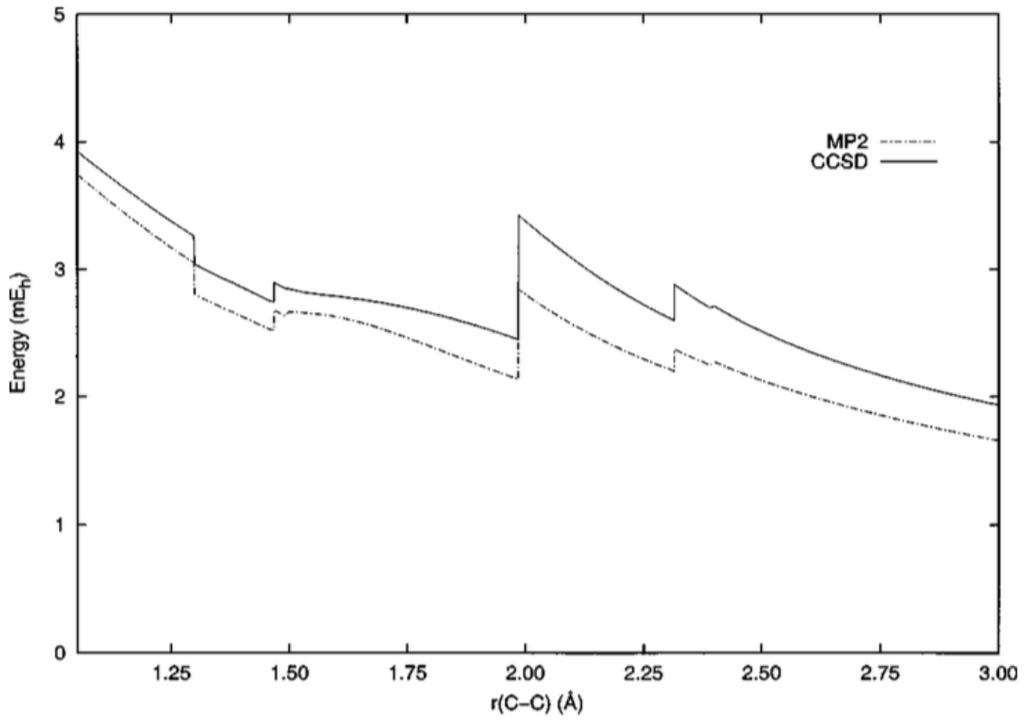


FIG. 7. LMP2 and LCCSD localization errors (in mE_h) for singlet ketene dissociation, where the four discontinuities discussed in the text are clearly visible.

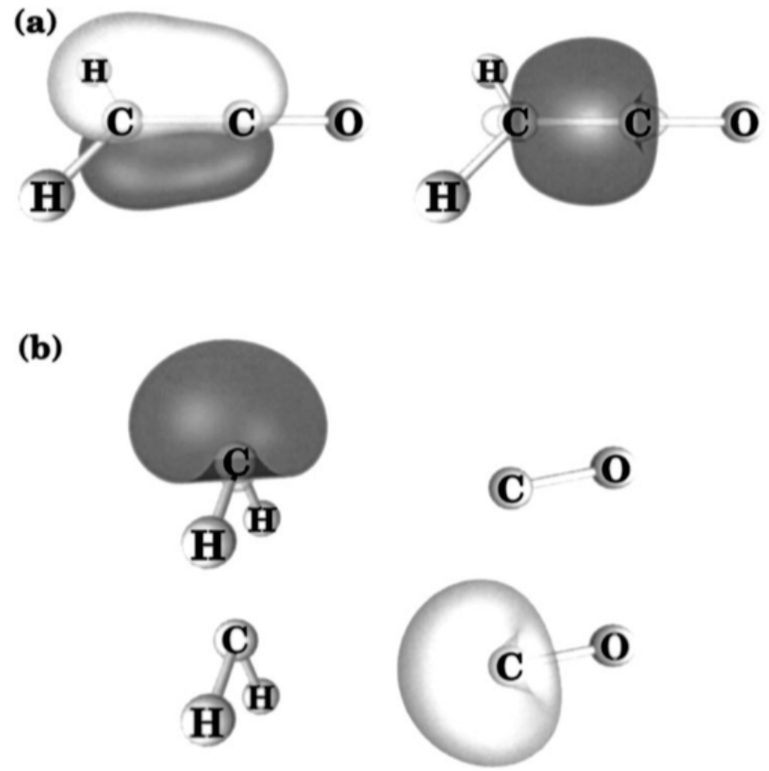


FIG. 8. Contour plots of the relevant Pipek–Mezey localized orbitals for singlet ketene: (a) The π and σ bonding orbitals near the equilibrium geometry and (b) the corresponding lone-pair dissociated MOs of singlet methylene and carbon monoxide.

- 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)]

Early PAO based LMP2: Accuracy

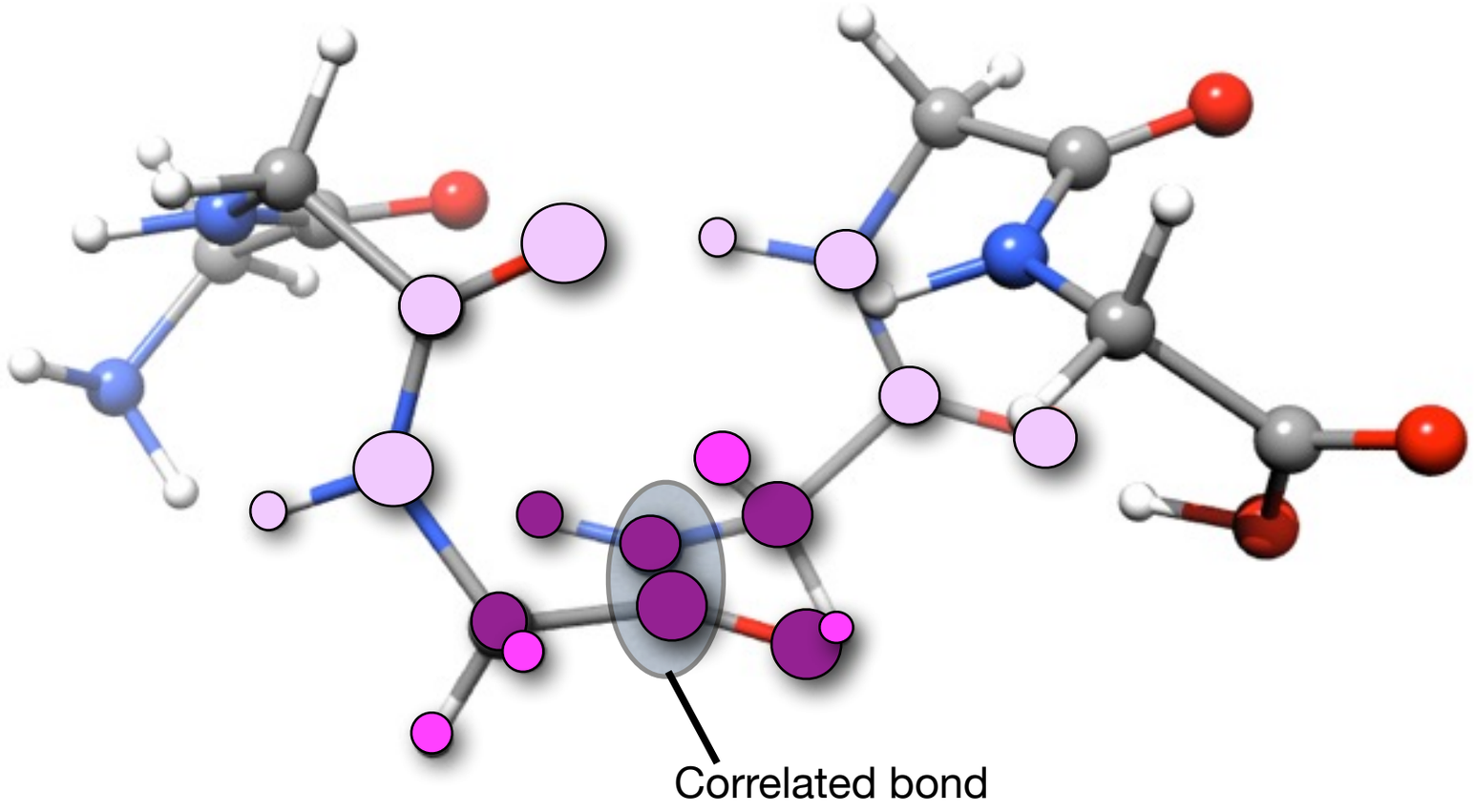
A new implementation of local second-order Møller-Plesset perturbation theory (LMP2) is presented for which asymptotically all computational resources (CPU, memory, and disk) scale only linearly with the molecular size. This is achieved by (i) using orbital domains for each electron pair that are independent of molecular size; (ii) classifying the pairs according to a distance criterion and neglecting very distant pairs; (iii) treating distant pairs by a multipole approximation, and (iv) using efficient prescreening algorithms in the integral transformation. The errors caused by the various approximations are negligible. LMP2 calculations on molecules including up to 500 correlated electrons and over 1500 basis functions in C_1 symmetry are reported, all carried out on a single low-cost personal computer. [S0021-9606(99)32037-7]

physically justified neglect of configurations. The effect of these truncations on absolute and relative energies, potential energy curves of weakly interacting systems, equilibrium geometries, and harmonic vibrational frequencies is well-known and well-documented.[10,15,17,24] Typically, the loss of correlation energy relative to the corresponding nonlocal wave function amounts to about 1.5%–2% for a double-zeta (cc-pVDZ) basis set and 0.5% for a triple zeta (cc-pVTZ) basis set. This is usually negligible compared to the basis set

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 (e.g. 99.9%) result?

How Large do Domains have to be?



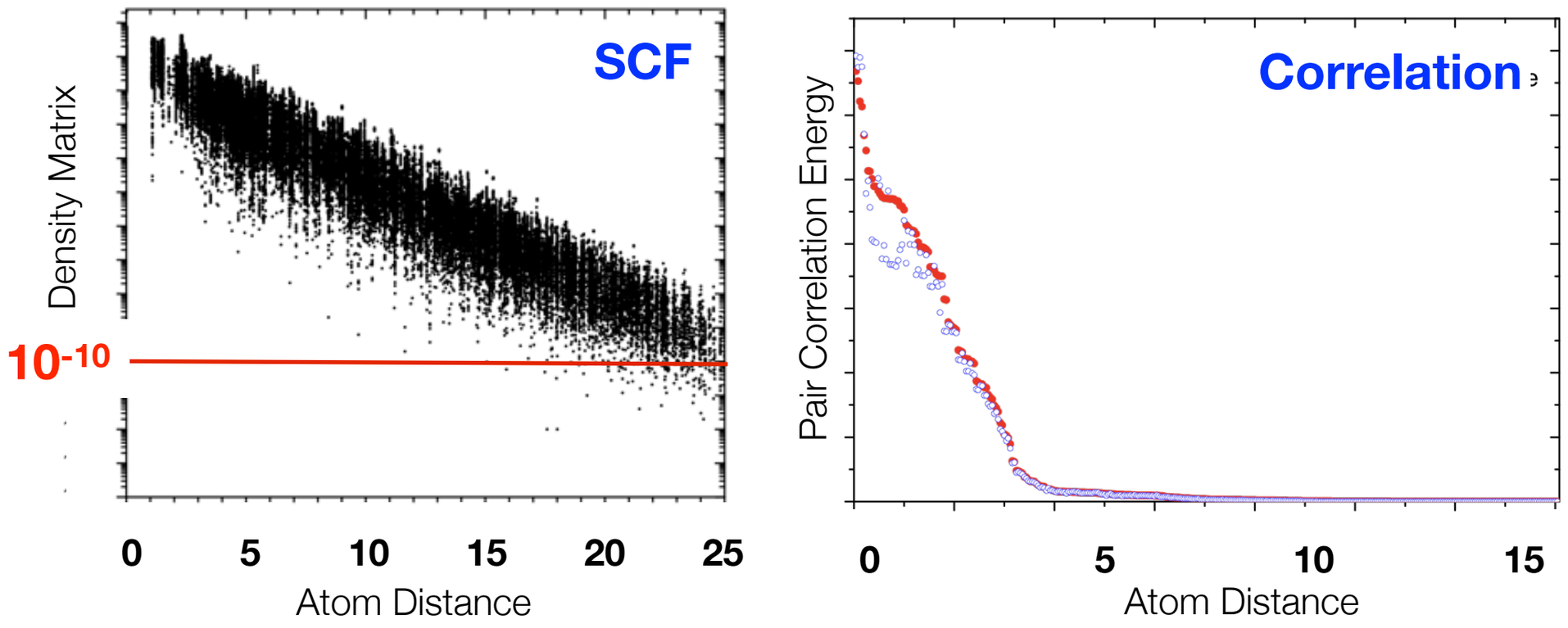
T_{DO}=0.1	98.4% E_{corr}	N^{av}_{PAO}=115
T_{DO}=0.01	99.7% E_{corr}	N^{av}_{PAO}=588
T_{DO}=0.001	99.9% E_{corr}	N^{av}_{PAO}=935

- 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!

$$M = \begin{pmatrix} & \\ & \end{pmatrix} \quad \mathbf{M' = U^\dagger M U} \Rightarrow \quad M' = \begin{pmatrix} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}$$

Natural Orbitals

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*

PER-OLOV LÖWDIN
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, and Institute of Mechanics and Mathematical Physics, Uppsala University, Uppsala, Sweden
(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 $\mathbf{U}$ which transforms this matrix to diagonal form with the eigenvalues $n_{kk}=n_k$:

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

We have further, in matrix form, $\boldsymbol{\gamma}=\mathbf{U}\mathbf{n}\mathbf{U}^\dagger$, and, if we introduce a new set of spin-orbitals χ_k by the matrix relation $\boldsymbol{\chi}=\boldsymbol{\psi}\mathbf{U}$, 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 $\boldsymbol{\gamma}^2=\boldsymbol{\gamma}$ 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

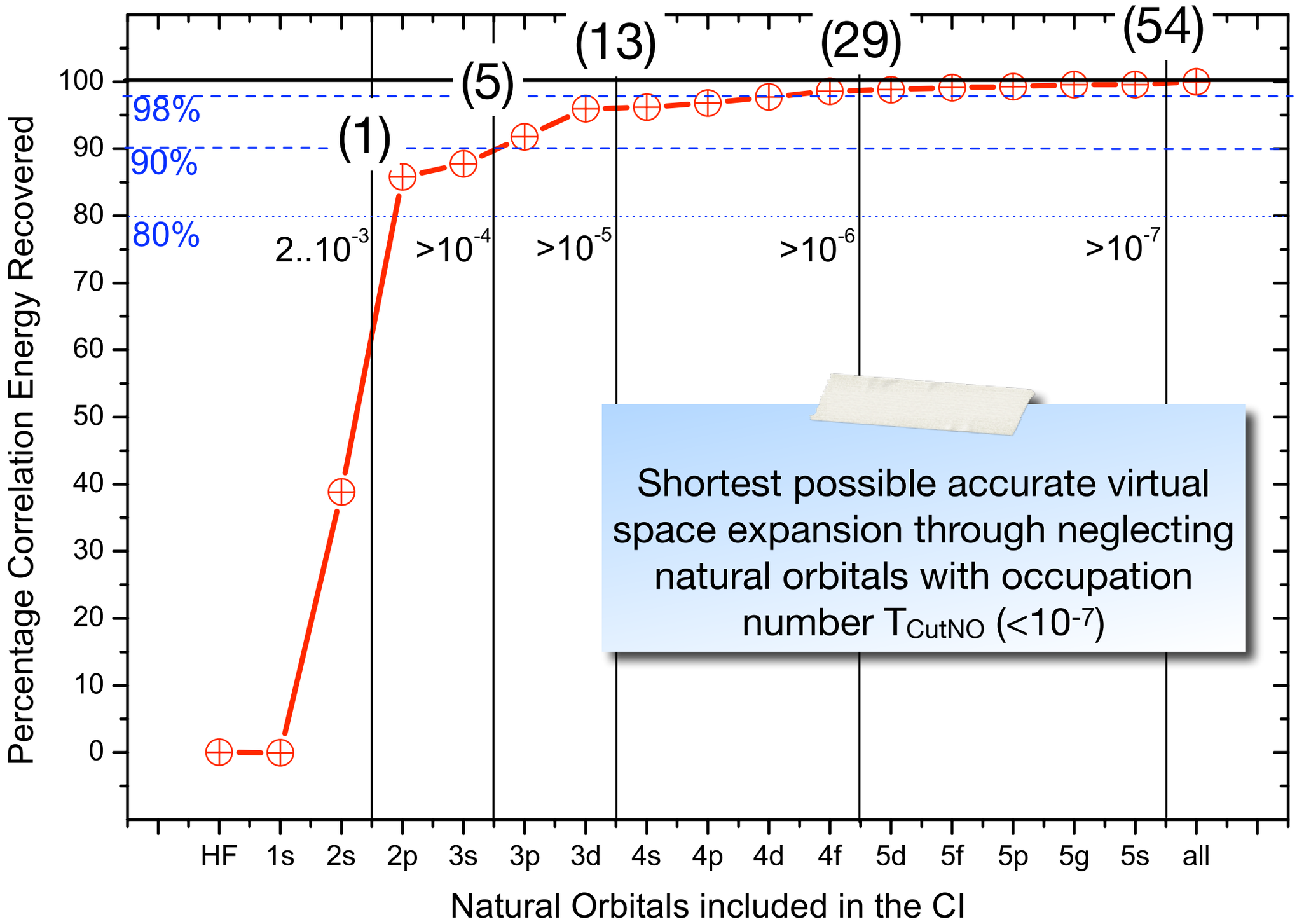
$$\Sigma_k\gamma_k^2=\Sigma_k n_k^2-\sum_{l\neq k}|\gamma_{kl}|^2\leq\Sigma_k n_k^2,$$

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.

The Natural Expansion of He



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^+

C. EDMISTON*
University of Wyoming, Laramie, Wyoming
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.

Early Applications of Pair Natural Orbitals

INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY, NO. 5. 341–348 (1971)

Ionization Energies of Water from PNO–CI Calculations

WILFRIED MEYER
Institut für Theoretische Physikalische Chemie, Universitäet Stuttgart, Germany

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 58, NUMBER 3 1 FEBRUARY 1973

PNO–CI Studies of electron correlation effects. I. Configuration expansion by means of nonorthogonal orbitals, and application to the ground state and ionized states of methane

Wilfried Meyer

Pair Natural Orbitals and the Virtual Space

✓ Exact density $$\mathrm{D}_{\mathrm{ab}} = \sum_{\mathrm{P}\equiv\mathrm{ij}} \mathrm{D}^{(\mathrm{P})}_{\mathrm{ab}}$$

a,b= canonical virtual orbitals

$\mathrm{P} \equiv (\mathrm{ij})$ Pair label

✓ Diagonalize each pair density individually

$$\mathbf{D}^{(\mathrm{P})}\mathbf{d}^{(\mathrm{P})} = \mathbf{n}^{(\mathrm{P})}\mathbf{d}^{(\mathrm{P})}$$

✓ PNO expansion $$\left|\tilde{\mathrm{a}}_{\mathrm{P}}\right\rangle = \sum_{\mathrm{a}} \mathrm{d}^{(\mathrm{P})}_{\mathrm{a}\tilde{\mathrm{a}}_{\mathrm{P}}} \left|\mathrm{a}\right\rangle$$ (exact without truncation)

- PNOs are orthogonal to all occupied orbitals
- PNOs of a given pair are orthonormal
- PNOs of different pairs are not orthogonal

$$\left\langle \tilde{\mathrm{a}}_{\mathrm{P}} \mid \tilde{\mathrm{b}}_{\mathrm{Q}} \right\rangle \equiv \mathrm{S}^{(\mathrm{P},\mathrm{Q})}_{\tilde{\mathrm{a}}_{\mathrm{P}},\tilde{\mathrm{b}}_{\mathrm{Q}}} = \sum_{\mathrm{ab}} \mathrm{d}^{\mathrm{P}}_{\mathrm{a}\tilde{\mathrm{a}}_{\mathrm{P}}} \mathrm{d}^{\mathrm{Q}}_{\mathrm{b}\tilde{\mathrm{b}}_{\mathrm{Q}}} \underbrace{\left\langle \mathrm{a} \mid \mathrm{b} \right\rangle}_{\delta_{\mathrm{ab}}} = (\mathbf{d}^{\mathrm{P}})^{\mathrm{T}}\mathbf{d}^{\mathrm{Q}}$$

- PNOs based on local occupied orbitals are also local

Pair Natural Orbitals and the Virtual Space

✓ Truncation according to $\mathrm{n}_{\mathrm{a}}^{\mathrm{P}} < \mathrm{T}_{\mathrm{CutPNO}}$

- Asymptotically constant number of PNOs per pair
- Minimal error for a given expansion length

✓ Estimate of PNO error: $\Delta \mathrm{E}_{\mathrm{PNO}} = \sum_{\mathrm{P}} \varepsilon_{\mathrm{P}}^{(\mathrm{full})} - \varepsilon_{\mathrm{P}}^{(\mathrm{selected})}$

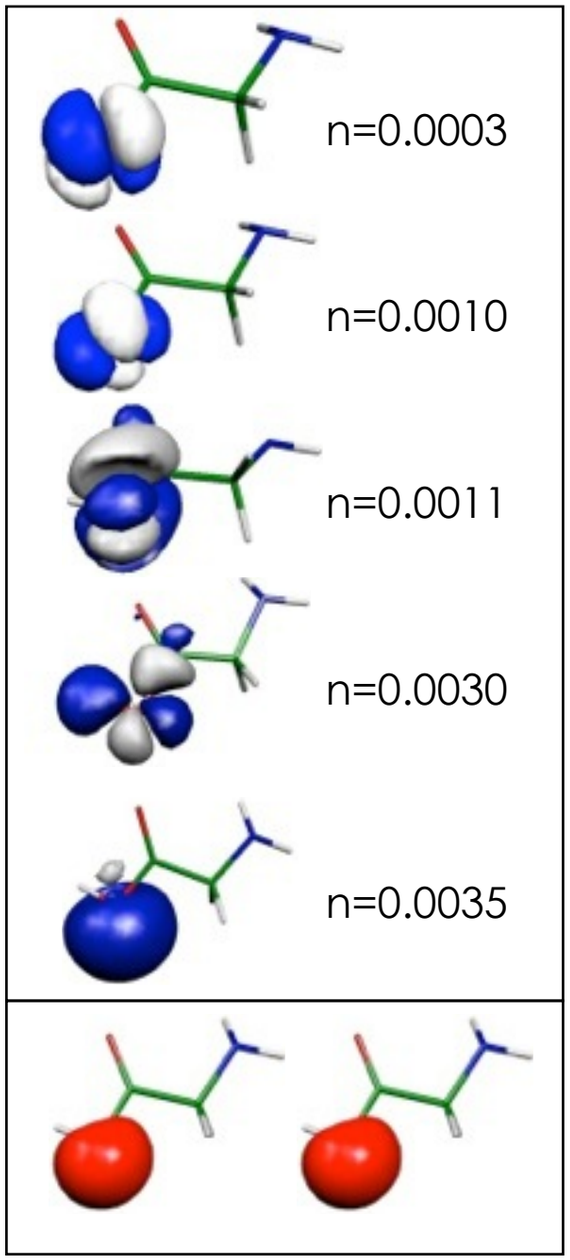
✓ After truncation, try to expand the PNOs of one pair in terms of another pair PNOs:

$$\left|\mathrm{a}_{\mathrm{P}}\right\rangle \approx \sum_{\mathrm{b}_{\mathrm{Q}}} \mathrm{c}_{\mathrm{b}_{\mathrm{Q}}\mathrm{a}_{\mathrm{P}}} \left|\mathrm{b}_{\mathrm{Q}}\right\rangle$$

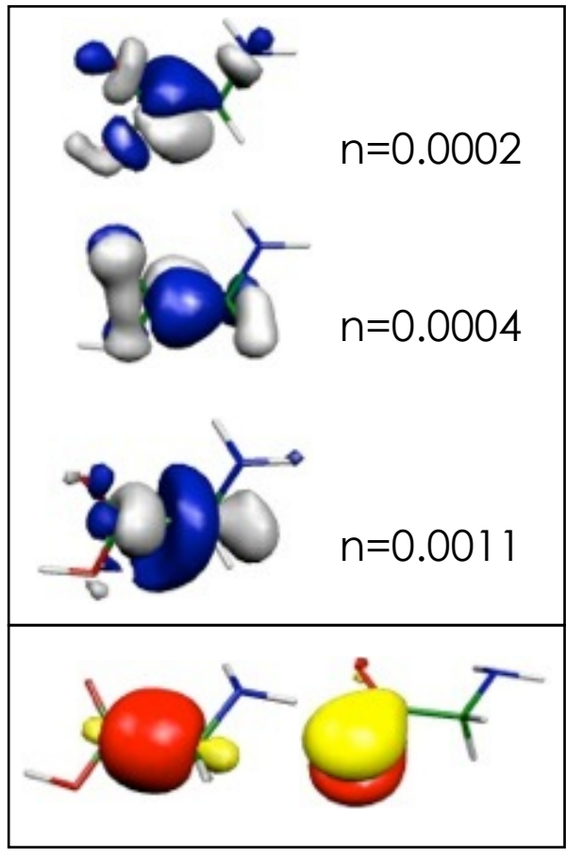
$$\mathrm{c}_{\mathrm{b}_{\mathrm{Q}}\mathrm{a}_{\mathrm{P}}} = \left\langle \mathrm{b}_{\mathrm{Q}} \mid \mathrm{a}_{\mathrm{P}} \right\rangle = \mathrm{S}^{(\mathrm{Q},\mathrm{P})}_{\mathrm{b}_{\mathrm{Q}},\mathrm{a}_{\mathrm{P}}}$$

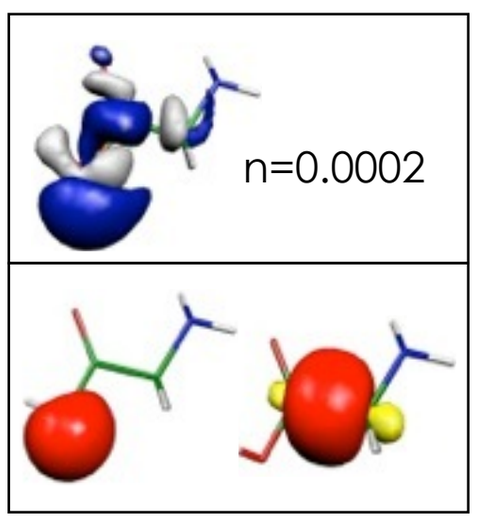
- Expansion is approximate for truncated PNO expansions! (it can be **very** bad)
- The overlap is a **projector**

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

Obstacles

✓ At threshold 0, each pair dimension = full VMO

✓ Need to know the exact density to get PNOs

✓ Many more PNOs than VMOs

➧ Nightmare!

➧ Absurd!

➧ Integral generation is frightening

➡ PNO method that expand PNOs in virtual MOs are possible (and maybe sometimes desirable! e.g. first generation LPNO methods), but it only becomes efficient and linear scaling with further approximations

Domain Based **L**ocal **P**air **N**atural **O**rbital Methods

✓ Logical approximation: Expand the PNOs in terms of local virtual orbitals, e.g. PAO's taken from large pair-specific domains

$$\left|\mathrm{a}_{\mathrm{ij}}\right\rangle = \sum_{\tilde{\mu}_{\mathrm{ij}}} \mathrm{d}^{(\mathrm{ij})}_{\mu_{\mathrm{ij}}\mathrm{a}_{\mathrm{ij}}} \left|\tilde{\mu}_{\mathrm{ij}}\right\rangle$$

✓ The pair density is approximate and comes from (semi-canonical) local MP2:

$$\mathbf{D}^{(\mathrm{ij})} = \mathbf{T}^{(\mathrm{ij})}\mathbf{T}^{(\mathrm{ij})+} + \mathbf{T}^{(\mathrm{ij})+}\mathbf{T}^{(\mathrm{ij})}$$

$$\mathrm{T}^{\mathrm{ij}}_{\tilde{\mu}_{\mathrm{ij}}\tilde{\nu}_{\mathrm{ij}}} = -\frac{\left(\mathrm{i}\tilde{\mu}_{\mathrm{ij}} \mid \mathrm{j}\tilde{\nu}_{\mathrm{ij}}\right)}{\mathrm{F}_{\mathrm{ii}} - \mathrm{F}_{\mathrm{jj}} - \varepsilon_{\tilde{\mu}_{\mathrm{ij}}} - \varepsilon_{\tilde{\nu}_{\mathrm{ij}}}}$$

➡ The generated PNOs are rather approximate, but experience shows that only minor improvements are possible by making more elaborate choices; the domain approximation is is more problematic.

Local Correlation with PNOs: PNO-MP2

Recall: $$\mathbf{R}^{ij} = \mathbf{K}^{ij} - \mathbf{K}^{ji} + \boldsymbol{t}^{ij}\overline{\boldsymbol{F}}\tilde{\boldsymbol{S}}^{(ij,ij)} + \tilde{\boldsymbol{S}}^{(ij,ij)}\overline{\boldsymbol{F}}\boldsymbol{t}^{ij} - \sum_{k}\left(\tilde{\boldsymbol{S}}^{(ij,ik)}\boldsymbol{t}^{ik}\tilde{\boldsymbol{S}}^{(ik,ij)}F_{kj} + F_{ik}\tilde{\boldsymbol{S}}^{(ij,ikj)}\boldsymbol{t}^{kj}\tilde{\boldsymbol{S}}^{(kj,ij)}\right)$$

- Throwing out negligible electron pairs (ij) does not change the equations
  - Just the same with PNOs as with PAOs, only the overlap projector now refers to PNO's:

$$\tilde{S}_{\tilde{a}\tilde{b}} = \left\langle \tilde{a} \,|\, \tilde{b} \right\rangle$$

Thus there is an emerging **„cooking recipe“**:

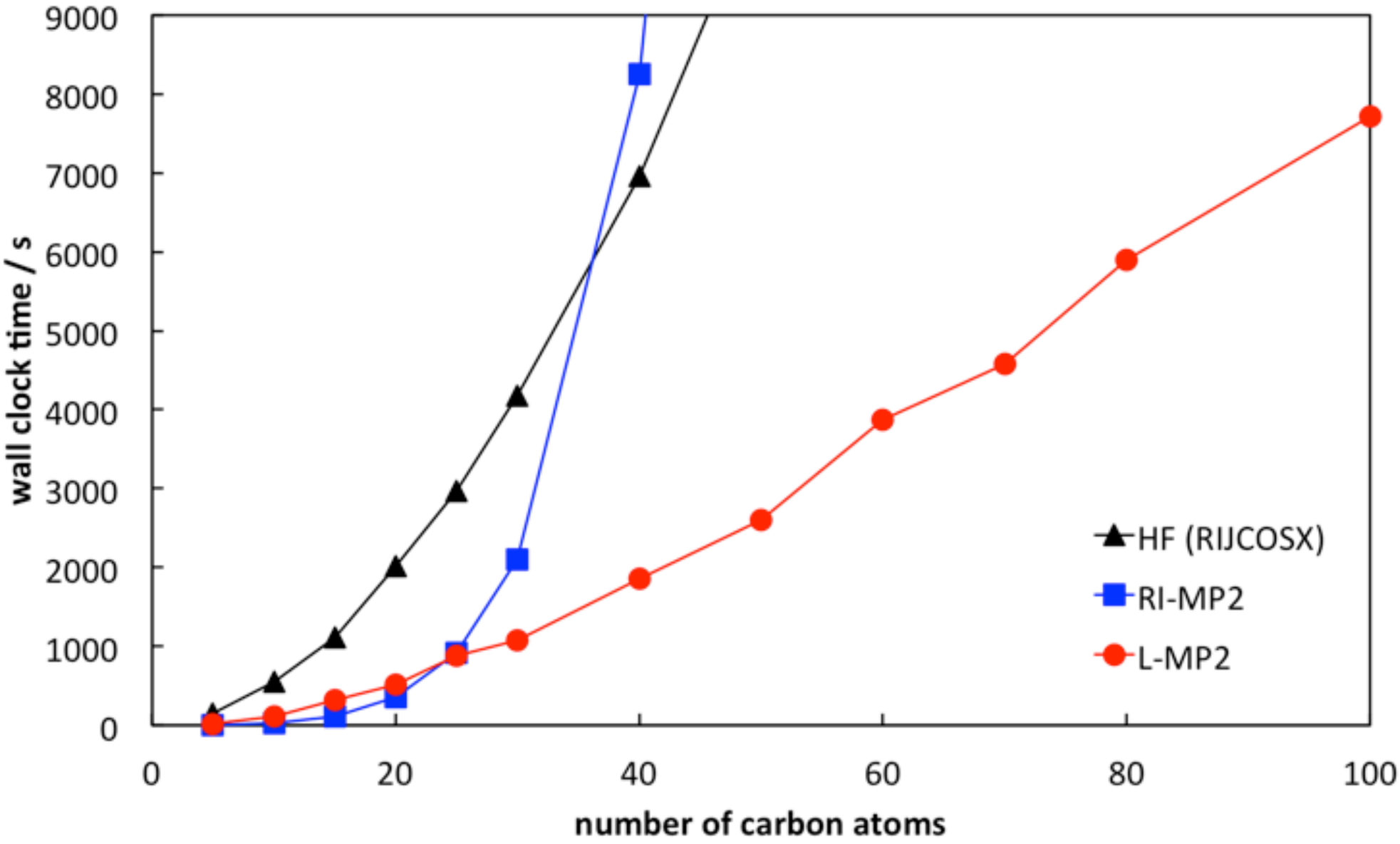
- Whenever two pairs are „connected“ there will be mismatched dimensions on the matrices to be multiplied: insert the pair-pair overlap in these terms.
- In reality it is not quite that simple …

FN; Hansen, A.; Liakos, D. G. *JCP* **2009**, *131* (DOI: 10.1063/1.3086717).
FN; Wennmohs, F.; Hansen, A. *JCP* **2009**, *130* (DOI: 10.1063/1.3173827).

Steps in DLPNO-MP2

- ✓ Perform **HF** calculation
- ✓ **Localize** occupied MOs – separately for core and valence
- ✓ Construct normalized redundant **PAOs**
- ✓ Select PAO **domains** based on DOI (T_{CutDO})
- ✓ **Screen** *ij*-pairs based on a dipole approximation of the pair energy
- ✓ For every pair domain, construct **quasi-canonical non-redundant PAOs**
- ✓ Calculate the **semi-canonical amplitudes**
- ✓ **Diagonalize** the pair density
- ✓ **Keep PNO**s with occupation > T_{CutPNO}
- ✓ **Solve** MP2 residual equations in PNO basis

DLPNO-MP2: Efficiency and Scaling



- ALWAYS faster than even accelerated Hartree-Fock
- Early crossover with the canonical RI-MP2 method!

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

Assessment of DLPNO-MP2 Approximations in Double-Hybrid DFT

Hagen Neugebauer, Peter Pinski, Stefan Grimme, Frank Neese,* and Markus Bursch*

Cite This: *J. Chem. Theory Comput.* 2023, 19, 7695–7703

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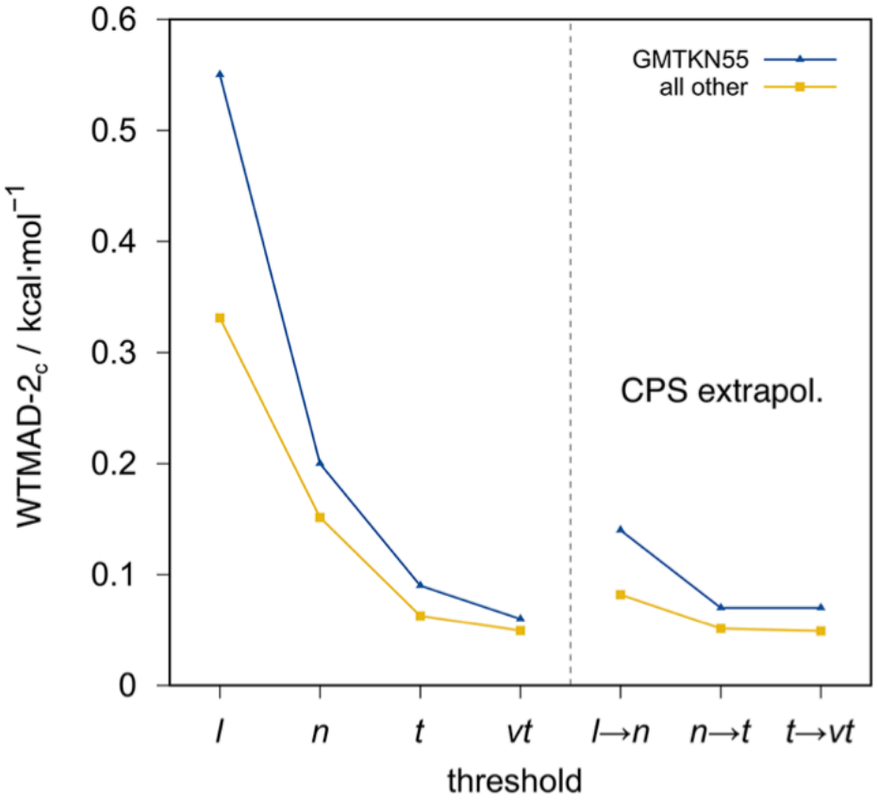
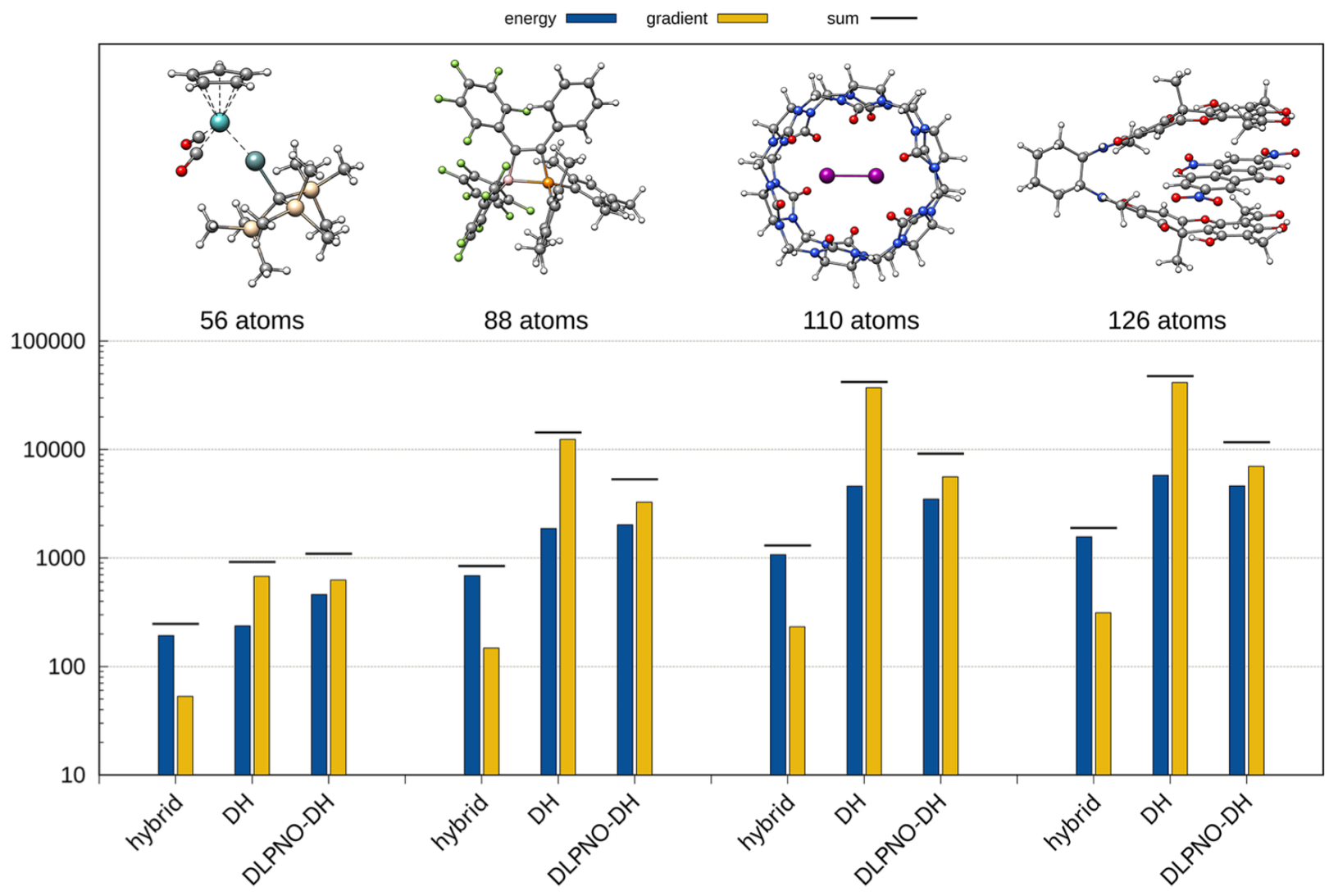




Practical Implementation:

A (somewhat) Formal Treatment of Sparsity

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. $(i\tilde{\mu} \mid K)$

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?

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

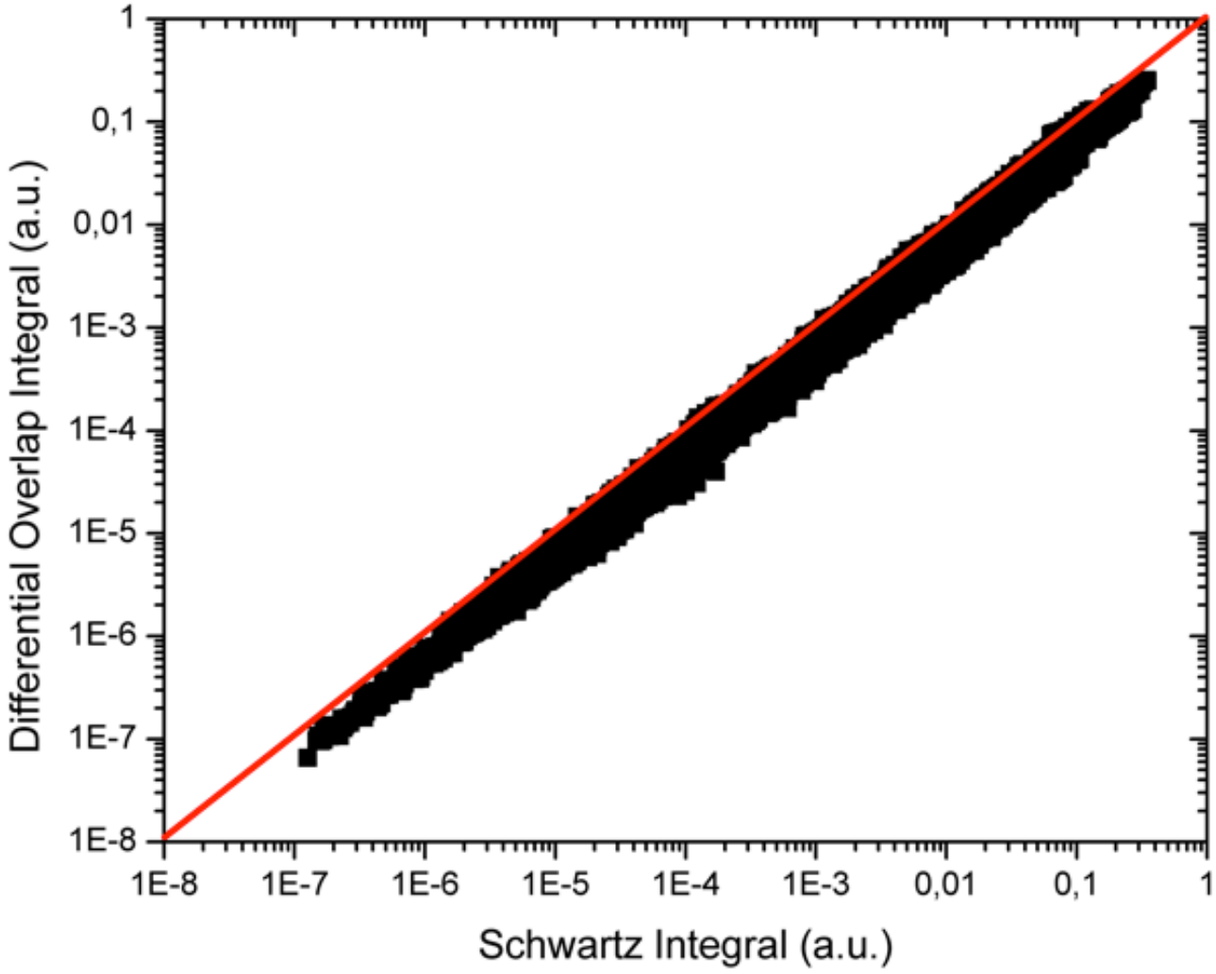
Want a simple substitute for the SPI to implement multiplicative sparsity

The Differential Overlap Integral (DOI)

Our 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

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

Inversion:

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

Contraction:

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

shells atoms

Union & Dissection:

$$\mathbf{L}_1(f \to g) \quad \mathbf{L}_2(f \to g) \qquad \mathbf{L}_3 = \mathbf{L}_1 \cup \mathbf{L}_2 \qquad \mathbf{L}_3 = \mathbf{L}_1 \cap \mathbf{L}_2$$

Chaining

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

Can, for example, be put into a C++ object library that implements sparse map operations

Implementing Sparsity:,*Linked Index Principle*‘

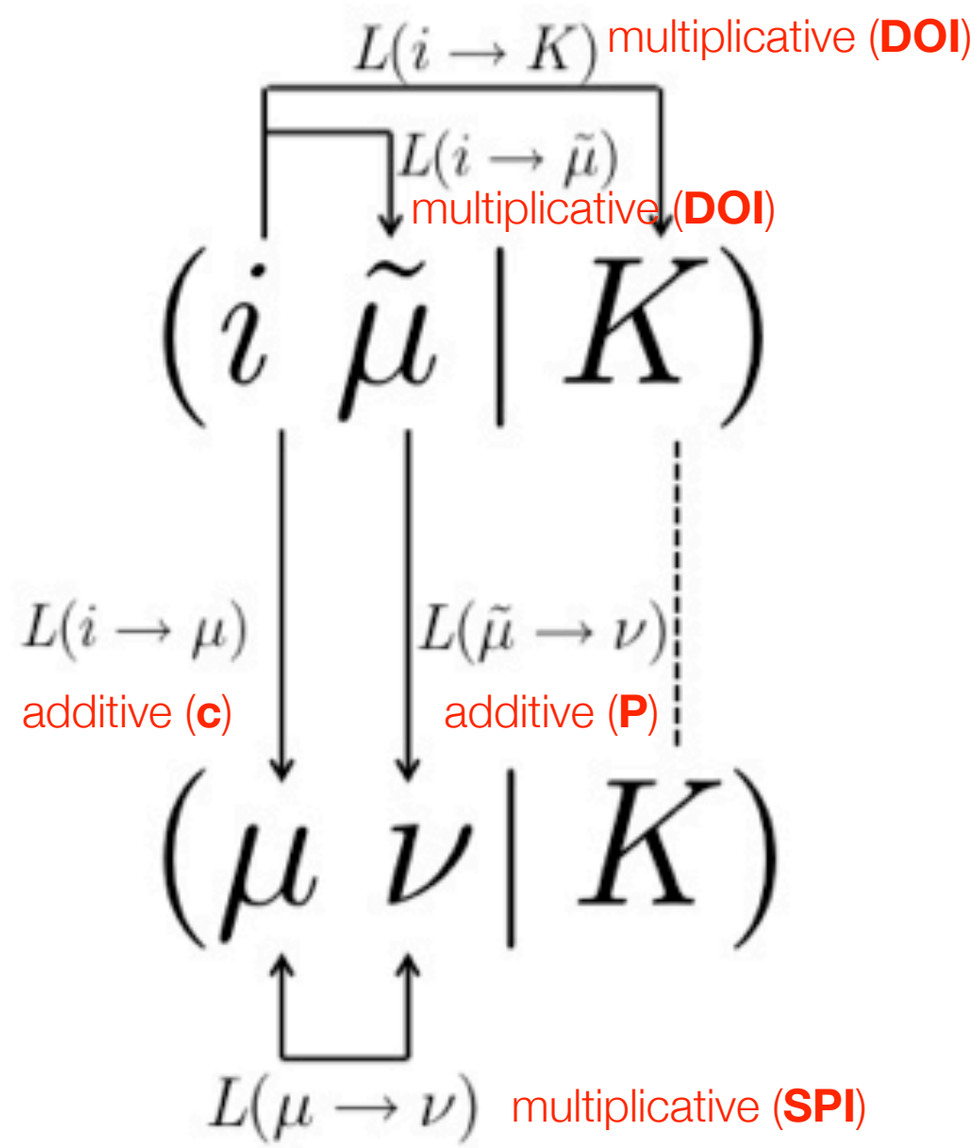
In order to reach linear scaling there MUST be an uninterrupted path of sparsity relationships that connects each index of a given object (integral, amplitude) to each other index)

Example: Three-Index Integral transformation

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

Chain of sparsity relationships exist

Linear scaling is possible



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

Linear Scaling 3-Index Transformation

```
Loop over auxiliary basis function shell K_S                    <-- O(N)
   # primitive integral transformation
   Loop over basis functions μ∈L_K(K→μ)
     Loop over basis functions ν∈L_K(K→ν)
       Compute integrals (μν|K)
       Buffer integrals I_K(μν)=(μν|K)
     End Loop ν
   End Loop μ
   # actual transformation
   Loop over MOs i∈L_K(K→i)
     Loop ν∈L_K(K→ν)
       (iν|K)=0
       Loop μ∈ L_K(K→μ)∩L_i(i→μ)   (iν|K)+= c^L(μ,i)*I_K(μν)
     End Loop ν
   End Loop i
   Loop over PAOs μ̃ ∈L(K→μ̃)
     Loop over MOs i∈L(K→i)
       (iμ̃|K)=0
       Loop ν∈L(K→ν)∩L(μ̃→ν)   (iμ̃|K)+= P_νμ̃ *(iν|K)
       Store (iμ̃|K)
     Loop over MOs i∈L(K→i)
   End Loop μ̃
End Loop K
```

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

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

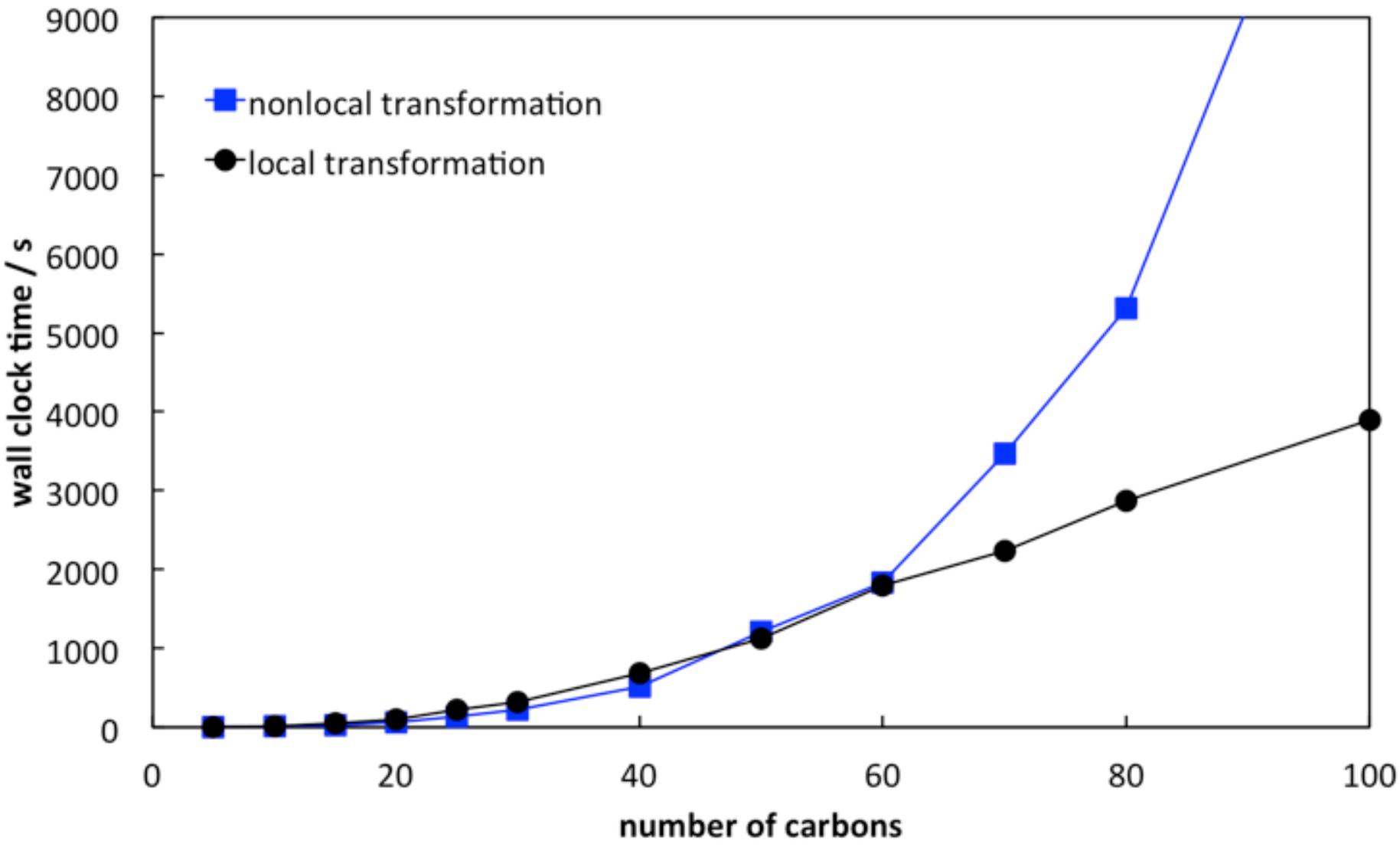
$$\mathbf{L}(K \to \nu) = \mathbf{L}(K \to i) \subset \mathbf{L}(i \to \tilde{\mu}) \subset \mathbf{L}(\tilde{\mu} \to \nu)$$

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

All O(1) operations on the current auxiliary shell

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

Local Correlation Analytic Derivatives

Golden Rule

You should never approximate a derviative. If you want an accurate results you MUST take the derivative of the approximation!

$$\boldsymbol{g}(analytic) = \frac{\partial E(analytic)}{\partial \boldsymbol{x}}$$

$$E(analytic) \rightarrow E(approx)$$

$$\boldsymbol{g}(analytic) \rightarrow \boldsymbol{g}(approx)$$

$$\boldsymbol{g}(approx) = \frac{\partial E(approx)}{\partial \boldsymbol{x}}$$

The Canonical MP2 Lagrangian

$$\mathcal{L} = E_{SCF} + \frac{1}{2}\sum_{ijab} t_{ab}^{ij} \langle ij||ab\rangle + \sum_{ab} D_{ab}F_{ab} - \sum_{ij} D_{ij}F_{ij} + \sum_{ai} z_{ai}F_{ai} + \sum_{pq} X_{pq}(S_{pq} - \delta_{pq})$$

SCF Energy | **Hylleraas Functional (correlation energy)** | **SCF condition** | **Orthonormality condition**

RHS of Z-vector $\mathrm{L}_{\mathrm{ai}} = \mathbf{R}(\mathbf{D}^{\mathrm{ur}})_{\mathrm{ai}} + 2\sum_{\mathrm{jbc}} \left\langle \mathrm{aj} \,||\, \mathrm{cb} \right\rangle \mathrm{t}_{\mathrm{cb}}^{\mathrm{ij}} - 2\sum_{\mathrm{jkb}} \left\langle \mathrm{kj} \,||\, \mathrm{ib} \right\rangle \mathrm{t}_{\mathrm{ab}}^{\mathrm{kj}}$

Response operator $\mathbf{R}\left(\mathbf{D}^{\mathrm{ur}}\right)_{\mathrm{pq}} = \sum_{\mathrm{rs}} 2\mathrm{D}_{\mathrm{rs}}^{\mathrm{ur}} \left\langle \mathrm{pr} \,||\, \mathrm{qs} \right\rangle$

Unrelaxed density $\mathbf{D}_{\mathrm{ij}}^{\mathrm{ur}} = -\sum_{\mathrm{k}} \mathbf{T}^{\mathrm{ik}}\mathbf{T}^{\mathrm{jk}}$ $\qquad$ $\mathbf{D}_{\mathrm{ab}}^{\mathrm{ur}} = \sum_{\mathrm{i<j}} \mathbf{T}^{\mathrm{ij}+}\mathbf{T}^{\mathrm{ij}} + \mathbf{T}^{\mathrm{ij}}\mathbf{T}^{\mathrm{ij}+}$

Relaxed density $\mathbf{D} = \mathbf{D}^{\mathrm{ur}} + \mathbf{Z}$

Two-particle density $\Gamma_{\mathrm{pqrs}}^{\mathrm{PT2}} = \mathrm{D}_{\mathrm{pq}}\mathrm{P}_{\mathrm{rs}} - \frac{1}{2}\mathrm{D}_{\mathrm{pr}}\mathrm{P}_{\mathrm{qs}} + \Gamma_{\mathrm{pqrs}}^{\mathrm{NS}}$

DLPNO-MP2 Lagrangian

$$\mathrm{L} = \underbrace{\mathrm{E}_{\mathrm{SCF}}}_{\text{SCF Energy}} + \underbrace{\frac{1}{2}\sum_{\mathrm{ijab}} \mathrm{T}_{\mathrm{ab}}^{\mathrm{ij}} \left\langle \mathrm{ij} \,||\, \mathrm{ab} \right\rangle + \sum_{\mathrm{ab}} \mathrm{D}_{\mathrm{ab}} \mathrm{F}_{\mathrm{ab}} - \sum_{\mathrm{ij}} \mathrm{D}_{\mathrm{ij}} \mathrm{F}_{\mathrm{ij}}}_{\text{Hylleraas Funcitonal}}$$

$$+ \underbrace{\sum_{\mathrm{ai}} \left(\mathrm{z}_{\mathrm{ai}} \mathrm{F}_{\mathrm{ai}} + \mathrm{c.c.} \right)}_{\text{SCF condition}} + \underbrace{\sum_{\mathrm{pq}} \mathrm{x}_{\mathrm{pq}} \left(\mathrm{S}_{\mathrm{pq}} - \delta_{\mathrm{pq}} \right)}_{\text{Orthnormality condition}}$$

$$\underbrace{+\Delta \mathrm{E}_{\mathrm{pre}}}_{\text{Pair Pr escreening}} + \underbrace{\Delta \mathrm{E}_{\mathrm{PNO}}}_{\text{PNO Error Correction}} + \underbrace{\sum_{\mathrm{ai}} \left(\mathrm{z}_{\mathrm{ai}}^{\mathrm{loc}} \mathrm{s}_{\mathrm{ai}}^{\mathrm{loc}} + \mathrm{c.c.} \right)}_{\text{localization condition}} + \underbrace{\sum_{\mathrm{i<j}} \sum_{\tilde{\mathrm{a}}\tilde{\mathrm{b}}'} \left(\nu_{\tilde{\mathrm{a}}\tilde{\mathrm{b}}'}^{\mathrm{ij}} \mathrm{D}_{\tilde{\mathrm{a}}\tilde{\mathrm{b}}'}^{\mathrm{ij}} + \mathrm{c.c.} \right)}_{\text{Discarded PNO condition}}$$

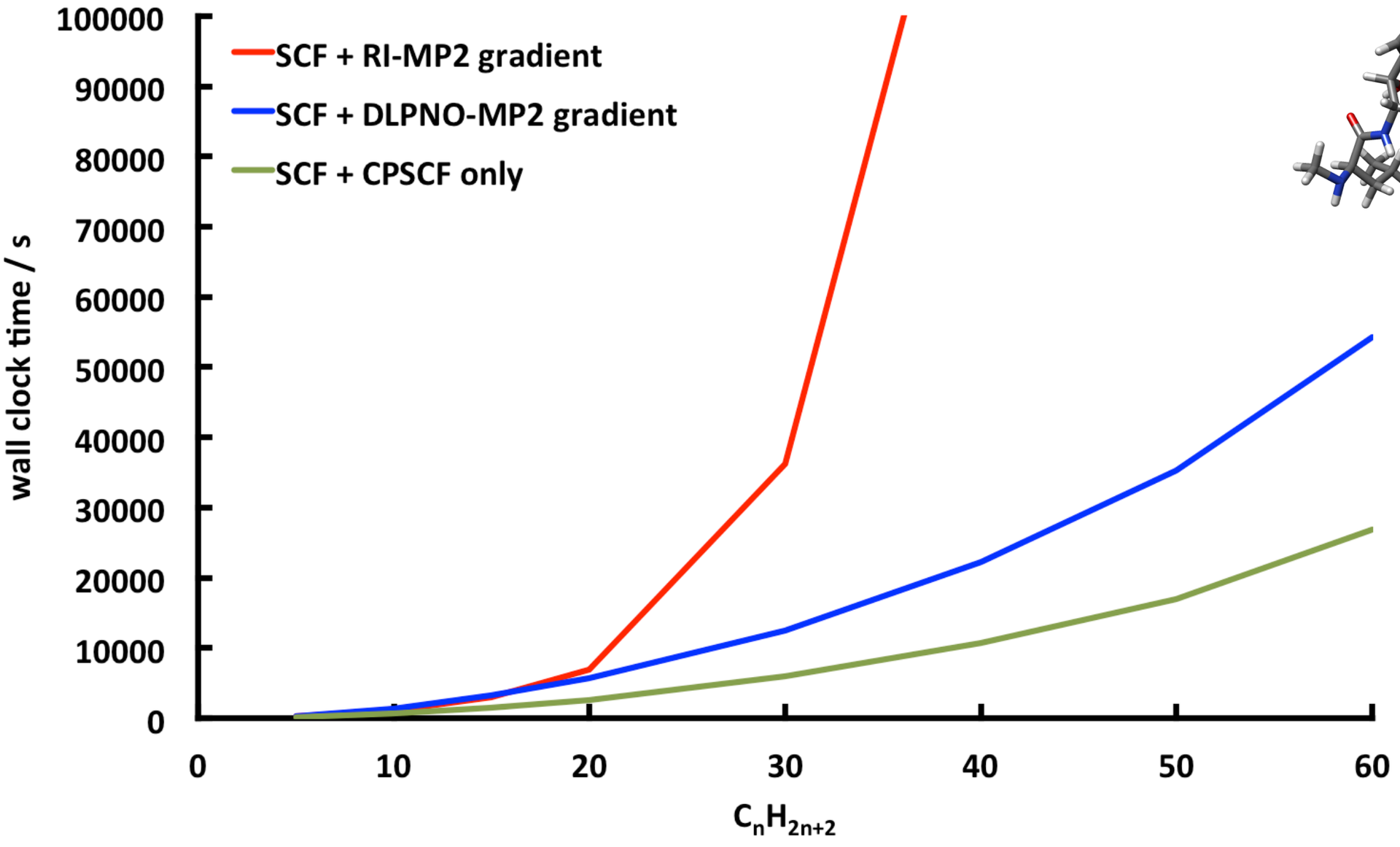
additional terms!

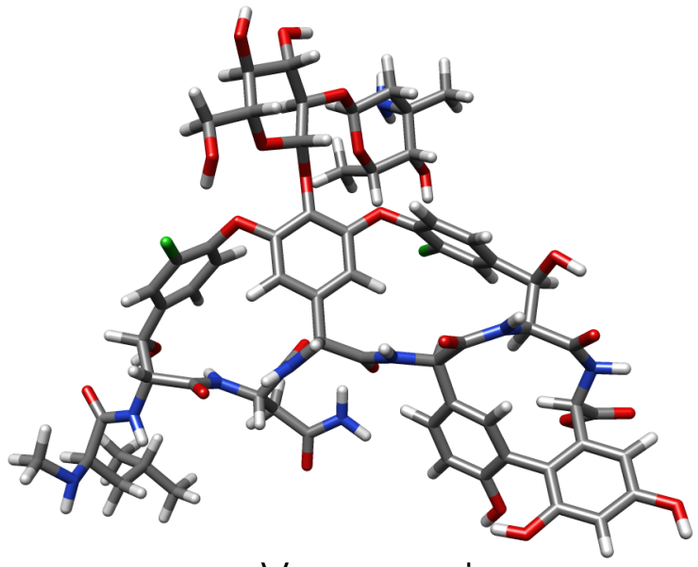
$$\underbrace{+ \sum_{\mathrm{i<j}} \sum_{\tilde{\mathrm{a}}''\tilde{\mathrm{b}}''} \left(\omega_{\tilde{\mathrm{a}}''\tilde{\mathrm{b}}''}^{\mathrm{ij}} \mathrm{R}_{\tilde{\mathrm{a}}''\tilde{\mathrm{b}}''}^{\mathrm{ij}} + \mathrm{c.c.} \right)}_{\text{semi-canonical condition}} + \underbrace{\sum_{\mathrm{i<j}} \sum_{\tilde{\mathrm{a}}''\tilde{\mathrm{b}}''} \left(\tilde{\mathrm{x}}_{\tilde{\mathrm{a}}''\tilde{\mathrm{b}}''}^{\mathrm{ij}} \left(\mathrm{S}_{\tilde{\mathrm{a}}''\tilde{\mathrm{b}}''}^{\mathrm{ij}} - \delta_{\tilde{\mathrm{a}}''\tilde{\mathrm{b}}''} \right) \right)}_{\text{PNO orthonormality}}$$

$$\breve{\mathbf{R}}^{ij} = \mathbf{K}^{ij} + \mathbf{F}\breve{\mathbf{T}}^{ij} + \breve{\mathbf{T}}^{ij}\mathbf{F} - (F_{ii} + F_{jj})\breve{\mathbf{T}}^{ij} = \mathbf{0}$$

$\left| \tilde{\mathrm{a}}_{\mathrm{ij}} \right\rangle =$ Retained PNOs $\quad \left| \tilde{\mathrm{a}}'_{\mathrm{ij}} \right\rangle =$ Discarded PNOs $\quad \left| \tilde{\mathrm{a}}''_{\mathrm{ij}} \right\rangle =$ All PNOs

Performance of the gradient



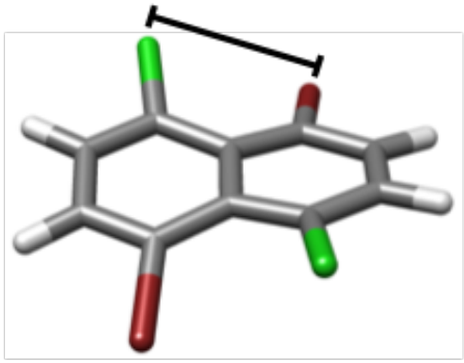


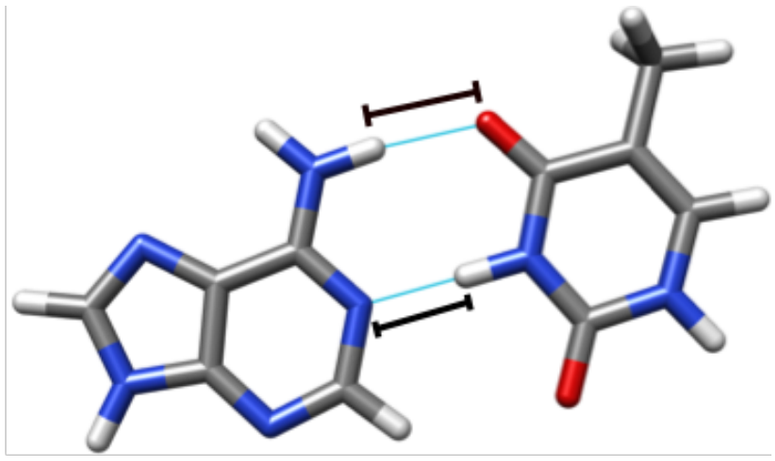
Vancomycin
(176 atoms)
SCF and Gradient in
100 h on 1 CPU core.

def2-TZVP / 1 CPU / 6 GB allowed memory usage. RIJCOSX-SCF/CPSCF

Accuracy of Optimized Structures

$r_{Cl\text{-}Br}$ / pm
313.3
313.4
313.4

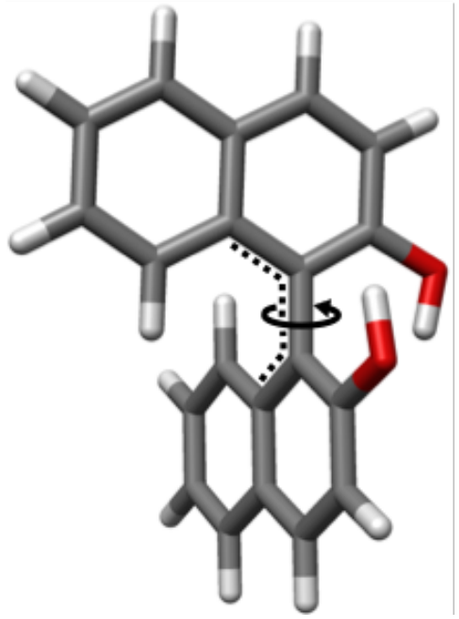


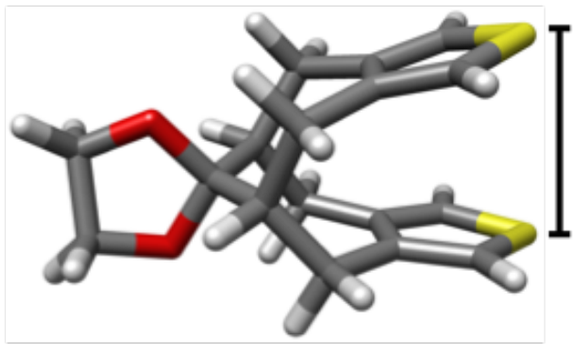


$r_{H\text{-}O}$ / pm
190.7
191.0
190.8

$r_{N\text{-}H}$ / pm
177.1
177.7
177.3

$\vartheta_{C\text{-}C\text{-}C\text{-}C}$ / °
77.13
77.67
77.70





$r_{S\text{-}S}$ / pm
383.8
386.7
384.6

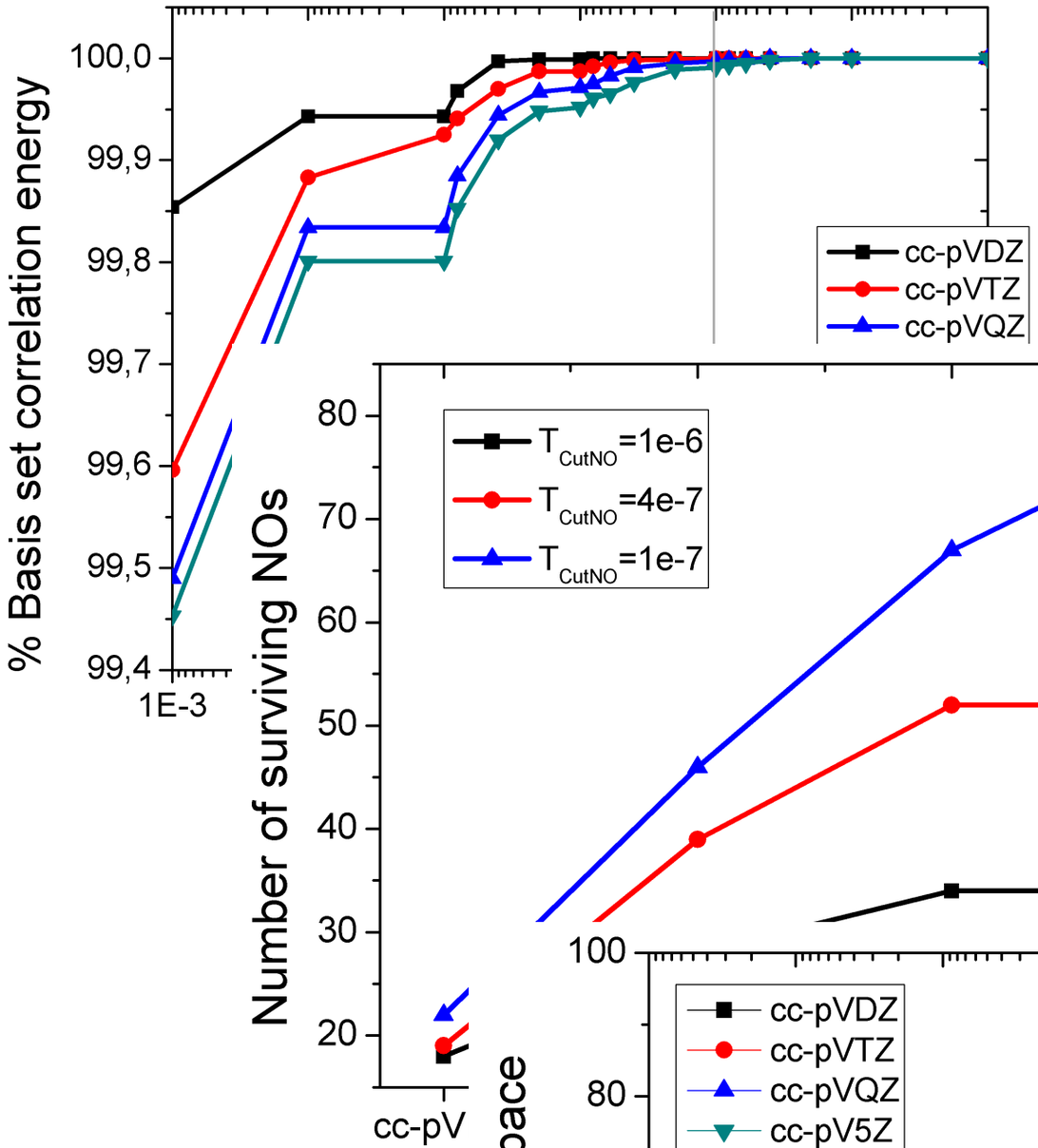
RI-MP2
NormalPNO
TightPNO

Errors for covalent bonds:

	lenghts / pm		angles / °	
MAX	0.1	0.05	0.22	0.06
RMS	0.03	0.01	0.03	0.01

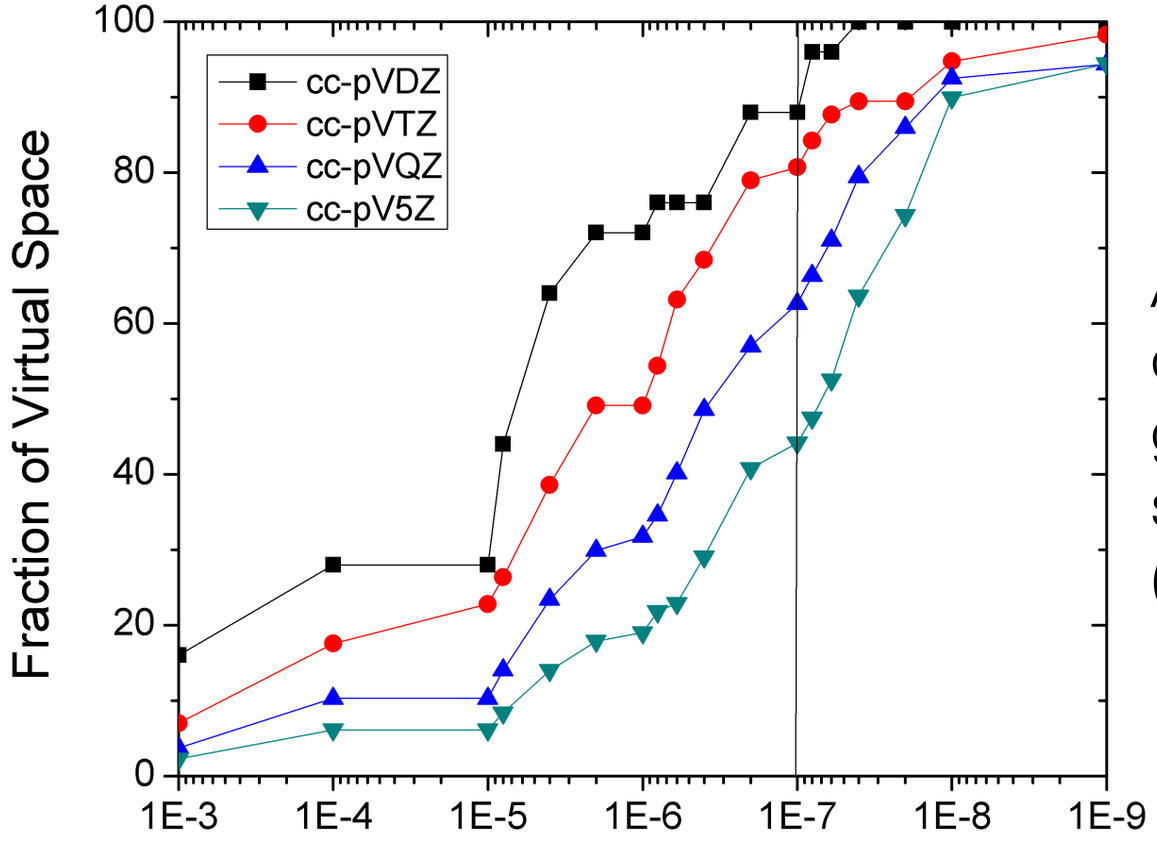
Basis Set Convergence in PNO Calculations

Li-Dimer @ 1.5 Angström



At fixed threshold one recovers less E_c as the basis set is approaching completeness … $T_{CutNO}=10^{-7}$ is fine even for large bases

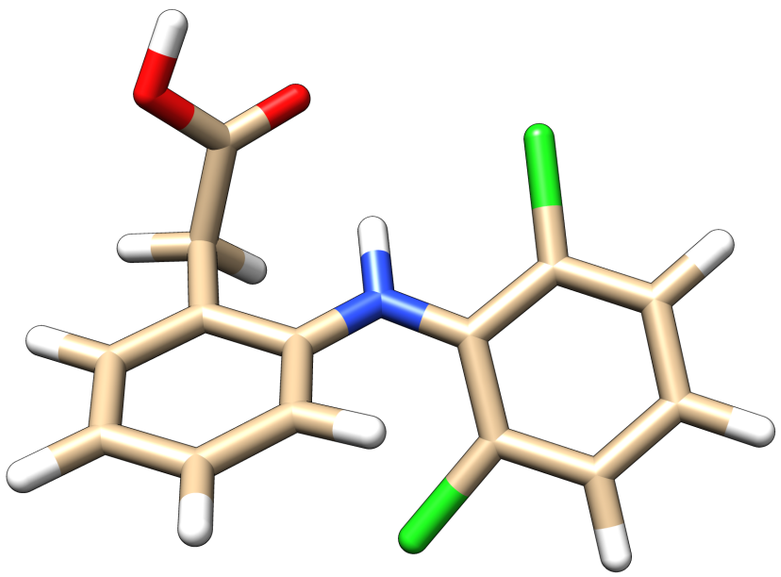
At fixed threshold the number of NOs *is* approaching a constant as the the basis set saturates



At fixed threshold the fraction of the virtual space treated gets smaller as the basis set saturates
(cost reduction ~ (fraction)^4)

Real Life Basis Set Behavior of DLPNO-CCSD(T)

In real life convergence of the PNO expansion is *more* favorable than for, say He, since weakly interacting electron pairs saturate more quickly with basis set!



Diclophenac

(30 atoms)

	N_{Bas}	N_{PNO}^{av}	Fraction	Time(s)	
cc-pVDZ	329	19	5.7	723	
cc-pVTZ	723	27	3.7	3782	(5.2x)
cc-pVQZ	1383	32	2.3	13676	(3.6x)
cc-pV5Z	3243	36	1.1	46675	(3.4x)
cc-pV6Z	3669	39	1.0	144141	(3.0x)

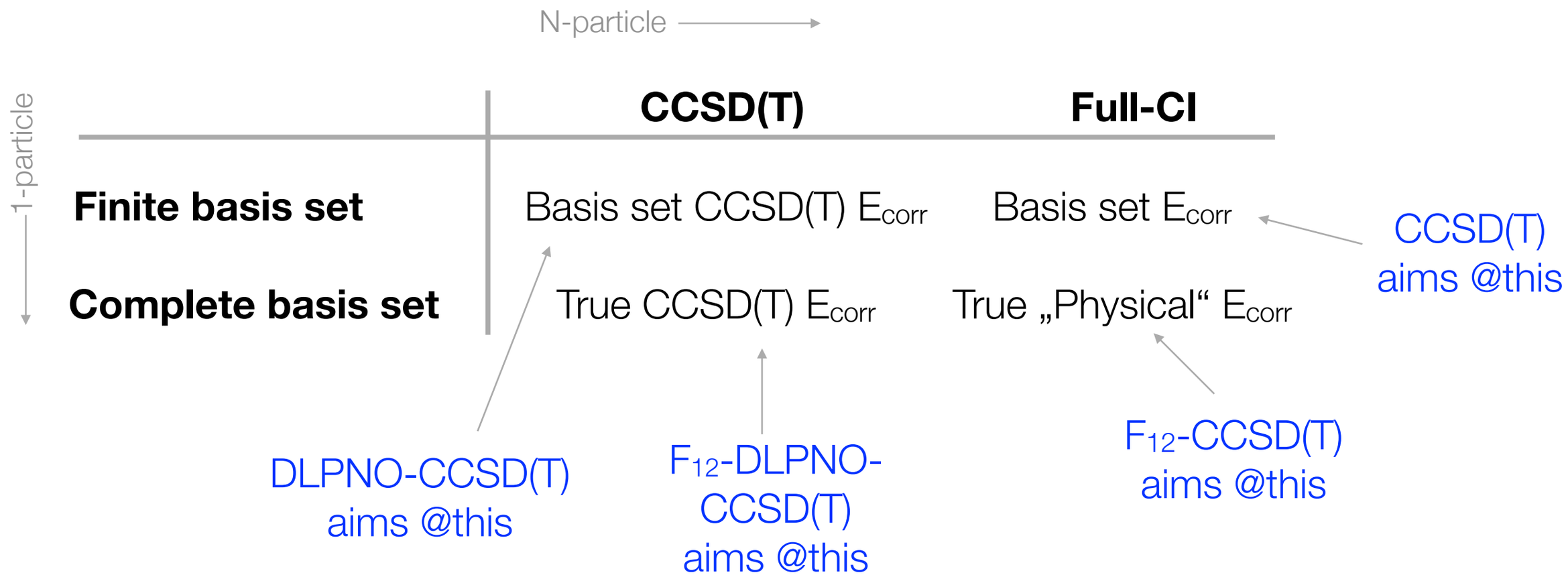
=1.6 days/16 cores

Savings ~10^8!

Increase of computer time with cardinal number: DLPNO-CCSD(T) **~factor 3-4**

Canonical CCSD(T) **~factor 10-100**

PNO Truncation, Basis Sets, Correlation Energy

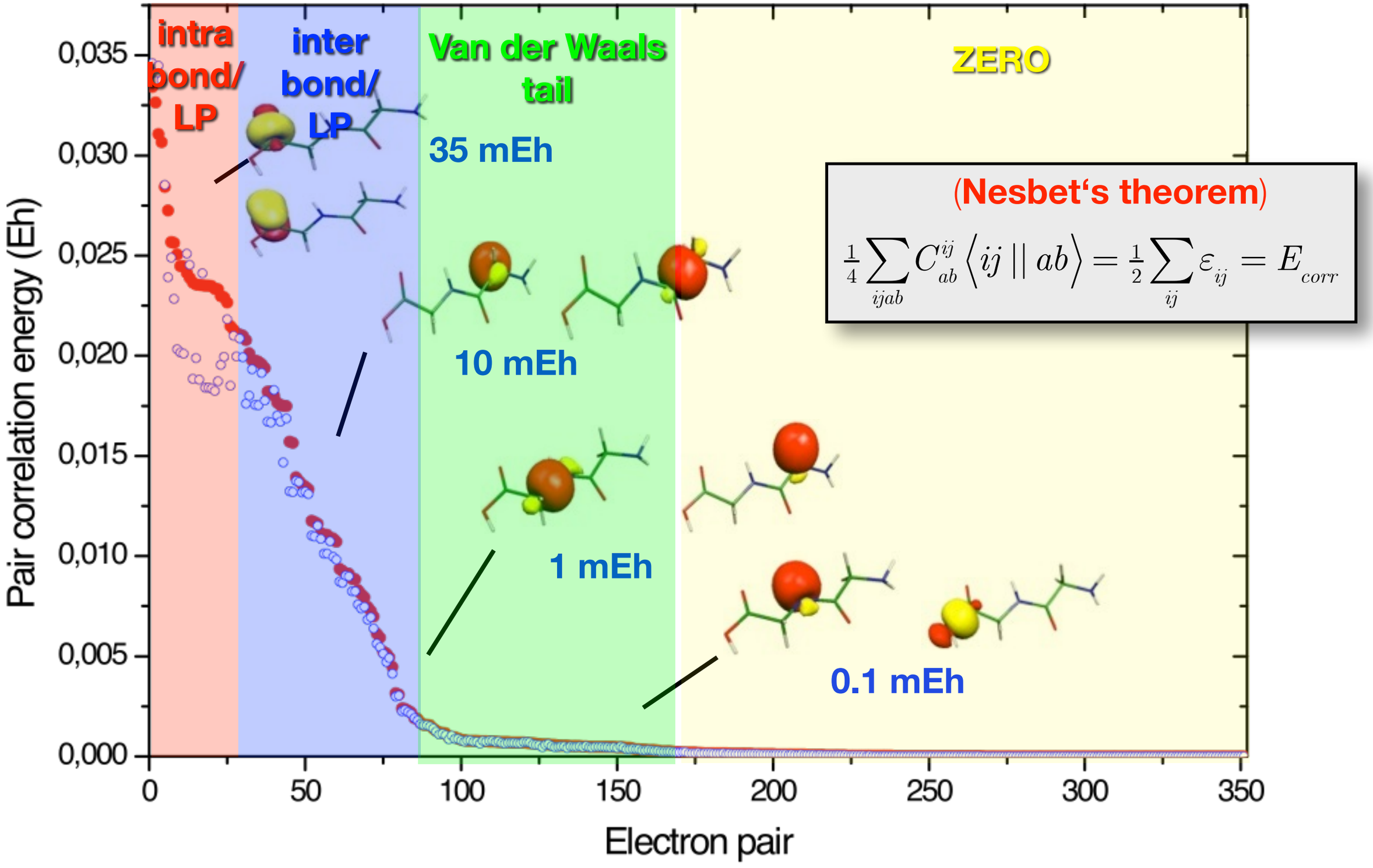


- ➡ **One should only judge DLPNO-CCSD(T) relative to how well it approximates CCSD(T) energy in the same basis set!**
- ➡ **Extrapolation to the 1-particle (basis set) limit is something separate**
- ➡ **Extrapolation to the N-particle (full CI) limit is something separate**

Chemical Interpretation: Local Energy Decomposition

W Schneider; G Bistoni, M Sparta, M Saitow, C Riplinger, A Auer, FN, **2016**, *JCTC,* in press

Decomposing the Correlation Energy

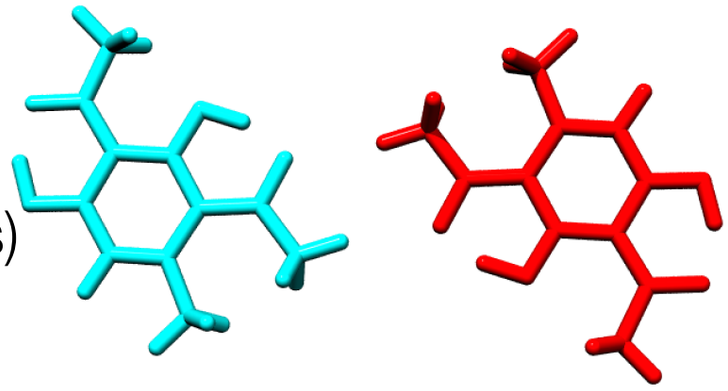


(Nesbet's theorem)

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

Local Energy Decomposition

Key step:
User defined fragmentation
(arbitrary number of fragments)



```
* xyz 0 1
  N(1)  -0.009  -0.010   0.002854
  H(1)   1.012  -0.012   0.030497
  H(1)  -0.297   0.969   0.023325
  H(1)  -0.273  -0.368  -0.917511
  O(2)  -1.080  -1.506  -1.855969
  H(2)  -1.437  -1.910  -1.048847
  H(2)  -1.564  -1.941  -2.576109
*
```

Total Energy:

$$E_{tot} = E_{HF} + E_C$$
$$= E_{HF}^{intra} + E_C^{intra} + E_{HF}^{inter} + E_C^{inter}$$

Intra-Molecular

$$E_{HF}^{(X)} = V_{NN}^{(X)} + T_e^{(X)} + V_{eN}^{(X)} + V_J^{(X)} + V_X^{(X)}$$
$$= \sum_{A_X<B_X} \frac{Z_A^{(X)} Z_B^{(X)}}{\left|\mathbf{R}_A^{(X)} - \mathbf{R}_B^{(X)}\right|} + 2\sum_i \left\langle \psi_i^{(X)} \mid -\tfrac{1}{2}\nabla_i^2 \mid \psi_i^{(X)} \right\rangle - 2\sum_{i_X, A_X} \left\langle \psi_i^{(X)} \mid \frac{Z_A^{(X)}}{\left|\mathbf{r} - \mathbf{R}_A^{(X)}\right|} \mid \psi_i^{(X)} \right\rangle$$
$$+ \sum_{i \le j} \frac{4}{1+\delta_{ij}} \left(\psi_i^{(X)} \psi_i^{(X)} \mid \psi_j^{(X)} \psi_j^{(X)} \right) - \sum_{ij} \frac{2}{1+\delta_{ij}} \left(\psi_i^{(X)} \psi_j^{(X)} \mid \psi_i^{(X)} \psi_j^{(X)} \right)$$

$$E_C^{(X)} = \sum_{i_X \le j_X} \varepsilon_{ij}^{(X)}$$ *(Through assignment of occupied local orbitals to fragments)*

W Schneider; G Bistoni, M Sparta, M Saitow, C Riplinger, A Auer, FN, **2016**, *JCTC,* in press

Grouping of *Inter*molecular Terms

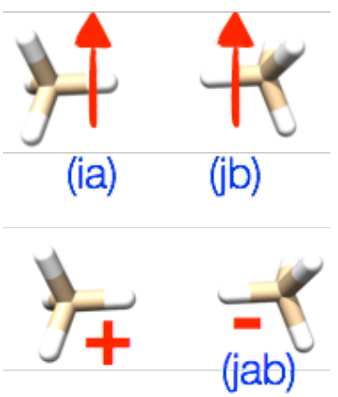
The individual terms get very large and lead to less than illuminating decompositions of small energy differences. Hence, we re-group the inter-molecular terms into intuitively appealing and physically sensible contributions:

Electrostatic interaction:

$$E^{(X,Y)}_{el-stat} = \underbrace{V^{(X,Y)}_{Nuc-nuc} + V^{(X,Y)}_{J}}_{repulsive} + \underbrace{V^{(X,Y)}_{eN} + V^{(Y,X)}_{eN}}_{attractive}$$

Exchange interaction:

$$E^{(X,Y)}_{exch} = \underbrace{-2\sum_{i_X j_Y}(i_X j_Y \mid i_X j_Y)}_{always\ "attractive"}$$



Pure dispersion

$$\varepsilon^{(DISP)}_{i_X j_Y} = \sum_{a_X b_Y}(i_X \tilde{a}_X \mid j_Y \tilde{b}_Y)\tilde{T}^{ij}_{\tilde{a}_X \tilde{b}_Y}$$

Dynamic-Polarization

$$\varepsilon^{(DPOL)}_{i_X j_Y} = \sum_{a_X b_X}(i_X \tilde{a}_X \mid j_Y \tilde{b}_X)\tilde{T}^{ij}_{\tilde{a}_X \tilde{b}_X} + \sum_{a_Y b_Y}(i_X \tilde{a}_Y \mid j_Y \tilde{b}_Y)\tilde{T}^{ij}_{\tilde{a}_Y \tilde{b}_Y}$$

Exchange Dispersion

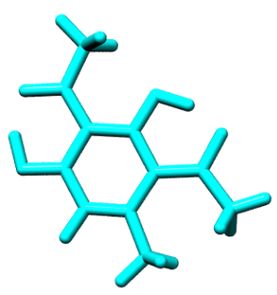
$$\varepsilon^{(xDISP)}_{i_X j_Y} = \sum_{a_Y b_X}(i_X \tilde{a}_Y \mid j_Y \tilde{b}_X)\tilde{T}^{ij}_{\tilde{a}_Y \tilde{b}_X}$$

(Through localization of PNOs and assignment to fragments)

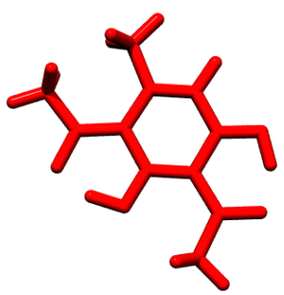
W Schneider; G Bistoni, M Sparta, M Saitow, C Riplinger, A Auer, FN, **2016**, *JCTC,* in press

Features of the LED

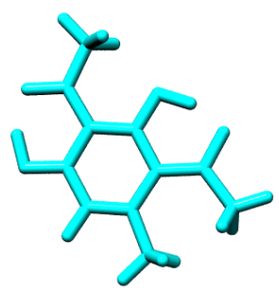
- ✓ Like any other decomposition scheme, individual contributions are ***not observable*** and have been chosen according to subjective ‚reasonable' criteria
- ✓ The decomposition is ***not perturbative*** and works along the *entire potential energy surface*, no matter how strong the interaction is (e.g. also for the onset of ***bond formation*** and ***arbitrary amounts of charge transfer***)
- ✓ No additional computational cost, no complex programming
- ✓ At interaction distance, the fragments are **electronically and geometrically relaxed**
  - ➡ Dissociation energy needs to correct for that



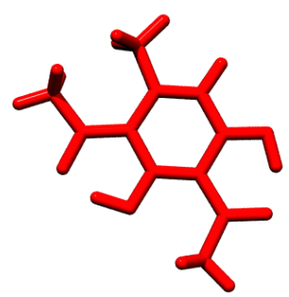
$E_{HF}^{(X)}(\bar{R}), E_{C}^{(X)}(\bar{R})$



$E_{HF}^{(Y)}(\bar{R}), E_{C}^{(Y)}(\bar{R})$



$E_{HF}^{(X)}(\infty), E_{C}^{(X)}(\infty)$



$E_{HF}^{(Y)}(\infty), E_{C}^{(Y)}(\infty)$

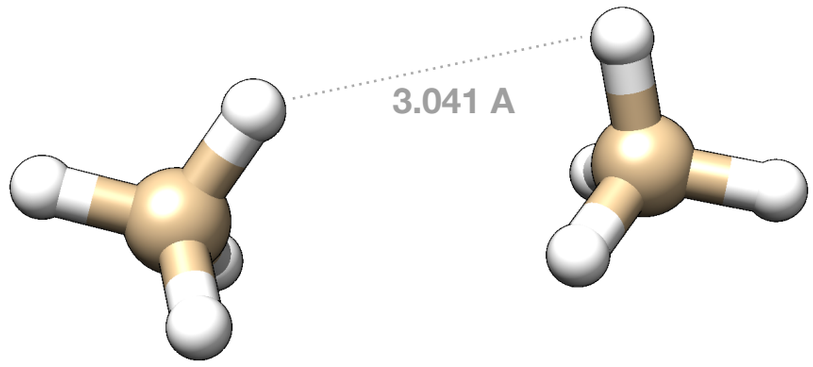
$E_{el-stat}^{(X,Y)}(\bar{R}), E_{exch}^{(X,Y)}(\bar{R}), E_{C}^{(X,Y)}(\bar{R})$

$= 0$

$E_{HF}^{(X)}(\bar{R}) - E_{HF}^{(X)}(\infty)$ **local virial ratio!**

W Schneider; G Bistoni, M Sparta, M Saitow, C Riplinger, A Auer, FN, **2016**, *JCTC,* in press

Methane-Dimer



	$E_{HF\text{-}intra}$ (Eh)	$E_{C\text{-}intra}$ (mEh)	E_{elstat} (kcal/mol)	E_{exch} kcal/mol	$E_{C\text{-}inter}$ kcal/mol
aug-cc-pVDZ	-80.396901	-392.12	-0.78	-0.40	-0.94
aug-cc-pVTZ	-80.424045	-454.70	-0.78	-0.40	-1.03
aug-cc-pVQZ	-80.429250	-470.98	-0.79	-0.40	-1.04
aug-cc-pV5Z	-80.430638	-476.071	-0.79	-0.40	-1.04

Med. Conv. **Slow Conv.** **Fast convergence**

(Note: all of these terms are zero at infinity)

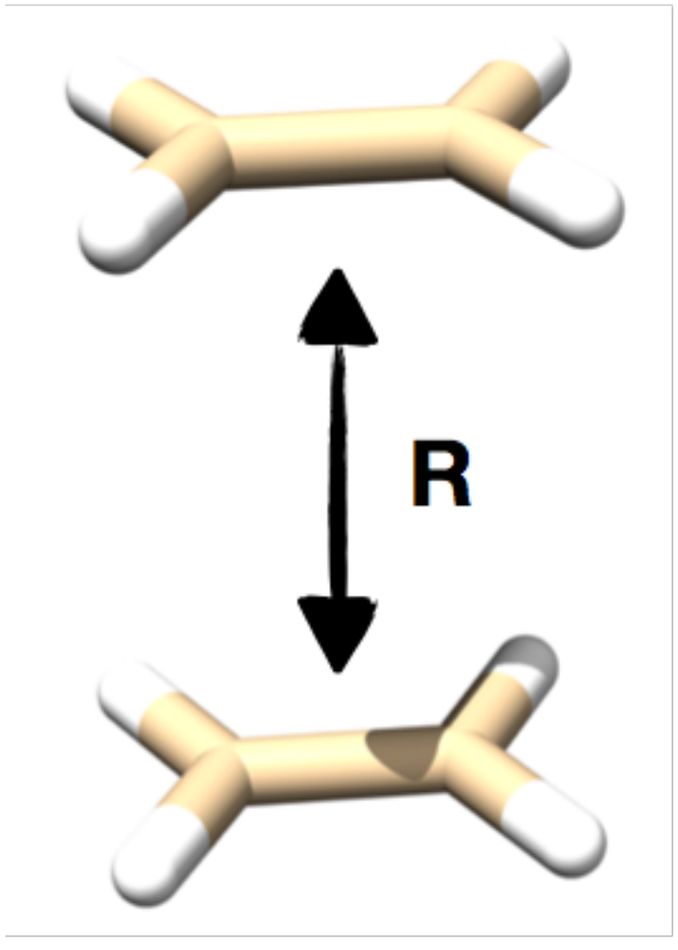
„raw“ interaction energy=-2.23 kcal/mol

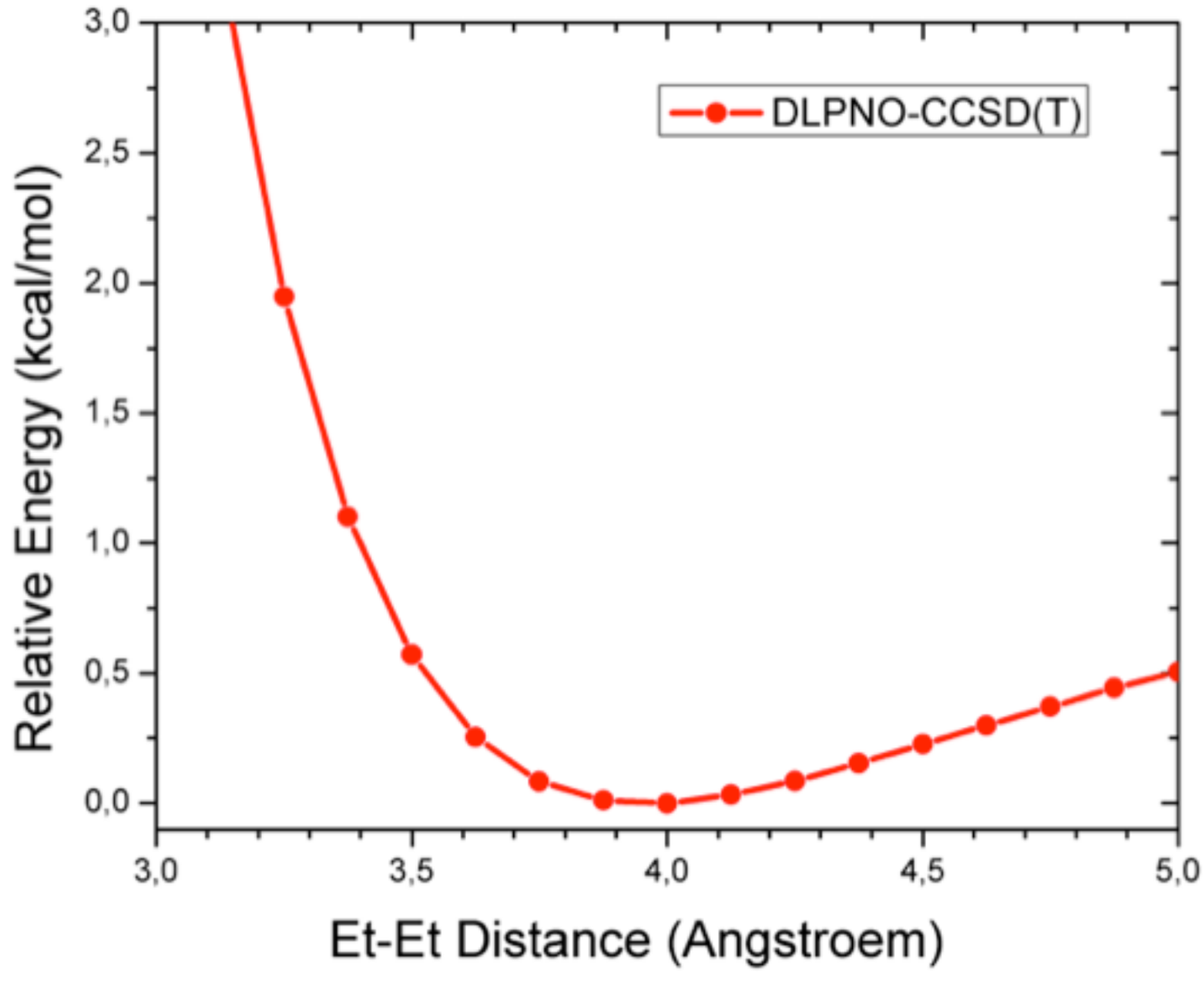
~50% correlation,
~35% electrostatics,
~15% exchange

This number overestimates the interaction energy since we need to take account of electronic and geometric relaxation

W Schneider; G Bistoni, M Sparta, M Saitow, C Riplinger, A Auer, FN, **2016**, *JCTC,* in press

What about π-π Interactions?





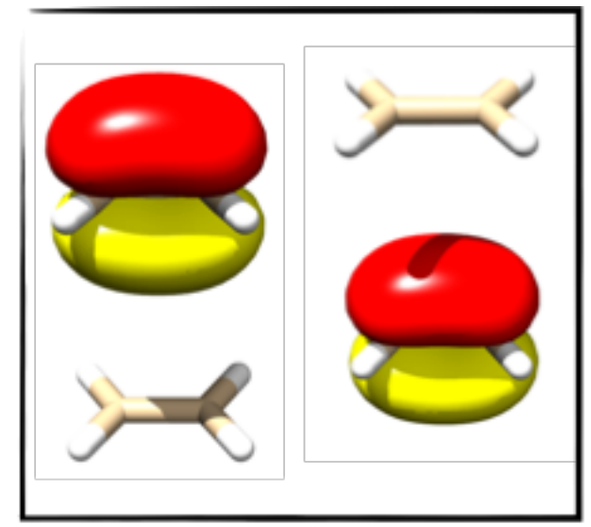
W Schneider; G Bistoni, M Sparta, M Saitow, C Riplinger, A Auer, FN, **2016**, *JCTC,* in press

Example: Ethene-Ethene

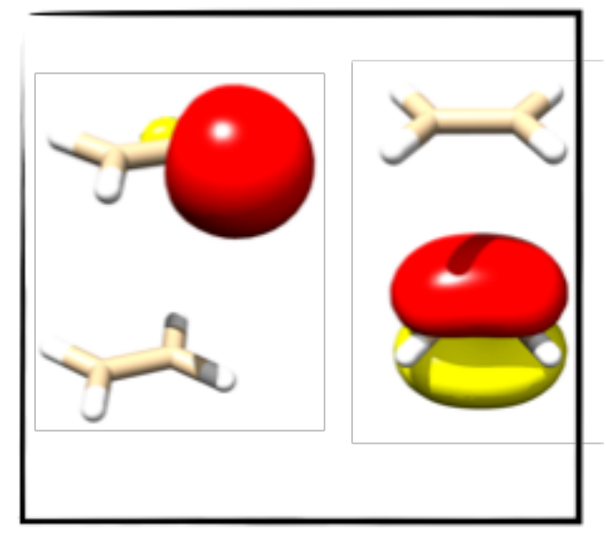
```
FRAGMENTS     2,1 =  -0.001688259898 Eh
     genuine pi-pi interaction
     1: pair   29( 11,  5) =  -0.000516971903 Eh (= 30.62 per cent)

     pi - C-H interaction
     2: pair   67( 15,  5) =  -0.000083397327 Eh (=  4.94 per cent)
         … times 8 = 40 per-cent

     Rest is C-H/C-H interactions = 30%
```



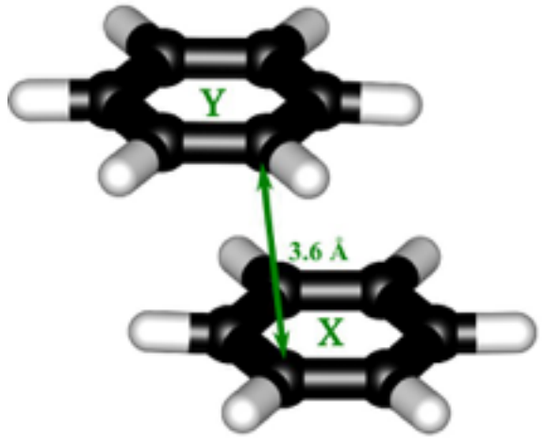
```
Overall breakdown of contributions:
Induced Dipole-Dipole      ~70%
Charge Transfer            ~30%
```



π–π interactions are NOT dominated by genuine π–π interactions. They account for about 30%. About 40% of the interaction energy comes from the interaction of the pi-orbitals with the neighboring C-H bonds and another 30% from the interactions of the C-H bonds with each other

W Schneider; G Bistoni, M Sparta, M Saitow, C Riplinger, A Auer, FN, **2016**, *JCTC,* in press

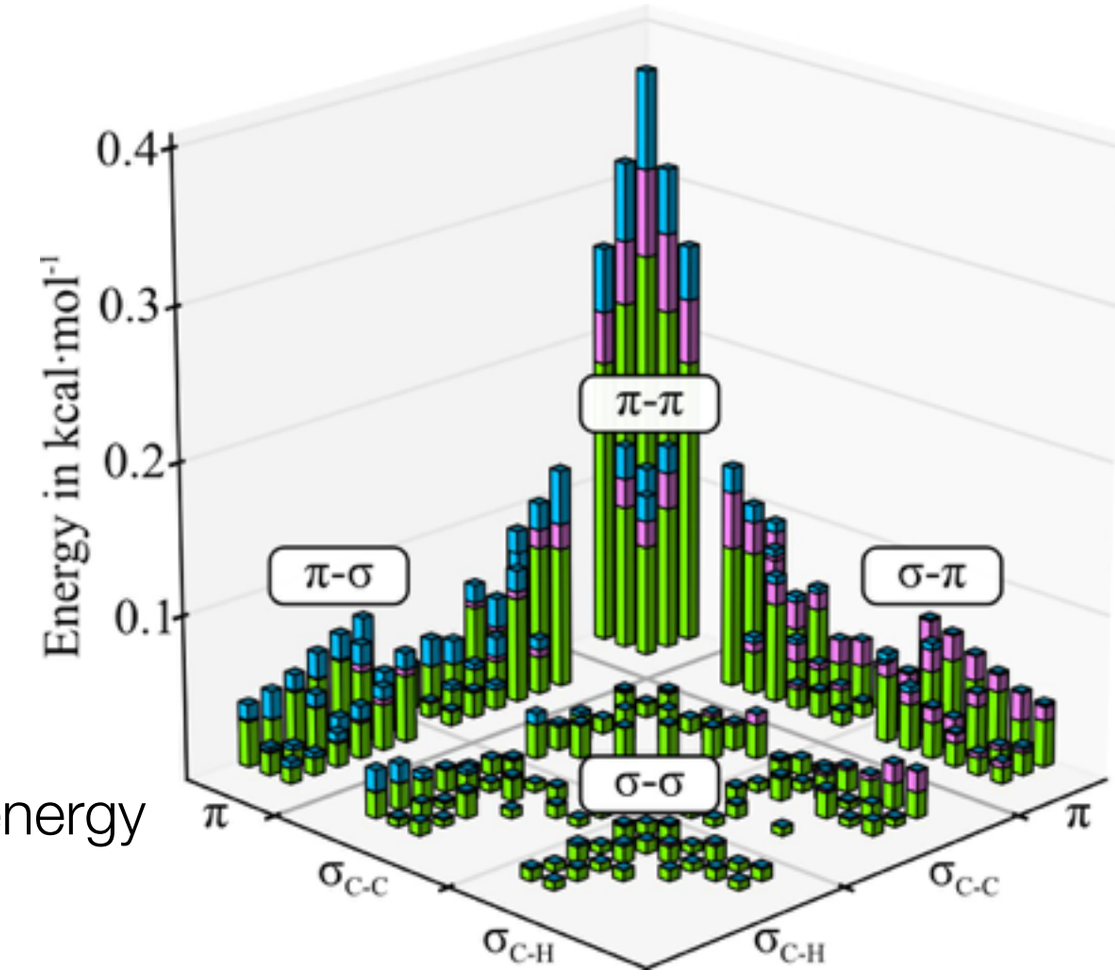
Benzene Dimer



Total DLPNO-CCSD(T)7cc-pVQZ interaction energy

2.07 kcal/mol

(inside experimental error)



30% π-π (9 pairs)
50% π-σ (72 pairs)
20% σ-σ (144 pairs)

W Schneider; G Bistoni, M Sparta, M Saitow, C Riplinger, A Auer, FN, **2016**, *JCTC,* in press