Local Correlation Approaches

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Problem with Wavefunction Methods

So why don't we use these accurate ab initio methods for our everyday theoretical chemistry?

Explosive cost

\[ \propto O^7(N) \]
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

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)


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


And the early coupled cluster work (mostly CCD)


… 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 $E_c \approx 10\ Eh=6270\ \text{kcal/mol}$

➡ Chemical accuracy is $\approx 1\ \text{kcal/mol}$

➡ The target accuracy **MUST** be 99.9 to 99.99% of $E_c$

➡ Error cancellation is NOT better than $\approx 1$ order of magnitude
Principles of Local Correlation Theory

Pretty much all local correlation methods:

\[ E_{\text{corr}} = \sum_{\text{Chunks } K=1}^{N_K} \delta E_K \approx \sum_{\text{Chunks } K' = 1}^{N_K' < N_K} \delta E_K^{(\text{approx})} \]

where „chunks“ =

- Fragments
- Atoms
- Atom Pairs
- Orbitals
- Orbital Pairs
- ...

Approximation 1

Approximation 2
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

\[ \hat{H}_{BO} (\Phi_{HF} + \sum \limits_{ia} C^i_a \Phi^a_i + (\frac{1}{2}!)^2 \sum \limits_{ijab} C^{ij}_{ab} \Phi^{ab}_{ij} + ...) = E \left( C^a_0 \Phi_{HF} + \sum \limits_{ia} C^i_a \Phi^a_i + (\frac{1}{2}!)^2 \sum \limits_{ijab} C^{ij}_{ab} \Phi^{ab}_{ij} + ... \right) \]

Multiply with the HF function from the left:

\[
\begin{align*}
\langle \Phi_{HF} | \hat{H}_{BO} | \Phi_{HF} \rangle &+ \sum \limits_{ia} C^a_i \langle \Phi_{HF} | \hat{H}_{BO} | \Phi^a_i \rangle + \frac{1}{4} \sum \limits_{ijab} C^{ab}_{ij} \langle \Phi_{HF} | \hat{H}_{BO} | \Phi^{ab}_{ij} \rangle \\
= &\quad \sum \limits_{ia} C^a_i \langle \Phi_{HF} | \Phi^a_i \rangle + \frac{1}{4} \sum \limits_{ijab} C^{ab}_{ij} \langle \Phi_{HF} | \Phi^{ab}_{ij} \rangle \\
= &\quad E \left( \langle \Phi_{HF} | \Phi_{HF} \rangle + \sum \limits_{ia} C^a_i \langle \Phi_{HF} | \Phi^a_i \rangle + \frac{1}{4} \sum \limits_{ijab} C^{ab}_{ij} \langle \Phi_{HF} | \Phi^{ab}_{ij} \rangle \right)
\end{align*}
\]

Thus:

\[
\frac{1}{4} \sum \limits_{ijab} C^{ij}_{ab} \langle ij || ab \rangle = \frac{1}{2} \sum \limits_{ij} \varepsilon_{ij} = E_{corr}
\]

(Nesbet's theorem)

If we know the precise values of the double excitation coefficients we know the EXACT correlation energy! It is a sum of PAIR CORRELATION ENERGIES
Approximation 1: Pair Approximation

\[ E_{corr} = \frac{1}{4} \sum_{ijab} C_{ab}^{ij} \langle ij \| ab \rangle = \frac{1}{2} \sum_{ij} \varepsilon_{ij} \]
The Leading Term of Electron Correlation

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

**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)

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

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

Use the bipolar expansion in real spherical harmonics:

\[
(i_a | j_b) \approx \sum_{l_a} \sum_{l_b} \sum_{m=l_a}^{l_b} \sum_{l'<l} d_{l_a l_b}^m Q_{l_a m}^{i_a} Q_{l_b m}^{j_b} \frac{R_{l_a + l_b + 1}}{4\pi} \frac{(2l_a + 1)(2l_b + 1)}{(l_a + m)(l_b + m)(l_a - m)(l_b - m)} (-1)^l m (l_a + l_b)!
\]

Distance between the center of the charge distributions

\[
Q_{lm}^{i_a} = \int r^l S_{lm}(\theta, \phi) \rho_{i_a}(r) dr
\]

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**

\[
(i_a | j_b) \propto R^{-3} \Rightarrow \varepsilon_{ij}^{SC-MP2} \propto R^{-6}
\]

This is the **pure dispersion (induced dipole-induced dipole) interaction**.
Chemically Speaking: How Local is the Correlation?

\[ \Delta E = +1.9 \pm 0.5 \text{ kcal/mol} \quad \text{Exp.} \]
-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!

Δ = 0.2 kcal/mol
Δ = 4.6 kcal/mol
Δ = 6.2 kcal/mol

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

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

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

\[
|\hat{\mu}\rangle = (1 - \sum_i |i\rangle \langle i|) |\mu\rangle
\]

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** \( \{\mu\}_{ij} \) is the union of the individual orbital domains

\[ \{\mu\}_{ij} = \{\mu\}_i \cup \{\mu\}_j \]
Orthonormal Localized Virtual Orbitals


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

\[
L = \sum_i \left| \left\langle \psi_i | (\mathbf{r} - \mathbf{R}_i)^4 | \psi_i \right\rangle \right|^2
\]

\[
\mathbf{R}_i = \left\langle \psi_i | \mathbf{r} | \psi_i \right\rangle
\]

- 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

✓ Jørgensen 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:

\[ \psi_i, \psi_j \Rightarrow P, Q \]

\[ \psi_a, \psi_b \Rightarrow \overline{P}, \overline{Q} \]

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

› Expansion of the correlation energy:

\[ E_C = \sum_P E_P + \sum_{P<Q} \Delta E_{PQ} \]

\[
\begin{align*}
E_P &= \frac{1}{2} \sum_{i<j \in P} \sum_{ab} (t_{ab}^{ij} + t_{ba}^{ij}) \langle ij \mid \parallel ab \rangle \\
\Delta E_{PQ} &= \frac{1}{2} \sum_{i \in P, j \in Q, P} \sum_{ab} (t_{ab}^{ij} + t_{ba}^{ij}) \langle ij \mid \parallel ab \rangle - E_P - E_Q
\end{align*}
\]

still exact!

The DEC family of methods

- Local approximations

\[ E_P \approx \frac{1}{2} \sum_{i<j \in P} \sum_{a,b \in \bar{P}} (t_{ab}^{ij} + t_{ai}^i t_{bj}^j) \langle ij \parallel ab \rangle \]

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 \( \text{FOT} \)

\[ E_P \approx \frac{1}{2} \sum_{i<j \in P} \sum_{a,b \in \bar{P}} (t_{ab}^{ij} + t_{ai}^i t_{bj}^j) \langle ij \parallel ab \rangle \]

- Orbital truncation step

Truncate the AO contributions to the occupied and virtual MOs according to a completeness relation with threshold \( \delta \). 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

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

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

### Table

<table>
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<th>no. alanines</th>
<th>$E_{corr}$ (au)</th>
<th>$\Delta E_{corr}$ (au)</th>
<th>% of $E_{corr}$</th>
<th>orb. spread (Å)</th>
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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

\[ E_C = \sum_{ia} t^i_a f_{ia} + \frac{1}{4} \sum_{ijab} (t^i_{ab} + t^i_a t^j_b) \langle ij \parallel ab \rangle \]

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

\[ E_C = \sum_i \delta E_i \quad \delta E_i = \sum_a t^i_a f_{ia} + \frac{1}{4} \sum_{jab} (t^i_{ab} + t^i_a t^j_b) \langle ij \parallel ab \rangle \]

let the occupied orbital be localized.

Replace:

\[ \psi_i (r) = \sum_{\mu} c_{\mu i} \mu (r) \rightarrow \psi_i (r) \approx \sum_{\mu \in \{i\}} c_{\mu i} \mu (r) \]

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

The Cluster in Molecules (CIM) Approach

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

$\rightarrow$ Environment $[i]=[i, j_{1i}, j_{2i}, \ldots, j_{Ni}]$

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

$\rightarrow$ 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

$\rightarrow$ 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 $N_{\text{occ}}$ 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 integrals are computed multiple times
An Integral-Direct Linear-Scaling Second-Order Møller–Plesset Approach

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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 \textit{two different types of sparsity}

\textbf{Additive}

\[ f_i = \sum_k x_{ki} g_k \]

\textit{e.g.} \( i \rangle = \sum_\mu c^{i \mu}_\mu | \mu \rangle \)

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

\textbf{Sparse Map:} \( L(f \rightarrow g) = \{ L_1, L_2, \ldots, L_M \} \) (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:

\[ SPI_{ik} \equiv \sqrt{fg \mid fg} = \sqrt{\int \int \frac{f_i(r_1)g_k(r_1)f_i(r_2)g_k(r_2)}{|r_1 - r_2|} dr_1 \; dr_2} \]

- ✓ 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)

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

\[
DOI_{ik} = \sqrt{\int |f_i(r)|^2 |g_k(r)|^2 \, dr}
\]

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

\[(i \tilde{\mu} \mid K) = \sum_{\mu \nu} c_{\mu \tilde{\mu}}^{L} \tilde{P}_{\nu \tilde{\mu}}(\mu \nu \mid K)\]

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:**

$$\mathbf{L}(f \rightarrow \nu) \rightarrow \mathbf{L}(f \rightarrow \nu_s)$$

shells

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

atoms

**Union & Dissection:**

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

**Chaining**

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

We have developed a C++ object library that implements sparse map operations
Example 2: Linear Scaling 3-Index Transformation

\[
(i\tilde{\mu} \mid K) = \sum_{\mu} c^L_{\mu i} \tilde{P}_{\mu\tilde{\mu}} (\mu\nu \mid K)
\]

Loop over auxiliary basis function shell \(K_s\)

# primitive integral transformation
Loop over basis functions \(\mu \in L_K(K \rightarrow \mu)\)
   Loop over basis functions \(\nu \in L_K(K \rightarrow \nu)\)
      Compute integrals \((\mu \nu \mid K)\)
      Buffer integrals \(I_K(\mu \nu) = (\mu \nu \mid K)\)
   End Loop \(\nu\)
End Loop \(\mu\)

# actual transformation
Loop over MOs \(i \in I_K(K \rightarrow i)\)
   Loop over \(\nu \in L_K(K \rightarrow \nu)\)
      \((i\nu \mid K) = 0\)
      Loop \(\mu \in L_K(K \rightarrow \mu)\) \& \(I_1(i \rightarrow \mu)\) \((i\nu \mid K) = c^L(\mu, i) \times I_K(\mu \nu)\)
   End Loop \(\nu\)
End Loop \(i\)

Loop over PAOs \(\tilde{\mu} \in L(K \rightarrow \tilde{\mu})\)
   Loop over MOs \(i \in L(K \rightarrow i)\)
      \((i\tilde{\mu} \mid K) = 0\)
      Loop \(\nu \in L(K \rightarrow \nu)\) \& \(L(\tilde{\mu} \rightarrow \nu)\) \((i\tilde{\mu} \mid K) = -P_{\nu\tilde{\mu}} (i\nu \mid K)\)
      Store \((i\tilde{\mu} \mid K)\)
   End Loop \(\tilde{\mu}\)
End Loop \(K\)

\(O(N)\) operations on the current auxiliary shell

\(L(K \rightarrow i) = L^{-1}(i \rightarrow K)\)

\(L(K \rightarrow \mu) = L(K \rightarrow i) \subset L(i \rightarrow \mu)\)

\(L(K \rightarrow \nu) = L(K \rightarrow i) \subset L(i \rightarrow \tilde{\mu}) \subset L(\tilde{\mu} \rightarrow \nu)\)

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

\[ E^{(2)} = \min(2 \langle \Psi^{(1)} | H | \Psi^{(0)} \rangle + \langle \Psi^{(1)} | H_0 - E_0 | \Psi^{(1)} \rangle) \]

It readily leads to an orbital invariant formulation of MP2

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

\[ H = H_0 + V \quad H_0 = F, \quad V = H - H_0 \]

Local MP2 Theory

\[
\langle \Psi^{(1)} | H | \Psi^{(0)} \rangle = \frac{1}{4} \sum_{ijab} C_{ab}^{ij} \langle ij || ab \rangle
\]

\[
\langle \Psi^{(1)} | H_{0} - E_{0} | \Psi^{(1)} \rangle = \frac{1}{8} \sum_{ijabc} C_{ab}^{ij} F_{cb} C_{ac}^{ij} - \frac{1}{8} \sum_{ijkab} C_{ab}^{ij} F_{jk} C_{ab}^{ik}
\]

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

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

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:

\[
\Psi^{(1)} = \frac{1}{4} \sum_{ij\mu\nu} C_{\mu\nu}^{ij} \Phi_{ij}^{\mu\nu}
\]
Local MP2 Theory

The residual becomes:

\[
R_{\mu\nu}^{ij} = \langle ij \parallel \tilde{\mu} \tilde{\nu} \rangle + \sum_c (F_{\mu\kappa} C_{\kappa\tau}^{ij} \tilde{S}_{\tau\nu} + \tilde{S}_{\mu\kappa} C_{\kappa\tau}^{ij} F_{\tau\nu}) - \sum_k (F_{ik} \tilde{S}_{\mu\kappa} C_{\kappa\tau}^{kj} \tilde{S}_{\tau\nu} + F_{kj} \tilde{S}_{\mu\kappa} C_{\kappa\tau}^{ik} \tilde{S}_{\tau\nu}) = 0
\]

or:

\[
R_{ij} = K_{ij} + (FC_{ij}^{\tilde{S}} + \tilde{SC}_{ij}^{\tilde{F}}) - \sum_k (f_{ik} \tilde{SC}_{kj}^{\tilde{S}} + f_{kj} \tilde{SC}_{ik}^{\tilde{S}}) = 0
\]

With the PAO overlap matrix \( \tilde{S}_{\mu\nu} = \langle \tilde{\mu} \parallel \tilde{\nu} \rangle \)

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.

---

Local MP2 Theory

Using the domains, the residual becomes

\[ R_{ij}^{ij} = K_{ij}^{ij} + (F_{(ij)}^{(ij)} C_{ij}^{ij} \tilde{S}_{(ij,ij)} + \tilde{S}_{(ij,ij)} C_{ij}^{ij} F_{(ij)}) - \sum_k (f_{ik} \tilde{S}_{(ij,kj)}^{(ij,kj)} C_{kj}^{ik} \tilde{S}_{(kj,ij)}^{(kj,ij)} + f_{kj} \tilde{S}_{(ij,ik)}^{(ij,ik)} C_{ik}^{ik} \tilde{S}_{(ik,ij)}^{(ik,ij)}) = 0 \]

Where all matrices are now local:

\[
\begin{align*}
R_{\mu\nu}^{ij} &\rightarrow R_{\mu\nu}^{ij} \\
K_{\mu\nu}^{ij} &\rightarrow K_{\mu\nu}^{ij} \\
F_{\mu\nu}^{(ij)} &\rightarrow F_{\mu\nu}^{(ij)} \\
\tilde{S}_{\mu\nu}^{(ij,kl)} &\rightarrow \tilde{S}_{\mu\nu}^{(ij,kl)}
\end{align*}
\]

\[ \checkmark \quad \text{Sub-matrices can either be stored or constructed on the fly} \]

Two more steps are necessary to reach linear scaling

1. **Discard weakly interacting electron pairs:**
   In almost all local treatments done by distance criteria \((R_{ij}=\text{distance between orbital centroids})\)

2. **Discard small terms in the sum over } k\text{ by analyzing } f_{ik}, f_{jk}\text{**
   Threshold } F_{\text{Cut}} \sim 10^{-5} \text{ Eh}
Amplitude Update

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

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

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

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

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:

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

And in each iteration update the amplitudes according to:

$$C^{ij}_{\tilde{\mu}\tilde{\nu}} \leftarrow C^{ij}_{\tilde{\mu}\tilde{\nu}} - \frac{R^{ij}_{\tilde{\mu}\tilde{\nu}}}{\varepsilon_{\tilde{\mu}} + \varepsilon_{\tilde{\nu}} - f_{ii} - f_{jj}} \quad (\tilde{\mu}\tilde{\nu} \in \{ij\})$$
Hierarchical treatment of electron pairs, multipole approximations, careful thresholding lead to efficient, linear scaling algorithms.
Problems with PAO based treatments


FIG. 7. LMP2 and LCCSD localization errors (in mEh) 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:

Calculation of smooth potential energy surfaces using local electron correlation methods

Ricardo A. Mata and Hans-Joachim Werner

Improvements of Local MP2

1. **RI/DF Approximation of $K_{ij}$**

2. **Pseudospectral construction of $K_{ij}$**
   RB Murphy, MD Beachy, RA Friesner, MN Ringnalda J. Chem. Phys., **1995**, **103**, 1481

3. **Laplace Transformation**

...
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?

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.

- $T_{DO}=0.1$ 98.4% $E_{corr}$  $N_{avPAO}=115$
- $T_{DO}=0.01$ 99.7% $E_{corr}$  $N_{avPAO}=588$
- $T_{DO}=0.001$ 99.9% $E_{corr}$  $N_{avPAO}=935$
Virtual Space Compaction: Pair Natural orbitals
Exploit Sparsity!

Compress Data!

\[ M = \begin{pmatrix} \vdots \end{pmatrix} \xrightarrow{M' = U^T MU} \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \]
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 Hermitian, and it is therefore possible to find a unitary matrix $U$ which transforms this matrix to diagonal form with the eigenvalues $n_{kk} = n_k$:

$$U^* \gamma U = n = \text{diagonal matrix.} \quad (72)$$

We have further, in matrix form, $\gamma = U^n U^*$, and, if we introduce a new set of spin-orbitals $\chi_k$ by the matrix relation $\chi = \psi U$, or

$$\chi_k = \sum \alpha \psi_\alpha U_{ik}, \quad (73)$$

we may rewrite the density matrix in the form

$$\gamma(x'_1|x_1) = \sum_k n_k \chi_k^*(x'_1) \chi_k(x_1). \quad (74)$$

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

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.
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 $\psi_k$ to occur in the expansion of the total wave function $\Psi$. If only $M$ of the numbers $\gamma(k)$, $k = 1, 2, 3, \ldots$, are essentially different from zero, then the number of essential terms in (66) is given by the corresponding number of possible configurations: $M! / M! (M-N)!$. 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 $\psi_k$ 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

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

which fulfills the inequality of $0 \leq \vartheta < 1$. In considering different basic sets $\psi_1, \psi_2, \psi_3, \ldots$ for the description of the same total wave function $\Psi$, it is clear that the natural spin-orbitals $\chi_k$ are characterized by having the smallest $\vartheta$ value possible. According to (72), we have $\gamma = U n U^\dagger$ and $\gamma^2 = U n^2 U^\dagger$, leading to $\text{Tr}(\gamma^2) = \text{Tr}(n^2)$ and

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

with the final result

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

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 $\vartheta$, 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 $T_{\text{CutNO}} (< 10^{-7})$
Pseudonatural Orbitals as a Basis for the Superposition of Configurations. I. He$_2^+$

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AND

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(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$_2$ 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

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

\[ T_{ab}^{ij} = -\frac{K_{ab}^{ij}}{\varepsilon_a - \varepsilon_b - \varepsilon_i - \varepsilon_j} \]

\[
\begin{align*}
D_{ij} &= \frac{1+\delta_i}{\mathcal{N}} (\tilde{T}_i^j - T_i^j + \tilde{T}_i^j T_i^j) \\
\tilde{T}_i^j &= \frac{1}{1+\delta_j} (4T_i^j - 2T_i^j - )
\end{align*}
\]

\[ \mathcal{N} = 1 + \langle \tilde{T}_i^j | T_i^j \rangle \]

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

\[ D_{ij} d_{ij} = n_{ij} d_{ij} \]

\[ |\tilde{a}_i^{ij} \rangle = \sum_{a} a_{a}^{ij} |a\rangle \]

\[ |a\rangle = \sum_{\tilde{a}_i^{ij}} a_{\tilde{a}_i^{ij}} |\tilde{a}_i^{ij}\rangle \]

PNOs with occupation numbers below \( T_{\text{CutPNO}} \) are neglected

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

\[ G_{ij} = F + K_{ij} - J_{ij} \]

\[ G_{ij} = F + K_{ij} + K_{ij} - \frac{1}{2} J_{ij} + \frac{1}{2} J_{ij} \]
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:

\[
T_1 + T_2 = \sum_{ia} t_{\tilde{a}_i} a_i^+ a_i + \frac{1}{4} \sum_{ijab} t_{\tilde{a}_i \tilde{a}_j} a_i^+ a_i^+ a_j a_i
\]

- PNO’s for doubles are made from DLPNO-MP2 and cut with \(T_{\text{CutPNO}}\)
- PNO’s for singles are identical to the PNOs of the diagonal pairs and cut with \(0.01T_{\text{CutPNO}}\)

The **PNOs** are expanded in large PAO domains (using \(T_{\text{CutDO}}\)) for domain construction and \(T_{\text{CutMKN}}\) for aux-domain construction

\[
\left| \tilde{a}_{ij} \right\rangle = \sum_{\tilde{\mu} \in \{ij\}} d_{\tilde{a} \tilde{a}}^{ij} \left| \tilde{\mu} \right\rangle
\]
PNO based Correlation Equations

PNO-CI Wavefunction:

\[ \psi = \psi_{\text{HF}} + \sum_{i} t_{i}^\psi \psi_{i}^r + \sum_{i \leq j} \sum_{c, d} T_{c,d}^\psi \psi_{c,d}^r \]

\[ \bar{T}^\psi = d^\psi + T^\psi d^\psi \]

\( \Rightarrow \) very compact Linear, scaling number of doubles amplitudes (reduction > factor > 10^7)

PNO-CI Doubles Residual:

\[ \sigma_{a \bar{a}}^{\delta \bar{\delta}} = \bar{K}_{a \bar{a}}^{\delta \bar{\delta}} + K(\bar{T}^\psi)_{a \bar{a}} + (d^\psi | F d^\psi T^\psi + \bar{T}^\psi d^\psi F d^\psi )_{a \bar{a}} \]

\[ \sum_{\ell} (F_{\ell \bar{\ell}}^\prime (S_{\ell \bar{\ell}} + \bar{T}^\psi S_{\ell \bar{\ell}})_{a \bar{a}} | F_{\ell \bar{\ell}}^\prime (S_{\ell \bar{\ell}} + \bar{T}^\psi S_{\ell \bar{\ell}})_{a \bar{a}} ) + \sum_{\ell \bar{\ell}} (\ell \bar{\ell}) (S_{\ell \bar{\ell}} + \bar{T}^\psi S_{\ell \bar{\ell}})_{a \bar{a}} \]

\[ \sum_{\ell} \left\{ S_{\ell \bar{\ell}} (2 \bar{T}^\psi + \bar{T}^\psi T^\psi )_{a \bar{a}} + \frac{1}{2} J_{a \bar{a}} d^\psi + \frac{1}{2} J_{a \bar{a}} (\bar{T}^\psi + \bar{T}^\psi T^\psi )_{a \bar{a}} \right\} \]

\[ \sum_{\ell} \left\{ \frac{1}{2} S_{\ell \bar{\ell}} T^\psi + d^\psi + \frac{1}{2} d^\psi + J_{a \bar{a}} S_{\ell \bar{\ell}} + \frac{1}{2} d^\psi + J_{a \bar{a}} S_{\ell \bar{\ell}} \right\} \]

\[ S_{a \bar{a}}^{\delta \bar{\delta}, \alpha \bar{\alpha}} = \langle \tilde{a} | \tilde{b} \rangle \langle \tilde{a} | \tilde{b} \rangle_{a \bar{a}} \]

Natural Triple Excitations

Our suggestion: Natural triples orbitals (TNO’s)

✓ Three-pair density: \[ D_{ijk} = \frac{1}{3} (D_{ij} + D_{ik} + D_{jk}) \]

\((The \ operator \ \hat{D}_{ijk} = \sum \langle \bar{a}_{ij} | \bar{a}_{ij} \rangle + \sum \langle \bar{a}_{ik} | \bar{a}_{ik} \rangle + \sum \langle \bar{a}_{jk} | \bar{a}_{jk} \rangle \ projects \ onto \ the \ joint \ PNO \ space \ of \ the \ three \ pairs)\)

✓ Formation of the three pair density in the PAO basis is linear scaling:

✓ Eigenfunctions: \[ D_{ijk} x_{ijk} = n_{ijk} x_{ijk} \] (cut-off below a given \( n_{ijk}(\text{min}) \) just as for PNOs)

✓ Recanonicalize: \[ x_{ijk} + F x_{ijk} \]

✓ Amplitudes are projected into the TNO basis: \[ T_{\bar{a}_{ijk}, \bar{b}_{ijk}}^{ij:TNO} = S_{\bar{a}_{ijk}, \bar{c}_{ij}}^{ijk,ij} T_{\bar{c}_{ij}, \bar{d}_{ij}}^{ij:PNO} S_{\bar{b}_{ijk}, \bar{d}_{ijk}}^{ijk,ij} \]

→ 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

Scaling of LPNO-CCSD

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

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)

(In)sensitivity to the Nature of the Localized Orbitals

3.2.3 Dependence of the results on the localization method

A further dependence of the results could result from the localization method. This subject was investigated on two test systems with two different basis sets. The results in Table 1 demonstrate that the dependence of the LPNO-CEPA/1 energies on the localization method is extremely weak – correlation energies only differ by a few hundredth of a kcal/mol despite the fact that the Pipek-Mezey procedure keeps the π/σ-separation while the Foster-Boys localization produces banana-type bonds in benzene. Moreover, with basis sets that contain diffuse functions the Pipek-Mezey localization algorithm produces some very poorly localized orbitals that will eventually be problematic for local correlation methods that use real-space criteria for truncation. An example is one of the C-H bonds in benzene as shown in Figure 7. Obviously, the Pipek-Mezey procedure leads to LMOs in this case that show artificial delocalized tails while the Foster-Boys procedure behaves as expected. It is gratifying to observe that despite the unphysical behavior of the Pipek-Mezey MOs, the LPNO-CEPA/1 results obtained are almost identical to those that are based on the Foster-Boys orbitals (Table 1). Since we consider the Foster-Boys localization criteria to be more physically sound, our default procedure is based on this method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Molecule</th>
<th>(E_{\text{tot}}) [Eh]</th>
<th>(E_{\text{tot}}) (LPNO-CEPA/1) - (E_{\text{tot}}) (CEPA/1) [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPNO-CEPA/1 benzene</td>
<td>benzene</td>
<td>-231.555559</td>
<td>0.51</td>
</tr>
<tr>
<td>(cc-pVDZ)</td>
<td>octahedran</td>
<td>-463.079091</td>
<td>1.46</td>
</tr>
<tr>
<td>LPNO-CEPA/1 benzene</td>
<td>benzene</td>
<td>-231.586412</td>
<td>0.53</td>
</tr>
<tr>
<td>(aug-cc-pVDZ) octahedran</td>
<td>-463.145835</td>
<td>1.63</td>
<td>1.79</td>
</tr>
</tbody>
</table>
Basis Set Dependence of DLPNO Methods

\[ N_{PNO} \propto \sqrt{N_{bas}} \]
DLPNO-CCSD(T): Summary

1. **(relative) Simplicity.** Only one critical cut-off ($T_{\text{CutPNO}}$); local approximations
   only 'boost' efficiency. $T_{\text{CutPNO}}$ can be used 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**