Linear Scaling Coupled Cluster Theory

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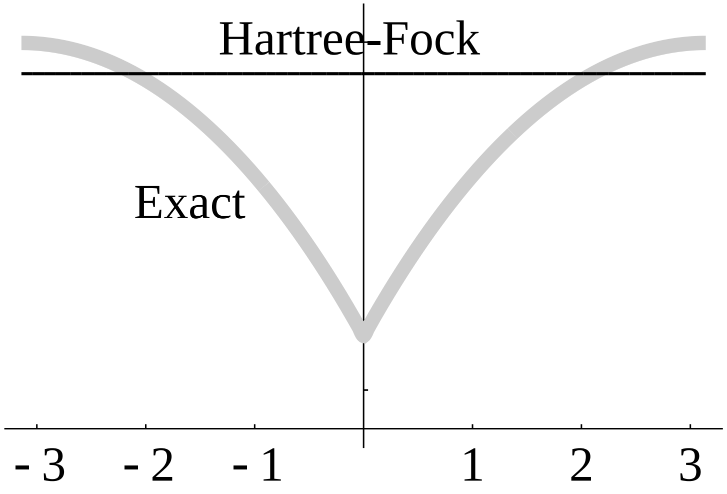
Electron Correlation

The Wavefunction for small interelectronic distances $z_2 - z_1$:



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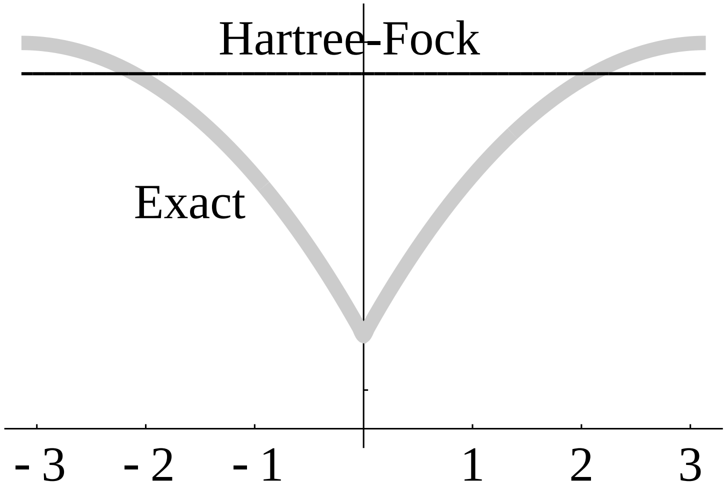

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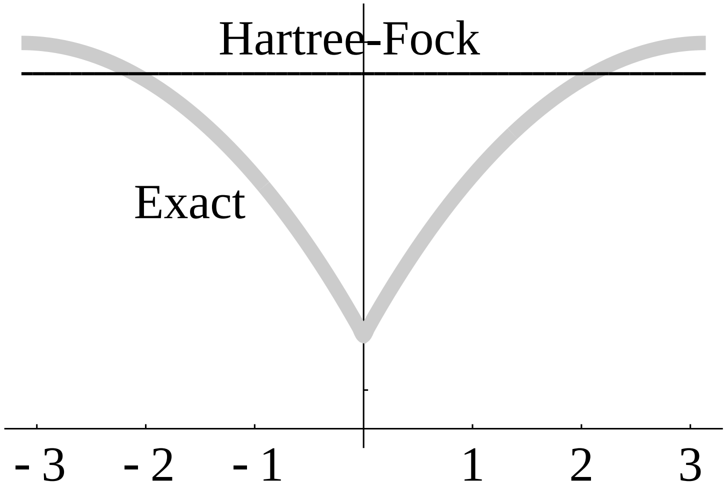

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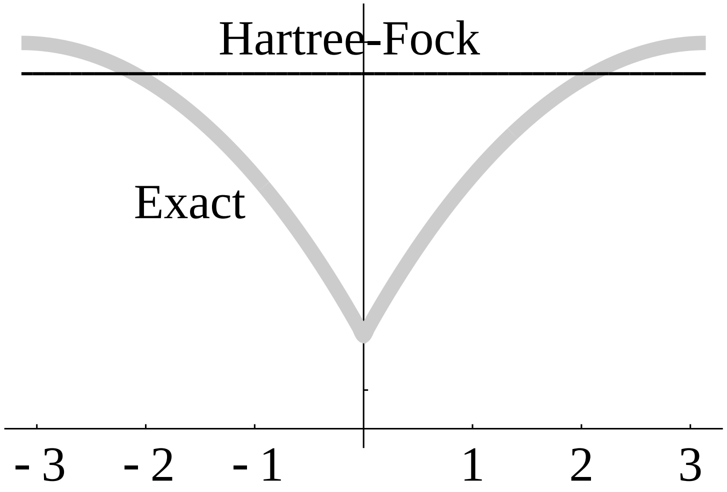

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- Present in all chemical systems

- Short-range effect
  $\propto R^{-6}$ (dispersive forces in intermolecular perturbation theory)

Canonical Electron Correlation Methods

Dynamical Electron Correlation described by Pair-Excitations from occupied into unoccupied (virtual) Molecular Orbitals.

Simplest Theory of Electron Correlation:

Møller-Plesset Perturbation Theory of 2nd Order

$$\Psi = \Psi_{\mathrm{HF}} + \frac{1}{2} \sum_{ij} \sum_{ab} T^{ij}_{ab} \Phi^{ab}_{ij}$$

Φ^{ab}_{ij} *Doubly excited Determinants*: $i, j \rightarrow a, b$

T^{ij}_{ab} *Amplitudes* (Coefficients, determined by perturbation theory)

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- Number of Amplitudes grows with 4th power of molecular size: $\mathcal{O}(\mathcal{N}^4)$
- Computational cost increases with 5th power of molecular size: $\mathcal{O}(\mathcal{N}^5)$

The Scaling Problem of Electron Correlation Methods

Hierarchy of Electron Correlation Methods:

Method	Nominal	with Prescreening	CPU($2\mathcal{N}$)/CPU($\mathcal{N}$)
HF	$\mathcal{N}^4$	$\mathcal{N} - \mathcal{N}^2$	$2 - 4$
MP2	$\mathcal{N}^5$	$\mathcal{N}^3$	8
CCSD	$\mathcal{N}^6$	$\mathcal{N}^6$	64
CCSD(T)	$\mathcal{N}^7$	$\mathcal{N}^7$	128
CCSDT-1b	$\mathcal{N}^7$	$\mathcal{N}^7$	128
CCSDT	$\mathcal{N}^8$	$\mathcal{N}^8$	256

- **Computational Cost (CPU, Memory, Disk) increases dramatically with Molecular Size ! ($\mathcal{N}^x$ Scaling Wall)**

- The more accurate the method, the higher the scaling.

- **Even the largest Supercomputers provide no solution to this problem:**

512 nodes $\equiv$ Factor of 2.45 in $\mathcal{N}$
1024 nodes $\equiv$ Factor of 2.69 in $\mathcal{N}$

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Why Local Correlation Methods ?

- Dynamical Correlation Effects are *Short Range* (Dispersion energy $\propto r^{-6}$)
- Scaling problem of conventional methods is an artifact of the *canonical* (delocalized) Molecular Orbitals that are used to describe occupied and virtual MO spaces...

$\Rightarrow$ **SOLUTION:** Use of *local basis* to span occupied and virtual MO spaces

- Short range nature of dynamical correleation effects can be fully exploited
- $\mathcal{O}(\mathcal{N})$ Algorithms become possible
- Molecules with 50–100 atoms in application range of present high-accuracy local correlation methods

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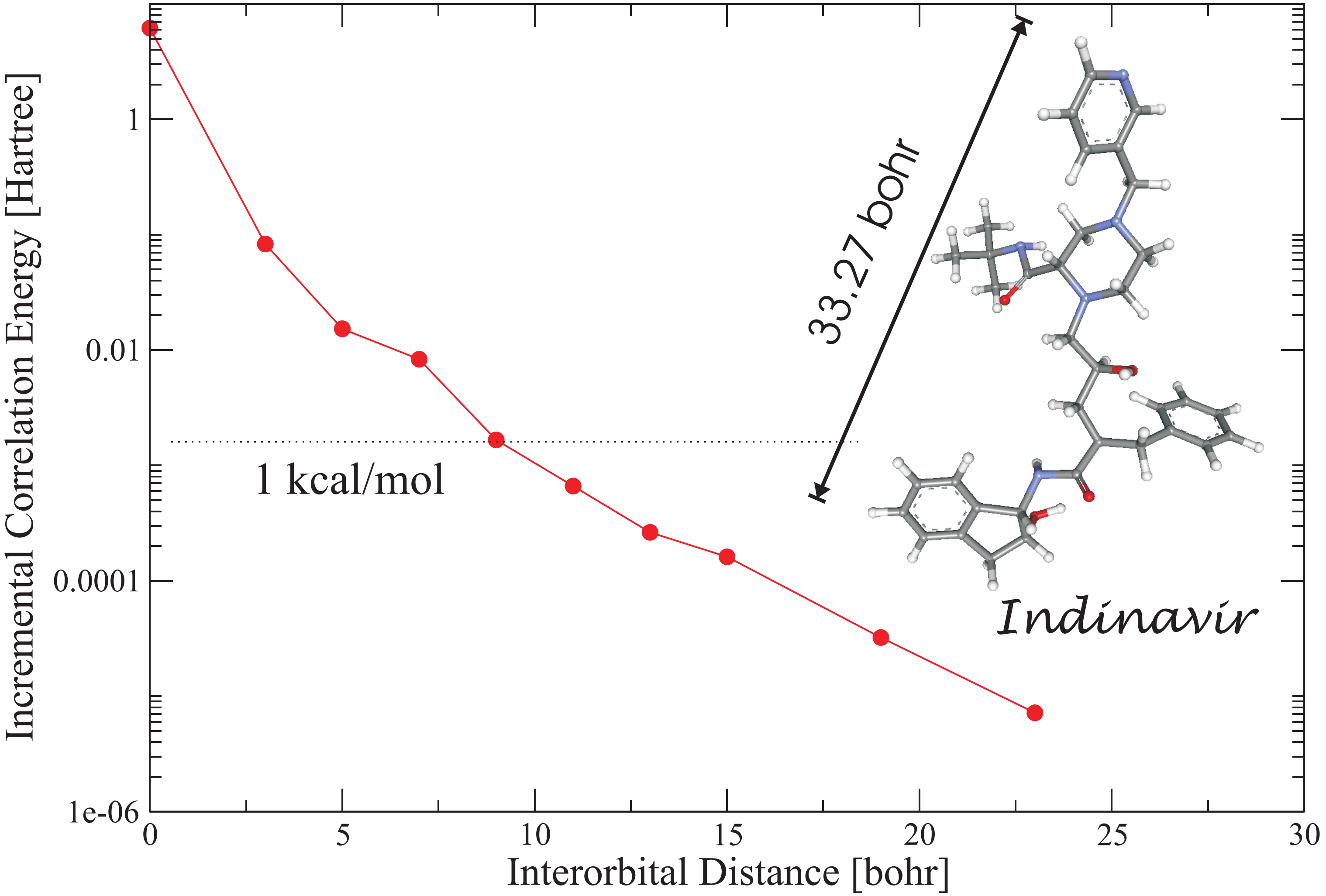
Distance Histogram of Correlation Energy



⇒ For $R = 0 \implies$ 98.26 % of the correlation energy is obtained!

Brief History of Local Correlation Methods

Sinanoglu (1964), Nesbet (1965), Kutzelnigg, Ahlrichs (1968)
Otto and Ladik (1982), Laidig, Purvis, Bartlett (1982-1985)
Kapuy and Kozmuta (1983, 1991)
Pulay (1983), Saebø and Pulay (1985-1988)
Kirtman and Dykstra (1986)
Stollhoff, Fulde, Vasilopoulos (1986)
Murphy, Beachy, Friesner, Rignalda (1995)
Reynolds, Martinez, Carter (1996)
Knab, Förner, Cicek, Ladik (1996)
Maslen and Head-Gordon (1998)
local CCSD: Hampel, Werner (1996)
linear scaling local MP2: Schütz, Hetzer, Werner (1999)
linear scaling, local CCSD: Schütz, Werner (2000)
linear scaling, local CCSD(T): Schütz (2000)
linear scaling, local CCSDT-1b: Schütz (2001)

The Local Basis for the Occupied Space

- **Localized Molecular Orbitals (LMOs):**
  generated from *occupied* Hartree-Fock orbitals by *Unitary Transformation*
  $\Rightarrow$ Mutual Orthogonality is preserved

- Various Localization Procedures (presently two implemented):
  - **Boys:**
    Maximize distances between centers of charge
  - **Pipek-Mezey:**
    Minimize number of atoms with significant LMO contributions

- Localization procedure has hardly any influence on the outcome of a Local Correlation calculation !

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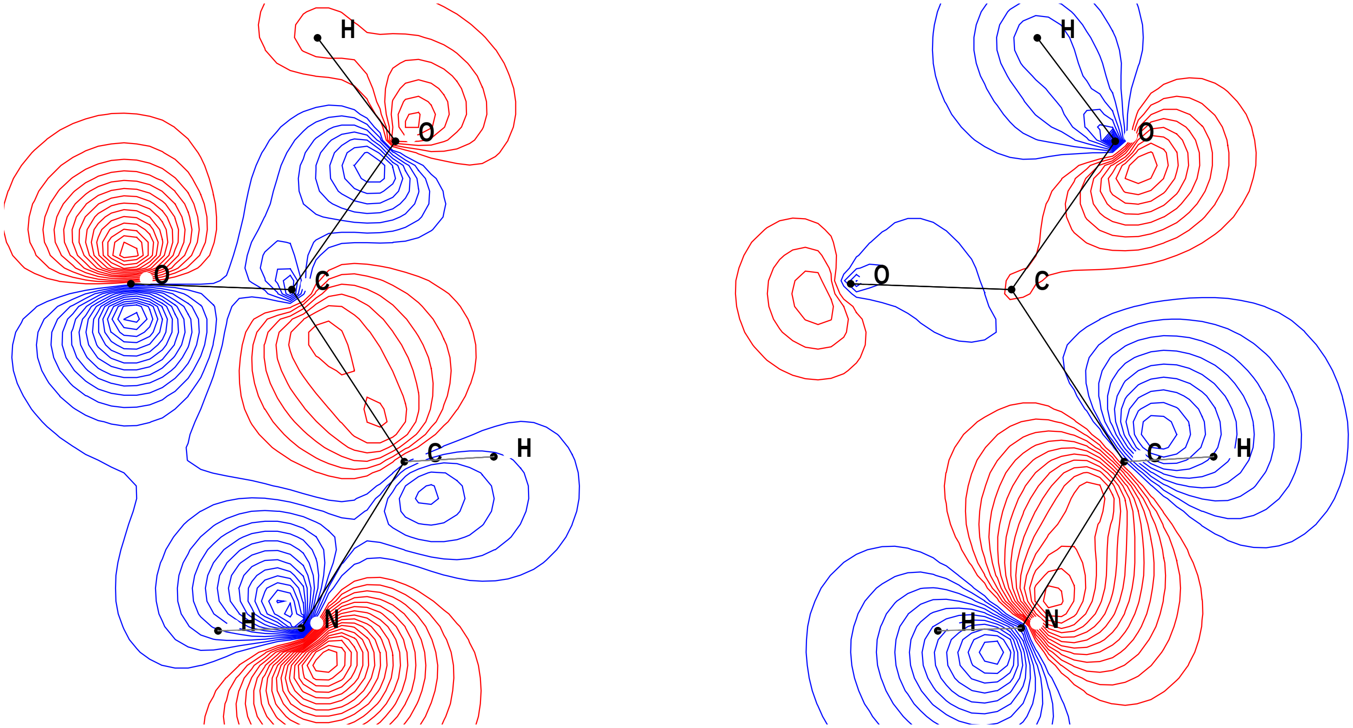
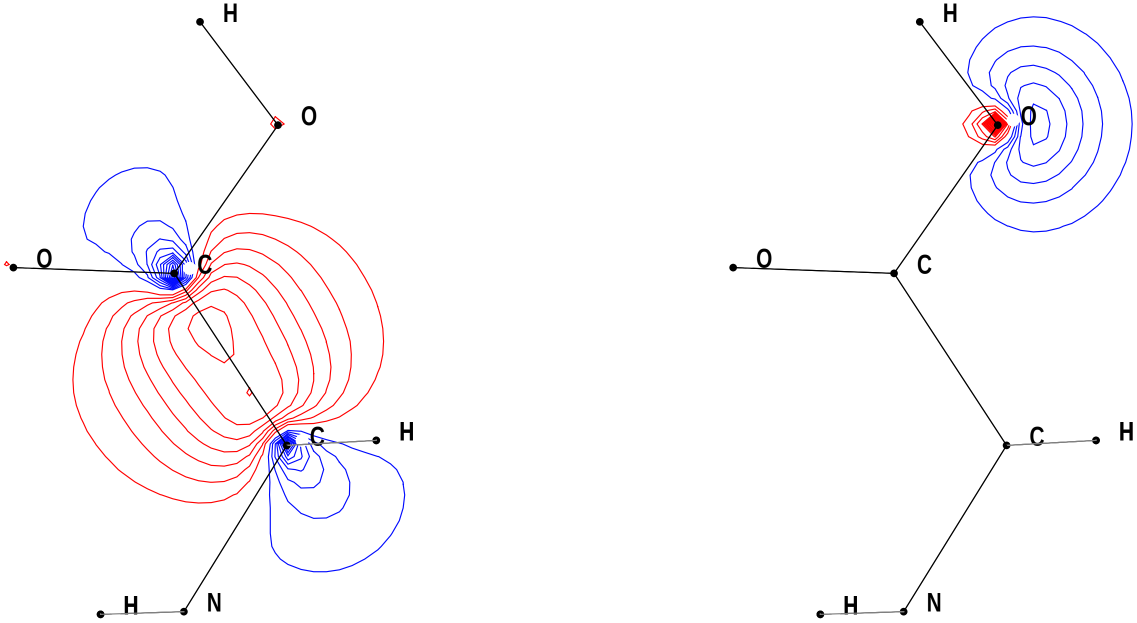
Glycine Molecule: Canonical MOs...



- ...entirely delocalized...

- destroys local character of dynamical correlation

Glycine Molecule: ... and Localized MOs (LMOs)



- Typically localized on one or two atoms...

⇒ appropriate for description of dynamical correlation effects

GOTO LMP2

The projected AO Basis for the virtual space (PAOs)

- Localization of virtual MOs (by unitary transformation) not possible

⇒ Mutual orthogonality has to be abandonned

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- The original, inherently local AO basis is used

- The occupied space is projected out

$$|\tilde{\phi}_r\rangle \quad = \quad \left(1 - \sum_{i=1}^{m} |\phi_i\rangle\langle\phi_i|\right) \; |\chi_r\rangle$$

⇒ Orthogonality between occupied and virtual space is maintained

⇒ PAO basis spans *exactly* the same space as the original virtual canonical Hartree-Fock MOs

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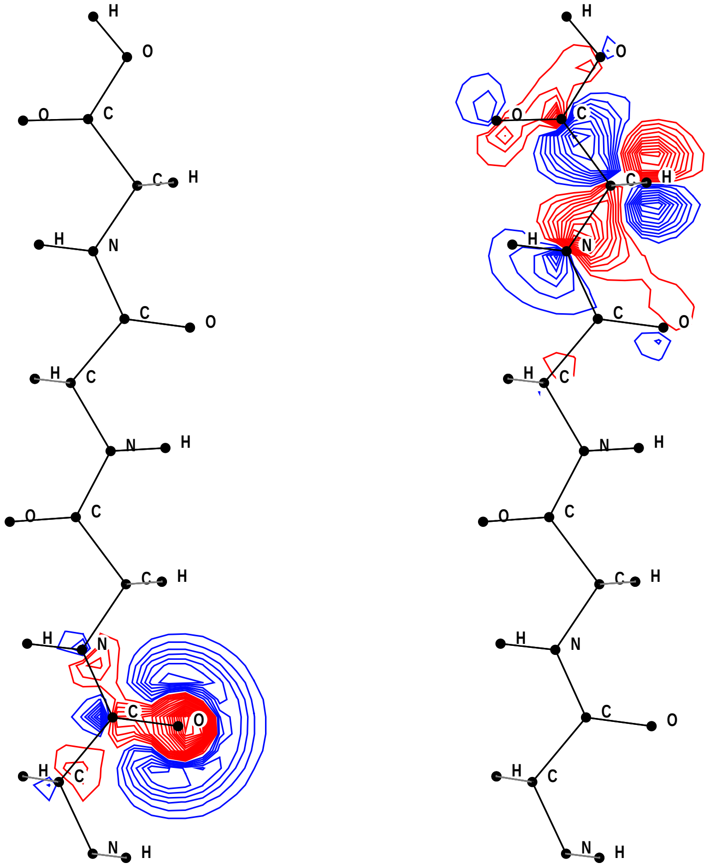
Properties of PAOs

- PAOs can be assigned to individual atoms
- Inherently local
- Not orthogonal
- Linear dependencies (# PAOs = # AOs)

(Gly)$_4$-Peptide PAOs



Excitation Domains

($\tilde{\phi}_r \leftarrow \phi_i$: Exponential decay with respect to separation between ϕ_i and $\tilde{\phi}_r$)

- To each LMO ϕ_i an Orbital Domain $[i]$ is assigned.
  - (comprises all PAOs $\tilde{\phi}_r$ of atoms spatially close to the related LMO ϕ_i)
  - Orbital Domains are generated fully automatically (Boughton-Pulay)

- Single Excitations Φ_i^r restricted to Orbital Domains $r \in [i]$

- Pair Excitations Φ_{ij}^{rs} restricted to *Pair Domains* $r, s \in [ij] = [i] \cup [j]$

- Triple Excitations Φ_{ijk}^{rst} restricted to *Triple Domains* $r, s, t \in [ijk] = [ij] \cup [k]$

- The sizes of all domains are $\mathcal{O}(1)$!

$\Rightarrow$ **Number of amplitudes per Orbital/Paar/Triple $\mathcal{O}(1)$!**

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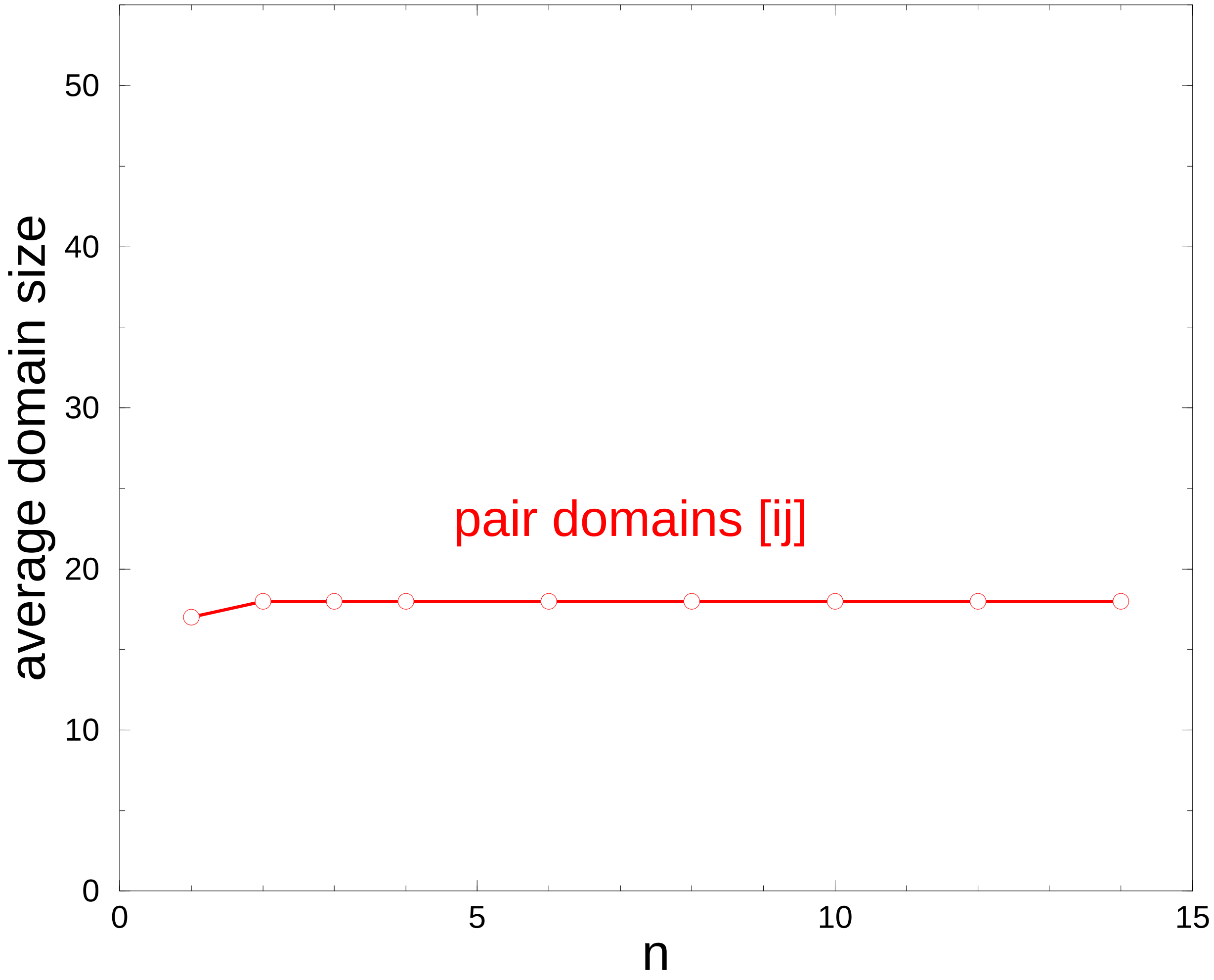

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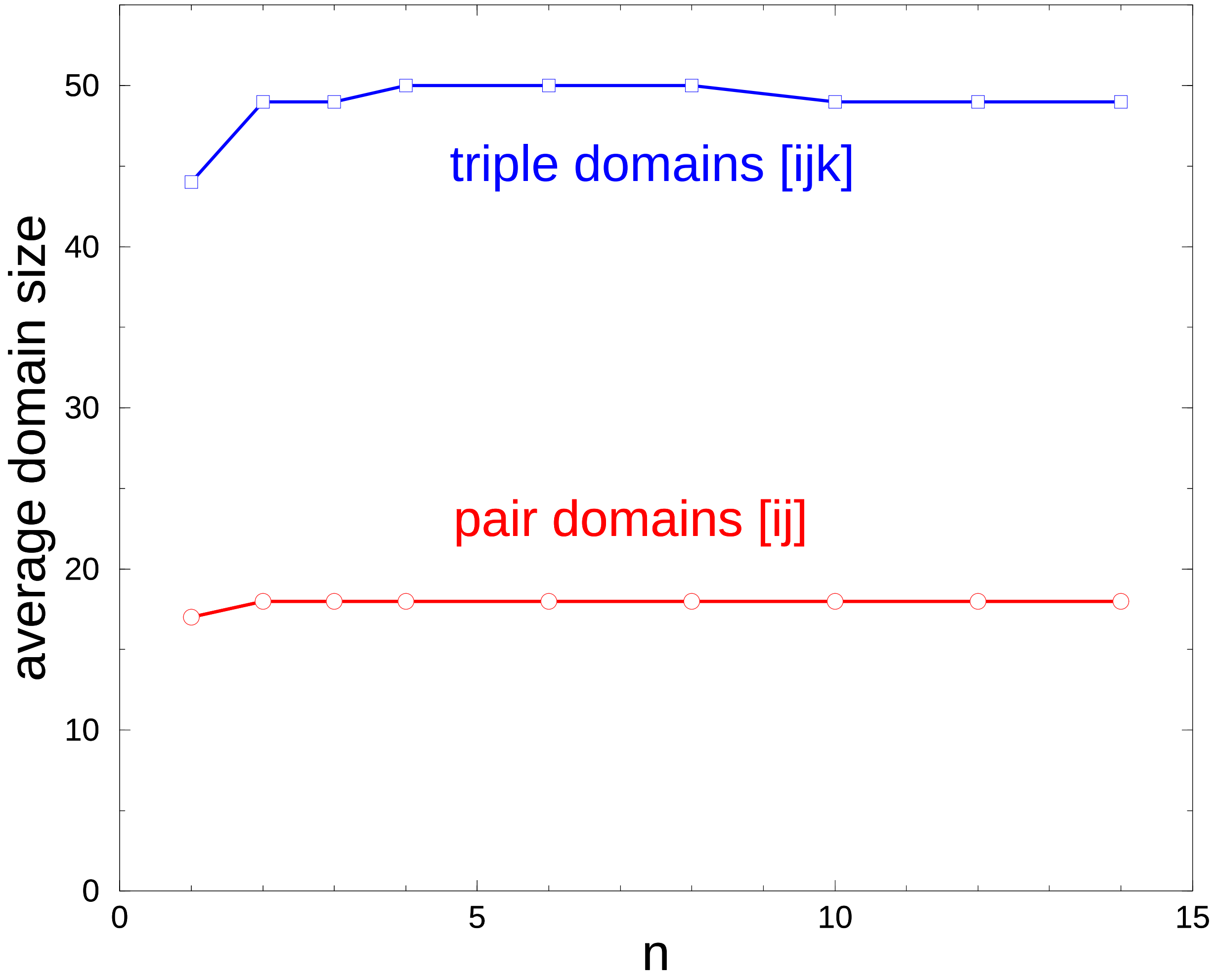

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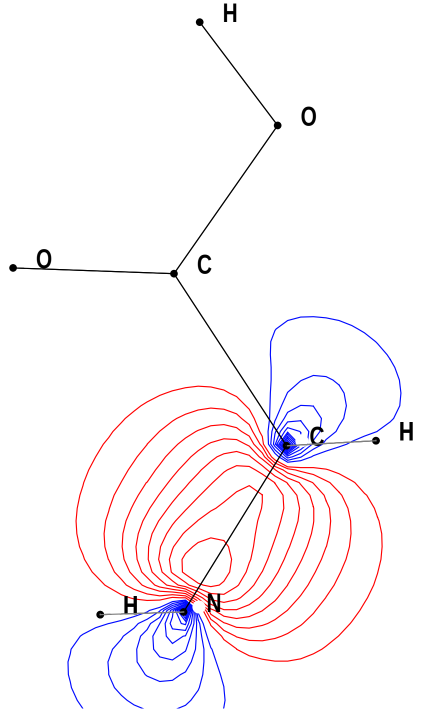

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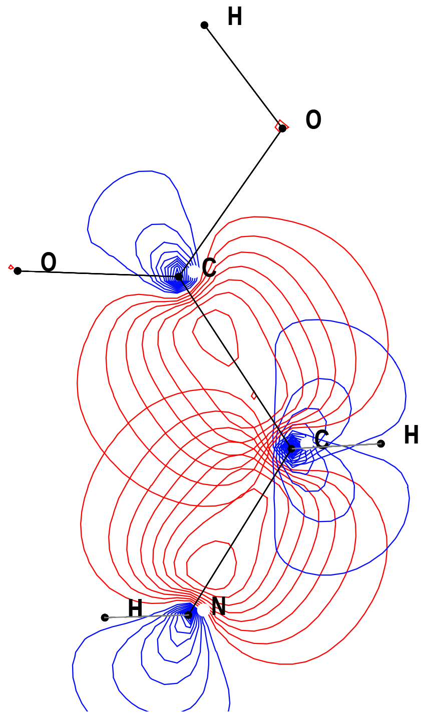

- LMOs have at least one atom in common

- Cover 90-95% of the correlation energy

- Treatment at highest correlation level: LCCSD, LCCSD(T)

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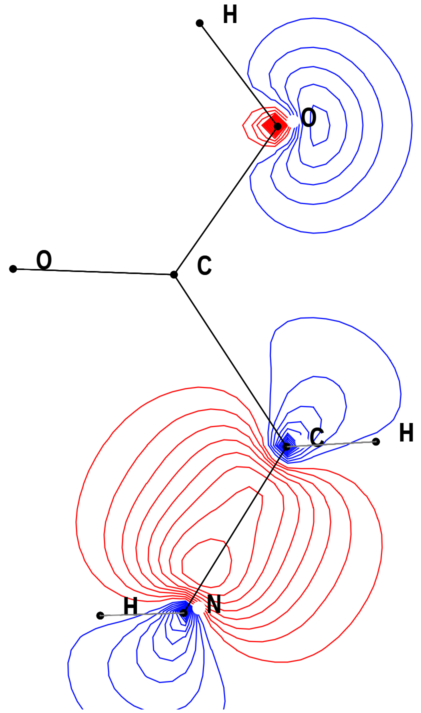
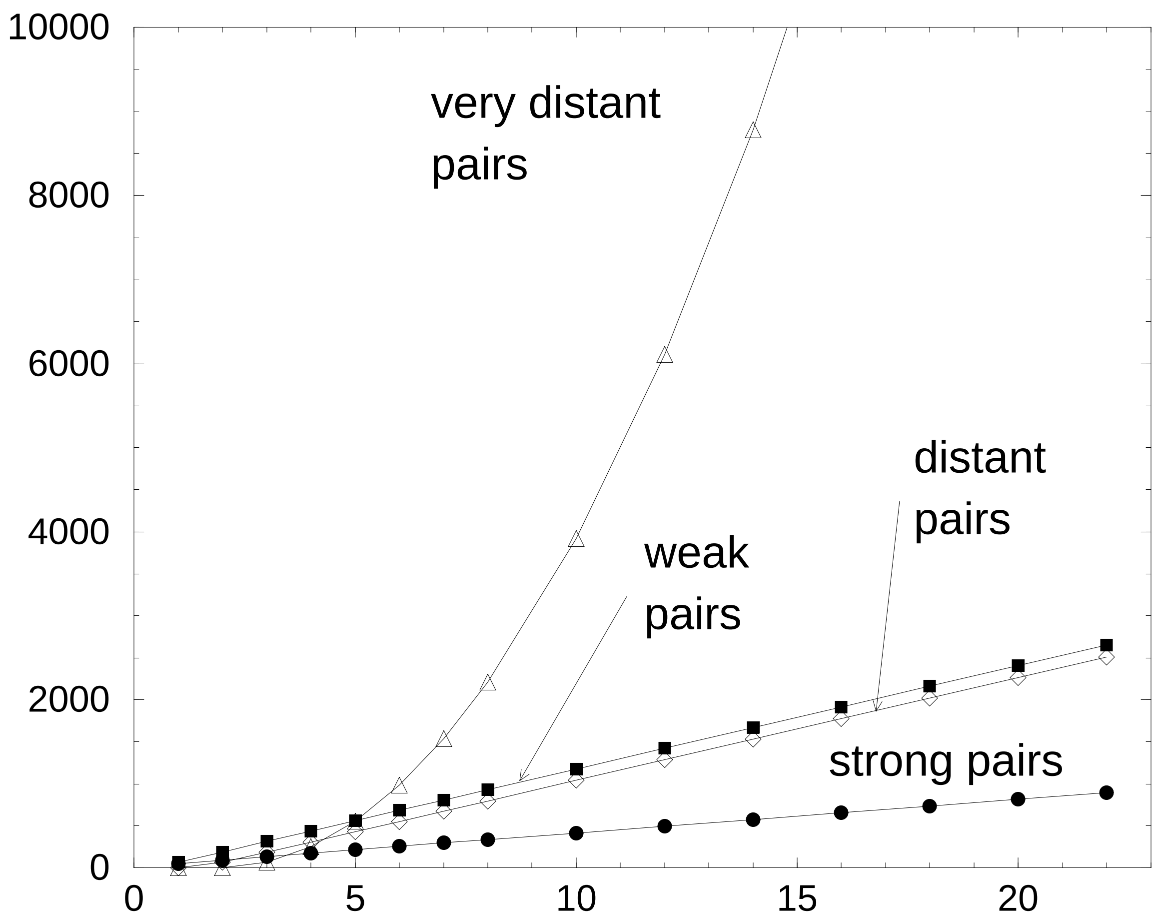


- LMOs separated by at least one chemical bond
- Cover 5-10% of the correlation energy
- Treatment at the LMP2 level

Hierarchy of the Electron Pairs



- Number of Pairs entering each correlation level (LMP2/LCCSD) are $\mathcal{O}(\mathcal{N})$

- Only the number of very distant Pairs are $\mathcal{O}(\mathcal{N}^2)$ (these are dropped from the calculation)

Local MP2

$$\begin{aligned}\mathbf{R}^{ij} &= \mathbf{K}^{ij} + \mathbf{F}\mathbf{T}^{ij}\mathbf{S} + \mathbf{S}\mathbf{T}^{ij}\mathbf{F} - \sum_k \mathbf{S}\left[F_{ik}\mathbf{T}^{kj} + F_{kj}\mathbf{T}^{ik}\right]\mathbf{S} \;:= \; \mathbf{0} \\ E^{(2)} &= \sum_{ij}\sum_{rs\in[ij]}(2T^{ij}_{rs} - T^{ij}_{sr})K^{ij}_{rs}\end{aligned}$$

- Fock Matrix is NOT diagonal, amplitudes are coupled via **F**
- virtual orbitals NOT orthogonal ⇒ Couplings via $\mathbf{S}$

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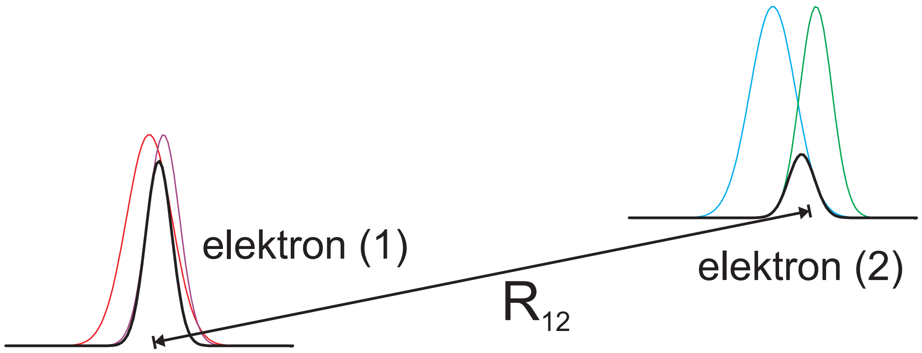
⇒ Computational cost $\mathcal{O}(\mathcal{N})$!

Screening of Electron Repulsion Integrals

$\int\int \qquad r \qquad dr\,dr$



- cheap estimate of integral based on Schwarz inequality

$$|(\mu\rho|\nu\sigma)| \leq [(\mu\rho|\mu\rho)(\nu\sigma|\nu\sigma)]^{\frac{1}{2}}$$

- $(\mu\rho|\nu\sigma)$ decreases exponentially with distance between χ_μ & χ_ρ, χ_ν & χ_σ

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$\Rightarrow$ Number of relevant integrals scales with $\mathcal{O}(\mathcal{N}^2)$.

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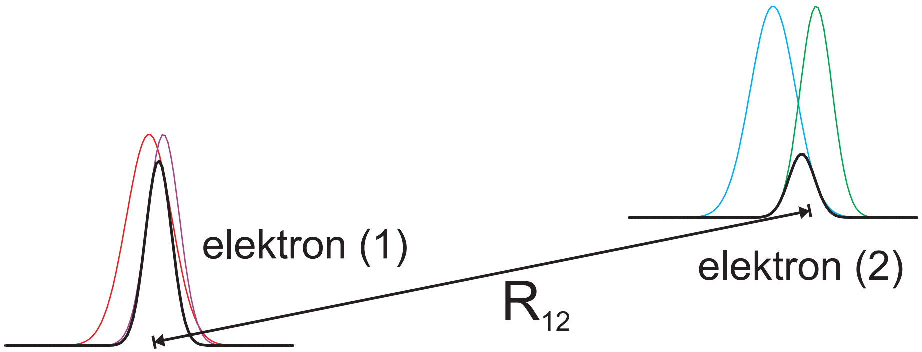

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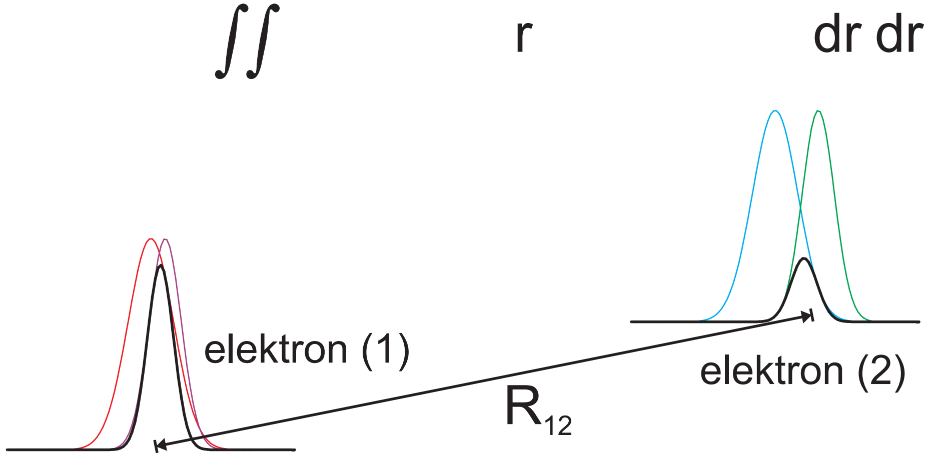

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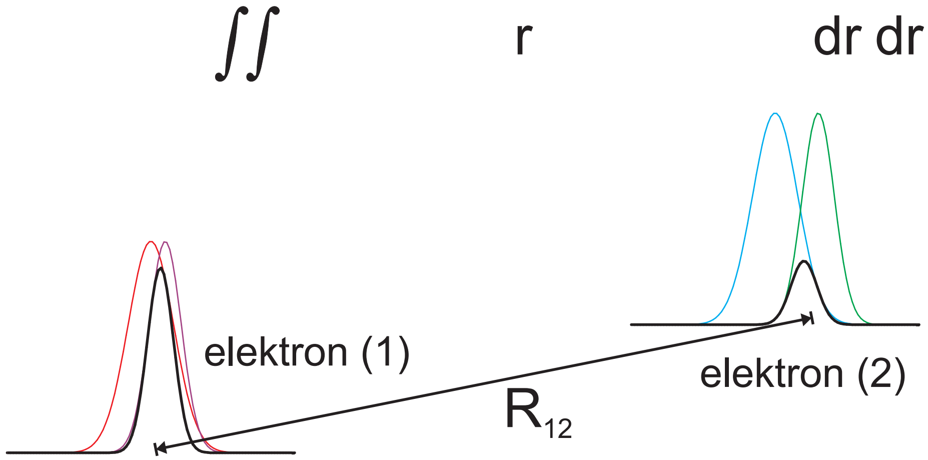

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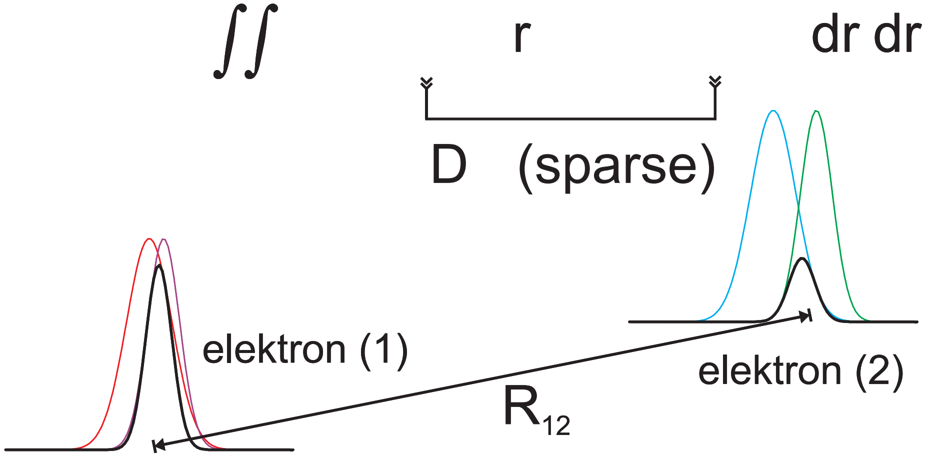

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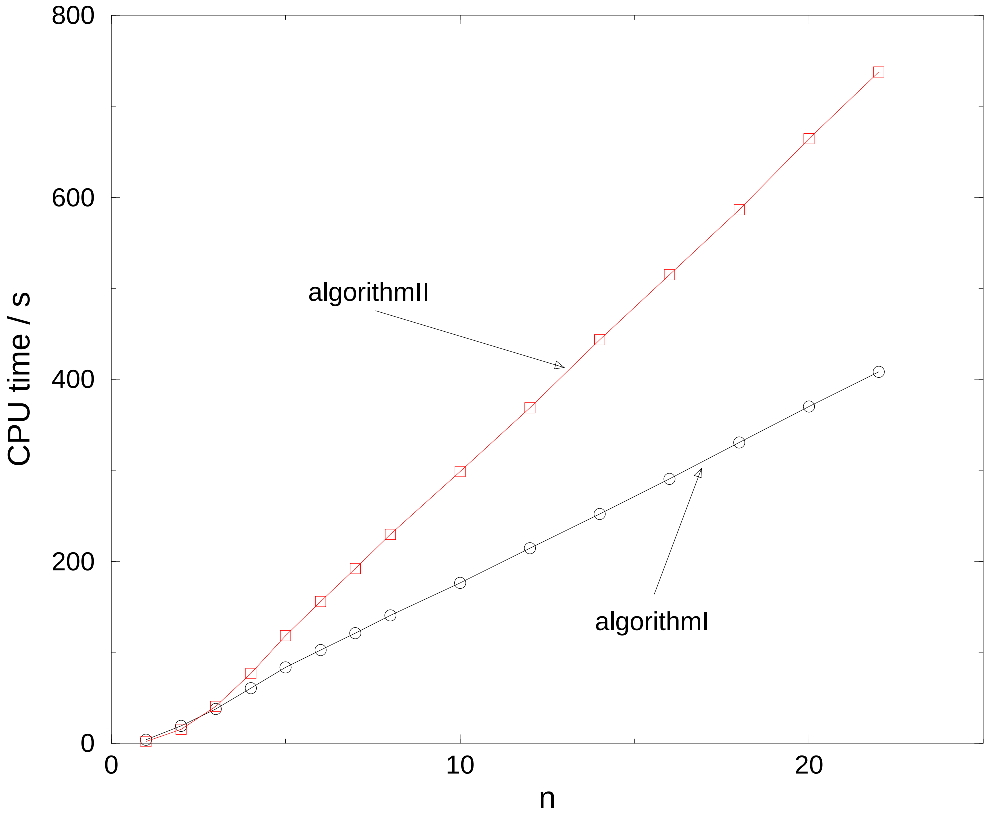
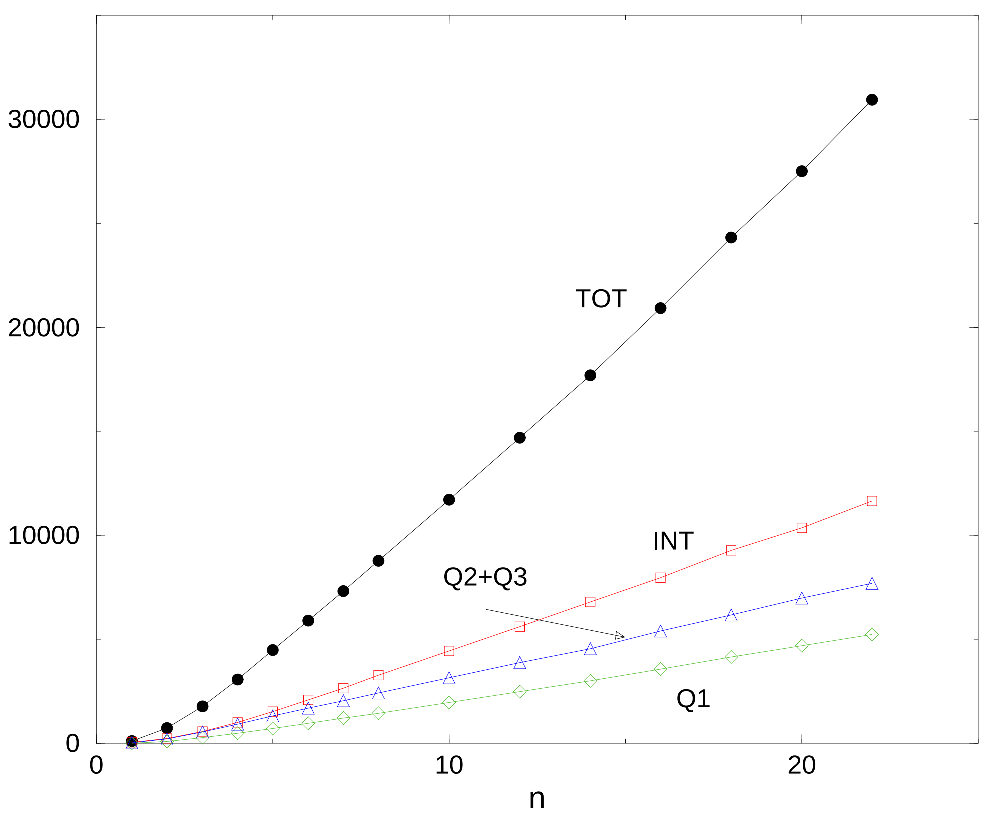
$\Rightarrow$ With Integral/Density product prescreening
$\rightarrow$ $\mathcal{O}(\mathcal{N})$ scaling for exchange-type contractions

LMP2 Scaling behaviour, CPU-time

System: Glycine-Polypeptid [Gly]$_n$ / VDZ Basis ([Gly]$_{22}$: 1586 BF/492 El.)
Hardware: Linux Pentium II/450 MHz



Iterative Solution of Amplitude Equations

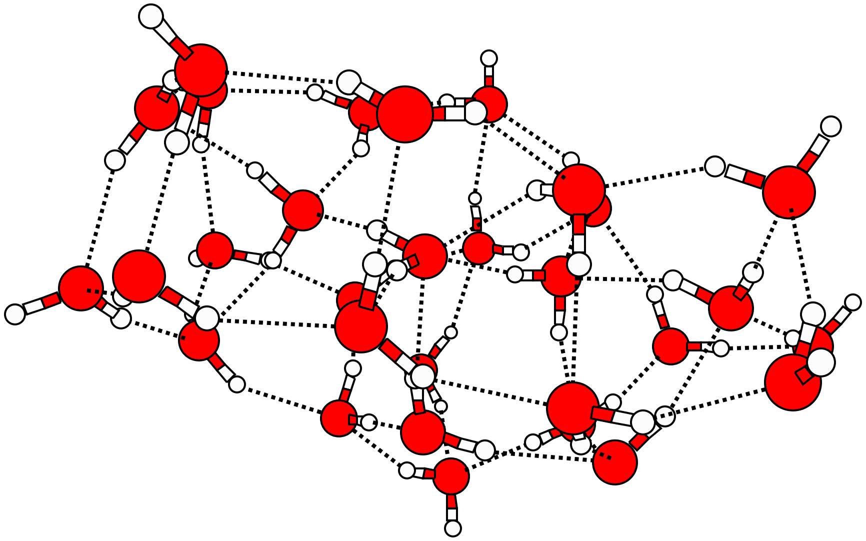


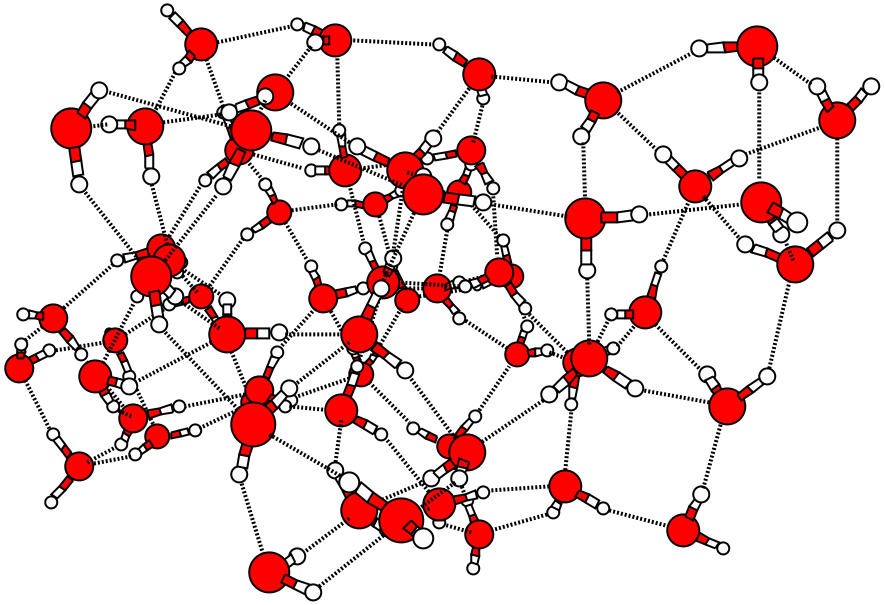
Direct Integral Transformation

GOTO LCCSD

LMP2 CPU-times for 3-D Water Clusters

System: $(H_2O)_n$, $n = 30, 60$ /VDZ Basis:





n=30 / 720 BF
Memory: 9.92 MW
$t(\mathbf{K}^{ij}) = 4.3$ h
$t(\mathrm{iter}) = 12$ min

n=60 / 1440 BF
Memory: 27.21 MW (1.49)
$t(\mathbf{K}^{ij})$=15.7 h (1.84)
$t(\mathrm{iter})$=39 min (1.29)

For comparison: LinK in linear scaling SCF :[1]
Scaling between $(H_2O)_{50}$ and $(H_2O)_{100}$: 1.83

---

[1] Ochsenfeld, White and Head-Gordon, J.Chem.Phys. 109, 1663 (1998)

GOTO LCCSD

Coupled Cluster Theory

- CC wave function generated from reference wave function Φ_0 by an *exponential excitation operator*:

$$\Psi^{\mathrm{CC}} = \exp(\hat{T})\Phi_0, \quad \exp(\hat{T}) = 1 + \hat{T} + \frac{1}{2!}\hat{T}\hat{T} + \frac{1}{3!}\hat{T}\hat{T}\hat{T}\ldots$$

- Products of excitation operators $\Rightarrow$ size consistency

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  (for CCSD model: Truncation after double excitations ⇒ $\hat{T} = \hat{T}_1 + \hat{T}_2$)

- CC Equations: Projection of the Schrödinger eq. onto subspaces of(Zero-, One-, Two-… fold excitations)

$$\begin{aligned} E &= \langle \Phi_0 | \hat{H} \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle, \\ r_r^i &= \langle \Phi_i^r | (\hat{H} - E) \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle \ = \ 0, \\ R_{rs}^{ij} &= \langle \bar{\Phi}_{ij}^{rs} | (\hat{H} - E) \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle \ = \ 0. \end{aligned}$$

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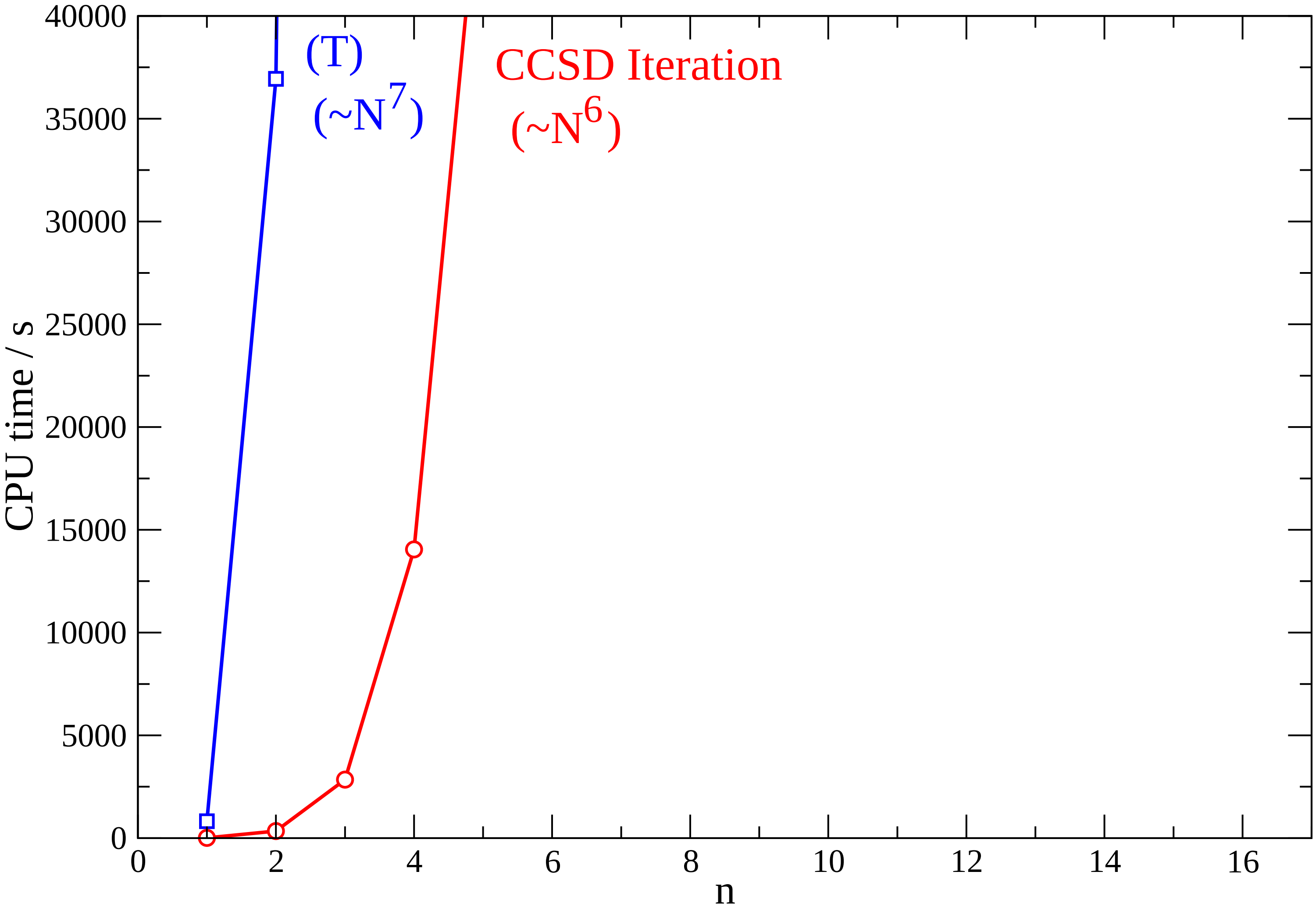
Scaling of CPU-time for for Local Coupled Clusters

System: Glycine-Polypeptide $[\mathrm{Gly}]_n$ / VDZ Basis: ($[\mathrm{Gly}]_{16}$: 1160 BF/360 El.)
Hardware: 1 GHz Athlon PC



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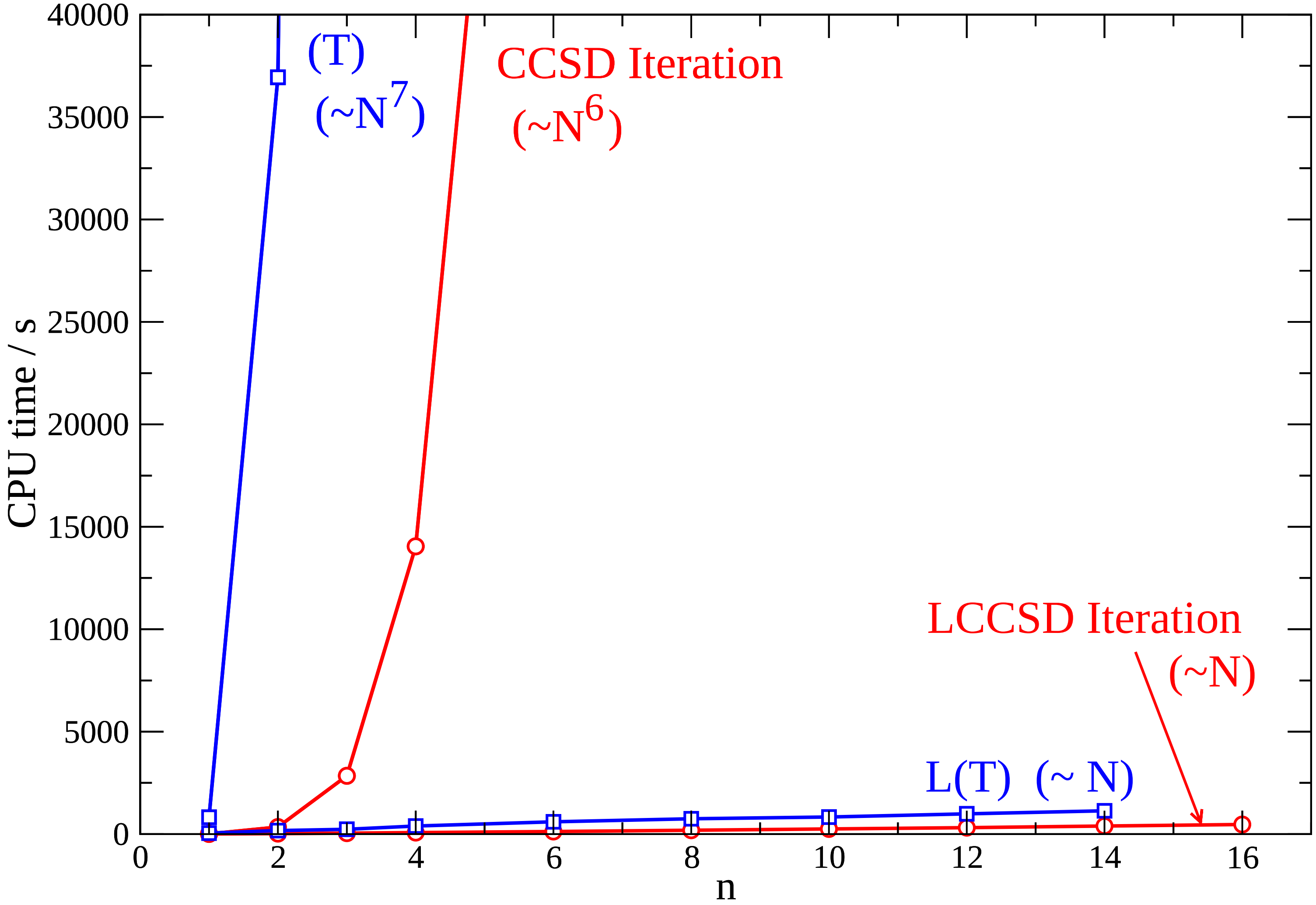

Scaling of CPU-time for Integral Transformations

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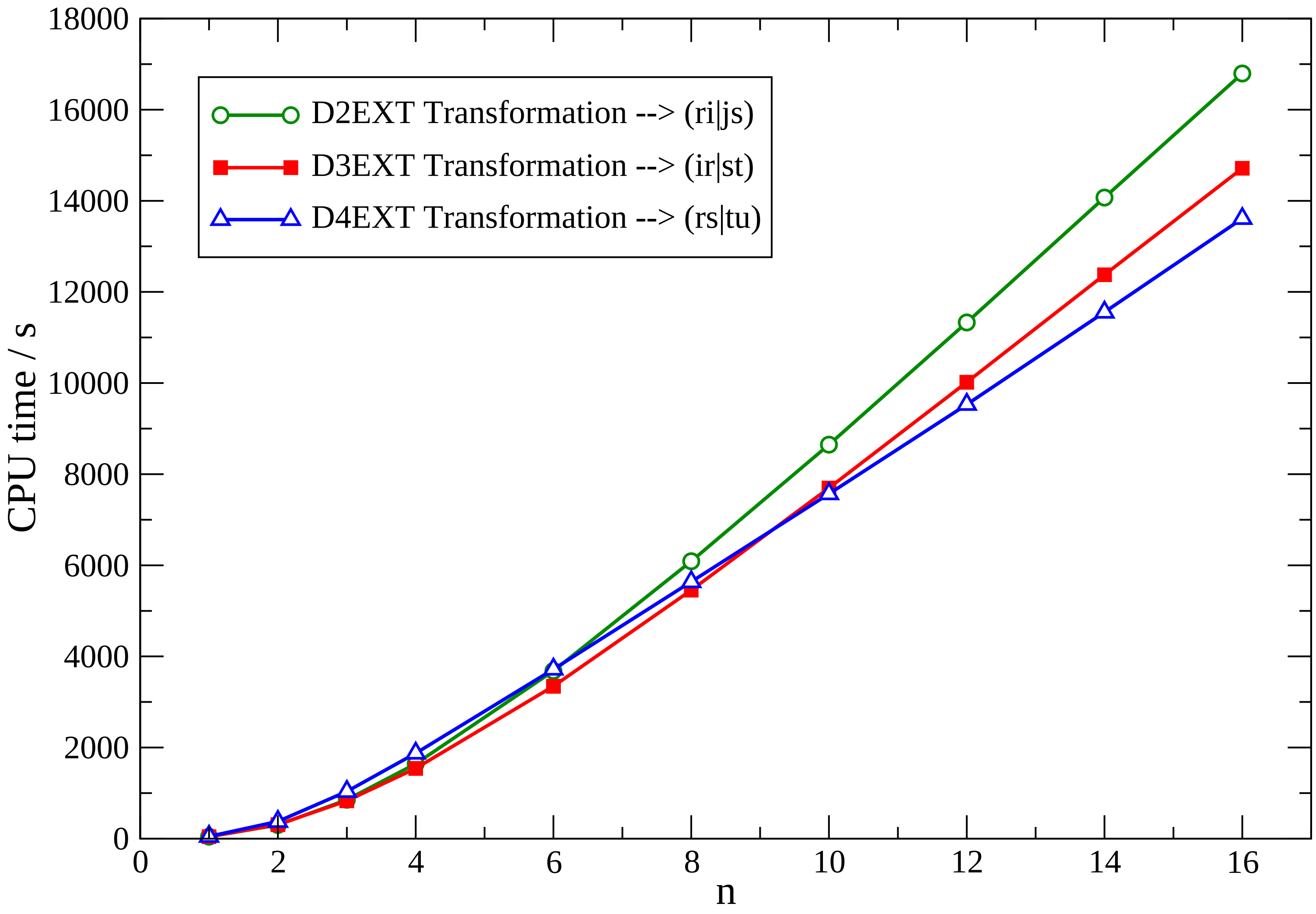
Hardware: 1 GHz Athlon PC



External Exchange Matrices in LCCSD

$$K(\mathbf{C}^{ij})_{rs} = \sum_{tu} C^{ij}_{tu}(rt|su), \quad \text{mit } C^{ij}_{rs} = T^{ij}_{rs} + t^i_r t^j_s$$

- Single contribution of 4-ext integrals
- No couplings of amplitudes via $K(\mathbf{C}^{ij})_{rs}$
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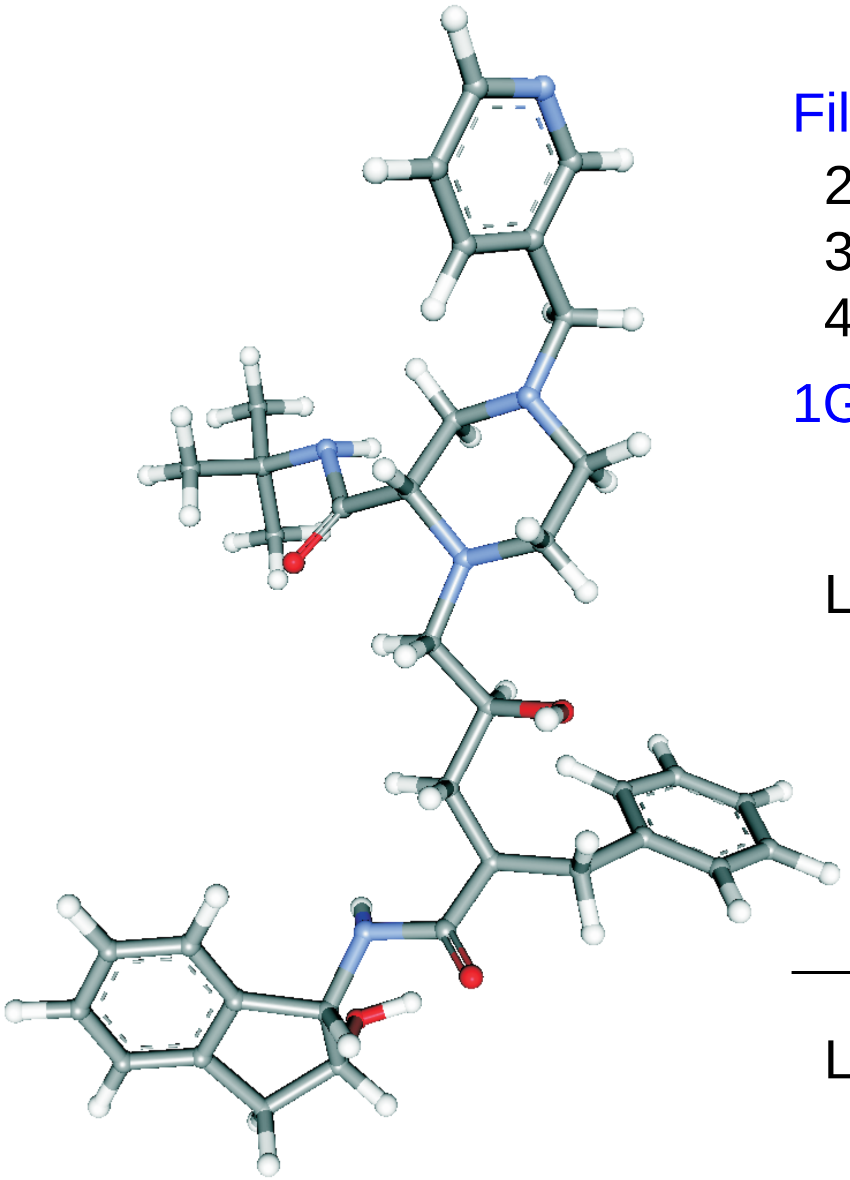
Local case:

- Very compact set of 4-ext integrals, $\propto \mathcal{N}$
  (Number of external exchange matrices = Number of Strong Pairs)
  (r, s, t, u restricted to Pair Domain $[ij]$)
- Computational complexity $\propto n_P L_P^4 \propto \mathcal{N}$

An example: Indinavir 865 BF (VDZ)



Filesize:

2-ext	150 MB	(1.35 GB w/o Multipoles)
3-ext	4.41 GB	
4-ext	1.84 GB	

1GHz Athlon PC

LCCSD	DTRAF:	23.0	h
	D3EXT:	17.7	h
	D4EXT (new):	25.8	h
	KEXT_4EXT (new):	47	s/it
	(DKEXT (old):	15.5	h /it)
	LCCSD one it:	36.7	min
L(T0)	-0.221283 (96.9 %)	2.1	h

The “Resolution of the Identity” (RI) Approximation[2]

Example: Exchange integrals (as used in LMP2):

$$K_{rs}^{ij} = (ri|js) = \int \tilde{\phi}_r(\mathbf{r_1})\phi_i(\mathbf{r_1})\frac{1}{|\mathbf{r_2}-\mathbf{r_1}|}\phi_j(\mathbf{r_2})\tilde{\phi}_s(\mathbf{r_2})d\mathbf{r_1}d\mathbf{r_2}$$

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[2] O. Vahtras, J.Almlöf, M.W. Feyereisen, CPL 213, 514 (1993)

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and minimization of the Coulomb self-repulsion of the residual $\rho - \check{\rho}$ leads to the equation system

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and the integral approximation

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- For $\mathcal{O}(\mathcal{N})$ scaling via density prescreening:
  - sparse test densities must involve auxiliary index A.
  - not available for RI-LMP2 (available for RI-LMP2 gradients though)

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$\Rightarrow$ $(ri|A)$ and $(A|B)$ become *short range* integrals:$\Rightarrow$ $\mathcal{O}(\mathcal{N})$ scaling restored

$(A|B) = \int \Xi_A(\mathbf{r}) \hat{P} \Xi_B(\mathbf{r}) d\mathbf{r}$ (like kinetic energy integrals)

$(ri|A) = \int \Xi_A(\mathbf{r}) \chi_r(\mathbf{r}) \phi_i(\mathbf{r}) d\mathbf{r}$ (three-index overlap integrals)

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[3] F.R. Manby, P.J. Knowles, A.W. Lloyd, JCP 115, 9144 (2001)

Linear Scaling with RI-Approximation

- $(A|B)$ and $(ri|A)$ are two- and three-index *Coulomb* integrals $\Rightarrow \propto \mathcal{O}(\mathcal{N}^2)$

- For $\mathcal{O}(\mathcal{N})$ scaling via density prescreening:
  - sparse test densities must involve auxiliary index A.
  - not available for RI-LMP2 (available for RI-LMP2 gradients though)

- Alternative: Use of Poisson functions as auxiliary basis[3]

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- Catch: The fitted Poisson density does not carry any charge or multipole moments

$\Rightarrow$ Mixed auxiliary basis (Poisson plus few ordinary Gauss functions)

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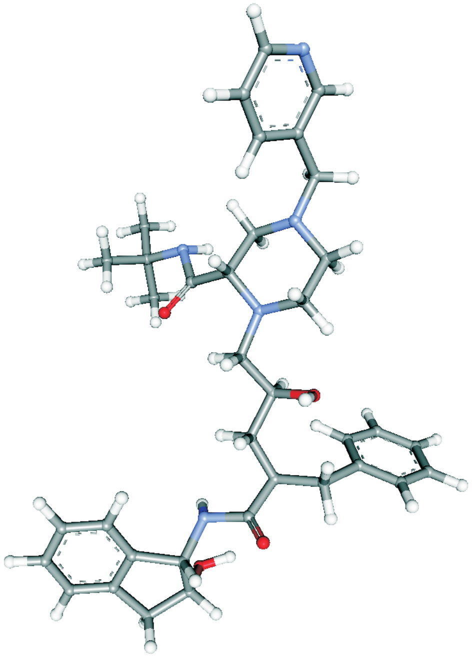
RI-Local MP2



Indinavir 865 BF (VDZ), # fitting functions: 3920

CPU times on single Processor Athlon/1GHz:

LMP2	2.6 h
RI-LMP2	1.5 h
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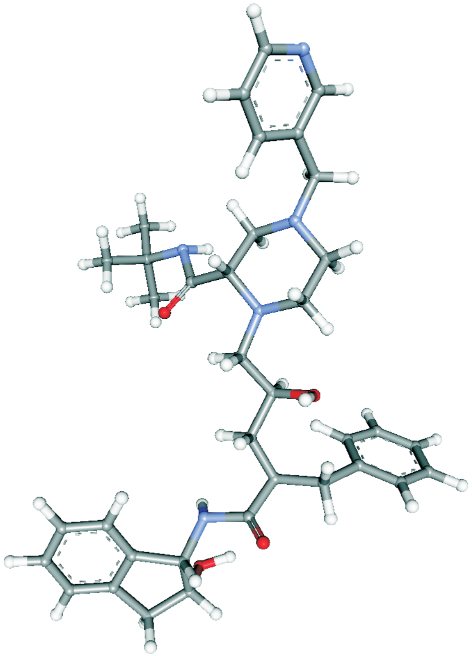

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  - Computational savings (relative to “conventional” local formalism) much more dramatic than for energy
  - MP2 geometry optimizations for large molecules now become feasible
  - Focus of future applications: Molecular clusters
- Under development: Use of RI-Ansatz in local Coupled Cluster Theory (Elimination of costly initial integral transformations)

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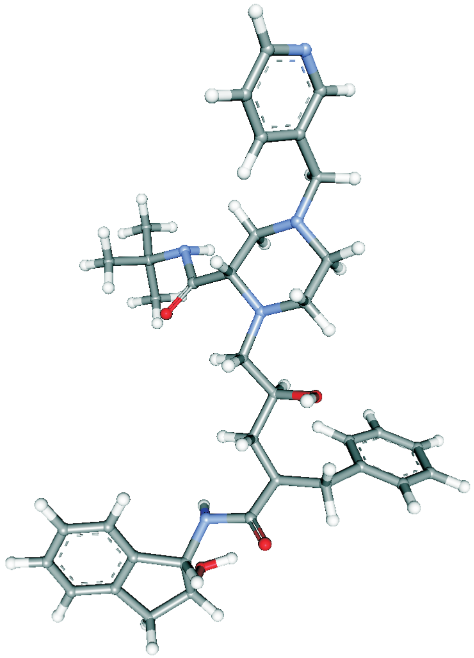

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Accuracy of the Local Approximation

Test Suite: **Reaction Energies of 50 different chemical Reactions**
(compiled by Dr. A. Schäfer, BASF AG)

- DFT (Becke-Perdew, B3-LYP) for geometries and (harmonic) vibrational frequencies (ZPE and finite Temperature corrections)
- Single point energies for electronic contribution to reaction energies, using CCSD(T), LCCSD(T), LCCSD(T)$|$LMP2
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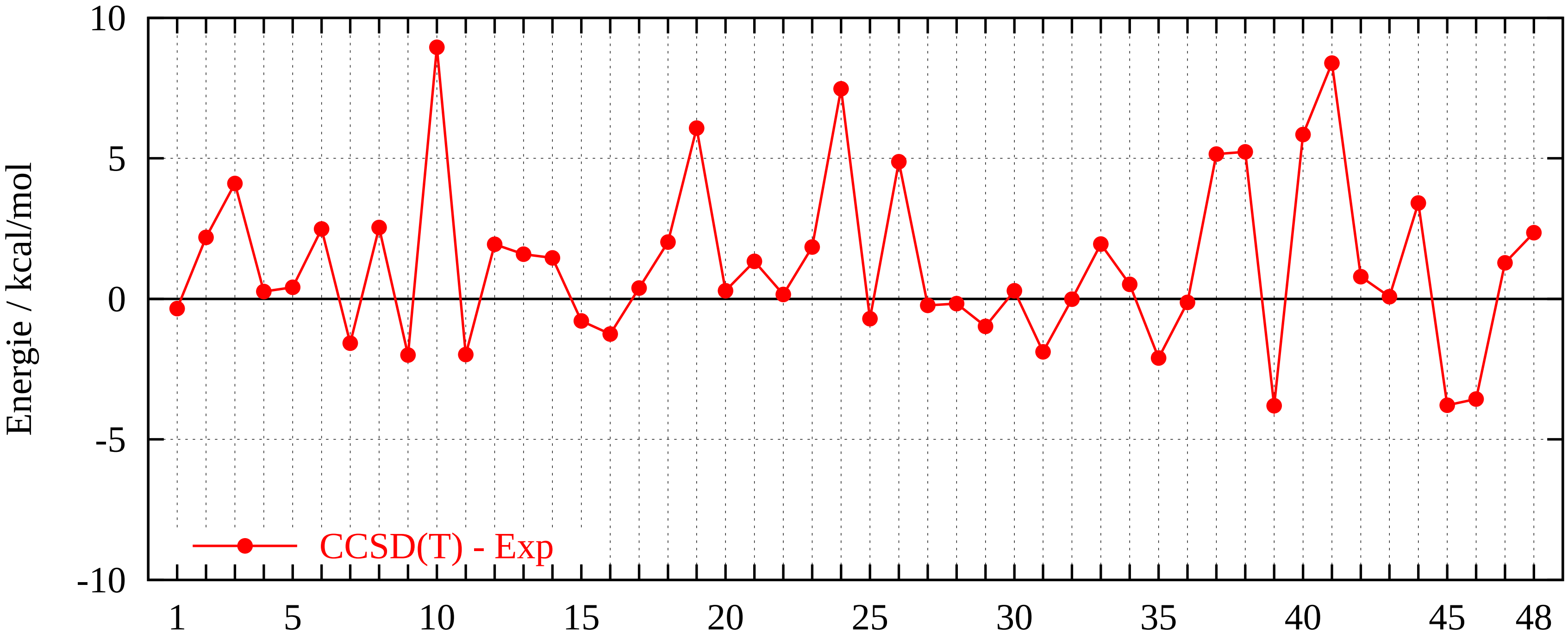

- Deviation CCSD(T) from Experiment

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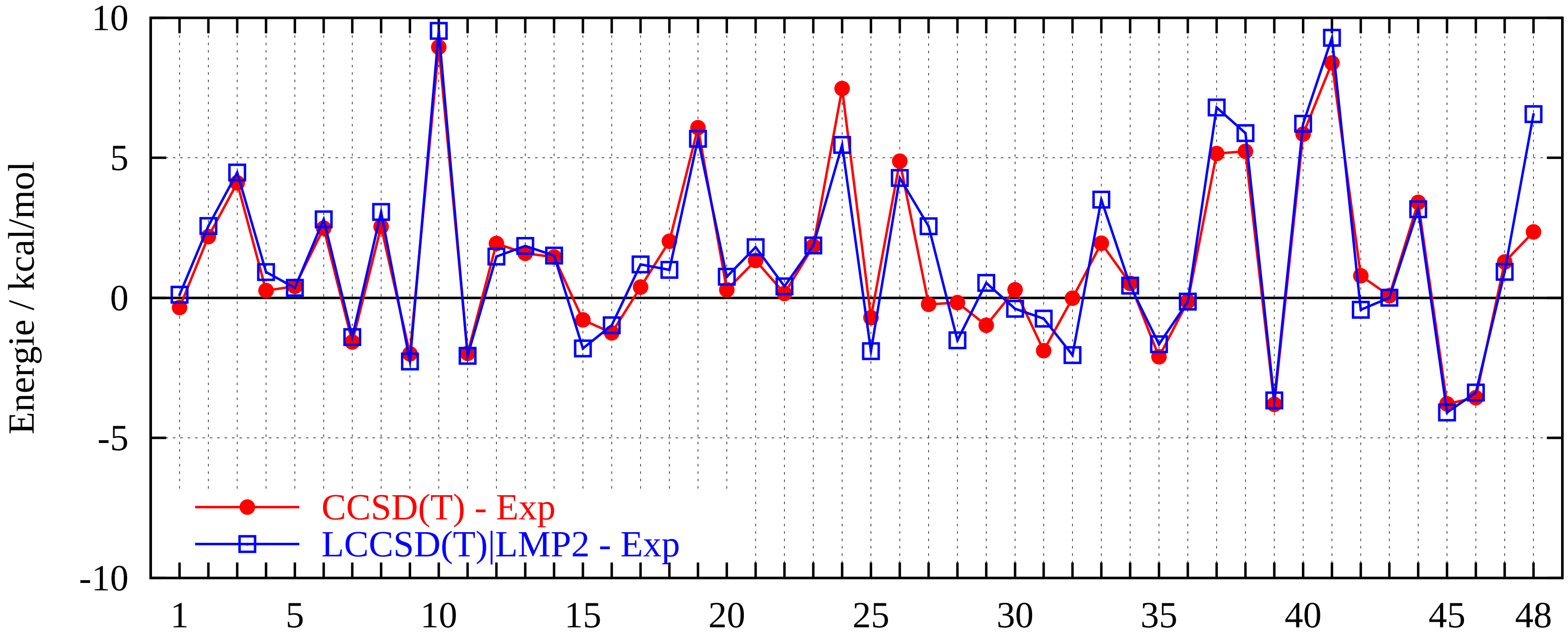

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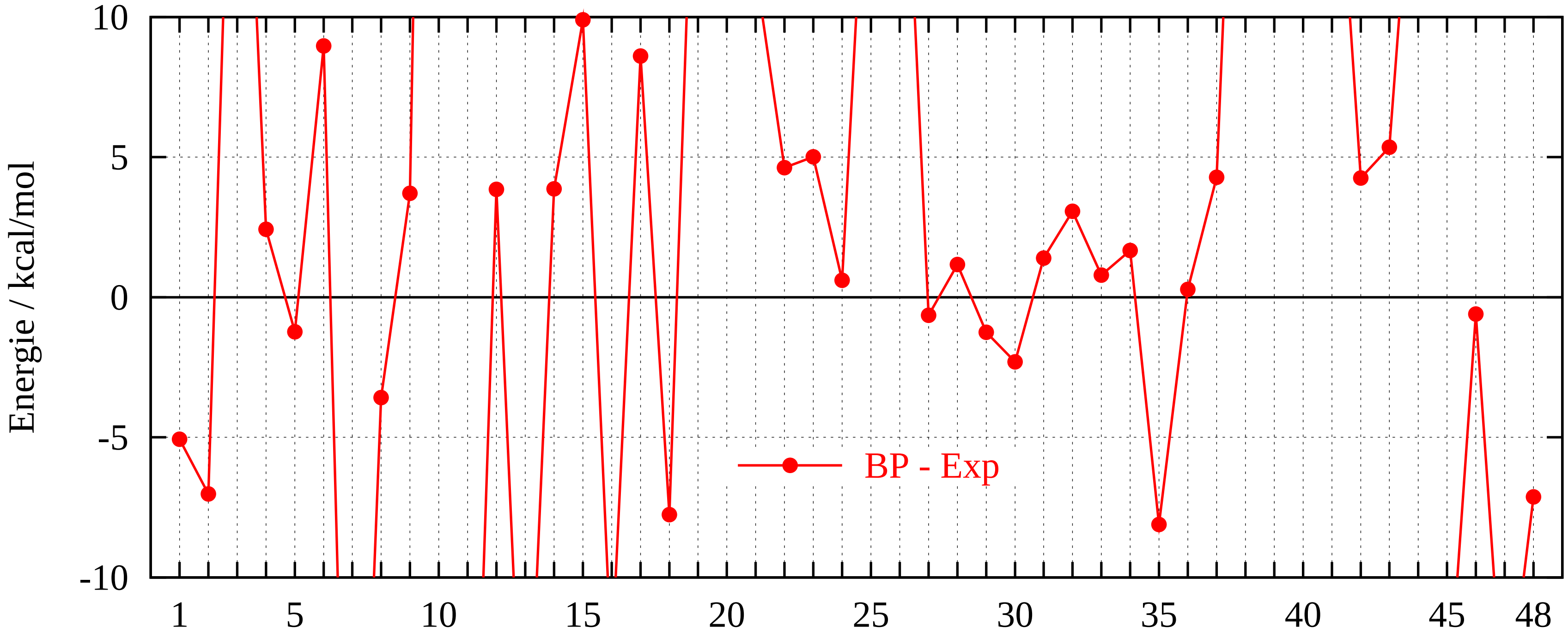
Reaction Energies DFT (Testset50)



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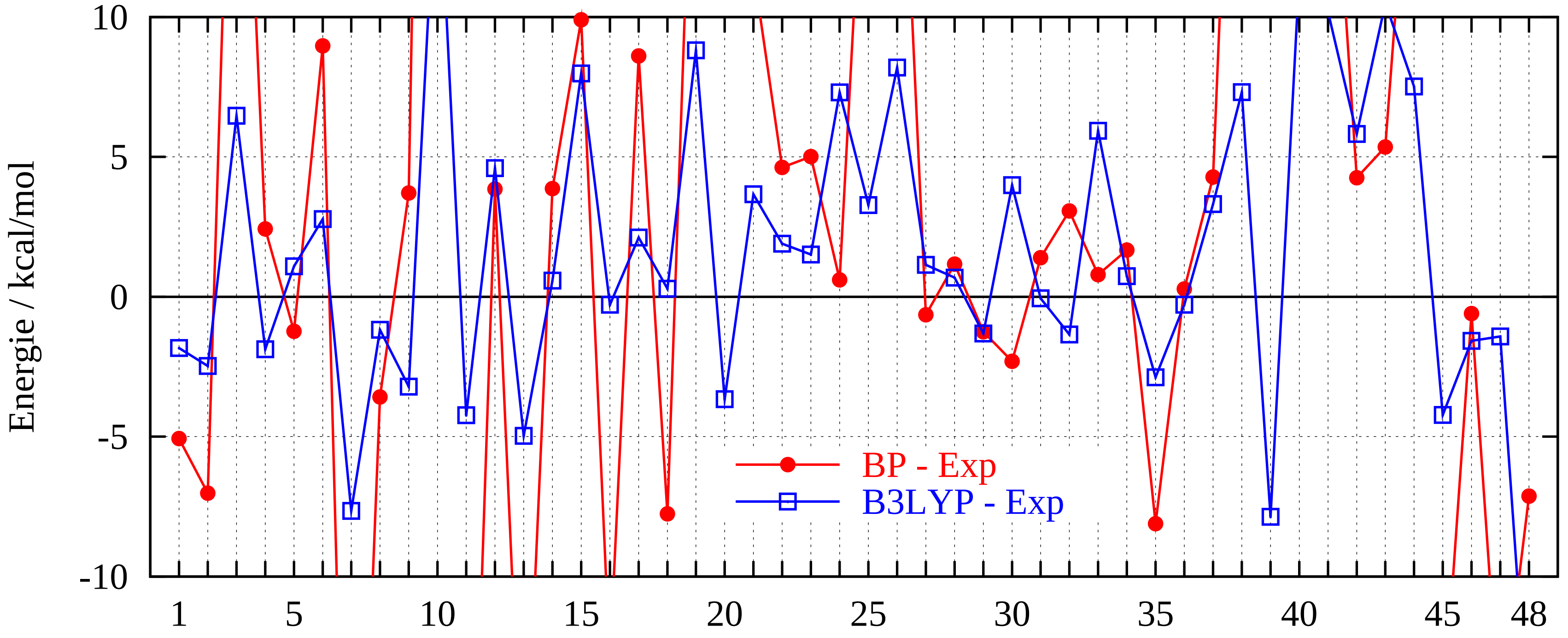

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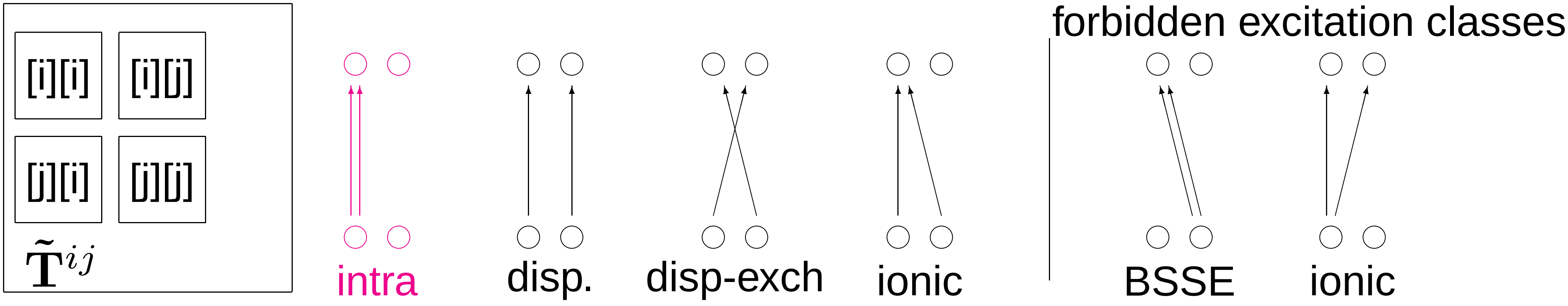
$(H_2O)_2$: Partitioning of the LMP2 Interaction Energy

1. Separation of intra- and intermolecular Electron Pairs

2. For intermolecular Pairs: Partitioning of the amplitude matrices $\mathbf{T}^{ij}$ along Orbital Domain Boundaries
   - dispersive components
   - ionic components
   - exchange-disperison



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  $\Rightarrow$ No Basis Set Superposition Error (BSSE) for local correlation methods!

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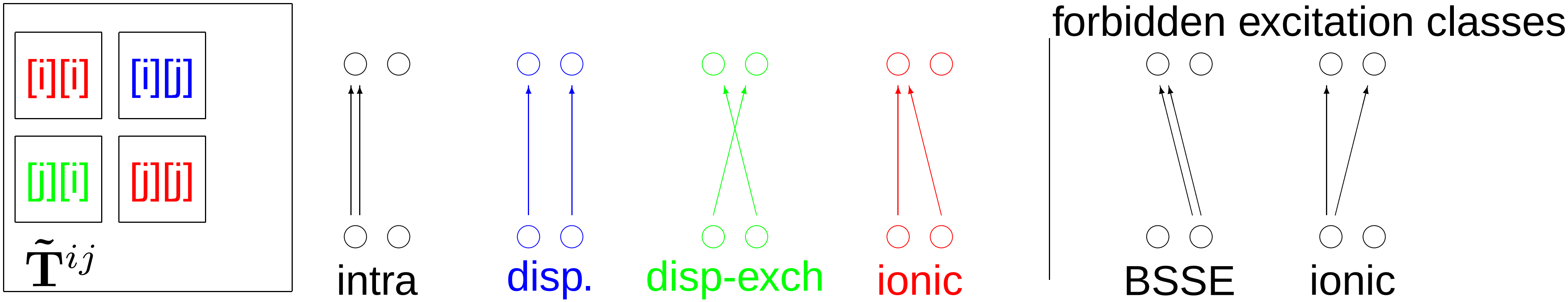

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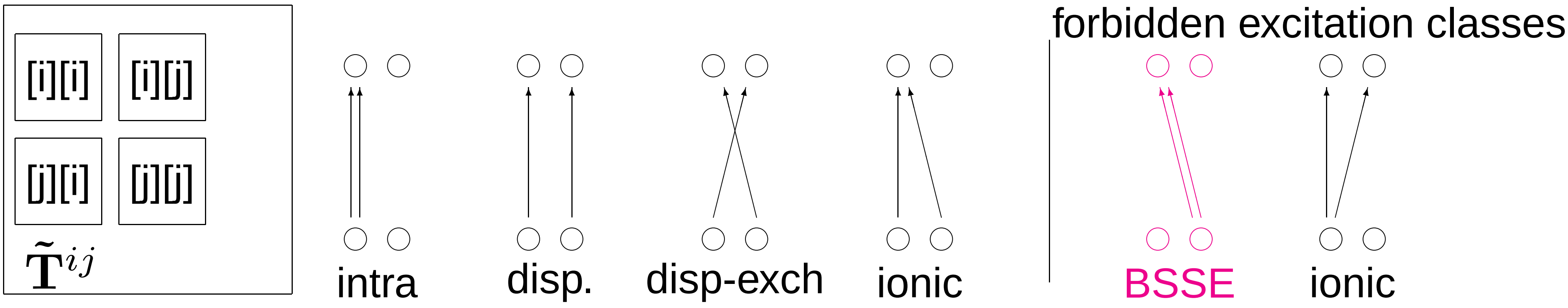

[i][i] [i][j]
[j][i] [j][j]
$\tilde{\mathbf{T}}^{ij}$

intra
disp.
disp-exch
ionic

forbidden excitation classes

BSSE
ionic

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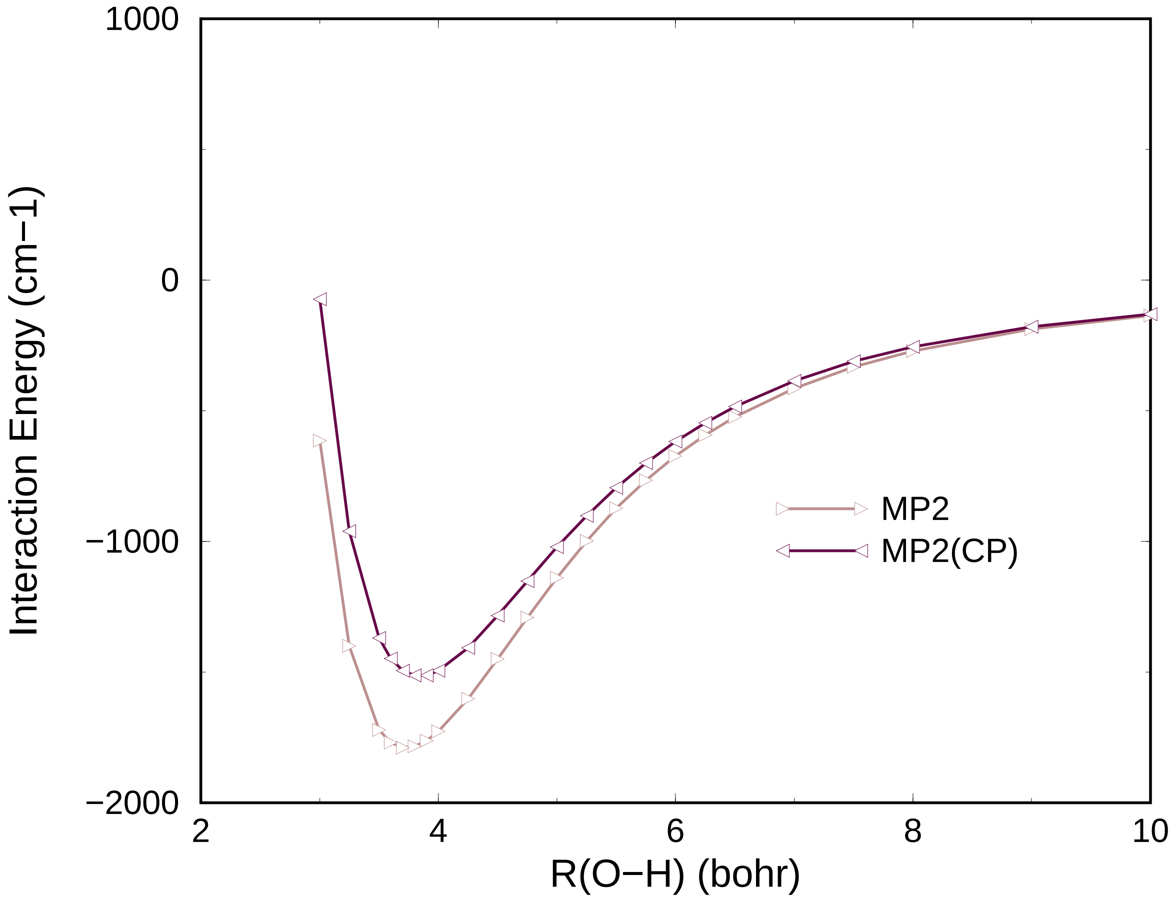

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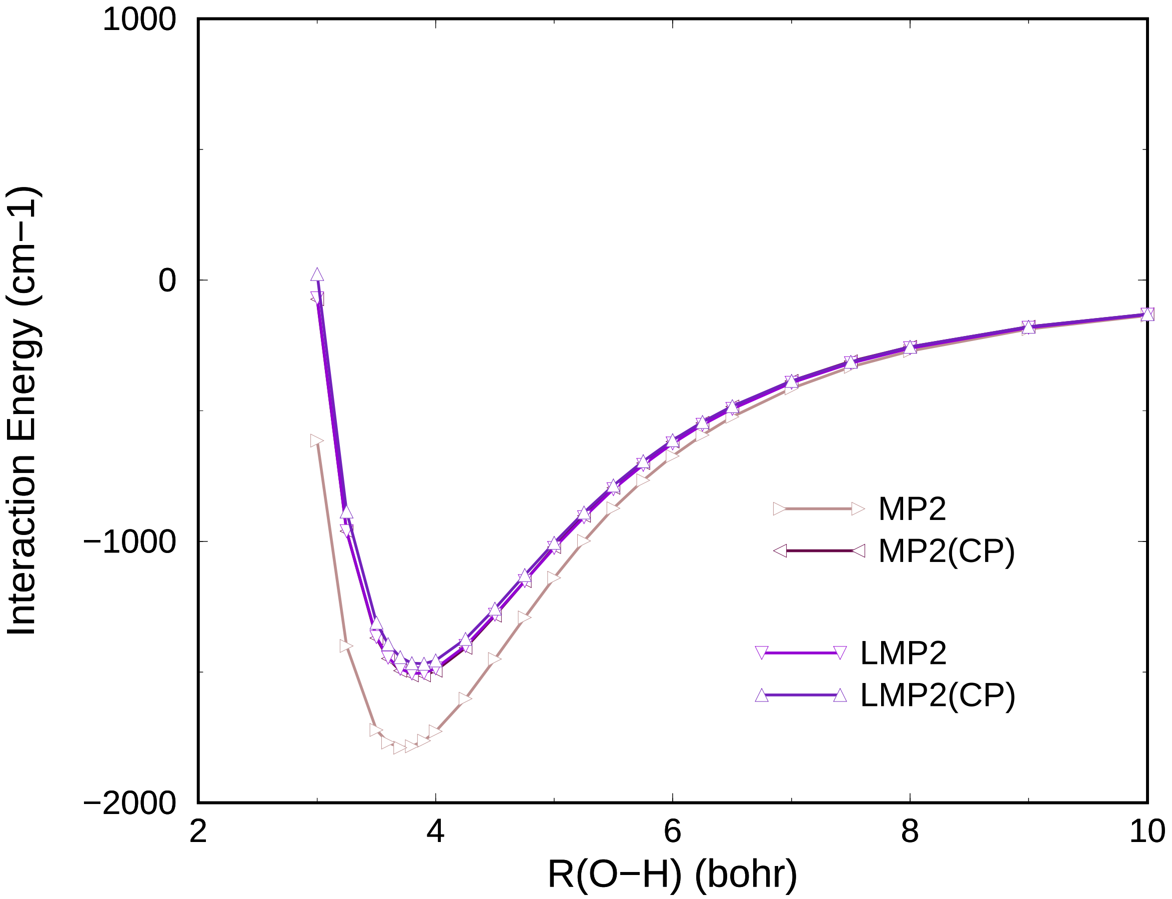

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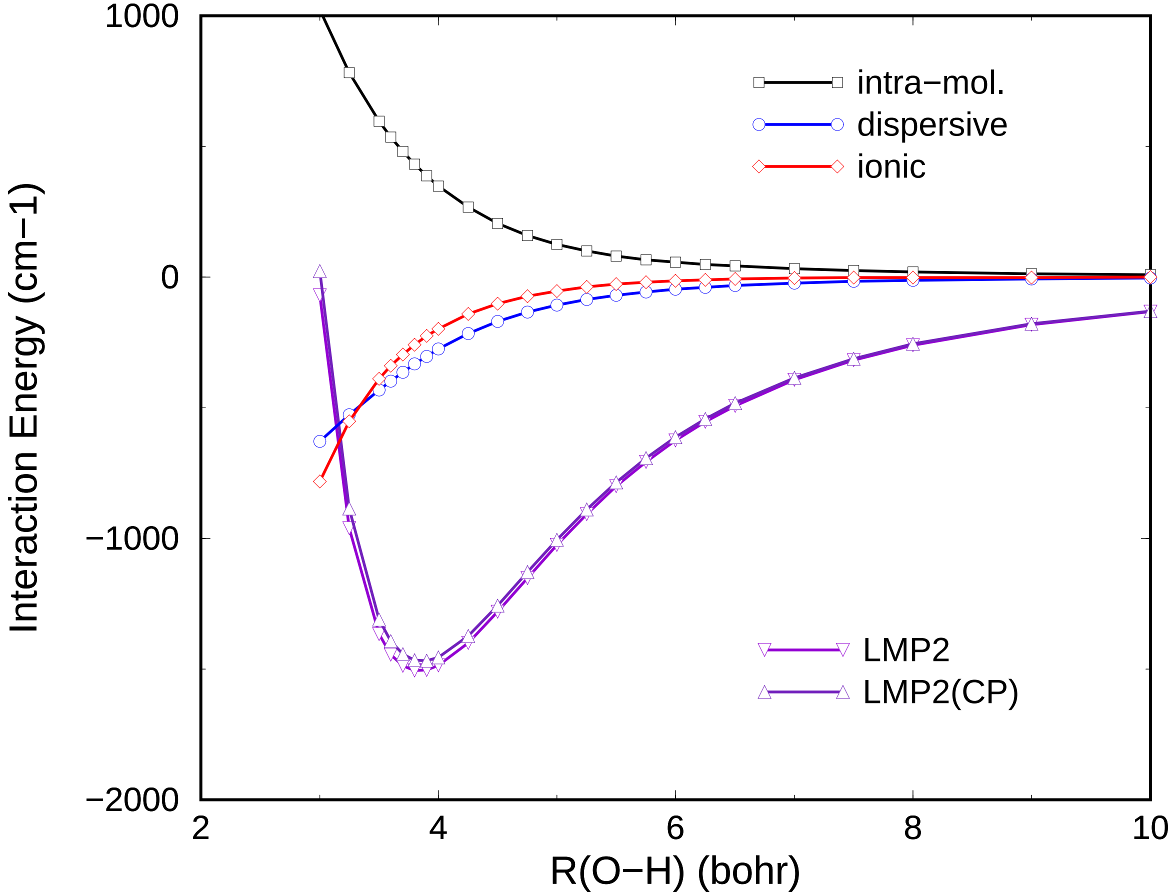

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- Energy Partitioning: *intramolecular* component (repulsiv)
  dispersive component (attractive, decaying as $\propto \frac{1}{R^6}$
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Conclusions

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Problems:

- Delocalized systems

- Bigger basis sets: VDZ → VTZ: factor of 16 in computational cost