Wavefunction Correlation Methods: From the Basics to the Frontiers

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Challenges in Theoretical Chemistry

▶ **Large (+extended) Systems**:
- ★ Proteins, Nucleic Acids
- ★ Extended π-Systems
- ★ Solids + surfaces

...

▶ **High Accuracy Needed**
- ★ Chemical phenomena are happening on a scale of relative energies of ~1 kcal/mol

▶ **Conformational Complexity**
- ★ Multiple minima separated by shallow barriers lead to a large conformational space and dynamics

▶ **Relativistic effects**
- ★ Heavy atoms
- ★ Advanced spectroscopies (EPR, XAS)

▶ **Excited states**

▶ **Intermolecular interactions (including environment modeling)**

H-bonding

π-stacking

Conformational variables

Conformational variables
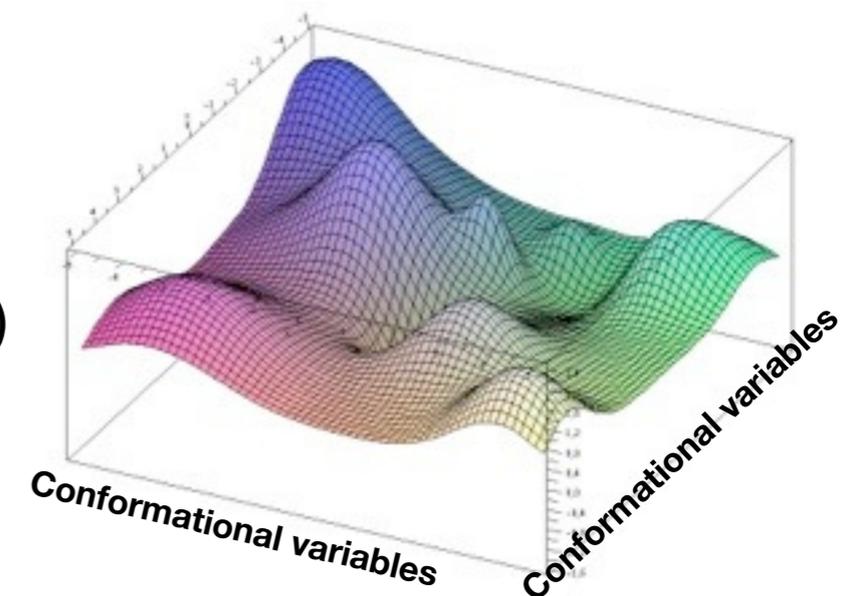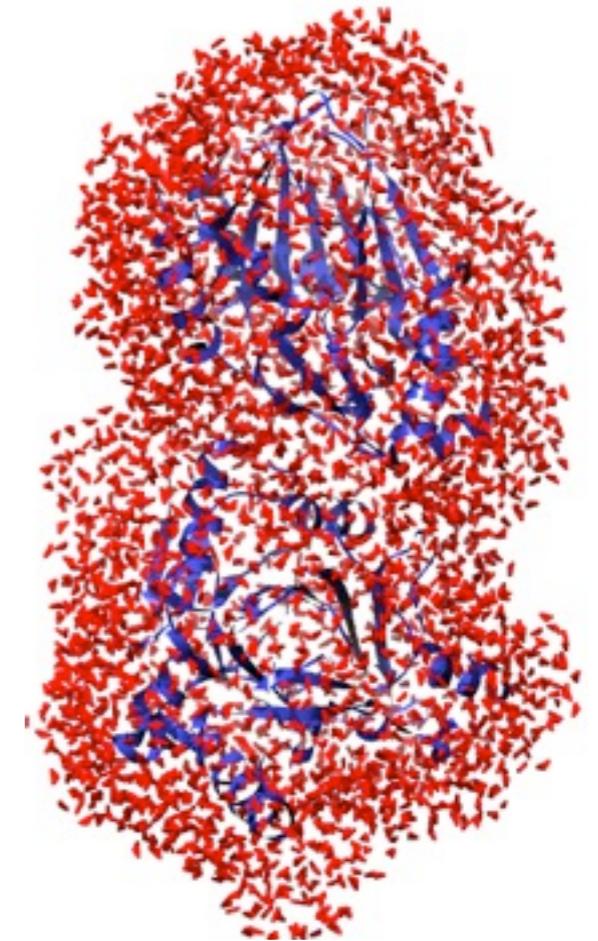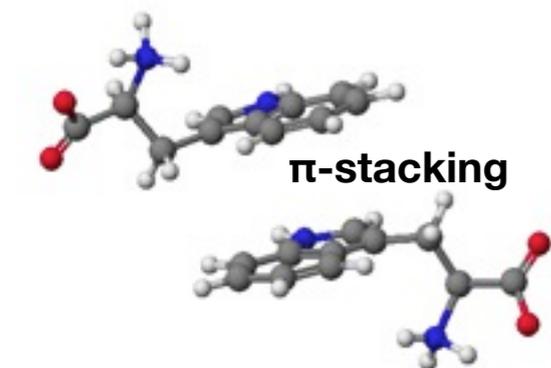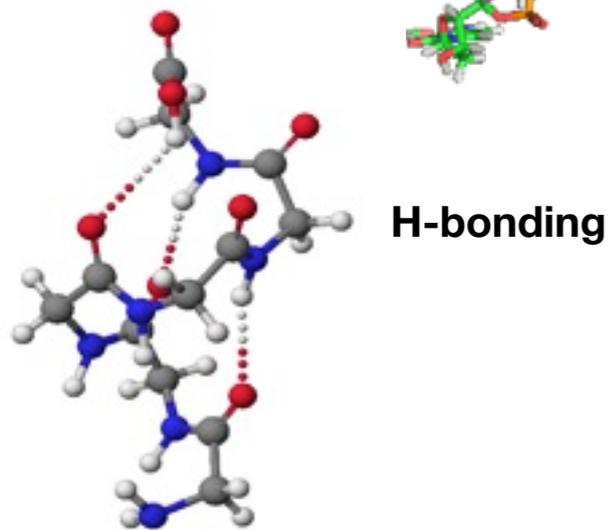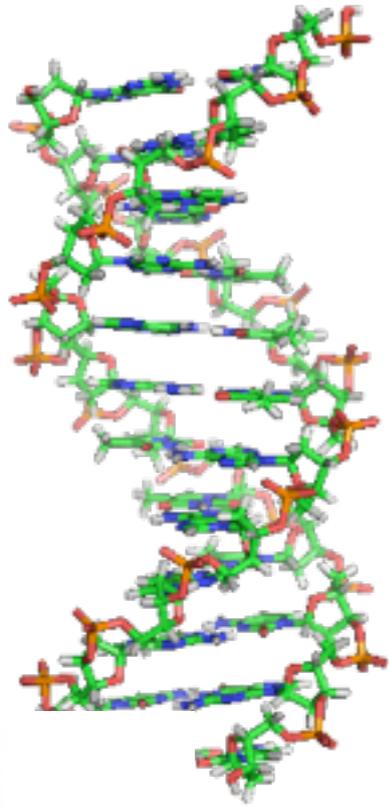
The Underlying Simplicity
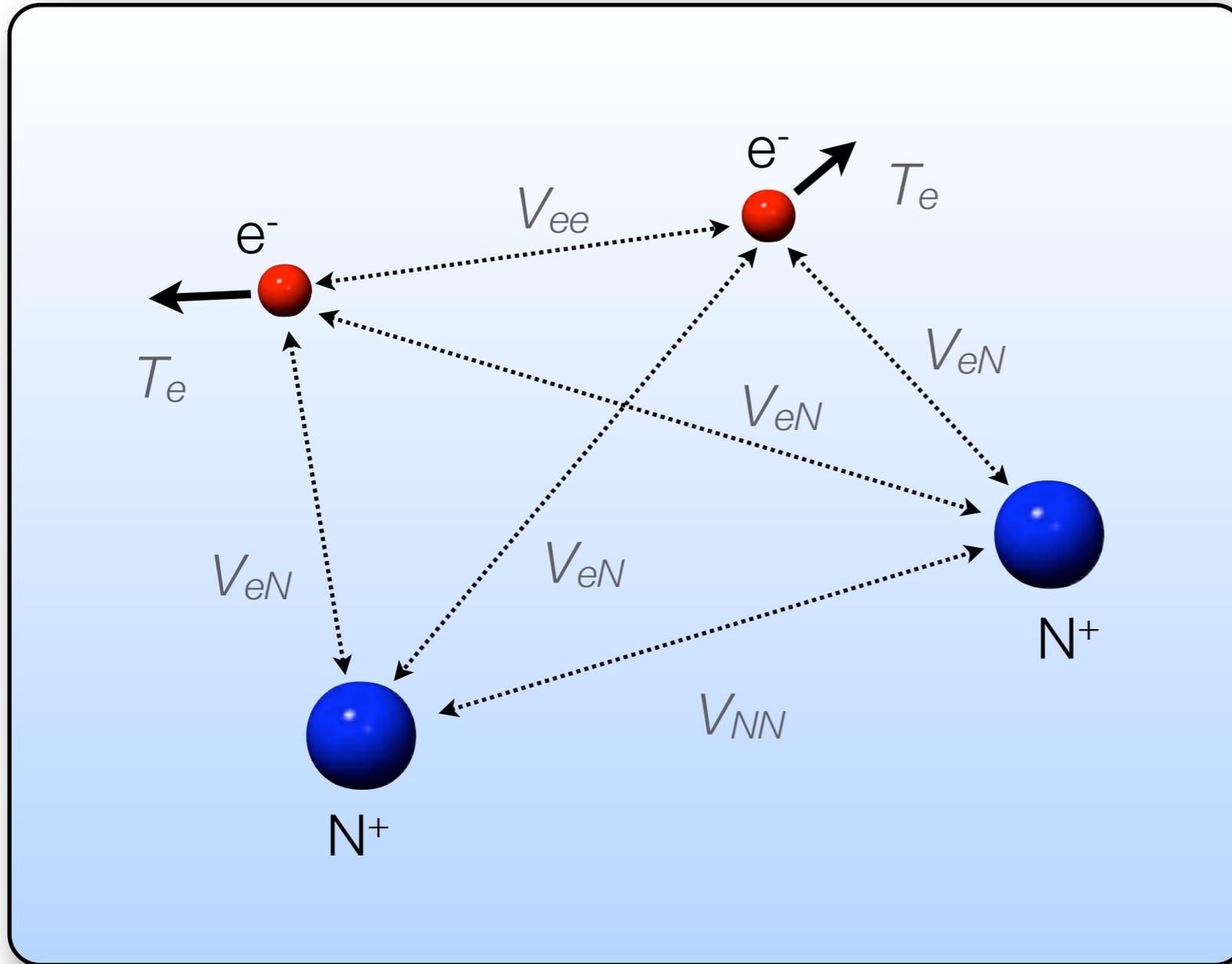
Just 2 Laws:

1. Coulomb's Law
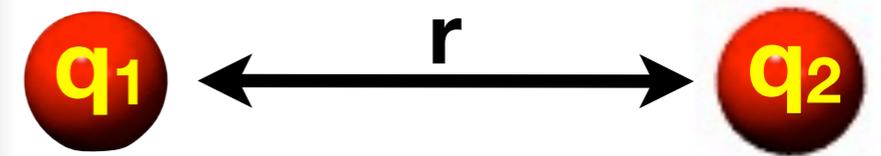
$$E = \frac{1}{4\pi\varepsilon_0} \frac{q_1\, q_2}{\left| \mathbf{r}_1 - \mathbf{r}_2 \right|}$$

2. Kinetic Energy

$$E = \frac{1}{2} m v^2 = \frac{p^2}{2m}$$

$$E = T_e + T_N + V_{eN} + V_{NN} + V_{ee}$$

Approximate Methods

$$\hat{H}(\mathbf{x}, \mathbf{R})\Psi(\mathbf{x}_1, ..., \mathbf{x}_N \mid \mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{x}_1, ..., \mathbf{x}_N \mid \mathbf{R})$$

cost

Hartree-Fock

Density Functional Theory

Semi-Empirical

Force Fields

Configuration Interaction (Many Body Perturbation) Coupled Cluster

Multireference CI, PT, CC

accuracy

Exact Solution of the BO-Problem
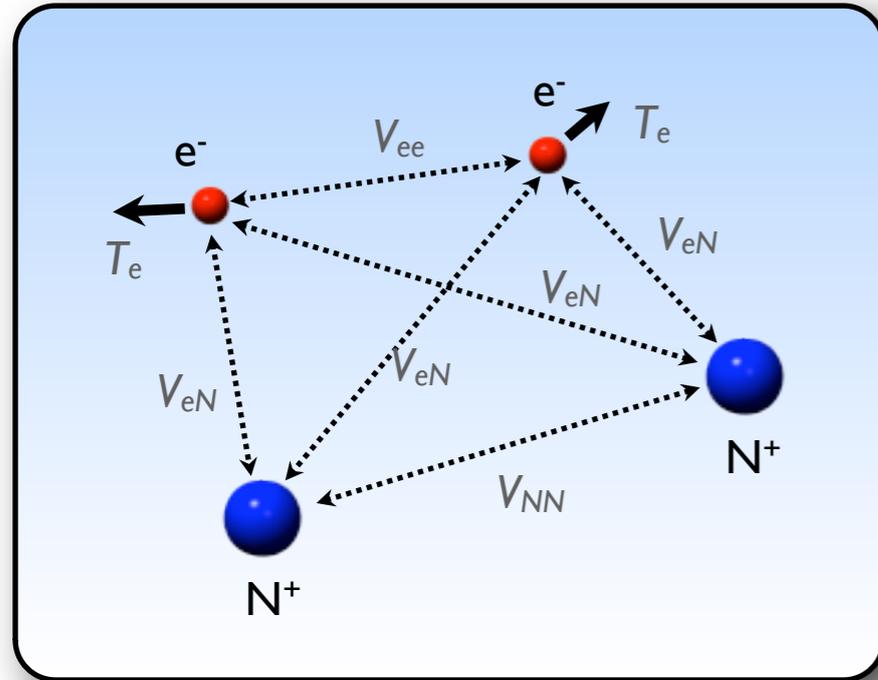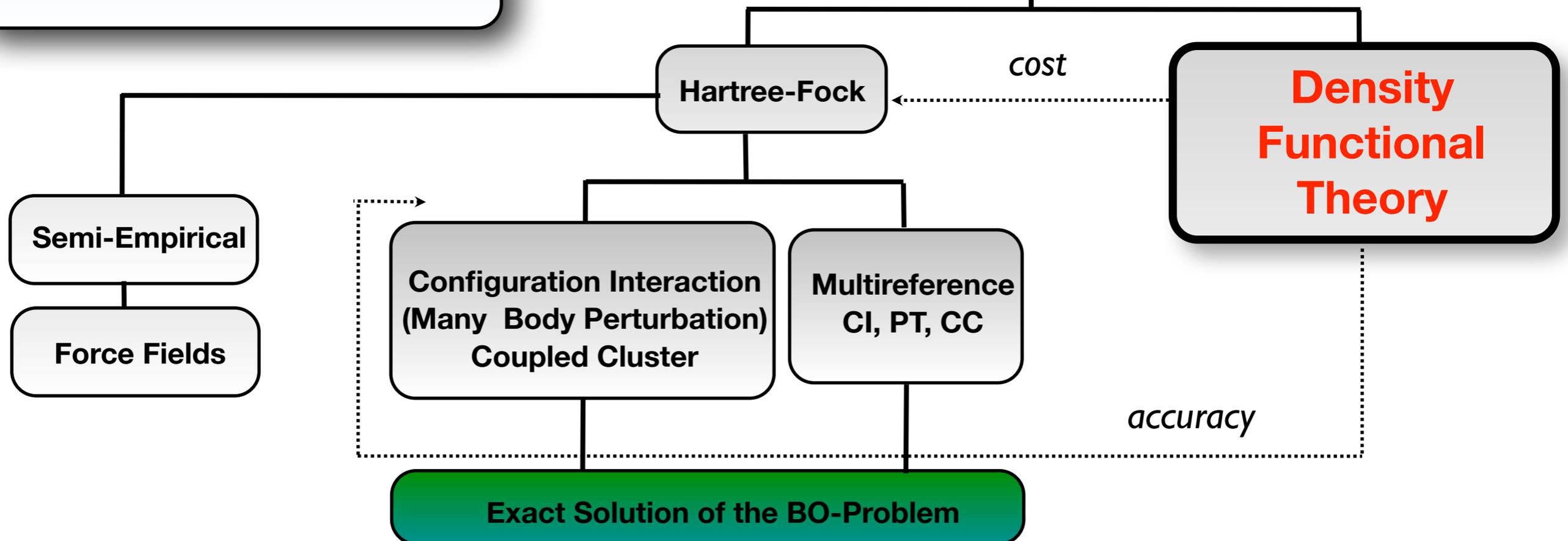
Wavefunction vs DFT Methods

FN, A. Hansen, F. Wennmohs, S.- Grimme (**2009**) *Acc. Chem. Res.* <u>42</u>, 641
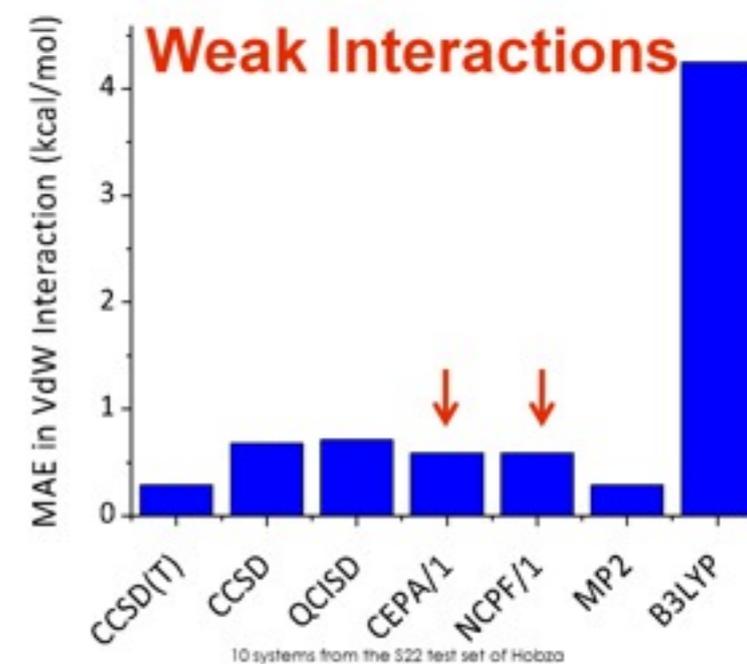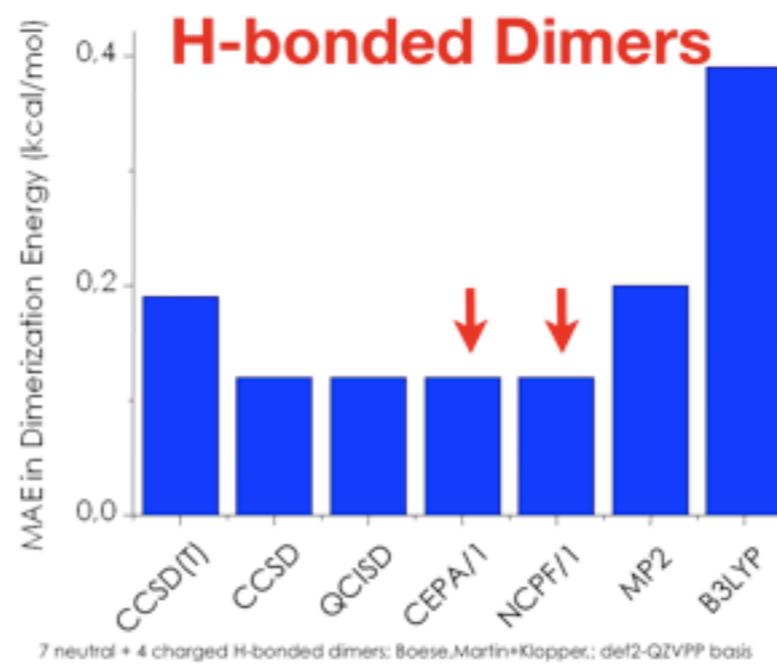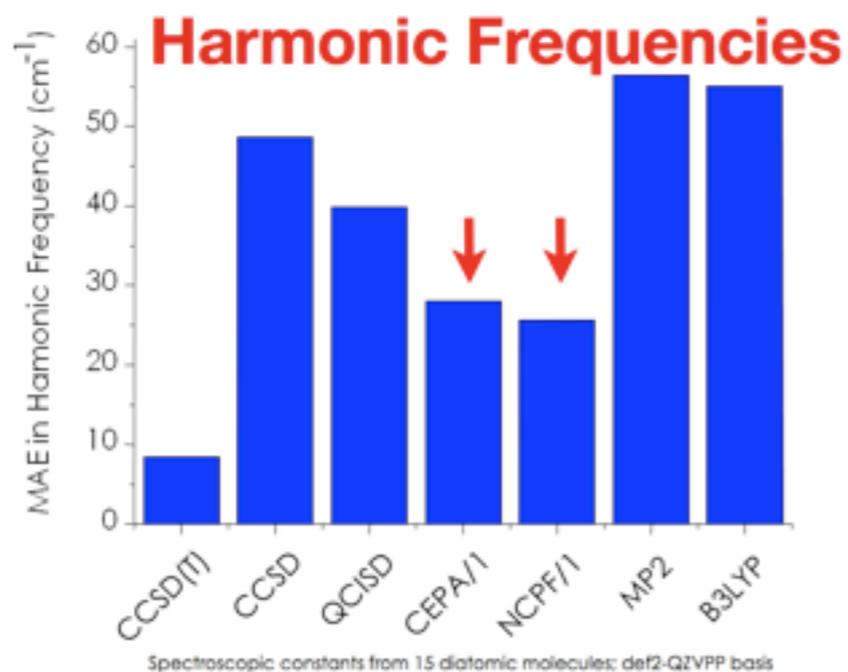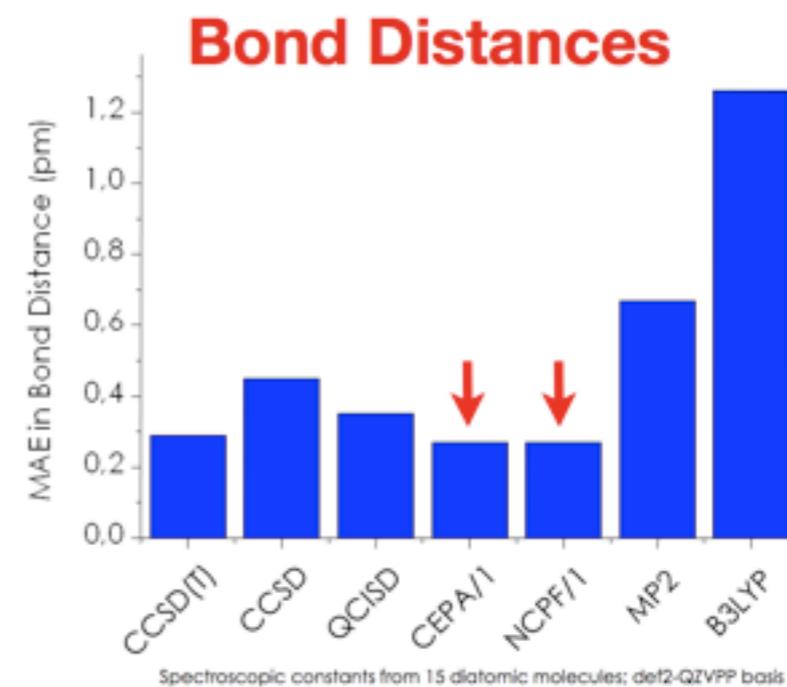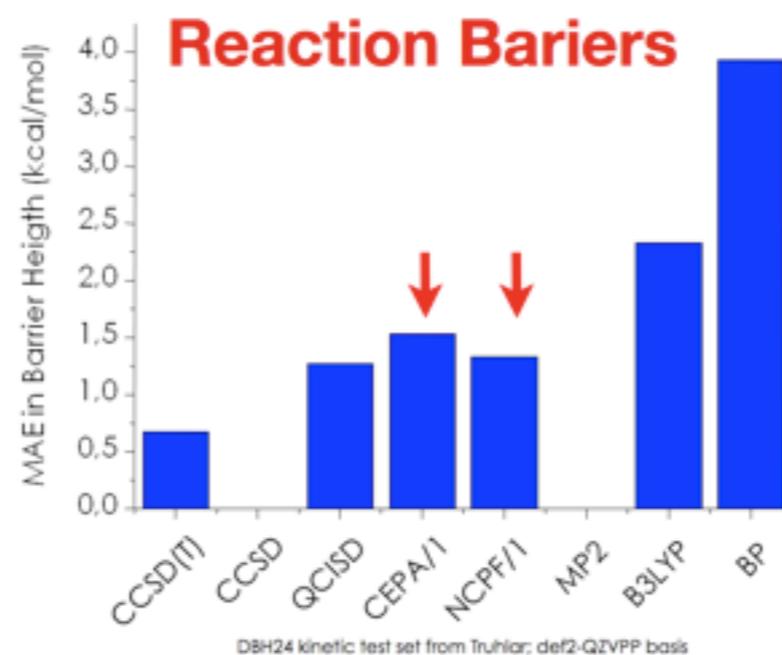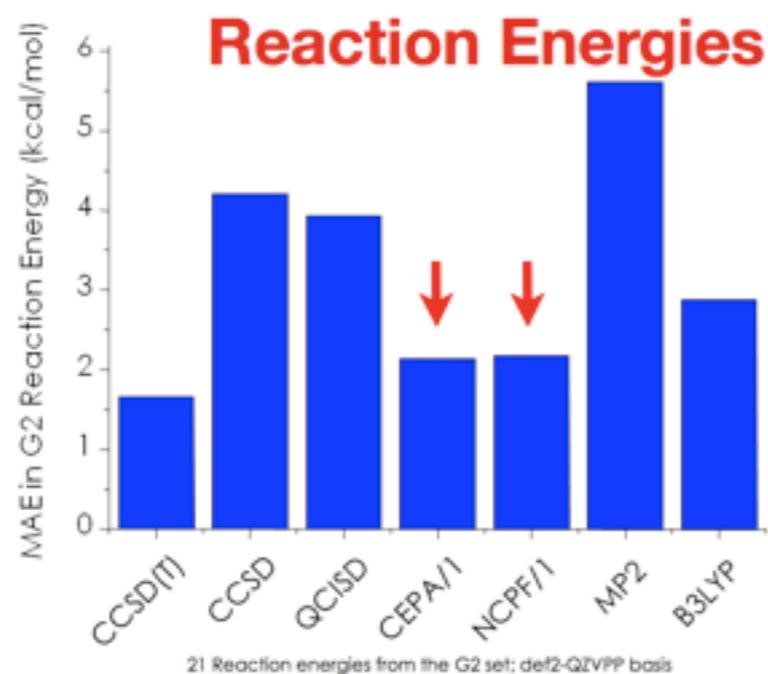
The Exact Energy

Exact Energy =
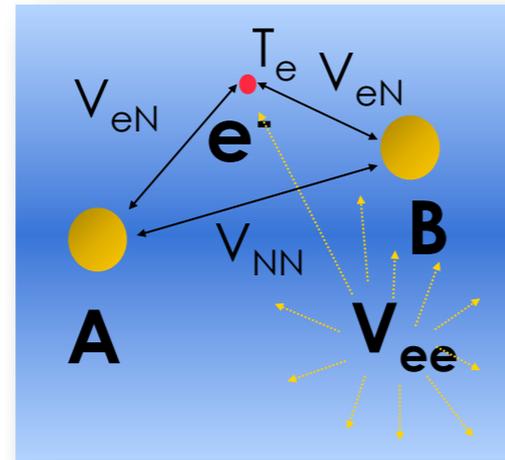
"Mean Field"
Hartree-Fock

$+$
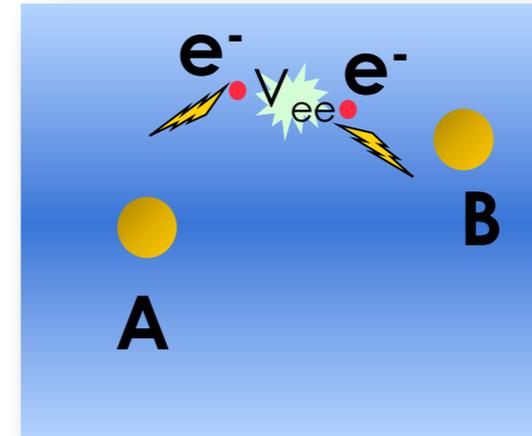
Instantaneous electron-
electron interaction

Correlation energy= $\quad \dfrac{1}{2} \displaystyle\sum_{i,j \text{ Electron pairs}} \quad \varepsilon_{ij}(\uparrow\uparrow) \quad + \quad \varepsilon_{ij}(\uparrow\downarrow)$

Fermi-Correlation   **Coulomb-correlation**

| *Relatively easy due to "Fermi hole" in the mean-field* | *Extremely hard to calculate due to interelectronic cusp at the coalescence point* $r_1 = r_2$ |

Definition of the Correlation Energy

The Hartree-Fock model is characterized by:

✓ The use of a single Slater determinant which describes a system of N quasi-independent electrons (independent particle or mean field model!)

✓ The orbitals are optimized to achieve the lowest possible energies.

✓ The method is variational. It provides an upper bound to the exact solution of the Born-Oppenheimer hamiltonian (usually >99.7% of the exact nonrelativistic energy is recovered): **not good enough :-(**

✓ The remaining energy error is called **correlation error** and arises from „instantaneous" electron-electron interactions (as opposed to the mean-field interaction present in HF theory).

✓ Thus, we *define* the **correlation energy** as (Löwdin):

$$E_{corr} = E_{excact} - E_{HF}$$

This definition is quite problematic but is still the widely accepted one.

Basic idea of wavefunction based correlation methods:

multideterminantal Ansatz

Solving the many particle Schrödinger equation is then a trivial exercise:

Assume: **complete set** of N-electron expansion functions **{Φ}** available.

Ansatz:
$$\Psi(\mathbf{x}_1,...,\mathbf{x}_N) = \sum_I C_I \Phi_I(\mathbf{x}_1,...,\mathbf{x}_N)$$

Variational principle:
$$E[\Psi] = \frac{\langle \Psi \mid H \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} = \frac{\sum_{IJ} C_I^* C_J H_{IJ}}{\sum_{IJ} C_I^* C_J S_{IJ}}$$

Perform variation:
$$\mathbf{HC} = E\mathbf{SC}$$

Lowest eigenvalue = exact ground state energy

First Problem: *Where to get a complete many particle expansion basis from?*

We can construct a complete (infinite) N-electron expansion set from the (<u>presumed exact!</u>) solutions of the HF equations by replacing 1,2,...,N electrons in the HF Slater determinant by virtual orbitals (so called excitations - not to be confused with actual excited STATES)!

$$\Psi = C_0 \Phi_{HF} + \underbrace{\sum_{ia} C_a^i \Phi_i^a}_{Singles} + \left(\frac{1}{2!}\right)^2 \underbrace{\sum_{ijab} C_{ab}^{ij} \Phi_{ij}^{ab}}_{Doubles} + \left(\frac{1}{3!}\right)^2 \underbrace{\sum_{ijkabc} C_{abc}^{ijk} \Phi_{ijk}^{abc}}_{Triples} + ... + (n - fold\ exc.)$$

conventions:

i,j,k,l : internal (occupied) orbitals (occupied in the HF determinant)

a,b,c,d : external (virtual) orbitals (unoccupied in the HF determinant)

p,q,r,s : general orbitals (occupied or unoccupied)

μ,ν,κ,τ : basis functions

Capital symbols   : N-particle space

Lowercase symbols   : 1-particle space

The Boiling „Electron Sea"

$$\frac{1}{2} P_{ij} P_{ab} \sum_{klcd} \langle kl \| cd \rangle t^{ik}_{ac} t^{lj}_{db}$$

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{ia} C^i_a |\Psi^a_i\rangle + \frac{1}{4} \sum_{ijab} C^{ij}_{ab} |\Psi^{ab}_{ij}\rangle + \frac{1}{36} \sum_{ijkabc} C^{ijk}_{abc} |\Psi^{abc}_{ijk}\rangle + \dots$$
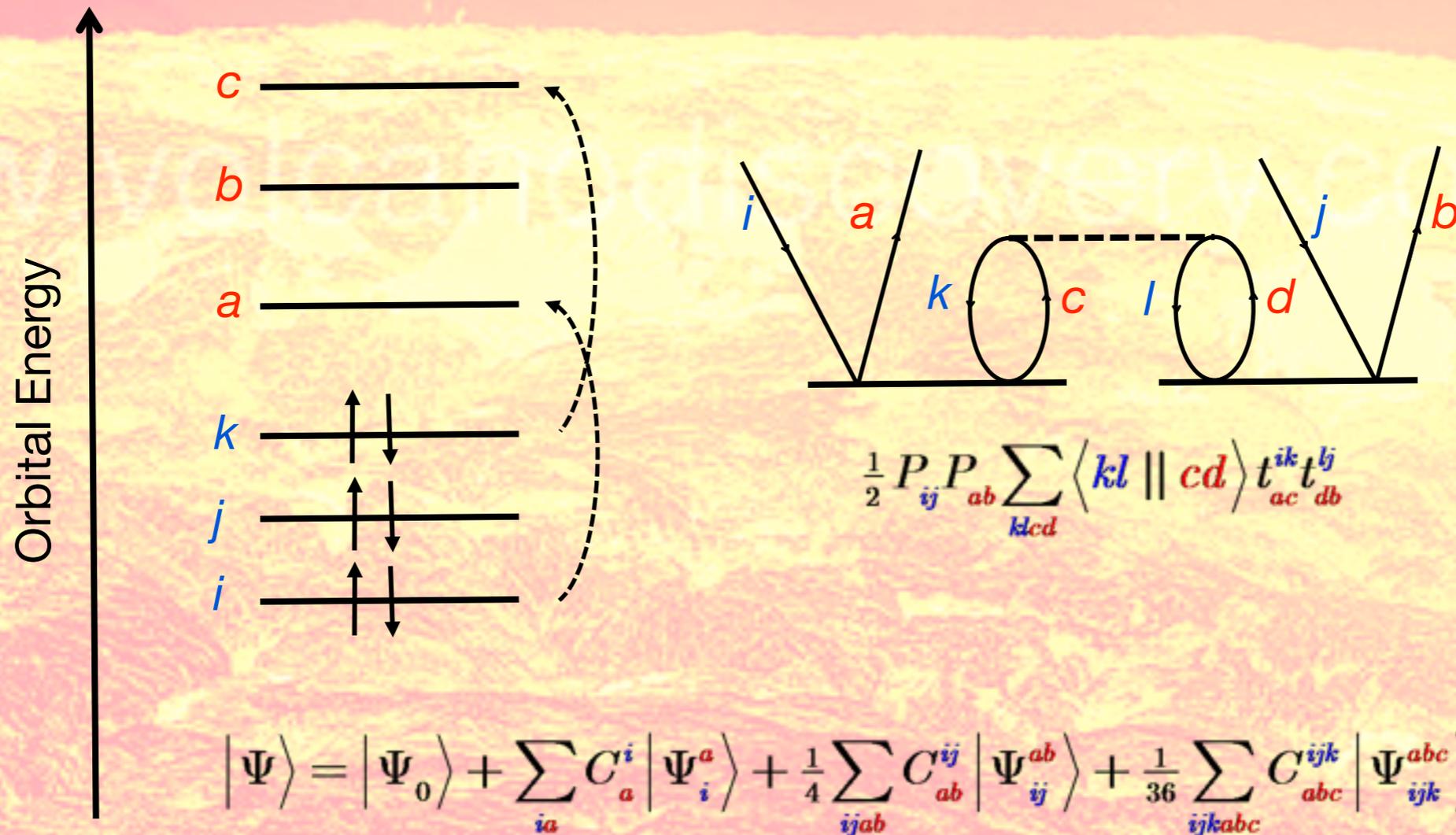
Let us look at: $\mathbf{HC} = E\mathbf{SC}$

in terms of our infinite set of excited determinants. First we recognize that since the HF orbitals are assumed to be orthonormal we get **S=1.**

If we order the determinants according to excitation level 0, 1 (S), 2 (D), 3 (T), 4 (Q), ... Owing to Slater's rules, the structure of the Hamilton matrix is:

$$\mathbf{H} = \begin{pmatrix} E_{HF} & \langle 0|\hat{H}|S\rangle & \langle 0|\hat{H}|D\rangle & 0 & 0 \\ & \langle S|\hat{H}|S\rangle & \langle 0|\hat{H}|D\rangle & \langle S|\hat{H}|T\rangle & 0 \\ & & \langle D|\hat{H}|D\rangle & \langle D|\hat{H}|T\rangle & \langle D|\hat{H}|Q\rangle \\ & & & \langle T|\hat{H}|T\rangle & \langle T|\hat{H}|Q\rangle \\ & & & & \ddots \end{pmatrix}$$

Thus, the Hamiltonian has a nice **block structure** in the determinantal basis.

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

Insert the expansion

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

Multiply with the HF function from the left:

$$C_0\underbrace{\left\langle\Phi_{HF}\mid\hat{H}_{BO}\mid\Phi_{HF}\right\rangle}_{E_{HF}} + \sum_{ia} C_i^a\underbrace{\left\langle\Phi_{HF}\mid\hat{H}_{BO}\mid\Phi_i^a\right\rangle}_{F_{ia}} + \tfrac{1}{4}\sum_{ijab} C_{ij}^{ab}\underbrace{\left\langle\Phi_{HF}\mid\hat{H}_{BO}\mid\Phi_{ij}^{ab}\right\rangle}_{\left\langle ij||ab\right\rangle}$$

$$E_{HF} + E_{corr}\longrightarrow \quad = E\left(C_0\underbrace{\left\langle\Phi_{HF}\mid\Phi_{HF}\right\rangle}_{1} + \sum_{ia} C_i^a\underbrace{\left\langle\Phi_{HF}\mid\Phi_i^a\right\rangle}_{0} + \tfrac{1}{4}\sum_{ijab} C_{ij}^{ab}\underbrace{\left\langle\Phi_{HF}\mid\Phi_{ij}^{ab}\right\rangle}_{0}\right)$$

$$F_{ia} = h_{ia} + \sum_j \left\langle ij\,||\,aj\right\rangle \qquad \text{Matrix element of the HF operator}$$

$$\varepsilon_{ij} = \tfrac{1}{2}\sum_{ab} C_{ab}^{ij}\left\langle ij\,||\,ab\right\rangle \qquad \textbf{\textcolor{red}{pair-correlation energy}}$$

$$\left\langle ij\,||\,ab\right\rangle = \left\langle ij\mid ab\right\rangle - \left\langle ij\mid ba\right\rangle = (ia\mid jb) - (ib\mid ja)$$

antisymmetrized two-electron integral.

We get:
$$\sum_{ia} C_a^i F_{ia} + \tfrac{1}{2} \sum_{ij} \varepsilon_{ij} = C_0 E_{corr}$$

However, if the orbitals really do satisfy the **canonical HF equations**

$$F\psi_i = \varepsilon_i \psi_i$$

then we see immediately by multiplying from the left with ψ_a and integrating:

$$\left\langle \psi_a \mid F \mid \psi_i \right\rangle = \varepsilon_i \left\langle \psi_a \mid \psi_i \right\rangle = 0$$

Note: this does <u>not</u> imply that the coefficients on the single excitations in the exact wavefunction are zero! They are not zero for HF orbitals. (there is a set of orbitals for which the singles coefficients are zero, the so called **Brueckner orbitals**).

Thus, for HF orbitals the matrix elements of the BO Hamiltonian with single excited determinants is zero! (**Brillouin's theorem**)

Finally:
$$\tfrac{1}{4} \sum_{ijab} C_{ab}^{ij} \left\langle ij \mid\mid ab \right\rangle = \tfrac{1}{2} \sum_{ij} \varepsilon_{ij} = C_0 E_{corr}$$
(**Nesbet's theorem**)

If we would know the precise values of the double excitation coefficients we would know the EXACT correlation energy!

✓ Too bad that we don't know the exact values of the double coefficients :-(since each coefficient of a given excitation level directly depends on the coefficients of the higher (up to 2 levels) and lower (up to two levels) excitation levels (consequently all coefficients are indirectly dependent on each other!).
Later we will see how we can determine pretty accurate approximations to the crucial double excitation coefficients!

✓ The expansion is **still infinite** and therefore pretty academic! In practice all we can do is of course to truncate the expansion by <u>not</u> using an infinite set of orbitals but a finite one. Then the determinantal expansion also becomes finite.
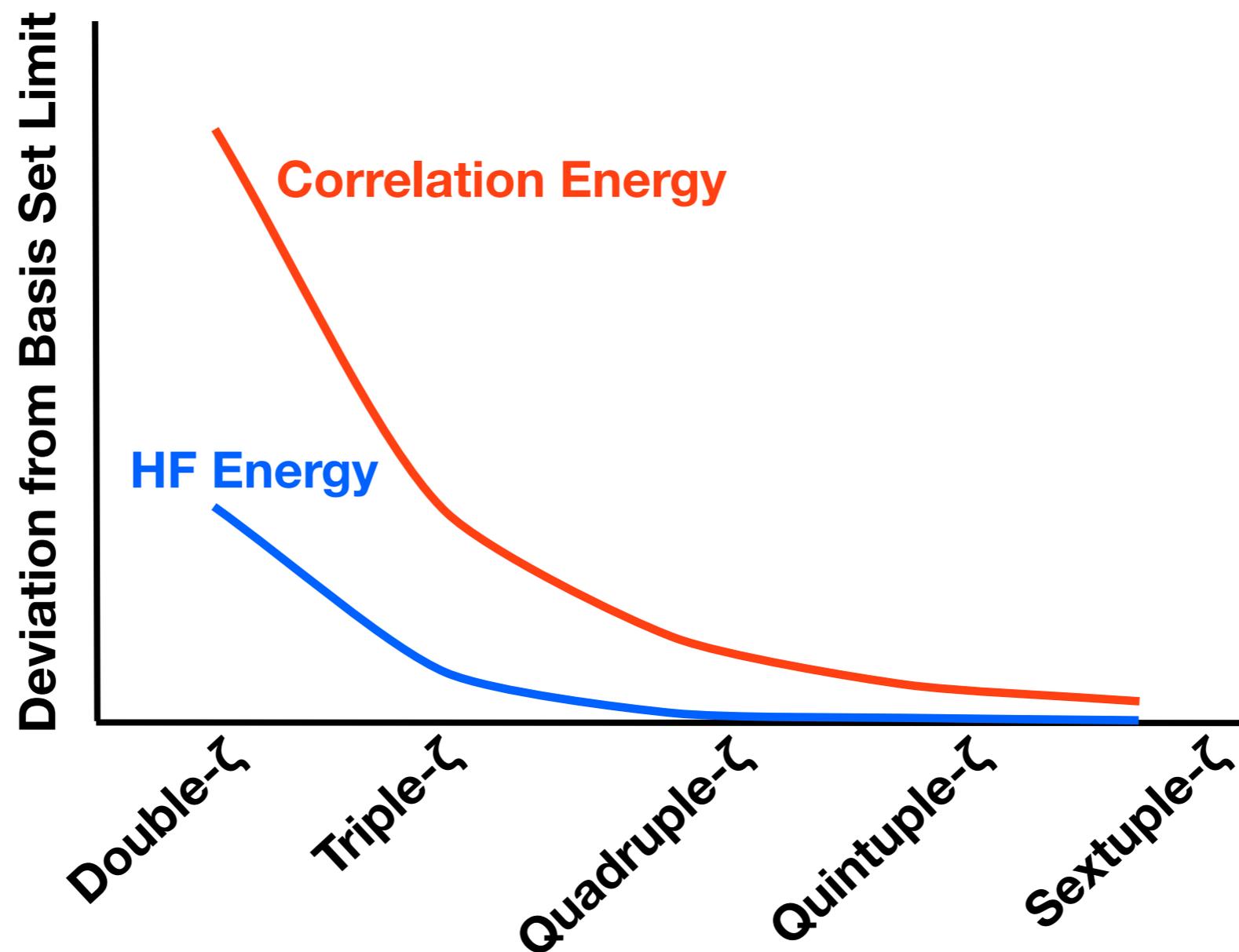
✓ Then we do not obtain the exact correlation energy from the full-CI but the **basis set correlation energy** and hope that we can get to the **basis set limit**

✓ In the Hartree-Fock theory that is not too hard. Unfortunately for CI the correlation energy **converges very slowly with the basis set**! *(F12-methods, extrapolation)*

Let us determine how many terms we have in the expansion if we assume N occupied and $V=N-M$ (M=size of the basis) virtual HF orbitals at our disposal. For excitation level n:

Number of ways to choose n out of N electrons to be excited: $\begin{pmatrix} N \\ n \end{pmatrix}$

Number of ways to choose n out of V acceptor orbitals (virtual): $\begin{pmatrix} V \\ n \end{pmatrix}$

Combine the two and sum over all excitation levels n up to N:

$$N_{\text{det}}(FCI) = \sum_{n=1}^{N} \begin{pmatrix} N \\ n \end{pmatrix} \begin{pmatrix} V \\ n \end{pmatrix} = \sum_{n=1}^{N} \frac{N!}{n!(N-n)!} \frac{(M-N)!}{n!(M-N-n)!} = \begin{pmatrix} M \\ N \end{pmatrix}$$

Using Stirling's formula: $k! \approx k^{k+\frac{1}{2}} \sqrt{2\pi + 1} \exp(-k)$

$$\begin{pmatrix} M \\ N \end{pmatrix} \approx \sqrt{\frac{M}{(2\pi+1)N(M-N)}} \left(\frac{M-N}{N} \right)^{N} \left(\frac{M}{M-N} \right)^{M}$$

Too Much!

Truncated Configuration Interaction

Nesbet's theorem implied a special role of the double excitations for the correlation problem (and an analysis of many body perturbation theory would confirm that). Hence, one might contemplate an **Ansatz** that only contains double excitations:

$$\left| \Psi \right\rangle = \left| \Psi_{HF} \right\rangle + \frac{1}{4} \sum_{ijab} C_{ab}^{ij} \left| \Phi_{ij}^{ab} \right\rangle$$

The coefficients of the double excitations were estimated to first order as (**MP2**):

$$C_{ab}^{ij(1)} = -\frac{\left\langle ij \, || \, ab \right\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

But what about calculating these coefficients variationally? → **Configuration Interaction**

$$\mathbf{HC} = E\mathbf{SC} \rightarrow \begin{pmatrix} E_{HF} & \mathbf{H}_{0D} \\ \mathbf{H}_{0D} & \mathbf{H}_{DD} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{C}_D \end{pmatrix} = E \begin{pmatrix} 1 \\ \mathbf{C}_D \end{pmatrix}$$

Large-dimensional eigenvalue problem → iterative solution (**Davidson algorithm**)

Size Consistency

If we treat a supersystem consisting of non-interacting subsystems, we should obtain the sum of the individual subsystem energies. Is that the case for CID?

$$E_{corr} = \frac{\left\langle \Psi_{HF} + \Psi_{corr} \left| \hat{H} - E_{HF} \right| \Psi_{HF} + \Psi_{corr} \right\rangle}{\left\langle \Psi_{HF} + \Psi_{corr} \middle| \Psi_{HF} + \Psi_{corr} \right\rangle}$$

Now, for localized orbitals, it is easy to show that the **numerator** gives:

$$\left\langle \Psi_{HF} + \Psi_{corr} \mid H \mid \Psi_{HF} + \Psi_{corr} \right\rangle = \left\langle \Psi_{HF} + \Psi_{corr}^{(A)} + \Psi_{corr}^{(B)} \mid H \mid \Psi_{HF} + \Psi_{corr}^{(A)} + \Psi_{corr}^{(B)} \right\rangle \equiv \boxed{X_A + X_B}$$

For the **denominator** we have:

$$\left\langle \Psi_{HF} + \Psi_{corr} \mid \Psi_{HF} + \Psi_{corr} \right\rangle \equiv \boxed{1 + Y_A + Y_B}$$

Hence:
$$E_{corr} = \frac{X_A + X_B}{1 + Y_A + Y_B} \boxed{\neq E_{corr}(A) + E_{corr}(B)}$$
$$\approx \left(X_A + X_B \right)\left[1 - \left(Y_A + Y_B + ... \right) \right]$$

Truncated CI is <u>NOT</u> size consistent

(and hence useless for chemistry)

For a single minimal basis H_2 molecule we found that the CID matrix was of the form:

$$\mathbf{H} = \begin{pmatrix} 0 & V \\ V & \Delta \end{pmatrix}$$

$$\Delta = \left\langle \Psi_D \mid \hat{H} \mid \Psi_D \right\rangle - \left\langle \Psi_{HF} \mid \hat{H} \mid \Psi_{HF} \right\rangle$$

$$V = \left\langle \Psi_0 \mid \hat{H} \mid \Psi_D \right\rangle$$

— σ^*

— σ
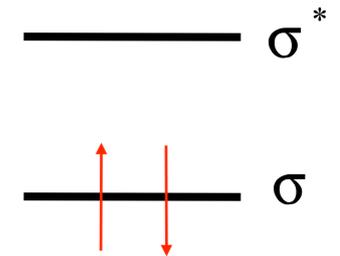
Ground state of the minimal basis H_2 system

With the lowest eigenvalue:

$$E_0 = \tfrac{1}{2}\left(\Delta - \sqrt{\Delta^2 + 4V^2} \right)$$

It is easy to show that for N noninteracting H_2 molecules CID gives:

$$E_0 = \tfrac{1}{2}\left(\Delta - \sqrt{\Delta^2 + 4NV^2} \right)$$

Which is **not** size consistent. We return to N=2 and study what is missing from CID.

Obviously, one step beyond CID is to include higher excitations. In the minimal basis 2x H_2 model system this would be a „**simultaneous pair excitation**" in which both H_2's are put in their excited state.

$$|0\rangle \qquad |D_A\rangle \qquad |D_B\rangle \qquad |Q\rangle = |D_A + D_B\rangle$$
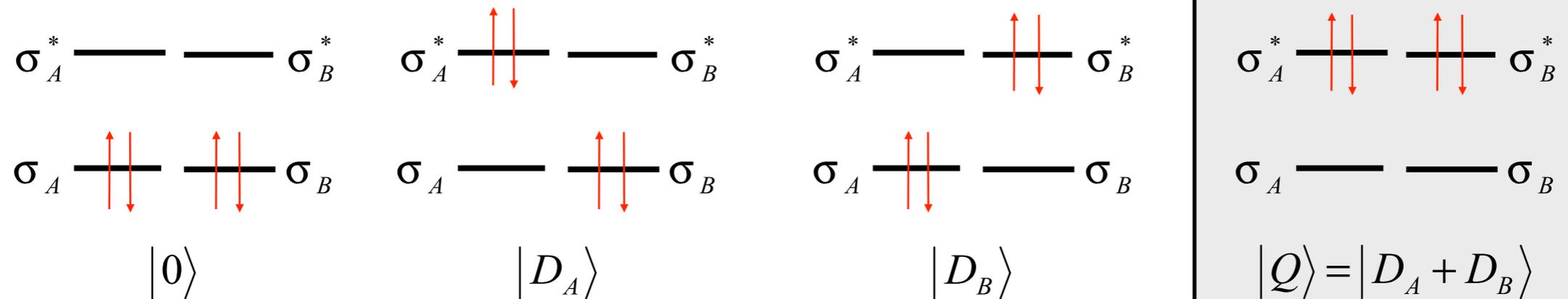
Matrix-elements:

$$\langle D_A|\hat{H}|D_A\rangle = \langle D_B|\hat{H}|D_B\rangle = \langle 0|\hat{H}|0\rangle + \Delta \qquad \text{Diagonal doubles}$$

$$\langle Q|\hat{H}|Q\rangle = \langle 0|\hat{H}|0\rangle + 2\Delta \qquad \text{Diagonal quadruple}$$

$$\langle 0|\hat{H}|D_A\rangle = \langle 0|\hat{H}|D_B\rangle = \langle \sigma\sigma\|\sigma^*\sigma^*\rangle = V \qquad \text{Doubles/ground state}$$

$$\langle 0|\hat{H}|Q\rangle = 0 \qquad \text{Quadruple/ground state}$$

$$\langle D_A|\hat{H}|Q\rangle = \langle D_B|\hat{H}|Q\rangle = V \qquad \text{Quadruple/doubles} = \text{Doubles/ground state!}$$

In order to solve the problem we form again the symmetry adapted linear combination of the two doubles: $|D\rangle = \frac{1}{\sqrt{2}}\left(|D_A\rangle + |D_B\rangle\right)$

The variational principle leads us then to the CI matrix (the configurations are in the order |0>, |D>, |Q>):

$$\mathbf{H} = \begin{pmatrix} 0 & \sqrt{2}V & 0 \\ \sqrt{2}V & \Delta & \sqrt{2}V \\ 0 & \sqrt{2}V & 2\Delta \end{pmatrix}$$

The lowest root is (without proof; look in a formula collection or use a computer algebra system):

$$E_0 = \Delta - \sqrt{\Delta^2 + 4V^2}$$
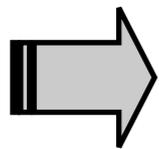
➡️ This is **twice the energy of a single H$_2$**. Thus, the **inclusion of the quadruple excitation restores the size consistency**!

Furthermore:

$$C_Q = \frac{\sqrt{2}V}{\underbrace{E - 2\Delta}_{C_D/2C_0}} C_D = \frac{1}{2C_0} C_D^2$$
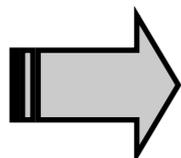
➡️ For noninteracting subsystems, **the coefficients of the quadruples are exactly products of doubles coefficients**!

Conclusions and Generalization

We had 3 key results in studying the $2xH_2$ problem:

1. *Inclusion of the simultaneous pair excitation exactly restores the size consistency.*

2. *The product of the simultaneous pair excitation was exactly proportional to the square of the coefficients of the double excitations (also follow from MBPT).*

3. *The matrix elements of the quadruple excitation with the doubles was equal to the matrix elements of the doubles with the ground state. Both sets of determinants differ by a double substitution from each other.*

Now we want to **generalize** these findings and restart from the full-CI equations.
Ansatz:

$$\left| \Psi \right\rangle = \left| \Psi_{HF} \right\rangle + \left| \Psi_D \right\rangle + \left| \Psi_Q \right\rangle$$

$$\left| \Psi_D \right\rangle = \frac{1}{4} \sum_{ijab} C_{ab}^{ij} \left| \Phi_{ij}^{ab} \right\rangle$$

$$\left| \Psi_Q \right\rangle = \frac{1}{576} \sum_{ijklabcd} C_{abcd}^{ijkl} \left| \Phi_{ijkl}^{abcd} \right\rangle$$

Insert into the Schrödinger equation and multiply from the left with the HF wavefunction gives the energy expression:

$$H\left(\left|\Psi_{HF}\right\rangle + \left|\Psi_D\right\rangle + \left|\Psi_Q\right\rangle\right) = E\left(\left|\Psi_{HF}\right\rangle + \left|\Psi_D\right\rangle + \left|\Psi_Q\right\rangle\right)$$

$$\left\langle\Psi_{HF}\right| \rightarrow E = E_{HF} + E_{corr} = E_{HF} + \left\langle\Psi_{HF} \mid H \mid \Psi_D\right\rangle$$

$$= E_{HF} + \frac{1}{4}\sum_{ijab} C_{ab}^{ij}\left\langle ij \mid\mid ab\right\rangle$$

Multiplication from the left with a double excitation (X is a **compound label X=(ij,ab)**) gives the **amplitude equation:**

$$\underbrace{\left\langle\Psi_X \mid H \mid \Psi_{HF}\right\rangle}_{\langle ij\mid\mid ab\rangle} + \underbrace{\left\langle\Psi_X \mid H \mid \Psi_D\right\rangle}_{} + \underbrace{\left\langle\Psi_X \mid H \mid \Psi_Q\right\rangle}_{} = EC_X$$

doubles/doubles   doubles/quadruples
interaction   interaction

In order to break the full-CI hierarchy we have to approximate the doubles/quadruples interaction! Let us try to use the insights gained from the H$_2$-dimer

$$\left|\Psi_D\right\rangle = \sum_X C_X \hat{E}_X \left|\Psi_{HF}\right\rangle$$

$$\left|\Psi_Q\right\rangle \approx \frac{1}{2}\sum_{X,Y} C_X C_Y \hat{E}_X \hat{E}_Y \left|\Psi_{HF}\right\rangle$$

(the E's are second quantized excitation operators)

BIG approximation 1: „disconnected quadruples"

We then insert into the amplitude equation:

$$\left\langle \Psi_D \mid H \mid \Psi_Q \right\rangle = \tfrac{1}{2} \sum_{Y,Z} C_Y C_Z \left\langle \Psi_X \mid \hat{H}\hat{E}_Y \hat{E}_Z \mid \Psi_{HF} \right\rangle$$

$$\approx C_X \sum_{Y} C_Y \left\langle \Psi_X \mid H\hat{E}_X \hat{E}_Y \mid \Psi_{HF} \right\rangle$$

$$\approx C_X \sum_{Y} C_Y \left\langle \Psi_{HF} \mid H\hat{E}_Y \mid \Psi_{HF} \right\rangle$$

BIG approximation 2: Matrix element transfer

$$= C_X \sum_{Y} C_Y \left\langle \Psi_{HF} \mid H \mid \Psi_Y \right\rangle = \boxed{C_X E_{corr}}$$

Hence, we arrive at a key result (MANY treatments arrive just there!):

$$\underbrace{\left\langle \Psi_X \mid H \mid \Psi_{HF} \right\rangle}_{\langle ij\|ab\rangle} + \underbrace{\left\langle \Psi_X \mid H \mid \Psi_D \right\rangle} + \underbrace{\left\langle \Psi_X \mid H \mid \Psi_Q \right\rangle} = E C_X$$

$$\left\langle \Psi_X \mid H \mid \Psi_{HF} \right\rangle + \left\langle \Psi_X \mid H \mid \Psi_D \right\rangle + E_{corr} C_X = \underbrace{E}_{E_{HF}+E_{corr}} C_X$$

$$\left\langle \Psi_X \mid H \mid \Psi_{HF} \right\rangle + \left\langle \Psi_X \mid H \mid \Psi_D \right\rangle = E_{HF} C_X$$

These are the **CEPA/0-equations.** You would have arrived there upon neglect of the normalization of the denominator in the Ritz functional as well ... or in many other ways! They also look like CID equation shifted with a diagonal shifted by E_{corr}

Exclusion principle violating terms

We have been a bit too hasty in making one-specific simplification: *we can only perform a double excitation on top of another double excitation if the two double excitations are truly „**disconnected**" (share* <u>no</u> *orbital label). Hence, we have to repair that:*

$$C_X \sum_Y C_Y \left\langle \Psi_{HF} \mid H\hat{E}_Y \mid \Psi_{HF} \right\rangle \to C_X \sum_Y C_Y \left\langle \Psi_{HF} \mid H\hat{E}_Y \mid \Psi_{HF} \right\rangle - C_X \sum_{Y \subset X} C_Y \left\langle \Psi_{HF} \mid H\hat{E}_Y \mid \Psi_{HF} \right\rangle$$

$$= C_X \left(E_{corr} - \sum_{Y \subset X} C_Y \left\langle \Psi_{HF} \mid H\hat{E}_Y \mid \Psi_{HF} \right\rangle \right)$$

$$\equiv C_X \left(E_{corr} - \Delta_X^{(EPV)} \right)$$
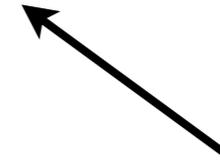
read: „joint with", e.g. shares orbital labels

The shifts are called „**Exclusion principle violating terms**".

Inserting into the full-CI equations now gives us the celebrated „**Coupled Electron Pair**" (**CEPA**) equations:

$$\left\langle \Psi_X \mid H \mid \Psi_{HF} \right\rangle + \left\langle \Psi_X \mid H \mid \Psi_D \right\rangle = \left(E_{HF} + \Delta_X^{(EPV)} \right) C_X$$

They are simply shifted CI equations. Without proof, the best CEPA method is **CEPA/1**:

$$\Delta_X^{(EPV)} = \Delta_{ijab}^{(EPV)} = \frac{1}{2} \sum_k \varepsilon_{ik} + \varepsilon_{jk}$$

$$\varepsilon_{ij} = \frac{1}{2} \sum_{ab} \left\langle ij \mid\mid ab \right\rangle C_{ab}^{ij}$$

Pair correlation energy $\quad E_{corr} = \frac{1}{2} \sum_{ij} \varepsilon_{ij}$

Accurate Theoretical Chemistry with Coupled Pair Models

FRANK NEESE,[*,†,‡] ANDREAS HANSEN,[†] FRANK WENNMOHS,[†]
AND STEFAN GRIMME[§]

☺ CEPA is beautiful ☺

For the overwhelming majority of cases CEPA is within 1-2 kcal/mol of CCSD(T) and systematically better than QCISD and CCSD.

Both are very close to experiment if large basis sets are used

Generalization of CEPA

In deriving CEPA we made two major approximations:

✓ Expressing the quadruples in terms of disconnected doubles amplitudes

✓ Expressing doubles/quadruples matrix elements in terms of pair correlation energies

The first approximation is physically sound, the second is mathematically sloppy. So let us avoid the second approximation. This is most easily done by introducing the **excitation operators**:

$$\hat{C}_1 = \sum_{ia} C_a^i a_a^+ a_i$$

$$\hat{C}_2 = \tfrac{1}{4} \sum_{ijab} C_{ab}^{ij} a_a^+ a_b^+ a_j a_i$$

Now we also include the singles and make the **Ansatz**:

$$\left| \Psi_S \right\rangle = \hat{C}_1 \left| \Psi_{HF} \right\rangle$$

$$\left| \Psi_D \right\rangle = \hat{C}_2 \left| \Psi_{HF} \right\rangle$$

$$\left| \Psi_Q \right\rangle \approx \hat{C}_2 \hat{C}_2 \left| \Psi_{HF} \right\rangle$$

This Ansatz leads immediately to what we consider as the most proper CEPA version: the **quadratic configuration interaction with singles and doubles, QCISD**). *(This is <u>NOT</u>, how this method was historically perceived.)*

$$E_{QCISD} = E_{HF} + \tfrac{1}{4}\sum_{ijab}\left\langle ij \,||\, ab\right\rangle C_{ab}^{ij}$$

$$E_{corr}\,C_a^i = \left\langle \Psi_i^a \mid H(1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_1\hat{C}_2)\mid \Psi_{HF}\right\rangle$$

$$E_{corr}\,C_{ab}^{ij} = \left\langle \Psi_{ij}^{ab} \mid H(1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_2\hat{C}_2)\mid \Psi_{HF}\right\rangle$$

These equations contain disconnected triples in the singles equation and disconnected quadruples in the doubles equation. Once the matrix elements are evaluated (perhaps best in terms of diagrams) and properly solved, the result are size consistent, unitarily invariant correlation energies of excellent quality.

Instead of putting in **products of excitation operators** „by hand", we can choose an Ansatz that incorporates them from the beginning:

$$\left|\Psi_{CC}\right\rangle = \exp(\underbrace{\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ...}_{\hat{T}})\left|\Psi_{HF}\right\rangle$$

$$= (1 + \hat{T} + \tfrac{1}{2}\hat{T}^2 + \tfrac{1}{3!}\hat{T}^3 + ...)\left|\Psi_{HF}\right\rangle$$

$$\hat{T}_1 = \sum_{ia} t_a^i \left\{ a_a^+ a_i \right\}$$

$$\hat{T}_2 = \tfrac{1}{4} \sum_{ijab} t_{ab}^{ij} \left\{ a_a^+ a_b^+ a_j a_i \right\}$$

$$\hat{T}_3 = \tfrac{1}{36} \sum_{ijkabc} t_{abc}^{ijk} \left\{ a_a^+ a_b^+ a_c^+ a_k a_j a_i \right\}$$

In the limit where either all C-operators or all T-operators are included in the treatment, the CI and CC wavefunctions are identical and CC is a more complicated way of parameterizing the full-CI wavefunction. For truncation of the C-operator series or the T-operator series the CC expansion is more complicated but much more accurate.

We have purposely renamed the CI coefficients **C** to cluster amplitudes **t** and the *C*-operators to *T*-operators to:
a) follow the conventions used in the literature and
b) emphasize that the two types of quantities are different

✓ This is the famous „**Coupled Cluster Expansion**".

✓ In CI theory the unknowns are the **CI coefficients C** of the single, double, triple,... excitations which are determined from the variational principle.

✓ In Coupled Cluster theory the unknowns are the „**cluster amplitudes**" *t* for the single, double, triple,... excitation operators.

While these t's and C's appear to be closely related there is an important difference which becomes obvious upon expanding the linear and nonlinear terms in the power series expansion of the exponential. Restricting, the cluster operator at the moment to the T_1 and T_2 terms:

$$\exp(\hat{T}_1 + \hat{T}_2) = 1 + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + +\hat{T}_1\hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2 + ...$$

Thus, at each **spin-orbital excitation level n** the coupled cluster expansion has amplitudes arising from „genuine" (**connected**) n-tuple excitations and those (**disconnected**) parts which arise as products of lower excitations. In CI theory each n-tuple excitation is only associated with a single coefficient.

(In other words - if the CC T-operator is truncated, the model still contains highly excited determinants. This is <u>not</u> the case for the CI model where each determinant in the treatment comes with its own coefficient. In the CC model the coefficients of the higher excitations are approximated as products of coefficients of lower excitations!)

$$\hat{C}_1 = \hat{T}_1$$

$$\hat{C}_2 = \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_2$$

$$\hat{C}_3 = \tfrac{1}{6}\hat{T}_1^3 + \hat{T}_1\hat{T}_2 + \hat{T}_3$$

$$\hat{C}_4 = \tfrac{1}{24}\hat{T}_1^4 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_3 + \hat{T}_4$$

Solution of the CC Equations

✓ Inserting the CC Ansatz into the variational functional:

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle e^T \Psi_0 | \hat{H} | e^T \Psi \rangle}{\langle e^T \Psi | e^T \Psi \rangle}$$

shows that this is a **hopeless idea** – the expansion **does not terminate**.

✓ Thus, an alternative is needed and is readily derived from inserting the CC-Ansatz into the Schrödinger equation:

$$\hat{H}_{BO} | \Psi \rangle = E | \Psi \rangle$$

$$\hat{H}_{BO} e^T | \Psi_0 \rangle = E e^T | \Psi_0 \rangle$$

✓ The amplitudes are determined by projecting onto the Schrödinger equation. In CI that gave the same results as the variational treatment. In CC theory this is evidently not so.

$$E_{CC} = \langle \Psi_0 | \hat{H}_{BO} e^T | \Psi_0 \rangle$$

$$0 = \langle \Psi_X | \hat{H}_{BO} e^T | \Psi_0 \rangle$$

Ψ_X is some excited determinant

✓ The correlation energy results from projection with the HF determinant

$$E_{corr} = \tfrac{1}{4} \sum_{ij} t_{ab}^{ij} \langle ij \, || \, ab \rangle$$

some diagrams in the doubles equation:

$$-P(ij)t_{im}^{ab}f_{me}t_j^e \qquad -P(ij)t_{im}^{ab}\langle mn||je\rangle t_n^e \qquad -\tfrac{1}{2}P(ij)t_{im}^{ab}\langle mn||ef\rangle t_{jn}^{ef}$$

$$-P(ij)t_{im}^{ab}\langle mn||ef\rangle t_j^e t_n^f \qquad \tfrac{1}{2}\langle mn||ij\rangle t_{mn}^{ab} \qquad \langle mn||ij\rangle t_m^a t_n^b$$

$$\tfrac{1}{2}P(ij)t_{mn}^{ab}\langle mn||ie\rangle t_j^e \qquad P(ij)t_m^a t_n^b \langle mn||ie\rangle t_j^e \qquad \tfrac{1}{4}t_{mn}^{ab}t_{ij}^{ef}\langle mn||ef\rangle$$

$$\tfrac{1}{2}t_m^a t_n^b t_{ij}^{ef}\langle mn||ef\rangle \qquad \tfrac{1}{2}t_{mn}^{ab}t_i^e t_j^f\langle mn||ef\rangle \qquad t_m^a t_n^b t_i^e t_j^f\langle mn||ef\rangle$$

$$\tfrac{1}{2}t_{ij}^{ef}\langle ab||ef\rangle \qquad t_i^e t_j^f\langle ab||ef\rangle \qquad -\tfrac{1}{2}P(ab)t_{ij}^{ef}\langle am||ef\rangle t_m^b \qquad -P(ab)t_i^e t_j^f\langle am||ef\rangle t_m^b$$

$$P(ij)P(ab)t_{im}^{ae}\langle mb||ej\rangle \qquad -P(ij)P(ab)t_{im}^{ae}\langle mn||ej\rangle t_n^b \qquad P(ij)P(ab)t_{im}^{ae}\langle mb||ef\rangle t_j^f$$

$$-P(ij)P(ab)t_{im}^{ae}\langle mn||ef\rangle t_n^b t_j^f \qquad \tfrac{1}{2}P(ij)P(ab)t_{im}^{ae}t_{jn}^{bf}\langle mn||ef\rangle \qquad -P(ij)P(ab)t_i^e t_m^a\langle mb||ej\rangle$$

$$-P(ab)t_m^a\langle mb||ij\rangle \qquad P(ij)t_i^e\langle ab||ej\rangle$$

Source: Gauss J. (**1998**) in: von Schleyer, P.v.R. et al. *Encyclopedia Computational Chemistry*, pp 615-636.

Triple Excitations

In recent years it has become possible for small molecules to pursue very accurate calculations which explicitly include the triple and quadruple excitations in CCSDT and CCSDTQ. However, in the majority of cases, these calculations are simply too expensive as already CCSDT features an effort which scales as $O(N^8)$. On the other hand it is clear that one has to go beyond CCSD if high accuracy (i.e. „chemical accuracy" of 1-3 kcal/mol) should be reached.

The compromise is the „gold standard" **CCSD(T) model** in which a perturbative correction to the connected triple excitations is calculated based on the converged amplitudes of a CCSD calculation. The correction features an asymptotic $O(N^7)$ effort and reads:

$$\Delta E^{(T)} = -\frac{1}{36} \sum_{ijkabc} t_{abc}^{ijk} \left(t_{abc}^{ijk} + \tilde{t}_{abc}^{ijk} \right) \left(\varepsilon_a + \varepsilon_b + \varepsilon_c - \varepsilon_i - \varepsilon_j - \varepsilon_k \right)$$

$$t_{abc}^{ijk} = -P(ijk)P(abc) \frac{\sum_d t_{ad}^{ij} \langle bc \,||\, dk \rangle - \sum_l t_{ab}^{il} \langle lc \,||\, jk \rangle}{\varepsilon_a + \varepsilon_b + \varepsilon_c - \varepsilon_i - \varepsilon_j - \varepsilon_k}$$

$$\tilde{t}_{abc}^{ijk} = -P(ijk)P(abc) \frac{t_a^i \langle bc \,||\, jk \rangle}{\varepsilon_a + \varepsilon_b + \varepsilon_c - \varepsilon_i - \varepsilon_j - \varepsilon_k}$$

Convergence of CC Energies

Deviation from full-CI (CO molecules, cc-pVDZ basis, frozen core) in mE_h for CI and CC models with various excitation levels:

	CI	CC
SD	30.804	12.120
SDT	21.718	1.011[a]
SDTQ	1.775	0.061
SDTQP	0.559	0.008
SDTQPH	0.035	0.002

a: 1.47 mE_h for CCSD(T)
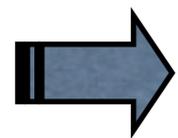
➡ For a given excitation level, the CC models are about one order of magnitude more accurate than CI models (which becomes even more significant for larger molecules)!

source: Gauss, J.; Lecture notes for „Coupled Cluster Theory", Workshop, Mariapfarr, Austria, 2004.

High Accuracy Thermochemistry with CC

Using the most accurate modern CC methods together with large basis sets and corrections for relativistic effects, one can calculate the atomization energy for small molecules to better than 1 kcal/mol.

Example: **CO molecule, atomization energy** [kcal/mol]:

```
HF-Level                 :  174.40 kcal/mol
Correlation (CCSD(T))    :   85.30
Zero-Point Vibration     :   -3.10
Spin-Orbit Coupling      :   -0.29
Scalar Relativity        :   -0.17
Correlation (>CCSD(T))   :   -0.04
Non Born-Oppnheimer      :    0.03
------------------------------------------------
Sum(Theory)                  256.29
Experiment                   256.2
```

source: From Gauss, J.; Lecture notes for „Coupled Cluster Theory", Workshop, Mariapfarr, Austria, 2004.

Problem with Wavefunction Methods

Explosive cost
Wall clock time $\propto O(N^7)$

Aim of the Development

Premises

✓ **Coupled cluster *would* be the method of choice if it *would* be applicable in reasonable turnaround times to molecules of current chemical interest.**

... this means 50-200 atoms (QM/MM for larger)

... currently these studies are done with DFT (mostly B3LYP)

... if the accuracy of DFT is in question, typically CC calculations on model systems are called upon

Conclusions

✓ Produce methodology that is as black box as DFT or canonical CC

✓ The method must be computationally affordable (Not *much* more expensive than the gold standard B3LYP)

✓ The method must be generally applicable to properties, open shells, transition metals, ...

Premises

✓ **Cou** ... **ble in**
   reas ... **st.**

... thi ...

... currently these studies are done with DFT (mostly B3LYP)

... if t ... systems

are c ...

> **Efficient and accurate local approximations to coupled-electron pair approaches: An attempt to revive the pair natural orbital method**
>
> Frank Neese,[1,2,a] Frank Wennmohs,[1] and Andreas Hansen[1]
>
> *J. Chem. Phys.*, **2009**, 130, 114108

> THE JOURNAL OF CHEMICAL PHYSICS 131, 064103 (2009)
>
> **Efficient and accurate approximations to the local coupled cluster singles doubles method using a truncated pair natural orbital basis**
>
> Frank Neese,[a] Andreas Hansen, and Dimitrios G. Liakos
> *Lehrstuhl für Theoretische Chemie, Universität Bonn, Wegelerstr. 12, D-53115 Bonn, Germany*
>
> (Received 27 April 2009; accepted 18 June 2009; published online 10 August 2009)

Conclusio ...

✓ Produce methodology that is as black box as DFT or canonical CC

✓ The ... ve
   than ...

✓ The ... ition
   meta ...

> **An efficient and near linear scaling pair natural orbital based local coupled cluster method**
>
> Christoph Riplinger and Frank Neese[a]
> *Max Planck Institut für Chemische Energiekonversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr, Germany*
>
> (Received 28 September 2012; accepted 13 December 2012; published online XX XX XXXX)

The *ORCA* Project

Hartree-Fock

RHF,UHF,ROHF,CASSCF
Direct, Semidirect, Conventional,
RI-Approx., Newton-Raphson

Semiempirical

INDO/S,MNDO,AM1,PM3,NDDO/1

Density Functional

LDA, GGA, Hybrid Functionals
Double hybrid functionals,
RI-Approx., Newton-Raphson
RKS,UKS,ROKS

Electron Correlation

MP2/RI-MP2
CCSD(T),QCISD(T),CEPA,CPF
(all with and without RI, Local)
MR-MP2, MR-MP3, MR-MP4(SD)
MR-CI, MR-ACPF, MR-AQCC

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Excited States

TD-DFT/CIS+gradients
MR-CI/DDCI/SORCI

Relativistic Methods

1st-5th Order Douglas-Kroll-Hess
Zero'th Order Regular Approximation (ZORA)
Infinite Order Regular Approximation (IORA)
Picture Change Effects, All electron basis sets,
(Effective core potentials)

Molecular Properties

Analytical Gradients(HF,DFT,MP2) + Geometries + Trans. States
Polarizabilities, Magnetizabilities (Coupled-Perturbed HF/KS)
COSMO Solvation Model Throughout
IR, Raman and Resonance Spectra (Numerical Frequencies)
EPR-Parameters (g,A,D,J,Q)
Mössbauer-Parameters (δ,ΔE_Q)
ABS,CD,MCD Spectra
Population Analysis, NBOs, Localization, Multipole Moments,...

Saving Time in Electronic Structure Calculations

Exploit Sparsity!
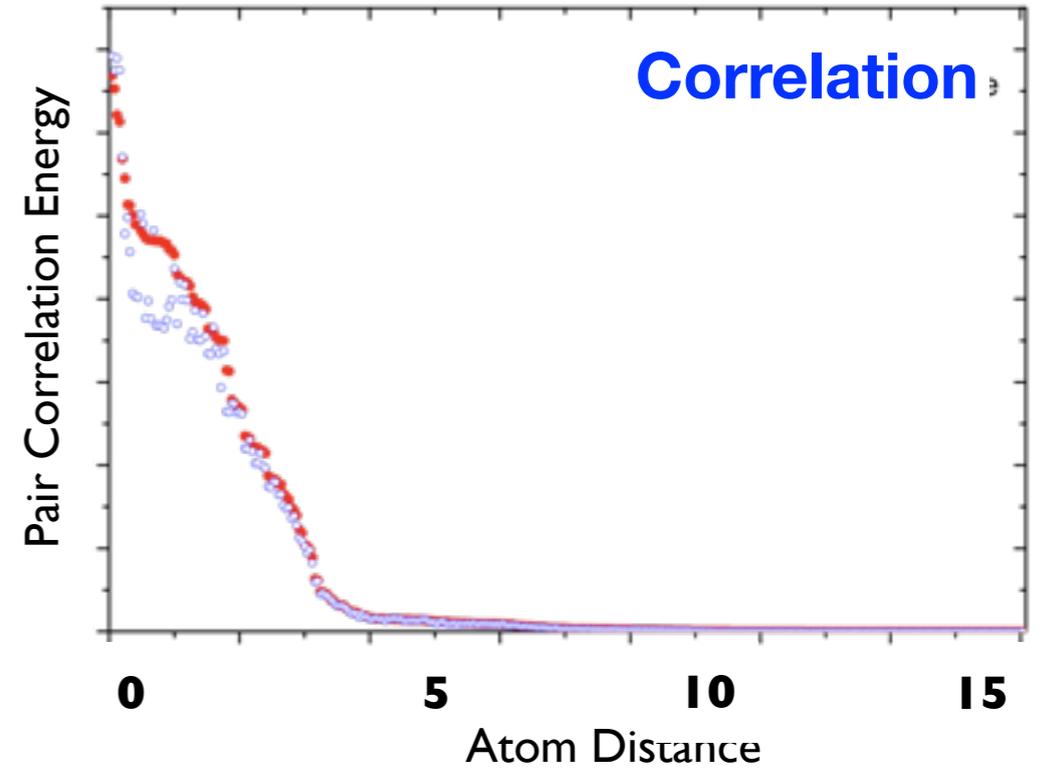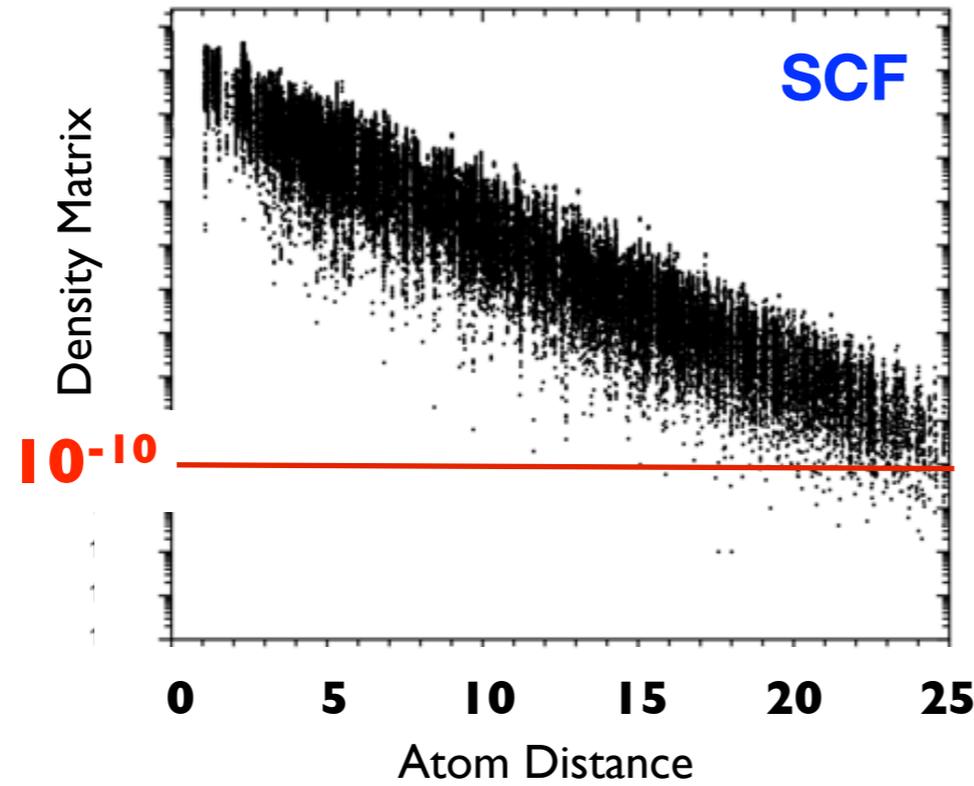
Compress Data!

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

Canonical Virtual Orbitals and Correlation

Canonical virtual orbitals are a „chaotic" space for correlating electron pairs

MO120   MO140   MO98
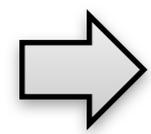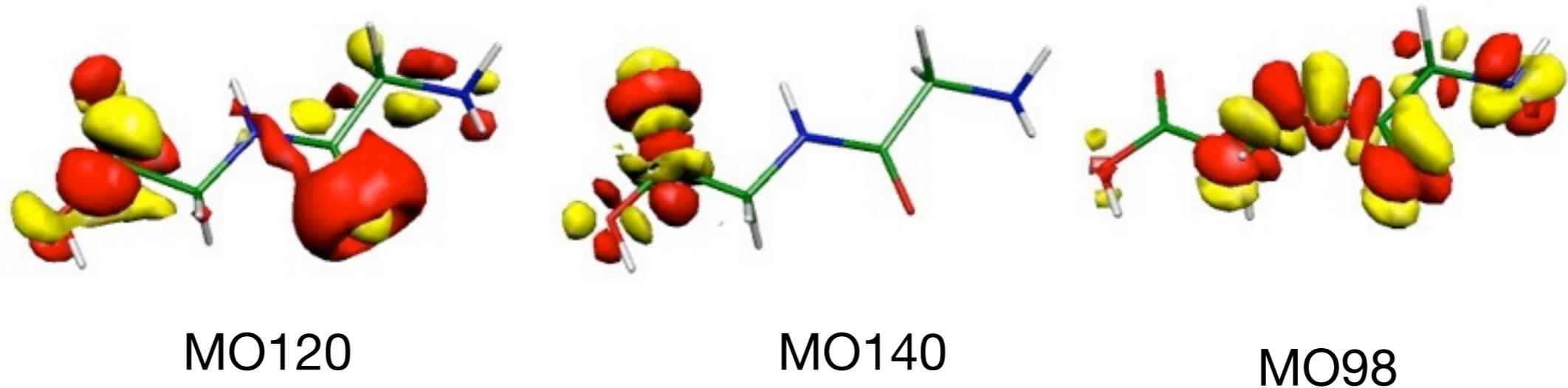
⇒ Truncation schemes based on canonical MOs are unlikely to be highly successful

Projected atomic orbitals, PAOs, Pulay, P. *CPL*, **1983**, 100, 151 $$\left|\tilde{\mu}\right\rangle=\left(1-\sum_i\left|i\right\rangle\left\langle i\right|\right)\left|\mu\right\rangle$$
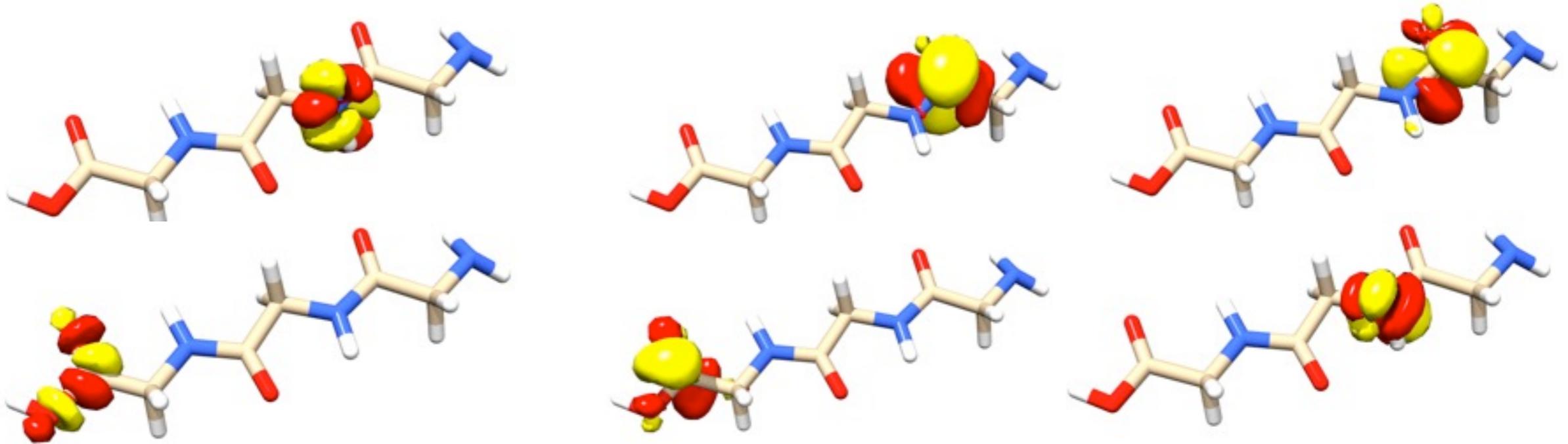
⇒ Only the PAOs of „**domains**" close to a given occupied orbitals are taken

⇒ **Pair domains** are constructed from individual orbital domains

⇒ Solid local basis for electron correlation! Leads to **linear scaling** when done properly (Pulay, Werner, Schütz)

⇒ If domains are chosen to be accurate they contains >10-20 atoms and then the calculations still become expensive or not feasible

⇒ An even more compact set is obtained by using **pair natural orbitals** (Meyer, Kutzelnigg, Staemmler, Taylor). *Local* **PNOs** (FN)

Most Compact Expansion: Natural Orbitals

Shortest possible accurate virtual space expansion through neglecting natural orbitals with occupation number T_{CutPNO} ($<10^{-7}$)
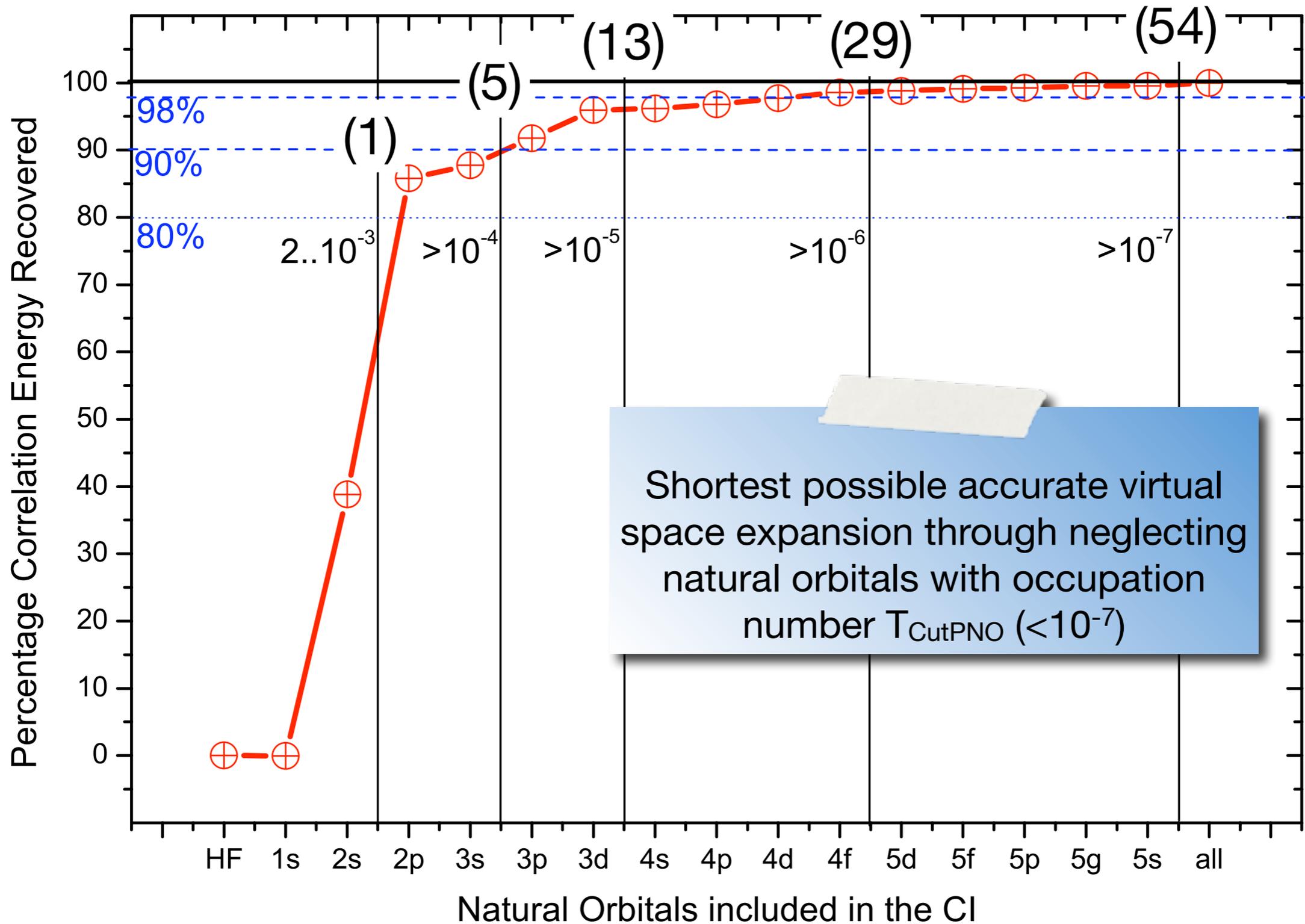
The Beauty of Pair Natural Orbitals

- ‣ Small number of significant PNOs per electron pair
- ‣ Vanishing (0-5) PNOs for weak pairs (But see talk of HJ Werner)
- ‣ Located in the same region of space as the internal pair but as delocalized as necessary
- ‣ Asymptotically basis set independent number of PNOs for each pair

n=0.0003

n=0.0010

n=0.0011

n=0.0030

n=0.0035

n=0.0002

n=0.0004

n=0.0011

n=0.0002

FN; Wennmohs, F.; Hansen, A. *J. Chem. Phys.* **2009**, 130, 114108
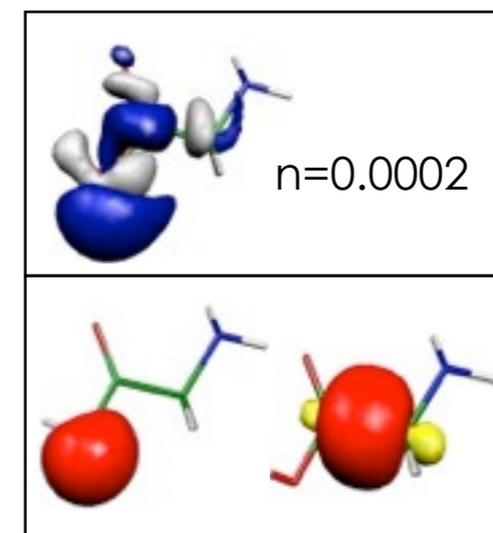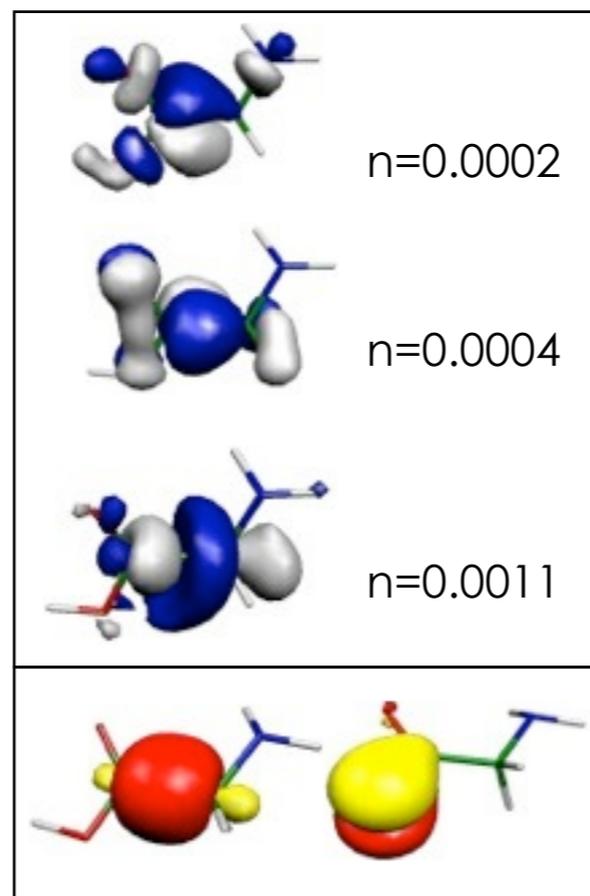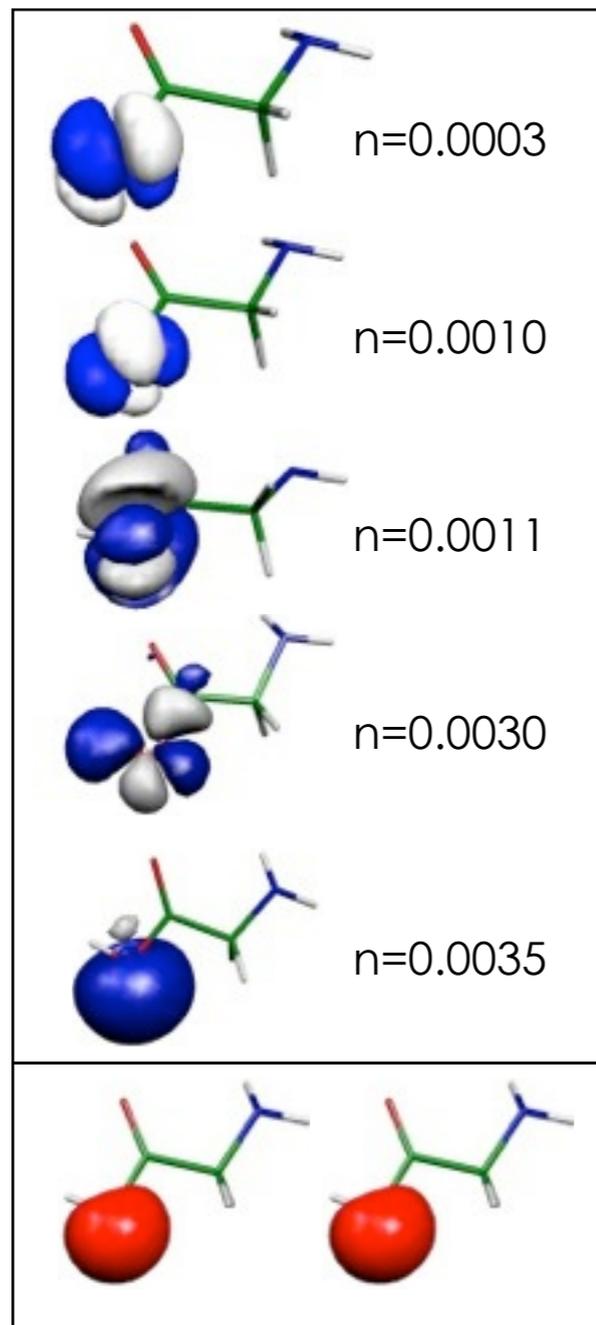
Convergence of LPNO-CCSD

LPNO$_1$-CCSD
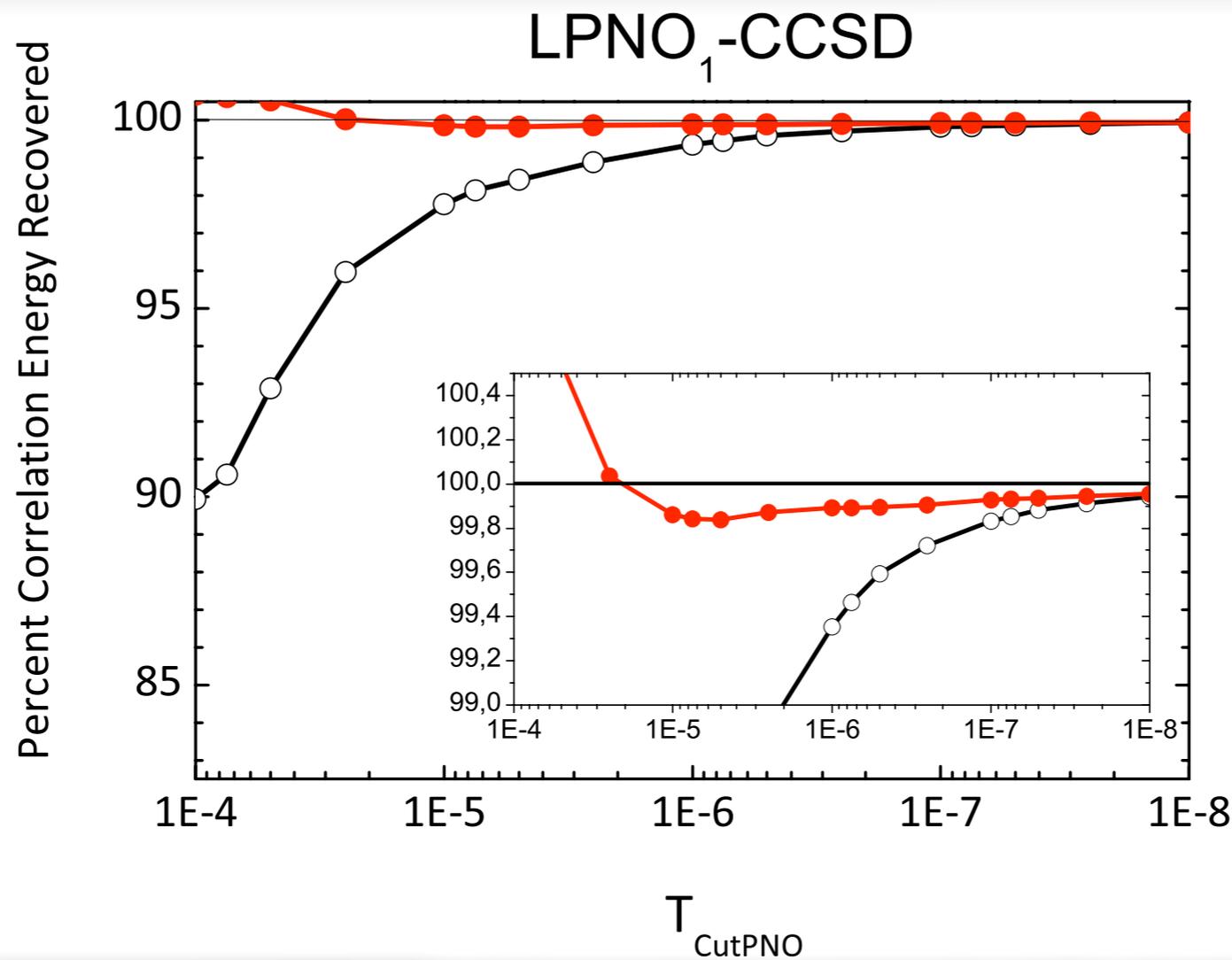
- ✓ Typically 99.8-99.9% of the canonical correlation energy is recovered in LPNO-(CEPA,QCISD, CCSD)
- ✓ Energetics of the canonical counterpart methods is reproduced to 1 kcal/mol or better
- ✓ The methods are robust and completely black box in character (as the canonical counterparts).

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

FN; A. Hansen, D.G. Liakos,, *J. Chem. Phys.*, **2009** 131, 064103

Cyclohexane/cc-pVTZ

Attractive Features of the LPNO Approach

(1)   Simplicity. Only one critical cut-off (T_{CutPNO}); local approximations only ‚boost'

efficiency. T_{CutPNO} can be use to control the absolute desired accuracy

(2)   No real-space cut-offs or fragmentation necessary

(3)   No redundant integral generation or amplitude optimizations

(4)   No reliance on sparsity

(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)   With (moderately) conservative thresholds only 0.1-0.3% of E_c is lost. Reproduces

the canonical result to within a few 0.1 kcal/mol

(8)   Very weak or no dependence on the localization method. Well localized internal

space not even required

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

(10)   Black box character

Canonical:
! cc-pVTZ CCSD
LPNO:
! cc-pVTZ cc-pVTZ/C DLPNO-CCSD

n=0.0003

n=0.0010

n=0.0011

n=0.0030

n=0.0035
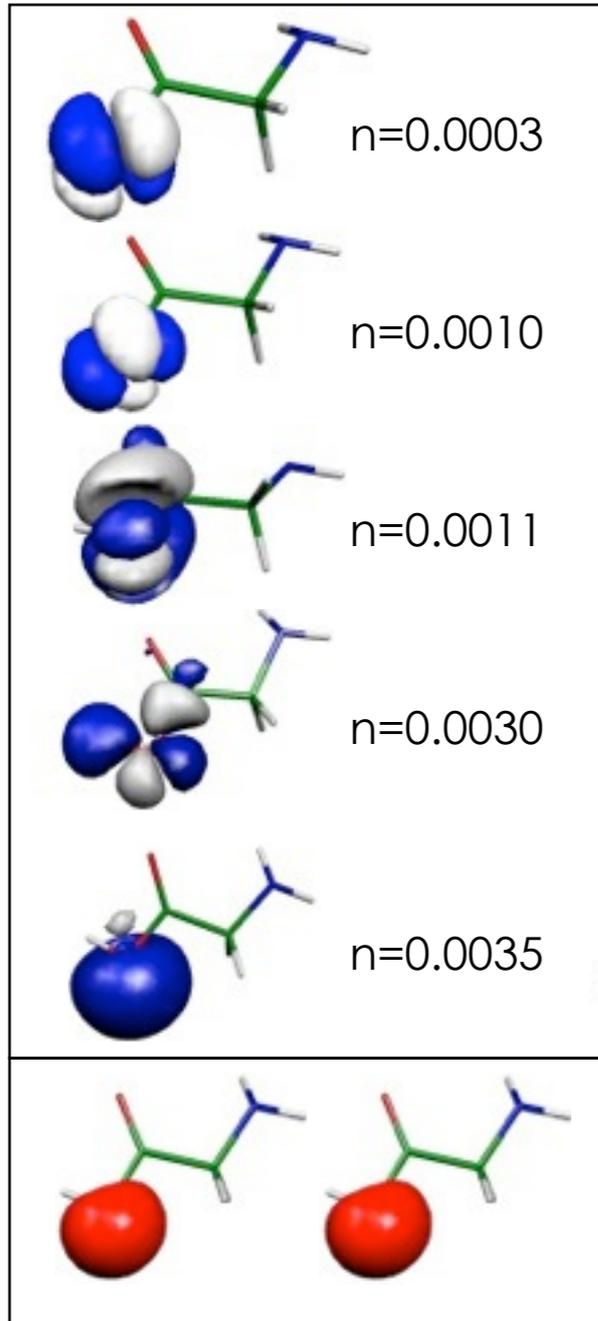
PNOs are localized in the same region of space as the internal orbitals that they correlate

⟹ PNOs can be mapped onto domains

⟹ How large are these domains?

$T_{MKN}=0.1$

$T_{MKN}=0.01$

$T_{MKN}=0.001$

Correlated bond
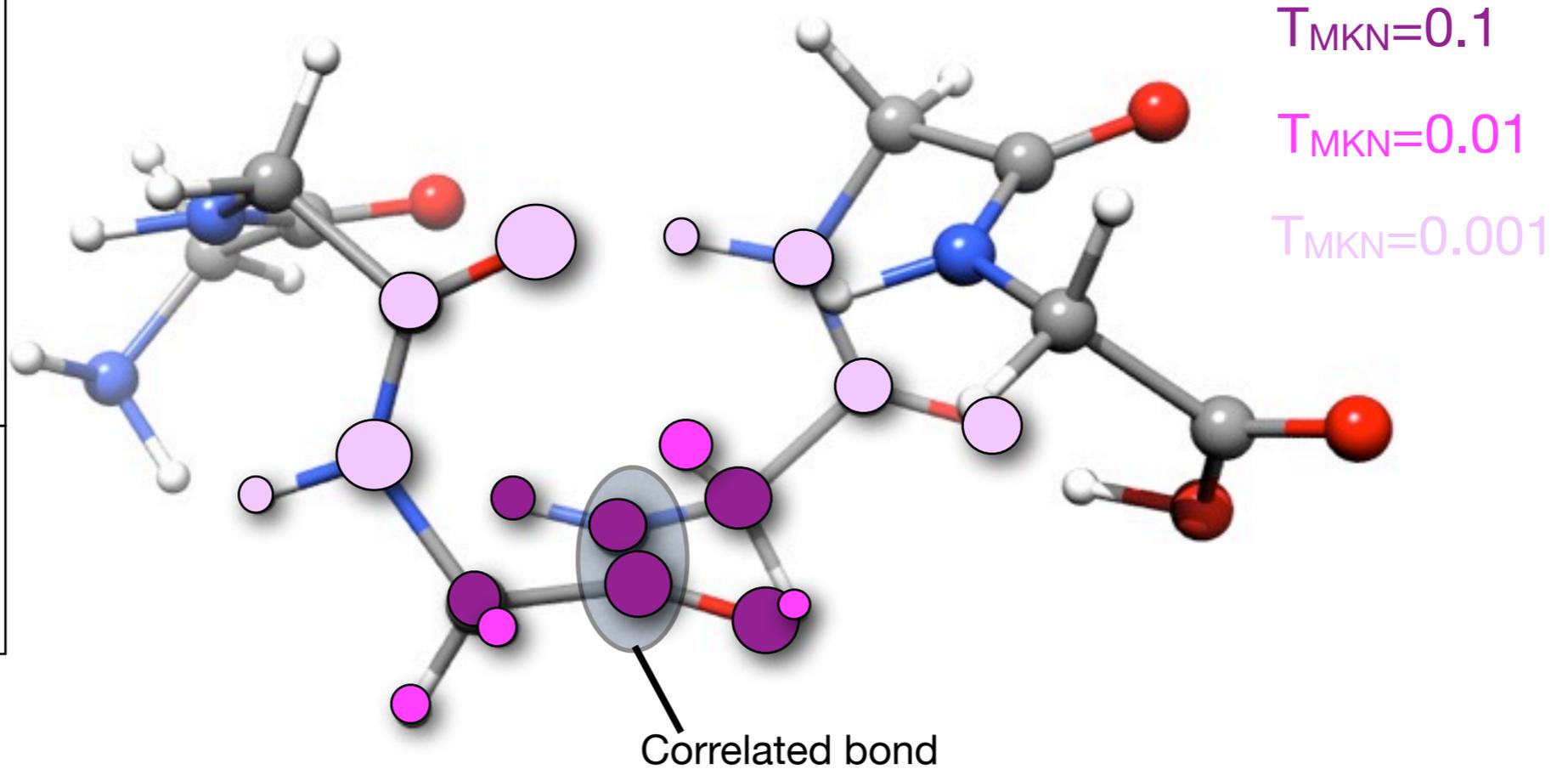
(ICQC, 2009)

The best of Both Worlds DLPNO

✓ **The original LPNO-Method** Expanded the PNOs in terms of virtual MOs. Hence, the PNOs were local but the expansion basis was not

▶ undesirable fifth order scaling steps limited the applicability of the method to about 100 atoms

▶ **Expansion of the PNOs in terms of PAOs eliminates all bottlenecks and leads to (near) linear scaling LPNO-CCSD ('Domain Based' LPNO, DLPNO)**

LPNO-CCSD
$$\left| \tilde{a}_{ij} \right\rangle = \sum_{a} d_{a\tilde{a}}^{ij} \left| a \right\rangle$$

DLPNO-CCSD
$$\left| \tilde{a}_{ij} \right\rangle = \sum_{\tilde{\mu} \in \{ij\}} d_{\tilde{\mu}\tilde{a}}^{ij} \left| \tilde{\mu} \right\rangle$$

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

Dr. Christoph Riplinger

Pair Natural Orbital Construction

Pair density construction: LMP2 amplitudes
$$T^{ij}_{\tilde{\mu}\tilde{\nu}} = -\frac{(i\tilde{\mu} \mid j\tilde{\nu})}{\varepsilon_{\tilde{\mu}} + \varepsilon_{\tilde{\nu}} - F_{ii} - F_{jj}}$$

$$\mathbf{D}^{ij} = \tilde{\mathbf{T}}^{ij+}\mathbf{T}^{ij} + \tilde{\mathbf{T}}^{ij}\mathbf{T}^{ij+} \quad \tilde{T}^{ij} = \frac{1}{1+\delta_{ij}}(4\mathbf{T}^{ij} - 2\mathbf{T}^{ij+})$$

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

$$\mathbf{D}^{ij}\mathbf{d}^{ij} = \mathbf{n}^{ij}\mathbf{d}^{ij}$$

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

Problem: if this is done for *each* electron pair, the cost will be significant since even in a local MP2 context the amplitude construction becomes expensive.

Solution: Use a **pair prescreening** to estimate which pairs are worthwhile computing and obtain a reliable estimate of the pair truncation effect

tail to be estimated
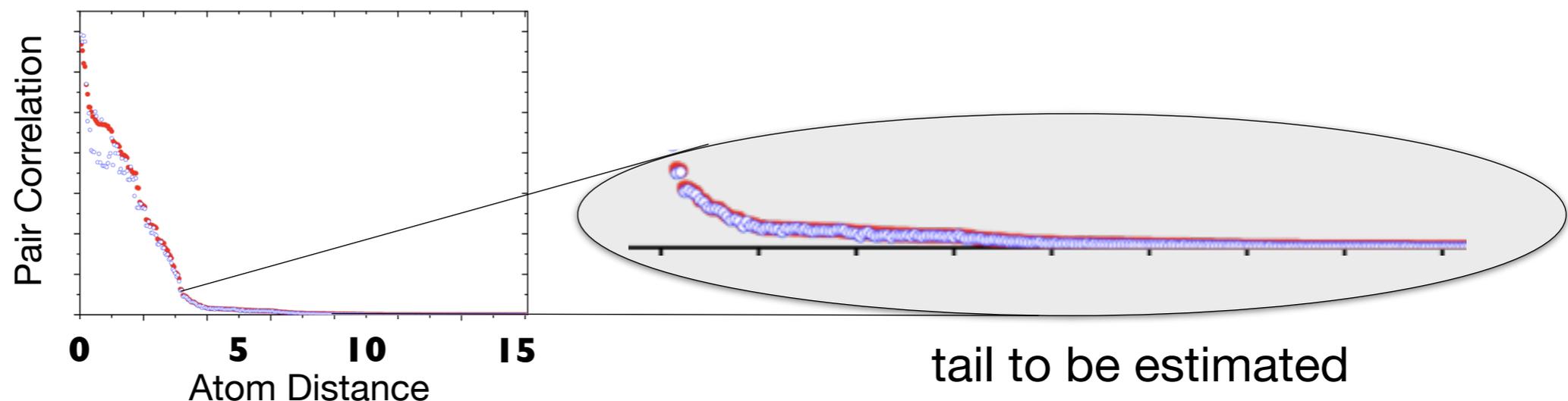
Electron Pair Prescreening

✓ **MP2** pair correlation energy:

<div style="text-align:center">„Coulomb"   „Exchange"→0</div>

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

▸ Introduce a set of **orbital specific virtual orbitals** (=PNOs of diagonal pairs) and drop the exchange part

✓ **Long range** part

$$\varepsilon_{ij}^{SC-OSV} \approx -4\sum_{ab} \frac{(i\tilde{a}_i \mid j\tilde{b}_j)^2}{\varepsilon_{\tilde{a}_i} + \varepsilon_{\tilde{b}_j} - F_{ii} - F_{jj}}$$

„Orbital specific virtuals" (OSVs)

✓ **Multipole Expansion**

$$\varepsilon_{ij}^{OSV-DIP} = \frac{8}{R_{ij}^6} \sum_{ab} \frac{\left(\left\langle i \mid \mathbf{r} \mid \tilde{a}_i \right\rangle\left\langle j \mid \mathbf{r} \mid \tilde{b}_j \right\rangle\right)^2}{\left(\varepsilon_{\tilde{a}_i} + \varepsilon_{\tilde{b}_i} - F_{ii} - F_{jj}\right)}$$

▸ Very small effort: only OSVs and dipole integrals (Generation in O(*N*) time)

Hetzer, G.; Pulay, P.; Werner, HJ *Chem. Phys. Lett.*, **1998**, <u>290</u>, 143   Riplinger, C. FN *J. Chem. Phys*, **2013**, <u>138</u>, 034106

Numerical Example: Benzene Dimer

Riplinger, C. FN *J. Chem. Phys*, **2013**, 138, 034106
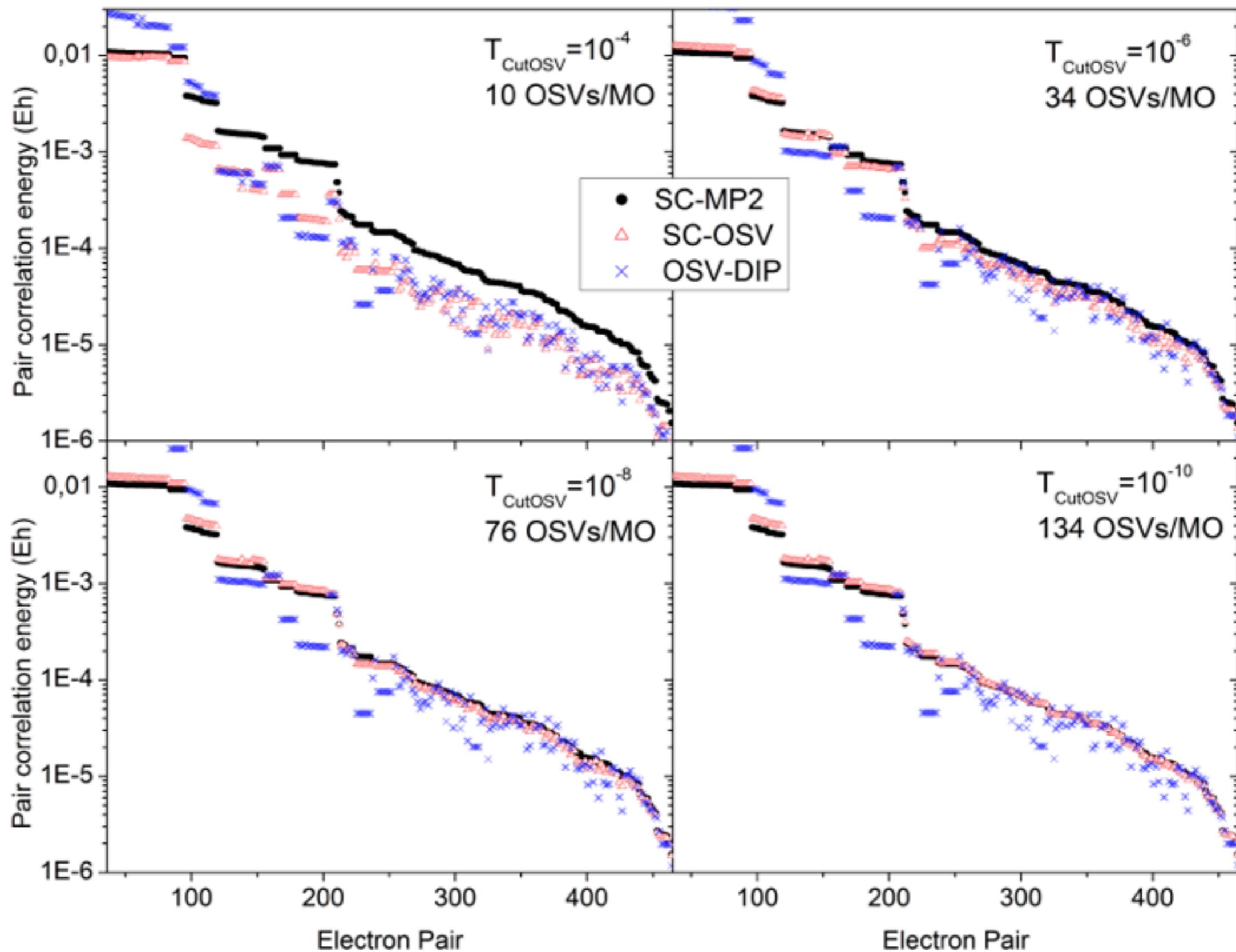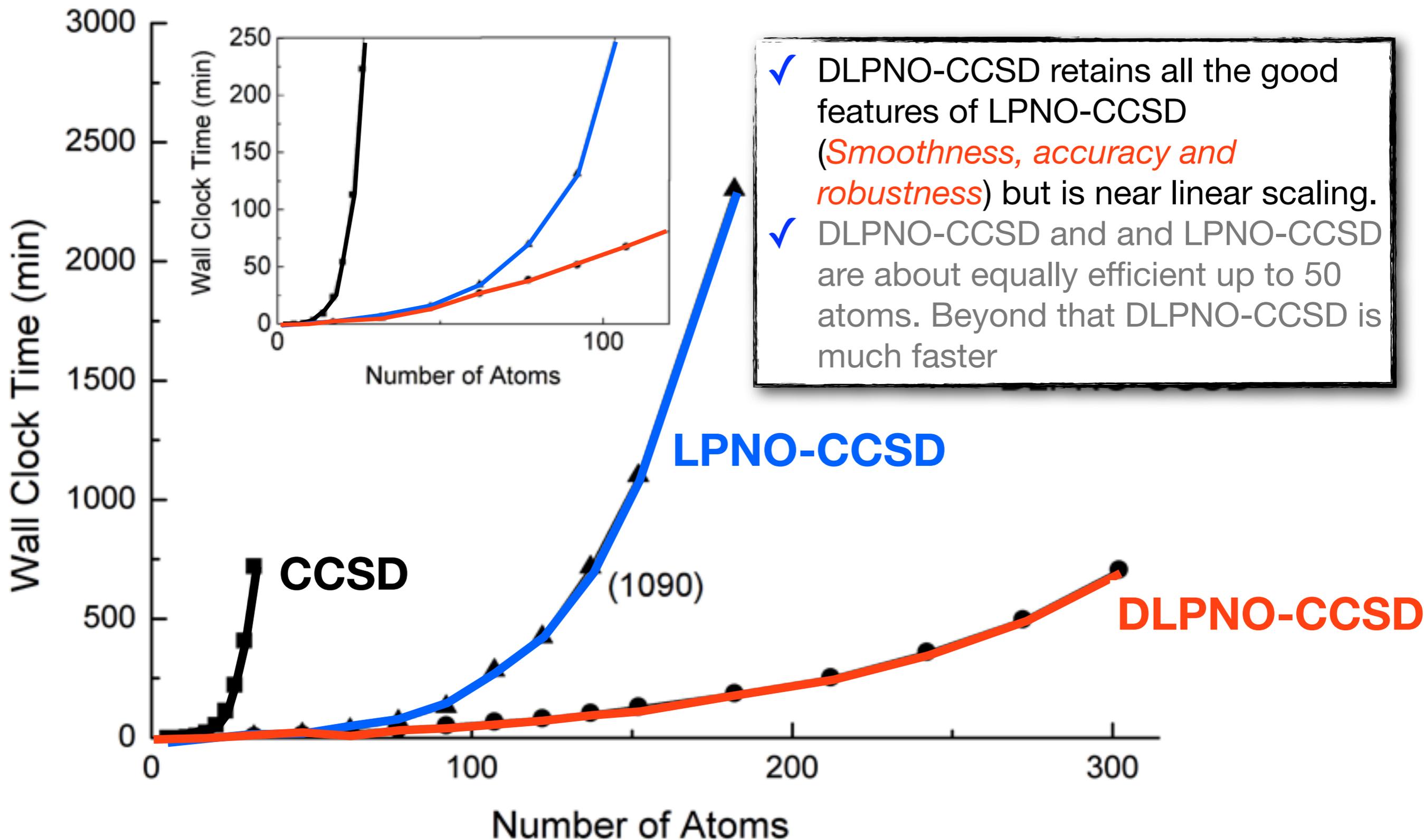
✓ DLPNO-CCSD retains all the good features of LPNO-CCSD (*Smoothness, accuracy and robustness*) but is near linear scaling.

✓ DLPNO-CCSD and and LPNO-CCSD are about equally efficient up to 50 atoms. Beyond that DLPNO-CCSD is much faster

Calculations on some larger molecules

Heme-CO

Vancomycin
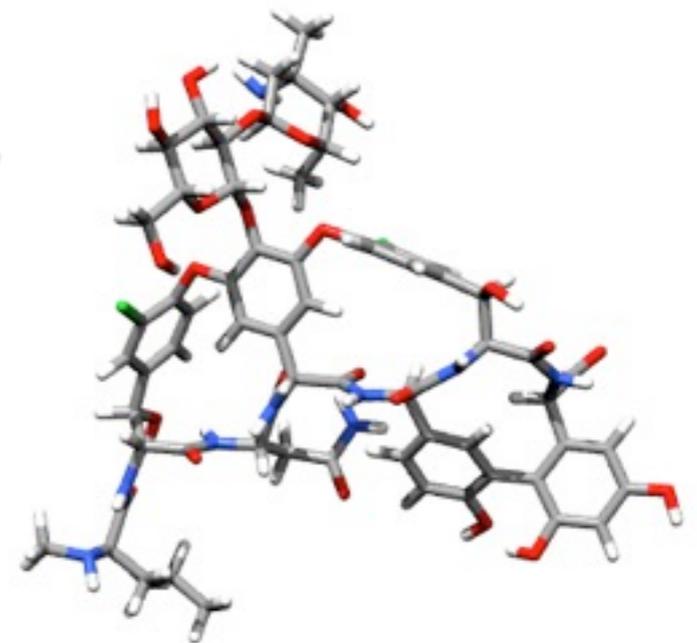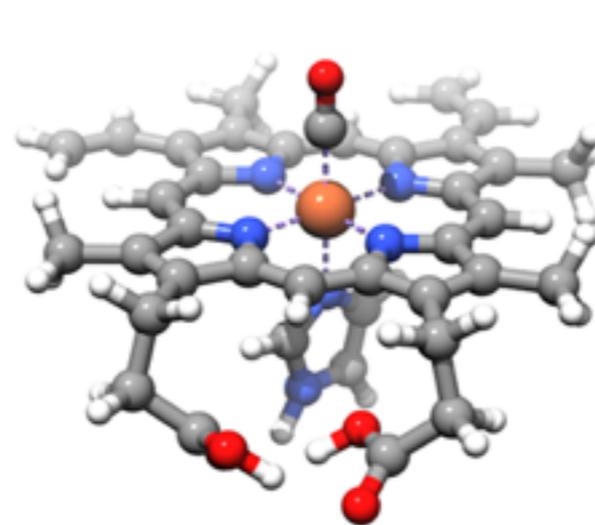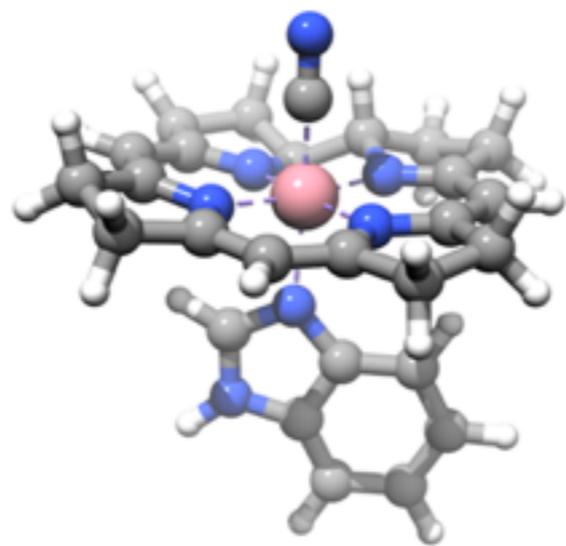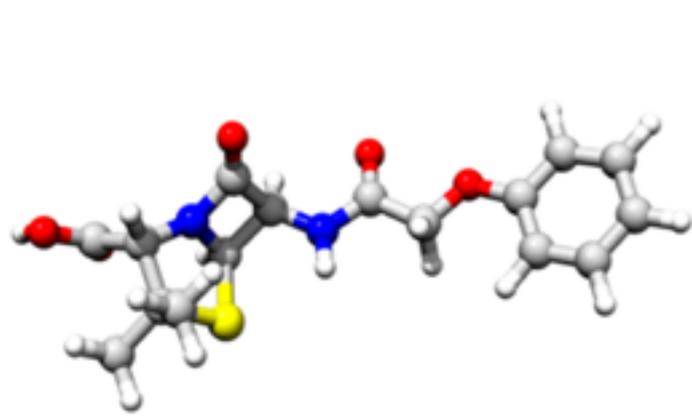
Accuracy of the correlation energy
Penicillin/def2-TZVPP

Canonical CCSD (1006 basis functions;
12 days on 16 cores)

−4.3799 Eh

DLPNO-CCSD (4 hours on 1 core)

−4.3781 Eh

74 Atoms
212 correlated electrons
def2-SVP
782 Basis functions

176 Atoms
542 correlated electrons
SV(P)
1797 Basis functions

t_{SCF}=**4.6 h**
t_{PNO-CC}=**31 h**

t_{SCF}=**? h**
t_{PNO-CC}=**14 h**

def2-TZVP (=3593 BF)

t_{PNO-CC}=**121 h**
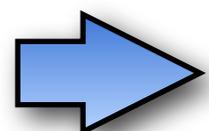
➡ **>200 atoms/>4000 basis functions** can be treated well

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

$$C_{150}H_{302} = 452 \text{ atoms}$$

def2-TZVPP Basis Set =   **8878** Basis Functions

20460 Auxiliary basis functions

... LPNO-CCSD runs through on a single processor in just a few days.
... future highly parallelized codes will be able to treat huge molecules efficiently thus pushing the boundaries of computational chemistry
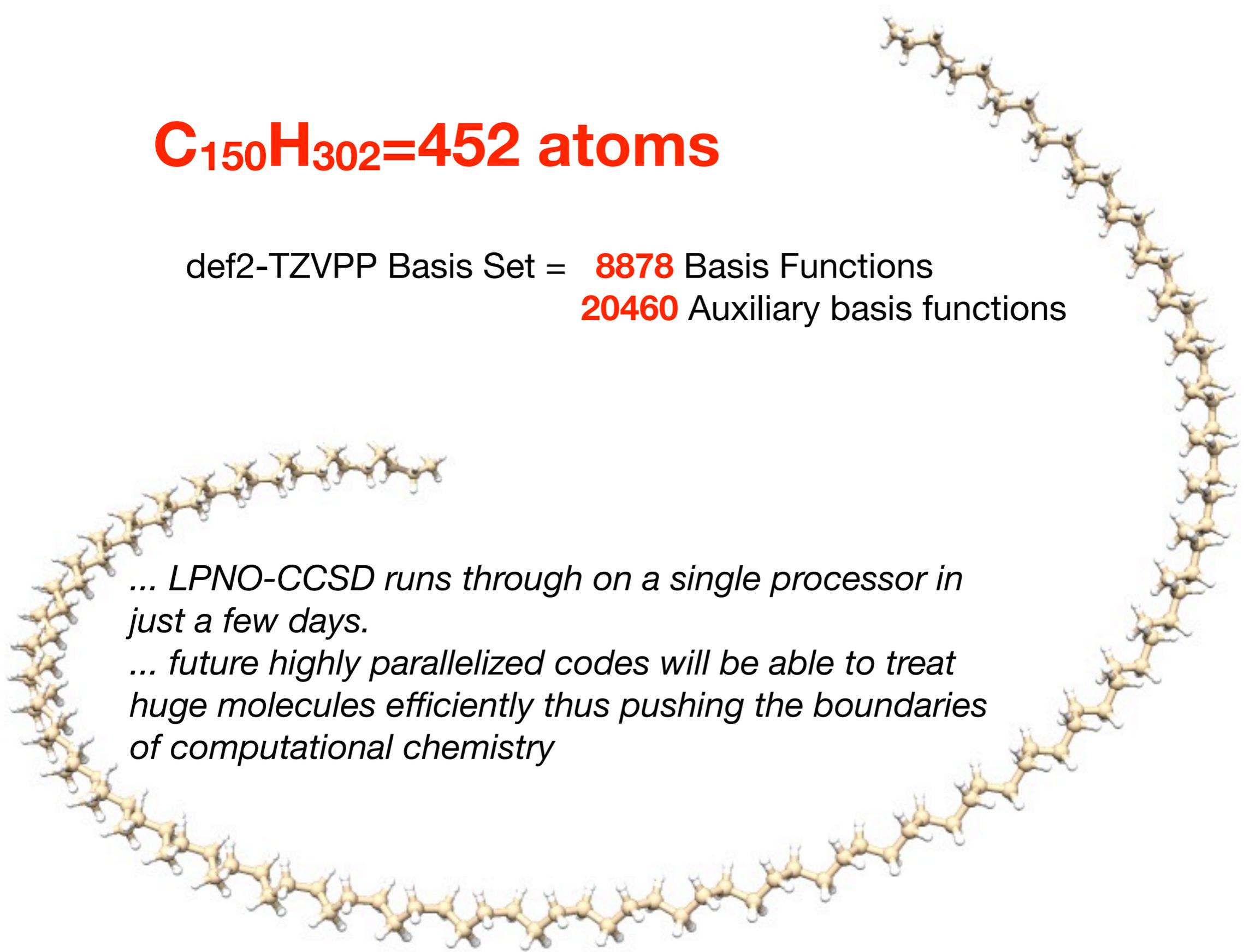
Real World Applications

Asymmetric Hydrogenation Catalysts
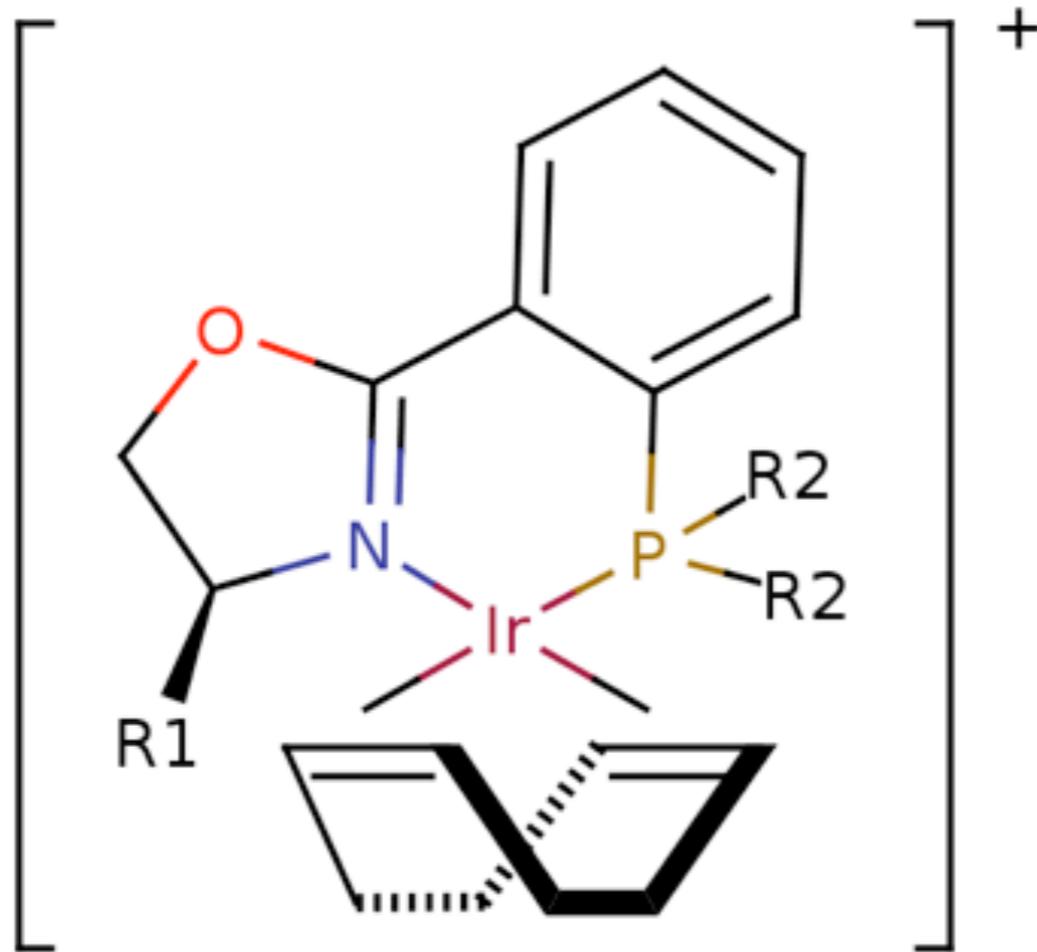
Pfaltz, A.; Drury, W.J. *PNAS*, **2004**, 101, 5723
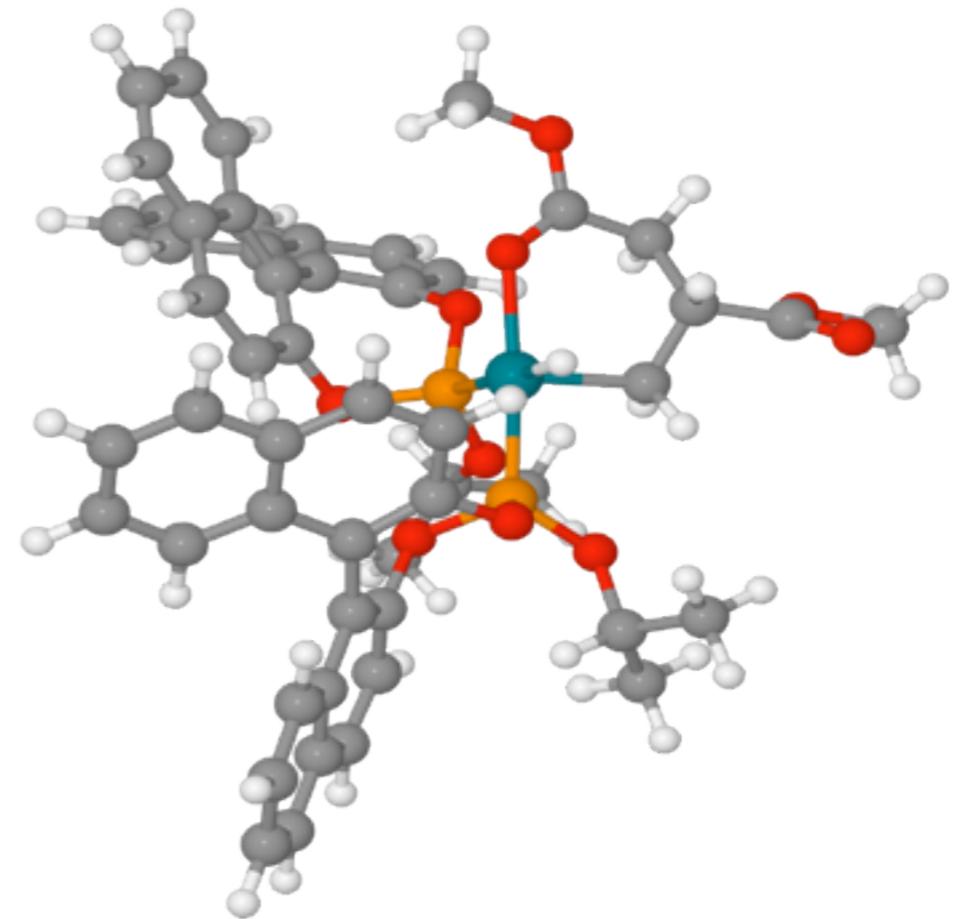
M. T. Reetz, A. Meiswinkel, G. Mehler, K. Angermund, M. Graf, W. Thiel, R. Mynott, and D. Blackmond, J. Am. Chem. Soc. 127, 10305-10313 (2005)

Dr. Manuel Sparta

Local ‚Natural' Triple Excitations

The highly successful perturbative triple excitation correction **(T)** involves:

$$W^{ijk}_{abc} \leftarrow \underbrace{\sum_d (ia \mid bd) t^{jk}_{dc}}_{I^i_{ab,d} T^{jk}_{dc}} - \underbrace{\sum_l (kc \mid jl) t^{il}_{ab}}_{T^i_{ab,l} L^{jk}_{l,c}} + (5 \;\; permutations)$$

✓ In a local context only a linear number of pairs must be included in the triples correction
✓ The problem, again, is to represent the virtual space

PAO based domain treatment (Schütz & Werner): Linear scaling achievable

OSV based treatment (Chan, Werner et al.): Linear scaling achieved

Fragment based approach by Kallay, Piecuch: Linear scaling achieved

Approach by Pulay: Not strictly linear scaling but very accurate

DLPNO-CCSD:

    ✓ Domains are available but are too large for the Schütz & Werner approach (>500 basis functions/pair)

Natural Triple Excitations

Our suggestion: **Natural triples orbitals**

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

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

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

✓ Eigenfunctions: $\mathbf{D}^{ijk}\mathbf{x}^{ijk} = n^{ijk}\mathbf{x}^{ijk}$ (cut-off below a given n^{ijk}(min) just as for PNOs)

✓ Recanonicalize: $\mathbf{x}^{ijk+}\mathbf{F}\mathbf{x}^{ijk}$

✓ Amplitudes are projected into the TNO basis: $T^{ij;TNO}_{\tilde{a}_{ijk},\tilde{b}_{ijk}} = S^{ijk,ij}_{\tilde{a}_{ijk},\tilde{c}_{ij}} T^{ij;PNO}_{\tilde{c}_{ij},\tilde{d}_{ij}} S^{ijk,ij}_{\tilde{b}_{ijk},\tilde{d}_{ij}}$

➡ Problem is that projection of existing PNO integrals onto the TNO basis is not good enough (sad history :-( )

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

Dr. Christoph Riplinger

➡ *Linear scaling implementation achieved*

Riplinger, C. FN *J. Chem. Phys*, **2013**, submitted

Consistency checks
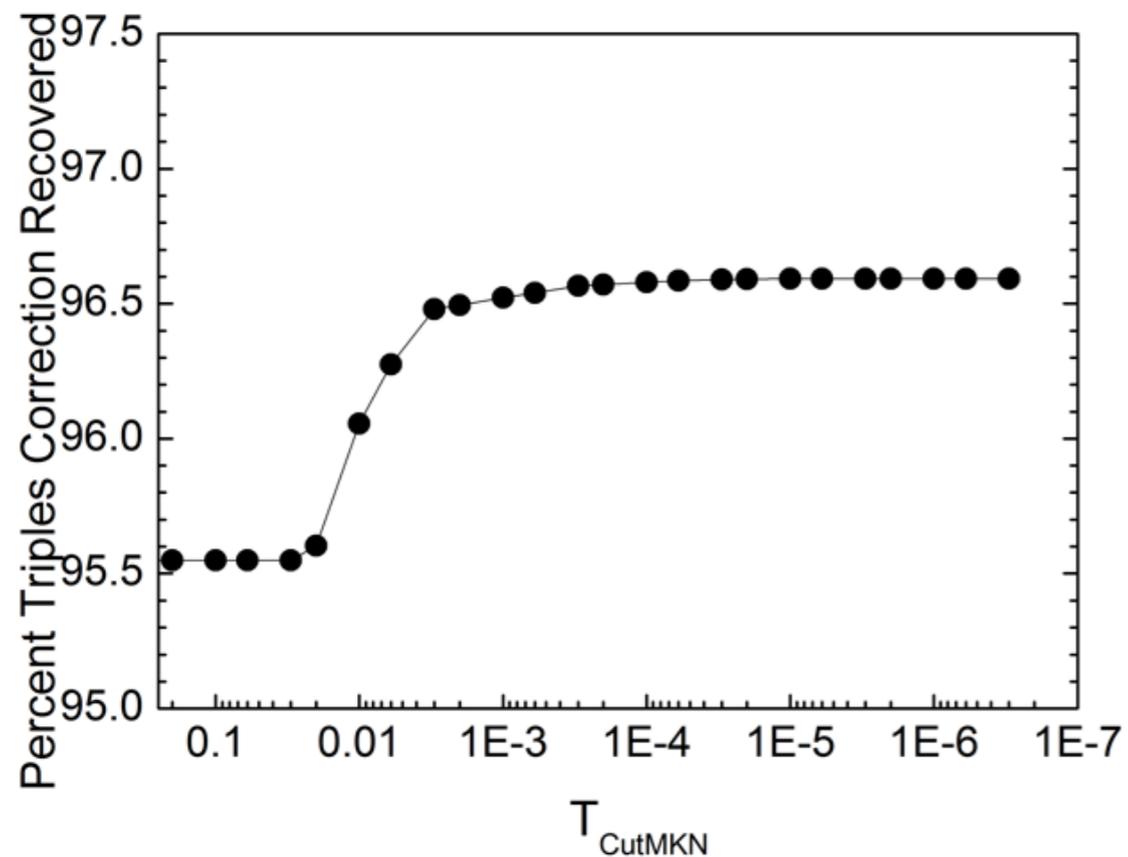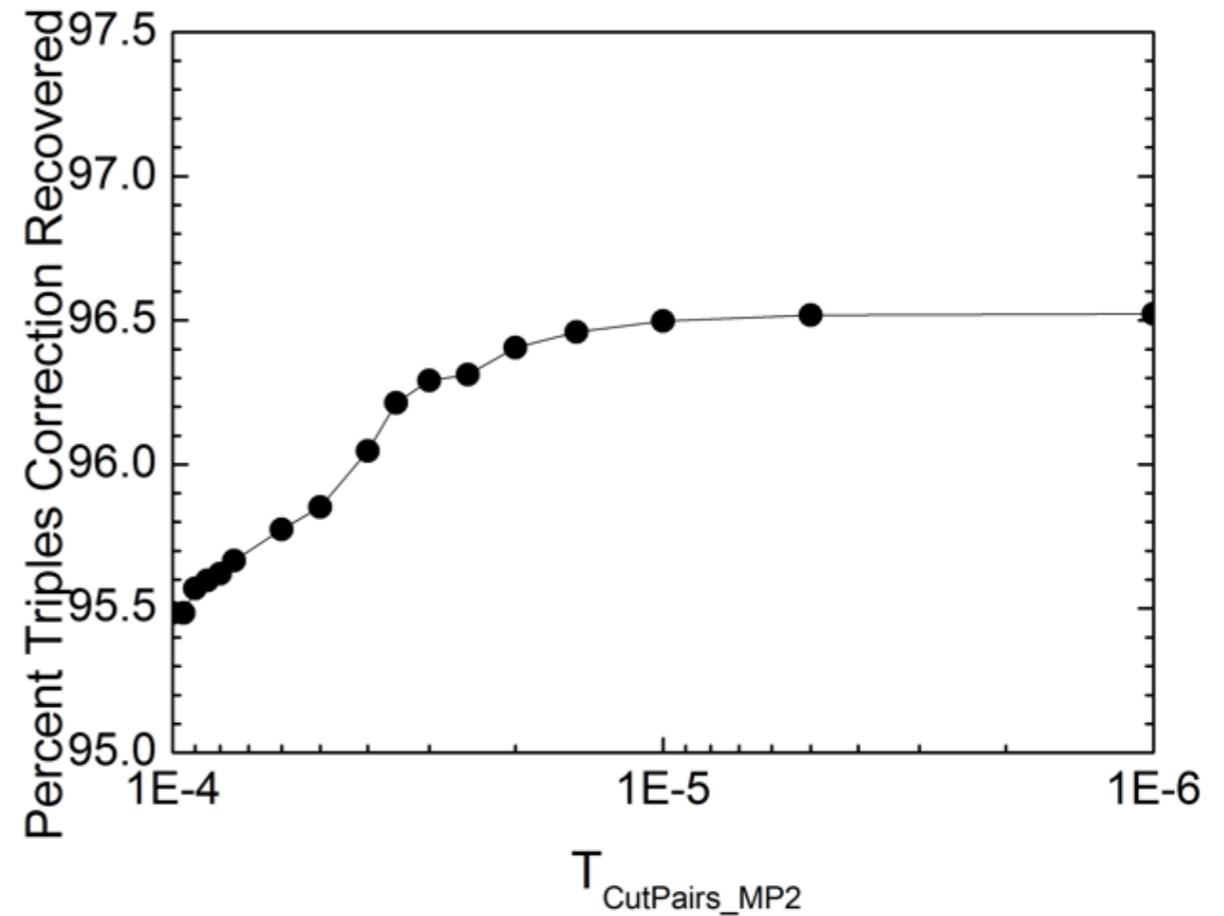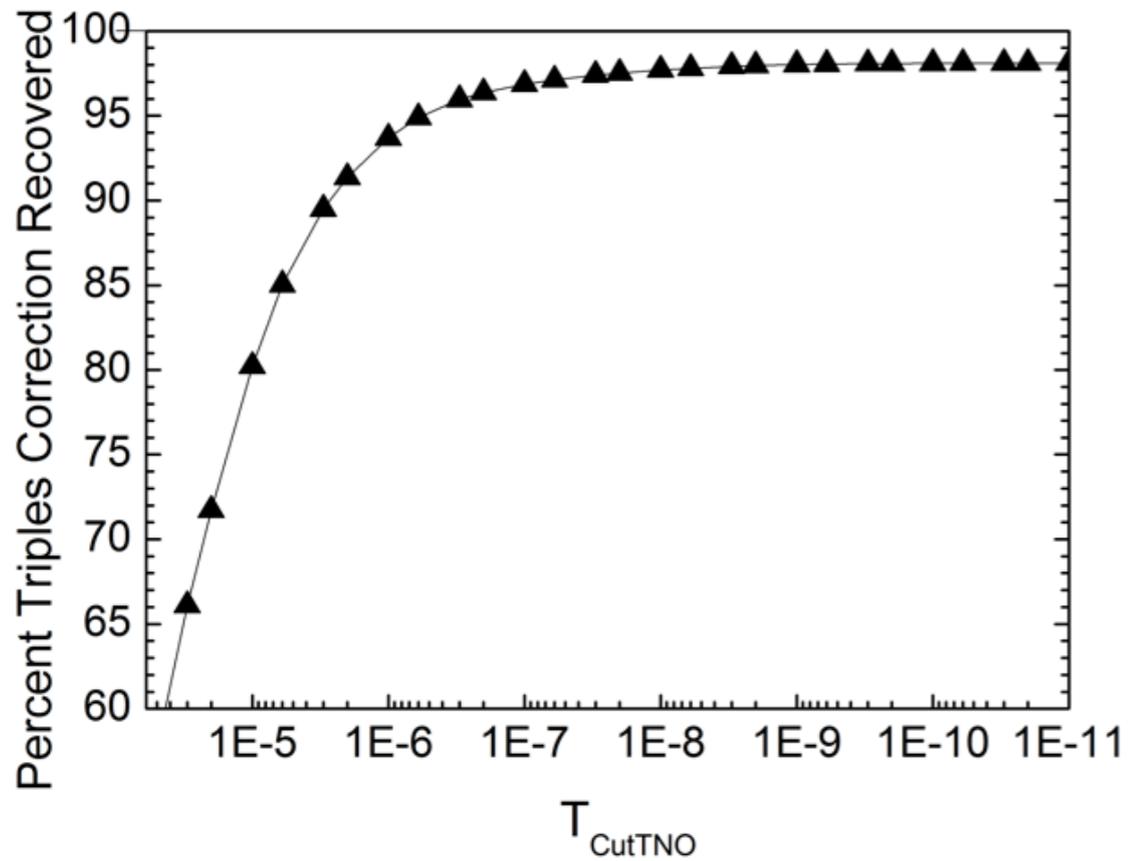
- ✓ Local (T_0) converges smoothly to about 97-98% of (T_0)
- ✓ Sufficient to include MP2 pairs at 0.1 $T_{CutPairs}$
- ✓ Domains are converged at the default T_{CutMKN}

Error Statistics

Reaction & Isomerization Energies (ISO34 set; relative to canonical CCSD/CCSD(T_0))

kcal/mol	MAD	MAX	ME
DLPNO-CCSD	0.41	2.10	-0.23
DLPNO-CCSD(T)	0.50	1.70	-0.06

✓ The additional error due to the triples is limited
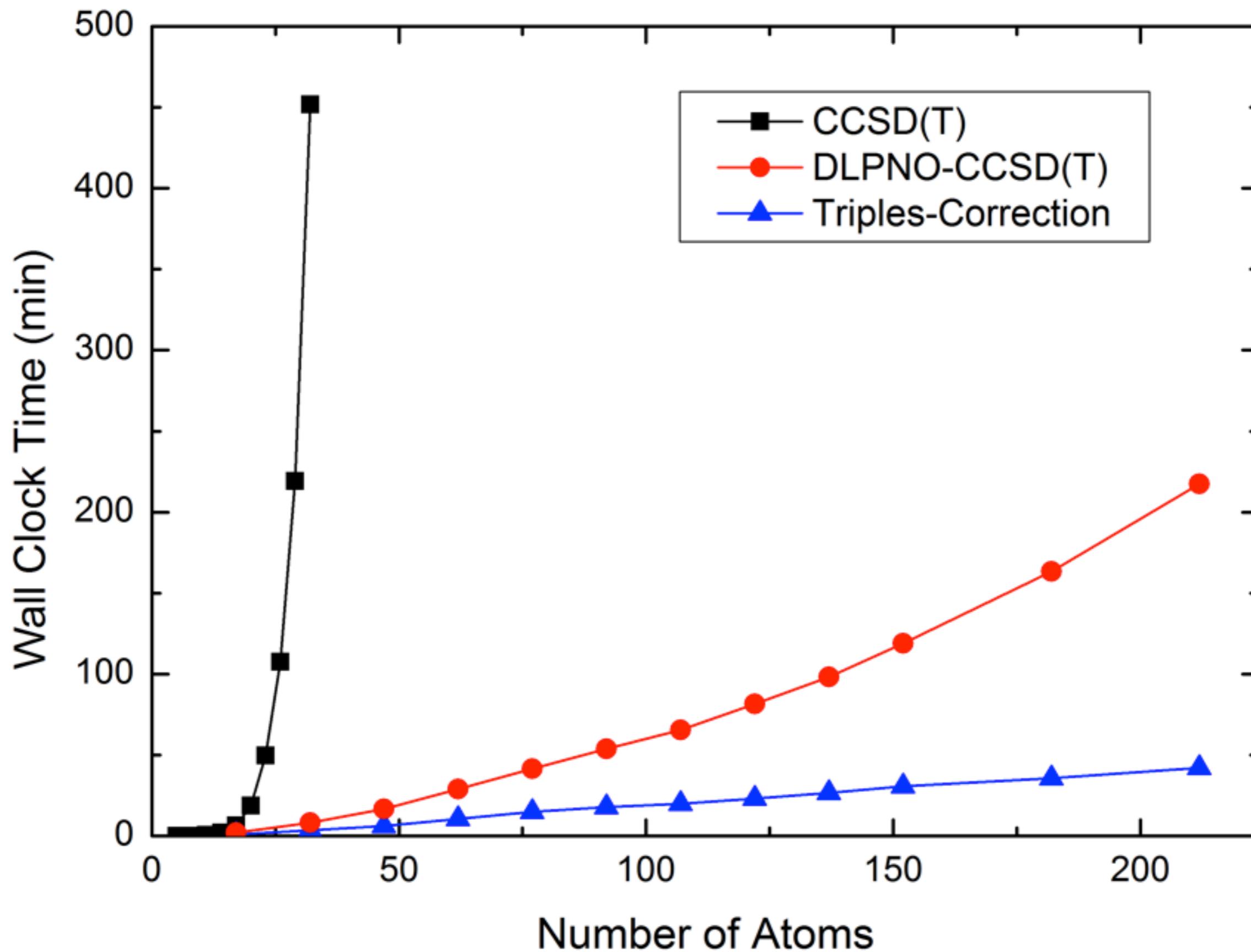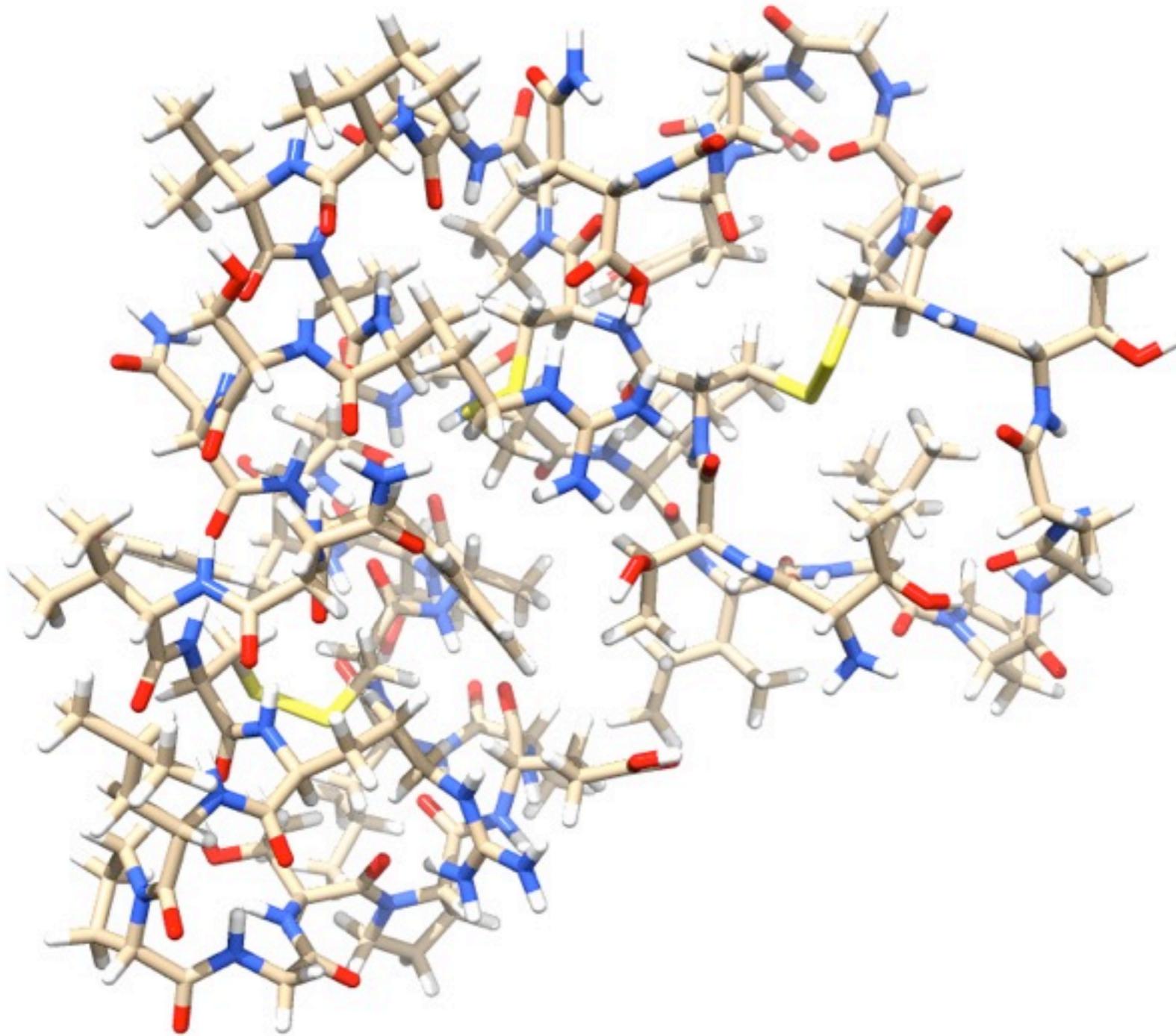
Crambin

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

Canonical computation time
~5 Million Years

DLPNO-CCSD(T)
~3 weeks/1 Core
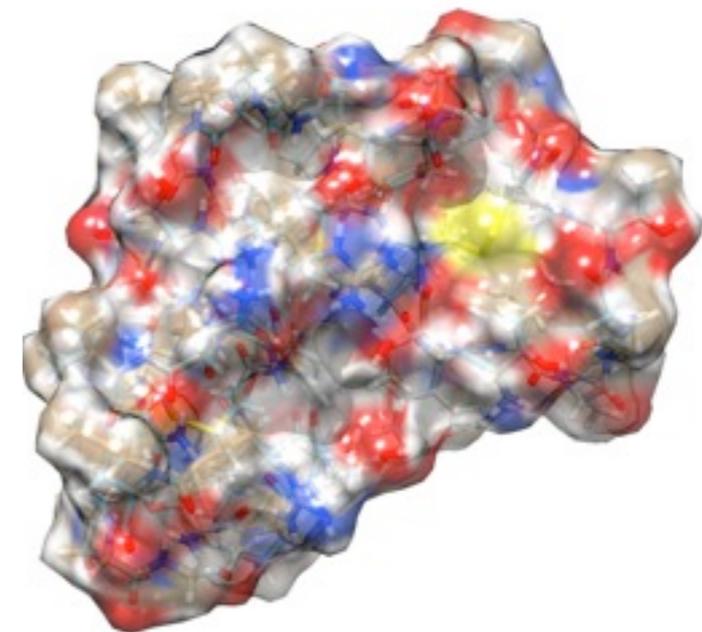
Riplinger, C. FN *J. Chem. Phys*, **2013**, submitted

✓ PHBH is a flavoprotein monooxygenase that catalyzes the hydroxylation of the substrate p-hydroxybenzoate by the cofactor flavin hydroperoxide

✓ 10 representative snapshot of the reaction were selected by MD simulation.

✓ For each snapshot GS and TS were optimized

✓ QM/MM calculations of the active site (49 atoms) embedded into the point charge distribution to account for the rest of the protein

✓ Computation of (T) accounts for ~30% of the computation time

✓ Almost >2/3rd of the (large) triples effect is recovered by DLPNO-CEPA/1
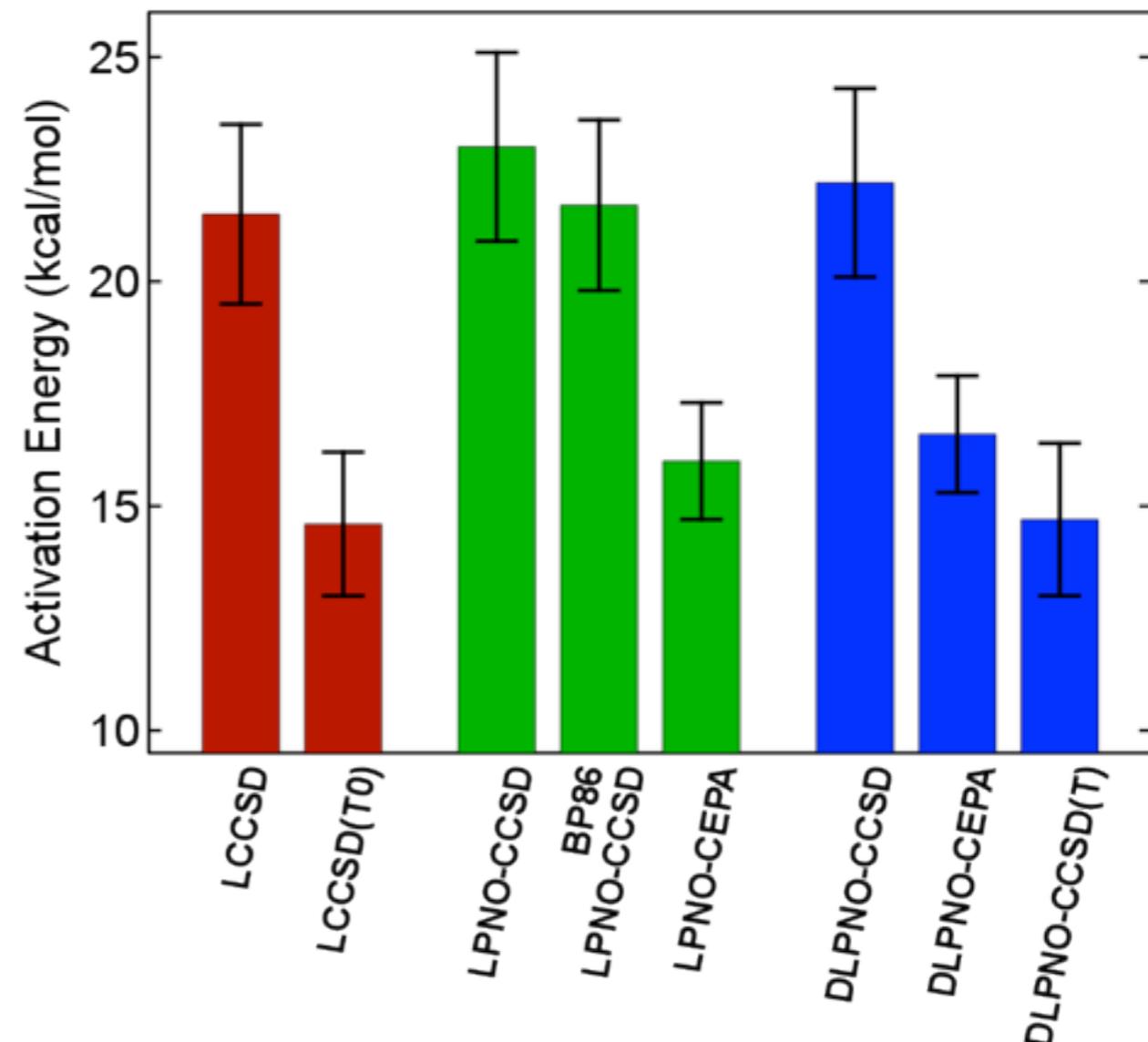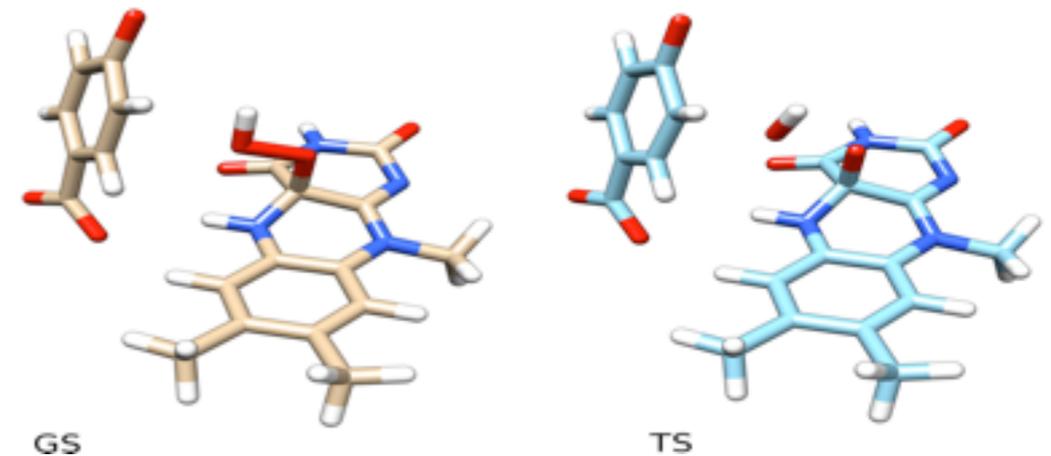
Dr. Manuel Sparta

Towards Applications: V_2O_5

$V_2O_9H_8$

$V_6O_{20}H_{10}$

$V_{10}O_{31}H_{12}$

$V_4O_{18}H_{16}$

$V_{12}O_{40}H_{20}$

$V_{20}O_{62}H_{24}$

Structure oprimization with high-level wavefunctions (LPNO-CCSD)
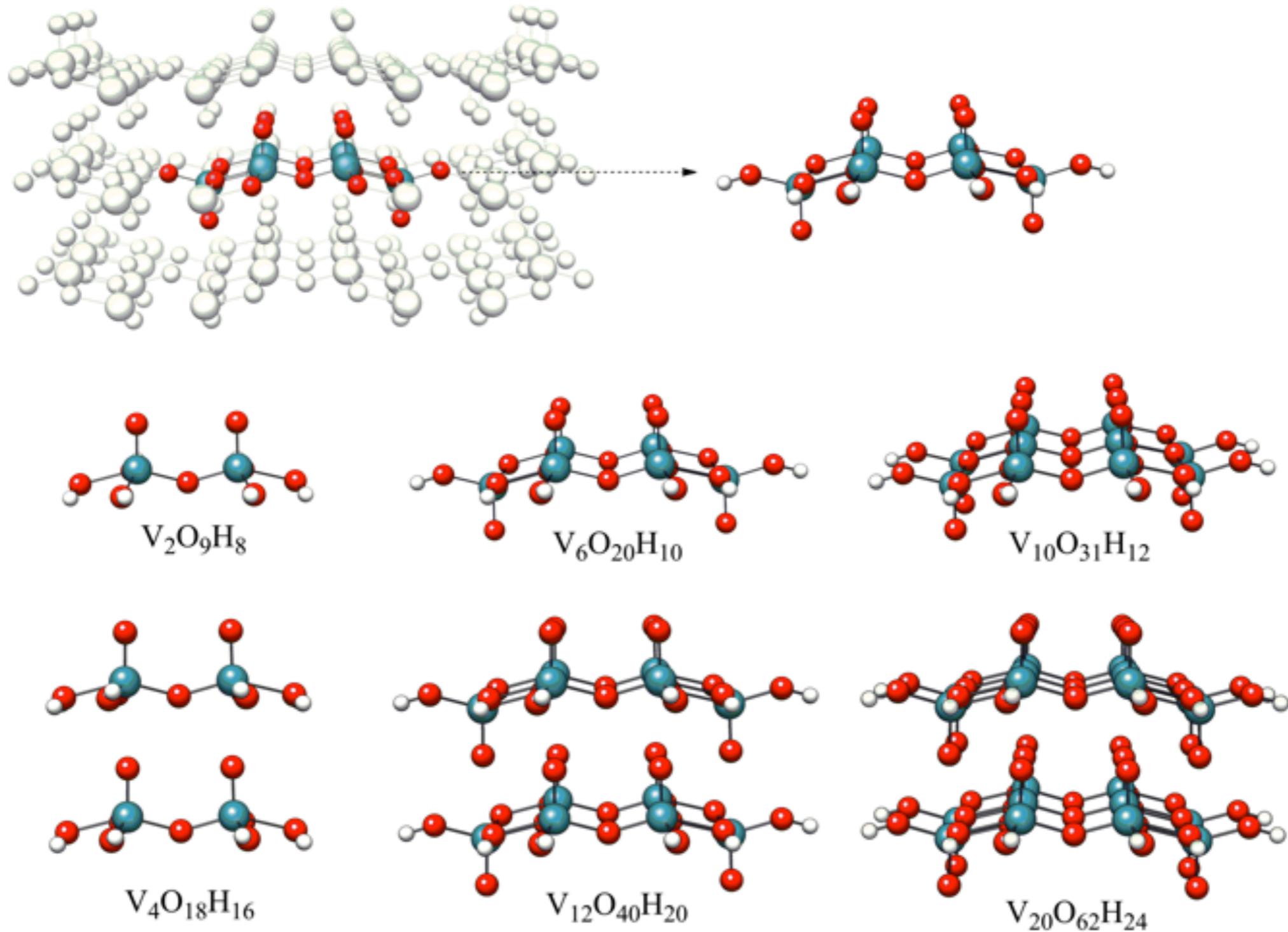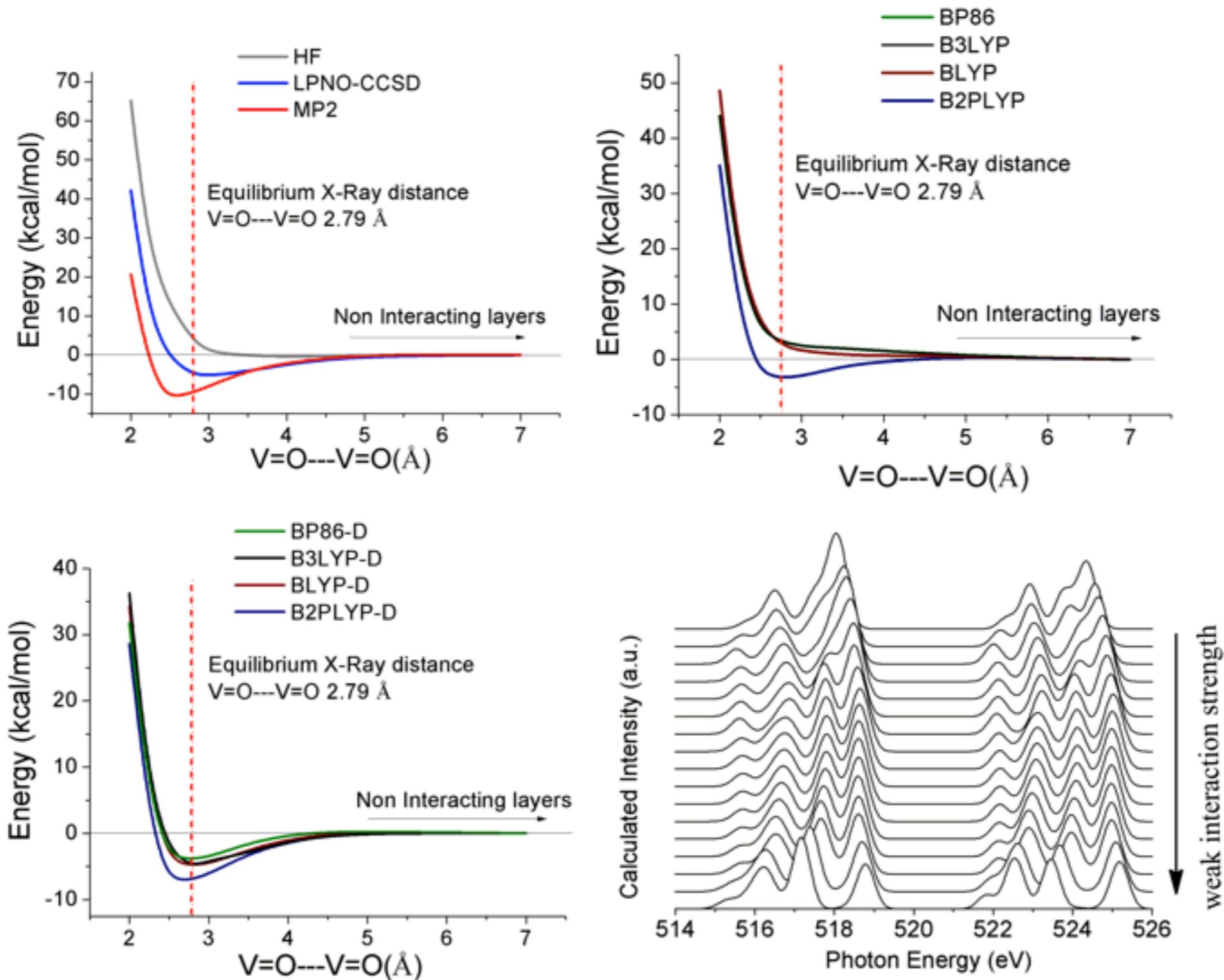
D Maganas; M Hävecker; A Knop-Gericke; M Roemelt; R Schlögl; A Trunschke; FN, PCCP **2013**, 15, 7260-76.

Summary & Conclusions

★ LPNO based correlation methods provide a highly reliable, robust and systematic route towards wavefunction calculations on large molecules.

★ Deviations from canonical results are small. Presently ~200-600 atoms can be treated.

★ Parallelized closed (and open-shell) codes are available.

★ Extensions to properties, F_{12}, excited states etc. are coming forward

We are always looking for highly motivated Ph. D. students and postdocs to join the team!

Have fun with

.... ORCA

http://www.cec.mpg.de/downloads

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