Introduction to Coupled Cluster Theory

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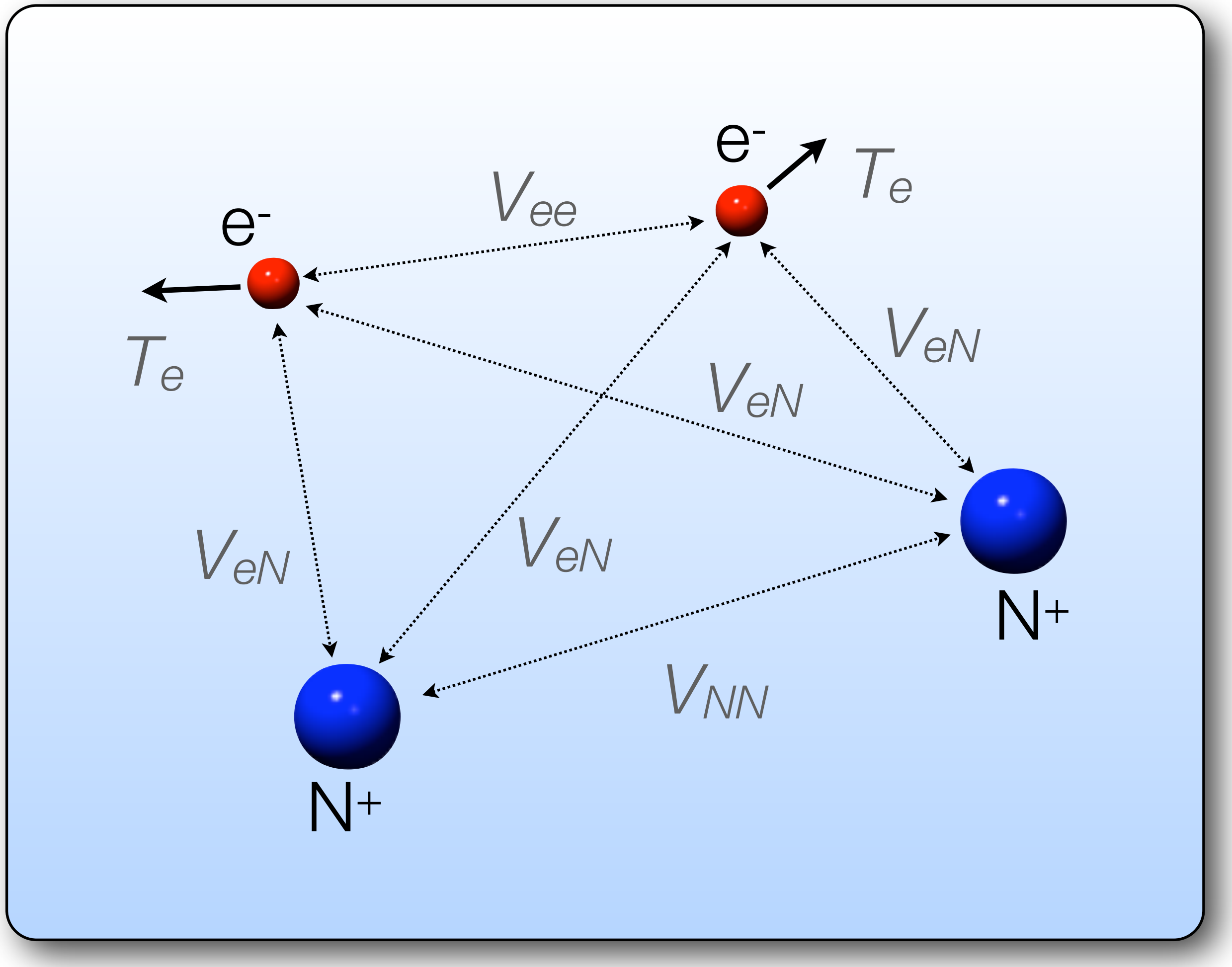
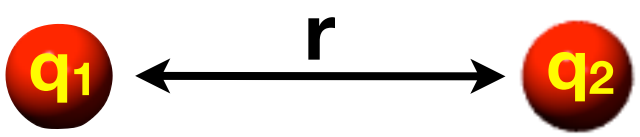
The Molecular Schrödinger Equation



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

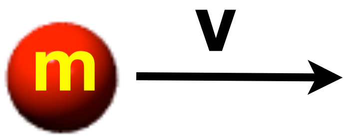
Only 2 Laws

1. Coulomb Law



$$E = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}$$

2. Kinetic Energy



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

The Molecular Hamiltonian

The Hamiltonian in **first quantization:**

$$\hat{H} = \underbrace{\frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{|\boldsymbol{R}_A-\boldsymbol{R}_B|}}_{V_{NN}} + \underbrace{\underbrace{\frac{1}{2}\sum_{i,A}\nabla_i^2}_{\hat{T}_e} - \underbrace{\sum_{i,A}\frac{Z_A}{|\boldsymbol{R}_A-\boldsymbol{r}_i|}}_{\hat{V}_{eN}}}_{\hat{h}} + \underbrace{\underbrace{\frac{1}{2}\sum_{i\neq j}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}}_{V_{ee}}}_{\hat{g}}$$

Introduce a complete one-particle basis {p} and write the **second-quantization** version:

$$\hat{H} = V_{NN} + \underbrace{\sum_{pq}\underbrace{\langle p|\hat{h}|q\rangle}_{=h_{pq}} E_p^q}_{\hat{h}} + \underbrace{\frac{1}{2}\sum_{pqrs}(pq|rs)\{E_r^s E_p^q - \delta_{rq}E_p^s\}}_{\hat{g}}$$

$E_p^q = q_\alpha^+ p_\alpha + q_\beta^+ p_\beta$ Replacement operator (generator of unitary group)

$h_{pq} = \int p(\boldsymbol{x})\hat{h}(\boldsymbol{x})q(\boldsymbol{x})d\boldsymbol{x}$ 1-electron Integrals $\boldsymbol{x}_i = (\boldsymbol{r}_i, \sigma_i)$

$g_{pqrs} = (pq|rs) = \int\int \frac{p(\boldsymbol{x}_1)q(\boldsymbol{x}_1)r(\boldsymbol{x}_2)s(\boldsymbol{x}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{x}_1 d\boldsymbol{x}_2$ 2-electron Integrals

Ansatz: The Hartree-Fock Method

The **Hartree-Fock** (HF) method is obtain by using the Variational principle with an Ansatz ffor a non-interacting N-particle wavefunction („**independent particle model**“)

Ψ = simple product of one-electron functions.

Satisfy the Pauli principle → „**Slater determinant**“

$$\Psi_{HF}(\boldsymbol{x}_1, \dots \boldsymbol{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\boldsymbol{x}_1) & \psi_1(\boldsymbol{x}_2) & \cdots & \psi_1(\boldsymbol{x}_N) \\ \psi_2(\boldsymbol{x}_1) & \psi_2(\boldsymbol{x}_2) & \cdots & \psi_2(\boldsymbol{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\boldsymbol{x}_1) & \psi_N(\boldsymbol{x}_2) & \cdots & \psi_N(\boldsymbol{x}_N) \end{vmatrix}$$

„Auxiliary“ one-electron functions = „**orbitals**“. They are the objects to be varied.

Variation under orthonormality constraint → Hartree-Fock equations

$$\psi_i = occupied\ \ spin\ orbitals\ (i = 1..N)$$

$$\psi_a = unoccpied\ \ spin\ orbitals\ (a = N+1..\infty)$$

Hartree-Fock Equations

$$\underbrace{\left\{ \underbrace{\hat{h}}_{one-electron} + \sum_j \underbrace{(jj|\circledast\circledast)}_{Coulomb} - \underbrace{(j\circledast|j\circledast)}_{Exchange} \right\}}_{Fock-Operator\ \hat{F}} \psi_i(\boldsymbol{x}) = \varepsilon_i \psi_i(\boldsymbol{x})$$

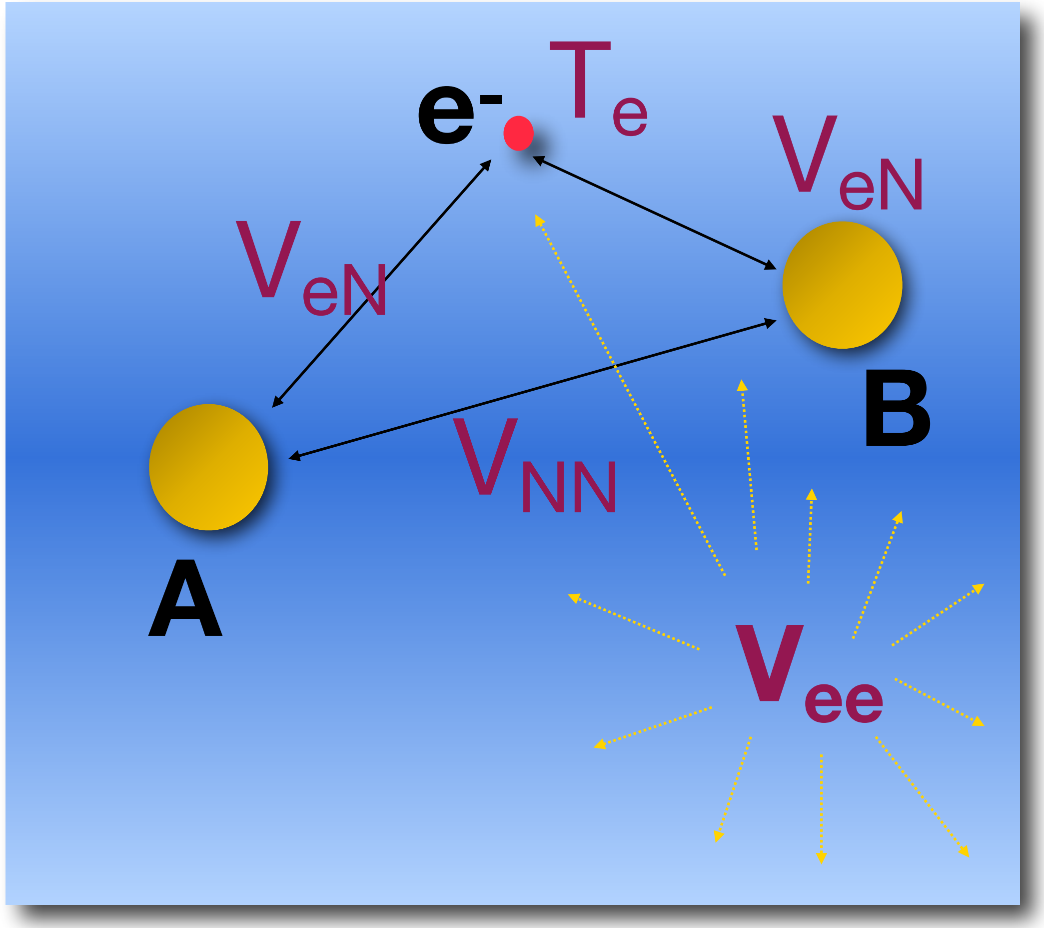
$$F_{pq} = \langle p|\hat{F}|q\rangle = h_{pq} + \sum_j \underbrace{(jj|pq)}_{Coulomb} - \underbrace{(jp|jq)}_{Exchange}$$

Convention: i,j,k,l = occupied orbitals (in reference determinant)
a,b,c,d = unoccupied orbitals (in reference determinant)
p,q,r,s= general orbitals

SCF-condition: $F_{ai} = 0$

➡ Tedious, but standard methodology

Interpretation of the Hartree-Fock Model



Each electron moves in the field created by the nuclei and the average field created by the other electrons („**mean field model**“) - this also called the „**Hartree-Fock sea**“ or "**Fermi vacuum**"

How Good is Hartree-Fock Theory?

Consider a Hartree-Fock calculation on the Neon atom (10 electrons)

```
Exact HF Energy                 : -128.547 Eh
Exact Experimental Energy : -129.056 Eh
```

(NOTE: exact experimental energy= sum of the ten ionization potentials)

Good News: HF recovers 99.6% of the exact energy (after subtraction of relativistic effects ~99.8%)

Bad News: The conversion factors work against us!

1 Eh = 27.21 eV

1 eV = 23.06 kcal/mol

= 8065 cm^{-1}

0.2% = 319 kcal/mol error! In chemistry one aims at 1 kcal/mol accuracy.

➡ Accurate quantum chemsitry is the struggle for the last 0.2%

Correlation Energy: $E_C = E_{exact} - E_{HF} \ (< 0)$

Beyond Hartree-Fock: The Exact Solution

Introduce a **multideterminantal Ansatz** and use the variational principle.

Let us *assume* that we have a **complete set** of N-electron expansion functions **{Φ}** available. Then the exact wavefunction can be written as:

$$\boxed{\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)=\sum_I C_I\Phi_I(\mathbf{x}_1,\ldots,\mathbf{x}_N)}$$

Variational Principle

$$E[\mathbf{C}]=\frac{\left\langle\Psi\,|\,H\,|\,\Psi\right\rangle}{\left\langle\Psi\,|\,\Psi\right\rangle}=\frac{\sum_{IJ}C_IC_J\left\langle\Phi_I\,|\,H\,|\,\Phi_J\right\rangle}{\sum_{IJ}C_IC_J\left\langle\Phi_I\,|\,\Phi_J\right\rangle}$$

$$\frac{\partial E}{\partial C_K}=0$$ (for all K)

$$\boxed{\begin{aligned}\mathbf{HC}&=E\mathbf{SC}\\ H_{IJ}&=\left\langle\Phi_I\,|\,H\,|\,\Phi_J\right\rangle\\ S_{IJ}&=\left\langle\Phi_I\,|\,\Phi_J\right\rangle\end{aligned}}$$

DONE!

The lowest Eigenvalue is

the exact solution

What are the Expansion Functions?

Replace, 1,2,...N spin-orbitals at the time in the HF determinant (**Full-CI Expansion**):

$$\boxed{\Psi = C_0 \Phi_{HF} + \underbrace{\sum_{ia} C^i_a \Phi^a_i}_{Singles} + \underbrace{\left(\tfrac{1}{2!}\right)^2 \sum_{ijab} C^{ij}_{ab} \Phi^{ab}_{ij}}_{Doubles} + \underbrace{\left(\tfrac{1}{3!}\right)^2 \sum_{ijkabc} C^{ijk}_{abc} \Phi^{abc}_{ijk}}_{Triples} + \ldots + (n - fold\ exc.)}$$

Excited Determinants:

$$\Phi_{HF} = \left| \psi_1 \ldots \psi_i \ldots \psi_j \ldots \psi_k \ldots \psi_N \right|$$

$$\Phi^a_i = \left| \psi_1 \ldots \psi_a \ldots \psi_j \ldots \psi_k \ldots \psi_N \right|$$

$$\Phi^{ab}_{ij} = \left| \psi_1 \ldots \psi_a \ldots \psi_b \ldots \psi_k \ldots \psi_N \right|$$

$$\Phi^{abc}_{ijk} = \left| \psi_1 \ldots \psi_a \ldots \psi_b \ldots \psi_c \ldots \psi_N \right|$$

orthonormal: **S**=**1**.

Note:if any two upper or any two lower indices are equal the determinant is zero! (Pauli principle!)

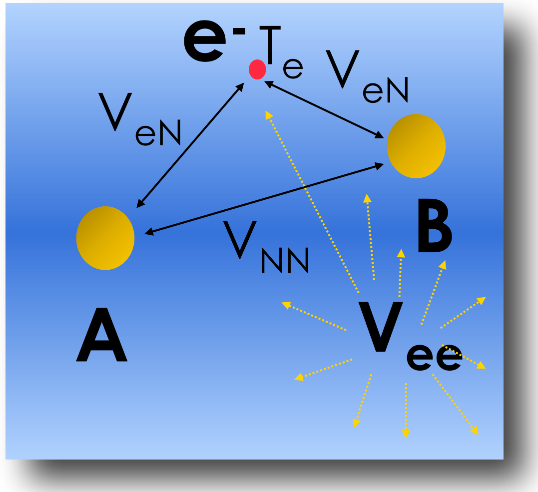
Permutation Symmetry:

$$\Phi^{ab}_{ij} = -\Phi^{ba}_{ij} = -\Phi^{ab}_{ji} = \Phi^{ba}_{ji}$$

$$C^{ij}_{ab} = -C^{ij}_{ba} = -C^{ji}_{ab} = C^{ji}_{ba}$$

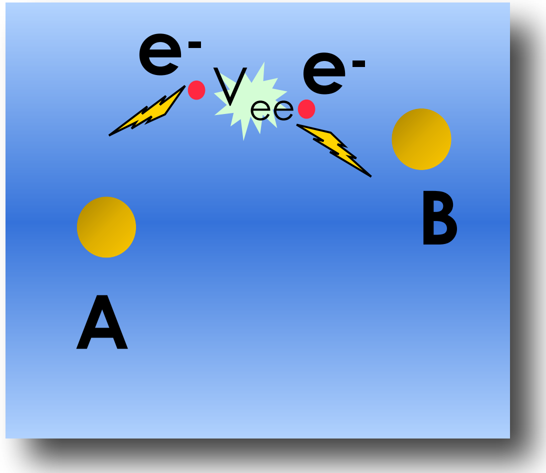
Components of the Exact Energy

Exact Energy =



“Mean Field”
Hartree-Fock

+



Instantaneous electron-electron interaction

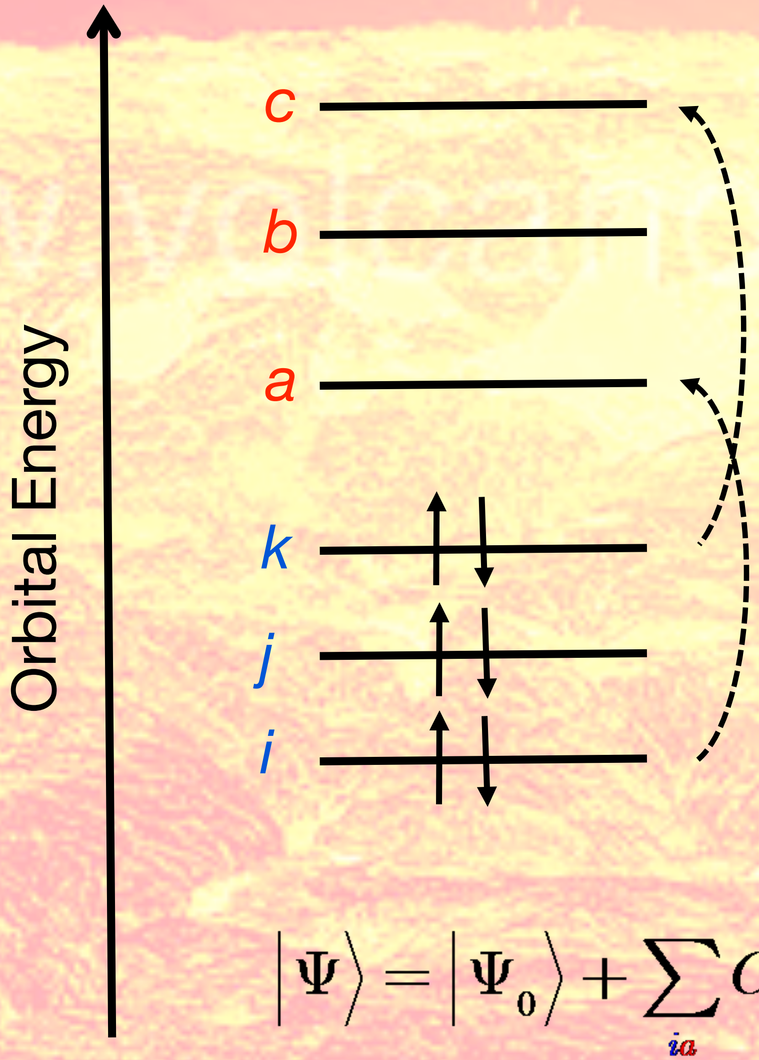
Correlation energy= $\frac{1}{2}\sum_{i,j \text{ Electron pairs}} \varepsilon_{ij}(\uparrow\uparrow) + \varepsilon_{ij}(\uparrow\downarrow)$

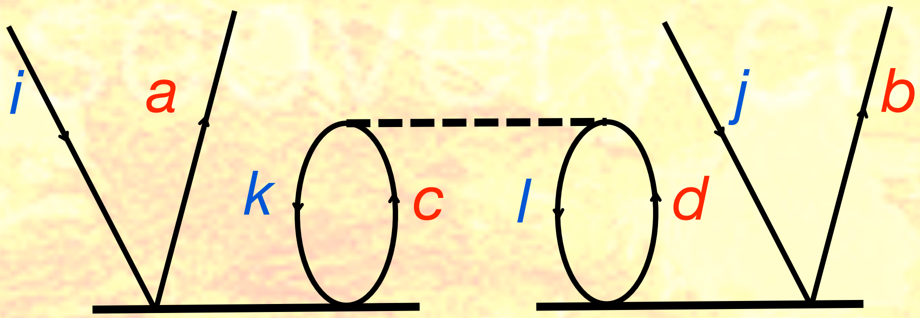
Fermi-Correlation ↑

Relatively easy due to “Fermi hole” in the mean-field

Coulomb-correlation ↑

Extremely hard to calculate due to interelectronic cusp at the coalescence point $\boldsymbol{r}_1=\boldsymbol{r}_2$





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

$$\left|\Psi\right\rangle = \left|\Psi_0\right\rangle + \sum_{ia} C_a^i \left|\Psi_i^a\right\rangle + \frac{1}{4}\sum_{ijab} C_{ab}^{ij}\left|\Psi_{ij}^{ab}\right\rangle + \frac{1}{36}\sum_{ijkabc} C_{abc}^{ijk}\left|\Psi_{ijk}^{abc}\right\rangle + \dots$$

Size of the Full-CI Matrix

Let us determine how many terms we have in the expansion if we assume *N* occupied and *V*=*M*-*N* (*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: $k! \approx k^{k+\frac{1}{2}} \sqrt{2\pi + 1} \exp(-k)$

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

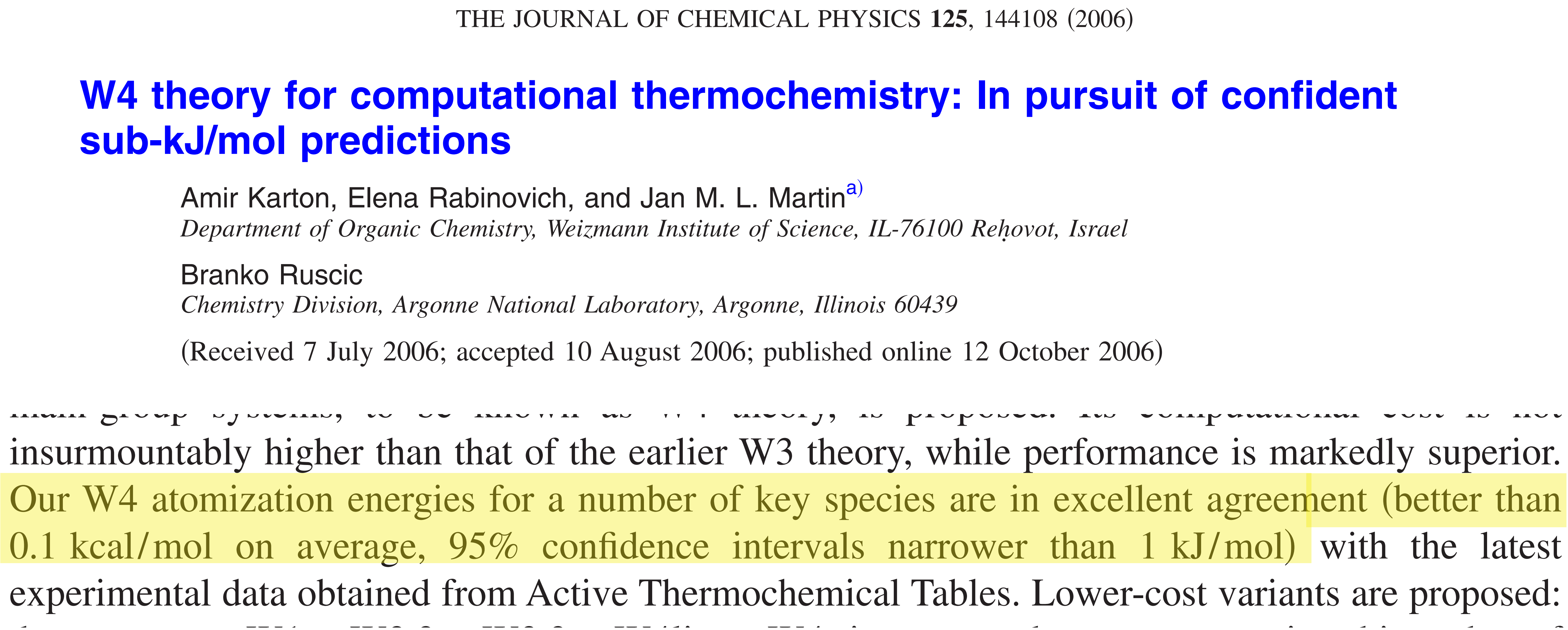
Full CI: An Example

Example: N=10, M=50

n	Number of Determinants
1	400
2	35100
3	1185600
4	19191900
5	16581806
6	806059800
7	2237227200
8	3460710825
9	2734388800
10	847660528
Σ	10272278170 ~ 10^{10}

- The size of the full CI matrix is HUGE even for moderately sized systems!
- About 10^{10} IS DOABLE today. Beyond that there are approximation (e.g. **Project C2**)

Accurate Solutions



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W4 theory for computational thermochemistry: In pursuit of confident sub-kJ/mol predictions

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insurmountably higher than that of the earlier W3 theory, while performance is markedly superior. Our W4 atomization energies for a number of key species are in excellent agreement (better than 0.1 kcal/mol on average, 95% confidence intervals narrower than 1 kJ/mol) with the latest experimental data obtained from Active Thermochemical Tables. Lower-cost variants are proposed:

... meaning the (non-relativistic) Schrödinger equation is solved to an accuracy of 0.0001 Eh which is ~99.9999% or ~1 part in 10^6!

... For **really** small systems (1-6 *electrons*), we can today reach „crazy accuracy“, e.g. Nakatsuji calculated the H_2^- ground state energy to be **-0.597 139 063 123 405 074 834 134 096 025 974 142 a.u.** (36 significant digits!)

Nakatsuji, JCP 113, 2949 (2000); Nakatsuji, Davidson, JCP 115, 2000 (2001).

Decomposition of the Exact Correlation Energy

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

Insert the **full CI expansion**

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

Multiply with the HF function from the left:

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

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

Thus:

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

(Nesbet's theorem)

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

Truncated Wavefunction Approximation

We have so far used two key ingredients

1. The **Variational Principle**
2. The **Expansion** of the many particle wavefunction starting from HF

We saw that the double excitation are particularly important.

➡ Try a **truncated wavefunction** together with the variational principle

$$\Psi_{CID} = \Psi_{HF} + \frac{1}{4}\sum_{ijab} C_{ab}^{ij}\Phi_{ij}^{ab}$$

Let us use a model system (minimal basis H_2) to study this approximation

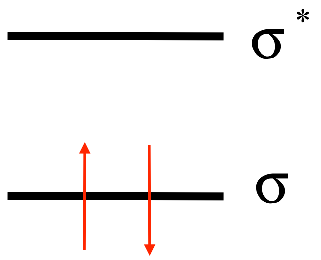
Point of Departure: Minmal Basis H_2

For a **single minimal basis H_2 molecule** the CID matrix is:

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

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

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



Ground state of the minimal basis H_2 system

With the lowest eigenvalue:

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

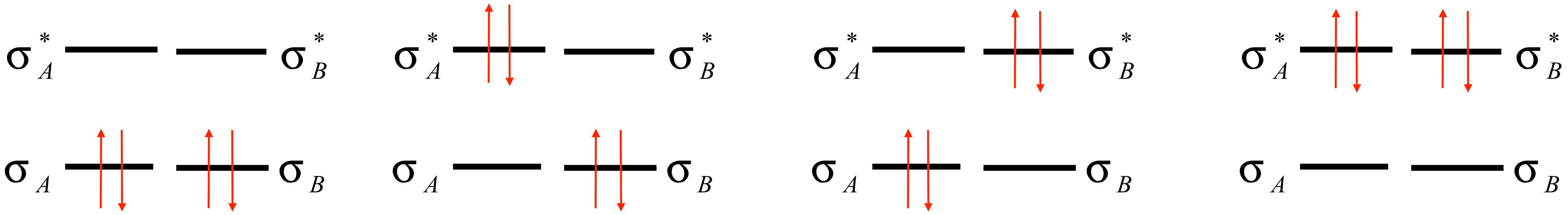
➡ Great, this is Full-CI. Now try 2 non-interacting H2's and *we should get twice this*

However, for **N noninteracting H_2 molecules** CID gives:

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

Which is **NOT size consistent** → Go 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.



$|0\rangle$ $|D_A\rangle$ $|D_B\rangle$ $|Q\rangle = |D_A + D_B\rangle$

Matrix-elements:

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

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

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

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

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

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

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):

$$\boxed{E_0 = \Delta - \sqrt{\Delta^2 + 4V^2}}$$

This is **twice the energy of a single H_2**. Thus, the **inclusion of the quadruple excitation restores the size consistency**!

Furthermore:

$$\boxed{C_Q = \frac{\sqrt{2}V}{\underbrace{E - 2\Delta}_{C_D/2C_0}} C_D = \frac{1}{2C_0} C_D^2}$$

For noninteracting subsystems, **the coefficients of the quadruples are exactly products of doubles coefficients**!

Conclusions and Generalizations

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 (as predicted less rigorously but more generally by perturbation theory).
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 which are written in intermediate normalization (we neglect odd excitations at the moment):

$$\left|\Psi\right\rangle = \left|\Psi_{HF}\right\rangle + \left|\Psi_{D}\right\rangle + \left|\Psi_{Q}\right\rangle + \ldots$$

Approximation 1: Statistically Uncorrelated Excitations

CI-Equations:

$$\left\langle \Psi_X \middle| \hat{H} \middle| \Psi_{HF} + \Psi_D + \Psi_Q + \ldots \right\rangle = E \left\langle \Psi_X \middle| \Psi_{HF} + \Psi_D + \Psi_Q + \ldots \right\rangle$$

$$\left\langle \Psi_X \middle| \hat{H} \middle| \Psi_{HF} \right\rangle + \left\langle \Psi_X \middle| \hat{H} \middle| \Psi_D \right\rangle + \left\langle \Psi_X \middle| \hat{H} \middle| \Psi_Q \right\rangle = EC_X$$

Approximate the quadruples as a product of doubles („**disconnected quadruples**“):

Approximation 1:

$$\left| \Psi_Q \right\rangle \cong \tfrac{1}{2} \sum_{X,Y} C_X C_Y \underbrace{\hat{E}_X \hat{E}_Y \left| \Psi_0 \right\rangle}_{\left| \Psi_{X+Y} \right\rangle}$$

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

compound label X=(ij,ab)

Approximation 2:

$$\left\langle \Psi_X \middle| \hat{H} \middle| \Psi_{Y+Z} \right\rangle \cong \delta_{XY} \left\langle \Psi_X \middle| \hat{H} \middle| \Psi_{X+Z} \right\rangle + \delta_{XZ} \left\langle \Psi_X \middle| \hat{H} \middle| \Psi_{Y+X} \right\rangle$$

Fully disjointed excitations: $\rightarrow \delta_{XY} \left\langle \Psi_0 \mid \hat{H} \mid \Psi_Z \right\rangle + \delta_{XZ} \left\langle \Psi_0 \mid \hat{H} \mid \Psi_Y \right\rangle$

Problem: If X+Z or Y+Z share common labels, the excitation is not possible (**Exclusion principle violating terms**)

Approximate Full-CI Equations

$$
\begin{aligned}
\left\langle \Psi_X \,|\, \hat{H} \,|\, \Psi_Q \right\rangle &\cong \tfrac{1}{2} \sum_{Y,Z} C_Y C_Z \left\{ \delta_{XY} \left\langle \Psi_0 \,|\, \hat{H} \,|\, \Psi_Z \right\rangle + \delta_{XZ} \left\langle \Psi_0 \,|\, \hat{H} \,|\, \Psi_Y \right\rangle \right\} \\
&= C_X \sum_Y C_Y \left\langle \Psi_X \,|\, \hat{H} \,|\, \Psi_{X+Y} \right\rangle \\
&= C_X \underbrace{\sum_Y C_Y \left\langle \Psi_0 \,|\, \hat{H} \,|\, \Psi_Y \right\rangle}_{E_{corr}} - C_X \underbrace{\sum_{Y \subset X} C_Y \left\langle \Psi_0 \,|\, \hat{H} \,|\, \Psi_Y \right\rangle}_{\text{Exclusion Principle Violating Terms}} \\
&= C_X \left(E_{corr} - \Delta_X^{(EPV)} \right)
\end{aligned}
$$

Beautiful simplification of the full-CI equation:

$$
\begin{aligned}
&\left\langle \Psi_X \,|\, \hat{H} \,|\, \Psi_{HF} \right\rangle + \left\langle \Psi_X \,|\, \hat{H} \,|\, \Psi_D \right\rangle + \left\langle \Psi_X \,|\, \hat{H} \,|\, \Psi_Q \right\rangle = C_X \left(E_{HF} + E_{corr} \right) \\
\approx &\left\langle \Psi_X \,|\, \hat{H} \,|\, \Psi_{HF} \right\rangle + \left\langle \Psi_X \,|\, \hat{H} \,|\, \Psi_D \right\rangle + C_X \left(E_{corr} - \Delta_X^{(EPV)} \right) = C_X \left(E_{HF} + E_{corr} \right) \\
&\boxed{= \left\langle \Psi_X \,|\, \hat{H} \,|\, \Psi_{HF} \right\rangle + \left\langle \Psi_X \,|\, \hat{H} \,|\, \Psi_D \right\rangle = C_X \left(E_{HF} + \Delta_X^{(EPV)} \right)}
\end{aligned}
$$

(**Coupled-Electron Pair Approximation, CEPA**): CI problem with a shifted diagonal

Drop the Crude Approximations

X ≡ (ijab)
Y ≡ (klcd)
Z ≡ (mnef)
x ≡ (ia)
y ≡ (kc)

⇒

$$\left\langle \Psi_X \middle| \hat{H} \middle| \Psi_Q \right\rangle \cong \tfrac{1}{2} \sum_{klcd} \sum_{mnef} C_{kl}^{cd} C_{mn}^{ef} \left\langle \Psi_{ij}^{ab} \middle| \hat{H} \middle| \Psi_{klmn}^{cdef} \right\rangle$$

$$\left\langle \Psi_x \middle| \hat{H} \middle| \Psi_T \right\rangle \cong \sum_{kc} \sum_{mnef} C_k^c C_{mn}^{ef} \left\langle \Psi_i^a \middle| \hat{H} \middle| \Psi_{kmn}^{cef} \right\rangle$$

But it is more elegant to write that in terms of the C-operators, giving:

$$\left\langle \Psi_X \middle| \hat{H} \middle| \Psi_Q \right\rangle \cong \left\langle \Psi_{ij}^{ab} \middle| \hat{H} \middle| \tfrac{1}{2} \hat{C}_2 \hat{C}_2 \Psi_0 \right\rangle$$

$$\left\langle \Psi_x \middle| \hat{H} \middle| \Psi_T \right\rangle \cong \left\langle \Psi_i^a \middle| \hat{H} \middle| \hat{C}_1 \hat{C}_2 \Psi_0 \right\rangle$$

Thus, the "**Quadratic CI Singles + Doubles**" (QCISD) equations for the energy and the determination of the coefficients:

$$E_{QCISD} = \left\langle \Psi_{HF} \mid \hat{H}_N \mid \Psi \right\rangle = E_{HF} + \sum_{ia} F_{ia} C_a^i + \tfrac{1}{4} \sum_{ijab} \left\langle ij \,||\, ab \right\rangle C_{ab}^{ij}$$

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

$$E_{corr} C_{ab}^{ij} = \left\langle \Psi_i^a \mid \hat{H}_N (1 + \hat{C}_1 + \hat{C}_2 + {\color{red} \tfrac{1}{2} \hat{C}_2 \hat{C}_2}) \mid \Psi_{HF} \right\rangle$$

From QCISD to the full Coupled Cluster Hierarchy

Coupled Cluster Theory Incorporates excitation products from the beginning:

$$\boxed{\begin{aligned}|\Psi_{CC}\rangle &= exp(T)|\Psi_0\rangle = exp\left(\underbrace{T_1 + T_2 + T_3 + \cdots}_{T}\right)|\Psi_0\rangle \\ &= \left(1 + T + \tfrac{1}{2}T^2 + \tfrac{1}{3!}T^3 + \cdots\right)|\Psi_0\rangle\end{aligned}}$$

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.

$$T_1 = \sum_{ia} t_a^i a^+ i$$

$$T_2 = \frac{1}{4}\sum_{ijab} t_{ab}^{ij} a^+ b^+ ji$$

$$T_3 = \frac{1}{36}\sum_{ijab} t_{abc}^{ijk} a^+ b^+ c^+ kji$$

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 not quite the same.

CI theory: **CI coefficients *c*** of the single, double, triple,... excitations

CC theory: „**cluster amplitudes“ *t*** for the single, double, triple,... excitation operators.

Coupled Cluster versus CI

$$\boxed{|\Psi_{FCI}\rangle = (1 + \underset{\text{CI}}{C})|\Psi_0\rangle = \underset{\text{CC}}{exp(T)}|\Psi_0\rangle}$$

Connection of CI and CC

$$C_1 = T_1$$

$$C_2 = \frac{1}{2}T_1^2 + T_2$$

$$C_3 = \frac{1}{6}T_1^3 + T_1T_2 + T_3$$

$$C_4 = \frac{1}{24}T_1^4 + \frac{1}{2}T_2^2 + \frac{1}{2}T_1^2T_2 + T_1T_3 + T_4$$

Model	**Parameters**	**Effort**
CCD : T_2	$O(N^4)$	$O(N^6)$
CCSD : T_1+T_2	$O(N^4)$	$O(N^6)$
CCSD(T) : $T_1+T_2+(T_3)$	$O(N^6)$	$O(N^7)$
CCSDT : $T_1+T_2+T_3$	$O(N^6)$	$O(N^8)$
CCSDTQ: $T_1+T_2+T_3+T_4$	$O(N^8)$	$O(N^{10})$

CC is size consistent
at any truncation level!
CI is not

Convergence of the CC Hierarchy vs CI

Deviation from full-CI (CO molecule, 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 at least 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.

Energy and Amplitude Determination

✓ **Variational principle:**

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

➡ **Hopeless idea** – the expansion **does not terminate** and the resulting equations are just to complex to be soluble.

✓ **Projection:**

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

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

$$\langle \Psi_0 \left| \hat{H} e^T \right| \Psi_0 \rangle = E$$ **Energy equation**

$$\langle \Psi_X \left| \hat{H} e^T \right| \Psi_0 \rangle \equiv \sigma_X = 0$$ **Amplitude equations**

Linked Form of Coupled Cluster Equations

Baker-Campbell-Haussdorff Expansion:

$$e^{-T}\hat{H}e^{T} = \hat{H} + [\hat{H},T] + \frac{1}{2!}\left[[\hat{H},T],T\right] + \frac{1}{3!}\left[\left[[\hat{H},T],T\right],T\right] + \frac{1}{4!}\left[\left[\left[[\hat{H},T],T\right],T\right],T\right]$$

Since both H and T are expressed in second quantization, the terms are of the form:

$$[q^{+}ps^{+}r, b^{+}ja^{+}i] = 0$$

Unless, there is at least one coincidence among p,q,r,s and i,j,a,b

This leads to rewriting

$$[\hat{H},T] = (\hat{H},T)_C + (\hat{H},T)_D - \underbrace{(T,\hat{H})_C}_{=0} - (T,\hat{H})_D = (\hat{H},T)_C$$

"Connected expansion"

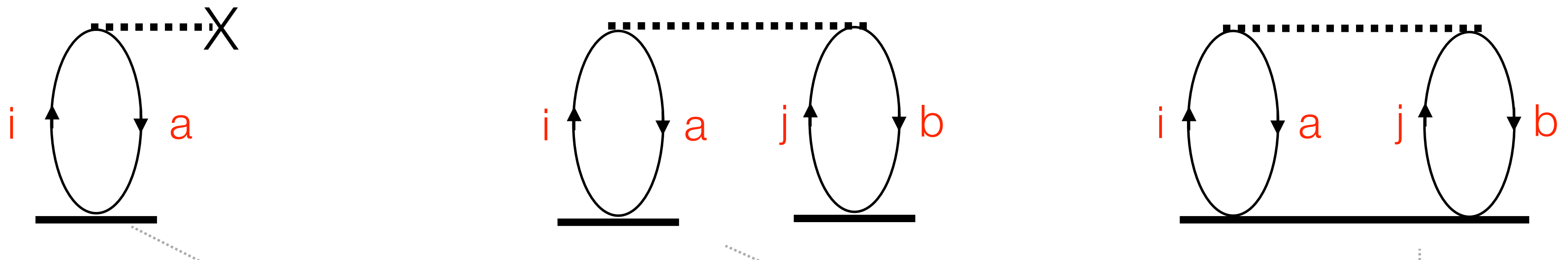
$$\hat{H}T = (\hat{H},T)_C + (\hat{H},T)_D$$

Graphical Evaluation of Energy Expression

The connected expansion allows one to use powerful graphical techniques for matrix element evaluation

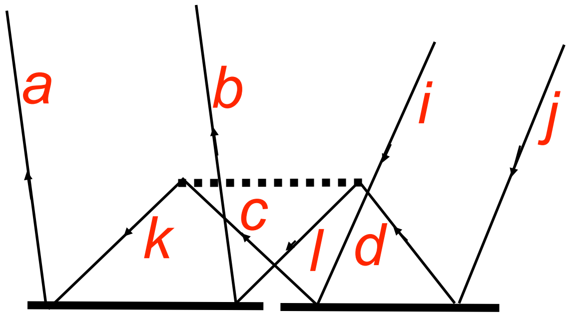
$$\langle \Psi_0 | e^{-T}\hat{H}e^{T} | \Psi_0 \rangle = \langle \Psi_0 \left| \left(\hat{H}e^{T}\right)_C \right| \Psi_0 \rangle = E$$

$$\langle \Psi_X | e^{-T}\hat{H}e^{T} | \Psi_0 \rangle = \langle \Psi_X \left| \left(\hat{H}e^{T}\right)_C \right| \Psi_0 \rangle = 0$$



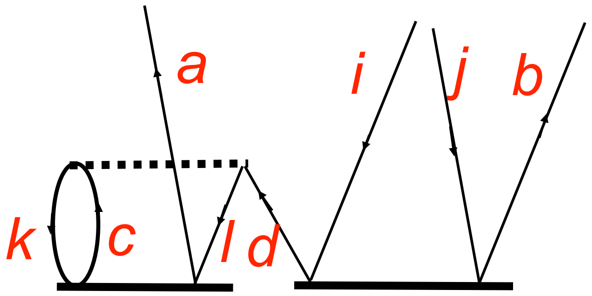
$$\boxed{E = E_{HF} + \sum_{ia} F_{ia} t_a^i + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle \left(2 t_a^i t_b^j + t_{ab}^{ij}\right)}$$

Graphical Evaluation of the Amplitude Equations

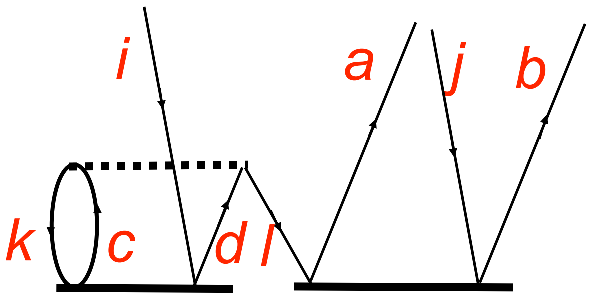


$$\frac{1}{2}\sum_{klcd}\langle kl||cd\rangle t^{kl}_{ab}t^{ij}_{cd}$$

(2 equivalent diagrams each having the prefactor 1/4)



$$-P_{ab}\sum_{klcd}\langle kl||cd\rangle t^{kl}_{ca}t^{ij}_{db}$$



$$-P_{ij}\sum_{klcd}\langle kl||cd\rangle t^{ik}_{cd}t^{lj}_{ab}$$

CCD Equations:

$$\Delta^{ij}_{ab}t^{ij}_{ab} = \langle ij||ab\rangle + u^{ij}_{ab} + v^{ij}_{ab}$$

$$u^{ij}_{ab} = \frac{1}{2}\sum_{cd}\langle ab||cd\rangle t^{ij}_{cd} + \frac{1}{2}\sum_{kl}\langle ij||kl\rangle t^{kl}_{ab} - P_{ij}P_{ab}\sum_{kc}\langle kb||ic\rangle t^{kj}_{ac}$$

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

- ➡ Up to CCSD(T), maybe CCSDT, doable by hand,
- ➡ Higher-order CC equations derived and implemented by Automatic Code Generation (Project A2)

Practical Implementation

For example: $\sigma_{ab}^{ij} \leftarrow \sum_{kc} \langle kb||ic\rangle t_{ac}^{kj}$

Write as matrices: $\langle kb||ic\rangle = \langle kb|ic\rangle - \langle kb|ci\rangle \quad = (ki|bc) - (kc|bi)$

$$= \left(\boldsymbol{J}^{ki}\right)_{bc} - \left(\boldsymbol{K}^{ki}\right)_{cb}$$

$$t_{ac}^{kj} = \left(\boldsymbol{t}^{kj}\right)_{ac}$$

Sigma-vector contribution:

$$\sigma_{ab}^{ij} \leftarrow \langle kb||ic\rangle t_{ac}^{kj} = \left\{\left(\boldsymbol{J}^{ki}\right)_{bc} - \left(\boldsymbol{K}^{ki}\right)_{cb}\right\}\left(\boldsymbol{t}^{kj}\right)_{ac}$$

$$= \left[\boldsymbol{t}^{kj}\left(\boldsymbol{J}^{ki+} - \boldsymbol{K}^{ki}\right)\right]_{ab}$$

- Efficient storage using internal indices as "slow" indices
- Efficient contraction as matrix multiplications using BLAS level 3 operations
- Automatic code generation for supercomputers pursued in project A2

Coupled Cluster Summary

1. Coupled cluster models are the **most sophisticated** electron correlation models available which among those based on expansions in determinants.
2. Coupled cluster theory is a **nonlinear model** which approximates higher excitations as products of lower excitations through an **exponential parameterization**.
3. Coupled cluster theory is perfectly **size consistent** and **unitarily invariant** but **not variational.**
4. The **CCSD model** is perhaps the best model based on single and double excitations at the same asymptotic cost as CISD. QCISD is easier and very close in accuracy.
5. High accuracy models („chemical accuracy“ ~ 1 kcal/mol) require the inclusion of **connected triple excitations**. The **CCSD(T) model** is an excellent tradeoff between accuracy and computational effort and is *de facto* the standard for high accuracy work.

Moving on from there

Coupled Cluster Lagrangian:

$$\mathcal{L} = \langle \Psi_0 | (1 + \hat{\Lambda}) e^{-T} \hat{H} e^{T} | \Psi_0 \rangle + \sum_{ia} F_a^i z_a^i$$

$$\hat{\Lambda} = \hat{\Lambda}_1 + \hat{\Lambda}_2 + \cdots = \sum_{ia} \lambda_a^i i^+ a + \frac{1}{4} \sum_{ijab} \lambda_{ab}^{ij} i^+ j^+ ab + \cdots$$

Molecular structures

$$\frac{\partial \mathcal{L}}{\partial \boldsymbol{R}} = 0$$

Vibrations, Reactions

$$H_{KL} = \frac{\partial^2 \mathcal{L}}{\partial R_K \partial R_L}$$

Molecular properties

$$\frac{\partial \mathcal{L}}{\partial \kappa} = \sum_{pq} D_{pq} \langle p | \hat{h}^{(\kappa)} | q \rangle$$

Excited States

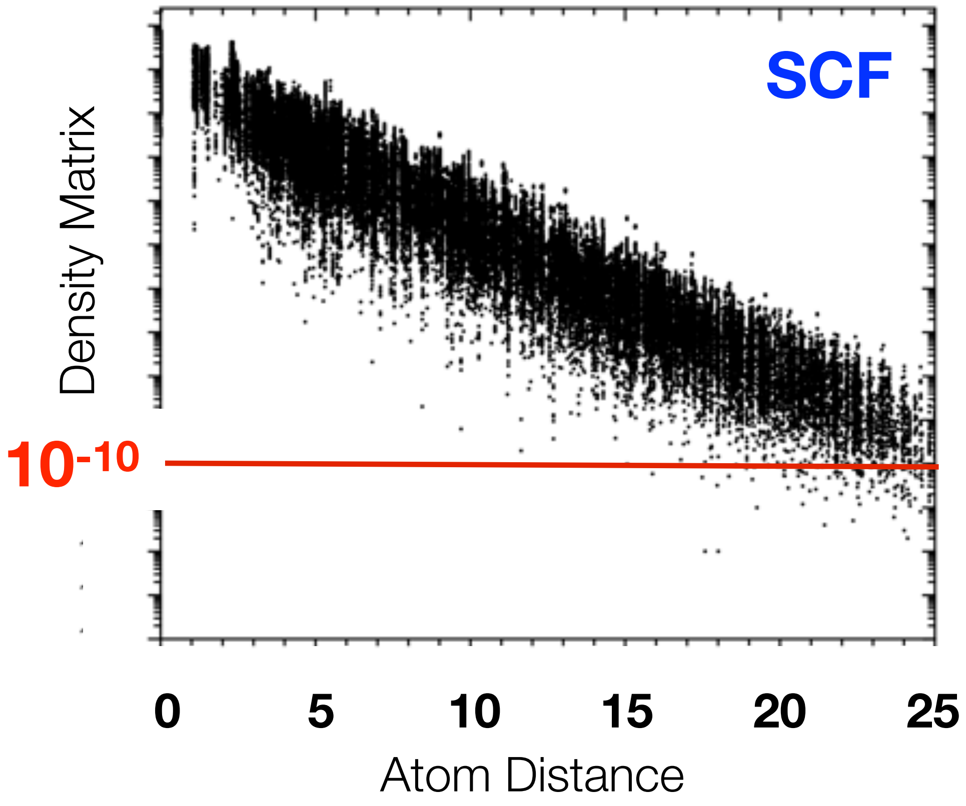
$$|\Psi_I\rangle = (\hat{R}_1 + \hat{R}_2 + \cdots) |\Psi_{CC}\rangle$$

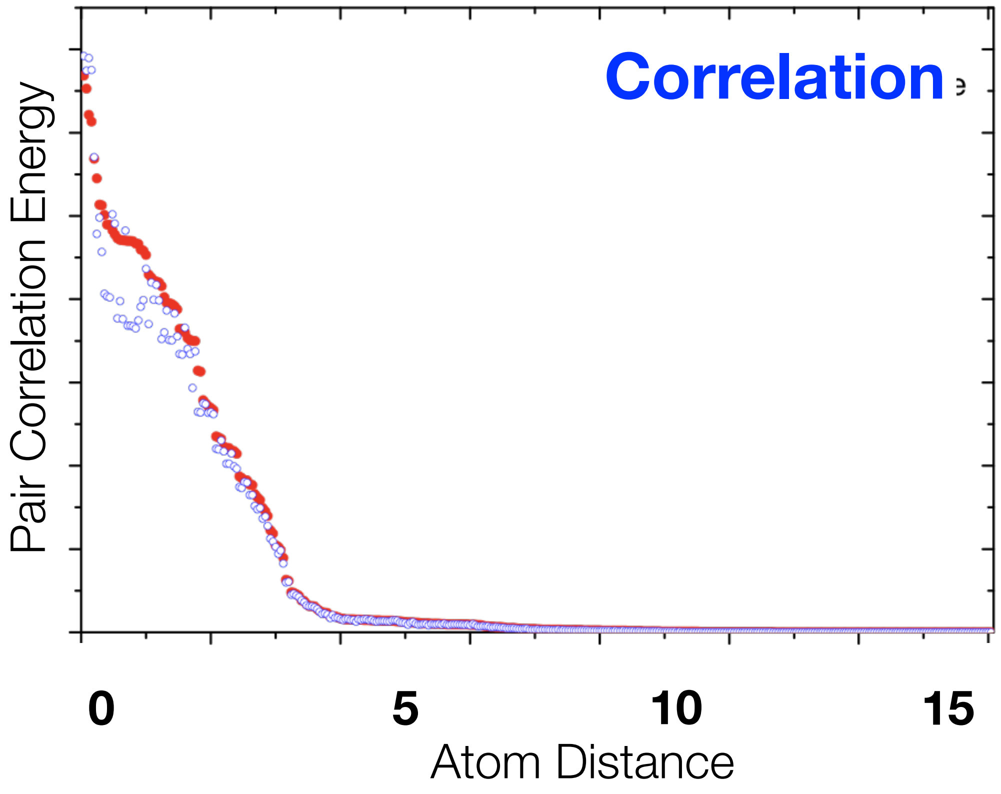
- All approachable with the exact same formalism and techniques

Problem with Coupled Cluster Methods

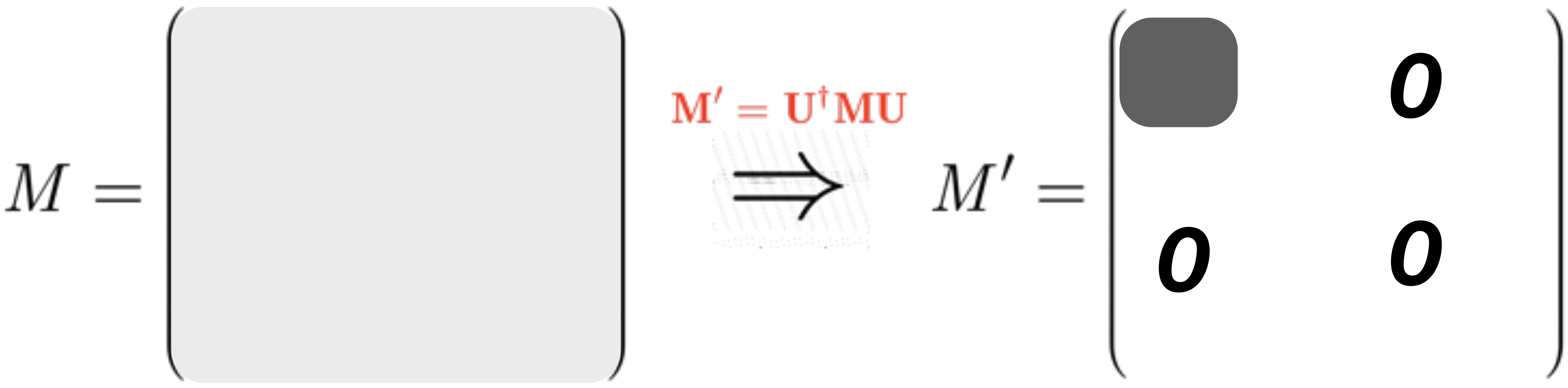
Saving Time in Electronic Structure Calculations

Exploit Sparsity!

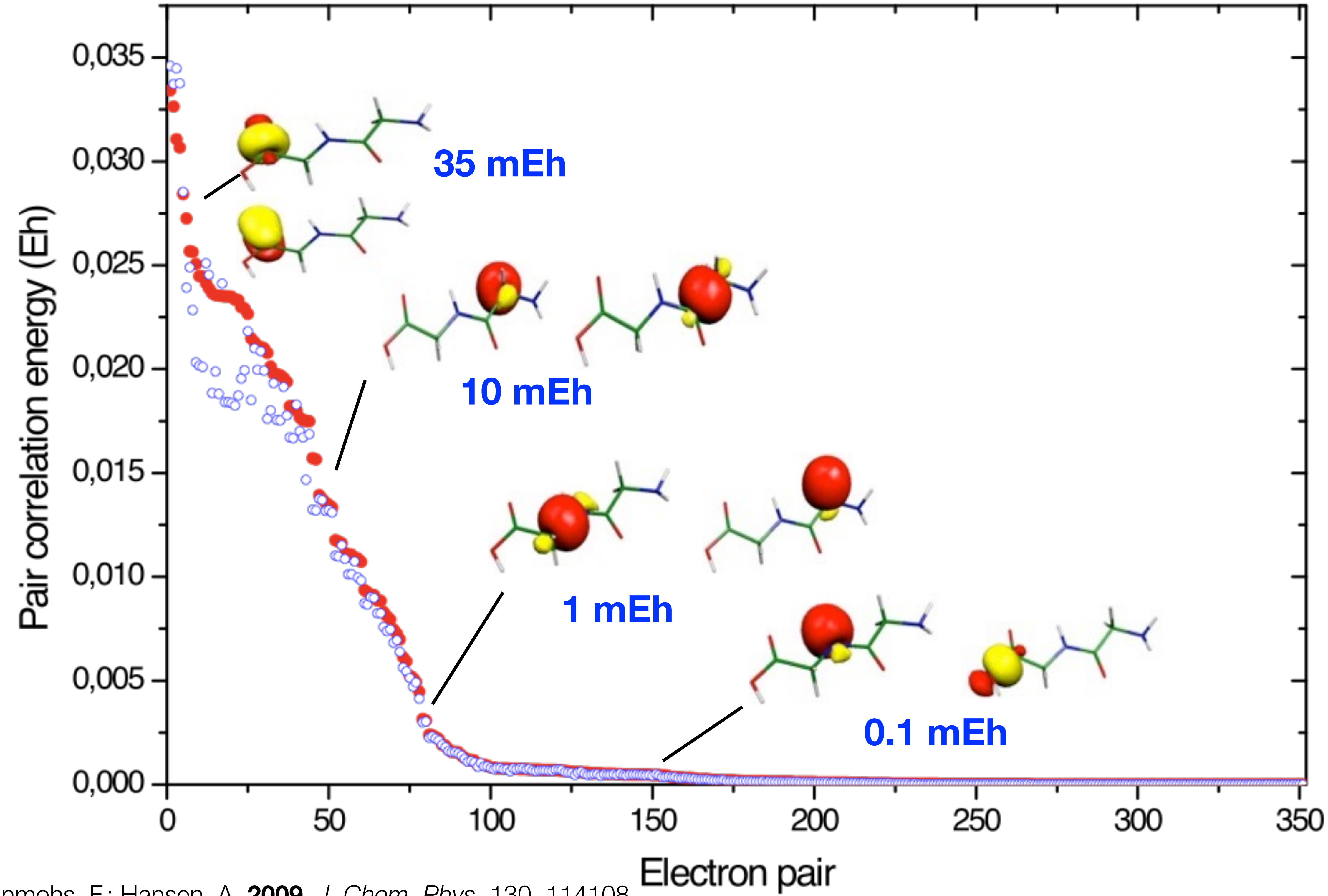




Compress Data!

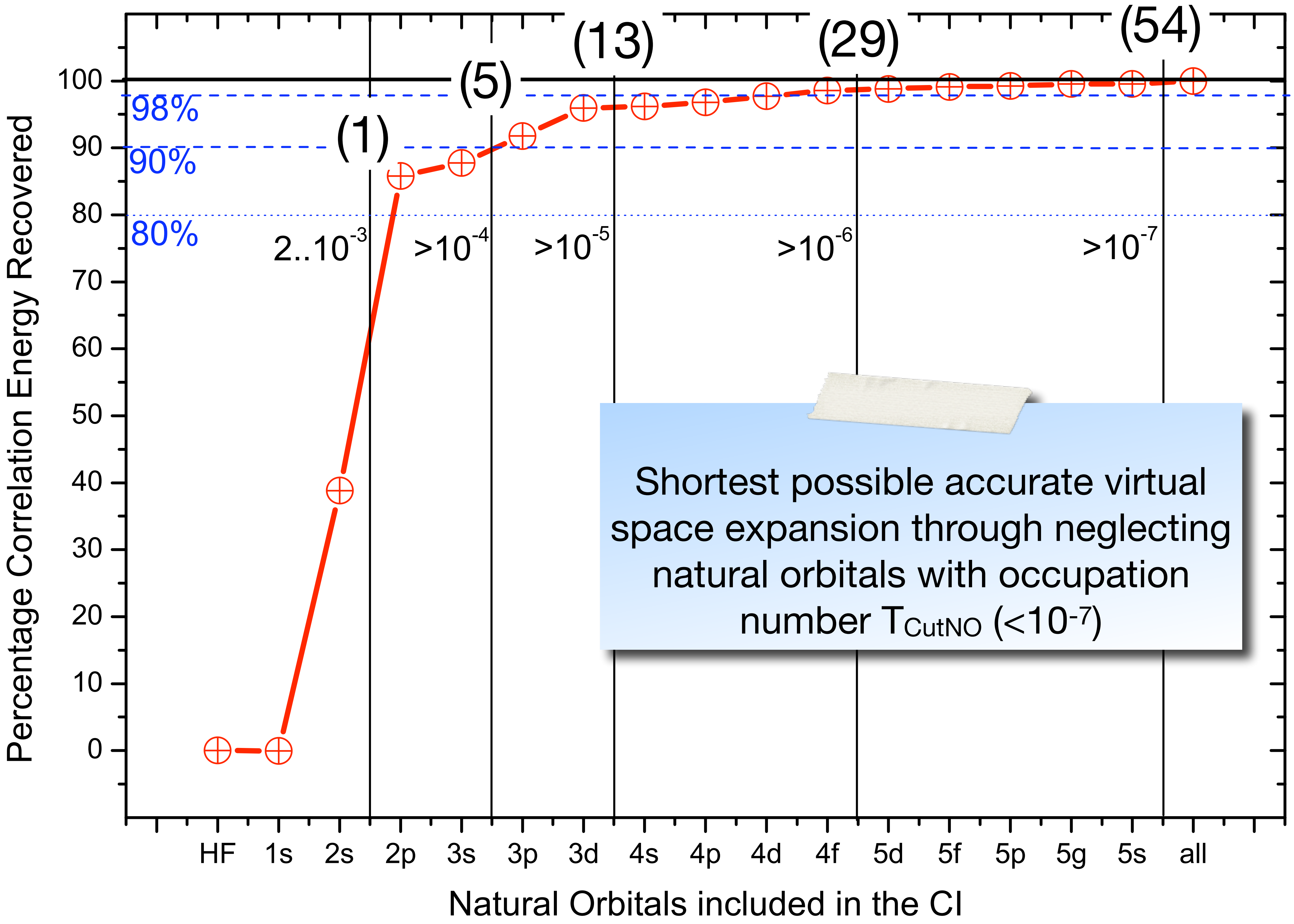


Approximation 1: Locality of Pair Correlation Energies



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

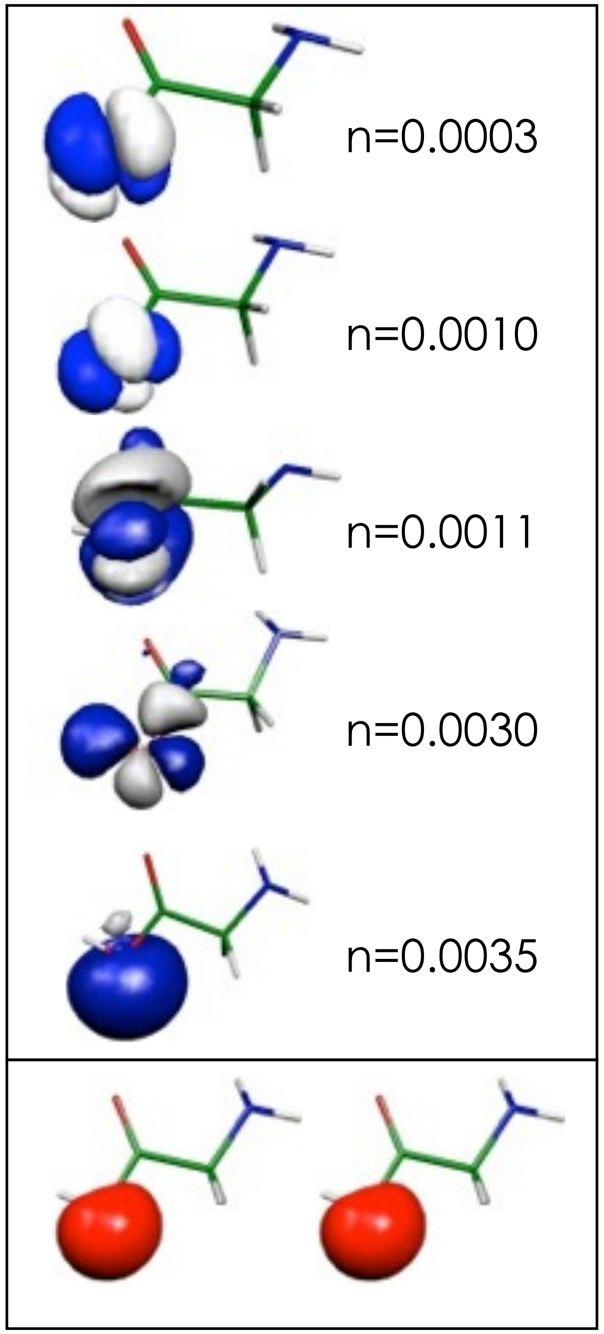
The Natural Expansion of He

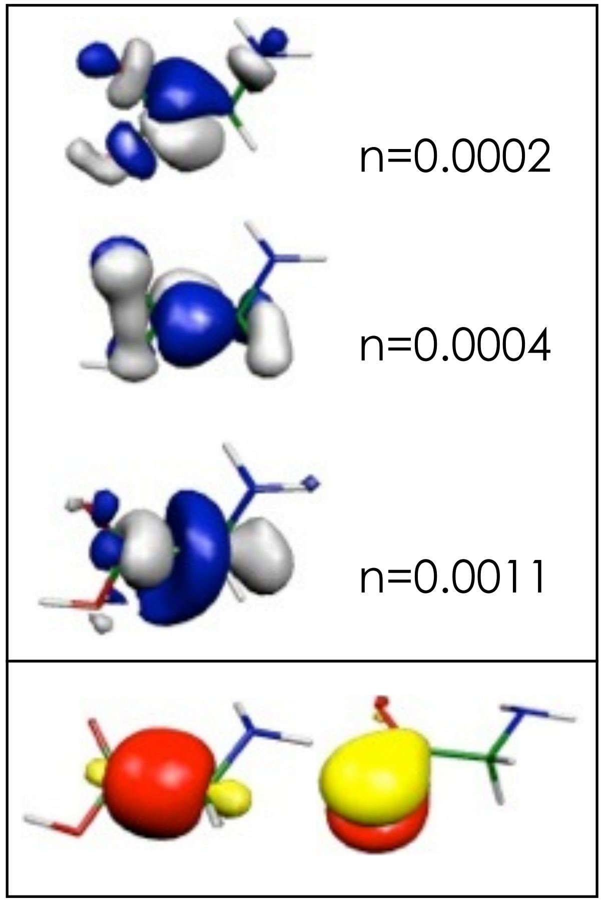


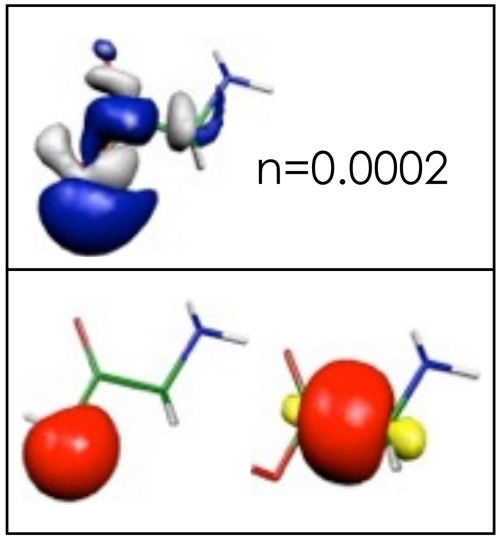
Shortest possible accurate virtual space expansion through neglecting natural orbitals with occupation number T_{CutNO} ($<10^{-7}$)

Pair Natural Orbitals (PNOs)

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

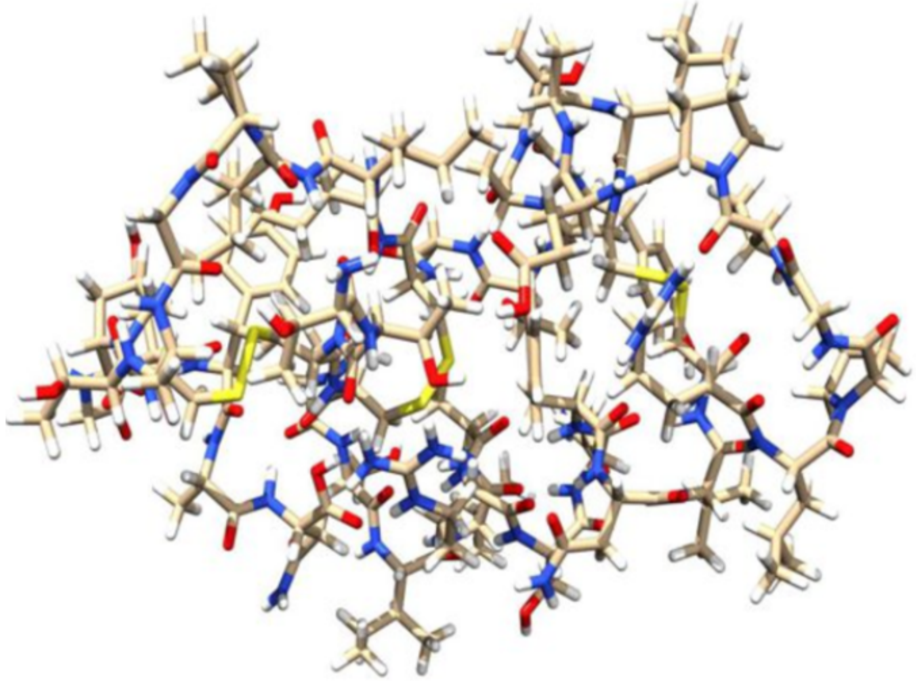






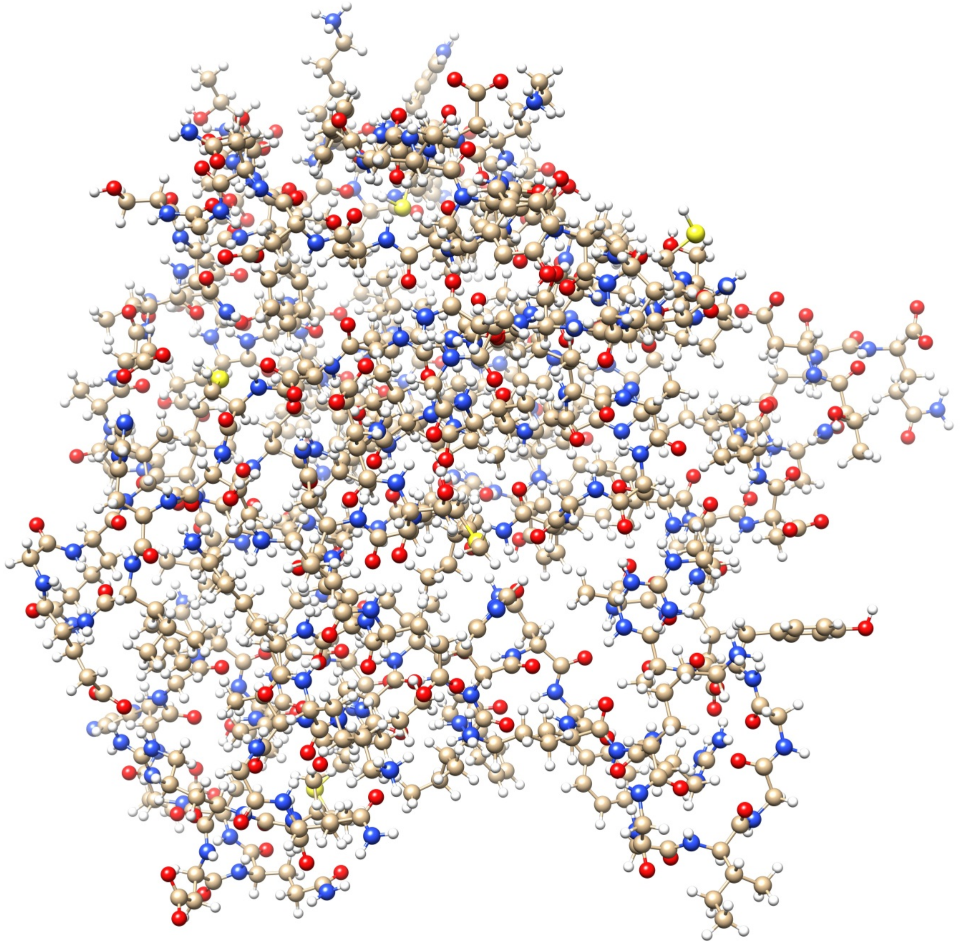
FN; Wennmohs, F.; Hansen, A. *J. Chem. Phys.* **2009**, 130, 114108

Huge Calculations with linear DLPNO-CCSD(T)



Crambin/def2-TZVP
644 atoms
12705 Basis functions
10 d/4 cores

$C_{350}H_{702}$/def2-TZVP
1052 atoms
15062 Basis functions
18h/4 cores

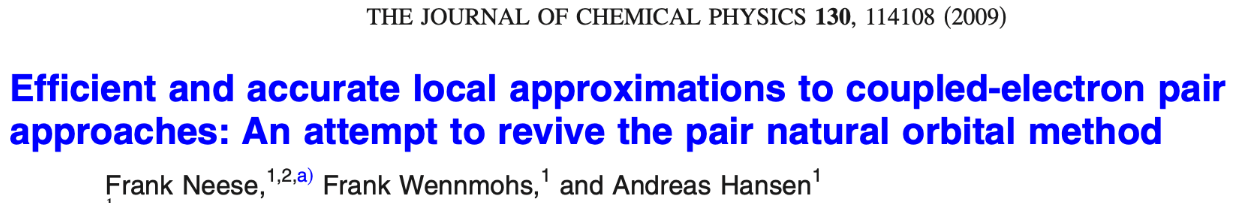


Integrase/cc-pVDZ
2380 atoms
22621 Basis functions
62h/64 cores

(CIM-DLPNO-CCSD(T))
Y. Guo, FN, 2017

C. Riplinger, P. Pinski, U. Becker, E.F. Valeev, FN, **2016**, 144, 024109

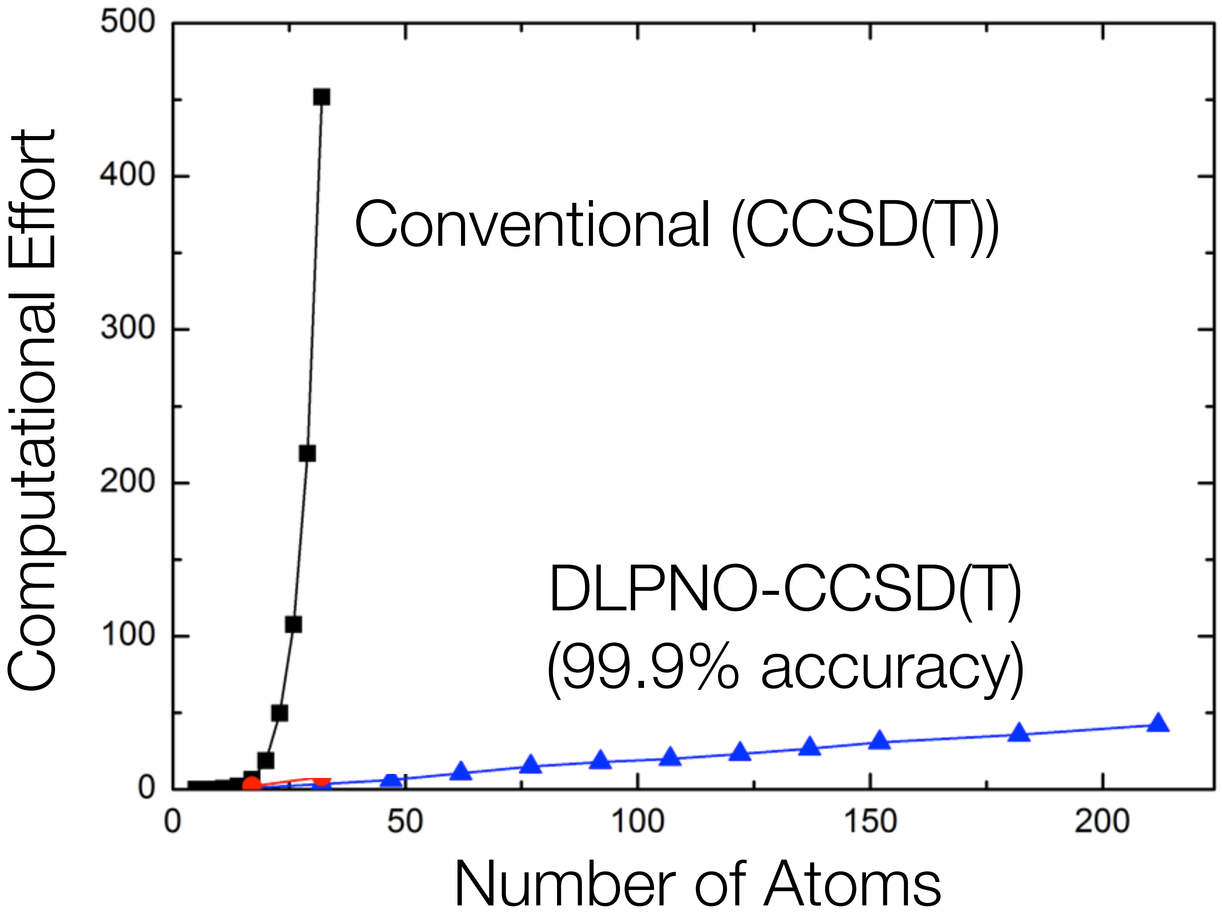
Impact of DLPNO-CCSD(T)

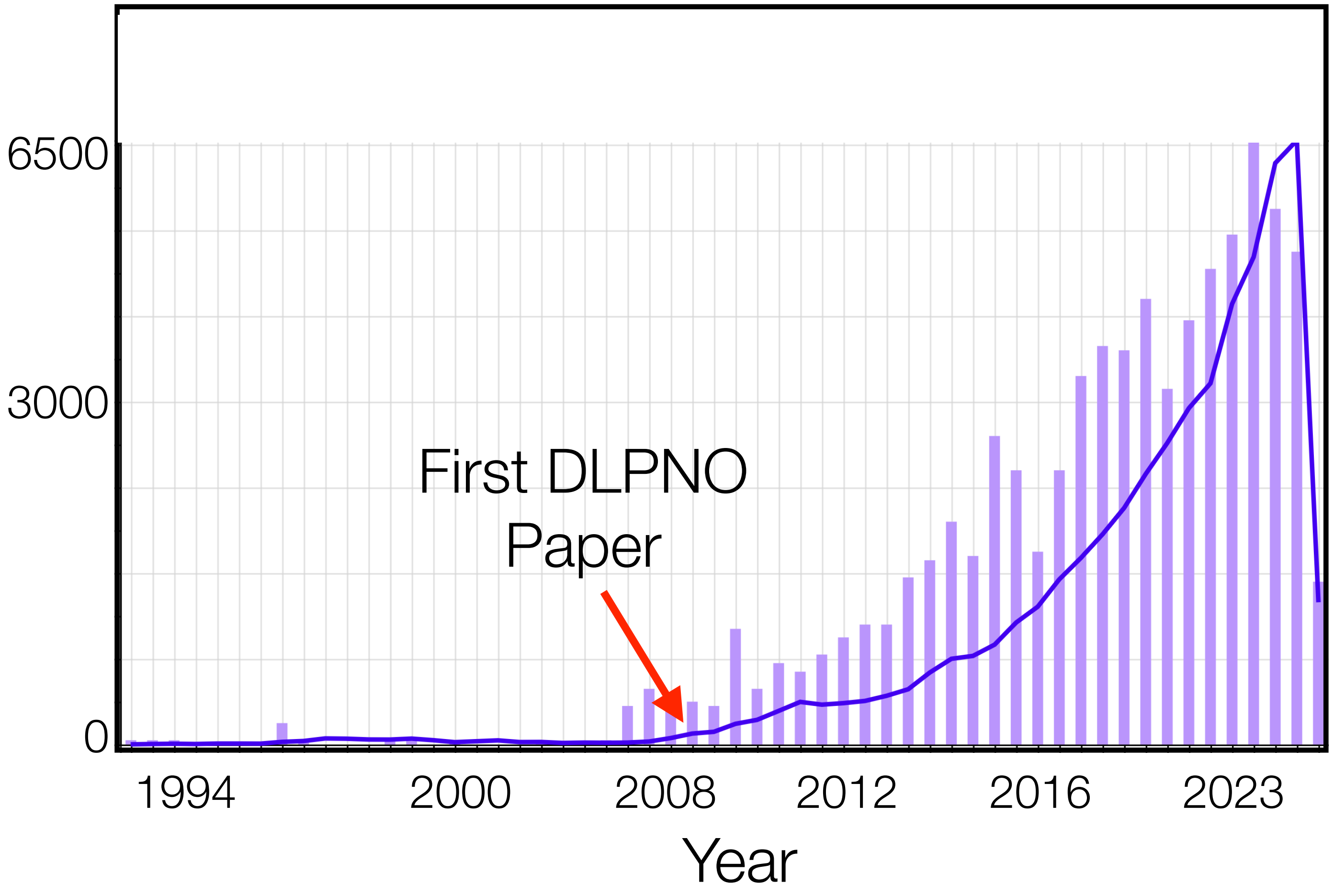


THE JOURNAL OF CHEMICAL PHYSICS **130**, 114108 (2009)

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]





Zitationen: „Pair Natural Orbital“

Neese, F.; Hansen, A.; Liakos, D. G. *JCP* **2009**, *131*.
Riplinger, C.; Neese, F. *JCP* **2013**, *138*.
Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *JCP* **2013**, *139*.
Riplinger, C.; Pinski, P.; Becker, U.; Valeev, E. F.; Neese, F. *JCP* **2016**, *144*
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