

# **From CI to CEPA to perturbation — being well-dressed may be important**

Peter Reinhardt

Laboratoire de Chimie Théorique, Université Paris VI, 75252 Paris CEDEX 05,

`Peter.Reinhardt@upmc.fr`

# Presentation

- Introduction
- Theoretical part
  - Coupled Cluster, CI, dressed CI, and dressed perturbation theory
  - Construction of localized orbitals
- Applications
- Conclusions et perspectives

# Introduction

# Introduction

Either

**Obtain the same result as with canonical orbitals, but more efficiently**

Correlation methods invariant to orbital rotation: CCSD, CI, ACPF, CEPA-0,  
(MP2 in invariant formulation)

# Introduction

Either

**Obtain the same result as with canonical orbitals, but more efficiently**

Correlation methods invariant to orbital rotation: CCSD, CI, ACPF, CEPA-0, (MP2 in invariant formulation)

Or

**Exploit localization without direct comparison to the canonical case**

Localization-dependent schemes: perturbation theory, CEPA-2, CEPA-3, Full CEPA, CCSD(T)

# CCSD, CI, and dressed perturbation schemes

Starting point: CISD or CCSD

- Both invariant under orbital rotations
- CI variational, CCSD projection

**Advantages:** CCSD size consistent, CI standard eigenvalue problem

**Problematic:** CI not size consistent, CCSD non-linear equations

# CCSD, CI, and dressed perturbation schemes

Starting point: CISD or CCSD

- Both invariant under orbital rotations
- CI variational, CCSD projection

**Advantages:** CCSD size consistent, CI standard eigenvalue problem

**Problematic:** CI not size consistent, CCSD non-linear equations

- Get rid of the quadratic terms in the CCSD scheme  $\longrightarrow$  CEPA-0 as LCCSD
- Add linked diagrams **via the correlation energy** in order to compensate the unlinked diagrams  $\longrightarrow$  CEPA-0 as dressed CI

# CCSD, CI, and dressed perturbation schemes

Starting point: CISD or CCSD

- Both invariant under orbital rotations
- CI variational, CCSD projection

**Advantages:** CCSD size consistent, CI standard eigenvalue problem

**Problematic:** CI not size consistent, CCSD non-linear equations

More delicately:

- Get rid of the quadruple excitations, **which are not a product of double excitations**, or add **only the necessary** diagrams to cancel the unlinked diagrams in CI  $\longrightarrow$  (SC)<sup>2</sup>CI or Full CEPA



# CCSD, CI, and dressed perturbation schemes

Linear system of equations :

$$\sum_I \langle \Phi_0 | \mathbf{H} | \Phi_I \rangle c_I = H_{0I} c_I = E_{\text{Corr}}$$
$$H_{0I}^\dagger + (H_{II} - E_{HF} + \Delta_I) c_I + \sum_{J \neq I} H_{IJ} c_J = 0$$

in a base of SD determinants  $I = \Phi_{ij}^{ab}$  with **diagonal dressing** :  $\Delta_I$

# CCSD, CI, and dressed perturbation schemes

Linear system of equations :

$$\sum_I \langle \Phi_0 | \mathbf{H} | \Phi_I \rangle c_I = H_{0I} c_I = E_{\text{Corr}}$$
$$H_{0I}^\dagger + (H_{II} - E_{HF} + \Delta_I) c_I + \sum_{J \neq I} H_{IJ} c_J = 0$$

in a base of SD determinants  $I = \Phi_{ij}^{ab}$  with **diagonal dressing** :  $\Delta_I$

- Without dressing ( $\Delta_I = 0$ ) : CEPA-0
- ACPF :  $\Delta_I = -\frac{2}{n_e} E_{\text{Corr}}$
- (SC)<sup>2</sup>CI:  $\Delta_{ij}^{ab} = -\sum_{\text{EPV}(i,j,a,b)} \langle \Phi_0 | \mathbf{H} | \Phi_{kl}^{cd} \rangle c_{kl}^{cd}$

# CCSD, CI, and dressed perturbation schemes

Linear system of equations :

$$\sum_I \langle \Phi_0 | \mathbf{H} | \Phi_I \rangle c_I = H_{0I} c_I = E_{\text{Corr}}$$
$$H_{0I}^\dagger + (H_{II} - E_{HF} + \Delta_I) c_I + \sum_{J \neq I} H_{IJ} c_J = 0$$

in a base of SD determinants  $I = \Phi_{ij}^{ab}$  with diagonal dressing :  $\Delta_I$

- Without dressing ( $\Delta_I = 0$ ) : CEPA-0
- ACPF :  $\Delta_I = -\frac{2}{n_e} E_{\text{Corr}}$
- (SC)<sup>2</sup>CI:  $\Delta_{ij}^{ab} = -\sum_{\text{EPV}(i,j,a,b)} \langle \Phi_0 | \mathbf{H} | \Phi_{kl}^{cd} \rangle c_{kl}^{\text{cd}}$   
 $= -\sum_{\text{EPV}(i,j,a,b)} \langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ijkl}^{\text{abcd}} \rangle c_{kl}^{\text{cd}}$

# CCSD, CI, and dressed perturbation schemes

Diagonal of the CEPA problem

$$\sum_I \langle \Phi_0 | \mathbf{H} | \Phi_I \rangle c_I = H_{0I} c_I = E_{\text{Corr}}$$

$$H_{0I}^\dagger + (H_{II} - E_{HF} + \Delta_I) c_I = 0$$

# CCSD, CI, and dressed perturbation schemes

Diagonal of the CEPA problem

$$E_{\text{Corr}} = - \sum_I \frac{H_{0I}^2}{H_{II} - E_{HF} + \Delta_I}$$

Epstein-Nesbet perturbation theory

# CCSD, CI, and dressed perturbation schemes

Diagonal of the CEPA problem

$$E_{\text{Corr}} = - \sum_I \frac{H_{0I}^2}{H_{II} - E_{HF} + \Delta_I}$$

Epstein-Nesbet perturbation theory

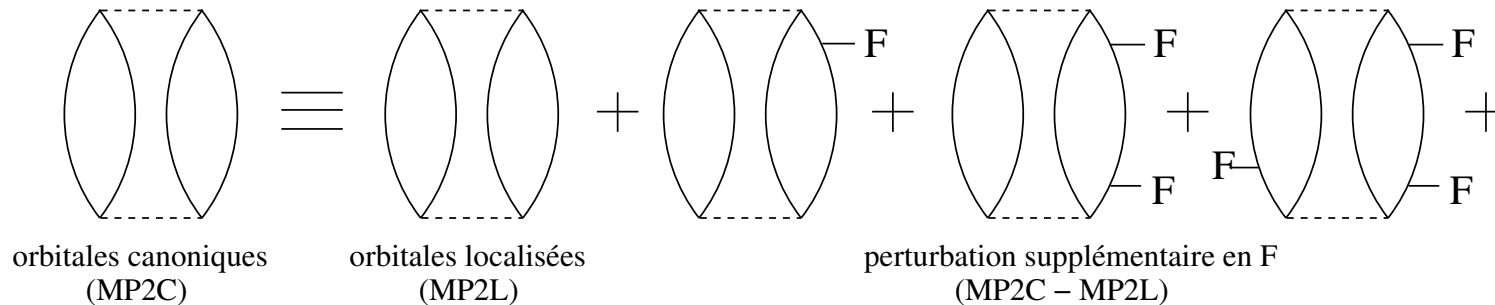
- Epstein-Nesbet perturbation theory:
  - $H_0$  as the diagonal of  $H$  in the space of determinants
  - infinite same-index summation of MP diagrams.
  - additional elements of J and K, still fast.

# MP2 in localized orbitals

- Fock operator is not any more diagonal
- Additional perturbation series  $\mathbf{V}^F$  with

$$\mathbf{H}_0 = \sum_{\mu} F_{\mu\mu} a_{\mu}^{\dagger} a_{\mu}$$

$$\mathbf{V}^F = \sum_{i \neq j} F_{ij} a_i^{\dagger} a_j + \sum_{a \neq b} F_{ab} a_a^{\dagger} a_b$$



# MP2 in localized orbitals

- Fock operator is not any more diagonal
- Additional perturbation series  $\mathbf{V}^F$  with

$$\mathbf{H}_0 = \sum_{\mu} F_{\mu\mu} a_{\mu}^{\dagger} a_{\mu}$$

$$\mathbf{V}^F = \sum_{i \neq j} F_{ij} a_i^{\dagger} a_j + \sum_{a \neq b} F_{ab} a_a^{\dagger} a_b$$

- MP2C : system of linear equations

$$\langle 0 | \mathbf{H} | \Phi_{ij}^{ab} \rangle = (ia|jb) - (ib|ja) \delta_{\sigma_i \sigma_j} = \sum_k (c_{kj}^{ab} F_{ik} + c_{ik}^{ab} F_{kj}) -$$

$$- \sum_c (c_{ij}^{cb} F_{ac} + c_{ij}^{ac} F_{kj})$$

$$E_{Corr} = \sum_{ijab} c_{ij}^{ab} (2(ia|jb) - (ib|ja))$$



# Our version of Epstein-Nesbet

- Localized orbitals
- “common formula” :

$$EN2 = - \sum_I \frac{\langle 0 | \mathbf{H} | I \rangle^2}{\langle I | \mathbf{H} - E_{HF} | I \rangle}$$

# Our version of Epstein-Nesbet

- Localized orbitals
- “common formula” :

$$EN2 = - \sum_I \frac{\langle 0 | \mathbf{H} | I \rangle^2}{\langle I | \mathbf{H} - E_{HF} | I \rangle}$$

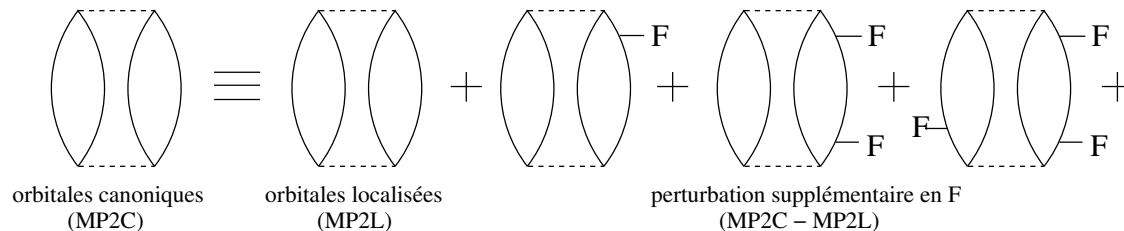
- Inclusion of EPV diagrams as diagonal dressing :  $\langle I | \mathbf{H} - E_{HF} + \Delta_I | I \rangle$

# Our version of Epstein-Nesbet

- Localized orbitals
- “common formula” :

$$EN2 = - \sum_I \frac{\langle 0 | \mathbf{H} | I \rangle^2}{\langle I | \mathbf{H} - E_{HF} | I \rangle}$$

- Inclusion of EPV diagrams as diagonal dressing :  $\langle I | \mathbf{H} - E_{HF} + \Delta_I | I \rangle$
- Inclusion of non-diagonal Fock matrix elements through **MP2C – MP2L**

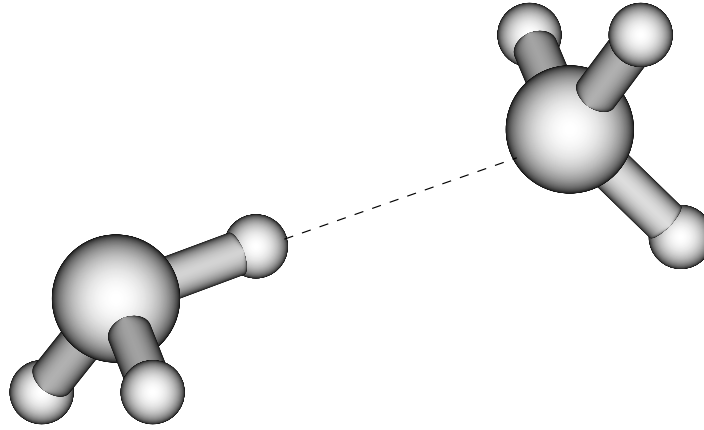


- 3 independent ingredients : F, same-index summation, EPV

**NOT Epstein-Nesbet in canonical orbitals !**

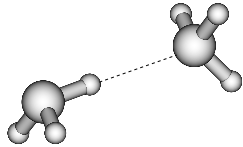
# Applications

- $\text{NH}_3$  dimer: different localizations

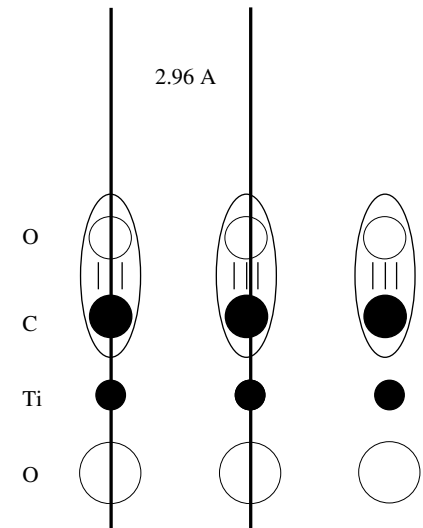
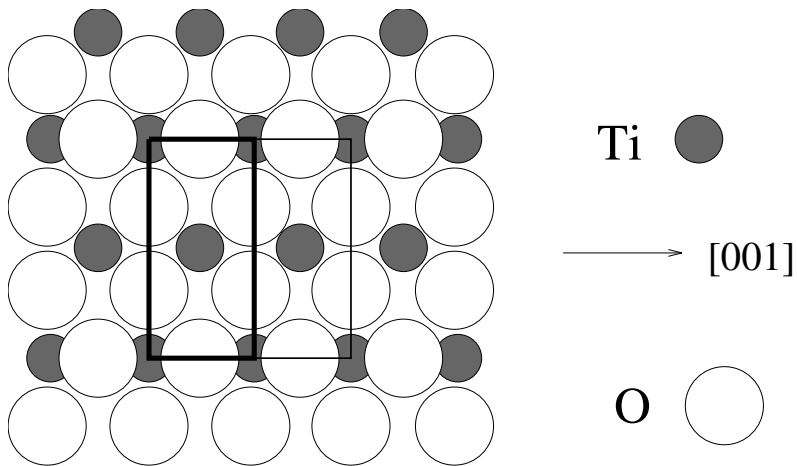


# Applications

- $\text{NH}_3$  dimer: different localizations

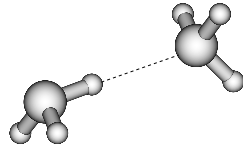


- CO on  $\text{TiO}_2$ : different dressings

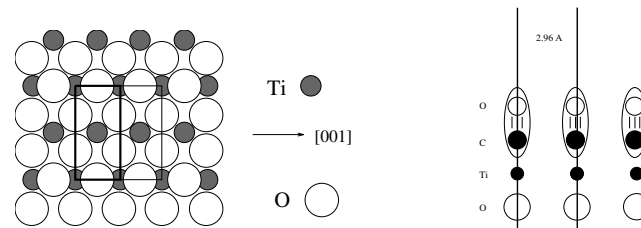


# Applications

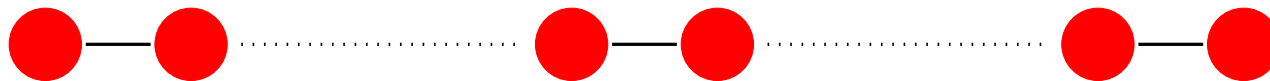
- $\text{NH}_3$  dimer: different localizations



- CO on  $\text{TiO}_2$ : different dressings



- Two-electron systems:  $(\text{H}_2)_n$ ,  $(\text{LiH})_n$  toward periodic systems



# Dependance on the employed localisation

Continuous path from Pipek-Mezey localization to Boys localization

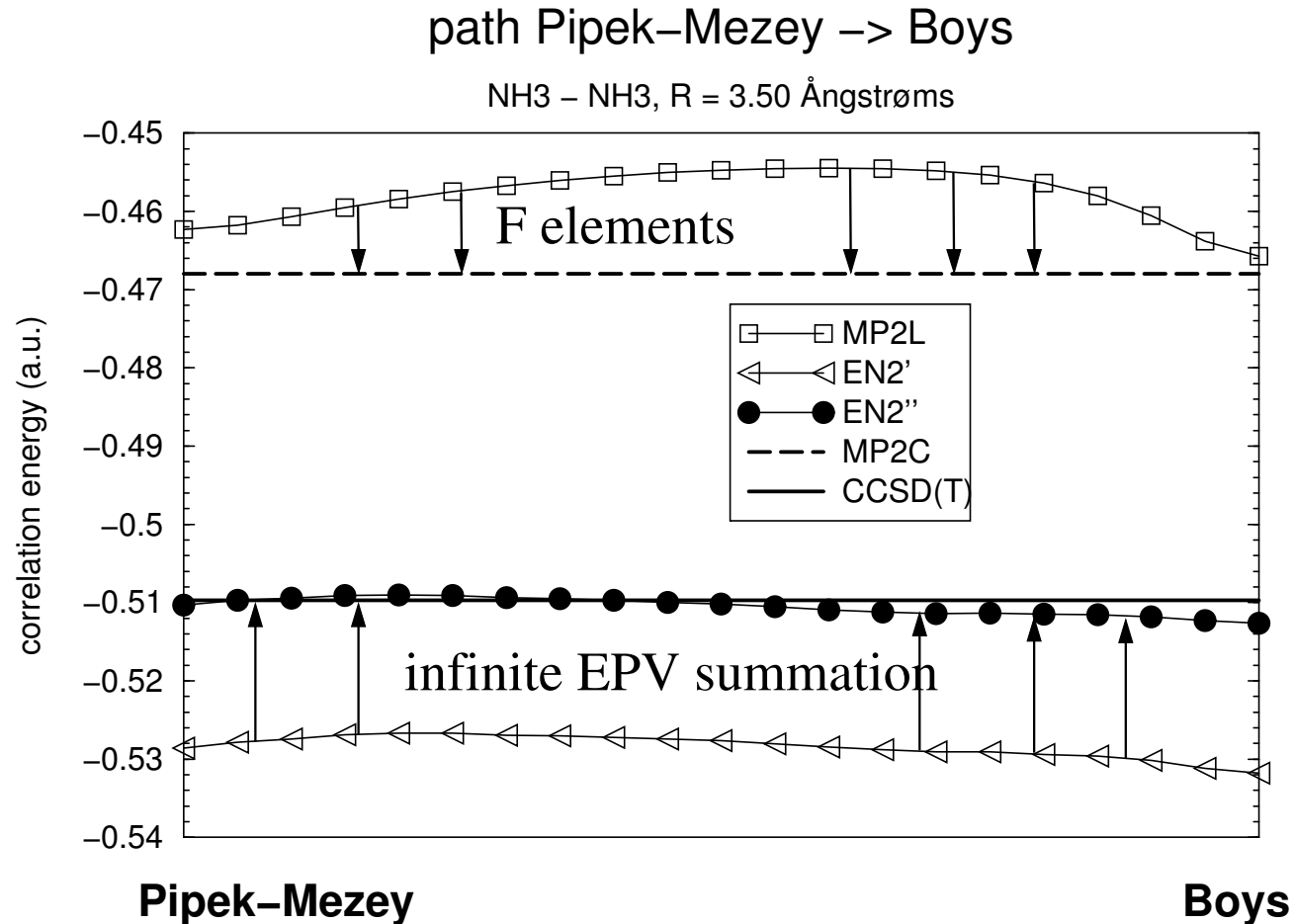
- Via parametrisation of the transformation  $\mathbf{T}$  between the two localisation schemes :

$$\mathbf{T} = \mathbf{U}^\dagger \begin{pmatrix} e^{i\lambda_1} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & e^{i\lambda_n} \end{pmatrix} \mathbf{U}$$

- Parameter  $\alpha$  for  $\lambda_i \rightarrow \alpha\lambda_i$ , thus  $\mathbf{T}(\alpha)$
- Pipek-Mezey localisation:  $\alpha = 0$
- Boys pour localisation:  $\alpha = 1$ .

# Dependance on the employed localisation

Continuous path from Pipek-Mezey localization to Boys localization

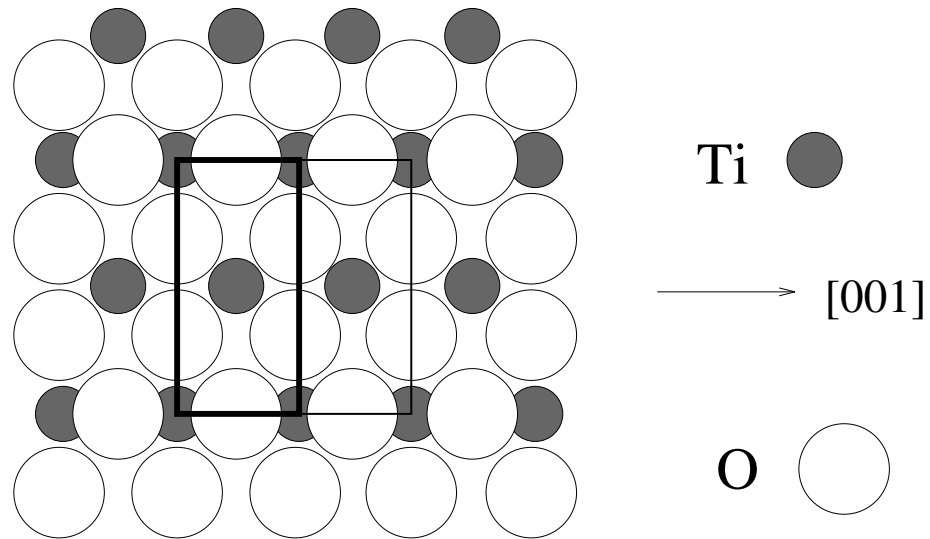


Infinite EPV summation (SC<sup>2</sup>CI)



# CO on TiO<sub>2</sub>

- TiO<sub>2</sub>(110) is a common catalyst; structured surface,

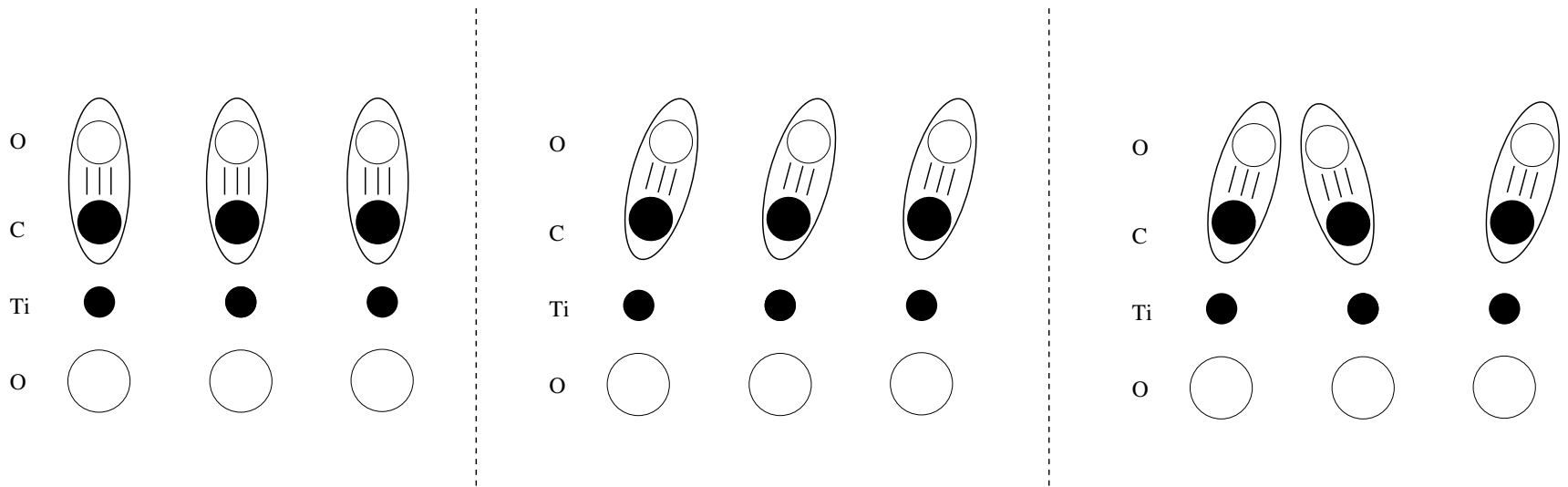


- repulsive CO – CO interaction
- 1D arrangement

# CO on TiO<sub>2</sub>

Model:

- C–C distance imposed by the substrate
- possible orientations: V-shaped or parallel:



- free CO molecules
- metastable  $2 CO \longrightarrow C + CO_2$
- minimum for a T-shaped configuration; O pointing toward the CO triple bond (A.vdPol, A.vdAvoird, P.E.S.Wormer, JCP, 92 (1990) 7498)

# Orbital localization

Multi-step localization without canonical orbitals: Super-CI

- Iteration on 3 steps: orthogonalization
- construction of a Fock matrix
- CI of mono-excited determinants

# Orbital localization

Multi-step localization without canonical orbitals: Super-CI

- Iteration on 3 steps: orthogonalization
- construction of a Fock matrix
- CI of mono-excited determinants
  
- Monomer in monomer basis, canonical orbitals  $\longrightarrow$  virtual orbitals
- Monomer in multimer basis, canonical orbitals  $\longrightarrow$  occupied orbitals
- Multimer in Multimer basis, localization via Singles CI
- Monomer in Multimer basis, localization via Singles CI

Orbital freezing/deleting affects orbitals of same shape

- Leading to localized occupied AND virtual orbitals, all orthogonal

# CO on TiO<sub>2</sub>

- aug-cc-pvtz basis set
- Simulated by a dimer, checked (RHF and correlation) with the trimer
- interaction energy between neighbors in a.u.

angle	RHF		CCSD(T)	
	dimers	trimer	dimer	trimer
parallel				
60.	0.01724	0.01711	0.005461	0.005394
70.	0.01317	0.01313	0.003536	0.003489
80.	0.01207	0.01207	0.002867	0.002834
90.	0.01193	0.01195	0.002726	0.002698
v-shaped				
80.	0.01613	0.01569	0.004348	0.004150
70.	0.03363	0.03259	0.011603	0.011143
60.	0.09034	0.08748	0.036671	0.035374

# CO on TiO<sub>2</sub>

Dimer interaction energy (a.u.)

	MP2C	CEPA-0	ACPF	CCSD(T)
parallel				
60.	0.005510	0.005629	0.005771	0.005461
70.	0.003321	0.003709	0.003811	0.003536
80.	0.002420	0.003042	0.003131	0.002867
90.	0.002185	0.002903	0.002990	0.002726
v-shaped				
80.	0.003792	0.004536	0.004644	0.004348
70.	0.010531	0.011836	0.012006	0.011603
60.	0.034467	0.037017	0.037332	0.036671

# CO on TiO<sub>2</sub>

The same for the dressed Epstein-Nesbet perturbation

angle	CEPA-0(appr.)	ACPF(appr.)	(SC) <sup>2</sup> CI(appr.)	CCSD(T)
parallel				
60.	0.002562	0.003710	0.004947	0.005461
70.	0.000751	0.001786	0.002916	0.003536
80.	-0.000036	0.000966	0.002064	0.002867
90.	-0.000222	0.000771	0.001858	0.002726
v-shaped				
80.	0.000944	0.002049	0.003256	0.004348
70.	0.006808	0.008227	0.009768	0.011603
60.	0.029276	0.031083	0.033047	0.036671

# CO on TiO<sub>2</sub>

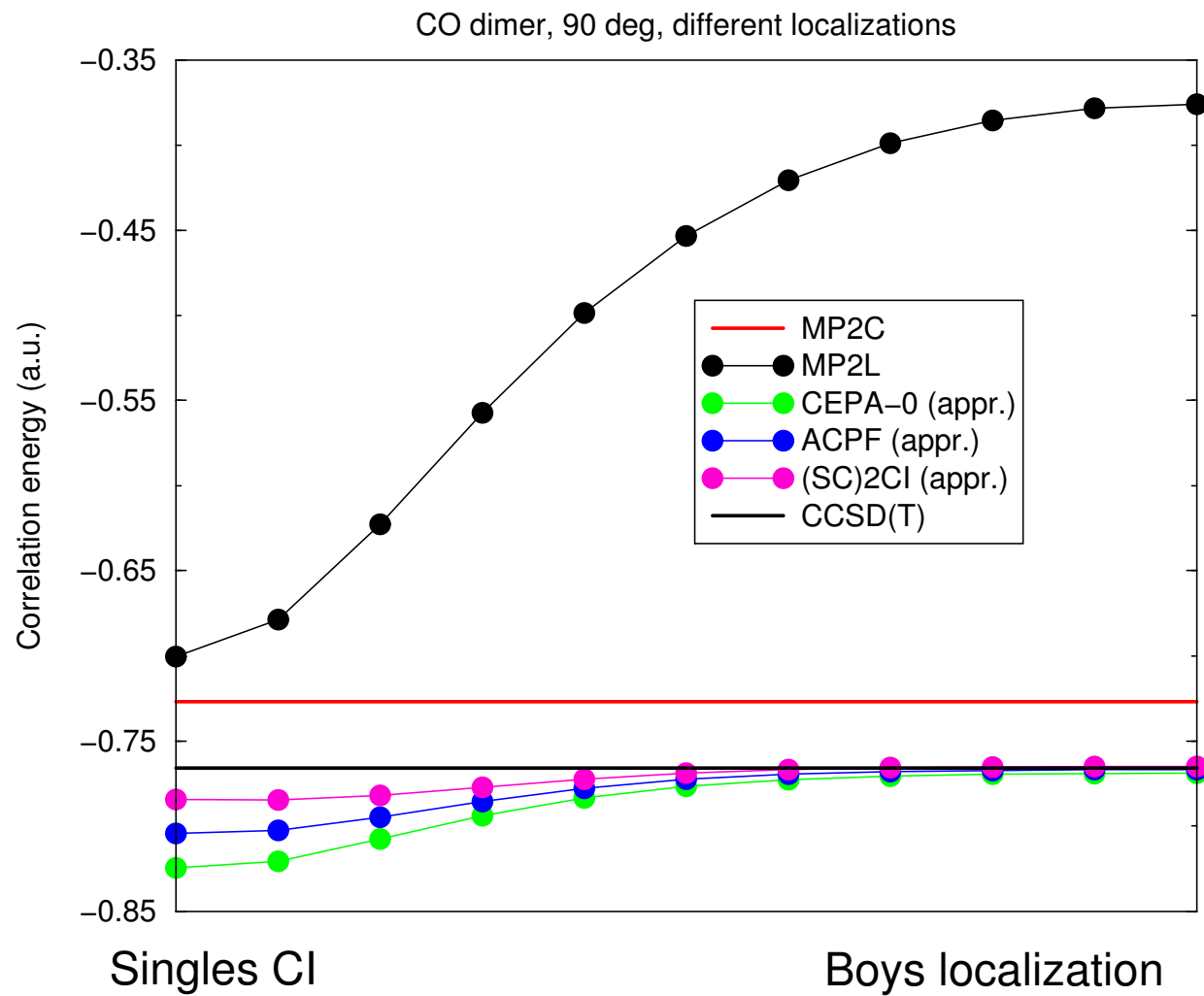
The dimer system only — correlation energy in a.u.

angle	MP2C	MP2L	CEPA-0	ACPF	(SC) <sup>2</sup> CI	CCSD(T)
parallel						
60.	-0.7263	-0.6912	-0.8360	-0.8024	-0.7831	-0.7660
70.	-0.7264	-0.6947	-0.8378	-0.8033	-0.7836	-0.7658
80.	-0.7267	-0.6957	-0.8384	-0.8038	-0.7840	-0.7659
90.	-0.7268	-0.6956	-0.8385	-0.8041	-0.7843	-0.7660
v-shaped						
60.	-0.7431	-0.6710	-0.8410	-0.8123	-0.7956	-0.7785
70.	-0.7335	-0.6844	-0.8385	-0.8067	-0.7884	-0.7712
80.	-0.7289	-0.6916	-0.8382	-0.8046	-0.7853	-0.7677
100.	-0.7260	-0.6970	-0.8385	-0.8036	-0.7837	-0.7653
110.	-0.7256	-0.6972	-0.8385	-0.8035	-0.7836	-0.7651
120.	-0.7255	-0.6966	-0.8384	-0.8035	-0.7836	-0.7650



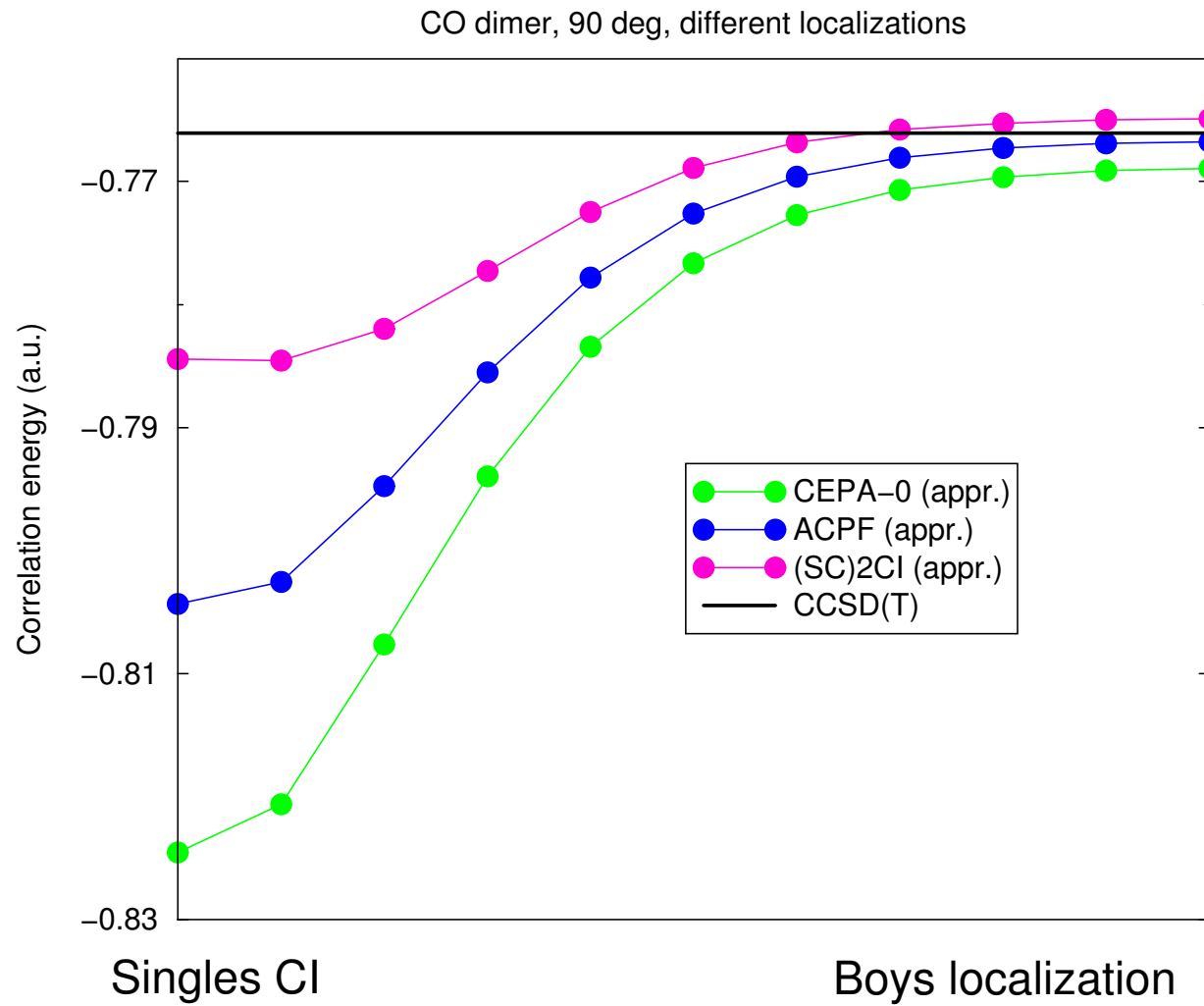
# CO on TiO<sub>2</sub>

## Different localizations



# CO on TiO<sub>2</sub>

## Different localizations



# CO on TiO<sub>2</sub>

Interaction energies (90 deg dimer) :

	MP2C	CEPA-0	ACPF	(SC) <sup>2</sup> CI	CCSD(T)
Singles CI	0.002185	-0.000222	0.000771	0.001858	0.002726
Boys localization		0.001889	0.001916	0.001941	

# Hydrogen systems

Linear approach :

- $E_{Corr}/N = E_{Corr}(N + 1) - E_{Corr}(N)$
- Standard molecular programmes, all methods

# Hydrogen systems

Linear approach :

- $E_{Corr}/N = E_{Corr}(N + 1) - E_{Corr}(N)$
- Standard molecular programmes, all methods

Hydrogen molecules

- Distances  $R - 2R$



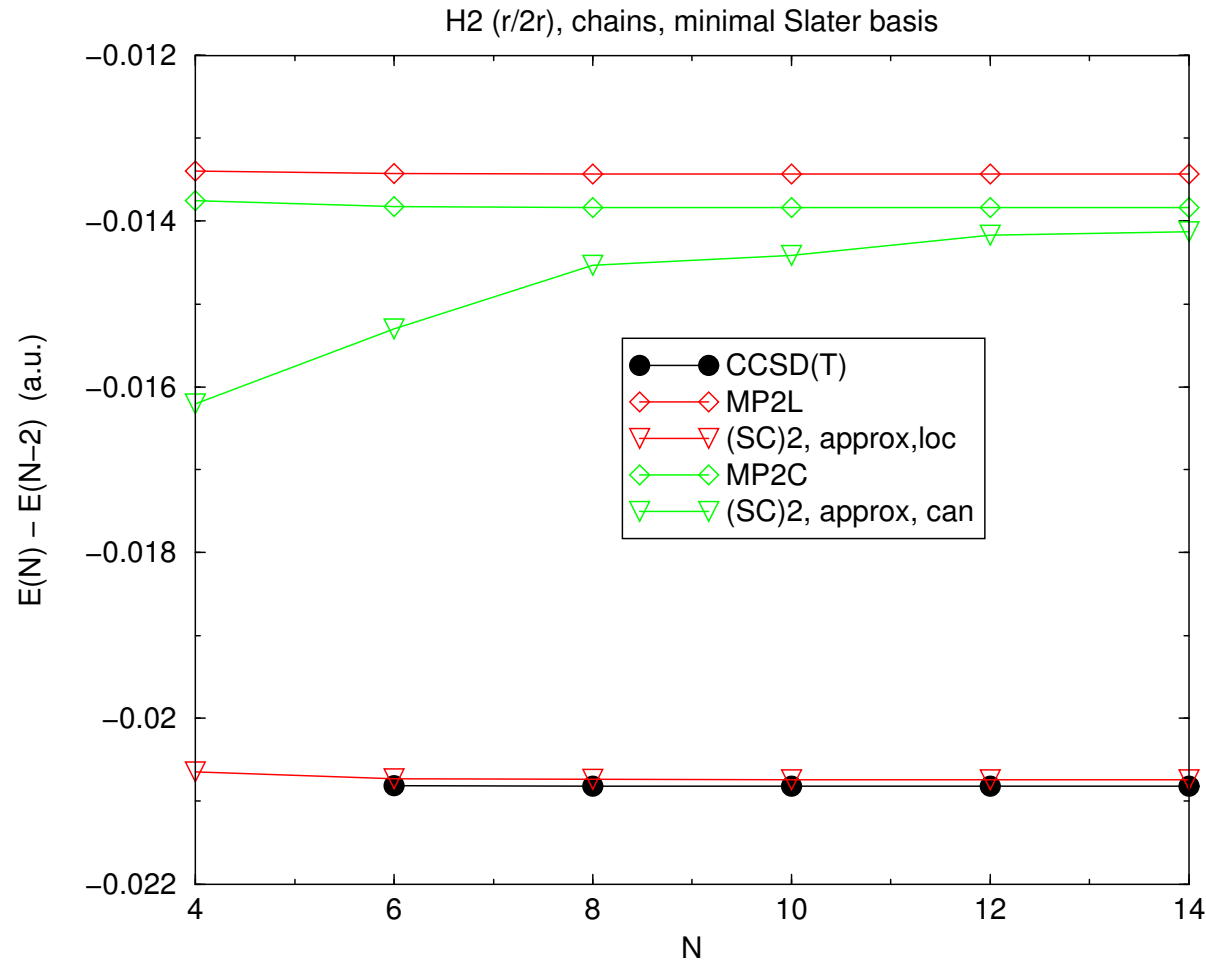
- Different basis sets, Gaussians, Slater

# Some results

- Slater basis, taken from ADF
- Linear approach

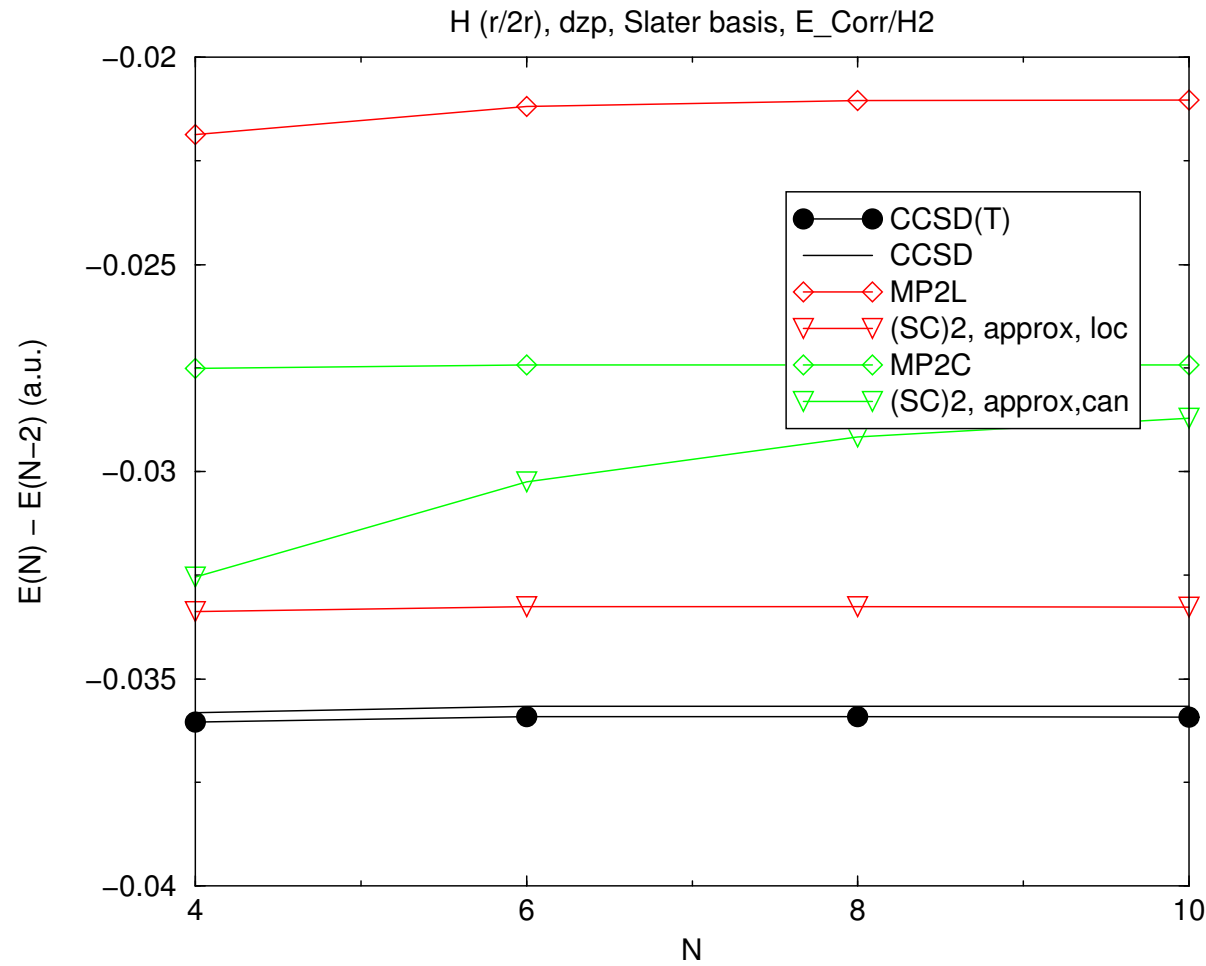
# Some results

- Slater basis, taken from ADF
- Linear approach



# Some results

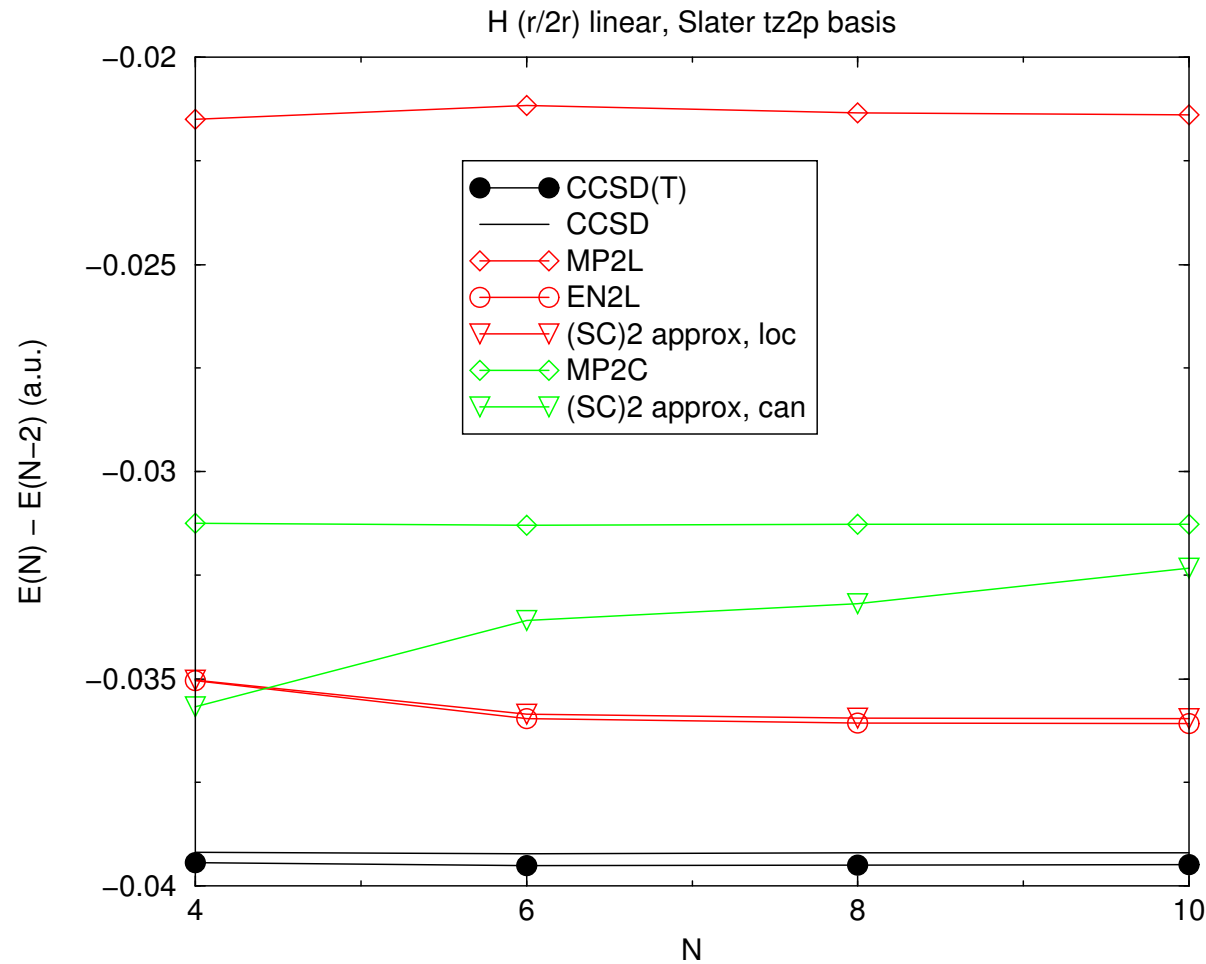
- Slater basis, taken from ADF
- Linear approach





# Some results

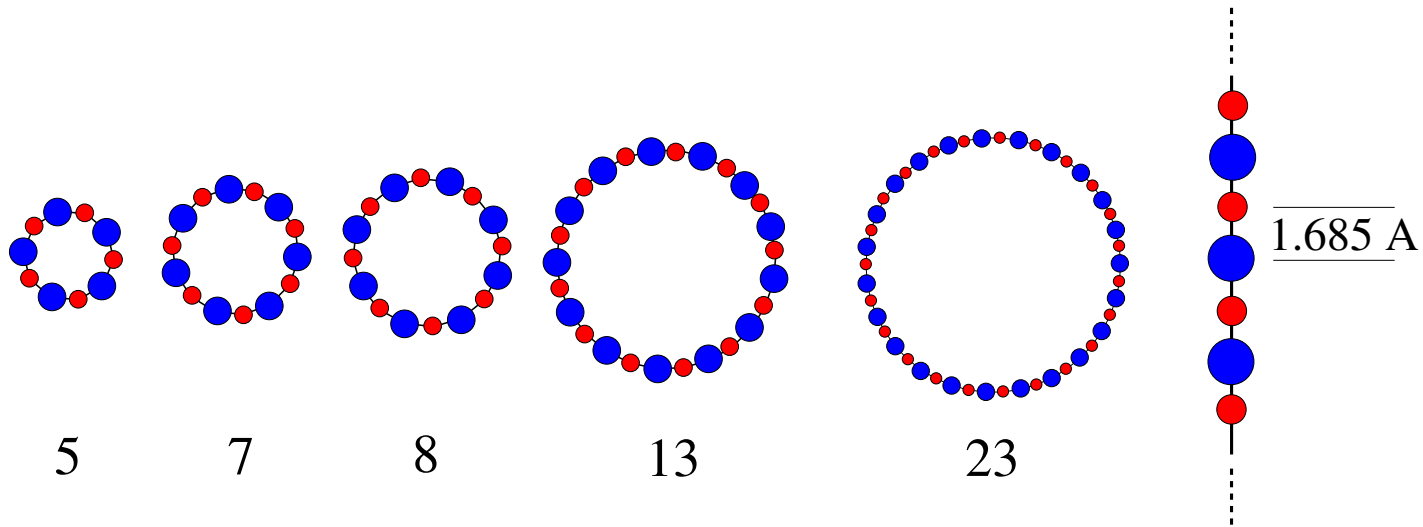
- Slater basis, taken from ADF
- Linear approach



# Some results

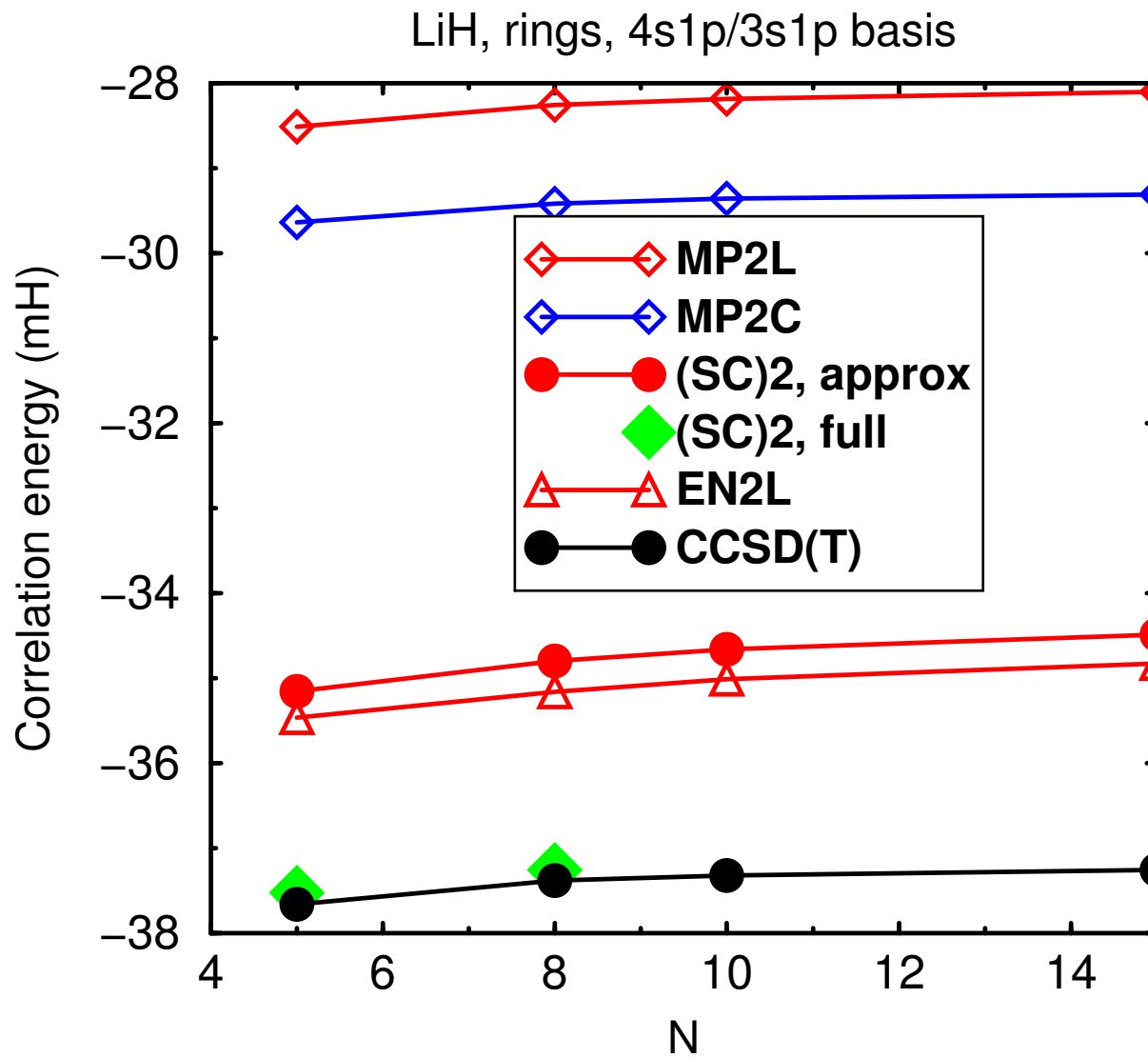
- Slater basis, taken from ADF
- Linear approach

# Li hydride



- Rings in a **tzp basis**(4s1p (Li), 3s1p (H))

# Li hydride



# Conclusions and perspectives

- Correlation in localized orbitals does not need to reproduce the same results as in canonical orbitals — we should aim at CCSD(T) through perturbation theory for joining efficiency and error minimization.
- Sum important contributions as good as possible: (SC)<sup>2</sup>CI on the Epstein-Nesbet instead of ACPF.
- How should we localize ?
- Little number of electrons per site: dressing becomes unimportant.
- What will be results on real periodic systems?
- Construction of orthogonal localized (and virtual) orbitals for extended systems is a major drawback.

# Acknowledgement

Members of different institutions :



LCT, UMR 7616, Université Paris VI, Paris

# Acknowledgement

Members of different institutions :



LCT, UMR 7616, Université Paris VI, Paris

I.R.S.A.M.C., Toulouse, France :

- Jean-Paul Malrieu
- Daniel Maynau
- Fernand Spiegelmann, Jean-Louis Heully, Jean-Pierre Daudey

# Acknowledgement

Members of different institutions :



LCT, UMR 7616, Université Paris VI, Paris

I.R.S.A.M.C., Toulouse, France :

- Jean-Paul Malrieu
- Daniel Maynau
- Fernand Spiegelmann, Jean-Louis Heully, Jean-Pierre Daudey



MPIPKS Dresden, Germany (1998–1999)

- Prof. Peter Fulde, Michael Dolg, Martin Albrecht, Beate Paulus



# Dressings

Linear system of equations :

$$\sum_I \langle \Phi_0 | \mathbf{H} | \Phi_I \rangle c_I = H_{0I} c_I = E_{\text{Corr}}$$
$$H_{0I}^\dagger + (H_{II} - E_{\text{HF}} + \Delta_I) c_I + \sum_{J \neq I} H_{IJ} c_J = 0$$

Global dressings :

---

CISD

$$-E_{\text{Corr}}$$

ACPF

$$-\frac{2}{n_e} E_{\text{Corr}}$$

AQCC

$$-E_{\text{Corr}} \left( 1 - \frac{(n_e - 2)(n_e - 3)}{n_e(n_e - 1)} \right)$$

AQCC-v

$$-E_{\text{Corr}} \left( 1 - \frac{(n_e - 2)(n_e - 3)}{n_e(n_e - 1)} \frac{(n_v - 2)(n_v - 3)}{n_v(n_v - 1)} \right)$$

$n_e$ : electrons;

$n_v$ : virtual orbitales

---

# Dressings

Linear system of equations :

$$\sum_I \langle \Phi_0 | \mathbf{H} | \Phi_I \rangle c_I = H_{0I} c_I = E_{\text{Corr}}$$

$$H_{0I}^\dagger + (H_{II} - E_{HF} + \Delta_I) c_I + \sum_{J \neq I} H_{IJ} c_J = 0$$

CEPA dressings :

---

CEPA-0

0

CEPA-2  $-\sum_{cd} \langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ijij}^{abcd} \rangle c_{ij}^{cd} = -\sum_{cd} \langle \Phi_0 | \mathbf{H} | \Phi_{ij}^{cd} \rangle c_{ij}^{cd} = -e(i,j)$

CEPA-3  $-\sum_{kcd} \langle \Phi_0 | \mathbf{H} | \Phi_{ik}^{cd} \rangle c_{ik}^{cd} - \sum_{kcd} \langle \Phi_0 | \mathbf{H} | \Phi_{kj}^{cd} \rangle c_{kj}^{cd} + \sum_{cd} \langle \Phi_0 | \mathbf{H} | \Phi_{ij}^{cd} \rangle c_{ij}^{cd} = -e(i)-e(j)+e(i,j)$

(SC)<sup>2</sup>CI  $-\sum_{\text{EPV}(i,j,a,b)} \langle \Phi_0 | \mathbf{H} | \Phi_{kl}^{cd} \rangle c_{kl}^{cd}$  (Full CEPA)

# Epstein-Nesbet in canonical orbitals

## Back

- MP2 and EN2 have the same numerator  $\langle 0 | \mathbf{H} | I \rangle^2$
- Denominator MP2 :

$$\langle I | \mathbf{H}_0 - E_0 | I \rangle = F_{ii} + F_{jj} - F_{aa} - F_{bb}$$

# Epstein-Nesbet in canonical orbitals

## Back

- MP2 and EN2 have the same numerator  $\langle 0 | \mathbf{H} | I \rangle^2$
- Denominator MP2 :

$$\langle I | \mathbf{H}_0 - E_0 | I \rangle = F_{ii} + F_{jj} - F_{aa} - F_{bb}$$

- Denominator Epstein-Nesbet :

$$\langle I | \mathbf{H} - E_{HF} | I \rangle = F_{ii} + F_{jj} - F_{aa} - F_{bb} - \tilde{J}_{ij} - \tilde{J}_{ab} + \tilde{J}_{ia} + \tilde{J}_{ib} + \tilde{J}_{ja} + \tilde{J}_{jb}$$

- Elements of  $J$  and  $K$  ( $\tilde{J}_{jb} = J_{jb} - K_{jb} \delta_{\sigma_j \sigma_b}$ )

# Epstein-Nesbet in canonical orbitals

## Back

- MP2 and EN2 have the same numerator  $\langle 0 | \mathbf{H} | I \rangle^2$
- Denominator MP2 :

$$\langle I | \mathbf{H}_0 - E_0 | I \rangle = F_{ii} + F_{jj} - F_{aa} - F_{bb}$$

- Localized orbitals  $s_1, s_2 \dots s_N$ ; canonical orbitals

$$\phi_1 = \frac{1}{\sqrt{N}} (s_1 + s_2 + \dots s_N)$$

- integrals  $J_{11} = (\phi_1 \phi_1 | \phi_1 \phi_1) \longrightarrow \frac{1}{N^2} \times N (s_1 s_1 | s_1 s_1) \sim 1/N$  for large systems
- Canonical orbitals : every single integral  $\longrightarrow 0$ , thus EN2  $\longrightarrow$  MP2
- Localized orbitales : **N** integrals  $(\phi_1 \phi_1 | \phi_1 \phi_1)$  remain at a constant size

# Epstein-Nesbet in canonical orbitals

## Back

- MP2 and EN2 have the same numerator  $\langle 0 | \mathbf{H} | I \rangle^2$
- Denominator MP2 :

$$\langle I | \mathbf{H}_0 - E_0 | I \rangle = F_{ii} + F_{jj} - F_{aa} - F_{bb}$$

- Localized orbitals  $s_1, s_2 \dots s_N$ ; canonical orbitals

$$\phi_1 = \frac{1}{\sqrt{N}} (s_1 + s_2 + \dots s_N)$$

- integrals  $J_{11} = (\phi_1 \phi_1 | \phi_1 \phi_1) \longrightarrow \frac{1}{N^2} \times N (s_1 s_1 | s_1 s_1) \sim 1/N$  for large systems
- Canonical orbitals : every single integral  $\longrightarrow 0$ , thus EN2  $\longrightarrow$  MP2
- Localized orbitales : **N** integrals  $(\phi_1 \phi_1 | \phi_1 \phi_1)$  remain at a constant size
- Epstein-Nesbet not size-consistent **in canonical orbitales**