

Reseau français de chimie théorique (IdF)

cours Master II : interactions intermoléculaires

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Plan du cours

- Introduction
- Termes classiques : électrostatique, induction et dispersion
- Méthodes supermoléculaires
- Décompositions : Heitler-London, CSOV, Morokuma
- Perturbation intermoléculaire (SAPT)

Introduction

règle empirique de Trouton (1884)

$$10 R T_{eb} \approx \Delta H_{vap} \approx \frac{n}{2} \epsilon \mathcal{N}_A$$

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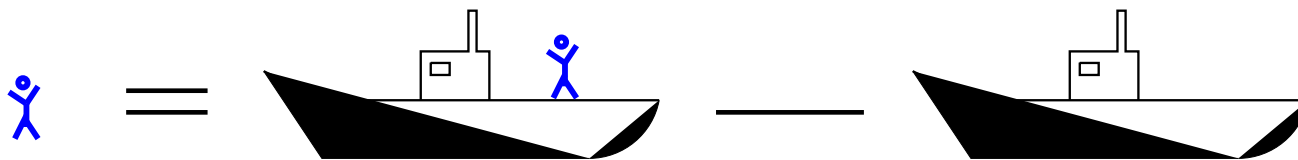
	T_{eb}/K	n	$(20T_{eb}/n)/\text{K}$	$(\epsilon_{exp.}/k)/\text{K}$	$\epsilon/(\text{kJ/mol})$
He	4.2	12	7	11	0.091
Ar	87	12	145	142	1.18
Xe	166	12	277	281	2.34
CH ₄	111.5	12	86	180–300	1.5–2.5
H ₂ O	373.2	4	1866	≈2400	≈20

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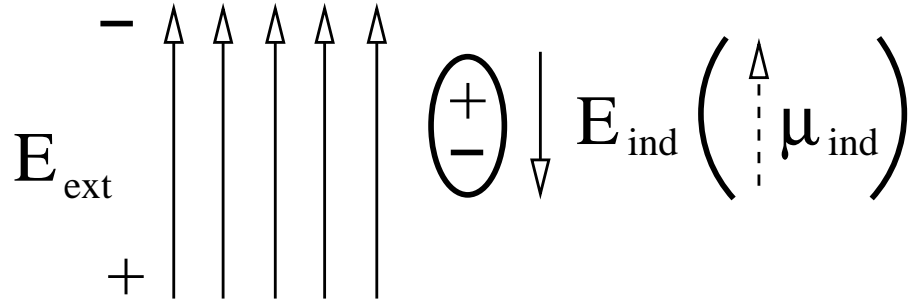


Termes classiques

Electrostatique

$$E_{Pol} = \int \int \frac{\rho_A(\vec{r}_1)\rho_B(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 \quad (1)$$

Induction



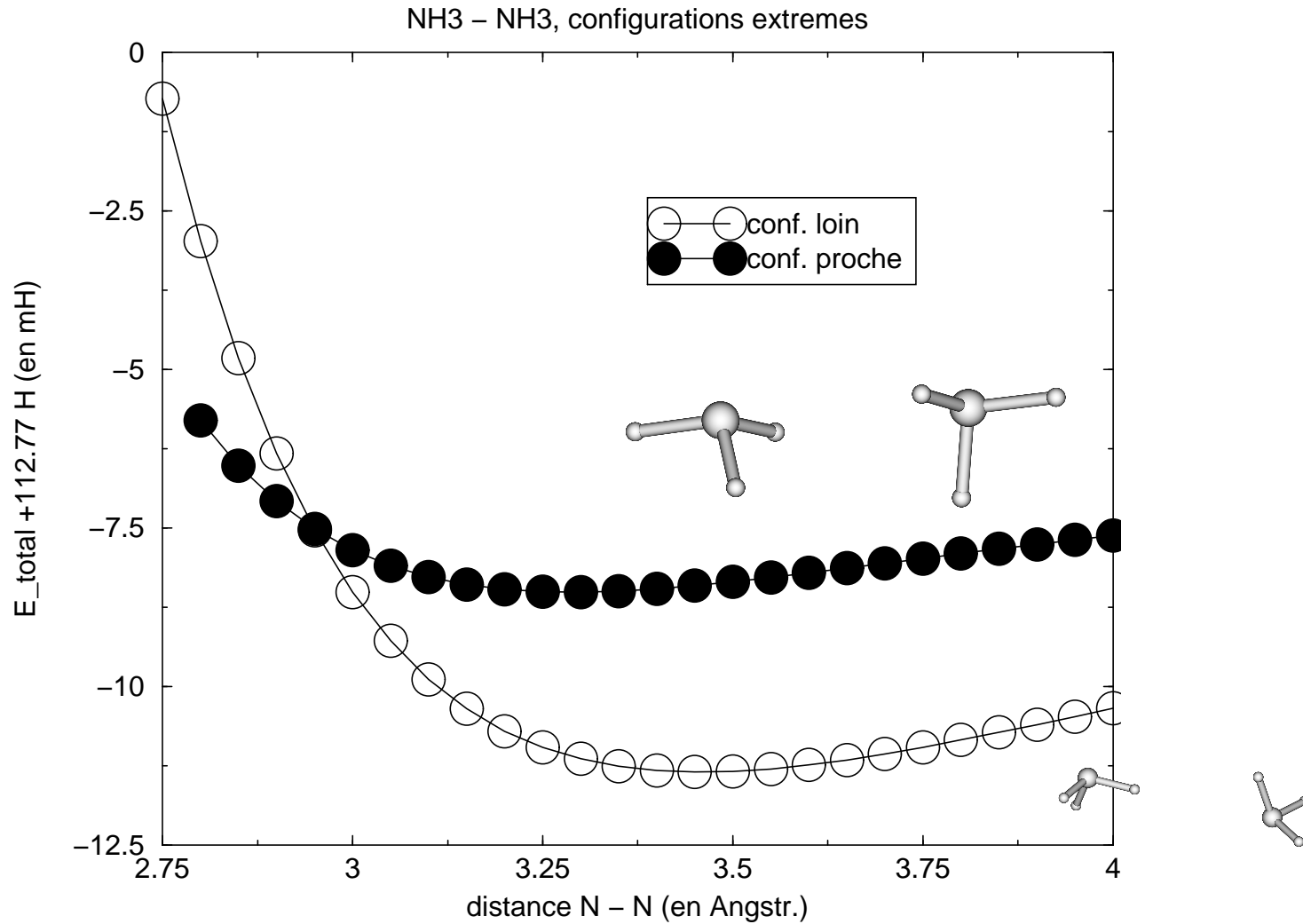
$$E_{ind} = -\vec{E} \cdot \vec{\mu} = -\vec{E} \alpha_B \vec{E} = -\alpha_B E^2$$

Dispersion (effet quantique)

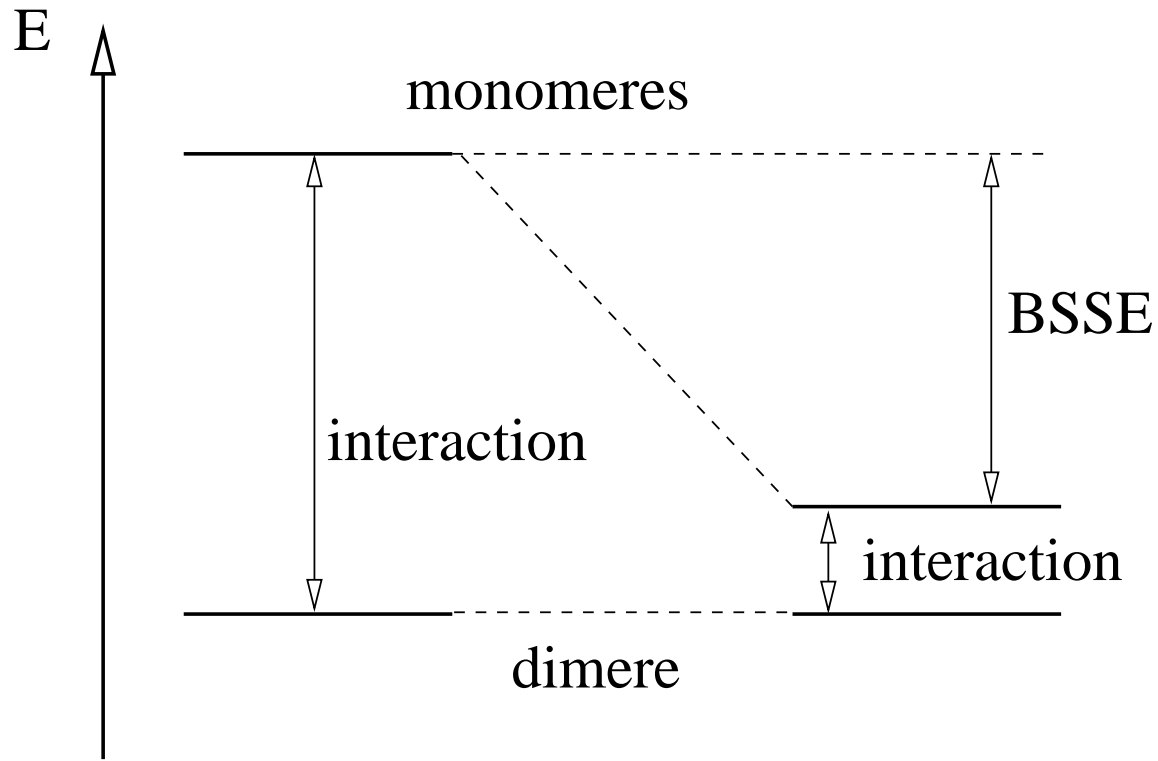
$$E_{Disp} = -\frac{C_6}{|\vec{R}_A - \vec{R}_B|^6} \quad (2)$$

Méthodes supermoléculaires

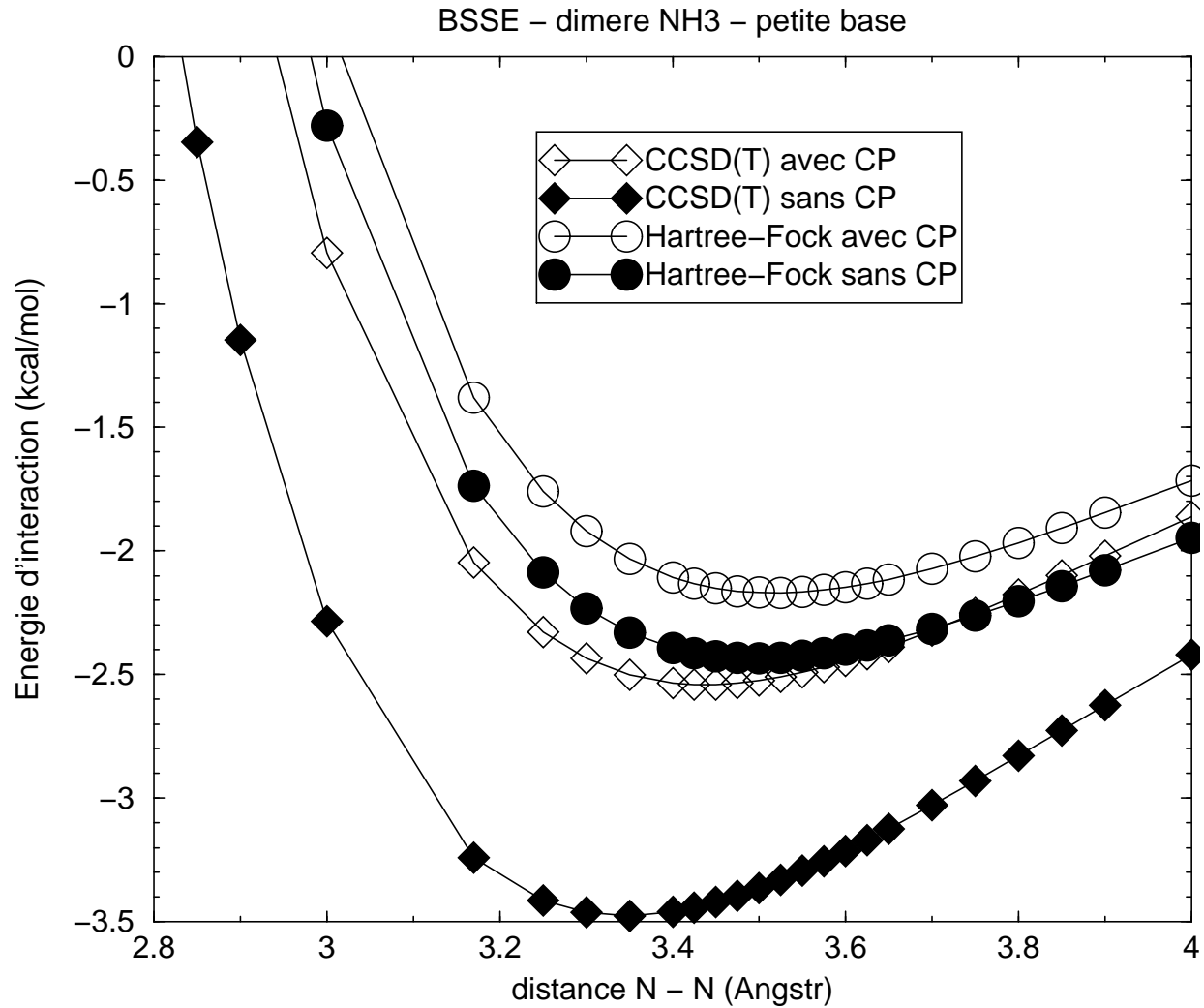
Interaction $\text{NH}_3 - \text{NH}_3$, MP2



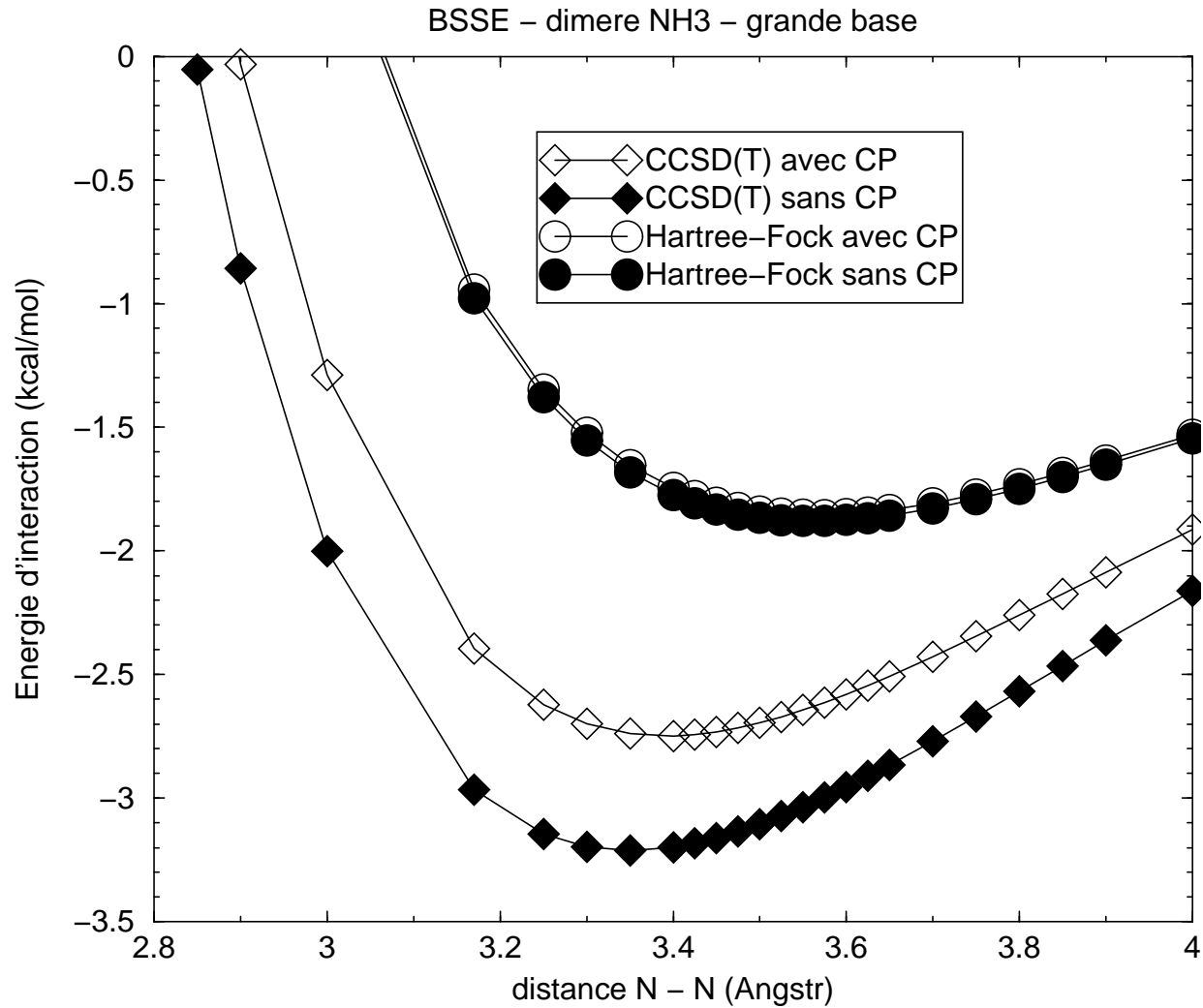
Méthodes supermoléculaires — BSSE



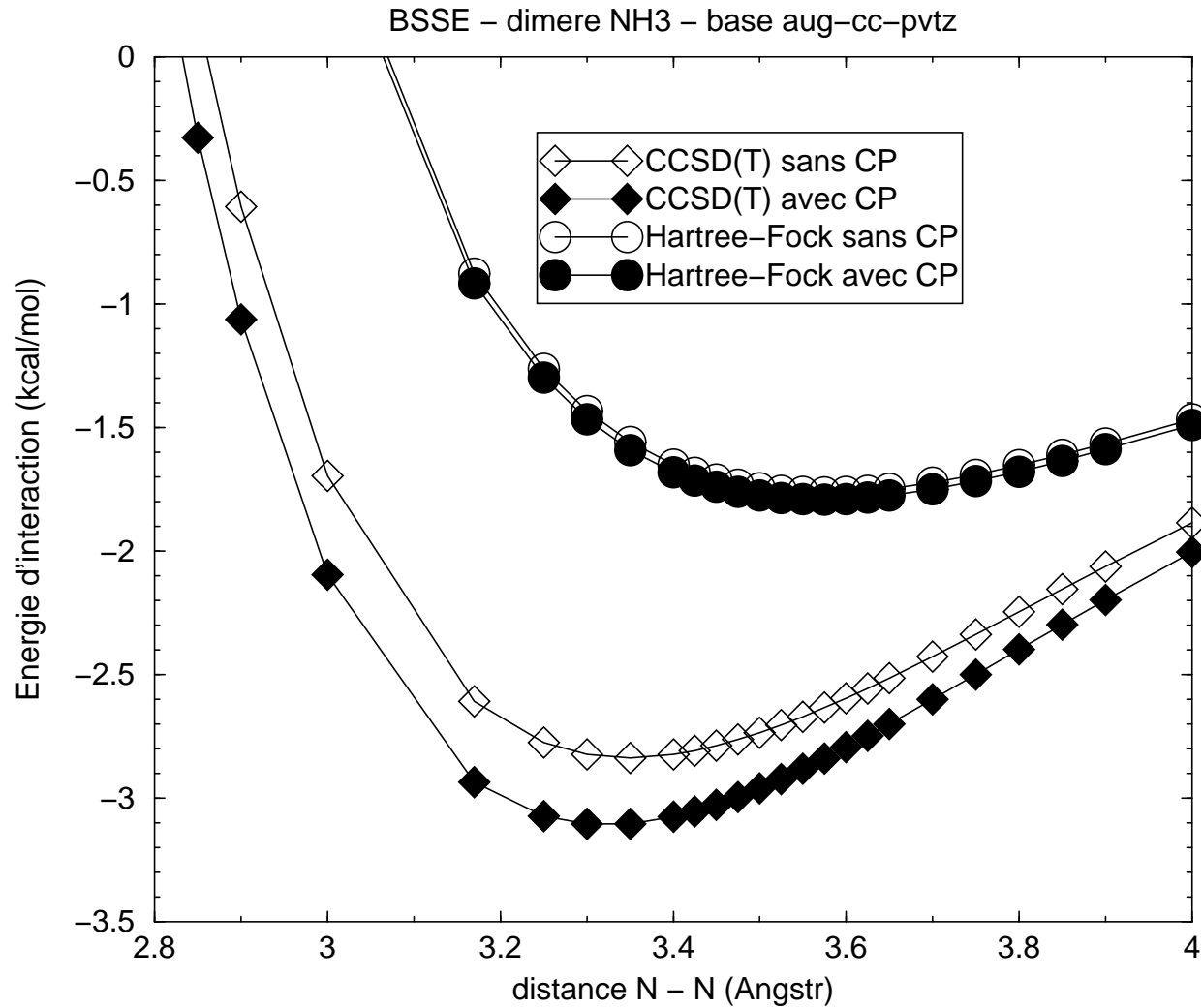
Méthodes supermoléculaires — BSSE



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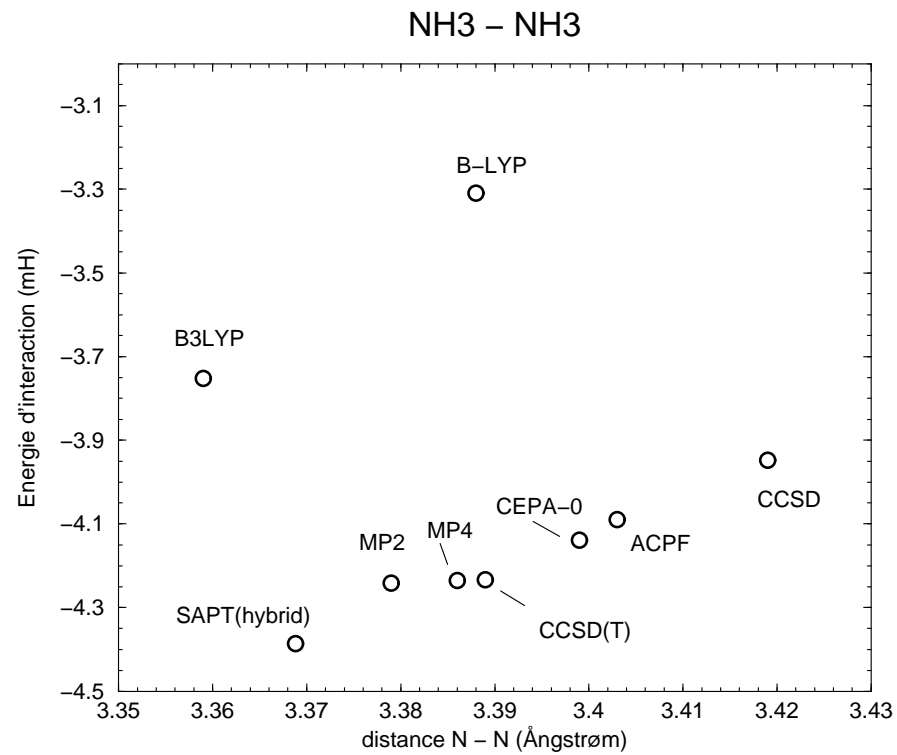
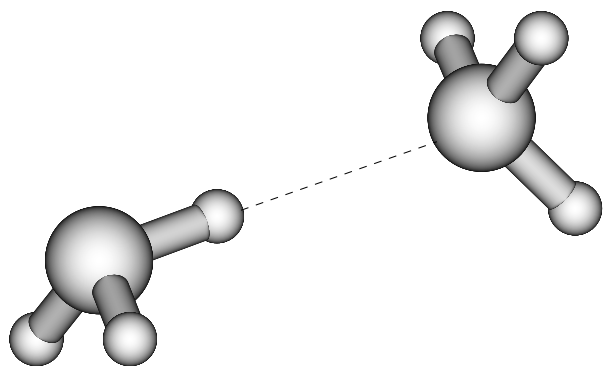
Méthodes supermoléculaires — BSSE



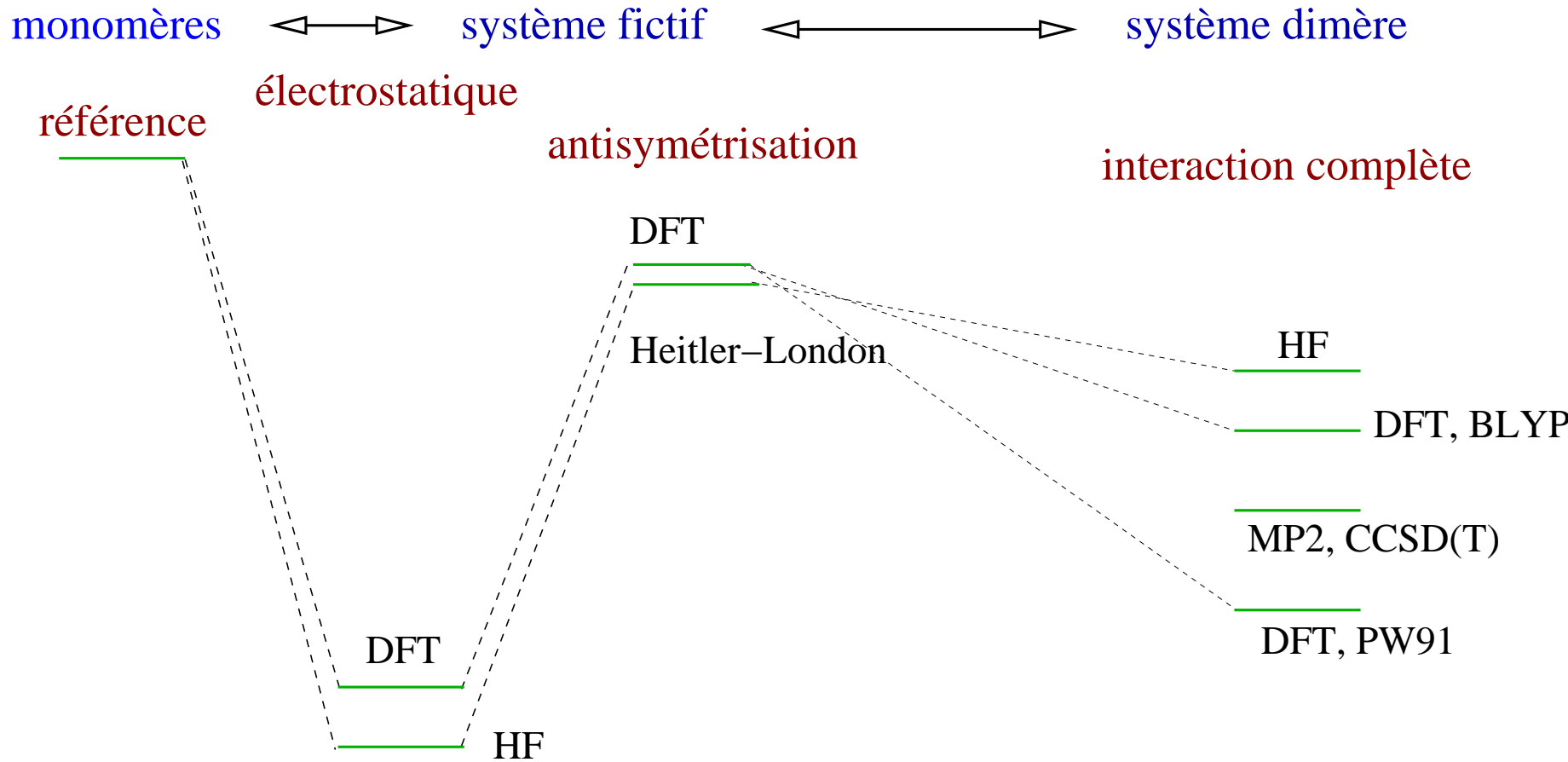
Méthodes supermoléculaires — BSSE

	sans	correction	avec	correction
	d (Å)	E_{int} (kcal/mol)	d (Å)	E_{int} (kcal/mol)
petite base				
Hartree-Fock	3.495	-2.43	3.518	-2.17
CCSD(T)	3.345	-3.48	3.438	-2.54
grande base				
Hartree-Fock	3.560	-1.88	3.564	-1.85
CCSD(T)	3.350	-3.21	3.390	-2.75
base aug-cc-pvtz				
Hartree-Fock	3.570	-1.79	3.572	-1.76
CCSD(T)	3.323	-3.10	3.348	-2.83

Décompositions



Heitler-London



Heitler-London

	2.80 Å	3.17 Å	3.40 Å	4.00 Å
Hartree-Fock :				
$E_{lec.stat.}$	-14.80	-6.64	-4.3	-1.75
Heitler-London :				
ΔT	150.61	58.27	31.57	5.98
ΔV	-96.42	-38.17	-20.82	-3.96
$\Delta \text{échange}$	-28.39	-12.26	-7.04	-1.50
E_{HL}	25.79	7.84	3.71	0.52
interaction orbitalaire :				
ΔT	-81.44	-36.37	-21.99	-6.49
ΔV	65.10	29.74	18.20	5.60
$\Delta \text{échange}$	9.72	4.52	2.70	0.65
$E_{orb.int.}$	-6.61	-2.11	-1.09	-0.24
ΔE	4.37	-0.91	-1.68	-1.47

Heitler-London

	2.80 Å	3.17 Å	3.40 Å	4.00 Å
Perdew-Wang 91 :				
$E_{lec.stat.}$	-15.07	-6.75	-4.33	-1.69
Heitler-London :				
ΔT	165.46	68.46	39.10	8.71
ΔV	-106.77	-45.41	-26.21	-5.91
$\Delta \text{échange}$	-35.14	-16.31	-9.99	-2.75
E_{HL}	23.55	6.74	2.90	0.05
interaction orbitalaire :				
ΔT	-107.17	-52.77	-33.69	-11.09
ΔV	83.41	41.27	26.30	8.68
$\Delta \text{échange}$	15.31	8.43	5.69	2.01
$E_{orb.int.}$	-8.45	-3.07	-1.70	-0.40
ΔE	0.03	-3.08	-3.13	-2.04

CSOV, RVS

	2.80 Å	3.17 Å	3.40 Å	4.00 Å
E_{CEX}	10.89	1.19	-0.59	-1.24
E_{POL} (A)	-1.75	-0.68	-0.41	-0.13
E_{POL} (B)	-1.31	-0.35	-0.16	-0.03
E_{CT} (A)	-0.22	-0.06	-0.03	-0.01
E_{CT} (B)	-3.20	-1.00	-0.47	-0.06
E_{BSSE} (A)	-0.04	-0.02	-0.01	0.00
E_{BSSE} (B)	-0.03	-0.01	-0.01	-0.01
ΔE	4.40	-0.90	-1.68	-1.47
$\Delta E(\text{BSSE})$	4.35	-0.92	-1.69	-1.48

Orthogonalisation

- Construction de l'espace virtuel ?

Orthogonalisation

- Occupées : orthogonalisation symétrique $\mathbf{S}^{-1/2}$:

$$\begin{aligned}\phi_i &= \sum_j \mathbf{S}_{ij}^{-1/2} \varphi_j \\ \langle \phi_i | \phi_j \rangle &= \sum_{kl} \mathbf{S}_{ik}^{-1/2} \langle \varphi_k | \varphi_l \rangle \mathbf{S}_{lj}^{-1/2} = \sum_{kl} \mathbf{S}_{ik}^{-1/2} \mathbf{S}_{kl} \mathbf{S}_{lj}^{-1/2} = \delta_{ij} \quad (5)\end{aligned}$$

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- Projection :

$$|\phi_{virt}\rangle = |\varphi_{virt}\rangle - \sum_{i \in occ} |\varphi_i\rangle \langle \varphi_i | \varphi_{virt}\rangle \quad (8)$$

Orthogonalisation

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- Projection :

$$|\phi_{virt}\rangle = |\varphi_{virt}\rangle - \sum_{i \in occ} |\varphi_i\rangle \langle \varphi_i | \varphi_{virt}\rangle \quad (10)$$

- Virtuelles : encore $\mathbf{S}^{-1/2}$.

Orthogonalisation

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- Projection :

$$|\phi_{virt}\rangle = |\varphi_{virt}\rangle - \sum_{i \in occ} |\varphi_i\rangle \langle \varphi_i | \varphi_{virt}\rangle \quad (12)$$

- Virtuelles : encore $\mathbf{S}^{-1/2}$.
- Orbitales auront des queues sur l'autre fragment.

Meilleures orbitales

- SCF de monomères dans les bases des monomères
- Gardons les orbitales virtuelles

Meilleures orbitales

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-
- SCF de monomères dans la base du dimère
 - Gardons les orbitales occupées

Meilleures orbitales

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- SCF de monomères dans la base du dimère
- Gardons les orbitales occupées

- Occupées : orthogonalisation symétrique $\mathbf{S}^{-1/2}$
- Occupées/virtuelles : projection
- Virtuelles : orthogonalisation symétrique $\mathbf{S}^{-1/2}$

Meilleures orbitales

SCF du dimère par IC de monoexcitations :

1. Construction de la matrice Fock
2. Construction d'une matrice IC de mono-excitations
3. Meilleure fonction d'onde : $\Psi = \Phi_0 + \sum_{ia} c_i^a \Phi_i^a$
4. Corrections des orbitales :

$$\phi'_i = \phi_i + \sum_a c_i^a \phi_a \quad (13)$$

$$\phi'_a = \phi_a - \sum_i c_i^a \phi_i \quad (14)$$

5. Orthogonalisation occ-occ, virt-virt
6. GO TO 1

Meilleures orbitales

SCF du dimère par IC de monoexcitations :

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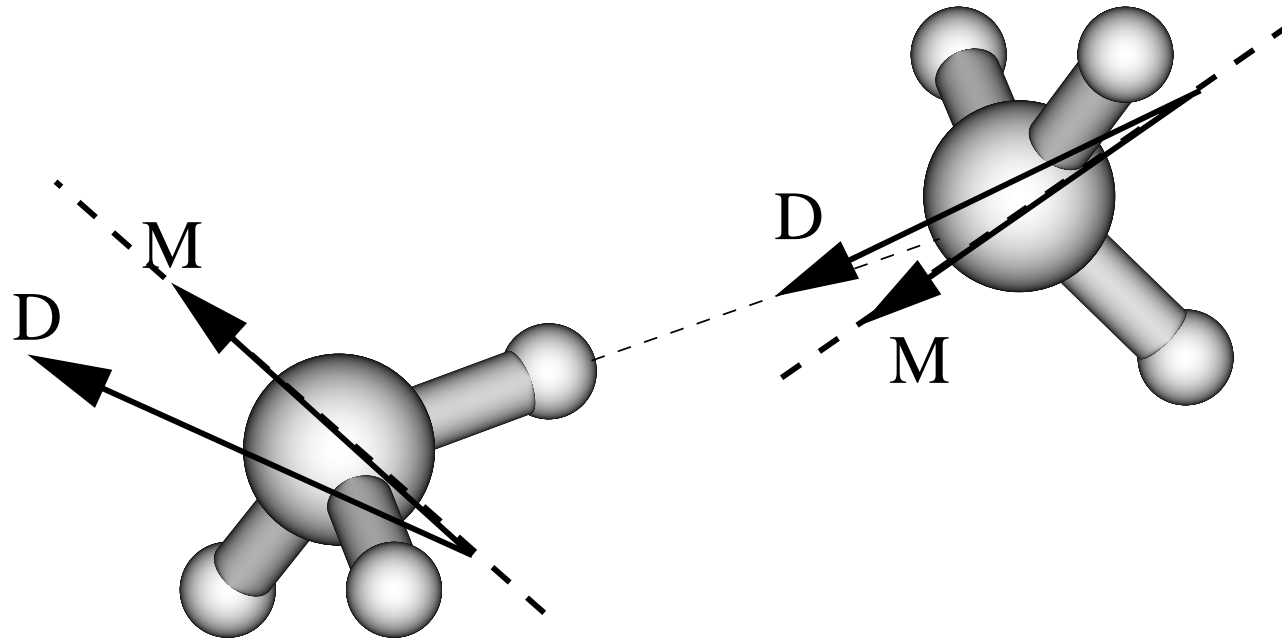
$$\phi'_i = \phi_i + \sum_a c_i^a \phi_a \quad (15)$$

$$\phi'_a = \phi_a - \sum_i c_i^a \phi_i \quad (16)$$

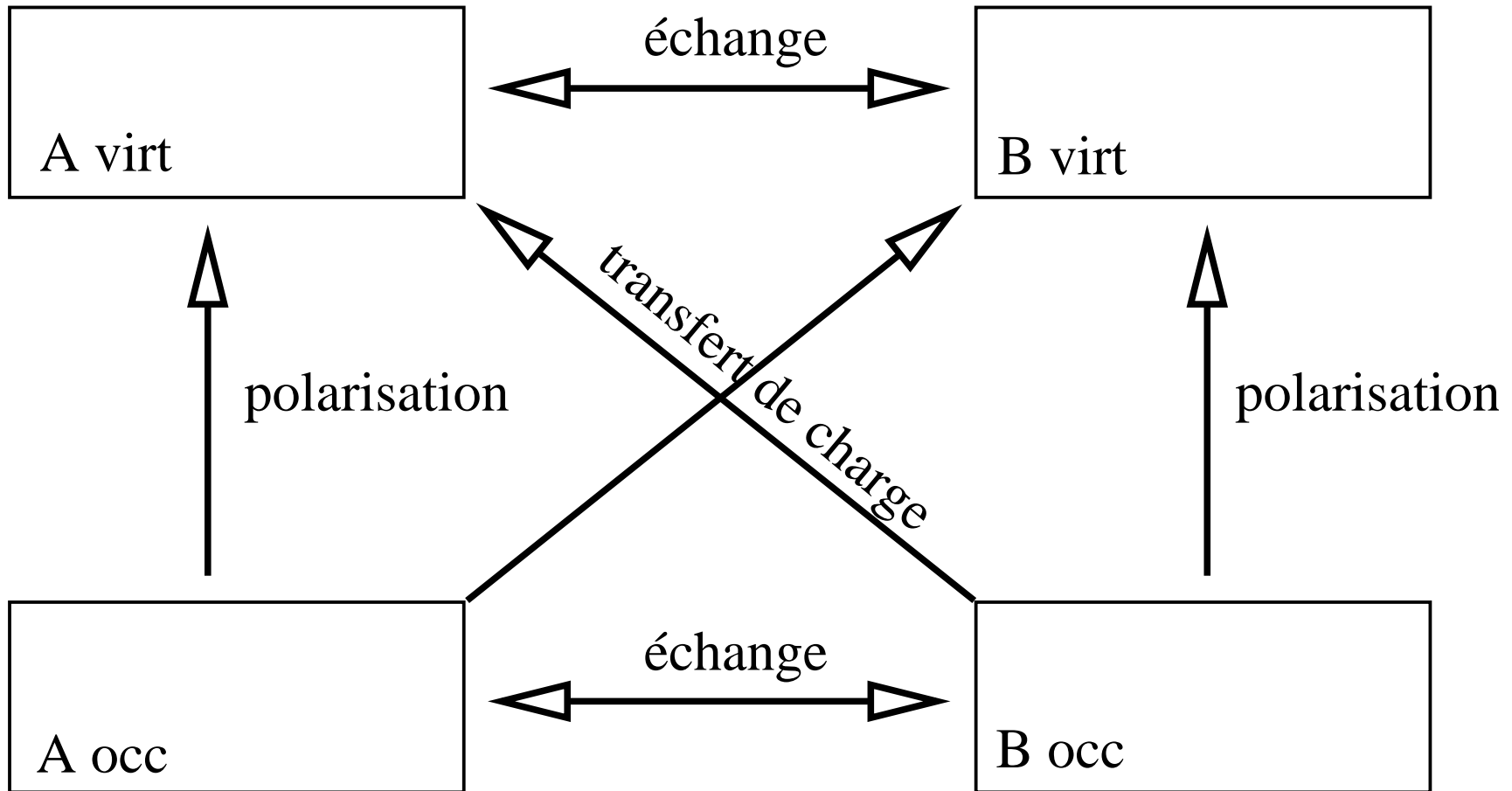
5. Orthogonalisation occ-occ, virt-virt
 6. GO TO 1
- Orbitales du dimère ressemblent le plus possibles aux orbitales des monomères.

Application

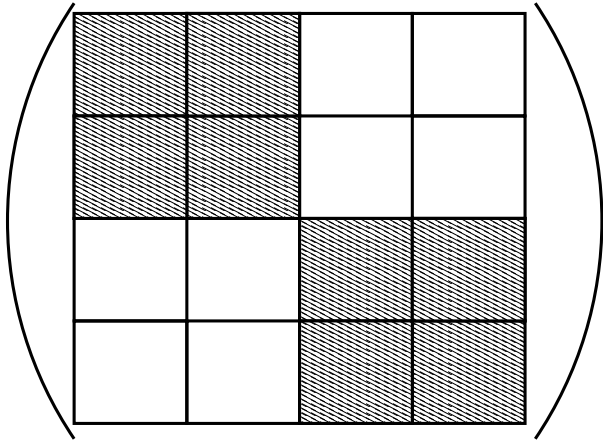
Evolution d'un moment dipolaire



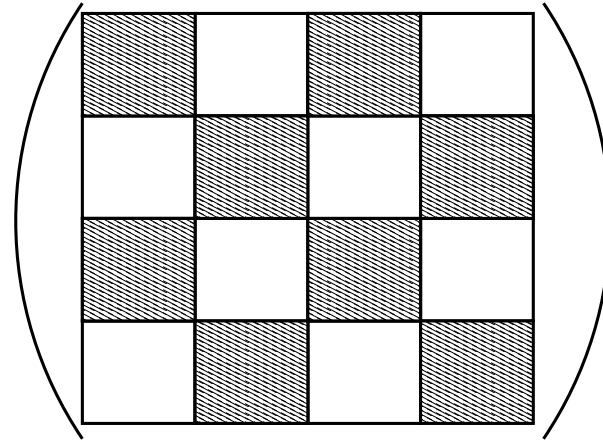
Décomposition de Morokuma



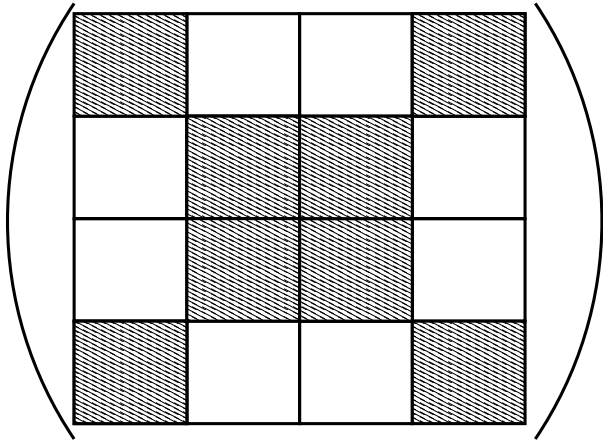
Décomposition de Morokuma



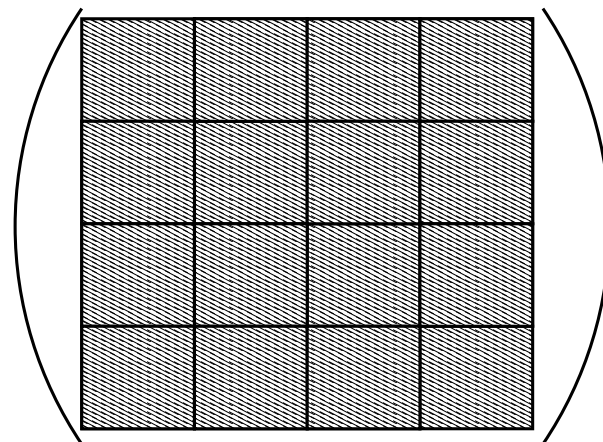
Polarisation



Echange



Transfert de charge

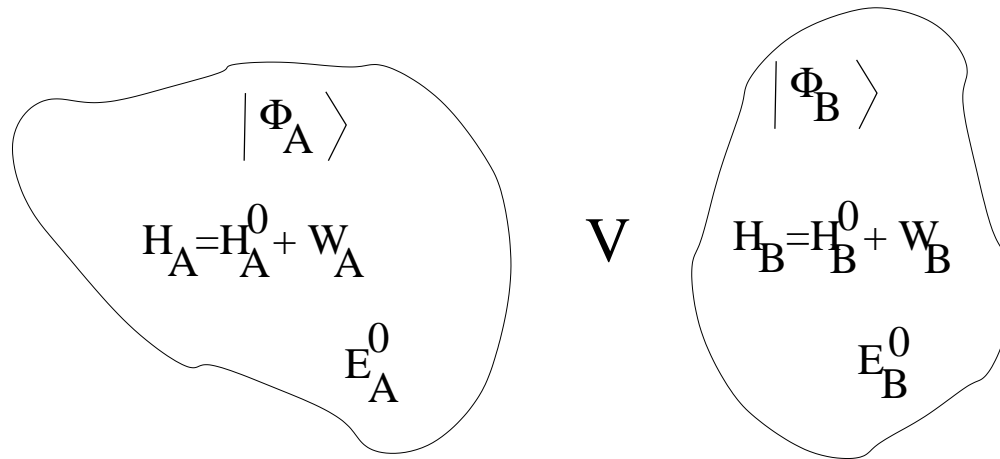


Tout

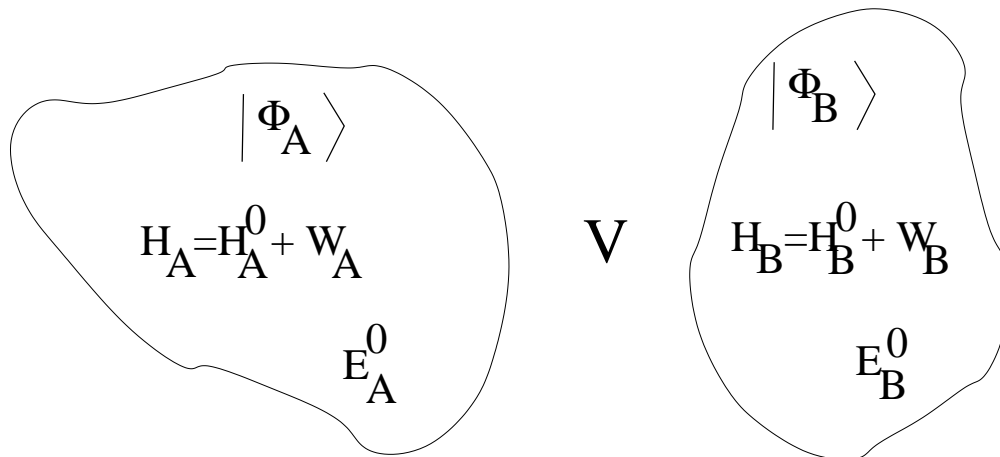
Décomposition de Morokuma

	2.80 Å	3.17 Å	3.40 Å	4.00 Å
E_{ES}	-15.09	-6.71	-4.33	-1.76
E_{PL}	-13.79	-1.81	-0.88	-0.21
E_{EX}	25.98	7.90	3.74	0.52
E_{CT}	-9.48	-2.02	-0.90	-0.14
E_{mix}	16.66	1.68	0.65	0.09
ΔE	4.29	-0.95	-1.71	-1.49
BSSE	0.09	0.05	0.03	0.02
$\Delta E(\text{BSSE})$	4.38	-0.91	-1.68	-1.47

SAPT (symmetry adapted perturbation theory)

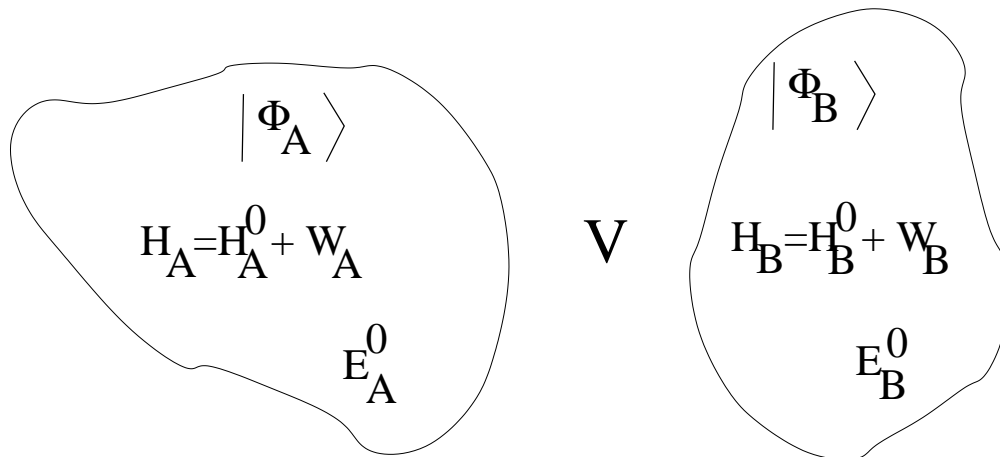


SAPT (symmetry adapted perturbation theory)



$$\begin{aligned} \mathbf{H} &= \mathbf{H}^A + \mathbf{H}^B + \mathbf{V} \\ &= \mathbf{H}_0^A + \mathbf{W}^A + \mathbf{H}_0^B + \mathbf{W}^B + \mathbf{V} \end{aligned} \quad (18)$$

SAPT (symmetry adapted perturbation theory)



$$\begin{aligned}
 \mathbf{H} &= \mathbf{H}^A + \mathbf{H}^B + \mathbf{V} \\
 &= \mathbf{H}_0^A + \mathbf{W}^A + \mathbf{H}_0^B + \mathbf{W}^B + \mathbf{V}
 \end{aligned}
 \tag{19}$$

Perturbation en \mathbf{V} , $\Phi^{(0)} = |\Phi_A\rangle \cdot |\Phi_B\rangle$, $E^{(0)} = E_A + E_B$

$$\begin{aligned}
 \Psi &= \Phi_0 + \sum_n \xi^n \Phi_{pol}^{(n)} \\
 E_{pol}^{(n)} &= \langle \Phi_0 | \mathbf{V} | \Phi_{pol}^{(n)} \rangle
 \end{aligned}$$

SAPT (symmetry adapted perturbation theory)

Antisymétrisation

$$E_{SRS}^{(n)} = \frac{1}{\langle \Phi_0 | \mathcal{A} \Phi_0 \rangle} \left[\langle \Phi_0 | \mathbf{V} | \mathcal{A} \Phi_{pol}^{(n-1)} \rangle - \sum_{k=1}^{n-1} E_{SRS}^{(k)} \langle \Phi_0 | \mathcal{A} \Phi_{pol}^{(n-k)} \rangle \right]$$

SAPT (symmetry adapted perturbation theory)

Antisymétrisation

$$E_{SRS}^{(n)} = \frac{1}{\langle \Phi_0 | \mathcal{A} \Phi_0 \rangle} \left[\langle \Phi_0 | \mathbf{V} | \mathcal{A} \Phi_{pol}^{(n-1)} \rangle - \sum_{k=1}^{n-1} E_{SRS}^{(k)} \langle \Phi_0 | \mathcal{A} \Phi_{pol}^{(n-k)} \rangle \right]$$

$$E_{SRS}^{(1)} = E_{pol}^{(1)} + E_{exch}^{(1)}$$

$$E_{SRS}^{(2)} = E_{pol}^{(2)} + E_{exch}^{(2)}$$

etc.

SAPT (symmetry adapted perturbation theory)

Antisymétrisation

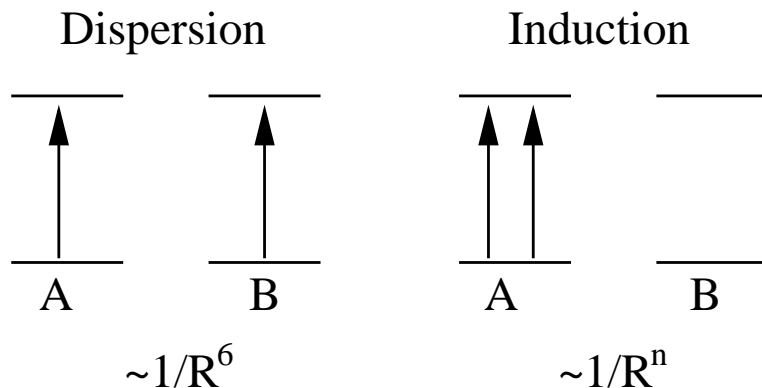
$$E_{SRS}^{(n)} = \frac{1}{\langle \Phi_0 | \mathcal{A} \Phi_0 \rangle} \left[\langle \Phi_0 | \mathbf{V} | \mathcal{A} \Phi_{pol}^{(n-1)} \rangle - \sum_{k=1}^{n-1} E_{SRS}^{(k)} \langle \Phi_0 | \mathcal{A} \Phi_{pol}^{(n-k)} \rangle \right]$$

$$E_{SRS}^{(1)} = E_{pol}^{(1)} + E_{exch}^{(1)}$$

$$E_{SRS}^{(2)} = E_{pol}^{(2)} + E_{exch}^{(2)}$$

etc.

Repartition 2e ordre en **Induction** et **Dispersion**



SAPT (symmetry adapted perturbation theory)

$$\begin{aligned} E_{int} = & \underbrace{E_{pol}^{(10)} + E_{pol,resp}^{(12)} + E_{pol,resp}^{(13)}}_{E_{pol}^{(1)}} + \\ & + \underbrace{E_{exch}^{(10)} + E_{exch,resp}^{(12)} + E_{exch,resp}^{(13)}}_{E_{exch}^{(1)}} + \\ & + E_{ind}^{(20)} + E_{ind}^{(22)} + E_{ind}^{(30)} + \text{termes d'échange} \\ & + E_{disp}^{(20)} + E_{disp}^{(21)} + E_{disp}^{(22)} + E_{ex-disp}^{(20)} \end{aligned} \quad (20)$$

SAPT (symmetry adapted perturbation theory)

$$\begin{aligned}
 E_{int} = & \underbrace{E_{pol}^{(10)} + E_{pol,resp}^{(12)} + E_{pol,resp}^{(13)}}_{E_{pol}^{(1)}} + \\
 & \underbrace{E_{exch}^{(10)} + E_{exch,resp}^{(12)} + E_{exch,resp}^{(13)}}_{E_{exch}^{(1)}} + \\
 & + E_{ind}^{(20)} + E_{ind}^{(22)} + E_{ind}^{(30)} + \text{termes d'échange} \\
 & + E_{disp}^{(20)} + E_{disp}^{(21)} + E_{disp}^{(22)} + E_{ex-disp}^{(20)} \quad (22)
 \end{aligned}$$

$$E_{int}^{(2)} = E_{int}(\text{HF-like}) + E_{Corr-inter}^{(20)} + E_{Corr-intra}^{(2m)} \quad (23)$$

$$\text{avec } E_{int}(\text{HF-like}) = E_{Pol}^{(10)} + E_{exch}^{(10)} + E_{ind}^{(20)} + E_{ind}^{(30)} + E_{exch-ind}^{(20)} + E_{exch-intra}^{(30)}$$

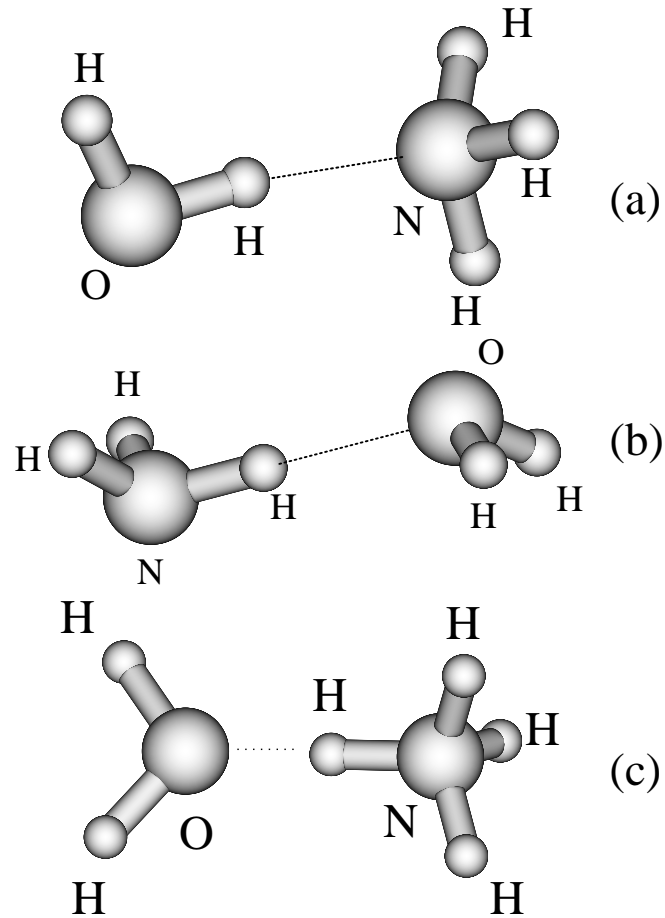
$$\text{et } E_{Corr-inter} = E_{disp}^{(20)} + E_{ex-disp}^{(20)} \quad .$$

$$\text{et } E_{Corr-intra} = E_{Pol,resp}^{(12)} + E_{Pol,resp}^{(13)} + E_{exch}^{(11)} + E_{exch}^{(12)}$$

SAPT, dimère NH_3

	2.80 Å	3.17 Å	3.40 Å	4.00 Å
$E_{Pol}^{(1)}$	-14.91	-6.62	-4.25	-1.69
$E_{exch.}^{(1)}$	27.23	8.76	4.28	0.65
induction (ordre 2)	-2.99	-1.05	-0.60	-0.17
dispersion	-4.40	-2.10	-1.36	-0.48
interaction	4.33	-1.40	-2.21	-1.79
SAPT(hybrid)	1.07	-2.49	-2.75	-1.89

SAPT, autres systèmes



SAPT, autres systèmes

	$\text{H}_2\text{O} \cdots \text{HNH}_2$ $R_{(N \cdots O)} = 3.300 \text{ \AA}$	$\text{HOH} \cdots \text{NH}_3$ 3.000 \AA	$\text{H}_2\text{O} \cdots \text{HNH}_3^+$ 2.700 \AA
niveau Hartree-Fock			
$E_{Pol}^{(10)}$ ($E_{exch}^{(10)}$)	-3.35 (+2.74)	-10.19 (+8.55)	-24.57 (+16.41)
$E_{ind}^{(20)}$ ($E_{exch-ind}^{(20)}$)	-0.93 (+0.50)	-4.16 (+2.43)	-12.09 (+4.62)
$E_{ind}^{(30)}$ ($E_{ex-ind}^{(30)*}$)	-0.92 (+0.49)	-3.76 (+2.12)	-6.23 (+2.10)
Corrélation			
$E_{disp}^{(20)}$ ($E_{exch-disp}^{(20)}$)	-1.34 (+0.19)	-2.75 (+0.56)	-3.99 (+0.63)
$E_{disp}^{(30)}$	0.03	0.07	0.08
$E_{Pol}^{(12)} + E_{Pol}^{(13)}$	0.08	0.23	1.63
$E_{exch}^{(1)}$	0.56	1.24	1.41
$E_{ind}^{(22)}$ ($E_{ex-ind}^{(22)*}$)	-0.15 (+0.08)	-0.50 (+0.29)	-1.08 (+0.41)
$E_{disp}^{(21)} + E_{disp}^{(22)}$	-0.21	-0.40	-0.24
$\frac{E_{exch-ind}^{(30)}}{E_{ind}^{(30)}} = \frac{E_{exch-ind}^{(22)}}{E_{ind}^{(22)}} = \frac{E_{exch-ind}^{(20)}}{E_{ind}^{(20)}}$			