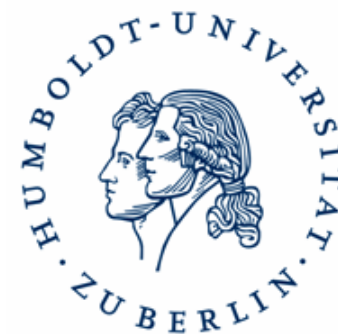


Quantum chemistry and wavefunction based methods for electron correlation

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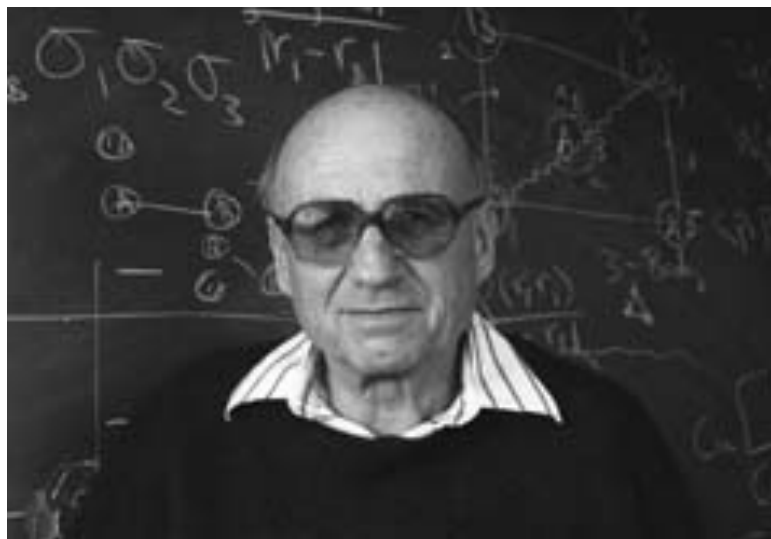
The Royal Swedish Academy of Sciences has awarded
The 1998 Nobel Prize in Chemistry in the area of quantum chemistry to

Walter Kohn, University of California at Santa Barbara, USA and
John A. Pople, Northwestern Univ., Evanston, Ill., USA (British citizen).

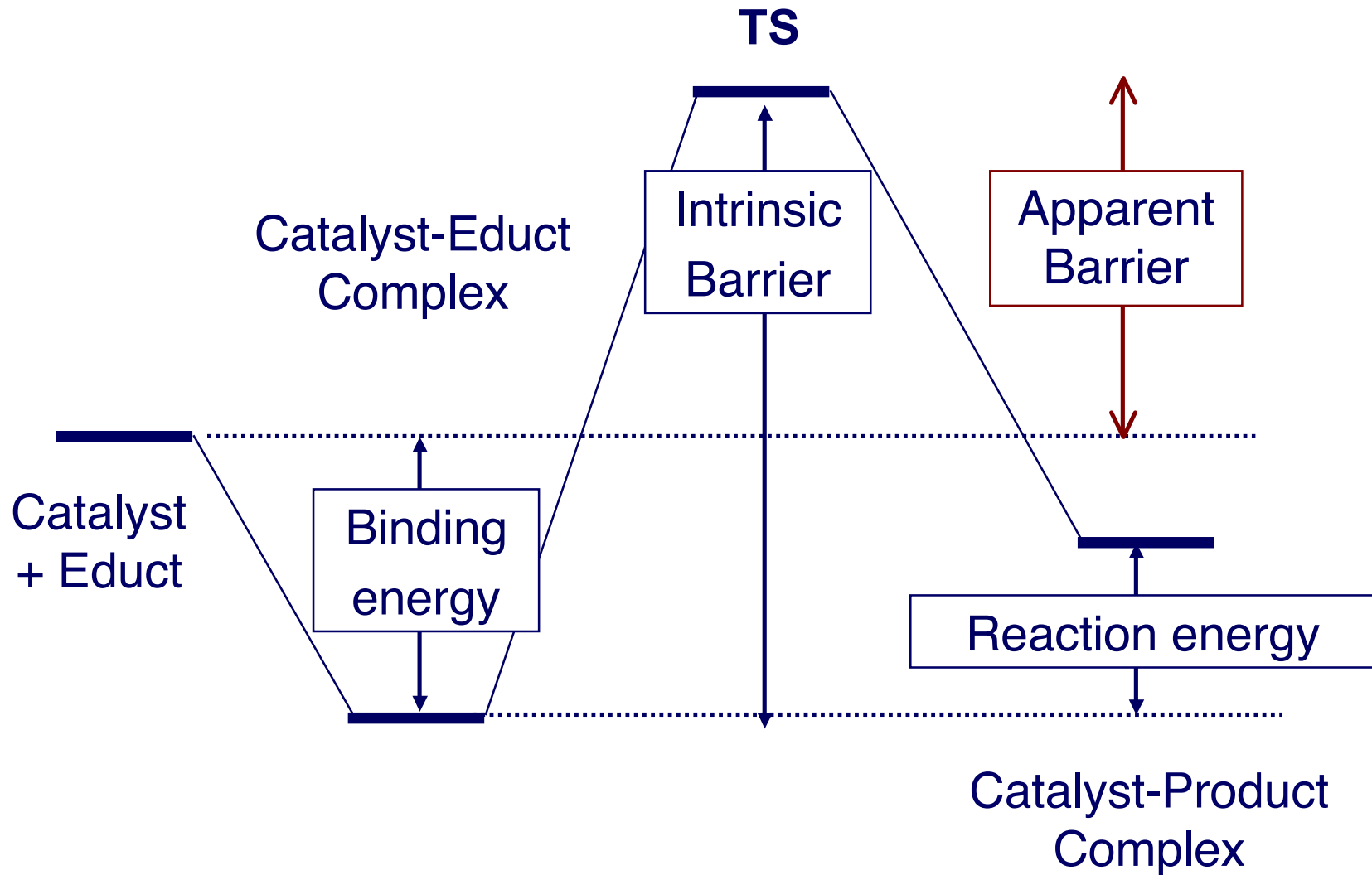


Citation:

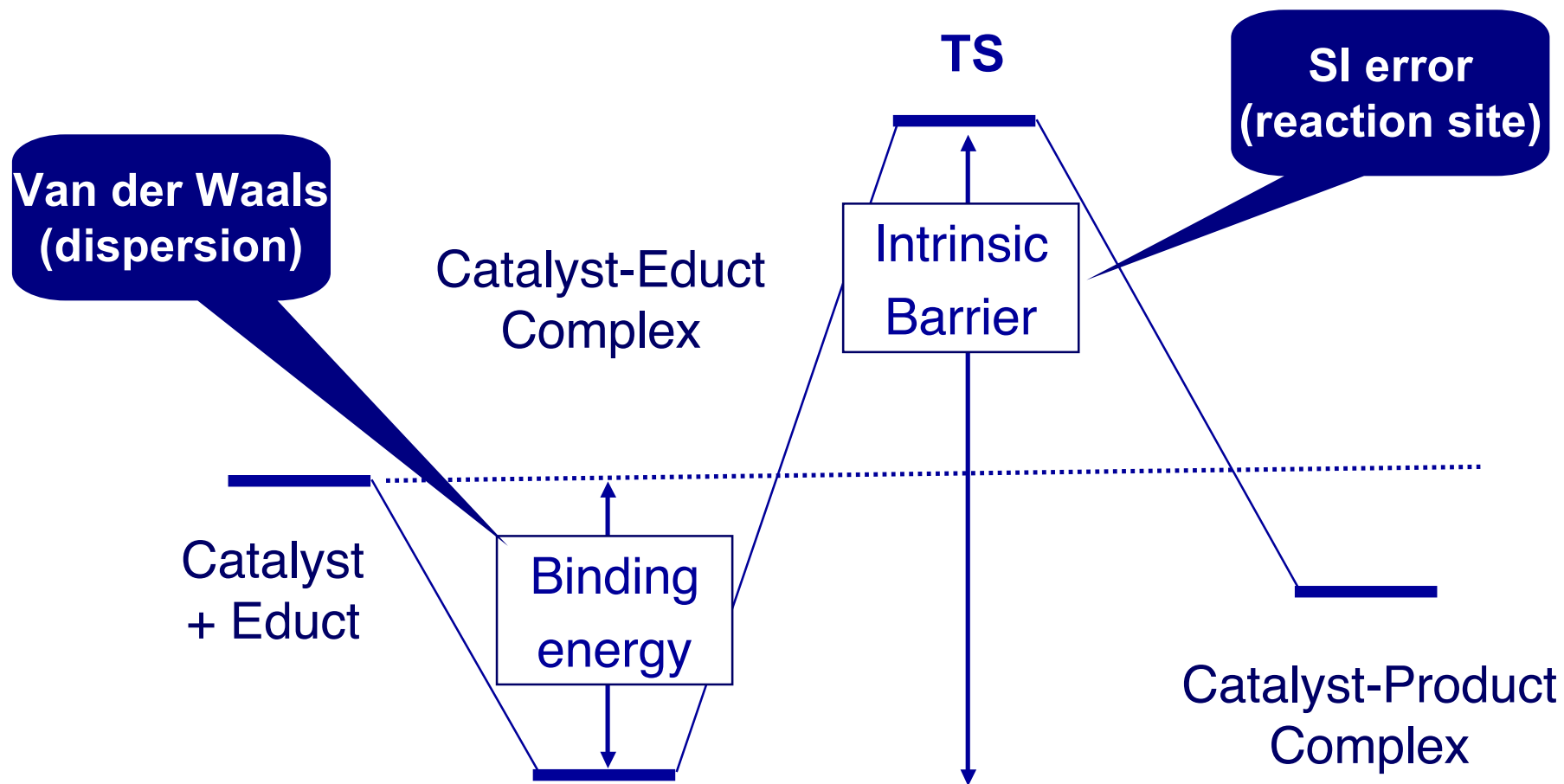
"to Walter Kohn for his development of the **density-functional theory** and to John Pople for his development of **computational methods in quantum chemistry**."



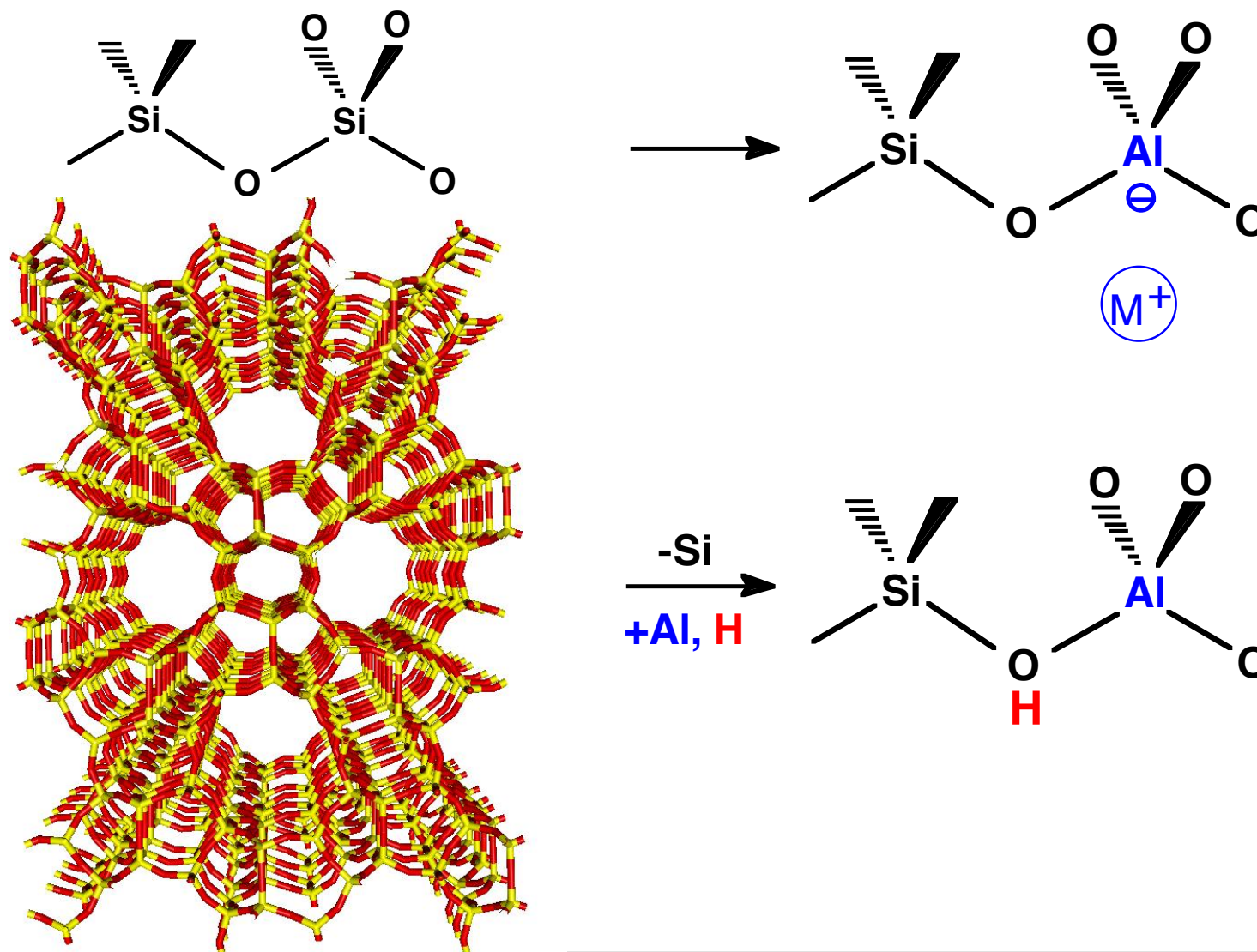
Surface Reaction



DFT problems with barriers



Zeolite catalysts: active sites (transition metal ions, protons) in a „surface-only“ silica matrix

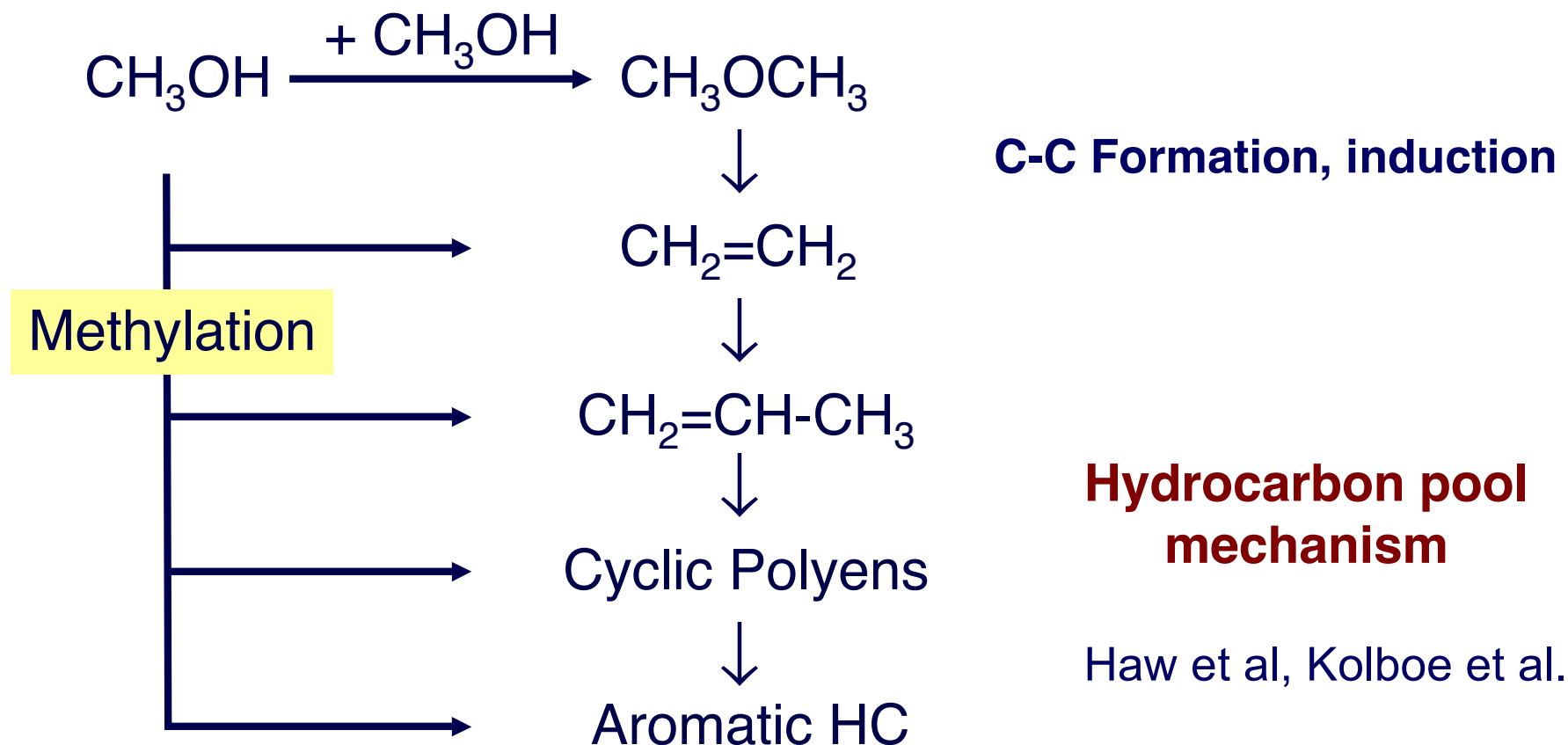


Zeolite catalysis: Methanol-to-hydrocarbons

Methanol from
different sources

MTG
MTO

Gasoline
Olefines

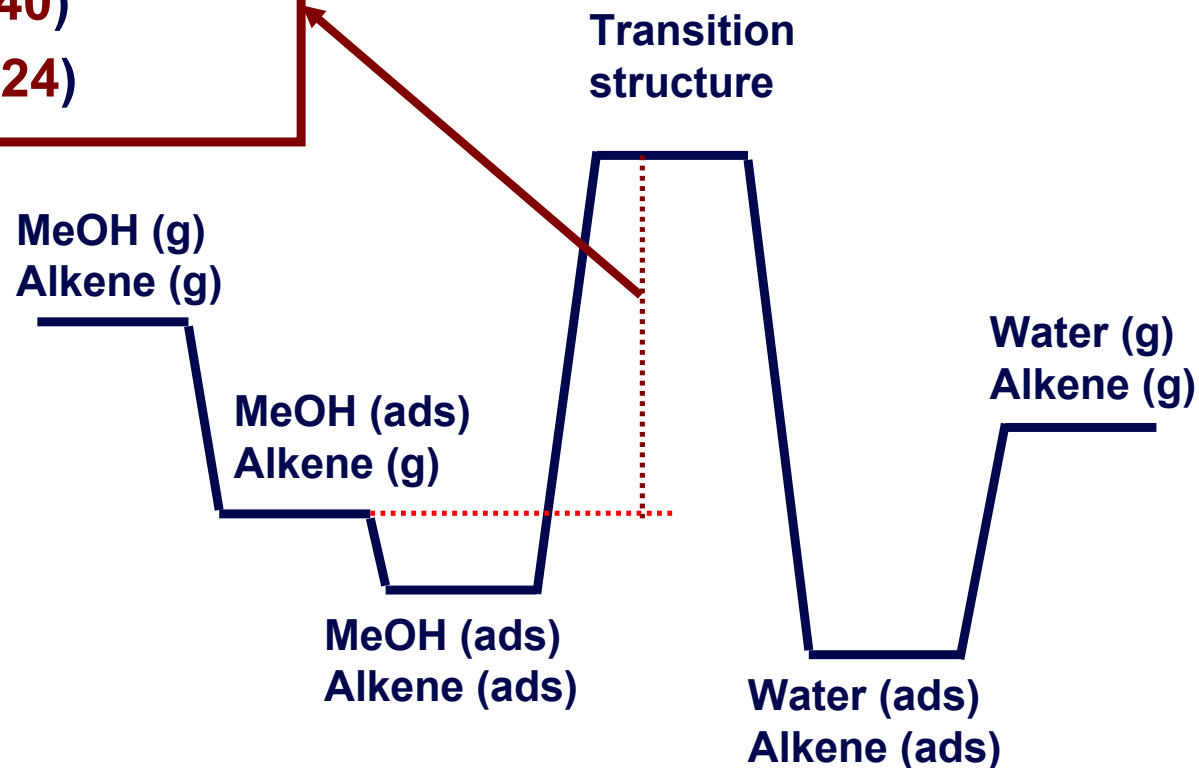


Review: Stöcker, Microp. and Mesop. Mat. 29 (1999) 3-48

Methylation of ethene, propene, trans-2-butene in H-MFI

Measured* Apparent Barrier

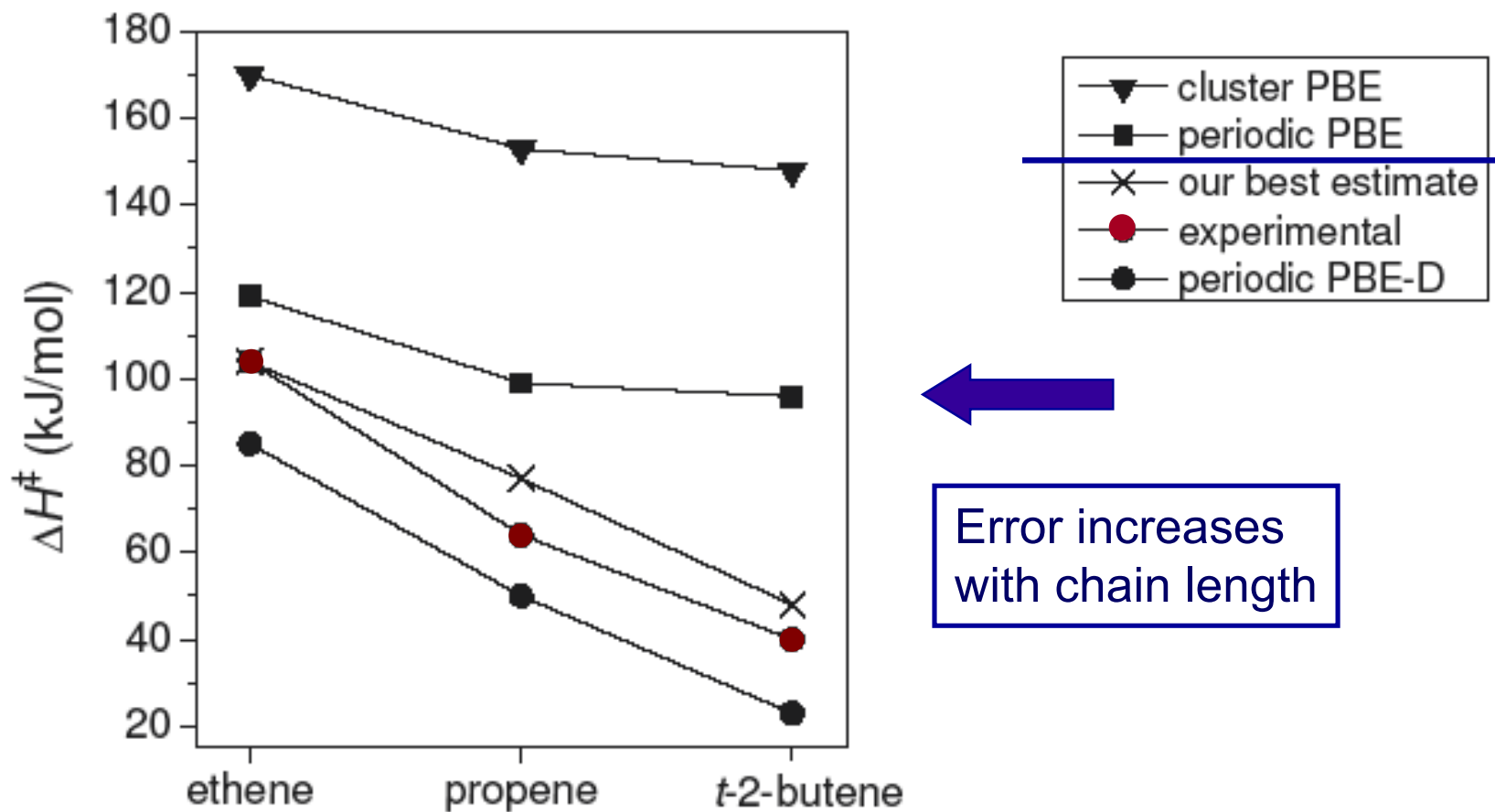
Ethene	104
Propene	64 (-40)
t-2-Butene	40 (-24)



*S. Svelle, P.A. Ronning, S. Kolboe, *J. Catal.* **2004**, *224*, 115.

S. Svelle, P.O. Ronning, U. Olsbye, S. Kolboe, *J. Catal.* **2005**, *234*, 385.

Methylation of alkenes in H-MFI - pbc DFT



Svelle, Tuma, Rozanska, Kerber, Sauer, JACS 131 (2009) 816

Pragmatic solution: DFT + Dispersion (DFT+D)

Many predecessors with DFT, HF+Disp, e.g. Ahlrichs and Scoles
Many more sophisticated schemes

$$E_{total} = E_{DFT} + E_{disp}$$
$$E_{disp} = -s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{C_6^{ij}}{r_{ij}^6} f_{damp}$$
$$f_{damp}(R) = \frac{1}{1 + e^{-\alpha(R/R_0 - 1)}}$$

$$s_6 = 1.4/1.3/0.7 \text{ for BLYP/BP86/PBE}$$

Grimme, *J. Comput. Chem.*, **2004**, *25*, 1463; **2006**, *27*, 1787.

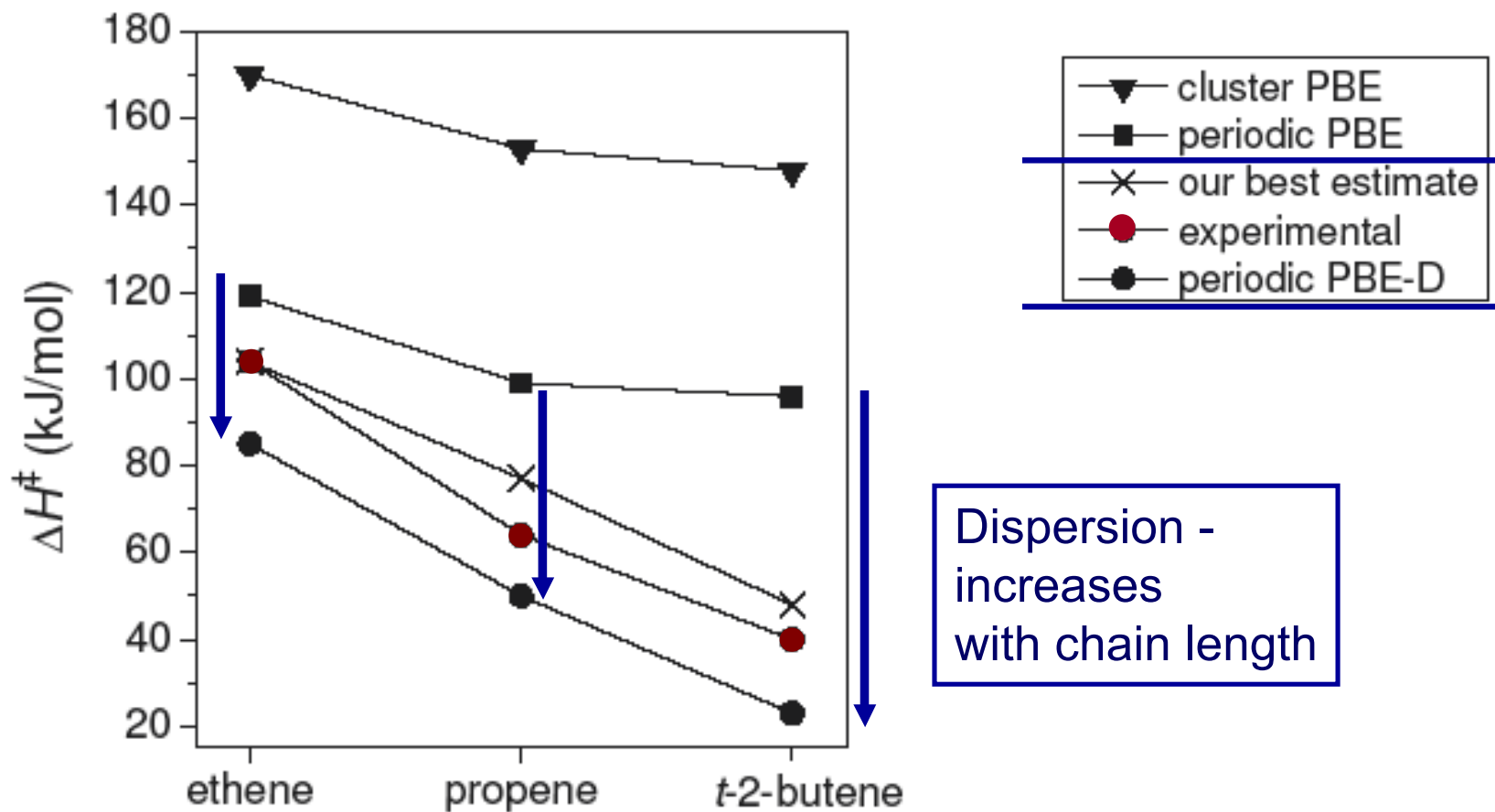
Parameters are as good for solids (condensed systems) as for molecules

Note, however, Mg^{2+} very different from Mg, whereas O^{2-} similar to O

Implementation of Ewald sum for $1/r^6$ for periodic systems

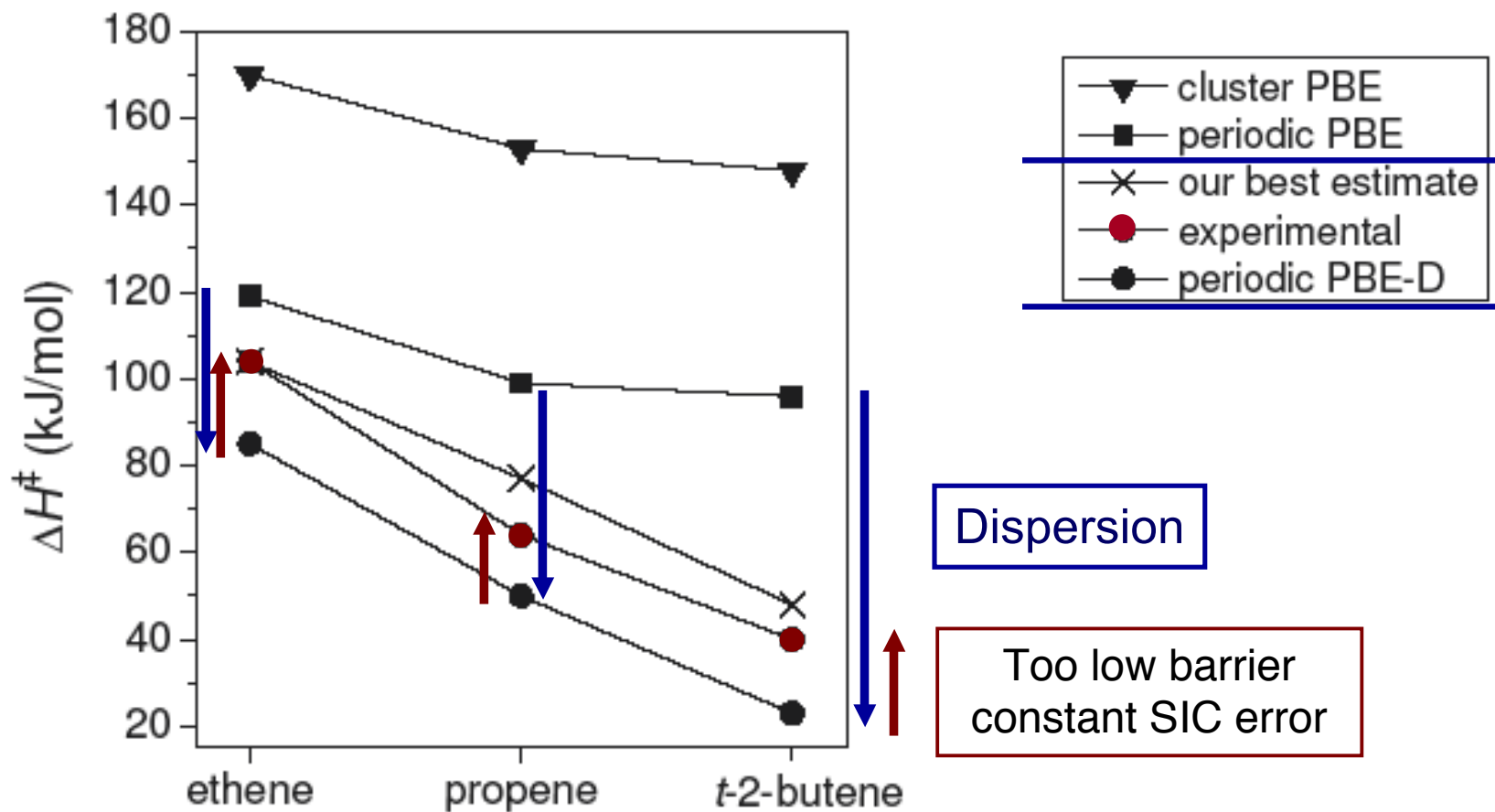
Kerber, Sierka, Sauer, *J. Comput. Chem.* **29** (2008) 2088.

Methylation of alkenes in H-MFI - pbc DFT+D



Svelle, Tuma, Rozanska, Kerber, Sauer, JACS 131 (2009) 816

Methylation of alkenes in H-MFI - pbc DFT+D



Svelle, Tuma, Rozanska, Kerber, Sauer, JACS 131 (2009) 816

Errors on energy barriers (Truhlar et al.)

kcal/mol

TABLE 5: Mean Errors for HTBH38 and NHTBH38 Database^{a,b,c}

methods	heavy atom transfer (12)		NS ^d (16)		unimol and assoc ^e (10)		hydrogen transfer (38)	
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE
PBE1PBE	-6.62	6.62	-1.87	2.05	-0.58	2.16	-4.22	4.22
B3LYP	-8.49	8.49	<u>-3.25</u>	<u>3.25</u>	-1.42	2.02	<u>-4.13</u>	<u>4.23</u>
MP2	11.76	11.76	<u>0.74</u>	<u>0.74</u>	4.71	5.44	<u>3.69</u>	<u>4.14</u>
TPSSh	-11.51	11.51	-5.78	5.78	-2.94	3.23	-5.97	5.97
BLYP	-14.66	14.66	-8.40	8.40	-3.38	3.51	-7.52	7.52
TPSS	-14.65	14.65	-7.75	7.75	-3.84	4.04	-7.71	7.71
PBE	-14.93	14.93	<u>-6.97</u>	<u>6.97</u>	-2.94	3.35	<u>-9.32</u>	<u>9.32</u>

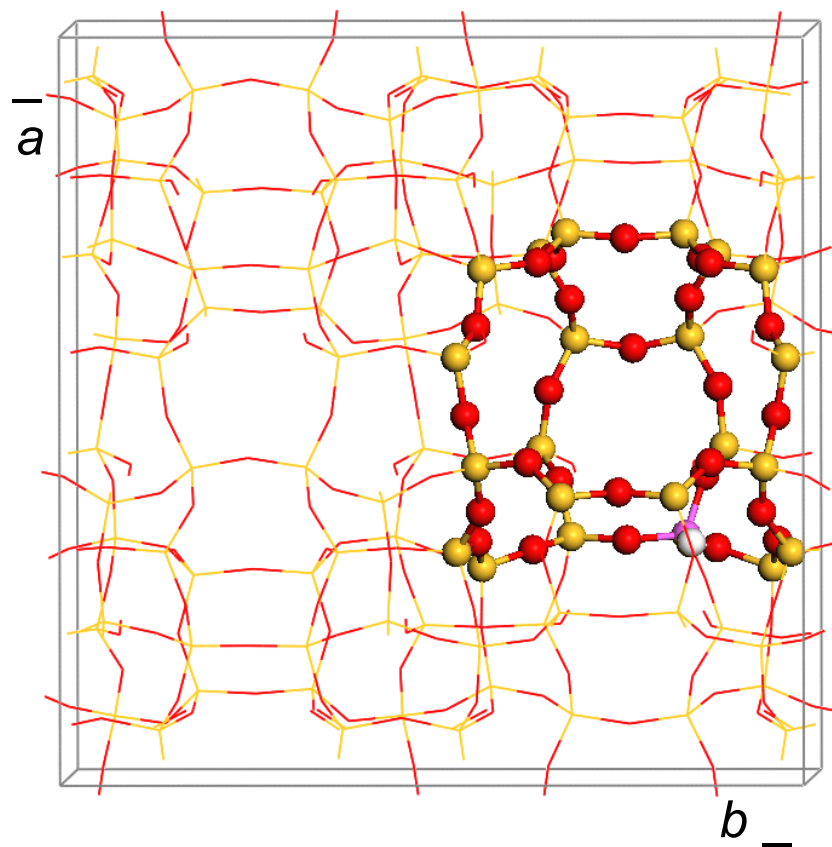
Nucleophilic substitution

Reference data:

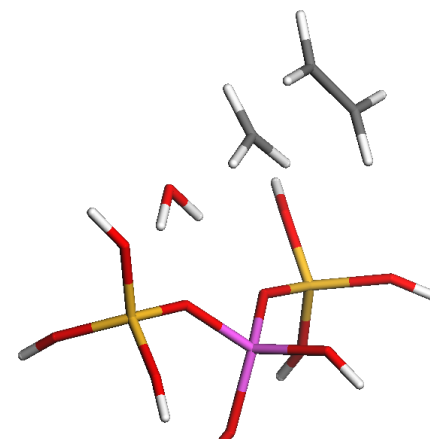
CCSD(T) with extrapolation to complete basis set limit („W1 theory“)

Divide and Conquer - Models and Methods

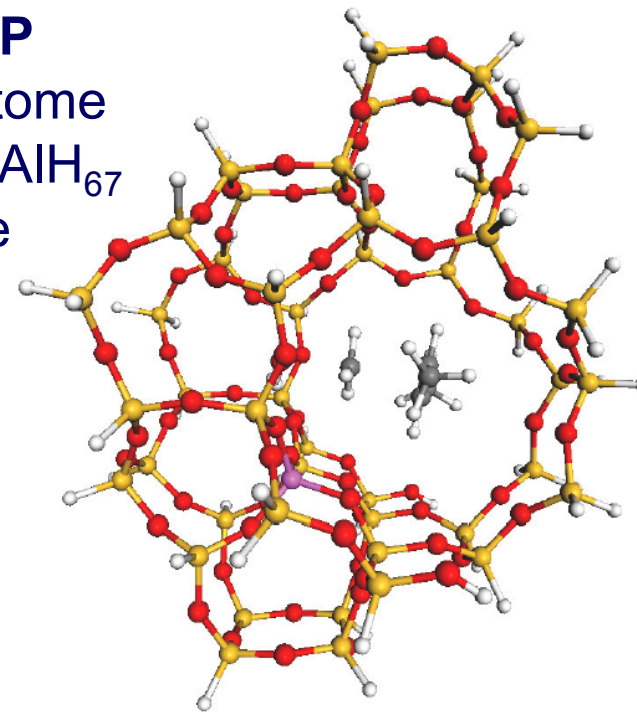
DFT (PBE/plane waves), VASP
20.2x20.5x13.5 Å; 96 +18 atoms
Periodic Boundary Conditions



CCSD(T)/cbs
17+17 Atome
 $C_3O_{11}Si_2AlH_{17}$
MOLPRO



MP2/TZVP
123+67Atome
 $C_3O_{72}Si_{47}AlH_{67}$
CC2 code



Hybrid high level : low level method

Hybrid MP2(cluster):PBE+D(pbc) + Δ CCSD(T) method

$$E_{\text{hybrid}}(\mathbf{S}, \mathbf{C}) = E_{\text{DFT+D}}(\mathbf{S}) + \underbrace{[E_{\text{MP2}}(\mathbf{C}) - E_{\text{DFT+D}}(\mathbf{C})]}_{\text{High level correction}}$$

Step 0: PBE+D optimization, periodic boundary conditions (pbc)

Frequency calculation for stationary points, ZPVE

Step 1: Hybrid MP2(cluster):PBE+D(pbc) optimization

Step 2: Basis set extrapolation to CBS limit, single point

Step 3: CCSD(T)-MP2, small cluster model

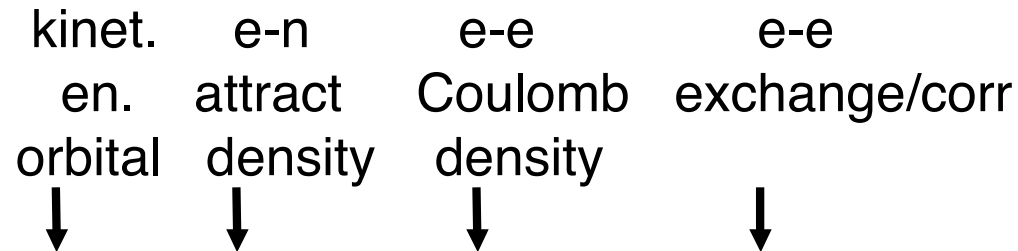
Tuma, Sauer, *CPL* 2004, 387, 388; *PCCP*, 2006, 8, 3955

Kerber, Sierka, Sauer, *J. Comput. Chem.* 2008, 29, 2088

Reuter/Scheffler, *PRL* 98 (2007) 176103 (CO/Cu(111))

Stoll, *JPC A* 113 (2009) 11483 (Be, Mg crystals)

Energy as functional of orbitals or electron density



$$E^{\text{HF}} = E_{\text{T}} + E_{\text{N}} + \boxed{E_{\text{J}} + E_{\text{X}}^{\text{Fock30}} \text{ (orbital)}} \quad \text{Self-interaction cancels}$$

$$E^{\text{DFT}} = E_{\text{T}} + E_{\text{N}} + E_{\text{J}} + E_{\text{XC}} \text{ (density)}$$

functional of density only

$$E_{\text{XC}}^{\text{LDA}} = E_{\text{X}}^{\text{Dirac30}} + E_{\text{C}}^{\text{VWN}}$$

functional also of density gradient (Generalized Gradient Approximation)

$$E_{\text{XC}}^{\text{BLYP}} = E_{\text{X}}^{\text{Dirac30}} + \Delta E_{\text{X}}^{\text{B88}} + E_{\text{C}}^{\text{LYP}}$$

Self-interaction correction

Hartree-Fock E_J + E_X^{F30} (orbital)

$$\rho(x) = \left| \begin{array}{l} \frac{1}{2} \iint \rho(x_1) \frac{1}{r_{12}} \rho(x_2) dx_1 dx_2 - \frac{1}{2} \sum_{i,j} \iint i^*(x_1) j^*(x_2) \frac{1}{r_{12}} j(x_1) i(x_2) dx_1 dx_2 \\ \sum_{i=1}^N i(x) i^*(x) \\ i = j \end{array} \right. \begin{array}{l} \frac{1}{2} \sum_{i,j} [\langle ij|ij \rangle - \langle ij|ji \rangle] \\ [\langle ii|ii \rangle - \langle ii|ii \rangle] = 0 \end{array}$$

Coulomb and exchange terms cancel - self-interaction correction (SIC)

Kohn-Sham E_J + E_{XC} (density)

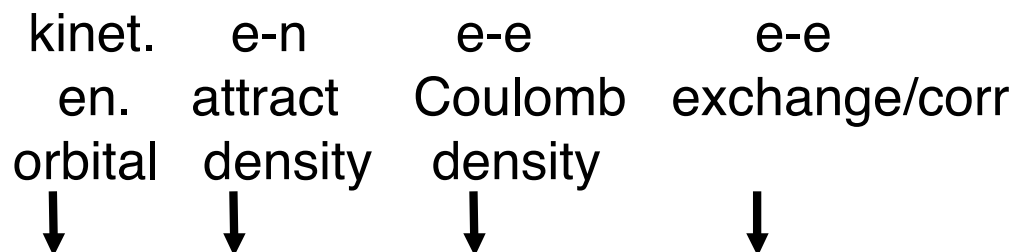
$$\frac{1}{2} \iint \rho(x_1) \frac{1}{r_{12}} \rho(x_2) dx_1 dx_2 + \int dx \rho(x) V_{XC}[\rho, \nabla \rho]$$

$$\frac{1}{2} \langle ii|ii \rangle + \langle i|V_{XC}[\rho, \nabla \rho]|i \rangle \neq 0$$

Coulomb and exchange do not cancel - self-interaction error

$$* \iint i^*(x_1) j^*(x_2) \frac{1}{r_{12}} i(x_1) j(x_2) dx_1 dx_2 = \langle ij|ij \rangle$$

Energy as functional of orbitals or electron density



$$E^{\text{HF}} = E_{\text{T}} + E_{\text{N}} + \boxed{E_{\text{J}} + E_{\text{X}}^{\text{Fock30}} \text{ (orbital)}} \quad \text{Self-interaction cancels}$$

$$E^{\text{DFT}} = E_{\text{T}} + E_{\text{N}} + E_{\text{J}} + E_{\text{XC}} \text{ (density)}$$

functional of density only

$$E_{\text{XC}}^{\text{LDA}} = E_{\text{X}}^{\text{D30}} + E_{\text{C}}^{\text{VWN}}$$

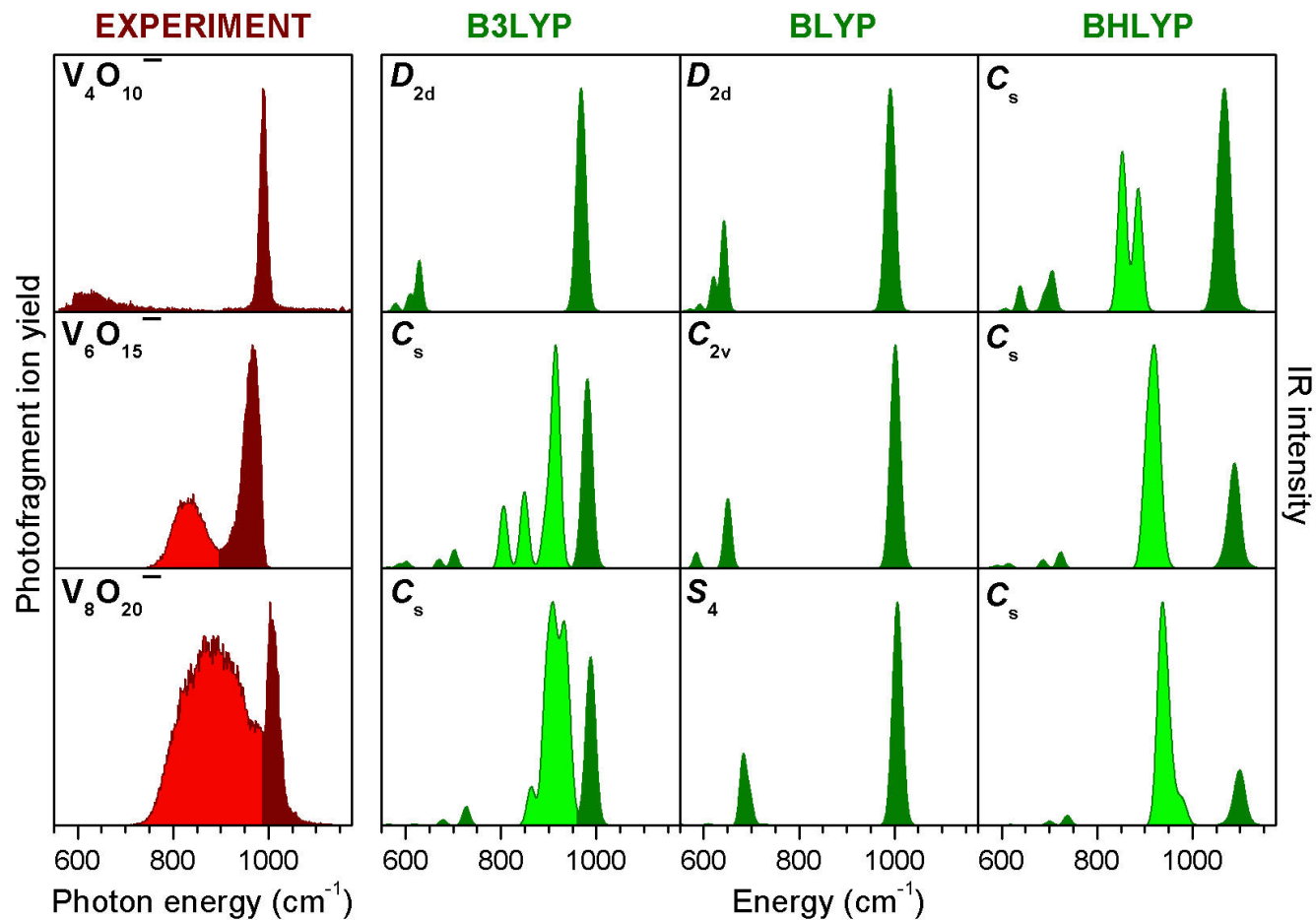
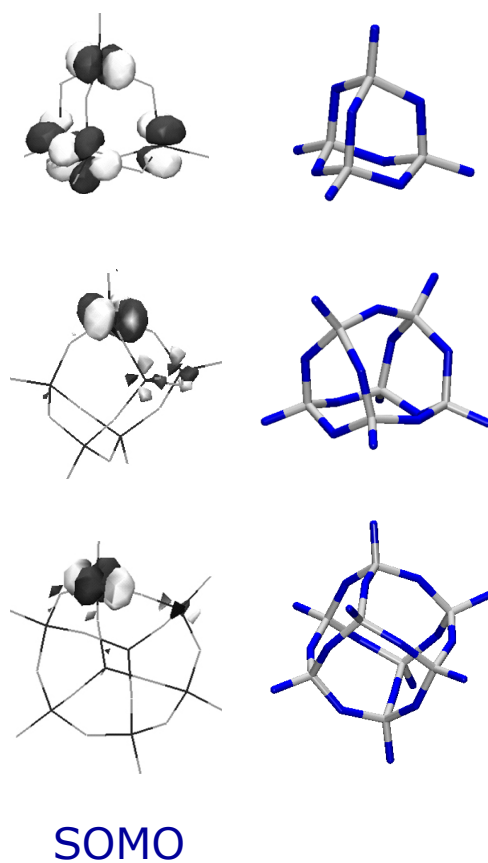
functional also of density gradient (Generalized Gradient Approximation)

$$E_{\text{XC}}^{\text{BLYP}} = E_{\text{X}}^{\text{Dirac30}} + \Delta E_{\text{X}}^{\text{B88}} + E_{\text{C}}^{\text{LYP}}$$

orbital-density **hybrid functional**

$$E_{\text{XC}}^{\text{B3LYP}} = a_0 E_{\text{X}}^{\text{F30}} + (1 - a_0) E_{\text{X}}^{\text{D30}} + a_{\text{X}} \Delta E_{\text{X}}^{\text{B88}} + (1 - a_{\text{C}}) E_{\text{C}}^{\text{VWN}} + a_{\text{C}} E_{\text{C}}^{\text{LYP}} \quad \text{Self-interaction cancels partially}$$

Cluster anions $(V_2O_5)_n^-$

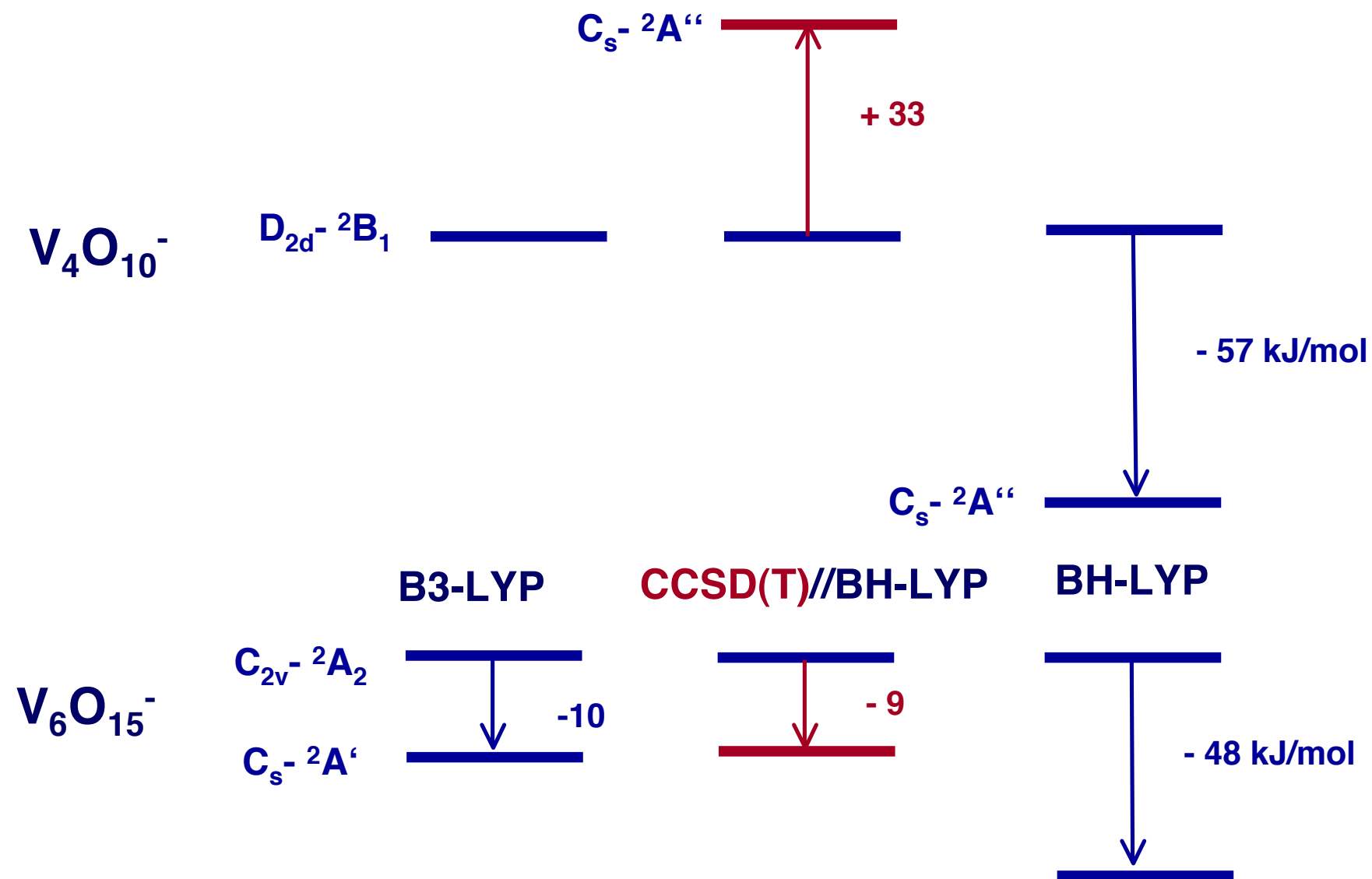


**Size-dependent
electron localization**

20% 0% 50%

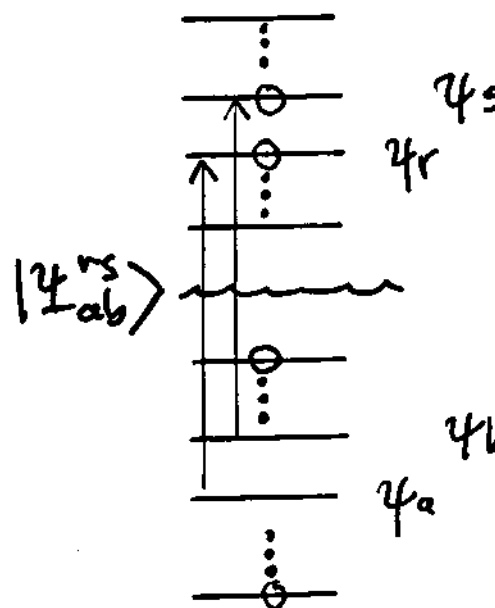
Fock-exchange in functional

CCSD(T) calculations confirm most stable structures



Orbital functional for electron correlation: 2nd order Møller-Plesset perturbation theory

$$E_C^{MP2}[\psi] = - \sum_{a < b} \sum_{r < s} \frac{\langle ab || rs \rangle^2}{\epsilon_r + \epsilon_s - \epsilon_a - \epsilon_b}$$

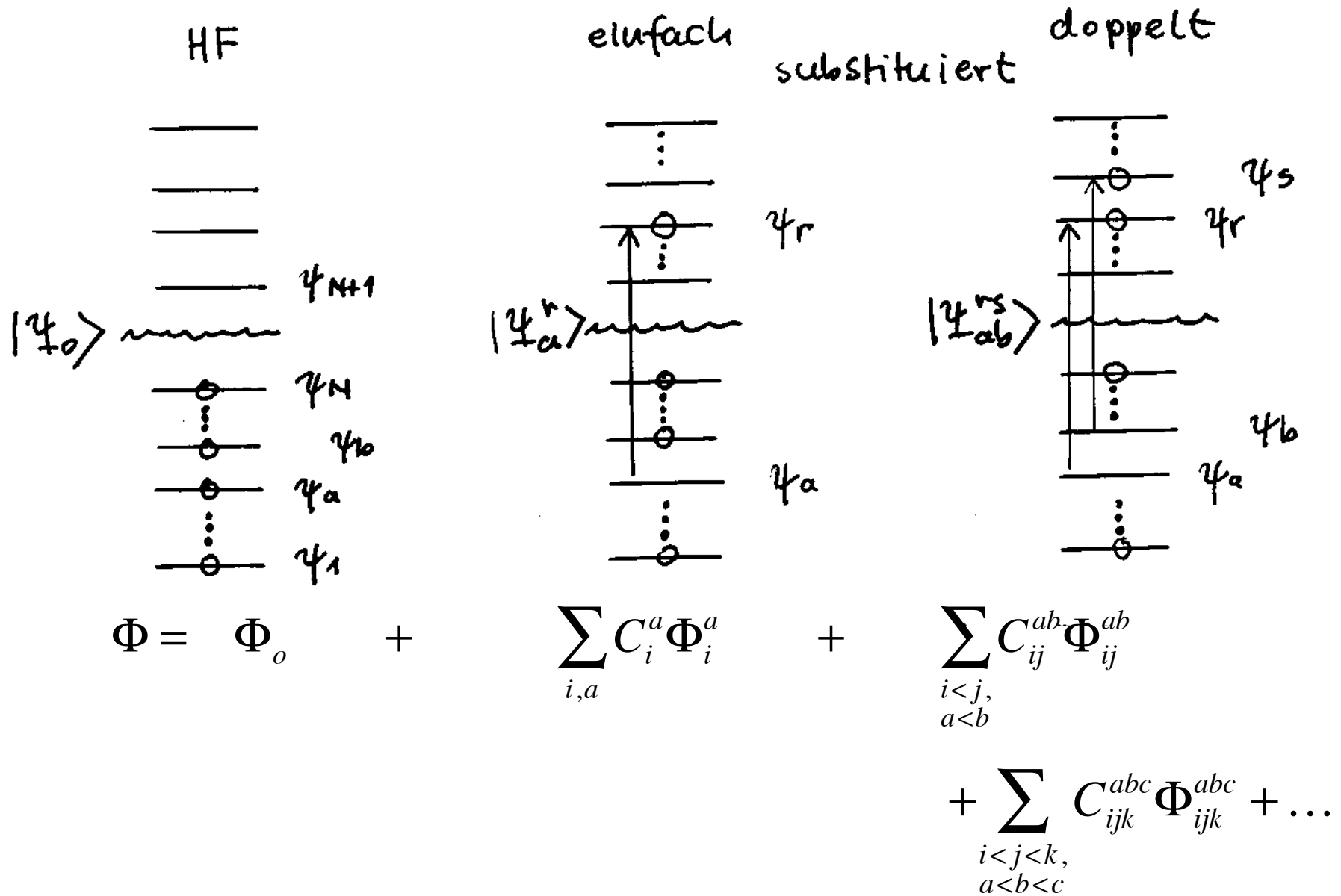


Covers dispersion

Functionals including this term and Fock exchange: double hybrid

$$E^{\text{DFT}} = E_{\text{T}} + E_{\text{N}} + E_{\text{J}} + E_{\text{XC}}[\rho] + a_{\text{x}} E_{\text{X}}^{\text{F30}} + a_{\text{MP2}} E_{\text{C}}^{\text{MP2}}$$

Wave function expansion



Wave function expansion

$$\Phi = \sum_n C_n \Phi_n = \Phi_o + \sum_{i,a} C_i^a \Phi_i^a + \sum_{\substack{i<j, \\ a<b}} C_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{\substack{i<j<k, \\ a<b<c}} C_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

Result depends on

- configuration space „full configuration interaction“
- size of one-particle space (M, given by the basis set)
how many configurations of a given substitution level ?

$$\frac{M!}{N!(M-N)!} = 4 \cdot 10^{11} \quad \text{for CH}_4 \quad \text{DZP basis } M=70, N=10$$

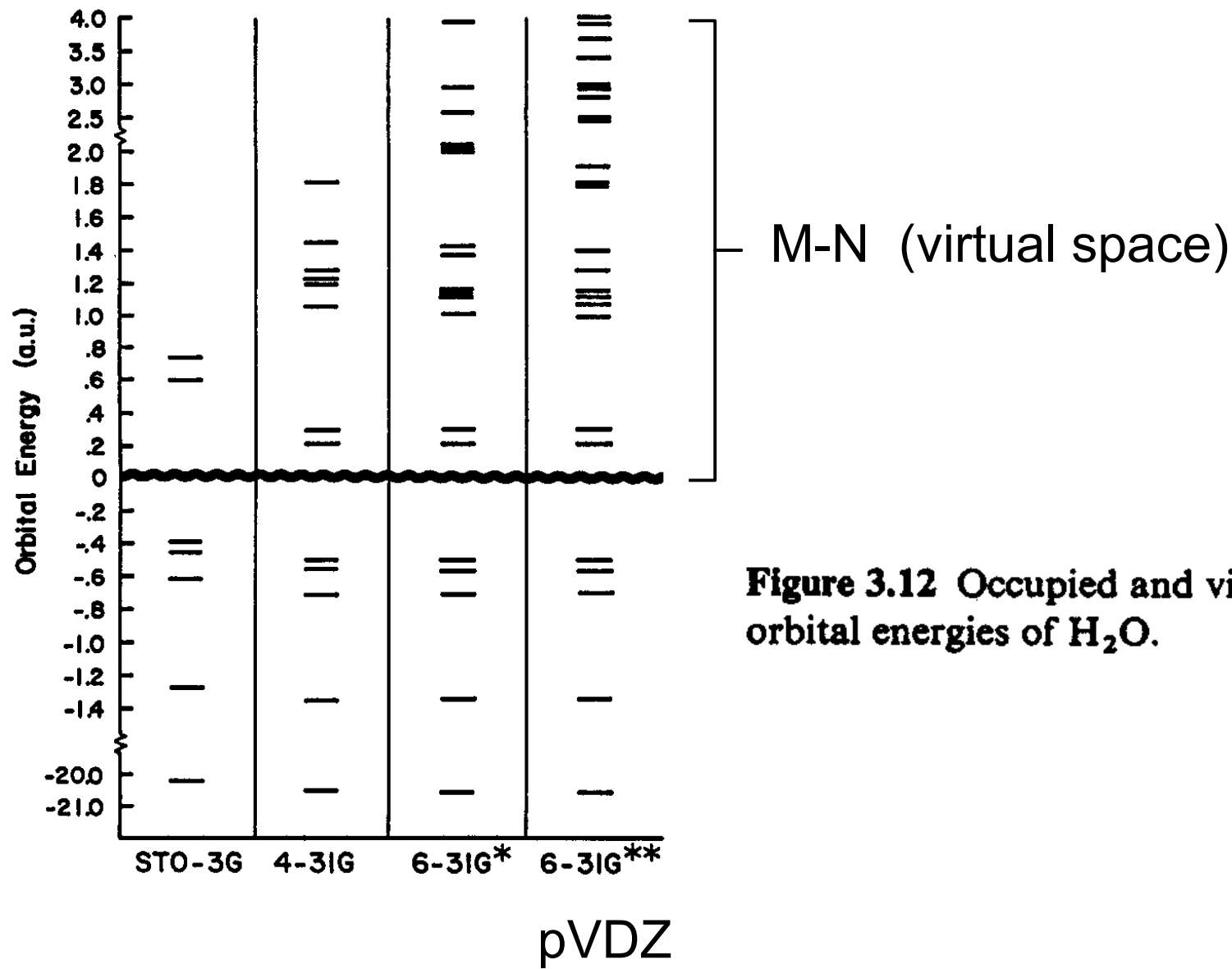
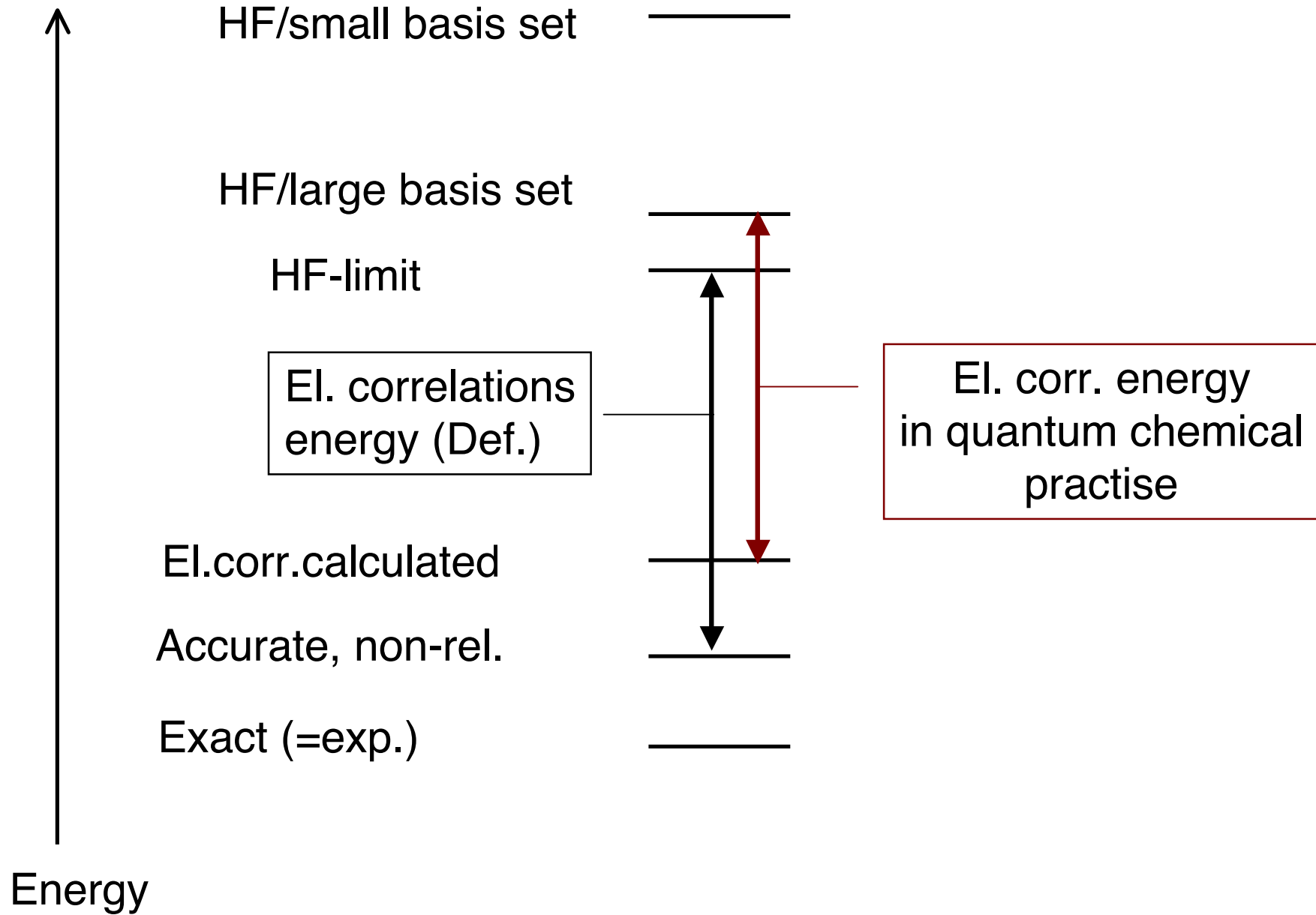


Figure 3.12 Occupied and virtual orbital energies of H₂O.



Electron correlation - „Post Hartree Fock“

$$\Phi = \Phi_o + \sum_{i,a} C_i^a \Phi_i^a + \sum_{\substack{i<j, \\ a<b}} C_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{\substack{i<j<k, \\ a<b<c}} C_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

$$\langle ab || rs \rangle = \langle ab | rs \rangle - \langle ab | sr \rangle \quad \int \psi_a^*(x_1) \psi_b^*(x_2) \frac{1}{r_{12}} \psi_r(x_1) \psi_s(x_2) dx_1 dx_2 = \langle ab | rs \rangle$$

$$E_{corr} = E - E^{HF} = \sum_{\substack{r<s \\ a<b}} C_{ab}^{rs} \langle \Psi_0 | \hat{H} | \Psi_{ab}^{rs} \rangle = \sum_{\substack{r<s \\ a<b}} C_{ab}^{rs} \langle ab || rs \rangle$$

You only need double substitution to calculate the exact correlation energy, but to determine the doubles coefficients exactly, you need all substitutions

Many body perturbation theory (MBPT)

$$H_0 = \sum_{\zeta} F(\zeta)$$

Φ_0 -- Determinant consisting of canonical HF orbitals

$$E^{(0)} = \sum_i \varepsilon_i$$

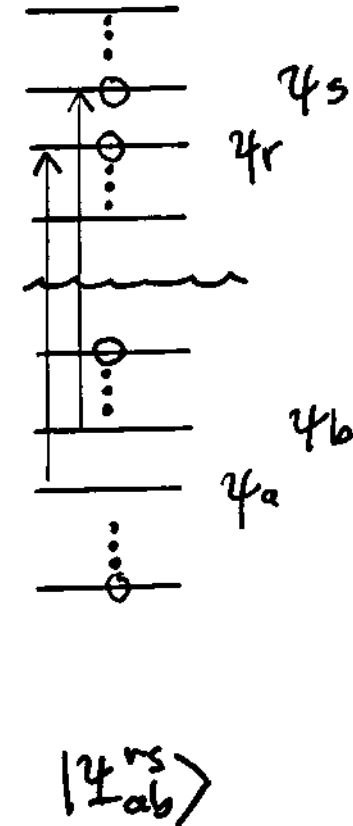
$$E^{(0)} + E^{(1)} = E^{HF}$$

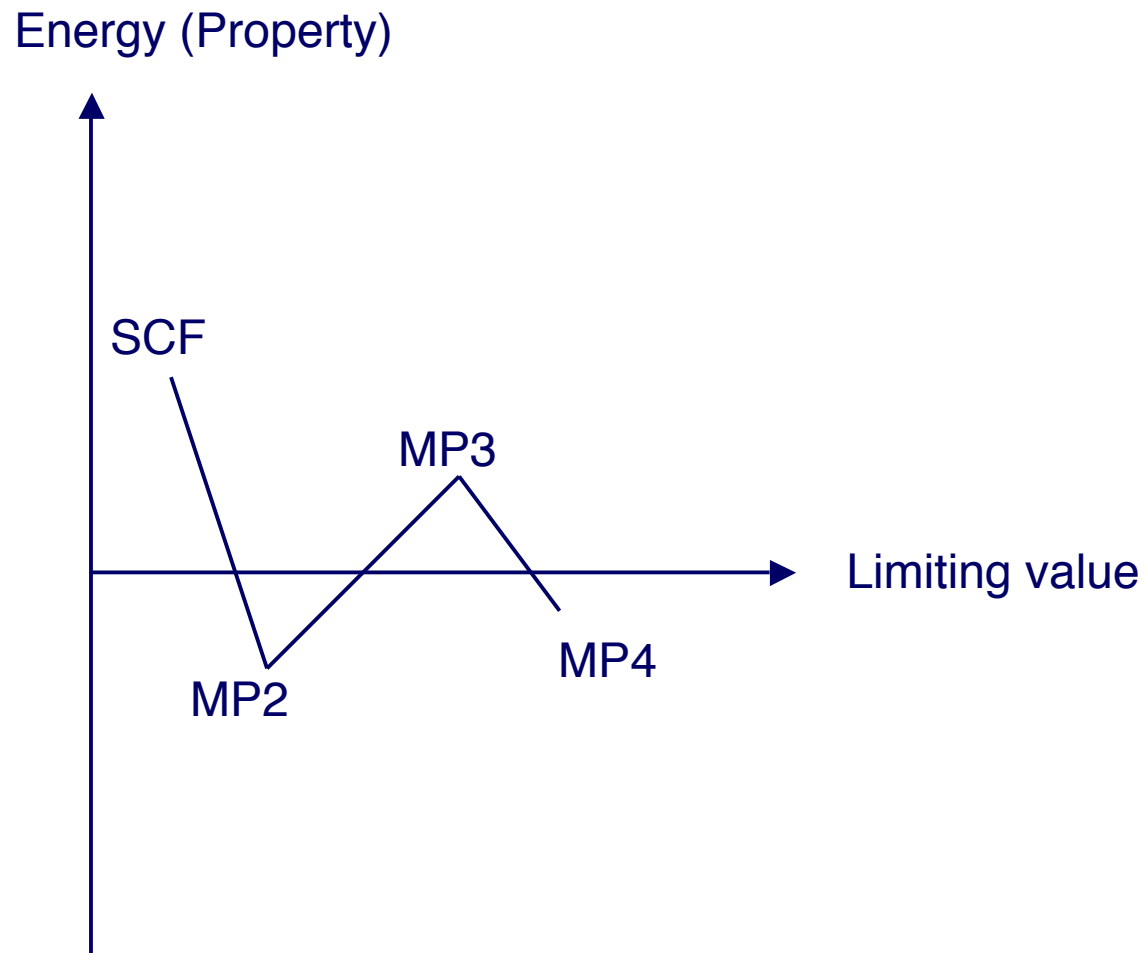
$$\langle \Phi_0 | \hat{H} | \Phi_a^r \rangle = 0 \quad (\text{Brillouin Theorem})$$

$$\langle \Phi_0 | \hat{V} | \Phi_{ab}^{rs} \rangle = \langle \Phi_0 | \hat{H} | \Phi_{ab}^{rs} \rangle = \langle ab || rs \rangle = \sum_{\mu\nu\kappa\lambda} c_{\mu a} c_{\nu b} c_{\kappa r} c_{\lambda s} \langle \mu\nu || \kappa\lambda \rangle$$

$$E_{corr} = E^{(2)} = - \sum_{a < b} \sum_{r < s} \frac{\langle ab || rs \rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b} \langle ab || rs \rangle = E^{MP2}$$

$$E_{XC}^{MP2} = E_X^{F30} + E_C^{MP2}$$





Typical oscillating behaviour of results obtained with the MP method

Coupled Cluster Expansion

$$\Psi = e^T \Phi_0 = (1 + T + \frac{1}{2} T^2 + \frac{1}{3!} T^3 + \dots) \Phi_0$$

$$e^T = 1 + T_1 + (T_2 + \frac{1}{2} T_1^2) + (T_3 + T_2 T_1 + \frac{1}{3!} T_1^3) + (T_4 + \frac{1}{2} T_2^2 +$$

$$T_1 \Phi_0 = \sum_i \sum_m t_i^m \Phi_i^m \quad \text{t - Amplitudes}$$

$$T_1^2 \Phi_0 = \sum_{i,j} \sum_{m,n} t_i^m t_j^n \Phi_{ij}^{mn} \quad \text{disconnected (unlinked) doubles}$$

$$T_2 \Phi_0 = \sum_{i,j} \sum_{m,n} t_{ij}^{mn} \Phi_{ij}^{mn} \quad \text{connected (linked) doubles}$$

The presence of disconnected (double) substitution ensures size-consistency

Coupled Cluster Energy

$$E = \langle \Phi_0 | H | 1 + T_1 + (T_2 + \frac{1}{2} T_1^2) \Phi_0 \rangle$$

(if HF orbitals are used)

$$E_{corr} = \sum_{i < j} \sum_{m < n} (t_{ij}^{mn} + t_i^m t_j^n - t_i^n t_j^m) \langle ij || mn \rangle$$

Equations for determination of „amplitudes“ (coefficients)

$$\sum_{im} t_i^m \langle \Phi_i^p | H | \Phi_i^m \rangle + \sum_{ij, mn} (t_{ij}^{mn} + t_i^m t_j^n - t_i^n t_j^m) \langle \Phi_i^p | H | \Phi_{ij}^{mn} \rangle +$$

$$\sum (t_{ij}^{mn} t_k^o + \dots t_i^m t_j^n t_k^o - \dots) \langle \Phi_i^p | H | \Phi_{ijk}^{mno} \rangle = E t_i^p$$

Iterative solution

CC-SD equation (HF-Orbitale)

$$\langle \Phi_i^m | H | (T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{6} T_1^3) \Phi_0 \rangle = E \cdot t_i^m$$

$$\begin{aligned} \langle \Phi_{ij}^{mn} | H | (1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{6} T_1^3 + \frac{1}{2} T_2^2 + \frac{1}{2} T_1^2 T_2 + \frac{1}{24} T_1^4) \Phi_0 \rangle \\ = E \cdot (t_{ij}^{mn} + t_i^m t_j^n - t_i^n t_j^m) \end{aligned}$$

CCSD(T) - (T)riple-contribution according to MP4 equation,
but T1 and T2 amplitudes are taken from CCSD equations

Wavefunction-based methods for electron correlation

I. According to the way, the expansion coefficients are determined

variational: Configuration Interaction (CI methods)

Size-consistency problem

CIS (CI with singles) for excited states

perturbation theory: Møller-Plesset

MP2, MP4-SDTQ

system of equations: Coupled Cluster (iterative)

CCSD; **CCSD(T)**

Wavefunction-based methods for electron correlation

II. Substitutions included in wavefunction expansion

all in given one-particle basis:	full CI
up to quadruple:	MP4-SDTQ
up to connected triple substitution: (an expensive standard method)	CCSD(T)
up to doubles:	CI-SD → CPF
doubles only: (the simplest wavefunction-based standard method))	MP2
singles only: (simplest method for excited states)	CI-S

TABLE 1. Statistical Data (in kcal mol⁻¹) for 21 Reaction Energies (Small Molecules) Calculated with Different Quantum Chemical Methods with the def2-QZVPP Basis Set^a

	deviation from CCSD(T) (exp.) reference		
	MAD	MD	MAX
CCSD(T)	(1.76)	(-0.82)	(6.73)
CCSD	3.41 (4.78)	-3.02 (-3.84)	14.13 (17.23)
QCISD	3.07 (4.44)	-2.71 (-3.53)	12.11 (16.27)
CEPA/1	1.08 (2.53)	-0.35 (-1.17)	2.99 (7.14)
NCPF/1	1.03 (2.42)	-0.26 (-1.08)	2.44 (6.84)
SCS-MP3	2.22 (3.01)	-1.21 (-2.03)	7.06 (11.91)
SCS-MP2	3.41 (2.78)	-0.34 (-1.17)	9.58 (15.36)
MP2	5.54 (4.99)	-2.76 (-3.58)	26.39 (33.12)
B2PLYP	2.68 (2.45)	0.55 (-0.28)	6.33 (7.93)
B3LYP	3.18 (2.91)	1.72 (0.90)	8.72 (7.26)

Neese et al., Acc. Chem. Res. 42 (2009) 641-648

The scaling problem

Table 7.4 Formal scaling behavior, as a function of basis functions N , of various electronic structure methods

Scaling behavior	Method(s)
N^4	HF
N^5	MP2
N^6	MP3, CISD, MP4SDQ, CCSD, QCISD
N^7	MP4, CCSD(T), QCISD(T)
N^8	MP5, CISDT, CCSDT
N^9	MP6
N^{10}	MP7, CISDTQ, CCSDTQ

Electron correlation: requires better (larger) basis sets than Hartree Fock or DFT

Polarisation functions indispensable/diffuse functions recommended

Pople school (GAUSSIAN)	correlation consistent Dunning	
6-311G**	cc-pVDZ	3s2p1d/2s1p
6-311+G(2df,p)	cc-pVTZ	4s3p2d1f/3s2p1d
6-311+G(3df,2p)	cc-pVQZ	5s4p3d2f1g/4s3p2d1f
+ diffuse s-function	aug - diffuse functions (one for each angular momentum)	

Dunning (aug)-cc-pVnZ Basis Sets

	s	p	d	f	g	h	No.AO X/H
cc-pVDZ	<u>3/2</u>	<u>2/1</u>	1/0				14/05
cc-pVTZ	<u>4/3</u>	<u>3/2</u>	2/1	1/0			30/14
cc-pVQZ	<u>5/4</u>	<u>4/3</u>	3/2	2/1	1/0		55/30
cc-pV5Z	<u>6/5</u>	<u>5/4</u>	4/3	3/2	2/1	1/0	91/55
aug-cc-pVDZ	4/3	3/2	2/0				23/09
aug-cc-pVTZ	5/4	4/3	3/2	2/0			46/23
aug-cc-pVQZ	6/5	5/4	4/3	3/2	2/0		80/46
aug-cc-pV5Z	7/6	6/5	5/4	4/3	3/2	2/0	127/80

l/k refers to first row atom/h atom

How to reach the basis set limit for a given method?

- Use basis sets of increasing size
- Reaching the basis set limit faces the scaling problem
- More expensive methods generally need larger basis sets to reach limit
- Extrapolation formulas available

Basis set extrapolation - CBS limit

(aug)-cc-pVXZ

$$E_{\text{corr},X} = E_{\text{corr,lim}} + AX^{-3}$$

$$E_{\text{corr,lim}} = \frac{X^3}{X^3 - (X-1)^3} E_{\text{corr},X} - \frac{(X-1)^3}{X^3 - (X-1)^3} E_{\text{corr},X-1}$$

Two-point extrapolation

A. Halkier et al., CPL 286 (1988) 243

other and more sophisticated schemes, see refs. in

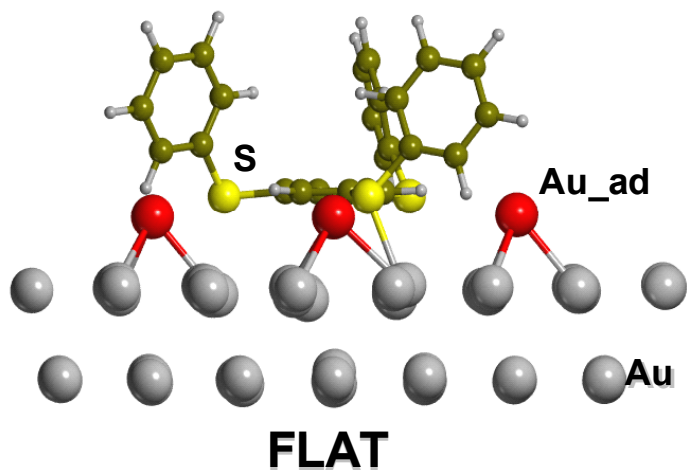
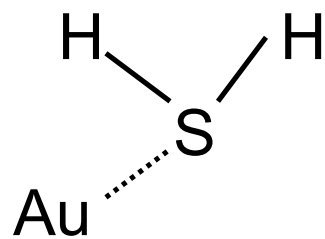
T. H. Dunning, Jr., JPC A 104 (2000) 9062

Note: You need to extrapolate also the Hartree-Fock energy

O₂ dissociation energy (kJ/mol)

Method	Basis set	D _e	D ₀
Obsd		505	494
UCCSD(T)FC	cc-pVTZ	476	
	cc-pVQZ	490	
	CBS(T,Q)	501	
	aug-cc-pVTZ	481	
	CBS	501	
	CBS+cv	503	
G2	G2	494	484

EMSL Computational Results DataBase - 255 Molecules, 41 Atoms
<http://www.emsl.pnl.gov:2080/proj/crdb/>

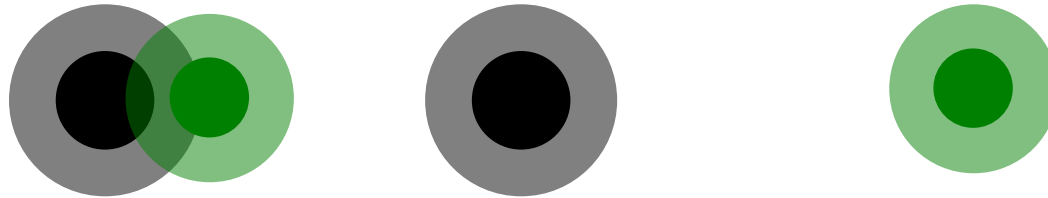


Au-S bond distance (pm) and H₂S-Au interaction energies (kJ/mol)

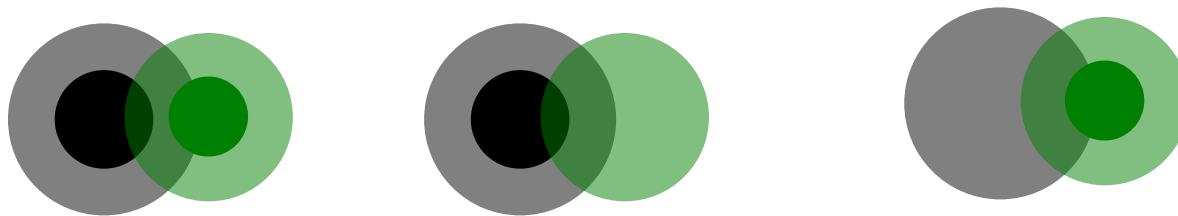
	$R_{\text{Au-S}}$	ΔE
PBE/TZVPP	247	-53.8
PBE+D ^b /TZVPP//PBE	247	-56.9
B3LYP/TZVPP//B3LYP	260	-26.5
B3LYP+D ^b /TZVPP	260	-30.7
CCSD(T)//B3LYP+D ^a	ΔE	$\Delta E/\text{CBS}(X,Y)$
aug-pVDZ	-27.4	-
aug-pVTZ	-32.8	-34.7 (D,T)
aug-pVQZ	-35.4	-37.0 (T,Q)
aug-pV5Z	-36.7	-37.7 (Q,5)

^b Au C₆ parameters from Tonigold and Gross

Basis Set Superposition Error



$$\Delta E = E_{AB} - (E_A + E_B)$$

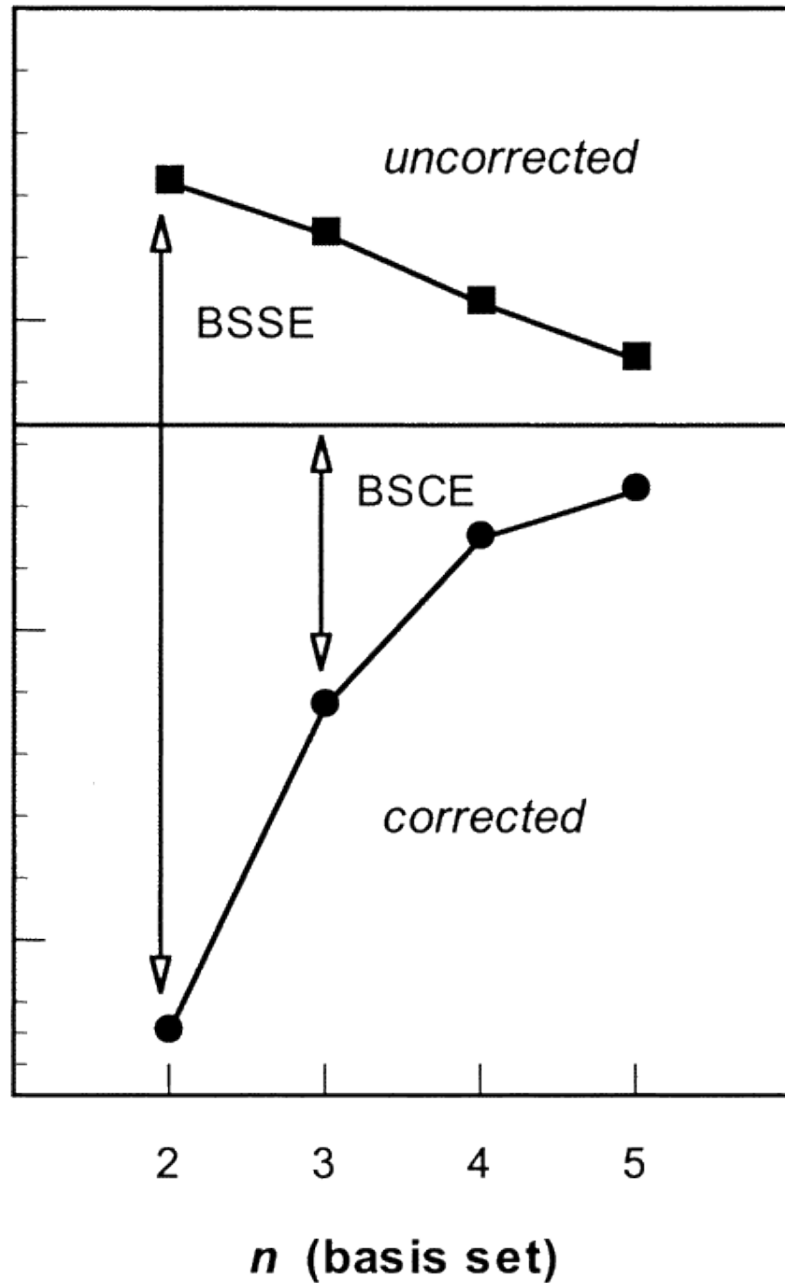


$$\Delta E^c = E_{AB} - (E_{A(B)} + E_{(A)B})$$

$$\varepsilon_A = (E_A - E_{A(B)}) \quad \varepsilon_B = (E_B - E_{(A)B})$$

Boys Bernardi function counterpoise method

BSSE



$D_e(\infty)$

BSSE

Basis set superposition error

BSCE

Basis set convergence error

Thom H. Dunning Jr.

"A road map for the calculation
of molecular binding energies"

J Phys Chem A 2000, 104, 9062-9080

Notes on BSSE

- BSSE for two subsystems is an indicator of balanced basis sets
- For small basis sets BSSE correction may lead to larger deviations from experiment (or basis set limit)
- BSSE corrected results are less basis set dependent
- There may be other errors (BSCE)
- Sizeable for intermolecular complexes, but also present for chemical bonds
- BSSE elimination is not always easy. How do you correct an energy barrier for BSSE?
- There is no BSSE for plane wave basis sets

There are cases, for which the Hartree Fock determinant is not a sufficiently good starting point

Stretched, almost dissociated bonds (H_2 example)

Biradicals, polynuclear transition metal compounds

Almost degenerate states (partially occupied d-shells)

Multireference cases

CAS (Complete Active Space) SCF

MC (Multi-configuration) SCF

+ MR (Multireference)-CI(SD)

The challenge of transition metal oxides

GGA functionals (PBE) are often not good enough, but hybrid functionals (B3LYP, PBE0, HSE) are one order of magnitude more expensive (with plane waves and pbc two orders of magnitude)

GGA functionals yield more delocalized electronic structures (delocalization of holes), preference for polar structures and too low energy barriers.

Partially occupied d-shells, the presence of more than one TM site and the decoupling of electron pairs in bond breaking processes requires a multi-reference treatment

- DFT limited to high-spin, low spin states require broken symmetry approximation
- in general, CCSD(T) is not good enough and not suitable as benchmark
- ab initio multi-reference methods cannot treat large enough systems reliably.

T_1 diagnostics

Is CCSD(T) applicable?

Is a single determinant a good reference function?

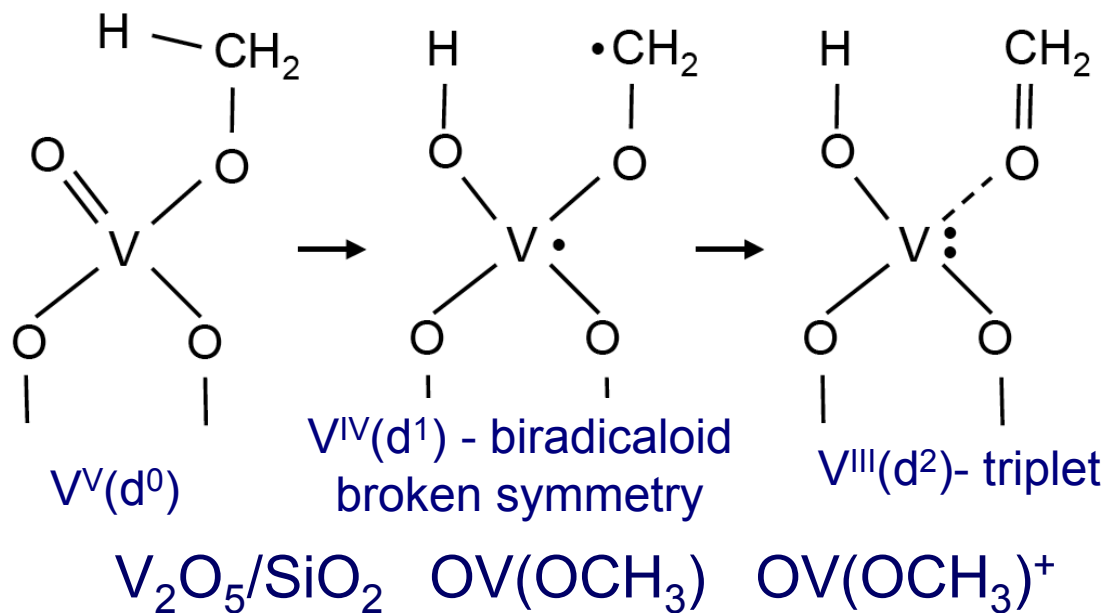
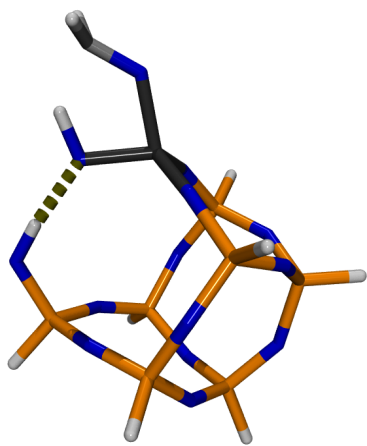
$$\Psi = \left[1 + T_1 + \left(T_2 + \frac{1}{2} T_1^2 \right) + \left(T_2 T_1 + \frac{1}{3!} T_1^3 \right) + \dots \right] \Phi_0$$

$$T_1 \Phi_0 = \sum_i \sum_m t_i^m \Phi_i^m$$

$$T_1 = \|\mathbf{t}_1\| / \sqrt{N_e} \quad \|\mathbf{t}_1\| = \sum_i \sum_m (t_i^m)^2$$

$T_1 > 0.02$ not a clear single reference state

H-Transfer: surface complex - gas phase model



Calculated

$E^\#, B3LYP$

$E^\#, CCSD(T)$

Observed

$E^\#_{intrinsic} (0 K)$

broken symmetry

doublet

154

147

80

(137)

131

T1=0.07

137±10

estimate

52±11

Döbler, Pritzsche, Sauer, JACS 127 (2005) 10861

**If you would like to join our group as
postdoc or PhD student -**

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