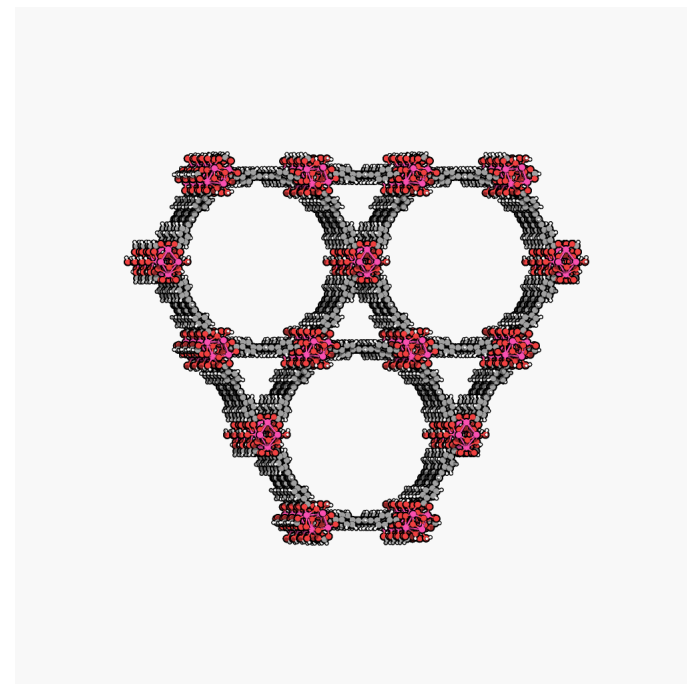
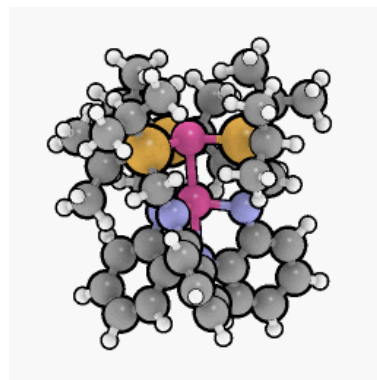
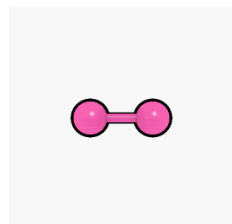


Multiconfigurational Wave Function Theory: A perspective on the examination of transition metals in porous materials

Varinia Bernales



Current Topics in Theoretical Chemistry School

September 24th, 2016

Trujillo - Peru



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Electron Correlation

$$\mathbf{E}_{\text{FCI}} - \mathbf{E}_{\text{HF}} = \mathbf{E}_{\text{Corr}}$$

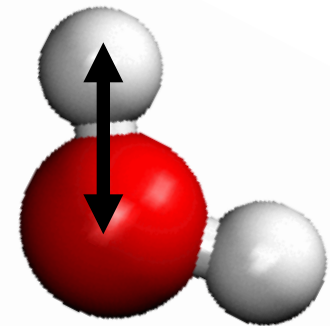
Electron Correlation

- Two types of electron correlation

Basis Set Correlation for H₂O with a DZ Basis

Geometry	E_{corr} (hartree) ^a
R_e	-0.148028
1.5 R_e	-0.210992
2.0 R_e	-0.310067

^aData from Harrison, 1983.



*Dynamical correlation, electrons instantaneously avoid each other.
It should become less important at stretches geometries → electrons are further apart
But in this table, the correlation energy increases with the stretching ... Why?*

**Non-dynamical
Correlation**

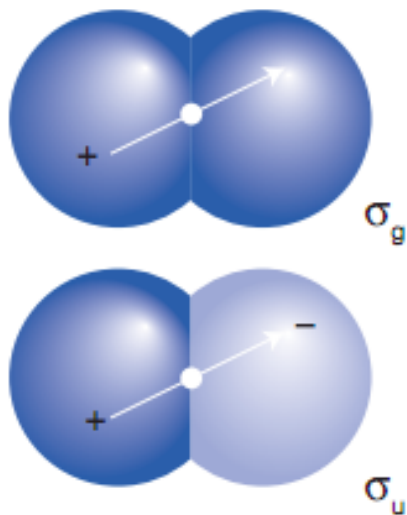
What Causes the *Nondynamical* Correlation?

- Recall the correlation energy is the difference between Full CI and Hartree-Fock.
- We know Hartree-Fock neglects instantaneous electron-electron repulsions (“dynamical correlation”).
- What else is it missing? It does not account for nearly degenerate electron configurations



Simplest Example of Degeneracy: Stretched H_2

- For minimal basis H_2 , only two $1s$ functions, one on each H atom: ϕ_A, ϕ_B . Restricted Hartree-Fock orbitals determined completely by symmetry. Let overbars denote β spin.



$$\phi_{\sigma} = \frac{1}{\sqrt{2(1 + S_{12})}} (\phi_A + \phi_B)$$

$$\phi_{\sigma^*} = \frac{1}{\sqrt{2(1 - S_{12})}} (\phi_A - \phi_B)$$

Slater determinant

$$|\phi_{\sigma} \bar{\phi}_{\sigma}\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{\sigma}(1) & \bar{\phi}_{\sigma}(1) \\ \phi_{\sigma}(2) & \bar{\phi}_{\sigma}(2) \end{vmatrix}$$



Determinant Expansion

Slater determinant $|\phi_\sigma \bar{\phi}_\sigma\rangle = \frac{1}{\sqrt{2}} [\phi_\sigma(1)\bar{\phi}_\sigma(2) - \phi_\sigma(2)\bar{\phi}_\sigma(1)]$

- The expanded determinant looks like the sum of four determinants made of atomic spin orbitals:

$$|\phi_\sigma \bar{\phi}_\sigma\rangle = \frac{1}{2(1 + S_{12})} [|\phi_A \bar{\phi}_A\rangle + |\phi_A \bar{\phi}_B\rangle + |\phi_B \bar{\phi}_A\rangle + |\phi_B \bar{\phi}_B\rangle]$$

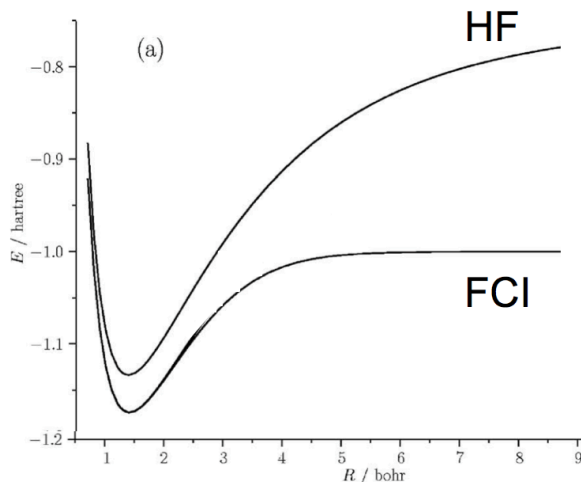
So what's the problem?

The **first** and **last terms** are **ionic valence bond structures** and should not contribute to the wavefunction (they place both electrons on one of the hydrogens) as $R_{AB} \rightarrow \infty$.

However, they are required by RHF. Thus, RHF does not work for bond-breaking processes in general.



Configuration Interaction



*Configuration interaction (CI) is perhaps the easiest electronic structure theory method to understand but the hardest to implement efficiently.**

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{ra} c_a^r|\Phi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \sum_{r<s<t,a<b<c} c_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \dots$$

The number of excited Slater Determinants increases **factorially** with the number of electrons and basis functions

*An Introduction to Configuration Interaction Theory. C. David Sherrill

*Figure modified from *J. Chem. Phys.* **2007**, *126*, 244104.

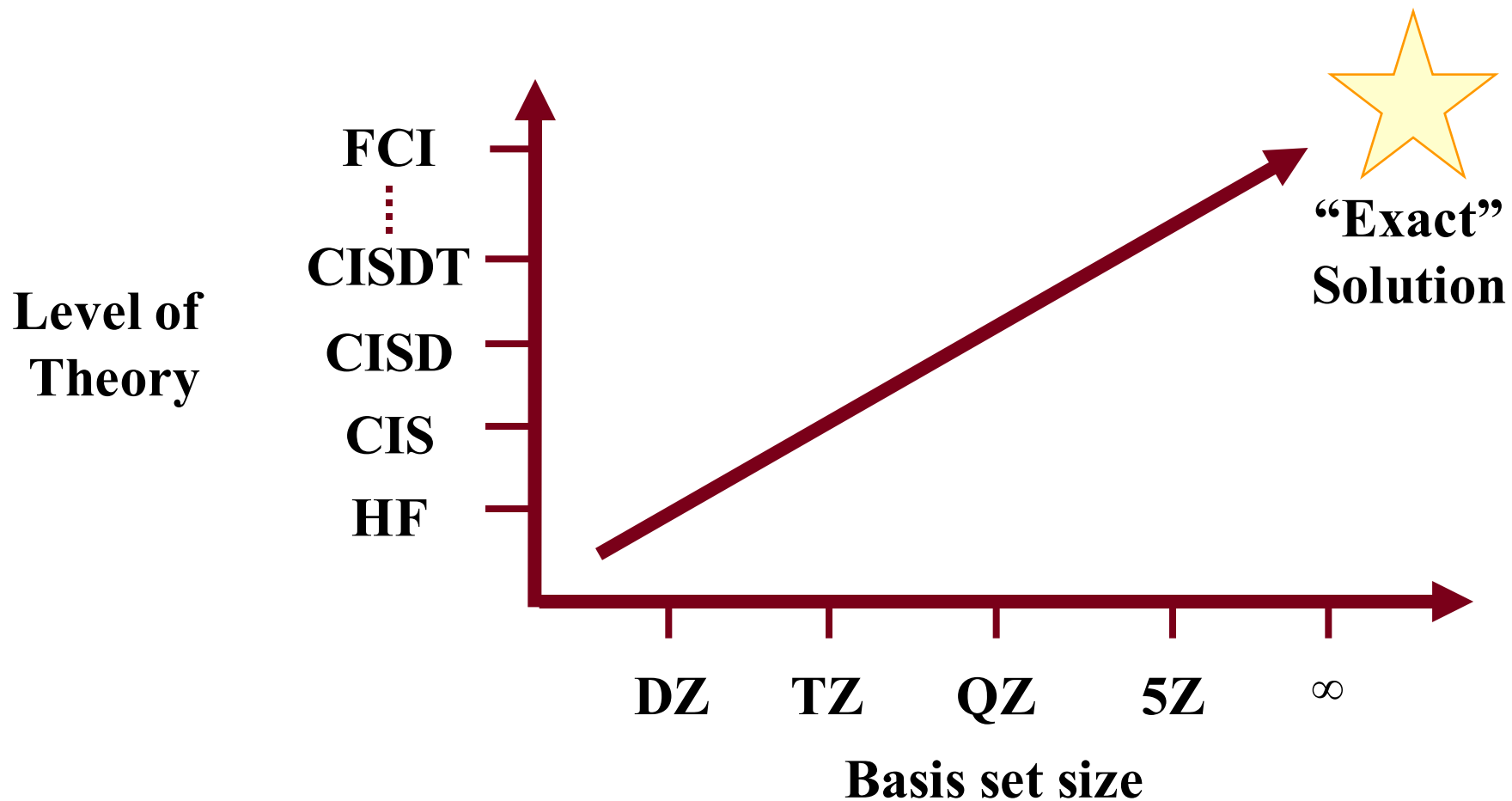
Note that the basis set in Figure is aug-cc-pV6Z



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Systematically Improved Accuracy with CI



Conceptual Test

If you compare the geometry of a molecule computed at the HF level compared to the same molecule computed at the CI level, in general, do you expect the bond lengths at the CI level to be longer or shorter than those at the HF level?

Explain your reasoning.



A single determinant: Is it not enough?

- Molecules with partially broken bonds
- Transition metal compounds
- Compounds of strongly electronegative first-row atoms (e.g. F and O)
- Large conjugated systems
- Majority of excited states



MCSCF

- We need to **include all nearly degenerate electron configurations** (or determinants) in our starting (“**reference**”) wavefunction
- Need to find orbitals which minimize the energy of the mixture of near-degenerate determinants: this is multi-configurational self-consistent-field (MCSCF)
- But not the short-range problems that arise as $R_{12} \rightarrow 0$: the so-called dynamical correlation.
- Describe the *nondynamical* (or “*static*”) correlation that comes from configurational near-degeneracies or from deficiencies in the HF orbitals.
- Need to use multi-configurational references for subsequent treatment of dynamical correlation; multi-reference CI, multi-reference PT, multi-reference CC, ...
- Or perhaps some sort of DFT on top of MCSCF (not discussed here)*

J. Chem. Phys.* **2012, *137*, 044104

J. Chem. Theory Comput.* **2014, *10*, 3669



MCSCF Configuration Space

- First simplifying assumption: we will choose a subspace of MOs, the active space, from which all configurations will be built.
- Then include all configurations generated by allocating electrons to these orbitals: a Full CI in the AS.
- A nice naïve approach would be the valence AOs for all atoms, but this quickly gets very large ...



Orbital Spaces for CAS Wave Functions

- Reduce the choice to active orbitals and electrons. (will usually have some doubly occupied orbitals – the **inactive space**.)
- Should include all orbitals where the occupation number change significantly during a process (like a reaction, excitation, ionization), or where the occupation number differ significantly from two or zero.

Virtual



Active



Inactive

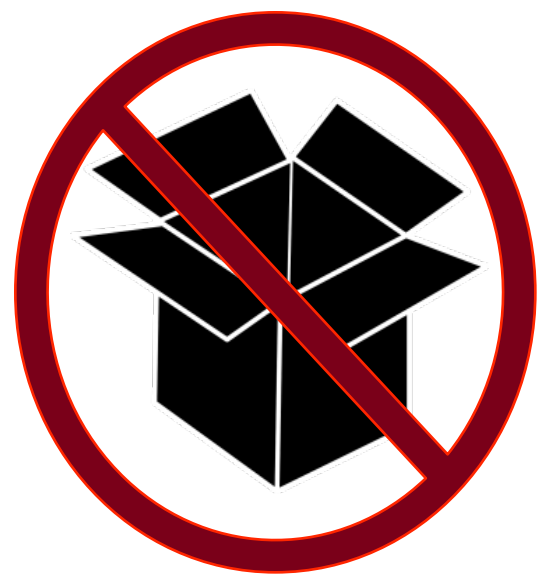


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Choosing active spaces

- Sometimes the problem seems simple: H_2 ground-state potential curve will need $(\sigma_g, \sigma_u)^2$, or the two $1s$ orbitals, as the AS. Bigger diatomic seem similarly easy: N_2 ground-state will need $(\sigma_g, \pi_u, \pi_g, \sigma_u)^6$ or the $2p$ orbitals.
- In most polyatomic the full valence will be too large.
- Spectroscopy of C_6H_6 : use the six p MOs.
- Breaking a C–H or C–C bond in a hydrocarbon: use σ, σ^* .
- **Identify the orbitals involved in the process.**
- **You may have to refine this choice – Clearly, we are very far from a black-box approach!**



Optimization of MCSCF Wave Functions

- Wave function:

$$\Psi = \sum_m \Phi_m c_m$$

- Or:

$$|0\rangle = \sum_m |m\rangle c_m$$

- Objective: to optimize the MOs and the MC coefficient using the variational principle

$$E = \frac{\langle 0 | \hat{H} | 0 \rangle}{\langle 0 | 0 \rangle}$$

Non-relativistic Hamiltonian (Second Quantization)

- Hamiltonian

$$\hat{H} = \sum_{ij} h_{ij} \hat{E}_{ij} + \frac{1}{2} \sum_{ijkl} g_{ijkl} (\hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il})$$

- Where,

$$h_{ij} = \int \phi_i^*(\mathbf{x}) \hat{h}(\mathbf{x}) \phi_j(\mathbf{x}) d\mathbf{x}$$

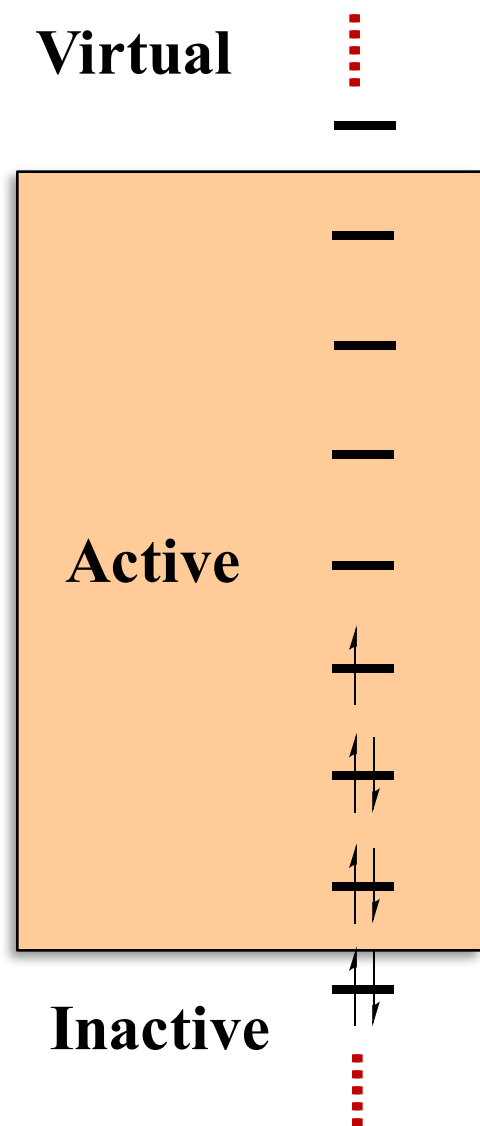
$$g_{ijkl} = \int \phi_i^*(\mathbf{x}_1) \phi_k^*(\mathbf{x}_2) \hat{G}(\mathbf{x}_1, \mathbf{x}_2) \phi_j(\mathbf{x}_1) \phi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

- Are the one- and two-electron integrals.
- “Excitation operator” $\hat{E}_{ij} = \hat{a}_{i\alpha}^\dagger \hat{a}_{j\alpha} + \hat{a}_{i\beta}^\dagger \hat{a}_{i\beta}$

The CASSCF Method

Complete Active Space SCF

For $S = 0$



Active Space	Slater Determinants
2 e ⁻ in 2 Orbitals	4
4 e ⁻ in 4 Orbitals	36
6 e ⁻ in 6 Orbitals	400
8 e ⁻ in 8 Orbitals	4 900
10 e ⁻ in 10 Orbitals	63 504
12 e ⁻ in 12 Orbitals	853 776
14 e ⁻ in 14 Orbitals	11 778 624
16 e ⁻ in 16 Orbitals	165 636 900
18 e ⁻ in 18 Orbitals	2 363 904 400
20 e ⁻ in 20 Orbitals	34 134 779 536



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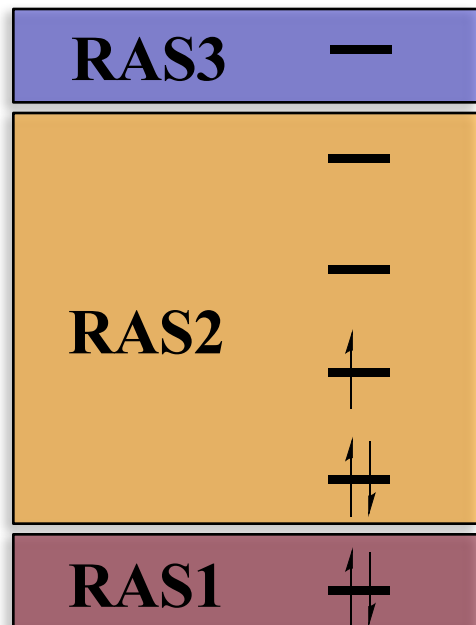
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Bigger active spaces?

Virtual



Restricted Active Space Self-Consistent Field



Inactive Orbitals $n_{occ} = 2$

RAS1 orbitals: Max number of holes

RAS2 orbitals: $n_{occ} = \text{varies}$

RAS3 orbitals: Max number of electron

A CAS plus excitations out of some doubly occupied orbitals into some virtual orbitals.

Inactive



CAS: RAS1 and RAS3 are empty

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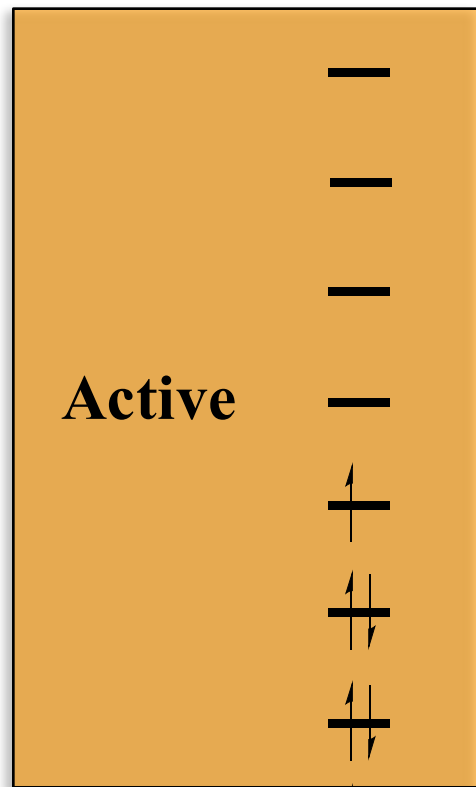


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The GASSCF Method

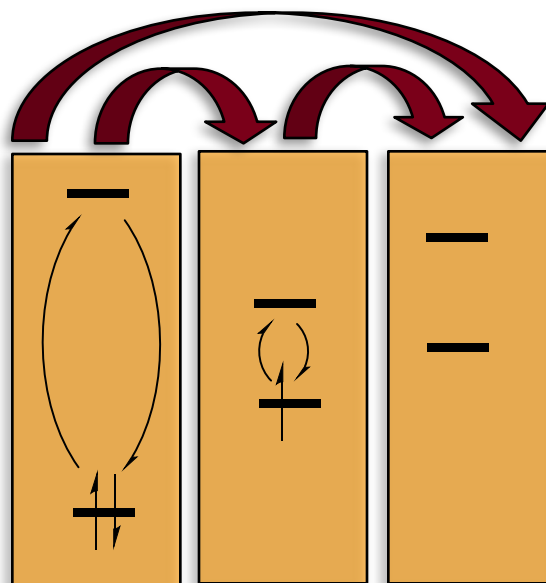
Generalized Active Space SCF

Virtual



Active

Inactive



Infinite number of subspaces

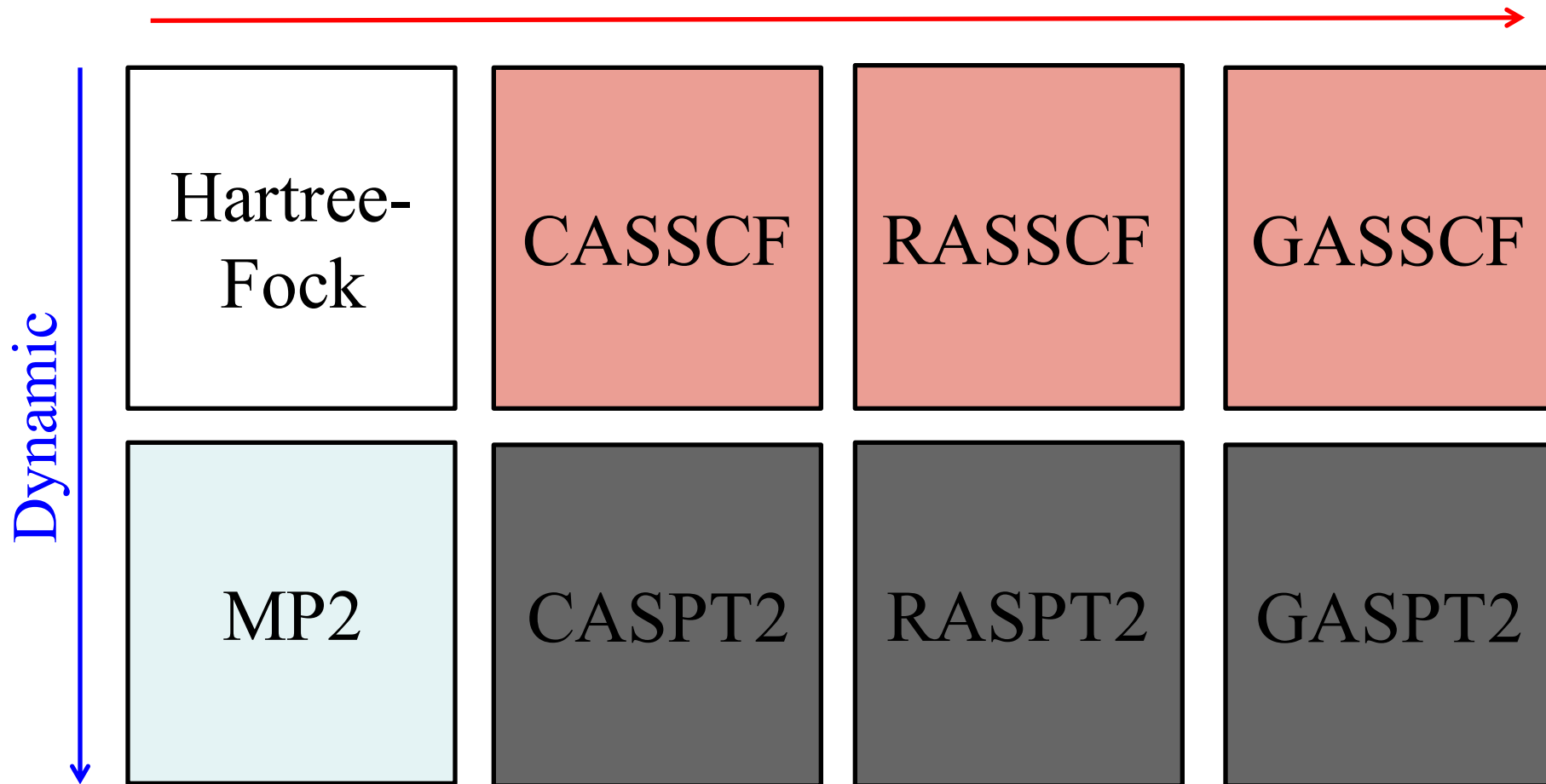


Advantages:

1. Elimination of ineffective configurations
2. Exploration of larger active spaces

... and CASSCF alone isn't enough!

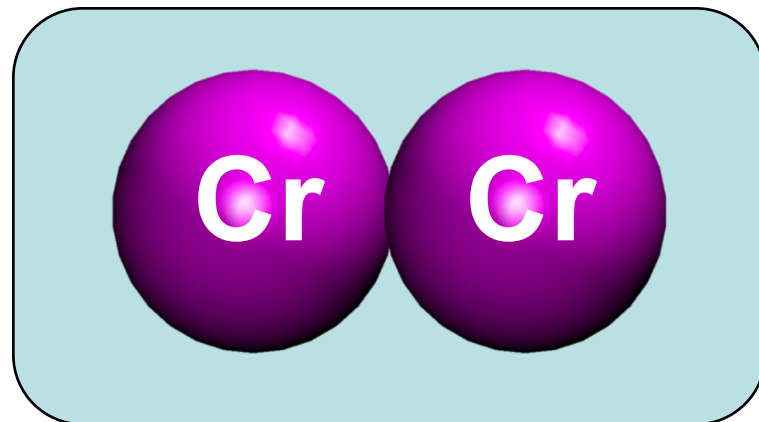
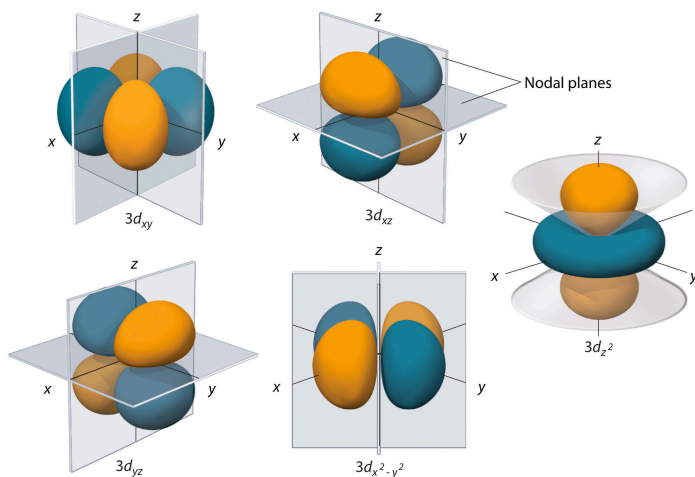
Static





Chromium Dimer (*golden case*)

- Five $3d$ orbitals and $4s$



- $\text{Cr}_2 \rightarrow$ sextuple bond?

The bond order between two atoms

- **Bonding orbital (BO)** and **antibonding orbital (AO)**



- If occupation of **BO** is $\eta_b = 2 - x$ occupation of **AO** $\eta_a = x$
; $\eta_b + \eta_a = 2$

- **Effective Bond Order (EBO)**
$$\text{EBO} = \frac{\sum \eta_b - \sum \eta_a}{2}$$

- To be compared with the **Formal Bond Order (FBO)**

Chromium Dimer

- The Golden case: its ground state is highly multiconfigurational in character: The weight of the closed-shell HF configuration in the total wavefunction is only **45%** at the equilibrium geometry
- CASSCF/CASPT2(12,12)
- **Cr–Cr bond length:** 1.66 Å (1.68 Å)*
- **Bond energy:** 38 kcal/mol (35 kcal/mol)*
- The **EBO** is 4.45, not 6
- The weakening of the bond is caused by two factors
 - Different size of the $3d$ and $4s$
 - $4s-4s$ is larger than $3d-3d$

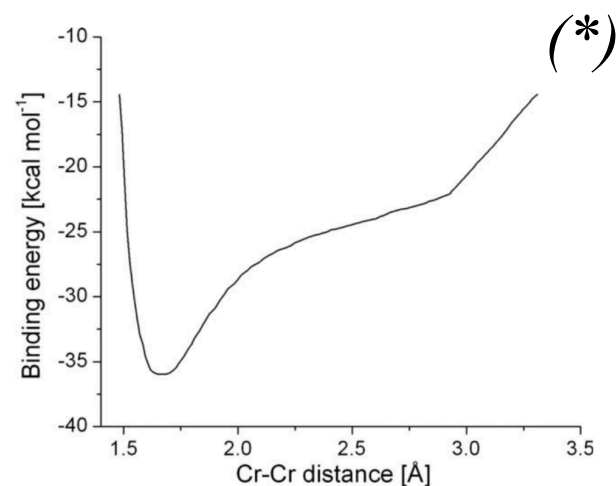


Fig. 1. The experimental potential energy curve for Cr₂ [21].

Chromium Dimer

- DFT: B3LYP/cc-pVTZ

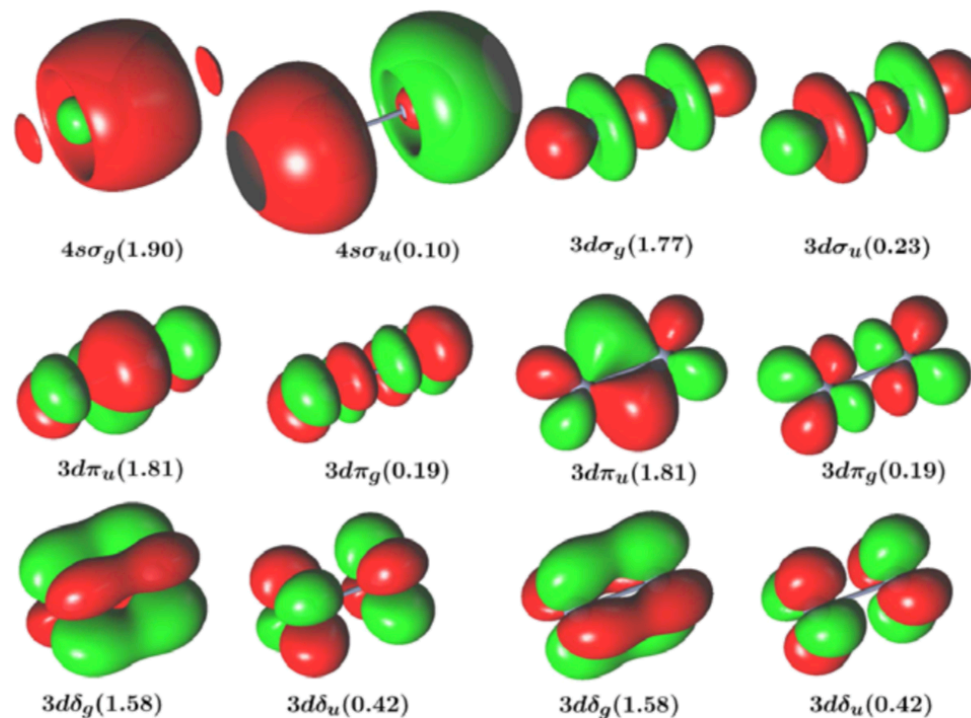
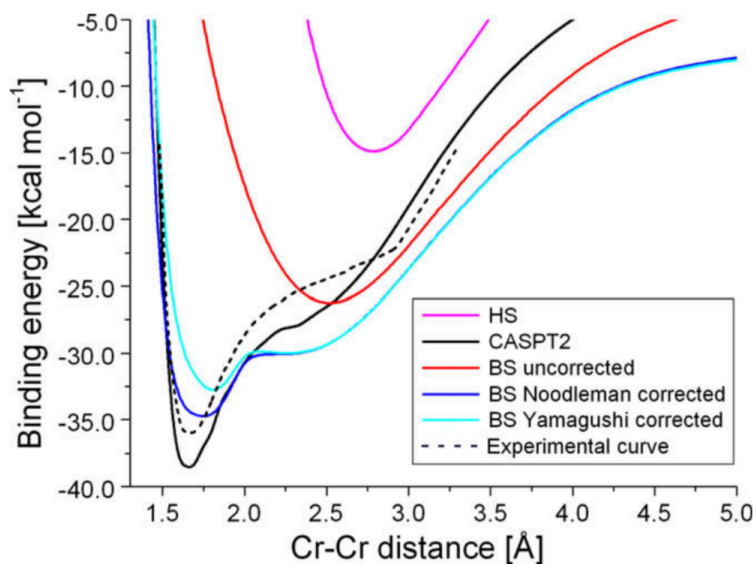
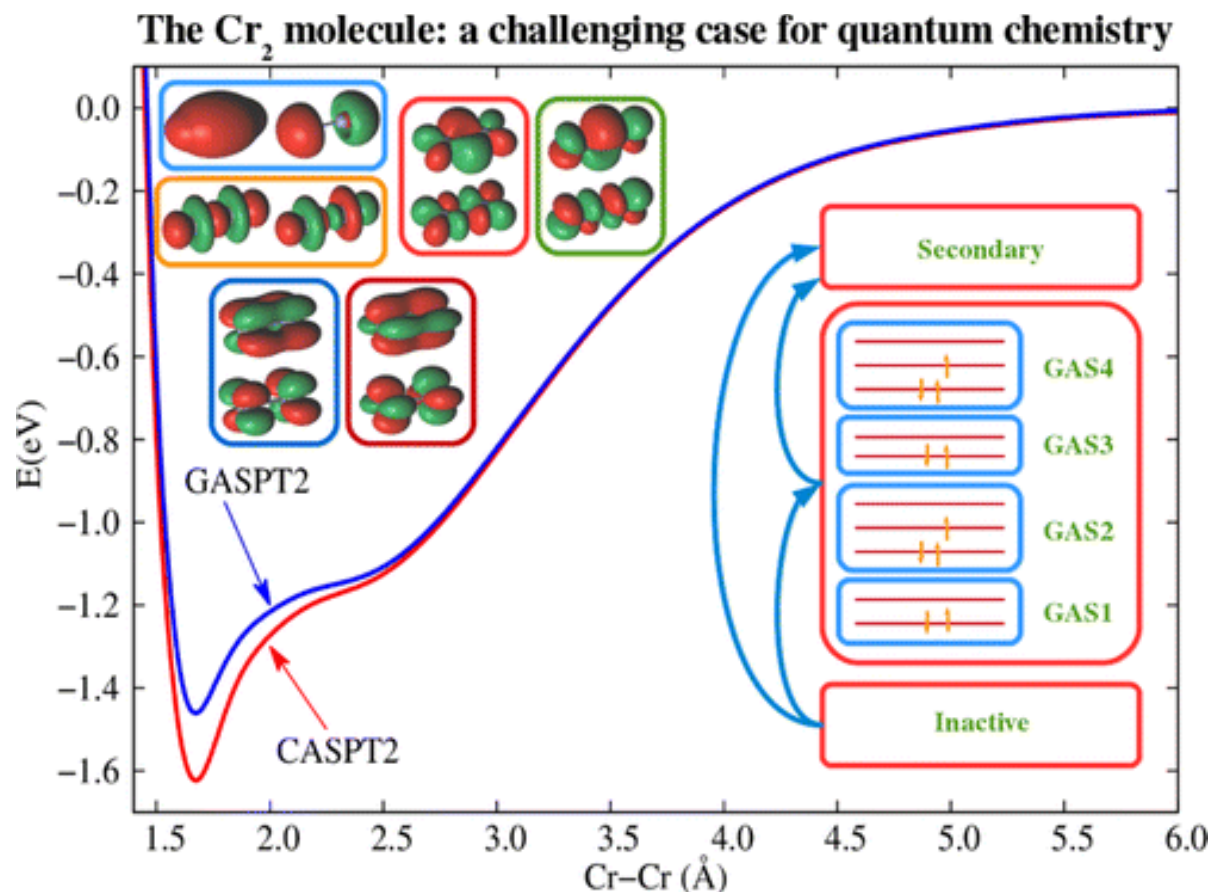


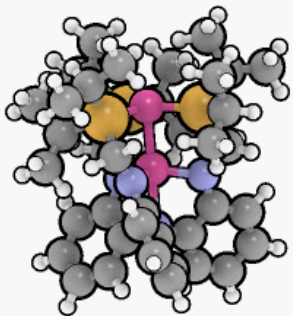
Fig. 2. The natural orbitals for the chromium diatom. Orbital labels and occupation numbers are given below each orbital (contour lines at the density 0.07 e/au³).



Cr₂ – GASPT2

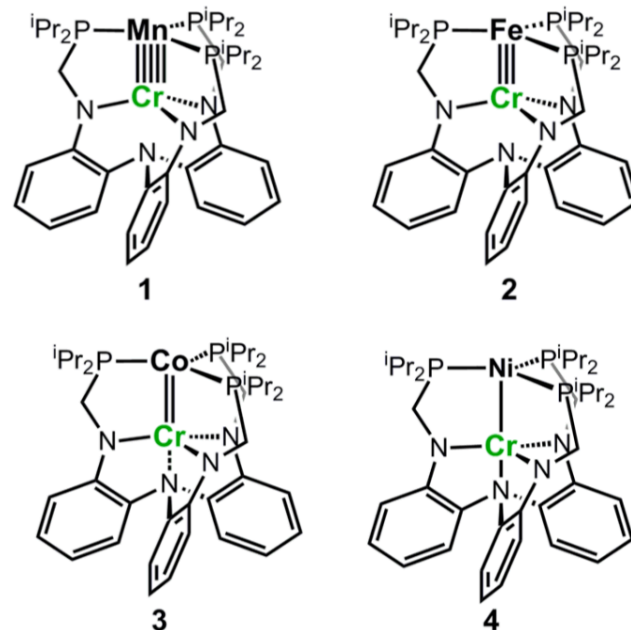
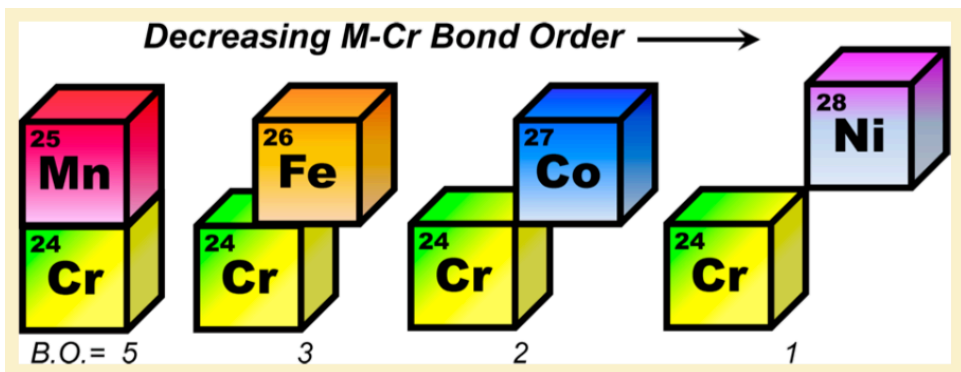
- The user defines an arbitrary number of AS.
- With min and max number of electron per AS.
- GAS allows to remove the ineffective configurations





Molecular Problems

- More Multiple Bonds!



	1 MnCr	2 ^a FeCr	3 ^a CoCr	4 NiCr
M-Cr (Å)	1.8192(9)	1.943(1) 1.944(1)	2.135(1) 2.145(1)	2.4105(7)
r^b	0.78	0.83	0.92	1.04

J. Am. Chem. Soc. **2013**, *135*, 13142.

Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Why is important?

More than one metal can favor multiple one-electron transfer processes

Molecular Problems

- Methodology
- Gas-phase geometry optimization with the PBE functional (Turbomole)*
 - Def2-TZVPP for metals
 - Def2-TZVP for non C nor H
 - Def2-SVP for C and H
- Followed by CASSCF/CASPT2 on top of the DFT optimized geometries (MOLCAS)
 - ANO-RCC-VTZP for metals
 - ANO-RCC-VDZP for non C nor H
 - ANO-RCC-MB for C and H

How do we chose the active spaces?

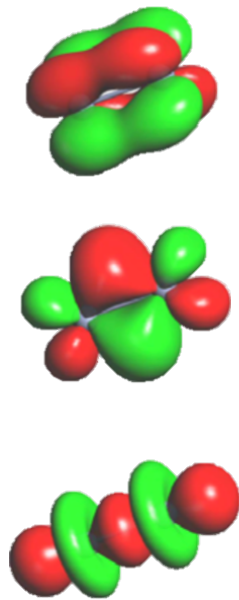
- Let us think ...
- What do we want to achieve?
 - Electronic structure of the MM bond
- We have two metal centers : five $3d$ orbitals
- Then, let us count the number of electrons
- Cr formal oxidation state is +3 and M is zero.

15 orbital were necessary: 3d for Cr; 3d for M and also 4d!! Second shell effects

	MnCr	FeCr	CoCr	NiCr
M	7e	8e	9e	10e
Cr	3e	3e	3e	3e
Total e	10e	11e	12e	13e

How can we distribute these electrons?

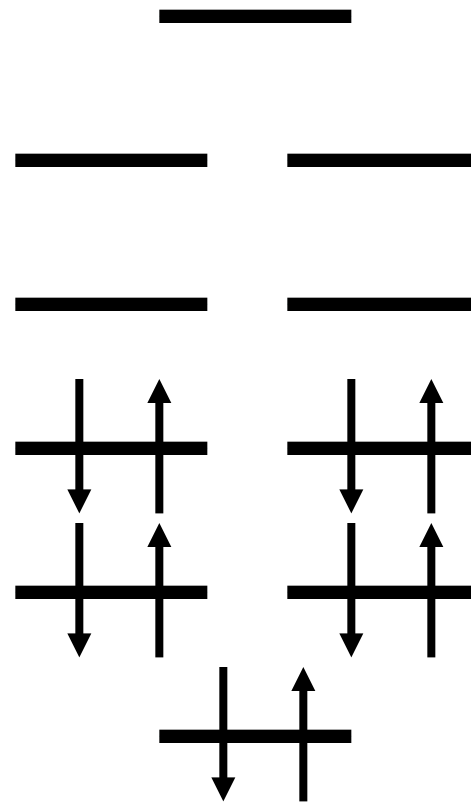
- We have:



$$\delta(d_{xy}, d_{x^2-y^2})$$

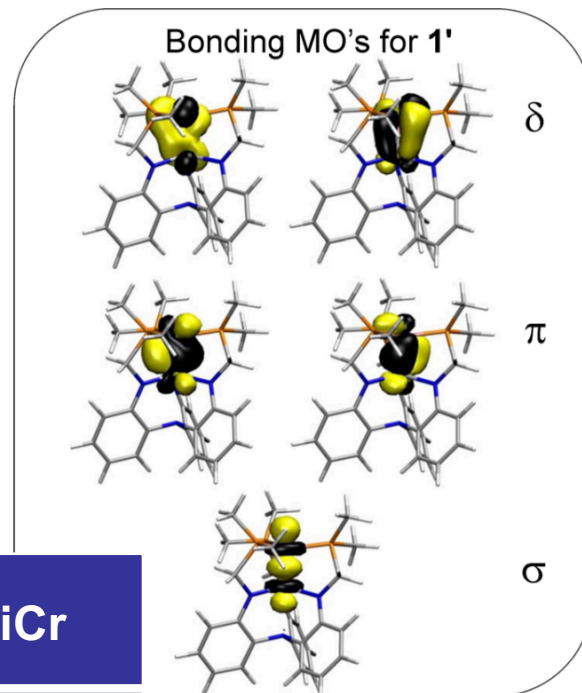
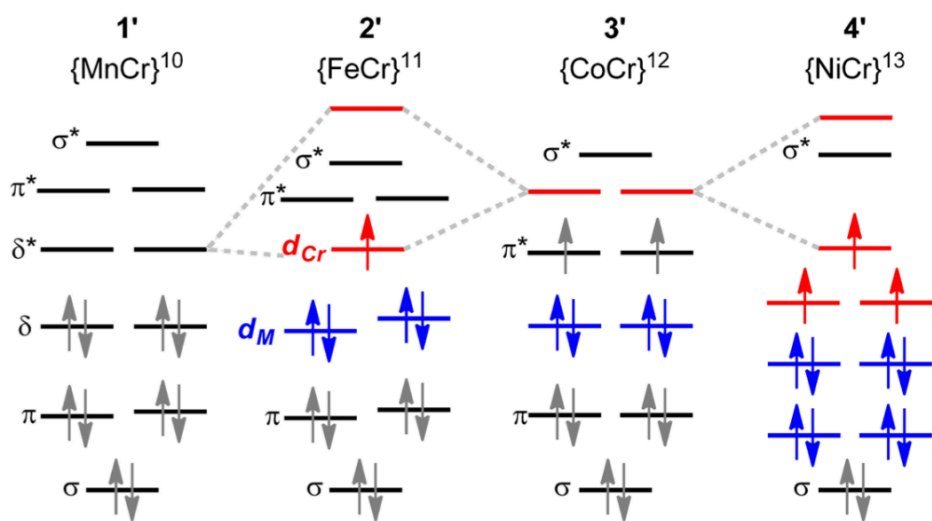
$$\pi(d_{xz}, d_{yz})$$

$$\sigma(d_z^2)$$

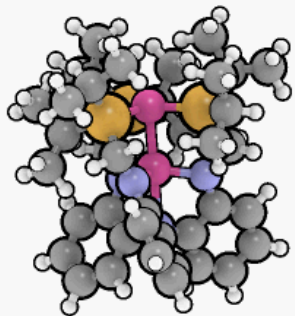


Molecular Problems

- More Multiple Bonds!



Partial O.S.	MnCr	FeCr	CoCr	NiCr
M	0.9	0.6	0.5	0.3
Cr	2.1	2.4	2.5	2.7



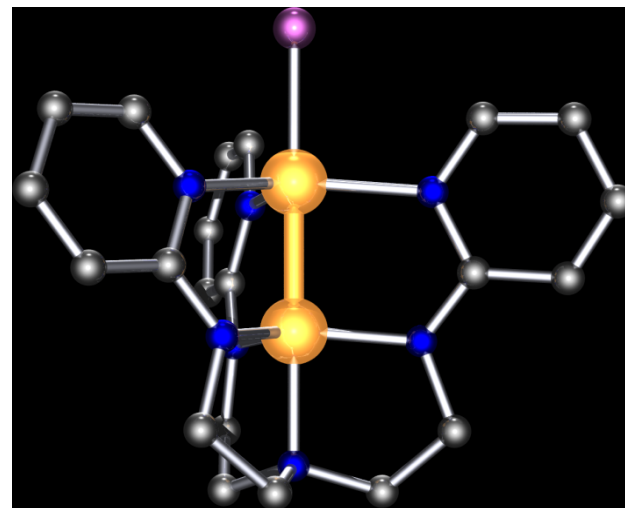
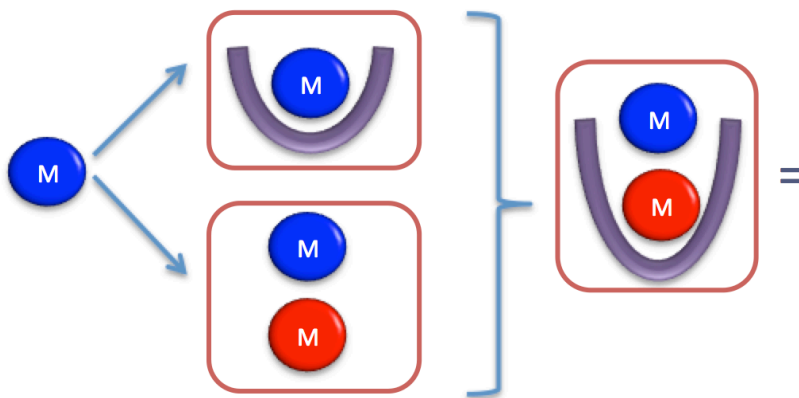
Molecular Problems

- Comparison with DFT

SI Table 2. Calculated relative energies of 1-MnCr for various possible spin states at DFT, CASSCF, and CASPT2 levels of theory.

Spin state	DFT (PBE) (kcal/mol)	CASSCF (kcal/mol)	CASPT2 (kcal/mol)	Percent of main configuration
singlet	0	0	0	54 %
triplet	8.50	6.932	17.130	59 %
quintet	18.81	19.851	44.864	73 %
septet	32.31	19.337	66.782	88 %

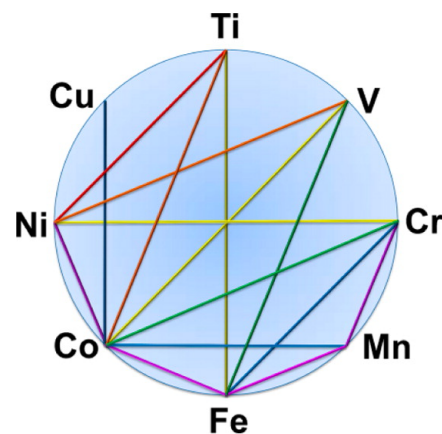
What can theory help with?



*Fundamental understanding of structure / bonding
electronic / magnetic properties*

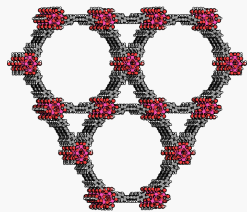
Applications

highly tailored for function / catalysis?



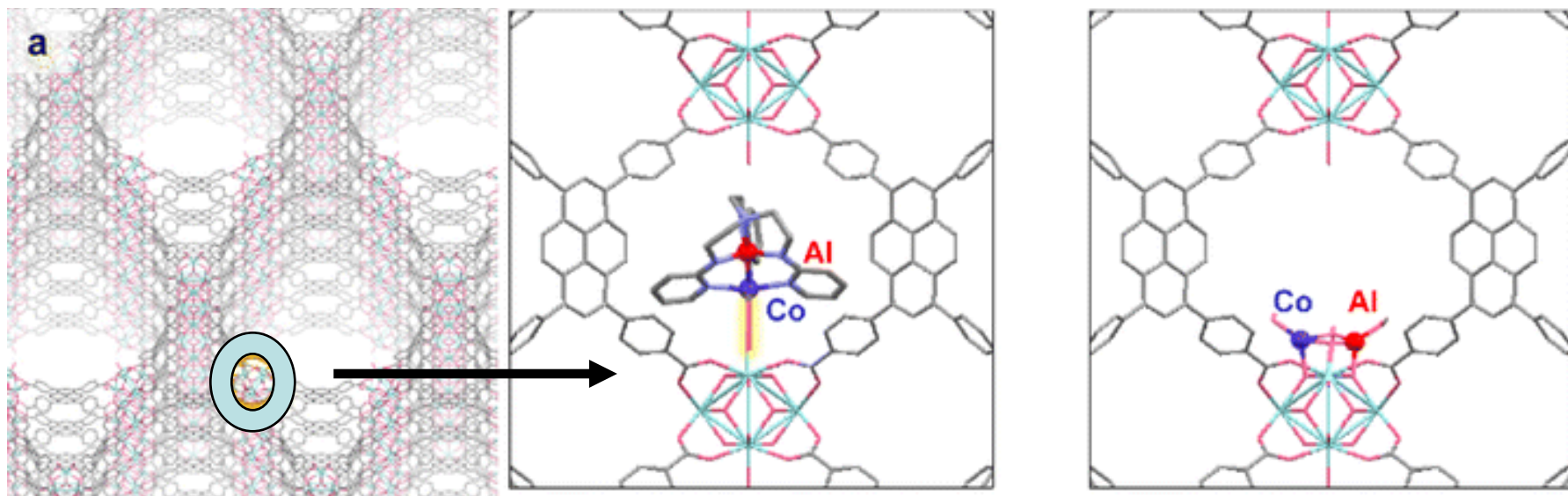
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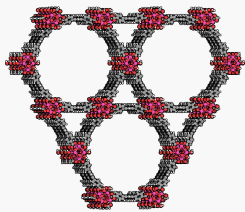


Let's move to Larger Systems Now

MOF

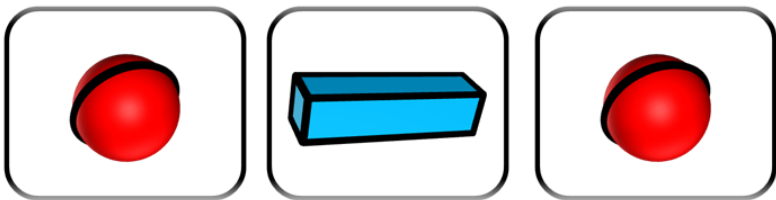


Molecular complexes are deposited on porous materials

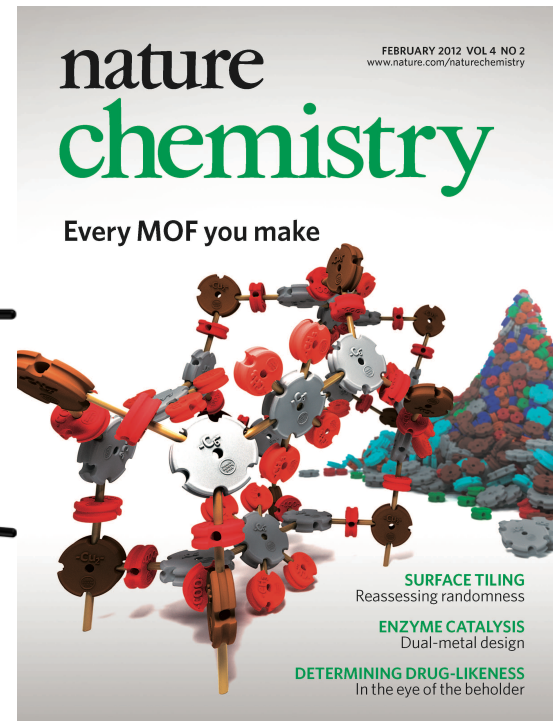
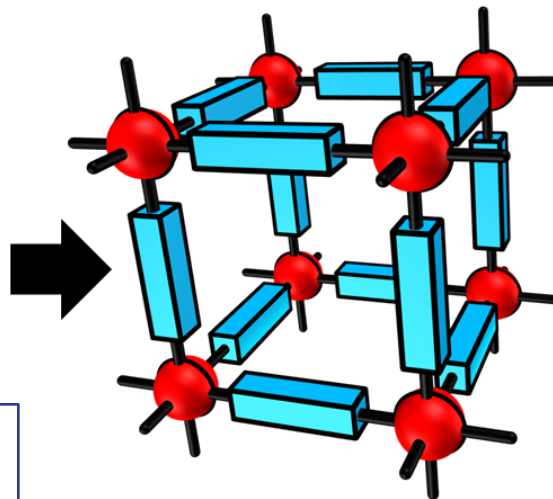


Metal Organic Frameworks

- well-ordered crystalline structures
- **Modular building blocks** can be interchanged leading to materials with novel properties
- The number of **possible combinations is enormous...**

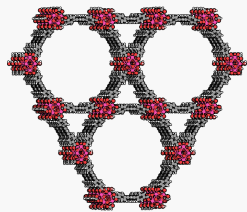


metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures.



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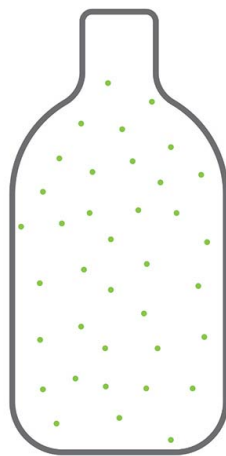
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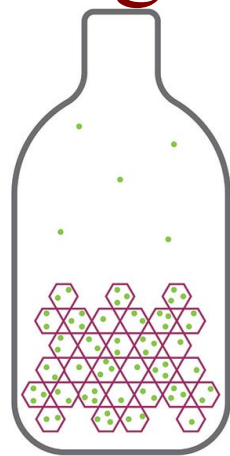
“One gram” of NU-1000 has the surface area of a soccer field

- Enormous internal **surface areas**

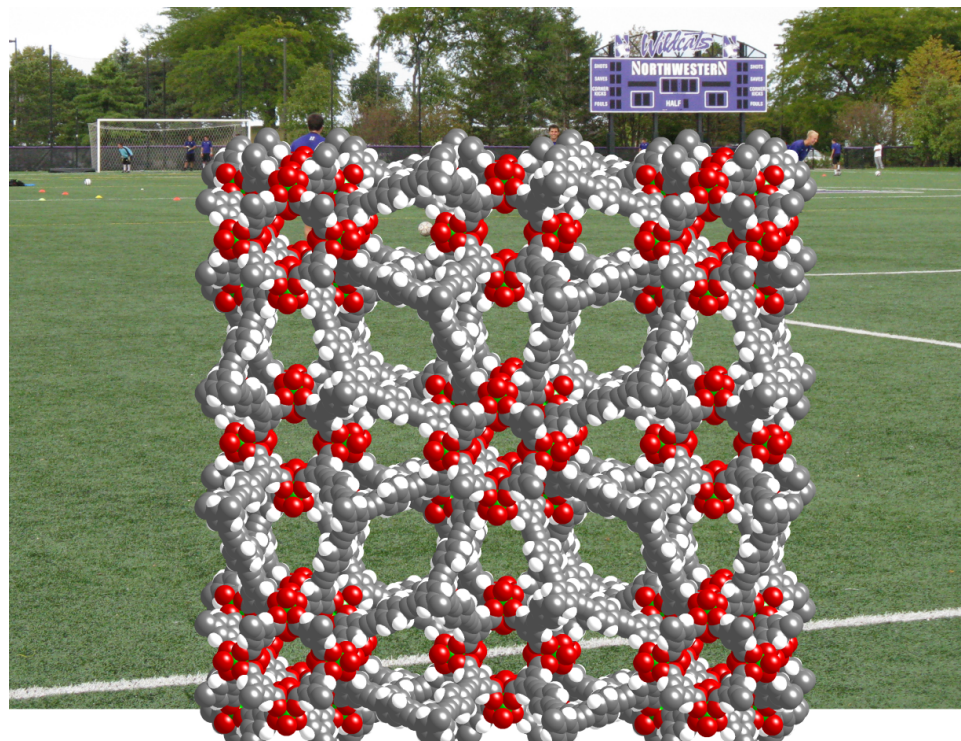
Gas Storage



gas storage tank

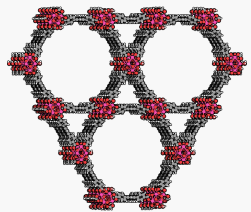


MOF-loaded tank



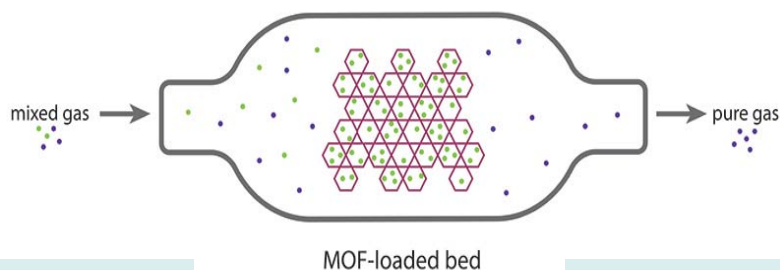
- Gas molecules: CO_2 , CO , N_2 , NO_2 , H_2S , C_2H_4 , C_2H_6
- Gas molecules can interact with the linker or the metal-oxide building block

“One gram” of NU-1000 has the surface area of a soccer field



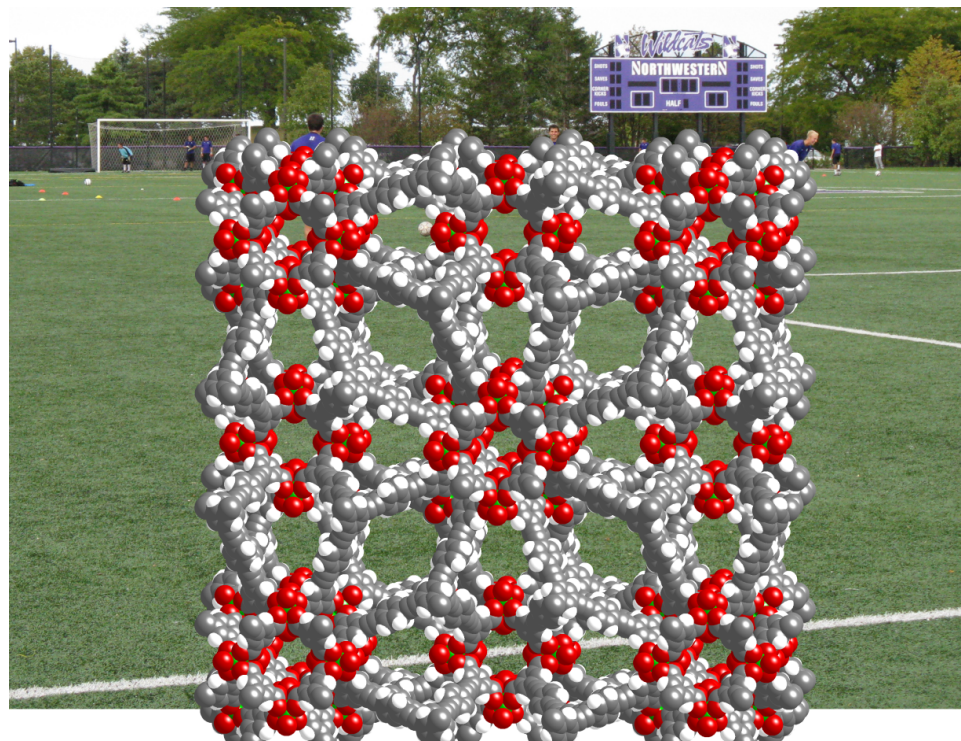
- Enormous internal **surface areas**

Gas Separation

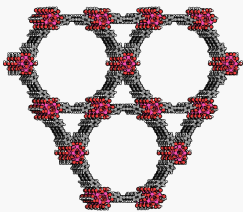


Reactants

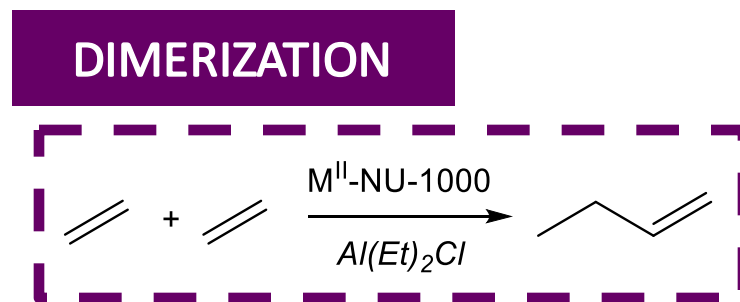
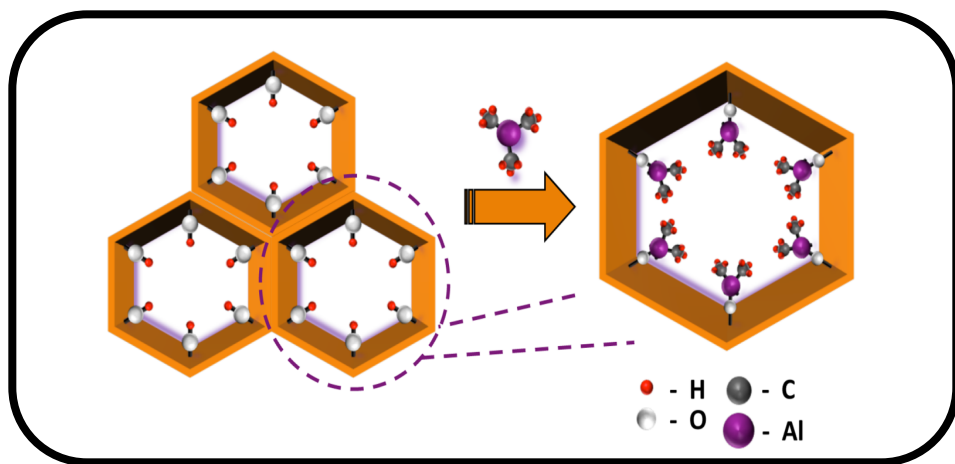
Products



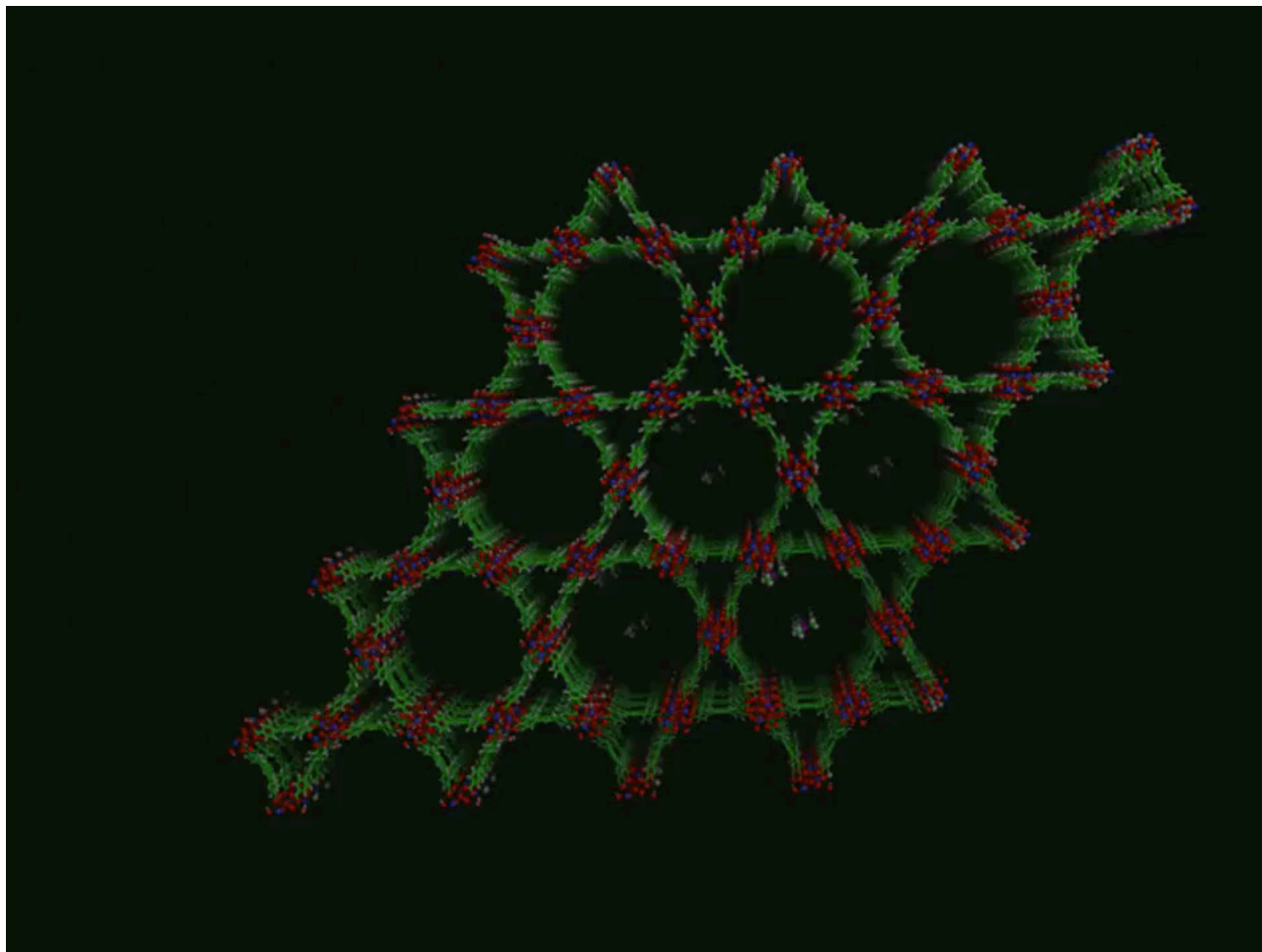
- Now, what happens if instead of separating we want to pass reactants through?



Catalytic Activity for Ethylene Dimerization: Decorated MOF with Co and Ni



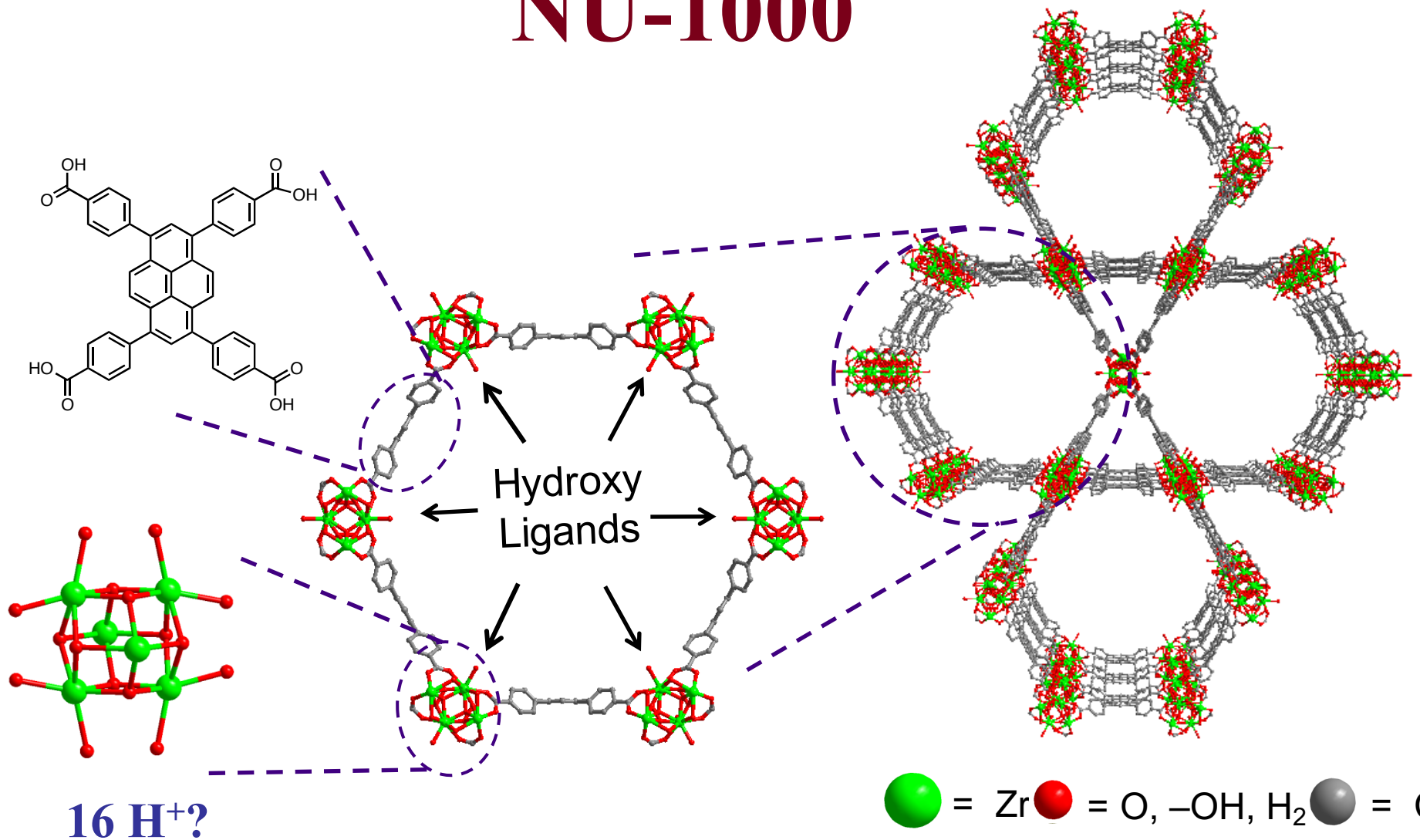
NU-1000



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NU-1000



J. Am. Chem. Soc. **2013**, *135*, 10294
Proton topology: *J. Phys. Chem. Lett.* **2014**, *5*, 3716.



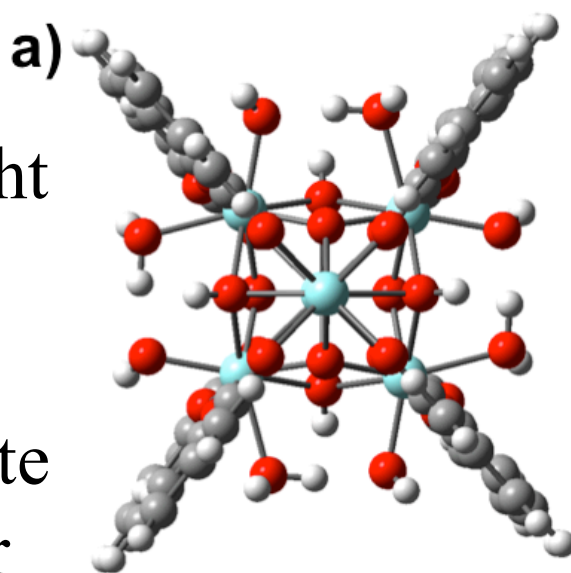
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The Model: NU-1000

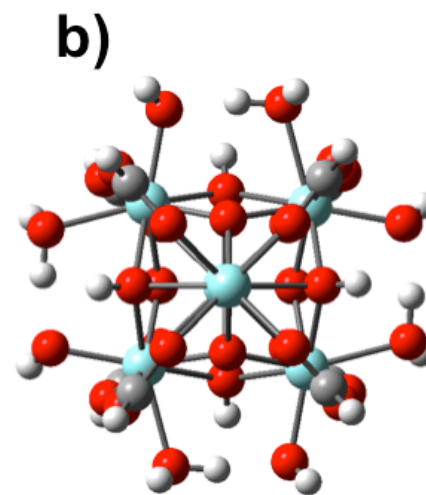
Different models for different problems!

- Cluster model:

- Zr_6 -node coordinated to eight organic ligands
- Ligands can be cropped to benzoate (a), formate (b), or acetate.



Deposition of M(II)



Catalysis

Deposition of M(II):

Cobalt(II) d^7

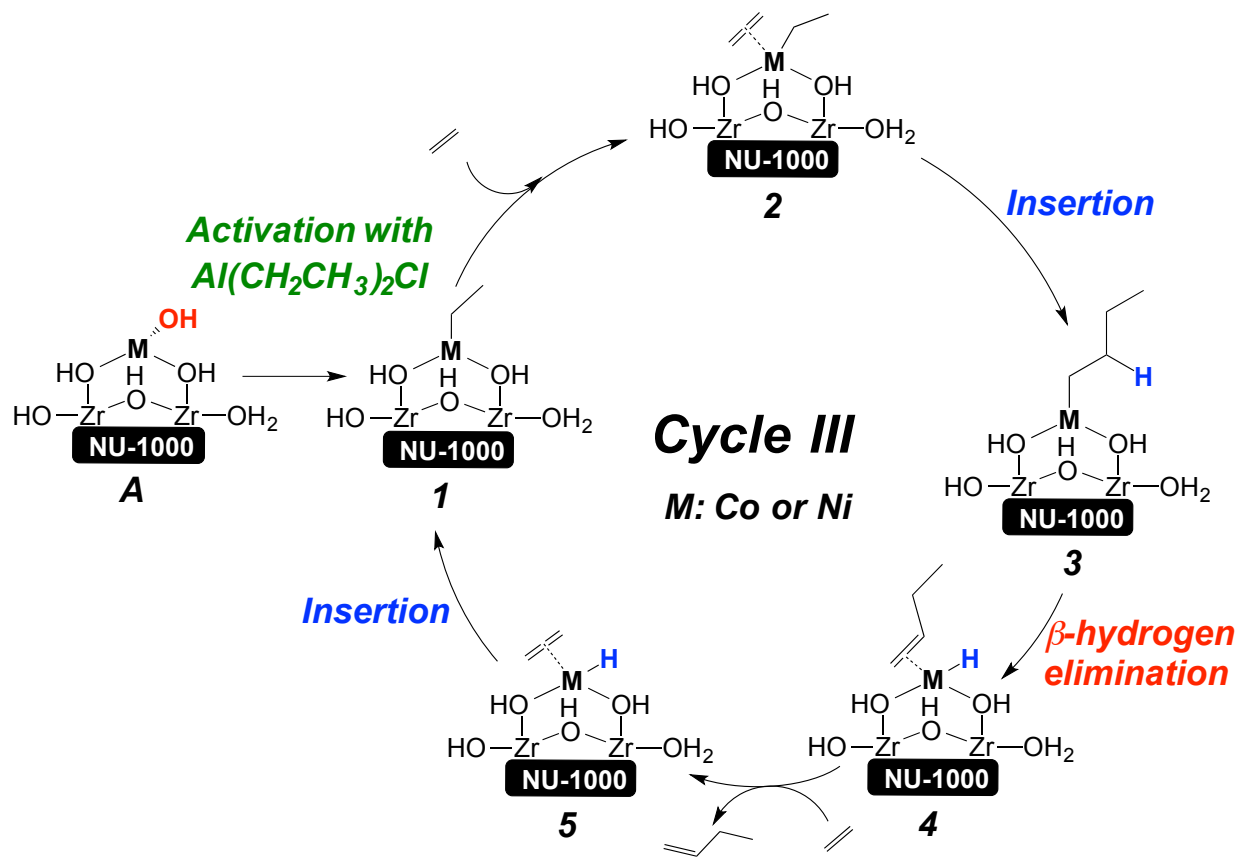
Nickel(II) d^8



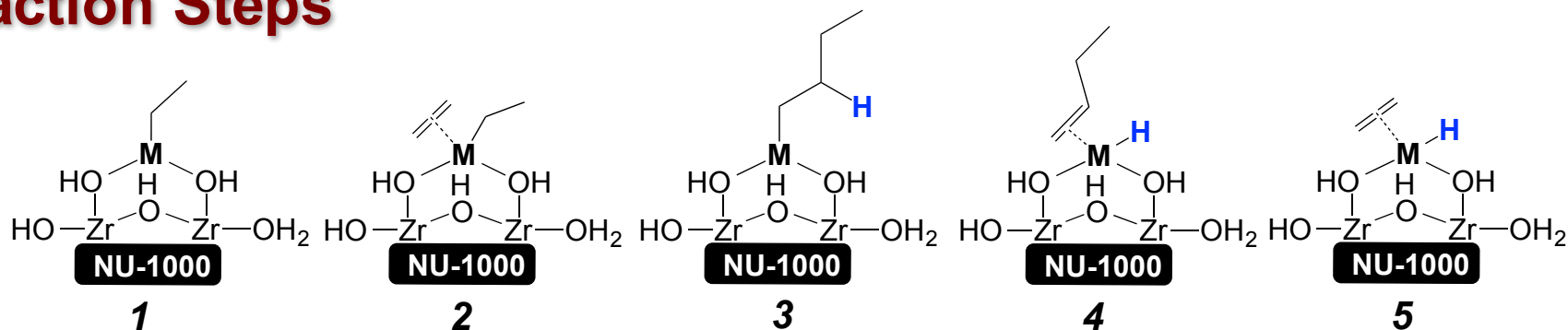
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Most Energetically Favorable Pathway for Ethylene Dimerization



Reaction Steps

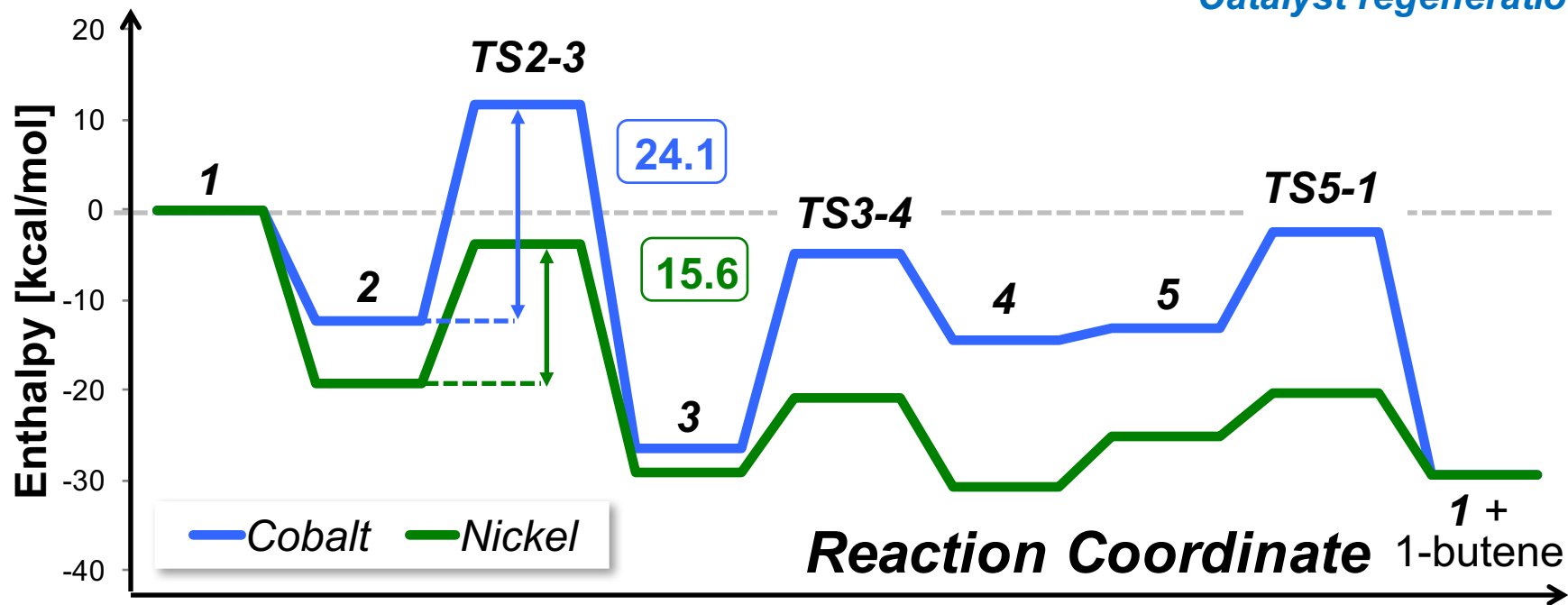


Ethylene Coordination

Insertion

β -H elimination

Product release
Catalyst regeneration



Why are Co and Ni so Different?

✧ Insertion Step: TS2-3

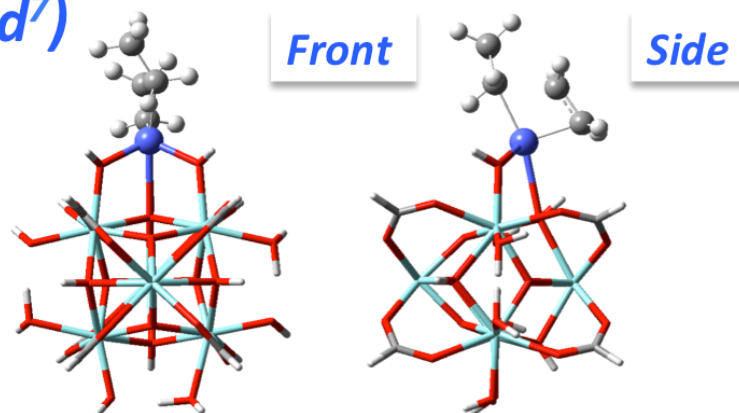
Co–Zr₆:

- Metal center is high-spin
- Geometry is trigonal bipyramidal

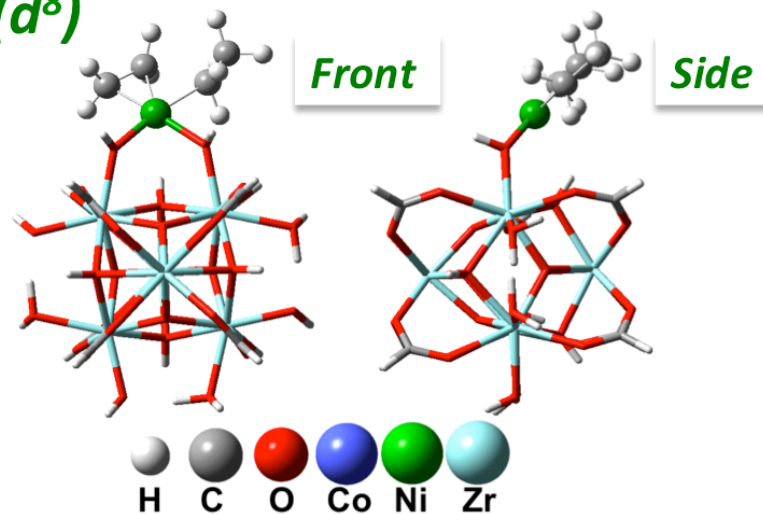
Ni–Zr₆:

- Metal center is low-spin
- Geometry is square-planar

Cobalt (d^7)

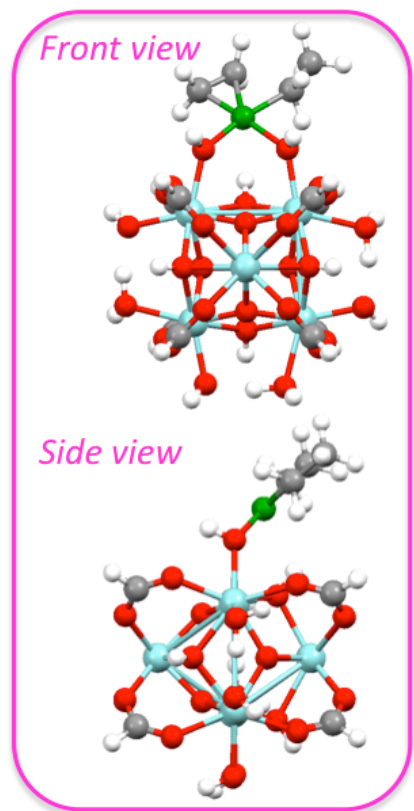


Nickel (d^8)

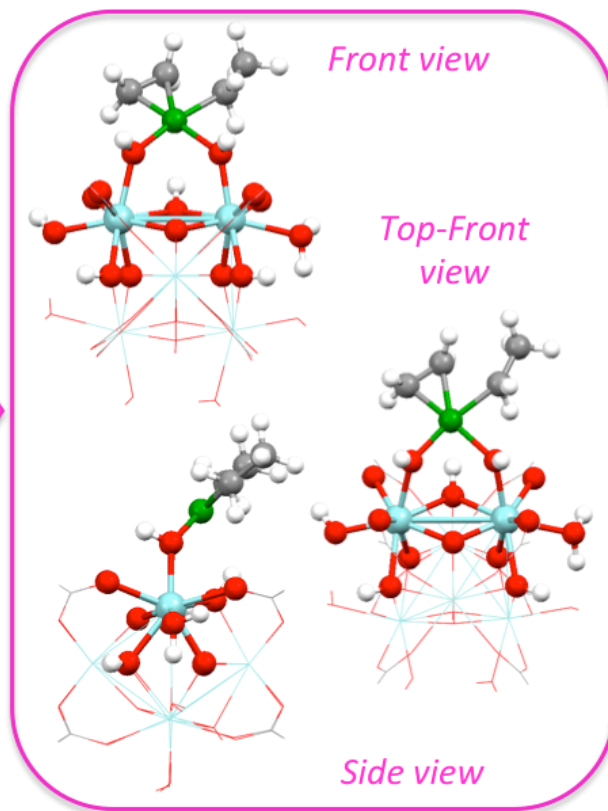


Cluster Model

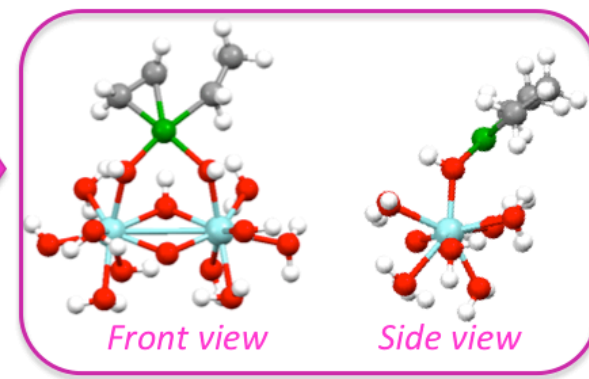
a) Formate-cluster Model



b) Selected Atoms



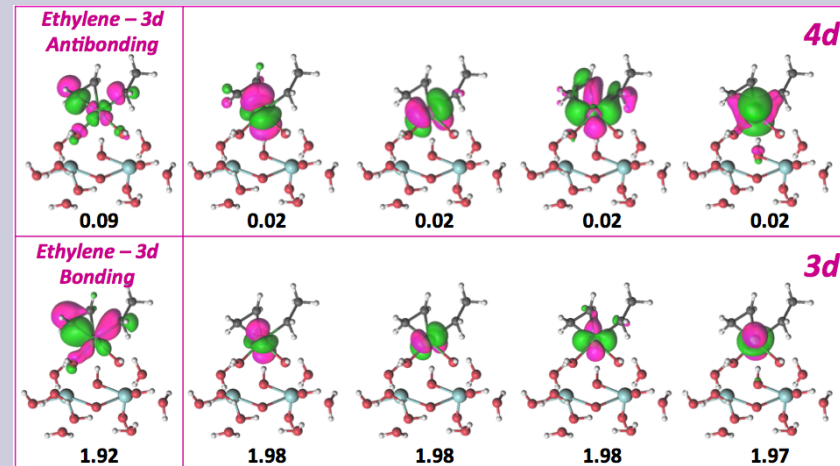
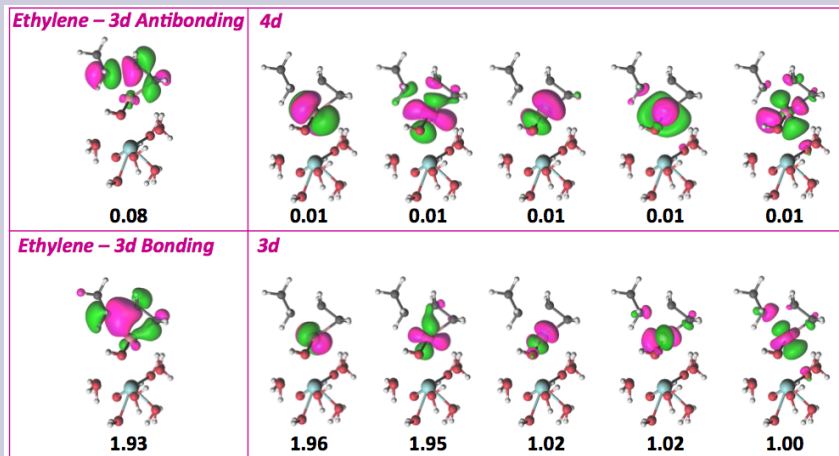
c) Small-cluster Model



Active Space

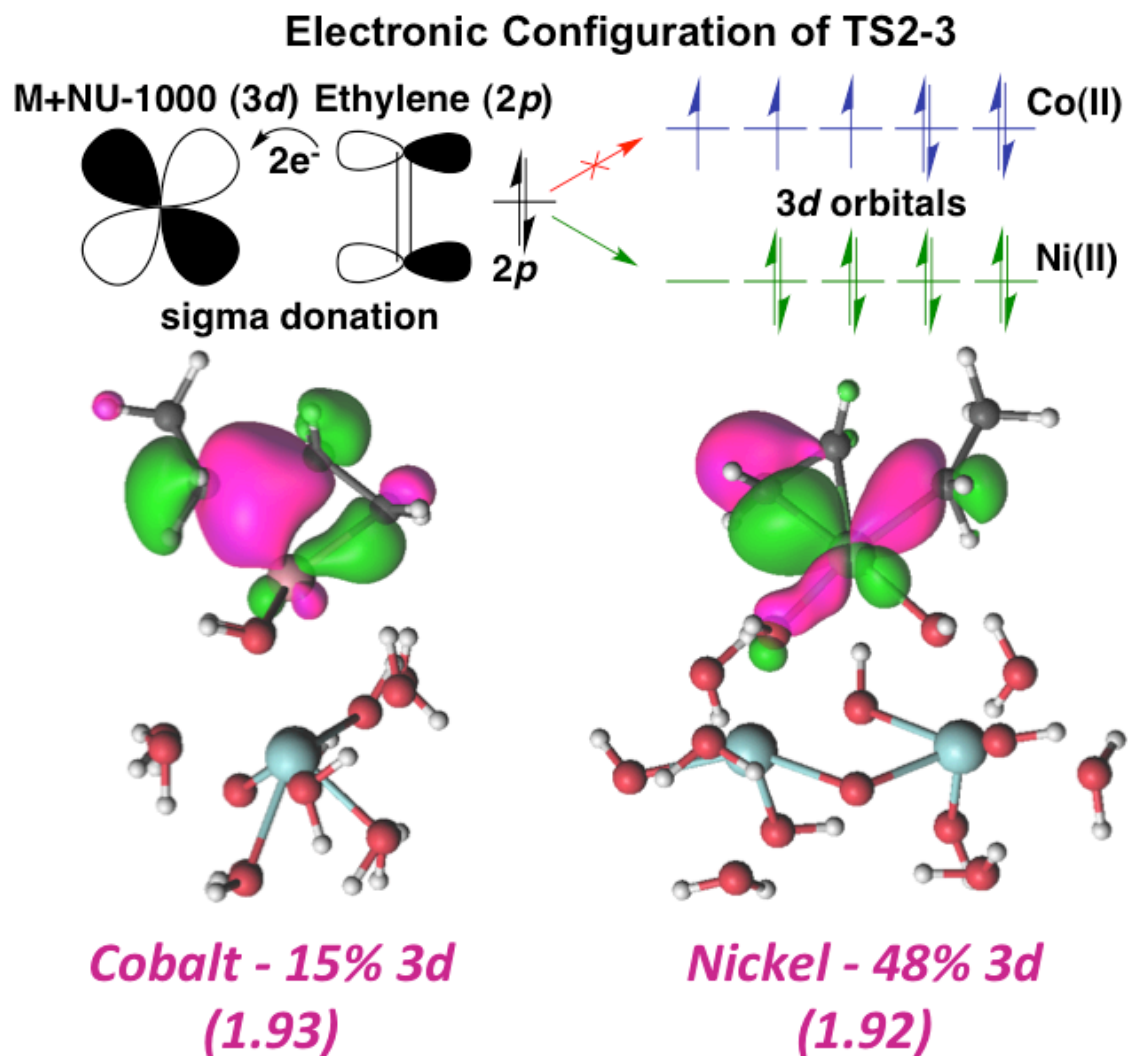
Transition State TS2-3 (Quartet):
CAS(9,12) – 91%.

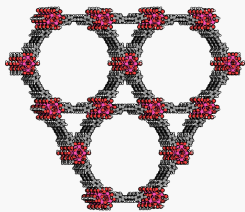
Transition State TS2-3 (Singlet):
CAS(10,10) – 92%



Electronic Structure Analysis

- CASSCF/CASPT2
- Ni(II) empty d orbital stabilizes $\pi \rightarrow \sigma$ bond formation in TS structure



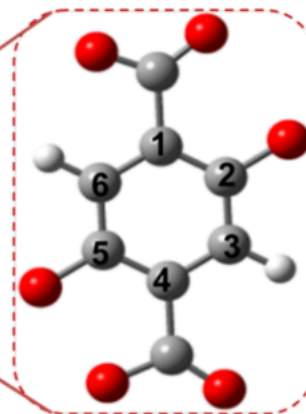
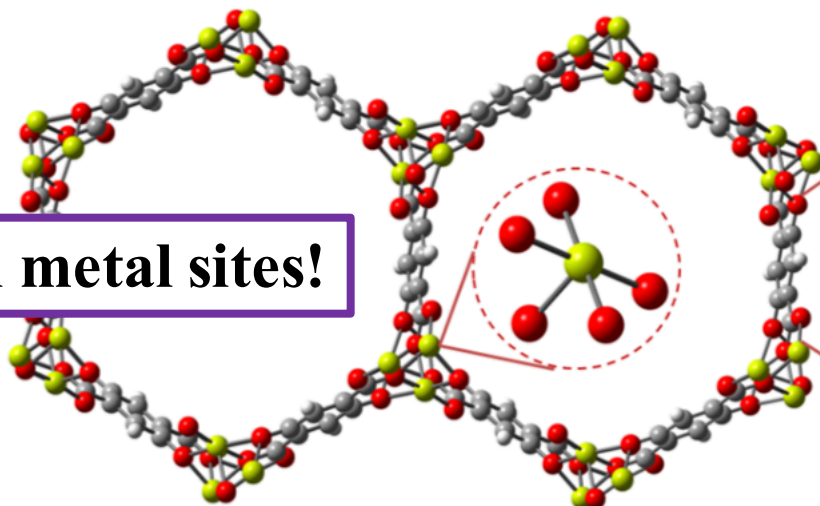


Creation of a reactive Fe(IV)=O Species

- The Chemical Problem:

To convert
Ethane into Ethanol

Open metal sites!



MOF-74
M-MOF(dobdc)₂
M=Mg and Fe

(dobdc⁴⁻ = 2,5-dioxido-1,4-
benzenedicarboxylate)

J. Am. Chem. Soc., 2015, 137, 5770.

*hexagonal channels with a diameter of about 1.1 nm



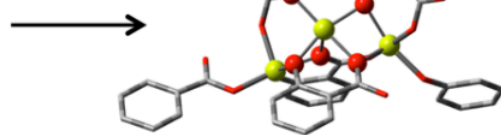
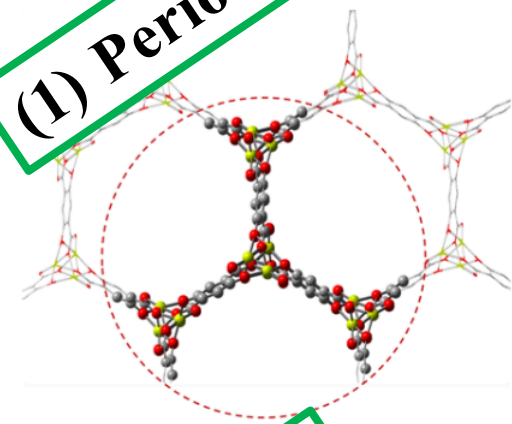
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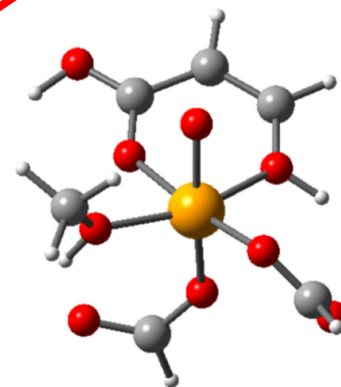
Creation of a reactive Fe(IV)=O Species

• The model:

(1) Periodic DFT



(3) CASSCF/CASPT2



(2) DFT

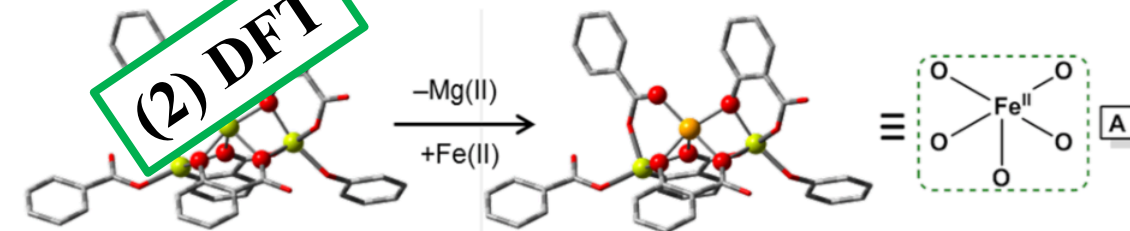
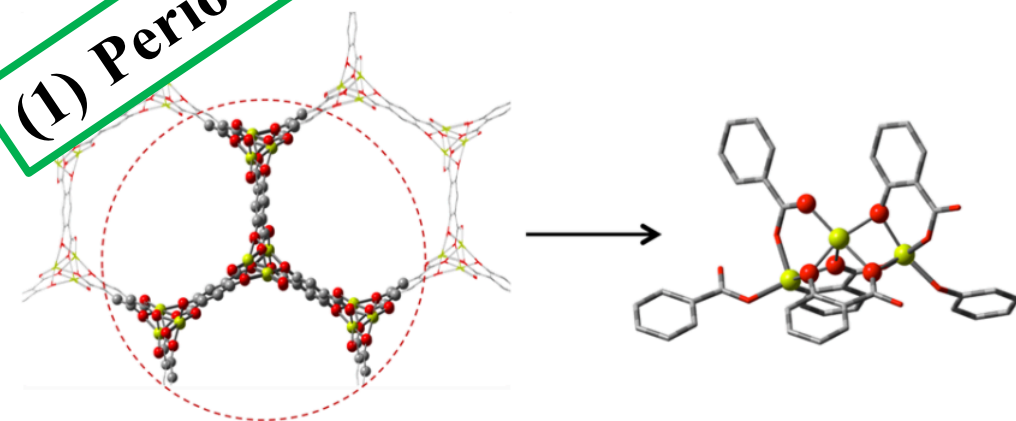


Figure 3. The 26-atom mononuclear model of B' used for multireference calculations. [Color code: orange = Fe, red = O, gray = C, and white = H].

Creation of a reactive Fe(IV)=O Species

(1) Periodic DFT

- The model:



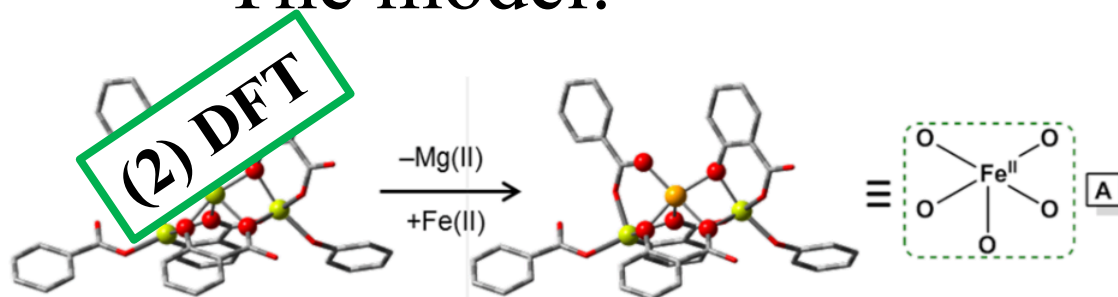
Periodic Calculations:

Mg₂(dobdc) optimized with
VASP (PBE).

More details in:
Nat. Chem. **2014**, 6, 590– 595

Creation of a reactive Fe(IV)=O Species

- The model:



**An 88-atoms model was
extracted from the periodic
calculation**

Neutrality of the cluster was
ensured by adding H atoms

DFT Calculation:

Catalytic reaction was
modeled by using *Gaussian 09*
with the M06-L density
functional and the def2-TZVP
all-electrons basis set.

*(Comparison with B3LYP)**

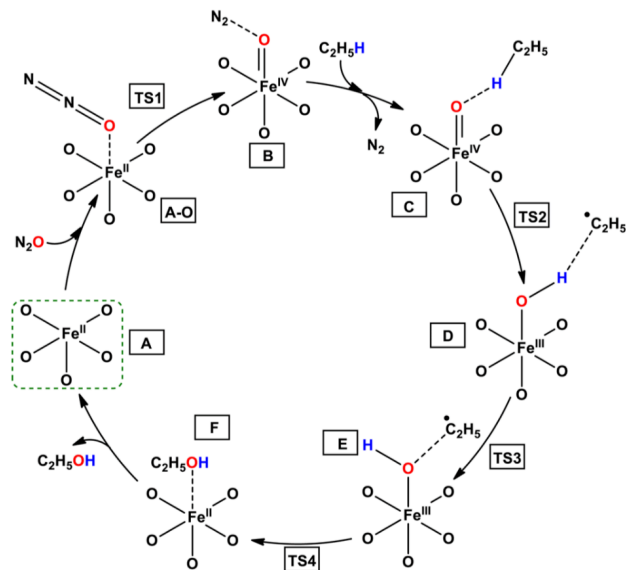
**J. Am. Chem. Soc.*, 2015, 137, 5770.



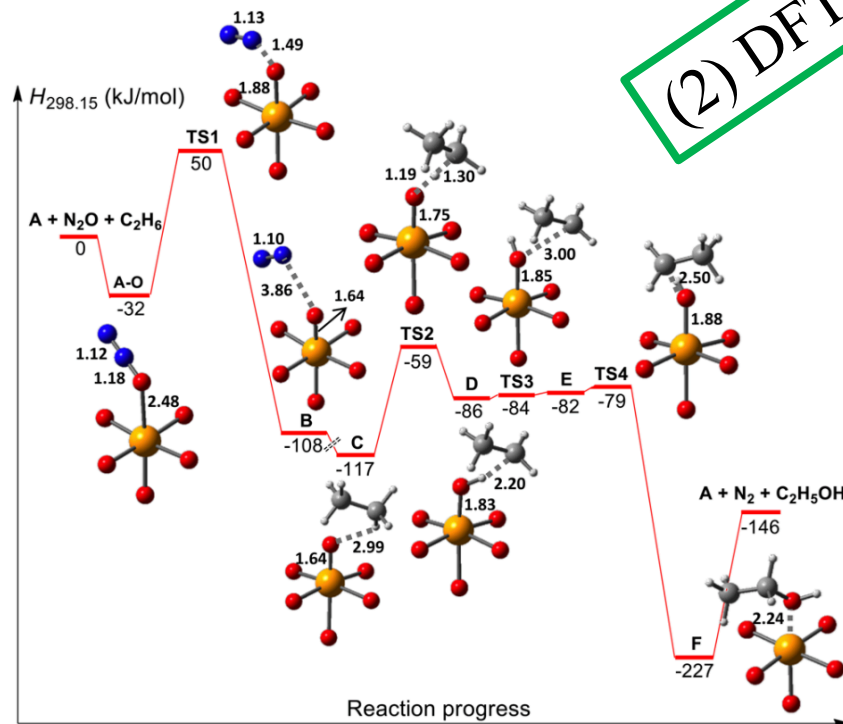
Creation of a reactive Fe(IV)=O Species

- The study:

Scheme 2. Proposed Mechanism for the Oxidation of Ethane to Ethanol in $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})^a$



^aThe first coordination sphere of the 88-atom cluster is shown along with the guest species bound to it.



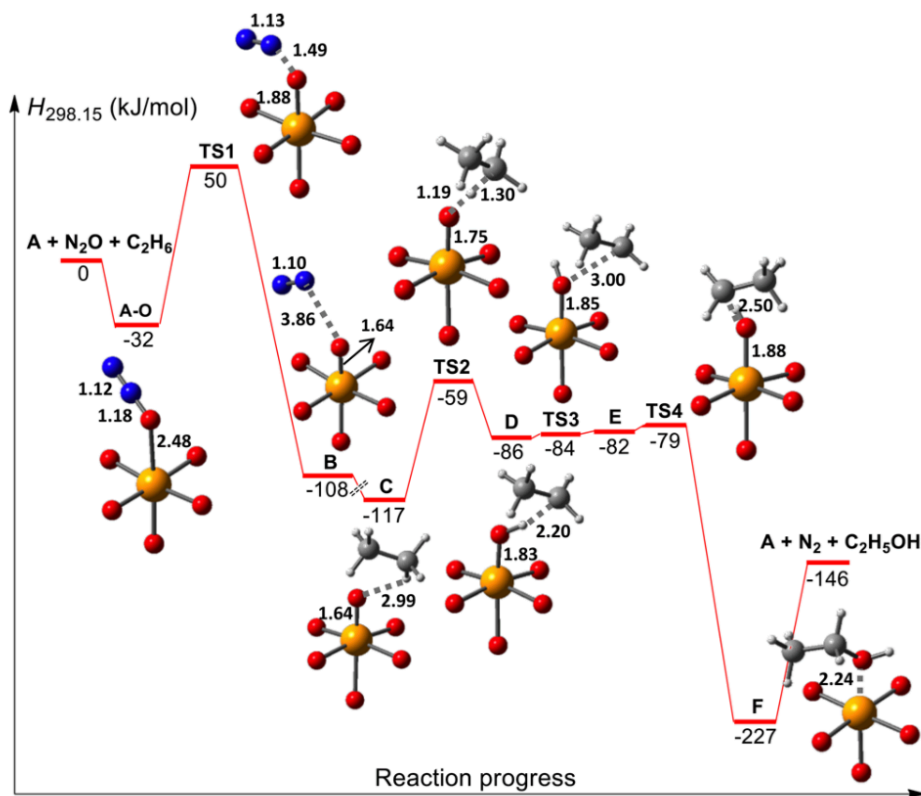
Creation of a reactive Fe(IV)=O Species

- The study:

Reaction Steps:

- (1) Formation of the Fe(IV)=O species.
- (2) C–H bond activation
- (3) Radical rebound to form ethanol.
- (4) Release the product

Key intermediates: **B** and **TS2**



Creation of a reactive Fe(IV)=O Species

(3) CASSCF/CASPT2

• TS2 model:

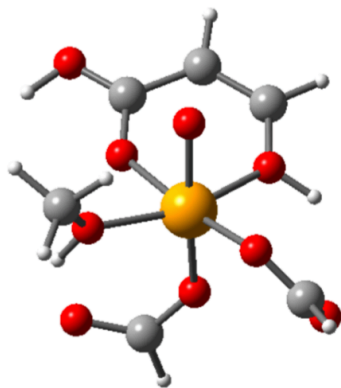


Figure 3. The 26-atom mononuclear model of **B'** used for multireference calculations. [Color code: orange = Fe, red = O, gray = C, and white = H].

Validation of the small model

Key intermediates: **B** and **TS2**

Both state-specific (SS) and state-averaged (SA) complete active space self-consistent field (CASSCF) calculations were performed. MOLCAS package.
Same basis set as in MCr example

Fe(IV)=O Species

- How to select the AS?
 - CASSCF(18e,12o)
 - Excluding the doubly occupied 3p and the σ^* molecular orbitals of the active space, the electronic structure of the dominant configuration state is:

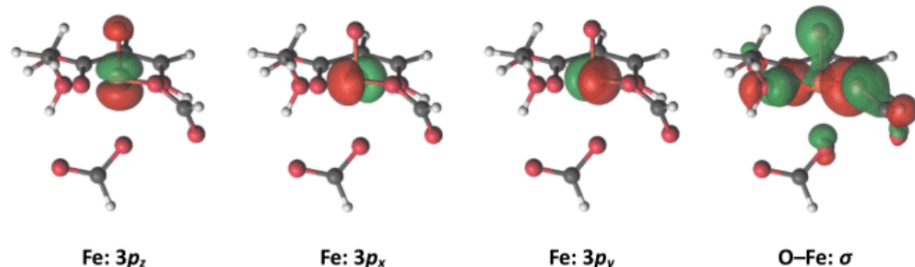
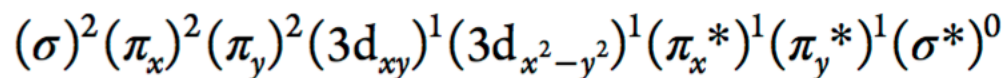
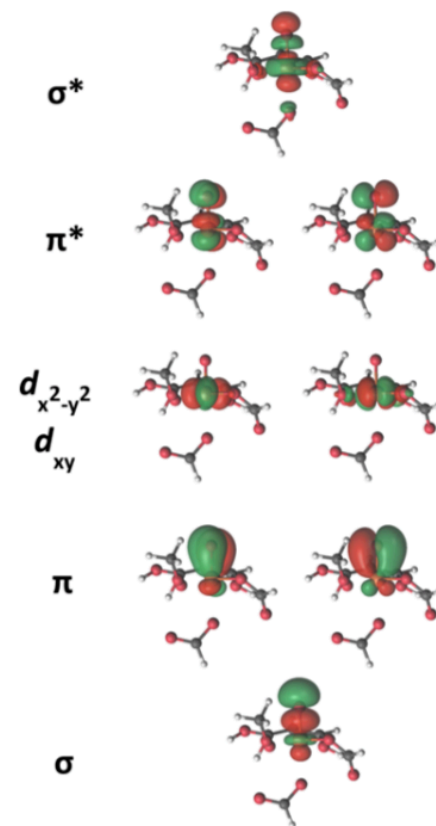


Figure S1. The four additional doubly occupied molecular orbitals included in CAS(18, 12) of B'.



J. Am. Chem. Soc., 2015, 137, 5770.

^aThe four extra orbitals correspond to the σ bonding orbitals of the Fe with the ligand



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Fe(IV)=O Species

- Intermediate **B'**
(without the N₂)

(3) CASSCF/CASPT2

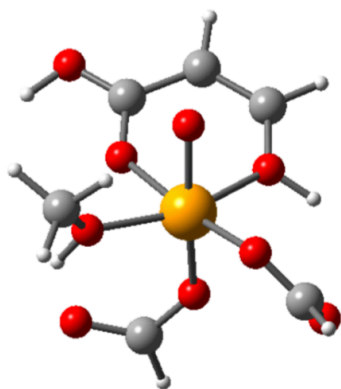
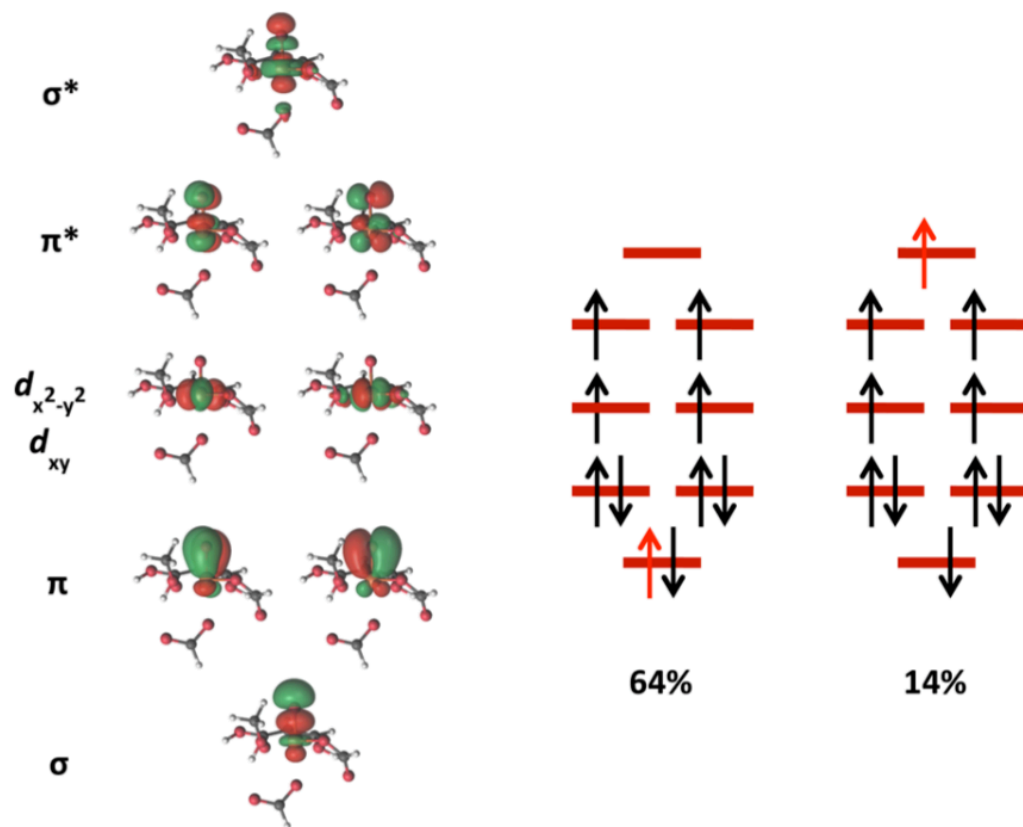


Figure 3. The 26-atom mononuclear model of B' used for multireference calculations. [Color code: orange = Fe, red = O, gray = C, and white = H].



TS2: C–H bond activation

- How to select the AS?
 - CASSCF(12e,11o)
 - four singly occupied 3d orbitals of Fe.
 - Three doubly occupied molecular orbitals involving the 2p orbitals of O.
 - Two unoccupied 3p orbitals of O and the σ/σ^* molecular orbitals between Fe and the evolving –OH group.
 - The four dominant configurations of **TS2** are given in Table S6.

J. Am. Chem. Soc., 2015, 137, 5770.

^aThe four extar orbitals correspond to the σ bonding orbitals of the Fe with the ligand



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TS2: C–H bond activation

- TS2

Table S6. Dominant configurations of **TS2** calculated by CASSCF(12, 11). '2' stands for a doubly occupied molecular orbital, 'u' (as in "up") for a singly occupied orbital containing an electron with α spin, and 'd' (as in "down") for a singly occupied orbital containing an electron with β spin.

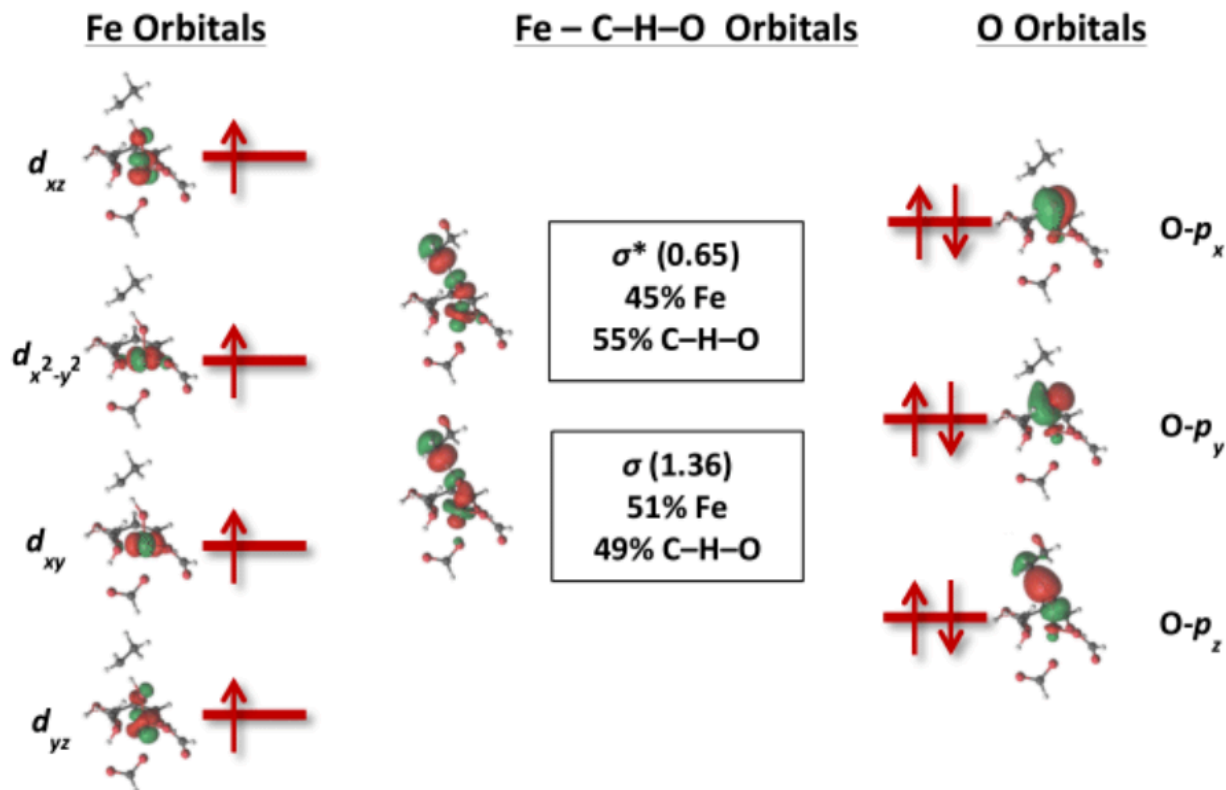
Configuration ^a	Weight (%)
222uuuu2000	51
222uuuu0200	17
222uuuuu00	14
222uuuuud00	11

^aOrdering of the orbitals:

$(2p_z-0)(2p_x-0)(2p_y-0)(3d_{xz}-\text{Fe})(3d_{yz}-\text{Fe})(3d_{xy}-\text{Fe})(3d_{x^2-y^2}-\text{Fe})$ $(\sigma)(\sigma^*)$ $(3p_x-0)(3p_y-0)$

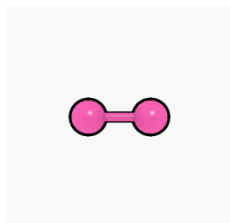
TS2: C–H bond activation

- TS2

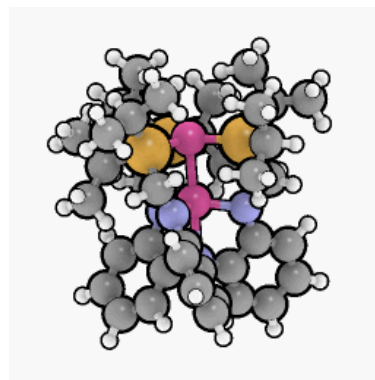


What Level of Theory Can We Apply?

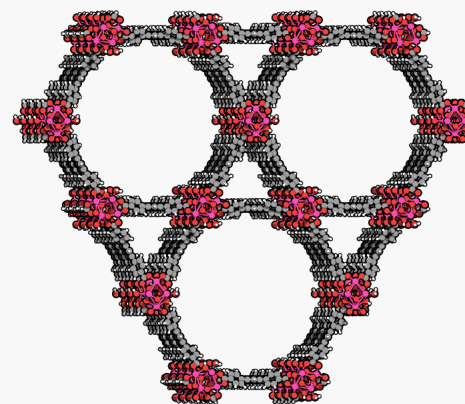
Small
Cluster



Molecular Systems
Medium Cluster



Periodic Systems



Hartree-Fock
Multireference
Post Hartree-Fock
DFT

Mainly DFT
CASSCF/CASPT2*
GASSCF/GASPT2

Periodic DFT or QM/MM



Thanks for your attention!

The Gagliardi
Group



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Recommended Books

