An Introduction to Multiconfigurational Wave Function Theory

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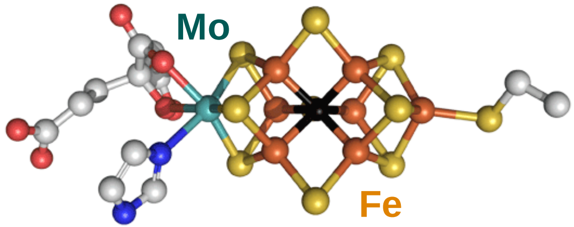
June 29, 2019
Current Topics in Theoretical Chemistry School

Quito - Ecuador

- **Grand Challenge:** How can we represent transition metal-based systems in an accurate fashion?

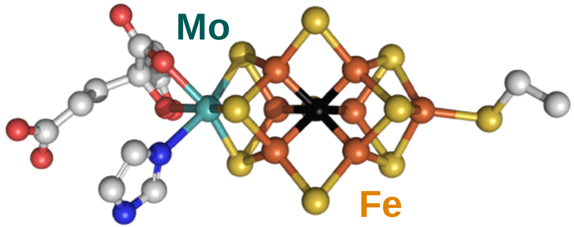


FeMo nitrogenase is responsible for the conversion of N_2 into ammonia

This catalyst presents multiple metal centers with multiple unpaired electrons

One may want to understand how these particular arrangement of iron centers influence the catalytic activity

- **Grand Challenge:** How can we represent transition metal-based systems in an accurate fashion?



FeMo nitrogenase is responsible for the conversion of N_2 into ammonia

This catalyst presents multiple metal centers with multiple unpaired electrons

Naïve question: What will happen if we try to optimize this molecule using HF or DFT?

(*See Phys. Chem. Chem. Phys.* **2019**, *21*, 2480)

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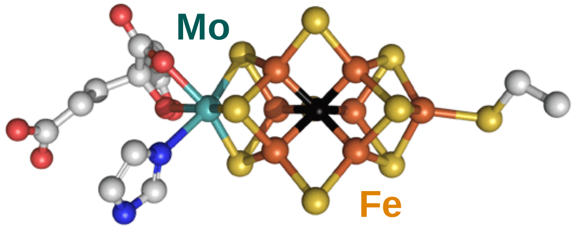
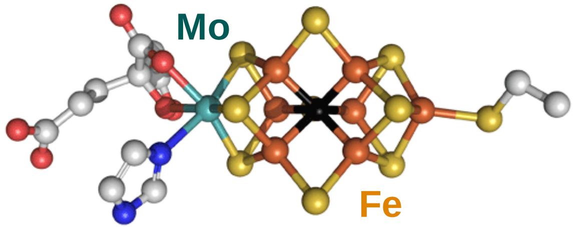


FeMo nitrogenase is responsible for the conversion of N_2 into ammonia

This catalyst presents multiple metal centers with multiple unpaired electrons

HF and DFT use a **single determinant** to represent the possible electron configurations and they fail because **multiple configurations are needed** to represent the nature of the systems

- **Grand Challenge:** How can we represent transition metal-based systems in an accurate fashion?



How can we properly treat these systems?
What are the current limitations?

Löwdin defined electron correlation as the difference between the exact nonrelativistic energy and the restricted Hartree-Fock (RHF) energy in a complete basis set.

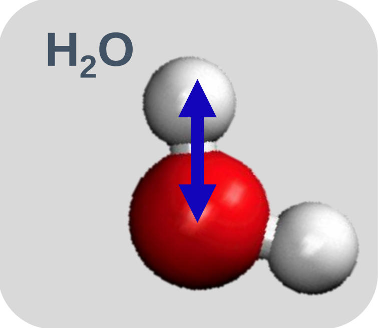
$$E_{FCI} - E_{HF} = E_{Corr}$$

Phys. Rev. **1955**, *97*, 1509

ELECTRON CORRELATION: TYPES OF ELECTRON CORRELATION

Basis set correlation for water with DZ basis

O-H	ε_{corr} (a.u.)	ε_{corr} (kcal/mol)
R_e	-0.148028	-92.9
$1.5R_e$	-0.210992	-132.4
$2.0R_e$	-0.310067	-194.6



Stretching the O-H bond

Dynamical correlation *arises from electrons instantaneously avoid each other.*

- *At dissociation the electrons are further apart. Thus, this difference should become less important*
- *But in this table, the correlation energy increases with the stretching … Why?*

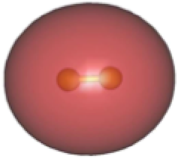
Non-dynamical Correlation

Chem. Phys. Lett. **1983**, *95*, 386-391.

Simplest Example of Degeneracy: Stretched H_2

- Using only two 1s functions, one on each H atom (minimal basis): ϕ_A and ϕ_B. RHF orbitals are determined by symmetry. β spin is denoted by an overbar.

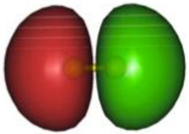
σ



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

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

σ*



Slater determinant

$$\left|\phi_\sigma\overline{\phi_\sigma}\right\rangle = \frac{1}{2^{1/2}}\begin{vmatrix}\phi_\sigma(1) & \overline{\phi_\sigma}(1)\\ \phi_\sigma(2) & \overline{\phi_\sigma}(2)\end{vmatrix}$$

Determinant Expansion

Slater determinant

$$\left|\phi_\sigma\overline{\phi_\sigma}\right\rangle = \frac{1}{2^{1/2}}\left[\phi_\sigma(1)\overline{\phi_\sigma}(2) - \phi_\sigma(2)\overline{\phi_\sigma}(1)\right]$$

The expanded determinant can be reorganize as the sum of four determinants made of atomic spin-orbitals:

$$\left|\phi_\sigma\overline{\phi_\sigma}\right\rangle = \frac{1}{2(1+S_{12})}\left[\left|\phi_A\overline{\phi_A}\right\rangle + \left|\phi_A\overline{\phi_B}\right\rangle + \left|\phi_B\overline{\phi_A}\right\rangle + \left|\phi_B\overline{\phi_B}\right\rangle\right]$$

So what's the problem?

The **first** and **last terms are ionic structures** and should not contribute to the wave function (they place both electrons on one of the hydrogens: $H^- + H^+$) as $R_{AB} \rightarrow \infty$.

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

DETERMINANT EXPANSION

Slater determinant

$$|\phi_\sigma\overline{\phi_\sigma}\rangle = \frac{1}{2^{1/2}}[\phi_\sigma(1)\overline{\phi_\sigma}(2) - \phi_\sigma(2)\overline{\phi_\sigma}(1)]$$

The expanded determinant can be reorganize as the sum of four determinants made of atomic spin-orbitals:

$$|\phi_\sigma\overline{\phi_\sigma}\rangle = \frac{1}{2(1+S_{12})}[|\phi_A\overline{\phi_A}\rangle + |\phi_A\overline{\phi_B}\rangle + |\phi_B\overline{\phi_A}\rangle + |\phi_B\overline{\phi_B}\rangle]$$

We can fix this by adding coefficients in front of the determinants, as a linear combination

$$|\Psi\rangle = C_{ion}|\Phi_{ion}\rangle + C_{cov}|\Phi_{cov}\rangle$$

We can vary these coefficients to produce a correct wavefunction at dissociation $C_{ion} = 0$*; at equilibrium* $C_{ion} = C_{cov}$

What Causes the Non-dynamical Correlation?

- Many researchers have found it useful to subdivide correlation effects further as:

$$E_{Corr} = E_{dyn} + E_{static}$$

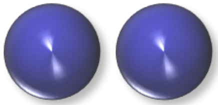
- Dynamic correlation arises from electrons avoiding one another at short range to minimize repulsion or correlating their motion at large distances to produce dispersion interactions.

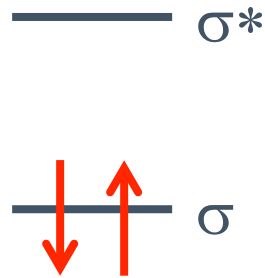
- Static correlation (also called non-dynamical, near-degeneracy, left-right, or first-order) energy arises from near-degeneracies of the Hartree-Fock occupied and virtual orbitals.

What Causes the Non-dynamical Correlation?

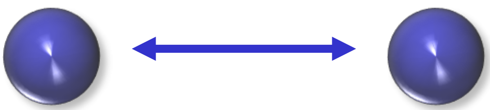
At equilibrium – dynamic correlation

H_2





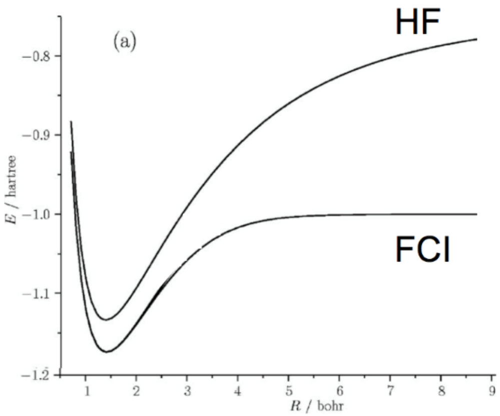
At dissociation – static correlation



H H

QC bond representation involves bonding and antibonding orbitals

Configuration Interaction



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

$$|\Psi\rangle = C_0|\Phi_0\rangle + \sum_{ra} C_a^r\,|\Phi_a^r\rangle + \sum_{a<b.r<s} C_{ab}^{rs}\,|\Phi_{ab}^{rs}\rangle + \sum_{a<b.<c\ r<s<t} C_{abc}^{rst}\,|\Phi_{abc}^{rst}\rangle + \cdots$$

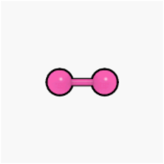
The number of excited Slater Determinants increases **factorially** with the number of electrons and basis functions

**D. Sherril – From Modern Quantum Chemistry by A. Szabo, N. S. Ostlund*

CONCEPTUAL TEST I

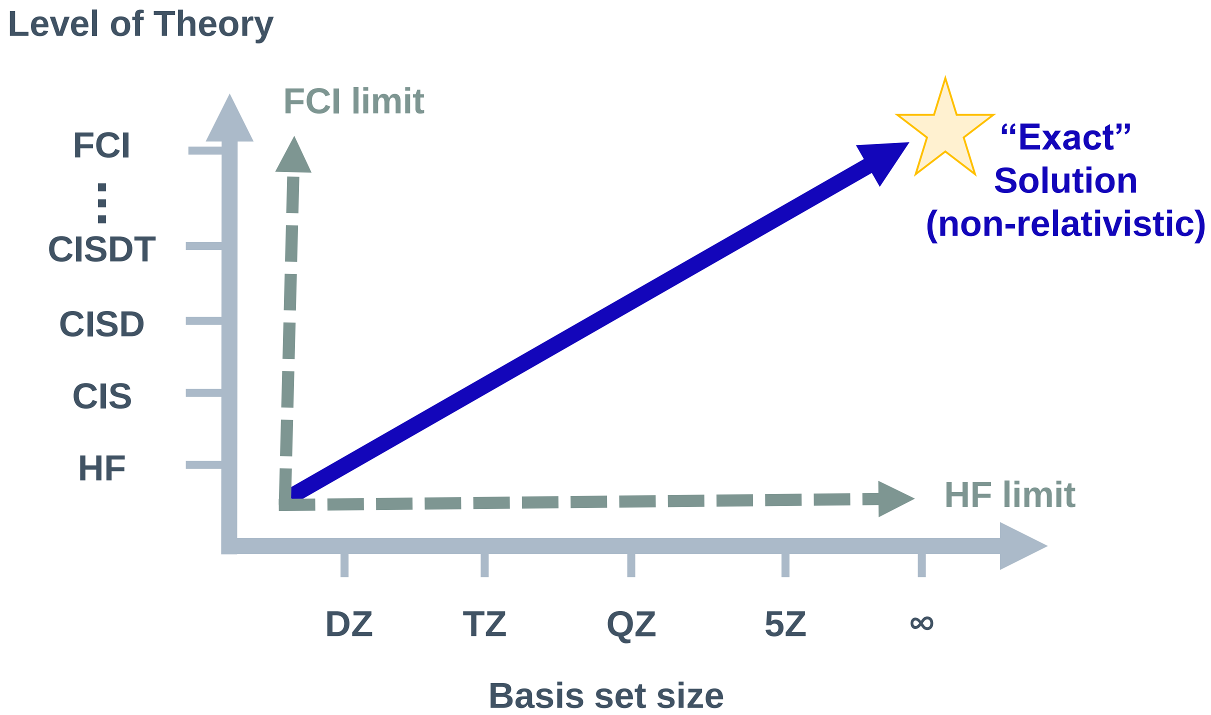
If you compare the geometry of a molecule optimized at the HF level and the same molecule optimized at the CI level

Do you expect the bond lengths at the CI level to be longer or shorter than those at the HF level?



Explain your reasoning.

SYSTEMATICALLY IMPROVED ACCURACY WITH CI



Full CI wave functions
How many n-tuple excitations are there?

- CI method completely general with respect to the choice of configurations

- **Full CI: full set of determinants generated by distributing all electrons among all orbitals**

- Number of SD (N_{det}): product of number of determinants for the α and β electrons separated

$$N_{det} = \binom{n}{k}^2$$

Let's see what happen for $n = k$ (and S = 0)

n:orbitals
k:electrons

Full CI Expansion

For $S = 0$

(2k,2n)	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

bottleneck

CI WAVE FUNCTION

- Linear combination of Slater Determinants

$$|C\rangle = \sum_i C_i |i\rangle$$

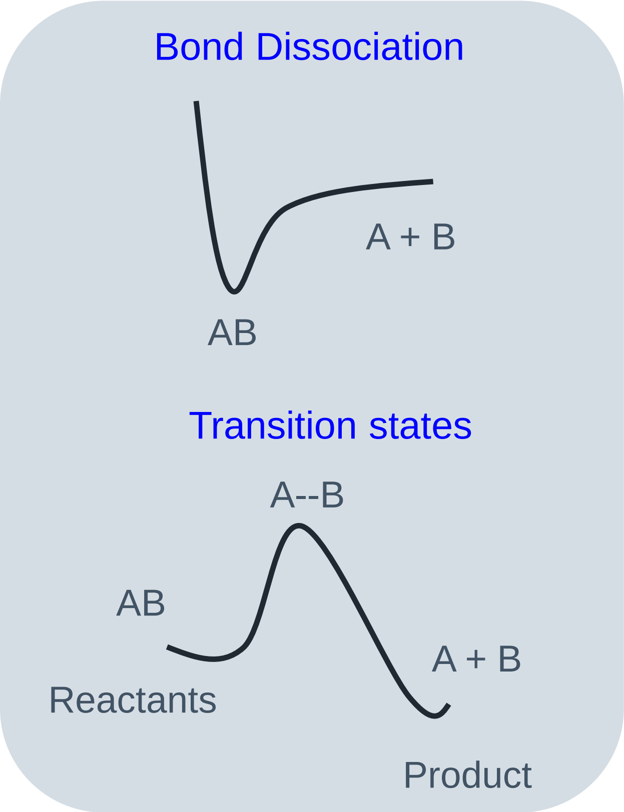
- C_i coefficients determined by a variational optimization of the expectation value of the electronic energy

$$\frac{\partial}{\partial C_i} \frac{\langle \boldsymbol{C} | \hat{H} | \boldsymbol{C} \rangle}{\langle \boldsymbol{C} | \boldsymbol{C} \rangle} = 0$$

- Accurate wave functions for small molecules. Difficult to apply to large molecules: rapid growth in number of configurations
- **A solution is to truncate the CI expansion**
- **Caveat:** when one truncates the CI expansion, the CI wavefunction suffers from **lack of size-extensivity.**

IS A SINGLE DETERMINANT ENOUGH?

- Bond breaking processes
- Species with radical character
- Excited states
- Any species that present near-degenerancies



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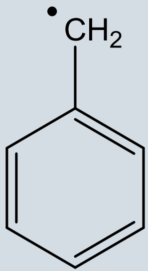
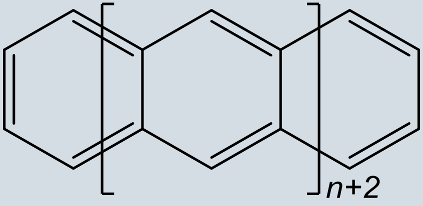
Radical



Conjugated systems



IS A SINGLE DETERMINANT ENOUGH?

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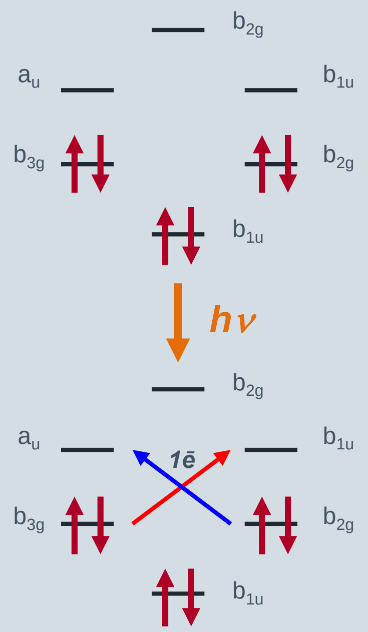
- Any species that present near-degenerancies

Ground State (1^1A_g)
Dominant configurations 89%



First Excited State (1^1B_{2u})
Two dominant configurations 40%

J. Phys. Chem. Lett. **2019**, 10, 75−81

IS A SINGLE DETERMINANT ENOUGH?

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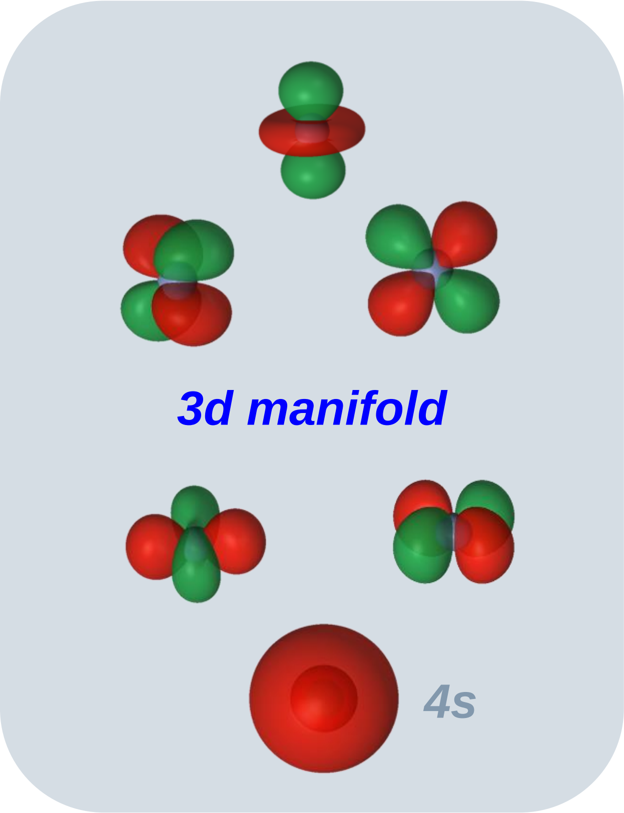
- Any species that present near-degenerancies



IS A SINGLE DETERMINANT ENOUGH?: MULTICONFIGURATIONAL SCF

- Our reference wavefunction includes all nearly degenerate electron configurations

- MCSCF: optimizes the orbitals which minimize the energy of this set of near-degenerate determinants

- Describe the static correlation that arises from near-degenerancies between two or more configurations

- But does not fix the short-range problems that arise as $R_{12 \to 0}$: dynamical correlation.

- Since the MCSCF wavefunction is used as a reference wavefunctions; we need a subsequent treatment to account for 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

Optimization of MCSCF Wave Functions

- MCSCF Wave function:

$$\Psi^{\text{MCSCF}} = C_0|0\rangle + C_1|1\rangle + C_2|2\rangle + \ \dots = \sum_i c_i|i\rangle$$

$$E^{\text{MCSCF}} = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2}\sum_{pqrs} g_{pqrs} d_{pqrs} + V_{NN}$$

$$h_{pq} = \int \varphi_p(\mathbf{r}_1)\left(-\frac{1}{2}\nabla_1^2 - \sum_{\substack{\text{nuclei}\\ A}} \frac{Z_A}{r_{1A}}\right)\varphi_q(\mathbf{r}_1)d\mathbf{r}_1$$

1- electron integral

$$g_{pqrs} = \iint \varphi_p(\mathbf{r}_1)\varphi_r(\mathbf{r}_2)\left(\frac{1}{r_{12}}\right)\varphi_q(\mathbf{r}_1)\varphi_s(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

2-electron integrals

pqrs: Molecular orbitals indices

$a^\dagger$: creation operator, a: annihilation operator (*see second quantization*)

Optimization of MCSCF Wave Functions

- MCSCF Wave function:

$$\Psi^{\mathrm{MCSCF}} = C_0|0\rangle + C_1|1\rangle + C_2|2\rangle + \ \ldots = \sum_i c_i|i\rangle$$

$$E^{\mathrm{MCSCF}} = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2}\sum_{pqrs} g_{pqrs} d_{pqrs} + V_{NN}$$

$$D_{pq} = \sum_{I,J} C_I C_J \langle I|a_p^\dagger a_q|J\rangle$$

1-body density matrix element

$$d_{pqrs} = \sum_{I,J} C_I C_J \langle I|a_p^\dagger a_r^\dagger a_s a_q|J\rangle$$

2-body density matrix elements

pqrs: Molecular orbitals indices

$a^\dagger$: creation operator, a: annihilation operator (*see second quantization*)

Optimization of MCSCF Wave Functions

- MC wave function:

$$\Psi^{\mathrm{MC}} = c_0\Phi_0 + c_1\Phi_1 + c_2\Phi_2 + \ \ldots = \sum_i c_i\Phi_i$$

- Or:

$$|0\rangle = \sum_i c_i |i\rangle$$

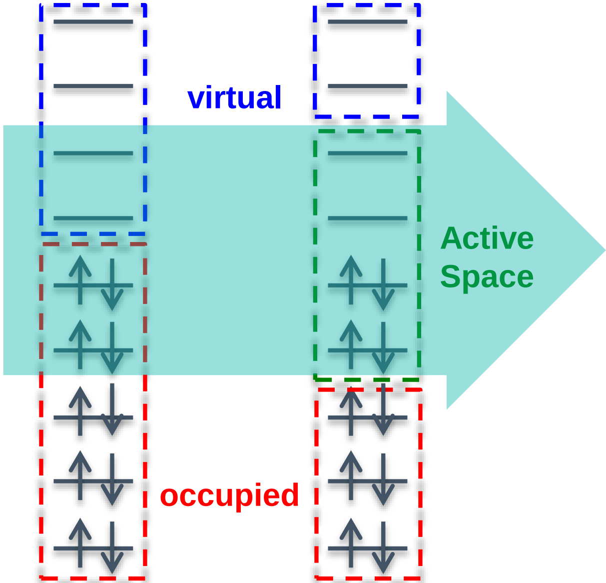
- Objective: to optimize the MOs and the CI coefficient variationally

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

MCSCF Configuration Space

How can we generate the MCSCF wavefunction?

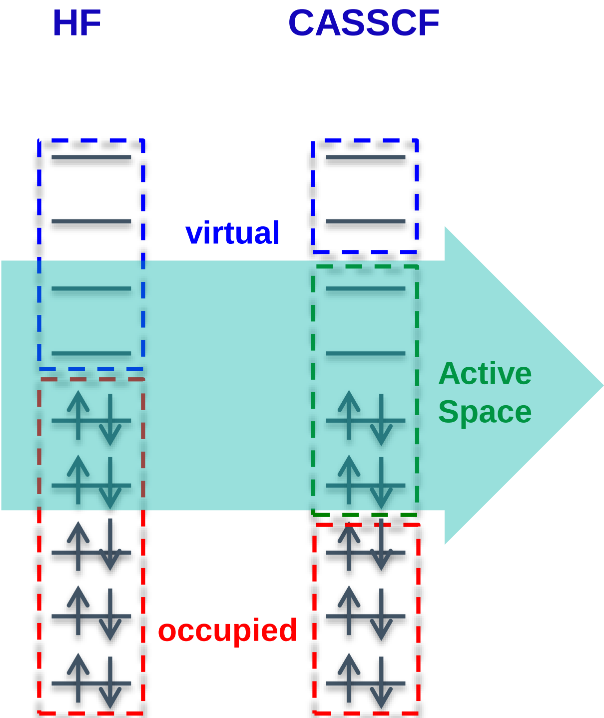
- Remember that we will face similar problems to the CI expansion.
- Let us choose a subspace of MOs (active space), from which all configurations can be built by distributing the electrons in these orbitals: a Full CI in the AS.
- We could select all the valence AOs for all atoms, but this quickly gets very large … Let us think of an alternative …



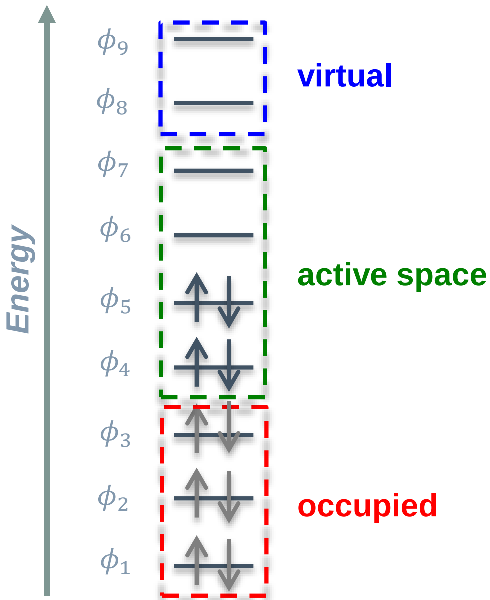
Complete Active Space SCF

- We can reduce the number of active orbitals and electrons. *(Mostly doubly occupied orbitals can be left outside of the AS.)*
- We need to understand which orbitals change their occupation significantly during the process under study

Small CASSCF as a test
Rule of thumb:
0.2< Occupation number <1.98



CASSCF Notation: CAS(4,4)



$$\psi^{CAS} = C_1 \left| \phi_1^2 \phi_2^2 \phi_3^2 \phi_4^2 \phi_5^2 \right\rangle$$

CAS: Orbitals divided in three classes: inactive, active and secondary. It is written as:

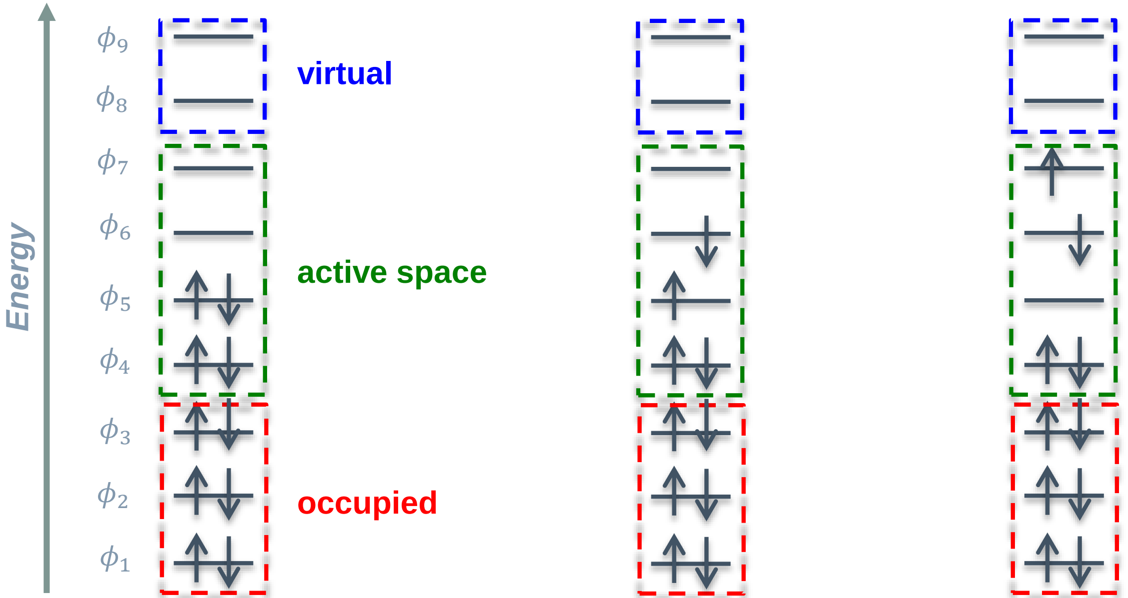
CAS(n,m)

With n active electrons and m active orbitals

Notes:

- Inactive orbitals are doubly occupied in all configurations
- Active space considers all possible occupation of orbitals.
- Virtual orbitals (or secondary orbitals) are unoccupied in all configurations

CASSCF Notation: CAS(4,4)



$$\psi^{CAS} = C_1\left|\phi_1^2\phi_2^2\phi_3^2\phi_4^2\phi_5^2\right\rangle + C_2\left|\phi_1^2\phi_2^2\phi_3^2\phi_4^2\phi_5^1\phi_6^1\right\rangle + C_3\left|\phi_1^2\phi_2^2\phi_3^2\phi_4^2\phi_6^1\phi_7^1\right\rangle + \ldots$$

Notes:

- Inactive orbitals are doubly occupied in all configurations
- Active space considers all possible occupation of orbitals.
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Choosing the Active Space

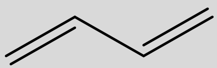
- Identify the orbitals involved in the process.
- You may have to refine this choice – Clearly, we are very far from a black-box approach!

How to Select Active Space for Multiconfigurational Quantum Chemistry?
Int. J. Quantum Chem. **2011**, *111*, 3329.

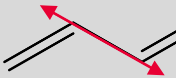
(See AutoCAS: https://reiher.ethz.ch/software/autoCAS.html for automated AS selection)

For the same molecule, different active spaces can be required

1,3-butadiene



Excited states: π and π* shell



Bond dissociation: σ/σ*, π/π* shell

The active space is not simply a matter of selecting the number of electrons and orbitals.

We need to be able to represent the right character

CHEAT-SHEET: HOW TO SELECT AN ACTIVE SPACE?

Main group:

- For **Li, Be, B, C**: choose 2s, 2p as active (four orbitals).
- For **N, O, F**: 2s can be left inactive (three orbitals).
- A long alkyl chain with an active end group only needs orbitals there to be active.
- Conjugated systems should include all π valence orbitals

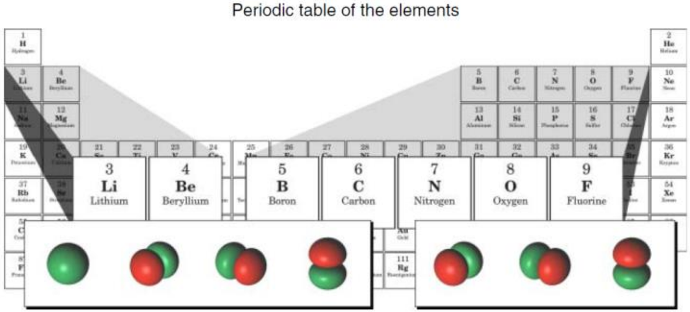


Figure 9.6 The standard active space selection for second-row atoms. For the initial set of elements, Li-C, the 2s and 2p near degeneracy has to be considered. However, for N and onward the 2s orbital can be left inactive.

Image from "Multiconfigurational Quantum Chemistry" book
By Bjorn Olof Roos, Roland Lindh, Per Åke Malmqvist, Valera Veryazov and Per-Olof Widmark.

CHEAT-SHEET: HOW TO SELECT AN ACTIVE SPACE?

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Transition Metal group:

- Available valence orbitals: **nd, (n+1)s, (n+1)p, n=3,4,5**
- Calculations never show much populations of (n+1)p orbitals
- The 18-electron rule is well obeyed in many cases: Ni(CO)4, Fe(CO)5, Cr(CO)6, etc.
- **All orbitals that have *d*-character should be included. Do not forget the ligand.**

Second shell effects:
TM with-more-than half-filled 3d shell

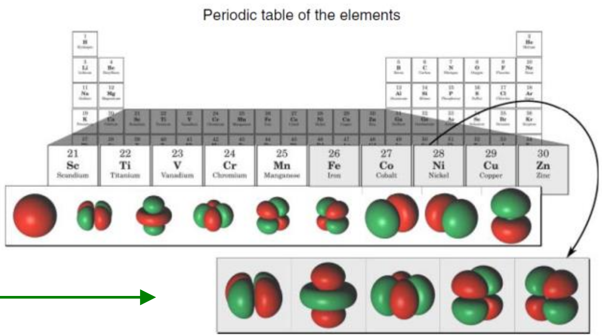

Figure 9.7 The standard active space selection for transition metals. For the first-row transition metals we have 4s, 3d, and 4p as active orbitals. For elements with more than five d-electrons, a second complete 3d′-shell might be required. This effect decreases for higher row transition metals.

Image from "Multiconfigurational Quantum Chemistry" book
By Bjorn Olof Roos, Roland Lindh, Per Åke Malmqvist, Valera Veryazov and Per-Olof Widmark.

CHEAT-SHEET: HOW TO SELECT AN ACTIVE SPACE?

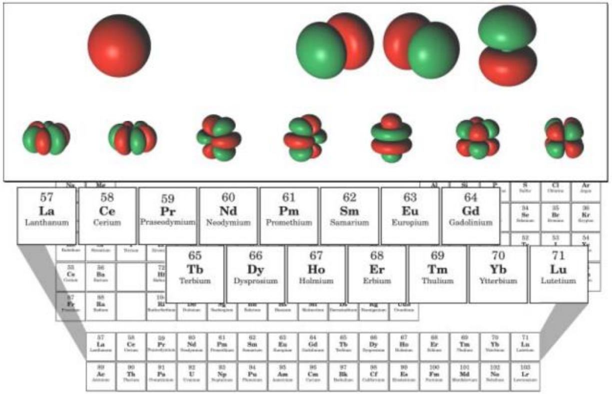

Figure 9.8 The standard active space selection for lanthanides. For the lanthanides, we have 6s, 4f, 5d, and 6p as active orbitals. The 5d-shell normally only is required in the worst case.

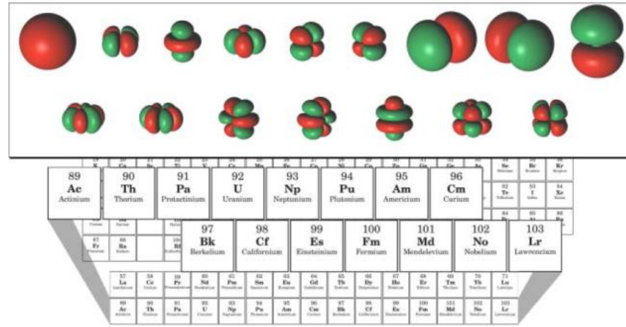

Figure 9.9 The standard active space selection for actinides. For the actinides, we have 7s, 5f, 6d, and 7p as active orbitals.

Lanthanides group:

- The 4f shell is inert but has to be kept active.
- **6s, 4f, 5d, 6p the most important orbitals**. In the worst case the 5d shell.
- Often very ionic complexes: Only 4f active.
- Covalent bonds difficult because large demands on the active space!

Actinides group:

- **In principle: 5f, 6d, 7s, 7p active (16 orbitals).**
- Actinides are often highly charged (high oxidation states): only 5f active.
- But: covalent bonding is not unusual. Example uranyl, UO_2^{2+}, which needs a 12 in 12 active space. U(VI) can be treated as single reference.

Image from "Multiconfigurational Quantum Chemistry" book By Bjorn Olof Roos, Roland Lindh, Per Åke Malmqvist, Valera Veryazov and Per-Olof Widmark.

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- Calculations never show much populations of (n+1)p orbitals
- The 18-electron rule is well obeyed in many cases: Ni(CO)4, Fe(CO)5, Cr(CO)6, etc.
- **All orbitals that have *d*-character should be included. Do not forget the ligand.**

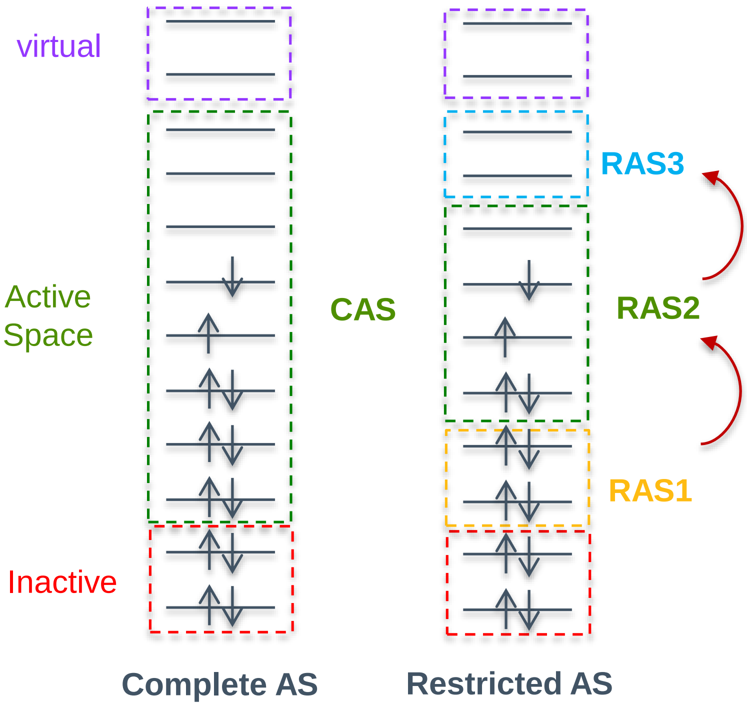
Lanthanides group:

- The 4f shell is inert but has to be kept active.
- **6s, 4f, 5d, 6p the most important orbitals**. In the worst case the 5d shell.
- Often very ionic complexes: Only 4f active.
- Covalent bonds difficult because large demands on the active space!

Actinides group:

- **In principle: 5f, 6d, 7s, 7p active (16 orbitals).**
- Actinides are often highly charged (high oxidation states): only 5f active.
- But: covalent bonding is not unusual. Example uranyl, UO_2^{2+}, which needs a 12 in 12 active space. U(VI) can be treated as single reference.

The active space does not limit the size of molecules



Complete vs Restricted Active Space

CAS: Orbitals divided in three classes: inactive, active and secondary. It is written as:

CAS(n,m)

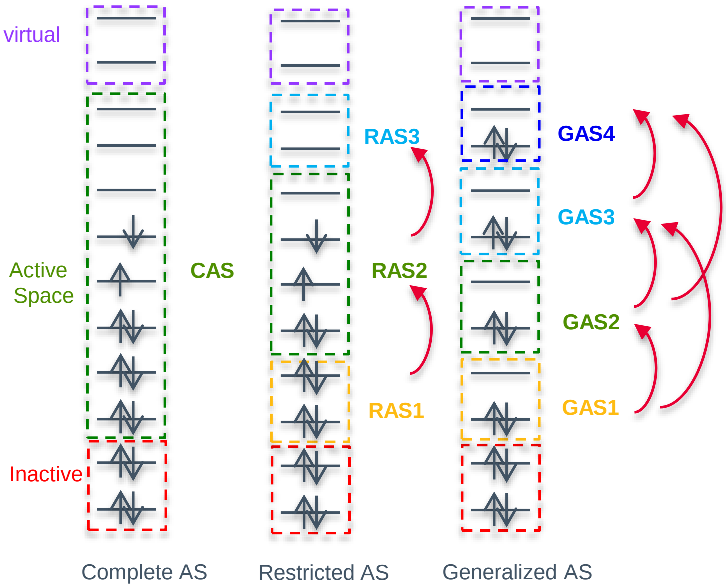
RAS: Additional subdivision of the active orbitals in three categories: RAS1 RAS2 and RAS3. It is written as:

$RAS(n,m; e_{RAS1},e_{RAS3})$

n: number of electrons
m: number of orbitals
e_{RAS1}: max. number of holes
e_{RAS3}: max. number of particles

CASSCF: Chem. Phys. **1980**, *48*, 157.
RASSCF/RASPT2: J. Chem. Phys. **2008**, *128*, 204109.

GASSCF METHOD: PUSHING THE ACTIVE SPACE LIMITS



Bigger active spaces?

GASSCF Approach

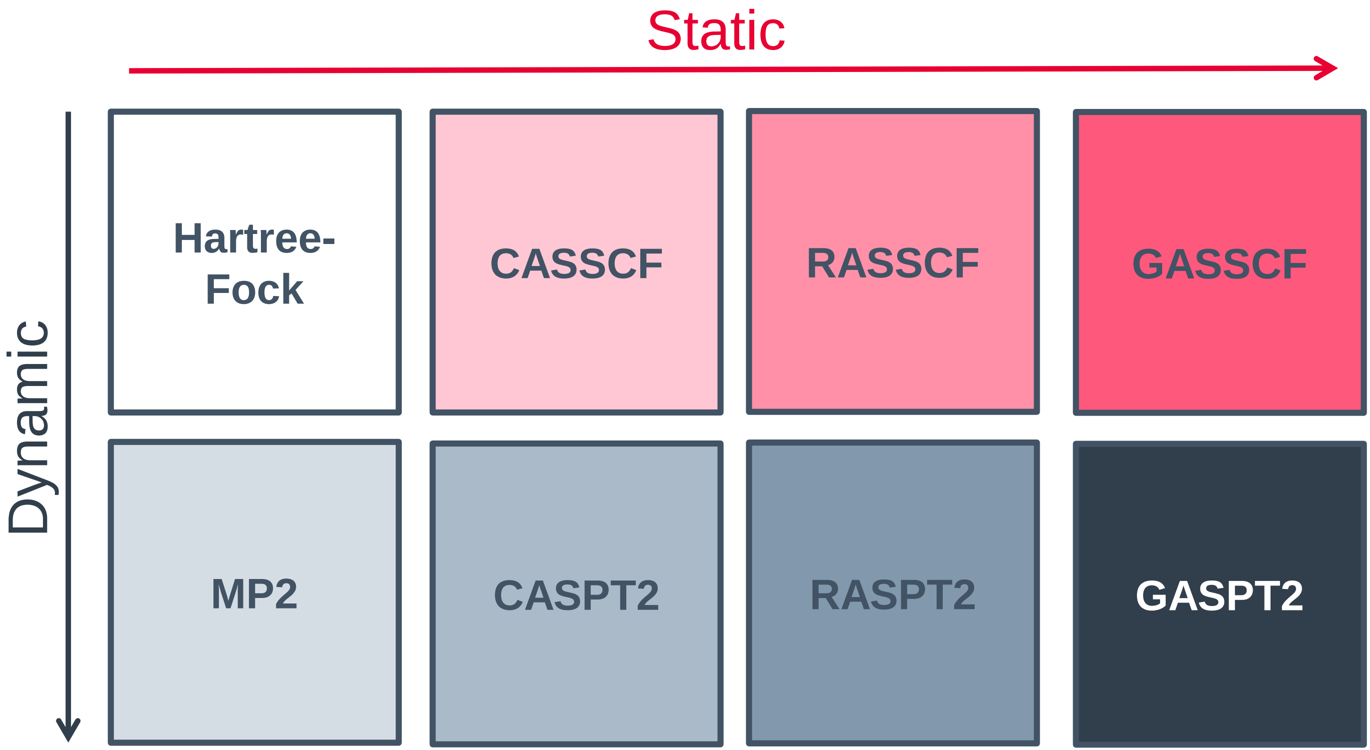
Infinite number of subspaces

<u>Advantages</u>:

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

RASSCF/RASPT2: J. Chem. Phys. **2008**, *128*, 204109.
GASSCF: J. Chem. Phys. **2011**, *135*, 044128.
GASPT2: J. Chem. Theory Comput. **2016**, *12*, 3208

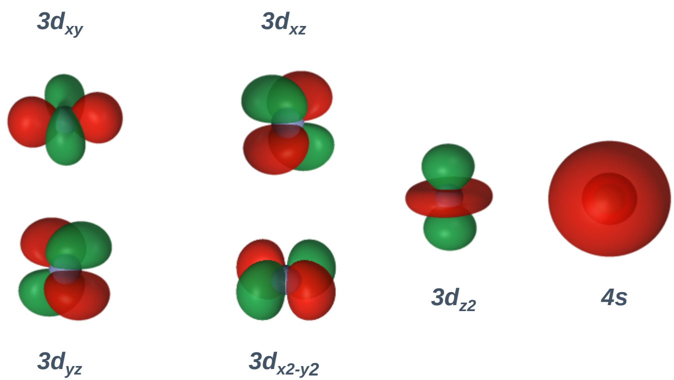
… AND CASSCF ALONE ISN'T ENOUGH!

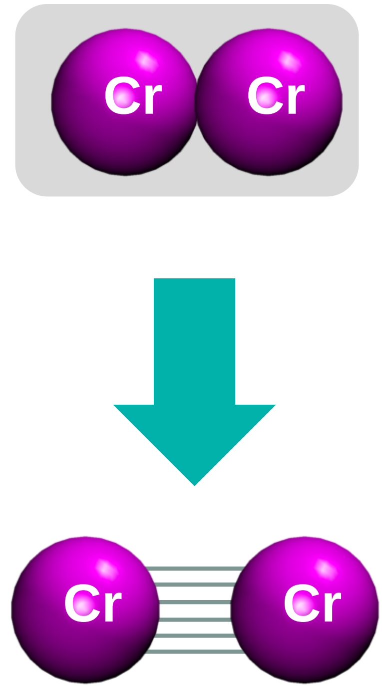


Courtesy of Professor B. Vlaisavljevich

CHROMIUM DIMER (GOLDEN CASE)

- Five 3*d* orbitals and 4*s*: $(3d)^5(4s)^1$





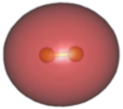
- Cr_2 → sextuple bond?

  Then, we should expect:
  - short bond length
  - large bond energy

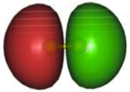
Formal Bond Order and Effective Bond Order

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

If occupation of BO is $\eta_{bo} = 2 - x$,



the occupation of AO is $\eta_{ao} = x$;



$$\eta_{bo} + \eta_{ao} = 2$$

- Effective Bond Order (EBO)

$$EBO = \frac{\sum \eta_{bo} - \sum \eta_{ao}}{2}$$

To be compared with the Formal Bond Order (FBO)

Angew. Chem. Int. Ed. **2007,** *46*, 1469.

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(12,12)/CASPT2

Cr–Cr bond length: 1.66 A (1.68 A)*
Bond energy: 38 kcal/mol (35 kcal/mol)*
The EBO is 4.45, not 6

Weakening of the bond is caused by:
- Multireference character.
- Different size of the 3d and 4s. 4s-4s is larger than 3d-3d

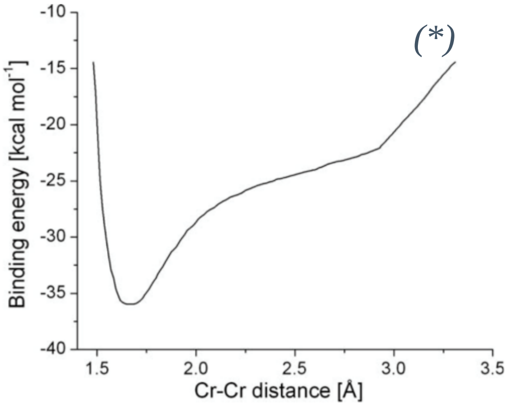
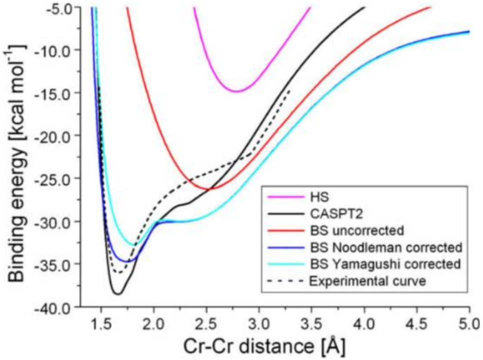


Fig. 1. The experimental potential energy curve for Cr_2 [21].

Angew. Chem. Int. Ed. **2007,** *46,* 1469
J. Phys. Chem*. **1993, *97*, 816.

Chromium Dimer

- DFT: B3LYP/cc-pVTZ



Active Orbitals / CAS(12,12)

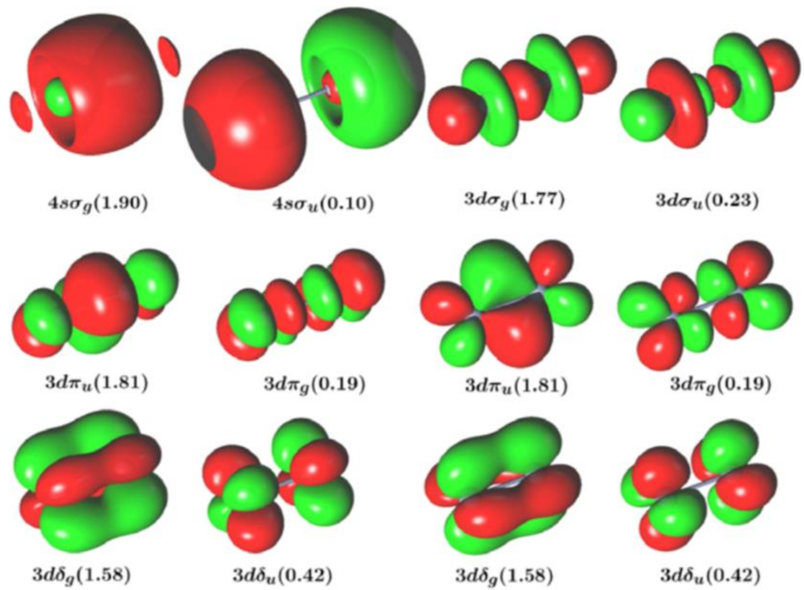


Fig. 2. The natural orbitals for the chromium diatom. Orbital labels and occupation numbers are given below each orbital (contour lines at the density 0.07 e/au^3).

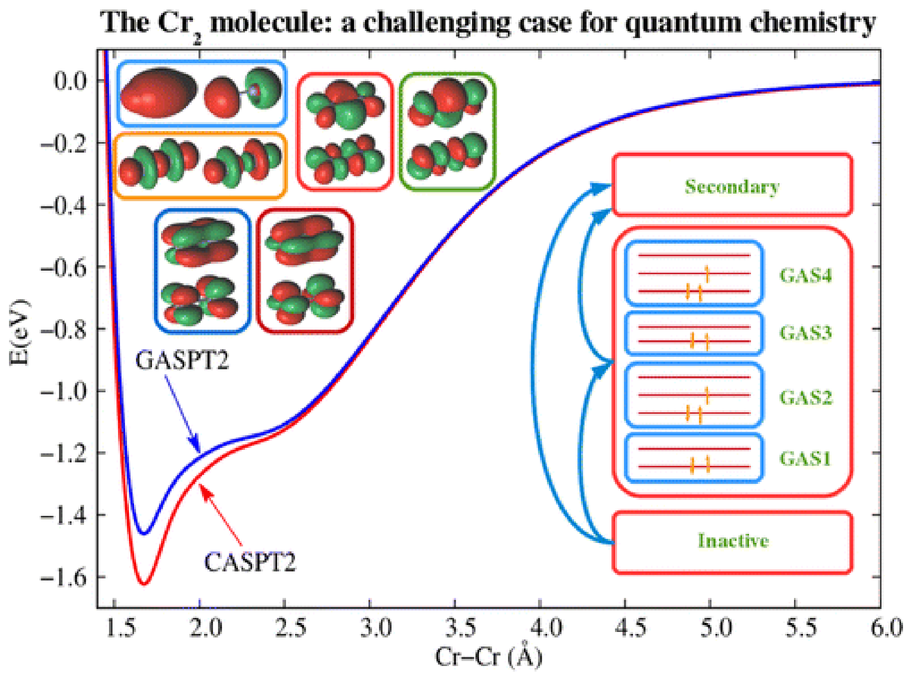
DFT is unable to capture the multireference character of the wavefunction

HS: high-spin
BS: broken-symmetry
CASPT2: CASSCF(12,12)/CASPT2

Chemical Physics Letters 471 (2009) 1–10

CR_2 – GASPT2

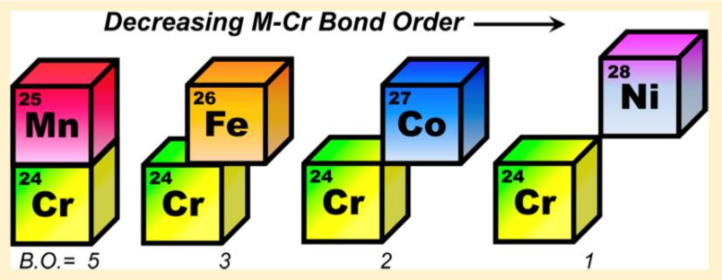
- The user defines an arbitrary number of AS.
- With min and max number of electron per AS.
- GAS allows removal of ineffective configurations

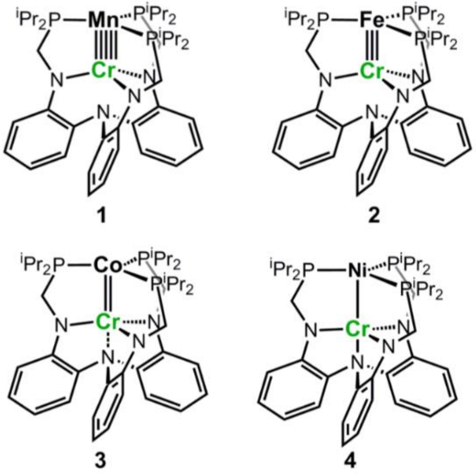


CASSCF/CASPT2(12,12): 28 784 CSF
GASSCF/GASPT2(12,12): 1 516 CSF

J. Chem. Theory Comput. **2016**, *12*, 3208.

- 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

Why is this important?
More than one metal can favor multiple one-electron transfer processes

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

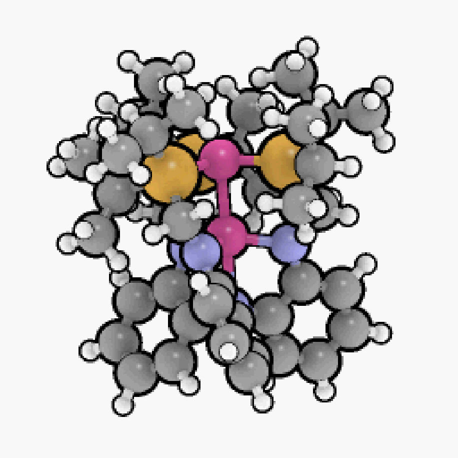
Pauling, L. The Nature of the Chemical Bond, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Molecular Complex Example: Workflow

DFT geometry optimization → **CASSCF** → **CASPT2**

PBE functional (Turbomole)
Basis set:

- 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

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

How do we choose the active spaces?

15 orbitals are necessary:
3d for Cr; *3d* for M and also *4d*!!
Second shell effects (*3d'*)

Let us think …

What do we want to achieve?

Electronic structure of the MM bond

We have **two metal** centers : five ***3d* orbitals**

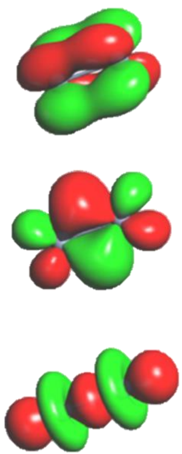
Then, let us count the number of electrons

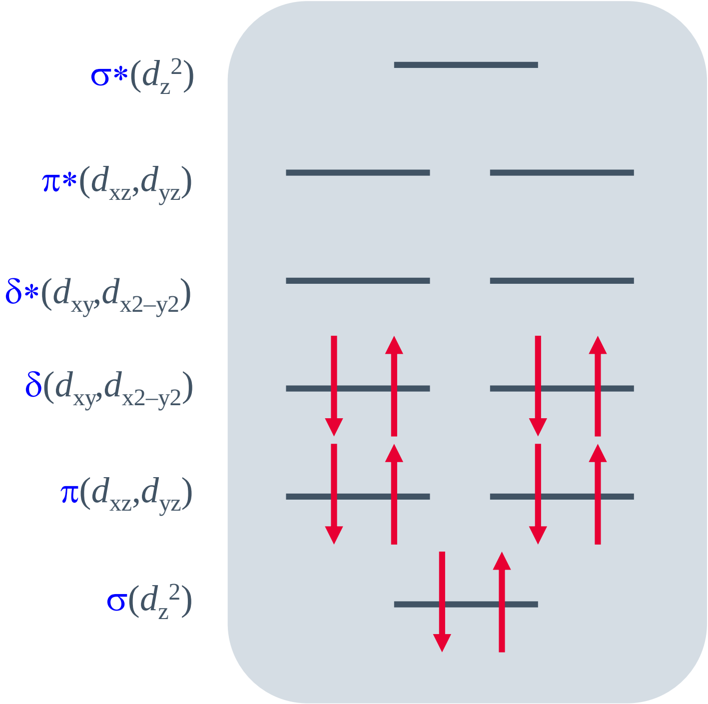
Cr formal oxidation state is +3 and M is zero.

Number of ē	MnCr	FeCr	CoCr	NiCr
M	7	8	9	10
Cr	3	3	3	3
Total electrons	10ē	11ē	12ē	13ē

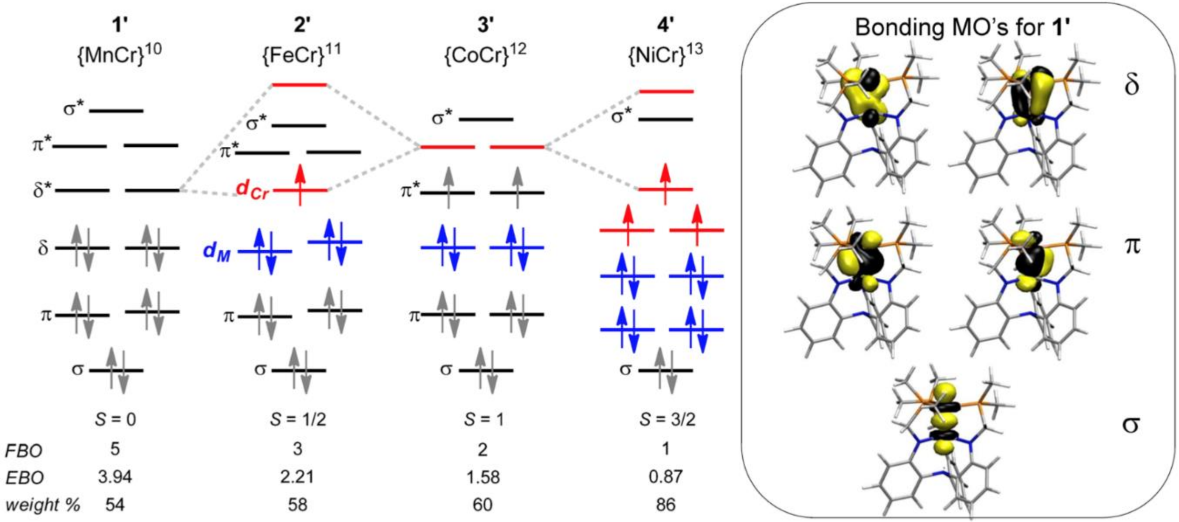
How can we distribute these electrons?

- We have:





- More Multiple Bonds!

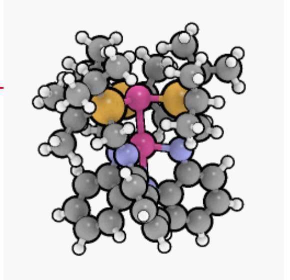


Partial O.S.	MnCr	FeCr	CoCr	NiCr
M	0.9	0.6	0.5	0.3
Cr	2.1	2.4	2.5	2.7

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

MOLECULAR PROBLEMS: DFT AND CASSCF/CASPT2

- MnCr complex



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

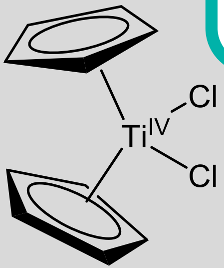
Spin state	**DFT (PBE) (kcal/mol)**	**CASSCF (kcal/mol)**	**CASPT2 (kcal/mol)**	**Percent of main configuration**
singlet	0	0	0	54 %
triplet	8.50	6.932	17.130	59 %
quintet	18.81	19.851	44.864	73 %
septet	32.31	19.337	66.782	88 %

- Remember that CASSCF lacks dynamical correlation.
- DFT energies should be compared to CASPT2 energies.

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

22 $3d^24s^2$
Ti
Titanium
47.867

How many electrons and orbitals are needed to run a successful CAS?

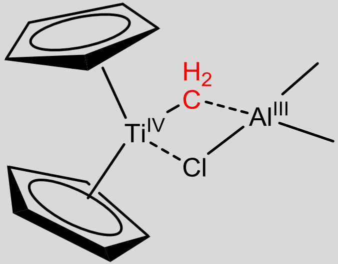


Answer:

- Ti(IV) has no *d* electrons (d^0)
- This is a single reference system

CONCEPTUAL TEST III

How many electrons and orbitals are needed to run a successful CAS?



Tebbe's reagent

Answer:

- Ti(IV) has no *d* electrons (*d*^{0})
- This is a single reference system
- Although the –CH_2 group presents radical character…
  Do not forget about the ligands!!

CASSCF(2,2), the HF determinant corresponds to the dominant configuration with a 91% weight [CAS(12,12) a 88%]

What Have we learnt today?

Key learning points in the lecture:

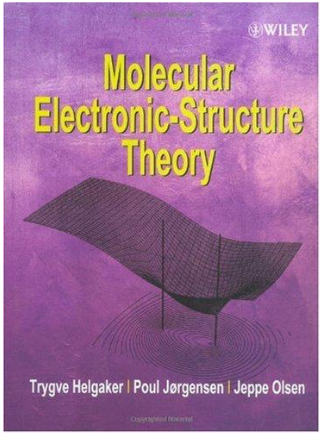
- Multireference methods are used to generate appropriate reference states when single reference methods, such as HF or DFT fail
- Multiconfigurational wavefunctions are represented as a linear combination of Slater determinants or configuration state functions (CSF) to approximate the exact electronic wavefunction.
- In MCSCF, orbitals and CI coefficient are variationally optimized to minimize the energy.
- CASSCF-like methods uses a FCI window (active space) to generate all electron configurations. Remember that direct comparison with DFT must be done after dynamical correlation is included (through CI, PT, CC, or DFT, etc.)

What Have we learnt today?

Key learning points in the lecture:

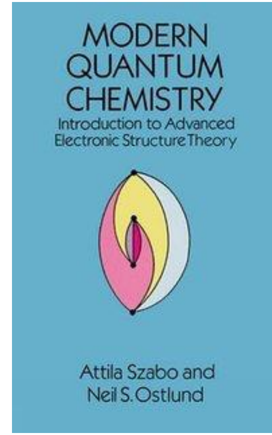
- We discussed key rules to select active spaces depending on the nature of the systems and the question we want to answer.

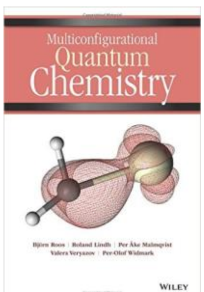
Recommended Books

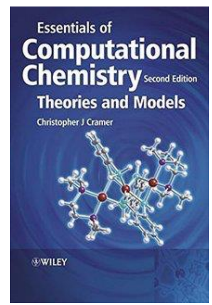


From Molecular Electronic-Structure Theory
by T. Helgaker, P. Jorgensen and J. Olsen, Ed. Wiley 2000.
Chapters 11;12

From Modern Quantum Chemistry:
By A. Szabo, N. S. Ostlund, Ed. Dover Publications 1996.
Chapters 4; Appendix C







THANK YOU FOR YOUR ATTENTION

ACKNOWLEDGEMENTS:

CORE R&D GROUP AT DOW

GAGLIARDI GROUP

AMONG OTHERS

Seek Together™