

The background of the slide features a large, faint, circular watermark of the University of Toronto seal. The seal contains the text "UNIVERSITY OF TORONTO" around the perimeter and "VERITAS" in the center, with a sunburst design above it.

QUANTUM CHEMISTRY FOR TRANSITION METALS



Outline

I Introduction

II Correlation

- Static correlation effects
- MC methods
- DFT

III Relativity

- Generalities
- From 4 to 1 components
- Effective core potential



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I Introduction

II Correlation

- Static correlation effects
- MC methods
- DFT

III Relativity

- Generalities
- From 4 to 1 components
- Effective core potential





Introduction

GROUP

1

IA

PERIOD

1

1

1.0079

H

HYDROGEN

2

IIA

4

9.0122

Be

BERYLLIUM

3

6.941

Li

LITHIUM

13

IIIA

5

10.811

B

BORON

14

IVA

6

12.011

C

CARBON

15

VA

7

14.007

N

NITROGEN

16

VIA

8

15.999

O

OXYGEN

17

VIIA

9

18.998

F

FLUORINE

18

IIIA

10

20.180

Ne

NEON

11

22.990

Na

SODIUM

12

24.305

Mg

MAGNESIUM

19

39.098

K

POTASSIUM

20

40.078

Ca

CALCIUM

21

44.956

Sc

SCANDIUM

22

47.867

Ti

TITANIUM

23

50.942

V

VANADIUM

24

51.996

Cr

CHROMIUM

25

54.938

Mn

MANGANESE

26

55.845

Fe

IRON

27

58.933

Co

COBALT

28

58.693

Ni

NICKEL

29

63.546

Cu

COPPER

30

65.38

Zn

ZINC

31

69.723

Ga

GALLIUM

32

72.64

Ge

GERMANIUM

33

74.922

As

ARSENIC

34

78.96

Se

SELENIUM

35

79.904

Br

BROMINE

36

83.798

Kr

KRYPTON

37

85.468

Rb

RUBIDIUM

38

87.62

Sr

STRONTIUM

39

88.906

Y

YTTRIUM

40

91.224

Zr

ZIRCONIUM

41

92.906

Nb

NI OBIUM

42

95.96

Mo

MOLYBDENUM

43

(98)

Tc

TECHNETIUM

44

101.07

Ru

RUTHENIUM

45

102.91

Rh

RHODIUM

46

106.42

Pd

PALLADIUM

47

107.87

Ag

SILVER

48

112.41

Cd

CADMIUM

49

114.82

In

INDIUM

50

118.71

Sn

TIN

51

121.76

Sb

ANTIMONY

52

127.60

Te

TELLURIUM

53

126.90

I

IODINE

54

131.29

Xe

XENON

55

132.91

Cs

CAESIUM

56

137.33

Ba

BARIUM

57-71

La-Lu

Lanthanide

72

178.49

Hf

HAFNIUM

73

180.95

Ta

TANTALUM

74

183.84

W

TUNGSTEN

75

186.21

Re

RHENIUM

76

190.23

Os

OSMIUM

77

192.22

Ir

IRIDIUM

78

195.08

Pt

PLATINUM

79

196.97

Au

GOLD

80

200.59

Hg

MERCURY

81

204.38

Tl

THALLIUM

82

207.2

Pb

LEAD

83

208.98

Bi

BISMUTH

84

(209)

Po

POLONIUM

85

(210)

At

ASTATINE

86

(222)

Rn

RADON

87

(223)

Fr

FRANCIUM

88

(226)

Ra

RADIUM

89-103

Ac-Lr

Actinide

104

(267)

Rf

RUTHERFORDIUM

105

(268)

Db

DUBNIUM

106

(271)

Sg

SEABORGIUM

107

(272)

Bh

BOHRNIUM

108

(277)

Hs

HASSIUM

109

(276)

Mt

MEITNERIUM

110

(281)

Ds

DARMSTADIUM

111

(280)

Rg

ROENTGENIUM

112

(285)

Cn

COPERNICIUM

113

(...)

Uut

UNUNTRIUM

114

(287)

Fl

FLEROVIUM

115

(...)

Uup

UNUNPENTIUM

116

(291)

Lv

LIVERMORIUM

117

(...)

Uus

UNUNSEPTIUM

118

(...)

Uuo

UNUNOCTIUM

RELATIVE ATOMIC MASS (1)

GROUP IUPAC

GROUP CAS

ATOMIC NUMBER

SYMBOL

ELEMENT NAME

Metal

Semimetal

Nonmetal

Alkali metal

Alkaline earth metal

Transition metals

Lanthanide

Actinide

Chalcogens element

Halogens element

Noble gas

STANDARD STATE (25 °C; 101 kPa)

Ne - gas

Hg - liquid

Fe - solid

Tc - synthetic

<http://www.periodni.com>

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.05 Yb YTTERBIUM	71 174.97 Lu LUTETIUM
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ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM
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(1) Pure Appl. Chem., 81, No. 11, 2131-2156 (2009)
Relative atomic masses are expressed with five significant figures. For elements that have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element. However three such elements (Th, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

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Introduction

Transition metal are elements with valence d (or f) orbitals (« d-block »)

High degeneracy (5-fold degenerate d orbitals)

Ligands only small lifting of degeneracy

A lot of possible oxidation and spin states

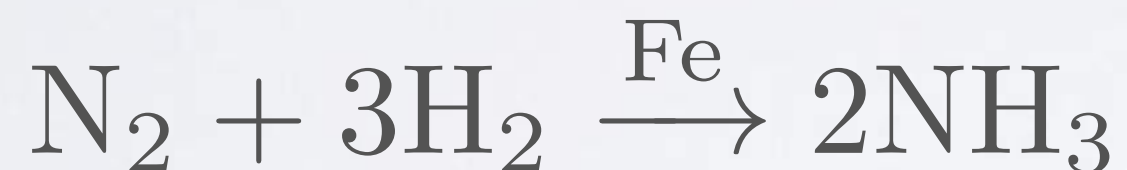
Magnetic properties

Usually absorb visible light



Introduction

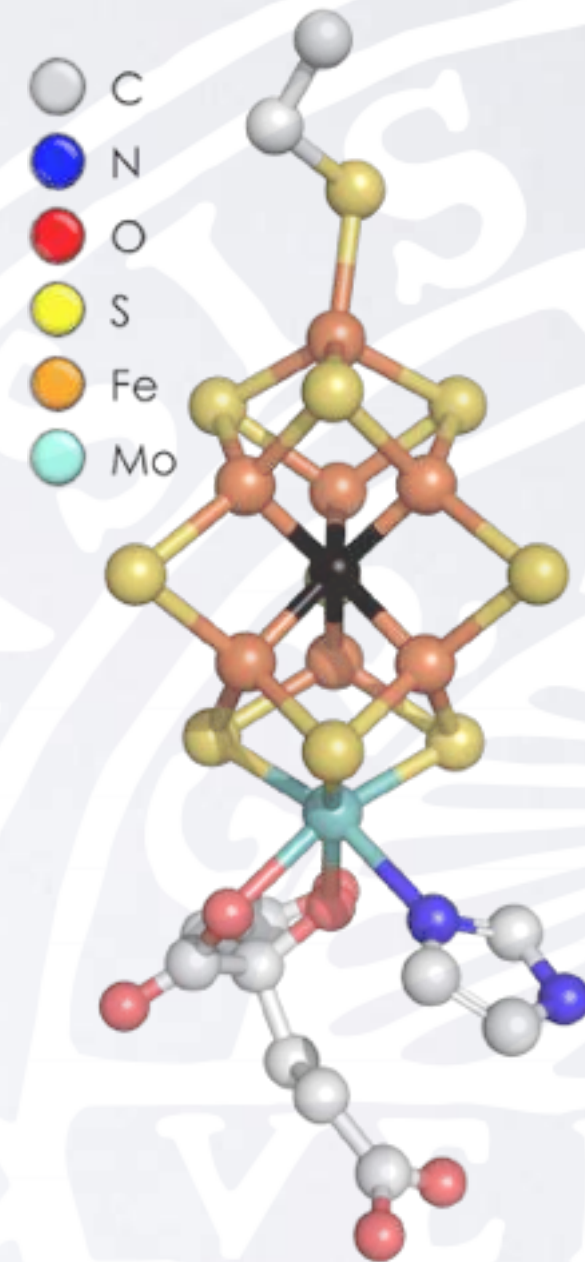
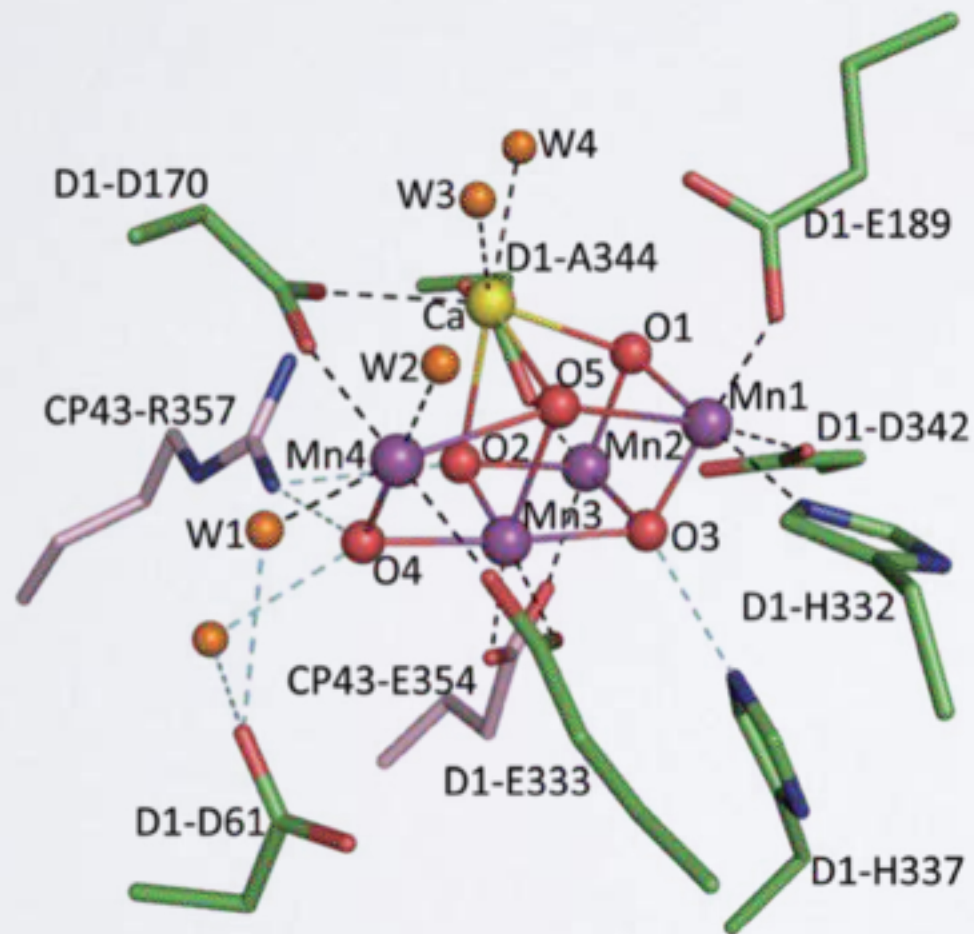
Transition metal are prominent catalysts
both in industry





Introduction

Transition metal are prominent catalysts
and in nature





Introduction

Why are they challenging for quantum chemistry?

High degeneracy (5-fold degenerate d orbitals)

Ligands only small lifting of degeneracy

A lot of possible oxidation and spin states

Magnetic properties

Usually absorb visible light

And somewhat heavy!



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Correlation

Metals have a high electronic density

Large correlation effects

valence (4s, 3d, 4p)

semi-core (3s, 3p)

core (1s, 2s, 2p)

dynamic and static

somewhat constant

constant

By default core correlation is neglected in most QC programs



The « multiconfigurational propensity » periodic table

1 H																	2 He
3 Li 2s	4 Be 2s											5 B 2p	6 C 2p	7 N 2p	8 O 2p 24	9 F 2p	10 Ne 2p
11 Na 3s	12 Mg 3s											13 Al 3p	14 Si 3p	15 P 3p	16 S 3p	17 Cl 3p	18 Ar 3p
19 K 4s	20 Ca 4s	21 Sc 3d	22 Ti 3d	23 V 3d	24 Cr 3d 312	25 Mn 3d 96	26 Fe 3d 1043	27 Co 3d 1390	28 Ni 3d 629	29 Cu 3d	30 Zn 3d	31 Ga 4p	32 Ge 4p	33 As 4p	34 Se 4p	35 Br 4p	36 Kr 4p
37 Rb 5s	38 Sr 5s	39 Y 4d	40 Zr 4d	41 Nb 4d	42 Mo 4d	43 Tc	44 Ru 4d	45 Rh 4d	46 Pd 4d	47 Ag 4d	48 Cd 4d	49 In 5p	50 Sn 5p	51 Sb 5p	52 Te 5p	53 I 5p	54 Xe 5p
55 Cs 6s	56 Ba 6s	57 La 4f	58 Ce 4f 13	59 Pr 4f	60 Nd 4f 19	61 Pm	62 Sm 4f 105	63 Eu 4f 90	64 Gd 4f 293	65 Tb 4f 229 221	66 Dy 4f 179 89	67 Ho 4f 132 20	68 Er 4f 85 20	69 Tm 4f 56	70 Yb 4f	71 Lu 4f	
87 Fr	88 Ra 7s	89 Ac 5f	90 Th 5f	91 Pa 5f	92 U 5f	93 Np 5f	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	



Correlation

QC methods

~~HF (SCF)~~

~~MP2~~

~~CISD~~

CCSD

DFT

~~MCSCF~~

MRPT2

MRCISD

~~MRCOCSO~~

...



Correlation

DFT rules hegemonically over inorganic chemistry
but accuracy not always that good



Ligand field theory

Simple picture of TM binding

Often high local symmetry (square planar, tetrahedral, octahedral)

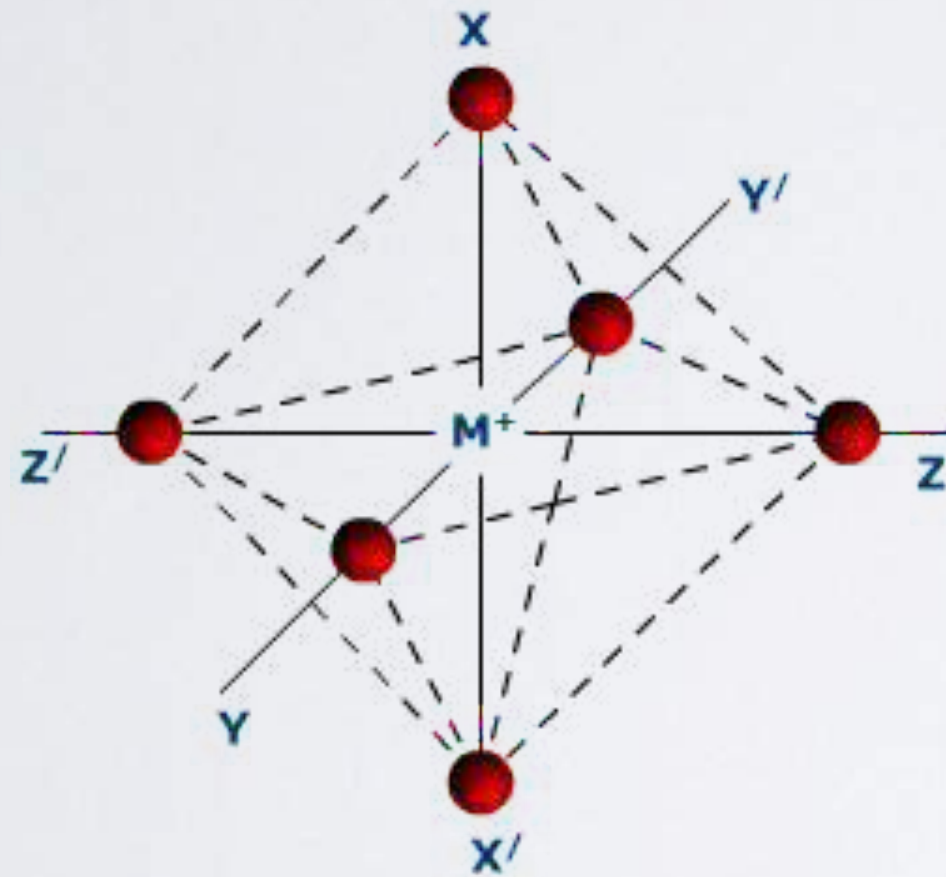
Central to designing of active space

Central to understanding of inorganic chemistry

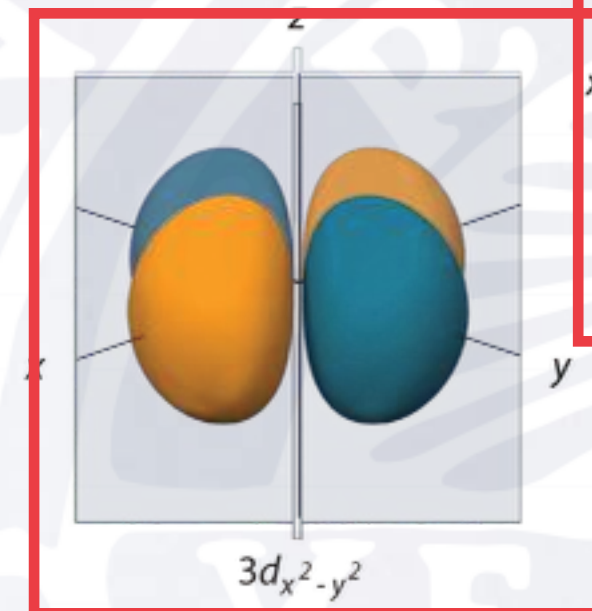
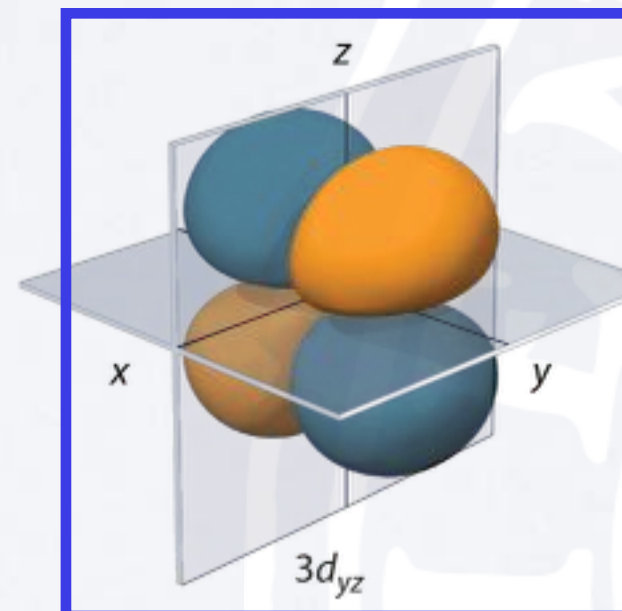
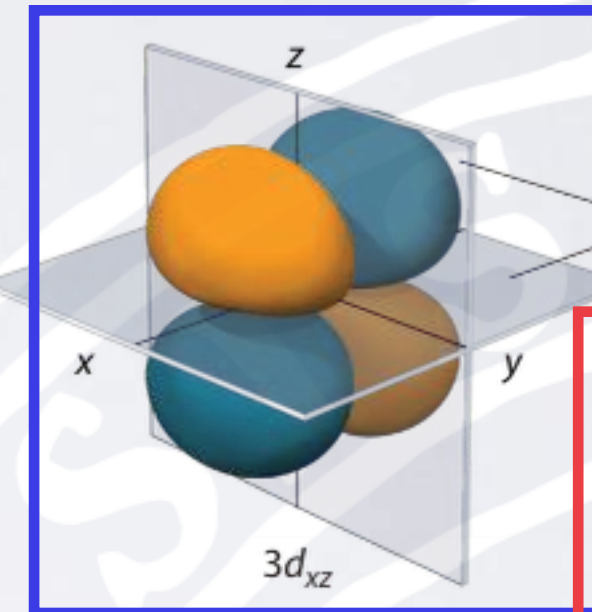
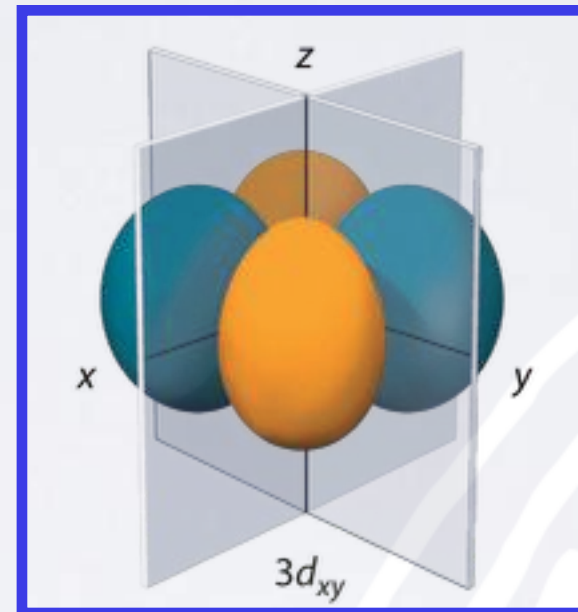
« Lewis structure » of TM



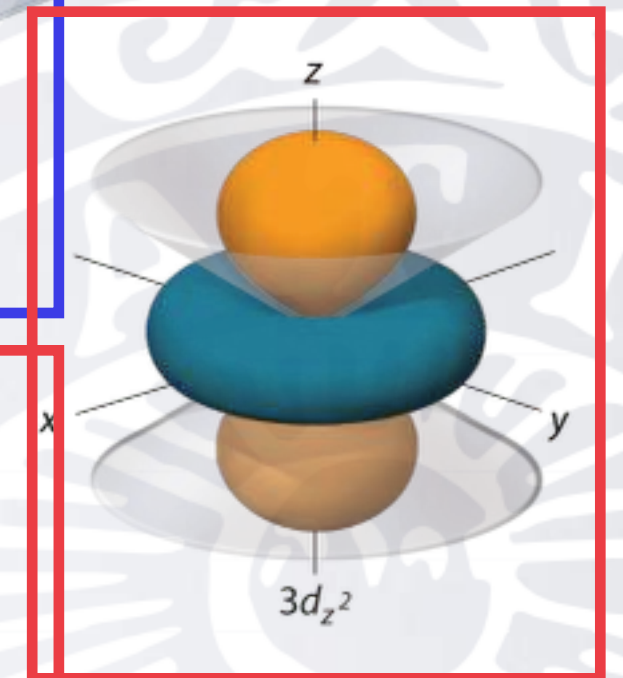
Ligand field theory



π



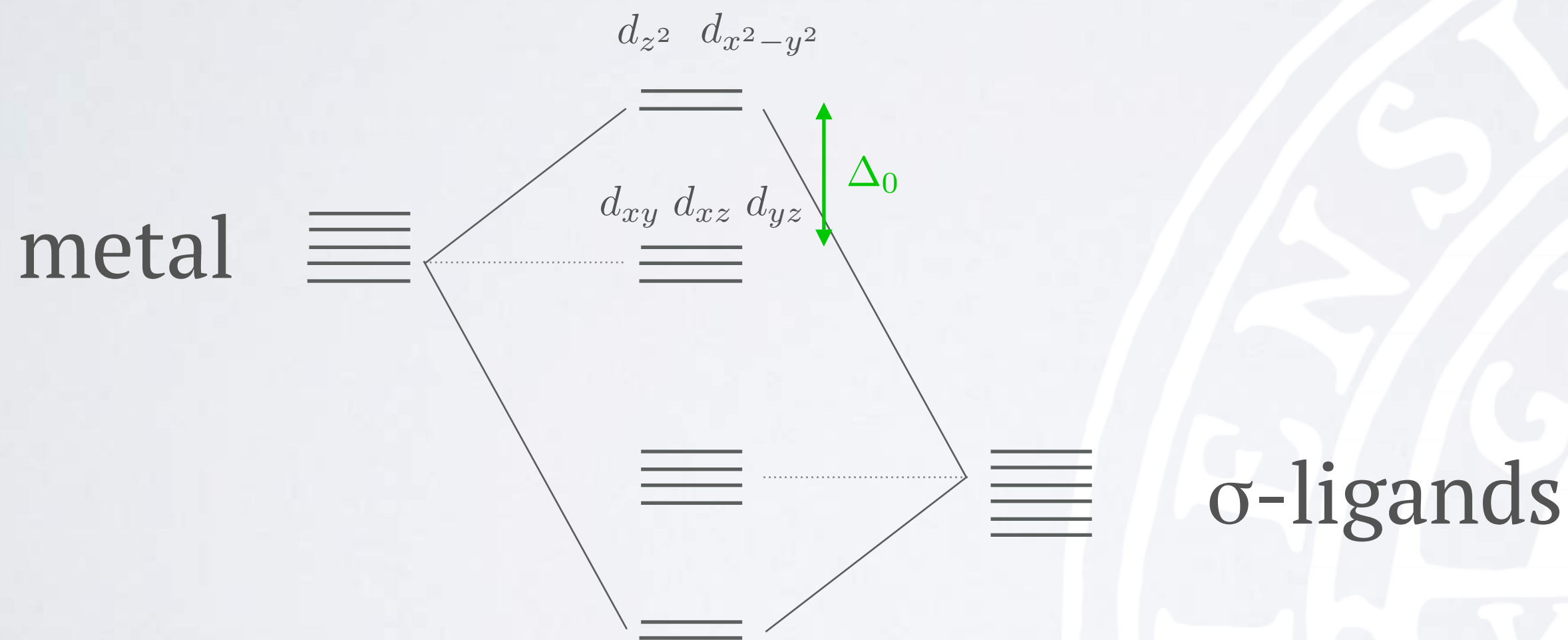
σ





Ligand field theory

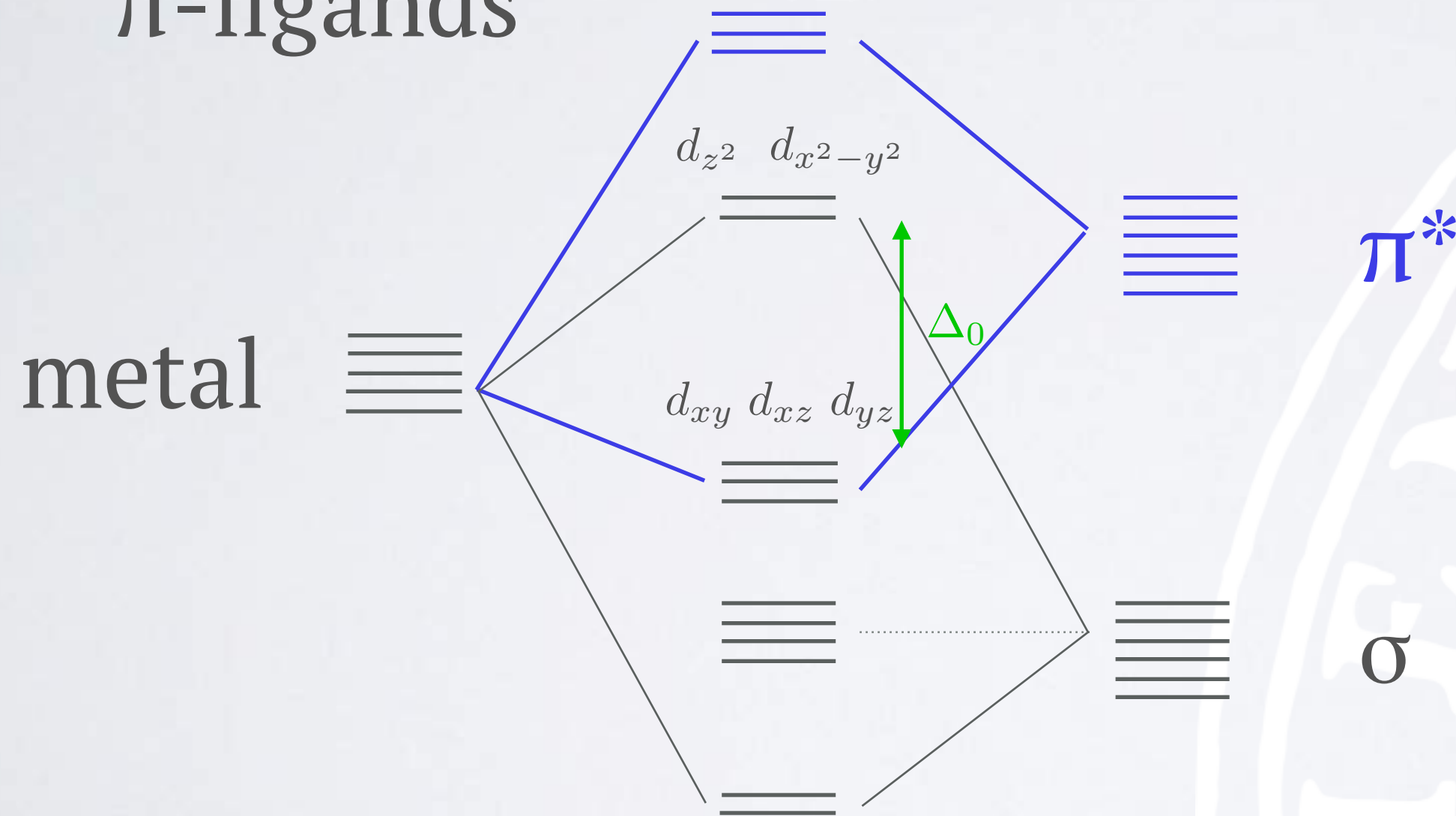
σ -ligands





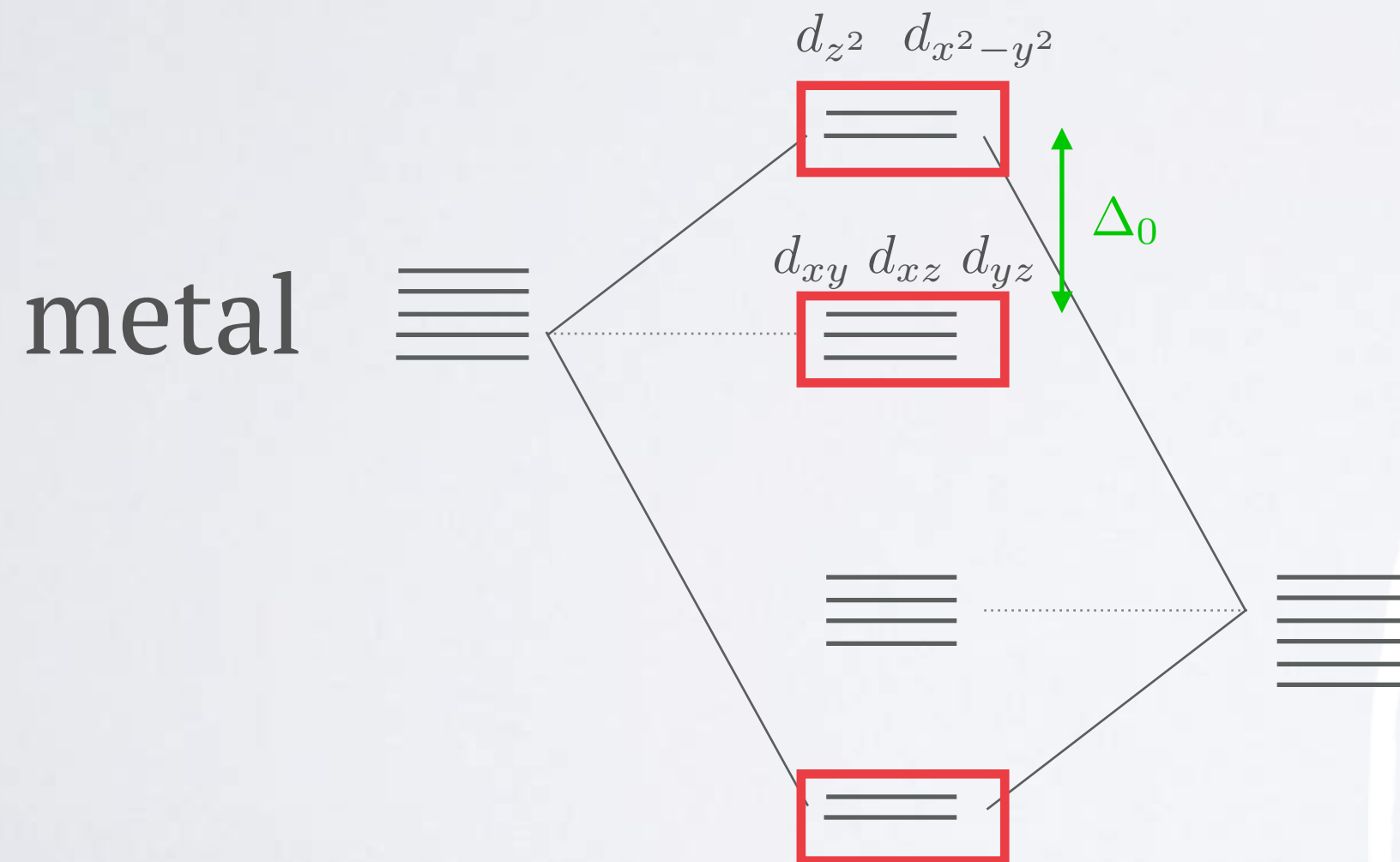
Ligand field theory

π -ligands





Active space theory σ -ligands



no correlating partner
for pure d orbitals

Add corresponding 4d
(important for late TM)

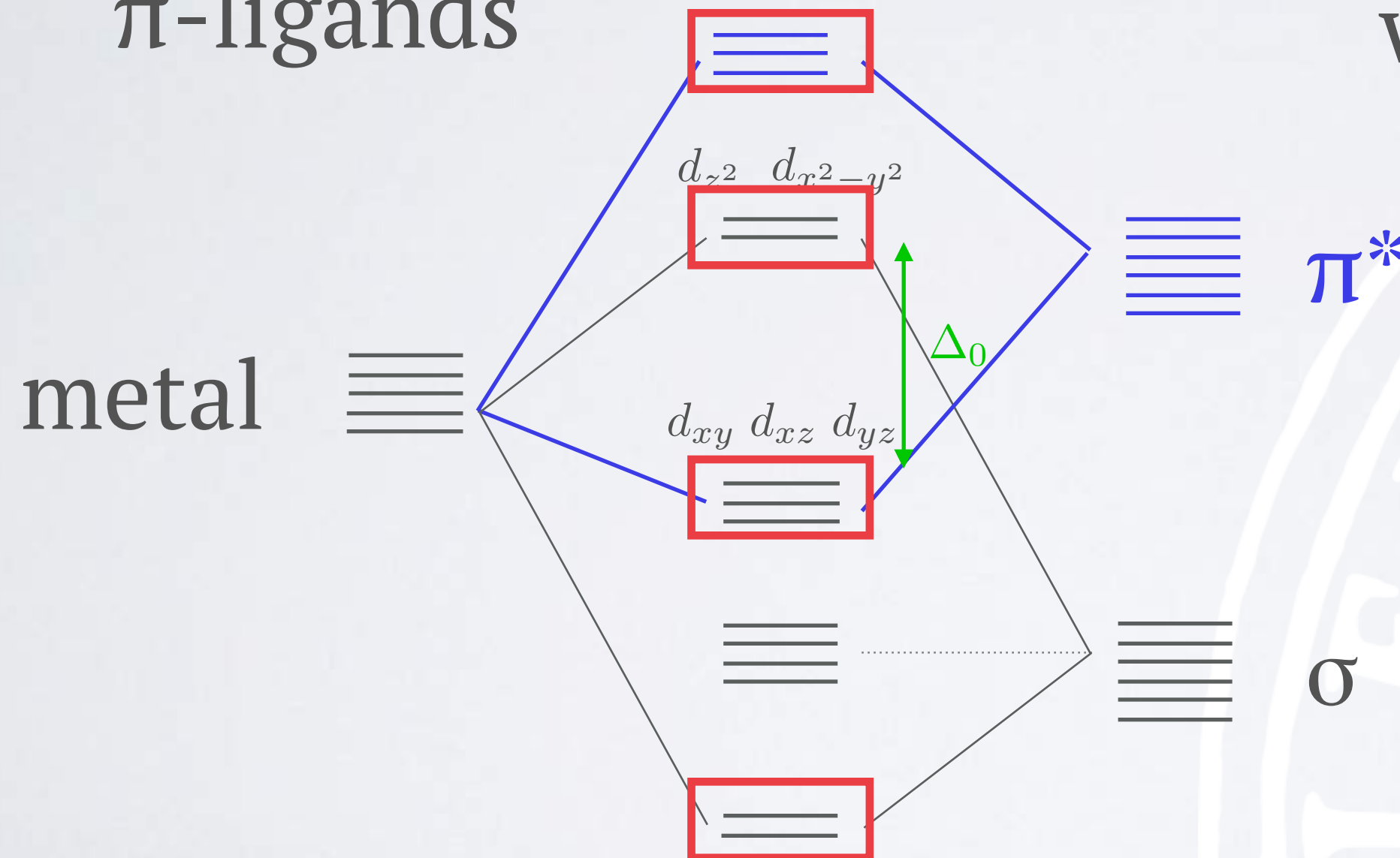
double-shell effect

σ -ligands



Correlation - MC methods

Active space theory π -ligands



Often π^* orbitals mixed
with 4d (double-shell)

Warning also remaining
 π^* for photochemistry



Active space theory

MOLECULAR PHYSICS, 10 July 2003, Vol. 101, No. 13, 2083–2094



Taylor & Francis
Taylor & Francis Group

The CASPT2 method in inorganic electronic spectroscopy: from ionic transition metal to covalent actinide complexes*

KRISTINE PIERLOOT[†]

Department of Chemistry, University of Leuven,
Celestijnenlaan 200F, B-3001 Heverlee-Leuven, Belgium

(Received 15 October 2002; accepted 20 November 2002)

During the past ten years, the CASSCF/CASPT2 method has been applied with considerable success to a substantial number of problems related to the electronic spectroscopy of transition metal complexes, thus providing a definite breakthrough of *ab initio* quantum chemistry in this domain. This will be illustrated in the present contribution by means of a few representative cases from the field of inorganic, organometallic and bio-chemistry. Furthermore, CASPT2 results obtained for the excitation energies of the ions UO_2^{2+} and $\text{UO}_2\text{Cl}_4^{2-}$ will be presented, indicating that the method is also applicable with comparable accuracy for molecules with very heavy metals (provided that relativistic effects are accounted for). We will also show that the success of the method is critically dependent upon its judicious application, in particular upon the choice of the orbitals to be included in the reference active space. A link will be made between the latter choice and the specific electronic structure of the metal–ligand interactions.



Correlation - MC methods

Accuracy CASPT2 vs CCSD(T)?

CASPT2 most often good, rarely bad

Depends a lot on the quality of the settings

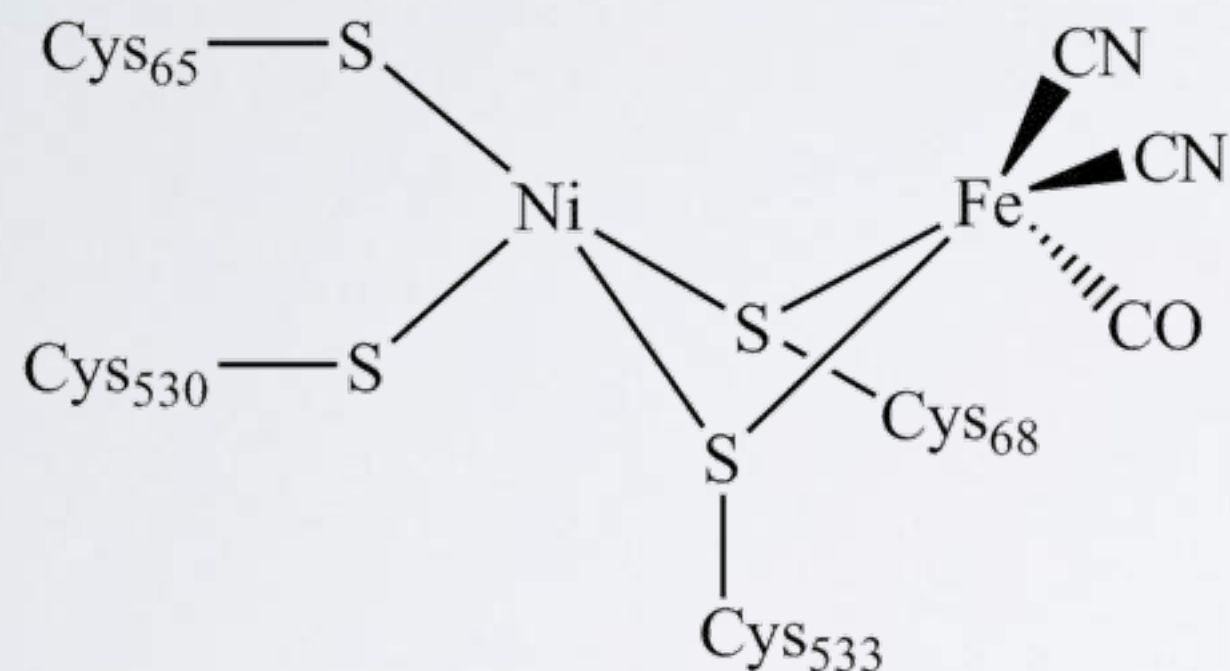
CCSD(T) often excellent, sometimes terrible

T1 diagnostic

Think about what you're doing!



Accuracy CASPT2 vs CCSD(T)?



[Ni-Fe] Hydrogenase

Ni can be singlet or triplet
Very large variations
among DFT

CCSD(T) have large T1 value
but comes from Fe!!!

CCSD(T) better reference for
spin on Ni than CASPT2

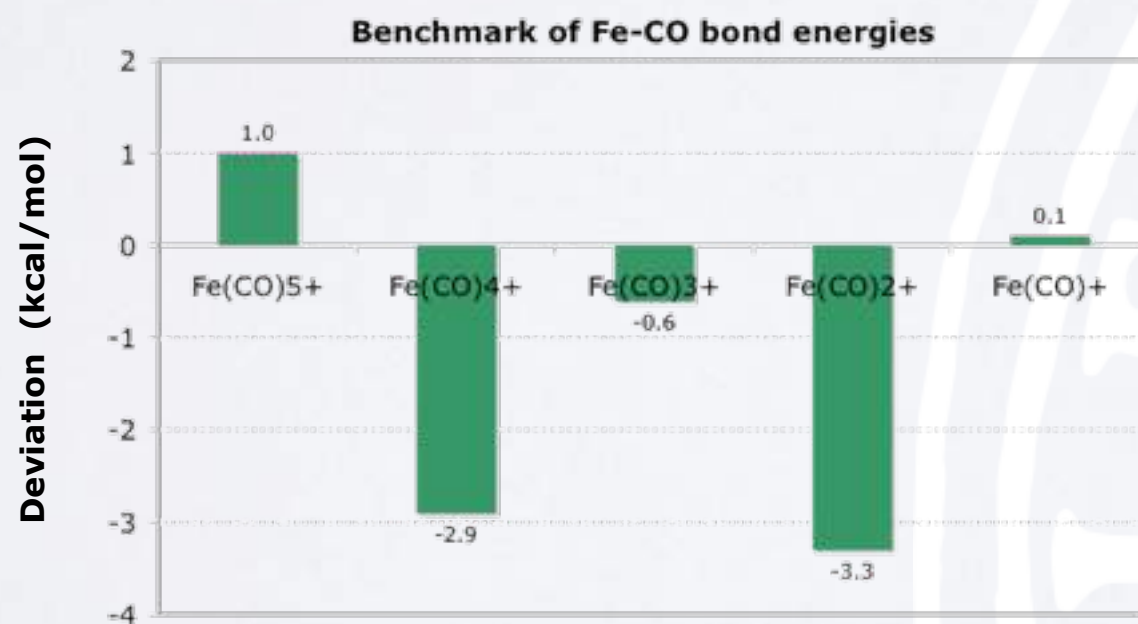


Correlation - DFT

DFT is less sensitive to static correlation than many advanced post-HF methods

Error cancellation with self-interaction

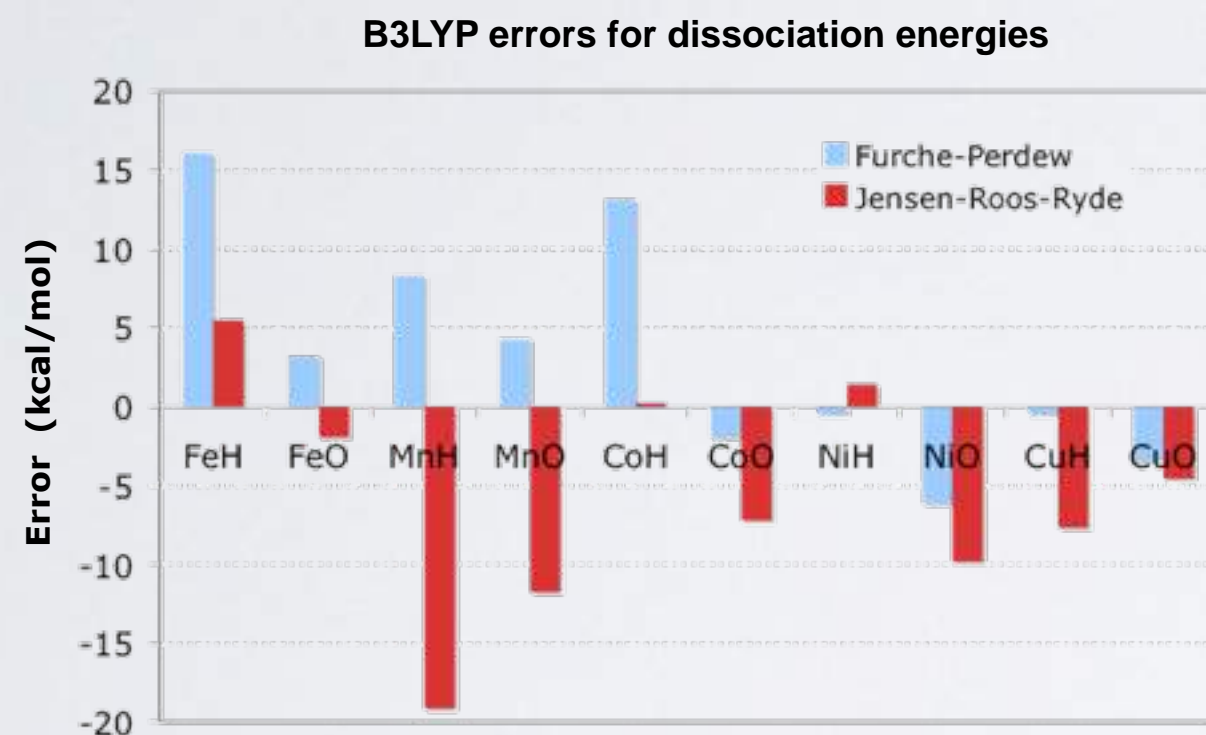
Early investigations hybrid DFT promising





Correlation - DFT

Later investigations... less promising



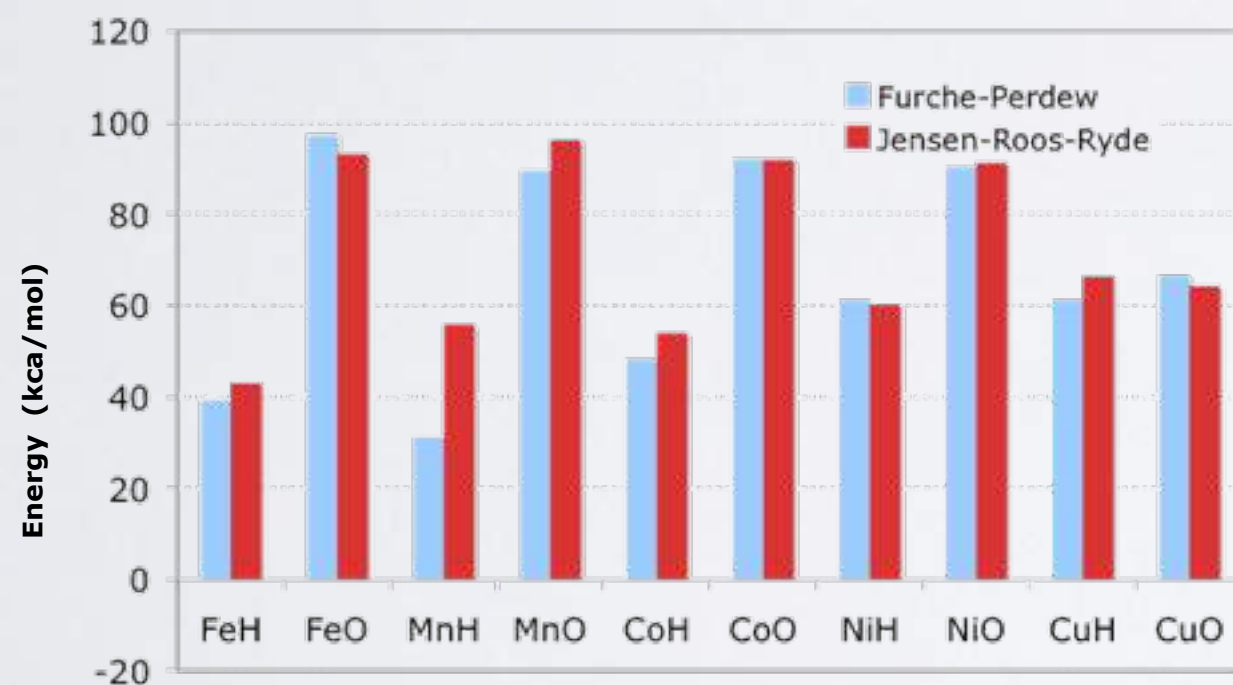
Large deviations
also large deviation between
studies



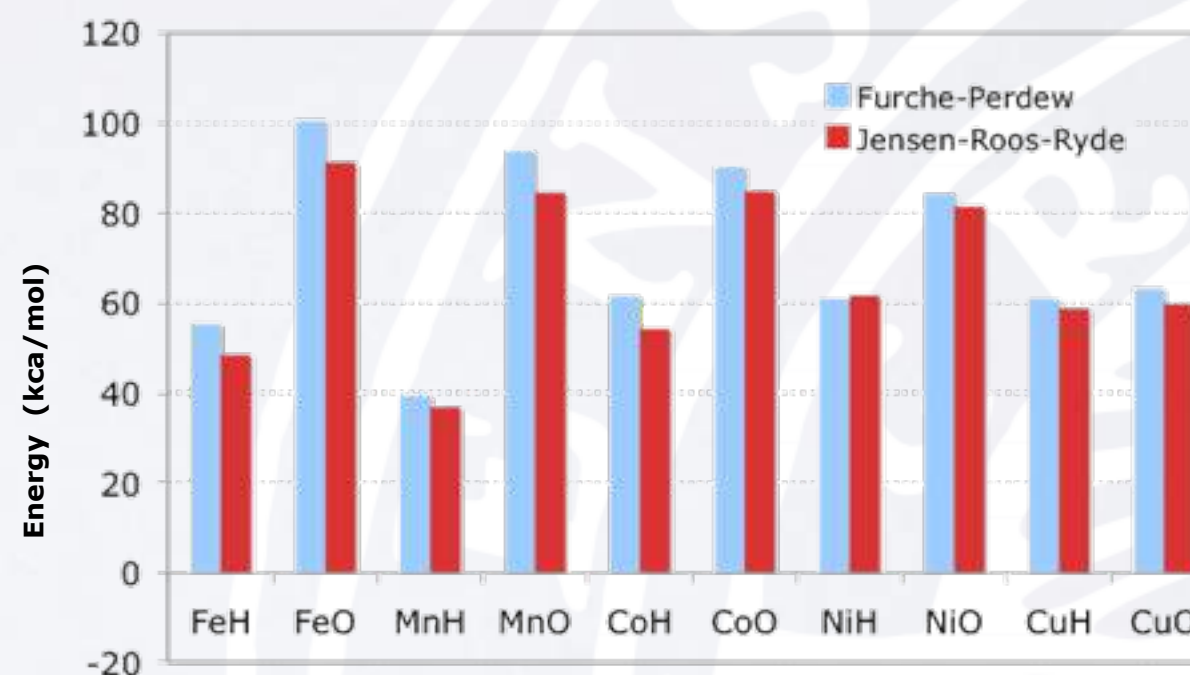
Correlation - DFT

Difficult to benchmark TM systems
Flawed experimental data
Difficult to converge densities

Experimental benchmarks



B3LYP results for dissociation energies



Mixed set - Furche & Perdew, *J. Chem. Phys.* **2006**, 124, 044103.
Diatomics - Jensen, Roos & Ryde, *J. Chem. Phys.* **2007**, 126, 014103.



DFT convergence

For TM, many possible GS: difficult to converge
if converged, is it right one?

Starting iterations, occupy virtual level (Fermi)

Help finding other orbital solutions

Slower but more chance to find the lowest state

But then, one wants faster convergence



DFT convergence

Orbital rotation = single excitation

Perturbative idea : inverse of orbital energy

Low Homo-Lumo gap \Rightarrow difficult convergence

Hartree-Fock exchange increases gap

Can use level shift to artificially increase gap

Can converge to wrong state

Use quadratic convergence (costly)



Correlation - DFT

DFT functional

Result usually very sensitive to functional choice

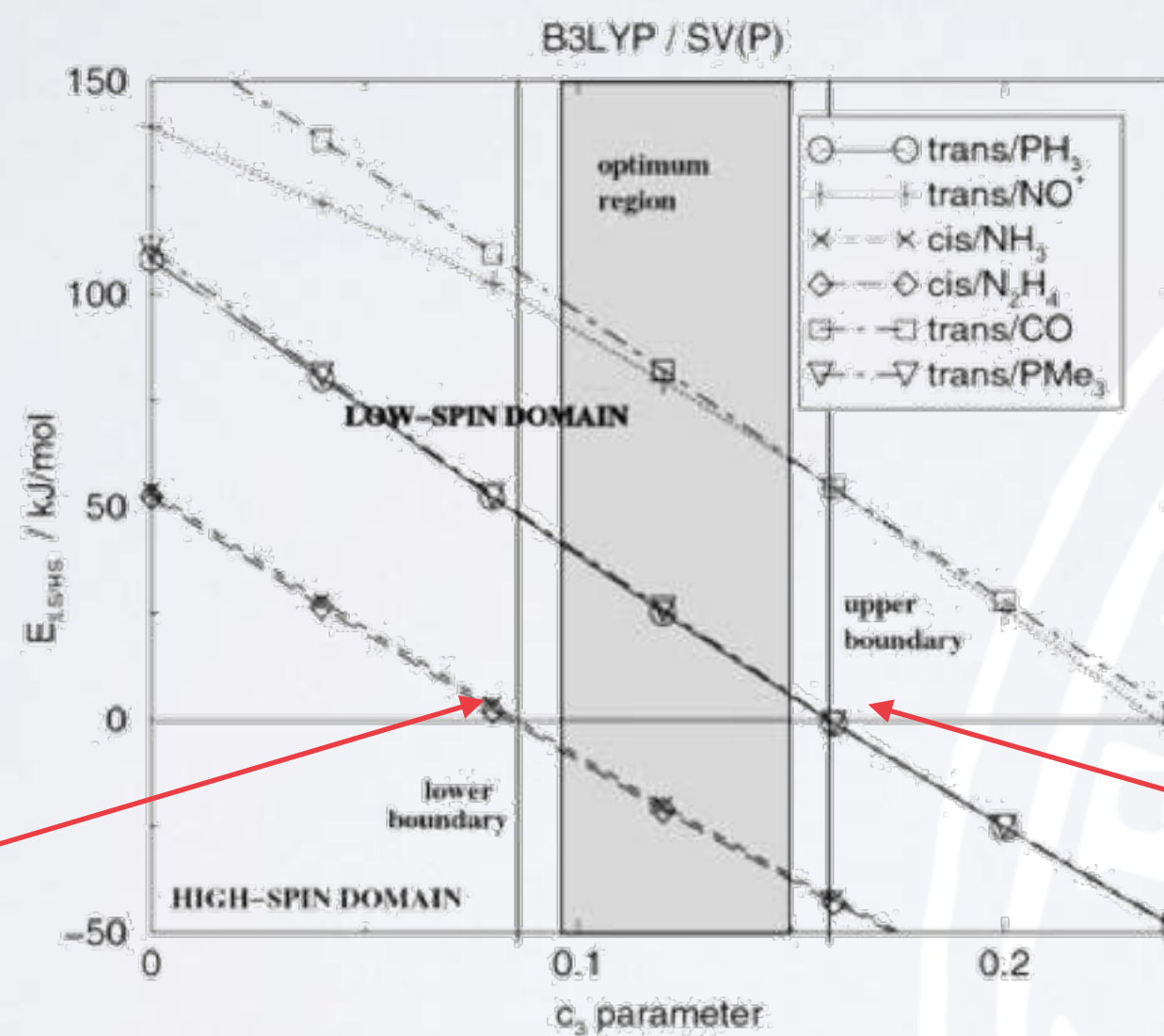
Even bond length can vary a lot

Cannot use double-hybrids



Correlation - DFT

HF exchange fundamental in the accuracy of functionals



Known to be
high spin

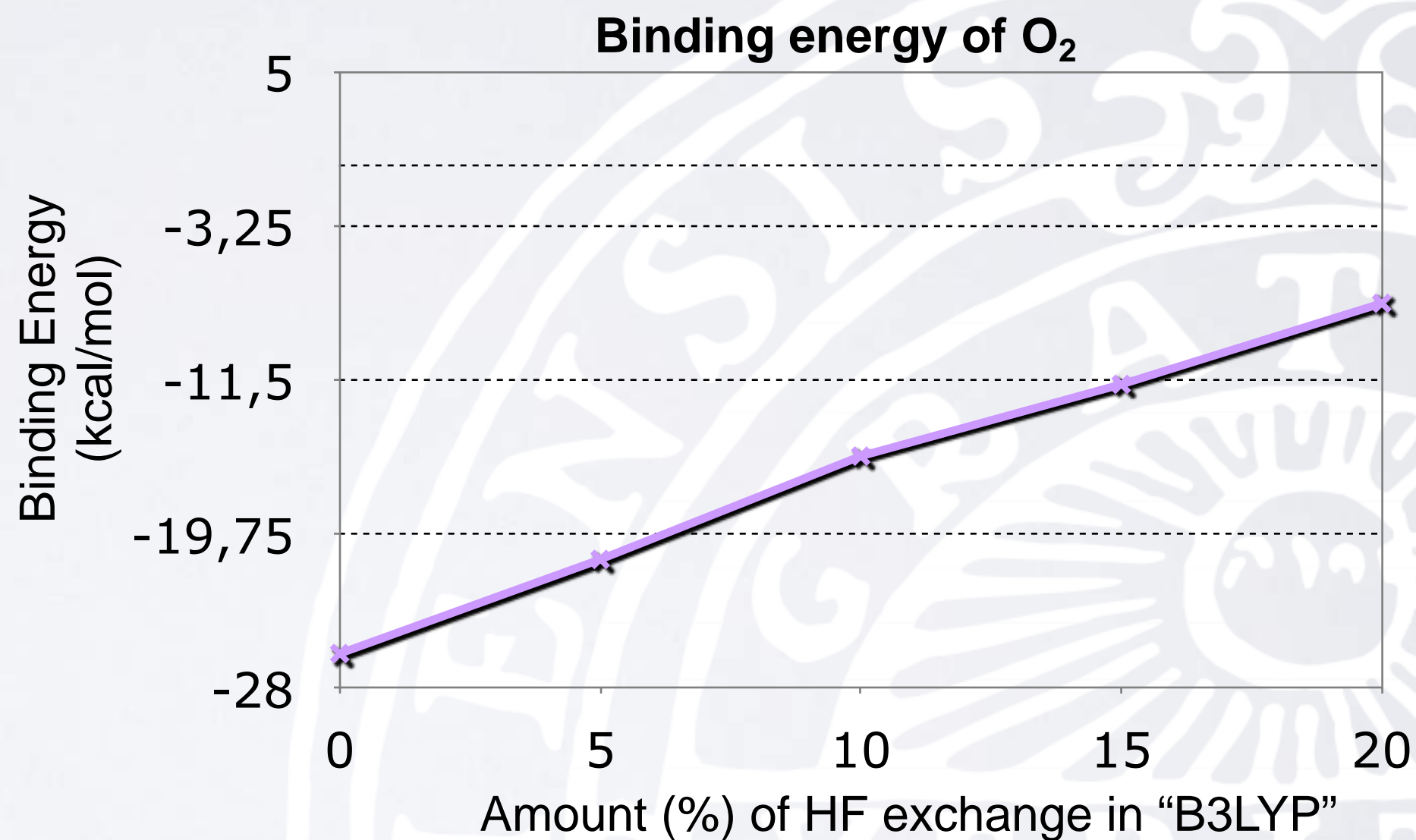
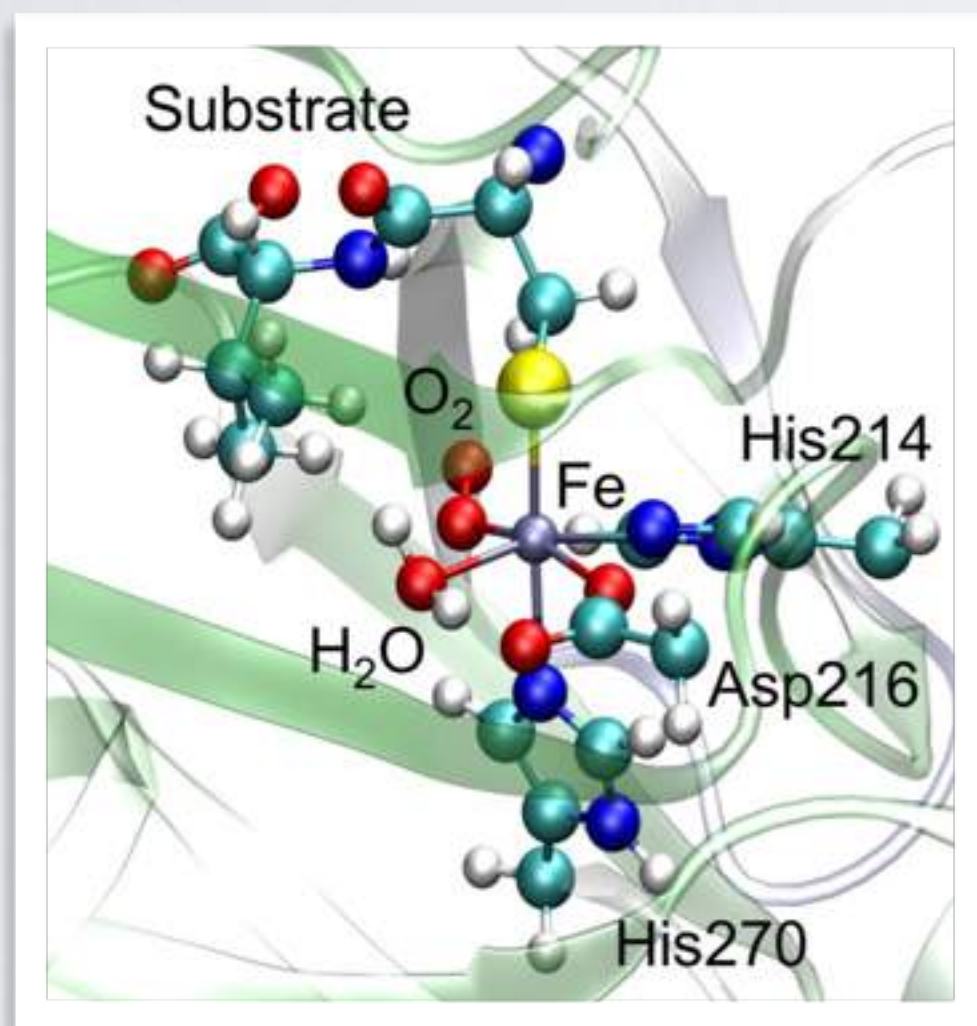
Reduced HF exchange
compared to main
group elements

Known to be
low spin



Correlation - DFT

HF exchange fundamental in the accuracy of functionals





Benchmark

JCTC

Journal of Chemical Theory and Computation

Article

pubs.acs.org/JCTC

Tests of Exchange-Correlation Functional Approximations Against Reliable Experimental Data for Average Bond Energies of 3d Transition Metal Compounds

Wenjing Zhang,^{†,‡} Donald G. Truhlar,^{*,‡} and Mingsheng Tang[†]

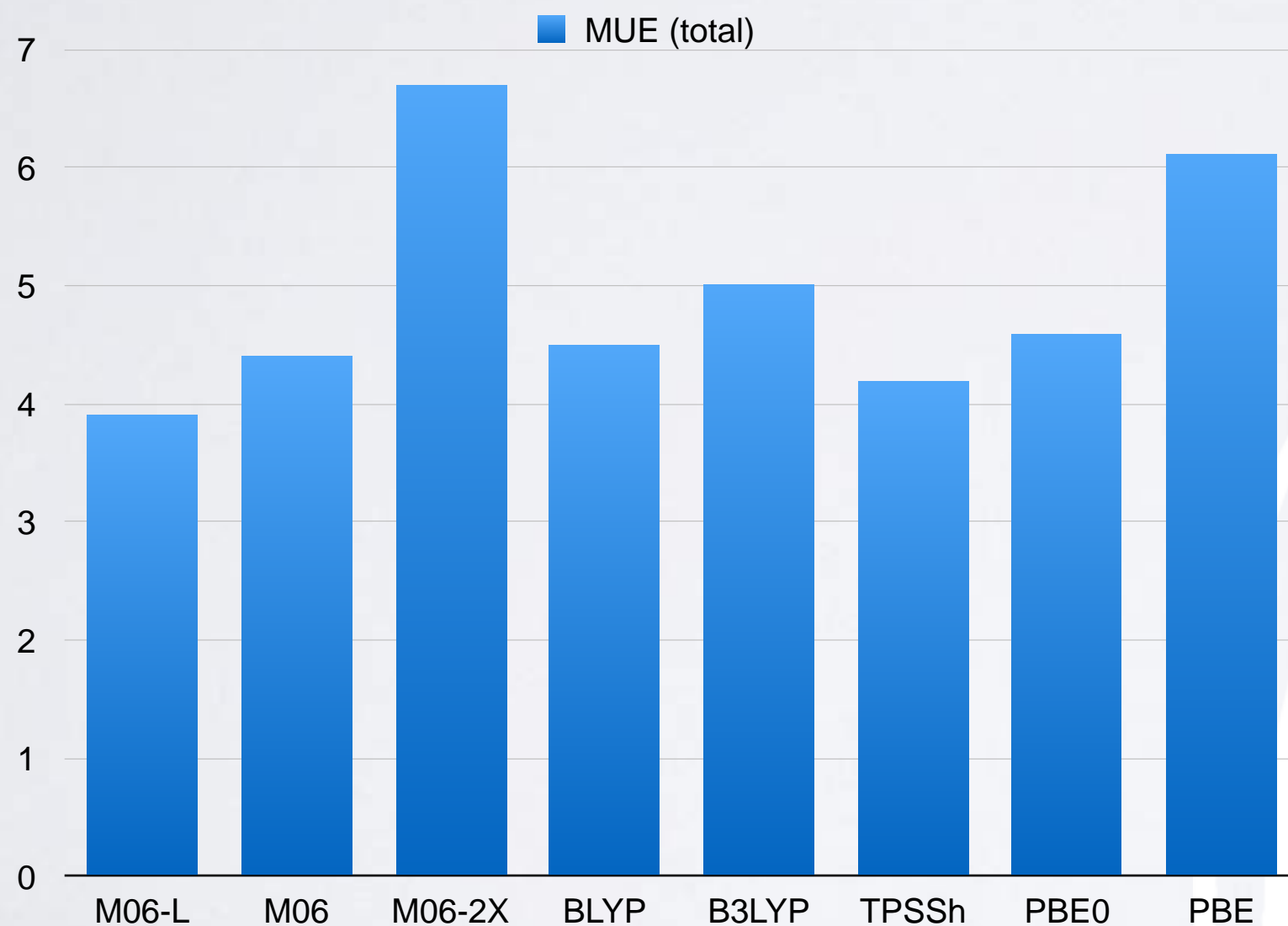
[†]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan Province 450001, P. R. China

[‡]Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States



Correlation - DFT

Benchmark



Modern functionals better
for TM systems

M06, TPSSh...

Depends a lot on system

M06

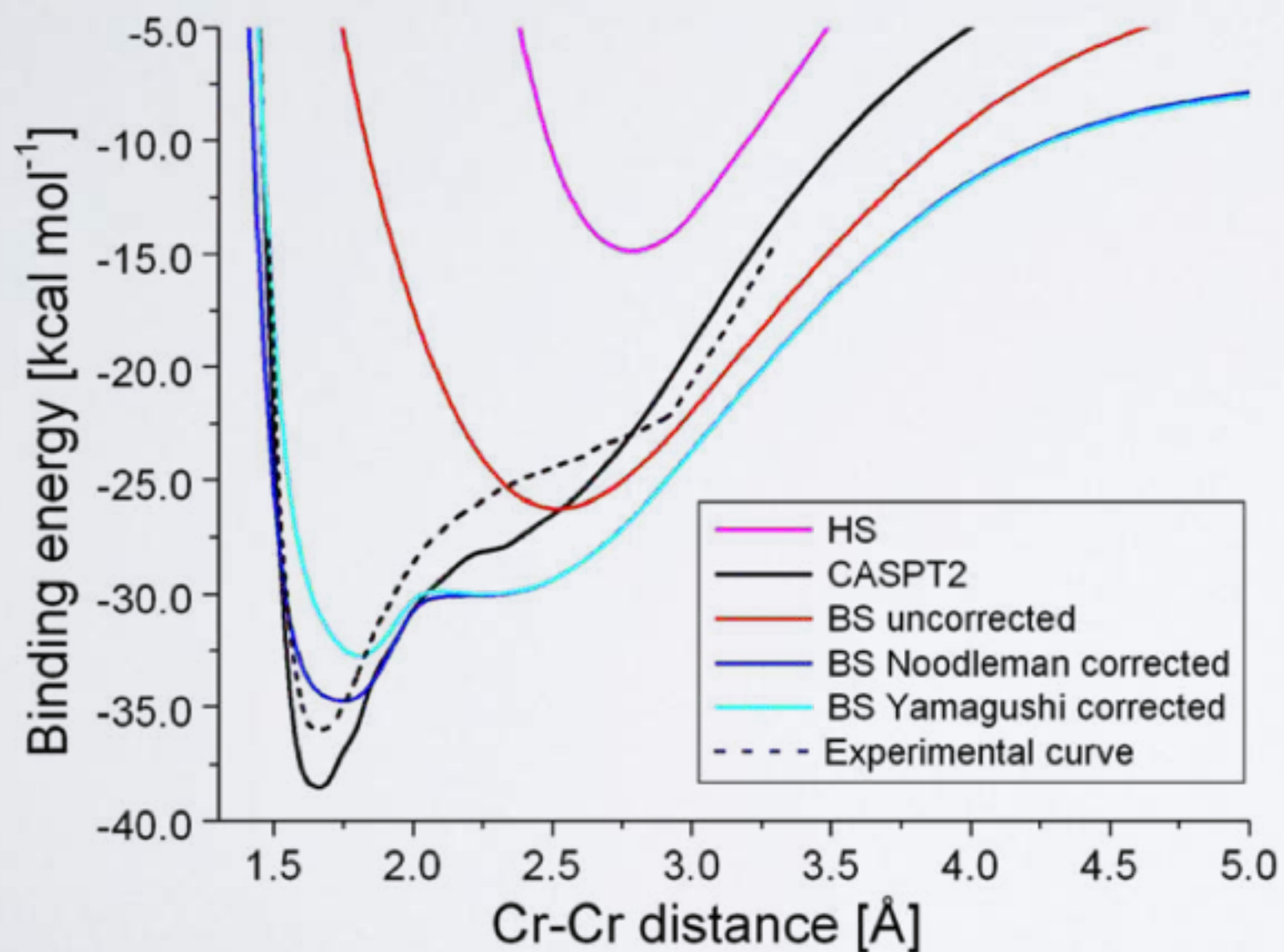
M-C: 1.9 kcal/mol

M-O: 9.7 kcal/mol



Correlation - DFT

Nightmare: metal dimers



Cr₂ archetypal QC « nightmare »

Even post-HF methods have
hard time

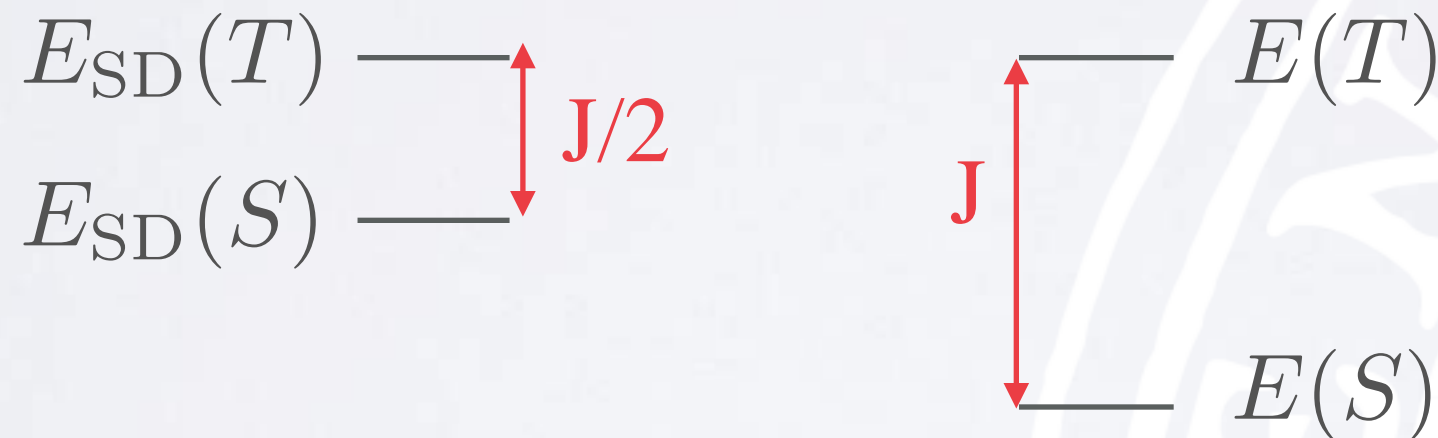
DFT with broken-symmetry
terrible

Large spin contamination



Broken symmetry correction for 2 unpaired electrons

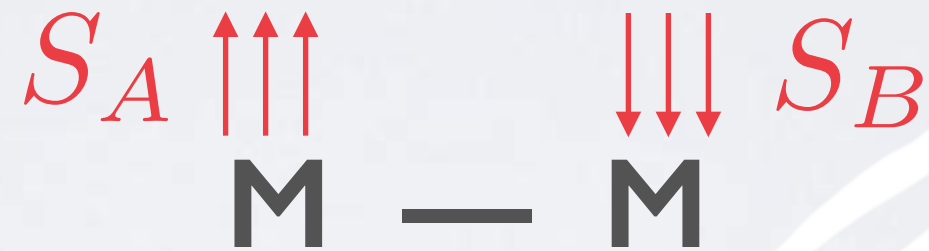
$$E_{\text{SD}}(S) = \frac{E(S) + E(T)}{2} = \frac{E(S) + E_{\text{SD}}(T)}{2} \quad \uparrow \quad \downarrow$$



One can compute the « right » singlet from the BS solution



Broken symmetry correction for N unpaired electrons



Heisenberg Hamiltonian

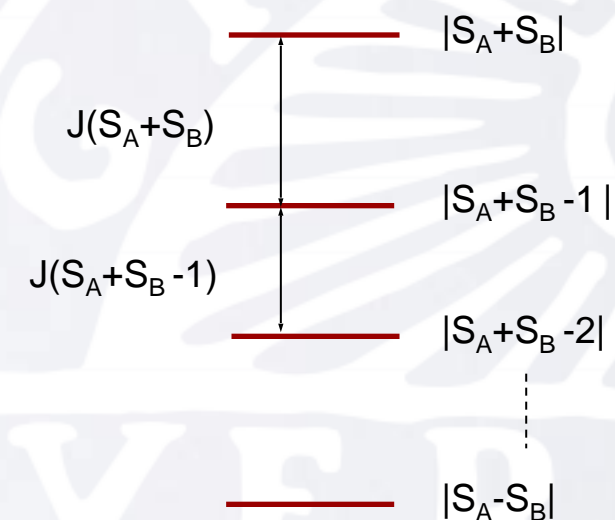
$$E(\text{HS}) = JS_AS_B$$

$$E_{\text{SD}}(\text{LS}) = JS_A(-S_B)$$

$$J = \frac{E(\text{HS}) - E_{\text{SD}}(\text{LS})}{2S_AS_B}$$

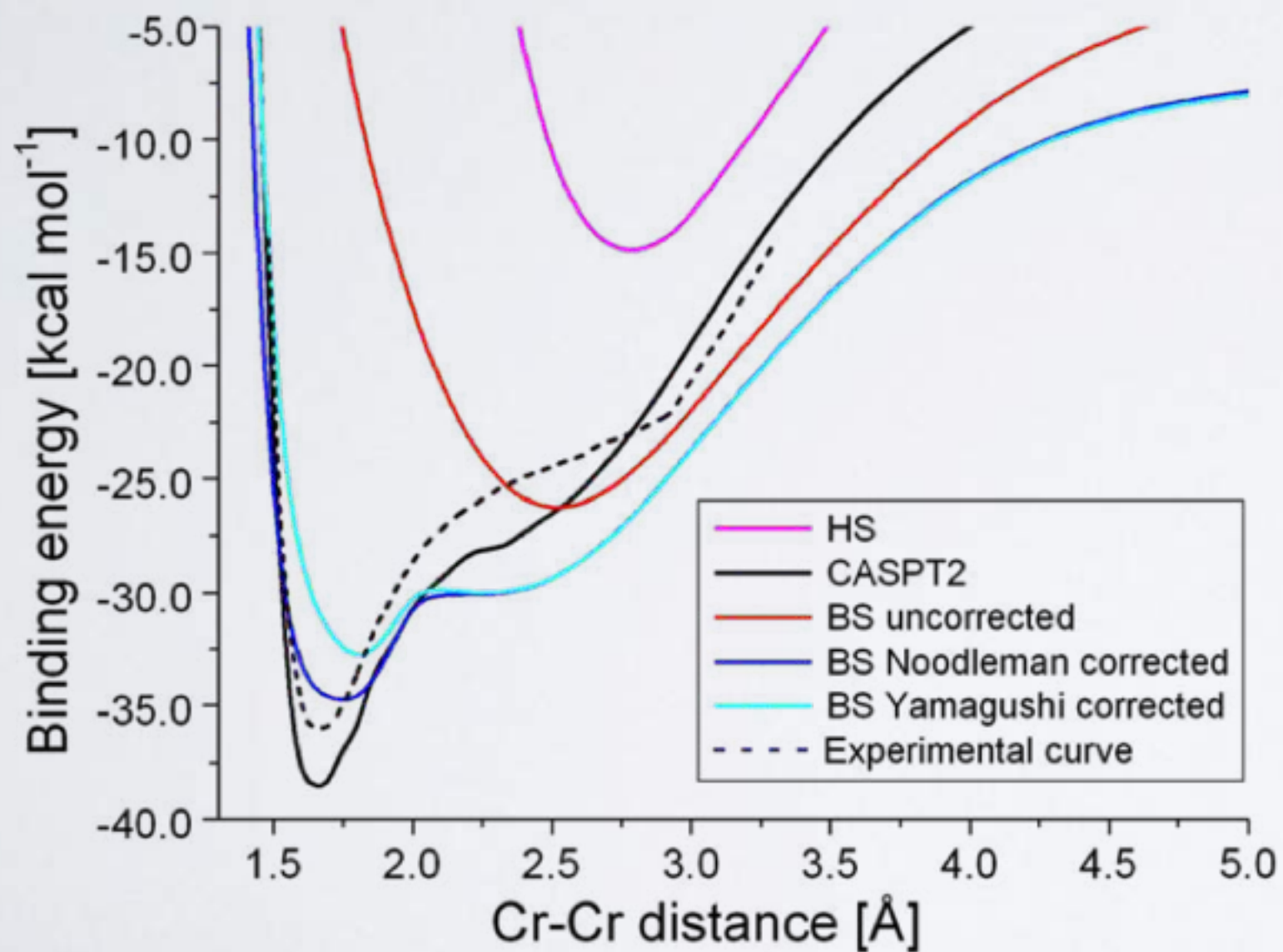
Landé interval rule

$$\Delta E(S, S-1) = -JS$$





Nightmare: metal dimers



$$S_A = S_B = \frac{5}{2}$$

$$J = -\frac{2}{25} (E(HS) - E_{SD}(LS))$$

Landé interval (5 steps)

$$E(LS) = E(HS) + 15J$$

With spin contamination correction: reasonable!



Correlation - Summary

Transition metal very challenging

Very few methods usable (DFT, CASPT2, CCSD(T))

DFT works surprisingly well

In some cases, large deviations between functionals

Care has to be taken (even in DFT)

Right spin? Right state?



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Relativity - Principles

Relativistic quantum mechanics

Space-time equivalency (x, y, z, ct)

Nothing can go faster than light

Schrödinger equation: 1st derivative time, 2nd derivative position

not correct!



Relativity - Principles

How important are relativistic effects?

Without relativity, $N=137$: 1s electron faster than light

Effects already noticeable before but still mainly in 1s

1s « slowed » by relativistic effects

orbital expands

But core orbital constant during reactions!



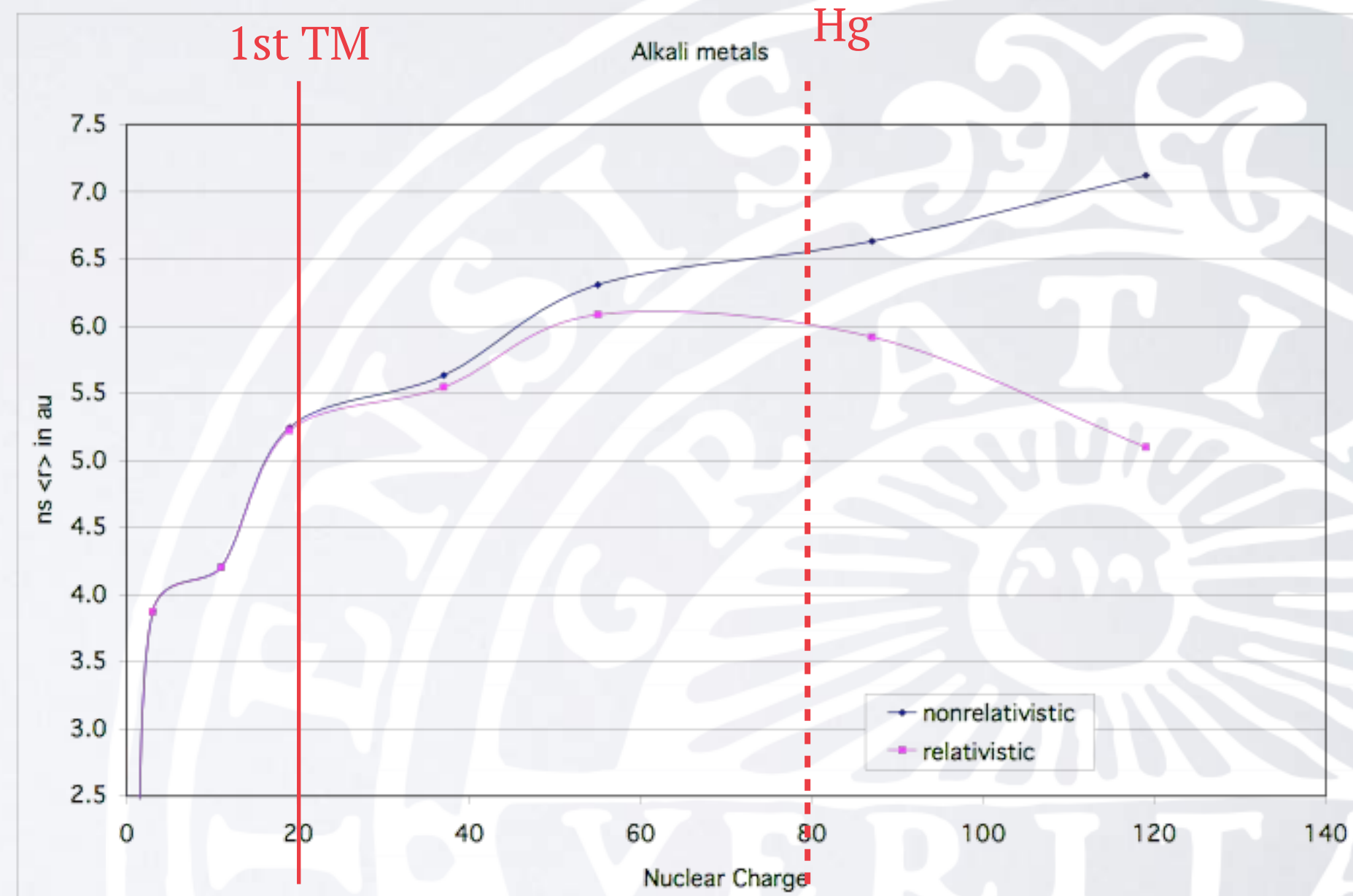
How important are relativistic effects?

1s expanded : less
screening of nuclear
charge

Valence s contract

Valence p, d expand

Scalar relativistic effects





How important are relativistic effects?

Spin only comes naturally in relativistic theory

Spin interacts with the magnetic field generated by the electron in the orbital

Spin-orbit coupling!

Couple spin states (singlet and triplet mixing)

Break orbital degeneracy (p and d)



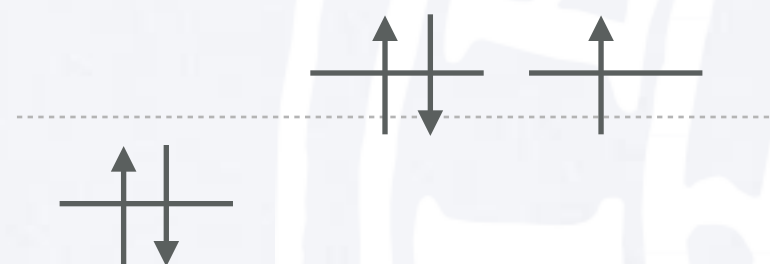
How important are relativistic effects?

Break p and d degeneracy



Not much difference if all occupied

Else (open-shell, multiconfigurational), stabilizes

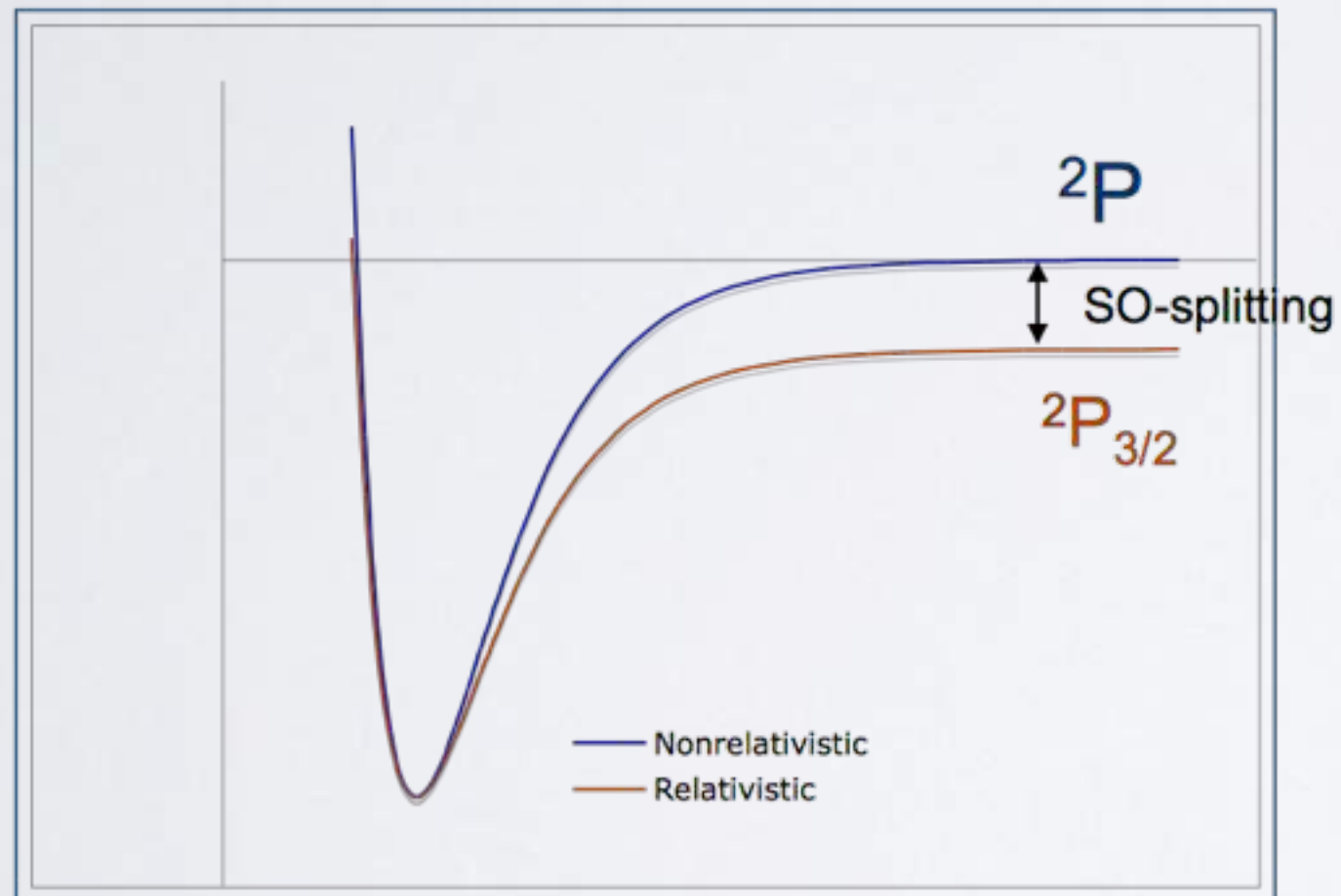




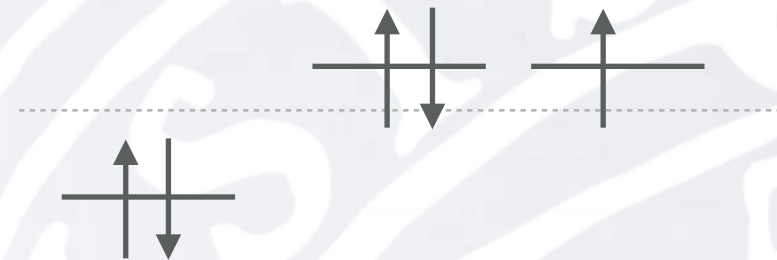
Relativity - Principles

How important are relativistic effects?

Break p and d degeneracy



HI dissociation





Relativity - Dirac

Relativistic quantum mechanics

Good solution brought by Dirac equation

Already there some approximations (Coulomb, finite-size nuclei...)

Can be solved in similar way as Schrödinger

Main software : DIRAC

HF, DFT, MP2, CCSD, MCSCF...



Relativity - Dirac

Dirac equation

Wavefunctions are now 4-components

Large and small component

2 spin states for each

Small component corresponds to positron

First prediction!

Not so interesting for chemistry...



Relativity - From 4 to 1 component

Decoupling small component (2-component methods)

ZORA (zeroth order regular approximation)

Douglas-Kroll

Perturbative, usually 2nd order

Can also go further and remove spin dependence

Only scalar relativistic effects (neglect spin-orbit) 

Very little change of the traditional codes 



Relativity - From 4 to 1 component

Basis set...

Because different radial extent, need special basis sets

For example ANO-RCC basis in MOLCAS (made for Douglas-Kroll)



Relativity - and back!

One can instead start by non-relativistic and add corrections

« Perturbative »

Diagonalization of spin-orbit Hamiltonian for SA-CASSCF/MS-CASPT2 for example

The way to add spin-orbit on top of scalar ZORA or Douglas-Kroll



Relativity - Effective core potential

Pragmatic:

Core electrons effect constant (with or without relativity)

Outer electrons just feel a field from the core

Neglect core electrons and add effective core potential

Can include scalar relativistic effect



Relativity -Effective core potential

Effective core potential

Very cheap (only valence or sub-valence electrons)

Only scalar effects

Can be extended to add spin-orbit

Accuracy can vary but usually good

Many ECP to choose from (Lanl2, Stuttgart...)

Parametrized to fit atomic 4-components values



Relativity -Summary

Importance of relativistic effect

Scalar (contraction and expansion of orbitals)

Already for 1st line TM

Clearly from 2nd line TM

Spin-orbit coupling

If spin-crossing (phosphorescence, ...)

Heavy open-shells (or multi-conf)



Relativity -Summary

Dirac (4-c)

Exact but very heavy

ZORA/Douglas-Kroll (2-c)

Very accurate, heavy

ZORA/Douglas-Kroll (scalar)

Only scalar, as fast as
non-relativistic

+ perturbative spin-orbit

Good for weak spin-orbit
coupling

ECP

Very cheap, approximate