Electronic Structure and Reactivity of the σ-Complex of Benzene and $Fe^{IV}O$, a Model of the Cytochrome P450 Active Site

DFT, CASSCF and CASPT2 modeling

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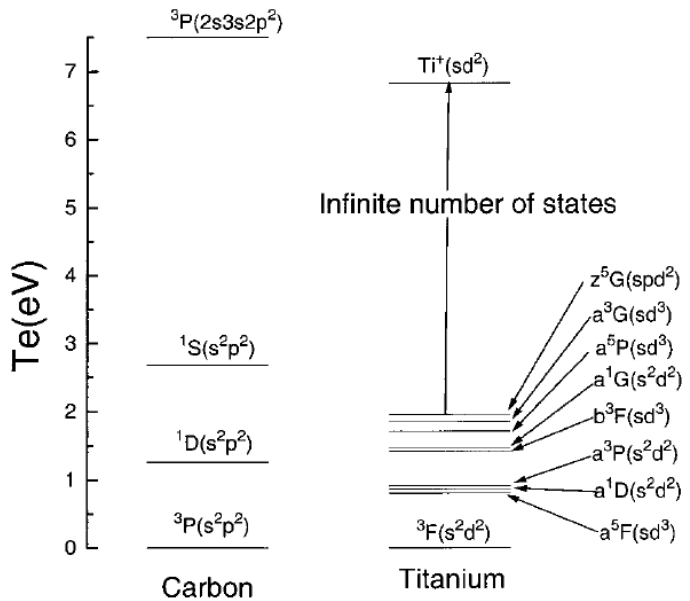
Lecture plan

Modeling difficulties

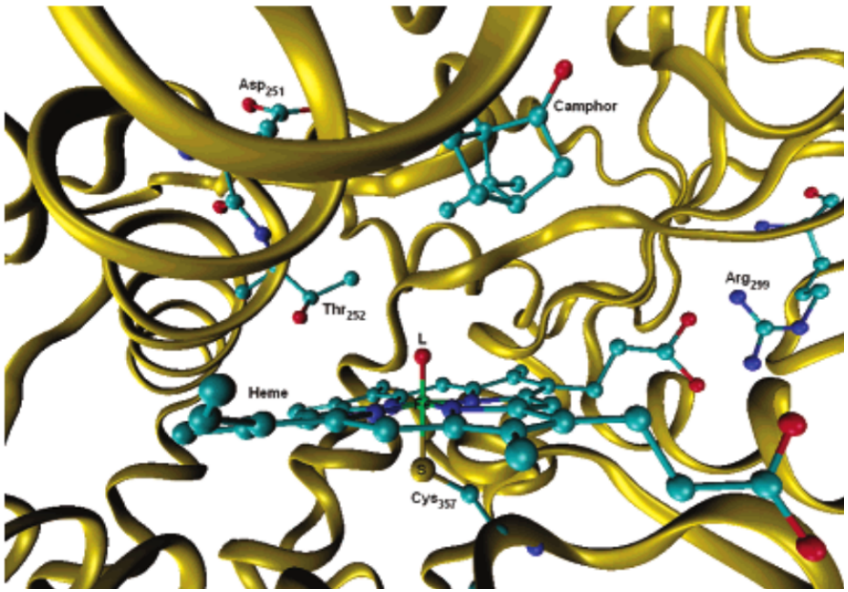
Problems in accurately describing transition-metal containing molecules:



- degeneracy of atomic terms
- separations of lowest states configurations
  - stabilization of the 3d orbital relative to 4s orbital
  - preference for high-spin d shells
- differential correlation effect
  - valence – valence
  - valence – core
  - core – core

Protein's characterization

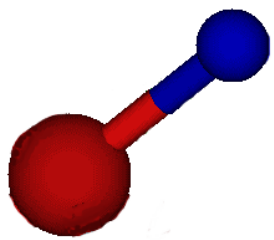
Cytochrome P450 features make them one of the most interesting problem in quantum chemistry:



- activation of inert C-H bonds
- model for creative mimetic chemistry
- detoxification
- biosynthesis
- drug metabolism
- involvement in brain chemistry
- wide spread in nature
- Cpd I – short life time

Modeling stages

- Stage I:
  iron(III) oxide – FeO^+
  - A. Fiedler, D. Schröder
  - J.F. Harrison
- Stage II:
  σ-complex benzene-FeO
  - K. Yoshizawa, Y. Shiota
  - Karolina Kwapień
- Stage III:
  σ-complex CpdI-benzene
  - S.P. de Visser, Sason Shaik
  - Mariusz Radoń



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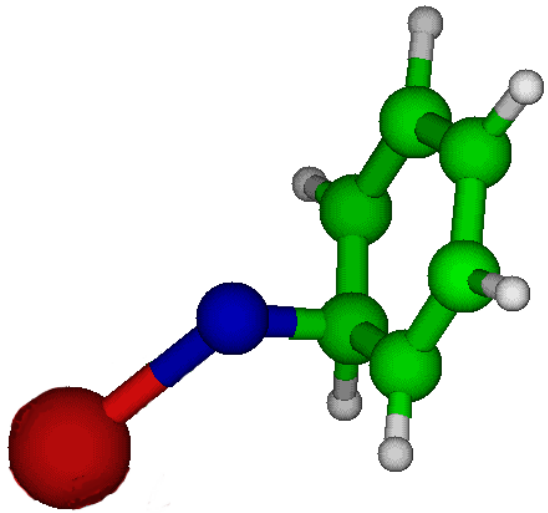

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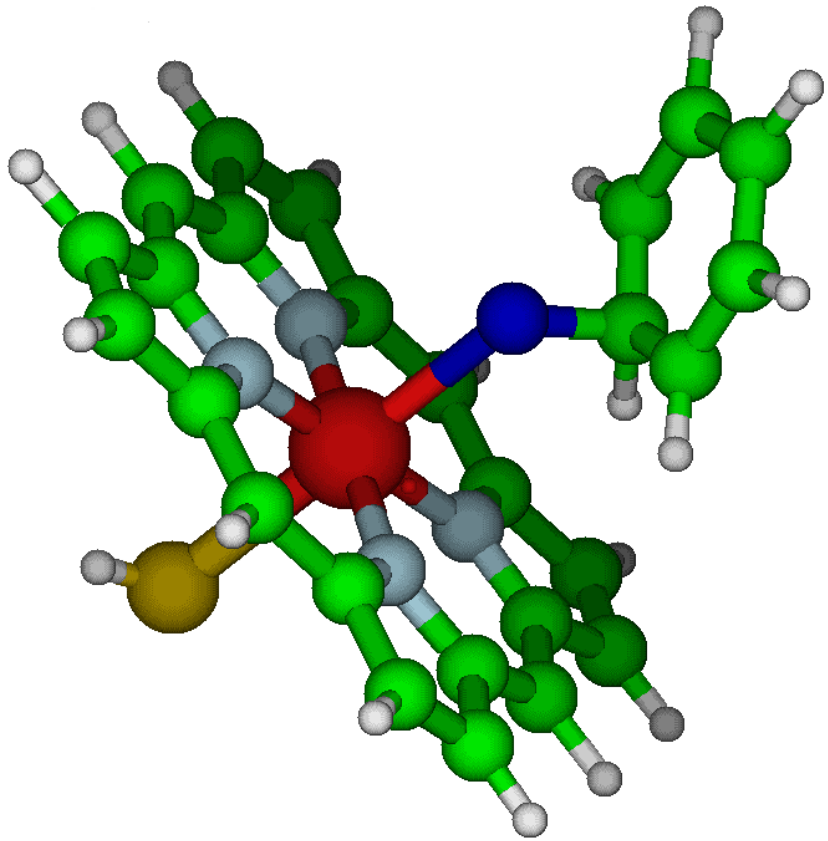


DFT – *Density Funtional Theory*

Quantum mechanical theory used to investigate the electronic structure of many-body systems

- wavefunction substituted by electron density

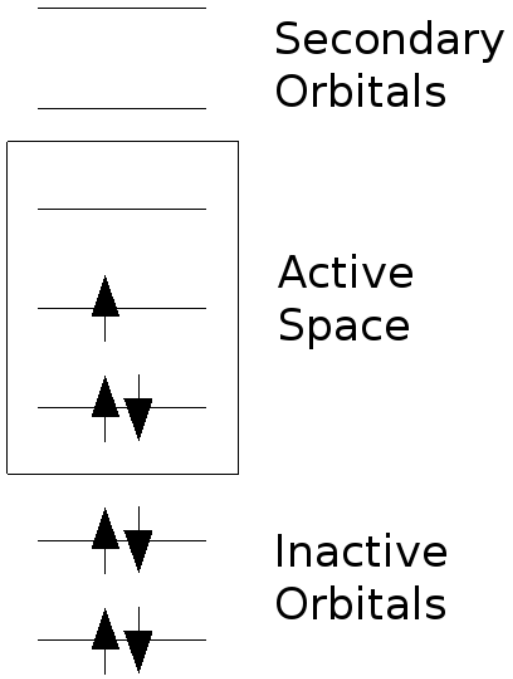
$$\psi_0 \Leftrightarrow \rho_0 \tag{1}$$

- lower computational cost
- qualitatively good predictions

CASSCF – *Complete Active Space SCF*

Complete Active Space Self Consistent Field

- multi-configuration approach
- active orbitals
- energy connected to chosen set of orbitals
- static electron correlation energy take into account



CASPT2 – *CAS Perturbation Theory of the Second Order*

Second-order perturbation theory with a complete active space self-consistent field reference function

- multireference perturbation approach
- includes dynamic correlation energy
- CASSCF function as a reference function
- includes second-order energy correction

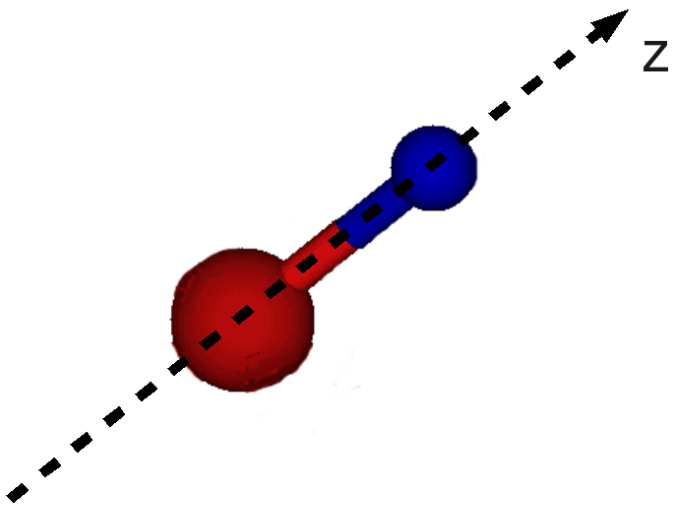
double–shell effect

Correlation effect important in systems with transition metals

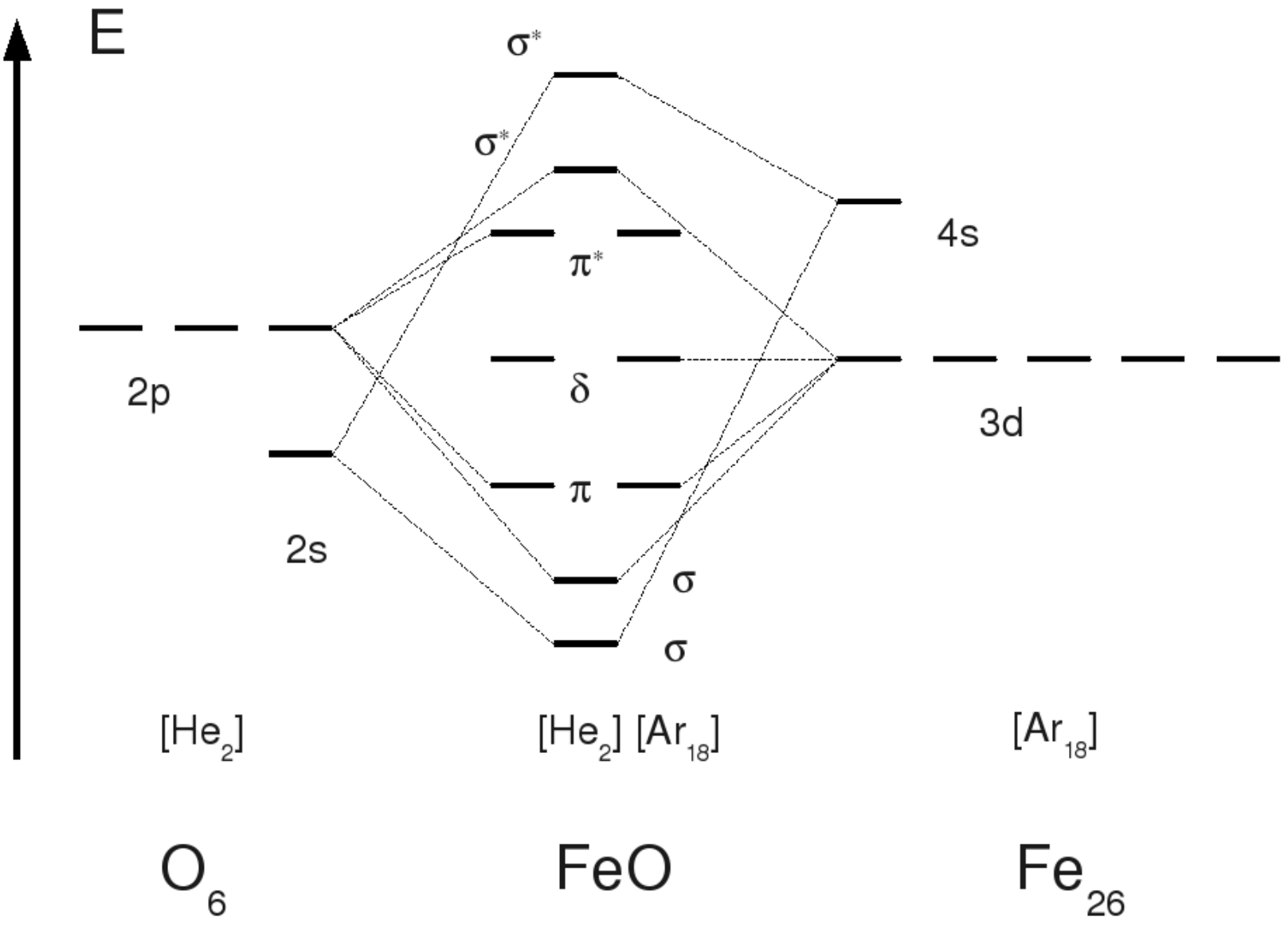
- especially important in high d orbital occupancy systems
- need to take second d shell in to account
- atomic correlation effect
- influence on CASPT2 calculations (e.g. charge transfer)

Used programs

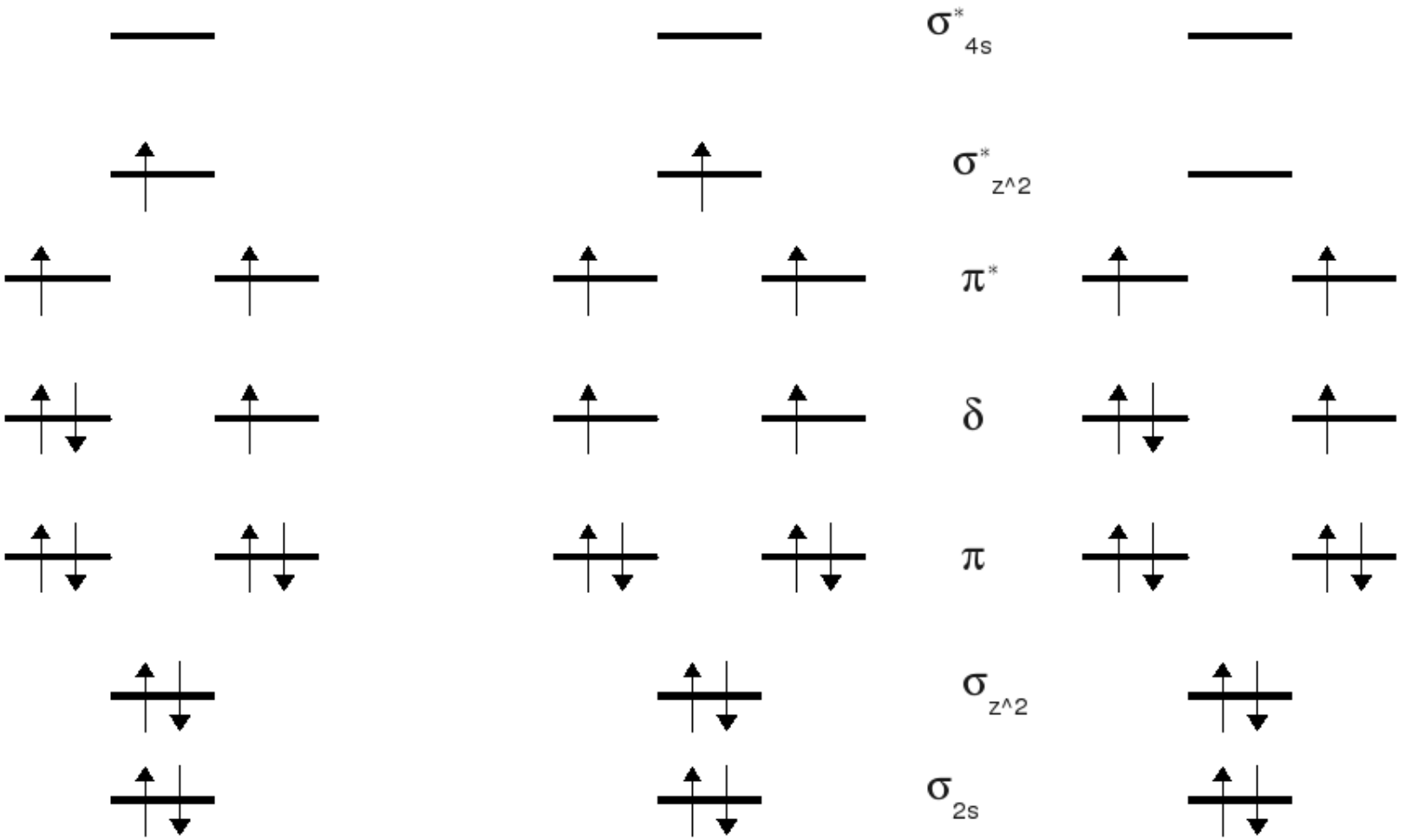
- Gaussian:
  - functional: B3LYP
  - basis set: 6-311G**
- Molcas:
  - symmetry: C_2
  - basis set Fe:
    ANO-rcc...7s6p5d3f2g1h.
  - basis set O:
    ANO-rcc...4s3p2d1f.
- Molden
- Turbomol



Orbital energy diagram



Considered configurations

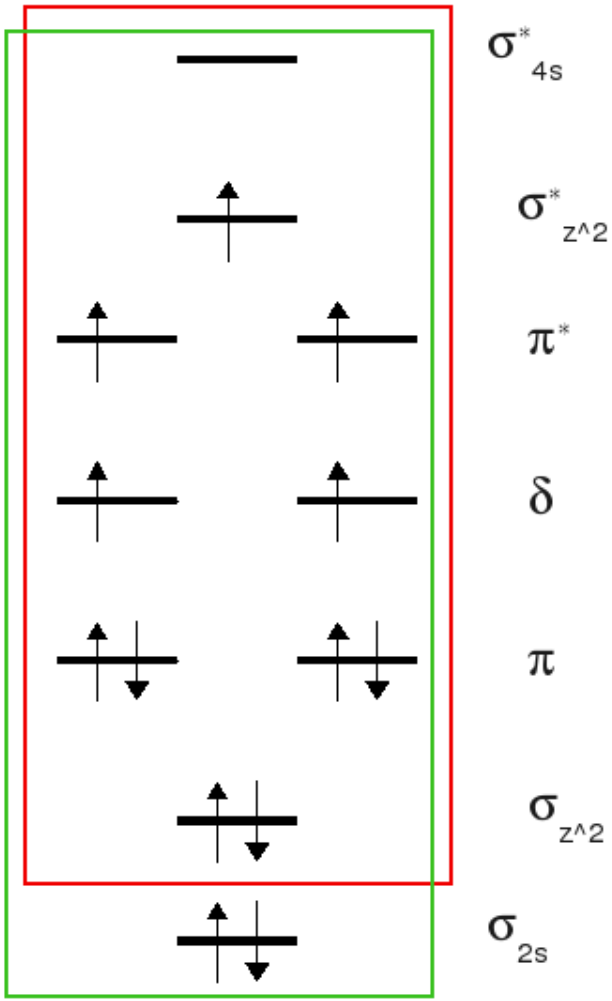


$FeO(^5\Delta)$ $FeO^+(^6\Sigma^+)$ $FeO^+(^4\Delta)$

Considered configurations

11in9
13in10

11in14 =
11in9 + ds
13in15 =
13in10 + ds



$FeO^+(^6\Sigma^+)$

Ionization energy

	Ionization energy [eV]
Exp.	8,9 $\pm 0,16$
DFT	7,93

	Ionization energy [eV]			
	12in9	*12in14*	*12in10*	*12in15*
CASSCF	6,82	7,24	6,82	7,36
CASPT2	7,98	8,39	7,97	8,18

Energy difference sextet–quartet

	Energy [eV]
Exp.	???
DFT	0,76

	Energy [eV]			
	12in9	*12in14*	*12in10*	*12in15*
CASSCF	0,95	0,70	0,77	0,22
CASPT2	0,63	0,64	0,63	0,76

Achievements

- Stage I (iron(III) oxide – FeO^+):
  - stable active orbitals sets found
  - geometry and orbitals optimized
  - comparison DFT, CASSCF and CASPT2 done
  - double–shell effect examined
- Stage II (σ-complex benzene-FeO):
  - stable active orbitals set found
  - geometry and orbitals optimized
- Stage III (σ-complex CpdI-benzene):
  - geometry optimized

Perspectives

- Stage II (σ-complex benzene-FeO):
  - results analysis
  - results presentation
- Stage III (σ-complex CpdI-benzene):
  - active space to define
  - search for radical an cationic species
  - final calculations

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