# Structure and bonding in transition metal containing systems:

# Natural Orbital Functional and wavefunction-based calculations

F. Ruipérez, J. M. Matxain, X. Lopez, J. M. Ugalde, M. Piris, E. Matito

# TRANSITION METAL DIMERS

Small metal clusters:

- Model for surface science
- Applications in optics, biomedicine, catalysis
- Comparison between theory and experiment
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## Chromium: $Cr_2$

- Complicated electronic structure
- Difficult to describe theoretically
- Test of quantum chemical methods

# COMPUTATIONAL METHODS

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- ☛ Relativistic effects
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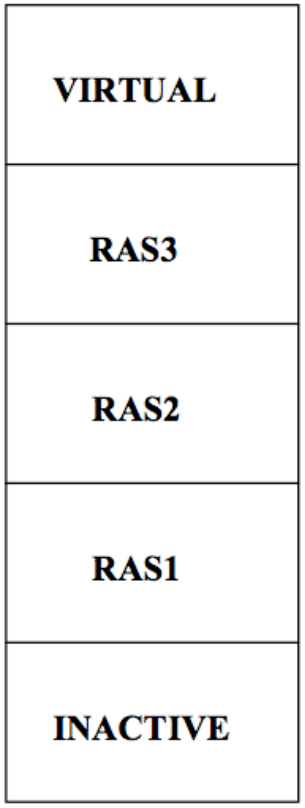
# CASSCF AND RASSCF



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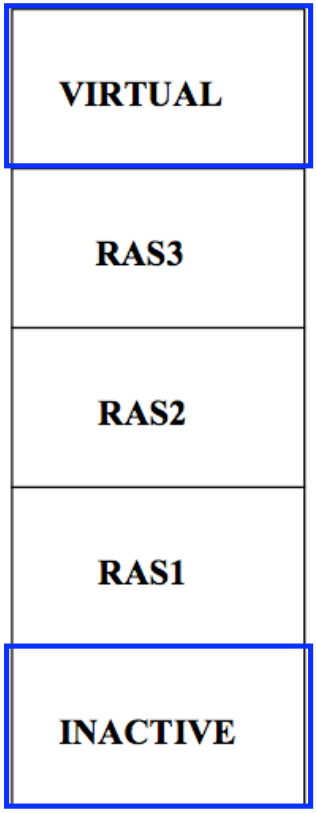


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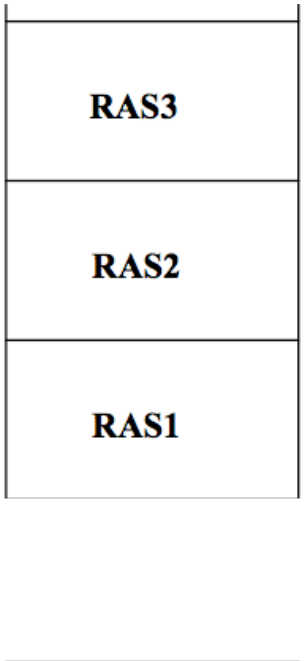


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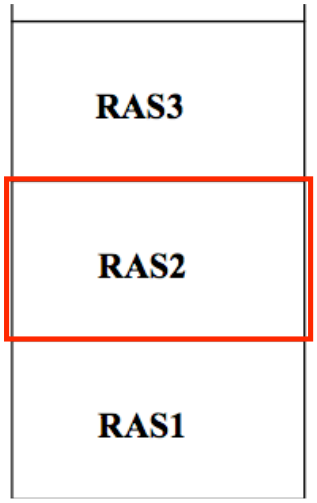


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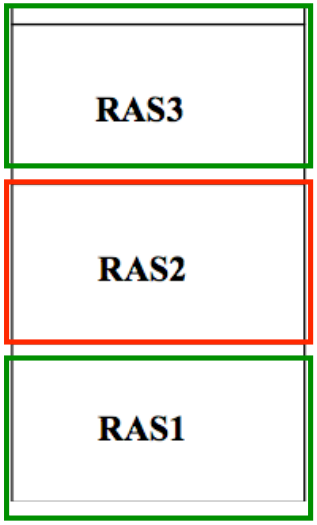


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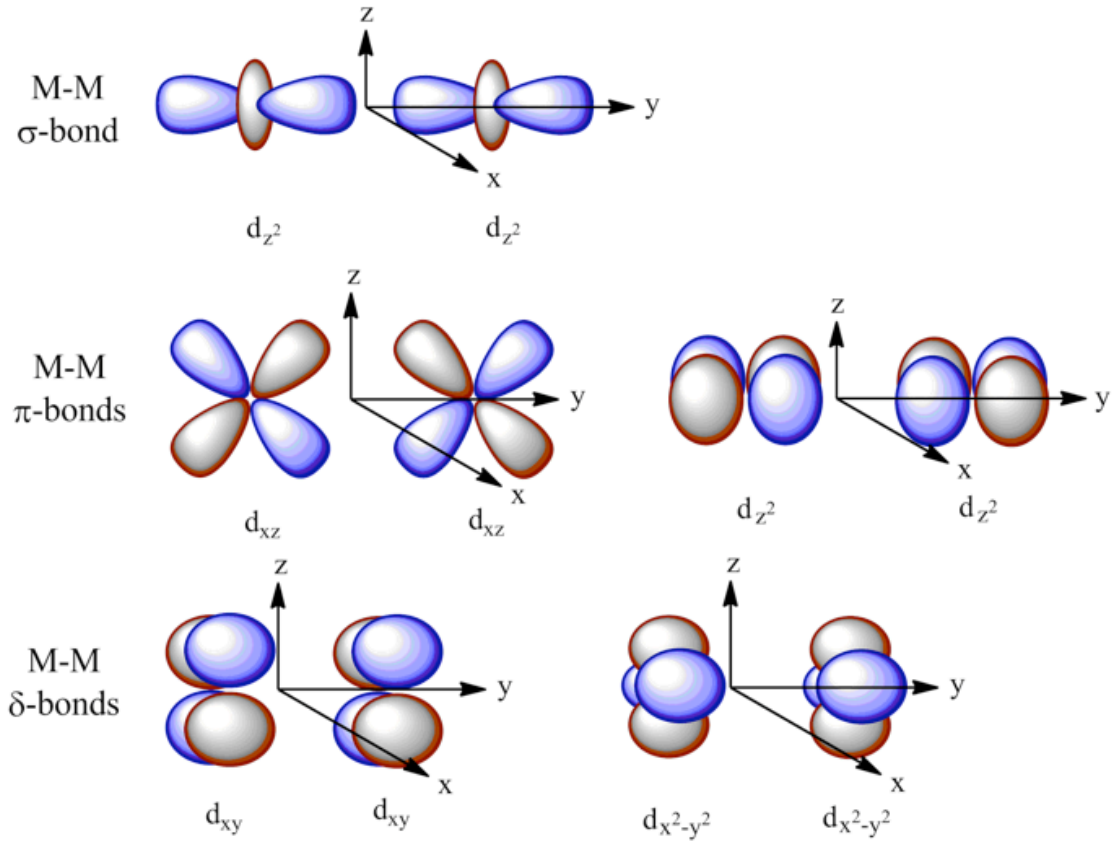

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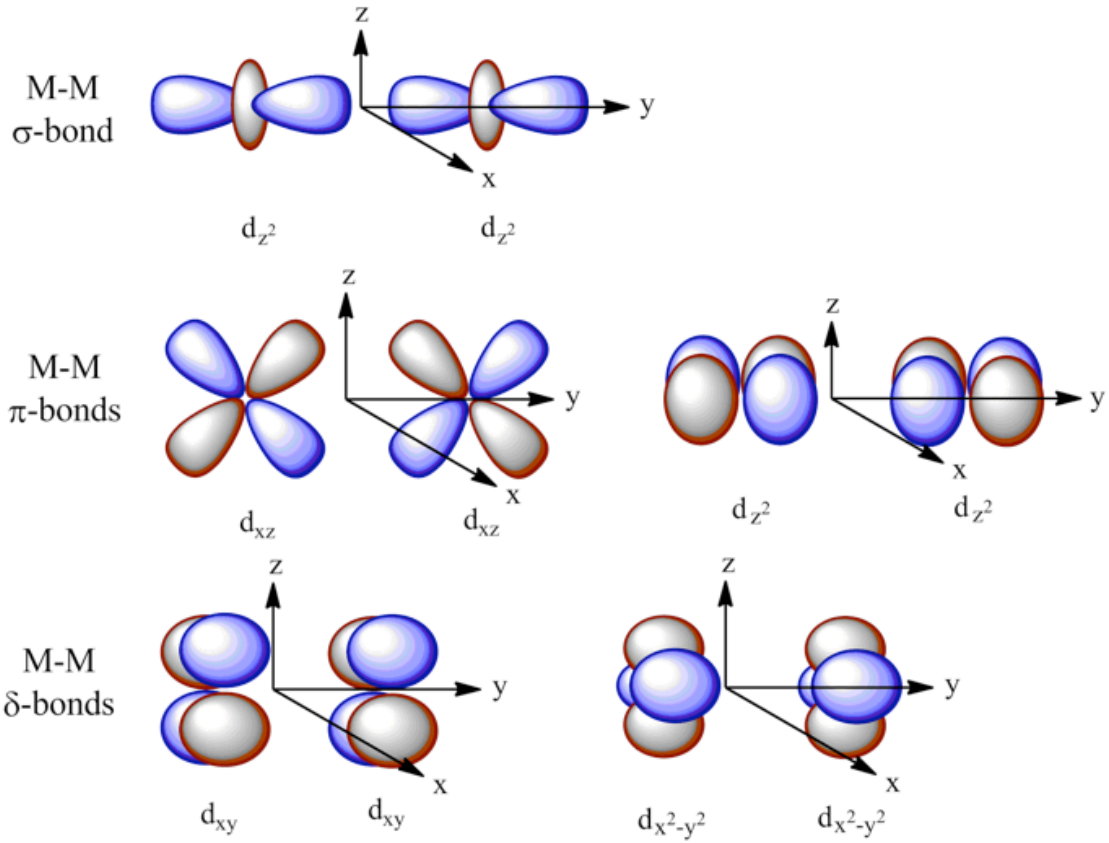
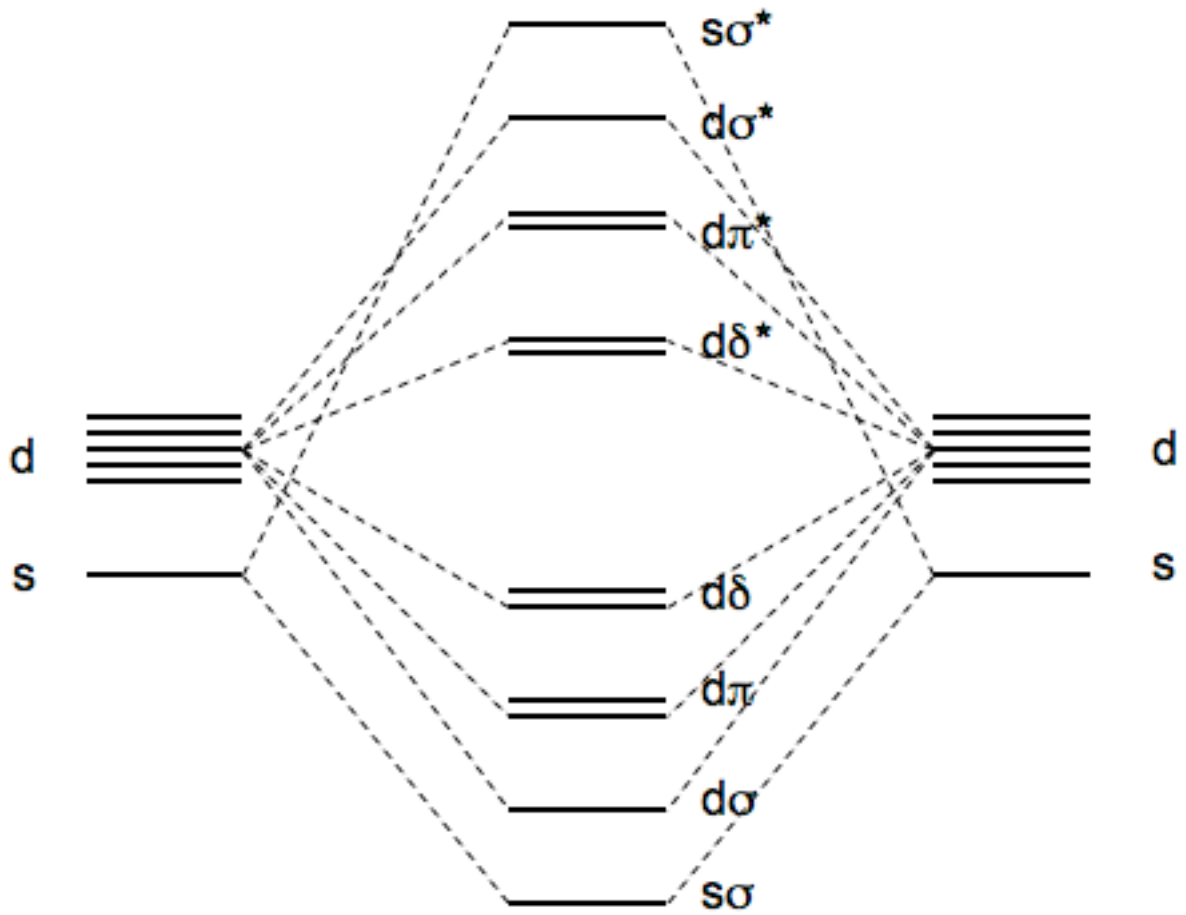



*d* orbitals: sigma, pi and delta bonds  *s* orbital: sigma bond

# ACTIVE SPACE

12 MOs composed of *d* and *s* atomic orbitals



# NATURAL ORBITAL FUNCTIONAL THEORY

$$E^{PNOF5} = \sum_{p=1}^{N}\left[n_p\left(2H_{pp} + J_{pp}\right) - \sqrt{n_{\tilde{p}}n_p}K_{p\tilde{p}}\right] + \sum_{p,q=1}^{N}{}'' n_q n_p \left(2J_{pq} - K_{pq}\right)$$

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  - ✓ Bond lengths, dipole moments and dissociation energies accurately represented

# Chromium dimer: $Cr_2$

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Ground state: $^1\Sigma_g^+$ highly multiconfigurational

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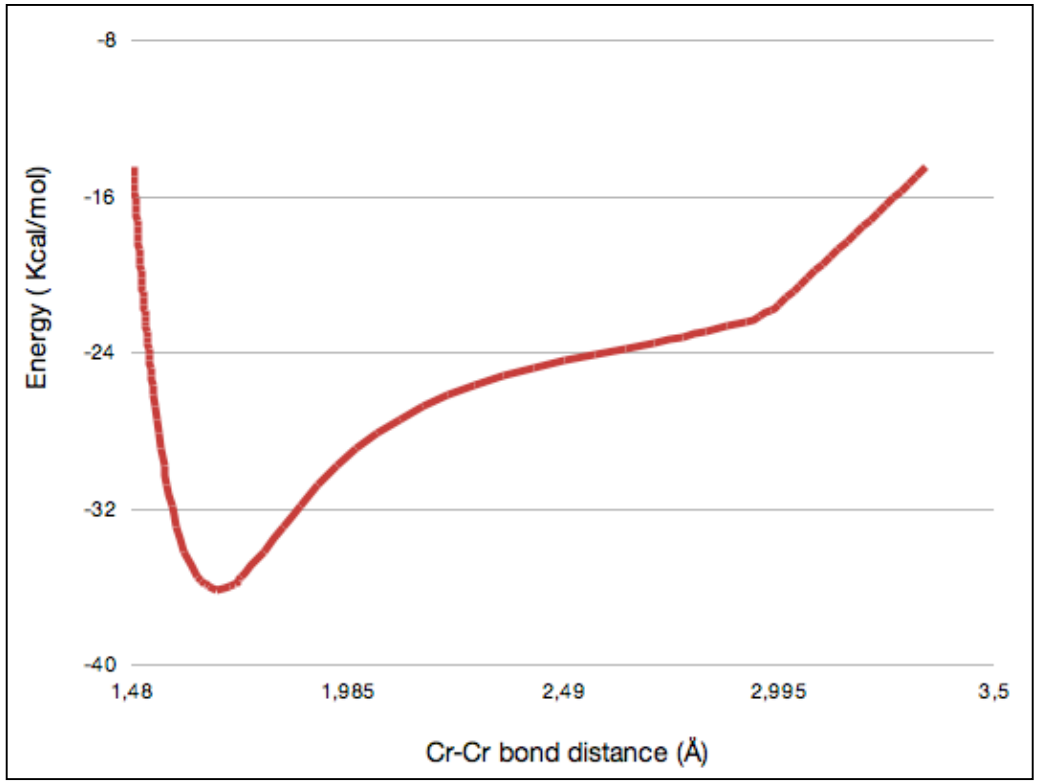

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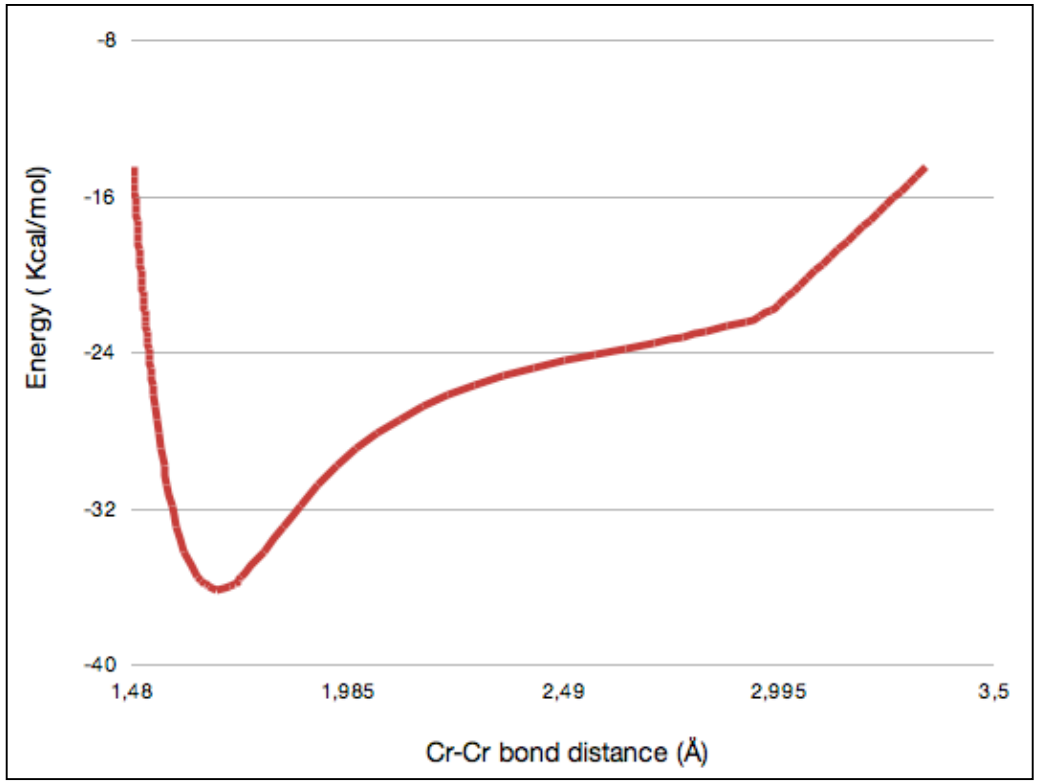

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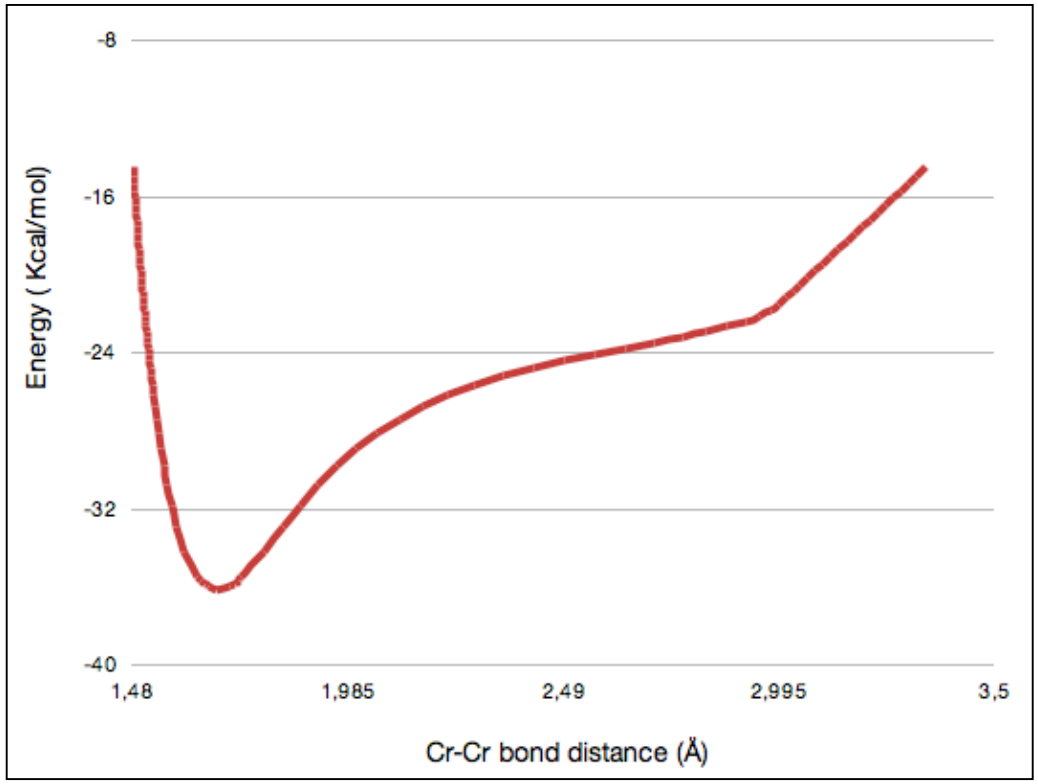

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## Natural Orbital Functional Theory:

- PNOF5: good qualitatively, reasonable quantitatively

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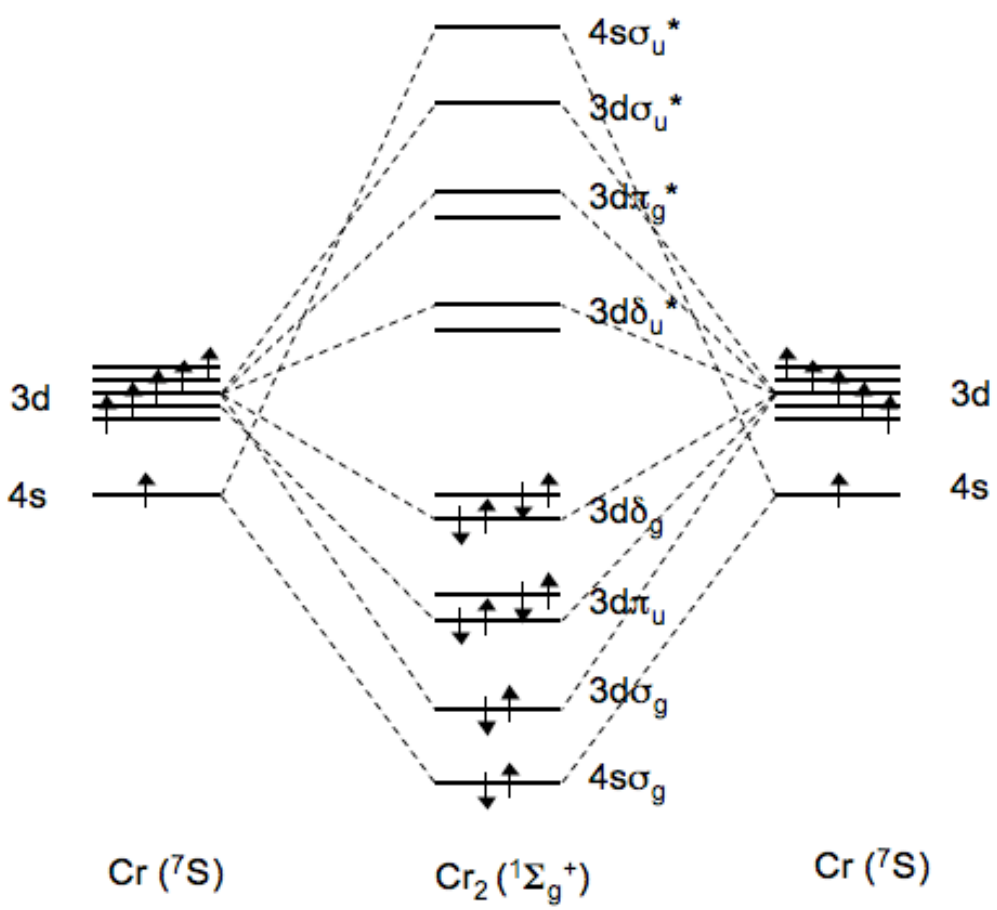


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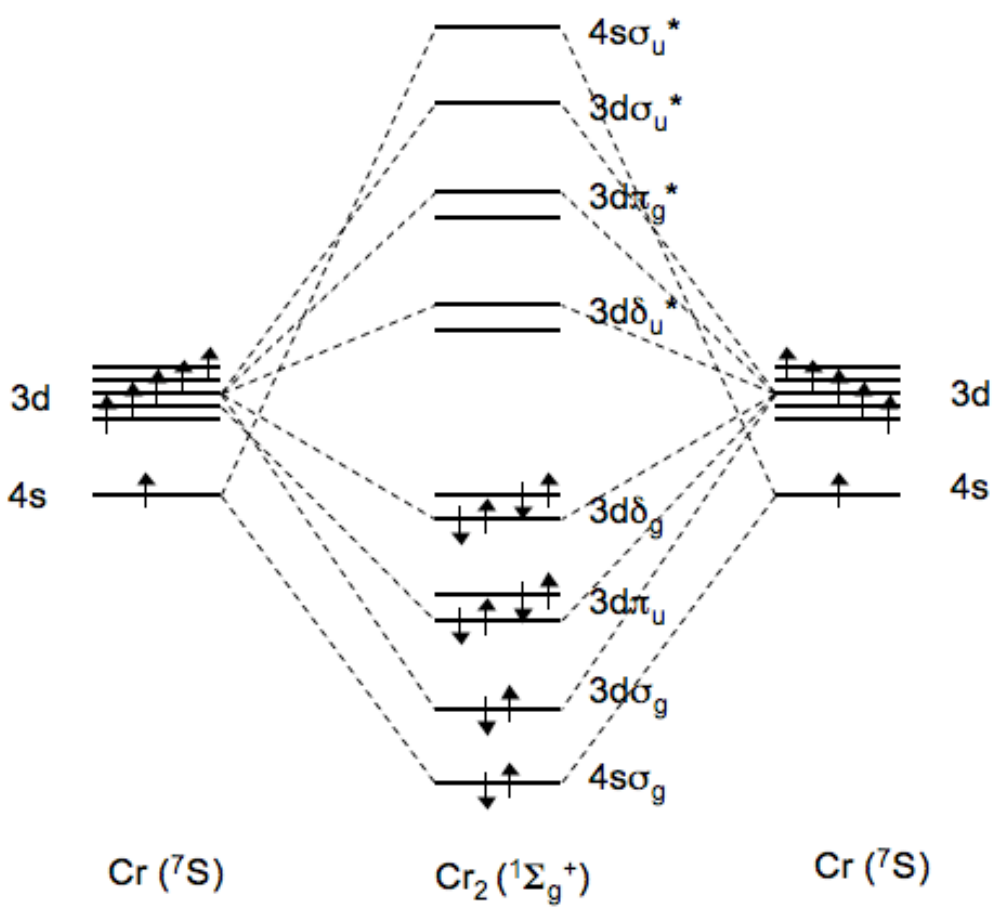


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- ECP: valence *3s3p3d4s* (*8s7p6d*)/[*6s5p3d*]
- All-electron basis set: (*14s11p6d3f*)/[*8s6p4d1f*]

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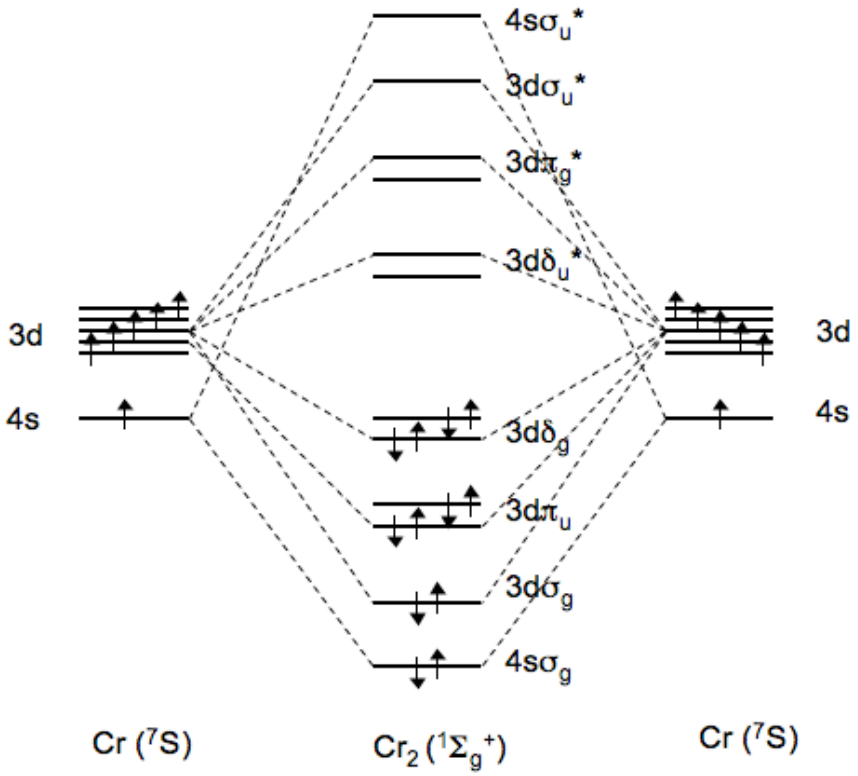

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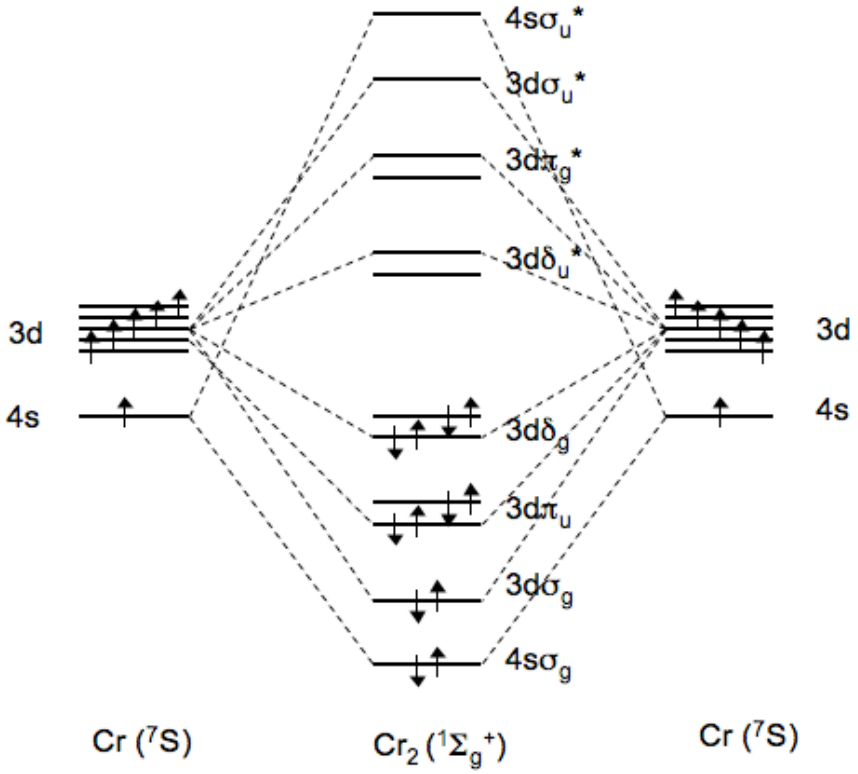


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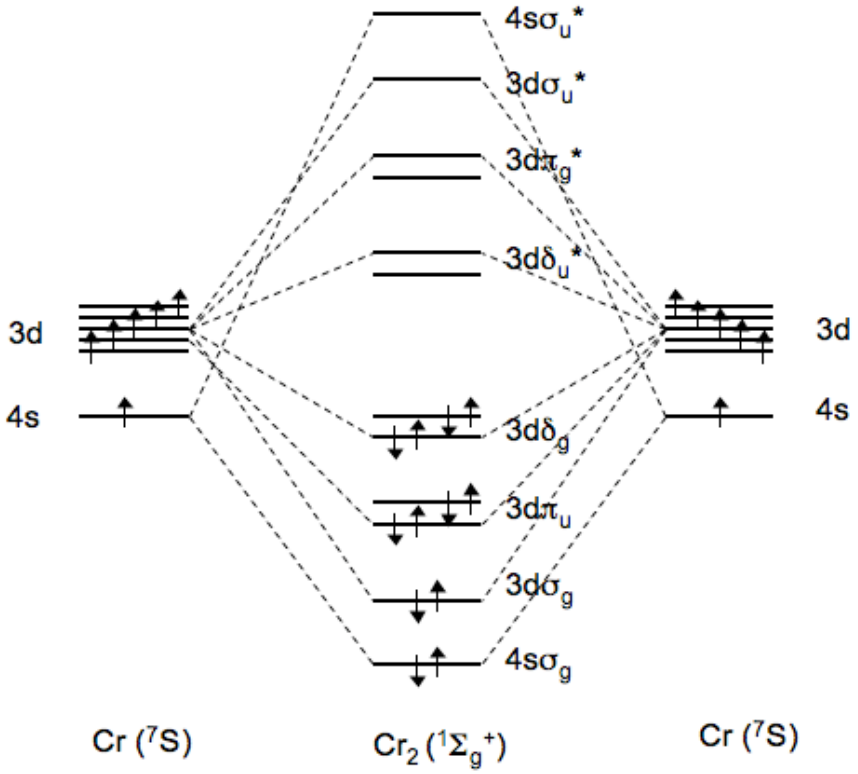


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## Quintuple bond

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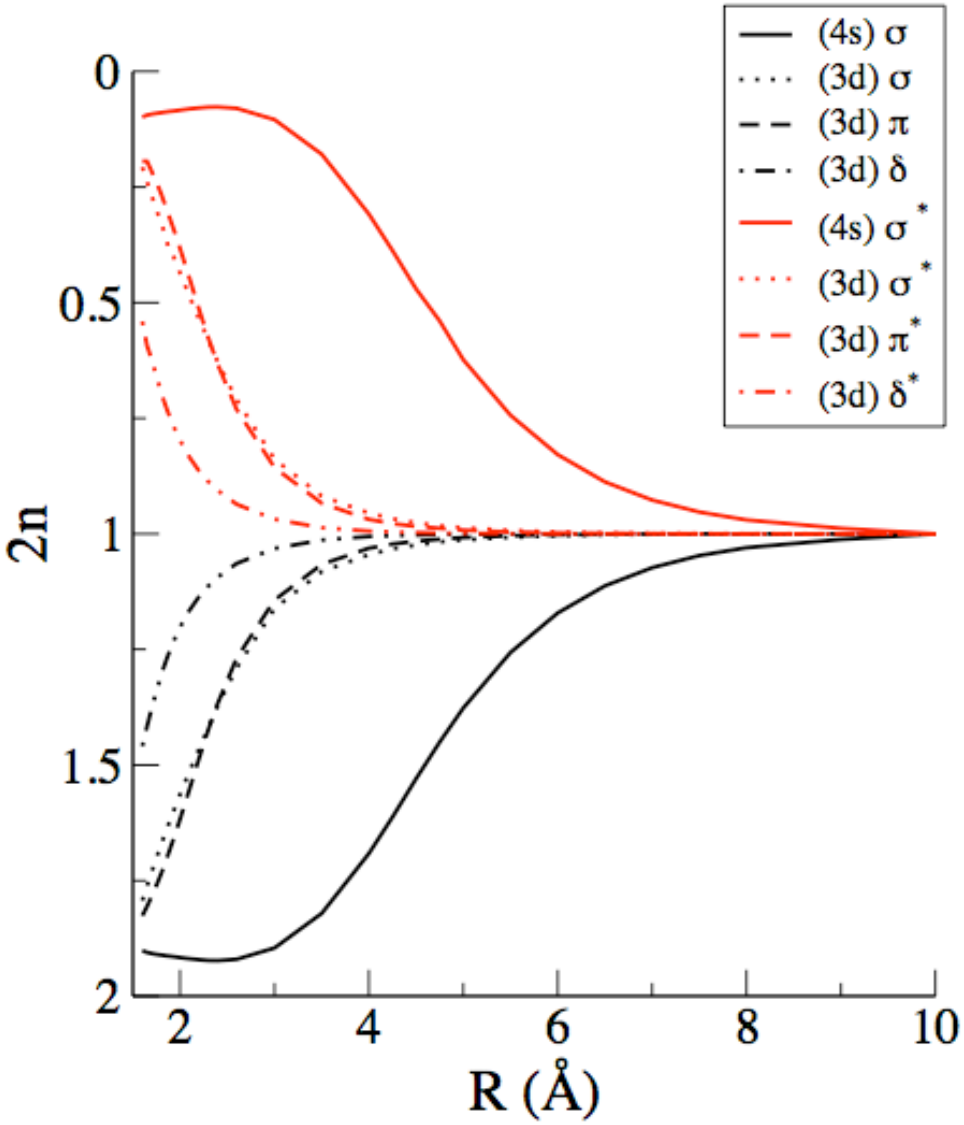


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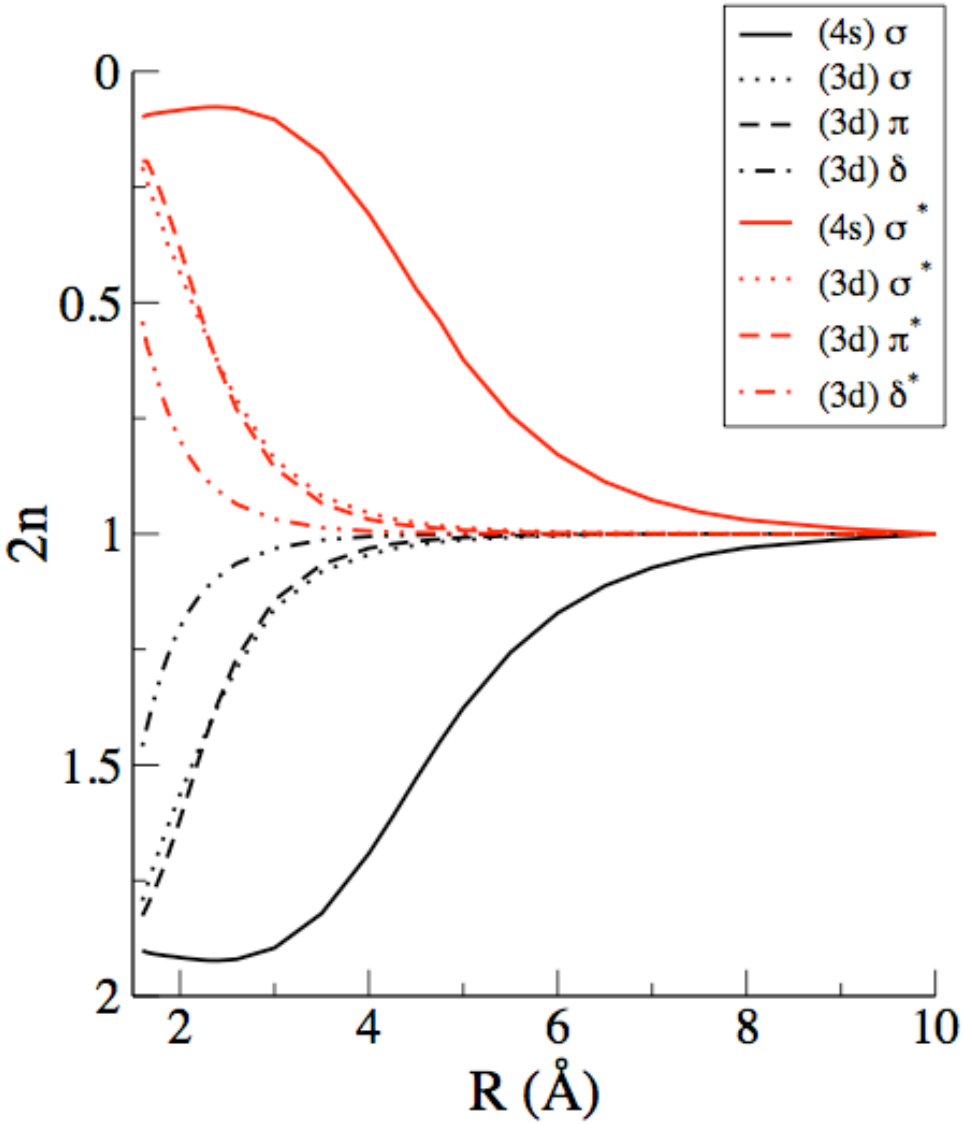


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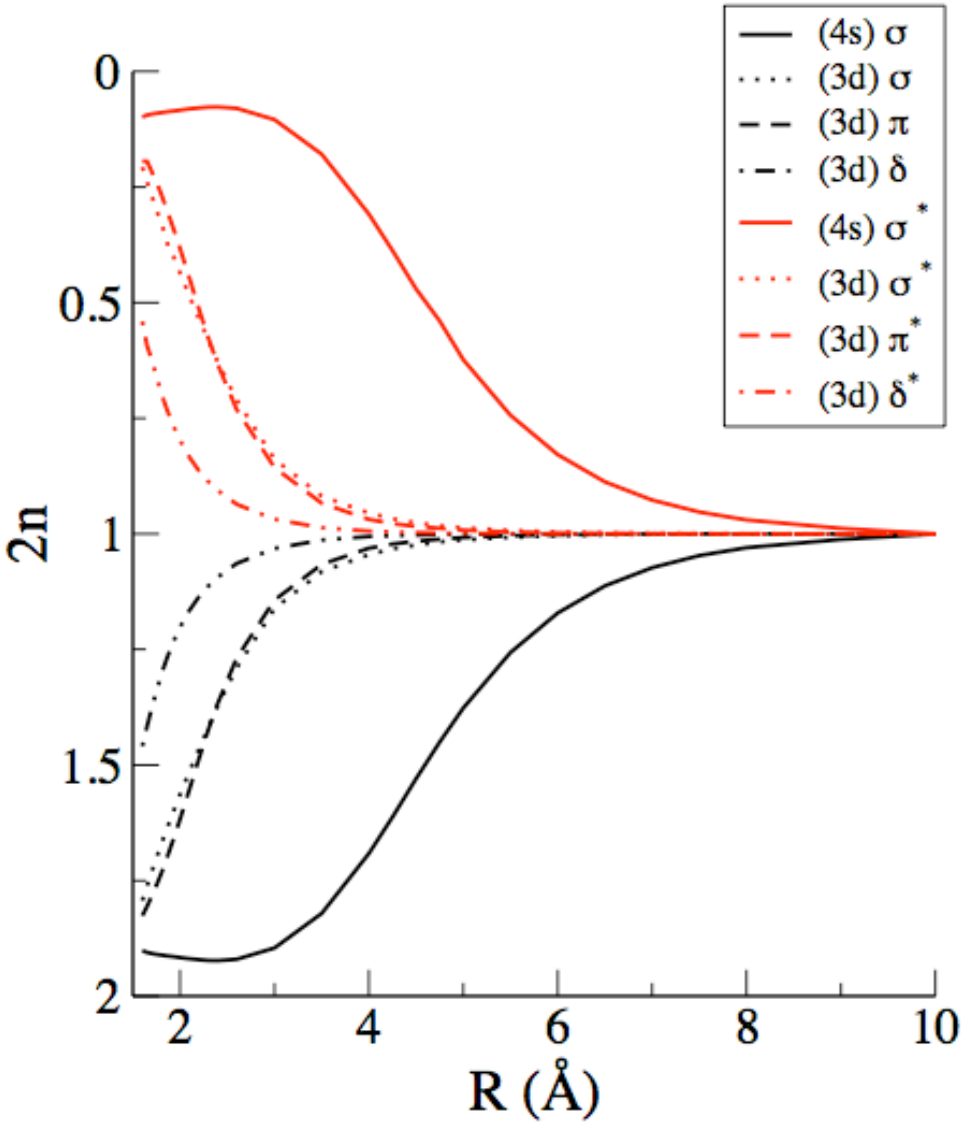


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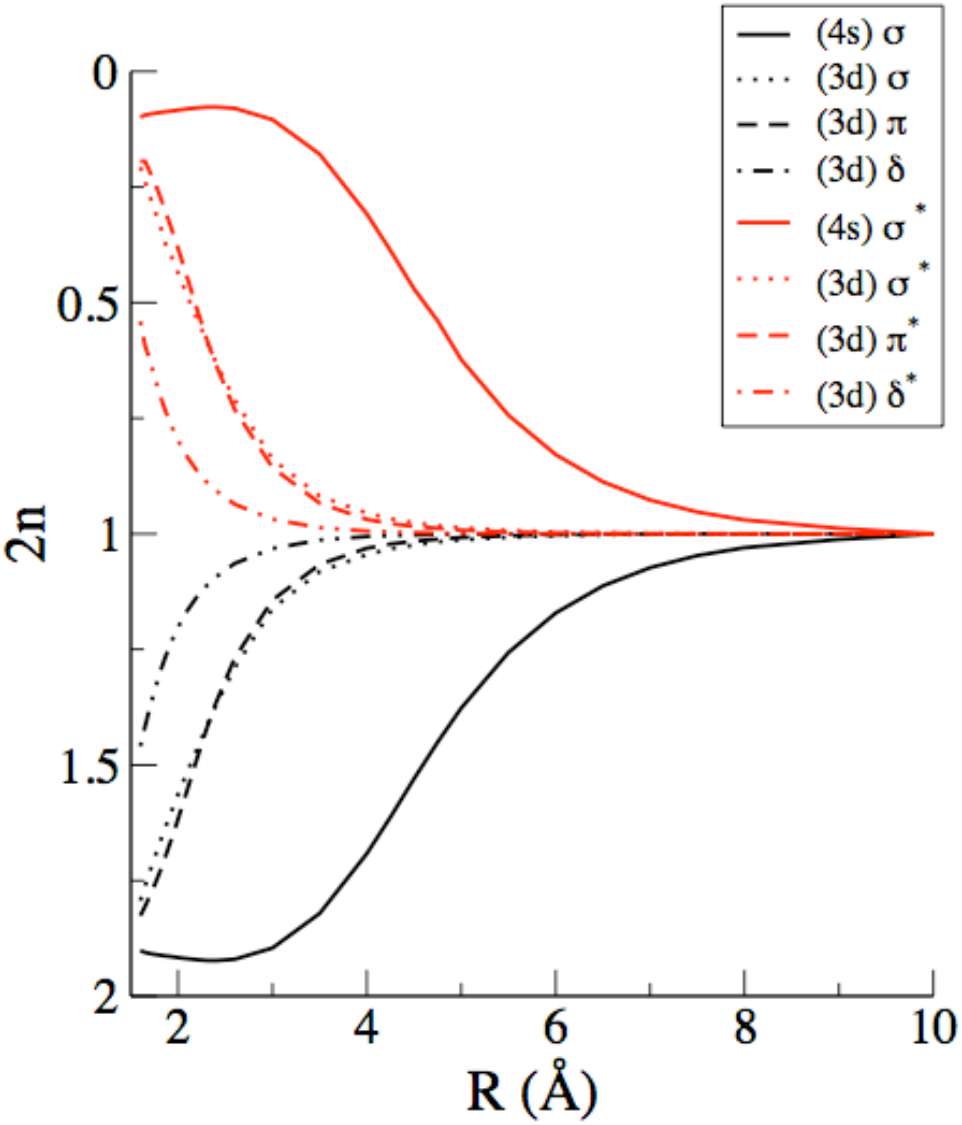


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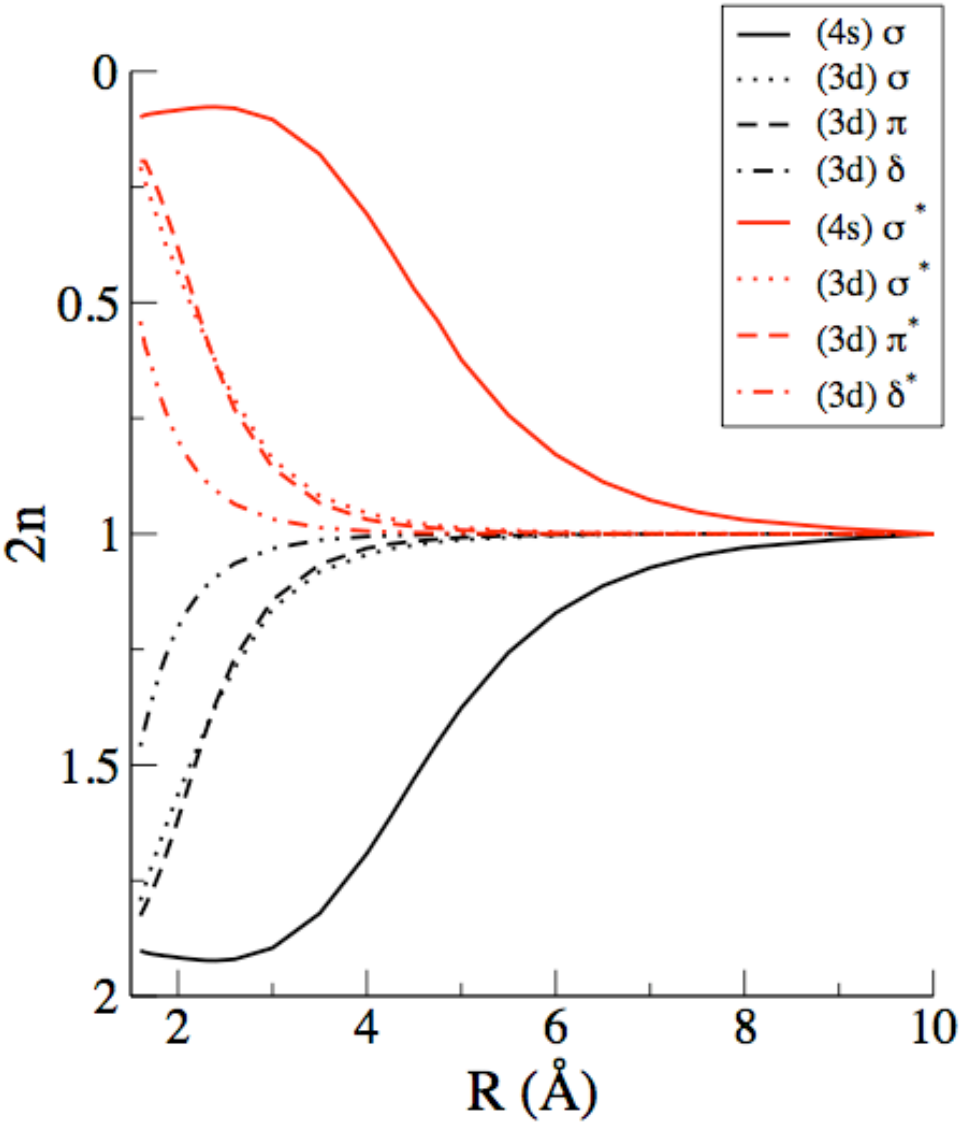


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PNOF5 properly reproduces $Cr_2$ dissociation

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| | PNOF5 | | CASSCF | | CASPT2 | | |
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| | ECP | AE | ECP | AE | ECP | AE | Exp. |
| $R_e$ | 2.10 | 1.90 | 3.19 | 3.18 | 2.64 | 2.43 | 1.68[a] |
| $\omega_e$ | 163 | 264 | 73 | 84 | 160 | 326 | 470[a] |
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All-electron calculations: still important discrepancies

- CASSCF: negligible changes
- CASPT2: improvement
- PNOF5: improvement as in CASPT2
  - much better $R_e$
  - same $D_e$

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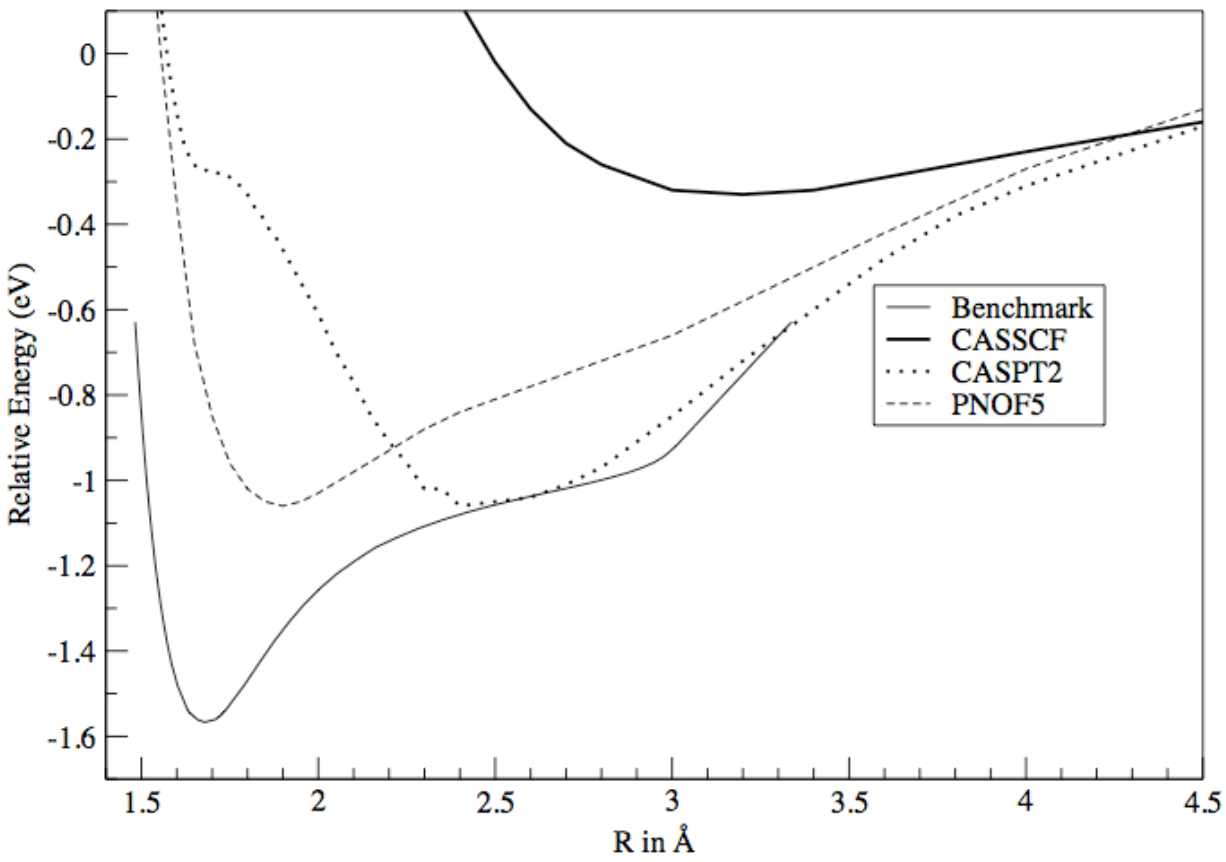

# Iron-sulfur clusters

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Present in metalloproteins and metalloenzymes:

- Electron transfer processes
- Small molecule activation
- Radical-based catalytic transformations
- DNA repair
- Signal transduction

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Fe has variable oxidation states:

- Unpaired electrons coupled by magnetic interactions
- Dense manifold of ferro- and antiferromagnetic states
- Comprehension of Fe-Fe intracluster interactions

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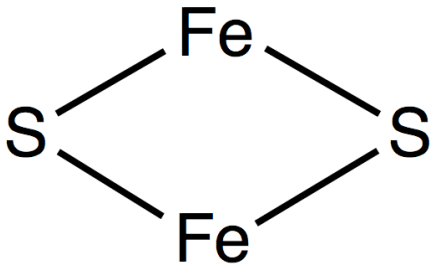
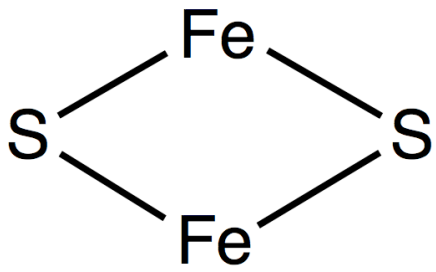



Symmetry: $D_{2h}$ → Ground state: $^1A_g$

# COMPUTATIONAL METHODS

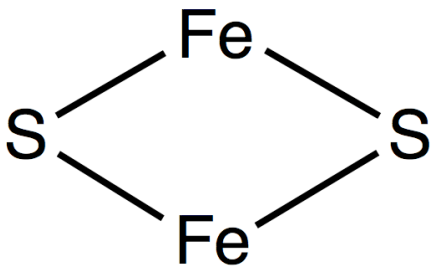



Symmetry: $D_{2h}$ → Ground state: $^1A_g$

CASSCF/CASPT2 calculations:

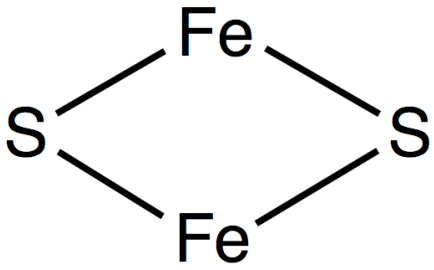
- Active space: Fe(3d), S(3p)
  - ✓ Neutral: 24 electrons in 16 orbitals
  - ✓ Cation: 22 electrons in 16 orbitals
- Basis sets
  - ✓ All-electron ANO-RCC-TZ

# COMPUTATIONAL METHODS




CASPT2 geometry optimization

# COMPUTATIONAL METHODS




CASPT2 geometry optimization

Neutral:

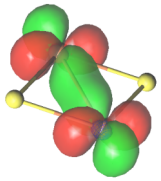
- R(Fe-Fe): 2.411 Å
- R(S-S): 3.656 Å
- R(Fe-S): 2.190 Å

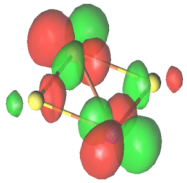
Cation:

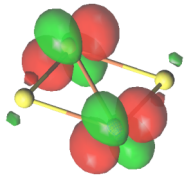
- R(Fe-Fe): 2.486 Å
- R(S-S): 3.418 Å
- R(Fe-S): 2.113 Å

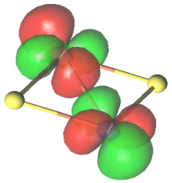
# $Fe_2S_2$

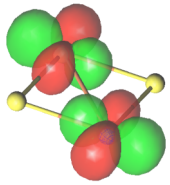
## Iron 3d orbitals and occupations

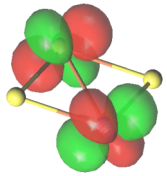

σ: 1.183

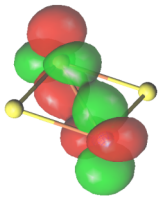

π: 0.886

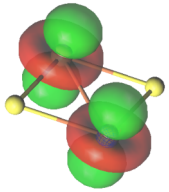

δ: 0.926

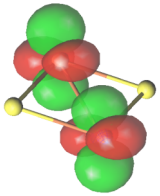

σ*: 0.819

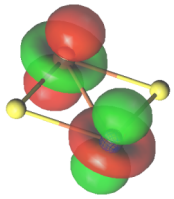

π*: 1.116


δ*: 1.076


π: 1.999

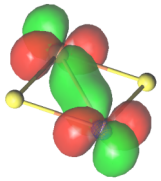

δ: 1.028

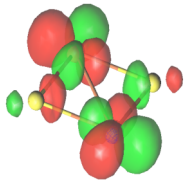

π*: 1.999

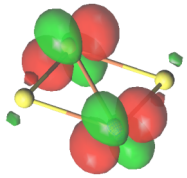

δ*: 0.973

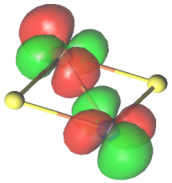
# $Fe_2S_2$

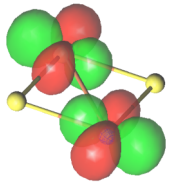
## Iron 3d orbitals and occupations

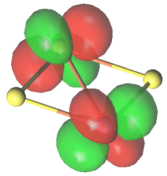

σ: 1.183

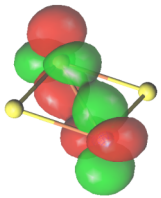

π: 0.886

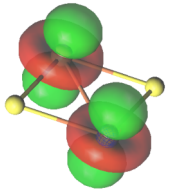

δ: 0.926


σ*: 0.819

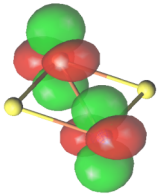

π*: 1.116

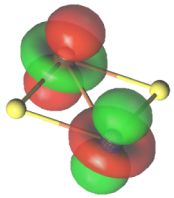

δ*: 1.076


π: 1.999


δ: 1.028

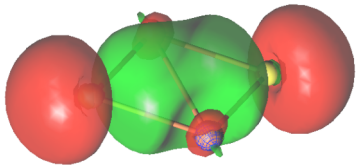
12 electrons in iron: $Fe^{2+}$


π*: 1.999

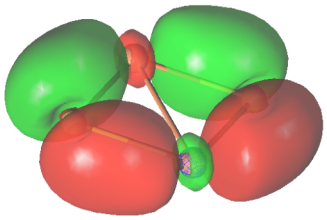

δ*: 0.973

# $Fe_2S_2$

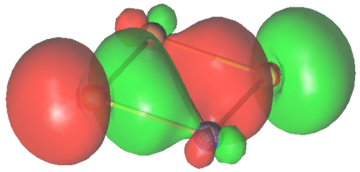
## Sulfur 3p orbitals and occupations



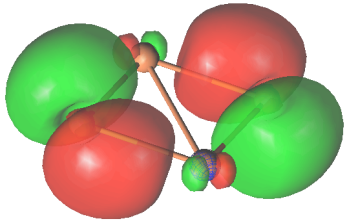
σ: 2.000



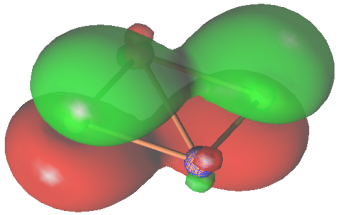
π: 1.999



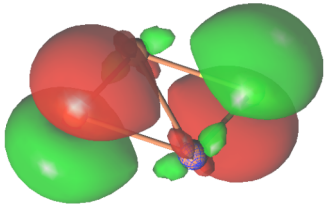
σ*: 1.998



π*: 2.000



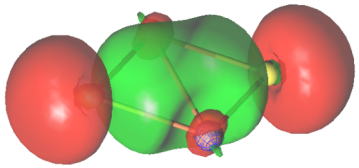
π: 2.000



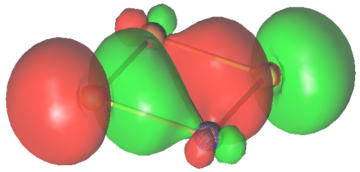
π*: 1.999

# $Fe_2S_2$

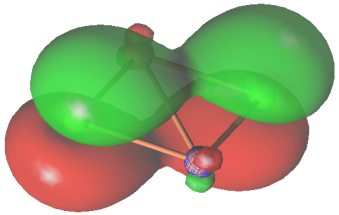
## Sulfur 3p orbitals and occupations



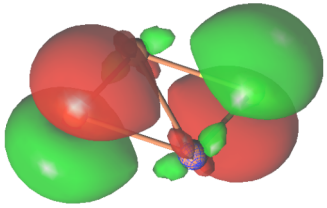
σ: 2.000



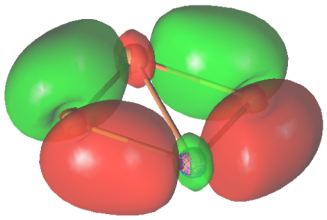
σ*: 1.998



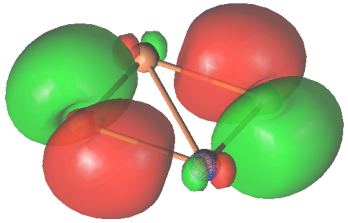
π: 2.000



π*: 1.999



π: 1.999

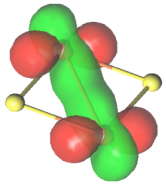


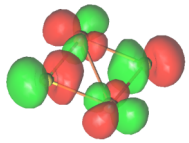
π*: 2.000

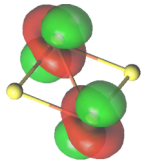
12 electrons in sulfur: $S^{2-}$

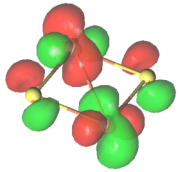
# $Fe_2S_2^{2+}$

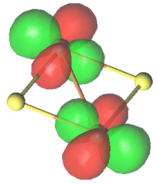
## Iron 3d orbitals and occupations

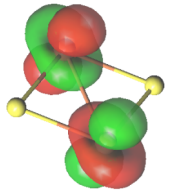

σ: 1.367

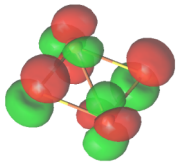

π: 0.597

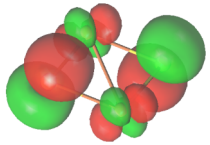

δ: 1.012

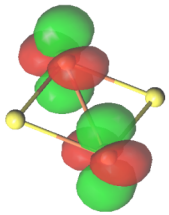

σ*: 0.704

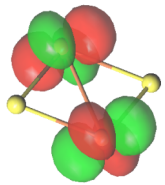

π*: 1.537


δ*: 1.004


π: 0.919

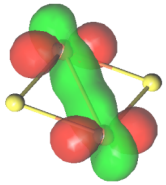

δ: 1.868

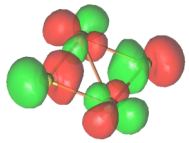

π*: 1.155

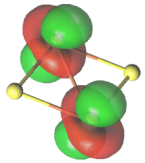

δ*: 1.555

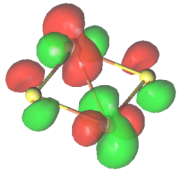
# $Fe_2S_2^{2+}$

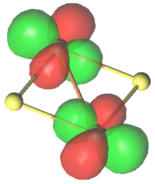
## Iron 3d orbitals and occupations

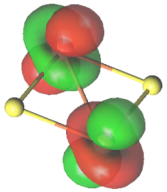

σ: 1.367

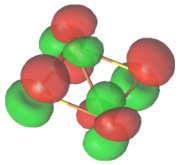

π: 0.597

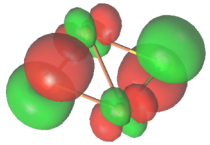

δ: 1.012


σ*: 0.704

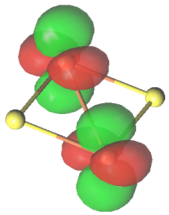

π*: 1.537

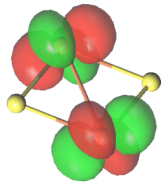

δ*: 1.004


π: 0.919


δ: 1.868

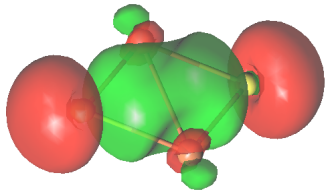
12 electrons in iron: $Fe^{2+}$


π*: 1.155

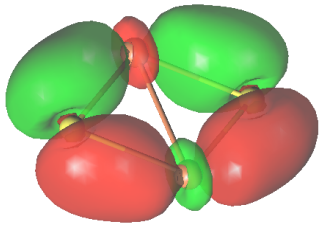

δ*: 1.555

# $Fe_2S_2^{2+}$

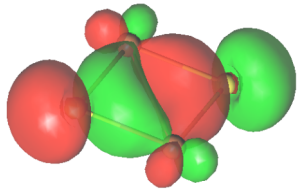
## Sulfur 3p orbitals and occupations



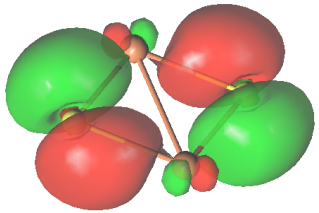
σ: 1.995



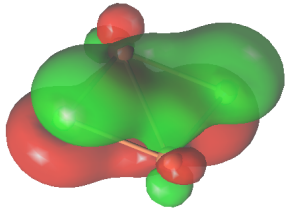
π: 1.950



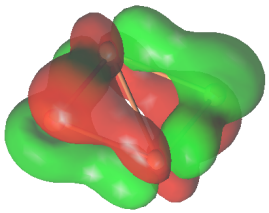
σ*: 1.901



π*: 1.974



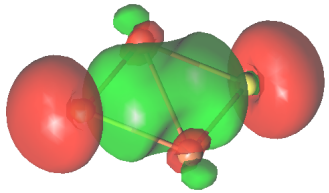
π: 1.882



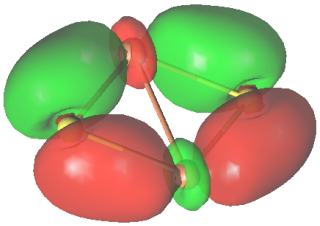
π*: 0.620

# $Fe_2S_2^{2+}$

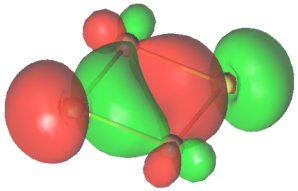
## Sulfur 3p orbitals and occupations



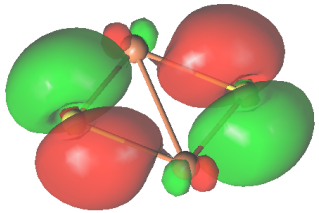
σ: 1.995



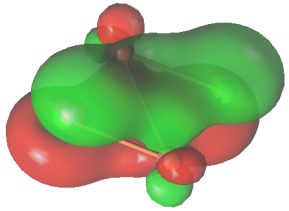
π: 1.950



σ*: 1.901

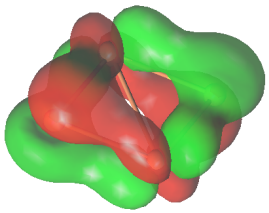


π*: 1.974



π: 1.882

10 electrons in sulfur: $S^-$



π*: 0.620

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- ✓ Iron-sulfur clusters:
  - CASSCF/CASPT2 in progress. PNOF5 to be done
  - Interaction with cystein chain ligands (-$SCH_3$)
  - Extension to bigger clusters

# ACKNOWLEDGEMENT

Financial support comes from Eusko Jaurlaritza (Basque Government) and the Spanish Office for Scientific Research.
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Thank you for your attention