

# Density functional theory studies at a Fe(II) spin-crossover complex

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## Scientific Questions

### Why do we want to investigate?

- Spin-crossover molecules are interesting for data storage and digital display due to spin state switching and changing the refractive index.
- Try understanding the switching mechanism triggered by external stimuli [1, 2].
- Investigate the changes in bond lengths and the associated electronic structure.
- On which timescale do those changes appear? Look inside the switching dynamics.

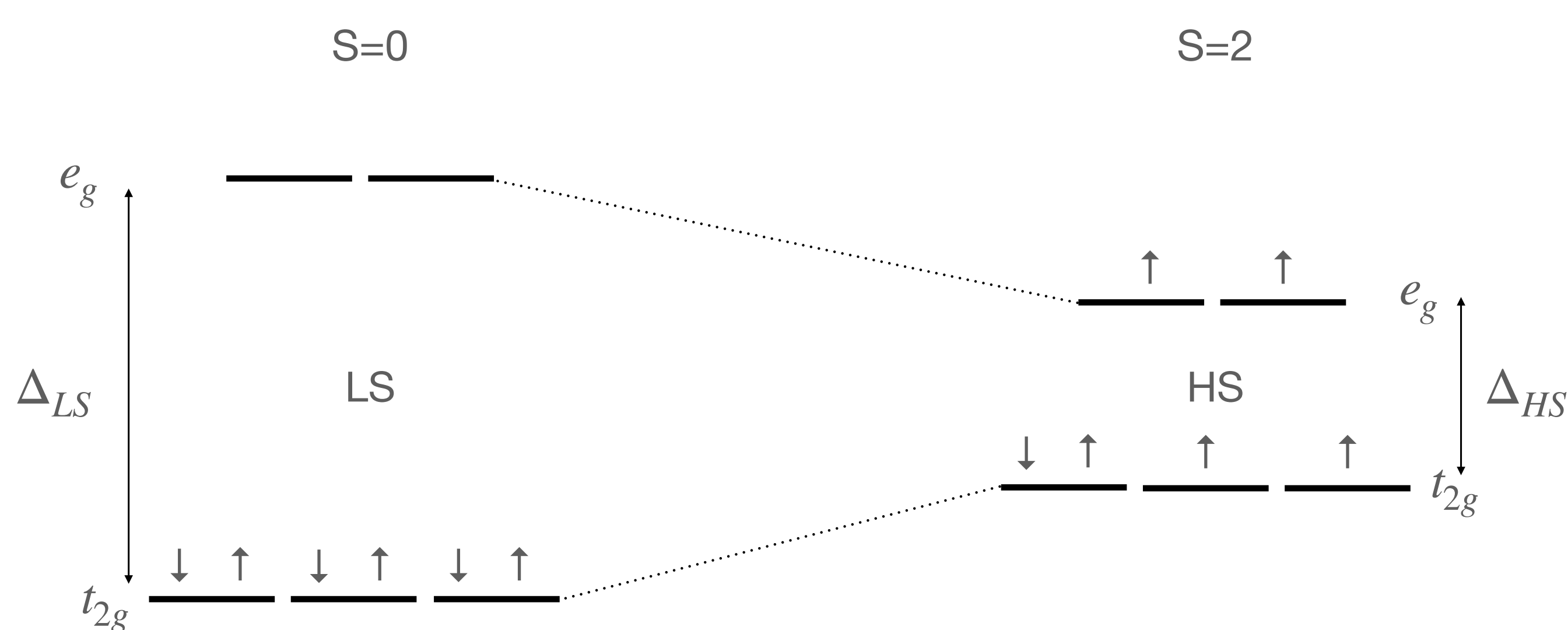
## Spin-Crossover

### Spin-crossover molecules (SCO):

- Spin switching from a low-spin (LS,  $S = 0$ ) to a high-spin (HS,  $S = 2$ ) state due to external stimuli, e.g., light, pressure, temperature, X-rays [3, 4].
  - Expansion of Fe-N bond length from LS to HS
  - X-Ray absorption spectroscopy (XAS) can distinguish between molecules' LS and HS states by splitting the  $L_3$ -peak.
  - Pump-probe experiments enable to study of the dynamics of switching.
- A criterion for future applications as a solid: Abrupt phase transition with switching between LS and HS.

## Schematic Energy States

### Symmetric Octahedral Ligand Field



### Asymmetric Octahedral Ligand Field

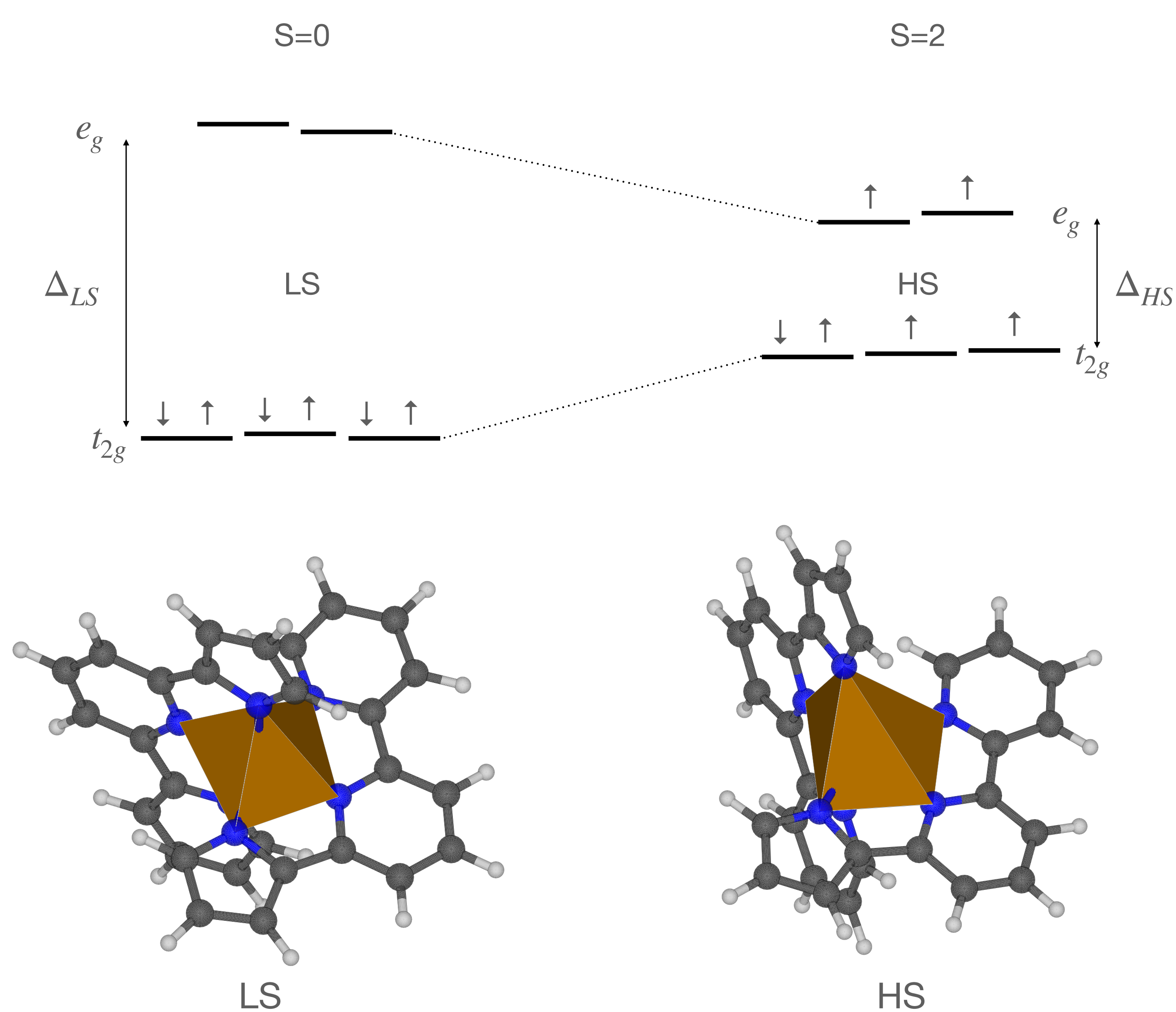


Figure: Ligand Fields of a symmetric and asymmetric environment; top: symmetric octahedron, middle: asymmetric octahedron, bottom: octahedron for both structures (vol HS/vol LS:1.30)

## Calculation Methods

### Density functional theory (DFT) calculations:

Code: FHI-Aims Code [5]:

- Ab initio all-electron full-potential electronic structure code
- Based on numeric atom-centered orbitals

Functional: B3LYP [6]

Working Assumptions:

- Single-molecule, no crystal
- Static DFT is sufficient
- Hybrid functional works well

## Fe(II)-Complex

### Our Molecule:

- Fe(II)-core in a surrounding octahedral nitrogen
- Complex includes 2 1-pyrroline (pyrrole) and 4 pyridine rings
  - Pyridine rings  $C_5H_5N$  (6-membered ring)
  - Pyrrole rings  $C_4H_4N$  (5-membered ring)
  - Asymmetric structure repeats the octahedral degeneracy
- Spin state switching elongates the Fe-N bond and distortion of the nitrogen octahedron.
  - Rotation of one ligand concerning each other about the iron atom
  - Twist of the plane of one ligand about Fe-N (pyridine)

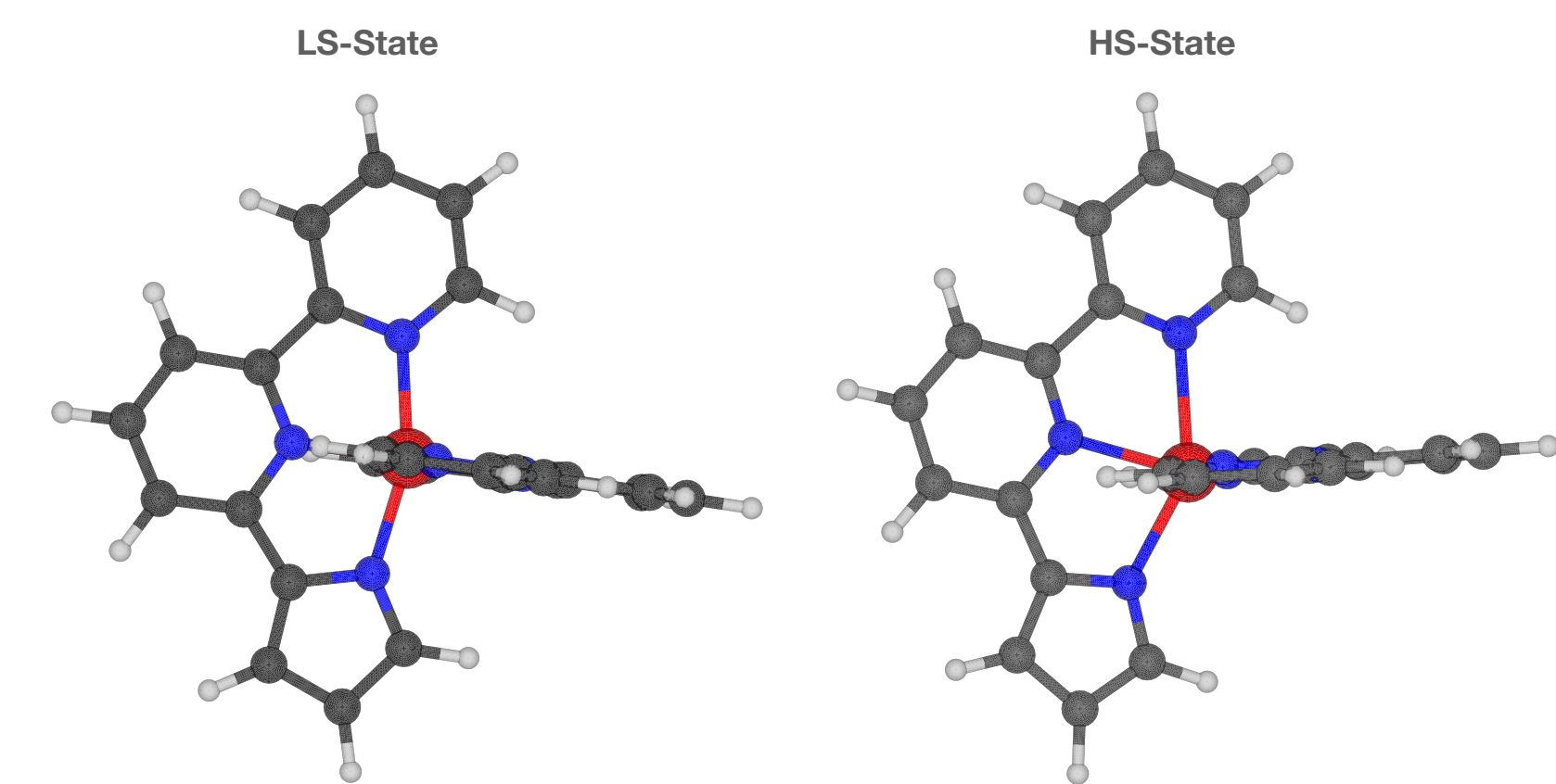


Figure: Comparison of LS- and HS-state bondings

## Bonding Length and Angles

Table: Simulated bond lengths

Bonding	(LS)[Å]	(HS)[Å]
Fe-N(pyridine)1	1.922	2.169
Fe-N(pyridine)2	1.922	2.169
Fe-N(pyridine)3	2.015	2.315
Fe-N(pyridine)4	2.015	2.315
Fe-N(pyrrole)5	1.989	2.093
Fe-N(pyrrole)6	1.990	2.093

### Comparison of LS and HS:

- Structural differences between HS and LS
- Asymmetric bonding for Fe-N for pyrrole and pyridine
- LS and HS are asymmetric

Table: Simulated angles[°] in octahedral environment

Bonding	(LS)[°]	(HS)[°]
N(pyridine)1-Fe-N(pyridine)2	179.98	153.78
N(pyridine)2-Fe-N(pyrrole)6	160.65	147.40
N(pyridine)3-Fe-N(pyrrole)5	160.64	147.41
N(pyridine)2-Fe-N(pyridine)3	79.78	70.88
N(pyridine)1-Fe-N(pyridine)4	79.79	70.88
N(pyridine)2-Fe-N(pyrrole)5	80.87	76.53
N(pyridine)1-Fe-N(pyrrole)6	80.87	76.53

## Potential Energy Surfaces

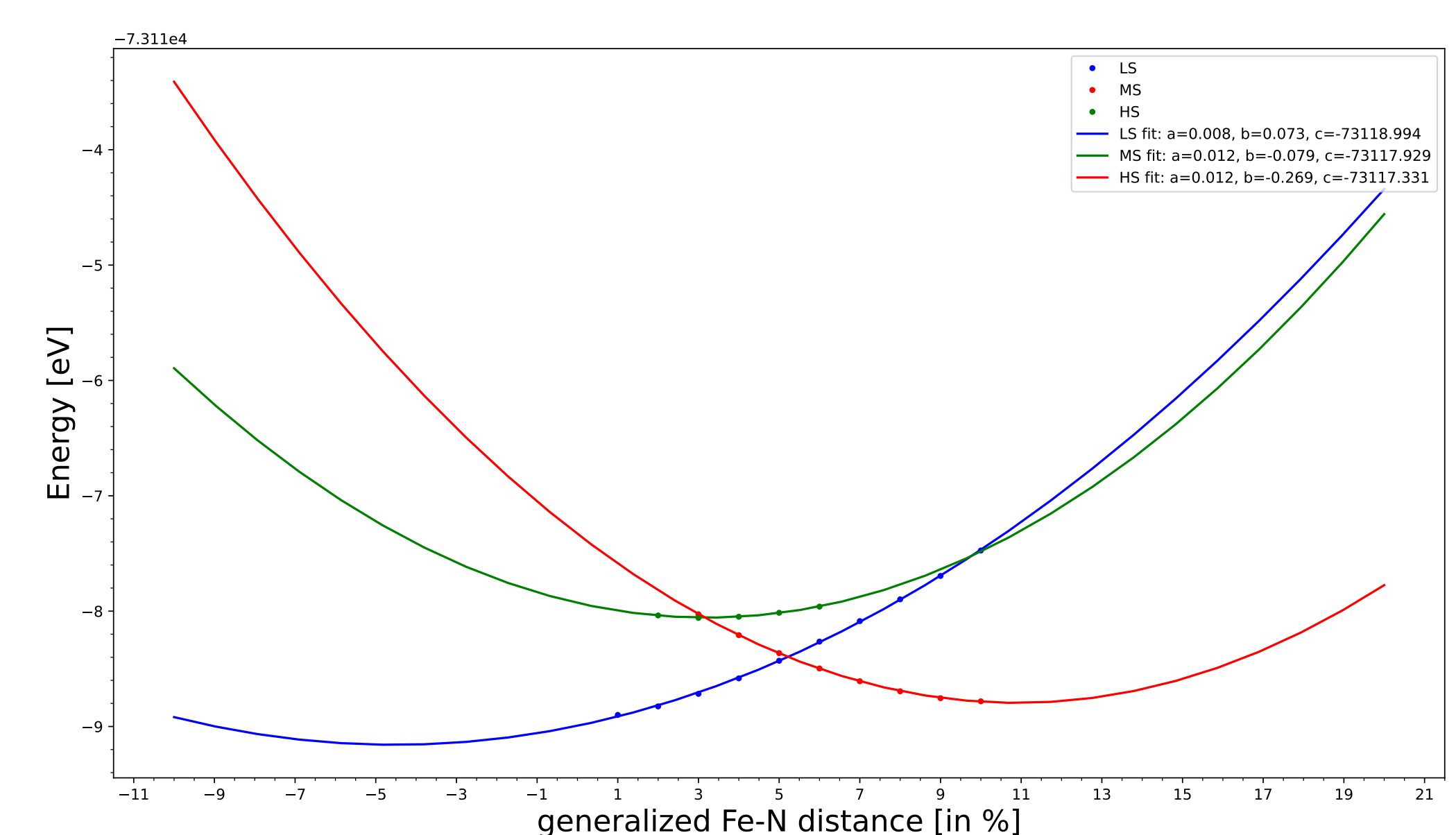


Figure: Comparison of LS-/MS- and HS-state with different generalized Fe-N distances

## Conclusion and Outlook

### Conclusion:

- Increase of bond length and decrease of bonding angle from LS to HS (geometrical switching).
  - Identification of the pyridine and pyrrole Fe-C and C-C bonding differences.
    - Note: No symmetric bonds in B3LYP
- ⇒ Qualitative description of switching mechanism through DFT calculations.

### Outlook:

- Calculating and investigating XAS features for a deeper understanding.
- Comparison of lifetime of states and simulation of the time dependency.

## References

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