Electronic Structure of Open-Shell Tetrahedral $\{Fe(NO)_2\}^9$ Complexes

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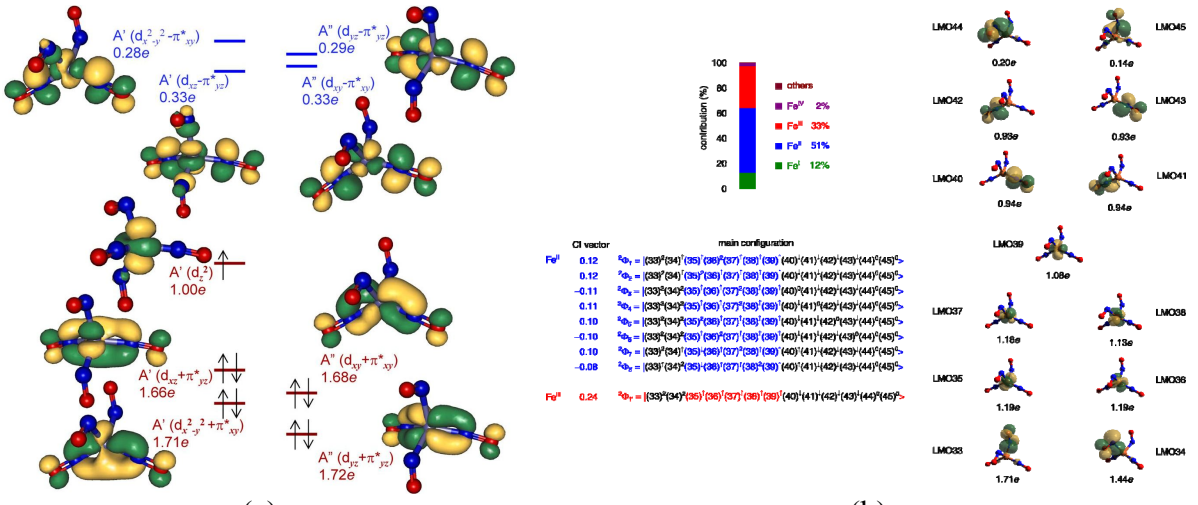
The electronic structure of typical $\{Fe(NO)_2\}^9$ compounds are investigated using multireference theories including complete active space self-consistent field (CASSCF) and N-electron valence state perturbation theory up to the second order (NEVPT2). Geometry optimizations at CASSCF(9,9) and NEVPT2(9,9) using numerical gradients with double-zeta basis set and LANL2 effective core potentials give agreeable structural parameters compared to the experimental X-ray data and the geometries optimized using symmetry adapted cluster/configuration interaction (SAC-CI) method, while NEVPT2 theory significantly improved the overestimated bondlengths at CASSCF level. It is also observed that density functional theories may incorrectly predict the geometries of $\{Fe(NO)_2\}^9$ compounds due to the failure to generate correct spin density. Natural orbital diagrams are demonstrated, and orbital localization using CASSCF wavefunction suggests that the charge of iron is between Fe^{II} and Fe^{III}.



(a) (b)

Figure 1. (a) Natural orbital diagrams of $Fe(NO)_4^-$ optimized at NEVPT2(9,9) level. (b) Boys localization and charge assignment for $Fe(NO)_4^-$.

References

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