measurements, electron density, multipolar refinements

MS46 Computational tools for theoretical chemistry in crystallography

Chairs: Martin Lutz, Martyn Winn

MS46-O1 Recent Advancements in the Development of X-ray Constrained Wave Function Strategies

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As well known, the wave function is a fundamental entity that intrinsically contains all the information of a system in the most compact way. For this reason the possibility of determining wave functions from experimental data has been a tantalizing perspective that motivated different research groups over the years.

Among the modern strategies proposed in this context, the X-ray constrained wave function (XC-WF) method introduced by Jayatilaka [1] is undoubtedly the most noteworthy. This technique can be considered as the most promising advancement of the pioneering strategies introduced by Clinton *et al.* [2] and it consists in extracting single Slater determinants that, other than minimizing the Hartree-Fock energy of the systems, reproduce sets of experimental structure factors within a predefined accuracy.

In our group, the XC-WF approach has been extended in order to extract Extremely Localized Molecular Orbitals (ELMOs) from experimental X-ray diffraction data [3-4], namely Molecular Orbitals that are strictly localized on small molecular fragments (e.g., atoms or bonds) and that are consequently very close to the traditional chemical picture of molecules. Determining XC-ELMOs is straightforward and the new strategy can be seen as an alternative tool to determine experimental electron densities, combining the quantum mechanical rigor of the wave function-based approaches with the chemical interpretability of the popular multipole model.

More recently, always starting from the concept of ELMOs, we have also devised a preliminary X-ray constrained Valence Bond method. This technique, other than being the first attempt of introducing a multi-determinant wave function *ansatz* in the Jayatilaka approach, has allowed us to successfully study the charge distribution of the syn-1,6:8,13-Biscarbonyl[14]annulene at different pressures [5], theoretically confirming the partial rupture of the aromaticity experimentally observed when pressure is increased [6].

An overview of our techniques recently developed in the framework of the XC-WF approach will be presented.

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Keywords: X-ray Constrained Wave Function, Electron Density, Extremely Localized Molecular Orbitals, Valence Bond Theory

MS46-O2 Synergistic 'Substrate Activation' and 'Oxygen Activation' in Salicylate Dioxygenase from QM/MM Simulations

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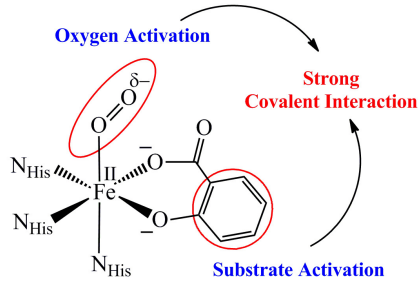
Salicylate 1,2-Dioxygenase (SDO) is the first enzyme discovered to catalyze the oxidative cleavage of a monohydroxylated aromatic compound, salicylate, in contrast to the well-known electron-rich substrates. We have investigated the mechanism of dioxygen activation in SDO by QM/MM calculations. Our study reveals that the non-heme Fe^{II} center in SDO activates salicylate and O_2 synergistically by a strong covalent interaction to facilitate the reductive cleavage of O_2. A covalent Salicylate-Fe^{II}-O_2 complex is the reactive oxygen species in this case, where the electronic structure is best described as between the two limiting cases, Fe^{II}-O_2 and Fe^{II}-O_2^- with partial electron transfer from the activated salicylate to O_2 via the Fe center. Thus, SDO employs a synergistic strategy of 'substrate activation' and 'oxygen activation' to carry out the catalytic reaction, which is unprecedented in the family of iron dioxygenases. Moreover, O_2 activation in SDO happens without the assistance of a proton source. Our study essentially opens up a new window in the mechanism of O_2 activation.

[1] S. Roy and J. Kästner Angew. Chem. Int. Ed. 55, 1168 (2016)



(His = Histidine)

Figure 1. Dioxygen is activated in Salicylate 1,2-Dioxygenase (SDO) by a stron covalent interaction with the non-heme iron cofactor and the substrate.

Keywords: DIOXYGENASE, METALLOENZYMES, QM/MM, ACTIVATION