Can we reach the heaven of chemical accuracy by climbing Jacob's Ladder? A DFT validation study for Non-heme Iron complexes

by

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Introduction: Jacob's Ladder classification

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'Heaven'
Chemical Accuracy

fully non-local

hybrid meta GGA
hybrid GGA

meta GGA

GGA

LSDA

- **M06-2X, M06, M06L**
- **B3LYP-D3, B97D, wB97xD**
- **B3LYP, X3LYP, B3P86**
- **MPWB95,BB95,TPSS**
- **BP86, BLYP, PBE**
- **LSDA**

'Earth'
Hartree Fock Theory

DFT functional forms gets more complex but the energies get more accurate (and computationally more expensive as one climbs the rungs of Jacob's Ladder .

Introduction

- The Jacob's Ladder is a metaphorical description of the classification of DFT functionals based on their chemical accuracy starting from the "earth" of Hatree-Fock approximation to the "heaven" of chemical accuracy.

- This concept is generally applied to identify the best DFT functional that should be used predict the energy for a molecule within chemical accuracy (±1 kcal/mol).

- Hence, if the energy of a given molecular structure is a function of its the electron density (which ultimately determine the geometry) as the fundamentals of DFT teach us, then we can infer that "climbing" the Jacob's Ladder should also lead us to the most accurate description of the structure and electronic properties of a given molecule/complex.

Aim of this work

- Hence in this work, the aim was to:

(i) Investigate whether climbing higher up the rungs of the Jacob's Ladder actually results in improved accuracy of predicting structural and electronic properties of Fe(II)complexes;

(ii) Determine which rung of the Jacob's Ladder best predicts the structure and electronic properties of Fe(II) complexes used as catalysts for the activation of C-H bonds in organic substrates and

(iii) To ultimately identify the optimal DFT functional for carrying out QSAR studies of the catalytic behaviour of Fe(II) complexes used in alkane oxidation.

Computational Details

- Five representative **Fe(II) complexes** were selected from the CCD and starting structures of these were geometry optimized using various DFT functionals.

- 16 functionals covering the whole spectrum of Jacob Ladder Classification of DFT functionals were tested.

- The structural and electronic properties of the resulting optimized structures were compared to that of **corresponding crystal structures**.

- For all the calculations, the Gen/ECP basis set and Gaussian 09 Rev. D01 on the CHPC was used for all the calculations

Structures of Selected Fe(II) Complexes

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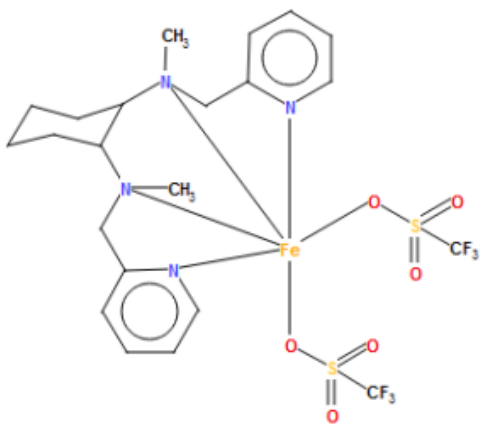

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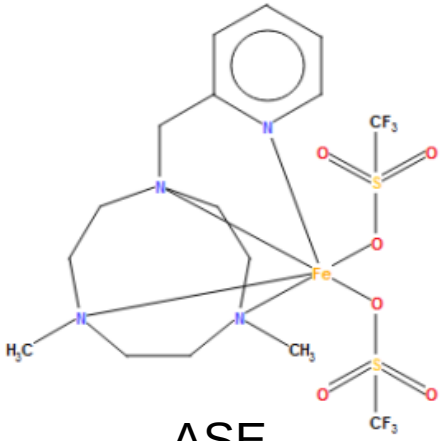

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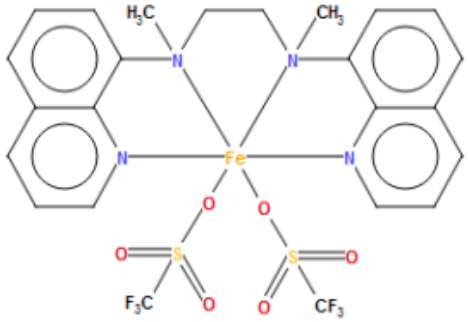

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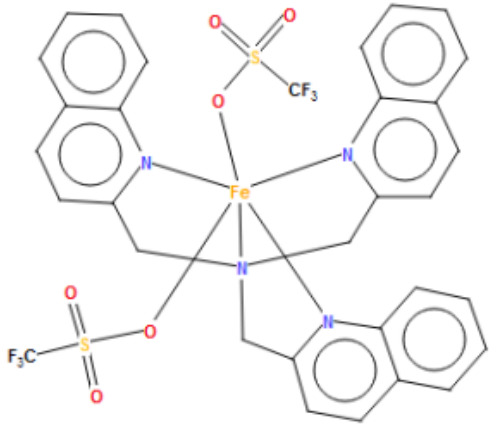

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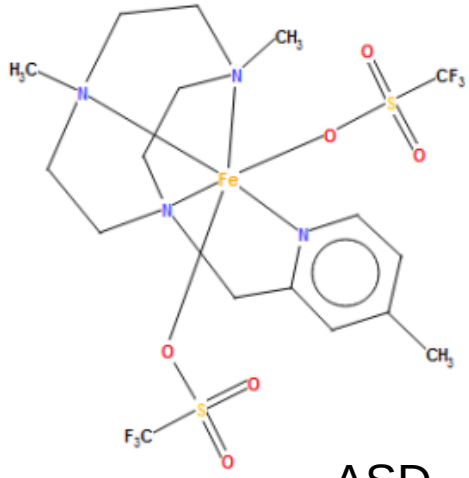

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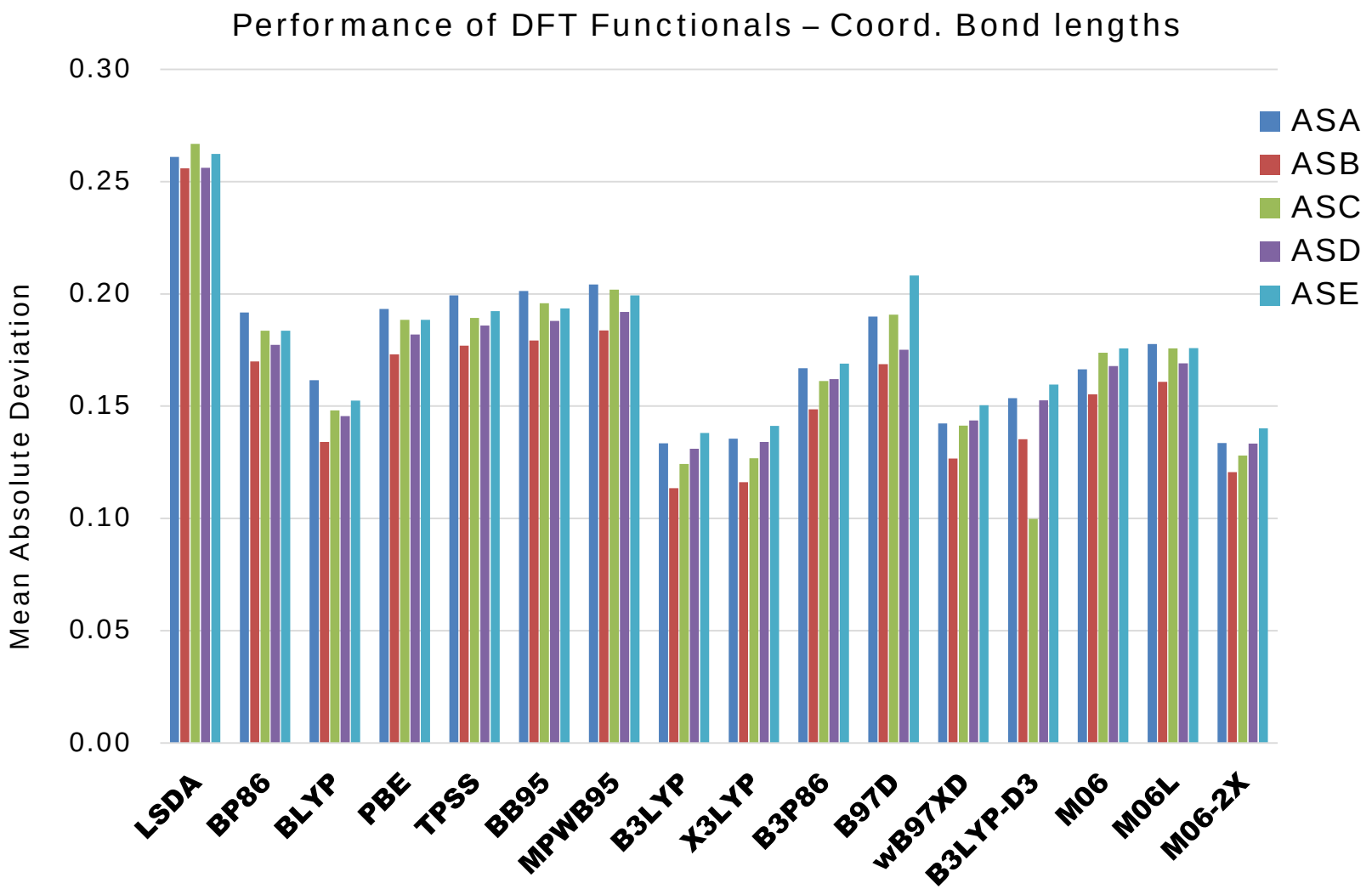
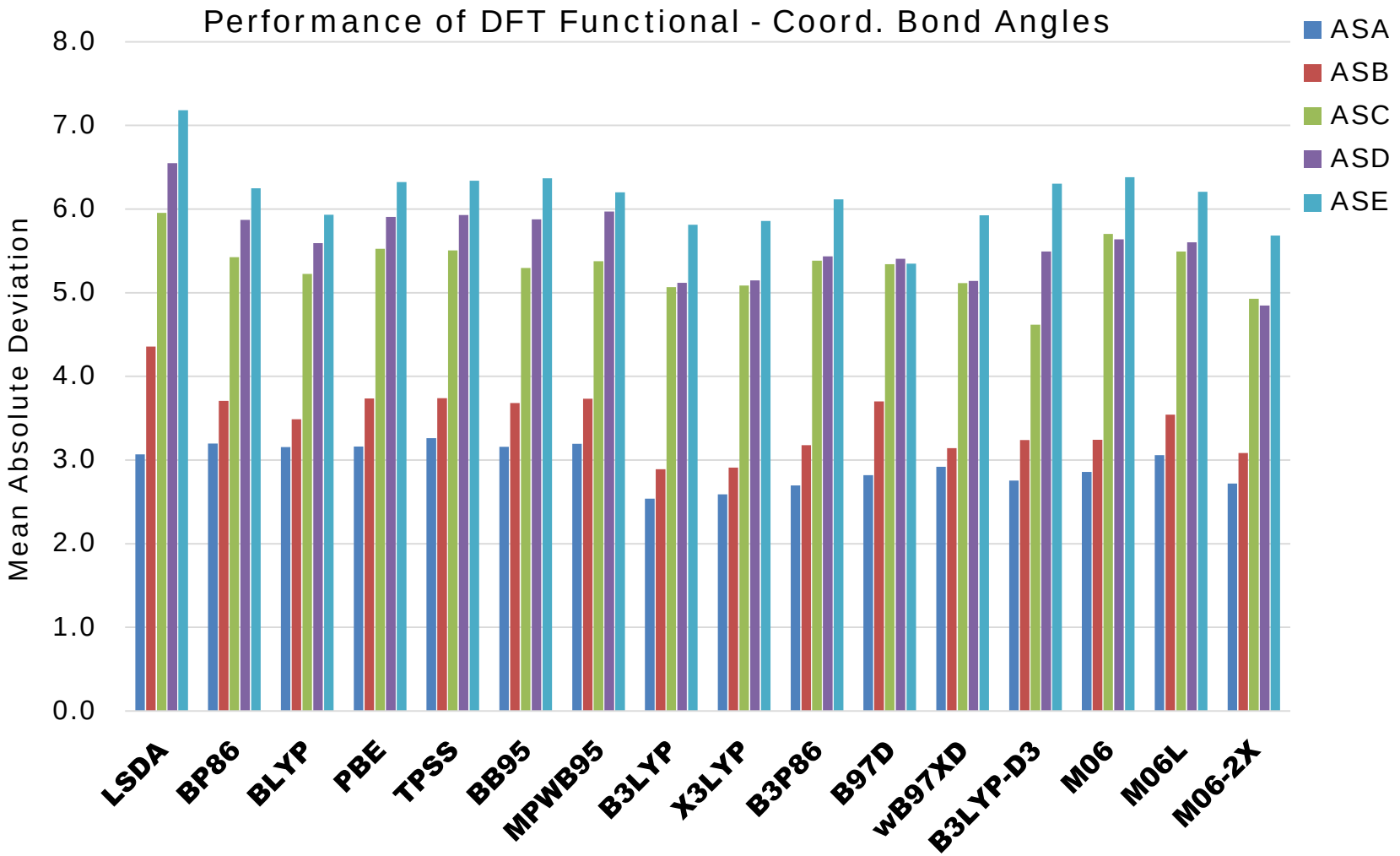
Results and Discussion



Results and Discussion



Results and Discussion

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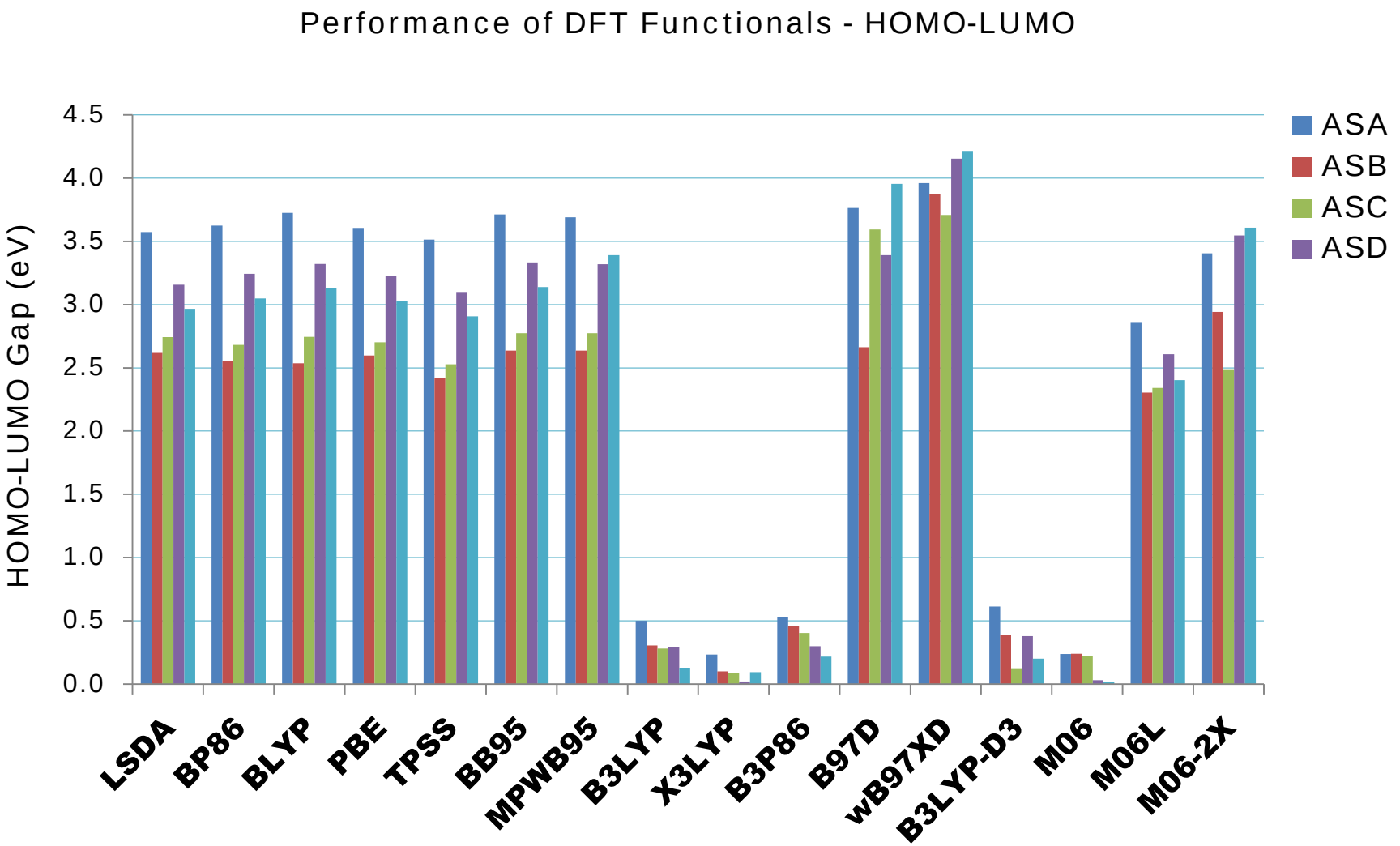
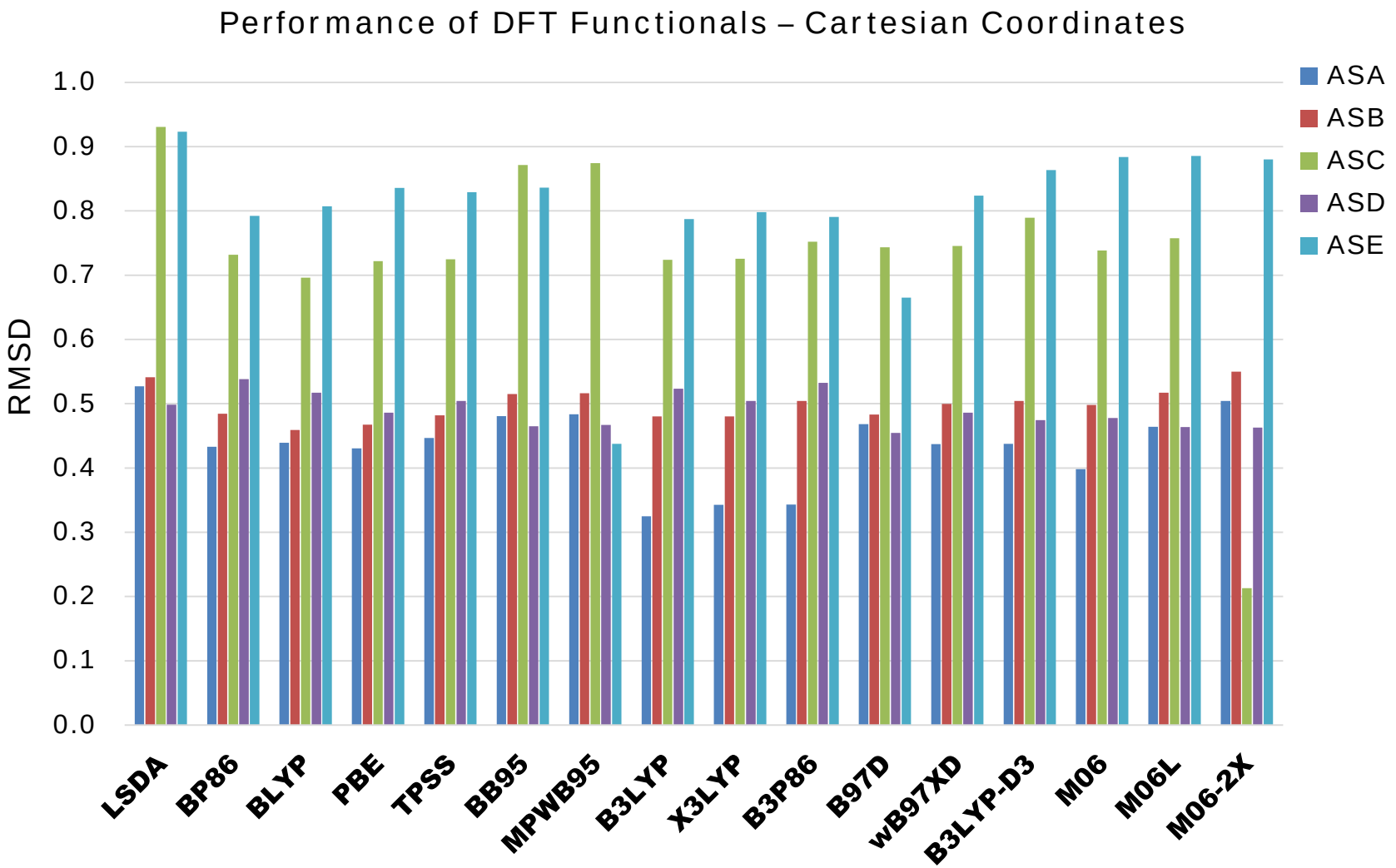
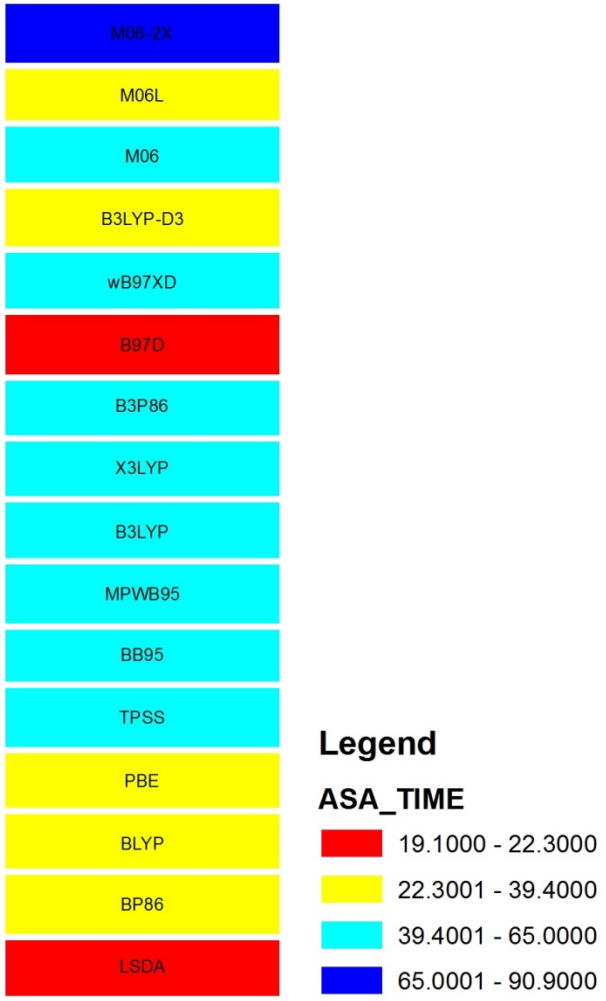


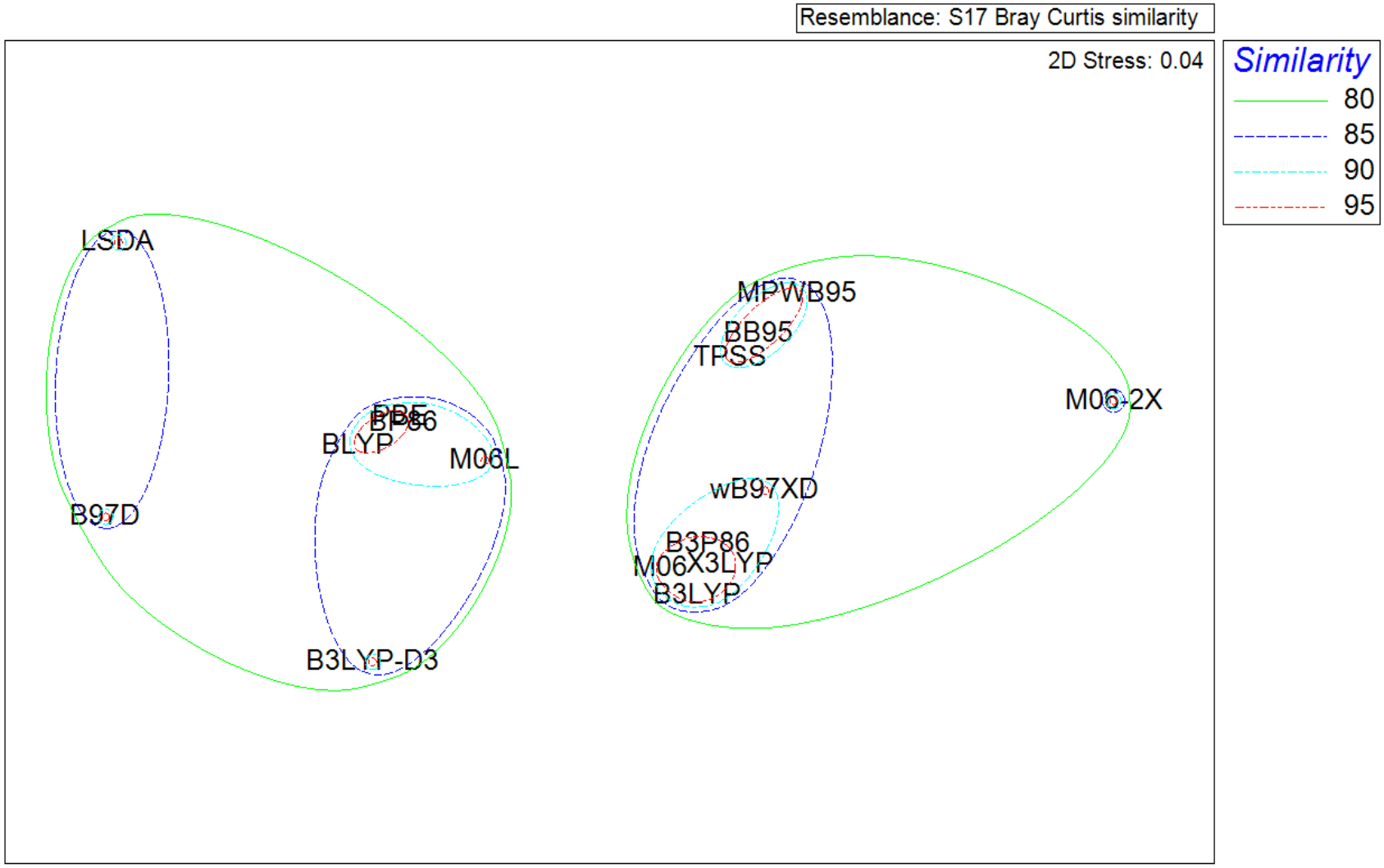
Results and Discussion



Results and Discussion



Summary of Results



Conclusions and Recommendations

- Despite their position in the Jacob's Ladder and corresponding longer computational time, the hybrid meta-GGA functionals (M06, M06L and M06-2X) had larger errors in predicted properties compared to the much cheaper hybrid GGA functionals (B3LYP, X3LYP, B3P86). This demonstrates that the position of a DFT method on the Jacob's Ladder does not necessarily correlate with its accuracy.

- So the most accurate and complex functional may not always be the best functional as one may originally think according to the Jacob's Ladder concept.

- In general, the hybrid GGA and the hybrid meta-GGA functionals performed better than other DFT functionals in reproducing the bond lengths for all Fe(II) complexes investigated irrespective of bond type.

- Is there a way of predicting these before carrying out any DFT calculation?

Conclusions

- Although several validations of DFT functionals have been carried out in literature, this work shows that there is need to develop a rigorous way of choosing the appropriate DFT method to use in modelling the properties of a molecule.

- This has been alluded to recently by several publications in literature a classical example of which is the report by Michael G. Medvev *et al* titled “Density Functional Theory is straying from the path towards the exact functional”, Science 2017, 355, aah5975.

Acknowledgements

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Thank you