Poster

Ab initio crystal structure prediction (CSP) of magnetic metal-organic frameworks (MOFs)

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Magnetic systems play an essential role in modern life, serving as the foundation for the advancements of technology ranging from electric engines to data storage systems. This fundamental dependency motivates the exploration for materials that demonstrate beneficial and unique magnetic properties. While there are several magnetic materials that are well-established, i.e. inorganic magnets (derived from transition and rare-earth metals), they still encounter limitations in terms of tuneability [1]. Enhancing the tuneability of magnetic properties involves modifying the characteristics of the material, often depends on the alignment of magnetic ions within its structure, arranged in 1D, 2D, and 3D chains [2].

Metal-organic frameworks (MOFs), consisting of transition metal ions (nodes) linked together by organic linker molecules, present exciting prospects for the advancement of new magnetic materials. Understanding the notion of topological diversity of MOFs, which can be amplified by several factors such as combination of metal-linker, is pivotal in its design as it signifies the extensive connectivity inherent in the framework. By tailoring MOFs with specific topologies, we can adjust the relative orientation of magnetic metal centers [3], thus providing a systematic approach to target desired magnetic properties.

As the exploration of different combination of nodes (metal ions) and linkers becomes pivotal in studying magnetic MOFs, the search for techniques that can effectively carry this task is also increasing. Traditionally, this task has been addressed through experimental screening. However, this is becoming increasingly difficult due to the vast array of available organic linker molecules and the diversity of potential nodes, which can range from single-metal ions to metal clusters. Therefore, a theoretical approach backed by robust computing performance is the most suitable techniques to fulfil this task. This will enable theoretical investigations to support and offer explanations to the magnetic phenomena observed and make predictions for experimental verification.

Our approach for theoretical investigation of magnetic MOFs is crystal structure prediction (CSP) based on *ab initio* random structure searching (AIRSS) [4] and Wyckoff Alignment of Molecules (WAM) [5]. This approach allows us to generate entirely new crystal structures starting just from molecular diagrams of individual nodes and linkers. The incorporation of WAM into AIRSS accelerates the search for structures by reducing the dimension of the search space through symmetry imposition on trial structure, thereby speeding up the searching process. The validity of this approach has been confirmed through successful reproduction of existing MOF structures [5], and followed by successful design of novel functional MOFs with application as rocket fuels [6].

To assess the likelihood of the generated structures existing under experimental conditions, it is crucial to evaluate their energy ranking. For this task, periodic density functional theory (DFT) is used. However, considering the magnetic ordering of metal ions within the MOFs lattice, a more sophisticated periodic DFT is needed. Therefore, various functional types (GGA, hybrid, range-separated hybrids) will need to be tested, along with additional enhancements such as Hubbard U correction [7]. Ultimately, this approach will enable comprehensive structure searches of magnetic MOFs, allowing for the identification of experimentally relevant structures with high computational accuracy.

[1] Thorarinsdottir, A. E. & Harris, T. D. (2020). *Chem. Rev.,* **120**, 8716.

[2] Miller, J. S. (2011). *Chem. Soc. Rev.,* **40**, 3266.

[3] Cheng, X. N., Zhang, Y. Y., Zheng, Y. Z., Chen, X. M. (2007). *Advanced Materials,* **19**, 1494.

[4] Pickard, C. J. & Needs, R. J. (2011). *J. Phys. Condens. Matter,* **23**, 053201.

[5] Darby, J. P., Arhangelskis, M., Katsenis, A. D., Marrett, J. M., Friščić, T., Morris, A: J. (2020). *Chem. Mater.,* **32**, 5835.

[6] Xu, Y., Marret, J. M., Titi, H. M., Darby, J. P., Morris, A. J., Friščić, T., Arhangelskis, M. (2023). *J. Am. Chem. Soc.,* **145**, 3515.

[7] Anisimov, V. I., Zaanen, J., Andersen, O. K. (1991). *Phys. Rev. B.,* **44**, 943.