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Using polyhedral distortions to understand structure-property behaviour.

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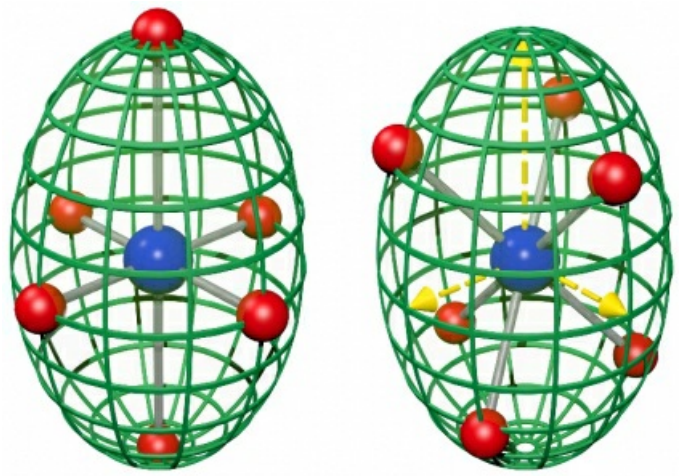
Polyhedra are prevalent in crystallography; we seek to rationalise structures in terms of tetrahedra, octahedra and other regular shapes. Indeed, many structure-property relationships can be described in terms of interactions between rigid coordination spheres, such as perovskite phase transitions and negative thermal expansion. Often, however, polyhedra are not rigid instead displaying some degree of distortion; analysing this can be difficult, particularly if the polyhedron shows deviations both in terms of both bond lengths and angles. Often, these distortions can give rise to complex electronic effects, resulting in useful magnetic materials. While local symmetry mode analysis can give a comprehensive structural picture in many cases, it is often difficult to interpret if multiple distortion modes act cooperatively. Alternatively, continuous shape measures [1] can be used to quantify deviations from a reference polyhedron, but this reference is not always trivial to define. Here, we present a much simpler measure of polyhedron distortion, based on the fitting of ellipsoids to coordination environments.

We have applied this new general method to a range of metal oxide materials, revealing new insights into their properties; from a switching bistability in symmetry-disallowed perovskite phase transitions to a weak off-centre 'd5-effect' for Fe3+ ions, that could potentially be exploited in multiferroic materials.[2] We have implemented the method in the python package PIEFACE.

While the method has currently been applied to metal oxides, it could easily be generalised to other materials that obey a polyhedral description, including coordination complexes, framework materials and organic molecules.

[1] Alvarez, S. et al. (2005). Coordination Chemistry Review, 249, 1693-1708.
[2] Cumby, J. and Attfield, J. P. (2017). Nature Communications, 8, 14235.



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