MS45 What is inside the black box?

MS45-04
The Crystal Isometry Principle
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Abstract
'Black box' approaches to the prediction of properties are greatly hindered by ambiguities in data representation [1]. A crystal structure can be represented by infinitely many different bases and motifs. Crystal Structure Prediction produces numerous near-duplicates among millions of simulated crystals, obtained as slightly different approximations of the same local energy minimum, which must be distinguished from genuinely different structures [2].
Since crystal structures are determined in a rigid form, their strongest equivalence is rigid motion or isometry also including reflections. Their classification up to isometry requires invariants and metrics that are continuous under perturbations because any conventional or reduced basis may double in size under small perturbations.
Density functions [3], the isoset (a complete invariant of periodic structures) [4], Average Minimum Distances (AMD) open up the 'black box' of crystallographic data with unambiguous representations of periodic structures [5]. The simplest Gaussian regression on AMD invariants [6] achieved the state-of-the-art Mean Absolute Error (less than 5kJ/mole, 0.05eV/atom) on 5679 crystals [2].
Pointwise Distance Distributions (PDD) are stronger invariants, which can be continuously compared by the Earth Mover's Distance. This distance was used for visualising the Inorganic Crystal Structure Database [7]. More than 200 billion pairwise comparisons between all 660K+ periodic crystals (full 3D structure; no disorder) in the Cambridge Structural Database (CSD) was completed over two days on a modest desktop PC.
PDD computations detected five pairs of entries that have identical geometry but differ by one pair of atoms, for example, Cd<->Mn in HIFCAB vs JEPLIA [8, section 7]. Since these coincidences seem physically impossible, five journals are now investigating the integrity of publications based on these duplicates.
These experiments justify the Crystal Isometry Principle, which states that any periodic crystal is uniquely determined by its geometric structure. Indeed, replacing any atom with a different one inevitably perturbs distances between neighbours. Then all periodic crystals live in a common Crystal Isometry Space (CRISP), so that Mendeleev's periodic table representing individual elements, categorised by atomic number and group, can be extended into a continuous space for all solid crystalline materials. For instance, diamond and graphite, both consisting purely of carbon, have different locations in CRISP.
In the case of 2-dimensional lattices [9], the first map of CRISP shows that among all real crystals in the CSD about 45% of 2-dimensional lattices are oblique and nicely fill the expected continuous space [10] except towards the point representing very thin long cells.

References
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Ambiguity and discontinuity of reduced cells

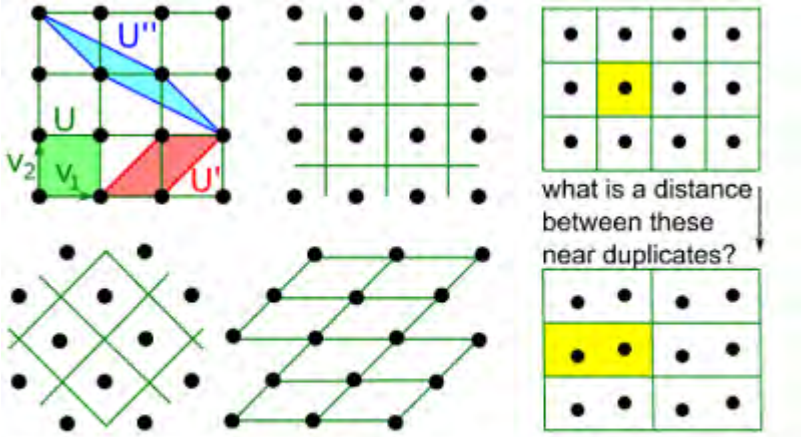

Figure 1. Left: the square lattice can be given by many bases.

Right: reduced cells are discontinuous under perturbations.

Invariants of crystals and maps of 2D lattices

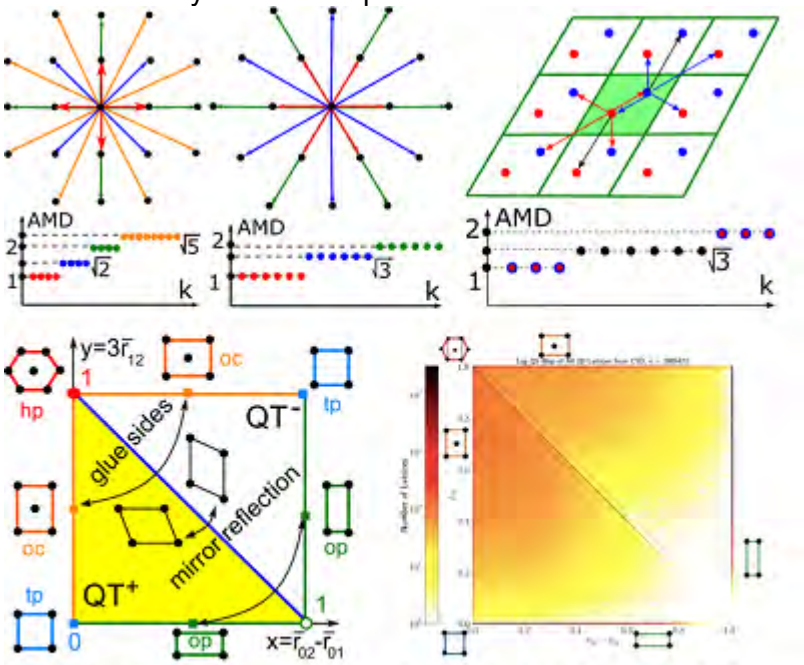

Figure 2. Top: the AMD sequence of distances from motif points to k neighbours for the square lattice, hexagonal lattice, a honeycomb structure (with averages over motif points).

Bottom left: the space of all 2D lattices up to isometry and scaling. Bottom right: the log scale density map of 2D lattices in all periodic crystals from the Cambridge Structural Database.