

Computational methods Introduction Solid state chemistry has developed an increasing focus on complex or functional materials. Describing systems where a large number of configurations may exist locally requires a significant number of parameters to be determined. XRD would not be amenable to this, as an example, as it measures diffraction arising from structured materials so point defects are not measurable.

Computational methods can assist in this area. Sufficiently advanced models can accurately reproduce experimental data, with the calculation of properties not readily determined by experimental methods. The exponential growth in computing power over recent decades has allowed increasingly complex systems and phenomenon to be calculated in a reasonable timeframe.

In this chapter, basic concepts and formulae pertaining to the modelling of crystal structures are outlined. Mathematical techniques used to efficiently optimize these systems are then presented. This overview is brief and primarily discusses techniques used in this report, as more comprehensive reviews are already available. Gale2003,Jensen2007,Catlow2013

Potential models The implementation of accurate potential models is vital if the results of atomistic modelling studies are to accurately reproduce experimental findings. These models describe the energy of a system as a function of nuclear coordinates.

Whilst in principle the internal energy of a system is dependant on the momentum and position in space of all nuclei and electrons within the system, the huge number of interactions this entails are not feasible to consider explicitly for all but the simplest of systems.

Instead, the system is treated as a series of distinct ions, and the energy terms are subdivided by the number of bodies in a given interaction: $U = \sum_{i=1} U_i + 12 \sum_{i=1} \sum_{j=1} U_{ij} + 16 \sum_{i=1} \sum_{j=1} \sum_{k=1} U_{ijk} + \dots$

Single body interactions are usually implemented where an external forcefield is to be applied to a system, such as the application of an external electric field. They can also be used in the implementation of the Einstein model, in which there is no interatomic interactions, and instead species are modelled as being attached to their lattice sites by harmonic springs.

Single body terms are not used in the course of this study, but are referenced here for completeness sake.

Two-body interactions The two-body terms in Equation eq:taylor are those which account for interactions between individual pairs of ions or atoms. It is convenient to further subdivide these interactions into Coulombic (long-range) and short-range terms as so: equation $U_{ij} = \Phi_{Coulombic} + \Phi_{short-range} eq : two - body$