Multipoles and interaction potentials in ionic materials from planewave-DFT calculations

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Potentials for oxides which transfer well between different materials have to account explicitly for many-body contributions to the interionic forces, such as dipole and quadrupole polarization effects and the compression and deformation of an oxide ion by its immediate coordination environment. Such complex potentials necessarily involve many paramters. Here we examine how the results of *ab-initio* electronic structure calculations, based upon planewave Density Functional Theory (DFT) methods, on general configurations of ions derived from Molecular Dynamics simulations at finite temperature, may be used to parameterize an "Aspherical Ion" (AIM) potential. Dipoles and quadrupoles on the individual ions are obtained *via* a transformation of the Kohn-Sham orbitals to localised orbitals on each ion, which enables a distorted charge density for each ion to be obtained. The dipoles and quadrupoles appearing in polarization parts of the AIM potential are fit to those obtained from the *ab-initio* calculations in this way. The remaining parts of the potential, describing short-range repulsive interactions between ions with compressed and deformed charge densities, are fit to the *ab-initio* forces and the stress tensor. By using a sufficiently large data set on which to carry out this optimisation, an excellent potential is obtained, which accurately transfers between different phases and to mixtures.