Poster

Combining Molecular Dynamics Simulations with Topological Analysis of the Bonding in Crystalline Systems

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In recent years, computer modelling and simulations become more and more indispensable in scientific research, as an alternative or a complementary method to the experimental one. In particular, ab initio Molecular Dynamics (AIMD), based on Hartree-Fock (HF) or Density Functional Theory (DFT), has become established since its early days as an important tool for simulations of an increasingly wider range of problems in geology, condensed matter physics, chemistry and biology.[1,2] This method combines the quantum- mechanical static description given by ab initio theories such as HF and DFT with a classical evolution of the nuclear coordinates in the phase space, thus allowing a dynamic characterization of structural and electronic properties of a condensed matter system. In the Born-Oppenheimer method, the nuclear positions are propagated using forces evaluated at the self-consistent electronic ground state for each instantaneous arrangement of the nuclei.

In this work, the implementation of an original Born-Oppenheimer molecular dynamics module is presented, which is able to perform structural optimization based on AIMD concepts,[3] together with simulations of large-scale and complex condensed-phase systems for sufficiently long time scales at the level of hybrid DFT functionals, in the microcanonical, canonical and isobaric-isothermal ensembles.[4] The information contained in the trajectory of the dynamics is then extracted through a series of post-processing algorithms, that provide the radial pair distribution function, as well as the diffusion coefficient and the vibrational density of states of the system.[4] This package of new algorithms is fully integrated in the CRYSTAL code, a program for quantum-mechanical simulations of materials, whose peculiarity stems from the use of atom-centered basis functions within a linear combination of atomic orbitals to describe the wave function.

Within this framework, the use of a localized basis set is of great advantage to analyse the chemical properties of condensed matter systems. More specifically, the quantum theory of atoms in molecules and crystals (QTAIMAC), through topological analysis of the electron density, often complemented by the evaluation of its Laplacian, provides a general and robust theoretical framework to characterize chemical bonding features from a computed wave function.[5,6] This methodology, embedded in the CRYSTAL code (TOPOND module), is capable to treat crystalline systems using basis functions up to *f* and *g* type orbitals,[7,8] paving the way for an effective QTAIMAC analysis of chemical bonding of lanthanide and actinide materials.

Therefore, combining the dynamical evolution in microcanonical, canonical or isobaric-isothermal ensemble with the topological analysis of the chemical bonding, the evolution of the bonds interactions along a dynamical trajectory can be studied, allowing a full and coherent characterization of the electronic properties during dynamic processes induced by temperature or pressure variations, as, for example, in the case of phase transitions.

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