

Editorial

First-Principles Prediction of Structures and Properties in Crystals

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The term “first-principles calculations” is a synonym for the numerical determination of the electronic structure of atoms, molecules, clusters, or materials from ‘first principles’, i.e., without any approximations to the underlying quantum-mechanical equations that govern the behavior of electrons and nuclei in these systems. In principle, these calculations allow us to learn about structural, mechanical, electronic, optical, and many more properties of molecules and materials without having to resort to any empirical or effective models. Of course, solving the quantum many-particle problem is very hard; the application of the clamped nuclei or Born–Oppenheimer approximations removes the atomic nuclei from the problem but leaves behind the many-electron problem that is still impossible to solve analytically for any interesting system.

Quantum chemists have risen to the challenge since the late 1920s by developing a succession of approximate approaches that, crucially, can be extended systematically towards solving the full many-electron problem. For small molecular systems, the best of these methods (such as coupled cluster theory) can determine electronic properties such as the ionization potential as accurately and precisely as the best experiments. These approaches cannot be scaled well to extended, crystalline systems, and it was the development of density functional theory (DFT) in the 1960s that opened the door to accurate “first-principles” calculations of crystalline materials. DFT comes with its own methodological challenges and restrictions, first and foremost that a crucial component of the electron–electron interaction, the exchange–correlation energy, is only known in a myriad of approximations and cannot be extended systematically towards the true expression. Nonetheless, DFT calculations have shown from the beginning that they provide a reasonably accurate means to reproduce and explain experimentally measured properties of crystals [1].

However, the challenge of whether first-principles calculations can evolve from an *explanatory* to a truly *predictive* tool was acknowledged, most colorfully in John Maddox’s famous statement in the late 1980s about the “continuing scandal in the physical sciences”—the failure to predict the crystal structures of materials on the basis of their chemical composition alone [2]. This ‘scandal’ has been tackled over the last two decades: more accurate calculations, smarter algorithms that borrow from data science, biological evolution, and machine learning, all combined with increased computing power, allowing us to use DFT for truly predictive purposes [3–5].

Yet, challenges remain: complex chemical compositions, variable external conditions (such as pressure), defects, or properties that rely on collective excitations—all represent computational and/or methodological bottlenecks. This Special Issue comprises a collection of papers that use DFT to tackle some of these challenges and thus highlight what can (and cannot yet) be achieved using first-principles calculations of crystals.

In Reference [6], Geng et al. have used evolutionary algorithms to predict crystal structures and electronic properties of binary Na–S compounds under pressure. This material class is of interest for

use in battery materials, but the authors show that high pressure favors the formation of metallic compounds with intriguing superconducting properties. Their work searches for stable and metastable phases across different pressures and a wide range of chemical compositions, and the authors use quantum chemical approaches and density functional perturbation theory to obtain the full picture of the new compounds' electronic structure and superconductivity.

In Reference [7], Higgins et al. present a methodological advancement of a crystal structure prediction tool based on genetic algorithms, which accounts for the magnetic as well as the crystal structure of a material by treating the localized magnetic moments as degrees of freedom on par with the atomic positions and unit cell dimensions. They demonstrate that their approach can predict complex magnetic structures that can form at the interfaces of magnets and semiconductors.

In Reference [8], Derzsi et al. predict the structural, electronic, and magnetic properties of an elusive metal halide, AgCl_2 . They show that structure prediction can be done both in a physically biased way (following imaginary phonon modes of reasonable candidate structures) and in an unbiased way (exploring configurational space using evolutionary algorithms). The authors examine in detail the difficulties of DFT to properly capture the charge transfer and magnetic properties of this compound and place the resultant most stable structure in a wider context of metal halide compounds.

In Reference [9], Khan et al. explore the electronic and transport properties of Mn-doped ZnTe. The host material is a promising thermoelectric, and the authors show that this is also true for the doped materials, whilst doping reduces the electronic band gap towards values that are useful for optoelectronic applications. The combination of defects, magnetism, and transport properties makes this a very challenging problem.

In Reference [10], Peng et al. tackle a methodological issue of DFT: how best to describe non-local electronic correlations of the London dispersion type. They introduce a new dispersion-corrected exchange-correlation functional that relies on a single adjustable parameter, q , which is present in the exchange part of the functional. The authors use the new approach to optimize the mass densities of a test set of molecular and layered materials and show that it outperforms two standard density-based dispersion correction methods.

In Reference [11], Chen et al. study the properties of a class of metal-iridium compounds, $X_3\text{Ir}$, for a set of early $3d$ and $4d$ transition metals. They focus on physical properties such as elastic moduli and sound velocities and are able to identify trends between the different metals, relate their calculations to experimental data, and correlate them to details of the electronic structures of the compounds.

In Reference [12], Peng et al. survey a large set of possible point defects in an exemplary III–V semiconductor, InAs. These calculations necessitate the use of large supercells of the host material crystal structure, and the authors consider a wide range of possible local charge states for the different defects. How to treat such charged point defects in a fully periodic framework remains a point of interest to the community, and the present work contributes to the body of work from first-principles calculations in this area.

In summary, this Special Issue highlights several of the frontiers of first-principles calculations in crystals: the prediction of crystal structures of materials, which remains the foundation to determine any and all of their properties; treating symmetry-breaking events such as defect formation or doping, which can significantly change materials' properties; calculating collective atomic or electronic excitations, which requires perturbative approaches that relegate the standard DFT calculation to a small first step; and developing new and improved ways to capture exchange-correlation effects in many-electron systems. The present papers show that impressive progress has been made on all these frontiers to allow truly predictive first-principles studies of crystalline materials and their properties.

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