Discovering materials with first-principles computational methods

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Predicting the arrangement of atoms in materials is of fundamental importance for the discovery and design of new materials. The discovery and development of stronger, cheaper, lighter, etc., functional materials can help to extend the steady progress of technology to which we have become accustomed, and to enable future technologies. It is increasingly being recognised that computational modelling can play a key role in this enterprise via searching for structures. The great challenge of computational materials discovery is that exploring the potential energy surface of a material (the "structure space") is fundamentally combinatorial in nature, and there is no hope of a complete enumeration of the energy minima which represent stable and metastable structures.

Only fully quantum mechanical calculations suffice to deliver the accuracy required for the wide range of inter-atomic bonding that may be encountered during the searches. First-principles density functional theory (DFT) methods offer a high-level quantum mechanical description of the electronic structure at a cost that is affordable for the many thousands of structures that must be considered in the course of a reliable search.

In recent years there has been an explosion of activity aimed at combining structure searching with DFT methods, supported by the increasing availability of computing resources and the stability and efficiency of modern DFT codes. Early first-principles searches for crystal structures were performed for small unit cells by Schön and Jansen [1] and methods based on, for example, "Evolutionary Algorithms" [2, 3, 4], "Swarm Intelligence" [5], "Basin Hopping" [6], and "Minima Hopping" [7] have been used. We introduced the simple and highly effective "*Ab initio* Random Structure Searching" (AIRSS) method [8]. These methods derive from ideas about global optimization developed within the computational mathematics community. There is, however, no consensus on the most efficient algorithms for finding low-energy structures using first-principles DFT methods.

Modern DFT codes are highly optimised for relaxing structures to a local minimum in the energy. A search typically starts from a set of structures with controlled degrees and types of randomness. Very bad structures can be eliminated during the optimisation, and methods for jumping out of local minima are often employed. The success of a particular search depends much more on the details of how it is performed than the general type of searching algorithm used. The basic operations performed on the structures during the searches in the different methods are all rather similar. The initial structures should be carefully prepared by, for example, controlling the initial atomic separations, placing molecular units within the simulation cell rather than individual atoms, or constraining the symmetry (based on the idea that low energy structures normally have symmetry).

It is now possible to search for the structures of bulk crystals, nanoclusters, crystalline surfaces, interfaces, point defects, etc, using these methods. We don't even demand to know the precise chemical composition, the identities of the elements present is often enough, as the stable structures can be predicted for different chemical compositions.

Searching can lead to the discovery of new compounds and new types of inter-atomic bonding. Various examples of the success of structure searches using first-principles methods are described in Refs. [9] and [10]. Searching with first-principles DFT methods has met with many successes, and only a very few of them can be mentioned here.

(1) Very recently the prediction from AIRSS [11] that at high pressures ammonia decomposes into NH_4^+ and NH_2^- ions has been verified experimentally [12].

(2) AIRSS was used to determine the structure of the high pressure phase III of hydrogen, which has been sought for over 20 years [13]. The most promising models for the recently discovered phase IV of hydrogen emerged from AIRSS calculations [13].

(3) The USPEX evolutionary code [2] was used to predict "transparent dense sodium" at high pressures, with a double-hexagonal-close-packed structure, which was confirmed by experiment [14].

(4) USPEX was used to identify stoichiometries of stable sodium chlorides [15].

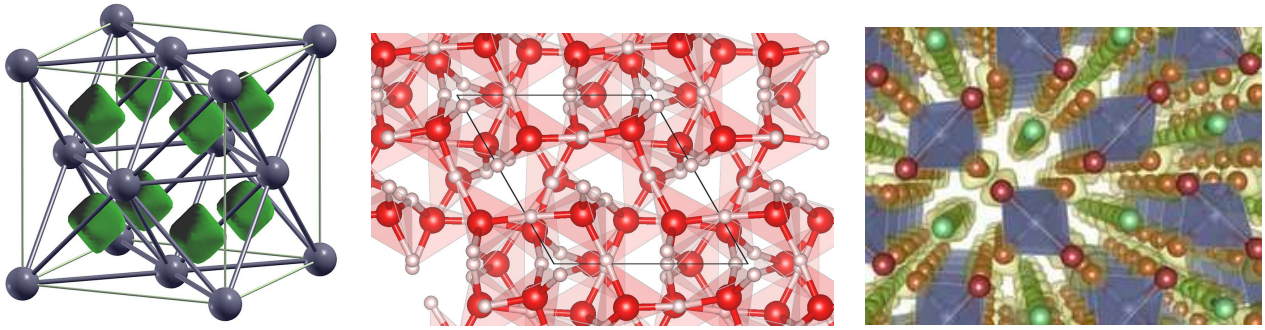

Figure 1: It was thought that structures at very high pressures would be simple, but AIRSS has predicted that even at at terapascal pressures they can be very interesting. Terapascal pressures are of interest in planetary science and are investigated at laboratories such as the National Ignition Facility (NIF) in the USA. Left: the fcc phase of carbon at 25 TPa is an electride in which some electrons occupy interstitial positions [Martinez-Canales *et al.*, Phys. Rev. Lett. 108, 045704 (2012)]. Centre: translucent tetrahedra are used to highlight 4-fold coordination in the $P3_12_1$ structure of water ice at 1 TPa, and at about 5 TPa the decomposition of water is predicted [Pickard *et al.*, Phys. Rev. Lett. 110, 245701 (2013)]. Right: the $P4/nbm$ "all-nitrogen metallic salt" structure at 2.5 TPa consists of partially charged $N_2^{\delta+}$ pairs and $N_5^{\delta-}$ tetrahedra [Sun *et al.*, Phys. Rev. Lett. 111, 175502 (2013)].

(5) Using an evolutionary search, Kolmogorov *et al.* predicted the first semiconducting metal boride and a superconducting iron boride [16].
(6) Zhu *et al.* [17] used the CALYPSO swarm intelligence method [18] and AIRSS to study reactions of xenon with iron and nickel, which suggested that xenon could be present in the Earth's inner core, providing a possible resolution of the "missing Xe paradox".
(7) Using the Minima-Hopping method, Amsler *et al.* [19] found a pure carbon sp^3-bonded material ("Z-carbon") that can explain features of "cold compressed graphite" found experimentally.
(8) The prediction of a semiconducting structure for dense lithium [20] using CALYPSO has been confirmed experimentally [21].

Another idea is to use experimental data to aid the searches. Even when a structure cannot be solved directly from diffraction data, information such as the size and shape of the unit cell or a set of likely space groups can often be obtained. Successful DFT searches aided by experimental data include, for example:
(1) A combination of high pressure experimental studies and evolutionary crystal structure prediction using the USPEX code led to the structural identification of a B_{28} form of elemental boron [22], which had been synthesized in 1965.
(2) AIRSS with experimental cell and space group constraints found the correct structure of phase II of ammonia dihydrate, which could not be determined from the neutron difraction data [23]. The experimental structure of semiconducting lithium, see (8) above, was solved using the same approach [21].

Using structures from databases is also helpful. Various databases of experimental structures are available, and it should now be possible to develop much larger databases using structures from DFT calculations.

Twenty-five years ago Nature editor John Maddox famously wrote that "One of the continuing scandals in the physical sciences is that it remains impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition" [24]. Scientists can now claim to have laid this scandal to rest. Applications of structure searching with first-principles methods appear almost limitless, and they are certain to play a major role in materials modelling.

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