Computer modeling in materials chemistry*

C. R. A. Catlow

The Royal Institution of Great Britain, London W1S 4BS, UK

Abstract: This short article concerns the application of computer modeling techniques to the growing field of materials chemistry, where modeling techniques are widely used in an increasingly predictive manner. The article focuses on modeling at the atomic and molecular level.

Keywords: Computer modeling; materials chemistry; interatomic potentials; electronic structure methods; crystal structure prediction; surface structures; interface structures.

INTRODUCTION

During the last 20 years, computer modeling techniques have had substantial impact on almost all areas of science and technology. This short article concerns their applications to the growing field of materials chemistry, where modeling techniques are widely used in an increasingly predictive manner. We will focus on modeling at the atomic and molecular level, although we recognize the importance of atomistic modeling making links to modeling at larger lengths and time scales.

As the field has been extensively reviewed in recent years by the present author and others, the account here is very brief. The reader will find detailed accounts of both techniques and applications in references [1–4].

SCOPE

Materials chemistry is concerned with the synthesis and characterization of materials with specific chemical and physical functionalities. It relates to areas of major technological importance including catalysis, sensors, and new energy technologies. It increasingly focuses on the design and understanding of materials at the atomic level, where atomistic modeling techniques make a vital contribution. The range of applicability of these techniques is now very large and includes modeling (and increasingly prediction) of the following:

- structures of both crystalline and amorphous solids
- surface structure and crystal morphologies
- molecular sorption and diffusion on surfaces and within microporous materials
- structures and properties of both point and extended defects
- mechanical properties of materials
- nanocluster structures
- fundamental processes relating to materials synthesis
- reactivity both on and within solids

This list is not exhaustive, but it includes many of the most topical areas of current activity. Examples of recent applications will be summarized later.

METHODOLOGIES

Modeling in materials chemistry uses the full range of tools available to the computational chemist and physicist. These comprise two broad categories of technique:

Methods based on interatomic potentials, where we do not attempt to solve the Schrödinger equation for the system, but use a potential which expresses the potential energy of the system, $V(r_A...r_N)$ as a function of the nuclear coordinates $(r_A...r_N)$ (or some combination of these). The potentials themselves may be derived from an electronic structure method or from empirical or semi-empirical procedures. More detailed discussions are available in references [1–4] and in the older literature (e.g., ref. [5]).

Potential models may be implemented in several different types of simulation procedure, of which the most important are:

Energy minimization, which is conceptually the simplest procedure and involves locating the minimum energy (or free energy) structure of the material simulated. The method is simple and robust, but is limited in several respects, including the omission of any explicit representation of thermal motions and perhaps most fundamentally the impossibility of ever guaranteeing that the minimum identified is the "global" rather than a local minimum. Approaches to ameliorate the local minimum problem include the use of simulated annealing (SA) and genetic algorithm (GA) methods; and careful use of these techniques may give a high degree of confidence that the global minimum has been located, but there can never be a guarantee. SA and GA methods, in conjunction with energy minimization, are, however, being used increasingly on structure predictions as discussed in further detail below.

Monte Carlo methods, which are essentially techniques of computational statistical mechanics and involve the generation of a representative set of configurations of the system simulated from which ensemble averages may be calculated. Detailed discussions are available in references [6,7].

Molecular dynamics is potentially the richest of the simulation techniques as it yields explicit dynamic information as well as structural data. The method is, again, conceptually simple; essentially, it consists of a numerical iterative solution of the classical equations of motion of the system simulated, using a specified time step, which is successively applied and after which velocities and coordinates are updated. The main limitation of the method is that using currently available computer power, it is rarely possible to explore "real times" of greater than 10–100 ns (although these time scales are constantly lengthening owing to growth in computer performance). This limitation means that, for example, when applying the techniques to solid-state diffusion, only systems with high diffusion coefficients (like the so-called fast ion conductors) can be effectively modeled. The method has, however, been very widely and successfully applied in materials modeling, as discussed in references [1–4].

For many of the systems of importance in current materials chemistry, including "hard solids" (e.g., aluminosilicates and oxides) and "soft solids" (e.g., polymers and molecular crystals), high-quality interatomic potentials are available; for many problems concerning structural and dynamical properties of materials they are the natural and appropriate techniques. They are, however, limited as they cannot, of course, be used to model any properties that depend explicitly on electronic structure; although some potential models have been developed that can model bond-breaking and -making, studies of reactivity are generally beyond the scope of such methods, which require recourse to the techniques discussed below.

Electronic structure methods, by definition, attempt to solve the Schrödinger equation at some level of approximation. There are now two broad classes of widely used methodologies; first, **Hartree–Fock** (HF) methods that have been developed largely in the molecular quantum chemistry community, but which have also been widely and successfully applied to solids; secondly, **density functional theory** (DFT), which rests on the pioneering work of Kohn and Sham [8,9] and which has been

extensively applied in condensed matter and increasingly in molecular studies. DFT methods tend to scale with system size better than HF techniques and have become increasingly popular as the field has moved increasingly toward applications to large complex systems. However, both HF and DFT techniques have a continuing role in modeling studies of materials.

Electronic structure techniques can be applied to molecules or clusters, to periodic systems, and to "embedded" clusters. The latter techniques, which have a long history, involve treating a local state, e.g., a defect or the active site of a catalyst at a high quantum mechanical level, with a more approximate (usually interatomic potential) based treatment of the surrounding lattice. A good recent account of these techniques is given in reference [10].

APPLICATIONS

The range of applications is now very extensive. Here, we list a number of recent highlights from the work of the author and colleagues that illustrate the range and scope of the field.

- *Crystal structure prediction*, in which SA and GA methods or topological modeling are combined with electron microscopy (EM), have enjoyed notable success in recent years. Examples include the work of Woodley et al. on oxide materials [11] and of Foster, Bell et al. on microporous materials [12].
- *Modeling of surface and interface structures*, where complex surface structures can now be modeled, as in the recent work of Whitmore et al. on ZnO [13] and where there are increasing capabilities for modeling complex interfaces, as in the recent work of de Leeuw et al. on silica/apatite interfaces [14].
- *Elucidation of complex defect structure*, as in the work of Braithwaite et al. on H-containing defect in mantle minerals [15].
- *Design of organic templates* for hydrothermal synthesis of microporous materials employing the *de novo* design methods pioneered by Lewis, Willock et al. [16].
- *Elucidation of the mechanisms of catalytic reactions*, as in recent work on micro- and mesoporous titanosilicate, oxidation catalysts [17] and oxide, methanol synthesis catalysts [4,18].

FUTURE PROSPECTS

The field is developing rapidly, and its horizons widen with developments in technique, algorithms, and computer power. The emphasis is increasingly on prediction and design, and there is no doubt that computational techniques will play an even more prominent role in future developments in materials chemistry.

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