

J-CAMD 080

Computer modelling: Future directions

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Received 21 June 1989

Accepted 10 October 1989

Key words: Simulation; Potentials; Interfaces; Biomolecules; Diffusion

SUMMARY

Recent developments in computing and in the theory of simulation have extended greatly the successes of the modelling of ionic crystals pioneered by Mott and Littleton. This has changed the way in which computer experiments are brought to bear on an increasing range of solid-state phenomena. Yet applied science creates new demands, both in the form of new types of system and in terms of the complexity and subtlety of what is studied. The author's brief survey looks at some of the successes and gaps from interfaces and catalysts to neurotransmitters and from superconductors to slags.

SUCCESS IN MODELLING: IONIC SOLIDS

The seminal paper of Mott and Littleton, now fifty years old, showed how simple defects in alkali halides could be modelled accurately. This was achieved by systematic approximations which recognised the roles of short-range repulsion and of electronic and ionic polarisation. It was for the same alkali halide systems that a more extensive range of defect studies was developed in the 1960s and 1970s, partly as excellent test systems for techniques, and partly as tests of ideas about potentials. Modelling, in the sense of almost all of this meeting, uses the concept of interatomic potentials for at least part of the solution to a problem, a part which can be critical.

Within this scope, the part of modelling which ignores electrons explicitly (but builds them into potentials) has had a surprising range of successes. These have been reviewed elsewhere [1], and include (i) predictions of stable phases, including those at extreme conditions, as in shock waves, (ii) predictions of defect energies (formation energies, motion energies, binding energies), (iii) predictions of defect vibrational behaviour, including entropies (so free energies can be obtained), (iv) predictions of absolute diffusion rates (both for quantum and classical diffusion [2]), and even (v) estimates of some energies for which the electron is an essential component, as in charge transfer or in small polaron behaviour (for references see Ref. 3). The last group of calculations are practical solely because a dominant energy is that of polarisation, and so obtainable by

simpler calculations. What is particularly impressive overall is the accuracy achieved (i.e. agreement with unambiguous quantitative experimental data) by relatively simple methods. This, in effect, confirms the value of the shell model as a general description and as a framework for both a priori and empirical parameterisation.

WHAT MATERIALS PROBLEMS REMAIN?

The list in the former section may suggest that all is in hand. Yet there are striking gaps. Despite much recent progress (and this is a very fast-moving field; see e.g. Ref. 4 for a recent example), neither metals nor semiconductors have simple algorithms of comparable accuracy. Nor have computer methods – despite dramatic developments – reached the stage where large biomolecules can be handled with useful predictive accuracy. We may characterise the gaps by two observations. First, we may ask what new materials have emerged in the last few years, and whether we can model them? A list might include:

- Superionic conductors (Li_3N ; RbA_4I_5 ; β -alumina; ZrO_2)
- High dielectric constant resonators ($\text{Ba}_2\text{Ti}_9\text{O}_{20}$)
- Superconductors: High field (PbMo_6S_8)
 - Magnetic (SmRh_4B_4)
 - Heavy fermion systems (CeCu_2Si_2 , UBe_{13})
 - Thin films of technological quality (NbN , Nb_3Sn)
 - Oxide superconductors, both CuO-based and Cu-free
- Intercalation compounds (based on C_nK or Li_xTiS_2)
- Hydrogen-storage systems ($\text{LaNi}_5\text{:H}$)
- Mixed valence compounds (SmS)
- Large coercive force magnets ($\text{Fe}_{14}\text{Nd}_2\text{B}$)
- Semimagnetic semiconductors (EuO , $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$)
- Spin glasses
- Charge density waves (NbSe_3)
- Organic charge transfer conductors (TTF-TCNQ)
- Polymeric conductors (polyacetylene, etc.).

In this long list, there is still only a handful of systems that can be modelled in the sense that reliable quantitative predictions are practical and have been demonstrated. The second question concerns expectations: Superionics are exactly the sort of system we might claim we can model. Yet can one point to a case where a better superionic was made because of modelling? This question – which cannot be ignored – is answered in part by observing that it is the framework which modelling provides, plus the estimates from modelling which ensure a realistic perspective, which enable better superionics to be developed. As noted later for oxide superconductors, what modelling offers at least is a reference calculation, where the limits are partly (perhaps primarily) from the difficulties of preparation methods.

MODELLING DIFFUSION: QUANTUM AND CLASSICAL DIFFUSION

Since this is discussed elsewhere in the meeting, I shall merely make some remarks on recent calculations [2]. First, in favourable cases classical diffusion can be predicted consistently and accurately by both molecular dynamics and by Vineyard theory. The results are in excellent accord with experiment where the experiments can be made cleanly. Examination of the theory shows, amongst other things, why prefactors can be larger than on the common 'approach frequency' arguments and how prefactors and activation energies can be related through rules such as the Meyer–Neldel rule. Secondly, in favourable cases, quantum diffusion can be predicted successfully by either quantum molecular dynamics (where what is predicted is the analogue of a saddle-point occurrence probability) or by explicit calculation of quantum jump probabilities. Such predictions are very sensitive to chosen interatomic potentials, and some issues of interpretation remain. Thirdly, in special cases the issue of potentials can be avoided by combining molecular dynamics with direct treatment of the electrons. This has been done for H in Si [5]; in such cases the atomic dynamics is classical, but the electrons are treated quantum mechanically. Fourthly, it is not difficult to identify cases where the atomic dynamics can be done quantum mechanically, especially if there is only a single quantum particle. One approach is to treat the quantum particle like a new type of electron, and to use the standard variational approaches of Hartree–Fock methods, suitably modified. This would be analogous to the treatment of electrons and holes in complex defects [6]. Suitable cases for analysis might be H-associated defects in silicon, where both the temperature range of interest and my initial analysis suggest quantum effects will be important.

MODELLING SUPERCONDUCTORS

This area is the subject of an extended description at this meeting. My remarks therefore cover only two specific points. First, there are now several papers which have used methods for ionic insulators in the context of superconductors, which must surely be ideal non-insulators. How can this be justified? Secondly, how can one hope to do useful modelling of these superconductors? Here one can exploit the idea of a *reference calculation*. The oxide superconductors resemble closely the ionic oxide ceramics in many respects. Indeed, the two types can be particularly similar above T_c in the regime in which processing is done. A close look at the various terms in the energy as a function of ionic positions confirms that (for several key results at least) one might expect predictions for an ionic model (the 'reference crystal') to correspond to what is observed for a real superconductor. This idea has been used by several groups, though their assumptions are not always explicit. The 'reference crystal' concept allows one to separate out those features which depend on the ionic radii, on the factors which tend to encourage anion-like and cation-like behaviour, and other such features, from those features which are specifically dependent on the unique superconducting behaviour.

INTERFACES

One major success of the modelling of ionic crystals has been the understanding of grain boundary structure and of surface phenomena such as segregation. A second area, that of metal/oxide interfaces, has also made significant progress: the main factors involved (especially the im-

age terms in the total energy) have been identified, their implications analysed. Codes to exploit these ideas are now near to completion, and will find application in several areas of microelectronics (e.g. radiation-enhanced adhesion, electrostatic bonding, and controllable adhesion), in coating technology (e.g. oxide film spalling, brazes, contacting ionic conductors) and in catalyst optimisation by influencing the morphology of supported metal catalysts [7]. Another key area – that of the aqueous/oxide interface – is understood only at a much lower level, and will surely attract attention.

WHERE IS THE CHEMISTRY?

When one uses interatomic potentials, these are a substitute for chemistry; all the details of the electronic wavefunction are removed. Yet there is no doubt that interatomic forces depend strongly on electronic state. This is especially so for defects, though even for highly-excited solids there may be profound effects. What is left out when simple potentials or molecular mechanics methods are used? How can one couple in the electronic degrees of freedom?

In the late 1960s and early 1970s a number of approaches were tried. These were mainly designed to handle only a small number of electrons in detail, i.e. they mixed interatomic potentials and the Schrödinger equation in some way. There were exceptions to this, but mainly in cases where a potential was implicit (e.g. when there is a weak pseudopotential one may not have to derive the effective interatomic potential explicitly to find the relaxed geometry). Approaches to defect problems have been generalised greatly, including methods which combine the best self-consistent methods with a proper treatment of long-range distortion and polarisation.

More recently, Car and Parrinello [8] have introduced a simultaneous treatment of atomic dynamics and of all valence electrons. This exploits several ideas, namely (i) the use of local density functional theory to give total energies, (ii) the realisation that the coefficients in the plane wave expansion of the density can be treated as dynamical variables in much the same way as the particle coordinates, and (iii) the use of quenched molecular dynamics to obtain minimum energy configurations (dynamics without quenching can also be done, and has been extremely successful [5]). This method has encouraged many related methods, notably because it does not require the user to identify the symmetry in advance.

There are several variants of the Car–Parrinello method; indeed, there were simple attempts with rather similar features (the use of quenched molecular dynamics; the combined electronic and lattice minimisation) in the 1960s and 1970s, but at a far less powerful level. However, there are also approaches which use neither the local density functional approach (which is a problem for excited states) nor the plane wave basis (which is not helpful for some systems). In particular (see the next section) there are some very direct approaches which allow one to exploit a more favourable LCAO basis set. Other workers too have suggested floating Gaussians (also quite an old concept) would be extremely effective.

SPECIAL ORGANICS: CONDUCTING POLYMERS AND BIOMOLECULES

Here it is helpful to give an example. A new approach [9] combines a well-established semi-empirical method (CNDO in this case, though INDO and MINDO could be used, and would be needed for hydrated and some other systems) with molecular dynamics. This is therefore a Har-

tree-Fock-based method (although CNDO and similar schemes can be derived systematically from local density functional theory too [10]) with a limited LCAO basis. Simple calculations can be done on a personal computer. Specific examples of calculations showing the power of the approach are these:

(a) *Conducting polymers.* The polymer area includes conductors whose conductivity is close to that of copper, some of the very best insulators, and semiconductors. Here, in the important case of *trans*-polyacetylene, most of the work on the solitons, which carry the current, has been done with a simple model (SSH) due to Su, Schrieffer and Heeger [11]. This has been very fruitful, but has several weaknesses. The new code [12] avoids many of the weaknesses, whilst agreeing very well in several areas (like the qualitative variation of dimerisation across the soliton; the quantitative result is fitted in the SSH model but predicted by quantum chemistry here). One new prediction concerns the soliton velocity. This can be measured directly using the molecular dynamics option, with self-consistency maintained at each stage. In fact, since fields can be applied to the

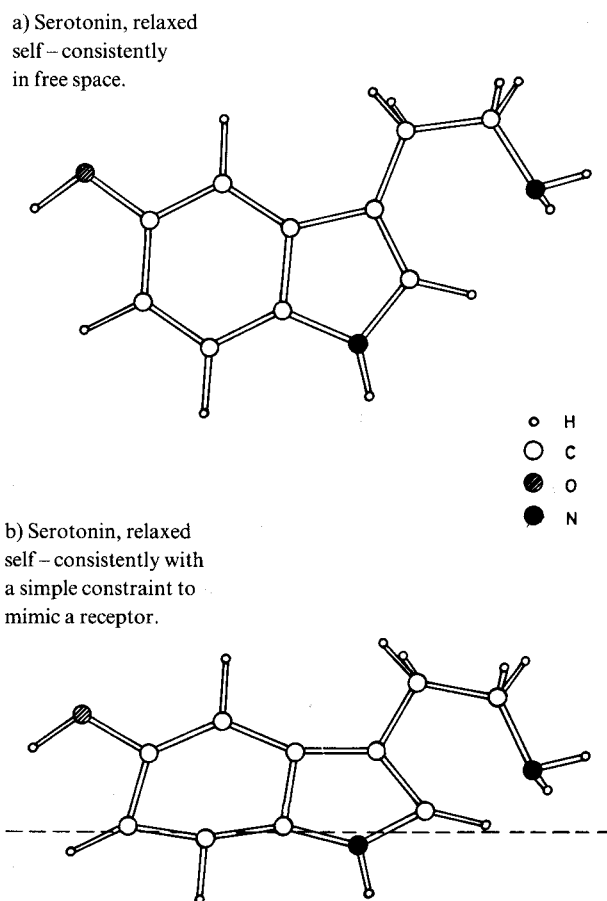


Fig. 1. The serotonin molecule, with its electronic structure and geometry optimised self-consistently. (a) shows the free molecule; (b) shows the molecule distorted into a new optimised geometry in the presence of an external potential which mimics a simple receptor.

carriers (or to the atoms) in the new code, the soliton mobility can be obtained by computer experiment. Further, the image terms (needed when looking at electrode effects) can also be included to examine metal/organic contacts.

(b) *Biomolecules*. The example here is serotonin, a molecule related to LSD and which takes part in the control of sleep and sexual activity. It has low symmetry – indeed, almost all previous calculations use a greatly simplified geometry. One key question is how this molecule interacts with a receptor; here most discussions use a ‘jigsaw’ description, where a neurotransmitter and a receptor interact in a purely geometrical way. Our calculations [12] go beyond this in several respects. First, the geometry optimisation can be done *with a model of the receptor in place*, so one does not merely look at a free space geometry and compare with a hypothetical receptor. An example is shown in the figure, where the receptor here is merely an attractive plane (more complicated forms are easily included) which clearly distorts the shape. Secondly, a comparison of the ground (singlet) state with an excited state (the lowest triplet) shows that excitation leads to a geometry change and to charge transfer, so that the molecule will surely show some level of ionic polarisability. This means that localised charges in the receptor can provide selectivity, not only the geometric matching usually discussed.

OTHER FUTURE DEVELOPMENTS?

There are three themes which should be noted here. First, what are the difficult topics, the areas where technical challenges are critical? I would note four as examples:

- (i) Highly non-stoichiometric systems;
- (ii) Complex liquids, by which I mean slags and related silicate melts and especially aqueous systems, including interfaces with electrolytes;
- (iii) Behaviour near phase transitions;
- (iv) Behaviour at high temperatures and pressures, between the regions accessed by static methods and yet where molecular dynamics may be inefficient.

In all these areas, there are central concepts which need to be clarified. There are, of course, still problems relating to technical tools – e.g. how one locates a saddle point for, say, an enzymal process, where the saddle point is far from obvious from symmetry.

The second theme concerns how the modelling will be used and its role in technological problems. The atomistic part often needs to be linked to classical physics in applied area, for instance with the diffusion equation in oxidation problems, or with mechanical (stress development) codes in coatings studies. More complex situations arise too, e.g. when one may wish to exploit predictions to help to texture the grain structure of an oxide superconductor.

The third theme concerns the developments in materials science which should be foreseen. No one can speak confidently here, but two areas which do spring to mind. Firstly there is *nanotechnology*, including methods of lithography and the relative importance of different processes which become important when only a few diffusive jumps are needed to cover the scale lengths involved. Secondly, the interface between biotechnology and condensed matter studies is sure to grow (for example for monitoring metabolic phenomena and responses), together with those analogous areas in which both organic and inorganic components are used in microelectronics.

ACKNOWLEDGEMENT

This work was supported in part by the Underlying Programme of long term research of the UKAEA.

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