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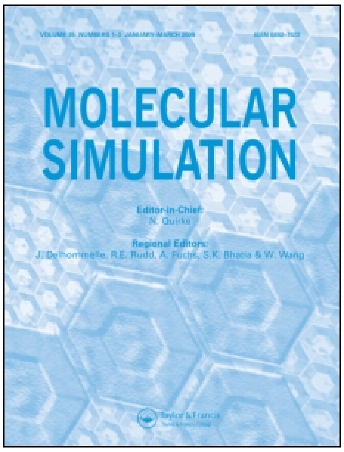

Molecular Simulation

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Guest Editorial

A. H. Harker; R. W. Grimes

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GUEST EDITORIAL

This issue of *Molecular Simulation* contains papers presented at a meeting on *The Practical Calculation of Interionic Potentials in Solids* held at the University of Keele on April 3rd and 4th 1989, under the sponsorship of the Science and Engineering Research Council's Collaborative Computational Project Number 5. The aim of the meeting was to review the strengths and weaknesses of the available methods for computing inter-ionic potentials, and to compare *ab initio* methods with empirical fitting procedures. Other points which were highlighted for special attention were the adequacy of two-body potentials; the influence of the crystalline environment on the ions; the importance of relativistic effects; and the transferability of potentials between systems.

Throughout the meeting, there was an emphasis on the application of the potentials, and a recognition of the limitations of empirical fitting procedures, which cannot be expected to yield potentials which are valid for extreme conditions or for defect or diffusion saddle-point problems (see the paper by Harding). The meeting revealed a degree of convergence between empirical and theoretical methods: for complex minerals Parker suggested modifications to potentials to account for coordination number and Madelung potential, which paralleled the effect of environment terms discussed by Grimes, Pyper and Fowler. With potentials which include such features, transferability is increased.

The extension beyond two-body forces figured in many papers (Parker, Leslie, Morton-Blake, Vessal, Jackson, Janssen). In developing empirical potentials for a single system, it becomes necessary to reduce the number of free parameters if one is to avoid overfitting. In this respect, neither *ab initio* calculation nor fitting procedures are entirely satisfactory. Both determine the two-body term externally and fix some or all of its parameters as part of the *n*-body potential. More research is also needed into the best functional forms to adopt for these interactions.

Of the *ab initio* techniques discussed, the electron-gas theory (Allan) and molecular orbital method (Grimes, Fowler, Harker, Janssen) were fairly familiar, the Relativistic Integrals Program (Pyper) and spin-coupled theory (Cooper) less so. Some of the differences between these approaches were not discussed – in particular, the differences between self-consistent and frozen ion schemes. It is clear that for complicated systems (Janssen) it is hard to analyse the results in a way which allows the transfer of parameters between systems. One particularly interesting point is that electron-gas models, when compared with spin-coupled theory, prove to have the correct functional form, but require numerical parameters which differ from those of standard theories. Relativistic effects cannot, it seems, be included merely by using fixed ionic charge densities computed relativistically in otherwise non-relativistic calculations. For dispersive interaction energies one requires accurate ionic polarisabilities (Fowler) which can be used in van der Waals terms, with recognition (Pyper) of the modifications needed at shorter ranges. There was some discussion of the possibility that electron gas approaches might be extended to deal with dispersive interactions.

Although there was some enthusiasm at the meeting for extending the theoretical approaches to deal with open-shell systems and magnetic terms, there are obviously still difficulties with the present schemes. If the practitioners of the several calculation methods were to derive *ab initio* potentials and compute, say, a defect formation energy or an activation energy for diffusion, then even in an archetypal ionic crystal there would be a wide spread of results. It is hoped that the papers presented here will lead to fruitful studies of the reasons for such discrepancies, and thereby lead to advances in this important field.

The guest editors are grateful to the editorial board for this opportunity to air their prejudices, and to those who attended the meeting at Keele thereby making it a success and these proceedings possible.

This issue of *Molecular Simulation* contains the first part of the papers presented at the meeting. The remainder will be published in a future issue of *Molecular Simulation*.

A.H. Harker - Harwell
R.W. Grimes - Keele