

Review of CCP5 Polarisability Meeting

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A meeting on the use of polarisability for describing systems involving cooperative interactions was held recently at Birkbeck College, University of London. This conference was the second in a series organised by the SRC's Collaborative Computing Project Five (CCP5), which is concerned with computational aspects of molecular dynamics and Monte Carlo simulation techniques. The aim of the meeting was to review the systems for which it has been found necessary to include cooperative effects and to compare the various methods used to assess the non-pair-additive contribution.

The use of atomic polarisability to account for non-pair-additive effects was wide ranging from such dense crystals as Uranium oxide to that of water in biological systems. The need for the inclusion of quite complicated polarisation effects was shown by both D. Frankel (Amsterdam) and P. Madden (Cambridge) in their interpretation of collision induced effects in light scattering spectra.

The relative importance of non-pair-additive terms was shown by J. Murrell (Sussex) who found that the three-body energy terms in quantum mechanical calculations of alkali halides were significant compared with the two-body terms. J. Quinn (Birkbeck) presented data from liquid water simulations showing that although the four-body energies were small, the three-body terms contributed to approximately 10% of the total energy. Although this latter fraction of 10% would appear to be significant and difficult to ignore, the four-body terms were an order of magnitude smaller and hence not so essential to an accurate simulation.

In calculating the energy of formation and migration of defects in solids, C.R.A. Catlow (University College, London) needed to account for multibody interactions as the rigid ion models failed to reproduce satisfactorily experimental energies. Both the use of the shell model and a

modification of the rigid ion model to reproduce the known dielectric constant lead to a much closer agreement of theory with experiment. M. Dixon (Oxford) also emphasised the use of the shell model in simulations of molten salts. Although the physical validity of this well-known model was criticised, it does lead to good agreement with known energies whereas the point polarisable ion model leads to a polarisation catastrophe in these dense ionic systems.

Specific algorithms for the inclusion of polarisability were described by H. Berensden (Gronigen) and P. Barnes (Birkbeck College, London). Both speakers have developed models for liquid water in which the need to take into account the cooperative nature of the hydrogen bond is important. Berensden uses a system of point charges which change in value due to the potential acting upon them from all other charges in the liquid. Barnes uses a self-consistent interactive procedure in which the dipole moments of each water molecule is updated due to the electropole field of all surrounding molecules.

The meeting ended with several topics of more general interest for molecular dynamics and Monte Carlo simulations. D. Beveridge (Hunter College, N.Y.) showed data from extensive simulations on liquid water in which convergence of some thermodynamic quantities - especially the specific heat - did not occur until well beyond the usually acceptable number of MC configurations. The rate of convergence was considerably increased by the use of force bias and preferential sampling techniques although at the expense of extra computation. M. Mezei (H. College, N.Y.) and P. Claveire (Paris) showed the importance of establishing that the multipole expansion (often used to describe the electronic configuration of a molecule) does actually converge for the system being studied.

Recent computational improvements have been made through the use of vector processors (like the CRAY at DL) to decrease the time of simulations which involve cooperative effects so that they become comparable with the simpler effective pairwise potentials. Increases in computational speed by factors of three to ten over the CDC 7600 have been found by both Berensden and Barnes by vectorisation of their algorithms. The versatility of computer graphics for displaying complex three-dimensional

surfaces was seen in a demonstration by Quinn (Birkbeck College).

This meeting underlines the usefulness of the SRC's collaborative computing projects in that a group of scientists all using very computer intensive simulation techniques were able to compare and discuss the various methods available for the best method of simulating 'reality' in the most efficient manner.