

# HOW TO DERIVE THE INTERATOMIC POTENTIALS NEEDED FOR SIMULATION STUDIES

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## **Conference Organisers**

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## **ABSTRACTS OF ORAL PRESENTATIONS**

### *Ab initio* databases for testing empirical potentials

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A subjective view has always to be taken of the nature of the interatomic interactions for the purpose of constructing interatomic potentials so that a specific potential will embody particular forms of interactions such as two-, three- and higher-body interactions or many-body interactions. The strengths of these interactions are determined by fitting to the available experimental data. In many cases, such experimental data is extremely limited and may have only marginal relevance to the atomic environments modelled in the simulation. Hence, the accuracy of the resulting interatomic potential in the regions of phase space to be investigated is normally not known. Since one of the common difficulties associated with constructing interatomic potentials is the lack of a significant amount of reliable experimental data that can be used to parametrise the potentials, the use of *ab initio* methods to provide accurate energies and interatomic forces for any arrangement of atoms can obviously make a significant contribution to the process of constructing potentials by providing data in those regions of phase space which are most important for the processes to be studied. Several strategies have been adopted for using *ab initio* data in parametrising interatomic potentials. *Ab initio* molecular dynamics simulations provide enormous datasets for

fitting interatomic potentials <sup>[1]</sup> but it is far from clear that fitting to such data for, say, a liquid will produce a potential that is accurate for a surface. Perhaps the more relevant, and demanding, question is whether a single interatomic potential *is* suitable for both the bulk and the surface. In our approach <sup>[2,3]</sup> we have generated a database of energies for 183 configurations of aluminium atoms with coordination numbers between 0 and 12. The database covers a range of interatomic separations and dimensionalities of structures. The size of the database is of significance because it allows the process of parametrising an interatomic potential and testing the accuracy of the resulting potential to be separated. This step is crucial in order to avoid the problem of overfitting a potential to the dataset, which is liable to produce a potential which is not accurate for atomic configurations outside the original dataset.

We have considered the ability of two- and three-body potentials and of many-body (glue model) potentials to accurately reproduce the energies of our database. We find that interatomic potentials with two- and three-body terms are totally incapable of describing the variation of energy over the whole range of coordination number, though they may work reasonably well over a small range. In contrast, glue models describe the trends over the whole range of coordination number extremely well. However, glue models still show significant errors for individual structures and, hence, they may give incorrect predictions for specific physical properties.

[1] F. Ercolessi and J.B. Adams, to be published in *Europhys Lett* (1994)

[2] I.J. Robertson, M.C. Payne and V. Heine, *Europhys Lett* **15** , 301 (1991)

[3] I.J. Robertson, V. Heine and M.C. Payne, *Phys. Rev. Lett.* **70** , 1944 (1993)

### **A modern valence bond approach for interionic potentials**

David.L. Cooper

Department of Chemistry, University of Liverpool

An attractive approach to intermolecular forces is to build the total wavefunction for a weakly-bound molecular complex from those of the unperturbed interacting fragments. A modern valence bond strategy is described which treats properly the overlap between the fragments whilst avoiding basis set superposition error. Recent results are presented for LiH..He. Analogous methodology has been employed to calculate two-body interionic potentials. Preliminary results are presented for binary oxides, chlorides and fluorides of alkali- and alkaline-earth metals. Factors discussed include the stabilisation of anions in a suitable Madelung potential, lattice symmetry, electron correlation in the fragments, and compression effects due to nearest neighbours.

### **Bond order potentials for covalent systems**

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An angularly-dependent many-atom expansion has recently been derived for the bond energy within the Tight Binding model for electronic structure. It accounts properly for directional bonding in covalent materials. The background theory and essential concepts are presented. The method has been successfully applied to *sp*-valent systems, *d*-valent transition metals and refractory carbides. In particular, for silicon, structural energy differences, elastic constants, surface reconstruction, the Jahn-Teller distortion at a vacancy, defect formation energies, the structure of the liquid and small clusters have all been modelled.

The Bond Order Potential is compared with recent density matrix method <sup>[1]</sup>. The two methods are found to be comparable for semiconducting systems, though the Bond Order Potential is much more rapidly convergent for conducting systems.

[1] Li, X-P., Nunes, R.W. and Vanderbilt, D. *Phys. Rev. B* **47** 10891 (1993)

### **Anisotropic atom-atom potentials for molecules**

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The forces between polyatomic molecules are traditionally represented by the isotropic atom-atom potential model. However, the implicit assumption that the atoms interact as if they were spherical is a poor approximation for some elements. This paper outlines some of the progress being made in developing anisotropic atom-atom potentials, which can represent the effects of lone pair and  $\pi$  electron density on intermolecular interactions. It is difficult to determine the form of an atom's anisotropy empirically, and so it has to be derived from the molecular charge distribution, using recently developed theories of intermolecular forces. This can be done for each major contribution to the intermolecular potential for small polyatomics, resulting in more accurate intermolecular potentials. For organic molecules, at the moment, only the electrostatic contribution can be routinely described in this way, through a distributed multipole analysis. However, computational studies using such an accurate electrostatic model, in conjunction with simple approximations for the other contributions, have been useful for understanding the structures of van der Waals complexes, biochemical interactions and molecular crystal structures.

The development of new computer codes is gradually allowing anisotropic atom-atom potentials to be used routinely for an increasing range of types of simulation. Nevertheless, it will often be desirable, and adequate, to approximate an accurate potential by a simpler isotropic site-site form, with additional sites representing the anisotropic features. Assuming the isotropic atom-atom potential, without careful consideration of the distribution of charge in the molecule, can lead to problems in deriving quantitatively adequate potentials for many molecules, and can even lead to conceptual problems.

### **Realistic description of many-body polarisation effects in simulations of ionic systems**

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In order to represent the many-body aspects of polarisation interactions in ionic systems we have developed molecular dynamics algorithms based upon the Car-Parrinello strategy, in which distortions of the electronic structure of an ion due to interionic interactions are represented in a simplified way. Additional degrees of freedom which represent this structure are added to the ionic coordinates and the equations of motion extended accordingly, so that these variables are updated to their self-consistent, adiabatic values as the ions move, without the need for explicit energy minimisation <sup>[1]</sup>. The representation of the induced moments is not constrained by a particular model of the interionic interactions, as in the standard Shell Model. Short-range corrections to the asymptotic induction and dispersion terms are parametrised on the basis of *ab initio* electronic structure calculations.

The polarisable ion model accounts, *inter alia*, for the fact that MX<sub>2</sub> systems (where M is a group II or IIB metal) crystallise into *layered* structures, for large radius ratios <sup>[2]</sup>. It also reproduces distinctive features of short- and intermediate-range order in MX<sub>2</sub> melts, which have been detected in neutron scattering experiments, but eluded explanation <sup>[3,4]</sup>. The distinctive role played by the induction effects in pushing highly polarisable anions into asymmetric sites is also detected in a range of oxides. It seems that this simple extension of the ionic model accounts for many properties which have been regarded as ‘covalent’. Besides simple dipole polarisation, recent extensions of the method allow a representation of induced quadrupoles and of the fact that some ions, like the oxide ion, change their effective radius in response to changes in their environment.

[1] M. Wilson and P.A. Madden *J. Phys. Condens. Matt.*, **5**, 2687 (1993)

[2] M. Wilson and P.A. Madden *J. Phys. Condens. Matt.* **6**, 159 (1994)

[3] M. Wilson and P.A. Madden *J. Phys. Condens. Matt.* **6**, A151 (1994)

[4] M. Wilson and P.A. Madden *Phys. Rev. Lett.* **72**, 3033 (1994)

### Derivation and properties of force related atomic multipoles

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“Force related” procedures refer to the use of atomic polar tensors (atp) and related quantities for predicting intermolecular electrostatic interactions. The parameters consist of atomic charges, multipoles, and charge-flux parameters obtained from quantum calculations of electrostatic properties. The derivation of parameters in this way provides a number of advantages over earlier procedures:

- (1) the parameters produce both interaction forces and energies simultaneously; accurate forces are of especial importance in molecular dynamics simulations or in optimising intermolecular geometries,
- (2) the derivation gives both multipoles and charge flux, the latter needed to reproduce the directional dependence of electrostatic forces about molecules and dependence of charges on molecular geometry,
- (3) they generally give accurate electrostatic potentials around molecules,
- (4) they are uniquely derivable from well-defined quantum observables, such as the atp,
- (5) the atomic multipoles reproduce the molecular multipoles exactly within the computational method employed, and
- (6) they correctly reproduce the asymptotic behaviour of the intermolecular interactions at large separations.

In this paper the general mathematical properties of force related multipoles, as well as charge flux, will be reviewed. The recently developed method for computing these parameters for molecules of arbitrary symmetry will be outlined. The computed values of the resulting multipoles for some simple molecules such as water and formamide may be compared directly to those predicted by other methods. For pairs of molecules the interaction energies retaining successively higher order terms in the multipole expansion are presented. The same comparison may be performed with the multipole expansions defined by other approaches. Finally the properties of molecular crystals (lattice vector lengths and angles, and lattice energies) are given for differing types of multipole expansions. We focus particularly on the formamide crystal. The results show that the force related formulation provides a general, consistent, and accurate procedure for modelling intermolecular electrostatic interactions.

### **Towards a general strategy for global interatomic potentials for elemental solids, surfaces and clusters**

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Many problems of molecules and solids can be tackled within the Born-Oppenheimer approximation in which structure and dynamics are determined by a potential which depends on the internuclear distances. There is a hierarchy of assumptions that can be made about these potentials ranging from the simplest (optimistic), which is that the potential is pair-additive, to the most complicated (pessimistic), that no useful analytical function can be found. Between these two

extremes many functions have been investigated and the one we have been studying for elemental solids is a 2-body plus 3-body potential with simple analytical functions for each term.

We have been mainly concerned with the following question. If we fit with high accuracy the properties of a solid, taking more than one solid phase if these are known, will we obtain potentials which are useful for studying surfaces and clusters? We recognise that in this approach our cluster potentials are not electronic state specific, so for small clusters in particular they will have limited use.

The parameters in our potentials reproduce the following solid state data: cohesive energy, lattice constant, phonon frequencies, elastic constants and vacancy formation energy. In addition the potential must reproduce the correct order of cohesive energies of different solid structures where these are known, or, at the least, make the fitted structure the most stable.

Examples will be given to show the outcome of this procedure for simple metals and transition metals and for group 4 solids.

This work has been carried out in the School of Chemistry and Molecular Sciences at the University of Sussex with the help of several postgraduates and postdoctoral workers.

I acknowledge particularly the work of Dr R.L. Johnston , currently a Royal Society University Research Fellow.

### **Interionic potentials for oxides**

J.H. Harding

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Oxides are important materials. They range from the classical refractory ceramics such as MgO and Al<sub>2</sub>O<sub>3</sub> to complex mineral silicates. So diverse a range of materials has been tackled by a wide range of potential models. It is not proposed to review them all here. Rather, the objective of the talk is to discuss what criteria one might look for in a potential and what special features there are for oxides. Both empirical and calculated potentials will be considered. Questions of the meaning of ionicity will be reviewed and the modelling of oxide ions in the crystalline environment will be discussed .

### **The computer modelling of oxide surfaces**

M.J. Gillan , I. Manassidis and S. Pugh

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The talk will present the results of recent *ab initio* calculations on the surfaces of a variety of oxide materials. The results allow a critical examination of the predictions of interatomic potential models for the energetics and structure of oxide surfaces. The comparisons to be presented provide strong support for the reliability of current models.

## Future directions in empirical potential derivation

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Recent developments in the field of empirical potential derivation for ionic materials will be reviewed, with particular reference to the fitting of shell models. Examples of both “simultaneous” and “relaxed” fitting, as implemented in the program GULP will be given, indicating their merits over previous fitting methods.

Improved reliability of empirical potentials may be achieved by fitting many structures concurrently, rather than sequentially. The quality of a purely empirical oxygen-oxygen potential derived in this way will be examined for the energy of an oxygen interstitial in alumina, as compared with existing potentials and *ab initio* calculation. Compatibility of bulk and gas phase data for empirical fitting within the ionic model will also be addressed.

To date the majority of empirical potentials have been derived for application in athermal simulations. However, with the increasing use of free energy methods and molecular dynamics the future lies in fitting at finite temperatures. Results will be presented for the alkaline earth hydroxides in which potentials have been derived under the experimental conditions. The implications of lattice dynamics for theoretical calculations of interatomic potentials will be examined in this context.

I would like to thank Drs. Tim Bush and Andrew Rohl for their contribution in many of the examples that will be presented, and to thank the Royal Society for funding.

## ABSTRACTS OF POSTER PRESENTATIONS

### Polarisation effects on amino-acid and peptide conformation

D.A. Mac Dónaill and D.A. Morton-Blake

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Notwithstanding recent advances in the simulation of polarisable environments <sup>[1,2]</sup>, in vacuo models are still widely employed in simulations involving supposedly “inert” solvents or environments <sup>[e.g.3]</sup>. In the calculations reported here a modified CNDO/2 method <sup>[4]</sup> was used to calculate the conformational energy surface of zwitterionic glycine and of the glycyl dipeptide in a simulated polarisable environment. The results were compared with in vacuo simulations.

While the calculated global minimum for the in vacuo glycine zwitterion corresponds to an eclipsed conformation, the allowance of even a small degree of environmental polarisability inverts

the relative stabilities of the staggered and eclipsed forms. For the dipeptide, the C5 minimum resists small increases from zero polarisability, while the C7 minimum shifts to a nearby, related position. The latter result may explain apparently contradictory structural inferences drawn from i.r. and n.m.r. spectroscopy.

The calculations indicate that in vacuo models can be unreliable, even for supposedly “inert” media, and thus short-range potentials fitted to such calculations are also unreliable. Environmental polarisability should be explicitly considered in the calculation of short-range potentials.

[1] S. Ten-no, F. Hirata and S. Koto, *Chem. Phys. Lett.*, **214**, 391 (1993).

[2] S. Ten-no, F. Hirata and S. Koto, *J. Chem. Phys.*, **100**, 7443 (1994).

[3] C. Aleman and J. Percy, *Int. J. Pept. Prot. Res.*, **43**, 258 (1994).

[4] R. Constanciel and O. Tapia: *Theoret. Chim. Acta* **48**, 75 (1978).

### **The search for global potential energy functions for metallic elements**

Jason E. Hearn, Catherine R. Griffiths and Roy L. Johnston

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This poster presents some applications of the Murrell-Mottram type of 2-plus-3-body potential to metallic elements. For calcium, it has proven possible to derive a potential which gives a good fit to the phonon frequencies, elastic constants and vacancy energies of both the low temperature fcc and the high temperature bcc allotropes. This potential is currently being used to study the fcc-bcc phase transition of Ca. For sodium, which adopts the bcc structure at ambient temperature and pressure, a potential, derived by fitting lattice dynamical properties of the solid, has been used to predict the structures and relative stabilities of small clusters  $(\text{Na})_n$ , where  $n \leq 20$ . In agreement with other studies of sodium cluster growth icosahedral-based structures are generally found to be the most stable. The M+M potential has also been shown to give good results for transition metals such as iron (both the bcc and fcc forms) and Cu, Ag, Au. This is not surprising, since many-body forces are expected to be more significant for transition metals than for the simple Group 1 and 2 metals.

### **Empirical tight-binding parameters for silicon-boron, with applications**

Paul B. Rasband, Andrew P. Horsfield and Paulette Clancy

Department of Chemical Engineering, Cornell University, Ithaca, New York

Empirical Tight-Binding, when used with the recent developments in distance-scaling functions, is a very powerful tool for the study of point defects in semiconducting matter. Accurate information on relaxed structures, formation, binding, and migration energies and entropies, valence band structure, and more can be obtained through such potentials.

Our group has used the Goodwin-Skinner-Pettifor functional forms with Si-B ETB parameters to study the interaction between boron and silicon point defects, emphasising questions which deal with boron diffusion during semiconductor processing. The parameters were fitted to *ab initio* (LDA pseudopotential) data obtained using the Corning code. The structure of the occupied bands for zinc blende SiB are reproduced very well; the root-mean-square error for the 56 fitted band energies is 0.16eV. The three parameters involved with the repulsive potential have been fitted directly to formation energies for boron-defect pairs.

In addition to a description of the parameter fitting and evaluation, we will present results of migration energy studies for vacancy and interstitial mediated diffusion paths.

### **Empirical tight-binding parameters for silicon-boron, with application to boron-defect pairs in crystalline silicon**

Paul B. Rasband , Andrew P. Horsfield and Paulette Clancy

School of Chemical Engineering, Cornell University, Ithaca, NY

A set of Empirical Tight-Binding parameters for use with well-established functional forms has been produced to describe the interactions between Si and B atoms, complete with a quantum mechanical treatment of valence electrons. The functional forms adopted to describe the distance scaling of orbital interactions and ion-ion repulsion have been used successfully by other authors to treat Si-Si and C-C interactions. Here Si-B parameters are presented which have been chosen to reproduce ground-state band structures and total energies obtained from *ab initio* calculations. While the parameter fitting was done for tetrahedral configurations, the functions used have proven to be very flexible in the case of Si-Si interactions, suggesting that these Si-B parameters are transferable to other structures. In addition to a discussion regarding the parameter development, this work also presents some examples of the application of the Si-B ETB model in studying defect-dopant pair formation. The ultimate objective of this ETB parameter development is to provide a means of accurately predicting formation and migration energies and entropies of neutral and charged species involved in the diffusion of boron during the production of semiconductor devices.

### **Dynamics of adsorbed ammonia molecules on titanium dioxide (rutile) surfaces**

Dietmar Paschek and Alfons Geiger

Department of Physical Chemistry, University of Dortmund, Germany

The dynamics of adsorbed ammonia molecules on titanium dioxide (rutile) surfaces has been studied by molecular dynamics simulations in conjunction with  $^1H$ - and  $^2H$ -NMR measurements.

The  $^2H$ -spectra show an amazing dependence of the signal shape on the degree of coverage. At low coverage Pake-type solid state powder spectra occur. If the coverage becomes larger than

about 0.75 monolayers, they change to orientationally averaged singlets, characteristic of a liquid-like mobility of the adsorbed molecules.

The results of our molecular dynamics simulations are consistent with these NMR measurements and give a simple explanation for the observed mobility increase. The  $\langle 110 \rangle$  surface consists of lines of  $\text{Ti}^{4+}$  adsorption sites, separated by linear walls of oxygen atoms. Because of the strong lateral repulsive interaction between ammonia molecules adsorbed on neighbouring sites, the lateral and orientational mobility increases drastically in the coverage range between 0.6 and 0.8 monolayers. In parallel, the distribution functions characterising the positions and orientations of the adsorbed molecules change strongly.

Our simulations serve as a practical tool for obtaining more detailed microscopic information from NMR data than would be possible by using conventional model calculations.

### **Non-additive intermolecular forces in molecular systems: what can we learn from the spectroscopy of van der Waals trimers?**

Andreas Ernesti and Jeremy M. Hutson

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Over the last few years, very accurate pair potentials have been developed for prototype systems such as Ar-HF and Ar-HCl by fitting to extensive high-resolution microwave, far-infrared and mid-infrared spectra of van der Waals dimers. These are now the best-characterised of all potential energy surfaces involving molecules (as opposed to atoms), and have been used very successfully to calculate collisional properties such as pressure broadening cross sections and molecular beam scattering results.

In order for accurate pair potentials to be useful in simulations, we need to understand many-body forces as well. Although there has been a great deal of work on non-additive forces in purely atomic systems, it has proved very difficult to find sources of information on non-additivity in systems containing molecules. Now, for the first time, the spectroscopy of van der Waals complexes is starting to provide such information.

Several experimental groups (Gutowsky, Saykally, Nesbitt) have now been able to measure high-resolution microwave, far-infrared and mid-infrared spectra of trimers such as  $\text{Ar}_2 - \text{HCl}$  and  $\text{Ar}_2 - \text{HF}$ . Since all the pair potentials are very well known, the spectroscopic results can be compared with calculations based on pairwise-additive potentials. We have developed the computational methods needed to do this. We have shown that calculations using trimer potentials based on pairwise additivity give significant discrepancy with experiment (typically 2 to 3  $\text{cm}^{-1}$  error in the bending frequencies of the trimers). These discrepancies are about a factor of 5 larger than can be attributed to uncertainties in the pair potentials. We have investigated various sources of non-additive forces, including anisotropic triple-dipole dispersion forces and exchange overlap forces. We have concluded that the most important contribution to the changes in spectroscopic

properties comes from a new type of non-additive force, which does not exist in purely atomic systems: this is the electrostatic interaction between the permanent multipoles of the HX molecule and an exchange quadrupole that develops on Ar<sub>2</sub> at short range. This is a very general effect: in any system containing molecules, short-range exchange and overlap effects modify the charge distributions of the monomers, and thus modify the electrostatic interaction with a third molecule.

In future work, we hope to be able to *determine* details of the non-additive forces from the trimer spectra.

### **The effect of defects on the stability of heteroepitaxial ceramic interfaces using pair potentials**

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Static simulation techniques have been used to examine the defect chemistry in the heteroepitaxial ceramic interfaces BaO(100)/MgO(100) and CeO<sub>2</sub>(111) $\alpha$  – Al<sub>2</sub>O<sub>3</sub>(001). Reduced ion density at the interface is seen to enhance the stability of the BaO(100)/MgO(100) interface. Interfacing CeO<sub>2</sub> with  $\alpha$  – Al<sub>2</sub>O<sub>3</sub> promotes the migration of oxygen from the interfacial plane to the surface, a process that may be of importance in catalytic reactions.

### **Simulation of lithium insertion into metal oxides**

Andrew W.J. Smith, M.G.B. Drew, R.J. Hobson and V. Padyaychy

Department of Chemistry, University of Reading

Computer simulation techniques are an increasingly useful tool for various problems associated with solid state chemistry. They are most useful when used in conjunction with experimental techniques such as X-ray and neutron diffraction. However, they can also be helpful to investigate processes where there is little experimental information available, such as diffusion processes in solids.

Initially work was conducted to reproduce known crystal structures using a simple force field. The traditional Born model was used consisting of the electrostatic and non-bonded terms. The 6-12 Lennard-Jones potential (LJ) was used for the non-bonded terms containing the parameters  $\epsilon$  and  $R$ . However, for accurate reproduction of crystal data an in-house program, PARAM was developed which optimises the  $R$  parameter in the LJ potential. This has enabled more complicated structures to be studied by static relaxation methods and by Monte Carlo techniques. Starting

values for  $\epsilon$  and  $R$  were taken from the Universal Force Field (UFF) [1]. A function  $F^2$  is defined as the sum of the square of the partial derivatives of the potential energy along the axes  $a$ ,  $b$  and  $c$ . During parametrisation  $F^2$  is minimised with respect to the  $R$  parameters. The Simplex method was used to perform the minimisation.

This work has provided parameters suitable to model diffusion of lithium in some metal oxide host structures such as  $\text{TiO}_2$  and  $\text{ReO}_3$  and these results will be presented.

This work has been supported by the Defence Research Agency.

[1] A.K. Rappe et al., *J. Am. Chem. Soc.* **114**, 10024-10035 (1992)

### **Modelling of inorganic systems**

Malcolm D. Shakesby and Michael G.B. Drew

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Potentials are being developed for rigid model and shell model calculations of a range of simple metal oxides using a variety of parametrisation procedures. We are particularly concerned with the interaction of gases within the oxides and therefore have concentrated upon development of potentials to evaluate the interaction of the gases within the solid. These potentials allow calculation of the preferred binding sites of the adsorbates in the system and their mobility through the system.

Of particular interest is the interaction of hydrogen with these solids and the problems encountered with deriving parameters for  $\text{H}_2$ ,  $\text{H}^+$ ,  $\text{H}^-$  and  $\text{OH}^-$  will be discussed. Many of the properties of absorption in metal solids are due to defects in the solid and the effect of such defects upon the calculations will be described.

### **A periodic Hartree-Fock treatment of $\text{VO}_2$ : derivation of interatomic potentials**

B. Slater and M.G.B. Drew

Department of Chemistry, University of Reading

We present central force potentials derived from an *ab initio* study of the metallic, rutile-type phase of  $\text{VO}_2$ . Relaxation of the unit cell at constant pressure reproduces the lattice constants to within 4%. These potentials have been used to study a first order semiconductor  $\rightarrow$  metallic phase transition which occurs at 340K. Below the transition temperature the regular rutile structure is significantly distorted, exhibiting alternate short and long metal-metal distances. We have performed Monte Carlo simulations using the derived potentials which are able to reproduce the subtle structural changes associated with this transition. Analysis of the configurations reveals that the phase transition is initially mediated by the oxygen anions.

### **Computational sorption studies of alkanes in zeolites**

Michael G.B. Drew and Paul M. Hobbs

Department of Chemistry, University of Reading

Alkane sorption in a pentasil zeolite has been studied through simulations. A series of alkanes, including methane, propane, n-butane, iso-butane and three hexane isomers, were studied in silicalite. Statistical mechanical principles have been employed to predict sorption equilibria at low occupancy. Henry's constants and isosteric heats of sorption were calculated, using the CERIOUS<sup>[1]</sup> software package from Molecular Simulations, through the evaluation of configurations with a Monte Carlo integration scheme. A range of Lennard-Jones parameters for carbon, hydrogen, silicon and oxygen was used. The effects of using united atoms in the alkane and of removing the silicon atoms from the zeolite were estimated. An optimised set of parameters was obtained by fitting to experimental data for n-hexane and was then subsequently used with other alkanes. The results were in good agreement with experimental values in the literature<sup>[2]</sup>.

[1] CERIOUS molecular modelling software for materials research from Molecular Simulations Inc. of Burlington, MA, and Cambridge UK.

[2] J.R. Hufton and R.P. Danner, *AIChE Journal* **39** (6), 945-961 (1993)

### **RMC with interatomic potentials: modelling the structure and dynamics of an amorphous system?**

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The Reverse Monte Carlo (RMC) method<sup>[1]</sup> has achieved significant success at modelling the structure of a range of disordered materials in recent years. One of the prime examples of this has been the simulation of experimental neutron diffraction, X-ray diffraction and EXAFS data simultaneously in the production of structural models of the four-component fast-ion conducting glass,  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ <sup>[2]</sup>. This study will show the progress currently being made in developing an *ab initio* determination of an interatomic potential from a final structural model created with RMC. The challenge to overcome and the potential benefits of this approach will be described.

[1] R.L. McGreevy and M.A. Howe (1992) *Ann. Rev. Mater. Sci.* **22**, 217.

[2] J.D. Wicks, L. Börjesson, G. Bushnell-Wye, W.S. Howells and R.L. McGreevy (1994) *Phys Rev Lett* in press.

### **Significance of higher order many-body interaction energy terms in water clusters and bulk water<sup>1</sup>**

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The magnitudes of the 2- through 6-body energy terms and their contribution to the interaction energy of small ring water clusters (n=2 to 6) are computed at the Hartree-Fock (HF) and second through fourth order many-body perturbation (MP2, MP4) levels of theory. Each water molecule in the ring acts both as a proton donor and a proton acceptor resulting in one hydrogen bond per water molecule. This fact increases the polarisation of each fragment due to its neighbours and enhances, accordingly, the total as well as the individual many-body interactions. We have found that 3-body terms have a significant contribution (as high as 30%) to the interaction energy of the larger clusters and that 4-body and higher order terms are negligible. Electron correlation accounts for a 10 to 20% increase in the individual 2-body terms and a much larger increase of 75% for the 3-body and 200% for the small 4-body terms. The MP4 results are found to differ only slightly (<20%) from the corresponding MP2 results.

Many-body energy terms higher than two are, however, less significant for configurations resembling bulk water which have, on the average, two hydrogen bonds per water molecule.

### **Deriving intermolecular potentials for predicting the crystal structures of polar molecules**

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Most successful work on crystal structure modelling and prediction has concentrated on the crystal structures of non polar molecules. Attempts to extend the isotropic atom-atom potential method to polar molecules, however, have met with only limited success. This can be attributed to the fact that for polar molecules, the electrostatic contribution to the intermolecular potential will dominate the lattice energy, particularly if hydrogen bonding occurs within the crystal.

The electrostatic contribution to the intermolecular potential can be accurately described using a theoretically rigorous distributed multipole model for the charge distribution, which describes the molecular charge distribution as a set of point multipoles, usually on every atomic site.

The ability of a distributed multipole model, together with literature isotropic atom-atom repulsion-dispersion potentials, to model the crystal structures of a diverse range of polar organic molecules is investigated. This potential provides surprisingly good structure predictions and thus provides a benchmark and starting point for further optimisation.

This poster describes improvements on this set of isotropic atom-atom repulsion-dispersion potentials by least squares fitting to a set of crystal structures and lattice energies.

### **Extracting and validating force fields for disordered polymeric materials from neutron scattering data**

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Many of the useful properties of polymeric materials ultimately depend on the connectivity and flexibility characters of the chain molecules. In general these features can be described in terms of 2, 3 and 4-body intramolecular potentials relating to bond stretching, valence angle bending and dihedral rotation respectively. For each of these contributions, the various force fields proposed to date depend on a number of “empirical” constants describing the detailed shape of the potential. These constants have been derived either from fits to spectroscopic and thermodynamic data or from *ab initio* calculations; in both cases the parameters are obtained on relatively simple model systems. The resulting force field expressions form the basis for the definition of the chain conformation in all theoretical predictions and atomistic modelling of polymer behaviour and properties. Although the assumption is made that these potentials work equally well for simple molecules and for systems as complex as polymers, such an assumption is not entirely justified and may seem somewhat arbitrary.

In this work we shall present a new approach that allows the determination of force field parameters from experimental neutron diffraction data obtained over a large  $Q$  range, through a tight coupling of computer modelling predictions with experimental neutron scattering results. The method is based on the generation of a model single chain through the assignment of analytical expressions for the force fields of interest and on the systematic variation of the parameters constituting these analytical expressions to minimise the difference between predicted and experimental diffraction patterns. Particular attention will be devoted to the torsional term, since this is the term responsible for the degree of flexibility of the chain. We will present the sensitivity and the potential of this analysis strategy in a few case studies, specifically chosen for the varying level of stiffness of the polymer chains under investigation.

### **Potential models for multi-component oxides: hexa-aluminates**

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The phase equilibria and crystal chemistry of multi-component hexa-aluminates shows a considerable variation as a function of composition. Our interest is in rationalising this variation through

an understanding of the structural stability as a function of stoichiometry and defect chemistry, which may be obtained from atomistic computer simulations. Our recent experiences in the use of interatomic potential models for the simulation of complex multi-component oxides are discussed with particular reference to alkaline earth hexa-aluminates,  $MAl_2O_19$  ( $M=Ca, Sr, Ba$ ). We have found that simply transferring parameters from models of binary oxides is not necessarily valid, and that the usual test of reproducing the experimental crystal structural parameters is not by itself sufficient. A re-examination of the potential model for  $SrAl_{12}O_{19}$  revealed the need to include a consideration of cation coordination, as had been found desirable in simulations of spinels. Furthermore, it is also found that when the consideration of cation coordination is limited within the spinel-structured blocks in the structure of hexa-aluminates as well as when an appropriate set of binary oxide potential models is transferred, the thermodynamic stabilities of the related complex compounds are correctly predicted.

### **The conformation of DNA containing chemically modified base pairs**

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N-nitroso compounds are known to chemically modify normal DNA bases and result in mutations which either are corrected by repair proteins or lead to misreading of the code and possibly carcinogenesis. Molecular dynamics simulations of normal oligonucleotide sequences are commonly used to study conformation and dynamics. In order to undertake simulations of the modified sequences, we have extended the AMBER force field to allow for the  $O^6$ -methyl- and  $O^6$ -ethyl-guanine bases.

Our simulations show that the AMBER force field produces stable oligonucleotide double helices over 2,400 picoseconds. The normal sequence behaves as expected with Watson-Crick hydrogen bonds between the base pairs. The modified sequences with ethylguanine-cytosine base pairs leads to local disruption of the base pair because of the chemical modification of the guanine base but all other base pairs retain their normal conformation. The resulting modified base pair has only two hydrogen bonds and adopts the so-called wobble conformation. The resulting structure is likely to be less stable than the normal hydrogen bonding pattern and is likely to be recognised as different by a repair protein.

### **Potentials for B-metal compounds: the stannates $MSnO_3$ ( $M=Ca,Sr,Ba$ ) and $SnO_2$**

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Reliable potentials for B-metal oxides and halides have been notoriously difficult to obtain. We report a consistent set of potentials for alkaline earth stannates and tin (IV) dioxide. Results are presented relating to structure, defect properties and redox behaviour.

### **Thermoelastic and dielectric properties of KCl and NaCl crystals in the quasiharmonic approximation: fully automatic approach**

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Detailed general expressions are derived for the 1st and 2nd order derivatives of the Helmholtz free energy of an arbitrary crystal with respect to both internal and external strains in the quasiharmonic approximation (QHA). This enables one to calculate a wide range of thermoelastic and dielectric properties of any non-primitive crystal for arbitrary temperature and general stress conditions by means of a single calculation since our final formulae contain just lattice summations similar to those used to study crystal phonon spectra and higher order elastic constants.

The pairwise potential energy of the crystal is taken from the theory of deformable dipoles by K.B.Tolpygo which includes the usual shell model as a special case. We prove by proper microscopic consideration that microscopic and macroscopic expressions for the elastic energy of any piezoelectric crystal coincide. The theory was implemented in a friendly computer code which fully exploits the crystal symmetry. Special attention is paid to the most efficient numerical realisation of the method.

Numerical results are presented for rock salts KCl and NaCl for which elastic and dielectric properties versus temperature and pressure were studied. The calculations clearly show that empirical pair potentials of Catlow et al are in reasonably good agreement with most of the zero-pressure data. However, these potentials must be revised if experimentally observed high-pressure properties of these crystals are to be reproduced. Our calculations in the vicinity of the melting point demonstrate that the transition is controlled only by the isothermal elastic constant  $C_{11}$ . It decreases so catastrophically rapidly with increase of temperature that it leads to an immediate violation of the stability condition  $C_{11} > C_{12}$  for isothermal elastic constants. In addition, we show that by means of the quasiharmonic approximation physically correct qualitative results could be expected much further than half of the melting temperature.

### **Parametrisation of empirical potentials in the presence of a distributed multipole electrostatic model**

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The commonly used Buckingham form for the repulsion-dispersion potential can be parameterized in terms of its well depth, minimum energy separation and a steepness parameter. This gives an easy framework for the computer modeller to think about the significance of each potential in a given atomistic problem. Although formally called a repulsion-dispersion potential, the real function of the parametrised potential in a model is to account for all the interactions not explicitly calculated. In this paper it is shown how explicit treatment of the electrostatic term in polar organic crystals allows a better parametrisation of the potential to be made. Potentials are fitted to a set of experimental structures and sublimation energies. Different potentials are compared by the net deviation from the X-ray structure on relaxation for the crystals fitted.

### **Pseudopotential for the excess electron in polar liquid**

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The methodology for building a pseudopotential between an excess electron and polar molecule in the electronic ground state is presented. The proposed form of the pseudopotential has four contributions:

$$V(r, R) = V_c + V_r + V_{ex} + V_p$$

The  $V_c$  term corresponds to the Coulomb potential,  $V_r$  term to repulsion according to the Pauli principle requiring the orthogonality of the wave function of the excess electron to all occupied orbitals of the molecule,  $V_{ex}$  term stands for exchange interaction whose origin lies in indistinguishability of the excess electron and molecular electrons. The last term  $V_p$  is the polarisation part of potential that results from polarisation effects due to excess electron charge.

The methodology is illustrated in a working example of the development of pseudopotential for the excess electron and methanol molecule. In this case the electrostatic part was approximated by a sum over partial charges located on sites of the molecule. The repulsion and exchange components were based on molecular electronic density while the polarisation part was proposed in a non-spherical form described by polarisation tensor. The electronic calculations were based on UHF *ab-initio* method with double-zeta (9s5p/4s) gaussian basis set.

### **Application of pseudopotentials for the path integral simulation of excess electron in methanol**

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The question of how the excess electron is bonded to molecules or atoms in a medium in which it solvates still remains unanswered. The computer simulation techniques that rely on fully atomic description of the solvent and fully quantum description for the excess electron are in the best position to answer all questions about nature and behaviour of the excess electron. Despite many difficulties and uncertainties inherently bound to these methods, the main reason why these methods did not result in a full model is a fact that they were applied to a very narrow range of solvents. Regarding the electron in non-polar media, only atomic noble gases were investigated, while in polar media the simulations were performed for water, ammonia and quite recently methanol. In this poster we report some results of our Path Integral simulations of excess electron in methanol. The simulations are based on the developed pseudopotential which describes the interaction between the excess electron and methanol molecule. Besides standard results of the simulation like the various radial distribution functions, we show the records that suggest that the electron in methanol is involved in a kind of bonding which fulfil the energetical as well as geometrical definition of the hydrogen bond. We conclude our contribution with the sketch of an investigation programme that should be undertaken to support or discard the hypothesis.

#### **Developments in the surface descriptions of silicates**

Paul Baram

School of Chemistry, University of Bath

#### **Derivation of empirical potential parameters for oxide ferroelectric perovskites**

Martin Exner

The Royal Institution, London

#### **Modelling phosphate biominerals**

Marina G. Taylor

Department of Zoology, University of Reading

#### **Use of diamond anvil data in the derivation of potentials**

John Stuart

Department of Chemistry, University College London

#### **Derivation of potentials for molecular ionic materials**

Peter Wilde <sup>1</sup> and Gillian B. Telfer <sup>2</sup>

<sup>1</sup> Department of Chemistry, University of Keele <sup>2</sup> Department of Chemistry, Strathclyde University

**On the determination of force field parameters using weak coupling to experimental data**

S.L. Njo

Department of Chemistry, Swiss Federal Institute, Zurich

**Computational studies of supported platinum catalysts - developing interatomic potentials from *ab initio* calculations on model platinum clusters**

P. Wolohan

Department of Chemistry, University of Reading

**Modelling the hydrogen peroxide-water system**

Matthias Stein

Department of Chemistry, Manchester University

**DMA derived electrostatic charges from density functional methods**

Peter Winn

Department of Chemistry, University of Essex

**Simulations of nitroimidazole bioreductive agents**

Jon Wright

Department of Chemistry, University of Essex