Computational Modelling of Inorganic Solids

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This report covers papers published in 2011 dealing with the application of computational techniques to inorganic solids. It deals mainly with continuous solids that are ionic in nature; work on metals and MOFs is excluded. Special attention is given to solids used in solid oxide fuel cells, iron-based superconductors, zeolites and systems of interest to the life and earth sciences. Relevant advances in computational methods are also covered.

Highlights

The first highlight deals with modelling the important aqueous calcium carbonate system. Knowledge of the growth of the polymorphs of calcium carbonate and the equilibria between carbonate ions and protonated forms (hydrogen carbonate and carbonic acid) aids our understanding of the formation of carbonate minerals, biominalisation (for example mollusc shells) and the formation of scale in hard water areas. Gale et al. have developed a new reactive force field which allows them to study this system in microsolvated and bulk water conditions. An interatomic potential approach is used as this enables longer timescales to be covered in molecular dynamics calculations and gives a better description of the interaction of water with the species than standard DFT. As an example of this work, Figure 1 shows the interaction of bulk water with the surface of calcite as determined through molecular dynamics. In addition the authors show that metastable carbonic acid diffuses to the surface of the water where the C=O group can occupy a hydrophobic environment. The results also lend validity to models that assume that the carbonate anion is involved in crystal growth even under conditions where it is not the dominant equilibrium species.

Computer screening for potentially useful molecules is well-established in drug research. A second highlight is a paper which applies a screening technique to the design of high performance piezoelectric materials. Armiento et al. have written scripts that automate the submission of batches of calculations on perovskites. The results are screened according to the following criteria:

1. The perovskite must be non-metallic and have a sufficiently large band gap to avoid current leakage when a potential is applied.
2. The energy differences between different distortions of the perovskite structure (tetragonal, rhombohedral and rotational) must be small <0.5 eV overall.
Fig. 1. An instantaneous configuration of the basal surface of calcite in contact with water taken from the molecular dynamics simulation of the interface as shown from two directions.

1 Introduction

As usual there are several special issues of journals relevant to this topic. The
October 2011 issue of Journal of Physics – Condensed Matter \(^5\) contains a Special Section on Computational Materials Science dedicated to Jürgen Hafner. The October 2011 issue of Physica Status Solidii B \(^4\) dedicated to Professor Manfred Fähnlie and covering the topic ‘Recent developments in magnetism and modern magnetic materials’ contains a number of computational papers. A special issue of Journal of Catalysis \(^5\) on ‘Molecular Approach to Heterogeneous Catalysis’ includes articles using a computational approach.

A review in Solid State Nuclear Magnetic Resonance \(^6\) covers the development and use of calculations of solid state NMR parameters.

Molecular quantum chemists have long been aware that standard quantum chemistry methods are not good at dealing with cases involving long bonds. The classic example is the difficulty in correctly predicting the ground state of \(H_2\) as it nears dissociation. Recently, solid state programs have begun to include a method DFT-D \(^7\)-\(^10\) for dealing with cases where van der Waals interactions are important. Interatomic potential terms, often based on the Lennard-Jones potential, are added to DFT calculations. In the literature surveyed here this has proved particularly useful for studying molecules in zeolites.

Simple oxides are still the subject of much research both as test cases for new methods and in investigating new aspects of their properties. Studies on hydroxides, halides and oxyhalides are included in the same section as oxides. Publications in this area include two interesting studies on oxyhydroxides, MOOH \(^11\),\(^12\). Much work has been done on F-doping of oxides and now work on N-doped solids is increasing. Some of these are included in the oxides section.

Calculations on chalcogenides are becoming more numerous and are also included.

The number of papers on cuprate superconductors is decreasing but iron-based superconductors remain of interest with the mechanism of superconductivity still not entirely understood.

An area still attracting a lot of interest is solids used, or of potential use, in fuel cells. This is an area where theory can play a major role in elucidating diffusion paths and mechanisms.

Finally, some examples of solid state calculations applied to problems in biology and geology including the first highlight and two papers on the diffusion of iron in the lower mantle are reported.

The total number of papers published is very large and the author apologises to those whose work I has been overlooked.

### 2 Methods

There have been a number of papers dealing with ways of improving calculations, new ways of analysing data, comparison of functionals and improved graphical interfaces.

Bridging the gap between atomic scale and macroscale modelling has been an active area of interest over the past few years. Volker et al.\(^13\) have suggested a method for linking atomic level calculations to a phase-field model. This model is applied to the ferroelectric materials \(\text{PbTiO}_3\) and \(\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3\). Another area that has attracted much interest for some years is the prediction of crystal structures. This is an important field in pharmaceuticals where obtaining the correct polymorph of a drug can be essential. Much of this work is concerned with organic molecules and not covered here, but some recent work on methods is notable. Lonie and Zurek\(^14\),\(^15\)
have written a program, XTALOPT, under GNU public licence for crystal structure prediction. Cai et al. discuss an improved model for creating computer models of amorphous solids using reverse Monte Carlo with the invariant environment refinement technique. Fitting partial pair-correlation functions rather than the total correlation improved the results.

Games consoles employ sophisticated high resolution graphics. To manipulate these efficiently they use highly parallel graphics-processing units (GPUs). GPUs also provide an efficient way to process large blocks of data in parallel and computational programs are now being written to take advantage of this ability. For example, Maintz et al. have proposed using graphics-processing units to speed up DFT calculations and have written a modification for VASP using this approach.

In DFT calculations, choice of functional can be an important factor in obtaining useful results. For example, LDA calculations are known to underestimate the band gap and can falsely predict solids to be metallic. A number of studies have compared pure DFT functionals with GGA + U and/or hybrid functionals. The consensus appears to be that + U or hybrid methods reproduce properties better than pure DFT functionals. This is especially true of strongly correlated systems, in particular compounds of transition metals. Amongst hybrid functionals, B3LYP often gives the best result. De La Pierre et al. have compared the functionals LDA, PBE, PBESOL, B3LYP, PBE0 and WC1LYP in CRYSTAL09 for calculations on forsterite (Mg$_2$SiO$_4$). They conclude that hybrid functionals perform better than LDA and GGA and that B3LYP performs better than the other hybrid functionals. Maschio et al. compare the performance of LDA, PBE, PBESOL, B3LYP and PBE0 in describing the infrared spectrum of spessartine (Mn$_3$Al$_2$Si$_3$O$_{12}$). Again they conclude that hybrids outperform LDA and GGA and that B3LYP is the best-performing hybrid functional. Chen et al. have compared GGA, GGA + U and PBE0 functionals for calculations on Co$_3$O$_4$. GGA underestimates the band gap and PBE0 overestimates it. Yu modifies the exchange functional of B3LYP to obtain better agreement with the band gaps of GaN and ZnO. Tran and Blaha report the implementation of screened hybrid functionals in the program WIEN2K. This method eliminates long range Hartree-Fock exchange which can cause problems by screening the HF exchange using the Yukawa potential. Compared to PBE0, the results with the screened potential YS-PBE0 were better for small band gap solids but worse for large band gap solids. This group also put forward an optimal; GGA functional for molecules and solids and consider the merits and limits of the modified Becke-Johnson, mBJ, exchange potential.

Grimme et al. discuss the effect of damping functions on calculations using DFT-D.

Having performed a DFT calculation, it is often important to analyse the results to obtain properties for comparison with experiment or gain insight into the reasons for a particular electronic or geometric structure. Yu et al. have put forward a method for solids containing defects in which the total energy of a supercell is decomposed into individual atomic contributions. They show for example that the effect of interstitial oxygen on Ti atoms in bulk Ti is confined to the first two shells around the O atom. Kozlowski and Plime have shown that an algorithm designed for the decomposition of electron density is also suitable for analysis of ELF (electron localisation function) and MEP (molecular electrostatic potential). ELF results for diamond and ZnS are given. Baranov and Kohout report implementation as part of DGRID of a method of obtaining localisation and delocalisation indices. Elk was
used to provide the wave functions. Otero-de-laRoza and Luana\textsuperscript{33} describe techniques developed for fitting energy against volume. Ghosh et al\textsuperscript{34} have used periodic DFT calculations with branch-following and bifurcation techniques to map paths on the DFT energy landscape as a function of applied load and consider this method has potential to provide insight into mechanisms driving structural phase transitions. Shelley et al\textsuperscript{35} have tackled electronic transport properties. Following DFT calculations, the ground state wave functions are transformed to localised (Wannier) functions. Short range Hamiltonians in this basis can be combined to form model Hamiltonians for $>10,000$ atoms which can then be used to calculate quantum conductance. The method has been implemented in Wannier90\textsuperscript{36}.

Björkman\textsuperscript{37} has written a program that will produce the geometrical set-up for a number of packages from information in CIF files. J-ICE\textsuperscript{38} is a free on-line GUI which visualises crystal structure using Jmol. The resulting structures can be saved in formats suitable for several programs and it is also possible to load output into J-ICE to view the structure produced in calculations.

3 Simple compounds

3.1. Oxides, Hydroxides, Hydrides and Halides

Hydroxides and halides are included here with oxides as this allows a discussion of studies dealing with both oxides and hydroxides and those involving halide-doped oxides and oxyhalides without having to split the results between two sections.

Starting with oxides, there are still new insights to be found from calculations on simple oxides. Dileep et al\textsuperscript{39} use DFT calculations to identify additional peaks in the pre-edge EELS structure of ZnO as O defect states in the band gap lying just below the conduction band. Han et al\textsuperscript{40} consider the effect of doping with Mg and Al on the band gap of ZnO (wurtzite). Magnetic properties of C-doped ZnO were calculated by Shi et al\textsuperscript{41}. Burbano et al\textsuperscript{42} present a new potential for use with CeO$_2$ for problems where even now ab initio calculations are not feasible. Hanken et al\textsuperscript{43} use DFT + U calculations to explore different cation and charge ordering in U$_{1-x}$Ce$_x$O$_2$. Nolan et al\textsuperscript{44} use the screened exchange hybrid functional HSE06 to look at the effect of C- and N-doping on the electronic structure of NiO. Zhukov et al\textsuperscript{45} have used a plane wave method to study the effect of doping anatase with N and either V or Na. They find impurity levels in the band gap but note that an increase in optical absorption only occurs above 3eV. Velikokhatnyi and Kumta\textsuperscript{46} have used VASP and the GGA DFT method to study the effect of fluorine-doping of SnO$_2$ and find an increase in the density of electronic states at the Fermi level with increase in fluoride concentration. It should be noted however that the calculations were pure DFT without an added U and as such overestimated the band gap. Allen et al\textsuperscript{47} find that in order to describe the structure of SnO correctly they need to include van der Waals corrections, based on an ionic model, in their DFT calculations, PBE-vdW. In SnO there is a lone pair on Sn which affects the geometry giving a layer structure. This method should be of use for other layered structures. Nazir et al\textsuperscript{48} use the PLAPW method to study BaCoO$_2$. They find that with an LSDA functional a ferromagnetic semimetallic state is predicted to have the lowest energy but with the addition of a +U term, the ground state is semiconducting and antiferromagnetic. The antiferromagnetic ordering chosen is that in which successive layers of Co ions have opposite spins.

Iron oxides and hydroxides are ubiquitous and much-studied, but still present
problems for the computational chemist. Guo and Hubbard\textsuperscript{11} used DFT + U in both a plane wave (VASP) and a locally confined atomic orbital (SIESTA) representation to study $\alpha$- and $\gamma$-Fe$_2$O$_3$, $\alpha$- and $\gamma$-FeOOH and Fe$_3$O$_4$. They find both approaches predict the correct energy ordering and magnetic states, but prefer the plane wave method for producing a phase diagram.

Demichelis et al\textsuperscript{12} have published a review of work on aluminium hydroxides over the last five years. Using the all-electron code CRYSTAL09, they show that hybrid DFT calculations using B3LYP can be used to investigate the relative energies and vibrational spectra of the known hydroxides, AlOOH and Al(OH)$_3$. After allowance for broadening of the vibrational peaks (particularly the OH stretch) in the experimental spectra, the calculated patterns of peaks are a reasonable fit. Location of the H atoms is a problem for XRD studies here, as in the iron hydroxides, and calculation can provide a suggested lowest energy position for H. The calculated structures of doyleite and nordstrandite are given in Figure 2.

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Corno et al\textsuperscript{50} look at hydrogen substitution by fluorine in LiBH$_4$ as a possible hydrogen storage material but find that their calculations predict a separation of F and H such that F ions prefer to substitute on the same ion rather than disperse through the solid. Zavorotynska et al\textsuperscript{51} have used DFT calculations to study vibrations of BH$_4^-$ in alkali metal borohydrides.

Morgan and Madden\textsuperscript{52} use molecular dynamics (MD) and a rigid ion potential to model defect behaviour in AgI. Wang et al\textsuperscript{53} have calculated the electronic structure and magnetism of chromium halides. They find that a +U term is necessary to correctly predict magnetic ordering in CrCl$_3$. Singh et al\textsuperscript{54} used GGA to study elastic properties of thallium halides, TICl and TIBr.

### 3.2. Chalcogenides

Calculations on chalcogenides are becoming more popular, perhaps because of increased computer power and/or because of the discovery of chalcogenide superconductors. Ben Nasr et al\textsuperscript{55} have studied the electronic structure and optical
properties of Sb$_2$S$_3$ using GGA. Romero et al$^{56}$ have calculated properties of CuGaS$_2$
and Kocak$^{57}$ et al properties of PrS, PrSe and PrTe. Zhou et al$^{58}$ report DFT
calculations using a GGA functional on the novel chalcogenidehalide Hg$_2$Cd$_2$S$_3$Br$_2$.
Liu et al$^{59}$ use CASTEP to determine the nature of the conduction and valence bands
in Ba$_4$In$_4$S$_{{19}}$, Ba$_4$In$_2$S$_8$ and Ba$_4$Ga$_2$S$_8$ and conclude that the S$_2^{2-}$ ions contribute
mainly to the top of the valence band and the bottom of the conduction band and hence these ions determine the band gap. Aguilera et al$^{60}$ compared GGA + U +
G$_0$W$_0$ to the many body perturbational GW approach in studying the band formed by
Ti substituting on In sites in MgIn$_2$S$_4$ and concluded that GGA + U +
G$_0$W$_0$ was justified when sufficient computer resource to run GW was not available. Ti forms a
fully-occupied band in the band gap. Without U, DFT calculations predicted a
metallic compound.

3.3. Other

Nitrides of Group 13 elements doped with transition metals to form dilute magnets
can be half-metallic. Such compounds are used for example in spin valves. Amin et
al$^{61}$ have studied Cr-doped AlN, GaN and InN and find that Al$_{0.75}$Cr$_{0.25}$N and
Ga$_{0.75}$Cr$_{0.25}$N are half metallic. Hao et al$^{62}$ have studied ZrC and ZrN at high
pressures using DFT. They find a pressure-induced transition from an NaCl-type
structure to a CsCl-type structure.

DFT calculations on actinide nitrides are an active field now that such
calculations are feasible and because of interest in these compounds for fast breeder
reactors. Bocharov et al$^{63}$ have modelled oxygen incorporation into UN, a
promising nuclear fuel that is degraded by the presence of oxygen impurities.

Derzsi et al$^{64}$ find that LDA + U performs better than GGA in reproducing the
unit cell constants of the unusual Ag(II) compound AgSO$_4$.

Calculations of NMR parameters can be useful in assigning spectra where there is
ambiguity in assignment from purely experimental results. Such calculations can
also be used to analyse contributions to chemical shifts and to aid in structure
determination. Castets et al$^{65}$ calculate NMR chemical shifts for LiFePO$_4$OH and
FePO$_4$.H$_2$O paying particular attention to the Fermi contact shifts arising from
interaction with Fe$^{3+}$. 0 K spin densities are obtained from VASP and (for values at
the nucleus) WIEN2k and then scaled using the experimental magnetic
susceptibility. Mali et al$^{66}$ investigated polymorphs of Li$_3$FeSiO$_4$ using Mössbauer
and NMR and analysed contributions to the $^6$Li chemical shifts using DFT/GIPAW
calculations. First principal calculations of NMR parameters are also used by
Pallister et al$^{67}$ to help in the signal assignment of the $^{17}$O spectrum of the
polymorphs of MgSO$_4$.

DFT calculations$^{68}$ on the novel tungstate compounds CeBiW$_2$O$_8$ and SmBiW$_2$O$_8$
indicate that these are indirect band gap materials.

Cerium ions are often used as an analogue for plutonium ions in studies
concerned with nuclear waste. Gilbert and Harding$^{69}$ use interatomic potential
calculations to explore the validity of this model for ions trapped in zirconolite,
CaZrTi$_2$O$_7$. They find that whereas Ce$^{4+}$ is partly reduced in zirconolite, this would
not be expected for Pu$^{4+}$.

Matar et al$^{70}$ predict that Na$_2$OsO$_4$ develops a magnetic moment when in the less
stable K$_2$NiF$_4$ phase whereas it is magnetically silent in the Ca$_3$IrO$_4$ phase.

4. Perovskites and spinels
Perovskites display a wide range of useful magnetic and electronic properties acting as superconductors, ferroelectrics etc. Many theoretical studies aim to explore these properties and search for these and possibly new properties in new solids with perovskite-type structures. Markkula et al. have studied the band structure and composition of MnVO$_3$ in order to understand the spin-spin coupling mechanisms that lead to the observed incommensurate spin ordering. Li et al. have studied electrical and magnetic properties of the perovskite structure BiCu$_3$Fe$_4$O$_{12}$ using GGA + U and including local orbitals. They compare the ferrimagnetic state with Cu and Fe ions interacting antiferromagnetically with each other but with ferromagnetic coupling between ions of the same type with several states in which Fe ions couple antiferromagnetically and Ce ions are decoupled. They conclude that in the ferrimagnetic state, charge is transferred from Fe to Cu via the O2p orbitals, giving Cu$^{2+}$ whereas in the antiferromagnetic states, Cu is present as Cu$^{3+}$. Trang et al. have studied the electronic and magnetic properties of CaMnO$_3$ in bulk, slab and nanocluster forms. Gong and Liu use the modified Becke-Johnson exchange potential and an LDA correlation functional to study LaMnO$_3$ and obtain improved results for the band gap over GGA. Ahmad et al. use hybrid DFT to study the stability of LaMnO$_3$ and that of the possible oxides formed from its decomposition - La$_2$O$_3$, MnO, Mn$_2$O$_3$, MnO$_2$ and Mn$_3$O$_4$. Ali et al. have studied the magnetic properties of PrCoO$_3$ and NdCoO$_3$.

Huang et al. have calculated properties of YAlO$_3$. Cherrad et al. use LDA calculations to obtain properties of Ca$_3$SnO, Ba$_3$SnO and Sr$_3$SnO hoping to inspire experimentalists to work on these compounds. Gheboubi et al. have calculated the properties of BiScO$_3$ using DFT. Gao et al. use GGA + U calculations to confirm a revised structure of the double perovskite, Sr$_3$InReO$_6$. A lowest energy structure of BaFeO$_2$F with fluoride ions arranged trans to each other in the octahedron around Fe and forming lines of F-Fe-F perpendicular in successive layers has been identified using hybrid DFT calculations.

Benedek et al. report calculations on the surface structure of LiMn$_2$O$_4$. Using GGA + U, they find the lowest energy surface to be Li-terminated (001). Illustrating the advances possible as computer power increases, their work includes molecular dynamics simulations to explore surface reconstruction. Ragavendran et al. also report DFT studies on surfaces of LiMn$_2$O$_4$. They concentrate on surfaces which are likely to be important for crystal growth and do not include (001) but agree in finding that surfaces with buried Mn are more stable. Jiang et al. have studied the electronic spectrum of MgAl$_2$O$_4$ containing oxygen vacancies. Shukla et al. use atomistic simulation to study MgAl$_2$O$_4$ with the inverse spinel structure. They find that cation ordering and volume changes affect the properties in opposite ways so that for up to 50% inversion, elastic properties are unchanged and that thermal conductivity is unchanged over the whole range of inversion. Rezende et al. use interatomic potential calculations to study doping by and subsequent reduction of rare earth ions in BaAl$_2$O$_4$. In a later paper this group consider the concentration dependence of rare earth doping in this aluminate.

Matar’s group have studied the ionic character of hydrogen in perovskite and K$_2$NiF$_4$ phases CsCaH$_2$, Cs$_2$CaH$_4$ and CsCa$_2$H$_4$ and used Ni substitution on the Mg sites to explore the ionic character of hydrogen in RbMgH$_3$.

5. Superconductors and multiferroics
Iron-based high Tc superconductors have again been of much interest, the mechanism of superconductivity being still a matter of debate. Sefat and Singh\textsuperscript{90} have written a short review of these materials including what is known of their magnetism and electronic structure. A number of theoretical papers on the iron-based and cuprate superconductors have been published in the Special Issue of Journal of Physics and Chemistry of Solids\textsuperscript{93} on Spectroscopies in Novel Superconductors. Harshman \textit{et al}.\textsuperscript{92} have analysed a range of high Tc superconductors and propose that the value of Tc is determined by the Coulomb interaction between layers and is independent of energy band dispersion or proximity to the Fermi level. Maiti \textit{et al}.\textsuperscript{97} compare s-wave and d-wave ordering in Fe-based superconductors and conclude that spin pairing in these materials is due to spin fluctuation exchange.

One approach to understanding these materials is to look at the electronic structure of known examples and closely-related solids. Such calculations in 2011 include those on EuFe\textsubscript{2}P\textsubscript{2},\textsuperscript{98} K\textsubscript{3}Fe\textsubscript{1.8}Se\textsubscript{2},\textsuperscript{99} KFe\textsubscript{2}Se\textsubscript{2}, KFe\textsubscript{2}Se\textsubscript{2} and KFe\textsubscript{2}Te\textsubscript{2},\textsuperscript{100} AFe\textsubscript{2}Se\textsubscript{2} (A = Cs, K, Rb, Tl),\textsuperscript{101} Ca\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{6}\textsubscript{y},\textsuperscript{102} La\textsubscript{2}O\textsubscript{3}Fe\textsubscript{2}Se\textsubscript{2} and La\textsubscript{2}O\textsubscript{3}Co\textsubscript{2}Se\textsubscript{2},\textsuperscript{103} LaFeAsO\textsubscript{1.06},\textsuperscript{104} transition metal-doped LaFeAsO\textsubscript{1.06},\textsuperscript{105} (Sr,Mg)\textsubscript{2}As\textsubscript{2},\textsuperscript{106} Fe\textsubscript{2}As\textsubscript{2}Sr\textsubscript{2}Mg\textsubscript{2}O\textsubscript{6} (where A is a Group 1 or Group 2 metal),\textsuperscript{103} Co\textsubscript{2}As\textsubscript{2}Sr\textsubscript{2}Sc\textsubscript{2}O\textsubscript{6} and Co\textsubscript{2}P\textsubscript{2}Sr\textsubscript{2}Sc\textsubscript{2}O\textsubscript{6},\textsuperscript{107} a\textsubscript{1-x}(FeAs)\textsubscript{x} (where A is a Group 1 or Group 2 metal).\textsuperscript{105, 106} Calculations on structurally related but iron-free superconductors have been reported by Shein \textit{et al}.\textsuperscript{108} (LiCu\textsubscript{2}P\textsubscript{2}) and Shein and Ivanovskii\textsuperscript{109} (SrPt\textsubscript{2}As\textsubscript{2}).

Evarestov \textit{et al}. present phonon calculations for SrTiO\textsubscript{3} and for BaTiO\textsubscript{3}, BaZrO\textsubscript{3} and BaHfO\textsubscript{3} and conclude that the hybrid functional PBE0 gives results closest to experiment for both plane wave and LCCO methods. Gao \textit{et al}.\textsuperscript{110} conclude that GGA/PW91 functionals and ultrasoft pseudopotentials describe the properties of BaTiO\textsubscript{3} well. Lv \textit{et al}.\textsuperscript{111} discuss the best method and pseudopotential for calculations on PbTiO\textsubscript{3} using CASTEP. Ganesh and Cohen\textsuperscript{112} predict a tetragonal ground state for PbCrO\textsubscript{3} from DFT + U calculations. Cr d orbital ordering is stabilised by the crystal field produced. In a search for lead-free ferroelectrics to replace materials such as PZT, Bennett \textit{et al}.\textsuperscript{113} use DFT calculations to investigate SnAl\textsubscript{6}O\textsubscript{3}N\textsubscript{0.5}O\textsubscript{1}. They predict that this material will be ferroelectric and possibly a good piezoelectric material. Jia \textit{et al}.\textsuperscript{114} investigated the pressure-induced spin transition in the potential multiferroic, BiCoO\textsubscript{3}. Ordering in multiferroic BaMn\textsubscript{2}O\textsubscript{4} has been investigated using GGA and GGA + U by Li \textit{et al}.\textsuperscript{115} They find that the solid contains two types of manganese ions with slightly different charges but with a large difference in the minority e\textsubscript{g} occupancy. This charge ordering leads to partial ferroelectric polarisation.

6. Applications to fuel cells, batteries

Solid oxide fuel cells continue to attract much interest. Properties of actual or potential electrode and electrolyte materials are investigated. Computation can also offer insights into the mechanism of ionic conduction, a field that has for some time been the focus of Islam’s group. In 2011 this group published studies on a number of systems. A combination of \textsuperscript{17}O MAS NMR and DFT modelling was used to explore the diffusion of oxide ions through La\textsubscript{x}Y\textsubscript{1-x}Ge\textsubscript{2}O\textsubscript{3}, an oxide ion conductor and possible electrolyte for solid oxide fuel cells\textsuperscript{116}. A novel substitution-mediated mechanism is proposed. DFT was used in conjunction with diffraction to study Li...
intercalation in Li$_{1+x}$V$_{1-x}$O$_2$. Paths for Li ion diffusion in LiFeSO$_4$F were studied using atomistic simulations. This paper also considers NaFeSO$_4$F and finds that whereas Li ion diffusion is three-dimensional, Na ion diffusion is only one-dimensional.

Catti’s group have used hybrid DFT calculations to study lithium salts used in this context. They validate a proposed scheme of electrochemical reactions to explain the electrode functionality of LiFeO$_2$ and model the Li-rich phases of the lithium conductor, Li$_3$La$_2$C$_2$TiO$_7$ (LLTO). Blanc et al use DFT calculations in conjunction with NMR studies to explore the structural and defect chemistries of Sr- and Mg-doped LaGaO$_3$, a promising electrolyte for solid oxide fuel cells. The diffusion of lithium ions through TiO$_2$ in both anatase and amorphous forms has been studied by Yildirim et al. Diffusion of an isolated ion is found to be higher for anatase but at the maximum Li intercalation ratio, diffusion is higher for amorphous TiO$_2$.

Suthirakun et al use DFT calculations to study n- and p-type doped SrTiO$_3$ under conditions relevant to its use as an anode catalyst in solid oxide fuel cells. For this purpose, the material must have high mixed ionic/electronic conductivity and the authors suggest this can be achieved through doping with both p-type and n-type dopants on the B site. Chen et al use GGA in VASP and molecular dynamics to study oxygen reduction and oxide diffusion mechanisms in Sr-doped LaMnO$_3$ (LSM). Addition of a U term made little difference to the O$_2$ adsorption energy. LSM is a mixed ionic/electronic cathode material in low temperature solid oxide fuel cells. The results of these calculations indicate that O$_2$ reduction occurs via peroxide and superoxide and is more favourable on Mn cations than on Sr cations. Oxide ions were found to diffuse faster through the bulk than along the surface of the solid. Petkovic et al use DFT calculations as a complement to experiment in their study of possible cathode materials La$_{1-x}$A$_x$Fe$_{1-y}$Co$_y$O$_3$. Sekizawa et al have investigated the effect of Li content on the cathode-active Li$_{6}$Ni$_{0.3}$Mn$_{0.7}$O$_{2}$.

7 Zeolites

Zeolites were the great triumph for molecular mechanics, but these days the majority of calculations use DFT or MM/DFT methods. The papers quoted here generally use periodic calculations of the zeolite. However there are a large number of papers where the interaction of molecules with zeolites are studied using a representative cluster for the zeolite. The mechanisms of absorption, desorption and catalysis within zeolites are particularly popular.

The positions of guest cations in zeolites have been studied by Guesmi’s group,$^{29,30}$ (Ni$^{2+}$), Schuessler et al,$^{131}$ (La$^{3+}$), Chu et al,$^{132}$ (Na$^+$).

Reyniers’ group have used a QM/MM method based on combining MP2, hybrid DFT and interatomic potential calculations with statistical thermodynamics to study n-alkanes and linear alkenes in H-FAU, H-BEA, H-MOR and H-ZSM-5. In both cases, the adsorption strength increases in the order H-FAU < H-BEA < H-MOR < H-ZSM-5 and varies linearly with the number of carbon atoms. 2-alkenes are found to adsorb more strongly than 1-alkenes Garcia-Perez et al have used a Monte Carlo method with the alkanes modelled using a united atom approach to study the absorption of ethane, propane and mixtures on the external surface of silicalite-1. They conclude that the absorption is ideal and that excess absorption on zeolite surfaces depends on the cut as well as the orientation of the zeolite crystal.
Goltl and Hafner have looked at alkane absorption in Na-exchanged chabazite comparing DFT (GGA), two variants of DFT-D (one due to Grimme and one with a van der Waals exchange-correlation functional) and a random phase approximation method (RPA). The most accurate description is found at the RPA level with HF exchange energies.

ZSM-5 is a high Si:Al ratio zeolite used in a number of catalytic processes. Zazza et al have used DFT and DFT-D to study the interaction of methane with aluminium-free ZSM-5. Their calculations indicate that methane does not react within silicate cages and that Al-free ZSM-5s do not catalyse the dissociation of methane inside straight micropores. Brønsted acidity is important for catalytic activity in zeolites. With H⁺ as the balancing cation, ZSM-5 can be used as an acid catalyst. Nguyen et al have studied the absorption of butanol isomers in HZSM-5. They use DFT with an additional interatomic potential to allow for van der Waals interactions and find steric restraints and van der Waals interaction with the framework to be the dominant interactions. Cheng et al have studied the absorption and diffusion of fructose in HZSM-5 and conclude that in order to obtain an accurate reaction energy barrier, it is necessary to include dispersion effects.

Brüggeman et al use DFT to study the reduction of NOₓ with ammonia on H-ZSM5. Other reactions are catalysed by ZSM-5 with transition metal ions. Izquierdo et al have studied the catalytic decomposition of NO₂ and NO with Cu-ZSM-5. using DFT and molecular mechanics. Li et al studied the direct oxidation of benzene to phenol with N₂O on extra-framework Fe in ZSM-5 using DFT with the functional PBE and an additional Lennard-Jones potential to allow for van der Waals interaction. They identify a preferred catalytic pathway using Fe²⁺ at two particular sites in 6-rings.

Potassium loaded zeolite A is ferromagnetic despite being composed of non-magnetic elements. Nohara et al model this system by constructing Wannier functions for the potassium electrons which turn out to be superatomic orbitals in the host cage.

Pinto et al use DFT calculations to show that the presence of water in the pores of ETS-4 promotes adsorption of NO at pentacoordinated Ti²⁺ framework ions.

8 Biological and Geological Applications

The equilibria involved in the formation of the various polymorphs of calcium carbonate and the reaction of acid with carbonate are important both for biomineralisation and the geological carbon cycle. Gale et al report a reactive force field to model speciation in the aqueous-calcium carbonate system (see highlight). The two most frequently-occurring surfaces of natural calcium carbonate are stepped surfaces. Aquilano et al use interatomic potential calculations to obtain the surface energy and attachment energy of these and two flat surfaces and consider the attachment of L-alanine to calcite surfaces. They conclude that the explanation of the enantiospecificity of adsorption lies in the compatibility between the substrate and the polar properties of the adsorbed layer. Bakri and Zaoui used DFT to study the structure of dolomite under high pressure and predict a phase change with increasing pressure to first a calcite III-like structure and then to an aragonite II-like structure.

Pan et al use DFT calculations to corroborate the positions of Cr and H incorporated into stishovite obtained by EPR. Prencipe et al have studied the high
pressure thermal expansion of beryl. Vigneresse et al.\textsuperscript{150} describe the chemical character of magmas in terms of hard-soft acids-bases. The parameters used for this are electronegativity, hardness, electrophilicity and polarisability. DFT calculations are used to provide some of these parameters. The description provides insights into the affinity of elements for different phases during igneous activity. Saha et al.\textsuperscript{151} and Ammann et al.\textsuperscript{152} use ab initio calculations to study the diffusion of Fe ions in the lower mantle.

Combinations of liposomes and silica (liposils) are strong candidates for drug storage and release. Folliet et al.\textsuperscript{153} have used solid state NMR spectroscopy together with geometry optimisation and NMR parameter calculations and molecular dynamics to characterise the organic/inorganic interface in liposols.

References

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