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Computational Modelling of Inorganic Solids

5 Elaine Ann Moore*

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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.

15 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, biomineralisation (for example mollusc shells) and the formation of scale in hard water areas. Gale et al¹ 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 al² 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 Matter³ contains a Special Section on Computational Materials Science dedicated to Jürgen Hafner. The
 50 October 2011 issue of Physica Status Solidi B⁴ dedicated to Professor Manfred Fähnle and covering the topic ‘Recent developments in magnetism and modern magnetic materials’ contains a number of computational papers. A special issue of Journal of Catalysis⁵ on ‘Molecular Approach to Heterogeneous Catalysis’ includes articles using a computational approach.

55 A review in Solid State Nuclear Magnetic Resonance⁶ 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 H₂ as it
 60 nears dissociation. Recently, solid state programs have begun to include a method DFT-D⁷⁻¹⁰ 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.

65 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.
 70 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 superconduction still not entirely understood.

75 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
 80 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,
 85 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 al¹³ have suggested a method for linking atomic level calculations to a phase-field model. This model is
 90 applied to the ferroelectric materials PbTiO₃ and PbZr_{0.5}Ti_{0.5}O₃. 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}

95 have written a program, XTALOPT, under GNU public licence for crystal structure prediction. Cai et al¹⁶ 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.

100 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 al¹⁷ have proposed using graphics-processing units to speed up
105 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
110 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 al¹⁸ have compared the functionals LDA, PBE, PBESOL, B3LYP, PBE0 and WC1LYP in CRYSTAL09 for calculations on forsterite
115 (Mg₂SiO₄). They conclude that hybrid functionals perform better than LDA and GGA and that B3LYP performs better than the other hybrid functionals. Maschio et al¹⁹ compare the performance of LDA, PBE, PBESOL, B3LYP and PBE0 in describing the infrared spectrum of spessartine (Mn₃Al₂Si₃O₁₂). Again they conclude that hybrids outperform LDA and GGA and that B3LYP is the best-performing
120 hybrid functional. Chen et al²⁰ have compared GGA, GGA + U and PBE0 functionals for calculations on Co₃O₄. GGA underestimates the band gap and PBE0 overestimates it. Yu²¹ modifies the exchange functional of B3LYP to obtain better agreement with the band gaps of GaN and ZnO. Tran and Blaha²² report the implementation of screened hybrid functionals in the program WIEN2K. This
125 method eliminates long range Hartree-Fock exchange which can cause problems by screening the HF exchange using the Yukawa potential²³. 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 solids²⁴ and consider the merits and limits of the
130 modified Becke-Johnson, mBJ²⁵, exchange potential²⁶.

Grimme et al²⁷ 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
135 a particular electronic or geometric structure. Yu et al²⁸ 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. Kozłowski and Plime²⁹ have shown that an algorithm designed for the
140 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 Kohout³⁰ report implementation as part of DGRID³¹ of a method of obtaining localisation and delocalisation indices. Elk³² was

used to provide the wave functions. Otero-de-laRoza and Luana³³ describe techniques developed for fitting energy against volume. Ghosh et al³⁴ 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 al³⁵ 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 Wannier90³⁶.

Bjorkman³⁷ has written a program that will produce the geometrical set-up for a number of packages from information in CIF files. J-ICE³⁸ 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 al³⁹ 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 al⁴⁰ 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 al⁴¹. Burbano et al⁴² present a new potential for use with CeO₂ for problems where even now ab initio calculations are not feasible. Hanken et al⁴³ use DFT + U calculations to explore different cation and charge ordering in U_{1-x}Ce_xO₂. Nolan et al⁴⁴ 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 al⁴⁵ 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 Kumta⁴⁶ have used VASP and the GGA DFT method to study the effect of fluorine-doping of SnO₂ 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 al⁴⁷ 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 al⁴⁸ use the PLAPW method to study BaCoO₂. 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 Hubbard¹¹ used DFT + U in both a plane wave (VASP) and a locally confined atomic orbital (SIESTA) representation to study α - and γ -Fe₂O₃, α - and γ -FeOOH and Fe₃O₄. They find both approaches predict the correct energy ordering and magnetic states, but prefer the plane wave method for producing a phase diagram.

Fig/2 Calculated structures of doyleite and nordstrandite. Al, gray; O, red; H, white.”Reprinted with permission from Physico-Chemical Features of Aluminium hydroxides Asodeled with the Hybrid B3LYP Functional and Localised Basis Functions, Raffaella Demichelis,, Yves Noë, Piero Ugliengo, Claudio M. Zicovich-Wilson, and Roberto Dovesi, *The Journal of Physical Chemistry C*, 2011, **115**, 13107 – 13134. Copyright 2011 American Chemical Society.”

Demichelis et al¹² 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. Ferreira et al⁴⁸ used DFT calculations to compare two possible structures of γ -Al₂O₃ and conclude the spinel-type structure is more favourably energetically.

Corno et al⁵⁰ look at hydrogen substitution by fluorine in LiBH₄ 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 al⁵¹ have used DFT calculations to study vibrations of BH₄⁻ in alkali metal borohydrides.

Morgan and Madden⁵² use molecular dynamics (MD) and a rigid ion potential to model defect behaviour in AgI. Wang et al⁵³ have calculated the electronic structure and magnetism of chromium halides. They find that a +U term is necessary to correctly predict magnetic ordering in CrCl₃. Singh et al⁵⁴ used GGA to study elastic properties of thallium halides, TlCl and TlBr.

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 al⁵⁵ have studied the electronic structure and optical

properties of Sb_2S_3 using GGA. Romero et al⁵⁶ have calculated properties of CuGaS_2 and Kocak⁵⁷ et al properties of PrS , PrSe and PrTe . Zhou et al⁵⁸ report DFT calculations using a GGA functional on the novel chalcogenidehalide $\text{Hg}_2\text{Cd}_2\text{S}_2\text{Br}_2$. Liu et al⁵⁹ use CASTEP to determine the nature of the conduction and valence bands in $\text{Ba}_{12}\text{In}_4\text{S}_{19}$, $\text{Ba}_4\text{In}_2\text{S}_8$ and $\text{Ba}_4\text{Ga}_2\text{S}_8$ 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 al⁶⁰ compared GGA + U + G_0W_0 to the many body perturbational GW approach in studying the band formed by Ti substituting on In sites in MgIn_2S_4 and concluded that GGA + U + G_0W_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 al⁶¹ have studied Cr-doped AlN , GaN and InN and find that $\text{Al}_{0.75}\text{Cr}_{0.25}\text{N}$ and $\text{Ga}_{0.75}\text{Cr}_{0.25}\text{N}$ are half metallic. Hao et al⁶² 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 al⁶³ have modelled oxygen incorporation into UN, a promising nuclear fuel that is degraded by the presence of oxygen impurities.

Derzsi et al⁶⁴ 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 al⁶⁵ calculate NMR chemical shifts for $\text{LiFePO}_4\cdot\text{OH}$ and $\text{FePO}_4\cdot\text{H}_2\text{O}$ 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 al⁶⁶ investigated polymorphs of $\text{Li}_2\text{FeSiO}_4$ using Mössbauer and NMR and analysed contributions to the ^6Li chemical shifts using DFT/GIPAW calculations. First principal calculations of NMR parameters are also used by Pallister et al⁶⁷ to help in the signal assignment of the ^{17}O spectrum of the polymorphs of MgSO_4 .

DFT calculations⁶⁸ on the novel tungstate compounds CeBiW_2O_9 and SmBiW_2O_9 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 Harding⁶⁹ use interatomic potential calculations to explore the validity of this model for ions trapped in zirconolite, $\text{CaZrTi}_2\text{O}_7$. They find that whereas Ce^{4+} is partly reduced in zirconolite, this would not be expected for Pu^{4+} .

Matar et al⁷⁰ predict that Na_2OsO_4 develops a magnetic moment when in the less stable K_2NiF_4 phase whereas it is magnetically silent in the Ca_2IrO_4 phase.

4. Perovskites and spinels

275 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 al⁷¹ 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 al⁷² have studied 280 electrical and magnetic properties of the perovskite structure $\text{BiCu}_3\text{Fe}_4\text{O}_{12}$ 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 285 antiferromagnetically and Cu 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 al⁷³ have studied the electronic and magnetic properties of CaMnO_3 in bulk, slab and nanocluster forms. Gong and Liu⁷⁴ use the modified Becke-Johnson exchange 290 potential and an LDA correlation functional to study LaMnO_3 and obtain improved results for the band gap over GGA. Ahmad et al⁷⁵ use hybrid DFT to study the stability of LaMnO_3 and that of the possible oxides formed from its decomposition - La_2O_3 , MnO , Mn_2O_3 , MnO_2 and Mn_3O_4 . Ali et al⁷⁶ have studied the magnetic properties of PrCoO_3 and NdCoO_3 .

295 Huang et al⁷⁷ have calculated properties of YAlO_3 . Cherrad et al⁷⁸ use LDA calculations to obtain properties of Ca_3SnO , Ba_3SnO and Sr_3SnO hoping to inspire experimentalists to work on these compounds. Ghebouli et al⁷⁹ 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, $\text{Sr}_2\text{InReO}_6$ ⁸⁰. A lowest energy structure of 300 BaFeO_2F 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 calculations⁸¹.

Benedek et al⁸² report calculations on the surface structure of LiMn_2O_4 . Using GGA + U, they find the lowest energy surface to be Li-terminated (001). Illustrating 305 the advances possible as computer power increases, their work includes molecular dynamics simulations to explore surface reconstruction. Ragavendran et al⁸³ also report DFT studies on surfaces of LiMn_2O_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 al⁸⁴ have studied the 310 electronic spectrum of MgAl_2O_4 containing oxygen vacancies. Shukla et al⁸⁵ use atomistic simulation to study MgAl_2O_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 al⁸⁶ use 315 interatomic potential calculations to study doping by and subsequent reduction of rare earth ions in BaAl_2O_4 . In a later paper this group consider the concentration dependence of rare earth doping in this aluminate⁸⁷.

Matar's group^{88,89} have studied the ionic character of hydrogen in perovskite and K_2NiF_4 phases CsCaH_3 , Cs_2CaH_4 and CsCa_2H_4 and used Ni substitution on the Mg 320 sites to explore the ionic character of hydrogen in RbMgH_3 .

5. Superconductors and multiferroics

Iron-based high T_c superconductors have again been of much interest, the mechanism of superconductivity being still a matter of debate. Sefat and Singh⁹⁰

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 Solids⁹¹ on Spectroscopies in Novel Superconductors. Harshman et al⁹² have analysed a range of high T_c superconductors and propose that the value of T_c is determined by the Coulomb interaction between layers and is independent of energy band dispersion or proximity to the Fermi level. Maiti et al⁹³ 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_2P_2 ⁹⁴, $\text{K}_x\text{Fe}_{1.6}\text{Se}_2$ ⁹⁵, KFe_2S_2 , KFe_2Se_2 ⁹⁶, KFe_2Se_2 and KFe_2Te_2 ⁹⁷, AFe_2Se_2 ($\text{A} = \text{Cs}, \text{K}, \text{Rb}, \text{Ti}$)⁹⁸, $\text{Ca}_4\text{Al}_2\text{O}_{6-x}\text{Fe}_2\text{As}_2$ ⁹⁹, $\text{La}_2\text{O}_3\text{Fe}_2\text{Se}_2$ and $\text{La}_2\text{O}_3\text{Co}_2\text{Se}_2$ ¹⁰⁰, LaFeAsO ¹⁰¹, transition metal-doped LaFeAsO ¹⁰², H-doped LaFeAsO_{1-y} ¹⁰³, $\text{Fe}_2\text{AS}_2\text{Sr}_4\text{Mg}_2\text{O}_6$ and $\text{Fe}_2\text{AS}_2\text{Sr}_4\text{Ti}_2\text{O}_6$ ¹⁰⁴, $\text{Co}_2\text{As}_2\text{Sr}_4\text{Sc}_2\text{O}_6$ and $\text{Co}_2\text{P}_2\text{Sr}_4\text{Sc}_2\text{O}_6$ ¹⁰⁵, $\text{A}_x(\text{FeAs})_{1-x}$ (where A is a Group 1 or Group 2 metal)¹⁰⁶, $\text{BaFe}_{1.85}\text{Co}_{0.15}\text{As}_2$ ¹⁰⁷. Calculations on structurally related but iron-free superconductors have been reported by Shein et al¹⁰⁸ (LiCu_2P_2) and Shein and Ivanovskii¹⁰⁹ (SrPt_2As_2).

Evarestov et al present phonon calculations for SrTiO_3 ¹¹⁰ and for BaTiO_3 , BaZrO_3 and BaHfO_3 ¹¹¹ and conclude that the hybrid functional PBE0 gives results closest to experiment for both plane wave and LCCO methods. Gao et al¹¹² conclude that GGA/PW91 functionals and ultrasoft pseudopotentials describe the properties of BaTiO_3 well. Lv et al¹¹³ discuss the best method and pseudopotential for calculations on PbTiO_3 using CASTEP. Ganesh and Cohen¹¹⁴ predict a tetragonal ground state for PbCrO_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 et al¹¹⁵ use DFT calculations to investigate $\text{SnAl}_{0.5}\text{Nb}_{0.5}\text{O}_3$. They predict that this material will be ferroelectric and possibly a good piezoelectric material. Jia et al¹¹⁶ investigated the pressure-induced spin transition in the potential multiferroic, BiCoO_3 . Ordering in multiferroic BiMn_2O_5 has been investigated using GGA and GGA + U by Li et al¹¹⁷. They find that the solid contains two types of manganese ions with slightly different charges but with a large difference in the minority e_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 ^{17}O MAS NMR and DFT modelling was used to explore the diffusion of oxide ions through $\text{La}_8\text{Y}_2\text{Ge}_6\text{O}_{27}$, an oxide ion conductor and possible electrolyte for solid oxide fuel cells¹¹⁸. A novel substitution-mediated mechanism is proposed. DFT was used in conjunction with diffraction to study Li

intercalation in $\text{Li}_{1+x}\text{V}_{1-x}\text{O}_2$ ¹¹⁹. Paths for Li ion diffusion in LiFeSO_4F were studied using atomistic simulations¹²⁰. This paper also considers NaFeSO_4F 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. They¹²¹ 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, $\text{Li}_3\text{La}_2\text{O}_7(\text{TiO}_3)_2$ (LLTO)¹²². Blanc et al¹²³ 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 al¹²⁴. 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 al¹²⁵ 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 al¹²⁶ use GGA in VASP and molecular dynamics to study oxygen reduction and oxide diffusion mechanisms in Sr-doped LaMnO_4 (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 al¹²⁷ use DFT calculations as a complement to experiment in their study of possible cathode materials $\text{La}_{1-x}\text{A}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$. Sekizawa et al¹²⁸ have investigated the effect of Li content on the cathode-active $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$.

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^{129,130} (Ni^{2+}), Schuessler et al¹³¹ (La^{3+}), Chu et al¹³² (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-alkanes¹³³ and linear alkenes¹³⁴ in H-FAU, H-BEA, H-MOR and H-ZSM-5. In both cases, the adsorption strength increases in the order $\text{H-FAU} < \text{H-BEA} < \text{H-MOR} < \text{H-ZSM-5}$ and varies linearly with the number of carbon atoms. 2-alkenes are found to adsorb more strongly than 1-alkenes Garcia-Perez et al¹³⁵ 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 Hafner¹³⁶ have looked at alkane absorption in Na-exchanged chabazite comparing DFT (GGA), two variants of DFT-D (one due to Grimme⁸ and one with a van der Waals exchange-correlation functional¹³⁷) 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 al¹³⁸ 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 al¹³⁹ 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 al¹⁴⁰ 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 al¹⁴¹ use DFT to study the reduction of NO_x with ammonia on H-ZSM5. Other reactions are catalysed by ZSM-5 with transition metal ions. Izquierdo et al¹⁴² have studied the catalytic decomposition of NO₂ and NO with Cu-ZSM-5. using DFT and molecular mechanics. Li et al¹⁴³ 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 al¹⁴⁴ model this system by constructing Wannier functions for the potassium electrons which turn out to be superatomic orbitals in the host cage.

Pinto et al¹⁴⁵ use DFT calculations to show that the presence of water in the pores of ETS-4 promotes adsorption of NO at pentacoordinated Ti⁴⁺ 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 al¹ 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 al¹⁴⁶ 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 Zaoui¹⁴⁷ 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 al¹⁴⁸ use DFT calculations to corroborate the positions of Cr and H incorporated into stishovite obtained by EPR. Prencipe et al¹⁴⁹ have studied the high

pressure thermal expansion of beryl. Vigneresse et al¹⁵⁰ describe the chemical character of magmas in terms of hard-soft acids-bases. The parameters used for this
 465 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 al¹⁵¹ and Ammann et al¹⁵² use ab initio calculations to study the diffusion of Fe ions in the lower mantle.

470 Combinations of liposomes and silica (liposils) are strong candidates for drug storage and release. Folliet et al¹⁵³ 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.

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