8   HIGHLIGHT OF THE MONTH

Applying Ab Initio Calculations in Mineralogy

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There are at least five university departments of Earth Sciences in Britain where some ab initio simulations are being carried out on minerals, and a few more university and other institutions in the rest of the world. The number of people involved in ab initio calculations of silicates and related phases becomes larger if one includes chemists making calculations on zeolite catalysts, a few zeolites being in fact minerals. There are also others, often physicists, who have done calculations on quartz and other simple silicates as test or demonstration calculations rather than being focused on solving specific mineralogical problems. One can therefore discern an embryonic community of ab initio computationalists beginning to make a contribution in mineralogy. Incidentally a mineral is any material occurring naturally in the earth. Minerals include many phases with very complex structure and crystal chemistry, particularly among the aluminosilicates, and including some of interest in materials science in connection with high performance ceramics.

How can ab initio calculations be a useful tool in mineralogy ? This was the topic of a recent CECAM workshop (23-28 June 1997) which was enlivened by a good mixture of experimental

mineralogists, several developers of ab initio codes, and of course a number of practitioners. One theme was mutual education. Up till now one might characterise the community of ab initio computationalists as largely a cosy club of physicists interested in the basics of electronic structure and bonding in condensed matter, knowledgeable about density functional theory, electron correlation, pseudopotentials etc. But here was an embryonic community wanting numbers to such and such accuracy from a black box. Of course they cannot have that, at least not in the foreseeable future, and so what they will need is substantial support. Where is that support to come from, and the interfacing with their complex crystal structure packages etc? It is no answer to say that mineralogists should become physicists; and so we came to the complex issue of commercialisation of codes. Commercialisation of codes has come and will continue, and the question for us is really how to engage with it constructively in a way that also benefits the basic science community. Another point that became evident is that the user community in mineralogy also has specific needs, particularly regarding complicated space group symmetries, large cells with low symmetry, all components of the stress tensor, among others. The mineralogical community is indeed very grateful to the people who have developed various codes, which are drawn on for various purposes, e.g. computation of total energies for processes modelled in large supercells in one case, or the determination of electric field gradients at the nucleus for the interpretation of NMR spectra in another, and so on. One can also make the point the other way round: history has shown in other fields of computational science that codes can get rapidly dropped or superseded if the developers lose touch with the evolving needs of their user community. In addition to the codes being already used in the mineralogical community, the new SIESTA code by Ordejon et al., based on local orbitals which allows calculations of state-of-the-art accuracy at one extreme to very much faster ones of lower accuracy ('quick and dirty') at the other extreme was presented at the workshop and was thought to be potentially very useful for modelling minerals.

Applications in mineralogy can be divided broadly into two streams. One is to design computer experiments to elucidate basic understanding of e.g. phase changes or diffusion processes. We may term this basic mineral physics. For example there are many displacive phase transitions where one may picture the energy as a double well: as the temperature is lowered, the material flops from a more symmetrical structure to the 'left' or 'right' into a less symmetrical structure represented by each of the wells. A puzzle presented at the workshop is that there are marked differences in some cases in the transition along the temperature and the pressure axis: one would like to understand these and the crossover between them.

However more significant for mineralogy and earth sciences generally is simply to get numbers that are difficult, extremely tedious, or impossible to measure in the laboratory. Most obvious are data at the high temperatures and pressures present in the earth's mantle. (A quick teach-in. 'Crust' is the top 30 km of the earth made up of rather low density, complex phases. 'Mantle' is the next 3000 km consisting of a few high density phases where the convection driving the plate tectonics takes place. 'Core' consists of an iron alloy in the middle, liquid and solid respectively in the outer and inner core. The temperature and pressure at the core/mantle boundary are roughly 3500 K and 1.3 Mbar.) Accurate ab initio calculations of elastic constants would

be very valuable in connection with interpreting seismic data, and phonon spectra for thermal enthalpies and entropies. Elastic constants are surprisingly difficult to measure for minerals, partly because there are an awful lot of them, e.g. 21 for a triclinic crystal. A problem of high pressure research is the absence of an absolute pressure scale beyond a few kilobars where one can use a known weight loading with negligible friction. In principle ab initio calculations depending only on the electron mass and charge and other fundamental constant could provide an absolute scale. The challenge was thrown out to calculate either the equation of state of some reference crystal whose lattice constants can be monitored, or the pressure of some phase transition as a marker preferably as a function of temperature. The simulation of materials at high temperature is clearly of great importance (and of difficulty for ab initio calculations!).

Most of what mineralogists would like is way beyond what ab initio calculation can deliver in the near future and a recurring theme in the workshop was to use ab initio calculations to calibrate simulations with empirical interatomic potentials. The latter tend to give good interatomic distances, but the database to which they have been fitted contains virtually no information about relative energies, e.g. about Al in tetrahedral and octahedral coordinations. For example an ab initio calculation of the energy difference between two phases of $ZrSiO_4$ was the first step in a subsequent simulation of radiation damage in a sample with thousands of atoms. The project concerns the use of $ZrSiO_4$ as a host for disposal of plutonium and other actinides.

Almost all naturally occurring minerals are complex solid solutions of two, three or four major components. The synthesis of samples with known composition can be an extremely time consuming and expensive process, but an accurate knowledge of their thermodynamic functions (enthalpy and entropy) is essential for understanding geological processes. There is scope for computer modelling, based perhaps on ab initio calculations on some chosen configurations. Another question is whether one can obtain accurate enough results for solid solutions by defining an average atom, and how would this be done when the components are chemically rather different and have different radii leading to strong strain effects.

Clearly ab initio simulations are not going to solve all the problems of the Earth Sciences but the picture emerged from the workshop that, yes, there are certainly worthwhile research projects for this technique. One young post-doc finds herself besieged by requests for calculations in a department new to ab initio calculations. Another workshop participant spoke of attending an earth sciences conference and seeing a dozen possible projects.

So finally a brief highlight from recent work. Michael Haiber reported an investigation of proton transport in the high pressure phases olivine, forsterite and spinel of Mg_2SiO_4, which may contribute to electrical conduction in the earth's mantle. The three structures are very similar but Mullikan orbital analysis suggested that one of the four oxygen sites in forsterite has a somewhat higher negative charge than the others and indeed a proton gets trapped there with no diffusion observed in ab initio simulations up to 1400 K. However the proton has chains of hydrogen-bond sites with double-well potentials between neighbouring oxygen atoms in one

direction in olivine, and a three-dimensional network of such bonds in spinel. At 1500K there was rapid diffusion in spinel in a two-step process, a jump from one oxygen to the other in the hydrogen bond in about 100 fs and a migration around the oxygen atom to another hydrogen bond in 250 fs. The process has a considerable entropy of activation, a free energy of 0.25 eV being (computationally) measured compared with a barrier energy of 0.17 eV. The electrical conductivity is given by the Einstein relation from the diffusion observed in the simulation. The results show how useful properties of minerals can be obtained at high T and P from ab initio simulation, and how small differences in structure can result in large differences in behaviour.

Vienna–Keele collaboration supported by the Psi-k Network

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Funding from the Psi-k Network has made possible a fruitful collaboration between the groups of Mike Gillan (Keele University, U.K.) and Jürgen Hafner (Technical University, Vienna). The collaboration builds on the shared interests of the two groups in the *ab initio* treatment of liquid and solid metals, but has given benefits which go well beyond this. *Ab initio* techniques developed in Vienna have greatly helped the work of the Keele group on metals, and also in other areas. At the same time, the U.K. experience in parallel implementation of *ab initio* codes has benefited the Vienna group.

Both research groups have a strong background in the *ab initio* theory of metals, using density-functional theory and the pseudopotential approach. At Keele, there has been a major effort over the past four years to apply *ab initio* molecular dynamics simulation to liquid-metal alloys. This research was stimulated by experimental work – particularly by the group of John Enderby at Bristol – on the dramatic variations of structure and electrical properties of liquid alloys with composition. Using the CASTEP code[1] written in Cambridge, and its parallel version CETEP[2], the Keele group had made fairly extensive investigations of structure and transport properties of the liquid alloys Ga-Se[3,4] and Ag-Se[5−7] over a wide composition range, working closely with the Enderby group. Because of the need to include d-electrons, the Ag-Se work was computationally demanding, and relied heavily on the Edinburgh Cray T3D. At the same time, the Vienna group had made major advances in technique for treating metallic systems, which were implemented in the VASP code written by Georg Kresse and Jürgen Furthmüller[8]. The code has been used for liquid simple metals (Na, Ge)[8], liquid transition metals (V,Cu)[10], the transition from a liquid metal to an amorphous semiconductor by the rapid quenching of Ge[11], and the metal non−metal transition in liquid Hg [12].

Because of the common interests, it was clear that collaboration would be extremely beneficial to both groups. To get this moving, Mike Gillan and Janusz Holender (the post-doc working with him on liquid metals) made a three-day visit to Hafner's group in Vienna in November 1995. This visit was made possible by travel and subsistence funding from the Psi-k Network, and brought immediate benefits. Naturally, the two groups got to know each other's scientific work much better. But much more importantly, there was time, even in three days, for detailed discussion of the *ab initio* techniques being used by the two groups. The idea that emerged from these discussions was that the two groups should work together to produce a massively parallel version of the VASP code.

Here, a word is needed about U.K. work on parallel coding of DFT-pseudopotential calculations. Back in 1990, it was realised by Volker Heine, Mike Payne and others in the U.K. that parallel coding was going to play a major role in *ab initio* simulation, and a collaboration was set up to explore this. Initially known as the Grand Challenge consortium, but now called the U.K. Car-Parrinello consortium (UKCP), this collaboration obtained research-council funding to buy a share of a 64-node Meiko Computing Surface at Edinburgh Parallel Computing Centre. This enabled UKCP to build up a major expertise in parallel *ab initio* computations, and CETEP was the DFT-pseudopotential code that emerged from this. The Keele group was a founder-member of UKCP, and made significant contributions to CETEP.

Because VASP has important advantages over CASTEP/CETEP for metals, the potential benefits of parallelising VASP were clear. In making this happen, an important step was a two-week visit of Holender to Vienna in 1996, which was funded by the Psi-k Network. In the end, the comprehensive parallelisation of VASP has been brought to fruition by Georg Kresse, during a 10-month period spent at Keele October 1996 – August 1997. During this period, Kresse has also played a key role in the liquid-metal work of the Keele group, as well as making a number of important technical advances.

Scientific work at Keele for which the collaboration has been crucial includes work on liquid selenium and on liquid and solid iron. Some work on ℓ-Se and ℓ-Te had been done by the two groups before the collaboration was up and running[13], and this had shown that the two systems pose problems for density-functional theory. In the solid, both elements crystallise to form helical chains, with strong covalent bonds within the chains and much weaker bonds between the chains. It is the weak bonds that cause the problem. One sign of this is that the local density approximation (LDA) underestimates the equilibrium lattice parameter for Se perpendicular to the chain axis by about 10 % [14]. Fortunately, this huge error is almost entirely corrected by the generalised gradient approximation (GGA). The LDA also turns out to give pretty mediocre results for the radial distribution function in ℓ-Se (the results are even worse for ℓ-Te). Through the collaboration, we have been able to study this problem in depth for ℓ-Se, and we have shown that GGA produces a big improvement for the liquid as well. This collaborative work led to a joint conference paper [1] which has already been published, and a lengthy paper on ℓ-Se which has been submitted to Phys. Rev. B [2] (reports benefiting from the collaboration are cited in square brackets – see separate list below). A further long paper on defects in ℓ-Se is about to be submitted [3].

In addition to this work on ℓ-Se, the parallel VASP code produced by the collaboration has played a crucial role in our work on liquid and solid iron. Work on iron is being done in both groups, but particularly relevant is a collaborative project between Keele and the group of David Price in London (Geological Sciences Department, University College London). In this project, we are using *ab initio* simulation to help understand the properties of iron in the Earth's core. Specifically, we are using the calculations to shed light on the viscosity of liquid iron in the Earth's outer core, and the pressure-dependent melting point and the phase diagram of solid iron under Earth's-core conditions. Using the VASP code, we have been able to show that DFT-pseudopotential calculations reproduce very well some of the key experimental data on solid and liquid iron at high pressures and temperatures, and we have obtained estimates for the viscosity of the liquid in the outer core. Some of the work has already been reported in a paper

presented at one of the Royal Society of Chemistry's Faraday Discussions [4], and a paper has also been submitted to Nature [5]. In addition, we have used VASP to do *ab initio* calculations on the melting of aluminium, in order to prove the techniques that will be used to study the high-pressure melting of iron, and a paper is in preparation on this [6].

We also want to mention that the parallel VASP code is playing an important part in the work of the Keele group on oxide surfaces, and a joint paper with the Vienna group on this is in course of publication [7]. The work of Georg Kresse at Keele has also led to a number of significant technical advances, including: the parallel *ab initio* implementation of Jonsson's 'nudged elastic band' method for finding transition states; and the implementation of Blöchl's 'projected augmented wave' technique within the VASP code.

In conclusion, we want to thank the Psi-k Network for the travel and subsistence funding which enabled our collaboration to establish itself. The benefits of this funding are already clear from the work reported by the collaboration, and their effect will be felt for many years to come.

Publications benefiting from the collaboration

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