

CAN WE TRUST THE SHELL MODEL?

M.J. Gillan

*Physics Department, Keele University
Keele, Staffordshire ST5 5BG, U.K.*

I am not a great believer in staring at your navel. Trying something out in practice is usually better than hours of self-questioning. Nevertheless, from time to time a moment of introspection can be good for the soul. Sometimes you need to ask: Is this method that I have used for so long really what it seems?

The shell model for the energetics of ionic materials [1] has been used enthusiastically for many years. But there has always been the odd awkward customer who has seen fit to question its basis. We know that ions in crystals are electronically polarised by the electric fields due to neighbouring ions. We know that they are also polarised simply because neighbouring ions press against them. These two physical facts form the basis of the shell model. Each ion is represented by a massive core and a massless shell, both charged, coupled by a harmonic spring. The short-range interactions between ions are usually assumed to act between the shells. Both the field polarisation and the polarisation due to short range interactions are incorporated in this simple model.

It is easy to pick holes. Polarisation of an ion really occurs by distortion of the orbitals occupied by the valence electrons. Can the distortion of a p -orbital in an oxygen ion really be adequately represented by the simple relative displacement of core and shell charges? What about the redistribution of electrons in the unfilled d -shell of a cobalt ion? Such doubts have not prevented the shell model from being routinely applied to oxide materials (including, incidentally, cobalt oxide) [2]. Matters are not helped when you look at the shell model parameters. Very often the shell model is parameterised by fitting to selected experimental data for bulk crystals - things like the lattice parameter or the dielectric and elastic constants. The shells are supposed to represent valence electrons - in spite of which, the cation shell charges that emerge from fitting very often have positive values (examples can be seen in ref. [3]). What is this supposed to mean? Strange shell charges might not matter if the shell model was only applied in situations close to those it has been fitted to. In practice, though, it has been widely used for things like the properties of surfaces - which are about as different from bulk crystals as you could imagine. This raises all kinds of questions. You could imagine that a material might be fully ionic in the bulk, but only partially ionic at the surface, for example. There is plenty to keep you awake at night!

It looks as though worries like these will very soon be a thing of the past, thanks to first principles-methods. The idea of first-principles simulations is to solve Schroedinger's equation to determine the electronic ground state of the system. These methods have become so accurate and reliable in the last few years that they can now be used as an independent way of testing and constructing interaction models. The problem in the past in parameterising an interaction model using experimental data was that usually only data on the perfect crystal would be available. First-principles methods give you the means to calculate the energy for any configuration of the

ions that may be relevant. First-principles calculations on the structure and energy of defects and surfaces can now be used to provide a direct test of shell model predictions.

Two main first-principles approaches are being used. The work we are doing at Keele [4,5] is based on density functional theory (DFT) and pseudopotentials. Other groups, particularly at Daresbury Laboratory, at ICI, and at the Royal Institution in London, are making use of Hartree-Fock methods [6,7]. I will say something first about our own work, and then mention the Hartree-Fock methods later.

The basis of the density functional method is the idea that you can write the total energy as a unique functional of the density distribution of the electrons. This leads naturally to a simple approximation for the electronic exchange and correlation energy. The approximation assumes that at each point in the system there is a density of exchange and correlation energy and that this density depends only on the density of electrons at that point - this is called the local density approximation (LDA). There is now a wide range of results which shows that the LDA gives very accurate results for many systems and situations. The idea of the pseudopotential method is to set up the calculations in such a way that only the valence electrons have to be explicitly treated. This makes sense because the atomic cores are usually almost completely inert and have no effect on the energetics of the system. The pseudopotential for any atom represents the effective interaction of the valence electrons with the atomic cores. Nowadays, pseudopotentials are constructed from first principles, and there is no loss of rigour in following the pseudopotential approach.

A number of research groups have written DFT-pseudopotential codes for calculating the total ground state energy of materials. In the U.K., the most important is the code CASTEP written by Mike Payne and his group at Cambridge with the support of a CCP9 project. This is now becoming widely used, both in the U.K. and in the rest of Europe. In the last two years, as part of the U.K. Car-Parrinello project, this code has been rewritten in parallel form to run on machines like the Intel iPSC/860 at Daresbury Laboratory and the Meiko Computing Surface 'Maxwell' at the Edinburgh Parallel Computing Centre [8]. This code already has a number of important scientific achievements to its credit, including a study of the famous 7x7 reconstruction on the silicon (111) surface, which involved simulations on 400 silicon atoms [9,10].

At Keele, we have been using the code CETEP on the parallel machines at both Edinburgh and Daresbury to study the energetics and structure of defects and surfaces in oxide materials. As a by-product of these calculations, we have obtained some extremely instructive insights into the validity of shell-model potentials for these materials. But before saying anything about these results, it is worth taking a look at how the DFT pseudopotential method does for the properties of the perfect crystals. As an example, Table 1 shows some of the results we obtained for the equilibrium lattice parameter, the bulk modulus, and some of the vibrational frequencies of perfect crystal MgO. When you look at the results, you should bear in mind that these calculations are done completely from first principles and contain no adjustable parameters at all. You can see that results like these are certainly reliable enough for constructing interaction models.

We have used these methods to look at the energetics of point defects in both MgO and Li₂O.

The dominant thermally produced defects in MgO are Schottky defects, in other words vacancies on the magnesium and oxygen sublattices. In lithium oxide, the dominant defects are cation Frenkel defects, in other words lithium vacancies and interstitials. What we have aimed to do is to calculate from first principles the energy of formation of these defects and their migration energies - the energy barriers that the defects have to get over as they jump from one site to another in the lattice. Of course, when you do calculations on defects, you have to use systems containing many ions. The calculations are all done in periodic boundary conditions so that, in effect, what we are doing is calculations on periodically repeating arrays of defects. Since the defects carry net charges, we have to be very careful about correcting for the effective Coulomb interaction between defects and their periodic images. Even with such corrections, you need to do calculations on systems of about 50 ions in the repeating cell to obtain reliable results. In addition, because of the large polarisation effects for charged defects, it is important to get the system mechanically relaxed so that the forces on all the ions are extremely small.

Table 2 shows some of the results we have obtained for the energies of Schottky defects in MgO and Frenkel defects in Li₂O. These results are compared with the predictions of shell model potentials, and also, in some cases, with experimental results. The point about these comparisons is that the agreement between the first principles results and the predictions of the shell model are actually very close, even in cases where experimental results do not exist. This already provides useful support for the validity of the shell model, at least for these problems. Further support comes when you look at the relaxed structure of the defects. What we find is that the relaxed positions of the ions surrounding the defects - both the equilibrium defects and the migration saddle points - is extremely similar in the shell model and first principles calculations. Put another way, this means that if you take the relaxed structure predicted by shell-model calculations, and put it into the first-principles calculations, then you find that the first-principles forces on the ions are all extremely small.

The shell model thus comes through with flying colours for the point defects we have looked at. But you might argue that point defects are not so very far from the perfect crystal structure. A much more severe test is provided by crystal surfaces. Here, the ions at the surface find themselves in an environment which is completely different from what they see in the bulk. One of the cases we have been looking at is the structure of the basal-plane surface of alpha-alumina. This is a particularly dramatic case, because the shell model potentials predict a huge relaxation of the surface structure [11,12]. For example, the spacing between the plane of the surface aluminiums and the plane of oxygens beneath it is predicted to be at least 50 % less than in the bulk crystal. These predictions are based on the assumption that the material is completely ionic even at the surface - in other words, that the ions are Al³⁺ and O²⁻. But the Madelung potential must be completely different at the surface from what it is in the bulk. The charge transfer between ions might well be strongly influenced by the Madelung potential, and it is easy to imagine that the degree of ionicity at the surface might be considerably less than what is found in the bulk. The first-principles calculations give us a way of answering this question.

We have done a series of calculations on the relaxed surface structure of the basal-plane surface of Al_2O_3 . The calculations have been done in slab geometry, so that each slab of material is separated from the next slab by a vacuum layer. It turns out that quite thin slabs of typically 6 Å thickness and similar thicknesses of vacuum are quite enough to get fully converged results. Remarkably, when we relax the surface structure we find very similar results to what is predicted by the empirical shell-model potentials. To show this, table 3 gives the surface inter-planar spacings predicted by the two methods. The agreement is, indeed, not exact, but the systematics of the spacing changes is identical in the two calculations. The predictions for the relaxed surface energy are also in rather good agreement. For this particular surface, the first-principles calculations predict a surface energy of 1.76 J m^{-2} , while the shell model prediction [11] is 2.03 J m^{-2} .

I have not said anything yet about Hartree-Fock methods. A big effort to develop Hartree-Fock codes for treating periodically repeating systems has been put in by the group of Pisani and co-workers at the University of Turin in collaboration with Vic Saunders at Daresbury Laboratory. This has led to the widely used code CRYSTAL [6,13], which has been used in a range of calculations on both ionic crystals and other materials. It is already clear that the Hartree-Fock method too gives very good predictions for the properties of bulk crystals of materials like MgO and Al_2O_3 . Calculations on defects and surfaces in ionic materials are not yet as far advanced as those using DFT-pseudopotential methods. Part of the reason for this seems to be that it is less easy with the Hartree-Fock methods to get the calculations fully converged with respect to the size of the basis set. However, there will be great advantages in being able to compare the predictions of two completely independent methods, and there is every sign that the Hartree-Fock approach will also give very reliable results. The CRYSTAL code has already seen very important use in the construction of interaction models [7,14].

So can we trust the shell model? It is probably too early to be sure, but so far it has emerged unscathed from the rigorous testing provided by first principles calculations. I certainly do not expect to see first-principles methods put the shell model out of business. The ability to do rapid static and dynamical shell-model simulations on ionic materials will be important for many years to come. What will happen, though, is that the first-principles methods will allow us to distinguish much better between good and bad shell-model potentials, and will improve the quality of good shell models still further.

References

- [1] B. G. Dick and A. W. Overhauser, *Phys. Rev.*, **112**, 90 (1958)
- [2] C. R. A. Catlow, C. M. Freeman, M. S. Islam, R. A. Jackson, M. Leslie and S. M. Tomlinson, *Phil. Mag. A*, **58**, 123 (1988)
- [3] C. R. A. Catlow, M. J. Norgett and T. A. Ross, *J. Phys. C*, **10**, 1627 (1977)
- [4] A. De Vita, M. J. Gillan, J. S. Lin, M. C. Payne, I. Štich and L. J. Clarke, *Phys. Rev. Lett.*,

68, 3319 (1992)

- [5] A. De Vita, I. Manassidis, J. S. Lin and M. J. Gillan, *Europhys. Lett.*, **19**, 605 (1992)
- [6] L. Salasco, R. Dovesi, R. Orlando, M. Causà and V. R. Saunders, *Molec. Phys.*, **72**, 267 (1991)
- [7] J. D. Gale, C. R. A. Catlow and W. C. Mackrodt, preprint
- [8] L. J. Clarke, I. Štich and M. C. Payne, preprint
- [9] I. Štich, M. C. Payne, R. D. King-Smith, J.-S. Lin and L. J. Clarke, *Phys. Rev. Lett.*, **68**, 1351 (1992)
- [10] I. Štich, M. C. Payne, A. De Vita, M. J. Gillan and L. J. Clarke, *Proc. NATO ARW 'Computation for the Nanoscale'*, in press
- [11] W. C. Mackrodt, *J. Chem. Soc. Faraday Trans. 2*, **85**, 541 (1989)
- [12] P. W. Tasker, *Adv. Ceram.*, **10**, 176 (1988)
- [13] M. Causà, R. Dovesi, C. Pisani and C. Roetti, *Phys. Rev. B*, **33**, 1308 (1986)
- [14] N. M. Harrison and M. Leslie, *Molec. Simulation*, **9**, 171 (1992)

	calculated	experimental
a_0 (Å)	4.17	4.22
B (Mbar)	1.54	1.55 - 1.62
TO(Γ) (THz)	12.39	12.23
TA(X) (THz)	8.65	8.96
LA(X) (THz)	12.57	12.65
TO(X) (THz)	13.24	13.15
LO(X) (THz)	16.36	16.61

Table 1: Calculated and experimental values of lattice parameter a_0 , bulk modulus B and five phonon frequencies of MgO. Phonon modes are the transverse optic mode at the Γ point and the transverse and longitudinal acoustic and optic modes at the X point of the Brillouin zone.

		first-principles	shell-model	experimental
MgO	E_S	6.88	7.72	...
	ΔE_m (cation vacancy)	2.39	2.07	2.2, 2.28
	ΔE_m (anion vacancy)	2.48	2.11	2.42, 2.61
Li ₂ O	E_F	2.20	2.12	1.58, 2.53
	ΔE_m (cation vacancy)	0.34	0.21	0.40, 0.49
	ΔE_m (cation interstitial)	0.58

Table 2: First-principles, shell-model and experimental results for the Schottky energy E_S and the cation and anion vacancy migration energies ΔE_m of MgO, and the Frenkel energy E_F and the cation vacancy and interstitial migration energies ΔE_m of Li₂O (all energies in eV). All calculated results are for a 32-ion system of MgO and a 48-ion system of Li₂O.

	First principles Slab	Empirical Semi-infinite
aluminium	-86 %	-59 %
oxygen	+3 %	+2 %
aluminium	-54 %	-49 %
aluminium	+25 %	+26 %
oxygen		

Table 3: Percentage changes of interplanar spacing due to relaxation of the α -alumina basal-plane surface. Planes of atoms are specified in the left-hand column, the topmost plane being the layer of aluminiums on the surface; changes of spacing are given between successive planes. Results are given for the present first-principles calculations and for shell-model calculations on the surface of the semi-infinite crystal reported by Mackrodt [11].