

Ab initio total energy studies of minerals using density functional theory and the local density approximation

BJÖRN WINKLER

Mineralogisch-Petrographisches Institut der Christian-Albrechts Universität, Olshausenstr. 40, D 24098 Kiel 1, Germany

VICTOR MILMAN

Molecular Simulations, 240/250 The Quorum, Barnwell Road, Cambridge CB5 8RE, UK

AND

MICHAEL C. PAYNE

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

Abstract

Ab initio total energy calculations based on the local density approximation (LDA) and using a conjugate-gradient solver for the Kohn-Sham equations have been performed for cordierite, brucite, $(\text{Mg}(\text{OH})_2)$ and diaspore (AlOOH). The calculated fractional coordinates of all structures are in good agreement with experimental diffraction data. The angle of the non-linear hydrogen bond in diaspore is reproduced well. The Raman active OH stretching frequency in brucite has been calculated using the frozen phonon approach and the calculated stretching frequency is in very good agreement with the observed value. The energetically most favourable calculated orientation of the proton-proton vector of an H_2O molecule incorporated in the structural channels of cordierite agrees with findings deduced from spectroscopic data, and the calculated energy of hydration is in reasonable agreement with calorimetric data. It is therefore concluded that *ab initio* total energy calculations can confidently be used to predict properties of hydrogen bonded structures, which is difficult with conventional parameterized static lattice energy minimization calculations. An extension to the model is necessary to improve the agreement of the predicted to the observed lattice parameters for small structures.

KEYWORDS: total energy calculations, local density approximation, brucite, diaspore, cordierite, hydrogen bond, CASTEP.

Introduction

In computational mineralogy, microscopic models based on a parameterized description of the interatomic interactions are used to address a large variety of problems, including, to name but a few, isotope fractionation, Al/Si ordering, equations of state, structural phase transitions and lattice dynamics (Price and Parker, 1988; Winkler and Bührer, 1990; Winkler *et al.*, 1991; Dove *et al.*, 1993). The complexity of the models used in such

calculations ranges from rigid-ion models, in which only short-range repulsive and long-range Coulomb interactions are incorporated, to sophisticated core-shell models, which may utilize multi-shell, multi-body interactions.

These models are predictive if the parameterization of the interactions is transferable between different structures. Typical cases where the transferability is generally questionable are those which involve drastic changes in the crystal structure, such as changes in coordination numbers. It is also very

difficult to develop transferable potentials which take into account electronic effects commonly encountered in structures with transition metal ions, such as Jahn-Teller distortions. Furthermore, work over the last few years has shown that the development of a transferable potential describing simultaneously the geometric and dynamic aspects of hydrogen bonds is very difficult (Abbott *et al.*, 1989; Abbott, 1991; Collins, 1990; Winkler *et al.*, 1991).

To avoid problems due to an incorrect parameterization, *ab initio* (quantum mechanical) total energy calculations are increasingly applied to problems previously addressed by static lattice energy minimization techniques. Such calculations are predictive, as they are, in principle, parameter free. The underlying physics and constraints are well understood. They can, in principle, be used to investigate phenomena which are due to the electronic system, such as electric field gradients (Blaha *et al.*, 1985; Schwarz *et al.*, 1990; Singh *et al.*, 1992) or the origins of ferroelectricity and related phenomena (Cohen, 1992).

Currently a number of *ab initio* approaches are used and developed in parallel: very useful summaries of several techniques are given in books by Devreese and van Camp (1985) and Meyer and Pontikis (1991). Here, calculations based on the density functional theory (DFT), using the local density approximation (LDA), will be described. An excellent introduction to the method used here has been given by Gillan (1991). DFT asserts that the ground state energy of a system of interacting electrons moving in an external potential (due to the nuclei) is a unique function of the electron density, and that for a given external potential a minimization of the sum of the kinetic energy of the electrons and their mutual interaction energy will lead to the exact ground state energy associated with the given external potential. Problems arise due to the difficulty in obtaining the exchange-correlation part of the inter-electronic interaction energy. Here it is common to use the known exchange-correlation energy density of a homogeneous electron gas evaluated for the local density of the actual inhomogeneous system. This approach is called the local density approximation (LDA).

For a numerical self-consistent solution, the problem is reformulated to yield a set of Schrodinger equations for non-interacting particles, called the Kohn-Sham equations. Solving these equations self-consistently is computationally very demanding and necessitates an effective description of the wave functions. This has led to the development of different approaches. The method used in the present study relies on the fact that the change in the eigenstates of the electrons close to the core due to different chemical/crystallographic

environments is generally negligible, and it is only their influence on the eigenstates of the valence electrons which is of interest from a chemical point of view. This allows the use of effective (pseudo-)potentials for the valence electrons, i.e. the potential in which the valence electrons move, and which is due to the nucleus and the electrons close to the core, is calculated once only.

Ab initio total energy calculations are employed like conventional static lattice minimization calculations: the structural parameters of a trial structure are varied, so that the equilibrium ground state is obtained, which is characterized by the absence of any remaining forces on either the atoms or the bulk and by a minimal energy. The properties of the relaxed structure can then be derived from the dependence of the total energy on the structural parameters. *Ab initio* calculations have not superseded static lattice energy minimization techniques yet, as they are computationally much more expensive. With conventional static lattice energy minimization techniques even complicated structures with a few hundred atoms and sophisticated core-shell models are relaxed in a few seconds using modern workstations. Similar *ab initio* calculations for a structure with 50 atoms would take a few months of super-computing time. This has restricted the routine application of *ab initio* calculations to high symmetry structures with small unit cells. It also prevents the routine calculation of the changes in the total energy due to small displacements of the atoms in complex structures. With parameterized models such calculations yield the dynamical matrix in the harmonic or quasi-harmonic approximation. This is fundamental, as the eigenvalues of the dynamical matrix correspond to the frequencies of lattice vibrations and the associated eigenvectors describe the respective atomic displacements. These results then can be used to obtain thermodynamic properties or atomic displacement (thermal) parameters. In contrast to this, *ab initio* methods are generally limited to the calculation of harmonic phonon frequencies for lattice vibrations whose eigenvectors are known. The respective technique is called the frozen phonon approximation, and relies on the calculation of the total energy after imposing the displacement vector associated with the lattice vibration. While the calculation of phonon dispersion curves and phonon density of states of minerals from conventional lattice dynamics calculations is well established, the calculation of phonon dispersion curves via the frozen phonon approach necessitates the use of super cells, quickly exhausting the available computational resources for all but very small, highly symmetric structures. It should be noted, though, that the results obtained by this method are generally in excellent agreement with

experiment. In addition a number of groups are currently developing techniques which will allow frequency and eigenvector calculations without relying on the frozen phonon approximation (Wei and Chou, 1992; Gonze *et al.*, 1994).

In the present summary of our current work, we will briefly describe results pertaining to minerals obtained with a modern DFT-LDA package, CASTEP. Here we were mainly concerned with the modelling of molecular water and OH-groups in minerals. It has been mentioned above that this is a problem which is not easily addressed with conventional core-shell model calculations. We wanted to investigate in detail the reliability of such calculations and the possible need for a further extension of the model, as we would like to use calculations such as those presented here to understand neutron molecular spectroscopic data recently obtained for a variety of minerals (Winkler and Hennion, 1994; Line *et al.*, 1994; Winkler *et al.*, 1994b). We have therefore calculated the Raman active OH-stretching frequency in brucite, $\text{Mg}(\text{OH})_2$, the atomic coordinates in the non-linear hydrogen bond in diaspore, AlOOH , and the orientation of an H_2O molecule in cordierite. An in-depth discussion of details, such as the convergence behaviour, will be published elsewhere.

Technical details

The software package CASTEP (CAmbridge Serial Total Energy Package), which has been described elsewhere (Teter *et al.*, 1989; Payne *et al.*, 1992), and associated programs for symmetry analysis, were used for the calculations presented here. CASTEP is a pseudopotential total energy code which employs Perdew and Zunger (1981) parameterization of the exchange-correlation energy, supercells and special points integration over the Brillouin zone, and a plane-wave basis set for the expansion of the wavefunctions. The calculations were performed using norm conserving nonlocal pseudopotentials of the form suggested by Kleinman and Bylander (1982), where the pseudopotentials were taken from the CASTEP data base.

An application of the pseudopotential method for first-row elements has long been a problem. In these atoms there are no core states of the same symmetry as the valence $2p$ orbitals. As a result there is no effective screening and valence electrons feel the full potential of the ionic core. It is still possible to apply formally any standard scheme (Kerker, 1980; Bachelet *et al.*, 1982) and construct a pseudopotential for p angular momentum. This potential will be very deep, but still softer than the pure Coulomb potential of the ion. The same procedure can be also used to generate a hydrogen pseudopotential (Bachelet *et al.*,

1982). The problem with thus constructed potentials comes from the fact that we are using a plane wave basis set, and the representation of a very hard potential requires an exceedingly large number of plane waves. For hydrogen it has been shown that the use of a pseudopotential is not advantageous compared to the Coulomb (local) potential (Needs, priv. comm.).

Therefore, the main difficulty here is a poor convergence of the oxygen pseudopotential. We employed the optimization scheme based on the minimization of the kinetic energies of pseudo-orbitals beyond a certain critical wave vector (Lin *et al.*, 1992). This approach has been shown to produce a reliable oxygen pseudopotential for studies of oxides (de Vita *et al.*, 1992a,b). For Mg and Al no optimization is needed, as the original Kerker (1980) scheme produces soft potentials, and the overall convergence of the calculations for minerals with respect to the number of plane waves depends mainly on the properties of oxygen and hydrogen potentials. All these potentials have been shown to be transferable over the required energy range and free of the 'ghost' states which are sometimes introduced by the Bylander-Kleinman representation (Gonze *et al.*, 1990).

To obtain equilibrium structures for a given set of lattice constants, ionic and electronic relaxations were performed using the adiabatic or 'Born-Oppenheimer' approximation, where the electronic system is always in equilibrium with the ionic system. Relaxations were continued until the total energy had converged. In the present calculations kinetic cut-off energies between 594 and 1500 eV have been used. The Monkhorst-Pack scheme (Monkhorst and Pack, 1976) was used to sample the Brillouin zone. Seven points were used in the irreducible part of the Brillouin zone for brucite, 4 or 8 points for diaspore, and, due to limitations imposed by the availability of computational resources, only one point for cordierite. The symmetries of the structures were generally maintained by using an option to symmetrise the wave functions or by using constraints for the displacements of atoms on special positions. Some calculations have been performed without these constraints and gave identical results.

Results

Brucite

As an example of a hydrogen-containing mineral without hydrogen bonds we chose brucite, $\text{Mg}(\text{OH})_2$ (Fig. 1). Brucite has only five atoms in the unit-cell (Zigan and Rothbauer, 1967). All atoms are located on special positions, and only the z coordinates of the oxygen and hydrogen atoms are not fixed by

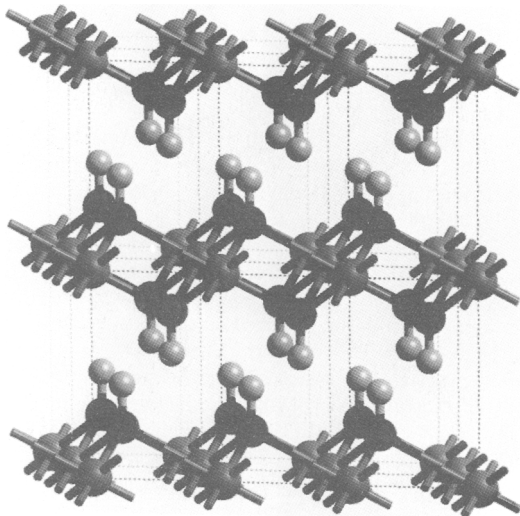


Fig. 1. The structure of brucite

symmetry. Starting from the experimentally determined structure (Zigan and Rothbauer, 1967) we performed a number of calculations with different lattice constants. The calculated pressure–volume relation indicated that, due to the finite basis set, corrections to the calculated pressure and total energy were necessary. We performed corrections according to the scheme proposed by Francis and Payne (1990). The correction term was obtained by varying the kinetic cut-off energy from 594 to 606 eV and from 500 to 1500, where both calculations gave the same correction term to within a few percent.

The predicted equilibrium lattice constants at zero pressure are $a = 3.00$ and $c = 4.57$ Å. For these lattice constants the z coordinates of the atoms are given in Table 1. A comparison between experimental and calculated data shows that every aspect of the structure is calculated about 4.5% too small. As the c/a ratio, the fractional coordinates and the OH stretching frequency (see below) are in good agreement with experimental data, it is reasonable to infer that the relative strengths of the interatomic interactions are predicted correctly, and that the too small cell parameters are due to a common phenomenon in LDA termed ‘overbinding’. This implies that a further extension to the model, a gradient correction, is necessary. This is similar to what has been observed by Lee *et al.* (1992) for ice, and our own preliminary gradient corrected calculations carried out at the time of writing show that the incorporation of a gradient correction yields lattice constants which are very close (less than 0.5%) to the experimental data.

Methods to obtain phonon dispersion curves have recently been described by Wei and Chou (1992). In the present study we only calculate the Raman active

Table 1. The experimentally determined (Zigan and Rothbauer, 1967) and calculated structure of brucite

	exp.	calc.	difference [%]
a [Å]	3.142(1)	3.00	−4.5
c [Å]	4.766(2)	4.57	−4.2
c/a	1.517	1.523	0.5
O(z)	0.2216(7)	0.2201	
H(z)	0.4303(12)	0.4356	
O–H [Å]	0.995	0.985	
Mg–O [Å]	2.102(3)	2.002	
O–O [Å]	2.787	2.655	
ν_{OH} , Raman [cm^{-1}]	3653	3633	−0.5
ν_{OH} , infrared [cm^{-1}]	3698	3642	−1.5

OH-stretching frequency at the Γ point, using the ‘frozen phonon’ approach (Kunc, 1985). Factor group analysis shows that there are two OH stretching vibrations, one Raman (A_{1g}) and one infrared (A_{2u}) mode, which have a simple eigenvector where both oxygen and protons move only parallel to [001]. We simplified the eigenvectors by taking into account the fact that oxygen has a much larger mass than hydrogen. Hence the total energy was calculated as a function of a hydrogen displacement parallel to [001] only, while all other structural parameters were fixed. The resultant $\Delta E = f(u)$ curve is shown in Fig. 2. In the harmonic approximation the change in energy, ΔE , is related to a phonon which is described by the mass weighted displacements, $m_i |u_i|^2$ of the i -atoms and the frequency, ω , by:

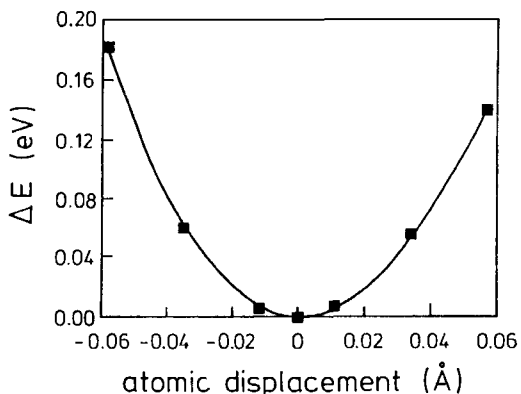


Fig. 2. The change of the total energy of brucite as a function of the proton position.

$$\Delta E = \frac{1}{2}\omega^2 \sum m_i |u_i|^2 \quad (1)$$

The change of the energy can be expanded in terms of u :

$$\Delta E = au^2 + bu^3 + \dots \quad (2)$$

where a fit of $\Delta E = f(u) = au^2 + bu^3$ is also shown in Fig. 2. From the excellent fit ($R = 0.999$) we obtain $a = 48.5(5) \text{ eV/\AA}^2$, and $b = -86(8) \text{ eV/\AA}^3$. In the harmonic approximation only the quadratic term is retained, and the phonon frequency is:

$$f = \frac{\omega}{2\pi} = \frac{\sqrt{a}}{2\pi} \quad (3)$$

This corresponds to a Raman frequency of 3633 cm^{-1} . The experimental value is 3653 cm^{-1} (Ryskin, 1974). A compression of a bond is energetically more unfavourable than a stretch; this causes the asymmetry of the $\Delta E = f(u)$ curve in Fig. 2. This asymmetry also shows that the infrared frequency will be slightly larger than the Raman frequency, as the corresponding infrared mode can be derived to a first approximation from the calculated values by averaging, for a given $|u|$, over ΔE for compression and stretching, and then refitting to obtain a' . This approximation treats the two hydroxyl groups as two independent oscillators having a phase shift of π for the infrared mode and being in phase for the Raman mode. In such an averaging the bu^3 term vanishes, and the resultant $\Delta E' = f(u)$ curve gives $a' = 48.8 \text{ eV/\AA}^2$, and, within this crude approximation, an infrared stretching frequency of 3642 cm^{-1} . The experimental value is 3698 cm^{-1} (Ryskin, 1974).

Diaspore

Diaspore, $\alpha\text{-AlOOH}$, is a strongly hydrogen bonded system (Fig. 3). Diaspore also has a simple structure (Busing and Levy, 1958; Hill, 1979) with only three kinds of atoms, but with its 16 atom unit-cell it approaches the dimensions of more interesting complex silicates. The atoms in diaspore lie on two planes at $z = \frac{1}{4}$ and $\frac{3}{4}$. The hydrogen bond is non-linear, i.e. the direction of the O-H bond and the O...O vector enclose an angle of 12° . The calculations performed for diaspore are computationally considerably more expensive than those for brucite. Hence we did not minimize the energy with respect to the lattice constants as extensively as for brucite. A comparison of the calculated stress tensor suggests that the calculated equilibrium lattice parameters would be too short by about 4–5% as well. We relaxed all the atomic positions, and the calculated atomic coordinates for fixed experimentally determined lattice parameters are given in Table 2. A comparison of the calculated to the observed (Busing and Levy, 1958) fractional atomic coordinates shows that, again similar to brucite, the topology of the

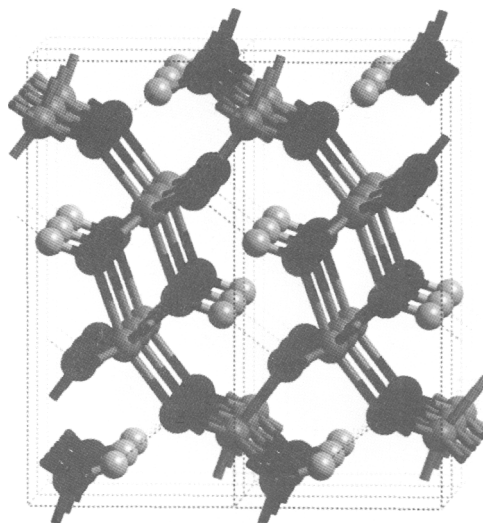


Fig. 3. The structure of diaspore

structure is reproduced well. For the OH distance the experimental value corrected for thermal motion (1.005 \AA) has been taken from the work of Busing and Levy (1958), the calculated value using the observed lattice constants is slightly larger (1.03 \AA). The non-linearity of the OH...O group has been mentioned before. In the model the observed angle is 11.5° . This agrees well with the experimental value of 12.1° .

Table 2. The experimentally determined (Busing and Levy, 1958) and calculated structure of diaspore

	exp.	calc
a [\AA]	4.401(1)	fixed
b [\AA]	9.421(4)	fixed
c [\AA]	2.845(1)	fixed
A1(x)	0.0451(8)	0.0449
A1(y)	0.8554(3)	0.8561
O1(x)	0.7120(5)	0.7109
O1(y)	0.1989(2)	0.1986
O2(x)	0.1970(5)	0.1944
O2(y)	0.0532(2)	0.0527
H(x)	0.4095(9)	0.4145
H(y)	0.0876(4)	0.0891
O-H [\AA]	1.0051 ^a	1.03
O2...O1 [\AA]	2.650	2.655
angle H-O ₁ -O ₁ [$^\circ$]	12.1	11.8

^a value corrected for thermal motion (Busing and Levy, 1958)

Cordierite

The calculations for cordierite have been described in detail by Winkler *et al.* (1994a). They consisted of a constant volume relaxation of the atomic coordinates of anhydrous and hydrous cordierite, and of an isolated water molecule. These very extensive calculations showed that for a static model, the energetically most favoured orientation of the proton-proton vector of a molecule incorporated into the structural channels was indeed parallel to [001], which had previously been inferred from spectroscopic data (Farrel and Newnham, 1967). The calculations also showed that the water molecule was only very weakly hydrogen bonded, which had been the subject of a previous discussion (Stout, 1975; Langer and Schreyer, 1976; Stout, 1976). We obtained the energy of hydration from the difference of the lattice energies, taking into account the energy of the isolated water molecule. This demands a high precision of the calculations, as the lattice energies are of the order of -20 keV, while the energies of dehydration are of the order of a few hundred meV. Considering that we are looking for very small differences of large numbers and that due to the very large system size the sampling of reciprocal space was very coarse, the calculated energy of hydration (0.4 eV) was in reasonably good agreement with the observed value (0.21 eV) (Carey and Navrotsky, 1992). Next to these specific points, these calculations have shown that the numerical methods used can also cope with large structures, as nearly 200 internal degrees of freedom have been relaxed very efficiently.

Discussion

The calculations for both brucite and diasporite showed that at zero pressure the calculated lattice parameters are about 4–5% smaller than the experimentally determined values. Although brucite is a layer-like structure, the ‘shrinkage’ was homogeneous and the *cla* ratio was modelled very well. Using the same pseudopotentials and the same code, de Vita *et al.* (1992a,b) predicted lattice constants which were in better agreement with experimental data for other oxides. Therefore, it is not some flaw in the oxygen pseudopotential which causes the ‘shrinkage’. Also, the description of the hydrogen is not the cause of the problem, as Hammer *et al.* (1993a,b) successfully modelled hydrogen adsorption on metallic surfaces. Hence the lattice constants are too small due to a general ‘overbinding’ often encountered in LDA calculations, which seems to become important if the structures are small and have oxygen and hydrogen as major constituents. The incorporation of gradient corrections, which also

have been necessary for ice (Lee *et al.*, 1992) then becomes essential. This has been corroborated by gradient-corrected calculations performed at the time of writing, which give lattice constants which agree to within 0.5% with the experimental data.

In the current calculations, the fractional atomic coordinates were reproduced well. This is typical of DFT-LDA calculations, and is especially encouraging in the case of the non-linear hydrogen bond in diasporite, as this is a result which cannot easily be obtained using conventional models. For brucite the calculations yield a stretching frequency of the O-H group very close to the observed value. The cordierite calculations have shown that properties of large complex silicates can be tackled with *ab initio* calculations if enough computing power is available. These calculations all have addressed problems which would be difficult to solve with parameterized models. As it is reasonable to expect that the cost of computing power will continue to decrease in the future, it is very likely that quantum-mechanical models will supersede parameterized conventional static lattice energy minimization calculations in the near future. Furthermore, next to problems involving hydrogen bonds, *ab initio* calculations can help in the interpretation of Mössbauer and NMR spectroscopic experiments, which are currently interpreted mostly on the basis of phenomenological models. Here, parameter-free models will remove any ambiguities in the interpretation. That these calculations will give reasonable results for minerals has been substantiated by calculations of the electric field gradients and asymmetry parameters for the *M1* and *M2* sites in forsterite, where good agreement with experimental data has been achieved (Winkler and Blaha, unpublished data). Earlier, Schwarz *et al.* (1990) and Singh *et al.* (1992) used this approach to show which one of competing models for the interpretation of NMR spectra of high T_c superconductors was correct. Furthermore surface properties and energetics of defect structures, which are very difficult to model with parameterized models, but are important as they allow the departure from idealized infinite perfect crystal models, have already successfully been addressed by quantum mechanical calculations. (Hammer *et al.*, 1992; de Vita *et al.*, 1992a,b; Gunderson *et al.*; 1993, Bass *et al.*, 1993; Milman *et al.*, 1994).

For the replacement of parameterized dynamic calculations which include temperature, such as molecular dynamics simulations (MDS), computing power has to become much cheaper to allow the simulation of large enough dynamic ensembles. The algorithms for molecular dynamics calculations within the framework of LDA already exist (Car and Parrinello, 1985; Payne *et al.*, 1992), and

diffusion paths have already been successfully calculated (Milman *et al.*, 1994). Such simulations will then allow the derivation of thermodynamic properties at any pressure-temperature conditions from the phonon density of states, as has been demonstrated for classical MDS by Winkler and Dove (1992).

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