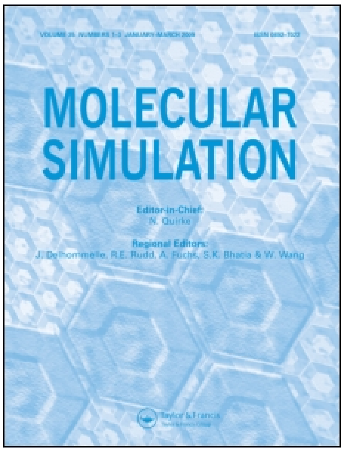

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The calculation of structural, elastic and phase stability properties of minerals using first principles techniques: A comparison of HF, DFT and Hybrid functional treatments of exchange and correlation

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THE CALCULATION OF STRUCTURAL, ELASTIC AND PHASE STABILITY PROPERTIES OF MINERALS USING FIRST PRINCIPLES TECHNIQUES: A COMPARISON OF HF, DFT AND HYBRID FUNCTIONAL TREATMENTS OF EXCHANGE AND CORRELATION

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We benchmark the performance of four treatments of electron exchange and correlation in the prediction of structural and elastic properties of a range of minerals. The treatments used are the Hartree–Fock (HF) theory, the local density approximation (LDA) and the generalised gradient approximation (GGA) to the density functional theory (DFT) and Becke's three parameter hybrid functional (B3LYP). We find that the hybrid functional, B3LYP method yields computed elastic properties in significantly better agreement to experiment than HF or DFT–LDA and performs at least as well, if not better than the most successful DFT–GGA functionals. We suggest that B3LYP is a simple, reliable and computationally efficient tool for the *ab initio* simulation of mineral systems.

Keywords: Hybrid functionals; DFT; B3LYP; LDA; GGA; HF

INTRODUCTION

Many mining and mineral processing techniques exploit differences in physical and chemical properties between various minerals to achieve their effective

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separation. The ability, or viability to effectively separate the various mineral phases can have a substantial impact on downstream "value-adding" processes that ultimately lead to commercial products. It is therefore important to understand, at the molecular level, the physical and chemical changes that occur during the processing of complex mineral ores. Experiments to probe these effects can be difficult to perform and interpret, as they often need to be carried out under extreme conditions, and so we can turn to the use of simulation as a complimentary technique for understanding the behaviour of these complex systems.

In many industrial applications, knowledge of the structure and phase stability of the mineral is required. As the mineralogical systems involved can be rather complex, any additional information that can be provided by simulation is invaluable in determining the stability of a sample and its behaviour under processing conditions such as grinding and milling which can subject the mineral to extreme pressures. Simulations have already provided useful information on the phase stability of minerals at extremely high pressures and together with experimental studies, can help clarify the behaviour and structure of a mineral at these conditions [1].

Before modelling mineral systems, it is essential to have some guide as to the reliability and transferability of available simulation techniques, particularly when computing properties in the absence of experimental data or where the property of interest is very sensitive to the theoretical treatment used. The growing body of theoretical work has shown that *ab initio* modelling techniques can provide a reliable method of computing the ground state electronic configurations for a wide variety of materials. The most common methods are based on either the Hartree–Fock (HF) or Density Functional Theory (DFT) within either the local density approximation (LDA) or its improvement, the generalised gradient approximation (GGA). The major approximation with these methods is in the treatment of electron exchange and correlation. Recently, Becke's three parameter hybrid functional (B3LYP) [2], a method combining HF and DFT originally developed in molecular studies, has been shown to be more reliable than pure HF or DFT for the prediction of optical properties such as the band gap [3]. A recent study has suggested that the hybrid functional techniques may be more reliable for the calculation of structural and elastic properties of minerals although this study only considered oxides [4].

In this study, we have benchmarked the performance of B3LYP with the HF and DFT treatments of exchange and correlation for the calculation of structural and elastic properties for a range of minerals including sulphides, oxides, halides, carbides and semi-conductors. The computing of elastic properties can be important in understanding geological processes, particularly those occurring at deep levels within the earth, and also effects arising from high temperatures and pressures generated during crushing and grinding. We have also computed the pressure required for the B1 (rock salt) to B2 (body centred) phase transition for a selection of minerals where this value has been measured experimentally.

METHOD

Computational Method

All calculations in this study have been performed using the CRYSTAL98 [5] code. The crystalline orbitals describing the wavefunction of the system are built from a linear combination of atomic orbitals (LCAO) [5]. Atom centred GAUSSIAN functions with *s*, *p* or *d* symmetry are used to describe the atomic orbitals. The main approximation is due to the basis set. To minimise the effect of this approximation, we have used high quality basis sets for each of the minerals studied. These basis sets have been generated and thoroughly tested in previous work on the individual minerals examined here (see Ref. [6] and references therein).

Four treatments of exchange and correlation were used. These were HF (where electron exchange is treated exactly within the single determinant approximation but correlation is neglected) [7], the LDA to DFT [8], the GGA to DFT and B3LYP [2]. The B3LYP functional used combines the non-local Lee-Yang-Parr [9] correlation functional with a mixture of the exact exchange energy and Becke's gradient correction to the LDA [10] as proposed by Stephens *et al.* [11]. The LDA functional calculations have been performed using the Perdew–Zunger parameterisation of the Ceperley and Alder quantum Monte Carlo simulations [12] and the GGA calculations have been performed using the functional developed by Perdew, Burke and Ernzerhof [13].

The *k*-space sampling was performed using Pack–Monkhurst grids [5,14]. For the cubic systems, we have used a shrinking factor 8 yielding 29 symmetry non-equivalent points in the irreducible Brillouin zones of the bulk crystals. For calculations performed on the NiO system, we have used the AF2 antiferromagnetic arrangement, which has been reported to be the ground state [15].

The truncation to the Coulomb and exchange series resulting from the use of local basis functions, is controlled by a series of five parameters, details of which can be found elsewhere [5,16]. These parameters have been set to very high tolerances (ITOLS 1–5 were set to 8 8 8 8 16, respectively, compared to the default value of 5 5 5 5 10) to minimise numerical errors.

TABLE I Lattice parameter a (Å), bulk modulus B_0 (GPa) and its derivative B' calculated with different treatments of exchange and correlation. Percentage errors in brackets, experimental errors listed where quoted

		B3LYP		*GGA*		*LDA*		*HF*		*Expt*	*Expt Error*
C-diamond	a	3.59	(0.5)	3.59	(0.6)	3.55	(−0.5)	3.57	(0.1)	3.567*	
	B_0	435.70	(−1.4)	431.40	(−2.4)	(474.50)	(7.4)	490.00	(10.9)	442†	(0.7)
	B_0'	3.45	(−13.8)	4.05	(1.3)	4.11	(2.8)	3.38	(−15.5)	4†	(15.8)
Si diamond	a	5.49	(1.1)	5.48	(0.8)	5.41	(−0.4)	5.51	(1.5)	5.4305*	
	B_0	90.25	(−7.8)	92.13	(−5.9)	100.00	(2.1)	104.80	(7.0)	97.9‡	
	B_0'	4.24	(1.9)	4.31	(3.5)	4.12	(−1.1)	3.75	(−9.9)	4.16‡	
CaO	a	4.85	(0.8)	4.84	(0.6)	4.71	(−2.0)	4.87	(1.2)	4.8108*	
	B_0	113.29	(2.1)	110.69	(−0.3)	134.90	(21.5)	117.90	(6.2)	111‡	(0.9)
	B_0'	3.70	(−11.9)	3.72	(−11.3)	4.32	(2.9)	3.92	(−6.6)	4.2‡	(4.8)
NaCl	a	5.75	(1.9	5.75	(1.9)	5.52	(−2.1)	5.80	(2.9)	5.6402*	
	B_0	24.22	(1.8)	23.90	(0.4)	29.17	(22.6)	22.24	(−6.6)	23.8b	(31.5)
	B_0'	3.78	(−22.9)	3.76	(−23.3)	4.17	(−15.0)	3.93	(−19.9)	4.9‡	(79.6)
NaCl B2	a	5.63		5.61		5.39		5.69			
	B_0	29.39	(−6.8)	29.10	(−7.1)	29.78	(−6.4)	25.31	(−10.9)	36.2‡	(11.6)
	B_0'	6.81	(70.2)	6.44	(60.9)	4.70	(17.5)	6.23	(55.7)	4‡	assumed
LiF	a	4.05	(0.7)	4.09	(1.7)	3.94	(−2.2)	4.01	(−0.4)	4.027¶	
	B_0	67.29	(1.2)	64.42	(−3.1)	81.41	(22.4)	75.50	(13.5)	66.5‡	
	B_0'	4.01	(14.5)	3.72	(6.4)	4.08	(16.6)	4.28	(22.3)	3.5‡	
KF	a	5.42	(1.5)	5.40	(1.0)	5.17	(−3.2)	5.46	(2.1)	5.344§	
	B_0	29.56	(0.9)	35.61	(21.5)	41.24	(40.7)	29.47	(0.6)	29.3‡	
	B_0'	4.30	(−20.4)	3.80	(−29.6)	5.02	(−7.0)	4.30	(−20.4)	5.4‡	
KCl	a	6.44	(2.3)	6.41	(1.8)	6.10	(−3.1)	6.55	(4.1)	6.2931*	
	B_0	16.10	(−22.6)	16.30	(−21.7)	23.92	(15.0)	15.33	(−26.3)	20.8‡	
	B_0'	4.35	(−13.0)	4.32	(−13.6)	5.32	(6.4)	4.18	(−16.4)	5‡	
LiCl	a	5.22	(1.5)	5.19	(1.0)	5.01	(−2.6)	5.29	(2.9)	5.143‖	
	B_0	30.21	(−5.3)	31.05	(−2.7)	39.80	(24.8)	28.35	(−11.1)	31.9‡	
	B_0'	4.26	(25.4)	4.26	(25.4)	4.86	(43.0)	4.15	(22.0)	3.4‡	
NaF	a	4.68	(0.9)	4.73	(2.0)	4.53	(−2.3)	4.64	(0.1)	4.6342*	
	B_0	44.80	(−4.1)	43.75	(−6.3)	59.55	(27.5)	47.35	(1.4)	46.7‡	
	B_0'	4.33	(−16.7)	3.99	(−23.2)	4.26	(−18.1)	4.61	(−11.3)	5.2‡	
NiO	a	4.22	(1.1)	4.17	(−0.2)	4.06	(−2.8)	4.27	(2.1)	4.177*	

TABLE I – *continued*

		B3LYP		*GGA*		*LDA*		*HF*		*Expt*	*Expt Error*
	B_0	205.90	(3.5)	225.15	(13.1)	268.09	(34.7)	202.10	(1.6)	199‡	
	B_0'	4.31	(5.2)	4.22	(2.9)	4.53	(10.5)	4.02	(−2.0)	4.1‡	
MgO	a	4.25	(0.9)	4.28	(1.6)	4.19	(−0.5)	4.21	(−0.1)	4.2117*	
	B_0	156.30	(0.2)	145.64	(−6.6)	160.84	(3.1)	173.57	(11.3)	156‡	(5.8)
	B_0'	3.91	(−16.7)	3.58	(−23.8)	3.79	(−19.3)	3.76	(−19.9)	4.7‡	(42.6)
CaF2	a	5.52	(1.0)	5.53	(1.2)	5.35	(−2.0)	5.53	(1.2)	5.4638*	
	B_0	82.82	(2.2)	79.38	(−2.0)	100.14	(23.6)	85.14	(5.1)	81‡	(1.5)
	B_0'	4.03	(−22.7)	4.00	(−23.5)	4.31	(−17.5)	4.06	(−22.3)	5.22‡	(6.7)
CaS	a	5.77	(1.5)	5.72	(0.6)	5.58	(−1.9)	5.88	(3.5)	5.684#	
	B_0	57.52	(1.4)	57.32	(1.1)	69.98	(23.4)	54.98	(−3.0)	56.7‡	
	B_0'	3.87	(−21.1)	4.32	(−11.9)	4.51	(−8.0)	3.89	(−20.7)	4.9‡	
SiC	a	4.41	(1.3)	4.42	(1.3)	4.37	(0.2)	4.40	(1.0)	4.358*	
	B_0	210.00	(−7.5)	204.32	(−10.0)	219.61	(−3.3)	238.31	(5.0)	227‡	(1.3)
	B_0'	3.52	(−14.1)	3.61	(−12.1)	3.57	(−13.0)	3.31	(−19.3)	4.1‡	(2.4)

* Adapted from Ref. [21].
† Adapted from Ref. [29].
‡ Adapted from Ref. [24].
¶ Adapted from Ref. [25].
§ Adapted from Ref. [26].
|| Adapted from Ref. [27].
Adapted from Ref. [28].

For each cubic system, at least 20 single point energy calculations were performed on cell volumes ranging ± 10% from the experimental volume. To reduce numerical errors in the potential energy surface, the most compact volume was selected as the reference geometry for the selection of the bielectronic integrals. For further details, see Ref. [5].

Calculation of Elastic Properties

The Bulk modulus (B) of a material is given by the expression:

$$B = -V\left(\frac{\partial^2 U}{\partial V^2}\right) \tag{1}$$

where V is the volume and U is the internal energy.

By fitting a polynomial to the single point energy calculations and using Eq. (1), a value for the bulk modulus can be computed. An alternate method for extracting the Bulk modulus is to use an equation of state (EOS), such as the Murnaghan [17] EOS (2)

$$U(V) = \left(\frac{B_0 V_0}{B_0'}\right)\left(\frac{1}{(B'-1)}\left(\frac{V_0}{V}\right)^{(B_0'-1)} + \frac{V}{V_0}\right) + U_0 \tag{2}$$

where U is the total internal energy, V is the unit cell volume, V_0 is the volume of minimum energy, B_0 is the zero-pressure bulk modulus, B' is the pressure derivative of the bulk modulus and U_0 is the minimum energy.

To calculate phase transition pressures of selected minerals, we minimised the enthalpy (H), with respect to the cell parameters (and hence volume, V) for a

TABLE II Summary of average errors

	B3LYP	*LDA*	*GGA*	*HF*
Cell parameter				
Average error	1.21	1.85	1.16	1.66
Std deviation	0.49	1.02	0.58	1.32
B_0				
Average error	4.30	17.41	6.51	7.53
Standard deviation	5.51	12.42	6.94	6.59
B_0'				
Average error	18.77	12.95	17.54	18.37
Std deviation	15.68	10.37	15.17	12.61

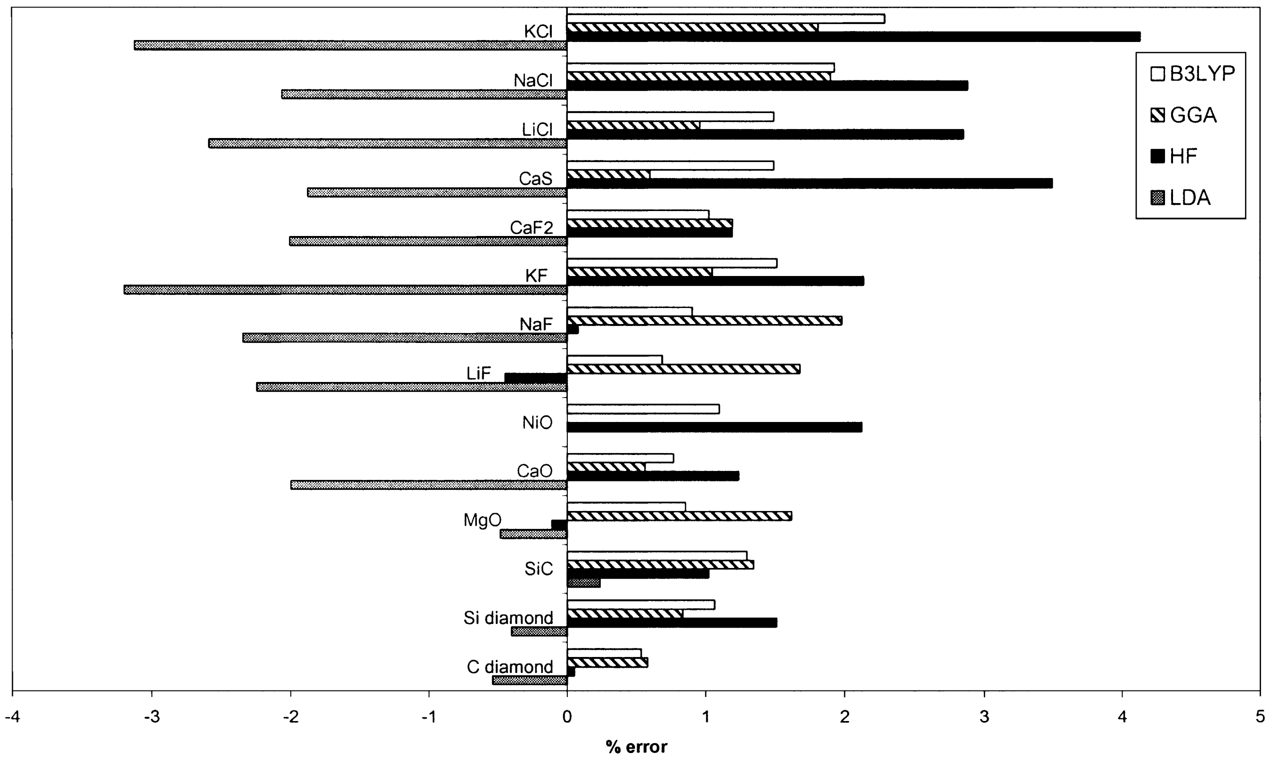

FIGURE 1 Percentage error in calculation of the cell parameter.

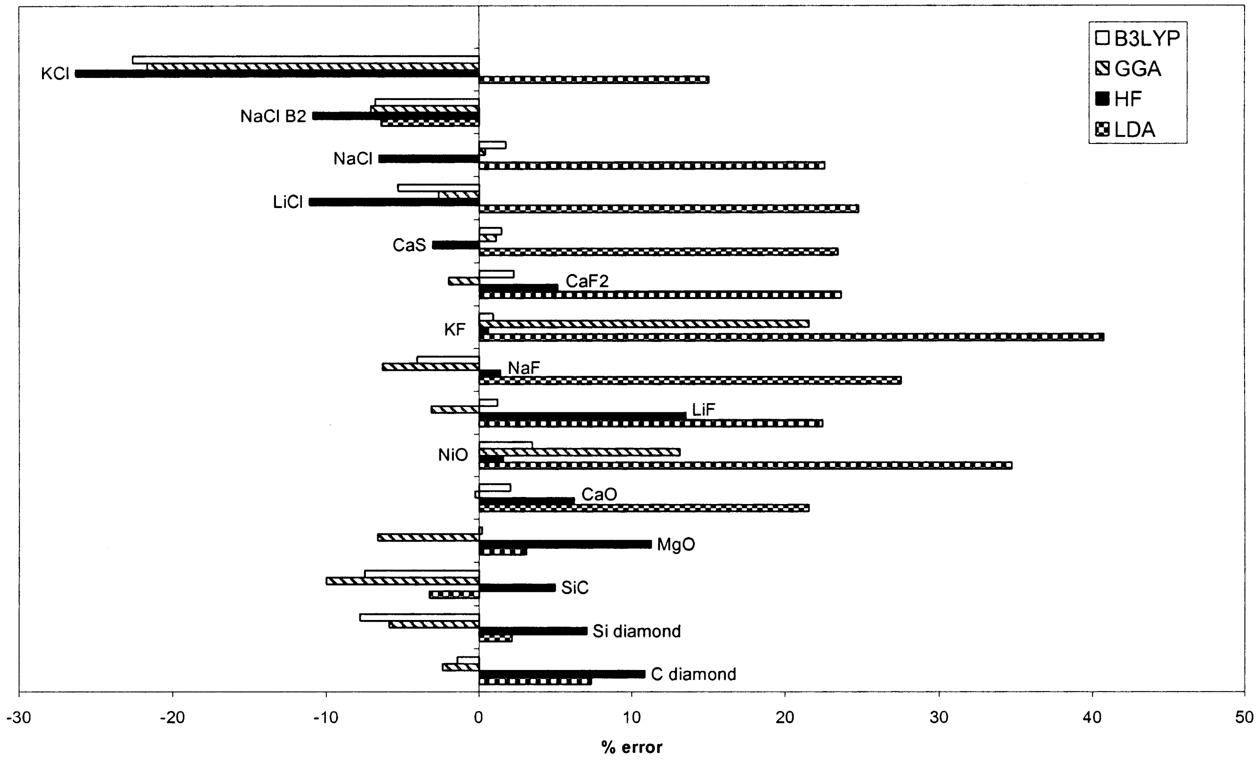

FIGURE 2 Percentage error in calculation of the Bulk Modulus (B_0).

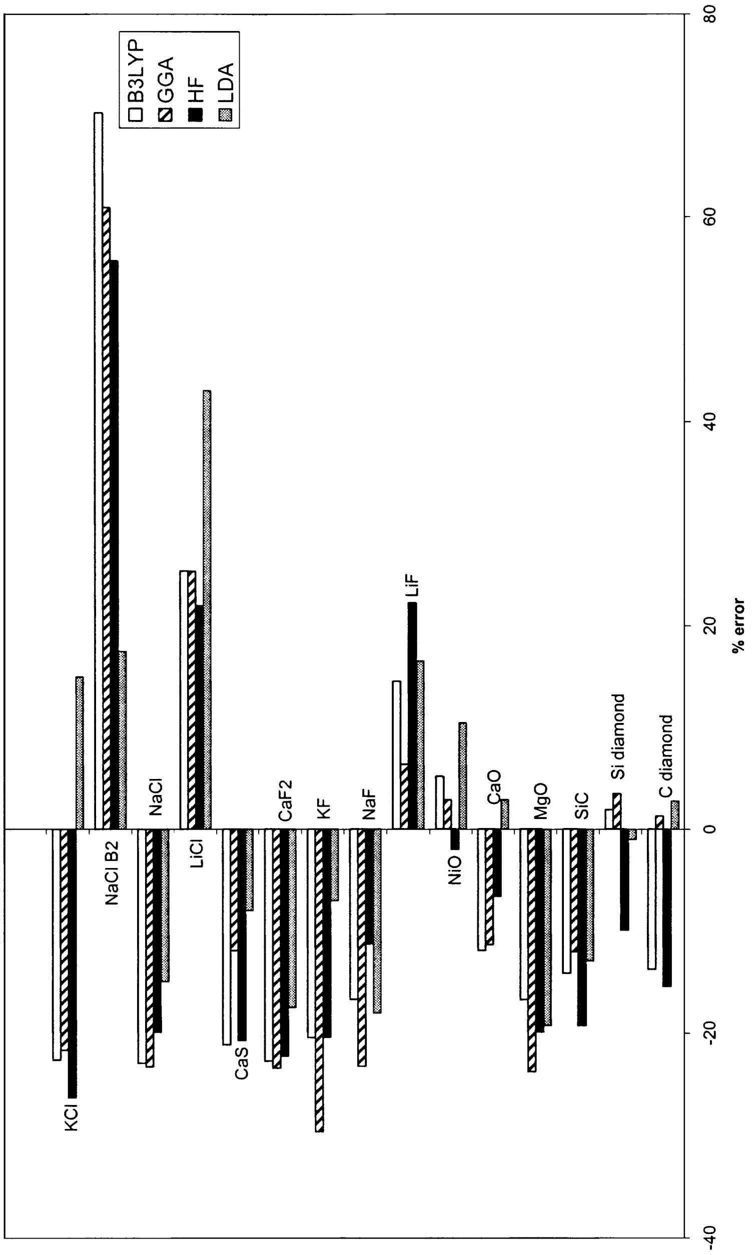

FIGURE 3 Percentage error in calculation of the derivative of the Bulk Modulus (*B*′).

range of pressures (P) in both the B1 and B2 phases as given in Eq. (3).

$$H = U + PV \tag{3}$$

The pressure of transformation is then given by the intersection of the enthalpy functions for the two phases.

RESULTS

The cell parameter, bulk modulus and its derivative were computed using the different treatments of exchange and correlation. Results are given in Table I. The average of the absolute error and its standard deviation for each of the parameters, are given in Table II, and the resulting errors with respect to the experimentally determined parameters are shown in Figs. 1–3.

We find that the computed cell length tends to be the most reliably predicted parameter, with the average error for all treatments of exchange and correlation being less than 2%. This is typical for such systems [4,18], however, a number of systematic trends with regards to the prediction of the cell parameters can be identified. Firstly, the HF approximation tends to overestimate cell parameters by about 1–2%, due to the neglect of interelectronic correlation effects, as reported previously [19]. DFT incorporates correlation effects in an approximate way with the result that the [20] LDA *overbinds* cells leading to an underestimation of the cell parameter by a similar amount. The GGA overcorrects for the *overbinding* of the LDA leading to a slight overestimate (about 1.2%) of the cell parameters. B3LYP yields cell parameters very similar to GGA–DFT.

We performed tests to compute the bulk modulus by fitting the results from the single point energy calculations to a range of polynomials from second order (quadratic) to sixth order. The values obtained from the polynomials were found to be sensitive to the order of the polynomial and the number of points fitted. Further tests using the Murnaghan EOS gave a more stable figure and consequently, we have used this EOS for the calculation of the results presented in this study.

In the case of the computed bulk modulus, LDA typically overestimates the bulk modulus by a significant amount (10–30%). HF, B3LYP and GGA tend to predict bulk moduli that are in better agreement with experiment but there are no obvious trends; for some materials, the bulk modulus is overestimated whilst for others, it is underestimated. However, it is important to note that in many cases, the experimental error is quoted to be as large as 10% (or even 32% in the case of NaCl [21]).

When comparing the performance of the theoretical simulations with experimental results such as the bulk modulus or its derivative, it must be borne in mind that the experimental measurement of such properties is very difficult. In the case of B', it is often assumed to be equal to 4. It is interesting to note that for most systems, HF, LDA, GGA and B3LYP give predicted B' in excellent agreement with each other but deviate by as much as 20–30% from the experimental value. Whilst we would expect some error from the fitting procedure used to extract B', it is worth noting that the experimental errors, when quoted, are sometimes quite large; the worst case being NaCl, which is quoted with an 80% error. This makes comparison with calculation difficult.

Finally, we have computed the pressure of the B1–B2 phase transformation for a selection of systems where the experimental value is well known namely, NaCl and CaO. For NaCl, we compute a phase transition pressure of 35 GPa when using B3LYP, compared to an experimental value of 30 GPa [22]. GGA and LDA give values of 27 and 24 GPa, respectively. For CaO, B3LYP gives a transition pressure of 70 GPa compared with the experimental value of 65 GPa [23]. These results suggest that the calculations performed using the B3LYP can be a reliable method for predicting phase transition pressures.

CONCLUSION

In the current study, we have benchmarked the performance of some of the most widely used first principles techniques for the calculation of the structural, elastic and phase stability properties of minerals. We find that it is possible to perform reliable simulations of a wide range of minerals with a good degree of confidence. In particular, we find that the structural properties such as the cell parameter can be computed using any of the methods tested to an accuracy of within 2% of the experimental value.

When calculating elasic properties, we find that the use of the Murnaghan EOS offers a simple and reliable method for extracting the bulk modulus and its derivative from a set of single point energy calculations with a greater robustness than alternative techniques such as fitting to polynomials. Comparisons with experiment can be difficult because the uncertainty in the experimental results is often very large. Nonetheless, for systems where these properties have been measured carefully, the agreement between experiment and theory is good. In addition, the good agreement of the predicted B' values between the different functionals is encouraging as this suggests that the *ab initio* calculations can provide a guide to the value of B' in minerals where large experimental uncertainties exist.

Our study reveals that the hybrid functional, B3LYP method yields computed values of the lattice constant and bulk modulus in significantly better agreement to experiment than HF or DFT–LDA and performs at least well, if not better than the most successful GGA functionals. Our tests also indicate that the B3LYP method may be useful as reliable method for predicting phase transition pressures.

In the light of the results presented here for elastic properties and elsewhere for band gap calculations, we suggest that the B3LYP is a simple, reliable and computationally efficient tool for the *ab initio* simulation of mineral systems.

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