All-atom ab initio energy minimization of the kaolinite crystal structure

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ABSTRACT

Calculations that minimize the energy and optimize the geometry of all atomic coordinates for two proposed kaolinite crystal structures were performed using a first-principles, quantum chemical code based on local density functional theory. All calculations were performed using published unit-cell parameters. Inner- and interlayer H atom positions agree well with those determined by Bish (1993) from neutron diffraction data and confirm a unit cell with $C_1$ symmetry.

INTRODUCTION

Accurate interpretation of high-quality crystal-structure refinements and spectroscopic data on adsorption at the molecular or atomistic scale would benefit from independent calculations of mineral structures and surfaces based on quantum-chemical approaches. One approach has been to use empirical or partial ab initio determinations of crystal structures and surface molecular configurations (Sherman 1991; Hess and Saunders 1992; Kubicki et al. 1996). However, the recent evolution in high-performance computers and ab initio quantum chemistry codes offers new, accurate, and inexpensive routes to understanding mineral structures (Winkler et al. 1995a; Brodholt et al. 1996; Smrcok and Benco 1996) and mineral surface-contaminant interactions such as those of interest in radioactive and chemical-waste remediation. The purpose of this study is to evaluate the local density functional computational method for accurate reproduction of structure and bonding in a sheet aluminosilicate mineral as a foundation for future study of surface relaxation phenomena for the extended mineral, water, and adsorbate complex. Typically, layered sheet structures, such as those representing clay minerals, are difficult to treat using the simpler empirical forcefield methods. Low symmetry, hydrogen bonding, and large localized charge separations require the more sophisticated and exact methods provided by the molecular orbital approach.

Here, we report the first all-atom geometry optimization of kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, using a periodic density functional method that was developed to run on massively parallel (MP) computers. The kaolinite Al octahedral sheet contains both interlayer OH groups that form hydrogen bonds with the adjacent Si tetrahedral sheet and inner OH groups associated with vacant octahedral Al sites. The interlayer and inner OH groups have been suggested (Giese and Costanzo 1986; Cygan et al. 1997b) to be significant in the surface electrostatics that influence the formation of host-guest complexes and thus may play an important role as a model in evaluating the transport of hazardous wastes. Numerous studies, both experimental (Adams 1983; Young and Hewat 1988; Bish and Von Dreele 1989; Bish 1993) and theoretical (Giese and Datta 1973; Giese 1982; Hess and Saunders 1992), have addressed the heavy atom positions and proton orientations in kaolinite; however, no optimization calculations involving all atoms of the unit cell in a periodic structure have been conducted.

Detailed and accurate quantum mechanical studies of the adsorption of small molecules onto hydrated mineral surfaces requires calculation of extended periodic surfaces. The alternative approach, using truncated clusters containing sites of interest, does not accurately represent the long-range interactions in the crystal. Boundary effects can lead to calculated adsorption energies that depend on cluster size and thus are not comparable with experimentally determined energies. The main purpose of the present study is to establish that the first-principles, periodic, density functional method is useful in reproducing the bulk structure and bonding in layered aluminosilicate minerals. Ultimately, we plan to apply the methods developed in simulating the bulk structure of kaolinite to the surface structure, and then to bulk and surface structures of other important layered aluminosilicate minerals.

METHODS AND RESULTS

The first-principles periodic bulk calculations used the local density approximation (Kohn and Sham 1965) to density functional theory (Hohenberg and Kohn 1964) in a Gaussian-based linear combination of atomic orbitals (LCAO) basis. The calculations were performed using the QUEST (quantum electronic structure) code, designed and written (Sears and Schultz, unpublished manuscript) for massively parallel, distributed-memory computer architectures. QUEST has been used successfully in bulk (Nelson et al. 1995), surface (Feibelman 1987), and molecular (Jennison et al. 1997) applications. Local density