Applications of *ab initio* quantum mechanical potential surfaces to mineral physics calculations

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Introduction

Recent studies have reported on the use of *ab initio* potential surfaces using a range of basis sets from a minimal STO-3G to a robust 6-31G* in the solid state physics of minerals and mineral surfaces (Lasaga, 1993, and reference therein). This paper explores the effects of electron correlations on the *ab initio* calculations and also expands the application to other mineral physics calculations such as albite and corundum by choosing the appropriate molecular clusters. Ultimately, the understanding of bonding and atomic processes in minerals will have to be based on extensive use of quantum mechanical calculations. One of the central aims of these calculations is to establish at what level *ab initio* quantum mechanical calculations can serve as a framework for the studying of the physics and chemistry of minerals. In particular, one must consider the effect of the size of the molecular clusters, the size of the basis sets, as well as the effects of electron correlation on the various properties being calculated. In addition, the representation of the quantum mechanical potential surface data by a potential that is easily used by others in molecular dynamics or mineral physics calculations, is another important problem. We will discuss some new representations involving the so-called EPEN/2 or QPEN potentials.

SiO$_2$

Various clusters have been chosen to model the local structure of quartz and cristobalite, among them the most commonly used ones are H_4SiO_4 and $H_6Si_2O_7$. Lasaga and Gibbs (see Lasaga, 1993) have carried out *ab initio* potential surface calculations at the STO-3G and 6-31G* levels based on these clusters and they were able to reproduce some of the physical properties of quartz and cristobalite quite well. Nonetheless, a recent study (Xiao and Lasaga, 1994) found that some of the calculated structural and physical properties are strongly basis set dependent. For example, two fully optimized conformations were found for the $H_6Si_2O_7$ cluster (Figure 1 a,b) by using the relatively small 3-21G* basis sets (Burkhard *et al.*, 1991; Kubicki and Sykes, 1993). Once larger (e.g. 6-31G*) basis sets as well as electron correlations are included, Figure 1 a) becomes unstable and there is only one energy minimum, which is shown in Figure 1 b). Figure 2 shows the calculated potential surfaces of $H_6Si_2O_7$ as a function of the Si-O-Si angles using different basis sets. It is important to point out that the Si-O-Si angles in conformation II are smaller than those in conformation I because of the formation of the two H···O bridges, and our calculated Si-O-Si angle at the MP2/6-31G* level, which is regarded as the most accurate one, is only
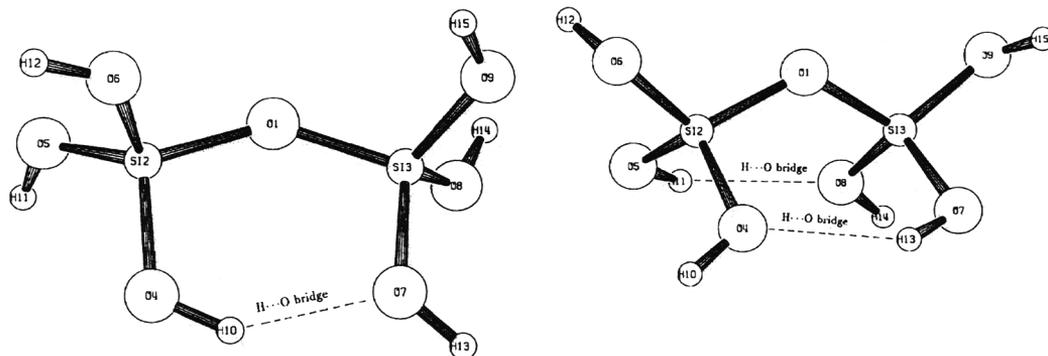
FIG. 1 $H_6Si_2O_7$ cluster. a) Conformation I which has one H···O bridge; b). Conformation II which has two H···O bridges.
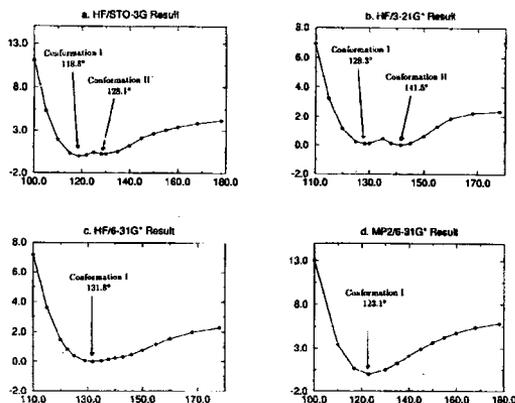
FIG. 2. Calculated $H_6Si_2O_7$ potential surface as a function of the Si-O-Si angle. Energies in Kcal/mol and angles in degrees. a) HF/STO-3G result; b) HF/3-21G* result; c) HF/6-31G* result; d) MP2/6-31G* result.

123.1°. In this case, the hydrogen bonds are exerting a strong effect on the malleable Si-O-Si angle. This indicate that care must be taken when using potential energies from lower level calculations. It also suggests that some restrictions should be applied to the optimizations of $H_6Si_2O_7$ cluster (to eliminate the unrealistic H···O hydrogen bonds) in order to mimic the local structure of quartz properly. Our new calculations on $H_6Si_2O_7$ as well as others such as H_6Si_2O disiloxane (which avoids the hydrogen bond problem) show that such considerations on the effects of basis set, cluster size, and optimization limitations are necessary for achieving accurate and consistent results.

Albite

The quantum mechanical potential surface calculations can be similarly applied to other minerals such as albite. Various clusters containing Si-O-Si and Si-O-Al with and without Na^+ have been used to mimic the local structure of albite and to generate the potential surface. The optimized geometries show they can reproduce details of the experimental structure of albite (e.g. the Si-O and Al-O bond lengths, the various Si-O-Al and Si-O-Si angles) nicely. We again carry out our calculations by using different basis sets plus electron correlation. The quantum

mechanical surfaces are used to generate a potential function that can be used in other mineral physics calculations. Some of the physical properties of albite, such as the compressibility, can be reproduced within 10% of the experimental value. The agreement is remarkable considering that there are no 'fudge' parameters in our treatment.

Corundum

Similar calculations will also be presented on corundum. The agreements between theory and experiment are promising.

Conclusion

Ab initio quantum mechanical calculations have been shown to provide a fundamental framework for mineral physics calculations. The results and potential surfaces being generated in this study are important for the complementary work carried out in the application of *ab initio* molecular orbital calculations to the study of adsorption kinetics, mineral diffusion, and surface geochemistry (water–rock kinetics) as well as for molecular dynamics and mineral physics calculations for melts and for high pressure crystal structures.

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