

Interatomic potentials for zeolites. Derivation of an ab-initio shell model potential

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Interatomic potentials for zeolites Derivation of an *ab-initio* shell model potential

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We have developed a new method for deriving parameters for the shell model of silica polymorphs. All parameters for the shell model are derived in a self-consistent way from *ab-initio* potential energy surfaces, polarisabilities, and dipole moments of small clusters. This yields an *ab-initio* partial-charge-shell model potential.

1. INTRODUCTION

There has been a long history in attempts to derive interatomic potentials for silica polymorphs [1]..[6]. The most often employed models in the parameterisations are the rigid-ion [7] and the shell model [8]. Initially the parameters for both models were completely or partially derived from experimental data of small systems like α -quartz. The applicability of those potentials based on experimental data turned out to be of limited value for properties not used explicitly in the parametrisation [9]. To obtain a potential which has no bias due to the incorporation of experimental data, parametrisation schemes have been developed for a rigid-ion model based on information which is obtained from *ab-initio* potential energy surfaces of small clusters [2,5,6].

Here we present the first *ab-initio* shell model potential for silica polymorphs which is derived from *ab-initio* potential energy surfaces, polarisabilities and dipoles of small clusters. The performance of our potential will be illustrated by presenting potential predictions for the structures of α -quartz, stishovite and coesite. The results will be compared with results obtained with the shell model potential of Jackson and Catlow [1] and with the rigid-ion model potential of Kramer *et. al.*[2], which will respectively be referred to as the JC potential and the KFBS potential.

2. METHOD

In our approach all potential parameters are derived from *ab-initio* potential energy surfaces, polarisabilities and dipole moments of small clusters. The clusters employed in our procedure are $\text{Si}(\text{OH})_4$ and $(\text{HO})_3\text{SiOSi}(\text{OH})_3$, referred to as respectively the monomer and the dimer. The O atoms in the clusters are described as polarisable, using the shell model.

The interactions between the atoms in the clusters are described with the following energy function: [1]

$$E^{pot} = \sum_{\substack{i,j \\ i < j}} [A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}] + \sum_{\substack{i,j \\ i < j}} \frac{q_i q_j}{r_{ij}} + \frac{1}{2} \sum_i k (r_{i,shell} - r_{i,core})^2 \quad (1)$$

The O-O interaction only acts through the shells, the Si-O interaction acts between the O shell and the Si ion. The third term is the harmonic interaction, which acts between core and shell of the same O atom. The Coulomb term includes, besides interactions of the atomic charges, also electrostatic interactions between cores and shells belonging to different atoms. All parameters in (1) are derived in an iterative procedure consisting of several fit procedures. This procedure is described in detail elsewhere [10] and will be outlined below. The O-O parameters are determined from a potential energy surface of the monomer which is obtained by varying two opposite O-Si-O angles while keeping the Si and O atoms in D_{2h} symmetry. The Si-O parameters are derived from a potential energy surface of the monomer in which the Si-O distances are symmetrically stretched while keeping the Si and O in T_d symmetry. During these fits the shell positions are determined by minimising the energy of the cluster with respect to the shell positions. The shell and atomic charges are determined from respectively the *ab-initio* polarisabilities and dipole moments of dimer configurations with variable Si-O-Si angle and fixed remaining angles and distances. The *ab-initio* data of the monomers and the dimers are respectively calculated with second order Møller Plesset and SCF with a high quality basis set using GAUSSIAN [11]. In our procedure all parameters, except the harmonic spring constant, denoted as k , are directly derived from *ab-initio* data. The value k is determined by the one that gives the smallest possible errors in the fit procedures. The accuracy of the obtained potential is illustrated by presenting the predicted structures and properties of α -quartz, coesite, and stishovite. Those calculations are done with the code THBREL [12].

3. RESULTS

To determine the k value we optimised parameter sets for a range of k values and we choose the value $k = 34.89 \text{ eV } \text{Å}^{-2}$ which gave the lowest errors in the fit procedures. Table 1 gives the parameter set belonging to this k , which is used in the calculations of the silica polymorphs.

Table 1
Our parameterset for the shell model, $q_{Si} = 2.7226$,
 $q_{O_s} = -2.0125$, $q_{O_c} = 0.6512$.

| $\alpha_i \alpha_j$ | A (eV) | ρ (Å) | C (eV Å ⁶) | k (eV Å ⁻²) |
|--------------------------------|--------|------------|------------------------|-------------------------|
| O _s -O _s | 266757 | 0.173411 | 0.0 | - |
| Si-O _s | 18122 | 0.17077 | 0.0 | - |
| O _c -O _s | - | - | - | 34.98 |

The results in tables 2 and 3 show that for α -quartz our potential is of reasonable accuracy; some elastic tensor elements are even closer to experiment than the predictions of both other potentials, even though no empirical data has been used whatsoever.

Table 2

Calculated properties of α -quartz compared with experiment and the predictions of the KFBS potential [2] and the JC potential [1]. Lengths are in Å, elastic constants (C_{ij}) are in 10^{10} N/m². Values closest to experiment are in italics. References denote experiment.

| quantity | exp | this work | KFBS | JC |
|-------------------------------|-------|-------------|--------------|--------------|
| α quartz [13,14] | | | | |
| $\bar{a}=b$ | 4.913 | 4.751 | <i>4.941</i> | 4.836 |
| c | 5.405 | 5.213 | <i>5.449</i> | 5.347 |
| u | 0.469 | 0.460 | <i>0.465</i> | 0.464 |
| x | 0.415 | 0.395 | 0.427 | <i>0.408</i> |
| y | 0.272 | 0.288 | <i>0.272</i> | 0.278 |
| z | 0.120 | 0.094 | <i>0.124</i> | 0.108 |
| d _{Si-O₁} | 1.614 | 1.621 | 1.605 | <i>1.614</i> |
| d _{Si-O₂} | 1.605 | 1.623 | 1.598 | <i>1.610</i> |
| γ | 120 | <i>120</i> | <i>120</i> | <i>120</i> |
| \angle Si-O-Si | 143.7 | 131.9 | 148.5 | <i>139.1</i> |
| C ₁₁ | 8.68 | <i>8.85</i> | 9.06 | 9.47 |
| C ₁₂ | 0.70 | 1.67 | <i>0.81</i> | 1.84 |
| C ₁₃ | 1.91 | 1.15 | 1.53 | <i>1.97</i> |
| C ₁₄ | -1.80 | -1.73 | <i>-1.77</i> | -1.45 |
| C ₃₃ | 10.58 | 11.26 | <i>10.70</i> | 11.61 |
| C ₄₄ | 5.82 | <i>5.46</i> | 5.03 | 5.00 |
| C ₆₆ | 3.99 | 3.59 | <i>4.12</i> | 3.81 |
| ϵ_{11}^0 | 4.45 | 2.42 | 1.95 | <i>4.74</i> |
| ϵ_{33}^0 | 4.81 | 2.46 | 1.99 | <i>5.01</i> |
| ϵ_{11}^∞ | 2.36 | 1.81 | - | <i>2.12</i> |
| ϵ_{33}^∞ | 2.36 | 1.82 | - | <i>2.14</i> |

Table 3

Calculated properties of silica polymorphs compared with experiment and the predictions of the KFBS potential [2] and the JC potential [1]. Lengths are in Å. Values closest to experiment are in italics. References denote experiment.

| quantity | exp | this work | KFBS | JC |
|---|------------|---------------|--------------|---------------|
| coesite [15] | | | | |
| a | 7.136 | 7.019 | 7.271 | <i>7.115</i> |
| b | 12.369 | 12.138 | 12.493 | <i>12.291</i> |
| c | 7.174 | 6.832 | <i>7.138</i> | 6.805 |
| $\langle d_{\text{Si-O}} \rangle$ | 1.611 | <i>1.612</i> | 1.601 | 1.607 |
| β | 120 | <i>120.03</i> | 120.7 | 119.5 |
| $\langle \angle \text{Si-O-Si}_1 \rangle$ | <i>180</i> | <i>180</i> | <i>180</i> | <i>180</i> |
| $\langle \angle \text{Si-O-Si}_2 \rangle$ | 143.6 | 134.2 | 150.5 | <i>138.7</i> |
| stishovite [16] | | | | |
| a | 4.171 | 4.089 | <i>4.149</i> | 4.025 |
| c | 2.665 | 2.591 | <i>2.662</i> | 2.775 |
| $d_{\text{Si-O}_1}$ | 1.809 | 1.714 | <i>1.790</i> | 1.728 |
| $d_{\text{Si-O}_2}$ | 1.757 | 1.750 | <i>1.755</i> | 1.782 |
| α | 90 | <i>90</i> | <i>90</i> | <i>90</i> |

A large error is found for the Si-O-Si angle in all structures studied, which might be due to the lack of an appropriate Si-O-Si bending term in our potential. For coesite and stishovite our potential performs as well as for α -quartz, while the KFBS potential and JC potential become less accurate for coesite and stishovite respectively, which indicates that despite the error in the Si-O-Si angle, our potential might have a higher transferability. Preliminary calculations on the low frequent phonon spectra and thermodynamic properties for α -quartz, done with the code PARAPOCS [17], show that our potential outperforms the KFBS potential for those properties.

4. CONCLUSIONS

We have derived the first fully *ab-initio* partial charge shell model potential from both *ab-initio* potential energy surfaces and *ab-initio* electrostatic data of small clusters, and we have shown that this potential gives reasonable agreement with experiments for a range of properties of α -quartz, coesite and stishovite.

We also conclude that our potential needs some further improvement, because for three silica polymorphs considered our potential predicts an Si-O-Si angle which is too small. We think that this indicates the lack of an appropriate (*ab-initio*) Si-O-Si bending term in our model. Notwithstanding this limitation, our potential predictions for several properties of the studied silica polymorphs, provides an improvement over both the predictions of the JC and KFBS potentials.

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