Encoding First Principles Electronic Structure Information in Pair Potentials for SiO₂. I. Parameterization

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Abstract

Potentials generally used in molecular dynamics (MD) simulation of SiO₂ properties customarily are calibrated to a combination of computed molecular electronic structure data and experimental crystalline data. The present study tests parameterization to data from high-level, first-principles electronic structure calculations *alone*. The issue is crucial to the success of multi-scale simulations. They require a consistent embedding of the so-called quantum mechanical region (forces from gradients of quantum mechanical total energies) in a classical interionic potential region. We parameterized a widely used form of effective interionic potential for SiO₂ from a high quality calculated data for H₄SiO₄ and H₆Si₂O₇ clusters and for α-quartz.

Introduction

The broad success of molecular dynamics (MD) simulation of condensed phase properties rests upon inter-ionic potentials as effective substitutes for the explicit quantum mechanics of bonding by electrons [1, 2]. SiO₂ is a technologically and scientifically important example [3]. Though there are many parameterized interactions for SiO₂ [4, 5], the issues of interest in multiscale simulations, our focus, are easily illustrated with the so-called TTAM [6] and BKS [7, 8] pair potentials. (The acronyms refer to the respective sets of authors.) These potentials are heavily cited in the materials literature, a fact that suggests they are viewed as successful by the materials simulation community [9].

As published, the TTAM and BKS potentials were parameterized to first-principles electronic structure results for a small cluster in combination with experimental data for α-quartz [6-8]. The "TTAM / BKS" form is

$$U_{ij} = \frac{\kappa q_i q_j}{r_{ij}} + \alpha_{ij} \exp\left[-\beta_{ij} r_{ij}\right] - \frac{\gamma_{ij}}{r_{ij}^6} \qquad (1)$$

where the ions i, j have relative displacement r_{ij}. Energies are in eV, lengths in Å, the q_i are in units of electron charge magnitude, and κ is the conversion from electrons² per Å to eV (~ 14.402). From their functional forms, the three terms are called Coulomb, Buckingham, and van der Waals terms, respectively. (Our notation differs from the originals to facilitate comparative presentation.)

Of course, three-body interactions are known to be important for ceramics [8, 10, 11], but the realism of the potential is not the issue. Rather, we have a single, fundamental concern: given a successful, popular form of potential, what are the effects of using different first-principles electronic structure inputs for parameterization? The context is multi-scale simulations. In them, the forces in a relatively small region, the so-called QM region, come from some choice of approximate Quantum Mechanics. The QM region is embedded in a much larger collection of particles whose dynamics are determined by inter-ionic potentials, the "CM region". Brenner [12] has given a comprehensive discussion of the issues of potential parameterization for ordinary MD simulations. Obviously those simulations do not involve embedding a QM region, the procedure we ultimately have in mind.

Both BKS and TTAM used the same broad approach to parameterization but with significant differences in detail. Each group picked a terminated SiO₄ cluster but with different terminations. Each then found multiple parameter sets that fit the potential to Hartree-Fock (HF) results for the structure and energetics of their cluster. From among those parameter sets, each group chose the one set that yielded the best fit to a selected set of calculated crystalline properties. Details differ, but that is the essential scheme.

For a multi-scale calculation to be unequivocally predictive, the calibration to experimental data would have to be eliminated. Achieving that freedom from experimental calibration is closely related to the primary focus of this paper. From that perspective the objective is to obtain the parameter set for a given potential that provides the best possible reproduction of calculated QM properties. This is equivalent to pursuing the implied logic of the BKS / TTAM approach to its end.

The computed data reported in Ref. [13] show that this is not an easy task. That study treated "chemically or physically appealing" clusters. It found a wide variation in calibration data sets even if one restricts consideration to such clusters. The variation has two broad sources. First, there is no unique choice of plausible reference clusters. Moreover, results for any particular cluster vary substantially with choices of methodology (level of refinement of approximation, basis set size, etc.). The other extreme for a calibration system, the perfect crystal alone, was studied in Ref. [14]. Comparison of the crystalline and cluster results in those two papers makes clear that calibration of the

same potential form will yield significantly *different* parameters.

As an example of reference data differences, the best-quality molecular calculations of Ref [15] give a range of 1.557 - 1.748 Å for the equilibrium Si-O bond length in 12 clusters $H_nSi_xO_y$. This range is in sharp contrast with the α-quartz companion study [14], which obtained values of 1.628 - 1.638 Å. Clearly the question is, do these differences affect the MD results for a many particle system significantly? We show here that the answer is unambiguously affirmative and characterize the differences.
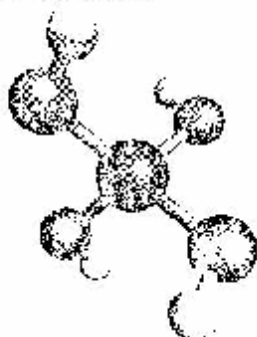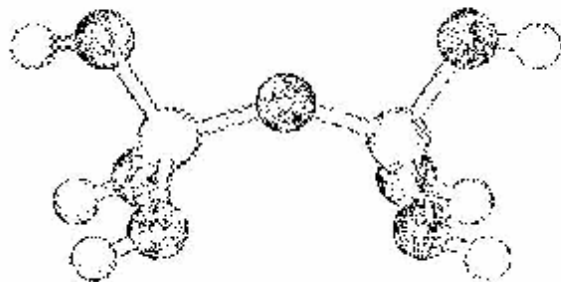

Figure (1): H_4SiO_4 (BKS).

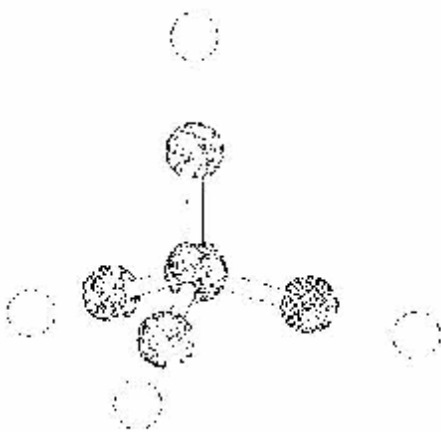Figure (2): $H_6Si_2O_7$ (TTAM)

Figure (3): $SiO_4^{?} - 4e^{?}$ (TTAM)

Parametrizations
A. Cluster Energetics

First we consider the consequences of parameterizing to cluster energetics alone. This approach is appealing in part because of its strong connection with chemical transferability concepts.

Use of cluster forces is considered below. It is helpful to distinguish what we will call BKS-type and TTAM-type parameterizations. These differ by the absence of non-coulombic Si-Si interactions in BKS-type fits (BKS: coast system 0) versus their presence in TTAM. Notice, however, that our use of "TTAM type" does not signify an atom-by-atom additive parameterization, the procedure used by TTAM.

Because there is no unique *a priori* choice of parameterizing cluster, we used two intuitively relevant choices. For BKS-type fits, we chose the cluster BKS [7, 8] used, H_4SiO_4 (FIG. 1). Fitting purely to it is a test of the robustness of the BKS procedure without recourse to experimental crystalline data as a corrective. For TTAM-type fits, we chose $H_6Si_2O_7$ (FIG. 2). It tests the significance of including a real Si-Si interaction in a silica-like cluster. In contrast, were we to apply the logic of the TTAM atom-by-atom parameterization approach to their cluster, $SiO_4^{4-} + 4e^+$ (FIG. 3) alone, the odd result would be a non-Coulomb Si-Si interaction from a cluster with only one Si. We also did not use the cluster employed by TTAM for technical reasons: the bare terminating charges cause problems. See Ref. [15] for details.

For reference, all the calculations on the BKS cluster, H_4SiO_4, were done at the highest level of refinement [CCSD(T) with the richest basis set, aug-cc-pVDZ; see Ref. 15 for nomenclature and details]. Our fitting followed the BKS prescription for handling the terminating H atoms. They were treated as scaled silicons in the pair potential $Q_H = Q_{Si}/4$, with no other interaction. We calculated energies on a grid of 15 geometries around the computed equilibrium configuration: a single Si-O bond stretched by ± 0.4, ± 0.2 Å, all four Si-O bonds uniformly dilated by ± 0.4, ± 0.2 Å, and one O-Si-O bond angle distorted by ± 6°, ± 4°, ± 2°. The BKS cluster introduces an unanticipated, spurious term and an effect. As shown in Ref [15], a high-level calculation of the equilibrium H_4SiO_4 geometry has two distinct O-Si-O angles, 103.3° and 114.2°. This behavior, which did not occur in the original BKS calculation, is a consequence of H-termination and the resulting O-H interaction. The two distinct angles force the fitted O-O potential to compromise between its shorter and longer equilibrium O-O distances. The only way to do that with a pairwise potential (which has only a single extremum), eq. (6), is via parameters that give an unphysical potential. Such behavior showed up severely in the actual parameterization: the fitted O-O potential has a local *maximum* at the minimum, 103.3°, of the CCSD(T) energy as a function of the smaller O-Si-O angle.

The BKS cluster energies as a function of geometric configuration and relative to the equilibrium energy are listed in Table I. These were fit to the BKS/TTAM form eq. (1) by least squares

and the use of the code ROBFIT [15]. The fitting is difficult in two specific senses. It is hard to avoid spurious negative parameters. In particular, it is easy to obtain $\gamma_{O-O} < 0$. In the original BKS parameterization γ_{O-O} was set to zero in the cluster part of the fit, and then determined entirely from the crystalline part of their fitting procedure. Working with cluster data alone precludes this remedy.

Table (1): Energy shifts (Hartree) for the unconstrained BKS cluster, H_4SiO_4 from CCSD(T).

One R_{Si-O}	+0.2 Å	+0.4 Å	-0.2 Å	-0.4 Å		
ΔE	0.0163496	0.0487257	0.0324494	0.1953456		
All R_{Si-O}	-0.2 Å	+0.4 Å	-0.2 Å	-0.4 Å		
ΔE	0.0702095	0.2053619	0.1402291	0.8431855		
$\angle O-Si-O$	-6°	+4°	12°	-2°	-4°	-6°
ΔE	0.0015581	0.0007114	0.0001836	0.0001944	0.0008015	0.0018650

It is unclear how to weight configurations that are energetically far from equilibrium in the fitting. Note Table 1 again. The issue does not seem to have been addressed in earlier work. Eventually we settled on an inverse linear weighting $w_i = (F_i - E_0) = (F_i - E_0)$ where E_0 is the calculated equilibrium total energy and F_i are the energies of the strained configurations, with $i = 1$ the strained configuration nearest in energy to F_0. The resulting parameters are in Table II. We do not recommend these parameters for materials simulations because of the unphysical O-O local maximum just discussed as well as the general grounds mentioned earlier.

Table (2): Parameters of the BKS type for Silica from fitting to energetics of the unconstrained H_4SiO_4; see text for cautionary notes. Q_i in units of electron charge, α_{ij} in eV, β_{ij} in Å^{-1}, γ_{ij} in eV-Å^6.

	Q_i	α_{ij}	β_{ij}	γ_{ij}
Si-Si	2.0267	0	0	0
Si-O		18003.799	4.74237	133.7542
O-O	$-Q_{Si}/2$	1388.7787	3.93408	242.4551

One way to evade the problem of two O-O equilibrium separations is to use the "tetrahedrally constrained" ("tc") cluster results from Ref. [13]. Those calculations used the same method and basis on a BKS H_4SiO_4 cluster constrained to tetrahedral O-Si-O geometry with the terminating Hs cyclic at the dihedral angle found by BKS. The imposed symmetry of course resolves the O-O problem but at a considerable cost in strain energy; see Ref. [13]. The symmetry constraint also decouples the bond stretch (T_d) and angular (D_2) modes of motion for fitting. Calculated energies on a grid of 14 bond lengths and 17 angles went into the fit. The resulting parameters are in Table III.

Table (3): Parameters of the BKS type for Silica energetics for H_4SiO_4 constrained to tetrahedral geometry; see text for details. Units as in Table II.

	Q_i	α_{ij}	β_{ij}	γ_{ij}
Si-Si	2.4	0	0	0
Si-O		7293.45	4.7938	25.980
O-O	$-Q_{Si}/2$	1301.93	2.6898	329.428

In addition to the general caution about recommending any of these parameter sets, there is a strong reason to distrust this particular set. The minimum of the fitted energy occurs at a notably larger angle, about 117°, than the minimum in the reference data. Curiously, the published BKS parameters have the same aw. FIG. 4 displays the problem. Notice in particular that the fitted parameters give a potential that replicates the bond stretch energies much better than the published parameters but that both sets miss the minimum in the angular energies. (Notice that the zeros of energy have been shifted to match in FIG. 4. The published BKS and TTAM parameters give a zero of energy that is drastically different from the separated atom limit of the molecular or crystalline calculations.)

Turning to the TTAM-type fitting, we chose $H_6Si_2O_7$ as the reference molecule in part because it had been used as a surrogate for silica energetics since at least the work of Newton and Gibbs [16]. A pertinent review from that period is by Gibbs [17]. More recently Wong-Ng et al. [18] modeled some aspects of silica fracture mechanics based on Restricted Hartree-Fock (RHF) calculations for $H_6Si_2O_7$. Moreover, this molecule does provide information on the Si-Si interaction. In the present work, the calculated molecular energies (in the CCSD approximation) were for 12 conformations: equilibrium plus 11 stretches of a single Si-O bond [13]. This relatively small sample of configurations illustrates the limits imposed by computational cost. In particular, detailed exploration of the weak dependence on the central Si-O-Si angle would have been very costly. See Ref. [13] for details. However, the relative success of a quantum mechanical Hamiltonian

parameterized to the stretching data alone [19] was encouraging.

TTAM-type fitting for clusters is complicated by the fact that β_i values in the vicinity of the TTAM value tend to make the total potential energy rather insensitive to the prefactor α_{ij}. If Q_{si} also is kept as a variational parameter, this fitting instability generally worsens. Since the primary issue for this part of the study was the Si-Si interaction, we would have preferred to address the issue by fixing all of the other parameters (Si-O, O-O) to the published TTAM values. Then with a starting value for Q_{si}, the parameters α_{SiSi}, β_{SiSi} and γ_{SiSi} could be fitted. This approach fails because the Si-Si distances are always such that the Si-Si potential is sampled only in its tail. The potential is quite flat there and the fitting is ill-posed. Two other fits do work, at least in the sense of providing a reasonably close representation of the CCSD energy as a function of bond distance. One is to fit only the Si-O parameters; the other is to fit both Si-O and Si-Si parameters. For the latter case we tried both $Q_{si} = 2.4$ and 2.6 with relatively little effect on the overall quality of fit. In both cases all other parameters were fixed at published TTAM values. Notice that implicitly this forces a reliance on experimental data. The parameters that result are in Table IV.

Table (4): Parameters of the TTAM type for Silica from fits to $H_6Si_2O_7$. See text regarding Q_{si}

	Q	α_{ij}	β_i	γ_{ij}
Si-Si	2.4 (chosen)	8.729×10^5	15.2147	4500.541
Si-O		19657.686	4.39225	10.039
O-O	$-Q_{si}/2$	1388.92	2.8166	214.877
Si-Si	2.6 (chosen)	8.729×10^5	15.3263	3970.636
Si-O		10062.449	4.35223	107.517
O-O	$-Q_{si}/2$	1338.92	2.8464	214.877

B. Cluster Forces

Since proper embedding of a QM region in an MD simulation is the objective, fitting to computed forces (energy gradients) might be superior to fitting to computed energies. The two approaches obviously are equivalent on an arbitrarily dense grid. But on a finite grid, the forces at a point correspond to the infinitely dense mesh limit of energy differences at multiple grid points. Therefore if computed forces are available from the electronic structure calculation it is uneconomical to ignore them. Also there is a seemingly trivial but operationally important advantage to calibration against computed forces. In fitting to computed energies, the zero of energy in the electronic structure calculation (cluster or solid) differs from the zero for the same over pair potentials by a constant. Since that constant offset is unknown a priori, it must be obtained by the fitting procedure even though it is irrelevant so far as embedding the dynamics is concerned.

Obviously that does not happen with calibration to forces.

Most modern molecular codes provide "analytic gradients". This is quantum chemistry jargon which signifies that, for each nuclear configuration, the code computes force components from analytical expressions for the gradient of whatever approximation to the QM total energy was chosen. Typically the gradient components are with respect to internal nuclear coordinates, a tedious nuisance but not a true barrier. Such is the case with the ACES-II code [20] we used. Analytical gradients are relatively uncommon in periodic codes. Fitting function algorithms, such as in the code GTOFF we used [21], have a particularly difficult technical problem of dealing with so-called Pulay forces associated with the fitting functions. Thus GTOFF does not have analytical gradients, so this part of the study was restricted to the molecular clusters.

Once again, we primarily used the "ref" H_4SiO_4 BKS cluster. Gradients for distortions of H_4SiO_4 with the published BKS parameters, turn out to be closer to the CCSD(T) gradients than might have been supposed. See FIG. 5. Notice that the fitted parameters reproduce the T_d force components from the electronic structure calculations almost exactly, whereas the published parameters are too stiff. However the fitted parameters do only a little better than published ones for the D_{2d} force component. The comparison is a bit surprising because

the original BKS fit used cluster reference energies computed at a lower level of theoretical refinement, RHF, than was used here, CCSD(T). Details are in Ref. [13].

With the published parameters as a starting point, we are able to generate a set of fitted parameters that reproduces the T_d gradients almost exactly but still has a problem with D_{2d} gradients. The resulting parameters are displayed in Table V. As was shown in FIG. 4, the energetics that these parameters yield reproduce the CCSD(T) T_d motion energetics quite well (without any zero of energy), but misloate the minimum in the D_{2d} motion.

Table (5): Parameters of the BKS type for Silica from fitting to forces for the H_4SiO_4 cluster constrained to have tetrahedral core geometry; see text for details. Units as in Table II.

	Q	α_i	β_i	γ_{ij}
Si-Si	2.40	0	0	0
Si-O		7149.17	4.4864	27.661
O-O	$-Q_{si}/2$	1359.30	2.8086	213.820

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