

## Nonlocal Pseudopotentials in Molecular-Dynamical Density-Functional Theory: Application to SiO<sub>2</sub>

Douglas C. Allan and Michael P. Teter

*Applied Process Research, Corning Glass Works, Corning, New York 14831*

(Received 26 May 1987)

Silicon dioxide is fundamental in geology, in the electronic materials industry, and in the glass industry. We have carried out an *ab initio* total-energy minimization study of the structure and bonding of alpha cristobalite using nonlocal pseudopotentials in a Car-Parrinello-type molecular-dynamical method. The electronic energy is expressed in the local-density approximation. The use of a separable nonlocal pseudopotential preserves the  $O(M \ln M)$  scaling of the computation for  $M$  plane waves. The resulting theoretically computed minimum-energy structure agrees well with experiment.

PACS numbers: 71.10.+x, 61.16.-d, 61.60.+m

In spite of the predominant role SiO<sub>2</sub> plays in geology, electronic devices, and the glass manufacturing industry, there have been few first-principles studies of the bonding and structure of silica. This lack stems from the relatively complex structures in which silica is found, as well as the difficulty of handling the oxygen ion with pseudopotentials and plane waves. In this paper we will show how both of these problems are solved by coupling new developments in density-functional theory with nonlocal pseudopotentials which are separable in momentum space.

It has long been a desire of condensed-matter theorists to be able to predict the structure and excitations of real materials entirely from first principles, with virtually no experimental input. In recent years this ambitious goal has to some extent been realized.<sup>1</sup> Two important breakthroughs have led to the current state of the art. First came the development of a tractable description of electron interactions and energies through density-functional theory and the local-density approximation.<sup>2,3</sup> Second was the development of realistic and transferable pseudopotentials which can be produced with no experimental input.<sup>4,5</sup> This pseudopotential density-functional total-energy method has been applied to an enormous variety of systems with great success.<sup>6</sup>

Having available realistic energies and realistic forces on atoms, one would like to go beyond static or quasi-static calculations and study the actual dynamics of atomic motion with the quantum-mechanical treatment of electron bonding. The standard plane-wave method would require about two to eight diagonalizations of a large Hamiltonian matrix to achieve self-consistency in the electronic charge density. These several diagonalizations would have to be repeated for each update of the ion coordinates, leading to a very time-consuming calculation. For this reason, such calculations have not been performed. Nevertheless, the ability to perform molecular dynamics within the local-density approximation is desirable both for the dynamical studies of atomic motion as well as for the ability to perform simulated annealing on the ions to find efficiently and reliably the minimum-energy structure over many coordinate variations.

This bottleneck was broken when Car and Parrinello (CP) suggested combining the molecular dynamics on the ions with a fictitious dynamics for the electrons which simultaneously minimizes the energy with respect to electron and ion degrees of freedom.<sup>7</sup> The molecular-dynamical method of minimizing the energy with respect to electron degrees of freedom is equivalent to using an iterative scheme for diagonalizing the Hamiltonian matrix, with the added advantage that for small displacements of the ion on every time step the electron states change little and can be approximately re-minimized with only a single iteration. Ordinarily the number of computational steps in such a scheme would scale as  $O(M^2)$  for  $M$  basis states for each time step, simply from the matrix multiplication required to obtain the forces for updating the electron coordinates. By the use of plane waves, however, the operation of the potential on the wave function becomes a convolution which can be computed by fast Fourier transforms, thus reducing  $O(M^2)$  to  $O(M \ln M)$ . As  $M$  reaches 5000 or more, the savings in computation time is substantial.

The original CP method has been improved by the use of a harmonic-oscillator integration scheme<sup>8</sup> in place of the Verlet algorithm.<sup>9</sup> The harmonic-oscillator algorithm can allow a factor of 10 fewer time steps to gain a particular convergence,<sup>8</sup> which allows application of the method to larger systems of interest. Another modification to CP involves use of Gram-Schmidt orthogonalization in place of the Lagrange-multiplier solution by the Rychaert<sup>7,10</sup> method. This can turn out to have important consequences when the initial trial wave functions have an accidental symmetry, because the Gram-Schmidt orthogonalization can break an accidental symmetry which would remain unbroken by the Lagrange multiplier solution.<sup>11</sup> These modifications of the original CP method have successfully been applied to the study of the  $\Sigma=5$  (001) twist grain boundary in Ge<sup>12</sup> and to the Ge(100) surface.<sup>13</sup>

Nevertheless, not all elements are adequately treated with a local pseudopotential. To perform reliable calculations including such elements as oxygen a nonlocal pseudopotential is required. Operation of a nonlocal potential on the wave function is not a convolution, and so

it naively would require  $O(M^2)$  steps. By choosing the nonlocal potential to be separable in momentum space, however, the operation on the wave function scales as  $O(M)$ . A separable nonlocal pseudopotential different from ours has been used previously in studies of Si<sup>14</sup> and Se.<sup>15</sup> We have used a form of separable potential proposed by Kleinman and Bylander<sup>16</sup> (KB) and found it very successful. This paper describes the implementation of the KB separable pseudopotential and its application to a study of the structure and bonding of alpha cristobalite.

We begin by comparing the form of the plane-wave matrix elements of a nonseparable nonlocal pseudopotential with the KB pseudopotential. KB call the usual nonseparable nonlocal pseudopotential "semilocal" (SL)

$$\langle \mathbf{q} | V_{\text{SL}} | \mathbf{q}' \rangle = \sum_l 4\pi(2l+1)P_l(\cos(\theta_{\mathbf{q}\mathbf{q}'})) \int_0^\infty dr r^2 j_l(qr) j_l(q'r) \delta V_l(r),$$

where  $j_l$  is a spherical Bessel function and by the definition the nonlocal correction  $\delta V_l(r)$  goes to zero just beyond the core radius of the pseudopotential.  $P_l$  is a Legendre polynomial and the angle  $\theta_{\mathbf{q}\mathbf{q}'}$  is the angle between the momentum vectors  $\mathbf{q}$  and  $\mathbf{q}'$ . By contrast, the KB separable momentum matrix elements are of the form

$$\langle \mathbf{q} | V_{\text{NL}} | \mathbf{q}' \rangle = \sum_l 4\pi(2l+1)P_l(\cos(\theta_{\mathbf{q}\mathbf{q}'})) \int_0^\infty dr r^2 j_l(qr) \phi_l(r) \delta V_l(r)$$

Here  $\phi_l(r)$  is the atomic radial pseudo wave function in the reference state used to generate the nonlocal pseudopotential. By construction the KB NL pseudopotential reduces to the SL type when applied to the reference state, so either choice of pseudopotential identically reproduces the all-electron properties of a reference atomic state. In spite of the fact that the SL and NL pseudopotentials are different operators, they both have the highly desirable transferability of norm-conserving pseudopotentials.<sup>4,5</sup> This follows from the fact that both operators, which are actually corrections to the local pseudopotential, vanish for radii larger than the pseudopotential core radius.

The model yields a good description of crystalline Si, with a lattice constant which is too small by 1.2%. Applying the model to study the equilibrium structure of alpha cristobalite provides a much more stringent test. Alpha cristobalite has four SiO<sub>2</sub> molecules in a tetragonal unit cell of space group  $P4_12_12$ , or  $D_4^4$ .<sup>19</sup> A perspective drawing of the structure is given in Fig. 1. The Si atoms occur at a special Wyckoff position with one degree of freedom, but the O atoms occur at the general position which therefore has three degrees of freedom. For these initial studies we use the minimal unit cell of twelve atoms and allow both the Si and O atom positions and the  $\mathbf{a}$  and  $\mathbf{c}$  axis length scales to vary in order to minimize the total energy. By symmetry there is one Si position and one O position in the unit cell, the rest of the positions being equivalent under symmetry transformations. With one degree of freedom for Si, three for O,

because it is nonlocal in the angular coordinates but local in the radial coordinate. The KB pseudopotential, by contrast, is nonlocal (NL) in both the angular coordinates and the radial coordinate. Being separable in momentum space means that the momentum matrix elements are expressible in the form

$$\langle \mathbf{q} | V | \mathbf{q}' \rangle = \sum_i f_i(q) g_i(q')$$

for some functions  $f$  and  $g$ , and the number of such functions is much smaller than the number of plane waves  $M$ . In our case the local pseudopotential and the nonlocal corrections  $\delta V_l(r)$  for angular momentum  $l$  are norm-conserving pseudopotentials.<sup>4,5,17</sup> In the typical implementation<sup>18</sup> the momentum matrix elements are nonseparable and are of the form

$$\times \int_0^\infty dr r^2 j_l(q'r) \phi_l(r) \delta V_l(r) / \int_0^\infty dr r^2 [\phi_l(r)]^2 \delta V_l(r).$$

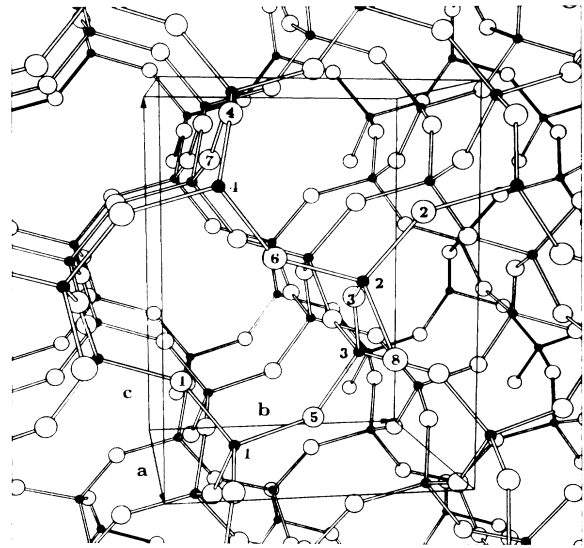


FIG. 1. A perspective drawing of the alpha-cristobalite structure projected down the  $\mathbf{a}$  cell edge. The tetragonal unit cell is outlined. Silicon atoms are smaller and blackened. The twelve atoms (four Si and eight O) inside the unit cell are numbered in accord with the symmetry operation which gives each atom as listed in the *International Tables for Crystallography* (Ref. 20). Sixfold (six Si and six O atoms) rings of bonds in the chair configuration can be seen in both face-on and edge-on views.

and two length scales, there are a total of six degrees of freedom to describe the crystal when its full symmetry is imposed. These studies retain the space-group symmetry and use one special point<sup>21</sup> at  $\mathbf{k}=(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  in units of the primitive reciprocal-lattice translations. The simpler calculation which uses only  $\mathbf{k}=(0,0,0)$  gives unrealistic results when compared with the experimentally measured structure.

The basis includes plane waves out to a kinetic energy of 20.75 hartrees which includes about 5240 plane waves at  $\mathbf{k}=(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ . The gradients of energy with respect to primitive cell translation lengths are corrected to obtain the desired derivatives at constant resolution from the actually computed gradients at constant plane-wave number  $M$ . This is accomplished by the estimation of  $\partial E(M)/\partial M$  numerically and the computation of

$$\left(\frac{\partial E}{\partial l}\right)_{\text{total}} = \left(\frac{\partial E}{\partial l}\right)_M + \left(\frac{\partial E}{\partial M}\right) \left(\frac{\partial M}{\partial l}\right)$$

with  $\partial M/\partial l = M/l$ ,  $l = \mathbf{a}, \mathbf{b}$ , or  $\mathbf{c}$  lengths. This correction prevents the lattice from contracting in response to an unphysical force arising from the improved description of the wave function for the same number of plane waves and a smaller unit cell.<sup>22</sup>

The minimum-energy configuration is found by simulated annealing, treating electron wave functions, ion coordinates, and lattice length scales as dynamical variables which respond to forces given by gradients of the total energy. We use the term annealing in the sense of a continuous removal of kinetic energy from the ions, done in the present work, as opposed to a steepest descent quench which simply follows the gradients to find a minimum. In the present case we did not observe local minima so that a steepest-descent quench would probably have succeeded. The results of this simulation and a comparison with the experimentally determined ion locations and lattice parameters<sup>23</sup> are given in Table I.

The resulting agreement is excellent. It is well to re-

TABLE I. Experimental (Ref. 23) and theoretical unit-cell parameters for alpha cristobalite, and their percent difference. The numbers in parentheses are the standard deviations of the last significant digit for the time-of-flight neutron powder diffraction data. The atom locations are given in units of the primitive translation lengths  $\mathbf{a} = \mathbf{b}$  and  $\mathbf{c}$ .

Parameter	Experiment (10 K)	Theory	$\Delta$ (%)
Si $x=y$ ( $z=0$ )	0.3047(2)	0.3030	-0.56
O $x$	0.2381(2)	0.2380	-0.04
$y$	0.1109(2)	0.1112	+0.27
$z$	0.1826(1)	0.1825	0.05
$a$ (Å)	4.9570(1)	4.959	+0.04
$c$ (Å)	6.8903(2)	6.906	+0.23

member that the only experimental inputs to the calculation are the atomic numbers of Si and O, the space group, and the number of atoms in the unit cell. None of the six structural coordinates given in Table I are related by symmetry or fixed by symmetry.

In addition to yielding a minimum-energy structure, the method gives the related local-density-approximation eigenvalues and eigenstates. Figure 2 shows the resulting valence pseudoelectron charge density in an O—Si—O bonding plane. Symmetry allows four different O—Si—O bond angles, all of which turn out to be near the tetrahedral angle of 109°. The plane of the bonds plotted in Fig. 2 includes the atoms labeled 1, 1, and 5 in Fig. 1; in the theoretical structure these atoms form an angle of 108.13°.

The first three panels resolve the valence pseudocharge density into contributions from various sets of bands, as described in the caption. This figure shows that the valence charge separates into O(2s)-like, O—Si-bonding-like, and O(2p)-like nonbonding charge in alpha cristobalite, as has been seen in other silica studies.<sup>24</sup> In particular the lowest set of bands [Fig. 2(a)] provides O(2s)-like core states which reside mostly on the O atoms, the next higher set [Fig. 2(b)] provides charge density of O(2p)-like character which lies along the

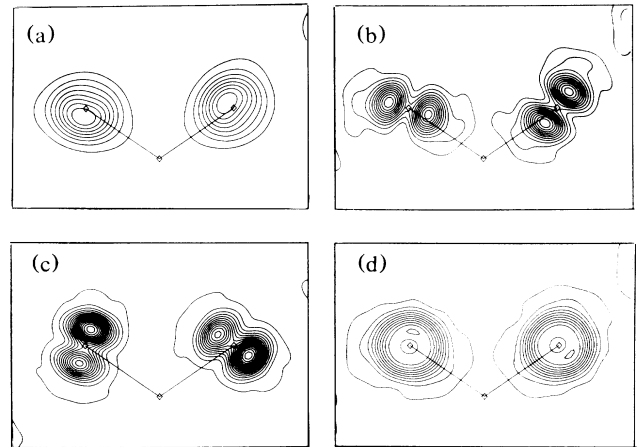


FIG. 2. A contour plot of valence pseudocharge densities in an O—Si—O bonding plane, in units of  $e \text{ \AA}^{-3}$ . Lozenges show the locations of O and Si atoms, and straight lines show the bonds. The average charge density is 64 electrons per cell or  $0.376 e \text{ \AA}^{-3}$ . In panels (a), (b), and (c) the contours are drawn starting at  $0.25 e \text{ \AA}^{-3}$  and are spaced by  $0.25 e \text{ \AA}^{-3}$ . In panel (d) the contours start at  $0.50 e \text{ \AA}^{-3}$  and are spaced by  $0.50 e \text{ \AA}^{-3}$ . (a) The lowest eight bands, constituting the O(2s)-like core states; highest contour is 2.0. (b) The next eight bands (9–16), constituting the O(2p)-like and Si bonding states; highest contour is 2.75. (c) The upper sixteen valence-band states, constituting the O(2p)-like nonbonding states; highest contour is 4.0. (d) The total charge density (sum over all 32 valence bands); highest contour, centered on the O atom, is 5.5 (the off-center contour near the maximum is at 4.5).

bond, and the highest set of valence bands [Fig. 2(c)] provides charge density of O(2p)-like character which lies perpendicular to the bond. The total charge density [Fig. 2(d)] shows that a majority of charge is localized near the O atom.

In this paper we have incorporated a particularly efficacious form of nonlocal pseudopotential for use in the molecular-dynamical method of computing electronic structure and total energies within the local-density and pseudopotential approximations. This computational scheme is fully self-consistent in the electronic charge density and is *ab initio*. The resulting method, which includes a molecular-dynamical treatment of ion motion as well, has been used to find a minimum-energy structure for alpha cristobalite. In comparison with low-temperature neutron diffraction studies of the structure, the resulting minimum-energy structure is in excellent agreement with experiment. The nature of the bond formation is also revealed by the resulting pseudo wave functions and their charge densities. This theoretical tool can now be used to study the structure at nonzero temperature and in the presence of structural defects and impurities.

We are grateful to Yaneer Bar-Yam for discussing, before publication, an optimal oxygen pseudopotential and considerations of basis-set convergence. We also acknowledge helpful discussions with David P. DiVincenzo.

<sup>1</sup>For example, J. D. Joannopoulos, in *Physics of Disordered Materials*, edited by D. Adler, H. Fritsche, and S. R. Ovshinsky (Plenum, New York, 1985), p. 19, and references therein.

<sup>2</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

<sup>3</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

<sup>4</sup>See description of *ab initio* pseudopotential development given in Ref. 1.

<sup>5</sup>D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).

<sup>6</sup>See examples in Ref. 1; also M. L. Cohen, in *Computer-Based Microscopic Description of the Structure and Properties of Materials*, edited by J. Broughton, W. Krakow, and S. T. Pantelides, MRS Symposia Proceedings Vol. 63 (Materi-

als Research Society, Pittsburgh, PA, 1986), pp. 107–115.

<sup>7</sup>R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

<sup>8</sup>M. C. Payne, J. D. Joannopoulos, D. C. Allan, M. P. Teter, and D. H. Vanderbilt, *Phys. Rev. Lett.* **56**, 2656 (1986).

<sup>9</sup>L. Verlet, *Phys. Rev.* **159**, 98 (1967).

<sup>10</sup>J. P. Ryckaert, G. Ciccotti, and H. J. C. Berendsen, *J. Comput. Phys.* **23**, 327 (1977).

<sup>11</sup>M. C. Payne, M. Needels, and J. D. Joannopoulos, "Symmetry Breaking in the Molecular Dynamics Method for *Ab Initio* Total Energy Calculations" (unpublished).

<sup>12</sup>M. C. Payne, P. D. Bristowe, and J. D. Joannopoulos, *Phys. Rev. Lett.* **58**, 1348 (1987).

<sup>13</sup>M. Needels, M. C. Payne, and J. D. Joannopoulos, *Phys. Rev. Lett.* **58**, 1765 (1987).

<sup>14</sup>R. Car and M. Parrinello, in *Proceedings of the Eighteenth International Conference on the Physics of Semiconductors, Stockholm, Sweden, 1986*, edited by O. Engstroem (World Scientific, Singapore, 1987), Vol. 2, p. 1165; R. Car, M. Parrinello, and W. Andreoni, in *Proceedings of the First NEC Symposium on Fundamental Approaches to New Material Phases, Tokyo, Japan, October 1986*, edited by S. Sugano, Y. Nishina, and S. Ohnishi (Springer-Verlag, New York, 1987).

<sup>15</sup>D. Hohl, R. O. Jones, R. Car, and M. Parrinello, *Chem. Phys. Lett.* (to be published).

<sup>16</sup>L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).

<sup>17</sup>The oxygen pseudopotential is generated using core radii of 0.8 bohr for  $l=0$  and 1 following careful testing of this potential by Yaneer Bar-Yam. This results in a much smoother pseudopotential requiring fewer plane waves in its expansion.

<sup>18</sup>J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).

<sup>19</sup>H. D. Megaw, *Crystal Structures: A Working Approach* (W. B. Saunders, Philadelphia, 1973), pp. 259–262.

<sup>20</sup>*International Tables for Crystallography*, edited by Th. Hahn (Reidel, Dordrecht, 1983), Vol. A, p. 358.

<sup>21</sup>R. A. Evarestov and V. P. Smirnov, *Phys. Status Solidi (b)* **119**, 9 (1983).

<sup>22</sup>P. Gomes Dacosta, O. H. Nielsen, and K. Kunc, *J. Phys. C* **19**, 3163 (1986). We thank David H. Vanderbilt for pointing out this correction term to us.

<sup>23</sup>J. J. Pluth, J. V. Smith, and J. Faber, Jr., *J. Appl. Phys.* **57**, 1045 (1985).

<sup>24</sup>J. R. Chelikowsky and M. Schlüter, *Phys. Rev. B* **15**, 4020 (1977), and references therein.