PHYSICAL REVIEW B VOLUME 39, NUMBER 5 15 FEBRUARY 1989-I

Ab initio pseudopotential solid-state calculations of highly electronegative first-row elements

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(Received 23 December 1987; revised manuscript received 12 August 1988)

Density-functional pseudopotential total-energy calculations have been a powerful tool in studies of the electronic and structural properties of semiconductors and simple metals. The inclusion of highly electronegative first-row elements such as oxygen and fluorine has not, in general, been tractable. In this paper we address the inherent difficulties and demonstrate that they can be overcome. Focusing on oxygen-silicon systems the precision of our method is demonstrated particularly through the study of angular stability of Si—O—Si bridge bonds in silica. The results predict bending to an equilibrium angle of 140°±5°, as observed, with an energy gain of only ~0.15 eV.

Silicon dioxide both in crystalline and amorphous forms has attracted extensive experimental and theoretical interest.[1] As the quintessential glass, the nature of its structure is of fundamental interest[2] as are the interesting phase transitions between crystalline polymorphs.[3] Defect structural properties and their interaction with electronic excitation are both of fundamental and practical importance because of the many practical uses of glasses from culinary to the choice large-gap insulator in silicon electronic devices. In crystalline silicon itself, oxygen is the most common impurity. Its high density in commercial Czochralski-grown material has made its structural and dynamical properties as an interstitial, and in agregation (the "thermal donors"), of great interest for silicon processing and properties. *Ab initio* theoretical studies of oxygen are difficult as for other first-row highly electronegative elements. Fluorine, the most electronegative first-row element, is also of great technological importance since it is used extensively in the microelectronics industry for etching silicon.

In the last few years *ab initio* density-functional-theory total-energy calculations have made significant contributions to our understanding of structural and dynamical properties of defects, surfaces, interfaces, phase transitions, and amorphous solids. Highly electronegative first-row atoms like oxygen and fluorine have not been studied because of their compact valence *p* orbitals. Such compact orbitals, which also have a small binding energy and are directly involved in bonding, lead to charge densities which are difficult to represent numerically. While the compact orbitals suggest a localized orbital basis, plane waves provide an unbiased basis set for the comparison of different geometries, particularly relevant for the low-symmetry geometries of silicon dioxide, its defects, and oxygen as an impurity in silicon. Indeed, experience has demonstrated that optimization of exponents of localized basis sets for low-symmetry defects with large atomic displacements is a very difficult task. Thus we adopt a plane-wave basis set.

Pseudopotentials are used extensively in the study of material properties due to simplifications that enable realistic calculations while retaining high accuracy. Pseudopotentials reduce the number of electrons and the number of basis states required to represent the electrons relevant for structural properties of materials. Originally developed to simply remove the core electrons, *ab initio* pseudopotentials are now constructed to retain specific atomic valence-electron properties such as eigenvalues and wave functions outside of a small core region. Thus, pseudopotentials may also be constructed without a specific angular-momentum core state. Still, the use of pseudopotentials for softening the electron-nucleus interaction is less effective for atoms where core states do not exist for a particular angular-momentum state, such as the *p* orbitals of oxygen or fluorine. The absence of core states is responsible for the existence of compact nodeless *p*-orbital wave functions.

Because of the difficulty in representing the oxygen wave functions, the only realistic total-energy calculations including oxygen, prior to the developments described herein, were studies[4] of BeO and MgO whose remarkably small cells reduce this difficulty dramatically.

In this paper we directly address the problem of convergence of oxygen pseudopotentials for total energies in a plane-wave basis.[5] We extensively test the convergence of existing potentials and display the essential intractability of calculations for SiO_2. We modify the existing potentials to obtain dramatically improved convergence in basis size. We then demonstrate the accuracy of calculated results for structural properties of silicon dioxide. In particular, we study the instability of Si—O—Si bridge bonds to angular distortion and obtain excellent agreement with experimental values for the equilibrium angle.

In the usual approach to generating pseudopotentials, atomic properties of the pseudopotential are carefully matched to the results of atomic all-electron calculations. In our approach to optimizing pseudopotentials for use in plane-wave total-energy calculations, we recognize that to insist on accurate duplication of the O 2*p* atomic wave function would ultimately not allow any reduction in difficulty. Since our objective is to reduce the number of basis states required, we generate a potential with smoother atomic wave functions, and adopt the approach of directly testing the structural properties of materials rather than atomic properties. We find that our specific potential which has smoother wave functions yields structural properties consistent with those obtained from conventional pseudopotentials. This comparison ensures that the *ab initio* nature of our approach is retained. Ultimately, the theoretical results obtained with these potentials are also in good agreement with experiment.

Four pseudopotentials were generated for comparison and extensive evaluation of accuracy in representing structural properties and in convergence tests in the number of plane waves in the basis set. The first potential (BHS) is the one recommended by Bachelet, Hamann, and Schläte[6] who adjusted their potential for optimal representation of atomic term values and wave functions. The second potential (BHS-V) is a potential developed by Vanderbilt[7] for optimal Fourier representation. The wave function remains modified only within the same core region used by Bachelet *et al.* In this way the Vanderbilt "smoother" potential still retains a faithful representation of the wave functions. Third, we chose a potential (labeled "New") designed to give different smoother wave functions. For direct comparison with the other potentials we used the same norm-conserving potentials but increased the core radii. The core radii used are 0.8 a.u. for both *s* and *p* nonlocal potentials as opposed to (BHS) 0.49 and 0.27 for *s* and *p*, respectively. The new core radii lie near the maximum amplitude of the wave functions, especially the *p*-orbital radial wave-function peak at 0.81 a.u. This creates some wiggles in the potential and distortion in the pseudo-wave-function. The fourth potential (New-V) applies the Vanderbilt potential smoothing to the new larger core radii.

Initial calculations, particularly the convergence tests, were performed on the β-cristobalite form of silicon dioxide. It has the diamond structure and is easily described as a silicon crystal with oxygen atoms inserted between silicon nearest neighbors and expanded to the equilibrium 1.62-Å Si—O bond length. It thus consists of silicon atoms bonded tetrahedrally to oxygen atoms, in turn bonded to silicon atoms. In this structure the angle of the bridge Si—O—Si bonds is 180°. By using this well-defined high-symmetry crystal, convergence could be obtained for all potentials. At the same time, this high-symmetry structure is the reference geometry for study of the instability that bends the Si—O—Si chains in SiO_2.

Total energies[8] are obtained using density-functional theory with local-electron-gas approximation for exchange and correlation. Density-functional particle eigenvalues and eigenfunctions for use in total-energy Brillouin-zone integrals were evaluated at special **k** points. Because of the highly ionic nature of the bonding, or equivalently the narrow bands and large gap, fewer special **k** points were needed for convergence than similar calculations for crystalline silicon. For the high-symmetry cristobalite, two **k** points in the reduced zone were adequate as verified by tests using ten **k** points.

Basis sets for convergence tests consist of plane waves up to a particular energy cutoff E_1 and additional plane waves up to E_2 (fixed to be twice E_1) used in second-order (Löwdin) perturbation theory. The use of the Löwdin perturbation theory was tested thoroughly for convergence. The values of E_2 used for tests of convergence range from 10 to 80 Ry. For example, the number of plane waves used directly and in perturbation theory ranged from (150;400) to (3300;9350) for the lowest to highest energy cutoffs (E_1;E_2) from (5 Ry;10 Ry) to (40 Ry;80 Ry). We do not adjust the values of E_1 and E_2 independently because such careful adjustments may lead to convergence particular to the properties directly evaluated.

In order to evaluate structural parameters for convergence tests, the total energy of the β-cristobalite crystal was calculated for three different bond lengths (lattice constants) for each of the four oxygen potentials and eight basis sets. Using these calculations, convergence of binding energy and approximate equilibrium lattice constant and bulk modulus were obtained.

Changing the lattice constant leads to different numbers of plane waves within the same energy cutoff. Thus, the constant energy cutoffs lead to changes in the number of plane waves which cause discrete changes in the total energy. Corrections may be made by extrapolating using the actual energy cutoff corresponding to the last plane wave used. For the purposes of this work, such corrections were not applied, which is responsible for the apparent "noise" in the data. The noise is more severe for

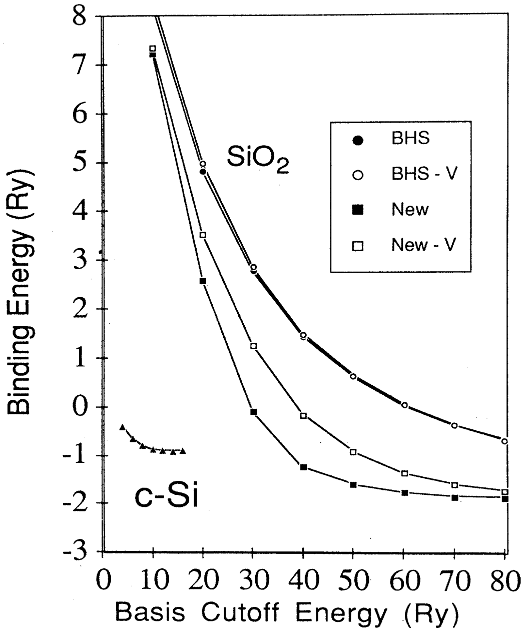

FIG. 1. Convergence of the binding energy of silicon dioxide (per SiO_2 unit) with respect to free atoms as a function of the plane-wave basis-set cutoff E_2. Each curve shows the results of calculations using a different oxygen pseudopotential as described in the text. Convergence using the new oxygen pseudopotential is substantially improved. The binding energy per unit cell of silicon is also plotted for comparison of the difficulty of different calculations.

bond lengths and particularly bulk moduli (for Si as well as SiO_2).

The binding energy of SiO_2 at a particular lattice constant is shown in Fig. 1 as a function of basis-set size for the different pseudopotentials. The differences between the convergence of the four oxygen potentials are dramatic. The convergence of the BHS oxygen potential is very slow; convergence is poor even at the highest energy cutoff used (40 Ry;80 Ry). The smoother potential BHS-V is essentially identical in its convergence properties. The new potential (New) with smoother atomic wave functions displays dramatically improved convergence of the binding energy. The use of Vanderbilt smoothing applied to the new potential (New-V) appears to be counterproductive, leading to convergence intermediate between the original BHS potential and the unsmoothed potential (New). This worsening of convergence is likely due to improvement in the accuracy of the Vanderbilt potential for the same core radii. It should still be possible to further increase the core radii with Vanderbilt smoothing and achieve similar convergence to the unsmoothed potential since the wave functions would then be smoother as well. In the same figure we plot the convergence of analogous calculations for crystalline silicon for a comparison of scale of difficulty.

In Figs. 2 and 3 we show the lattice constant and effective bulk modulus again plotted for different basis sizes. These figures give us a more quantitative measure of the accuracy of these calculations for structure properties. We see that the best convergence is obtained by the new potential in the range (20 Ry;40 Ry)–(30 Ry;60 Ry) while the normal or smoothed BHS potential does not converge until (35 Ry;70 Ry)– · · · , where the ellipsis indicates that equivalent convergence is not attained at even (40 Ry;80 Ry), especially for the bulk modulus.

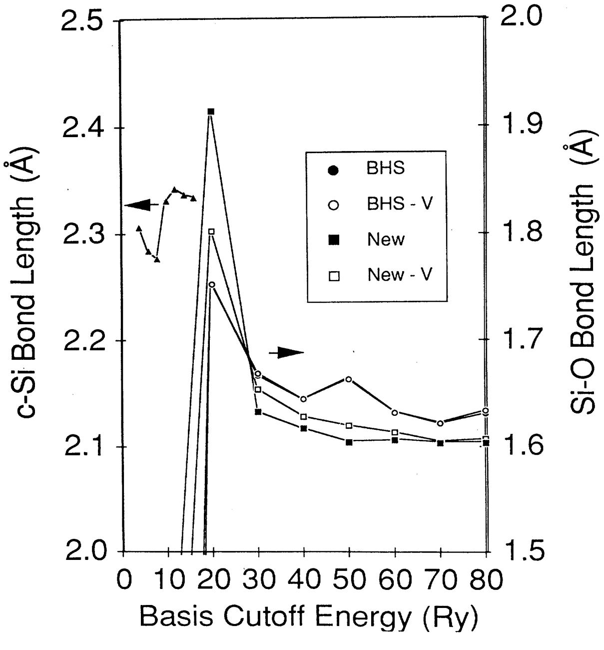

FIG. 2. Convergence of the Si—O bond length in silicon dioxide as a function of the plane-wave basis-set cutoff (the solid circles are not completely visible since they almost overlap the open circles). For comparison, Si—Si bond-length convergence is shown. Scale on the right is for the Si—O bond length, scale on the left for the Si—Si bond length.

The comparison of converged results of these calculations with experimental values is most significant for the Si—O bond length. The agreement here is excellent, the calculated result for the Si—O bond length is 1.60 Å compared with 1.61–1.62 Å experimentally. Converged binding energies are known to be too large in local-density-functional theory by ~10% because of the great difference comparing atomic and crystal systems. In these calculations the binding energy is too deep by 35% (1.75 Ry per SiO_2 compared with 1.3 Ry experimentally). The bulk modulus shown in Fig. 3 corresponds to the structure with straight Si—O—Si bonds and may not be compared with experimental values. The accuracy of total-energy calculations for silicon-dioxide materials using the oxygen pseudopotential described here is further demonstrated in recently reported quantum-molecular-dynamics calculations on α-cristobalite.[9]

The above tests show that accuracy is not sacrificed in the new potential while dramatic improvements in convergence can be obtained. Motivated by these results we adopt the new potential as the basis of further calculations. As a first application we calculate the instability of β-cristobalite in forming Si—O—Si bond angles less than 180°. Experimentally, the known low-temperature structures of silicon dioxide are found to have bent Si—O—Si bonds. Interesting phase transitions to high-temperature structures result in the averaged straightening of the Si—O—Si bridges.

The calculation of bond angles and particularly the energy difference between straight and bent-angle bonds requires much higher accuracy than the calculations previously discussed. Smaller energy differences are involved,

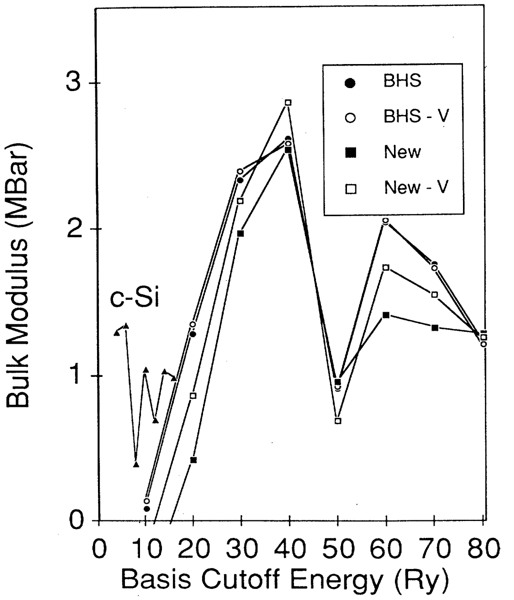

FIG. 3. Convergence of the bulk modulus of β-cristobalite as a function of the plane-wave basis-set cutoff.

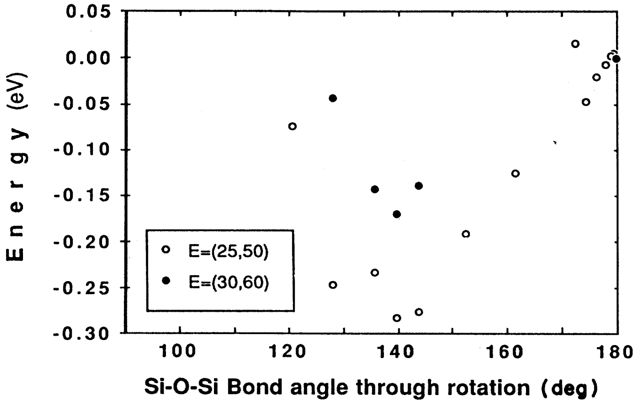

FIG. 4. Study of the instability of silicon dioxide to Si—O—Si bond-angle distortion. Values are plotted for two different basis sets. The minimum-energy angle is in excellent agreement with the 140° angle found in SiO_2.

while the nature of the bonding changes substantially. In Fig. 4 we show the energy as a function of bond angle for a uniaxial alternating clockwise, counterclockwise rotation of silicon tetrahedra. This rotation preserves the tetrahedral coordination and changes the bond angles. The rotation also results in changes in unit-cell volume and the accompanying changes in numbers of plane waves cause the appearance of noise. Results are plotted for two energy cutoffs $E_2=50$ and 60 Ry as indicated. Significantly, at this much-smaller energy scale these calculations correctly reproduce the experimental Si—O—Si angle which is found in a variety of systems to be in the range $140^{\circ}{}^{+5^{\circ}}_{-10^{\circ}}$.

An additional test of bond-angle change was performed by a direct bending of bond angles including changes in the O—Si—O bond angles. The energy was found to increase monotonically resisting this type of angular distortion in which the Si—O—Si bond-angle energy gain competes with the loss from O—Si—O bond-angle changes.

The difficulties with representing the oxygen potential wave functions which are addressed in this paper arise in other atoms which have compact valence wave functions due to an absence of the corresponding core levels. Silicon-fluorine systems have already been investigated[5] and results are comparable to those of oxygen reported here. The same type of pseudopotentials are likely to be particularly useful for nitrogen, carbon, as well as nickel, copper, and magnesium.

This work was supported in part by U.S. Office of Naval Research (ONR) Contract No. N00014-84-C-0396.

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