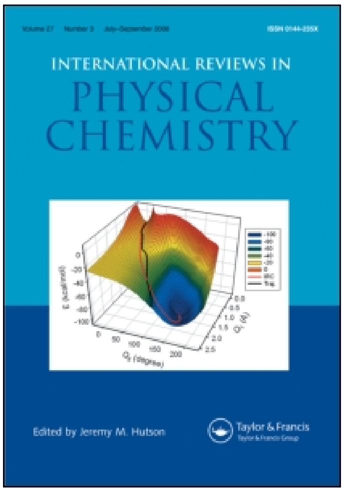

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Computer modelling of silicates

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We describe the basic methodologies and applications of computer modelling methods applied to the simulation of silicates and aluminosilicates. We discuss the use of distance least squares (DLS), electrostatic, Born-model and quantum mechanical methods. We consider applications to the simulation of the structures and defect properties of silicates. We include discussions of recent work on zeolites and on Mg_2SiO_4.

1. Introduction

The diversity and complexity of silicate minerals provides a powerful incentive for the development of theoretical methods for modelling their structures and properties. Further motivation follows from the need for information on the behaviour of silicate minerals under conditions where experimental investigation is difficult: a good example is provided by very high pressure studies, which pose severe experimental problems, but which are needed in order to understand the geophysics of the earth's mantle. The last few years have seen a considerable expansion in modelling studies of silicates, owing both to the growing appreciation of the potential of these methods and to the expansion in computer power; indeed the growth in computational resources has been an essential feature in allowing the modelling of such materials. In this review, we will discuss the current status of this rapidly developing field. Our main theme will be the simulation of crystalline silicate *structures*; but we will also discuss the calculation of other properties, including elastic and dielectric constants and phonon dispersion curves. We will then consider the important area of point defect calculations. And at the more fundamental level we will need to consider the difficult and controversial problems concerning bonding in silicates. We note that the modelling of amorphous silicates is also an active area, but is outside the scope of this review. The interested reader is referred to the recent review by Soules (1982).

There have been four distinct types of method used in modelling silicates. The first is *empirical procedures* based on measured bond lengths, of which the most notable has been the distance least squares (DLS) method; the second, purely *electrostatic calculations*; the third, *Born-model techniques* in which both the electrostatic and short-range energies are considered, with the latter usually treated by simple parametrized potentials; and finally, *quantum mechanical methods* have been used, including both semi-empirical and *ab initio* techniques.

In the sections which follow we will first describe each of the techniques and survey those classes of minerals for which calculations have been reported. We aim to give a critical account of the types of information given by the different techniques and a survey of areas where progress may be expected in the near future. First, however, it is necessary to summarize briefly the types of structure adopted by silicate minerals.

2. Structural classification of silicates and aluminosilicates

The traditional means of classification of these minerals is according to the mode of linkage of the constituent (Si, Al)O_4 tetrahedra. Most, if not quite all, structures then fall naturally into one of four main categories. We will describe each category without being exhaustive, giving examples of structures that have been modelled using the techniques outlined in the Introduction and which will be discussed in greater detail below. For a more detailed account of structural mineralogy we refer the reader to Deer *et al.* (1982).

(i) *Orthosilicates*

These consist of isolated tetrahedra which are connected to different kinds of coordination polyhedra (e.g. octahedra) rather than to other tetrahedra. The most familiar mineral in this group is olivine, the magnesium end member of which, Mg_2SiO_4, has been the subject of several simulations. Other minerals in this group are the zircons, (e.g. $ZrSiO_4$), and the garnets; calculations on both of these structural classes are discussed in Section 3.3. Note that in these minerals, little or no substitution of Si by Al is found.

Closely related to this group are structures which incorporate pairs of tetrahedra, forming isolated Si_2O_7 group. An important mineral group with this mode of linkage is epidote. Si_2O_7 groups are also found in the spinelloids which are structurally closely related to both olivine and spinel and are exemplified by β-olivine which has been modelled by Baur (1977) and Parker and Price (1985).

(ii) *Metasilicates*

Into this group fall those structures containing SiO_4 tetrahedra linked together to form chains. Minerals with single-chain structures include the pyroxene family, e.g. diopside and enstatite, and the related pyroxenoids (wollastonite, rhodonite and pyroxmangite) which differ from pyroxenes principally in the number of tetrahedra forming the repeat unit in the chain (see figure 1). Born-model calculations on these structures were reported by Catlow *et al.* (1982).

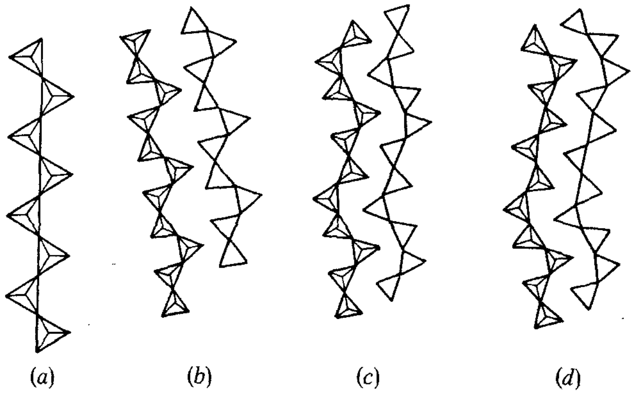

Figure 1. Structure of pyroxene and pyroxenoides: (*a*) pyroxene; (*b*) wollastonite; (*c*) rhodonite; (*d*) pyroxmangite.

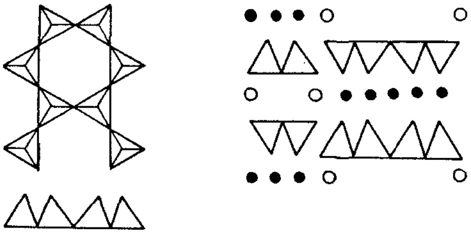

Figure 2. Amphibole structure: (*a*) double chain linkage; (*b*) stacking of double chains.

There are several ways in which pyroxene chains may be linked together to form double chains but the simplest, with every second tetrahedron in one pyroxene chain being linked to a tetrahedron in the other chain, is found in the important amphibole group of minerals (figure 2).

(iii) *Phyllosilicates*

In the phyllosilicates, the tetrahedra share vertices to form sheets, which may be combined with other sheets to form composite layers which then provide the principal structural feature of this group. Two principle subgroups of the sheet silicates, the micas and clays, are generally recognized, although of course there may be substantial differences within each subgroup.

The idealized composite layer structure of the mica family (figure 3) of which muscovite and biotite are perhaps the best known, consists of two sheets of SiO_4 tetrahedra with their apices pointing inwards; these are joined by a plane of cations whose octahedral coordination is completed by additional hydroxyl ions. The net negative charge of this composite layer is compensated by interlayer cations such as K, Na and Ca.

It is possible to stack successive composite layers in a considerable variety of ways and this leads to numbers of different polytypes, within the same mineral ty . Polytype formation is not well understood but may depend on such factors as the composition and distribution of cations within the octahedral plane. Theoretical studies of this problem would clearly be of value although few have been reported to date (but see the work of Price *et al.* (1984, 1985), who have coupled their ANNNI (axial next-nearest neighbour Ising) model with lattice energy calculations of possible polytypic structures in the Mg_2SiO_4 system).

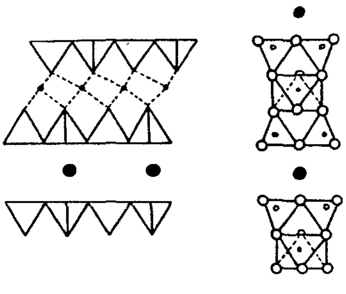

Figure 3. Idealized mica structure in which sheets of tetrahedra sandwich octahedrally coordinated cations (large black dots).

The taxonomy of micas is very extensive. Their chemical composition may be written as $X_2Y_{4-6}Z_8O_{20}(OH)_4$ where X denotes the interlayer cations, typically K, Na and Ca (or possibly Rb, Cs, Ba); Y denotes the octahedral cations, usually Al, Mg or Fe (but Mn, Cr, Ti and even Li have been found) and Z denotes the tetrahedral sites which mainly contain Si, with some Al, although Fe and Ti have been suspected. Note also that F has been found to substitute for some of the OH groups. Theoretical studies of the energetics of these replacements are reported by Jenkins and co-workers; they will be described in Section 3.2.

The clay minerals, broadly speaking, differ from the micas mainly through having interlayer water molecules. There are four principle subgroups of clays: kaolinites, illites, semectites and vermiculites. The latter has been studied theoretically by Jenkins and co-workers and will be considered in a later section. Otherwise, clays have received relatively little attention from theoreticians although they are continuing sources of interest owing to their useful catalytic properties, in which they in some ways resemble the zeolites discussed in the next section.

(iv) *Tectosilicates*

The fourth major group of silicates comprises those structures in which the tetrahedra are linked to form *framework* structures. Minerals in this group form some of the most abundant species: feldspars, the major component of igneous rocks, silica—SiO_2—minerals themselves, i.e. quartz, tridymite, cristobalite, coesite, etc., and the zeolites which are amongst the commercially most important of minerals. Surprisingly enough, the feldspars have received little theoretical attention, perhaps because efforts to model quartz have, until recently, been unsuccessful. Because of their industrial significance, on the other hand, zeolites have been the subject of a number of calculations.

Zeolites display a variety of structural types, which differ in their linkage topology. The primary feature is the existence of rings or nets of tetrahedra which can be joined in a variety of ways. These are commonly four, six or eight-membered rings as found in those zeolites which contain the sodalite unit as a primary feature, such as zeolite-A, faujasite and chabazite, but the pentasil zeolites, e.g. silicate ZSM-5 and ZSM-11, are so called because they contain 5-membered rings.

Smith (1979 *et seq.*) has investigated the different ways the nets may be joined, in an effort to enumerate systematically the possible structures. So far only a small number of those possible have been found in nature or synthesized.

Chemically, the presence of Al in the tetrahedral site is balanced by extra non-framework cations such as Na, K, Sr, etc., in the cavities and channels formed in the framework structure. The water in hydrous zeolites is located in these cavities as well, although it is usually possible to remove all of it. The cavities and channels vary in size and shape according to the actual structure but are large enough to accommodate substantially sized hydrocarbons and other organic molecules. Indeed, as is well known, zeolites are often used as molecular sieves, filtering out undesirable molecules through a judicious choice of channel size. The existence of the cavities and channels results in zeolites having a very large internal 'surface' area which thus makes them important as catalysts, since the catalytically active sites are usually found on the surface of crystals. For a more complete description of the uses and structure of zeolites the reader may refer to the *Proceedings of the Sixth International Zeolite Conference* (Olson and Bisio 1984). We will discuss several examples of recent calculations on zeolites in Section 3.3.

3. Techniques and applications

As outlined in the Introduction, modelling techniques range from semi-empirical procedures, based on bond lengths, to quantum mechanical methods, using the Hartree–Fock formalism. Each of these approaches is now described, with examples taken from the recent literature.

3.1. *DLS modelling of aluminosilicates*

The philosophy behind DLS (*D*istance *L*east *S*quares) modelling is one of geometric refinement. There is a wealth of experiment data, from crystal structure determinations, on bond lengths in aluminosilicates, and the DLS program (Meier and Villiger 1969, Baerlocher *et al.* 1978) makes use of this database by optimizing atomic coordinates and unit cell parameters to provide a best fit to the prescribed or input bond lengths.

From an initial set of atomic positions (which may be chosen at random, subject to symmetry constraints) the function,

$$R=\sum_j W_j^2\,[D_j^{\text{Prescribed}}-D_j^{\text{Calculated}}]^2$$

where the D_j are bond lengths or distances, and W_j are weighting factors, is minimized, by the method of least squares, with respect to the atomic coordinates and, possibly, if desired, to the unit cell parameters. The function R is usually called 'the residual' and is a minimum at the best fit to the set of prescribed distances. A useful feature of the DLS program is that for framework structures, the topology of the framework can be used to generate the set of prescribed distances: for example the T–O bond length is input and the various independent T–O–T linkages are described. The program then calculates several O–O and T–T bond lengths from default values of the bond angles used by the program (which may be overriden). The program also uses symmetry constraints which must be explicitly included as part of the input data. Thus although the residuals of calculations in two different space-groups may be compared, DLS can never change the symmetry during its optimization.

Nevertheless, the combination of a topological input facility and an initial random generation of coordinates can be advantageous in that the optimized results may sometimes be used as a starting model for structure refinement. This approach has been used for zeolites and will be discussed below.

Different weighting factors are commonly applied for different bond lengths in order to allow for the fact that the observed bond lengths show varying degrees of spread; in addition they may be used to alter the relative importance of the different distances used in the fit. There has been some discussion in the literature concerning the best weighting factors to use. A common choice has been to make them proportional to bond strengths (Meier and Villiger 1969, Dempsey and Strens 1976) for cation–oxygen bond lengths, although this cannot be used to find weights for oxygen–oxygen and cation–cation bond lengths.

A more appropriate scheme, proposed by Baur (1977) and Bish and Burnham (1984) may be to use force constant data, where this is known from infrared or Raman studies. It should be noted that the various ways of finding weighting factors usually produce numerical values which appear somewhat different, but just what effect the different weights have on the final optimized structure is not really clear. Bish and Burnham (1985) report some unsatisfactory features in their simulation of the hypothetical antidiopside structure, including lack of convergence.

Unpublished work on dehydrated zeolite A by Cormack and Smith found that DLS could not reproduce the large differences in the T–O–T angles unless the prescribed distances incorporated the necessary features from the onset. Changing the cell parameter resulted in a change in the shape of the SiO_4 tetrahedra, rather than an adjusment of T–O–T bond angles. They were unsuccessful in finding a weighting scheme that kept the SiO_4 tetrahedra unaltered in shape.

These points illustrate the basic limitations in the use of DLS, since the selection of distances and bond lengths to be used is obviously of prime importance. Notwithstanding this, however, DLS simulations have been used with profit, especially when combined with other methods such as lattice energy calculations or as an aid to structure refinement. Dollase and Baur (1976), for example, used DLS to unravel the structure of a meteoritic low tridymite structure. Although the first model produced by DLS was not completely compatible with the data, it elucidated sufficient detail so that an additional calculation allowed the diffraction data to be satisfactorily refined.

Recently Bish and Burnham (1984) have combined DLS structures for a range of binary olivines with cohesive energy calculations to investigate the energetics of ordering in the M1-M2 cation sites. In each of the eight cases they investigated, they found that the calculated site preferences agreed with the observed distributions. They also concluded, significantly, that omitting repulsive terms, i.e. considering only electrostatic energies, did not lead to the same predictions; furthermore, neither did consideration of just the individual M1 and M2 site energies for the ordered and anti-ordered distributions.

An area which has recently seen a great deal of activity using the DLS approach is the structural chemistry of zeolites. Detailed structural refinements are available, in many cases, only through Rietveld analysis of neutron diffraction data of powders, since single crystals are very difficult to prepare. A trial model (i.e. an initial set of atomic coordinates) is invariably needed for this method and where the topology of the framework is known this can easily be provided from a DLS model using the appropriate bond lengths. Indeed, it has been suggested (e.g. Gramlich-Meier and Meier 1982) that DLS methods may be used to discard hypothetical frameworks that cannot be optimized. The feasibility of trial models produced in this way has been discussed by Olson *et al.* (1981) in considering ZMS-5 (see also Kokotailo *et al.* 1978 b); trial coordinates for ZSM-11 were calculated by considering the possible topologies and linkages of the ZSM-5 structural chains, consistent with the observed unit cell parameters (Kokotailo *et al.* 1978 a). However, in view of the experience of Bish and Burnham (1984) with their weighting factors and the fact that Al, Si ordering may lead to substantially different bond lengths from the average ones supplied to the DLS program, a certain amount of caution is required.

The case of zeolite-rho perhaps serves as an illustration. McCusker and Baerlocher (1984) did DLS refinements in both Im3m and I$\bar{4}$3m for the room temperature, hydrated, structure and found a substantially lower residual, R, for I$\bar{4}$3m (0·03% compared with 0·45% for Im3m). However, on refining the powder X-ray data in I$\bar{4}$3m, no significant change from Im3m symmetry was found and a refinement in the latter space group produced no increase in the error indices. Although the final refinement was still regarded as poor, they concluded that the appropriate space-group should be Im3m, contrary to the predictions from the DLS models. Parise *et al.* (1984) used DLS to find the structure of (dehydrated) zeolite-rho as a function of cell size. They reported that the residual for I$\bar{4}$3m was always lower than that for Im3m except around $a = 15{\cdot}0$ Å, which was around the largest cell size investigated experimentally.

Considerable changes to the framework are found on changing the lattice parameter (through incorporation of different non-framework cations), but the comparison of the experimental coordinates with those calculated by DLS seemed poor.

It would seem that whilst one important use for DLS is to provide atomic coordinates from any given framework topology, this technique may not be able to evaluate adequately, or consistently, such details of the structure as bond lengths and bond angles. An obvious role for the DLS program is thus to provide an initial structure which can then be used in an energy minimization calculation using the techniques described in later sections. This approach would make good use of various computational techniques available and would take one step further the combination of DLS and lattice energy calculations reported by Burnham and co-workers.

3.2. *Electrostatic calculations*

In this simplest of theoretical approaches, one may calculate the total electrostatic contribution to the lattice energy and the Madelung potential at individual sites in the crystals. The value E_i, of the latter potential at site i is given by

$$E_i=\sum_j \frac{q_j}{r_{ij}} \qquad (1)$$

The sum is over all other ions of charge q_j in the crystal; r_{ij} is the separation between the i and the j ions. The electrostatic contribution to the lattice energy, $E_{\mathrm{L}}^{\mathrm{elec}}$, is then given by;

$$E_{\mathrm{L}}^{\mathrm{elec}}=\tfrac{1}{2}\sum_i q_i E_i \qquad (2)$$

where the sum is over all ions in the unit cell. We note that the Madelung potentials, may of course be calculated for sites that are not normally occupied in the crystal.

Care must be taken in carrying out the $1/r_{ij}$ summations in equation (1). The series, which must be taken to infinity, is only slowly convergent when handled in real space. However, a transformation, due originally to Ewald, solves the convergence problem by a notional division of the array of point charges into two components: the first is a set of Gaussians centred on the point charges; the second consists of a set of point charges embedded in oppositely charged Gaussians. The addition of the two components, of course, generates the original point-charge array. The value of the procedure is that the second component results in a contribution for the electrostatic potential which converges rapidly when summed in real space, whereas the first component can also be made rapidly convergent by a transformation to reciprocal space. Detailed discussions of the procedure are given in the review of Tosi (1964) and the report of Catlow and Norgett (1976). The Ewald technique forms the basis of most modern computational codes for evaluating electrostatic energies in crystals.

Other summation procedures have been used in earlier work. Evjen's method, for example, obtains Madelung potentials at a point by calculating the potentials due to successive shells surrounding the point. The shell should be chosen so as to be neutral with zero dipole moment, i.e. their contribution to the potential at the centre is due to higher-order multipole moments. This leads to rapid convergence. The method is, however, less readily automated than the Ewald procedure which is consequently generally preferred in modern computer codes.

The computational expense of electrostatic summations has led to search for reliable approximate methods. One of the most detailed studies was that of Jenkins and Hartman (1979) (see also Jenkins (1982)) who have attempted to derive techniques which allow summations to be performed for whole classes of structure. This is straightforward provided we ignore variations in the coordinates of the different members of each class of structure; that is, on passing from one member to another we simply substitute one set (or more) of ions by others of different charge without changes in coordinates. The electrostatic energy is then simply, and obviously, a sum of terms of the type $a_{ij}.q_iq_j$ where i and j refer to different ions of the unit cell. Using this approach, Jenkins and collaborators obtained useful results on a number of micas; these included a study of the energetics of expansion of phyllosilicates (following earlier studies of Giese (1974)) which was used to estimate the magnitude of interlayer binding.

Calculations of this nature are doubtless of use and allow a large number of structures to be examined rapidly; although with the continued growth in computer power, full electrostatic energy calculations on very large units cells are becoming routine and inexpensive. Moreover, the role of purely electrostatic energy calculations is unquestionably limited. Detailed modelling studies require the inclusion of a representation of the short-range energies, the topic taken up in the next section.

3.3. *Born-model calculations*

This category differs from the previous one in that non-coulombic terms in the interionic potentials are included, following Born's original model for ionic solids. Indeed, the aim is to derive potentials that give an accurate representation of the energy of the crystal (either perfect or defective) as a function of all atomic coordinates. The scope of calculations employing the full potential is, as noted, far greater than those in which the electrostatic terms alone are considered. The construction of such potentials is, however, a demanding task. In the discussion which follows, we first consider the models that have been used in describing the short-range potentials; we then consider the important question of the modelling of polarizability. Having described the potential models we are then in a position to discuss the types of calculation which may be performed. Here we pay greatest attention to our own recent work; a recent review of other calculations is available from Burnham (1985).

3.3.1. *Potential models*

By potential models, we mean those in which the cohesive energy of the solid is described as a function of the unit cell dimensions and atomic coordinates, and where the interatomic forces are calculable from the derivatives of the interatomic potentials which are written as functions of interatomic separations.

In contrast, *force constant model* descriptions of the solid provide only the derivative of the potential energy at the interatomic separations or bond angle in the perfect structure (and not at other separations or bond angles). Force constant models have been developed for SiO_2 by Streifler and Barsch (1975, 1976). The simplest type of potential model treats atoms or ions as hard spheres, to which radii are assigned. Models of this type are discussed by O'Keefe and Hyde (1978), and O'Keefe (1977), following Glidewell (1975). Detailed predictions of the properties of solids, especially those not directly related to structural stability, e.g. dynamical or transport properties, require a more sophisticated description of the interatomic potentials and we discuss such potentials below.

(i) *Non-coulombic terms*

The non-coulombic component of the potential is a complex quantity with several components, of which the most important are: (i) the short-range repulsions that come into play when atomic charge clouds overlap; (ii) the longer-range attractive forces due to dispersive interactions; and (iii) effects of covalent bonding. Despite this complexity, simple analytical functions have generally been used to describe these terms. A favoured function, widely used in potentials for ionic crystals, is the Buckingham potential:

$$V(r) = A\exp(-r/\rho) - Cr^{-6} \tag{3}$$

in which an exponential repulsive (Born–Mayer) function is supplemented by an attractive r^{-6} term. The latter has the correct analytical form for a dispersive interaction, although in practice, other attractive terms are very probably included in this term. The function is of the two-body, central-force type, i.e. the potential depends on the distance between pairs of particles and includes no angle-dependent forces. This feature is common to other analytical functions, e.g. the Morse and Lennard-Jones potentials that have been used in modelling solids. It is a major restriction when attempting to model silicates, for which angle-dependent, covalent forces are certainly significant.

Notwithstanding the previous comment, a number of workers have developed interatomic potentials for silicates using central-force potentials. Parker and co-workers (Parker 1982, 1983, Parker *et al.* 1984) derived potentials based on fully ionic models with Buckingham potentials acting between Si–O and O–O pairs (they found it unnecessary to include such functions between Si–Si pairs). Their models perform surprisingly well, as discussed below, in predicting structural properties of a number of silicate structures based on isolated SiO_4 tetrahedra or on silicate rings and chains. Potential models have also been derived for Mg_2SiO_4 by Catti (1981) and Matsui and Busing (1984 a, b). However, application of pair-potential models to framework structured silicates, e.g. SiO_2, leads to serious failures. These are essentially associated with the omission of terms in the potential constraining the SiO_4 units to retain tetrahedrality, i.e. the absence of an explicit contribution from covalent effects. A particularly simple solution of this problem was chosen by Sanders *et al.* (1984) who added to the Born model potential, energy terms of the type:

$$E(\theta) = K_b(\theta - \theta_0)^2 \tag{4}$$

where θ refers to O–Si–O bond angles and θ_0 is the tetrahedral angle; K_b is an harmonic force constant. It was found that the inclusion of these terms led to accurate modelling of the structure and properties of α-quartz, and, indeed, of other polymorphs of silica. Further details will again be given below, but the success of this approach will undoubtedly allow a much wider range of silicates and aluminosilicates to be treated in this manner.

(ii) *Polarization*

Detailed modelling studies require a treatment of polarization, including both displacement, due to relaxation of ions from their regular lattice sites, and electronic, due to deformation or distortion of the electron cloud, for example in the calculation of defect energetics. Displacement polarizability is accounted for naturally, through the equilibration of the structure around the defect during energy minimization (see

Section 3.3.2 below). The discussion that follows is concerned with the electronic contribution to ion polarizability. In silicates it may be necessary to consider oxide ion polarizability, and in some cases that of the extra-framework cations. The most successful treatments of polarizability in solid-state studies have been based on the shell model originally described by Dick and Overhauser (1958). This is a simple mechanical model of an atom or ion in which, as illustrated in figure 4, a massless 'shell' is connected by an harmonic spring to a 'core' in which the mass of the atom is concentrated; the former represents the polarizable valence shell electrons and the latter, the nucleus and unpolarizable core electrons. The development of a dipole moment is described in terms of the displacement of the shell relative to the core. The polarizability, α, is calculated as:

$$\alpha = Y^2/(k+R) \tag{5}$$

where Y is the shell charge, k is the harmonic force constant and R represents the damping of the polarizability due to the short-range forces.

Despite its crudity, the shell model includes one vital feature of polarizability in the solid state: polarization and short-range repulsive forces are coupled, if short-range forces are assumed to act between shells. This coupling acts so as to dampen the polarization and its omission, as in simpler point-dipole models, results in excessively large values of this term, manifested by inadequacy in calculated dielectric and lattice dynamical properties of the solid; and in extreme cases by instabilities known as the polarization catastrophe (Faux 1971, Faux and Lidiard 1971). In contrast, shell model potentials perform well in reproducing elastic and dielectric properties of materials, as well as phonon dispersion curves.

(iii) *Parametrization*

Potential models require 'parametrization', i.e. for each structure or compound values must be assigned to the variable parameters (e.g. A, ρ and C in equation (3)) in the description of the short-range potential and in the polarization terms. In modelling silicates, as indeed many other materials, the main approach used has been to 'fit'

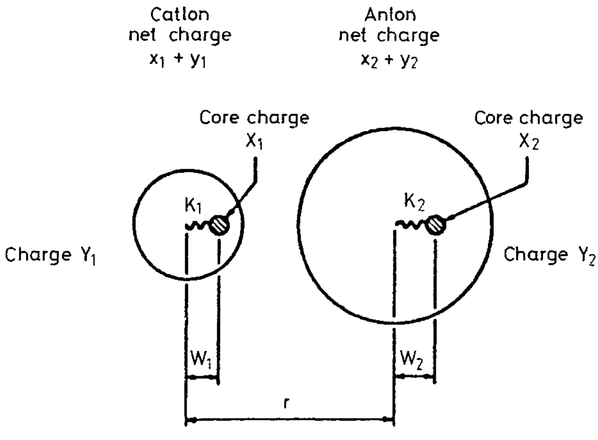

Figure 4. Schematic representation of the shell model.

parameters to bulk crystal properties. In many silicates, the structure itself is characterized by several parameters, all of which can be used as data to which potential parameters may be fitted. In practice, the procedure is to calculate, with a given potential, the forces acting on atoms in the crystal (and the forces of dilation or compression acting on the whole unit-cell) and adjust the potential parameters via a least-squares fitting routine until the calculated forces are a minimum, i.e. the potential gives the crystal as close as possible to equilibrium with the observed structure.

The above procedure was used with success by Parker (1982) and Parker *et al.* (1984) in obtaining pair potentials for silicates, as discussed below. The reliability of the empirical fitting procedure is, however, greatly increased when elastic, dielectric and lattice dynamical data are available in addition to structural properties. Such data were used by Price and Parker (1984) in a detailed study of Mg_2SiO_4. This work is of considerable interest as it provided some support for the superiority of interatomic potentials based on partial charges.

(iv) *Extension to simple Born-model treatment*

The siliceous mineral for which there is the greatest amount of reliable crystal data is, of course, α-SiO_2. As other workers had found, Sanders *et al.* (1984), and Sanders (1984), in a recent, detailed study of the potential for this material, established very clearly the inadequacy of two-body potential models; it is not possible using such models to reproduce structural, elastic and dielectric data. However, when bond bending terms (around the O–Si–O angles) of the type described in equation (4) were included, it proved possible to derive a potential model that satisfactorily calculates these data and is compatible with the observed structure of α-SiO_2. The potential parameters for the model, which included polarizability on the oxygen ions, are summarized in table 1 (*a*). Calculated and experimental crystal properties are given in table 1 (*b*) which also gives the results of the best fit that could be achieved using two-body potentials; the success of former and the inadequacy of the latter is clear. In addition the calculated phonon dispersion curves are in fair agreement with experiment for the bond-bending potential as shown in figure 5 which illustrates results for the $[\eta, \eta, 0]$ branch. In contrast, two-body models performed badly in the calculation of lattice dynamical properties.

Further evidence for the viability of bond-bending potentials in the modelling of framework-structured silicates will be provided in the following section. 'Empirical' potentials of this type do, however, have the inherent limitation that their reliability is guaranteed only for interatomic spacings close to those in the perfect lattice of the crystal used in deriving the parameters; although the success of empirical potentials in modelling the defect properties of a wide range of oxides and halides (Catlow *et al.* 1977, 1979) suggests that this limitation may not be too serious in practice. Nevertheless, there is a powerful incentive for developing theoretical methods for parametrizing interatomic potentials. In studies of simpler oxides and halide materials, considerable use has been made of electron gas models of the atom in deriving pair-potentials; a detailed discussion is given by Mackrodt and Stewart (1977, 1979). Greater reliability might be expected from the use of the *ab initio*, Hartree–Fock calculations. Indeed, this is a rapidly developing field, with studies reported recently by Mackrodt *et al.* (1980), and Saul *et al.* (1985). One aspect of this work that seems to be increasingly clear is the need to include the effect of the crystal environment when carrying out quantum mechanical calculations on pair potentials. Several studies have shown that failure to include these terms may lead to unreliable results.

Table 1

(*a*) Potential parameters for SiO_2, quartz (from Leslie *et al.* 1984)

Short-range potentials: $V(r) = A\exp(-r/\rho) - Cr^{-6}$

	Si...O	O...O
A(eV)	1283·9	22764·0
ρ(Å)	0·3205	0·149
C(eV Å^{-6})	10·66	27·88

Bond-bending force constant, O–Si–O, $V = k_b(\theta - \theta_0)^2$, ($k_b = 2{\cdot}097$ eV/rad^2)

	shell charge (|e|)	spring constant (eV Å^{-2})
Si	4·00	9999999·9
O	−2·8482	79·88

(*b*) Experimental and calculated crystal properties of α–quartz

Elastic constants (10^{11} dyne cm^{-2}):

	Expt.	*Calculated*	
		3-body	2-body
C_{11}	8·683	8·815	6·204
C_{33}	10·598	10·605	7·466
C_{12}	0·709	0·276	0·770
C_{13}	1·193	1·151	1·629
C_{46}	5·826	5·296	3·301
C_{66}	3·987	4·269	2·737
C_{14}	−1·806	−1·666	−1·012
Static dielectric constant			
ε_{11}	4·520	4·452	5·513
ε_{33}	4·640	4·812	6·086
High-frequency dielectric constant			
ε_{∞}	2·40	2·04	2·07

To date, although there have been several quantum mechanical studies of bonding in silicates (see 3.4), these methods have not been extensively applied to the study of interatomic potentials. Such studies should, we believe, be encouraged.

This concludes our study of interatomic potential models for silicates. The development of such models obviously raises the wider question on bonding in these compounds to which we return later. We continue with an account of the application of the potentials to the study of silicate structures.

3.3.2. *Structure prediction and calculation of crystal properties*

Given viable interatomic potential models, crystal structures may be predicted using energy minimization techniques. In concept, the procedure is simple: structural parameters (cell-dimensions and unit-cell coordinates) are varied until the minimum energy configuration is generated. A variety of algorithms are available for carrying out the computational, minimization procedure. The most successful are 'Newton'

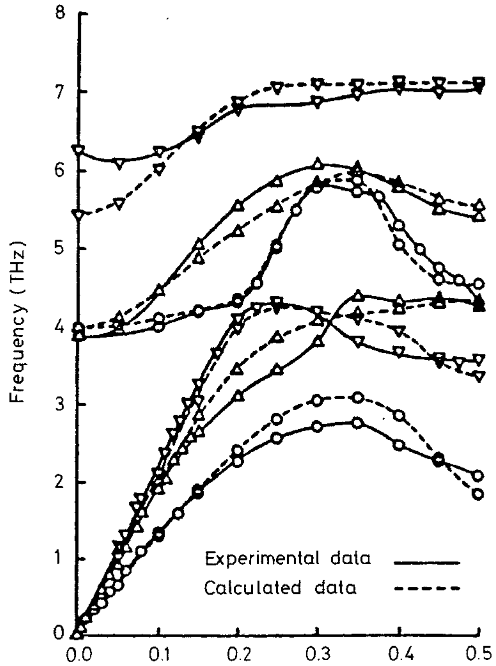

Figure 5. Phonon spectrum for α-quartz along $[\eta,\eta,0]$. (Sanders *et al.* 1984.) (Not all optical branches included.)

methods, in which second derivatives of the lattice energy with respect to particle coordinates are calculated. The iterative minimization procedure is then carried out with the vector $\mathbf{x}^{(p+1)}$ of unit-cell coordinates in the $(p+1)$th iteration being related to that in the pth iteration by the relationship:

$$\mathbf{x}^{(p+1)}=\mathbf{x}^{(p)}-(W^{-1})^{(p)}\mathbf{g}^{(p)} \tag{6}$$

where $\mathbf{g}^{(p)}$ is a gradient vector containing the derivatives of the energy with respect to coordinates and $W^{(p)}$ is a matrix, whose elements W_{ij} are the second derivatives of the energy with respect to coordinates, i.e.

$$W_{ij}=\frac{\partial^2 E}{\partial x_i \partial x_j}$$

Such methods are rapidly convergent, but have the disadvantage that the second derivative matrix must be calculated, stored and inverted. There are procedures for 'updating' the inverse of the matrix, without recalculation, each iteration. Nevertheless, the need to store the (inverse) matrix becomes a serious problem with large complex structures. The matrix is of dimension $3N \times 3N$ ($6N \times 6N$ if a shell model description is included), where N is the number of atoms in the unit cell. Thus for a cell containing 300 atoms, approximately 1 megaword of cpu memory is needed; this is approaching the limit of even the largest modern computer. For this reason it is necessary, in studies of very complex structures, to use alternative minimization procedures, which employ only first derivatives. The conjugate gradient method of Fletcher and Powell (1963) has proved to be one of the most effective, although such methods are invariably more slowly convergent than Newton procedures.

Full structure prediction includes minimization with respect to cell dimensions as well as unit cell coordinates. In the energy minimization studies of silicates reported by the present authors the following procedures have been adopted. First, the atom positions are equilibrated, with the given unit cell. Next, the cell dimensions are adjusted in the following manner for the lattice vector **a**:

$$\left.\begin{aligned} a'_x &= (1+\varepsilon_{ii})a_x + \varepsilon_{ij}a_y + \varepsilon_{ik}a_z \\ a'_y &= \varepsilon_{ij}a_x + (1+\varepsilon_{jj})a_y + \varepsilon_{jk}a_z \\ a'_z &= \varepsilon_{ik}a_x + \varepsilon_{jk}a_y + (1+\varepsilon_{kk})a_z \end{aligned}\right\} \tag{7}$$

where ε is the bulk strain matrix, acting on the unit cell; similar results obtain for **b** and **c**.

The lattice energy is then minimized with respect to coordinates in the new unit cell, after which cell dimensions are again adjusted. This 'double-iterative' procedure is then continued until the unit cell strains have been eliminated. In practice it is rarely necessary to adjust the cell dimensions more than four times.

These techniques have now been applied to several classes of silicate which will be classified according to the structure of the silicate sublattice, as described in Section 2.

(i) *Orthosilicates*

The greatest amount of work has been reported on Mg_2SiO_4. The structure of this important mineral is shown in figure 6: it is based on an hcp (hexagonal close-packed) oxygen sublattice with Mg occupying octahedral sites and Si tetrahedral sites—indeed distinct SiO_4 units can be identified in the structure. As is evident from the figure, the oxygen sublattice is extremely 'puckered'. Pair potential models developed by Parker and co-workers (1982, 1984) were surprisingly successful in reproducing the structure of this mineral, including the complex puckering of the oxygen sublattice. However, the fully ionic, pair-potential models did have definite deficiencies, with one of the Si–O bond lengths being in error by 0·15 Å. Notable improvements were effected by Price and Parker (1984) who used partial ion charges; they also employed Morse potentials in addition to Born–Mayer functions to describe the Si–O interaction. Using such potential models, they were able to reproduce very accurately the structure of this crystal. In addition, elastic and dielectric constants were well reproduced. Recently, Parker and Price (1985) have studied the energetics of the phase transition from the α structure to the high pressure spinel phase. This calculation performed well in

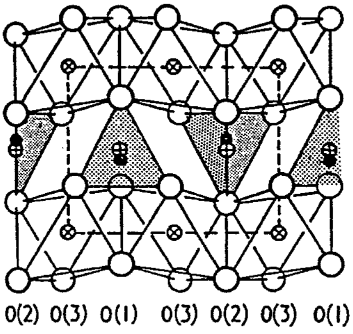

Figure 6. Projection of the structure of olivine showing 'puckered' oxygen plane.

reproducing the energies of the transition: a calculated value of 20 kJ mol^{-1} was obtained compared with an experimental value of 22 kJ mol^{-1}. However, Parker found that the calculated energy of the transition was exceptionally sensitive to the potential parameters. Thus a change in the value of 'ρ' of 10^{-4} in the Born–Mayer potential led to a change in of 7 kJ mol^{-1}. Clearly, the calculation of phase transition energies makes exceptional demands on interatomic potentials. It is apparent that there is considerable scope for more detailed studies on the interatomic potentials, especially in silicates.

(ii) *Metasilicates*

Calculations have been reported on both ring and chain-structured metasilicates. In the former category the mineral beryl ($Al_2Be_3Si_6O_{18}$), based on a six-membered ring, the three-membered ring structure $Na_2Be_2Si_3O_{19}$ and α-$Sr_3Si_3O_9$ were studied by Parker *et al.* (1984). Pair-potential models could adequately reproduce the main features of these structures although in some cases calculated bond lengths deviated from experimental values by as much as 0·2 Å.

The chain-structured metasilicates were also extensively studied by Parker *et al.* (1984) and Catlow *et al.* (1982). The former work again demonstrated the viability of pair-potential models in reproducing reasonably the structural properties of several minerals including wollastonite ($CaSiO_3$) and rhodonite ($MnSiO_3$). A detailed study was made of four pyroxenoid structures (diopside, β-wollastonite, rhodonite and pyroxmangite). Each structure adopts a different mode of linking the tetrahedra together in the $(SiO_3)_n$ chains (see figure 1). The relative energies of these different repeat units, as a function of ion size, were studied by Catlow *et al.* (1982). The results of the study are shown graphically in figure 7. The wollastonite and rhodonite structures were calculated to be more stable than diopside and pyroxmangite. However, in view of the sensitivity of phase transition energies to potential parameters as revealed by Parker's study of olivine, discussed above, it would be desirable to repeat these calculations with a variety of potentials.

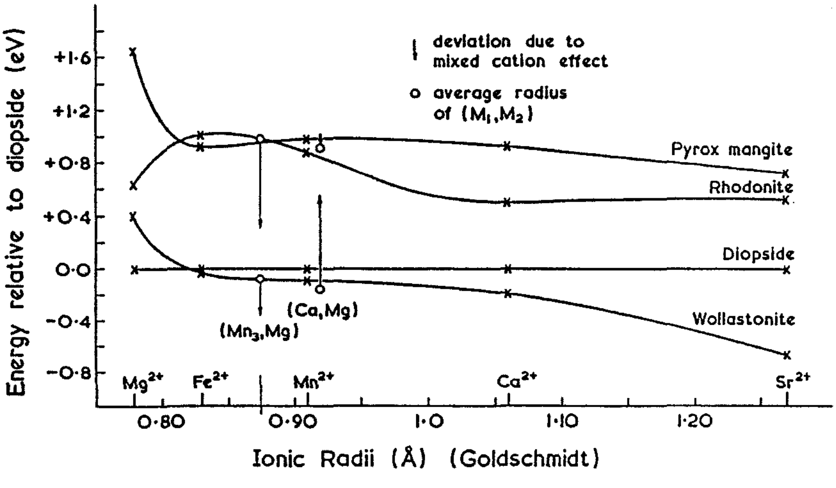

Figure 7. Energy of $MSiO_3$ unit (eV) relative to diopside. Smallest energy represents most stable configuration.

(iii) *Framework-structured silicates*

As discussed in Section 3.2.1, it is clear that two-body potentials are not so successful for the more open framework structures adopted by SiO_2 and many other aluminosilicates, for example, zeolites, a very important class of mineral. We saw, however, that inclusion of bond-bending terms did allow us to model successfully the structure and properties of α-quartz. Moreover, we found that the same potential could also reproduce well the structures of other polymorphs of SiO_2. In particular, energy minimization studies gave equilibrated structures for coesite, tridymite and α-cristobalite that were close to those observed experimentally (i.e. cell dimensions to within 1% and atomic coordinates to within 0·1 Å of the experimental values). These results encourage confidence in the applicability of this bond-bending potential for SiO_2 to other systems, such as the zeolites which we discuss next.

Studies of zeolites have been of two types. First, calculations have been performed with fixed frameworks with respect to which the extra-framework cation positions have been optimized. Secondly, full energy-minimization studies have been reported, in which the minimum energy position of both framework and non-framework atoms are calculated.

In the former category, there is the detailed study of the cation distribution in faujasites undertaken by Sanders (1984) and Sanders and Catlow (1983). Faujasites are one of the most important classes of zeolite and their structures are based on the well known cubo-octahedral cages connected via their six-rings as shown in figure 8. Diffraction studies have shown that the charge compensating extra framework cations are distributed predominantly over sites adjacent to six rings, with a small fraction occupying ill-defined positions in the super cage. There are three distinct types of six-ring sites: S_I' sites are within the cubo-octahedra (β-cages) and neighbour those six-rings which are directly linked to six-rings in other β-cages; S_I sites are within the hexagonal prisms created by the linking of the six-rings, while S_{II} sites are adjacent to unlinked six-rings. Sanders (1984) and Sanders and Catlow (1983) reported a detailed study of the cation distribution over these sites. They concentrated on the case where Si/Al = 1·4 in K-faujasite. This ratio was chosen because there had been a detailed study of the possible Si/Al ordering schemes over the tetrahedral sites reported by Klinowski *et al.* (1982) and Melchior *et al.* (1982), and one of the main aims of these calculations was to test the sensitivity of the distribution of the extra-framework cations to that of the Si and Al ions.

An initial examination of Madelung potentials showed that the S_{II} sites were by far the most energetically favoured. This accords well with experiment as S_{II} sites were found to be fully occupied in the diffraction studies of Mortier *et al.* (1976). Subsequent

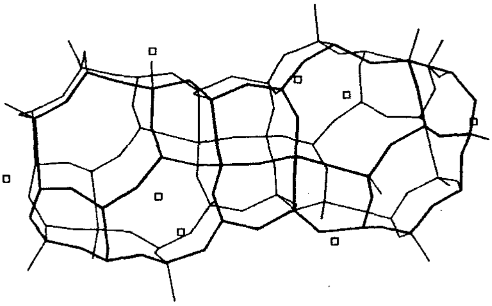

Figure 8. Linkage of cubo-octahedra in faujasite.

calculations therefore carefully examined the distribution of the remaining K^+ cations over the S_I and S_I' sites. In performing these calculations it was necessary to take into account the observation of Mortier *et al.* (1976), that a proportion of the K^+ cations (approximately six per unit cell) are located in ill-defined sites in the supercage (i.e. the large voids in the structure). Sanders (1984) therefore performed calculations in which six cations were placed in the centre of the supercage (in the faujasite structure) and the remaining ions were permuted over the S_I and S_I' sites. Detailed energy minimization with respect to the cation positions was then performed on the more energetically promising configurations.

The results showed that for most Si/Al ordering schemes, the favoured configurations had equal occupancy of the S_I and S_I' sites. This, in fact, accords with the experimental work of Mortier *et al.* (1976); moreover, the minimum energy positions occupied by the K^+ ions are close to those reported in that study. The details of the cation distribution are sensitive to the nature of the Si/Al ordering. Thus the calculations came up with the surprising prediction that for certain Si/Al distributions it was possible to have simultaneous occupancy of neighbouring S_I and S_I' sites, despite the unfavourable cation–cation repulsion energy. However, the calculations also showed that after energy minimization, the lattice energies of the different Si/Al ordering schemes were all similar. It seems that the extra-framework cations can readjust their positions in response to changes in the Al distribution, so as largely to remove any change in the total energy of the system.

The results suggest that any strong preference for a particular ordering scheme, such as the well known aluminium avoidance principle, formulated as Lowenstein's rule, may have a kinetic, rather than thermodynamic, basis. Indeed, preliminary calculations on Na-zeolite A (Sanders, unpublished work) have suggested that Al–O–Al linkages are not energetically prohibitive. Sanders (1984) and Sanders *et al.* (1984) also studied the cation distribution in zeolite A (in which the cubo-octahedra are linked through their four-rings). The particular system on which they concentrated was (dehydrated) Sr-zeolite A, where there had been some controversy (Pluth and Smith 1982, Firor and Seff 1978) concerning the distribution of Sr between six and eight-ring sites, these latter being created when the cubo-octahedra are linked together. Sander's conclusion clearly showed that the most energetically favoured cation distribution confined the Sr^{2+} to the six-ring sites, in agreement with the structural study of Pluth and Smith (1982). Indeed, the detailed cation distribution predicted by the calculations accorded well with that experimental study.

Sr-zeolite A was also the subject of an energy minimization study in which the framework, as well as the extra-framework, atoms were relaxed (Sanders 1984). As noted earlier, the simple two-body potentials fail badly when used in energy minimization studies of framework-structured silicates. However, when the 'bond-bending' potential described earlier was used, the results were again encouraging. The energy-minimized structure was found to be close to that observed experimentally. Moreover, the calculations found intriguing variations in the framework geometry, depending on whether or not an adjacent (non-framework) cation site was occupied by an Sr^{2+} ion. This type of information on *local* structure is not accessible from Bragg diffraction studies, although it could, in principle, be obtained from local structure probes, such as EXAFS.

As yet unpublished work of Jackson has shown that full energy minimization studies are also successful when applied to Na-Zeolite A. In addition, a very recent study by Hope (1985) has shown that it is possible to reproduce adequately the structure of pentasil zeolites such as the pure silica zeolite, silicalite, by energy minimization procedures using the 'bond-bending' potential. It seems, therefore, that present potentials and methodology are capable of modelling successfully the complex properties of zeolites; and there is clearly great scope for further work in this field.

There have been relatively few calculations on other framework silicates (except for SiO_2). Studies of alkali cation positional disorder in feldspars have been reported by e.g. Brown and Fenn (1979), but their model was largely electrostatic. In view of the success of the calculations on zeolites, further studies of feldspars would clearly be of interest.

(iv) *Defect calculations*

Although defect calculations have been very extensively applied to studies of ionic halides and oxides, there has been very little work on silicates. Lasaga (1980) used Mott–Littleton-like procedures to examine vacancy energies in magnesium olivine. His results are collected in table 2 where they are compared with recent work of Doherty in Catlow (1986). The very considerable difference reflects the use of a partially ionic model in Lasaga's work, unlike Doherty's study, where the potential model used fully ionic charges—the P1 potential of Price and Parker (1984).

Table 2.

(*a*) Vacancy energies (eV) in Mg_2SiO_4

Species	Mg(1)	Mg(2)	Si	O(1)	O(2)	O(3)
I†	23·842	25·609	90·256	25·558	23·617	23·280
II‡	3·854	6·404	—	1·422	1·455	0·592

(*b*) Interstitial energies (eV) in Mg_2SiO_4

Species	Type of site	Interstitial energy	Frenkel energy
Mg	Tetrahedral	−18·192 to −18·505	5·34
Mg	Octahedral	−14·023	9·82
Si	Tetrahedral	−67·203 to −67·920	22·34
O	Tetrahedral	−15·961 to −16·629	6·65

† These vacancy energies have been obtained using CASCADE (Leslie 1982).

‡ These values were quoted by Lasaga (1980).

Doherty's study employed the CASCADE code (Leslie 1982). This program uses a generalized Mott–Littleton procedure of the type that has been successfully applied to a wide range of oxide and halide crystals (see e.g. Catlow and Mackrodt (1982) for a discussion of the techniques and application of defect calculations). The most important feature of these calculations is the accurate treatment of lattice relaxation around the defect. This is achieved by a procedure known as the 'two-region' method, in which a region of crystal immediately surrounding the defect and containing typically 100–200 ions is treated atomistically with atomic coordinates being adjusted until a minimum energy configuration is attained. Interatomic potentials must, of course, be specified between the atoms in this region. In contrast, in the more distant regions of the crystal, where the defect forces are weak, the relaxation may be treated by pseudo-continuum procedures which calculate the polarization due to the effective charge of the defect.

Table 3. Schottky† energies (eV) for Mg_2SiO_4.

Species	Energy	Species	Energy
Mg(1)O(1)	49·400 (7·761)	SiO(1)O(1)	141·372 (20·607)
Mg(1)O(2)	47·459 (5·820)	SiO(1)O(2)	139·431 (18·666)
Mg(1)O(3)	47·122 (5·483)	SiO(1)O(3)	139·094 (18·329)
Mg(2)O(1)	51·165 (9·527)	SiO(2)O(2)	137·490 (16·725)
Mg(2)O(2)	49·224 (7·586)	SiO(2)O(3)	137·153 (16·388)
Mg(2)O(3)	48·248 (7·248)	SiO(3)O(3)	136·816 (16·051)

† Schottky energy is defined as the sum of the vacancy energies concerned and the lattice energy. The figure in parentheses is the Schottky energy, and the figure above is the sum of the vacancy energies of the species concerned. The lattice energy can be obtained using the potentials employed for Mg_2SiO_4. The value for MgO is −41·639 eV, and for SiO_2 is −120·765 eV.

There is now abundant evidence that, given sufficiently large sizes of the inner region, reliable defect energies may be calculated if good interatomic potentials are available. For further discussion, we again refer to Catlow and Mackrodt (1982).

In Doherty's work, interstitial, as well as vacancy, energies were calculated. Frenkel (table 2) and Schottky energies (table 3) may therefore be obtained. The most important finding was that the lowest-energy defect reactions involve the creation of Mg^{2+} Frenkel pairs which have a formation energy of about 5 eV. The calculations also suggest that the Mg^{2+} interstitial ions are mobile with an activation energy of ~0·35 eV. This would predict an Arrhenius energy of about 3 eV for Mg^{2+} diffusion, and this is within the range of experimentally determined values.

Whilst defect calculations on silicates are clearly at an early stage, the recent work on olivine is promising and suggests that the calculations could have a considerable role in advancing our knowledge of transport processes in these materials.

3.3.3. *Born-model calculations: an overview*

In view of their flexibility and range of applications, Born-model calculations will unquestionably have a continuing and expanding role to play in simulation studies of silicates. There remain, however, a number of problems which require further attention if the scope of such calculations is to be fully realized.

(i) *The question of ionicity*

Models based on formal ionic charges have performed surprisingly well. Nevertheless, there is a well founded consensus that silicates have a large covalent contribution to their bonding. Indeed, for the case of SiO_2, figures of 50% are commonly quoted for the percentage covalent character. Catlow and Stoneham (1983) following Cochran (1971) argued that a non-ionic electron density distribution does not invalidate the use of Born-type models; and the success of the modelling work on silicates must support this argument. It should be recalled that no potential model is more than a mathematical description of the lattice energy of the crystal as a function of atomic coordinates, and that the 'validity' of a model is simply a question of the extent to which it succeeds in this aspect. The electrostatic potential in the crystal will influence, for example, the distribution of extra-framework species in framework-structured silicates. The success of calculations on cation distribution in zeolites again suggests that Born-model potentials are acceptable in this respect. Nevertheless, there will no doubt be further attempts to derive potentials based on partial ionic charges. These in turn raise problems, first as to the choice of the effective charges—a notoriously difficult problem—and, secondly, to their use in defect studies where there are serious conceptual difficulties associated with point defects with non-integral charges.

(ii) *The use of bond-bending terms*

Again, we have found that the simple bond-bending term applied to O–Si–O bond angles results in apparently viable potentials. But is this the best type of function? And should it be confined to Si–centred bond angles? There is no definite answer to these questions, each of which requires further investigation.

(iii) *Parametrization*

To date, structural data have been the main source of empirical information on potentials. There is a need for assessment of potential models with reference to a much wider range of data, including elastic and dynamical properties.

3.4. *Quantum mechanical calculations*

The last few years has seen a considerable growth in the use of quantum mechanical calculations in investigating structure and bonding in silicates. Much of this work has been undertaken by Gibbs and collaborators (see e.g. Newton and Gibbs 1980, Gibbs *et al.* 1981) and by Tossell (1985). A good review is available from Gibbs (1982). In the present article, we cannot attempt a comprehensive account of this growing field; rather we wish to summarize the type of information yielded by these methods which we may then contrast with that available from the other techniques discussed earlier in this review. First, however, we present a brief summary of quantum mechanical methods that have been used.

3.4.1. *Quantum mechanical techniques*

Almost all calculations have been based on a small-cluster model, that is, a molecule which can be used as a model for bonding in silicates. The simplest molecule which allows tetrahedral silicon to be studied is $Si(OH)_4$; similarly $Si(OH)_6$ may be taken as a model for octahedral silicon. Larger molecules are then used when, for example, the properties of the Si–O–Si bond are being investigated (for which calculations have been performed on $H_6Si_2O_7$). In general, the molecules have not been 'embedded' i.e. there has been no attempt to account for the perturbation of the molecule, which is representing a fragment of the crystal, by the remainder of the surrounding crystal. We return to this point below.

The energy is calculated as a function of its geometry. In performing such calculations, greatest use has in recent years been made of *ab initio* methods in which all the matrix elements needed for solution of the Hartree–Fock equations, for a given basis set, are fully calculated. Gaussian basis sets have commonly been used, especially those in which Slater functions (STOS) are approximated by sums of Gaussian functions (see Gibbs (1982) for details). For larger molecules, computational constraints encourage the use of methods based on more approximate methods. For example, Tossell and Gibbs (1978, 1979) and Lasaga (1982) used the semi-empirical, CNDO procedure (which parameterizes certain many-electron integrals and ignores others) to study $H_6Si_2O_7$. It is likely, however, that with the continued increase in computer power, the need to use semi-empirical procedures will decline.

To date relatively few calculations have gone beyond the Hartree–Fock approximation in studies of silicate molecules. However, configurational interaction (CI) methods, which are now being extensively used in studies of small molecules, will, we consider, find a role in this field with the increasing availability of supercomputers.

3.4.2. *Results*

The main type of information yielded by the quantum mechanical calculations reported to data are as follows.

(i) *Structural properties*

Geometry optimization (the location of the minimum energy configuration of the molecule) can be readily performed for small molecules. The resulting bond lengths and bond angles can be compared with experiments. Thus Newton and Gibbs (1980) and Gibbs *et al.* (1981) calculated an SiO bond length of 1·65 Å in their *ab initio* study of H_4SiO_4; the value compares well with those measured in a range of monosilicates. A more complex example was the study by Meagher *et al.* (1980) of the energetics of $H_6Si_2O_7$ as a function of the Si–O–Si bond angles. The minimum energy was found for a bond angle of 140°, but the potential well is very shallow. This accords reasonably with experimental structural studies as a wide range of Si–O–Si bond angles are observed in silicates, but they are generally in the range of 140–160° (although some larger values are observed). Calculations on small molecules can therefore reveal general features of experimental structural studies. However, it is impossible for studies of such molecules to provide information on specific structures. The calculations should therefore be seen as providing general guidance as to the structural chemistry of silicates rather than detailed predictions on particular compounds.

(ii) *Bonding*

One of the simplest types of information concerning bonding is provided by electron density maps. These are particularly revealing when displayed as 'deformation density' maps, i.e. plots of the difference between the calculated electron density and that predicted from a superposition of non-interacting atoms. Such calculated maps, which immediately reveal bonding effects, may be compared with corresponding experimental plots available from high-quality X-ray studies. In general, it is found that the agreement between theory and experiments (where available) is good. Examples are given in the work of Hill *et al.* (1983).

Attempts may be made to partition electron density betwen different atoms, although this procedure is far from ambiguous. A number of prescriptions are available for partitioning calculated wave functions as discussed by Catlow and Stoneham (1983). Gibbs (1982) reports that effective charges of $\sim 2+$ for Si in silicates are typical for such calculations.

The most detailed and specific information concerning bonding relates to the contribution of different orbitals to the wave function. An example is the role of 3d orbitals—a long-standing controversy—in the bonding of silicates. Thus Newton and Gibbs (1980) found significant 3d orbital contribution to the bonding in H_4SiO_4 in line with earlier arguments of Pauling (1980).

(iii) *Interatomic potentials models*

By performing calculations on total energies as a function of geometry and fitting the resulting energies to analytical potential functions it is possible to extract effective potentials. Thus Newton *et al.* (1980) and Newton and Gibbs (1980), in calculations on $H_6Si_2O_7$, extracted Si–O bond-stretching and Si–O–Si bond-bending force constants which were approximately $100\,N\,m^{-1}$ and $10\,N\,m^{-1}$ respectively. Interatomic potentials (of which force constants are the derivatives) could equally well have been obtained. Recent applications to interatomic potentials in quartz are reported by Lasaga and Gibbs (1987).

In the opinion of the present authors, this is one of the most promising areas for future development. Quantum mechanical methods will, we consider, be increasingly used to obtain reliable interatomic potential models which are then employed in Born-model calculations of the type discussed in the previous section. Another development which we see as important is the use of 'embedded' quantum mechanical cluster calculations, in which the cluster is surrounded by a matrix of point charges which represent the effect of the remaining lattice. The work of Vail *et al.* (1984), Vail (1985) and Saul *et al.* (1985) has shown that greatly improved accuracy is achieved by these procedures. Indeed, omission of this effect can lead to the evaluation of an unsatisfactory wave function, with correspondingly erroneous results.

In summary, quantum mechanical methods provide valuable information, particularly on those fundamental aspects of bonding in silicates. There is, of course, no conflict between quantum mechanical approaches and those described in the previous section that were based on effective potentials. Indeed, the former can reinforce the latter by providing more reliable potential parameters.

4. Conclusions

The use of modelling methods is evidently a rapidly developing field in the study of the structural chemistry of silicates. Moreover, with expansion in computer power and increase of sophistication of programming, an exciting future is opening for the field in which there will be increasing studies of problems of greater complexity. Defect and surface studies are as yet in their infancy; great progress is to be expected in these fields. Indeed, simulations should have a major impact on our understanding of transport properties of minerals and in particular will allow us to predict the effect of temperature, pressure and chemical composition on diffusion and conductivity in these materials. Molecular dynamics techniques which have already been applied to silicate melts will find an increasing range of application in the study of high-temperature silicates; we also envisage a further major growth area in the use of simulations in studying the properties of silicates under conditions of high temperature and pressure—conditions which have great relevance geophysically, but where experimental studies are difficult or impossible.

A third area where expansion of the field is to be expected concerns the modelling of complex aluminosilicates. We have seen the value of simulation techniques in studying zeolites. Further work on these important materials may be expected together with the application of the techniques to other framework structures, such as feldspars, and to the clay minerals. Finally, we recall the central role of interatomic potentials in this field. The development of increasingly versatile and reliable models must be a priority in the future; we see an increasing part to be played by quantum mechanical studies in such developments.

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References

BAERLOCHER, C., HEPP, A., and MEIER, W. M., 1977, *DLS-76 Manual* (Zurich: Institut für Kristollographie und Petrographie, ETH).

BAUR, W. H., 1977, *Physics Chem. Miner.*, **2**, 3–20.

BISH, D. L., and BURNHAM, C. W., 1984, *Am. Miner.*, **69**, 1102–1109.

BROWN, G. E., and FENN, P. M., 1979, *Physics Chem. Miner.*, **4**, 83–100.

BURNHAM, C. W., 1985, *Microscopic to Macroscopic*, edited by S. W. Kiefer and A. Navrotsky (*Rev. Mineral*, **14**, 347).

CATLOW, C. R. A., and NORGETT, M. J., 1976, UKAEA Report, AERE-M2936.

CATLOW, C. R. A., and MACKRODT, W. C., (editors) 1982,*Computer Modelling of Solids* (Lecture Notes in Physics vol. 166) (Berlin: Springer).

CATLOW, C. R. A., DOHERTY, M., PRICE, G. D., SANDERS, M. J., and PARKER, S. C., 1986, *Mater. Sci. Forum*, **7**, 163. (Proceedings of Meeting on Transport in Silicates and Oxides, London, September 1984).

CATLOW, C. R. A., NORGETT, M. J., MACKRODT, W. C., and STONEHAM, A. M., 1979, *Phil. Mag.*, **40**, 161.

CATLOW, C. R. A., NORGETT, M. J., and ROSS, T. A., 1977, *J. Phys.* C, **10**, 1627.

CATLOW, C. R. A., and STONEHAM, A. M., 1983, *J. Phys.* C, **16**, 4321–4338.

CATLOW, C. R. A., THOMAS, J. M., PARKER, S. C., and JEFFERSON, D. J., 1982, *Nature*, **295**, 658.

CATTI, M., 1981, *Acta crystallogr.* A, **37**, 72; *Physics Chem. Miner.*, **7**, 20–25.

CATTI, M., 1982, *J. Phys. Chem. Solids*, **43**, 1111–1118.

COCHRAN, W., 1971, *Crit. Rev. Solid St. Sci.*, **2**, 1.

DEER, W. A., HOWIE, R. A., and ZUSSMAN, J., 1982, *Rock Forming Minerals*, second edition (London: Longman).

DEMPSEY, M. J., and STRENS, R. G. J., 1976, *The Physics and Chemistry of Minerals and Rocks*, edited by R. G. J. Strens (London: J. Wiley), pp. 443–59.

DICK, B. G., and OVERHAUSER, A. W., 1958, *Phys. Rev.*, **112**, 90.

DOLLASE, W. A., and BAUR, W. H., *Am. Miner.*, **61**, 971–978.

FAUX, I. D., 1971, *J. Phys.* C, **4**, L211.

FAUX, I. D., and LIDIARD, A. B., 1971, *Z. Naturf.* (a), **26**, 56.

FIROR, R. L., and SEFF, K., 1978, *J. Am. chem. Soc.*, **100**, 3091–3096.

FLETCHER, R., and POWELL, M. J. D., 1963, *Computer J.*, **6**, 16.

GIBBS, G. V., 1982, *Am. Miner.*, **67**, 421–450.

GIBBS, G. V., MEAGHER, E. P., NEWTON, M. D., and SWANSON, D. K., 1981, *Structure and Bonding in Solids*, Volume 1, edited by M. A. O'Keefe and A. Navrotsky (New York: Academic Press), pp. 195–225.

GIESE, R. F., 1974, *Nature*, **248**, 580.

GLIDEWELL, C., 1975, *Inorg. chem. Acta*, **12**, 219.

GRAMLICH, V., and MEIER, W. M., 1971, *Z. Kristallogr. Kristallgeom.*, **133**, 134–49.

HILL, R. J., NEWTON, M. D., and GIBBS, G. V., 1983, *Solid-St. Chem.*, **47**, 185–200.

HOPE, A. T. J., 1985, Ph.D. Thesis, University of London (University College).

JENKINS, H. D. B., 1982, *Computer Simulation of Solids*, edited by C. R. A. Catlow and W. C. Mackrodt, Lecture Notes in Physics, No. 116 (Berlin: Springer-Verlag), Chap. 16.

JENKINS, H. D. B., and HARTMAN, P., 1979, *Phil. Trans. R. Soc.* A, **293**, 169.

KLINOWSKI, J., RAMDAS, S., THOMAS, J. M., FYFE, C. A., and HARTMAN, J. S., 1982, *J. chem. Soc. Faraday Trans*, II, **78**, 1025.

Kokotailo, G. T., Chu, P., Lawton, S. L., and Meier, W. M., 1978 a, *Nature*, **275**, 119.

Kokotailo, G. T., Lawton, S. L., Olson, D. H., and Meier, W. M., 1978 b, *Nature*, **272**, 437.

Lasaga, A. C., 1980, *Am. Miner.*, **65**, 1237–1248.

Lasaga, A. C., and Gibbs, G. V., 1987, *Phys. Chem. Mineral* (in the press).

Leslie, M., 1982, SERC Daresbury Laboratory Report DL/SCI/TM31T.

Mackrodt, W. C., and Stewart, R. F., 1977, *J. Phys.* C, **10**, 1431.

Mackrodt, W. C., and Stewart, R. F., 1979, *J. Phys.* C, **12**, 431.

Mackrodt, W. C., Stewart, R. F., Campbell, J. C., and Hillier, I. M., 1980, *J. Phys. Paris*, **67**, 64.

McCusker, L., and Baerlocher, C., 1984, *Zeolites*, edited by D. H. Olson and A. Bisio (London: Butterworths).

Matsui, M., and Busing, W. R., 1984 a, *Phys. Chem. Miner.*, **11**, 55; 1984 b, *Am. Miner*, **69**, 1090.

Meagher, E. P., Swanson, D. K., and Gibbs, G. V., 1980, Abstract in *EOS*, **61**, 408.

Meier, W. M., and Villiger, H., 1969, *Z. Kristallogr. Kristallgeom.*, **129**, 411–423.

Melchior, M. T., Vaughen, D. E. W., and Jacobsen, A. J., 1982, *J. Am. chem. Soc.*, **104**, 4859.

Mortier, W. J., Pluth, J. J., and Smith, J. V., 1976, *Z. Kristallogr. Kristallgeom.*, **143**, 319.

Newton, M. D., and Gibbs, G. V., 1980, *Phys. Chem. Miner.*, **6**, 221–246.

Newton, M. D., O'Keefe, M., and Gibbs, G. V., 1980, *Phys. Chem. Miner.*, **6**, 305–312.

O'Keefe, M., 1977, *Acta Crystallogr.* A, **33**, 924.

O'Keefe, M., and Hyde, B. G., 1978, *Acta Crystallogr*, B, **34**, 27.

Olson, D. H., and Bisio, A., (eds.), 1984, *Zeolites* (Proceedings of the 6th International Conference on Zeolites) (London: Butterworths).

Olson, D. H., Kokotailo, G. T., Lawton, S. L., and Meier, W. M., 1981, *J. phys. Chem.*, **85**, 2238–43.

Parise, J. B., Gier, T. E., Corbin, D. R., and Cox, D. E., 1984, *J. phys. Chem.*, **88**, 1635–1639.

Parker, S. C., 1982, Ph.D. Thesis, University of London (University College).

Parker, S. C., 1983, *Solid St. Ionics*, **8**, 189.

Parker, S. C., and Price, G. G., 1985, *Physica* B, **131**, 290.

Parker, S. C., Catlow, C. R. A., and Cormack, A. N., 1984, *Acta crystallogr.* B, **40**, 200–208.

Pauling, L., 1980, *Am. Miner.*, **65**, 321.

Pluth, J. J., and Smith, J. V., 1982, *J. Am. chem. Soc.*, **104**, 6977.

Price, G. D., and Parker, S. C., 1984, *Phys. Chem. Miner.*, **10**, 209–216.

Price, G. D., Parker, S. C., and Yeomans, J., 1985, *Acta crystallogr.* B, **41**, 231–239.

Price, G. D., and Yeomans, J., 1984, *Acta crystallogr.* B, **40**, 448–454.

Sanders, M. J., 1984, Ph.D. Thesis, University of London (University College) also published as UKAEA Report AERE-TP 1102.

Sanders, M. J., Leslie, M., and Catlow, C. R. A., 1984, *J. chem. Soc. Chem. Comm.*, p. 1271.

Sanders, M. J., and Catlow, C. R. A., 1983, *Proceedings of the 6th International Zeolite Conference*, edited by D. Olsen and S. Bisio (London: Butterworths), p. 131.

Sanders, M. J., Catlow, C. R. A., and Smith, J. V., 1984, *J. phys. Chem.*, **88**, 2796–2797.

Saul, P., 1985, Ph.D. Thesis, University of London (University College).

Saul, P., Catlow, C. R. A., and Kendrick, J., 1985, *Phil. Mag.* B, **51**, 107–117.

Smith, J. V., 1977, *Am. Miner.*, **62**, 703–709.

Smith, J. V., 1978, *Am. Miner.*, **63**, 960–969.

Smith, J. V., 1979, *Am. Miner.*, **64**, 551–562.

Smith, J. V., and Bennett, J. M., 1981, *Am. Miner.*, **66**, 777–788.

Smith, J. V., and Bennett, J. M., 1984, *Am. Miner.*, **69**, 104–111.

Soules, T. F., 1982, *J. Non. Cryst. Solids*, **49**, 29.

Streifler, M. E., and Barsch, G. R., 1975, *Phys. Rev.* B, **12**, 4553–4566.

Streifler, M. E., and Barsch, G. R., 1976, *J. geophys. Research*, **81**, 2453–2466.

Tosi, M. P., 1964, *Solid State Physics*, Volume 16, edited by F. Seitz and K. Turnbull (New York: Academic Press), p. 1.

Tossell, J. A., 1980, *Am. Miner.*, **65**, 163–173.

Tossell, J. A., 1985, *Physica* B, **131**, 283–289.

Tossell, J. A., and Gibbs, G. V., 1977, *Phys. Chem. Miner.*, **2**, 21–57.

Tossell, J. A., and Gibbs, G. V., 1978, *Acta crystallogr.* A, **34**, 463–472.

Vail, J. M., 1985, *Phil. Mag.* B, **51**, 100–106.

Vail, J. M., Harker, A. H., Harding, J. H., and Saul, P., 1984, *J. Phys.* C, **17**, 3401.