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Publisher: Taylor & Francis

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Philosophical Magazine Part B

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tphb20>

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Published online: 27 Sep 2006.

To cite this article: J. D. Gale (1996) Empirical potential derivation for ionic materials, Philosophical Magazine Part B, 73:1, 3-19, DOI: [10.1080/13642819608239107](https://doi.org/10.1080/13642819608239107)

To link to this article: <http://dx.doi.org/10.1080/13642819608239107>

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Empirical potential derivation for ionic materials

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[Received 5 July 1994 and accepted in revised form 7 December 1994]

ABSTRACT

A program has been developed for the derivation of empirical interatomic potentials, with particular regard to ionic materials and the use of shell models, incorporating two new methods of fitting. Concurrent fitting of multiple structures is found to enhance greatly the reliability of the derived potentials and can lead to a physically sensible O-O potential without the use of constraints. Inclusion of gas-phase cluster information appears to be beneficial even within an ionic model. By combining free-energy minimization with empirical fitting based on displacements, rather than gradients, it is now possible to determine interatomic potentials with correct treatment of thermal effects and the zero-point energy.

§ 1. INTRODUCTION

The aim of this contribution is to highlight the recent progress made in the empirical derivation of interatomic potentials for applications in the solid state and to examine the future directions for improvement. Here we shall be specifically concerned only with ionic materials, and in particular oxides, as opposed to organics and semiconductor materials where empirical potential development is more advanced and has resulted in widely used parameterizations such as MM2 (Allinger 1977) and valence force field (VFF) (Lifson and Stern 1982). This is aided by the factor that such systems are characterized primarily by regular geometries that largely conform to well defined concepts such as valence shell electron pair repulsion (VSEPR). Forces are predominantly local in their nature as a result of the high degree of covalency. For ionic systems the dominant factor is electrostatics, typically making a contribution to the energy an order of magnitude greater than the short-range forces. Hence a different approach is called for.

The first modelling of ionic materials was done with empirical potentials in the form of the Born-Mayer and Born-Landé equations in which the short-range repulsive energy is a simple function of the nearest-neighbour distance. The ultimate in empirical modelling was, however, Kapustinskii's (1956) equation which gives the lattice energy without even knowing the structure!

Although there have been a number of innovations since this early work, much of the essence of the method remains unchanged, particularly in the choice of functional forms. One area, which is beyond the scope of this article, with potential for future development is the choice of model. Here we address the problem of obtaining the best parameters regardless of what particular functional form has been selected.

§2. FUNDAMENTAL CONSIDERATIONS OF EMPIRICAL FITTING

Empirical fitting quite simply consists of a least-squares procedure, minimizing the difference between the observable and calculated properties:

$$F = \sum [f(\text{obs}) - f(\text{calc})]^2.$$

Properties consist of the crystal structure, which is a prerequisite for fitting, supplemented by any of or all the following: elastic constants, high-frequency and static dielectric constants, lattice energy and piezoelectric constants.

In theory we can use phonons; however, care is needed as the ordering of modes may change during fitting. Consequently when fitting phonons it is necessary to specify a reasonable approximation to the relevant eigenvector so that the frequencies for fitting can be selected on the basis of maximum overlap with each normal mode. One exception is in systems where there is one distinctive frequency well separated from other modes, such as a single hydroxyl group.

One straightforward application of phonon fitting is to ensure that the structure that you are fitting is a minimum and not a higher-order stationary point. This can be achieved because at the gamma point the first three frequencies in ascending numerical order must be equal to zero for a genuine minimum.

A principal limitation of empirical fitting is that, for many complex oxides, only the crystal structure is known accurately, via either powder X-ray or neutron refinement. Measurement of other properties often requires reasonably sized single crystals, particularly for elastic constants and phonons. In some cases even the structure cannot be readily used in fitting, particularly where the material is non-stoichiometric or contains impurities. Experimental lattice energies also have a high degree of uncertainty owing to the second electron affinity of oxygen.

However, we cannot fully refine empirical potentials just based on a crystal structure as we shall obtain the answer that all our potential parameters with units of energy will tend to zero as this trivial solution gives zero gradients exactly, but this is not very useful! This problem can be circumnavigated by transferring a known potential from a different system, normally the oxygen–oxygen potential, or by fixing the charge state of the ions. By making these somewhat arbitrary choices we can no longer be certain that we shall obtain the truly optimum parameter set.

Many 'empirical' potential sets have been derived for oxides to date (Lewis and Catlow 1985); however, the vast majority were obtained from the starting point of the oxygen–oxygen potential derived by Catlow (1977) which came from Hartree–Fock calculations on the interaction of two O^- ions. Hence there has not actually been a genuinely all empirical set of potentials for oxides until very recently (Bush, Gale, Catlow and Battle 1994).

A second limitation of empirical fitting is that in terms of the energy against distance curve the above properties sample only the well depth, its position and its curvature. Hence extrapolation about the minimum is restricted to second-order quadratic accuracy. Fitted short-range potentials although they may act over a specified range are really influenced only by the first one or two shells of atoms and hence the potential is effectively sampled only at a small number of distances. Thus there is no guarantee that bulk-derived potentials are ideal for treatment of defects, such as interstitials or vacancies, or even for application to surfaces where there is substantial relaxation on cleavage.

Theoretical methods are becoming increasingly important in deriving potentials, through fitting of energy hypersurfaces, because it supplies information about a

wider variety of separations, although there is the restriction that the self-consistent field may be readily convergent only within typically $\pm 20\%$ of the equilibrium lattice parameter. There is a particular advantage to fitting energy hypersurfaces. In an empirical fit there are an infinite number of possible optimized potential sets resulting from the infinite number of choices of relative weighting factors for structural and curvature-related information. When utilizing an energy hypersurface no relative weighting factor is necessary unless we wish to improve the quality of the fit in a particular region of configuration space.

In the past most of the theoretical potential derivations have been based on clusters; so the problem has been to deal with cluster termination effects and differences in properties such as ionicity between the bulk and clusters. For example in the work of Van Beest, Kramer and van Santen (1990) after fitting to *ab initio* cluster models for aluminosilicates it was necessary to adjust empirically a number of parameters to achieve successful results for bulk calculations. These problems can now be overcome by using energy hypersurfaces obtained directly for the bulk material from programs such as CRYSTAL (Dovesi *et al.* 1988) as a starting point for potential derivation (Gale, Catlow and Mackrodt 1992). We shall demonstrate later that even potentials derived from a fully correlated relativistic quantum-mechanical method cannot be used in athermal simulations with the expectation of obtaining perfect agreement with experiment.

We shall now review the models and approaches to empirical parameterization that have been used to date which lead naturally to the question of how we may further improve interatomic potential derivation in future. This work is the result of the experience that has been gained in fitting through the development of the program GULP (Gale 1992–1994) over the last few years and owes much to the suggestions of the users. The availability of an input-file-driven program for empirical fitting has greatly accelerated the process of potential derivation for oxides through the automation of many procedures, which are to be documented in this article, combined with the inclusion of crystal symmetry to reduce the size of many problems.

§3. POTENTIAL MODELS

Although the discussion of empirical fitting that will follow is generally applicable to many models, it is worth stating the model that will be used in many of the examples for clarity. The exact many-body energy may be decomposed into a series of terms containing the n -body components:

$$E(1, \dots, N) = \sum_i E(i) + \sum_{i,j} E(i, j) + \sum_{i,j,k} E(i, j, k) + \sum_{i,j,k,l} E(i, j, k, l) + \dots$$

We shall assume that five-body and higher-order terms are negligible and subsequently neglect them. Of the remaining terms the two-body term is the dominant contribution to the binding energy and for ions i and j , with charges q_i and q_j , we can write the two-body energy as

$$E(i, j) = \varphi_{ij}(r_{ij}) + \frac{q_i q_j}{r_{ij}}.$$

The electrostatic term is only conditionally convergent in real space and is thus evaluated via a partial transformation into reciprocal space following the method developed by Ewald. The choice of real and reciprocal space cut-offs may be related to a single parameter η which can be defined as so to minimize the sum of the

number of terms to be calculated in real and reciprocal space (Jackson and Catlow 1988). Further refinement can be achieved by introducing a factor for the relative expense of calculation of the two types of term. The 'short-range' energy term is chosen to be a functional form that describes both the Pauli repulsion at short distances and the dispersive interaction at long range. For ionic materials this is generally chosen to take the form of a Buckingham potential:

$$\varphi_{ij}(r_{ij}) = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}.$$

The only problem with the Buckingham potential is that the energy tends to minus infinity as the distance goes to zero; so the barrier must be sufficiently large that this region is inaccessible, particularly in molecular dynamics. This can be overcome by use of a four-range Buckingham, which also introduces a further degree of freedom by being able to specify the position of the energy minimum.

Crucial to the success in modelling oxide materials is the use of a dipolar shell model which allows the polarization of ions in an electric field to be mimicked. This is particularly important for being able to fit dielectric properties and thus to calculate defect energetics. In the dipolar shell model due to Dick and Overhauser (1958) a massless shell, on which all pair potentials act, is coupled by a harmonic force to a core from which it is coulombically screened:

$$E(\text{core-shell}) = \frac{1}{2} K_{\text{cs}} r^2.$$

For partially covalent materials with regular coordination environments, such as silicate frameworks, three-body terms are normally included to introduce an energy penalty for deviation from tetrahedral coordination (Sanders, Leslie and Catlow 1984). Similarly four-body terms may be added to stabilize planar coordination geometries.

In theory the charges on the ions may be chosen, normally based on either an *ab initio* calculation or more approximate methods such as electronegativity equalization (Baekelandt, Mortier, Lievens and Schoonheydt 1991), or they can be regarded as fittable parameters. In practice it is far more convenient to assume formal charges as this makes a wider range of defect calculations possible, as defects will necessarily possess an integer charge, and also removes one degree of freedom.

§4. SIMULTANEOUS FITTING

In conventional fitting, as has been widely used within this community in the past, we calculate the gradients and properties at the experimental crystal structure and vary the potential parameters to minimize the error in these calculated quantities, taking the experimental gradients to be zero at the observed atomic coordinates.

A problem arises when using any form of shell model, be it dipolar or a breathing shell. Formally we can equate the core of an ion with the nucleus as it is assigned the atomic mass in dynamical calculations. Hence we know from a crystal structure the desired core positions to which we wish to fit, formally speaking provided that the diffraction data was obtained using neutrons. However, in the case of the shells we have no *a priori* information about where to place them, except in the rare case where the electron density has been determined precisely by crystallography and we can obtain the ion dipoles directly. In many cases the shells have been assumed to be coincident with the cores for early empirical potential fits, which is often true for

high-symmetry crystallographic sites. For low-symmetry sites this is clearly an erroneous assumption which, as it will be demonstrated later, leads to a poor quality of fit.

There are two approaches to handling the general case in shell model fitting. Firstly we could perform an optical (shell-only) energy minimization at each point in the fitting procedure and calculate the residual sum of squares as before. Alternatively we could include the symmetry-reduced shell model coordinates, and radial parameters if appropriate, as variables in the fit so that they are adjusted to obtain the lowest possible sum of squares. The inclusion of the shell coordinates as fitted parameters is countered by adding an equal number of conditions that the corresponding gradients must be zero. Hence the inclusion of the shell model leads to no change in the difference between the number of observables and fitted parameters.

These above two methods yield slightly different results if properties other than the crystal structure are included in the fit as in the first technique the shells are purely minimized with respect to the energy, whereas in the second case the shells are optimized in regard to the sum of the squares of the residuals.

Experience in applying these two approaches suggests that the latter method is more readily convergent and computationally efficient. The ability to relax shells during potential derivation has been automated in the program GULP and has been given the name 'simultaneous fitting'.

One example of where simultaneous fitting has proved to be crucial is in determining interatomic potentials for aluminophosphates. These materials also raise other questions, such as can we really expect the ionic model to handle unphysically large formal charge states as +5? Work on deriving potential parameters for berlinite (Gale and Henson 1994) suggests that a formally charged model is in fact feasible and performs as well as other more physical partially charged models (table 1 shows a comparison of calculated and experimental properties for berlinite). The shell model can allow the simulation of a significantly covalent material using an ionic model because of the similarity between polarization and covalency unless the electron density distribution is considered. In this example the dipolar shell model can subsume covalent effects because of the low symmetry at oxygen; however, for more regular structures a breathing shell would be necessary.

Modelling of silicates within the ionic model employing formal charges is now well established (Catlow and Cormack 1987); however, earlier attempts to extend the scope of such calculations to their aluminophosphate analogues had proved unsuccessful because the cores and shells were concentric during fitting. In the case of berlinite, conventional fitting, in which the cores and shells are assumed to be coincident, gives a final sum of squares of 884977.0 whereas simultaneous fitting yields 22.02, indicating that an improvement of several orders of magnitude may be achieved in extreme cases. This demonstrates that, for the shell model to be effective in subsuming errors in charge states, it is necessary to allow the core and shell to separate during fitting.

§ 5. TRANSFERABILITY OF EMPIRICAL POTENTIALS

A successful potential model must be transferable to as many different structures as possible. If it only reproduces the structure to which it was fitted, then it is of little practical use. For empirical fitting, reliability and transferability can obviously be improved by including as much information as possible, although we are often restricted for solid-state simulations by the lack of non-structural data for many

Table 1. Comparison of experimental and calculated structure and properties for berlinite.

	Experimental	Gale and Henson (1994)	Van Beest <i>et al.</i> (1990)
a (Å)	4.942 3	4.910 9	4.999 1
b (Å)	10.944 6	10.956 4	11.123 6
Al, x	0.466 5	0.467 0	0.464 7
P, x	0.466 9	0.469 8	0.463 1
O(1), x	0.416 1	0.408 3	0.433 4
O(1), y	0.292 2	0.289 1	0.294 4
O(1), z	0.397 6	0.397 2	0.402 5
O(2), x	0.415 3	0.417 9	0.422 2
O(2), y	0.257 9	0.260 0	0.251 2
O(2), z	0.883 5	0.882 2	0.889 3
C_{11} (GPa)	63.4	81.8	87.5
C_{12} (GPa)	2.3	15.9	13.0
C_{13} (GPa)	5.8	22.2	19.1
C_{14} (GPa)	-12.1	-10.9	-12.4
C_{33} (GPa)	55.8	106.7	104.0
C_{44} (GPa)	43.2	44.0	48.8
C_{66} (GPa)	30.6	32.9	37.4
ϵ_{11}^0	5.47	5.25	1.92
ϵ_{33}^0	5.37	5.42	1.94
$\epsilon_{11}^{\text{hf}}$	4.60	2.08	1.00
$\epsilon_{33}^{\text{hf}}$	4.48	2.11	1.00
d_{11} (10^{12} C N $^{-1}$)	-3.30	-2.30	-1.57
d_{14} (10^{12} C N $^{-1}$)	1.62	1.09	0.24

compounds. Conversely, accurate information about gas-phase clusters is much more readily available from sources such as the JANAF tables or alternatively high-level quantum-mechanical calculations. This begs the question, can we simultaneously fit both cluster and bulk material data, as has been done for systems such as silicon (Bolding and Andersen 1990), to obtain a common potential applicable to both? The ionicity will certainly differ between the two phases and, as the electrostatics are the dominant influence, this may preclude a combined fit within the ionic model.

We shall consider the example of magnesium oxide here, it being the best-characterized oxide material, theoretically at least. In considering the ionicity we shall concern ourselves with Mulliken charges. This is not to say that these are uniquely correct, but they are the most widely reported and we are interested in making comparisons only. A large number of *ab initio* Hartree-Fock studies on clusters indicate that the Mulliken charges for the MgO diatomic molecule are close to +0.8 and -0.8 for magnesium and oxygen respectively (Ziemann and Castleman 1991). As the size of such clusters increases, so does the Mulliken population although the trend cannot be extrapolated to formal charges for infinite cluster size.

At the other extreme, periodic Hartree-Fock (Causa, Dovesi, Pisani and Roetti 1986) and local-density approximation (LDA) plane-wave pseudopotential calculations (De Vita *et al.* 1992) indicate that the bulk solid is close to being fully ionic, although recent all-electron LDA calculations using Gaussian basis sets appear to disagree with this view (Birkenheuer, Boettger and Röscher 1994). The cluster limit and bulk results can be reconciled provided that the basis set exponents are reoptimized for each cluster size. For example, the standard 6-31G* basis set yields charges

of only ± 1.437 when used in a bulk Hartree-Fock calculation, whereas similar quality bulk-optimized basis sets yield much higher ionicities.

On balance there would appear to be a significant change in ionicity on going from the diatomic to the bulk for MgO. We shall now examine whether this makes information from the two phases incompatible in a fitting procedure. Two fits have been performed; in the first the Mg-O potential and shell model parameters are fitted to just the bulk structure, elastic and dielectric constants, while in the second the bond length and stretching frequency of the diatomic molecule are also fitted. In both cases the O-O short-range potential is held fixed at that obtained by Bush *et al.* (1994).

The results of these two fits in terms of the potentials derived and quality of fit are shown in tables 2 and 3 respectively. Both sets of potentials perform similarly for the bulk material; however, for the diatomic species the bulk-only fit is clearly inadequate. Particularly surprising is that despite underestimating the MgO bond length the frequency is also only two thirds of the experimental value, whereas it might have been expected to be too high as a result.

The difference in the potentials is primarily in the shell model parameters, and not the short range Mg-O repulsion. In the bulk-only fit the core and shell are always concentric; so the spring constant only contributes to the on-diagonal elements of the second-derivative matrix. Hence the shell model purely adsorbs errors in the calculated curvature-related properties. In the combined fit the shell model is fundamental in obtaining the correct diatomic molecule bond length as well making for a more reliable fit.

Table 2. Potential parameters derived for magnesium oxide based on either only bulk information or the combined use of gas phase and bulk data (potential cut-off, 12.0 Å).

Fit type	Bulk only	Bulk and gas phase
A (Mg-O) (eV)	2 053.405	2 143.768
ρ (Mg-O) (Å)	0.268 88	0.267 34
A (O-O) (eV)	25.31	25.31
ρ (O-O) (Å)	0.693 7	0.693 7
C (O-O) (eV Å ⁶)	32.32	32.32
K_{cs} (O) (eV Å ⁻²)	15.898	41.822
q_s (O) (electrons)	-2.000 0	-2.394 5
α (O) (Å ³)	3.623	2.129

Table 3. Calculated observables for bulk and gas-phase diatomic magnesium oxide.

	Experiment	Bulk only	Bulk and gas phase
Bulk			
a (Å)	4.212	4.224	4.226
C_{11} (GPa)	297	309.2	314.1
C_{14} (GPa)	156	199.4	198.8
ϵ_{11}^0	9.86	11.38	11.69
ϵ_{11}^∞	2.96	2.96	2.37
Cluster			
r (Å)	1.672	1.550	1.647
ν (cm ⁻¹)	902	593.2	901.3

Comparison of the two oxygen-in-crystal polarizabilities with both theoretical estimates for MgO of 1.826 \AA^3 (Fowler and Madden 1985) and experiment-based estimates of 1.689 \AA^3 (Fowler and Pyper 1985) indicates that the inclusion of molecular data enhances the parameterization of the shell model. It would appear from these preliminary results not only that is the combined fitting of cluster and bulk data possible, even for ionic oxides, but also that it is highly desirable.

§6. RELAXED FITTING

In the previous section we have demonstrated that the problem of the shell positions can be dealt with, but now we turn to address the question of how to improve the fitting process fundamentally. Practical experience has shown that, in conventional fitting, lowering the sum of squares is not a guarantee of better results when the potentials are actually applied to energy minimization. The main criterion used for deciding the accuracy of a potential model is normally not the forces at the experimental geometry, but instead the displacements of the optimized structure away from the experimental configuration.

If the gradient vector is \mathbf{g} and the Hessian matrix is \mathbf{H} , then the displacements Δ that would occur on optimization, assuming the local energy surface is quadratic, will be given by

$$\Delta = \mathbf{H}^{-1} \mathbf{g}.$$

Hence we could minimize the displacement vector with respect to the fitted parameters in place of the gradients. However, in many cases the quadratic approximation is not sufficient and in some cases the Hessian may not even be positive definite; so we would have to include further tests to ensure that the fit is valid.

There is also a second flaw in the conventional approach to fitting in that the curvature-related properties are only strictly calculable directly from the second-derivative matrix when the gradients are zero. Unless the fit to the structure is already perfect, then trying to reproduce elastic and dielectric constants at the experimental structure is far from ideal.

Both of the above difficulties can be resolved by performing a full optimization of the structure with a subsequent property calculation for each point during the fitting procedure. This method, which has become known as 'relaxed' fitting, thus yields the exact displacements and genuine physical properties.

A type of system for which relaxed fitting has been important is ferroelectric and piezoelectric materials, in which these properties depend on a subtle low-symmetry distortion away from the perovskite structure involving the off-centring of a cation leading to a net dipole within the unit cell. Previously fitting to these structures yielded models which on subsequent relaxation led to the regular high-symmetry form.

Cherry, Islam and Catlow (1995) have managed to derive a potential set that correctly models the distorted structure of LaCrO_3 by use of relaxed fitting. The potentials for La–O and O–O were taken from Bush *et al.* (1994) and only the Cr–O potential was fitted, first by conventional and subsequently by relaxed fitting. In their work the static dielectric constant was fitted alongside the structure. As table 4 shows, the static dielectric constant is the most sensitive second-derivative property in distinguishing between the low- and high-symmetry configurations, the latter being a high-order stationary point possessing seven imaginary modes with three unique frequencies ($3 \times 149.5i$, $1 \times 142.8i$ and $3 \times 63.4i \text{ cm}^{-1}$).

Table 4. Comparison of the calculated structure and properties for LaCrO_3 at the minimum-energy and high-symmetry configurations based on the potentials of Cherry *et al.* (1995).

	Optimized structure	High symmetry	Experiment
a (Å)	5.528	5.502	5.476
b (Å)	7.788	7.780	7.752
c (Å)	5.508	5.502	5.512
La, x (fraction)	0.023 5	0.000 0	0.019 6
La, z (fraction)	0.998 2	0.000 0	0.995 4
O, x (fraction)	0.489 6	0.500 0	0.493 5
O, z (fraction)	0.040 2	0.000 0	0.067 6
C_{11} (GPa)	415	525	—
C_{33} (GPa)	511	525	—
C_{12} (GPa)	171	186	—
C_{23} (GPa)	194	186	—
C_{13} (GPa)	138	153	—
C_{55} (GPa)	133	153	—
ϵ_{11}^0	68.2	−102.5	57.0

In the past, fitting has tended to proceed in a sequential manner, in that structures were fitted one at a time and then the potentials obtained transferred to any subsequent mixed-cation structures. This approach suffers in that errors arising either from uncertainties in empirical data fitted or from limitations of the model being employed propagate in an uncontrolled fashion. As previous empirical parameterization studies in other areas have demonstrated, fitting to as many different structures as possible concurrently greatly improves the transferability of the fitted variables and minimizes the effects of errors in any particular piece of information.

Recently Bush *et al.* (1994) have applied the combination of relaxed fitting and multiple structures to the problem of binary and ternary oxides. A wide range of binary oxides were concurrently fitted and the resulting interatomic potentials then applied to a number of ternary oxides with gratifying success with errors being typically less than 1%.

As has been previously mentioned, most earlier work on oxides needed some theoretical input to fix the O–O potential as empirical fitting to one structure tends to yield nonsensical parameters as there is insufficient sampling of the O–O repulsion and the attractive dispersion term can become very large through being correlated to the repulsive potential. Of particular significance is that Bush *et al.* (1994) were able to obtain a genuinely empirical O–O potential having allowed it to fit without constraints. Furthermore the coefficients of the Buckingham potential are physically reasonable with the dispersion term of $32.32 \text{ eV } \text{\AA}^6$ being close to the quantum-mechanical value of $36.1 \text{ eV } \text{\AA}^6$ for O^{2-} in magnesium oxide (Fowler 1990).

The exponential repulsion term of the O–O potential turns out to be negligibly small in comparison with previous interatomic potentials. However, this is not necessarily surprising as the electrostatic repulsion, which will demonstrate the long-range force, already represents an upper bound for this component and the true short-range energy will not be sampled in a perfect oxide structure.

Because of the interest in oxygen interstitials the exact nature of the O–O potential at short distances is important, however. To try to assess the performance of different interatomic potentials we can turn to quantum-mechanical methods. We have considered the energy of an oxygen interstitial in alumina as a suitable case

for comparison. It should be stressed that the aim of the exercise is to compare potentials and not to obtain an accurate energy for this defect.

While we can readily perform a Mott–Littleton calculation to obtain defect energies based on pair potentials, we cannot yet perform an exact parallel quantum-mechanical calculation. Hence we have devised a system for which this is possible. A finite cluster of point charges have been created to mimic the bulk Madelung potential at and around the interstitial site. The oxygen ions surrounding the interstitial are included explicitly in the quantum-mechanical calculation which was performed using solid-state optimized triple-zeta basis sets with polarization functions and a MP2 correlation correction. The counterpoise method was used to determine the approximate basis set superposition error contribution.

In the ionic model calculation, pair potentials likewise interact only between the interstitial ion and all the ions immediately surrounding this ion. No nuclear coordinates are optimized in the calculation; however, in the pair potential model an optical relaxation is performed to parallel the electronic polarization in the quantum study.

The quantum-mechanical estimate of the energy of introduction of an oxygen dianion interstitial was 4.14 eV after all corrections. This is comparable with the value of 5.18 eV obtained from the widely used Catlow (1977) O–O potential. The potential of Bush *et al.* (1994) with minimal short-range O–O interaction is in remarkably good agreement with the quantum-mechanical result yielding a value of 4.03 eV, further demonstrating that it is possible to obtain physically reasonable parameters by purely empirical means.

§ 7. BEYOND ATHERMAL FITTING

The vast majority of simulations performed on ionic materials to date have been athermal, in that the question of temperature is not explicitly considered. In practice, thermal effects are normally subsumed into the interatomic potentials through the experimental data that were used in the fitting procedure. The resulting potentials correspond to an effective temperature which is a weighted average of the temperatures at which all the pieces of data were measured. Strictly speaking, the convolution of thermal effects is valid only if all experimental quantities are measured at the same temperature.

With the increasing desire to perform simulations in which the temperature is an explicitly specified variable it is necessary to abandon such athermal parameterizations in future in favour of more rigorous treatments. This requires that interatomic potentials are derived by fitting to structures with each observable calculated at the temperature corresponding to the empirical data being employed. In turn this implies that properties and optimized structures must be calculated with the inclusion of thermal forces.

There are several approaches to explicit inclusion of the temperature in simulations of which the most commonly employed for ionic materials are free-energy minimization and molecular dynamics. Fitting based on molecular dynamics is both impractical, because of the computational expense and the statistical uncertainties, and incorrect because of the neglect of quantum effects in the low-temperature region.

Within the quasiharmonic approximation it is possible to calculate the free energy of a crystal based on the phonon contributions to the internal energy and entropy integrated across the Brillouin zone. The internal pressure is given by the derivative of the Helmholtz free energy with respect to the cell volume. By isotropically expanding the unit cell the Gibbs free energy can be obtained at the point at which

the externally applied pressure equals the phonon pressure. The free energy may then be minimized subject to the constraint on the pressure. This approach has been used in the study of silicates (Jackson, Parker and Tschaufeser 1992) although it has thus far been limited by having to use athermally derived interatomic potentials such that the effect of temperature is included twice over.

Free-energy minimization may be readily used in conjunction with relaxed fitting to provide a means of fitting at finite temperatures and has been implemented within the program GULP.

Often the effects of temperature are neglected as the thermal expansion coefficient is small. A class of materials where this approximation breaks down is for layered materials in which the layers are predominantly bound by only van der Waals forces. In such cases the cell parameters in one direction will be strongly temperature dependant.

A preliminary investigation of the application of free-energy fitting to the layered hydroxides portlandite ($\text{Ca}(\text{OH})_2$) and brucite ($\text{Mg}(\text{OH})_2$), which adopt the hexagonal CdI_2 structure, has been performed. The room-temperature crystal structures for both materials and the elastic constants for $\text{Ca}(\text{OH})_2$ were fitted using a minimal shrinking factor of two within the Monkhorst-Pack (1976) special points scheme, resulting in the parameters given in table 5. Work is currently in progress to examine the effect of increasing the density of the integration mesh.

In table 6 the experimental data are compared with those calculated at 0 and 298 K, and also the result of a conventional athermal energy minimization. The results for the free-energy minimization at absolute zero and the internal-energy minimization differ owing to the contribution of the zero-point vibrations, both to the energy and to the gradients. It is clear that the neglect of zero-point effects can lead to significant errors, in these examples by up to 0.1 Å in the cell parameters, and must be taken into consideration when comparing quantum-mechanically optimized bulk geometries with experimental data extrapolated to absolute zero.

The thermal expansion coefficients for the cell parameters of the two minerals have been determined by performing free-energy minimizations up to 600 K. As would be expected, the thermal expansion coefficients for the c parameters of 1.42×10^{-4} and $1.99 \times 10^{-4} \text{ Å K}^{-1}$ for portlandite and brucite respectively are an order of magnitude greater than those for the a parameter. These values represent the best linear fit to the data up to 600 K; however, the curves are found to be significantly quadratic. An interesting feature of the thermal expansion is that for brucite, containing layers of the smaller Mg^{2+} cations, the structure actually contracts in the a - b plane up to about 200 K.

One deficiency of the present model is that, while the hydroxyl stretching frequencies are in good agreement with those measured experimentally for brucite, allowing for anharmonic corrections, those for portlandite are significantly in error. Inclusion of the frequencies in the fitting procedure may improve this aspect. However, the model is qualitatively correct in reproducing the decrease in the stretching frequencies with the application of pressure (Kruger, Williams and Jeanloz 1989).

A limitation to the application of free-energy minimization to empirical fitting so far has been the need to calculate the first and second derivatives of the dynamical matrix. So far numerical differentiation has primarily been used, although this suffers from being computationally expensive and inherently less accurate. The introduction of analytical derivatives in the future based on either moment expansions (Montroll 1942) or perturbation theory will enable fitting with explicit inclusion of temperature to become a routine technique.

Table 5. Potential parameters derived for a core-only model from fitting at 298 K to experimental data for portlandite and brucite.

	Type	A (eV)	ρ (Å)	C (eV Å ⁶)	D_e (eV)	a (Å ⁻¹)	r_0 (Å)	r_{\min} (Å)	r_{\max} (Å)
Ca-O	Buckingham	2097.7	0.3018	0.0	—	—	—	0.0	10.0
Mg-O	Buckingham	1862.9	0.2747	0.0	—	—	—	0.0	10.0
O-O	Buckingham	22764.3	0.1490	30.72	—	—	—	0.0	18.0
O-H	Buckingham	616.71	0.25	0.0	—	—	—	1.2	10.0
O-H	Morse (Coulomb subtracted)	—	—	—	5.539	2.3669	0.9240	0.0	1.2

Table 6. Comparison of experimental and calculated structure and properties for $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$.

	Experimental	298 K	0 K	Athermal
$\text{Ca}(\text{OH})_2$				
a (Å)	3.592	3.612	3.607	3.595
a (Å)	4.906	4.933	4.900	4.845
O, z (fraction)	0.234 0	0.240 0	0.241 5	0.244 1
H, z (fraction)	0.425 6	0.434 5	0.437 3	0.442 3
ν (OH) (cm^{-1})	3618	3708	3702	3694
ν (OH) (cm^{-1})	3644	3737	3735	3732
C_{11} (GPa)	99.3	123.1	125.4	129.9
C_{12} (GPa)	36.2	37.7	38.8	41.1
C_{13} (GPa)	29.7	8.2	9.6	12.2
C_{33} (GPa)	32.6	29.3	32.6	38.5
C_{44} (GPa)	9.8	10.4	11.3	13.2
C_{66} (GPa)	31.6	42.7	43.3	44.4
$\text{Mg}(\text{OH})_2$				
a (Å)	3.142	3.149	3.149	3.141
c (Å)	4.766	4.748	4.709	4.611
O, z (fraction)	0.221 6	0.219 4	0.220 9	0.224 8
H, z (fraction)	0.430 3	0.422 3	0.425 6	0.434 0
ν (OH) (cm^{-1})	3655	3669	3662	3641
ν (OH) (cm^{-1})	3700	3693	3691	3687

Theoretically derived interatomic potentials are implicitly at absolute zero and thus require the use of free-energy minimization to correct for zero-point energy effects and thermal expansion if their results are to be compared with experiment.

An alternative approach can be taken to understanding the influence of phonon and thermal effects. When we calculate the energy for a given set of nuclear positions using an interatomic potential, we are not normally calculating an instantaneous energy as would be obtained from a quantum-mechanical calculation. The energy and properties calculated are more commonly a mean field average over the vibrational motions about the nuclear positions, even at absolute zero. If we assume that there is a Gaussian probability distribution for each atom about its mean position, then the relationship between the effective pair potential ϕ_{ij} and the potential ϕ_{ij} that would be obtained theoretically is

$$\phi_{ij}(r_{ij}^0) = \left(\frac{\alpha_i \alpha_j}{\pi^2} \right)^{3/2} \int \exp[-\alpha_i(r_i - r_i^0)^2] \int \exp[-\alpha_j(r_j - r_j^0)^2] \phi_{ij}(r_{ij}) dr_i dr_j.$$

This is the basis of a further method for performing free-energy calculations in which the Gaussian exponent coefficients α are treated as variational parameters (LeSar, Najafabadi and Srolovitz 1991).

Both empirical and theoretical potentials must take proper account of zero-point and thermal effects if we are to perform more accurate temperature-dependent simulations in future.

§ 8. POTENTIAL DERIVATION FOR COMPLEX SYSTEMS

As the complexity of the systems of interest increases, so does the number of interatomic potentials to be determined. Difficulties abound in that many potential

parameters may be highly correlated and hence choices need to be made about which species should have a non-Coulombic interaction or where three-body potentials should be used. For example a given triad of atoms can be treated by three two-body potentials or two two-body potentials and one three-body potential.

There is also a danger that, when trying to fit several new potentials at once, we could have chosen a set of initial variables which reside in a local minimum in parameter space which is not the global minimum. One approach to this problem is to try either a stochastic sampling method, such as Monte Carlo methods, or a technique which can overcome local barriers, for example simulated annealing via molecular dynamics, as a precursor to the normal least-squares procedure.

Stochastic approaches are probably favourable here as this eliminates the need to invent fictitious masses and will allow a more rapid and wider search of parameter space to be performed. Some studies have suggested that genetic algorithms can be superior to Monte Carlo techniques for locating local minima (Gallagher, Sambridge and Drijkoningen 1991).

An alternative approach to improving the fitting of complex systems is to combine the benefits of both theoretical and empirical methods. This is illustrated by the work of Rohl and Gale (1995) on the modelling of solids containing molecular ions. As an example we shall consider the alkali-metal and alkaline-earth sulphates.

A full theoretical determination of interatomic potentials based on periodic *ab initio* methods for the aforementioned sulphates would be time consuming, as there are many technical factors relating to the accuracy that must be considered in both Hartree–Fock and density functional approaches, such as basis set optimization, plane-wave cut-off, correlation corrections, non-local functionals and pseudo-potential derivation. Likewise a purely empirical potential derivation is hindered by the need to handle both intramolecular potentials for the sulphate group and interspecies potentials.

Intramolecular potentials for the sulphate group as an isolated species can be readily obtained from molecular quantum-mechanical calculations where the size of the basis set and the method of treatment of both the exchange and the correlation energies can be readily extended to high accuracy. In practice, this is not necessary as some of the potential parameters have to be empirically corrected in the final refinement anyway to allow for changes induced by the crystalline environment. In the case in question, MP2/6-31G* calculations were used for the cluster energy as the incompleteness in both the basis set and the correlation level leads to a partial cancellation of errors. The effect of the crystalline environment is partially accounted for in the molecular energy surface determination by embedding the ion in a point-charge array such that the system is charge neutral. Deformations of the sulphate ion corresponding to both the symmetric and asymmetric stretch within the point group C_{2v} were used to fit a Morse potential for the S–O bond, while a three-body term was used to fit the bending modes. The charge distribution obtained from the Mulliken analysis for the cluster calculation was used to assign partial charges of +1.36 and –0.84 for sulphur and oxygen respectively within the sulphate ions, although all intramolecular interactions were Coulomb subtracted.

Having obtained an initial set of parameters for the sulphate ion theoretically, the metal–sulphate and O–O intermolecular potentials were then obtained by empirical refinement. The resulting potentials (table 7) prove to be reliable across a wide range of sulphates for both structural and elastic properties as demonstrated in table 8 for a number of examples. Although the sulphate potentials eventually became

Table 7. Potential parameters for metal sulphates derived by combined use of theoretical and empirical methods (all intermolecular potentials have a cut-off of 10.0 Å, except O–O which is 15.0 Å owing to the longer-range C term).

[illegible]

Table 8. Calculated and experimental structure and properties for selected metal sulphates.

Compound	Observable	Experiment	Calculated
BaSO ₄	<i>a</i> (Å)	8.884	8.888
	<i>b</i> (Å)	5.456	5.471
	<i>c</i> (Å)	7.157	7.143
	<i>C</i> ₁₁ (GPa)	95.1	101.6
	<i>C</i> ₂₂ (GPa)	83.6	87.6
	<i>C</i> ₃₃ (GPa)	110.6	117.7
	<i>C</i> ₄₄ (GPa)	18.1	16.2
	<i>C</i> ₅₅ (GPa)	29.0	35.0
	<i>C</i> ₆₆ (GPa)	27.7	28.5
	<i>C</i> ₁₂ (GPa)	51.3	44.2
	<i>C</i> ₁₃ (GPa)	33.6	27.9
	<i>C</i> ₂₃ (GPa)	32.8	29.6
CaSO ₄	<i>a</i> (Å)	6.993	6.896
	<i>b</i> (Å)	6.245	6.332
	<i>c</i> (Å)	6.995	7.018
Na ₂ SO ₄	<i>a</i> (Å)	9.829	9.763
	<i>b</i> (Å)	12.302	12.303
	<i>c</i> (Å)	5.868	5.962
	<i>C</i> ₁₁ (GPa)	67.4	65.3
	<i>C</i> ₂₂ (GPa)	105.0	103.3
	<i>C</i> ₃₃ (GPa)	80.4	74.4
	<i>C</i> ₄₄ (GPa)	23.6	22.7
	<i>C</i> ₅₅ (GPa)	18.0	13.5
K ₂ Mg ₂ (SO ₄) ₃	<i>C</i> ₆₆ (GPa)	14.8	13.9
	<i>a</i> (Å)	10.031	9.919

partially empiricized, having a physically reasonable starting point for some of the potential parameters makes the fit much more tractable and less likely to yield an incorrect local minimum during the least-squares procedure, with minimal computational expense.

§9. CONCLUSIONS

Despite the advances in the accuracy of the theoretical treatment of solids in recent years, it is likely that empirical methods of interatomic potential derivation will remain important for some time to come. In order to model many ionic systems reliably, it is necessary to use a dipolar shell model and in many cases a quadrupolar shell model is desirable. It has been shown that the simultaneous optimization of shell parameters during fitting is essential.

Empirical fitting based on displacements of the energy-minimized configuration from the experimental structure is found to be superior to conventional fitting in which zero gradients at the experimental geometry is the aim, once a reasonable initial set of potential parameters has been generated such that optimizations are convergent. The relaxed fitting approach appears to be particularly appropriate for the modelling of low-symmetry structures.

In order to obtain empirical potentials for use in dynamical simulations, it is important that proper regard is paid to the temperature at which the experimental data were measured. Free-energy methods based on lattice dynamics offer the most convenient method for fitting at finite temperatures and this is a direction that must be explored further in the future to improve the reliability of empirical methods.

ACKNOWLEDGMENTS

I would like to thank the Royal Society for funding and to acknowledge the many people who have contributed to the development of the fitting aspects of GULP through using it and supplying me with feedback, in particular Dr Tim Bush and Dr Andrew Rohl. Also I would like to thank Mike Cherry for communicating his work on LaCrO_3 .

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