Development of a new force field for open shell ions: application to modelling of $LaMnO_3$

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A new type of force-field, based on the angular overlap model, has been developed in order to model compounds containing ‘non-spherical’ ions; the model has been successfully applied to $LaMnO_3$, with the Mn–O bond distances within the distorted MnO_6 octahedra and the lattice parameters being reproduced to within 0.33% of those determined experimentally.

There have been many successes over the last thirty years in the modelling of oxides using simple interatomic potentials based on the ionic model, particularly when ion polarisability is accounted for *via* the shell model.[1–3] Such calculations have typically used potentials comprising a Buckingham term to describe the short-range interaction between two ions along with the Coulomb term (evaluated *via* an Ewald sum) for the long-range interaction. Although potential parameters may be derived theoretically, particularly from fitting to *ab initio* energy surfaces, most have been obtained by empirical fitting to experimental data including structural and physical properties. However, the Coulomb and Buckingham potentials are purely radial, and consequently can only accurately model structures that contain spherical ions, representing a major limitation on the applicability of these methods to transition metal oxides. In order to extend the scope of structural modelling to include topical materials that contain ‘non-spherical’ (especially Jahn–Teller) ions, for example, manganates and cuprates which require accurate Mn^{3+}–O^{2-} and Cu^{2+}–O^{2-} potentials, we have developed a new short range potential. In this communication, we show that we are now able to model $LaMnO_3$, which contains the Jahn–Teller Mn^{3+}: $3d^4$ cation, which will clearly enable predictive computational chemistry to be applied to the area of colossal magnetoresistance (CMR) research. We expect the same basic method to be applicable in the case of Cu^{2+}: $3d^9$, and thus in the area of high T_c superconductivity.

The driving force for the distortions of the coordination sphere of Mn^{3+} and Cu^{2+} is associated with the Jahn–Teller effect, which removes a degeneracy in the electronic energies. In order to model the irregular coordination geometry associated with these ‘non-spherical’ ions, we chose to add a contribution to the lattice energy that corresponds to this energy-level splitting. Adding a ligand field stabilisation energy, and implementing numerical gradients, has previously proved[4] successful in the framework of molecular mechanics as applied to gas phase coordination complexes. Our model implements an adaptation of the angular overlap model (AOM).[5] The resulting parameterised interatomic energy term, E_{LF}, and its analytical gradients have been incorporated within the General Utility Lattice Program (GULP),[6,7] which is widely used for modelling ionic solids. One significant feature of our approach was to change the AOM formalism in order to introduce rotational invariance into the model, which is essential for application to energy minimisation studies. Thus, the GULP code creates a 5 × 5 overlap matrix for each transition metal ion,

$$H_{dd'} = \sum_{\text{ligands}} A e^{-r/\rho} \Gamma_{d} \Gamma_{d'} \qquad (1)$$

by taking the products of the angular contributions to the overlap integrals, Γ_d,[8] between the transition metal ion d-orbital and the orbitals of any surrounding ligand. A and ρ, which will subsequently be denoted with the subscript LF, are parameters that depend upon the transition metal and the ligand. From the eigenvalues of $H_{dd'}$, we can compute the approximate energy level diagram that results when the orbitals of the surrounding ligands overlap the d-orbitals of the transition metal ion *via* a σ-bonding interaction. In this way, we can calculate E_{LF}, for each transition metal ion, which is simply a weighted sum over these energy levels (eigenvalues). The second important modification of the AOM is the inclusion of an exponential distance dependence, rather than just inclusion of the nearest neighbour ions, such that a ligand that is further away makes a smaller contribution to E_{LF}. Moreover, the use of the exponential provides a way to decrease cut-off discontinuities and removes the need to specify which ligands belong to the first coordination sphere.

The mixing of the orbitals lowers the populated ‘ligand’ energy levels, creating a more stable environment. To conserve energy, the sum of the energy levels of the d-orbitals must increase. Because we do not explicitly consider the ‘ligand’ energy levels, the stabilising energy E_{LF} is calculated by summing up the energy levels of the unoccupied d-orbitals; thus, if there are 10 d-electrons there are no unoccupied states and no stabilisation energy. To avoid singularities (for example, when one or two electrons occupy d-orbitals that are three-fold degenerate) we have also allowed partial occupancies (or a non-zero probability that an electron can populate a higher energy state) through the use of a Fermi function. The Fermi energy, E_f, defined to be that which gives the required number of d-electrons, can only be expressed implicitly, and so it is calculated by an iterative method. Because we treat spin-up and spin-down separately, there are two Fermi energies, and E_{LF} for each transition metal ion is therefore a double summation over the weighted energy levels. The ‘electronic temperature’ of the Fermi function is fixed at room temperature in the present work.

Table 1 Buckingham parameters (B) for the interaction between the cations and the oxygen shells, O_s^{2-}, and the new force field parameters (LF) obtained for the Jahn–Teller interaction between the Mn^{3+} ion and the surrounding oxygen cores, O_c^{2-}. A cut-off radius of 10 Å was used for the cation–anion short-range potentials

	i	A_i/eV	ρ_i/Å
La^{3+}–O_s^{2-}	B	4317.17	0.2987
Mn^{3+}–O_s^{2-}	B	1265.17	0.3176
Mn^{3+}–O_c^{2-}	LF	8.98	0.3300

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Table 2 Structural data of $LaMnO_3$ within the *Pnma* space group

	Calculated (this work)			Observed (ref. 10)			Calculated (ref. 2)		
	a/Å	b/Å	c/Å	a/Å	b/Å	c/Å	a/Å	b/Å	c/Å
Unit cell parameters	5.7483	7.7199	5.5298	5.743	7.695	5.537	5.553	7.818	5.528
Fractional co-ordinates	x	y	z	x	y	z	x	y	z
La^{3+}	0.5457	0.2500	0.0044	0.550	0.250	0.009	0.521	0.250	0.002
Mn^{3+}	0.0000	0.0000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000
O^{2-}	0.9782	0.2500	0.9333	0.989	0.250	0.929	0.981	0.250	0.938
O^{2-}	0.6889	0.5344	0.7787	0.691	0.539	0.775	0.716	0.532	0.785

Table 3 The three unique Mn–O bond distances within the MnO_6 octahedron and two unique tilt angles of the MnO_6 octahedra within $LaMnO_3$ together with the electronic data of the Mn^{3+} ion

	Calculated			Observed (ref. 10)			Calculated (ref. 2)		
Mn–O/Å	1.9038	1.9689	2.1830	1.901	1.965	2.189	1.987	1.992	1.995
Mn–O–Mn/°	154.71	157.18		154.46	156.61		158.68	159.28	
Calculated energy levels/eV			0.001		0.001	0.001		0.440	0.696
Calculated occupations/e			1.000		1.000	1.000		0.993	0.007

To test the applicability of this new approach, we have parameterised a potential model including the AOM description for $LaMnO_3$. This material, which shows a substantial Jahn–Teller distortion of the MnO_6 octahedron, is of importance both for its relevance to CMR and for its use as the cathode material in solid oxide fuel cells. The total lattice energy is the sum of E_{LF} and the energy created by the two-body potential:

$$V = \frac{qq'}{r} + Ae^{-r/\rho} - \frac{C}{r^6} \qquad (2)$$

where the first term represents the Coulomb interactions. The remaining terms constitute the Buckingham potential representing the anion–anion and cation–anion short-range interactions. We choose to use formal ionic charges for q and q', although the charge on the transition metal ion may not be quite as high,[9] as this leads to greater transferability. The potential parameters, A_B, ρ_B and C_B, together with A_{LF} and ρ_{LF} used in the formulation of the angular overlap model, may be derived using standard empirical fitting techniques.[6]

Our strategy was to perform a 'relaxed fit', whereby we minimise the square of the differences between the observed[10] and calculated lattice parameters and ionic positions. Initially only the Mn^{3+}–O^{2-} Buckingham parameter A_B was refined whilst we tested a range of trial parameter values (A_{LF} and ρ_{LF}) for our new force field. In these preliminary calculations we used an equivalent exponential dependence for both the Buckingham and 'AOM' interaction between Mn^{3+} and the surrounding O^{2-} ions (*i.e.* $\rho_B = \rho_{LF}$) and the Buckingham parameters for the La^{3+}–O^{2-} interaction were held at the values determined previously.[1] To help find suitable potential parameters, the data used in the least squares fit included the Mn–O bond distances within the MnO_6 octahedron. Once our calculated Mn–O bond distances were reasonable, we refined the cation–anion parameters A_B and ρ_B along with A_{LF} and ρ_{LF}, again using a relaxed fit but with the calculated structure constrained within the experimentally determined *Pnma* space group. To increase the transferability of our potential parameters, we used the O^{2-}–O^{2-} Buckingham parameters[1] that were previously refined to be consistent with a range of binary and ternary oxides.

In Table 1 we report the potential parameters obtained for the best fit to the structural properties of $LaMnO_3$. The structural parameters of $LaMnO_3$ obtained using our new force field are presented in Tables 2 and 3, along with those calculated from previously published force field parameters[2] and the observed values.[10] As shown in Table 3, after minimising the lattice energy, our calculated Mn–O bond distances within the distorted MnO_6 octahedron are within 0.006 Å of those observed, and the tilt of these octahedra is within 0.6° of that observed. Comparison with the bond lengths obtained when the previously published Buckingham potential parameters[2] were used to model $LaMnO_3$ shows quite clearly that that the Mn^{3+} ion cannot be represented as a spherical ion and emphasises the progress made in the present study.

In Table 3, we also present the energy levels and their respective occupancies. With an 'electronic' temperature within the Fermi function set to that of room temperature, we note that there is a small probability (0.007) of an electron being in the highest energy level. The splitting of these energy levels is of the correct order of magnitude (although possibly too small) compared to typical orbital splittings for first row transition metals with weak field ligands, although no constraint was placed on these energies during fitting. As expected, the energies of the three non-bonding t_{2g} orbitals do not change whereas there is a Jahn–Teller splitting (~ 0.25 eV) of the anti-bonding e_g energy levels.

To summarise, we have shown that we can model Jahn–Teller distortions within $LaMnO_3$, the parent compound of the manganese perovskites that display CMR. This is the first time that a code primarily based on the inter-atomic potentials has been able to reproduce the Jahn–Teller distortion within this material. Furthermore, we have subsequently shown that our potential parameters are transferable, in that they have been used to reproduce the structure of Mn_2O_3 (with the calculated lattice parameters coming within 0.4% of the experimental value). The basic strategy described above increases the range of compounds that can be modelled using computationally inexpensive methods to include some of the most technologically important inorganic compounds studied in the last twenty years.

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