Environment Dependent Dynamic-Charge Interatomic Potential for MgO

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Abstract

Classical atomistic simulations of materials require an accurate description of the interatomic interactions. We present the environment dependent dynamic-charge (EDD-Q) transfer model of Muralidharan et al. for MgO. The parametrization of EDD-Q is formulated from Density Functional Theory (DFT) calculations on stoichiometric MgO clusters containing different coordination environments. Furthermore, the charge transfer scheme utilizes information from Mulliken population analysis of clusters which have been deformed along selected vibrational modes. We show that our potential accurately predicts atomic charges determined by DFT.

Introduction

The use of MgO as a technological material has shown considerable interest in obtaining information from ab initio and Density Functional Theory (DFT) calculations.2–7 A drawback to such approach is systems exceeding 100-1000 atoms cannot be investigated in a timely manner due to computational requirements of such methods. Thus it becomes paramount to develop an interatomic potential (IAP) which is parametrized to reproduce as closely as possible the quantum mechanical behavior. Such an approach would allow for classical atomistic simulations (CAS) which can accurately emulate higher-level calculation.

Existing IAP of ionic solids, like MgO, have been parameterized from empirical data.8,9 In such an approach the treatment of MgO can be divided into two types: 1. A Born-Mayer like potential which treats a system as a collection of rigid ions in which no polarization of the cation or anion is accounted for 2. A core-shell model where the core of a species is treated as a heavy mass with no charge and a massless shell containing charge that are connected via a harmonic spring. Both treatments have shown considerable ability to reproduce equilibrium properties and defect energies.8–12 Additionally, Aguado et al. developed an interatomic potential for MgO from ab initio MD based on aspherical ion model and reproduced many thermal properties.13,14 However, these IAP do not account for charge transfer. Another shortcoming of these potentials is that they have been fitted to empirical equilibrium data.
This suggests that non-equilibrium events are not accurately captured in the parametrization. As a consequence there is an absence of information which prevents adequate observation of forming and breaking bonds in CAS.

In this work we adapt the environment dependent dynamic-charge (EDD-Q) transfer model presented by Muralidharan et al. The model incorporates into the IAP parametrization the charge fluctuations on a given species based on local chemical environments. This is beneficial in that the information of charge transfer is obtained from ab initio calculations. Other approaches such as DQEq, QEq, and ReaxFF include a charge transfer model but differ in that they dynamically calculate atomic charges based on chemical potential equilibration principles. We choose to implement EDD-Q for MgO due to the rather simplicity of its expression form in comparison to DQEq, QEq, and ReaxFF.

**Background**

As a template for the functional form of the IAP we adapt the one proposed by Muralidharan et al. As shown eq. 1 the IAP consist of an embedding term, pairwise term, and electrostatic term. The embedding expression represents the energy associated with inserting an atom into a background electron density. However, Muralidharan et al. express the embedding term as a function of atomic charge. The two additional terms correspond to the pairwise and coulombic interactions, respectively.

\[ U_i = E(q_i) + \frac{1}{2} \sum_{j \neq i}^{N} \phi_{ij} + \frac{1}{2} \sum_{j \neq i}^{N} q_i q_j, \]  

\[ E(q_i) = A_i q_i \ln q_i^2 \]  

\[ \phi_{ij} = \frac{C_{ij}}{r_{ij}^{20}} - \frac{D_{ij}}{r_{ij}^6} \]  

where,  

The parameters \( A_i, C_{ij}, \) and \( D_{ij} \) are all fitting parameters to reproduce the correct energetics. The procedure for fitting the charge transfer model requires the use of Mulliken populations on individual atoms. Although Mulliken populations can result in unreasonable values for large basis sets, previous work has shown that for metal oxides large basis sets can produce sufficient values. The final expressions for charges are functions of bond distance and bond angle. This permits the calculation of charge in terms of chemical environment. It is also convenient to weight the Mulliken atomic charges to yield the correct energies.

**Methodology**

A series of geometry optimization, frequency analysis, and single point calculations are performed on \( \text{Mg}_2\text{O}_2, \text{Mg}_6\text{O}_6, \text{Mg}_9\text{O}_9, \) and \( \text{Mg}_{13}\text{O}_{13} \) (see Figure 1). The neutral stoichiometric MgO clusters have been selected based on reported stable clusters of Recio et al. These ground state structures were calculated using Hartree-Fock (HF) and second order Moller-Pleset (MP2) corrections with 6-31G* basis set. In this work we perform DFT calculations with B3LYP functional and 6-31G* basis set. The resulting geometries and energies are compared to those of Recio et al. and match in good agreement (see Table 1). DFT calculations are performed using the software package Gaussian 09.

After obtaining ground state structures for MgO clusters we carry out vibrational frequency analysis. These results will provide the necessary paths for deforming each cluster. For each MgO cluster we identify three primary modes of vibration, these correspond to the highest intensities. This is done since it can be expected that less active modes will contribute minimally in the charge transfer scheme and the sampling of different combinations of bond lengths and angles is surveyed. Single point energy calculations are performed in increments of varied bond lengths and angles along selected vibrational modes. These calculations provide the Mulliken population data required for fitting. The fitting procedure occurs in two steps, the first with determining the functional form for variation in charge as a function of bond distance and angle. The second is the fitting of parameters for the pairwise term and weighted...
charges to yield the correct energies\(^0\). This is carried out in a least-squares fitting fashion.

\[ \text{Figure 1: Resulting optimized geometries of MgO nanoclusters. (a) Mg}_2\text{O}_2, (b) Mg}_6\text{O}_6, (c) Mg}_9\text{O}_9, (d) Mg}_{13}\text{O}_{13} \]

**Results**

The resulting optimized geometry results for the test clusters is reported in Figure 1 along with Table 1 displaying energies and bond lengths. In Figure 2 the Mulliken population analysis of Mg\(_2\)O\(_2\) is shown for three different vibrational modes.

<table>
<thead>
<tr>
<th>Table 1: MgO cluster bond length and energy</th>
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<tr>
<td>Mg(_2)O(_2)</td>
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<tr>
<td>Mg(_6)O(_6)</td>
</tr>
<tr>
<td>Mg(_9)O(_9)</td>
</tr>
<tr>
<td>Mg(<em>{13})O(</em>{13})</td>
</tr>
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</table>

The affine transformation, that being the isotropic expansion, of Mg\(_6\)O\(_6\) can be seen in Figure 3, this mode is the simplest to show visually. Due to the large number of bond lengths and angles we do not show the plots of Mulliken atomic charges for large clusters of the selected deforming vibrational modes.

\(^0\)This step will be carried out in later work

\[ \text{Figure 2: Mulliken population analysis (in units of elementary charge, } e) \text{ of Mg}_2\text{O}_2 \text{ vibrational modes selected. (a) 273.63 cm}^{-1}, (b) 666.23 \text{ cm}^{-1}, (c) 656.82 \text{ cm}^{-1} \]
Figure 3: Mulliken population analysis of Mg₆O₆. Vibrational mode corresponds to affine transformation (isotropic expansion).

The data from Figure 2-4 permits fitting the charge on the Mg—O bond. In order to limit the number of computations only first nearest neighbors are calculated by using a cutoff of \( r_c = 3.2 \text{Å} \). This can be thought of as an accurate description since most charge transfer should occur between bonded atoms. The charge associated with a bond and angle can be calculated as:

\[
\Delta q_{\text{MgO}}^i = q_o \left( 1 - \tanh \left( \frac{r_{ij}}{r_o} - \sigma_1 \right) \right) + \sum_{k \neq j} \Delta q_{\text{OMgO}}^{jk}
\]

where

\[
\Delta q_{\text{OMgO}}^{jk} = \left( \rho \sin^2 \theta_{ijk} \exp(-\theta_{ijk}) \right) \tanh \left( \frac{r_{ij} - \sigma_2}{r_o} \right)
\]

\[
+ \left( \phi \exp(-\theta_{ijk}^2 \sin^2 \theta_{ijk}) \right) \tanh \left( \frac{r_{ij} - \sigma_3}{r_o} \right)
\]

In the above equations \( r_{ij} \) is the interaction distance and \( \theta_{ijk} \) the bond angle. All other parameters are used for fitting. The term \( \epsilon_i \) ensures that no charge transfer will occur beyond first nearest neighbors. We can now write the charge on Mg and O as:

\[
q_i^{\text{Mg}} = q_s^{\text{Mg}} + \sum_{i=1,N} \epsilon_i \Delta q_i^{\text{MgO}}
\]

\[
q_j^{\text{O}} = q_s^{\text{O}} - \sum_{j=1,N} \epsilon_i \Delta q_j^{\text{MgO}}
\]

where,

\[
\epsilon_i = \begin{cases} 
1 & r_{\text{MgO}} \leq r_c \\
0 & \text{otherwise} 
\end{cases}
\]

The fitting parameters can be seen in Table 2. In order to test the quality of the fitting procedure we have compared the values calculated from eq. 4-7 to DFT results for a MgO₂ molecule. The results shown in Figure 4 correspond to the Mulliken charge predicted by our fitting. There is significant underestimation of the atomic charge on MgO₂ molecule. This could be a result of the least-squares fitting procedure because the parameters might be satisfactory for a transient state. In other words the parameters are not being individually adjusted enough to yield an extremely close fit. On method to circumvent this is applying a genetic algorithm for fitting.

<table>
<thead>
<tr>
<th>Table 2: EDD-Q parameters for MgO</th>
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<tr>
<td>( q_s^{\text{Mg}}(e) )</td>
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<tr>
<td>2.51</td>
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<tr>
<td>( \rho_1(\text{e}) )</td>
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<tr>
<td>0.146</td>
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Figure 4: Comparison between DFT and EDD-Q of Mulliken charge on MgO₂ as Mg—O bond is varied(angle fixed).

There still exist a significant amount of work to be carried out. The parameterization of the
embedding and pairwise terms to the energies of the clusters will require the charge calculated to be weighted. Furthermore, the addition of more DFT calculations for non-stoichiometric clusters may contribute to a better outcome of the fit. The benchmarking of the developed EDD-Q potential for Mg to other empirical based IAP is also required.

**Conclusion**

The optimization and vibrational mode analysis of clusters Mg$_2$O$_2$, Mg$_6$O$_6$, Mg$_9$O$_9$, and Mg$_{13}$O$_{13}$ has been demonstrated and agrees with the work of Recio et al. These results have been used to initiate the procedure for a fitting MgO to the EDD-Q transfer model. We demonstrate the charge transfer portion of the interatomic potential and compare its predicted results to that of DFT calculations for MgO$_2$. As a first attempt the results are fairly close but furthur refinement is definently needed. This may be approached by using a genetic algorithm fit rather than least-squares. Future work will focus on fitting the energetics to match that of the cluster training set used.

**Acknowledgement**

We would like to Keith Runge and Pierre Deymier for their useful insight to many technical aspects.

**References**


