Electrostatic effects on cluster simulation of ionic crystals and surfaces

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Abstract. Local perturbations in ionic solids and surfaces are often studied with cluster models embedded in an electrostatic Madelung potential. This potential is usually represented by a finite set of point charges whose values are defined by using several different methods. Local properties seem to a large amount independent from the criteria adopted for defining the Madelung potential. In this study, the cluster electrostatic potential is defined unambiguously on the basis of a periodic calculation of the unperturbed crystal; this permits us to understand the reasons for the insensitivity of local properties to the quality of the Madelung potential.

1. Introduction

Chemical phenomena in complex systems have, in many cases, a moderately local nature. The description of the physical system can then concentrate on a subsystem. A localized approach is computationally preferable, as it limits the dimension of the model, so permitting higher levels of theory to be used. When the subsystem is weakly interacting with the environment, many approaches have been proposed: the quantum mechanical treatment of the structure and dynamics of molecules in solution is usually based on an “averaged” treatment of the interaction with the solvent environment: successful examples of such techniques are the “polarizable continuum model” [1] and “frozen solvent density” [2]. A lot of theoretical effort has been dedicated to the partition method in systems where, in a chemical language, strong covalent, ionic or metallic bonds are active between the atoms belonging to the molecular subsystem and the atoms in the surroundings. Among the approaches proposed for this kind of situations, the most elegant and sophisticated is due to C. Pisani and coworkers [3]: the “moderately large embedded cluster” (MLEC) method, and its computational implementation [4], treats the separation between the subsystems as a block partition of the one-particle Green function, represented in a localized basis set: the blocks describing the surroundings are frozen while the block describing the sub-system, the perturbed cluster, is self-consistently relaxed. The success of this partition method has been demonstrated by a large set of applications in complex localized perturbations, like defects in covalent and ionic crystals and surfaces [5]. The limit to the diffusion of the MLEC approach is probably due to its computational complexity: other methods, theoretically simpler and computationally easier, are commonly used for treating molecular subsystems strongly “embedded” in their environment, also if the cluster boundary conditions are not entirely under
control. Let us consider as an example the ONIOM method [6], that is a “non embedding” method: the localized nature of the perturbation is described by the cooperative use of several models, having different dimension and different accuracy level. The Fragment Molecular Orbital method [7] can be considered a surprisingly simple “embedding” method: the subsystems are treated as isolated clusters, their dangling bonds are described by localized orbitals, only the Hartree potential of the surroundings is considered, and the cluster wave functions are super-iteratively optimized considering pairs (and even triplets) of clusters in which the large model is subdivided. The “density embedding” methods [8] have an intermediate theoretical and computational complexity: the separation between subsystems, or between the central subsystem and the surroundings, is operated using the electronic density, that is a physical-mathematical object by far more easily manageable than the wave function, as the success of density functional theory has demonstrated. The “density embedding” method has proven to be successful in describing local perturbations in cases where the chemical “bonds” are very delocalized, like in metal surfaces [9].

Local perturbations and defects in ionic crystals and surfaces are very important in many relevant fields, like catalysis and materials science: the “electrostatic embedding” methods are well established in this area [10]: isolated clusters represent the locally perturbed sub-system, while the electrostatic effect of the surroundings, the “Madelung field”, is included in the cluster potential. We have developed an original method for deriving the Madelung field unambiguously from the electrostatic potential calculated for the unperturbed crystal or surface [11,12]. More recently we have studied the core excitation of transition metal oxides, like TiO$_2$ and V$_2$O$_5$ [13,14]. During this study we could critically revise other representations of the Madelung field. Surprisingly, local observables are quite insensitive to the details of the Madelung potential. The present study is devoted to the comprehension of the reasons for this finding.

2. Results and Discussion

2.1 Point charge representation of the Madelung field.

Recently we studied in details the effect of electrostatics on “bulk” properties of ionic and semi-ionic systems: core excitation energies, as measured in electron energy loss spectroscopy, are a good probe of the local electronic structure of solids. We calculated core excitation energies following an original method [15], defined within the Time Dependent Density Functional approximation [16]. In the case of 1s and 2s excitations of Mg and 1s excitations of O in MgO [17] large clusters were embedded in about 300 point charges, optimized by F. Illas [18] in such a way as to reproduce the Madelung field of +2 and -2 point charges. In the same study, for the O centered cluster, formal +2 -2 non optimized charges were used. The quality of the results did not depend critically on the value of the point charges: much more important are the size of the cluster, the quality of the basis set and the adopted exchange-correlation potential [19]. In another application of this method, we considered core excitations in Titanium Oxide [13] and Vanadium Oxide [14]. For TiO$_2$ we embedded the cluster model in a set of about 500 point charges, optimized to reproduce the Madelung field generated by formal charges [20]: during this study we confirmed a substantial non-sensitivity of the results from the specific value of the point charges used. When we studied core excitations of V$_2$O$_5$ [14] we obtained a good agreement with the experimental data without embedding the cluster models in a set of point charges: due to the partially covalent character of this crystal, we saturated the formal “dangling bonds” with hydrogen atoms; the cluster models were neutral. Again we were surprised by the independency of local observables from the Madelung field, because V$_2$O$_5$ has a partially ionic character: in periodic calculations the Mulliken net charges of oxygens are in the range -0.8 to -1.0. Influence and importance of the inclusion of point charges in cluster calculations of solids have been discussed in details by F. Illas [21] and G. Pacchioni [10]. In the present work we contribute to this analysis by using the charges derived from a periodic calculation; we discuss also some observables of the perfect periodic system, where the Madelung potential is considered more accurately.
2.2 Test cases

Magnesium oxide, in the most stable face-centred cubic phase, has been adopted as a prototype of fully ionic materials. MgO bulk and surfaces have been the subject of several theoretical studies [22,23] that agree on its fully ionic character. This allows us to build clusters with well defined formal charges, both for bulk and surface models. On the basis of our previous studies we choose a \( \text{Mg}_8\text{O}_8^{14+} \) cluster for the bulk study: this cluster has a medium size, in the range of those utilized for the simulation of core excitations [17]. With this cluster we studied the formation energy of a point defect in which a \( \text{Ca}^{2+} \) ion replaces an \( \text{Mg}^{2+} \) ion. As regards surfaces, we consider the basal (100) plane and CO adsorption energy thereon. Experimental and computational studies [23] show that the most stable adsorption geometry is vertical, carbon side, on top of Mg. We simulate the surface with \( \text{Mg}_8\text{O}_{18} \) and \( \text{Mg}_{12}\text{O}_{24} \) clusters, and compare charged and neutral clusters. For both systems we use as a reference super-cell periodic models: a 3x3x3 super-cell in the Ca bulk substitution, and a 3x3 super-cell for the CO surface adsorption. The equilibrium geometries of the systems has been studied by using the super-cell model. Then the same geometries of the defects has been utilized in cluster calculations: both periodic and cluster calculations are performed with Crystal06 [24,25]. A Gaussian type basis set, of triple-zeta quality, previously utilized in several studies of ionic systems and surfaces [22], has been adopted. The CO molecule is described with a split valence basis set plus polarization functions (6-31G**[23]). The hybrid B3LYP [26] hamiltonian has been adopted, that gives reasonably good results in describing solid state structural properties. The definition of the point charge set, and the fitting of charges to reproduce the periodic potential are performed with Crystal98 [27].

The treatment of Coulomb interactions in LCAO calculations of bulk and surface periodic systems [28] allows an easy definition of \( V^{\text{ext}} \), the potential generated by the lattice external to the cluster:

\[
V^{\text{ext}}(r)=\sum_{\lambda g} \rho_{\lambda}(r-s_{\lambda},g) + Z_{\lambda} |r-s_{\lambda}|^{-1}
\]

where \( \rho_{\lambda}(r-s_{\lambda},g) \) is the electronic density attributed to atom \( \lambda \) located at position \( s_{\lambda} \) in the unit cell \( g \), with nuclear charge \( Z_{\lambda} \). Atomic density \( \rho_{\lambda} \) is expanded in a series of shell multipoles, up to the sixth order. For defining \( V^{\text{ext}} \), the sum \( \sum_{\lambda g} \) runs on atomic centres not belonging to the selected cluster. A set of point charges \( \{q\} \), located at the \( r \) positions, is then used for fitting \( V^{\text{ext}}(r), \) where \( r \) belongs to the domain \( \{r\} \). Set \( \{q\} \) includes 500 to 1500 charges: the total charge of set \( \{q\} \) is fixed to \(-Q\), where \( Q \) is the cluster charge, for getting a globally neutral model; the global charge \(-Q\) is also constrained in the fitting procedure by a Lagrange multiplier. We also explored the possibility to add a penalty function during the fitting procedure for maintaining low the moduli of the \( \{q\} \) charges, as well as the possibility of fitting only the charges farthest from the cluster center: none of these two criteria affects significantly the calculated observables. Observables do not depend critically on the number of charges: all studies in this field employ several hundreds of charges [10]. An alternative procedure to generate the potential at the cluster site has been proposed by Truong and co-workers [29]: a set of point charges can be put on the surface of a sphere containing the cluster. The fitting domain \( \{r\} \) has a spherical shape in the bulk test, and a cylindrical shape in the surface test. Table 1 summarizes the results for the bulk substitution of \( \text{Ca}^{2+} \) for \( \text{Mg}^{2+} \) ion. The reference formation energy of the defect (+125.8 kcal/mol) has been checked with a larger super-cell model: with a 3x3x6 super-cell this value does not change. The bare, charged \( \text{Mg}_8\text{O}_8^{14+} \) cluster gives the same result; the cluster embedded in non-optimized point charges gives a very different defect formation energy; however by optimizing point charges it is possible to obtain again the reference formation energy. For understanding the reasons of the behaviour of the defect energy, we can analyze the electrostatic potential in Figures 1, 2 and 3. Figure 1 shows the total lattice potential, just for locating the position of ions, along a linear path that goes along the main axis of the \( \text{Mg}_8\text{O}_8^{14+} \) cluster. Figure 2 shows in an expanded scale the external \( V^{\text{ext}}(r) \) as defined in equation (1): potential \( V^{\text{ext}}(r) \) is essentially constant, and point charges reproduce reasonably well this situation as shown in figures 2 and 3. This feature of the external potential has already been observed during the analysis of
the Madelung field in the Crystal88 program [30]: it is due to the compensation of positive and negative charges around a cluster that has the same symmetry of the crystal. The constant behaviour of $V_{\text{ext}}(r)$ explains its limited effect on the local observables, like core excitation or point defect formation energy. The peculiarity of highly symmetric Mg$_{13}$O$_6^{14+}$ cluster is that it is easy to reach a self consistent field (SCF) convergency during the LCAO calculation: this is not always the case: for negatively charged clusters the SCF process is much more difficult and there risks to fall in an electronic state different from the bulk situation: in this case point charges are necessary for obtaining the correct SCF convergence. The problem of the point charge fields arises at the cluster border, as shown clearly in figures 2 and 3. Proximity to point charges, negative in this example, gives origin to a near-singularity that can destabilize the SCF procedure: point charges close to the cluster border require special attention: a successful procedure consists in omitting the point charges close to the cluster.

Table 1. Formation energy of the Ca$^{2+}$ defect in bulk MgO. In the last column the Root Mean Square deviation between $V_{\text{ext}}$ potential and the point charges potential is reported (in atomic units)

|                     | Defect energy (kcal/mol) | True vs point charges potential R.M.S. |
|---------------------|--------------------------|---------------------------------------|
| Periodic supercell (3x3x3) | 125.8                    |                                       |
| Isolated Mg$_{13}$O$_6^{14+}$ | 125.7                    |                                       |
| Mg$_{13}$O$_6^{14+}$ + charges | 27.6                     | 1.9 $10^{-1}$                         |
| Mg$_{13}$O$_6^{14+}$ + optimized charges | 114.7                    | 1.0 $10^{-2}$                         |
| Mg$_{13}$O$_{13}$ + optimized (charges+sphere) | 125.4                    | 1.0 $10^{-2}$                         |

Figure 1. Total electrostatic potential of bulk MgO along the linear Mg-O-Mg-O-Mg path. Distances in bohr, potential in a.u.(1 a.u. = 27.21 volts). There is high positive potential around each nucleus. The potential becomes negative in a spherical region around Oxygen anions at 4 and 12 bohrs, approximately. Mg cations, located at 0, 8 and 16 bohrs approximatively, show potential oscillations due to the more structured 1s 2sp core.

Figure 2. External potential $V_{\text{ext}}(r)$ calculated along the same linear path Mg-O-Mg-O-Mg. Units are the same as in figure 1, but the potential is expanded by a factor 15. Continuous line: $V_{\text{ext}}(r)$ from the periodic calculation; dashed, thin line: potential due to a set of point charges fitting $V_{\text{ext}}(r)$; dashed, thick line: potential due to a set of charges fitting a classical Madelung field.
According to classical electrostatics [31], any field in a space region can be reproduced by a suitable surface charge on a closed surface: a good approximation of a continuous surface charge is obtained by putting some hundreds of charges on the surface of a sphere [29]. In our experience, the best results in reproducing $V^{\text{ext}}(r)$ can be obtained using simultaneously a set of charges on a sphere around the cluster and a set of point charges located at the ion positions. In our analysis of the bulk defect formation energy we observed a large sensitivity of the results to the dimension of the fitting domain $\{r\}$: the best results reported in table 1 are obtained using a spherical $\{r\}$ with a radius of 5.5 bohrs, less than the geometrical radius of the cluster that is 8 bohrs [32]. This result shows absolute general fragility of the cluster-plus-charges procedure, that can be attenuated only working with larger clusters [17].

The surface example shows different features, due to a different behaviour of surface electrostatic potential with respect to the bulk Madelung potential. Figure 4 shows the geometry of the cluster surrounded by about 500 point charges. The results of our calculation for CO adsorption on MgO (100) models are summarized in Table 2, while Figure 5 shows the potential energy surface, that is the trend of the adsorption energy versus the adsorption distance. In our case SCF convergence can be easily reached also for bare clusters, but the adsorption energies obtained by bare cluster calculations depend very much on the cluster features: the positive cluster Mg$_{9}$O$_{5}^{+}$ gives -34 kcal/mol while the neutral Mg$_{9}$O$_{9}$ cluster gives -8.4 kcal/mol. If these clusters are embedded in sets of point charges the adsorption energy converges steadily to -12 kcal/mol. The reference adsorption energy calculated with the periodic 3x3 super-cell model is -7.5 kcal/mol: this is the result of a “one-side” adsorption on a slab model [33]. The two-side slab model gives the same adsorption energy, -7.5 kcal/mol, so we can assume that there is no influence of the dipolar moment across the slab. The inter-molecular repulsion between the co-adsorbed CO molecules in the 3x3 super-cell ($\theta=1/9=0.11$) model is +0.6 kcal/mol, that is consistent with the -6.3 kcal/mol adsorption energy calculated with a 6x6 super-cell ($\theta=1/36=0.028$): so a reasonable limit value for the single molecule adsorption energy, at the present level of accuracy B3LYP density functional with double zeta basis set plus polarization functions is in the interval [-6.9,-6.2] kcal/mol. All cluster calculations with point charge representations of the surface Madelung potential give an adsorption energy of [-13.1,-12.1] kcal/mol: the same results are steadily obtained by two different clusters, one neutral and one positively charged. This analysis allows us to assume that the point charge representation of the surface is very useful for obtaining a stable surface electronic structure, which is important for the study of surface phenomena, but the local electronic structure described by the cluster model is slightly different from that described by a periodic super-cell model. Also in the case of almost fully ionic crystals, clusters are more “flexible” than periodic slabs, so giving a stronger response to the local perturbation due to the weakly adsorbed molecular probe.
Figure 4. CO on the Mg$_9$O$_5$$^{8+}$ cluster embedded in a set $\{q\}$ of point charges. The molecular drawing is made with the Moldraw program [34]

|                        | Adsorption energy (kcal/mol) | True vs point charges potential R.M.S. |
|------------------------|-----------------------------|----------------------------------------|
| Periodic super-cell (3X3) | -7.5                        |                                        |
| Isolated Mg$_9$O$_5$$^{8+}$ | -32.0                       |                                        |
| Mg$_9$O$_5$$^{8+}$ + charges | -13.1                       | 4.4 $10^{-1}$                          |
| Mg$_9$O$_5$$^{8+}$ + optimized charges | -12.4                       | 6.3 $10^{-4}$                          |
| Mg$_9$O$_5$$^{8+}$ + optimized (charges + sphere) | -12.4                       | 9.9 $10^{-6}$                          |
| Isolated Mg$_9$O$_9$  | -8.4                        |                                        |
| Mg$_9$O$_9$ + charges  | -12.8                       | 5.3 $10^{-4}$                          |
| Mg$_9$O$_9$ + optimized charges | -12.1                       | 5.2 $10^{-4}$                          |
Figure 5. Adsorption energy of CO on MgO(100) as a function of the distance between the Carbon and Magnesium atoms. The zero energy corresponds to infinite distance. Solid line with squares: periodic model; dash-dotted line: cluster plus optimized charges; dotted line: cluster plus non-optimized charges; thin solid line: isolated cluster.

3. Conclusions

The present paper presents a method for defining unambiguously the electrostatic fields around clusters, simulating local phenomena in ionic bulk and surfaces, by means of sets of point charges obtained by best-fitting the electrostatic potential generated from periodic calculations. In the simulation of bulk processes using highly symmetric clusters, there is no direct effect of the external Madelung field, because the potential is nearly constant so that the electrostatic field vanishes. If the cluster model is embedded in a set of point charges, for making easier the SCF convergence, then the results depend strongly on the computational parameters. In the case of surfaces the results are more stable, in the sense that the cluster embedded in any reasonable set of charges gives about the same adsorption energy, close to that obtained in the periodic super-cell model, but it converges to a different limit. The message suggested by the present study is very clear: even in strongly ionic systems like MgO, where the electron localization is maximum, border problems due to cluster limitations cannot be disregarded if high accuracy is required. So there is room and need for studying the most sophisticated embedding schemes [3,8], and even for proposing new methods.

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