



An approach for inclusion of crystal polarization in embedded cluster calculations: application to CaF_2

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Abstract

A methodology is presented which allows for self-consistent treatment of lattice polarization effects in ab initio embedded cluster calculations of defects in insulating crystal. This approach uses molecular mechanics or shell model potentials for classical ions near the quantum cluster and a modification of the dielectric continuum method for polarization of the rest of the crystal. Anion interstitial and vacancy in CaF_2 crystal have been considered as test cases for the proposed method. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Ab initio embedded cluster method is a valuable tool for theoretical studies of defects and physico-chemical processes in the bulk and on the surface of crystals (for examples and references, see Refs. [1–4]). In this approach, a defect or a surface active site is modeled as a cluster treated quantum-mechanically. This cluster is embedded in the potential produced by the rest of the crystal lattice. This potential normally includes Coulomb (or Madelung), exchange and repulsion contributions. In many instances, especially for charged defects, polarization of the lattice is also an important part of the embedding potential. Although the basic principles of treatment of embedded clusters in the self-consistently polarized lattice are well known [5–7], the problem is so complex that approximations are certainly needed.

The main idea which makes the solution of this problem computationally feasible is to divide the infinite crystal containing a point defect into three regions as shown in Fig. 1a. Region I is quantum-mechanical cluster (shown as empty circles in Fig. 1a) where the electron configuration and positions of ions may differ significantly from those in the ground state of the perfect crystal. Region II is the surrounding classical region, where the ions are represented as classical particles (black circles in Fig. 1a), e.g., rigid ions or cores and shells, interacting with each other by means of pair potentials. These ions may be arbitrarily displaced from their lattice sites and polarized. Region III is the crystal remainder, where displacement and polarization of ions are usually treated as point dipoles using the continuous or Mott–Littleton approximation [8]. These general ideas have been implemented in a number of computer codes allowing for quantum treatment of a crystal defect with self-consistent lattice polarization [9–11]. The ICECAP computer code [9] employing accurate ab initio treatment of the cluster wave func-

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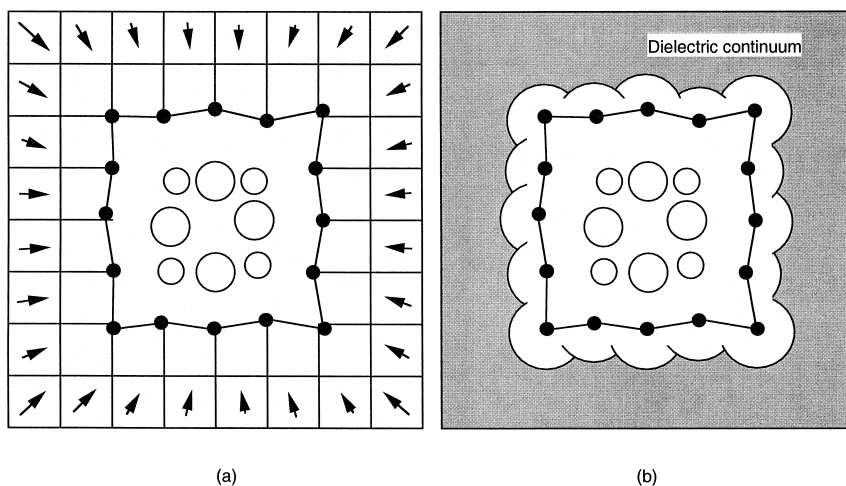


Fig. 1. Two different approaches for treatment of crystal polarization in zone III: (a) traditional Mott–Littleton method; (b) dielectric continuum approach.

tion has been successfully used in many studies of defects in crystals (for reviews, see Refs. [3,12]). Despite this progress, some problems regarding accuracy, applicability and computational efficiency have not been yet solved. In particular, in its current version, ICECAP can use only Hartree–Fock method with Rayleigh–Schrödinger many-body perturbation correction to calculate electronic structure in region I; due to unavailability of analytical energy gradients, geometry optimization in region I is still a tedious job.

Our goal here is to develop a computationally practical method for treating lattice polarization and the electronic structure of the cluster in a self-consistent manner. Such a method should allow *ab initio* representation of the cluster wavefunction with good basis sets and accurate treatment of the electron correlation, e.g., via MP2, non-local density functional methods or any multiconfigurational methods. In addition, it should have analytical energy derivatives with respect to positions of cluster atoms and the possibility to treat defects in arbitrary lattices including defects on crystal surfaces. Obviously, none of existing computational methods satisfy these strict requirements. A motivation for our interest in this problem comes from our studies of chemical processes at solid–liquid interfaces and in zeolites. With recently developed CECILIA model [13,14] we were able to model realistically the influence of the sol-

vent on interfacial reactions. As many crystals of interest have highly polarizable lattices, e.g., dielectric constant of TiO_2 is even higher than that of water, the treatment of the crystal lattice polarization on the same footing as that of the solvent becomes important.

In Section 2, we describe the proposed method that satisfies the above requirements. In Section 3 we test this model by applying it to CaF_2 (fluorite) crystal. This crystal has been used as a model substance in a variety of experimental and theoretical studies of radiation damage of insulating crystals. Similarly to the alkali halides, CaF_2 crystal is highly ionic and has a close-packed crystal structure. In such cases the embedded cluster approach is known to be very accurate. Therefore, we can concentrate on the description of polarization effects. We will test our method by comparing to experiment [15,16] formation energies of the anion vacancy and interstitial. Being charged defects, they induce significant polarization of the surrounding lattice.

2. Methodology

The physical model used in our approach (see Fig. 1b) is similar to that described above (e.g., in the ICECAP model [9]). The most significant difference is in the way we treat region III. Instead of representing polarization in this region as an array of

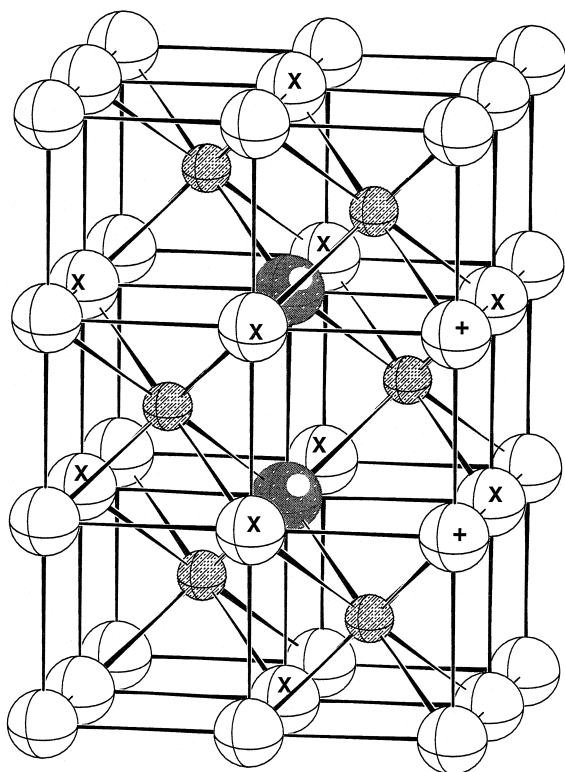


Fig. 2. A piece of the CaF_2 crystal lattice showing details of our embedded cluster model (see text).

discrete dipoles, we use the dielectric continuum approach which assumes that region III is a uniform medium characterized by a dielectric constant ϵ and separated from regions I and II by a sharp boundary. This approximation neglects the atomistic structure of region III and tensor character of its dielectric properties. This results in some loss of accuracy as compared to ICECAP-like techniques. However, these simplifications yield several computational advantages. In particular, geometry optimizations can be routinely performed due to the availability of analytical energy derivatives. The algorithms for construction of the boundary, representation of the polarization by apparent surface charges, and inclusion of the non-linear polarization potential in the Hamiltonian of the region I have been well developed for studies of solvent effects in liquids [17]. In this Letter we will use the GCOSMO dielectric continuum model [18] for treating polarization in region III. It is worth to mention that the possibility to use the simplest di-

electric continuum model (a point charge in the spherical cavity with a properly fitted radius) to represent crystal polarization has been demonstrated by Mott and Littleton [8] and also in Refs. [19,20].

Although the method outlined above is quite general, below we use the CaF_2 crystal as an example to illustrate all aspects of the model in a typical application setting. The quantum cluster (region I) $[\text{Ca}_6\text{F}_2]^{+10}$ used in this study is shown by hatched balls in Fig. 2. In order to reduce the number of active electrons and dimension of the quantum problem we employed a standard large core LANL pseudopotential with double-zeta basis set for Ca^{2+} ions [21] while all-electron D95 + (2d) basis set [22] was used for F ions. We have used Hartree–Fock approximation for the cluster wave function with MP2 electron correlation correction added to the total energy.

For anion vacancy calculations, one of cluster's F^- ions has been removed and the classical zone II was made of ten F^- ions marked with 'x' in Fig. 2. For interstitial calculations, an additional quantum F^- ion has been placed in the interstitial site and two more classical F^- (labelled with '+' in Fig. 2) have been added to the zone II. The energy of the classical region II was calculated in a rigid ion approximation. Born–Mayer analytical form was chosen for the pair interaction potentials between ions (Ca^{2+} and F^-) in region II and ionic cores or nuclei (Ca^{2+} and F^{9+}) in region I. The parameters of the potentials listed in Table 1 have been derived from calculations of the perfect cluster with one quantum F^- ion. They satisfy the following criteria [2]: (1) the equilibrium geometry of the cluster simulating the perfect lattice coincides with the corresponding fragment of the infinite lattice; (2) the total energy of the cluster behaves symmetrically with respect to displacements of the ions in the equivalent directions both inward

Table 1
Parameters of short-range pair interaction potentials for CaF_2 (atomic units), $f_{ab}(r) = C_1 \exp(-C_2 r) - C_3 r^{-6}$

a	b	C_1	C_2	C_3
F^{-1}	Ca^{+2}	136.78	2.0376	–
F^{+9}	Ca^{+2}	302.09	2.2744	96.670
Ca^{+2}	Ca^{+2}	2059.2	2.7007	161.42
F^{-1}	F^{+9}	109.97	2.0740	57.704

and outward from the border of the cluster. In this way the inequivalence in the interaction of the ions on the cluster boundary with the quantum-mechanical ions inside the cluster and with the classical ions outside the cluster is corrected.

The crystal lattice outside regions I and II described above was attributed to region III. 49 nearest Ca^{2+} ions in this region acted on electrons localized in the quantum cluster by means of the LANL pseudopotentials [21]. Use of the nonlocal pseudopotentials (as opposed to simple point charge approximation) for positive ions is essential to avoid unphysical delocalization of the cluster wave function. The rest of the zone III was treated in the point charge approximation ($Q_{\text{Ca}} = +2$, $Q_{\text{F}} = -1$). The contribution to the Madelung potential from 312 ions lying within 12 Å distance from the quantum cluster was calculated explicitly. The potential from the rest of the infinite lattice was modeled by 240 point charges situated on the sphere of radius 6 Å around the cluster using the SCREEP algorithm [23]. This model represents the Madelung potential inside cluster with the error of < 0.07 hartree.

We used the GCOSMO (generalized conductor-like screening model) solvation model [18] as a basis in our description of the dielectric continuum in zone III. This is a generalization of the COSMO model originally introduced by Klamt and Shüürmann [24] for studying solvent effects. The GCOSMO model has demonstrated its accuracy and applicability in a number of studies of solvent effects on structure, reactivity and spectroscopy (see Ref. [25] and references therein). The surface of the dielectric cavity has been constructed from spheres centered on ideal lattice positions of ions in regions I and II. To define the size and the shape of the GCOSMO cavity, we have used atomic radii which yield correct solvation energies for ions in water: 1.72 Å for Ca^{2+} and 1.28 Å for F^- . The value of 6.85 has been used for the dielectric constant of CaF_2 [26]. The boundary of the cavity was divided into 244 surface elements and surface charge distribution was approximated by effective point charges in the center of each surface element. The surface charges satisfy the matrix equation [18]

$$\mathbf{q} = -\frac{\varepsilon - 1}{\varepsilon} \mathbf{A}^{-1} \phi, \quad (1)$$

where ε is a dielectric constant and matrix elements of the matrix \mathbf{A} are given by [24]:

$$A_{uv} = \frac{1}{|\vec{t}_u - \vec{t}_v|},$$

$$A_{uu} = 1.07 \sqrt{\frac{4\pi}{S_u}},$$

where t_u is a position vector of a surface charge and S_u is an area of the corresponding surface element. The scaling of surface charges in Eq. (1) can be thought as an approximation to the rigorous Polarizable Continuum Model (PCM) approach. According to our estimates, even for systems with dielectric constant as low as 5, the error in calculated polarization energy does not exceed more than 10%.

In the original GCOSMO model, vector ϕ contains potentials on surface elements from the solute. In the case of a defect in crystal, polarization would occur only if the charge distribution in the cluster differs from that characteristic for the perfect lattice. Therefore, for potential ϕ in Eq. (1) we take the difference

$$\phi = \Phi - \Phi_0 \quad (2)$$

between the potential on surface element from the defective crystal Φ and from the perfect crystal Φ_0 , respectively. Generally, potentials Φ and Φ_0 include contributions from the quantum cluster, from classical zone II and the Madelung potential from zone III. However, the latter contribution obviously cancels out in Eq. (2). Note that in our method the potential from the electronic charge distribution is calculated exactly without using any multipole expansion as in the ICECAP program. The non-linear (with respect to the cluster wavefunction) polarization potential produced by charges (1) was added directly to the Fock matrix of the cluster [18]. Thus, LCAO coefficients of the cluster wave function and polarization charges converged simultaneously in the same SCF procedure. This is in contrast to previous algorithms [9,11] in which quantum (region I) and classical (regions II and III) parts of the program work iteratively until self-consistency is reached. Expressions for the total energy of the cluster and its first and second derivatives with respect to nuclear coordinates are basically the same as in the GCOSMO model [27]. For geometry optimizations with the polarization correction on, the

GCOSMO surface remained fixed. Therefore the reference potential of the perfect cluster Φ_0 needed to be determined only once.

This method has been implemented in our locally modified version of the GAUSSIAN92/DFT program [28].

3. Results and discussion

We have calculated the equilibrium geometry of perfect clusters of various shape and size including up to 12 F^- ions in the quantum zone. In all cases we found that deviations of optimized positions of ions from the perfect lattice geometry are $< 0.01 \text{ \AA}$. The same stands also for the defective clusters: the equilibrium structure and the defect formation energy are virtually independent on the size and shape of the quantum cluster. Furthermore we have found that the equilibrium geometry of a cluster simulating perfect CaF_2 (111) surface agrees well with that found in recent periodic Hartree–Fock calculations of the surface atomic and electronic structure [29]. This confirmed a good quality of the computational method reported above and allowed us to turn our attention to defect studies.

In defect calculations, geometry of the clusters modeling vacancy and interstitial have been first optimized without taking into account the lattice polarization. Positions of ions in zones I and II have been fully relaxed to zero force. Although the clusters are asymmetric and no symmetry constraints have been applied during the geometry optimization, the relaxation of the ions around defects was found to be symmetrical within 0.01 \AA precision. This provides an additional evidence towards the accuracy of our embedded cluster method. The magnitudes of

displacements are following: eight F^- ions and six Ca^{2+} around the interstitial move by 0.17 \AA outwards and by 0.20 \AA inwards, respectively. Four Ca^{2+} and six F^- around the vacancy move by 0.25 \AA outwards and by 0.14 \AA inwards, respectively. The displacements of more distant ions were found to be $< 0.01 \text{ \AA}$.

Formation energies of the anion vacancy and interstitial calculated using different levels of approximations are listed in Table 2. Formation energies are defined as a difference in total energy between defective and perfect clusters taking into account the self-energy of removed or added F^- ion. Electron correlation correction appears to be positive for the interstitial and negative for the vacancy and therefore it is relatively small for the pair of defects. If the polarization of the lattice is neglected, the calculated energy of the Frenkel pair formation is significantly overestimated by $\sim 3.6 \text{ eV}$. When polarization has been taken into account without reoptimizing the geometry, the error reduced to $\sim 1.2 \text{ eV}$. We found that reoptimization of the cluster geometry with inclusion of the crystal polarization does not noticeably change the equilibrium geometry of the defects. The displacements change by $< 0.01 \text{ \AA}$ and the total energy change by only $\sim 0.02 \text{ eV}$. Such small influence of polarization on geometry and electronic structure is consistent with previous studies on molecules in solution. This finding seems to justify a common procedure to simply add the lattice polarization energy to the total energy of the cluster without geometry reoptimization [31,32]. However, there are known instances when polarization of the surrounding considerably changes the topology of the solute potential energy surface [33,34]. In such cases, geometry of the cluster and polarization should be determined self-consistently.

Table 2
Formation energies of Frenkel defects in CaF_2 (eV)

	HF	HF + MP2	HF + MP2 + polarization	Experiment	Theory ^a
I_a (interstitial F^-)	-3.71	-3.37	-4.93		-4.41 to -3.24
V_a (F^- vacancy)	10.06	9.66	8.91		5.87–7.09
$I_a + V_a$	6.35	6.29	3.98	2.7 ^b , 2.8 ^c	2.63–2.67

^aWith different sets of shell model parameters fitted to experiment in Ref. [30].

^bRef. [15].

^cRef. [16].

We attribute the residual error in defect formation energies to the choice of parameters, i.e., pair potentials in Table 1 and atomic radii. To provide perfect match of boundary conditions between zones I–II and II–III, the pair-potentials used in zone II should be consistent with the quantum-mechanical method used in the zone I (this is achieved in our study), and yield by themselves, correct geometrical, energetic and dielectric properties of the perfect crystal [9,35]. Further work is needed for development of molecular mechanics parameters satisfying these conditions. Although the use of atomic radii taken from solvation studies in water is a reasonable initial guess, more work is certainly needed in this direction as well. However this problem is less severe since the dependence of results on the choice of atomic radii can be significantly reduced and the anisotropy of the crystal polarization can be better taken into account by simply increasing the size of the region II. Such increase does not have a noticeable influence on the speed and cost of calculations.

4. Summary

We have presented a simple method based on the dielectric continuum approximation for treatment of the crystal lattice polarization in ab initio embedded cluster calculations. Results of test calculations show good agreement with previous theoretical and experimental data. The advantage of our method is in its flexibility and computational efficiency. It allows treatment of defects in crystal lattices with arbitrary symmetry, including defects on surfaces. The electronic structure of the quantum zone can be treated with various electronic structure methods. If needed, all crystal lattice can be treated in fully classical approximation. The classical region can be described in both rigid ion and shell model approaches. Efficient geometry optimization can be performed with available energy derivatives. The additional cost for using self-consistent lattice polarization in zone III is only $\sim 10\%$. This method can be used for various defect related problems in material science, surface physics and chemistry. It is worth to mention that this way of treating crystal polarization perfectly suits for studying chemistry at solid–liquid interfaces with the CECILIA model [13]. The price we pay for

these advantages is complete neglect of atomic structure and anisotropy when dealing with polarization in region III. Although such neglect seems to be justified when explicitly treated regions I and II are chosen big enough, more work is needed for clear understanding of the accuracy of such an approximation and of the dependence of results on cluster size.

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