

Cluster modeling of metal oxides: the influence of the surrounding point charges on the embedded cluster

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Abstract

An ab initio study has been performed to investigate the influence of the surrounding point charges on the calculated electronic properties of the embedded NiO cluster. The employment of the nominal charges ± 2.0 would cause overestimation of the crystal potential even for the so-called ionic oxide NiO. Several criteria, namely, the charge, potential, dipole moment and charge density consistence for determining the magnitude of point charges self-consistently have been proposed and examined. When the embedding point charges are spherically expanded, giving the embedding point charges a continuous distribution of charge density, a good agreement is reached between the calculated properties of the embedded cluster model and those of the bulk solid after charge density consistence is fulfilled. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Metal oxides form a class of systems of important applications [1,2]. In catalysis, oxides are commonly used either as support materials or as catalytically active components. The importance of metal oxides cannot be overestimated as numerous catalytic reactions proceed over the surfaces of metal oxides. Nevertheless, mechanisms of basic surface reactions have not yet been fully established and theoretical modeling of metal oxides represents a serious challenge to quantum chemistry [3–5].

From the viewpoint of an embedded cluster model,

a bulk solid could be regarded as a sum of two fragments. One is a cut-out cluster, which will be explicitly treated in quantum chemical calculations, the other is the surrounding of the cut-out cluster. Accordingly, in order to establish a reasonable embedded cluster model, one has to answer two questions: (1) how to cut out a cluster; and (2) how to suitably account for the cluster–lattice interactions? For the first question, we have proposed three principles, namely, the neutrality principle, the stoichiometric principle and the coordination principle, according to which a neutral, stoichiometric cut-out cluster with the minimal amount of dangling bonds is preferred [6]. Our ab initio study for ZnO solid has shown the efficiency of these principles [7]. For the second question, when the surrounding of a cut-out cluster is approximately simulated by a point charge

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cluster (PCC), the cluster lattice interaction can be described by means of the Madelung potential. In principle, the magnitude of Madelung potential is proportional to the values of the point charges. So far, however, no systematic work has been found in the literature regarding the question of how to determine the values of the point charges. It is common to assume the full ionicity of a metal oxide and use the nominal charges for the respective ions [8,9]. Since most of the metal oxides are not purely ionic, but covalent to some extent, the choice of full ionicity is apparently not justified. Therefore, how to determine the charges of ions in metal oxides is of great importance for a successful embedded cluster modeling of metal oxides.

There have been some relevant papers published in the literature [10–13]. Starting from the simple ionic model to the sophisticated ab initio configuration interaction approach, Illas et al. [10] have investigated the ionicity of alkaline earth metal oxides. They claimed that the degree of covalency for the simple oxides from MgO to BaO never exceeds 5%. Investigations on CO chemisorption at the MgO(001) surface, however, give indirect evidence for a reduced ionicity of the MgO substrate. Neyman and Rösch [11] found that a reduction of the assumed ionicity from ± 2 to ± 1.5 of the MgO crystal brings the calculated vibrational frequency shifts of CO/(Mg₉O₉) from 54 to 17 cm⁻¹, which leads to a much better agreement with the experiment finding of 14 cm⁻¹. Stimulated by this discovery, Rösch et al. [12] have performed a first principle local density functional investigation on the extended, two-dimensional periodic slab models of the MgO(001) surface. The detailed analysis of the charge distribution and its influence on the electrical field above the surface reveals a charge separation significantly (10–20%) below the nominal ionic value of ± 2 . Previously, we studied the CO chemisorption on a NiO(100) surface with the DV-X_α embedded cluster method [13]. We found that a better description of the chemisorptive behavior was obtained when charge-consistence between the embedding point charges and the in-cluster Ni and O ions was accomplished by changing the embedding point charges from the nominal values of ± 2.0 to ± 1.72 .

In this Letter, several criteria, namely, the charge consistence, potential consistence, dipole moment

consistence and charge density consistence for determining the magnitude of point charges self-consistently have been proposed and examined. Merits and demerits of these criteria have been compared and contrasted. This has shown that when the embedding point charges are spherically expanded, which furnishes the embedding point charges with a continuous distribution of charge density, a good agreement is reached between the calculated properties of the embedded cluster model and those of the bulk solid after the requirement of charge density consistence is fulfilled.

2. Theoretical background for the embedded cluster model

Suppose that the solid could be divided into two parts, i.e. a cut-out cluster (index C) and its surroundings (index S). Neglecting the electron exchange between C and S, the zeroth-order wavefunction of bulk solid Ψ_{bulk} could be approximated in terms of Φ_C and Φ_S as a simple product and the interaction energy E_{CS} can be given by the first-order correction from the direct electrostatic interaction [14]. When the surroundings S are approximated by a PCC, the total energy of such an ideal system can be expressed as

$$\begin{aligned}
 E = & \left\langle \Phi_C \left| \sum_{i \in C} T_i - \sum_{i \in C} \sum_{a \in C} \frac{Z_a}{r_{ia}} \right. \right. \\
 & - \sum_{i \in C} \sum_{p \in S} \frac{Q_p}{r_{ip}} + \left. \sum_{1 > j \in C} \frac{1}{r_{ij}} \Phi_C \right\rangle \\
 & + \sum_{a > b \in C} \frac{Z_a Z_b}{R_{ab}} + \sum_{a \in C} \sum_{p \in S} \frac{Z_a Q_p}{R_{ap}} \\
 & + \sum_{p > q \in S} \frac{Q_p Q_q}{R_{pq}}, \quad (1)
 \end{aligned}$$

in which i, j label the electrons in cluster C; a, b label the nuclei in cluster C; and p, q label the positions of the point charges in surroundings S. T_i is the electronic kinetic energy of electron i . Z_a refers to the nuclear charge and r refers to the distance. So $-Z_a/r_{ia}$ is the electron–nuclear attraction in cluster C, while $-Q_p/r_{ip}$ corresponds to the

interaction between the point charge Q_p in surroundings S and the electron i in cluster C. The value of the point charge Q_p modifies the core Hamiltonian of the cluster in terms of one-electron integrals $-\sum_{i \in C} \sum_{p \in S} Q_p / r_{ip}$. Thus different Q_p of the surroundings S will result in different Φ_C of the cluster C. The charges used for embedding and the charges derived from the wavefunctions of the embedded cluster should be self-consistent.

3. Self-consistent criteria for determining the values of point charges

Suppose atom A is located at position a of cluster C, the electron count of atom A is given by

$$N_a = \int \rho_C(i) dv_i, \quad i \in A, \quad (2)$$

and the charge on atom A is

$$Q_a = Z_a - N_a. \quad (3)$$

When the surroundings S are approximated by a PCC, for the point p , one has

$$\rho_S^p(k) = N_p \delta(r_k - R_p), \quad k \in p. \quad (4)$$

Then the charge on point p is

$$Q_p = Z_p - N_p. \quad (5)$$

If atom A of cluster C and point p of the surroundings S are equivalent in the bulk solid, it would be anticipated that charge on point p should be equal to charge on atom A. That is

$$Q_p = Q_a. \quad (6)$$

Since ρ_C is given by Φ_C , while different Q_p will induce different Φ_C , one needs to reach charge consistence. That is the charges used for embedding should be consistent with the charges derived from the wavefunctions of the embedded cluster.

Suppose point p is equivalent to atom A and point q is equivalent to atom B, it is required that

$$R_{ab} = R_{pq}. \quad (7)$$

When the point charges p, q are fixed at the geometry of the bulk solid, the optimized geometry for cluster C could be in accordance with that for the surroundings S, after choosing suitable values of the

Q_p s. We call this potential consistence, i.e. the interaction potential produced by the point charges is balanced by that produced by the equivalent atoms at the equilibrium lattice positions (R_e).

We may take dipole moment consistence as a criterion for determining the embedding charge. The dipole moment of a discrete set of point charges Q_p s is given in classical physics by

$$\mu_S = \sum_{p \in S} Q_p R_p. \quad (8)$$

For a cluster with a discrete set of nuclear charges Z_a s and a continuous electronic density $\rho_C(i)$, the dipole moment is

$$\mu_C = \sum_{a \in C} Z_a r_a - \int \rho_C(i) r_i dv_i. \quad (9)$$

Assuming $|\mu_S| = |\mu_C|$, we will have Q_p . Again, different Q_p will induce different μ_C , we need to reach dipole moment consistence.

From Eqs. (2)–(5) it is clear that the basic difference between a point charge and a real atom lies in the fact that a real atom possesses a continuous distribution of charge density, while a point charge does not. Therefore, we try to spherically expand the point charge, so as to furnish it with a continuous distribution of charge density. Since in principle, the chemical properties of a system are intrinsically dependent on the electron density distribution, we expect that charge density consistence will help us to construct a better cluster model. The spherical expansion of a point charge Q_p can be processed as follows.

The spherical function is

$$\varphi_s(r) = \left(\frac{2\alpha}{\pi} \right)^{3/4} e^{-\alpha r^2}. \quad (10)$$

We then have a spherically expanded point charge with a charge density $q_p(r)$ in the form of

$$q_p(r) = Q_p (\varphi_s(r))^2, \quad (11)$$

$$Q_p = \int q_p(r) dv. \quad (12)$$

Defining the charge density of atom A as $q_a(r)$, we have

$$Q_a = \int q_a(r) dv. \quad (13)$$

When $Q_p = Q_a$, comparing Eq. (12) with Eq. (13), we have

$$q_p(r) \approx q_a(r). \quad (14)$$

In practice, the exponent α for the spherical charge is given by

$$\alpha = \frac{3}{2\langle R \rangle^2}, \quad (15)$$

where $\langle R \rangle$ is the ionic radius.

Taking NiO [15] as an example, we have

$$\begin{aligned} \langle R_{\text{Ni}^{2+}} \rangle &= 0.824 \text{ \AA}, \quad \alpha_{\text{Ni}} = 0.6186 \text{ \AA}^{-2}; \\ \langle R_{\text{O}^{2-}} \rangle &= 1.26 \text{ \AA}, \quad \alpha_{\text{O}} = 0.2646 \text{ \AA}^{-2}. \end{aligned} \quad (16)$$

4. Ab initio calculations for the embedded NiO cluster: the influence of the surrounding point charges on the embedded cluster

NiO solid is an NaCl-type crystalline, with a nearest Ni–O distance of 2.084 Å [16]. In the calculations, a NiO dimer was cut out from the NiO lattice and was embedded into a symmetric ($11 \times 11 \times 12$) PCC. The values of the point charges Q_p s were changed from 0.0 to ± 2.0 , in order to investigate the influence of the magnitude of the point charges on the calculated electronic properties of the embedded cluster.

The metal basis sets used in this study are derived from the Wachters (14s9p5d) primitive sets [17], which are contracted to [8s4p3d] by using Wachters' contraction Scheme 3. To these basis sets two additional diffuse p functions were added, which were optimized by Wachters to describe the 4p orbitals and which are scaled by a factor of 1.25 to make them more suitable for molecular calculations [17]. As suggested by Hay [18], a diffuse 3d function was also added to give a balanced description of the transition metal atom involving different d occupation. This leads to a final metal basis set of the form (14s11p6d)/[8s6p4d]. The O basis set is derived from the van Duijneveldt (9s5p) primitive set [19], which is contracted to [4s3p] based on a (5211) contraction of the s space and a (311) contraction of the p space. These basis sets are at least of double- ζ quality and are frequently employed in the theoretical literature.

Spin-unrestricted Hartree–Fock (UHF) calcula-

tions were performed on the triplet NiO cluster model using GAUSSIAN 94 [20], since previous calculations showed that the ground state of NiO is a triplet [21,22]. The spin contamination effect is found to be small, with the two spin-unpaired electrons being almost solely on Ni d orbitals.

Table 1 presents the results of our ab initio UHF calculations for the embedded NiO cluster model. The results show that:

(1) For the free NiO molecule, the calculated charge on the Ni atom (0.527) is far smaller than the nominal value 2.0, indicating the free NiO molecule would be quite covalent. The optimized Ni–O bond length (1.784 Å) is far shorter than that in NiO crystal (2.084 Å).

(2) When the NiO dimer is embedded into the electric field of the PCC, the computed charge on Ni increases considerably, indicating the increase of the ionicity of Ni–O bonding. Notably, the electronic properties of the embedded cluster, e.g. atomic populations, energy level of the HOMO (highest occupied molecular orbital), the energy gap ΔG between the HOMO and LUMO (lowest unoccupied molecular orbital) and dipole moment, etc., show large dependence on the magnitude of the embedding point charges.

(3) When the Q_p s are set to be the nominal charges ± 2.0 , the influence of the surrounding electric field is so strong that the optimized Ni–O distance (2.747 Å) is far longer than that in the crystal (2.084 Å). However, the calculated absolute charges on the Ni or O atom are smaller than the nominal value of 2.0. All of these points indicate that the external field is overestimated and the interaction between the cluster and the lattice point charges is non-balanced. We need to reach a certain consistence between the cut-out cluster and the surroundings.

(4) Reducing the Q_p s from ± 2.0 to ± 1.77 , we found that the calculated charges of Ni and O are also ± 1.77 , meeting the requirement of charge consistence. The calculated properties of the embedded cluster differ moderately upon geometry optimization, implying that the results from charge consistence are more reasonable than those from the nominal values of ± 2.0 . However, the Ni–O bond still becomes longer upon optimization, showing that the effect of the embedding electric field is still overestimated.

Table 1
Ab initio UHF calculations for the embedded NiO dimer

Q_p	$Q_{\text{Ni/O}}$	HOMO (au)	LUMO (au)	ΔG (au)	μ_c (debye)	μ_s (debye)	$R_{\text{Ni-O}}$ (Å)
0.00	± 0.527 ± 0.716	-0.3113 -0.3325	-0.0314 -0.0445	0.2799 0.2880	5.64 7.55	-	2.084 1.784*
± 2.00	± 1.823 ± 1.790	-0.4870 -0.4947	0.0487 0.0027	0.5357 0.4974	19.95 25.75	20.02	2.084 2.747*
± 1.99	± 1.821 ± 1.788	-0.4864 -0.4932	0.0496 0.0046	0.5360 0.4977	19.93 25.65	19.92	2.084 2.740*
± 1.77	± 1.768 ± 1.739	-0.4596 -0.4635	0.0664 0.0494	0.5259 0.5129	19.54 22.20	17.72	2.084 2.408*
± 1.36	± 1.641 ± 1.641	-0.3978 -0.3978	0.0610 0.0608	0.4588 0.4587	18.61 18.62	13.62	2.084 2.086*
± 1.67 (10spc)	± 1.669 ± 1.671	-0.4395 -0.4390	-0.0382 -0.0362	0.4013 0.4027	18.63 18.37	18.65	2.084 2.051*

The nearest Ni–O distance in NiO solid is 2.084 Å [16]. $Q_{\text{Ni/O}}$ refers to the Mulliken charges. The asterisk (*) stands for the results under the optimized geometry.

Fig. 1 schematically represents a comparison between the attractive potential curves produced by a real ion and by its equivalent point charge. When $Q_p = Q_a$, it is derived from Eq. (13) that $Q_p > q_a$. Since the attractive potential produced by point charge Q_p has the form of $-Q_p/r$ and the attractive potential produced by atom A with a charge density of $q_a(r)$ is in the form of $-q_a(r)/r$, the two attractive potential curves could never coincide in such a case as shown in Fig. 1a. When the atoms of an embedded cluster are located at the equilibrium lattice positions, the embedded cluster suffers a non-balanced interaction with its environmental PCC. In other words, charge consistence would still lead to an overestimation of the influence of the surroundings.

(5) Choosing the Q_p s equal ± 1.99 , the calculated dipole moment of the NiO dimer and that of the PCC are equal, meeting the requirement of dipole moment consistence. The calculated charge on the Ni atom is lower than the value of the point charge. The Q_p is just slightly lower than the nominal value. This suggests that taking dipole moment consistence as criterion would over-emphasize the ionicity of a

metal oxide. It should be noted that overlap densities from the atomic orbitals of the same atom like $\chi_i^A \chi_j^A$ make an important contribution to the dipole moment but no contribution to the populations because $S_{ij}^A = 0$. So choosing dipole moment consistence as a criterion will always encounter $Q_p > Q_a$, as shown in Fig. 1a. Therefore dipole moment consistence would also lead to an overestimation of the influence of the surroundings.

(6) When the Q_p s are set to be ± 1.36 , potential consistence is encountered. The optimized Ni–O distance is in good accordance with that in crystalline NiO. This indicates the attractive potential produced by the point charges is now balanced by that produced by the equivalent atoms at the equilibrium lattice position (R_e) after choosing a suitable value of Q_p . That is

$$-\frac{Q_p}{r} = -\frac{q_A(r)}{r} \quad (r = R_e).$$

But, as expected, the value of the point charge is lower than the calculated charge of the in-cluster Ni atom, i.e. $Q_p < Q_a$. The corresponding attractive po-

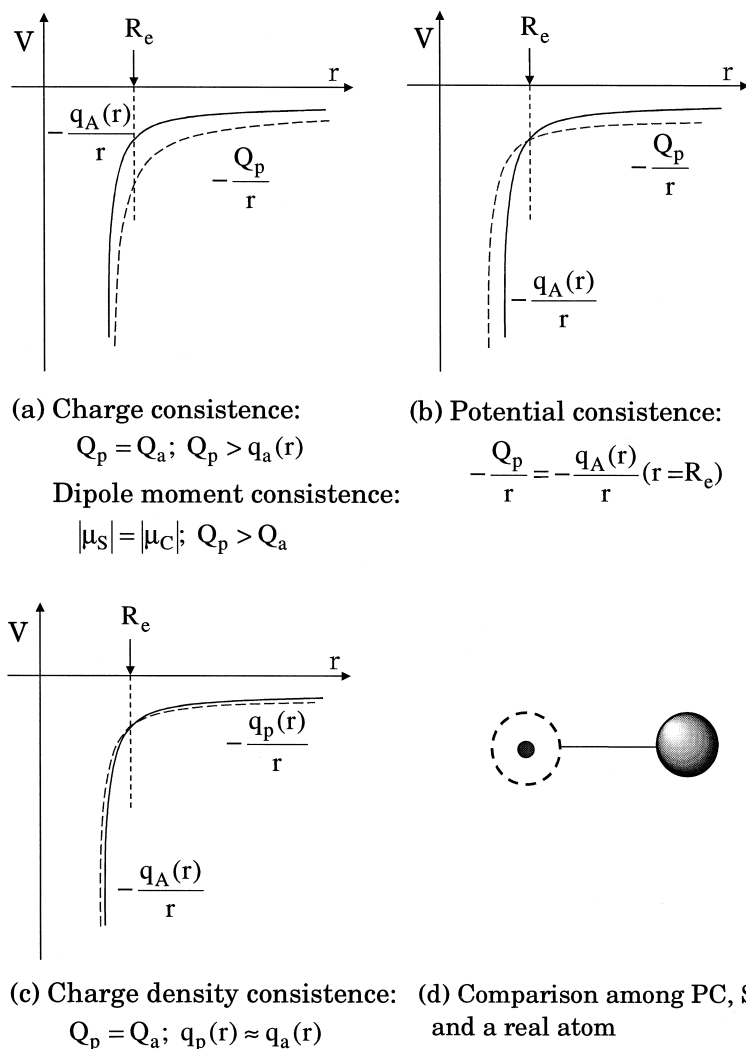


Fig. 1. Schematic comparison between the attractive potential curves produced by a real ion and its equivalent point charge.

tential curves are presented in Fig. 1b. $|Q_p|$ 1.36 is far lower than the nominal value of 2.0. This may be attributed to the difference between a point charge and a real ion, i.e. a real ion possesses a continuous distribution of charge density, while a point charge does not.

(7) When a spherical expansion is performed on the nearest 10 point charges neighboring the NiO dimer, we furnish these point charges with a continuous distribution of charge density. Then when charge consistency is encountered between the embedded cluster and its surroundings, we have Q_p 's of ± 1.67 . The optimized geometry is in accordance with the

experimental result, fulfilling the requirement of potential consistency; while the calculated dipole moment of the embedded NiO dimer is also close to that of the surrounding, reaching the dipole moment consistency. As expected, a better agreement is reached between the calculated properties of the embedded cluster and those of the bulk solid, when the charge density consistency is met.

5. Conclusions

In this Letter we have proposed and compared several criteria for the self-consistent determination

of the magnitude of the point charges employed in the embedded cluster modeling of metal oxides. An ab initio case study has been performed to show the influence of the values of the point charges chosen on the calculated electronic properties of the embedded NiO cluster. The calculation results show that the electronic properties of an embedded cluster depend largely on the values of the embedding point charges; that the choice of nominal values would lead to the overestimation of the crystal potential and certain consistence criterion between the cut-out cluster and the embedding point charges should be required and that the employment of point charges to represent the surrounding lattice will give a biased description of the embedded cluster with respect to the bulk solid, even if charge consistence, dipole moment consistence or potential consistence is accomplished. Considering that a real ion possesses a continuous distribution of charge density, we performed a spherical expansion of the point charges in the vicinity of the cut-out cluster. A good simulation of the bulk solid or solid surface is encountered, when charge density consistence is encountered. We call this model the SPC model. We have studied several representative chemisorption systems, e.g. CO/MgO, O/MgO, CO/ZnO, O/ZnO, H₂/ZnO, and H₂/TiO₂, with the SPC cluster model method and have investigated the effects of the size and symmetry of the PCC, the size dependence of the cluster model, basis sets and electron correlation in the theoretical description of chemisorptive bonding. Based on the findings in this Letter and those presented elsewhere, the main points of our so-called SPC cluster model can be summarized as follows: a stoichiometric cut-out cluster with the fewest dangling bonds embedded in a symmetric PCC and spherically expanded point charge surrounding with the charges self-consistently determined. Our case studies of chemisorption on the metal oxides of different degrees of ionicity demonstrated the efficiency of the SPC cluster model.

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