

SPC cluster modeling of metal oxides: ways of determining the values of point charges in the embedded cluster model*

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Abstract Several criteria for determining self-consistently the magnitude of point charges employed in the embedded cluster modeling of metal oxides have been proposed and investigated. Merits and demerits of these criteria have been compared. *Ab initio* study has been performed to show the influence of the values of point charges chosen on the calculated electronic properties of the embedded MgO cluster. The calculation results demonstrate that the electronic properties of the embedded cluster are of great dependence on the magnitude of the embedding point charges; that the employment of the nominal charges, ± 2.0 , would cause overestimation of the crystal potential even in the case of the so-called purely ionic oxide, MgO; and that certain requirements for the consistence between the embedded cluster and the embedding point charges should be reached. It is further found that errors for the calculated properties of the embedded cluster still exist with respect to those of bulk solid even in the case that self-consistence in terms of charge, dipole moment, or electrostatic potential was met between the cut-out cluster and the embedding point charges. As far as spherical expansion is performed upon the embedding point charges, which furnishes the embedding point charges with a continuous distribution of charge density, a global agreement is reached between the calculated properties of the embedded cluster model and those of the bulk solid.

Keywords: metal oxides, cluster-surface analogy, embedded cluster model, SPC cluster model.

Metal oxides are one kind of material of important applications^[1,2]. For the cluster modeling of metal oxides with quantum chemical methods, the ways go into three groups^[3,4], i. e. the bare cluster model, the saturated cluster model and the embedded cluster model. The bare cluster model is simply a small portion of substrate atoms, cut out from the bulk solid. In the saturated cluster model, the possible dangling bonds in the bare cluster are terminated with hydrogens, pseudo-hydrogens, or some other atoms; while in the embedded cluster model, the bare cluster is embedded in the point charge array which adopts the periodic lattice position of bulk solid. Although rigorous calculations of a bare cluster can give reasonable results for highly localized properties of these systems, the appropriate treatment of the influence of the bulk solid is vital for an overall quantitative agreement with experiments. It is generally believed^[3-5] that the embedded cluster model is more suitable for modeling of an ionic oxide where the orbital overlaps and orbital interactions are smaller; while the saturated cluster model is better for a covalent oxide in which the dangling bonds are eliminated by saturators like hydrogens. In fact, on one hand, hydrogens would be located at lattice sites so as to fulfill the "geometric requirements" of the bulk, the "electronic

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requirement" can hardly be fulfilled owing to the differences in the electronic properties between hydrogens and the lattice atoms to be replaced by hydrogens; on the other hand, the embedded cluster model can give reasonably good description of an ideal ionic surface, would, however, result in an overestimation of the electrostatic interaction between the metal oxide surface and the polar adspecies. When the embedded cluster model is used to study chemisorption, the replacement of lattice atoms with point charges would lead to a biased description of the stability of the ionic adspecies. Thereby, it is of great importance to find a way suitable for describing the effect of lattice field. What is more, since most of metal oxides are intermediates between purely ionic and covalent solids, it is urgent to develop new embedding techniques which could be applied to the modeling of an ordinary metal oxide.

In the viewpoint of cluster model methods, a bulk solid can be regarded as a summation 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: (i) how to cut out a cluster, and (ii) how to suitably account for the cluster-lattice interaction. For the first question, we have proposed three principles, namely neutrality principle, stoichiometrical principle and coordination number principle, according to which a neutral, stoichiometrical cut-out cluster with the minimal amount of dangling bonds is preferred. Our *ab initio* case study for ZnO solid has shown the efficiency of these principles¹⁾. For the second question, when the surrounding of a cut-out cluster is approximately simulated by a point charge 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 point charges. So far, however, no systematic work has been found in the literature regarding how to determine the values of point charges. It is common to assume the full ionicity of a metal oxide and use the nominal charges for the respective ions^[6,7]. 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 not only of key importance for a successful embedded cluster modeling of metal oxides, but also a basic subject in chemistry.

This paper investigates several ways of determining the values of point charges in the embedded cluster model, and proposes the so-called SPC cluster model.

1 Theoretical background for the embedded cluster model

The heart of cluster model methods is how to suitably introduce the influence of bulk solid. Suppose that the solid could be localized into two parts, i. e. a cut-out cluster (index C) and its surrounding (index S). The wave functions of bulk solid, Ψ_{bulk} , could be represented in terms of Φ_{C} and Φ_{S} . That is

$$\Psi_{\text{bulk}} = MA |\Phi_{\text{C}}\rangle + |\Phi_{\text{S}}\rangle, \quad (1.1)$$

where M is a normalization factor and A is an antisymmetrizer. Supposing that Φ_{C} and Φ_{S} fulfill the strong orthogonality requirement

$$\langle \Phi_{\text{C}} | \Phi_{\text{S}} \rangle = \delta_{\text{CS}}. \quad (1.2)$$

1) Lu, X., Xu, X., Wang, N. Q. et al., Cluster modeling of ZnO: coordination number principle for cluster modeling of metal oxides, *Chem. J. Chin. Univ.* (in the press).

Then the total energy of the bulk solid can be expressed as

$$E = E_C + E_S + E_{CS}. \quad (1.3)$$

In the cluster modeling of an ionic oxide solid, the surrounding of a cut-out cluster can be represented approximately by an array of point charges. The total energy of such an ideal system, consisting of the PCC and the embedded cluster, can be expressed as

$$E = \left\langle \Phi_C \left| \sum_{i \in C} T_i - \sum_{i \in C} \sum_{\alpha \in C} \frac{Z_\alpha}{r_{i\alpha}} - \sum_{i \in C} \sum_{p \in S} \frac{Q_p}{r_{ip}} + \sum_{i > j \in C} \frac{1}{r_{ij}} \right| \Phi_C \right\rangle + \sum_{\alpha > \beta \in C} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + \sum_{\alpha \in C} \sum_{p \in S} \frac{Z_\alpha Q_p}{R_{\alpha p}} + \sum_{p > q \in S} \frac{Q_p Q_q}{r_{pq}}, \quad (1.4)$$

in which i and j label the electrons in cluster, C , α and β label the nuclei in cluster C , while p and q label the positions of point charges in surrounding S , T_i is the electronic kinetic energy of electron i ; Z_α refers to nuclear charge and r refers to distance. So $-\frac{Z_\alpha}{r_{i\alpha}}$ is the electron-nuclear attraction in cluster C ; while $-\frac{Q_p}{r_{ip}}$ corresponds to the interaction between the point charge Q_p in surrounding S and the electron i in cluster C . The value of point charge Q_p modifies the core Hamiltonian of the cluster in terms of one-electron integrals $-\sum_{i \in C} \sum_{p \in S} \frac{Q_p}{r_{ip}}$. Thus different Q_p of surrounding S will deduce different Φ_C of cluster C . The charges used for embedding and the charges derived from the wave functions of the embedded cluster should be self-consistent. Previously, we studied the CO chemisorption on NiO(100) surface with the DV- X_c embedded cluster method^[8]. We found that a better description of the chemisorptive behavior could be obtained when charge-consistence between the embedding point charges and the in-cluster Ni and O ions was accomplished by reducing the embedding point charges from the nominal values of ± 2.0 to ± 1.72 .

2 Self-consistence criteria for determining the values of point charges

In the framework of MO-LCAO method, molecular orbital $\Phi(r)$ can be expressed as linear combinations of atomic orbital $\chi(r)$; that is

$$\Phi_m(r) = \sum_A \sum_{i \in A} C_{Ai}^m \chi_{Ai}(r), \quad (2.1)$$

where m labels molecular orbitals, i and j label atomic orbitals, A and B label atoms. Performing Mulliken population analysis, we have

$$P_{ij}^t \equiv \sum_m n_m C_{Ai}^m C_{Bj}^m, \quad S_{Ai, Bj} = \int \chi_{Ai}(r) \chi_{Bj}(r) dr. \quad (2.2)$$

$$n = \sum_A n_A, \quad n_A = \sum_{i \in A} \sum_j P_{ij}^t S_{Ai, Bj}, \quad (2.3)$$

where n is the total electron count of the molecule and n_A is the electron count of atom A . Then the Mulliken charge on atom A is $Q_A = Z_A - n_A$.

If the point charge Q_p is equivalent to atom A in lattice, charge consistence requires that $Q_p = Q_A$.

Mulliken population analysis is widely used in the literature due to its simplicity. However, it divides the overlap populations $S_{Ai, Bj}$ equally, adding half to A or B atom, and thus is frequently criticized. For an ideal ionic solid, the overlap populations between atoms should be zero or

negligible. In such a case, the Mulliken charges obtained by well-balanced basis sets should be able to describe an ionic crystal reasonably.

Based on eq. (2.1), one may further perform a density analysis as

$$\rho(r) = \sum_m n_m \Phi_m^*(r) \Phi_m(r), \quad n = \int \rho(r) d\tau. \quad (2.4)$$

Similar to Mulliken population analysis, Mulliken electron density of atom A can be defined as

$$\rho_A(r) = \sum_{i \in A} \sum_j P_{ij}^t \chi_{Ai}(r) \chi_{Bj}(r). \quad (2.5)$$

The charge density of atom A can be expressed as

$$q_A(r) = Z_A - \rho_A(r). \quad (2.6)$$

Therefore, the charge of atom A is obtained as

$$Q_A = \int q_A(r) d\tau. \quad (2.7)$$

Apparently the intrinsic difference between a real atom and a point charge lies in the fact that the charge of a real ion possesses a radial distribution, while a point charge is only a point.

Since charges on the atoms are not eigenvalues of wave functions, they are intrinsically non-measurable. In other words, charge is a theoretical construct which cannot be defined unambiguously in terms of experimental observables. In this paper, we have investigated several ways of determining the values of point charges in terms of charge consistence, dipole moment consistence, potential consistence and charge density consistence. Fig. 1 schematically presents a comparison between the attractive potential curves produced by a real ion and its equivalent point charge for the above four cases.

2.1 Charge consistence

Define charge consistence as that the point charge in surrounding S is equal to the charge on its equivalent atom in cluster C, i. e. $Q_p = Q_A$. It is derived from eq. (2.7) that $Q_p > Q_A$. Since the attractive potential produced by point charge Q_p has the form of $-\frac{Q_p}{r}$, and the attractive potential produced by atom A with charge density of $q_A(r)$ is in the form of $-\frac{q_A(r)}{r}$, the two attractive potential curves could never coincide in such a case as shown in fig. 1(a). 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 surrounding.

2.2 Dipole moment consistence

The dipole moment of a discrete set of point charges Q_p is given in classical physics by

$$\mu_S = \sum_{p \in S} Q_p r_p. \quad (2.8)$$

For a cluster having a discrete set of charges Z_a from the nuclei and a continuous charge density $\rho(r)$ from the electrons, the dipole moment is

$$\mu_C = \sum_{a \in C} Z_a r_a - \int \rho(r) \cdot r d\tau. \quad (2.9)$$

Assuming $|\mu_S| = |\mu_C|$, we will have Q_p . Again, different Q_p will induce different μ_C , we need to reach the dipole moment consistence. It should be noted that overlap densities like

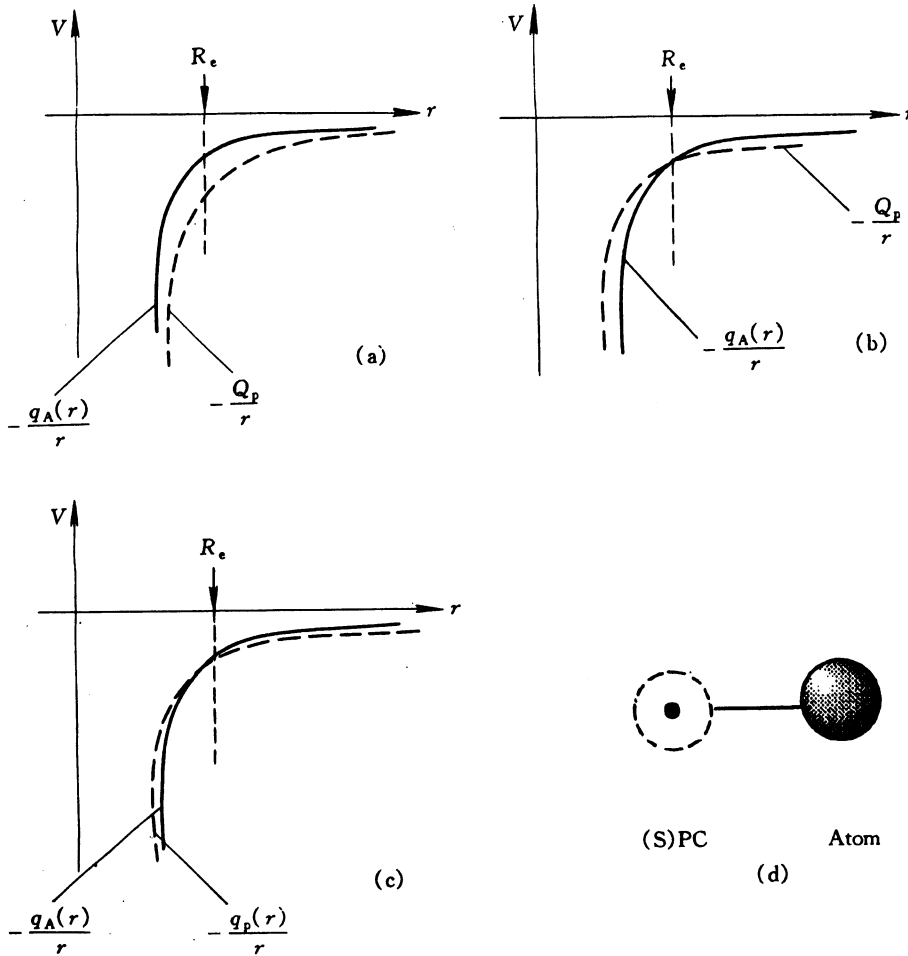


Fig. 1. Simulation of attractive potential in bulk with point charge. (a) Charge consistence: $Q_p = Q_A$; $Q_p > q_A(r)$. Dipole moment consistence: $|\mu_s| = |\mu_c|$, $Q_p > Q_A$. (b) Potential consistence: $-\frac{Q_p}{r} = -\frac{q_A(r)}{r}$ ($r = R_e$); $Q_p < Q_A$. (c) Charge density consistence: $Q_p = Q_A$; $q_p(r) \approx q_A(r)$. (d) Comparison among PC, SPC and a real atom.

$\chi_{Ai}\chi_{Aj}$ make a very important contribution to the dipole moment but no contribution to populations because $S_{Ai,Aj} = 0$. So choosing dipole moment consistence as a criterion will always encounter $Q_p > Q_A$, as shown in fig. 1(a). Therefore dipole moment consistence would also lead to an overestimation of the influence of the surrounding.

2.3 Potential consistence

Since in the cases of charge consistence and dipole moment consistence, the attractive potential produced by the point charges differs from that produced by the substrate atoms, the optimized geometry for cluster C would differ from that for surrounding S. Thereby, we have to consider potential consistence, i. e. the attractive potential produced by point charges is forced to be equal to that produced by the equivalent atoms at the equilibrium lattice position (R_e) after choosing a suitable value of Q_p . That is

$$-Q_p/r = -q_A(r)/r \quad (r = R_e). \tag{2.10}$$

Unfortunately we now have $Q_p < Q_A$. The corresponding attractive potential curves are presented in figure 1(b).

2.4 Charge density consistence

From fig. 1(b), one may notice that in the case of potential consistence, the two attractive potential curves do not coincide at non-equilibrium positions. This drawback would be attributed to the basic difference between a point charge and a real atom, i. e. a real atom possesses a continuous distribution of charge density, while a point charge does not (fig. 1(d)). We try to spherically expand the point charge, so as to furnish it with a continuous distribution of charge density. Since in principle, 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 point charge Q_p can be processed as follows.

The spherical function is

$$\varphi_s(r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}. \quad (2.11)$$

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

$$q_p(r) = Q_p(\varphi_s(r))^2, \quad (2.12)$$

$$Q_p = \int q_p(r) d\tau. \quad (2.13)$$

When $Q_p = Q_A$, comparing eq. (2.13) with eq. (2.7), we have

$$q_p(r) \approx q_A(r). \quad (2.14)$$

Since the radii of the spherical charge and the exponent α satisfy

$$\alpha = \frac{2}{\pi \langle r \rangle^2}, \quad (2.15)$$

substituting the ionic radii $\langle R \rangle$, which can be easily found in a text book, for the radii of spherical charge $\langle r \rangle$, we have

$$\alpha = B/\langle R \rangle^2. \quad (2.16)$$

Taking $\text{MgO}^{[9]}$ as an example, when $B = 1.5$, we have $\langle R_{\text{Mg}^{2+}} \rangle = 0.0844 \text{ nm}$, $\alpha_{\text{Mg}} = 0.5897$ and $\langle R_{\text{O}^{2-}} \rangle = 0.126 \text{ nm}$, $\alpha_{\text{O}} = 0.2646$.

3 *Ab initio* calculations for the embedded MgO cluster—Influence of the magnitude of point charges on the embedded cluster

MgO solid is a NaCl-type crystalline with the nearest Mg-O distance of $0.2104 \text{ nm}^{[10]}$. In the calculations, a MgO dimer was cut out from MgO lattice and was embedded into a $(10 \times 10 \times 10 - 2)$ point charge cluster (PCC). The values of the point charges Q_p 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. Table 1 presents the results of our *ab initio* RHF calculations for the embedded MgO cluster model. The results show the following points:

(1) For a free MgO molecule, the Mulliken charge on Mg atom is far smaller than 2.0 , indicating that the free MgO molecule would be quite covalent. The optimized Mg-O bond length (0.1799 nm) is far shorter than that in MgO crystal (0.2104 nm).

(2) When the MgO dimer is embedded into the electric field of PCC, the Mulliken charge of Mg increases considerably, indicating the increase of the ionicity of Mg-O bonding. Notably, the

Table 1 *ab initio* RHF calculations for the embedded MgO dimer^{a)}

Q_p	EE (a. u.)	HOMO (a. u.)	ΔG (a. u.)	Mulliken populations			μ_c /C·m	μ_s /C·m	R_{Mg-O} /nm
				Mg	O	Mg-O ^{b)}			
± 0.0	-19.106 6	-0.262	0.211	+0.748	-0.748	1.367	-21.21	-	0.210 4
	-19.645 9	-0.284	0.227	+1.021	-1.021	1.531	-28.82		0.179 9*
± 0.5	-19.746 2	-0.272	0.233	+1.301	-1.301	1.243	-51.54	16.84	0.210 4
	-20.062 5	-0.285	0.255	+1.359	-1.359	1.167	-47.67		0.186 3*
± 2.0	-21.917 8	-0.440	0.472	+1.784	-1.784	0.316	-65.84	67.41	0.210 4
	-22.223 2	-0.427	0.444	+1.820	-1.820	0.341	-90.76		0.292 6*
± 1.75	-21.546 7	-0.404	0.435	+1.750	-1.750	0.480	-65.08	59.01	0.210 4
	-21.519 0	-0.402	0.431	+1.749	-1.749	0.477	-71.05		0.232 1*
± 1.40	-21.030 8	-0.351	0.372	+1.682	-1.682	0.604	-63.41	47.20	0.210 4
	-21.029 7	-0.351	0.372	+1.682	-1.682	0.604	-63.51		0.210 7*
± 1.95	-21.843 1	-0.433	0.465	+1.778	-1.778	0.428	-65.71	65.74	0.210 4
	-22.096 1	-0.417	0.434	+1.810	-1.810	0.359	-90.03		0.291 2*
± 1.67	-21.391 6	-0.392	0.363	+1.668	-1.668	0.419	-62.78	62.81	0.210 4
	(10spc) -21.395 4	-0.393	0.365	+1.667	-1.667	0.421	-62.38		0.208 8*

a) Mg: $3s^2$, O: $2s^2 2p^4$. Basis sets: CEP-31G^[11] (calculated with Gaussian 92^[11] and Hondo8^[12]). b) Hondo8 bond order (EE, Electronic energy; ΔG , HOMO-LUMO gap; * results under optimized geometry).

electronic properties of the embedded cluster, e. g. atomic populations, total energy of electrons, energy level of the highest occupied molecular orbital (HOMO), the energy gap between HOMO and the lowest unoccupied molecular orbital (LUMO), and dipole moment, etc., show large dependence on the magnitude of the embedding point charges.

(3) When Q_p is set to be the nominal charges, ± 2.0 , owing to the overestimation of the external field, the interaction between the cluster and the lattice point charges is non-balanced. The influence of the surrounding electric field is so strong that the optimized Mg-O distance is far longer than that in crystal. However, the calculated Mulliken charges on Mg and O atoms are smaller than the nominal value 2.0.

(4) Reducing Q_p from ± 2.0 to ± 1.75 , we found that the calculated Mulliken charges of Mg and O were also ± 1.75 , meeting the requirement of charge consistence. The calculated properties of the embedded cluster only differ slightly from geometry optimization, implying that results from charge consistence are more reasonable than those from the nominal values ± 2.0 . However, the Mg-O bond stretches slightly longer upon optimization, showing that the effect of embedding electric field is still overestimated.

(5) When Q_p is chosen to be equal to ± 1.95 , the calculated dipole moment of MgO dimer is equal to that of the PCC array (65.71×10^{-30} C·m), meeting the requirement of dipole moment consistence. The calculated Mulliken charge on Mg atom is lower than the value of the point charge. Q_p is just slightly lower than the nominal value. This suggests that taking dipole moment consistence as a criterion would overemphasize the ionicity of a metal oxide.

(6) When Q_p is set to be ± 1.40 , potential consistence is encountered. The optimized Mg-O distance is in good accordance with that in MgO crystalline. But, as expected, the value of point charge is lower than the calculated Mulliken charge of the in-cluster Mg atom, i. e. $Q_p < Q_A$,

and $|Q_p| = 1.40$ is far lower than the nominal value 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 spherical expansion is performed on the nearest 10 point charges neighboring the MgO dimer, we furnish these point charges with a continuous distribution of charge density. Then when charge consistence is encountered between the embedded cluster and its surrounding, we have $|Q_p| = \pm 1.67$. The optimized geometry is in accordance with the experimental result, fulfilling the requirement of potential consistence; while the calculated dipole moment of the embedded MgO dimer is also close to that of the surrounding, reaching the dipole moment consistence. As expected, a global agreement is reached between the calculated properties of the embedded cluster and those of the bulk solid when the charge density consistence is met.

4 Conclusions

In this paper we have proposed and compared several criteria for the self-consistent determination of the magnitude of point charges employed in embedded cluster modeling of metal oxides. *Ab initio* study has been performed to show the influence of the values of point charges chosen on the calculated electronic properties of the embedded MgO cluster. The calculation results show that the electronic properties of an embedded cluster depend largely on the values of the embedding point charges; that even for MgO which is believed to be in full ionicity, the choice of nominal values will lead to the overestimation of the crystal potential, and a 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 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 spherical expansion of the point charges in the vicinity of the cut-out cluster. A good simulation of bulk solid or solid surface is encountered when charge density consistence is encountered.

We have studied several representative chemisorption systems, e. g. CO/MgO, CO/ZnO, H₂/ZnO, H₂/TiO₂ with SPC cluster model method and have investigated the effects of basis sets, electron correlation, size of cluster model, size and symmetry of point charge cluster on the theoretical description of chemisorptive bonding. Based on the findings in this paper and those presented elsewhere¹⁾, the main points of our so-called SPC cluster model can be summarized as follows: a stoichiometric cut-out cluster embedded in a symmetric PCC, and a spherically expanded point charge surrounding with charges being self-consistently determined. Our studies of chemisorption on the metal oxides of different degrees of ionicity demonstrated the efficiency of the SPC cluster model.

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