

## Cluster modeling of metal oxides: how to cut out a cluster?

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### Abstract

Three principles have been proposed for the cluster modeling of metal oxides, i.e. the neutrality principle, stoichiometry principle and coordination principle. A stoichiometric cluster model is recommended, for it possesses the correct atomic ratio of bulk solid and it automatically meets the requirement of neutrality. Particular attention has been focused on how to cut out a stoichiometric cluster which has as few dangling bonds as possible so as to fulfill the requirement of the coordination principle. A case study for the applications of these three principles to the modeling of ZnO solid has shown their efficiency in setting up a better cluster model of a given size. © 1998 Elsevier Science B.V. All rights reserved.

### 1. Introduction

Solids or solid surfaces have been analyzed in terms of cluster models for more than 30 years [1–7]. However, the situation is not so satisfactory. For the modeling of metal oxides, the models go into three groups [5–7], i.e. bare cluster model, embedded cluster model and saturated cluster model. Bare clusters are simply parts of the bulk. This procedure reduces the problem of an infinite solid to the common problem of molecules, and hence standard and well-documented *ab initio* computational methods for molecules can be used to explore the properties of solids and the chemistry on surfaces. It is clear, however, that the simulation with a bare cluster can only be justified if the structures of stable clusters

and of the bulk are similar. For more delicate calculations, it should be advantageous to embed the bare cluster into the potential produced by the rest of the bulk (i.e., embedded cluster model) or to saturate the free valencies at those sites of the bare cluster, which are not supposed to represent the real solid (i.e., saturated cluster model). It is clear, however, that a crude procedure of cutting out a cluster from the solid will create spurious electronic states at the border of the cluster, which are hard to correct in the subsequent embedding or saturation. Cutting-out a cluster suitably is a prerequisite for a good cluster modeling of a solid. It has been concluded that the cutout should be made as follows [6]: (1) a fixed number of electrons can uniquely be assigned to it; (2) a subset of CGTF (contracted Gaussian-type functions) can be attributed to it; (3) differential overlap and resonance integrals between its orbitals and those of the surroundings should be negligible.

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In this Letter, three practical rules, namely the neutrality principle, stoichiometry principle and coordination principle, are presented for a better, yet simple choice of a cluster model of a given size. The efficiency of these three principles is demonstrated by a case study of the cluster modeling of ZnO solid.

## 2. Three principles for cluster modeling

The ways of modeling depend largely on the properties of the particular system in question. Metal oxides differ significantly from each other in the properties, such as crystal structure, electronic structure, etc. This fact makes it difficult to set up unified principles for the cluster modeling of metal oxides. Fortunately, there do exist some basic rules which all metal oxides should obey. These are the neutrality principle, stoichiometry principle and coordination principle. Chemically, the coordination principle would be the most important, especially for covalent crystals. Thereby, clusters are frequently built by shells of ions around the central ion which represents the binding site. For example,  $[\text{ZnO}_4]^{6-}$  was used as a model in the simulation of bulk ZnO [8–10] and  $[\text{MgO}_5]^{8-}$  was used as a model for the 5-fold-coordinated Mg site on the MgO(001) surface [11,12]. In this way, the coordination principle will inevitably result in a charged cluster, which is not an adequate model to study chemisorption, for the unrealistic electric properties of such a charged cluster will shift artificially the energies of the frontier orbitals of the cluster and will create spurious static interactions with the adsorbate. The neutrality principle will be fulfilled with the help of hydrogen-saturation or embedding with a point charge cluster of the opposite total charge, whereas the stoichiometry principle can never be fulfilled in such a charged cluster model. The breaking-down of the stoichiometry principle will bring about some artificial DOS (density of states) of the excess atoms [13]. Thereby, we recommend choosing a stoichiometric cluster. In this way, the neutrality requirement is reached automatically. The remainder is how to minimize the edge effect of a cluster of a given size so as to fulfill the requirement of the coordination principle. In principle, the fewer dangling bonds a cluster has, the smaller the edge effect is. Consequently, a cutout cluster should

possess as few dangling bonds as possible and should maintain the strongest bonds within it. In the following section, we will take ZnO solid as an example to verify the three principles introduced above. The reason we choose ZnO solid for the case study lies in the fact that ZnO is such a partially ionic solid that the cutting-out procedure should be more severe here than when applied to a highly ionic solid in which electrons are highly localized around the nuclei. Therefore conclusions reached here would be more general.

## 3. Case study: cluster modeling of ZnO

### 3.1. Charged cluster models: $[\text{ZnO}_4]^{3q-}$ ( $3q = 6, 4, 3, 2, 0$ )

ZnO crystallizes in the hexagonal structure of the wurtzite type, in the bulk of which all Zn and O ions are coordinated with four counter-ions [14]. Therefore, the  $[\text{ZnO}_4]^{6-}$  cluster, in which the  $\text{Zn}^{2+}$  site is surrounded by its four nearest-neighbor  $\text{O}^{2-}$  anions with a local symmetry of  $C_{3v}$ , is a model frequently employed to simulate bulk ZnO [8–10]. Though the ionicity of ZnO remains unanswered [15], it is generally agreed that the real charge of Zn in bulk ZnO should be smaller than 2. Therefore, it would be inadequate to assume the full ionicity of ZnO as in  $[\text{ZnO}_4]^{6-}$ . Suppose that the valency of a Zn atom in bulk ZnO is  $+q$ , while keeping the absolute charges on Zn and O equal, i.e.  $|\text{Zn}:\text{O}| = 1:1$ , as demanded by the stoichiometry and neutrality of the solid, the  $\text{ZnO}_4$  cut-out cluster should be charged as  $[\text{ZnO}_4]^{3q-}$ . Since a different choice of  $q$  will result in a different amount of electrons in the cluster, one has to face the problem of how to determine the value of  $q$ . Moreover, in an ab initio calculation, one can only define the total amount of electrons of the whole system. There is no guarantee that the stoichiometric requirement,  $|\text{Zn}:\text{O}| = 1:1$ , is really satisfied in such a case. Table 1 presents the results of ROHF calculations for the  $[\text{ZnO}_4]^{3q-}$  cluster with a charge of  $3q = 6, 4, 3, 2$  and 0, respectively. The outcomes of these calculations could be summarized as follows:

(1) A charged, non-stoichiometric cluster is unstable as indicated by the positive value of the HOMO (highest occupied molecular orbital) level. There is a tendency to ionize.

Table 1  
ROHF calculations for  $[\text{ZnO}_4]^{3q-}$  clusters

$3q$	ROHF <sup>a</sup> (au)	HODO <sup>b</sup> (eV)	HOMO <sup>c</sup> (eV)	LUMO <sup>d</sup> (eV)	$\Delta G^e$ (eV)	Mulliken charges		
						Zn	O	Zn:O
6	-122.51742	17.42	25.15	37.70	12.55	0.28	-1.57	1:5.61
4	-124.14690	2.49	14.26	19.18	4.92	0.52	-1.13	1:2.17
3	-124.53428	-4.00	8.51	14.11	5.6	0.68	-0.92	1:1.35
2	-125.01254	-11.31	2.13	8.82	6.68	0.56	-0.64	1:1.14
0	-124.99618	-26.02	-11.08	-2.77	8.31	0.76	-0.19	1:0.25

<sup>a</sup>ROHF calculations are performed using the GAUSSIAN94 package [16]. The geometries for these clusters are taken from bulk experimental data [11]; basis set: Zn, Ar core + (3s 2p 5d)/[1s 1p 1d] [17]; O, CEP-31G [18].

<sup>b</sup>HODO refers to the highest occupied d orbital of Zn.

<sup>c</sup>Highest occupied molecular orbital.

<sup>d</sup>Lowest unoccupied molecular orbital.

<sup>e</sup> $\Delta G = |\text{LUMO} - \text{HOMO}|$ .

(2) The simple way of reducing  $q$  to zero so as to reach neutrality does not lead to a realistic model of bulk ZnO. The  $[\text{ZnO}_4]^0$  cluster possesses an over-stabilized 3d band of the Zn atom (HODO, highest occupied d orbital of Zn, -26.02 eV (calc.)) with respect to the bulk one (central of d band, -15.4 eV (expt.)) [19].

(3) As shown by the Mulliken charges, those clusters with  $q = 2$  or 0 encounter a serious drawback in reproducing the fact,  $|\text{Zn:O}| = 1:1$ ; while those clusters with  $q$  being around 1 have a  $|\text{Zn:O}|$  ratio close to 1, but their HOMOs are unreasonably positive owing to their unrealistic electric properties for the breaking-down of the neutrality principle.

### 3.2. $(\text{ZnO})_x$ ( $x = 3, 4, 5, 6, 10, 13$ )

Fig. 1 presents a set of stoichiometric  $(\text{ZnO})_x$  ( $x = 3, 4, 5, 6, 10, 13$ ) clusters, which adopt the geometry of bulk oxide [11]. As such, the clusters are simply segments of the bulk. For those larger clusters such as  $(\text{ZnO})_{13}(\text{o})$ , there are four layers. Since the third-layer atoms are directly below the second layer, and the fourth-layer ones directly below those of the first, only the first and second layers are shown in Fig. 1. The notation, 'Zn(7:0:6:0); O(0:6:0:7)', for  $(\text{ZnO})_{13}(\text{o})$  indicates the numbers of Zn and O atoms in each layer, i.e. seven Zn atoms in the first layer, six O atoms in the second layer, and so on. For a given  $x$ , there are a number of different choices for cutting out a cluster. The model should work best if the edge effect is the smallest. In a

perfect ZnO solid, every Zn or O is 4-fold coordinated. Cutting out a cluster will result in dangling bonds of 3, 2 or 1 on the border atoms of the cluster. Defining  $N_d$  as the total amount of dangling bonds of a cutout cluster, then we have  $\beta = N_d/2x$ , which is the average dangling bonds on each in-cluster atom. It is expected that for a given  $x$ , the cluster with the minimum  $N_d$  should have the smallest edge effect and should be the most stable. Along with the increase of  $x$ , there are more and more inner atoms, the corresponding  $\beta$  should decrease and the cluster should be getting more and more close to the solid. Ab initio calculations for the cluster models in Fig. 1 are in good agreement with the above expectations. The calculation results are summarized in Table 2, in which there is the RHF total energy, ZnO-unit RHF energy (i.e., RHF/ $x$ ), energy level of the HOMO and the energy gap between the HOMO and LUMO (i.e.,  $\Delta G$ ). The Mulliken charges are labeled on the respective atoms of clusters in Fig. 1.

From Table 2, it is quite clear that the topologic parameter  $N_d$  is well connected with the calculated total energy of the cluster of the same size and  $\beta$  associates well with the calculated ZnO-unit energy, which measures the relative stability of the clusters of different size. As shown by the data in Table 2, the cluster with the least dangling bonds (smallest  $N_d$ ) is the most stable (lowest total energy) among those of the same size. The largest  $\beta$  corresponds to the highest ZnO-unit energy, thereby the least stable cluster; and the smallest  $\beta$  corresponds to the lowest ZnO-unit energy, as such, the most stable cluster.

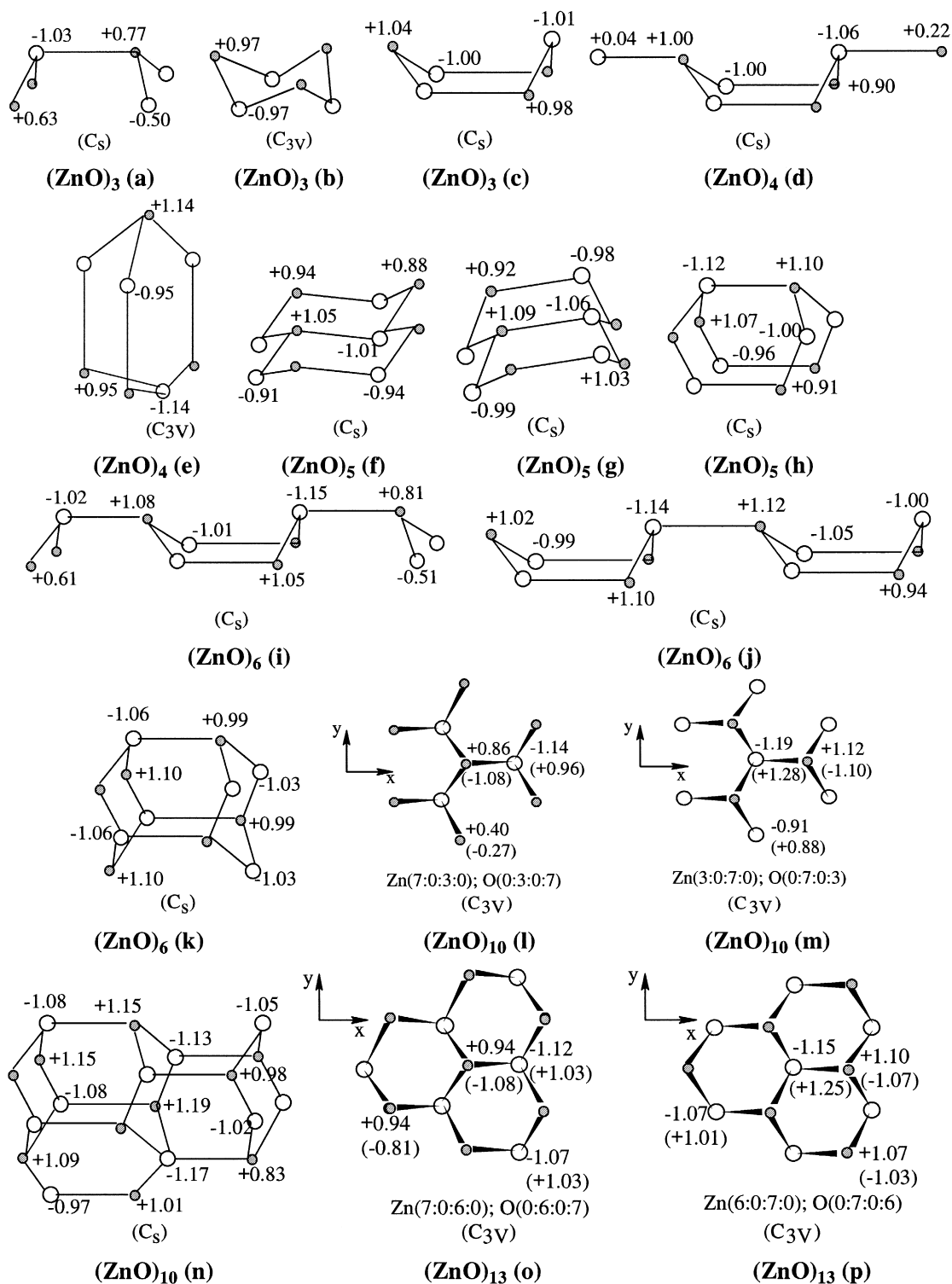


Fig. 1. Geometries of  $(\text{ZnO})_x$  cluster models (open circles, oxygen atoms; shaded circles, zinc atoms). Mulliken charges are shown on the atoms.

Table 2  
Ab initio RHF<sup>a</sup> calculations for (ZnO)<sub>x</sub> clusters

<i>x</i>		<i>N<sub>d</sub></i>	$\beta = N_d/2x$	RHF (au)	RHF/ <i>x</i> (au)	<i>E<sub>coh</sub></i> <sup>b</sup> (eV)	HOMO (eV)	$\Delta G$ <sup>c</sup> (eV)
3	a	14	2.33	−236.8208106	−78.9402702	1.591	−7.03	4.70
	b	12	2.00	−237.0258259	−79.0086086	−0.269	−9.42	9.06
	c	12	2.00	−237.0305163	−79.0101721	−0.311	−8.72	8.21
4	d	16	2.00	−315.9310569	−78.9827642	0.435	−6.44	3.89
	e	14	1.75	−316.0772598	−79.0193150	−0.560	−8.86	7.74
5	f	18	1.80	−395.0835573	−79.0167115	−0.489	−8.54	5.82
	g	18	1.80	−395.1207196	−79.0241439	−0.691	−8.45	7.17
	h	18	1.80	−395.1222968	−79.0244594	−0.700	−8.71	7.62
6	i	24	2.00	−473.9766610	−78.9961102	0.072	−6.45	4.71
	j	22	1.83	−474.1927842	−79.0321307	−0.909	−9.19	8.72
	k	18	1.50	−474.2448721	−79.0408120	−1.145	−7.29	5.36
10	l	38	1.90	−789.8244796	−78.9824480	0.443	−6.20	3.85
	m	30	1.50	−790.3876660	−79.0387666	−1.089	−8.50	6.73
	n	26	1.30	−790.6178681	−79.0617868	−1.716	−6.48	4.02
13	o	32	1.23	−1027.4239008	−79.0326077	−0.922	−6.47	3.52
	p	24	0.92	−1027.9996935	−79.0768995	−2.127	−7.61	−5.96
Bulk <sup>d</sup>							−4.68	3.3

<sup>a</sup>Zn basis set: HW/ECP Ar + [1s 1p 1d] [17]; O basis set: CEP-31G [18].

<sup>b</sup> $E_{\text{coh}} = \text{RHF}/n - E_{\text{ZnO}}^{\text{a}}$ ;  $E_{\text{ZnO}}^{\text{a}} = E_{\text{Zn}}^{\text{a}}(1\text{S}) + E_{\text{O}}^{\text{a}}(3\text{P}) = -78.9987410$  (au).

<sup>c</sup> $\Delta G = |\text{HOMO} - \text{LUMO}|$ .

<sup>d</sup>See Refs. [20–23].

Associating  $\beta$  with the ZnO-unit energy reveals that the well-known edge effect would be further divided into two effects, i.e. the size effect (dependence on the size of the cluster) and the shape effect (dependence on the shape of the cluster). The fact that the three clusters with  $x = 5$  have the same amount of dangling bonds but differ substantially with respect to their RHF energy should be attributed to the fine shape effect.

Taking the summation of the HF energies of atomic Zn(<sup>1</sup>S) and O(<sup>3</sup>P), denoted as  $E_{\text{ZnO}}^{\text{a}}$ , as a reference, we may have the cohesive energy of a cluster defined as  $E_{\text{coh}} = \text{RHF}/x - E_{\text{ZnO}}^{\text{a}}$ . The four clusters, (ZnO)<sub>3</sub>(a), (ZnO)<sub>4</sub>(d), (ZnO)<sub>6</sub>(i) and (ZnO)<sub>10</sub>(l), have ZnO-unit RHF energies higher than  $E_{\text{ZnO}}^{\text{a}}$ , indicating that these clusters are thermodynamically unstable. Inspection of the geometries of these clusters in Fig. 1 reveals that there exist 1-fold coordinated atoms in all of them. We ascribe the unstableness of these clusters to the existence of the

1-fold coordinated atoms. Mulliken charges provide another simple, yet useful tool of measuring the reliability of a cluster model. In contrast to the results from the charged cluster models  $[\text{ZnO}_4]^{3q-}$ , the Mulliken charges from the stoichiometric (ZnO)<sub>x</sub> are reasonable. The calculated absolute charges on Zn and O are approximately equal, with  $q$  close to 1.0. The fact that the Mulliken charges on the 1-fold coordinated atoms are significantly lower than those of the other atoms suggests that a cutting-out procedure, which will produce this kind of extremely low coordinated atoms, should be avoided.

The experimental value of the band gap of ZnO solid, i.e. 3.3 eV [24], could be taken as a criterion to judge the suitability of a cluster to model the solid. We notice, however, that for the clusters of a given size, the calculated energy gap ( $\Delta G$ ) for the cluster with the largest  $N_d$  is closer to the experimental value than that for the one with the smallest  $N_d$ . Detailed analysis reveals that the dangling bonds

greatly destabilize these clusters, which results in smaller  $\Delta G$ s. Therefore, the seeming agreement between the computed  $\Delta G$ s from the clusters, with lower-coordinated atoms and the experimental gap should be an artifact. In fact, the LUMO is always destabilized by the HF method, a larger  $\Delta G$  should be anticipated within Koopman's approximation.

It is of particular importance to examine the stability of the calculated data with respect to changes in the cluster size, so as to judge the reliability of the cluster models. For the cluster modeling of a metal surface, this has been a subject of intensive investigations [1,25–27]. The computed properties of clusters have been found to oscillatingly approach to those of bulk [1,25–27]. For the cluster modeling of metal oxides, there are only a few papers devoted to this problem [28,29,20]. Owing to the localized nature of electronic structures of metal oxides, it is generally assumed that converged calculation results can economically be reached with a medium-size cluster. However, Martins et al. have examined the size dependence with bare clusters of  $(\text{ZnO})_x$  ( $x = 3, 4, 5, 6$ ) [20] and found that the HOMO – LUMO gap and the HOMO energy oscillate with the cluster size [20]. In fact, it is hard to draw a clear conclusion from the data in Table 2, if the shapes of the clusters were chosen arbitrarily.

On the other hand, we now have a set of clusters,  $(\text{ZnO})_3$ (c),  $(\text{ZnO})_4$ (e),  $(\text{ZnO})_5$ (h),  $(\text{ZnO})_6$ (k) and  $(\text{ZnO})_{10}$ (n), which are the most stable ones of each given size. We believe that this set of clusters provide a more suitable starting-point to study the cluster-size dependence of the computed properties, since the shape effects are now under control. It is interesting to compare our results with those found by Martins et al. [20]. Their cluster models  $(\text{ZnO})_x$  ( $x = 3, 4, 5, 6$ ) are in the same geometrics as those labeled (c), (d), (f) and (i) in Fig. 1, which are not all the most stable clusters of a given size. Therefore, the quite strong oscillation observed by them should be regarded as a mixture of size effect and shape effect. Our calculated electronic properties of bare  $(\text{ZnO})_x$  ( $x = 3–13$ ) are summarized in Table 2. As it is expected, the electronic properties, such as band gap and work function values, calculated for small clusters are larger than the experimental bulk values [21–23]. Examining the data for the most stable clusters of different sizes, however, we only see a

mild size dependence for the calculated the HOMO – LUMO energy gap and the HOMO energy. These properties tend to approach smoothly to the corresponding bulk values, i.e. band-gap of 3.3 eV [24] and work function of 4.68 eV [23], with increasing cluster size.

Finding a cluster which has the minimal value of  $\beta$  would be nontrivial. We suspect that for the case of  $x = 13$ , the cluster  $(\text{ZnO})_{13}$ (p) may not have the minimal  $\beta$  and that is why the behavior of cluster  $(\text{ZnO})_{13}$ (p) is somewhat out of the expectation. A program which makes use of graph theory to search for a cluster with the minimal  $\beta$  in a given size is in construction [30]. Furthermore, it should be noted that a good cluster model should preserve the local symmetry of the active sites and should maintain the strongest bonds within it.

Fig. 2 presents the DOS of these most stable

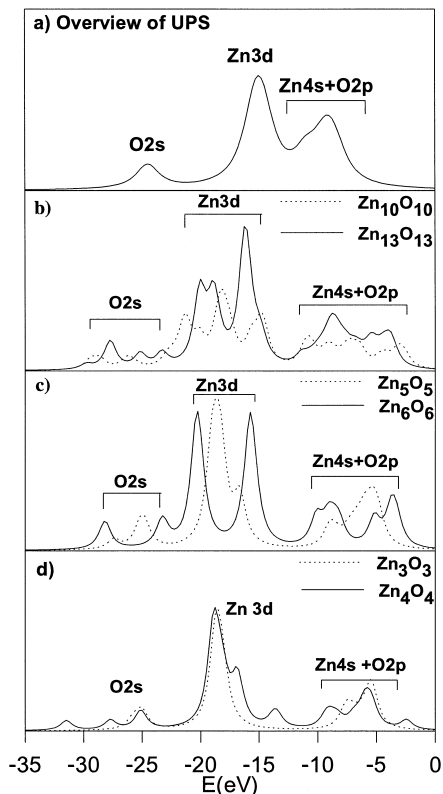


Fig. 2. Comparison between DOS of  $(\text{ZnO})_x$  clusters and UPS data of ZnO solid: (a) overview of the experimental UPS [20,21] ( $E_f = 0$  eV); (b–d) DOS of  $(\text{ZnO})_x$  clusters. The orbital energy is relative to  $-4.0$  eV.

clusters, which are obtained by performing a Lorentz expansion for the distinctively discrete MOs of the molecular clusters. An overview of the UPS spectra for the ZnO solid is also included for comparison (assuming Koopman's theorem). The experimental spectra [21] can be divided into three main peaks: the first peak between 0.0 and  $\sim -8.5$  eV below the valence-band edge is due to emission from the Zn(4s) and O(2p) derived orbitals; the second, the most intense peak from  $\sim -8.5$  to  $\sim -11.5$  eV is due to the Zn(3d) levels; and the third peak at around  $-20.0$  eV is due to the O(2s) band [22]. Fig. 2 schematically demonstrates that the electronic structures of those molecular clusters are in qualitative accordance with that of the bulk solid. The difference in the fine structures of the DOS represent the more or less edge effects while small bare clusters are employed to simulate the solid. Saturation or embedding is important for a partially covalent oxide like ZnO. In fact, in the cluster model study of heterolytic adsorption of  $H_2$  on the ZnO(10 $\bar{1}$ 0) surface, the bare clusters chosen in this way are found to be able to qualitatively predict the surface reactivity. Embedding is vital for a quantitative description of the reaction energy [31].

Similar investigation has been performed on the cluster modeling of MgO solid with  $(MgO)_x$  ( $x = 2-16$ ) [32]. The calculation results are in much better agreement with the expectation from  $N_d$  or  $\beta$  than those in the ZnO case. The electronic as well as the adsorptive properties which emerged from the cluster models with minimal  $\beta$  in the MgO case are much less size dependent than those in the ZnO case. The reasons should be that MgO solid is more ionic and symmetric than bulk ZnO, thereby the cutting out is less severe in the MgO case.

We believe that the outcomes derived from cluster modeling of metal oxides bulk solid should hold true for the modeling of surfaces, only one should take into consideration the intrinsic dangling bonds on the surface atoms. Moreover, in the case that two clusters of a given size have the same amount of dangling bonds, the one possessing more surface atoms should be preferred. One may even go into the details to count dangling bonds on metal cation or oxygen separately. Indeed dangling bonds on O would influence the properties of the clusters to a greater extent than dangling bonds on metal cation,

since O is negatively charged with orbitals lying higher. We believe that the topologic parameters  $N_d$  and  $\beta$  provide meaningful criteria to cut out a better cluster model, without paying for the high cost of detailed preliminary calculations. A good cut-out cluster is not only itself a good bare cluster model, but also a suitable starting-point for embedding or saturation.

#### 4. Conclusions

In the cluster modeling of metal oxides, there exist three principles which we should consciously follow. They are the neutrality principle, stoichiometric principle and coordination principle. Owing to the infinite structure of a solid, it is impossible to cut out a cluster which fulfills the requirements of all these three principles. We have to sacrifice one for the other according to the nature of solid. We recommend choosing a stoichiometric cluster which offers a correct ratio of anion vs. cation and meets the requirement of neutrality. In this Letter, attention has been focused on how to cut out a stoichiometric cluster which has a few dangling bonds as possible. We have shown the good correlation between the topologic parameters  $N_d$  and  $\beta$  with the stability of clusters and provide an efficient way to set up a better cluster model of a given size.

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