

Theoretical studies of nickel clusters and chemisorption of hydrogen

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First principles calculations of high- and low-symmetry clusters (up to Ni₈₇) are reported. Macroscopic properties [ionization potential (IP), electron affinity (EA), and bandwidth] are not sensitive to cluster symmetry and, except for EA, are converged to bulk values by Ni₈₇. Even for Ni₈₇ the EA is over 2.5 eV smaller than the IP; the origin of this effect is discussed. The chemisorption of hydrogen is considered on the low-symmetry clusters, where it is found that threefold and fourfold sites are most favored with bond energies of ~3 eV for both types of sites. Geometries are not cluster sensitive with $R(\text{NiH})$ values of 1.57, 1.62, and 1.78 Å for twofold, threefold, and fourfold sites, respectively. Vibrational frequencies for these sites are 1420, 1212, and 592 cm⁻¹, respectively.

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INTRODUCTION

Recent improvements in methods of creating and characterizing supported catalysts have led to a new role for theoretical investigations of the electronic properties of metal clusters. In addition to their usefulness as models for chemisorption processes on infinite metal surfaces, such studies can contribute to the elucidation of properties of highly dispersed metal clusters. In this paper we first examine and compare the properties of several clusters of nickel atoms, ranging from Ni₁₃ to Ni₈₇. Our emphasis is on the convergence of surface-related properties to the bulk limit, with the intention (a) of determining conditions (i.e., type of adsorbate, property to be modelled, etc.) under which a finite cluster may model the infinite system, and (b) of finding useful criteria for designing a cluster to better mimic the semiinfinite system. In the final section of this paper we use some of these clusters to analyze in detail the chemisorption of atomic hydrogen on nickel.

CALCULATIONAL DETAILS

The ability to economically apply *ab initio* methods to clusters as large as Ni₈₇ results from a fundamental simplifying approximation based on earlier work. In particular, we found that the lower electronic states of Ni₂^{1,2} and Ni₈² have a localized 3d⁹ configuration on each Ni atom, with the remaining electrons in delocalized (conduction band) orbitals dominated by the 4s-like component on each Ni atom. The 3d band spectrum and orbital character are nearly independent of the conduction band occupation and, in fact, these orbitals are of only minor importance in the bonding. These findings suggest a simplification in which the conduction band is studied separately from the 3d bands. To avoid bias towards a particular 3d⁹ configuration on each atom, we averaged over

the five possible 3d⁹ spatial configurations. To retain the effect of this 3d⁹ field without having to treat these orbitals explicitly, we replaced the 3d⁹ field with an effective potential.³ This reduces the conduction band problem to one electron per Ni atom, allowing a significant truncation in the basis set required, and an enormous increase in the size of the clusters that can be economically considered. For a given Ni_n cluster in this description, all orbitals were solved for self-consistently (Hartree-Fock) for a number of states of the neutral, positive ion, and negative ion systems. Since most states possessed open shell orbitals, it was necessary to use the proper variational technique⁴ to ensure that each state was a correct spin eigenfunction.

Two different systematic schemes were used to select clusters. Cubic clusters (*O_h* symmetry) were formed by selecting an atom of the face-centered-cubic (fcc) Ni structure (2.487 Å bond distance⁵) and taking the first *k* shells of atoms surrounding a central atom. Here we report the first six cases (*k* = 1-6), numbering 13, 19, 43, 55, 79, and 87 atoms. Two clusters of lower symmetry, *D_{2h}*, were obtained by selecting two adjacent atoms of the fcc structure and surrounding each of them simultaneously with *k* shells of atoms in the same manner as above. The first two such clusters, Ni₂₀ and Ni₂₈ are considered here.

As a test of the validity of the use of averaged atom 3d⁹ potentials, we solved for the optimum bond length for the Ni₁₃ cluster. The computed minimum is at 2.41 Å, in reasonable agreement with the bulk value of 2.487 Å, suggesting that this one-electron description includes the dominant bonding interactions between atoms.

WORK FUNCTION AND ELECTRON AFFINITY

Both the IP and EA are of considerable importance in chemisorption and we summarize these properties for the

TABLE I. Comparison of calculated cluster properties. All energies are in eV.

	Number of shells	Number of atoms	Multiplicity of ground state	Ionization potential ^a		Bandwidth		Electron affinity	
				DZ ^b SCF (KT)	DZ + P ^b SCF (KT)	DZ ^b SCF	DZ + P ^b SCF	DZ ^b SCF	DZ + P ^b SCF
<i>O_h</i>	0	1	2	7.63 (7.63)	7.63 (7.63)	—	—	—	—
	1	13	2	6.18 (6.39)	4.76 (5.14)	12.6	10.5	2.62	1.28
	2	19	2	7.45 (7.67)	4.99 (5.36)	12.5	11.3	3.49	1.60
	3	43	4	5.10 (5.19)		15.4		2.07	
	4	55	6	5.52 (5.68)		16.5		2.91	
	5	79	4	5.92 (5.76)		16.1		3.16	
	6	87	2	4.86 (5.05)		16.3		2.75	
∞	∞		5.2 ^c	5.2 ^c	—		5.2 ^c	5.2 ^c	
<i>D_{2h}</i>	1	20	3	5.88 (5.77)	4.25 (4.68)	14.3	11.9	2.28	0.81
	2	28	1	5.63 (5.74)		14.6		2.61	
	∞	∞		5.2 ^c	5.2 ^c	—		5.2 ^c	5.2 ^c

^aValues in parentheses are from Koopman's Theorem. Values not in parentheses are from Hartree-Fock calculations on both neutral and ion states.

^bDZ (double zeta) results are for basis sets with two *s*-like contracted functions per center; DZ + P results are for basis sets consisting of the DZ basis augmented with a single *p*-like Gaussian in each direction on each center (basis set used in Ref. 3).

^cReference 10.

eight clusters in Table I. Koopman's Theorem (KT) and self-consistent values for each property are listed for comparison. The KT values are obtained as orbital energies from calculations on the ground state and as such they ignore contributions due to electron correlation in both neutral and ion states, and orbital contractions occurring in the ion. Accuracy of these values depends in general on the degree to which the correlation error (a bias towards the ion state) cancels the orbital shape error (a bias towards the neutral). As these values are quite close to the Hartree-Fock values listed (which include only orbital contraction), both sources of error in the KT results are apparently quite small.

The convergence of IP values towards the bulk work function of 5.2 eV⁶ is not monotonic, but for $N \geq 43$, it is within 0.5 eV of this value. The EA on the other hand, is still 2.5 eV smaller than the bulk value, even for $N = 87$! The reason for this may be seen by examining the energy expressions for the EA and IP of each system. For a neutral doublet state, in which only orbital *o* is singly-occupied, the IP and EA (of orbital *o*) differ by:

$$IP - EA = J_{oo} \quad (1)$$

where J_{oo} is the Coulomb interaction between the two electrons of orbital *o* (self-energy) in the anion. For a neutral state with *m* singly occupied orbitals in addition to *o*, Eq. (1) becomes

$$IP - EA = J_{oo} + \sum_{n=1}^m K_{no}$$

where K_{no} are exchange integrals ($K_{no} \leq 0.01$ hartrees). In this sum, the dominant term is J_{oo} , the self-energy for orbital *o*. In Table II, we see that J_{oo} is within 0.2 eV of the calculated (self-consistent) IP - EA for various clusters. For these Ni clusters, we find that $J_{oo}(\text{eV}) \approx 14.4/R(\text{\AA})$ for orbitals near the fermi energy. Thus, for a cluster of radius *R*, we expect:

$$IP - EA = 14.4/R(\text{\AA})$$

and consequently the convergence is slow. For a cluster of

1146 atoms ($R = 14.4 \text{\AA}$), the EA - IP is 1 eV, and to obtain an IP - EA of 0.1 eV, a cluster of 144 \AA radius or almost 10^6 atoms is needed.

The significance of these results for chemisorption is as follows. For electronegative adsorbates (e.g., H, CH₃, OH) the charge transfer is away from the cluster and hence it is the IP of the cluster that is relevant in determining bond energy. On the other hand, for electropositive adsorbates (such as Na, K, Li) the charge transfer should be towards the bulk and hence the EA is more relevant in determining bond energy. Since the cluster electron affinity is significantly less than that of the bulk, we would expect bond energies of electropositive species to be less on small aggregates than on the bulk surface. Electronegative species may well behave the same in both systems. Note that these results are *not* theoretical artifacts, the difference between IP and EA arises from the non-vanishing value of the self-energy and should be experimentally observable.⁷ It has been suggested⁸ that electron tunnelling spectroscopy could provide a direct test of these predictions. Metal drops of $\sim 50 \text{\AA}$ would allow determination of the threshold for successive charge transfer to each drop.

SURFACE ELECTRON DENSITY

A property of interest both for understanding the surface properties of bulk metals and of clusters is the calculated surface electron density. In Fig. 1 we show electron populations as a function of shell radius for the largest cubic clusters, $N = 55, 79$, and 87 atoms. Two factors appear to control the surface density in these clusters:

TABLE II. Convergence of IP - EA with cluster size.

Cluster	Neutral state	$J_{oo}(\text{eV})$	IP - EA (eV)	$14.4/R(\text{eV})$
Ni ₁₉	² A ₁	3.96	3.71	4.09
Ni ₄₃	² T _{2g}	3.09	2.99	3.34
Ni ₅₅	² T _{1g}	2.92	2.75	2.90

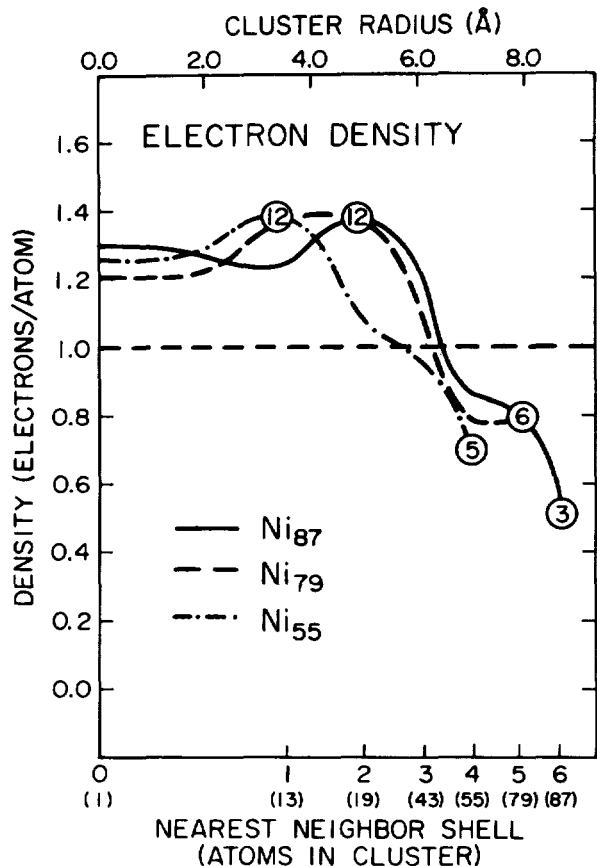


FIG. 1. Electron density per atom for the three largest cubic clusters, plotted as a function of nearest neighbor shell. The outermost shells possessing full coordination of 12 atoms are indicated (note that this point coincides for Ni_{79} and Ni_{87}) as well as the coordination of the "surface" layer atoms. Horizontal dashed line represents the average bulk density.

(i) As the number of shells possessing full coordination (12 nearest neighbors for a bulk fcc atom) increases, the fluctuations in electron density as a function of radius are reduced.

(ii) Absolute cluster size does not fully determine surface density as indicated by the Ni_{79} and Ni_{87} results. The coordination number of the surface atoms is of considerable importance in determining the magnitude of the density of electrons at the surface.

The implications of these results for the bulk are as follows.

(i) Surface atoms should be electron deficient with the deficiency largest for least dense (high index) surfaces.

(ii) The outermost layer with complete coordination has a higher density than either the surface or the deeper bulk atoms, resulting in density reminiscent of Friedel oscillations. This may result in other properties fluctuating in this region. For example, the interlayer spacing may be larger than the bulk value in the outermost layers but slightly smaller in layers below the surface. Similarly, interstitials may concentrate in different surface layers depending on their electrophilic (or nucleophilic) character.

(iii) Corner atoms at steps or kinks have low coordination and should be particularly electron deficient and thus reactive towards nucleophiles.⁹

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CONDUCTION BAND DENSITY OF STATES

In studies of the chemisorption of H, S, and O on small (<10 atoms) metal clusters we have found that these "covalent bonded"¹⁰ adsorbates interact with band orbitals of widely differing energies, all having density in the adsorbate bond region. It would appear that an ideal cluster for studying these species should possess an evenly distributed density of states.

In Fig. 2 we show an approximate density of states for each of the clusters, composed of (occupied) orbital energies of the cluster ground states. Distinctly different trends occur for the cubic and the non-cubic cluster series. For each series, there is an increase in density near the Fermi level in agreement with nearly free electron band theory, however for almost all cubic clusters, the spectrum is very discontinuous. The high symmetry causes a bunching of degenerate levels, making the smaller cubic clusters possibly unacceptable as models for chemisorption. The D_{2h} clusters on the other hand are non-degenerate and even Ni_{20} shows a more uniform density of states than a 55-atom cubic cluster. This suggests using spheroidal clusters of D_{2h} symmetry (breaking all degeneracies but retaining enough symmetry to simplify the calculation).

APPLICATION: H ON Ni_{20} AND Ni_{28}

As was mentioned in the previous section, a cluster with an evenly distributed density of states is important when modelling the chemisorption of atomic hydrogen. The Ni_{20} and Ni_{28} noncubic clusters are the smallest of the eight discussed here that meet this criterion. Both clusters also yield accurate IP values, a property of importance for modelling adsorption of such an electronegative species. The Ni_{20} cluster has sites representative of (100), (110), and (111) planes, while the Ni_{28} cluster is entirely composed of (111) planes, and has slightly higher coordination of the surface atoms. Most chemisorption sites of interest on the low-index planes are represented on each cluster, allowing a single cluster to be used to compare

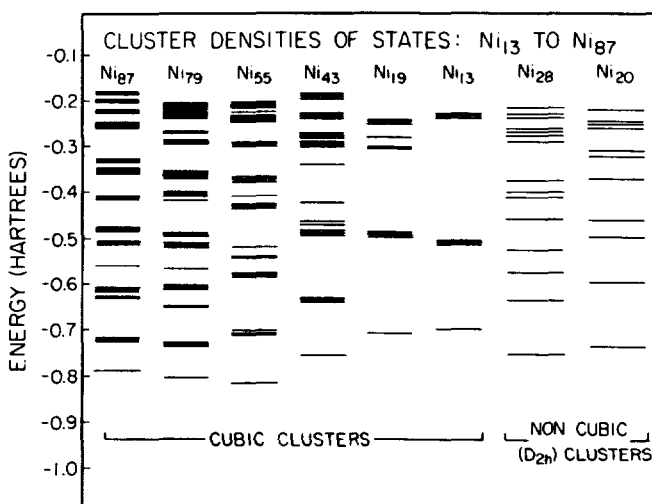


FIG. 2. Approximate densities of states for both cubic and D_{2h} clusters. Levels are obtained as orbital energies from Hartree-Fock calculations. Degenerate levels have been plotted as multiplets to indicate actual state density. Only occupied states are shown.

TABLE III. Bond parameters for H binding sites.

Cluster	Site	Description			Bond length (Å)		Vibrational frequency		Chemisorption energy	
		Surface	Ligancy of H	Ligancy of surface Ni atoms ^a	R_{\perp} ^b	$R_{(\text{NiH})}$ ^c	(cm^{-1})	(meV)	(kcal)	(eV)
Ni ₂₀	B	[001]	1	7	1.50	1.50	2286	283	36	1.56
	F	[110]	1	5	1.49	1.50	2262	280	33	1.43
	C	[112]	1	7	1.49	1.49	(1864)	(231)	(23)	(1.00)
	A	[001]	2	7,7	0.99	1.59	1428	177	63	2.73
		[001] with 3d electrons	2	7,7	1.03	1.61	1503	186	66	2.86
	G	[001]	2	5,5	0.99	1.59	(1393)	(173)	(50)	(2.17)
	E	[110]	2	6,6	0.93	1.55	(1300)	(161)	(36)	(1.56)
	H	[112]	2	5,5	0.96	1.57	1419	176	54	2.43
	I	[111]	3	5,5,5	0.78	1.63	1248	155	74	3.21
	D	[111]	3	7,6,6	0.79	1.64	(1057)	(131)	(49)	(2.12)
J	[001]	4	5,7,7,5	0.30	1.78	592	73	70	3.04	
Ni ₂₈	K	[001]	2	5,5	0.94	1.56	1332	165	51	2.23
	L	[111]	2	7,7	0.93	1.55	1419	176	57	2.47
	E	[110]	2	7,7	0.95	1.57	(1278)	(158)	(30)	(1.31)
	M	[111]	3	5,5,9	0.72	1.61	(1185)	(147)	(52)	(2.25)
	D	[111]	3	9,7,7	0.69	1.59	(1269)	(157)	(49)	(2.11)
	N	[111]	3	5,7,7	0.79	1.64	1216	151	72	3.14
	I	[111]	3	7,7,7	0.73	1.61	1172	145	63	2.75

^aNumber of nearest neighbor atoms for the Ni atoms(s) at the binding site. Where nonequivalent surface atoms are present, values are given for each type.

^bOptimum distance from H to the plane representing the surface.

^cOptimum distance from H to atoms at site.

bond energies at different sites. In addition, since the two clusters have sites in common, the effect of increasing cluster size may be monitored.

In Table III we have assembled bond properties for each of the sites considered on both clusters. In addition, we present results for one site on Ni₂₀ in which all valence electrons (4s¹3d⁹) were included on four Ni atoms surrounding the bonding site.

The salient features in this table are as follows.

(i) The effect of the 3d electrons on the adsorbate bond is minor. Each parameter is affected by, at most, ~5%, lending support to the idea that bonding properties in Ni are determined by the 4s electrons.

(ii) For both clusters, bond energies increase with ligancy of the H atom. For both clusters, the largest bond energies (D_e) are for threefold (111) and fourfold (100) sites, with average bond energies of 3.03 and 3.04 eV, respectively.

(iii) Geometric parameters are not cluster sensitive, as different R(NiH) values for a given site vary by no more than ± 0.05 Å. Average values for twofold, threefold, and fourfold sites are 1.57, 1.62, and 1.78 Å, respectively.

(iv) Vibrational frequencies are also insensitive to cluster size, but serve as "fingerprints" for different types of sites as frequencies vary from 2275 and 1420 cm^{-1} to 1212 and 592 cm^{-1} for onefold, twofold, threefold, and fourfold sites, respectively.

To illustrate the importance of a continuous band spectrum, we show in Fig. 3 how the Ni₂₈ spectrum is modified by the presence of the H atom at various sites (the sites represented in the figure are adjacent on the cluster face). By taking the overlap of each Ni₂₈H orbital with the original Ni₂₈ orbitals,

we can relate the spectrum at each site to that of a neighboring site and also to that of the Ni₂₈. In all cases, the overlap was very high, and the Ni part of each Ni₂₈H orbital may be expressed almost exactly (99+%) as a linear combination of the original Ni₂₈ orbitals.¹¹

Two very important modifications are noticeable in the figure. At each site, a new level appears near $-0.5 h$ and a high-lying cluster level is pushed above the Fermi level (i.e. unoccupied). The new level is found to have predominantly H character (>50%), while the destabilized level is always the highest level with large density in the bonding region.

The interaction of the remaining orbitals is also of interest. At each site, certain of the levels are excluded by symmetry from interacting with the H atom and these are indicated in the figure by heavy dashed lines. For the most part, these levels are not affected by the H atom. The remaining levels are "pushed away" from the new H level in order to remain orthogonal.

Qualitatively, very similar results are obtained on applying this analysis to the Ni₂₀ spectrum.¹² The principal difference lies in the position of the new H level. For the smaller cluster, the position of this level is not so invariant, ranging from less than 0.5 h to over 0.6 h. The reason for this is seen by comparing the density of states for both clusters in the 0.4–0.6 h range (Fig. 2). The Ni₂₈ cluster has essentially twice as many levels with which the H atom may interact, and thus the position of the H level is less constrained.

That both clusters do not fully mimic the bulk is indicated by the behavior of levels near the Fermi energy. In Fig. 3, it is the second highest Ni₂₈ levels that are destabilized at sites N and L. For both sites K and I, a deeper doubly occupied

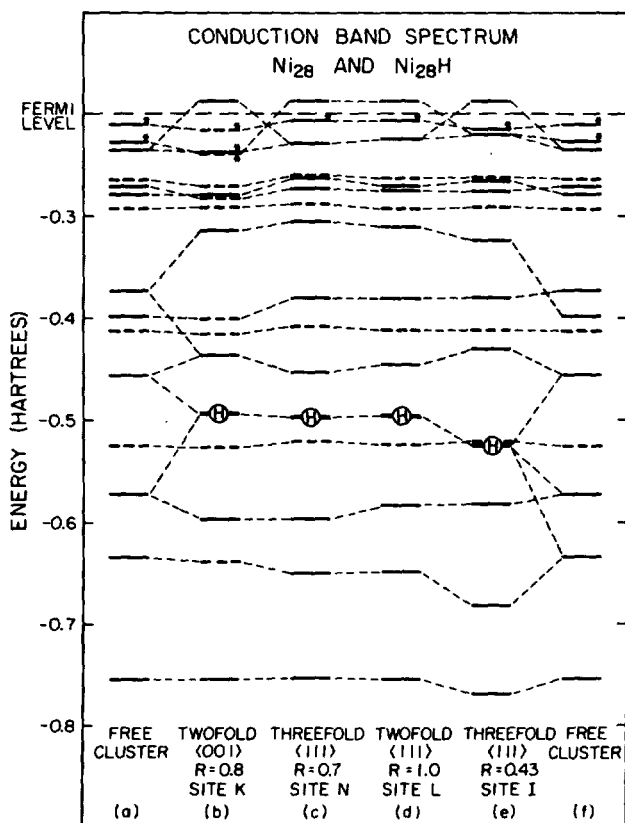


FIG. 3. Spectrum of states for Ni_{28} and $Ni_{28}H$ clusters. Levels connected by light dashed lines are of similar orbital character. The H on a level indicates the orbital with maximum H character. Dashed levels are for orbitals unable to interact with the H atom by symmetry. The location of the "Fermi level" is arbitrary and is used only to differentiate between occupied and unoccupied orbitals. Asterisks indicate singly occupied orbital levels.

orbital is forced to give up an electron. For site K this produces a quartet state, while at site I, two of these single-occupied orbitals collapse to form a net doublet. Thus, cluster "bonds" must be broken to accommodate the H at these sites. This occurrence is reflected in part by the smaller binding energy at sites K and I than at nearly equivalent sites L and N. Similar, but more drastic, excitations lead to weaker binding energies at the other Ni_{28} threefold sites. These sites, along with sites on Ni_{20} that are similarly affected, are listed in parentheses in Table III.

In comparing with experimental results we find the following.

(i) UPS studies of H on $Ni(111)^{13,14}$ and $Ni(110)^{14}$ indicate a single broad level appears at about 6 eV below the Fermi level. Our studies on Ni_{28} place this level at about 7 eV and suggest that its position should not change significantly at different sites.

(ii) Very little ir or HRELS data is available for chemisorbed H. The observed value for H on (100) Ni is 75 meV,¹⁵ in excellent agreement with the value (73 meV) we predict for fourfold binding on this plane.

(iii) Work function measurements detect a small (0.1–0.2 eV) increase in the work function for the low index faces upon adsorption of H_2 .¹⁶ Qualitatively, this is in agreement with results presented here which indicate destabilization of the highest levels.

(iv) Binding energies have been measured for each low index face and are essentially invariant at ~ 2.75 eV per H atom.^{16,17} Our present Ni_{20} and Ni_{28} values predict slightly higher values, and suggest that fourfold and threefold sites should give very comparable binding energies.

(v) Very little structural data for H on Ni is available. Small clusters have been generated, however, possessing bulklike sites. The complex $H_3Ni_4(\eta^5-C_5H_5)_4$ possesses threefold sites for which an $R(NiH)$ value of 1.69 Å has been found,¹⁸ in reasonable agreement with our value of 1.64 Å.

(vi) Recently, Himpsel and Eastman¹⁹ have observed an $sp(A_1)$ surface state on $Ni(111)$ whose photoemission is attenuated on adsorption of O and H. Such an observation is more consistent with the band structure behavior predicted here from 4s–H bonding than usual models of H–3d bonding.²⁰

CONCLUSION

In summary, we find that large clusters can mimic certain bulk properties, but that for modelling chemisorption size alone is not a useful criterion for choosing a model. For electropositive (electron donating) adsorbates, even very large clusters may be inadequate. On the other hand, a relatively small cluster of 20 atoms is useful for studying the bonding of an electronegative adsorbate. For hydrogen, increased cluster size seems important only from the standpoint of providing a more continuous state density. This would perhaps provide a more accurate placement of the "H" level and avoid sites with unusually weak bonds (due to promoting the electron out of a deep orbital). Geometric parameters and basic qualitative features of the bonding process are not greatly affected by cluster size, and thus, it appears possible that this treatment may be extended to a variety of systems where such data are of fundamental significance.

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