Theoretical studies of nickel clusters and chemisorption of hydrogen

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First principles calculations of high- and low-symmetry clusters (up to Ni$_{14}$) 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 Ni$_{14}$. Even for Ni$_{10}$ 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 $R$(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 Ni$_{13}$ to Ni$_{17}$. Our emphasis is on the convergence of surfacel-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 semi-infinite 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 Ni$_{14}$ results from a fundamental simplifying approximation based on earlier work. In particular, we found that the lower electronic states of Ni$_{12}$ and Ni$_{13}$ have a localized 3d$^8$ 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 3d$^8$ configuration on each atom, we averaged over the five possible 3d$^8$ spatial configurations. To retain the effect of this 3d$^8$ field without having to treat these orbitals explicitly, we replaced the 3d$^8$ field with an effective potential. 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 technique 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 distance) 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, 45, 55, 79, and 87 atoms. Two clusters of lower symmetry, D$_{4h}$, 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, Ni$_{59}$ and Ni$_{94}$, are considered here.

As a test of the validity of the use of averaged atom 3d$^8$ potentials, we solved for the optimum bond length for the Ni$_{13}$ 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.

<table>
<thead>
<tr>
<th>Number of shells</th>
<th>Number of atoms</th>
<th>Multiplicity</th>
<th>Ionization potential*</th>
<th>Bandwidth</th>
<th>Electron affinity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>DZ(^b) SCF (KT)</td>
<td>DZ + P(^b) SCF (KT)</td>
<td>DZ(^b) SCF</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>6.73 (7.63)</td>
<td>4.76 (5.14)</td>
<td>2.62 1.28</td>
</tr>
<tr>
<td>1</td>
<td>13</td>
<td>2</td>
<td>6.18 (6.39)</td>
<td>4.99 (5.36)</td>
<td>1.25 1.13</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
<td>2</td>
<td>4.75 (5.67)</td>
<td>12.6</td>
<td>10.5 3.49</td>
</tr>
<tr>
<td>3</td>
<td>43</td>
<td>4</td>
<td>5.10 (5.19)</td>
<td>15.4</td>
<td>2.07</td>
</tr>
<tr>
<td>4</td>
<td>55</td>
<td>6</td>
<td>5.52 (5.68)</td>
<td>16.5</td>
<td>2.91</td>
</tr>
<tr>
<td>5</td>
<td>79</td>
<td>4</td>
<td>5.92 (5.76)</td>
<td>16.1</td>
<td>3.16</td>
</tr>
<tr>
<td>6</td>
<td>87</td>
<td>2</td>
<td>4.86 (5.05)</td>
<td>16.3</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.2(^a)</td>
<td>5.2(^a)</td>
<td>5.2(^a)</td>
</tr>
</tbody>
</table>

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

\(^b\)DZ (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).

Reference 10.

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eight clusters in Table I. Koopmans' 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 eV 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:

\[
\text{IP} - \text{EA} = J_{oo}
\]

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

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

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 \( J_{oo}(eV) = 4.4/R(\text{Å}) \) for orbitals near the Fermi energy. Thus, for a cluster of radius \( R \), we expect:

\[
\text{IP} - \text{EA} = 14.4/R(\text{Å})
\]

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

The significance of these results for chemisorption is as follows. For electronegative adsorbates (e.g., H, CH\(_3\), 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.\(^a\) It has been suggested\(^b\) that electron tunnelling spectroscopy could provide a direct test of these predictions. Metal drops of ~50 Å 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.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Neutral state</th>
<th>IP - EA (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(_{10})</td>
<td>( 3.74 )</td>
<td>3.96</td>
</tr>
<tr>
<td>Ni(_{12})</td>
<td>( 3.74 )</td>
<td>3.09</td>
</tr>
<tr>
<td>Ni(_{15})</td>
<td>( 3.74 )</td>
<td>2.92</td>
</tr>
</tbody>
</table>
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" 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_{5h} clusters on the other hand are non-degenerate and even N_{19} shows a more uniform density of states than a 55-atom cubic cluster. This suggests using spheroidal clusters of D_{5h} symmetry (breaking all degeneracies but retaining enough symmetry to simplify the calculation).

APPLICATION: H ON N_{20} AND N_{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 N_{19} and N_{20} on cubic 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 N_{19} cluster has sites representative of (100), (110), and (111) planes, while the N_{20} 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

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<table>
<thead>
<tr>
<th>Cluster</th>
<th>Site</th>
<th>Surface</th>
<th>Ligancy of H</th>
<th>Ligancy of surface Ni atoms</th>
<th>Bond length (Å)</th>
<th>Vibrational frequency (cm⁻¹)</th>
<th>Chemisorption energy (meV, kcal, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>[001]</td>
<td>1</td>
<td>7</td>
<td></td>
<td>1.50</td>
<td>1.50</td>
<td>2286, 283, 36, 1.56</td>
</tr>
<tr>
<td>F</td>
<td>[110]</td>
<td>1</td>
<td>5</td>
<td></td>
<td>1.49</td>
<td>1.50</td>
<td>2262, 280, 33, 1.43</td>
</tr>
<tr>
<td>C</td>
<td>[112]</td>
<td>1</td>
<td>7</td>
<td></td>
<td>1.49</td>
<td>1.49</td>
<td>(1644), (231), (23), (1.00)</td>
</tr>
<tr>
<td>A</td>
<td>[001]</td>
<td>2</td>
<td>7.7</td>
<td></td>
<td>0.99</td>
<td>1.59</td>
<td>1428, 177, 63, 2.73</td>
</tr>
<tr>
<td>Ni₉₀</td>
<td>G</td>
<td>[001]</td>
<td>2</td>
<td>5.5</td>
<td>0.99</td>
<td>1.59</td>
<td>(1393) (7), (173), (50)</td>
</tr>
<tr>
<td>E</td>
<td>[110]</td>
<td>2</td>
<td>6.6</td>
<td></td>
<td>0.93</td>
<td>1.55</td>
<td>(1300), (161), (36)</td>
</tr>
<tr>
<td>H</td>
<td>[112]</td>
<td>2</td>
<td>5.5</td>
<td></td>
<td>0.96</td>
<td>1.57</td>
<td>1419, 176, 54, 2.43</td>
</tr>
<tr>
<td>I</td>
<td>[111]</td>
<td>3</td>
<td>5.55</td>
<td></td>
<td>0.78</td>
<td>1.63</td>
<td>1248, 155, 74, 3.21</td>
</tr>
<tr>
<td>D</td>
<td>[111]</td>
<td>3</td>
<td>7.66</td>
<td></td>
<td>0.79</td>
<td>1.64</td>
<td>(1057), (131), (49)</td>
</tr>
<tr>
<td>J</td>
<td>[001]</td>
<td>4</td>
<td>5.7, 7.7, 5</td>
<td></td>
<td>0.30</td>
<td>1.78</td>
<td>592, 73, 70, 3.04</td>
</tr>
<tr>
<td>Ni₉₄</td>
<td>K</td>
<td>[001]</td>
<td>2</td>
<td>5.5</td>
<td>0.94</td>
<td>1.56</td>
<td>1322, 165, 51, 2.23</td>
</tr>
<tr>
<td>L</td>
<td>[111]</td>
<td>2</td>
<td>7</td>
<td></td>
<td>0.93</td>
<td>1.55</td>
<td>1419, 176, 57, 2.47</td>
</tr>
<tr>
<td>E</td>
<td>[110]</td>
<td>2</td>
<td>7.7</td>
<td></td>
<td>0.95</td>
<td>1.57</td>
<td>(1278), (158), (30)</td>
</tr>
<tr>
<td>M</td>
<td>[111]</td>
<td>3</td>
<td>5.59</td>
<td></td>
<td>0.72</td>
<td>1.61</td>
<td>(1185), (147), (52)</td>
</tr>
<tr>
<td>D</td>
<td>[111]</td>
<td>3</td>
<td>7.7, 7.7</td>
<td></td>
<td>0.69</td>
<td>1.59</td>
<td>(1265), (157), (49)</td>
</tr>
<tr>
<td>N</td>
<td>[111]</td>
<td>3</td>
<td>5.7</td>
<td></td>
<td>0.79</td>
<td>1.64</td>
<td>1216, 151, 72, 3.14</td>
</tr>
<tr>
<td>I</td>
<td>[111]</td>
<td>3</td>
<td>7.7, 7.7</td>
<td></td>
<td>0.73</td>
<td>1.61</td>
<td>1172, 145, 63, 2.75</td>
</tr>
</tbody>
</table>

*Number of nearest neighbor atoms for the Ni atoms(s) at the bonding site. Where nonequivalent surface atoms are present, values are given for each type.

Optimum distance from H to the plane representing the surface.

Optimum distance from H to atoms at 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 (Dₑ) 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 Ni₉₄ 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 Ni₉₄H orbital with the original Ni₉₄ orbitals, we can relate the spectrum at each site to that of a neighboring site and also to that of the Ni₉₄. In all cases, the overlap was very high, and the Ni part of each Ni₉₄H orbital may be expressed almost exactly (99+%) as a linear combination of the original Ni₉₄ orbitals.

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 Ni₉₄ spectrum. 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 Ni₉₄ 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 Ni₉₄ levels that are destabilized at sites N and L. For both sites K and I, a deeper doubly occupied
(iv) Binding energies have been measured for each low index face and are essentially invariant at ~0.75 eV per H atom.16,17 Our present Ni$_{50}$ and Ni$_{49}$H 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$_3$Ni$_4$ (sp$^2$-C$_6$H$_5$)$_n$ 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 photoluminescence 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 modeling chemisorption size alone is not a useful criterion for choosing a model. For electron-donating (electron donating) adsorbates, even very large clusters may be inadequate. On the other hand, a relatively small cluster of Ni atoms is useful for studying the bonding of an electron-positive 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 coverage 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.

ACKNOWLEDGMENTS

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2Contribution No. 5909.
9The IP and EA values discussed here are vertical values. For very small clusters geometry changes in cation and anion may alter experimental
(adiabatic) IP and EA values. However, by \( N = 43 \) such geometry effects should be less important.

9. R. C. Jacevic, Ford Motor Co. (private communication).

10. A. Somorjai, J. Colloid Interface Sci. 58, 150 (1977), and references cited therein.

11. The term "covalently bonded" is used here to distinguish those adsorbrates from those possessing formal "dative" bonds such as CO, NO, or \( \text{C}_2\text{H}_4\).

12. To obtain overlaps, Ni\(_{25}\)H orbitals were renormalized following removal of H atom contributions, and projected onto all Ni\(_{25}\) orbitals.


