



ELECTRONIC PROPERTIES OF METAL CLUSTERS (Ni_{13} TO Ni_{87}) AND IMPLICATIONS FOR CHEMISORPTION^{*†}

Carl F. Melius[†]

Sandia Laboratories, Livermore, California 94550

and

Thomas H. Upton and William A. Goddard III^{*}

Contribution No. 5814 from the Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, California 91125

(Received 26 July 1978 by A.A. Maradudin)

First principles calculations of the electronic properties of Ni clusters (up to Ni_{87}) are reported. It is found that the ionization potential (IP) converges to bulk values (work function) by Ni_{43} , whereas the electron affinity (EA) is off by 2.5 eV, even for Ni_{87} . The conduction band of ~16 eV appears converged by Ni_{87} . It is found that the electron density for surface atoms is significantly lower than the bulk value. The significance of these results for chemisorption on small metallic clusters and for modelling of chemisorption on bulk surfaces is discussed.

1. Introduction

Recently, there has been a number of papers in which metal clusters were used to study various aspects of chemisorption¹. A recurring theme in these studies has been the extent to which the cluster actually mimics bulk chemisorption behavior, yet few studies have dealt directly with the electronic properties of the clusters themselves^{1d}. This communication addresses this problem with a discussion of the valence electronic properties of small nickel clusters ranging in size from 13 to 87 atoms. Specifically, we consider the convergence to the bulk limit of those properties expected to be important in chemisorption processes such as ionization potential (IP), electron affinity (EA), bandwidth, and surface electron density.

2. Computational Details

Previous calculations² on Ni_2 and Ni_8 including all valence electrons indicated that (i) nickel atoms in the bulk are stabilized in what is effectively a localized $3d^9$ atomic configuration on each Ni; (ii) the remaining electrons are contained in delocalized band orbitals (referred to here as conduction band or 4s orbitals) dominated by the 4s-like component on each Ni atom; (iii) the 3d electrons are of only minor importance (20 to 25%) in Ni-Ni bonding; and

(iv) these 3d orbitals interact only weakly with the conduction band orbitals (that is, the 3d band spectrum is nearly independent of the distribution of orbitals in the conduction bands). From these studies we concluded that it is valid to study the conduction electrons independently of the 3d electrons of nickel. To do this while avoiding a bias towards a particular $3d^9$ configuration on each atom we average over the five possible $3d^9$ spatial configurations. Consequently the field of this average d^9 configuration can be replaced with an effective potential³ reducing the conduction band problem to one electron per Ni atom (and allowing a corresponding truncation in the basis set for describing these orbitals)⁴. All calculations reported here were carried out at the Hartree-Fock (HF) level; however, since most states possessed open-shell orbitals, it was necessary to use the proper variational technique¹⁴ to ensure that each state was a correct spin eigenfunction.

The clusters studied were selected by assuming the face-centered cubic (fcc) Ni structure (2.487 Å bond distance⁵) and selecting the first n shells of atoms surrounding a particular atom. Here we report the six cases with n = 1 to n = 6, numbering 13, 19, 43, 55, 79, and 87 atoms. As a test of the validity of this description, 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,

* Supported in part by a grant (DMR74-04965) from the National Science Foundation.

† Supported in part by a contract [AT(29-1)-789] from the U.S. Department of Energy.

suggesting that the dominant interactions between atoms are included.

3. Densities of States

In Fig. 1 we show the orbital energies

inherent in the cubic symmetry of the cluster. As an alternative approach we have built lower symmetry clusters (D_{2h}) by adding shells simultaneously to two nearest atoms. The smallest units here are Ni₂₀ and Ni₂₈, leading to the band spectra indicated in Fig. 1. Here

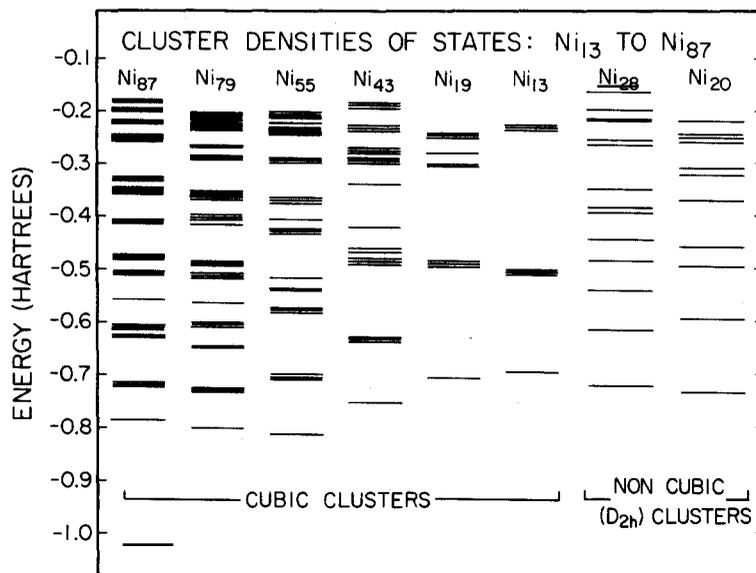


FIG. 1: Approximate densities of states for both cubic and D_{2h} clusters. Levels are obtained as orbital energies from Hartree-Fock calculations. Degenerate levels have been plotted as multiplets to indicate actual state density. Only occupied states are shown.

obtained for the ground state of each of the six cubic clusters. As each level represents an approximate ionization potential (Koopmans' Theorem), the range of energies shown in each case represents an effective cluster density of states (levels that are doubly or triply degenerate have been plotted as closely spaced groups of lines to indicate this degeneracy). The 13- and 19-atom clusters show a very discrete spectrum, and only the clusters larger than 43 atoms show a rather continuous density of states. For these clusters there is an increase in density near the Fermi level, in agreement with the ideas of simple, nearly free-electron band theory⁶.

In studies of the chemisorption of atoms such as H⁷ and O⁸ on metal clusters, we have found that several "band" orbitals of widely differing orbital energies are changed greatly upon chemisorption. As a result of such studies, we have concluded that a good cluster for modelling chemisorption on the solid surface should exhibit a density of states that is as continuous as possible. Based on these considerations, the 13-, 19-, and 43-atom clusters are quite inadequate and even the 79- and 87-atom clusters are barely satisfactory. This bunching of levels is partly due to the high degree of degeneracy

we see that uniform densities of states may be obtained with small clusters, suggesting the use of such less symmetric clusters for studies of chemisorption.

4. Work Function, Electron Affinity, and Bandwidth

In Table I we summarize values for these properties as a function of cluster size. For the Ni clusters the IP from using Koopmans' Theorem (KT) is close to the HF value, indicating that the effects of orbital relaxation and of differential electron correlation between neutral and ion states (the primary sources of error in the KT result) are small.

The convergence of IP values towards the bulk work function is not monotonic, but for $N \geq 43$, it is within 0.5 eV of the experimental work function¹⁰. The EA, on the other hand, is still 2.5 eV smaller than the experimental work function, even for $N = 87$. The reason for this is that the IP and EA differ (for any particular singly-occupied orbital) by the orbital self-energy J_{ii} (the coulomb interaction of two electrons occupying the same orbital i), where $IP = EA + J_{ii}$. Here $J_{ii}(\text{eV}) \approx 14.4/R(\text{\AA})$, where R is the radius of the cluster. Thus, for $N = 87$ with $R = 6.1 \text{ \AA}$,

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 ^a		Electron Affinity	
			DZ ^b	DZ + P ^b	DZ ^b	DZ + P ^b	DZ ^b	DZ + P ^b
			SCF (KT)	SCF (KT)	SCF	SCF	SCF	SCF
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

^a Values not in parentheses are from self-consistent calculations on both the neutral and ion states; values in parentheses are from use of Koopmans' Theorem.

^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. 4).

^c Reference 10.

the self-energy is about 2.4 eV. From this expression we see that to obtain IP - EA = 1 eV requires $R = 14.4 \text{ \AA}$ (a cluster of 1146 atoms) and that IP - EA = 0.1 eV requires 1.1×10^6 atoms! Thus extremely large clusters are required before this characteristic property of a metal (IP = EA) is achieved.

For studying the chemisorption of atoms more electronegative than Ni, such as H, N, O, F, Cl, or S, it is the IP of the cluster that is more important as it controls the degree of charge transfer to the adsorbate. On the other hand, for electropositive adsorbates such as Na, K, and Cs, it is the EA of the surface complex that should be more important, since charge transfer is to the surface. Thus small clusters of metal atoms should possess similar properties to bulk metals for electronegative adsorbates, but they may have unique properties of their own for electropositive adsorbates.

The conduction bandwidth appears to be essentially converged to ~16 eV by $N = 87$. There are no established experimental values available for this property, but measurable energy state density has been found as much as 10-11 eV below the fermi level¹¹.

5. Cluster Electron Density

A particularly important property to be evaluated in comparing clusters with the bulk is the distribution of electron density at and near the surface. Using the wavefunctions for the 87-atom cluster, we show in Fig. 2 the charge population of each atom as a function

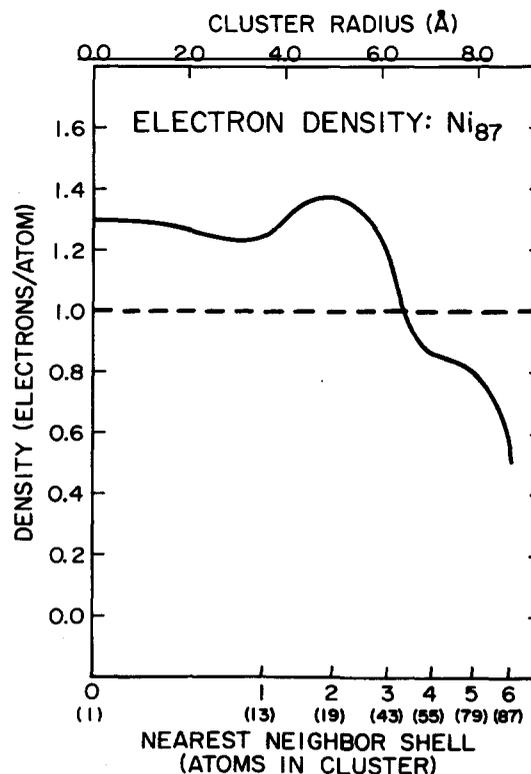


FIG. 2: Electron density per atom for 87-atom cluster plotted as a function of nearest-neighbor shell. Dashed line indicates the average bulk density.

of shell radius. Similar results are found for the N = 43, 55, and 79 clusters¹².

The implications of these results for the infinite system are:

- i) The surface atoms may be electron-deficient with the deficiency greater for less dense surfaces [i.e., $\rho(111) > \rho(100) > \rho(110)$], which may relate directly to changes in work function and reactivity for different surfaces.
- ii) The layers just below the surface may have electron densities greater than the bulk. Thus electronegative interstitials may be more localized in these near-surface regions, while electropositive interstitials may have a significant barrier to moving from the bulk to the surface layer.
- iii) The structure near the surface may have a non-uniform behavior corresponding to the non-uniform density. For example, these results would suggest that a larger spacing should occur between the outermost layers while some layers slightly below the surface may be closer together than the bulk spacing.
- iv) Corner atoms at steps and kinks should be even more electron-deficient than the remaining surface atoms and hence more reactive towards nucleophiles, as has also been suggested by other investigators¹³.
- v) To better mimic surface atoms, the outer atoms of the cluster should have

coordination numbers approaching those of the actual surface. In this respect, the 79-atom cluster should be a more successful surface model than the 87-atom cluster.

- vi) As an extension of (iv) above, the complexes with a low coordination number for the outer shell may be more appropriate as models for the reactivity of steps and kinks than the infinite surface.

6. Summary

From studies of the change in conduction band states of metallic clusters as a function of cluster size, we have obtained data on the convergence of electronic properties towards bulk values. We find that although there is convergence of almost all properties, the rate at which these values change towards the bulk value varies widely. We have attempted to determine the nature of these variations in such a manner as to provide insight into how well the surface may be represented in a theoretical study of chemisorption. In addition, the implications of these results on the behavior of different infinite metal surfaces is considered. We find that small clusters have some properties differing from bulk surfaces, perhaps leading to changes in their chemisorptive and catalytic properties.

REFERENCES

1. (a) FASSAERT, D. J. M. and van der AVOIRD, Surf. Sci. 55, 313 (1976); (b) A. B. ANDERSON, J. Am. Chem. Soc. 100, 1153 (1978); (c) G. A. OZIN, W. J. POWER, T. H. UPTON, and W. A. GODDARD III, J. Am. Chem. Soc. 100, 4750 (1978); (d) R. P. MESSMER, S. K. KNUDSON, K. H. JOHNSON, J. B. DIAMOND, and C. Y. YANG, Phys. Rev. B 13, 1396 (1976).
2. (a) C. F. MELIUS, T. H. UPTON, and W. A. GODDARD III, Solid State Commun., in preparation; (b) C. F. MELIUS, J. W. MOSKOWITZ, A. P. MORTOLA, M. B. BAILLIE, and M. A. RATNER, Surf. Sci. 59, 279 (1976).
3. C. F. MELIUS, B. D. OLAFSON, and W. A. GODDARD III, Chem. Phys. Lett. 28, 457 (1974).
4. Basis sets used were the same (4s and 4p) as those used in S. P. WALCH and W. A. GODDARD III, J. Am. Chem. Soc. 100, 1338 (1978).
5. W. P. PERASON, A Handbook of Lattice Spacings and Structures of Metals and Alloys (Pergamon Press, New York, 1958).
6. See, for example, C. KITTEL, Introduction to Solid State Physics (John Wiley & Sons, New York, 1971).
7. W. A. GODDARD III, Physical Chemistry Division Talk No. 30, 176th National Meeting of the American Chemical Society, Anaheim, California, 12-17 March 1978.
8. S. P. WALCH AND W. A. GODDARD III, Solid State Commun. 23, 907 (1977).
9. P. J. HAY, T. H. DUNNING, JR., and W. A. GODDARD III, J. Chem. Phys. 62, 3912 (1975).
10. A. A. HOLSCHER, Surf. Sci. 4, 89 (1966).
11. See, for example, C. S. FADLEY and D. A. SHIRLEY, Phys. Rev. Lett. 21, 980 (1968).
12. This behavior is reminiscent of Friedel oscillations found in the jellium model. For a discussion, see W. A. HARRISON, Solid State Theory (McGraw-Hill, New York, 1970), p. 184.
13. G. A. SOMORJAI, J. Colloid Interfac. Sci. 58, 150 (1977) and references cited therein.
14. W. J. HUNT, W. A. GODDARD III, and T. H. DUNNING, JR., Chem. Phys. Lett. 6, 147 (1970). Closed-shell states appeared only in the direct calculation of certain positive and negative ion states.