

CNDO Calculations for Small Clusters of Ni Atoms
and Hydrogen Atoms Chemisorbed on the Clusters

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The starting point for CNDO (complete neglect of differential overlap) methods is Roothaans's¹ LCAO SCF equations, which are simplified by ignoring and approximating large numbers of integrals so that the computations for a large molecule can be carried out on a computer in a reasonable length of time, i.e., from a few minutes to one hour. The CNDO procedure used was basically a modification of that by Pople et al.² The modifications mainly consist in recognizing d orbitals as being sufficiently different from s and p orbitals as to require separate treatment. The diagonal F matrix elements are like those of Baetzold³ in which the d orbitals have different orbital exponential coefficients from the s and p orbitals. In the off diagonal F matrix elements a different parameter was used to represent the resonance integrals for d electrons from that used for s and p electrons as in the work of Clack et al.⁴ Slater type orbitals⁵ were used. All valence shell electrons in the 3d, 4s and 4p orbitals of nickel were included while all inner shell electrons were treated as part of a non-polarizable core.

The input parameters used for nickel atoms are listed in Table 1. These were chosen on the basis of giving reasonable values of equilibrium bond length, d orbital occupancy⁶, binding energy, Fermi level, and d band width for a cluster of nickel atoms⁶. The hydrogen atom parameters are those given by Pople et al.²

Table 2 shows a comparison of the calculated properties of an octahedral Ni₆ cluster with bulk Ni properties. Reasonable agreement of calculated and experimental properties is found. The s and p electrons were primarily responsible for producing the Ni-Ni bonds so the parameters for these electrons had the

greatest effect on calculated properties.

Table 1

Nickel atom parameters for an initial configuration of $3d^8, 4s^2, 4s^0$;
 β -resonance integral, ξ -orbital exponential coefficient,
 I -ionization potential, and A -electron affinity

β_s	— 6
β_d	— 10
ξ_s	1.8
ξ_d	2.5
$(I_s + A_s)/2$	4.3
$(I_p + A_p)/2$	1.3
$(I_d + A_d)/2$	10.0

Table 2

Comparison of calculated values for octahedral Ni_6
using the standard parameter set with bulk nickel properties

	Ni_6 by CNDO	Bulk Ni
r_{eq}	2.5 Å	2.5 Å
d electrons per atom	9.46	9.4
binding energy (normalized)	3.7 eV	4.4 ⁽⁸⁾
HOMO (Fermi level)	-7.7 eV	-5.22 ⁽⁹⁾ , -4.75 ⁽¹⁰⁾ eV
d band width	3.3	2.7 ⁽¹¹⁾ , 5 ⁽¹²⁾ , 4 ⁽¹³⁾ eV

The calculations were made for the interaction of a hydrogen atom with a (111) surface of a cluster of 10 nickel atoms. The hydrogen atom is located 1.6 Å directly above a nickel atom or 1.0 Å above the center of a triangular hole on the (111) face. These distances are the calculated equilibrium distances for the interaction of hydrogen atoms with small nickel clusters of a similar

configuration. In all cases the nickel-nickel distance is 2.5 Å as in bulk nickel.

The results are given in Table 3. These CNDO calculations give a much greater binding energy for a hydrogen atom over a hole than directly over a surface atom. The calculated binding energy over a hole of 73 kcal per mole is in good agreement with the experimental value¹⁴ of 67 kcal per mole. These

Table 3

CNDO calculation for H adsorbed on (111) Ni

	Binding energy	H atom charge	Bond order			
			s	p	d	Total
H over Ni atom	26 kcal	- 0.23e	0.158	0.282	0.095	0.535
H over hole	73 kcal	- 0.03e	0.334	0.510	0.082	0.926

results are apparently the opposite of those of Fassaert et al.¹⁵ who found adsorption over a surface atom favored in an extended Huckel molecular orbital (EHMO) calculation. However, in the EHMO calculation the H atom is much closer to the plane of the three Ni atoms forming the hole than in the CNDO calculation reported here. Positioning the H atom for an EHMO calculation in the equilibrium position indicated by these CNDO calculations could possibly result in better agreement for the two methods. The H atom carries a negative charge for both positions which would result in a negative surface potential in agreement with experimental measurements¹⁴.

The bond orders indicate that the nickel s and p orbitals are largely responsible for the bonding with the d orbitals playing a relatively minor role. Although previous theoretical considerations^{16,17} have emphasized the role of d orbitals in chemisorption, these results are not in agreement with that view for hydrogen adsorption on nickel. That hydrogen adsorption is mainly involved with the nickel sp band electrons is supported by theoretical calculations of conductivity changes upon hydrogen adsorption¹⁸.

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