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PARAMETER SELECTION IN CNDO CALCULATIONS FOR SMALL NICKEL CLUSTERS

By

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Abstract

A method of doing CNDO calculations for a cluster of transition metal atoms is presented. The calculations include all s, p and d orbitals in the valence shell. Parameter selection and the effect of individual parameters on calculated properties are discussed. Initial input parameters include the initial electron configuration of the atoms, resonance integral for s and d electons, orbital exponential coefficients for s and d Slater type orbitals, and ionization potentials and electron affinities for s, p and d orbitals. Calculations for an octahedral Ni_6 cluster gave an equilibrium bond length of 2.5 Å, 9.46 d electrons per atom, a binding energy of 3.7 eV per atom, the Fermi level at -7.7 eV, and a d-band width of 3.3 eV. These results are in approximate agreement with bulk properties. 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.

Introduction

The properties of small clusters of metal atoms are important to considerations of vapor phase nucleation, thin film properties and dispursed metal catalysts. All of these areas involve working with high surface area materials. Because the surface to volume ratio in metal clusters is large their properties are expected to differ from those of bulk metals. However, just how the properties of small clusters and bulk metals differ is not well understood. More experimental and theoretical guidelines are needed the help define the relationship between these two classes of materials. It is the purpose of this paper to contribute to the understanding of metal clusters by presenting a semi-empirical quantum mechanical method of calculating the properties of small clusters. In addition to leading to a better understanding of metal clusters it is hoped that the method developed will also serve as a basis for calculations on the interaction of adsorbed molecules

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with a metal cluster. In tnis paper the emphasis will be on presenting the method and the selection of the empirical parameters.

Relatively few quantum mechanical calculations for metal clusters have been made. Because of the large number of electrons involved ab-initio calculations for transition metals are not yet feasible. Extended Huckel calculations have been made for a few diatomic metal molecules[1,2], small clusters and strings of atoms[3] and clusters of up to 13 nickel atoms[4]. Calculations using a CNDO procedure have appeared for only very small clusters of Ag and Pd atoms[3]. The widespread use of semi-empirical molecular orbital methods to treat a wide variety of chemical structures has lead to some general guidelines for their use. The exact values of quantities such as ionization potentials, spectral transition energies, and dipole moments are usually not accurate; close agreement between calculation and experiment being regarded as merely a happy accident. However, trends in values for similar compounds are often well reproduced by the calculations. Equilibrium bond angles and charge distributions are usually given more accurately than energies. The extended Huckel method has not usually been successful in giving equilibrium internuclear distances whereas the CNDO methods have[5]. For this reason a CNDO procedure has been chosen for this work.

Some properties of metal clusters have been calculated[6] using pair-wise additive potentials of the Lennard-Jones type for the atom interactions. These calculations showed a strong dependence on the number of atoms included. Calculations of equilibrium forms of clusters have been made[7] assuming that the contribution to the total binding enegy by each atom is directly proportional to its coordination number. The validty of this rather common assumption has received very little consideration. It is hoped that the type of calculation presented here can be used to check this assumption.

CNDO Method

The starting point for CNDO (complete neglect of differential overlap) methods is ROOTHAANS's[8] LCAO SCF equations, which are simplified by ignoring and approximating large numbers of integrals so that the computations for large molecule can be carried out on a computer in a reasonable length of time, *i.e.*, from a few minutes to one hour. In the CNDO method of POPLE *et al.*[5,9~12] the matrix equation

$$(F-E)C = 0 \qquad\qquad (1)$$

is solved with the matrix elements

$$F_{\mu\mu} = U_{\mu\mu} + \left[P_{AA} - (1/2)P_{\mu\mu} \right] \gamma_{AA} + \sum_{B \neq A} (P_{BB} - Z_B)\gamma_{AB} \tag{2}$$

$$F_{\mu\nu} = \beta^0_{AB}S_{\mu\nu} - 1/2P_{\mu\nu}\gamma_{AB} \qquad (\mu \neq \nu) \tag{3}$$

with the symbols as defined in reference 5. These equations were not designed to handle transition metal atoms so a few modifications are in order. These principly consist in recognizing d orbitals as being sufficiently different from s and p orbitals to require special treatment in calculations for transition metals[2,3,13]. The energy of an electron in ϕ_μ on atom A is given by the term

$$U_{\mu\mu} = \int \phi_\mu^* \left[-(1/2)\nabla^2 - Z_A/r \right] \phi_\mu d\tau \tag{4}$$

is replaced in the semi-empirical expression for the case where ϕ_μ is an s orbital by

$$U_{ss} = -(1/2)(I_s + A_s) - (N - 1/2)\gamma_{ss} - M\gamma_{sd} \tag{5}$$

Here I_s is the ionization potential from orbital ϕ_s, A_s the electron affinity, N the number of s and P electrons, and M the number of d electrons for a base configurative $(sp)^N (d)^M$. This equation is obtained by averaging the value of U_{ss} in the two equations

$$U_{ss} = -I_s - (N-1)\gamma_{ss} - M\gamma_{sd} \tag{6}$$

$$U_{ss} = -A_s - N\gamma_{ss} - M\gamma_{sd} \tag{7}$$

which are for the processes of loosing and gaining an electron from the base configuration $(sp)^N(d)^M$. In a similar manner the expression for U_{dd} is obtained as

$$U_{dd} = -(1/2)(I_d + A_d) - N\gamma_{sd} - (M - 1/2)\gamma_{dd} . \tag{8}$$

The core attraction integrals, V^{AB}, which are given by

$$V^{AB} = \int \phi_\mu^* (Z_B/r_B)\phi_\mu d\tau \tag{9}$$

are then replaced by electron repulsion integrals so that

$$V_{ss}^{AB} = N_B\gamma_{ss}^{AB} + M_B\gamma_{sd}^{AB} \tag{10}$$

and

$$V_{dd}^{AB} = N_B\gamma_{ds}^{AB} + M_B\gamma_{dd}^{AB}. \tag{11}$$

The two center electron repulsion integrals are given by

$$\gamma_{ds}^{AB} = \iint \phi_d(1)\phi_d(1)(1/r_{12})\phi_s(2)\phi_s(2)d\tau_1\tau_2. \tag{12}$$

Electron repulsion integrals involving only s orbitals are readily calculated so all d orbitals in electron repulsion integrals were replaced by s orbitals with the same orbital coefficient. Thus, the following expression were used

$$\gamma_{dd} = \gamma_{s's'} \tag{13}$$

$$\gamma_{sd} = \gamma_{ss'}, \tag{14}$$

where orbital s' has the same orbital coefficient as orbital d. All d orbirals of an atom are treated as being equivalent. The degree of approximation introduced this way is shown in the comparisons in Table 1.

TABLE 1   Electron Repulsion Integrals
The orbital exponent is 1.8 in all cases

Integrals	One center integrals	Two center integrals (electron 1 on center A, electron 2 on center B)
$(3s(1)\,3s(1)\,/\,3s(2)\,3s(2))$	0.4689	0.2107
$(3d_{xz}(1)(3d_{xz}(1)/\,3d_{xz}(2)\,3d_{xz}(2))$	0.5023	0.2200
$(3d_{z^2}(1)\,3d_{z^2}(1)/\,3d_{z^2}(2)\,3d_{z^2}(2))$	0.5524	0.2663
$(3d_{x^2}(1)\,3d_{x^2}(1)/\,3d_{x^2}(2)\,3d_{x^2}(2))$	0.5524	0.1941

In the off diagonal terms the constant β_{AB}^0 in $F_{\mu\nu}$ is given by

$$\beta_{AB}^0 = (1/2)(\beta_A^0 + \beta_B^0), \tag{15}$$

where β_A^0 is given by $\beta_A^0(s)$ or $\beta_B^0(d)$ depending on whether μ is an s or d orbital and likewise β_B^0 is replaced by $\beta_B^0(s)$ or $\beta_B^0(d)$.

For both diagonal and off diagonal elements s and p orbitals are treated as equivalent. The basic equations produced by these approximations are

$$F_{\mu\mu}^A(s) = -(1/2)(I_s^A + A_s^A) - (N^A - 1/2)\gamma_{ss}^A - M_A\gamma_{ss'}^A$$
$$-(1/2)P_{\mu\mu}\gamma_{ss}^A + \sum_\lambda P_{\lambda\lambda}\gamma_{\mu\lambda} - \sum_{B\neq A}(N^B\gamma_{ss}^{AB} + M_B\gamma_{ss'}^{AB}) \tag{16}$$

$$F_{\mu\mu}^A(d) = -(1/2)(I_d^A + A_d^A) - (M^A - 1/2)\gamma_{s's'}^A - N^A\gamma_{s's}^A$$
$$-(1/2)P_{\mu\mu}\gamma_{s's'}^A + \sum_\lambda P_{\lambda\lambda}\gamma_{\mu\lambda} - \sum_{B\neq A}(N^B\gamma_{s's}^{AB} + M^B\gamma_{s's'}^{AB}) \tag{17}$$

$$F_{\mu\nu}^{AB} = (1/2)(\beta_A^0 + \beta_B^0)S_{\mu\nu} - (1/2)P_{\mu\nu}\gamma_{\mu\nu}^{AB}. \tag{18}$$

Slater type orbital were used. All valence shell electrons in the $3d$, $4s$, and $4p$ orbitals were included while all inner shell electrons were treated as part of a non-polarizable core.

The computer program used in these calculations was producd by modifying the program given in reference 5. The integrals involving $4s$ and $4p$ orbitals were calculated by the method used in that program.

In using the program for clusters of metal atoms it was found that the results usually diverged rather than converging to a constant charge density and energy. When a small variation from a uniform charge distribution occured on one side of the cluster it was over-corrected for in the next iteration so that a larger variation appeared on the other side of the cluster. This quickly developed into a large permanent oscillation. To prevent this the program was modified to store the density matrix P after each iteration as PO. On the next iteration if the new total energy increased or changed in absolute magnitude by more than 2 atomic units, the new density matrix was discarded and density matrix elements given by

$$P_{\mu\nu} = PO_{\mu\nu} + 0.1 \left(P_{\mu\nu}(\text{new}) - PO_{\mu\nu} \right) \tag{19}$$

were used. This procedure eliminated the divergence problem. The criterion used for convergence was that the energy not change by more than 10^{-4} atomic units.

The calculations were performed on the FACOM 230–60 computer at Hokkaido University Computing Center.

Parameter Selection

The parameters for which values must be selected are the orbital exponential coefficients ξ_s and ξ_d for $4s$ and $3d$ electrons, $(1/2)(I_s + A_s)$, $(1/2)(I_p + A_p)$, $(1/2)(I_d + A_d)$, β_s, β_d and the values of M and N in the initial configuration. The orbital exponential coefficients, ξ, occur in the radial part of the Slater orbital in the form

$$R_{nl}(r) = (2\xi)^{n+1/2} \left[(2n)! \right]^{-1/2} r^{n-1} \exp(-\xi r) \tag{20}$$

The basic philosophy used in selecting parameters for this semi-empirical method was to choose values in a physically reasonable range to best fit known bulk properties of nickel. An octahedral cluster of 6 nickel atoms was chosen as a basis for fitting parameters for several reasons. This is about as large a cluster as can be conveniently worked with. It takes the program about 5 minutes to reach convergence with Ni_6 whereas larger clusters take much longer. The atoms in the octahedral Ni_6 cluster have the same geometric arrangement as in the bulk metal and have an average coordination number of 4 nearest neighbours. This is considerably lower

G. BLYHOLDER

than the coordination number of 12 in the bulk metal but even a cluster of 13 atoms where a central atom has all 12 of its nearest neighbours only has an average coordination number of 5.5. Linear strings and planer arrangements of atoms have much lower coordination numbers than 4 as well as lacking any elements of a three dimensional structure. The properties considered included the number of d electrons (9.4 in the bulk metal), equilibrium internuclear distance (2.5 Å in the bulk), Fermi level, binding energy, and d band width.

Various schemes for determining orbital exponential coefficients have been proposed by SLATER[14], BURNS[15], CLEMENTI[16] and GOUTERMAN[17]. The values suggested by these authors are listed in Table 2. It may be noted that the values of ξ_s go from 1.1 to 1.8 and the values of ξ_d from 2.5 to 4.2. Any value within these ranges was regarded as reasonable to try for these calculations.

TABLE 2　Values of orbital exponential coefficients
for s and d orbitals for the configuration
$3d^8 4s^2$ for Ni

Author	ξ_s	ξ_d
Slater	1.1	2.5
Burns	1.8	3.5
Clementi	1.43	4.2
Gouterman	1.47	3.0

In estimating values for $(1/2)(I+A)$ the ionization potential, I, is regarded as a valence state value, and is an average over spectroscopic states. There is enough data to make reasonable estimates for I but there is very little data for electron affinities and so few observations of suitable spectro-

TABLE 3　Values estimated for $(1/2)(I+A)$ in eV from
CLACK, HUSH and YANDLE and values in
parenthisis estimated from I values in BALL-
HAUSEN and GRAY with the assumption $A=0$

Orbital type	Configuration	
	$d^8 s^2$	$d^9 s^1$
$3d$	6.2	(5.0)
$4s$	4.3 (4.5)	(3.8)
$4p$	1.3 (2.5)	(2.0)

scopic states that values for A are very approximate. Estimated values for $(1/2)(I+A)$ obtained from CLACK, HUSH, and YANDLE[13] and estimated values using I given by BALLHAUSEN and GRAY[18] with the assumption that $A=0$ are given in Table 3. These latter values are lower limits to values that would be obtained using the I values in BALLHAUSEN and GRAY. Clearly they give values somewhat higher than the others.

Values of β_d from -1 to -30 have been used[2,13] and values of β_s from -0.5 to -35 for transition metals have been used[13]. Calculations for nickel clusters with initial configurations d^8s^2 and $d^{9.4}s^{0.6}$ are reported herein.

RESULTS

The most successful set of parameters is listed in Table 4. Hereafter this will be referred to as the standard set and any parameter may be assumed to have the standard value unless otherwise specified. A com-

TABLE 4 Most successful parameter set, used as the standard set

Initial configuration $3d^8\ 4s^2\ 4p^0$	
β_s	-6
β_d	-10
ξ_s	1.8
ξ_d	2.5
$(1/2)\ (I_s+A_s)$	4.3
$(1/2)\ (I_p+A_p)$	1.3
$(1/2)\ (I_d+A_d)$	10.0

TABLE 5 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
HOMO (Fermi level)	-7.7 eV	$-5.22,\ -4.75\ eV$
d band width	3.3	2.7, 5, 4 eV

parison between calculated properties for an octahedral 6 atom nickel cluster and experimental or calculated bulk nickel properties is shown in Table 5. The number of d electrons for atom k, N_k^d is defined as

$$N_k^d = \sum_{d\text{-orbitals}} n_\mu^d, \tag{21}$$

where

$$n_\mu^d = \sum_{MO's} n_i c_{\mu i}^2, \tag{22}$$

where n_i is the number of electrons in molecular orbital i. The total difference between the energy for the Ni_6 cluster and 6 separated Ni atoms is 0.271 atomic units. In order to get a meaningful number to compare to the experimental cohesive energy of the metal (4.4 eV)[19] it was assumed, as has been done previously[7], that the bindingy energy of an atom is directly proportional to the number of nearest neighbors. Thus, the calculated normalized binding energy per atom is obtained by multiplying 0.271 a.u. by 12/4 and dividing by the number of atoms in the cluster.

For a discrete set of molecular orbitals there is no unequivocal definition of a Fermi level. The Fermi level here is taken as the energy of the highest occupied molecular orbital (HOMO). Experimental values of the Fermi level have been given as -5.22 eV[20] and -4.75 eV[21].

In Table 5 the calculated d band width has been taken as the difference in energy between the lowest orbital with strong d character and the HOMO since this energy range contains over 90% of the d electron density. There is a small amount of d character in lower energy occupied orbitals and higher energy unoccupied orbitals which are largely s and p in character. The CNDO calculation gives a d band width within the range of values calculated by FLETCHER[22] (2.7 eV), HANUS[23] (5 eV) and YAMASHITA et al.[24] (4 eV).

In general the values in Table 5 indicate that the CNDO method can give quite reasonable values for properties of metal clusters. A curve showing the variation of total energy with interatomic distance for the Ni_6 cluster is shown in Figure 1. The values of the standard parameters were selected so as to have the calculated r_{eq} close to the bulk distance of 2.5 Å.

In the course of selecting the best parameters calculations were made over a wide range of parameter values. In Table 6 some of the these runs which illustrate the effect of particular parameters on the properties of a Ni_6 cluster are listed. In lines 2 to 5 of Table 6 the value of ξ_s is increased from 1.5 to 1.8 while all other parameters are held constant. As
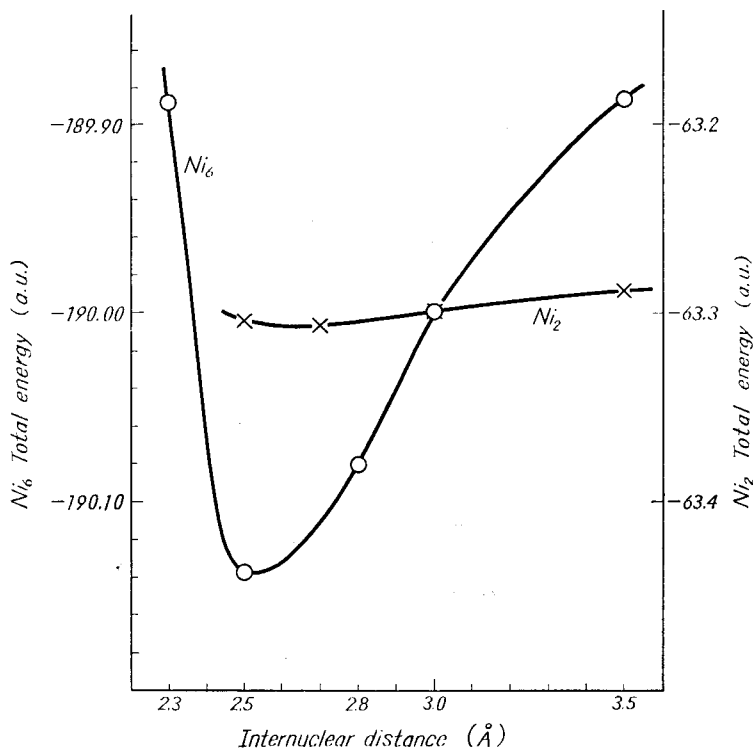
Figure 1. Energy vs. bond length for octahedral Ni_6 and for Ni_2 with standard parameters.

ξ_s increases the total energy of the cluster becomes more negative since the energy holding an s electron is becoming larger. At the same time the Fermi level as measured by the HOMO decreases in energy a little, the lowest occupied molecular orbital, which is largely of s and p character increases in energy. This last effect indicates that the spread of the sp band is decreasing, presumably due to less overlap of the s and p orbitals as the orbital exponential coefficient is increased. Finally the d band filling increases as ξ_s increases. This last effect of ξ_s, however, depends on the values of the other parameters as lines 8 to 10 show. Here the d band filling decreases as ξ_s increases. The trends in the other properties are the same as in lines 2 to 5. This difference may be due to the fact that for the parameters in the second case (lines 8 to 10) the d band is higher in energy with respect to the s band so that contraction of the spread of the s band has a different effect. This does however illustrate that the qualitative effect of a parameter on some properties does depend on the

TABLE 6 Calculated properties of Ni_6 for various parameter selections. All have an initial configuration of d^8s^2

line number	β_s	β_d	ξ_s	ξ_d	$\dfrac{(I_s+A_s)}{2}$	$\dfrac{(I_p+A_p)}{2}$	$\dfrac{(I_d+A_d)}{2}$	r	E_T	P_d	LOWEST ORBITAL	LOWEST d	HOMO	LUMO	normalised binding energy
					(eV)	(eV)	(eV)	Å	(au)		(au)	(au)	(au)	(au)	(eV)
1	−6	−10	1.8	2.5	4.3	1.3	10.0	2.5	−190.136	9.46	−0.54	−0.40	−0.28	−0.07	3.7
2	−5	−10	1.5	2.5	4.3	1.3	10.0	2.5	−182.22	8.68	−0.71	−0.55	−0.21	+0.00	0.5
3	−5	−10	1.6	2.5	4.3	1.3	10.0	2.5	−184.91	9.19	−0.60	0.45	−0.21	+0.01	1.2
4	−5	−10	1.7	2.5	4.3	1.3	10.0	2.5	−187.51	9.28	−0.54	−0.44	−0.25	−0.02	1.8
5	−5	−10	1.8	2.5	4.3	1.3	10.0	2.5	−189.92	9.51	−0.46	−0.46	−0.27	−0.06	0.7
6	−6	−10	1.8	3.0	4.3	1.3	10.0	2.5	−215.44	8.40	−0.67	−0.67	−0.23	+0.02	16.7
7	−6	−10	1.8	3.5	4.3	1.3	10.0	2.5	−239.57	8.65	−0.73	−0.73	−0.28	0.00	21.4
8	−5	−10	1.1	2.5	3.0	1.0	7.0	2.5	−161.09	8.62	−0.83	−0.36	−0.18	−0.02	—
9	−5	−10	1.3	2.5	3.0	1.0	7.0	2.5	−169.255	8.60	−0.77	−0.40	−0.23	−0.07	—
10	−5	−10	1.5	2.5	3.0	1.0	7.0	2.5	−176.42	8.2	−0.74	−0.56	−0.22	0.00	11.6
11	−5	−10	1.8	2.5	4.3	1.3	10.0	2.8	−189.934	9.55	−0.38	−0.38	−0.25	−0.07	0.9
12	−5	−10	1.8	2.5	4.3	1.3	10.0	3.0	−189.934	9.70	−0.35	−0.35	−0.28	+0.01	0.9
13	−5	−10	1.8	2.5	4.3	1.3	10.0	3.5	−189.870	10.0	−0.26	−0.26	−0.26	+0.08	0.1
14	−4	−10	1.8	2.5	4.3	1.3	10.0	2.5	−189.751	9.50	−0.42	−0.42	−0.25	−0.04	—
15	−5	−10	1.8	2.5	4.3	1.3	6.2	2.5	−182.12	8.97	−0.51	−0.38	−0.24	−0.03	8.7
16	−5	−15	1.8	2.5	4.3	1.3	6.2	2.5	−182.33	9.15	−0.50	−0.38	−0.22	0.00	11.6
17	−5	−15	1.825	2.5	4.3	1.3	6.2	2.5	−182.91	9.04	−0.49	−0.39	−0.23	−0.01	11.2
18	−5	−25	1.825	2.5	4.3	1.3	6.2	2.5	−183.46	9.00	−0.53	−0.53	−0.23	+0.02	18.6
19	−6	− 6	1.8	2.5	4.3	1.3	10.0	2.5	−190.00	9.52	−0.53	−0.37	−0.27	−0.07	1.8
20	−6	− 6	1.8	2.5	4.3	1.3	10.0	2.8	−190.005	9.53	−0.40	−0.40	−0.25	−0.07	1.9
21	−6	− 6	1.8	2.5	4.3	1.3	10.0	3.0	−189.968	9.56	−0.39	−0.39	−0.28	−0.01	1.4
22	−6	− 1	1.8	2.5	4.3	1.3	10.0	2.5	−189.86	9.60	−0.51	−0.35	−0.26	−0.06	0.0
23	−6	− 1	1.8	2.5	4.3	1.3	10.0	2.8	−189.92	9.65	−0.37	−0.37	−0.25	−0.08	0.7
24	−6	− 1	1.8	2.5	4.3	1.4	10.0	3.0	−189.94	9.53	−0.38	−0.38	−0.28	−0.01	1.0

specific value of the other parameters.

Lines 1, 6 and 7 of Table 6 show the effect of changing ξ_d. As the d orbitals are contracted by increasing ξ_d the total energy, energy of the lowest orbital, and the energy of the lowest d M. O. all decrease. While the HOMO shows no consistent change the average number of d electrons shows a large decrease.

The effect of β_s with all clusters having their atoms 2.5 Å apart is shown in lines 1, 5 and 14. As β_s increases, the total energy, energy of the lowest orbital, and energy of the HOMO all decrease. The energy of the lowest d MO and the average number of d electrons show small changes with no consistent trend. Lines 5 and 11 to 13 give a value of 2.9 Å for r_e indicating that as β_s decreases from 6 to 5 the value of r_e increases by 16%.

The effect of changing β_d with other parameters constant may be seen in the results on the pairs of lines 15, 16 and 17, 18 and the set in lines 1, 19 and 22. Increasing β_d increases the total energy and the binding energy but has relatively little effect on the other parameters. Lines 19 to 21 indicate a r_{eq} of 2.8 Å with all parameters standard except for β_d which is -6 instead of the standard -10. Lines 22 to 24 give $r_{eq} \geq 3.0$ Å with $\beta_d = -1$ while the standard $\beta_d = -10$ gives $r_{eq} = 2.5$ Å. Thus, r_{eq} increases as β_d decreases.

The effect of changing $(1/2)(I_d + A_d)$ may be seen in lines 5 and 15. Increasing $(1/2)(I_d + A_d)$ decreases the total energy, increases the number of d electrons, decreases the level of the lowest d MO, and changes other properties relatively little. Changes in $(1/2)(I_s + A_s)$ and $(1/2)(I_p + A_p)$ had relatively little effect on the calculated properties. This occurs because these terms contribute only a very small percentage to the F matrix terms.

Most of the parameter sets in Table 6 use a value of ξ_s around 1.8. It is also possible to get reasonable, but not quite as good, results with ξ_s at 1.3 or 1.4. A variety of runs based on this value of ξ_s are given in Table 7. With ξ_s about 1.3 or 1.4 it is necessary to increase the value of $(1/2)(I_d + A_d)$ to about 14 eV to get an average number of d electrons close to that in bulk nickel. This is somewhat higher than the values that would be estimated from Table 3. In general, the trends produced by parameter variation in Table 7 are like those outlined above for Table 6. The effect of the parameters in Table 7 or r_{eq} is shown in Figure 2. It is seen that these parameters give r_{eq} values of 3 Å and greater, which are somewhat greater than the bulk metal value of 2.5 Å. From the curves in Figure 2 it is evident that increasing β_s decreases r_{eq}, increasing β_d has

TABLE 7 Calculated properties of Ni$_6$ for various parameter selections

| line number	Initial Configuration	β_s β_d	ξ_s ξ_d	$\frac{(I_s+A_s)}{2}$ (eV)	$\frac{(I_p+A_p)}{2}$ (eU)	$\frac{(I_d+A_d)}{2}$ (eV)	r (Å)	E_T (au)	$\bar{P}_d$	LOWEST ORBITAL (au)	LOWEST d (au)	HOMO (au)	LUMO (au)	normalized binding energy (eV)
25	d^8 s^2	−5 −10	1.3 2.5	4.3	1.3	14.0	2.3	−181.50						—
26	d^8 s^2	−5 −10	1.3 2.5	4.3	1.3	14.0	2.5	−183.58	9.10	−.74	−.50	−.23	−0.4	—
27	d^8 s^2	−5 −10	1.3 2.5	4.3	1.3	140	2.7	−184.79						—
28	d^8 s^2	−5 −10	1.3 2.5	4.3	1.3	14.0	3.0	−185.62						—
29	d^8 s^2	−5 −10	1.3 2.5	4.3	1.3	14.0	3.2	−185.80						—
30	d^8 s^2	−5 −10	1.3 2.5	4.3	1.3	14.0	3.5	−185.81						3.9
31	d^8 s^2	−5 −15	1.3 2.5	4.3	1.3	14.0	2.3	−181.68						—
32	d^8 s^2	−5 −15	1.3 2,5	4.3	1.3	14.0	2.5	−183.73	9.17	−.74	−.44	−.24	−.03	—
33	d^8 s^2	−5 −15	1.3 2.5	4.3	1.3	14.0	2.7	−184.90						—
34	d^8 s^2	−5 −15	1.3 2.5	4.3	1.3	14.0	3.0	−185.69						—
35	d^8 s^2	−5 −15	1.3 2.5	4.3	1.3	14.0	3.2	−185.80						—
36	d^8 s^2	−5 −15	1.3 2.5	4.3	1.3	140	3.5	−185.84						4.4
37	d^8 s^2	−7 −10	1.3 2.5	4.3	1.3	14.0	2.3	−182.71						—
38	d^8 s^2	−7 −10	1.3 2.5	4.3	1.3	14.0	2.5	−184.64	8.7	−1.07	−.65	−.27	−.12	—
39	d^8 s^2	−7 −10	1.3 2.5	4.3	1.3	14.0	2.7	−185.70	8.8					—
40	d^8 s^2	−7 −10	1.3 2.5	4.3	1.3	14.0	3.0	−186.36	8.8					—
41	d^8 s^2	−7 −10	1.3 25	4.3	1.3	14.0	3.2	−186.42						12.2
42	d^8 s^2	−7 −10	1.3 2.5	4.3	1.3	14.0	3.5	−186.26						—
43	d^8 s^2	−5 −10	1.3 2.5	3.0	1.0	7.0	2.5	−169.26	8.6	−.77	−.40	−.23	−.07	—
44	d^8 s^2	−5 −10	1.3 2.5	3.0	1.0	7.0	3.0	−172.18						1.2
45	d^8 s^2	−5 −10	1.3 2.5	3.0	1.0	7.0	3.5	−171.25						—
46	d^8 s^2	−5 −10	1.4 2.5	4.3	1.3	14.0	2.5	−187.10	9.42	−.66	−.42	−.26	−.04	—
47	d^8 s^2	−5 −10	1.4 2.5	4.3	1.3	14.0	2.7	−187.94						—
48	d^8 s^2	−5 −10	1.4 2.5	4.3	1.3	14.0	3.0	−188.42	9.53					—
49	d^8 s^2	−5 −10	1.4 2.5	4.3	1.3	14.0	3.2	−188.44						2.0
50	d^8 s^2	−5 −10	1.4 2.5	4.3	1.3	14.0	3.5	−188.42						—
51	d^8 s^2	−7 −10	1.4 2.5	4.3	1.3	14.0	2.7	−188 60	9.2	−.87	−.51	−.30	−.11	—
52	d^8 s^2	−7 −10	1.4 2.5	4.3	1.3	14.0	3.0	−188.92						8.6
53	d^8 s^2	−7 −10	1.4 25	4.3	1.3	14.0	3.2	−188.88						—
54	$d^{9.4}$ $s^{0.6}$	−5 −10	1 3 3.0	3.3	1.0	4.4	2.5	−226.14						—
55	$d^{9.4}$ $s^{0.6}$	−5 −10	1.3 3.0	3.3	1.0	4.4	2.7	−226.30						—
56	$d^{9.4}$ $s^{0.6}$	−5 −10	1.3 3.0	3.3	1.0	4.4	2.8	−226.33	9.44	−.74	−.55	−.36	−.18	7.4
57	$d^{9.4}$ $s^{0.6}$	−5 −10	1.3 3.0	3.3	1.0	4.4	3.0	−226.28						—
58	$d^{9.4}$ $s^{0.6}$	−5 −10	1.3 3.0	3.3	1.0	4.4	3.5	−226.09						
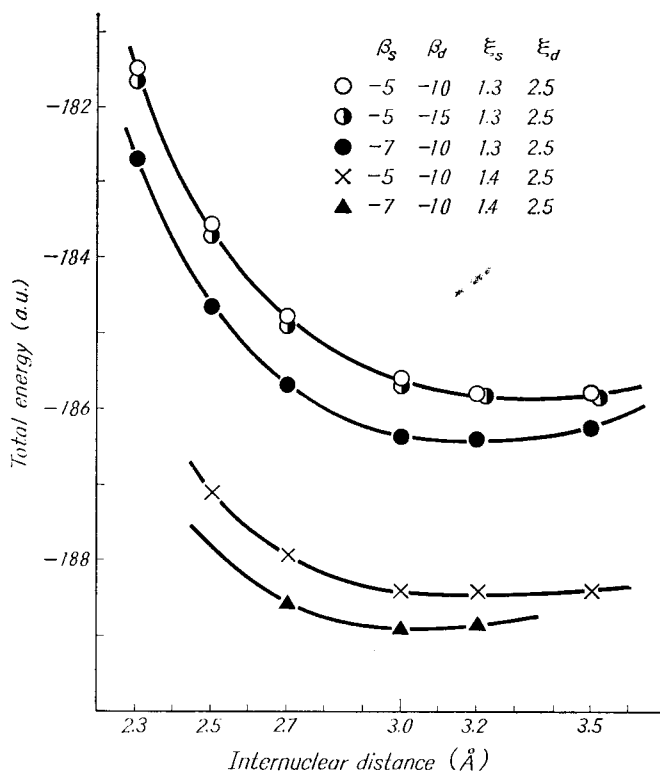
Figure 2. Energy vs. bond length for octahedral Ni₆ for various parameters.

little effect on r_{eq}, increasing $(1/2)(I_a + A_d)$ increase r_{eq}, and increasing β_s decreases r_{eq}.

The results of using an initial configuration with $d^{9.4}s^{0.6}$ are on lines 54 to 58 of Table 7. The reason for trying this configuration is that it matches that for bulk nickel. The results are not unreasonable in that r_{eq} is 2.8 Å and the average number of d electrons is 9.44 but the lowest d M.O. and the HOMO are somewhat too low. The normalized binding energy is also about 50% too high.

Conclusion

In summary the CNDO method presented has shown itself to be capable of producing reasonable values for the equilibrium interatomic distance, average number of d electrons, d band width, FERMI level, and binding energy. Since the s and p orbitals are primarily responsible for producing

the Ni–Ni bond, the values of β_s and ξ_s are most important in determining the internuclear distance. The width of the sp band is strongly dependent on β_s as is also the binding energy. The d band width had fairly reasonable values for most parameter sets; becoming much too large only when ξ_d was increased to 3.0 and 3.5 from the standard value of 2.5. The value of 10 eV used for $(1/2)(I_d + A_d)$ in order to get an average number of d electrons of about 9.4 is larger than the value of 6.2 estimated in Reference 13 but in view of the almost complete lack of electron affinity data this number is very approximate and the data in Reference 18 would lead to a higher estimate. The FERMI level as measured by the HOMO was surprisingly constant for a wide range of parameter selections.

Acknowledgement

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Parameter Selection in CNDO Calculations for Small Nickel Clusters

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