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AB INITIO LCAO/MO CLUSTER-TYPE CALCULATION OF
THE SELF CONSISTENT ELECTRONIC SCREENING
CHARGE DENSITY AROUND A SINGLE HYDROGEN
IMPURITY IN A NICKEL CRYSTAL.

RICE UNIVERSITY, PH.D., 1978

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Ab Initio LCAO/MO Cluster-Type Calculation of the
Self Consistent Electronic Screening Charge Density around a
Single Hydrogen Impurity in a Nickel Crystal

by

Russell Woodward Simpson

A THESIS SUBMITTED
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THESIS DIRECTOR'S SIGNATURE

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RICE UNIVERSITY
HOUSTON, TEXAS

FEBRUARY 1978

ABSTRACT

Ab Initio LCAO/MO Cluster-Type Calculation of the Self Consistent Electronic Screening Charge Density around a Single Hydrogen Impurity in a Nickel Crystal

Russell Woodward Simpson

The electronic structure for a Ni_6 cluster embedded in bulk Ni by use of a spin-averaged local-exchange self-consistent-field Ni crystal potential is calculated with an ab initio LCAO/MO variational method. A single H impurity is added at the cluster center (FCC octahedral interstitial site) and the H- Ni_6 electronic structure calculated iteratively until the change in charge density from the Ni_6 charge density is self-consistent within a radius of 2.0 a.u. from the proton. Plots of the charge density identify bonding and non-bonding cluster orbitals. The screening charge density is isotropic out to a radius of 1.0 a.u. and strongly anisotropic farther from the proton. A modified Mulliken population analysis indicates that the Ni 4s and 4p electrons play a much larger role than the Ni 3d electrons in screening the impurity. The variational basis is improved by adding functions on more distant Ni layers. The density of states for a Ni_{38} cluster agrees well with the Ni crystal DOS. For H- Ni_{38} , a non self-consistent charge density increase is found to be greater than the H- Ni_6 increase, and more like the atomic H charge density. These cluster results are compared to other H impurity screening calculations.

TABLE OF CONTENTS

ABSTRACT	ii
TABLE OF CONTENTS	iii
LIST OF FIGURES	v
LIST OF TABLES	vii
ACKNOWLEDGEMENTS	viii

Chapter	Page
---------	------

I.	INTRODUCTION	1
II.	THE LCAO MOLECULAR CLUSTER METHOD FOR A PERFECT CRYSTAL	
	A. Variational Method	7
	B. Pure Nickel Cluster Hamiltonian	11
	C. Symmetrized Basis Functions	13
	D. Calculation of Integrals	27
	E. Orthogonality to Core States	30
III.	RESULTS FOR PURE NICKEL CLUSTERS	
	A. Convergence in Orthogonality Layers of Eigenvalues and Charge Density	34
	B. Convergence in Valence Layers of Eigenvalues and Charge Density	37
	C. Density of States	41
IV.	THE LCAO MOLECULAR CLUSTER METHOD FOR A SINGLE HYDROGEN IMPURITY	
	A. Self-Consistency in Charge Density	46
	B. Octahedral Site Basis Functions	48

TABLE OF CONTENTS (continued)

Chapter	Page
C. Hydrogen Impurity Hamiltonian	51
D. Calculation of Integrals	53
V. RESULTS FOR HYDROGEN IMPURITY CLUSTERS	
A. First Approximate Calculation	54
B. Self Consistency in Charge Density Change ...	56
C. Molecular Orbital Charge Density Plots	60
D. Density of States	69
E. Three-Valence-Layer Cluster Ni_{38}	71
VI. DISCUSSION	
A. Electronic Screening of the Proton	75
B. Possible Improvements in the Cluster Method	79
Appendix A. GAUSSIAN INTEGRALS	81
Appendix B. OVERLAPPING ATOMIC POTENTIAL	88
Appendix C. EWALD DECOMPOSITION OF CRYSTAL POTENTIAL	94
Appendix D. DENSITY OF STATES SMOOTHING FUNCTIONS	97
Appendix E. WEIGHTING SCHEME FOR AVERAGING OVER DIRECTIONS (100), (110), (111)	99
Appendix F. MULLIKEN POPULATION ANALYSIS	100
REFERENCES	102

LIST OF FIGURES

Figure	Page
1. H impurity surrounded by 6 Ni atoms and 32 Ni core-states	4
2. Flowchart overview of molecular cluster approach ..	6
3. Flowchart of steps in LCAO molecular cluster calculation for a perfect crystal	10
4. Block diagonalization of 54x54 Hamiltonian matrix for 1 layer of 6 Ni atoms	16
5. Symmetrized orbitals a_{1g}	18
6. Symmetrized orbitals t_{1u}	19
7. Symmetrized orbitals t_{2g}	20
8. Symmetrized orbitals e_g	21
9. Symmetrized orbitals e_g	22
10. Nickel 3d atomic and "optimized" orbitals	26
11. Zero integrals and integrals equivalent by symmetry	28
12. Convergence of a_{1g} roots with number of orthogonality layers	35
13. Convergence of octahedral site charge density of the one-valence-layer Ni_6 cluster with number of orthogonality layers	38
14. Convergence of octahedral site charge density with number of valence layers	40
15. Density of states for Ni_{38} compared to the Ni crystal DOS	42

LIST OF FIGURES (continued)

Figure	Page
16. Flowchart of steps in LCAO molecular cluster calculation for a crystal with a single hydrogen impurity	47
17. Range comparison of two octahedral site Gaussian Type Orbital (GTO) basis sets	50
18. Change in electron density in the (100) direction for the one-valence-layer H-Ni ₆ cluster	55
19. Radial charge density change for the one-valence-layer H-Ni ₆ cluster	58
20. Ni 3d basis function density plot	61
21. Ni 4s and 4p basis functions density plots	62
22. Ni ₆ and H-Ni ₆ 1a _{1g} molecular orbital density plots	64
23. Ni ₆ and H-Ni ₆ 2a _{1g} molecular orbital density plots	67
24. Ni ₆ and H-Ni ₆ 3a _{1g} molecular orbital density plots	68
25. Density of states for H-Ni ₆ compared to the Ni ₆ DOS	70
26. Change in electron density for H-Ni ₆ and H-Ni ₃₈ clusters	73
27. Change in electron density for several impurity calculations	76
28. Radial charge density change for several calculations	78

LIST OF TABLES

Table	Page
I. Gaussian exponential parameters α and the linear coefficients of nickel atomic orbital expansions ...	24
II. Location and number of atoms in clusters of nickel atoms centered on the octahedral interstitial site	36
III. Approximately self-consistent charge density change due to a hydrogen impurity in nickel	59
IV. Mulliken population analysis of a_{1g} molecular orbitals for Ni_6 and $H-Ni_6$ clusters	65

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Chapter I

INTRODUCTION

The interactions of hydrogen with metals need to be understood in order to control metallic embrittlement and corrosion. The materials most affected are those which contain hydrocarbon fuels and hydrogen itself as a fuel.¹ Theoretical studies of the electronic structure of dilute metal-hydrogen systems are recommended as promising by the American Physical Society study group on radiation effects on materials.² Recently calculations have been made for concentrated systems containing enough hydrogen to form metal hydrides.³⁻⁶ The extreme case of dilution is one hydrogen impurity in a metal crystal. The screening of the proton by the electronic charge density is very important in dilute solutions.⁷ The charge density surrounding a proton immersed in "jellium," a smeared out average charge density of the nuclei in a solid, has been calculated.⁸⁻⁹ The discrete nuclei have been used in model calculations of one hydrogen atom in palladium¹⁰ and in nickel.¹¹ These previous efforts have motivated the current ab initio calculation of the electronic structure of a hydrogen atom in a transition metal crystal.

The presence of the hydrogen as a point defect destroys the translational symmetry of a perfect metal crystal. Only if identical defects are introduced in a "superlattice" with a Large Unit Cell (LUC)¹² can the band structure methods

which depend on periodic boundary conditions be used.

However the LCAO molecular cluster method can be applied to a single point defect. Chaney has employed this variational method to study the F color center in lithium fluoride.^{13, 14}

The linear combination of atomic orbitals (LCAO) method has had its greatest difficulty reduced by the introduction of Gaussian Type Orbitals (GTO) as basis functions.^{15, 16} The simple transformation properties of GTO's facilitate the calculation of multi-center integrals, as shown in Appendix A. This extended LCAO method has been applied successfully to compounds (LiF^{17, 18} and CaO¹⁹), semiconductors (Si^{18, 20, 21, 22, 23}), polyethylene²⁴, (SN)_x in a one-dimensional chain and in a three-dimensional crystal²⁵, simple metals (Li^{16, 26, 27}, Na^{20, 28}, K^{28, 29}, and Al³⁰), and transition metals (Ni^{31, 32}, Fe³³, Cr³⁴). Molecular cluster methods have been used in studies on both amorphous²³ and crystalline¹⁸ silicon.

Nickel has been chosen as a specific hydrogen host transition metal for which a Self Consistent Field (SCF) calculation³¹ had been made. For their LCAO band structure, Callaway and Wang used a local density exchange approximation,³⁵ with different exchange potentials for majority and minority spins. The Coulomb potential Fourier coefficients were self-consistent to .001 Hartree.

Nickel dissolves only 4.5×10^{-5} atomic ratio of hydrogen at room temperature,³⁶ so a LUC band structure

calculation would require a prohibitively large unit cell. The hydrogen occupies an interstitial site with octahedral coordination in the nickel lattice.¹ We will consider clusters of nickel atoms surrounding a hydrogen atom at the octahedral site, which is the center of the nickel Face Centered Cubic (FCC) unit cell. Fig. 1 shows a cluster of 38 nickel atoms around one hydrogen atom. The $(1\bar{1}\bar{1})$ crystal planes of nickel atoms are clearly depicted.

The potential energy of the entire nickel crystal is utilized in the cluster Hamiltonian in order to minimize artificial effects due to the "surface" of the clusters. The spin-restricted cluster Hamiltonian is that of Callaway and Wang³¹ with the majority and minority spin exchange potentials averaged. Thus the molecular cluster is "embedded" in the bulk nickel crystal. In order to study the perturbation of the hydrogen atom, calculations of the one-electron energies, wave functions, and charge density are made of the same size clusters with hydrogen present and without it.

Simpson, Lane, and Chaney³⁷ have previously reported the hydrogen-induced charge density for a cluster of 6 nickel atoms with nearby nickel core-states included for orthogonalization. Fig. 1 shows this configuration with the two types of nickel states drawn different sizes. The valence states of the 6 nickel atoms must be orthogonal to all lower lying core-states in the crystal and the 32 nickel core-states partially accomplish this, as will be explained

later.

The charge density in this first attempt was not self-consistent. This effort is an extension to include charge density self-consistency, larger clusters of nickel atoms, and more surrounding layers of orthogonal nickel core-states. Fig. 2 shows a flow chart of this overall approach. In Chapter II, the application of the LCAO molecular cluster method to a perfect nickel crystal is explained, and the results are presented in Chapter III. The iterative technique used to achieve self-consistency of the hydrogen impurity charge density is given in Chapter IV. The resulting energies and charge densities are compared in Chapter V to the pure nickel cluster values. Chapter VI is a discussion of the physical insights gained.

Fig. 2. FLOWCHART OVERVIEW OF MOLECULAR CLUSTER APPROACH

Chapter II

THE LCAO MOLECULAR CLUSTER METHOD FOR A PERFECT CRYSTAL

A. Variational Method

A variational method is employed to determine approximate eigenfunctions of the one-electron Schrodinger equation,

$$H \psi_i(\vec{r}) = E_i \psi_i(\vec{r}) \quad . \quad (1)$$

A trial wave function is expanded as a linear combination of "atomic" orbitals (LCAO),

$$\psi_i(\vec{r}) = \sum_{j=1}^N a_{ij} \phi_j(\vec{r}) \quad . \quad (2)$$

However the orbitals $\phi_j(\vec{r})$ need not be limited to atomic orbitals.

The expansion coefficients a_{ij} can be determined by a variational procedure which minimizes the eigenvalues E_i . Substitution of Eq. 2 into Eq. 1 and multiplication by $\phi_i^*(\vec{r})$, obtains

$$\phi_i^*(\vec{r}) H \sum_j a_{ij} \phi_j(\vec{r}) = \phi_i^*(\vec{r}) E_i \sum_j a_{ij} \phi_j(\vec{r}) \quad . \quad (3)$$

Then upon integrating,

$$\sum_j a_{ij} \langle \varphi_i | \mathcal{H} | \varphi_j \rangle = \sum_j a_{ij} E_i \langle \varphi_i | \varphi_j \rangle, \quad (4)$$

for each orbital $\varphi_i(\vec{r})$, $i = 1, \dots, N$. We define the Hamiltonian matrix element

$$\mathcal{H}_{ij} \equiv \langle \varphi_i | \mathcal{H} | \varphi_j \rangle = \int d^3r \varphi_i^*(\vec{r}) \mathcal{H} \varphi_j(\vec{r}), \quad (5)$$

and the overlap matrix element

$$S_{ij} \equiv \langle \varphi_i | \varphi_j \rangle = \int d^3r \varphi_i^*(\vec{r}) \varphi_j(\vec{r}). \quad (6)$$

The set of equations in Eq. 4 then become

$$\sum_{j=1}^N a_{ij} (\mathcal{H}_{ij} - E_i S_{ij}) = 0, \quad i = 1, \dots, N. \quad (7)$$

This set of linear homogenous equations for the coefficients a_{ij} can have non-trivial solutions only if the secular equation

$$\det |\mathcal{H}_{ij} - E_i S_{ij}| = 0, \quad (8)$$

is satisfied. Multiplying by the overlap matrix inverse we see by

$$\det |S_{ik}^{-1} \mathcal{H}_{kj}| = \det |E_i S_{ij}|, \quad (9)$$

that the product matrix $S_{ik}^{-1} H_{kj}$ should be diagonal. The unitary transformation which accomplishes this diagonalization also transforms the unit matrix into the expansion coefficients a_{ij} , each row i corresponding to an eigenvalue E_i .

Therefore in any LCAO method one calculates the Hamiltonian and overlap matrices and then diagonalizes $S_{ik}^{-1} H_{kj}$ to obtain minimum eigenvalues E_i and their eigenvectors $\psi_i = \sum_j a_{ij} \phi_j$. In the molecular cluster LCAO method we employ a basis set of "atomic" orbitals which have been combined into molecular orbitals. Each "molecule" is a cluster of nickel atoms. Fig. 3 shows a graphic flow chart of the steps in the LCAO molecular cluster method as applied to a perfect crystal of nickel. In Section B of this chapter the Hamiltonian is discussed further. Section C describes the advantages of symmetrized basis functions and the method of their construction from "atomic" orbitals and in turn, from Gaussian Type Orbitals (GTO). In Section D the calculation of multicenter integrals is outlined. The Orthogonalized Linear Combination of Atomic Orbitals (OLCAO), a convenient variation in the LCAO method, is presented in Section E.

Fig. 3 FLOWCHART OF STEPS IN LCAO MOLECULAR CLUSTER CALCULATION FOR A PERFECT CRYSTAL.

B. Pure Nickel Cluster Hamiltonian

The one-electron Hamiltonian used for the pure nickel clusters is

$$\mathcal{H}^{Ni} = -\frac{1}{2} \nabla^2 + V^{Ni}(\vec{r}) \quad , \quad (10)$$

where $V^{Ni}(\vec{r})$ is the average over the majority and minority spins of the Self Consistent Field (SCF) nickel crystal potential of Callaway and Wang³¹. The nickel crystal potential is utilized in the Hamiltonian in order to avoid artificial effects due to the "surface" of the clusters. In order to facilitate the computation of multicenter integrals, the crystal potential is expanded in a Fourier series as

$$V^{Ni}(\vec{r}) = \sum_{\vec{K}} V^{Ni}(\vec{K}) \cos \vec{K} \cdot \vec{r} \quad . \quad (11)$$

For each reciprocal lattice vector $\vec{K}$, the Fourier coefficient of the SCF potential is given by

$$V^{Ni}(\vec{K}) = V^{OAP}(\vec{K}) + \overline{\Delta V}^{SCF}(\vec{K}) \quad . \quad (12)$$

Here $V^{OAP}(\vec{K})$ is a Fourier coefficient of an Overlapping Atomic Potential formed by the superposition of the charge densities of neutral nickel atoms ($3d^9 4s^1$) in a face centered cubic (FCC) lattice. The lattice constant *

* The lattice is not allowed to relax upon introduction of the impurity, so the constant repulsive energy of the nickel nuclei is not included in the Hamiltonian.

$a = 6.644$ a.u. is that used by Callaway and Wang to construct $V^{OAP}(\vec{K})$ as the starting potential for their calculation. $\overline{\Delta V}^{SCF}(\vec{K})$ is the average of the crystal potential increments for the two spins which transform the starting potential to the SCF potential.

The Fourier coefficients of the OAP are given by

$$V^{OAP}(\vec{K}) = \frac{1}{N\Omega} \int d^3r \, e^{-i\vec{K}\cdot\vec{r}} \left\{ \left[\sum_{\mu} V_{\text{atomic}}^{\text{Coulomb}}(\vec{r} - \vec{R}_{\mu}) \right] + V^{\text{exchange}}(\vec{r}) \right\}. \quad (13)$$

The real-space Coulomb potential is the sum over each nickel atom μ of

$$V_{\text{atomic}}^{\text{Coulomb}}(\vec{r}) = -\frac{Z}{|\vec{r}|} + \int d^3r' \frac{\rho_{\text{atomic}}(\vec{r}')}{|\vec{r} - \vec{r}'|}, \quad (14)$$

where the atomic number Z is 28 for nickel, and $\rho_{\text{atomic}}(\vec{r}')$ is the electronic charge density of a neutral nickel atom ($3d^9 4s^1$). Atomic units with $\hbar = m = e = 1$ are used, so the unit of energy is 1 Hartree = 27.2 eV and the unit of length, 1 Bohr radius = .529 Å.

The exchange potential is approximated by the Slater X_{α} local density exchange term with $\alpha = 2/3$, which is the Kohn-Sham³⁵ value.[‡]

[‡] Callaway and Wang found $\alpha = 2/3$ to give a ferromagnetic band structure in better agreement with experiments than that of $\alpha = .972$ which had been used in an earlier non-self consistent calculation.

$$V_{(\vec{r})}^{\text{exchange}} \simeq \frac{2}{3} \left\{ -3 \left[\frac{3}{8\pi} \rho_{\text{crystal}}(\vec{r}) \right]^{1/3} \right\} = - \left[\frac{3}{\pi} \rho_{\text{crystal}}(\vec{r}) \right]^{1/3}, \quad (15)$$

where $\rho_{\text{crystal}}(\vec{r})$ is the superposition of atomic charge densities. The OAP calculation is described in more detail in Appendix B.

For narrow GTO's the real-space region very near a nickel nucleus is important and the Fourier sum must contain many more terms in reciprocal-space than are necessary for diffuse GTO's. An Ewald-type procedure similar to that described by Chaney et al.,¹⁶ is used to separate the potential into a more rapidly convergent Fourier series and a real-space portion. Appendix C contains an explanation of this procedure.

The crystal potential Fourier series in Eq. 11 has been truncated at 923 independent reciprocal-space vectors. These comprise all vectors with $|\vec{K}| \leq 32(\frac{2\pi}{a})$ which lie in the unique 1/48th sector of the Brillouin Zone. The convergence of this Fourier potential was checked by increasing the number of independent reciprocal space vectors to 3223, i.e. all vectors with $|\vec{K}| \leq 50(\frac{2\pi}{a})$. The 4s and 3d eigenvalues only changed by .001 Hartree.

C. Symmetrized Basis Functions

The symmetry properties of the crystal Hamiltonian are exploited in order to reduce the size of the secular equation to be diagonalized. No translational symmetry is

assumed, since it will not be present when the defect is considered. However, the point group symmetry of clusters centered on the octahedral site is that of the full octahedral group O_h . This means that a symmetry operator R of the octahedral point group will commute with the Hamiltonian $\mathcal{H}$,

$$R \mathcal{H} = \mathcal{H} R \quad . \quad (16)$$

If these products are expanded in a matrix representation based on eigenfunctions of R , we have:

$$\sum_j R_{ij} \mathcal{H}_{jk} = \sum_j \mathcal{H}_{ij} R_{jk} \quad . \quad (17)$$

Since this representation is based on eigenfunctions of R , R has a diagonal matrix and each sum becomes a single term, i.e.

$$R_{ii} \mathcal{H}_{ik} = \mathcal{H}_{ik} R_{kk} \quad . \quad (18)$$

Therefore

$$(R_{ii} - R_{kk}) \mathcal{H}_{ik} = 0 \quad . \quad (19)$$

This implies that the matrix element $\mathcal{H}_{ik}$ between basis functions of different symmetry eigenvalues R_{ii} and R_{kk} must be zero. The Hamiltonian can therefore be "block diagonalized" into non-interacting blocks by constructing basis functions which are eigenfunctions of the octahedral

symmetry group.

For example a cluster of 6 nickel atoms with 1s, 2s, 3s, and 4s basis functions, 2p, 3p, and 4p basis functions (x, y, and z) and 3d basis functions (xy, xz, yz, $2z^2 - x^2 - y^2$, and $x^2 - y^2$) would give rise to a 54x54 secular equation.

$$6 \text{ atoms} \times \left(1 \frac{s \text{ orbital}}{\text{atom}} + 3 \frac{p \text{ orbitals}}{\text{atom}} + 5 \frac{d \text{ orbitals}}{\text{atom}} \right) = 54 \text{ orbitals} . \quad (20)$$

But this Hamiltonian matrix can be block diagonalized into four 1x1, three 2x2, seven 3x3, two 4x4, and three 5x5 submatrices. Many of these are degenerate, so only one 2x2, three 3x3, one 4x4, and one 5x5 need be diagonalized.

Fig. 4 indicates this decomposition schematically.

The basis functions for the variational calculation are linear combinations of atomic orbitals into molecular orbitals (LCAO/MO). Each "molecule" consists of nickel atoms surrounding the empty octahedral site. A cluster layer is made up of the nickel lattice sites which are transformed into each other under the 48 operations of the full octahedral point group. For each layer λ and irreducible representation Γ of the symmetry group we construct symmetrized basis functions

$$\Phi_{\lambda\Gamma} = \sum_{\mu}^{N_{\lambda}} a_{\mu\Gamma}^{lmn} \chi(\vec{R}_{\mu}, l, m, n) , \quad (21)$$

where $\vec{R}_{\mu}$ is the location of the μ th atom in layer λ .

FIG. 4. Block diagonalization of 54x54 Hamiltonian matrix for 1 layer of 6 Ni atoms. The submatrices which must be diagonalized are shaded and their rank is indicated. Matrix elements which are not in the diagonal blocks are all equal to zero.

χ is an atomic orbital at that site with parameters l, m, n , to be described later.

A symmetrized orbital for a layer is the set of atomic orbitals constructed by applying all 48 operations of the octahedral point group to a prototype atomic wave function at one layer site, e.g. to a p_x function at $(\frac{a}{2}, 0, 0)$. This procedure generates the proper orbitals at each of the lattice sites, e.g. six operations each transform the p_x at $(\frac{a}{2}, 0, 0)$ to a p_y at $(0, \frac{a}{2}, 0)$. The symmetrizing coefficients $a_{\mu\Gamma}^{lmn}$ are a product of the number of group operations creating the atomic orbital $\chi(\vec{R}_\mu, l, m, n)$ with a matrix element of the irreducible representation Γ .

If these coefficients are zero for all sites in a layer, then the type of atomic orbitals being considered cannot in that layer transform according to the irreducible representation used, (e.g. the representation a_{1u} has no symmetrized basis functions in layer 1).

Symmetrized basis functions of layer 1 are portrayed three dimensionally in Figs. 5-9. For the representations t_{1u} and t_{2g} of dimension three, only those symmetrized basis functions having the x-axis as a special symmetry axis have been shown in Fig. 6 and 7. Mere rotation of the x-axis to the y- or z-axis produces the other basis partners. For the representation e_g of dimension two, however, both sets of basis functions are shown in Fig. 8 and 9. If the orbital resulting from rotating the x-axis into the y-axis for a basis function shown in Fig. 8 has the sign of each

FIG. 5. Symmetrized orbitals a_{1g} . Cluster basis functions are constructed from Ni atomic wave functions at 6 lattice sites to transform according to the totally symmetric a_{1g} , or "s-type", irreducible representation of the octahedral point group. The positive lobes of the atomic wave functions are shaded in the figure, negative lobes are unshaded, and the magnitude is noted beside any lobe which has a relative magnitude other than 1.

FIG. 6. Symmetrized orbitals t_{1u} . These "p-type" cluster basis functions are triply degenerate and only those basis functions which are symmetric about the x-axis are shown. Each basis function shown has two partners symmetric about the y- and z-axes.

FIG. 7. Symmetrized orbitals t_{2g} . These "d_{xy}-type" cluster basis functions are triply degenerate and only those basis functions which are symmetric about the x-axis are shown.

FIG. 8. Symmetrized orbitals e_g . These " $d_{z^2-y^2}$ -type" cluster basis functions are doubly degenerate with the " $d_{2x^2-y^2-z^2}$ -type" basis functions shown in Fig. 9.

FIG. 9. Symmetrized orbitals e_g . These " $d_{2x^2-y^2-z^2}$ - type" cluster basis functions are doubly degenerate with the " $d_{z^2-y^2}$ - type" basis functions shown in Fig. 8.

atomic wave function reversed, then is superimposed with the orbital resulting from rotating the x-axis into the z-axis, their sum is the corresponding basis function in Fig. 9.

The nickel atomic orbitals $\chi(\vec{R}_\mu, l, m, n)$ in Eq. 21 are a linear combination or "contraction" of Gaussian Type Orbitals (GTO's),

$$\chi(\vec{R}_\mu, l, m, n) = \sum_i b_i^{lmn} \theta(\vec{R}_\mu, \alpha_i, l, m, n). \quad (22)$$

A single GTO with exponential parameter α and center $\vec{A}$ is defined as

$$\theta(\vec{A}, \alpha, l, m, n) = x_A^l y_A^m z_A^n \exp(-\alpha r_A^2), \quad (23)$$

where $x_A^l \equiv (x - A_x)^l$.

The atomic orbitals used are nickel 1s, 2s, 2p, 3s, 3p, 3d, 4s, and 4p atomic wave functions. The exponential parameters were determined by Wachters³⁸ in a self consistent field (SCF) calculation for the free nickel atom. The linear coefficients are also Wachters', with the exception of the 3d orbitals which have coefficients adjusted to the nickel crystalline environment. Table I lists the values we use.

The nickel 3d coefficients are determined by calculating an "optimized orbital" for the crystalline environment.²⁷ The five d-type GTO's are used as independent basis functions in a variational calculation

TABLE 1. Gaussian exponential parameters α and the linear coefficients of nickel atomic orbital expansions.

α	1s	2s	3s	4s
284878.	2.81225	-.878829	.351532	-.0878829
41997.9	5.14358	-1.56817	.585449	-.125453
9627.67	8.68657	-2.70157	1.00443	-.207813
2761.96	13.3757	-4.19519	1.58575	-.323125
920.488	17.8059	-6.04330	2.26654	-.460930
341.805	18.4924	-7.09103	2.77273	-.569957
138.023	11.6158	-6.50531	2.55339	-.520895
59.2587	2.92051	-1.65266	.804944	-.172771
20.3712	.0973156	3.67510	-2.24502	.491430
8.59400	-.00722617	2.09226	-1.71596	.383488
2.39417	.000754465	.0718525	.947526	-.263843
.918169	-.000173810	-.00589618	.386581	-.190864
.130176	.00000926743	.000321271	.00170521	.0886276
.046392	-.00000213729	-.0000676809	-.000218004	.0399346

α	2p	3p	4p
1774.18	48.4183	-17.8901	2.79021
423.403	63.9796	-23.7904	3.64111
138.311	70.3550	-27.1657	4.25267
53.1703	57.7665	-23.2224	3.56922
22.3874	30.1852	-13.2927	2.14627
9.92848	7.39624	-1.85521	.207251
4.11625	.410763	3.05861	-.521330
1.71031	-.00225823	1.54098	-.332239
.672528	.000833392	.203495	-.0128568
.146588	.0	.0	.0617564
.044447	.0	.0	.0182839

α	3d
48.9403	40.5986
13.7169	23.8299
4.63951	8.73160
1.57433	1.54599
.486409	.180801

with the nickel SCF crystal potential. The eigenvector with a 3d-band eigenvalue (-.1870 Hartree) contains the linear coefficients we use in our cluster 3d "optimized" orbital. The three shortest range GTO's have had their linear coefficients changed by less than +/- 1% from the nickel free atom values. The longest and next longest range GTO's have coefficients changed by +16% and -9%, respectively. This adjustment to the crystalline environment gives the cluster 3d basis functions somewhat longer range than the nickel free atom wave functions, as shown in Fig. 10.

The basis set described so far is a minimal basis set for a nickel crystal calculation plus the Ni 4p excited state basis function. This basis set cannot adequately represent the wave functions in the region immediately surrounding a hydrogen impurity. The variational freedom of the basis set must be increased at the cluster center. This is done by introducing four single GTO's at the octahedral site as independent basis functions. The single GTO's are all s-type and transform according to a_{1g} the totally symmetric representation. The exponential parameters and their selection criteria are given in Section IV-C on the augmented basis set for the hydrogen impurity clusters.

This basis set including the additional four single GTO's in the representation a_{1g} is used in calculations for the pure nickel clusters and for the hydrogen impurity clusters. In this way, only the Hamiltonian is changed when comparing clusters with and without hydrogen.

FIG. 10. Nickel 3d atomic and "optimized" orbitals. The radial parts of the wave functions are plotted vs the distance r from the nucleus. The wave functions are multiplied by 10 for r between 2.0 and 4.0 a.u.

D. Calculation of Integrals

Integrals involving GTO's are evaluated using the expressions given in Appendix A. Matrix elements are to be calculated over the symmetrized orbitals described in the previous section, rather than over "single" GTO's. The symmetrized orbitals are defined in terms of atomic orbitals, which are "contractions" or linear combinations of GTO's. Three techniques are employed to reduce the number of integrals over single GTO's which must be evaluated.

Those integrals which must be zero because of the symmetry and location of the atomic orbitals are identified so they need not be evaluated. There are reflection planes through p and d atomic orbitals across which these orbitals are odd, e.e. spatially reflected with opposite sign. An integral over an odd orbital with an orbital even with respect to that plane must be zero. Fig. 11a shows two such examples.

The number of integrals over "contracted" atomic orbitals is further reduced by using the translational and rotational symmetry of the crystal lattice to recognize equivalent integrals. The atomic orbitals are translated so the one with the lower orbital quantum number is at the origin, then rotated to produce a relative separation with components

$$\overline{AB}_x \quad A_x \geq A_y \geq A_z \geq 0 \quad (24)$$

FIG. 11. Zero integrals and integrals equivalent by symmetry.

p_z at (000) , s at $(0a0)$

d_{xy} at (000) , p_y at $(0a0)$

FIG. 11a. Orbitals which have zero overlap integrals by their symmetry and relative placement.

p_y at $(0a0)$

d_{xy} at $(a00)$

p_y at (000)

d_{xy} at $(a00)$

$-p_x$ at (000)

$-d_{xy}$ at $(aa0)$

FIG. 11b. Orbitals which are first translated, then rotated to the standard form used to recognize integrals which are equivalent.

For example Hamiltonian and overlap integrals over a P_y orbital located at $(0, a, 0)$ and a d_{xy} orbital at $(a, 0, 0)$ are equivalent to integrals over a $-P_x$ orbital at the origin and a $-d_{xy}$ orbital at $(a, a, 0)$. The p orbitals may be nickel 2p, 3p, or 4p atomic orbitals, and a is the FCC lattice constant. This example is shown in Fig. 11b.

An integral "request list" as suggested by Clementi and Davis³⁹ has been incorporated to store Hamiltonian and overlap integrals over "contracted" atomic orbitals at given separation distances. When integrals are needed to sum up a matrix element, the request list is first searched and only if the integrals are not stored must they be evaluated. The integrals are identified by a coded number containing the atomic orbital types and their relative separation. This information is "packed" in the form

$$\begin{aligned} ID = & (n_A - l_A) \times 10^6 + (l_A + 1) \times 10^5 \\ & + (n_B - l_B) \times 10^4 + (l_B + 1) \times 10^3 \\ & + \left\{ \frac{AB_x}{a/2} - 9 \right\} \times 10^2 + \left\{ \frac{AB_y}{a/2} - 9 \right\} \times 10^1 + \left\{ \frac{AB_z}{a/2} - 9 \right\}, \end{aligned} \quad (25)$$

where the principal and orbital quantum numbers of the atomic orbital at lattice site $\vec{A}$ are n_A and l_A , those at $\vec{B}$ are n_B and l_B , and $\overline{AB}$ is the distance in a.u. between $\vec{A}$ and $\vec{B}$. Even though Gaussian techniques have made

multicenter integral calculation relatively simple, it is much quicker to look up an integral than to recalculate it.

E. Orthogonality to Core States

The infinite crystal potential exploited in a cluster Hamiltonian includes the potentials of Ni atoms both inside and outside the cluster. When the cluster basis functions extend to these exterior Ni sites which have no basis functions located on them, the linear variational scheme will attempt to represent the Ni core-states (1s, 2s, 2p, 3s, and 3p) at these sites. This distorts the eigenfunctions of the valence-states within the cluster and lowers their eigenvalues by as much as .5 Hartree.

To avoid this deterioration of the accuracy of the valence-state energies, the cluster basis set can be augmented with Ni core-state basis functions in "cushion layers" surrounding the layers of complete nickel atoms. The valence functions are required in the matrix diagonalization to be orthogonal to these cushion layer functions and do not mimic their core-states. This method was used by Menzel et al.¹⁸ In their cluster calculation of the electronic structures of pure silicon and lithium fluoride crystals.

Ching and Lin²¹ employed the technique of Orthogonalized Linear Combination of Atomic Orbitals (OLCAO)

In their study of the electronic energy bands of Si III. The orthogonalization of valence basis functions to core basis functions is done with the aim of reducing the size of the secular equation to be diagonalized for this infinite crystal, rather than to avoid contamination of valence eigenfunctions by core-states. Both of these purposes are served by the OLCAO scheme in Ching, Lin, and Huber's later paper ²³ on the electronic structure of amorphous silicon which contains cluster calculations.

The OLCAO method is used in most of the present work, after having included the "cushion layer" of core-states in the secular equation diagonalization during the earlier phases of work. The nickel energy eigenvalues calculated by these two different methods of handling core-states differ by no more than .0009 Hartree. Similarly Ching and Lin ²¹ found that Si III energies calculated by the OLCAO method agreed within .0008 Hartree with energies gotten by using the usual LCAO method with all core-states included. We find the OLCAO root always to be the lower of any such eigenvalue pair being considered. Since the OLCAO valence eigenfunctions are orthogonal to atomic core functions, their energies are slightly lower than those of the LCAO valence eigenfunctions which are orthogonal to the LCAO crystal core eigenfunctions.

The orthogonalized valence basis functions ϕ'_i are given by

$$\phi_i' = \phi_i + \sum_k b_{ik} \phi_k^c, \quad (26)$$

where ϕ_i and ϕ_k^c are the non-orthogonal valence and core basis functions respectively.

Orthogonality means that for the overlap matrix elements S_{ij}'

$$S_{ij}' = \langle \phi_i' | \phi_j^c \rangle = 0. \quad (27)$$

This gives rise to a set of simultaneous linear equations for the coefficients b_{ik}

$$\sum_k b_{ik} S_{kj} = -S_{ij}, \quad (28)$$

where

i runs over all valence basis functions,

j runs over all core basis functions,

and the k summation is over all core basis functions.

Then the Hamiltonian matrix element between the orthogonalized valence basis functions ϕ_i' and ϕ_j' is

$$H_{ij}' = H_{ij} + \sum_k b_{ik} H_{kj} + \sum_l b_{jl} H_{il} + \sum_k \sum_l b_{ik} b_{jl} H_{kl}. \quad (29)$$

Substituting S for H gives the relationship for the orthogonalized basis overlap S_{ij}' .

Solving the linear equations before diagonalizing the smaller orthogonalized valence function secular equation is a faster computation but requires that the same number of integrals be evaluated over the non-orthogonal basis

functions.

Although the original impetus was to eliminate from the secular equation matrix elements over core basis functions from outside the cluster, this formalism is not so restricted. Therefore the valence basis functions are made orthogonal to the core basis functions within the cluster also, further reducing the dimensionality of the secular equation.

Chapter III

RESULTS FOR PURE NICKEL CLUSTERS

A. Convergence in Orthogonality Layers of Eigenvalues and Charge Density

The Orthogonalized Linear Combination of Atomic Orbitals (OLCAO) technique of preventing the valence eigenfunctions from being contaminated by core-state character was presented in Section II-C. The number of layers of orthogonal core basis functions necessary for accurate valence energies is determined by comparison of roots of the irreducible representation a_{1g} which have been calculated with clusters containing different orthogonal layers. Fig. 12 shows the convergence of these eigenvalues with increasing number of orthogonal layers. The three a_{1g} roots of layer 1 are stable to within .002 Hartree when orthogonal to core-states in layers 1 through 6. Table II shows that the minimum distance squared (in units of $a^2/4 = 11.04$ a.u.) between layers 1 and 6 is $6 \times a^2/4 = 66.21$ a.u.² Similarly all the valence roots of layer 2 have converged to within .002 Hartree when made orthogonal to core-states on all 9 layers within 8.1 a.u. of layer 2.

The orthogonality layer convergence is determined by the longest range GTO, the Ni 4s orbital with an exponential parameter of .046. If the nickel 4s atomic orbital were to

FIG. 12. Convergence of a_{1g} roots with number of orthogonality layers. For each cluster the valence root with lowest energy is labeled $1a_{1g}$. (a) one-valence-layer Ni_6 cluster. (b) two-valence-layer Ni_{14} cluster.

TABLE II. Location and number of atoms in clusters of nickel atoms centered on the octahedral interstitial site. Atom site is in units of $a/2 = 3.322a.u.$ The distance squared to each layer from layers 0, 1, 2, and 3 is in units of $(a/2)^2 = 11.04a.u.^2$

layer label	atom site	number atoms in layer	total number atoms in cluster	distance squared to atom from layers L=0,1,2,3			
				L=0	L=1	L=2	L=3
0	0,0,0	0	0	0			
1	1,0,0	6	6	1	0		
2	1,1,1	8	14	3	2	0	
3	2,1,0	24	38	5	2	2	0
4	2,2,1	24	62	9	6	2	2
5	3,0,0	6	68	9	4	6	2
6	3,1,1	24	92	11	6	4	2
7	3,2,0	24	116	13	8	6	2
8	4,1,0	24	140	17	10	10	4
9	3,2,2	24	164	17	12	6	6
10	3,3,1	24	188	19	14	8	6
11	4,2,1	48	236	21	14	10	6
12	4,3,0	24	260	25	18	14	8
13	5,0,0	6	266	25	16	18	10
14	5,1,1	24	290	27	18	16	10
15	3,3,3	8	298	27	22	12	14
16	5,2,0	24	322	29	20	18	10
17	4,3,2	48	370	29	22	14	12

be replaced with an optimized orbital²⁷ not containing the extremely long .046 GTO, far fewer orthogonality layers would probably be required. The convergence with orthogonality layers of the one layer charge density at the empty octahedral site is shown in Fig. 13. The charge densities due to one root, the sum of two roots, and the sum of all three a_{1g} roots of layer 1 are shown to be converged well within .001 a.u. when six orthogonal layers have been used. Since only the totally symmetric representation can have charge at the cluster center, the top line in Fig. 13 is the total charge density for the one layer clusters. The total density is changed much less by changes in orthogonality layers than any of its three summands. Even when the valence states are distorted by admixtures of core-states from outside the cluster (i.e. few orthogonality layers) the charge density merely shifts among valence states within a constant total density.

B. Convergence in Valence Layers of Eigenvalues and Charge Density

When clusters having different numbers of valence layers are compared, they have different numbers of eigenvalues. The extra roots of a larger cluster begin to fill in around the smaller number of roots the energy range which corresponds to the energy band in a band structure.

FIG. 13. Convergence of octahedral site charge density of the one-valence-layer Ni_6 cluster with number of orthogonality layers. The partial charge densities due to one and two roots are shown as well as the total charge density of the three a_{1g} roots.

This change in both number and position of the eigenvalues with increasing cluster size makes very difficult any discussion of convergence in valence layers of eigenvalues.

However the totally symmetric representation a_{1g} always has the lowest lying root for any cluster size. For clusters containing one, two, and three valence layers, this lowest root is $-.392$, $-.421$, and $-.423$ Hartree respectively. The spreading effect of increasing numbers of roots is seen here. In a sense, these roots "repel" each other in the diagonalization of the secular equation. The roots which have larger overlap between their primary basis functions will separate more than those with less interaction (smaller overlap integral). By way of comparison, the bottom of the spin-averaged 4s energy band is $-.458$ Hartree in Callaway and Wang's calculation.^{3/}

The convergence of octahedral site charge density with number of valence layers is shown in Fig. 14. The clusters used in this calculation are orthogonal to the near neighbor core-states of the outer valence layers. The largest cluster consists of layers 1,2,3, and 5 because layers 4 and 5 are equidistant from the octahedral site, but layer 5 has fewer atoms. As the number of valence roots (all in the representation a_{1g}) increase from 3 to 6 to 12 to 15, the charge density changes by $.011$, $.007$, and $.001$ a.u. respectively.

FIG. 14. Convergence of octahedral site charge density with number of valence layers. The fourth valence layer is layer number 5 in Table II, as explained in Sec. III-B.

C. Density of States

The density of states (DOS) for a three valence layer cluster is shown in Fig. 15. This cluster of 38 valence atoms is orthogonal to 11 layers of core-state atoms. The total cluster size is 236 nickel atoms. The 115 eigenvalues of the 10 representations have been Gaussian broadened in order to produce a smooth DOS curve. Each root is represented by a Gaussian of .012 Hartree full width at half maximum normalized to the orbital occupation number of the root. The DOS function is

$$n(E) = \sum_i \frac{d_i}{\sqrt{\pi/\alpha}} \exp \left[-\alpha (E - E_i)^2 \right], \quad (30)$$

where d_i is the orbital occupation number, E_i is the orbital eigenvalue, and the parameter α is calculated from w , the full width of the Gaussian at half its maximum value, by

$$\exp \left[-\alpha \left(E_i + \frac{w}{2} - E_i \right)^2 \right] = \frac{1}{2}, \quad (31)$$

$$-\alpha \left(\frac{w}{2} \right)^2 = -\ln 2, \quad (32)$$

$$\alpha = \frac{4 \ln 2}{w^2}. \quad (33)$$

This smoothing technique has been used by Messmer et al.⁴⁰

FIG. 15. Density of states for Ni_{38} compared to the Ni crystal DOS. Each cluster root is broadened by a Gaussian of .012 Hartree full width at half maximum. The crystal DOS is the majority spin DOS of Callaway and Wang (Ref. 31) with adjustments described in Sec. III-C.

and Jennings ^{4/}et al. In their cluster-type calculations. The Gaussian smoothed DOS function used by Messmer et al. is equivalent to ours, as is shown in Appendix D. They have interpreted this broadened DOS function as simulating the effect of adding more shells of atoms to the cluster, while preserving the spectral density and width of the d-band that is characteristic of the small cluster. It is as if many new eigenvalues were to be inserted into the already closely spaced energy levels of the small cluster.

However as valence layers are added to make larger clusters, a new "inserted" eigenvalue will repel surrounding roots of the same irreducible representation as mentioned in Section III-B. Thus some of the eigenvalues of the three layer cluster do not fall in the domain of the smoothed one layer cluster DOS. With this reservation, it is certainly useful to regard the Gaussian broadened function as a smoothed DOS histogram.

The majority spin DOS from the band structure calculation of Callaway and Wang ^{3/} is shown in the bottom part of Fig. 15. The majority spin DOS curve was arbitrarily chosen for comparison, since the minority spin DOS curve is essentially the same shape, but shifted to higher energies by about .03 Hartrees. To account for the minority spin electrons, the majority spin DOS was doubled in the band structure DOS in Fig. 15. The Fermi level has been placed at the average position of the majority and minority spin Fermi levels relative to their DOS curves.

It would be less appropriate to compare our spin-restricted results to Callaway and Wang's total spin DOS which is the sum of majority and minority spin DOS curves. The superposition of these two curves washes out important features that they possess in common, although displaced in energy. This is in agreement with the Stoner-Wohlfarth ferromagnetism model⁴² that considers the majority and minority spin bands to be equal but shifted rigidly with respect to each other by the exchange splitting energy. This energy splitting is not included in our spin-restricted Hamiltonian. Therefore our results should be compared with either of the single-spin results of Callaway and Wang.

In Fig. 15 the three layer cluster DOS agrees rather well with the band structure DOS. The occurrence of two major peaks and three minor peaks is in agreement in both energy and relative heights. The cluster DOS even shows a suggestion of the shoulder in the crystal DOS at $-.07$ Hartree. The $.19$ Hartree d-band width for the three layer cluster agrees well with the $.21$ Hartree width of the band structure. Jennings *et al.*⁴¹ and Messmer *et al.*⁴⁰ found that the d-band width they calculated for small nickel clusters was about one-half the band value. Use of the infinite crystal potential has presumably aided our cluster calculation in this regard. The major difference between the two curves is the slope of the upper edge of the first peak.

In the next chapter the application of the variational

method to nickel clusters which contain a hydrogen impurity
is described.

Chapter IV

THE LCAO MOLECULAR CLUSTER METHOD FOR A SINGLE HYDROGEN IMPURITY

A. Self-Consistency in Charge Density

Clusters containing a single hydrogen impurity are used in a variational calculation like that of the pure nickel clusters. Only the Hamiltonian is changed so that comparisons of hydrogen impurity clusters with pure nickel clusters are straightforward. The electronic charge density is the property of most interest. The charge density change induced by a single octahedral hydrogen impurity is expected to be significant only in the region near the impurity. To describe this localized property a cluster smaller than would be needed for the change in density of states might be adequate.

The change in charge density is to be made self-consistent by an iterative technique as shown in Fig. 16. The initial approximation to the charge density change is the unperturbed hydrogen atom density. This density change is used in the initial impurity Hamiltonian as described in Section C of this chapter. The impurity matrix elements are added to the corresponding pure nickel matrix elements, then new eigenvalues, wave functions and charge density are calculated. The difference between this density and the

FIG. 16. FLOWCHART OF STEPS IN LCAO MOLECULAR CLUSTER CALCULATION FOR A CRYSTAL WITH A SINGLE HYDROGEN IMPURITY.

pure nickel cluster density is of course not equal to the assumed hydrogen atom density. Therefore, it is "curve-fitted" with Gaussians as described in Section IV-C, and further iterations are performed. When the density change "in" agrees with the density change "out" of an iteration, the hydrogen impurity charge density is self-consistent. The criteria for agreement are given in Sec. V-B.

B. Octahedral Site Basis Functions

The charge density very near the hydrogen impurity should respond primarily to the proton rather than to the lattice of nickel nuclei. Then to a first approximation the density, which has cubic symmetry, will be dominated by a totally symmetric term. Near the hydrogen impurity we expect the largest response to be in the totally symmetric irreducible representation a_{1g} of the cubic (octahedral) point group. Therefore the nickel basis set is augmented with single GTO's for more variational freedom. This augmented basis set is used for both pure nickel and hydrogen impurity clusters.

The GTO exponential parameters were chosen from Gaussian expansion sets used by Sambe⁴³ for the hydrogen atomic 1s state. Some trial and error was necessary to find a small number of GTO's which adequately spanned the region of interest. Trial basis sets were Sambe's linear

combination of five Gaussians, the same five Gaussians used independently as single GTO's, a set of three single GTO's, and a set of four single GTO's.

The single "contracted" function was found to be too restrictive. As expected, it can only reproduce a hydrogen-atom-shaped wave function. However when the five Gaussians were used independently as a basis set, the longest range Gaussian (exponential parameter $\alpha = 0.0978$) was not negligible at the second nearest neighbor sites and caused orthogonality problems. Since the impurity wave function was not expected to require such a long range correction, this basis function was not used.

The basis set with three single GTO's (exponential parameters = 13.7, 2.03, and 0.455) was judged to be adequate. However the coefficients of these three GTO's in the eigenvectors was found to alternate in sign. To determine whether an even number of single GTO's in a basis set would "cancel out" differently than an odd number, a basis set of four single GTO's was examined. The exponential parameters (12.5, 3.47, 1.11, 0.393) were chosen to span roughly the same space as the three GTO basis set, as shown in Fig. 17. The results were found to be equivalent for the two basis sets. The four single GTO's are employed as the octahedral site basis set in the representation a_{1g} in all pure nickel clusters and hydrogen impurity clusters.

$$\alpha_1 = 12.5 , \quad \alpha_2 = 3.47 , \quad \alpha_3 = 1.11 , \quad \alpha_4 = 0.393$$

$$\alpha_1 = 13.7 , \quad \alpha_2 = 2.03 , \quad \alpha_3 = 0.455$$

FIG. 17. Range comparison of two octahedral site Gaussian Type Orbital (GTO) basis sets. For each gaussian with non-linear parameter α_i , $r^2 \exp(-\alpha_i r^2)$ is normalized to its maximum value.

C. Hydrogen Impurity Hamiltonian

The one-electron Hamiltonian for a hydrogen impurity in a nickel cluster can be written as a sum of the Hamiltonian for the pure nickel cluster and a potential energy term arising from the defect as

$$\mathcal{H}_{H-Ni} = \mathcal{H}_{Ni} + V_H . \quad (34)$$

The matrix elements over the pure nickel cluster Hamiltonian have been previously determined. Only matrix elements over the hydrogen impurity potential need be calculated. The potential energy for the hydrogen impurity can be separated into Coulomb and exchange terms,

$$V_H = V_H^{\text{Coulomb}} + V_H^{\text{exchange}} . \quad (35)$$

The Coulomb potential term is

$$V_H^{\text{Coulomb}}(\vec{r}) = -\frac{1}{|\vec{r}|} + \int d^3r' \frac{\Delta\rho_H(\vec{r}')}{|\vec{r}-\vec{r}'|} , \quad (36)$$

which is composed of the Coulomb attraction to the proton at the cluster origin plus the electronic repulsion due to the increased charge density due to the hydrogen impurity. The charge density increase around the hydrogen impurity is approximated by Gaussian functions determined by a non-linear curve fitting technique⁴⁴ as

$$\Delta\rho_H(\vec{r}) \approx \sum_i f_i \exp(-\alpha_i r^2) . \quad (37)$$

For the first iteration the unperturbed hydrogen atomic charge density is assumed for the density increase $\Delta\rho_H(\vec{r})$. In all subsequent iterations the density increase calculated from the wave functions is not spherically symmetric. Therefore the Gaussian fit in Eq. 37 is made to a weighted average of the anisotropic density increases in three different directions. The averaging method is described in Appendix E.

The exchange potential term depends on the local density approximation. Since this exchange is proportional to the cube root of the local charge density, it does not vary linearly with the increase in charge density. The difference between the exchange potential due to the total charge density of a hydrogen-nickel cluster and the density of a pure nickel cluster,

$$V_H^{exchange}(\vec{r}) = - \left\{ \left[\frac{3}{\pi} \rho_{total}(\vec{r}) \right]^{1/3} - \left[\frac{3}{\pi} \rho_{Ni}(\vec{r}) \right]^{1/3} \right\}, \quad (38)$$

is used as the exchange term in the impurity potential. Thus in the vicinity of the hydrogen impurity the exchange potential due to the pure nickel cluster density is replaced by the exchange potential of the total charge density of the hydrogen-nickel cluster. A Gaussian fit weighted over three directions as explained in Appendix E is made to this exchange term as

$$- \left\{ \left[\frac{3}{\pi} \rho_{total}(\vec{r}) \right]^{1/3} - \left[\frac{3}{\pi} \rho_{Ni}(\vec{r}) \right]^{1/3} \right\} \simeq \sum_j g_j \exp(-\beta_j r^2). \quad (39)$$

D. Calculation of Integrals

The formulae used to evaluate multicenter integrals with the hydrogen impurity Hamiltonian are given in Appendix A. All integrals except the electron repulsion integral were required for the pure nickel cluster Hamiltonian as well.

The number of integrals to be calculated is reduced by using the rotational point group symmetry of the cluster to recognize equivalent integrals. For the pure nickel clusters a similar technique which also exploited the crystalline translational symmetry was employed.

The hydrogen impurity potential integrals are much faster to calculate than the nickel crystal Hamiltonian integrals, which involve a Fourier expansion with 923 terms. For this reason the techniques of the integral "request list" and the identification of integrals which are zero by orbital symmetry as described in Section II-B are not applied to the calculation of impurity integrals for impurity clusters.

In the next chapter, results of the hydrogen impurity cluster calculations are examined.

Chapter V

RESULTS FOR HYDROGEN IMPURITY CLUSTERS

A. First Approximate Calculation

A first approximation to the increase in charge density arising from the addition of a hydrogen atom to a nickel crystal has been reported previously.³⁷ The 38 atom cluster shown in Fig. 1 was used for this calculation, with one layer of 6 nickel atoms and two layers of 32 nickel core-states. As discussed in Section III-A, six orthogonality layers of nickel core-states are required for convergence of the eigenvalues. However the charge density near the octahedral site is much less affected than are the individual eigenvalues by the incomplete orthogonality to nickel crystal core-states exterior to the cluster. More important to the change in charge density is the requirement that it be self-consistent as described in Section IV-A. Also, the first approximation contained only the charge density increase in the totally symmetric irreducible representation a_{1g} of the octahedral point group. As shown in Figure 18, the self-consistency requirement most affects the charge density increase near the octahedral hydrogen site, while the inclusion of other representations (notably t_{1u}) is only important at distances greater than 1.0 a.u. from the hydrogen.

FIG. 18. Change in electron density in the (100) direction for the one-valence-layer H-Ni₆ cluster. (a) the linear response density increase in the symmetry a_{1g} is plotted versus distance from the impurity along the (100) axis $\circ$ — $\circ$, (b) the a_{1g} part of the SCF H-Ni₆ cluster density increase $\times$ — $\times$, (c) the a_{1g} and t_{1u} part of the SCF H-Ni₆ cluster density increase $\triangle$ — $\triangle$, (d) free hydrogen atom charge density — — —, (e) curve-fit to the free hydrogen atom charge density

The first approximation to the electron density change was calculated only for the (100) near-neighbor nickel direction. Of course the true electron density is not really isotropic. The change in charge density is nearly isotropic near the proton, but beyond 1.0 a.u. is increasingly anisotropic due to the near-neighbor nickel atoms. Therefore the spherical Gaussian expansion of charge density increase (Section IV-C, Eq. 36) to be used in the hydrogen impurity Hamiltonian is curve-fitted to a weighted average over the (100), (110), and (111) directions. This averaging technique represents the anisotropic change in charge density by a radial function in which the variation in each direction is weighted approximately by the number of directions that are equivalent under the symmetry operations of the cluster. The weighting scheme is described in Appendix E.

B. Self Consistency in Charge Density Change

The "radial" charge density change is

$$r^2 \Delta \rho_i(r) = r^2 [\rho_i(r) - \rho_o(r)] \quad , \quad (40)$$

between iteration i and the pure nickel cluster starting point. When the radial charge density increase for iteration i equals that for iteration $i+1$ at all distances

r , perfect self consistency is achieved. In practice of course, limits are placed on both the range of r and the agreement required for the radial charge density change. Most of the charge anisotropy and most of the charge density change lie farther than 1.0 a.u. from the hydrogen nucleus. Therefore the radial charge density criterion is a more stringent requirement than agreement of the charge density change.

Fig. 19 shows that for the approximately self-consistent one valence layer cluster, the largest difference in $r^2\Delta\rho$ between iterations is .008 a.u. in the direction (100) at $r = 2.0$ a.u.. The maximum difference in the curve-fits to the direction-weighted averages of radial density increase is only .002 a.u. at $r = 2.0$ a.u.. Almost all of the discrepancy between the two iterations is in the (100) direction and arises from the t_{1u} representation. Since there are no octahedral site GTOs in the representation, charge density must be built up near the hydrogen impurity using the tails of the t_{1u} nickel basis functions. Thus the charge density near the octahedral site is not independent of the charge density near the near-neighbor nickel sites. This limitation of the variational freedom of the basis set in the representation t_{1u} is probably the cause of the larger differences in radial density increase found in this representation.

Table III contains the approximately self-consistent charge density increase at distances up to 2.0 a.u. from the

FIG. 19. Radial charge density change for the one-valence-layer H-Ni₆ cluster. This plot shows both the degree of self consistency attained and the anisotropy required for the H-Ni₆ cluster. r is the distance from the H impurity along the (100), (110), and (111) directions. The average over these three directions of the radial density increase is performed using the weighting scheme described in Appendix E. The "in" values are those used as input to the final iteration and the "out" values are the resulting radial density increases in all three directions and averaged over directions.

TABLE III. Approximately self-consistent charge density change due to a hydrogen impurity in nickel. The input and output values of the density change for this iteration are printed for comparison. Values for the (100), (110), and (111) directions and for a curve-fit to a weighted average over these directions are given for each radius r from the hydrogen impurity site. Units for the charge density change are electrons/a.u.³ and units for r are a.u. The cluster is the one-valence-layer H-Ni₆ cluster.

r	(100)		(110)		(111)		Curve-Fit	
	IN	OUT	IN	OUT	IN	OUT	IN	OUT
.0	.212	.211	.212	.211	.212	.211	.212	.211
.166	.184	.183	.184	.183	.184	.183	.184	.183
.332	.133	.132	.133	.132	.133	.132	.132	.132
.498	.0932	.0927	.0931	.0925	.0930	.0925	.0927	.0921
.664	.0674	.0671	.0671	.0668	.0670	.0667	.0676	.0673
.830	.0502	.0500	.0496	.0494	.0494	.0492	.0500	.0500
.997	.0383	.0382	.0372	.0372	.0369	.0369	.0371	.0371
1.163	.0295	.0296	.0278	.0279	.0274	.0274	.0277	.0276
1.329	.0228	.0231	.0203	.0204	.0198	.0198	.0206	.0206
1.495	.0179	.0183	.0141	.0143	.0136	.0137	.0149	.0151
1.661	.0148	.0155	.0093	.0095	.0087	.0088	.0104	.0107
1.827	.0139	.0152	.0056	.0059	.0051	.0051	.0068	.0072
1.993	.0157	.0179	.0030	.0032	.0024	.0024	.0042	.0046

octahedral site. The results of the last two iterations are printed side by side for comparison. For each iteration the weighted average over directions is given in addition to the density increase in the (100), (110), and (111) directions.

C. Molecular Orbital Charge Density Plots

Plots of the charge density due to a single molecular orbital (MO) are helpful in determining the physical nature of a molecular orbital. The pure Ni_6 cluster symmetrized basis function consisting of one layer of nickel 3d atomic wave functions in the representation a_{1g} is shown in Fig. 20. The charge density is plotted for a cross-section in the xy plane indicated by the drawing at the bottom of Fig. 20. This plane is covered by a series of reference lines of zero charge density, and the charge density is plotted above its base reference line. Each plot simulates a three-dimensional display of a vertical "height" proportional to charge density above a horizontal cross-sectional plane. The density curves are marked with a short vertical dash in regions where the wave function ψ is negative. Thus the positive and negative lobes of an atomic 3d function can be distinguished around each nickel nucleus.

In Fig. 21 the 4s and 4p symmetrized basis functions are displayed in the same manner. The long range $\text{Ni } 4p$ atomic functions overlap strongly to produce the basis

FIG. 20a. Ni 3d basis function density plot. Charge density is plotted above a real space cross-section as explained in Sec. V-C.

FIG. 20b. Orientation of the real space cross-section through the Ni_6 cluster used in Figs. 20 - 24.

FIG. 21a. Ni 4s basis function density plot.

FIG. 21b. Ni 4p basis function density plot.

function with greatest charge density at the octahedral site. These plots do not include the core contributions. The latter are mixed into the valence functions when orthogonality to the nickel core-states is imposed. These contributions are only significant near the nickel nuclei.

The molecular orbital (MO) with the lowest energy in group representation a_{1g} is shown in Fig. 22 for both the hydrogen-nickel and the pure nickel clusters, each consisting of one Ni valence layer. The pure nickel cluster MO consists almost entirely of the Ni 4s basis functions shown in Fig. 21a. The small admixture of other valence basis functions merely reduces the charge density at the octahedral site, spreading the charge density more evenly throughout the plane.

The hydrogen-nickel MO with the lowest energy is also primarily 4s in nature, but strongly mixed with all the other valence basis functions. A molecular orbital can be decomposed into its constituent atomic orbitals using a modification of the Mulliken population analysis⁴⁵⁻⁴⁷ as explained in Appendix F. The charge in this MO is divided among the a_{1g} basis functions including the four single GTO's at the impurity site. The portions of charge assigned to each basis function are .4 Ni-4s, .3 GTO's, .2 Ni-4p, and .1 Ni-3d. This population analysis is suggestive of changes in MO character when the hydrogen impurity is added. Table IV compares the MO populations for hydrogen-nickel and pure nickel clusters of one valence layer. When the hydrogen

FIG. 22a. Ni_6 $1a_{1g}$ molecular orbital density plot.

FIG. 22b. H-Ni_6 $1a_{1g}$ molecular orbital density plot.

TABLE IV. Mulliken population analysis of a_{1g} molecular orbitals for Ni_6 and $H-Ni_6$ clusters.

Basis functions	$1a_{1g}$		$2a_{1g}$		$3a_{1g}$	
	Ni_6	$H-Ni_6$	Ni_6	$H-Ni_6$	Ni_6	$H-Ni_6$
Impurity site GTO's	.0	.3	.0	.1	.1	.1
Nickel 4s	1.0	.4	.1	.4	.1	.1
Nickel 4p	.0	.2	.6	.3	.2	.2
Nickel 3d	.0	.1	.3	.2	.6	.6

impurity is added to the cluster, the two lowest-energy MO's change character strongly and form H-Ni bonding orbitals. The second lowest root $2 a_{1g}$ in each type of cluster is shown in Fig. 23. The Ni 4s component of the $2 a_{1g}$ wavefunction is opposite in sign to the other components at the octahedral impurity site, resulting in lower charge density than that of the $1 a_{1g}$ wavefunction.

The $3 a_{1g}$ root lies in that range of cluster energies identified with the d-band and retains that d-character when the hydrogen impurity is added. This Ni 3d MO is essentially non-bonding both to the hydrogen impurity and among nickel atoms. Fig. 24 shows a low ridge of charge extending between nickel atoms. This small amount of charge is indicated by arrows in the directions toward the near neighbor nickel atoms not shown in the same xy plane.

Since the totally symmetric representation a_{1g} is the only representation whose wavefunctions can be non zero at the impurity site, the three MO's just discussed contain all the electronic charge in the near vicinity of the proton. The amount of electronic charge increase associated exclusively with the impurity site is .8 electron, calculated by doubly occupying the fractions of MO's assigned in Table IV to the impurity site GTO's.

FIG. 23a. Ni_6 $2a_{1g}$ molecular orbital density plot.

FIG. 23b. H-Ni_6 $2a_{1g}$ molecular orbital density plot.

FIG. 24a. Ni_6 $3a_{1g}$ molecular orbital density plot.

FIG. 24b. $H-Ni_6$ $3a_{1g}$ molecular orbital density plot.

D. Density of States

Changes in the density of states (DOS) due to the inclusion of a hydrogen atom can be seen by comparing the DOS of the one-valence-layer cluster Ni_6 with that of H-Ni_6 . Fig. 25 shows that the lowest root $1a_{1g}$ shifts energy downward .08 a.u. The highest energy root shown in the H-Ni_6 cluster is +.37 a.u. above the Fermi energy, but the corresponding $4a_{1g}$ root in the Ni_6 cluster lies at +.68 a.u.

Tanabe, Adachi, and Imoto have made cluster calculations⁴⁸ for Ni_5 and H-Ni_5 using the Self Consistent Charge (SCC) approximation to a fully self-consistent procedure, in which the charges assigned by Mulliken population analysis are iterated to self-consistency.⁴⁹ Their interest was in chemisorption, so the nickel clusters represent a surface and do not enclose the hydrogen. Also the potential arises from the cluster atoms only, without any contribution from the bulk nickel in which it is embedded.

In spite of these differences, their H-Ni_5 cluster is geometrically identical to our H-Ni_6 cluster with one nickel atom removed. They see the same effect of lowering the bottom valence a_{1g} root, although by much more, .35 a.u. In addition the H-Ni_5 d-band has split into two major peaks due to the different charge environment of the "bottom" Ni atom which is not equivalent to the other four Ni atoms in this C_{4v} symmetry. However the H-Ni_6 cluster, in which all six

FIG. 25. Density of states for H-Ni_6 compared to the Ni_6 DOS. The lowest root (which is $1a_{1g}$) is shifted .08 a.u. downward from the Ni_6 cluster to the H-Ni_6 cluster.

Ni atoms are equivalent, also suggests this growth of a separate peak at the bottom of the d-band.

Ultraviolet Photoemission Spectra (UPS) experiments have found a wide level of enhanced emission at -0.2 a.u. when hydrogen is chemisorbed on nickel.^{50,51} This probably corresponds to the H-Ni_6 $1a_{1g}$ level and other a_{1g} levels which would be introduced if more hydrogen atoms were included.

When the number of hydrogen atoms is increased to equal the nickel atoms, nickel hydride is formed. In the NiH band structure calculated by Switendick,³ a hydrogen peak appears -0.25 a.u. below the Fermi energy.

E. Three-Valence-Layer Cluster Ni_{38}

In order to see how well the Ni_6 cluster represents bulk nickel, a larger cluster of 38 nickel atoms has been examined. The Ni_{38} cluster consists of all the nickel atoms shown in Fig. 1 used as valence atoms. In addition, 198 surrounding nickel core "atoms" must be included to impose orthogonalization to all core-states within 8.1 a.u., as explained in Sec. III-A.

The Ni_{38} charge density within 2.0 a.u. of the octahedral site was found to be similar to the Ni_6 density there. However when the SCF H-Ni_6 electron density increase was applied to the H-Ni_{38} cluster, the resulting increase in

charge density was not only unlike the input, it was greater than free hydrogen atom density, as shown in Fig. 26. Since the SCF density increase for a one-valence-layer cluster was clearly not self-consistent for a three-valence-layer cluster, the atomic hydrogen charge density was assumed as the input density increase, so that the density increase arising from it could be examined. This "linear response" of the H-Ni_{38} cluster to the free hydrogen atomic density is also shown in Fig. 26.

The output charge density increase tends to overshoot the SCF density increase when the input charge density increase differs from the SCF density change. When the assumed density increase is larger than the SCF increase, the wavefunctions are "repelled" by this excessive charge and are consequently too small in that region. The resulting density increase is therefore smaller than the SCF increase. Clearly, when the assumed density increase is too small, the resulting density increase will be larger than the SCF value. Fortunately rapid convergence to the SCF density increase can be achieved by averaging the input and output values of a given iteration for use as the input to the next iteration.

Therefore the SCF density increase for the H-Ni_{38} should be bracketted by the free atomic hydrogen density as an upper limit and the H-Ni_6 SCF density increase as a lower limit. The H-Ni_{38} linear response is possibly not a lower limit to the H-Ni_{38} SCF density increase at all radii,

FIG. 26. Change in electron density for H-Ni₆ and H-Ni₃₈ clusters. (a) SCF H-Ni₆ cluster — — —, (b) H-Ni₃₈ result when density change (a) is input — · —, (c) curve-fit to free hydrogen atom —, (d) H-Ni₃₈ result when density change (c) is input · · · · ·, (e) H-Ni₆ result when density change (c) is input - - - - -. The linear responses to the free hydrogen density are results (d) and (e).

because its exact shape may not be correct. Only after the gross density features have converged, can the smaller changes in slope necessary for self-consistency be determined. The details of the density increase curve at distances greater than 1.0 a.u. will depend on the representations other than a_{1q} .

Chapter VI

DISCUSSION

A. Electronic Screening of the Proton

The screening of a proton by the electronic cloud it attracts has been studied in "jellium" for a range of metallic electronic charge densities.^{8,9} In the "jellium" model the positive ions are smeared out to form a uniform background. The background electronic charge densities are commonly expressed in terms of r_s , the radius of a sphere containing one electron. For the nickel cluster octahedral density of .019, the appropriate r_s is 2.3 a.u. The electronic charge increase above a background density of $r_s = 2.2$ a.u. as calculated by Almladh et al.⁸ is compared in Fig. 27 to the self-consistent one-valence-layer density increase described in Chapter V. Also shown in Fig. 27 are the results of Shaw's calculation of the screening of a hydrogen atom in a nickel crystal¹¹ and the free hydrogen atom charge density. Both Almladh's jellium result and Shaw's discrete ion result have greater density increase near the impurity than the hydrogen atomic charge density. The cluster density increase by contrast is lower than the free hydrogen density.

The H-Ni₆ cluster increase in density is also shown extrapolated linearly from the lowest two non-zero radial

FIG. 27. Change in electron density for several impurity calculations. (a) SCF H-Ni₆ cluster — — —, (b) nonlinear jellium by Almladh — — —, (c) discrete ions by Shaw ·····, and (d) free hydrogen atom ———.

data points. This is considered to be a minimum value for the density intercept because the limited GTO basis cannot describe the hydrogenic cusp accurately within 0.1 a.u. of the impurity. This extrapolated intercept is .24 a.u., or 75% of the free hydrogen atom value. The linear response H-Ni₆ cluster value was 55% of the free hydrogen density. Linear response underestimates the increase in charge density for the cluster method, just as it does for the jellium model.⁸

The tails of density functions in Fig. 27 are difficult to distinguish. The radial density functions plotted in Fig. 28 show differences in that region. The points along the jellium curve are enclosed by error limits which reflect the uncertainty in values taken from a density change graph in the paper by Almladh et al.⁸ The range cut-off at 2.0 a.u. is the limit of reliability in the cluster calculations due to increasing charge density anisotropy when farther from the impurity and increasing importance of density changes due to the core-functions when closer to the near-neighbor nickel atoms. At 2.0 a.u. the radial density increase due to the jellium model has decreased to become the lowest of the four functions. The amount of charge enclosed within this radius is found by integrating under each of the radial density curves. For Shaw's calculation, the charge is increased .93 electron within 2.0 a.u., for Almladh's $r_s = 2.2$ a.u. jellium, the increase is .90 electrons, while for the H-Ni₆ cluster, it is .67 electron.

FIG. 28. Radial charge density change for several calculations. (a) curve-fit to SCF H-Ni_6 —, (b) the a_{1g} part of the H-Ni_{38} linear response to the free hydrogen atom density — — —, (c) free hydrogen atom density — · — · —, (d) discrete atoms by Shaw — · — · —, (e) nonlinear jellium by Almbladh (error limits show the uncertainty in data derived from a graph in Ref. 8) — — —.

The free hydrogen atom contains .79 electron within 2.0 a.u.

The proton is screened more by Ni-4s and 4p functions than by Ni-3d, as can be seen by the composition of the screening states $1a_{1g}$ and $2a_{1g}$ in Table IV. This is in accord with the experimental result that Ni-3d electrons play a much smaller role than 4s electrons in hydrogen-nickel chemisorptive bonding.⁵⁰

B. Possible Improvements in the Cluster Method

The relaxation of the nickel lattice around the hydrogen impurity has been neglected in this work. In addition the hydrogen has been fixed at the octahedral interstitial site, thus allowing no study of its diffusion. Both of these interesting variations on the current problem might be more easily accomplished if the integral calculations were done in real space, rather than Fourier space. Then with a real-space potential, both the nickel atoms and the hydrogen impurity might be moved from their currently fixed positions.

The variational freedom of the basis set is barely above minimal in the present calculation. Each of the atomic nickel wave functions used as basis functions is a single linear combination of Gaussians. The Ni-4p functions are added to the minimal occupied atomic nickel wave functions, but in the representation t_{1u} in particular, this

seems not to have added sufficient variational freedom. The effect of the additional hydrogen potential was to increase the t_{1u} wave functions rather rigidly inside the Ni_6 cluster. Additional freedom in the variational functions could be obtained by adding at the impurity site single GTO's of p-type for the t_{1u} representation. For all representations, each nickel atomic orbital could be released from its frozen linear combination of Gaussians to a sum of a few "contracted" Gaussian parts which would be allowed to rearrange in the variational calculation.

The preceding paragraphs are some possible improvements on the current cluster method. As a first step, this method has enabled the ab initio calculation of the charge density and density of states in a pure transition metal. It has provided impurity wavefunctions, induced charge density, and the changed density of states for the extreme case of dilution: one hydrogen atom dissolved in a nickel crystal.

Appendix A

GAUSSIAN INTEGRALS

A single GTO with exponential parameter α and center $\vec{A}$ is defined as

$$\Theta(\vec{A}, \alpha, l, m, n) \equiv x_A^l y_A^m z_A^n \exp(-\alpha r_A^2), \quad (A1)$$

where $x_A^l \equiv (x - A_x)^l$.

The convenience of GTO's is that the product of two GTO's collapses to a third GTO with a different center.⁵² For example the product of two s-type GTO's is

$$\Theta(\vec{A}, \alpha_1, 0, 0, 0) \Theta(\vec{B}, \alpha_2, 0, 0, 0) = \exp\left(\frac{-\alpha_1 \alpha_2 \overline{AB}^2}{\gamma}\right) \Theta(\vec{P}, \gamma, 0, 0, 0), \quad (A2)$$

where $\gamma \equiv \alpha_1 + \alpha_2$, (A3)

and $\vec{P} \equiv \frac{\alpha_1 \vec{A} + \alpha_2 \vec{B}}{\gamma}$. (A4)

1. General Product of GTO's

When the GTO's are not 1s orbitals, factors such as $x_B^{l_1} x_B^{l_2}$ appear in the product. We rewrite these factors in terms of x_p , the coordinate relative to $\vec{P}$. The convention

$$\overline{AB} \equiv \vec{A} - \vec{B} \quad (A5)$$

is used throughout this paper. So we have

$$X_A = X_P + \overline{PA}_x \quad (A6)$$

and the extra factors can be cast into the form⁵³

$$\begin{aligned} X_A^{l_1} X_B^{l_2} &= (X_P + \overline{PA}_x)^{l_1} (X_P + \overline{PB}_x)^{l_2} \\ &= \sum_i f_i(l_1, l_2, \overline{PA}_x, \overline{PB}_x) X_P^i, \end{aligned} \quad (A7)$$

where $f_i(l, m, a, b)$ is the coefficient of x^i in the expansion

$$(x+a)^{l_1} (x+b)^{l_2} = \sum_{i=0}^{l_1+l_2} f_i(l_1, l_2, a, b) x^i, \quad (A8)$$

and is given by

$$f_i(l, m, a, b) \equiv \sum_{j=\max(0, i-m)}^{\min(i, l)} \binom{l}{j} \binom{m}{i-j} a^{l-j} b^{m+j-i}. \quad (A9)$$

Then we have in general for the product of two GT0's

$$\begin{aligned} \Theta(\vec{A}, \alpha_1, l_1, m_1, n_1) \Theta(\vec{B}, \alpha_2, l_2, m_2, n_2) = \\ \exp\left(\frac{-\alpha_1 \alpha_2 \overline{AB}^2}{\delta}\right) \Theta(\vec{P}, \gamma, 0, 0, 0) \sum_i \sum_j \sum_k, \end{aligned} \quad (A10)$$

$$\text{where } \sum_i \equiv \sum_i f_i(l_1, l_2, \overline{PA}_x, \overline{PB}_x) X_P^i$$

and similarly for $\sum_j, \sum_k$ in the y- and z-directions.

2. Overlap Integral

The overlap integral is given by Clementi and Davis³⁸

$$\begin{aligned} \text{as } OI &\equiv \langle \theta(\vec{A}, \alpha_1, l_1, m_1, n_1) | \theta(\vec{B}, \alpha_2, l_2, m_2, n_2) \rangle \\ &= \left(\frac{\pi}{8}\right)^{3/2} \exp\left(\frac{-\alpha_1 \alpha_2 \overline{AB}^2}{8}\right) \sum_x \sum_y \sum_z, \quad (A11) \end{aligned}$$

$$\text{where } \sum_x \equiv \sum_{i=0}^{[\frac{1}{2}(l_1+l_2)]} f_{2i}(l_1, l_2, \overline{PA}_x, \overline{PB}_x) \frac{(2i-1)!!}{2^i 8^i}.$$

The notation $[m]$ means the largest integer less than or equal to m , and the double factorial is

$$(2i-1)!! \equiv 1 \cdot 3 \cdot 5 \cdots (2i-1). \quad (A12)$$

3. Kinetic Energy Integral

The kinetic energy integral is defined as³⁸

$$KEI \equiv \langle \theta(\vec{A}, \alpha_1, l_1, m_1, n_1) | -\frac{\nabla^2}{2} | \theta(\vec{B}, \alpha_2, l_2, m_2, n_2) \rangle. \quad (A13)$$

The operator ∇^2 changes only the GTO centered at $\vec{B}$, so denoting the overlap integral between $\theta(\vec{A}, \alpha_1, l_1, m_1, n_1)$ and $\theta(\vec{B}, \alpha_2, l_2, m_2, n_2)$ by $S(l_2, m_2, n_2)$,

$$\begin{aligned} KEI &= \alpha_2 \left\{ 2(l_2 + m_2 + n_2) + 3 \right\} S(l_2, m_2, n_2) + \\ &\quad - 2\alpha_2^2 \left\{ S(l_2+2, m_2, n_2) + S(l_2, m_2+2, n_2) + S(l_2, m_2, n_2+2) \right\} + \\ &\quad - \frac{1}{2} \left\{ l_2(l_2-1) S(l_2-2, m_2, n_2) + m_2(m_2-1) S(l_2, m_2-2, n_2) + \right. \\ &\quad \left. + n_2(n_2-1) S(l_2, m_2, n_2-2) \right\}. \quad (A14) \end{aligned}$$

4. Fourier Potential Integral

The integral over the Fourier representation of a potential has been given by Chaney and Dorman²⁸ as

$$\begin{aligned} \text{FPI} &\equiv \left\langle \theta(\bar{A}, \alpha_1, l_1, m_1, n_1) \left| \sum_{\vec{K}}^{K_{\max}} V_K \cos K r \right| \theta(\bar{B}, \alpha_2, l_2, m_2, n_2) \right\rangle \\ &= (8\pi)^{\frac{3}{2}} \exp\left(-\frac{\alpha_1 \alpha_2 \bar{A} \bar{B}^2}{8}\right) \sum_{\vec{K}}^{K_{\max}} V_K I(K_x) I(K_y) I(K_z), \end{aligned} \quad (\text{A15})$$

where

$$I(K_x) = \sum_{i=0}^{l_1+l_2} f_i(l_1, l_2, \bar{P}A_x, \bar{P}B_x) \exp\left(\frac{-K_x^2}{48}\right) \frac{\lambda_i(K_x)}{(28)^{\frac{i+1}{2}}} \text{He}_i\left(\frac{K_x}{\sqrt{28}}\right),$$

and

$$\lambda_i(K_x) = \begin{cases} (-1)^{\frac{i}{2}} \cos(K_x \bar{P}A_x) & \text{if } i \text{ is even} \\ -(-1)^{\frac{i+1}{2}} \sin(K_x \bar{P}A_x) & \text{if } i \text{ is odd} \end{cases},$$

and He_i is a Hermite polynominal.

$I(K_y)$ and $I(K_z)$ are similarly defined.

5. Nuclear Attraction Integral

Huzinaga⁵⁴ has given an expression for the nuclear attraction integral as

$$\begin{aligned}
 NAI &= \langle \Theta(\vec{A}, \alpha_1, l_1, m_1, n_1) \left| \frac{1}{r_c} \right| \Theta(\vec{B}, \alpha_2, l_2, m_2, n_2) \rangle \\
 &= \left(\frac{2\pi}{\gamma} \right) \exp \left(-\frac{\alpha_1 \alpha_2 \overline{AB}^2}{\gamma} \right) \sum_{i,r,u} \sum_{j,s,v} \sum_{k,t,w} F_\nu(\gamma \overline{PC}^2),
 \end{aligned}
 \tag{A16}$$

where

$$\nu \equiv i + j + k - 2(r + s + t) - (u + v + w)$$

and

$$\sum_{i,r,u} \equiv \sum_{i,r,u} \frac{(-1)^{i+u} i! f_i(l_1, l_2, \overline{PA}_x, \overline{PB}_x) \overline{PC}_x^{i-2(r+u)}}{r! u! (i-2r-2u)! (4\gamma)^{r+u}}$$

with summations over the ranges:

$$\begin{aligned}
 i &= 0 \rightarrow l_1 + l_2 \\
 r &= 0 \rightarrow \left[\frac{i}{2} \right] \\
 u &= 0 \rightarrow \left[\frac{1}{2}(i-2r) \right]
 \end{aligned}$$

and $\sum_{j,s,v}$ and $\sum_{k,t,w}$ are similarly defined in terms of y and z components. F_ν is the incomplete Gamma function and can be evaluated by a series expansion and recursion relations.⁵²

6. Electron Repulsion Integral

The electron repulsion integral from Taketa⁵⁵ is

$$ERI = \langle \Theta(\vec{A}, \alpha_1, l_1, m_1, n_1) \Theta(\vec{B}, \alpha_2, l_2, m_2, n_2) \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \cdot \Theta(\vec{C}, \alpha_3, l_3, m_3, n_3) \Theta(\vec{D}, \alpha_4, l_4, m_4, n_4) \rangle$$

$$= \frac{2\pi^2}{\delta_1 \delta_2} \left(\frac{\pi}{\delta_1 + \delta_2} \right)^{\frac{1}{2}} \exp \left[\frac{-\alpha_1 \alpha_2 \overline{AB}^2}{\delta_1} + \frac{-\alpha_3 \alpha_4 \overline{CD}^2}{\delta_2} \right]$$

$$\sum_{\substack{i_1, i_2 \\ r_1, r_2 \\ u}} \sum_{\substack{j_1, j_2 \\ s_1, s_2 \\ v}} \sum_{\substack{k_1, k_2 \\ t_1, t_2 \\ w}} F_\nu \left(\frac{\delta_1 \delta_2}{\delta_1 + \delta_2} \overline{PQ}^2 \right),$$

where

(A17)

$$\delta_1 \equiv \alpha_1 + \alpha_2, \quad \delta_2 \equiv \alpha_3 + \alpha_4$$

and

$$\vec{Q} \equiv \frac{\alpha_3 \vec{C} + \alpha_4 \vec{D}}{\delta_2}$$

and

$$\nu \equiv i_1 + i_2 + j_1 + j_2 + k_1 + k_2 - 2(r_1 + r_2 + s_1 + s_2 + t_1 + t_2) + (u + v + w)$$

$$\sum_{\substack{i_1, i_2 \\ r_1, r_2 \\ u}} \equiv \sum_{\substack{i_1, i_2 \\ r_1, r_2 \\ u}} \frac{(-1)^{i_1+u} i_1! i_2! [i_1 + i_2 - 2(r_1 + r_2)]! \overline{PQ}_x^{i_1 + i_2 - 2(r_1 + r_2 + u)}}{r_1! r_2! (i_1 - 2r_1)! (i_2 - 2r_2)! u! [i_1 + i_2 - 2(r_1 + r_2 + u)]!} \cdot f_{i_1}(l_1, l_2, \overline{PA}_x, \overline{PB}_x) \cdot f_{i_2}(l_3, l_4, \overline{QC}_x, \overline{QD}_x),$$

with summations over the ranges:

$$\begin{aligned}
 i_1 &= 0 \rightarrow l_1 + l_2 & i_2 &= 0 \rightarrow l_3 + l_4 \\
 r_1 &= 0 \rightarrow [i_1/2] & r_2 &= 0 \rightarrow [i_2/2] \\
 u &= 0 \rightarrow \left[\frac{1}{2} (i_1 + i_2) - (r_1 + r_2) \right]
 \end{aligned}$$

and y and z component sums are similarly defined.

Typographical errors can easily occur in the complicated expressions for any of these integrals. Several of the references cited contain misprints. A convenient guide to checking these integral expressions is the outline of the derivation for the ERI expression given by Wright.⁵⁶

Appendix B

OVERLAPPING ATOMIC POTENTIAL

An Overlapping Atomic Potential (OAP) is formed by the superposition of the charge densities of neutral nickel atoms ($3d^9 4s^1$) for use as a starting potential,⁵⁹ as explained in Sec. II-B. The nickel atoms are located in a face entered cubic (FCC) lattice with lattice constant $a = 6.644$ a.u.

A Fourier series form of the OAP is desired, with coefficients

$$V(\vec{K})^{OAP} = V(\vec{K})_{Coulomb}^{OAP} + V(\vec{K})_{exchange}^{OAP} . \quad (B1)$$

The Coulomb term is

$$V(\vec{K})_{Coulomb}^{OAP} = \frac{1}{N\Omega} \int d^3\vec{r} \, e^{-i\vec{K}\cdot\vec{r}} \sum_{\mu} V(\vec{r}-\vec{R}_{\mu})_{Coulomb}^{atomic} , \quad (B2)$$

where N is the number of real-space cells in the integration, Ω is the cell volume, and $\vec{R}_{\mu}$ is the location of the μ^{th} atom.

Since $\vec{K}$ is a reciprocal-lattice vector

$$\sum_{\mu} e^{-i\vec{K}\cdot\vec{R}_{\mu}} = N . \quad (B3)$$

So we have

$$\begin{aligned}
 V_{\text{Coulomb}}^{\text{OAP}}(\vec{K}) &= \frac{1}{N\Omega} \int d^3r e^{-i\vec{K}\cdot\vec{r}} \sum_{\mu} V_{\text{Coulomb}}^{\text{atomic}}(\vec{r}-\vec{R}_{\mu}) \\
 &= \frac{1}{N\Omega} \int d^3r \sum_{\mu} e^{-i\vec{K}\cdot(\vec{r}+\vec{R}_{\mu})} V_{\text{Coulomb}}^{\text{atomic}}(\vec{r}) \\
 &= \frac{1}{\Omega} \int d^3r e^{-i\vec{K}\cdot\vec{r}} V_{\text{Coulomb}}^{\text{atomic}}(\vec{r}) \left(\sum_{\mu} \frac{e^{-i\vec{K}\cdot\vec{R}_{\mu}}}{N} \right) \\
 &= \frac{1}{\Omega} \int d^3r e^{-i\vec{K}\cdot\vec{r}} V_{\text{Coulomb}}^{\text{atomic}}(\vec{r}) . \quad (B4)
 \end{aligned}$$

The Coulomb potential for each nickel atom is

$$V_{\text{Coulomb}}^{\text{atomic}}(\vec{r}) = -\frac{Z}{|\vec{r}|} + \int d^3r' \frac{\rho_{\text{atomic}}(r')}{|\vec{r}-\vec{r}'|} . \quad (B5)$$

Consider the integral

$$\begin{aligned}
 \int d^3r \frac{e^{-i\vec{K}\cdot\vec{r}}}{|\vec{r}|} &= 2\pi \int_0^{2\pi} d\theta \sin\theta \int_0^{\infty} r^2 dr \frac{e^{-iKr\cos\theta}}{r} \\
 &= \lim_{\lambda \rightarrow 0} 2\pi \int_{-1}^1 du \int_0^{\infty} r dr e^{-iKu - \lambda r} \\
 &= \lim_{\lambda \rightarrow 0} 2\pi \int_{-1}^1 du \left(\frac{1}{(\lambda + iKu)^2} \right) \\
 &= 2\pi \int_{-1}^1 \frac{du}{-K^2 u^2} = \frac{2\pi}{K^2} \left[u^{-1} \right]_{-1}^1 \\
 &= \frac{4\pi}{K^2} . \quad (B6)
 \end{aligned}$$

We use this integral with Eq. (B4) and Eq. (B5),

$$\begin{aligned}
 V_{\text{Coulomb}}^{\text{OAP}}(\vec{K}) &= \frac{1}{\Omega} \int d^3r \left\{ \frac{-Z e^{-i\vec{K} \cdot \vec{r}}}{|\vec{r}|} + e^{-i\vec{K} \cdot \vec{r}} \int d^3r' \frac{\rho_{\text{atomic}}(r')}{|\vec{r} - \vec{r}'|} \right\} \\
 &= \frac{-4\pi Z}{\Omega K^2} + \frac{1}{\Omega} \int d^3r' \rho_{\text{atomic}}(r') \int d^3r \frac{e^{-i\vec{K} \cdot (\vec{r} + \vec{r}')}}{|\vec{r}|} \\
 &= \frac{-4\pi Z}{\Omega K^2} + \frac{1}{\Omega} \int d^3r' \rho_{\text{atomic}}(r') e^{-i\vec{K} \cdot \vec{r}'} \left(\int d^3r \frac{e^{-i\vec{K} \cdot \vec{r}}}{|\vec{r}|} \right) \\
 &= \frac{-4\pi Z}{\Omega K^2} + \frac{4\pi}{\Omega K^2} \int d^3r' \rho_{\text{atomic}}(r') e^{-i\vec{K} \cdot \vec{r}'} \\
 &= \frac{-4\pi Z}{\Omega K^2} + \frac{8\pi^2}{\Omega K^2} \int_0^\infty r'^2 dr' \rho_{\text{atomic}}(r') \int_{-1}^1 du e^{-iKr'u} \\
 &= \frac{-4\pi Z}{\Omega K^2} + \frac{8\pi^2}{\Omega K^2} \int_0^\infty r'^2 dr' \rho_{\text{atomic}}(r') \left[\frac{e^{-iKr'}}{-iKr'} + \frac{e^{iKr'}}{iKr'} \right] \\
 &= \frac{-4\pi Z}{\Omega K^2} + \frac{16\pi^2}{\Omega K^3} \int_0^\infty r dr \rho_{\text{atomic}}(r) \sin Kr. \quad (B7)
 \end{aligned}$$

But for $\vec{K} = 0$, we must use

$$\begin{aligned}
 V_{\text{Coulomb}}^{\text{OAP}}(\vec{K}=0) &= \lim_{\vec{K} \rightarrow 0} \left\{ \frac{-4\pi Z}{\Omega K^2} + \frac{16\pi^2}{\Omega K^3} \int_0^\infty r dr \rho_{\text{atomic}}(r) \left(Kr - \frac{(Kr)^3}{3!} + \dots \right) \right\} \\
 &\quad (B8) \\
 &= \lim_{\vec{K} \rightarrow 0} \left\{ \frac{-4\pi Z}{\Omega K^2} + \frac{4\pi}{\Omega K^2} \left(\int_0^\infty 4\pi r^2 dr \rho_{\text{atomic}}(r) \right) - \frac{16\pi^2}{6\Omega} \int_0^\infty r^4 dr \rho_{\text{atomic}}(r) \right\}.
 \end{aligned}$$

Since the integral in the second term gives the atomic number Z , the two terms containing K^2 cancel, leaving

$$V_{\text{Coulomb}}^{\text{OAP}}(\vec{R}=0) = -\frac{8\pi}{3\Omega} \int_0^\infty r^4 dr \rho_{\text{atomic}}(r) \quad (B9)$$

To calculate the nickel atomic charge density, we use Slater-Type Orbitals (STO) with experimental parameters and linear coefficients determined by Clementi⁵⁷.

$$R_i(r) = \sum_j C_{ij} r^{l-1} \exp(-\alpha_j r) \quad , \quad (B10)$$

$$\text{so } \rho_{\text{atomic}}(r) = \frac{1}{4\pi} \sum_i n_i |R_i(r)|^2 \quad , \quad (B11)$$

where n_i is the orbital occupation number. Substituting into Eq. (B9) gives

$$\begin{aligned} V_{\text{Coulomb}}^{\text{OAP}}(\vec{R}=0) &= \frac{-8\pi}{3\Omega} \int_0^\infty r^4 dr \sum_i \frac{n_i}{4\pi} \left[\sum_j C_{ij} r^{l-1} \exp(-\alpha_j r) \right] \left[\sum_m C_{im} r^{p-1} \exp(-\alpha_m r) \right] \\ &= \frac{-2\pi}{3\Omega} \sum_i \sum_j \sum_m n_i C_{ij} C_{im} \int_0^\infty dr r^{l-1+p-1+4} \exp(-[\alpha_j + \alpha_m]r) \\ &= \frac{-2\pi}{3\Omega} \sum_i \sum_j \sum_m n_i C_{ij} C_{im} \frac{(l+p+2)!}{(\alpha_j + \alpha_m)^{l+p+3}} \quad (B12) \end{aligned}$$

The same substitution into Eq. (B8) leads to more complicated, but still algebraic forms for $V_{\text{Coulomb}}^{\text{OAP}}(\vec{R})$. We shall not list these forms because there are seven separate cases to consider.

The exchange term in Eq. (B1) is

$$\begin{aligned}
 V_{\text{exchange}}^{\text{OAP}}(\vec{K}) &= \frac{1}{N\Omega} \int d^3r \, e^{-i\vec{K} \cdot \vec{r}} V_{\text{exchange}}(\vec{r}) \\
 &= \frac{1}{\Omega} \int_{\text{cell}} d^3r \, e^{-i\vec{K} \cdot \vec{r}} V_{\text{exchange}}(\vec{r}) \quad . \quad (\text{B13})
 \end{aligned}$$

We approximate the integral over the unit cell by an integral over the equal volum Wigner-Seitz sphere with radius $r_{\text{ws}} = 2.6 \text{ a.u.}$. Then applying the Kohn-Sham exchange approximation³⁵

$$\begin{aligned}
 V_{\text{exchange}}(\vec{r}) &\simeq \frac{2}{3} \left\{ -3 \left[\frac{3}{8\pi} \rho_{\text{crystal}}(\vec{r}) \right]^{\frac{1}{3}} \right\} \\
 &= - \left[\frac{3}{\pi} \rho_{\text{crystal}}(\vec{r}) \right]^{\frac{1}{3}} \quad . \quad (\text{B14})
 \end{aligned}$$

We have

$$\begin{aligned}
 V_{\text{exchange}}^{\text{OAP}}(\vec{K}) &= \frac{-1}{\Omega} \int_0^{2\pi} d\varphi \int_{-1}^1 du \int_0^{r_{\text{ws}}} r^2 dr \, e^{-iKru} \left(\frac{3}{\pi} \rho_{\text{crystal}}(r) \right)^{\frac{1}{3}} \\
 &= \frac{-2\pi}{\Omega} \int_0^{r_{\text{ws}}} r^2 dr \left(\frac{3}{\pi} \rho_{\text{crystal}}(r) \right)^{\frac{1}{3}} \left[\frac{e^{-iKru}}{-iKr} \right]_{u=-1}^{u=1} \\
 &= \frac{-4\pi}{\Omega K} \int_0^{r_{\text{ws}}} r dr \left(\frac{3}{\pi} \rho_{\text{crystal}}(r) \right)^{\frac{1}{3}} \sin Kr \quad . \quad (\text{B15})
 \end{aligned}$$

For $\vec{K} = 0$, we use

$$V_{\text{exchange}}^{OAP}(\vec{R}=0) = \frac{-4\pi}{\Omega} \int_0^{r_{ws}} r^2 dr \left(\frac{3}{\pi} \rho_{\text{crystal}}(r) \right)^{1/3} . \quad (B16)$$

The directional crystal charge density is a superposition of 321 nickel atomic charge densities,

$$\rho_{\text{crystal}}(\vec{r}) = \sum_{\mu=1}^{321} \rho_{\text{atomic}}(\vec{r} - \vec{R}_{\mu}) . \quad (B17)$$

The radial crystal charge density $\rho_{\text{crystal}}(r)$ is the weighted average of the directional crystal charge densities in the directions (100), (110), (111), and (210). The integrals in Eq. (B15) and (B16) are done with 96 point Legendre-Gaussian quadrature.

Appendix C

EWALD DECOMPOSITION OF CRYSTAL POTENTIAL

An Ewald-type procedure similar to that described by Chaney et al.¹⁶ is used to obtain a Fourier series that is more rapidly convergent than that for the full crystal potential. When a GTO exponential parameter α is greater than 7.5, the real space region very near a nickel nucleus is important and the summation in reciprocal space must be carried to many more terms than for more diffuse GTO's. For this case, we separate the crystal potential into two parts

$$\begin{aligned} V_c(\vec{r}) &= V_\ell(\vec{r}) + [V_c(\vec{r}) - V_\ell(\vec{r})] \\ &= V_\ell(\vec{r}) + V_d(\vec{r}), \end{aligned} \quad (C1)$$

where $V_\ell(\vec{r})$ is a localized potential which has a Coulomb singularity $-Z/r$ at each nucleus and is negligible outside of a unit cell centered at that nucleus.

For the localized potential we use

$$V_\ell(\vec{r}) = \frac{-Z}{|\vec{r}|} e^{-\beta_1 r^2} + \frac{\alpha}{|\vec{r}|} [e^{-\beta_1 r^2} - e^{-\beta_2 r^2}], \quad (C2)$$

where $\beta_1 = 88.1261$, $\beta_2 = 9.53958$, $\alpha = 35.7264$.

This function goes to the limit $-Z/r$ as $r \rightarrow 0$, and at $r=2$ a.u. it is smaller than 10^{-15} .

The Fourier coefficients of the first term in $V_\ell(\vec{r})$ are given by:

$$\begin{aligned} V_\ell^1(\vec{K}) &= \frac{4\pi}{K\Omega} \int_0^\infty dr \left(-\frac{Z}{r} e^{-\beta_1 r^2} \right) r \sin(Kr) \\ &= -\frac{4\pi Z}{K\Omega} \left\{ \int_0^\infty dr e^{-\beta_1 r^2} \sin(Kr) \right\}. \end{aligned} \quad (C3)$$

An integral table⁵⁸ relates the definite integral to the hypergeometric function, ${}_1F_1$. So we have

$$V_\ell^1(\vec{K}) = -\frac{2\pi Z}{\Omega \beta_1} {}_1F_1\left(1, \frac{3}{2}, -\frac{K^2}{4\beta_1}\right), \quad (C4)$$

and ${}_1F_1$ is evaluated using a series expansion.

We now can obtain $V_\ell(\vec{K})$ since the Fourier coefficients of the other terms in Eq. (C2) are calculated in the same manner as the first term. We subtract this Fourier representation of the local potential from the perfect crystal Fourier potential giving

$$V_d(\vec{K}) = V_c(\vec{K}) - V_\ell(\vec{K})$$

Matrix elements over $V_d(\vec{K})$ are calculated in exactly the same way as those over $V_c(\vec{K})$, as given in Appendix A.

We still have to evaluate the matrix elements over the localized part of the potential, $V_\ell(\vec{r})$. This integral is done in real space and after simplification of Gaussians, involves terms like

$$NAI \equiv \langle \theta(\vec{A}, \alpha_1, l_1, m_1, n_1) | \frac{1}{r_c} | \theta(\vec{B}, \alpha_2, l_2, m_2, n_2) \rangle, \quad (C6)$$

which is the Nuclear Attraction Integral (NAI). This integral is evaluated in terms of the incomplete gamma function, as shown in Appendix A.

In short, when a narrow GTO is involved, matrix elements over the perfect crystal potential are calculated in two parts: a real space integral (NAI) over the localized potential $V_\ell(\vec{r})$ and a Fourier space integral over the difference potential $V_d(\vec{R})$.

Appendix D

DENSITY OF STATES SMOOTHING FUNCTIONS

We have used the Gaussian smoothed DOS function

$$n(E) = \sum_i \frac{d_i}{\sqrt{\pi/\alpha}} \exp[-\alpha(E-E_i)^2] , \quad (D1)$$

where d_i is the orbital occupation number, E_i is the orbital eigenvalue, and the parameter α is calculated from w , the full width of the Gaussian at half its maximum value, by:

$$\exp[-\alpha(E_i + \frac{w}{2} - E_i)^2] = \frac{1}{2} , \quad (D2)$$

$$-\alpha(\frac{w}{2})^2 = -\ln 2 , \quad (D3)$$

$$\alpha = \frac{4 \ln 2}{w^2} . \quad (D4)$$

We tried smoothed DOS functions using $w = .008, .010, .012$, and $.014$ Hartrees, and found $w = .012$ Hartrees the best to join adjacent roots smoothly without hiding separate roots. Messmer et al.⁴⁰ have used the Gaussian broadened DOS function

$$n(E) = \sum_i \frac{d_i}{\sqrt{\pi/2\sigma^2}} \exp[-\frac{(E-E_i)^2}{2\sigma^2}] , \quad (D5)$$

where d_i and E_i are defined as Eq. (B1) and σ is a broadening parameter chosen to give "sufficient resolution of structure." Messmer et al. chose $\sigma = .01$ Rydberg = .005 Hartree for their Ni_{13} cluster.

These two smoothed DOS functions would be equivalent if

$$\alpha = \frac{4 \ln 2}{W^2} = \frac{1}{2 \sigma^2} \quad , \quad (D6)$$

that is, if

$$\sigma = \frac{W}{\sqrt{8 \ln 2}} = \frac{W}{2.355} \quad . \quad (D7)$$

For $W = .012$ Hartrees, we have $\sigma = .012/2.355 = .005$ Hartrees. Since this is exactly the broadening parameter chosen by Messner et al. , their cluster calculations use a Gaussian smoothed DOS function equivalent to ours.

Appendix E
WEIGHTING SCHEME FOR AVERAGING
OVER DIRECTIONS (100), (110), AND (111)

The hydrogen impurity Hamiltonian described in Sec. IV-C contains an average of the charge density increase (Eq. 36) and an average of the change in the exchange term (Eq. 37) due to the inclusion of hydrogen. The weighting scheme for averaging over three independent directions is chosen to approximately reflect the number of directions equivalent by cluster symmetry. The variation in the (111) direction is weighted with the integer 8, the (110) variation weighted with 12, and the (100) variation weighted with 4. The density change and exchange difference are thought to be less accurate in the near-neighbor (100) direction, so the 6 equivalent (100) direction are only weighted 4. Then the weights are in simple ratios:

$$\frac{w(110)}{w(100)} = \frac{12}{4} = 3, \quad (E1)$$

$$\frac{w(111)}{w(100)} = \frac{8}{4} = 2. \quad (E2)$$

The resulting radial variation is then curve-fitted with spherical Gaussians as in Eq. 36 or Eq. 37.

Appendix F

MULLIKEN POPULATION ANALYSIS

Mulliken population analysis of a molecular orbital (MO) is a method of dividing the electronic charge of the MO among the "atomic" orbitals which are used as basis functions.⁴⁵⁻⁴⁷ The MO is a linear combination of atomic orbitals (LCAO),

$$\psi = \sum_j a_j \phi_j \quad . \quad (F1)$$

Since both the MO ψ and the AO ϕ_j are normalized functions,

$$\langle \psi | \psi \rangle = 1 = \sum_j \left[a_j^2 + 2 \sum_{k>j} a_j a_k S_{kj} \right], \quad (F2)$$

where S_{kj} is the overlap integral between ϕ_k and ϕ_j .

A gross atomic orbital population can be defined as

$$N_j \equiv a_j^2 + \gamma \left(2 \sum_{k \neq j} a_j a_k S_{jk} \right), \quad (F3)$$

such that

$$\sum_j N_j = 1 \quad . \quad (F4)$$

The a_j^2 term in Eq. F3 is the net atomic orbital population and the overlap population is the term in parenthesis.

Mulliken has used $\gamma = 1/2$, dividing the overlap population

equally between ϕ_j and ϕ_k . However gross AO populations less than zero can occur when a_j and a_k differ greatly in magnitude.

It seems reasonable to assign to each AO ϕ_j a portion of the overlap population which is proportional to the magnitude of its MO coefficient a_j . This modified Mulliken population analysis uses the factor

$$\gamma = \frac{|a_j|}{|a_j| + |a_k|} \quad (F5)$$

The resulting gross AO population N_j is much less likely to be negative than one calculated by the original Mulliken population analysis. This behavior makes the modified gross AO population easier to interpret as an indicator of MO character and more suitable as a weighting factor in a local density of states (LDOS).

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