Spin-polarized self-consistent local orbital method and its application to ferromagnetic Ni(001) slabs
by Xueyuan Zhu

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Physics
Montana State University
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Abstract:
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spin-polarized adaptation of the self-consistent local orbital method developed by Arlinghaus, Gay and
Smith. A new correlation potential derived from a recent analysis of correlation energy for the
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minor role.
SPIN-POLARIZED SELF-CONSISTENT LOCAL ORBITAL METHOD
AND ITS APPLICATION TO FERROMAGNETIC Ni(001) SLABS

by

Xueyuan Zhu

A thesis submitted in partial fulfillment
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of
Doctor of Philosophy
in
Physics

MONTANA STATE UNIVERSITY
Bozeman, Montana
August 1983
ii

APPROVAL

of a thesis submitted by

Xueyuan Zhu

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

August 1, 1983

Date

Chairman, Graduate Committee

Approved for the Major Department

August 1, 1983

Date

Head, Major Department

Approved for the College of Graduate Studies

12 Aug. 1983

Date

Graduate Dean
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ACKNOWLEDGEMENTS

The author gladly takes this opportunity to thank Professor John Hermanson, who suggested and supported the research reported here, for his unlimited advice and patient discussions during the past 2 years.

Sincere thanks also to Robert Motsch and Philip Adolf. It would have been impossible to finish such an intensive work without the assistance they provided at the Scientific Sub-System computer facility at Montana State University.
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ABSTRACT

The electron structure and magnetism of one, three and five-layer Ni(001) slabs are calculated by our spin-polarized adaptation of the self-consistent local orbital method developed by Arlinghaus, Gay and Smith. A new correlation potential derived from a recent analysis of correlation energy for the spin-polarized electron liquid by Vosko, Wilk and Nusair, has been employed in these calculations. The magnetic moments of the surface-layers are 0.98, 0.69 and 0.65 μ_B/atom for these three slabs, respectively. At the inner planes of three and five-layer slabs the bulk moment limit (0.56 μ_B/atom) are approached due to the increased atomic coordinations. The contributions of dehybridization and band-narrowing to this "surface magnetism enhancement" have been determined by repeating the calculations with sp-d matrix elements omitted. The results show that the dehybridization only plays a minor role.
CHAPTER I

INTRODUCTION

Recently, the number of experimental and theoretical studies of magnetism on d-band metal surfaces has increased very rapidly, due to the development of promising new techniques for detecting electron spin-polarization on surfaces, including photoemission (Ref. 1-4), tunneling (Ref. 5), field-emission spectroscopies (Ref. 6-7), scattering of spin-polarized electrons (Ref. 8), electron-capture spectroscopy (Ref. 9-10), Hall-effect measurements (Ref. 11), and ferromagnetic resonance (Ref. 12).

Magnetism is one of the most fundamental and technologically important physical phenomena. The theoretical interest of surface magnetism has attracted more and more theorists during the past several years. The successful local spin-density approximation and the full self-consistent methods for electronic band structure provide great opportunities in this new area.

In the early 70's, there were some very interesting but contradictory measurements on very thin ferromagnetic slabs and interfaces. Liebermann et al. (Ref. 19) reported "dead" magnetism for less than about 2.5 layers of Ni deposited on a Cu substrate.
Bergmann's (Ref.11) anomalous Hall effect measurement supported the existence of "dead" layers. But the spin polarized photoemission measurement by Pierce et al. (Ref.8) showed that even a Ni monolayer deposited on Cu is magnetized. Rau's (Ref.9-10) electron capture spectroscopy measurement agreed with this, but pointed out that the magnetism of Ni overlayer has a reduced moment.

Stoner first proposed the band-structure theory of magnetism (Ref.20-21). C. S. Wang and J. Callaway successfully realized a self-consistent spin-polarization calculation for bulk Ni (Ref.22).

A thin film is somewhat different from a real semi-infinite surface; however, a thick enough thin-film model can accurately simulate the surface properties with great convenience in computation.

In 1980, C. S. Wang and Freeman (Ref.23-24) first used a self-consistent LCAO method to calculate the magnetism of a 9-layer Ni(100) slab. They did not find any magnetically "dead" layers, but a 20% surface-moment deficit (0.44\(\mu_B\)) compared with the bulk-like central-layer moment. They attributed this deficit to a vacancy of a majority-spin \(\tilde{M}_3\) surface state.

Recently, Jepsen, Madsen and Andersen (Ref.25-26) reported the results for the magnetic behavior of one (Ni1), three (Ni3) and five-layer (Ni5) slabs of Ni(100) computed by the LAPW method. In the 5-layer slab case, the magnetic moment of each layer was 0.61, 0.55 and 0.65 \(\mu_B\) from central to surface layer. This result shows
10% enhancement of the surface magnetism compared with the central layer. They obtained an unoccupied $\bar{M}_3$ majority-spin surface state, but they believe it was not enough to cause a surface magnetic deficit. They pointed out: "The essential mechanism behind this is the narrowing at the surface of the $3z^2-r^2$, xz and yz bands and the broadening of the $x^2-y^2$ and xy bands." They predicted: "The spin moment at the (100) surface of a Ni crystal is enhanced over the bulk value by roughly 10% to about 0.63 $\mu_B$ per atom, and the enhancement is mostly of $E_g(x^2-y^2)$ character, and to a small extent, $T_{2g}(xy)$ character."

D. S. Wang, Krakauer and Freeman have used a LAPW method and presented some newer results of Ni(001) and Ni(110) slabs (Ref. 27-28). They claimed that they also found surface magnetism enhancement which is due to a full majority-spin $\bar{M}_3$ surface state.

Some other groups computed the magnetism of Ni/Cu, Cu/Ni interfaces and Ni(100) monolayer (Ref. 29-31).

Starting in the summer of 1981, we adopted the SCLO method (Ref. 32-34) of Smith, Gay and Arlinghaus of General Motor Research Laboratories, and successfully calculated one, three and five-layer slabs of Ni(100). The results agreed excellently with Jepsen et al.

Plummer et al. and Erskine (Ref. 35-37) published their spin-polarized photoemission results for the Ni(100) surface. They pointed
out the existence of some surface states. Some of these surface states had been predicted by Dempsey and Kleinman (Ref. 38) previously. Unfortunately until now there has been no way to distinguish the magnetic moments of different layers.
CHAPTER 2

METHODOLOGY

Exchange and Correlation (XC) Potentials

In single electron theory, the many-body effect is approximated by a mean field. Hartree and Fock (HF) (Ref. 39-40) first introduced the "exchange potential," which is due to the anti-symmetric exchange property of the wavefunction of a spin-1/2 particle system. Their method is called the HF approximation, and the exchange energy or potential is named the HF energy or potential.

The "correlation energy" of an interacting electron gas is defined as the difference between the HF energy and any better approximation to the total energy. So, the total potential of a single electron is, combining the potentials,

\[ V^\sigma(\vec{r}) = \phi(\vec{r}) + V_X^\sigma(\vec{r}) + V_C^\sigma(\vec{r}) \]  

(1)

where \( \phi(\vec{r}) \) is the electrostatic potential

\[ \phi(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - \sum Z \frac{1}{|\vec{r} - \vec{m}|} \]  

(2)

In local-spin-density theory (Ref. 41-43), the exchange energy
can be written as

$$\varepsilon_x = \varepsilon_x(r_s, \zeta)$$  \hspace{1cm} (3)

where

$$r_s = (3/4\pi \rho)^{1/3}, \quad \rho(\tilde{r}) = \rho_+(\tilde{r}) + \rho_-(\tilde{r}),$$  \hspace{1cm} (4)

and

$$\zeta = (\rho_+ - \rho_-)/ (\rho_+ + \rho_-)$$  \hspace{1cm} (5)

Thus, the exchange potential will be

$$V^\sigma_x = \frac{\partial}{\partial \rho_\sigma} (\rho \varepsilon_x) = \varepsilon_x + \rho \frac{\partial \varepsilon_x}{\partial r_s} \frac{\partial r_s}{\partial \rho_\sigma} + \rho \frac{\partial \varepsilon_x}{\partial \zeta} \frac{\partial \zeta}{\partial \rho_\sigma}$$  \hspace{1cm} (6)

Since

$$\frac{\partial r_s}{\partial \rho_\sigma} = - \frac{r_s}{3}$$  \hspace{1cm} (7)

and

$$\rho \frac{\partial \zeta}{\partial \rho_\pm} = \pm (1 \mp \zeta),$$  \hspace{1cm} (8)
The exchange energy is given by an analytic form

\[ V_x^\pm = \varepsilon_x - \frac{r_s^3}{3} \frac{\partial \varepsilon_x}{\partial r_s} \pm \frac{1}{2} (1 + \xi) \frac{\partial \varepsilon_x}{\partial \xi} \]  

(9)

This tells us that the exchange energy favors a ferromagnetic ground state in which the imbalance between \( \rho_+ \) and \( \rho_- \) would decrease the total energy of the system.

For \( \rho_+ = \rho_- \), we introduce the paramagnetic exchange energy

\[ \varepsilon_x^p = - \frac{3}{2} \left( \frac{3}{\pi} \right)^{1/3} \rho^{1/3} \]  

(10)

Then Eq(9) becomes

\[ \varepsilon_x^\pm = \varepsilon_x^p (1 + \xi) \]  

(11)

The exchange energy per electron at a certain spatial point, where the density \( \rho \) and polarization \( \xi \) are defined, is

\[ \varepsilon_x (r_s, \xi) = \varepsilon_x^p (r_s) \left\{ \frac{1}{4} \left( 1 + \xi \right)^{1/3} \left( 1 - \xi \right)^{1/3} - \left( 1 + \xi \right)^{1/3} \right\}/2 \]  

(12)

Since

\[ \varepsilon_x - \frac{r_s^3}{3} \frac{\partial \varepsilon_x}{\partial r_s} = \frac{4}{3} \varepsilon_x (r_s, \xi) \]  

(13)

\[ (1 + \xi) \frac{\partial \varepsilon_x}{\partial \xi} = 2 \frac{3}{3} \varepsilon_x^p (1 + \xi) \left\{ \frac{1}{4} \left( 1 + \xi \right)^{1/3} \left( 1 - \xi \right)^{1/3} \right\}, \]  

the exchange potential is
Kohn and Sham (Ref. 44) first obtained this result in 1965. We may notice that it is only 2/3 of Slater's exchange potential (Ref. 45) which overestimated the exchange effect and caused unreasonably large theoretical values of magnetic moments (Ref. 46-48).

In the 1930's, Wigner (Ref. 49-50) calculated the correlation energy for both high and low-density limits of a paramagnetic electron system. Pines (Ref. 51-52) first suggested an interpolation formula

\[ V_c = \frac{4}{3} \frac{\epsilon_p}{x} (1 + \xi) \frac{1}{3} = -2\sqrt[3]{3\rho_{\pm}/\pi} \]

Kohn and Sham (Ref. 44) first obtained this result in 1965. We may notice that it is only 2/3 of Slater's exchange potential (Ref. 45) which overestimated the exchange effect and caused unreasonably large theoretical values of magnetic moments (Ref. 46-48).

In the 1930's, Wigner (Ref. 49-50) calculated the correlation energy for both high and low-density limits of a paramagnetic electron system. Pines (Ref. 51-52) first suggested an interpolation formula

\[ \epsilon_c = \frac{-0.88}{r_s + 7.8} \]

for the metallic density (1.9 < r_s < 5.6). Thus, one can obtain a corresponding Wigner potential for paramagnetic system.

\[ V_c = \frac{\rho \epsilon_c}{d\rho} = -\frac{0.56\rho^{2/3} + 0.0059\rho^{1/3}}{(0.079 + \rho^{1/3})^2} \]

We adapted the correlation energy from a recent study of the spin-polarized electron liquid by Vosko, Wilk and Nusair (Ref. 53). They used a Pade method to interpolate the correlation energy data from the high to low-density regions, where the results of the RPA (Ref. 54-56) and Monte Carlo methods, (Ref. 57) are available, respectively.
We suppose the spin-dependent correlation energy can be written as

$$\varepsilon_c(r_s, \zeta) = \varepsilon_c(r_s, 0) + \frac{1}{2} \alpha_c(r_s) \zeta^2$$  \hspace{1cm} (17)

and both $\varepsilon_c(r_s, 0)$ and $\alpha_c(r_s)$ can be interpolated as

$$\varepsilon_c(r_s, 0) = -AF(r_s/R)$$  \hspace{1cm} (18)

$$\alpha_c(r_s) = A\alpha F(r_s/R_\alpha)$$  \hspace{1cm} (19)

where

$$F(x) = (1+x^3) \ln(1+\frac{1}{x})$$  \hspace{1cm} (20)

Since

$$F(x) - \frac{x}{3} F'(x) = \ln(1+\frac{1}{x})$$  \hspace{1cm} (21)

The spin-polarized correlation potential becomes

$$V_c = -A \ln(1+\frac{R}{r_s}) + \alpha_c(r_s) \zeta + \beta_c(r_s) \zeta^2$$  \hspace{1cm} (22)

where

$$\beta_c(r_s) = \frac{1}{2} A\alpha \ln(1+\frac{R}{r_s}) - \alpha(r_s)$$  \hspace{1cm} (23)

We find $A=48.6$ mRyd, $R=15$, and $A_\alpha=31.1$ mRyd, $R_\alpha=16.4$ which can fit Vosko's data for $\varepsilon_c$ and $\alpha_c$ to better than 1 mRyd.
Table 1. The paramagnetic correlation energy (mRyd) of Vosko et al, and Zhu-Hermanson's fit with A=48.6 mRyd and R=15

<table>
<thead>
<tr>
<th>rs</th>
<th>Vosko et al</th>
<th>Zhu-Hermanson</th>
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<tbody>
<tr>
<td>0.5</td>
<td>154.13</td>
<td>151.4</td>
</tr>
<tr>
<td>1.0</td>
<td>120.04</td>
<td>120.0</td>
</tr>
<tr>
<td>2.0</td>
<td>89.57</td>
<td>90.2</td>
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<tr>
<td>3.0</td>
<td>73.77</td>
<td>74.5</td>
</tr>
<tr>
<td>4.0</td>
<td>63.57</td>
<td>62.5</td>
</tr>
<tr>
<td>5.0</td>
<td>56.27</td>
<td>56.4</td>
</tr>
<tr>
<td>10.0</td>
<td>37.09</td>
<td>36.1</td>
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Table 2. The spin-stiffness of the correlation energy (mRyd), \( a_c(r_s) \), of Vosko et al., Zhu-Hermanson, and von Barth-Hedin

<table>
<thead>
<tr>
<th>( r_s )</th>
<th>Vosko et al</th>
<th>Zhu-Hermanson*</th>
<th>von Barth-Hedin</th>
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<tr>
<td>0.5</td>
<td>100.1</td>
<td>99.6</td>
<td>122.7</td>
</tr>
<tr>
<td>1.0</td>
<td>79.4</td>
<td>79.4</td>
<td>94.7</td>
</tr>
<tr>
<td>2.0</td>
<td>60.1</td>
<td>60.2</td>
<td>68.2</td>
</tr>
<tr>
<td>3.0</td>
<td>49.8</td>
<td>49.9</td>
<td>53.7</td>
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<td>4.0</td>
<td>43.0</td>
<td>43.0</td>
<td>44.2</td>
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<tr>
<td>5.0</td>
<td>38.0</td>
<td>38.0</td>
<td>37.3</td>
</tr>
<tr>
<td>6.0</td>
<td>34.2</td>
<td>34.2</td>
<td>32.0</td>
</tr>
</tbody>
</table>

* Zhu-Hermanson's fit uses the parameters

\[ A_\alpha = 31.1 \text{ mRyd} \]

and

\[ R_\alpha = 16.4. \]
We can expand the exchange potential as
\[ V_x^+ = V_x^P \left( 1 \pm \frac{1}{3} \zeta + \frac{1}{9} \zeta^2 + \cdots \right) \]  
(24)

From Eq(22) and Eq(24), we find that the XC potential difference between up and down-spin is
\[ \Delta V_{xc} = \Delta V_x + \Delta V_c \]  
(25)

where
\[ \Delta V_x = -\frac{2}{3} V_x^P(r_s) \zeta \]  
(26)
\[ \Delta V_c = 2\alpha_c(r_s) \zeta \]  
(27)

This shows that the exchange potential favors spin-polarization but the correlation potential opposes this tendency. The final balance between these two competing potentials will build up a stable magnetic moment in some metals.

Comparing our data with the commonly used von Barth-Hardin (BH) correlation potential, we find that the BH potential overestimates the spin-polarization stiffness \( \alpha_c \) at the most important density region \( 0.5 < r_s < 2.0 \) for Ni. For Ni, we tested both the Vosko and BH potentials and we find that the BH potential leads to a reduction of the magnetic moment, by 1\%, and a reduction of the spin-splitting, by 2-8\% (Ref.58).
Geometry and Symmetry

Because of the existence of a surface, the 3-D periodicity of the bulk structure will be broken in the z-direction which is perpendicular to this surface. If we use a periodically-repeated thin-slab model to simulate the bulk-surface system, then we can recover the periodicity in the z-direction and employ the Fourier transformation technique again. Thus the problem will be much simpler mathematically than that of a real semi-infinite system.

Essentially, a NiS slab is good enough to describe a surface system, since the central layer's features are very close to the bulk's. Usually, we assume the distance between two slabs, "ELZ", to be about 10 times the lattice constant, "ALAT", of the surface structure. Thus, we have determined a 3-D unit cell with a volume of $ALAT^2*ELZ$. Inside this unit cell, the number of atoms is equal to the number of layers comprising the slab.

On the Ni(001) surface, the x and y axes are defined to be along the bulk [100] and [010] directions as shown in Fig.1.

In this real space coordinate system, we ordered the atomic orbitals of each layer as below:

1. 1s
2. 2s
3. 2p(x)
4. 2p(y)
5. 2p(y)

13. 3d(yz)
14. 3d($x^2-y^2$)
15. 4s
16. 4p(x)
In this coordinate system the $\bar{\Sigma}$ line is parallel to the x axis and the $\bar{\Lambda}$ line is at $45^\circ$ (see Fig. 1). Our symmetry labels conform to the character table of Alldredge and Kleinman (Ref.59). We add primes to denote the odd symmetries under z-reflection.

Because of the symmetry property, we only need to consider the 1/8 irreducible region of the square Brillouin zone. To study the magnetism of the slab, we calculated the charge densities of both spins by summing the square of wavefunctions over 15 or 36k points in the irreducible zone:

$$\rho^\sigma(\vec{r}) = \sum_{i} \sum_{k_{11}} \psi^\sigma_{i,k_{11}}(\vec{r})^2$$

The 15 and 36k point samples are shown in Fig. 2.

For the Ni(100) slab, the point group is $D_{4h}$, i.e., $(C_{4v} \times R_z)$, where $C_{4v}$ is the square group and $R_z$ is a z-reflection group with 2
elements, I and $\sigma_z$. The operations of these 2 elements are

\[
I : x \ y \ z \\
\sigma_z : x \ y \ -z
\]

$C_{4v}$ has 8 elements in 5 classes. Their operations are

\[
I : x \ y \ z \\
C_4^2 : -x \ -y \ z \\
2C_4^1 : -y \ x \ z \\
\quad \quad y \ -x \ z.
\]

\[
2\sigma_{x,y} : x \ -y \ z \\
\quad \quad : -x \ y \ z \\
2\sigma_{x+y} : -y \ -x \ z \\
\quad \quad y \ x \ z.
\]

In $k$-space, the wavevector group (Ref.60) of the high-symmetry points and lines are

\[
\vec{\Gamma}, \vec{M}: \{ I, C_4^2, 2C_4^1, 2\sigma_{x,y}, 2\sigma_{x+y} \} \ast \{ I, \sigma_z \}
\]

\[
\vec{X}: \{ I, C_4^2, \sigma_{x+y}, \sigma_{x-y} \} \ast \{ I, \sigma \}
\]

\[
\vec{\Delta}: \{ I, \sigma_{x-y} \} \ast \{ I, \sigma_z \}
\]

\[
\vec{\Sigma}: \{ I, \sigma_{x} \} \ast \{ I, \sigma_z \}
\]

\[
\vec{Y}: \{ I, \sigma_{x+y} \} \ast \{ I, \sigma_z \}.
\]

However, there is only $R_z$ symmetry for general $k_{11}$ points.

At $\vec{\Gamma}$ and $\vec{M}$, there is $C_{4v}$ symmetry plus $R_z$. The irreducible
representations and basis functions of $C_{4v}$ are (Ref. 61).

$$\tilde{r}_1, \tilde{M}_1 : 1; z; 3z^2-r^2$$

$$\tilde{r}_2, \tilde{M}_2 : xy(x^2-y^2)$$

$$\tilde{r}_3, \tilde{M}_3 : xy$$

$$\tilde{r}_4, \tilde{M}_4 : x^2-y^2$$

$$\tilde{r}_5, \tilde{M}_5 : x, y; xz, yz$$

For a Ni(001) slab with more than one layer, there are two types of plane, A and B, which are displaced by a vector $\tilde{n}_0$ with respect to each other (see Fig. 1). For the A-plane, one of the lattice points is defined at the origin. We emphasize that the basis function $xy(x^2-y^2)$ of the $\tilde{M}_2$ symmetry has the same symmetry as B-plane's xy band at the $\tilde{M}$ point (see Fig. 3). But the A-plane's xy band at $\tilde{M}$ point belongs to $\tilde{M}_3$ symmetry. This was pointed out in Ref. 59.

For the X point, there is $C_{2v}$ symmetry plus $R_z$; its representations and basis functions are

$$\tilde{X}_1 : 1; z; xy; 3z^2-r^2$$

$$\tilde{X}_2 : x+y; x-y; x^2-y^2$$

$$\tilde{X}_3 : (x+y)z$$

$$\tilde{X}_4 : (x-y)z$$

In addition to $R_z$ reflection symmetry, there are other mirror-plane reflection $\sigma_{x-y}$, $\sigma_x$ and $\sigma_{x+y}$ for high symmetry lines $\tilde{A}$, $\tilde{\Sigma}$ and $\tilde{Y}$ respectively. We will denote with 1 even $xy$-parity functions,
and with 2 those odd on these lines. Since all symmetrical and
genral points have $\sigma_z$ reflection symmetry, we are able to separate
the Hamiltonian and overlap matrixes into even and odd parts, re-
ducing the diagonalization time by a factor of four.

Atomic Orbitals, Potentials and Preliminary Calculation

Because of the localization of d-electrons, the atomic orbital
basis is a reasonable choice for d-band metals calculations. To
simplify the calculation of Hamiltonian and overlap matrix elements,
our localized atomic orbitals are restricted to be linear combinations
of Gaussians of various angular momenta.

$$a_i(\vec{r}) = Y_{\ell m}(\theta, \phi) r^\ell \sum_j D_{ij} \exp(-\alpha_i r^2)$$

(29)

For Ni or Cu, we built a minimum basis set with 15 occupied atomic
orbitals, 1s, 2s, 2p, 3s, 3p, 3d and 4s for each layer, which have
been expanded into linear combinations of Gaussians. To increase
the variational freedom, three diffuse single Gaussians are added to
simulate the virtual orbitals, 5s, 4p and 4d, in the outer atomic
region. Since our basis of 24 functions per layer is much smaller
than that used in LAPW calculations for Ni slabs (45-55/layer), a con-
siderable reduction of computing time is realized.

The procedure for computing the coefficients $D_{ij}(i)$ and scale
factors $\alpha_j(i)$ of different orbitals is described in Ref. 62 and the
App. A of Ref. 32. In Table 3., we list the scale factors \( \alpha_j \) and coefficients \( D_j \) of \( s \), \( p \), and \( d \) orbitals respectively.

The starting potential for the calculations is made by overlapping atomic-charge densities. In computing the matrix elements of this potential, it is expedient to first compute the matrix elements of a potential made up of overlapping (spherically symmetric) atomic potentials

\[
W(\mathbf{r}) = \sum_{\mathbf{m}} v(\mathbf{r} - \mathbf{m})
\]

(30)

where \( v(\mathbf{r} - \mathbf{m}) \) is the atomic potential and the sum runs over all atomic sites denoted by position vector \( \mathbf{m} \). The atomic potential consists of a nuclear term plus an electronic term

\[
v(\mathbf{r}) = -\frac{Z}{r} + u_e(\mathbf{r})
\]

(31)

To eliminate the divergent behavior of the nuclear term, we construct a "total atomic potential"

\[
u(\mathbf{r}) = \frac{Z}{r} \left\{ \exp(-r^2) - 1 \right\} + u_e(\mathbf{r})
\]

(32)

which has no singularity at the origin and is suitable for approximation by a Gaussian expansion. Thus, the potential of Eq(31) can be
Table 3-1. The scale factors $\alpha_j$ and coefficients $D_j$ for s orbitals

<table>
<thead>
<tr>
<th>$\alpha_j$</th>
<th>$D_j$ of 1s</th>
<th>$D_j$ of 2s</th>
<th>$D_j$ of 3s</th>
<th>$D_j$ of 4s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0700000</td>
<td>0.0000000</td>
<td>0.0000000</td>
<td>0.0000000</td>
<td>0.0000000</td>
</tr>
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<td>0.1197705</td>
<td>0.0000000</td>
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<td>0.6124116</td>
</tr>
<tr>
<td>0.3348712</td>
<td>0.0000000</td>
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<td>-1.7346211</td>
<td>-0.1321180</td>
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<td>0.9677963</td>
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<td>0.0000000</td>
<td>-3.6407412</td>
<td>-1.3487436</td>
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<td>2.8920765</td>
<td>0.0000000</td>
<td>8.1439547</td>
<td>7.1295201</td>
<td>2.1434983</td>
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<tr>
<td>8.0913675</td>
<td>0.0000000</td>
<td>13.6110435</td>
<td>7.9676855</td>
<td>2.0088771</td>
</tr>
<tr>
<td>22.9389906</td>
<td>0.0000000</td>
<td>-33.5437246</td>
<td>-20.6783054</td>
<td>-8.8727049</td>
</tr>
<tr>
<td>84.7615438</td>
<td>-33.5437246</td>
<td>-20.6783054</td>
<td>-8.8727049</td>
<td>-2.1661321</td>
</tr>
<tr>
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<td>-20.6783054</td>
<td>-8.8727049</td>
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<td>-2.1661321</td>
</tr>
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<td>14937.9479113</td>
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<td>-20.6783054</td>
<td>-8.8727049</td>
<td>-2.1661321</td>
</tr>
</tbody>
</table>

* For 5s, there is only a nonzero coefficient $D_4=0.3438588$. 
Table 3-2. The scale factors $a_j$, and coefficients $D_j$ for p orbitals

<table>
<thead>
<tr>
<th>$a_j$</th>
<th>$D_j$ of 2p</th>
<th>$D_j$ of 3p</th>
<th>$D_j$ of 4p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20000000</td>
<td>0.00000000</td>
<td>0.00000000</td>
<td>0.39018618</td>
</tr>
<tr>
<td>0.97695586</td>
<td>0.00000000</td>
<td>1.45907504</td>
<td>0.00000000</td>
</tr>
<tr>
<td>3.10329134</td>
<td>0.00000000</td>
<td>7.28542502</td>
<td>0.00000000</td>
</tr>
<tr>
<td>8.77150789</td>
<td>-15.44961730</td>
<td>-2.03813930</td>
<td>0.00000000</td>
</tr>
<tr>
<td>25.76669530</td>
<td>-90.19915233</td>
<td>-39.54596233</td>
<td>0.00000000</td>
</tr>
<tr>
<td>75.69081569</td>
<td>-154.96140933</td>
<td>-61.41105038</td>
<td>0.00000000</td>
</tr>
<tr>
<td>222.34514410</td>
<td>-132.62741105</td>
<td>-50.80341581</td>
<td>0.00000000</td>
</tr>
<tr>
<td>653.14876914</td>
<td>-121.75582077</td>
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<td>0.00000000</td>
</tr>
</tbody>
</table>

Table 3-3. The scale factors $a_j$ and coefficients $D_j$, for d orbitals

<table>
<thead>
<tr>
<th>$a_j$</th>
<th>$D_j$ of 3d</th>
<th>$D_j$ of 4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32650127</td>
<td>0.11350223</td>
<td>0.36798313</td>
</tr>
<tr>
<td>1.07087955</td>
<td>1.24523880</td>
<td>0.00000000</td>
</tr>
<tr>
<td>3.51233862</td>
<td>10.11723233</td>
<td>0.00000000</td>
</tr>
<tr>
<td>11.51999081</td>
<td>34.43106498</td>
<td>0.00000000</td>
</tr>
<tr>
<td>37.78399602</td>
<td>56.63202625</td>
<td>0.00000000</td>
</tr>
</tbody>
</table>
written as
\[ \nu(r) = -\frac{Z}{r} \exp(-r^2) + u(r) \] (33)

By using a spherically symmetric atomic charge distribution, of which the valence occupancy is 3d\textsuperscript{9}s\textsuperscript{1}, we evaluated the "total atomic potential" and the exchange-correlation potential within the local density approximation and fit them with Gaussian expansions
\[ u(r) = \sum \Sigma D_j \exp(-\alpha_j r^2) \] (34)
of which the scale factors \( \alpha_j \) and coefficients \( D_j \) are shown in Table 4.

Using the Gaussian-fitted atomic orbitals and potential, the overlap, potential and kinetic matrix elements
\[ O_{ij}(m) = \langle a_i(\vec{r}) | a_j(\vec{r}-\vec{m}) \rangle \] (35)
\[ V_{ij}(\bar{m}) = \sum \Sigma h < a_i(\vec{r}) | \nu(\vec{r}-\bar{m}) | a_j(\vec{r}-\bar{m}) > \] (36)
\[ T_{ij}(\bar{m}) = < a_i(\vec{r}) | -\frac{1}{2} \nabla^2 | a_j(\vec{r}-\bar{m}) > \] (37)
Table 4. The scale factors and coefficients of the "total atomic potential" and the exchange-correlation potential

<table>
<thead>
<tr>
<th>$\alpha_j$</th>
<th>$D_j$ of &quot;total atomic potential&quot;</th>
<th>$D_j$ of exchange-correlation potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03914699</td>
<td>-0.12777584</td>
<td>-0.12777584</td>
</tr>
<tr>
<td>0.04697784</td>
<td>0.57211627</td>
<td>0.57211627</td>
</tr>
<tr>
<td>0.05637515</td>
<td>-0.79273327</td>
<td>-0.79273327</td>
</tr>
<tr>
<td>0.30159735</td>
<td>-0.56404984</td>
<td>-0.31901655</td>
</tr>
<tr>
<td>0.58600651</td>
<td>-0.72613003</td>
<td>0.02401055</td>
</tr>
<tr>
<td>1.13861621</td>
<td>19.61831961</td>
<td>-1.50464864</td>
</tr>
<tr>
<td>2.21234211</td>
<td>17.89941822</td>
<td>0.39559214</td>
</tr>
<tr>
<td>4.29860171</td>
<td>6.51648261</td>
<td>-2.42642719</td>
</tr>
<tr>
<td>8.35222393</td>
<td>16.57933076</td>
<td>5.67341046</td>
</tr>
<tr>
<td>16.22845037</td>
<td>6.09909345</td>
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</tr>
<tr>
<td>31.53203310</td>
<td>16.71051295</td>
<td>2.54603849</td>
</tr>
<tr>
<td>61.26703961</td>
<td>0.62789667</td>
<td>-3.10908090</td>
</tr>
<tr>
<td>119.04243950</td>
<td>15.30555297</td>
<td>4.49476725</td>
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<tr>
<td>231.30058986</td>
<td>-2.15282248</td>
<td>-5.15269496</td>
</tr>
<tr>
<td>449.41924153</td>
<td>10.56605143</td>
<td>-7.91111706</td>
</tr>
</tbody>
</table>
can be computed by closed forms (Ref. 63-65). For example, a 2-center Gaussian integral

\[ I = \int \exp\{-\alpha(\vec{r}-\vec{A})^2\} \cdot \exp\{-\beta(\vec{r}-\vec{B})^2\} \, d\vec{r} \quad (38) \]

can be simplified to a single-center Gaussian integral, since

\[ \exp\{-\alpha(\vec{r}-\vec{A})^2 - \beta(\vec{r}-\vec{B})^2\} = c \exp\{-(\alpha+\beta) \cdot (\vec{r}-\vec{D})^2\} \quad (39) \]

where

\[ c = \exp\{ -\frac{\alpha\beta}{\alpha + \beta} \cdot \frac{r^2}{AB} \} \quad (40) \]

\[ D = \frac{\alpha\vec{A} + \beta\vec{B}}{\alpha + \beta} \quad (41) \]

\[ \vec{r}_{AB} = \vec{A}-\vec{B} \quad (42) \]

With this advantage of Gaussian integrals, even an N-center integral can be reduced to a single-center one by algebraic manipulation.

As mentioned before, we used an overlapping atomic potential in place of the potential due to the overlapping atomic charge densities, to calculate the starting potential matrix elements. The slowly-varying
nonzero differences

\[ \Delta V(\mathbf{r}) = V\{ \sum_{\mathbf{n}} \rho_{\text{atom}}(\mathbf{r} - \mathbf{n}) \} - \sum_{\mathbf{n}} V(\mathbf{r} - \mathbf{n}) \]  

(43)

and their Fourier coefficients:

\[ \Delta V(\mathbf{q}) = \int \Delta V(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} \]  

(44)

can be computed by using the program "ITQP". After summing \( \Delta V(\mathbf{q}) \) with \( S_{ij}(\mathbf{m}, \mathbf{q}) \) over fundamental discrete reciprocal lattice points, we obtain the potential matrix elements changes

\[ \Delta V_{ij}(\mathbf{m}) = \sum_{\mathbf{q}} \Delta V(\mathbf{q}) \cdot S_{ij}(\mathbf{m}, \mathbf{q}) \]  

(45)

where

\[ S_{ij}(\mathbf{m}, \mathbf{q}) = \langle a_i(\mathbf{r}) | e^{i\mathbf{q} \cdot \mathbf{r}} | a_j(\mathbf{r} - \mathbf{m}) \rangle \]  

(46)

In order to save computing time for evaluating potential matrix elements, we also used a screened "total atomic potential"

\[ u_s(\mathbf{r}) = \sum_j D_j \exp\{-(\alpha_j + \gamma) \mathbf{r}^2\} \]  

(47)
The difference

\[ \Delta V(\mathbf{r}) = \sum_{\mathbf{n}} \{ u(\mathbf{r}-\mathbf{n}) - u_s(\mathbf{r}-\mathbf{n}) \} \]  

(48)

can also be treated by Eq(44) and Eq(45), then we get another contribution to the starting matrix elements \( \Delta V_{ij}(\mathbf{m}) \).

Because of the 2-D translation symmetry on the surface, the calculation of Eq(44) can be simplified tremendously as

\[ \Delta V(q) = \sum_{\mathbf{n}} f e^{-i\mathbf{q} \cdot \mathbf{r}} (1-e^{-\gamma(\mathbf{r}-\mathbf{n})^2}) u(\mathbf{r}-\mathbf{n}) \, dr \]  

(49)

Let \( \mathbf{r}' = \mathbf{r} - \mathbf{n} \), then

\[ \Delta V(q) = \sum_{\mathbf{n}} e^{-i\mathbf{q} \cdot \mathbf{n}} f e^{-i\mathbf{q} \cdot \mathbf{r}'} (1-e^{-\gamma \mathbf{r}'^2}) u(\mathbf{r}') \, dr' \]  

(50)

where the atomic integral is not hard to work out, and

\[ \sum_{\mathbf{n}} e^{i\mathbf{q} \cdot \mathbf{n}} = \sum_{\mathbf{n}_z} e^{iqz} \sum_{\mathbf{n}_a, \mathbf{n}_b} e^{i\mathbf{q}_a \cdot \mathbf{n}_a, \mathbf{n}_b} \]  

(51)

For A-planes ( \( z = 0, +2, +4 \ldots \) ), we have

\[ \sum_{\mathbf{n}_a} e^{i\mathbf{q}_a \cdot \mathbf{n}_a} = 1 \]  

(52)
and for B‐planes \((z=+1, +3\ldots)\), we have

\[
\sum_{\tilde{n}} e^{i\tilde{q}\cdot\tilde{n}} = e^{i\tilde{q}\cdot\tilde{n}_0} \tag{53}
\]

So, for a 5‐layer slab, we will have

\[
\sum_{\tilde{n}} e^{i\tilde{q}\cdot\tilde{n}} = 1+2\cos(\frac{q_z a}{\sqrt{2}})\cos(\tilde{q}_{\parallel} \cdot \tilde{n}_0) + 2\cos(\sqrt{2}q_z a) \tag{54}
\]

This calculation is processed by the program "CHKQC".

4. Bloch Basis Function

Because of the 2‐D translation symmetry parallel to the slab surface, \(K_{11}\) is a good quantum number. We therefore construct a Bloch function

\[
\phi_j(k_{11}, \tilde{r}) = \frac{1}{\sqrt{N}} \sum_{\tilde{n}} e^{i\tilde{k}_{\parallel} \cdot \tilde{n}} a_j(\tilde{r} - \tilde{n}_n) \tag{55}
\]

for an orbital of type \(j\) in each unit cell. Here \(j\) is a compound index giving the orbital type and the plane to which the orbital belongs.

So, the total number of these Bloch basis functions are 24, 72 and 120 for 1, 3 and 5‐layer Ni slabs, respectively.

The Hamiltonian matrix elements of given \(K_{11}\) are
\[ H_{ij}(K_{11}) = \langle \phi_1(k_n, \overline{x}) | H | \phi_j(k_n, \overline{x}) \rangle \]

\[ = \sum_{\tilde{m}} e^{i\mathbf{k}_n \cdot \mathbf{\tilde{m}}} \langle a_1(\overline{x}) | H | a_j(\overline{x} - \mathbf{\tilde{m}}) \rangle \]

\[ = \sum_{\tilde{m}} e^{i\overline{k}_n \cdot \mathbf{\tilde{m}}} H_{ij}(\mathbf{\tilde{m}}) \tag{56} \]

and the overlap will be a non-diagonal Hermitian matrix

\[ S_{ij}(K_{11}) = \langle \phi_1(k_n, \overline{x}) | \phi_j(k_n, \overline{x}) \rangle \]

\[ = \sum_{\tilde{m}} e^{i\overline{k}_n \cdot \mathbf{\tilde{m}}} S_{ij}(\mathbf{\tilde{m}}) \tag{57} \]

Bloch basis functions are not orthogonal to each other in the local orbital method.

Since the slab Hamiltonian is block diagonal in \( K_{11} \), the slab eigenfunctions are simply linear combinations of Bloch functions of a given \( K_{11} \).

\[ \psi_{i, \overline{k}_n}(\overline{x}) = \sum_{j=1}^{m} u_{ij}(\overline{k}_n) \phi_j(\overline{k}_n, \overline{x}) \tag{58} \]

Thus, we obtain the Schrödinger equation

\[ H U = E S U \tag{59} \]
or

\[
\sum_{l} H_{ll}(\tilde{k}_{n}) U_{ll}(\tilde{k}_{n}) = E_{l}(\tilde{k}_{n}) \sum_{l} S_{jl}(\tilde{k}_{n}) U_{ll}(\tilde{k}_{n})
\]  \quad (60)

Unfortunately, the eigenvector \( U \) no longer has clear physical meaning, because the orthogonality only can be defined as

\[
\sum_{m} \sum_{n} U_{jm}(\tilde{k}_{n}) S_{mn}(\tilde{k}_{n}) U_{nj}(\tilde{k}_{n}) = \delta_{ij}
\]  \quad (61)

To interpret the meaning of the projection of a eigenvector, Mulliken (Ref. 66) suggested that for \( j \)th eigenvector

\[
U_{jm}(\tilde{k}_{n}) \sum_{n} S_{mn}(\tilde{k}_{n}) U_{nj}(\tilde{k}_{n}) = p_{jm}
\]  \quad (62)

is the projected content of the \( m \)th basis function.

But, some negative Mulliken projections found in our calculation, were forcing us to transform to the orthogonal basis set which was introduced by Lowdin (Ref. 67). Since the overlap \( S \) is a positive-definite Hermitian matrix, it can be transformed to a diagonal matrix \( D \), in which all the elements are positive, i.e.

\[
M^{+} S M = D
\]  \quad (63)
where

\[
D = \begin{bmatrix}
    d_1 \\
    & d_2 \\
    &   & \ddots \\
    &   &   & d_m
\end{bmatrix}  \tag{64}
\]

We define two new matrixes

\[
S^{-\frac{1}{2}} = M D^{-\frac{1}{2}} M^+ \tag{65}
\]

and

\[
S^{+\frac{1}{2}} = M D^{+\frac{1}{2}} M^+ \tag{66}
\]

where

\[
D^{-\frac{2}{3}} = \begin{bmatrix}
    1/\sqrt{\alpha_1} \\
    & 1/\sqrt{\alpha_2} \\
    &   & \ddots \\
    &   &   & 1/\sqrt{\alpha_m}
\end{bmatrix}  \tag{67}
\]
Then, we have
\[ S^{-\frac{1}{2}} S S^{-\frac{1}{2}} = I \]  \hspace{1cm} (69)

and the Schrodinger equation \( H U = E S U \) can be changed into
\[ H' U' = E U' \]  \hspace{1cm} (70)

where
\[ H' = S^{-\frac{1}{2}} H S^{-\frac{1}{2}} \]  \hspace{1cm} (71)
\[ U' = S^{\frac{1}{2}} U \]  \hspace{1cm} (72)
Thus, we have avoided the negative projection. Since the new basis functions are linear combinations of the old basis functions, they no longer are pure s, p, or d functions.

**Self-Consistent Method and Paramagnetic Band Calculation**

The self-consistent local orbital method, developed by Arlinghaus, Gay and Smith, is one of the most successful computational methods which have been applied to d-band metal surfaces. The paramagnetic electronic band structure calculation is started from an overlapping atomic configuration, in which the slab charge distribution is computed by summing the atomic electronic densities of atoms at different sites

\[
\rho_o(\vec{r}) = \sum_{\text{atom}} \rho(\vec{r}-\vec{m})
\]  

(74)

This distribution has been used to calculate the starting Hamiltonian matrix elements and it will be used as a reference charge distribution in the forthcoming iteration procedure also.

The existence of surfaces gives rise to an extensive electronic-
charge rearrangement from the overlapping atomic picture, so it is important to construct a self-consistent slab charge distribution through iterations. In each iteration, from a new slab charge distribution, we are able to calculate a new slab potential which will be used to correct the old Hamiltonian.

Essentially, our SC method is based on the Fourier technique. The differences between the new charge density and the reference overlapping atomic density

$$\Delta \rho_n(\vec{r}) = \rho_n(\vec{r}) - \rho_0(\vec{r})$$

(75)

and the difference between the new XC potential and that calculated from reference

$$\Delta V_n^{xc}(\vec{r}) = V_n^{xc}(\vec{r}) - V_0^{xc}(\vec{r})$$

(76)

are treated by Fourier transformation

$$\Delta \rho_n(q) = \int \Delta \rho_n(\vec{r}) e^{-i \vec{q} \cdot \vec{r}} d\tau$$

(77)

and

$$\Delta V_n^{xc}(q) = \int \Delta V_n^{xc}(\vec{r}) e^{-i \vec{q} \cdot \vec{r}} d\tau$$

(78)
Since the Fourier component of the electrostatic potential is

\[ \phi_n(\bar{q}) = \frac{4\pi n(\bar{q})}{q^2} \quad (79) \]

then,

\[ \Delta\phi_n(\bar{q}) = -\frac{4\pi \Delta n(\bar{q})}{q^2} \quad (80) \]

Since \( \Delta n(\bar{q}=0)=0 \) (the system is neutral), a limiting process is required to determine \( \Delta\phi(\bar{q}=0) \)

\[ \Delta\phi_n(\bar{q}=0) = \lim_{q_z \to 0} \left\{ 4\pi \Delta n(\bar{q}_n=0, q_z)/q_z^2 \right\} \quad (81) \]

Thus, the Fourier components of the total potential difference in the nth iteration are:

\[ \Delta V_n(\bar{q}) = \Delta\phi_n(\bar{q}) + \Delta V_{XC}^n(\bar{q}) \quad (82) \]

At this point, we apply a convergence technique to treat \( \Delta V_n(\bar{q}) \) as

\[ \Delta V'_n(\bar{q}) = \Delta V'_{n-1}(\bar{q}) + QEF*(\Delta V_n(\bar{q}) - \Delta V'_{n-1}(\bar{q})) \quad (83) \]
where \( QF \) is a convergence factor and \( \Delta V_n'(\vec{q}) \) will be stored for the next iteration. For Ni1, we choose \( QF \) equal to 0.1, but for Ni5, 0.01-0.02 only. Using a bigger factor caused a divergence due to charge transfer between the central and surface layers.

After summing \( \Delta V_n'(\vec{q}) \) with \( S_{ij}(\vec{m}, \vec{q}) \) over reciprocal lattice points, we obtain an nth "compensation" Hamiltonian with matrix elements

\[
\Delta H_{ij}^n(\vec{m}) = \sum_{\vec{q}} \Delta V_n'(\vec{q}) S_{ij}(\vec{m}, \vec{q})
\]

At the beginning of the next iteration, \( \Delta H_{ij}^n(\vec{m}) \) is added to \( H_{ij}^n(\vec{m}) \) to get the \( (n+1) \) th Hamiltonian

\[
H_{ij}^{n+1}(\vec{m}) = H_{ij}^n(\vec{m}) + \Delta H_{ij}^n(\vec{m})
\]

In this new iteration, the eigenvalues \( E_{ij}^{n+1}(K_{11}) \) and the expansion coefficients \( U_{ij}^{n+1}(K_{11}) \) are given by the solution of the Schrodinger equation

\[
\sum_{l} H_{jl}^{n+1}(\vec{k}_i) U_{il}^{n+1}(\vec{k}_i') = E_{ij}^{n+1}(\vec{k}_i) \sum_{l} S_{ij}(\vec{k}_i, \vec{k}_i') U_{il}^{n+1}(\vec{k}_i')
\]

where

\[
S_{ij}(\vec{k}_i') = \sum_{\vec{m}} e^{-i \vec{k}_i' \cdot \vec{m}} a_i(\vec{r}) |a_j(\vec{r} - \vec{m})>
\]
where QF is a convergence factor and \( \Delta V_n(\vec{q}) \) will be stored for the next iteration. For Ni1, we choose QF equal to 0.1, but for Ni5, 0.01-0.02 only. Using a bigger factor caused a divergence due to charge transfer between the central and surface layers.

After summing \( \Delta V_n(\vec{q}) \) with \( S_{ij}(\vec{m}, \vec{q}) \) over reciprocal lattice points, we obtain an \( n \) th "compensation" Hamiltonian with matrix elements

\[
\Delta H_{ij}^n(\vec{m}) = \sum_{\vec{q}} \Delta V_n'(\vec{q}) S_{ij}(\vec{m}, \vec{q})
\]  

At the beginning of the next iteration, \( \Delta H_{ij}^n(\vec{m}) \) is added to \( H_{ij}^n(\vec{m}) \) to get the \( n+1 \) th Hamiltonian

\[
H_{ij}^{n+1}(\vec{m}) = H_{ij}^n(\vec{m}) + \Delta H_{ij}^n(\vec{m})
\]

In this new iteration, the eigenvalues \( E_{i1}^{n+1}(\vec{k}_{11}) \) and the expansion coefficients \( U_{i1}^{n+1}(\vec{k}_{11}) \) are given by the solution of the Schrödinger equation

\[
\sum_{1}^{n+1} H_{jj1}(\vec{k}_{11}) = E_{i1}^{n+1}(\vec{k}_{11}) \sum_{1}^{n+1} S_{ij1}(\vec{k}_{11}) U_{i1}^{n+1}(\vec{k}_{11})
\]

where

\[
S_{ij}(\vec{k}_{11}) = \sum_{\vec{m}} e^{-i\vec{k}_{11} \cdot \vec{m}} a_{i}(\vec{x}) a_{j}(\vec{x} - \vec{m})
\]
After computing the Fermi level, the new valence charge distribution can be calculated by

\[ \rho_{n+1}^V(\vec{r}) = \sum_{i=\text{valence}} |\psi_{i\vec{k}_n}(\vec{r})|^2 \]  

The core states are so localized that the core charge density is assumed to be unchangeably "frozen" during the "growing" of the valence electron-band structure. Summing \( \rho^V \) and \( \rho^C \), we obtain the \( n+1 \) th total charge distribution

\[ \rho_{n+1}(\vec{r}) = \rho_{n+1}^V(\vec{r}) + \rho_{n+1}^C(\vec{r}) \]  

and the \( n+1 \) th potential distribution

\[ V_{n+1}(\vec{r}) = V(\rho_{n+1}(\vec{r})) \]  

Usually, if the "on-site" 3d orbitals' compensation Hamiltonian matrix elements
we conclude that a "self-consistent" treatment of the paramagnetic electron band structure calculation has been achieved.

Spin-polarization Band Calculation

After the paramagnetic band calculation is completed, we use the converged Hamiltonian and a "complete spin-split technique" to start a spin-polarization calculation. In fact, the final results for different slabs present an approximately full majority 3d-band, except in few cases where the top of this band, $\bar{M}_{(xy)}$ surface state, is only a little higher than the Fermi level.

So, we believe that Hund's rule is still approximately satisfied in the thin-slab's magnetism problem.

After much testing, we finally used a splitting energy difference

$$\Delta E = (E_{d\text{-band top}}^P - E_F^P)/2$$

(93)

to split a converged single paramagnetic band to be a full majority-spin d-band and a partially occupied minority-spin d-band by

$$E_+^{\text{o}}(\vec{k}_n) = E_F^P - \Delta E$$

(94)
After computing the spin densities \( \rho_+ (\vec{r}) \) and \( \rho_- (\vec{r}) \), the spin-XC potentials \( V^+_{\text{XC}} (\vec{r}) \) and \( V^-_{\text{XC}} (\vec{r}) \) can be evaluated by the local density formula. The total charge density

\[
\rho (\vec{r}) = \rho_+ (\vec{r}) + \rho_- (\vec{r})
\]

is still useful for constructing the electrostatic potential, which is the same for both spins.

A unit convergence factor, \( Q_F = 1 \), is applied in this artificial spin-split processing which we would like to call the "complete spin-split method". Finally, we get two spin-polarization starting compensation Hamiltonian matrices

\[
\Delta H^+_{ij} (\vec{m}) = \sum_{\vec{q}} \Delta V^+ (\vec{q}) S_{ij} (\vec{m}, \vec{q})
\]

and

\[
\Delta H^-_{ij} (\vec{m}) = \sum_{\vec{q}} \Delta V^- (\vec{q}) S_{ij} (\vec{m}, \vec{q})
\]
From the next iteration, a natural spin-polarization calculation will be continued until a stable magnetic moment and a self-consistent charge distribution are obtained. Using this complete spin-split method only 15-20 iterations are needed.

Discrete Fourier Transformation (DFT) Method (Ref. 68)

Because of the 3-D even symmetries of the charge density and the XC potential, it is only necessary to calculate their values for the 1/8 inequivalent mesh points in a slab unit cell. In our calculation, the surface lattice constant, ALAT is divided into 10 segments (Fig. 4), and the slabs' repeat distance, ELZ is divided into Nz (about 100) segments. The coordinates of the mesh points are:

\[ x_i^j, y_i^j = (i-1/2)\Delta x \quad (i = 1, 2\cdots) \quad (99) \]

and

\[ z_j = (j-1/2)\Delta z \quad (j = 1, 2\cdots) \quad (100) \]

With these \((10*10*N_z)/8\) spatial values of a function \(f(F)\), a discrete Fourier transformation method determines \((10*10*N_z)/8\) fundamental Fourier coefficients \(F(\bar{q}_n)\) at reciprocal lattice points \(\bar{q}_n\). These \(\bar{q}_n\)
points are defined in an 1/8 rectangular parallelepiped centered at the origin of reciprocal space. Increasing the number of direct-space mesh points, will increase the number of these fundamental Fourier coefficients, i.e. it enlarges the fundamental rectangular parallelepiped in the reciprocal space.

Because the discussion is simpler, the properties of one dimension DFT are set forth below.

Let \( f(x) \) be even and periodic in \( x \) with period \( a \), i.e.

\[
f(-x) = f(x)
\]  

(101)

and

\[
f(x+a) = f(x)
\]  

(102)

so that

\[
f(x) = A_0/2 + \sum_{n=1}^{\infty} A_n \cos(q_n \cdot x)
\]  

(103)

where

\[
q_n = \frac{2\pi n}{a}
\]  

(104)
and

\[
A_n = \frac{2}{a} \int_0^{a/2} f(x) \cos(q_n \cdot x) \, dx,
\]

(105)

We set \( \Delta X = \frac{a}{2N} \), and use a summation

\[
A_n = \frac{2}{a} \sum_{i=1}^{N} f(x_i) \cos(\frac{2\pi n}{a} \cdot x_i) \Delta x
\]

(106)

to replace the integral (105). Then, we can get some important conclusions:

\[
A_{-n} = A_n
\]

(107)

\[
A_{n+2N} = -A_n
\]

(108)

\[
A_N = A_{3N} = A_{5N} = \cdots = 0
\]

(109)

and

\[
f(x_i) = A_0 + \sum_{n=1}^{N-1} A_n \cos(q_n \cdot x_i)
\]

(110)
Thus, the first $N$ Fourier coefficients can be thought of as "fundamental". The extension to 3-D is obvious, and it was mentioned in the beginning of this section.

Using a finer direct-space mesh, one can improve the results computed by a rough mesh and obtain Fourier coefficients which represent the shorter-wavelength features of $f(x)$. Actually, due to the slow variation of the charge density difference and the XC potential difference, increased accuracy of the long-wavelength coefficients is the predominant consequence of refining the mesh.
CHAPTER 3

RESULTS

General Feature of Band Structure

The computed electronic energy bands of ferromagnetic Ni1, Ni5 are shown in Fig. 5-10. For Ni1, majority-spin and minority-spin bands are separated to two figures, Fig. 5 and 6, in which the dashed lines present the odd z-reflection states and the full lines represent the even, as well as 1 and 2 denote the even and odd xy-reflection parities respectively. For Ni5 (Fig. 7-10), four figures are used to present majority-even, majority-odd, minority-even and minority-odd states in z-reflection, and the dashed and full lines represent the odd and even xy-reflection parities respectively.

In all of these figures, the Fermi levels is chosen as the energy zero. The work-functions computed by different groups are displayed in Table 5.

Physically, a thicker thin-slab model would give a deeper one-dimensional potential well, until a real bulk-surface limit is obtained. Compared to the experimental value and other groups' results, ours
Table 5. The work functions (eV) of one, three and five-layer Ni(001) slabs, calculated by Zhu-Hermanson, Jepsen et al., and Freeman et al.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Zhu and Jepsen, Madsen and Andersen</th>
<th>Freeman, D.S. Wang and Krakauer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni1</td>
<td>4.78(4.68)</td>
<td>5.7</td>
</tr>
<tr>
<td>Ni3</td>
<td>4.97(4.99)</td>
<td>5.3</td>
</tr>
<tr>
<td>Ni5</td>
<td>4.99</td>
<td>5.4</td>
</tr>
</tbody>
</table>

* The results of Zhu-Hermanson are computed in a 15k sampling in the irreducible segment of the surface B-Z, and the data quoted in parenthesis are from a 36k sampling.

** The experimental value of Ni(001) surface is 5.0-5.2 eV (Ref. 69-70).
seems to be more reasonable.

The shape similarity between the majority and minority-spin bands is not surprising. The band shape is mostly determined by the geometry of the crystal structure, but the exchange splitting and some other details are determined by spin-polarization. We recall that the band shape of a paramagnetic Cu(001) slab is almost the same as that of a Ni(001) slab, even though their electronic occupation configurations, $3d^{10}4s^1$ and $3d^94s^1$, are different. Except for their relative positions and band widths, we could not identify them by their shapes.

We prefer to measure the slabs' 3d-band width at the $\bar{M}$ point, where the $k$-dependent bonding difference gives rise to an antibonding surface state $\bar{M}(xy)$ at the 3d-band top, and a well-bonded constructive state $\bar{M}(x^2-y^2)$ at the bottom.

In Table 6, we list the spin-band widths and exchange splitting of Ni1, Ni3 and Ni5.

From table 6, we find that the width of the majority-spin 3d-band is narrower than that of the minority-spin for every slab, and that increasing the slab thickness increases both spins' 3d-band widths. At the same time, we notice that the 3d-band widths of Ni5 are very close to the bulk limits (Ref.22).

We may explain the relative narrowing of the majority-spin band compared to the minority-spin's by its relative localization in a deeper
Table 6. The 3d-band widths and exchange splitting of one, three and five-layer Ni(001) slabs

<table>
<thead>
<tr>
<th></th>
<th>d-band width (eV)</th>
<th>exchange splitting (eV)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Majority</td>
<td>Minority</td>
<td>d-band top</td>
</tr>
<tr>
<td>Ni1</td>
<td>3.1</td>
<td>3.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Ni3</td>
<td>4.3</td>
<td>4.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Ni5</td>
<td>4.6</td>
<td>4.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

* In this table, the 3d-band widths are measured by the differences between the highest $\bar{M} (xy)$ and the lowest $\bar{M} (x^2 - y^2)$. 
atomic potential well. This majority-spin potential deepening is due to the exchange-splitting effect and is more important at the high electron-density core region.

When we calculate the spin charges by integrating the spin densities on a real space mesh, the minority-spin charge always has a better accuracy due to its better spatial expansion feature.

The broadening of a thicker slab's band width is due to the increasing atomic coordination. The band width of Ni5 shows that it is good enough to simulate a real semi-infinite surface system.

We also noticed that the surface-layer's magnetic moments values (in $\mu_B$), are very close to the average exchange-splittings values (in eV) in the region near the Fermi-level. Stoner's itinerant electron magnetism theory predicted this relation more than 30 years ago.

We also find a large $k$-dependent exchange-splitting dispersion, i.e. the exchange-splitting of a specific band is bigger at its top than that at the bottom (see Table 6). The monolayer slab offers us a very clear picture of this dispersion. For example, the exchange-splitting is 1.02 eV at $\bar{M}_3$ and 0.84 eV at $\bar{X}_3$.

Table 7 shows the exchange-splitting data of all 3d-bands of Ni1 at the high-symmetry $k$-points $\bar{F}$, $\bar{M}$ and $\bar{X}$.

We can attribute this exchange-splitting dispersion to the $k$-dependent bonding difference of each band. For example, the $xy$ band is very destructive at the $\bar{M}$ point, but is constructively bonded
Table 7. The exchange-splitting (eV) of 3d orbitals of monolayer Ni(001) slab at $\bar{\Gamma}$, $\bar{M}$ and $\bar{X}$

<table>
<thead>
<tr>
<th></th>
<th>$\bar{\Gamma}$</th>
<th>$\bar{M}$</th>
<th>$\bar{X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3z^2-r^2$</td>
<td>0.76 (0.74)</td>
<td>0.91 (0.89)</td>
<td>0.84 (0.82)</td>
</tr>
<tr>
<td>$xy$</td>
<td>0.84 (0.80)</td>
<td>1.02 (0.97)</td>
<td>0.75 (0.72)</td>
</tr>
<tr>
<td>$xz, yz$</td>
<td>1.02 (0.95)</td>
<td>0.94 (0.88)</td>
<td></td>
</tr>
<tr>
<td>$(x-y)z$</td>
<td></td>
<td></td>
<td>1.03 (0.96)</td>
</tr>
<tr>
<td>$(x+y)z$</td>
<td></td>
<td></td>
<td>0.91 (0.84)</td>
</tr>
<tr>
<td>$x^2-y^2$</td>
<td>1.08 (1.06)</td>
<td>0.86 (0.84)</td>
<td>1.03 (1.00)</td>
</tr>
</tbody>
</table>

* The data quoted in parenthesis are computed by using von Barth-Hedin potential.
at point \( \bar{r} \) by the valence-charge overlapping. In other words, compared to \( \bar{r}_3 \), \( \bar{M}_3 \) is more localized in the core region, where the exchange potential spin-difference is bigger than that at the outer region.

The most important feature of different Ni(001) slabs' spin-polarization band structures is that their majority-spin 3d-bands are full. We find that for NiI or Ni3 the 3d-band tops, \( \bar{M}_3 \) (xy) or \( \bar{M}_2 \) (xy) is below the Fermi level, and for Ni5 it is just on this critical level.

Hund's rule for ferromagnetic atoms says that the majority-spin d-levels must be full, and the magnetic moment is equal to the number of minority-spin d-holes. From this rule, we can see that Ni's atomic magnetic moment is 2 \( \mu_B \), because its atomic configuration is 3d^84s^2.

For crystals, the hybridization between d-band and sp-band makes the problem very complicated, but the existence of a full majority-spin 3d-band suggests us that Hund's rule might still be powerful in our slab magnetism problem. Based on this fact, we developed a "complete splitting technique" to start every slab spin-polarization computation.

For Ni5, there is a large valence charge transferring between two A planes during the first few iterations. Using a proper convergence factor, this charge-transfering can be controlled and a layer-by-layer
charge neutrality can be built up within only about 10 iterations. It means that the different layers' total valence charge integrals in a slab unit cell all equal the atomic valence electron number 10, even though the electronic structures experience a dramatic change.

Table 8 shows the converged layer-valence charges of Ni1, Ni3 and Ni5 slabs.

The density of states (DOS) can be projected onto each plane of a slab. For Ni5, both the 3d-band shapes and widths of the inner planes are very close to those of the bulk DOS, but the surface DOS is in the shape of a triangle which shows a big 3d-band narrowing due to the reduction of coordination at the surface region.

From the planar DOS projections, which are shown in Fig 11-15, we also noticed that the upper DOS limits of all inner and surface layers sharply coincide at the same energy. This means that the narrowed surface 3d-bands' have been pushed up by the electrostatic force which is demanded to keep the charge neutrality at the surface.

Using the local atomic orbital method, the crystal electronic band-structure can be analyzed by an atomic picture. Although all bands are hybridized by different atomic orbitals, we still label them by the names of their dominant atomic orbitals.

We use the Lowdin projections to calculate the electronic occupancies of the converged band structure of Ni1, Ni3 and Ni5; these are shown in Table 9.
Table 8. Layer-valence charges of one, three and five-layer slabs

<table>
<thead>
<tr>
<th></th>
<th>Monolayer ($\text{36k}_{11}$)</th>
<th>Three-layer ($\text{36k}_{11}$)</th>
<th>Five-layer ($\text{15k}_{11}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>10.00</td>
<td>9.98</td>
<td>10.01</td>
</tr>
<tr>
<td>$S-1$</td>
<td>10.03</td>
<td></td>
<td>9.99</td>
</tr>
<tr>
<td>$S-2$</td>
<td></td>
<td></td>
<td>10.01</td>
</tr>
</tbody>
</table>
In general, the sp-electron occupation is slightly less in a thinner slab or in a surface layer than in a thicker slab or on the inner planes. These dehybridizations are also related to the atomic coordination band narrowing. However, this dehybridization is not remarkable, for instance, only 2% reduction occurs from central to surface layer for Ni5.

Magnetic Moment and Its Surface Enhancement

The most important result of our calculations is that the Ni(001) thin-slabs' surfaces are not magnetically "dead", but have larger magnetization than the inner planes.

This "surface magnetism enhancement" is based on an ideal model of the crystal slab with a spacing equal to the normal Ni bulk lattice constant; i.e., without any consideration about the surface reconstruction. Although this model is only approximate, some obtained results, for example, the existence of a full majority-spin 3d-band, would be expected in a more realistic surface problem.

To describe the layer-by-layer magnetism, a planar (layer) magnetic moment is defined as:

\[ M_L = Q_L^+ - Q_L^- \]  \hspace{1cm} (111)

where the layer spin-charges, \( Q_L^+ \) and \( Q_L^- \) are evaluated by spatial integration of the self-consistent spin densities. The integration region
Table 9. The electron occupation numbers of Ni(001) slabs

<table>
<thead>
<tr>
<th></th>
<th>s</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.89 (0.42)</td>
<td>0.30 (0.15)</td>
<td>8.77 (8.26)</td>
</tr>
<tr>
<td>Ni3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.70</td>
<td>0.44</td>
<td>8.81</td>
</tr>
<tr>
<td>S-1</td>
<td>0.59</td>
<td>0.54</td>
<td>8.79</td>
</tr>
<tr>
<td>Ni5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.70 (0.43)</td>
<td>0.44 (0.29)</td>
<td>8.84 (8.29)</td>
</tr>
<tr>
<td>S-1</td>
<td>0.59 (0.46)</td>
<td>0.53 (0.42)</td>
<td>8.82 (8.29)</td>
</tr>
<tr>
<td>S-2</td>
<td>0.58 (0.46)</td>
<td>0.52 (0.43)</td>
<td>8.74 (8.28)</td>
</tr>
</tbody>
</table>

* This table's data are calculated by the Lowdin projection.

** The data quoted in the parenthesis are computed by Krakauer and Freeman.
is a slab unit cell bounded by parallel planes midway between the atomic planes (see Fig. 16). The surface moment also included the contribution of the "vacuum" region.

\[
Q_2^\sigma = \int_{z_1}^{z_2} \rho^\sigma(E)\,d\tau
\]  

(112)

This definition is slightly different from other workers' for instance Freeman and Krakauer only integrate the spin-densities in a muffin-tin sphere. Because the magnetic moment is principally due to the 3d electron occupancy, this difference should not give any significant discrepancy.

The total slab moment is determined by the difference between the numbers of occupied energy levels of majority and minority-spin. These energy levels are quadratically interpolated at 20,000 random points within the surface Brillouin zone, by using the diagonalization results at 45k points in the 1/8 irreducible segment of this zone.

Our results for layer magnetic moments are given in Table 10. From this table, we find that the layer moment increases as the coordination is reduced, from 0.61 \( \mu_B \) at the central layer of Ni3 and Ni5 to 0.98 \( \mu_B \) for monolayer. This tendency is also shown in Fig. 17, where both the atomic and bulk limits can be approached.

The surface layers of Ni3 and Ni5 have enhanced moments, with increases of 16\% and 8\% compared with the central layer's value. A
Table 10. The layer magnetic moments of one, three and five-layer slabs

<table>
<thead>
<tr>
<th></th>
<th>Zhu and Hermanson</th>
<th>Jepsen, Madsen and Andersen</th>
<th>Krakauer and Freeman</th>
<th>Noffke and Fritsche</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni1 (36k\textsubscript{11})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.98 (0.94)</td>
<td>0.95</td>
<td>0.86</td>
<td>0.90</td>
</tr>
<tr>
<td>Ni3 (36k\textsubscript{11})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.71 (0.76)</td>
<td>0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-1</td>
<td>0.61 (0.64)</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni5 (15k\textsubscript{11})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.66 (0.65)</td>
<td>0.65</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>S-1</td>
<td>0.55 (0.54)</td>
<td>0.58</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>S-2</td>
<td>0.61 (0.59)</td>
<td>0.61</td>
<td>0.69</td>
<td></td>
</tr>
</tbody>
</table>

* In Zhu and Hermanson's column, the data quoted in parenthesis are the results of last self-consistent iteration. The data outside the parenthesis have been renormalized by the results of a Monte Carlo quadratic interpolation technique.

** In Krakauer and Freeman's column, the data have been improved by a linear analytic triangle method.
small oscillation of the moment is seen in the Ni5 case, where the sub-surface layer's value is 0.55 \( \mu_B \).

Essentially the bulk magnetization, 0.56 \( \mu_B \) (Ref.71-72), is observed on all inner layers (even for Ni3), and the surface moment enhancement is obtained by different groups with different methods. Our results are in best agreement with those of Jepsen et al.

We note a deficiency of the recent results of Krakauer and Freeman, who first started the slab magnetism calculation several years ago. They used a linear analytic triangle method to "improve" the "self-consistent" results, which are 14% to 28% larger than the final improved values (see Table 10). Perhaps this is a signal of the lack of self-consistency.

**Mechanism of Surface Magnetism Enhancement**

Obviously, the surface magnetism enhancement should be attributed to the reduction of coordination at the surface. Physically this reduction will cause the band narrowing and the sp-d band dehybridization in the surface region.

We already noticed that after band-narrowing the charge neutrality on the surface layer is still satisfied, and the narrowed d-bands are pushed up by an electrostatic force which tends to keep the balance between the negative electron charge and the positive nuclear charge on each layer.
For all Ni(OOl) slabs, we also found that there is a full or almost full majority-spin d-band, and that any layers have approximately equal d-occupation number $N_d$, which is 8.74, 8.82 and 8.84 from central to surface layer of NiS, as well as 8.77, 8.81 and 8.84 for the surfaces of Ni1, Ni3 and Ni5 respectively. So, using these d-occupation numbers cannot explain why decreasing the coordination increases the magnetic moment. The independence of the layer d-electron number and the coordination is found by both Lowdin and Mulliken projections, and by both SCLO and LAPW methods.

Basically, we believe that the sp-d dehybridization will increase the d-occupation number, and the band-narrowing will decrease the d-occupation. These two opposing changes cause a quasi-constancy of the layer d-character.

By setting the sp-d matrix elements of the final self-consistent Hamiltonian equal to zero, we recomputed the magnetism and orbital occupancies. The results, shown in Table 11, show a remarkable increase of $N_{sp}^O$ due to the coordination reduction, which displays a behavior comparable to the magnetic moment (see Fig. 18). From this behavior, we can conclude that the band-narrowing controls the surface magnetism enhancement.

From Table 11 we noticed that $N_{d+}^O$ is very close to 5 on all layers, and the magnetic moment $M^O$ is nearly equal to $N_{sp}^O$, which is essentially the number of d holes. Thus, Hund's rule, which was
designed for atomic systems, still applied to the sp-d unhybridized magnetic slabs system.

We also noticed that the fractional d character of the nominal d-band, \( f_d \), increases from 0.942 at the center of NiS to 0.974 at the surface of NiS (the largest number is found for the monolayer, 0.980). It cancels the decrease of \( N_d \) at the surfaces caused by the band-narrowing.

We would suggest that the bulk limit of \( f_d \) is about 0.4. So, the magnetic moment increases about 60% from the bulk limit to that of NiI, but \( f_d \) increases only 4%. From the central to surface layer of Ni5, these two increases are 9% and 1% respectively. If the \( f_d \) factor can approximately describe the dehybridization character, which is due to the coordination reduction, then we believe the sp-d dehybridization plays only a minor role in the surface magnetism enhancement.

Surface States and Photoemission Experiments

In the ARPS (angle resolved photoemission spectroscopy) method (Ref. 73-75), both the incident light and the output electron beam, which is collected by a detector, are set on a mirror plane (MP). This MP is determined by the surface normal direction and the high symmetry line on which the energy spectrum is to be measured. A very simple theory proves that the final electron state, from which the
Table 11. Occupation numbers and magnetic moments computed in the absence of sp-d hybridization.

<table>
<thead>
<tr>
<th></th>
<th>( N_{\text{sp}}^0 )</th>
<th>( N_{d}^0 ) (Nd)</th>
<th>( M^0(\mu_B) )</th>
<th>( N_{d^+}^0 )</th>
<th>( f_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni1</td>
<td>S</td>
<td>1.02</td>
<td>8.95 (8.77)</td>
<td>1.06</td>
<td>5.00</td>
</tr>
<tr>
<td>Ni3</td>
<td>S</td>
<td>0.82</td>
<td>9.12 (8.81)</td>
<td>0.88</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>S-1</td>
<td>0.75</td>
<td>9.25 (8.74)</td>
<td>0.76</td>
<td>5.00</td>
</tr>
<tr>
<td>Ni5</td>
<td>S</td>
<td>0.80</td>
<td>9.07 (8.84)</td>
<td>0.88</td>
<td>4.97</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>0.72</td>
<td>9.31 (8.82)</td>
<td>0.68</td>
<td>4.99</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>0.71</td>
<td>9.27 (8.74)</td>
<td>0.71</td>
<td>4.99</td>
</tr>
</tbody>
</table>

* "\( f_d \)" is the ratio \( N_d / N_{d^+}^0 \), the fractional d character of nominal d-band.

*** The occupation data are computed in the Lowdin projection.

*** The quoted data, \( N_d^0 \), are from regular calculations including sp-d hybridization.
output electron beam is obtained, has even parity with respect to the mirror plane reflection (MPR). So called s/p-polarization of incident light is determined by whether the polarization is perpendicular/parallel to the MP. Thus, the interaction Hamiltonian term $\vec{A} \cdot \vec{P}$ has even parity for p-light and odd for s-light respect to MPR.

In order to guarantee the transition matrix element

$$<f|\vec{A} \cdot \vec{P}|i>$$

is not zero, the initial state must have the same parity as the interaction Hamiltonian.

Plummer and Eberhardt, and Erskine (Ref.35-37), observed two majority-spin surface-states (SS), at the $\bar{\text{M}}$ and $\bar{\Gamma}$, and by using the MP technique they also found a continuous odd-parity surface-band (SB) between these two SS. Dempsey and Klieman first predicted the existence of this SB by using a non-self-consistent computational method, in 1977. In our Ni5 result, these two SS, $\bar{\text{M}}_3 (xy)$ and $\bar{\Gamma}_5 (yz)$ are also obtained, with 100% and above 60% surface character respectively.

The extremely strong surface character of $\bar{\text{M}}_3 (xy)$ is due to the extension of the $xy$ orbital parallel to the slab surface; the next layer's $xy$ orbital is in a different symmetry $\bar{\text{M}}_2$. The z-direction extension of the $yz$ orbital increases $\bar{\Gamma}_5$'s bulk character.
Our calculation also assigned to the $\Gamma_4 (x^2-y^2)$ state a very strong surface character (above 90%). Because of the selection rule which was first pointed out by Hermanson (Ref. 76), it can not be reached by photoemission probes.

We find no evidence for the (even) minority-spin SB near $E_F$ invoked by Plummer and Eberhardt. The observed emission may be due to a bulk-like majority-spin band with slightly enhanced surface amplitude.
CHAPTER 4
SUMMARY

Very accurate calculation on the magnetism of Ni(001) slabs has been achieved by our spin-polarized self-consistent local orbital method. The results are in excellent agreement with those of LAPW methods (Ref. 26,28). Our method not only provides a computational efficiency, which surpasses that of other methods, but also intuitive physical insight due to its use of the atomic picture.

We find that three and five-layer slabs of Ni(001) show an enhanced surface magnetism compared with the "bulk" behavior exhibited by the inner layers. This enhancement is mainly due to the band-narrowing at the surface layer where the atomic coordination is reduced.

The effect of the surface-dehybridization between sp and d bands has been studied by repeating the calculation with the sp-d matrix elements omitted. The final results show that the effect of the dehybridization is not comparable to that of the band-narrowing.

We also find that the nominal d-band occupancy is independent of the variation of the atomic coordination at different layers. Referring to the charge-neutrality at all layers, our result doesn't
support the surface sp to d charge transfer which was obtained by Tersoff and Falicov's parametrized method.

We find a $\tilde{\Sigma}_2$ surface state band which has been observed by angle-resolved photoemission spectroscopy (Ref. 35-37).
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REFERENCES

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APPENDIX A

FIGURES
o A-plane sites
x B-plane sites
$\vec{n}_0$ A-B plane displacement vector
$\vec{a}, \vec{b}$ Lattice vector

Fig. 1 The geometry and the coordinate system of the slab surface.
Fig. 2 The 15 and 36k samples in 1/8 irreducible region of surface B-Z.
Fig. 3 The $d_{xy}$-orbital's shapes on A and B-planes at the M point.
Fig. 4 The xy-plane mesh in 1/4 unit cell.
Fig. 5 The majority-spin band of Nil
Fig. 6 The minority-spin band of Nil
Fig. 7 The majority-spin band of Ni$_5$ (even in z-reflection).
Ni$_5$ MAJORITY-SPIN BANDS (Odd in z)

Fig. 8 The majority-spin band of NiS (odd in z-reflection).
Fig. 9 The minority-spin band of Ni$_5$ (even in z-reflection).
Fig. 10 The minority-spin band of Ni$_5$ (odd in $z$-reflection).
Fig. 11 The total density of states for Ni₁.
Fig. 12 The total density of states for Ni$_3$. 
Fig. 13 The total density of states for Ni5.
Fig. 14 The plane-projected DOS for Ni₃.
Fig. 15 The plane-projected DOS for Ni5.
Fig. 16 The muffin-tin sphere and planar charge integral regions.
<table>
<thead>
<tr>
<th>Film</th>
<th>Total NN</th>
<th>$M (\mu_B)$</th>
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<tbody>
<tr>
<td>$Ni_0$</td>
<td>0</td>
<td>2.00</td>
</tr>
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<td>$Ni_1$</td>
<td>8(4,4)</td>
<td>0.98</td>
</tr>
<tr>
<td>$Ni_3$</td>
<td>13(8,5)</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>16(12,4)</td>
<td>0.61</td>
</tr>
<tr>
<td>$Ni_5$</td>
<td>13(8,5)</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>17(12,5)</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>18(12,6)</td>
<td>0.61</td>
</tr>
<tr>
<td>Bulk</td>
<td>18(12,6)</td>
<td>0.56</td>
</tr>
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</table>

*Fig. 17* The magnetic moment $M (\mu_B)$ vs. the number of first-second neighbor atoms.
Fig. 18 The magnetic moment $M(\mu_B)$ and $sp$-occupation number (electron) vs. the number of nearest-neighbor atoms.
APPENDIX B

COMPUTATIONAL FLOWCHARTS
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cop.2 Spin-polarized self-consistent local orbital method and its application...