

ABSTRACT

Surface Magnetism of Ni(001), Co(001), and Fe(001):
An Embedding Green Function Approach

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Self-consistent spin-polarized surface embedded Green function (SEGF) calculations have been performed for the Ni(001), Co(001), and Fe(001) surfaces. Results are reported for three-layer slabs embedded onto the bulk crystals. The work functions, surface magnetic moments, and other electronic properties are compared with experiment and other theoretical work. The calculated Fe(001) work function is in good agreement with experiment and slab calculations, while the Ni(001) and Co(001) work functions are in fair agreement. Enhanced magnetic moments are obtained for the top layer of atoms, in agreement with experiment. Calculated surface states and surface resonance bands for each surface have been analyzed and compared with theoretical and experimental results.

Surface Magnetism of Ni(001), Co(001), and Fe(001):
An Embedding Green Function Approach

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DEDICATION

To Yezabel, Robert, Marlene, Bernie, Ginny, and Bayley.

Robert, Daddy is free to play now . . .

CHAPTER ONE

Introduction

God made solids, but surfaces were the work of the Devil

—Wolfgang Pauli

After the discovery of the electron in 1897, P. Drude developed a theory concerning metallic conduction based on the kinetic theory of gases. This model, although generally successful, failed to account for quantum mechanical effects. With the advent of quantum mechanics in the 1920s, physicists had the tools to accurately describe many microscopic condensed matter systems. During the 1930s, a time of rapid innovation in surface physics, Tamm, Goodwin, and Shockley theorized the existence of localized electron states at surfaces.¹ Other strides were made by Bardeen, Lennard-Jones, Mott, and Schottky.²⁻⁵

Because the many-body Schrödinger equation for a solid cannot be solved analytically, properties of solids were initially computed from the simplest of models. However, advances in engineering, chemistry, physics, and technology ushered in the computing age, which allowed scientists to adopt modeling techniques of greater and greater sophistication. A history of the major algorithms that provided the basis for the modeling techniques are discussed within this chapter.

The time-independent Schrödinger equation for a crystal may be written as:

$$\hat{H}\Psi = \sum_{i=1}^n \left(-\frac{\hbar^2}{2m} \nabla_i^2 \Psi - Ze^2 \sum_{\mathbf{R}} \frac{1}{|\mathbf{r}_i - \mathbf{R}|} \Psi \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi = E\Psi, \quad (1.1)$$

where Ψ is the many-electron wavefunction. This N-body problem is intractable for real crystals, which possess on the order of 10^{23} electrons and nuclei; present mathematical techniques and modern supercomputers are simply not up to the task.

A simplification of the physical problem was necessary to improve the predictive capability of various methods and to advance scientific knowledge.

Hartree formulated an algorithm that allowed a great advance in modeling crystals by approximating the many-electron wavefunction as a product of one-electron functions. He also assumed that the effects of the other $N-1$ electrons on a single electron could be approximated by the electrostatic action of the average charge density.⁶ Using these assumptions, the many-body equation reduced to a set of one-electron equations known as the Hartree equations:

$$-\frac{\hbar^2}{2m}\nabla_i^2\psi_i(\mathbf{r}) + U^{ion}(\mathbf{r})\psi_i(\mathbf{r}) + \left[e^2 \sum_{j \neq i} \int d\mathbf{r}' |\psi_j(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (1.2)$$

Although these Hartree equations are computationally complicated, certain electron-electron interactions, such as exchange and correlation effects, are still not included.

One shortcoming of the Hartree approach is that the product wavefunction is not antisymmetric with respect to electron interchange. Fock and Slater independently improved upon the Hartree method by using an antisymmetrized wavefunction Ψ in the form of a Slater determinant to account for the Pauli exclusion principle.^{7,8} By minimizing the ground state energy with respect to the one-particle wavefunctions ψ_i , the Hartree-Fock (H-F) equations were obtained:

$$-\frac{\hbar^2}{2m}\nabla_i^2\psi_i(\mathbf{r}) + U^{ion}(\mathbf{r})\psi_i(\mathbf{r}) + U^{el}(\mathbf{r})\psi_i(\mathbf{r}) - e^2 \sum_j \int d\mathbf{r}' \psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r}) \frac{\delta_{s_i s_j}}{|\mathbf{r} - \mathbf{r}'|} = \varepsilon_i \psi_i(\mathbf{r}). \quad (1.3)$$

The last term on the left hand side of the H-F equations is known as the exchange term and is non-zero only for parallel electron spins. This is a nonlocal operator whereby electrons of like spin avoid each other. The effect of the operator is to exclude electronic charge of like spin from a region surrounding each electron. The exclusion of negative charge appears as an attractive interaction in the Hamiltonian. This region of

excluded charge is known as the exchange hole. As a result, the exchange interaction among electrons of equal spin is taken into account; however, the exchange interaction for electrons of opposite spin is omitted.⁹ The Hartree and Hartree-Fock formulations work well for isolated atoms, but neither approach is adequate for crystals because of the way the exchange-correlation potential is approximated.⁶

These methods were succeeded by the jellium model in which the solid is approximated by a system of interacting electrons and a smeared out positively-charged background. The jellium model improves upon the physics of electron correlation effects, but it omits the binding of electrons by the ionic cores and can give qualitatively wrong results (*e.g.*, negative surface energies).⁹

The next major development in electronic structure methods for solids was the development of pseudopotential techniques. The pseudopotential is an effective potential containing both the lattice potential and a repulsive term simulating the effect of the Pauli exclusion principle.⁹ Pseudopotential methods have proved to be very reliable in the study of metals with free electron Fermi surfaces.¹⁰

Density functional theory (DFT) was the next development that sought to incorporate a periodic lattice potential with accurate electron-electron interactions.⁹ Based on a theorem of Pierre Hohenberg and Walter Kohn, DFT assumes that all properties of the many-body system are determined by the ground-state charge density.¹¹ In particular, the many-body ground state energy can be written as

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] - \sum_{\mathbf{R}} Ze \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{R} - \mathbf{r}'|} + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})], \quad (1.4)$$

where $\rho(\mathbf{r})$ is the ground state charge density, $T[\rho(\mathbf{r})]$ is the kinetic energy of a non-interacting electron gas, and $E_{xc}[\rho(\mathbf{r})]$ is the exchange-correlation energy.¹

This many-body problem can be reduced to a set of one-electron Schrödinger-like equations written in atomic units ($e = 1, m = 1, \hbar = 1$) as

$$-\frac{1}{2}\nabla^2\psi_i(\mathbf{r}) + V_{eff}(\mathbf{r})\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}).^1 \quad (1.5)$$

The effective potential, V_{eff} , includes all the interaction terms: the Coulomb potential, exchange (Pauli exclusion), and correlation (the potential due to the effect of a given electron on the overall charge distribution).⁹

If an infinitesimal volume element of a real crystal is sampled, the electron density within the sampled volume is most likely inhomogeneous. The exact exchange-correlation energy for such an element is unknown; however, the exchange-correlation energy for a homogeneous gas is known. One approximation would be to take the exchange-correlation energy due to an infinitesimal volume of the inhomogeneous electron gas and approximate it by that of a homogeneous electron gas of the same average density. This approximation is easily inserted into the DFT equations because the energy densities of homogeneous electron gases have been calculated for all densities of interest.¹² This approximation is known as the local density approximation (LDA). Spin effects have also been incorporated into the LDA, which allow spin-dependent properties such as surface magnetic moments to be calculated.

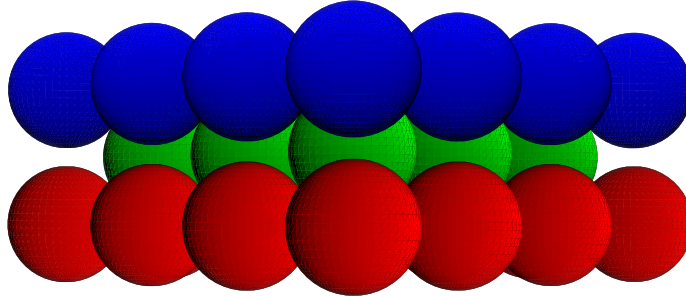


FIG. 1.1. Geometry of a three-layer slab lattice. Vacuum regions bound the top and bottom of the slab.

Creating a surface breaks the three-dimensional periodicity of a crystal, causing the task of finding solutions to the LDA Schrödinger equation to become more difficult. Most successful methods use either a slab or a slab-superlattice geometry (Figs. 1.1 and 1.2) to calculate the surface electronic structure. For these geometries, the LDA Schrödinger equation is solved self-consistently for a slab of up to about nine atomic layers thickness. When a slab calculation has reached self-consistency, the center layer is usually compared with bulk properties found experimentally.

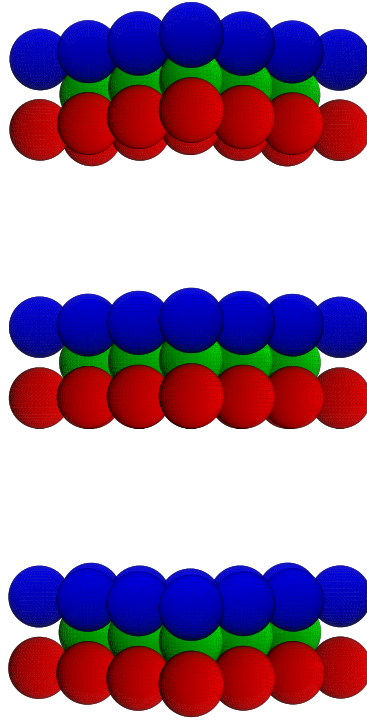


FIG. 1.2. Geometry of a slab-superlattice. Vacuum is between layers.

Unlike a true semi-infinite system, these geometries allow surfaces to interact with one another. Therefore, although slab methods are usually satisfactory in predicting aggregate properties, such as the work function and charge density, they poorly describe most individual properties, such as surface state energies. Because the band-

structure from slab calculations is discrete instead of continuous, identifying surface states is rather arbitrary because bulk bands and band gaps are absent.

The Surface Embedded Green Function (SEGF) method, developed in 1983 by Benesh and Inglesfield, overcomes the deficiencies of slab-based calculations.¹³ Using this theoretical method, many material surfaces have been studied with remarkable success when compared with experimental results.^{13–15} Until now, only two studies of the magnetic properties of iron have been performed using the SEGF method.^{16,17} This dissertation will address the problems with earlier calculations and will provide a detailed study of the surface electronic and magnetic properties of Ni(001), Co(001), and Fe(001).

CHAPTER TWO

The SEGF Method

Calculating the electronic properties of complicated systems requires great computing effort even with the latest advances in computing and physical modeling. As the computational capabilities of CPUs have increased, numerical models developed to study physical phenomena have also increased in complexity. Improved physical understanding has led to better models and improved algorithms that facilitate those computations. Although slab and slab-superlattices are the favored methods for modeling surfaces, neither model represents a true physical surface. This chapter outlines a methodology in which a true surface is modeled while conserving computational resources.

2.1 Motivation

Although modeling a three-dimensional crystal is difficult, it is far less challenging than accurately representing a surface. No closed-form solution exists for many-body problems with more than two bodies. The many-body problem for a crystal contains more than 10^{23} electrons and nuclei. Additionally, a surface creates further complications due to the loss of three-dimensional periodicity. Because a surface atom has fewer near neighbors than its bulk crystal counterpart, the electronic structure at the surface is expected to differ from the bulk. Therefore, it is expected that physical properties which depend upon the electronic structure will also be different at the surface.

Surfaces often exhibit reconstruction, in which atoms positioned at the surface crystal rearrange, forming different lattice structures from the underlying crystal (*e.g.*, W(100) which reconstructs to $\sqrt{2} \times \sqrt{2} - R45^\circ$ pattern). Vertical relaxations can also occur due to the reduced coordination of the surface atoms, thereby altering the

surface charge density and affecting the work function. Forces that bind surface atoms together differ from those in the substrate. Magnetic properties may also change at the surface. A surface may acquire a net magnetization while the bulk remains magnetically neutral, as is the case for the (001) face of vanadium.

The problems and limitations associated with slab methods are well known. When slab methods were developed, computing technology was not as advanced as today and the model needed to be computationally feasible. Another algorithmic approach is described below that is computationally compact and accurate without the limitations of slab-only methods. By grafting a thin slab onto a bulk crystal, a method is derived that models a true surface.

2.2 *Surface Embedding*

The Surface Embedding Green Function (SEGF) method separates the semi-infinite system (Fig. 2.1) into a surface region (I) and a substrate region (II). The substrate is the perfect three-dimensional bulk crystal. Because the bulk crystal is included in the calculation through the embedding potential, there is no need to use a thick slab to mimic the bulk crystal. Therefore, the number of computed crystal layers can be greatly reduced as compared with slab methods. The SEGF method conserves computer resources, allowing for the study of more complicated structures. By being less computationally intensive, the SEGF method is able to iterate to self-consistency faster than slab methods. The goal of the SEGF method is to allow an accurate calculation of the surface electronic structure without making the compromises of slab methods.

By obtaining the ground state energy of a system, other properties of physical interest can be determined. For all but the simplest of systems, the exact many-body system wavefunction (Ψ) is unknown. To find the ground state energy, generally the best approach has been to guess a form for Ψ that approximates the exact wavefunc-

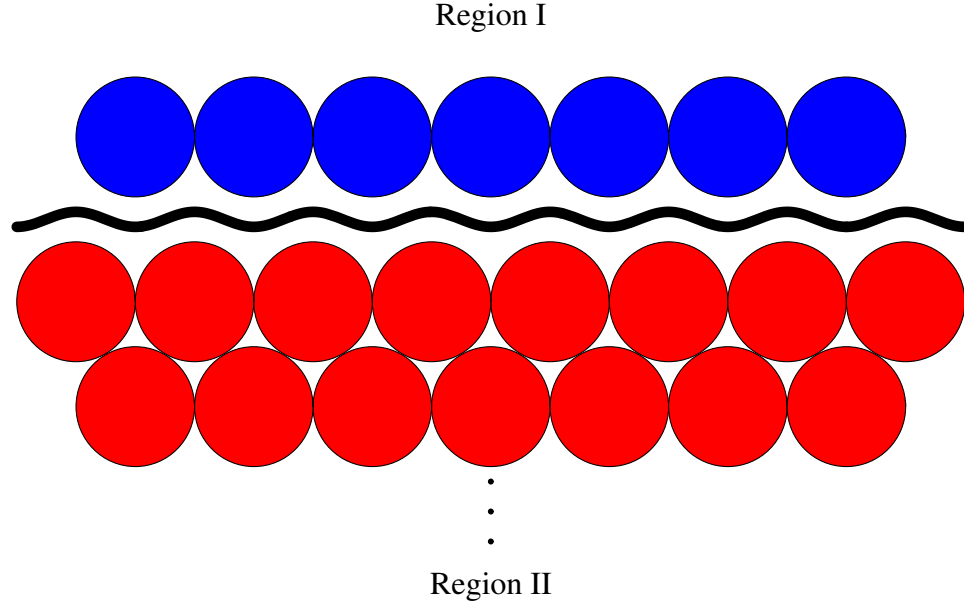


FIG. 2.1. Side view of SEGf crystal representation. The undulating solid black line represents the boundary between the surface and bulk regions.

tion. If Ψ is not known, as is the case for a crystal, the ground state energy (E) is bound by:

$$E \leq \frac{\langle \Phi(\mathbf{r}) | \hat{H} | \Phi(\mathbf{r}) \rangle}{\langle \Phi(\mathbf{r}) | \Phi(\mathbf{r}) \rangle}, \quad (2.1)$$

where $\hat{H}$ is the Hamiltonian and $\Phi(\mathbf{r})$ is the approximate wavefunction for the entire system. Eq. 2.1 is often used when encountering systems where iterative methods are employed to find the ground state energy. A variational method will be used to calculate the ground state energy for the SEGf method.

Although Ψ is unknown, the energy computed by guessing the form of the ground state wavefunction can provide a good estimate of the ground state energy. For good choices of Φ , the estimated ground state energy will differ only slightly from the true ground state energy. In fact, a decent choice of wavefunction with error ε will introduce an error in the true ground state energy on the order of ε^2 .¹⁸

2.3 SEGF Formalism

The SEGF method defines a trial function $\phi(\mathbf{r})$ in the surface region and matches it along an embedding surface onto the substrate wavefunction $\psi(\mathbf{r})$, which is an exact solution to the bulk Schrödinger equation.

Using Eq. 2.1 and the following definition for Ψ :

$$\Psi(\mathbf{r}) = \begin{cases} \phi(\mathbf{r}), & \text{in Region I} \\ \psi(\mathbf{r}), & \text{in Region II} \end{cases}, \quad (2.2)$$

the expectation value for the Hamiltonian is (using atomic units, where $e = \hbar = m = 1$ and ε is the bulk energy eigenvalue):

$$E = \frac{\int_I d\mathbf{r} \phi^* H \phi + \varepsilon \int_{II} d\mathbf{r} |\psi|^2 + \frac{1}{2} \int_S d\mathbf{r} \phi^*(\mathbf{r}_S) \frac{\partial \phi}{\partial n_S} - \frac{1}{2} \int_S d\mathbf{r} \phi^*(\mathbf{r}_S) \frac{\partial \psi}{\partial n_S}}{\int_I d\mathbf{r} |\phi|^2 + \int_{II} d\mathbf{r} |\psi|^2}, \quad (2.3)$$

where the normal derivative points into the substrate. Because the trial function is permitted to have a discontinuous derivative at the interface, the two surface integrals in the previous equation are required. These integrals express the discontinuity in $\partial\Psi/\partial n_S$ arising from the kinetic energy operator.¹⁹

An expression is desired that explicitly solves for the ground state energy in terms of only the trial function in the surface region. Eliminating the integrals through the substrate is accomplished by using the bulk Green function (G_0). The Green function for the perfect crystal is required to satisfy a Neumann boundary condition on the embedding surface:

$$\frac{\partial G_0(\mathbf{r}_S, \mathbf{r}')}{\partial n_S} = 0. \quad (2.4)$$

The surface-inverse of the Green function is defined by:

$$\int_S d\mathbf{r}'_S G_0^{-1}(\mathbf{r}_S, \mathbf{r}'_S) G_0(\mathbf{r}'_S, \mathbf{r}''_S) = \delta(\mathbf{r}_S - \mathbf{r}''_S). \quad (2.5)$$

Utilizing this definition and the continuity of the trial function on the embedding interface, an equation relating the substrate function derivative to the amplitude can be found:

$$\frac{\partial \psi(\mathbf{r}_S)}{\partial n_S} = -2 \int_S d\mathbf{r}'_S G_0^{-1}(\mathbf{r}_S, \mathbf{r}'_S) \phi(\mathbf{r}'_S). \quad (2.6)$$

An expression for the volume integral in terms of the trial function is also required. Inglesfield has shown that:

$$\int_{II} d\mathbf{r} |\psi|^2 = - \int_S d\mathbf{r}_S \int_S d\mathbf{r}'_S \phi^*(\mathbf{r}_S) \frac{\partial G_0^{-1}(\mathbf{r}_S, \mathbf{r}'_S)}{\partial \varepsilon} \phi(\mathbf{r}'_S) .^{20} \quad (2.7)$$

The expectation value for the energy can now be expressed entirely in terms of the trial function ϕ and the bulk Green Function G_0 ; thus, a true variational expression for E has been found. In terms of the trial function ϕ and G_0 , Eq. 2.3 becomes:

$$E = \frac{\int_I d\mathbf{r} \phi^* H \phi + \int_S d\mathbf{r}_S \int_S d\mathbf{r}'_S \phi^*(\mathbf{r}_S) \left(G_0^{-1} - \varepsilon \frac{\partial G_0^{-1}}{\partial E} \right) \phi(\mathbf{r}'_S)}{\int_I d\mathbf{r} |\phi|^2 - \int_S d\mathbf{r}_S \int_S d\mathbf{r}'_S \phi^*(\mathbf{r}_S) \frac{\partial G_0^{-1}}{\partial E} \phi(\mathbf{r}'_S)} . \quad (2.8)$$

The trial function, ϕ , is expanded as:

$$\phi(\mathbf{r}) = \sum_i a_i \chi_i(\mathbf{r}) , \quad (2.9)$$

where $\chi_i(\mathbf{r})$ are the basis functions. E is then minimized with respect to small changes in ϕ , resulting in the following equation:

$$\sum_j \left(H_{ij} + (G_0^{-1})_{ij} + (E - \varepsilon) \frac{\partial (G_0^{-1})_{ij}}{\partial E} \right) a_j = E \sum_j O_{ij} a_j , \quad (2.10)$$

where:

$$\begin{aligned} H_{ij} &= \int_I d\mathbf{r} \chi_i^*(\mathbf{r}) H \chi_j(\mathbf{r}) + \int_S d\mathbf{r} \chi_i^*(\mathbf{r}_S) \frac{\partial \chi_j(\mathbf{r}'_S)}{\partial n_S} , \\ (G_0^{-1})_{ij} &= \int_S d\mathbf{r}_S \int_S d\mathbf{r}'_S \chi_i^*(\mathbf{r}_S) G_0^{-1}(\mathbf{r}_S, \mathbf{r}'_S) \chi_j(\mathbf{r}'_S) , \end{aligned}$$

and

$$O_{ij} = \int_I d\mathbf{r} \chi_i^*(\mathbf{r}) \chi_j(\mathbf{r}) . \quad (2.11)$$

G_0^{-1} now appears in Eq. 2.10 in the form of an extra potential added to the surface Hamiltonian. Matrix elements for G_0^{-1} (the embedding potential) provide all the substrate information for the surface calculation. The formulation for this calculation is now entirely in terms of ϕ and G_0^{-1} . No approximations have been made, and this method is exact. Eq. 2.10 is evaluated at $E = \varepsilon$ to further simplify the problem.

By calculating the Green function for the surface instead of the individual wave-functions, the ground state surface properties are obtained without carrying around the excess baggage of the numerous ϕ 's needed. The Green function, G , may be represented by a basis function expansion:

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_{i,j} g_{ij}(E) \chi_i(\mathbf{r}) \chi_j^*(\mathbf{r}') . \quad (2.12)$$

The related Green function equation for the surface is obtained by the variational method. A matrix equation is then computed, similar to Eq. 2.10. If we choose to evaluate G at energy $E = \varepsilon$, we obtain

$$\sum_k [H_{ik} + (G_0^{-1})_{ik} - E O_{ik}] g_{kj}(E) = \delta_{ij} . \quad (2.13)$$

Once the g_{kj} s are computed, the Schrödinger equation is solved and the physical properties of interest, such as the charge density, the local density of states, and work function, are found.

2.4 Basis Functions

Basis functions are chosen to resemble the spatial behavior of ϕ and G in the surface region. Since ϕ and G are expected to vary when traversing the surface region, a wise choice of basis will minimize the number of functions required for a given level of accuracy, thus minimizing the time required to complete the calculation. Constructing a basis with one type of function for the surface region is difficult because the number of coefficients needed to represent the surface would be very large. Instead, linearized augmented plane waves (LAPWs) are chosen as basis functions.²¹ In accordance with the LAPW method, the surface layer is broken up into three regions: the muffin-tin (MT) region, the interstitial region, and the vacuum region. This choice of basis has certain advantages over other expansions, namely, the functions are continuous and differentiable everywhere, and are sufficiently flexible to produce matrix elements that are nearly independent of energy.

2.4.1 Muffin-Tin Spheres

The muffin-tin (MT) region is defined by a sphere centered around an atomic site and extending out until touching nearest neighbor spheres. MT basis functions for G and ϕ are composed of spherical harmonics times a radial function and its energy derivative:

$$\begin{pmatrix} \chi_{m,n}^+(\mathbf{r}) \\ \chi_{m,n}^-(\mathbf{r}) \end{pmatrix} = \sum_L \left(\begin{pmatrix} A_{L,\alpha}^+(\mathbf{k}) \\ A_{L,\alpha}^-(\mathbf{k}) \end{pmatrix} \times u_{l,\alpha} + \begin{pmatrix} B_{L,\alpha}^+(\mathbf{k}) \\ B_{L,\alpha}^-(\mathbf{k}) \end{pmatrix} \times \dot{u}_{l,\alpha} \right) Y_L(\Omega) \times \begin{pmatrix} i^l \\ i^{l-1} \end{pmatrix}, \quad (2.14)$$

where the $\pm$ solutions match onto odd(-)/even(+) interstitial plane waves (with respect to reflection in the $z = 0$ plane) at the MT-interstitial boundary. u_l and $\dot{u}_l$ are radial and energy derivative solutions to the scalar-relativistic Dirac equations with no spin-orbit coupling.²² The A and B coefficients are determined by matching χ and $\partial\chi/\partial r$ across the MT boundary. The energy derivative is used because $u_{l,\alpha}$ is approximately linear over an energy range centered on the energy parameter E_l for each atom(α): $u_l(E) = u_l(E_l) + (E - E_l)\dot{u}_l(E_l)$.²³ Values for E_l are chosen so that the energy lies in the center of the band with that l character, although the use of $\dot{u}_l$ ensures that band eigenvalues are relatively insensitive to the choice of E_l . The basis functions for each spin state are calculated individually, and thus the spin indices are missing in Eq. 2.14.

The usual practice has been to include terms up to $l = 8$ for the MT expansions. However, for this study, terms in the MT expansion were increased to $l = 12$. When terms up to $l = 12$ are used instead of $l = 8$, the error at the MT-interstitial interface was reduced by an order of magnitude. Because spin-polarized calculations have an extra degree of freedom, it was felt that the extra digit of accuracy was needed.

2.4.2 Interstitial Region

In the interstitial region, where the charge density and potential are expected to be slowly-varying, the LAPWs are plane waves of the form:

$$\left. \begin{array}{l} \chi_{m,n}^+(\mathbf{r}) \\ \chi_{m,n}^-(\mathbf{r}) \end{array} \right\} = \sqrt{\frac{2}{\Omega}} e^{i\mathbf{k}_m \cdot \mathbf{R}} \times \begin{cases} \cos(k_n z), & n \text{ even}, \\ \sin(k_n z), & n \text{ odd}, \end{cases} \quad (2.15)$$

where,

$$k_n = \frac{n\pi}{\widetilde{D}}. \quad (2.16)$$

Ω is the volume of the slab unit cell, and $\widetilde{D}$ is chosen to be slightly larger than D , the slab thickness. $\widetilde{D}$ is used rather than D in order to allow greater freedom in derivative at the boundary of the interstitial region. Because the interstitial χ s are used in a finite Fourier expansion, it is expected that discontinuities at the vacuum-interstitial boundary and the MT-interstitial boundary will always exist. Finite Fourier expansions tend to overshoot at the discontinuity and lead to an uneven distribution of error (see Fig. 2.2). If the basis functions were not allowed to extend beyond $\pm D/2$, minor errors may occur with matching at the boundary. Allowing the expansion to extend out past the interstitial region adds greater accuracy in matching by allowing a greater range in matching conditions.

2.4.3 Vacuum Region

In the vacuum region, the wavefunctions are expected to exponentially decay away from the surface. The vacuum basis functions are expressed as:

$$\left. \begin{array}{l} \chi_{m,n}^+(\mathbf{r}) \\ \chi_{m,n}^-(\mathbf{r}) \end{array} \right\} = \left[\left[\begin{array}{l} \alpha_{m,n}^+(\mathbf{k}) \\ \alpha_{m,n}^-(\mathbf{k}) \end{array} \right] \times v_m(z) + \left[\begin{array}{l} \beta_{m,n}^+(\mathbf{k}) \\ \beta_{m,n}^-(\mathbf{k}) \end{array} \right] \times \dot{v}_m(z) \right] e^{i\mathbf{k}_m \cdot \mathbf{R}}. \quad (2.17)$$

The Schrödinger equation is solved in the vacuum region at an energy E_v with the planar-averaged potential in order to find v_m and the energy derivative $\dot{v}_m$. α and β are chosen in order to preserve the continuity of χ and $\partial\chi/\partial z$ at the vacuum-slab boundary.



FIG. 2.2. The first six approximations of a step function using a finite Fourier series expansion. Note the overshoots at the discontinuities.²⁴

2.5 Embedding Potential

Because the potential and charge density are slowly-varying in the interstitial region, the logical choice is to embed there; however, the resulting interface is very complicated (see Fig. 2.3). Computing the matrix elements along this undulating surface is difficult; however, calculating the matrix elements along a planar surface is relatively simple. Therefore, it is desirable to transfer the embedding surface from the complicated surface to a flat one (see Fig. 2.4). Thus, the computational difficulties arising from the undulating surface are circumvented. Provided this shift is performed correctly, the bulk crystalline properties will still have the same influence on the surface.¹³

The embedding potential may be thought of as a pseudopotential that replaces the exact physical potential in such a way as to preserve the physical influence of the core and valence electrons. Pseudopotentials may be created using different approaches provided they accurately model the influence of the original potential. The embedding potential is analogous to the method of images used in electrostatics, in

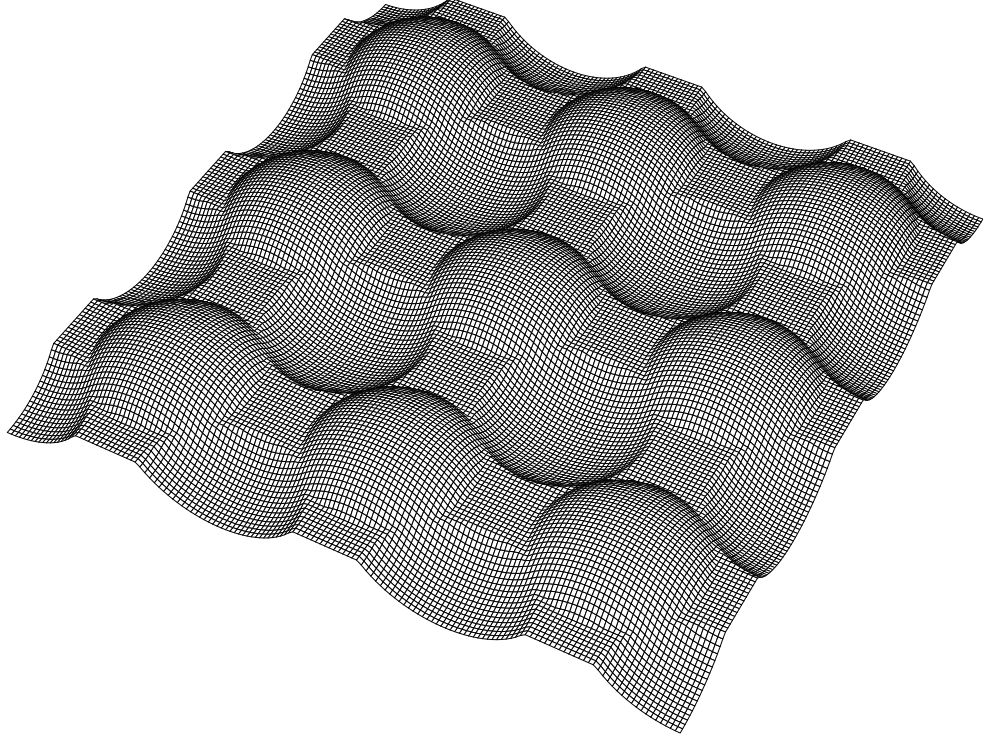


FIG. 2.3. A BCC(001) embedding surface.

which imaginary charges are placed in the excluded region in such a way as to give the correct physics in the region of interest.

The embedding potential is generated by employing a scattering method and using previously tabulated values for the bulk atomic potentials. The bulk crystal is assumed to have a muffin-tin form and the potentials inside the muffin-tins are assumed to be spherically symmetric. Scattering phase shifts are then used to determine the reflection properties of the perfect crystal lattice from which the embedding potential can be computed.

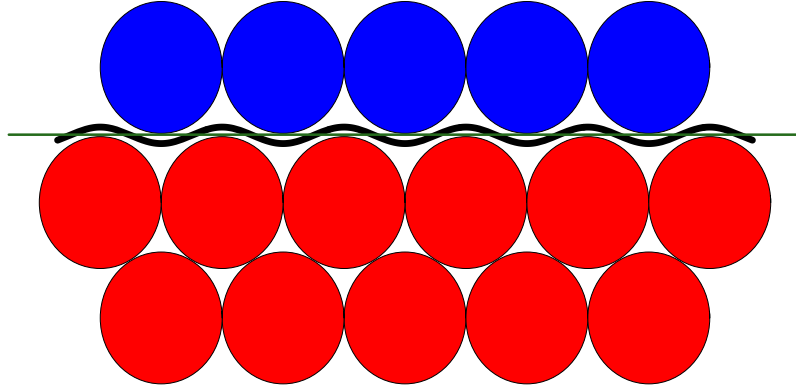


FIG. 2.4. The transferred embedding surface is represented by the flat line between the surface slab (blue circles) and the substrate (red circles).

To show how the reflection properties can be calculated, consider a plane wave $e^{i[\mathbf{k}+\mathbf{G}]\cdot\mathbf{R}}e^{ik_z z}$ incident on the surface, where $\mathbf{k}$ is any wavevector, k_z is the z -component of $\mathbf{k}$, $\mathbf{G}$ is a surface reciprocal lattice vector, and $\mathbf{R}$ is the x - y planar component of $\mathbf{r}$. When the plane wave scatters, the wavefunction can be written as ($z < 0$):

$$\psi(\mathbf{r}) = e^{i[\mathbf{k}+\mathbf{G}]\cdot\mathbf{R}}e^{ik_z z} + \sum_{\mathbf{G}'} R_{\mathbf{G}',\mathbf{G}} e^{i[\mathbf{k}+\mathbf{G}']\cdot\mathbf{R}} e^{\gamma_{\mathbf{G}'} z}, \quad (2.18)$$

where $R_{\mathbf{G}',\mathbf{G}}$ is the reflection matrix and $k_{\mathbf{G}'}^2 - \gamma_{\mathbf{G}'}^2 = k_{\mathbf{G}}^2 - k_z^2$. At the flat boundary surface, the Fourier components are given by:

$$\begin{aligned} \psi_{\mathbf{G}'} &= \delta_{\mathbf{G}',\mathbf{G}} + R_{\mathbf{G}',\mathbf{G}}, \\ \psi'_{\mathbf{G}'} &= \gamma_{\mathbf{G}'}(-\delta_{\mathbf{G}',\mathbf{G}} + R_{\mathbf{G}',\mathbf{G}}). \end{aligned} \quad (2.19)$$

By inverting Eq. 2.6, an expression for G_0^{-1} can be obtained in terms of the reflection matrix:

$$G_0^{-1} = \gamma \frac{(1 - R)}{(1 + R)}. \quad (2.20)$$

Using the layer-doubling method,²⁵ the reflection matrix is calculated using the muffin-tin substrate potential. In spin-polarized calculations, separate spin-up and spin-down embedding potentials are calculated for use in the SEGF program.

2.6 Surface Brillouin Zone

The goal of this work is to determine the electronic structure of materials within certain design limits. Even by using the Green function, calculating the electronic properties for even the simplest of materials is computationally difficult. A simplification to the problem may be introduced by limiting the choices of materials to periodic ones. Computational difficulties will also be eased through symmetry considerations.

The periodic arrangement of potentials in a crystal lattice allows the use of Born von-Karman (periodic) boundary conditions when solving the Schrödinger equation. The resulting solutions are of Bloch form and are labeled by their wavevector ($\mathbf{k}$) and their band index ($\mathbf{n}$). Because the electrons are labeled by wavevectors, reciprocal space is used when calculations are made.

With computational efficiency as a design goal, the calculations are performed in the smallest region of reciprocal space possible, the irreducible portion of the Brillouin Zone, to ensure that computer resources are conserved. Because the introduction of the surface breaks vertical symmetry, the component of $\mathbf{k}$ perpendicular to the surface is no longer a good quantum number, and the bulk Brillouin Zone transforms into the surface Brillouin Zone (see Fig. 2.5). Therefore, the surface Brillouin Zone (SBZ) is used when calculating relevant physical quantities. Having established the geometry, the next step is to define the grid for the SBZ over which aggregate quantities can be integrated.

Cunningham has provided a method to generate efficient sets of points and weighting factors over the SBZ that give accurate representations of periodic functions.²⁶ The points are referred to as special $\mathbf{k}$ -points. Choosing the number of points used

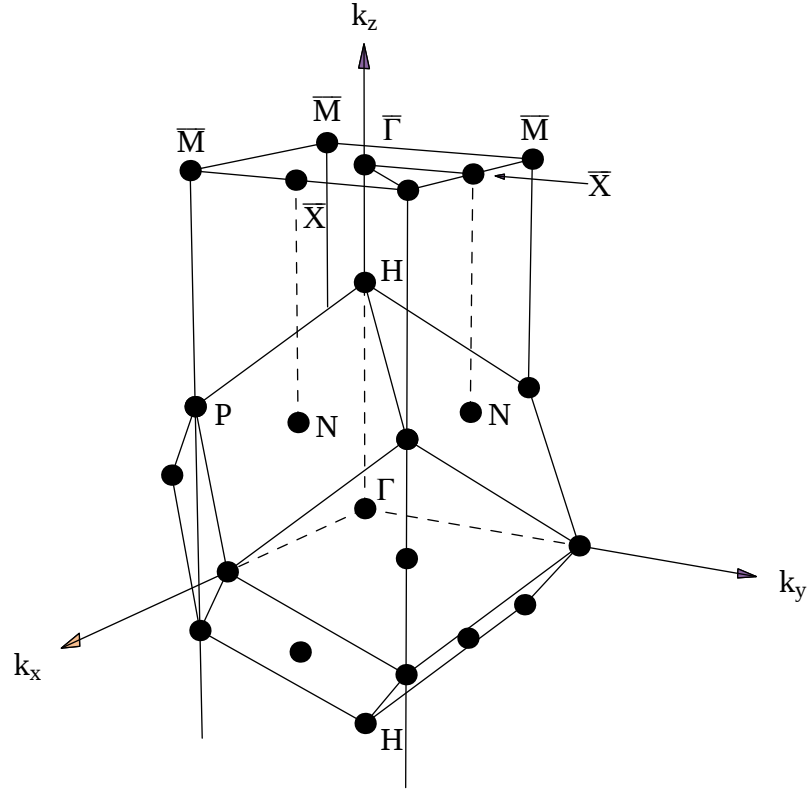


FIG. 2.5. Projection of the bulk Brillouin Zone (bottom) onto the surface Brillouin Zone (top) for a bcc lattice.

in a calculation is left to the individual performing the calculation. Small point sets are chosen to keep computational time and resources to a minimum, yet large enough to represent the crystal accurately. Metals with partially-filled bands, like the $3d$ transition metals considered in this study, or those that possess significant structure close to the Fermi level require a larger numbers of special $\mathbf{k}$ -points because the occupations of bands may differ significantly at adjacent $\mathbf{k}$ -points. A 36 special $\mathbf{k}$ -point set in the irreducible portion of the SBZ was used for all materials in this study (see Fig. 2.6).

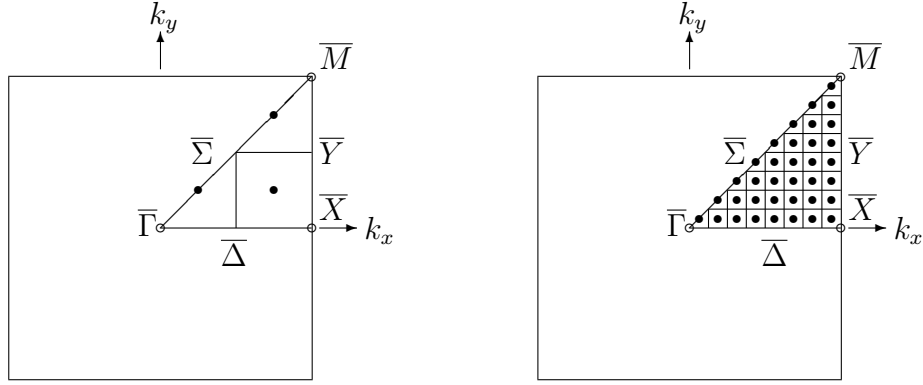


FIG. 2.6. Surface Brillouin Zone for three and thirty-six special $\mathbf{k}$ -point sets (filled circles) within the irreducible portion of a square surface Brillouin Zone

2.7 Self Consistency

Many methods for performing electronic structure calculations have been developed. These methods usually involve solving a set of one-electron equations. In these methods, trial wavefunctions for each electron are used to establish an interaction potential, which is then used to find the individual wavefunctions. When this iterative process yields no change between the input and output potentials (or charge densities), self-consistency is said to have been reached. This procedure is known as the self-consistent field approximation. A self-consistent calculation is necessary because the electron states must be known in order to compute the potential, which must be known to compute the states.²⁷

The SEGF method is no different in this respect: a set of one-electron equations are used to find the ground state energy. The SEGF potential depends on the charge density which depends on the Green function. Instead of attempting to solve the whole problem in a single calculation, the ground state energy is reached using an iterative approach.

A separate computer program is used to calculate a starting charge density or potential that is either paramagnetic or spin-polarized. For this study, the charge

density was used for the input. A third computer program was used to calculate the energy-dependent embedding potential. Once these steps were completed, the self-consistent iterative process began. The Coulomb potential was obtained from the input charge density by solving Poisson's equation in the surface layer using a method developed by Weinert.²⁸ The exchange-correlation potential (spin-dependent) is then added to the Coulomb potential and the total potential ($V_{in} = V_{Coulomb} + V_{XC}$) is complete. V_{in} is used in the scalar-relativistic Dirac equation for the surface Green function to determine a new charge density ρ_{out} , which is then used to compute an output potential (V_{out}).

For most initial guesses of ρ_{in} , the ρ_{out} will not match coefficient for coefficient. If this were the case, there would be no need to iterate because ρ_{in} would be the ground state charge density. In general, this is not the case and the output charge density could be used as the new input, creating a feedback loop that iterates to the ground state charge density. However, an unattenuated feedback loop with the SEGF method is not stable due to the strength of the Coulomb potential in the surface region. A large Coulomb potential tends to attract too much charge on one cycle and overcompensate on the next cycle by depleting the surface of charge because the SEGF method does not require charge conservation. Large charge density oscillations drive the calculation away from convergence. To overcome this, attenuated feedback or mixing may be used to iterate to the ground state without driving large charge density oscillations.

Two mixing schemes are generally used to aid convergence: simple mixing and Broyden's method. Simple mixing attenuates feedback linearly, adding a small amount of ρ_{out} to ρ_{in} :

$$\rho_{in}^{m+1} = (1 - \beta)\rho_{in}^m + \beta\rho_{out}^m, \quad (2.21)$$

where m is the current iteration and β is a mixing factor. β can range from 0 to 1 but is normally very small. For this study, β ranged between 0.0001 and 0.02.

Another convergence technique is the Broyden method, which is a non-linear method for finding the minimum of a multivariate function in which previous cycles are used to help locate the ground state. In theory, because of the greater number of degrees of freedom, the Broyden method should reduce the number of iterations needed to find the ground state charge density.

2.8 Charge Density

Once the ground state energy of the system has been found, physical quantities which describe the system can be extracted, providing information about the electronic structure. Usually this can be accomplished by using the local density of states (LDOS) for the system. The LDOS describes the distribution of electron energy levels throughout the surface. The LDOS is defined as:

$$\sigma_{\mathbf{k}}(\mathbf{r}, E) = \sum_n |\psi_{\mathbf{k},n}|^2 \delta(E - E_n) , \quad (2.22)$$

when the energy states are discrete, and

$$\sigma_{\mathbf{k}}(\mathbf{r}, E) = \int_{-\infty}^{E_F} dE' |\psi_{\mathbf{k}}(\mathbf{r}, E')|^2 \delta(E - E') , \quad (2.23)$$

when the states lie in the bulk continuum.

The LDOS is used rather than the density of states because experimental efforts to study surfaces probe electronic properties at particular positions rather than aggregate properties. For example, scanning tunneling microscopy measures energy levels of electron states on a plane. Of interest are surface states which are electronic states that exist in bulk band gaps, which can be identified from the LDOS.

In metals, valence electrons are not bound to their parent nuclei and their wavefunctions extend throughout the crystal. Because of the enormously large number (10^{23}) of valence electrons in a metal, their wavefunctions form an almost continuous energy spectrum. Their spatial extent makes calculating individual wavefunctions difficult. Even with state-of-the-art computers, calculating an enormously large num-

ber of wavefunctions is impossible. Models that use wavefunctions store only enough of them for an adequate physical description.

Alternatively, the LDOS may be calculated by use of a Green function. The Green function contains all of the information about the physics of the surface and substrate. To understand how the LDOS is calculated, consider the bilinear formula for the Green function:

$$G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}', E) = \sum_n \frac{\psi_{\mathbf{k},n}^*(\mathbf{r}') \psi_{\mathbf{k},n}(\mathbf{r})}{E - E_n \pm i\alpha}, \quad \text{for } \alpha > 0. \quad (2.24)$$

Using the formal identity,

$$\lim_{\alpha \rightarrow 0} \frac{1}{x \pm i\alpha} = P\left(\frac{1}{x}\right) \mp i\pi\delta(\mathbf{x}), \quad (2.25)$$

(where P stands for the principal part), the LDOS may be written in terms of $G_{\mathbf{k}}$:

$$\sigma_{\mathbf{k}}(\mathbf{r}, E) = \frac{1}{\pi} \text{Im } G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}; E + i\varepsilon). \quad (2.26)$$

To compute the charge density at a given $\mathbf{k}$ -point, the following integral is used:

$$\rho(\mathbf{r}) = \int_{-\infty}^{E_F} dE \sigma_{\mathbf{k}}(\mathbf{r}, E), \quad (2.27)$$

where the integration is computed just above the real axis to avoid any poles. A total density of states or total charge density is computed by performing a weighted sum of contributions from the LDOS throughout the SBZ using the scheme outlined in Fig. 2.6.

With the Green function, and by extension the LDOS, the valence charge density can be constructed in the different LAPW regions using the expansions:

$$\rho(\mathbf{r}) = \begin{cases} \sum_{m,n} \rho_{mn} e^{i\mathbf{G}_m \cdot \mathbf{R}} \times \begin{cases} \cos(k_n z) \\ \sin(k_n z) \end{cases} & , \text{ with } \mathbf{r} \text{ in the interstitial region,} \\ \sum_L \rho_L(\mathbf{r}) Y_L(\theta, \phi) & , \text{ with } \mathbf{r} \text{ in the MT spheres,} \\ \sum_m \rho_m(z) e^{i\mathbf{G}_m \cdot \mathbf{R}} & , \text{ with } \mathbf{r} \text{ in the vacuum.} \end{cases} \quad (2.28)$$

Electrons that comprise the core charge reside in the inner shells of each crystalline atom and are relatively inert. The energy bands occupied by core electrons are the very low energy, narrow bands in the solid which have nearly the same character as isolated atoms. Unlike valence electrons, the wavefunctions for the core electrons are appreciable only near a particular atom.

The core electrons states are found by calculating wavefunctions for the fully relativistic Dirac equation using a spherical potential. The SEGF formulation assumes that the core charge is negligible past the MT boundary; however for small muffin-tin radii, this is not strictly true. For the surfaces studied herein, a non-negligible (albeit small) amount of core charge was found to extend into the interstitial region. A method to add the core charge to the other regions was implemented (see Appendix A). Once these contributions are computed, the total charge density is determined by adding the valence and core charge contributions:

$$\rho(\mathbf{r}) = \rho(\mathbf{r})_{core} + \rho(\mathbf{r})_{valence}.$$

2.9 Work Function

To remove an electron from a solid, energy must be expended to transport the electron from the bulk lattice, through the surface, and into the vacuum. The minimum amount of energy required to do this at absolute zero is known as the work function. An accurate measurement of the work function should be performed on a crystal with an infinite surface, but in practice, measurements like this are made such that the electron is extracted far enough from the edges of the crystal to avoid stray fields and edge effects.

At the surface, the configuration of electrons differs from the bulk crystal. In fact, valence electrons at the surface spill out into the vacuum region, resulting in a surface layer total charge that shifts from neutral to slightly positive. The resulting dipole layer produces an electric field that works against the removal of electrons from the

crystal. Therefore, to remove an electron from a surface, the electron must have enough energy to traverse the dipole layer (D). Quantitatively, the work function (ϕ) is defined as:

$$\phi = D - E_F . \quad (2.29)$$

Because the Fermi level and the surface distribution of charge are both properties of the material, the work function provides a characteristic value that is likely to be unique. Other factors that influence ϕ include the arrangement of surface atoms and the natural repulsion of nearby electrons. The accuracy of the calculated work function is often taken to be a standard measure of the accuracy of an electronic structure calculation.

CHAPTER THREE

The Surface Magnetism of Ni(001)

Hund's rules elegantly explain how electrons are arranged in an isolated atom or ion. The essential feature is that electrons organize themselves such that partially-filled shells maximize their spin, achieving the lowest energy state possible for a given electron count. In the absence of external $\mathbf{E}$ and $\mathbf{B}$ fields, a net spin imbalance occurs if the valence shell is unfilled, giving rise to magnetic moments in free atoms. However, aggregations of atoms or ions (*e.g.*, atomic gases) are not generally spontaneously magnetic due to the random alignment of individual magnetic moments.

Solids with unfilled valence shells are generally paramagnetic. The individual atoms within the solid may possess non-zero magnetic moments, but these moments fail to interact in such a way as to produce a net macroscopic moment. However, when certain solids are cooled below their critical temperatures, the individual moments align and the crystal spontaneously magnetizes. Modeling cooperative behavior such as magnetism from first principles remains a difficult problem.

Magnetic solids are generally classified in two crystalline orderings: ferromagnetic or antiferromagnetic. Ferromagnetic crystals, such as the $3d$ transition metals in this study, favor alignment of the local magnetic moments (see Fig. 3.1(a)). Ferromagnetic solids have a net magnetization in the absence of applied fields. A subtype of the ferromagnetic crystal, ferrimagnets have antiparallel but unequal magnetic moments in each sublattice, thus retaining a net magnetization. In an antiferromagnetic crystal (see Fig. 3.1(b)), the magnetic moments are ordered, but the ordering is antiparallel such that atomic moments produce a total macroscopic moment of zero.

Advances in physical understanding have led to improved methods for describing magnetic behavior in solids. From these, one major fact is clear: the Coulombic

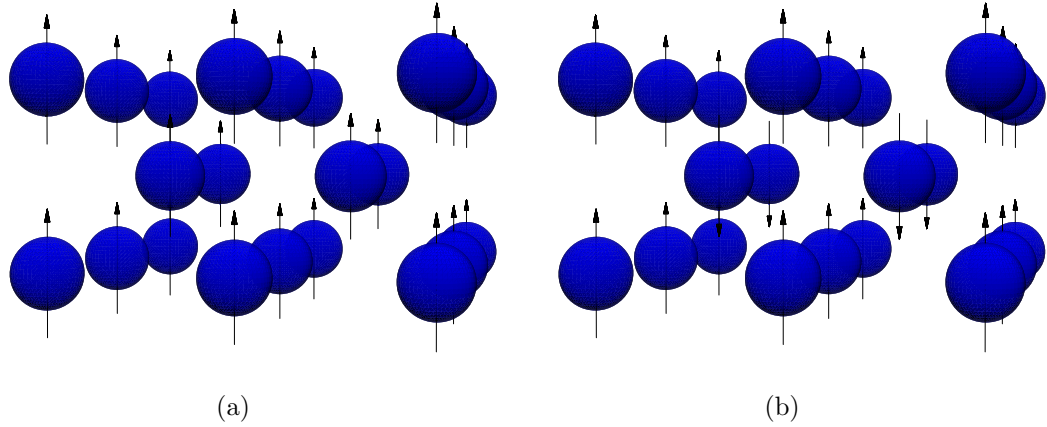


FIG. 3.1. Ferromagnetic and antiferromagnetic bcc crystals. Arrows show the magnetic moment for each atom.

and intra-atomic exchange interactions are the causes behind magnetic ordering in solids. Other physical interactions like dipole-dipole and spin-orbit coupling, while important, are not sufficiently energetic to explain spontaneous magnetization. By introducing spin polarization into physical models, electrons are allowed to populate different spin states. This single improvement allows magnetic behavior to be studied computationally.

For the $3d$ transition metals in the present study (iron, nickel, and cobalt), it is generally accepted that their ferromagnetic order is due to the narrowing of the d bands. When the crystals of these materials have temperatures below their Curie temperatures, the band of majority-spin states lies below the Fermi energy, while the minority-spin band lies partially above the Fermi energy. As a result, the valence electrons preferentially populate the spin-up bands at the expense of spin-down states. For each material, the spin-state populations differ; thus, variations in the strength of their magnetic moments are expected. Of the elements studied here, iron possesses the largest bulk magnetic moment.

From the earliest of times, some solids were known to possess macroscopic magnetizations. However, until fairly recently, the surfaces of solids were thought to be

non-magnetic because early theoretical studies of spin-polarized iron and nickel found the surfaces to be magnetically dead.²⁹ This is now known to be incorrect, and the origin of surface magnetism can be easily explained using a simple model developed by E.C. Stoner and J.C. Slater, which combines the molecular field concept with Fermi statistics.³⁰

For the bulk, the Coulomb interaction and any small applied external magnetic field can be shown to split the band eigenstates into spin-up and spin-down components.¹ Unequal populations give rise to a magnetic moment which can then be computed. The magnetic susceptibility ($\chi = \partial M / \partial H$) is given by:

$$\chi = \frac{\mu_0^2 \rho(E_F)}{1 - U\rho(E_F)}, \quad (3.1)$$

where U is the Coulomb interaction and $\rho(E)$ is the density of electronic states. When the Stoner criterion is satisfied ($U\rho(E_F) > 1$), the crystal is ferromagnetic.¹

Surface magnetism can be predicted by modifying the Stoner model for a surface, and using the surface density of states combined with an intra-atomic exchange parameter which gives the correct bulk magnetic moments.¹ The surface Stoner model predicts that the 3d transition metals iron, nickel, and cobalt, along with paramagnetic vanadium and anti-ferromagnetic chromium, will order ferromagnetically at the surface. These predictions are confirmed by other theoretical methods and experiment which have shown that iron, nickel, and cobalt have magnetic order at their surfaces.^{31–35}

3.1 Computational Details

A self-consistent calculation of the electronic structure of the Ni(001) surface was performed using the spin-polarized SEGf method. With a face centered cubic (fcc) crystal structure, the lattice vectors describing the surface mesh were rotated by 45° from the bulk axes to construct the smallest possible unit cell (see Fig. 3.2). As a

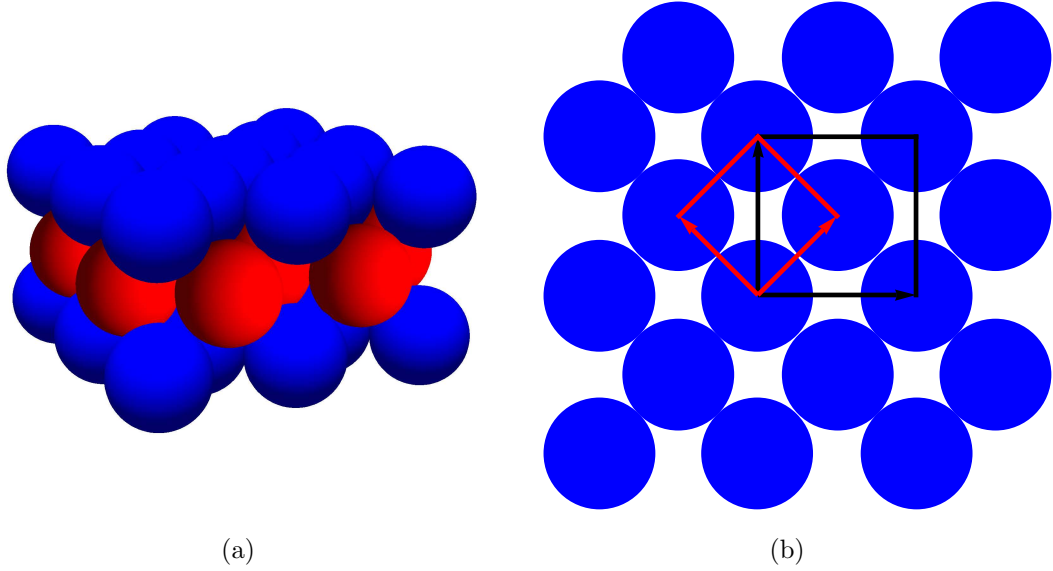


FIG. 3.2. To the left is a three-layer representation of an fcc crystal structure. The figure to the right is a simplified view of the top layer of an fcc(001) crystal. The black arrows show the conventional bulk lattice vectors, while the red arrows are the primitive surface vectors.

result, the rotated lattice spacing is 4.63 a.u. rather than the bulk lattice spacing of 6.55 a.u.

Using the tabulated bulk potentials of Moruzzi, Janak, and Williams,³⁶ the majority and minority-spin embedding potentials were constructed. A total of 180 LAPWs were used for the variational calculation. Basis functions in the MT region contained angular momentum components up to $l = 12$. For the expansion of the interstitial charge density, 2000 plane waves were used. In the irreducible portion of the surface Brillouin Zone, 36 special $\mathbf{k}$ -points were employed. The von Barth-Hedin parametrization for the exchange-correlation potential was used.³⁷ The potential and charge density in the vacuum region were expanded at 100 grid points up to 10 a.u. from the surface. Self consistency was defined when the maximum difference between the input and output potentials was less than 0.1 eV.

Previous paramagnetic SEGF surface studies used one- or two-layer embedded slabs with great success. However, with the magnetic crystals for this study, a three-

layer slab was used because bulk spin-densities appear to be restored at the third interior layer.

3.2 Work Function

The resulting work function as calculated by the SEGF method is 5.76 eV, which is in fair agreement with the experimentally measured work function of 5.2 eV.³⁸ Another Green function method³³ calculated a work function of 5.75 eV, while a seven-layer slab FLAPW calculation³⁹ obtained a value of 5.37 eV. Jepsen *et al.* used a five-layer slab LAPW method and a von Barth-Hedin approximation for exchange and correlation resulting in a work function of 5.35 eV.⁴⁰ A thin-slab LAPW calculation found a work function of 5.5 eV for a five-layer slab.⁴¹ Because of the fair agreement of the calculated SEGF work function with the experimental value, there is confidence that the rest of the computed quantities are likely to compare favorably with experimental results. Worthy of note is that the spin-polarized SEGF method has computed a work function near the experimental value while only using a three-layer slab. The other computational work cited all used much thicker slabs without embedding; thus, they do not model the semi-infinite problem correctly because such slabs have vacuum regions on both sides. A comparison of work functions and surface magnetic moments is found in Table 3.1.

3.3 Charge and Spin Density

Nickel was one of the first magnetic surfaces to be studied using self-consistent methods to determine its surface magnetic moment. Early studies errantly found magnetically dead surface layers^{42,43} while the bulk crystal remained ferromagnetically ordered. Feder *et al.*⁴⁴ studied the surface magnetic structure of Ni(001) using polarized electron diffraction, finding an enhancement of the surface magnetic moment by five percent with respect to the bulk.

Theory and experiment have now established that narrowed $3d$ bands are the primary reason for an enhancement of the magnetic moment at the surface. In the present work, we have obtained a spin moment at the surface of $0.69 \mu_B$ in good agreement with experiment.⁴⁴ This represents about a seven percent enhancement of the surface moment over that in the sub-surface layer.

Table 3.1. Ni(001) magnetic moments for the surface (S), subsurface ($S - 1$), and ($S - 2$) sub-surface layers and work function.

Calculation Method	S	$S - 1$	$S - 2$	Work Function (eV)
Three-layer SEGF	0.69	0.61	0.64	5.76
Seven-layer FLAPW ³⁹	0.68	0.60	0.59	5.37
Four-layer TB-LMTO ³³	0.69	0.64	0.66	5.75
Five-layer LMTO method ³²	0.59	0.58	0.57	5.02
Five-layer LAPW method ⁴⁰	0.65	0.59	0.62	5.35
Five-layer LAPW ⁴¹	0.73	0.68	0.69	5.5

Our SEGF calculated spin densities compare favorably with other theoretical and experimental studies (see Table 3.1). As seen in several other calculations,^{33,40,41} there is a Friedel-type oscillation in the magnetic moments between surface layers. The spin-polarized SEGF method performed very well with a three-layer slab as compared with other calculations that used much thicker slabs for their results.

For the bulk, the magnetic moment is $0.56 \mu_B$, as found experimentally,⁴⁵ and $0.58 \mu_B$ via theoretical methods.⁴⁶ Without performing a four-layer calculation, we are unable to determine the magnetic moment for the fourth layer ($S - 3$), but based on the results presented, it would likely be closer to the bulk moment.

In a study of Ni(001), Krakauer *et al.*⁴¹ argue that independent of size effects and $\mathbf{k}$ -point sampling, the charge density, except at the surface layer, will be charge neutral throughout the other layers, and the surface magnetic moment will be enhanced. Krakauer *et al.*⁴¹ found that the d orbital contribution to the charge density was the

Table 3.2. Surface, subsurface, and sub-subsurface layer valence charge for Ni(001).

Calculation Method	S	$S - 1$	$S - 2$
Three-layer SEGF	9.10	9.29	9.26
Five-layer LAPW film method ⁴¹	9.01	9.17	9.17
Five-layer LAPW ⁴⁰	9.08	9.24	9.25
Nine-layer TB-LMTO ⁴⁷	9.70	10.10	9.99

same from layer to layer, but the s and p orbital contributions at the surface layer were less than in the subsurface layers. Therefore, it was concluded that the s and p orbitals were responsible for the vacuum spill out of charge, and thus, responsible for determining the work function of the material. For the present work, an orbital charge decomposition was not performed; however, the valence charge was computed and compared with that of the Krakauer *et al.* total valence charge to evaluate their claim. Our SEGF calculated results have 9.10 electrons in the surface layer MTs, while the subsurface and sub-subsurface layers have 9.29 and 9.26 electrons, respectively (Table 3.2). A recent nine-layer tight-binding LMTO⁴⁷ calculation did not find charge neutrality throughout the layers. The results from Chakraborty *et al.*⁴⁷ indicate that the two topmost surface layers differ from the other layers, and that the magnetic moment for Ni(001) has a larger Friedel-type oscillation in the top three surface layers as seen in Table 3.1.

3.4 Surface Electronic Structure

3.4.1 Surface States and Resonances

3.4.1.1 Physical Description. When the symmetry of a three-dimensional infinite lattice is broken, as is the case for a surface, solutions to the Schrödinger equation no longer occur in 3D Bloch form. For the bulk, all components of $\mathbf{k}$ are good quantum

numbers, but at the surface, $\mathbf{k}_\perp$ can no longer be used because of the loss of periodicity perpendicular to the surface. Therefore, the bulk wavefunction at a surface can be written in the following form:

$$\psi(\mathbf{r}) = u(r_\parallel) e^{i\mathbf{k}_\parallel \cdot \mathbf{r}_\parallel} e^{-\kappa r_\perp}. \quad (3.2)$$

At the slab-vacuum boundary, electronic wavefunctions should be continuous; however, real values for κ would cause $\psi(\mathbf{r})$ to grow exponentially in amplitude in a direction perpendicular to the surface. If an eigenfunction of the Hamiltonian could be found in the vacuum region that decays away from the crystal, and that simultaneously matches to a bulk solution to the Schrödinger equation along the embedding surface, then this function would be a valid one-particle wavefunction. An important feature of this type of wavefunction is that the electronic state is not required to exist in a bulk energy band. Provided $\psi(\mathbf{r})$ and its logarithmic derivative can be matched onto any solution to the Schrödinger bulk equation (even a solution in a band gap), a localized electronic state will exist. States of this nature are confined to a short range near the surface because they exist in bulk band gaps or symmetry gaps. Electronic states of this type are known as surface states.

Another type of state that can exist at the vacuum boundary is a surface resonance. Such states lie within the bulk bands, but have amplitudes that are enhanced at the surface. In photoemission studies, surface resonances appear as peaks in the spectra, similar to the appearance of true surface states. Thus, the results from bulk bandstructure calculations must be used to discriminate between surface resonances and surface states.

3.4.1.2 Local Density of States. From the self-consistent charge density, the local densities of states (LDOS) were computed and plotted along the lines of high symmetry in the surface Brillouin Zone (SBZ). From these LDOS plots, the surface

states and resonances were found for both majority- and minority-spin states and further characterized by parity. Peaks in the LDOS are candidate surface states or

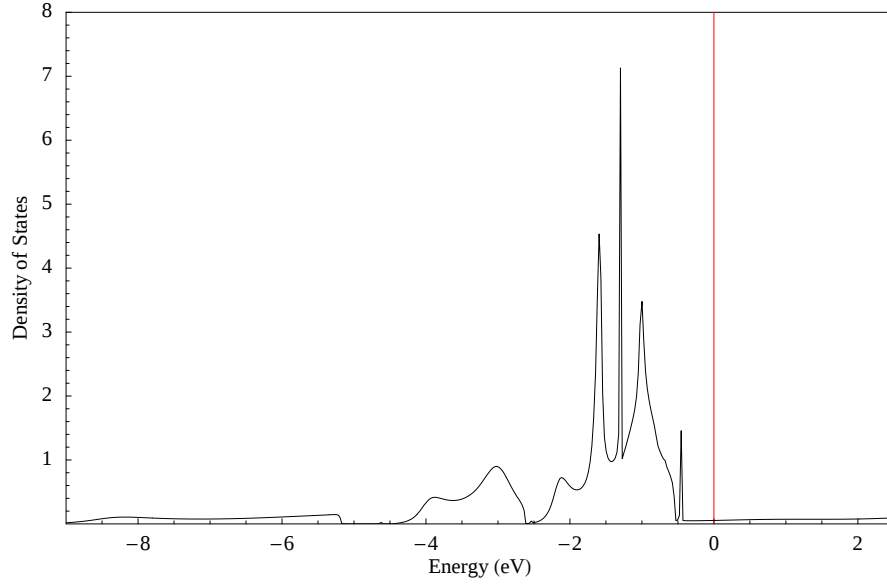


FIG. 3.3. The LDOS for the surface layer of Ni(001) at $\bar{\Gamma}$. The vertical red line denotes the Fermi Level.

resonances. An example LDOS plot for the surface layer is shown in Fig. 3.3. In order to categorize each state, some criteria for identifying a surface state or resonance must be established. Any peak in the LDOS that lies in an absolute gap in the surface bandstructure is a surface state by definition. Also, any state that lies in a relative gap of the same symmetry is also a surface state. For states that lie within the projected surface bandstructure, those peaks with high amplitude were included in the analysis.

Bulk energy bands along the lines of high-symmetry were projected onto the two-dimensional Brillouin Zone (see Fig. 2.5 for the 2D Brillouin zone for Ni(001)). Detailed analyses of the electronic structure along these lines of high symmetry are included in the following sections. Both the $\bar{\Delta}$ line (connecting $\bar{\Gamma}$ to $\bar{X}$) and the $\bar{\Sigma}$

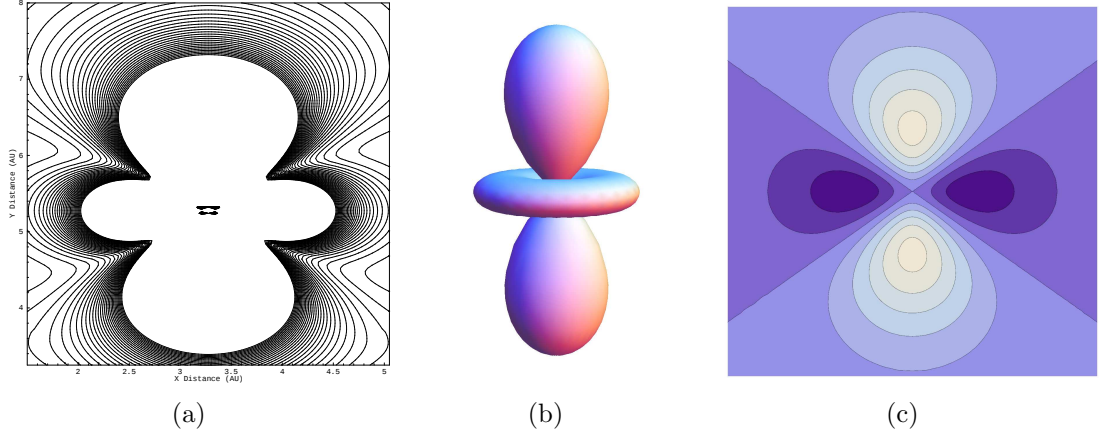


FIG. 3.4. (a) A charge density contour plot at $\bar{\Gamma}$, -1.6 eV below the Fermi level. (b) Graphical representation of a $3d_{z^2}$ orbital. (c) Contour plot of a $3d_{z^2}$ orbital.

line (connecting $\bar{M}$ to $\bar{\Gamma}$) allow even and odd symmetry for the projected bands and surface states. This is not the case for the $\bar{Y}$ line that extends from $\bar{X}$ to $\bar{M}$, as there is no reflection symmetry in the 3D Brillouin Zone along this line. Therefore, a delineation between the even- and odd-symmetry bulk bands is not possible along $\bar{Y}$, but the surface states and resonances can still be classified as having either even or odd parity. The symmetries of the projected bandstructures, surface states, and surface resonances are provided in the graphs.

For each peak in the LDOS, the valence charge density was plotted using a small energy range centered around the peak. In order to analyze these charge densities, several contour plots were made so that the symmetry of each state could be determined. Previously, this plotting would have been very laborious as each computer-generated plot had its inputs altered via a text editor and human; but over the course of this study, software was developed (see Appendix B.3) to allow systematic plotting of all peaks in the LDOS.

By analyzing the charge density profiles, information about the symmetry of the state can be determined and plotted. An example is shown in Fig. 3.4(a), in which charge density contours are plotted for a peak in the LDOS at $\bar{\Gamma}$ at 1.6 eV below the

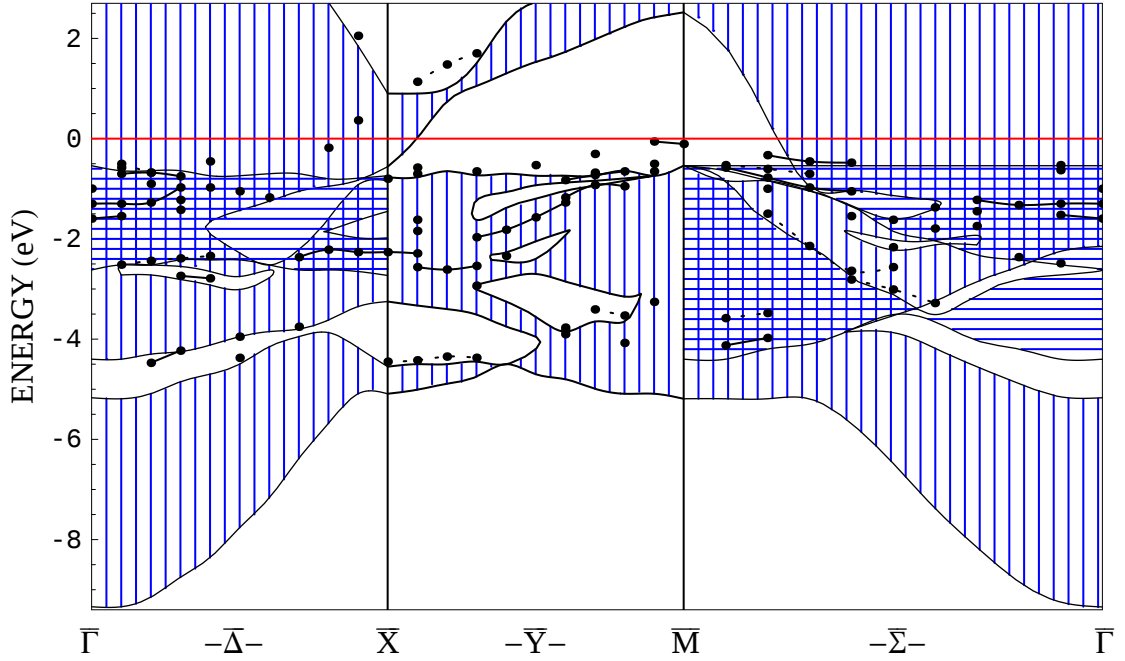


FIG. 3.5. Majority-spin bandstructure for Ni(001) that includes surface states and resonances along the two-dimensional lines of high symmetry. Vertical shading represents even-symmetry projected bulk bands while the horizontal shading indicates odd-symmetry bulk bands. Solid lines represent even-symmetry and dashed lines are odd-symmetry surface states and resonances.

Fermi level. The contour closely resembles a $3d_{z^2}$ orbital (Figs. 3.4(b) and 3.4(c)). Using the charge density contours of a given state together with the character table for the point group, the state's symmetry can be deduced. The results for Ni(001) are plotted in Figs. 3.5 and 3.6.

3.4.2 $\bar{\Delta}$

The high-symmetry line on the square surface Brillouin Zone traversing from $\bar{\Gamma}$ to $\bar{X}$ is labeled as the $\bar{\Delta}$ line (see Fig. 2.6). Eleven evenly spaced $\mathbf{k}$ -points were used to analyze the surface electronic structure along $\bar{\Delta}$. At each $\mathbf{k}$ -point, the LDOS was computed for energies well below the Fermi level to almost 3 eV above. For each of

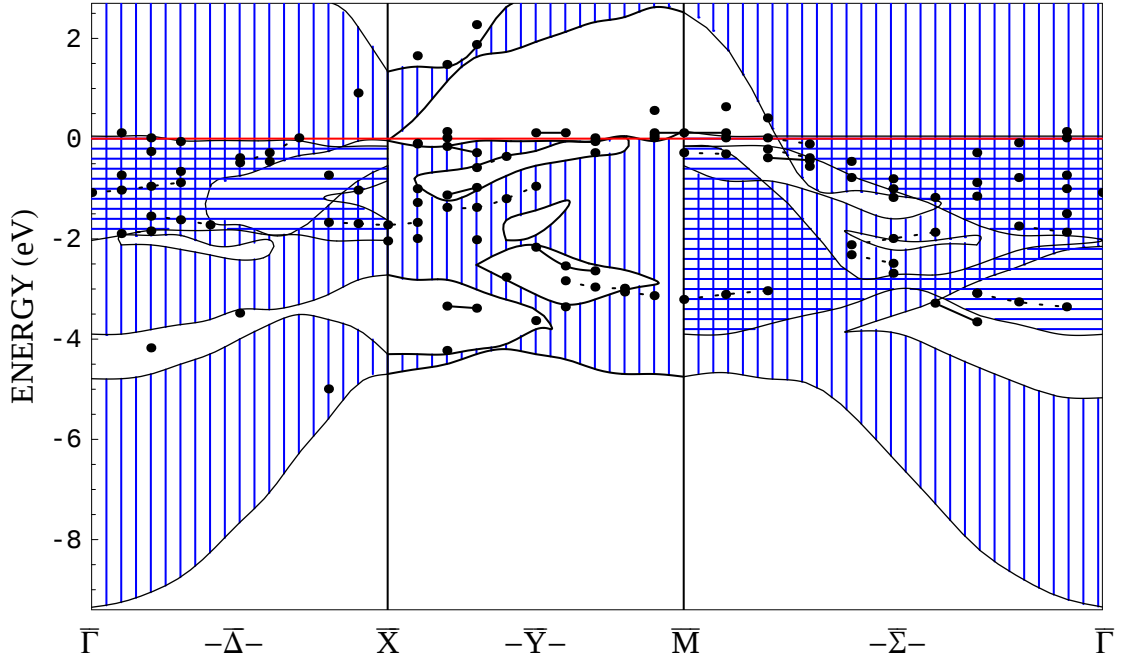


FIG. 3.6. Minority-spin bandstructure for Ni(001) that includes surface states and resonances along the two-dimensional lines of high symmetry. Vertical shading represents even-symmetry projected bulk bands while the horizontal shading indicates odd-symmetry bulk bands. Solid lines represent even-symmetry and dashed lines are odd-symmetry surface states and resonances.

the eleven discrete points sampled along $\bar{\Delta}$, over four hundred discrete LDOS values were calculated so as to not miss any peaks in the LDOS. If a peak in the LDOS was identified as a surface state or resonance, the charge density profile was plotted for the $\mathbf{k}$ -point and energy.

As seen in Figs. 3.7(a) and 3.7(b), there is an absolute band gap that traverses the entire $\bar{\Delta}$ line for both spin states. At $\bar{\Gamma}$ the majority gap is centered at -4.78 eV and has a width of 0.38 eV. For about three-quarters of the way along the line, the center of the gap rises as the width of the gap narrows. By $\bar{X}$ the gap is centered at -3.9 eV and is 0.65 eV wide. The $\bar{\Delta}$ minority band gap is very similar to the majority case. For minority spin along $\bar{\Delta}$, the gap is -4.35 ± 0.45 eV at $\bar{\Gamma}$ and is 3.51 ± 0.70 eV

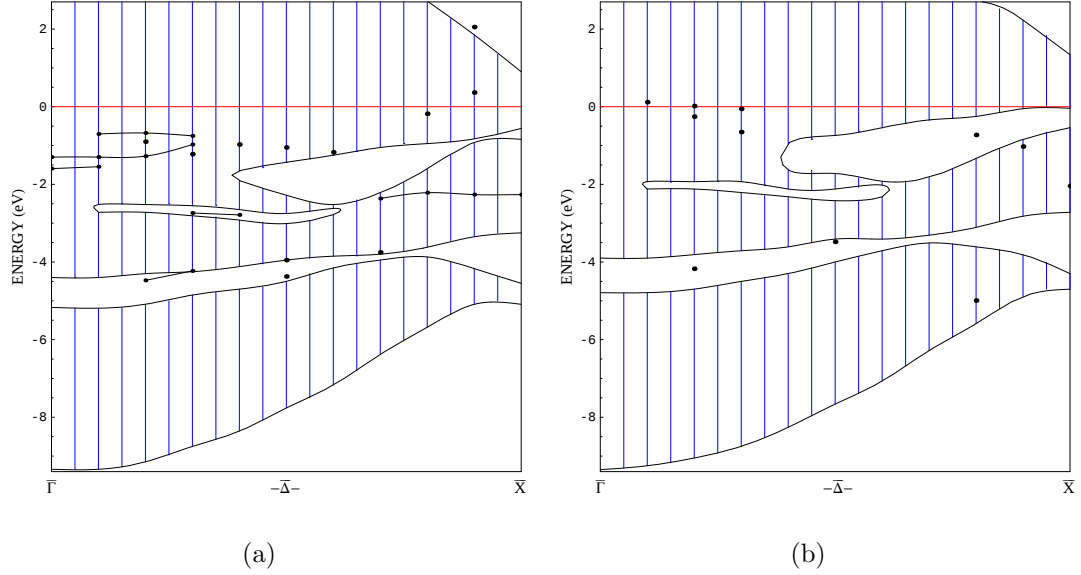


FIG. 3.7. Even-symmetry surface bands, resonances, and bulk band projections for Ni(001) majority and minority spin along $\bar{\Delta}$. Vertical shading represents even-symmetry projected bulk bands. Solid lines represent even-symmetry surface states and resonances.

by $\bar{X}$. Both spin states also have a narrow gap that begins near $\bar{\Gamma}$ and continues to over sixty percent of the distance to $\bar{X}$.

For $\bar{\Delta}$ majority spin, several surface states are found in the gap that traverses the $\bar{\Delta}$ line (see Fig. 3.7(a)). There is also a short surface state band about one quarter of the distance from $\bar{\Gamma}$. Two surface resonance bands are found starting at $\bar{\Gamma}$ at 1.6 eV and 1.3 eV below the Fermi level. These bands are similar to those found by Krakauer *et al.*; however, each of their bands were about 0.5 eV higher than the ones found using the SEGf method.²¹ There is a $\bar{\Delta}_1$ band starting at $\bar{X}$ that is about 2.28 eV below the Fermi level. This band runs about a quarter of the distance toward $\bar{\Gamma}$. A five-layer LAPW calculation found a similar band near $\bar{X}$ around 2 eV below the Fermi level.⁴⁰

Photoemission experiments by Plummer and Eberhardt show a surface band that runs from $\bar{X}$ back one-third along $\bar{\Delta}$ that is 0.1 eV below the Fermi level.⁴⁸ Although

previous calculations have failed to obtain this surface band,⁴⁰ the present results show two individual states in the vicinity of the band observed experimentally.

In Fig. 3.7(b), there are several individual surface resonance states near E_F that appear one-tenth to three-tenths of the way along $\bar{\Delta}$ from $\bar{\Gamma}$. Jepsen *et al.*⁴⁰ obtained an even-symmetry minority-spin band from $\bar{\Gamma}$ to less than half the distance to $\bar{X}$ near the Fermi level that is very similar to the states identified in this study. A nine-layer FLAPW³⁹ calculation identified a surface band running all along $\bar{\Delta}$ near the Fermi level.

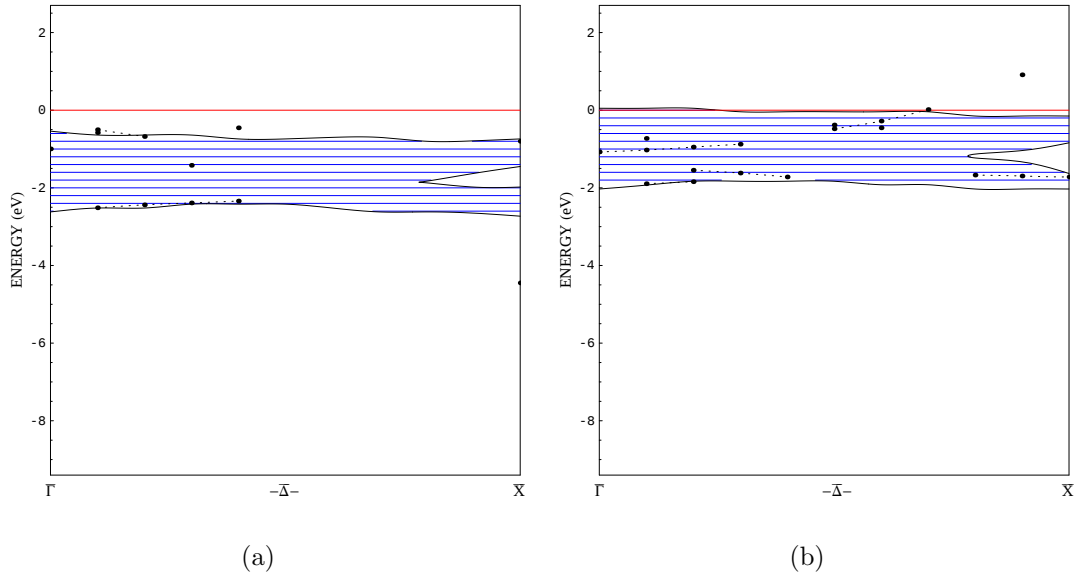


FIG. 3.8. Odd-symmetry surface bands, resonances, and bulk band projections for Ni(001) majority and minority spin along $\bar{\Delta}$. Horizontal shading indicates odd-symmetry projected bulk bands. Dashed lines are odd-symmetry surface states and resonances.

The graphs in Fig. 3.8 possess no absolute gaps along $\bar{\Delta}$, but both odd-symmetry majority and minority spins have relative gaps that open around four-fifths of the way to $\bar{X}$. For the majority-spin case (Fig. 3.8(a)), the gap starts 1.45 eV below the Fermi level at $\bar{X}$ and is 0.53 eV wide. The gap for minority spin in Fig. 3.8(b) is 0.79 eV wide and starts 0.84 eV below the Fermi level for Ni(001).

There is a $\bar{\Delta}_2$ surface resonance band near $\bar{\Gamma}$ that is 1.8 eV below E_F (see Fig. 3.8(a)). Otherwise, there are several surface states and surface bands. The most prominent surface state is found two-tenths of the $\bar{\Delta}$ distance. This state lies 0.45 eV below E_F and is of $\bar{\Delta}_2$ character. This resonance band was not identified in any previous theoretical work. Jepsen *et al.* found several low-lying resonance bands near $\bar{X}$ and another one near the Fermi level that stretches through most of $\bar{\Delta}$.⁴⁰

3.4.3 $\bar{Y}$

As seen in Fig. 2.6, the $\bar{Y}$ line traverses from $\bar{X}$ to $\bar{M}$. Of the three lines of symmetry analyzed in this chapter, $\bar{Y}$ is the only one whose projected bulk bands cannot be broken down into even and odd states due to the lack of reflection symmetry along this line. Although the projected bands lack parity, the surface states can still be divided into even and odd states. Because the projected bulk bands lack symmetry,

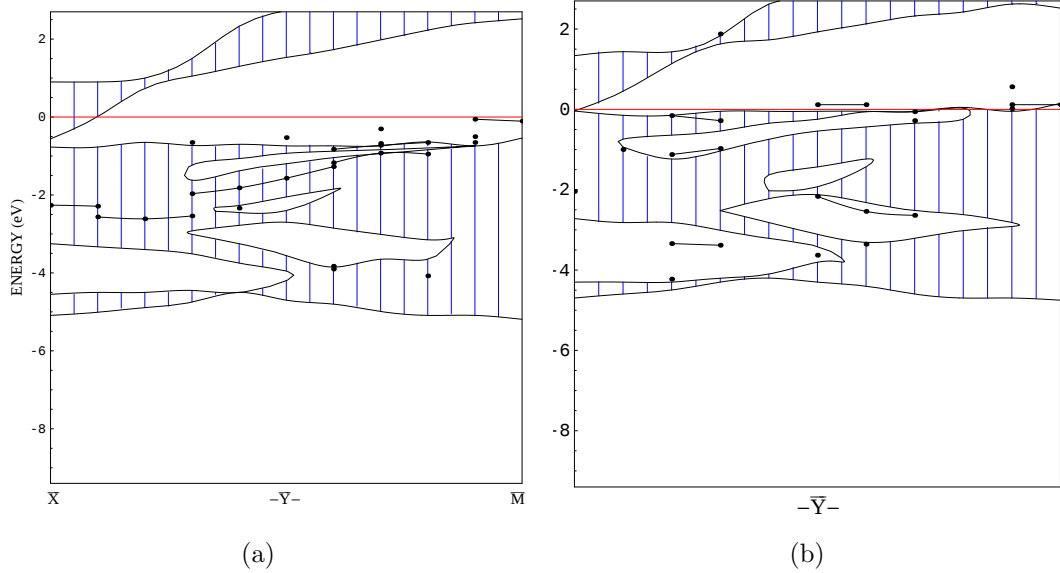


FIG. 3.9. Even-symmetry surface bands, resonances, and bulk band projections for Ni(001) majority and minority spin along $\bar{Y}$. Vertical shading represents projected bulk bands. Solid lines represent even-symmetry surface states and resonances.

all band gaps along $\bar{Y}$ are absolute gaps. Therefore, any states found in these gaps are surface states.

Fig. 3.9(a) shows several surface states and bands along $\bar{Y}$. There are surface states along the edge of the bulk band below the Fermi level across most of $\bar{Y}$. Several of these states are some of the most prominent states found in our results. There is a very short $\bar{Y}_1$ band starting at $\bar{X}$ approximately 2.3 eV below the Fermi level. A band of the same character lies just below where the previous band ends and continues farther along $\bar{Y}$. Wang and Freeman found a band approximately 4 eV below the Fermi level running about halfway along $\bar{Y}$ starting from $\bar{X}$, and another band near the Fermi level for most of $\bar{Y}$.³⁹

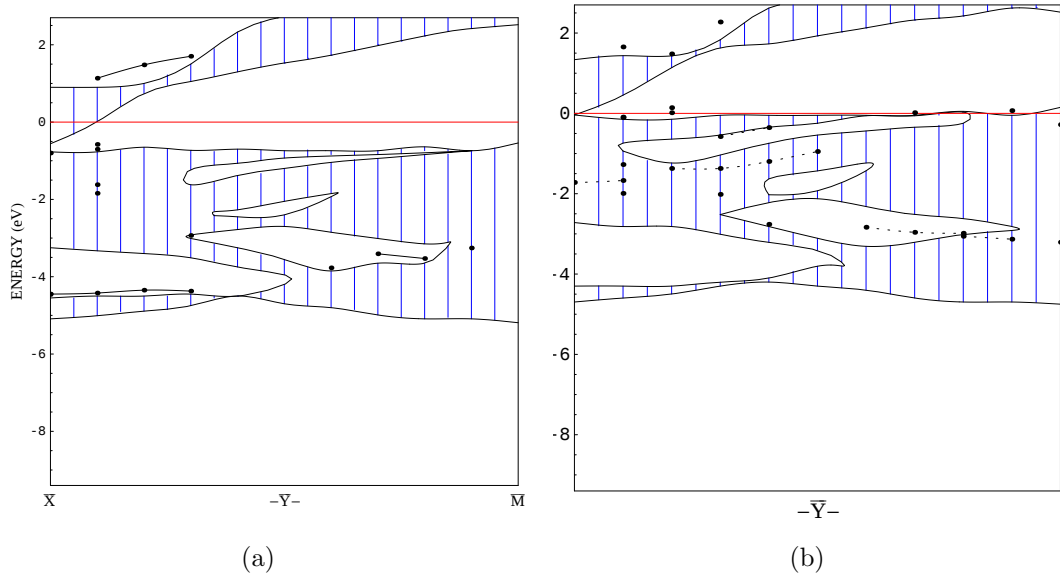


FIG. 3.10. Odd-symmetry surface bands, resonances, and bulk band projections for Ni(001) majority and minority spin along $\bar{Y}$. Vertical shading represents projected bulk bands. Dashed lines represent odd-symmetry surface states and resonances.

For the minority-spin states, Fig. 3.9(b) shows several short surface bands along $\bar{Y}$. Several of these bands are consistent with those found by Wang and Freeman.³⁹

Another study found a surface band near the Fermi level, with the band connecting across $\bar{X}$ to $\bar{\Delta}$, and extending about halfway along $\bar{Y}$.⁴⁰

There are two $\bar{Y}_2$ majority-spin surface bands of interest. The first band starts 4.45 eV below the Fermi level and is of $\bar{X}'_1$ character (Fig. 3.10(a)). The other band starts about 1.13 eV above the Fermi level and rises to 1.7 eV. Both bands have relatively low amplitude. The lower-lying surface band compares well with the band found using the FLAPW method.^{39,40}

There is an odd-symmetry band around 1.7 eV below E_F that is a continuation of a band that originated along $\bar{\Delta}$ (Fig. 3.10(b)). There is a lower-lying band in an absolute gap past the midpoint of the $\bar{Y}$ line that has a relatively low amplitude at the surface. There are also many single surface states and resonances that are not banded together throughout this line. A band was found near this energy by Jepsen *et al.*; however their band dispersed much farther along $\bar{Y}$.⁴⁰ They also found a band that peaked about 1 eV above the Fermi level near $\bar{M}$.⁴⁰ The latter band starts at $\bar{M}$ and continues about thirty percent of the way to $\bar{X}$. It is similar to a band found by Wang and Freeman.³⁹

3.4.4 $\bar{\Sigma}$

$\bar{\Sigma}$ is defined as the line from $\bar{M}$ to $\bar{\Gamma}$ (see Fig. 2.6). The bandstructure plots in Figs. 3.5 and 3.6 show that both spin states have several absolute gaps along this symmetry line. The largest of these for either spin state is the even-symmetry gap that opens at $\bar{\Gamma}$ and continues over half way along $\bar{\Sigma}$. While the even-symmetry energy gap widths at $\bar{\Gamma}$ for both spins are about the same (Fig. 3.11), the absolute gap for majority spin is not as large. This is because the odd-symmetry majority band is about 0.5 eV lower than the same band for minority spin.

A plot of the surface states and resonances along with the projected bulk bandstructure can be found in Fig. 3.11. There are two surface bands of $\bar{\Sigma}_1$ symmetry near

$\bar{M}$ that are close to the Fermi level. The lower of the two skirts along the bottom of the gap and is relatively weak. However, the upper one, which eventually becomes a resonance band and dies out midway along $\bar{\Sigma}$, is very prominent. This is consistent with Plummer and Eberhardt's experimental findings that the more prominent states were located away from $\bar{\Gamma}$. Similar bands were found by Jepsen, *et al.*, but their LAPW study also found several surface bands⁴⁰ dispersing along $\bar{\Sigma}$ that were not found in this SEGF study. Also, a nine-layer FLAPW study obtained a surface band starting around 5 eV below the Fermi level at $\bar{\Gamma}$ and rising by more than 1 eV about halfway along $\bar{\Sigma}$.³⁹ This is similar to a very short band obtained by the spin-polarized SEGF calculation. Similar to the majority-spin state case, a prominent

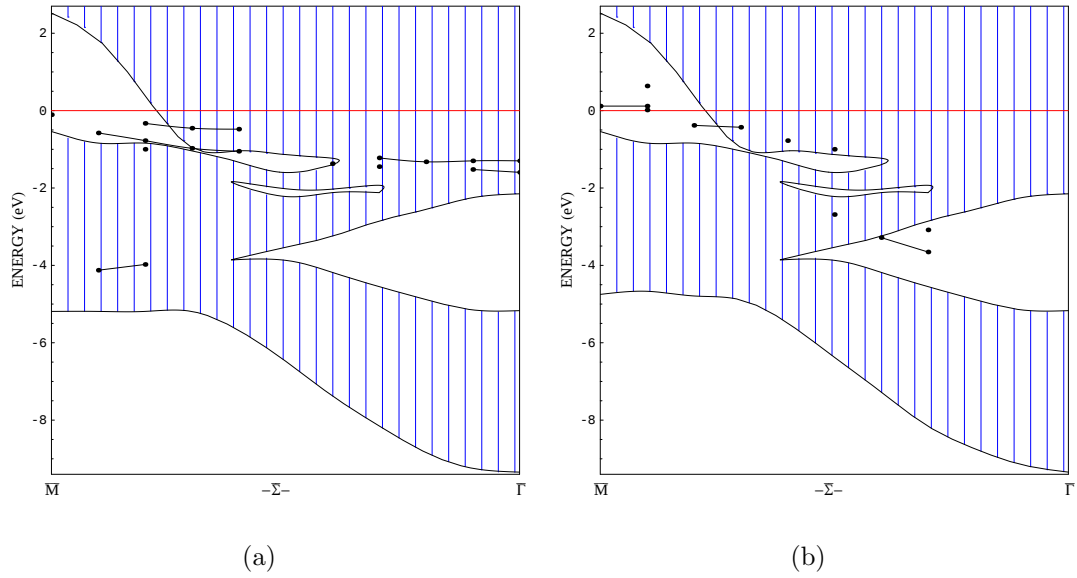


FIG. 3.11. Even-symmetry surface bands, resonances, and bulk band projections for Ni(001) majority and minority spin along $\bar{\Sigma}$. Vertical shading represents even-symmetry projected bulk bands. Solid lines represent even-symmetry surface states and resonances.

surface state band was found 0.55 eV below the Fermi level about one-quarter of the way to $\bar{\Gamma}$ (Fig. 3.11(b)).

There are several weak states that connect across $\bar{M}$ to a $\bar{Y}$ band about 0.1 eV above E_F . Several lone resonances are found throughout $\bar{\Sigma}$. A photoemission experiment conducted by Erskine found a surface band starting at $\bar{\Gamma}$ near the Fermi level that dispersed two-thirds of the way to $\bar{M}$.⁴⁹ The present resonance band near the Fermi level compares well with the experimental band.

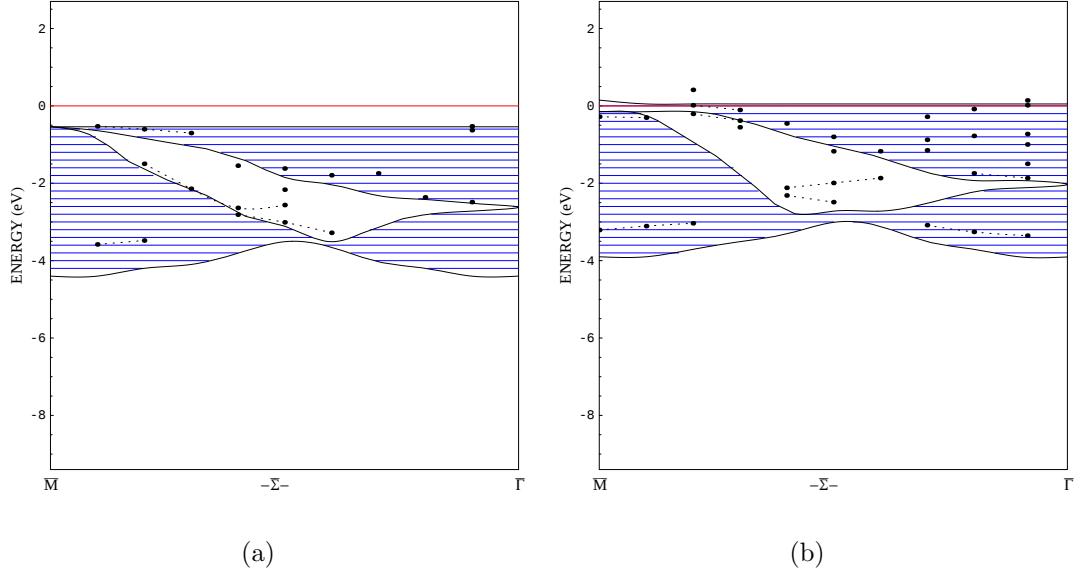


FIG. 3.12. Odd-symmetry surface bands, resonances, and bulk band projections for Ni(001) majority and minority spin along $\bar{\Sigma}$. Horizontal shading indicates odd-symmetry projected bulk bands. Dashed lines are odd-symmetry surface states and resonances.

As for the odd states (Fig. 3.12), the SEGF method obtained two surface bands in the gap along $\bar{\Sigma}$. There are many surface and resonance states along this line, in agreement with earlier calculations. The LAPW study found more states which were classified as surface states/resonances, especially close to $\bar{M}$ —although without the bulk states present, their identification is not certain. In the Wang and Freeman study, a majority-spin surface band was found at $\bar{M}$ near E_F that is similar to the one found with the SEGF method.³⁹ A photoemission experiment found a surface band near the Fermi level starting near the middle of $\bar{\Sigma}$ and continuing to $\bar{\Gamma}$.⁴⁸ The band

was identified as a majority-spin state according to criteria laid out by Plummer and Eberhardt.⁴⁸ The present calculations did not reveal such a band. A minority-spin resonance band was found 3 eV below the Fermi level at $\bar{M}$ that disperses upward by 1.09 eV near the mid-point of $\bar{\Sigma}$. At that point the band breaks away from the underlying bulk bands and projects into the relative gap (Fig. 3.12(b)). Surface states/resonances at this energy were found in an LAPW study,⁴⁰ but the curvature of the band found by the SEGf method is opposite to their results. Another minority-spin resonance band is found near the Fermi level close to $\bar{\Gamma}$. Wang and Freeman's calculation found a band that follows the relative gap along $\bar{\Sigma}$ and mirrors the SEGf calculated odd-symmetry, majority-spin surface band.³⁹

The spin-polarized SEGf calculation for the Ni(001) surface has produced a work function that is in good agreement with experiment. An enhancement of the surface magnetic moment of seven percent was found to be in excellent agreement with experiment. Many of the surface state and resonance bands agreed with the locations found by experimental means. Because the SEGf method treats the semi-infinite problem correctly, fewer layers were needed when compared with slab methods to compute the electronic properties of the (001) surface of ferromagnetic nickel.

CHAPTER FOUR

The Surface Magnetism of Co(001)

4.1 Computational Details

The crystal structure of naturally occurring cobalt is hexagonal close-packed, but when heated to around 750°C, a phase transition occurs that alters the crystal structure to fcc. Under the right conditions, the fcc structure remains intact when cooled. The fcc crystal structure was chosen for this study due to the availability of tabulated values which allowed for the generation of an embedding potential.

The electronic structure of Co(001) was computed using the spin-polarized SEGF method. The embedding potential was constructed from tabulated values for bulk ferromagnetic cobalt.³⁶ Lattice vectors describing the Co(001) surface were rotated by 45° so the smallest unit cell could be chosen. The rotated lattice vectors and muffin-tin radius are 4.62 a.u. and 2.31 a.u., respectively.

Choosing a surface slab with too many layers wastes computational resources for an SEGF calculation because the extra layers provide less information than the embedding potential. A slab that is too thin fails to provide an adequate physical description of the surface environment. Paramagnetic SEGF studies have found that one- or two-layer slabs are usually thick enough for results that compare favorably with experiment. One or two layers are likely to be inadequate for spin-polarized Co(001) because previous calculations have found that spin densities are not restored to bulk values by the third interior layer. Therefore, a three-layer embedded slab was chosen to model the Co(001) surface.

A total of 180 LAPWs were used for the expansion of the surface Green function. The charge density and potential expansions in the interstitial region employed 2000 plane waves. To sample the irreducible portion of the surface Brillouin Zone,

36 special $\mathbf{k}$ -points were employed. For the exchange-correlation potential, the von Barth-Hedin parametrization³⁷ was used. In the MT region, radial functions and energy-derivative functions were expanded with angular momenta up to $l = 12$. The core electrons were calculated fully relativistically and the valence electrons scalar-relativistically. Convergence was considered achieved when the input and output potentials differed by less than 0.1 eV.

4.2 Work Function

The work function was previously described in Section 2.9. Calculated work functions are often viewed as a measure of a calculation's accuracy, because the work function is specific to the particular material and the electronic configuration at the surface. For the self consistent spin-polarized SEGF calculation, a work function of 5.48 ± 0.02 eV resulted for the (001) face of cobalt as compared with an experimental value of 5.0 eV.⁵⁰ Other studies^{33,51} have calculated work function values ranging from 5.05 eV to 5.52 eV.

4.3 Charge and Spin Density

As stated in Section 4.1, cobalt in an fcc crystalline form is not naturally occurring and not easily manufactured. This is the main reason there are very few electronic structure studies of this surface. Nonetheless, there are many theoretical treatments that compute the work function and spin densities without providing details of the bandstructure at the surface. These studies have all found an enhanced magnetic moment for Co(001) at its surface.

Using the values obtained from the converged SEGF calculation, a magnetic moment of $1.81 \mu_B$ resulted. This represents an eleven percent surface enhancement over the accepted bulk value of $1.64 \mu_B$. As seen in Table 4.1, the spin density at the surface is in agreement with those computed using slab and Green function methods.

Table 4.1. Co(001) magnetic moments for the surface (S), subsurface ($S - 1$), and ($S - 2$) sub-subsurface layers and work function.

Calculation Method	S	$S - 1$	$S - 2$	Work Function (eV)
Three layer SEGF	1.81	1.52	1.74	5.48
Five-layer FLAPW ⁵¹	1.85	1.65	1.66	5.05
Nine-layer FLAPW ⁵¹	1.86	1.64	1.65	5.17
Four-layer TB-LMTO ³³	1.84	1.63	1.66	5.52
Nine-layer TB-LMTO ⁴⁷	1.76	1.46	1.58	

Other theoretical studies have found a surface enhancement over the bulk moment ranging from seven to thirteen percent,^{33,51} while a nine-layer tight-binding linearized muffin-tin orbitals method (TB-LMTO) found an enhancement of seven percent⁴⁷ as compared with the accepted bulk value. All of the referenced studies exhibit some Friedel oscillation in the magnetic moments near the surface. Table 4.1 clearly shows that the spin-polarized SEGF results are in excellent agreement with the other cited surface magnetic moment calculations.

Table 4.2. Surface, subsurface, and sub-subsurface layer valence charge for Co(001).

Calculation Method	S	$S - 1$	$S - 2$
Three layer SEGF	8.01	8.27	8.18
Five-layer FLAPW ⁵¹	8.05	8.27	8.27
Nine-layer FLAPW ⁵¹	8.04	8.27	8.27
Four-layer TB-LMTOprotect ³³	8.66	9.01	9.00
Nine-layer TB-LMTO ⁴⁷	8.66	9.14	9.00

As stated in the previous chapter, except at the surface, the total valence charge within a layer is expected to be the same even though the magnetic moments might differ. The spin-polarized SEGF method calculated the valence charge to be 8.27 electrons per MT for the subsurface layer and 8.18 electrons MT for the sub-subsurface layer respectively (see Table 4.2). The SEGF computed values for the valence charge

in the surface and subsurface layers are very close to those obtained in the five-layer and nine-layer FLAPW calculations.⁵¹ However, the total muffin-tin charge found in the sub-subsurface layer is somewhat lower than that obtained in the FLAPW studies. A further comparison with the FLAPW results for the layered charge broken into spin components shows that the FLAPW results had relatively constant values (4.96 for majority spin and 3.31 for minority spin) from the subsurface layer inward.⁵¹ The SEGF results do not follow this pattern and neither does the TB-LMTO study.⁴⁷

A possible explanation for the apparent charge shift could be the embedding potential, which is constructed from pretabulated values. If the underlying bulk bands are not accurate, the minority-spin bulk bands could be wider or have a greater percentage below the Fermi level. This would allow more minority-spin electrons to populate and would reduce the magnetic moment at the embedding layer. Electron screening will reduce this error away from the embedding surface. It is likely that an excess of minority-spin charge in the subsurface layer has influenced the positioning of surface states and the surface charge distribution; thus, affecting the calculated work function. Further investigation is warranted.

4.4 *Electronic Structure*

4.4.1 *Surface States and Resonances*

Section 3.4.1 describes the origin of surface states and surface resonances. Once the SEGF charge density has converged, it may be used to analyze the electronic structure of the surface.

The Co(001) local densities of states along the lines of symmetry (Fig. 2.5) were computed and plotted. Each plotted peak corresponds to a state with high amplitude in the top few surface layers. Deciding how to classify the plotted surface state/resonance peaks has been discussed previously (see Section 3.4.1.2). Peaks in the LDOS that are in absolute or relative gaps are surface states by definition. Surface reso-

nances which are strongly peaked states in the projected bulk bands are harder to classify. Charge density plots have been used to determine the parity of each state. These criteria resulted in the surface states and resonances plotted in Figs. 4.1 and 4.2.

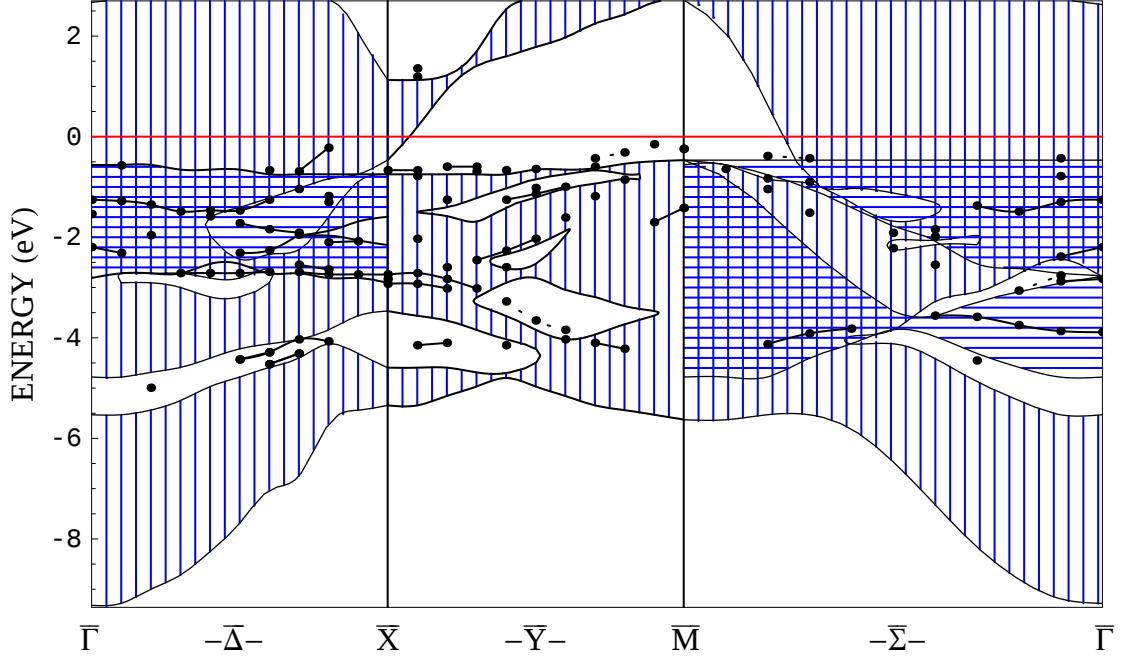


FIG. 4.1. Majority-spin bandstructure for Co(001) that includes surface states and resonances along the two-dimensional lines of high symmetry. Vertical shading represents even-symmetry projected bulk bands while the horizontal shading indicates odd-symmetry bulk bands. Solid lines represent even-symmetry and dashed lines are odd-symmetry surface states and resonances.

4.4.2 $\bar{\Delta}$

Beginning with the $\bar{\Delta}$ line, which runs from $\bar{\Gamma}$ to $\bar{X}$ (Fig. 2.6), eleven evenly spaced points were used to analyze the surface electronic structure. Bulk band states were projected onto the two dimensional surface with vertical shading representing even-

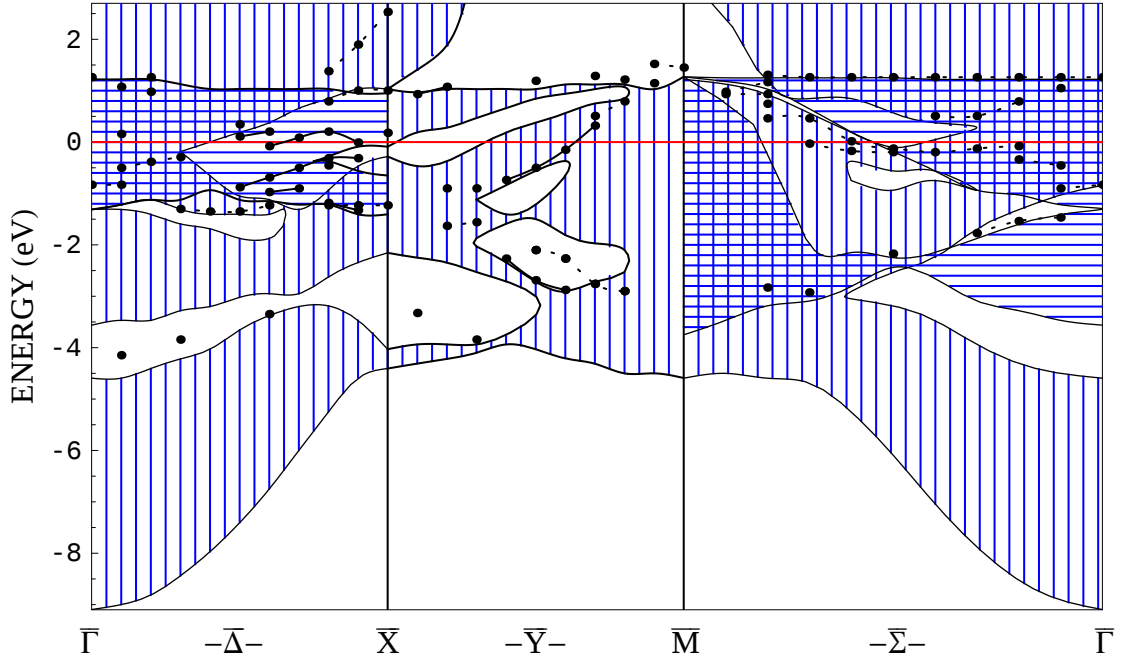


FIG. 4.2. Minority-spin bandstructure for Co(001) that includes surface states and resonances along the two-dimensional lines of high symmetry. Vertical shading represents even-symmetry projected bulk bands while the horizontal shading indicates odd-symmetry bulk bands. Solid lines represent even-symmetry and dashed lines are odd-symmetry surface states and resonances.

symmetry bulk bands, while odd-symmetry bulk bands are indicated by horizontal shading (*e.g.*, Fig. 4.1). Graphs of this type are seen throughout this section. Individual surface states and resonances were plotted as points, and surface bands are indicated by lines that connect surface states sampled along the $\bar{\Delta}$ line.

These graphical representations are used to compare other theoretical studies and, more importantly, experimental results that may provide researchers with other avenues of inquiry. By comparing the theoretical with the experimental results, a model's accuracy may be evaluated. Also, any discrepancies between the model and reality should result in further investigation of possible physics or computational error

that may be in the model. It is also possible upon further analysis to find that the experiment erred in some way.

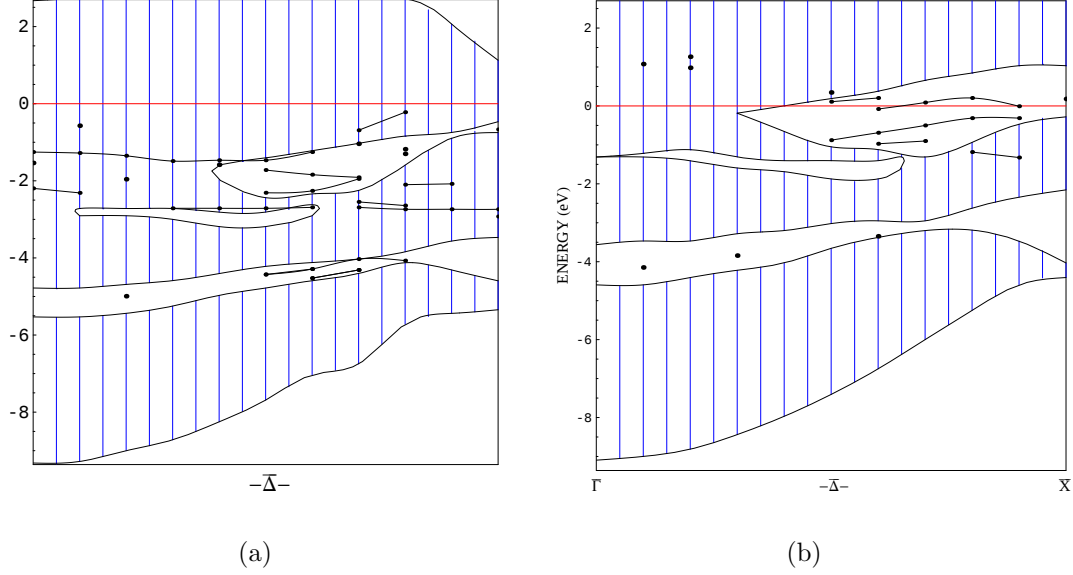


FIG. 4.3. Even-symmetry surface bands, resonances, and bulk band projections for Co(001) majority and minority spin along $\bar{\Delta}$. Vertical shading represents even-symmetry projected bulk bands. Solid lines represent even-symmetry surface states and resonances.

Beginning with the even-symmetry states along the $\bar{\Delta}$ line, there is an absolute gap that runs across all of the $\bar{\Delta}$ line. For the majority-spin case, this gap is located at $E_F - 5.16 \pm 0.38$ eV, as seen in Fig. 4.3(a), while the minority-spin gap, Fig. 4.3(b) is located at $E_F - 4.87 \pm 0.52$ eV. For both spin states, the gaps then rise in energy along the whole $\bar{\Delta}$ line. In both cases, the gaps begin to pinch off near $\bar{X}$, but then widen into a larger gap at $\bar{X}$ than at $\bar{\Gamma}$.

For majority spin, there are a few surface state bands within this absolute gap near the central portion of the $\bar{\Delta}$ line as seen in Fig. 4.3(a). At $\bar{\Gamma}$, there are two resonance bands at 2.2 eV and 1.25 eV below the Fermi level. The one closer to E_F extends over halfway along $\bar{\Delta}$ and is relatively flat. At $\bar{X}$, there is a resonance band 2.76 eV below E_F which is similar to a FLAPW-predicted resonance band near

3 eV below E_F .⁵¹ For the FLAPW study, these resonance band states were the only concentration of majority-spin states along the $\bar{\Delta}$ line. Also of interest, is that the bulk energy levels included through the embedding potential are shifted about 1 eV downward compared with the FLAPW lowest plotted electron energy states.

For the minority-spin case, as seen in Fig. 4.3(b), the surface states and resonances are mainly located near E_F in the relative gap and span from $\bar{X}$ halfway back to $\bar{\Gamma}$. This is very similar to the two bands identified in the FLAPW study.⁵¹ Otherwise, the SEGF method mainly found a few prominent surface states near $\bar{\Gamma}$.

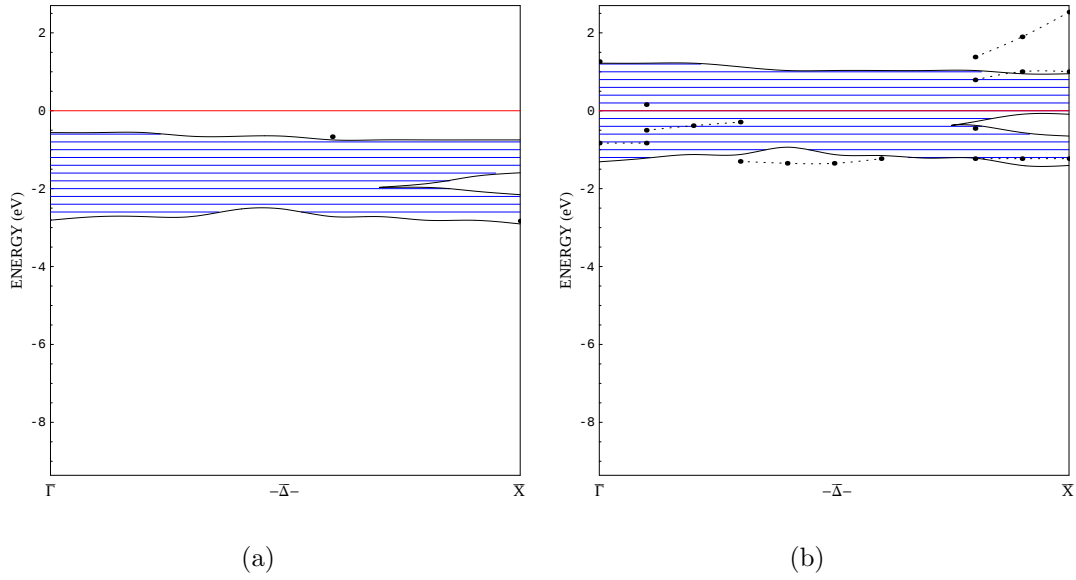


FIG. 4.4. Odd-symmetry surface bands, resonances, and bulk band projections for Co(001) majority and minority spin along $\bar{\Delta}$. Horizontal shading indicates odd-symmetry projected bulk bands. Dashed lines are odd-symmetry surface states and resonances.

For the odd-symmetry case, only a single majority state was found according to the surface state/resonance criteria (Fig. 4.4(a)). This finding is similar to the FLAPW study, which did not identify any surface states or resonances along $\bar{\Delta}$. For the minority-spin case (Fig. 4.4(b)), several surface resonances were found, with the most prominent one stretching from $\bar{X}$ more than half the distance to $\bar{\Gamma}$ along the bottom

of the projected bandstructure. There are also bands located from 0.5 eV to 0.9 eV below E_F at or near $\bar{\Gamma}$ that disperse less than halfway along $\bar{\Delta}$ before dying out. At $\bar{X}$, there are two bands located above E_F . The FLAPW study found a single, short resonance band located less than 1 eV above E_F .

4.4.3 $\bar{Y}$

As seen in Fig. 2.6, the $\bar{Y}$ line traverses from $\bar{X}$ to $\bar{M}$. Of the three lines of symmetry analyzed, $\bar{Y}$ is the only one whose projected bulk bands cannot be broken down into even and odd states due to the lack of reflection symmetry in the 3D Brillouin Zone along this line. Although the projected bulk bands have mixed symmetry, the $\bar{Y}$ line is a reflection line for the 2D reciprocal lattice; thus, the surface states can be divided into even and odd states according to their symmetry. The even-symmetry surface bands, surface states, and surface resonances are shown in Fig. 4.5.

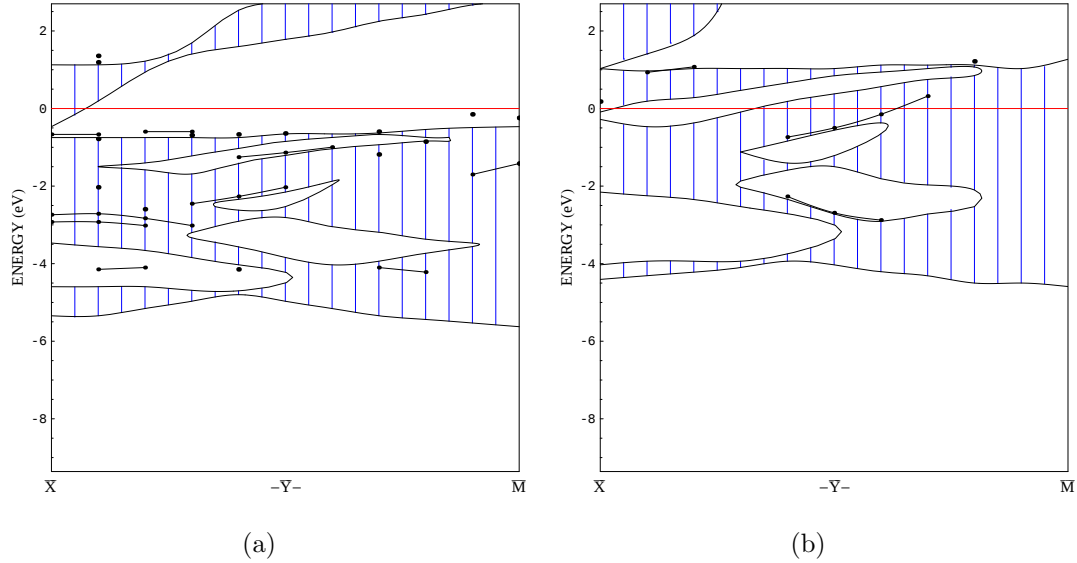


FIG. 4.5. Even-symmetry surface bands, resonances, and bulk band projections for Co(001) majority and minority spin along $\bar{Y}$. Vertical shading represents projected bulk bands. Solid lines represent even-symmetry surface states and resonances.

Beginning with the majority-spin even states along $\bar{Y}$ (see Fig. 4.5(a)), there are two resonance bands starting at $\bar{X}$ that are 2.93 and 2.76 eV below E_F . The lowest-lying band has a larger amplitude in the LDOS. One-tenth of the way from $\bar{X}$ to $\bar{Y}$ is a very prominent surface state that is 0.69 eV below E_F . At the bottom of the absolute gap that is positioned nearest to E_F in Fig. 4.5(a) there are many surface states that extend along $\bar{Y}$ up to three-fifths of the way to $\bar{M}$. In an FLAPW study, Li *et al.* found an extended band near $\bar{M}$ located approximately 2 eV below the Fermi level.⁵¹ This even-symmetry majority-spin band is similarly placed as the short resonance band we find 1.42 eV below E_F .

In contrast, the even-symmetry, minority-spin plot (Fig. 4.5(b)) contains only a few surface states and resonances. There is a low-lying surface band in an absolute gap in the middle of $\bar{Y}$ and a resonance band near E_F . The latter band is somewhat similar to a band in the FLAPW study,⁵¹ although that band was slightly closer to $\bar{M}$.

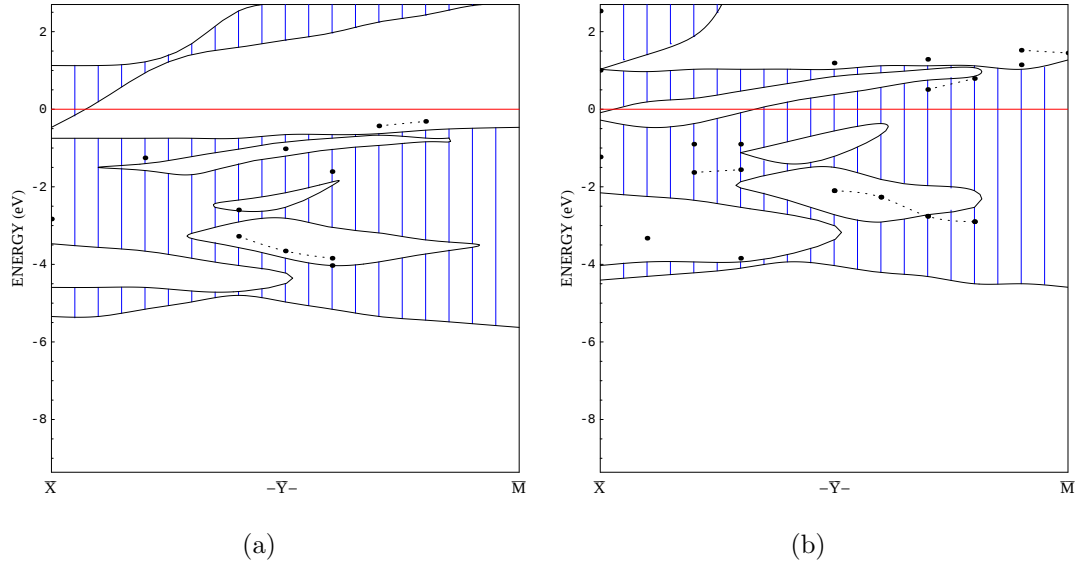


FIG. 4.6. Odd-symmetry surface bands, resonances, and bulk band projections for Co(001) majority and minority spin along $\bar{Y}$. Vertical shading represents projected bulk bands. Dashed lines represent odd-symmetry surface states and resonances.

As for the odd-symmetry surface states along $\bar{Y}$ (see Fig. 4.6(a) and Fig. 4.6(b)), both spin states have a single resonance state below the Fermi level at 2.83 eV and 1.23 eV, respectively. No majority-spin surface states or resonances appear at $\bar{M}$, while a single minority-spin surface state above E_F is observed there. Both spin types have a few resonance and surface bands along $\bar{Y}$. This contrasts with the FLAPW results where short bands were found at $\bar{M}$ for both spin states. For majority spin, the band near $\bar{M}$ was below E_F , but was above for the minority-spin case. The minority surface state/resonance band near the center of $\bar{Y}$ is very similar to one found in the FLAPW paper.⁵¹

4.4.4 $\bar{\Sigma}$

Fig. 2.6 describes the $\bar{\Sigma}$ line between $\bar{\Gamma}$ and $\bar{M}$. $\bar{\Sigma}$ is a factor of $\sqrt{2}$ longer than the others because it is along the diagonal of the square Brillouin Zone. While there

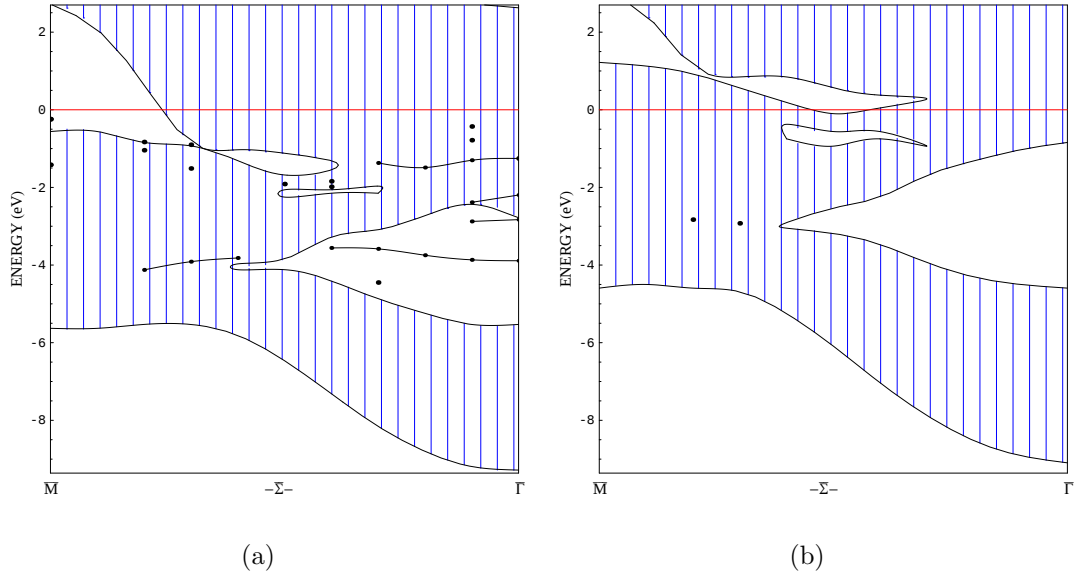


FIG. 4.7. Even-symmetry surface bands, resonances, and bulk band projections for Co(001) majority and minority spin along $\bar{\Sigma}$. Vertical shading represents even-symmetry projected bulk bands. Solid lines represent even-symmetry surface states and resonances.

is an absolute gap for both spin states along $\bar{\Sigma}$, the even bands possess larger gaps that are partially overlapped by odd-symmetry bands as seen in Figs. 4.1 and 4.2. Based on the criterion for choosing surface states, the SEGF method yielded the states plotted in Fig. 4.7(a) for even-symmetry majority-spin states and Fig. 4.7(b) for minority-spin states. There are a number of even-symmetry majority-spin surface states and resonance bands along $\bar{\Sigma}$. Many of these bands exist below E_F , starting at $\bar{\Gamma}$ and dispersing toward $\bar{M}$. The lowest-lying band at $\bar{\Gamma}$ is not very pronounced, having a minor LDOS peak. Nonetheless, it is included in the graph because it lies in a band gap, and is thus a surface state band by definition. This contrasts with the FLAPW study which found a greater concentration of surface bands and resonances below the Fermi level at $\bar{M}$, but nothing at $\bar{\Gamma}$.⁵¹ With the minority-spin states, only two resonance states are found throughout the $\bar{\Sigma}$ line. The previously-cited FLAPW study did find surface states and resonances near both ends of the $\bar{\Sigma}$ line.

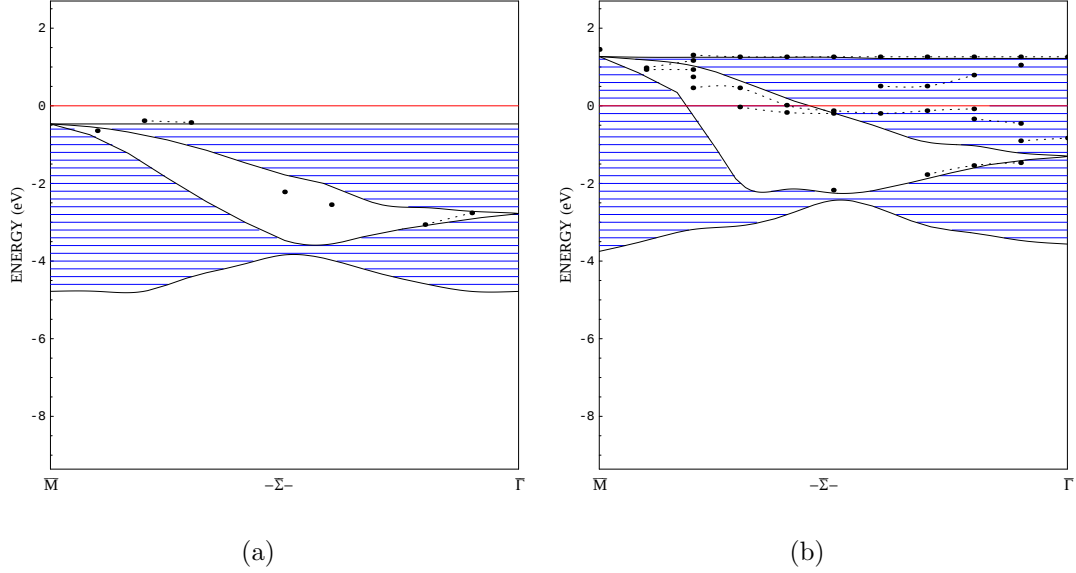


FIG. 4.8. Odd-symmetry surface bands, resonances, and bulk band projections for Co(001) majority and minority spin along $\bar{\Sigma}$. Horizontal shading indicates odd-symmetry projected bulk bands. Dashed lines are odd-symmetry surface states and resonances.

For the odd-symmetry states, there are few majority-spin surface states and resonances (Fig. 4.8(a)), and no surface states or resonances at either $\bar{\Gamma}$ or $\bar{M}$. This contrasts with the FLAPW results in which there are two bands that are below E_F dispersing downward along $\bar{\Sigma}$.⁵¹ Similar results can be seen in the FLAPW minority-spin results.⁵¹ No similar bands are observed in the present study (see Fig. 4.8(b)). There are several resonance and surface state bands near and above E_F between $\bar{M}$ and $\bar{\Gamma}$. There is also a weak surface band slightly above the highest projected bulk band starting at $\bar{\Gamma}$ and traversing most of $\bar{\Sigma}$.

Unfortunately, there are not many theoretical electronic structure studies of this surface with which to compare. While the exact locations of the surface states and resonances did not always agree with the FLAPW calculation by Li *et al.*, there was general agreement regarding the concentration of these states. Both studies found a greater concentration of even-symmetry states for majority spin. Odd-symmetry minority-spin states have their greatest concentration along $\bar{\Sigma}$ for both calculations. Finally, Li *et al.* argue that the novel surface properties of Co(001) are due to the concentration of minority-spin surface states near E_F as compared with the lower-lying majority-spin states.⁵¹ The present spin-polarized SEGF results are in substantial agreement regarding this observation.

CHAPTER FIVE

The Surface Magnetism of Fe(001)

5.1 Computational Details

Of the three surfaces studied, iron is the only one in a body-centered-cubic (bcc) configuration. As seen in Fig. 5.1, the bcc(001) surface is more open compared with the (001) surface of an fcc crystal. The bcc surface atoms, such as Fe(001), have fewer nearest neighbors than atoms on fcc(001) surfaces such as Ni(001) and Co(001). The bcc(001) geometry is thought to enhance the surface magnetic moment in iron by thirty percent⁵² over the bulk value of $2.216 \mu_B$.⁵³

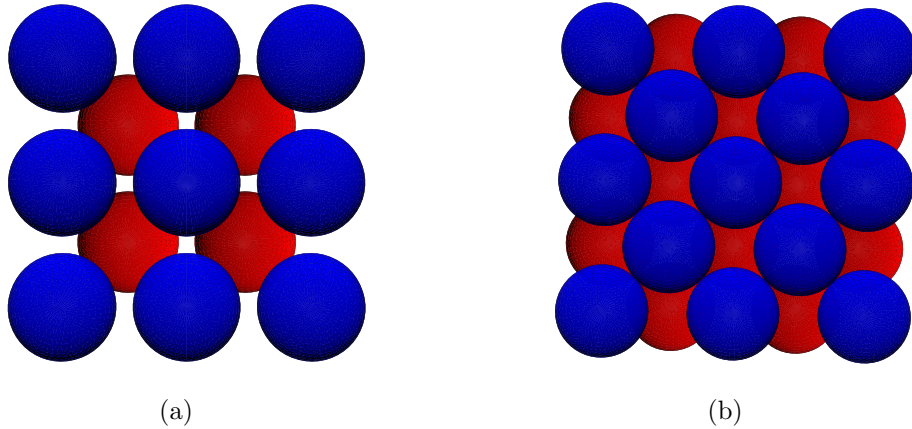


FIG. 5.1. Comparison between the openness of the bcc and fcc 001 crystal faces.

To determine how many atomic layers were needed to accurately model the surface, other studies were examined. Several theoretical treatments^{31–34} have found that the magnetic moment for Fe heals to its bulk value by the fourth layer. Because of this, a three-layer slab embedded onto bulk iron was used for this study.

The bulk muffin-tin potentials of Moruzzi, Janak, and Williams³⁶ were used to calculate the Fe(001) embedding potential for both spin states. A lattice spacing of

5.27 a.u. and a muffin-tin radius of 2.282 a.u. were used. Each of the (001) atomic layers forms a square lattice. The unit cell thickness was 9.834 a.u. The irreducible portion of the surface Brillouin Zone was discretized using 36 special $\mathbf{k}$ -points.

The vacuum region was defined from the top of the surface layer muffin-tin sphere and extended away from the surface in a linear grid of 100 points that were spaced 0.1 a.u. apart. The vacuum layer was chosen to be of sufficient thickness that the charge density was negligible farther away from the slab.

Wavefunctions were expanded using 180 LAPWs. The von Barth-Hedin³⁷ parametrization for exchange and correlation was used. Lastly, self consistency was defined when the maximum difference between the input and output potential at geometric boundaries was less than 0.1 eV.

5.2 Work Function

Because the work function is a general indicator of the quality of the calculation, it is one of the first physical properties extracted and compared with other results. For Fe(001), our spin-polarized SEGF calculated work function was 4.70 ± 0.14 eV. This compares favorably with the experimental value of 4.5 eV.⁵⁴ Using a seven-layer slab and the same von Barth-Hedin parametrization for the exchange-correlation potential, Ohnishi *et al.*³¹ obtained a calculated work function of 4.29 eV using a seven-layer slab (see Table 5.1). A tight-binding, linearized muffin-tin orbital slab calculation (TB-LMTO) by Aldén *et al.*³³ resulted in a calculated work function in agreement with experiment.

An earlier master's thesis presented the results of a spin-polarized SEGF calculation for a single-layer slab of Fe(001).¹⁶ For the single-layer slab, the work function was calculated to be 5.18 eV. By using a three-layer slab and by extending the core charge (see Appendix A), a significant improvement for the work function was obtained. By improving the treatment of the semi-infinite problem, quantities like the

work function can be computed using a thinner embedded slab than in slab-only calculations. As a result, fewer computer resources are used and the system is able to iterate toward a self-consistent solution more quickly.

5.3 Spin Density

For the three-layer SEGF calculation, a net spin moment of $2.65 \mu_B$ was found for the surface layer, which represents a twenty percent increase over the experimental bulk value $2.216 \mu_B$.⁵³ A comparison of the spin moments and work functions for various calculations is provided in Table 5.1. The trend for the majority of the results is the absence of Friedel-like oscillations in the magnetic moment from layer to layer. However, a more recent calculation by Chakraborty *et al.*⁴⁷ does reveal a small oscillation that is more consistent with the SEGF results.

The SEGF calculated values for the magnetic moments for the subsurface and sub-surface layer are puzzling because the computed values for the work function and surface magnetic moment are in good agreement with experiment. The results from nickel and cobalt agree well with experiment and with other computational methods. It is not known why the layer adjacent to the embedding surface is paramagnetic while the surface layer is ferromagnetic. It is worth noting that none of the studies referenced in Table 5.1 have calculated values for the bulk magnetic moment that are in agreement with the experimental value of $2.216 \mu_B$.⁵³

Table 5.1. Fe(001) magnetic moments for the surface (S), subsurface ($S - 1$), and ($S - 2$) sub-surface layers and work function.

Calculation Method	S	$S - 1$	$S - 2$	Work Function (eV)
Three-layer SEGF	2.65	1.86	0.05	4.70
Single-layer SEGF	2.62			5.18
Seven-layer FLAPW ³¹	2.98	2.35	2.39	4.29
Five-layer TB-LMTO ³³	2.97	2.30	2.37	4.50
Seven-layer LMTO ³²	2.87	2.34	2.33	4.30
Nine-layer TB-LMTO ⁴⁷	2.95	2.2	2.39	

In order to explain for the low spin density in the layer adjacent to the embedding surface, the valence charge was analyzed for the three top surface layers and compared with other theoretical results. Since the SEGF method does not require charge neutrality, the valence charge analysis may shed light on the current issue because the valence charge determines the magnetic moments.

The converged spin-polarized SEGF results show that, at the surface, a valence charge of 6.74 electrons for the surface MT. The SEGF value compares well to the 6.78 electrons calculated using a seven-layer FLAPW method.³¹ A more recent nine-layer TB-LMTO⁴⁷ study computed a surface layer charge of 7.50 electrons per unit cell, with 6.51 electrons attributed to d electron states.

In the layer adjacent to the embedding surface, the results are somewhat different. The sub-surface layer has 6.97 electrons per MT as computed with the SEGF method. This compares favorably with the 7.05 electrons calculated using a seven-layer FLAPW slab;³¹ however, a TB-LMTO calculation obtained 8.01 electrons. Thus, the paramagnetic SEGF result at the sub-surface layer of Fe(001) is not due to a deficit in the number of valence electrons. It may point to a flaw in converging the embedding potential for such an open surface.

5.4 Surface Electronic Structure

5.4.1 Surface States and Resonances

Surface states and resonances were plotted along the lines of high symmetry over the surface Brillouin Zone for both majority and minority spin. Fig. 2.5 shows the bulk energy bands along the lines of high symmetry that were projected onto the two-dimensional Brillouin Zone. The composite graphs can be seen in Figs. 5.2 and 5.3. For each surface state in an absolute or relative band gap, the charge density profile was plotted and the symmetry was determined by consulting the appropriate character table. The same analysis was performed for surface resonance states. Each

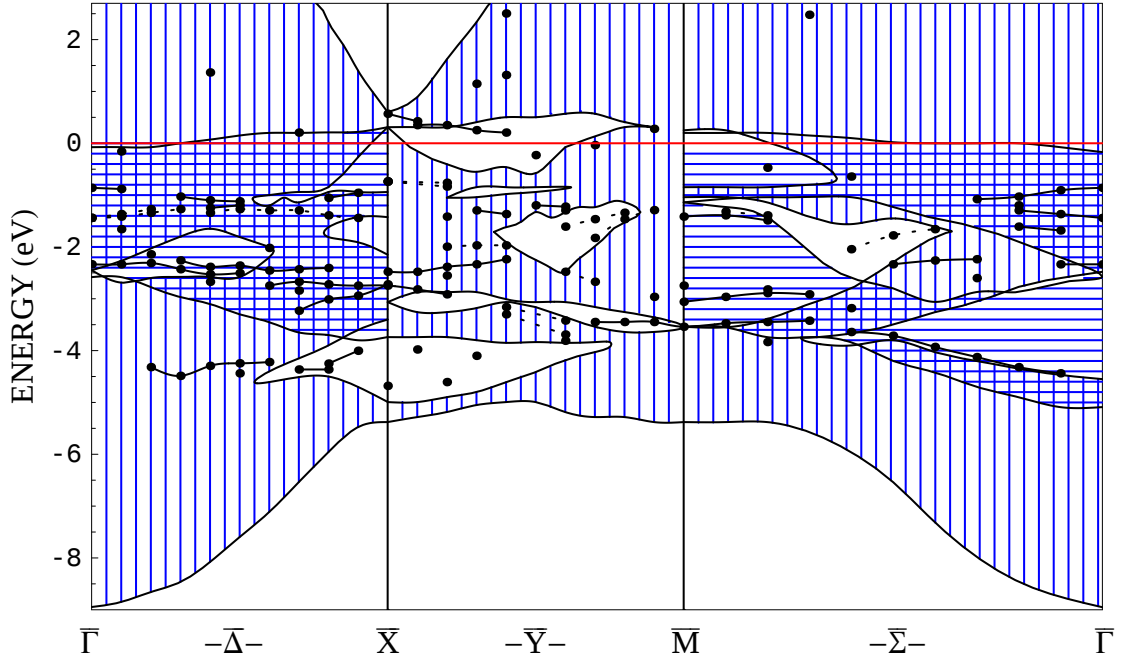


FIG. 5.2. Majority-spin bandstructure for Fe(001) that includes surface states and resonances along the two-dimensional lines of high symmetry. Vertical shading represents even-symmetry projected bulk bands while the horizontal shading indicates odd-symmetry bulk bands. Solid lines represent even-symmetry and dashed lines are odd-symmetry surface states and resonances.

line was divided into ten evenly spaced intervals using eleven $\mathbf{k}$ -points. At each of these $\mathbf{k}$ -points, the LDOS was calculated in order to locate surface states and resonances. Analysis of the spin-polarized SEGF results for Fe(001) along each line of high symmetry are presented in the following subsections.

5.4.2 $\bar{\Delta}$

Fig. 5.4 shows the projected bandstructure and surface states of even symmetry along $\bar{\Delta}$ for both majority- and minority-spin states. At $\bar{X}$, both spin states have two even-symmetry gaps. The lowest energy majority gap is centered at $E_F - 4.37$ eV and is 1.25 eV wide, while the second gap is centered at $E_F - 0.315$ eV and is 0.625 eV wide.

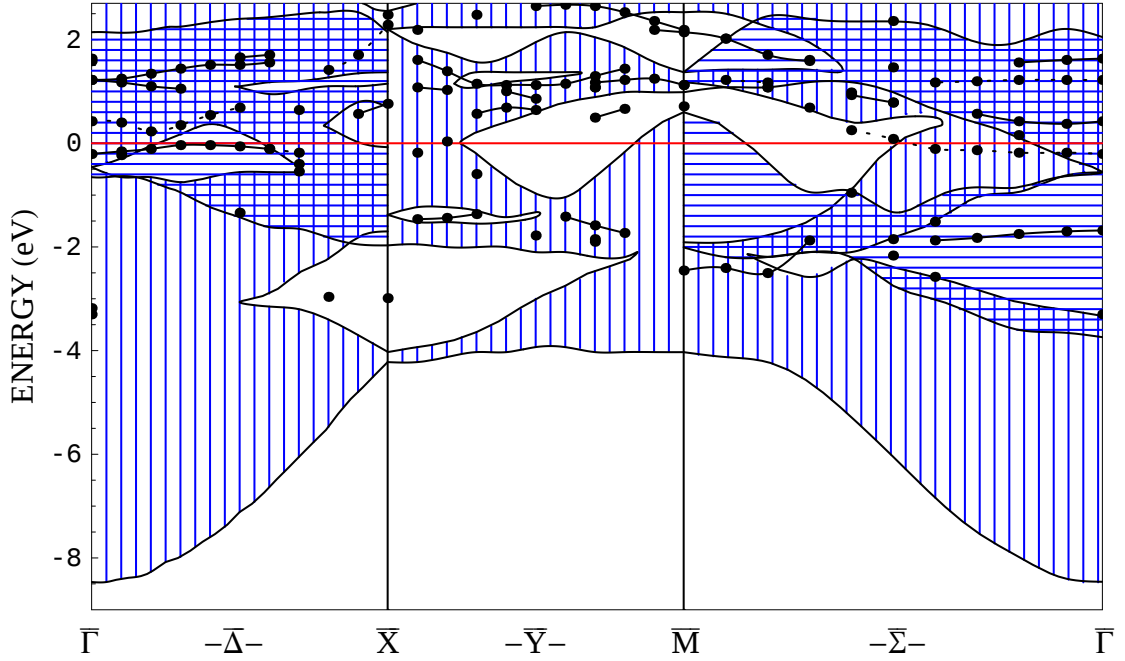


FIG. 5.3. Minority-spin bandstructure for Fe(001) that includes surface states and resonances along the two-dimensional lines of high symmetry. Vertical shading represents even-symmetry projected bulk bands while the horizontal shading indicates odd-symmetry bulk bands. Solid lines represent even-symmetry and dashed lines are odd-symmetry surface states and resonances.

The projected bulk bands are in excellent agreement with other calculations^{31,35,55,56} in regards to their shape and placement of band gaps along $\bar{\Delta}$.

For majority spin (Fig. 5.4(a)) at $\bar{\Gamma}$, two surface resonances are present. There is a $\bar{\Gamma}_1$ surface state band predicted at 2.3 eV below E_F that disperses into the relative gap and is present until the gap closes about halfway along $\bar{\Delta}$. This state is very close to a $\bar{\Gamma}$ state found in photoemission studies about 2.2 eV below E_F .³⁵ A seven-layer FLAPW calculation³¹ also identified an even-symmetry, majority-spin surface resonance near the calculated band. In their photoemission experiment, Turner and Erskine³⁵ found an Fe(001) surface resonance at $\bar{\Gamma}$ that was 3.2 eV below E_F . This state has not been identified in either the present SEGF calculation or any other

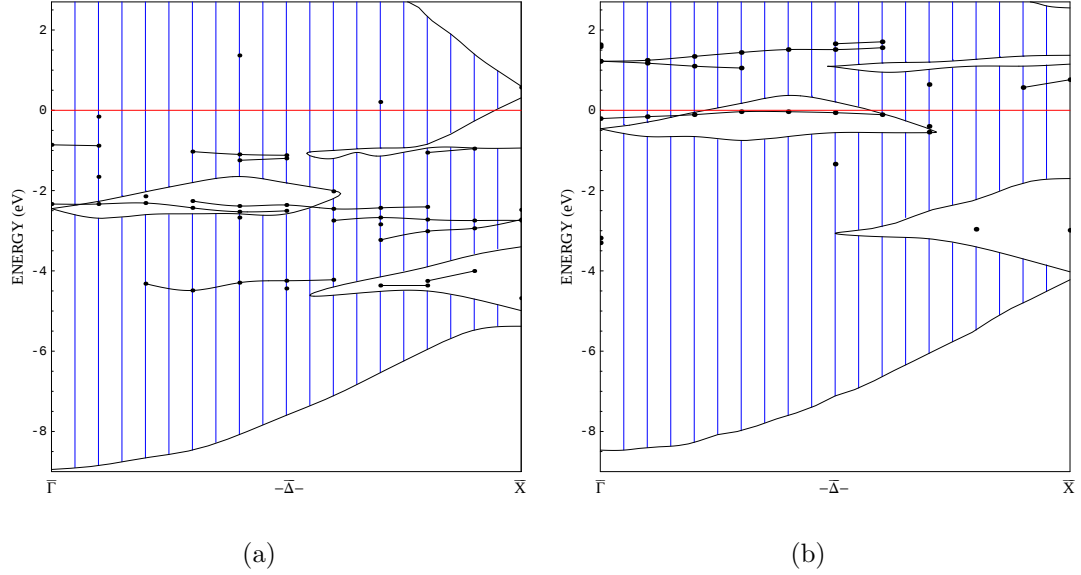


FIG. 5.4. Even-symmetry surface bands, resonances, and bulk band projections for Fe(001) majority and minority spin along $\bar{\Delta}$. Vertical shading represents even-symmetry projected bulk bands. Solid lines represent even-symmetry surface states and resonances.

theoretical treatment.^{31,55} Both Wang and Freeman⁵⁵ and Ohnishi *et al.*³¹ identified a surface resonance between 4 eV and 4.5 eV below E_F that is not seen in the present results. The spin-polarized SEGf method found a peak in the LDOS at nearly the same energy as the one found using slab methods; however, the peak amplitude of this state was not strong enough for a positive identification to be made. Slab methods usually identify surface states based on how much charge a particular state has near the surface of the slab. The layer-by-layer charge contribution is usually added and then a cutoff percentage is chosen to identify states as being surface states or resonances. There is really no true determination of a surface state by this method because of the absence of the bulk states and band gaps.

At $\bar{X}$, a majority-spin surface state was found at 4.7 eV below E_F near the bottom of an absolute gap. This surface state is very similar to a surface state observed in photoemission experiments.³⁵ Slab calculations have also identified a surface state that is positioned similarly to our results.^{31,55} Slightly higher in energy at 2.75 and

2.5 eV below E_F , two surface resonance states are identified via the SEGF method. The lower-lying resonance state is found to split in two, and each of the resulting bands disperse toward $\bar{\Gamma}$.

The LDOS calculations for Fe(001) indicate a minority-spin surface state band just below the Fermi level in the relative gap along $\bar{\Delta}$ (see Fig. 5.4(b)). This is in excellent agreement with photoemission data³⁵ and slab calculations.^{31,55} In our SEGF results the band disperses from $\bar{\Gamma}$ to over halfway to $\bar{X}$; however, the Turner and Erskine³⁵ photoemission results show the band running throughout $\bar{\Delta}$. Wang and Freeman's seven-layer slab⁵⁵ results identify this band at roughly $E_F - 1$ eV. The positioning of this band from the present SEGF calculation is remarkable considering the inaccuracy in the sub-surface magnetic moment. It is clear that the iron valence electrons screen off imperfections with a very short healing length.

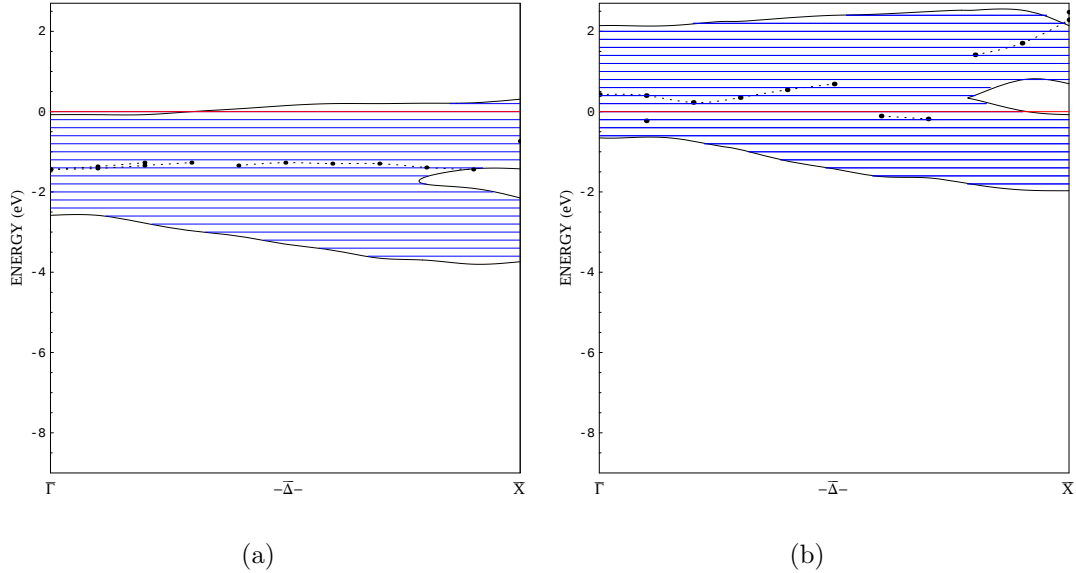


FIG. 5.5. Odd-symmetry surface bands, resonances, and bulk band projections for Fe(001) majority and minority spin along $\bar{\Delta}$. Horizontal shading indicates odd-symmetry projected bulk bands. Dashed lines are odd-symmetry surface states and resonances.

While the FLAPW method⁵⁵ fails to identify any surface states or resonances for the odd-symmetry states of either spin, the SEGf calculation has positively identified surface resonance bands for odd-symmetry states for both majority and minority spin (see Fig. 5.5). A photoemission experiment found a majority-spin surface state band below the projected bulk bandstructure at $\bar{\Gamma}$. By $\bar{X}$ this band evolves into a majority-spin resonance band. For minority spin, experiments show a resonance band below E_F all along $\bar{\Delta}$. This is in contrast to Fig. 5.5(b) which shows the resonance band above E_F starting at $\bar{\Gamma}$ and dispersing halfway to $\bar{X}$.

A general trend for all of the majority-spin results presented here is a greater concentration of surface states and resonances below the Fermi level. For minority spin, the surface states and resonance bands are concentrated near or above the Fermi level. These concentrations result in an enhanced magnetic moment at the surface since more majority-spin electronic levels are occupied because they fall below the Fermi energy.

5.4.3 $\bar{Y}$

$\bar{Y}$ is a line of high-symmetry in the two-dimensional Brillouin zone that traverses from $\bar{X}$ to $\bar{M}$ (Fig. 2.6). The projected surface bands, surface states, and surface resonances are shown in Figs. 5.6 and 5.7. Due to the absence of bulk reflection symmetry, the projected bulk bands cannot be characterized having even or odd symmetry, which is reflected in the graphs in this section.

An analysis of the projected bands reveals several absolute gaps for both spins along the $\bar{\Delta}$ line as shown in Fig 5.6. For the majority-spin case, the first gap is 1.25 eV wide centered at 4.37 eV below E_F . For the minority-spin case, a gap opens at $\bar{X}$ as well. This gap is centered around 2.97 eV below E_F and is 2.84 eV wide. Previous studies^{31,35,55} have produced gaps in agreement with our results.

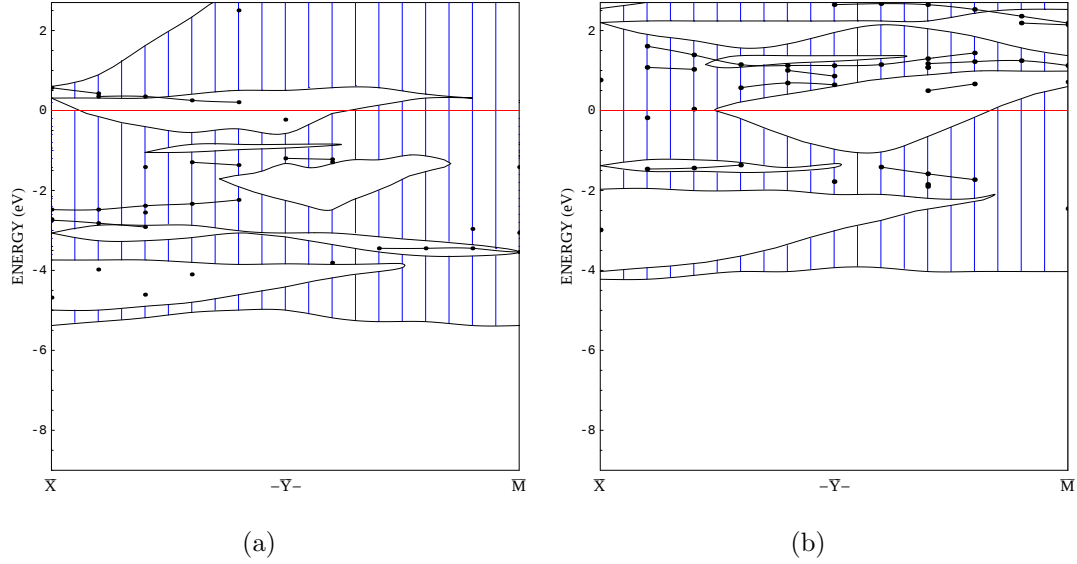


FIG. 5.6. Even-symmetry surface bands, resonances, and bulk band projections for Fe(001) majority and minority spin along $\bar{Y}$. Vertical shading represents projected bulk bands. Solid lines represent even-symmetry surface states and resonances.

Starting at $\bar{X}$, there are two even-symmetry majority-spin resonance bands 2.5 and 2.75 eV below E_F and a third one positioned just above E_F . All disperse along $\bar{Y}$ (Fig. 5.6(a)). Turner and Erskine's photoemission analysis³⁵ for the $\bar{Y}$ line failed to discriminate the symmetry of their experimental surface states and resonances, so direct comparison with experiment is difficult. Photoemission found a surface state approximately 4 eV below E_F , which is slightly higher than the E_F -4.7 eV state computed using the spin-polarized SEGf method. However, the seven-layer FLAPW results³¹ are in agreement with our results. At $\bar{X}$, the lowest-lying surface state is located at E_F -2.99 eV. This state has been identified as an even-symmetry minority-spin state and is in excellent agreement with the photoemission findings.³⁵

At $\bar{M}$ there is a surface band 3.5 eV below E_F that disperses in an absolute band gap toward $\bar{X}$ with little change in energy (Fig. 5.6(a)). This result contrasts with photoemission data of Turner and Erskine,³⁵ in which a band was observed between 3 and 4 eV below E_F that also dispersed toward $\bar{X}$. However, their $\bar{M}$ state starts as

a resonance band before crossing into the gap closer to $\bar{X}$. This band is also seen in the FLAPW results.³¹

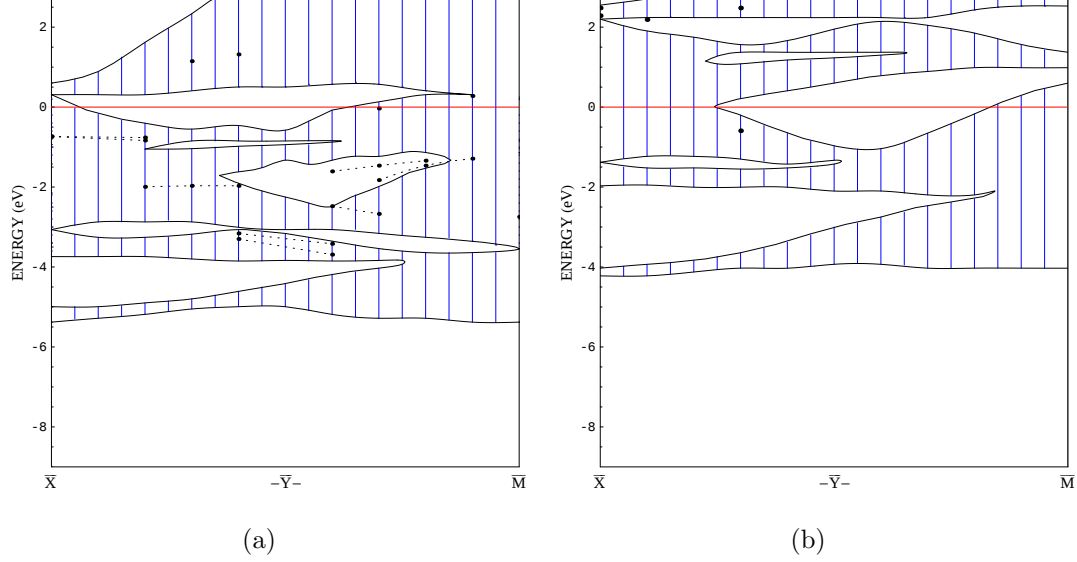


FIG. 5.7. Odd-symmetry surface bands, resonances, and bulk band projections for Fe(001) majority and minority spin along $\bar{Y}$. Vertical shading represents projected bulk bands. Dashed lines represent odd-symmetry surface states and resonances.

Odd-symmetry majority- and minority-spin surface bandstructure is displayed in Fig. 5.7. For $\bar{X}$ (Fig.5.7(a)), there is an odd-symmetry state 0.78 eV below E_F . Turner and Erskine's photoemission results³⁵ show a majority-spin state 0.5 eV below E_F that disperses downward in energy toward $\bar{M}$, which is very similar to the present SEGf results. In contrast, the seven-layer FLAPW calculation has this state positioned about 1 eV below E_F . For odd-symmetry minority-spin states, only a few surface resonances have been identified, which contrasts with photoemission results that showed two bands dispersing all along $\bar{Y}$.³⁵

5.4.4 $\bar{\Sigma}$

The $\bar{\Sigma}$ line is the longest of the three high-symmetry lines under consideration, as it is half the diagonal of the square Brillouin Zone. Projected bulk bands along this

line have absolute gaps for both majority- and minority-spin states. At $\bar{\Gamma}$, both spins have band gaps that open below the Fermi level and extend over halfway through the zone (see Fig 5.8).

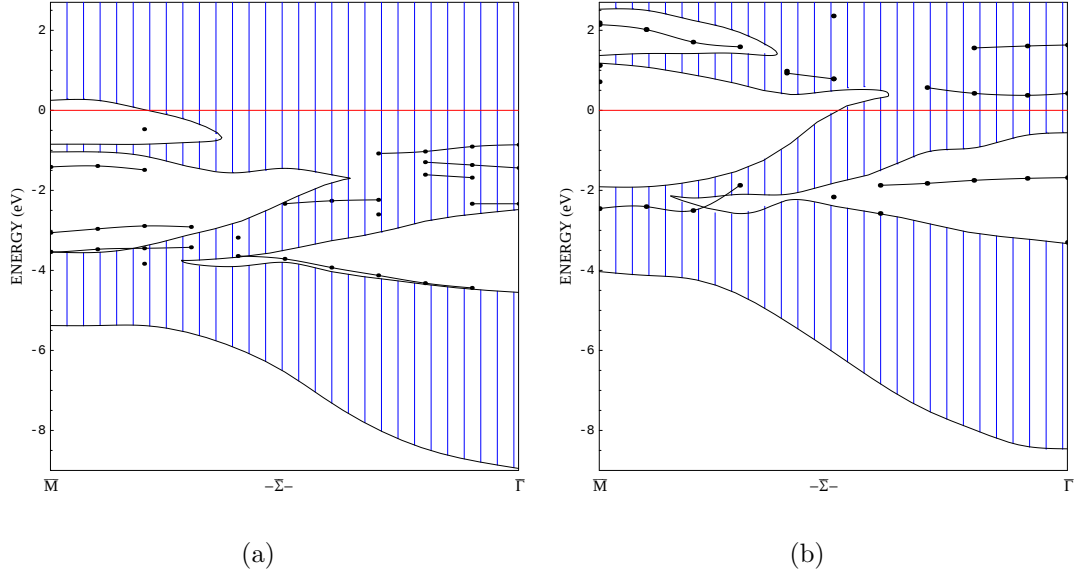


FIG. 5.8. Even-symmetry surface bands, resonances, and bulk band projections for Fe(001) majority and minority spin along $\bar{\Sigma}$. Vertical shading represents even-symmetry projected bulk bands. Solid lines represent even-symmetry surface states and resonances.

There are a pair of relatively large projected bulk band gaps at $\bar{M}$ for both majority and minority spin. As seen in Fig. 5.8, the center of each majority-spin band gap is below the corresponding minority-spin gap. For majority spin, we find three even-symmetry bands in the lower band gap. The lower two bands are between 3 and 4 eV below E_F , while the highest band is located at $E_F - 1.41$ eV. All disappear before traversing halfway along $\bar{\Sigma}$. The photoemission results of Turner and Erskine³⁵ indicate a surface state 1.2 eV below E_F , which compares favorably to the highest SEGf computed state in the band gap at $\bar{M}$. Turner and Erskine also found a surface resonance 3.2 eV below E_F , which is in close agreement with the current results. The FLAPW calculation³¹ has positioned a similar state 4 eV below E_F

which disperses sharply downward in energy. This is in sharp contrast to both the SEGF and photoemission results. For minority spin at $\bar{\Gamma}$, there is a single calculated surface resonance band 2.75 eV below E_F . Both photoemission results³⁵ and the seven-layer FLAPW calculation³¹ position this state at approximately E_F-2 eV.

Close to $\bar{\Gamma}$ there is an even-symmetry surface state band that begins at $E_F-4.38$ eV and disperses along the bottom of the band gap to two-thirds of the way to $\bar{M}$ before the gap closes (Fig. 5.8(a)). This band is in excellent agreement with the photoemission results of Turner and Erskine.³⁵ Higher in energy at $\bar{\Gamma}$, these results show several resonance bands dispersing toward $\bar{M}$ (Fig. 5.8(a)). The topmost band occurs at 0.85 eV below E_F . The photoemission study places a resonance band between E_F and E_F-1 eV, but the dispersion is upward in energy.³⁵ However, a seven-layer FLAPW calculation³¹ found the same downward dispersion as the present results.

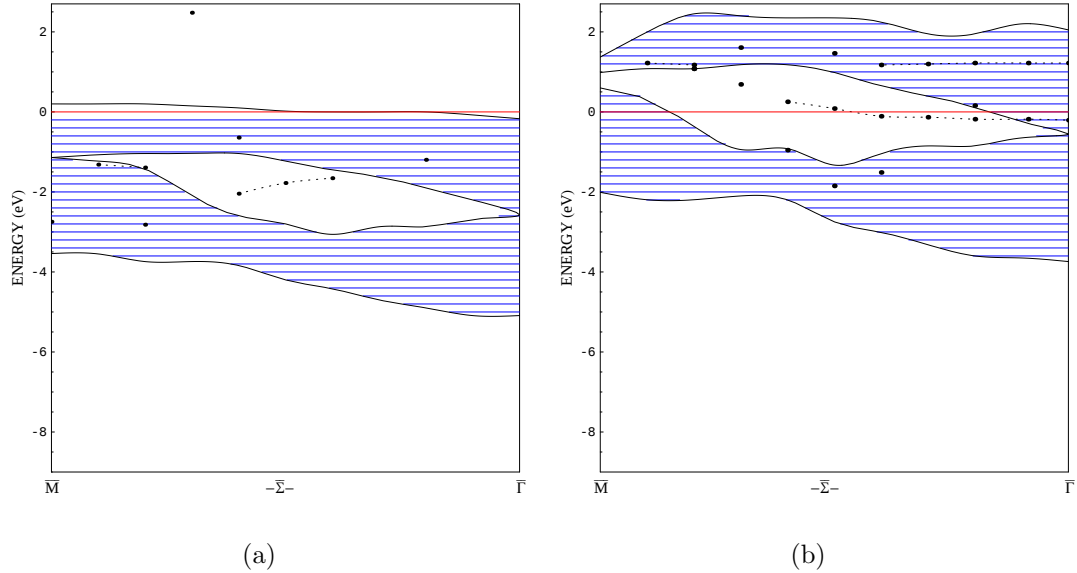


FIG. 5.9. Odd-symmetry surface bands, resonances, and bulk band projections for Fe(001) majority and minority spin along $\bar{\Sigma}$. Horizontal shading indicates odd-symmetry projected bulk bands. Dashed lines are odd-symmetry surface states and resonances.

For the odd-symmetry states along $\bar{\Sigma}$, there is a short surface band in the middle of $\bar{\Sigma}$ (Fig. 5.9(a)), that disperses upward from $\bar{M}$ to $\bar{\Gamma}$. This is in contrast to the photoemission data³⁵ and the seven-layer FLAPW calculation³¹ which both show a surface band running the whole length of $\bar{\Sigma}$ and dispersing downward. However, the odd-symmetry minority-spin state found right below E_F at $\bar{\Gamma}$ dispersing upward in the relative bulk symmetry gap, is in good agreement the photoemission results.³⁵ There is a slight difference in where the surface state band crosses E_F . The SEGF results show the crossing closer to $\bar{\Gamma}$ than the experimental results of Turner and Erskine.³⁵ The SEGF results are also in agreement with the seven-layer FLAPW calculation.³¹

This study has found good agreement when comparing the experimental value for the work function with the SEGF calculated result. There is an enhancement of the surface magnetic moment in line with that established by experiment. Positioning of surface state bands and surface resonance bands are quite impressive considering the spin density issue with the sub-surface layer. By treating the semi-infinite problem correctly, we have found remarkable agreement with experiment and other calculations despite a problem with the sub-surface magnetic moment.

CHAPTER SIX

Summary

Spin-polarized SEGF calculations were performed for the Ni(001), Co(001), and Fe(001) surfaces with a correction to the computer code that allowed the core charge to extend past the muffin-tin boundary. By correctly treating the semi-infinite problem, the identification of surface states is trivial compared with slab methods where the usual identification of surface states is performed by choosing states that have charge localized in the top two or three layers. Our calculations also do not suffer from the problem of interactions between states on opposing surfaces. In a previous paper, Benesh and Inglesfield demonstrated how a surface state arising on the two surfaces of a seven-layer Al(001) slab was split into two hybridized states (split by nearly 1 eV) due to the interaction across the finite width of the slab.⁵⁷

Our calculated work function for Ni(001) was in fair agreement with experiment. This disagreement could be due the fact that natural nickel has a lattice expansion at the surface of about four percent. The surface magnetic moment was in excellent agreement with experiment and other calculations. We found a Friedel-type oscillation in the layer-by-layer spin moments that was seen in several other calculations. It would be interesting to perform another SEGF calculation with four or more layers to determine when the oscillations die off and compare the lowest surface layer with the experimental value for the bulk moment. Our identification of surface states and resonances were in agreement with experiment and other calculations.

The computed work function for the metastable fcc(001) face of cobalt was improved compared with our computed value for nickel. The calculated spin density was in excellent agreement with other calculations and the layer-by-layer spin moments had Friedel-type oscillations seen in other theoretical results. We were not able to

compare our surface electronic structure with experiment. There was general agreement with an FLAPW slab calculation regarding the concentration of surface states and resonances along the high-symmetry lines in the surface Brillouin Zone.

The results for Fe(001) were mixed. Our calculated work function was in good agreement with experiment, even though the calculated magnetism in the third layer was almost paramagnetic rather than ferromagnetic. The good results for the surface layer was almost certainly due to the electron screening of the imperfections with a short healing length. The calculated surface electronic structure was in very good agreement with experiment and surpassed other calculations for several surface state and resonance bands.

The poor magnetic moment in the third layer of Fe(001) is cause of some concern. The corresponding magnetic moments for Ni(001) and Co(001) were in good agreement with other studies. Iron was the only bcc crystal in this study, and possesses the largest fraction of interstitial volume (Fig. 5.1). We have assumed that if the bulk bandstructure compared well with other published bulk bandstructures, then the embedding potential was a good representation of the bulk. It is possible that the expansion used for the embedding potential is inadequate for such an open surface. Also, the electrostatic boundary condition imposed along the embedding surface (where the potential is set to zero), may not be appropriate for such an open surface. One way to check would be to perform a calculation for the Ni(110) surface to determine if the third layer has a magnetic moment that deviates greatly from experiment or other calculations.

APPENDICES

APPENDIX A

Core Charge

An initial spin-polarized study of Fe(001) for a one-layer slab¹⁶ yielded results uncharacteristic of previous paramagnetic SEGF studies.^{13–15} Fe(001) is known to possess a bulk magnetic moment of $2.216 \mu_B$ and has a surface moment that is enhanced by thirty percent over the bulk value. The spin polarized SEGF calculation resulted in a spin moment of $2.62 \mu_B$ and a work function of 5.18 eV, in poor agreement with the experimental value of 4.4 eV. Other self consistent calculations using slab methods found that the spin density healed close to the bulk Fe value by the fourth interior layer. Thus, it was thought that a three-layer calculation using the spin polarized SEGF method would provide better results. Unfortunately, this was not the case, and poor spin densities resulted upon convergence; however, the calculated work function was in good agreement with experiment.

An analysis of the SEGF output files showed that the charge densities and potentials at the MT-interstitial boundaries were mismatched. A difference of less than 1.5×10^{-3} a.u. was observed in each of the majority and minority-spin charge densities at the MT-interstitial boundary. In addition, the MT charge density was found to be consistently greater than the interstitial charge density, and even larger differences occurred in the total potential. Because of small differences in the charge density and larger differences in the potential, the potential routines were considered the source of the error.

The exchange-correlation potential, which scales as $\rho^{1/3}$, was checked to determine if any error existed in the routine. Thorough testing showed the exchange-correlation potential gave excellent results for a wide range of charge densities, and more importantly, gave consistent results for the inputs that were fed in from the MT and

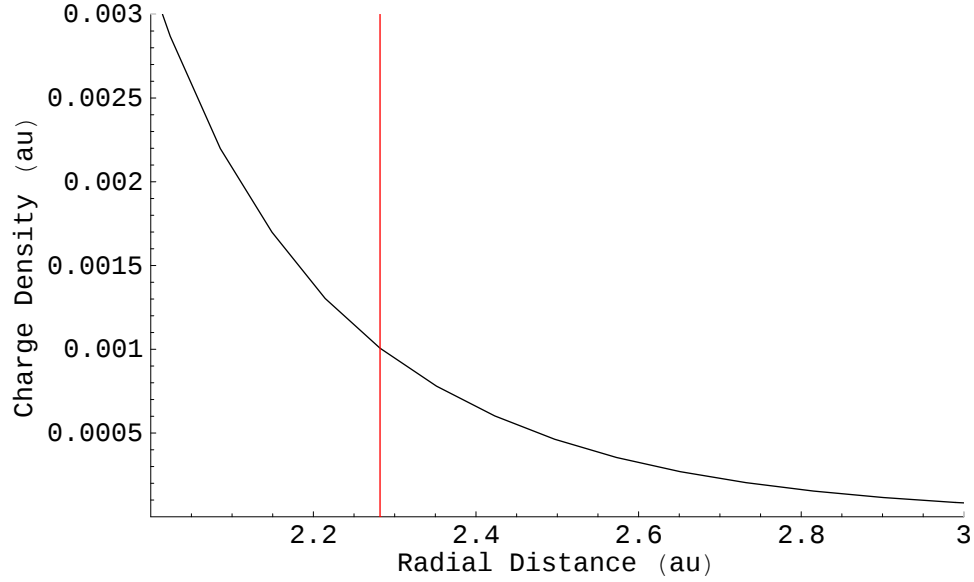


FIG. A.1. Radial variation in the core charge for Fe(001) near the MT edge.

interstitial regions. The Coulomb potential was then checked for continuity, resulting in a small error (1×10^{-4} Hartree), which was not enough to explain the larger error in the output.

The charge density components were then examined. The basis functions were checked at the MT-interstitial boundary and no continuity errors were detected that were large enough to explain the mismatch. By raising the MT expansion from $l = 8$ to $l = 12$, the basis function matching error decreased and led to better continuity in the charge density and potential. However, the matching of the total potential improved by less than 1×10^{-4} Hartree.

The core charge density was then excluded from the calculation, isolating the valence charge in order to observe matching at the boundary. By removing the core charge, the matching accuracy improved by two orders of magnitude. Therefore, the matching error was found to result from non-negligible core charge extending past

Table A.1. MT radii variation for the 001 crystal faces for different elements.

Element	Lattice	Lattice Constant (a.u.)	MT radius (a.u.)
Aluminum	fcc	7.60	2.687
Platinum	fcc	7.42	2.622
Nickel	fcc	6.55	2.316
Cobalt	fcc	6.54	2.312
Iron	bcc	5.27	2.282

the MT boundary. In fact, the core charge density was found to match the missing difference at the MT-interstitial boundary, which was not apparent in previous SEGF calculations.^{13–15}

Most of the previous SEGF studies used crystals with larger MT radii than the elements in this study, which is likely the reason the core charge mismatch was not apparent. The 3*d* transition metals used for this study possessed MT radii that were thirteen to eighteen percent smaller than aluminum or platinum MT radii (see Table A.1) used in previous studies. Also, the amount of core charge at the MT boundary depends sensitively on the MT radius and number of core electrons. While a charge mismatch may have been negligible for Pt or Al, it should have greater significance in the case of paramagnetic nickel (see Fig. A.2).¹³

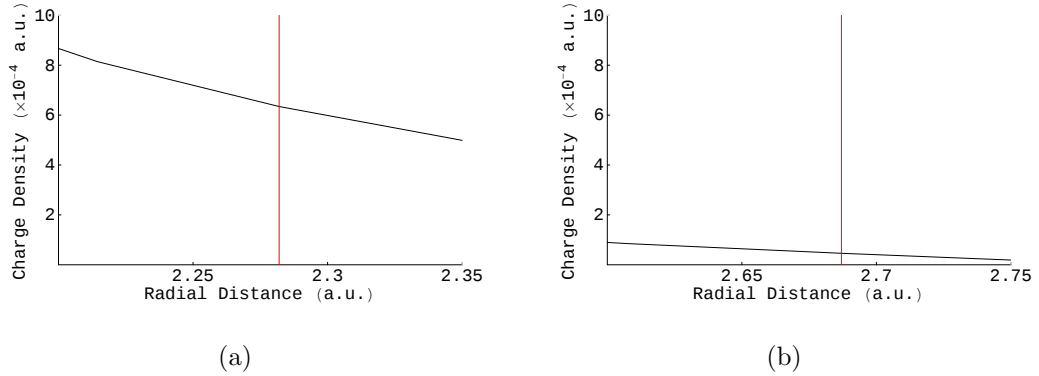


FIG. A.2. Core charge density for (a) Fe and (b) Al near their respective MT boundaries. The vertical red line is the MT radius for each element.

A method to solve this problem was developed: add the *leaky* MT charge to the interstitial and vacuum region. First, the exponential decay of the extended core charge density profile was confirmed by graphing the ρ_{core} from a SEGF calculation (Fig. A.3). By confirming the exponential decay, the core charge extending past the

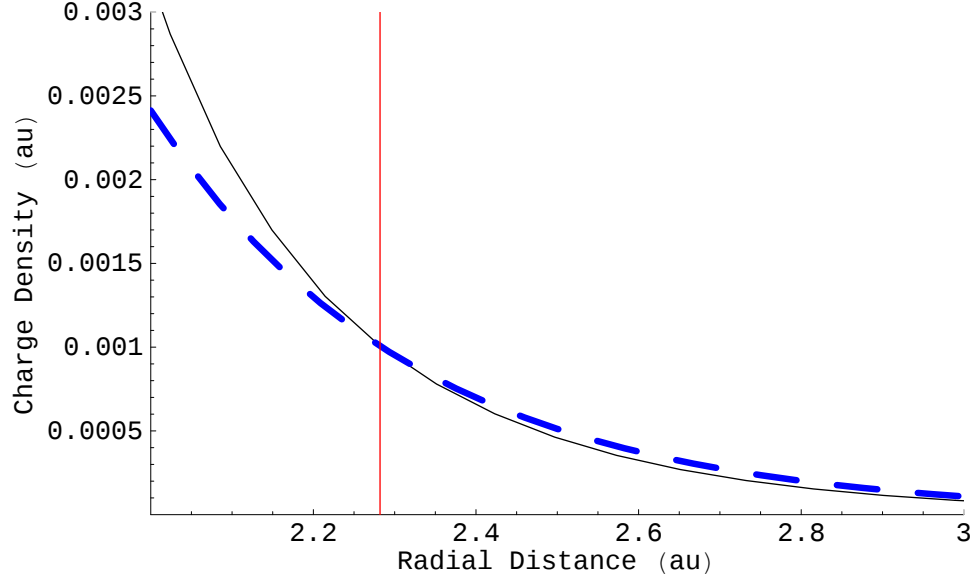


FIG. A.3. Radial core charge density of Fe(001) as calculated by SEGF (solid line) and calculated by the model (dashed line). The model charge density is used only outside the muffin-tin radius (red line).

MT sphere can be modeled in the following form:

$$\rho_n(r) = \beta_n e^{-\alpha_n r}, \quad (\text{A.1})$$

where β_n and α_n are constants determined by fitting the core charge at the MT surface and a point in the interstitial region where the charge has decayed to a threshold level ($\approx 10^{-6}$ a.u.). Once the coefficients were determined, the charge density was recomputed by adding the spin-dependent core charge contribution in the interstitial and vacuum regions. Coefficients for the total charge were then recalculated in these regions. While this solution is not perfect, the matching at the different interfaces has

been greatly improved. One remaining problem with this correction is that charge from touching MTs are not added to each other. This includes charge coming from substrate MTs which touch surface MTs. Nevertheless, the errors in both charge density and potential have been lowered dramatically and provide confidence that the resulting output for all computational cycles is accurate.

APPENDIX B

Data Analysis Software

The sample programs in this appendix were developed to automate data analysis tasks associated with this SEGF study. The programs have been developed for the Linux[®] operating system, but should work with little or no modification within any UNIX[®]-like operating system. The graphics were mostly generated with Wolfram *Mathematica*[®], but gnuplot was used as well.

B.1 Bandstructure Plotting

The following program generates bulk band graphs from the embedding program along the lines of high symmetry for a square SBZ. Gnuplot is required and the graphics are in encapsulated postscript format.

```
#!/usr/bin/perl -w

#####
# band_structure is a Perl script designed to generate graphs of the bulk
# band structure along varied points in a 2D surface BZ
# Interactive, but one could just as well use a configuration file and read it in.
# Requires the gnuplot plotting program
#####

use strict;
use diagnostics;
use File::Copy;

##### Scalar Variables #####

my $embed;          # embedding executable name
my $embed_file;     # name of input files
my $bulk_file;      # bulk input file
my $fermi_level;    # Fermi level
my $crystal;        # name of crystal and part of graph title
my $spin;           #
my $spin_label;     #
my $division;       # Number of points sampled along high symmetry lines
my $start;          #
my $final;          #
my $output;         # output from embedding program to be plotted
my $dir;            # directory to put the graphs and data
my $x;              # coordinate
my $y;              # coordinate
my $x_step;         # step size
my $y_step;         # step size
my $xhigh;          # max value
my $garbage;        # temporary value
my $energy;         # plotted energy
my $k;              #
my $run;            #
my $LINE;           #

my $flag = 0;

##### Arrays #####

my @lines;

##### Hash Tables #####
```

```

my %symmetry_point = (
    1 => [ "Gamma_Bar", 0.0,      0.0 ],
    2 => [ "X_Bar",      0.5,      0.0 ],
    3 => [ "M_Bar",      0.5,      0.5 ],
);

##### Main Program #####

print "Enter the name of the embedding program:\n";
chomp( $embed = <STDIN> );

print "Enter the name of the embedding input file:\n";
chomp( $embed_file = <STDIN> );

print "Enter the name of the bulk input file:\n";
chomp( $bulk_file = <STDIN> );

print "Enter the fermi-level in Hatrees:\n";
chomp( $fermi_level = <STDIN> );

print "Enter the element and crystal face:\n";
chomp( $crystal = <STDIN> );

print
    "Enter 0 for paramagnetic, 1 for majority spin or 2 for minority spin:\n";
chomp( $spin = <STDIN> );

if ( $spin == 0 ) {
    $spin_label = "Paramagnetic";
}
elsif ( $spin == 1 ) {
    $spin_label = "Majority";
}
else {
    $spin_label = "Minority";
}

if ( -e $embed_file ) {

    #file exists
}
else {
    print "$embed_file: File not found:$!\n" && die;
}

if ( -e $bulk_file ) {
    copy( $bulk_file, "fort.7" );
}
else {
    print "$bulk_file: File not found:$!\n" && die;
}

while ( $flag == 0 ) {
    print

```

```

        "Enter the starting point (1 - Gamma Bar, 2 - X Bar, 3 - M Bar):\n";
chomp( $start = <STDIN> );

if ( $symmetry_point{$start} ) {
    print "$symmetry_point{$start}[0] choosen as the starting point.\n";
    $flag = 1;
}
else {
    print "$start is not the correct value. Please try again.\n";
}

}

$flag = 0;

while ( $flag == 0 ) {

    print
        "Enter the ending point (1 - Gamma Bar, 2 - X Bar, 3 - M Bar):\n";

    chop( $final = <STDIN> );

    if ( $final == $start ) {
        print "Starting and ending points are the same.
            Please try again.\n";
    }
    elsif ( $symmetry_point{$final} ) {
        print "$symmetry_point{$final}[0] choosen as the end point.\n";
        $flag = 1;
    }
    else {
        print
            "Entered value $final has been entered incorrectly.
            Please try again.\n";
    }

}

print "Enter the number of steps between the first and the last points.\n";
chop( $division = <STDIN> );

$x_step
    = ( $symmetry_point{$final}[1] - $symmetry_point{$start}[1] ) / $division;
$y_step
    = ( $symmetry_point{$final}[2] - $symmetry_point{$start}[2] ) / $division;

$x = $symmetry_point{$start}[1];
$y = $symmetry_point{$start}[2];

$dir = $symmetry_point{$start}[0] . '-'
    . $symmetry_point{$final}[0] . '-'
    . $spin_label;
mkdir $dir;

```

```

open( EMBED_FILE, "+<$embd_file" );

@lines = <EMBED_FILE>;

$run = 0;

while ( $run <= $division ) {

    open( TEMP, ">temp" );

    $LINE = 0;
    while ( $LINE < 20 ) {
        print TEMP "$lines[$LINE]";
        $LINE++;
    }

    printf TEMP ( " %1.6fD+00 %1.6fD+00 1.000000D+00\n", $x, $y );

    close(TEMP);
    open( TEMP, "-temp" );
    '$embed < temp > embed_log';

    $output = "$dir/band_test" . "$run";

    open( BAND, "fort.3" );

    open( OUTPUT, "+>$output" );

    $xhigh = 0;

    while (<BAND>) {
        ( $garbage, $energy, $k ) = split(/\s+/);
        $energy = ( $energy - $fermi_level ) * 27.212; # 1 Hartree = 27.212 eV
        print OUTPUT "$k $energy\n";
        if ( $xhigh < $k ) {
            $xhigh = $k;
        }
    }
    close OUTPUT;
    open( PLOT, ">band_plot.gnu" );

    print PLOT
        "set term postscript landscape enhanced color 'Times-Roman' 14\n";
    print PLOT "load 'plot.gnu'\n";
    print PLOT "set output '$output.eps'\n";
    print PLOT "set xrange [0:$xhigh]\n";
    print PLOT "set yrange [-12:3]\n";

    if ( $spin == 0 ) {
        print PLOT
            "set title \"Band Structure of $crystal at $x, $y\"
            font \"Times-Roman,14\" \n";
    }
    else {

```

```

        print PLOT
            "set title \"Band Structure of $crystal ($spin_label spin)
              at $x, $y\" font \"Times-Roman,14\"\\n";
        }
    print PLOT "plot '$output' with points pointtype 7 pointsize 1\\n";

    close PLOT;
    'gnuplot band_plot.gnu';

    $x = $x + $x_step;
    $y = $y + $y_step;
    $run++;
}

```

B.2 Local Density of States

```
#!/usr/bin/perl

##### Description #####
# Determines the LDOS and generates graphs for points between 2 points
# on the SBZ.
# An input file fixes the parameters.
# Depending on the setup of the OS, some of this may need modification
# Graphics are generated using Mathematica, but additional subroutines could
# expand this to Gnuplot, etc...
# Note: The input data file is not currently checked for errors.
# Script now has the ability to increment energy ranges in order to have more
# points in the LDOS.
#####

##### Load Modules #####

use warnings;
use strict;
use diagnostics;
use Cwd;
use File::Copy;

##### Scalar Variables #####

my $sbz_type;      # SBZ type (currently only square geometry available)
my $segf_exe;      # Name of SEGF executable
my $segf_in5;      # Name of Stream 5 SEGF input file
my $embd_exe;      # Name of precompiled embedding executable
my $embd_in5;      # Stream 5 input file for embedding program
my $embd_in7;      # Stream 7 file for embedding program
my $embd_estart;    # Starting energy level for bands
my $embd_estop;     # Highest energy level for band construction
my $fermi_level;    # Fermi Level in Hartrees
my $bzdivisions;    # Number of divisions along a line in the SBZ
my $spin_type;      # Paramagnetic, majority, or minority
my $plot_var;       # y or n (plot generated using gnuplot)
my $plot_times
    ; # for a full plot of the ldos, the embedding energy range is divided
    # plotted when $embd_stop is reached
my $plot_prog;      # Plotting program (mathematica or gnuplot)
my $dir;
my $spin_state;
my $key;
my $sbz_start;
my $sbz_stop;
my $bz_x;
my $bz_xstart;
my $bz_xstop;
my $bz_xstep;
my $bz_y;
my $bz_ystart;
my $bz_ystop;
```

```

my $bz_ystep;
my $newdir;
my $embfile;
my $embd_estep;
my $embd_e1;
my $embd_e2;
my $run;
my $istep;
my $file_num;
my $segf_emb;
my $garbage;
my $iotyp;
my $icrtyp;
my $imix;
my $mtiop;
my $nspin;
my $log_flag;
my $mt;
my $mtfile;
my $hartree_energy;
my $im;
my $dos;
my $energy;
my $vacfile;
my $ch_int_dos;
my $intdos;
my $dos_emb;
my $LINE;

```

```

##### Array Variables #####

```

```

my @embd5;
my @segf5;

my @spin = ( 'majority', 'minority' );

```

```

##### Hash #####

```

```

my %sbz = (
  square => {
    lines_of_symmetry => {
      delta => [ 'gamma_bar', 'x_bar' ],
      y      => [ 'x_bar',      'm_bar' ],
      sigma => [ 'm_bar',      'gamma_bar' ],
    },
    gamma_bar => [ 0.0, 0.0 ],
    x_bar     => [ 0.5, 0.0 ],
    m_bar     => [ 0.5, 0.5 ],
  },
);

```

```
##### Main Program #####
```

```
open( DATA, "segf_data" );

chop( $sbz_type      = <DATA> );
chop( $segf_exe      = <DATA> );
chop( $segf_in5      = <DATA> );
chop( $embd_exe      = <DATA> );
chop( $embd_in5      = <DATA> );
chop( $embd_in7      = <DATA> );
chop( $embd_estart   = <DATA> );
chop( $embd_estop    = <DATA> );
chop( $fermi_level   = <DATA> ); # Fermi level in Hartrees
chop( $bzdivisions   = <DATA> );
chop( $spin_type     = <DATA> ); # $spin_type = paramagnetic, majority, minority
chop( $plot_var      = <DATA> )
    ; # $plot_var = y or n (plot generated using gnuplot)
chop( $plot_times    = <DATA> )
    ; # for a full plot of the ldos, the embedding energy range
      # is divided into pieces and plotted at the end
chop( $plot_prog     = <DATA> ); # mathematica or gnuplot

close DATA;

$dir = cwd();

foreach $spin_state (@spin) {

    # loop over each line of high symmetry in the Surface BZ
    foreach $key ( sort keys %{ $sbz{$sbz_type}->{lines_of_symmetry} } ) {

        $sbz_start = @{ $sbz{$sbz_type}->{lines_of_symmetry}->{$key} }[0];
        $bz_xstart = $sbz{$sbz_type}->{$sbz_start}->[0];
        $bz_ystart = $sbz{$sbz_type}->{$sbz_start}->[1];

        $sbz_stop = @{ $sbz{$sbz_type}->{lines_of_symmetry}->{$key} }[1];
        $bz_xstop = $sbz{$sbz_type}->{$sbz_stop}->[0];
        $bz_ystop = $sbz{$sbz_type}->{$sbz_stop}->[1];

        # make the directory to store the dos values

        $newdir = "$sbz_start" . "_to_" . "$sbz_stop" . "_" . "$spin_state";
        mkdir( $newdir, 0775 );

        $newdir = "$dir" . "/" . "$newdir";

        open( EMBED, "$embd_in5-$spin_state" );
        @embd5 = <EMBED>;
        close EMBED;

        open( SEGF5, "$segf_in5-$spin_state" );
        @segf5 = <SEGF5>;
```

```

close SEGF5;

$embd_estep = ( $embd_estop - $embd_estart ) / $plot_times;
$embd_e1     = $embd_estart;
$embd_e2     = $embd_estart + $embd_estep;

$bz_xstep = ( $bz_xstop - $bz_xstart ) / $bzdivisions;
$bz_ystep = ( $bz_ystop - $bz_ystart ) / $bzdivisions;

$bz_x = $bz_xstart;
$bz_y = $bz_ystart;

$run    = 0;
$istep  = 1;

copy( "$embd_in7-$spin_state", "fort.7" );

while ( $run <= $bzdivisions ) {

    if ( $run < 10 ) {
        $file_num = "0" . "$run";
    }
    else {
        $file_num = $run;
    }

    print "$bz_x $bz_y\n";
    while ( $istep <= $plot_times ) {

        open( ETEMP, ">etemp" );
        $LINE = 4;

        print ETEMP "$embd5[0]";
        print ETEMP "$embd5[1]";
        print ETEMP "$embd5[2]";

        if ( $embd_e1 < 0 && $embd_e2 > 0 ) {
            printf ETEMP (
                " %1.6fD+00 %1.6fD+00 1.000000D-06\n",
                $embd_e1, $embd_e2
            );
        }
        elsif ( $embd_e1 < 0 && $embd_e2 < 0 ) {
            printf ETEMP (
                " %1.6fD+00 %1.6fD+00 1.000000D-06\n",
                $embd_e1, $embd_e2
            );
        }
        else {
            printf ETEMP (
                " %1.6fD+00 %1.6fD+00 1.000000D-06\n",
                $embd_e1, $embd_e2
            );
        }
    }
}

```

```

while ( $LINE < 20 ) {
    print ETEMP "$embd5[$LINE]";
    $LINE++;
}

printf ETEMP ( "  %1.6fD+00 %1.6fD+00  1.000000D+00\n", $bz_x,
    $bz_y );

close ETEMP;

'$embd_exe < etemp > embd_log';    # runs the embedding code
$segf_emb = $segf5[6];
chop($segf_emb);
move( "fort.4", "$segf_emb" );

# b4 running the dos calculation, need to check if the bz point is at m-bar
if ( $bz_x == 0.5 && $bz_y == 0.5 )
{
    # at m-bar and set imix=5
    $_ = $segf5[0];
    chop($_);
    ( $garbage, $iotyp, $icrtyp, $imix, $mtiop, $nspin )
        = split(/\s+/);
    $segf5[0] = " $iotyp  $icrtyp  5  $mtiop  $nspin\n";
}
if ( $bz_x == 0.5 && $bz_y == 0.0 )
{
    # at x-bar and set imix=6
    $_ = $segf5[0];
    chop($_);
    ( $garbage, $iotyp, $icrtyp, $imix, $mtiop, $nspin )
        = split(/\s+/);
    $segf5[0] = " $iotyp  $icrtyp  6  $mtiop  $nspin\n";
}
else {
    $_ = $segf5[0];
    chop($_);
    ( $garbage, $iotyp, $icrtyp, $imix, $mtiop, $nspin )
        = split(/\s+/);
    $segf5[0] = " $iotyp  $icrtyp  -1  $mtiop  $nspin\n";
}

open( STEMP, ">stemp" );
print STEMP @segf5;
close STEMP;
system "$segf_exe < stemp > segf_log";

unlink "out12";    # deletes the output chden file

# the ldos values can now be extracted from segf_log
open( LOG, "segf_log" );
$log_flag = 0;

while (<LOG>)
{ # this loop goes through the log file to extract
  # the ldos info

```

```

chop($_);
if (/DENSITY OF STATES IN MUFFIN TINS/) {
    $mt = substr( $_, 69, 1 ); # determines the mt number
    $mtfile = "$newdir" . "/" . "bzrun"
        . "$file_num" . "mt_" . "$mt";
    open( MTFILE, ">>$mtfile" );

    while () {
        chop( $_ = <LOG> );
        if (/^$/ )
        { # after the data is read in, a blank line follows.
            last
                ; # this kicks control out of the while loop
        }
        s/D/E/g
            ; # perl doesn't understand DP formatted numbers
        ( $hartree_energy, $im, $dos )
            = /(\S+)\s+(\S+)\s+(\S+)/;
        $energy = ( $hartree_energy - $fermi_level )
            * 27.212; # Zeroing the Fermilevel(eV)
        $dos = $dos / 27.212;

        print MTFILE "$energy $dos\n";
    }

    # use the subroutine plot to provide graphs for
    # data analysis
    close MTFILE;

    if ( $istep == $plot_times ) {
        if ( $plot_prog eq "mathematica" ) {
            plot_mathematica( $mtfile, $newdir );
        }
        else {
            plot_gnuplot($mtfile);
        }
    }
}

elsif (/AVERAGE DOS OVER PLANE AT/) {
    $_ = <LOG>;
    $vacfile = "$newdir" . "/" . "bzrun"
        . "$file_num" . "_vac";
    open( VACFILE, ">>$vacfile" );

    while () {
        $_ = <LOG>;
        if (/^$/ ) {
            last;
        }
        s/D/E/g;
        ( $hartree_energy, $im, $dos )
            = /(\S+)\s+(\S+)\s+(\S+)/;
        $energy

```

```

        = ( $hartree_energy - $fermi_level ) * 27.212;
        $dos = $dos / 27.212;

        print VACFILE "$energy $dos\n";
    }
    close VACFILE;
    if ( $istep == $plot_times ) {
        if ( $plot_prog eq "mathematica" ) {
            plot_mathematica( $vacfile, $newdir );
        }
        else {
            plot_gnuplot($vacfile);
        }
    }
}
elsif (/DOS IN EMBEDDED REGION/) {
    $log_flag = 1;
    $embfile = "$newdir" . "/" . "bzrun"
        . "$file_num" . "_emb";
    $intdos = "$newdir" . "/" . "bzrun"
        . "$file_num"
        . "_delta_int";
    open( EMBFILE, ">>$embfile" );
    open( INTDOS, ">>$intdos" );

    while ( ) {
        chop( $_ = <LOG> );
        if (/^$/ ) {
            last;
        }
        s/D/E/g;
        ( $hartree_energy, $im, $dos_emb, $ch_int_dos )
            = /(\S+)\s+(\S+)\s+(\S+)\s+(\S+)/;
        $energy
            = ( $hartree_energy - $fermi_level ) * 27.212;
        $dos_emb = $dos_emb / 27.212;
        $ch_int_dos = $ch_int_dos / 27.212;

        print EMBFILE "$energy $dos_emb\n";
        print INTDOS "$energy $ch_int_dos\n";
    }
    close EMBFILE;
    close INTDOS;
    if ( $istep == $plot_times ) {
        if ( $plot_prog eq "mathematica" ) {
            plot_mathematica( $embfile, $newdir );
            plot_mathematica( $intdos, $newdir );
        }
        else {
            plot_gnuplot($embfile);
            plot_gnuplot($intdos);
        }
    }
}
}

```

```

        if ( $log_flag == 1 )
        {      # finished reading the ldos and go to the next point
                last;
        }

    }

    close LOG;
    $embd_e1 = $embd_e2;
    $embd_e2 = $embd_e2 + $embd_estep;
    $istep++;

}

$run++;
$bz_x      = $bz_xstart + $run * $bz_xstep;
$bz_y      = $bz_ystart + $run * $bz_ystep;
$istep     = 1;
$embd_e1   = $embd_estart;
$embd_e2   = $embd_estart + $embd_estep;

}

}

}

##### Subroutines #####

sub plot_gnuplot {

    my $output;

    open( PLOT, ">dos.gnu" );
    $output = "$_[0]" . ".eps";
    print PLOT
        "set term postscript landscape enhanced color 'Times-Roman' 14\n";
    print PLOT "load 'dosplot.gnu'\n";
    print PLOT "set output '$output'\n";

    if ( $_[1] != 0 ) {
        print PLOT "set xrange [-13:3]\n";
        print PLOT "set yrange [0:~]\n";
    }

    print PLOT "set title \"$_[0] at ($bz_x, $bz_y)\" \"Times-Roman,14\"\\n";
    print PLOT "set xlabel \"Energy (eV)\" \"Times-Roman,14\"\\n";
    print PLOT "set ylabel \"DOS (# states/eV)\" \"Times-Roman,14\"\\n";
    print PLOT "plot '$_[0]' with lines\\n";
    close PLOT;
    system "gnuplot dos.gnu";
}

```

```

}

sub plot_mathematica {

    my $e_low;
    my $e_high;
    my $ldos;
    my $ldos_low;
    my $ldos_high;
    my $math_plot;

    my @hartree_energy;
    my @ldos;

    open( LDOS, "$_[0]" );

    while (<LDOS>) {
        ( $hartree_energy, $ldos ) = split(/\s+/);
        push( @hartree_energy, $hartree_energy );
        push( @ldos,          $ldos );
    }

    @ldos      = sort { $a <=> $b } @ldos;
    $e_low     = int( $hartree_energy[0] ) + 1.0;
    $e_high    = int( pop(@hartree_energy) ) + 1.0;
    $ldos_high = int( pop(@ldos) ) + 1.0;
    $ldos_low  = $ldos[0];

    if ( $ldos_low >= 0 || $ldos > -1.0e-03 )
    {
        # Sometimes a low ldos is computed
        $ldos_low = 0.0;
    }
    else {
        $ldos_low = int($ldos_low) - 1;
    }

    $math_plot = "$_[0]" . "mathematica";

    open( MPLOT, ">$math_plot" );

    print MPLOT "ldos = ReadList[\"$_[0]\",{Number,Number}];\n";
    print MPLOT "ldosplot = ListPlot[ldos,PlotJoined->True,Frame->True,\n";
    print MPLOT "ImageSize->{600,450},\n";
    print MPLOT "AspectRatio->0.65,Axes->False,PlotStyle->RGBColor[1,0,0],\n";
    print MPLOT "PlotRegion->{{0.05,0.97},{0.05,0.90}},\n";
    print MPLOT
        "FrameStyle->{{Automatic},{Automatic},{Automatic},{Automatic}},\n";
    print MPLOT "FrameTicks -> {Automatic, Automatic, None, None},\n";
    print MPLOT
        "PlotRange -> {{$e_low, $e_high}, {$ldos_low, $ldos_high}},\n";
    print MPLOT "Axes->False,\n";
    print MPLOT "PlotLabel->\"LDOS at point ($bz_x, $bz_y)\",\n";
    print MPLOT "FrameLabel->{\"Energy (eV)\",\"DOS (# states/eV)\"},\n";

```

```
print MPlot "DisplayFunction->Identity];\n";  
print MPlot "Export[\"$math_plot.eps\",ldosplot,\"EPS\"];\\n";  
  
close MPlot;  
  
system "/usr/local/bin/math < $math_plot > test_log";  
  
}
```

B.3 Charge Density Contour Plots

```
#!/usr/bin/perl

# Extracts peaks in the LDOS, generates charge density and potential
# output, and finally plots them in Mathematica using a modified
# version of the newplot.f plotting program.

##### Load Modules #####

use warnings;
use strict;
use diagnostics;
use Cwd;
use File::Copy;

##### Scalar Variables #####

my $sbz_type;           # 2D geometry of the Surface BZ (e.g. square)
my $fermi_level;        # Fermi level in Hartrees
my $ldos_directory_top_level; # Directory where the LDOS data is stored
my $data_file_name_prefix; # Prefix for the LDOS data files
my $bz_start;           # Surface Brillouin starting point
my $bz_stop;            # Surface Brillouin stopping point
my $segf_executable;    # SEGF executable to run
my $segf_input_file;    # Stream 5 file for SEGF exe
my $embd_executable;    # Embedding executable to run
my $embd_input_file
    ;                  # Embedding input file for majority spin/paramagnetic calc
my $embd_bulk;          # Embedding bulk input file
my $spin_type;          # 1 = Paramagnetic 2 = Spin-polarized
my $embd_input_file2;   # Minority spin embedding input file
my $embd_bulk2;         # Minority spin embedding bulk file
my $newplot_executable; # Program to generate charge density plotting points
my $newplot_in1;        # Newplot input file (point of view for cd plotting)
my $newplot_in2;        # Newplot input file
my $newplot_in1_minority;
my $newplot_in2_minority;
my $sbz_x_start;        # SBZ starting point on x-axis
my $sbz_x_stop;         # SBZ stopping point on x-axis
my $sbz_y_start;        # SBZ starting point on y-axis
my $sbz_y_stop;         # SBZ stopping point on y-axis
my $segf_emb;           # Name for Paramagnetic/Majority spin embedding potential
my $segf_emb2;          # Name for Minority spin embedding potential
my $newdir;             # Directory to store data
my $dir;                # Directory (cwd)
my $sbz_x;              # See $x_start
my $sbz_y;              # See $y_start
my $sbz_xstep;          # Delta step along x-axis (10 points)
my $sbz_ystep;          # Delta step along y-axis (10 points)
my $file_num;           # Names files according to delta point
my $file;               # File name
my $file_full;          # Full path to LDOS input file
```

```

my $peak_count;      # Number of peaks in an LDOS file
my $chden_dir;       # Directory path for plots
my $ldos_data_file;  # Path + file for LDOS
my $hartree_energy;  # Energy of a point in LDOS
my $ldos;            # LDOS value
my $he_minus;        # Energy on left side of analyzed LDOS value
my $he_plus;         # Energy on right side of analyzed LDOS value
my $ldos_minus;      # LDOS on left side of analyzed LDOS value
my $ldos_plus;       # LDOS on right side of analyzed LDOS value
my $count2;          # Counting variable
my $newplot_file;    # File name for newplot output
my $newplot_file2;
my $i;               # Counting variable
my $spin_state;
my $key;
my $sbz_start;
my $sbz_stop;
my $ldos_directory;
my $embd_delta;
my $k;

##### Arrays #####

my @segf5;           # Stream 5 input file for SEGF
my @ldos_file;       # Stores each line of LDOS input file
my @chden_file;

my @spin = ( 'majority', 'minority' );

##### Hash #####

my %sbz = (
  square => {
    lines_of_symmetry => {
      delta => [ 'gamma_bar', 'x_bar' ],
      y     => [ 'x_bar',     'm_bar' ],
      sigma => [ 'm_bar',     'gamma_bar' ],
    },
    gamma_bar => [ 0.0, 0.0 ],
    x_bar     => [ 0.5, 0.0 ],
    m_bar     => [ 0.5, 0.5 ],
  },
);

##### Main #####

open( DATA, "chden_plotting_data" );

```

```

chop( $sbz_type           = <DATA> );
chop( $spin_type          = <DATA> );
chop( $fermi_level        = <DATA> );
chop( $ldos_directory_top_level = <DATA> );
chop( $data_file_name_prefix = <DATA> );
chop( $segf_executable    = <DATA> );
chop( $segf_input_file    = <DATA> );
chop( $embd_executable    = <DATA> );
chop( $embd_input_file    = <DATA> );
chop( $embd_bulk          = <DATA> );

if ( $spin_type == 2 ) {
    chop( $embd_input_file2 = <DATA> );
    chop( $embd_bulk2      = <DATA> );
}

chop( $newplot_executable = <DATA> );
chop( $newplot_in1       = <DATA> );    # sets view point 1
chop( $newplot_in2       = <DATA> );    # sets view point 2

if ( $spin_type == 2 ) {
    chop( $newplot_in1_minority = <DATA> );
    chop( $newplot_in2_minority = <DATA> );
}

open( SEGF5, "$segf_input_file" );
@segf5 = <SEGF5>;
close SEGF5;
$segf_emb = $segf5[6];
chop($segf_emb);

if ( $spin_type == 2 ) {
    $segf_emb2 = $segf5[7];
    chop($segf_emb2);
}

$dir = cwd();

foreach $spin_state (@spin) {

    # loop over each line of high symmetry in the Surface BZ
    foreach $key ( sort keys %{ $sbz{$sbz_type}->{lines_of_symmetry} } ) {

        $sbz_start    = @{ $sbz{$sbz_type}->{lines_of_symmetry}->{$key} }[0];
        $sbz_x_start  = $sbz{$sbz_type}->{$sbz_start}->[0];
        $sbz_y_start  = $sbz{$sbz_type}->{$sbz_start}->[1];

        $sbz_stop     = @{ $sbz{$sbz_type}->{lines_of_symmetry}->{$key} }[1];
        $sbz_x_stop   = $sbz{$sbz_type}->{$sbz_stop}->[0];
        $sbz_y_stop   = $sbz{$sbz_type}->{$sbz_stop}->[1];

        $sbz_x = $sbz_x_start;
        $sbz_y = $sbz_y_start;
    }
}

```

```

$sbz_xstep = ( $sbz_x_stop - $sbz_x_start ) / 10;
$sbz_ystep = ( $sbz_y_stop - $sbz_y_start ) / 10;

$newdir = "$sbz_start" . "_to_" . "$sbz_stop" . "_" . "$spin_state";
mkdir( $newdir, 0775 );
$newdir = "$dir" . "/" . "$newdir";

for ( $file_num = 0; $file_num <= 10; $file_num++ ) {

    $ldos_directory = "$ldos_directory_top_level" . "/"
        . "$sbz_start" . "_to_"
        . "$sbz_stop" . "_"
        . "$spin_state";
    if ( !-d $ldos_directory ) {
        die "Cannot find $ldos_directory: $!\n";
    }

    $file = $file_num * 2;
    if ( $file < 10 ) {
        $file = "0" . "$file";
    }
    $file_full = "$ldos_directory/" . "bzrun" . "$file" . "mt_1";
    $peak_count = 0;

    $chden_dir = "$newdir/" . "bzrun" . "$file" . "mt_1";
    mkdir( $chden_dir, 0777 );

    open( FILE, "$file_full" );

    # $ldos_count = `wc -l < $file_full`;
    @ldos_file = <FILE>;
    close FILE;

    $ldos_data_file = "$chden_dir" . "_data_file";
    open( LDOS_DATA, ">$ldos_data_file" );

    # Loop over the LDOS file and find peaks in the LDOS
    for ( $i = 2; $i < ( $#ldos_file + 1 ); $i++ ) {

        ( $hartree_energy, $ldos ) = split( /\s+/, $ldos_file[$i] );
        ( $he_minus, $ldos_minus )
            = split( /\s+/, $ldos_file[ $i - 1 ] );
        ( $he_plus, $ldos_plus )
            = split( /\s+/, $ldos_file[ $i + 1 ] );

        if ( $ldos > 0.2
            && $ldos > $ldos_minus
            && $ldos > $ldos_plus )
        {

            print LDOS_DATA "$hartree_energy $ldos\n";

            if ( $peak_count < 10 ) {
                $newplot_file = "chden_math_peak_0"

```

```

        . "$peak_count"
        . "_view1"
        . "_bzrun" . "$file";
    }
    else {
        $newplot_file = "chden_math_peak_"
        . "$peak_count"
        . "_view1"
        . "_bzrun" . "$file";
    }

    if ( $peak_count < 10 ) {
        $newplot_file2 = "chden_math_peak_0"
        . "$peak_count"
        . "_view2"
        . "_bzrun" . "$file";
    }
    else {
        $newplot_file2 = "chden_math_peak_"
        . "$peak_count"
        . "_view2"
        . "_bzrun" . "$file";
    }

    if ( $spin_state eq 'minority' ) {
        $embd_delta = 0.001;
    }
    else {
        $embd_delta = 0.00001;
    }

    $k = 0;

    while ( !-e "$chden_dir/$newplot_file" . '.eps'
        || ( stat("$chden_dir/$newplot_file.eps") ) [7]
        < 100000 )
    {

# run embd and generate embedding potential around the ldos
        embed_run(
            $sbz_x,          $sbz_y,
            $hartree_energy, $fermi_level,
            $embd_executable, $embd_input_file,
            $embd_bulk,      $segf_emb,
            $embd_delta
        );

        if ( $spin_type == 2 ) {
            embed_run(
                $sbz_x,          $sbz_y,
                $hartree_energy, $fermi_level,
                $embd_executable, $embd_input_file2,
                $embd_bulk2,      $segf_emb2,
                $embd_delta
            );
        }
    }

```

```

    );
}

# run segf to generate charge density data
'$segf_executable < $segf_input_file > segf_log';
unlink 'out12';

#      $count = 'wc -l < fort.20';
open( CHDEN, 'fort.20' );
@chden_file = <CHDEN>;
close CHDEN;

if ( $spin_type == 2 ) {

    open( CHDEN2, '>fort.2' );

    for (
        $count2 = ( $#chden_file + 1 ) / 2;
        $count2 < ( $#chden_file + 1 );
        $count2++
    )
    {
        print CHDEN2 $chden_file[$count2];
    }

    close CHDEN2;
}

if ( $spin_state eq 'minority' ) {
    move 'fort.2', 'fort.1';
}
else {
    move 'fort.20', 'fort.1';
}

# run newplot to generate charge density points

if ( $spin_state eq 'majority' ) {
    newplot_run(
        $newplot_in1,    $newplot_executable,
        $newplot_file,   $chden_dir,
        $sbz_x,          $sbz_y,
        $hartree_energy, $embd_delta
    );

    newplot_run(
        $newplot_in2,    $newplot_executable,
        $newplot_file2,  $chden_dir,
        $sbz_x,          $sbz_y,
        $hartree_energy, $embd_delta
    );
}
else {

```

```

        newplot_run(
            $newplot_in1_minority, $newplot_executable,
            $newplot_file,         $chden_dir,
            $sbz_x,                 $sbz_y,
            $hartree_energy,        $embd_delta
        );

        newplot_run(
            $newplot_in2_minority, $newplot_executable,
            $newplot_file2,        $chden_dir,
            $sbz_x,                 $sbz_y,
            $hartree_energy,        $embd_delta
        );
    }

    $k++;
    if ( $spin_state eq 'minority' ) {
        $embd_delta = 0.002 * $k;
    }
    else {
        $embd_delta = 0.0005 * $k;
    }

    print "$k $embd_delta\n";

    if ( $k > 50 ) {
        last;
    }

}

$peak_count++;

}

}

close LDOS_DATA;
$sbz_x = $sbz_x + $sbz_xstep;
$sbz_y = $sbz_y + $sbz_ystep;

}

}

}

##### Subroutines #####

sub embed_run {

```

```

my $e1;
my $e2;
my $LINE;

my $sbx      = shift;
my $sby      = shift;
my $energy    = shift;
my $fe        = shift;
my $exe       = shift;
my $input     = shift;
my $bulk_file = shift;
my $emb       = shift;
my $delta     = shift;

my $embed_energy = ( $energy / 27.212 ) + $fe;

my @embd5;

$e1 = $embed_energy - $delta;
$e2 = $embed_energy + $delta;

copy $bulk_file , "$dir/fort.7";
open( EMBED, "$input" );
@embd5 = <EMBED>;
close EMBED;

open( ETEMP, ">etemp" );
$LINE = 4;

print ETEMP "$embd5[0]";
print ETEMP "$embd5[1]";
print ETEMP "$embd5[2]";

printf ETEMP ( "  %1.6fD+00  %1.6fD+00  1.000000D-05\n", $e1, $e2 );

while ( $LINE < 20 ) {
    print ETEMP "$embd5[$LINE]";
    $LINE++;
}

printf ETEMP ( "  %1.6fD+00  %1.6fD+00  1.000000D+00\n", $sbx, $sby );
close ETEMP;

'$exe < etemp > embd_log';    # runs the embedding executable
move "fort.4", "$emb";
unlink "$dir/fort.7";

}

sub newplot_run {

my $garbage;
my $x1;

```

```

my $x2;
my $y1;
my $y2;
my $xlow;
my $xhigh;
my $ylow;
my $yhigh;

my $input      = shift;
my $exe        = shift;
my $output     = shift;
my $directory  = shift;
my $x          = shift;
my $y          = shift;
my $energy     = shift;
my $delta      = shift;

'$exe < $input > newplot_log';

open( CHDEN_FILE, "fort.7" );
open( CHDEN_MATH, ">$directory/$output" );

print CHDEN_MATH "Needs[\"Graphics'MultipleListPlot'\"];\n";
print CHDEN_MATH "chdengraph = MultipleListPlot[\n";

$_ = <CHDEN_FILE>;
chop($_);
( $garbage, $x1, $y1, $x2, $y2 ) = split(/\s+/);
print CHDEN_MATH "{{{$x1,$y1},{$x2,$y2}},\n";
$xlow = $x1;
$ylow = $y1;
$xhigh = $x2;
$yhigh = $y2;

# reads points to plot
while (<CHDEN_FILE>) {
    chomp;
    ( $garbage, $x1, $y1, $x2, $y2 ) = split(/\s+/);
    print CHDEN_MATH "{{{$x1,$y1},{$x2,$y2}},\n";

    if ( $xlow > $x1 ) {
        $xlow = $x1;
    }
    if ( $xlow > $x2 ) {
        $xlow = $x2;
    }

    if ( $ylow > $y1 ) {
        $ylow = $y1;
    }
    if ( $ylow > $y2 ) {
        $ylow = $y2;
    }
}

```

```

        if ( $xhigh < $x1 ) {
            $xhigh = $x1;
        }
        if ( $xhigh < $x2 ) {
            $xhigh = $x2;
        }

        if ( $yhigh < $y1 ) {
            $yhigh = $y1;
        }
        if ( $yhigh < $y2 ) {
            $yhigh = $y2;
        }
    }

    print CHDEN_MATH "PlotStyle->{{Thickness[0.001]}}\n";
    print CHDEN_MATH
        "FrameLabel->{\\"X Distance (AU)\", \\"Y Distance (AU)\"}\n";
    print CHDEN_MATH ",SymbolShape->None\n";
    print CHDEN_MATH ",PlotJoined->True";
    print CHDEN_MATH
        ",PlotLabel->\\"Charge Density Plot ($x,$y)\\"\\n for
        Energy $energy\\n (Energy Delta = $delta)\\"\\n";
    print CHDEN_MATH
        ",Frame->True,\nPlotRange->{{$xlow,$xhigh},{ $ylow,$yhigh}}\n";
    print CHDEN_MATH ",AspectRatio->1\n";
    print CHDEN_MATH ",ImageSize->{500,500},DisplayFunction->Identity];\n";
    print CHDEN_MATH
        "Export[\\\"$directory/$output.eps\\",chdengraph,\\\"EPS\\"];\\n";

    close CHDEN_FILE;
    close CHDEN_MATH;

    '/usr/local/bin/math < $directory/$output > test_log';
}

```

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