



Self-consistent localized-orbital study of chemisorbed oxygen on Fe(001)
by Hong Huang

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Physics

Montana State University

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Abstract:

The electronic structure and magnetism of a $p(1 \times 1)$ chemisorbed oxygen layer on the Fe(001) surface was studied by the SCLO method. The interface geometry was suggested by a previous LEED analysis. We found a good agreement between the calculated DOS and the UPS data. We found the oxygen atoms have significant bonding to both the surface and subsurface Fe atoms, and atomic bonding pictures were derived. We did not find a magnetically dead layer of Fe surface, consistent with the spin-resolved photo emission experiments on Fe-based glass. The calculated work function change disagrees with the experiments, and this may be due to oxygen incorporation. The surface-state bands were predicted. Comparing these bands with ARPES may clarify the chemisorption/oxidation model.

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OF CHEMISORBED OXYGEN ON FE(001)

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A thesis submitted in partial fulfillment
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of
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in
Physics

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of a thesis submitted by

Hong Huang

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TABLE OF CONTENTS

	page
APPROVAL.....	ii
STATEMENT OF PERMISSION TO USE.....	iii
ACKNOWLEDGMENT.....	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
ABSTRACT.....	viii
CHAPTER 1. INTRODUCTION.....	1
CHAPTER 2. METHODOLOGY.....	11
Slab Model.....	11
Local Density Approximation.....	14
Matrix Form of the Schrodinger Equation.....	20
Gaussian Expansion of Atomic Wave Function and Potential.....	23
Starting-matrix Calculation.....	27
Symmetry.....	36
Self-consistent Iteration.....	51
Lowdin Representation.....	57
CHAPTER 3. RESULTS AND DISCUSSION.....	65
Two-level Bonding Model.....	65
Density of States.....	71
Atomic-orbital Occupancies.....	83
Magnetism.....	88
Charge and Spin Densities.....	89
Surface-state Bands.....	90
CHAPTER 4. SUMMARY AND FUTURE WORK.....	97
Summary.....	97
Suggestions for Future Study.....	98
REFERENCES CITED.....	100

LIST OF TABLES

	page
1. Atomic Wave Function and Point Group Representation.....	40
2. Representation matrices for C_{4v} Group.....	44
3. Representation matrix for Z-Reflection Group.....	45
4. Occupation Numbers for Fe, and O/Fe, Slabs.....	86
5. Magnetic Moments for Fe, and O/Fe, slabs.....	87

LIST OF FIGURES

	page
1. Slab model for p(1x1) O/Fe(001). Side View.....	12
2. Slab Model for p(1x1) O/Fe(001).Top view.....	13
3. Application of C_{4v} Symmetry.....	46
4. Application of Z-Reflection Symmetry.....	47
5. Two-level Bonding. Weak Coupling.....	69
6. Two-level Bonding. Strong Coupling.....	70
7. Layer-projected DOS's of O/Fe(001).....	76
8. Surface 3d-orbital DOS's of O/Fe(001).....	77
9. Subsurface 3d-orbital DOS's of O/Fe(001).....	78
10. Central-layer 3d-orbital DOS's of O/Fe(001).....	79
11. Planar Bonding I.....	80
12. Planar Bonding II.....	81
13. Vertical Bonding.....	82
14. Charge-density Contours.....	93
15. Spin-density Contours.....	94
16. Symmetric Surface Bands.....	95
17. Antisymmetric Surface Bands.....	96

ABSTRACT

The electronic structure and magnetism of a $p(1 \times 1)$ chemisorbed oxygen layer on the Fe(001) surface was studied by the SCLM method. The interface geometry was suggested by a previous LEED analysis. We found a good agreement between the calculated DOS and the UPS data. We found the oxygen atoms have significant bonding to both the surface and subsurface Fe atoms, and atomic bonding pictures were derived. We did not find a magnetically dead layer of Fe surface, consistent with the spin-resolved photoemission experiments on Fe-based glass. The calculated work function change disagrees with the experiments, and this may be due to oxygen incorporation. The surface-state bands were predicted. Comparing these bands with ARPES may clarify the chemisorption/oxidation model.

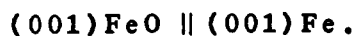
CHAPTER 1

INTRODUCTION

One of the major goals of surface science is to understand the microscopic mechanism of chemical corrosion, for which O/Fe is a very important example. The study of this system, however, was not possible until a few decades ago when ultra-high-vacuum techniques began to be applied so that the oxidation processes could be brought under control. Since then, extensive studies [1-15] have been performed on this system, both experimentally and theoretically. It is generally agreed that the dissociative chemisorption of oxygen on iron is the first step of oxidation of Fe, followed by incorporation of O into the selvedge to form a two-dimensional oxide. Finally this thin oxide layer begins to grow inward towards the bulk. However, there is no consensus regarding the adsorbed structure, the saturation coverage, the sticking probability, and the nature of the oxidation products, etc. Several experimental studies have been reported on the chemisorption and oxidation of the Fe(001) surface. Here we review them briefly.

Simmons and Dwyer [5] used low-energy-electron-diffraction (LEED) and Auger-electron spectroscopy (AES) to study the structural changes and kinetics of the oxidation of Fe(001) at room temperature. At first, the clean iron sample showed a sharp p(1x1) LEED pattern. When oxygen was deposited on the surface, half-order c(2x2) LEED spots gradually appeared, and their intensity and sharpness were maximized when AES indicated that half a monolayer of oxygen was formed on the surface. With further exposure (up to 10 L, 1 L=10⁻⁶ Torr-second), the half-order LEED spots gradually went away. The disappearance of the c(2x2) spots occurred simultaneously with the shift of the AES iron peaks. The LEED pattern became p(1x1) at 10 L, but the relative intensity of the integral-order spots was different from the corresponding diffraction features of the clean surface. This can be interpreted as (though the original interpretation of the authors was somewhat different) chemisorbed oxygen at alternate four-fold sites on the Fe(001) surface diffusing to sites beneath the Fe surface, followed by oxide nucleation. The shift of AES iron peaks indicated that the oxide is formed. This oxide, however, is amorphous rather than well ordered. The p(1x1) LEED pattern, therefore, is not due to this oxide but is due to the underlying iron substrate. The experiment also showed that further oxygen

exposure caused gradual weakening of all reflections, and no diffraction features were observed for exposures above 20 L. This is probably due to the fact that the amorphous oxide is thicker than the mean free path of the incident electrons, so no LEED pattern of the underlying Fe can be seen. After heating the sample mildly for a few minutes at this coverage, the $p(1 \times 1)$ LEED pattern showed up again. AES indicated that no change in oxygen concentration occurred during heating. The reappearance of LEED spots is interpreted as the result of a disorder-order transition of FeO. The epitaxial relationship between the FeO oxide layer and the Fe substrate is



AES also indicated that the concentration of oxygen at this stage was about 4 times higher than the value for the $c(2 \times 2)$ oxygen adlayer. This is exactly the amount of oxygen needed to form two layers of FeO with NaCl structure on the Fe substrate. The coincidence of the iron substrate and the oxide overlayer reflections suggests that the oxide has a lattice parameter 4.5% smaller than the value for FeO bulk. So it is expected that this epitaxial structure will change when the oxide layer becomes thicker. After 75 L exposure and mild heating of the sample, in addition to the spots of Fe(001), there

appeared hexagonal LEED spots which suggest an ordered FeO(111) layer epitaxially grown on the Fe(001) surface.

Brucker and Rhodin [8] studied the same system by using ultraviolet photoemission spectroscopy (UPS), LEED, and work-function-change measurements. For exposures less than 1.5 L, they reported little change (a small attenuation) of Fe d-band-peak emission compared to the corresponding data from a clean Fe sample. An additional peak centered about 5.5 eV below E_F appeared due to the 2p band of dissociatively chemisorbed oxygen. The LEED pattern at this stage showed a clear $0\ c(2 \times 2)$ structure on the Fe(001) surface. This was interpreted by the authors as confirming that a half monolayer of oxygen was formed on the Fe surface. The work function at this stage reached its maximum, about 0.2 eV above the clean surface value. For large exposures, the 5.5 eV peak broadened substantially, and the d-band emission was sharply attenuated. At 60 L the photoelectron energy distribution was very similar to that of FeO. Regarding the LEED patterns, further exposure caused the $c(2 \times 2)$ spots to fade out gradually at 4 L, and after that the $p(1 \times 1)$ spots disappeared at 7 L. The LEED pattern changes agreed well with those reported by Simmon and Dwyer, but not the exposures at which the LEED patterns changed. These changes suggest the beginning of the oxidation after 1.5 L.

exposure, and the formation of a few layers of amorphous oxide, as concluded by Simmon and Dwyer. The work function began to decrease after 1.5 L exposure, and reached a minimum value 0.05 eV higher than the work function of the clean Fe surface at 7 L exposure. This corresponds to the incorporation of oxygen beneath the iron surface, which leads to a reversal of the surface dipole, causing the work function to decrease. The authors concluded that below 1.5 L exposure, the system is in the dissociative chemisorption stage. Beyond that, a few layers of FeO are formed. Further exposure leads to the formation of a superstructure and the three-dimensional bulk oxide.

Legg, Jona, Jepson and Marcus [9] performed a LEED analysis in order to study the geometrical aspect of the chemisorption of oxygen on the Fe(001) surface. AES was also used to calibrate oxygen concentration on the surface and to monitor the possible existence of impurities. They reported that no fractional-order LEED spots were observed for oxygen chemisorbed on a clean Fe surface even when they varied oxygen-exposure procedures and thermal histories of the sample in order to produce the oxygen c(2x2) structure reported by other workers (Some faint half-order spots existed, but only when AES indicated the presence of large amounts of carbon on the surface). Exposure to oxygen caused no change in the geometry of the

LEED pattern but only changes in the intensities of the diffracted beams, consistent with the formation of the $0 \times 0 \times p(1 \times 1)$ structure on the Fe(001) substrate surface. The background remained low and contrast high up to 6-10 L, then the background increased and the LEED spots grew progressively broader with increasing exposure. After high exposures of 25 L or more, it was always possible to revert to the $0 \times 0 \times p(1 \times 1)$ structure by annealing it, but they never succeeded in reducing the oxygen concentration below one full monolayer by heating it. They found that 6 L oxygen exposure provided a complete and well ordered $p(1 \times 1)$ O/Fe(001) structure. By dynamical LEED calculation and intensity vs. voltage analysis, they determined that the O-Fe interlayer distance is 0.48 Å, with oxygen atoms occupying the 4-fold hollow sites in close proximity to substrate Fe atoms. The first Fe-Fe interlayer spacing is apparently expanded by 8% compared with bulk metal. This chemisorption model of O/Fe is shown in Fig.1 and Fig.2 except that the 7-layer slab geometry there should be replaced by semi-infinite geometry.

Recently, Sakisaka, Miyano and Onchi [10] used electron-energy-loss-spectroscopy (EELS) in conjunction with LEED, AES, secondary-electron emission spectroscopy (SES), and work-function-change measurements to study chemisorption and initial oxidation of Fe(001). Three

stages of oxidation were identified: (1) dissociative chemisorption below 3 L, (2) incorporation of O atoms into the selvedge between 3 and 20 L, and (3) oxidation above 20 L, leading to the formation of $\gamma\text{-Fe}_2\text{O}_3$. Of special interest is the change in surface electronic properties from that characteristic of the metal to that of the oxide observed by EELS. An energy-loss peak characteristic of the chemisorbed oxygen was observed at 6 eV below 3 L, being ascribed to the transition between the bonding and antibonding states. The clean surface energy-loss peaks at about 5 and 8 eV were weakened substantially at this stage, but the 2 eV energy-loss peak remained unchanged until the exposure was in the range at 3-20 L. The authors interpreted the former peaks as involving $\text{Fe } 3d_{xy, xz, yz}$ and the latter as involving $\text{Fe } 3d_{z^2, x^2-y^2}$. Thus the $\text{Fe } 3d_{xy, xz, yz}$ orbitals play a major role in the chemisorption bond, and for the incorporation process the $\text{Fe } 3d_{z^2, x^2-y^2}$ orbitals are involved. The EELS spectrum in the oxide phase was characterized by peaks due to the $\text{O}^{2-} 2p \rightarrow \text{Fe}^{3+} 3d$ charge-transfer transition. The $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \text{FeO}$ phase transition at 570 C was also confirmed by monitoring an energy-loss peak due to a $d \rightarrow d$ transition. The work-function-change measurement showed that the work function increased steeply up to 3 L, reaching a maximum of $\Delta\Phi = +0.25$ eV at 3 L, then decreased

to a minimum of $\Delta\Phi = +0.02$ eV at 20 L, and finally increased again to a limiting value $\Delta\Phi = 0.4$ eV at 350 L. The initial increase of the work function is due to charge transfer to the chemisorbed oxygen, creating a surface dipole layer, thus increasing the energy barrier for electrons coming out of the surface. The subsequent decrease of the work function is due to the oxygen incorporation, leading to an oxide layer. The final increase of the work function is related to the in-depth oxidation. The work-function-change measurement thus agreed with the three-stage oxidation process confirmed by EELS analysis. The LEED pattern seen at the chemisorption stage is $p(1 \times 1)$, agreeing with the observation of Legg *et al* [9]. However, the coverage calibration, with 3 L exposure corresponding to a coverage of 0.35 and 20 L corresponding to a coverage of 1, does not agree with the calibration of any other group.

After reviewing the results of experimental investigations, it is realized that the geometrical aspect of oxidation is still controversial. For example, it is agreed that at some stage of oxidation there is a $p(1 \times 1)$ structure of the O/Fe(001) system. The question is: does this $p(1 \times 1)$ structure correspond to the chemisorption of oxygen on the Fe(001) surface, or to the incorporation of oxygen beneath the Fe(001) surface, forming amorphous or

ordered FeO? Although we know that the oxygen eventually goes inside the Fe surface, the exact nature, extent and geometry of the oxygen incorporation remains unknown. The task of theoretical investigation, therefore, is to pick some experimental models, to study and possibly to predict the properties of the system, to compare with further experiments, and then to justify or refine the model. We chose the model proposed by Legget et al for oxygen chemisorption on the Fe(001) surface.

A few electronic structure calculations have been performed using cluster models of the O/Fe(001) chemisorption system. In spin-polarized computations for the cluster O-Fe₅, Anderson [13] obtained oxygen 2p levels 6 eV below the highest occupied level, and an equilibrium Fe-O interlayer spacing of 0.48 Å, when the oxygen was placed in the four-fold hollow site. Ribarsky, in an unrestricted Hartree-Fock cluster calculation [14], predicted a vertical spacing of 0.38 Å. In recent X-ray cluster calculations [15], Adachi et al used a 9-atom substrate to study the level structure of O/Fe(001) versus the Fe-O bond site and bond length. For an interlayer spacing near 0.5 Å, three O 2p levels were obtained in the energy range 5 to 7 eV below E_F. The d-band density of states (DOS) was reduced near E_F due to the Fe-O bonding.

None of the calculations reviewed above included the effects of adsorbate-adsorbate interactions in the extended O/Fe(001) system. This interaction broadens the O 2p levels, leading to two-dimensional energy bands. These bands hybridize at general points in the irreducible wedge of the surface Brillouin zone (IBZ) but have definite reflection parity along the Σ and Δ symmetry lines. They should be detectable using angle-resolved photoemission spectroscopy (ARPES) [16]. The use of polarized light in conjunction with the selection rules [17] should aid in their identification.

Here we report calculations of the electronic structure of a p(1x1) O/Fe(001) slab using the self-consistent localized-orbital (SCLO) method developed by Smith, Gay and Arlinghaus [18-20]. In addition to the calculation of O/Fe(001) [21], we also did a number of slab calculations: Ni/Cu(001) [22], Cu/Ni(001) [23], H/Ni(001) [24], Pd/Fe(001) [25], and Fe/Cu(001) [26]. Because this method incorporates an atomic orbital basis, a simple picture of the surface bond can be developed from the numerical results. By treating electron-spin polarization explicitly, we were able to study the magnetic behavior of this system as well as the influence of the magnetism on the bonding and energy band structure. The SCLO method is discussed in detail in the next chapter.

CHAPTER 2

METHODOLOGY

Slab Model

The semi-infinite surface can be simulated theoretically by an atomic slab with infinite extension in the XY (surface) plane and a finite number of layers in the Z direction (normal to surface). See Fig.1 and Fig.2. In our study, we calculated electronic properties of the slab by applying the Schrodinger equation to it without any adjustable parameters. The only physical inputs are the atomic positions m and nuclear charges Z . Atomic positions are assumed to have translation symmetry in the XY plane and reflection symmetry in the Z direction. The slab may be considered thick enough to represent the real surface if the calculated electronic properties at the center layer are bulk like [27,28].

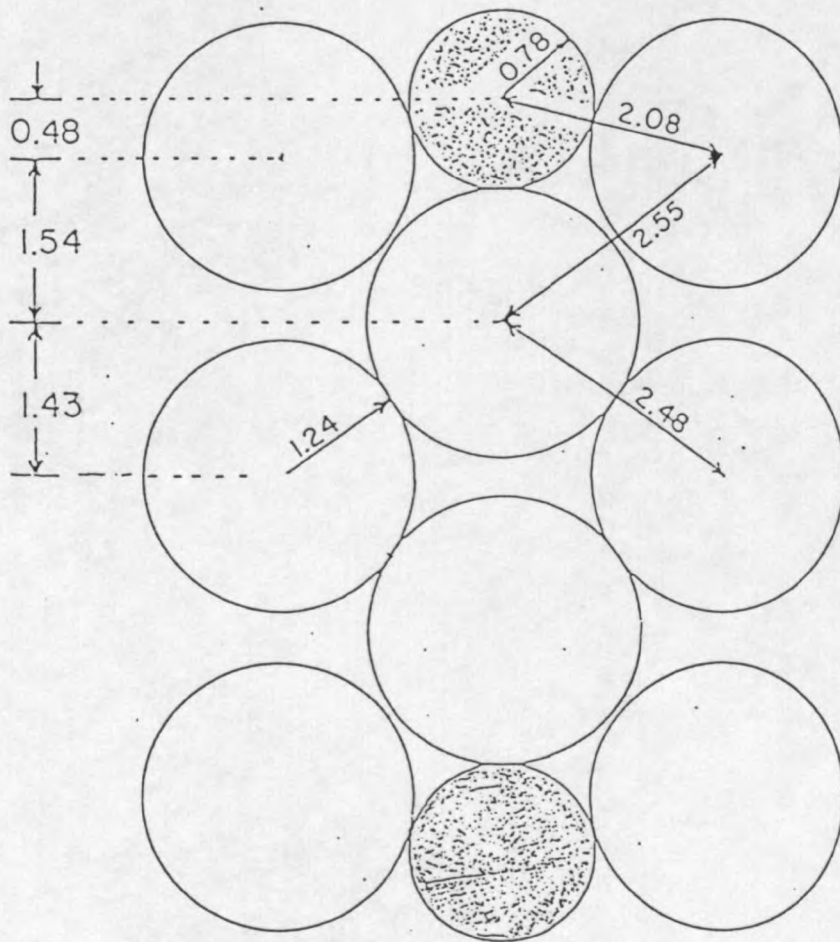


Fig.1 Slab model for p(1x1) O/Fe(001). Side View. Cross section along (110) plane. Distances in angstroms.

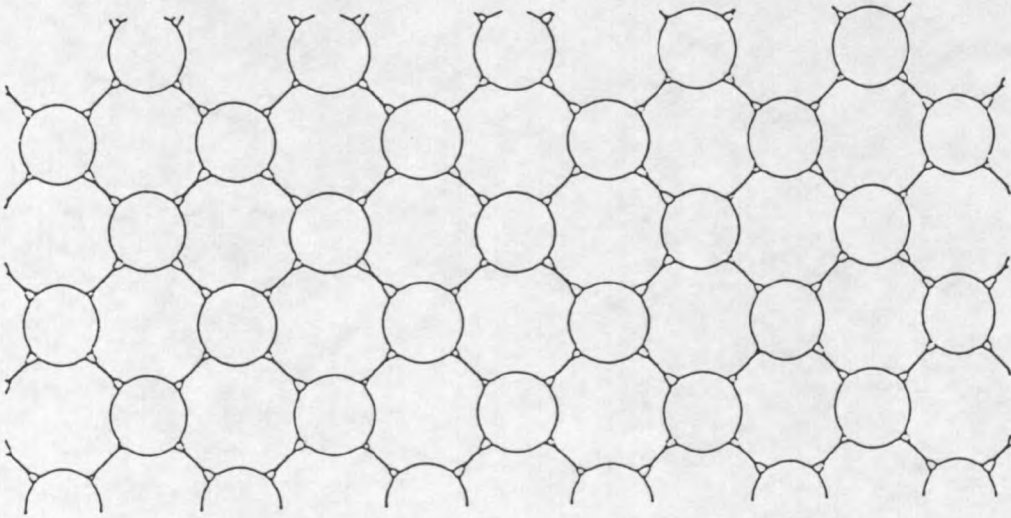


Fig.2 Slab model for p(1x1) O/Fe(001). Top View.

Local Density Approximation

The electronic wave function of the system obeys the Schrodinger equation

$$H \Psi(r_1, s_1, \dots, r_n, s_n) = E \Psi(r_1, s_1, \dots, r_n, s_n), \quad (1)$$

where

$$H = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_m \frac{Z_m}{|r_i - m|} \right) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{r_{ij}}, \quad (2)$$

m is the atomic position and N is the number of electrons in the system. Atomic units (a.u.) are used. This is valid in the non-relativistic approximation, namely, for all elements with atomic number $Z < 50$ [27], thus including 3d and 4d transition metals, which we are most interested in.

In the single-electron approximation, due to Pauli's exclusion principle, the wave function can be written as a Slater determinant

$$\Psi(r_1, s_1, \dots, r_n, s_n) = \frac{1}{(n!)}^{1/2} \times \begin{vmatrix} \phi_1(1) & \dots & \phi_n(1) \\ \vdots & & \vdots \\ \phi_1(n) & \dots & \phi_n(n) \end{vmatrix}, \quad (3)$$

where

$$\phi_i(j) = \psi_i(r_j) \chi_i(s_j), \quad (4)$$

that is, the single-electron wave function is the product of an orbital function and a spin function.

To minimize the total energy of the system $\langle \Psi | H | \Psi \rangle$, the single-electron wave function must obey the Hartree-Fock equation [29,30,31]:

$$\begin{aligned} & [-1/2\nabla^2 - \sum_m Z_m / |r_i - m| + \sum_j \int \psi_j^*(r') \psi_j(r') d^3r' / |r - r'|] \psi_i(r) \\ & - \sum_j [\delta s_i s_j \int \psi_j^*(r') \psi_i(r') d^3r' / |r - r'|] \psi_j(r) = E \psi_i(r). \end{aligned} \quad (5)$$

The first term in this equation is the kinetic energy, the second one is the potential energy due to the nucleus, the third one is the Coulomb interaction potential between electrons, and the fourth one is exchange potential between parallel-spin electrons, due to Pauli's exclusion principle.

In the Local Density Approximation (LDA) [32-35], the exchange potential can be written as a function of the local electron density for each spin:

$$V_{x\uparrow\text{or}\downarrow} = -[(3/\pi)\rho_{\uparrow\text{or}\downarrow}(r)]^{1/3} \quad (6)$$

To derive the above expressions [36], first let us consider the extreme case of a homogeneous electron gas under the influence of a constant potential field. We can use plane waves to represent wave functions:

$$\psi_i(r) = \exp(ik_i \cdot r) \quad (7)$$

Then the exchange term in the Hartree-Fock equation becomes

$$\begin{aligned}
& \sum_j \left[\int \exp(-i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3 r' \right] \exp(i\mathbf{k}_j \cdot \mathbf{r}) \\
&= \left[\sum_j \int \exp(i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}) / r d^3 r \right] \exp(i\mathbf{k}_i \cdot \mathbf{r}) \\
&= 4\pi \left[\sum_{\mathbf{k}_j < \mathbf{k}_F} 1 / (\mathbf{k}_j - \mathbf{k}_i)^2 \right] \psi_i(\mathbf{r}) \\
&\rightarrow 1 / (2\pi^2) \left[\int_{\mathbf{k}_j < \mathbf{k}_F} 1 / (\mathbf{k}_j - \mathbf{k}_i)^2 d^3 \mathbf{k}_j \right] \psi_i(\mathbf{r}) \\
&= (\mathbf{k}_F / \pi) F(\mathbf{k}_i / \mathbf{k}_F) \psi_i(\mathbf{r}) \tag{8}
\end{aligned}$$

where

$$F(x) = 1 + [(1-x^2)/2x] \ln |(1+x)/(1-x)|. \tag{9}$$

The exchange energy term is k_i -dependent. There are several ways to average this k_i -dependence, for example, inside the Fermi sphere $k_i < k_F$, which is the Slater approximation and which gives $\langle F \rangle = 1.5$ [37], or at the Fermi sphere $k_i = k_F$, which is the Kohn-Sham approximation and which gives $\langle F \rangle = 1$ [33]. We use the latter since it can be derived, alternatively, based on the variational principle thus in a more rigorous way [33].

The value of the Fermi wavevector is related to the charge density by

$$k_F = (3\pi^2 \rho)^{1/3} \tag{10}$$

for each spin since the summation in the exchange term of Eq.(5) is over a particular spin only. So the exchange energy for the homogeneous electron gas is given by the Eq.(6).

Now we consider the electrons moving in a slowly varying potential field. The fundamental assumption is that the above expression for exchange energy of a homogeneous system is valid locally even in the case of a slowly varying inhomogeneous system. This is the essential idea behind the Thomas-Fermi method for atoms [38,39]. It is expected that the LDA will be a good approximation for solids in the interstitial region, where the potential and the electron density do change slowly and where most of the charge rearrangement occurs when the solid is formed from isolated atoms.

The LDA is not only an approximation for the Hartree-Fock exchange potential, it also incorporates many-body correlation effects. The motion of electrons is highly correlated. Following each electron as it moves through the system is a depression in the distribution of other electrons. The depression is called the exchange-correlation hole. In the Hartree-Fock equation, the instantaneous interaction between any pair of electrons $1/r_{ij}$ is treated as the interaction between one electron and the distribution of another electron. In particular,

the two antiparallel-spin electrons are allowed to be at the exactly same space point (Slater determinant for two antiparallel-spin electrons does not vanish when $r_1=r_2$) which will never happen in the real physical system. Thus Coulomb interaction between electrons is overestimated in this way, especially in the high density region, although for parallel-spin electrons the exchange energy partly makes up this deficiency. Further improvement is needed for both parallel and antiparallel electrons by adding a term called the correlation energy to the Hamiltonian.

The correlation term in LDA is also a function of the local electron density of both spins, ρ_\uparrow and ρ_\downarrow , or equivalently, it is a function of r_s and p , where

$$r_s = [3 / (4\pi \times (\rho_\uparrow + \rho_\downarrow))]^{1/3}, \quad (11)$$

which is the average distance between electrons, and

$$p = (\rho_\uparrow - \rho_\downarrow) / (\rho_\uparrow + \rho_\downarrow), \quad (12)$$

which is the polarization parameter.

Our correlation potential was adapted from studies of the spin-polarized homogeneous electron liquid by Vosko, Wilk and Nusair [40]. They used a Pade technique to interpolate accurate results for the random-phase-approximation (RPA) [40-45] correlation energy, valid for small r_s , to low density, where Monte Carlo results

[46,47] are available. To determine a convenient form of the correlation energy, the paramagnetic correlation energy per electron [40] was first fitted as [48-50]

$$e(r_s, 0) = -AF(r_s/R), \quad (13)$$

where

$$F(x) = (1+x^3) \ln(1+1/x) + 2/x - x^2 - 1/3, \quad (14)$$

A is 48.6 mRy, and R is 15. We also fit the spin stiffness α to Eq.(13) with $A'=31.1$ mRy and $R'=16.4$. The spin-dependent correlation energy can be written as [40]

$$e(r_s, p) = e(r_s, 0) + \alpha p^2 / 2. \quad (15)$$

Then

$$\begin{aligned} & V_{\text{cfor}\downarrow} \\ &= \frac{\partial (p e_c)}{\partial p_{\uparrow} \text{or} \downarrow} \\ &= -A \ln(1+R/r_s) \pm \alpha p + \beta p^2, \end{aligned} \quad (16)$$

where

$$\beta = 1/2 A' \ln(1+R'/r_s) - \alpha. \quad (17)$$

To sum up, in LDA, the single-electron wave function obeys

$$[-1/2\nabla^2 - \sum_{\mathbf{m}} Z_{\mathbf{m}}/|\mathbf{r}-\mathbf{m}| + \int \rho(\mathbf{r}') d^3\mathbf{r}'/|\mathbf{r}-\mathbf{r}'| + V_{\text{xc}}(\rho(\mathbf{r})^{1/2})] \psi(\mathbf{r}) = E \psi(\mathbf{r}). \quad (18)$$

Symbolically,

$$H(\rho(\mathbf{r}))\psi = E\psi. \quad (19)$$

In order to know the wave function, we have to know $\rho(\mathbf{r})$ first. But $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \sum_{\text{occupied}} \psi_i(\mathbf{r})^2. \quad (20)$$

So in order to know $\rho(\mathbf{r})$, we have to know $\psi_i(\mathbf{r})$ first. This indicates we have to solve Eq.(18) self-consistently.

Matrix Form of the Schrodinger Equation

The Schrodinger equation

$$H(\mathbf{r})\psi_j(\mathbf{r}) = E\psi_j(\mathbf{r}) \quad (21)$$

can be written in matrix form with an appropriate choice of basis. The basis functions we choose here are the Bloch lattice sums of atomic wave functions:

$$\phi_i(\mathbf{r}, \mathbf{k}) = \sum_{\mathbf{m}} \exp(-i\mathbf{k}\cdot\mathbf{m}) a_i(\mathbf{r}-\mathbf{m}), \quad (22)$$

where \mathbf{k} is in the irreducible Surface Brillouin Zone, \mathbf{m} is a lattice site within one layer of the slab, and $a_i(\mathbf{r}-\mathbf{m})$ is the i th atomic wave function located at lattice site \mathbf{m} . The subscript i indicates both the atomic orbital and the

layer at which the atom is located. Since d-electrons of transition metals are tightly bound by the nucleus nearby, they behave somewhat like the corresponding atomic d-electrons. Therefore, the introduction of the lattice can be considered as a perturbation. Thus the atomic wave functions are good candidates for the basis set in this case. There are 19 atomic functions for each Fe atom in the cell: 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 5s, and 9 atomic functions for each O atom in the cell: 1s, 2s, 2p, 3s, 3p. Among them the Fe 4p, 5s and the O 3s, 3p orbitals are not occupied in isolated atoms. We add them to increase variational freedom [51] in describing charge rearrangement in the interstitial and surface regions of the solids. The extended virtual orbitals of the surface atom are especially important, for without them we could not describe the charge expansion into vacuum properly, and thus could not get the correct work function. Trial calculation shows that whether or not we include the Fe 4d orbitals is not crucial in the calculation.

The eigenfunction of the Schrodinger equation is expanded into atomic Bloch functions with a given k since k is a good quantum number:

$$\psi_j(r, k) = \sum_i c_{ij} \tilde{\phi}_i(r, k) \quad (23)$$

We plug (22) and (23) into (21), multiply $a_1(r)$ from the left, and perform the integration, obtaining

$$\sum_i [H_{1i}(k) - E_j O_{1i}(k)] c_{ij} = 0, \quad i=1, N \quad (24)$$

where

$$H_{1i}(k) = \sum_m \exp(-ik \cdot M) \langle a_1(r) | H(r) | a_i(r-M) \rangle, \quad (25)$$

$$O_{1i}(k) = \sum_m \exp(-ik \cdot M) \langle a_1(r) | a_i(r-M) \rangle. \quad (26)$$

Symbolically, the equation in matrix form is

$$HC = EOC. \quad (27)$$

This is a generalized diagonalization problem.

After we diagonalize (24) for every k , we get all $\psi_j(k)$ and $E_j(k)$. We then count energy levels $E_j(k)$ from low to high up to the total number of the valence electrons (the meaning of valence electron, as opposed to core electron, will be explained later) of the slab cell times the number of k points. Summing over all occupied states, we get the charge density, and thus the new potential. We keep running until the potential is self-consistent.

Gaussian Expansion of Atomic Wave Function and Potential

In the central-field approximation, the atomic wave function can be written as [29]

$$a(r) = R_{n,1}(r) Y_{1,m}(\theta, \phi), \quad (28)$$

where

$$R_{n,1}(r) = \sum_j D_{n,j} g_1(\alpha_j, r), \quad (29)$$

$$g_1(\alpha_j, r) = \frac{2^{1+7/4} \alpha_j^{1/2+3/4}}{\pi^{1/4} [1 \times 3 \times \dots \times (2l+1)]^{1/2}} r^1 \exp(-\alpha_j r^2), \quad (30)$$

and $g_1(\alpha_j, r)$ is a normalized radial Gaussian primitive [52]. What we want is a set of α_j and D_j ($j=1, N$) which best represents an atomic wave function with a given, finite N .

The procedure to get these α 's and D 's is as follows:

- 1) Solve the LDA Equation for an atom with a spherically symmetric potential $V(r)$,

$$V(r) = -Z/r + (4\pi/r) \int \rho(r') r'^2 dr' + V_{xc}(r), \quad (31)$$

obtaining the self-consistent $V(r)$ numerically [53].

- 2) Choose α 's for the Gaussian basis set as

$$\alpha_j = \alpha_1 \beta^{j-1} \quad j=1, N \quad (32)$$

These are even-tempered Gaussians [52] which almost cover the whole spectrum of relevant Gaussians.

- 3) Resolve the atomic LDA equation with matrix form [54] using the given Gaussian basis set:

$$\sum_j (H_{ij} - ES_{ij})D_j = 0, \quad i=1, N \quad (33)$$

obtaining $E_1 < E_2 < \dots < E_n$ and the corresponding D 's.

- 4) Vary α_1 and β , repeating 2) 3) above to minimize E_1 , to get the best α 's and D 's for Ψ_1 (1s).
- 5) Add two more Gaussians to the above basis, solve the $N+2$ dimensional equation of the atom, vary α_{n+1} and α_{n+2} to minimize E_2 , and use the Schmidt procedure to make this best 2s function orthogonal to the 1s function.
- 6) Repeat the procedure for all occupied atomic wave functions for a given angular momentum.
- 7) Repeat the procedure for all occupied atomic wave functions with different angular momenta.
- 8) Add virtual orbitals for s and p functions (a single diffuse Gaussian for each orbital) to provide maximum variational freedom in describing charge rearrangement when the atomic slab is constructed.

This describes how we obtain the atomic wave functions. Under the assumption of atomic configurations ($3d^7 4s^1$ for Fe and $2s^2 2p^4$ for O), we can determine the atomic charge

distribution, and therefore the atomic potential. The atomic potential can be separated into two parts [55]: the first one contains a singularity at the origin, and the second is finite everywhere, so it can be expanded into Gaussians:

$$V(r) = V_1(r) + V_2(r), \quad (34)$$

$$V_1(r) = -(Z/r) \exp(-r^2), \quad (35)$$

$$V_2(r) = (Z/r)(1 - \exp(-r^2)) + V_{\text{Coulomb}} + V_{\text{xc}}. \quad (36)$$

Now we are ready to expand V_2 into Gaussians. But before doing that, we first rename $V_2(r)$ as $V(r)$, and name its expansion as $V'(r)$:

$$V'(r) = \sum_j D_j g(\alpha_j, r), \quad (37)$$

where the α 's obey Eq. (32), that is, they are even-tempered Gaussians.

A least-squares-fitting procedure is used to optimize the expansion. That is, we try to find $V'(r)$ such that

$$\int [V(r) - V'(r)]^2 \omega(r) r^2 dr = \text{Min}, \quad (38)$$

where $\omega(r)$ is a weighting factor, and we set $\omega(r) = r$.

$V(r)$ and $V'(r)$ have to obey

$$\int V(r)^2 \omega(r) r^2 dr = \int V'(r)^2 \omega(r) r^2 dr = \text{Const}. \quad (39)$$

(38) with (39) is equivalent to

$$\int V(r)V'(r)\omega(r)r^2 dr = \text{Max.} \quad (40)$$

When (37) is used to expand $V'(r)$ in (40), we have

$$I(\alpha, D) = \sum_j D_j \int V(r)g(\alpha_j(r))\omega(r)r^2 dr = \sum_j D_j P_j = \text{Max.}, \quad (41)$$

where

$$P_j = \int V(r)g(\alpha_j, r)\omega(r)r^2 dr. \quad (42)$$

Squaring (40), we have

$$I^2(\alpha, D) = \sum_i \sum_j D_i D_j P_i P_j = \text{Max.} \quad (43)$$

(37) is also used to expand (39), and we have

$$\begin{aligned} & \sum_i \sum_j D_i D_j \int g(\alpha_i, r)g(\alpha_j, r)\omega(r)r^2 dr \\ &= \sum_i \sum_j D_i D_j S_{ij} = \text{Const.}, \end{aligned} \quad (44)$$

where

$$S_{ij} = \int g(\alpha_i, r)g(\alpha_j, r)\omega(r)r^2 dr. \quad (45)$$

Subtracting $\omega \times (44)$ from (43) ($\omega = \text{Constant}$), we have

$$F(D_1, \dots, D_n) = \sum_i \sum_j D_i D_j (O_{ij} - \omega S_{ij}) = \text{Max.}, \quad (46)$$

where $O_{ij} = P_i P_j$.

Differentiating F with respect to all D 's, and setting the results equal to 0, we have the secular equation

$$\sum_j (O_{ij} - \omega S_{ij}) D_j = 0. \quad i=1, N \quad (47)$$

By solving (47), we find D 's corresponding to maximum ω and F .

As in the wave function fitting, we vary α to get $\text{Max}(\omega_{\text{max}})$.

We then repeat the procedure for the expansion of V_{xc} .

Starting-matrix Calculation

The starting-matrix calculation is a very important step in the whole calculation. Without the right starting Hamiltonian matrix, the iteration would take longer computing time. Furthermore, it could be trapped at wrong points.

Since the solid is formed by bringing isolated atoms together, it is natural to begin with the atomic charge distribution,

$$\rho_0(\mathbf{r}) = \sum_m \rho_{\text{atom}}(\mathbf{r}-\mathbf{m}). \quad (48)$$

Notice that

$$V_{xc}(\mathbf{r}) = V_{xc}(\rho_0(\mathbf{r})^{1/3}) \quad (49)$$

is a non-linear function of the lattice sum of the charge density (48). (49) with (48) is called the overlapping-atomic-charge potential. So (49) will not equal the lattice sum of individual atomic potentials

The potential $V(r)$ consists of two parts (48, 50):

$$V_{xc}(r) = \sum_m v_{xc}(\rho(r-m)^{1/3}), \quad (50)$$

which is called the overlapping atomic potential. If we take the overlapping atomic potential as the starting potential for mathematical convenience, we have to compensate for that by adding a term equal to the difference between the overlapping-atomic-charge potential (50) and the overlapping atomic potential (49).

The starting matrix consists of four terms:

$$1) \langle a_i(r) | -1/2\nabla^2 | a_j(r-n) \rangle \quad (51)$$

$$2) \langle a_i(r) | [\sum_m v(r-m)] \exp(-r\gamma^2) | a_j(r-n) \rangle \quad (52)$$

$$3) \langle a_i(r) | [\sum_m v(r-m)] (1 - \exp(-r\gamma^2)) | a_j(r-n) \rangle \quad (53)$$

$$4) \langle a_i(r) | V_{xc}[\sum_m \rho(r-m)] - \sum_m v_{xc}[\rho(r-m)] | a_j(r-n) \rangle \quad (54)$$

where γ is chosen as 0.15.

All wave functions are expanded into Kubic-Harmonic-Gaussians

$$G(r) = g(r)K(x, y, z) \quad (55)$$

where K is a Kubic Harmonic [39], or linear combination of Spherical Harmonics, such as

$$S, X, Y, Z, 3Z^2-R^2, X^2-Y^2, XZ, YZ, XY.$$

The potential $V(r)$ consists of two parts (34,35,36): $-(Z/r)\exp(-r^2)$, which diverges at the origin, and a non-singular part, which is expanded into Gaussians.

Term 1 is the kinetic energy, term 2 is the screened overlapping atomic potential, term 3 is the difference between screened and unscreened potentials, and term 4 is the difference between the overlapping-atomic-charge potential and the overlapping atomic potential.

Before we go into calculation of Term 1 and 2, we would like first to examine how an integral, with two Gaussians located at different sites (called a two-center integral),

$$I = \int \exp(-\alpha r^2) \exp(-\beta(r-n)^2) d^3r, \quad (56)$$

can be done analytically.

This integral can be decomposed as the product of 3 terms with the same integrand form, that is, the product of three two-center integrals:

$$I = I_x \times I_y \times I_z, \quad (57)$$

where

$$I_x = \int \exp(-ax^2) \exp(-\beta(x-x_n)^2) dx, \quad (58)$$

and similar expressions hold for I_y and I_z .

It is not difficult to show that

$$\begin{aligned} I_x &= \exp[-(\alpha\beta/(\alpha+\beta))n_x^2] \int \exp(-(\alpha+\beta)(x-\beta n_x/\alpha+\beta)^2) dx \\ &= (\pi/\alpha)^{1/2} \exp[-(\alpha\beta/(\alpha+\beta))n_x^2], \end{aligned} \quad (59)$$

and similar results hold for I_y and I_z .

Thus a two-center integral is reduced to a one-center integral, which can be done in closed form. Similarly, a three-center integral, which is involved in term 2, can be reduced to two-center form, and then to one-center form.

The two- and three-center Gaussian integrals which include multiplicative polynomials (Kubic Harmonics are linear combinations of the polynomials), for example,

$$I = \int x \exp(-\alpha r^2) (y-y_n) \exp(-\beta(r-n)^2) d^3r, \quad (60)$$

can also be calculated in closed form [56-58].

The above conclusion is also valid for three-center integrals with the singular part of the potential at one of the centers [56-58]

$$I = \langle G_i(r) | \exp(-(r-m)^2) / |r-m| | G_j(r-n) \rangle. \quad (61)$$

The second derivative of G is a linear combination of polynomial-multiplied Gaussians:

$$\begin{aligned}
& \nabla^2 G(\mathbf{r}) \\
& = \nabla^2 g(\mathbf{r}) K_j(\mathbf{x}, \mathbf{y}, \mathbf{z}) \\
& = \sum_{\mathbf{l}} C_{\mathbf{l}} g(\mathbf{r}) P_{\mathbf{l}}(\mathbf{x}, \mathbf{y}, \mathbf{z}). \tag{62}
\end{aligned}$$

Then, since

$$a_i(\mathbf{r}) = \sum_{\mathbf{m}} D_{i,\mathbf{m}} G_{i,\mathbf{m}}(\mathbf{r}), \tag{63}$$

the kinetic energy term (51) may be written as

$$-(1/2) \sum_{\mathbf{m}} \sum_{\mathbf{n}} \sum_{\mathbf{l}} D_{i,\mathbf{m}} D_{j,\mathbf{n}} C_{\mathbf{l},\mathbf{j},\mathbf{n}} \langle G_{i,\mathbf{m}}(\mathbf{r}) | g_{\mathbf{n}}(\mathbf{r}-\mathbf{n}) P_{\mathbf{l},\mathbf{j},\mathbf{n}}(\mathbf{r}-\mathbf{n}) \rangle. \tag{64}$$

Once we know the integrals $\langle G_i(\mathbf{r}) | g(\mathbf{r}-\mathbf{n}) P_j(\mathbf{r}-\mathbf{n}) \rangle$, which are in fact worked out and tabulated [56-58], only algebraic manipulation is needed in order to calculate the kinetic energy term. No numerical integration is needed, which, in the case of very localized wave function, would be very time-consuming because a very fine mesh would be required to describe such wave functions.

The same is true for the potential energy calculation (52) except that a three-center-integral tabulation [56-58] is used and we need to sum over all atomic sites contributing to the potential. No numerical integration is involved in this case either. That is the reason why we expand the atomic wave function and atomic potential into Gaussians [59].

In the calculation of the potential term (52), we screened the atomic potential by multiplying it an exponential factor $\exp(-\gamma r^2)$, so that fewer atomic sites contribute to the overlapping atomic potential. But this screening effect is artificial. To include the difference between screened and unscreened potentials we use term 3 (53).

Term 3 is computed by Fourier Transformation. That is, in order to calculate

$$\delta V_{ij}(n) = \langle a_i(r) | \delta V(r) | a_j(r-n) \rangle, \quad (65)$$

we first calculate

$$\delta V(Q) = 1/V_{\text{cell}} \int_{\text{cell}} \delta V(r) \exp(-iQ \cdot r) d^3r \quad (66)$$

and

$$S_{ij}(n, Q) = \langle a_i(r) \exp(-iQ \cdot r) | a_j(r-n) \rangle. \quad (67)$$

Then, by summing over Q space, we get

$$\begin{aligned} \delta V_{ij}(n) \\ = \sum_Q \delta V(Q) S_{ij}(n, Q). \end{aligned} \quad (68)$$

$S_{ij}(n, Q)$ is also a kind of two-center integral, and it can be integrated in closed form [58].

Since $\delta V(r)$ is a slowly varying function in real space, $\delta V(Q)$ will vanish at large Q (large Q means rapid

oscillation in the integrand, leading to phase cancellation). It is this slowly varying property which makes it possible to expand $\delta V(r)$ into plane waves with only a modest number of Q 's:

$$\begin{aligned}
 \delta V(Q) &= 1/V_{\text{cell}} \int_{\text{cell}} \left[\sum_{m=-\infty}^{\infty} \delta v(r-m) \right] \exp(-iQ \cdot r) d^3r \\
 &= 1/V_{\text{cell}} \int_{\infty} \left[\sum_{m=\text{cell}} \delta v(r-m) \right] \exp(-iQ \cdot r) d^3r \\
 &= 1/V_{\text{cell}} \int_{\infty} \left[\sum_{m=\text{cell}} \exp(-iQ \cdot m) \right] \int_{\infty} \delta v(r-m) \exp(-iQ \cdot (r-m)) d^3r \\
 &= 1/V_{\text{cell}} \int_{\infty} \left[\sum_{m=\text{cell}} \exp(-iQ \cdot m) \right] \int_{\infty} \delta v(r) \exp(-iQ \cdot r) d^3r \quad (69)
 \end{aligned}$$

Now $\int \delta v(r) \exp(-iQ \cdot r) d^3r$ is independent of lattice site m , and can be reduced to a one-dimensional numerical integration:

$$\begin{aligned}
 &\int_{\infty} \delta v(r) \exp(-iQ \cdot r) d^3r \\
 &= (2/Q) \int_0^{\infty} V_{\text{atomic}}(r) (1 - \exp(-\gamma r^2)) \sin(Qr) r dr. \quad (70)
 \end{aligned}$$

We also apply the Fourier transformation technique to term 4 (54). In this case, we have to perform a three-dimensional numerical integration to calculate

$$\delta V'(Q) = 1/V_{\text{cell}} \int_{\text{cell}} \delta V'(r) \exp(-iQ \cdot r) d^3r. \quad (71)$$

Fortunately, $\delta V'(r)$, the difference between the overlapping-atomic-charge potential (49) and the

overlapping atomic potential (50), is also slowly varying. Although near the nucleus, both atomic charge and atomic potential have their maximum value and change most rapidly, very little atomic charge overlaps there, which makes $\delta V'(r)$ small. In fact, $\delta V'(r)$ has its largest contribution in the interstitial region where it varies slowly. As the result of this slowly varying nature, we only need to include modest numbers of mesh points, both in real space and reciprocal space for the integrations.

Here we would like to point out that in our matrix element calculation, we did not use the nearest-neighbor approximation, as is often used by other workers. We calculate the matrix element $\langle a_i(r) | H(r) | a_j(r-n) \rangle$ for any i, j, n as small as 10^{-6} (The largest matrix element is of order 10^{+2} , for comparison), no matter how far apart

the atoms are. In fact, we calculate up to 15th nearest neighbors ($|n|=27$ a.u.) for the most diffuse 5s atomic wavefunctions located at the same lattice plane.

Finally, we want to discuss the relation between the number of points in real space and Q space [60]. For simplicity, we only consider the one-dimensional case. The generalization to the three-dimensional case is obvious.

A periodic function in real space with period X can be expanded into a Fourier series as

$$f(x) = \sum_n F(n) \exp(-i2\pi nx/X), \quad (72)$$

where

$$F(n) = (1/X) \int_0^X f(x) \exp(i2\pi nx/X) dx, \quad (73)$$

for $f(x)$ given at continuous x . If, on the other hand, $f(x)$ is given only at discrete x values, as is always true in numerical calculation by computer, $F(n)$ will be changed from an integral to a summation:

$$F(n) = (1/N) \sum_{j=1}^N f((j-1/2)\Delta x) \exp(i2\pi(j-1/2)n/N) \quad (74)$$

where $f(x)$ is sampled at N equally spaced points, and $x_1 = 0.5 \Delta x$, as in our numerical integration.

It is easy to show that

$$F(n+N) = -F(n), \quad \text{for } n=1, N \quad (75)$$

that is, there are only N F 's which are distinct. Thus the number of points in real space equals the number of points in reciprocal space. If the information in the real space is limited, we can not gain more insight by using more points in the reciprocal space.

Symmetry

Here we would like to discuss the symmetry properties of the system. Without using the symmetry, the calculation would be much more time-consuming.

First of all, there is a translation symmetry of the potential in the XY plane, that is, $V(\mathbf{r}+\mathbf{R})=V(\mathbf{r})$, where \mathbf{R} is any lattice-displacement vector in the plane. Thus, we only need to consider one unit cell. Every physically observable quantity behaves exactly the same in any other cell. The wave function in different cells, however, obeys the Bloch condition: $\Psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R})=\exp(-i\mathbf{k}\cdot\mathbf{R})\Psi_{\mathbf{k}}(\mathbf{r})$. Thus we need to introduce a good quantum number, the 2-dimensional \mathbf{k} vector, to represent the wave function. The basis then is \mathbf{k} dependent. The Hamiltonian matrix is block-diagonal in \mathbf{k} . The number of \mathbf{k} vectors, in principle, is infinite for the system with infinite extension. Fortunately, only a few of them (6 special \mathbf{k} points [61] in the irreducible wedge of the surface Brillouin zone (IBZ), or 36 in the whole first surface Brillouin zone), according to our tests, are necessary to iterate to self-consistency, and 45 \mathbf{k} points in the IBZ are needed for the last iteration, based on which we can interpolate the energy and wave function for other \mathbf{k} 's. On the other hand, the introduction of \mathbf{k} makes the effective Hamiltonian [62]

lose its C_{4v} symmetry for a general k point, and this makes diagonalization more difficult.

In the Z direction, there is no translation symmetry, due to the existence of the surface. The unit cell has to include all layers of the slab. That is the reason why we need atomic basis function for every layer, as mentioned above. What we have now for our model is one slab with vacuum at both sides. However, in order to perform the three-dimensional Fourier transformation to calculate charge density and therefore potential, we must repeat the slab in the Z direction. The space between slabs is so large (~ 100 a.u. compared with ~ 5 a.u. between nearest neighbors) that there is no interaction at all between slabs. There is no need to introduce a k vector in the Z direction, or equivalently, there is no $E(k_z)$ dispersion, so we only need to consider $k_z=0$.

The point group of the Hamiltonian of the (100) surface for F.C.C. or B.C.C. crystalline structures is $C_{4v} \times R = D_{4h}$.

The C_{4v} group has 8 symmetry operations and 5 classes. They are:

	E	C_2	C_4	C_4'	σ_h	σ_v	σ_d	σ_d'	
X	X	-X	Y	-Y	X	-X	Y	-Y	
Y	Y	-Y	-X	X	-Y	Y	X	-X	(76)

The R group has 2 symmetry operations. They are:

$$\begin{array}{ccc}
 & E & \sigma_z \\
 Z & Z & -Z
 \end{array} \quad (77)$$

Because of the C_{4v} symmetry of $V(r)$, k 's in the IBZ would be sufficient to represent all k 's involved in V_{eff} in the whole first BZ. For any k which is in the BZ but not in the IBZ we can always perform some kind of C_{4v} operation to place it in the IBZ without changing the physical situation. The only things changed are the XY coordinate which is indeed arbitrary within a 90-degree rotation, and right-left-hand-coordinate convention.

For the effective Hamiltonian $H=E_k+V(r)+K \cdot p$ [62], the C_{4v} symmetry is retained only at Γ and M.

At X the symmetry for V_{eff} is C_{2v} , which has 4 operations and 4 classes. They are:

$$\begin{array}{ccccc}
 & E & C_2 & \sigma_h & \sigma_v \\
 X & X & -X & X & -X \\
 Y & Y & -Y & -Y & Y
 \end{array} \quad (78)$$

At Δ , Σ and Y, the symmetry is reduced to E and σ_h (for Δ) or σ_v (for Y) or σ_d (for Σ):

$$\begin{array}{ccc}
 & E & \sigma_h \\
 X & X & X \\
 Y & Y & -Y
 \end{array} \quad (79)$$

$$\begin{array}{ccc}
 & E & \sigma_v \\
 X & X & -X \\
 Y & Y & Y
 \end{array} \quad (80)$$

$$\begin{array}{ccc}
 & E & \sigma_d \\
 X & X & Y \\
 Y & Y & X
 \end{array} \quad (81)$$

At a general k point, however, there is no point group operation which will leave the effective Hamiltonian invariant. So the only symmetry left is the Z reflection symmetry, which leads us to make even and odd linear combinations of atomic wave functions located at opposite sides of the slab. There is no coupling between these even and odd functions, thus reducing the dimension of the matrix by a factor of 2.

The atomic orbitals belonging to the different representation of the group of the wave vector [62] is shown in Table 1.

Table 1 Atomic Wave Function and Point Group Representation

Point Group	Atomic Wave Function	
	Site(0,0)	Site(c/2,c/2)
Γ_1	$S, Z, 3Z^2 - R^2$	$S, Z, 3Z^2 - R^2$
Γ_2	NULL	NULL
Γ_3	$X^2 - Y^2$	$X^2 - Y^2$
Γ_4	XY	XY
Γ_5	(X, Y) (XZ, YZ)	(X, Y) (XZ, YZ)
M_1	$S, Z, 3Z^2 - R^2$	XY
M_2	NULL	$X^2 - Y^2$
M_3	$X^2 - Y^2$	NULL
M_4	XY	$S, Z, 3Z^2 - R^2$
M_5	(X, Y) (XZ, YZ)	(X, Y) (XZ, YZ)
X_1	$S, Z, X^2 - Y^2, 3Z^2 - R^2$	X, XZ
X_2	XY	Y, YZ
X_3	X, XZ	$S, Z, X^2 - Y^2, 3Z^2 - R^2$
X_4	Y, YZ	XY
Δ_1	$S, X, Z, XZ, X^2 - Y^2, 3Z^2 - R^2$	$S, X, Z, XZ, X^2 - Y^2, 3Z^2 - R^2$
Δ_2	Y, XY, YZ	Y, XY, YZ
Y_1	$S, Y, YZ, X^2 - Y^2, 3Z^2 - R^2$	X, XY, XZ
Y_2	X, XY, XZ	$S, Y, YZ, X^2 - Y^2, 3Z^2 - R^2$
Σ_1	$S, X+Y, Z, XY, XZ+YZ, 3Z^2 - R^2$	$S, X+Y, Z, XY, XZ+YZ, 3Z^2 - R^2$
Σ_2	$X-Y, XZ-YZ, X^2 - Y^2$	$X-Y, XZ-YZ, X^2 - Y^2$

In the irreducible wedge of the first BZ, $[\Delta X Y M \Sigma]$, the knowledge of [76],[77-81] and Table 1 helps us to identify the atomic orbitals involved in any energy level. Furthermore, the band structure can be interpolated between calculated eigenvalues having the same symmetry properties. These interpolated energy bands can then be compared directly with the experimental data obtained from angle-resolved-photoemission spectroscopy.

The Hamiltonian of the system is invariant under all operations of the point group D_{4v} . This fact is applied in the starting-matrix-element calculation. We only need to calculate

$$H_{ij}(n) = \langle a_i(r) | H(r) | a_j(r-n) \rangle \quad (82)$$

for n in $1/8$ of the plane. Then by applying the C_{4v} symmetry of $V(r)$, we can obtain $H_{ij}(n)$ for n in all other parts of the plane. Furthermore, once we know $\langle a_i(r-m) | H(r) | a_j(r-n) \rangle$ for some $n-m$ (Here we changed the origin of the coordinate from the atom where a_i is located to the atom in the central layer), we can easily obtain the corresponding matrix element for $(n'-m')_z = -(n-m)_z$ with $m'_z = -m_z$ and $(n'-m')_{\parallel} = (n-m)_{\parallel}$ by applying the Z-reflection symmetry of $H(r)$. The procedure is the following:

Define

$$H_{ij}(n) = \langle a_i(r) | H(r) | a_j(r-n) \rangle. \quad (83)$$

Performing a C_{4v} operation on r 's, we have

$$H_{ij}(an) = \langle a_i(ar) | H(ar) | a_j(a(r-n)) \rangle. \quad (84)$$

By C_{4v} symmetry of the Hamiltonian, we have

$$H(ar) = H(r). \quad (85)$$

$a_i(a(r-n))$ can be expanded as

$$a_i(a(r-n)) = \sum_p D_{pi}(a) a_p(r-n). \quad (86)$$

So

$$\begin{aligned} & H_{ij}(an) \\ &= \langle \sum_p D_{pi} a_p(r) | H(r) | \sum_q D_{qj} a_q(r-n) \rangle \\ &= \sum_p \sum_q D_{pi}^* D_{qj} H_{pq}(n) \\ &= \sum_p \sum_q (D_{ip})^+ H_{pq}(n) D_{qj}. \end{aligned} \quad (87)$$

In matrix form,

$$H' = D^+ H D. \quad (88)$$

Thus, once we know the transformation properties of the wave function (86), we can easily obtain the transformation properties of matrix elements. By rotating or reflecting the lattice site n involved in the matrix element, the calculated results for lattice site n in the

1/8 of the XY plane can be generalized into the whole plane with only some algebraic manipulation.

An example of this transformation is given in Fig.3.

The coefficients $D(\alpha)$ for all C_{4v} elements α can be easily worked out by applying (76) to all atomic wave functions. Table 2 gives D 's for C_4 and σ_v . For all other operations, the D matrix can be obtained by multiplication of the D 's already known. Thus,

$$C_2 = C_4 \times C_4, \quad (89)$$

$$C_4^3 = C_4 \times C_4 \times C_4, \quad (90)$$

$$E = C_2 \times C_2, \quad (91)$$

$$\sigma_h = C_2 \times \sigma_v, \quad (92)$$

$$\sigma_d = C_4 \times \sigma_h, \quad (93)$$

$$\sigma_d^3 = C_2 \times \sigma_d. \quad (94)$$

A similar argument allows one to apply reflection symmetry $H(-z) = H(z)$ to get $\langle a_i(r-m') | H(r) | a_j(r-n') \rangle$ once we know $\langle a_i(r-m) | H(r) | a_j(r-n) \rangle$ with $(n'-m')_z = -(n-m)_z$, $m'_z = -m_z$ and $(n'-m')_{\parallel} = (n-m)_{\parallel}$. $D(\sigma_z)$ is shown in Table 3.

An example of this transformation is given in Fig.4.

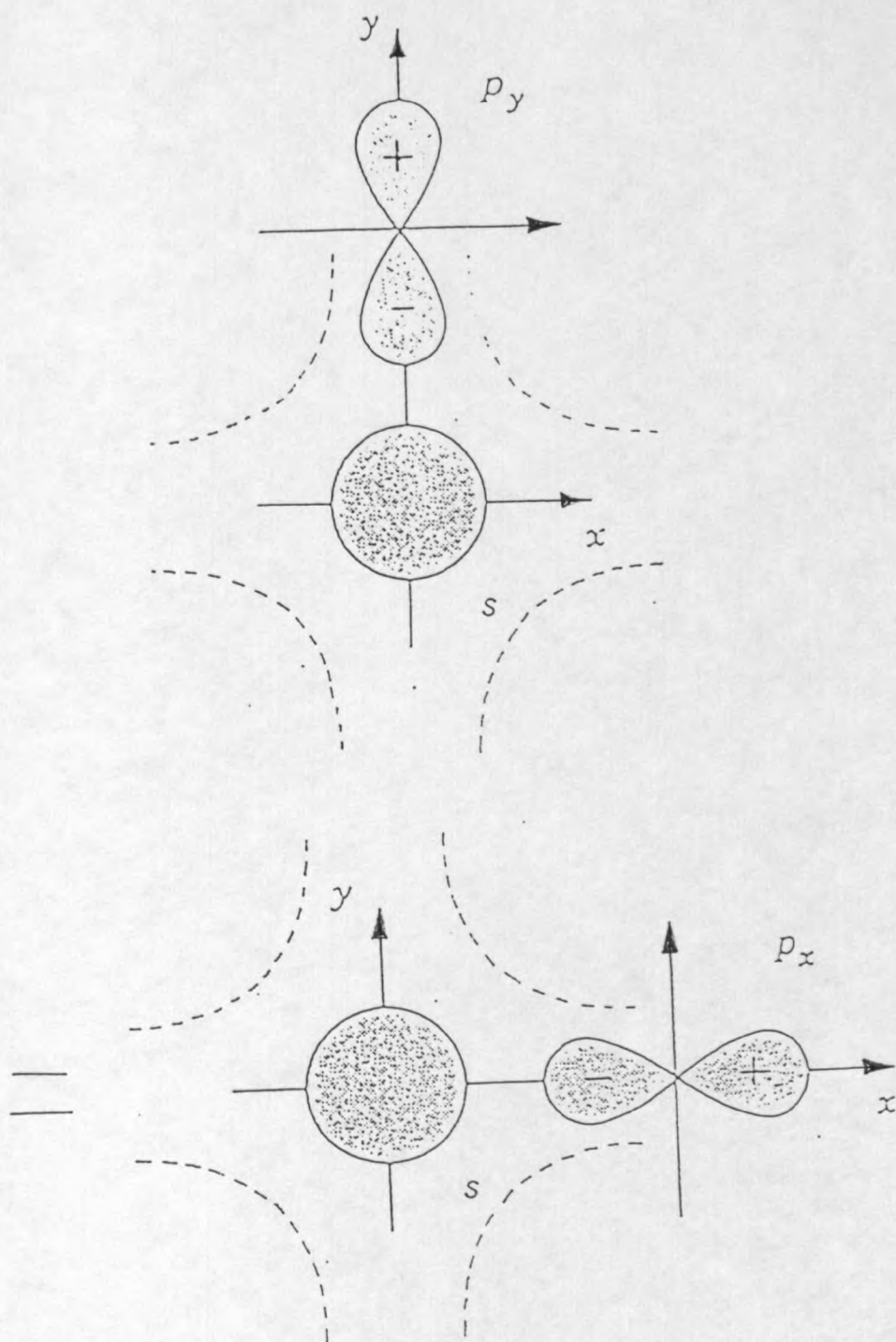


Fig.3 Application of C_{4v} symmetry of the crystal potential in the matrix-element calculation. $\langle s(\mathbf{r}) | H(\mathbf{r}) | p_y(\mathbf{r}-\mathbf{n}) \rangle = \langle s(\mathbf{r}) | H(\mathbf{r}) | p_x(\mathbf{r}-\mathbf{n}') \rangle$, where $\mathbf{n}=(0, a)$ and $\mathbf{n}'=(a, 0)$. Dashed lines represent a C_{4v} -symmetric potential.

