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## Field Adsorption of Hydrogen on Metal Surfaces

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by Xiaoming Ye

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Dalhousie University Halifax, Nova Scotia, Canada May, 1992

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## Contents

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: ',

ę

|   | Lis                                    | t of Figures                               | vi   |  |  |
|---|--|--|------|--|--|
|   | Lis                                    | t of Tables                                | ix   |  |  |
|   | Ab                                     | stract                                     | x    |  |  |
|   | List                                   | t of Symbols                               | xi   |  |  |
|   | Ack                                    | cnowledgements                             | xiii |  |  |
| 1 | Int                                    | roduction                                  | 1    |  |  |
| 2 | Ele                                    | ctric Fields at Metal Surfaces             | 4    |  |  |
|   | <b>2</b> .1                            | Infinite Metal Planes                      | 4    |  |  |
|   | 2.2                                    | Various Tip Geometries                     | ·Ĵ   |  |  |
|   | 2.3                                    | Paraboloidal Tip in Parabolic Coordinates  | 14   |  |  |
|   | 2.4                                    | Hemispherical Protrusion                   | 21   |  |  |
|   | 2.5                                    | Jellium Model                              | 23   |  |  |
|   | 2.6                                    | Metal Atom on Jellium Surface              | 28   |  |  |
|   | 2.7                                    | Jellium Model with Crystal Structure       | 28   |  |  |
|   | 2.8                                    | Charged Clusters                           | 33   |  |  |
| 3 | Theoretical Models of Field Adsorption |  |      |  |  |
|   | 3.1                                    | Field Adsorption on A Jellium Metal        | 43   |  |  |
|   | 3.2                                    | Spin Density Functional Theory of Clusters | 47   |  |  |
|   | 3.3                                    | Electric Field in Cluster Model            | 54   |  |  |

.

,

| 4 | Theoretical Results 5   |   |     |  |  |  |  |  |
|---|---|---|-----|--|--|--|--|--|
|   | 4.1   | $H, H_2, H_3$ and Their Ions $\ldots$                               | 57  |  |  |  |  |  |
|   | 4.2   | Field Adsorption of $H$ on $Rh(111)$                                | 67  |  |  |  |  |  |
|   | 4.3   | Field Adsorption of $H_2$ on $Rh(111)$                              | 80  |  |  |  |  |  |
|   | 4.4   | Field Adsorption of $H_3$ on $Rh(111)$                              | 85  |  |  |  |  |  |
|   | 4.5   | Field Adsorption of NO on Rh Dimer                                  | 90  |  |  |  |  |  |
| 5 | Summary 1   |   |     |  |  |  |  |  |
| A | A An Exact Solution of Laplace's Equation with Boundary Conditions      |   |     |  |  |  |  |  |
|   | at A Finite Tip Surface and Screen in Parabolic Coordinates             |   |     |  |  |  |  |  |
| В | Der   | ivation of One Dimensional Electron Density                         | 108 |  |  |  |  |  |
|   | B.1 Derivation of One Dimensional Electron Density in Cartesian Coordi- |   |     |  |  |  |  |  |
|   |   | nates   | 108 |  |  |  |  |  |
|   | B.2   | Derivation of One Dimensional Electron Density in Cylindrical Coor- |     |  |  |  |  |  |
|   |   | dinates   | 112 |  |  |  |  |  |
|   | Ref   | erences   | 116 |  |  |  |  |  |

•

t }

1

## List of Figures

•

| 1  | A diagram of hyperbolic coordinates.   | 6  |
|----|--|----|
| 2  | Field emitter geometry and equipotential surface   | 8  |
| 3  | Diagram showing the geometry of the tip and its image                                      | 10 |
| 4  | A schematic of the geometry used in the numerical analysis                                 | 12 |
| 5  | Normalised equipotential contours plotted for a specimen modelled as                       |    |
|    | a line(a), and as one with shape(b). $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ | 13 |
| 6  | Parabolic coordinates  | 15 |
| 7  | A sketch of the geometry of parabolic tip  | 20 |
| 8  | Field and potential on hemispherical protrusion  | 22 |
| 9  | A schematic view of flat jellium surface   | 25 |
| 10 | Effective potential and charge density on jellium surface                                  | 26 |
| 11 | Induced charge density distribution on jellium surface                                     | 27 |
| 12 | Electric field strength for $Ti$ and $Nb$ adsorbed on jellium surface                      | 29 |
| 13 | External electrostatic potential   | 30 |
| 14 | Screening charge at $Ag(001)$ surface with field $F = 0.01 \dots \dots$                    | 31 |
| 15 | Change in potential at $Ag(001)$ surface with field $F = 0.01a.u.$                         | 32 |
| 16 | Electric field strength profile generated by doubly charged $Rh_4$ cluster                 | 35 |
| 17 | Electric field strength profile generated by doubly charged $Rh_5(100)$                    |    |
|    | cluster  | 36 |
| 18 | Electron density difference between the doubly charged and the neutral                     |    |
|    | $Rh_5(100)$ cluster  | 37 |
| 19 | Electric potential contour of doubly charged $Rh_5(100)$ cluster                           | 38 |
| 20 | Electron density difference between the singly charged and the neutral                     |    |
|    | $Rh/Rh_5(100)$ cluster   | 39 |

| 21 | Electron density difference between the doubly charged and $Rh/Rh_5(100)$        |    |
|----|--|----|
|    | cluster.   | 40 |
| 22 | Electric potential contour of singly charged $Rh/Rh_5(100)$ cluster              | 41 |
| 23 | Electric potential contour of doubly charged $Rh/Rh_5(100)$ cluster              | 42 |
| 24 | Potential energy of $H_2$ in a uniform electric field, $F_0$                     | 61 |
| 25 | Potential energy of $H_2^+$ in a uniform electric field, $F_0$                   | 62 |
| 26 | Potential energy of $H_3^+$ in a uniform electric field, $F_0 = 1.5V/\text{\AA}$ | 63 |
| 27 | Contour plot of field-induced charge transfer for $H_2$                          | 64 |
| 28 | Contour plot of field-induced charge transfer for $H_2^+$                        | 65 |
| 29 | Contour plot of field-induced charge transfer for $H_3^+$                        | 66 |
| 30 | Field adsorption of atomic hydrogen on a jellium metal with $r_s = 2.0$ .        | 71 |
| 31 | Change in state density of atomic hydrogen on a jellium metal with               |    |
|    | $r_s = 3.0.$   | 72 |
| 32 | Potential energy of the $Rh - H$ dimer in a constant electric field, $F_0$ .     | 74 |
| 33 | Electron density difference contour plot for the $Rh - H$ dimer without          |    |
|    | a field  | 75 |
| 34 | Electron density difference contour plot for the $Rh - H$ dimer in $F_0 =$       |    |
|    | 3.0V/Å   | 76 |
| 35 | Geometries of field-free adsorption of various hydrogen species                  | 77 |
| 36 | Geometries of field adsorption of linear hydrogen species on a $Rh$ atom         |    |
|    | resulting from the LSDA calculations.  | 78 |
| 37 | Geometries of field adsorption of linear hydrogen species on a $Rh$ atom         |    |
|    | resulting from the non-local calculations.                                       | 79 |
| 38 | Potential energy of the linear $Rh - H - H$ trimer                               | 82 |
|    |  |    |

• 1

•

ţ

\_

| 39 | Electron density difference contour plot for linear $Rh - H - H$ trimer    |    |
|----|--|----|
|    | without a field  | 83 |
| 40 | Electron density difference contour plot for linear $Rh - H - H$ trimer    |    |
|    | in $F_0 = 3.0V/Å$  | 84 |
| 41 | Potential energy of $Rh - H - H - H$ as a function of $Rh - H_3$ distance  | 86 |
| 42 | Potential energy of $Rh - H - H - H$ as a function of $RhH - H_2$ distance | 87 |
| 43 | Electron density difference contour plot for $Rh - H - H - H$ quadrumer    |    |
|    | without a field  | 88 |
| 44 | Electron density difference contour plot for $Rh - H - H - H$ quadrumer    |    |
|    | in $F_0 = 2.0V/Å$  | 89 |
| 45 | Binding energy between $NO$ and $Rh$ surface in the presence of an         |    |
|    | electric field.  | 92 |
| 46 | Field-induced charge transfer, $F_0 = 0.3V/\text{\AA}$                     | 93 |
| 47 | Field-induced charge transfer, $F_0 = -0.3V/\text{\AA}$                    | 94 |
| 48 | Electron density difference contour plot for linear $Rh2 - NO$ without     |    |
|    | field  | 95 |
| 49 | Electron density difference contour plot for linear $Rh2 - NO$ in $F_9 =$  |    |
|    | 0.3V/Å   | 96 |
| 50 | Electron density difference contour plot for linear $Rh2 - NO$ in $F_0 =$  |    |
|    | -0.3V/Å  | 97 |
| 51 | Contour plot for the difference of $Rh2-NO$ with and without a positive    |    |
|    | field  | 98 |
| 52 | Contour plot for the difference of $Rh2 - NO$ with and without a neg-      |    |
|    | ative field  | 99 |

I.

د د

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a

## List of Tables

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**—**į

¥ ; 1 ]

a with a

| 1 | Binding | characteristics | of $H_2$ , | linear | and | triangular | $N_3$ | and | their | ions. | 60 |
|---|---------|-----------------|------------|--------|-----|------------|-------|-----|-------|-------|----|
|   |         |                 |            |        |     |            |       |     |       |       |    |

7

## Abstract

Various methods of generating electric fields in the vicinity of a metal surface are reviewed. In addition, the classical solution to Laplace's equation in parabolic coordinates is derived and quantum mechanical results for charged clusters are presented.

The Local Density Approximation jellium model and the Local Spin Density Approximation cluster model are used to calculate the adsorption of hydrogen on a jellium metal and on a  $R^{1}$  cluster in the presence of electric fields. Calculated binding energies and geometries are in good agreement with experimental data.

An extension of the LSDA cluster model to field adsorption of NO on Rh dimer is implemented with results that compare well with the latest experiment.

### List of Symbols

- E Total energy
- $E_F$  Fermi energy
- $\epsilon_F$  -Fermi energy
- $U_c$  Electron-electron interaction energy
- $U_{xc}$  Exchange-correlation energy
- $\epsilon_{\nu}$  Energy eigenvalue
- F Electric field strength
- $F_0$  Constant electric field strength
- $N_e$  Total number of electrons
- Q Total charge quantity
- n(r) Electron density
- $\rho(r)$  Charge density
- $\sigma_0$  Surface charge density
- $\Phi$  Electrostatic potential
- $V_c$  Electron-electron interaction potential
- $V_{xc}$  Exchange-correlation potential (in cluster model)
- $\mu_{xc}$  Exchange-correlation potential

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- $v_{eff}$  Effective potential
- $\psi_\nu\,$  Eigenfunction of one-electron wave equation
- $\phi_{\nu}$  Molecular orbital wave function (in cluster model)
- $\chi_l$  The *l*th Gaussion function in basis set
- $DV X\alpha$  The discrete Variational  $X\alpha$  method
- LDA Local density approximation
- LSDA Local spin density approximation
- ASED-MO The atom superposition and electron delocalization molecular orbital method
- **CI** Configuration interaction
- **FSGO** Floating spherical Gaussian orbitals

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### **1** Introduction

High electric fields, as they occur in zeolite cavities, at electrolyte interfaces, and at the tips of field ion and field emission microscopes [1], are known to alter the physics and chemistry of atoms and solids drastically so that some new pathways may be established in chemical reactions and particularly in heterogeneous catalysis. It is thus necessary to make as thorough an investigation as possible into electric fields generated in the vicinity of a surface, and in particular around a metal tip. In Chapter 2, we will review the attempts that have been made to calculate the field, and give details for the solution to Laplace's equation in parabolic coordinates and for charged clusters.

Hydrogen adsorbs on metal and semiconductor surfaces in either atomic or molecular form in ontop, bridge and multicoordinated hollow sites. Adsorption energies for atomic hydrogen range from 2 to 4 eV; molecular hydrogen, on the other hand is weakly physisorbed with adsorption energies less than 0.15 eV [2]. The bonding of hydrogen to the surface of transition metals has received extensive attention in the last years. Nevertheless no definite answer on the nature of the bonding seems to be available at present. The motivation to investigate adsorption of hydrogen on transition metal surfaces arises from various sources: (1) heterogeneous catalysis in which a great part of the reactions involve hydrogen as a reactant or product molecule. The synthesis of ammonia, of hydrocarbons or alcohols by means of the Fischer-Tropsch reaction, or solidification of unsaturated fatty acids are only some examples. This kind of catalytic reaction such as hydrogenation and dehydrogenation or hydrogenolysis is believed to gain even more interest in the future as increasingly amounts of fuel will be produced on the basis of coal or natural gas liquefication. (2) materials science and metallurgy where in particular hydrogen has long been known as a major source of embrittlement and fracture phenomena. (3) the use of hydrogen as a working fluid in energy conversion and storage devices made of certain alloys or intermetallic compounds [2].

Electric fields of the order of volts per angstrom, i.e. of the same order of magnitude as intra-atomic fields, dramatically effect the electronic properties of the surface layers of metals and semiconductors. For instance, on clean metals electric fields reduce the activation barrier of evaporation, eventually to zero at the evaporation field strength. Electric fields also change the binding characteristics of adsorbates. For instance, the binding energies of rare gases, weakly physisorbed in the field-free case, increase by at least an order of magnitude due to field- induced chemisorption [3,4]. Likewise, for adsorbed molecules dissociation may become enhanced or inhibited as the field is increased changing reaction pathways. Hydrogen is no exception to this scenario. Two effects in particular have so far defied a detailed theoretical explanation: (1) the reduction of the evaporation field strength in the presence of hydrogen, and (2) the appearance of a  $H_3^+$  species in the field ion mass spectrum [5,6,7,8,9,10].

We will report theoretical studies of the adsorption characteristic of atomic and molecular hydrogen as a function of electric field strength. In Chapter 3 we describe ,in detail, the theoretical tools we have been using, e.g. Local Density Approximation jellium model and the Local Spin Density Approximation cluster model. The inclusion of the electric field effects in our models, is simplified due to two facts: (1) electric fields are always enhanced at kink sites, terraces and in front of single atoms on closed packed planes. We can therefore restrict calculations to on top sites, and (2) molecules are usually aligned along the field direction. Thus only such geometries are taken into consideration.

The major results are presented in Chapter 4. We will see that the binding

energy of atomic hydrogen, H, is reduced as the field is increased, whereas  $H_2$  is bound more strongly. As a result, dissociative adsorption and associative desorption are modified considerably. Within the present theoretical framework one will also be able to propose a reaction pathway for the formation of a linear  $H_3$  species at metal surfaces in high electric fields. We will also comment on the reduction of the metal evaporation field strength by 10 - 15% in the presence of hydrogen. Finally, the LSDA method will be extended to field adsorption of NO on a Eh dimer so as to explain the latest experimental data.

Chapter 5 summarizes our main results and gives an outlook to future work.

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### **2** Electric Fields at Metal Surfaces

In this chapter, we investigate the electrostatic field in front of a metal surface. We begin by reviewing results obtained with classical electromagnetic theory for an infinite planar metal, a parabolic tip and a hemispherical protrusion. We then review jellium model calculations discussing just a flat jellium surface. After that we look at the electric field distribution around a metal atom on a jellium surface. Next we illustrate jellium model calculation that includes the lattice structure. Lastly we present results for charged clusters.

#### 2.1 Infinite Metal Planes

Consider two parallel infinite metal planes carrying uniform opposite surface charge. The electrostatic field may be generated by integrating Poisson's equation

$$\nabla \cdot \vec{F} = 4\pi\rho \tag{1}$$

resulting in

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$$F_z = 4\pi\sigma \tag{2}$$

where  $F_z$  is the z-component of the electric field which is constant between these two planes and drops to zero at the surfaces and  $\sigma$  is the surface charge density.

#### 2.2 Various Tip Geometries

The metal electrodes used in Scanning Tunnelling Microscopy, Field Emission Microscopy and Field Ion Microscopy are actually tips rather than an infinite plane. A number of studies have been reported with respect to the electric field strength and the electric field distribution on metal tip surfaces. Eyring, Mackeown and Millikan [11] assumed that the tip is hyperboloidal in shape and the screen is an infinite plane, shown in Figure 1. The solution to Laplace's equation in hyperbolic coordinates yields for the electrostatic potential

$$\Phi = \Phi_0 \frac{\log[(1 + \cos\beta)/(1 - \cos\beta)]}{\log[(1 + \cos\beta_0)/(1 - \cos\beta_0)]}$$
(3)

and thus the electric field at the apex of the tip is given by

$$F_{\beta,Apex} = -\frac{2\Phi_0}{alog[(1+\cos\beta_0)/(1-\cos\beta_0)]} \cdot \frac{1}{1-\cos^2\beta_0}$$
(4)

where  $\beta = \beta_0$  is the equation for the tip surface in hyperbolic coordinates and  $\Phi_0$  is the potential difference between the tip and the screen which is kept at zero potential and has the surface equation  $\beta = \pi/2$ . *a* is a constant determined by the tip dimensions.

The electron micrographs of field-ion tips show that a hyperboloid is not a good approximation. Although the shapes of these tips vary greatly, their general characteristics are fitted quite well by a paraboloid. Becker [12] assumed that both the tip and the screen were paraboloidal and used parabolic equations for tip and screen in Cartesian coordinates instead of solving Laplace's equation in parabolic coordinates. The resulting field is given by

$$F_z = \frac{2V_0}{\rho(1+2r/\rho)^{1/2} ln(1+2h/\rho)}$$
(5)

where  $V_0$  is the tip voltage, h is the tip to screen distance, r is the distance off the tip axis and  $\rho$  is the radius of curvature of the specimen tip. At the vertex of the tip, r = 0 and



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Figure 1: A diagram of hyperbolic coordinates.

$$F_{Apex} = \frac{2V_0}{\rho ln(1+2h/\rho)} \tag{6}$$

Dyke and Dolan [13] suggested that a family of equipotential surfaces surrounding a charged isolated sphere on an orthogonal cone shown in Figure 2 be used to describe the tip surface and found that it could fit well to the typical cathode geometries.

If it is assumed that the screen is another equipotential from the same family, the potential distribution may be written:

$$\Phi = \frac{V_0}{h^n} [r^n - a^{2n+1}r^{-n-1}] P_n(\cos\theta)$$
(7)

where r and  $\theta$  are ordinary plane polar coordinates referred to the center of the sphere as origin and the pole of the sphere opposite its contact with the cone as zero direction; h is the distance between the tip and the screen,  $V_0$  the applied potential, a the radius of the sphere, and  $P_n$  the Legendre function with n chosen so that the function vanishes when  $\theta$  is equal to the exterior half angle  $\alpha$  of the cone. The electric field at the tip apex is

$$F_{Apex} = \frac{V_0}{R^n r_0^{1-n}} [n + (n+1)(\frac{a}{r_0})^{2n+1}]$$
(8)

where the  $r_0$  is the value of r at  $\theta = 0$  on the surface which approximates the tip and the  $V_0$  is the potential difference between core and anode.

Based upon a combination of solving Laplace's equation for the region between the tip and the screen and finding a distribution of charges which gives a family of equipotentials of which one coincides with the tip surface and one with the screen, Birdseye and Smith [14] obtained their solution for the electric field by using the image method. They assume that the tip is smooth and axially symmetrical, and that it may be described by a curved surface r = R(z) in cylindrical coordinates. The

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Figure 2: A comparison between (a) typical field emitter geometries from electron micrographs and (b) equipotential surfaces surrounding a charged, isolated sphere on orthogonal cone. (c) is an enlarged profile of a typical field emitter fitted with an equipotential surface from Equation (7), using the values n = 0.10,  $a = 1.235 \times 10^{-5} cm$ , and  $r_0 = 4.00 \times 10^{-5} cm$ . From [13]

tip, its electrostatic "image" and the screen are shown diagrammatically in Figure 3 Under the condition  $r \ll z$ , they managed to derive the potential

$$\Phi = \frac{V_0}{2\ln R(z) + L/[(z+2h)^2 + R^2]^{1/2}} [2\ln r + \frac{L}{[(z+2h)^2 + r^2]^{1/2}}]$$
(9)

where  $V_0$  is the potential applied to the tip and L is its length, and h is the distance between the tip and screen. The electric field F is given by

$$F_n = -\frac{V_0[1+R'^2]^2}{L+2\ln R(z+2h)} \left[\frac{2}{R}(z+2h) - \frac{LR}{(z+2h)^2}\right]$$
(10)

where  $R' = \partial R(z)/\partial z$  and n is the normal to the surface.

The condition  $r \ll z$ , however, does not hold for the region far from the z axis or at the apex of the tip. In the latter region they determined the electric field by approximating the tip as an ellipsoid and solving the Laplace's equation in ellipsoidal coordinates with an assumption that the screen is at infinity. The solution is

$$F_n = -\frac{V_0}{[\rho^2 + R(z)^2]^{1/2} \ln \frac{1}{2} [\rho/c]^{1/2}}$$
(11)

where  $\rho$  is the radius of curvature of the specimen tip and c is the semi-major axis of the ellipsoid fitted to the tip, respectively. This also gives the field at the apex where R(z) = 0 as:

$$F_{Apex} = -\frac{v_0}{\rho \ln[R(L)/L]} \tag{12}$$

Apart from those works that have treated only analytical solutions for the electric field, some numerical studies have also been pursued. Gipson, Yannitell and Eaton [15], for example, have developed a numerical finite element method with which quite complex geometrics and varying material properties can be handled. In accordance



Figure 3: Diagram showing the geometry of the tip and its image From [14]

with their approach, the tip is assumed to be spherical with the shank and variations in the basic geometry including changes in the shank angle and tip radius of the specimen can be implemented by subroutine modifications to the finite element program. The geometry used to perform the numerical analysis and some results are shown in Figure 4 and Figure 5.

Quite recently, Tagawa, Takenobu, Ohmae and Umeno [16] have carried out computer simulations of the electric field distribution by using a charge simulation method in which charges on the surface of the tip are replaced by charges arranged inside the tip and errors in the potentials caused by the arrangement of charges can be examined at the check points that are distributed over the tip surface. In addition, they set up two experimental methods, i.e., the field emitted electron method and the thermionic electron method for measuring the local field strength of the tip surface and obtained reasonable agreement with the computer simulation.



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Figure 4: A schematic of the geometry used in the numerical analysis. From [15]



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Figure 5: Normalised equipotential contours plotted for a specimen modelled as a line(a), and as one with shape(b). From [15]

#### 2.3 Paraboloidal Tip in Parabolic Coordinates

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To verify Becker's result in parabolic coordinates and to establish a model for the study of field adsorption on a paraboloidal jellium metal in the future, we assume that the tip and the screen have the shape of a paraboloid of revolution and solve the Laplace equation in parabolic coordinates which are related to the Cartesian coordinates by the relations:

$$x = \alpha \beta \cos \phi$$
  

$$y = \alpha \beta \sin \phi$$
 (13)  

$$z = 1/2(\alpha^2 - \beta^2)$$

where  $0 \le \alpha < \infty, 0 \le \beta < \infty, -\pi < \phi \le \pi$ . The parabolic coordinates and the intersections of coordinate surfaces with the XZ- and XY-planes are shown in Figure 6.

In parabolic coordinates, the Laplace's equation reads

$$\nabla^2 \Phi = \left\{ \frac{1}{\alpha^2 + \beta^2} \left[ \frac{1}{\alpha} \frac{\partial}{\partial \alpha} \alpha \frac{\partial}{\partial \alpha} + \frac{1}{\beta} \frac{\partial}{\partial \beta} \beta \frac{\partial}{\partial \beta} + \left( \frac{1}{\alpha^2} + \frac{1}{\beta^2} \right) \frac{\partial^2}{\partial \phi^2} \right] \right\} \Phi = 0 \qquad (14)$$

and can be solved, subject to the given boundary conditions  $\Phi = \Phi_1(const.)$  when  $\alpha = \alpha_1$  which is the metal tip surface, and  $\Phi = \Phi_2$  when  $\alpha = \alpha_2(const.)$ , i.e. on the screen far from the tip. Note that for tip and screen of infinite size, the boundary conditions imply that the potential will be dependent on  $\alpha$  only, 50 ensure that  $\Phi$  is constant at the boundaries. For tip and screen of finite size, a strict derivation, see Appendix A, shows that the solution to the Laplace's equation (14) is a two dimensional quantity, and a numerical test has been performed resulting in that both cases approach to each other when  $\alpha_2$  is large enough. We take account of the infinite case only in the text. The Laplace's equation may thus be reduced to:



Figure 6: Parabolic Coordinates. –The vertices of all parabolas lie on the Z-axis at distances  $-\beta^2/2$  and  $\alpha^2/2$ , respectively, and all of them have a common focus at the origin of the Cartesian coordinate system. The coordinate surfaces are: (1) paraboloids of revolution extending in the direction of the positive Z-axis ( $\beta = const.$ ); (2) paraboloids of revolution extending toward the negative Z-direction ( $\alpha = const.$ ); (3) planes through the Z-axis ( $\phi = const.$ ).

$$\frac{d}{d\alpha}\alpha \frac{d}{d\alpha}\Phi(\alpha) = 0 \tag{15}$$

and the solution to this equation is given by

$$\Phi = c_1 \ln \alpha + c_2 \tag{16}$$

where  $c_1$  and  $c_2$  can be determined in terms of boundary conditions:  $\Phi_1 = c_1 \ln \alpha_1 + c_2$ and  $\Phi_2 = c_1 \ln \alpha_2 + c_2$ . We thus obtain, by solving the nonhomogeneous algebraic equations for  $c_1$  and  $c_2$ ,

$$c_1 = \frac{-(\Phi_1 - \Phi_2)}{\ln \alpha_2 / \alpha_1} \tag{17}$$

and

$$c_2 = \frac{\Phi_1 \ln \alpha_2 - \Phi_2 \ln \alpha_1}{\ln \alpha_2 / \alpha_1} \tag{18}$$

The electric field which has only an  $\alpha$  component  $F_{\alpha}$  and surface charge density are given by

$$F_{\alpha} = -\frac{1}{\sqrt{\alpha^2 + \beta^2}} \frac{\partial \Phi}{\partial \alpha}$$
  
=  $\frac{\Phi_1 - \Phi_2}{\ln \alpha_2 / \alpha_1} \cdot \frac{1}{\sqrt{\alpha^2 + \beta^2}} \cdot \frac{1}{\alpha}$  (19)

and

$$\sigma = -\frac{1}{4\pi} \nabla \Phi \Big|_{\alpha_1}$$
  
=  $\frac{\Phi_1 - \Phi_2}{4\pi \ln \alpha_2 / \alpha_1} \cdot \frac{1}{\sqrt{\alpha_1^2 + \beta^2}} \cdot \frac{1}{\alpha_1}$  (20)

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respectively. Combining the expressions of  $F_{\alpha}$  and  $\sigma$  gives rise to

$$F_{\alpha} = 4\pi\sigma \frac{\sqrt{\alpha_1^2 + \beta^2}}{\sqrt{\alpha^2 + \beta^2}} \cdot \frac{\alpha_1}{\alpha}$$
(21)

Before going further, we consider some geometry factors around the apex of the tip, (see Figure 7)  $r_0$  is the curvature radius which can be determined by setting  $\beta = 0$  and  $\alpha = \alpha_1$  in the expression (13), and is given by

$$r_0 = \alpha_1^2 \tag{22}$$

Note that setting  $\beta = 0$  actually means the positive z axis. In a similar fashion, we have

$$r_0 + 2l = \alpha_2^2 \tag{23}$$

where l denotes the distance between the apex of the tip and the screen. Substitution of  $r_0$  and l into the expression of  $c_1$  leads to

$$c_1 = \frac{-(\Phi_1 - \Phi_2)}{1/2\ln(1 + 2l/r_0)} \tag{24}$$

Since the field along the z axis has the maximum value, attention would be paid to this z component of the field. Taking the z component of the field only into account requires that we set  $\beta = 0$  in the expressions of  $F_{\alpha}$ . In doing so the expression of  $F_{\alpha}$ may be further reduced to

$$F_{\alpha} = \frac{\Phi_1 - \Phi_2}{\ln \alpha_2 / \alpha_1} \cdot \frac{1}{\alpha^2}$$
(25)

Substituting  $r_0$  and l into the above gives

$$F_{\alpha} = 4\pi\sigma_0 \frac{r_0}{2z}$$
  
=  $4\pi\sigma_0 \frac{r_0}{r_0 + 2z'}$  (26)

where

$$\sigma_0 = \frac{\Phi_1 - \Phi_2}{4\pi \ln \alpha_2 / \alpha_1} \cdot \frac{1}{\alpha_1^2}$$
(27)

is the surface charge density at the apex of the tip and  $z' = z - r_0/2$  is the distance measured from the apex of the tip, respectively. The electric field  $F_{Apex} = 4\pi\sigma_0$  at z' = 0, the apex of the tip.

If we take  $r_0$  approaching to infinity, i.e.  $r_0 \gg l$ , which implies that the tip turns to a flat plane, the field on the tip surface becomes approximately

$$F \approx \frac{\Phi_1 - \Phi_2}{l} \tag{28}$$

This result is in agreement with that between the two infinite charged metal sheets.

More generally, the curvature radius of the tip,  $r_0$ , is much less than the distance between tip and screen l. The typical values for  $r_0$ , l and  $\Delta \Phi = \Phi_1 - \Phi_2$  are  $r_0 = 10^2 \text{\AA}, l = 10^2 \text{ cm}$  and  $\Delta \Phi = 10 kV$  respectively. Thus the field at the apex of the tip is of order  $V/\text{\AA}$ . we note that it is now possible to make tips with a single atom at the apex, i.e. with a curvature of an angstrom! We present, in Figure 7, the profiles of electric field and potential along the z-axis in the parabolic co-ordinates and by comparison, their counterparts for infinite metal sheets. The electric field strength at the apex of a parabolic tip is equal to that in the infinite case but will decrease as  $z^{-1}$ , and on the other hand, the electric field in the infinite system has a constant strength of  $4\pi\sigma$ . We define the surface charge quantity as the integral

$$Q = \int \sigma ds \tag{29}$$

where

$$ds = 2\pi\alpha_1\beta \cdot \sqrt{\alpha_1^2 + \beta^2} \cdot d\beta \tag{30}$$

is the area element of the tip surface in the parabolic co-ordinates. Completing the integration within the finite region leads to

$$Q = \int_{0}^{\beta_{0}} \sigma ds = \frac{\Delta \Phi}{\ln(1 + l/r_{0})} \cdot \frac{\beta_{0}^{2}}{2}$$
(31)



Figure 7: A sketch of the geometry of parabolic tip (upper part), and the profiles of electric field and potential in both parabolic  $(F_{\alpha}, \Phi_{\alpha})$  and planar  $(F_{plane}, \Phi_{plane})$  geometries (lower part).

#### 2.4 Hemispherical Protrusion

It has been known that the surface of a solid is not mathematically flat. To see how much electric fields are modified by roughness and to compare the classical result with the quantum one in the future, we consider a hemispherical protrusion, or spherical boss, of radius R on top of an infinite plane, see Figure 8. The electric potential is, according to D.J. Rose [17], and Landau and Lifshitz [18] given by

$$\Phi = -4\pi\sigma_0 z (1 - R^3/r^3)$$
(32)

Differentiating this potential with respect to r along the z axis yields the electric field

$$F_z = 4\pi\sigma_0(1 + 2\frac{R^3}{z^3})$$
(33)

Locally the excess charge redistributes itself into

$$\sigma = \sigma_0 (1 - R^3/r^3) \tag{34}$$

on the infinite plane, and

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$$\sigma = 3\sigma_0 z/R \tag{35}$$

on the surface of the protrusion. We note that at the apex of the boss the electric potential is zero and the field is three times its value at infinity. For z = 2R above the apex, potential and field values agree to within 20 percent of their values laterally far from the boss.



Figure 8: Electric field (left scale) and potential (right scale) as a function of distance at a metal surface with a spherical boss of radius R (see insert) far from the boss (dashed lines) and along the apex of the boss (solid lines). From [3]

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#### 2.5 Jellium Model

So far we have described electric fields by using classical electromagnetic theory which assumes that the surface of a metal is a mathematical plane or spheroid with excess surface charges where the normal component of the electric field drops discontinuously to zero at such planes, at least for a perfect conductor. On real surfaces, however, there is a dipole layer resulting from a relaxation of the lattice and a rearrangement of the electron distribution. As a consequence, the singular surface charge density will be smeared out and the electric field will vary smoothly over distances of a few angstroms. A simple model that bears out these features is the jellium model of a metal in which we assume that the ionic lattice is replaced by a uniform positive charge density  $n_+$ that drops to zero abruptly half a lattice constant above the topmost layer of ion cores. It is given in terms of the Wigner-Seitz radius as

$$n_{+} = \frac{3}{4\pi} (r_{s}/a_{0})^{3} \tag{36}$$

where  $r_s$  is given in units of the Bohr radius  $a_0$ .

Lang and Kohn [19,20,21] performed the first self-consistent quantum mechanical calculation of charge density and electric field distribution at a metal surface for such a structureless jellium model using the local density approximation to density functional theory. A systematic study of this problem was recently performed by Gies and Gerhardts [22] and also by Schreier and Rebentrost [23]. We present the results of a density functional calculation for a jellium surface in Figure 9 [24].

In panel (a) we show the selfconsistent electron distribution in the absence of an external field with the local deviation from charge neutrality, i.e. the dipole layer, given in panel (b). In panel (c) we have added some excess charge,  $\delta\rho$ , that gives rise to the external field in panel (d). We note that the field decays smoothly into the
metal with appreciable strength left at the position of the top most ion layer. This can be viewed as partial penetration of the field into the metal, or as incomplete expulsion of the field from the metal. To compare these quantum mechanical calculations with classical results from Maxwell's theory, we note that the plane at which boundary conditions are imposed on the classical fields, i.e. the discontinuous drop of the normal component of the electric field to zero, is given by the center of gravity of the excess charge  $\delta \rho$ , i.e. roughly the point where the field has dropped to half its value at infinity. For future reference we note here that this plane does not remain constant but moves towards the ion cores as the asymptotic field strength increases, due to the fact that the electrons are pushed into the metal increasing the field penetration and the Friedel oscillations.

Figure 10 shows results for the self-consistent effective potential and electron density of a neutral and two oppositely charged surfaces. We can see electrons are pulled out of or pushed into the jellium in terms of the negatively and positively applied electric fields, respectively. Also plotted in Figure 11 are the normalized induced charge densities characterized by their center of mass  $z_0$  which determines the position of the image plane for an external point charge in front of the surface.



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Figure 9: A schematic view of (a) the charge distribution at a metal surface without a fields ( $F_0 = 0$ ), the positive jellium background is indicated,  $Z_d$  and  $d_n$  are the dynamic and static image plane positions; (b) the surface dipole layer  $\rho^s = n_+^s - n_-^s$  for  $F_0 = 0$ , constructed from (a); (c) the field-induced surface charge  $\delta\rho$ ; and (d) the applied electric field at a metal surface. From [24]



Figure 10: Self-consistent effective potential of (a) a positively charged, (b) neutral, and (c) negatively charged surface. The induced surface charge density is  $\pm 4.77 \times 10^{-3} e/Å^2$ . From [22]



Figure 11: Normalized self-consistent induced charge density for (a) a positively and and (c) a negatively charged surface.  $z_0$  and  $\lambda$  are the center of mass and spread, respectively. From [22]

#### 2.6 Metal Atom on Jellium Surface

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It is believed that imaging of single atoms in the field ion microscope occurs as a result of local field enhancement around kink sites and around single metal atoms on flat crystal planes. These local electric fields of the order of V/Å arise, via Poisson's equation, from local enhancements of the surface electron density. The electric field distribution around isolated atoms on a flat jellium surface have recently been calculated selfconsistently within the framework of the local density approximation of density functional theory by Kreuzer, Wang and Lang [25]. They find a field enhancement by a factor 1.5 to 2 some 1-2Å above an adsorbed metal atom instead of a factor 3 at the apex of a boss on top of a flat metal plane. The detailed comparison between this quantum mechanical calculation and the corresponding classical theory is shown in Figure 12 and also in the contour plot of Figure 13. Calculated evaporation field strengths, i.e. 3.0V/Å for Ti and 3.5V/Å for Nb, agree very well with experimental data.

### 2.7 Jellium Model with Crystal Structure

It has been noted that the jellium model of metals does not account for the crystalline structure. To see how big the local variations in the electron and field distributions along the surface are, Inglesfield calculated the screening of an external electric field at Al(001) and Ag(001) surfaces by using an embedding technique and the linearized augmented plane wave method for including the substrate, i.e. the real atomic structure [26,27]. One can find, see Figure 14 and Figure 15, that the screening charge lies on top of the surface atoms and the lateral variation in the electric field is rather small and indeed, negligible a few angstroms above the topmost lattice sites [24].



Figure 12: Electric field strength along the line through the center of the adatoms. Upper part:  $Ti \ (r_s = 3.0 \text{ bohr at } d = 2.5 \text{ bohr})$  in  $F_0 = 2.6V/\text{\AA}$ . Lower part:  $Nb \ (r_s = 3.0 \text{ bohr at } d = 2.75bohr)$  in  $F_0 = 3.0V/\text{\AA}$ . Curves A and B: without and with the adatom; curve C: classical result; from [4]



Figure 13: External electrostatic potential. Upper panels for Ti and Nb based on the quantum mechanical calculations; lower panels are classical results in terms of the semispherical projection model; from [25]

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Figure 14: Screening charge at Ag(001) surface with electric field F = +0.01a.u. The solid lines are contours of decreased electron density, and the dashed lines increased density; from [27]



Figure 15: Change in potential at Ag(001) surface with field F = 0.01a.u. From [27]

#### 2.8 Charged Clusters

Electric fields can also be generated by charging a cluster of metal atoms which we describe using a finite cluster model based on spin density functional theory. If we do this by adding charges to the cluster, in practice by taking electrons away from the neutral cluster, the net positive charges will distribute themselves over the surface of the cluster. To fulfill this task, The self-consistent calculations for the neutral cluster and the ionized one are performed, respectively by running the LSD program. Taking the difference of the electron densities between the neutral and the ionized systems gives rise to the induced electron density which will result in the local electric potentials and fields illustrated in this section. A Fortran program has been coded for this purpose and will be elaborated in section 3.3. By choosing an appropriate geometry, e.g. a pyramidal shape, we can ensure that most of the extra charge resides on the top atom of the cluster and a strong electric field is produced in its vicinity. We have investigated the maximum fields generated on various cluster configurations and their distances from the top atom of the cluster. We note that the highest field strength is found, shown in Figure 16, to be 2.7 V/Å and 1.4 Å away from the top atom in the doubly charged  $Rh_4$  tetrahedron modelling the Rh(111) lattice structure. For a singly charged  $Rh_5(110)$  cluster, however, the maximum field is  $1.35V/\text{\AA}$  and located at about 1.6 Å the top atom. We know that the electric field on a semi-infinite flat plane is perpendicular to the plane and goes outwards uniformly. Figure 17 shows the field profile produced by a doubly charged  $Rh_5(100)$  cluster that models a small part of the flat plane. It is clear that the electric field generated by means of charging a cluster will fall off rapidly, with an exception of  $Rh_5(100)$ , rather than approach a constant as it does in front of a single atom on top of an extended metal surface described in preceding sections. We next plot the charge distribution for a doubly

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charged cluster of five Rhodium atoms which form one layer of a Rh(100) plane and find very similar characteristics to the embedded Ag(001) surface, i.e. the electron density is smoothed and the lateral variation in the electric field is rather small a few angstroms away from the top atoms (see Figure 18 and Figure 19. We have also obtained the electron density distributions (see Figure 20 and Figure 21) and potential contour plots (see Figure 22 and Figure 23) for both singly and doubly charged  $Rh_6$  clusters which have one more Rhodium atom on top of the  $Rh_5(100)$ cluster. In general, one can generate fields of about 1 - 2V/Å one or two angstroms away from the top atom in the cluster, i.e. at the position where atomic hydrogen will adsorb.



Figure 16: Electric field strength profile generated by doubly charged  $Rh_4$  cluster



Figure 17: Electric field strength profile generated by doubly charged  $Rh_5(100)$  cluster

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Contour lines are -0.0005, -0.0001, -0.00005, 0.000001, 0.000005, 0.00001, 0.00005, 0.0001, 0.0005, 0.001, 0.005, 0.01 per a.u. of volume. Crosses mark the nuclei of the atoms.



Figure 19: Electric potential contour of doubly charged  $Rh_5(100)$  cluster. Contour interval is 0.02 a.u. Crosses mark the nuclei of the atoms.





Contour lines are  $\pm 0.001$ ,  $\pm 0.00075$ ,  $\pm 0.0005$ ,  $\pm 0.00025$ ,  $\pm 0.0001$ ,  $\pm 0.000075$ ,  $\pm 0.00005$ ,  $\pm 0.000025$ ,  $\pm 0.00001$  per a.u. of volume. Crosses mark the nuclei of the atoms.

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Contour lines are  $\pm$  0.001,  $\pm$  0.0005,  $\pm$  0.0001,  $\pm$  0.00005,  $\pm$  0.00001 per a.u. of volume. Crosses mark the nuclei of the atoms.



Figure 22: Electric potential contour of singly charged  $Rh/Rh_5(100)$  cluster. Contour interval is 0.005 a.u. Crosses mark the nuclei of the atoms.

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Figure 23: Electric potential contour of doubly charged  $Rh/Rh_5(100)$  cluster. Contour iunterval is 0.01 a.u. Crosses mark the nuclei of the atoms.

# **3** Theoretical Models of Field Adsorption

As we discussed in the preceding chapter, the electric fields at metal surfaces are greatly enhanced around kink sites and around single metal atoms on flat crystal planes. We also mentioned that the quantum mechanical calculations of the selfconsistent charge density and electric field distribution have been done for both a flat jellium surface and a jellium surface with one metal atom adsorbed on it by employing the local density approximation to density functional theory.

To understand field adsorption of molecules, one would like to calculate the electronic structure of an adsorbed molecule in the local field at kink sites or around single atoms on densely packed planes of transition metals. Unfortunately, such a complete calculation is not available at the present time. We will therefore resort to two approaches, both of which are based on density functional theory to determine the electronic structure and the local electric field selfconsistently. In the first place, we use the jellium model to describe field adsorption of atomic hydrogen. Next we use a cluster model for field adsorption of both atomic and molecular hydrogen species. Accordingly, this chapter is divided into two sections in order to account for these two models in detail.

#### 3.1 Field Adsorption on A Jellium Metal

For the field adsorption of atomic hydrogen we will use the jellium model to represent a densely packed metal surface on which we will study the chemisorption of atomic hydrogen as a function of applied field using local density functional theory [19,20, 21,28]. This model does not account for p and d electrons in the metal and obviously neglects all effects due to the lattice structure of the surface. In its present form the program is also restricted to single atom adsorption. In this model we assume that the ionic lattice can be smoothed into a uniform positive charge density  $n_+$ , given by (36) that drops to zero abruptly half a lattice constant above the topmost layer of ion cores. We will study the local electron and field distribution first for a bare metal surface and then adding a hydrogen atom [29] in front of this jellium metal within the framework of density functional theory. The latter determines the exact ground state electron density as the selfconsistent solution of the equations

$$n(z) = \frac{m}{\pi\hbar^2} \sum_{\nu} (\epsilon_F - \epsilon_{\nu}) \Theta(\epsilon_F - \epsilon_{\nu}) |\psi_{\nu}(z)|^2$$
(37)

$$(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + v_{eff}[n;z] - \epsilon_{\nu})\psi_{\nu}(z) = 0$$
(38)

where  $\epsilon_{\nu}$  and  $\psi_{\nu}$  are, respectively, the energy eigenvalues and normalized eigenfunctions of an electron in the one dimensional effective potential  $v_{eff}$  which, in turn, is a functional of the electron density n(z). The present expression of one dimensional electron density, Equation 37, can be derived exactly in both Cartesian and cylindrical coordinates, see Appendix B for details. In the local density approximation, the effective potential

$$v_{eff}[n;z] = \Phi(z) + \mu_{xc}(n(z))$$
 (39)

is the sum of the electrostatic potential as seen by an electron, determined from Poisson's equation

$$\frac{d^2}{dz^2}\Phi(z) = 4\pi e[n_+ - n(z)]$$
(40)

which can be integrated analytically, leading to the solution

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$$\Phi(z) = \Phi(-\infty) - 4\pi \int_{-\infty}^{z} dz'(z-z')(n(z') - n_{+}(z'))$$
(41)

and the exchange and correlation contribution,  $\mu_{xc}$  which, in the local density approximation with a Wigner form for the correlation, is given by

$$\mu_{xc}(n(z)) = -\frac{e^2}{a_0} \left( \frac{0.611}{r_s(n)} + 0.147 \frac{4r_s(n) + 23.4}{[r_s(n) + 7.8]^2} \right)$$
(42)

where  $r_s(n)$  is defined by  $(4\pi/3)[r_s(n)]^3 = 1/n$ .

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A static electric field  $F_0$  applied perpendicular to the jellium surface is characterized by the surface charge density

$$\sigma_0 = e \int_{-\infty}^{\infty} (n_+ \Theta(-z) - n(z)) dz = F_0 / 4\pi$$
(43)

where  $\Theta(-z)$  is a step function defined by  $\Theta(z) = 1$  when z > 0 and  $\Theta(z) = 0$  when z < 0. The profiles of the electron density, the induced charge density and electric field at the flat jellium surface are shown in Figure 10 and Figure 11.

To study chemisorption of an atom on jellium, it is again required to solve the one electron equation (38) where, however, the effective potential needs to be written, for the metal-adatom system consisting of a semi-infinite uniform positive background, a nucleus of charge Z, and the gas of interacting electrons, as  $v_{eff}[n^{MA};r]$ . Hereafter the superscripts M and MA refer, respectively, to the bare metal and the combined metal-adatom system. We note the fact that the metal screens out the effects of the adatom on the charge density and potential, except in the vicinity of the adatom such that this kind of locality of the disturbance in the potential can be conveniently treated, for the continuum states, by using a Lippmann-Schwinger integral equation

$$\psi^{MA}(r) = \psi^{M}(r) + \oint dr' G^{M}(r,r') \delta v_{eff}(r') \psi^{MA}(r')$$
(44)

where  $\psi^{M}$  is the solution of Equation 38 in the absence of the adsorbed atom,  $G^{M}$  is the Green's function of the bare metal and  $\delta v_{eff}$  is the difference of the effective potential (39) with and without the adsorbed atom. Because  $\delta v_{eff}$  approaches zero rapidly outside the adatom, we can restrict the integral in Equation 44 to a sphere centered at the adatom, bounded by a surface S outside of which  $\delta v_{eff}$  is negligible.

To include an external electric field, we must add an excess surface charge to the metal. This is done first in the bare metal problem by imposing the condition

$$\sigma = e \int_{-\infty}^{\infty} (n_{+}\Theta(-z) - n^{M}(z, F_{0})) dz = F_{0}/4\pi$$
(45)

on the charge density of the bare metal. Note that this equation is similar to Equation 43, but we this time write the electron density as  $n^M(z, F_0)$  that is constructed by wavefunctions  $\psi^M(z, F_0)$  through Equation 37 and depends upon the field strength,  $F_0$ , far from the surface. In the presence of the adatom one then requires that outside the sphere S

$$n^{MA}(r, F_0) \to n^M(r, F_0) \qquad for \ |r| \to \infty$$
 (46)

which acts as a boundary condition on the solution of (44). Thus, the effect of the external electric field is imposed in the metal-adatom system through the condition (46).

While the external electric field does not change the structure of the one electron equations, it does affect the numerical procedure. In the absence of external electric fields, the effective potential of a bare metal,  $v_{eff}[n^M, z]$ , will approach a constant for  $z \to \infty$ , usually taken as the zero of energy. However, in the presence of an external electric field of asymptotic strength  $F_0$ ,  $v_{eff}[n^M, z]$  will grow as  $eF_0z$  for large z. It is then advantageous to choose the Fermi energy as the energy reference,  $\epsilon_F = 0$ . With

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this choice the energies of all occupied levels are negative.

The one electron differential equation corresponding to the Lippmann-Schwinger integral equation can be solved exactly by direct numerical integration outward from the adatom nucleus. These solutions  $\psi_{Eml}(r)$  are represented as an r-dependent linear combination of free-particle solutions

$$\psi_{Eml}(r) = \sum_{l'=|m|}^{\infty} [C_{Emll'}(r)j_{l'}(pr) + S_{Emll'}(r)h_{l'}^{+}(pr)]Y_{l'm}(\Omega)$$
(47)

where  $p = \sqrt{E}$ , and  $j_{l'}$  and  $h_{l'}^+$  are the spherical Bessel functions. These solutions are characterized by their angular behavior near the nucleus and do not satisfy the boundary conditions embodied in the Lippmann-Schwinger equation. Within the sphere S, however, the desired solution  $\psi_{Emk}(r)$  may be expanded in terms of these fundamental solutions

$$\psi_{Emk}(r) = \sum_{l'=|m|}^{\infty} \alpha_{Emkl'} \psi_{Eml'}(r)$$
(48)

where the coefficients  $\alpha_{Emkl'}$  are obtained by substituting this equation into the Lippmann-Schwinger integral equation (44).

## 3.2 Spin Density Functional Theory of Clusters

To account for the local lattice effects for adsorption around isolated atoms on densely packed surfaces or at kink sites, we will use a finite cluster model based on spin density functional theory. Because the number of metal atoms is rather small in such calculations for practical reasons, long range metallic effects such as image forces are not included in this model. The current model which employs the local spin density approximation to the exchange and correlation potential was first established by Sambe and Felton [30,31], later on modified by Dunlap [32,33] and then by Salahub [34,35,36,37,38]. In their original version of this model, Sambe and Felton used the  $X\alpha$  potential as the local density functional approximation and expanded the  $X\alpha$  potential as well as the electron density appearing in the Coulomb potential in terms of some auxiliary Gaussian functions so as to circumvent those cumbersome integrals caused by the  $X\alpha$  potential and to reduce the number of two-electron integrals arising from Coulomb interaction. Upon calculating matrix elements analytically, a group of self-consistent- field equations can be solved iteratively and the chemically interesting quantities such as total energy, ionization energy and equilibrium geometry, can be obtained. Consequently, the muffin-tin approximation for the potential that is inherent to the multiple scattering method and therefore unreliable in studies of molecular geometry has been removed. Furthermore, the large number of sample points per atom necessary in the  $DV - X\alpha$  method will no longer be demanded.

The one electron equation and molecular orbitals, in the electric field caused by nuclei of charges  $Z_p$  at positions  $R_p$ , are determined by variational minimization of the Local Density Functional total energy expression,

$$E = \sum_{i} n_{i} \int dr^{3} \phi_{i}^{*}(r) [-\frac{1}{2} \nabla^{2} - \sum_{p} \frac{Z_{p}}{|r - R_{p}|}] \phi_{i}(r) + U_{c} + U_{xc} + \sum_{p>q} \frac{Z_{p} Z_{q}}{|R_{p} - R_{q}|}$$
(49)

where  $n_i$  is the occupation number of the *i*th orbital  $\phi_i$ . The electron-electron interaction energy is

$$U_{c} = \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} dr^{3} dr'^{3}$$
(50)

where

$$\rho(r) = \sum_{i} n_i \phi_i^*(r) \phi_i(r) \tag{51}$$

is the charge density when the *i*th molecular orbital is occupied by  $n_i$  electrons (at this point, we only take into account the case where there is no net spin polarization of the electrons for simplicity) and the exchange-correlation energy is, for example in the  $X\alpha$  approximation, given by

$$U_{xc} = -\alpha \frac{3}{4} \left(\frac{81}{8}\pi\right)^{1/3} \int \rho(r)^{4/3} dr^3$$
(52)

For open shell systems, the wave functions and total electron density,  $\rho$ , can be divided into spin-up and spin-down components, and the exchange-correlation energy will be spin dependent.

We now display the one-electron equation, in atomic units,

$$(-\frac{1}{2}\nabla^{2} + v_{eff}[\rho; r] - \epsilon_{\nu})\phi_{\nu}(r) = 0$$
(53)

where the effective potential comprises electron-nuclear attraction, electron- electron repulsion and exchange-correlation potentials, and can be written explicitly,

$$v_{eff}[\rho(r);r] = \sum_{p} \frac{-Z_{p}}{|r-R_{p}|} + V_{c}(r) + V_{xc}(\rho(r))$$
$$V_{c}(r) = \int \frac{\rho(r')}{|r-r'|} dr'^{3}$$
$$V_{xc}(\rho(r)) = -3\alpha [(3/8\pi)\rho(r)]^{1/3}$$
(54)

where we have used the  $SCF - X\alpha$  approximation and will be doing this throughout all our derivations. We next will expand the electron density and the exchangecorrelation potential by a least-squares fit to Gaussian functions centered at the nuclei, respectively.

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$$\rho(r) \approx \sum_{i} a_{i} f_{i}(r) \tag{55}$$

$$V_{xc}(\rho(r)) \approx \sum_{j} b_{j} g_{j}(r)$$
(56)

Hence the effective potential becomes

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$$\tilde{v}_{eff} = \sum_{p} -\frac{Z_{p}}{|r-R_{p}|} + \tilde{V}_{c} + \tilde{V}_{xc}$$
$$\tilde{V}_{c} = \sum_{i} a_{i} \int \frac{f_{i}(r')}{|r-r'|} dr'^{3}$$
$$\tilde{V}_{xc} = \sum_{j} b_{j}g_{j}(r)$$
(57)

where a tilde indicates a fitted quantity. In order to solve the one-electron equation

$$\left(-\frac{1}{2}\nabla^2 + \tilde{v}_{eff} - \epsilon_{\nu}\right)\phi_{\nu}(r) = (\tilde{H} - \epsilon_{\nu})\phi_{\nu}(r) = 0$$
(58)

We employ the Rayleigh-Ritz variational method with linear variational functions

$$\phi_{\nu} = \sum_{l} \chi_{l} C_{l\nu} \tag{59}$$

where  $\chi_l$  are Hermite-Gaussion functions centered at the nuclei. This leads to the secular equation:

$$\sum_{l} (\tilde{H}_{kl} - \epsilon_{\nu} S_{kl}) C_{k\nu} = 0$$
(60)

where the  $\tilde{H}_{kl}$  is the fitted Hamiltonian matrix elements,

$$\tilde{H}_{kl} = \int \chi_k \tilde{H} \chi_l dr^3 \tag{61}$$

and the  $S_{kl}$  is normally called an overlap integral,

$$S_{kl} = \int \chi_k \chi_l dr^3 \tag{62}$$

since its value is, in certain cases, an indication of the extent to which the two functions  $\chi_k$  and  $\chi_l$  occupy the same space. The electron density is given by, in terms of the solutions of Equation (60),

$$\rho = \sum_{kl} \sum_{\nu} n_{\nu} C_{k\nu} C_{l\nu} \chi_k \chi_l \tag{63}$$

To solve the equations (57) to (63), we start from the expansion coefficients  $a_i$ and  $b_j$  which determine the fitted Hamiltonian  $\tilde{H}$ . Upon solving the secular equation, a new electron density and a new exchange-correlation potential are obtained. The expansion coefficients  $a_i$  and  $b_j$  are recalculated by least-squares fitting to these new quantities and thus an iteration is performed.

Our electron density fitting equations follow from taking account of the second order effect in the calculation of the coulomb energy  $U_c$ . Consequently, the most accurate approximation to  $U_c$  results from minimizing a positive definite quantity  $\delta_c$ :

$$\delta_c = \frac{1}{2} \int \int \frac{(\rho(r) - \tilde{\rho}(r))(\rho(r') - \tilde{\rho}(r'))}{|r - r'|} dr^3 dr'^3 \tag{64}$$

subject to the normalization constraint:

$$\int \tilde{\rho}(r)dr^3 = \sum_i a_i \int f_i(r)dr^3 = N_e$$
(65)

where the  $N_e$  is the total number of electrons. Introducing a Lagrange multiplier  $\lambda$  to this restrictive minimization, we can obtain  $\tilde{\rho}$  with a fit

$$a = F^{-1} \cdot (t + \lambda n)$$
  
$$\lambda = (N_e - n \cdot F^{-1} \cdot t)/n \cdot F^{-1} \cdot n \qquad (66)$$

where

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$$F_{ij} = \int \frac{f_i(r)f_j(r')}{|r - r'|} dr^3 dr'^3$$
  

$$t_i = \int \frac{\rho(r)f_i(r')}{|r - r'|} dr^3 dr'^3$$
  

$$n_i = \int f_i(r)dr^3$$
(67)

The exchange-correlation potential has been fitted on the three-dimensional grid of points around each nucleus of the atom with a radial distribution consisting of every tenth point of the Herman-Skillman mesh [39]. The angular mesh consists of the twelve vertices of a regular icosahedron [40]. In the present program, we chose the local exchange-correlation potential fitted by Vosko, Wilk and Nusair [41] to the Ceperley-Alder [42] Monte Carlo treatment of the electron gas. This local potential has been tested and compared with various other exchange-correlation potentials within the same computational scheme by Baykara, McMaster and Salahub [35], and believed to be close to the limit attainable in a local method. In addition to the local density approximation, a nonlocal correction that involves the gradient of the density as well as the density itself proposed by Perdew [43,44] to the exchange-correlation functional has been added to the latest version of the computing program [45] during the course of preparation of this thesis.

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To apply the model described to the treatment of large clusters containing transition metal atoms, which is a necessary step in understanding complex chemisorption and catalytic phenomena, there is a need for simplification of the LSD calculations. One of the obvious ways is to take into account only the valence electrons of the cluster, assuming they move in an unchanging potential due to the atomic core electrons. The model core potential that has been originally proposed by Huzinaga and Bonifacic [46], and then developed for the spin-polarized local-spin-density method by Andzelm, Radzio and Salahub [34] is employed in our calculations so that we represent the valence orbitals using truncated basis sets and replace operators of the core-valence interaction by simple, preferably one-electron, analytical potentials.

#### **3.3 Electric Field in Cluster Model**

In earlier cluster calculations based on the semi-empirical ASED-MO method [47,48] the electric field as calculated for a flat jellium surface was imposed on the cluster. This method successfully explained field-induced chemisorption of rare gases [49] and field evaporation of metals [50]. In the same way, we can also include an electric field in the LSDA cluster calculations. In fact, some subroutines have been written and added to the LSD program. Unfortunately, this is no longer a self-consistent calculation. For the cluster calculations carried out in this work, we employ a different and simpler scheme to include field effects. Because we are interested in field adsorption around single metal atoms on top of closed packed surfaces or around kink sites, we take a cluster consisting of a single metal atom and the adsorbing atom or molecule. This cluster is then put into a constant external field will lead to a net field expulsion over the volume of the metal atom and to a field enhancement in front of it where field adsorption of the additional atoms or molecules takes place.

To incorporate the uniform electric field in the cluster model, we add

$$V_F(z) = F_0 z \tag{68}$$

to the effective potential (54) in the one-electron equation and

$$U_F = -\sum_p Z_p F_0 z_p \tag{69}$$

to the total energy expression (49). We note that the fitted Hamiltonian  $\tilde{H}$ , and correspondingly the fitted Hamiltonian matrix elements  $\tilde{H}_{kl}$ , will now depend on the field. A modified LSD program containing such a uniform electric field still guarantees

self-consistency and the resulting electron density reflects the field effect.

To evaluate the local electric potential and field, we must solve Poisson's equation

$$\nabla \cdot \vec{F} = -\nabla^2 \Phi = -4\pi\rho(r) + \sum_p Z_p \cdot 4\pi\delta(r - R_p)$$
(70)

Thus the electric potential and the field are given by

$$\Phi = \sum_{p} \frac{Z_{p}}{|r - R_{p}|} - \int \frac{\rho(r')dr'}{|r - r'|} = \Phi_{N} + \Phi_{e}$$
(71)

and

$$\vec{F} = \sum_{p} \frac{Z_{p}(r - R_{p})}{|r - R_{p}|^{3}} + \nabla \Phi_{e} = \vec{F}_{N} + \vec{F}_{e}$$
(72)

where  $\Phi_N$  and  $\vec{F}_N$  are the potential and the field due to the positive charges of the ion cores, and  $\Phi_e$  and  $\vec{F}_e$  are the potential and the field arising from the electrons.

To evaluate  $\Phi_e$ , we express the electron density in terms of the Hermite-Gaussian basis functions,  $\chi_l$ , as

$$\rho(r) = \sum_{l,m} \sum_{\nu} n_{\nu} C_{l\nu} C_{m\nu} \chi_{l}(r) \chi_{m}(r)$$
(73)

where  $n_{\nu} = 1$  or 0 and the  $C_{l\nu}$ 's are determined self-consistently in the LSD program. The integrals in  $\Phi_e$  can then be done explicitly. To evaluate, for instance, the zcomponent of  $\vec{F}_e$ , we have to take a derivative with respect to z yielding

$$F_{e,z} = \sum_{l,m} \sum_{\nu} n_{\nu} C_{l\nu} C_{m\nu} (-1)^{m} \frac{2\pi}{a+b} \sum_{k_{1}} \sum_{k_{2}} \sum_{k_{3}} \left(\frac{b}{\sqrt{a+b}}\right)^{k} \\ h(l_{1},m_{1},k_{1},-\frac{a}{b})h(l_{2},m_{2},k_{2},-\frac{a}{b})h(l_{3},m_{3},k_{3},-\frac{a}{b}) \\ (\partial_{K_{z}}^{k_{1}} \partial_{K_{y}}^{k_{2}} \partial_{K_{z}}^{k_{3}+1} \int_{0}^{1} e^{-K^{2}t^{2}} dt) \cdot \left(\frac{ab}{a+b}\right)^{\frac{l+m-k}{2}} H_{l_{1}+m_{1}-k_{1}}\left(\sqrt{\frac{ab}{a+b}}R_{x}\right)$$

$$H_{l_2+m_2-k_2}(\sqrt{\frac{ab}{a+b}}R_y)H_{l_3+m_3-k_3}(\sqrt{\frac{ab}{a+b}}R_z) \cdot e^{-\frac{ab}{a+b}R^2}$$
(74)

where  $H_{l_1+m_1-k_1}$  are Hermite polynomials, a and b are exponents of basis functions centered at  $\vec{A}$  and  $\vec{B}$ , respectively, and  $\vec{R} = \vec{B} - \vec{A}$  is a vector pointing from  $\vec{A}$  to  $\vec{B}$ . The other symbols are defined as follows:

$$l = l_1 + l_2 + l_3$$
  

$$m = m_1 + m_2 + m_3$$
  

$$k = k_1 + k_2 + k_3,$$
(75)

the summation over  $k_1$ ,  $k_2$  and  $k_3$  limits the range from zero to  $l_1 + m_1$ ,  $l_2 + m_2$  and  $l_3 + m_3$ , respectively, and

$$\vec{K} = \sqrt{a+b}(\vec{r} - \frac{a\vec{A} + b\vec{B}}{a+b})$$
(76)

The auxiliary functions  $h(l_1, m_1, k_1, -\frac{a}{b})$  are given by

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$$h(l_1, m_1, k_1, -\frac{a}{b}) = \sum_{\max\{0, k_1 - m_1\}}^{\min\{l_1, k_1\}} \binom{l}{i} \binom{m}{k_1 - i} (-\frac{a}{b})^i$$
(77)

Source codes to include field effect, and plotting routines for electron densities and field distributions, have been written and are available upon request.

# **4** Theoretical Results

## 4.1 $H, H_2, H_3$ and Their Ions

To assess the reliability of the local spin density approximation (LSDA) as outlined in the preceding chapter, we have compiled, in Table 4.1, bond length, total electronic energies, binding energies, and ionization energies for the various hydrogen species and their ions. For atomic hydrogen LSDA is not too reliable yielding an ionization energy of 13.02eV instead of the exact value of 13.59eV; a similar discrepancy exists for the ionization energy of  $H_2$  with half an electron volt difference. For the molecular species, bond lengths calculated in LSDA are typically too long by as much as 0.1Aand binding energies are overestimated about 0.1 eV. Although binding energies for linear and triangular  $H_3$  are 0.5eV higher, ionization energies for linear and triangular  $H_3$  and binding energies for linear and triangular  $H_3^+$  are in good agreement with CI calculations  $\mathbb{CXP}$  [52] and SL [53]. The latter, being specifically designed for  $H_3$ , employ much larger basis sets and ought to be more reliable. We also note that CI calculations based on the Gauss'90 package [54] give rather poor results as does an approach based on a basis of floating spherical Gaussian orbitals [55]. Our calculations confirm that  $H_3$  is unstable in nature and easily dissociates into  $H_2$  plus H, but that  $H_3^+$ , especially in its triangular form, is quite stable as also seen in field ionization experiments [5]. Lastly we notice that nonlocal calculations have improved all local results.

As a first step towards the understanding of field effects on hydrogen we calculate the electronic properties of  $H_2$ ,  $H_2^+$  and  $H_3^+$  in a constant electric field using LSDA. In the basis set for hydrogen we included 1s, 2s, 2p type gaussian orbitals. In Figure 24 we show the potential energy, i.e. the energy difference,  $\Delta E = E(H_2, F) - 2E(H, F =$ 0) as a function of the H - H distance for various field strengths. We note a steady decrease in the minimum, with the bond length increasing slightly. The Schottky barrier of dissociation disappears at 5.14 V/Å. The early FSGO [55] calculation put the dissociation field strength between 5.6 and 6.0 V/Å. If we assume that field-induced dissociation is a thermally activated process with a rate constant given by

$$k = \nu exp(-Q(F)/k_BT) \tag{78}$$

with the prefactor of standard magnitude, i.e.  $\nu = 10^{13}s^{-1}$ , we estimate dissociation setting in at field strengths of the order of  $4.5V/\text{\AA}$  at room temperature. We also calculated the polarisability of  $H_2$  to be  $\alpha(F = 0)=7.6$  a.u. to be compared with the exact value of 5.61 a.u. The polarisability increases to 19 a.u. at  $F = 5.14V/\text{\AA}$ .

We next look at the  $H_2^+$  ion. Figure 25 shows the potential energy similarly defined for  $H_2$ . We also see a steady decrease in the minimum of the total energy with a small increase in bond length. The Schottky barrier of dissociation disappears at 1.5V/Å. Hiskes' exact calculation [56] reported that the required field for the dissociation range from  $10^{-3}V/Å$  for the uppermost vibrational state to 2V/Å for the ground state. Hanson [57] obtained a similar result , 1.8 - 2.0V/Å for the disappearance of the activation barrier.

Taking account of the fact that  $H_2^+$  and  $H_3^+$  have the same binding energy, we expect that they would be dissociated at about the same electric field strength. The LSDA calculation has verified this prediction, see Figure 26.  $H_3^+$  will decay, at a field somewhat larger than 1.5V/Å, into  $H_2$  and a proton.

The contour plot of Figure 27, based on electron density difference

$$\Delta \rho = \rho(H_2, F) - \rho(H_2, F = 0), \tag{79}$$

displays the field-induced charge transfer in the direction opposite to the electric field

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strength. In similar fashion, Figure 28 and Figure 29 show the field-induced charge transfer for  $H_2^+$  and  $H_3^+$ , respectively.

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|                       | H <sub>2</sub> | $H_2^+$ | $H_3(L)$ | $H_3^+(L)$ | $H_3(T)$ | $H_3^+(T)$ |
|-----------------------|----------------|---------|----------|------------|----------|------------|
| Bond length (Å)       |                |         |          |            |          |            |
| exact                 | 0.74           | 1.06    |          |            |          | İ          |
| CI(SL)                |                |         | 0.93     |            | 1.11     |            |
| CI(CKP)               |                |         |          | 0.81       |          | 0.88       |
| FSGO                  | 0.70           | 1.00    |          |            |          | 0.83       |
| CI(Gauss'90)          | 0.75           |         | 0.94     | 0.81       |          |            |
| LSDA                  | 0.78           | 1.16    | 0.95     | 0.87       | 1.10     | 0.94       |
| Non-local             | 0.77           | 1.15    | 0.95     | 0.86       | 1.10     | 0.94       |
| $E_{total} (eV)$      |                |         |          |            |          |            |
| exact                 | -31.94         | -16.38  |          |            |          |            |
| CI(SL)                | -31.92         |         | -45.08   |            | -42.78   |            |
| CI(CKP)               | -31.88         |         |          | -34.72     |          | -36.44     |
| FSGO                  | -27.84         | -13.73  | ]        | ļ          |          | -31.64     |
| CI(Gauss'90)          | -31.32         |         | -44.23   | -34.11     |          |            |
| LSDA                  | -30.85         | -15.89  | -44.00   | -33.70     | -41.87   | -35.28     |
| Non-local             | -32.00         | -16.60  | -45.61   | -34.88     | -43.36   | -36.45     |
| $E_{binding} (eV)$    |                |         |          |            |          |            |
| exact                 | 4.75           | 2.79    |          |            |          |            |
| CI(SL)                | 4.74           |         | -0.44    |            | -2.74    |            |
| CI(CKP)               | 4.70           |         |          | 2.84       |          | 4.56       |
| FSGO                  | 4.75           | 2.19    |          |            |          | 3.80       |
| CI(Gauss'90)          | 4.13           |         | -0.67    | 2.79       |          |            |
| LSDA                  | 4.82           | 2.88    | 0.14     | 2.85       | -1.99    | 4.43       |
| Non-local             | 4.72           | 2.95    | -0.03    | 2.87       | -2.28    | 4.45       |
| $E_{ionization} (eV)$ |                |         |          |            |          |            |
| exact                 | 15.43          |         |          |            |          |            |
| CI                    |                |         | 10.36    |            | 6.34     |            |
| CI(Gauss'90)          |                |         | 10.12    |            |          |            |
| LSDA                  | 14.96          |         | 10.29    |            | 6.59     |            |
| Non-local             | 15.40          |         | 10.73    |            | 6.91     |            |

Table 1: Binding characteristics of  $H_2$ , linear and triangular  $H_3$  and their ions.

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Figure 24: Potential energy of  $H_2$  in a uniform electric field,  $F_0$ , as a function of the H - H distance. Solid line:  $F_0 = 0V/\text{\AA}$ , long-dashed line:  $F_0 = 3.0V/\text{\AA}$ , short-dashed line:  $F_0 = 4.5V/\text{\AA}$ , dot line:  $F_0 = 5.14V/\text{\AA}$ .



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Figure 25: Potential energy of  $H_2^+$  in a uniform electric field,  $F_0$ , as a function of the internuclei distance. Solid line:  $F_0 = 0V/\text{\AA}$ , long-dashed line:  $F_0 = 1.0V/\text{\AA}$ , short-dashed line:  $F_0 = 1.5V/\text{\AA}$ , dot line:  $F_0 = 2.0V/\text{\AA}$ .



Figure 26: Potential energy of  $H_3^+$  in a uniform electric field,  $F_0 = 1.5V/\text{\AA}$ , as a function of the internuclei distance between the two hydrogen atoms further away along the field.



Figure 27: Contour plot of field-induced charge transfer for  $H_2$ . Applied electric field strength is  $5.14V/\text{\AA}$  and points to right. Contour lines are  $\pm 0.01, \pm 0.005 \pm 0.001, \pm 0.0005, \pm 0.0001$  per a.u. of volume. Crosses mark the nuclei of the atoms.



Figure 28: Contour plot of field-induced charge transfer for  $H_2^+$ . Applied electric field strength is 1.5V/Å and points to right. Contour lines are  $\pm$  0.01,  $\pm$  0.005,  $\pm$  0.001,  $\pm$  0.0005,  $\pm$  0.0001 per a.u. of volume. Crosses mark the nuclei of the atoms.



Figure 29: Contour plot of field-induced charge transfer for  $H_3^+$ . Applied electric field strength is  $1.5V/\text{\AA}$  and points to right. Contour lines are  $\pm$  0.01,  $\pm$  0.005,  $\pm$  0.001,  $\pm$  0.0005,  $\pm$  0.0001 per a.u. of volume. Crosses mark the nuclei of the atoms.

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## 4.2 Field Adsorption of H on Rh(111)

For the field adsorption of atomic hydrogen we present results modeling the metal by (1) a jellium and (2) a small cluster of metal atoms. In Figure 30 we show the potential energy curves of H on jellium with  $r_s = 2.0$  for various field strengths. Similarly to the earlier calculations [58,59] in the absence of external electric fields we find that the asymptotic energy for H far from the jellium surface is only -12eVinstead of -13.59eV. This is due to the fact that the theory does not account for the change in spin polarisation as a function of distance from the jellium. It describes chemisorption at distances less than 2-3 angstroms properly, i.e. in particular at the minimum of the potential energy and at distances where the hydrogen atom is no longer polarised. However, the change to the polarized state at large distances is not allowed for. To correct for this obvious shortcoming of the calculation, one therefore restricts the jellium calculations to distances around the minimum of the potential energy curve and adjusts its asymptotic value to the correct one. This can also be done in the presence of an external electric field. However, in this situation we are less interested in the binding energy than in the activation energy as defined by (78). We see from Figure 30 that for fields larger than about 3V/Å the Schottky barrier is well within the range where the calculations are trustworthy.

We note in Figure 30 that as the field is increased, the position of the binding minimum remains essentially unchanged at 0.5Å above the jellium edge, i.e. about 1 - 1.5Å above the topmost ion cores. The activation energy for field desorption is, however, decreasing continuously, suggesting that atomic hydrogen can no longer be field adsorbed at field strengths beyond 6V/Å. Slight changes occur when one takes  $r_s = 3.0$ , confirming earlier results in the field free case which found that the total energy has a flat plateau for  $r_s$  between 2 and 4. Figure 31 shows the change of the state density of 1s below the Fermi level of the jellium metal. As the field strength increases, the peak of the 1s state shifts up getting closer to the Fermi level.

To get an idea of the importance of the p- and d-electrons of transition atoms and of the lattice structure we now report the results of LSDA cluster calculations for *Rhodium*. In a first calculation we have mimicked the (111) surface of *Rh* by a tetrahedral cluster of 4 Rh atoms with a H atom on its apex, see 35. It is known that atomic hydrogen adsorbes preferentially at multi-coordinated sites in the fieldfree case. Nevertheless we have used the on top geometry because in the presence of a field, adsorption is preferrable at on top sites, i.e. at kinks and steps. In the absence of a field we find the binding energy for H on  $Rh_4$  to be 2.36eV (compared to 1.6eV on jellium with  $r_s = 3$  bohr and 2.0eV for  $r_s = 2$  bohr) with H located 1.67Å from the top Rh atom (compared with 1.6Å on jellium if we assume that the first lattice plane is half a lattice constant, i.e. 1.35Å below the jellium edge). In a third calculation, also based on LSDA, we look at the Rh - H dimer. We find a binding energy of 3.3eV at a distance of 1.59Å, i.e. somewhat stronger binding at shorter distances for the dimer than for the cluster because the single Rh in the dimer has more electrons available for binding to hydrogen. The further reduction in binding as one goes to jellium is largely due to the lack of p- and d- electrons which form the bonding orbital with the s-electron of hydrogen in the dimer. We list, in Table 4.2, binding lengths and energies for various atomic hydrogen adsorption on transition metals based on either experiments or cluster calculations. We note that the binding distances range from 1.6Å to 2Å and binding energies from 2 to 4 eV. The LSDA result is in good agreement with these listed values.

Within the dimer model we next include field effects by placing the dimer in a uniform external field. This overestimates the field effect on Rh, because of the

absence of the field expulsion by conduction electrons in an extended metal cluster. Nevertheless, the calculation has its merits as an estimate. In Figure 32 we plot the potential energy curves for the Rh - H dimer as a function of the separation for various field strengths. It suggests that for  $F_0$  somewhat larger than 3.5V/Å the dimer no longer exists. This is indeed the range above which field adsorption of hydrogen on metals can no longer be observed. The fact that a dimer model yields good answers confirms a long held belief [60,61] that the local fields and thus the local electronic structure around adsorption sites (kink sites, steps etc.) are more important than long range metallic effects for the understanding of field adsorption. It is at first sight surprising that the jellium model predicts too large a maximum field strength for hydrogen field adsorption, i.e. of the order of 5 - 6V/Å instead of 3 - 3.5V/Å, considering the fact that similar calculations for field evaporation of metal atoms yielded good agreement with experiment [25]. However, we should bear in mind that hydrogen adsorption takes place at very short distances from the topmost ion core of the metal, i.e. in the region of the classical image plane where the local field varies rapidly. The local structure must therefore be known rather accurately, a task that the jellium model of a metal cannot provide.

The changes in the bonding characteristics as one increases the field from 0.0 to  $3.0V/\mathring{A}$  are clearly depicted in Figure 33 and 34 where we have plotted the change in density upon adsorption

$$\Delta \rho = \rho(Rh - H) - \rho(Rh) - \rho(H) \tag{80}$$

As the field is applied the bonding orbitals spread out with a significant charge transfer from the region between Rh and H to the outer side of the Rh nucleus, thus weakening the binding.

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The geometries and energies of field-free adsorption are summarized in Figure 35 with field effects displayed in Figure 36 and Figure 37.

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The contour plots of Figure 34 also give an indication why the presence of a field adsorbed hydrogen reduces the evaporation field strength of most metals. We recall that for field evaporation the metal surface is charged positively, i.e. the surface electron density is depleted resulting in a steepening of the electron profile and a shift of the image plane towards the interior of the metal [22,23]. As a result, the electron density behind the top most metal atom is enhanced, in particular if it sits in a kink site or on a smooth surface. Returning to the effect of adsorbed hydrogen we note from Figure 34 that a similar charge transfer occurs from the adsorbed hydrogen into the region behind the metal atom. Thus, in general a smaller field is necessary to cause the field evaporation of metals in the presence of adsorbed hydrogen. One might speculate that for metals or semiconductors where the charge transfer from the adsorbed hydrogen occurs into a bonding orbital between the top most atom and the next layer down, a stabilisation of the metal or semiconductor surface against field evaporation might ensue as a result of hydrogen adsorption. We hope to give a comprehensive discussion of this point elsewhere later on.



Figure 30: Field adsorption of atomic hydrogen on a jeilium metal with  $r_s = 2.0$ . Solid line:  $F_0 = 0V/\text{\AA}$ , long-dashed line:  $F_0 = 3.0V/\text{\AA}$ , short-dashed line:  $F_0 = 5.0V/\text{\AA}$ , dot line:  $F_0 = 6.0V/\text{\AA}$ .



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|                        | $R(\check{A})$ | $E_{binding}(eV)$ |
|------------------------|----------------|-------------------|
| $Pd_4H^{a}$            | 1.65           | 3.51              |
| $Pd_4H^{b}$            | 1.77           | 3.67              |
| $Pd_4H^{c}$            | 1.75           | 4.71              |
| $PdH(expt.)^{d}$       | 2.0            | 2.7               |
| $Ag_4H^{c}$            | 1.96           | 3.59              |
| $Ni_4H^{c}$            | 1.65           | 4.62              |
| $Ni_n H^{e}$           | 1.61           | 2.86              |
| $NiH(expt.)^{f}$       | 1.76-1.84      | 2.74              |
| $H/Ni(111)^{g}$        | 1.61           | 1.94              |
| $H/Ni(111)^{h}$        | 1.81-1.87      | 2.50-2.66         |
| $H/Rh(110)^{i}$        | 1.86           |                   |
| $H/Rh(001)^{j}$        | 2.00           | 2.57              |
| $H/Rh(111)(expt.)^{k}$ |                | 2.65              |
| $H/Rh(110)(expt.)^{l}$ |                | 2.65              |
| $H/Rh_{4}(111)(Atop)$  | 1.67           | 2.36              |
| H - Rh dimer           | 1.59           | 3.32              |

Table 2: Atomic hydrogen adsorption on transition metals

<sup>a)</sup> H is at the pseudo-three fold sites on Pd(110), Ref. [62]. <sup>b)</sup> Short bridge sites on  $Pd(110, \text{Ref. [62]. }^{c)}$  Three fold sites on Pd(111), Ref. [63]. <sup>d)</sup> Ref. [64,65]. <sup>e)</sup> Ref. [66]. <sup>f)</sup> Ref. [67]. <sup>g)</sup> CI calculation on top sites, Ref. [68]. <sup>h)</sup> CI calculation on three fold and bridge sites Ref. [68]. <sup>i)</sup> Pseudo-three fold sites, Ref. [69]. <sup>j)</sup> Four fold hollow sites, Ref. [70]. <sup>k)</sup> Ref. [71]. <sup>l)</sup> Ref. [72].



Figure 32: Potential energy of the Rh - H dimer in a constant electric field,  $F_0$ . Solid line:  $F_0 = 0V/\text{\AA}$ , long-dashed line:  $F_0 = 2.0V/\text{\AA}$ , short-dashed line:  $F_0 = 3.0V/\text{\AA}$ , dot line:  $F_0 = 3.5V/\text{\AA}$ 



Figure 33: Electron density difference contour plot for the Rh - H dimer without a field.

Contour lines are  $\pm$  0.01,  $\pm$  0.005,  $\pm$  0.001,  $\pm$  0.0005,  $\pm$  0.0001 per a.u. of volume. Crosses mark the nuclei of the atoms.





Contour lines are  $\pm 0.01$ ,  $\pm 0.005$ ,  $\pm 0.001$ ,  $\pm 0.0005$ ,  $\pm 0.0001$  per a.u. of volume. Crosses mark the nuclei of the atoms.



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Figure 35: Geometries of field-free adsorption of various hydrogen species on jellium, a single Rh atom and as tetrahedron  $Rh_4$ . Internuclear distances are in angstroms and energies in eV.



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Figure 36: Geometries of field adsorption of linear hydrogen species on a Rh atom resulting from the LSDA calculations.



Figure 37: Geometries of field adsorption of linear hydrogen species on a Rh atom resulting from the non-local calculations.

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## 4.3 Field Adsorption of $H_2$ on Rh(111)

We have used the LSDA method to calculate the binding energy of a linear Rh - H - Hspecies and of  $H_2$  linearly adsorbed on top of a tetrahedron of Rh. Such a geometry is of course very unlikely in the absence of a field. However, as soon as a field is applied, it will align the molecular dipole moment, i.e. the molecular axis along it. We will therefore only study field effects for this geometry.

In the absence of a field we find from LSDA a binding energy of 0.66 and 0.54 eVon a single Rh atom and on a  $Rh_4$  tetrahedron respectively, with the first hydrogen a distance of 1.88 (1.90) Å from the top Rh atom and the second H a further 0.79Å away, roughly the bonding distance in the free  $H_2$  molecule, see Figure 35. These numbers indicate physisorption for molecular hydrogen. We note that our non-local calculation improves the result a great deal giving such a value as 0.06eV which is in very good agreement with experiment and other calculations [73]. The (negligible) weakening of the Rh - H bond as one goes from a single Rh to a  $Rh_4$  cluster is again the result of a charge transfer into the internal Rh bonds.

We next look at the effect of a uniform electric field on the binding characteristics of a linear Rh - H - H species, see Figure 38. As the field is increased, the distance between the Rh and the inner H shrinks and the H - H separation increases enhancing the binding between the Rh and the  $H_2$  but diminishing the H - H binding energy. For fields of the order of 3V/Å the activation barrier for  $H_2$  dissociation dissappears. Some relevant numbers can be found in Figure 36 and Figure 37. We note that a surprising transition for  $H_2$  from physisorption in zero field to chemisorption in a strong electric field 3V/Å can be seen, particularly from the non-local calculations. This phenomenon is referred to as field-induced chemisorption that is important even for the most inert atom, namely helium [3,49]. The changes in the bonding characteristics are demonstrated in the contour plots, Figures 39 and 40, of the density differences

$$\Delta \rho = \rho(Rh - H - H) - [\rho(Rh) + 2\rho(H)]. \tag{81}$$

We should stress that this is a new, field-induced dissociation channel for an upright  $H_2$  species leading to only one H atom adsorbed rather than two as a result of the stretching of an  $H_2$  molecule physisorbed parallel to the surface.



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Figure 38: Potential energy the linear  $Rh_H - H$  trimer as a function of the H - H distance with the Rh - H distance at 1.5Å. Solid line:  $F_0 = 0V/Å$ , dashed line:  $F_0 = 2.0V/Å$ , dot line:  $F_0 = 3.0V/Å$ .



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Figure 39: Electron density difference contour plot for linear Rh - H - H trimer without a field.

Contour lines are  $\pm$  0.05, $\pm$  0.01, $\pm$  0.005,  $\pm$  0.001, $\pm$  0.0005,  $\pm$  0.0001 per a.u. of volume. Crosses mark the nuclei of the atoms.





Contour lines are  $\pm$  0.05, $\pm$  0.01, $\pm$  0.005, $\pm$  0.001,  $\pm$  0.0005, $\pm$  0.0001 per a.u. of volume. Crosses mark the nuclei of the atoms.

## 4.4 Field Adsorption of $H_3$ on Rh(111)

The bond lengths and binding energies for field-free adsorption of a linear  $H_3$  molecule on either a  $Rh_4$  cluster or on a single Rh atom are given in Figure 35. This suggests interpreting  $H_3$  adsorption as chemiscrption of an H atom on Rh with a  $H_2$  molecule physisorbed on top of it. Dissociation energies support this, i.e. 0.1eV for Rh - Hplus  $H_2$  and 3.28eV for Rh plus  $H_3$ . It is also evident in the contour plot, Figure 43, which bears an astounding similarity to that of the Rh - H species in Figure 33. Clearly this is not the lowest energy state for the adsorption of 3 hydrogen atoms on a metal surface.

What we want to show next is that the linear  $H_3$  configuration in an on top position will be stabilized in the presence of an electric field. We therefore put the Rh - H - H - H cluster into a uniform electric field of 2V/Å and calculate the binding energy as a function of the  $Rh - H_3$  distance keeping the distance between the second and the third H atoms at its field-free value. The minimum remains at the same  $\frac{1}{K}$  osition but the activation barrier against thermal field desorption is reduced to less than 1eV, see Figure 41. If we vary next the distance between the first and the second H atoms we find that a substantial contraction occurs with a significant increase in the corresponding H - H bond strength implying a field stabilisation of the linear  $H_3$  molecule, see Figure 34. The relevant bond lengths and binding energies are summarized in Figure 35 and 36. The corresponding non-local results can be found in Figure 37.



Figure 41: Potential energy of Rh - H - H - H as a function of the  $Rh - H_3$  distance keeping the second and the third H atoms at their field-free value. The distance between the first and the second H atoms is fixed at 1.9Å without a field and at 1.2Å in  $F_0 = 2.0V/Å$ , respectively. Solid line is for the field-free adsorption and dashed line for field adsorption in  $F_0 = 2.0V/Å$ .



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Figure 42: Potential energy of Rh - H - H - H as a function of the distance between the first and the second H atoms keeping last two H atoms at their field-free value. The distance between Rh and the first H atom is fixed at 1.6Å all the way. Solid line is for the field-free adsorption and dashed line for field adsorption in  $F_0 = 2.0V/Å$ .





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Contour lines are  $\pm 0.05, \pm 0.01, \pm 0.005, \pm 0.001, \pm 0.0005, \pm 0.0001$  per a.u. of volume. Crosses mark the nuclei of atoms.



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Figure 44: Electron density difference contour plot for Rh - H - H - H quadrumer in  $F_0 = 2.0V/Å$ .

Contour lines are  $\pm$  0.01, $\pm$  0.005, $\pm$  0.001, $\pm$  0.0005,  $\pm$  0.0001 per a.u. of volume. Crosses mark the nuclei of the atoms.

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## 4.5 Field Adsorption of NO on Rh Dimer

As a further application of the LSDA cluster model for field adsorption of molecules on metal, we extend our calculation to the Rh - NO system. Lately, Madenach [74] has done an experiment using Atom Probe Desorption Mass Spectrometry. He found that for NO adsorbed on a Rh tip, a positive electric field with the strength of 0.3V/Å weakens the surface binding energy by about 0.1eV and a similar negative electric field otherwise strengthens the binding energy by about 0.1eV; see Figure 45. In our calculation, the two Rh atoms are put at their equilibrium position, 2.1Å apart from each other and the Nitrogen-Oxygen dimer are aligned on top of one Rh atom with Oxygen in the far end. The calculated equilibrium geometry for such a system shows that the distance between Nitrogen and the top Rh is 1.8Å and Oxygen is 1.16Å farther away from Nitrogen, basically remaining at their bonding distance in the isolated case. The field-free binding energy between Rh dimer and NO dimer is 2.90eV instead of the experimentally measured value 1.1eV. This discrepancy essentially results from the fact that the LSDA model overestimates binding energy and also due to the small size of the Rh cluster. A constant electric field of  $\pm 0.3V/Å$ across this linear Rh - NO system does not cause an appreciable change of the geometry. However, the positive field decreases the binding energy to 2.83eV and the negative field increases the binding energy to 3.02eV. Consequently, the LSDA calculation reproduces the experimental trend very well.

In order to understand the variations of the binding energy and the electric field effect, we recall that in the field-free circumstances the bonding of NO to Rh dimer is accompanied by a transfer of 5s and 4d electrons of Rh to the  $2\pi$  anti-bonding orbital of NO. With a positive field the transfer is partially reversed due to the fact that the  $2\pi$  level of NO is raised relative to the metal band by the field energy, leading

to the weakening of the binding. In contrast a negative field will enhance such a transfer of electrons, as a result, strengthening the binding. Contour plots Figure 46 and Figure 47 defined by

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$$\Delta \rho = \rho(Rh2 - NO, F = \pm 0.3V/\text{\AA}) - \rho(Rh2 - NO, F = 0)$$
(82)

show the field-induced charge transfer, respectively. A positive field pushes the electrons towards Rh and a negative field pulls them out of Rh leaving more electrons in the NO area. We have also plotted the difference of electron density

$$\Delta \rho = \rho(Rh2 - NO) - \rho(Rh2) - \rho(NO) \tag{83}$$

in the absence and the presence of the electric field. Figure 48 shows that in the field-free case electrons pile into the bonding region of the top Rh and NO. In Figure 49 and Figure 50 we see a tiny redistribution of electrons in the opposite direction responding to these positive and negative external electric fields. The effect of a positive field may be seen more clearly from Figure 51 taken in terms of the difference of Figure 49 and Figure 48. There is an accumulation of electrons on NO's  $5\sigma$  orbital and a little drain of electrons out of the NO's  $2\pi$  orbital indicating an increase of bonding for NO dimer and therefore a less surface binding. Quite the contrary can be observed if a negative field is applied, see Figure 52 that is the difference of Figure 50 and Figure 48.

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Figure 45: Binding energy between NO and Rh surface in the presence of an electric field.



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Figure 46: Field-induced charge transfer,  $F_0 = 0.3V/\text{\AA}$ Contour lines are  $\pm 0.01, \pm 0.005, \pm 0.001, \pm 0.0005, \pm 0.0001$  per a.u. of volume. Crosses mark the nuclei of the atoms in order of Rh, N and O from bottom to top. The electric field points up.



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Figure 47: Field-induced charge transfer,  $F_0 = -0.3V/\text{\AA}$ Contour lines are  $\pm 0.01, \pm 0.005, \pm 0.001, \pm 0.0005, \pm 0.0001$  per a.u. of volume. Crosses mark the nuclei of the atoms in order of Rh, N and O from bottom to top. The electric field points down.

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Figure 48: Electron density difference contour plot for linear Rh2 - NO without field. Contour lines are  $\pm 0.1, \pm 0.05, \pm 0.01, \pm 0.005, \pm 0.001$  per a.u. of volume. Crosses mark the nuclei of the atoms in order of Rh, N and O from bottom to top.

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Contour lines are the same as in Fig. 48. Crosses mark the nuclei of the atoms in order of Rh, N and O from bottom to top. The electric field points up.



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Contour lines are the same as in Fig. 48. Crosses mark the nuclei of the atoms in order of Rh, N and O from bottom to top. The electric field points down.



Figure 51: Contour plot for the difference of Rh2 - NO with and without a positive field.

Contour lines are  $\pm 0.01, \pm 0.005, \pm 0.001, \pm 0.0005, \pm 0.0001$  per a.u. of volume. Crosses mark the nuclei of the atoms in order of Rh, N and O from bottom to top. The electric field points up.



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Figure 52: Contour plot for the difference of Rh2 - NO with and without a negative field.

Contour lines are the same as in Fig. 51. Crosses mark the nuclei of the atoms in order of Rh, N and O from bottom to top. The electric field points down.

#### 5 Summary

The main conclusions of this study are as follows: (1) Adsorption of atomic hydrogen on metal surfaces is weakened in the presence of electric fields. The maximum field strength of the order of 3V/Å is reproduced by a simple dimer model whereas field effects on adsorbed hydrogen are underestimated on a jellium surface. (2) The binding energy between molecular  $H_2$  and Rh is strongly increased in the presence of an electric field, leading to field-induced chemisorption.  $H_2$  linearly adsorbed in an on top position will be dissociated in fields of the order of 3V/Å. (3)  $H_3$  linearly adsorbed will be stabilized in fields of the order of 2V/Å.

In fields of less than 3V/Å we therefore have present on the surface (i) chemisorbed, i.e. immobile atomic hydrogen, and (ii) we <sup>1</sup>/<sub>1</sub>y, field-stabilized chemisorbed  $H_2$ , most likely mobile even at temperatures of the order of 50K. The  $H_2$  molecule will then migrate up the gradient along the metal tip. If it encounters a chemisorbed H atom, it might hop on top forming a field-stabilized linear  $H_3$  species. Once ionized by electron impact from the gas phase, it will remain stable as  $H_3^+$  after leaving the surface as is well known from gas phase spectroscopy. The local density approximation to density functional theory, having been implemented for a jellium surface and a cluster of transition metal atoms, turns out to be a good method resulting in the reliable geometry and the variation of binding energy in the presence of the electric field. This method constantly overestimates the binding energy due to its local property. As far as the ionization energy of molecular species is concerned, the calculated results are in very good agreement with CI calculation and experiments [80]. The addition of non-local approximation to the local exchangecorrelation functional is expected to yield further improvements in some cases. This is particularly true as used in calculations for binding energy of physisorbed systems.

101

We now understand field adsorption as field-induced chemisorption. In this field, however, a lot of work still remains to be done to understand effects such as local field enhancements and, ultimately, image formation in the field ion microscope, and new reaction pathways in heterogeneous catalysis.

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## Appendices

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## A An Exact Solution of Laplace's Equation with Boundary Conditions at A Finite Tip Surface and Screen in Parabolic Coordinates

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A typical solution to Laplace equation in parabolic coordinates [75]  $\nabla^2 \Phi(\alpha, \beta) = 0$  is

$$\Phi(\alpha,\beta) = \cos(m\phi)J_m(\kappa\alpha)[a_m(\kappa)I_m(\kappa\beta) + b_m(\kappa)K_m(\kappa\beta)]$$
(84)

where  $J_m$  is Bessel function of the *m*th order, and  $I_m(Z)$  and  $K_m(Z)$  are definded, in terms of  $J_m$  and Hankel function  $H_m$ , by

$$I_m(Z) = (-i)^m J_m(iZ)$$
  

$$K_m(Z) = (\pi/2)i^{m+1} H_m(iZ)$$
(85)

We choose m = 0 components of (84), since we are interested in only ground state solution in the rotationally symmetric tip. We thus have a simplified form of solution that is given by

$$\Phi(\alpha,\beta) = J_0(\kappa\alpha)[a_0(\kappa)I_0(\kappa\beta) + b_0(\kappa)K_0(\kappa\beta)]$$
(86)

In terms of superposition of these special solutions (86), we are in a position to construct a general solution which satisfies our specific boundary conditions:  $\Phi(\alpha, \beta_1) =$ 0, grounded and  $\Phi(\alpha, \beta_2) = \Phi_2$ , bias potential within the region  $\vartheta \le \alpha \le \alpha_2$ . Each special solution can be written as

$$\Phi^{[n]}(\alpha,\beta) = J_0(\kappa_n\alpha)[a_n I_0(\kappa_n\beta) + b_n K_0(\kappa_n\beta)]$$
(87)

On the tip surface,  $\beta = \beta_1$ , we impose a condition  $\Phi_{[n]} = 0$  on Equation (87) and obtain a relation

$$a_n I_0(\kappa_n \beta_1) + b_n K_0(\kappa_n \beta_1) = 0$$
(88)

or

$$b_n = -\frac{I_0(\kappa_n \beta_1)}{K_0(\kappa_n \beta_1)} \cdot a_n \tag{89}$$

Substitution of this expression into Equation (87) leads to

$$\Phi^{[n]}(\alpha,\beta) = J_0(\kappa_n\alpha)a_n[I_0(\kappa_n\beta) - \frac{I_0(\kappa_n\beta_1)}{K_0(\kappa_n\beta_1)}K_0(\kappa_n\beta)]$$
(90)

A general solution of Laplace's equation can be obtained in terms of superposition of Equation (90),

$$\Phi(\alpha,\beta) = \sum_{n=1}^{\infty} \Phi^{[n]}(\alpha,\beta)$$
(91)

On the screen,  $\beta = \beta_2$  (>  $\beta_1$ ), we impose another condition

$$\Phi(\alpha,\beta_2) = \sum_{n=1}^{\infty} \Phi^{[n]}(\alpha,\beta_2) = \Phi_2 = constant$$
(92)

If we write

$$\kappa_n = \frac{x_{0n}}{\alpha_2}$$

$$C_n = a_n [I_0(\kappa_n \beta_2) - \frac{I_0(\kappa_n \beta_1)}{K_0(\kappa_n \beta_1)} K_0(\kappa_n \beta_2)]$$
(93)

and substitute them into the boundary condition (92), we then have

$$\Phi_2 = \sum_{n=1}^{\infty} C_n J_0(x_{0n} \frac{\alpha}{\alpha_2}), \qquad (0 < \alpha < \alpha_2)$$
(94)

where Fourier-Bessel expansion [76] has been used and  $x_{0n}$ s are the positive roots of the equation  $J_0(x) = 0$  [77]. The coefficients  $C_n$  are defined by

$$C_{n} = \frac{2\Phi_{2}}{\alpha_{2}^{2}J_{1}^{2}(x_{0n})} \int_{0}^{\alpha_{2}} \alpha J_{0}(x_{0n}\frac{\alpha}{\alpha_{2}})d\alpha$$
(95)

Combination of Equation (93) and Equation (95) gives an expression for  $a_n$  and substitution of which into Equation (91) will lead to the general solution

$$\Phi(\alpha,\beta) = \frac{2\Phi_2}{\alpha_2^2} \sum_{n=1}^{\infty} \frac{J_0(\kappa_n \alpha)}{J_1^2(\kappa_n \alpha_2)} \cdot \frac{I_0(\kappa_n \beta) K_0(\kappa_n \beta_1) - I_0(\kappa_n \beta_1) K_0(\kappa_n \beta)}{I_0(\kappa_n \beta_2) K_0(\kappa_n \beta_1) - I_0(\kappa_n \beta_1) K_0(\kappa_n \beta_2)} \cdot \int_0^{\alpha_2} r J_0(\kappa_n r) dr$$
(96)

Having derived electric potential  $\Phi(\alpha, \beta)$ , let us now turn to the derivation of the electric field which results from the gradient of  $\Phi$ 

$$\vec{F} = -\nabla\Phi(\alpha, \beta) \tag{97}$$

where

$$\nabla = \frac{\hat{\alpha}}{h_1} \frac{\partial}{\partial \alpha} + \frac{\hat{\beta}}{h_2} \frac{\partial}{\partial \beta} = \frac{1}{\sqrt{\alpha^2 + \beta^2}} (\hat{\alpha} \frac{\partial}{\partial \alpha} + \hat{\beta} \frac{\partial}{\partial \beta})$$
(98)

With a help of the recurrence relations of modified Bessel functions [76]

$$\frac{\partial}{\partial Z} J_0(Z) = -J_1(Z)$$

$$\frac{\partial}{\partial Z} I_0(Z) = I_1(Z)$$

$$\frac{\partial}{\partial Z} K_0(Z) = -K_1(Z)$$
(99)

we obtain the expression for electric field,

$$\vec{F}(\alpha,\beta) = -\frac{2\Phi_2}{\alpha_2^2} \cdot \frac{1}{\sqrt{\alpha^2 + \beta^2}} \sum_{n=1}^{\infty} \frac{1}{J_1^2(x_{0n})} \cdot \frac{\int_0^{\alpha_2} \kappa_n r J_0(\kappa_n r) dr}{I_0(\kappa_n \beta_2) K_0(\kappa_n \beta_1) - I_0(\kappa_n \beta_1) K_0(\kappa_n \beta_2)}$$

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$$\times \{J_{1}(\kappa_{n}\alpha)[I_{0}(\kappa_{n}\alpha)K_{0}(\kappa_{n}\beta_{1}) - I_{0}(\kappa_{n}\beta_{1})K_{0}(\kappa_{n}\beta)](-\hat{\alpha}) + J_{0}(\kappa_{n}\alpha)[I_{1}(\kappa_{n}\beta)K_{0}(\kappa_{n}\beta_{1}) + I_{0}(\kappa_{n}\beta_{1})K_{1}(\kappa_{n}\beta)](\hat{\beta})\}$$
(100)

The integral part of Equation (100) can be carried out analytically

$$\int_0^{\alpha_2} \kappa_n r J_0(\kappa_n r) dr = \alpha_2 \cdot J_1(x_{0n}) \tag{101}$$

and substitution of this result back into the electric field (100) will lead to

$$\vec{F}(\alpha,\beta) = F_{\alpha}\hat{\alpha} + F_{\beta}\hat{\beta}$$
(102)

in which the two components of electric field end up with

$$F_{\alpha} = \frac{2\Phi_2}{\alpha_2^2} \cdot \frac{1}{\sqrt{\tilde{\alpha}^2 + \tilde{\beta}^2}} \sum_{n=1}^{\infty} \frac{J_1(x_{0n}\tilde{\alpha})}{J_1(x_{0n})} \\ \times \frac{I_0(x_{0n}\tilde{\beta})K_0(x_{0n}\tilde{\beta}_1) - I_0(x_{0n}\tilde{\beta}_1)K_0(x_{0n}\tilde{\beta})}{I_0(x_{0n}\tilde{\beta}_2)K_0(x_{0n}\tilde{\beta}_1) - I_0(x_{0n}\tilde{\beta}_1)K_0(x_{0n}\tilde{\beta}_2)}$$
(103)

and

$$F_{\beta} = -\frac{2\Phi_2}{\alpha_2^2} \cdot \frac{1}{\sqrt{\tilde{\alpha}^2 + \tilde{\beta}^2}} \sum_{n=1}^{\infty} \frac{J_0(x_{0n}\tilde{\alpha})}{J_1(x_{0n})} \\ \times \frac{I_1(x_{0n}\tilde{\beta})K_0(x_{0n}\tilde{\beta}_1) + I_0(x_{0n}\tilde{\beta}_1)K_1(x_{0n}\tilde{\beta})}{I_0(x_{0n}\tilde{\beta}_2)K_0(x_{0n}\tilde{\beta}_1) - I_0(x_{0nn}\tilde{\beta}_1)K_0(x_{0n}\tilde{\beta}_2)}$$
(104)

where

$$\tilde{\alpha} = \alpha/\alpha_2, \qquad 0 \le \tilde{\alpha} \le 1$$

$$\tilde{\beta} = \beta/\alpha_2, \qquad \tilde{\beta}_1 \le \tilde{\beta} \le \tilde{\beta}_2 \qquad (105)$$

and

$$\tilde{\beta}_1 = \beta/\alpha_2, \qquad \tilde{\beta}_2 = \beta/\alpha_2$$
 (106)

At this point, it turns out that both the electrostatic potential and the electric field are two dimensional quantities due essentially to the finite size of the metal tip and the screen. For an infinite system, however, the electrostatic potential is only  $\beta$ -dependent as we see in the text.

In order to pursue numerical solution of Equations (103) and (104), one has to determine the parameters  $\beta_1$ ,  $\beta_2$ ,  $\alpha_2$  and  $\Phi_2$  which should satisfy the experimental conditions. Such a test has been performed and the result showed that electric field approached to its counterpart in the infinite case as long as the  $\alpha_2$  is large enough.

## **B** Derivation of One Dimensional Electron Density

#### **B.1** Derivation of One Dimensional Electron Density in Cartesian Coordinates

Consider a box which has a square cross section and is infinitely stretched along the z direction. For electrons confined in such a box, the wave function and the electron density are given by

$$\Psi(x, y, z) = \sqrt{\frac{2}{L}} \sin(\frac{\pi x}{L}n) \cdot \sqrt{\frac{2}{L}} \sin(\frac{\pi y}{L}m) \cdot \psi_i(z)$$
(107)

and

$$n(x,y,z) = \sum_{occ} |\Psi(x,y,z)|^2 = \sum_{i} \sum_{m} \sum_{n} \frac{2}{L} \sin^2(\frac{\pi x}{L}n) \cdot \frac{2}{L} \sin^2(\frac{\pi y}{L}m) \cdot |\psi_i(z)|^2 \quad (108)$$

respectively, where L denotes the size of the box cross section with  $0 \le x \le L$  and  $0 \le y \le L$  and the sum is over all occupied energy states which possess the energy

$$E_{inm} = \epsilon_i + \frac{\hbar^2 \pi^2}{2\mu L^2} (n^2 + m^2)$$
(109)

For the ground state, all energy levels below the Fermi energy  $E_F$  would be occupied. Thus we have a restriction for the eigenstate energy,

$$E_{inm} \le E_F \tag{110}$$

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$$\frac{\hbar^2 \pi^2}{2\mu L^2} (n^2 + m^2) \le E_F - \epsilon_i$$
(111)

We now put on the right hand side those constant factors and use  $K^2$  to represent them, e.g.,

$$K^{2} = \frac{2\mu L^{2}}{\pi^{2}\hbar^{2}} (E_{F} - \epsilon_{i})$$
(112)

Thus we have

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$$n^2 + m^2 \le K^2 \tag{113}$$

In order to work out the sum for n(x, y, z), we turn to an integral over m and n instead of doing the summation. As a result, the electron density may be written as,

$$n(x,y,z) = \sum_{i} |\psi_{i}(z)|^{2} \int_{0}^{B} \int_{0}^{A} \frac{4}{L^{2}} \sin^{2}(\frac{\pi x}{L}n) dn \cdot \sin^{2}(\frac{\pi y}{L}m) dm \qquad (114)$$

where  $A = n_{max} = \sqrt{K^2 - m^2}$  and  $B = m_{max} = K$ . The integral over n can be evaluated at first and the double integration can be reduced to

$$\frac{4}{L^2} \int_0^K \sin^2(\frac{\pi y}{L}m) dm \int_0^{\sqrt{K^2 - m^2}} \sin^2(\frac{\pi x}{L}n) dn = \frac{4}{L^2} \int_0^K dm \sin^2(\frac{\pi y}{L}m) \times \left[\frac{\sqrt{K^2 - m^2}}{2} - \frac{L}{4\pi x} \sin(\frac{2\pi x}{L}\sqrt{K^2 - m^2})\right]$$
(115)

The substitution: u = m/K and  $a = K\pi y/L$  will be put into the above integral and the integration of the first term of it follows

$$\frac{4}{L^2} \int_0^K dm \sin^2(\frac{\pi y}{L}m) \frac{\sqrt{K^2 - m^2}}{2} = \frac{2K^2}{L^2} \int_0^1 du \sin^2(au) \sqrt{1 - u^2}$$

$$= \frac{2K^2}{L^2} \int_0^1 \sqrt{1 - u^2} \cdot \frac{1}{2} (1 - \cos 2au) du$$
  
$$= \frac{K^2}{L^2} [\int_0^1 \sqrt{1 - u^2} du - \int_0^1 \cos 2au \cdot \sqrt{1 - u^2} du]$$
  
$$= \frac{K^2}{L^2} [(\frac{u}{2}\sqrt{1 - u^2} + \frac{1}{2}\sin^{-1}u)]_0^1 - \frac{\pi}{4a} J_1(2a)]$$
  
$$= \frac{K^2}{L^2} [\frac{\pi}{4} - \frac{\pi}{4a} J_1(2a)]$$
(116)

The second term of the integral (115) turns out to be

$$\frac{1}{L\pi x} \int_{0}^{K} dm \sin^{2}(\frac{\pi y}{L}m) \sin(\frac{2\pi x}{L}\sqrt{K^{2}-m^{2}})$$
$$= \frac{K}{L\pi x} \int_{0}^{1} du \sin^{2} au \cdot \sin b\sqrt{\frac{1}{L}-u^{2}}$$
$$= \frac{K}{2L\pi x} [\int_{0}^{1} \sin b\sqrt{1-u^{2}} du - \int_{0}^{1} \cos 2au \cdot \sin b\sqrt{1-u^{2}} du]$$
(117)

where u = m/K,  $a = K\pi y/L$  and  $b = 2\pi x K/L$  respectively and replacement of the integrand by

$$\sin^2 au \cdot \sin b\sqrt{1 - u^2} = \frac{1}{2}(1 - \cos 2au) \sin b\sqrt{1 - u^2}$$
$$= \frac{1}{2}\sin b\sqrt{1 - u^2} - \frac{1}{2}\cos 2au \cdot \sin b\sqrt{1 - u^2}$$
(118)

has been made use of. The second integral of Equation (117) can be evaluated immediately by looking up the Tables of Integrals [78]

$$\int_0^1 \cos 2au \cdot \sin b\sqrt{1 - u^2} dv = \frac{\pi b}{2\sqrt{b^2 + 4a^2}} J_1(\sqrt{b^2 + 4a^2})$$
(119)

The first integral of Equation (117), however, needs to be carried through, using the variable transform

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$$1 - u^{2} = v^{2}$$
  
$$du = d\sqrt{1 - v^{2}}, \qquad (120)$$

in which case we obtain

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$$\int_{0}^{1} \sin b\sqrt{1 - u^{2}} = \int_{1}^{0} \sin bv \cdot d\sqrt{1 - v^{2}}$$
  
=  $(\sqrt{1 - v^{2}} \sin bv)|_{1}^{0} - \int_{1}^{0} \sqrt{1 - v^{2}} d \sin bv$   
=  $-\int_{1}^{0} \sqrt{1 - v^{2}} b \cos bv dv$   
=  $\int_{0}^{1} b\sqrt{1 - v^{2}} \cos bv dv$   
=  $\frac{\pi}{2} J_{1}(b)$  (121)

Combination of Equation (119) and Equation (121) yields

$$\frac{K}{L\pi x} \int_0^1 du \sin^2 a u \cdot \sin b \sqrt{1 - u^2} = \frac{K}{2L\pi x} [\frac{\pi}{2} J_1(b) - \frac{\pi}{2} \frac{b}{\sqrt{b^2 + 4a^2}} J_1(\sqrt{b^2 + 4a^2})]$$
(122)

Putting Equation (116) and Equation (122) together will lead to

$$\frac{K^{2}}{L^{2}}\left[\frac{\pi}{4} - \frac{\pi}{4a}J_{1}(2a)\right] - \frac{K}{2L\pi x}\left[\frac{\pi}{2}J_{1}(b) - \frac{\pi}{2}\frac{b}{\sqrt{b^{2} + 4a^{2}}}J_{1}(\sqrt{b^{2} + 4a^{2}})\right]$$

$$= \frac{\pi}{4}\frac{K^{2}}{L^{2}} - \left[\frac{K}{4Ly}J_{1}\left(\frac{2\pi K}{L}y\right) + \frac{K}{4Lx}J_{1}\left(\frac{2\pi K}{L}x\right)\right]$$

$$+ \frac{K}{4L}\frac{J_{1}\left(\frac{2\pi K}{L}\sqrt{x^{2} + y^{2}}\right)}{\sqrt{x^{2} + y^{2}}}$$

$$\stackrel{\doteq}{=} \frac{\pi}{4}\frac{K^{2}}{L^{2}} \qquad L \to \infty \qquad (123)$$

1 1 . where we have made use of the expansion of the Bessel function

$$J_n(Z) = \frac{Z^n}{2^n} \sum_{l=0}^{\infty} \frac{(-1)^l Z^{2l}}{2^{2l} l! \Gamma(n+l+1)}$$
(124)

We have now worked out the original double integral. Next we substitute the expression of  $K^2$  (112) into (123) and insert them into Equation (114) so that the resulting electron density ends up with

$$n(x, y, z) = \frac{\mu}{2\pi\hbar^2} \sum_{i} (E_F - \epsilon_i) |\psi_i(z)|^2$$
(125)

It is clear that the density is no longer x and y dependent. This result agrees completely with that obtained by means of a plane wave expansion.

# **B.2** Derivation of One Dimensional Electron Density in Cylindrical Coordinates

We write the Schrodinger Equation for the planar jellium model in cylindrical coordinates

$$\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho}+\frac{\partial^2}{\partial z^2}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}\right]+V_{eff}[n;z]-E\}\Psi(\rho,z,\phi)=0$$
(126)

where the  $V_{eff}$  is the effective potential and E is the molecular orbital energy, respectively. The variable separation can be accomplished by substituting

$$\Psi(\rho, z, \phi) = A e^{im\phi} J_m(k\rho) \psi_i(z)$$
(127)

into Schrodinger Equation (126). Thus we have

$$\{-\frac{\hbar^2}{2\mu}[-k^2 + \frac{\partial^2}{\partial z^2}] + V_{eff}[n;z] - E\}\psi_i(z)J_m(k\rho)e^{im\phi} = 0$$
(128)

$$\frac{1}{\rho}\frac{d}{d\rho}\rho\frac{d}{d\rho}J_{m}(k\rho) + (k^{2} - \frac{m^{2}}{\rho^{2}})J_{m}(k\rho) = 0$$
(129)

and Equation

$$\frac{1}{\rho^2} \frac{d^2}{d\phi^2} e^{im\phi} = -\frac{m^2}{\rho^2}$$
(130)

Dividing through Equation (128) by  $J_m(k\rho)e^{im\phi}$  yields

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dz^2}\psi_i(z) + V_{eff}[n;z]\psi_i(z) = (E - \frac{k^2\hbar^2}{2\mu})\psi_i(z)$$
(131)

that is eigenvalue equation in which  $\psi_i(z)$  is the eigenfunction and  $(E - k^2 \hbar^2/2\mu)$  is the corresponding eigenvalue, respectively. For ground state, the molecular orbital energy should satisfy

$$E \le E_F \tag{132}$$

where the  $E_F$  is defined as Fermi energy. It is further put into the form

$$k^2 \le \Gamma^2 \tag{133}$$

by substitutions

$$E_i = E - \frac{k^2 \hbar^2}{2\mu} \tag{134}$$

and

$$\Gamma^{2} = \frac{2\mu}{\hbar^{2}} (E_{F} - E_{i})$$
(135)

The electron density is given by

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$$n(z,\rho,\phi) = \sum_{occ} |\Psi(z,\rho,\phi)|^2$$
  
=  $\sum_{i} \sum_{m} \sum_{k} |\psi_i(z)|^2 J_m^2(k\rho)| e^{im\phi}|^2 A^2$  (136)

where A is a normalization factor which may be obtained by integrating  $\Psi^*(\vec{r})\Psi(\vec{r})$ over the whole space. Having assumed  $\psi_i(z)$  is normalized, we can prove that  $A^2 = k/2\pi$  provided that the Bessel functions and plane wave functions be normalized to  $\delta$  function [79], e.g.,

$$\int_0^\infty \int_0^{2\pi} A^2 J_m(k'\rho) J_m(k\rho) e^{i(m-m')\phi} \rho d\rho d\phi = A^2 \frac{2\pi}{k} \delta(k-k') \delta_{mm'}$$
(137)

We now rewrite the electron density in terms of the normalized wave functions

$$n(z,\rho,\phi) = \sum_{i} \sum_{m} \sum_{k} |\psi_{i}(z)|^{2} J_{m}^{2}(k\rho) \frac{k}{2\pi}$$

$$= \sum_{i} |\psi_{i}(z)|^{2} \int_{0}^{\Gamma} \frac{k}{2\pi} dk \sum_{m=-\infty}^{\infty} J_{m}^{2}(k\rho)$$

$$= \sum_{i} |\psi_{i}(z)|^{2} \int_{0}^{\Gamma} \frac{1}{4\pi} dk^{2}$$

$$= \sum_{i} |\psi_{i}(z)|^{2} \frac{\Gamma^{2}}{4\pi}$$

$$= \frac{\mu}{2\pi\hbar^{2}} \sum_{i} (E_{F} - E_{i}) |\psi_{i}(z)|^{2}$$
(138)

where we have made use of the summation theorem of Bessel function [78] which is given by

$$J_0^2(z) + 2\sum_{m=1}^{\infty} J_m^2(z) = 1$$
 (139)

and

$$J_{-m}(z) = (-1)^m J_m(z)$$
(140)

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Note that we have not taken the spin into account and the resulting electron density (138) is z dependent only as it is in Cartisian coordinates and takes the same form as that obtained by Gies and Gerhardts [22].

### References

- R. Gomer, Field Emission and Field Ionization (Harvard University Press, Cambridge, Massachusetts, 1961).
- [2] K. Christmann, Surf. Sci. Rep. 9 (1988) 1-163.
- [3] H.J. Kreuzer, in Chemistry and Physics of Solid Surfaces VIII, eds. R. Vanselow and R. Howe (Springer-Verlag, Berlin, 1990) p.133.
- [4] H.J. Kreuzer, in Surface Science of Catalysis: In-Situ Probes and Reaction Kinetics, eds. D. Dweyer and F. Hoffmann (ACS Books, Washington, 1991)
   p.268.
- [5] T.C. Clements and E.W. Müller, J. Chem. Phys. 37 (1962) 2684.
- [6] M.G. Inghram, A. Jason, B. Halpern and R. Gomer, J. Chem. Phys. 52 (1970)
   227.
- [7] E.W. Müller and T.T. Tsong, Prog. Surface Sci. 4 (1973) 1.
- [8] F.W. Röllgen, H. Heinen and H.D. Beckey, Z. Naturforsch. A29 (1974) 773.
- [9] N. Ernst and J.H. Block, Phys. Rev. B29(1984) 7092.
- [10] N. Ernst and G. Ehrlich, in *Microscopic Methods in Metals*, ed. U. Gonser, Vol. 40 of Topics in Current Physics (Springer-Verlag, Berlin, 1986) p.75.
- [11] S.S. Mackeown, C.F. Eyring and R.A. Millikan, Phys. Rev. 31 (1928) 900.
- [12] J.A. Becker, Bell System Tech. J. 30 (1951) 907.

- [13] W.P. Dyke and W.W. Dolan, in Advances in Electronics and Electron Physics VIII (Academic Press, New York, 1956) p.89.
- [14] P.J. Birdseye and D.A. Smith, Surf. Sci. 23 (1970) 198.
- [15] D.W. Yannitell, G.S. Gipson and H.C. Eaton, J. Phys. D: Appl. Phys. 12 (1979) 987.
- [16] N. Ohmae, M. Tagawa, S. Takennobu and M. Umeno, Appl. Phys. Lett. 50 (1987) 545.
- [17] D.J. Rose, J. Appl. Phys. 27 (1956) 215.
- [18] L.D. Landau and E.M. Lifshitz, Electrodynamics of Continuous Media (Pergamon Press, Oxford, 1960).
- [19] N.D. Lang and W. Kohn, Phys. Rev. B1 (1970) 4555.
- [20] N.D. Lang and W. Kohn, Phys. Rev. B3 (1971) 1215.
- [21] N.D. Lang and W. Kohn, Phys. Rev. B7 (1973) 3541.
- [22] P. Gies and R.R. Gerhardts, Phys. Rev. B33 (1981) 982.
- [23] F. Schreier and F. Rebentrost, J. Phys. C: Solid State Phys. 20 (1983) 2609.
- [24] S.H. Payne, K. Watanabe and H.J. Kreuzer, Surf. Sci. 202 (1988) 521.
- [25] L.C. Wang, H.J. Kreuzer and N.D. Lang Phys. Rev. B (in press).
- [26] J.E. Inglesfield, Surf. Sci. 188 (1987) L701.
- [27] G.C. Aers and J.E. Inglesfield, Surf. Sci. 217 (1989) 367.

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- [28] N.D. Lang, in Solid State Physics, Vol. 28 (Academic Press, New York, 1978) p.270.
- [29] N.D. Lang and A.R. Williams, Phys. Rev. B18 (1978) 616.
- [30] H. Sambe and R.H. Felton, J. Chem. Phys. 61 (1974) 3862.
- [31] H. Sambe and R.H. Felton, J. Chem. Phys. 62 (1975) 1122.
- [32] J.W.D. Connolly, B.I. Dunlap and J.R. Sabin, J. Chem. Phys. 71 (1979) 3396.
- [33] J.W.D. Connolly, B.I. Dunlap and J.R. Sabin, J. Chem. Phys. 71 (1979) 4993.
- [34] E. Radzio, J. Andzelm and D.R. Salahub, J. Chem. Phys. 83 (1985) 4573.
- [35] B.N. McMaster, N.A. Baykara and D.R. Salahub, Molecular Phys. 52 (1984) 891.
- [36] E. Radzio, J. Andzelm and D.R. Salahub, J. Comp. Chem. 6 (1985) 520.
- [37] J. Andzelm and D.R. Salahub, International J. Quantum Chem. 29 (1986) 1091.
- [38] G. Chiarello, J. Andzelm, N. Russo, R. Fournier and D.R. Salahub, Surf. Sci.
   202 (1988) L621.
- [39] F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Englewood Cliffs, New Jersey, 1963).
- [40] A.H. Stroud, Approximate Calculations of Multiple Integrals (Prentice-Hall, Englewood Cliffs, New Jersey, 1971).
- [41] L. Wilk, S.H. Vosko and M. Nusair, Can. J. Phys. 58 (1980) 1200.
- [42] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. 45 (1980) 566.

- [43] J.P. Perdew and Y. Wang, Phys. Rev. B33 (1986) 8800.
- [44] J.P. Perdew, Phys. Rev. B33 (1986) 8822.

- [45] D.R. Salahub et al., in Theory and Applications of Density Functional Approaches to Chemistry (Springer-Verlag, 1991).
- [46] V. Bonifacic and S. Huzinaga, J. Chem. Phys. 60 (1974) 2779.
- [47] A.B. Anderson and R.G. Parr, J. Chem. Phys. 53 (1969) 3375.
- [48] A.B. Anderson, J. Chem. Phys. 60 (1973) 2477.
- [49] H.J. Kreuzer, K. Nath and A.B. Anderson, Surf. Sci. 176 (1986) 261.
- [50] H.J. Kreuzer and K. Nath, Surf. Sci. 183 (1987) 591.
- [51] T. Živković and Z.B. Maksić, J. Chem. Phys. 49 (1968) 3083.
- [52] T.G. Csizmadia, J.C. Polanyi, R.E. Kari, A.C. Roach and M.A. Robb, J. Chem. Phys. 52 (1970) 6205.
- [53] P. Siegbahn and B. Liu, J. Chem. Phys. 68 (1978) 2457.
- [54] M.J. Frisch et al., GAUSSIAN 90 (Gaussian Inc., Pittsburgh, 1990).
- [55] T. Steinke, W. Gründler and P. Walther, J. Comp. Chem. 11 (1990) 548.
- [56] J.R. Hiskes, Phys. Rev. 122 (1961) 1207.
- [57] G.R. Hanson, J. Chem. Phys. 62 (1975) 1161.
- [58] H. Hjelmberg, B.I. Lundquist, O. Gunnarsson and J.K. Norskov, Surf. Sci. 89 (1979) 196.

- [59] J.K. Norskov and N.D. Lang, Phys. Rev. B21 (1980) 2131.
- [60] T.T. Tsong and E.W. Müller, Phys. Rev. Lett. 25 (1970) 911.
- [61] T.T. Tsong and E.W. Müller, J. Chem. Phys. 55 (1967) 2884.
- [62] I. Papai and D.R. Salahub, Surf. Sci. 236(1990) 241.
- [63] D.R. Salahub, V. Russier and C. Mijoule, Phys. Rev. B42 (1990) 5046.
- [64] G. Ertl, H. Conrad and E.E. Latta, Surf. Sci. 41 (1974) 435.
- [65] M. Skottke, G. Ertl, R.J. Behm, V. Penka and W. Moritz, J. Chem. Phys. 87 (1987) 6191.
- [66] T.H. Upton and W.A. Goddard III, Phys. Rev. Lett. 42 (1979) 472.
- [67] G. Ertl, K. Christmann, O. Schober and M. Neumann, J. Chem. Phys. 60 (1974)
   4528.
- [68] H. Yang and J.L. Whitten, J. Chem. Phys. 89 (1988) 5329.
- [69] K. Lebnberger et al, Surf. Sci. 217 (1989) 511.
- [70] P.J. Feibelman, Phys. Rev. B43 (1990) 9452.
- [71] P.A. Thiel, J.T. Yates Jr. and W.H. Weinberg, Surf. Sci. 84 (1979) 427.
- [72] M. Ehsasi and K. Christmann, Surf. Sci. 194 (1988) 172.
- [73] C. Holmberg, P. Nordlander and J. Harris, Surf. Sci. 175 (1986) L753.
- [74] R. Madenach (private communication.).

1

the to apply to a state of the 
- [75] P.M. Morse and H. Feshback, Methods of Theoretical Physics (McGraw-Hill, New York, 1953).
- [76] N.N. Levedev, Special Functions and Their Applications (Prentice-Hall, 1965).
- [77] M. Abramowitz and I.A. Stegun, Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables (Washington, U.S. Govt. Print. Off., 1964).
- [78] I.S. Gradshteyn and I.M. Ryzhik, Table of Integrals, Series and Products (Academic Press, 1965).
- [79] G. Arfken, Mathematical Methods for Physicists (Academic Press, 1985).
- [80] H. Andren, X. Ye and H.J. Kreuzer (in preparation).

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