THE DENSITY FUNCTIONAL THEORY AND THE ELECTRONIC STRUCTURE OF METAL SURFACES

THESIS

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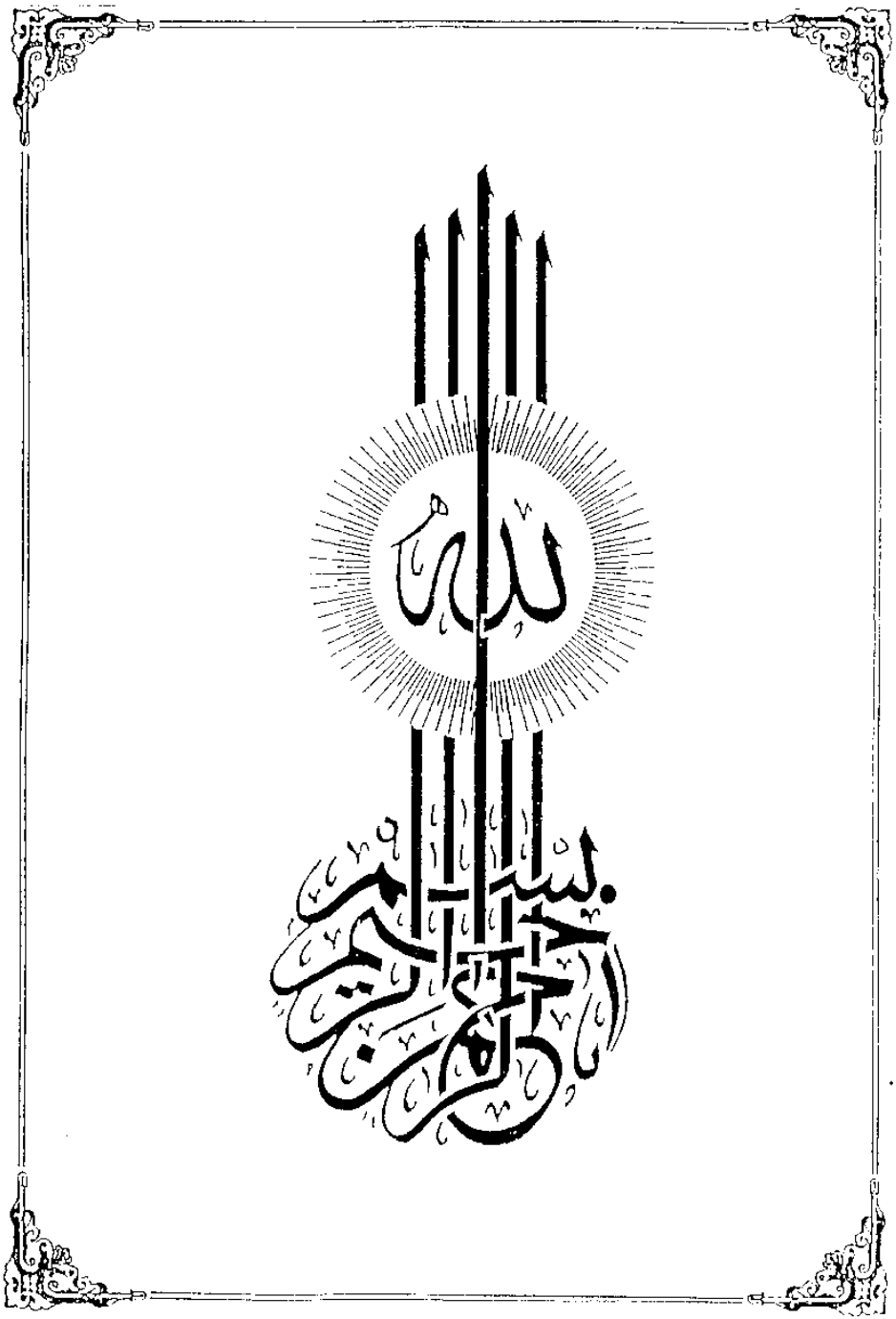

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SUMMARY

SUMMARY

The aim of this thesis is to study the metal surface dipole moments and work function in the linear potential model as an approximation to the effective potential at a metal surface.

Jellium metal surface properties such as the surface dipole barrier and work function are obtained in the linear potential model. The metal surface position and field strength are determined, respectively, by the requirement of overall charge neutrality condition and the constraint set on the electrostatic potential by the Budd-Vannimenus theorem. The calculation are primarily analytic and these properties are given in terms of universal functions of the field strength. The results obtained employing the Ceperly Alder expression for the correlation energy closely approximate those of Lang and Kohn.

A brief review of the density functional theory is given in section (2.1)of chapter II. In section (2.2) we present the definitions of Jellium metal surface and the various surface properties and sum rules which are to be employed in this work.

In chapter III we present the detailed derivations of semi-analytic expression of the metal surface dipole moment in the linear potential model. An analytic expression for the surface dipole barrier $\Delta\phi$ is obtained in terms of the slope parameter y_f.

CHAPTER I

INTRODUCTION

We consider here the linear potential model [9, 10] approximation to the effective potential at a metal surface (see Fig.1) for a given value of the field strength, the metal surface position is fixed by requiring overall charge neutrality. The field strength may then be determined by application of the (BVT). The choice of the BVT criteria as the constraint is governed by the fact that its application in previous work [2, 3] consistently lead to good results for the work function.

We redrive the analytic expressions for the surface dipole barrier $\Delta\phi$ and work function in the linear potential approximation of a metal. An analytic expression for the surface dipole barrier $\Delta\phi$ is obtained, in the linear potential model, in terms of the slope parameter y_f. This is then solved by application of Budd-Vannimenus (BV) [14] theorem to this model problem. The slope parameter y_f in this case is adjusted so as to satisfy the condition on the electrostatic potential V_{es} set by the BV theorem, while the metal-surface position is simultaneously fixed by the requirement of charge neutrality.

Thesis outline :-

In this thesis we are concerned principally with the study of the metal surface dipole moments in the linear potential approximation within the context of the density functional theory.

A brief review of the density functional theory is given in section (2.1) of chapter (II). In section (2.2) we present definitions of Jellium metal surface and the various surface properties and sum rules which are to be employed in this work.

In chapter III we present the detailed derivations for the semi-analytical expressions for the electronic charge density, the Jellium edge position, the surface dipole barrier, and the electrostatic potential, in the linear potential model.

An analytic expression for the surface dipole barrier $\Delta\phi$ is obtained in terms of the slope parameter y_f. In section (4.1) of chapter IV we employ this analytic expression for the surface dipole barrier by application of the Budd-Vannimenus (BV) theorem to this model problem.

Finally, in section (4.2), we summarize our conclusion and make suggestions for future work.

CHAPTER II

THEOREMS AND DEFINITIONS

The vanishing of the first variation of $E[\rho]$ about the correct density may be expressed by,

$$\delta E[\rho] = 0 \qquad (2\text{-}1\text{-}9)$$

Employing a Lagrange multiplier μ (which can be shown to be corresponding to the chemical potential of the system) to incorprate the constraint that the total number of the particles is conserved.

This variational principle implies that, for the correct density,

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\vec{r})} = v_{es}(\vec{r}) + \frac{\delta T_S[\rho]}{\delta \rho(\vec{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \qquad (2\text{-}1\text{-}10)$$

where $v_{es}(\vec{r})$ is the total electrostatic potential of the system due to all charges. i.e.

$$v_{es}(\vec{r}) = v(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \qquad (2.1.11)$$

Thus the density may be obtained by solution of Eq. (2-1-10) in conjunction with Eq. (2-1-11).

However, since the kinetic energy $T_S[\rho]$ within this theorem corresponds to a system of non-interacting electrons, solution of Eq. (2-1-10) is equivalent to solving self consistently a set of single particle Schrödinger like equations for non-interacting electrons moving in an effective potential $v_{eff}(\vec{r})$ whose solution gives the exact ground state density, and hence the energy, of the

2.2 Definitions of Jellium metal surface properties:

In this section we introduce the definitions of the electron density, surface dipole barrier, work function and surface energy as applied to the Jellium model of a metal surface. In this model the positive ions are assumed to be replaced by a uniform semi-infinite charge background of density $\rho_+(x) = \frac{k_f^3}{3\pi^2}\Theta(-x + a)$ ending abruptly at the metal surface position (a). Here k_f is the bulk Fermi momentum defined in terms of the Wigner-Seitz radius as in [12].

$$k_f = \frac{1}{\alpha r_s} \quad , \quad \alpha^{-1} = \left(\frac{9\pi}{4}\right)^{1/3}$$

and

$$\frac{k_f^3}{3\pi^2} = \bar{\rho} \text{ is the bulk density.}$$

Because of the reduction in symmetry in this problem, the Hamiltonian of the system is different inside and outside the metal surface, and therefore the electron momentum perpendicular to the surface is no longer a good quantum number. However, since Jellium metal has no structure parallel to the surface, the momentum parallel to the surface is a good quantum number.

Consequently, the electronic wave function can be written as

$$\psi_k(\vec{r}) = \left(\frac{1}{A}\right)^{1/2} \psi_k(x)\, \exp(i\vec{k}_{\parallel}.\vec{x}_{\parallel}) \qquad (2\text{-}2\text{-}1)$$

$$\rho_T(x) = \rho_e(x) - \rho_+(x) \qquad (2\text{-}2\text{-}4)$$

must satisfy the neutrality condition for the system. This condition is given by

$$\int_{-\infty}^{\infty} \rho_T(x)\, dx = 0 \qquad (2\text{-}2\text{-}5)$$

It has been shown [13] that this charge neutrality condition is equivalent to a phase shift sum rule due to Sugiyama [10] according to which the weighted Fermi surface average of the asymptotic phase shift $\delta(k)$ of the electronic wave function must equal to $-\pi/4$.

$$\int_0^{k_f} dk\, k\, \delta(k) \Big/ \int_0^{k_f} k\, dk = -\pi/4. \qquad (2\text{-}2\text{-}6)$$

The Jellium edge position (a) may be determined either by the charge neutrality condition or by employing the Sugiyama sum rule. Application of the latter condition leads to a simple expression for the Jellium edge position in terms of the asymptotic phase shift $\delta(k)$, which is

$$a = -\frac{3\pi}{8k_f} - \frac{3}{k_f^3} \int_0^{k_f} k\, \delta(k)\, dk \qquad (2\text{-}2\text{-}7)$$

Due to the fact that the electronic density decays into the vacuum well beyond the Jellium edge, a double layer is formed in the region about the surface. An electron trying to escape from the metal will thus experience a dipole barrier of height

$$\Delta\phi = 4\pi \int_{-\infty}^{\infty} x\, \rho_T(x)\, dx = v_{es}(\infty) - v_{es}(-\infty) \qquad (2\text{-}2\text{-}8)$$

where $v_{es}(x)$ is the electrostatic potential due to the total charge distribution of the system, and is determined as the solution to Poisson's equation

$$\frac{d^2 v_{es}}{dx^2} = -4\pi\, \rho_T(x) \qquad (2\text{-}2\text{-}9)$$

with the choice of the boundary conditions $v_{es}(-\infty) = v'_{es}(-\infty) = 0$, together with the charge neutrality condition, this solution may be written as

$$v_{es}(x) = \Delta\phi - 4\pi \int_{\infty}^{x} dx' \int_{\infty}^{x'} dx'' \, \rho_T(x'') \qquad (2\text{-}2\text{-}10)$$

The contribution to the effective potential $v_{eff}(x)$, other than the electrostatic potential $v_{es}(x)$, are due to the exchange and correlation effects (see Eq. (2-1-14)). In the deep interior of the metal where the electron density is uniform,

$$v_{eff}(x) \longrightarrow v_{es}(-\infty) + v_{xc}(\rho) \qquad (2\text{-}2\text{-}11)$$

where $v_{xc}(\rho) = d[\rho\epsilon_{xc}(\rho)]/d\rho$, since $E_{xc}[\rho]$ is known for the homogeneous electron gas system.

Very far outside the surface, exchange and correlation effects are insignificant so that

$$v_{eff}(x \longrightarrow \infty) = v_{es}(\infty) \qquad (2\text{-}2\text{-}12)$$

In the intermediate region it is not possible to give an explicit expression for $v_{eff}(x)$ since the functional $E_{xc}[\rho]$ is unknown. Both from electrostatics and by a study [15] of the mass operator of a Fermi-level electron in a bounded electron gas we known that well outside the surface but such Eq. (2-2-12) is appropriate, the effective potential is of the image

$$v_{eff}(x) \simeq v_{es}(\infty) - 1/4x \qquad (2\text{-}2\text{-}13)$$

in this region.

The work function ϕ which is the energy required to remove a Fermi electron to infinity may be written as

$$\phi = \left[v_{eff}(\infty) - v_{eff}(-\infty) \right] - \frac{1}{2} k_f^2 \qquad (2\text{-}2\text{-}14)$$

Or equivalently as

$$\phi = \Delta\phi - \frac{1}{2} k_f^2 - \mu_{xc} \qquad (2\text{-}2\text{-}15)$$

where $\frac{1}{2} k_f^2$ is the Fermi energy and μ_{xc} is the exchange and correlation part of the chemical potential of the uniform electron gas defined [1] as

$$\mu_{xc} = \frac{d}{d\rho}(\rho\, \varepsilon_{xc}) \qquad (2\text{-}2\text{-}16)$$

where $\varepsilon_{xc} = \varepsilon_x + \varepsilon_c$ is the average exchange correlation energy per particle for the homogeneous electron gas system. In terms of