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QUANTUM MECHANICS OF EFFECTIVE POTENTIAL AT A METAL SURFACE

by

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Abstract

QUANTUM MECHANICS OF EFFECTIVE POTENTIAL AT A METAL SURFACE

by

Alexander Solomatin

Adviser: Professor Viraht Sahni

In this thesis we study the nonuniform electron density system at a metal-vacuum interface via the corresponding local effective potential confining the electrons, the metal being represented by the jellium and structureless pseudopotential models. The study is performed within conventional Kohn-Sham (KS) density-functional theory and its recently derived quantum-mechanical interpretation. In the latter, properties are determined in terms of the separate electron correlations due to the Pauli exclusion principle, Coulomb repulsion and the correlation contribution to the kinetic energy. We have derived the exact analytical structure, valid for self-consistent orbitals, of the KS theory exchange potential in the classically forbidden region. This structure is image-potential-like of the form $-\alpha_{KS_x}(\beta)/x$, where the parameter β^2 is the ratio of the surface barrier height to the metal Fermi energy. For a Wigner-Seitz radius of $r_s=4.1$, which is approximately that for which jellium metal is stable, the decay coefficient is precisely 1/4. Over the metallic range of densities $r_s=2-6$, the coefficient ranges from 0.195 to 0.274. Thus, if the asymptotic structure of the KS exchange-correlation potential is the image potential, then this structure is due principally to KS exchange effects, the KS correlation

contribution being an order of magnitude smaller. These results, then lead to the concept of an 'image' charge localized to the surface region for asymptotic positions of the electron. We have further derived the exact analytical structure in the vacuum of the Slater exchange potential, and of the Pauli-correlation and correlation-kinetic components of the KS exchange potential. These structures are all image-potential-like, decaying respectively as $-\alpha_S(\beta)/x$, $-\alpha_W(\beta)/x$ and $\alpha_{t_c}^{(1)}(\beta)/x$. The Pauli-correlation component constitutes the major fraction of the KS exchange potential asymptotically, but there is a finite correlation-kinetic contribution. It is only for metals of high density that the KS exchange potential is the same as its Pauli component. We have also determined the structure of the Pauli-correlation and correlation-kinetic components about the surface extending into the metal bulk. Once again, the KS exchange potential is comprised primarily of its Pauli component, the correlation-kinetic part being an order of magnitude smaller. Similar calculations for atoms then show the intershell bumps in the KS exchange potential to be due to correlation-kinetic effects. We have also constructed an approximate KS exchange potential for the metal surface via the concept of restricted functional differentiation developed by us. This potential is then shown to satisfy essentially all integral and differential sum rules for this property, as well as possess the correct asymptotic structure in the metal bulk and vacuum regions. Finally, we have constructed separate approximate KS exchange and correlation energy functionals such that the potentials improve upon the local density approximation by possessing the correct asymptotic structure in the vacuum.

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CHAPTER I

INTRODUCTION

This thesis is concerned with the electronic structure of the nonuniform electron gas at a metal surface (Kiejna and Wojciechowski, 1996; Lang, 1983) in its ground state. We work within the context of Hohenberg-Kohn-Sham (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) density-functional theory (Dreizler and Gross, 1990; Parr and Yang, 1989; March, 1992) in which the interacting electrons are represented by a system of ***noninteracting*** fermions confined to within the metal by a ***local*** (multiplicative) effective potential along the lines of the Sommerfeld (Sommerfeld, 1928; Fröhlich, 1936) model. In Kohn-Sham theory this local potential is rigorously defined, and represents electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and the correlation contribution to the kinetic energy. The definitions employed in the thesis, however, are those of both conventional Kohn-Sham theory as well as of its recently derived physical interpretation (Sahni, 1996; ibid., 1997). In the former, the potential is described strictly in mathematical terms as a functional derivative of a yet unknown exchange-correlation energy functional of the density $\rho(\mathbf{r})$ in which these correlations are incorporated. In the latter, the description of both the energy functional and potential is in terms of fields and source distributions that separately represent the different correlations which contribute to them. It is thus possible via the physical interpretation to study properties in terms of these correlations.

According to modern density-functional theory due to Hohenberg and Kohn, the ground state wavefunction Ψ of a system of interacting electrons in a local external potential $v(\boldsymbol{r})$ is a functional the ground-state density $\rho(\boldsymbol{r})$. Therefore, the expectation value of any observable, and hence the energy $E[\rho]$, is a unique functional of the density. In the Kohn-Sham (KS) version of the theory, the Hamiltonian of the Schrödinger equation is replaced by that of a system of ***noninteracting*** fermions whose ground state density and energy are that of the interacting system. The corresponding 'wavefunction' is a ***single*** Slater determinant of the KS orbitals. The noninteracting fermions are confined within and about the metal surface by a **local** or multiplicative effective potential $v_{eff}(\boldsymbol{r})$. The effective potential is comprised of a sum of the electrostatic potential due to the electronic density and positively charged ions of the metal, and an 'exchange-correlation' potential $v_{xc}(\boldsymbol{r})$. As a consequence of the variational principle for the energy, the potential $v_{xc}(\boldsymbol{r})$ is defined ***mathematically*** as the ***functional derivative*** with respect to arbitrary norm conserving density variations of the universal 'exchange-correlation' energy functional $E_{xc}^{KS}[\rho]$ of the density: $v_{xc}(\boldsymbol{r}) = \delta E_{xc}^{KS}[\rho]/\delta\rho(\boldsymbol{r})$. Since the fermions are noninteracting, the functional $E_{xc}^{KS}[\rho]$ incorporates correlations due to the Pauli exclusion principle, Coulomb repulsion, and the correlation contribution to the kinetic energy of the electrons. The functional derivative $v_{xc}(\boldsymbol{r})$ is also therefore representative of these correlations. The energy functional $E_{xc}^{KS}[\rho]$, and hence its derivative $v_{xc}(\mathbf{r})$, are at present unknown.

In recent work (Sahni, 1996; ibid., 1997a) a ***rigorous*** quantal interpretation of the KS theory exchange-correlation energy functional $E_{xc}[\rho]$ and its derivative $v_{xc}(\mathbf{r})$ has been developed. This ***physical*** interpretation, based on the ideas of Harbola and Sahni (Harbola and Sahni, 1989; Sahni and Harbola, 1990; Harbola and Sahni, 1993) and their formal extension by Holas and March (Holas and March, 1995), is in terms of a sum of two fields whose source distributions are quantal expectations of Hermitian operators. The first of these is derived via Coulomb's law from the quantal Fermi-Coulomb hole charge distribution, and is strictly representative of Pauli and Coulomb correlations. The second field arises from the difference of the kinetic-energy-density tensors of the interacting and noninteracting systems, and is therefore representative of the correlation-kinetic contribution. The functional derivative $v_{xc}(\mathbf{r})$ is the work done to move an electron in the sum of these fields. This work done is ***path-independent***, since the sum of the fields is conservative. The quantal exchange-correlation and correlation-kinetic components of the energy functional $E_{xc}^{KS}[\rho]$ can also be expressed separately in virial form in terms of these fields. The exchange-correlation component can be further split into its purely Pauli and Coulomb parts. The determination of the Pauli, Coulomb, and correlation-kinetic fields then leads to an understanding of the correlations which contribute to the KS exchange-correlation energy and potential.

A major component of the thesis is the ***exact analytical*** (Solomatin and Sahni, 1996; ibid., 1997a,b,c; Sahni, 1997b) determination of the effective potential in the classically forbidden region at a metal-vacuum interface, and of its constituents representing the different correlations which contribute to its structure. These analytical results are valid for the ***fully-self-consistent*** Kohn-Sham orbitals of the jellium (Bardeen, 1936) and structureless-pseudopotential (Perdew, 1995; Perdew et.al.,1990; Shore and Rose, 1991) models of a ***semi-infinite*** metal surface. The asymptotic structure in the vacuum is of significance from the perspective of various surface probes such as the scanning tunneling microscope (Persson and Baratoff, 1988), inverse (Yang et.al.,1991; Smith, 1988) and two-photon photoemission (Fischer et.al.,1990), the data on the binding energy and lifetime of image-potential-bound surface states (Davison and Steslicka, 1992) thereby produced, as well as for the interaction of ions and positrons with the metal surface. The analytical results derived in the thesis lead to a description of the physics which differs from that presently accepted in the literature, the latter conclusions having been arrived at via calculations that employ various approximations and which are ***numerical***.

To put our work in context, we describe here the principle results and conclusions of the work of others. Since the electrostatic potential at a metal surface, as determined by Poisson's equation, decays exponentially in the classically forbidden region just as does the density, the asymptotic structure of the effective potential is that of the Kohn-Sham theory exchange-correlation potential $v_{xc}(r)$. In their paper, Almbladh and von

Barth (Almbladh and von Barth, 1985) state ***without proof*** that for macroscopic systems, the exchange potential $v_x(r) = \delta E_x^{KS}[\rho]/\delta\rho(r)$, where $E_x^{KS}[\rho]$ is the Kohn-Sham exchange energy functional, tends ***exponentially*** to zero. They, thus conclude that the asymptotic structure of $v_{xc}(r)$ is a ***Coulomb correlation*** or polarization effect. Then determining this polarization ***classically***, they obtain the asymptotic structure of $v_{xc}(r)$ via the resulting single-particle density matrix to be the image potential $(-1/4x)$. The view that the asymptotic structure of $v_{xc}(r)$ is the image potential and that it is due to Coulomb correlations is supported by Sham (Sham, 1985) and the ***jellium-slab-metal*** calculations of Eguiluz et.al. (Eguiluz et.al., 1992a). In the work of these authors the exchange potential $v_x(r)$ decays asymptotically as $-1/x^2$. The calculations of Eguiluz et.al., for the exchange-correlation potential $v_{xc}(r)$, which are within the GW and random phase approximations, and in which the one-electron Green function is replaced by the density-functional theory noninteracting Green function, are performed ***numerically*** for ***specific*** metals. With these approximations, and to the distance of about two Fermi wavelengths from the surface considered, they obtain the asymptotic structure of $v_{xc}(r)$ to be the image potential. The calculations of Sham (Sham, 1985), are based on Rudnick's (Rudnick, 1970) thesis in whose work various approximations are made for the determination of the self-energy. These approximations include using the one-electron Green function for an electron in free space to represent the electron in the classically forbidden region, as well as the use of the infinite barrier model (Bardeen, 1936) of a metal surface. As a consequence, the $-1/x$ behavior of $v_{xc}(r)$ is again attributed to Coulomb correlation effects. We refer the reader to the original literature for details of the various approximations made in these calculations.

On the other hand, Harbola and Sahni (Harbola and Sahni, 1989b) determined ***numerically*** and for a ***specific*** high density metal the work done $W_x^{KS}(r)$ in the field $\mathcal{E}_x^{KS}(r)$ of the ***dynamic*** and ***delocalized*** (Sahni and Bohnen, 1984; ibid., 1985; Harbola and Sahni, 1988) Fermi hole charge at a metal surface, and observed it to be essentially the image potential at about eight Fermi wavelengths from the surface. ($W_x^{KS}(r)$ is the Pauli-correlation component of the KS exchange-correlation potential $v_{xc}(r)$) Since the total charge of the Coulomb hole is zero, the field due to it vanishes for asymptotic positions of the electron in the vacuum region far from the metal. Harbola and Sahni thus concluded that the asymptotic image potential structure of $v_{xc}(r)$ was due entirely to ***Pauli correlations***, and that the decay coefficient was 1/4 for ***all*** metals. To further support their viewpoint, Harbola and Sahni (Harbola and Sahni, 1993) also showed ***numerically***, again for a ***specific*** high density metal, that the asymptotic structure of the exchange potential $v_x(r)$ is also image-potential-like about three Fermi wavelengths from the surface.

In light of these different conclusions with regard to the physical origin of the asymptotic structure of the exchange-correlation potential $v_{xc}(\mathbf{r})$, Dobson (Dobson, 1995) in a recent review has stated: "There is much remaining to be said on this issue, and since both sides of the argument have so far only presented numerical evidence, this question still remains to be settled once and for all by a rigorous analytical analysis". We provide here much of the requisite rigorous analytical analysis. We note that at present there is ***no rigorous analytical derivation*** of the asymptotic structure of $v_{xc}(\mathbf{r})$. In this thesis we derive the exact analytical structure of the ***exchange*** potential $v_x(\mathbf{r})$ and show it to be image-potential-like of the form $-\alpha_{KS_x}(\beta)/x$, where the coefficient $\alpha_{KS_x}(\beta)$ depends upon the parameter β where β^2 is the ratio of the metal surface barrier height to its Fermi energy. In fact it turns out that for $\beta = \sqrt{2}$, which corresponds to a Wigner-Seitz radius $r_s = 4.1$ for which approximate value jellium-metal is stable, the coefficient $\alpha_{KS_x}(\beta)$ is precisely $1/4$. Over the metallic range of densities, the coefficient α_{KS_x} ranges from 0.195 for $r_s = 2.0$ to 0.274 for $r_s = 6.0$. Thus, if the asymptotic structure of $v_{xc}(\mathbf{r})$ is the image potential, then for stable jellium this structure is entirely due to the Kohn-Sham exchange effects. For other metals, the structure is due to both KS exchange and correlation, being principally due to the former, the latter contributing only weakly. It can also be shown (Solomatin and Sahni, 1996; ibid., 1997a,b,c) ***analytically*** that for jellium-slab-metal the exchange potential $v_x(\mathbf{r})$ must decay as $-x^{-2}$. This confirms the result of the exchange-only calculation of Eguiluz et.al.

We have also derived the ***exact analytical*** structure of the work $W_x^{KS}(\mathbf{r})$ and shown it to be image-potential-like of the form $-\alpha_w(\beta)/x$, but with a coefficient $\alpha_w(\beta)$ which differs from that of the Kohn-Sham coefficient $\alpha_{KS_x}(\beta)$. The value of approximately 1/4 for α_w obtained by Harbola and Sahni (Harbola and Sahni, 1989b) for the specific high density metal considered is essentially correct. However, for other metals, the coefficient $\alpha_w(\beta)$ is not 1/4. It turns out (Levy and March, 1997) that the work $W_x^{KS}(\mathbf{r})$ also represents the Pauli-correlation component of the KS exchange potential $v_x(\mathbf{r})$. The remaining component represents ***part*** of the correlation-kinetic piece of the KS exchange-correlation potential $v_{xc}(\mathbf{r})$. Thus, we learn that both the Pauli and correlation-kinetic components of the exchange potential $v_x(\mathbf{r})$ are ***long-ranged*** and decay asymptotically as $-x^{-1}$ and x^{-1}, respectively.

The knowledge of the delocalized nature of the Fermi hole at a metal surface for asymptotic positions of the electron in the vacuum together with the results derived for the asymptotic structure of the KS exchange potential then lead to an understanding (Solomatin and Sahni, 1996; ibid., 1997a,b,c) of the physical origin of an 'image' charge localized to the surface region. Note that the asymptotic electron is here part of the nonuniform electron gas, and that this 'image' charge is an intrinsic property of the system and not a distribution induced due to the presence of an external test charge. We have also investigated (Solomatin and Sahni, 1997a) the structure of the KS exchange potential and its Pauli and correlation-kinetic components at and about the surface. This part of the structure of the effective potential is of significance for properties such as the surface energy, curvature energy, and work function.

A second component of the thesis is the construction of an approximate though accurate Kohn-Sham theory exchange potential by a new prescription developed by us (Solomatin et.al., 1994; Solomatin and Sahni, 1995). In the conventional approach to Kohn-Sham theory, the unknown exchange and exchange-correlation energy functionals of the density are approximated, and the corresponding approximate potentials obtained therefrom by functional differentiation. However, in approximating these energy functionals, the rigor of the Hohenberg-Kohn theorems is lost, and consequently the bounds for the energy thus obtained are no longer rigorous. It turns out that although the Kohn-Sham theory exchange energy functional of the density is unknown, the exchange energy can be expressed explicitly in terms of the Kohn-Sham orbitals. In this thesis we have developed a new method whereby an approximate exchange potential is derived from the ***exact*** exchange energy expression via ***restricted functional differentiation***. The rigor of the Hohenberg-Kohn theorems is thereby preserved, and the energy bounds are thus rigorous. The approximate exchange potential obtained in this manner is then shown to satisfy essentially all sum rules required of this potential as well as to possess the correct asymptotic structure both in the metal bulk and vacuum regions. An approximate exchange and correlation energy functional have also been constructed (Sahni and Solomatin, 1997) such that their functional derivative possesses the correct asymptotic structure in the bulk and vacuum regions.

We begin in Chapter II by defining properties within the context of Schrödinger and Kohn-Sham theories. We then describe the quantum-mechanical interpretation of Kohn-Sham theory. As the various derivations and calculations are performed for the semi-infinite jellium and structureless-pseudopotential models of a metal surface, these models too are described in this chapter.

As the leading term of the KS exchange potential $v_x(\mathbf{r})$ is $(1/2)V_x^S(\mathbf{r})$, where $V_x^S(\mathbf{r})$ is the Slater exchange potential, we initially study the Slater potential in Chapter III. We first derive an expression for the Slater potential, different from that existing in the literature (Harbola and Sahni, 1987), which allows for its easy and accurate numerical determination throughout space. Employing this expression we then determine (Solomatin and Sahni, 1996; ibid., 1997b) the ***exact analytical*** asymptotic structure of the Slater potential in the classically forbidden region and show it to decay in an image-potential-like manner as $-\alpha_S(\beta)/x$. To make the derivation accessible, we initially derive the result for orbitals of a model effective potential. We then prove that the result is equally valid for the self-consistently determined orbitals. We also confirm the correctness of the analytical expression numerically.

From the integral equation (Sham, 1985) relating the KS exchange-correlation potential $v_{xc}(\mathbf{r})$ to the self-energy $\Sigma(\mathbf{r},\mathbf{r}';\epsilon)$ of many-body theory, we derive in Chapter IV the ***exact analytical*** asymptotic structure of the KS exchange potential $v_x(\mathbf{r})$ in the classically forbidden region. As was the case for the Slater potential, we first derive this result for model potential orbitals, and then prove it valid for the self-consistent KS orbitals. As noted above, the structure is also image-potential-like of the form $-\alpha_{KS_x}(\beta)/x$. We then compare the Slater $\alpha_S(\beta)$ and KS $\alpha_{KS_x}(\beta)$ decay coefficients over the metallic range of densities. We next prove ***analytically***, that for jellium-slab metal, the KS exchange potential $v_x(\mathbf{r})$ must decay as $-1/x^2$, and explain why this is the case. Finally, we prove that two approximate exchange potentials in the literature, one due to Sham (Sham, 1985) and the other by Solomatin et.al. (Solomatin et.al., 1994), possess the correct asymptotic structure in the vacuum.

In Chapter V we study the Pauli component $W_x^{KS}(\mathbf{r})$ of the KS exchange potential $v_x(\mathbf{r})$ at a metal surface. We begin by deriving an expression for the field $\mathcal{E}_x^{KS}(\mathbf{r})$ due to the Fermi hole charge which is different from that in the literature (Harbola and Sahni, 1989). This expression allows for the exact analytical determination of the asymptotic structure in the vacuum of the work $W_x^{KS}(\mathbf{r})$ done in this field. This asymptotic structure of the work $W_x^{KS}(\mathbf{r})$ is also image-potential-like of the form $-\alpha_W(\beta)/x$. This analytical result is then confirmed numerically. For metallic densities the coefficient $\alpha_W(\beta)$ differs from the KS exchange potential decay coefficient $\alpha_{KS_x}(\beta)$. However, in this asymptotic region the Pauli component constitutes a substantial fraction of the exchange potential $v_x(r)$, the two becoming essentially equivalent for very high density systems ($r_s \leq 2.0$). The expression derived for the field $\mathcal{E}_x^{KS}(r)$ also allows for its easy and accurate numerical determination as well as that of the work $W_x^{KS}(r)$ throughout space. For accurate model effective potential orbitals, we then determine and study the structure about the surface of the field $\mathcal{E}_x^{KS}(r)$ and the work done $W_x^{KS}(r)$ in it for both a high and low density metal. As a consequence, the asymptotic value of the work $W_x^{KS}(r)$ in the metal-bulk is also determined. Once again, it is only for very high density metals that this asymptotic value approaches the $-k_F/\pi$ value of the KS exchange potential.

In Chapter VI we derive an approximate KS exchange potential from the exact exchange energy functional via restricted functional differentiation. We then show that this potential satisfies various integral and differential sum rules as well as possess the correct asymptotic structure in the vacuum and metal-bulk. We next determine this potential ***analytically*** for the orbitals of the infinite barrier model. We also demonstrate how it can be determined for the orbitals of an arbitrary effective potential, and provide a physical interpretation of it in terms of an effective Fermi hole charge. In this chapter we also construct approximate exchange and correlation energy functionals which improve upon the local density approximation by ensuring that the asymptotic structure of the functional derivative in the vacuum region is correct.

In Chapter VII we study the correlation-kinetic component $W_{t_c}^{(1)}(\mathbf{r})$ of the KS exchange potential $v_x(\mathbf{r})$ at a metal surface and in atoms. Since the asymptotic structure in the vacuum of the potential $v_x(\mathbf{r})$ and its Pauli component $W_x^{KS}(\mathbf{r})$ are exactly known, so is the ***exact analytical*** structure of the correlation-kinetic component $W_{t_c}^{(1)}(\mathbf{r})$ known. In this chapter we determine the long-range structure of $W_{t_c}^{(1)}(\mathbf{r})$ in the vacuum and metal bulk regions. Then by assuming the KS exchange potential to be approximated by that derived by restricted functional differentiation in Chapter VI, we determine the structure of the correlation-kinetic field $\mathcal{Z}_{t_c}^{(1)}(\mathbf{r})$ and potential $W_{t_c}^{(1)}(\mathbf{r})$ at and about the metal surface. Lastly, by assuming the KS exchange potential in atoms to be that of the optimized potential method (Sharp and Horton, 1953), we determine the corresponding field $\mathcal{Z}_{t_c}^{(1)}(\mathbf{r})$ and potential $W_{t_c}^{(1)}(\mathbf{r})$ for the representative atoms of Ne and Ar. These calculations then show that the intershell bumps of the KS exchange potential, whose origin has been of considerable interest in the literature, arise due to correlation-kinetic effects.

As noted above, there is at present no rigorous analytical proof that the asymptotic structure of the KS exchange-correlation potential $v_{xc}(\mathbf{r})$ in the vacuum is the image potential. If the asymptotic structure of $v_{xc}(r)$ is assumed to be the image potential, it is then possible to determine (as in Chapter VIII) an ***analytical*** expression for the KS correlation potential $v_c(r)$ in this region. The structure of $v_c(r)$ asymptotically is also image-potential-like of the form $-\alpha_{KS,c}(\beta)/x$, but the decay coefficient $\alpha_{KS,c}(\beta)$ is an order of magnitude smaller than its exchange counterpart $\alpha_{KS,x}(\beta)$. Thus, KS Coulomb correlation effects contribute weakly to the image potential structure of $v_{xc}(r)$. The fact that the image potential structure of $v_{xc}(r)$ is independent of metal parameters, whereas its exchange and correlation components separately are dependent on them, is then explained by the concept of an 'image' charge localized to the surface region, and the correlations which contribute to this charge.

Finally, in Chapter IX we summarize our results and the conclusions arrived at, and discuss current and possible directions for future work. In particular, we think the next important step is the determination of the Coulomb hole structure at a metal surface as a function of electron position. This hole charge distribution would then enable the determination of the Coulomb correlation contribution to the surface and curvature energy and potential, as well as provide the asymptotic structure of the latter in the vacuum.

CHAPTER II

KOHN-SHAM DENSITY-FUNCTIONAL THEORY AND ITS QUANTUM-MECHANICAL INTERPRETATION

To contrast the definitions of various properties within Schröginger and Kohn-Sham theories, and in light of the fact that the quantum-mechanical interpretation of the latter is in terms of the system wavefunction, we begin with definitions within Schrödinger theory.

2.1 Definitions Within Schrödinger Theory

Within the adiabatic approximation, the Hamiltonian of a metal (in atomic units) is

$$\hat{H} = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_i v(\mathbf{r}_i) + \frac{1}{2}\sum_{ij}{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{n,m}{}' \frac{Z^2}{|\mathbf{R}_n - \mathbf{R}_m|} \quad , \qquad \text{(II-1)}$$

where $\{\mathbf{r}, \mathbf{R}\}$ are the electronic and nuclear co-ordinates, Z the nuclear charge, and where the ***local*** external potential $v(\mathbf{r})$ is

$$v(\mathbf{r}) = -\sum_n \frac{Z}{|\mathbf{r} - \mathbf{R}_n|} \quad . \qquad \text{(II-2)}$$

The corresponding time-independent Schrödinger equation for the N-electron system is then

$$\hat{H}\Psi(\mathbf{x}_1,\ldots\mathbf{x}_N) = E\Psi(\mathbf{x}_1,\ldots\mathbf{x}_N) \quad , \tag{II-3}$$

where Ψ and E are the normalized electronic wavefunction and energy, respectively. (Here $\mathbf{x} = \mathbf{r}\sigma$, where σ is the electron spin coordinate. The integral $\int d\mathbf{x} \equiv \sum_\sigma \int d\mathbf{r}$).

The electronic density $\rho(\mathbf{r})$, which is N times the probability of an electron being at $\mathbf{r}$, is the expectation value of the Hermitian density operator $\hat{\rho} = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$:

$$\begin{aligned}\rho(\mathbf{r}) &= N\sum_\sigma \int \Psi^*(\mathbf{r}\sigma, \mathbf{x}_2,\ldots\mathbf{x}_N)\Psi(\mathbf{r}\sigma, \mathbf{x}_2,\ldots\mathbf{x}_N)d\mathbf{x}_2,\ldots d\mathbf{x}_N \\ &= \langle\Psi|\hat{\rho}|\Psi\rangle \quad ,\end{aligned} \tag{II-4}$$

such that $\int \rho(\mathbf{r})d\mathbf{r} = N$.

The energy E is the expectation of the Hamiltonian:

$$\begin{aligned}E &= \langle\Psi|\hat{H}|\Psi\rangle \\ &= T + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{ee} + \frac{1}{2}\sum_{n,m} \frac{Z^2}{|\mathbf{R}_n - \mathbf{R}_m|} \quad ,\end{aligned} \tag{II-5}$$

where

$$T = \langle\Psi|\sum_i -\frac{1}{2}\nabla_i^2|\Psi\rangle \quad , \tag{II-6}$$

is the kinetic energy, and

$$E_{ee} = \langle\Psi|\frac{1}{2}\sum_{i,j}{}' \frac{1}{|r_i - r_j|}|\Psi\rangle \quad , \tag{II-7}$$

the electron-interaction energy.

The energy E_{ee} may also be expressed in terms of the ***pair-correlation density*** $g(\mathbf{r},\mathbf{r}')$ which is defined in terms of the Hermitian pair-correlation operator $\hat{P}(\mathbf{r},\mathbf{r}') = \sum_{i,j}{}' \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}')$ as

$$g(\mathbf{r},\mathbf{r}') = <\Psi|\hat{P}(\mathbf{r},\mathbf{r}')|\Psi>/\rho(\mathbf{r}) \quad . \tag{II-8}$$

The pair-correlation density is the density at $\mathbf{r}'$ for an electron at $\mathbf{r}$. For nonuniform electronic density systems, it is a ***dynamic*** charge distribution whose structure changes as a function of electron position. Its total charge for arbitrary electron position is $\int g(\mathbf{r},\mathbf{r}')d\mathbf{r}' = N - 1$. It is a property that arises as a result of correlations between electrons due to the Pauli exclusion principle and Coulomb repulsion. Thus, it may also be written as the density $\rho(\mathbf{r}')$ at $\mathbf{r}'$ plus the reduction in the density at $\mathbf{r}'$ due to these correlations. The reduction in density about an electron which occurs as a result of Pauli and Coulomb correlations is the quantal ***Fermi-Coulomb hole*** charge distribution $\rho_{xc}(\mathbf{r}, \mathbf{r}')$. Thus, we may write

$$g(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') + \rho_{xc}(\mathbf{r}, \mathbf{r}') \quad , \qquad \text{(II-9)}$$

and consequently the charge of the Fermi-Coulomb hole is

$$\int \rho_{xc}(r, r')dr' = -1 \quad . \qquad \text{(II-10)}$$

The electron-interaction energy is then the energy of interaction between the electronic and pair-correlation densities:

$$E_{ee} = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})g(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \quad . \qquad \text{(II-11)}$$

Employing the form of $g(\mathbf{r}, \mathbf{r}')$ as given by Eq.(II-9), the energy E_{ee} may be written as the sum

$$E_{ee} = E_H + E_{xc} \quad , \qquad \text{(II-12)}$$

where E_H is the Coulomb self-energy

$$E_H = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \quad , \qquad \text{(II-13)}$$

and E_{xc} is the quantal exchange-correlation energy

$$E_{xc} = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \quad , \tag{II-14}$$

which is the energy of interaction between the density and Fermi-Coulomb hole charge distribution.

The kinetic energy T may also be expressed in terms of the ***kinetic-energy-density tensor*** $t_{\alpha\beta}(\mathbf{r})$ which is a real, symmetric tensor defined as

$$t_{\alpha\beta}(\mathbf{r};[\gamma]) = \frac{1}{4}\left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right]\gamma(\mathbf{r}',\mathbf{r}'')\Big|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}} \quad . \tag{II-15}$$

where $\gamma(\mathbf{r},\mathbf{r}')$ is the spinless single-particle density matrix whose definition is

$$\gamma(\mathbf{r},\mathbf{r}') = N\sum_\sigma \int \Psi^*(\mathbf{r}\sigma,\mathbf{x}_2,\ldots \mathbf{x}_N)\Psi(\mathbf{r}'\sigma,\mathbf{x}_2,\ldots \mathbf{x}_N)d\mathbf{x}_2\ldots d\mathbf{x}_N. \tag{II-16}$$

The density matrix $\gamma(r,r')$ is the expectation value of the Hermitian operator (Sahni and Krieger, 1975; Sahni et. al., 1975) $\hat{X}$:

$$\gamma(r,r') = \langle\Psi|\hat{X}|\Psi\rangle \quad , \tag{II-17}$$

where

$$\hat{X} = \hat{A} + i\hat{B} \quad , \tag{II-18}$$

$$\hat{A} = \frac{1}{2}\sum_i [\delta(r_j-r)T_j(a) + \delta(r_j-r')T_j(-a)] \tag{II-19}$$

$$\hat{B} = \frac{i}{2}\sum_j [\delta(r_j - r)T_j(a) - \delta(r_j - r')T_j(-a)] \quad . \tag{II-20}$$

$T_j(a)$ is a translation operator such that

$$T_j(a)\Psi(\ldots r_j \ldots) = \Psi(\ldots r_j + a \ldots) \quad , \tag{II-21}$$

and $a = r' - r$. The single-particle density matrix constructed from the wavefunction Ψ is not idempotent. Its diagonal matrix element is the density: $\gamma(\mathbf{r}, \mathbf{r}) = \rho(\mathbf{r})$. The trace of the kinetic-energy-density tensor is the scalar kinetic-energy-density: $t(\mathbf{r}) = \sum_\alpha t_{\alpha\alpha}(\mathbf{r}) \geq 0$, so that the kinetic energy

$$T = \int t(\mathbf{r})d\mathbf{r} \quad . \tag{II-22}$$

The quantal properties of the pair-correlation density $g(\mathbf{r}, \mathbf{r}')$ and the correlation-kinetic-energy density tensor $t_{\alpha\beta}(\mathbf{r})$ are fundamental to the physical interpretation of KS theory. However, prior to describing the interpretation we define properties within the context of conventional Kohn-Sham density-functional theory.

2.2 Kohn-Sham Density-Functional Theory

In KS density-functional theory of the ground state, one constructs a model system of ***noninteracting*** fermions whose density and energy are the same as that of the interacting system described by Schrödinger theory. As such the ground-state energy functional $E[\rho]$ is partitioned as

$$E[\rho] = T_s[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r} + E_{ee}^{KS}[\rho] + \frac{1}{2}\sum_{n,m}{}' \frac{Z^2}{|\mathbf{R}_n - \mathbf{R}_m|} \quad , \qquad \text{(II-23)}$$

where $T_s[\rho]$ is the corresponding kinetic energy of the noninteracting system. The KS theory electron-interaction energy functional $E_{ee}^{KS}[\rho]$ can be further partitioned as

$$E_{ee}^{KS}[\rho] = E_H[\rho] + E_{xc}^{KS}[\rho] \quad , \qquad \text{(II-24)}$$

because the Coulomb self-energy functional $E_H[\rho]$ of Eq. (II-13) is known, and this then defines the 'exchange-correlation' energy functional $E_{xc}^{KS}[\rho]$. A comparison of Eq.(II-24) with Eq.(II-12) in conjunction with the energy expression Eq.(II-5) shows that $E_{xc}^{KS}[\rho]$ is comprised of the sum of the quantal exchange-correlation $E_{xc}[\rho]$ and correlation-kinetic $T_c[\rho]$ energy components:

$$E_{xc}^{KS} = E_{xc}[\rho] + T_c[\rho] \quad , \qquad \text{(II-25)}$$

where

$$T_c[\rho] = T[\rho] - T_s[\rho] \quad . \qquad \text{(II-26)}$$

On application of the variational principle to the ground-state energy functional of Eq.(II-23) for arbitrary norm conserving variations of the density, one obtains the KS equation

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{ee}(\mathbf{r}) \right] \psi_i(\mathbf{x}) = \epsilon_i \psi_i(\mathbf{x}) \, ; \qquad i = 1, \ldots N \quad , \qquad \text{(II-27)}$$

so that the electrons all move in a ***local*** effective potential $v_{eff} = v(\mathbf{r}) + v_{ee}(\mathbf{r})$. Here $v_{ee}(\mathbf{r})$ is the ***local*** (multiplicative) potential in which ***all*** the electron correlations are incorporated. As a consequence of the variational principle, this potential is the functional derivative of $E_{ee}^{KS}[\rho]$:

$$v_{ee}(\mathbf{r}) = \frac{\delta E_{ee}^{KS}[\rho]}{\delta\rho(\mathbf{r})} \quad . \tag{II-28}$$

With $E_{ee}^{KS}[\rho]$ partitioned as in Eq.(II-24), the potential $v_{ee}(\mathbf{r})$ can be written as

$$v_{ee}(\mathbf{r}) = v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad , \tag{II-29}$$

which defines the density-functional theory Hartree potential $v_H(\mathbf{r})$ as the functional derivative

$$v_H(\mathbf{r}) = \frac{\delta E_H[\rho]}{\delta\rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad , \tag{II-30}$$

and the KS theory 'exchange-correlation' potential $v_{xc}(\mathbf{r})$ as the functional derivative

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}^{KS}[\rho]}{\delta\rho(\mathbf{r})} \quad . \tag{II-31}$$

The ground-state 'wavefunction' corresponding to this noninteracting system is then a ***single*** Slater determinant $\Phi\{\psi_i(\mathbf{x})\}$ of the lowest occupied orbitals. The idempotent Dirac (Dirac, 1930) single-particle density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$, ground-state density $\rho(\mathbf{r})$, and noninteracting system kinetic energy $T_s[\rho]$ that result from this Slater determinant are

$$\gamma_s(\mathbf{r},\mathbf{r}') = \langle\Phi\{\psi_i(x)\}|\hat{X}|\Phi\{\psi_i(x)\}\rangle = \sum_i\sum_\sigma \psi_i^*(\mathbf{r}\sigma)\psi_i(\mathbf{r}'\sigma) \quad , \tag{II-32}$$

$$\rho(\mathbf{r}) = \gamma_s(\mathbf{r},\mathbf{r}) = \sum_i\sum_\sigma |\psi_i(\mathbf{r}\sigma)|^2 \quad , \tag{II-33}$$

and

$$T_s[\rho] = \sum_i \int \psi_i^*(x)\left[-\frac{1}{2}\nabla^2\right]\psi_i(x)dr = \int t_s(r)dr \quad , \tag{II-34}$$

respectively, and where $t_s(r)$ is defined in a manner analogous to $t(r)$ but in terms of $\gamma_s(r,r')$ instead. The ground-state energy is then determined from the functional of Eq.(II-23) by adjusting the nuclear positions $\mathbf{R}_n$ till a minimum is determined. Furthermore, the highest occupied eigenvalue (Perdew et.al., 1982; Levy et.al., 1984; Almbladh and von Barth, 1985) of the KS differential equation has the ***physical interpretation*** of being the removal energy, so that in principle properties such as the ionization potential, electron affinity and the work function can be determined directly via its solution. The KS exchange correlation energy functional $E_{xc}^{KS}[\rho]$ is at present unknown, and thus so is its functional derivative $v_{xc}(r)$.

Finally, the energy $E_{xc}^{KS}[\rho]$ can be split into its exchange $E_x^{KS}[\rho]$ and correlation $E_c^{KS}[\rho]$ energy components:

$$E_{xc}^{KS}[\rho] = E_x^{KS}[\rho] + E_c^{KS}[\rho] \quad , \tag{II-35}$$

so that the resulting local exchange and correlation potentials are the functional derivatives

$$v_x(r) = \frac{\delta E_x^{KS}[\rho]}{\delta\rho(r)} \tag{II-36}$$

and

$$v_c(\boldsymbol{r}) = \frac{\delta E_c^{KS}[\rho]}{\delta\rho(\boldsymbol{r})} , \tag{II-37}$$

respectively.

2.2.1 Kohn-Sham Theory Exchange Energy and Potential

As with the exchange-correlation energy functional $E_{xc}^{KS}[\rho]$, the explicit dependence of the KS exchange energy functional $E_x^{KS}[\rho]$ on the density $\rho(\mathbf{r})$ is at present unknown. However, its dependence on the KS orbitals $\psi_i(\mathrm{x})$ or equivalently on the corresponding Fermi hole charge $\rho_x^{KS}(\mathbf{r}, \mathbf{r}')$ is known explicitly. The pair-correlation density $g_s(\mathbf{r}, \mathbf{r}')$ derived from the Slater determinant of the KS orbitals $\Phi\{\psi_i\}$ which is

$$g_s(\mathbf{r}, \mathbf{r}') = <\Phi\{\psi_i\} \mid \hat{P}(\mathbf{r}, \mathbf{r}') \mid \Phi\{\psi_i\}> / \rho(\mathbf{r}) = \rho(\mathbf{r}') + \rho_x^{KS}(\mathbf{r}, \mathbf{r}') , \tag{II-38}$$

defines the Fermi hole charge. The Fermi hole in turn is defined in terms of the idempotent Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ as

$$\rho_x^{KS}(\mathbf{r}, \mathbf{r}') = -|\gamma_s(\mathbf{r}, \mathbf{r}')|^2/2\rho(\mathbf{r}) , \tag{II-39}$$

and satisfies the constraints of charge neutrality

$$\int \rho_x^{KS}(r,r')dr = -1 , \tag{II-40}$$

negativity

$$\rho_x^{KS}(r,r') \leq 0 , \tag{II-41}$$

and value at electron position

$$\rho_x^{KS}(r,r) = -\frac{\rho(r)}{2} \quad . \tag{II-42}$$

The exchange energy $E_x^{KS}[\rho]$ is the energy of interaction between the density and the Fermi hole charge:

$$E_x^{KS}[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho_x^{KS}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \quad . \tag{II-43}$$

The corresponding exchange potential $v_x(\mathbf{r})$ is then the functional derivative of $E_x^{KS}[\rho]$. However, for the analysis of the asymptotic properties at a metal surface, it is best to express this functional derivative in terms of the Slater (Slater, 1951) potential $V_x^S(\mathbf{r})$ defined as

$$V_x^S(\mathbf{r}) = \int \frac{\rho_x^{KS}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \quad . \tag{II-44}$$

The exchange energy is then

$$E_x^{KS}[\rho] = \frac{1}{2}\int \rho(\mathbf{r})V_x^S(\mathbf{r})d\mathbf{r} \quad , \tag{II-45}$$

and the KS-exchange potential

$$v_x(\mathbf{r}) = \frac{\delta E_x^{KS}[\rho]}{\delta\rho(\mathbf{r})} = \frac{1}{2}V_x^S(\mathbf{r}) + \frac{1}{2}\int \rho(\mathbf{r}')\frac{\delta V_x^S(\mathbf{r}')}{\delta\rho(\mathbf{r})}d\mathbf{r}' \quad . \tag{II-46}$$

Note that the leading term of the exchange potential is $(1/2)V_x^S(\mathbf{r})$.

The exchange potential $V_x^S(\mathbf{r})$ can also be defined (Shaginyan, 1993) in terms of variations of the effective potential $v_{eff}(\mathbf{r})$ of the KS equation via the chain rule as

$$v_x(\mathbf{r}) = \int \frac{\delta E_x^{KS}[\rho]}{\delta v_{eff}(\mathbf{r}')} \frac{\delta v_{eff}(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}' \quad , \tag{II-47}$$

where $v_{eff}(\mathbf{r}) = v(\mathbf{r}) + v_{ee}(\mathbf{r})$. This expression for $v_x(\mathbf{r})$ is equivalent to the exchange potential obtained via the optimized potential method (Sharp and Horton, 1953; Talman and Shadwick, 1976). The differential equation of this method is

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \qquad i = 1, \ldots N \tag{II-48}$$

and is of the same form as the KS equation Eq.(II-27). However, in this method an optimized local effective potential is determined by minimizing the Hartree-Fock theory expression for the energy $\langle H \rangle_{HF}$ with respect to arbitrary variations of the effective potential. ($\langle H \rangle_{HF}$ is the expectation of the Hamiltonian $\hat{H}$ taken with respect to the Slater determinant $\Phi\{\phi_i\}$). The exchange potential $v_x(\mathbf{r})$ is then obtained by subtracting from this effective potential the external $v(\mathbf{r})$ and Hartree $v_H(\mathbf{r})$ potentials. The variation

$$\frac{\delta < H >_{HF}}{\delta v_{eff}(\mathbf{r})} = \sum_i \int \frac{\delta < H >}{\delta \phi_i(\mathbf{r}')} \frac{\delta \phi_i(\mathbf{r}')}{\delta v_{eff}(\mathbf{r})} d\mathbf{r}' = 0 \quad , \tag{II-49}$$

leads to the following integral equation for the exchange potential:

$$\sum_i \int d\mathbf{r}' \left[v_x(\mathbf{r}') - v_{x,i}(\mathbf{r}') \right] G_i(\mathbf{r}', \mathbf{r}) \phi_i(\mathbf{r}') \phi_i^*(\mathbf{r}) = 0 \quad , \tag{II-50}$$

where $G_i(\mathbf{r}, \mathbf{r}')$ is the Green function

$$G_i(\mathbf{r}, \mathbf{r}') = \sum_j{}' \frac{\phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}')}{\epsilon_j - \epsilon_i} \quad , \tag{II-51}$$

and where $v_{x,i}(\mathbf{r})$ is the Hartree-Fock theory orbital-dependent potential (Slater, 1951)

$$v_{x,i}(\mathbf{r}) = \int \frac{\rho_{x,i}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad , \tag{II-52}$$

with

$$\rho_{x,i}(\mathbf{r}, \mathbf{r}') = -\sum_j \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}) \phi_i(\mathbf{r}') / \phi_i(\mathbf{r}) \quad , \tag{II-53}$$

being the orbital-dependent Fermi hole charge at $\mathbf{r}'$ for an electron at $\mathbf{r}$. The orbitals $\phi_i(\mathbf{r})$ are determined by self-consistent solution of the differential and integral equations. The optimized potential method falls within the rubric of 'exchange-only' (Sahni and Levy, 1986) density-functional theory since it is the Hartree-Fock theory energy expression that is minimized. As such the corresponding orbitals $\phi_i(\mathbf{r})$ differ from the KS orbitals $\psi_i(\mathbf{r})$. Furthermore, since there is the added constraint that the effective potential be local, these orbitals also differ from those of Hartree-Fock theory. Thus, the total ground-state energy of the optimized potential method is a rigorous upper bound to the Hartree-Fock theory value.

Finally, we note that within the Kohn-Sham theory representation (Levy, 1979; Payne, 1979; Dreizler and Gross Sect 6.2, 1990; Holas et. al., 1993) of Hartree-Fock theory, it is also possible to define (Holas and March, 1996) an exchange energy functional $E_x^{KSHF}[\rho]$ and potential $v_x^{KSHF}(r) = \delta E_x^{KSHF}[\rho]/\delta\rho(r)$, whereby the HF density and energy are obtained.

2.2.2 Kohn-Sham Theory Correlation Energy and Potential

The KS theory Coulomb hole $\rho_c^{KS}(\mathbf{r}, \mathbf{r}')$ is defined (Sahni, 1996; ibid., 1997) as the difference

$$\rho_c^{KS}(\mathbf{r}, \mathbf{r}') = \rho_{xc}(\mathbf{r}, \mathbf{r}') - \rho_x^{KS}(\mathbf{r}, \mathbf{r}') \quad , \qquad \text{(II-54)}$$

so that it satisfies the constraint

$$\int \rho_c^{KS}(r,r')dr' = 0 \quad . \qquad \text{(II-55)}$$

The correlation energy $E_c^{KS}[\rho]$ is then the sum

$$E_c^{KS}[\rho] = U_c[\rho] + T_c[\rho] \quad , \qquad \text{(II-56)}$$

where

$$U_c[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho_c^{KS}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad , \qquad \text{(II-57)}$$

is the energy of interaction between the densities $\rho(\mathbf{r})$ and $\rho_c^{KS}(\mathbf{r}, \mathbf{r}')$. The corresponding KS correlation potential $v_c(\mathbf{r})$ is the functional derivative

$$v_c(\mathbf{r}) = \frac{\delta E_c^{KS}[\rho]}{\delta\rho(\mathbf{r})} = \frac{1}{2}V_c^S(\mathbf{r}) + \frac{1}{2}\int \rho(\mathbf{r}')\frac{\delta V_c^S(\mathbf{r}')}{\delta\rho(\mathbf{r})}d\mathbf{r}' + \frac{\delta T_c[\rho]}{\delta\rho(\mathbf{r})} \quad , \qquad \text{(II-58)}$$

where

$$V_c^S(\mathbf{r}) = \int \frac{\rho_c^{KS}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \quad , \qquad \text{(II-59)}$$

is the Slater correlation potential.

2.3 Quantum-Mechanical Interpretation of Kohn-Sham Theory

As noted, the KS theory electron-interaction energy $E_{ee}^{KS}[\rho]$ and potential $v_{ee}(\mathbf{r})$ account for electron correlations due to the Pauli exclusion principle and Coulomb repulsion as well as the correlation-kinetic contribution. The physical interpretation of this energy functional and its derivative is in terms of fields whose source distributions are quantal expectations of Hermitian operators. The interpretation, furthermore, distinguishes between the ***purely*** quantal (Pauli and Coulomb) electron-interaction and correlation-kinetic components.

The electron-interaction potential $v_{ee}(\mathbf{r})$ is the work done to bring an electron from infinity to its position at $\mathbf{r}$ against a field $\mathcal{F}(\mathbf{r})$:

$$v_{ee}(\mathbf{r}) = \frac{\delta E_{ee}^{KS}[\rho]}{\delta\rho(\mathbf{r})} = -\int_{\infty}^{\mathbf{r}} \mathcal{F}(\mathbf{r}') \cdot d\mathbf{l}' \quad . \qquad \text{(II-60)}$$

The field $\mathcal{F}(r)$ is conservative so that $\nabla\times\mathcal{F}(r) = 0$. Thus, the work done in this field is ***path-independent.***

The field $\mathcal{F}(r)$ can be split into its electron-interaction $\mathcal{E}_{ee}(r)$ and correlation-kinetic components $\mathcal{Z}_t(r)$:

$$\mathcal{F}(r) = \mathcal{E}_{ee}(r) + \mathcal{Z}_t(r) . \tag{II-61}$$

The field $\mathcal{E}_{ee}(\mathbf{r})$ is strictly representative of Pauli and Coulomb correlations, and is determined via Coulomb's law from the pair-correlation density $g(\mathbf{r}, \mathbf{r}')$ which is its source charge distribution. Thus, the field $\mathcal{E}_{ee}(\mathbf{r})$ is given as

$$\mathcal{E}_{ee}(\mathbf{r}) = \int \frac{g(\mathbf{r}, \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}' , \tag{II-62}$$

and the work done $W_{ee}(\mathbf{r})$ in this field is

$$W_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{E}_{ee}(\mathbf{r}') \cdot d\mathbf{l}' . \tag{II-63}$$

With $g(\mathbf{r}, \mathbf{r}')$ written in terms of the density $\rho(\mathbf{r}')$ and the Fermi-Coulomb hole charge $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ of Eq.(II-9), the field $\mathcal{E}_{ee}(\mathbf{r})$ is the sum of the Hartree $\mathcal{E}_{H}(\mathbf{r})$ and exchange-correlation $\mathcal{E}_{xc}(\mathbf{r})$ fields:

$$\mathcal{E}_{ee}(\mathbf{r}) = \mathcal{E}_{H}(\mathbf{r}) + \mathcal{E}_{xc}(\mathbf{r}) , \tag{II-64}$$

where

$$\mathcal{E}_{H}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}' \quad \text{and} \quad \mathcal{E}_{xc}(\mathbf{r}) = \int \frac{\rho_{xc}(\mathbf{r}, \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}' . \tag{II-65}$$

The work $W_{ee}(\mathbf{r})$ is then the sum of the work $W_{H}(\mathbf{r})$ and $W_{xc}(\mathbf{r})$ done to move an electron in the Hartree and exchange-correlation fields:

$$W_{ee}(\mathbf{r}) = W_H(\mathbf{r}) + W_{xc}(\mathbf{r}) \quad , \tag{II-66}$$

where

$$W_H(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{E}_H(\mathbf{r}') \cdot d\mathbf{l}' \quad \text{and} \quad W_{xc}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{E}_{xc}(\mathbf{r}') \cdot d\mathbf{l}' \quad . \tag{II-67}$$

Now since the density $\rho(\mathbf{r})$ is a ***static*** charge distribution whose structure does not change as a function of electron position, the Hartree field may be written as $\mathcal{E}_H = -\nabla W_H(\mathbf{r})$, where

$$W_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad . \tag{II-68}$$

Note that the scalar potential $W_H(\mathbf{r})$ is the same as the density-functional theory Hartree potential $v_H(\mathbf{r})$ of Eq.(II-30).

The field $\mathbf{Z}_{t_c}(\mathbf{r})$, representative of the correlation-kinetic contribution, is defined in terms of a field $\mathbf{z}(\mathbf{r};[\gamma])$ whose component $z_\alpha(\mathbf{r})$ is derived from the kinetic-energy-density tensor as

$$z_\alpha(\mathbf{r};[\gamma]) = 2\sum_{\beta=1}^{3} \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r};[\gamma]) \quad . \tag{II-69}$$

The field $\mathbf{z}(\mathbf{r};[\gamma])$ is for the ***interacting*** system since the tensor involves the density matrix $\gamma(\mathbf{r},\mathbf{r}')$ of Eq.(II-16). With the field $\mathbf{z}(\mathbf{r};[\gamma_s])$ derived similarly from the tensor $t_{\alpha\beta}(\mathbf{r};[\gamma_s])$ written in terms of the idempotent Dirac density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ of KS theory, the field $\mathbf{Z}_{t_c}(\mathbf{r})$ is then defined as

$$\mathbf{Z}_{t_c}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})}\left[\mathbf{z}(\mathbf{r};[\gamma_s]) - \mathbf{z}(\mathbf{r};[\gamma])\right] \quad . \tag{II-70}$$

The source of the field $\mathbf{Z}_{t_c}(\mathbf{r})$ is therefore the difference between the kinetic-energy-density tensors for the non-interacting and interacting systems. The corresponding work $W_{t_c}(\mathbf{r})$ done in this field is

$$W_{t_c}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathbf{Z}_{t_c}(\mathbf{r}') \cdot d\mathbf{l}' \quad . \tag{II-71}$$

The KS theory electron-interaction potential $v_{ee}(\mathbf{r})$ is then the sum

$$v_{ee}(\mathbf{r}) = W_{ee}(\mathbf{r}) + W_{t_c}(\mathbf{r}) \quad , \tag{II-72}$$

and the 'exchange-correlation' potential $v_{xc}(\mathbf{r})$ the sum

$$v_{xc}(\mathbf{r}) = W_{xc}(\mathbf{r}) + W_{t_c}(\mathbf{r}) \quad . \tag{II-73}$$

The sum of the work $[W_{ee}(\mathbf{r}) + W_{t_c}(\mathbf{r})]$ is path-independent since $\nabla v_{ee}(\mathbf{r}) = -\boldsymbol{\mathcal{F}}(\mathbf{r})$. Equivalently, it is the sum $[W_{xc}(\mathbf{r}) + W_{t_c}(\mathbf{r})]$ that is path-independent since $\nabla \times \boldsymbol{\mathcal{E}}_H(\mathbf{r}) = 0$. For systems of a certain symmetry such as closed shell atoms, open-shell atoms in the central-field approximation, jellium metal clusters, jellium and stabilized-jellium metal surfaces, etc., the work $W_{xc}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ are ***separately*** path-independent since $\nabla \times \boldsymbol{\mathcal{E}}_{xc}(\mathbf{r}) = \nabla \times \mathbf{Z}_{t_c}(\mathbf{r}) = 0$.

The KS theory electron-interaction energy functional $E_{ee}^{KS}[\rho]$ can also be expressed in terms of the fields corresponding to the quantal electron-interaction and correlation-kinetic energy components. The quantal electron-interaction energy component Eq.(II-7) is

$$E_{ee}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \mathcal{E}_{ee}(\mathbf{r}) \quad , \tag{II-74}$$

which can be reduced further to its Coulomb self-energy Eq.(II-13) and exchange-correlation energy (Eq.(II-14)) components as

$$E_{H}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \mathcal{E}_{H}(\mathbf{r}) \quad , \tag{II-75}$$

and

$$E_{xc}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \mathcal{E}_{xc}(\mathbf{r}) \quad , \tag{II-76}$$

respectively. The correlation-kinetic-energy component of Eq.(II-26) is

$$T_{c}[\rho] = \frac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})\boldsymbol{r} \cdot \mathbf{Z}_{t_c}(\mathbf{r}) \quad . \tag{II-77}$$

Thus, we see that KS theory can be described entirely in terms of two fields (and their source distributions), these fields accounting separately for the quantal electron-correlation and correlation-kinetic contributions.

2.3.1 Quantum-Mechanical Interpretation of Kohn-Sham Theory Exchange Energy and Potential

A *rigorous* physical interpretation in terms of fields and source distributions can be provided for the exchange energy functional and its derivative for the three cases considered in section 2.2.1 viz. that of (a) the Kohn-Sham theory for the fully interacting system, (b) the Kohn-Sham theory representation of Hartree-Fock theory, and (c) the Kohn-Sham exchange-only theory. In each case there is a field representative of Pauli correlations and one that represents kinetic effects. We describe the interpretation of each case below.

(a) Kohn-Sham theory

In KS theory the exchange potential $v_x(r)$, which is the derivative of the functional $E_x^{KS}[\rho]$, is (Levy and March, 1997) the sum of the Pauli $W_x^{KS}(r)$ and correlation-kinetic $W_{t_c}^{(1)}(r)$ components:

$$v_x(\mathbf{r}) = \frac{\delta E_x^{KS}[\rho]}{\delta \rho(\mathbf{r})} = W_x^{KS}(\mathbf{r}) - W_{t_c}^{(1)}(\mathbf{r}) \quad . \tag{II-78}$$

Here $W_x^{KS}(\mathbf{r})$ is the work done to move an electron in the field $\mathcal{E}_x^{KS}(\mathbf{r})$ determined via Coulomb's law from the Fermi hole charge $\rho_x^{KS}(\mathbf{r}, \mathbf{r}')$. Thus,

$$W_x^{KS}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{E}_x^{KS}(\mathbf{r}') \cdot d\mathbf{l}' \quad , \tag{II-79}$$

with

$$\mathcal{E}_x^{KS}(\mathbf{r}) = \int \frac{\rho_x^{KS}(\mathbf{r},\mathbf{r}')\,(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,d\mathbf{r}' \quad . \tag{II-80}$$

The Pauli component $W_x^{KS}(\mathbf{r})$ of the exchange potential $v_x(\mathbf{r})$ may also be expressed as

$$W_x^{KS}(\mathbf{r}) = \frac{1}{2}V_x^S(\mathbf{r}) + \int_{\infty}^{\mathbf{r}} d\mathbf{l}' \cdot \int d\mathbf{r}'' \frac{(\nabla'' - \nabla')\rho_x^{KS}(\mathbf{r}',\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|} \quad , \tag{II-81}$$

so that ***the leading term of this work done is*** $(1/2)\,V_x^S(\mathbf{r})$. The work $W_{t_c}^{(1)}(\mathbf{r})$ is that done to move an electron in the field $\mathbf{Z}_{t_c}^{(1)}(\mathbf{r})$:

$$W_{t_c}^{(1)}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathbf{Z}_{t_c}^{(1)}(\mathbf{r}') \cdot d\mathbf{l}' \quad , \tag{II-82}$$

with

$$\mathbf{Z}_{t_c}^{(1)}(\mathbf{r}) = \frac{\mathbf{z}(\mathbf{r};[\gamma_1^c])}{\rho(\mathbf{r})} \quad , \tag{II-83}$$

where $\gamma_1^c(\mathbf{r},\mathbf{r}')$ is the first-order correction to the KS density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ as obtained via perturbation theory by an expansion of the system wavefunction in terms of the electron-interaction coupling constant. Once again the sum of the work $[W_x^{KS}(\mathbf{r}) - W_{t_c}^{(1)}(\mathbf{r})]$ is path-independent since $\nabla \times [\mathcal{E}_x^{KS}(\mathbf{r}) - \mathbf{Z}_{t_c}^{(1)}(\mathbf{r})] = 0$. For systems with the symmetry discussed in the previous section, the work $W_x^{KS}(\mathbf{r})$ and $W_{t_c}^{(1)}(\mathbf{r})$ are separately path-independent. The expression for the exchange potential $v_x(r)$ of Eq.(II-78) is ***exact*** (Levy and March, 1997), because it incorporates ***all*** terms linear in the coupling constant. Higher-order perturbation theory leads to the correlation component of the KS energy and potential.

There is no explicit correlation-kinetic contribution to the KS exchange energy $E_x^{KS}[\rho]$. The contribution, however, is manifested via the KS orbitals, so that $E_x^{KS}[\rho]$ which is related to its functional derivative $v_x(\mathbf{r})$ by the virial (Levy and Perdew, 1985) theorem is expressed entirely in terms of the field $\mathcal{E}_x^{KS}(\mathbf{r})$ as

$$E_x^{KS}[\rho] = -\int \rho(\mathbf{r})\mathbf{r} \cdot \nabla v_x(\mathbf{r})d\mathbf{r} = \int \rho(\mathbf{r})\mathbf{r} \cdot \mathcal{E}_x^{KS}(\mathbf{r})d\mathbf{r} \quad , \tag{II-84}$$

with

$$\int \rho(\mathbf{r})\mathbf{r} \cdot \mathbf{Z}_{t_c}^{(1)}(\mathbf{r})d\mathbf{r} = 0 \quad . \tag{II-85}$$

(b) Kohn-Sham representation of Hartree-Fock theory

The KS 'exchange' energy functional $E_x^{KSHF}[\rho]$ which leads to the HF theory ground-state energy and density is defined as (Sahni, 1997; Holas and March, 1996)

$$E_x^{KSHF}[\rho] = E_x^{HF}[\rho;\gamma^{HF}] + T_c^{HF}[\rho] \quad , \qquad \text{(II-86)}$$

where $E_x^{HF}[\rho;\gamma^{HF}]$ is the HF theory exchange energy determined from the idempotent Dirac density matrix $\gamma^{HF}(\mathbf{r},\mathbf{r}')$ constructed from the HF orbitals $\phi_i^{HF}(\mathbf{x})$. (The definitions of these properties are the same as Eqs. II-32,39 and 43 with $\psi_i(\mathbf{x})$ replaced by $\phi_i^{HF}(\mathbf{x})$). The correlation-kinetic energy $T_c^{HF}[\rho]$ is defined as

$$T_c^{HF}[\rho] = T^{HF}[\rho] - T_s[\rho] \quad , \qquad \text{(II-87)}$$

where $T^{HF}[\rho]$ is the HF theory kinetic energy, and $T_s[\rho]$ the kinetic energy of noninteracting fermions obtained from orbitals of the KS equation which lead to the HF theory density and energy.

The exchange energy $E_x^{HF}[\rho;\gamma^{HF}]$ component is defined in terms of an electric field $\mathcal{E}_x^{HF}(\mathbf{r})$ derived via Coulomb's law from the HF theory Fermi hole $\rho_x^{HF}(\mathbf{r},\mathbf{r}')$ in the same manner as Eq. (II-84).

The correlation-kinetic energy $T_c^{HF}[\rho]$ component is expressed in terms of a field $\mathbf{Z}_{t_c}^{HF}(\mathbf{r})$ as

$$T_c^{HF}[\rho] = \frac{1}{2}\int d\mathbf{r}\,\rho(\mathbf{r})\,\mathbf{r}\cdot \mathbf{Z}_{t_c}^{HF}(\mathbf{r}) \quad , \tag{II-88}$$

where

$$\mathbf{Z}_{t_c}^{HF}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})}\Big[\mathbf{z}(\mathbf{r};[\gamma_s^{HF}]) - \mathbf{z}(\mathbf{r};[\gamma^{HF}])\Big] \quad , \tag{II-89}$$

the field $\mathbf{z}(\mathbf{r})$ is as defined by Eqs. (II-70) and (II-15), and where $\gamma_s^{HF}(\mathbf{r},\mathbf{r}')$ is the idempotent density matrix constructed from the orbitals of the KS equation which leads to the HF density and energy.

The KS exchange potential $v_x^{HF}(\mathbf{r})$ which generates the HF theory density and energy is

$$v_x^{HF}(\mathbf{r}) = \frac{\delta E_x^{KSHF}[\rho]}{\delta\rho(\mathbf{r})} = W_x^{HF}(\mathbf{r}) + W_{t_c}^{HF}(\mathbf{r}) \quad , \tag{II-90}$$

where $W_x^{HF}(\mathbf{r})$ and $W_{t_c}^{HF}(\mathbf{r})$ are respectively, the work done in the fields $\boldsymbol{\mathcal{E}}_x^{HF}(\mathbf{r})$ and $\mathbf{Z}_{t_c}^{HF}(\mathbf{r})$. The sum of the work $[W_x^{HF}(\mathbf{r}) + W_{t_c}^{HF}(\mathbf{r})]$ is ***path-independent*** since $\nabla \times [\boldsymbol{\mathcal{E}}_x^{HF}(\mathbf{r}) + \mathbf{Z}_{t_c}^{HF}(\mathbf{r})] = 0$.

(c) Kohn-Sham exchange-only theory

The exchange-only version of Kohn-Sham theory corresponds to the optimized potential method (OPM). The resulting exchange energy $E_x^{\mathrm{OPM}}[\rho;\gamma_s^{\mathrm{OPM}}]$ and potential $v_x^{\mathrm{OPM}}(\mathbf{r})$ are determined by self-consistent solution of the OPM integral and differential equations. The exchange energy is obtained through Eq. (II-43) via the Fermi hole $\rho_x^{\mathrm{OPM}}(\mathbf{r},\mathbf{r}')$ or density matrix $\gamma_s^{\mathrm{OPM}}(\mathbf{r},\mathbf{r}')$ constructed from the OPM orbitals $\phi_i^{\mathrm{OPM}}(\mathbf{r})$. The potential $v_x^{\mathrm{OPM}}(\mathbf{r})$ may be expressed as (Slamet and Sahni, 1997)

$$v_x^{\mathrm{OPM}}(\mathbf{r}) = W_x(\mathbf{r}) + W_{t_c}(\mathbf{r}) \quad , \qquad \text{(II-91)}$$

where $W_x(\mathbf{r})$ is the work done in the field $\mathcal{E}_x(\mathbf{r})$ determined via Coulomb's law from the Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$ constructed from the orbitals $\phi_i^{\mathrm{WF}}(\mathbf{r})$ of the Work Formalism (Sahni, 1995) (WF) differential equation. (This equation is the same as the KS differential equation with $v_{xc}(\mathbf{r})$ replaced by $W_x(\mathbf{r})$). With $\gamma_s^{\mathrm{WF}}(\mathbf{r},\mathbf{r}')$ the corresponding idempotent density matrix, the work $W_{t_c}(\mathbf{r})$ is that done in the field $\mathbf{Z}_{t_c}(\mathbf{r})$ where

$$\mathbf{Z}_{t_c}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})}\Big[\mathbf{z}\big(\mathbf{r};[\gamma_s^{\mathrm{OPM}}]\big) - \mathbf{z}\big(\mathbf{r};[\gamma_s^{\mathrm{WF}}]\big)\Big] \quad , \qquad \text{(II-92)}$$

and where the field $\mathbf{z}(\mathbf{r})$ is as defined previously in terms of the appropriate kinetic-energy density tensor. In this exchange-only case, the virial theorem (Levy and Perdew, 1985) leads to the energy relation

$$E_x^{OPM}[\rho;\gamma_s^{OPM}] - E_x^{WF}[\rho;\gamma_s^{WF}] = \int \rho(\mathbf{r})\mathbf{r} \cdot \mathbf{Z}_{t_c}(\mathbf{r})d\mathbf{r} \quad . \qquad \text{(II-93)}$$

We note that in the derivation of Eq.(II-91) it is assumed that the OPM and WF densities are equivalent, which is essentially the case for both finite and extended systems. However, the off-diagonal elements of $\gamma_s^{OPM}(\mathbf{r},\mathbf{r}')$ and $\gamma_s^{WF}(\mathbf{r},\mathbf{r}')$ are not assumed to be equivalent so that the field $\mathbf{Z}_{t_c}(\mathbf{r})$ is finite. Furthermore, the work $W_x(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ are separately path-independent.

To summarize, the exchange potential of Kohn-Sham theory (Eq.(II-78), that of its representation of HF theory (Eq.(II-90)), and of the OPM (Eq.(II-91)), are all comprised of two components. The first, representative of Pauli correlations, is the work done in a field determined by Coulomb's law from the Fermi hole charge constructed with the corresponding orbitals. The second, representative of correlation-kinetic effects, is the work done in a field determined from a corresponding kinetic-energy-density tensor. We note, however, that though in principle these potentials are different, in practice they are essentially equivalent for both finite atomic and extended metal surface systems.

2.3.2 Quantum-Mechanical Interpretation of Kohn-Sham Theory Correlation Energy and Potential.

With the KS theory Fermi and Coulomb holes as defined by Eq.(II-54), the exchange-correlation potential $v_{xc}(r)$ can also be expressed in terms of its ***separate*** Pauli, Coulomb and correlation-kinetic contributions as

$$v_{xc}(r) = \frac{\delta E_{xc}^{KS}[\rho]}{\delta\rho(r)} = W_x^{KS}(r) + W_c^{KS}(r) + W_{t_c}(r) \,, \tag{II-94}$$

where $W_c^{KS}(r)$ is the work done in the field $\mathcal{E}_c^{KS}(r)$ due to the Coulomb hole charge $\rho_c^{KS}(r,r')$:

$$W_c^{KS} = -\int_{\infty}^{r} \mathcal{E}_c^{KS}(r')\cdot dl' \;; \qquad \mathcal{E}_c^{KS}(r) = \int \frac{\rho_c^{KS}(r,r')(r-r')}{|r-r'|^3}\,dr' \,. \tag{II-95}$$

Since $v_{xc}(r)=v_x(r)+v_c(r)$, where $v_x(r)$ is given by Eq. (II-78), the ***exact*** expression for the derivative $v_c(r)$ is then

$$v_c(r) = \frac{\delta E_c^{KS}[\rho]}{\delta\rho(r)} = W_c^{KS}(r) + W_{t_c}(r) + W_{t_c}^{(1)}(r) \,, \tag{II-96}$$

where $W_{t_c}(r)$ and $W_{t_c}^{(1)}(r)$ are as defined previously. The Coulomb correlation energy $U_c[\rho]$ of Eq. (II-57) is also expressed in terms of the field $\mathcal{E}_c^{KS}(r)$ as

$$U_c[\rho] = \int dr\,\rho(r)\,r\cdot\mathcal{E}_c^{KS}(r) \,. \tag{II-97}$$

Perturbation theory expressions for $W_c^{KS}(r)$, $W_{t_c}(r)$, $U_c[\rho]$ and $T_c[\rho]$ can be derived but we do not give these here. We note, however, that the KS correlation potential $v_c(\boldsymbol{r})$ commences (Levy and March, 1997) in second order in coupling constant. The term quadratic in the coupling constant $v_{c,2}(\boldsymbol{r})$ is then

$$v_{c,2}(\boldsymbol{r}) = W_c^{(1)}(\boldsymbol{r}) - W_{t_c}^{(2)} , \qquad \text{(II-98)}$$

where the work $W_c^{(1)}(\boldsymbol{r})$ depends on the first-order correction to the pair-correlation density, and $W_{t_c}^{(2)}(\boldsymbol{r})$ on the second-order correction $\gamma_2^c(\boldsymbol{r},\boldsymbol{r}')$ of the density-matrix $\gamma(\boldsymbol{r},\boldsymbol{r}')$. Similarly, it can shown that for $E_c^{KS}[\rho]$ the term quadratic in the coupling constant is due to correlation-kinetic effects arising from the field of $\gamma_2^c(\boldsymbol{r},\boldsymbol{r}')$.

2.4 Jellium and Structureless-Pseudopotential Models of a Metal Surface

In the jellium model (Kiejna and Wojciechowski, 1996; Bardeen, 1936), the charge of ions is assumed smeared out into a uniform positive background of charge $\rho_+(\mathbf{r}) = \bar{\rho}\theta(-x + a)$ ending abruptly at the surface at $x=a$, and where $\bar{\rho} = k_F^3/3\pi^2$ is the bulk density, $k_F = 1/\alpha r_s$ is the Fermi momentum, $\alpha^{-1} = (9\pi/4)^{1/3}$, and r_s is the Wigner-Seitz radius. The jellium edge position is determined by the constraint of charge neutrality or equivalently by the Sugiyama sum rule (Sugiyama, 1960). The external potential $v(\mathbf{r})$ and the Coulomb interaction between ions (see Eq.(II-1) and Eq.(II-2)) are then expressed as

$$v_{\mathrm{jell}}(\mathbf{r}) = -\int \frac{\rho_+(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \ , \qquad \text{(II-99)}$$

and

$$\frac{1}{2}\sum_{n,m}{}' \frac{Z^2}{|\mathbf{R}_n-\mathbf{R}_m|} = \frac{1}{2}\int\int \frac{\rho_+(\mathbf{r})\rho_+(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \ , \qquad \text{(II-100)}$$

respectively. The KS theory total ground-state energy functional for this model is

$$E_{\mathrm{jell}}[\rho] = T_s[\rho] + E_{xc}^{KS}[\rho] + \frac{1}{2}\int\int \frac{[\rho(\mathbf{r})-\rho_+(\mathbf{r})][\rho(\mathbf{r}')-\rho_+(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \ , \qquad \text{(II-101)}$$

and the corresponding local effective potential is

$$v_{\mathrm{eff}}^{\mathrm{jell}}(\mathbf{r}) = \frac{\delta(E_{\mathrm{jell}}[\rho]-T_s[\rho])}{\delta\rho(\mathbf{r})} = v_{\mathrm{jell}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \ . \qquad \text{(II-102)}$$

If the Coulomb potential of the ionic cores is replaced by a local pseudopotential $\omega_{ps}(\mathbf{r})$, the energy functional is (Kiejna and Wojciechowski, 1996)

$$E_{\mathrm{pseudo}}[\rho] = E_{\mathrm{jell}}[\rho] + \frac{1}{2}\sum_{n,m} \frac{Z^2}{|\mathbf{R}_n-\mathbf{R}_m|} - \frac{1}{2}\int \frac{\rho_+(\mathbf{r})\rho_+(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int \rho(\mathbf{r})\delta v(\mathbf{r})d\mathbf{r} \ , \qquad \text{(II-103)}$$

where the 'difference potential' $\delta v(\mathbf{r})$ between the pseudopotential of a lattice of ions and the potential of the positive jellium background is

$$\delta v(\mathbf{r}) = \sum_{n} \omega_{ps}(\mathbf{r} - \mathbf{R}_n) + \int \frac{\rho_+(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad . \tag{II-104}$$

In the structureless-pseudopotential (stabilized-jellium) model (Perdew, 1995; Perdew et.al., 1990; Shore and Rose, 1991), the Wigner-Seitz unit cell is replaced by a sphere of radius $r_0 = Z^{1/3} r_s$. The stabilized-jellium energy functional is then obtained from the jellium model as

$$\underset{\text{stab-jell}}{E[\rho]} = \underset{\text{jell}}{E}[\rho] - \frac{3}{5} \frac{Z^{2/3}}{r_s} \int \rho_+(\mathbf{r}) d\mathbf{r} + \int \langle \delta v \rangle_{WS} \theta(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \quad , \tag{II-105}$$

where the second term is the spurious self-repulsion energy of the positive background in each cell, and the last term is the contribution of the 'difference potential' (see Eq.(I-103)). In this model, the difference potential is averaged over the Wigner-Seitz spherical cell. For the Ashcroft pseudopotential (Ashcroft, 1966), this average can be shown to be given as

$$\langle \delta v \rangle_{WS} = \frac{r_s}{3} \frac{d\epsilon_{jell}}{dr_s} \tag{II-106}$$

where ϵ_{jell} is the average energy per electron in the jellium model which is $\epsilon_{jell} = 3k_F^2/10 - 3k_F/4\pi + \epsilon_c(\bar{\rho})$ with $\epsilon_c(\bar{\rho})$ the average correlation energy per electron.

The potential $\langle \delta v \rangle_{WS} \theta(\mathbf{r})$ vanishes outside the positive background and is a constant inside. The KS theory effective potential for the stabilized-jellium model is

$$v_{eff}^{stab-jell}(\mathbf{r}) = \frac{\delta(E_{stab-jell}[\rho] - T_s[\rho])}{\delta\rho(\mathbf{r})} \tag{II-107}$$

$$= v_{jell}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}^{KS}(\mathbf{r}) + \langle \delta v \rangle_{WS} \theta(\mathbf{r}) \quad .$$

For the flat surface stabilized-jellium model, the potential $\langle \delta v \rangle_{WS} \theta(\mathbf{r}) = \langle \delta v \rangle_{WS} \theta(-x + a)$. Crystal face-dependent properties can be obtained by averaging the difference potential $\delta v(\mathbf{r})$ first over the direction parallel to the surface and then over the remaining direction inside the crystal. With this averaging

$$\langle \delta v \rangle_{face} = \langle \delta v \rangle_{WS} + \frac{3Z}{10 r_0} \left[1 - \frac{5}{3} \left(\frac{d}{r_0} \right)^2 \right] \quad , \tag{II-108}$$

where d is the distance between neighboring lattice planes parallel to the surface. For further details of the structureless-pseudopotential model and of its results, we refer the reader to the original literature (Perdew, 1995; Perdew et.al., 1990; Shore and Rose, 1991).

Within both the jellium and stabilized-jellium models, there is translational symmetry in the plane parallel to the surface, and since the effective potential in which the electrons move is local, the KS orbitals are of the form

$$\psi_k(\mathbf{r}) = \sqrt{\frac{2}{V}}\, e^{i\mathbf{k}_\parallel \cdot \mathbf{x}_\parallel}\phi_k(x) \quad , \tag{II-109}$$

where $(\mathbf{k}_\parallel, \mathbf{x}_\parallel)$ are the momentum and position vectors parallel to the surface, and (k, x) the components perpendicular to it. The Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ of Eq. (II-32) and the density $\rho(\mathbf{r})$ for these models are then

$$\gamma_s(\mathbf{r}, \mathbf{r}') = 2\int \frac{d\mathbf{k}}{(2\pi^2)_{\pi}}\phi_k^{*}(x)\phi_k(x')e^{i\mathbf{k}_\parallel \cdot (\mathbf{x}_\parallel - \mathbf{x}'_\parallel)}\Theta(\epsilon_F - \frac{k^2}{2}) \quad , \tag{II-110}$$

and

$$\rho(x) = \frac{1}{2\pi^2}\int_0^{k_F} (k_F^2 - k^2)\,|\phi_k(x)|^2 dk \quad , \tag{II-111}$$

where $\epsilon_F = k_F^2/2$ is the Fermi energy. The structure of the component $\phi_k(x)$ of the orbitals for the jellium and stabilized-jellium models in the asymptotic vacuum and metal-bulk regions is the same. The orbitals $\phi_k(x)$ of the two models differ only in the surface region.

CHAPTER III

THE SLATER EXCHANGE POTENTIAL AT A METAL SURFACE

The leading term of the KS exchange potential $v_x(\mathbf{r})$ is one-half of the Slater potential $V_x^S(\mathbf{r})$. (See Eqs. (II-44,46). We therefore initially focus on the Slater potential. In section 3.1 we derive (Solomatin and Sahni, 1996; ibid., 1997b) an expression for $V_x^S(\mathbf{r})$ valid for the jellium and structureless-pseudopotential models in terms of momentum space integrals. This allows for its easy and accurate numerical determination throughout space, because in dimensionless coordinates normalized to the Fermi momentum, these integrals are over the finite region from 0 to 1. Furthermore, as a consequence, knowledge of the precise structure of the delocalized Fermi hole charge deep in the metal bulk for asymptotic positions of the electron in the vacuum region is not necessary as it is in the work of others (Harbola and Sahni, 1987; Sahni, 1989). The expression for the Slater potential $V_x^S(\mathbf{r})$ derived also allows for the determination (Solomatin and Sahni, 1996; ibid., 1997b) of its ***exact analytical*** structure in the asymptotic vacuum region. To make this calculation accessible to the reader, we perform it initially for the accurate semi-analytical orbitals of a model effective potential (Sahni et.al., 1978) as described in section 3.2.1. The analytical result derived for the asymptotic structure of $V_x^S(\mathbf{r})$ is, however, equally valid for the ***fully self-consistently*** determined Kohn-Sham orbitals as proved (Solomatin and Sahni, 1996) in section 3.2.2.

3.1 Expression for the Slater Potential at a Jellium or Structureless-Pseudopotential Metal Surface

In this section we derive a general expression for the Slater potential $V_x^s(\mathbf{r})$ valid for the jellium or structureless-pseudopotential model of a metal surface.

With the Fermi hole $\rho_x^{KS}(\mathbf{r}, \mathbf{r}')$ defined as in Eq.(II-39), the Slater potential of Eq.(II-44) is

$$V_x^s(\mathbf{r}) = -\frac{1}{2\rho(\mathbf{r})} \int d\mathbf{r}' \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} . \qquad \text{(III-1)}$$

Substituting the single-particle density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ given by Eq.(II-110) and the density $\rho(\mathbf{r})$ from Eq.(II-111) into Eq.(III-1) we arrive at the following expression for the Slater potential

$$V_x^s(x) = -\frac{1}{2\rho(x)} \int dx' \, 4 \int \frac{d\mathbf{k}\, d\mathbf{k}'}{(2\pi)^4 \pi^2} \phi_{kk'}(x, x') \frac{e^{i(\mathbf{k}_\parallel - \mathbf{k}_\parallel) \cdot (\mathbf{x}_\parallel - \mathbf{x}'_\parallel)}}{|\mathbf{r} - \mathbf{r}'|} \qquad \text{(III-2)}$$

where

$$\phi_{kk'}(x, x') = \phi_k^*(x) \phi_k(x') \phi_{k'}^*(x') \phi_{k'}(x) . \qquad \text{(III-3)}$$

Now with $\mathbf{q} = \mathbf{k}_\parallel - \mathbf{k}'_\parallel$ and $\mathbf{X} = \mathbf{x}_\parallel - \mathbf{x}'_\parallel$, it can be shown that (Bardeen, 1936; Ma and Sahni, 1979),

$$\int d\mathbf{x}'_\parallel \frac{e^{i\mathbf{q} \cdot \mathbf{X}}}{|\mathbf{r} - \mathbf{r}'|} = 2\pi \frac{e^{-q|x - x'|}}{q} . \qquad \text{(III-4)}$$

Thus, we have

$$V_x^s(x) = -\frac{1}{2\rho(x)}\int dx'\, 4\int \frac{dk\,dk'}{(2\pi)^4\pi^2}\,\phi_{kk'}(x,x')\,\theta\left[\epsilon_F - \frac{k^2}{2}\right]\theta\left[\epsilon_F - \frac{k'^2}{2}\right] 2\pi\frac{e^{-q|x-x'|}}{q} \quad . \tag{III-5}$$

Now the product of the θ functions

$$\begin{aligned}\theta\left[\epsilon_F - \frac{k^2}{2}\right]\theta\left[\epsilon_F - \frac{k'^2}{2}\right] &= \theta\,(k_F^2 - k^2 - k_\parallel^2)\,\theta\,(k_F^2 - k'^2 - k_\parallel'^2) \\ &= \theta\,(\lambda^2 - k_\parallel^2)\,\theta\,(\lambda'^2 - k_\parallel'^2) \\ &= \theta\,(\lambda - k_\parallel)\,\theta\,(\lambda' - k_\parallel') \quad ,\end{aligned} \tag{III-6}$$

where $\lambda^2 = k_F^2 - k^2$, $\lambda'^2 = k_F^2 - k'^2$. The momentum space integrals of Eq.(III-5) may then be written as

$$\int_0^{k_F} dk \int_0^{k_F} dk' \int dk_\parallel \int dk_\parallel'\, \theta\,(\lambda - k_\parallel)\,\theta(\lambda' - k_\parallel')\,\phi_{kk'}(x,x')\,\frac{e^{-q|x-x'|}}{q} \quad . \tag{III-7}$$

In this equation we have two possibilities: $\lambda > \lambda'(k < k')$ or $\lambda < \lambda'(k > k')$. However, equation Eq.(III-7) is symmetric with respect to an interchange of k and k', so that we may assume $\lambda > \lambda'(k < k')$ and multiply the resulting equation by 2. Thus, we rewrite Eq. (III-7) as

$$2\int_0^{k_F} dk' \int_0^{k'} dk \int dk_\parallel \int dk_\parallel'\, \theta\,(\lambda - k_\parallel)\,\theta(\lambda' - k_\parallel')\,\phi_{kk'}(x,x')\,\frac{e^{-q|x-x'|}}{q} \quad , \tag{III-8}$$

where it is understood that $\lambda > \lambda'$. Substituting Eq.(III-8) into Eq.(III-5), the Slater potential may be written in dimensionless co-ordinates normalized to the Fermi momentum as

$$V_x^s(z) = -\frac{1}{\pi^3\rho(z)}\int_0^1 \frac{dk'}{(2\pi)}\int_0^{k'}\frac{dk}{(2\pi)}\phi_k^*(z)\phi_{k'}(z)\int dz'\,\phi_k(z')\phi_{k'}^*(z')I_{kk'}(z,z') \quad , \tag{III-9}$$

where

$$I_{kk'}(z,z') = \int d\mathbf{k}_\parallel \int d\mathbf{k}'_\parallel \frac{e^{-q|z-z'|}}{q}\,\theta(\lambda - k_\parallel)\,\theta(\lambda' - k'_\parallel) \quad . \tag{III-10}$$

In Eqs. (III-9) and (III-10), we have used the same notation for the dimensionless variables as before so that now $\lambda = (1-k^2)^{1/2}$, $\lambda' = (1-k'^2)^{1/2}$ etc., and $z = k_F x$. To determine the integral $I_{kk'}(z,z')$ we change the variables to

$$\mathbf{q} = \mathbf{k}_\parallel - \mathbf{k}'_\parallel \qquad \text{and} \qquad \mathbf{K} = \frac{1}{2}(\mathbf{k}_\parallel + \mathbf{k}'_\parallel) \quad , \tag{III-11}$$

so that

$$\mathbf{k}_\parallel = \mathbf{K} + \frac{1}{2}\mathbf{q} \qquad \text{and} \qquad \mathbf{k}'_\parallel = \mathbf{K} - \frac{1}{2}\mathbf{q} \quad . \tag{III-12}$$

Since the Jacobian of the transformation $J(\mathbf{q},\mathbf{K}) = \partial(\mathbf{k}_\parallel, \mathbf{k}'_\parallel)/\partial(\mathbf{q},\mathbf{K}) = 1$, we can rewrite Eq. (III-10) as

$$I_{kk'}(z,z') = \int d\mathbf{q}\frac{e^{-q|z-z'|}}{q}\int d\mathbf{K}\,\theta\left[\lambda - |\mathbf{K} + \frac{1}{2}\mathbf{q}|\right]\,\theta\left[\lambda - |\mathbf{K} - \frac{1}{2}\mathbf{q}|\right] \tag{III-13}$$

or equivalently as

$$I_{k,k'}(z,z') = 2\pi\int dq\, e^{-q|z-z'|}F(q) \quad , \tag{III-14}$$

where

$$F(q) = \int d\mathbf{K}\,\theta\left[\lambda - |\mathbf{K} + \frac{1}{2}\mathbf{q}|\right]\,\theta\left[\lambda - |\mathbf{K} - \frac{1}{2}\mathbf{q}|\right] \quad . \tag{III-15}$$

The integral over $\boldsymbol{K}$ has a simple geometrical interpretation. It is the area of the hatched region of Fig. 1(a) corresponding to all points in the $\boldsymbol{K}$-plane which belong simultaneously to circles of radii λ and λ' whose centers are a distance q apart. Since in Eq.(III-8) we assumed $\lambda > \lambda'$, there are three distinct cases for the $\boldsymbol{K}$-integral as shown in Figs. 1a, b, and c corresponding to the values of q being $\lambda - \lambda' < q < \lambda + \lambda'$, $q < \lambda - \lambda'$, and $q < \lambda + \lambda'$. For these cases we have from geometrical considerations

$$\begin{aligned} F(q) &= 0 && \text{for} \quad q \geq \lambda + \lambda' \\ &= \pi\lambda'^2 && \text{for} \quad q \leq \lambda - \lambda' \\ &= \pi\lambda'^2\theta\left[(\lambda^2 - \lambda'^2)^{1/2} - q\right] + S_\lambda(q) + S_{\lambda'}(q) && \text{for} \quad \lambda - \lambda' < q < \lambda + \lambda' \end{aligned} \qquad \text{(III-16)}$$

where

$$S_\lambda(q) = \lambda^2 \tan^{-1}\frac{\left(\lambda^2 - X_\lambda^2\right)^{1/2}}{X_\lambda} - X_\lambda\left(\lambda^2 - X_\lambda^2\right)^{1/2} \quad , \qquad \text{(III-17)}$$

$$S_{\lambda'}(q) = S_\lambda(q)\Big|_{\lambda \to \lambda'} \quad , \qquad \text{(III-18)}$$

$$X_{\lambda,\lambda'}(q) = \frac{1}{2}\left[q \pm \frac{\lambda^2 - \lambda'^2}{q}\right] \quad . \qquad \text{(III-19)}$$

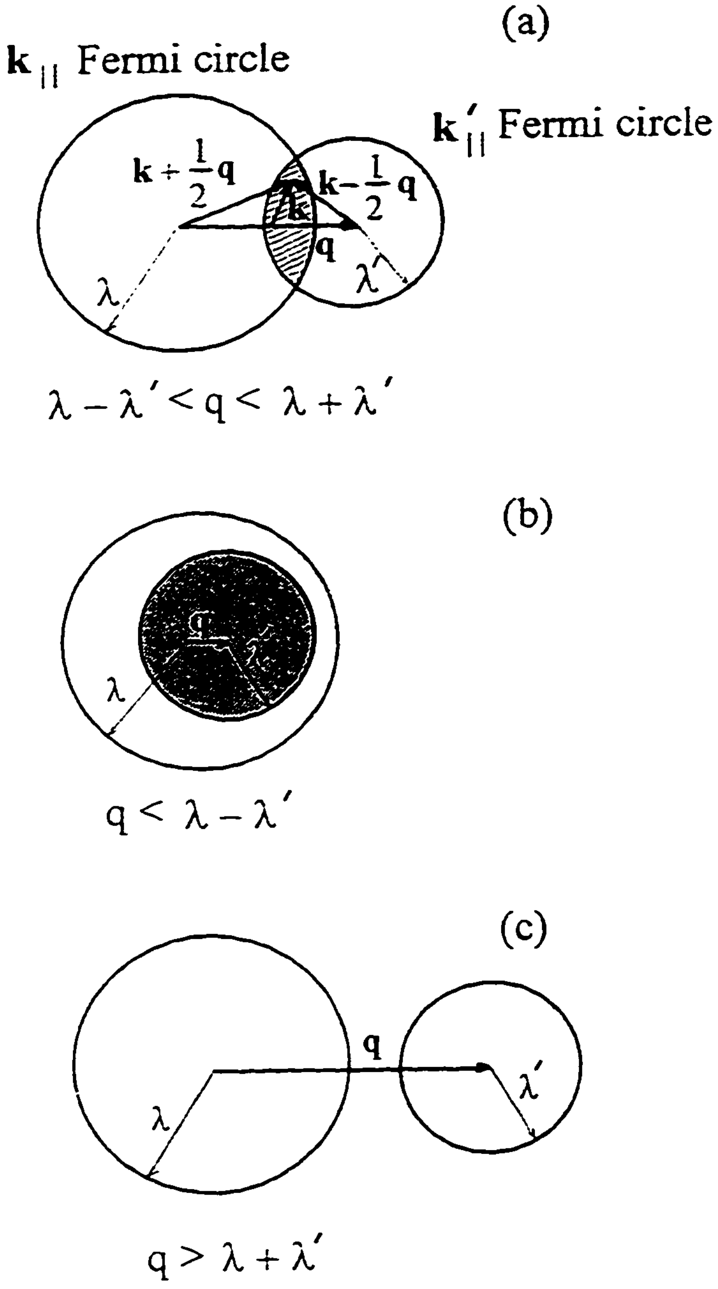

Fig. 1 The physical interpretation of the area of integration in Eq.(III-15). The hatched region corresponds to this area.

Thus, we may write $I_{kk'}(z, z')$ of Eq.(III-14) as

$$I_{k,k'}(z, z') = 2\pi \left[\pi\lambda'^2 \int_0^{(\lambda^2-\lambda'^2)^{1/2}} dq \; e^{-q|z-z'|} + \int_{\lambda-\lambda'}^{\lambda+\lambda'} dq \; e^{-q|z-z'|} \{ S_\lambda(q) + S_{\lambda'}(q) \} \right] \quad . \tag{III-20}$$

Substituting Eq.(III-20) into Eq.(III-9) we obtain finally

$$\frac{V_x^s(z)}{3k_F/2\pi)} = -\frac{4}{\pi\rho_n(z)} \int_0^1 dk' \int_0^{k'} dk \phi_k^*(z) \phi_{k'}(z) G(k, k'; z) \quad , \tag{III-21}$$

where $\rho_n(z) = 3 \int_0^1 (1-k^2) |\phi_k(z)|^2 dk$ is the density normalized to the bulk value,

$$G(k, k'; z) = \pi\lambda'^2 \int_0^{(\lambda^2-\lambda'^2)^{1/2}} dq \; J(q, z) + \int_{\lambda-\lambda'}^{\lambda+\lambda'} dq \; J(q, z) \{ S_\lambda(q) + S_{\lambda'}(q) \} \tag{III-22}$$

and

$$J(q, z) = 2 \int_{-\infty}^{\infty} dz' \; e^{-q|z-z'|} \; \phi_k(z') \phi_{k'}^*(z') \quad . \tag{III-23}$$

For orbitals generated by model effective potential, the integral $J(q,z)$ can be obtained analytically. The expression for the Slater potential $V_x^S(r)$ of Eq. (III-21) is then reduced to finite region momentum space integrals. This then allows for the accurate numerical determination of $V_x^S(r)$ throughout space.

3.2 Asymptotic Structure of the Slater Potential

We next determine the asymptotic structure of the Slater potential in the classically forbidden region. We perform our calculations for the orbitals of the jellium model of a metal surface since they allow for a more accessible derivation. In the stabilized-jellium model, the structure of the orbitals in the classically forbidden region and deep in the metal bulk are the same as those of the jellium model. They differ slightly only in the surface region. As such the analytical results for the asymptotic structure in the vacuum region which, as will be shown, depend only on the structure of the orbitals deep in the metal bulk are equally valid for both models.

3.2.1 Derivation for Model Effective Potential.

The effective potential $v_{eff}(z)$ we assume is that of the finite-linear-potential model (Sahni et.al., 1978) for which

$$v_{eff}(z) = \begin{cases} 0 & \text{for} \quad z \leq 0 \\ Fz & \text{for} \quad 0 \leq z \leq z_b \\ W & \text{for} \quad z \geq z_b \end{cases} . \tag{III-24}$$

The solution of the Schrödinger equation for this potential is

$$\phi_k(z) = sin\left[kz + \delta(k)\right]\theta(-z) + \left[B_k Ai(\zeta_k) + C_k Bi(\zeta_k)\right]\left[\theta(z) - \theta(z - z_b)\right] + D_k \exp(-\kappa_k z)\theta(z - z_b) , \tag{III-25}$$

where $k = \sqrt{2E}$, $\kappa_k = \sqrt{2(W-E)}$, $\zeta_k = zz_F^{-1/3} - \zeta_0$, $\zeta_0 = k^2 z_F^{2/3}$, $F = (k_F^2/2)/z_F$, $z_F = (k_F^2/2)z_b/W$, E is the energy, W the barrier height, and $Ai(\zeta_k)$ and $Bi(\zeta_k)$ the Airy functions. The phase factor $\delta(k)$ and the coefficients B_k, C_k and D_k are determined by the requirement of continuity of the wavefunction and its logarithmic derivative at $z = 0$ and $z = z_b$.

We first determine $J(q, z)$ of Eq.(III-23) for $z > 0$ for these orbitals to obtain (see Appendix A1)

$$
\begin{aligned}
J(q,z) = e^{-qz} \Bigg[& \frac{q\cos\delta_- + k_-\sin\delta_-}{q^2 + k_-^2} - \frac{q\cos\delta_+ + k_+\sin\delta_+}{q^2 + k_+^2} \\
& + 2\int_0^{z_b} dz'\, e^{qz'} \left\{B_k Ai(\zeta'_k) + C_k Bi(\zeta'_k)\right\} \left\{B_{k'} Ai(\zeta'_{k'}) + C_{k'} Bi(\zeta'_{k'})\right\} \\
& + \frac{2D_k D_{k'}}{\kappa_k + \kappa_{k'} - q} e^{-(\kappa_k + \kappa_{k'} - q)z_b} \Bigg] - \frac{4qD_k D_{k'}}{(\kappa_k + \kappa_{k'})^2 - q^2} e^{-(\kappa_k + \kappa_{k'})z} ,
\end{aligned}
\tag{III-26}
$$

where $k_{\mp} = k' \mp k$, and $\delta_{\mp} = \delta(k') \mp \delta(k)$. In the asymptotic large z region, the effective value of $q \sim 1/z$ due to the e^{-qz} factor in $J(q,z)$. Furthermore, since $k \sim k'$ for large z, the effective value of $k_- \sim 1/z$ due to the $e^{-\kappa_k z}$ factor. Expanding $J(q,z)$ of Eq.(III-26) in q we obtain for the asymptotic region

$$\begin{aligned} J(q,z) \underset{z\to\infty}{\sim} & \; e^{-qz}\left[\frac{q}{q^2+k_-^2}\cos\delta_- + \frac{k_-}{q^2+k_-^2} sin\delta_-\right] + e^{-qz}\left[-\frac{sin\delta_+}{k_+} - \frac{q\cos\delta_+}{k_+^2}\right. \\ & + \frac{2D_kD_{k'}}{\kappa_k+\kappa_{k'}} e^{-(\kappa_k+\kappa_{k'})z_s} \\ & \left. + 2\int_0^{z_s} dz' \left\{B_k Ai(\zeta_k') + C_k Bi(\zeta_k')\right\}\left\{B_{k'} Ai(\zeta_{k'}') + C_{k'} Bi(\zeta_{k'}')\right\}\right] \\ & - \frac{4qD_kD_{k'}}{(\kappa_k+\kappa_{k'})^2} e^{-(\kappa_k+\kappa_{k'})z} \quad . \end{aligned} \tag{III-27}$$

Next consider the contribution of $J(q,z)$ of Eq.(III-23) to the first integral in $G(k,k';z)$ of Eq.(III-22). The last term of Eq.(III-27) is exponentially small in the vacuum region and does not contribute. The contribution of the second set of terms is

$$\begin{aligned} & \frac{1-e^{-(\lambda^2-\lambda'^2)^{1/2}z}}{z}\left[-\frac{\sin\delta_+}{k_+} + \frac{2D_kD_{k'}}{\kappa_k+\kappa_{k'}} e^{-(\kappa_k+\kappa_{k'})z_s} + 2\int_0^{z_s} dz' \{\ \}\{\ \}\right] \\ & \mp \left[\frac{(\lambda^2-\lambda'^2)^{1/2} e^{-(\lambda^2-\lambda'^2)^{1/2}z}}{z} + 0\left[\frac{1}{z^2}\right]\right]\frac{\cos\delta_+}{k_+^2} \quad . \end{aligned} \tag{III-28}$$

Now $(\lambda^2-\lambda'^2)^{1/2}z \sim k_-^{1/2}z = (k_-z)^{1/2}z^{1/2} \gg 1$ for large z since $k_- \sim 1/z$. Thus, the contribution of Eq.(III-28) is of $0(1/z)$. The contribution of the first term of Eq.(III-20) to the first integral in $G(k,k';z)$, with $qz = u$ and $a = k_-z$, is

$$\cos\delta_{-}\int_{0}^{\infty} du \frac{u e^{-u}}{u^{2}+a^{2}} + a\sin\delta_{-}\int_{0}^{\infty} du \frac{e^{-u}}{u^{2}+a^{2}} + O\left[\frac{1}{z}\right] \quad . \qquad \text{(III-29)}$$

Next we note that the second term of $G(k,k';z)$ of Eq.(III-22) does not contribute to the leading order. This is because the integral is concentrated about its lower limit $\lambda - \lambda' \sim k_{-} \sim (1/z)$, because as noted previously $q \sim 1/z$. In the limit $q \to \lambda - \lambda'$, $X_{\lambda} \to \lambda$, $X_{\lambda'} \to -\lambda'$, so that $S_{\lambda,\lambda'} \to 0$. Thus, $G(k,k';z)$ is given by Eq.(III-29). We next consider the integral over k in Eq.(III-21) and rewrite it as $(1/z)\int_{0}^{\infty} da$. Again, since for large z, $k \sim k'$, we have $\kappa_{k} z = \kappa_{k'} z + ca$ where $c = k'/\kappa_{k'}$, so that $\phi_{k}(z) \sim \phi_{k'}(z)\exp(-ca)$. Substituting this $\phi_{k}(z)$ into Eq.(III-21) and using the fact that $\cos\delta_{-} \sim 1$ and $\sin\delta_{-} \sim 0$ for $k, k' \sim 1$, the Slater potential is then

$$V_{x}^{S}(z) \sim -\frac{2k_{F}}{\pi\rho_{n}(z)}\left[3\int_{0}^{1} dk' (1 - k'^{2})\phi_{k'}^{2}(z)\right]\left[\frac{1}{z}\int_{0}^{\infty} da \int_{0}^{\infty} du \frac{u e^{-ca-u}}{u^{2}+a^{2}} + O\left[\frac{1}{z^{2}}\right]\right] \quad .$$

(III-30)

The term in the first square parenthesis is the normalized density $\rho_{n}(z)$ and cancels the corresponding term in the denominator. Finally, on solving the double integral in the second square parenthesis and noting that the integral $\int_{0}^{1} dk'$ is concentrated near $k' \to 1$ for $z \to \infty$ so that $c \to 1/(\beta^{2}-1)^{1/2}$, we obtain the asymptotic structure of the Slater potential to be

$$\underset{x\to\infty}{V_{x}^{S}(x)} = -\frac{\alpha_{s}(\beta)}{x}; \qquad \alpha_{s}(\beta) = \frac{\beta^{2}-1}{\beta^{2}}\left[1 - \frac{\ln(\beta^{2}-1)}{\pi\sqrt{\beta^{2}-1}}\right] \quad , \qquad \text{(III-31)}$$

where $\beta^{2} = W/\epsilon_{F}$.

We note that in the above derivation employing the orbitals of the finite-linear-potential model, no approximations with regard to the structure of the Fermi hole have been made. Further, since the step-potential model (Bardeen, 1936; Sahni et.al., 1975; Sahni and Gruenebaum, 1977) is a special case of this effective potential, the analytical expression is equally valid for that model. In the following section we prove that the same expression is obtained for ***fully-self-consistently*** determined orbitals and effective potential.

The asymptotic decay of the Slater potential has also been investigated analytically by Juretschke (Juretschke, 1987) for the orbitals of the step-barrier model of a metal surface, but with an approximate form for the structure of the Fermi hole in the plane parallel to the surface. The resulting expression, however, is equivalent to that of Eq.(III-31).

3.2.2 Derivation for Self-Consistent Effective Potential.

To prove that the asymptotic structure of the Slater potential Eq.(III-31) is valid for the self-consistently determined effective potential, we divide the z axis into three parts: $z \leq -d$, $-d \leq z \leq d$, $z \geq d$, where d is an effective width of the surface region. In the first region, which corresponds to the metal bulk, the potential $v_{xc}(z)$ is constant. Consequently, the orbitals are of the form $\phi_k(z) = \sin[kz + \delta(k)]$, where the $\delta(k)$ are the self-consistent phase shifts. The contribution to $J(q, z)$ of Eq.(III-23) from this region is then

$$
\begin{aligned}
J(q,z) &= 2e^{-qz}\int_{-\infty}^{d} dz' e^{qz'} \sin[kz' + \delta(k)] \sin[k'z' + \delta(k')] \\
&= e^{-qz}e^{-qd}\left[\frac{q\cos(k_-d - \delta_-) - k_-\sin(k_-d - \delta_-)}{q^2 + k_-^2}\right. \\
&\qquad \left. - \frac{q\cos(k_+d - \delta_+) - k_+\sin(k_+d + \delta_+)}{q^2 + k_+^2}\right] \quad .
\end{aligned}
\tag{III-32}
$$

Note that this contribution is the same as the corresponding terms of Eq.(III-26) except that they are modified by the factor d. Now, due to screening, the surface region is small in comparison to the asymptotic electron position: $d \ll z$ for $z \to \infty$. Furthermore, again the effective value of $q \sim 1/z$, so that on expansion in q this contribution of $J(q,z)$ is,

$$
J(q,z) = e^{-qz}\frac{q}{q^2 + k_-^2}\cos\delta_- \quad , \tag{III-33}
$$

which is the same result as derived previously (see Eq.(III-27)). Recall, that it is this term which leads to the coefficient $\alpha_s(\beta)$.

In the region $-d \le z \le d$, the self-consistent orbitals will, of course, differ from those of the model effective potential considered. However, the contribution from this region to $J(q,z)$, which is

$$J(q,z) \;=\; 2\int_{-d}^{d} dz'\, e^{-q|z-z'|}\phi_k(z')\phi_{k'}(z') \quad , \qquad \text{(III-34)}$$

will be similar to the second set of terms of Eq.(III-27). Consequently, its contribution to $G(k,k'\,;z)$ (see Eq.(III-28)) is of $0(1/z)$, and therefore to $V_x^s(z)$ of $0(1/z^2)$.

In the region $z \geq d$, the orbitals of the model potential assumed previously were exponential (see Eq.(III-25)). If, however, we assume that the asymptotic structure of the effective potential which is that of $v_{xc} \sim -1/4x$, then the orbitals in this region are of the form $\phi_k(z) \sim z^{\nu_k} e^{-\kappa_k z}$ (Almbladh and von Barth, 1985). (For an electron at the Fermi level $\nu_{k_F} = 1/(4k_F\sqrt{\beta^2-1}\,))$. The expression for $J(q,z)$ in this region is

$$J(q,z) \;=\; \int_{d}^{\infty} dz'\, e^{-q|z-z'|}\phi_k(z')\phi_{k'}(z') \qquad \text{(III-35)}$$

$$\sim e^{-qz}\int_{d}^{z} dz'\, e^{qz'}(z')^{\nu_k+\nu_{k'}}e^{-(\kappa_k+\kappa_{k'})z'} + e^{qz}\int_{z}^{\infty} dz'\, e^{-qz'}(z')^{\nu_k+\nu_{k'}}e^{-(\kappa_k+\kappa_{k'})z'}$$

$$= \frac{e^{-qz}\left\{\Gamma(\nu_k+\nu_{k'}+1) - \Gamma\left[\nu_k+\nu_{k'}+1\,,\,(\kappa_k+\kappa_{k'}-q)z\right]\right\}}{(\kappa_k+\kappa_{k'}-q)^{\nu_k+\nu_{k'}+1}}$$

$$- \frac{e^{-qz}\gamma\left[\nu_k+\nu_{k'}+1\,,\,(\kappa_k+\kappa_{k'}-q)d\right]}{(\kappa_k+\kappa_{k'}-q)^{\nu_k+\nu_{k'}+1}} + \frac{e^{qz}\Gamma\left[\nu_k+\nu_{k'}+1\,,\,(\kappa_k+\kappa_{k'}+q)z\right]}{(\kappa_k+\kappa_{k'}+q)^{\nu_k+\nu_{k'}+1}} \, ,$$

$$\text{(III-36)}$$

where

$$\gamma(\alpha,x) \;=\; \int_{0}^{x} e^{-t}t^{\alpha-1}\,dt \quad , \qquad \text{(III-37)}$$

and

$$\Gamma(\alpha,x) = \int_x^\infty e^{-t} t^{\alpha-1}\, dt \quad , \tag{III-38}$$

are the incomplete gamma functions. Now (Spanier and Oldham, 1987)

$$\Gamma(\alpha,x) \sim x^{\alpha-1} e^{-x} \quad \text{as} \quad x \to \infty \quad .$$

so that

$$\underset{z\to\infty}{J(q,z)} = \frac{e^{-qz}\,\Gamma(\nu_k+\nu_{k'}+1)}{(\kappa_k+\kappa_{k'}-q)^{\nu_k+\nu_{k'}+1}} - \frac{2qz^{\nu_k+\nu_{k'}}}{(\kappa_k+\kappa_{k'})^2-q^2}\, e^{-(\kappa_k+\kappa_{k'})z} - \frac{e^{-qz}\,\gamma\left[\nu_k+\nu_{k'}+1\,,\,(\kappa_k+\kappa_{k'}-q)d\right]}{(\kappa_k+\kappa_{k'}-q)^{\nu_k+\nu_{k'}+1}} \quad . \tag{III-39}$$

(See Eq.(III-26) for a comparison with the corresponding terms of the finite-linear-potential model). The first and third terms of Eq.(III-39) give a $1/z$ contribution to $G(k,k';z)$, and consequently a $1/z^2$ contribution to $V_x^s(z)$. The second term has the functional dependence on z as $z^{\nu_k+\nu_{k'}} e^{-(\kappa_k+\kappa_{k'})z}$ instead of $e^{-(\kappa_k+\kappa_{k'})z}$ of the model potential. This term contributes exponentially to $G(k,k';z)$, and thus its contribution asymptotically to $V_x^s(z)$ vanishes.

Therefore, the asymptotic structure of the Slater potential for the self-consistently determined effective potential is the same as Eq.(III-31) derived previously. We emphasize again that this asymptotic structure of the potential in the vacuum region is governed and arises from the orbitals deep in the metal interior.

3.3 Numerical Confirmation of Analytical Asymptotic Expression

The correctness of the derivation can be shown by comparison of the asymptotic structure of the Slater potential $V_x^S(\mathbf{r})$ in the vacuum as determined by its general definition of Eq.(III-21) with the function $-\alpha_S(\beta)/x$ of Eq. (III-31). The expression for $V_x^S(\mathbf{r})$ in terms of momentum space integrals enables the easy numerical determination of $V_x^S(\mathbf{r})$ since the integrals are over the finite region from 0 to 1 in units normalized to the Fermi momentum. In Fig.2 we plot for Li metal (r_s=3.24) the Slater potential $V_x^S(\mathbf{r})$ in the vacuum as determined by this EXACT expression as well as the function $-\alpha_s(\beta)/z$. The calculations for the EXACT results are performed for the orbitals of the finite-linear-potential model for which the relationship between r_s and β is determined via energy minimization in the local density approximation for exchange and correlation (See Appendix of (Sahni, 1989). This value of β = 1.246. The same value of β is employed in the analytical expression for $\alpha_s(\beta)$. It is evident that the two curves merge by about ten Fermi wavelengths from the surface, thereby confirming the analytical results derived.

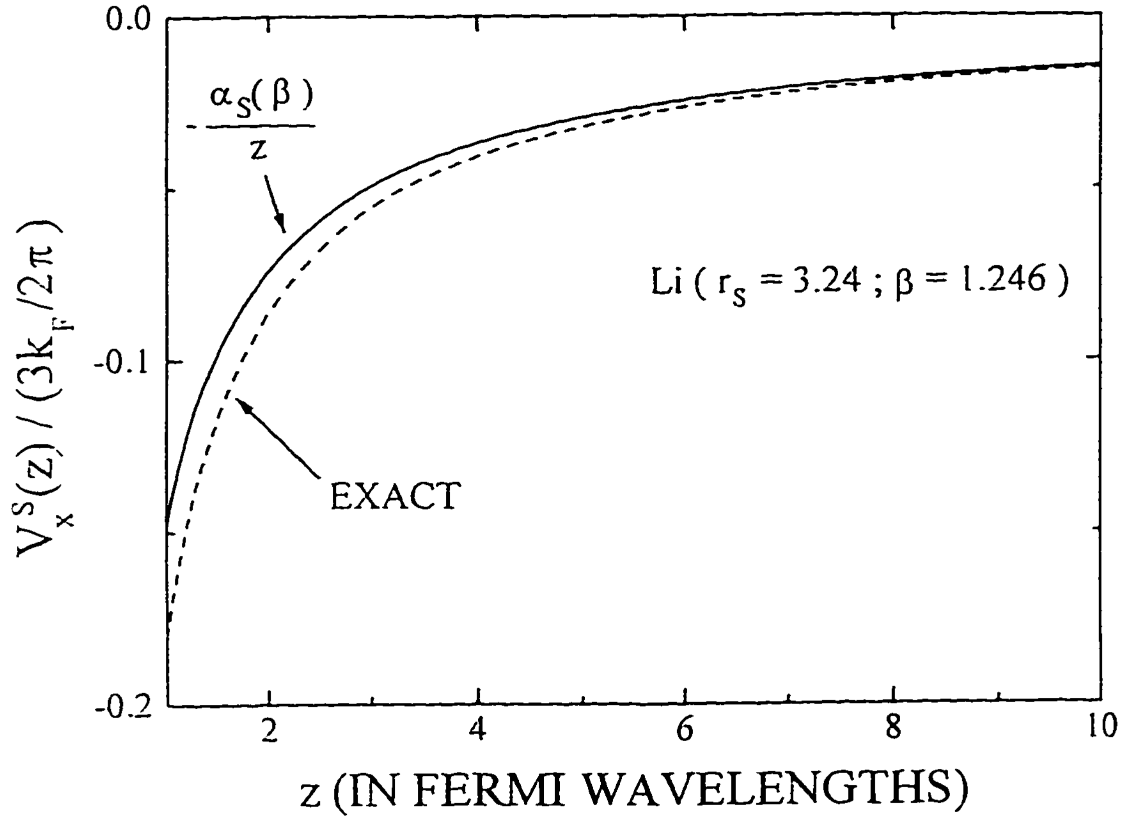

Fig. 2 Comparison of the EXACT Slater potential $V_x^S(z)$ (as determined by the general expression Eq.(III-21)) with the analytical expression $-\alpha_S(\beta)/z$ for asymptotic positions of electron in the vacuum.

3.4 Discussion of Results

In this chapter we have derived an expression for the Slater potential $V_x^S(r)$ at a metal surface which allows for its easy and accurate numerical determination throughout space. This semi-analytical expression differs from all previously derived expressions for the potential.

The other principal result of this chapter is the ***analytical*** confirmation that the asymptotic structure of the Slater exchange potential $V_x^S(r)$ in the classically forbidden region is ***long-ranged*** and image-potential-like of the form $-\alpha_S(\beta)/x$. The coefficient $\alpha_S(\beta)$ is, however, not 1/4 but approximately twice as large. For Wigner-Seitz radii of r_s = 2,4 and 6, the values of the coefficient $\alpha_S(\beta)$ are 0.390, 0.496 and 0.548, respectively.

For completeness we note that Harbola and Sahni (Harbola and Sahni, 1987) also investigated the asymptotic structure of the Slater potential at a metal surface. Their calculations (Sahni, 1989) of the Slater potential employing the orbitals of the finite-linear-potential model were performed for $r_s = 4.0$ with $\beta = 1.382$ for electron positions up to eight Fermi wavelengths ($\lambda_F = 6.93$Å) from the surface. The value of α_s of $3/(2\pi) \simeq 0.477$ was obtained by them whereas the exact result from Eq.(III-31) is 0.496. (In their original work employing the orbitals of the step-potential model for two values of β in which electron positions up to eight Fermi wavelengths were also considered, they had concluded that the Slater potential was not the image potential asymptotically but rather decayed with a coefficient $\alpha_s(\beta) = 3/(2\pi)$). These calculations were numerically complex because the Slater potential was written in a form involving a spatial integral over the semi-infinite crystal. Thus, accurate knowledge of the Fermi hole deep in the metal bulk was required, particularly for asymptotic positions of the electron in the vacuum region. The thrust of their work, however, was to show that the Slater potential did not decay as the image potential $-1/4x$.

CHAPTER IV

ANALYTICAL ASYMPTOTIC STRUCTURE OF KOHN-SHAM EXCHANGE POTENTIAL AT A METAL SURFACE

In this chapter, we present the ***exact analytical*** asymptotic structure of the 'exchange' potential $v_x(\mathbf{r})$ component of the Kohn-Sham theory 'exchange-correlation' potential $v_{xc}(\mathbf{r})$ in the classically forbidden region of a metal-vacuum interface. The asymptotic structure of $v_x(\mathbf{r})$ derived is valid for the ***self-consistent*** orbitals of both the semi-infinite jellium and structureless-pseudopotential models. We begin in section 4.1 by deriving a general expression for the asymptotic structure of the Kohn-Sham exchange potential in the classically forbidden region in terms of momentum-space integrals. As was the case for the Slater potential discussed in the previous chapter, this allows for the easy and accurate numerical determination of $v_x(\mathbf{r})$ in this region. This expression also allows for the determination of the exact asymptotic structure of $v_x(\mathbf{r})$ analytically. Again, to make our derivation more accessible, we first derive this result for the orbitals of the finite-linear-potential model, and then prove the expression to be valid for the fully self-consistent KS orbitals. We also prove in this chapter that two approximate exchange potentials, one due to us (Solomatin et.al., 1994) and the other to Sham (Sham, 1985), also possess the correct asymptotic structure in the vacuum. Finally, we prove ***analytically***, that for jellium-slab-metal, the exchange potential $v_x(\mathbf{r})$ decays as $-1/x^{-2}$.

4.1 Expression for Asymptotic Structure of Kohn-Sham exchange potential at a metal surface.

The relationship between density functional theory and many-body perturbation theory as established by Sham (Dreizler and Gross, 1990; Sham, 1985) is via the integral equation relating $v_{xc}(\mathbf{r})$ to the nonlocal exchange-correlation component $\Sigma_{xc}(\mathbf{r},\mathbf{r}';\omega)$ of the self-energy $\Sigma(\mathbf{r},\mathbf{r}';\omega)$. This equation is

$$\int dr' v_{xc}(r') \int d\epsilon G_s(r,r';\epsilon) G(r',r;\epsilon) = \int \int dr' dr'' \int d\epsilon G_s(r,r';\epsilon) \Sigma_{xc}(r',r'';\epsilon) G(r'',r;\epsilon), \tag{IV-1}$$

where $G(\mathbf{r},\mathbf{r}';\omega)$ is the one-particle Green function and $G_s(\mathbf{r},\mathbf{r}';\omega)$ the KS Green function. From this equation Sham (Sham, 1985) derived the asymptotic structure of $v_{xc}(\mathbf{r})$ to be

$$v_{xc}(\mathbf{r}) = \frac{1}{2\psi_k(\mathbf{r})} \int d\mathbf{r}' \Sigma_{xc}(\mathbf{r},\mathbf{r}';\epsilon_F) \psi_k(\mathbf{r}') + \frac{1}{2\psi_k^*(\mathbf{r})} \int d\mathbf{r}' \psi_k^*(\mathbf{r}') \Sigma_{xc}(\mathbf{r}',\mathbf{r};\epsilon_F) \quad , \tag{IV-2}$$

where the electron is at the Fermi level ϵ_F. The asymptotic structure of the exchange component $v_x(\mathbf{r})$ is obtained by substituting the self-energy $\Sigma_x(\mathbf{r},\mathbf{r}') = -\gamma_s(\mathbf{r},\mathbf{r}')/2|\mathbf{r}-\mathbf{r}'|$ into the above equation. Here $\gamma_s(\mathbf{r},\mathbf{r}') = 2\sum_k \psi_k^*(\mathbf{r})\psi_k(\mathbf{r}')$ is the idempotent density matrix constructed with the KS orbitals $\Psi_k(\mathbf{r})$. The resulting expression is recognized to be the orbital-dependent potential (Slater, 1951) $v_{x,k}(\mathbf{r})$ defined as

$$v_{x,k}(\mathbf{r}) = \int \frac{\rho_{x,k}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad , \tag{IV-3}$$

due to the orbital-dependent Fermi hole $\rho_{x,k}(\mathbf{r},\mathbf{r}')$ of Hartree-Fock theory which in turn is defined as

$$\rho_{x,k}(r,r') = \sum_{k'} \psi^{*}_{k'}(r)\psi_{k'}(r')\psi_k(r')/\psi_k(r) \ . \qquad \text{(IV-4)}$$

Employing the KS orbitals of Eq.(II-109), Harbola and Sahni (Harbola and Sahni, 1993) derived the expression for the orbital-dependent-potential $v_{x,1}(z)$ corresponding to the Fermi level electron with momentum perpendicular to the surface (in dimensionless variables) to be

$$\frac{v_{x,1}(z)}{(3k_F/2\pi)} = -\frac{4}{3\phi_1(z)}\int_{-\infty}^{\infty}\frac{dz'}{|z-z'|}\phi_1(z')\int_0^1 dk\,\phi^{*}_k(z')\phi_k(z)(1-e^{-\lambda|z-z'|}) \ , \qquad \text{(IV-5)}$$

where $\lambda = (1-k^2)^{1/2}$. Noting that

$$\frac{1-e^{-\lambda|z-z'|}}{|z-z'|} = \int_0^{\lambda} dq\, e^{-q|z-z'|} \ , \qquad \text{(IV-6)}$$

the expression for $v_{x,1}(z)$ can be written in the following form

$$\frac{v_{x,1}(z)}{(3k_F/2\pi)} = -\frac{2}{3\phi_1(z)}\int_0^1 dk\,\phi_k(z)\int_0^{\lambda} dq\,J(q,z) \ , \qquad \text{(IV-7)}$$

where

$$J(q,z) = 2\int_{-\infty}^{\infty} dz'\, e^{-q|z-z'|}\phi^{*}_k(z')\phi_1(z') \ . \qquad \text{(IV-8)}$$

The integral $J(q,z)$ can be performed analytically for orbitals generated by model effective potentials. The expression for $v_{x,1}(z)$ then reduces to finite-range momentum-space integrals.

4.2 Analytical Asymptotic Structure of the Kohn-Sham Exchange Potential

As for the case of the Slater potential, we first derive the asymptotic structure of the KS exchange potential $v_x(r)$ for the orbitals of the finite-linear-potential model. Once again, as will be shown, the result depends upon the structure of the orbitals deep in the metal bulk. As such the result is equally valid for the structureless-pseudopotential model. We then prove the expression to be valid for the fully self-consistently determined orbitals.

4.2.1 Derivation for Model Effective Potential

We first determine $J(q,z)$ of Eq.(IV-8) for $z > 0$ for the orbitals of the finite-linear-potential model (Eq.(III-25)) to obtain

$$J(q,z) = e^{-qz}\left[\frac{q\cos\delta_- + k_-\sin\delta_-}{q^2+k_-^2} - \frac{q\cos\delta_+ + k_+\sin\delta_+}{q^2+k_+^2}\right.$$
$$+ 2\int_0^{z_0} dz'\, e^{qz'}\left\{B_k Ai(\zeta_k') + C_k Bi(\zeta_k')\right\}\left\{B_l Ai(\zeta_l') + C_l Bi(\zeta_l')\right\}$$
$$\left. + \frac{2D_k D_l}{\kappa_k+\kappa_l-q}\, e^{-(\kappa_k+\kappa_l-q)z_0}\right] - \frac{4qD_kD_l}{(\kappa_k+\kappa_l)^2-q^2}\, e^{-(\kappa_k+\kappa_l)z} \quad , \tag{IV-9}$$

where $k_\mp = l \mp k$, and $\delta_\mp = \delta(l) \mp \delta(k)$. In the asymptotic large z region, the effective value of $q \sim 1/z$ due to the e^{-qz} factor in $J(q,z)$. Furthermore, since $k \sim l$ for large z, the effective value of $k_- \sim 1/z$ due to the $e^{-\kappa_l z}$ factor. Expanding $J(q,z)$ of Eq.(IV-9) in q we obtain for the asymptotic region

$$J(q,z) \underset{z\to\infty}{\sim} e^{-qz}\left[\frac{q}{q^2+k_-^2}\cos\delta_- + \frac{k_-}{q^2+k_-^2}sin\,\delta_-\right] + e^{-qz}\left[-\frac{sin\,\delta_+}{k_+} - \frac{q\cos\delta_+}{k_+^2}\right.$$
$$+\frac{2D_kD_1}{\kappa_k+\kappa_1}e^{-(\kappa_k+\kappa_1)z_b} \tag{IV-10}$$
$$\left. +2\int_0^{z_b} dz'\left\{B_kAi(\zeta_k') + C_kBi(\zeta_k')\right\}\left\{B_1Ai(\zeta_1') + C_1Bi(\zeta_1')\right\}\right]$$
$$-\frac{4qD_kD_1}{(\kappa_k+\kappa_1)^2}e^{-(\kappa_k+\kappa_1)z} \quad .$$

Next consider the contribution of $J(q,z)$ of Eq.(IV-10) to the integral over q in Eq.(IV-7). The last term of Eq.(IV-10) is exponentially small in the vacuum region and does not contribute. The contribution of the second set of terms is

$$\frac{1-e^{-\lambda z}}{z}\left[-\frac{\sin\delta_+}{k_+} + \frac{2D_kD_1}{\kappa_k+\kappa_1}e^{-(\kappa_k+\kappa_1)z_b} + 2\int_0^{z_b} dz'\,\{\;\}\,\{\;\}\right] \tag{IV-11}$$
$$+\left[\frac{\lambda e^{-\lambda z}}{z} + 0\left(\frac{1}{z^2}\right)\right]\frac{\cos\delta_+}{k_+^2} \quad .$$

Now $\lambda z \sim k_-^{1/2}z = (k_-z)^{1/2}z^{1/2} \gg 1$ for large z since $k_- \sim 1/z$. Thus, the contribution of Eq.(IV-11) is of $0(1/z)$. The contribution of the first term of Eq.(IV-10) to the integral over q in Eq.(IV-7), with $qz = u$ and $a = k_-z$, is

$$\cos\delta_- \int_0^\infty du\frac{ue^{-u}}{u^2+a^2} + a\sin\delta_- \int_0^\infty du\frac{e^{-u}}{u^2+a^2} + 0\left(\frac{1}{z}\right) \quad . \tag{IV-12}$$

We next consider the integral over k in Eq.(IV-7) and rewrite it as $(1/z)\int_0^\infty da$. Since for large z, $k \sim 1$, we have $\kappa_k z = \kappa_1 z + ca$ where $c = 1/\kappa_1$, so that $\phi_k(z) \sim \phi_1(z)\exp(-ca)$. Substituting this $\phi_k(z)$ into Eq.(IV-7) and using the fact that $\cos\delta_{-} \sim 1$ and $\sin\delta_{-} \sim 0$ for $k \sim 1$ we derive the expression for $v_{x,1}(z)$ to be

$$v_{x,1}(z) \sim -\frac{3k_F}{2\pi}\frac{2}{3\phi_1(z)}\phi_1(z)\frac{1}{z}\int_0^\infty da \int_0^\infty du \frac{u e^{-ba-u}}{u^2+a^2} , \tag{IV-13}$$

or equivalently

$$v_x(x) = -\frac{\alpha_{KS,x}(\beta)}{x} \quad ; \quad \alpha_{KS,x}(\beta) = \frac{\beta^2-1}{2\beta^2}\left[1-\frac{\ln(\beta^2-1)}{\pi(\beta^2-1)^{1/2}}\right] . \tag{IV-14}$$

Thus, the asymptotic structure of the KS exchange potential is image-potential-like and *long-ranged*. (Note that the coefficient $\alpha_{KS,x}(\beta) = \alpha_S(\beta)/2$).

The above derivation also shows that for the extended metal surface system for which the energy spectrum is continuous, to leading order, the orbital-dependent-potentials $v_{x,k}(r)$ for electrons within a shell of thickness $(1/z)$ about the Fermi level are the same. Thus, their average taken over this shell, which is the exchange potential, is equivalent in leading order to the orbital-dependent-potential for electrons at the Fermi level. In the case of discrete systems such as atoms, it is of course more readily apparent that the asymptotic structure is due to the highest occupied orbital electrons.

4.2.2 Derivation for Self-Consistent Effective Potential

To prove that the asymptotic structure of the Kohn-Sham exchange potential

Eq.(IV-14) is valid for the self-consistently determined effective potential, we divide the z axis into three parts: $z \leq -d$, $-d \leq z \leq d$, $z \geq d$, where d is an effective width of the surface region. In the first region, which corresponds to the metal bulk, the potential $v_{ee}(z)$ is constant. Consequently, the orbitals are of the form $\phi_k(z) = \sin[kz + \delta(k)]$, where the $\delta(k)$ are the self-consistent phase shifts. The contribution to $J(q,z)$ of Eq.(IV-9) from this region is then

$$J(q,z) = 2e^{-qz} \int_{-\infty}^{d} dz' e^{qz'} \sin[kz' + \delta(k)] \sin[z' + \delta(1)]$$

$$= e^{-qz} e^{-qd} \left[\frac{q\cos(k_- d - \delta_-) - k_- \sin(k_- d - \delta_-)}{q^2 + k_-^2} - \frac{q\cos(k_+ d - \delta_+) - k_+ \sin(k_+ d + \delta_+)}{q^2 + k_+^2} \right] . \tag{IV-15}$$

Note that this contribution is the same as the corresponding terms of Eq.(III-26) except that they are modified by the factor d. Now, due to screening, the surface region is small in comparison to the asymptotic electron position: $d \ll z$ for $z \to \infty$. Furthermore, again the effective value of $q \sim 1/z$, so that on expansion in q this contribution of $J(q,z)$ is,

$$J(q,z) = e^{-qz} \frac{q}{q^2 + k_-^2} \cos\delta_- \ , \tag{IV-16}$$

which is the same result as derived previously (see Eq.(IV-10)). Recall, that it is this term which leads to the coefficient $\alpha_{KS_x}(\beta)$.

In the region $-d \le z \le d$, the self-consistent orbitals will, of course, differ from those of the model effective potential considered. However, the contribution from this region to $J(q, z)$, which is

$$J(q,z) = 2\int_{-d}^{d} dz' \, e^{-q|z-z'|} \phi_k(z') \phi_l(z') \quad , \tag{IV-17}$$

will be similar to the second set of terms of Eq.(IV-10). Consequently, its contribution to $v_x(z)$ is of $O(1/z^2)$.

In the region $z \ge d$, the orbitals of the model potential assumed previously were exponential (see Eq.(III-25)). If, however, we assume that the asymptotic structure of the effective potential which is that of $v_{xc} \sim -1/4x$, then the orbitals in this region are of the form $\phi_k(z) \sim z^{\nu_k} e^{-\kappa_k z}$. (For an electron at the Fermi level $\nu_{k_F} = 1/(4k_F\sqrt{\beta^2-1}\,)$). The expression for $J(q, z)$ in this region is

$$J(q, z) = \int_{d}^{\infty} dz' \, e^{-q|z-z'|} \phi_k(z') \phi_l(z') \tag{IV-18}$$

$$\sim e^{-qz} \int_{d}^{z} dz' \, e^{qz'} (z')^{\nu_k + \nu_l} e^{-(\kappa_k + \kappa_l)z'} + e^{qz} \int_{z}^{\infty} dz' \, e^{-qz'} (z')^{\nu_k + \nu_l} e^{-(\kappa_k + \kappa_l)z'}$$

$$= \frac{e^{-qz}\left\{\Gamma(\nu_k + \nu_l + 1) - \Gamma\left[\nu_k + \nu_l + 1, (\kappa_k + \kappa_l - q)z\right]\right\}}{(\kappa_k + \kappa_l - q)^{\nu_k + \nu_l + 1}}$$

$$- \frac{e^{-qz}\gamma\left[\nu_k + \nu_l + 1, (\kappa_k + \kappa_l - q)d\right]}{(\kappa_k + \kappa_l - q)^{\nu_k + \nu_l + 1}} + \frac{e^{qz}\Gamma\left[\nu_k + \nu_l + 1, (\kappa_k + \kappa_l + q)z\right]}{(\kappa_k + \kappa_l + q)^{\nu_k + \nu_l + 1}} , \tag{IV-19}$$

where

$$\gamma(\alpha,x) = \int_0^x e^{-t} t^{\alpha-1}\,dt \quad , \quad \Gamma(\alpha,x) = \int_x^\infty e^{-t} t^{\alpha-1}\,dt \quad , \tag{IV-20}$$

are the incomplete gamma functions. $\Gamma(\alpha,x) \sim x^{\alpha-1}e^{-x}$ as $x \to \infty$, so that

$$\begin{aligned} \underset{z\to\infty}{J(q,z)} = \frac{e^{-qz}\Gamma(\nu_k+\nu_1+1)}{(\kappa_k+\kappa_1-q)^{\nu_k+\nu_1+1}} - \frac{2qz^{\nu_k+\nu_1}}{(\kappa_k+\kappa_1)^2-q^2}\,e^{-(\kappa_k+\kappa_1)z} \\ - \frac{e^{-qz}\gamma\left[\nu_k+\nu_1+1,(\kappa_k+\kappa_1-q)d\right]}{(\kappa_k+\kappa_1-q)^{\nu_k+\nu_1+1}} \quad . \end{aligned} \tag{IV-21}$$

(See Eq.(IV-9) for a comparison with the corresponding terms of the finite-linear-potential model). The first and third terms of Eq.(IV-21) give a $1/z^2$ contribution to $v_x(z)$. The second term has the functional dependence on z as $z^{\nu_k+\nu_1}e^{-(\kappa_k+\kappa_1)z}$ instead of $e^{-(\kappa_k+\kappa_1)z}$ of the model potential. The contribution of this term asymptotically to $v_x(z)$ vanishes.

Therefore, the asymptotic structure of the KS exchange potential for the self-consistently determined effective potential is the same as Eq.(IV-14) derived previously. We emphasize again that this asymptotic structure of the potential in the vacuum region is governed and arises from the orbitals deep in the metal interior whose structure is $\phi_k(x) = \sin[kx+\delta(k)]$ irrespective of whether the effective potential at the surface is modelled or determined self-consistently.

4.3 Kohn-Sham and Slater Asymptotic Exchange Potential Decay Coefficients

In Fig. 3 we plot the Kohn-Sham asymptotic exchange potential coefficient $\alpha_{KS,x}(\beta)$ as a function of the barrier height parameter β. We also give the corresponding Wigner-Seitz radius r_s for both the jellium and stabilized-jellium models. As in the previous chapter, the relationship between the parameters β and r_s is through fully-self-consistent calculations (Sahni, 1989; Lang and Kohn, 1970; Fiolhais and Perdew, 1992) within the local density approximation for exchange-correlation. For completeness we also plot the Slater asymptotic structure coefficient $\alpha_S(\beta)$.

For metallic densities the Kohn-Sham coefficient ranges from 0.195 to 0.274. For $\beta = \sqrt{2}$, this coefficient is precisely 1/4. (The corresponding value of $\alpha_S(\beta)$ = 1/2). This value of β corresponds to a Wigner-Seitz radius of $r_s \sim 4.0$ which is that of Na. We note that the jellium model is stable for approximately this value of r_s. It is thus clear that for the metallic range of densities, the asymptotic structure of the Kohn-Sham exchange potential $v_x(r)$ is essentially the image potential.

The numerical studies of the asymptotic structure of the Slater and Kohn-Sham exchange potentials at a metal surface due to Harbola and Sahni also confirm the analytical results derived in the present work. The calculations of Harbola and Sahni (Harbola and Sahni, 1993) for the asymptotic structure of the Kohn-Sham exchange potential were performed for the finite-linear-potential model orbitals for a Wigner-Seitz radius $r_s = 2.0$ with $\beta = 1.130$. They observed an image-potential-like $-\delta/x$ dependence.

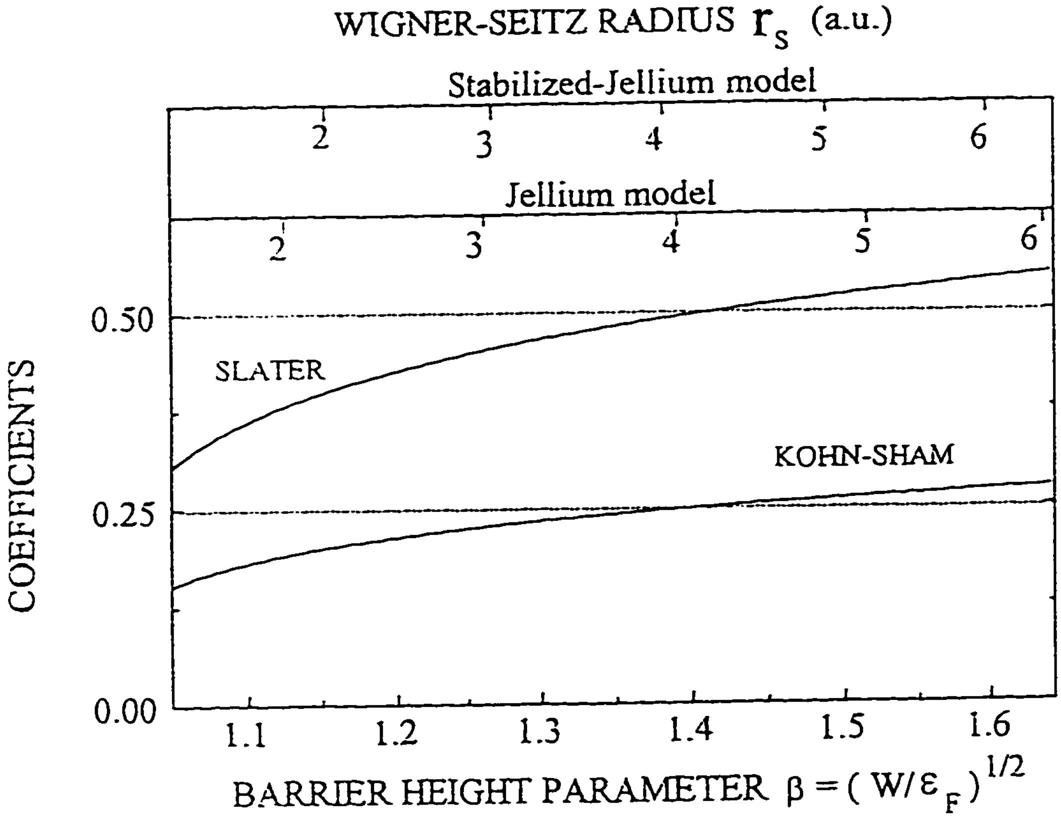

Fig. 3 The Slater and Kohn-Sham asymptotic exchange potential coefficients $\alpha_S(\beta)$ and $\alpha_{KS,x}(\beta)$ respectively, as a function of the barrier height parameter $\beta=(W/\epsilon_F)^{1/2}$, where W is the barrier height and ϵ_F the Fermi energy. The corresponding values of the Wigner-Seitz radius r_s for the jellium and stabilized-jellium models over the metallic range of densities are also given. The relationship between r_s and β is via self-consistent calculations in the local density approximation for exchange-correlation.

However, having performed their calculations to only about three Fermi wavelengths ($\lambda_F = 3.46\,\text{Å}$) from the surface, they concluded that $\delta = 1/4$. The correct value of the coefficient $\delta = 0.195$ for this value of β.

The near exactness of the coefficient obtained by Harbola and Sahni for specific values of the Wigner-Seitz radius is indicative of the accuracy of their numerical work, particularly in light of the highly delocalized nature of both the Fermi and orbital-dependent Fermi holes. The present work, however, provides the precise dependence of the coefficients on the metal parameters. Further, since this dependence is analytical, the coefficients can be determined for arbitrary bulk-metal density in addition to being valid for fully-self-consistent orbitals.

4.4 Asymptotic Structure of Exchange Potential for Jellium Slab Geometry

As noted previously, the asymptotic structure of the exchange potential $v_x(\mathbf{r})$ has also been examined by Sham (Sham, 1985) and Eguiluz et al (Eguiluz et.al., 1992) via the integral equation relating $v_x(\mathbf{r})$ to the self-energy $\Sigma_x(\mathbf{r}, \mathbf{r}')$, and they have concluded that the structure $\sim -x^{-2}$. The details of Sham's derivation are unavailable in the literature. However, the results of Eguiluz et al can be explained. In their numerical calculations these authors consider a slab configuration which they assume to be thick enough to represent a semi-infinite crystal. Thus, consider a slab of thickness L sufficiently large to make the energy spectrum continuous. The integral $J(q, z)$ of Eq.(IV-8) then extends from $-L$ to 0, so that for $z > 0$ (assuming the model effective potential),

$$J(q,z) = e^{-qz}\int_{-L}^{0} dz' e^{qz'}\sin[kz' + \delta(k)]\sin[k'z' + \delta(k')] \qquad \text{(IV-22)}$$

$$\underset{z\to\infty}{\sim} \frac{e^{-qz}q\left[\cos\delta_- - e^{-qL}\cos(\delta_- + k_- L)\right]}{q^2 + k_-^2} , \qquad \text{(IV-23)}$$

where the second term is the contribution from the surface at $-L$. Since in the asymptotic region $(z \to \infty)$, both q and $k_- \sim z^{-1}$, then qL and $k_- L \ll 1$. Then expanding about qL and $k_- L$ one obtains to leading order

$$J(q,z) \sim q^2 e^{-qz} L\cos\delta_- /(q^2 + k_-^2) , \qquad \text{(IV-24)}$$

which then leads to a $1/z^2$ dependence for the exchange potential $v_x(r)$ as obtained by Eguiluz et al. Thus, to obtain the correct asymptotic structure of the exchange potential for the semi-infinite crystal via numerical solution of the Sham integral equation, the slab thickness assumed must be much greater than the distance of the asymptotic electron from the surface. However, due to screening, whose manifestation is the partial cancellation of the exchange and correlation holes in the metal bulk, the structure of the exchange-correlation potential $v_{xc}(r)$ in finite thickness slab calculations should be equivalent to that obtained for the semi-infinite case.

4.5 Asymptotic Structure of Approximate Exchange Potentials

In this section we prove that two approximate exchange potentials in the literature also possess the correct asymptotic structure of $\frac{1}{2}V_x^s(r)$ at a metal surface. The first due to Sham (Sham, 1985) is

$$v_x^{Sham}(r) = \frac{\sum_k \delta(\epsilon_F-\epsilon_k)\left[\int dr' \Psi_k^*(r')\Sigma_x(r',r)\Psi_k(r) + c.c.\right]}{2\sum_k \delta(\epsilon_F-\epsilon_k)\,|\Psi_k(r)|^2} \;. \qquad \text{(IV-25)}$$

where $\sum_x(r,r')$ is the self-energy. The numerator of this expression can be written as

$$F(x) = \frac{1}{4}k_F\frac{\partial}{\partial k_F}\int\frac{dr'}{|r-r'|}\,|\gamma(r,r')|^2 \;, \qquad \text{(IV-26)}$$

where it is to be understood that the derivative acts ***only*** on the $\theta(\epsilon_F-\epsilon_k)$ in $\gamma(r,r')$. Following the same steps as in section 2.2.1, we obtain (in dimensionless co-ordinates)

$$F(z) = -\frac{2}{\pi^2}\frac{k_F}{\pi}\int_0^1 dk' \int_0^{k'} dk\,\phi_k^*(z)\phi_{k'}(z)\,H(k,k';z) \;, \qquad \text{(IV-27)}$$

where

$$H(k,k';z) = \int_0^{(\lambda^2-\lambda'^2)^{1/2}} dq J(q,z) + \frac{1}{\pi}\int_{\lambda-\lambda'}^{\lambda+\lambda'} dq J(q,z)\left\{C_\lambda(q)+C_{\lambda'}(q)\right\} \;, \qquad \text{(IV-28)}$$

$$C_\lambda(q) = \tan^{-1}\frac{(\lambda^2-X_\lambda^2)^{1/2}}{X_\lambda} \;, \qquad \text{(IV-29)}$$

$C_{\lambda'}(q) = C_\lambda(q)\big|_{\lambda\to\lambda'}$, and where $J(q,z)$, $X_{\lambda,\lambda'}$ and λ, λ' are as defined in Chapter III. (In deriving Eq.(IV-28), the integral corresponding to Eq.(III-15) involves instead the product of a θ function and a δ function. As such it is the arc of the $k_\parallel'$ Fermi circle (see Fig. 1) that lies within the $k_\parallel$ Fermi circle that must be determined). Again, as in Section 2.2.1, the structure of *F(z)* for asymptotic positions of the electron can be obtained to be

$$\underset{z\to\infty}{F(z)} = -\frac{2}{\pi^2}\frac{k_F}{\pi}\int_0^1 dk'\,\phi_{k'}^2(z)\left[\frac{1}{z}\int_0^\infty da\int_0^\infty du\,\frac{ue^{-ca-u}}{u^2+a^2}+0\left(\frac{1}{z^2}\right)\right] \quad . \qquad \text{(IV-30)}$$

On the other hand, the denominator of Eq.(IV-25) is the local density of states:

$$2\sum_k \delta(\epsilon_F-\epsilon_k)|\Psi_k(r)|^2 = \frac{2}{\pi}\int_0^1 dk\,|\phi_k(z)|^2 \quad . \qquad \text{(IV-31)}$$

On dividing Eq.(IV-30) by Eq.(IV-31), it is evident that the asymptotic structure of $v_x^{Sham}(x) = \frac{1}{2}V_x^s(x)$. The potential $v_x^{Sham}(r)$ also possesses the correct asymptotic behavior of $(-1/r)$ in atoms, but as noted by Sham, self-consistent calculations for such systems may not be feasible due to the vanishing of the denominator at the nodes of the wavefunctions.

The second approximate exchange potential $v_x^{(0)}(r)$ is derived (Solomatin, et.al., 1994) from the exact exchange energy functional $E_x[\rho]$, but determined by obtaining the functional derivative for a restricted class of density variations. The resulting general expression is

$$v_x^{(0)}(r) = [2d\rho(r)/dk_F]^{-1} \quad d[\rho(r)\,V_x^s(r)]/dk_F \quad , \qquad \text{(IV-32)}$$

whose leading term can readily be seen to be $\frac{1}{2}V_x^s(r)$. This approximate exchange potential will be discussed in detail in Chapter VI.

CHAPTER V

STRUCTURE OF THE PAULI COMPONENT OF THE KOHN-SHAM EXCHANGE POTENTIAL AT A METAL SURFACE

In this chapter we study the Pauli component $W_x^{KS}(r)$ of the KS exchange-correlation potential $v_{xc}(r)$ (see Eq. (II-94)) or equivalently of the exchange potential $v_x(r)$ (see Eq. (II-78)). The component $W_x^{KS}(r)$ is the work done to move an electron in the field $\mathcal{E}_x^{KS}(r)$ due to the Fermi hole $\rho_x^{KS}(r,r')$. We begin by deriving for the semi-infinite jellium metal surface an expression for the field $\mathcal{E}_x^{KS}(\mathbf{r})$ in terms of momentum-space integrals. As in the case of the Slater and Kohn-Sham potentials this allows for the easy and accurate numerical determination of the field, and therefore of the work $W_x^{KS}(\mathbf{r})$ throughout space. Again, in this manner, knowledge of the precise structure of the delocalized Fermi hole charge in the metal bulk, particularly for asymptotic positions of the electron in the vacuum region, is ***not*** necessary. The expression for the field $\mathcal{E}_x^{KS}(\mathbf{r})$ derived also allows for the determination of the ***exact analytical*** structure of the work $W_x^{KS}(\mathbf{r})$ in the asymptotic vacuum region. We perform the calculation of the asymptotic structure of $W_x^{KS}(\mathbf{r})$ for the accurate semi-analytical orbitals of the finite-linear-potential model. Again, as was the case for the Slater and KS potentials, the analytical result is equally valid for the ***fully self-consistently*** determined Kohn-Sham orbitals. This expression is also valid for the structureless-pseudopotential model of a metal surface. Finally, we study the structure of the field $\mathcal{E}_x^{KS}(\mathbf{r})$ and the work $W_x^{KS}(\mathbf{r})$ at and about the metal surface.

5.1 Expression for the Work $W_x^{KS}(\mathbf{r})$ at a Jellium or Structureless-Pseudopotential Metal Surface

In this section we derive a general expression for the work $W_x^{KS}(\mathbf{r})$ in the jellium or structureless-pseudopotential (stabilized-jellium) models of a metal surface. The electric field $\mathcal{E}_x^{KS}(\mathbf{r})$ of Eq.(II-80) due to the Fermi hole $\rho_x^{KS}(\mathbf{r}, \mathbf{r}')$ defined by Eq.(II-39) is then

$$\mathcal{E}_x^{KS}(\mathbf{r}) = \int d\mathbf{r}' \frac{x - x'}{|\mathbf{r} - \mathbf{r}'|^3} \frac{|\gamma_s(\mathbf{r}, \mathbf{r}')|^2}{2\rho(x)} \tag{V-1}$$

$$= -\frac{1}{2\rho(x)} \int dx' 4 \int\int \frac{d\mathbf{k}\, d\mathbf{k}'}{(2\pi)^4 \pi^2} \phi_{kk'}(x, x') \frac{(x - x')}{|\mathbf{r} - \mathbf{r}'|^3} e^{i\mathbf{q} \cdot \mathbf{X}} \theta(\epsilon_F - \frac{k^2}{2}) \theta(\epsilon_F - \frac{k'^2}{2}) \quad , \tag{V-2}$$

where

$$\phi_{kk'}(x, x') = \phi_k^*(x) \phi_k(x') \phi_{k'}^*(x') \phi_{k'}(x) \tag{V-3}$$

and $\mathbf{q} = \mathbf{k}_\parallel - \mathbf{k}'_\parallel$, $\mathbf{X} = \mathbf{x}_\parallel - \mathbf{x}'_\parallel$. Now the integral

$$\int d\mathbf{x}'_\parallel (x - x') e^{i\mathbf{q} \cdot \mathbf{X}} = -\frac{\partial}{\partial x} \int d\mathbf{x}'_\parallel \frac{e^{i\mathbf{q} \cdot \mathbf{X}}}{|\mathbf{r} - \mathbf{r}'|} = 2\pi \, \mathrm{sgn}(x - x') e^{-q|x - r'|} \quad , \tag{V-4}$$

so that

$$\mathcal{E}_x^{KS}(\mathbf{r}) = -\frac{1}{2\rho(x)} 4 \int\int \frac{d\mathbf{k}d\mathbf{k}'}{(2\pi)^4 \pi^2} \int dx' \phi_{kk'}(x, x') 2\pi \mathrm{sgn}(x - x') \, e^{-q|x - x'|} \theta\left[\epsilon_F - \frac{k^2}{2}\right] \theta\left[\epsilon_F - \frac{k'^2}{2}\right] \quad . \tag{V-5}$$

Apart from the *sgn*(x–x') factor in Eq.(V-5), this representation of the electric field is similar to Eq.(III-5) for the Slater potential. Following the same steps as in section 3.1

we can write the electric field $\mathcal{E}_x^{KS}(\boldsymbol{r})$ at a jellium metal surface as

$$\frac{\mathcal{E}_x^{KS}(z)}{3k_F^2/2\pi)} = -\frac{4}{\pi\rho_n(z)}\int_0^1 dk' \int_0^{k'} dk\,\phi_k^*(z)\phi_{k'}(z)H(k,k';z) \quad , \tag{V-6}$$

where

$$H(k,k';z) = \pi\lambda'^2 \int_0^{(\lambda^2-\lambda'^2)^{1/2}} dq\cdot q\,M(q,z) + \int_{\lambda-\lambda'}^{\lambda+\lambda'} dq\cdot q\,M(q,z)\{S_\lambda(q)+S_{\lambda'}(q)\} \quad , \tag{V-7}$$

$$M(q,z) = 2\int_{-\infty}^{\infty} dz'\,\mathrm{sgn}(z-z')\; e^{-q|z-z'|}\;\phi_k(z')\phi_{k'}^*(z') \quad , \tag{V-8}$$

and where $\rho_n(z)$ is the density normalized to the bulk value $\bar{\rho} = k_F^3/2\pi^2$. The work done $W_x^{KS}(z)$ is then

$$\frac{W_x^{KS}(z)}{(3k_F/2\pi)} = -\int_\infty^z \frac{\mathcal{E}_x^{KS}(z')}{(3k_F^2/2\pi)}dz' \quad . \tag{V-9}$$

For orbitals generated by model effective potentials, the spatial integral $M(q,z)$ of Eq.(V-8) can be determined analytically. Thus, for such orbitals, the field $\mathcal{E}_x^{KS}(z)$ is entirely in terms of finite-region momentum-space integrals, and therefore easily determined for all electron positions throughout space. Since the structure of the self-consistent orbitals in the asymptotic metal bulk (to within a phase factor) and vacuum regions is known, the integral $M(q,z)$ can also be determined analytically in these regions for such a calculation. Therefore, the integral has to be performed numerically only over a finite region of space. It is for this reason that a self-consistent calculation with $W_x^{KS}(z)$ as the exchange potential can be performed.

5.2 Analytic Asymptotic Structure of the Work $W_x^{KS}(\mathbf{r})$

In this section we derive the asymptotic structure of $W_x^{KS}(\mathbf{r})$ in the vacuum region in terms of the semi-analytical orbitals of finite-linear-potential model of a metal surface. The analytical result, however, is equally valid for fully self-consistently determined orbitals of both the jellium and structureless-pseudopotential models.

To determine the asymptotic structure of $W_x^{KS}(\mathbf{r})$ we employ the expression Eq.(V-9)) derived for it in the previous section. For the orbitals of Eq.(III-25) the integral for $M(q, z)$ of Eq.(V-8) can be solved analytically and its solution is given in Appendix 2. In the asymptotic large z region, the effective value of $q \sim 1/z$ due to the e^{-qz} factor in $M(q, z)$. Furthermore, since $k \sim k'$ for large z, the effective value of $k_- \sim 1/z$ due to the $e^{-\kappa_k z}$ factor. Expanding the expression for $M(q, z)$ for $z \geq z_b$ given in Appendix 2 in q we obtain for the asymptotic region

$$
\begin{aligned}
\underset{z\to\infty}{M(q, z)} \sim e^{-qz} & \left[\frac{q}{q^2 + k_-^2} \cos\delta_- + \frac{k_-}{q^2 + k_-^2} \sin\delta_- \right] \\
& + e^{-qz} \left[-\frac{\sin\delta_+}{k_+} - \frac{q\cos\delta_+}{k_+^2} + \frac{2D_k D_{k'}}{\kappa_k + \kappa_{k'}} e^{-(\kappa_k + \kappa_{k'})z_b} \right. \\
& \left. + 2\int_0^{z_b} dz' \left\{ B_k \mathrm{Ai}(\zeta'_k) + C_k \mathrm{Bi}(\zeta'_k) \right\} \left\{ B'_k \mathrm{Ai}(\zeta'_{k'}) + C'_k \mathrm{Bi}(\zeta'_{k'}) \right\} \right] \\
& - \frac{4D_k D'_k}{\kappa_k + \kappa'_k} e^{-(\kappa_k + \kappa'_k)z} \quad .
\end{aligned}
\tag{V-10}
$$

Next consider the contribution of $M(q,z)$ to the first integral of $H(k,k';z)$ of Eq.(V-7). The last term of Eq.(V-10) is exponentially small in the asymptotic vacuum region and does not contribute. The contribution of the second set of terms is

$$\frac{1-\left[1+(\lambda^2-\lambda'^2)^{1/2}z\right]e^{-(\lambda^2-\lambda'^2)^{1/2}z}}{z^2}\left[-\frac{\sin\delta_+}{k_+}+\frac{2D_kD_k'}{\kappa_k+\kappa_k'}e^{-(\kappa_k+\kappa_k')z_0}\right. \tag{V-11}$$

$$\left.+2\int_0^{z_0}dz'\{\}\ \{\}\right]+0\left(\frac{1}{z^3}\right) .$$

Now $(\lambda^2-\lambda'^2)^{1/2}z \sim k_-^{1/2}z=(k_-z)^{12}z^{1/2}\gg 1$ for large Z since $k_- \sim 1/z$. Thus, the contribution of Eq.(V-11) to the first integral of $H(k,k';z)$ is of $0(1/z^2)$. The contribution of the first term of Eq.(V-10) to the first integral of $H(k,k';z)$ with $qz=u$ and $a=k_-z$ is

$$\frac{1}{z}\left[\cos\delta_-\int_0^\infty du\frac{u^2e^{-u}}{u^2+a^2}+a\sin\delta_-\int_0^\infty du\frac{ue^{-u}}{u^2+a^2}\right]+0\left(\frac{1}{z^2}\right) . \tag{V-12}$$

We next note that the second term of $H(k,k';z)$ of Eq.(V-7) does not contribute to the leading order. This is because the integral is concentrated about its lower limit $(\lambda-\lambda')\sim k_-\sim(1/z)$, because as noted previously $q\sim 1/z$. In the limit $q\rightarrow\lambda-\lambda'$, $X_\lambda\rightarrow\lambda$, $X_\lambda'\rightarrow-\lambda'$ so that $S_{\lambda,\lambda'}\rightarrow 0$. Thus, $H(k,k';z)$ is given by Eq.(V-12). We next consider the integral over k in Eq.(V-6) and rewrite it as $(1/z)\int_0^\infty da$. Again, since for large z, $k\sim k'$, we have $x_kz=x_{k'}z+ca$ where $c=k'/x_{k'}$, so that $\phi_k(z)\sim\phi_{k'}(z)\exp(-ca)$. Substituting this $\phi_k(z)$ into Eq.(V-6) and using the fact that $\cos\delta_-\sim 1$ and $\sin\delta_-\sim 0$ for k, $k'\sim 1$, the potential $W_x^{KS}(z)$ of Eq.(V-9) is then

$$\frac{W_x^{KS}(z)}{(3k_F/2\pi)} \sim -\frac{4}{3}\int_{\infty}^{z} \frac{dz'}{z'^2\rho_n(z')} \left[3\int_0^1 dk'(1-k'^2)\phi_{k'}^2(z')\right] \left[\int_0^\infty da\int_0^\infty du\,\frac{u^2e^{-(ca+u)}}{u^2+a^2}\right] + 0\left(\frac{1}{z^2}\right) . \tag{V-13}$$

The term in the first square parenthesis is the density normalized to the bulk value and cancels the corresponding term in the denominator. Finally, on solving the double integral in the second square parenthesis, and noting that the integral $\int_0^1 dk'$ is concentrated near $k' \to 1$ for $z \to \infty$ so that $c \to 1/\sqrt{\beta^2-1}$, we obtain the asymptotic structure of $W_x^{KS}(x)$ to be

$$\underset{x\to\infty}{W_x^{KS}(x)} = -\frac{\alpha_w(\beta)}{x} , \tag{V-14}$$

where the coefficient

$$\alpha_w(\beta) = \frac{\beta^2-1}{\beta^2}\left[\frac{2}{\pi\sqrt{\beta^2-1}}\left(1-\frac{(\beta^2-1)\ln(\beta^2-1)}{\beta^2}\right)+\frac{\beta^2-2}{\beta^2}\right] \tag{V-15}$$

with $\beta^2 = W/\epsilon_F$. Thus, the structure of the component $W_x^{KS}(x)$ is image-potential-like and ***long-ranged.***

The proof of the fact that the above expression is valid for self-consistently determined orbitals is essentially the same as that given for the Slater potential in Chapter III. Once again, one can divide up the z axis into three parts: a metal bulk region, a surface region with a finite effective width, and the vacuum region. The critical point to note is that the asymptotic structure of the Slater, Kohn-Sham and $W_x^{KS}(r)$ potentials arises from the orbitals deep in the metal bulk. In a self-consistent calculation the orbitals in this region are again of the form $\phi_k(z) = \sin[kx + \delta(k)]$, so that the asymptotic structure of these potentials is governed by the term $e^{-qx} q \cos\delta_- / (q^2 + k_-^2)$ (see Eq.(V-10)), and leads to the corresponding coefficient and a $(1/x)$ decay. The contributions from the surface and vacuum regions is of $O(1/x^2)$ as in the model calculation discussed above.

5.3 Numerical Confirmation of Analytical Asymptotic Expression

In order to demonstrate the correctness of the derivation for the asymptotic structure of $W_x^{KS}(r)$ as given by Eq. (V-15), we plot in Fig.4 for Li metal (r_s = 3.24) the electric field $\mathcal{E}_x^{KS}(z)$ and potential $W_x^{KS}(z)$ outside the metal as determined by the general 'EXACT' expression (Eqs.(V-6)-(V-9)) for these properties derived in Section 5.2, as well as the quantities $\alpha_W(\beta)/z^2$ and $-\alpha_W/z$. The calculations for the EXACT results are performed for the orbitals of the finite-linear-potential model for which the relationship between r_s and β is determined via energy minimization in the local density approximation (see Appendix of (Sahni, 1989)). This value of β = 1.246. The same value of β is then employed in the analytical expressions. It is evident for both the field and potential that the analytical and EXACT results merge by about four Fermi wavelengths from surface.

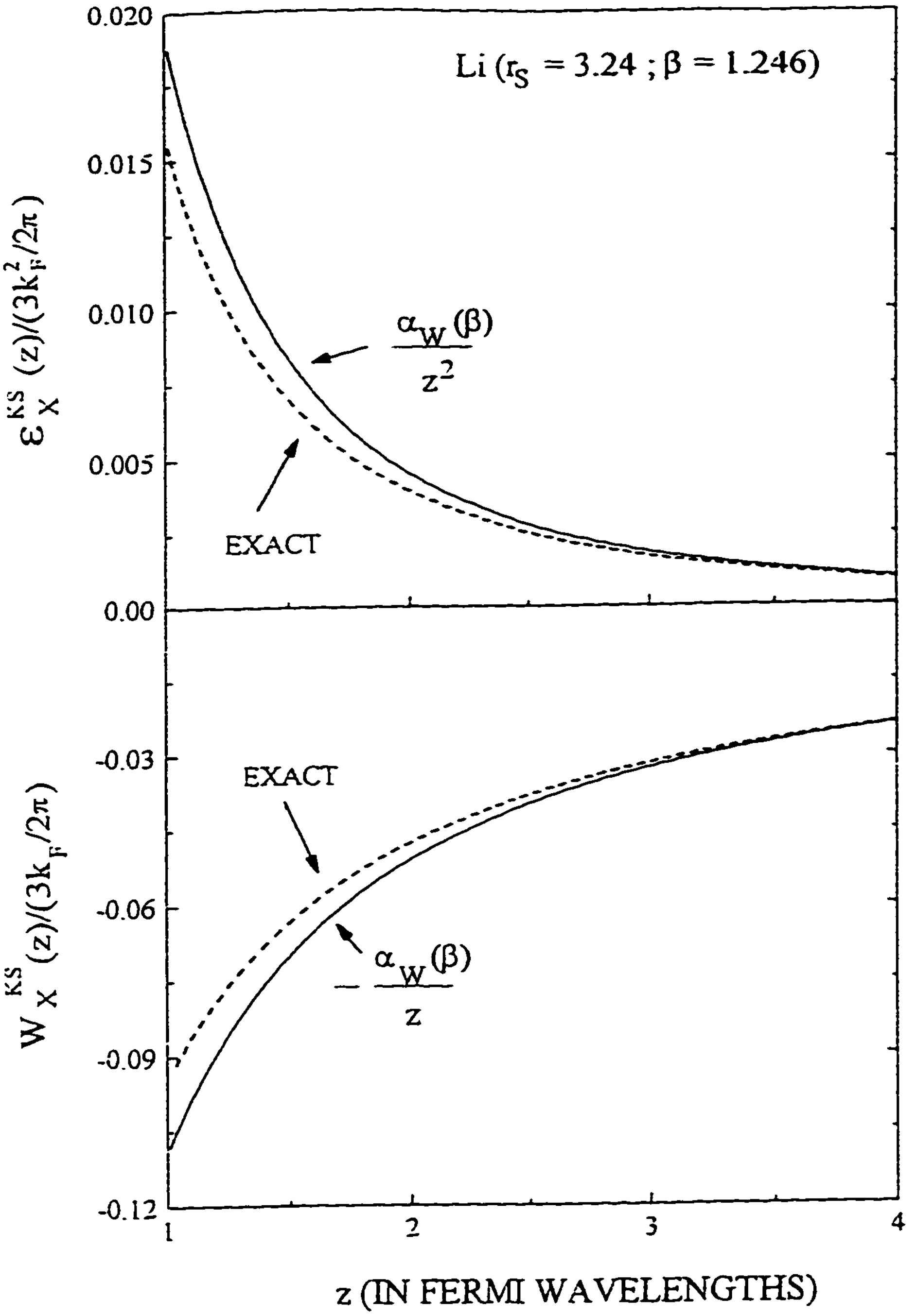

Fig. 4 Comparison of the EXACT field $\mathscr{E}_x^{KS}(z)$ and potential $W_x^{KS}(z)$ (as determined by the general expression Eq.(V-6)) with the analytical expressions $\alpha_w(\beta)/z^2$ and $-\alpha_w(\beta)/z$, respectively, for asymptotic positions of the electron in the vacuum.

5.4 Pauli Component Asymptotic Decay Coefficient

In Fig.5 we plot the Pauli component coefficient $\alpha_W(\beta)$ as a function of the barrier height parameter β. The corresponding values of the Wigner-Seitz radius r_s for both the jellium and structureless-pseudopotential models are also plotted. The relationship between β and r_s is determined as described in the previous chapters. For purposes of comparison we have also included the Slater $\alpha_S(\beta)$ and Kohn-Sham $\alpha_{KS,x}(\beta)$ decay coefficients.

For $r_s < 2.0$, the coefficient $\alpha_W(\beta) \approx \alpha_{KS,x}(\beta)$, so that for very high density metals the asymptotic structure of $v_x(\mathbf{r})$ is essentially due to its Pauli component $W_x^{KS}(\mathbf{r})$. For $r_s = 2$, 4 and 6, the values of $\alpha_W(\beta)$ are 0.217, 0.315 and 0.368, respectively, and differ from the corresponding KS exchange coefficients. The difference increases with decreasing metal bulk density.

The previous work of Harbola and Sahni (Harbola and Sahni, 1989b) on the asymptotic structure of $W_x^{KS}(z)$ was performed using the orbitals of the finite-linear-potential model for a value of β corresponding to $r_s = 2.0$. This calculation was numerical, and required accurate knowledge of the three-dimensional structure of the delocalized Fermi hole deep in the metal bulk. Their results showed that $W_x^{KS}(x) \sim -\alpha_w/x$, with $\alpha_w \sim 0.24$, and that this structure was achieved at about eight Fermi wavelengths from the surface. (The correct value of α_w as noted above is 0.217, with the structure $-\alpha_w/x$ being achieved at a distance of about four Fermi wavelengths).

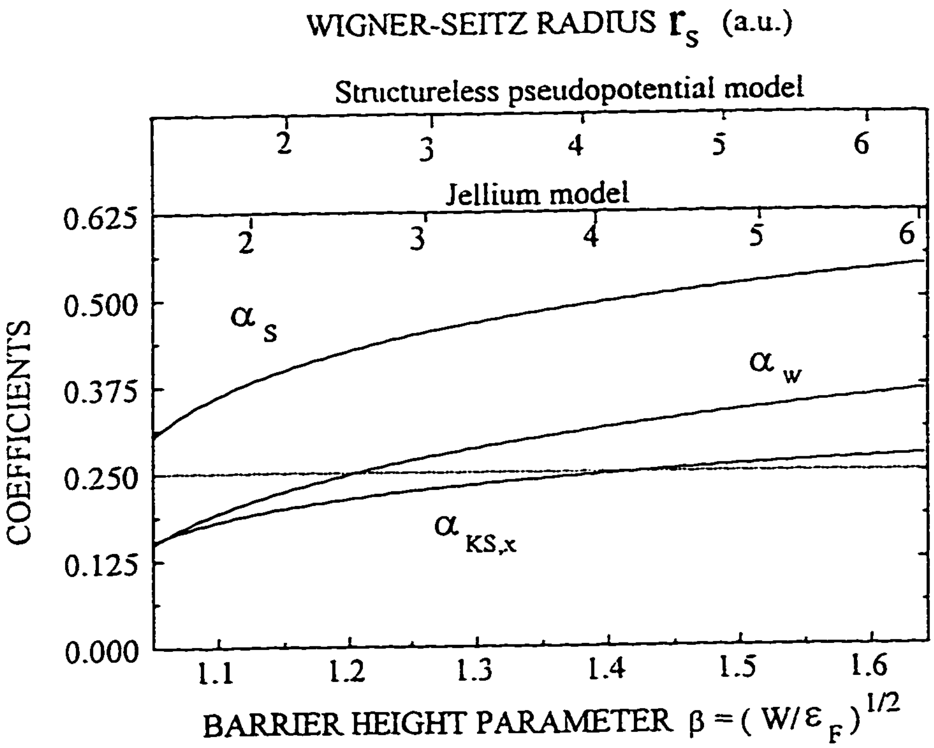

Fig. 5 The asymptotic structure coefficients $\alpha_{KS,x}(\beta)$, $\alpha_W(\beta)$ and $\alpha_S(\beta)$ as a function of the parameter $\beta=(W/\epsilon_F)^{1/2}$, where W is the barrier height and ϵ_F the Fermi energy. The corresponding values of the Wigner-Seitz radius r_s for the jellium and stabilized-jellium models over the metallic range of densities are also given. The relationship between r_s and β is via self-consistent calculations in the local density approximation for exchange-correlation.

Based on their results, these authors concluded that the asymptotic structure of the Kohn-Sham exchange potential for all metals was due entirely to Pauli correlations. As noted above, this is essentially the case only for $r_s \leq 2.0$.

5.5 Structure of Field $\mathcal{E}_x^{KS}(z)$ and Potential $W_x^{KS}(z)$ at a Metal Surface

The expression for the field $\mathcal{E}_x^{KS}(z)$ derived in Section 5.1 in terms of momentum space integrals (Eqs.(V-6)-(V-9)) allows for its easy and accurate numerical determination. This is particularly the case for model potential orbitals that are analytical or semi-analytical. In Fig. 6 we plot the field $\mathcal{E}_x^{KS}(z)$ for $r_s = 2.0$ and 6.0 for the orbitals of the finite-linear-potential model from -2 Fermi wavelengths inside to 4 Fermi wavelengths outside the surface. (The solution of the integral $M(q, z)$ of Eq.(V-8) for these orbitals is given in Appendix 2). Note that the Fermi wavelength for a metal of $r_s = 2.0$ is 3.46Å whereas that for $r_s = 6.0$ is 10.39Å. The barrier height parameter β is determined as previously by energy minimization within the local density approximation for the exchange-correlation energy functional.

Observe that the field $\mathcal{E}_x^{KS}(z)$ is greater at the surface for $r_s = 6$ than for $r_s = 2$. The reason for this is that for electron position near the jellium edge, the Fermi hole for low density metals is more localized in that region than it is for high density metals. For a comparison of the Fermi holes as a function of the rapidity of decay of the electron density at a metal surface, we refer the reader to the work of Sahni and Bohnen. The amplitude of the Bardeen-Friedel oscillations of the field $\mathcal{E}_x^{KS}(z)$ within the metal are also greater, as expected (Lang and Kohn, 1970) for the lower density metal.

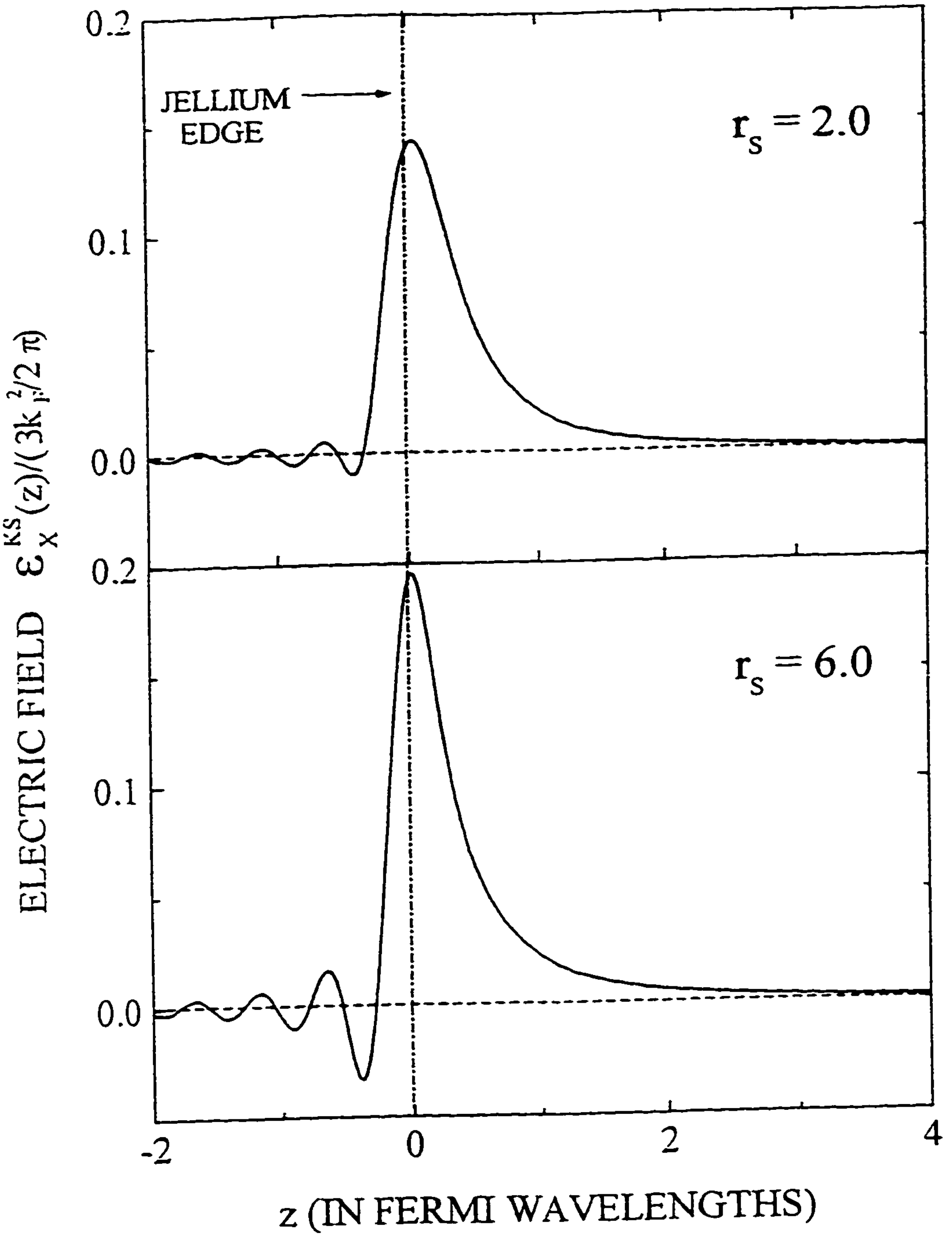

Fig. 6 Variation of the electric field $\mathcal{E}_x^{KS}(z)$ at a metal surface for metals of Wigner-Seitz radius r_s=2.0 and 6.0.

In Fig. 7 we plot the work $W_x^{KS}(z)$ for $r_s = 2.0$ and 6.0 over the same spatial range in Fermi wavelengths. Once again, the Bardeen-Friedel oscillations are more pronounced for the lower density metal. Asymptotically in the bulk, the potential $W_x^{KS}(z)$ does not approach -2/3 which is the limit for the Kohn-Sham potential $v_x(-\infty)$ in units of $(3k_F/2\pi)$. For $r_s = 2.0$ the limiting value of $W_x^{KS}(-\infty) = -0.716$, and for $r_s = 6.0$, $W_x^{KS}(-\infty) = -0.823$ (see Table I). The fact that the limiting value $W_x^{KS}(-\infty)$ is more negative for lower density metals is a reflection of the greater electric field at the surface. Further, the asymptotic coefficient $\alpha_W(\beta)$ is also greater than for high density metals. Thus, in integrating from $+\infty$ to inside the metal one obtains a greater limiting value.

TABLE I

The metal-bulk limiting value of the Pauli $W_x^{KS}(-\infty)$ component of the Kohn-Sham exchange potential $v_x(-\infty)$ as a function of the Wigner-Seitz radius r_s.

Wigner-Seitz radius r_s (a.u.)	$W_x^{KS}(-\infty)/(3k_F/2\pi$
2.0	- 0.716
4.0	- 0.788
6.0	- 0.823

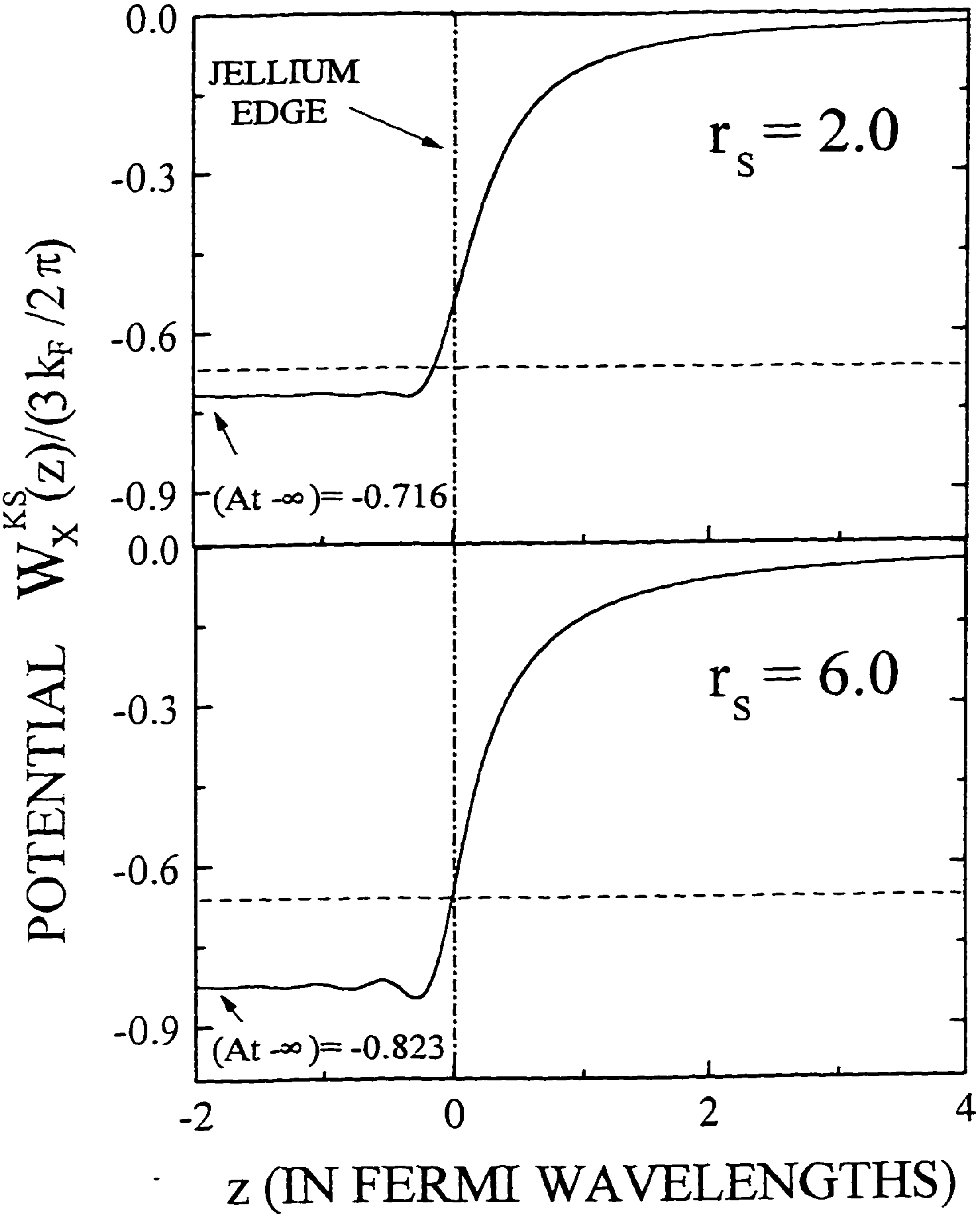

Fig. 7 Variation of the potential $W_x^{KS}(z)$ at a metal surface for metals of Wigner-Seitz radius r_s=2.0 and 6.0.

The calculations of Harbola and Sahni (Harbola and Sahni, 1989c) for the determination of the asymptotic limit of $W_x^{KS}(z)$ in the metal bulk were performed for $r_s = 1.0$. They obtained $W_x^{KS}(-\infty)/(3k_F/2\pi) = -0.669$. However, in their calculation they assumed that in the region beyond six Fermi wavelengths outside the surface the potential $W_x^{KS}(z)$ was the image potential. Thus, their limiting value is not exact because the coefficient $\alpha_w(\beta)$ is not 1/4 for $r_s = 1.0$. These authors also noted that for lower density metals the limiting value of $W_x^{KS}(z)$ in the bulk was not (-2/3). However, they attributed this to a lack of self-consistency of the orbitals. Of course, we now understand that the work $W_x^{KS}(\mathbf{r})$ is not the Kohn-Sham exchange potential $v_x(\mathbf{r})$, and that over the metallic range of densities there is a finite correlation-kinetic contribution to the potential. It is only for very high density systems, with the inhomogeneity of the kind at a surface, that the potentials $W_x^{KS}(\mathbf{r})$ and $v_x(\mathbf{r})$ are essentially equivalent. This is consistent with the fact (Wang et. al., 1990) that for very slowly varying densities for which the local density approximation is valid, the corresponding Kohn-Sham exchange potential $v_x(\mathbf{r})$ and the work $W_x^{KS}(\mathbf{r})$ are equivalent.

5.6 Summary of Results

In this chapter we have studied the structure of the Pauli $W_x^{KS}(\mathbf{r})$ component of the Kohn-Sham exchange potential $v_x(\mathbf{r})$ at a metal surface employing accurate representations of the KS orbitals. By deriving an expression for the field $\mathcal{E}_x^{KS}(\mathbf{r})$ due to the Fermi hole in terms of momentum-space integrals, valid for both the jellium and structureless-pseudopotential models, it has been possible to study the work done $W_x^{KS}(\mathbf{r})$

in this field over a substantial region of space about the surface and for arbitrary simple metal. The expression derived also allows for the determination of the ***exact analytical*** asymptotic structure of the work $W_x^{KS}(\mathbf{r})$ in the vacuum region that is valid for both models and ***self-consistently*** determined orbitals. It turns out that in the asymptotic vacuum region, the potential $W_x^{KS}(\mathbf{r})$ is ***long-ranged*** and decays as $-\alpha_w(\beta)/x$, where the parameter β depends upon the barrier height and Fermi energy. For metallic densities, the coefficient $\alpha_w(\beta)$ differs from the coefficient $\alpha_{KS,x}(\beta)$ of the KS potential $v_x(\mathbf{r})$. The coefficients $\alpha_w(\beta)$ and $\alpha_{KS,x}(\beta)$, however, approach each other for very high density metals.

As a consequence of the difference in the vacuum asymptotic structures of $v_x(z)$ and of its Pauli component $W_x^{KS}(z)$, the latter does not approach the Kohn-Sham value of (-2/3) (in units of $3k_F/2\pi$) in the asymptotic metal bulk region. The higher the density, the more closely this value is approached. Thus,it is only for slowing varying densities, i.e. for very high 'metallic' bulk densities, that the potentials $v_x(\mathbf{r})$ and $W_x^{KS}(\mathbf{r})$ are equivalent throughout space.

CHAPTER VI

CONSTRUCTION OF APPROXIMATE KOHN-SHAM THEORY POTENTIALS

In KS density-functional theory, the many-body effects are incorporated in the exchange-correlation functional $E_{xc}^{KS}[\rho]$ of the density $\rho(r)$. The corresponding local potential representing electron correlations is then determined by functional differentiation of this functional for arbitrary norm conserving variations of the density. However, when this as yet unknown functional is approximated, the rigor of the Hohenberg-Kohn theorems is lost. As a consequence, the corresponding approximate potential and density then lead to a total energy which is no longer a rigorous upper bound to the ground state energy of the system.

This chapter is comprised of two components. In the first we propose an approach whereby the rigor of the upper bound is maintained. It consists of determining an approximate ***exchange*** potential from the ***exact*** exchange energy functional through functional differentiation by considering only a restricted class of norm conserving density variations. In the second we construct approximate exchange and correlation energy functionals which improve upon the local density approximation by ensuring that the resulting functional derivatives have the correct KS asymptotic structure in the vacuum.

6.1 Exchange Potential from Restricted Functional Differentiation

We begin by constructing an approximate exchange potential from restricted functional differentiation of the exact exchange energy functional.

To explain this class of density variations, we take the example of free electrons confined to move in a one-dimensional box of length L. The electrons could equally well be considered as confined by a finite potential barrier, in which case the density $\rho_L(\boldsymbol{r})$ would extend from $+\infty$ in the vacuum to $-L$ in the metal bulk. The variations we consider are akin, in the jellium surface problem, to changes in $\rho_L(\boldsymbol{r})$ induced by the change of L to $L+\delta L$. The corresponding change in the exchange energy $E_x([\rho_L];L)$ is then

$$\frac{d}{dL}E_x([\rho_L];L) = K(L) - \frac{1}{4}\int d\boldsymbol{r}d\boldsymbol{r}' \, \frac{\frac{d}{dL}|\gamma_L(\boldsymbol{r},\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \ , \tag{VI-1}$$

where $K(L)$ is a constant. Since the exchange energy is a functional of $\rho_L(\boldsymbol{r})$, we can also write

$$\frac{d}{dL}E_x([\rho_L];L) = K(L) + \int d\boldsymbol{r} \, \frac{\delta E_x([\rho_L];L)}{\delta\rho_L(\boldsymbol{r})} \cdot \frac{d}{dL}\rho_L(\boldsymbol{r}) \ . \tag{VI-2}$$

A comparison of Eqs.(VI-1) and (VI-2) then leads to the expression for the functional derivative as

$$\frac{\delta E_x([\rho_L];L)}{\delta\rho_L(r)} = -\frac{1}{4}\int\frac{dr'}{|r-r'|}\cdot\frac{\frac{d}{dL}|\gamma_L(r,r')|^2}{\frac{d}{dL}\rho_L(r)} + f(r) \quad , \tag{VI-3}$$

where the function $f(r)$ satisfies the condition

$$\int dr\, f(r)\cdot\frac{d\rho_L(r)}{dL} = 0 \quad . \tag{VI-4}$$

The total number of electrons is held constant. This relates L to k_F, the Fermi momentum, so that $\frac{d}{dL}=\frac{dk_F}{dL}\cdot\frac{d}{dk_F}$. Thus, we can take the limit $L\to\infty$ in Eq.(VI-3), and write the functional derivative as

$$v_x(r) = v_x^{(0)}(r) + f(r) \quad , \tag{VI-5}$$

where

$$v_x^{(0)}(r) = \frac{1}{2\frac{d\rho(r)}{dk_F}}\cdot\frac{d}{dk_F}\left(\rho(r)\,V_x^S(r)\right) \quad , \tag{VI-6}$$

and $V_x^S(r)$ is the Slater potential defined by Eq.(II-44). Thus, the intrinsic nonlocality of the problem is explicitly incorporated into the expression for $v_x(r)$.

The right hand side of Eq. (VI-5) is an exact representation of the functional derivative $v_x(r)$. The exactly known component $v_x^{(0)}(r)$ of Eq. (VI-6) defines an approximate KS exchange potential at a jellium metal surface. In Section 6.1.1 we study the exchange potential $v_x^{(0)}(\mathbf{r})$ for systems for which the density $\rho(\mathbf{r})$ and the Slater potential $V_x^S(\mathbf{r})$ can be written in the form $a(k_F)h(z)$, where $z=k_Fx$. We show that $v_x^{(0)}(\mathbf{r})$ satisfies a number of important sum rules, and possesses the correct asymptotic structure both in the vacuum and metal-bulk regions. In section 6.1.2 we apply the general Eq.(VI-6) to determine $v_x^{(0)}(\mathbf{r})$ for the orbitals of the finite-linear potential model. Finally, in section 6.1.3 we provide a physical interpretation for the potential $v_x^{(0)}(\mathbf{r})$.

6.1.1 Satisfaction of Sum Rules and Correct Asymptotic Structure

In the simple case of a system for which the density $\rho(\mathbf{r})$ and the Slater potential $V_x^S(\mathbf{r})$ can be written in the form $a(k_F)h(z)$ where $z = k_Fx$, we can evaluate the k_F-derivatives in Eq.(VI-6) explicitly. We, thus, obtain the following form of the approximate exchange potential

$$v_x^{(0)}(\mathbf{r}) = \frac{1}{A(\mathbf{r})} \cdot \left[\frac{2}{3} V_x^S(\mathbf{r}) + \frac{\mathbf{r} \cdot \nabla\left[\rho(\mathbf{r}) V_x^S(\mathbf{r})\right]}{6\rho(\mathbf{r})} \right] , \tag{VI-7}$$

where $A(\mathbf{r}) = 1 + \mathbf{r} \cdot \nabla\rho(\mathbf{r}) / 3\rho(\mathbf{r})$. This makes explicit the fact that $v_x^{(0)}(\mathbf{r})$ is determined in closed form by $V_x^S(\mathbf{r})$ and $\rho(\mathbf{r})$ plus their first derivatives. For purposes of establishing asymptotic properties, an entirely equivalent form of Eq.(VI-7) is

$$v_x^{(0)}(\mathbf{r}) = \frac{1}{2} V_x^S(\mathbf{r}) + \frac{1}{2} \rho(\mathbf{r}) \hat{D}(\mathbf{r}) V_x^S(\mathbf{r}) , \tag{VI-8}$$

where the operator $\hat{D}(\mathbf{r})$ is defined as

$$\hat{D}(\mathbf{r}) = \frac{1 + \mathbf{r}\cdot\nabla}{\nabla\cdot\big(\mathbf{r}\rho(\mathbf{r})\big)} \quad . \tag{VI-9}$$

We employ Eq.(VI-7) to establish the asymptotic form of $v_x^{(0)}(\mathbf{r})$ in the metal bulk. In this limit we can disregard the spatial derivatives of $\rho(\mathbf{r})$ and $V_x^S(\mathbf{r})$, so that

$$\underset{z\to-\infty}{v_x^{(0)}(\mathbf{r})} = \frac{2}{3}\cdot V_x^S(\mathbf{r}) = v_x(-\infty) = -\frac{k_F}{\pi} \ . \tag{VI-10}$$

As to the asymptotic form of $v_x^{(0)}(\mathbf{r})$ in the classically forbidden region, Eq.(VI-8) is the appropriate tool and yields

$$\underset{z\to+\infty}{v_x^{(0)}(\mathbf{r})} = \frac{1}{2}\,V_x^S(\mathbf{r}) = \underset{z\to+\infty}{v_x(\mathbf{r})} = -\frac{k_F\alpha_{KS,x}(\beta)}{z} \ . \tag{VI-11}$$

Thus, we have demonstrated that $v_x^{(0)}(\mathbf{r})$ exhibits the correct asymptotic structure of the KS exchange potential both in the vacuum region and in the metal bulk. This also means that the second term in Eq.(VI-5) is short-ranged and localized at the surface.

Having determined the asymptotic structure of $v_x^{(0)}(\mathbf{r})$ at a metal surface we procede to discuss the other properties of this potential. It is worth noting that Ou-Yang and Levy (Ou-Yang and Levy, 1990; ibid., 1991) have established three specific conditions satisfied by the exact KS exchange potential $v_x(\mathbf{r})$. These are (i) the virial theorem (Levy and Perdew, 1985) relating the exchange energy to its functional derivative (see Eq.(II-84)), (ii) the scaling condition

$$v_x(\mathbf{r};[\rho_\lambda]) = \lambda\, v_x(\lambda\mathbf{r};[\rho]) \tag{VI-12}$$

where $\rho_\lambda(\mathbf{r}) = \lambda^3\rho(\lambda\mathbf{r})$, and (iii) the second derivative condition

$$\frac{\delta v_x(\boldsymbol{r})}{\delta\rho(\boldsymbol{r}')} = \frac{\delta v_x(\boldsymbol{r}')}{\delta\rho(\boldsymbol{r})} , \tag{VI-13}$$

which is one of symmetry in an interchange of $\boldsymbol{r}$ and $\boldsymbol{r}'$. This last condition guarantees that $v_x(\boldsymbol{r})$ is the functional derivative of some functional of the density $\rho(\boldsymbol{r})$. Furthermore, a hierarchy of equations (Nagy, 1993; Ou-Yang and Levy, 1991) can be obtained by functional differentiation of the virial theorem of Eq. (II-84), the first of which being

$$v_x(\boldsymbol{r})+\boldsymbol{r}\cdot\nabla v_x(\boldsymbol{r})+\int d\boldsymbol{r}'\rho(\boldsymbol{r}')\boldsymbol{r}'\cdot\nabla'\left[\frac{\delta v_x(\boldsymbol{r}')}{\delta\rho(\boldsymbol{r})}\right] = 0 . \tag{VI-14}$$

It can be shown (Ou-Yang and Levy, 1990) that an exchange potential that satisfies the above three conditions is the exact KS exchange potential.

The conditions (i)-(iii) can also be employed to test approximate exchange potentials. We can readily see that the exchange potential $v_x^{(0)}(\boldsymbol{r})$, which is completely determined by the density $\rho(\boldsymbol{r})$ and the Slater potential $V_x^S(\boldsymbol{r})$, satisfies the scaling condition of Eq.(VI-12). We now prove (Solomatin and Sahni, 1995) that $v_x^{(0)}(\boldsymbol{r})$ satisfies the virial theorem of Eq.(II-84). On substituting $v_x^{(0)}(\boldsymbol{r})$ for $v_x(\boldsymbol{r})$ into Eq.(II-84) and using the vector identity

$$\nabla\cdot\Phi\boldsymbol{A} = \boldsymbol{A}\cdot(\nabla\Phi) + \Phi\nabla\cdot\boldsymbol{A} \tag{VI-15}$$

the right-hand side of Eq.(II-84) becomes

$$\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r}\cdot\nabla v_x^{(0)}(\mathbf{r})=\int d\mathbf{r}\nabla\cdot\left[\mathbf{r}\rho(\mathbf{r})v_x^{(0)}(\mathbf{r})\right]-\int d\mathbf{r}\left(\nabla\cdot\left[\mathbf{r}\rho(\mathbf{r})\right]\right)v_x^{(0)}(\mathbf{r}) \quad . \tag{VI-16}$$

The first term on the right-hand side is then reduced to a surface integral by Gauss's theorem, which then vanishes. Substituting for $v_x^{(0)}(\mathbf{r})$ from Eq.(VI-8), we then have

$$\int d\mathbf{r}\,\rho(\mathbf{r})\mathbf{r}\cdot\nabla v_x^{(0)}(\mathbf{r})=-\frac{1}{2}\int d\mathbf{r}\left(\nabla\cdot\left[\mathbf{r}\rho(\mathbf{r})\right]\right)V_x^S(\mathbf{r})-\frac{1}{2}\int d\mathbf{r}\,\rho(\mathbf{r})(1+\mathbf{r}\cdot\nabla)\,V_x^S(\mathbf{r}) \quad . \tag{VI-17}$$

Once again, using the vector identity of Eq.(VI-15), the right-hand side becomes

$$\begin{aligned}&-\frac{1}{2}\int d\mathbf{r}\nabla\cdot\left(\mathbf{r}\rho(\mathbf{r})V_x^S(\mathbf{r})\right)+\frac{1}{2}\int d\mathbf{r}\,\rho(\mathbf{r})\,\mathbf{r}\cdot\nabla V_x^S(\mathbf{r})\\&-\frac{1}{2}\int d\mathbf{r}\,\rho(\mathbf{r})\,(1+\mathbf{r}\cdot\nabla)\,V_x^S(\mathbf{r}) \quad ,\end{aligned} \tag{VI-18}$$

where the first term again vanishes after conversion to a surface integral. The remaining terms reduce to

$$-\frac{1}{2}\int d\mathbf{r}\,\rho(\mathbf{r})\,V_x^S(\mathbf{r}) = -E_x[\rho] \quad , \tag{VI-19}$$

which proves the satisfaction of the theorem by the exchange potential $v_x^{(0)}(\mathbf{r})$.

We next demonstrate that with a local approximation for the functional derivative of the Slater potential, the exchange potential $v_x^{(0)}(\mathbf{r})$ satisfies the second derivative condition as well as the sum rule of Eq.(VI-14).

The functional derivative of $v_x^{(0)}(\mathbf{r})$ can be written as

$$\frac{\delta v_x^{(0)}(\mathbf{r})}{\delta\rho(\mathbf{r})} = \frac{1}{2}\left[\frac{\delta V_x^S(\mathbf{r})}{\delta\rho(\mathbf{r}')} + \delta(\mathbf{r}-\mathbf{r}')\,\hat{D}(\mathbf{r})\,V_x^S(\mathbf{r})\right] + \frac{1}{2}\rho(\mathbf{r})\frac{\delta\left[\hat{D}(\mathbf{r})\,V_x^S(\mathbf{r})\right]}{\delta\rho(\mathbf{r}')} \quad . \tag{VI-20}$$

In turn, the functional derivative of $V_x^S(\mathbf{r})$ can be represented by the sum of its local and nonlocal parts

$$\frac{\delta\, V_x^S(\mathbf{r})}{\delta\,\rho(\mathbf{r}')} = \delta(\mathbf{r}-\mathbf{r}')\,\hat{D}(\mathbf{r})\,V_x^S(\mathbf{r}) + g(\mathbf{r},\mathbf{r}') \quad . \tag{VI-21}$$

The functional derivative of the operator $\hat{D}(\mathbf{r})$ is

$$\frac{\delta\,\hat{D}(\mathbf{r})}{\delta\,\rho(\mathbf{r}')} = -\frac{\nabla\cdot\left[\mathbf{r}\,\delta(\mathbf{r}-\mathbf{r}')\right]}{\nabla\cdot\left[\mathbf{r}\,\rho(\mathbf{r})\right]}\hat{D}(\mathbf{r}) \quad . \tag{VI-22}$$

Approximating the functional derivative of the Slater potential $V_x^S(\mathbf{r})$ by its local part and employing Eq.(VI-22), we have

$$\frac{\delta\, v_x^{(0)}(\mathbf{r})}{\delta\,\rho(\mathbf{r}')} = \delta(\mathbf{r}-\mathbf{r}')\,\hat{D}(\mathbf{r})\,V_x^S(\mathbf{r}) + \frac{1}{2}\rho(\mathbf{r})\,\hat{D}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}')\,\hat{D}(\mathbf{r})\,V_x^S(\mathbf{r}) - \frac{1}{2}\rho(\mathbf{r})\frac{\nabla\cdot\left[\mathbf{r}\,\delta(\mathbf{r}-\mathbf{r}')\right]}{\nabla\cdot\left[\mathbf{r}\,\rho(\mathbf{r})\right]}\hat{D}(\mathbf{r})\,V_x^S(\mathbf{r}) \quad . \tag{VI-23}$$

Eliminating the term involving

$$\nabla\cdot\left[\mathbf{r}\,\delta(\mathbf{r}-\mathbf{r}')\right] \sim \mathbf{r}\cdot\nabla\delta(\mathbf{r}-\mathbf{r}') \tag{VI-24}$$

by employing the equation

$$\hat{D}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}')f(\mathbf{r}) = \frac{\mathbf{r}\cdot\nabla\delta(\mathbf{r}-\mathbf{r}')}{\nabla\cdot\left[\mathbf{r}\rho(\mathbf{r})\right]}f(\mathbf{r}) + \delta(\mathbf{r}-\mathbf{r}')\,\hat{D}(\mathbf{r})f(\mathbf{r}) \quad , \tag{VI-25}$$

where $f(\mathbf{r})$ is an arbitrary function of $\mathbf{r}$, we have the result

$$\frac{\delta v_x^{(0)}(\mathbf{r})}{\delta\rho(\mathbf{r}')} = \delta(\mathbf{r}-\mathbf{r}')\,\hat{D}(\mathbf{r})\,v_x^{(0)}(\mathbf{r}) \quad , \tag{VI-26}$$

which shows the satisfaction of the second derivative condition.

Finally, by substituting Eq.(VI-25) into the sum rule of Eq.(VI-14), we have for the integral term

$$\begin{aligned}
&\int d\mathbf{r}'\,\rho(\mathbf{r}')\,\mathbf{r}'\cdot\nabla'\left[\frac{\delta v_x^{(0)}(\mathbf{r}')}{\delta\rho(\mathbf{r})}\right] = \int d\mathbf{r}'\,\rho(\mathbf{r}')\,\mathbf{r}'\cdot\nabla'\left[\delta(\mathbf{r}-\mathbf{r}')\hat{D}(\mathbf{r}')v_x^{(0)}(\mathbf{r}')\right] \\
&= \int d\mathbf{r}'\,\nabla'\cdot\left[\delta(\mathbf{r}-\mathbf{r}')\hat{D}\,v_x^{(0)}(\mathbf{r}')\rho(\mathbf{r}')\mathbf{r}'\right] - \int d\mathbf{r}'\,\delta(\mathbf{r}-\mathbf{r}')\hat{D}(\mathbf{r}')v_x^{(0)}\mathbf{r}')\nabla'\cdot[\mathbf{r}'\rho(\mathbf{r}')] \\
&= \hat{D}(\mathbf{r})\,v_x^{(0)}(\mathbf{r})\,\nabla\cdot\left[\mathbf{r}\rho(\mathbf{r})\right] = -\,v_x^{(0)}(\mathbf{r}) - \mathbf{r}\cdot\nabla v_x^{(0)}(\mathbf{r}) \quad ,
\end{aligned} \tag{VI-27}$$

where once again, Gauss's theorem is employed. This proves the satisfaction of the sum rule of Eq.(VI-14) for the derivative of the potential $v_x^{(0)}(\mathbf{r})$.

To summarize, the potential $v_x^{(0)}(\mathbf{r})$ satisfies exactly conditions (i) and (ii), and that of condition (iii) provided a local approximation is made for the functional derivative of the Slater potential. Furthermore, $v_x^{(0)}(\mathbf{r})$ has the correct asymptotic structure in the vacuum and metal bulk regions. We thus expect $v_x^{(0)}(\mathbf{r})$ to be an accurate approximation to the KS exchange potential $v_x(r)$ at a jellium metal surface.

6.1.2 Application to Infinite Barrier Model

We first illustrate the structure of the potential $v_x^{(0)}(r)$ for the infinite barrier model of a metal surface due to Bardeen (Bardeen, 1936). Although in this first approximation to a metal surface the electrons are confined to the region within the barrier, and asymptotic properties in the vacuum region cannot therefore be determined, the model has the principal attribute that the resulting density, Dirac density matrix, and essentially all surface properties can be determined in ***closed analytical form*** (Bardeen, 1936;Juretschke, 1953; Sahni et.al., 1975; Sahni and Gruenebaum, 1977; Miglio et.al., 1981). In the infinite barrier model of a metal surface, the density $\rho(z)$ and the Slater potential $V_x^S(r)$ can be written in the form $a(k_F)h(z)$. Closed form analytical expressions for the density $\rho(r)$, Dirac density matrix $\gamma(r,r')$ and Slater potential $V_x^S(r)$ are given in Appendix 3. Thus, we can employ Eq.(VI-8) to derive the analytical expression for $v_x^{(0)}(r)$ for this model (see Appendix 3). For purposes of completeness, we also determine the Pauli component of the KS exchange potential $W_x^{KS}(r)$. (See also Appendix 3).

Fig.8 plots the exchange potentials $v_x^{(0)}(r)$, $V_x^S(r)$ and $W_x(r)$ in units of $(3k_F/2\pi)$ versus the electron position $z = 2k_Fx$ in Fermi wavelengths. Observe that all three potentials are similar in that they exhibit the Bardeen-Friedel oscillations inside the metal and that they are finite and have finite slopes at the barrier. However, it is only $v_x^{(0)}(z)$ which has the correct asymptotic limit of -2/3 in the metal bulk.

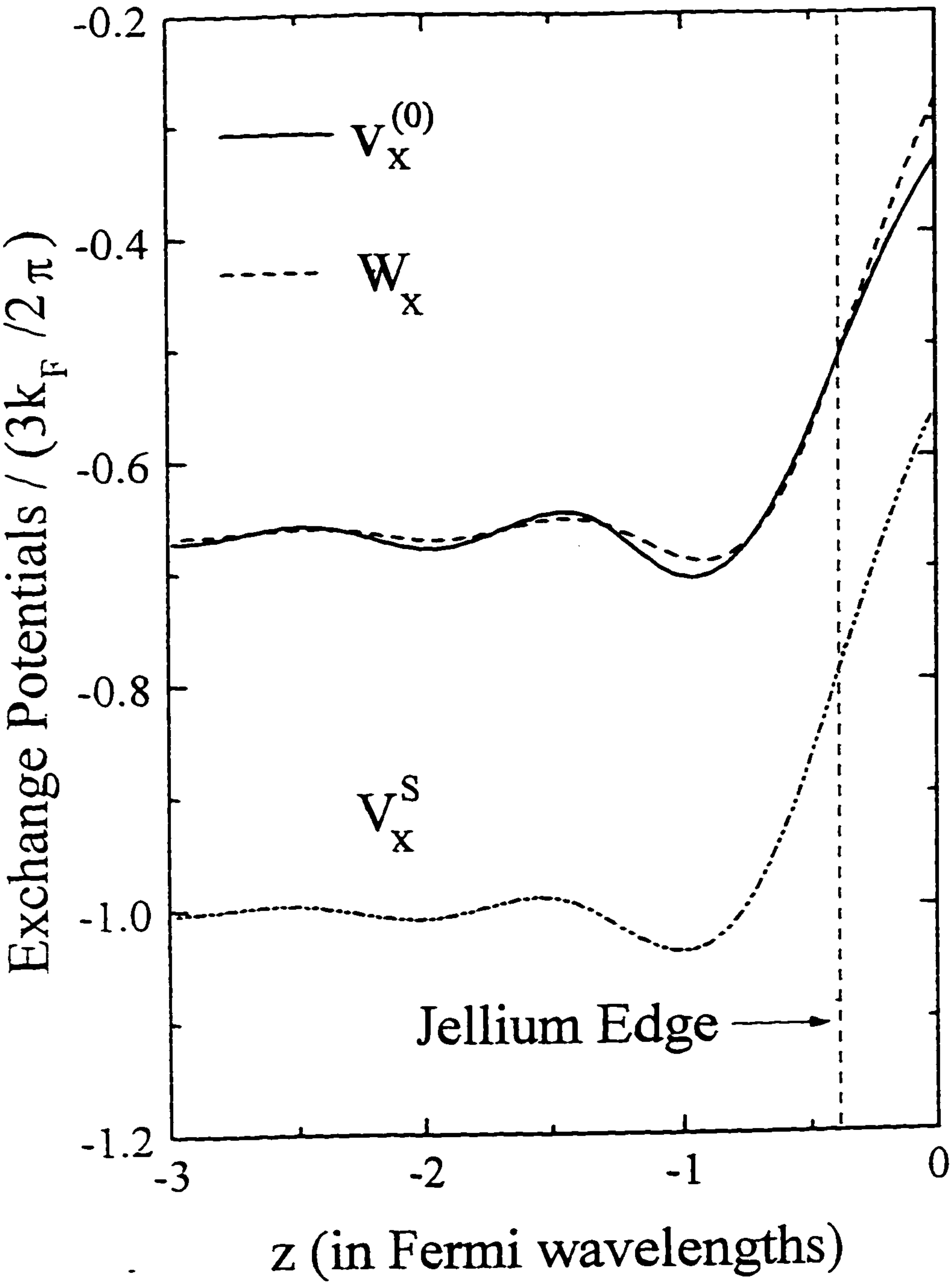

Fig. 8 Variation of the exchange potentials $v_x^{(0)}(z)$, $W_x(z)$ and $V_x^S(z)$ in units of $(3k_F/2\pi)$ versus the electron position z in Fermi wavelengths for the infinite barrier model.

The fact that the potentials have a finite slope at the barrier may be understood by examining the force field $\mathcal{E}_x^{KS}(z)$. This field is finite at the barrier. Thus, the structure of the potentials is similar to that of the local density approximation (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) exchange-correlation potential at the nucleus of atoms and molecules. Within this approximation (Slamet and Sahni, 1992; Sahni and Slamet, 1993; Sahni, 1995), the force field due to the Fermi-Coulomb hole charge is finite at the nucleus, so that the corresponding potential there has finite slope.

As we have noted, the expression for the exchange potential $v_x^{(0)}(\boldsymbol{r})$ of Eq.(V-8) is applicable to densities of the form $a(k_F)h(z)$. What this means is that the self-consistent change in the effective potential resulting from the (restricted) density variations is not accounted for in this expression. (It is, however, implicit in the general expression for $v_x^{(0)}(\boldsymbol{r})$ of Eq.(VI-6).) Thus, as in the case of the infinite barrier model, the effective potential of the electrons remains unchanged despite the variations in the density being performed to determine the functional derivative of the exchange energy. Because the density variations are achieved by a change in the Fermi momentum, which is equivalent to a change of scale, this expression for $v_x^{(0)}(\boldsymbol{r})$ could also be derived by scaling arguments. It is furthermore clear that what is required is a generalization of this expression to account for the change in effective potential due to the restricted variations in the density. In principle, one could evaluate the exchange potential $v_x^{(0)}(\boldsymbol{r})$ from Eq.(VI-6) for the orbitals of a model effective potential $v_{eff}(\boldsymbol{r})$. However, this approach requires the parameters of the effective potential to be known functions of the Fermi momentum. In the next section we present a general procedure that yields $v_x^{(0)}(\boldsymbol{r})$ for an arbitrary effective potential which can be implemented in a self-consistent calculation of jellium surface properties.

6.1.3 Determination of the Exchange Potential $v_x^{(0)}(r)$ for the Orbitals of Arbitrary Effective Potential

To use the general expression of Eq.(VI-6) for the exchange potential $v_x^{(0)}(r)$ one has to know the explicit dependence of the orbitals on the Fermi momentum k_F, or equivalently on the Wigner-Seitz radius r_S. An alternate route would be to evaluate $v_x^{(0)}(r)$ in terms of response functions of the system. The former approach would work well for sufficiently simple models (e.g. IBM and step barrier models), but it would not be useful for orbitals resulting from a self-consistent (e.g. LDA) calculation which are entirely numerical. The latter approach makes the numerical determination of $v_x^{(0)}(r)$ prohibitively difficult.

In this section we employ the finite-difference version of Eq.(VI-6) to evaluate $v_x^{(0)}(r)$ at a jellium metal surface. This method is sufficiently simple to be implemented numerically, and it does not require the explicit dependence of the orbitals on the Wigner-Seitz radius to be known. The finite-difference form of Eq.(VI-6) for the system corresponding to the Wigner-Seitz radius r_S can be written as

$$v_x^{(0)}(z) = -\frac{2}{\pi}\,\frac{d_+^4\cdot F_+(z) - d_-^4\cdot F_-(z)}{d_+^3\rho_+(z) - d_-^3\rho_-(z)} \quad , \tag{VI-28}$$

where $d_\pm = 1\mp\Delta r_S/r_S$, $\rho_\pm(z)$ is the normalized density of the system whose Wigner-Seitz radius is $d_\pm\cdot r_S$, and

$$F_\pm(z) = \int_0^1 dk' \int_0^{k'} dk\,\varphi_{k_\pm}^*(z)\,\varphi_{k'_\pm}(z)\,G_\pm(k,k';z) \quad . \tag{VI-29}$$

In Eq.(VI-28) $\varphi_{k_\pm}(z)$ are the orbitals of the system whose Wigner-Seitz radius is $d_\pm\cdot r_S$ and $G_\pm(z)$ is given by Eq.(III-22) with orbitals $\varphi_{k_\pm}(z)$.

We now apply the above procedure to the orbitals of the finite-linear potential model (see Eq.(III-25)). The parameters of the model potential are found by interpolation of the values given in the appendix of reference (Sahni, 1989), which in turn were determined by minimization of the energy for the fully-correlated system within the local density approximation for exchange-correlation.

In Fig.9 we plot the exchange potential $v_x^{(0)}(z)$ at the jellium surface of Li metal (r_S=3.24). For comparison we also provide the graph of the LDA exchange potential determined for the same set of orbitals. Notice that these potentials are close to each other at the surface and in the metal bulk. The amplitude of the Bardeen-Friedel oscillations exhibited by $v_x^{(0)}(z)$ is slightly greater than that of the LDA exchange potential. However, in the vacuum region the exchange potential $v_x^{(0)}(z)$ displays the correct

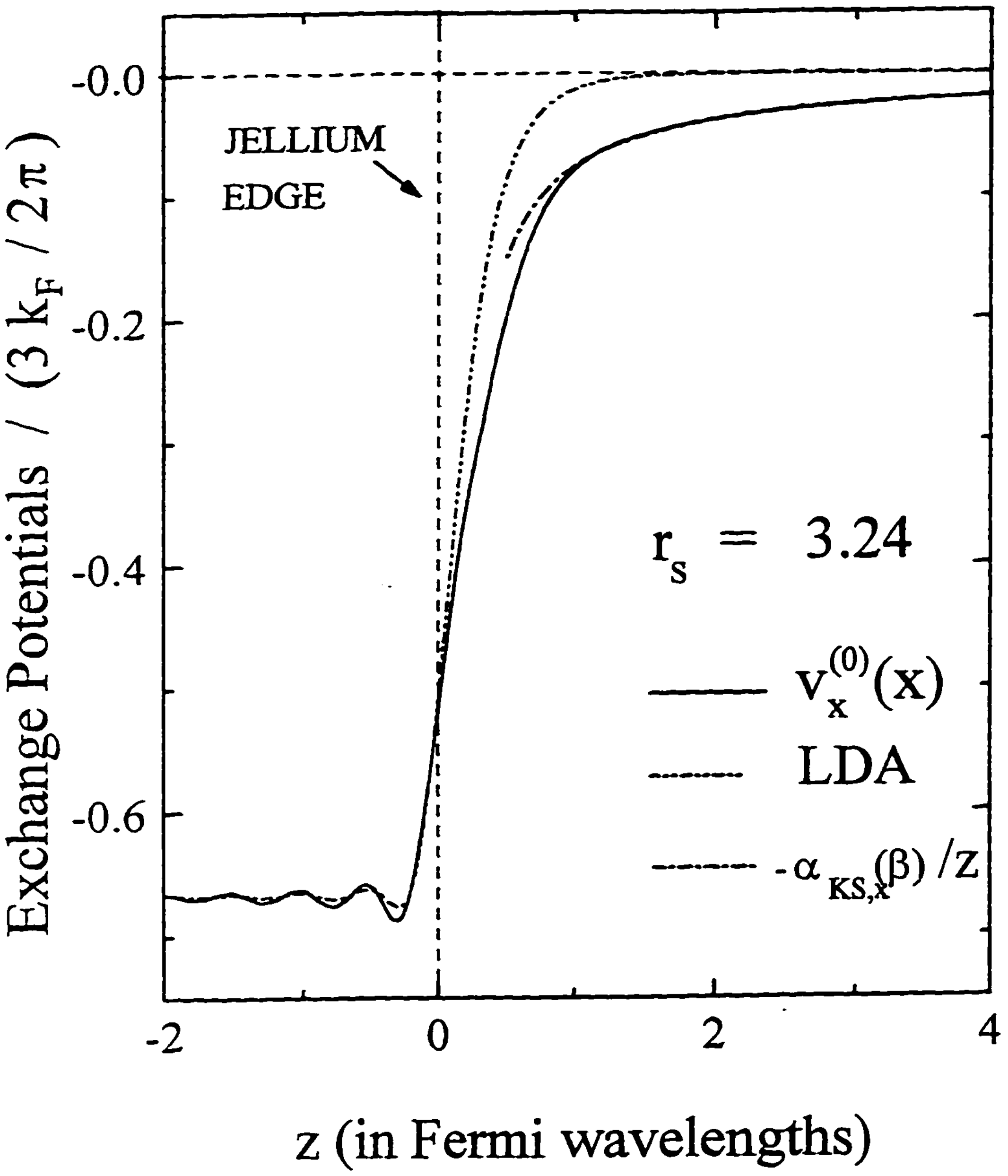

Fig.9 The approximate exchange potential $v_x^{(0)}(z)$ at the surface of Li metal of Wigner-Seitz radius r_s = 3.24. The exchange potential in the local density approximation (LDA) is also plotted, as is the exact asymptotic structure $-\alpha_{KS,x}(\beta)/z$ of the KS exchange potential $v_x(r)$.

asymptotic behavior of the KS exchange potential. Observe that the graph of $v_x^{(0)}(z)$ merges with the graph of the asymptotic function $-\alpha_{KS,x}(\beta)/x$ at about one Fermi wavelength from the jellium edge. Our studies show this to be true throughout the metallic range of densities. This property of the exchange potential $v_x^{(0)}(z)$ is in sharp contrast with the asymptotic behavior of the Slater potential studied in Chapter III. The latter was shown to merge with the exact Slater asymptotic function $-\alpha_S(\beta)/x$ only at about ten Fermi wavelengths from the jellium edge.

6.1.4 Physical Interpretation of Approximate Exchange Potential $v_x^{(0)}(\mathbf{r})$

In this section we provide a physical interpretation for the approximate exchange potential $v_x^{(0)}(\mathbf{r})$. In a manner similar to the Slater exchange potential $V_x^S(\mathbf{r})$, we define $v_x^{(0)}(\mathbf{r})$ as the potential due to some dynamic effective charge distribution $\rho_{eff}(\mathbf{r},\mathbf{r}')$:

$$v_x^{(0)}(\mathbf{r}) = \int d\mathbf{r}' \, \frac{\rho_{eff}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, , \tag{VI-30}$$

where the effective charge density (Fermi hole) is

$$\begin{aligned} \rho_{eff}(\mathbf{r},\mathbf{r}') = {} & \frac{\rho(z)}{2k_F\frac{d\rho(z)}{dk_F}}\left[(4+\frac{\mathbf{r}\cdot\nabla\rho(z)}{\rho(z)})\rho_x(\mathbf{r},\mathbf{r}')+\mathbf{r}\cdot(\nabla+\nabla')\rho_x(\mathbf{r},\mathbf{r}')\right] \\ & - \frac{\gamma_s(\mathbf{r},\mathbf{r}')}{2k_F\frac{d\rho(z)}{dk_F}}\cdot k_F\frac{\partial}{\partial k_F}\gamma_s(\mathbf{r},\mathbf{r}') \, , \end{aligned} \tag{VI-31}$$

and $\rho_x(\mathbf{r},\mathbf{r}')$ and $\gamma_s(\mathbf{r},\mathbf{r}')$ are the Fermi hole and the noninteracting single particle density matrix defined by Eqs.(II-39) and (II-32), respectively.

We can determine the total effective charge $Q_{eff}(z)$ by integrating the effective Fermi hole of Eq.(VI-31) over $\boldsymbol{r}'$. It is easy to see that the second term in parenthesis in Eq.(VI-31) does not contribute to the integral, so that

$$Q_{eff}(z) = \int d\boldsymbol{r}' \rho_{eff}(\boldsymbol{r},\boldsymbol{r}') = -\frac{1}{2}\left[1 + \frac{1}{k_F \frac{d}{dk_F} \ln\rho(z)}\right] . \tag{VI-32}$$

It is interesting to note that unlike the total charge of the exact Fermi hole $\rho_x(\boldsymbol{r},\boldsymbol{r}')$ which is independent of the position of an electron, $Q_{eff}(z)$ depends on z. We can evaluate $Q_{eff}(z)$ in two limiting cases: (i) in the bulk metal, and (ii) in the vacuum region. Far in the bulk metal we have

$$\left. k_F \frac{d\rho(z)}{dk_F} \right|_{z \to -\infty} = 3\bar{\rho} , \tag{VI-33}$$

and $Q_{eff}(z) = -2/3$. This value of $Q_{eff}(z)$ guaranties that $v_x^{(0)}(z)$ approaches the correct KS bulk limit of $-k_F/\pi$. In the vacuum region far from the metal surface

$$\left. k_F \frac{d\rho(z)}{dk_F} \right|_{z \to \infty} \propto z\rho(z) , \tag{VI-34}$$

and, hence, $Q_{eff}(z) = -1/2$. This limiting value of the effective Fermi hole gives rise to the correct asymptotic structure of $v_x^{(0)}(z)$ in the vacuum region.

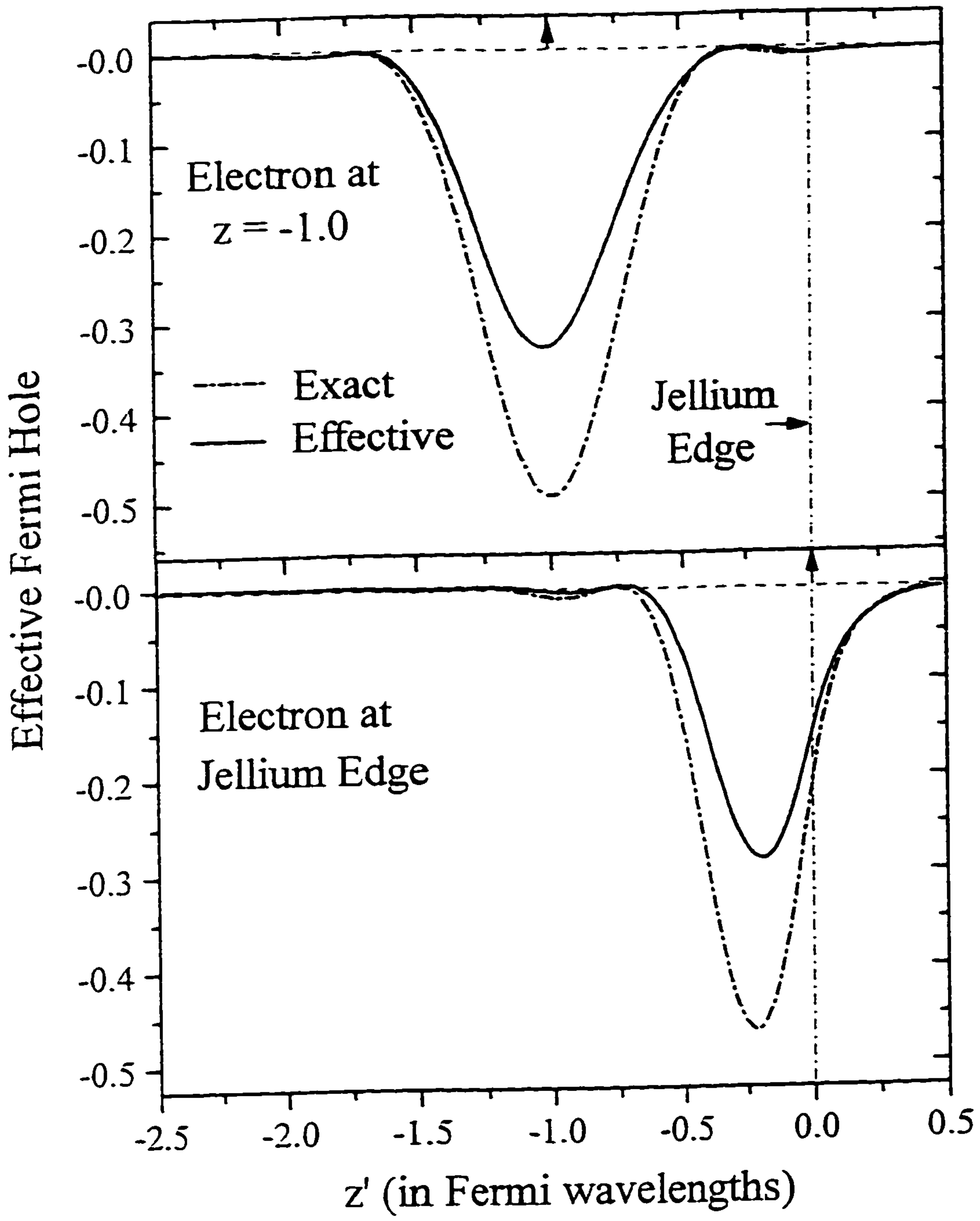

Fig. 10 Cross-sections of the exact and effective Fermi hole charge distributions in the plane perpendicular to the surface encompassing the electron for different electron positions. The electron position is indicated by an arrow.

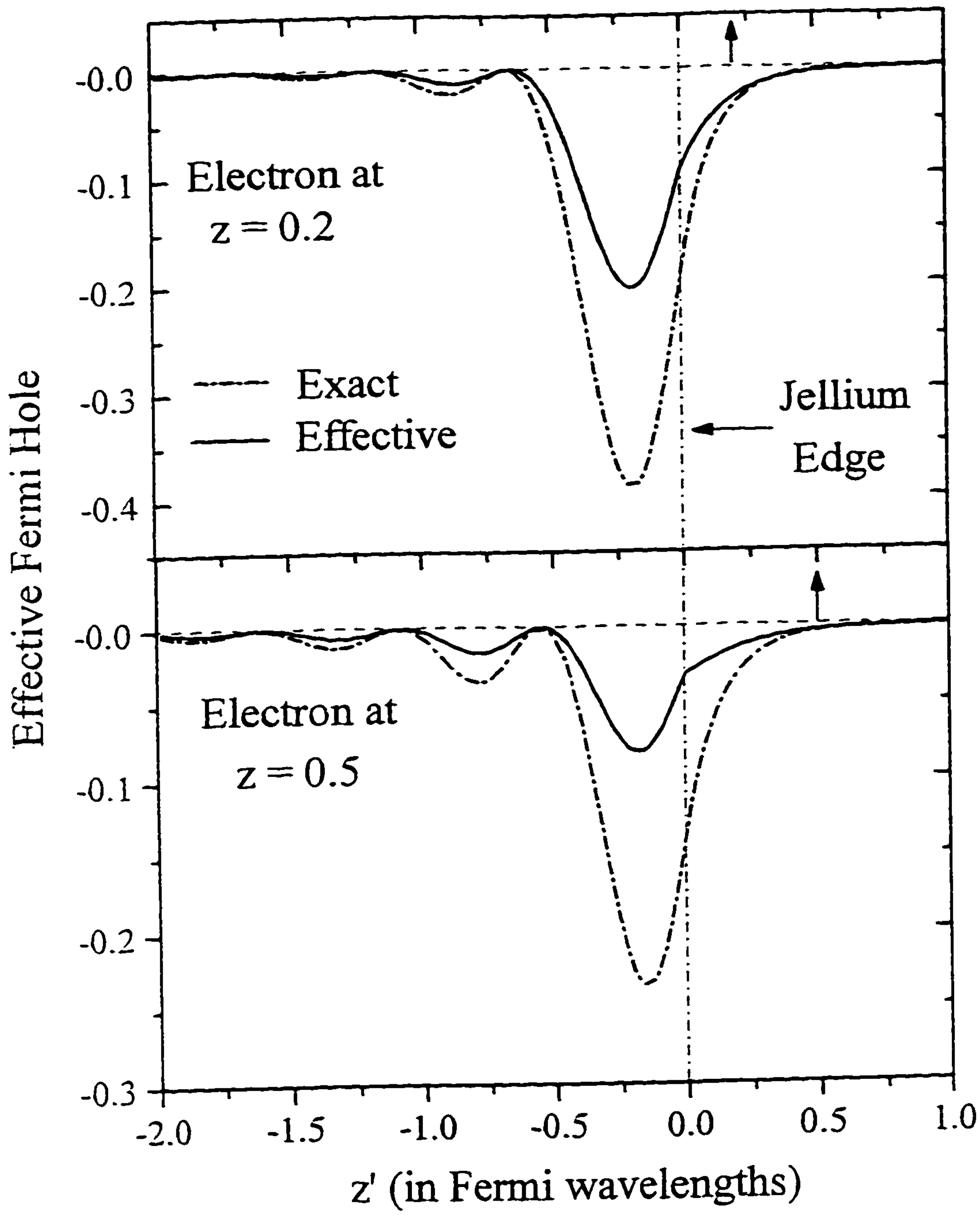

Fig 11 Cross-sections of the exact and effective Fermi hole charge distributions in the plane perpendicular to the surface encompassing the electron for different electron positions. The electron position is indicated by an arrow.

In Figs. 10 and 11 we plot cross-sections of the exact and effective Fermi holes in the plane perpendicular to the surface encompassing the electron for different electron positions employing the orbitals of the step-barrier potential (Bardeen, 1936; Sahni et.al., 1975).

It is evident from these figures that the structure of the effective Fermi hole is similar to that of the exact hole but smaller in magnitude. In the metal bulk it is spherically symmetric about the electron. As the electron moves across the surface into the vacuum region, the effective Fermi hole lags behind within the crystal as does the exact hole. There is, however, one important difference: whereas the exact Fermi hole is always negative, the effective hole does become positive at the local maxima of the charge.

Another unusual feature of Fig. 11 is the cusp in the curve representing $\rho_{eff}(z)$. However, this cusp is a result of the discontinuity of the effective potential, and as such is an artifact of the step barrier model.

6.2 Construction of Approximate Kohn-Sham Exchange Energy Functional and Derivative with Exact Asymptotic Structure

In this section we derive a local density approximation-like expression for the KS exchange energy functional and its derivative such that the latter possesses the correct asymptotic structure both in the classically forbidden and metal-bulk regions.

We begin by constructing an approximate expression $V_x^{S,app}(r)$ for the Slater potential $V_x^S(r)$ as

$$V_x^{S,app}(r) = \frac{3k_F}{2\pi}\left[p\rho_n^{1/3}(r) + \frac{\bar{\alpha}_s(\beta)}{\ln\rho_n^{1/3}(r) - \dfrac{\bar{\alpha}_s(\beta)}{p+1}} \right] \qquad \text{(VI-35)}$$

where

$$\bar{\alpha}_s(\beta) = \frac{4\pi}{9}(\beta^2-1)^{1/2}\alpha_s(\beta) \ , \qquad \text{(VI-36)}$$

$\alpha_s(\beta)$ is the Slater asymptotic decay coefficient of Eq. (III-31), $\rho_n(r)$ is the electron density normalized to the bulk value $\bar{\rho} = k_F^3/3\pi^2$, $\beta^2 = W/\epsilon_F$, and p is a free parameter. Note that for $p = -1$, the potential $V_x^{S,app}(r)$ is equivalent to the local density approximation of the Slater potential which is $-3k_F[\rho_n(r)] = -(3/2\pi)[3\pi^2\rho(r)]^{1/3}$.

It is easy to see that since $\lim_{z\to-\infty}\rho_n(z) = 1$, where $z = k_F x$, then for any value of the parameter p, the potential $V_x^{S,app}(r)$ reproduces the correct asymptotic structure of the exact Slater potential $V_x^S(\mathbf{r})$ in the metal bulk:

$$V_{x}^{S,app}(z) \underset{z\to-\infty}{=} \frac{3k_F}{2\pi}\left[\, p - p - 1 \,\right] = -\frac{3k_F}{2\pi} \; . \qquad \text{(VI-37)}$$

In the classically forbidden region we can write the normalized density as

$$\rho_n(z) \propto \exp\!\left[-2(\beta^2-1)^{1/2}z\right] \; , \qquad \text{(VI-38)}$$

where we have omitted the pre-exponential factor, which in general depends upon z. This factor leads to the higher order terms in the asymptotic expansion of $V_x^S(\mathbf{r})$ in the vacuum region. Thus, in the asymptotic vacuum region we have the result

$$V_{x}^{S,app}(z) \underset{z\to+\infty}{=} \frac{3k_F}{2\pi} \cdot \frac{\bar{\alpha}_s(\beta)}{\ln\rho_n^{1/3}(z)} \sim -\frac{\alpha_s(\beta)}{x} \qquad \text{(VI-39)}$$

for any value of p.

We next construct the approximate KS exchange energy $E_x^{app}[\rho]$ via the approximate Slater potential $V_x^{S,app}(\mathbf{r})$ as

$$\begin{aligned} E_x^{app}[\rho] &= \frac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})V_x^{S,app}(\mathbf{r}) \\ &= \frac{3k_F}{2\pi}\int d\mathbf{r}\rho(\mathbf{r})\left[\frac{p}{\bar{\rho}^{1/3}}\rho^{1/3}(\mathbf{r}) + \frac{\bar{\alpha}_s(\beta)}{\ln\left[\dfrac{\rho(\mathbf{r})}{\bar{\rho}}\right]^{1/3} - \dfrac{\bar{\alpha}_s(\beta)}{p+1}}\right] \; . \end{aligned}$$

$$\text{(VI-40)}$$

The functional derivative of $E_x^{app}[\rho]$ which is the approximate KS exchange potential $v_x^{app}(\mathbf{r})$ is then

$$v_x^{app}(r) = \frac{3k_F}{4\pi}\left[\frac{4p}{3}\rho_n^{1/3}(r) + \frac{\bar{\alpha}_s(\beta)}{\ln\rho_n^{1/3}(r) - \dfrac{\bar{\alpha}_s(\beta)}{p+1}} - \frac{\bar{\alpha}_s(\beta)}{3\left[\ln\rho_n^{1/3}(r) - \dfrac{\bar{\alpha}_s(\beta)}{p+1}\right]^2}\right] .$$

(VI-41)

It is readily seen that the potential $v_x^{app}(r)$ has the correct asymptotic structure $-[\alpha_s(\beta)/2]/x = -\alpha_{KS_x}(\beta)/x$ of Eq. (IV-14) in the vacuum for any value of the parameter p except for $p = -1$. The parameter p is determined by the requirement that $v_x^{app}(r)$ have the correct asymptotic structure of $-k_F/\pi$ of the KS exchange potential $v_x(r)$ in the bulk. Thus

$$\underset{z\to-\infty}{v_x^{app}(z)} = \frac{3k_F}{4\pi}\left[\frac{4p}{3} - p - 1 - \frac{(p+1)^2}{3\bar{\alpha}_s(\beta)}\right] = -\frac{k_F}{\pi} , \tag{VI-42}$$

so that the parameter s must satisfy the following equation

$$(p+1)\cdot\left[1 - \frac{p+1}{\bar{\alpha}_s(\beta)}\right] = 0 \tag{VI-43}$$

The first root of this equation $p = -1$ gives rise to the local density approximation exchange energy and corresponding derivative. The second root is

$$p = -1 + \bar{\alpha}_s(\beta) , \tag{VI-44}$$

which then leads to the following expressions for the exchange energy and derivative

$$E_x^{app}[\rho] = -\frac{3k_F}{4\pi}\bar{\rho}\int d\mathbf{r}\left[(1-\bar{\alpha}_s(\beta))\rho_n^{4/3}(\mathbf{r}) + \frac{\bar{\alpha}_s(\beta)\rho_n(\mathbf{r})}{1-\ln\rho_n^{1/3}(\mathbf{r})}\right] , \qquad \text{(VI-45)}$$

$$v_x^{app}(\mathbf{r}) = -\frac{k_F}{\pi}\left[(1-\bar{\alpha}_s(\beta))\rho_n^{1/3}(\mathbf{r}) + \frac{3\bar{\alpha}_s(\beta)}{4(1-\ln\rho_n^{1/3}(\mathbf{r}))} + \frac{\bar{\alpha}_s(\beta)}{4(1-\ln\rho_n^{1/3}(\mathbf{r}))^2}\right] . \qquad \text{(VI-46)}$$

A plot of $v_x^{app}(z)$ for Li metal (r_s=3.24) employing the orbitals of the finite-linear potential model is given in Fig. 12. The corresponding local density approximation (LDA) potential is also plotted. In the interior and about the surface of the metal the two potentials are equivalent. But outside the surface $v_x^{app}(z)$ improves upon the LDA significantly and approaches the exact structure asymptotically. We thus expect that properties such as the surface energy and work function obtained with $E_x^{app}[\rho]$ and $v_x^{app}(\mathbf{r})$ to be superior to those of the LDA. Such self-consistent calculations are in progress.

In a manner similar to that described above, it is possible to correct other exchange energy functionals more accurate than the LDA, such as the generalized gradient approximation (Perdew, 1985). It is also possible to obtain the correction to the LDA or other correlation energy functionals such that the correct asymptotic structure is ensured. In the following subsection we construct an approximate correlation energy functional and derivative with the correct asymptotic structure in the vacuum and metal-bulk regions.

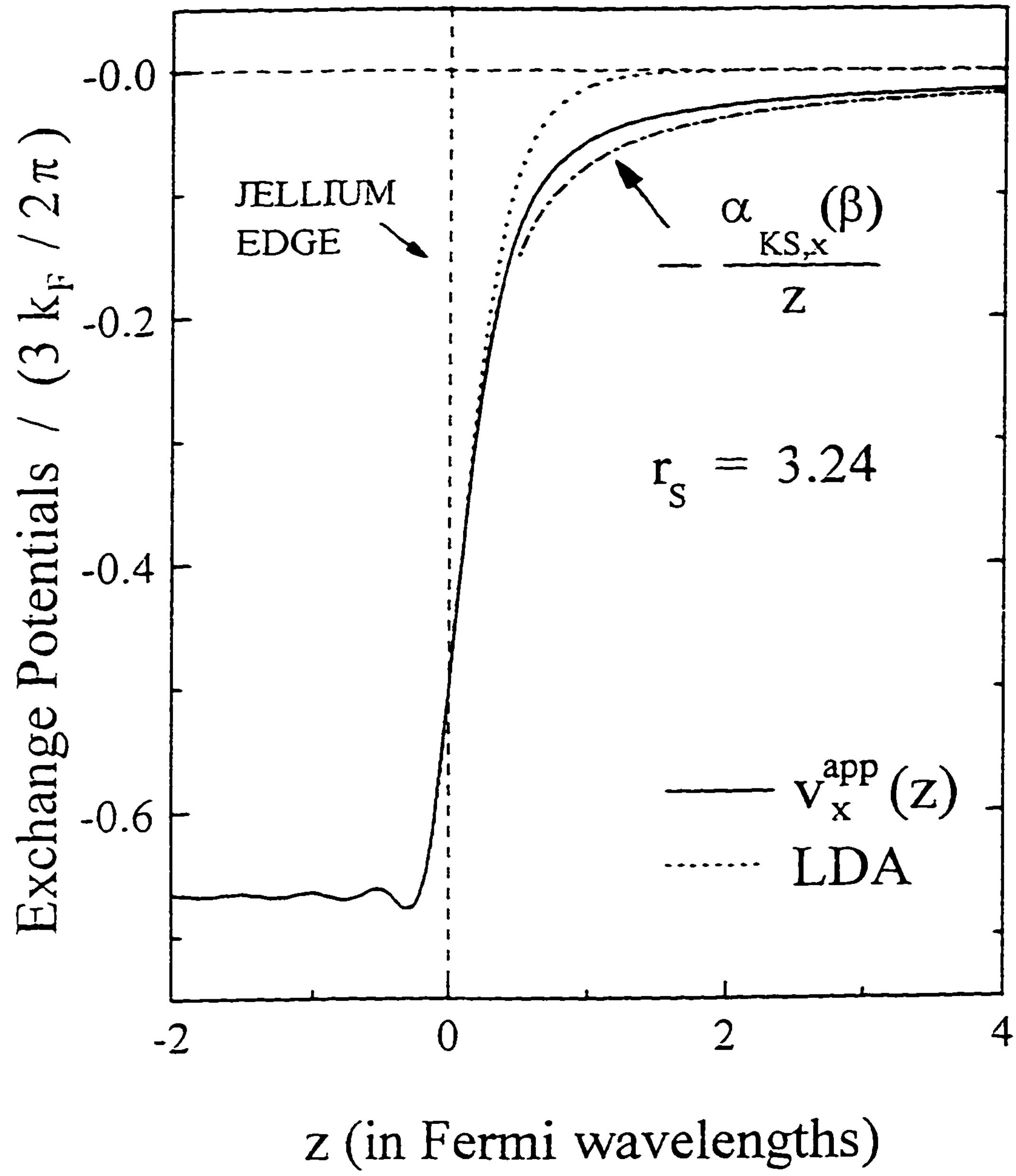

Fig. 12 Structure of the approximate local KS exchange potential $v_x^{app}(r)$ of Eq. (VI-46) for Li metal. The exchange potential in the local density approximation as well as the exact KS asymptotic structure of $-\alpha_{KS,x}(\beta)/z$ are also plotted.

6.3 Construction of Approximate Kohn-Sham Correlation Energy Functional and Derivative with Exact Asymptotic Structure.

In this section we construct an approximate correlation energy functional and derivative such that the latter possesses the correct asymptotic structure of $-\alpha_{KS,c}(\beta)/x$ in the vacuum region as well as the correct limit in the metal bulk.

We define the approximate correlation energy functional as

$$E_c^{app}[\rho] = \int d\mathbf{r}\rho_n(\mathbf{r})\bar{\epsilon}_c\{\rho_n(\mathbf{r})\} \quad , \tag{VI-47}$$

where

$$\bar{\epsilon}_c\{\rho_n(\mathbf{r})\} = \frac{3k_F}{2\pi}\left[q\epsilon_c\{\rho_n(\mathbf{r})\} + \frac{\bar{\alpha}_c(\beta)}{\ln\rho_n^{1/3}(\mathbf{r}) - \dfrac{\bar{\alpha}_c(\beta)}{p}}\right] , \tag{VI-48}$$

$$\bar{\alpha}_c(\beta) = \frac{4\pi}{9}(\beta^2-1)^{1/2}\alpha_{KS,c}(\beta) \quad , \tag{VI-49}$$

q and p are parameters to be determined, and $\epsilon_c\{\rho_n(\mathbf{r})\}$ is any commonly employed parametrization of the correlation energy of the uniform electron gas. For a discussion of the KS correlation potential decay coefficient $\alpha_{KS,c}(\beta)$, see Chapter VIII.

Since $\lim_{z\to-\infty}\rho_n(z) = 1$ $(z=k_F x)$, we have from Eq. (VI-48) that

$$\lim_{z\to-\infty}\bar{\epsilon}_c\{\rho_n(r)\} \equiv \epsilon_c^{bulk} \triangleq \epsilon_{c,b} = q\epsilon_{c,b}-p \quad , \tag{VI-50}$$

so that

$$p = (q-1)\epsilon_{c,b},$$

and therefore

$$\bar{\epsilon}_c\{\rho_n(r)\} = \frac{3k_F}{2\pi}\left[q\epsilon_c\{\rho_n(r)\} + \frac{\bar{\alpha}_c(\beta)}{\ln\rho_n^{1/3}(r) - \dfrac{\bar{\alpha}_c(\beta)}{(q-1)\epsilon_{c,b}}}\right] \cdot \tag{VI-51}$$

With the $\bar{\epsilon}_c\{\rho_n(r)\}$ of Eq. (VI-51) substituted into Eq. (VI-47) we then obtain for the functional derivative $v_x^{app}(r)$ to be

$$\frac{v_x^{app}(r)}{3k_F/2\pi} = \frac{\delta E_c^{app}[\rho]}{\delta\rho_n(r)}$$

$$= q\left[\epsilon_c\{\rho_n(r)\} + \rho_n(r)\frac{d\epsilon_c\{\rho_n(r)\}}{d\rho_n}\right] + \frac{\bar{\alpha}_c(\beta)}{\ln\rho_n^{1/3}(r) - \dfrac{\bar{\alpha}_c(\beta)}{(q-1)\epsilon_{c,b}}} \tag{VI-52}$$

$$- \frac{\bar{\alpha}_c(\beta)}{3\left[\ln\rho_n^{1/3}(r) - \dfrac{\bar{\alpha}_c(\beta)}{(q-1)\epsilon_{c,b}}\right]^2} \ .$$

In the vacuum region the density decays as Eq. (VI-38), so that

$$\lim_{z\to\infty} v_c^{app}(z) = \frac{3k_F}{2\pi}\frac{\bar{\alpha}_c(\beta)}{\ln\rho_n^{1/3} - \dfrac{\bar{\alpha}_c(\beta)}{(q-1)\epsilon_{c,b}}} = -\frac{\alpha_{KS,c}(\beta)}{x}\ , \tag{VI-53}$$

which is the correct asymptotic limit.

Finally, we determine the constant q by the requirement that $v_c^{app}(z)$ have the correct asymptotic limit in the metal bulk. Thus, from Eq. (VI-52)

$$\begin{aligned}\lim_{z\to\infty}\frac{v_c^{app}(r)}{(3k_F/2\pi)} &\equiv \epsilon_{c,b} + \left[\frac{d\epsilon_c\{\rho_n(r)\}}{d\rho_n}\right]_{\rho_n\to 1}\\ &= q\left\{\epsilon_{c,b} + \left[\frac{d\epsilon_c\{\rho_n\}}{d\rho_n}\right]_{\rho_n\to 1}\right\} - (q-1)\epsilon_{c,b} - \frac{(a-1)^2\epsilon_{c,b}^2}{3\bar{\alpha}_c(\beta)}\ ,\end{aligned} \tag{VI-54}$$

so that

$$q = 1 + \frac{3\bar{\alpha}_c(\beta)}{\epsilon_{c,b}^2}\left[\frac{d\epsilon_c\{\rho_n\}}{d\rho_n}\right]_{\rho_n\to 1}\ . \tag{VI-55}$$

The resulting expression for $\bar{\epsilon}_c\{\rho_n\}$ is then

$$\begin{aligned}\bar{\epsilon}_c\{\rho_n\} &= \frac{3k_F}{2\pi}\left[\left\{1+3\bar{\alpha}_c(\beta)\left[\frac{1}{\epsilon_c^2\{\rho_n(r)\}}\frac{d\epsilon_c\{\rho_n\}}{d\rho_n}\right]_{\rho_n\to 1}\right\}\epsilon_c\{\rho_n\}\right]\\ &+ \frac{3k_F}{2\pi}\left[\frac{\bar{\alpha}_c(\beta)}{\ln\rho_n^{1/3}(r) - \left[\dfrac{\epsilon_c\{\rho_n\}}{3d\epsilon_c\{\rho_n\}/d\rho_n}\right]_{\rho_n\to 1}}\right]\ ,\end{aligned} \tag{VI-56}$$

which when substituted into Eq. (VI-47) leads to the expression for the correlation energy. The corresponding expression for the functional derivative is given by Eq. (VI-52) with the value of q obtained from Eq. (VI-55). Note that there are no parameters in the expression for the approximate correlation energy and its derivative.

In a similar manner, an expression for the exchange-correlation energy $E_{xc}^{app}[\rho]$ and its derivative can be constructed. The expression for $\epsilon_{xc}\{\rho_n\}$ would be the same as Eq. (VI-56) with $\epsilon_c\{\rho_n\}$ replaced by $\epsilon_{xc}\{\rho_n\}$, and the $\alpha_{KS,c}(\beta)$ of $\alpha_c(\beta)$ of Eq. (VI-49) replaced by $\alpha_{KS,xc} = 1/4$.

CHAPTER VII

STRUCTURE OF THE CORRELATION-KINETIC COMPONENT OF THE KOHN-SHAM EXCHANGE POTENTIAL AT A METAL SURFACE AND IN ATOMS

In this chapter we study the correlation-kinetic component $W_{t_c}^{(1)}(\mathbf{r})$ of the KS exchange potential $v_x(\mathbf{r})$ at a metal surface and in atoms. (See Section 2.3.1) We begin with a discussion of the asymptotic structure of $W_{t_c}^{(1)}(\mathbf{r})$ both in the vacuum and bulk regions of a metal surface. Then by assuming the approximate exchange potential of Eq. (VI-6) derived by restricted functional differentiation to be KS exchange potential, we determine the structure of the correlation-kinetic field $\mathcal{Z}_{t_c}^{(1)}(\mathbf{r})$ and potential $W_{t_c}^{(1)}(\mathbf{r})$ at and about the surface. Finally, by assuming the KS exchange potential in atoms to be that of the optimized potential method, we determine the corresponding field $\mathcal{Z}_{t_c}^{(1)}(\mathbf{r})$ and potential $W_{t_c}^{(1)}(\mathbf{r})$ for this nonuniform density system.

7.1 Asymptotic Structure of the Correlation-Kinetic Component Potential $W_{t_c}^{(1)}(z)$ at a Metal Surface

The KS exchange potential $v_x(\mathbf{r})$ is the sum of a Pauli component $W_x^{KS}(\mathbf{r})$ and a correlation-kinetic component as expressed by Eq. (II-78). For the jellium and structureless pseudopotential models of a metal surface, we have derived in chapters IV and V the exact asymptotic structure of $v_x(\mathbf{r})$ and $W_x^{KS}(\mathbf{r})$ in the classically forbidden region. The analytical expressions for these structures, which are valid for self-consistently determined orbitals, show both potentials to decay in a $-x^{-1}$ image-potential-like manner but with different decay coefficients which depend upon the metal Fermi energy and surface barrier height. Thus, the asymptotic structure of the correlation-kinetic component $W_{t_c}^{(1)}(r)$ is also known ***exactly*** to decay as

$$\underset{x \to \infty}{W_{t_c}^{(1)}(x)} = \frac{\alpha_{t_c}^{(1)}(\beta)}{x} , \tag{VII-1}$$

where the decay coefficient is

$$\alpha_{t_c}^{(1)}(\beta) = \frac{\beta^2 - 1}{2\beta^2}\left[1 - 2\,\frac{\beta^2 - 2}{\beta^2} - \frac{4}{\pi\sqrt{\beta^2 - 1}}\left\{1 + \frac{4 - 3\beta^2}{\beta^2}\ln(\beta^2 - 1)\right\}\right] , \tag{VII-2}$$

and where $\beta^2 = W/\epsilon_F$. Thus, the correlation-kinetic potential $W_{t_c}^{(1)}(x)$ is also ***long-ranged***.

The coefficient $\alpha_{t_c}^{(1)}(\beta)$ as a function of β is plotted in Fig. 13. For completeness, the Slater $\alpha_S(\beta)$, KS exchange $\alpha_{KS_x}(\beta)$ and its Pauli component $\alpha_W(\beta)$ decay coefficients are also plotted. The value of the Wigner-Seitz radius r_s for the jellium and structureless pseudopotential models is also given, the relationship between r_s and β being determined as in the previous chapters. It is evident that correlation-kinetic effects are small for high and very high density metals, their contribution becoming larger for medium and low density metals. For jellium metal corresponding to r_s=2.0, 4.0 and 6.0, the values of the coefficient $\alpha_{t_c}^{(1)}(\beta)$ are 0.022, 0.066 and 0.094 respectively. For r_s=2.0 this contribution compared to the KS coefficient $\alpha_{KS_x}(\beta)$ is 11 percent whereas for r_s=6.0 it

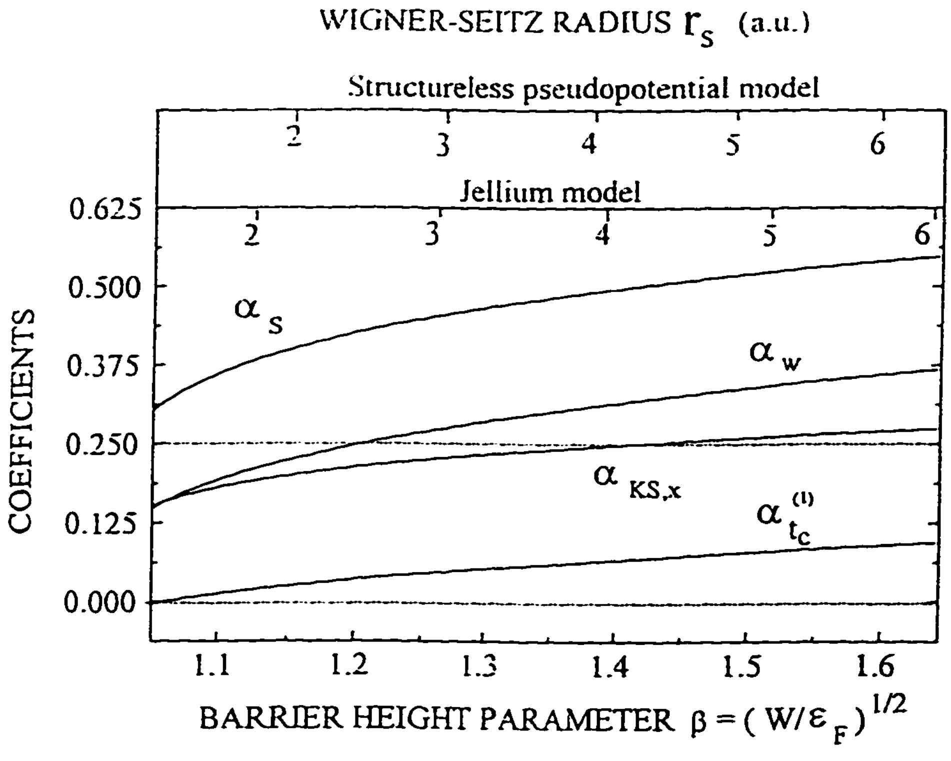

Fig. 13 Asymptotic structure coefficients $\alpha_S(\beta)$, $\alpha_{KS,x}(\beta)$, $\alpha_W(\beta)$ and $\alpha_{t_c}^{(1)}(\beta)$ as function of barrier height parameter $\beta=(W/\epsilon_F)^{1/2}$, where W is the barrier height and ϵ_F the Fermi energy. Corresponding values of the Wigner-Seitz radius r_s for jellium and structureless-pseudopotential models over the metallic range of densities are also given. The relationship between r_s and β is via self-consistent calculations in the local density approximation for exchange-correlation.

is 34 percent. Thus, it is only for very high density metals ($r_s \leq 2.0$) that the asymptotic structure of the KS exchange potential is governed primarily by Pauli correlations.

Recall that in chapter V we had determined the asymptotic structure of the Pauli component potential $W_x^{KS}(z)$ in the metal bulk, and that in this limit it differed from the exact KS exchange potential $v_x(z)$ value of $-2/3$. We thus see that in addition to Pauli correlations, there is a finite correlation-kinetic contribution to the KS exchange potential $v_x(z)$ in the bulk. This limiting value of the correlation-kinetic potential $W_{t_c}^{(1)}(-\infty)$ is given in Table II. It is evident from the Table that for very slowly varying densities

TABLE II

The metal-bulk limiting value of the correlation-kinetic component $W_{t_c}^{(1)}(-\infty)$ of the KS exchange potential $v_x(-\infty)$ as a function of the Wigner-Seitz radius r_s.

Wigner-Seitz radius r_s (a.u.)	$W_{t_c}^{(1)}(-\infty)/(3k_F/2\pi)$
2.0	0.049
4.0	0.121
6.0	0.156

($r_s \leq 2$, $\beta \rightarrow 1$) the correlation-kinetic contribution vanishes and the KS exchange potential $v_x(z)$ and its Pauli component $W_x^{KS}(z)$ become equivalent as must be the case. (Wang et.al., 1990). However, over the metallic range of densities (r_s = 2-6), there is a distinct correlation-kinetic contribution which increases with decreasing bulk density.

We next study the correlation-kinetic field $Z_{t_c}^{(1)}(\boldsymbol{r})$ and potential $W_{t_c}^{(1)}(\boldsymbol{r})$ at and about metal surfaces.

7.2 Structure of the Correlation-Kinetic Component Field $Z_{t_c}^{(1)}(z)$ and Potential $W_{t_c}^{(1)}(z)$ at a Metal Surface

In order to determine an accurate representation of the correlation-kinetic field $Z_{t_c}^{(1)}(\boldsymbol{r})$ and potential $W_{t_c}^{(1)}(\boldsymbol{r})$ at a metal surface, we assume the KS exchange potential $v_x(\boldsymbol{r})$ to be $v_x^{(0)}(\boldsymbol{r})$ of Eq. (VI-6) determined by restricted functional differentiation. The orbitals employed in the calculation of this potential are those of the finite-linear-potential model of Eq. (III-25) corresponding to Wigner-Seitz radii of r_s = 3.24 and 6.0. For the same set of orbitals we then determine the Pauli component field $\mathcal{E}_x^{KS}(\boldsymbol{r})$ and potential $W_x^{KS}(\boldsymbol{r})$. The differences $[\nabla v_x^{(0)}(\boldsymbol{r}) - \mathcal{E}_x^{KS}(\boldsymbol{r})]$ and $[v_x^{(0)}(\boldsymbol{r}) - W_x^{KS}(\boldsymbol{r})]$ are then the corresponding correlation-kinetic field $Z_{t_c}^{(1)}(\boldsymbol{r})$ and potential $W_{t_c}^{(1)}(\boldsymbol{r})$, respectively.

In Fig. 14 we plot the approximate KS exchange potential $v_x^{(0)}(z)$ and the Pauli component $W_x^{KS}(z)$. As noted in the previous chapter, $v_x^{(0)}(z)$ achieves the exact asymptotic structure of $v_x(z)$ in the vacuum by about one Fermi wavelength from the

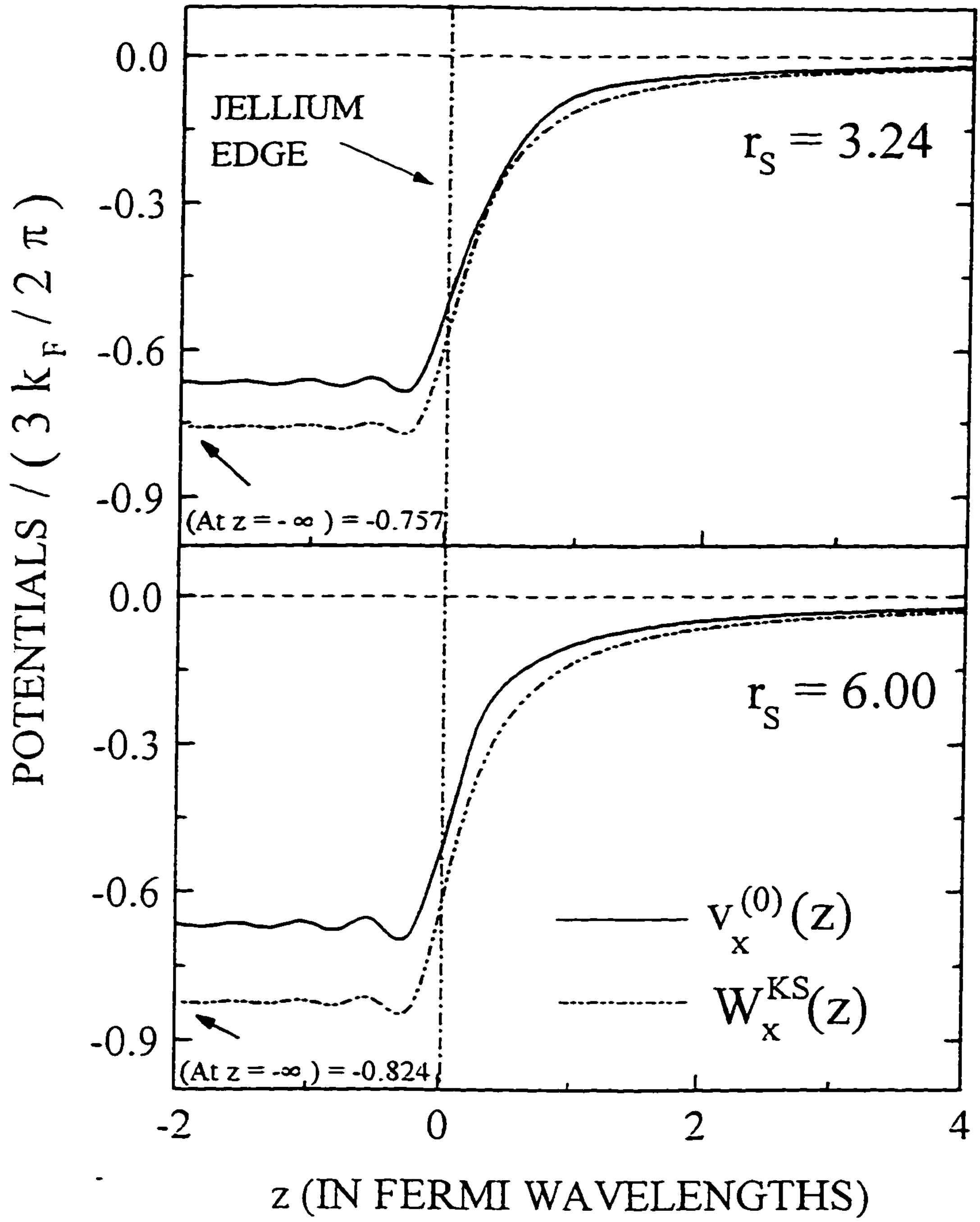

Fig. 14 The Kohn-Sham exchange potential $v_x^{(0)}(z)$, and the Pauli component potential $W_x^{KS}(z)$ at the surface of metals of Wigner-Seitz radii r_s=3.24 and 6.00.

surface. In the metal bulk, it has the correct limiting value of -2/3 (in units of $3k_F/2\pi$). As discussed in chapter V, for these metal densities, the Pauli component $W_x^{KS}(z)$ is distinct from the exchange potential $v_x^{(0)}(z)$. Its asymptotic structure in the vacuum is different as is its structure at the metal surface and metal bulk.

In Fig. 15 we plot the correlation-kinetic field $Z_{t_c}^{(1)}(z)$. As was the case for the Pauli field $\mathcal{E}_x^{KS}(z)$ (see Fig. 6), the field $Z_{t_c}^{(1)}(z)$ is also concentrated about the surface. It is long-ranged in the vacuum decaying asymptotically as $\alpha_{t_c}^{(1)}(\beta)/z^2$ as demonstrated in Fig. 16. In the metal it exhibits the requisite Bardeen-Friedel oscillations. The field $Z_{t_c}^{(1)}(z)$, however, is an order of magnitude smaller than the Pauli component field $\mathcal{E}_x^{KS}(z)$.

In Fig. 17 the correlation-kinetic potential component $W_{t_c}^{(1)}(z)$ is plotted. For these densities, the potential is entirely positive, possesses the correct asymptotic structure of Eq. (VII-1) in the vacuum, and exhibits the Bardeen-Friedel oscillations. Once again, the potential $W_{t_c}^{(1)}(z)$ is an order of magnitude smaller than the Pauli component $W_x^{KS}(z)$. For higher density metals, the component $W_{t_c}^{(1)}(z)$ will become less and less significant as $v_x(z) \sim W_x^{KS}(z)$. However, for metallic densities, the potential $W_{t_c}^{(1)}(z)$ is finite throughout space, and will therefore contribute to all surface properties.

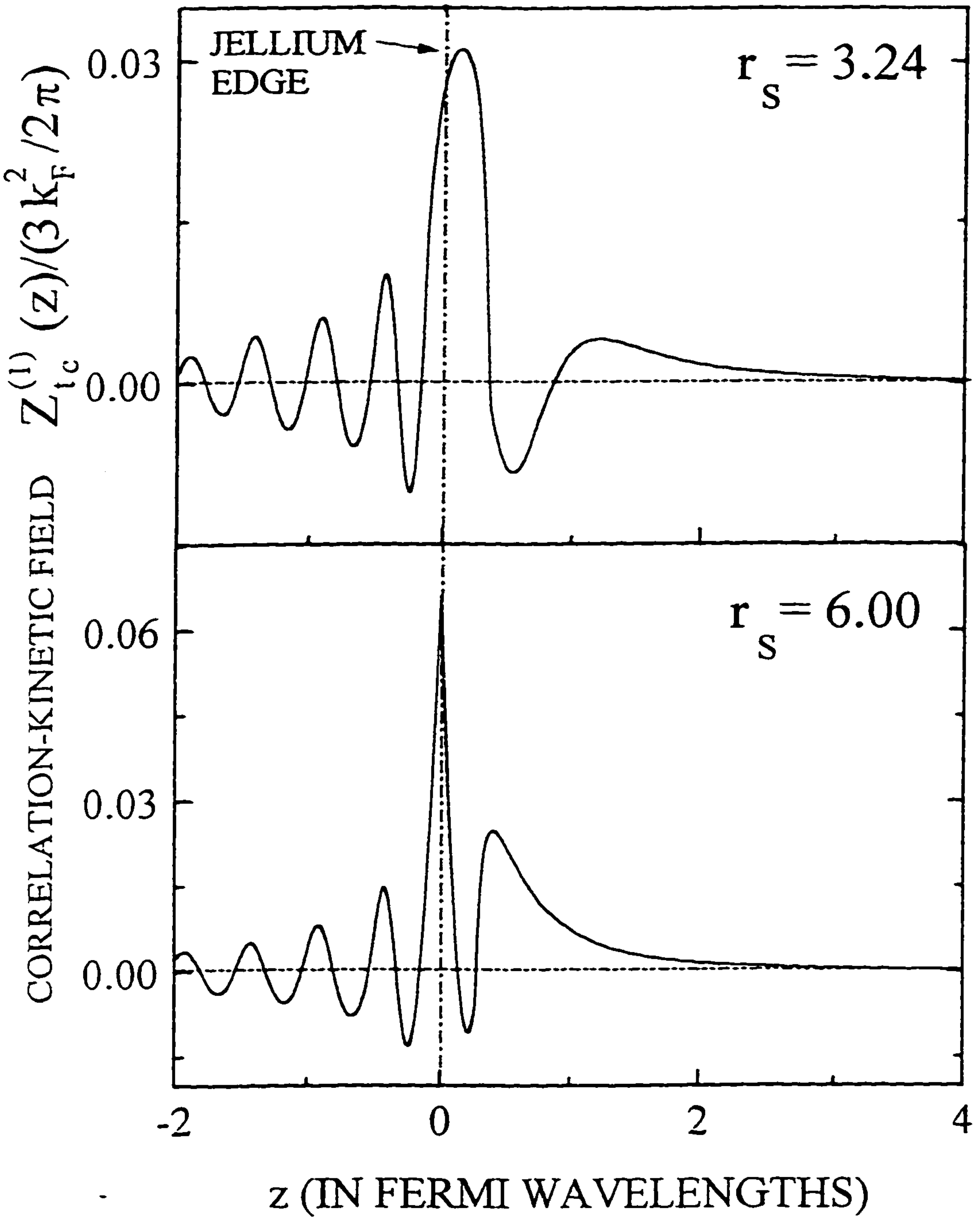

Fig. 15 The correlation-kinetic field $Z^{(1)}_{t_c}(z)$ at the surface of metals of Wigner-Seitz radii r_s=3.24 and 6.00.

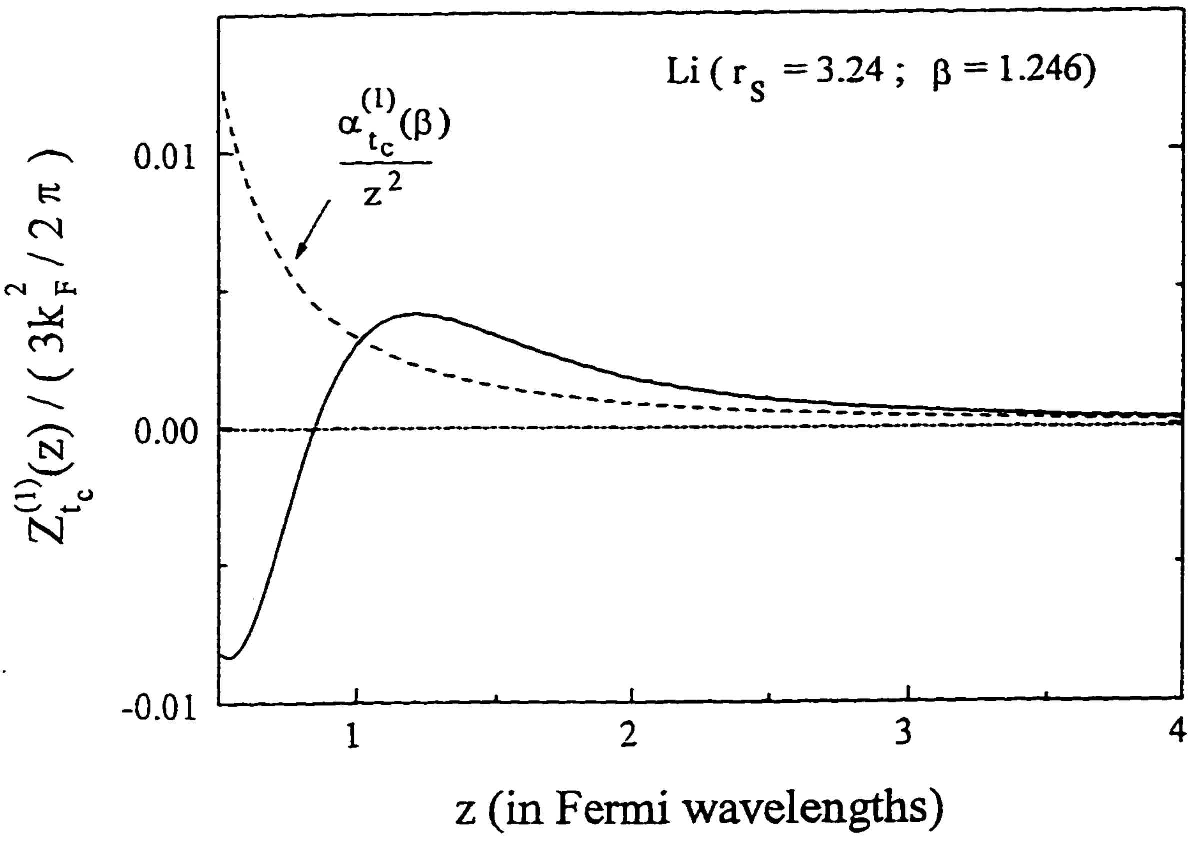

Fig. 16 Comparison of the asymptotic structure of the correlation-kinetic field $Z^{(1)}_{t_c}(z)$ at the surface of Li metal with its exact analytical asymptotic structure $\alpha^{(1)}_{t_c}(\beta)/z^2$.

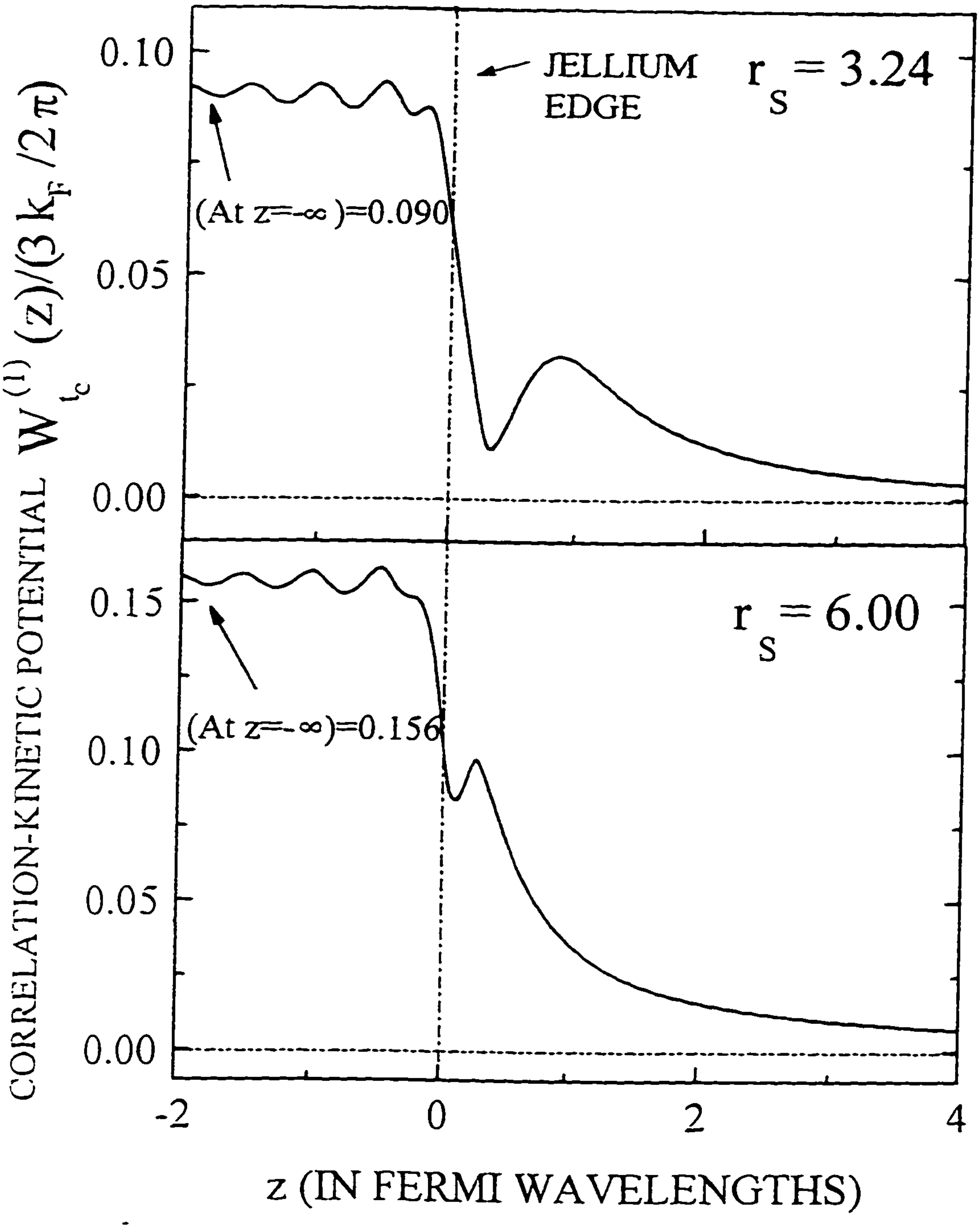

Fig. 17 The correlation-kinetic component potential $W_{t_c}^{(1)}(z)$ at the surface of metals of Wigner-Seitz radii r_s=3.24 and 6.00.

7.3 Structure of Correlation-Kinetic Component Field $Z_{t_c}^{(1)}(z)$ and Potential $W_{t_c}^{(1)}(r)$ in Atoms

To determine an accurate representation of the correlation-kinetic field $\mathbf{Z}_{t_c}^{(1)}(\mathbf{r})$ and potential $W_{t_c}^{(1)}(\mathbf{r})$ in atoms, we assume the KS exchange potential $v_x(\mathbf{r})$ to be that of the optimized potential method $v_x^{OPM}(\mathbf{r})$. We then determine the work $W_x(\mathbf{r})$ by self-consistent solution of the Work Formalism differential equation. In other words, we assume the 'exchange' problem to be defined by the case described by Eq. (II-90). We reiterate that the difference between the KS, OPM, and Work Formalism orbitals is minimal. The differences $[\nabla v_x^{OPM}(\mathbf{r}) - \mathcal{E}_x^{KS}(\mathbf{r})]$ and $[v_x^{OPM}(\mathbf{r}) - W_x^{KS}(\mathbf{r})]$ are then the corresponding correlation-kinetic field $\mathbf{Z}_{t_c}^{(1)}(\mathbf{r})$ and potential $W_{t_c}^{(1)}(\mathbf{r})$, respectively.

In Figs. 18 and 19 we plot the Pauli component field $\mathcal{E}_x^{KS}(\mathbf{r})$ due to the Fermi hole charge for Ne and Ar atoms. Note the shell structure as exhibited by the field, and that it exists primarily within the K-shell becoming less significant in the outer shells, decaying asymptotically as $-1/r^2$. In Figs. 20 and 21 we plot the corresponding correlation-kinetic component field $Z_{t_c}^{(1)}(r)$ for these atoms. In these graphs we have also indicated the radial probability density, so that it is evident that the field $Z_{t_c}^{(1)}(r)$ exists principally in the intershell regions and is oscillatory there. Furthermore, the magnitude of this field is greatest in the region between the K and L shells, becoming much smaller in the outer intershell regions. The field $Z_{t_c}^{(1)}(r)$ is also ***short-ranged*** in comparison to the Pauli field $\mathcal{E}_x^{KS}(r)$, vanishing at about the commencement of the outermost occupied shell. It is also interesting to note that there is a small component of this field present in the interior of the atom. Finally, observe that the field $Z_{t_c}^{(1)}(r)$ is much smaller, about

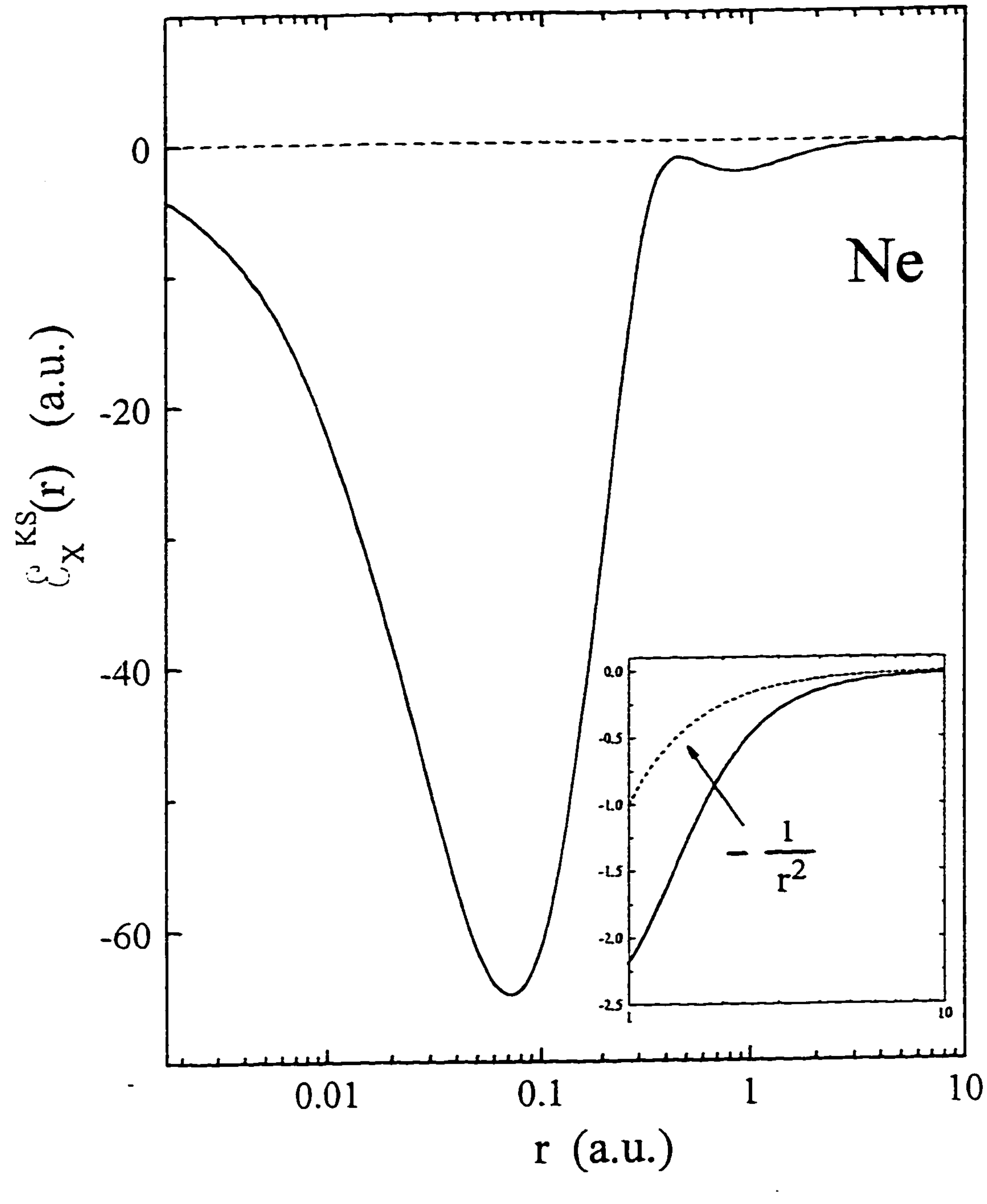

Fig. 18 The Pauli component field $\mathcal{E}_x^{KS}(r)$ for Ne atom.

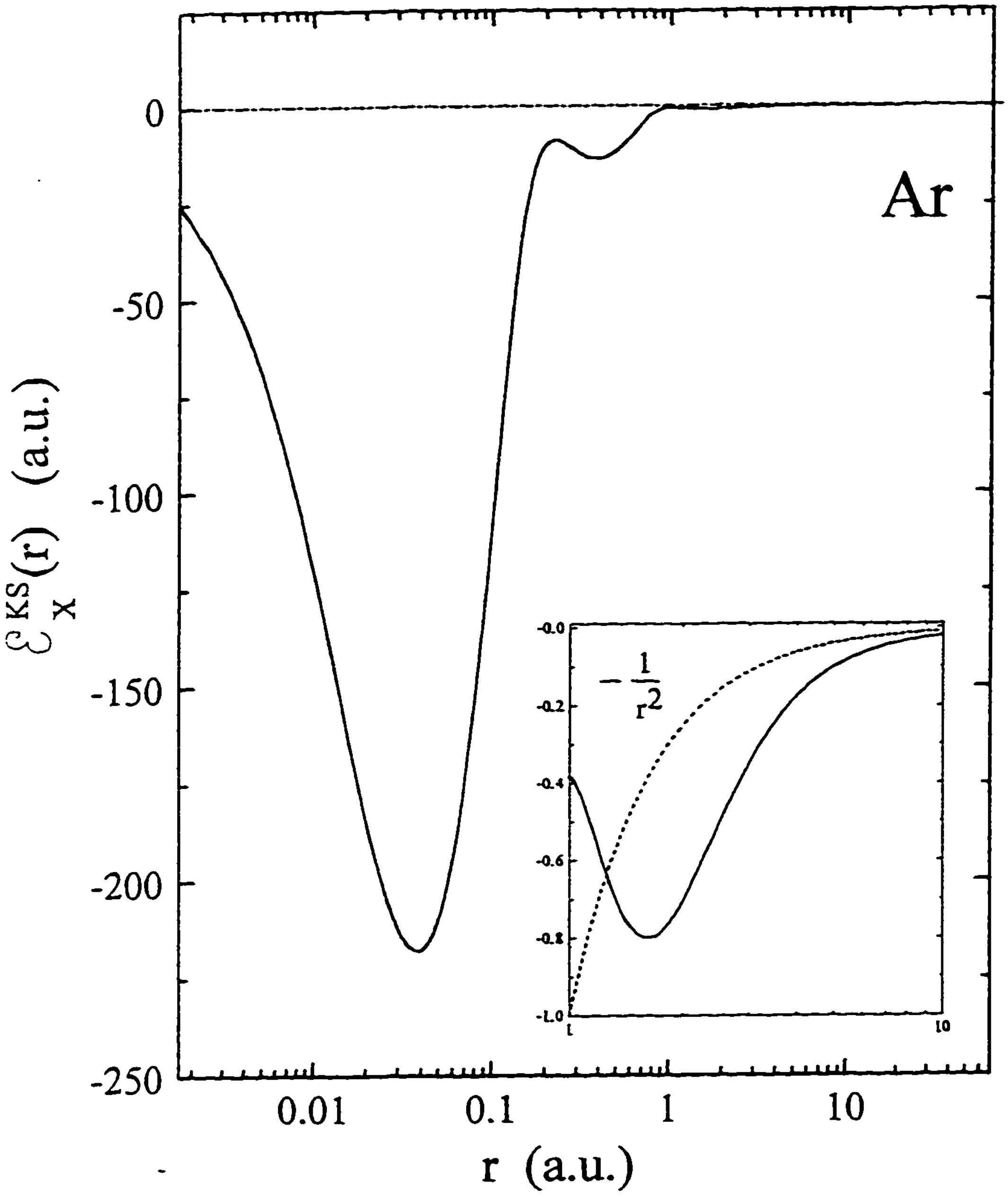

Fig. 19 The Pauli component field $\mathcal{E}_x^{KS}(r)$ for Ar atom.

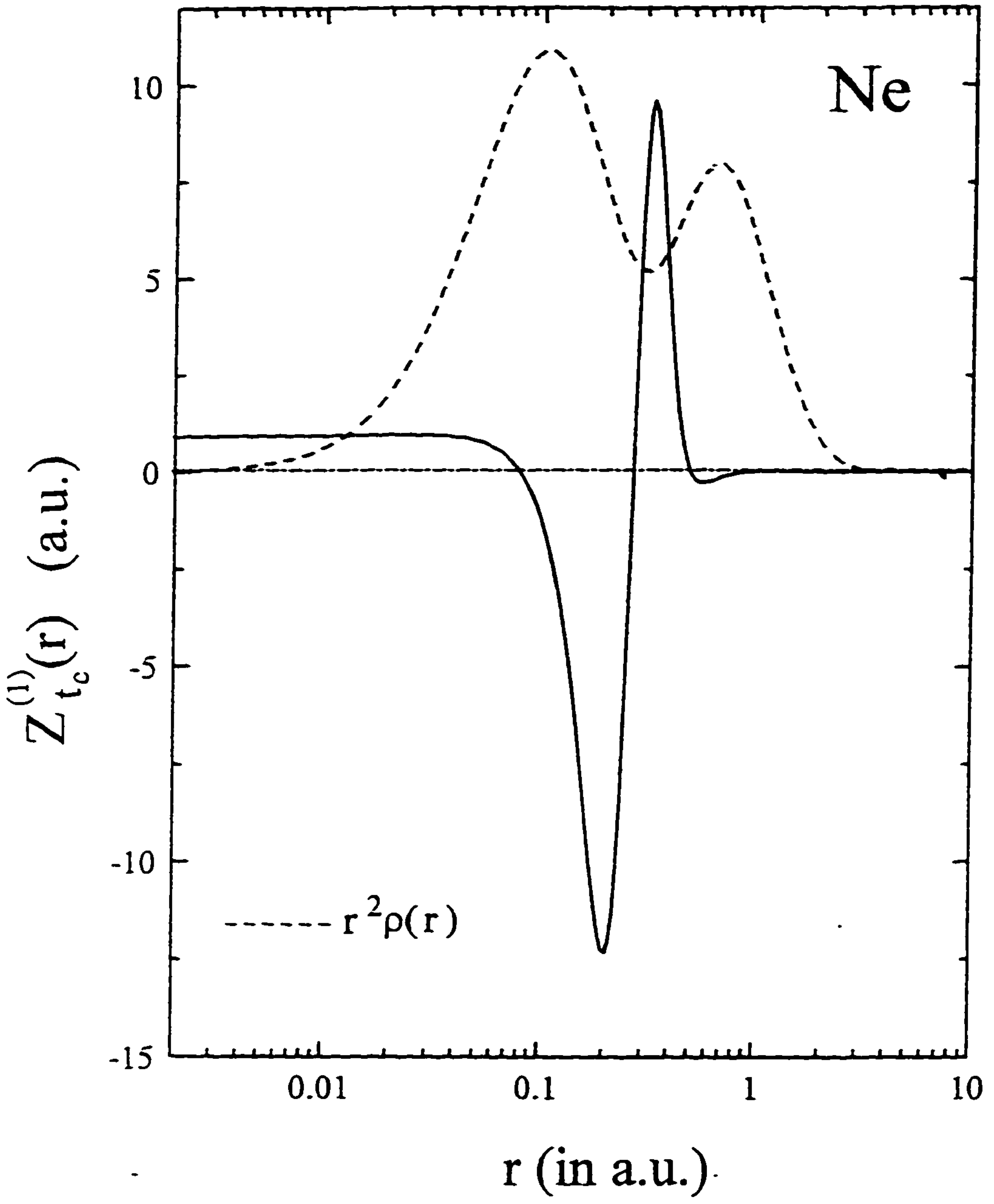

Fig.20 The correlation-kinetic component field $Z^{(1)}_{t_c}(r)$ for the Ne atom. The radial probability density is plotted as the dashed line.

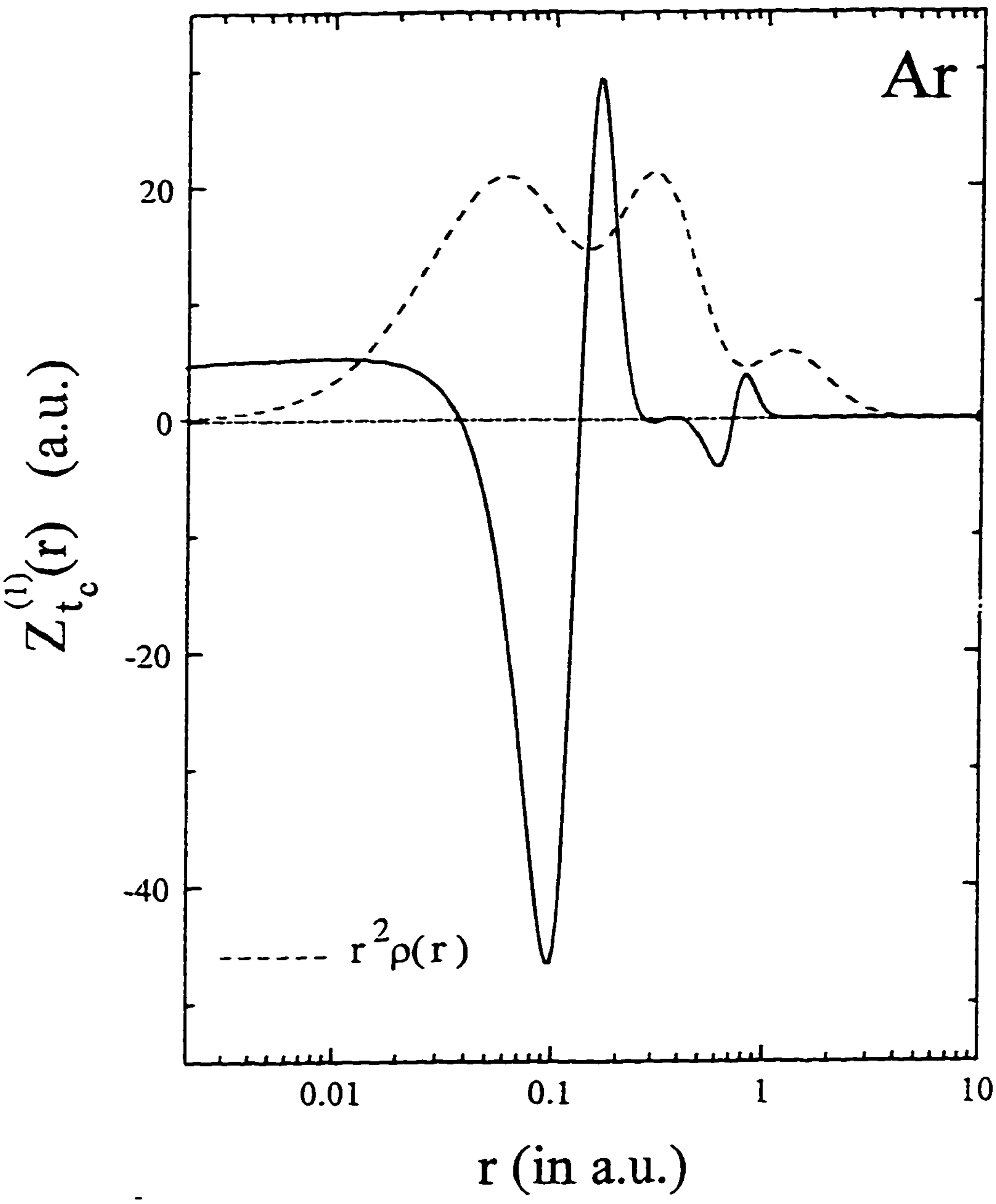

Fig.21 The correlation-kinetic component field $Z^{(1)}_{t_c}(r)$ for the Ar atom. The radial probability density is plotted as the dashed line.

a fifth of the magnitude of the Pauli field $\mathcal{E}_x^{KS}(r)$.

In Figs.22 and 23 we plot the Pauli $W_x^{KS}(r)$ and correlation-kinetic $W_{t_c}^{(1)}(r)$ components of the KS 'exchange' potential $v_x(r)$ for Ne and Ar, respectively. As is known (Harbola and Sahni, 1989a), the Pauli component $W_x^{KS}(r)$ exhibits shell structure, and is monotonic with positive slope since the field $\mathcal{E}_x^{KS}(r)$ is negative throughout space. It decays asymptotically as $-1/r$ in the classically forbidden region as does $v_x(r)$. Since the correlation-kinetic field $Z_{t_c}^{(1)}(r)$ is oscillatory and exists in the intershell regions, the corresponding potential $W_{t_c}^{(1)}(r)$ exhibits a dip in these regions, vanishing well within the outermost occupied shell. It is this correlation-kinetic component which then gives rise to the well-known bumps of the KS potential $v_x(r)$ in the intershell regions. Again, we note that there is a small component of this potential in the interior of atoms. Finally, observe that $W_{t_c}^{(1)}(r)$ is an order of magnitude smaller than the Pauli potential $W_x^{KS}(r)$. Thus, the correlation-kinetic effects contributing to the KS potential $v_x(r)$ are small. As such it is justified to represent the potential $v_x(r)$ in finite systems by its Pauli component $W_x^{KS}(r)$. The high accuracy of this approximation with regard to total ground and excited state energies, ionization potentials and electron affinities has been demonstrated in the literature (Sahni, 1996; Sahni et. al., 1992; Li et. al., 1989).

7.4 Discussion of Results

The KS 'exchange' potential $v_x(r)$ is comprised of a term $W_x^{KS}(r)$ representative of Pauli correlations, and another $W_{t_c}^{(1)}(r)$ which constitutes ***part*** of the correlation-kinetic

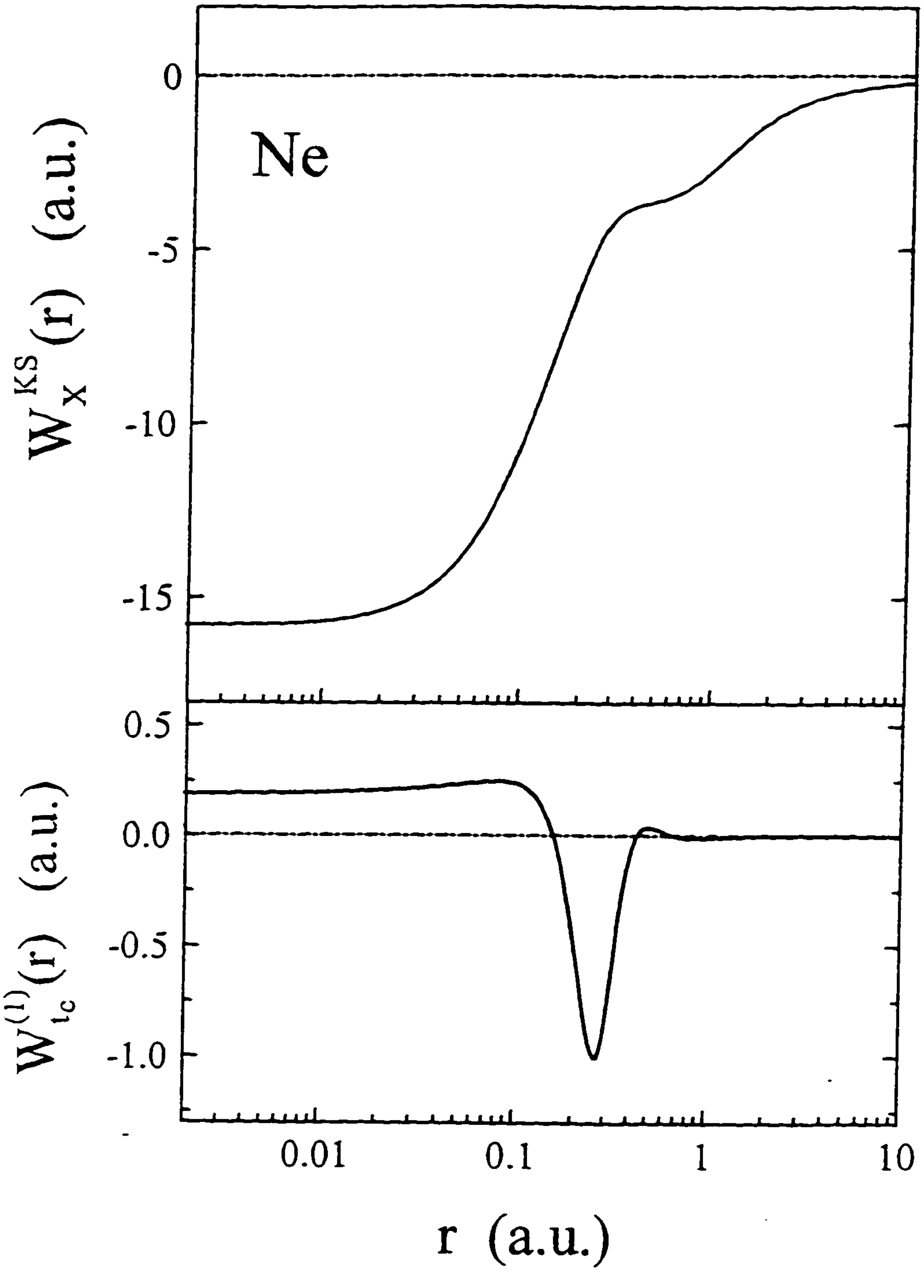

Fig.22 The Pauli $W_x^{KS}(r)$ and correlation-kinetic $W_{t_c}^{(1)}(r)$ potentials for the Ne atom.

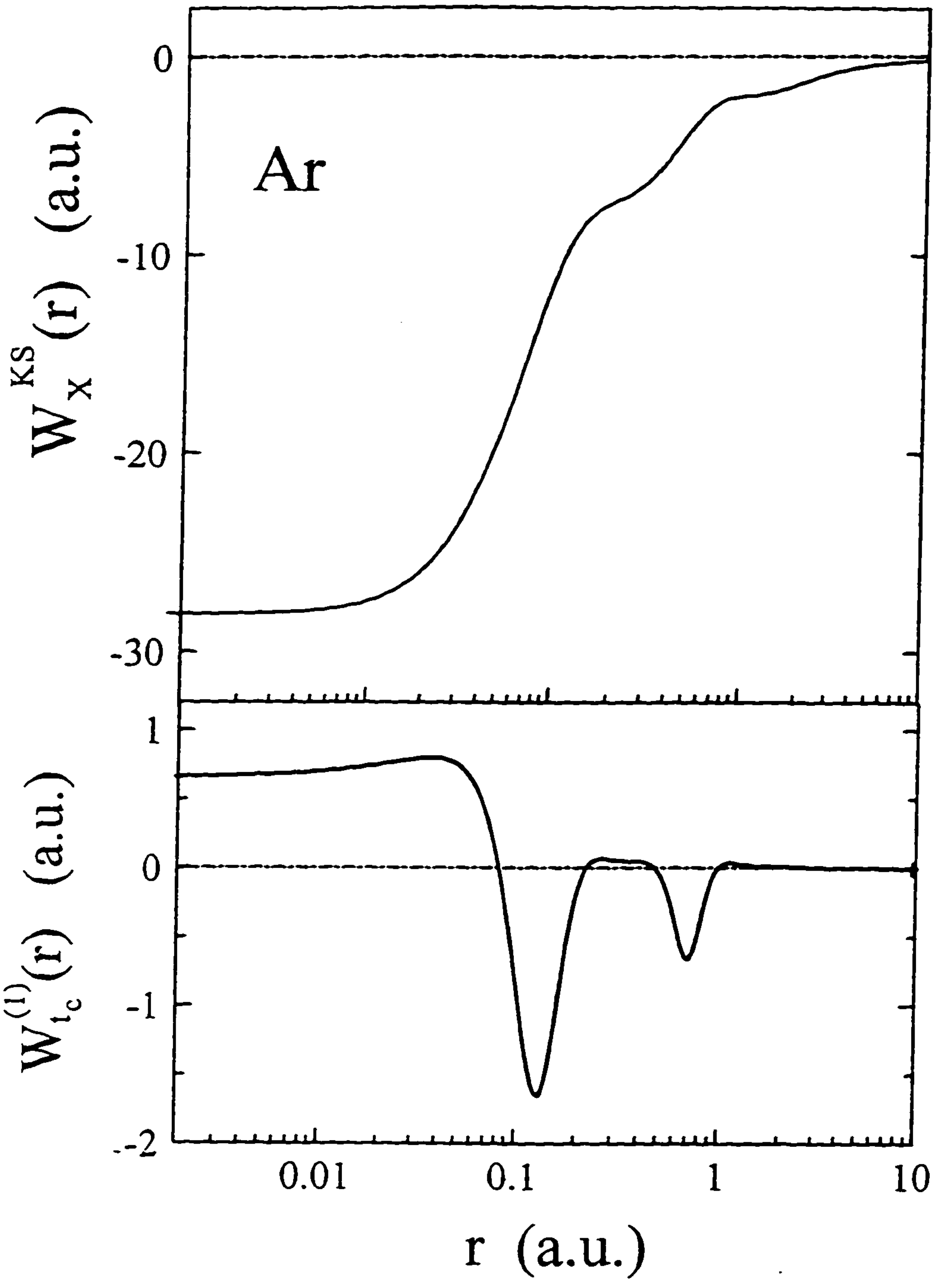

Fig.23 The Pauli $W_x^{KS}(r)$ and correlation-kinetic $W_{t_c}^{(1)}(r)$ potentials for the Ar atom.

effects. These components of the potential $v_x(\mathbf{r})$ arise respectively from fields $\mathcal{E}_x^{KS}(\mathbf{r})$ and $\mathbf{Z}_{t_c}^{(1)}(\mathbf{r})$ representative of these correlations. In this chapter we have studied the structure of the correlation-kinetic field $\mathbf{Z}_{t_c}^{(1)}(\mathbf{r})$ and potential $W_{t_c}^{(1)}(\mathbf{r})$ as applied to finite atomic and extended metal surface systems. For these systems, this field and potential are about an order of magnitude smaller than the corresponding Pauli components. In atoms, the field $\mathbf{Z}_{t_c}^{(1)}(\mathbf{r})$ exists principally in the intershell regions and is oscillatory there. This then gives rise to a trough in the resulting potential $W_{t_c}^{(1)}(\mathbf{r})$ in these regions. Since the Pauli component $W_x^{KS}(\mathbf{r})$ is monotonic with positive slope everywhere, the ***intershell bumps of the KS potential*** $v_x(\mathbf{r})$ ***can now be understood to be entirely a consequence of correlation-kinetic effects.*** Although there is a small component of the field $\mathbf{Z}_{t_c}^{(1)}(\mathbf{r})$ in the deep interior of atoms, this field is ***short-ranged***, vanishing within the last occupied shell. The asymptotic structure $-1/r$ of $v_x(\mathbf{r})$ in the classically forbidden region is therefore due entirely to its Pauli component $W_x^{KS}(\mathbf{r})$. Since the field $\mathbf{Z}_{t_c}^{(1)}(\mathbf{r})$ in atoms is small and short-ranged, the KS potential $v_x(\mathbf{r})$ can be approximated accurately by its Pauli component $W_x^{KS}(\mathbf{r})$. This is borne out in the literature (Sahni et. al., 1992; Li et. al., 1989). For example, total ground-state energies of atoms with this approximation lie within 25ppm of those of the OPM, being within 5ppm for atoms heavier than Kr.

At a metal surface, the correlation-kinetic field $\mathbf{Z}_{t_c}^{(1)}(\mathbf{r})$ is concentrated mainly in the surface region. The field, however, is ***long-ranged***. It decays asymptotically in the vacuum as $\alpha_{t_c}^{(1)}/x^2$, with the coefficient $\alpha_{t_c}^{(1)}$ dependent upon the metal Fermi energy and surface barrier height. It also extends deep into the metal, exhibiting the requisite Bardeen-Friedel oscillations there. The resulting correlation-kinetic potential $W_{t_c}^{(1)}(\mathbf{r})$ is therefore also ***long-ranged*** in the vacuum with a structure of $(\alpha_{t_c}^{(1)}/x)$. Further, it too exhibits the Bardeen-Friedel oscillations in the metal, and has a finite positive limiting value in the metal bulk. The Pauli component $W_x^{KS}(\mathbf{r})$ is also long-ranged, with a $-x^{-1}$ image-potential-like structure in the vacuum similar to that of the KS potential $v_x(\mathbf{r})$, but with a decay coefficient that is different. In the metal bulk, $W_x^{KS}(\mathbf{r})$ also has a finite (negative) limiting value which is close to but less than that of $v_x(\mathbf{r})$ which is $-k_F/\pi$. Thus, although the contribution of $v_x(\mathbf{r})$ to properties such as the surface energy and work function will be due principally to its Pauli component, we expect the correlation-kinetic contribution in this instant to be not insignificant.

CHAPTER VIII

ASYMPTOTIC STRUCTURE OF THE KOHN-SHAM CORRELATION POTENTIAL AND 'IMAGE' CHARGE AT A METAL SURFACE

8.1 Asymptotic Structure of the Kohn-Sham Correlation Potential at a Metal Surface

As derived in the previous chapters, the Slater potential $V_x^S(\boldsymbol{r})$, and the KS exchange potential $v_x(\boldsymbol{r})$ and its Pauli $W_x^{KS}(\boldsymbol{r})$ and correlation-kinetic $W_{t_c}^{(1)}(\boldsymbol{r})$ components, all vanish asymptotically as $-x^{-1}$ (or x^{-1}) but with different decay coefficients. If it is now ***assumed*** that the asymptotic structure of the KS exchange-correlation potential is the image potential, then the KS correlation potential $v_c(\boldsymbol{r})$ is also image-potential-like decaying as

$$\underset{x \to \infty}{v_c(\boldsymbol{r})} = -\frac{\alpha_{KS,c}(\beta)}{x} \quad , \qquad \text{(VIII-1)}$$

where the decay coefficient

$$\alpha_{KS,c}(\beta) = \left[1 - 4\alpha_{KS,x}(\beta)\right]/4 \quad , \qquad \text{(VIII-2)}$$

with $\alpha_{KS,x}(\beta)$ as defined by Eq. (IV-14). Note that the potential $v_c(\boldsymbol{r})$ then depends upon the metal properties through the parameter β.

In Fig. 24 we plot the coefficient $\alpha_{KS,c}(\beta)$ as a function of the parameter β. For completeness the Slater $\alpha_S(\beta)$, KS exchange $\alpha_{KS,x}(\beta)$, the Pauli $\alpha_W(\beta)$ and

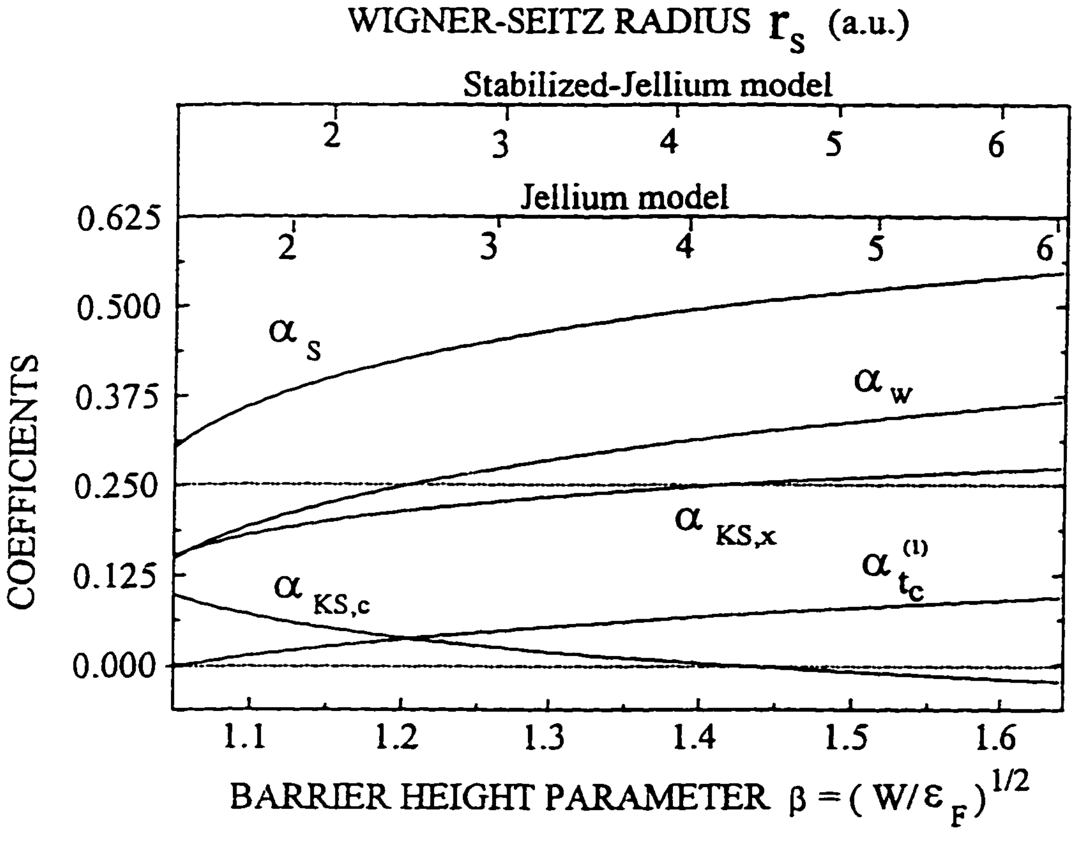

Fig. 24 Asymptotic structure coefficients $\alpha_S(\beta)$, $\alpha_{KS,x}(\beta)$, $\alpha_W(\beta)$, $\alpha_{t_c}^{(1)}(\beta)$, and $\alpha_{KS,c}(\beta)$ as function of barrier height parameter $\beta = (W/\epsilon_F)^{1/2}$, where W is the barrier height and ϵ_F the Fermi energy. Corresponding values of the Wigner-Seitz radius r_s for jellium and structureless-pseudopotential models over the metallic range of densities are also given. The relationship between r_s and β is via self-consistent calculations in the local density approximation for exchange-correlation.

correlation-kinetic $\alpha_{t_c}^{(1)}(\beta)$ component coefficients are also plotted. The Wigner-Seitz radii r_s for the jellium and structureless pseudopotential models are also quoted, where the relationship between r_s and β is as described previously. The corresponding values of the coefficients for $r_s = 2$, 4 and 6 in the jellium model are all given in Table III.

TABLE III

The asymptotic structure coefficients of the Slater potential $V_x^S(\mathbf{r})$: $\alpha_S(\beta)$, the KS exchange potential $v_x(\mathbf{r})$: $\alpha_{KS,x}(\beta)$, the potential $W_x^{KS}(\mathbf{r})$: $\alpha_W(\beta)$, the potential $W_{t_c}^{(1)}(\mathbf{r})$: $\alpha_{t_c}^{(1)}(\beta)$, and the KS correlation potential $v_c(\mathbf{r})$: $\alpha_{KS,c}(\beta)$, as a function of the Wigner-Seitz radius r_s for the jellium metal surface. The parameter $\beta = (W/\epsilon_F)^{1/2}$, where W is the barrier height and ϵ_F the Fermi energy. The relationship between the parameters β and r_s, is determined via a self-consistent calculation within the local density approximation.

Coefficients	Wigner-Seitz radius r_s (a.u.)		
	2	4	6
$\alpha_S(\beta)$	0.390	0.496	0.548
$\alpha_{KS,x}(\beta)$	0.195	0.248	0.274
$\alpha_W(\beta)$	0.217	0.315	0.368
$\alpha_{t_c}^{(1)}(\beta)$	0.022	0.066	0.094
$\alpha_{KS,c}(\beta)$	0.055	0.002	-0.024

For these values of r_s, the correlation potential coefficient $\alpha_{KS,c}(\beta)$ is 0.055, 0.002, and -0.024, respectively. Thus, when KS exchange and correlation are considered separately, the contribution of $v_c(\boldsymbol{r})$ to the asymptotic image potential structure is weak, being an order of magnitude smaller. For stable jellium ($r_s \sim 4.1$) the image structure is entirely due to the KS exchange potential.

As noted in the introduction, there is at present no rigorous analytical derivation of the asymptotic structure of the KS exchange-correlation potential $v_{xc}(\boldsymbol{r})$ or that of its correlation component $v_c(\boldsymbol{r})$ at a semi-infinite metal surface. Equivalently, in terms of the quantal interpretation, the structures of the work $W_{xc}(\boldsymbol{r})$, $W_c^{KS}(\boldsymbol{r})$, and $W_{t_c}(\boldsymbol{r})$ are unknown. What we do understand at this juncture is that the KS exchange potential $v_x(\boldsymbol{r})$ decays asymptotically as $-x^{-1}$, that this structure is due primarily to Pauli correlations via the work $W_x^{KS}(\boldsymbol{r})$, but that there is a finite correlation-kinetic contribution through the work $W_{t_c}^{(1)}(\boldsymbol{r})$. If, however, it is assumed that the asymptotic structure of $v_{xc}(\boldsymbol{r})$ is the image potential, then that of its component $v_c(\boldsymbol{r})$ is known and seen to contribute weakly to this structure. The separate contributions of Coulomb correlations via $W_c^{KS}(\boldsymbol{r})$ and the correlation-kinetic component $W_{t_c}(\boldsymbol{r})$ are even then still unknown.

8.2 'Image' Charge at a Metal Surface

One of the issues addressed in this thesis is the structure of the KS exchange-correlation potential $v_{xc}(\boldsymbol{r})$ for asymptotic positions of the electron in the classically forbidden region outside a metal surface, and the correlations which contribute to it. The asymptotic electron is here considered part of the N-electron nonuniform density system at the surface. The problem thus differs from that of the response of the N-electron metal to an ***external*** test charge in which the test charge is treated classically. In the latter case, there is a screening or image charge that is induced and localized at the surface. The structure of this charge is known exactly in classical physics and has also been determined (Lang and Kohn, 1973) within the local density approximation for exchange and correlation in KS theory. The work done to move the test charge in the field of the dynamic image charge is the image potential $-1/4x$. (In the density-functional theory calculation, the center of mass of the image charge defines the effective location of the metal surface, which then is the reference position for the image potential). The image potential structure thus calculated is, of course, a consequence of Coulomb correlations.

For the case when the asymptotic electron is considered part of the N-electron nonuniform system, it is also possible to think in terms of an 'image' charge localized to the surface giving rise to the asymptotic effective potential. Let us assume that the asymptotic structure of $v_{xc}(\boldsymbol{r})$ is the image potential, and therefore independent of any metal parameters. (Recall that the asymptotic structure of the KS exchange potential $v_x(\boldsymbol{r})$, and its Pauli $W_x^{KS}(\boldsymbol{r})$ and correlation-kinetic $W_{t_c}^{(1)}(\boldsymbol{r})$ components, all depend upon the metal Fermi energy and surface barrier height). Now the potential $v_{xc}(\boldsymbol{r})$ is the sum of the Pauli $W_x^{KS}(\boldsymbol{r})$, Coulomb $W_c^{KS}(\boldsymbol{r})$ and correlation-kinetic $W_{t_c}(\boldsymbol{r})$ work done (see Eq.

(II-73)). In turn, the total charge of the quantal Fermi-Coulomb $\rho_{xc}(\mathbf{r},\mathbf{r}')$ and KS Fermi $\rho_x^{KS}(\mathbf{r},\mathbf{r}')$ holes is -e, where e is the electronic charge, whereas that of the KS Coulomb hole $\rho_c^{KS}(\mathbf{r},\mathbf{r}')$ is zero. For asymptotic positions of the electron, the Fermi hole is ***delocalized*** and spread throughout the crystal. As such the field $\mathcal{E}_c^{KS}(\mathbf{r})$ due to the Coulomb hole can be thought of as being comprised of two components. The first due to the ***delocalized*** part of the Coulomb hole (of charge +e) in the metal bulk, and the second due to that part of the Coulomb hole (of charge -e) ***localized*** about the surface region. The component due to the delocalized part of the Coulomb hole then screens out the contribution of the delocalized Fermi hole field $\mathcal{E}_x^{KS}(\mathbf{r})$ to the image tail. With the added assumption that the correlation-kinetic field $\mathbf{Z}_{t_c}(\mathbf{r})$ decays faster than $-x^{-2}$, it is then the component due to the ***surface localized part*** of the Coulomb hole that gives rise to the image potential structure of $v_{xc}(\mathbf{r})$, and which therefore constitutes the 'image' charge at the surface. With this interpretation, the image potential structure can be attributed to Coulomb correlations, but only to those which contribute to that ***part*** of the Coulomb hole localized to the surface. In this manner, the asymptotic structure is also independent of metal parameters, and therefore the same for all metals.

CHAPTER IX

SUMMARY, CONCLUSIONS AND FUTURE WORK

In this thesis we have studied the nonuniform electron density system at metal surfaces, with the metal being represented by the jellium and structureless pseudopotential models. The study is within the context of both conventional Hohenberg-Kohn-Sham density functional theory as well as its recently explained (Sahni, 1997; ibid. 1996) rigorous physical interpretation. In conventional Kohn-Sham theory, the yet unknown exchange-correlation energy functional $E_{xc}^{KS}[\rho]$ of the density $\rho(\mathbf{r})$ and its functional derivative (potential) $v_{xc}(\mathbf{r}) = \delta E_{xc}^{KS}[\rho] / \delta\rho(\mathbf{r})$ incorporate correlations due to the Pauli exclusion principle, Coulomb repulsion, and the correlation contribution to the kinetic energy. The physical interpretation explains how these correlations are ***explicitly*** represented in the energy functional and its derivative. This description is in terms of fields and their sources which in turn are quantum-mechanical expectations of Hermitian operators. In this manner it is then possible to understand surface properties in terms of the correlations which contribute to them.

The leading term of the KS exchange potential $v_x(\mathbf{r}) = \delta E_x^{KS}[\rho]/\delta\rho(\mathbf{r})$, where $E_x^{KS}[\rho]$ is the KS exchange energy functional, is $\frac{1}{2} V_x^S(\mathbf{r})$ with $V_x^S(\mathbf{r})$ being the Slater potential. We have first derived the ***exact analytical*** asymptotic structure of $V_x^S(\mathbf{r})$ in the classically forbidden region. This result is valid for the ***fully self-consistently*** determined Slater orbitals. The structure of the potential is image-potential-like of the form

$-\alpha_S(\beta)/x$, where the parameter β^2 is the ratio of the metal surface barrier height to the Fermi energy. From an integral equation relating the KS exchange potential $v_x(\boldsymbol{r})$ to the exchange component of the many-body theory self-energy, we have also derived the ***exact analytical*** asymptotic structure of $v_x(\boldsymbol{r})$ in the vacuum. This structure is also image-potential-like of the form $-\alpha_{KS,x}(\beta)/x$ and valid for the ***fully self-consistently*** determined KS orbitals. It turns out that the coefficient $\alpha_{KS,x}(\beta) = \frac{1}{2}\alpha_S(\beta)$. Thus, at a metal surface, the KS exchange potential $v_x(\boldsymbol{r})$ decays as $\frac{1}{2}V_x^S(\boldsymbol{r})$. (This contrasts with the case of atoms, molecules, and metallic clusters where $v_x(\boldsymbol{r})$ decays as $V_x^S(\boldsymbol{r})$, the asymptotic structure of these potentials then being $-1/r$).

For metallic densities (r_s =2.0–6.0), the value of the coefficient $\alpha_{KS,x}(\beta)$ ranges from 0.195 to 0.274. It is precisely 0.250 for $\beta=\sqrt{2}$ corresponding to an $r_s \sim 4.1$ which is the approximate value for which jellium metal is stable. If it is ***assumed*** that the asymptotic structure of the KS exchange-correlation potential $v_{xc}(\boldsymbol{r})$ is the image potential, then the correlation potential too decays as $-\alpha_{KS,c}(\beta)/x$, where $\alpha_{KS,c}=[1-4\alpha_{KS,x}(\beta)]/4$, and is dependent on the metal parameters. The coefficient $\alpha_{KS,c}(\beta)$, however is an ***order of magnitude*** smaller than the exchange coefficient $\alpha_{KS,x}(\beta)$. The KS theory correlation contribution to the image potential is thus very small, the principal contribution to this structure being KS exchange.

The physical interpretation of the KS exchange potential $v_x(\boldsymbol{r})$ shows that it is comprised of a term $W_x^{KS}(\boldsymbol{r})$ representative of Pauli correlations, and a term $W_{t_c}^{(1)}(\boldsymbol{r})$ that constitutes ***part*** of the total correlation-kinetic contribution $W_{t_c}(\mathbf{r})$ We have derived the ***exact analytical*** asymptotic structure in the vacuum of both $W_x^{KS}(\mathbf{r})$ and $W_{t_c}^{(1)}(\mathbf{r})$, and shown them to be of the form $-\alpha_W(\beta)/x$ and $\alpha_{t_c}^{(1)}(\beta)/x$, respectively. These results too are valid for the ***self-consistently*** determined KS orbitals. We have also determined these components of $v_x(\mathbf{r})$ at and about the metal surface employing accurate KS orbitals. It turns out that although the structure of $v_x(\mathbf{r})$ about the surface and asymptotically in the vacuum and metal bulk regions is comprised primarily of its Pauli component, the correlation-kinetic contribution is not insignificant for medium and low density metals. It is only for high density systems ($r_s \leq 2.0$) that $v_x(\mathbf{r})$ is represented essentially by its Pauli component $W_x^{KS}(\mathbf{r})$. Thus, the uniform electron gas result of $-k_F/\pi$ for the KS exchange potential $v_x(\mathbf{r})$, which is the asymptotic metal bulk value, is not a consequence of Pauli correlations alone as is presently thought to be the case. There is also a small correlation-kinetic contribution. The Pauli and correlation-kinetic components of $v_x(\mathbf{r})$ in the metal-bulk have now been quantified.

We have also determined the Pauli $W_x^{KS}(\mathbf{r})$ and correlation-kinetic $W_{t_c}^{(1)}(\mathbf{r})$ components of $v_x(\mathbf{r})$ in atoms. We show that in contrast to the metal surface case where the correlation-kinetic part is ***long-ranged*** in the classically forbidden region, in atoms it is ***short-ranged*** decaying well within the last occupied shell. The correlation-kinetic contribution to the KS exchange potential is negligible in atoms. At a metal surface this component is far more significant as it is finite throughout space. Our calculations also explain that the intershell bumps in the structure of KS exchange potential $v_x(\mathbf{r})$ in atoms are a consequence of correlation-kinetic effects.

Based on the exact analytical result derived for the KS exchange potential $v_x(\mathbf{r})$ in the vacuum, it is possible to provide an alternative 'classical' interpretation of the asymptotic image potential structure of the exchange-correlation potential $v_{xc}(\mathbf{r})$ in terms of an 'image' charge localized to the surface region. The (assumed) image-potential structure of $v_{xc}(\mathbf{r})$ is ***independent*** of metal parameters and the same for all metals. Recall that $v_{xc}(\mathbf{r})$ is the sum of the work done $W_{xc}(\mathbf{r})$ in the field of the Fermi-Coulomb charge $\rho_{xc}(\mathbf{r},\mathbf{r}')$ obtained by the Coulomb's law, and the work $W_{t_c}(\mathbf{r})$ due to correlation-kinetic effects. For asymptotic positions of the electron in the vacuum, the Fermi-Coulomb hole is localized about the surface, an idea originally enunciated by Bardeen (Bardeen, 1964). However, a slightly deeper analysis can now be made. Since the Fermi hole $\rho_x^{KS}(\mathbf{r},\mathbf{r}')$ is ***delocalized*** in the metal for these asymptotic positions of the electron, we can surmise the structure of the Coulomb hole $\rho_c^{KS}(\mathbf{r},\mathbf{r}')$ as having a component ***delocalized*** in the metal and one that is ***localized*** to the surface. The field due to the delocalized part of the Coulomb hole screens out that of the delocalized Fermi hole. As such the asymptotic structure of $W_{xc}(z)$ arises from that part of the Coulomb hole or 'image' charge (of total charge -e) that is localized about the surface. For the determination of the asymptotic structure of $v_{xc}(z)$, we must also know how the correlation-kinetic work $W_{t_c}(z)$ decays. If the asymptotic structure of $v_{xc}(z)$ is the image potential due to the localized component of the Coulomb hole, then the asymptotic structure of $W_{t_c}(z)$ must decay more rapidly than x^{-1}. Thus, via this interpretation, the asymptotic structure of $v_{xc}(z)$ is due to the field determined by Coulomb's law from the localized component of the Coulomb hole charge. This field is not an induced field, but one that is an intrinsic property of the nonuniform electron density system at a metal-vacuum interface.

Finally, we have derived an approximate KS exchange potential $v_x^{(0)}(\mathbf{r})$ from the exact exchange energy functional $E_x^{KS}[\rho]$ via a restricted class of density variations. In this manner, the rigor of the Hohenberg-Kohn theorems is preserved, and the bounds to the total energy thus obtained will be rigorous. This expression is also shown to satisfy various integral and differential sum rules, and to possess the correct asymptotic structure in the vacuum and metal bulk regions. The expression has been employed with accurate KS orbitals to determine the structure of the correlation-kinetic component of the KS exchange potential. An approximate exchange and correlation energy functional are also constructed such that their functional derivative too possesses the correct asymptotic structure in both the classically forbidden and metal-bulk regions. The use of these energy functionals and potentials for the determination of the surface energy, curvature energy, work function of metals is in progress.

As discussed above, the asymptotic structure of $v_{xc}(\mathbf{r})$ in the vacuum can be thought of as arising from that ***part*** of the Coulomb hole localized to the surface, provided there is no correlation-kinetic contribution asymptotically. A further understanding of the overall structure of $v_c(\mathbf{r})$ and properties such as the surface correlation energy can therefore be achieved by determinig the structure of the Coulomb hole charge $\rho_c^{KS}(\mathbf{r},\mathbf{r}')$ as a function of electron position. (See (Slamet and Sahni, 1995) for such a study in atoms). This would also show how, for electron positions in the vacuum, the field due to the Coulomb hole component delocalized in the metal bulk screens out that of the delocalized Fermi hole. The work done in the field of the Coulomb hole component localized to the surface region is then the asymptotic structure of the Coulomb correlation part of $v_{xc}(\mathbf{r})$ in the vacuum. One approach to determining an accurate approximation to the Coulomb hole is to combine the random phase (Wikborg and Inglesfield, 1975) and generalized gradient (Perdew, 1993) expansion approximations. The former represents long-range and the latter short-range correlations accurately. Another approach would be to determine the quantal Fermi-Coulomb hole via a Monte Carlo calculation, and then subtract from it the KS Fermi hole. The KS orbitals and Fermi hole could be obtained from a model effective potential by adjusting the parameters so that the density is the same as that of the interacting system.

APPENDIX 1

INTEGRAL $J(q,z)$ OF EQ.(III-23) FOR ORBITALS OF THE FINITE LINEAR POTENTIAL MODEL

The solution of the integral

$$J(q,z) = 2\int_{-\infty}^{\infty} dz' e^{-q|z-z'|} \phi_k(z')\phi_{k'}^{*}(z') \quad ,$$

for the orbitals $\phi_k(z)$ of Eq. (III-25) of the finite-linear-potential model is the following.

For $z \leq 0$

$$\begin{aligned} J(q,z) = 2 & \left[\frac{q\cos(k_- z + \delta_-)}{q^2 + k_-^2} - \frac{q\cos(k_+ z + \delta_+)}{q^2 + k_+^2} \right] \\ & + e^{qz} \left[\frac{k_- \sin\delta_- - q\cos\delta_-}{q^2 + k_-^2} - \frac{k_+ \sin\delta_+ - q\cos\delta_+}{q^2 + k_+^2} \right. \\ & + \frac{2D_k D_k'}{q + \kappa_k + \kappa_k'} e^{-(q+\kappa_k+\kappa_{k'})z_0} \\ & \left. + 2\int_0^{z_0} dz' e^{-qz'} \left\{ B_k \mathrm{Ai}(\zeta'_k) + C_k \mathrm{Bi}(\zeta'_k) \right\} \left\{ B_k' \mathrm{Ai}(\zeta'_{k'}) + C_{k'} \mathrm{Bi}(\zeta'_{k'}) \right\} \right] \quad . \end{aligned}$$

For $0 < z < z_b$

$$\begin{aligned}
J(q,z) = e^{-qz} & \left[\frac{q\cos\delta_- + k_-\sin\delta_-}{q^2 + k_-^2} - \frac{q\cos\delta_+ + k_+\sin\delta_+}{q^2 + k_+^2} \right. \\
& \left. + 2\int_0^{z_b} dz' e^{qz'} \left\{ B_k \mathrm{Ai}(\zeta'_k) + C_k \mathrm{Bi}(\zeta'_k) \right\} \left\{ B_k' \mathrm{Ai}(\zeta'_{k'}) + C_{k'} \mathrm{Bi}(\zeta'_{k'}) \right\} \right] \\
+ e^{qz} & \left[\frac{2D_k D_{k'}}{q + \kappa_k + \kappa_{k'}} e^{-(q+\kappa_k+\kappa_{k'})z_b} \right. \\
& \left. + 2\int_z^{z_b} dz' e^{-qz'} \left\{ B_k \mathrm{Ai}(\zeta'_k) + C_k \mathrm{Bi}(\zeta'_k) \right\} \left\{ B_{k'} \mathrm{Ai}(\zeta'_{k'}) + C_{k'} \mathrm{Bi}(\zeta'_{k'}) \right\} \right] .
\end{aligned}$$

For $z \geq z_b$

$$\begin{aligned}
J(q,z) = e^{-qz} & \left[\frac{q\cos\delta_- + k_-\sin\delta_-}{q^2 + k_-^2} - \frac{q\cos\delta_+ + k_+\sin\delta_+}{q^2 + k_+^2} \right. \\
& + 2\int_0^{z_b} dz' e^{qz'} \left\{ B_k \mathrm{Ai}(\zeta'_k) + C_k \mathrm{Bi}(\zeta'_k) \right\} \left\{ B_k' \mathrm{Ai}(\zeta'_{k'}) + C_{k'} \mathrm{Bi}(\zeta'_{k'}) \right\} \\
& \left. - \frac{2D_k D_{k'}}{q - \kappa_k - \kappa_{k'}} e^{(q-\kappa_k-\kappa_{k'})z_b} \right] \\
& + \frac{4qD_k D_{k'}}{q^2 - (\kappa_k + \kappa_{k'})^2} e^{-(\kappa_k+\kappa_{k'})z} .
\end{aligned}$$

In the above expressions, $k_\mp = k' \mp k$ and $\delta_\mp = \delta(k') \mp \delta(k)$.

APPENDIX 2

INTEGRAL $M(q, z)$ OF EQ.(V-8) FOR ORBITALS OF THE FINITE LINEAR POTENTIAL MODEL

The solution of the integral

$$M(q, z) = 2\int_{-\infty}^{\infty} dz' \operatorname{sgn}(z - z') e^{-q|z-z'|} \phi_k(z') \phi^*_{k'}(z') \quad ,$$

for the orbitals $\phi_k(z)$ of Eq. (III-25) of the finite-linear-potential model is the following.

For $z \leq 0$

$$\begin{aligned} M(q, z) = 2 \Bigg[& \frac{k_- \sin(k_- z + \delta_-)}{q^2 + k_-^2} - \frac{k_+ \sin(k_+ z + \delta_+)}{q^2 + k_+^2} \\ & - e^{qz} \left[\frac{k_- \sin\delta_- - q\cos\delta_-}{q^2 + k_-^2} + \frac{k_+ \sin\delta_+ - q\cos\delta_+}{q^2 + k_+^2} \right. \\ & + \frac{2D_k D_k'}{q + \kappa_k + \kappa_k'} e^{-(q + \kappa_k + \kappa_{k'}) z_0} \\ & \left. + 2\int_0^{z_0} dz' e^{-qz'} \left\{ B_k \operatorname{Ai}(\zeta'_k) + C_k \operatorname{Bi}(\zeta'_k) \right\} \left\{ B_k' \operatorname{Ai}(\zeta'_{k'}) + C_{k'} \operatorname{Bi}(\zeta'_{k'}) \right\} \right] \end{aligned} \quad .$$

For $0 < z < z_b$

$$
\begin{aligned}
M(q,z) = e^{-qz}\Bigg[& \frac{q\cos\delta_- + k_-\sin\delta_-}{q^2+k_-^2} - \frac{q\cos\delta_+ + k_+\sin\delta_+}{q^2+k_+^2} \\
& + 2\int_0^{z_b} dz' e^{qz'} \left\{B_k \mathrm{Ai}(\zeta'_k) + C_k \mathrm{Bi}(\zeta'_k)\right\} \left\{B_k' \mathrm{Ai}(\zeta'_{k'}) + C_{k'} \mathrm{Bi}(\zeta'_{k'})\right\}\Bigg] \\
& - e^{qz}\Bigg[\frac{2D_k D_{k'}}{q+\kappa_k+\kappa_{k'}} e^{-(q+\kappa_k+\kappa_{k'})z_b} \\
& + 2\int_z^{z_b} dz' e^{-qz'} \left\{B_k \mathrm{Ai}(\zeta'_k) + C_k \mathrm{Bi}(\zeta'_k)\right\} \left\{B_{k'} \mathrm{Ai}(\zeta'_{k'}) + C_{k'} \mathrm{Bi}(\zeta'_{k'})\right\}\Bigg] \quad .
\end{aligned}
$$

For $z \geq z_b$

$$
\begin{aligned}
M(q,z) = e^{-qz}\Bigg[& \frac{q\cos\delta_- + k_-\sin\delta_-}{q^2+k_-^2} - \frac{q\cos\delta_+ + k_+\sin\delta_+}{q^2+k_+^2} \\
& + 2\int_0^{z_b} dz' e^{qz'} \left\{B_k \mathrm{Ai}(\zeta'_k) + C_k \mathrm{Bi}(\zeta'_k)\right\} \left\{B_k' \mathrm{Ai}(\zeta'_{k'}) + C_{k'} \mathrm{Bi}(\zeta'_{k'})\right\} \\
& - \frac{2D_k D_{k'}}{q-\kappa_k-\kappa_{k'}} e^{(q-\kappa_k-\kappa_{k'})z_b}\Bigg] \\
& - \frac{4(\kappa_k+\kappa_{k'})D_k D_{k'}}{q^2-(\kappa_k+\kappa_{k'})^2} e^{-(\kappa_k+\kappa_{k'})z} \quad .
\end{aligned}
$$

In the above expressions, $k_\mp = k' \mp k$ and $\delta_\mp = \delta(k') \mp \delta(k)$.

APPENDIX 3

EXCHANGE POTENTIALS IN INFINITE BARRIER MODEL

For the infinite barrier model (Bardeen, 1936), the effective potential $v_{eff}(r)$ in which electrons move is $v_{eff}(r) = 0$ for $x \leq 0$, and ∞ for $x > 0$, so that $\phi_k(x) = \theta(-x)\sin kx$. Thus, the density and Dirac density matrix are, respectively,

$$\rho(z) = \bar{\rho}n(z) \tag{A3-1}$$

$$n(z) = 1 - \frac{3j_1(z)}{z}\ , \tag{A3-2}$$

and

$$\gamma(r,r') = 3[\rho(s) - \rho(t)], \tag{A3-3}$$

where

$$\begin{aligned} z &= 2k_F x \\ s &= k_F|r-r'| \\ t &= k_F[(r-r')^2 + 4xx']^{1/2} \end{aligned} \tag{A3-4}$$

and $j_1(x) = (\sin x - x\cos x)/x^2$ is the first-order spherical Bessel function. (Note that although in this model, the density matrix and thus the exchange energy is in terms of functions which are the same as the density function, the functional dependence of the density matrix on the density is unknown. Therefore, it is not possible to determine the functional derivative directly from the exchange-energy expression for this model potential.) From charge neutrality the jellium edge is determined to be at

$z_a = 2k_F a = -3\pi/4$. The expressions for the Slater potential $V_x^S(r)$, the approximate functional derivative $v_x^{(0)}(r)$, and the Pauli component $W_x^{KS}(r)$ of the Kohn-Sham exchange potential $v_x(r)$, and the limiting properties of this potentials are derived to be as follows.

Slater Exchange Potential (Juretschke, 1953; Miglio et.al., 1981)

$$\frac{V_x^S(z)}{(3k_F/2\pi)} = -\frac{J(z)}{n(z)} , \tag{A3-5}$$

where

$$\begin{aligned} J(z) = {} & \frac{91}{30z^4}+\frac{1}{3z^2}+1-\frac{2z}{15}Si(-z)+\frac{4}{3z}Si(-2z)- \\ & \left[\frac{16}{5z^4}-\frac{64}{15z^2}+\frac{2}{15}-\frac{4}{z^3}Si(-2z)+\frac{4}{z^4}f(z)\right]\cos z- \\ & \left[\frac{56}{5z^3}+\frac{2}{15z}+\frac{4}{z^4}Si(-2z)+\frac{4}{z^3}f(z)\right]\sin z+\left[\frac{1}{6z^4}+\frac{2}{3z^2}\right]\cos 2z+\frac{1}{3z^3}\sin 2z , \end{aligned} \tag{A3-6}$$

$$Si(-z) = \int_{-z}^{\infty} dt\frac{\sin t}{t} , \tag{A3-7}$$

$$Ci(-z) = -\int_{-z}^{\infty} dt\frac{\cos t}{t} , \tag{A3-8}$$

$$f(z) = Ci(-2z) - \ln(-2z) - C \quad , \tag{A3-9}$$

and $C = 0.5772$ is the Euler constant. The limiting value of the potential at the barrier is

$$\lim_{z \to 0} \frac{V_x^S(z)}{(3k_F/2\pi)} = -\frac{5}{9} \quad , \tag{A3-10}$$

and in the metal bulk,

$$\lim_{z \to -\infty} \frac{V_x^S(z)}{(3k_F/2\pi)} = -1 \quad , \tag{A3-11}$$

so that the difference

$$\frac{V_x^S(-\infty) - V_x^S(0)}{(3k_F/2\pi)} = -\frac{4}{9} \quad . \tag{A3-12}$$

Approximate Functional Derivative $v_x^{(0)}(r)$

$$\frac{v_x^{(0)}(r)}{(3k_F/2\pi)} = -\frac{2}{3} \cdot \frac{P(z)}{1 - j_0(z)} \quad , \tag{A3-13}$$

where

$$\begin{aligned} P(z) = {} & 1 + \frac{1}{6z^2} - \frac{z}{6} Si(-z) + \frac{1}{z} Si(-2z) + \frac{1}{2z^2} \cos 2z - \\ & \left[\frac{2}{3z^2} + \frac{1}{6} + \frac{1}{z^2} f(z) \right] \cos z - \left[\frac{7}{6z} + \frac{1}{z^2} Si(-2z) \right] \sin z \quad , \end{aligned} \tag{A3-14}$$

and $j_0(x) = \sin x/x$ is the zeroth-order spherical Bessel function. The limits at the barrier and metal bulk, respectively, are

$$\lim_{z\to 0} \frac{v_x^{(0)}(z)}{(3k_F/2\pi)} = -\frac{1}{3} \quad , \qquad \text{(A3-15)}$$

and

$$\lim_{z\to -\infty} \frac{v_x^{(0)}(z)}{(3k_F/2\pi)} = -\frac{2}{3} \quad , \qquad \text{(A3-16)}$$

so that

$$\frac{v_x^{(0)}(-\infty)-v_x^{(0)}(0)}{(3k_F/2\pi)} = -\frac{1}{3} \quad . \qquad \text{(A3-17)}$$

Pauli Component $W_x^{KS}(r)$ of the Kohn-Sham Exchange Potential $v_x(r)$

To obtain the potential $W_x^{KS}(r)$, the force field $\mathcal{E}_x^{KS}(r)$ due to the Fermi hole $\rho_x(r,r')$ must first be determined. The field $\mathcal{E}_x(z)$ in the infinite barrier model is derived as

$$\frac{\mathcal{E}_x^{KS}(z)}{(3k_F^2/2\pi)} = \frac{R(z)}{n(z)} \quad , \qquad \text{(A3-18)}$$

where

$$R(z) = \int_0^\infty \frac{ds}{s^2} \int_{h(s,z)}^{s-z} dt\, t \left[1-\frac{t^2-s^2}{z^2}\right] \left[\frac{j_1(s)}{s}-\frac{j_1(t)}{t}\right]^2 \quad , \qquad \text{(A3-19)}$$

and $h(s,z)=-s-z$ for $s<-z/2$, and s for $s>-z/2$. Evaluating this integral, we obtain

$$\begin{aligned} R(z) = &-\frac{506}{105z^5}-\frac{2}{15z^3}+\left(\frac{2}{15}-\frac{z^2}{70}\right] Si(-z)-\frac{4}{3z^2}Si(-2z)+ \\ &\left[\frac{192}{35z^5}-\frac{484}{105z^3}+\frac{17}{105z}-\frac{z}{70}-\frac{4}{z^4}Si(-2z)+\frac{4}{z^5}f(z)\right]\cos z+ \\ &\left[\frac{472}{35z^4}-\frac{187}{105z^2}-\frac{1}{70}+\frac{4}{z^5}Si(-2z)+\frac{4}{z^4}f(z)\right]\sin z- \\ &\left[\frac{2}{3z^5}+\frac{2}{3z^3}\right]\cos 2z-\frac{4}{3z^4}\sin 2z \quad . \end{aligned} \tag{A3-20}$$

The limiting value of the field at the barrier is

$$\lim_{z\to 0}\frac{\mathscr{E}_x^{KS}(z)}{(3k_F^2/2\pi)} = -\frac{\pi}{21} \ , \tag{A3-21}$$

and its structure in the metal bulk is

$$\frac{\mathscr{E}_x^{KS}(z)}{(3k_F^2/2\pi)} \sim \frac{2j_0(z)}{z} \ . \tag{A3-21}$$

The potential $W_x(z)$ is then obtained as

$$W_x^{KS}(z) = -\int_0^z \mathscr{E}_x^{KS}(z')dz' \ . \tag{A3-22}$$

It has not been possible to solve this integral analytically, and as such, it is solved numerically. The solution leads to the result

$$\frac{W_x^{KS}(-\infty)-W_x^{KS}(0)}{(3k_F^2/2\pi)} = -0.3860 \ . \tag{A3-23}$$

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