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STUDY OF ELECTRON CORRELATIONS IN NON-UNIFORM DENSITY SYSTEMS VIA THE WORK FORMALISM OF ELECTRONIC STRUCTURE

by

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Abstract

STUDY OF ELECTRON CORRELATIONS IN NON-UNIFORM DENSITY SYSTEMS VIA THE WORK FORMALISM OF ELECTRONIC STRUCTURE

by

Marlina Slamet

Adviser: Professor Viraht Sahni

In this thesis we investigate electron correlations in nonuniform density systems via the work formalism of electronic structure. In the formalism, which is founded in Schrödinger theory, the system wavefunction is determined by solution of a Sturm-Liouville-type equation over both occupied and virtual states. Both the local potential representing electron correlations in this differential equation as well as the electron interaction energy arise by Coulomb's law from a quantum-mechanical source charge distribution. This source charge is the pair-correlation density. The potential is the work done to move an electron in the force field of the pair-correlation density, whereas the energy is the energy of interaction between the electronic and pair-correlation densities. We have investigated Coulomb correlation effects in the Helium atom in its ground-state by studying the structure of the dynamic Coulomb hole charge distribution as a function of electron position, and the local correlation potential to which it gives rise. These calculations confirm the tenet of the work formalism that the asymptotic structure of the effective potential of all nonuniform density systems in the classically forbidden region is a consequence only of the Pauli exclusion principle, and thus exactly determinable. A comparison of the work formalism correlation potential to the corresponding potential of Kohn-Sham density-functional theory then leads to insights into the structure of the latter. We have also studied electron correlations within the Pauli-correlated approximation in a nonspherically symmetric system as represented by a degenerate state of the Carbon atom. These calculations demonstrate the applicability of the work formalism to such systems without having to invoke the central-field approximation. Finally, we provide insights into electron correlations in the local density approximation of Kohn-Sham theory by rederiving the equations of the approximation via the work formalism. The derivation shows the presence of correlations in addition to those assumed by Kohn-Sham theory, and this constitutes the fundamental physical reason for the success of the approximation. This latter conclusion is confirmed by a study of these correlations by application to the inhomogeneous electron gas in atoms and at metal surfaces.

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Chapter I

INTRODUCTION

The Schrödinger theory (Schrödinger, 1926) provides the basis for the determination of the electronic properties of matter. For a system of N electrons in an external potential $v_{ext}(\boldsymbol{r})$ such as the nuclear potential in atoms and molecules, or the lattice potential in clusters and solids, the Schrödinger equation is

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v_{ext}(\boldsymbol{r}_i) + \frac{1}{2} \sum_{i,j \neq i} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \right] \Psi = E \Psi \ , \qquad \textbf{(I-1)}$$

where $\Psi(x_1, x_2, \ldots x_N)$ and E are the system wavefunction and energy, respectively, the latter being the expectation value of the Hamiltonian. The electron coordinate $x \equiv \boldsymbol{r}, \zeta$ where $\boldsymbol{r}$ is its spatial and ζ its spin coordinate. Due to the presence of the ***nonlocal*** electron interaction term, this 3N-dimensional differential equation cannot be solved in closed analytical form even for the simplest of many-electron systems such as the He atom. Thus, although electron correlations due to the Pauli exclusion principle are accounted for by the requirement of antisymmetry of the wavefunction, the explicit representation of Coulomb repulsion in the wavefunction is unknown. As a consequence the wavefunction must be approximated. Since the advent of quantum mechanics various methods have been developed to obtain approximate wavefunctions of many-electron systems, such as the Hartree (Hartree, 1928 a; *ibid.*, 1928 b; *ibid.*, 1928 c), Hartree-Fock (Fock, 1930 a; *ibid.*, 1930 b; Slater, 1930), and configuration interaction approximations (Szabo and Ostlund, 1989), and correlated wavefunction (Szabo and Ostlund, 1989), many-body perturbation theory (Szabo and Ostlund, 1989), and Monte Carlo (Kalos and Whitlock, 1985) techniques. The majority of these methods are based on the variational principle for the energy and thereby lead to rigorous upper bounds to the ground-state energy.

An alternate approach to the determination of electronic structure is Hohenberg-Kohn-Sham (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) density-functional theory (Parr and Yang, 1989; Dreizler and Gross, 1990; Kryachko and Ludeña, 1990; March, 1992). According to this theory, which is also derived via the variational principle, every observable (and hence the energy) can be written as a unique functional of the electronic density $\rho(x)$ which is defined as

$$\rho(x) = N \int \Psi^*(x, x_2, x_3, \ldots x_N)\ \Psi(x, x_2, x_3, \ldots x_N)\ dx_2 \ldots dx_N\ , \qquad \text{(I-2)}$$

such that $\int \rho(x)\, dx = N$. In the corresponding Kohn-Sham theory differential equation, which is equivalent to the Euler equation for the density, the operator representing ***all*** electron correlations including the correlation contribution to the kinetic energy is ***local*** (multiplicative). This then simplifies the calculations for the determination of the density which is now obtained from a Slater determinant of Kohn-Sham orbitals. However, as a result of the application of the variational principle, the local operator (potential) has a strictly ***mathematical*** definition in terms of a functional derivative. Furthermore, it is a functional derivative of an as yet unknown "exchange-correlation" energy functional which represents Pauli and Coulomb correlations as well as the correlation-kinetic-energy contribution. In Kohn-Sham theory it is this energy functional that is approximated.. However, in approximating the energy functional, as for example in the Local Density (Parr and Yang, 1989; Dreizler and Gross, 1990; Kryachko and Ludeña, 1990; March, 1992) or Gradient (Parr and Yang, 1989; Dreizler and Gross, 1990; Kryachko and Ludeña, 1990; March, 1992) or Generalized Gradient (Perdew, 1985; Gross and Dreizler, 1994) Expansion approximations, the rigor of the Hohenberg-Kohn theorems is lost, and the bounds to the energy obtained no longer rigorous. Substantial progress (Gross and Dreizler, 1994) in the development of accurate density-functional theory exchange, correlation and exchange-correlation energy functionals as well as of the properties of the exact functionals has, however been made, and the approximate functionals employed extensively. Another approach (Solomatin *et al.*, 1994) to approximate density-functional theory whereby the bounds obtained are still rigorous is to consider, for example in exchange-only theory, the ***exact*** exchange energy functional as written in terms of the Kohn-Sham orbitals, but to derive its functional derivative for a restricted class of density variations. Thus, even though the potential obtained is approximate, the total energy is determined through the exact exchange energy functional.

Recently, a theory of electronic structure, referred to as the work formalism, has been developed by Harbola and Sahni (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola and Sahni, 1993 a), a brief review of which has been given by Sahni (1995). The work formalism, which is founded in Schrödinger theory, is derived by arguments that are entirely ***physical*** and based on Coulomb's law. It leads ***in principle*** to the system wavefunction Ψ via a Sturm-Liouville differential equation. The relationship of the work formalism to Schrödinger theory and the system wavefunction is through the pair-correlation ***density*** which constitutes the fundamental quantity in the formalism. It represents the ***quantum-mechanical source charge*** distribution which gives rise via Coulomb's law to both the electron interaction energy as well as a ***local*** potential representing electron correlations. The wavefunction is then determined by solution of the resulting Sturm-Liouville equation in which the potential depends self-consistently on the wavefunction. The basic idea underlying the work formalism is the recognition of the fact that the pair-correlation density of nonuniform density systems is a ***nonlocal*** (dynamic) charge distribution whose structure changes as a function of electron position. Thus, the potential representing electron correlations is the work done to move an electron in the force field of the pair-correlation density. The electron interaction energy is in turn the energy of interaction between the electronic and pair-correlation densities. The applications of the work formalism thus far have led to highly accurate results both in comparison to experiment as well as to those of other theories.

The work formalism also overlaps with Kohn-Sham density-functional theory in that Pauli and Coulomb correlations between the electrons are represented by a local potential. The theory thus possesses all the attributes attendant to having a multiplicative operator representing electron correlations in the differential equation governing the system. Furthermore, whereas in Kohn-Sham theory the corresponding local potential is derived variationally to be a functional derivative, the potential in the work formalism is obtained directly via Coulomb's law. Thus, the work formalism also provides a physical interpretation for the potential of Kohn-Sham theory. In recent work (Holas and March, 1995) have reaffirmed the ideas of the work interpretation of the Kohn-Sham potential.

This thesis is concerned in the first part with a study of electron correlations in nonuniform density systems via the work formalism of electronic structure. These studies in turn lead to a further understanding of the formalism itself. The thesis is also concerned with the insights that the work formalism provides into the possibly most extensively used approximation scheme in the literature, viz. the local density approximation of Kohn-Sham theory. These insights provide an understanding of the electron correlations within this approximation that is more fundamental than that achieved by Kohn-Sham theory.

We begin in chapter II with a description of the general framework of the work formalism. We also discuss the theory within the Pauli-correlated approximation, and the ***universal*** nature of the asymptotic structure of the work formalism exchange-correlation potential. For ***all*** nonuniform density systems, the asymptotic structure of the potential is a consequence ***only*** of the Pauli exclusion principle, and as such ***exactly*** determinable. We also discuss Kohn-Sham theory and the interrelationship between it and the work formalism. We conclude this chapter by a brief description of some results of the application of the work formalism to nonuniform density systems in atoms and at metallic surfaces.

The majority of the applications of the work formalism thus far have been within the Pauli-correlated approximation. In chapter III we go beyond this approximation to study Coulomb correlation effects within the work formalism by application (Slamet and Sahni, 1995 a) to the ground state of the He atom. We study the structure of the dynamic Coulomb hole charge distribution as a function of electron position, and the resulting correlation potential of the work formalism that it gives rise to. This in turn leads to a further understanding of the structure of the corresponding correlation potential of Kohn-Sham theory.

As with most theories, the application of the work formalism to atoms has been performed within the central-field model. In chapter IV we investigate (Harbola *et al.*, 1991; Slamet *et al.*, 1994 a) the work formalism for non-spherical density atoms by application to a degenerate state of the Carbon atom in the Pauli-correlated approximation. The results of these calculations then also provide the explanation for why the central-field model of atoms is accurate.

In chapter V we describe how the work formalism leads to insights into the local-density approximation for exchange and correlation of Kohn-Sham density functional theory. We begin with the Kohn-Sham theory interpretation of electron correlations within this approximation, which is that of the ***uniform*** electron gas assumed to be valid locally. We then show by ***rigorously*** rederiving the equations of the local density approximation for exchange via the work formalism, that the representation of the electron correlations is superior to that previously assumed, and that the ***nonuniformity*** of the density is in fact ***explicitly*** accounted for by a term proportional to the gradient of the density. This then is the underlying reason for the accuracy of the approximation. We then demonstrate this understanding by application to the inhomogeneous electronic system in atoms and at metal surfaces. We have also performed (Slamet and Sahni, 1991a; Slamet and Sahni, 1992a) a similar analysis of the gradient expansion approximation for exchange of Kohn-Sham theory, which in turn leads to insights into the expansions for exchange-correlation and correlation. We do not, however, include a description of this analysis here, but instead refer the reader to the original literature. In the final chapter VI we summarize our conclusions and discuss directions for future work.

Chapter II

THE WORK FORMALISM OF ELECTRONIC STRUCTURE

2.1 General Description of the Work Formalism

The fundamental quantity in the work formalism (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola and Sahni, 1993 a; Sahni, 1995) is the pair-correlation ***density*** $g(\boldsymbol{r},\boldsymbol{r}')$ which is defined in terms of the wavefunction Ψ as

$$g(\boldsymbol{r},\boldsymbol{r}') = \frac{\left\langle \Psi \mid \sum_{i,j\neq i} \delta(\boldsymbol{r}-\boldsymbol{r}_i)\,\delta(\boldsymbol{r}'-\boldsymbol{r}_j) \mid \Psi \right\rangle}{\left\langle \Psi \mid \sum_{i} \delta(\boldsymbol{r}-\boldsymbol{r}_i) \mid \Psi \right\rangle} , \qquad \textbf{(II-1)}$$

where the numerator expectation value represents the probability of simultaneously finding electrons at $\boldsymbol{r}$ and $\boldsymbol{r}'$, and the denominator expectation is the electronic density $\rho(\boldsymbol{r})$:

$$\rho(\boldsymbol{r}) = \left\langle \Psi \mid \sum_{i} \delta(\boldsymbol{r}-\boldsymbol{r}_i) \mid \Psi \right\rangle \quad . \qquad \textbf{(II-2)}$$

Thus $g(\boldsymbol{r},\boldsymbol{r}')$ is the electronic density at $\boldsymbol{r}'$ when an electron is specified as being at $\boldsymbol{r}$, and as such incorporates the effects of Pauli and Coulomb correlations between the electrons. The total charge of the pair-correlation density for arbitrary electron position is then $\int g(\boldsymbol{r},\boldsymbol{r}')\,d\boldsymbol{r}' = N-1$. (In these equations and those to follow, the spin dependence is suppressed).

The physics underlying the work formalism is based on the fact that the pair-correlation density is a ***non local*** (dynamic) charge distribution whose structure changes as a function of electron position. The dynamic nature of this distribution must therefore be incorporated in the construction of the local potential in which the electrons move. Thus, the force field $\mathscr{E}(\boldsymbol{r})$ due to this charge, which by Coulomb's law is

$$\mathscr{E}(r) = \int \frac{g(r,r')\ (r - r')}{|r - r'|^3}\, dr' \quad , \tag{II-3}$$

must first be obtained. The potential $W(\boldsymbol{r})$ is then the work done on an electron to bring it from infinity to $\boldsymbol{r}$ against the force of this field:

$$W(r) = - \int_{\infty}^{r} \mathscr{E}(r') \cdot dl' \quad . \tag{II-4}$$

The total potential in which the electrons move is thus $[v_{ext}(r) + W(r)]$, and consequently the differential equation governing the system is

$$\left[-\frac{1}{2} \nabla^2 + v_{ext}(r) + W(r) \right] \phi_i(r) = \epsilon_i\ \phi_i(r) \quad . \tag{II-5}$$

This is a Sturm-Liouville (Morse and Feshbach, 1953) differential equation whose solutions form a complete set. As such, the wavefunction Ψ can, ***in principle*** be obtained (Löwdin, 1959) as an infinite linear combination of N-electron Slater determinants $\Phi_i\{\phi_i\}$ of the spin-orbitals $\phi_i(r)$ corresponding to the occupied and virtual states of the system:

$$\psi = \sum_i B_i \Phi_i\{\phi_i\} \quad , \tag{II-6}$$

where B_i are appropriately chosen coefficients. Note that since the spin-orbitals

$\phi_i(\mathbf{r})$ are generated self-consistently from the pair-correlation density, the effects of Pauli and Coulomb correlations are ***implicitly*** incorporated in their structure. The total energy E is then the expectation value of the Hamiltonian of Eq. (I-1) taken with respect to the wavefunction ψ . The electron interaction energy E_{ee} can also be written in terms of the pair-correlation density $g(\mathbf{r},\mathbf{r}')$ as the energy of interaction between it and the electronic density ,$\rho(\mathbf{r})$ so that

$$E_{ee} = <\psi|\ \frac{1}{2} \sum_{i,j}{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\ |\psi> = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\ g(\mathbf{r},\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\ d\mathbf{r}\ d\mathbf{r}' \quad . \qquad \textbf{(II-7)}$$

Thus, the pair-correlation density constitutes the ***quantum-mechanical source charge*** distribution which gives rise to ***both*** the local potential representing the correlations between the electrons as well as the electron interaction energy. Futhermore, by definition there is no self-interaction in this source charge distribution, and thus within the work formalism.

The equations of the work formalism Eqs. (II-5) and (II-7) can be put in a more recognizable form, and one in which the relationship to the Density-Functional Theory (Dreizler and Gross, 1990; Parr and Yang, 1989; March, 1992) is more explicit, by rewriting the pair-correlation density $g(\mathbf{r},\mathbf{r}')$ at $\mathbf{r}'$ for an electron at $\mathbf{r}$ as the sum of the density $\rho(\mathbf{r}')$ and the Fermi-Coulomb hole charge $\rho_{xc}(\mathbf{r},\mathbf{r}')$:

$$g(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}') + \rho_{xc}(\mathbf{r},\mathbf{r}') \quad . \qquad \textbf{(II-8)}$$

The Fermi-Coulomb hole can therefore be seen to represent the reduction in density about an electron due to correlations resulting from the Pauli exclusion principle and Coulomb repulsion. The Fermi-Coulomb hole satisfies the charge conservation constraint

$$\int \rho_{xc}(\boldsymbol{r},\boldsymbol{r}')\, d\boldsymbol{r}' = -1 \quad , \qquad \textbf{(II-9)}$$

for all electron positions $\boldsymbol{r}$. The force field $\mathscr{E}(\boldsymbol{r})$ can then be written as the sum of the Hartree $\mathscr{E}_H(\boldsymbol{r})$ and exchange-correlation $\mathscr{E}_{xc}(\boldsymbol{r})$ fields where

$$\mathscr{E}_H(\boldsymbol{r}) = \int \frac{\rho(\boldsymbol{r}')\,(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}' \quad \text{and} \quad \mathscr{E}_{xc}(\boldsymbol{r}) = \int \frac{\rho_{xc}(\boldsymbol{r},\boldsymbol{r}')\,(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}' . \qquad \textbf{(II-10)}$$

The potential $W(\boldsymbol{r})$ is now the sum of the potentials $W_H(\boldsymbol{r})$ and $W_{xc}(\boldsymbol{r})$ where

$$W_H(\boldsymbol{r}) = -\int_{\infty}^{\boldsymbol{r}} \mathscr{E}_H(\boldsymbol{r}') \cdot d\boldsymbol{l}' \quad \text{and} \quad W_{xc}(\boldsymbol{r}) = -\int_{\infty}^{\boldsymbol{r}} \mathscr{E}_{xc}(\boldsymbol{r}') \cdot d\boldsymbol{l}' , \qquad \textbf{(II-11)}$$

are respectively the work done on an electron against the Hartree and exchange-correlation fields. However, since the electronic density is a static charge distribution whose structure is independent of the electron position, the Hartree field can be written as $\mathscr{E}_H(\boldsymbol{r}) = -\nabla W_H(\boldsymbol{r})$ with

$$W_H(\boldsymbol{r}) = \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}' \quad , \qquad \textbf{(II-12)}$$

which then defines the scalar potential $W_H(\boldsymbol{r})$. Further, this potential $W_H(\boldsymbol{r})$ is path independent since $\nabla \times \mathscr{E}_H(\boldsymbol{r}) = 0$. With the assumption that the curl of the exchange-correlation field vanishes, i.e. so that the work is path-independent, the system differential equation is now

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\, d\boldsymbol{r}' + W_{xc}(\boldsymbol{r}) \right] \phi_i(\boldsymbol{r}) = \epsilon_i\, \phi_i(\boldsymbol{r}) . \quad \textbf{(II-13)}$$

The electron interaction energy E_{ee} is then the sum of the (Hartree) Coulomb self-energy E_H and the exchange-correlation energy E_{xc} where

$$E_H = \frac{1}{2}\int\int \frac{\rho(\boldsymbol{r})\,\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}' \quad \text{and} \quad E_{xc} = \frac{1}{2}\int\int \frac{\rho(\boldsymbol{r})\,\rho_{xc}(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}', \quad \textbf{(II-14)}$$

and where the latter is the energy of interaction between the density $\rho(\boldsymbol{r})$ and the Fermi-Coulomb hole charge $\rho_{xc}(\boldsymbol{r},\boldsymbol{r}')$.

The assumption of path-independence of the work $W_{xc}(\boldsymbol{r})$ is rigorously valid for symmetrical density systems such as spherically symmetric atoms and jellium metal surfaces and clusters, and non-spherically symmetric density systems in the central field approximation. There is as yet, however, no general proof of the path-independence of $W_{xc}(\boldsymbol{r})$ for systems of arbitrary symmetry in which the external potential is ***physically realistic***. Let us thus assume (Harbola, *et al.* 1991; Slamet *et al.*, 1994 a; Ou-Yang and Levy, 1990 a; Rasolt and Geldart, 1990; Harbola and Sahni, 1990 a) that there are systems for which the curl of the force field $\mathcal{E}_{xc}(\boldsymbol{r})$ does not vanish.

Now according to the Helmholtz theorem, the most general vector field has both a non-zero divergence and a non-zero curl, and can be derived from the negative gradient of a scalar potential and the curl of a vector potential. Therefore in general we can write the force field $\mathcal{E}_{xc}(\boldsymbol{r})$ due to the Fermi-Coulomb hole charge distribution as a sum of its irrotational $\mathcal{E}^I_{xc}(r)$ and solenoidal $\mathcal{E}^S_{xc}(r)$ components:

$$\mathcal{E}_{xc}(r) = \mathcal{E}^I_{xc}(r) + \mathcal{E}^S_{xc}(r) \tag{II-15}$$

$$= -\nabla \int \frac{\nabla' \cdot \mathcal{E}_{xc}(r')}{4\pi\,|r-r'|}\,dr' + \nabla \times \int \frac{\nabla' \times \mathcal{E}_{xc}(r')}{4\pi\,|r-r'|}\,dr' \,. \tag{II-16}$$

For systems for which the curl of the field vanishes, the solenoidal component $\mathcal{E}^S_{xc}(r)$ is obviously zero, and consequently the force field $\mathcal{E}_{xc}(r)$ is the same as its irrotational component $\mathcal{E}^I_{xc}(r)$. For systems for which the curl of the force field may not vanish (Ou-Yang and Levy, 1990 a; Rasolt and Geldart, 1990; Harbola and Sahni, 1990 a), the solenoidal component is simply ignored. As such the force field $\mathcal{E}_{xc}(r)$ for these systems is approximated as being equal to its irrotational component $\mathcal{E}^I_{xc}(r)$.

From Eq. (II-16) the irrotational component of the force field can be considered as negative gradient of a scalar effective exchange-correlation potential $W^{eff}_{xc}(r)$:

$$\mathcal{E}^I_{xc}(r) = -\nabla W^{eff}_{xc}(r) \,, \tag{II-17}$$

where the scalar potential

$$W^{eff}_{xc}(r) = \int \frac{\rho^{eff}_{xc}(r')}{|r-r'|}\,dr' \,, \tag{II-18}$$

is seen to arise from a scalar *(static)* effective Fermi-Coulomb hole source charge $\rho^{eff}_{xc}(r)$ which is

vector potential $\boldsymbol{A}_{xc}(\boldsymbol{r})$:

$$\mathcal{E}^{S}_{xc}(\boldsymbol{r}) = \nabla \times \boldsymbol{A}_{xc}(\boldsymbol{r}) \ , \tag{II-24}$$

where the vector potential

$$\boldsymbol{A}_{xc}(\boldsymbol{r}) = \int \frac{\boldsymbol{J}_{xc}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, d\boldsymbol{r}' \ , \tag{II-25}$$

is due to an exchange-correlation vector vortex source $\boldsymbol{J}_{xc}(\boldsymbol{r})$ given as

$$\boldsymbol{J}_{xc}(\boldsymbol{r}) = \frac{1}{4\pi} \nabla \times \mathcal{E}_{xc}(\boldsymbol{r}) \ . \tag{II-26}$$

The expression for the vector source can be further simplified to read

$$\boldsymbol{J}_{xc}(\boldsymbol{r}) = \frac{1}{4\pi} \int \left[\nabla \rho_{xc}(\boldsymbol{r},\boldsymbol{r}') \right] \times \frac{(\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3} \, d\boldsymbol{r}' \ . \tag{II-27}$$

The solenoidal component of the field can also be obtained directly from the vector vortex source as

$$\mathcal{E}^{S}_{xc}(\boldsymbol{r}) = \int \boldsymbol{J}_{xc}(\boldsymbol{r}') \times \frac{(\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3} \, d\boldsymbol{r}' \ . \tag{II-28}$$

It is evident that for systems (or regions of space) where the vortex source vanishes, the potentials $W^{eff}_{xc}(\boldsymbol{r})$ and $W_{xc}(\boldsymbol{r})$ are equivalent and path-independent. Thus, another way of obtaining the potential $W_{xc}(\boldsymbol{r})$ for such systems or regions (other than determining the line integral of Eq. (II-11)) is via a static effective charge distribution given by the divergence of the field due to the Fermi-Coulomb hole.

2.2 The Work Formalism in the Pauli-Correlated Approximation

When only correlations due to the Pauli exclusion principle are considered, and the ground-state wavefunction Ψ is a single Slater determinant of the occupied N spin-orbitals $\phi_i(\boldsymbol{r})$, the pair-correlation density is (from Eq. (II-1))

$$g_x(\boldsymbol{r},\boldsymbol{r}') = \rho(\boldsymbol{r}') + \rho_x(\boldsymbol{r},\boldsymbol{r}') \quad , \qquad \textbf{(II-29)}$$

where $\rho_x(\boldsymbol{r},\boldsymbol{r}')$ is the Fermi hole charge at $\boldsymbol{r}'$ for an electron at $\boldsymbol{r}$. The Fermi hole represents the reduction in density about an electron due to the Pauli-exclusion principle, and is defined in terms of the ***idempotent*** Dirac density matrix as

$$\rho_x(\boldsymbol{r},\boldsymbol{r}') = -\,|\gamma(\boldsymbol{r},\boldsymbol{r}')|^2 \,/\, 2\rho(\boldsymbol{r}) \quad , \qquad \textbf{(II-30)}$$

where $\gamma(\boldsymbol{r},\boldsymbol{r}') = \sum_i \phi_i^*(\boldsymbol{r})\,\phi_i(\boldsymbol{r}')$ with $\gamma(\boldsymbol{r},\boldsymbol{r}) = \rho(\boldsymbol{r})$. The Fermi hole satisfies the constraints of charge conservation

$$\int \rho_x(\boldsymbol{r},\boldsymbol{r}')\, d\boldsymbol{r}' = -1 \quad , \qquad \textbf{(II-31)}$$

value at electron position

$$\rho_x(\boldsymbol{r},\boldsymbol{r}) = -\,\rho(\boldsymbol{r})/2 \quad , \qquad \textbf{(II-32)}$$

and that of negativity

$$\rho_x(\boldsymbol{r},\boldsymbol{r}') \le 0 \quad . \qquad \textbf{(II-33)}$$

The local potential representing electron correlation is then $W(\boldsymbol{r}) = W_H(\boldsymbol{r}) + W_x(\boldsymbol{r})$, where the exchange potential $W_x(\boldsymbol{r})$ is the work done to move an electron in the force-field $\mathcal{E}_x(\boldsymbol{r})$ of the Fermi hole charge:

$$W_x(\boldsymbol{r}) = -\int_{\infty}^{\boldsymbol{r}} \mathcal{E}_x(\boldsymbol{r}') \cdot d\boldsymbol{l}' \quad \text{where} \quad \mathcal{E}_x(\boldsymbol{r}) = \int \frac{\rho_x(\boldsymbol{r}, \boldsymbol{r}')\,(\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\, d\boldsymbol{r}' . \qquad \textbf{(II-34)}$$

The differential equation governing the system in the Pauli-correlated approximation is then

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\, d\boldsymbol{r}' + W_x(\boldsymbol{r}) \right] \phi_i(\boldsymbol{r}) = \epsilon_i\, \phi_i(\boldsymbol{r}) . \qquad \textbf{(II-35)}$$

Note that this differential equation can also in principle be solved exactly since the dependence of the exchange potential $W_x(\boldsymbol{r})$ on the orbitals $\phi_i(\boldsymbol{r})$ is explicitly known. In practice, on application to atoms, it has been solved ***exactly*** (Li *et al.*, 1989; Sahni *et al.*, 1992). For systems for which the curl of the exchange force field does not vanish, a local effective exchange potential $W_x^{eff}(\boldsymbol{r})$ is obtained from the irrotational component of the field, or equivalently from a static effective exchange charge $\rho_x^{eff}(\boldsymbol{r}) = (1/4\pi)\, \nabla \cdot \mathcal{E}_x(\boldsymbol{r})$. Further, since the Fermi hole charge satisfies the constraint of charge conservation, so does the effective Fermi hole charge:

$$\int \rho_x^{eff}(\boldsymbol{r})\, d\boldsymbol{r} = -1 \quad . \qquad \textbf{(II-36)}$$

The electron interaction energy E_{ee} in either case is the sum of the Coulomb self energy E_H and the exchange energy E_x , where the latter is the energy of interaction between the electronic density and the Fermi hole charge: .

$$E_x = \frac{1}{2} \int\!\!\int \frac{\rho(\boldsymbol{r})\, \rho_x(\boldsymbol{r}, \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}' \quad . \qquad \textbf{(II-37)}$$

2.3 Asymptotic Structure of Exchange-Correlation Potential

An important attribute of the work formalism is that for ***all*** nonuniform electron gas systems whether in atoms, molecules, metallic surfaces or metallic clusters, the asymptotic structure of the exchange-correlation potential $W_{xc}(\boldsymbol{r})$ in the classically forbidden region is that of the exchange potential $W_x(\boldsymbol{r})$, and therefore exactly determinable. To understand this we first define the Coulomb hole charge $\rho_c(\boldsymbol{r},\boldsymbol{r}')$ as the difference between the Fermi-Coulomb $\rho_{xc}(\boldsymbol{r},\boldsymbol{r}')$ and Fermi $\rho_x(\boldsymbol{r},\boldsymbol{r}')$ hole charge distributions:

$$\rho_c(\boldsymbol{r},\boldsymbol{r}') = \rho_{xc}(\boldsymbol{r},\boldsymbol{r}') - \rho_x(\boldsymbol{r},\boldsymbol{r}') \quad , \qquad \textbf{(II-38)}$$

where the Fermi hole is determined within the Pauli-correlated approximation. The Coulomb hole charge gives rise to a correlation potential $W_c(\boldsymbol{r})$ which is the work done to move an electron in its force field $\mathcal{E}_c(\boldsymbol{r})$:

$$W_c(\boldsymbol{r}) = -\int_{\infty}^{\boldsymbol{r}} \mathcal{E}_c(\boldsymbol{r}')\cdot d\boldsymbol{l}' \quad \text{where} \quad \mathcal{E}_c(\boldsymbol{r}) = \int \frac{\rho_c(\boldsymbol{r},\boldsymbol{r}')\,(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}'. \qquad \textbf{(II-39)}$$

and to a correlation energy E_c which is the interaction energy between it and electronic density:

$$E_c = \frac{1}{2}\int\int \frac{\rho(\boldsymbol{r})\,\rho_c(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}' \quad . \qquad \textbf{(II-40)}$$

Now since the total charge of both the Fermi-Coulomb and Fermi holes is (negative) unity, the total charge of the Coulomb hole is $\int \rho_c(\boldsymbol{r},\boldsymbol{r}')\,d\boldsymbol{r}' = 0$. Thus, for asymptotic positions of the electron beyond where this charge exists there is no force field $\mathcal{E}_c(\boldsymbol{r})$ due to it, and therefore the correlation potential $W_c(\boldsymbol{r})$ vanishes in this region. The exchange-correlation potential $W_{xc}(\boldsymbol{r})$ then reduces to $W_x(\boldsymbol{r})$ which arises due to the finite charge of the Fermi hole. Therefore, the asymptotic structure of the fully-correlated system potential $W_{xc}(\boldsymbol{r})$, i.e. when both Pauli and Coulomb correlations are present, can be determined ***exactly*** by solving the problem in the Pauli-correlated approximation.

There is yet another important consequence of the above conclusion. In local effective potential theories, the highest occupied eigenvalue is governed principally by the asymptotic structure of the exchange-correlation potential. Since the asymptotic structure of $W_{xc}(\boldsymbol{r})$ is given by $W_x(\boldsymbol{r})$, it is meaningful to compare the highest occupied eigenvalue of the Pauli-correlated approximation differential equation to the experimental ionization potential and electron affinity. For the same reason it is also meaningful to compare transition energies obtained within the Pauli-correlated approximation of the work formalism to experiment. In contrast we note that the highest occupied eigenvalue of Hartree-Fock theory has the meaning of a removal energy only within the context of Koopmans' theorem (Koopmans, 1933) which requires the orbitals of the neutral and ionized systems to be the same.

2.4 Comparison with Kohn-Sham Theory

In Kohn-Sham (KS) theory (Parr and Yang, 1989; Dreizler and Gross, 1990; Kryachko and Ludeña, 1990; March, 1992), the ground-state energy $E[\rho]$, which is a universal functional of the density $\rho(\boldsymbol{r})$, is partitioned as follows:

$$E[\rho] = T_s[\rho] + \int v_{ext}(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r} + E_H[\rho] + E_{xc}^{KS}[\rho] \quad , \qquad \textbf{(II-41)}$$

where $T_s[\rho]$ is the kinetic energy of a system of ***noninteracting*** electrons having the same density distribution as the interacting system, the second term on the right is the expectation of the external potential $v_{ext}(\boldsymbol{r})$, $E_H[\rho]$ the Coulomb self-energy of Eq. (II-14), and $E_{xc}^{KS}[\rho]$ the Kohn-Sham theory exchange-correlation energy. Thus, $E_{xc}^{KS}[\rho]$ differs from the quantum-mechanical definition of the exchange-correlation energy E_{xc} of Eq. (II-14) in that as a result of the above partition it also accounts for the correlation contribution $T_c[\rho]$ to the kinetic energy.

On application of the variational principle for the energy to the functional of Eq. (II-41) for arbitrary variations of the density, one obtains the Kohn-Sham differential equation

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + v_{xc}(\boldsymbol{r})\right]\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r}) \quad , \qquad \textbf{(II-42)}$$

where the density-functional theory Hartree $v_H(\boldsymbol{r})$ and exchange-correlation $v_{xc}(\boldsymbol{r})$ potentials are the functional derivatives of $E_H[\rho]$ and $E_{xc}^{KS}[\rho]$, respectively:

$$v_H(\boldsymbol{r}) = \frac{\delta E_H[\rho]}{\delta\rho(\boldsymbol{r})} = \int\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' \quad , \qquad \textbf{(II-43)}$$

and

$$v_{xc}(\boldsymbol{r}) = \frac{\delta E_{xc}^{KS}[\rho]}{\delta\rho(\boldsymbol{r})} \quad . \qquad \textbf{(II-44)}$$

The ground-state density $\rho(\boldsymbol{r})$ of the system and the non-interacting kinetic energy are obtained from a ***single*** Slater determinant $\Phi\{\phi_i\}$ of the lowest occupied orbitals $\phi_i(\boldsymbol{r})$ of the Kohn-Sham differential equation:

$$\rho(\boldsymbol{r}) = \langle\Phi\{\phi_i\}|\sum_i \delta(\boldsymbol{r}_i - \boldsymbol{r})|\Phi\{\phi_i\}\rangle = \sum_i |\phi_i(\boldsymbol{r})|^2 \ , \qquad \textbf{(II-45)}$$

and

$$T_s[\rho] = \sum_i \int \phi_i^*(\boldsymbol{r}) \left[-\tfrac{1}{2}\nabla_i^2 \right] \phi_i(\boldsymbol{r})\, d\boldsymbol{r} \ . \qquad \textbf{(II-46)}$$

With the orbitals $\phi_i(\boldsymbol{r})$ and the density $\rho(\boldsymbol{r})$, the ground-state energy is then determined via the functional of Eq. (II-41). Furthermore, the highest occupied eigenvalue of the Kohn-Sham differential equation is (Perdew *et al.*, 1982; Levy *et al.*, 1984; Almbladh and von Barth, 1985) the negative of the removal energy. However, the exchange-correlation energy functional $E_{xc}^{KS}[\rho]$, and therefore its functional derivative $v_{xc}(\boldsymbol{r})$ and the highest occupied eigenvalue are at present unknown.

Analogous to the quantum-mechanical definitions, $E_{xc}^{KS}[\rho]$ can also be thought of as the energy of interaction between the density $\rho(\boldsymbol{r})$ and the Kohn-Sham Fermi-Coulomb hole charge $\rho_{xc}^{KS}(\boldsymbol{r}, \boldsymbol{r}')$. This hole charge differs from the quantum-mechanical hole in that its structure also incorporates the correlation contribution to the kinetic energy. The Kohn-Sham hole charge (Harris and Jones, 1974; Gunnarsson and Lundqvist, 1976; Langreth and Perdew, 1977) is defined in terms of the electron-electron-interaction coupling constant λ integral as

$$\int_0^1 d\lambda \; g_\lambda(\boldsymbol{r},\boldsymbol{r}') = \rho(\boldsymbol{r}') + \rho_{xc}^{KS}(\boldsymbol{r},\boldsymbol{r}') \quad , \tag{II-47}$$

where $g_\lambda(\boldsymbol{r},\boldsymbol{r}')$ is the pair-correlation density of a hypothetical system in an external potential $v_{ext,\lambda}(\boldsymbol{r})$ chosen such that the ground-state density $\rho_\lambda(\boldsymbol{r}) = \langle\Psi_\lambda|\sum_i \delta(\boldsymbol{r}_i - \boldsymbol{r})|\Psi_\lambda\rangle$ is identical with the true density $\rho(\boldsymbol{r})$ for all values of the constant λ.

It is evident from the above description of Kohn-Sham theory that a point of commonality between it and the work formalism is the equivalence of the DFT Hartree potential $v_H(\boldsymbol{r})$ of Eq. (II-43) to the potential $W_H(\boldsymbol{r})$ of Eq. (II-12). Thus, the functional derivative of the Coulomb self-energy $E_H[\rho]$ has the physical interpretation of being the work done to move an electron in the force field $\mathcal{E}_H(\boldsymbol{r})$ of the electronic density $\rho(\boldsymbol{r})$.

Before discussing the exchange-correlation potentials $W_{xc}(\boldsymbol{r})$ and $v_{xc}(\boldsymbol{r})$, we compare the work formalism with Kohn-Sham theory in the Pauli-correlated approximation. In this approximation the functional $E_{xc}^{KS}[\rho]$ in Eq. (II-41) and potential $v_{xc}(\boldsymbol{r})$ of Eq. (II-42) are replaced by the exchange energy functional $E_x^{KS}[\rho]$ and potential $v_x(\boldsymbol{r}) = \delta E_x^{KS}[\rho]/\delta\rho(\boldsymbol{r})$, respectively. The exchange energy $E_x^{KS}[\rho]$ can also be defined as the energy of interaction between the corresponding density and the Kohn-Sham Fermi hole, where in turn the latter is defined in terms of the indempotent Dirac density matrix formed from the exchange-only Kohn-Sham orbitals. Since the functional dependence of the density matrix $\gamma(\boldsymbol{r},\boldsymbol{r}')$ on $\rho(\boldsymbol{r})$ is unknown, the potential $v_x(\boldsymbol{r})$ cannot be determined as a functional derivative. In contrast the exchange potential $W_x(\boldsymbol{r})$ is known precisely since it is determined directly from the Fermi hole itself.

The exchange potential $v_x(\boldsymbol{r})$ of Kohn-Sham theory also satisfies the following three conditions (Ou-Yang and Levy, 1990 b; *ibid.*, 1991). These are (i) the virial sum rule relating the exchange energy to its functional derivative:

$$E_x^{KS}[\rho] + \int d\boldsymbol{r}\rho(\boldsymbol{r})\boldsymbol{r}\cdot\nabla v_x(\boldsymbol{r}) = 0 \quad , \qquad \textbf{(II-48)}$$

(ii) the scaling condition

$$v_x(\boldsymbol{r};[\rho_\lambda]) = \lambda v_x(\lambda\boldsymbol{r};[\rho]) \quad , \qquad \textbf{(II-49)}$$

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

$$\delta v_x(\boldsymbol{r})/\delta\rho(\boldsymbol{r}') = \delta v_x(\boldsymbol{r}')/\delta\rho(\boldsymbol{r}) \quad , \qquad \textbf{(II-50)}$$

which is one of symmetry in an interchange of $\boldsymbol{r}$ and $\boldsymbol{r}'$. As a consequence of this same symmetry of the pair-correlation ***function*** $h_x(\boldsymbol{r},\boldsymbol{r}') = g_x(\boldsymbol{r},\boldsymbol{r}')/\rho(\boldsymbol{r}')$, it can be ***analytically*** shown (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola and Sahni, 1993 a) that the potential $W_x(\boldsymbol{r})$ satisfies the virial sum rule. It is also ***analytically*** evident (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola and Sahni, 1993 a) that $W_x(\boldsymbol{r})$ satisfies the scaling condition. Again, since the dependence of the Dirac density matrix on the density is unknown, whether $W_x(\boldsymbol{r})$ satisfies the second derivative condition cannot be determined.

The Kohn-Sham exchange potential $v_x(\boldsymbol{r})$ is also defined in the literature (Sahni *et al.*, 1982; Sahni and Levy, 1986) as that obtained by the optimized potential method (Sharp and Horton, 1953; Talman and Shadwick, 1976) (OPM). In this method the electrons in an external potential $v_{ext}(\boldsymbol{r})$ are assumed to move in a local effective potential $V^{OPM}(\boldsymbol{r})$ which is then varied till the Hartree-Fock theory energy is minimized. The exchange potential $v_x(\boldsymbol{r})$, which is the difference between $V^{OPM}(\boldsymbol{r})$ and the DFT Hartree potential $v_H(\boldsymbol{r})$, satisfies the equations

$$\left[-\frac{1}{2}\nabla_i^2 + v_{ext}(\boldsymbol{r}) + V^{OPM}(\boldsymbol{r})\right]\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r}) \quad , \qquad \textbf{(II-51)}$$

and

$$\sum_i \int d\boldsymbol{r}'\left[v_x(\boldsymbol{r}') - v_{x,i}(\boldsymbol{r}')\right]G_i(\boldsymbol{r}',\boldsymbol{r})\phi_i(\boldsymbol{r}')\phi_i^*(\boldsymbol{r}) = 0 \quad , \qquad \textbf{(II-52)}$$

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

$$G_i(\boldsymbol{r},\boldsymbol{r}') = \sum_{j;j\neq i}\phi_j(\boldsymbol{r})\phi_j^*(\boldsymbol{r}')/\varepsilon_j - \varepsilon_i \quad , \qquad \textbf{(II-53)}$$

and where $v_{x,i}(\boldsymbol{r})$ is the orbital-dependent potential of Hartree-Fock theory. For atoms in the central field approximation, the exchange potential determined by the optimized potential method has been shown (Wang *et al.*, 1990) numerically to satisfy the virial sum rule. (The potentials of the original OPM calculation (Aashamar *et al.*, 1979; *ibid.*, 1978) do not satisfy the sum rule (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola and Sahni, 1993 a). The OPM code was subsequently refined (Wang *et al.*, 1990)). The total ground-state energies obtained, closely approximate but are an upper bound to the Hartree-Fock theory values. The local exchange potential which leads to the Hartree-Fock theory ground-state energy and density as defined (Parr and Yang, 1989; Dreizler and Gross, 1990; Kryachko and Ludeña, 1990; March, 1992) by the integral equation relating the potential to the irreducible self-energy has yet not been determined.

As will be shown in the section on results, the potential $W_x(\boldsymbol{r})$ and the exchange potential $v_x(\boldsymbol{r})$ of the optimized potential method are ***essentially equivalent*** for the nonuniform electron systems in atoms and at metallic surfaces. Together with the fact that $W_x(\boldsymbol{r})$ satisfies the virial sum rule and the scaling condition, the exchange potential of Kohn-Sham theory can then be accurately interpreted as the work done to move an electron in the force field of the Fermi hole charge.

The Kohn-Sham theory exchange-correlation energy functional $E_{xc}^{KS}[\rho]$ and its functional derivative $v_{xc}(\boldsymbol{r})$ satisfy in turn the virial sum rule (Averill and Painter, 1981; Levy and Perdew, 1985):

$$E_{xc}^{KS}[\rho] + \int d\boldsymbol{r}\,\rho(\boldsymbol{r})\,\boldsymbol{r}\cdot\nabla v_{xc}(\boldsymbol{r}) = -T_c \leq 0 \quad . \tag{II-54}$$

(Note that there is no exchange contribution T_x to the kinetic energy in Kohn-Sham theory. Thus, the sum rule satisfied by the Kohn-Sham theory correlation energy $E_c^{KS}[\rho]$ and its functional derivative $v_c(\boldsymbol{r}) = \delta E_c^{KS}[\rho]/\delta\rho(\boldsymbol{r})$ is the same as Eq. (II-54)). Once again as a result of the symmetry of the pair-correlation ***function*** $h(\boldsymbol{r},\boldsymbol{r}') = g(\boldsymbol{r},\boldsymbol{r}')/\rho(\boldsymbol{r}')$, the left hand side of this sum rule can be shown (Nagy, 1990; Harbola and Sahni, 1990 b) to vanish when $W_{xc}(\boldsymbol{r})$ is substituted for $v_{xc}(\boldsymbol{r})$. Thus, the exchange-correlation potential of the work formalism is not the Kohn-Sham theory potential. The reason for this is that $W_{xc}(\mathbf{r})$ is determined from the quantum-mechanical Fermi-Coulomb hole charge $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ which does not incorporate the correlation contribution to the kinetic energy $T_c[\rho]$ in its structure. [Even if one were to employ the Kohn-Sham Fermi-Coulomb hole charge $\rho_{xc}^{KS}(\mathbf{r}, \mathbf{r}')$, (which does include this contribution), to determine $W_{xc}(\mathbf{r})$, the left hand side of the sum rule would still vanish due to the symmetry of the pair-correlation function. This implies that the component of $\rho_{xc}^{KS}(\mathbf{r}, \mathbf{r}')$ due to the correlation-kinetic-energy does not contribute to the force field. Equivalently, Coulomb's law cannot account for the kinetic energy contributions to the potential]. Thus, the potential $W_{xc}(\mathbf{r})$ can be thought of as representing the exchange and purely Coulomb correlation components of the Kohn-Sham potential $v_{xc}(\mathbf{r})$. This fact has been confirmed (Holas and March, 1995) through the differential form of the virial theorem. The correlation-kinetic-energy contribution to the potential is also the work done in a field which is defined in terms of the kinetic energy density tensor.

2.5 Results of Application of the Work Formalism

The application of the work formalism has led to remarkably accurate results for both ground and excited state properties. It has also led to insights into other extensively employed approximation schemes. Given below is a brief description of these results:

(a) The total ground-state energies of atoms (Li *et al.*, 1989; Sahni *et al.*, 1992) from He(Z = 2) to Rn (Z = 86) in the Pauli-correlated approximation lie within 50 ppm of those of Hartree-Fock theory (Fischer, 1977). From ^{36}Kr to ^{71}Lu, the difference lies between 10 to 5 ppm, and from ^{72}Hf to ^{86}Rn the difference is less than 5 ppm. Thus, in essence the work formalism reproduces the ground-state energies of Hartree-Fock theory without recourse to the variational principle for the energy.

(b) The accuracy of the electronic density in the deep interior of atoms as determined by the work formalism in the Pauli-correlated approximation is demonstrated by the satisfaction of the Kato-Steiner electron-nucleus cusp condition (Kato, 1957; Steiner, 1963)

$$-\lim_{r\to 0} \frac{d\rho(r)/dr}{2Z\rho(r)} = 1 \quad , \qquad \textbf{(II-55)}$$

For the noble gas atoms up to Xe, the cusp condition is satisfied (Sen, 1994) to within 2 ppm. For Rn it is satisfied to 55 ppm. Comparison with Hartree-Fock theory is not meaningful in this case because in the work of Fischer the cusp ratio is fixed for the outward integration.

(c) The electronic density of atoms is also accurately determined within the Pauli-correlated approximation of the work formalism. As such, the ***complete shell structure*** is exhibited by the radial probability density of all the atoms. This then allows for the accurate determination (Slamet *et al.*, 1995 b) of core-valence separations. These results are indistinguishable from those of Hartree-Fock theory (Sen *et al.*, 1993).

(d) The highest occupied eigenvalues of atoms (He-Rn) obtained in the Pauli-correlated case are good approximations (Li *et al.*, 1989; Sahni *et al.*, 1992) to the experimental ionization potentials (Moore, 1970). For 66 of the 85 atoms considered these eigenvalues are superior to those of Hartree-Fock theory when compared to experiment. For the remaining atoms, the results of the two theories are essentially equivalent.

(e) For the negative atomic ions (Sen and Harbola, 1991; Sen, 1991; Li *et al.*, 1992) considered thus far (H^-, Li^-, Na^-, K^-, Rb^-, F^-, Cl^-, Br^-, I^-, B^-, C^-, O^-, Al^-, Si^-) the highest occupied eigenvalues of the work formalism in the Pauli-correlated approximation are once again more accurate than those of Hartree-Fock theory when compared to the experimental electron affinities.

(f) The transition energies (Sen, 1992) for atomic one- and two-electrons excited states for Na ($3^2S \rightarrow 4^2S$, 5^2S, 3^2P, and 4^2P) as obtained from eigenvalue differences are more accurate when compared to experiment than those of Hartree-Fock theory obtained from total energy differences.

(g) Static dipole and quadrupole polarizabilities of the Ne-isoelectronic sequence (F^-, Ne, Na^+, Mg^{2+}, Al^{3+}, Si^{4+}) equivalent to those of Hartree-Fock theory have been obtained via the work formalism (Sen, 1991; Samuel and Sen, 1992).

(h) It has been shown via the work formalism that the asymptotic structure of the effective potential in the vacuum region outside a metal surface (which is the exchange potential) (Sahni, 1989; Harbola and Sahni, 1989 b) has the image potential $(-1/4x)$ structure. We note that this result is consistent with that obtained through the optimized potential method (Harbola and Sahni, 1993 b), as well as through functional differentiation (Solomatin *et al.*, 1994; Solomatin and Sahni, 1995) of the exchange energy functional of Eq. (II-37) by considering variations restricted to a particular class of densities.

(i) The asymptotic structure of the exchange potential at metal surfaces has also been shown (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola and Sahni, 1993 b) to go in the interior of the metal to the Kohn-Sham value of $(-2/3)$ (in units of $3k_F/2\pi$).

(j) The application (Sen, 1994) of the work formalism exchange potential together with a recently developed optimized local correlation functional (Gritsenko *et al.*, 1993) has led to highly accurate ground-state energies of atoms and ionization potentials.

(k) It has been possible to explain (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola and Sahni, 1993 a) via the work formalism the physical reason why Slater theory and Slater's X_α method are in error.

Chapter III

COULOMB-CORRELATION EFFECTS IN THE HE ATOM

In this chapter we first investigate Coulomb-correlation effects in the He atom in its ground state by studying the structure of the ***dynamic*** Coulomb hole charge distribution $\rho_c(\mathbf{r}, \mathbf{r}')$ as a function of electron position. Instead of solving the work formalism differential equation Eq. (II-13) for the determination of an approximate wavefunction, we will assume the wavefunction known. The wavefunction employed in our calculations is the analytical 39-parameter correlated wavefunction of Kinoshita (Kinoshita, 1957) which is of the form

$$\Psi(r_1,r_2) = \Psi^K(s,t,R) \quad , \tag{III-1}$$

where $s = r_1 + r_2$, $t = -r_1 + r_2$, and $R = |\mathbf{r}_2 - \mathbf{r}_1|$. The Kinoshita wavefunction is given in Appendix A. This wavefunction leads to the same energy as that due to the 1078-parameter correlated wavefunction of Pekeris (Pekeris, 1959; *ibid.*, 1962) to seven significant figures, and to the expectations of various single particle operators from four-to-five significant figures. The wavefunction also satisfies the electron-nucleus (Kato, 1957; Steiner, 1963) cusp condition which is

$$\lim_{r_1 \to 0} \frac{d\bar{\Psi}(r_1,r_2)}{dr_1} = -Z\ \Psi(0,r_2) \quad , \tag{III-2}$$

where

$$\bar{\Psi}(r_1,r_2) = \frac{1}{4\pi} \int \Psi(\mathbf{r}_1,\mathbf{r}_2)\, d\Omega_{r_1} \tag{III-3}$$

and Z is the atomic number, to three significant figures. (This cusp condition can also be written in terms of the density as in Eq. (II-55)). It also satisfies the electron-electron cusp condition (Kato, 1957; Steiner, 1963) which is

$$\lim_{R \to 0} \frac{d\bar{\Psi}}{dR} = \frac{1}{2}\,\Psi(R=0) \quad , \tag{III-4}$$

where

$$\bar{\Psi}(R,\mathbf{r}_2) = \frac{1}{4\pi}\int \Psi(\mathbf{r}_2 + \mathbf{R},\mathbf{r}_2)\, d\Omega_{\mathbf{R}} \tag{III-5}$$

to two significant figures over most of the atomic region. For purposes of completeness we also determined the previously studied (Coulson and Neilsen, 1961; Lester and Krauss, 1964; Gavin and Bartell, 1966; March *et al.*, 1967) ***static*** Coulomb hole $\rho_c^{static}(R)$, where R is the magnitude of the interelectronic distance.

We next investigate the correlation potential $W_c(\mathbf{r})$ of the work formalism, which is the work done to move an electron in the force field $\mathcal{E}_c(\mathbf{r})$ of the ***dynamic*** Coulomb hole charge $\rho_c(\mathbf{r}, \mathbf{r}')$. Now in local potential theories of the He atom, it is possible to define a Fermi hole from which the exchange potential $W_x(\mathbf{r})$ can then be obtained. As such comparisons of the exchange $W_x(\mathbf{r})$, correlation $W_c(\mathbf{r})$, and exchange-correlation $W_{xc}(\mathbf{r})$ potentials for this atom as determined within the work formalism are also made. Such a comparison is important in order to confirm the tenet of the work formalism that the asymptotic structure of the exchange-correlation potential for ***all*** nonuniform density systems is that of the exchange potential alone.

Finally, we compare the potential $W_c(\mathbf{r})$ with the correlation potential $\mu_c(\mathbf{r})$

of Hohenberg-Kohn-Sham density-functional theory. We have determined the potential $\mu_c(\mathbf{r})$ by inverting the Kohn-Sham differential equation as in the work of Almbladh and Pedroza (1984), but have obtained the density and thereby the Kohn-Sham orbitals via the Kinoshita wavefunction. As noted earlier, the exchange-correlation potentials $W_{xc}(\mathbf{r})$ and $\mu_{xc}(\mathbf{r})$ differ fundamentally in that the former is purely representative of Fermi and Coulomb correlations whereas the latter incorporates in addition the correlation contribution T_c to the kinetic energy. Thus, since for the He atom the exchange potentials $W_x(\mathbf{r})$ and $\mu_x(\mathbf{r})$ of the work formalism and Kohn-Sham theory, respectively are the same, the difference between the correlation potentials of the two theories provides an estimate of the correlation-kinetic-energy contribution $\delta T_c / \delta \rho(\mathbf{r})$ to the Kohn-Sham potential.

The semi-analytical expressions for the density $\rho(\mathbf{r})$, Coulomb hole $\rho_c(\mathbf{r}, \mathbf{r}')$, correlation force field $\mathcal{E}_c(\mathbf{r})$ and correlation potential $W_c(\mathbf{r})$ as derived from the Kinoshita wavefunction are given in Appendix A.

3.1 Structure of Static Coulomb Hole

The static Coulomb hole $\rho_c^{static}(\mathbf{R})$ is defined (Benesch and Smith, 1971) in terms of the radial electron-electron distribution function $f(\mathbf{R})$, which is the probability of finding two electrons at $\mathbf{r}_1$ and $\mathbf{r}_2$ a distance $R = |\mathbf{r}_2 - \mathbf{r}_1|$ apart. In terms of the pair-correlation density $g(\mathbf{r}, \mathbf{r}')$ this probability can be written as

$$f(R) = \frac{1}{2} \int d\mathbf{r}\ \rho(\mathbf{r}) \left[\int g(\mathbf{r}, \mathbf{r} + \mathbf{R})\, d\Omega_{\hat{R}}\, R^2 \right] \quad . \tag{III-6}$$

In the above expression the term in square parentheses is the probability density a distance R from an electron at r. This is then weighted by the probability of finding an electron at r which in turn is then integrated over all possible electron positions. The factor of (1/2) ensures that the normalization (Benesch and Smith, 1971) of this distribution function is the number of electron pairs:

$$\int_0^\infty f(R)\, dR = \frac{N(N-1)}{2} \quad . \tag{III-7}$$

The static Coulomb hole $\rho_c^{static}(R)$ is defined as the difference

$$\rho_c^{static}(R) = f(R) - f_x(R) \quad , \tag{III-8}$$

where $f_x(R)$ is the radial distribution function when only Pauli correlations are assumed present as in Hartree-Fock theory. Since both distribution functions integrate to the number of electron pairs, the total charge

$$\int \rho_c^{static}(R)\, dR = 0 \quad , \tag{III-9}$$

and consequently the static Coulomb hole is both positive and negative.

In Fig. 1 we plot the radial distribution functions $f(R)$ and $f_x(R)$ for the He atom using the Kinoshita and Hartree-Fock (Fischer, 1977) wavefunctions, respectively, as well as the static Coulomb hole $\rho_c^{static}(R)$. In the region where $0 < R \leq 1$ *a.u.* the function $f(R)$ lies below $f_x(R)$ indicating thereby that in this region Coulomb correlations reduce the probability of two electrons being a certain distance apart from that of when these correlations are absent. Thus, in this region the Coulomb hole is negative. In the region beyond $R \geq 1$ *a.u.*, $f(R)$ lies above $f_x(R)$

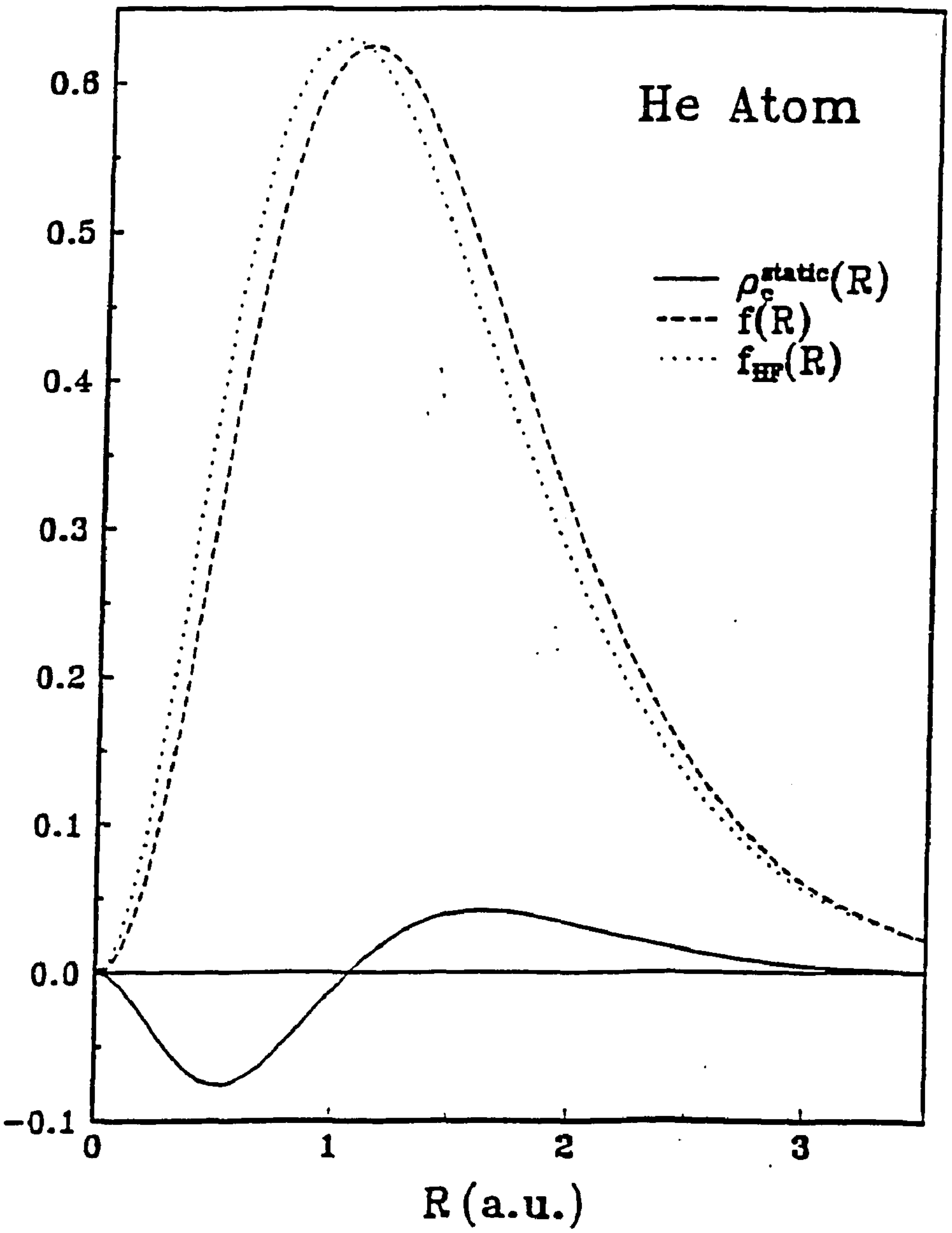

Fig. 1. The static Coulomb hole $\rho_c^{static}(R)$ as a function of the interelectronic distance R for the He atom. The radial electron-electron distribution functions $f(R)$ and $f_x(R)$ determined via the Kinoshita and Hartree-Fock wavefunctions, respectively, are also plotted. (From Fig. 1 of (Slamet and Sahni, 1995 a)).

so that the Coulomb hole is positive, indicating that as a result of Coulomb correlations there is an increase in the probability that the electrons are separated by a distance greater than ~ 1 *a.u.* The structure of the positive part of the hole describes the probability of this separation. Studies (Coulson and Neilsen, 1961; Lester and Krauss, 1964; Gavin and Bartell, 1966; March *et al.*, 1967) of the He isoelectronic sequence $Li^{+}, Be^{2+}, \ldots Ne^{8+}$ show that the region in which the Coulomb hole is positive increases with increasing atomic number as it must, but that the structure of the hole remains the same.

In the quantum-mechanical description of an atom, the probability of an electron being at some position changes as a function of its distance r from the nucleus. The static Coulomb hole does not describe the effects of Coulomb correlations as a function of this probability or equivalently of the nonuniformity of the electronic density. This is described by the dynamic Coulomb hole charge discussed below.

3.2 Structure of Dynamic Coulomb Hole

As noted earlier in Section 2.3 the dynamic Coulomb hole charge $\rho_c(\boldsymbol{r}, \boldsymbol{r}')$ at $\boldsymbol{r}'$ for an electron at $\boldsymbol{r}$ is defined as the difference between the Fermi-Coulomb $\rho_{xc}(\boldsymbol{r}, \boldsymbol{r}')$ and Fermi hole $\rho_x(\boldsymbol{r}, \boldsymbol{r}')$ charge distributions: $\rho_c(\boldsymbol{r}, \boldsymbol{r}') = \rho_{xc}(\boldsymbol{r}, \boldsymbol{r}') - \rho_x(\boldsymbol{r}, \boldsymbol{r}')$, where the Fermi hole is determined within the Pauli-correlated approximation such as Hartree-Fock theory or the exchange-only version of the work formalism. For the He atom in its ground state, there are no correlations due to the Pauli exclusion principle since the electrons have opposite spin. Thus the Hartree-Fock theory Slater-determinantal wavefunction reduces to that of the Hartree approximation which is a product of two spin-orbitals. The corresponding pair-correlation density for an electron at $\boldsymbol{r}$ is then the density due to the other electron at $\boldsymbol{r}'$, which is half the total density so that $g(\boldsymbol{r}, \boldsymbol{r}') = \rho(\boldsymbol{r}')/2$. However, when the pair-correlation density is written as in Eq. (II-8), it is appropriate to think in terms of a "Fermi hole" which is the negative of the self-interaction term in the density. Therefore for the He atom $\rho_x(\boldsymbol{r}, \boldsymbol{r}') = -\rho(\boldsymbol{r}')/2$, which is independent of the electron position. Such a concept derives from local effective potential theories in which the pair-correlation density constitutes the fundamental quantity, with both the density and the Fermi or Fermi-Coulomb holes giving rise to local potentials.

In Fig. 2 we plot a cross-section through the Coulomb $\rho_c(\boldsymbol{r}, \boldsymbol{r}')$, Fermi $\rho_x(\boldsymbol{r}, \boldsymbol{r}')$ and Fermi-Coulomb $\rho_{xc}(\boldsymbol{r}, \boldsymbol{r}')$ hole charge distributions for an electron at the nucleus $r = 0$ as determined via the Kinoshita wavefunction. Also plotted for purposes of comparison is the electronic density $\rho(\boldsymbol{r}')$. Observe that for this electron position all the hole charge distributions are spherically symmetric about the electron. At the position of the electron, the holes all also exhibit a cusp. (The cusp in the structure of the Fermi hole is a consequence of the cusp in the density). At and about the electron position the Fermi-Coulomb hole is more negative than the Fermi hole as must be the case. This is a consequence of the fact that when Coulomb correlations are introduced, an electron digs a hole about it that is deeper than when only Pauli

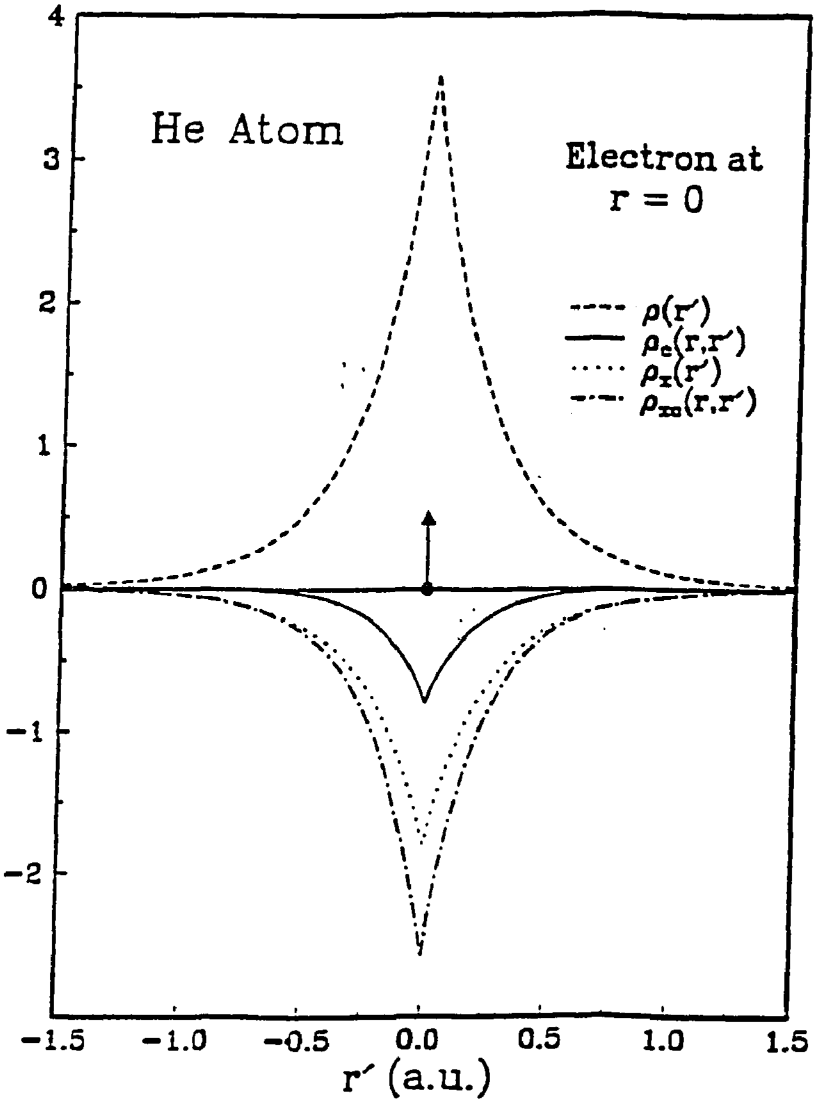

Fig. 2. Cross sections of the Coulomb $\rho_c(r, r')$, Fermi $\rho_x(r, r')$, and Fermi-Coulomb $\rho_{xc}(r, r')$ holes for the He atom as determined via the Kinoshita wavefunction for an electron at the nucleus $r = 0$, as indicated by the arrow. The nucleus is at the origin. The positive part of the Coulomb hole is not evident on the scale of the figure. The electronic density $\rho(r')$ is also plotted. (From Fig. 2 of (Slamet and Sahni, 1995 a)).

correlations are present. Thus, in the region about the electron, the Coulomb hole is negative. (This is also the case for all electron positions). However, near the surface of the atom $(\langle r \rangle = 0.929 \text{ a.u.})$ and in the classically forbidden region, the Fermi-Coulomb hole must lie above the Fermi hole since both these distributions satisfy the same charge conservation constraint. In these regions the Coulomb hole is then positive. (The positive part of the Coulomb hole is not evident on the scale of Fig. 2, but is clearly exhibited in the figures to follow). Thus, the Coulomb hole is both positive and negative, and integrates to a total charge of zero. The positive part of the hole indicates that for an electron at the origin, the other electron is outside the surface in the classically forbidden region of the atom.

Since the Fermi hole for this atom is independent of the electron position, we now focus our attention solely on the structure of the Coulomb hole for the other electron positions considered. In Fig. 3a we plot the Coulomb hole for an electron with a radial co-ordinate of $r = 0.566$ a.u. which is at the maximum of the radial probability density, and in Fig. 3b for an electron at $r = 0.8$ a.u. The polar angle θ of the electron position is taken to be zero. (For the structure of the Fermi holes discussed in the later chapters, the polar angle θ of the electron positions considered is similarly defined). The polar angles θ' of the Coulomb hole charge considered correspond to $\theta' = 0°$, $\theta' = 45°$ and $\theta' = 90°$ with respect to the nucleus-electron direction. Since the electron position is along the $\theta' = 0°$ direction, the Coulomb hole, (for this spherically symmetric atom), is independent of its azimuthal

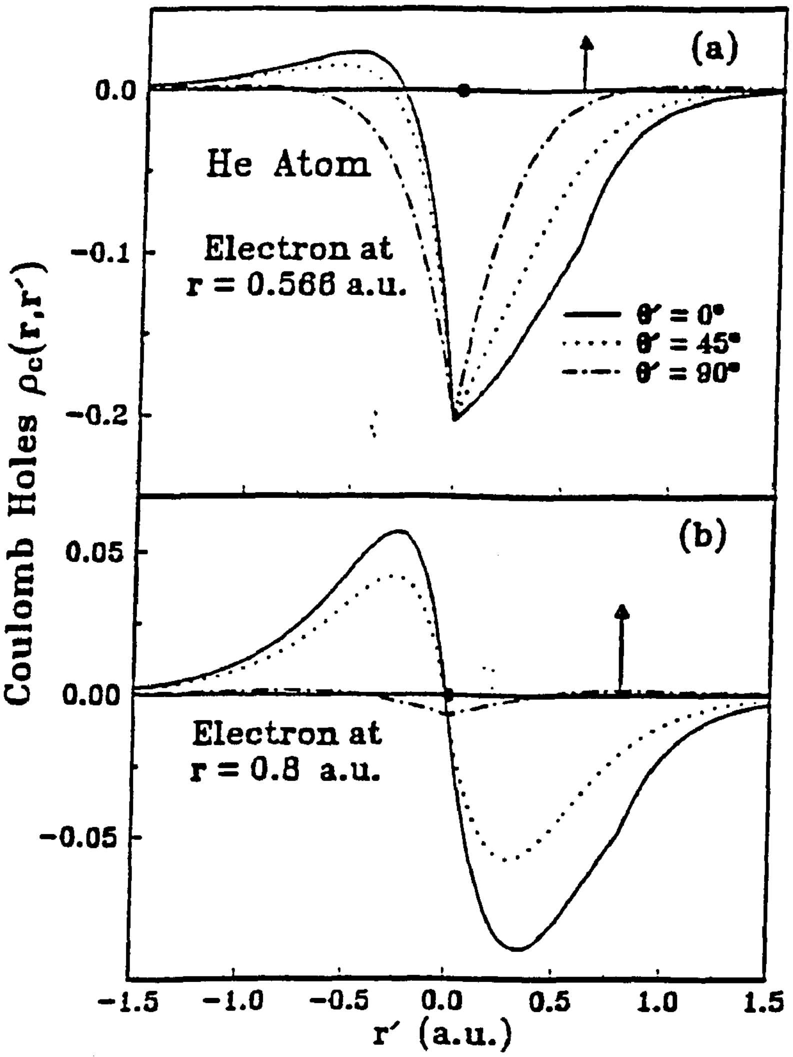

Fig. 3. The Coulomb hole $\rho_c(r,r')$ for the He atom in three different directions corresponding to $\theta' = 0$, $\theta' = 45°$, and $\theta' = 90°$ with respect to the nucleus-electron direction. The electron position corresponds to a polar angle of $\theta = 0$. In (a) the radial co-ordinate of the electron, as indicated by the arrow, is at the maximum of the radial probability density for the He atom at $r = 0.566\,a.u.$, whereas in (b) the electron is at $r = 0.8\,a.u.$ (From Fig. 3 of (Slamet and Sahni, 1995 a)).

angle ϕ'. For these electron positions the Coulomb hole is no longer spherically symmetric about the electron. Observe also the cusp in the structure of the Coulomb hole at the position of the electron. At and about these positions, the hole is principally negative. Its magnitude at the electron position diminishes with distance from the nucleus as a result of the decrease in the density. However, as the distance of the electron from the nucleus increases, a part of the hole that is positive emerges on the side of the atom opposite to that of the electron. The magnitude of this positive part is seen to increase relative to that of the negative part about the electron, with the positive part moving closer to the nucleus. This indicates that it is more probable for the other electron to be in this region.

In Fig. (4a, b, c) we plot the Coulomb hole for an electron in the surface region of the atom at $r = 1$ a.u., and in the classically forbidden region at $r = 1.5$ a.u., and $r = 5$ a.u., respectively. The trends discussed above continue as the distance of the electron from the nucleus increases further. The positive part of the Coulomb hole increases in magnitude about the nucleus, and the negative part around the electron position continues to decrease. For the electron at $r = 5$ a.u., (Fig. 4c), most of the Coulomb hole is positive, localized about the nucleus and essentially spherically symmetric about it. Thus, if one of the two electrons is in the asymptotic region, the other is localized about the nucleus.

In Fig. 5 we plot the center of mass $<r'>$ of the Coulomb hole $\rho_c(\boldsymbol{r}, \boldsymbol{r}')$ as

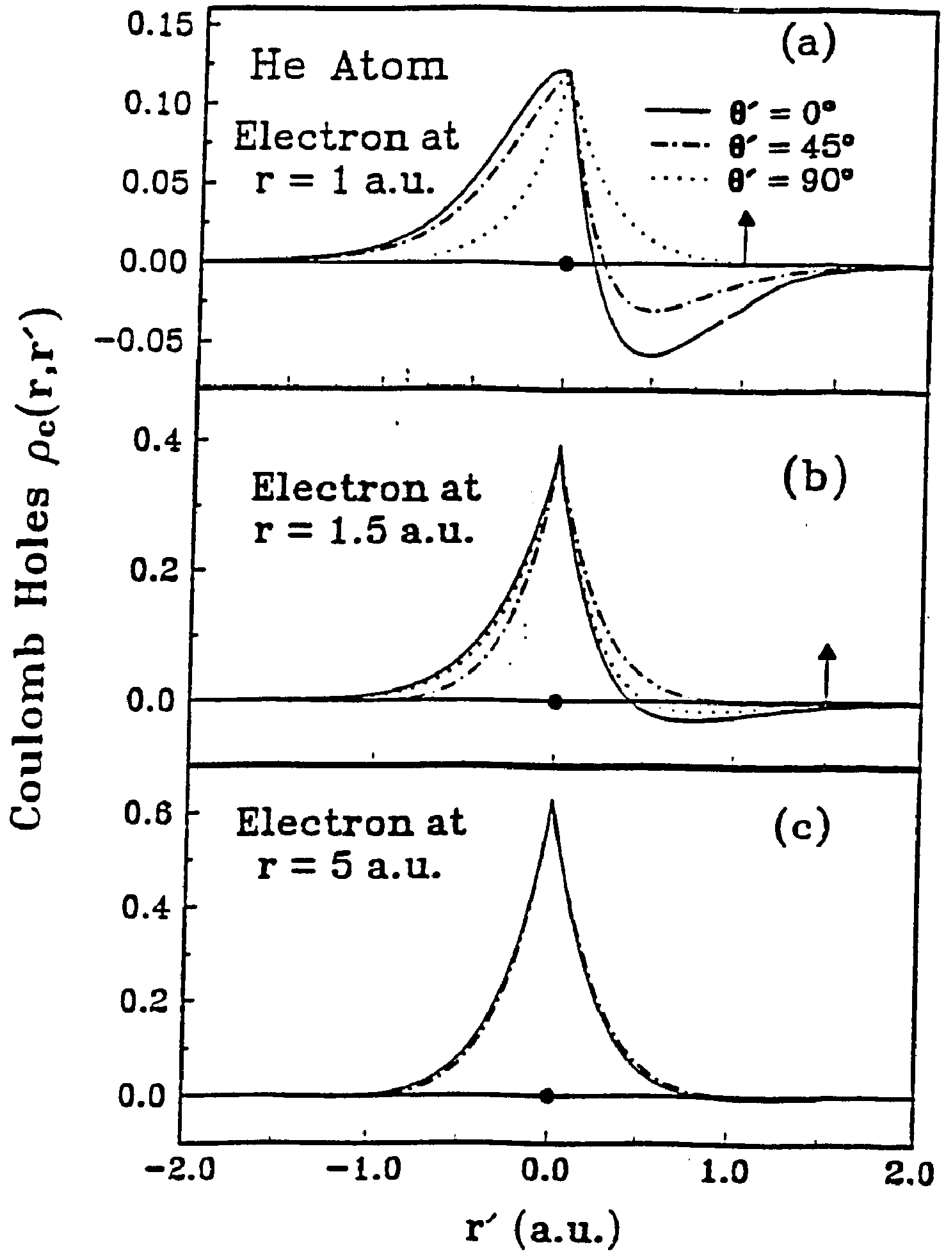

Fig. 4. The figure caption is the same as that of Fig. 3 except that in (a) the electron is at $r = 1\, a.u.$, in (b) at $r = 1.5\, a.u.$, and in (c) at $r = 5\, a.u.$ (From Fig. 4 of (Slamet and Sahni, 1995 a)).

a function of electron position. The center of mass lies along the nucleus-electron direction. However, it is always on the side of the nucleus opposite to that of the electron, but also always close to the nucleus. For asymptotic positions of the electron, it once again approaches the nucleus. The center of mass of the Fermi hole in this case is at the origin. However, for other atoms, (see Fig. 2 of Sahni and Harbola, 1990), the center of mass of the Fermi hole for most part lies on the same side of the nucleus as the electron. Furthermore, it follows the electron for positions within the atom, and lies considerably farther from the nucleus prior to approaching the origin for asymptotic electron positions.

As we have seen, the structure of the Coulomb hole charge changes from being essentially negative for electron positions in the deep interior of the atom to being essentially positive for asymptotic positions of the electron. This is a direct consequence of the fact that Coulomb repulsion depends upon the distance between the electrons. On the other hand, the Fermi hole is always negative irrespective of the electron position. The negative Fermi hole charge gives rise to a force field $\mathcal{E}_x(\mathbf{r})$ that is negative, and consequently the exchange potential $W_x(\mathbf{r})$ determined as the work done to bring an electron from infinity to its position at $\mathbf{r}$ in this field is also always negative. On the other hand, the Coulomb hole charge is both positive and negative, and changes from being nearly all negative to nearly all positive. Does the force field $\mathcal{E}_c(\mathbf{r})$ due to this charge distribution and the corresponding work done $W_c(\mathbf{r})$ in this field then go positive in certain regions of space? The structure of the

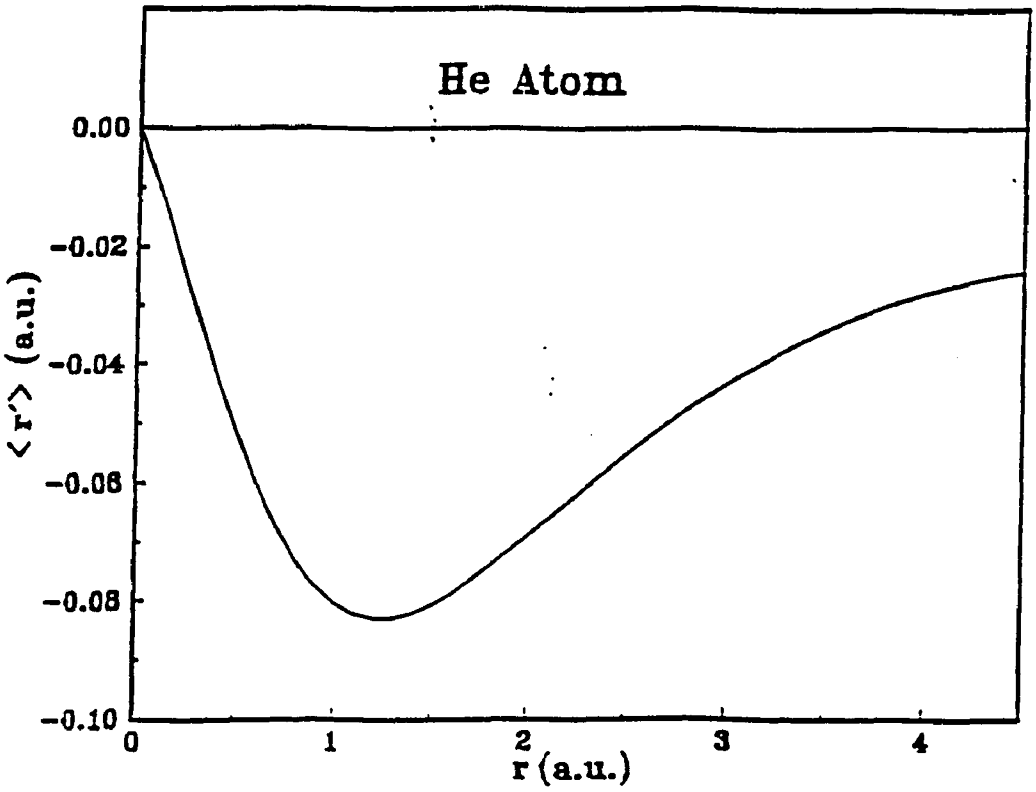

Fig. 5. The center of mass <r'> of the Coulomb hole $\rho_c(\mathbf{r}, \mathbf{r}')$ for the He atom as a function of electron position. (From Fig. 5 of (Slamet and Sahni, 1995 a)).

force field due to the Coulomb hole charge and the resulting correlation potential are discussed in the following section.

3.3 Structure of Correlation Potential of the Work Formalism

In order to study the structure of the He atom correlation potential $W_c(\mathbf{r})$, the Kinoshita wavefunction again was assumed. The structure of the resulting Coulomb $\rho_c(\mathbf{r}, \mathbf{r}')$, Fermi $\rho_x(\mathbf{r}, \mathbf{r}')$ and Fermi-Coulomb $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ hole charge distributions is then as determined previously. The resulting exchange $\mathcal{E}_x(\mathbf{r})$, correlation $\mathcal{E}_c(\mathbf{r})$ and exchange-correlation $\mathcal{E}_{xc}(\mathbf{r})$ force fields due to these charge distributions is plotted in Fig. 6. Observe that all the force fields vanish at the origin. This is a consequence of the fact for an electron at the nucleus, the charge distributions $\rho_c(\mathbf{r}, \mathbf{r}')$, $\rho_x(\mathbf{r}, \mathbf{r}')$ and $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ are all spherically symmetric about it. As such there is no force field at the position of the electron. The structure of the correlation field $\mathcal{E}_c(\mathbf{r})$ in the interior of the atom is similar to the exchange field $\mathcal{E}_x(\mathbf{r})$, although it is about an order of magnitude smaller. However, both the fields $\mathcal{E}_x(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$ are negative throughout space. This is an interesting result since the corresponding source charge distributions for these fields are strikingly different. The Fermi hole is negative for all electron positions and therefore the field $\mathcal{E}_x(\mathbf{r})$ is negative throughout. On the other hand the Coulomb hole is both positive and negative and can be substantially one or the other depending upon the position of the electron. The fact that the correlation field $\mathcal{E}_c(\mathbf{r})$ is negative is a consequence of the fact that the force field depends not only on the structure of the charge distribution but

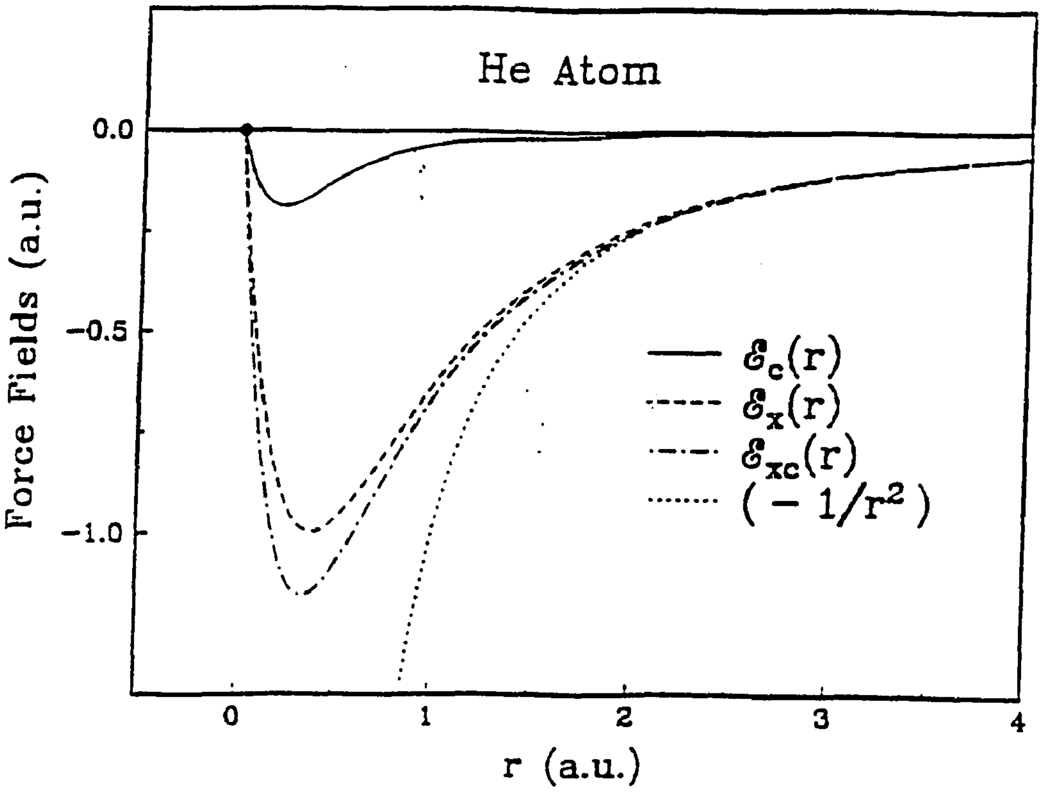

Fig. 6. The force-fields $\mathcal{E}_c(r)$, $\mathcal{E}_x(r)$ and $\mathcal{E}_{xc}(r)$ due to the Coulomb, Fermi, and Fermi-Coulomb hole charges, respectively, for the He atom. The function $(-1/r^2)$ is also plotted. (From Fig. 6 of (Slamet and Sahni, 1995 a)).

also on the inverse of the square of the distance between the charge and the electron. Thus, the part of the charge that lies farther from the electron contributes less to the field than the charge that is closer. For example, for an electron at $r = 1.5$ a.u., the positive part of the Coulomb hole (see Fig. 4b) is much larger in magnitude than its negative part. However, the positive part is localized about the nucleus far from the electron and therefore its contribution to the force field is less than that of the negative charge closer to the electron, with the result that the net force field at the electron position is negative. This explains why the correlation field $\mathcal{E}_c(r)$ is negative. The fact that the Coulomb hole goes substantially positive for asymptotic positions of the electron does, however, cause the correlation field $\mathcal{E}_c(r)$ to decay far more rapidly than the exchange field $\mathcal{E}_x(r)$. The correlation field $\mathcal{E}_c(r)$ (see Fig. 6) has essentially vanished by $r \sim 4$ a.u. whereas the exchange field $\mathcal{E}_x(r)$ decays asymptotically as $(-1/r^2)$. Thus, the exchange-correlation field $\mathcal{E}_{xc}(r)$ is asymptotically the same as its exchange component $\mathcal{E}_x(r)$, and decays as $(-1/r^2)$. This asymptotic structure may also be understood to be a consequence of the fact that the total charge of the Coulomb hole is zero, whereas that of the Fermi and Fermi-Coulomb holes is unity, and the fact that all these charge distributions are localized and essentially static about the nucleus for asymptotic positions of the electron.

In Fig. 7 we plot the correlation $W_c(r)$, exchange $W_x(r) = -\frac{1}{2}W_H(r)$, and exchange-correlation $W_{xc}(r)$ potentials. Observe that the potentials all approach the nucleus quadratically, and have zero slope at the origin as a consequence of the force

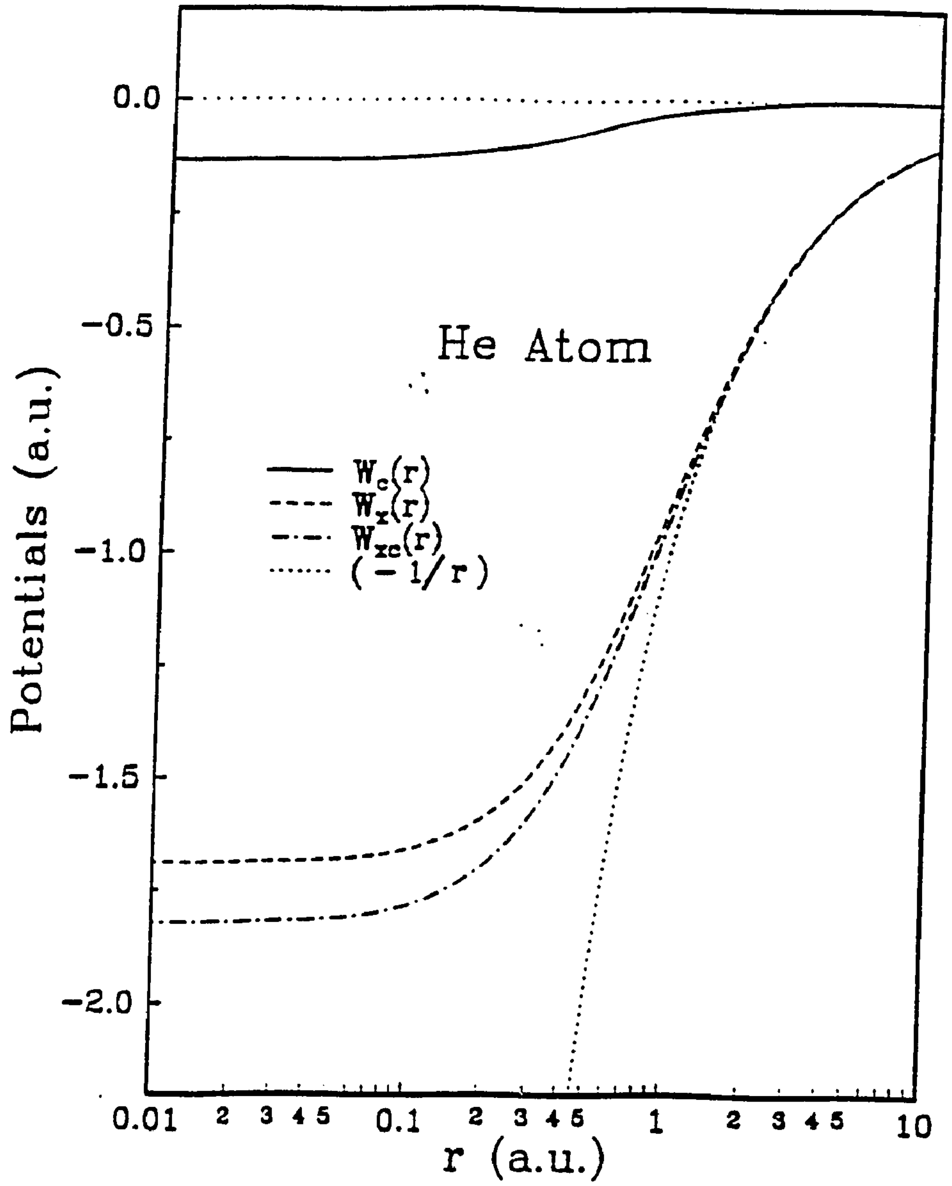

Fig. 7. The work formalism correlation $W_c(r)$, exchange $W_x(r)$ and exchange-correlation $W_{xc}(r)$ potentials for the He atom. The function $(-1/r)$ is also plotted. (From Fig. 7 of (Slamet and Sahni, 1995 a)).

fields vanishing there. In the interior of the atom, the structure of $W_c(\mathbf{r})$ is similar to that of $W_x(\mathbf{r})$, but is an order of magnitude smaller. Note that $W_c(\mathbf{r})$ is negative throughout space and monotonic, and therefore positive work must be done to move an electron against the force field of the Coulomb hole charge. Since the correlation field $\mathcal{E}_c(\mathbf{r})$ decays rapidly, the correlation potential $W_c(\mathbf{r})$ is also negligible by $r \sim 4$ a.u. The exchange $W_x(\mathbf{r})$ and exchange-correlation $W_{xc}(\mathbf{r})$ potentials, however, decay asymptotically as $(-1/r)$ as they must. This clearly demonstrates that the exchange-correlation potential $W_{xc}(\mathbf{r})$ of the work formalism reduces to its exchange component $W_x(\mathbf{r})$ asymptotically. Thus, the asymptotic structure of the many-body potential $W_{xc}(\mathbf{r})$ in the atom can be obtained by solution of the differential equation in the Pauli-correlated approximation. Furthermore, as a consequence, it is meaningful to compare the highest occupied eigenvalue of this differential equation to experiment.

3.4 Comparison with Correlation Potential of Kohn-Sham Theory

The correlation potential $\mu_c(\mathbf{r})$ for the He atom for an assumed density $\rho(\mathbf{r})$ can be determined either by the methods of Wang and Parr (1993), Jones and Trickey (1987), and van Leeuwen and Baerends (1994), or as in the original work of Almbladh and Pedroza (1984). We follow the latter procedure whereby $\mu_c(\mathbf{r})$ is obtained by inversion of the Kohn-Sham differential equation Eq. (II-42):

$$\mu_c(\mathbf{r}) = \epsilon + \frac{\nabla^2 \phi}{2\phi} + \frac{2}{r} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \mu_x(\mathbf{r}) \quad , \qquad \textbf{(III-10)}$$

where the Kohn-Sham orbital $\phi(\mathbf{r}) = [\rho(\mathbf{r})/2]^{1/2}$, the eigenvalue ε is taken to be the first ionization potential (Moore, 1970), and where the expression for the exchange potential $\mu_x(\boldsymbol{r})$ is the same as $W_x(\boldsymbol{r})$ discussed previously.

A plot of the potential $\mu_c(\boldsymbol{r})$ for the density corresponding to the Kinoshita wavefunction is given in Fig. 8. This potential is the same as that obtained from a Monte Carlo calculation (Umrigar, 1994; Alexander, 1994). For purposes of comparison we include in this figure.the potential $W_c(\boldsymbol{r})$. Observe (see inset) that $\mu_c(\boldsymbol{r})$ also approaches the nucleus quadratically and has zero slope at the origin. As is known, $\mu_c(\boldsymbol{r})$ is not a monotonic function and goes positive at $r \sim 0.3$ a.u., and then decays as a positive function. In recent work (Umrigar and Gonze, 1994), however, the use of a 491-term correlated wavefunction shows that $\mu_c(\boldsymbol{r})$ goes negative for $r > 4$ a.u. and vanishes asymptotically as a negative function. The potential $\mu_c(\boldsymbol{r})$ as determined by the Kinoshita wavefunction also goes negative but for these asymptotic positions of the electron its accuracy is obviously not as great. In contrast $W_c(\boldsymbol{r})$ is monotonic and always negative. Furthermore, in the interior of the atom the potential $\mu_c(\boldsymbol{r})$ is less attractive than $W_c(\boldsymbol{r})$.

It is thus evident that the structure of the Kohn-Sham Coulomb hole $\rho_c^{KS}(\boldsymbol{r}, \boldsymbol{r}')$ is different from that of the quantum-mechanical Coulomb hole $\rho_c(\boldsymbol{r}, \boldsymbol{r}')$ described in the previous section. It is, however, difficult to infer the structure of $\rho_c^{KS}(\boldsymbol{r}, \boldsymbol{r}')$ from that of the potential $\mu_c(\boldsymbol{r})$ via Coulomb's law. This is because, as discussed in Section 2.4, the component of $\rho_c^{KS}(\boldsymbol{r}, \boldsymbol{r}')$ due to the correlation contribution to the kinetic energy, $T_c[\rho]$, does not contribute to the correlation force-field.

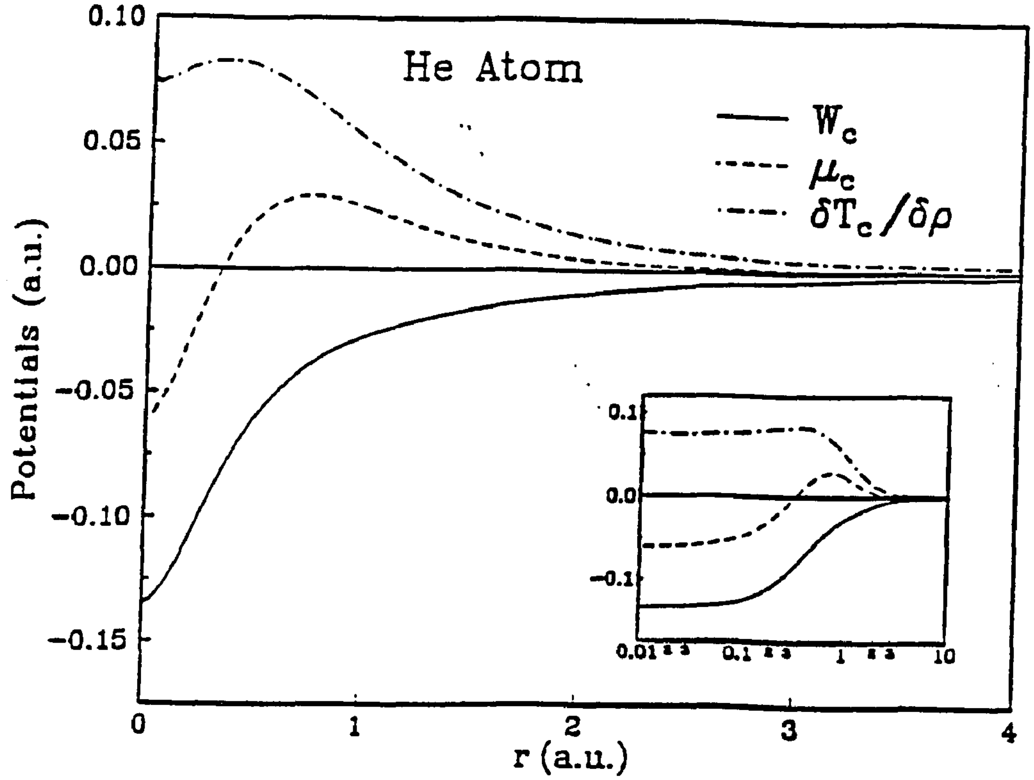

Fig. 8. The correlation potentials $W_c(r)$ and $\mu_c(r)$ of the work formalism and Kohn-Sham theory, respectively, for the He atom. The ansatz $\delta T_c/\delta\rho = \mu_c(r) - W_c(r)$ is also plotted. The inset is on a logarithmic scale to indicate the structure near the nucleus of the atom. (From Fig. 8 of (Slamet and Sahni, 1995 a)).

Equivalently, Coulomb's law cannot account for the kinetic energy contributions to the potential $\mu_c(\mathbf{r})$. (The components of $\rho_c^{KS}(\mathbf{r},\mathbf{r}')$ due to $T_c[\rho]$ do, however, contribute to the Kohn-Sham correlation energy $E_c^{KS}[\rho]$). The fact that the potential $\mu_c(\mathbf{r})$ is less attractive than $W_c(\mathbf{r})$ is consistent with $W_c(\mathbf{r})$ being strictly representative of Coulomb correlations whereas $\mu_c(\mathbf{r})$ includes in addition the correlation contribution $T_c[\rho]$ to the kinetic energy. Thus, it is reasonable to assume that the difference $[\mu_c(\mathbf{r}) - W_c(\mathbf{r})]$ is a good approximation to $\delta T_c[\rho]/\delta\rho(\mathbf{r})$, the contribution of $T_c[\rho]$ to $\mu_c(\mathbf{r})$. The result of this ***ansatz*** for $\delta T_c/\delta\rho$ is also plotted in Fig. 8. Observe that it is of the same order of magnitude as $\mu_c(\mathbf{r})$, and also not monotonic. It is, however, positive over the entire range of the figure. The fact that $\delta T_c/\delta\rho$ is a significant fraction of $\mu_c(\mathbf{r})$ is reflected in the corresponding values of the energies $T_c[\rho]$ and $E_c^{KS}[\rho]$. From Eq. (II-41), $E_c^{KS}[\rho] = -0.0422$ a.u. whereas from Eq. (II-40) of the work formalism $E_c = -0.0787$ a.u. Once again, since the exchange energies of Kohn-Sham theory and the work formalism are the same, we have $T_c[\rho] = E_c^{KS}[\rho] - E_c = 0.0365$ a.u. This value for $T_c[\rho]$ is the same as that determined by Ludeña *et al.* (1993) by means of local scaling transformations.

For completeness we note that Levy and Perdew (Dreizler and Gross, 1990; Parr and Yang, 1989; March, 1992) have provided explanations for the non-monotonicity and positiveness of the Kohn-Sham correlation potential $\mu_c(\mathbf{r})$. For a tightly bound closed shell atom they show that to leading order (e^4) in the electronic charge e in perturbation theory, the integral term in the correlation counterpart of the sum rule Eq.

(II-54) vanishes, and thus $\mu_c(\boldsymbol{r})$ cannot be monotonic since $\rho(\boldsymbol{r})$ is everywhere positive. The value of the integral turns out to be 0.0057 a.u., which is small. To explain that $\mu_c(\boldsymbol{r})$ goes positive in certain regions of space, they employ the fact that, as noted in Section 2.4, the highest occupied eigenvalue of the Kohn-Sham differential equation is the negative of the first ionization potential. On comparing the highest occupied eigenvalue of exchange-only Kohn-Sham theory to the ionization potential they find that the former is more negative than the latter for many atoms. Thus, in order to satisfy the ionization potential theorem, they conclude that the expectation value of $\mu_c(\boldsymbol{r})$ taken with respect to the highest occupied orbital is often positive. The present analysis shows the ***physical*** source of the nonmonotonicity and positiveness of $\mu_c(\boldsymbol{r})$ to be the correlation contribution to the kinetic energy. The purely Coulomb correlation component of $\mu_c(\boldsymbol{r})$ is well described by $W_c(\boldsymbol{r})$ just as the exchange potential $\mu_x(\boldsymbol{r})$ of Kohn-Sham theory is well described (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola and Sahni, 1993 a; Slamet *et al.*, 1994 a; Sahni, 1994 a) by $W_x(\boldsymbol{r})$.

3.5 Conclusions

In this chapter we have investigated Coulomb correlation effects in the He atom by studying the structure of the static and dynamic Coulomb hole charge distributions as determined by the Kinoshita wavefunction. The static Coulomb hole, which is defined in terms of the radial electron-electron distribution function, shows that due to Coulomb repulsion there is a decrease in probability that the two electrons will be separated by a distance less than one atomic unit, and an increase is this probability for greater separations. The dynamic Coulomb hole is defined directly in terms of the pair-correlation density, and thus describes the probability of finding one of the electrons given the position of the other. In contrast to the Fermi hole, which is negative over the entire region of the atom irrespective of electron position, the dynamic Coulomb hole is both negative and positive. At and about the test electron, the hole is always negative indicating the reduction in density about it due to Coulomb repulsion. The magnitude of this reduction in density depends upon the electronic density at that position. The positive part of the Coulomb hole then gives the positional probability of the other electron. A study of the dynamic Coulomb hole thus explains how the two electrons are correlated as a function of the nonuniform density of the atom. For example, when the test electron is in the high density interior of the atom, the hole is principally negative. The positive part of the hole is much smaller and lies in the surface region of the atom on the other side of the nucleus, and thus it is most probable that the other electron is there. When the test electron is in the low density classically forbidden region, the hole is principally positive and concentrated about the nucleus, thereby indicating the localization of the other electron there. At the position of the electron, the hole also exhibits a cusp in its structure reflective of the electron-electron cusp requirement of the wavefunction.

We have also investigated the structure of the correlation potential $W_c(\boldsymbol{r})$ of the work formalism for the He atom again employing the Kinoshita wavefunction. This potential is determined by Coulomb's law from the dynamic Coulomb hole charge distribution. It is the ***local*** potential representing Coulomb correlations in the Sturm-Liouville differential equation of the work formalism which leads to the wavefunction of the system. Although the structure of the Coulomb and Fermi holes is different in that the former is both positive and negative, and the latter entirely negative, the structure of $W_c(\mathbf{r})$ is similar to the exchange potential $W_x(\mathbf{r})$ due to the Fermi hole: it is entirely negative, has zero slope at the nucleus and is monotonic, but is an order of magnitude smaller. Since the total charge of the Coulomb hole is zero and because it is principally positive and localized about the nucleus for electron positions in the classically forbidden region, the potential $W_c(\mathbf{r})$ decays rapidly in this region. Thus, the asymptotic structure of the exchange-correlation potential $W_{xc}(\mathbf{r})$ is due to the exchange potential $W_x(\mathbf{r})$ itself, which as a consequence of the total charge of the Fermi hole being negative unity is $(-1/r)$. Further, these results confirm that the asymptotic structure of the many-body potential $W_{xc}(\mathbf{r})$ for nonuniform density systems can be obtained by solving the differential equation corresponding to the Pauli-correlated approximation within the work formalism.

The structure of $W_c(\mathbf{r})$ also sheds light on the physics underlying the structure of the correlation potential $\mu_c(\mathbf{r})$ of Kohn-Sham theory. The latter potential contains in addition the correlation contribution $T_c[\rho]$ to the kinetic energy and is thus less attractive. Further, it is not monotonic and goes positive within the atom, remaining positive asymptotically. Since the potential $W_c(\mathbf{r})$ is strictly representative of

Coulomb correlations and is everywhere negative and monotonic, the nonmonotonicity and positiveness of the Kohn-Sham correlation potential $\mu_c(\boldsymbol{r})$ can be attributed to the correlation-kinetic-energy. (Note that the Kohn-Sham exchange potential $\mu_x(\boldsymbol{r})$ is the same as $W_x(\boldsymbol{r})$ of the work formalism and is monotonic and negative. For other atoms, the exchange potential of the optimized potential method possesses bumps in the intershell region). Thus the result of the ansatz that the difference $[\mu_c(\boldsymbol{r}) - W_c(\boldsymbol{r})]$ is the correlation-kinetic-energy contribution $\delta T_c / \delta\rho(\boldsymbol{r})$ to the Kohn-Sham potential is then nonmonotonic and positive. The magnitudes of the functions $\delta T_c / \delta\rho(\boldsymbol{r})$ and $\mu_c(\boldsymbol{r})$ are also comparable. These results are consistent with the fact that the energy $T_c[\rho]$ is positive and comparable in magnitude to the Kohn-Sham correlation energy $E_c^{KS}[\rho]$.

Chapter IV

APPLICATION OF WORK FORMALISM TO NONSPHERICAL DENSITY ATOMS

The electronic charge densities of the majority of atoms in the Periodic Table are non spherically symmetric. However, in most calculations of electronic structure, the atoms are treated within the central-field model wherein these densities are sphericalized by ensemble averaging the different orientations. In order to determine more accurately the properties of atoms, their nonsphericity must be taken into account. (Janak and Williams, 1981; Kutzler and Painter, 1987). To do so in a meaningful manner it is important to understand the nonsphericity of the electronic charge distribution in terms of the correlations between the electrons. In this chapter we learn about electron correlations in nonspherical density atoms by investigating the work formalism for such systems.

From the discussion in chapter II it is evident that for both spherically-symmetric and non-spherically-symmetric density systems, the work formalism can be equivalently described in terms of a ***static*** effective exchange-correlation source charge distribution $\rho_{xc}^{eff}(\boldsymbol{r})$ that is given by the divergence of the force-field due to the Fermi-Coulomb hole charge. We thus begin this chapter by first studying the effective exchange charge $\rho_{x}^{eff}(\boldsymbol{r})$ of the spherically symmetric Argon atom. This charge distribution of course, gives rise to the same exchange potential $W_x(\boldsymbol{r})$ as that obtained by calculating the work done in the force field of the Fermi hole charge $\rho_x(\boldsymbol{r}, \boldsymbol{r}')$. We then determine the effective exchange charge $\rho_x^{eff}(\boldsymbol{r})$ and the potential $W_x^{eff}(\boldsymbol{r})$ for the nonspherical density system of the open-shell Carbon atom in its degenerate $1s^2\,2s^2\,2p_z^2$ state in a non-self-consistent calculation (Harbola *et al.*, 1991; Slamet *et al.*, 1994 a).

4.1 Structure of Effective Fermi hole in the Argon Atom

Since the potential seen by the electrons must possess the symmetry of the system, it is expected that the structure of the effective charge distribution from which the potential arises will be similar to that of the electronic density. In order to demonstrate this, we calculate the effective Fermi hole charge distribution $\rho_x^{eff}(\boldsymbol{r})$ for the spherically-symmetric ^{18}Ar atom. In Fig. 9 we plot the quantity $4\pi^2\rho_x^{eff}(\boldsymbol{r})$ together with the radial probability density $4\pi^2\rho(\boldsymbol{r})$. Observe that the effective charge distribution has structure similar to that of the radial probability density in that it closely follows the probability density in exhibiting the shell structure of the atom. (These are the *K*, *L*, and *M* shells). However, in contrast to the Fermi hole $\rho_x(\boldsymbol{r},\boldsymbol{r}')$ which is negative, the effective Fermi hole $\rho_x^{eff}(\boldsymbol{r})$ goes both positive and negative. The effective exchange potential $W_x^{eff}(\boldsymbol{r})$ arising from this static charge is the same as the potential $W_x(\boldsymbol{r})$ obtained as the work done against the force field of the Fermi hole, since the curl of the force field vanishes. This potential (Harbola and Sahni, 1989) is shown in Fig. 10 and its structure can be seen to also clearly delineate the atomic shells.

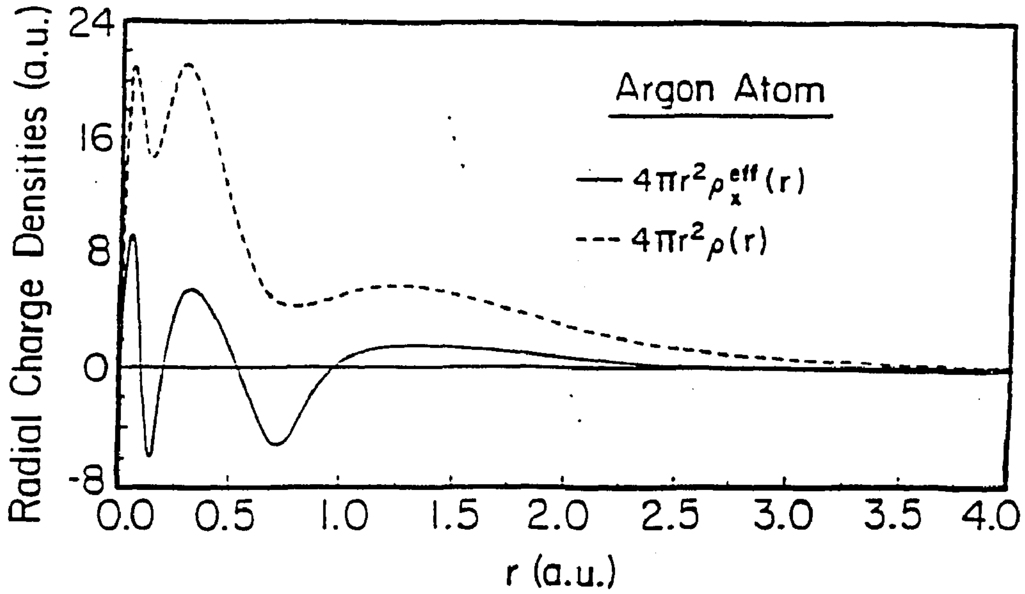

Fig. 9. Variation of the effective radial exchange charge $4\pi r^2 \rho_x^{eff}(r)$ and the radial probability density $4\pi r^2 \rho(r)$ for the Argon atom. (From Fig. 1 of (Harbola *et al.*, 1991)).

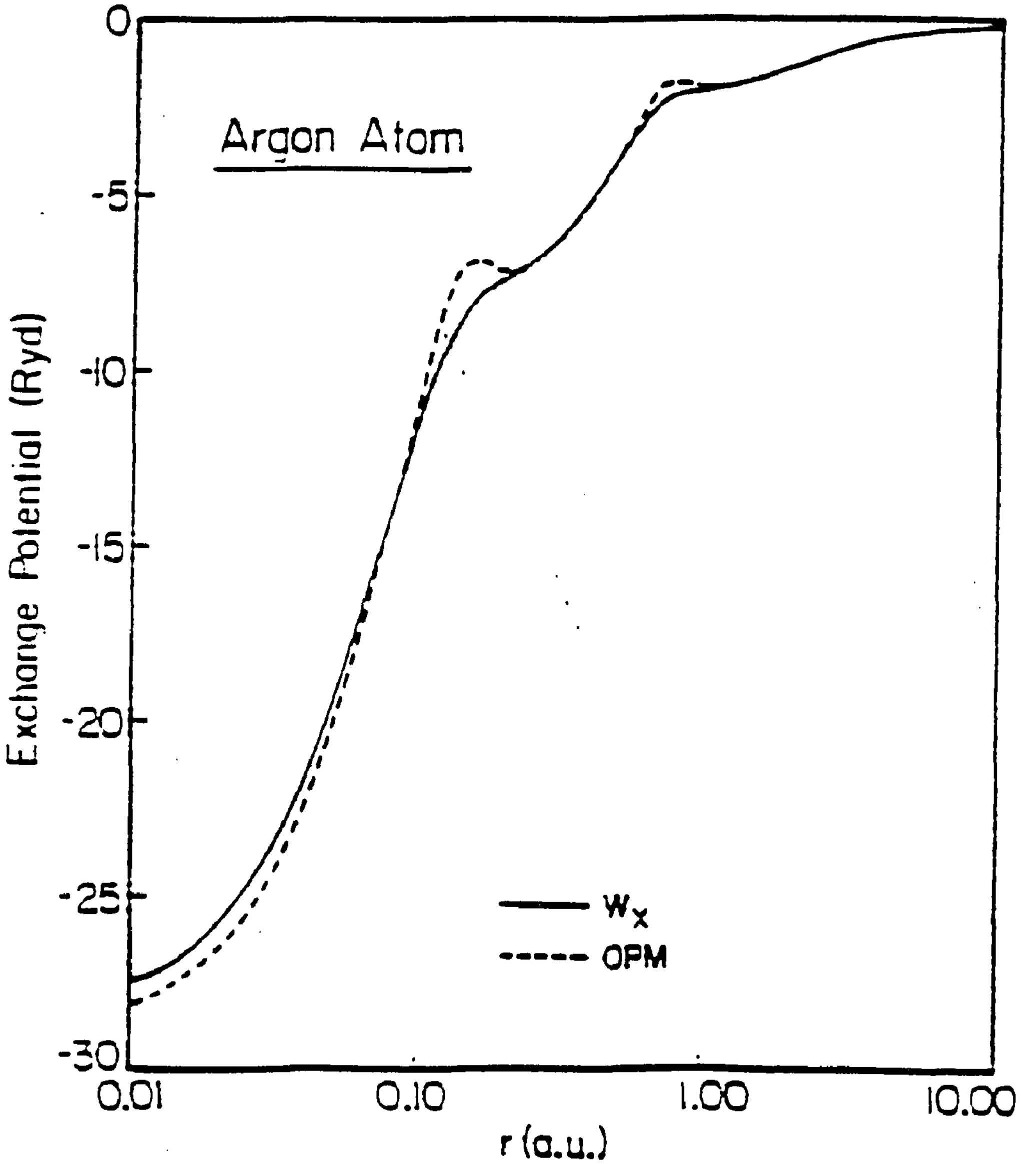

Fig. 10. Variation of the exchange potential $W_x(r)$ as a function of the electron position r for the Argon atom. The exchange potential as obtained by the optimized potential method (OPM) is also plotted. (From Fig. 1 of (Harbola and Sahni, 1989)).

4.2 Structure of Effective Fermi Hole and Exchange Potential in the Nonspherical Carbon Atom

We next consider the open-shell Carbon atom in its $1s^2 2s^2 2p_z^2$ degenerate ground state in the Pauli-correlated approximation. The orbitals are assumed to be hydrogenic so that

$$\begin{aligned}\phi_{1s}(r) &= \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Zr} \\ \phi_{2s}(r) &= \frac{1}{2\sqrt{2\pi}} Z^{3/2} \left(1 - \frac{Z}{2} r\right) e^{-Zr/2} \\ \phi_{2p_z}(r,\theta) &= \frac{1}{4\sqrt{2\pi}} Z^{5/2}\, r \cos\theta\, e^{-Zr/2}\end{aligned} \qquad \text{(III-1)}$$

with $Z = 6$. (This implies the electrons are non-interacting and that the total potential $\left[v_{ext}(\boldsymbol{r}) + W(\boldsymbol{r})\right]$ is central. Also implicit is the assumption that there exists some hypothetical external potential $v_{ext}(\boldsymbol{r})$ which gives rise to this total potential which is central. Of course, non-interacting electrons in a central potential are supposed to possess spherical densities. There is therefore, a further assumption that the electrons are in the degenerate state as a result of some perturbation, and that they remain in that state when the perturbation is removed. The assumption that the non-interacting electrons are in this degenerate state is therefore a means to simulate the non-sphericity of the density of an open-shell atom for which the total potential is not central). The electronic density $\rho(\boldsymbol{r})$ obtained from these orbitals has azimuthal symmetry and depends only on the co-ordinates $[(r,\theta) = q]$. Further, the curl of the force field $\mathcal{E}_x(\boldsymbol{r})$ due to the Fermi hole does not vanish. Thus, for this system, an effective exchange potential $W_x^{eff}(\boldsymbol{r})$ has to be determined from the irrotational component

$\mathcal{E}_x^I(r)$ of the field, with the solenoidal component $\mathcal{E}_x^S(r)$ being neglected. Brief details of the derivation and specific analytical and integral expressions for the various properties are given in Appendix B.

The highly non-spherically symmetric structure of the density $\rho(r)$ is demonstrated in Fig. 11 where the radial probability density $r^2\rho(q)$, as well as the quantity $r^2\ \rho_x^{eff}(r,\theta)$, is plotted for different directions corresponding to θ = 0°, 30°, 60° and 90°. Observe again how the effective charge distribution follows the probability density. For example, as the intershell probability diminishes for increasing θ , so does the effective charge distribution. To further demonstrate the similarity in structure between the effective charge and the probability density, we plot in the panels of Fig. 12 these charge distributions as a function of the angle θ for specific electron positions. These positions correspond to the maxima and intershell minimum of the radial probability distribution as well as a point in the classically forbidden region for θ = 0 (see Fig. 11). Once again observe that the effective charge essentially follows the probability density distribution. Thus the structure of the effective charge distribution for the non-symmetrical system is also similar to that of the probability density distribution. This non-symmetrical effective exchange charge also satisfies the charge conservation sum rule.

The Fermi hole $\rho_x(r,r') \equiv \rho_x(q,q')$ is also independent of the azimuthal angles ϕ and ϕ' . Thus, the force field $\mathcal{E}_x(r)$ due to the Fermi hole charge is independent of

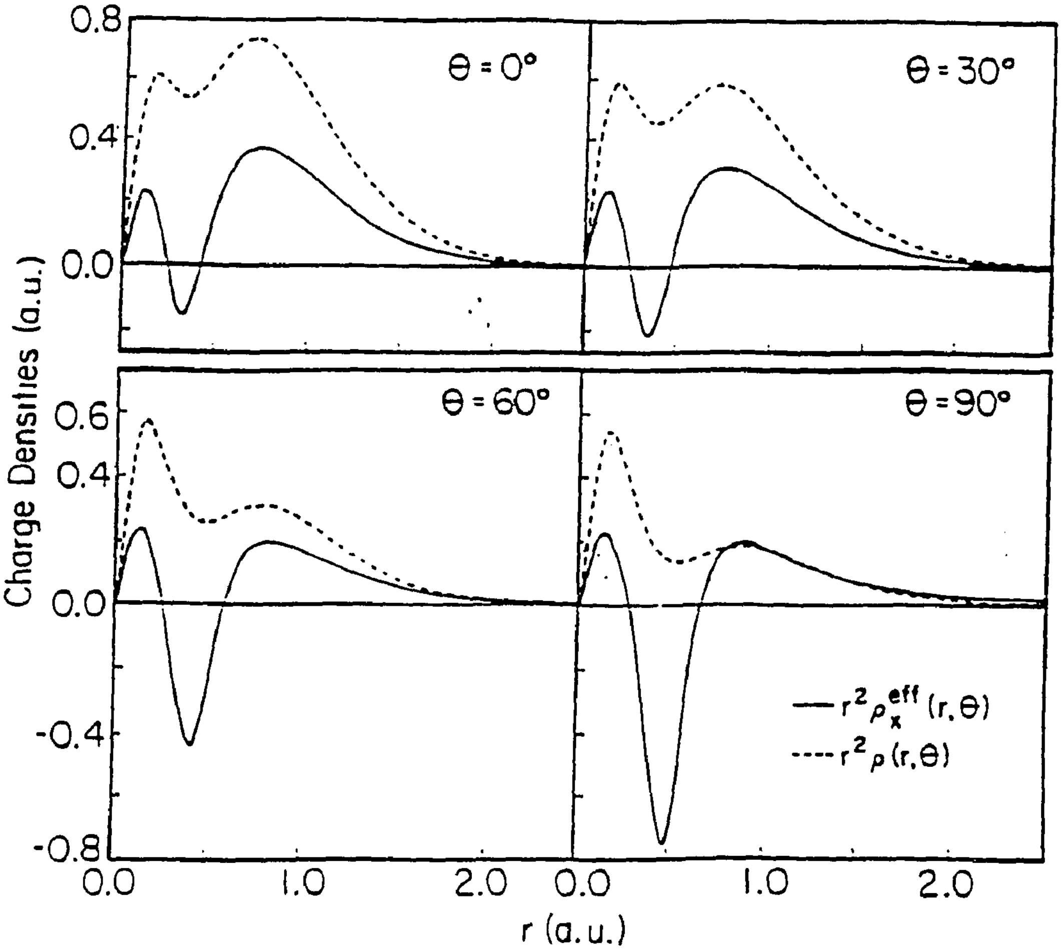

Fig. 11. Variation of the effective exchange charge density $r^2\rho_x^{eff}(r,\theta)$ and the probability density $r^2\rho(r,\theta)$ as a function of the radial distance r for different angles θ for the Carbon atom. (From Fig. 2 of (Harbola *et al.*, 1991)).

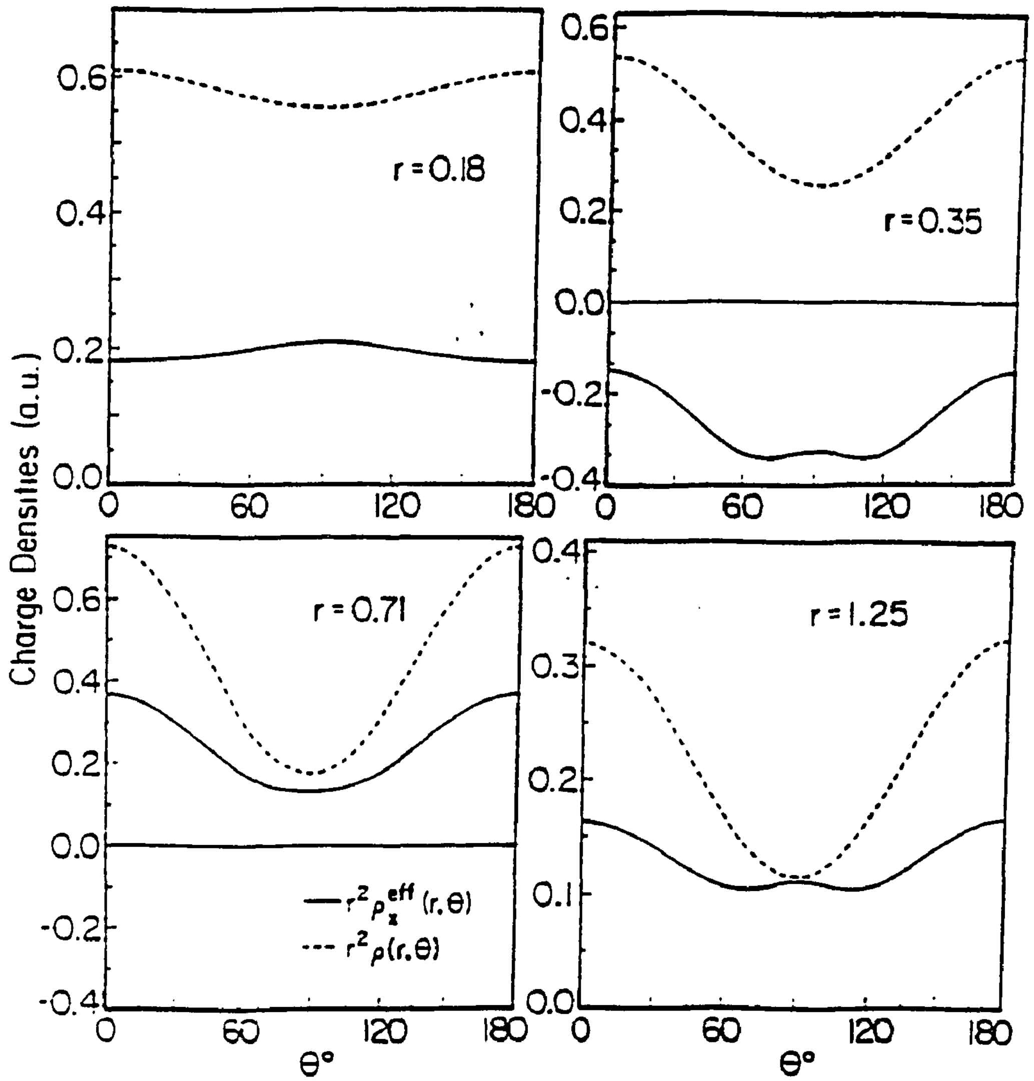

Fig. 12. Variation of the effective exchange charge density $r^2\rho_x^{eff}(r,\theta)$ and the probability density $r^2\rho(r,\theta)$ as a function of the angle θ for different positions r of the electron for the Carbon atom. (From Fig. 3 of (Harbola *et al.*, 1991)).

the angle ϕ and does not have an azimuthal component. (This is also the case for the irrotational $\mathcal{E}_x^I(r)$ and solenoidal $\mathcal{E}_x^S(r)$ components of the field). The force field is thus $\mathcal{E}_x(q) = \hat{i}_r \mathcal{E}_{x,r}(q) + \hat{i}_\theta \mathcal{E}_{x,\theta}(q)$, so that its curl is also independent of ϕ, and only has an azimuthal component: $\nabla \times \mathcal{E}_x = \hat{i}_\phi [\nabla \times \mathcal{E}_x(q)]_\phi$.

In Fig. 13 we plot the curl of the force field (or equivalently the vortex source) as a function of the radial distance r from the nucleus for different angles θ. The curl vanishes for $\theta = 0$, but its magnitude increases (Fig. 13 a) with increasing values of θ reaching a maximum for $\theta = 60°$. With a further increase in θ (Fig. 13 b) the magnitude of the curl decreases vanishing once again for $\theta = 90°$. Observe that the curl of the force field is finite within the atom (see Figs. 11 and 13), and vanishes in ***all*** directions for $r \gtrsim 2.0$ *a.u.* This can be understood from the fact that for finite systems, such as atoms, the Fermi hole charge is localized about the nucleus of each atom. Thus, in the classically forbidden region and right up to the surface of the atom, the vortex source and thus the solenoidal component of the force field is zero. The force field in these regions is thus equivalent to its irrotational component. The curl of the force field also vanishes at the origin. Therefore, in the classically forbidden region as well as at the origin and in the directions $\theta = 0$ and 90°, the effective exchange potential $W_x^{eff}(r)$ is equal to the potential $W_x(r)$ arises from the Fermi hole charge itself.

What the above analysis, together with the fact that the total charge of the

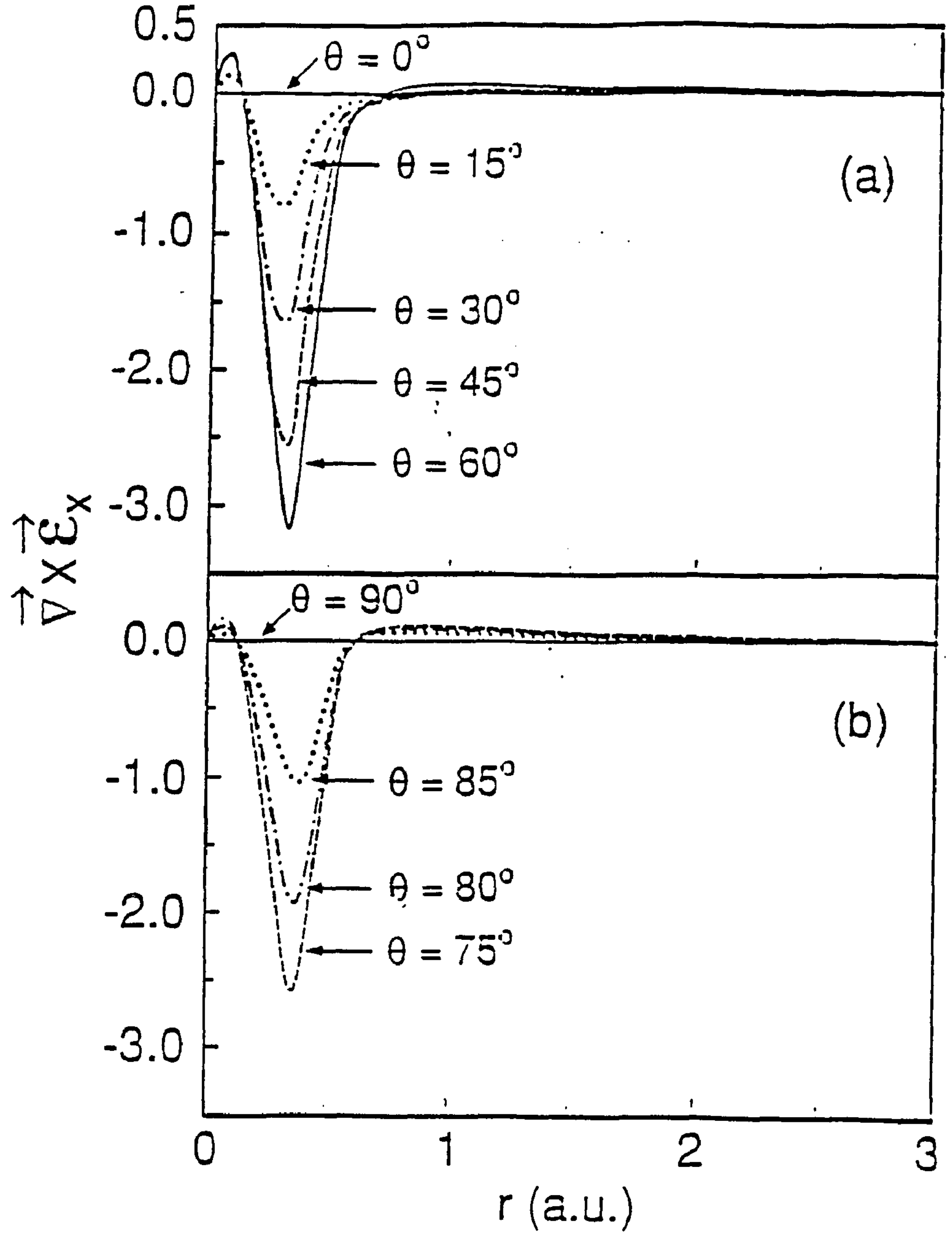

Fig. 13. Variation of the curl of the electric field $\nabla \times \mathcal{E}_x = \hat{i}_\phi [\nabla \times \mathcal{E}_x(r,\theta)]_\phi$ as a function of the electron position r from the nucleus for different angles θ for the Carbon atom. (From Fig. 2 of (Slamet *et al.*, 1994 a)).

Coulomb hole is zero, shows is that even for non-symmetrical density atoms the potential $W_{xc}(r)$ for fully-correlated case is in fact path-independent over substantial regions of configuration space. Furthermore, with a knowledge of the symmetry of a system, specific directions for which this is also the case can be determined. In addition the self-consistent determination of the structure of these atoms is facilitated since the local many-body potential in these regions and directions is then obtained directly from the Fermi-Coulomb hole charge itself rather than via the effective charge $\rho_{xc}^{eff}(r)$.

As we have seen, the vortex source function $J_x(r)$ is finite only within the atom. Therefore, the significant question which next needs to be answered is how the irrotational and solenoidal components of the force field compare to each other. This will answer what fraction of the many-body effects is incorporated in the effective Fermi hole charge $\rho_x^{eff}(r)$, and therefore how accurate the local effective exchange potential $W_x^{eff}(r)$ is.

In Figs. 14, 15 and 16 we compare the magnitudes $|\mathcal{E}_x^I(q)|$ and $|\mathcal{E}_x^S(q)|$ of the irrotational and solenoidal components of the force field as a function of the radial distance r for the different angles $\theta = 0°$, 30° and 60° respectively. In Fig. 14 which corresponds to $\theta = 0°$, there is only the irrotational component $|\mathcal{E}_x^I(q)|$ since in this direction the vortex source vanishes. This force field increases from a small value in the deep interior to a maximum within the *K*-shell of the atom. The structure

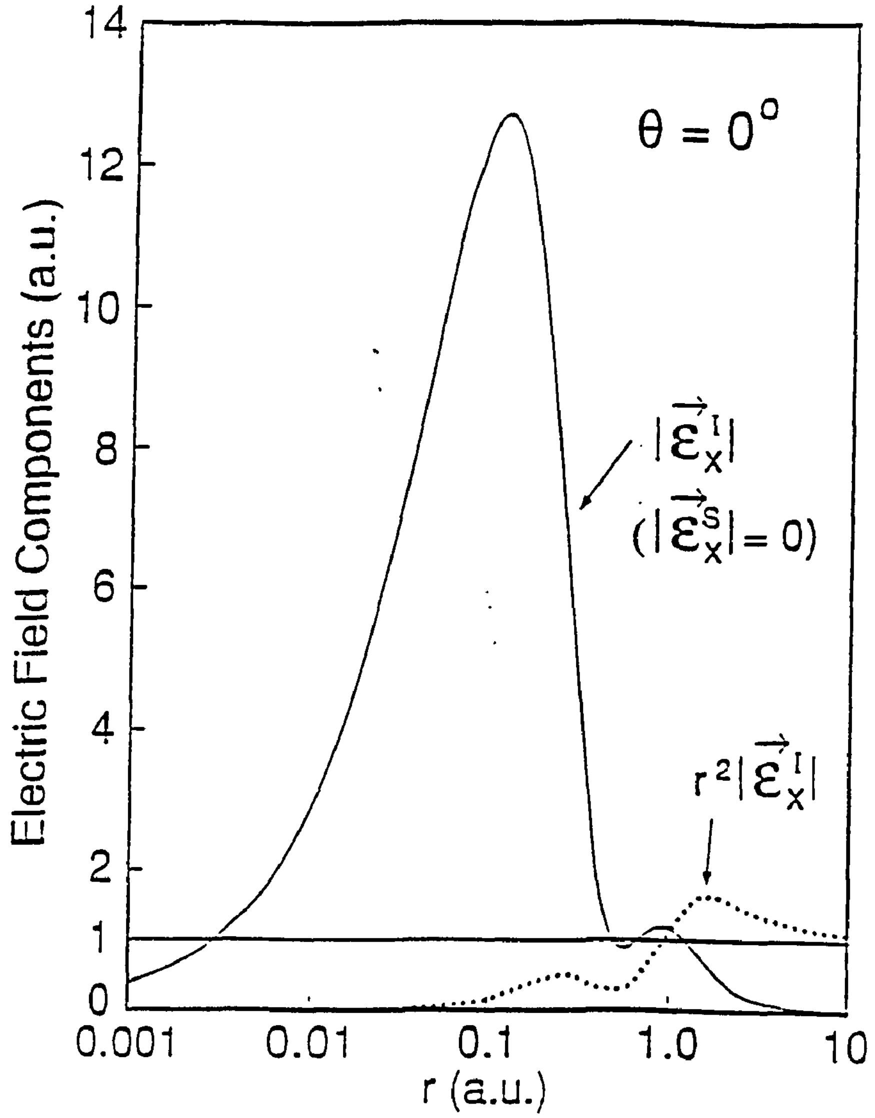

Fig. 14. The magnitudes of the irrotational $\left|\mathcal{E}_x^I(r,\theta)\right|$ and solenoidal $\left|\mathcal{E}_x^S(r,\theta)\right|$ components of the electric field $\mathcal{E}_x(r)$ as a function of electron position r for $\theta = 0°$ for the Carbon atom. The function $\left|\mathcal{E}_x^I(r,\theta)\right|$ is also plotted as the dashed line. (From Fig. 3 of (Slamet *et al.*, 1994 a)).

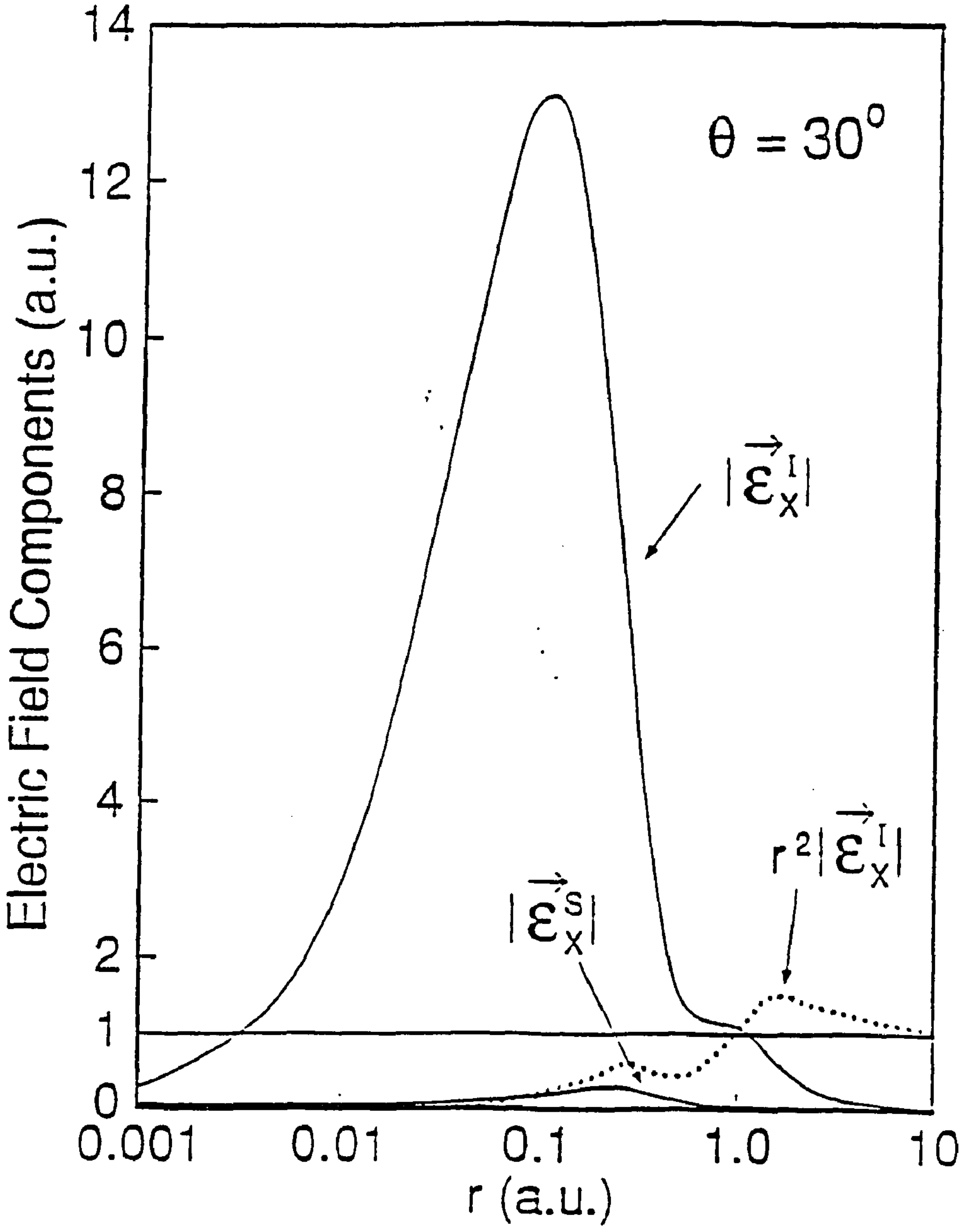

Fig. 15. The figure caption is the same as that of Fig. 14 with the exception that this figure is plotted for θ = 30° . (From Fig. 4 of (Slamet *et al.*, 1994 a)).

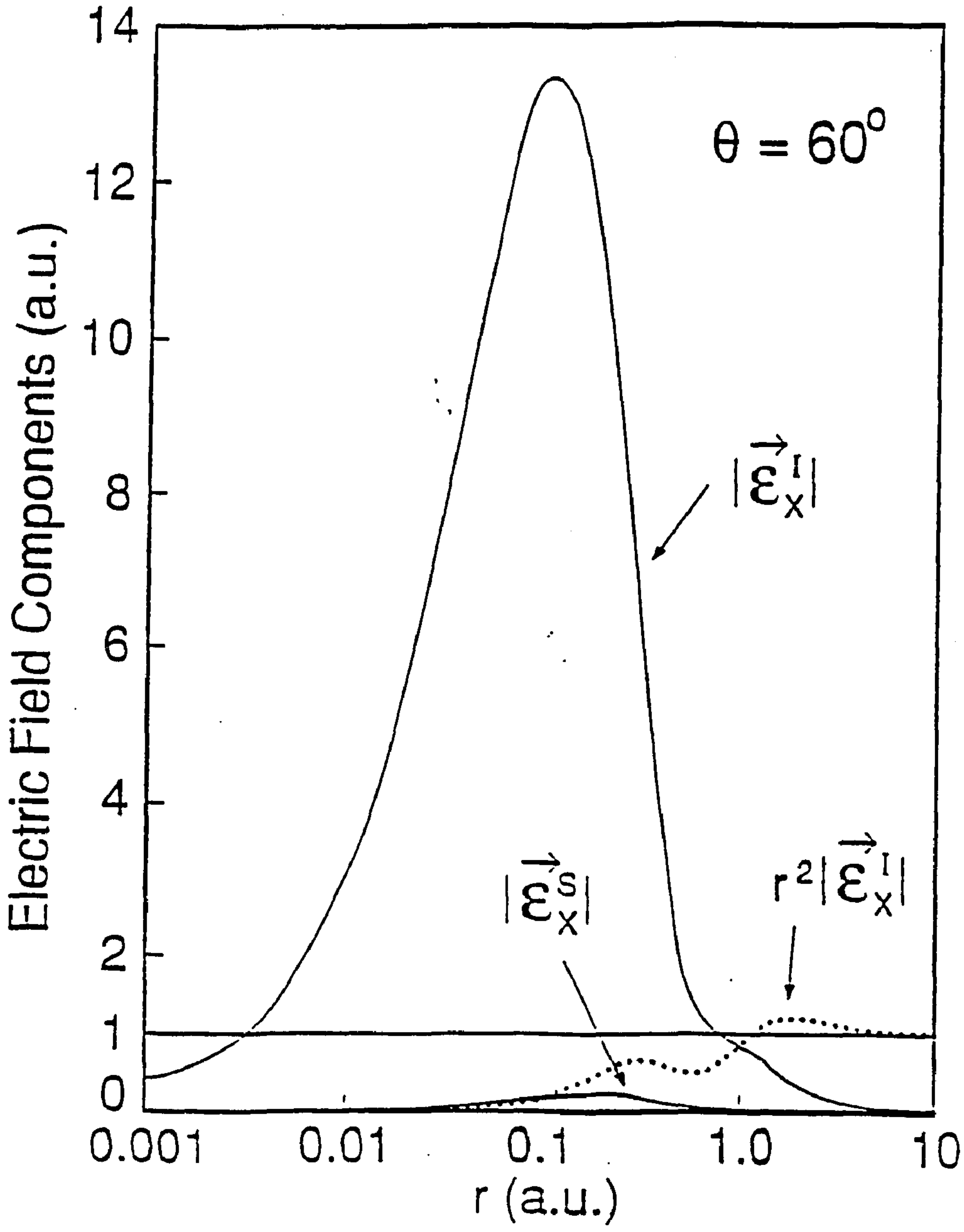

Fig. 16. The figure caption is the same as that of Fig. 15 with the exception that this figure is plotted for θ = 60° . (From Fig. 5 of (Slamet *et al.*, 1994 a)).

of the force field clearly delineates between the atomic shells, with its value in the L-shell being much smaller. In the figure the function $r^2|\mathcal{E}_x^I(q)|$ is also plotted as the dashed line. From this graph it is evident that the magnitude of the force field decays asymptotically as $1/r^2$ in the $\theta = 0°$ direction. Consequently the asymptotic structure of the effective potential $W_x^{eff}(r)$ in this direction must be $-1/r$. Figs. 15 and 16 correspond to $\theta = 30°$ and 60° for which the vortex source is finite (see Fig. 13), so that there is a solenoidal component $|\mathcal{E}_x^S(q)|$ of the field in these directions. Observe that the solenoidal component is negligible in the deep interior of the atom. It reaches a maximum at approximately the same electron position as that of the irrotational component. However, this maximum in $|\mathcal{E}_x^S(q)|$ is ***two orders*** of magnitude smaller than that of $|\mathcal{E}_x^I(q)|$. Further, the solenoidal component vanishes for $r \gtrsim 2.0\ a.u.$ as expected since the vortex source function vanishes in this region. These figures thus indicate that essentially all the many-body effects are incorporated in the effective Fermi hole charge $\rho_x^{eff}(r)$. Therefore, the potential $W_x^{eff}(r)$ is an accurate representation of the local exchange potential seen by the electrons within the atom, and will consequently lead to accurate ground-state energies. The structure of the irrotational component in the $\theta = 30°$ and 60° directions is similar to that for $\theta = 0°$, once again delineating between the shells and decaying asymptotically as $1/r^2$. Thus, as is the case for spherically symmetric atoms, the effective potential $W_x^{eff}(r)$ for open shell atoms must decay asymptotically as $-1/r$ in all directions. This is because the asymptotic structure of $W_x^{eff}(r)$ is due to the unit negative charge contained in $\rho_x^{eff}(r)$. Equivalently, since the vortex source vanishes in the classically forbidden region, the asymptotic structure of $W_x^{eff}(\mathbf{r})$ is the same as that of $W_x(\mathbf{r})$ which in turn arises from the unit negative charge of the Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$.

For electron positions in the deep interior of the atom (see Figs. 14 - 16), the magnitude of the irrotational component $|\mathcal{E}_x^I|$ though small is finite. This is the case even at $r = 0.001\ a.u.$ Thus, even at this electron position, the effective potential $W_x^{eff}(\mathbf{r})$ must have a small though finite slope. However, for an electron at the origin, the Fermi hole charge is spherically symmetric. As such the solenoidal as well as the irrotational components, and therefore the force field itself vanishes for this electron position. Thus, at the origin, the effective exchange potential $W_x^{eff}(\mathbf{r})$ is equivalent to the potential $W_x(\mathbf{r})$ and its slope there, as for spherically symmetric atoms, is zero. This is evident in Fig. 17 where we plot the effective exchange potential $W_x^{eff}(\mathbf{r})$ for the different values of θ . The slope of the potentials in all directions diminishes as the origin is approached, and is virtually zero even at $r = 0.01\ a.u.$

Also notice in the same figure that in all directions the potentials have similar structure increasing monotonically from the origin with a distinct change of slope in the intershell region clearly delineating between the *K*- and *L*- shells. The fact that the difference in the potential $W_x^{eff}(\mathbf{r})$ in different directions is small except for the intershell region explains why the central field model of atoms is so accurate. (For comparison see Fig. 10 for the exchange potential $W_x(\mathbf{r})$ for the spherically

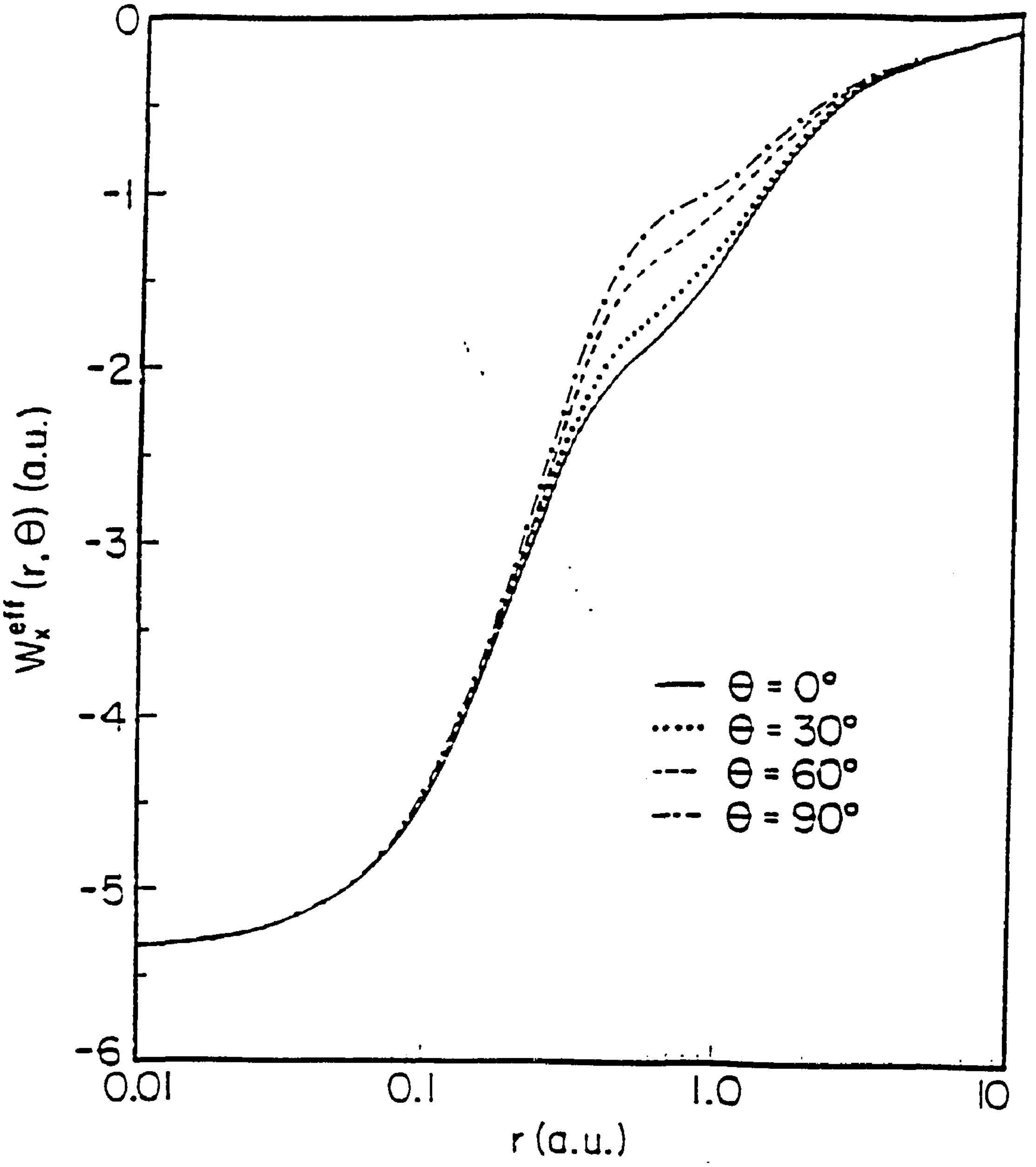

Fig. 17. Variation of the local path-independent effective exchange potential $W_x^{eff}(r,\theta)$ as a function of the radial distance r for different angles θ for the Carbon atom. (From Fig. 4 of (Harbola *et al.*, 1991)).

symmetric Ar atom). Asymptotically the effective exchange potentials decay to zero as $-1/r$ at different rates in the different directions. This is to be expected due to the non-spherical nature of the density. By $r = 10\ a.u.$ the potentials are all exact to two decimal places. The path independence of the potential is also aptly demonstrated by considering the potential at the nucleus of the atom where, independent of the direction of approach, it has a unique value ($-5.34\ a.u.$). We note that in comparison with this number obtained using hydrogenic functions, the corresponding value of the Kohn-Sham exchange potential $\mu_x^{OPM}(r)$ which is determined with the density for the carbon atom being spherically symmetrized is $-4.81\ a.u.$ (Talman and Shadwick, 1976; Aashamar *et al.*, 1978).

The different asymptotic decay rates of the potential $W_x^{eff}(r)$ (Fig. 17), and consequently of the potential $W_x(r)$, and also those of the corresponding force field $\mathcal{E}_x(r)$ (as indicated by the plots of $r^2 | \mathcal{E}_x^l(q) |$ in Figs. 14 - 16), can be explained more rigorously by a study of the center of mass $\langle r' \rangle$ of the Fermi hole for these electron positions. Since for the orbitals assumed, the Fermi hole has azimuthal symmetry, the center of mass always lies along the $z' (\theta = 0°)$ -axis irrespective of the co-ordinates (r,θ) of the electron. In Fig. 18 we plot $\langle r' \rangle$ as a function of the radial electron distance r for $\theta = 0°, 30°, 60°, 90°$. Observe that as for spherically symmetric atoms, the Fermi hole is centered behind the nucleus for small electron positions (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola, 1989). The center of mass then follows the electron within the atom. For asymptotic positions of

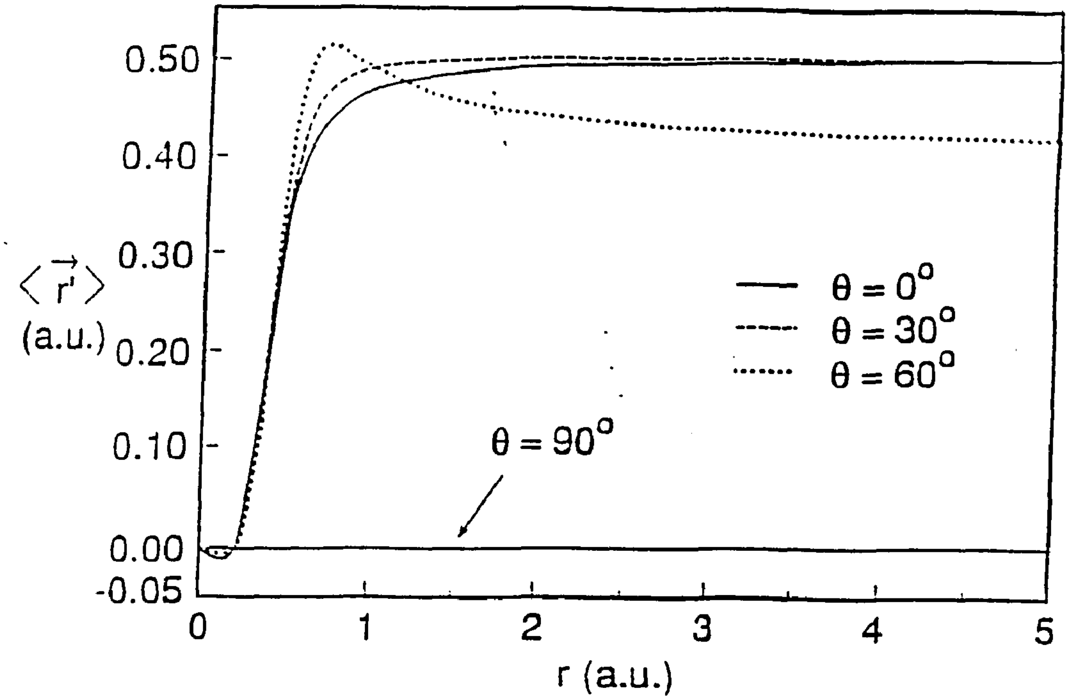

Fig. 18. The center of mass $\langle \mathbf{r}' \rangle$ of the Fermi hole as a function of the radial electron distance r for different directions $\theta = 0°$, 30°, 60° and 90° for the Carbon atom. Due to the azimuthal symmetry of the Fermi hole, its center of mass lies along the z′-axis irrespective of the co-ordinates (r,θ) of the electron. (From Fig. 6 of (Slamet *et al.*, 1994 a)).

the electron, the center of mass approaches a constant value which lies between 0 and 0.5 *a.u.* for $90° \leq \theta \leq 0°$ since the $\lim_{r \to \infty} \langle r' \rangle \sim \cos\theta / [1 + \cos^2\theta]$. That the center of mass approaches a constant can also be seen by plotting the Fermi hole for asymptotic positions of the electron. For these electron positions the changes in the structure of the Fermi hole are negligible and the charge has stabilized. In Fig. 19 we plot the cross-sections of the Fermi hole in the $\theta' = 0$ plane for asymptotic electron positions at $r = 20\,a.u.$ and $\theta = 0°, 30°, 60°, 90°$. From the figure it is evident that with the exception of the $\theta = 90°$ direction for which the Fermi hole is symmetric about the nucleus at the origin, the center of mass in other directions cannot be located at the nucleus. Thus, together with the fact that the total charge of the Fermi hole is negative unity, the different asymptotic values of its center of mass in different directions explains why the force field decays towards $-1/r^2$ with different decay rates in these directions. For wavefunctions more accurate than hydrogenic functions, the center of mass would either decay to zero or to a smaller constant value closer to the nucleus. Consequently so would the force field and potential achieve their asymptotic structures closer to the surface of the atom.

For the fully-correlated case when both Pauli and Coulomb correlations are considered, we reiterate that the Coulomb hole charge $\rho_c(r,r')$ and therefore the effective Coulomb hole $\rho_c^{eff}(r)$ are localized about the nucleus of the atom with total charge zero. Thus, asymptotically the effective correlation potential $W_c^{eff}(r)$ vanishes and the effective exchange-correlation potential $W_{xc}^{eff}(r)$ reduces to that of $W_x^{eff}(r)$.

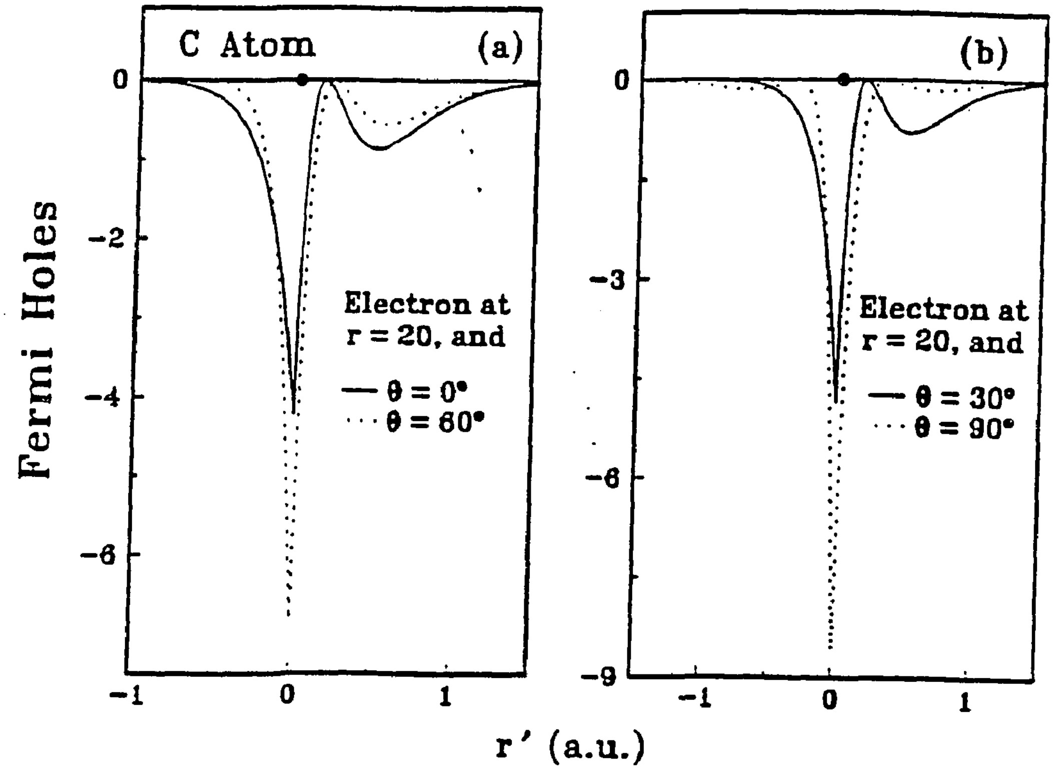

Fig. 19. Cross-sections of the Fermi hole $\rho_x(r,r')$ in the $\theta' = 0$ plane as a function of r' for different electron positions at $r = 20$ *a.u.* and $\theta = 0°$, $30°$, $60°$ and $90°$ for the Carbon atom. The nucleus at the origin is indicated by the small dark circle. (From Fig. 7 of (Slamet *et al.*, 1994 a)).

As noted above, the effective potential $W_x^{eff}(\boldsymbol{r})$ in turn is equivalent to the potential $W_x(\boldsymbol{r})$ in the classically forbidden region since there the vortex source $J_x(\boldsymbol{r})$ vanishes. Thus, as is the case for closed-shell atoms, the structure of the local exchange-correlation potential for open-shell atoms in the region near and outside the surface of the atom is also ***exactly*** known and given by $W_x(\boldsymbol{r})$. In the truly asymptotic region $W_x(r) = -1/r$ in ***all*** directions. Therefore the highest occupied eigenvalue of the differential equation when only Pauli correlations are considered should also gives rise to a good approximation to the ionization potential, electron affinity, and transition energy of atoms.

4.3 Conclusions

From our analysis of the work formalism as applied to a degenerate ground-state of the carbon atom in the Pauli-correlated approximation, we have learned the following.

The vector vortex source function $J_x(\boldsymbol{r})$ for the solenoidal component $\mathcal{E}_x^S(\boldsymbol{r})$ of the electric field $\mathcal{E}_x(\boldsymbol{r})$ due to the Fermi hole charge $\rho_x(\boldsymbol{r},\boldsymbol{r}')$ is finite only within the atom. This follows from the fact that for such finite systems the Fermi hole charge is localized in the atom about the nucleus. The vector source function vanishes in the classically forbidden region and along certain axes of symmetry. As such, the effective exchange potential $W_x^{eff}(\boldsymbol{r})$ in these regions and directions is equal to $W_x(\boldsymbol{r})$, the work done in the force field of the Fermi hole charge. Therefore, over the substantial fraction of configuration space corresponding to these electron positions, the work

$W_x(\mathbf{r})$ is path-independent. Furthermore, the self-consistent determination of the local exchange potential in the classically forbidden region and along these specific symmetry directions is facilitated since its structure for those electron positions can then be determined directly from the Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$ itself rather than via the effective charge $\rho_x^{eff}(\mathbf{r})$.

Although the solenoidal component $\mathcal{E}_x^S(\mathbf{r})$ of the force field is finite within the atom, it is ***two orders*** of magnitude smaller than the irrotational component $\mathcal{E}_x^I(\mathbf{r})$. This means that essentially all the many-body effects are incorporated in the effective Fermi hole charge $\rho_x^{eff}(\mathbf{r})$. Therefore, the potential $W_x^{eff}(\mathbf{r})$ is an accurate representation of the local exchange potential seen by the electrons within the atom, and will consequently lead to accurate ground-state energies. Furthermore, the fact that the difference in the potential $W_x^{eff}(\mathbf{r})$ in the different directions is small except for the intershell region explains why the central field model of atoms is so accurate.

For the fully-correlated case when both Pauli and Coulomb correlations are considered, we know that the Coulomb hole charge $\rho_c(\mathbf{r},\mathbf{r}')$, and therefore the effective Coulomb hole $\rho_c^{eff}(\mathbf{r})$ are localized about the nucleus of the atom with total charge zero. Thus, asymptotically the effective correlation potential $W_c^{eff}(\mathbf{r})$ vanishes and the effective exchange-correlation potential $W_{xc}^{eff}(\mathbf{r})$ reduces to that of $W_x^{eff}(\mathbf{r})$. As noted above, the effective potential $W_x^{eff}(\mathbf{r})$ in turn is equivalent to the potential $W_x(\mathbf{r})$ in the classically forbidden region since there the vortex source $J_x(\mathbf{r})$ vanishes. Thus, as is the case for closed-shell atoms, the structure of the local exchange-correlation potential for open-shell atoms in the region near and outside the surface of the atom is also ***exactly*** known and given by $W_x(\boldsymbol{r})$. In the truly asymptotic region $W_x(\boldsymbol{r}) = -1/r$ in ***all*** directions. The highest occupied eigenvalue of the differential equation when only Pauli correlations are considered should therefore be a good approximation to the ionization potential and electron affinity of atoms, and also give rise to accurate transition energies and polarizabilities.

For an electron at the nucleus, the Fermi-Coulomb hole charge is spherically symmetric. The vortex source, therefore, vanishes, and the effective potential $W_{xc}^{eff}(\boldsymbol{r})$ there is equal to $W_{xc}(\boldsymbol{r})$. Thus, the unique value of the potential at the origin can also be determined directly from the Fermi-Coulomb hole charge. Since the electric field $\mathcal{E}_{xc}(\boldsymbol{r})$ is also zero at this electron position, the effective potential $W_{xc}^{eff}(\boldsymbol{r})$ in the different directions all approach this unique value at the origin with diminishing slope, with the slope finally vanishing at that position.

Finally, as we have seen, even with the choice of hydrogenic orbitals the solenoidal component of the force field is negligible in comparison to the irrotational component. For self-consistently determined orbitals for which the distortion of the electron density from sphericity is expected to be far less pronounced, the solenoidal component will be still smaller. As a consequence, the effective exchange potential $W_x^{eff}(\boldsymbol{r})$ will be more accurate since essentially all the many-body correlation effects would then have been accounted for in the determination of its structure. A self-consistent solution within the Pauli-correlated approximation with the true electron-nucleus external potential would also answer whether there even exists a solenoidal component of the force field, and therefore whether the potential $W_x(\mathbf{r})$ for such non-symmetrical density systems is in fact path-independent throughout space.

Chapter V

PHYSICAL INTERPRETATION OF ELECTRON CORRELATION IN THE LOCAL-DENSITY APPROXIMATION (LDA)

In this chapter we rederive (Sahni, 1994 b; Sahni and Slamet, 1993; Slamet and Sahni, 1992 b) the equations of the local-density approximation (LDA) of Kohn-Sham theory via the work formalism. This derivation then leads to an understanding of the electron correlations within this approximation that is more fundamental than that achieved by Kohn-Sham theory. Now in the LDA as described by Kohn-Sham theory, each point of an inhomogeneous electronic density system is approximated as being homogeneous, but with a density corresponding to the local value at that point. In other words, the correlations between electrons as described by this picture are those of the uniform electron gas. Equivalently, the ***wavefunction*** for the non-uniform electron gas system at ***each*** electron position corresponds to that of a uniform electron gas with a density equal to the local value at that position. This description of the LDA leads naturally to the criticism which questions the efficacy of employing homogeneous electron gas wavefunctions in regions of space where the potential is rapidly varying and in the classically forbidden region where the wavefunction is exponential. On the other hand, the results of application (Jones and Gunnarsson, 1989) of the LDA are remarkably accurate, considerably more so than can be expected on the basis of the above description. Are the LDA results then simply fortuitious? The answer to this question is negative, since as will be explained, the LDA in fact goes beyond uniform electron gas theory and ***explicitly*** incorporates the non-uniformity of the electronic density in its representation of electron correlations. The LDA wavefunction thus incorporates to a significant degree the physics apropos to regions where the potential is varying, and this thereby is the reason for the accuracy of the results achieved. Furthermore, the above mentioned criticism, based on an erroneous understanding of electron correlations in the approximation, is therefore no longer valid.

In the following section we discuss the basis for the current understanding of electron correlations in the LDA as described by Kohn-Sham theory. In the section that follows we describe the work formalism interpretation of the correlations within this approximation.

5.1 Interpretation of the LDA via Kohn-Sham Theory

In Kohn-Sham theory, the exchange-correlation energy functional in the LDA is written as

$$E_{xc}^{LDA}[\rho] = \int \epsilon_{xc}^{(0)}\{\rho(\boldsymbol{r})\}\ \rho(\boldsymbol{r})\ d\boldsymbol{r} \tag{V-1}$$

$$= \frac{1}{2}\iint \frac{\rho(\boldsymbol{r})\rho_{xc}^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}}{|\boldsymbol{r}-\boldsymbol{r}'|}\ d\boldsymbol{r}\ d\boldsymbol{r}' \quad , \tag{V-2}$$

where $\epsilon_{xc}^{(0)}\{\rho(\boldsymbol{r})\}$ and $\rho_{xc}^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ are respectively, the average exchange-correlation energy per electron and the Fermi-Coulomb hole charge distribution for the ***uniform*** electron gas (as indicated by the superscript (0)). The explicit dependence of these expressions on the density $\rho(\boldsymbol{r})$ implies that each point of the non-uniform density is to be treated as if it were homogeneous but with a density that corresponds to the local value at that point. Since for the uniform electron gas the Fermi-Coulomb hole charge is spherically symmetric about an electron, the hole charge $\rho_{xc}^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ for the non-uniform electron gas is also spherically symmetric about the electron irrespective of its position in the system. Furthermore the hole $\rho_{xc}^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ also satisfies the charge conservation constraint of the exact Fermi-Coulomb hole. On the basis of the definitions (Eqs. (V-1) and (V-2)) of $E_{xc}^{LDA}[\rho]$ and the fact that $\rho_{xc}^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ by construction satisfies the charge conservation sum rule, one then assumes the correlations between electrons in the LDA to be those of the homogeneous electron gas. As a consequence the resulting Fermi-Coulomb hole charge is also always assumed to be spherically-symmetric about the electron. However, as will be shown in the following section, this is not the case.

In the expression for $E_{xc}^{LDA}[\rho]$ of Eq. (V-1) the values for the average exchange-correlation energy per electron $\epsilon_{xc}^{(0)}\{\rho(\boldsymbol{r})\}$ are determined from the solution of the Schrödinger equation for the uniform electron gas over a wide range of densities. This is done by Monte Carlo methods (Ceperley, 1978). A parametrized analytical fit to these numbers can then be used in the LDA energy functional. Since it is the Schrödinger equation that is being solved, the resulting $\epsilon_{xc}^{(0)}\{\rho(\boldsymbol{r})\}$ determined does not include the correlation contribution T_c to the kinetic energy. Thus, this contribution to the kinetic energy is not accounted for in the LDA exchange-correlation energy functional $E_{xc}^{LDA}[\rho]$ as described above. (We note, however, that the exchange-correlation energy per particle $\epsilon_{xc}^{(0)}\{\rho(\boldsymbol{r})\}$ commonly employed in the literature

(Perdew and Zunger, 1981; Ceperley, 1978) is not the same as the quantum-mechanical $\epsilon_{xc}^{(0)}\{\rho(\boldsymbol{r})\}$ described here. The expression used in the literature is the sum of $\epsilon_{x}^{(0)}\{\rho(\boldsymbol{r})\}$ which is the exchange energy density derived when only Pauli correlations are considered, and $\epsilon_{c}^{(0)}\{\rho(\boldsymbol{r})\}$ which is obtained from the difference between the fully interacting system ground-state energy and the Hartree-Fock theory energy corresponding to the same density. This correlation energy density $\epsilon_{c}^{(0)}\{\rho(\boldsymbol{r})\}$ therefore contains part of the correlation contribution to the kinetic energy.)

Finally, the LDA exchange-correlation potential $\mu_{xc}^{LDA}(\boldsymbol{r})$ which generates the orbitals for the construction of the density is obtained as the functional derivative of $E_{xc}^{LDA}[\rho]$:

$$\mu_{xc}^{LDA}(\boldsymbol{r}) = \frac{\delta E_{xc}^{LDA}[\rho]}{\delta \rho} = \frac{d}{d\rho}[\rho(\boldsymbol{r})\ \epsilon_{xc}^{(0)}\{\rho(\boldsymbol{r})\}] \quad , \qquad \text{(V-3)}$$

and the LDA differential equation

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + \mu_{xc}^{LDA}(\boldsymbol{r}) \right] \phi_i(\boldsymbol{r}) = \epsilon_i\ \phi_i(\boldsymbol{r}) \qquad \text{(V-4)}$$

then solved self-consistently for these orbitals.

For the case when only correlations due to the Pauli exclusion principle are considered, the LDA equations are obtained from the Hartree-Fock theory wavefunction for the uniform electron gas which is a Slater determinant of plane waves. The resulting average exchange energy per electron $\epsilon_{x}^{(0)}\{\rho(\boldsymbol{r})\}$ and Fermi hole charge distribution $\rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ to be substituted in the exchange-only counterpart $E_x^{LDA}[\rho]$ of Eqs. (V-1) and (V-2) can be determined analytically, and are given respectively by the expressions

$$\epsilon_x^{(0)}\{\rho(\boldsymbol{r})\} = -\frac{3k_F(\boldsymbol{r})}{4\pi} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}[\rho(\boldsymbol{r})]^{\frac{1}{3}} \quad , \tag{V-5}$$

and

$$\rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} = -\frac{1}{2}\,\rho(\boldsymbol{r})\left[\frac{9j_1^2(x)}{x^2}\right] \quad , \tag{V-6}$$

where $k_F(\boldsymbol{r}) = [3\pi^2\rho(\boldsymbol{r})]^{1/3}$ is the local value of the Fermi momentum, and $j_1(x) = [\sin x - x\cos x]/x^2$ is the first-order spherical Bessel function with $x = k_F R$ and $\boldsymbol{R} = \boldsymbol{r}' - \boldsymbol{r}$. (We note that the exchange energy of the LDA was originally proposed by Dirac (Dirac, 1930) as an extension to Thomas-Fermi theory (Thomas, 1927; Fermi, 1927; *ibid.*, 1928). Slater also tried to derive the LDA exchange potential within his theory (Slater, 1951), but the result differs by a factor of 3/2 although it has the right density dependence. The correct result was then confirmed by the subsequent work of Gaspar (1954), and Kohn and Sham (1965)). The LDA for exchange (X) potential $\mu_x^{LDA}(\boldsymbol{r})$ is then

$$\mu_x^{LDA}(\boldsymbol{r}) = \frac{\delta E_x^{LDA}[\rho]}{\delta\rho} = -\frac{k_F(\boldsymbol{r})}{\pi} = -\left(\frac{3}{\pi}\right)^{\frac{1}{3}}[\rho(\boldsymbol{r})]^{\frac{1}{3}} \, , \tag{V-7}$$

and the corresponding electron interaction potential $v_{ee}^{LDAX}(\boldsymbol{r})$ of Kohn-Sham theory is

$$v_{ee}^{LDAX}(\boldsymbol{r}) = v_H(\boldsymbol{r}) - \frac{k_F(\boldsymbol{r})}{\pi} \quad . \qquad \text{(V-8)}$$

We note that, as is the case with the Fermi-Coulomb hole charge $\rho_{xc}^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$, the Fermi hole $\rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is also spherically symmetric about the electron irrespective of its position, and that it satisfies all the constraints of the exact Fermi hole. Thus, once again it is on the basis of the definition of the LDA exchange energy functional $E_x^{LDA}[\rho]$, and the fact that the resulting Fermi hole by construction satisfies the requisite sum rules, that one assumes the electron correlations to be those of the uniform electron gas. This, however, is not how electrons are correlated within the LDA for exchange. In the following section we derive via the work formalism the explicit analytical representation of electron correlations within the local density and Pauli-correlated approximations.

5.2 Interpretation of the LDA via the Work Formalism

We begin our analysis of electron correlations in the LDA via the work formalism by first considering the case of correlations due to the Pauli exclusion principle. Further, let us initially consider the electrons to be correlated as described in the previous section by Kohn-Sham theory. In other words we assume the wavefunction to be a Slater determinant of plane waves, and then invoke the LDA by assuming these correlations to be valid at each point of the non-uniform density of the system. We refer to this approximation as the ***density-functional theory (DFT) Hartree approximation***, the reason for which will become clear shortly. With this wavefunction, the corresponding pair-correlation density (see Eq. (II-1)) is

$$g_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} = \rho(\boldsymbol{r}') + \rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} \quad , \tag{V-9}$$

where $\rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is given in Eq. (V-6), and is the Fermi hole in the description of the LDA via Kohn-Sham theory. Now since the Fermi hole charge $\rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is ***spherically symmetric*** about the electron irrespective of its position, there is no contribution of this charge to the force field at the electron position. The force-field $\boldsymbol{\mathcal{E}}^{(0)}(\boldsymbol{r})$ of the pair-correlation density $g_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ then arises only from the term $\rho(\boldsymbol{r}')$ of Eq. (V-9) so that

$$\boldsymbol{\mathcal{E}}^{(0)}(\boldsymbol{r}) = \int \frac{g_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}\;(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}' = \boldsymbol{\mathcal{E}}_H(\boldsymbol{r}) \quad , \tag{V-10}$$

the Hartree field. Therefore, the corresponding work done $W^{(0)}(\boldsymbol{r})$ is the Hartree potential $v_H(\boldsymbol{r})$:

$$W^{(0)}(\boldsymbol{r}) = v_H(\boldsymbol{r}) = \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}' \quad . \tag{V-11}$$

Thus, we see that electron correlations as represented by $g_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ give rise via Coulomb's law to the Hartree potential $v_H(\boldsymbol{r})$. The differential equation governing the system is then the density-functional theory Hartree approximation equation

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{r}) + v_H(\boldsymbol{r}) \right] \phi_i(\boldsymbol{r}) = \epsilon_i\, \phi_i(\boldsymbol{r}) \quad , \tag{V-12}$$

with $\rho(\boldsymbol{r}) = \Sigma_i\,|\phi_i(\boldsymbol{r})|^2$. The resulting electron interaction energy $E_{ee}^{(0)}$ which is the energy of interaction between the density and pair-correlation density is then

$$\begin{aligned} E_{ee}^{(0)} &= \frac{1}{2}\iint \frac{\rho(\boldsymbol{r})\, g_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}' \\ &= E_H[\rho] + \frac{1}{2}\iint \frac{\rho(\boldsymbol{r})\rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}' \qquad \text{(V-13)} \\ &= E_H[\rho] + E_x^{LDA}[\rho] \quad , \end{aligned}$$

which is the same expression as the electron interaction energy in the LDAX of Kohn-Sham theory (See Eq. (V-2)). Therefore, the expression for the total ground-state energy in the DFT Hartree approximation is also the same as that in the LDAX scheme. However, the ***numerical values*** of these ground-state energies are different because the orbitals employed to determine these energies are generated by different equations: the Hartree differential equation of Eq. (V-12), and the differential equation in the LDAX scheme. The energy in the DFT Hartree approximation will therefore be an upper bound to that in the LDAX. This is demonstrated in Table I where we have quoted the ground-state energies of noble gas and closed s-subshell atoms as determined via the DFT Hartree and local density approximations.

What we have therefore learned from the above analysis in the Pauli-correlated approximation is the following. If the electrons of the non-uniform system are assumed at each point to be correlated as in a uniform electron gas, then the corresponding pair-correlation density $g_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ gives rise via Coulomb's law to an electron interaction potential $v_{ee}(\boldsymbol{r})$ that is the Hartree potential $v_H(\boldsymbol{r})$ and not that of Eq. (V-8) of the Kohn-Sham LDAX scheme. Therefore, this is not how

TABLE I

Self-consistent ground-state energies of noble gas and closed s-subshell atoms within the Pauli-correlated approximation as obtained in the density-functional theory (DFT) Hartree approximation, the local-density approximation (LDA), the work formalism and Hartree-Fock theory. The negative values of the energies in Rydbergs are quoted. (From Table I of (Sahni; 1994 b)).

Atoms	**DFT Hartree**	**LDA**[(a)]	**Work formalism**[(b)]	**Hartree-Fock**[(c)]
^{2}He	2.64227	2.72364	2.86168	2.86168
^{4}Be	14.1050	14.2233	14.5714	14.5730
^{10}Ne	127.048	127.491	128.542	128.547
^{12}Mg	197.797	198.249	199.606	199.615
^{18}Ar	523.864	524.518	526.804	526.818
^{20}Ca	673.501	674.160	676.743	676.758
^{30}Zn	1772.59	1773.91	1777.82	1777.85
^{36}Kr	2745.47	2746.87	2752.03	2752.06
^{38}Sr	3124.62	3126.01	3131.52	3131.55
^{48}Cd	5456.02	5457.88	5465.09	5465.13
^{54}Xe	7221.86	7223.78	7232.10	7232.14
^{56}Ba	7872.98	7874.89	7883.51	7883.54
^{70}Yb	unbound	13381.6	13391.4	13391.5
^{80}Hg	18394.6	18397.7	18408.9	18409.0
^{86}Rn	21852.1	21855.2	21866.7	21866.8

(a) Tong and Sham, 1966
(b) Sahni *et al.*, 1992
(c) Fischer, 1977

electrons are correlated within the LDAX. (The same conclusions are arrived at for the more general case when both Pauli and Coulomb correlations are considered).

The true wavefunction corresponding to the LDAX is therefore not a Slater determinant of plane waves assumed valid locally. However, it is still a Slater determinant of single-particle orbitals since only Pauli correlations are being considered. Thus, in order to obtain the true pair-correlation density $g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ in the LDAX, we expand the general expression for $g_x(\boldsymbol{r},\boldsymbol{r}')$ of Eq. (II-29) in gradients of the density about the uniform electron gas result, and then assume these correlations to be valid locally. To do so one requires the corresponding expansion for the Dirac density matrix $\gamma(\boldsymbol{r},\boldsymbol{r}')$ because both terms of $g_x(\boldsymbol{r},\boldsymbol{r}')$ viz. the density $\rho(\boldsymbol{r})$ and the Fermi hole $\rho_x(\boldsymbol{r},\boldsymbol{r}')$ are defined in terms of it (see Eq. (II-30)). The details of the derivation of the expansion of $\gamma(\boldsymbol{r},\boldsymbol{r}')$ are given in Appendix C. The lowest-order correction to the off-diagonal elements of the density matrix $\gamma(\boldsymbol{r},\boldsymbol{r}')$ is of $O(\nabla)$, whereas that of the diagonal matrix element which is the density $\rho(\boldsymbol{r})$, is of $O(\nabla^2)$. Thus, the expansion of the pair-correlation density $g_x(\boldsymbol{r},\boldsymbol{r}')$ to lowest order in ∇ assumed valid locally, which is $g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$, is given as

$$g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} = \rho(\boldsymbol{r}') + \rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} + \rho_x^{(1)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} , \qquad \text{(V-14)}$$

where

$$\rho_x^{(1)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} = \frac{9}{4}\,\rho(\boldsymbol{r}) \left[\frac{j_0(x)\,j_1(x)}{k_F^3}\,\hat{\boldsymbol{R}}\cdot\nabla k_F^2\right] , \qquad \text{(V-15)}$$

$j_0(x) = (\sin x)/x$ is the zeroth-order spherical Bessel function, $\hat{\boldsymbol{R}} = \boldsymbol{R}/R$, and where the superscript (1) indicates the expression to be of $O(\nabla)$. To see whether $g_x^{LDA}\{r,r';\rho(r)\}$ is the correct pair-correlation density in the LDAX, we next determine the potential due to this charge distribution via Coulomb's law. The term $\rho_x^{(1)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is ***not spherically symmetric*** about the electron position, and thus contributes to the force field $\mathcal{E}^{LDAX}(\boldsymbol{r})$ due to $g_x^{LDA}\{r,r';\rho(\boldsymbol{r})\}$. This contribution (Wang *et al.*, 1990) is $\nabla k_F(r)/\pi$, so that

$$\begin{aligned}\mathcal{E}^{LDAX}(\boldsymbol{r}) &= \int \frac{g_x^{LDA}\{r,r';\rho(r)\}(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\,d\boldsymbol{r}' \\ &= \mathcal{E}_H(\boldsymbol{r}) + \nabla\left(\frac{k_F(r)}{\pi}\right) \quad .\end{aligned} \tag{V-16}$$

The work done $W^{LDAX}(\boldsymbol{r})$ to move an electron in this force field is then

$$W^{LDAX}(r) = v_H(r) - \frac{k_F(r)}{\pi} \quad , \tag{V-17}$$

which is the Kohn-Sham LDAX electron interaction potential $v_{ee}^{LDAX}(\boldsymbol{r})$ of Eq. (V-8). Thus, the system differential equation derived from the pair-correlation density $g_x^{LDA}\{r,r';\rho(\boldsymbol{r})\}$ via Coulomb's law is the same as that of the Kohn-Sham LDAX scheme. Further, note that the curl of the force field $\mathcal{E}^{LDAX}(\boldsymbol{r})$ vanishes. This explains why the potential $v_{ee}^{LDAX}(\boldsymbol{r})$ is path-independent. The corresponding expression for the electron interaction energy obtained from $g_x^{LDA}\{r,r';\rho(\boldsymbol{r})\}$ is also the same as that of Kohn-Sham LDAX theory. This potential energy E_{ee}^{LDAX} is the energy of interaction between the density $\rho(\boldsymbol{r})$ and the pair-correlation density $g_x^{LDA}\{r,r';\rho(\boldsymbol{r})\}$. However, the non-spherically symmetric component $\rho_x^{(1)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ does not contribute to the energy integral so that

$$\begin{aligned} E_{ee}^{LDAX} &= \frac{1}{2} \int\int \frac{\rho(\boldsymbol{r})\, g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}' \\ &= E_H[\rho] + E_x^{LDA}[\rho] \quad , \end{aligned} \tag{V-18}$$

which is the Kohn-Sham LDAX theory expression. Note that the numerical value of the electron interaction potential energy, and therefore of the total ground-state energy is also the same as the Kohn-Sham scheme since the orbitals are identical. Thus, we see that the pair-correlation density $g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is the correct representation of electron correlations in the local-density approximation for exchange.

From the expression for $g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ of Eq. (V-14) we also learn that the Fermi hole in the LDA $\rho_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is then

$$\rho_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} = \rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} + \rho_x^{(1)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} \quad , \tag{V-19}$$

and that it is not spherically symmetric about the electron position. The LDA Fermi hole satisfies the constraints of charge neutrality and value at the electron position since the non-spherical component $\rho_x^{(1)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ does not contribute to either sum rule. It does not, however, satisfy the constraint of negativity, and this is one source of error in the LDA. It is also important to note that it is the ***non-spherically symmetric*** component $\rho_x^{(1)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ of the LDA Fermi hole charge that generates the force-field and thereby the local exchange potential $\mu_x^{LDA}(\boldsymbol{r})$ and orbitals of the Kohn-Sham LDAX differential equation. However, it is only the ***spherically symmetric*** component $\rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ that contributes to the LDA exchange energy.

Based on what we have just learned in the LDA for exchange, we now know that when both Pauli and Coulomb correlations are considered, the Coulomb correlation effects in the LDA are also represented by a Coulomb hole charge $\rho_c^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ that is not spherically symmetric about the electron position. As such the LDA Coulomb hole can be written as

$$\rho_c^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} = \rho_c^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} + \rho_c^{(1)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} \quad , \tag{V-20}$$

where $\rho_c^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is its spherically symmetric component obtained from uniform electron gas theory, and $\rho_c^{(1)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is its non-spherically symmetric component which is a term of first-order in the gradient of the density. It is this latter term that gives rise to the LDA exchange-correlation potential and orbitals. As in the Pauli-correlated case, only the spherically symmetric component of the charge contributes to the energy. Thus, neither the Fermi nor Coulomb or Fermi-Coulomb hole charge distributions as determined within the LDA are spherically symmetric about the electron position. An expression for the non-spherically symmetric component of the LDA Coulomb hole has not yet been derived. We have, however, studied (Slamet and Sahni, 1994 b) the spherically symmetric component of the LDA Fermi-Coulomb and Coulomb holes to explain why the error in the LDA correlation energy for atoms is so large (Perdew and Zunger, 1981; Tong and Sham, 1966).

5.3 Application to Atoms

In this section we apply our understanding of electron correlations within the LDA to atoms in order to study the accuracy of various atomic ground-state properties obtained in this approximation. The calculations are performed within the Pauli-correlated approximation, the results presented being fully self-consistent. Since the explanation of how electrons are correlated in the LDA is achieved via the work formalism, the LDA results are compared with those of self-consistent computations performed within the work formalism (WF) for exchange.

In Fig. 20 we plot the cross-sections of the LDA Fermi hole $\rho_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ (Eq. (V-19)) and its spherically symmetric component $\rho_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ (Eq. (V-6)) in the electron-nucleus plane ($\theta = 0$) for three different electron positions in the high probability density regions of Be atom. The electron positions considered (indicated by the arrows) are at the nucleus $r = 0$, and at the positions of maximum radial probability density in the *K*- and *L*- shells which are at $r = 0.266\, a.u.$ and $r = 2.05\, a.u.$, respectively. The corresponding cross-sections of the exact Fermi hole of the work formalism are also plotted. In Fig. 21 we plot the Fermi holes for the electron positions in the low probability density regions of the atom, which are at $r = 1.1\, a.u.$ which is the position of the intershell minimum of the radial probability density, and $r = 4.1\, a.u.$ in the classically forbidden region. Observe in all these figures that the LDA Fermi hole is not spherically symmetric about the electron position. Furthermore, it develops decaying oscillations which demonstrates that it does not satisfy the constraint of negativity. The positive part of these oscillations have no physical meaning, since the effect of the Pauli-exclusion principle can only be in terms of a ***reduction*** in the density. Another consequence of the oscillations is that

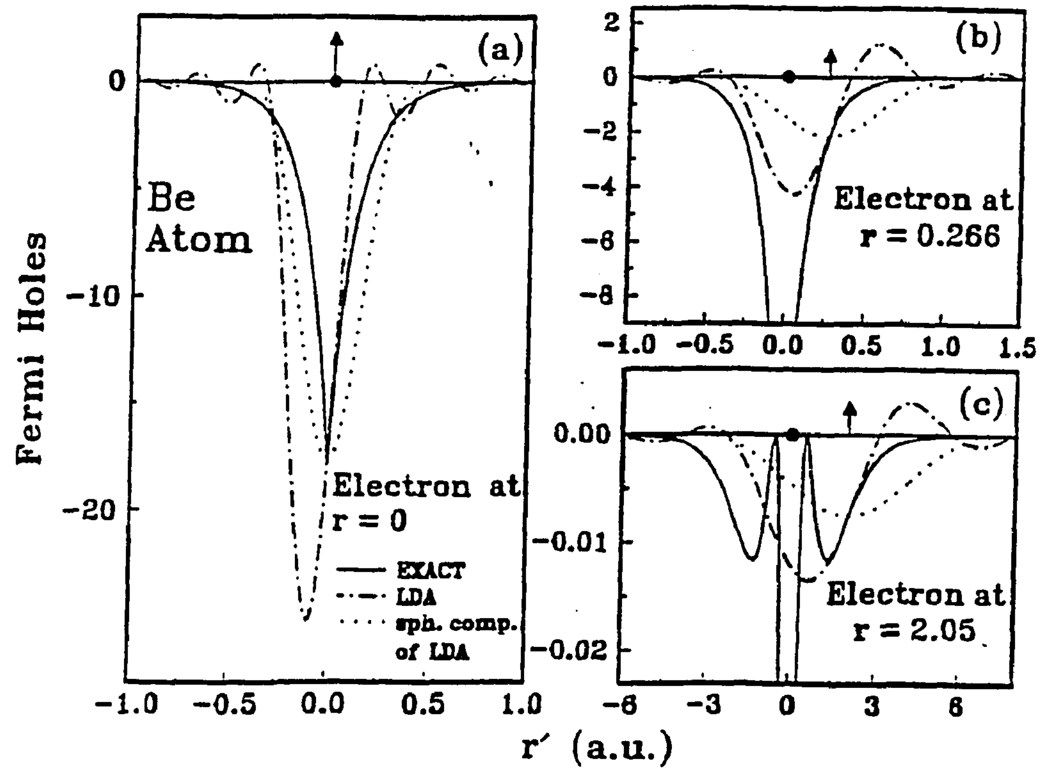

Fig. 20. Cross-sections in the nucleus-electron plane of the Fermi holes for the Be atom for different electron positions. The Fermi holes plotted are those of the exact, local-density approximation (LDA) for exchange, and its spherically symmetric component (sph. comp.). The electron positions, indicated by the arrow, are at (a) the nucleus, (b) and (c) at the first and second maximum of the radial probability density corresponding to the K- and L-shell, respectively, of the LDA for exchange.

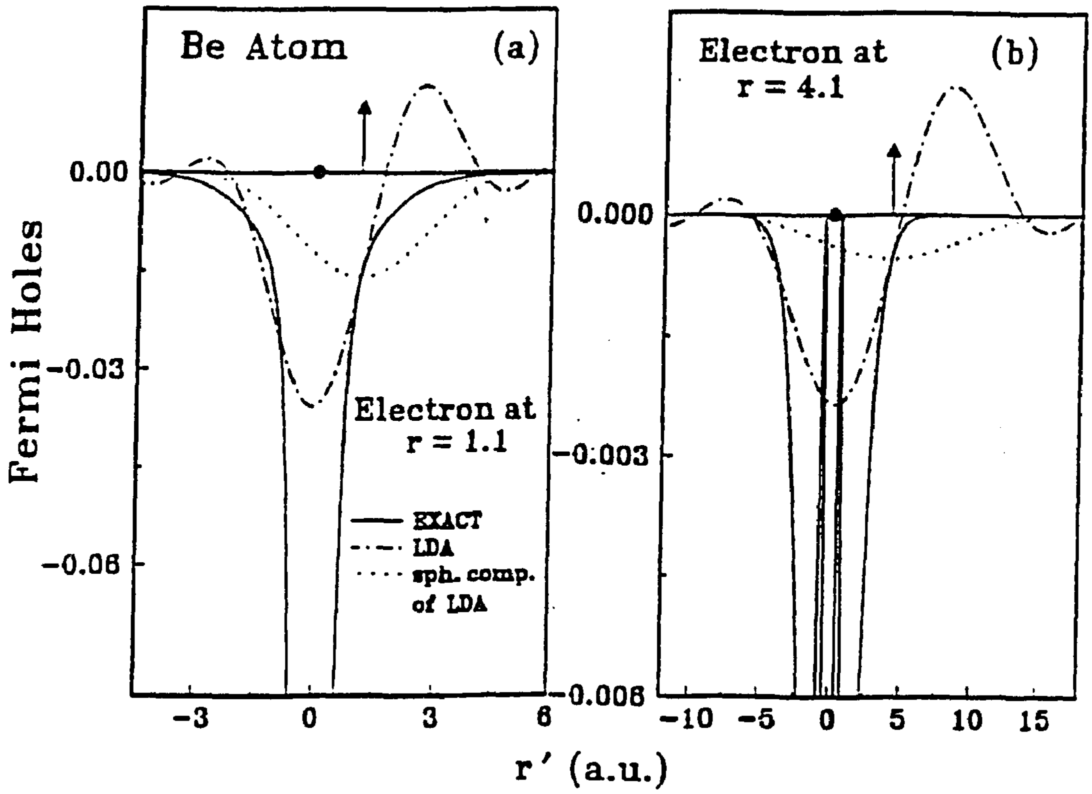

Fig. 21. The figure caption is the same as that of Fig. 20 except that in (a) the electron is at the intershell minimum of the radial probability density, and in (b) at a point in the classically forbidden region.

the LDA hole is not localized about the nucleus as is the case for the exact hole.

In the high density regions (Fig. 20) from which the principal contribution to the energy arises, observe that the LDA hole is a fair approximation to the exact hole, although it does not possess any of its structure (Fig. 20(c)). Consequently in the interior of the atom the potential $\mu_x^{LDA}(\boldsymbol{r})$ arising from this hole is a good approximation to $W_x(\boldsymbol{r})$. This is evident in Fig. 22 where we plot these exchange potentials as a function of electron position $\boldsymbol{r}$. As such the orbitals generated by the LDA differential equation with the total potential $[v_{ext} + v_H + \mu_x^{LDA}]$ in it are also accurate in the interior. This therefore explains why the LDA ground-state energies are as accurate as they are in comparison to the WF and Hartree-Fock theory results (see Table I on page 89). On the other hand, notice in Fig. 20 that the spherically symmetric component of the LDA hole is not very accurate for these positions. Since this is the component that contributes to the exchange energy expression, it is then obvious why the LDA exchange energy is in error by 13% when compared to the Hartree-Fock value.

Although the LDA exchange potential is in general accurate in the interior of the atom, its structure in the deep interior, particularly the way it approaches the nucleus, is inaccurate. This is evident in Fig. 23 where we plot the corresponding force field $\mathcal{E}_x(\boldsymbol{r})$ due to the LDA and exact Fermi holes. For an electron at the origin $\boldsymbol{r} = 0$, the exact Fermi hole is spherically symmetric (Fig. 20(a)), so that the

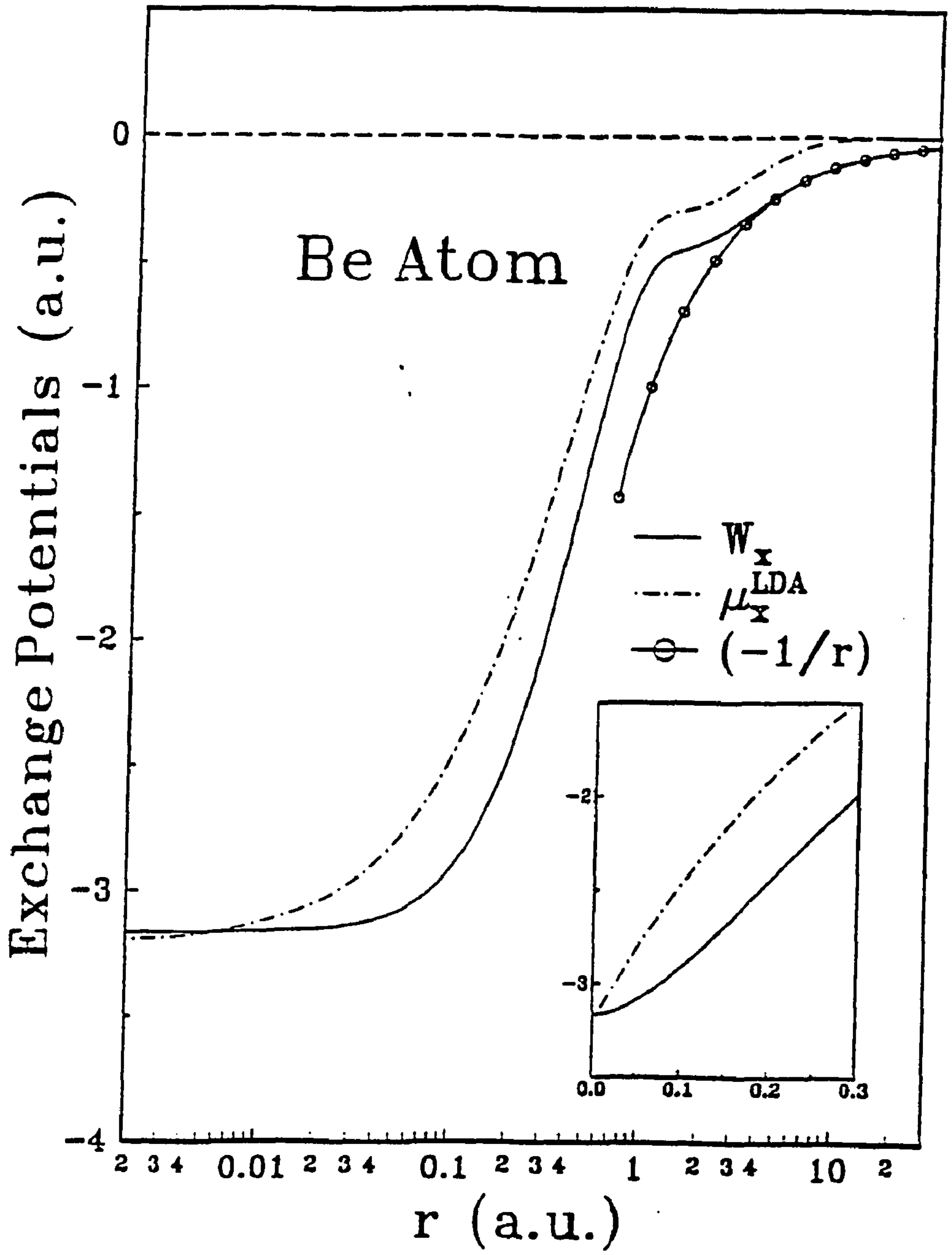

Fig. 22. Exchange potentials $W_x(r)$ and $\mu_x^{LDA}(r)$ for the Be atom as obtained within the work formalism and local-density approximation (LDA) for exchange, respectively. (From Fig. 3 of (Sahni, 1994 b)).

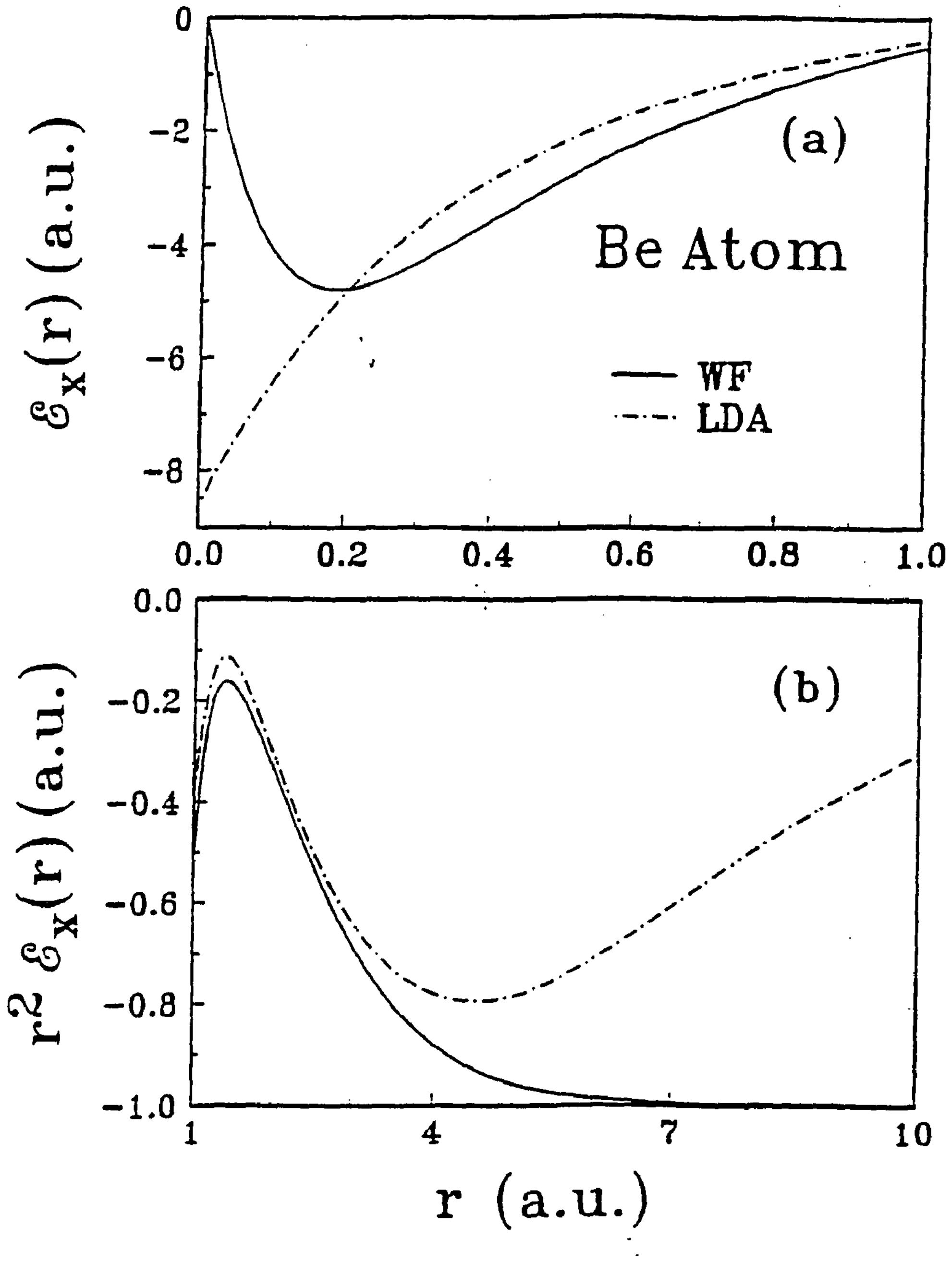

Fig. 23. (a) The force fields $\mathcal{E}_x(r)$ for the Be atom due to the Fermi holes obtained within the work formalism (WF) and local-density approximation (LDA) for exchange. (b) Plot of $r^2\mathcal{E}_x(r)$. (From Fig. 2 of (Sahni, 1994 b)).

corresponding WF force field there is zero (Fig. 23(a)). Thus, the potential $W_x(r)$ has zero slope at the nucleus (Fig. 22). On the other hand, the LDA Fermi hole is not symmetrical about the electron at the nucleus (Fig. 20(a)), and the LDA force field there is finite (Fig. 23(a)). Since a force field represents the slope of a potential, the LDA exchange potential $\mu_x^{LDA}(r)$ has a finite slope at the origin. (See Fig. 22 and its inset). This will also be the case when Coulomb correlations are incorporated within the LDA.

In the regions of low probability density (Fig. 21), the LDA Fermi hole is a poor approximation to the exact hole. The amplitude of the first positive oscillation is a substantial fraction of the primary negative part, and the oscillations extend for substantial distances beyond the surface of the atom. The error in the corresponding force field is therefore significant as may be observed from Fig. 23(b) where we plot $r^2\mathscr{E}_x(r)$. Whereas the WF result tends asymptotically to -1.0, the LDA result approaches zero. Thus, the potential $\mu_x^{LDA}(r)$ is in error in the classically forbidden region, decaying exponentially rather than as $-1/r$ (Fig. 22). Consequently, the highest occupied eigenvalue of the Kohn-Sham LDAX equation will be a poor approximation to the experimental ionization potential and electron affinity. The poorness of the source charge in these regions also causes its spherically symmetric component to be poor, particularly in the classically forbidden region. However, the contribution to the exchange energy from this region is minimal, so that the poorness of the LDA hole has little impact on the result for the exchange energy.

Finally, we note that the differences between electron correlations as represented by the pair-correlation densities $g_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$, $g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$, and $g_x(\boldsymbol{r},\boldsymbol{r}')$ are also reflected in the structure of the corresponding local effective potentials and the total ground state energies to which they give rise. In Fig. 24 we plot the potential $v_H(r) + W_x(r)$ of the WF, the potential $v_H(r) + \mu_x^{LDA}(r)$ of the LDA, and the potential $v_H(r)$ of the DFT Hartree approximation which are the electron interaction potentials due to $g_x(\boldsymbol{r},\boldsymbol{r}')$, $g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ and $g_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ respectively for the Beryllium atom. In Table I we quote the corresponding ground-state energies as obtained within these approximations, together with the energies for other noble gas and closed s-subshell atoms. The results of Hartree-Fock theory are also quoted. Note that the DFT Hartree and LDA energies are obtained from the LDA ground-state energy functional for exchange, whereas both the WF and Hartree-Fock theory results are the expectation values of the Hamiltonian taken with respect to the wavefunction corresponding to the Pauli-correlated case. It is evident from this Table that the WF ground-state energies are essentially equivalent to those of Hartree-Fock theory. Observe in Fig. 24 the striking difference between the potentials $v_H(r)$ and $v_H(r) + \mu_x^{LDA}(r)$. Thus, the effect of the additional correlations represented by the gradient term in $g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is significant. This difference is then reflected in the corresponding values of the ground-state energy, so that the results of the DFT Hartree approximation lie above those of the LDA (see Table I). A second point of comparison in Fig. 24 is of the potentials $v_H(r)$ and $v_H(r) + \mu_x^{LDA}(r)$ with that of the work formalism potential $v_H(r) + W_x(r)$. Once again it is a consequence of the

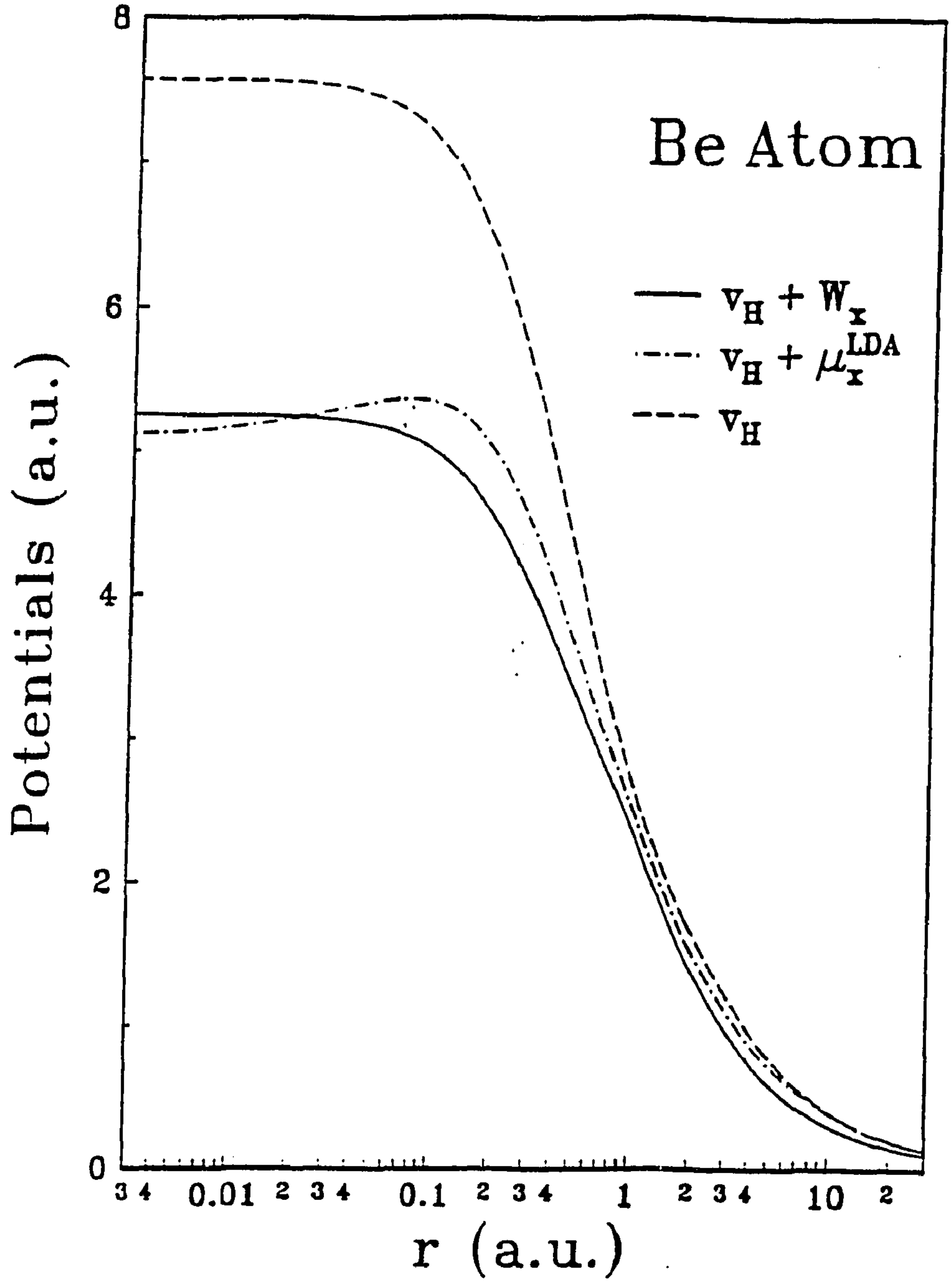

Fig. 24. Electron interaction potentials for the Be atom as obtained within the work formalism for exchange: $v_H(r) - W_x(r)$, the local-density appproximation (LDA) for exchange: $v_H(r) - \mu_x^{LDA}(r)$, and the density-functional theory Hartree approximation: $v_H(r)$. (From Fig. 4 of (Sahni, 1994 b)).

additional gradient term in $g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ that the electron interaction potential in the LDA is closer than the Hartree potential to that of the work formalism. As such the LDA ground-state energies are also more accurate. Thus, as the representation of electron correlations is improved in going from $g_x^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ to $g_x^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ to $g_x(\boldsymbol{r},\boldsymbol{r}')$, the corresponding ground-state energies also improve, as they must.

5.4 Application to Metal Surfaces

We next consider the structure of the LDA Fermi hole charge distribution $\rho_x^{LDA}(\boldsymbol{r},\boldsymbol{r}')$ as a function of electron position at a jellium metal surface. The structure of the exact Fermi hole at metallic surfaces is very different from that in atoms. The principal difference is that in atoms the hole is localized about the nucleus for all electron positions, whereas in metals the hole is delocalized as an electron is removed from within it. The detailed description of the behavior of the exact Fermi hole as an electron is removed from within the crystal to infinity outside is given elsewhere (Sahni, 1989; Sahni and Bohnen, 1984; *ibid.*, 1985; Harbola and Sahni, 1988). In particular as the electron passes through the surface, the Fermi hole develops oscillations in its structure and is left behind in the metal. For asymptotic positions of the electron in the classically forbidden region, the hole is completely delocalized and is spread throughout the crystal. It is this delocalized charge distribution which constitutes the quantum-mechanical source (Sahni, 1989; Harbola and Sahni, 1989 b) of the image potential at a metal surface. On the other hand, the asymptotic structure of the exchange potential due to the LDA Fermi hole charge is exponential, as is the case in atoms.

The orbitals employed in the present calculations of the source charge distribution are those generated by the linear-potential model (Sahni *et al.*, 1977 a; Sahni and Gruenebaum, 1977 b) of a metal surface. In this model the effective potential $v_{eff} = F x \Theta(x)$ where the field strength F is defined in terms of the slope parameter x_F and the Fermi energy E_F as $F = E_F / x_F$. The corresponding electronic wavefunctions in the direction perpendicular to the surface are

$$\begin{aligned} \Psi_k(x) &= B \{ \sin[kx + \delta(k)]\, \Theta(-x) + [\sin\delta(k) A_i(\zeta) / A_i(-\zeta_0)]\, \Theta(x) \} \\ B &= -(2/L)^{1/2} \qquad\qquad \text{(V-21)} \\ \delta(k) &= \cot^{-1}[\zeta_0^{-1/2} A_i'(-\zeta_0)/A_i(-\zeta_0)] \ , \end{aligned}$$

where $A_i(\zeta)$ is the Airy function, $A_i'(\zeta)$ its derivative, $\zeta_0 = (k_F x_F)^{2/3} k^2/k_F^2$, and $\zeta = x(2F)^{1/3} - \zeta_0$. With a change of variables to $y = k_F x$, $y_F = k_F x_F$, $q = k/k_F$ and $q' = k'/k_F$, the Fermi hole expressions are universal functions of the slope parameter y_F. For these orbitals, the exact and LDA surface exchange energies have been determined previously (Ma and Sahni, 1979; Sahni *et al.*, 1982). In the present work we choose for the density profile parameter (Sahni *et al.*, 1977 a; Sahni and Gruenebaum, 1977 b) a value of $y_F = 3$ which corresponds to a typical (Sahni *et al.*, 1981; Sahni and Gruenebaum, 1979) metallic density profile. For this density the LDA surface exchange energy is in error by 17%. For the expression for the exact Fermi hole charge distribution, we refer the reader to the original literature (Sahni and Bohnen, 1984; *ibid.*, 1985; Harbola and Sahni, 1988; Sahni *et al.*, 1977 a; Sahni and

Gruenebaum, 1977 b).

In Figs. 25 and 26 we plot cross-sections (in the plane perpendicular to the metal surface and encompassing the electron) of the exact universal function $\rho_x(r,r')/(\rho/2)$, together with the LDA and its spherically symmetric component counterparts for different electron positions. Here the electron is at $y = k_F x$, where x is the co-ordinate perpendicular to the surface, k_F is the bulk value of the Fermi momentum, and $\rho = k_F^3/3\pi^2$ is the bulk density. The Fermi hole is plotted as a function of the variable $y' = k_F x'$. In these figures the metal is to the left and the vacuum region to the right of the jellium edge located at the origin. A value of $y = 2\pi$ corresponds to a Fermi wavelength λ_F. For Al, $\lambda_F = 3.39 Å$ and for Cs $\lambda_F = 9.22 Å$. In Fig. 27 we plot the universal function $\mathcal{E}_x(y)/(3k_F^2/2\pi)$ as a function of electron position y, where $\mathcal{E}_x(y)$ is the force field due to the Fermi holes.

In Fig. 25(a) the electron is at a quarter Fermi wavelength inside the metal. It is evident from the graph that at this distance inside, the electron gas is sufficiently homogeneous so that the LDA, its spherically symmetric component, and exact holes are all essentially equivalent. As such the corresponding LDA force field (Fig. 27(a)) is a good approximation to the exact result. Consequently, since by this distance inside the metal, the exact exchange potential (Harbola and Sahni, 1989 a; Sahni and Harbola, 1990; Harbola, 1989) has essentially achieved its bulk value of $-k_F/\pi$

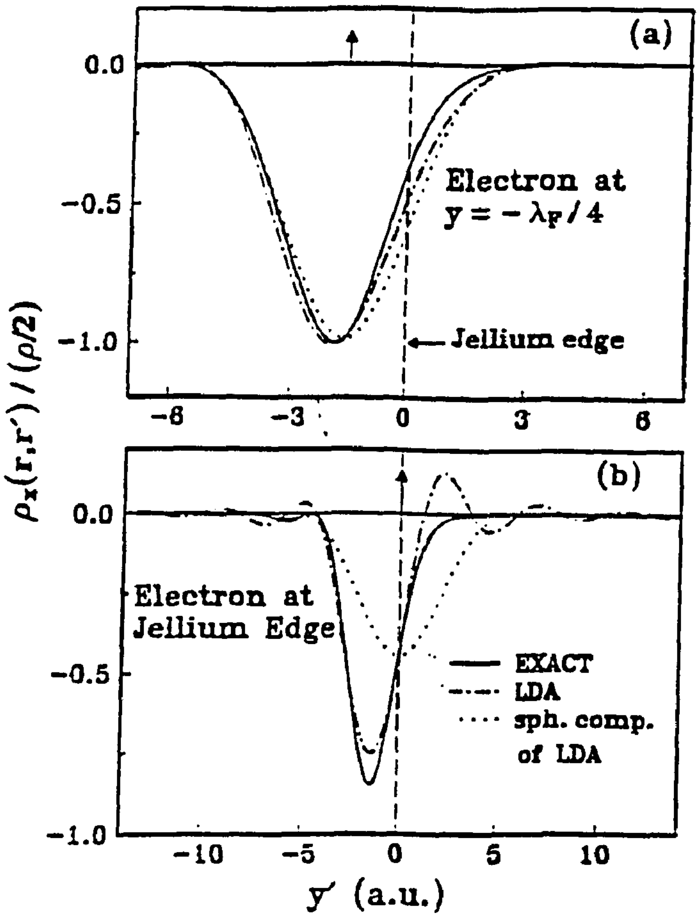

Fig. 25. Cross-sections through the exact Fermi hole in the plane perpendicular to the metal surface encompassing the electron for different electron positions. Similar cross-sections for the local density approximation (LDA) source charge distribution, and its spherically symmetric component (sph. comp.), are also plotted. In (a) the position of the electron, indicated by the arrow, is a quarter of a Fermi wavelength λ_F inside the metal whereas in (b) the electron is at the jellium edge. Note that the scales of the abscissa in these panels are different. (From Fig. 1 of (Slamet and Sahni, 1992 b)).

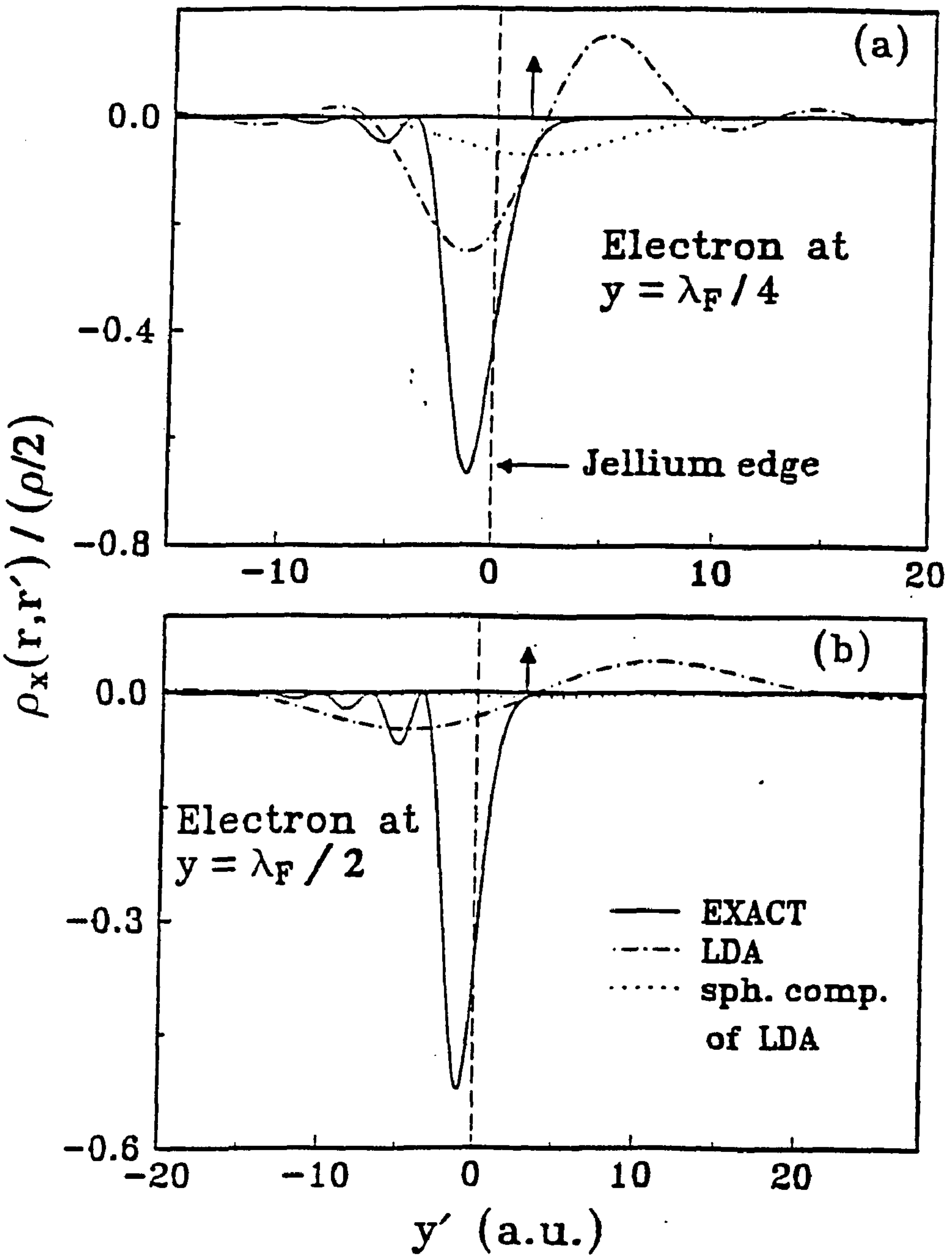

Fig. 26. The figure caption is the same as that of Fig. 25 except that in (a) the electron is at a quarter Fermi wavelength and in (b) a half Fermi wavelength outside the metal surface. (From Fig. 2 of (Slamet and Sahni, 1992 b)).

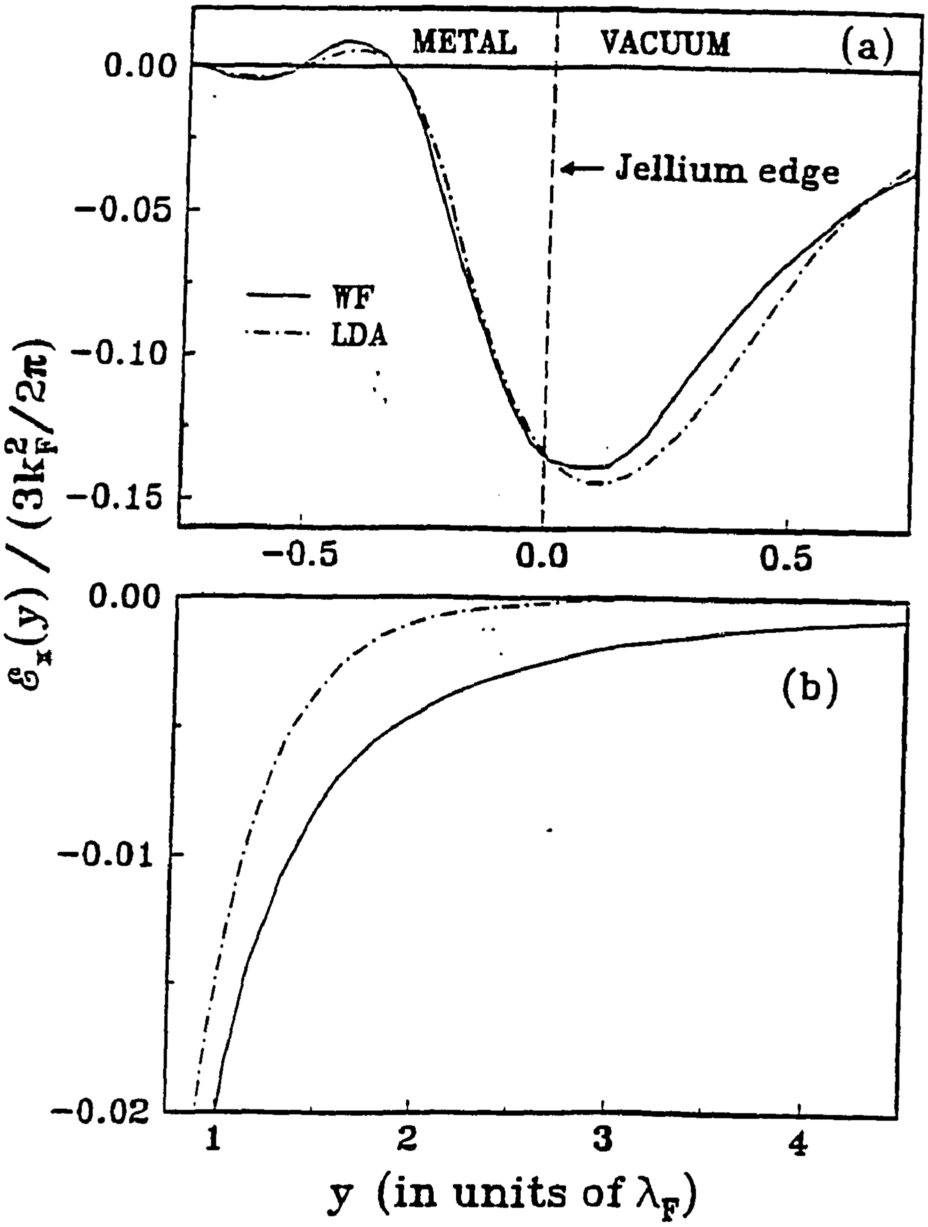

Fig. 27. Variation of the universal functions $\mathcal{E}_x(y) / (3k_F^2/2\pi)$ as a function of electron position y from the metal surface, where $\mathcal{E}_x(y)$ is the force field due to the Fermi hole as obtained within the work formalism (WF) and local-density approximation (LDA) for exchange, respectively.

relative to the reference vacuum level, and the LDA hole is the same as the exact hole, then so must the LDA potential approximate well the true value at this point. Further, since the spherically symmetric component of the LDA hole at this point is also essentially the same as the exact hole, its contribution to the surface exchange energy is also essentially exact.

In Fig. 25(b) the electron is at the jellium edge. Note that the exact Fermi hole lies principally inside the metal, and that in this region the LDA hole approximates it well. However, outside the metal the LDA hole, instead of vanishing, develops oscillations which continue well into the vacuum. Nevertheless, since the LDA hole for the most part approximates well the exact hole, the corresponding LDA force field at the surface is also fairly accurate, as can be seen in Fig. 27(a). On the other hand the spherically symmetric component of the LDA hole (which gives rise to the energy) is significantly in error, with half the hole charge lying outside the surface. Since the contributions to the surface exchange energy come principally from about and outside the metal surface, it is evident that the LDA surface exchange energy is going to be in error. More importantly we now begin to understand that a principal cause of the error in the LDA is the unphysical oscillations of its source charge distribution.

The case of electron positions at a quarter and half Fermi wavelength outside the metal surface is shown in Figs. 26(a) and (b) respectively. The LDA hole now no longer resembles the exact hole, with the amplitude of the LDA hole inside the metal becoming a progressively smaller fraction of the exact charge the further out the electron. The LDA hole also possesses none of the structure of the exact hole. In addition, the amplitude of the first positive oscillation outside is now essentially the same as that of the negative charge inside. Furthermore, the LDA hole extends for great distances into the vacuum region instead of being principally inside the metal. We thus see that it is this erroneous description of the physics of Pauli correlations for electron positions in the classically forbidden region that leads to the exponential decay of the LDA force field into the vacuum (see Fig. 27(b)). To focus on the asymptotic structure of the force fields outside the metal, we plot in Fig. 28 the universal function $2y^2 \mathcal{E}_x(y)/(3k_F^2/2\pi) \simeq 4x^2 \mathcal{E}_x(x)$. It is evident that whereas the WF force field decays as the image field $-1/4x^2$ asymptotically, the LDA force field has essentially vanished in this region. Even by one Fermi wavelength outside the metal surface the LDA force field, and consequently the LDA exchange potential, is in error. As such, the potential cannot, for example, give rise asymptotically to the image-potential surface states. The spherically symmetric component of the LDA hole for electron positions in the classically forbidden region is even more considerably in error, and this is reflected in the poorness of the LDA surface exchange energy.

5.5 Conclusions

In conclusion we note that the representation of electron correlations within the LDA of Kohn-Sham theory is far more physically realistic than previously understood to be the case. The approximation does not correspond to one in which the non

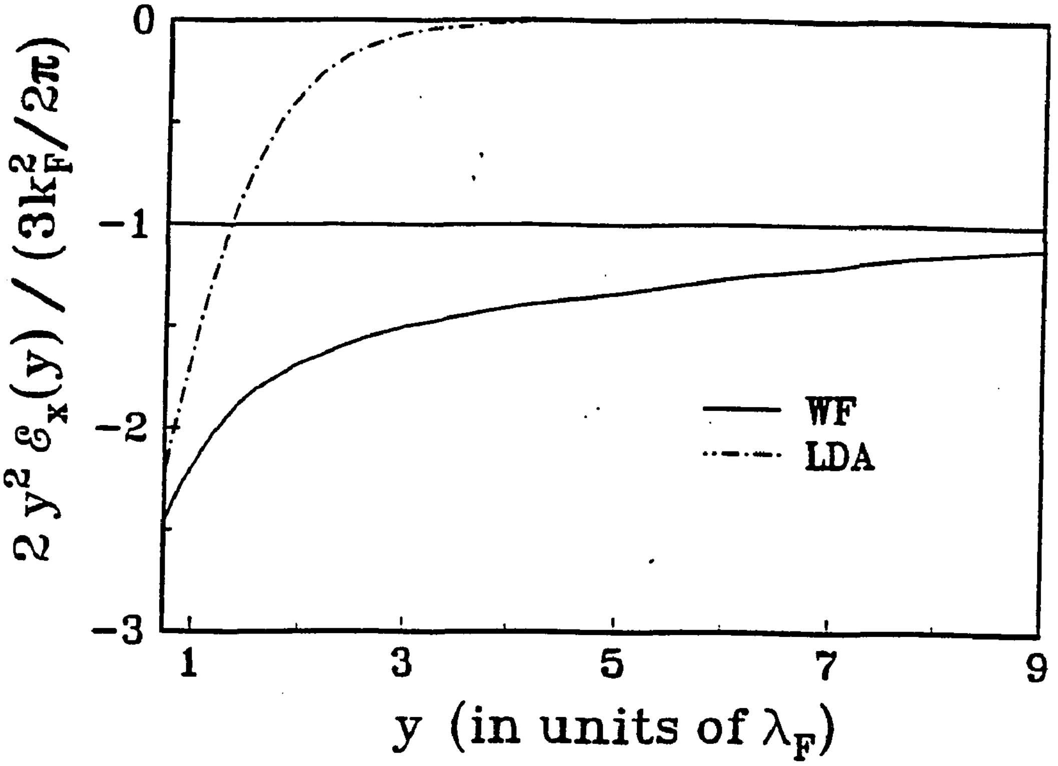

Fig. 28. Variation of the universal functions $2y^2\,\mathcal{E}_x(y)\,/\,(3k_F^2/2\pi)$ for asymptotic positions y of the electron outside the metal surface, where $\mathcal{E}_x(y)$ is the force field due to the Fermi hole as obtained within the work formalism (WF) and local-density approximation (LDA) for exchange, respectively.

-uniform electron gas is considered uniform at each point, but rather is one in which the non-uniformity of the electronic density is ***explicitly*** accounted for at each electron position. The LDA pair-correlation density $g^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ in fact contains a term proportional to the ***gradient of the density***, and may be written as

$$g^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} = g^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} + O(\nabla\rho) \quad , \tag{V-22}$$

where $g^{(0)}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\}$ is the uniform electron gas pair-correlation density. From this fact and its definition (see Eq.(II-1)) in terms of the corresponding LDA wavefunction $\Psi^{LDA}\{\boldsymbol{r}_1,\ldots\boldsymbol{r}_N;\rho(\boldsymbol{r})\}$ which is

$$g^{LDA}\{\boldsymbol{r},\boldsymbol{r}';\rho(\boldsymbol{r})\} = \frac{<\Psi^{LDA}\mid \sum'_{i,j} \delta(\boldsymbol{r}-\boldsymbol{r}_i)\,\delta(\boldsymbol{r}'-\boldsymbol{r}_j)\mid \Psi^{LDA}>}{<\Psi^{LDA}\mid \sum_i \delta(\boldsymbol{r}-\boldsymbol{r}_i)\mid \Psi^{LDA}>} \quad , \tag{V-23}$$

we learn that $\Psi^{LDA}\{\boldsymbol{r}_1,\ldots\boldsymbol{r}_N;\rho(\boldsymbol{r})\}$ explicitly incorporates elements of the physics appropriate to regions of space where the potential is rapidly varying as well as of the classically forbidden region. The fact that the LDA wavefunction possesses these properties is the fundamental reason for the accuracy achieved by the approximation.

As we have seen, when only correlations due to the Pauli-exclusion principle are considered, the LDA electron-electron interaction potential can be derived either via the functional derivative route of Kohn-Sham theory or through Coulomb's law in the work formalism. We expect this to also be the case when Coulomb correlations are included. However, as in the Pauli-correlated approximation, the precise description of how electrons are correlated when Coulomb correlations are present can only be achieved via the work formalism through the pair-correlation density, and not via Kohn-Sham LDA theory whose starting point is the uniform electron gas correlation energy functional.

The understanding of the LDA achieved by the work formalism also allows for a more accurate description of the explanation (Gunnarsson *et al.*, 1977; *ibid.*, 1979; Sahni *et al.*, 1988) for the success of the LDA given in the past. The starting point of this explanation is also the Kohn-Sham LDA exchange-correlation energy functional, with the subsequent assumption that the LDA Fermi-Coulomb hole is that derived from uniform electron gas theory. Further, it is noted that the exchange-correlation energy can be written in terms of the spherical average of this hole charge. It is then ***observed*** that in the interior of atoms, the spherically-averaged LDA (uniform electron gas theory) hole is a reasonable approximation to the spherical average of the exact hole. The approximate equivalence of these spherically-averaged holes is then given as the reason for the accuracy of the ground-state energies achieved by the LDA. However, we know now that the LDA Fermi-Coulomb hole is a far more accurate representation of electron correlations than that assumed on the basis of uniform electron gas theory. Thus, although the spherical averages of these holes turn out to be the same, we understand that the spherical average is in fact that of a more accurate representation of the hole charge. This is why the spherical average of the LDA hole is a good approximation to that of the the exact hole.

Chapter VI

CONCLUSIONS

In this thesis we have studied electron correlations in nonuniform density systems via the work formalism of electronic structure. In the formalism, the system wavefunction is in principle determined ***self-consistently*** from a ***local*** potential representing the electron correlations. The potential is in turn defined in terms of the wavefunction through the force field of the pair-correlation density. The pair-correlation density thus constitutes the quantum-mechanical source charge distribution that gives rise to both the potential describing the electron correlations as well as the electron interaction energy. In particular we have studied Coulomb correlation effects in the Helium atom, and investigated electron correlations in the Pauli-correlated approximation for a nonspherically-symmetric density system as described by a degenerate state of the Carbon atom. Thus we have seen, for example, how strikingly different the manifestation of electron correlations due to the Pauli exclusion principle and Coulomb's law (as represented by the corresponding Fermi and Coulomb hole charge distributions) are in such nonuniform density systems. Furthermore, we have learned that for systems for which the curl of the force field due to the Fermi-Coulomb hole charge distribution does not vanish, essentially all the physics of electron correlations are described by the irrotational component of the field. These studies have also led to insights into the corresponding potentials of Kohn-Sham density-functional theory, and provided the explanation for the accuracy of the central-field model of atoms. These insights into Kohn-Sham theory have recently been reaffirmed

(Holas and March, 1995). We have also rederived the local density approximation for exchange of density-functional theory via the work formalism. This derivation shows the electron correlations as represented by this approximation to be far more accurate than that assumed on the basis of Kohn-Sham theory. In fact we show that electron correlations within this approximation ***explicitly*** account for the nonuniformity of the density via a term proportional to its gradient. This then constitutes the underlying physical reason for the considerable success of the approximation. We have also investigated the gradient expansion approximation via the perspective of the work formalism but do not report these conclusions here.

The above studies have also provided further insights into the work formalism itself. For one, we have learned that inspite of the differing structures of the Fermi and Coulomb hole charge distributions, the corresponding exchange and correlation potentials obtained from them via Coulomb's law are similar and differ only in magnitude. Furthermore, the tenet of the work formalism that the asymptotic structure of the effective potential is a consequence only of Pauli correlations, is confirmed by example. The applicability and accuracy of the work formalism to nonspherical density systems has also been demonstrated.

Additional studies of the work formalism (as well as of Kohn-Sham theory) along the lines reported are being performed since accurate Monte Carlo generated wavefunctions of atoms upto twenty electrons now exist. Simultaneously, the self-consistent solution of the fully-correlated work formalism differential equation is being pursued. It is expected that the number of configurations necessary to achieve the same accuracy as that of the Monte Carlo calculations will be far less than that of standard configuration-interaction methods. The reason for this as noted is that the effects of the correlations due to the Pauli exclusion principle and Coulomb repulsion are implicitly incorporated in the structure of the self-consistently determined orbitals. These studies will then lead to a better understanding of the applicability of the work formalism to larger systems.

APPENDIX A

KINOSHITA WAVEFUNCTION AND VARIOUS PROPERTIES OBTAINED FROM IT

Wavefunction

The Kinoshita (Kinoshita, 1957) wavefunction for the He atom is

$$\Psi(r_1, r_2) = \Psi^K(s,t,R) = c_N \; e^{(-1.860556\,s)} \sum_{i=-1}^{6} R^{(i)}\, T_i \quad , \tag{A-1}$$

where $s = r_1 + r_2$, $t = -r_1 + r_2$, $R = |r_2 - r_1|$, and where the normalization constant $c_N = 1.364931021$, the subscript (i) represents the power of R in each term of the summation, and the terms T_i are

$$T_{-1} = 0.001292\,t^2 + 0.002071\,t^2 s \; , \tag{A-2}$$

$$\begin{aligned} T_0 = {} & 1 - 0.087026\,s + 0.030099\,t^2/s + 0.057891\,s^2 + 0.226660\,t^2 \\ & - 0.011656\,s^3 - 0.022154\,s\,t^2 + 0.001025\,s^4 + 0.005852\,s^2 t^2 \\ & + 0.000555\,t^4 - 0.000200\,s^3 t^2 \; , \end{aligned} \tag{A-3}$$

$$\begin{aligned} T_1 = {} & 0.467736 + 0.008079\,s - 0.155282\,t^2/s + 0.002128\,s^2 + 0.005221\,t^2 \\ & + 0.000252\,s^3 \, , \end{aligned} \tag{A-4}$$

$$\begin{aligned} T_2 = {} & -0.049206/s - 0.160571 + 0.039716\,t^2/s^2 + 0.028827\,s \\ & + 0.003594\,t^2/s - 0.002328\,s^2 + 0.003172\,t^2 \; , \end{aligned} \tag{A-5}$$

$$T_3 = 0.076577/s + 0.014535 - 0.000112\,s - 0.001060\,t^2 \quad , \tag{A-6}$$

$$T_4 = -0.013293/s^2 - 0.012758/s - 0.007997 - 0.000137\,s + 0.000105\,t^2 \, , \tag{A-7}$$

$$T_5 = 0.005655/s + 0.001326 \; , \tag{A-8}$$

$$T_6 = -0.000939/s - 0.000002 \; . \tag{A-9}$$

Density

The electronic density for the He atom is given as $\rho(\boldsymbol{r}) = 2\int \Psi^2(\boldsymbol{r}, \boldsymbol{r}_2)\, d\boldsymbol{r}_2$. By peforming the angular integration over $d\Omega_{\hat{r}_2}$ analytically we obtain

$$\rho(r) = 4\pi c_N^2 \int e^{[-2(1.860556)s]} \left[\sum_{k=-2}^{12} y_k(r,r_2)\, w_k(r,r_2) \right] (r_2)^2\, dr_2 \ , \qquad \textbf{(A-10)}$$

where

$$y_{-2} = \left(\ln b - \ln a\right)/(2rr_2) \ , \qquad \textbf{(A-11)}$$

$$y_{-1} = \left(\sqrt{b} - \sqrt{a}\right)/(r\,r_2) \ , \qquad \textbf{(A-12)}$$

$$y_0 = 2 \ , \qquad \textbf{(A-13)}$$

and for $k = 1, 2, \ldots 12$:

$$y_k = \left[b^{(k+2)/2} - a^{(k+2)/2} \right] / \left[r\,r_2(k+2) \right] \qquad \textbf{(A-14)}$$

$$a = r^2 + r_2^2 - 2\,r\,r_2 \ , \qquad \textbf{(A-15)}$$

$$b = r^2 + r_2^2 + 2\,r\,r_2 \ , \qquad \textbf{(A-16)}$$

and the terms w_k are

$$w_{-2} = T_{-1}^2 \ , \qquad \textbf{(A-17)}$$

$$w_{-1} = 2\ T_0\ T_{-1} \ , \qquad \textbf{(A-18)}$$

$$w_0 = T_0^2 + 2\ T_{-1}\ T_1 \ , \qquad \textbf{(A-19)}$$

$$w_1 = 2\ T_0\ T_1 + 2\ T_{-1}\ T_2 \ , \qquad \textbf{(A-20)}$$

$$w_2 = T_1^2 + 2\ T_0\ T_2 + 2\ T_{-1}\ T_3 , \qquad \textbf{(A-21)}$$

$$w_3 = 2\,T_0\,T_3 + 2\,T_{-1}\,T_4 + 2\,T_1\,T_2 \ , \qquad \textbf{(A-22)}$$

$$w_4 = T_2^2 + 2T_0T_4 + 2T_{-1}T_5 + 2T_1T_3 , \qquad \text{(A-23)}$$

$$w_5 = 2T_0T_5 + 2T_{-1}T_6 + 2T_1T_4 + 2T_2T_3 , \qquad \text{(A-24)}$$

$$w_6 = T_3^2 + 2T_1T_5 + 2T_2T_4 + 2T_0T_6 , \qquad \text{(A-25)}$$

$$w_7 = 2T_1T_6 + 2T_2T_5 + 2T_3T_4 , \qquad \text{(A-26)}$$

$$w_8 = 2T_2T_6 + 2T_3T_5 + T_4^2 , \qquad \text{(A-27)}$$

$$w_9 = 2T_3T_6 + 2T_4T_5 , \qquad \text{(A-28)}$$

$$w_{10} = T_5^2 + 2T_4T_6 , \qquad \text{(A-29)}$$

$$w_{11} = 2T_5T_6 , \qquad \text{(A-30)}$$

$$w_{12} = T_6^2. \qquad \text{(A-31)}$$

The expressions for s, t, and R in T_i are the same as those given above, but with r_l replaced by r.

Coulomb Hole

The Coulomb hole $\rho_c(\boldsymbol{r},\boldsymbol{r}')$ is determined by Eq.(II-38), where the Fermi-Coulomb hole $\rho_{xc}(\boldsymbol{r},\boldsymbol{r}') = [2\,|\,\Psi^K(\boldsymbol{r},\boldsymbol{r}')\,|^2/\rho(\boldsymbol{r})\,] - \rho(\boldsymbol{r}')$, and the Fermi hole is $\rho_x(\boldsymbol{r},\boldsymbol{r}') = -\,\rho(\boldsymbol{r}')/2$ as discussed in the text.

Correlation Force Field

The correlation force field $\mathcal{E}_c(\boldsymbol{r})$ due to the Coulomb hole is defined by Eq.(II-39). By performing the angular integration over $d\Omega_{r'}$ analytically, we obtain

$$\boldsymbol{\mathscr{E}}_c(\boldsymbol{r}) = \hat{\boldsymbol{e}}_r \, \mathscr{E}_c(r)$$
$$= \hat{\boldsymbol{e}}_r \, [\frac{4\pi c_N^2}{\rho(r)} \int e^{[-2(1.860556)s} \left(\sum_{k=-2}^{12} z_k(r,r') \, w_k(r,r') \right) (r')^2 \, dr'$$
$$- \frac{2\pi}{r^2} \int_o^r dr' \, (r')^2 \, \rho(r') \,] \, , \qquad \textbf{(A-32)}$$

where

$$z_{-2} = \left[h \left(a^{-3/2} - b^{-3/2}\right)/3 + d \left(a^{-1/2} - b^{-1/2}\right) \right] / (r r') \, , \qquad \textbf{(A-33)}$$

$$z_{-1} = \left[h \left(\frac{1}{a} - \frac{1}{b} \right) + d \left(\ln b - \ln a \right) \right] / (2 r r') \, , \qquad \textbf{(A-34)}$$

$$z_0 = \left[h \left(\frac{1}{\sqrt{a}} - \frac{1}{\sqrt{b}} \right) + d \left(\sqrt{b} - \sqrt{a} \right) \right] / (r r') \, , \qquad \textbf{(A-35)}$$

$$z_1 = \left[h \left(\ln a - \ln b \right) + d \left(a - b \right) \right] / (2 r r') \, , \qquad \textbf{(A-36)}$$

and for $k = 2, \ldots 12$:

$$z_k = - \left[\frac{h}{k-1} \left(a^{(k-1)/2} - b^{(k-1)/2} \right) / 3 + \frac{d}{k+1} \left(a^{(k+1)/2} - b^{(k+1)/2} \right) \right] / (r r') \, , \qquad \textbf{(A-37)}$$

where $h = \frac{r}{2} - \frac{(r')^2}{2r}$, and $d = \frac{1}{2r}$. The expressions for s, a, b, and w_k are the same as those given above, but with r_2 replaced by r'.

Correlation Potential

The correlation potential $W_c(r)$ is then obtained by Eq. (II-39) as

$$W_c(r) = - \int_{\infty}^{r} \mathscr{E}_c(r') \, dr' \quad . \qquad \textbf{(A-38)}$$

APPENDIX B

PROPERTIES OF CARBON ATOM
IN ITS $1s^2\ 2s^2\ 2p_z^2$ DEGENERATE STATE

In this appendix we give the analytical and integral expressions for the various properties discussed in chapter IV as derived for the hydrogenic orbitals (Eq. (IV-1)) assumed. To simplify the expressions we define $q \equiv (r,\theta)$, $q' \equiv (r',\theta')$, $z = r\cos\theta$, $z' = r'\cos\theta'$, $p = 1 - 3r$, and $p' = 1 - 3r'$. The functions $f_1(r,r')$ and $f_2(q,q')$ up to $f_5(q,q')$ are defined as

$$f_1(r,r') = e^{-3r'} p - e^{-3r} p' \quad , \qquad \text{(B-1)}$$

$$f_2(q,q') = e^{-3r} z' - e^{-3r'} z \quad , \qquad \text{(B-2)}$$

$$f_3(q,q') = z' p - z p' \quad , \qquad \text{(B-3)}$$

$$f_4(q,q') = z - z' + 3\, z\, [\, \hat{i}_r \cdot (\mathbf{r} - \mathbf{r}')\,] \quad , \qquad \text{(B-4)}$$

$$f_5(q,q') = z - z' + 3\, r \sin\theta\, [\, \hat{i}_\theta \cdot (\mathbf{r} - \mathbf{r}')\,] \quad . \qquad \text{(B-5)}$$

Electronic density

The electronic density has azimuthal symmetry so that

$$\rho(\mathbf{r}) = \rho(q) = \frac{432}{\pi}\, e^{-6r} A(q) \quad , \qquad \text{(B-6)}$$

where

$$A(q) = e^{-6r} + \frac{1}{8}(p^2 + 9z^2) \quad . \tag{B-7}$$

Fermi hole charge

The Fermi hole (Eq. (II-29)) is independent of the azimuthal angles ϕ and ϕ' so that

$$\rho_x(q,q') = -\frac{216}{\pi} e^{-6r'} \frac{B^2(q,q')}{A(q)} \quad , \tag{B-8}$$

where

$$B(q,q') = e^{-3(r+r')} + \frac{1}{8} (pp' + 9zz') \quad . \tag{B-9}$$

Gradient of Fermi hole charge

The gradient of the Fermi hole

$$\nabla\rho_x(q,q') = \hat{i}_r \frac{\partial\rho_x}{\partial r} + \hat{i}_\theta \frac{1}{r} \frac{\partial\rho_x}{\partial\theta} \quad , \tag{B-10}$$

where

$$\frac{\partial\rho_x}{\partial r} = -\frac{486\ B}{\pi\ A^2} e^{-6r'} [r e^{-3r} f_1 + e^{-3r} (1+3r) f_2 \cos\theta + \frac{1}{8} f_3 \cos\theta] , \tag{B-11}$$

and

$$\frac{1}{r} \frac{\partial\rho_x}{\partial\theta} = \frac{486\ B}{\pi\ A^2} e^{-6r'} \left[e^{-3r} f_2 \sin\theta + \frac{1}{8} p f_3 \sin\theta \right] . \tag{B-12}$$

Force Field

The force field due to the Fermi hole (Eq. (II-10) with ρ_{xc} replaced by ρ_x) has azimuthal symmetry and does not have an azimuthal component. Thus

$$\begin{aligned}\mathcal{E}_x(q) &= \hat{i}_r\ \mathcal{E}_{x,r}(q) + \hat{i}_\theta\ \mathcal{E}_{x,\theta}(q)\\ &= \hat{i}_r \int \rho_x(q,q')\ \frac{\hat{i}_r \cdot (\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\ d\boldsymbol{r}' + \hat{i}_\theta \int \rho_x(q,q')\ \frac{\hat{i}_\theta \cdot (\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\ d\boldsymbol{r}'\ .\end{aligned} \tag{B-13}$$

Curl of force field and vortex source function

The curl of the force field also has azimuthal symmetry but only an azimuthal component :

$$\begin{aligned}\nabla \times \mathcal{E}_x(\boldsymbol{r}) &= \hat{i}_\phi\ [\nabla \times \mathcal{E}_x(q)]_\phi\\ &= \hat{i}_\phi \left\{ \hat{i}_\phi \cdot \int \frac{\nabla \rho_x(q,q') \times (\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\ d\boldsymbol{r}' \right\}\end{aligned} \tag{B-14}$$

$$= \int \frac{[\hat{i}_\theta \cdot (\boldsymbol{r} - \boldsymbol{r}')]\,\dfrac{\partial \rho_x}{\partial r} - [\hat{i}_r \cdot (\boldsymbol{r} - \boldsymbol{r}')]\ \dfrac{1}{r}\ \dfrac{\partial \rho_x}{\partial \theta}}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\ d\boldsymbol{r}'. \tag{B-15}$$

The vortex source function (Eq. (II-26) with $\mathcal{E}_{xc}$ replaced by $\mathcal{E}_x$) is then

$$J_x(q) = \hat{i}_\phi\ J_{x,\phi}(q) = \hat{i}_\phi\ [\nabla \times \mathcal{E}_x(q)]_\phi\ /\ 4\pi \quad . \tag{B-16}$$

Effective Fermi hole charge

The effective Fermi hole (Eq. (II-19) with $\mathcal{E}_{xc}$ replaced by $\mathcal{E}_x$) is

$$\rho_x^{eff}(q) = \frac{\rho(q)}{2} + \frac{243}{2\pi^2 A^2} \int \frac{B\,e^{-6r'}}{|\boldsymbol{r} - \boldsymbol{r}'|^3} [\{\hat{i}_r \cdot (\boldsymbol{r} - \boldsymbol{r}')\} r\,e^{-3r} f_1 + e^{-3r} f_2 f_4 + \frac{1}{8} f_3 f_5]\, d\boldsymbol{r}' \,. \qquad \text{(B-17)}$$

Irrotational component of force field

As with the force field, its irrotational component (see Eq. (II-23) with ρ_{xc}^{eff} replaced by ρ_x^{eff}) has azimuthal symmetry, and only radial (r) and θ components:

$$\begin{aligned} \mathcal{E}_x^I(q) &= \hat{i}_r\, \mathcal{E}_{x,r}^I(q) + \hat{i}_\theta\, \mathcal{E}_{x,\theta}^I(q) \\ &= \hat{i}_r \int \rho_x^{eff}(q') \frac{\hat{i}_r \cdot (\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\, d\boldsymbol{r}' + \hat{i}_\theta \int \rho_x^{eff}(q') \frac{\hat{i}_\theta \cdot (\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\, d\boldsymbol{r}' \,. \end{aligned} \qquad \text{(B-18)}$$

Solenoidal component of force field

The solenoidal component of the force field (see Eq. (II-28) with J_{xc} replaced by J_x) also has azimuthal symmetry and only r and θ components :

$$\mathcal{E}_x^S(q) = \hat{i}_r\, \mathcal{E}_{x,r}^S(q) + \hat{i}_\theta\, \mathcal{E}_{x,\theta}^S(q) \quad , \qquad \text{(B-19)}$$

where

$$\mathscr{E}^{S}_{x,r}(q) = \int \frac{\left([\hat{i}_{\theta'}\cdot(\mathbf{r}'-\mathbf{r}'')]\,\dfrac{\partial\rho_x(q',q'')}{\partial r'} - [\hat{i}_{r'}\cdot(\mathbf{r}'-\mathbf{r}'')]\,\dfrac{1}{r'}\,\dfrac{\partial\rho_x(q',q'')}{\partial\theta'} \right)}{4\pi\,|\mathbf{r}-\mathbf{r}'|^3\;|\mathbf{r}'-\mathbf{r}''|^3} \times$$

$$\Big((\hat{i}_{\theta}\cdot\hat{i}_{\phi'})\,[\hat{i}_{\phi}\cdot(\mathbf{r}-\mathbf{r}')] - (\hat{i}_{\phi}\cdot\hat{i}_{\phi'})\,[\hat{i}_{\theta}\cdot(\mathbf{r}-\mathbf{r}')] \Big)\, d\mathbf{r}'\, d\mathbf{r}'' ,$$

(B-20)

and

$$\mathscr{E}^{S}_{x,\theta}(q) = \int \frac{\left([\hat{i}_{\theta'}\cdot(\mathbf{r}'-\mathbf{r}'')]\,\dfrac{\partial\rho_x(q',q'')}{\partial r'} - [\hat{i}_{r'}\cdot(\mathbf{r}'-\mathbf{r}'')]\,\dfrac{1}{r'}\,\dfrac{\partial\rho_x(q',q'')}{\partial\theta'} \right)}{4\pi\,|\mathbf{r}-\mathbf{r}'|^3\;|\mathbf{r}'-\mathbf{r}''|^3} \times$$

$$\Big((\hat{i}_{\phi}\cdot\hat{i}_{\phi'})\,[\hat{i}_{r}\cdot(\mathbf{r}-\mathbf{r}')] - (\hat{i}_{r}\cdot\hat{i}_{\phi'})\,[\hat{i}_{\phi}\cdot(\mathbf{r}-\mathbf{r}')] \Big)\, d\mathbf{r}'\, d\mathbf{r}'' .$$

(B-21)

Effective exchange potential

The local effective exchange potential (see Eq. (II-18) with ρ_{xc} replaced by ρ_x) is

$$W^{eff}_{x}(q) = \frac{1}{2}\int \frac{\rho(q')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + \frac{243}{2\pi^2}\int \frac{B(q',q'')\,e^{-6r''}}{A^2(q')\,|\mathbf{r}-\mathbf{r}'|\;|\mathbf{r}'-\mathbf{r}''|^3} \times$$

$$[\hat{i}_{r'}\cdot(\mathbf{r}'-\mathbf{r}'')]\; r'\,e^{-3r'} f_1(r',r'') + e^{-3r'} f_2(q',q'')\,f_4(q',q'') +$$

$$\frac{1}{8}\, f_3(q',q'')\,f_5(q',q'')\Big\}\; d\mathbf{r}'\, d\mathbf{r}'' \quad .$$

(B-22)

The six-dimensional integrals for the irrotational and solenoidal components of the force field and that for the effective exchange potential are performed by the Monte Carlo method (Lepage, 1978).

APPENDIX C

DERIVATION OF THE LDA FERMI HOLE VIA THE KIRZHNITS METHOD

In this appendix we derive the analytical expression for the Fermi hole in the local density approximation $\rho_x^{LDA}(\boldsymbol{r},\boldsymbol{r}')$ by the method of Kirzhnits (Kirzhnits, 1967). The derivation shows explicitly how and where the term proportional to the gradient of the density appears.

The Fermi hole $\rho_x(\boldsymbol{r},\boldsymbol{r}')$ is defined in terms of the Dirac density matrix $\gamma(\boldsymbol{r},\boldsymbol{r}')$ as

$$\rho_x(\boldsymbol{r},\boldsymbol{r}') = -\frac{|\gamma(\boldsymbol{r},\boldsymbol{r}')|^2}{2\,\rho(\boldsymbol{r})} \quad , \tag{C-1}$$

where

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = \sum_{j;\ \epsilon_j \le \epsilon_F} \phi_j^*(\boldsymbol{r})\ \phi_j(\boldsymbol{r}') \quad , \tag{C-2}$$

with the density $\rho(\boldsymbol{r}) = \gamma(\boldsymbol{r},\boldsymbol{r})$, and the orbitals ϕ_j's being the solutions of the single-particle Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2 + v(\boldsymbol{r})]\,\phi_j(\boldsymbol{r}) = \varepsilon_j\,\phi_j(\boldsymbol{r}) \ , \tag{C-3}$$

where $v(\boldsymbol{r})$ is a local operator.

The density matrix is then written in terms of the Fermi energy ε_F as

$$\begin{aligned}\gamma(\boldsymbol{r},\boldsymbol{r}') &= \sum_{j=1}^{\infty} \Theta(\varepsilon_F - \varepsilon_j)\ \phi_j^*(\boldsymbol{r})\ \phi_j(\boldsymbol{r}') \\ &= \sum_{j=1}^{\infty} \Theta(\varepsilon_F - \hat{t} - \hat{v})\ \phi_j^*(\boldsymbol{r})\ \phi_j(\boldsymbol{r}')\end{aligned} \tag{C-4}$$

where $\Theta(x)$ is the step function, and $\hat{t} = -\frac{1}{2}\nabla^2$ the kinetic energy operator. Defining the operator $\hat{T}_F(\boldsymbol{r}) = \frac{1}{2}k_F^2(\boldsymbol{r})$ for the local Fermi energy $T_F(\boldsymbol{r}) = \varepsilon_F - v(\boldsymbol{r})$, we then can write the density matrix as

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = \Theta(\hat{T}_F - \hat{t}) \sum_{j=1}^{\infty} \phi_j^*(\boldsymbol{r})\ \phi_j(\boldsymbol{r}')\ . \tag{C-5}$$

We then employ the completeness of the single-particle orbitals ϕ_j's, i.e. $\sum_{j=1}^{\infty} \phi_j(\boldsymbol{r})\,\phi_j^*(\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}')$, and represent the delta function $\delta(\boldsymbol{r}-\boldsymbol{r}')$ with the plane-wave orbitals to obtain

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = \frac{2}{(2\pi)^3} \int d\boldsymbol{k}\ \Theta(\hat{T}_F - \hat{t})\ e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\ e^{-i\boldsymbol{k}\cdot\boldsymbol{r}'}\ , \tag{C-6}$$

where the factor of 2 is for the spin. The step function $\Theta(\hat{T}_F - \hat{t}) \equiv \Theta(\hat{k}_F^2 - \hat{k}^2)$ can simply be written as $f(\hat{a}+\hat{b})$, where $f = \Theta$, $\hat{a} = -\hat{k}^2 = \nabla^2$, and $\hat{b} = k_F^2(\boldsymbol{r})$. Thus Eq. (C-6) becomes

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = \frac{2}{(2\pi)^3} \int d\boldsymbol{k}\ f(\hat{a}+\hat{b})\ e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\ e^{-i\boldsymbol{k}\cdot\boldsymbol{r}'}\ . \tag{C-7}$$

This leads to a mathematical problem of the following general nature: given the eigenfunction $|a\rangle$ of an operator $\hat{a}$, where $\hat{a}\,|a\rangle = a\,|a\rangle$ with $|a\rangle = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ and $a = -\boldsymbol{k}^2$, how can one compute the quantity $f(\hat{a}+\hat{b})\,|a\rangle$ if the operator $\hat{a}$ does not commute with $\hat{b}$: $[\hat{a},\hat{b}] \neq 0$. To tackle this problem we rewrite $f(\hat{a}+\hat{b})\,|a\rangle$ in terms of its Laplace (or Fourier) transformation

$$f(\hat{a} + \hat{b})\ |a\rangle = \int d\tau\ F(\tau)\ \hat{E}(\tau)\ |a\rangle \quad , \qquad \text{(C-8)}$$

where τ is a real (or imaginary) parameter, and $\hat{E}(\tau) = e^{\tau(\hat{a}+\hat{b})}$. Since $\hat{a}$ does not commute with $\hat{b}$, the operator $\hat{E}(\tau)$ does not simply equal to $\left(e^{\tau\hat{a}}e^{\tau\hat{b}}\right)$ nor $\left(e^{\tau\hat{b}}e^{\tau\hat{a}}\right)$. Thus, we introduce a supplementary operator $\hat{K}$ such that $\hat{E}(\tau)$ can be put into normal form which means a product in which all $\hat{k}$ operators are to the right of the $\hat{r}$ operators, so that the $\hat{k}$ and $\hat{r}$ operators can be treated as classical variables:

$$\hat{E}(\tau) = e^{\tau(\hat{a}+\hat{b})} = e^{\tau\hat{b}}\ \hat{K}(\tau)\ e^{\tau\hat{a}} \quad . \qquad \text{(C-9)}$$

Thus

$$\hat{E}(\tau)\ |a\rangle = e^{\tau\hat{b}}\ \hat{K}(\tau)\ e^{\tau\hat{a}}\ |a\rangle = e^{\tau\hat{b}}\ \hat{K}(\tau)\ e^{\tau a}\ |a\rangle\ , \qquad \text{(C-10)}$$

and consequently

$$\hat{E}(\tau)\ |a\rangle = e^{\tau(a+\hat{b})}\ \hat{K}(\tau)\ |a\rangle \quad . \qquad \text{(C-11)}$$

Note that the eigenvalue a has now replaced the operator $\hat{a}$ in the argument of the exponential function, and consequently it now commutes with the operator $\hat{b}$ such that the dependence on the commutators $[\hat{a},\hat{b}]$ appears only in tha operator $\hat{K}(\tau)$.

Now in order to determine $\hat{K}(\tau)$, we first determine an expression for the differential equation of $\hat{K}(\tau)$ by differentiating both sides of Eq. (C-9) with respect to τ . One then obtains

$$\frac{\partial \hat{K}}{\partial \tau} = e^{-\tau\hat{b}}\,\hat{a}\,e^{\tau\hat{b}}\,\hat{K} - \hat{K}\,\hat{a} \quad . \tag{C-12}$$

The expansion of $\hat{K}$ in powers of τ is obtained by expanding both of the exponential functions $e^{-\tau\hat{b}}$ of Eq. (C-12) in Taylor series. This results in

$$\begin{aligned} e^{-\tau\hat{b}}\,\hat{a}\,e^{\tau\hat{b}} &= (1 - \tau\hat{b} + \tfrac{1}{2!}\tau^2\hat{b}^2 - \tfrac{1}{3!}\tau^3\hat{b}^3 + \ldots)\,\hat{a}\,(1 + \tau\hat{b} + \tfrac{1}{2!}\tau^2\hat{b}^2 + \tfrac{1}{3!}\tau^3\hat{b}^3 + \ldots) \\ &= \hat{a} - \tau\,[\hat{b},\hat{a}] + \tfrac{\tau^2}{2!}[\hat{b},[\hat{b},\hat{a}]] - \ldots \end{aligned} \tag{C-13}$$

In general form

$$e^{-\tau\hat{b}}\,\hat{a}\,e^{\tau\hat{b}} = \sum_{n=0}^{\infty} \frac{(-\tau)^n}{n!} \underbrace{[\hat{b},[\hat{b},[\hat{b},\ldots,[\hat{b},\hat{a}]]\ldots]}_{n \text{ times}} \; . \tag{C-14}$$

By substituting Eq. (C-13) into Eq. (C-12) we obtain

$$\frac{\partial \hat{K}}{\partial \tau} = \left(\hat{a} - \tau\,[\hat{b},\,\hat{a}] + \frac{\tau^2}{2!}\,[\hat{b},\,[\hat{b},\,\hat{a}]\,] - \ldots\right)\hat{K} - \hat{K}\,\hat{a} \quad . \tag{C-15}$$

The solution $\hat{K}(\tau)$ of this differential equation will be determined via iteration whereby the $(i+1)th$ order solution of $\hat{K}$ is obtained from the $i\text{-}th$ order solution by substituting the latter into the right hand side of Eq. (C-15), and then integrating the differential equation. Thus $\hat{K}_{i+1} = \int \frac{\partial \hat{K}_{i+1}}{\partial \tau}\,d\tau = \int \hat{O}\,K_i\,d\tau$, where $\hat{O}\,\hat{K}_i$ is the entire right hand side of Eq. (C-15) with $\hat{K}_i$ substituted in it. The zeroth order solution of $\hat{K}$ implies that there is no dependence on the commutator $[\hat{b},\hat{a}]$, and thus it is determined by substituting $\tau = 0$ into Eq. (C-9), which results in: $\hat{K}_0 = 1$. The first order solution of $\hat{K}$ which implies that only the commutator $[\hat{b},\hat{a}]$ is considered to be non-zero, is then obtained as the integral over $\int d\tau$ of Eq. (C-12) which is then

$$\begin{aligned} \frac{\partial \hat{K}_1}{\partial \tau} &= \left(\hat{a} - \tau \; [\hat{b}, \hat{a}] \right) \hat{K}_0 - \hat{K}_0 \, \hat{a} \\ &= - \tau \; [\hat{b}, \hat{a}] \quad , \end{aligned} \tag{C-16}$$

and which results in

$$\hat{K}_1(\tau) = 1 - \frac{1}{2} \tau^2 \, [\hat{b}, \hat{a}] \; . \tag{C-17}$$

Then by using Eqs. (C-8), (C-11), and (C-17) we obtain

$$\begin{aligned} f(\hat{a} + \hat{b}) \, |a\rangle &= \left(\int d\tau \, F(\tau) \, e^{\tau(a + \hat{b})} \right) |a\rangle \\ &\quad - \frac{1}{2} \left(\int d\tau \, F(\tau) \, \tau^2 \, e^{\tau(a + \hat{b})} \right) [\hat{b}, \hat{a}] \, |a\rangle \; . \end{aligned} \tag{C-18}$$

Since the parameter τ acts as an operator for differentiating the function f with respect to its argument, the right hand side of Eq. (C-18) can be rewritten as

$$f(\hat{a} + \hat{b}) \, |a\rangle = f(a + \hat{b}) \, |a\rangle - \frac{1}{2} f''(a + \hat{b}) \; [\hat{b}, \hat{a}] \, |a\rangle \; , \tag{C-19}$$

where

$$\begin{aligned} f(a + \hat{b}) &= \Theta(k_F^2 - k^2) \; , \\ f'(a + \hat{b}) &= \delta(k_F^2 - k^2) \; , \\ \text{and} \quad f''(a + \hat{b}) &= \delta'(k_F^2 - k^2) \; . \end{aligned} \tag{C-20}$$

The commutator $[\hat{b}, \hat{a}]$ acting on $|a\rangle$ in the second term of the right hand side of Eq. (C-19), i.e. $[\hat{b}, \hat{a}] \, |a\rangle = - [k_F^2, \hat{k}^2] \, e^{i k \cdot r}$, is evaluated by employing the relationship $\hat{k} = \frac{1}{i} \nabla$ so that

$$[\hat{b},\hat{a}]\,|a\rangle = -\left(\nabla^2 k_F^2 + 2\,i\,\nabla k_F^2\cdot \boldsymbol{k}\right) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \,. \tag{C-21}$$

Since we are interested in determining the density matrix $\gamma(\boldsymbol{r},\boldsymbol{r}')$ only to lowest order in ∇, we drop the first term in the parentheses. Then by using Eqs. (C-7), (C-19)-(C-21) we obtain

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = \frac{2}{(2\pi)^3}\int d\boldsymbol{k}\left(\Theta(k_F^2-k^2) + \frac{1}{2}\,\delta'(k_F^2-k^2)\,2\,i\,\nabla k_F^2\cdot\boldsymbol{k}\right) e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}. \tag{C-22}$$

The integral of this equation can easily be solved by shifting the origin of the position vector $\boldsymbol{r}'$ to the tip of the position vector $\boldsymbol{r}$, such that $\boldsymbol{R} = \boldsymbol{r}' - \boldsymbol{r}$, and then choosing the direction of $\boldsymbol{R}$ along the z-axis such that $\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}') = -\,k\,R\cos\theta$. The first term of the integral of Eq. (C-22) is evaluated in a straightforward manner, and results in

$$\frac{2}{(2\pi)^3}\int d\boldsymbol{k}\;\Theta(k_F^2-k^2)\;e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} = \frac{k_F^3\,j_1(k_F R)}{\pi^2\,k_F\,R}\;, \tag{C-23}$$

where

$$j_1(x) = \frac{\sin x - x\cos x}{x^2} \tag{C-24}$$

is the first order spherical Bessel function. The second term of the integral of Eq. (C-22) is evaluated by partial integration and by rewriting

$$\delta'(k_F^2 - k^2) = -\frac{1}{2k}\,\frac{\partial}{\partial k}\delta(k_F^2 - k^2) \tag{C-25}$$

in order to first eliminate the first derivative of the delta function. Then by employing the relation

$$\delta[f(x)] = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|} \ , \tag{C-26}$$

where $f(x_i) = 0\,,\, f'(x_i) \neq 0\,,$ we have

$$\delta(k_F^2 - k^2) = \frac{\delta(k - k_F)}{2\,k_F} + \frac{\delta(k + k_F)}{2\,k_F} \ . \tag{C-27}$$

The second delta function on the right does not contribute to the integral so that finally one obtains

$$\begin{aligned}\frac{2}{(2\pi)^3}\int d\boldsymbol{k}\left(\frac{1}{2}\,\delta'(k_F^2 - k^2)\,2\,i\,\nabla k_F^2\cdot\boldsymbol{k}\right) e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} &= \\ (\nabla k_F^2\cdot\boldsymbol{R})\ \sin(k_F R)/4\pi^2 \ .\end{aligned} \tag{C-28}$$

Thus, to first order in ∇, the Dirac density matrix is

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = \frac{k_F^3}{\pi^2}\,\frac{j_1(k_F R)}{k_F R} + \frac{1}{4\,\pi^2}\left(\nabla k_F^2\cdot\hat{\boldsymbol{R}}\right)\sin(k_F R) \ . \tag{C-29}$$

It is thus evident from Eq. (C-29) that the density $\rho(\boldsymbol{r}) = \gamma(\boldsymbol{r},\boldsymbol{r})$ is of $O(\nabla^2)$ to lowest order in the gradients of the density. Since $j_1(x) \sim x/3$ for small x, then to $O(\nabla^0)$ the density $\rho(\boldsymbol{r})$ and local Fermi momentum $k_F(\boldsymbol{r})$ are related by the first term of Eq. (C-29) so that $\rho(\boldsymbol{r}) = k_F^3(\boldsymbol{r})/3\,\pi^2$.

Finally by using Eqs. (C-1), (C-4), (C-22), (C-23) and (C-29), we obtain the expression for the Fermi hole in the LDA as

$$\rho_x^{LDA}(\boldsymbol{r},\boldsymbol{r}') = -\frac{\rho(\boldsymbol{r})}{2}\left[\frac{9\,j_1^2(k_F R)}{(k_F R)^2} + \frac{9\,j_0(k_F R)\,j_1(k_F R)}{2\,k_F^3}\,(\boldsymbol{R}\cdot\nabla k_F^2)\right] , \tag{C-30}$$

where

$$j_0(x) = \frac{\sin x}{x} \qquad \text{(C-31)}$$

is the zeroth-order spherical Bessel function.

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