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QUANTAL DENSITY FUNCTIONAL THEORY

by

ZHIXIN QIAN

A dissertation submitted to the graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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Abstract

QUANTAL DENSITY FUNCTIONAL THEORY

by

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This thesis is concerned with studies in time-independent (TI) Quantal density functional theory (Q-DFT), and of its extension by us to the time-dependent (TD) case. Q-DFT is a description of the s-system of noninteracting Fermions with electronic density equivalent to that of Schrödinger theory. The total energy and corresponding local effective potential are defined in terms of classical fields whose sources are quantal expectations of Hermitian operators taken with respect to the Schrödinger wavefunction. The fields are separately representative of electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic and Correlation-Current-Density effects, the last two resulting, respectively, from the difference in the kinetic energy and current density of the Schrödinger and s-system. We demonstrate TI Q-DFT by application to the ground-state of the exactly solvable Hooke's atom, thereby explaining the contributions of the various electron correlations to the transformation from Schrödinger theory to the s-system. To make Q-DFT applicable, we develop a many-body perturbation theory within its framework. In this theory there exists a separate perturbation series representative of Pauli-Coulomb correlations and Correlation-Kinetic effects. At lowest-order, representative of Pauli correlations, the upper bound on the total energy is rigorous. We next derive via Q-DFT the analytical structure of the local effective potential in the classically forbidden asymptotic region of atoms, thereby delineating the separate Pauli, Coulomb, and Correlation-Kinetic contributions to this structure. Next, we demonstrate analytically and by numerical example, that Pauli and Coulomb correlations do not contribute to the discontinuity in the effective potential as the electron number passes through an integer value, but that it is solely a consequence of Correlation-Kinetic effects. Finally, we extend TI Q-DFT to the TD case by deriving the TD Schrödinger and s-system differential virial theorems. By extending adiabatic coupling constant perturbation theory to TD systems, we explain the relationship between Q-DFT and TD Kohn-Sham DFT in terms of electron correlations. We also derive various sum rules and integral virial theorems for the TD s-system. We conclude with directions for future research.

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Chapter 1

INTRODUCTION

Hohenberg-Kohn-Sham [1, 2] density-functional theory (DFT) [3-5] and its extension by Runge and Gross [6] to the time-dependent (TD) case [7-9] has become possibly the most extensively employed formalism for the determination of the electronic structure of atoms, molecules, clusters, surfaces, and solids. The basic theorem underlying DFT is that for a system of electrons in a ***local*** external potential represented by the operator $\hat{V}=\sum_i v(\mathbf{r}_i/\mathbf{r}_i t)$, there is a one-to-one correspondence between the electronic density $\rho(\mathbf{r}/\mathbf{r}t)$ and the potential $v(\mathbf{r}/\mathbf{r}t)$ to within a constant / time-dependent function. With the interaction between the electrons being known, a knowledge of the density thus uniquely specifies the external potential, and thereby fully defines the Hamiltonian. The wavefunction $\Psi(\mathbf{X}/\mathbf{X}t)$ ($\mathbf{X}=\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N$; $\mathbf{x}=\mathbf{r}\sigma$; $\sigma=$ spin coordinate) which is the solution of the resulting Schrödinger [10] equation is therefore a functional of the density, unique to within a TD phase in the TD case. As such, the expectation value of any quantum-mechanical operator $\hat{O}$ is a unique functional $O[\rho]$ of the density. Thus, in the time-independent (TI) case, the ground-state energy E which is the expectation value of the Hamiltonian, is a functional $E[\rho]$ of the ground-state density $\rho(\mathbf{r})$. In the TD case, the wavefunction $\Psi(\mathbf{X}t)$ with some initial condition $\Psi(\mathbf{X}t_0)$, corresponds to a stationary point of a quantum-mechanical action integral A. Since the wavefunction is a functional of the density $\rho(\mathbf{r},t)$, this action integral too is a functional $A[\rho]$. (The correspondence between the density and external potential in the TD case is restricted to external potentials that are Taylor expandable about the initial time t_0).

The second important theorem of Hohenberg-Kohn DFT is that the density $\rho(r)$ may be obtained via a variational principle for the energy involving arbitrary variations of the density. Thus, the true ground-state density is obtained via the Euler equation

$$\frac{\delta E[\rho]}{\delta \rho(r)} = 0 \ , \tag{1.1}$$

subject to the charge conservation requirement $\int \rho(r) dr = N$, where N is the number of electrons. Equivalently, the ground-state energy is obtained from the functional $E[\rho]$ for the true ground-state density $\rho(r)$. In the TD case, the action functional $A[\rho]$ must have a stationary point at the true TD density $\rho(r,t)$ with initial state $\Psi(Xt_0)$. Thus, the true density is obtained via the corresponding TD Euler equation

$$\frac{\delta A[\rho]}{\delta \rho(r,t)} = 0 \ , \tag{1.2}$$

with appropriate boundary conditions.

DFT is applied principally in its Kohn-Sham (KS) manifestation in which a model system of non-interacting Fermions with density equivalent to that of

Schrödinger theory -- the s-system -- is constructed. These noninteracting Fermions are all thus confined by the same local potential $v_s(\mathbf{r}/\mathbf{r}t)$, the density being determined via the orbitals $\phi_i(\mathbf{x}/\mathbf{x}t)$ $(i=1, \dots N)$ of the corresponding Schrödinger equation. Since the kinetic energy of the s-system is that of noninteracting Fermions, all the many-body effects are incorporated within KS theory into an electron-interaction energy $E_{ee}^{KS}[\rho]$ / action $A_{ee}^{KS}[\rho]$ functional. The many-body effects correspond to electron correlations due to the Pauli exclusion principle and Coulomb repulsion. In the TI case, there are additional correlations, referred to as Correlation-Kinetic effects, which are a consequence of the difference in kinetic energy of the interacting Schrödinger and noninteracting s-system. These effects too are incorporated in the functional $E_{ee}^{KS}[\rho]$. In the TD case, as we have shown [11, 12], there are still further correlations present in the functional $A_{ee}[\rho]$ that are a consequence of the difference in current density of the interacting and s-system, and which we refer to as Correlation-Current-Density effects. From the Euler equations (1.1) and (1.2), the electron-interaction component $v_{ee}(\mathbf{r}/\mathbf{r}t)$ of $v_s(\mathbf{r}/\mathbf{r}t)$ representative of these correlations is then defined as the functional derivative $\delta E_{ee}^{KS}/\delta\rho(\mathbf{r})$ or $\delta A_{ee}^{KS}/\delta\rho(\mathbf{r},t)$.

The explicit dependence of the wavefunction $\Psi(\mathbf{X}/\mathbf{X}t)$ on the density $\rho(\mathbf{r}/\mathbf{r}t)$ is unknown. As a consequence, the electron-interaction energy $E_{ee}^{KS}[\rho]$ and action $A_{ee}^{KS}[\rho]$ functionals are also unknown. Thus, how the various electron correlations are represented by these functionals is also unknown. A major area of research in DFT, therefore, is the development of accurate approximate energy / action functionals [7, 8, 13]. In these functionals the effects of the different correlations are then incorporated extrinsically, as for example in the Generalized Gradient Approximation [13]. The development of approximate functionals is further aided by the existence of numerous sum rules [14]. The approximate functionals can be molded to satisfy these sum rules as well as tested against them for accuracy. At present, however, there is no systematic procedure for improving upon an approximate functional. Furthermore, there are consequences to employing approximate electron-interaction energy / action functionals. For example, the rigor of the Hohenberg-Kohn theorems is lost, and the bound on the energy is no longer rigorous. As a result, it is possible to obtain total energies that lie below the true value. Another important consequence is that the correlations assumed in the construction of an approximate energy functional are not necessarily those of its functional derivative [15-17] as is the case for the well-known local / adiabatic-local density approximations. But it is the functional derivative that generates the density and from it the other properties of the system. The analysis of the results which are invariably based on the correlations assumed in the approximate functional can therefore be in error. Nevertheless, inspite of such consequences and limitations, approximate functionals leading to highly accurate results have been developed.

This thesis is concerned with an alternate prescription for the transformation from Schrödinger theory to that of the s-system which is termed Quantal density-functional theory (Q-DFT) [18-20]. Q-DFT is independent of KS-DFT. Stationary-state Q-DFT is based on the original ideas of Harbola and Sahni [21-26], their extension by Holas and March [27], and of further work by Sahni [18, 19]. It is a description of the s-system in terms of classical fields derived from quantal sources that are in turn expectations of Hermitian operators taken with respect to the system wavefunction. (The terminology Q-DFT is employed because the wavefunction is a functional of the density, and a system of equivalent density is being constructed). The local electron-interaction potential $v_{ee}(\mathbf{r})$ is the work done to move an electron in a conservative field $\mathcal{F}(\mathbf{r})$. This interpretation is rigorously derived from the differential virial theorems for the Schrödinger and s-system. The field $\mathcal{F}(\mathbf{r})$ may be decomposed into an electron-interaction $\mathcal{E}_{ee}(\mathbf{r})$ and a Correlation-Kinetic $\mathcal{Z}_{t_c}(\mathbf{r})$ component, the fields being representative of Pauli-Coulomb correlations and Correlation-Kinetic effects, respectively. These fields are explicitly defined. Furthermore, the electron-interaction E_{ee} and Correlation-Kinetic T_c energy components of the total energy can also be expressed in integral virial form in terms of these respective fields. In a similar manner, the transformation from the nonlocal Hartree-Fock [28-29] and Hartree [30] theories to s-systems with equivalent density and total energy can also be described [18] via Q-DFT. Q-DFT thus further provides a rigorous physical understanding of the KS-DFT electron-interaction energy functional $E_{ee}^{KS}[\rho]$ and of its functional derivative, as well as of the corresponding functional and potential of 'exchange-only' [31, 32] KS theory.

In Chapter 2 we give definitions within TI Schrödinger theory and the corresponding s-system of equivalent density. We also briefly summarize in this chapter KS-DFT and Q-DFT giving the key equations of these theories. In Chapter 3 we explain [20] the physics of transformation from Schrödinger theory to the s-system by considering the ground state of the exactly solvable Hooke's atom [33-35]. The example shows how the Pauli-Coulomb correlations and Correlation-Kinetic effects separately contribute to various properties of the s-system. In Chaper 4 we develop [36] a many-body perturbation theory within the context of Q-DFT. Since in Q-DFT the Pauli-Coulomb and Correlation-Kinetic contributions are separately delineated, a separate perturbation series exists for each effect. As with standard many-body perturbation theory, the bounds on the total energy at the lowest-order Pauli-correlated level are rigorous. Thus, in this manner, a systematic procedure for incorporating higher-order Coulomb correlation and Correlation-Kinetic effects is developed. In Chapter 5 we derive [37, 38] the analytical asymptotic structure of the local electron-interaction potential $v_{ee}(\mathbf{r})$ of the s-system for atoms via Q-DFT. The separate contributions of Pauli and Coulomb correlations and Correlation-Kinetic effects to this structure are thereby explicitly obtained. In Chapter 6 we address the issue of the discontinuity in the potential $v_{ee}(\mathbf{r})$ as the electron number passes through an integer value. In the context of KS-DFT, it is assumed that all the different electron correlations contribute to the discontinuity. We show [39, 40] via Q-DFT, both analytically and by example, that Pauli and Coulomb correlations do not contribute to the discontinuity and that it is solely a consequence of Correlation-Kinetic effects. In Chapter 7 we extend [11, 12] stationary-state Q-DFT to the TD case for arbitrary external potential $v(\mathbf{r},t)$. TD Q-DFT clearly shows that in addition to Correlation-Kinetic effects, there are Correlation-Current-Density effects that must be accounted for in the TD s-system. The TD local electron-interaction potential $v_{ee}(\mathbf{r},t)$ is interpreted, at each instant of time, as the work done to move an electron in a conservative field $\mathcal{F}(\mathbf{r},t)$. In addition to the electron-interaction $\mathcal{E}_{ee}(\mathbf{r},t)$ and Correlation-Kinetic $\mathcal{Z}_{t_c}(\mathbf{r},t)$ field components, there is now a Correlation-Current-Density $\mathcal{J}_c(\mathbf{r},t)$ field component to $\mathcal{F}(\mathbf{r},t)$. In this chapter we further derive [41] various sum rules and integral virial theorems valid for the TD s-system. Lastly, by extending adiabatic coupling constant perturbation theory to the TD case, we explain the relationship between TD Q-DFT and TD KS DFT in terms of electron correlations. The equations, interpretations, sum rules and theorems of TD Q-DFT reduce to those of the stationary state case for TI external potentials. References to the relevant work of others is made in each chapter. Finally, in Chapter 8 we discuss our conclusions and possible directions for future work.

Chaper 2

DEFINITIONS

2.1 Schrödinger Theory

For a system of N electrons in a local (multiplicative) external potential $\sum_i v(\boldsymbol{r}_i)$, the time-independent Schrödinger equation is

$$\hat{H}\Psi(X) = E\Psi(X) \ , \tag{2.1}$$

where the Hamiltonian $\hat{H} = \hat{T} + \hat{V} + \hat{U}$, with the kinetic energy operator

$$\hat{T} = \sum_i -\frac{1}{2}\nabla_i^2 \ , \tag{2.2}$$

the external potential operator

$$\hat{V} = \sum_i v(\boldsymbol{r}_i) \ , \tag{2.3}$$

and the electron-interaction operator

$$\hat{U} = \frac{1}{2}\sum_{i \neq j}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \ , \tag{2.4}$$

and where $\Psi(X)$ is the wavefunction, E the energy, $X = x_1, \cdots x_N$, $x \equiv \boldsymbol{r}, \sigma$ and σ the spin coordinate. The energy E is the expectation of the Hamiltonian:

$$E = \langle\Psi|\hat{H}|\Psi\rangle = T + \int v(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r} + E_{ee} \ , \tag{2.5}$$

where the kinetic energy

$$T = \langle \Psi | \hat{T} | \Psi \rangle \ , \tag{2.6}$$

the second term is the external energy E_{ext}, and

$$E_{ee} = \langle \Psi | \hat{U} | \Psi \rangle \ , \tag{2.7}$$

is the electron-interaction energy. The density $\rho(\boldsymbol{r})$ is N times the probability of a particle being at $\boldsymbol{r}$,

$$\begin{aligned} \rho(\boldsymbol{r}) &= N \sum_{\sigma} \int \Psi^{*}(\boldsymbol{r}\sigma, X^{N-1}) \Psi(\boldsymbol{r}\sigma, X^{N-1}) dX^{N-1} \\ &= \langle \Psi | \hat{\rho} | \Psi \rangle \ , \end{aligned} \tag{2.8}$$

where the density operator

$$\hat{\rho} = \sum_{i} \delta(\boldsymbol{r}_i - \boldsymbol{r}) \ , \tag{2.9}$$

with $X^{N-1} = x_2, \cdots, x_N$, $\int dX^{N-1} = \int dx_2 \cdots dx_N$ and $\int dx = \sum_{\sigma} \int d\boldsymbol{r}$.

The spinless single-particle density matrix $\gamma(\boldsymbol{r}, \boldsymbol{r}')$ is defined as

$$\begin{aligned} \gamma(\boldsymbol{r}, \boldsymbol{r}') &= N \sum_{\sigma} \int \Psi^{*}(\boldsymbol{r}\sigma, X^{N-1}) \Psi(\boldsymbol{r}'\sigma, X^{N-1}) dX^{N-1} \\ &= \langle \Psi | \hat{X} | \Psi \rangle \ , \end{aligned} \tag{2.10}$$

where the Hermitian operator

$$\hat{X} = \hat{A} + i\hat{B} \; , \tag{2.11}$$

$$\hat{A} = (1/2)\sum_j \left[\delta(\boldsymbol{r}_j - \boldsymbol{r})T_j(\boldsymbol{a}) + \delta(\boldsymbol{r}_j - \boldsymbol{r}')T_j(\boldsymbol{a})\right] \; , \tag{2.12}$$

$$\hat{B} = -(i/2)\sum_j \left[\delta(\boldsymbol{r}_j - \boldsymbol{r})T_j(\boldsymbol{a}) - \delta(\boldsymbol{r}_j - \boldsymbol{r}')T_j(-\boldsymbol{a})\right] \; , \tag{2.13}$$

$T_j(\boldsymbol{a})$ is a translation operator such that

$$T_j(\boldsymbol{a})\Psi(\cdots\, \boldsymbol{r}_j \,\cdots) = \Psi(\cdots\, \boldsymbol{r}_j + \boldsymbol{a} \,\cdots) \; , \tag{2.14}$$

and $\boldsymbol{a} = \boldsymbol{r}' - \boldsymbol{r}$. The single-particle density matrix constructed from the wavefunction Ψ is not idempotent. The diagonal matrix element of the density matrix is the density, $\rho(\boldsymbol{r}) = \gamma(\boldsymbol{r}, \boldsymbol{r})$.

The pair-correlation density $g(\boldsymbol{r}, \boldsymbol{r}')$ is the density at $\boldsymbol{r}'$ for an electron at $\boldsymbol{r}$, and is defined as the ratio of the expectations

$$g(\boldsymbol{r}, \boldsymbol{r}') = P(\boldsymbol{r}, \boldsymbol{r}')/\rho(\boldsymbol{r}) = \langle \Psi \,|\, \hat{P}(\boldsymbol{r}, \boldsymbol{r}') \,|\, \Psi \rangle \,/\rho(\boldsymbol{r}) \; , \tag{2.15}$$

where $\hat{P}(\boldsymbol{r}, \boldsymbol{r}')$ is the Hermitian pair-correlation operator

$$\hat{P}(\boldsymbol{r}, \boldsymbol{r}') = \sum_{i \neq j} \delta(\boldsymbol{r}_i - \boldsymbol{r})\delta(\boldsymbol{r}_j - \boldsymbol{r}') \; . \tag{2.16}$$

Note that in the definition of the pair-correlation density there is no self-interaction. The total charge of the pair density independent of electron position is

$$\int g(r,r')dr' = N-1 \ . \tag{2.17}$$

The pair-correlation density is a property that is due to electron correlations arising from the Pauli exclusion principle and Coulomb repulsion. Thus, it can also be interpreted as the density $\rho(r')$ at r' plus the reduction in this density at r' due to the electron correlations. The reduction in density about an electron that occurs as a result of the Pauli exclusion principle and Coulomb repulsion is the quantum-mechanical Fermi-Coulomb hole charge distribution $\rho_{xc}(r,r')$. Thus, we may write the pair-correlation density as

$$g(r,r') = \rho(r') + \rho_{xc}(r,r') \ , \tag{2.18}$$

and consequently the total charge of the Fermi-Coulomb hole for arbitrary electron position is

$$\int \rho_{xc}(r,r')dr' = -1 \ . \tag{2.19}$$

Note that the self-interaction contribution to the Fermi-Coulomb hole charge is cancelled by the density, so that the pair-correlation density as defined by Eq. (2.15) is self-interaction free.

The electron-interaction energy E_{ee} can be afforded a physical interpretation in terms of the pair-correlation density as the energy of interaction between it and the electronic density:

$$E_{ee} = \frac{1}{2}\int\int\frac{\rho(r)g(r,r')}{|r-r'|}drdr' \ . \qquad (2.20)$$

Using Eq. (2.18), the electron-interaction energy can be split further as

$$E_{ee} = E_H + E_{xc} \ , \qquad (2.21)$$

where E_H is the Coulomb self-energy.

$$E_H = \frac{1}{2}\int\int\frac{\rho(r)\rho(r')}{|r-r'|}drdr' \ , \qquad (2.22)$$

and E_{xc} is the quantum-mechanical exchange-correlation energy,

$$E_{xc} = \frac{1}{2}\int\int\frac{\rho(r)\rho_{xc}(r,r')}{|r-r'|}drdr' \ , \qquad (2.23)$$

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

The kinetic energy may be written in terms of the kinetic-energy-density tensor $t_{\alpha\beta}(r)$. This is a real, symmetric tensor defined in terms of the single-particle density matrix $\gamma(r,r')$ as

$$t_{\alpha\beta}(r;[\gamma]) = \frac{1}{4}\left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right]\gamma(r',r'')|_{r'=r''=r} \ . \qquad (2.24)$$

The trace of the kinetic-energy-density tensor is the scalar kinetic energy density $t(r) = \sum_\alpha t_{\alpha\alpha}(r)$. The kinetic energy T is then

$$T = \int dr t(r) \ . \tag{2.25}$$

2.2 Noninteracting Fermions with Equivalent Ground-State Density -- the S-system.

The differential equation corresponding to a system of noninteracting Fermions with ground-state density equivalent to that of Schrödinger theory -- the S-system -- is

$$[-\frac{1}{2}\nabla^2 + v_{eff}(r)]\phi_i(x) = \epsilon_i \phi_i(x) \ ; \qquad i=1,\cdots N \ , \tag{2.26}$$

where

$$v_{eff}(r) = v(r) + v_{ee}(r) \ , \tag{2.27}$$

and $v_{ee}(r)$ is the ***local*** electron-interaction potential incorporating all the many-body effects, $\phi_i(x)$ the single-particle orbitals, and ϵ_i the corresponding eigenvalues. The resulting density

$$\rho(r) = \langle \Phi\{\phi_i\} | \hat{\rho} | \Phi\{\phi_i\} \rangle = \sum_\sigma \sum_i |\phi_i(r\sigma)|^2 \ , \tag{2.28}$$

where $\Phi\{(\phi_i)\}$ is the Slater determinant of the orbitals $\phi_i(x)$.

The requirement that the S-system be one of equivalent ground-state density follows from the first Hohenberg-Kohn theorem which states that the wavefunction is a functional of the density: $\Psi(X) \equiv \Psi[\rho(r)]$, and that consequently all the information about a system is contained in the density. The existence of the s-system, however, is an assumption. The existence of such a system is referred to as noninteracting v-representability.

For the s-system, the idempotent Dirac density matrix $\gamma_s(r,r')$ is

$$\gamma_s(r,r') = \langle\Phi\{\phi_i\}|\hat{X}|\Phi\{\phi_i\}\rangle = \sum_i\sum_\sigma \phi_i^*(r\sigma)\phi_i(r'\sigma) \ , \qquad (2.29)$$

and the pair-correlation density $g_s(r,r')$ is

$$\begin{aligned} g_s(r,r') &= \langle\Phi\{\phi_i\}|\hat{P}|\Phi\{\phi_i\}\rangle/\rho(r) \\ &= \rho(r') + \rho_x(r,r') \ , \end{aligned} \qquad (2.30)$$

where $\rho_x(r,r')$ is the Fermi hole charge defined as

$$\rho_x(r,r') = -|\gamma_s(r,r')|^2/2\rho(r) \ . \qquad (2.31)$$

The total charge of the Fermi hole for arbitrary electron position is

$$\int \rho_x(r,r')dr' = -1 \ . \qquad (2.32)$$

Note that the s-system pair-correlation density is also self-interaction free. The s-system kinetic-energy density tensor $t_{s,\alpha\beta}(r,[\gamma_s])$ is defined in a manner similar to that of the interacting system (see Eq. (2.24)) but in terms of $\gamma_s(r,r')$, so that the scalar kinetic-energy density $t_s(r) = \sum_\alpha t_{s,\alpha\alpha}(r)$ and the noninteracting kinetic energy is

$$T_s = \langle \Phi\{\phi_i\} | \hat{T} | \Phi\{\phi_i\} \rangle = \int t_s(r) dr \ . \tag{2.33}$$

The ground-state energy is then

$$E = T_s + \int v(r)\rho(r) dr + E_{ee} + T_c \ , \tag{2.34}$$

or

$$E = \sum_i \epsilon_i - \int dr \rho(r) v_{ee}(r) + E_{ee} + T_c \ , \tag{2.35}$$

where T_c, refered to as the Correlation-Kinetic energy, is the difference $T - T_s$ between the kinetic energy of the interacting and noninteracting systems. It is the correlation contribution to the kinetic energy. Its definitions within the context of Kohn-Sham density functional theory and Quantal density functional theory are given in the following sections.

By employing the s-system it is possible to define the dynamic Coulomb hole charge $\rho_c(r, r')$ as

$$\rho_c(r, r') = \rho_{xc}(r, r') - \rho_x(r, r') \ , \tag{2.36}$$

so that the sum rule on the Coulomb hole is

$$\int \rho_c(r, r') dr' = 0 \ . \tag{2.37}$$

The electron interaction energy E_{ee} may also be written as

$$E_{ee} = E_H + E_x + E_c \; , \tag{2.38}$$

where the quantum mechanical exchange E_x and Coulomb E_c energies are respectively the energies of interaction between the density and the Fermi and Coulomb hole charges:

$$E_x = \frac{1}{2}\int\int \frac{\rho(r)\rho_x(r,r')}{|r-r'|}drdr' \; , \tag{2.39}$$

and

$$E_c = \frac{1}{2}\int\int \frac{\rho(r)\rho_c(r,r')}{|r-r'|}drdr' \; . \tag{2.40}$$

With the exception of the highest occupied eigenvalue $\epsilon_{\max}$, the eigenvalues of the s-system differential equation have no physical meaning. It has been shown [42-44] that $\epsilon_{\max}$ corresponds to minus the ionization potential or electron affinity.

2.3 Kohn-Sham Density-Functional Theory

Kohn-Sham (KS) [2] density-functional theory (DFT) is a particular description of the s-system which is based on the two theorems of Hohenberg and Kohn. As noted in the previous section, the first theorem states that the ground-state wavefunction is a functional of the ground-state density. Hence, the expectation of any operator is a unique functional of the ground-state density.

Thus, the ground-state energy is such a functional. The second theorem establishes the variational character of this energy functional: the ground-state energy is obtained for the ground-state density.

With the assumption of noninteracting v-representability, the ground-state energy functional $E[\rho]$ is partitioned as

$$E[\rho] = T_s[\rho] + \int v(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r} + E_{ee}^{KS}[\rho] \ , \tag{2.41}$$

where $T_s[\rho]$ is the kinetic energy functional of ***noninteracting*** fermions of density $\rho(\boldsymbol{r})$, and $E_{ee}^{KS}[\rho]$ is the KS electron-interaction energy functional in which ***all*** correlations including Correlation-Kinetic effects are incorporated. This functional may be further partitioned as

$$E_{ee}^{KS}[\rho] = E_H[\rho] + E_{xc}^{KS}[\rho] \ , \tag{2.42}$$

where $E_H[\rho]$ is the Coulomb self-energy defined previously. Comparison with Eqs. (2.5) and (2.21) for the energy expression in Schrödinger theory then defines the Kohn-Sham theory exchange-correlation energy functional $E_{xc}^{KS}[\rho]$ as the sum of the quantum-mechanical exchange-correlation energy E_{xc} and the correlation-kinetic energy $T_c[\rho]$:

$$E_{xc}^{KS}[\rho] = E_{xc}[\rho] + T_c[\rho] \ . \tag{2.43}$$

The KS exchange-correlation energy functional is conventionally further partitioned into the exchange energy E_x of Eq. (2.39) and the KS correlation energy functional $E_c^{KS}[\rho]$:

$$E_{xc}^{KS}[\rho] = E_x[\rho] + E_c^{KS}[\rho] \; . \tag{2.44}$$

It will be shown in Chapter 7 that $E_x[\rho]$ is representative not only of correlations due to the Pauli principle, but also of the lowest-order Correlation-Kinetic effects. The functional $E_c^{KS}[\rho]$ is therefore representative of Coulomb correlation and the higher-order Correlation-Kinetic effects. Within KS theory, it is understood that the Correlation-Kinetic energy T_c of Eq. (2.35) is also a functional of the density:

$$T_c[\rho] = T[\rho] - T_s[\rho] \; . \tag{2.45}$$

As a consequence of the Hohenberg-Kohn variational principle, the local electron-interaction potential $v_{ee}(\boldsymbol{r})$ potential is derived to be the functional derivative of $E_{ee}^{KS}[\rho]$:

$$v_{ee}(\boldsymbol{r}) = \delta E_{ee}^{KS}[\rho]/\delta\rho(\boldsymbol{r}) \; . \tag{2.46}$$

With the partition of $E_{ee}^{KS}[\rho]$ according to Eq. (2.44), the potential can be written as the sum

$$\begin{aligned} v_{ee}(\boldsymbol{r}) &= v_H(\boldsymbol{r}) + v_{xc}(\boldsymbol{r}) \\ &= v_H(\boldsymbol{r}) + v_x(\boldsymbol{r}) + v_c(\boldsymbol{r}) \; , \end{aligned} \tag{2.47}$$

where the Hartree potential is defined as

$$v_H(\boldsymbol{r}) = \frac{\delta E_H[\rho]}{\delta\rho(\boldsymbol{r})} = \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' , \tag{2.48}$$

and the exchange-correlation potential $v_{xc}(\boldsymbol{r})$, exchange $v_x(\boldsymbol{r})$, and correlation $v_c(\boldsymbol{r})$ potentials as

$$v_{xc}(\boldsymbol{r}) = \frac{\delta E_{xc}^{KS}[\rho]}{\delta\rho(\boldsymbol{r})} , \quad v_x(\boldsymbol{r}) = \frac{\delta E_x[\rho]}{\delta\rho(\boldsymbol{r})} , \quad v_c(\boldsymbol{r}) = \frac{\delta E_c^{KS}[\rho]}{\delta\rho(\boldsymbol{r})} , \tag{2.49}$$

respectively. The electron correlations that the KS exchange $v_x(\boldsymbol{r})$ and correlation $v_c(\boldsymbol{r})$ potentials are representative of are the same as those of their energy counterparts, and will be described more fully in Chapter 7.

2.4 Quantal Density-Functional Theory

Quantal density-functional theory (Q-DFT) [18-20] is a description of the s-system in terms of the wavefunction. The terminology Q-DFT is employed because the wavefunction is a functional of the ground-state density and the s-system is one of equivalent density. However, the fact that the wavefunction is such a functional is not employed, and therefore this description is independent of functionals of the density and their derivatives.

According to Q-DFT, the potential $v_{ee}(\boldsymbol{r})$ is the work done to move an electron from some reference point at ∞ to its position at $\boldsymbol{r}$ in the force of a conservative field $\mathcal{F}(\boldsymbol{r})$:

$$v_{ee}(r) = -\int_{\infty}^{r} \mathcal{F}(r')\cdot dl' \ . \tag{2.50}$$

Since $\nabla\times\mathcal{F}(r)=0$, the work done is ***path-independent***. The field $\mathcal{F}(r)$ is comprised of its quantum-mechanical electron-interaction $\mathcal{E}_{ee}(r)$ and correlation-kinetic $Z_{t_c}(r)$ components:

$$\mathcal{F}(r) = \mathcal{E}_{ee}(r) + Z_{t_c}(r) \ , \tag{2.51}$$

neither of which is necessarily conservative. Their sum, however, always is.

The field $\mathcal{E}_{ee}(r)$ is derived by Coulomb's law from the pair-correlation ***density*** $g(r,r')$ which constitutes its source so that

$$\mathcal{E}_{ee}(r) = \int \frac{g(r,r')(r-r')}{|r-r'|^3} dr' \ . \tag{2.52}$$

The field $Z_{t_c}(r)$ is the difference of two fields $z(r)$ and $z_s(r)$ which are derived from the kinetic-energy-density tensors $t_{\alpha\beta}(r)$ and $t_{s,\alpha\beta}(r)$ for the interacting Schrödinger and noninteracting systems, respectively. Thus

$$Z_{t_c} = \frac{1}{\rho(r)}[z_s(r;[\gamma_s]) - z(r;[\gamma])] \ , \tag{2.53}$$

where the component $z_\alpha(r)$ of the field $z(r)$ is

$$z_\alpha(\mathbf{r}) = 2\sum_\beta \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r};[\gamma]) \ , \tag{2.54}$$

The field $z_s(\mathbf{r})$ is similarly obtained from the idempotent Dirac density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$.

Finally, the electron-interaction E_{ee} and correlation-kinetic T_c energies may be expressed in virial form in terms of the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathbf{Z}_{t_c}(\mathbf{r})$ which give rise to them, respectively as

$$E_{ee} = \int \rho(\mathbf{r})\mathbf{r}\cdot\mathcal{E}_{ee}(\mathbf{r})d\mathbf{r} \qquad and \qquad T_c = \frac{1}{2}\int \rho(\mathbf{r})\mathbf{r}\cdot\mathbf{Z}_{t_c}(\mathbf{r})d\mathbf{r} \ . \tag{2.55}$$

For spherically symmetric atoms, open-shell atoms in the central field approximation [45], diatomic and linear-chain molecules, jellium and structureless pseudopotential models of metal surfaces and clusters, etc., the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathbf{Z}_{t_c}(\mathbf{r})$ are ***separately*** conservative. For such systems,

$$v_{ee}(\mathbf{r}) = W_{ee}(\mathbf{r}) + W_{t_c}(\mathbf{r}) \ , \tag{2.56}$$

where

$$W_{ee}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \mathcal{E}_{ee}(\mathbf{r}')\cdot d\mathbf{l}' \qquad and \qquad W_{t_c}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \mathbf{Z}_{t_c}(\mathbf{r}')\cdot d\mathbf{l}' \ . \tag{2.57}$$

The work done $W_{ee}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ are ***separately*** path-independent since $\nabla\times\mathcal{E}_{ee}(\mathbf{r}) = \nabla\times\mathbf{Z}_{t_c}(\mathbf{r}) = 0$.

Using the partitioning of $g(\boldsymbol{r},\boldsymbol{r}')$ of Eq. (2.18) into its local $\rho(\boldsymbol{r}')$ and nonlocal $\rho_{xc}(\boldsymbol{r},\boldsymbol{r}')$ parts, and the further partitioning of $\rho_{xc}(\boldsymbol{r},\boldsymbol{r}')$ into its Fermi $\rho_x(\boldsymbol{r},\boldsymbol{r}')$ and Coulomb $\rho_c(\boldsymbol{r},\boldsymbol{r}')$ components we may partition the field $\mathcal{E}_{ee}(\boldsymbol{r})$ into its Hartree $\mathcal{E}_H(\boldsymbol{r})$ and Pauli-Coulomb $\mathcal{E}_{xc}(\boldsymbol{r})$, Pauli $\mathcal{E}_x(\boldsymbol{r})$, and Coulomb $\mathcal{E}_c(\boldsymbol{r})$ components as

$$\begin{aligned} \mathcal{E}_{ee}(\boldsymbol{r}) &= \mathcal{E}_H(\boldsymbol{r}) + \mathcal{E}_{xc}(\boldsymbol{r}) \\ &= \mathcal{E}_H(\boldsymbol{r}) + \mathcal{E}_x(\boldsymbol{r}) + \mathcal{E}_c(\boldsymbol{r}) \ , \end{aligned} \tag{2.58}$$

where

$$\begin{aligned} \mathcal{E}_H(\boldsymbol{r}) &= \int \frac{\rho(\boldsymbol{r}')(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}' \\ \text{and} \quad \mathcal{E}_{xc}(\boldsymbol{r}) &= \int \frac{\rho_{xc}(\boldsymbol{r},\boldsymbol{r}')(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}' \ , \end{aligned} \tag{2.59}$$

and

$$\begin{aligned} \mathcal{E}_x^{KS}(\boldsymbol{r}) &= \int \frac{\rho_x^{KS}(\boldsymbol{r},\boldsymbol{r}')(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}' \\ \text{and} \quad \mathcal{E}_c^{KS}(\boldsymbol{r}) &= \int \frac{\rho_c^{KS}(\boldsymbol{r},\boldsymbol{r}')(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}' \ . \end{aligned} \tag{2.60}$$

The corresponding expression for the Hartree (Coulomb self-energy) and quantal exchange-correlation energies from Eqs. (2.22) and (2.23) are then

$$E_H = \int d\boldsymbol{r}\, \rho(\boldsymbol{r})\boldsymbol{r} \cdot \mathcal{E}_H(\boldsymbol{r}) \quad \text{and} \quad E_{xc} = \int d\boldsymbol{r}\, \rho(\boldsymbol{r})\boldsymbol{r} \cdot \mathcal{E}_{xc}(\boldsymbol{r}) \ . \tag{2.61}$$

In turn, the quantum-mechanical exchange E_x and Coulomb E_c energies are

$$E_x = \int dr\, \rho(r) r \cdot \mathcal{E}_x(r) \quad and \quad E_c = \int dr\, \rho(r) r \cdot \mathcal{E}_c(r) \,. \tag{2.62}$$

For systems of special symmetry, the individual fields are separately conservative so that we may write

$$\begin{aligned} v_{ee}(r) &= W_H(r) + W_{xc}(r) + W_{t_c}(r) \\ &= W_H(r) + W_x(r) + W_c(r) + W_{t_c}(r) \,, \end{aligned} \tag{2.63}$$

where

$$W_H(r) = -\int_{\infty}^{r} \mathcal{E}_H(r') \cdot dl' \equiv v_H(r) \quad and \quad W_{xc}(r) = -\int_{\infty}^{r} \mathcal{E}_{xc}(r') \cdot dl' \,. \tag{2.64}$$

and

$$W_x(r) = -\int_{\infty}^{r} \mathcal{E}_x(r') \cdot dl' \quad and \quad W_c(r) = -\int_{\infty}^{r} \mathcal{E}_c(r') \cdot dl' \,. \tag{2.65}$$

Thus, Q-DFT is a description of the s-system in terms of classical fields derived from quantal sources that are expectations of Hermitian operators. Both the electron-interaction potential $v_{ee}(r)$, and the electron-interaction E_{ee} and Correlation-Kinetic T_c energies are explicitly defined in terms of these fields.

Chapter 3

PHYSICS OF TRANSFORMATION FROM SCHRÖDINGER THEORY TO KOHN-SHAM DENSITY-FUNCTIONAL THEORY: APPLICATION TO AN EXACTLY SOLVABLE MODEL

3.1. Introduction

In this chapter, we illustrate the physics of transformation from Schrödinger theory to the s-system with equivalent density by application of Q-DFT to a ground-state of the Hooke's atom [33]. The external potential for this two-electron atom is harmonic: $v(\mathbf{r}) = \frac{1}{2}kr^2$, so that the Hamiltonian of the system is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}k(r_1^2 + r_2^2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} . \qquad (3.1)$$

For a certain infinite number of discrete oscillator strengths, the solution of the Schrödinger equation is analytical [34, 35]. For a value of $k = 1/4$, the ground-state wavefunction is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = Ce^{-R^2/2}e^{-r^2/8}(1 + r/2) \ , \qquad (3.2)$$

where $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $C = 1/[2\pi^{5/4}(5\sqrt{\pi} + 8)^{1/2}]$ =0.0291122 $a.u.$ the normalization constant. The energy $E = 2a.u.$.

With this wavefunction we have determined all the various properties of interest, the majority of them analytically. These are the density, pair-correlation density, Fermi-Coulomb and Coulomb hole charge distributions, the Schrödinger and noninteracting system kinetic-energy-density tensors and kinetic fields, the electron-interaction and Correlation-Kinetic fields, and the corresponding potentials and energies. The analytical expressions are given in Appendix A. In this manner we demonstrate the separate contributions and significance of each type of electron correlation to the energy and local effective potential.

The analytical expression for the density $\rho(\mathbf{r})$ obtained from the above wavefunction is given in Appendix A. The corresponding S-system orbital $\phi_i(\mathbf{r})$ can be expressed in terms of the density as

$$\phi_i(\mathbf{r}) = \sqrt{\rho(\mathbf{r})/2}\ ; \ i = 1,2\ . \qquad (3.3)$$

With the assumption that the local electron-interaction potential $v_{ee}(\mathbf{r})$ vanishes at infinity, the S-system differential equation can be inverted so that $v_{ee}(\mathbf{r})$ can also be written in terms of the density as

$$v_{ee}(\mathbf{r}) = \varepsilon_i + \frac{1}{2}\frac{\nabla^2\sqrt{\rho(\mathbf{r})}}{\sqrt{\rho(\mathbf{r})}} - \frac{1}{8}r^2\ , \qquad (3.4)$$

where $\varepsilon_i = 5/4$. The Hooke's atom wavefunction satisfies the electron-electron but not the electron-nucleus cusp condition. Furthermore, since we are concerned with the singlet ground-state of the atom, $\nabla\times\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) = \nabla\times\mathbf{Z}_{t_c}(\mathbf{r}) = 0$, so that the work done $W_{ee}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ are separately path-independent.

3.2. Model System Properties within Q-DFT.

A. *Pair-correlation density* $g(\mathbf{r},\mathbf{r}')$

For the ground-state of the Hooke's atom the Fermi hole is $\rho_x(\mathbf{r},\mathbf{r}') = -\rho(\mathbf{r}')/2$ so that the Coulomb hole is then $\rho_c(\mathbf{r},\mathbf{r}') = g(\mathbf{r},\mathbf{r}') + \rho(\mathbf{r}')/2$. The nonlocal nature of the pair-correlation density in this case is then due to the dynamic Coulomb hole charge. In Fig. 3.1 we plot the density $\rho(r)$ and the radial probability density $r^2\rho(r)$. Other than the lack of a cusp at the origin, the density, (and radial probability density), are similar to that of the He atom though different in magnitude. Also plotted in the figure are the quantal Fermi-Coulomb $\rho_{xc}(\mathbf{r},\mathbf{r}')$, and Fermi $\rho_x(\mathbf{r},\mathbf{r}')$ and Coulomb $\rho_c(\mathbf{r},\mathbf{r}')$ holes for an electron at the nucleus. Observe that the holes are all spherically symmetric about the electron. At the electron position $\mathbf{r}' = \mathbf{r}$ both the Fermi-Coulomb and Coulomb holes exhibit a cusp representative of the electron-electron cusp condition. These holes are also essentially all negative about the electron. The positive part of the Coulomb hole is not evident in the figure.

Since the Fermi hole for this model is independent of electron position, we consider only the Coulomb hole for other electron positions. In Fig. 3.2 we plot the Coulomb hole for electron positions at $r = 0.8\ a.u.$ in the interior of the atom, and at $r = 1.585\ a.u.$ which corresponds to the maximum of the radial probability density. The electron is along the z-axis corresponding to $\theta = 0°$. The cross sections through the Coulomb hole correspond to $\theta' = 0°$, $45°$ and $90°$

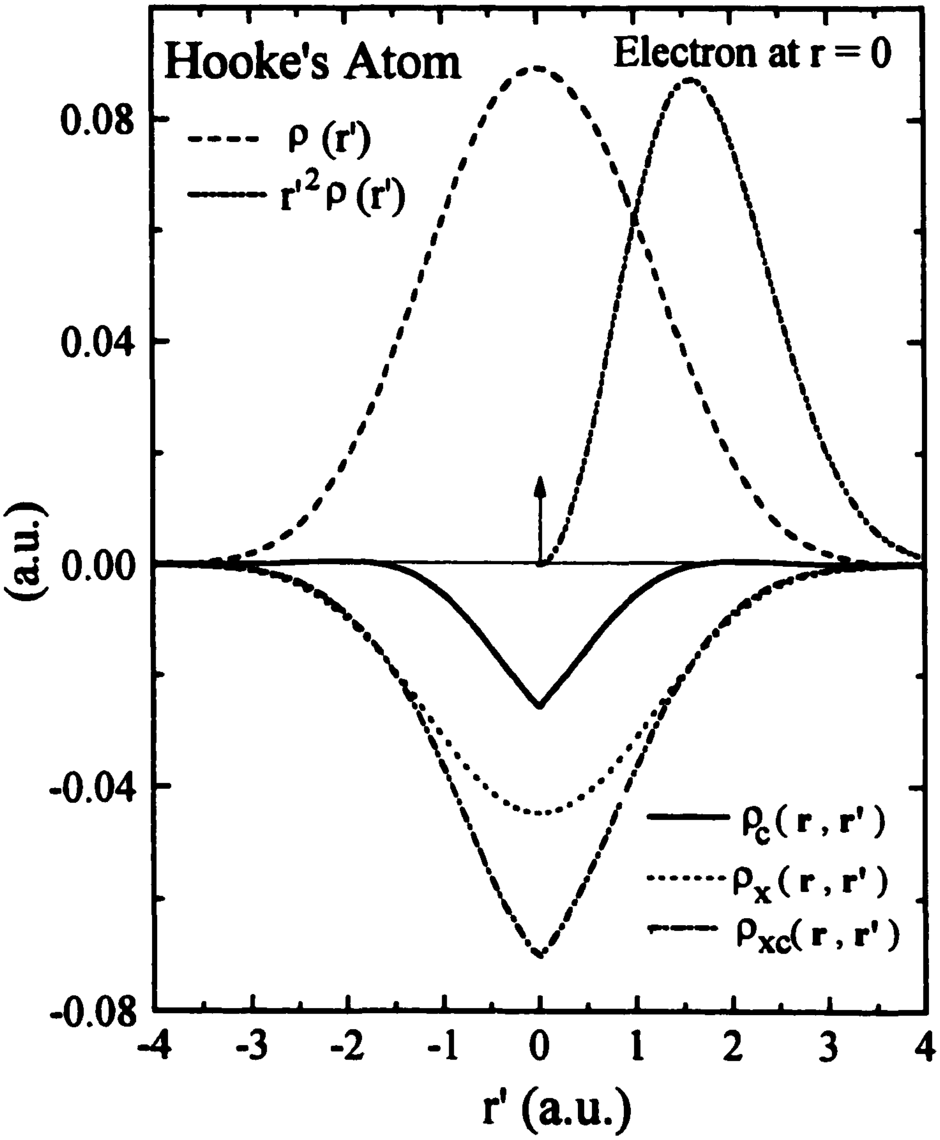


Figure 3.1: The density $\rho(r')$ and radial probability density $r'^2\rho(r')$ for the Hooke's atom. Cross sections through the quantal Fermi-Coulomb $\rho_{xc}(r,r')$ and KS theory Fermi $\rho_x(r,r')$ and Coulomb $\rho_c(r,r')$ holes for an electron at the nucleus (as indicated by the arrow) are also plotted.

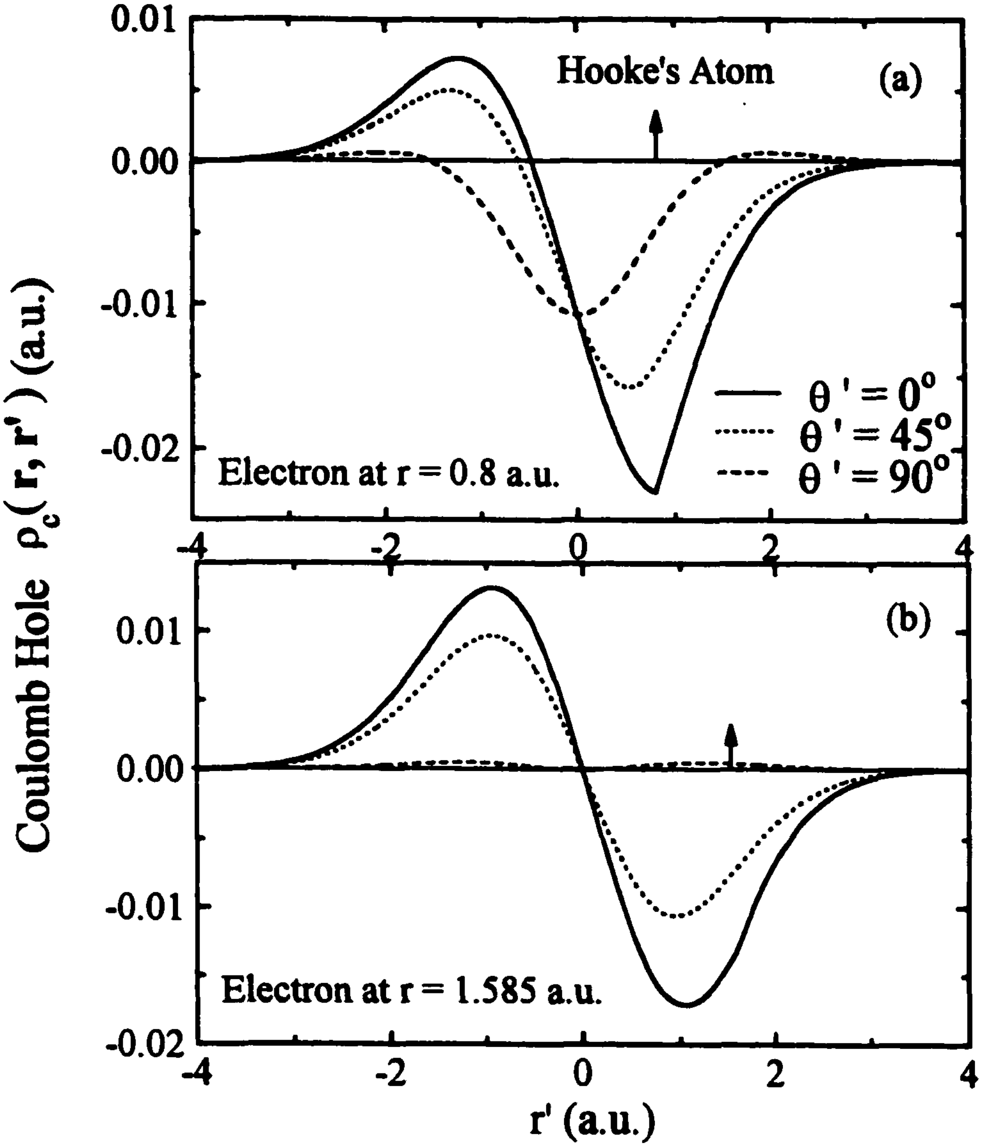


Figure 3.2: Cross-sections through the structure of the KS Coulomb hole $\rho_c(r,r')$ in different directions corresponding to $\theta' = 0°$, $45°$ and $90°$ with respect to the nucleus-electron direction for the Hooke's atom. The electron is on the z-axis corresponding to $\theta = 0°$ at $r = 0.8$ $a.u.$ in (a) and at $r = 1.585$ $a.u.$ in (b). The plots for $r' < 0$ correspond to the structure for $\theta = \pi$, $r' > 0$.

with respect to the electron-nucleus direction. (The graph for $r' < 0$ corresponds to the structure for $\theta = \pi$ and $r' > 0$). In Fig. 3.3 we present surface plots of the Coulomb hole along the lines of Pang et al [46] for the electron positions of Fig. 3.2. These plots are possible due to the spherical symmetry of the model atom. The cuts along the x- and y-axes correspond to $\theta' = 0°$ and $\theta' = 90°$. A study of Figs. 3.2 and 3.3 clearly shows the cusp in the Coulomb hole at the electron position, and the fact that it is no longer spherically symmetric about the electron. In Fig. 3.4 and 3.5 we consider electron positions near the surface ($\langle r \rangle = 3.489025\ a.u.$) of the atom at $r = 4.5 a.u.$, and in the classically forbidden region at $r = 18 a.u.$. Observe that as the electron position from the nucleus increases, the positive part of the Coulomb hole becomes more prominent on the other side of the nucleus (Figs. 3.2, 3.3 and 3.4a). For asymptotic positions of the electron (Figs. 3.4b and 3.5b), the positive part of the hole is concentrated about the nucleus. For these positions the hole becomes essentially a static charge as well as spherically symmetric about the nucleus. In Fig. 3.6 we plot the center of mass $\langle r' \rangle$ of the Coulomb hole as a function of electron position. The center of mass lies along the nucleus-electron direction, but is on the other side of the nucleus from the electron, approaching the nucleus asymptotically.

A comparison of the structure of the Hooke's atom Coulomb hole with that of the He atom [47] shows that although for certain electron positions there are

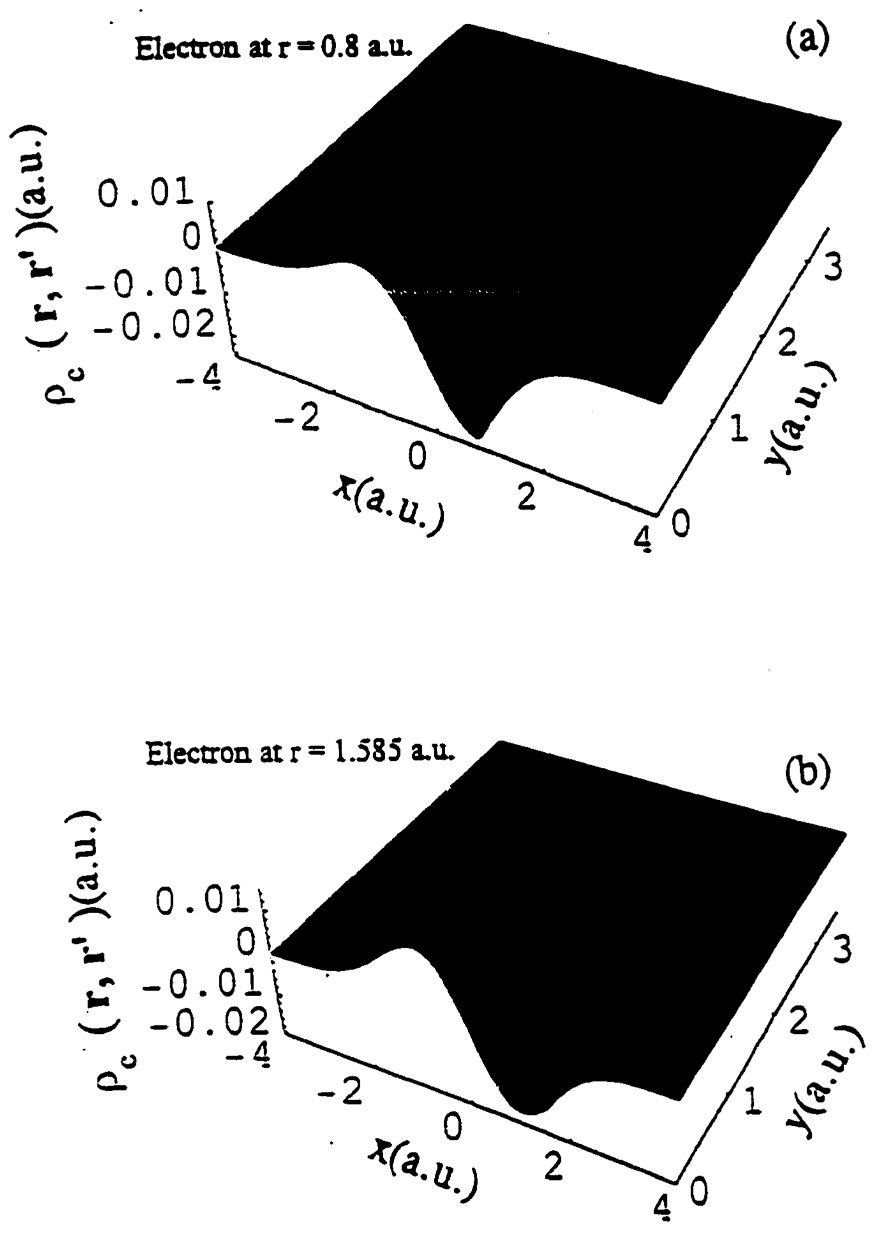


Figure 3.3: Surface plots of the Coulomb hole corresponding to the electron positions of Fig. 3.2 for the Hooke's atom. Here x' is the projection of r' on r, i.e. $x' = r'\hat{r}'\cdot\hat{r}$, and y' is the projection of r' on the direction perpendicular to r, i.e. $y' = r'[1-(\hat{r}'\cdot r)^2]^{1/2}$.

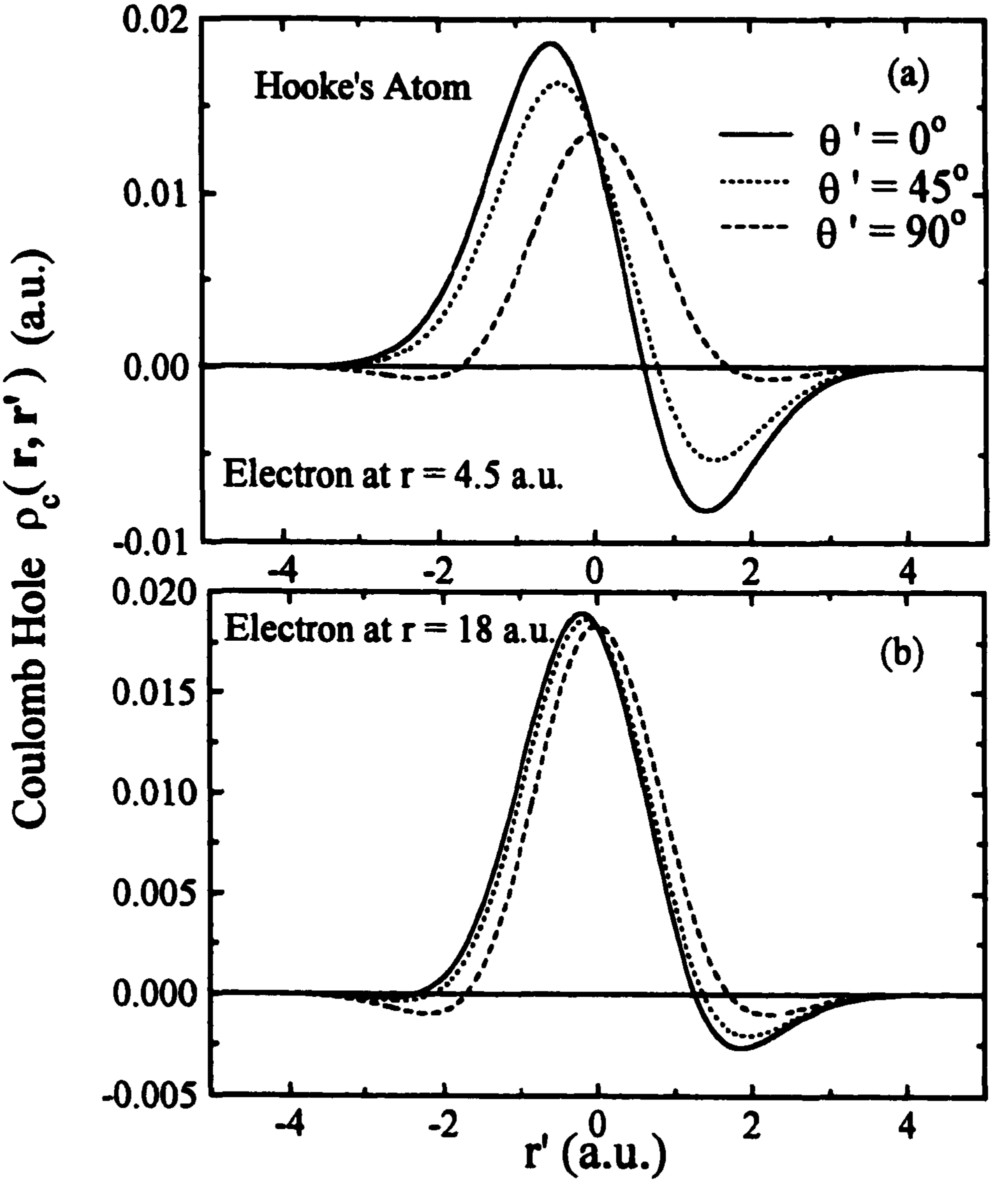
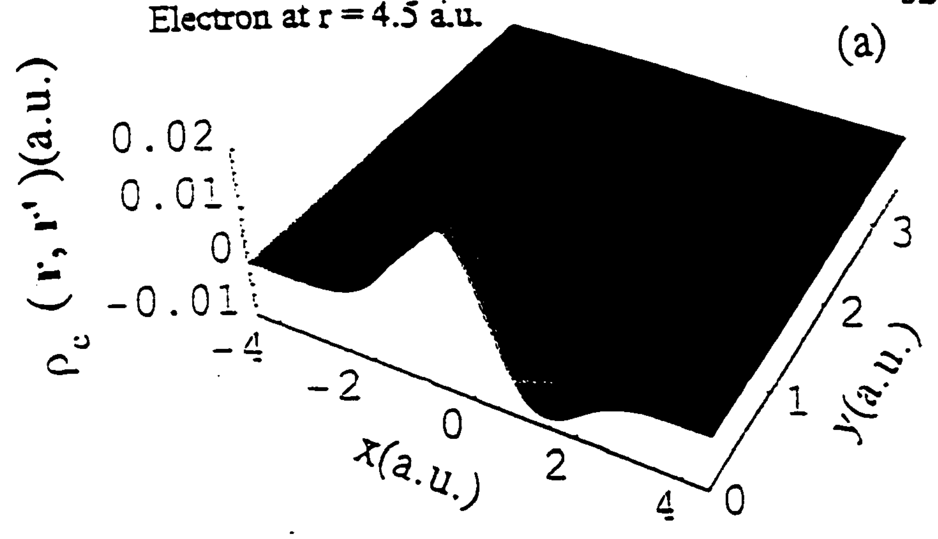


Figure 3.4: Same as in Fig. 3.2 except that in (a) the electron is at $r = 4.5\ a.u.$, and in (b) at $r = 18\ a.u.$.



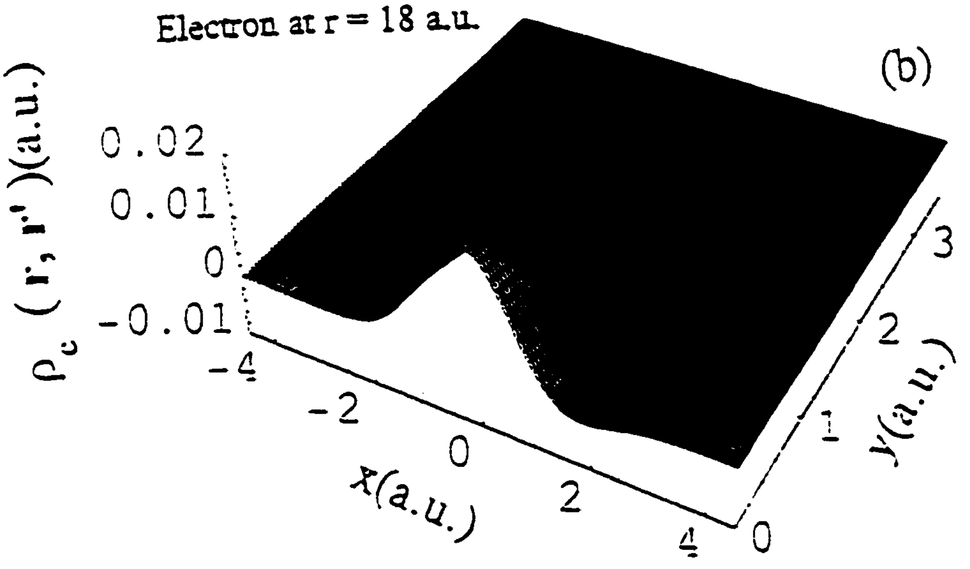


Figure 3.5: Surface plots of the Coulomb hole corresponding to the electron positions of Fig. 3.4.

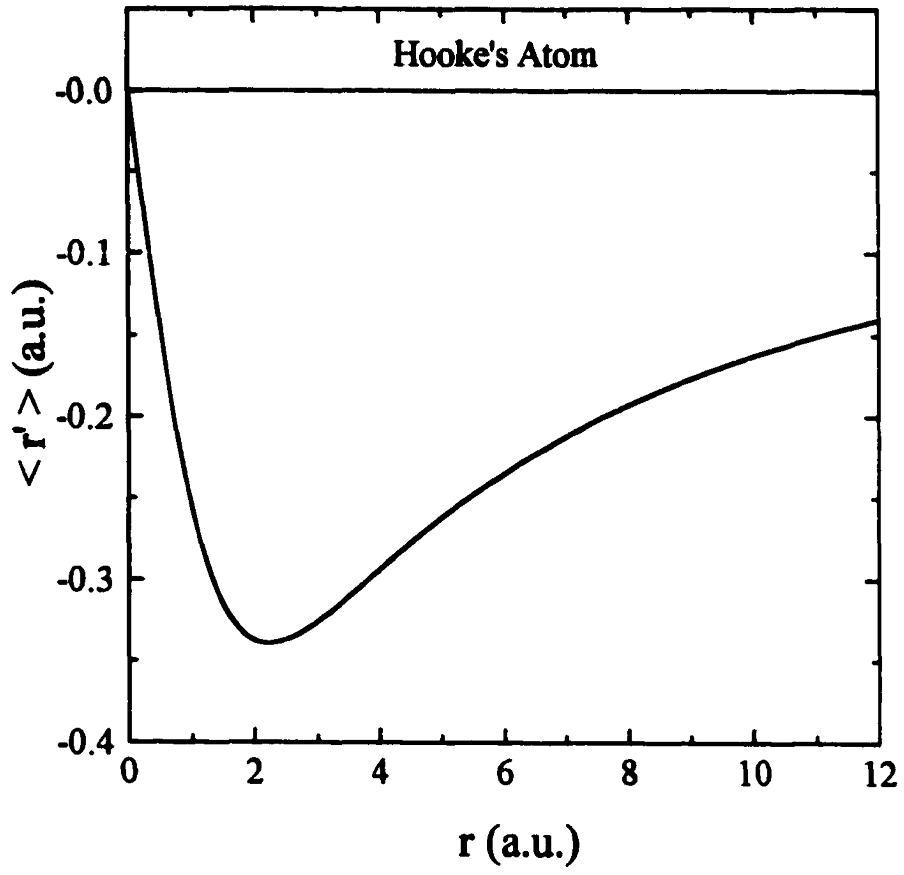


Figure 3.6: Center of mass $\langle r' \rangle$ of the KS Coulomb hole $\rho_c(r, r')$ as a function of electron position for the Hooke's atom.

qualitative differences, the overall structure is strikingly similar though different in magnitude inspite of the fact that the external potentials of the two atoms are different. *Ex post facto*, this must be so since electron repulsion is represented in each case by Coulomb's law. The Figs. 3.1-3.5 are a confirmation of this conclusion.

There is also a striking similarity between the surface plots of Figs. 3.3 and 3.5 with those of the pair-correlation function $h(\mathbf{r},\mathbf{r}')=g(\mathbf{r},\mathbf{r}')/\rho(\mathbf{r}')$ of the Ne atom plotted by Pang et al. [46] (The comparison is meaningful since for the Hooke's atom $\rho_c(\mathbf{r},\mathbf{r}')=[h(\mathbf{r},\mathbf{r}')-\frac{1}{2}]\rho(\mathbf{r}')$ and $\rho(\mathbf{r}')$ is monotonic). The one qualitative difference which appears is that of the presence of the second shell for the Ne atom. Other than that, the piling of charge on the other side of the nucleus from the electron position etc., are all similar.

B. Electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ and energy E_{ee}

In Fig. 3.7 we plot the fields $\mathcal{E}_{xc}(\mathbf{r})$, $\mathcal{E}_x(\mathbf{r})$, $\mathcal{E}_c(\mathbf{r})$ and the function $-1/r^2$. (The field $\mathcal{E}_H(\mathbf{r}) = -2\mathcal{E}_x(\mathbf{r})$ is not plotted). Observe that the fields all vanish at the nucleus. This is because the corresponding source charge distributions, viz, the Fermi-Coulomb, Fermi and Coulomb holes are all spherically symmetric about the electron for this electron position (see Fig. 3.1). The Pauli field $\mathcal{E}_x(\mathbf{r})$ is negative throughout space since the Fermi hole is a negative charge distribution. The Coulomb field is negative over most of space except the ***far***

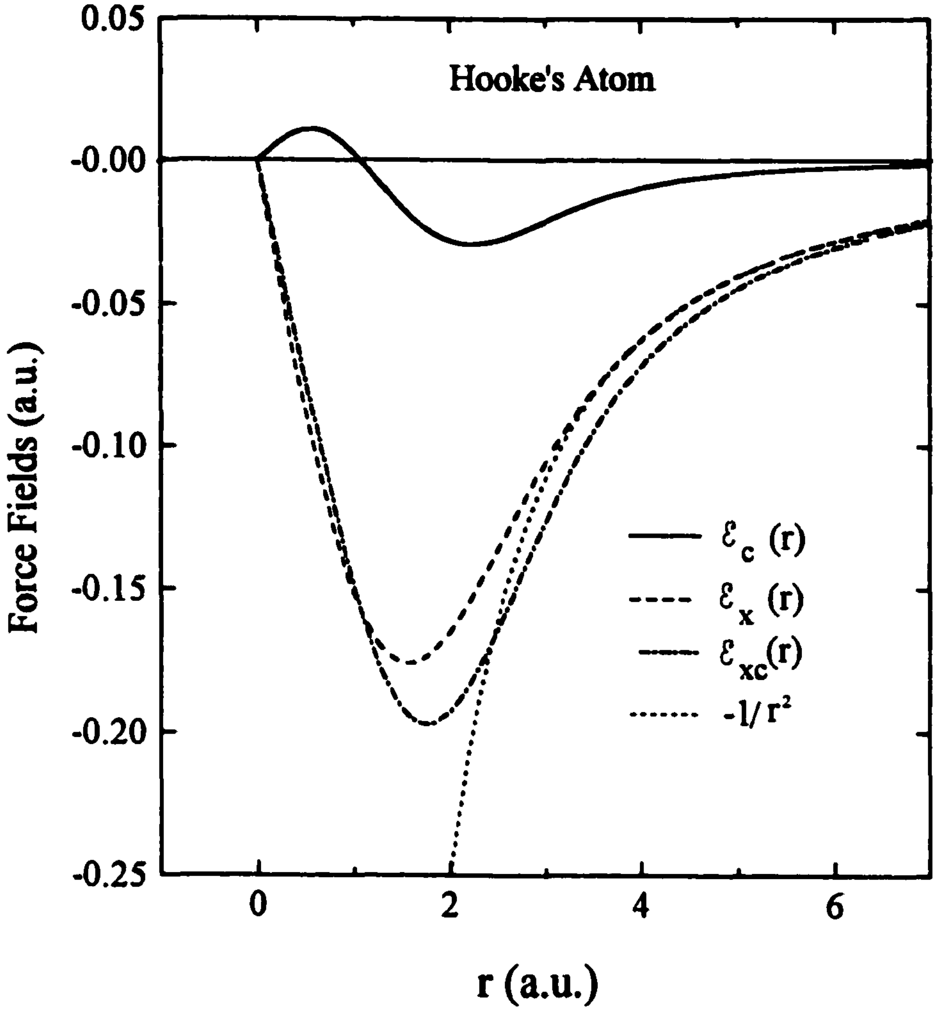


Figure 3.7: The quantal Pauli-Coulomb $\mathcal{E}_{xc}(r)$ and KS Pauli $\mathcal{E}_x(r)$ and Coulomb $\mathcal{E}_c(r)$ force fields for the Hooke's atom. The function $-1/r^2$ is also plotted.

interior. (This contrasts with the case of the He atom for which this field is negative throughout space). The quantal Pauli-Coulomb field $\mathcal{E}_{xc}(\boldsymbol{r})$ however, is negative over all space. Note that the fields $\mathcal{E}_{xc}(\boldsymbol{r})$ and $\mathcal{E}_{x}(\boldsymbol{r})$ are an order of magnitude larger than the field $\mathcal{E}_{c}(\boldsymbol{r})$. The signs of the various fields and their relative magnitudes are then reflected in the results for the corresponding energies: $E_{ee} = 0.447443\ a.u.$, $E_H = 1.030250\ a.u.$, $E_{xc} = -0.582807\ a.u.$, $E_x = -0.515125\ a.u.$ and $E_c = -0.0676820\ a.u.$. The corresponding values for the He atom [48] are $E_{ee} = 0.945819\ a.u.$, $E_H = 2.049137\ a.u.$, $E_{xc} = -1.103318\ a.u.$, $E_x = -1.024568\ a.u.$, and $E_c = -0.078750\ a.u.$. Note that although the He atom values for E_{ee} and its components E_H, E_{xc}, and E_x are about twice in magnitude as those of the Hooke's atom, the values of the Coulomb energy E_c are about the same.

The asymptotic structure of the various fields in the classically forbidden region is

$$\begin{gathered}
\mathcal{E}_{ee}(r) \xrightarrow[r\to\infty]{} \frac{1}{r^2} - \frac{4}{r^4}\ ;\ \mathcal{E}_{H}(r) \xrightarrow[r\to\infty]{} \frac{2}{r^2}\ ;\ \mathcal{E}_{xc}(r) \xrightarrow[r\to\infty]{} -\frac{1}{r^2} - \frac{4}{r^4}\ ; \\
\mathcal{E}_{x}(r) \xrightarrow[r\to\infty]{} -\frac{1}{r^2}\ ;\ \mathcal{E}_{c}(r) \xrightarrow[r\to\infty]{} -\frac{4}{r^4}\ .
\end{gathered} \tag{3.5}$$

The asymptotic structure of the fields $\mathcal{E}_{H}(\boldsymbol{r})$ and $\mathcal{E}_{x}(\boldsymbol{r})$ are to Gaussian accuracy. The $-1/r^2$ structure of the fields $\mathcal{E}_{xc}(\boldsymbol{r})$ and $\mathcal{E}_{x}(\boldsymbol{r})$ is a general result [19, 21-23] valid for any finite system. It is a consequence of the fact that the total charge of the quantal Fermi-Coulomb and Fermi holes is negative unity, and that these charge distributions which are localized about the nucleus become static in the limit of asymptotic positions of the electron.

C. *Electron-interaction potential* $W_{ee}(r)$

In Fig. 3.8a we plot the potential $W_c(r)$ and in Fig. 3.8b the potentials $W_{xc}(r)$, $W_x(r)$, and the function $-1/r$. Observe, that all the potentials have zero slope at the nucleus. This is a result of the fact that the corresponding field from which these potentials are derived all vanish at this electron position. The potentials $W_{xc}(r)$ and $W_x(r)$ are monotonic with positive slope as a result of the fact that the fields $\mathcal{E}_{xc}(r)$ and $\mathcal{E}_x(r)$ are negative. In contrast the potential $W_c(r)$ is not monotonic since the field $\mathcal{E}_c(r)$ changes sign. Furthermore, the potentials $W_{xc}(r)$ and $W_x(r)$ are an order of magnitude greater than $W_c(r)$ as a result of the magnitudes of the corresponding fields. We note that, for this specific system, the Pauli potential $W_x(r) = -\frac{1}{2} W_H(r)$.

The asymptotic structures of the potentials may be derived from Eq. (3.5) to be

$$W_{ee}(r) \underset{r\to\infty}{\to} \frac{1}{r} - \frac{4}{3r^3} \; ; \quad W_H(r) \underset{r\to\infty}{\to} \frac{2}{r} \; ; \quad W_{xc}(r) \underset{r\to\infty}{\to} -\frac{1}{r} - \frac{4}{3r^3} \; ;$$
$$W_x(r) \underset{r\to\infty}{\to} -\frac{1}{r} \; ; \quad W_c(r) \underset{r\to\infty}{\to} -\frac{4}{3r^3} \, . \tag{3.6}$$

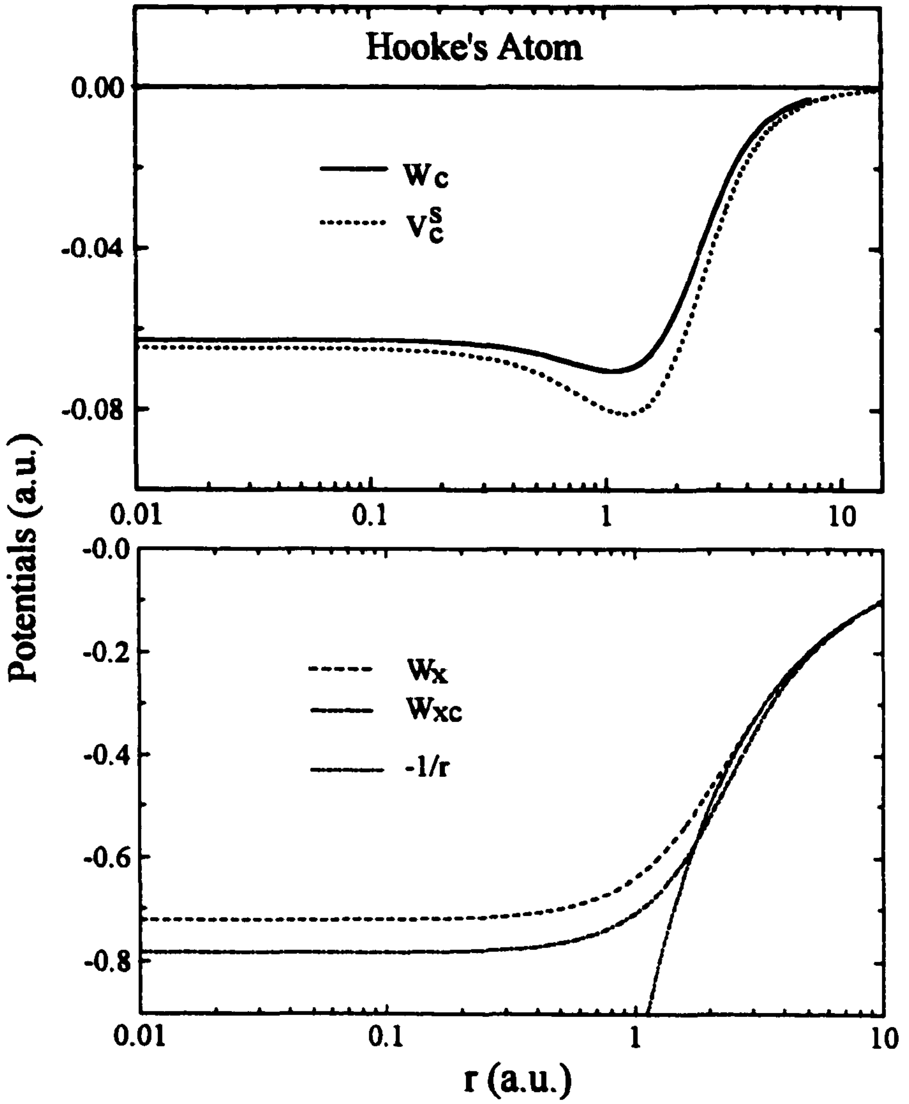


Figure 3.8: (a) The KS $W_c(r)$ and Slater $V_c^S(r)$ Coulomb potentials for the Hooke's atom. (b) The quantal Pauli-Coulomb $W_{xc}(r)$ and KS Pauli $W_x(r)$ potentials, and the function $-1/r$.

Once again, the asymptotic $-1/r$ structure of the potentials $W_{xc}(r)$ and $W_x(r)$ is the same for all finite systems for reasons explained previously. Note that the potential $W_c(r)$ due to the Coulomb hole decays in this case as $O\ (1/r^3)$. The asmptotic structure of $W_H(r)$ and $W_x(r)$ is again quoted to Gaussian accuracy.

With the Slater electron-interaction potential defined as

$$V^S_{ee}(r) = \int \frac{g(r,r')}{|r-r'|}\, dr' \ , \qquad (3.7)$$

we have also plotted in Fig. 3.8a the Slater correlation potential $V^S_c(r) = \int dr' \rho_c(r,r')/|r-r'|$. (The Slater [49] exchange potential $V^S_x(r) = \int dr' \rho_x(r,r')/|r-r'| = W_x(r)$ since the Fermi hole is a static charge in this model.) In Slater theory, the dynamic nature of the pair-correlation density is not accounted for, and as such $V^S_c(r)$ does not represent the potential energy of an electron. The error of $V^S_c(r)$ in comparison to the work $W_c(r)$ is evident from Fig. 3.8a. However, the asymptotic structure of the Slater exchange-correlation potential $V^S_{xc}(r) = \int dr' \rho_{xc}(r,r')/|r-r'|$ is $-1/r$, since the Fermi-Coulomb hole is then essentially a static charge distribution so that $V^S_{xc}(r) = W_{xc}(r)$ in this limit.

D. *Kinetic-energy-density tensors* $t_{\alpha\beta}(r\ ;\ [\gamma])$ *and* $t_{s,\alpha\beta}(r\ ;\ [\gamma_s])$

The source of the correlation-kinetic component is the difference between the kinetic-energy density tensors for the Schrödinger interacting $t_{\alpha\beta}(r\ ;\ [\gamma])$ and noninteracting $t_{s,\alpha\beta}(r\ ;\ [\gamma_s])$ systems. As a consequence of spherical symmetry, these tensors are of the form

$$t_{\alpha\beta}(r\ ;\ [\gamma]) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta}\, k(r)\ , \tag{3.8}$$

and

$$t_{s,\alpha\beta}(r\ ;\ [\gamma_s]) = \frac{r_\alpha r_\beta}{r^2} h(r)\ , \tag{3.9}$$

respectively, with the functions $f(r)$, $k(r)$, and $h(r)$ given in Appendix A, and with the detailed derivation given in Appendix B. Since the model is comprised of two electrons of opposite spin in the ground state, $t_{s,\alpha\beta}(r\ ;\ [\gamma_s])$ is the von Weizsäcker tensor [3-5]. Note that for the interacting system, there is an additional $\delta_{\alpha\beta}\, k(r)$ term which contributes only to the diagonal elements of the tensor. We note that this is the first time that the kinetic-energy-density tensor for an interacting nonuniform density system and of the equivalent noninteracting system have been determined, and that too analytically.

In Fig. 3.9a we compare the off-diagonal elements of the tensors by plotting the functions $f(r)$ and $h(r)$. Observe that they are essentially the same, vanishing at the nucleus, and decaying in a similar manner asymptotically. In Fig. 3.9b we compare the diagonal elements of the tensors by plotting the functions $h(r)$ and $f(r) + 3k(r)$. Note that the diagonal element of the interacting system tensor is now finite at the nucleus, and that the difference in this element of the two tensors occurs in the interior region of the atom. This then is the region from

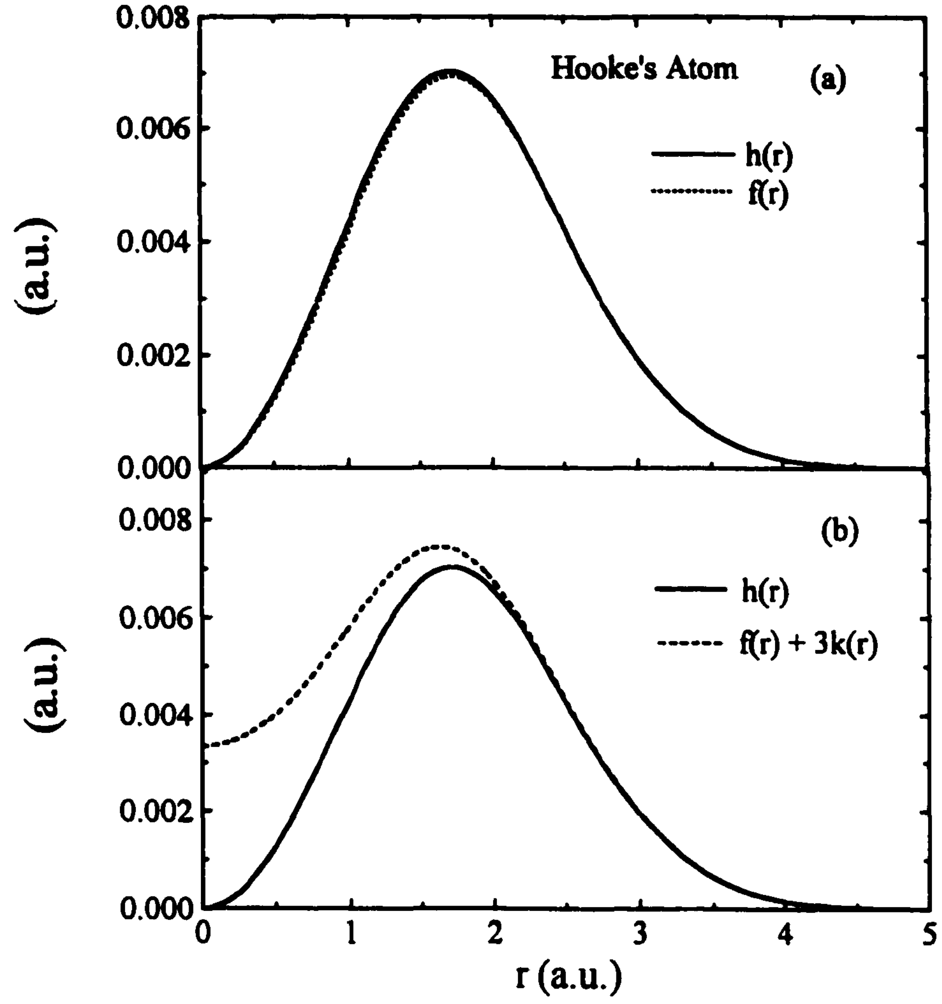


Figure 3.9: (a) The functions $f(r)$ and $h(r)$ of the off-diagonal elements of the interacting and noninteracting system kinetic-energy-density tensors $t_{\alpha\beta}(r;[\gamma])$ and $t_{s,\alpha\beta}(r;[\gamma_s])$ for the Hooke's atom, respectively. (b) The functions $f(r) + 3k(r)$ and $h(r)$ of the diagonal elements of the tensors $t_{\alpha\beta}(r;[\gamma])$ and $t_{s,\alpha\beta}(r;[\gamma_s])$, respectively.

which the correlation contribution to the kinetic energy must arise.

The trace of the kinetic-energy-density tensor is the kinetic-energy-density $t(\mathbf{r})$. Thus the fact that the interacting and noninteracting system tensors are essentially equivalent implies that the corresponding kinetic energies T and T_s are about the same. The value of $T = \int t(\mathbf{r})\, d\mathbf{r} = 0.664418\ a.u.$ and $T_s = \int t_s(\mathbf{r})\, d\mathbf{r} = 0.635245\ a.u.$. The difference $T - T_s$ is the correlation-kinetic energy T_c which is an order of magnitude smaller.

E. Correlation-Kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ and energy $T_c[\rho]$

The field $\mathcal{Z}_{t_c}(\mathbf{r})$ defined by Eq. (2.53) and its components $z_s(\mathbf{r}\ ;\ [\gamma_s])$ and $z(\mathbf{r}\ ;\ [\gamma])$ are plotted in Fig. 3.10. Both components vanish at the nucleus, with $z_s(\mathbf{r})$ being greater than $z(\mathbf{r})$ throughout space. As such $\mathcal{Z}_{t_c}(\mathbf{r})$ vanishes at the origin and is positive-definite over all space. In Fig. 3.11a we compare the field $\mathcal{Z}_{t_c}(\mathbf{r})$ to the Coulomb field $\mathcal{E}_c(\mathbf{r})$ and observe the two to be the same order of magnitude. The correlation-kinetic energy $T_c = 0.0291731\ a.u.$ (see also Eq. (2.55)) is therefore the same order of magnitude as the Coulomb energy $E_c = -0.0676820\ a.u.$. (Note that for the He atom $T_c = 0.0366420\ a.u.$.)

As noted the field $\mathcal{Z}_{t_c}(\mathbf{r})$ decays asymptotically as a positive function. Its precise asymptotic structure may be obtained from that of the components $z_s(\mathbf{r})$ and $z(\mathbf{r})$ which are

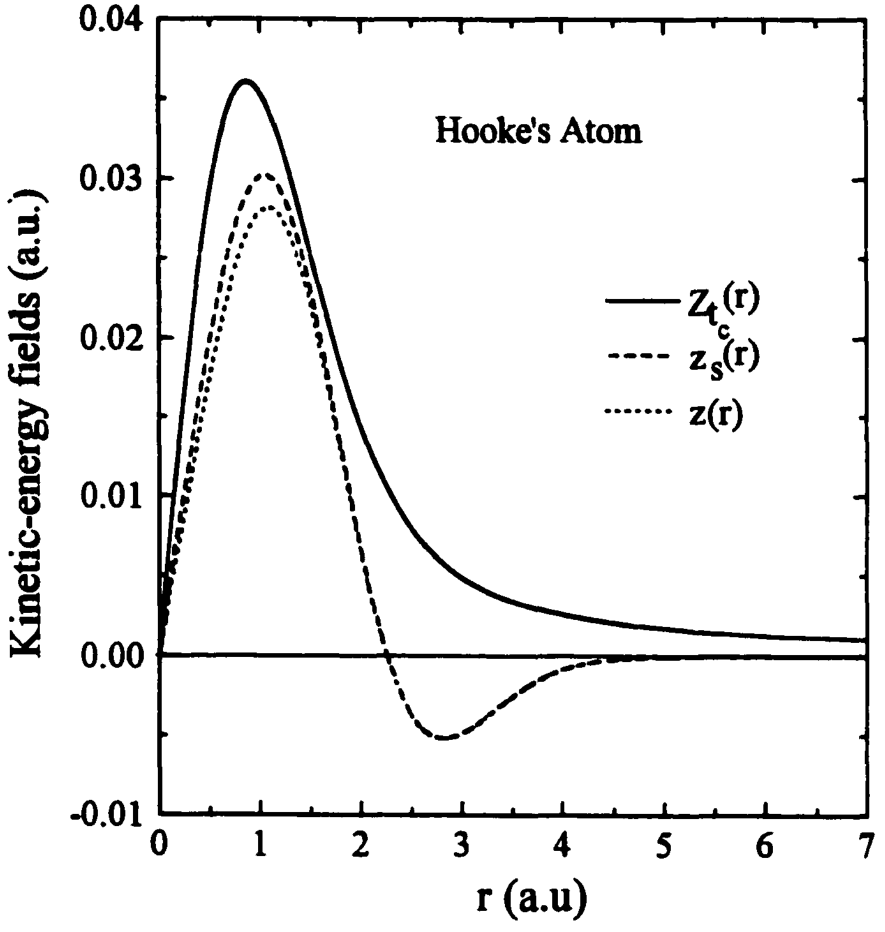


Figure 3.10: The correlation-kinetic field $Z_{t_c}(r)$, and its components $z_s(r\ ;\ [\gamma_s])$ and $z(r\ ;\ [\gamma])$ for the noninteracting and interacting systems for the Hooke's atom.

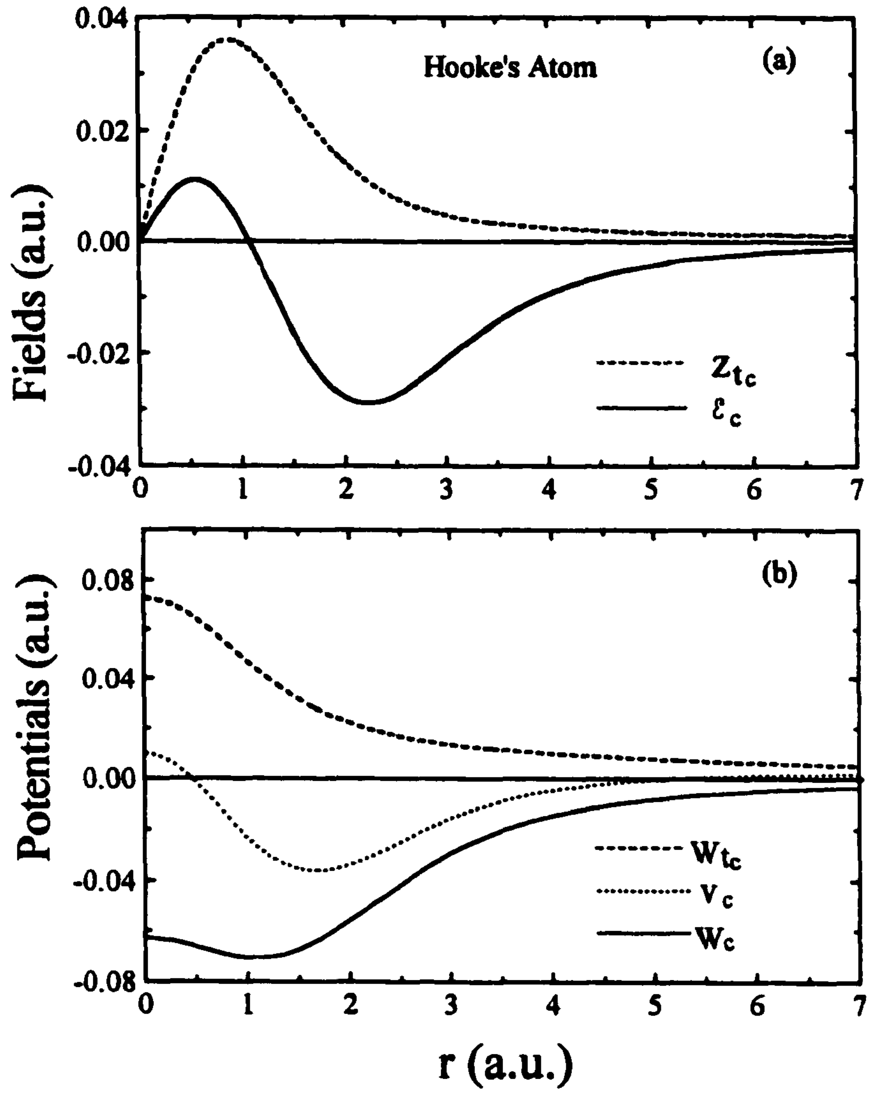


Figure 3.11: (a) The correlation-kinetic $\mathcal{Z}_{t_c}(\mathbf{r})$ and KS Coulomb $\mathcal{E}_c(\mathbf{r})$ fields for the Hooke's atom. (b) The correlation-kinetic $W_{t_c}(\mathbf{r})$ and KS Coulomb $W_c(\mathbf{r})$ potentials. The functional derivative $v_c(\mathbf{r}) = \delta E_c^{KS}[\rho]/\delta\rho(\mathbf{r})$ is also plotted.

$$z_s(r) \underset{r\to\infty}{\longrightarrow} -\frac{\sqrt{2\pi}\,\pi C^2}{4}\,\Big[\, r^5 + 4r^4 - 3r^3 - 24r^2 - 8r + 20 - \frac{20}{r} + \frac{8}{r^2} + \cdots \Big]\, e^{-r^2/2} \,, \tag{3.10}$$

and

$$z(r) \underset{r\to\infty}{\longrightarrow} -\frac{\sqrt{2\pi}\,\pi C^2}{4}\,\Big[\, r^5 + 4r^4 - 3r^3 - 24r^2 - 8r + 20 - \frac{16}{r} - \frac{8}{r^2} + \cdots \Big]\, e^{-r^2/2} \,. \tag{3.11}$$

Note the cancellation of terms of $O(r^5)$ to $O(r^0)$. The density $\rho(r)$ decays as

$$\rho(r) \underset{r\to\infty}{\longrightarrow} \sqrt{2\pi}\,\pi\, C^2 r^2 \left(1 + \frac{4}{r} \right) e^{-r^2/2} \,, \tag{3.12}$$

so that the field $Z_{t_c}(r)$ decays asymptotically as

$$Z_{t_c}(r) \underset{r\to\infty}{\longrightarrow} \frac{1}{r^3} - \frac{8}{r^4} \,. \tag{3.13}$$

The structure of the field $Z_{t_c}(r)$ for the He atom differs from the Hooke's model in that it is oscillatory, the difference arising due to the different external potentials. However, for both atoms, the field $Z_{t_c}(r)$ decays as a positive function. We have recently proved [37, 38] that for atoms with a Coulomb external potential, $Z_{t_c}(r)$ decays asymptotically as a positive function of $O(1/r^6)$.

F. *Correlation-Kinetic potential* $W_{t_c}(\mathbf{r})$.

The structure of the correlation-kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ dictates that of the corresponding potential $W_{t_c}(\mathbf{r})$. Since the field $\mathcal{Z}_{t_c}(\mathbf{r})$ vanishes at the nucleus, the potential $W_{t_c}(\mathbf{r})$ has zero slope there. Further, the field is positive, so that $W_{t_c}(\mathbf{r})$ is monotonic with negative slope over all space (see Fig. 3.11b). The potential decays asymptotically as

$$W_{t_c}(r) \underset{r\to\infty}{\rightarrow} \frac{1}{2r^2} - \frac{8}{3r^3} \, . \tag{3.14}$$

We have also plotted the Coulomb potential $W_c(\mathbf{r})$ in Fig. 3.11b to show it is the same order of magnitude as $W_{t_c}(\mathbf{r})$.

G. *Conventional Kohn-Sham theory correlation energy* $E_c^{KS}[\rho]$ *and its functional derivative* $v_c(\mathbf{r})$.

The KS electron-interaction energy functional $E_{ee}^{KS}[\rho]$ is conventionally written as a sum of the Coulomb self-energy $E_H[\rho]$ and KS exchange-correlation energy $E_{xc}^{KS}[\rho]$, the later being further split into its exchange $E_x[\rho]$ and correlation $E_c^{KS}[\rho]$ components. The corresponding KS Hartree $v_H(\mathbf{r})$, exchange-correlation $v_{xc}(\mathbf{r})$, exchange $v_x(\mathbf{r})$, and correlation $v_c(\mathbf{r})$ potentials are respectively the functional derivatives of $E_H[\rho]$, $E_{xc}^{KS}[\rho]$, $E_x[\rho]$ and $E_c^{KS}[\rho]$. The potential $v_H(\mathbf{r})$ is the same as $W_H(\mathbf{r})$ of Eq. (2.64) expressed in terms of the field $\mathcal{E}_H(\mathbf{r})$. The KS exchange energy $E_x[\rho]$ which is defined either via the virial theorem [50] in terms of $v_x(\mathbf{r})$, or as the energy of interaction between the density $\rho(\mathbf{r})$ and Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$

is the same as in Eq. (2.62) written in terms of the field $\mathcal{E}_x(\mathbf{r})$. The potential $v_x(\mathbf{r})$, however, is the sum [51-53]

$$v_x(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta\rho(\mathbf{r})} = W_x(\mathbf{r}) - W^{(1)}_{t_c}(\mathbf{r}) \ , \tag{3.15}$$

where $W^{(1)}_{t_c}(\mathbf{r})$ is the work done in the field $Z^{(1)}_{t_c}(\mathbf{r}) = z\,(\mathbf{r}\ ;\ [\gamma^c_1]\ )/\rho(\mathbf{r})$ with $\gamma^c_1\ (\mathbf{r},\mathbf{r}')$ being the first-order correction to the s-system density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ obtained via perturbation theory by an expansion of the wavefunction Ψ in terms of the electron-interaction coupling constant. The KS exchange potential thus contains part of the Correlation-Kinetic contribution. (A study of $W^{(1)}_{t_c}(\mathbf{r})$ for atoms and metal surfaces has recently been performed [54]). For the Hooke's atom in its ground-state, however, $v_x(\mathbf{r}) = W_x(\mathbf{r})$, so that

$$v_c(\mathbf{r}) = \frac{\delta E^{KS}_c\ [\rho]}{\delta\rho(\mathbf{r})} = W_c(\mathbf{r}) + W_{t_c}(\mathbf{r}) \ \ . \tag{3.16}$$

In Fig. 3.11b we have also plotted the KS correlation potential $v_c(\mathbf{r})$. It lies above $W_c(\mathbf{r})$ since it also contains the correlation-kinetic contribution. The corresponding KS correlation energy is $E^{KS}_c\ [\rho] = E_c[\rho] + T_c[\rho] = -0.0385089\,a.u.$. (The corresponding value of $E^{KS}_c\ [\rho]$ for He is $-\ 0.0421080\ a.u.$). Observe (Fig. 3.11a) that the fields $Z_{t_c}(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$, and (Fig. 3.11b) potentials $W_{t_c}(\mathbf{r})$ and $W_c(\mathbf{r})$, and thus the energies $E_c[\rho]$ and $T_c\ [\rho]$ cancel each other to a great degree. Thus, the Pauli potential $W_x(\mathbf{r})$ should be essentially equivalent to the KS exchange-correlation potential $v_{xc}(\mathbf{r})$. That this is the case is shown in Fig. 3.12 where the potentials $W_x(\mathbf{r})$ and $v_{xc}(\mathbf{r})$ are compared.

H. *Asymptotic structure of functional derivative $v_{xc}(r)$ in terms of electron correlations*

From the s-system differential equation for the Hooke's atom Eq. (3.4), the asymptotic structure of the functional derivative $v_{xc}(r)$ is

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}^{KS}[\rho]}{\delta\rho(\mathbf{r})} \xrightarrow[r\to\infty]{} -\frac{1}{r} + \frac{1}{2r^2} - \frac{4}{r^3} + \cdots \; . \qquad (3.17)$$

Here the leading $(-1/r)$ term is that of $v_x(\mathbf{r})$ or equivalently $W_x(\mathbf{r})$, and therefore due to Pauli correlations. The KS correlation potential then decays as

$$v_c(\mathbf{r}) \xrightarrow[r\to\infty]{} \frac{1}{2r^2} - \frac{4}{r^3} + \cdots \; . \qquad (3.18)$$

However, from Eqs. (3.14) and (3.16), we see that the term of $O(1/r^2)$ of Eq. (3.18) is a correlation-kinetic contribution. Furthermore, from Eqs. (3.6) and (3.14), we observe that the next lower order term $(4/r^3)$ of Eq. (3.18) is comprised of a Coulomb correlation component of magnitude $(4/3r^3)$ as well as a correlation-kinetic piece of magnitude $(8/3r^3)$. All lower order terms also comprise of a sum of Coulomb and correlation-kinetic contributions.

For a Coulomb external potential we have recently shown [38] (see also Chapter 5) that for atoms in which the N- and $(N-1)$-electron systems are

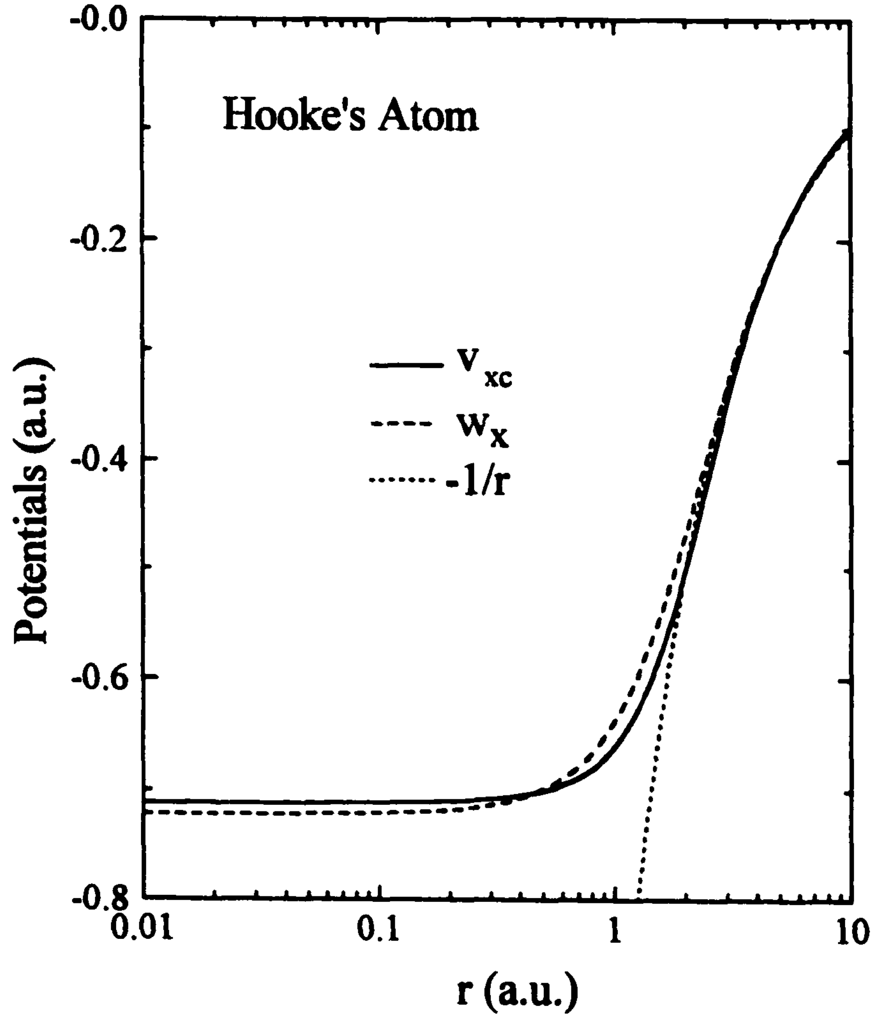


Figure 3.12: Comparison of KS Pauli $W_x(r)$ and exchange-correlation $v_{xc}(r) = \delta E_{xc}^{KS}[\rho]/\delta\rho(r)$ potentials for the Hooke's atom. The function $-1/r$ is also plotted.

orbitally nondegenerate, the structure of $v_{xc}(\mathbf{r}) \underset{r\to\infty}{\sim} -1/r - \alpha/2r^4 + 8\kappa_0\chi/5r^5$, where α is the polarizability, χ an expectation value of the $(N-1)$-electron ion, and $\kappa_0^2/2$ the ionization potential. The derivation shows the leading and second terms to arise ***directly*** from the Fermi and Coulomb hole charges, and the last to be a Correlation-Kinetic contribution. For atoms in which the N-electron system is orbitally degenerate, there are additional contributions of $O(1/r^3)$ and $O(1/r^5)$ due to Pauli correlations. Further, there is no $O(1/r^5)$ contribution due to Coulomb correlations. For completeness we note that at a metal-vacuum interface [54, 55], both the Pauli $W_x(\mathbf{r})$ and leading order Correlation-Kinetic $W_{t_c}^{(1)}(\mathbf{r})$ components (see Eq. (3.15)) contribute to the asymptotic structure of the KS exchange potential $v_x(\mathbf{r})$ in the classically forbidden and metal bulk regions.

3.3. Summary and Concluding Remarks

By application to a ground state of the Hooke's atom, we have illustrated in this chapter how to transform the Schrödinger equation to one of noninteracting Fermions with equivalent density. The transformation requires the construction of two fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathbf{Z}_{t_c}(\mathbf{r})$, which in this example are separately conservative, the former representative of correlations due to the Pauli exclusion principle and Coulomb repulsion, and the latter that of Correlation-Kinetic effects. The structure of these fields then leads to an *a priori* understanding of the corresponding potentials and magnitudes of the energies. In this manner, the Kohn-Sham theory exchange-correlation energy functional $E_{xc}^{KS}[\rho]$ and its functional derivative $v_{xc}(r)$ are also described in terms of the separate Pauli, Coulomb, and Correlation-Kinetic contributions. Here we have provided a complete description of the sources, fields, potentials and energies required for the construction of the equivalent noninteracting system.

The following is a summary of our results for the Hooke's atom. *(i)* The representation of electron interaction via the structure of the Coulomb hole is generally similar to that of the He atom. Furthermore, the Coulomb E_c and Correlation-Kinetic T_c energies also approximate well the corresponding values for the He atom. As such it is meaningful to test approximate exchange-correlation energy functionals and derivatives employing this model. *(ii)* The fact that ***both*** the Pauli-Coulomb $\mathcal{E}_{xc}(r)$ and Correlation-Kinetic $Z_{t_c}(r)$ fields vanish at the nucleus approaching it linearly indicates that the KS exchange-correlation potential $v_{xc}(r)$ is quadratic with zero slope there. *(iii)* That both the Pauli-Coulomb $\mathcal{E}_{xc}(r)$ and Pauli $\mathcal{E}_{x}(r)$ fields are negative-definite indicates that the corresponding component potentials $W_{xc}(r)$ and $W_x(r)$ of $v_{xc}(r)$ are monotonic with positive slope. *(iv)* That the field $Z_{t_c}(r)$ is positive-definite indicates that the Correlation-Kinetic component $W_{t_c}(r)$ is monotonic with negative slope. *(v)* The leading $(-1/r)$ asymptotic structure of $v_{xc}(r)$ is that of $W_x(r)$ and therefore due entirely to Pauli correlations. *(vi)* The next term of $O(1/r^2)$ is due to correlation-kinetic effects. *(vii)* Terms of $O(1/r^3)$ and lower are a sum of ***both*** Coulomb correlation and Correlation-Kinetic contributions. *(viii)* The structure of the

Coulomb $\boldsymbol{\mathcal{E}}_c(\boldsymbol{r})$ and correlation-kinetic $\boldsymbol{Z}_{t_c}(\boldsymbol{r})$ fields shows these effects to cancel so that the corresponding energies $E_c[\rho]$ and T_c are the same order of magnitude and opposite in sign. *(ix)* As a consequence of the cancellation of the fields $\boldsymbol{\mathcal{E}}_c(\boldsymbol{r})$ and $\boldsymbol{Z}_{t_c}(\boldsymbol{r})$, the Pauli potential $W_x(\boldsymbol{r})$ is essentially equivalent to the KS exchange-correlation potential $v_{xc}(\boldsymbol{r})$. *(x)* The off-diagonal elements of the Schrödinger and s-system kinetic-energy density tensors are essentially equivalent. *(xi)* The diagonal elements of the tensors differ only in the interior region of the atom. They are equivalent elsewhere. As such the contribution to the Correlation-Kinetic energy T_c arises from this region. *(xii)* Furthermore, the interacting and noninteracting system kinetic energies are essentially equivalent, so that T_c is an order of magnitude smaller.

Since the KS exchange-correlation energy functional $E_{xc}^{KS}[\rho]$ and its functional derivative $v_{xc}(\boldsymbol{r})$ are unknown, a focus of research has been the development of accurate approximate energy functionals and potentials. The quantum-mechanical interpretation via its application to the He atom as well as the present model calculation suggest another approach to the construction of accurate energy functionals and their derivatives. The ideas here is to employ an approximate wavefunction to approximate the Pauli-Coulomb $\boldsymbol{\mathcal{E}}_{xc}(\boldsymbol{r})$ and correlation-kinetic $\boldsymbol{Z}_{t_c}(\boldsymbol{r})$ fields since both $E_{xc}^{KS}[\rho]$ and $v_{xc}(\boldsymbol{r})$ are expressable in terms of them. One constraint on the fields is that their sum be curl free. Another restriction is that of the known asymptotic structure in the classically forbidden region. Any such approximation would, furthermore, be consistent in that the same total field, and thus the *same* approximate representation of electron correlations, will lead to both the energy as well as the potential. The potential could be determined self-consistently till the energy is minimized with respect to any parameters in the fields. The bound thus obtained on the ground-state energy would be rigorous since the Hamiltonian is unchanged.

The Hooke's atom also allows for the study of the physics of transformation from an excited state of the Schrödinger system to one of noninteracting Fermions with equivalent density. Such a calculation has recently been performed [56].

Chapter 4

AN ALTERNATE MANY-BODY PERTURBATION THEORY OF ELECTRONIC STRUCTURE

4.1. Introduction

In this chapter we develop a many-body perturbation theory of electronic structure within the framework of quantal density functional theory (Q-DFT). Since in Q-DFT, the contributions to the energy and local potential due to correlations arising from the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects are separately delineated, it is possible to develop a ***separate*** perturbation series for the latter two types of correlations. Thus, with the lowest order contribution being due to Pauli correlations, the Coulomb correlation and Correlation-Kinetic contributions can be ***systematically*** and ***separately*** incorporated to any order. As with standard many-body perturbation theory, at lowest order, the bound on the total energy is rigorous. Furthermore, as we will show, the Work Formalism Hartree-Fock approximation [18, 19] can be derived within this framework. At the end of this chapter, we also compare this calculational scheme with the Optimized Potential Method [57, 58], as well the integral equation of Sham and Schlüter [59, 60].

4.2. Sources of Fields in Terms of Green's Functions

The basic idea is to relate the fields of Q-DFT to many-body theory. Thus, we start by expressing the quantal sources in terms of the one particle Green's function $G_{\sigma\sigma'}(rt,r't')$ which is defined as

$$G_{\sigma\sigma'}(rt,r't') = -i\,\langle\Psi_0|\,T\{\psi_\sigma(r,t)\psi^+_{\sigma'}(r',t')\}\,|\Psi_0\rangle \,/\, \langle\Psi_0|\Psi_0\rangle \qquad (4.1)$$

where $|\Psi_0\rangle$ is the ground state of the interacting system, T is the time ordering operator and $\psi_\sigma(r,t)$, $\psi^+_\sigma(r,t)$ are the annihilation and creation operators, respectively. The single-particle density matrix $\gamma(r,r')$ is

$$\gamma_{\sigma\sigma'}(r,r') = -i\lim_{t\to t'^+} G_{\sigma'\sigma}(r't',rt)\ , \qquad (4.2)$$

where σ, σ' are spin indices. The density $\rho(r)$ is

$$\rho(r) = -i\sum_\sigma \lim_{t\to t'^+} G_{\sigma\sigma}(rt',rt)\ , \qquad (4.3)$$

The Dirac density matrix $\gamma_{s,\sigma\sigma'}(r,r')$ is similarly expressed in terms of $G_{s,\sigma\sigma'}(rt,r't')$, the noninteracting system Green's function, as

$$\gamma_{s,\sigma\sigma'}(r,r') = -i\lim_{t\to t'^+} G_{s,\sigma'\sigma}(r't',rt)\ , \qquad (4.4)$$

with

$$G_{s,\sigma\sigma'}(rt,r't') = -i\,\langle\Phi_0|\,T\{\psi_\sigma(r,t)\psi^+_{\sigma'}(r',t')\}\,|\Phi_0\rangle \,/\, \langle\Phi_0|\Phi_0\rangle \qquad (4.5)$$

where $|\Phi_0\rangle$ is the ground state Slater determinant of the noninteracting s-system. The density of the interacting system, which is the same as that of the noninteracing system, may therefore be written as

$$\rho(r) = -i \sum_{\sigma} \int \frac{d\omega}{2\pi} e^{i\omega\eta} G_{\sigma\sigma}(r,r,\omega) = -i \sum_{\sigma} \int \frac{d\omega}{2\pi} e^{i\omega\eta} G_{s,\sigma\sigma}(r,r,\omega) \ , \qquad (4.6)$$

where $G_{\sigma\sigma'}(r,r',\omega)$ ($G_{s,\sigma\sigma'}(r,r',\omega)$) are the Fourier transforms of $G_{\sigma\sigma'}(rt,r't')$ ($G_{s,\sigma\sigma'}(rt,r't')$), respectively:

$$G_{\sigma\sigma'}(r,r',\omega) = \int d(t-t') e^{i\omega(t-t')} G_{\sigma\sigma'}(rt,r't') \ . \qquad (4.7)$$

It is well known from conventional many-body theory [61] that

$$\begin{aligned} &[\omega + \frac{1}{2}\nabla^2 - v(r)] G_{\sigma\sigma'}(r,r',\omega) \\ &- \sum_{\mu} \int \Sigma_{\sigma\mu}(r,r'',\omega) G_{\mu\sigma'}(r'',r',\omega) dr'' = \delta(r-r')\delta_{\sigma\sigma'} \ , \end{aligned} \qquad (4.8)$$

where

$$\Sigma_{\sigma\sigma'}(r,r',\omega) = \int d(t-t') e^{i\omega(t-t')} \Sigma_{\sigma\sigma'}(rt,r't') \ , \qquad (4.9)$$

with $\Sigma(rt,r't')$ being the self-energy. With the definition

$$\bar{\Sigma}_{\mu\nu}(r,r',\omega) = \Sigma_{\mu\nu}(r,r',\omega) - \delta(r-r') v_{ee}(r) \delta_{\mu\nu} \ , \qquad (4.10)$$

Eq. (4.8) may be rewritten as

$$\begin{aligned} &[\omega + \frac{1}{2}\nabla^2 - v_s(r)] G_{\sigma\sigma'}(r,r',\omega) \\ &- \sum_{\mu} \int \bar{\Sigma}_{\sigma\mu}(r,r'',\omega) G_{\mu\sigma'}(r'',r',\omega) dr'' = \delta(r-r')\delta_{\sigma\sigma'} \ . \end{aligned} \qquad (4.11)$$

where

$$v_s(r) = v(r) + v_{xc}(r) . \tag{4.12}$$

The two Green's functions G and G_s are therefore related by the Dyson's equation

$$\begin{aligned} G_{\sigma\sigma'}(r,r',\omega) &= G_{s,\sigma\sigma'}(r,r',\omega) \\ &+ \sum_{\mu\nu} \int G_{s,\sigma\mu}(r,y,\omega)\tilde{\Sigma}_{\mu\nu}(y,y',\omega)G_{\nu\sigma'}(y',r',\omega)dydy' , \end{aligned} \tag{4.13}$$

because G_s satisfies the equation

$$[\omega + \frac{1}{2}\nabla^2 - v_s(r)]G_{s,\sigma\sigma'}(r,r',\omega) = \delta(r - r')\delta_{\sigma\sigma'} . \tag{4.14}$$

The Dyson's equation (4.13) can be written, in time space, as

$$\begin{aligned} G_{\sigma\sigma'}(rt,r't') &= G_{s,\sigma\sigma'}(rt,r't') \\ &+ \sum_{\mu\nu} \int G_{s,\sigma\mu}(rt,y\tau)\tilde{\Sigma}_{\mu\nu}(y\tau,y'\tau')G_{\nu\sigma'}(y'\tau',r't')dyd\tau dy'd\tau' . \end{aligned} \tag{4.15}$$

The two-particle density matrix $\rho_2(r_1,r_2;r_1',r_2')$ is defined as

$$\begin{aligned} \rho_2(r_1,r_2;r_1',r_2') = N(N - 1)/2 \sum_{\sigma_1\sigma_2} \int \Psi^*(r_1\sigma_1,r_2\sigma_2,X^{N-2}) \\ \Psi(r_1'\sigma_1,r_2'\sigma_2,X^{N-2})dX^{N-2} . \end{aligned} \tag{4.16}$$

The pair-correlation density $g(r,r')$ is related to the diagonal matrix element $\rho_2(r,r')$ of the two-particle density matrix via $\rho(r)g(r,r') = 2\rho_2(r,r')$ where

$$\rho_2(r,r') = \rho_2(r,r';r,r')$$
$$= N(N-1)/2 \sum_{\sigma\sigma'} \int \Psi^*(r\sigma, r'\sigma', X^{N-2}) \Psi(r\sigma, r'\sigma', X^{N-2}) dX^{N-2} \ . \tag{4.17}$$

The density matrix $\rho_2(r,r')$ can also be expressed as the expectation value of field operators in second quantization form as,

$$2\rho_2(r_1,r_2) = \sum_{\alpha\beta} \langle \Psi_0 | \psi_\alpha^+(r_1) \psi_\beta^+(r_2) \psi_\beta(r_2) \psi_\alpha(r_1) | \Psi_0 \rangle \ , \tag{4.18}$$

or

$$2\rho_2(r_1,r_2) = \lim_{t_3\to t_4^+} \lim_{t_4\to t_2^+} \lim_{t_2\to t_1^+}$$
$$\sum_{\alpha\beta} \langle \Psi_0 | \psi_\alpha^+(r_3t_3) \psi_\beta^+(r_4t_4) \psi_\beta(r_2t_2) \psi_\alpha(r_1t_1) | \Psi_0 \rangle \Big|_{r_3=r_1, r_4=r_2} \ . \tag{4.19}$$

Therefore, the density matrix $\rho_2(r_1,r_2)$ is expressible in terms of the two-particle Green's function, which is defined as

$$G^{(2)}_{\alpha\beta,\gamma\delta}(1,2;3,4)$$
$$= (-i)^2 \langle \Psi_0 | T\{ \psi_\alpha(1) \psi_\beta(2) \psi_\delta^+(4) \Psi_\gamma^+(3) \} | \rangle \ / \ \langle \Psi_0 | \Psi_0 \rangle \ , \tag{4.20}$$

where $1 \equiv r_1 t_1$ etc., as

$$2\rho_2(r_1,r_2) = -\lim_{t_3\to t_4^+} \lim_{t_4\to t_2^+} \lim_{t_2\to t_1^+} \sum_{\alpha\beta} G^{(2)}_{\alpha\beta,\alpha\beta}(1,2,3,4) \Big|_{r_3=r_1; r_4=r_2} \ . \tag{4.21}$$

4.3. Electron-Interaction Field $\mathcal{E}_{ee}(r)$

We next determine an expression for the electron-interaction field $\mathcal{E}_{ee}(r)$.

To do so we employ the Bethe-Salpeter equation [61, 62]. This equation which expresses the two-particle Green's function in terms of the one-particle Green's function and an effective two-particle interaction $\Gamma_{\alpha\beta\gamma\delta}$ is

$$\begin{aligned} G^{(2)}_{\alpha\beta,\gamma\delta}(1,2;3,4) &= G_{\alpha\gamma}(1,3)G_{\beta\delta}(2,4) - G_{\alpha\delta}(1,4)G_{\beta\gamma}(2,3) \\ &+ \sum_{\alpha'\beta'\gamma'\delta'} \int G_{\gamma'\gamma}(3',3)G_{\delta'\delta}(4',4) \\ &\Gamma_{\alpha'\beta'\gamma'\delta'}(1',2';3',4')G_{\alpha\alpha'}(1,1')G_{\beta\beta'}(2,2')d1'd2'd3'd4' , \end{aligned} \tag{4.22}$$

where $d1' = dr_1' dt_1'$ etc.. Substituting Eq. (4.22) into Eq. (4.21), one obtains

$$\begin{aligned} g(r_1,r_2)\rho(r_1) &= -\underset{t_3\to t_4^+\, t_4\to t_2^+\, t_2\to t_1^+}{\lim\lim\lim} \sum_{\alpha\beta} \{ [G_{\alpha\alpha}(r_1t_1, r_3t_3) G_{\beta\beta}(r_2t_2, r_4t_4) \\ &- G_{\alpha\beta}(r_1t_1, r_4t_4) G_{\beta\alpha}(r_2t_2, r_3t_3) \\ &+ \sum_{\alpha'\beta'\gamma'\delta'} \int G_{\gamma'\gamma}(3',3) G_{\delta'\delta}(4',4) \Gamma_{\alpha'\beta'\gamma'\delta'}(1',2',3',4') \\ &G_{\alpha\alpha'}(1,1') G_{\beta\beta'}(2,2') d1' d2' d3' d4'] \} |_{r_3=r_1, r_4=r_2} . \end{aligned} \tag{4.23}$$

Writing $G_{\alpha\beta}(1,2) = G(1,2)\,\delta_{\alpha\beta}$ etc., we have from Eq. (4.2)

$$\underset{t_3\to t_4^+\, t_4\to t_2^+\, t_2\to t_1^+}{\lim\lim\lim} \sum_{\alpha\beta} G_{\alpha\alpha}(r_1t_1, r_3t_3) G_{\beta\beta}(r_2t_2, r_4t_4) |_{r_3=r_1, r_4=r_2} = -\rho(r_1)\rho(r_2) . \tag{4.24}$$

and that

$$\begin{aligned} &\underset{t_3\to t_4^+\, t_4\to t_2^+\, t_2\to t_1^+}{\lim\lim\lim} \sum_{\alpha\beta} \frac{1}{\rho(r_1)} G_{\alpha\beta}(r_1t_1, r_4t_4) G_{\beta\alpha}(r_2t_2, r_3t_3) |_{r_3=r_1, r_4=r_2} \\ &= -\frac{1}{2} \frac{\gamma(r_1,r_2)\gamma(r_2,r_1)}{\rho(r_1)} . \end{aligned} \tag{4.25}$$

Again writing $G_{\gamma'\gamma}(3',3) = G(3',3)\,\delta_{\gamma'\gamma}$ etc., we have, from Eqs. (4.23), (4.24) and (4.25), the expression for the pair-correlation density to be

$$
\begin{aligned}
g(\mathbf{r}_1,\mathbf{r}_2) &= \rho(\mathbf{r}_2) - \frac{\gamma(\mathbf{r}_1,\mathbf{r}_2)\gamma(\mathbf{r}_2,\mathbf{r}_1)}{2\rho(\mathbf{r}_1)} \\
&- \frac{1}{\rho(\mathbf{r}_1)} \lim_{t_3 \to t_4^+} \lim_{t_4 \to t_2^+} \lim_{t_2 \to t_1^+} \sum_{\alpha\beta} \int G(3',\mathbf{r}_1 t_3)\, G(4',\mathbf{r}_2 t_4) \\
&\Gamma_{\alpha\beta\alpha\beta}(1',2';3',4')\, G(1,1')\, G(2,2')\, d1'd2'd3'd4' \ ,
\end{aligned}
\tag{4.26}
$$

where the effective two-particle interaction may be written diagrammatically as

$$(see\ page\ 61) \tag{4.27}$$

with

$$(see\ page\ 62) \tag{4.28}$$

and where the double lines are associated with G and the single with G_s. Note that an extra factor i^n is required for the nth-order interaction in the above diagrams. With the pair-correlation density $g(\mathbf{r},\mathbf{r}')$ given by Eq. (4.26) the electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ is determined via Coulomb's law Eq. (2.52) to any order.

4.4. The Correlation-Kinetic Field $Z_{t_c}(\mathbf{r})$

The correlation-kinetic field $Z_{t_c}(\mathbf{r})$ involves the difference between the kinetic-energy-density tensors for the non-interacting s-system and interacting system as

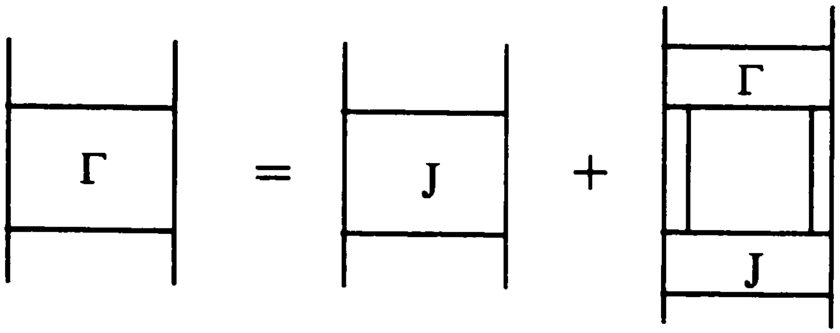


Figure 4.1: Equation (4.27) of Chapter 4

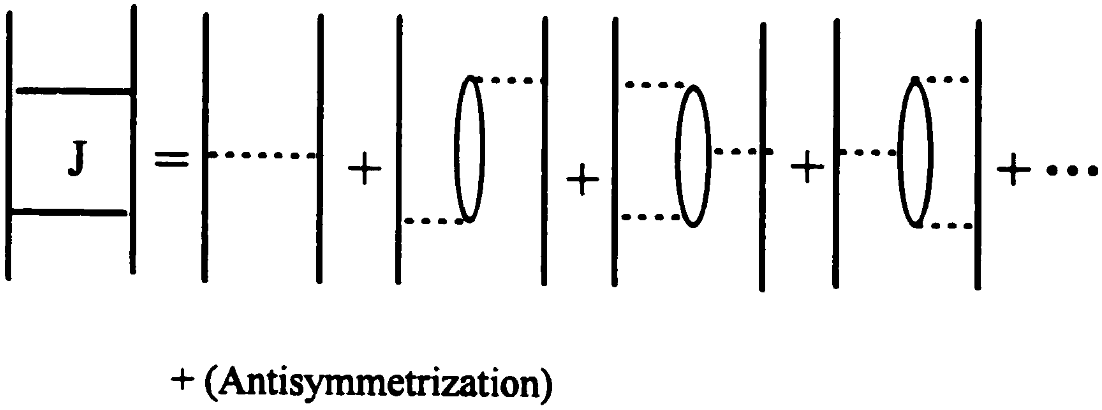


Figure 4.2: Equation (4.28) of Chapter 4

$$Z_{t_c,\alpha}(r) = 2\sum_{\beta}\frac{\partial}{\partial r_\beta}[t_{s,\alpha\beta}(r) - t_{\alpha\beta}(r)] \ . \tag{4.29}$$

Expressing the tensors in terms of the corresponding Green's functions, one obtains,

$$\begin{aligned} Z_{t_c,\alpha}(r) &= \frac{1}{\rho(r)}\sum_{\beta=1}^{3}\sum_{\sigma}\frac{\partial}{\partial r_\beta}\{[\frac{\partial^2}{\partial r_\alpha{}'\partial r_\beta{}''} + \frac{\partial^2}{\partial r_\beta{}'\partial r_\alpha{}''}] \\ &\lim_{t'\to t''^{+}} -i[G_{s,\sigma\sigma}(r''t'',r't') - G_{\sigma\sigma}(r''t'',r't')]_{r'=r''=r}\} \ . \end{aligned} \tag{4.30}$$

By using Dyson's equation Eq. (4.15), one has

$$\begin{aligned} Z_{t_c,\alpha}(r) &= \frac{i}{2\rho(r)}\sum_{\beta=1}^{3}\frac{\partial}{\partial r_\beta}\{[\frac{\partial^2}{\partial r_\alpha{}'\partial r_\beta{}''} + \frac{\partial^2}{\partial r_\beta{}'\partial r_\alpha{}''}]\sum_{\sigma}\lim_{t'\to t''^{+}} \\ &\sum_{\tau\lambda}\int\int dr_1 dt_1 dr_2 dt_2\, G_{s,\sigma\tau}(r''t'',r_1t_1)\tilde{\Sigma}_{\tau\lambda}(r_1t_1,r_2t_2)\,G_{\lambda\sigma}(r_2t_2,r't')|_{r'=r''=r}\} \end{aligned} \tag{4.31}$$

or, after Fourier transformation,

$$\begin{aligned} Z_{t_c,\alpha}(r) &= \frac{i}{4\pi\rho(r)}\sum_{\beta=1}^{3}\frac{\partial}{\partial r_\beta}\{[\frac{\partial^2}{\partial r_\alpha{}'\partial r_\beta{}''} + \frac{\partial^2}{\partial r_\beta{}'\partial r_\alpha{}''}]\sum_{\sigma}\sum_{\tau\lambda} \\ &\int\int dr_1 dr_2\int d\omega\lim_{\eta\to 0^{+}} e^{i\omega\eta}G_{s,\sigma\tau}(r'',r_1,\omega)\tilde{\Sigma}_{\tau\lambda}(r_1,r_2,\omega)\,G_{\lambda\sigma}(r_2,r',\omega)|_{r'=r''=r}\} \end{aligned} \tag{4.32}$$

For spin-independent interaction, one has,

$$G_{s,\alpha\beta}(r_1,r_2,\omega) = G_s(r_1,r_2,\omega)\,\delta_{\alpha\beta} \ , \tag{4.33}$$

$$G_{\alpha\beta}(r_1,r_2,\omega) = G(r_1,r_2,\omega)\,\delta_{\alpha\beta} \ , \tag{4.34}$$

$$\tilde{\Sigma}_{\alpha\beta}(r_1,r_2,\omega) = \tilde{\Sigma}(r_1,r_2,\omega)\delta_{\alpha\beta} , \tag{4.35}$$

Employing Eqs. (4.33-4.35) in Eq. (4.32) leads finally to

$$\begin{aligned} Z_{t_c,\alpha}(r) = {} & \frac{i}{2\pi\rho(r)}\sum_{\beta=1}^{3}\frac{\partial}{\partial r_\beta}\int d\omega \lim_{\eta\to 0^+} e^{i\omega\eta}\int dy \int dy'\tilde{\Sigma}(y,y',\omega) \\ & [\frac{\partial}{\partial r_\beta}G_s(r,y,\omega)\frac{\partial}{\partial r_\alpha}G(y',r,\omega) + \frac{\partial}{\partial r_\alpha}G_s(r,y,\omega)\frac{\partial}{\partial r_\beta}G(y',r,\omega)]. \end{aligned} \tag{4.36}$$

With the fields $\mathcal{E}_{ee}(r)$ and $Z_{t_c}(r)$ thus determined, the potential $v_{ee}(r)$ and the energies E_{ee} and T_c are obtained from Eqs. (2.50), (2.51) and (2.55), the orbitals $\phi_i(x)$ being generated by solution of the noninteracting s-system differential equation. The above formalism can be readily generalized to spin-dependent interactions.

4.5. Approximation Schemes

It is now possible to study an electronic system within a local effective potential formalism systematically in terms of the different correlations present. The ***zeroth-order*** approximation of the above perturbation theory comprises of neglecting Coulomb correlations and correlation-kinetic effects, and considering only those correlations which arise due to the Pauli exclusion principle, i.e. $G=G_s$, and $\Gamma=0$ in Eq. (4.26), and $Z_{t_c}=0$. In this case from Eq. (4.26), $g(r,r')=g_s(r,r')=\rho(r')+\rho_x(r,r')$, where the Fermi hole $\rho_x(r,r')=-|\gamma_s(r,r')|^2/2\rho(r)$, and $\int g_s(r,r')dr'=N-1$. The resulting Pauli field $\mathcal{E}_x(r)=$

$\int d\mathbf{r}' \rho_x(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^3$, and the exchange energy $E_x = \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}_x(\mathbf{r})$. Since the wavefunction in the zeroth-order approximation is a Slater determinant, the total energy is a *rigorous* upper bound. The zeroth-order corresponds to the Work Formalism Hartree-Fock approximation [18, 19]. Results obtained at the zeroth-order level are essentially equivalent to those of Hartree-Fock theory. For example [45], total ground-state energies of atoms are an upper bound and within $50ppm$ of those Hartree-Fock theory, differing by less than $10ppm$ for $Kr^{36}-Rn^{86}$. The corresponding highest occupied eigenvalues when compared with experimental ionization potentials are, however, superior. As another example [63], the total ground-state energies for anion (Li^-, B^-, C^-, F^-, Cl^-, Br^-)-positron bound states with the positron in the $1s$ orbital, are an upper bound to the Hartree-Fock values on the average by less than $90ppm$, the difference for $[Br^-, e^+_{1s}]$ being $5ppm$. It is emphasized that these results are derived from a local effective potential. For results at this order as applied to the nonuniform electron gas at a metal surface, see Refs. [54], [55] and [64].

As noted above, Coulomb correlation and correlation-kinetic effects can be considered separately. Thus, the *first-order* approximation which includes Coulomb correlations but no correlation-kinetic effects ($\mathbf{Z}_{t_c}(\mathbf{r}) = 0$) corresponds to

$$(see\ page\ 66) \tag{4.37}$$

The *first-order* correlation-kinetic field corresponds to assuming $G = G_s$ in Eq.

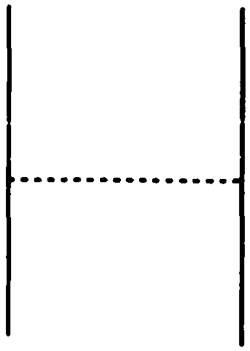
$\Gamma =$  $+$ (Antisymmetrization)

Figure 4.3: Equation (4.37) of Chapter 4

(4.36) and employing the lowest-order approximation for $\tilde{\Sigma}(\mathbf{r}, \mathbf{r}', \omega)$, i.e. $\tilde{\Sigma}_x(\mathbf{r}, \mathbf{r}', \omega) = \Sigma_x(\mathbf{r}, \mathbf{r}', \omega) - \delta(\mathbf{r} - \mathbf{r}')[v_{ee}(\mathbf{r}) - v_H(\mathbf{r})]$ where $\Sigma_x(\mathbf{r}, \mathbf{r}' \omega) = -\gamma_s(\mathbf{r}', \mathbf{r}, \omega)/2|\mathbf{r} - \mathbf{r}'|$.

The perturbation theory described above is in principle exact. A simplification occurs for systems of symmetry such that the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_{t_c}(\mathbf{r})$ are separately conservative. These fields are then separately conservative at each order, and the corresponding components of the potential path-independent. For systems of arbitrary symmetry for which the individual fields are not conservative, the energy at each order is obtained directly in terms of the fields via Eq. (2.55), but the potential is determined from their irrotational component [24, 25].

Finally, for finite systems, the asymptotic structure of $v_{ee}(\mathbf{r}) - v_H(\mathbf{r})$ is that of $W_x(\mathbf{r})$, the work done in the field $\mathcal{E}_x(\mathbf{r})$ of the Fermi hole charge $\rho_x(\mathbf{r}, \mathbf{r}')$ since the Coulomb correlation and correlation-kinetic contributions to $v_{ee}(\mathbf{r})$ decay more rapidly [38]. Irrespective of the order of calculation, this structure of $W_x(\mathbf{r})$ in the classically forbidden region is $-1/r$ because the total charge of the Fermi hole $\int \rho_x(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1$, and asymptotically this charge becomes static. Thus, at each order, the highest occupied eigenvalue of the noninteracting system differential equation will be governed primarily by the asymptotic structure of $W_x(\mathbf{r})$ and therefore be a good approximation to the experimental ionization potential or electron affinity. The exact asymptotic structure of $W_x(\mathbf{r})$ in the classically forbidden region of a semi-infinite jellium or structureless pseudopotential model of a metal surface has also been determined analytically [64] and shown to be image-potential-like of the form $-\alpha(\beta)/x$, where β^2 is the ratio of the barrier height to the Fermi energy. The perturbation theory developed here would allow the further contributions of Coulomb correlation and correlation-kinetic effects to the effective potential at a surface, and thus to properties such as the work function and surface energy, to be determined.

For completeness we note that, from Eq. (4.6) one has on integrating the Dyson equation Eq. (4.13) over all frequencies that,

$$\int d\omega \int d^3y \int d^3y'\, G_s(\mathbf{r},y,\omega)\tilde{\Sigma}(y,y',\omega)G(y',\mathbf{r},\omega) = 0 \,. \tag{4.38}$$

Substituting for $\tilde{\Sigma}$ from Eq. (4.10) into the above equation, one obtains

$$\begin{aligned} &\int d^3y\, v_{ee}(y) \int d\omega\, G_s(\mathbf{r},y,\omega)\, G(y,\mathbf{r},\omega) \\ &= \int d^3y \int d^3y' \int d\omega\, G_s(\mathbf{r},y,\omega)\, \Sigma(y,y',\omega)\, G(y',\mathbf{r};\omega) \,. \end{aligned} \tag{4.39}$$

This equation was first derived by Sham and Schlüter [59, 60]. It is an integral equation for the local electron-interaction potential $v_{ee}(\mathbf{r})$. The lowest order 'exchange-only' approximation of the Sham-Schlüter equation is obtained by employing $G(\mathbf{r},\mathbf{r}',\omega) = G_s(\mathbf{r},\mathbf{r}',\omega)$ and $\Sigma_x(\mathbf{r},\mathbf{r}',\omega) = -\gamma_s(\mathbf{r}',\mathbf{r})/2|\mathbf{r}-\mathbf{r}'|$, which leads to

$$\begin{aligned} &\int d^3y\, v_x(y) \int d\omega\, G_s(r,y,\omega)\, G_s(y,r,\omega) \\ &= -\int d^3y \int d^3y' \frac{1}{|y-y'|} \int d\omega\, G_s(r,y,\omega)\,\gamma_s(y',y)\, G_s(y',r;\omega) \ . \end{aligned} \tag{4.40}$$

By using the s-system Green's function $G_s(r,r',\omega)$ which is

$$G_s(r,r',\omega) = \sum_i \phi_i(r)\phi_i^*(r')\left[\frac{\theta(\epsilon_i-\epsilon_F)}{\omega-\epsilon_i+i\eta} + \frac{\theta(\epsilon_F-\epsilon_i)}{\omega-\epsilon_i-i\eta}\right] \ . \tag{4.41}$$

in Eq. (4.40) one obtains

$$\begin{aligned} &\sum_i \sum_j \phi_i(r)\phi_j^*(r)\frac{1}{\epsilon_j-\epsilon_i}\theta(\epsilon_F-\epsilon_i) \int\int dy\,dy' \frac{\gamma_s(y',y)}{2|y-y'|}\phi_i^*(y)\phi_j(y') \\ &= -\sum_i \sum_j \phi_i(r)\phi_j^*(r)\frac{1}{\epsilon_j-\epsilon_i}\theta(\epsilon_F-\epsilon_i) \int dy\, v_x(y)\phi_i^*(y)\phi_j(y) \ . \end{aligned} \tag{4.42}$$

which is just the integral equation of the optimized potential method (OPM) for the KS exchange potential $v_x(r)$. The OPM integral equation may be derived independently by minimizing the expectation value of the Hamiltonian as obtained via the s-system Slater determinant with respect to arbitrary variations of the local effective potential $v_{eff}(r)$ [57, 58]. As will be shown in Chapter 7, the KS exchange potential $v_x(r)$ and energy $E_x[\rho]$ are representative of electron correlations due to the Pauli principle as well as part of the Correlation-Kinetic effect. Thus, each higher-order term of Sham-Schlüter theory implicitly corresponds to a contribution of Coulomb correlation and Correlation-Kinetic contributions. In contrast, in lowest-order Q-DFT perturbation theory, the correlations are strictly due to the Pauli principle. Furthermore, there is a separate perturbation series for Coulomb correlation and Correlation-KInetic effects.

4.6. Conclusion

In conclusion, we have provided an alternate many-body perturbation theory within a local effective potential formalism with the following attributes:

(i) There is a systematic and separate perturbative incorporation of Coulomb correlation and correlation-kinetic effects to both the energy and potential.

(ii) In common with standard many-body perturbation theory, the ground-state energy at the zeroth-order or Pauli-correlated level is a rigorous upper bound.

(iii) At each order, the correlations assumed for the energy and potential are the same because both properties are derived from the same field.

(iv) At each order, the potential is orbital independent and free of self interaction.

(v) For finite systems, the asymptotic structure of the local electron-

interaction potential is that of the zeroth-order Pauli-correlated level and exactly known.

Chaper 5

ANALYTICAL ASYMPTOTIC STRUCTURE OF THE PAULI, COULOMB, AND CORRELATION-KINETIC COMPONENTS OF THE KOHN-SHAM THEORY EXCHANGE-CORRELATION POTENTIAL IN ATOMS

5.1. Introduction

In this chapter we derive [37, 38] for atoms in the classically forbidden region the analytical asymptotic structure of the Kohn-Sham exchange-correlation part $v_{xc}(\boldsymbol{r})$ of the local potential of the s-system. As noted in Chapter 2, this potential is defined within Kohn-Sham (KS) theory as the functional derivative $\delta E_{xc}^{KS}[\rho]/\delta\rho(\boldsymbol{r})$, where $E_{xc}^{KS}[\rho]$ is the KS exchange-correlation energy functional of the density $\rho(\boldsymbol{r})$. Our derivation is within the framework of Q-DFT in terms of the Schrödinger wavefunction Ψ. A principal advantage of Q-DFT is that it delineates the contribution of each type of correlation to ***both*** the energy and potential. In this manner it is then possible to derive the ***explicit*** contribution to the asymptotic structure of $v_{xc}(\boldsymbol{r})$ due to Pauli and Coulomb correlations, and Correlation-Kinetic effects. This understanding not only provides insights into the theory, but also allows for the meaningful construction of approximate exchange-correlation energy functionals and potentials which is one major focus of research in density-functional theory.

The systems we consider are those for which the N-electron atom may be orbitally degenerate, but the (N-1)-electron ion is always orbitally nondegenerate except for the twofold spin degeneracy e.g. B and Mg atoms and their ions. For the case when both the N- and (N-1)-electron systems are nondegenerate we obtain the asymptotic structure of $v_{xc}(r)$ to be

$$v_{xc}(r) \underset{r\to\infty}{\sim} -\frac{1}{r} - \frac{\alpha}{2r^4} + \frac{8\kappa_0\chi}{5r^5} + \cdots , \tag{5.1}$$

where α is the polarizability and χ an expectation value of the (N-1)-electron ion, and $\kappa_0^2/2$ the ionization potential. The $(-1/r)$ term is shown to arise ***directly*** from the s-system Fermi hole charge, and the $(-\alpha/2r^4)$ ***directly*** from the Coulomb hole. Neither Pauli nor Coulomb correlations contribute to $O(1/r^5)$. The last term is further shown [37] to be a Correlation-Kinetic contribution. For these assignations to $O(1/r^5)$, the wavefunction is expanded in the classically forbidden region to include terms involving the quadrupole moment tensor. For the case when the N-electron atom is orbitally degenerate, we obtain

$$v_{xc}(r) \underset{r\to\infty}{\sim} -\frac{1}{r} - \frac{Q}{r^3} - \frac{\alpha}{2r^4} + \frac{8\kappa_0\chi}{5r^5} - \frac{R}{r^5} + \cdots , \tag{5.2}$$

where the additional $O(1/r^3)$ and $O(1/r^5)$ terms are Pauli-correlation contributions, and Q and R multipole moments of the density. The physics of the other terms remains unchanged.

Prior to proceeding with our derivation, we briefly discuss the previous work of others. The first two terms of the structure of Eq. (5.1) have also been obtained quantum-mechanically by Almbladh and von Barth [44]. These authors first derive the differential equation for the quasiparticle amplitudes which are the interacting system counterparts of the single-particle orbitals of the non-interacting system. Then on comparison with the Kohn-Sham equation they determine $v_{xc}(r)$ to $O(1/r^4)$ to be

$$v_{xc}(r) = v_H^{(N-1)}(r) - v_H(r) - \frac{1}{2r^4}\sum_{\alpha\beta}\hat{r}_\alpha \hat{r}_\beta \alpha_{\alpha\beta} , \tag{5.3}$$

where $v_H(r) = \int dr' \rho(r')/|r-r'|$ and $v_H^{(N-1)}(r)$ are the Hartree potentials for the N- and (N-1)-electron systems, $\alpha_{\alpha\beta}$ is the polarizability tensor of the (N-1)-electron ion, subscripts α and β represent cartesian coordinates, and $\hat{r}_\alpha$ a component of the unit vector $\hat{r}$. For the case when both the N- and (N-1)-electron systems are nondegenerate, asymptotically the potentials $v_H^{(N-1)}(r) \underset{r\to\infty}{\sim} (N-1)/r$, and $v_H(r) \underset{r\to\infty}{\sim} N/r$ to expotential accuracy, and $\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta}$. The leading $-1/r$ term of Eq. (5.1) thus arises as the difference between two Hartree potentials. The authors, however, ascribe this term to the Fermi hole which has a total charge of (negative) unity, and thus to Pauli correlations. But the Fermi hole charge does not appear in the derivation so that the basis for the assignation is unclear. The $(-\alpha/2r^4)$ term is attributed to Coulomb correlations. However, this assignation is based on a comparison with a classical calculation of an ion and an asymptotic test charge. Once again, there is no direct relationship between this term and the Coulomb hole charge or other equivalent representation of

Coulomb correlations within KS theory. Of course, in the classical calculation, even the $-1/r$ term is due to Coulomb correlations. It is interesting to note that classically, higher order contributions [48] are of $O(1/r^6, 1/r^8)$, etc., and thus of even order. There are no terms of $O(1/r^5)$ in the classical calculation. Such terms are strictly a consequence of quantum effects.

The leading $(-1/r)$ term of $v_{xc}(r)$ has also been derived by Sham [60]. In the asymptotic limit, the integral equation relating $v_{xc}(r)$ to the nonlocal exchange-correlation component $\Sigma_{xc}(r, r'; \omega)$ of the self-energy $\Sigma(r, r'; \omega)$ (see Eq. (4.39)) reduces to

$$\begin{aligned} v_{xc}(r) &= \frac{1}{2\phi_i(r)} \int dr' \Sigma_{xc}(r, r'; \mu) \phi_i(r') \\ &+ \frac{1}{2\phi_i^*(r)} \int dr' \Sigma_{xc}(r, r'; \mu) \phi_i^*(r') \ , \end{aligned} \tag{5.4}$$

where $\phi_i(r)$ are the s-system orbitals, μ the chemical potential, and the electron is in the highest occupied orbital. By considering the leading exchange term in a diagramatical analysis, the $(-1/r)$ term is obtained, and thus this structure can be attributed to KS theory exchange effects.

Finally, according to Harbola and Sahni [21, 22], the asymptotic structure of $v_{xc}(r)$ is given by $W_x(r)$ which is the work done to move an electron in the field of the Fermi hole. The $(-1/r)$ structure is then obtained because the total charge of the Fermi hole is unity and the fact that it becomes an essentially static charge in the limit of asymptotic positions of the electron. The Coulomb hole does not contribute asymptotically to this order since its total charge is zero, and the field due to it vanishes in this region faster than $O(1/r^2)$.

5.2. Asymptotic Structure of Wavefunction, Single Particle Density Matrix, and Pair-Correlation Density.

In this section we derive the asymptotic structure of the wavefunction Ψ, the single-particle density matrix $\gamma(\boldsymbol{r},\boldsymbol{r}')$ and hence of the density $\rho(\boldsymbol{r})$, and the pair-correlation density $g(\boldsymbol{r},\boldsymbol{r}')$.

(a) Wavefunction

The ground-state Schrödinger equation for a system of N-electrons in a local external potential described by the operator $\hat{V}=\sum_i v(\boldsymbol{r}_i)$ is $\hat{H}\Psi=E_0\Psi$, where $\hat{H}=-(1/2)\sum_i\nabla_i^2+\sum_i v(\boldsymbol{r}_i)+(1/2)\sum_{ij}{}' 1/|\boldsymbol{r}_i-\boldsymbol{r}_j|$, and Ψ, E_0 the wavefunction and energy, respectively. The complete set of eigenfunctions and eigenenergies of the (N-1)-electron system are defined by the equation $\hat{H}^{(N-1)}\Psi_s^{(N-1)}=E_s^{(N-1)}\Psi_s^{(N-1)}$. We first expand the wavefunction Ψ in terms of the eigenfunctions $\Psi_s^{(N-1)}$:

$$\Psi(\boldsymbol{r}\sigma,\boldsymbol{x}_2,\cdots\boldsymbol{x}_N) = \sum_s C_{s\sigma}(\boldsymbol{r})\Psi_s^{(N-1)}(\boldsymbol{x}_2,\cdots\boldsymbol{x}_N) , \qquad (5.5)$$

and rewrite the N-electron Schrödinger equation as

$$\{-\frac{1}{2}\nabla^2 + v(\boldsymbol{r}) + \sum_{i=2}^{N}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}_i|} - \frac{1}{2}\sum_{i=2}^{N}\nabla_i^2 + \sum_{i=2}^{N} v(\boldsymbol{r}_i)$$
$$+ \frac{1}{2}\sum_{i\neq j\neq 1}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}\}\sum_s C_{s\sigma}(\boldsymbol{r})\Psi_s^{(N-1)} = E_0\sum_s C_{s\sigma}(\boldsymbol{r})\Psi_s^{(N-1)} \; . \tag{5.6}$$

For asymptotic positions of the electron we have by Taylor expansion

$$\frac{1}{|\boldsymbol{r}-\boldsymbol{r}_i|} = \frac{1}{r} + \frac{\boldsymbol{r}_i\cdot\boldsymbol{r}}{r^3} + \frac{1}{2}\sum_{\alpha,\beta} r_{i\alpha} r_{i\beta}\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\frac{1}{r} \; , \tag{5.7}$$

so that Eq. (5.6) may be rewritten as

$$\{-\frac{1}{2}\nabla^2 + v(\boldsymbol{r}) + \frac{N-1}{r}$$
$$+ \sum_{i=2}^{N}[\frac{\boldsymbol{r}_i\cdot\boldsymbol{r}}{r^3} + \frac{1}{2}\sum_{\alpha,\beta} r_{i\alpha} r_{i\beta}(\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\frac{1}{r})]\}\sum_s C_{s\sigma}(\boldsymbol{r})\Psi_s^{(N-1)} \tag{5.8}$$
$$+ \hat{H}^{(N-1)}\sum_s C_{s\sigma}(\boldsymbol{r})\Psi_s^{(N-1)} = E_0\sum_s C_{s\sigma}(\boldsymbol{r})\Psi_s^{(N-1)} \; ,$$

which reduces further to

$$[-\frac{1}{2}\nabla^2 + v(\boldsymbol{r}) + \frac{N-1}{r}]\sum_s C_{s\sigma}(\boldsymbol{r})\Psi_s^{(N-1)}$$
$$+ \sum_{i=2}^{N}[\frac{\boldsymbol{r}_i\cdot\boldsymbol{r}}{r^3} + \frac{1}{2}\sum_{\alpha,\beta} r_{i\alpha} r_{i\beta}(\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\frac{1}{r})]\sum_s C_{s\sigma}(\boldsymbol{r})\Psi_s^{(N-1)} \tag{5.9}$$
$$= \sum_s [E_0 - E_s^{(N-1)}]C_{s\sigma}(\boldsymbol{r})\Psi_s^{(N-1)} \; .$$

Multiplying Eq. (5.9) from the left by $\Psi_{s'}^{(N-1)*}$ and using the orthonormality condition $\langle\Psi_{s'}^{(N-1)}|\Psi_s^{(N-1)}\rangle = \delta_{ss'}$, we have

$$[-\frac{1}{2}\nabla^2 + v(r) + \frac{N-1}{r}]C_{s\sigma}(\mathbf{r}) + \frac{\mathbf{r}}{r^3}\cdot\sum_{s'} C_{s'\sigma}(\mathbf{r})\mathbf{P}_{ss'}$$
$$+ \frac{1}{2}\sum_{\alpha,\beta}(\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\frac{1}{r})\sum_{s'} C_{s'\sigma}(\mathbf{r})(Q_{ss'})_{\alpha\beta} = [E_0 - E_s^{(N-1)}]C_{s\sigma}(\mathbf{r}) \ , \tag{5.10}$$

where

$$\mathbf{P}_{ss'} = \sum_{i=2}^{N}\int \Psi_s^{(N-1)*}(x_2,\cdots x_N)\mathbf{r}_i\Psi_{s'}^{(N-1)}(x_2,\cdots x_N)\,d^{N-1}x \ , \tag{5.11}$$

and

$$(Q_{ss'})_{\alpha\beta} = \sum_{i=2}^{N}\int \Psi_s^{(N-1)*}(x_2,\cdots x_N)r_{i\alpha}r_{i\beta}\Psi_{s'}^{(N-1)}(x_2,\cdots x_N)\,d^{N-1}x \ . \tag{5.12}$$

Here $\mathbf{P}_{ss'}$ is the dipole moment and $(Q_{ss'})_{\alpha\beta}$ the quadrupole moment tensor of the (N-1) electron system. With the definitions

$$D_{ss'}(\hat{r}) = \hat{r}\cdot\mathbf{P}_{ss'} \ , \tag{5.13}$$

and

$$Q_{ss'}(\hat{r}) = \frac{1}{2}\sum_{\alpha,\beta}(3\hat{r}_\alpha\hat{r}_\beta - \delta_{\alpha\beta})(Q_{ss'})_{\alpha\beta} \ , \tag{5.14}$$

Eq. (5.10) becomes

$$[-\frac{1}{2}\nabla^2 + v(r) + \frac{N-1}{r}]C_{s\sigma}(\mathbf{r})$$
$$+ [\frac{1}{r^2}\sum_{s'}D_{ss'}(\hat{r}) + \frac{1}{r^3}\sum_{s'}Q_{ss'}(\hat{r})]C_{s'\sigma}(\mathbf{r}) = \epsilon_s C_{s\sigma}(\mathbf{r}) \ , \tag{5.15}$$

where $\epsilon_s = E_0 - E_s^{(N-1)}$. This is the same equation as derived by Almbladh and von

Barth for the quasiparticle amplitudes, but it is derived here via the wavefunction and carried to $O(1/r^3)$. The asymptotic structure of the coefficients $C_{s\sigma}(r)$ for $s \neq 0$ is then obtained from Eq. (5.15) as

$$C_{s\sigma}(r) = -[\frac{1}{r^2}D_{s0}(\hat{r}) + \frac{1}{r^3}Q_{s0}(\hat{r})]\ \frac{C_{0\sigma}(r)}{\omega_s}\ , \tag{5.16}$$

where $\omega_s = \epsilon_0 - \epsilon_s = E_s^{(N-1)} - E_0^{(N-1)}$ is an excitation of the (N-1)-electron system. Thus, the asymptotic structure of the wavefunction to $O(1/r^3)$ is derived.

(b) Single-particle density matrix

On substituting Eq. (5.16) for Ψ into Eq. (2.10) and using the orthonormality condition of the $\Psi_s^{(N-1)}$, we obtain the asymptotic structure of $\gamma(r, r')$ as

$$\begin{aligned}\gamma(r,r') &= N\sum_\sigma \sum_s C_{s\sigma}^*(r)C_{s\sigma}(r') \\ &= N\sum_\sigma C_{0\sigma}^*(r)C_{0\sigma}(r')\{1 + \sum_s{}' \frac{1}{\omega_s^2}[\frac{D_{s0}^*(\hat{r})}{r^2}\frac{D_{s0}(\hat{r}')}{r'^2} \\ &+ \frac{D_{s0}^*(\hat{r})}{r^2}\frac{Q_{s0}(\hat{r}')}{r'^3} + \frac{Q_{s0}^*(\hat{r})}{r^3}\frac{D_{s0}(\hat{r}')}{r'^2} + \frac{Q_{s0}^*(\hat{r})}{r^3}\frac{Q_{s0}(\hat{r}')}{r'^3}]\}\ .\end{aligned} \tag{5.17}$$

(Here $\sum_s{}' = \sum_{s\neq 0}$). The dipole-quadrupole cross terms in Eq. (5.17) can be shown to vanish by rewriting each term as

$$\sum_s{}' \frac{1}{\omega_s^2}\frac{D_{s0}(\hat{r})}{r^2}\frac{Q_{s0}^*(\hat{r}')}{r'^3} = \frac{1}{r^2}\cdot\frac{1}{r'^3}\sum_{\alpha\beta\lambda}\hat{r}_\alpha'\hat{r}_\beta' r_\lambda \langle\Psi_0^{(N-1)}|\hat{q}_{\alpha\beta}\frac{1-\hat{P}}{[\hat{H}-E_0^{(N-1)}]^2}\hat{d}_\lambda|\Psi_0^{(N-1)}\rangle \quad , \tag{5.18}$$

where $\hat{d}=\int r\delta\hat{\rho}(r)dr$, $\hat{q}_{\alpha\beta}=\int r_\alpha r_\beta\delta\hat{\rho}(r)dr$, $\delta\hat{\rho}(r)=\hat{\rho}(r)-\langle\Psi_0^{(N-1)}|\hat{\rho}(r)|\Psi_0^{(N-1)}\rangle$, $\hat{\rho}=\sum_i\delta(r-r_i)$, and $\hat{P}=|\Psi_0^{(N-1)}\rangle\langle\Psi_0^{(N-1)}|$ is the projector onto the (N-1)-electron ground state. (Note that the dipole $\hat{d}$ and quadrupole $\hat{q}_{\alpha\beta}$ moment operators are the same as in Eqs. (5.11) and (5.12) since the second term of the operator $\delta\hat{\rho}(r)$ does not contribute on account of the fact that the (N-1)-electron system is spherically symmetric). Now the operators $\hat{P}$, $\hat{H}$ and $\hat{q}_{\alpha\beta}$ are invariant under the inversion operator $\hat{I}$, while $\hat{d}_\lambda$ changes sign. Thus, the dipole-quadrupole term vanishes. The density matrix is then

$$\gamma(r,r') \underset{r,r'\to\infty}{\sim} N\sum_\sigma C_{0\sigma}^*(r)C_{0\sigma}(r') \times\{1+\sum_s{}'\frac{1}{\omega_s^2}[\frac{D_{s0}^*(\hat{r})}{r^2}\frac{D_{s0}(\hat{r}')}{r'^2}+\frac{Q_{S0}^*(\hat{r})}{r^3}\frac{Q_{s0}(\hat{r}')}{r'^3}]\} \; . \tag{5.19}$$

The asymptotic structure of the density $\rho(r)$ is given by the diagonal matrix element $\gamma(r,r)$ so that to $O(1/r^6)$,

$$\rho(r) \underset{r\to\infty}{\sim} N\sum_\sigma |C_{0\sigma}(r)|^2\{1+\sum_s{}'\frac{1}{\omega_s^2}[\frac{|D_{s0}(\hat{r})|^2}{r^4}+\frac{|Q_{s0}(\hat{r})|^2}{r^6}]\} \; . \tag{5.20}$$

For the systems considered, the leading term of $\gamma(r,r')$ as $r,r' \to \infty$ is from Eqs. (5.19) and (5.20),

$$\gamma(r,r') \underset{r,r' \to \infty}{\sim} \sqrt{\rho(r)}\,\sqrt{\rho(r')} \tag{5.21}$$

which is a well-known [65, 66] result.

(c) Pair-correlation density

From Eq. (2.15) we have that

$$\begin{aligned} P(r,r') = N(N-1) \sum_{\sigma\sigma'} \int & \Psi^*(r\sigma, r'\sigma', x_3, \cdots x_N) \\ & \times \Psi(r\sigma, r'\sigma', x_3, \cdots x_N)\, d^{N-2}x \end{aligned} \tag{5.22}$$

On substituting Eq. (5.5) for Ψ into the definition of $P(r,r')$ above

$$\begin{aligned} P(r,r') &= N(N-1) \sum_{\sigma\sigma'} \int [C_{0\sigma}^*(r)\Psi_0^{(N-1)*}(r'\sigma', x_3, \cdots x_N) \\ &\qquad + \sum_s{}' C_{s\sigma}^*(r)\Psi_s^{(N-1)*}(r'\sigma', x_3, \cdots x_N)] \\ &\qquad [C_{0\sigma}(r)\Psi_0^{(N-1)}(r'\sigma', x_3, \cdots x_N) \\ &\qquad + \sum_{s'}{}' C_{s'\sigma}(r)\Psi_{s'}^{(N-1)}(r'\sigma', x_3, \cdots x_N)]\, d^{N-2}x \\ &= N \sum_\sigma [\,|C_{0\sigma}(r)|^2 \rho^{(N-1)}(r') + \sum_s{}' C_{0\sigma}^*(r) C_{s\sigma}(r) \rho_{0s}^{(N-1)}(r') \\ &\quad + \sum_s{}' C_{s\sigma}^*(r) C_{0\sigma}(r) \rho_{s0}^{(N-1)}(r') + \sum_{ss'}{}' C_{s\sigma}^*(r) C_{s'\sigma}(r) \rho_{ss'}^{(N-1)}(r')]\ , \end{aligned} \tag{5.23}$$

where

$$\rho_{ss'}^{(N-1)}(\mathbf{r}') = (N-1)\sum_{\sigma'}\int \Psi_s^{(N-1)*}(\mathbf{r}'\sigma', \mathbf{x}_3, \cdots \mathbf{x}_N) \\ \Psi_{s'}^{(N-1)}(\mathbf{r}'\sigma', \mathbf{x}_3, \cdots \mathbf{x}_N)\, d^{N-2}\mathbf{x} \; . \qquad (5.24)$$

Thus, the asymptotic structure of the pair-correlation density $g(\mathbf{r},\mathbf{r}')$, on substituting for $C_{s\sigma}(\mathbf{r})$ from Eq. (5.16) is to $O(1/r^6)$

$$g(\mathbf{r},\mathbf{r}') \underset{r\to\infty}{\sim} \frac{1}{\rho(\mathbf{r})}\sum_{\sigma} |C_{0\sigma}(\mathbf{r})|^2 \{\rho^{(N-1)}(\mathbf{r}') \\ - 2Re\sum_{s}{}' \frac{1}{\omega_s}[\frac{D_{s0}(\hat{r})}{r^2} + \frac{Q_{s0}(\hat{r})}{r^3}]\rho_{s0}^{(N-1)}(\mathbf{r}') \\ + \sum_{ss'}{}' \frac{1}{\omega_s \omega_{s'}}[\frac{D_{s0}^*(\hat{r})D_{s'0}(\hat{r})}{r^4} + \frac{Q_{s0}^*(\hat{r})\,Q_{s'0}(\hat{r})}{r^6}]\rho_{ss'}^{(N-1)}(\mathbf{r}')\} \; . \qquad (5.25)$$

For the systems considered, the leading term of $g(\mathbf{r},\mathbf{r}')$ in the asymptotic limit is $\rho^{(N-1)}(\mathbf{r}')$, which is also a well-known [43, 66] result. Here we have provided the higher-order contributions.

5.3. Asymptotic Structure of the Electron-Interaction Potential $W_{ee}(\mathbf{r})$ and its Pauli $W_x(\mathbf{r})$ and Coulomb $W_c(\mathbf{r})$ Correlation Components.

We begin this section by determining the asymptotic structure of the quantum-mechanical electron-interaction component $W_{ee}(\mathbf{r})$ of the electron-interaction potential $v_{ee}(\mathbf{r})$. Substituting Eq. (5.25) for the pair-correlation density $g(\mathbf{r},\mathbf{r}')$ into Eq. (2.52) for the electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$, we obtain

$$\mathcal{E}_{ee}(\mathbf{r}) \underset{r\to\infty}{\sim} -\nabla\left[\frac{N-1}{r} - \sum_{s}{}' \frac{D_{s0}^{*}(\hat{r})D_{s0}(\hat{r})}{\omega_s}\frac{1}{r^4}\right] , \qquad (5.26)$$

to the accuracy of $O(1/r^6)$. Thus, asymptotically, the work done in this field is

$$W_{ee}(r) \underset{r\to\infty}{\sim} \frac{N-1}{r} - \frac{\alpha}{2r^4} , \qquad (5.27)$$

where

$$\alpha = 2\sum_{s}{}' \frac{D_{s0}^{*}(\hat{r})D_{s0}(\hat{r})}{\omega_s} , \qquad (5.28)$$

is the ground-state polarizability of the (N-1)-electron system. Note that the result for $W_{ee}(\mathbf{r})$ is to the accuracy of $O(1/r^5)$. In other words, there are no $O(1/r^5)$ contributions to $v_{ee}(\mathbf{r})$ due to Pauli and Coulomb correlations. The results of Eqs. (5.26) and (5.27) are valid for when the N-electron system is either orbitally degenerate or nondegenerate.

We next determine the separate Pauli and Coulomb correlation contributions to the asymptotic structure of $W_{ee}(\mathbf{r})$. It is evident that the N/r term of $W_{ee}(\mathbf{r})$ of Eq. (5.27) of the potential $v_{ee}(\mathbf{r})$ is due to the Hartree potential $v_H(\mathbf{r})$.

Since in the s-system, only the highest occupied orbital $\phi_N(\mathbf{x})$ contributes to the asymptotic structure, we have to exponential accuracy

$\gamma_s(\mathbf{r},\mathbf{r}') \underset{r\to\infty}{\sim} \sum_\sigma \phi_N^*(\mathbf{r}\sigma)\phi_N(\mathbf{r}'\sigma)$. Thus, asymptotically

$$\begin{aligned} \boldsymbol{\mathcal{E}}_x(\mathbf{r}) &\underset{r\to\infty}{\sim} \frac{4}{2\rho(\mathbf{r})}|\phi_N(\mathbf{r})|^2(\nabla\frac{1}{r})\int|\phi_N(\mathbf{r}')|^2 d\mathbf{r}' \\ &\underset{r\to\infty}{\sim} -\frac{\mathbf{r}}{r^3}, \end{aligned} \tag{5.29}$$

so that

$$W_x(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{1}{r} \tag{5.30}$$

to exponential accuracy. Thus, the $(-1/r)$ asymptotic structure of the electron-interaction potential $v_{ee}(\mathbf{r})$ is due entirely to Pauli correlations. As a consequence, (and from Eqs. (5.27) and (5.30)), we have

$$W_c(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{\alpha}{2r^4}, \tag{5.31}$$

so that the term of $O(1/r^4)$ in $v_{ee}(\mathbf{r})$ is strictly due to Coulomb correlations, arising from the Coulomb hole charge.

The Hartree $v_H(\mathbf{r})$ and Pauli $W_x(\mathbf{r})$ potentials will have higher order contributions for the case when the N-electron system is orbitally degenerate since the density $\rho(\mathbf{r})$ is no longer spherically symmetric. Expanding $1/|\mathbf{r}-\mathbf{r}'|$ in Legendre polynomials $P_n(x)$ we have

$$v_H(\mathbf{r}) \underset{r\to\infty}{\sim} \frac{N}{r} + \frac{Q}{r^3} + \frac{R}{r^5} + \cdots , \tag{5.32}$$

and

$$\mathcal{E}_x(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{\mathbf{r}}{r^3} - \frac{3\mathbf{r}}{r^5}Q - \frac{5\mathbf{r}}{r^7}R + \cdots , \tag{5.33}$$

so that

$$W_x(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{1}{r} - \frac{Q}{r^3} - \frac{R}{r^5} + \cdots , \tag{5.34}$$

where

$$Q = \int \rho(\mathbf{r}')r'^2 P_2(\cos\theta')d\mathbf{r}' , \tag{5.35}$$

$$R = \int \rho(\mathbf{r}')r'^4 P_4(\cos\theta')d\mathbf{r}' . \tag{5.36}$$

Note that the terms of $O(1/r^3)$ and $O(1/r^5)$ in $v_H(\mathbf{r})$ and $W_x(\mathbf{r})$ cancel out. Thus, for both the orbitally degenerate and non-degenerate N-electron systems, the asymptotic structure of $W_c(\mathbf{r})$ is the same to $O(1/r^5)$, and given by Eq. (5.31).

5.4. Asymptotic Structure of the Correlation-Kinetic Potential $W_{t_c}(\mathbf{r})$.

In this section we determine the asymptotic structure of the correlation-kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ and potential $W_{t_c}(\mathbf{r})$. These results have been previously derived [38] by us, employing quasiparticle amplitudes, and the physics and details of the calculations are the same. Primarily, the asymptotic structure of the density $\rho(\mathbf{r})$ and idempotent density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ are governed by the highest occupied orbital $\phi_N(x)$. Since the densities of the interacting and noninteracting systems are the same, the asymptotic structure of $\phi_N(r)$ is obtained from Eq. (5.20) as [44, 65, 43]

$$\begin{aligned}\phi_N(r) &= \sqrt{N}\sum_{\sigma} |\, C_{0\sigma}(r) \,| \\ &\times \{1+\sum_{s}{}' \frac{1}{\omega_s^{\,2}}[\frac{|D_{s0}(\hat{r})|^2}{r^4}+\frac{|Q_{s0}(\hat{r})|^2}{r^6}]\}^{1/2}.\end{aligned} \tag{5.37}$$

The asymptotic structure of $\gamma_s(r,r')$ is thus known. With that of $\gamma(r,r')$ given by Eq. (5.19), the asymptotic structure of the field $Z_{t_c}(r)$ of Eq. (2.53) is derived to be

$$Z_{t_c}(r) \underset{r\to\infty}{\sim} \frac{8\kappa_0\chi r}{r^7} \,, \tag{5.38}$$

where $\kappa_0^{\,2}/2 = E_0^{(N-1)} - E_0$ is the ionization potential, χ is an expectation of the spherically symmetric (N-1)-electron system defined by $\chi_{\alpha\beta} = \chi\delta_{\alpha\beta}$, where

$$\chi_{\alpha\beta} = \langle\Psi_0^{(N-1)}|\, d_\beta \frac{1-\hat{P}}{[\hat{H}-E_0^{(N-1)}]^2} d_\alpha \,|\,\Psi_0^{(N-1)}\rangle \,, \tag{5.39}$$

and where the operator d and $\hat{P}$ are defined in sect. 5.2b. Thus, the correlation-kinetic component of the potential $v_{ee}(r)$ decays asymptotically as

$$W_{t_c}(r) \underset{r\to\infty}{\sim} \frac{8\kappa_0\chi}{5r^5} \,. \tag{5.40}$$

5.5. Conclusions

There are two facets to this chapter. First, we have derived the asymptotic structure of the wavefunction, single-particle density matrix, the density, and pair-correlation density in the classically forbidden region of atoms. The results are specific to those atoms for which the N-electron system maybe orbitally degenerate, but the (N-1)-electron system is orbitally nondegenerate. The derivation differs from, as well as goes beyond that of previous work in that higher order quadrupole moment terms are included. In the second part of the paper, we have employed these expressions within Q-DFT which is described in terms of the wavefunction Ψ to derive the analytical asymptotic structure of the local potential of the s-system to terms of $O(1/r^5)$. Although terms of $O(1/r^4)$ have been obtained previously, the present derivation provides an independent confirmation of these results. However, the derivation via this interpretation provides the rigorous understanding that the $O(1/r)$ term is due to Pauli correlations, that of $O(1/r^4)$ due to Coulomb correlations, and that of $O(1/r^5)$ due to correlation-kinetic effects. For systems for which the N-electron atom is orbitally degenerate, Pauli correlations also contribute terms of $O(1/r^3)$ and $O(1/r^5)$. There are no quantum-mechanical Coulomb correlation contributions to $O(1/r^5)$. For these rigorous assignations to be made it was necessary to expand the wavefunction, density matrix, etc., to include terms up to the quadrupole moment. We note that the asymptotic structure derived is valid for the Coulomb external potential. For external potentials that are not Coulombic, such as in the Hooke's atom model (see Chapter 2), the asymptotic structure is different. The present procedure can be extended to systems where the (N-1)-electron system is degenerate, in which case the asymptotic structure will have an angular dependence [66]. We expect to extend our calculations to such systems in the future.

The KS exchange-correlation potential $v_{xc}(\boldsymbol{r})$ is also conventionally written as a sum of its exchange $v_x(\boldsymbol{r})$ and correlation $v_c(\boldsymbol{r})$ potentials, where $v_x(\boldsymbol{r}) = \delta E_x[\rho]/\delta\rho(\boldsymbol{r})$ and $v_c = \delta E_c^{KS}[\rho]/\delta\rho(\boldsymbol{r})$, and $E_x[\rho]$ and $E_c^{KS}[\rho]$ are the KS exchange and correlation energy functionals, respectively. Recently, it has been shown [51-53] that (see also Chapter 7),

$$v_x(\boldsymbol{r}) = -\int_{\infty}^{\boldsymbol{r}} \boldsymbol{R}(\boldsymbol{r}') \cdot d\boldsymbol{l}' \ , \tag{5.41}$$

$$\boldsymbol{R}(\boldsymbol{r}) = \boldsymbol{\mathcal{E}}_x(\boldsymbol{r}) - \boldsymbol{Z}_{t_c}^{(1)}(\boldsymbol{r}) \ , \tag{5.42}$$

where the field $\boldsymbol{Z}_{t_c}^{(1)}(\boldsymbol{r}) = \boldsymbol{z}(\boldsymbol{r};[\gamma_1^c])/\rho(\boldsymbol{r})$ with $\gamma_1^c(\boldsymbol{r},\boldsymbol{r}')$ being the first order correction to the density matrix $\gamma_s(\boldsymbol{r},\boldsymbol{r}')$ as obtained via perturbation theory by expansion of the system wavefunction in terms of the electron-interaction coupling constant. For the atomic systems considered in this chapter we can write

$$v_x(\boldsymbol{r}) = W_x(\boldsymbol{r}) - W_{t_c}^{(1)}(\boldsymbol{r}) \ , \tag{5.43}$$

where $W_{t_c}^{(1)}(\boldsymbol{r})$ is the work done in the field $\boldsymbol{Z}_{t_c}^{(1)}(\boldsymbol{r})$. Thus, $v_c(\boldsymbol{r}) = W_c(\boldsymbol{r}) + W_{t_c}(\boldsymbol{r}) + W_{t_c}^{(1)}(\boldsymbol{r})$. Solomatin and Sahni [54] have studied the field

$Z_{t_c}^{(1)}(r)$ and potential $W_{t_c}^{(1)}(r)$ in atoms numerically and shown them to be of much shorter range than $\mathcal{E}_x(r)$ and $W_x(r)$, vanishing within the last occupied shell. However, for the nonuniform electron gas at a metal surface, these authors have determined [54, 55, 64, 67-70] the potentials $v_x(r)$, $W_x(r)$ and $W_{t_c}^{(1)}(r)$ analytically, and shown that $W_{t_c}^{(1)}(r)$ is ***long-ranged*** both in the classically forbidden vacuum region as well as in the metal bulk. We have recently determined [53] the ***analytical*** asymptotic structure of $W_{t_c}^{(1)}(r)$ and that of the higher-order contributions to $v_c(r)$ in atoms.

Finally, the results derived help explain the accuracy of the results [45] for the ionization potential of atoms as obtained by the highest occupied eigenvalue of the Work-Formalism-Hartree-Fock approximation [18, 19]. In the Work-Formalism-Hartree-Fock approximation, the KS exchange-correlation potential $v_{xc}(r)$ is replaced by the work $W_x(r)$ done in the field $\mathcal{E}_x(r)$ of the Fermi hole generated by the corresponding differential equation. The highest occupied eigenvalue of the KS equation is [42-44] (minus) the ionization potential. Further, this eigenvalue is governed principally by the asymptotic structure of $v_{xc}(r)$. Now since Coulomb correlation and correlation-kinetic effects are of $O(1/r^4)$ and $O(1/r^5)$, respectively, the asymptotic structure of $v_{xc}(r) \underset{r\to\infty}{\sim} W_x(r)$. Thus, the asymptotic structure of $v_{xc}(r)$ is determined exactly by solving the Work-Formalism-Hartree-Fock differential equation. This then explains why the highest occupied eigenvalue of this differential equation [45] closely approximates the experimental ionization potential. For a comparison of the highest occupied Work-Formalism-Hartree-Fock eigenvalues to those of exact KS theory, see Ref. [19]

Chapter 6

A NEW INSIGHT INTO THE ORIGIN OF THE DERIVATIVE DISCONTINUITY IN DENSITY-FUNCTIONAL THEORY

6.1. Introduction

In Kohn-Sham theory, the electron-interaction energy functional $E_{ee}^{KS}[\rho]$ is representative of electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects. This functional is formally well-defined [42, 71] for both integer (N) and fractional ($N+\omega$; $0<\omega<1$) electron charge. As a consequence of its definition for fractional electron charge, the local electron-interaction potential $v_{ee}^{(N)}(\boldsymbol{r})$, which within KS theory is defined as the functional derivative $\delta E_{ee}^{KS}[\rho]/\delta\rho(\boldsymbol{r})$, exhibits a discontinuity as the electron number passes through an integer value. Thus, the discontinuity Δ is

$$\Delta = \lim_{\omega\to 0}[v_{ee}^{(N+\omega)}(\boldsymbol{r}) - v_{ee}^{(N)}(\boldsymbol{r})] \ . \tag{6.1}$$

The above discontinuity is an important feature of the ground-state energy functional, and intrinsic to the correct physical description of the dissociation of molecules and the band gap of semiconductors within the context of KS theory. In this chapter we show via Q-DFT that Pauli and Coulomb correlations do not contribute to the discontinuity, and that its physical origin is the Correlation-Kinetic effect. In this manner, we go beyond our previous work [39] and that of Harbola [72] within Q-DFT where it was concluded that all the different correlations contribute to the discontinuity. Prior to proving that the discontinuity is due to Correlation-Kinetic effects, we briefly review the current understanding of this fundamental property of the s-system.

6.2. Brief Review of Derivative Discontinuity

That the local electron-interaction potential $v_{ee}(r)$ exhibits a discontinuity as the electron number passes through an integer value was explained by Perdew et al [42]. They extended the definition of the ground-state energy functional for densities integrating to fractional particle number such that

$$\int \rho^{(N+\omega)}(r)dr = N + \omega \ , \quad N = integer \ ; \quad 0 \leq \omega \leq 1 \qquad (6.2)$$

by defining the ensemble density matrix

$$\hat{D} = (1 - \omega)\,|\Psi^{(N)}><\Psi^{(N)}| + \omega\,|\Psi^{(N+1)}><\Psi^{(N+1)}| \ , \qquad (6.3)$$

where $|\Psi^{(N)}><\Psi^{(N)}|$ and $|\Psi^{(N+1)}><\Psi^{(N+1)}|$ are N and $(N+1)$-electron density matrices, respectively. The ground-state energy functional for the fractionally charged system is then defined as

$$E^{(N+\omega)}[\rho] = F^{(N+\omega)}[\rho] + \int dr\rho^{(N+\omega)}(r)v(r) \ , \qquad (6.4)$$

where

$$F^{(N+\omega)}[\rho] = \min_{\hat{D}\to\rho^{(N+\omega)}} tr\hat{D}(\hat{T} + \hat{U}) \ , \qquad (6.5)$$

with the minimum being searched over all density matrices of the form of Eq.

(6.3), yielding the prescribed density $\rho^{(N+\omega)}(\boldsymbol{r})$. The minimum is obtained when $|\Psi^{(N)}\rangle$ and $|\Psi^{(N+1)}\rangle$ are the ***exact*** ground states of the N- and $(N+1)$-electron systems. The minimizing density, which is

$$\rho^{(N+\omega)}(\boldsymbol{r}) = tr\{\hat{D}\hat{\rho}\} , \tag{6.6}$$

is therefore obtained as

$$\rho^{(N+\omega)}(\boldsymbol{r}) = (1 + \omega)\rho^{(N)}(\boldsymbol{r}) + \omega\rho^{(N+1)}(\boldsymbol{r}) , \tag{6.7}$$

where $\rho^{(N)}(\boldsymbol{r})$ and $\rho^{(N+1)}(\boldsymbol{r})$ are the ground-state densities of the N- and $(N+1)$-electron systems. The energy minimum is given by

$$E_{N+\omega} = (1-\omega)E_N + \omega E_{N+1} \tag{6.8}$$

where E_N and E_{N+1} are the ground state energies of the N and $N+1$-electron systems.

According to Eq. (6.8), the ground state energy $E_{N+\omega}$ as a function of ω consists of straight line segments with possible derivative discontinuities at ***integer*** N. As the chemical potential $\mu(N)$ is defined as

$$\mu(N) = \frac{\partial E_N}{\partial N} , \tag{6.9}$$

we see that it can change discontinously at integer N. Since the Euler equation for the density

$$\frac{\delta}{\delta\rho}[E_N[\rho] - \mu(N)\int \rho(r')dr'] = 0 \ , \tag{6.10}$$

involves the functional derivative of the ground-state energy functional $E_N[\rho]$, this discontinuity will be exhibited by the derivative, and hence by the local electron interaction potential $v_{ee}(r)$.

By considering the fractionally charged s-system, it is possible to derive the discontinuity Δ of Eq. (6.1) to be the difference between the highest occupied eigenvalue $\epsilon_{N+1}^{(N+1)}$ of the $(N+1)$-electron system and the $(N+1)$th eigenvalue $\epsilon_{N+1}^{(N)}$ of the N-electron system. We next show how this result is derived.

The fractionally charged $(N+\omega)$ s-system with local potential $v_s^{(N+\omega)}(r)$ is defined by the equations

$$[-\frac{1}{2}\nabla^2 + v_s^{(N+\omega)}(r)]\phi_i^{(N+\omega)}(x) = \epsilon_i^{(N+\omega)}\phi_i^{(N+\omega)}(x) \ , \tag{6.11}$$

with

$$\rho^{(N+\omega)}(r) = \sum_{i=1}^{N} |\phi_i^{(N+\omega)}(r)|^2 + \omega|\phi_{N+1}^{(N+\omega)}(r)|^2 \ , \tag{6.12}$$

where the highest occupied orbital has the fractional charge ω. Equation (6.12) may equivalently be expressed as

$$\rho^{(N+\omega)}(r) = (1-\omega)\sum_{i=1}^{N} |\phi_i^{(N+\omega)}(r)|^2 + \omega\sum_{i=1}^{N+1} |\phi_i^{(N+\omega)}(r)|^2 \ . \tag{6.13}$$

Writing $v_s^{(N+\omega)}(r)$ in terms of its Hartree $v_H^{(N+\omega)}(r)$ and KS exchange-correlation $v_{xc}^{(N+\omega)}(r)$ potentials, we have

$$\begin{aligned} v_s^{(N+\omega)}(r) &= v(r) + v_{ee}^{(N+\omega)}(r) \\ &= v(r) + v_H^{(N+\omega)}(r) + v_{xc}^{(N+\omega)}(r) \ , \end{aligned} \tag{6.14}$$

where

$$v_H^{(N+\omega)}(r) = \int \frac{\rho^{(N+\omega)}(r')}{|r-r'|} dr' \ . \tag{6.15}$$

Equations (6.14) and (6.15) then define $v_{xc}^{(N+\omega)}(r)$. Assuming the system under consideration to be finite, we impose the condition that $v_s^{(N+\omega)}(r)$ vanish at infinity:

$$\lim_{r\to\infty} v_s^{(N+\omega)}(r) = 0 \ . \tag{6.16}$$

Since the external and Hartree potentials also vanish in this limit we then have

$$\lim_{r\to\infty} v_{xc}^{(N+\omega)}(r) = 0 \ . \tag{6.17}$$

With this result, the s-system orbital densities in general decay asymptotically as

$$|\phi_i(r)|^2 \underset{r\to\infty}{\to} e^{-2(-2\epsilon_i)^{1/2} r} \ . \tag{6.18}$$

The highest occupied fractionally charged orbital $\phi_{N+1}^{(N+\omega)}(r)$ has the slowest decay so that the asymptotic structure of the $(N+\omega)$ system density is

$$\rho^{(N+\omega)}(r) \underset{r\to\infty}{\rightarrow} e^{-2(-2\epsilon_{N+1}^{(N+\omega)})^{1/2}r}. \tag{6.19}$$

On the other hand, the asymptotic decay of the N- and $(N+1)$-electron system densities is [43]

$$\rho^{(N)}(r) \underset{r\to\infty}{\rightarrow} e^{-2(2I_N)^{1/2}r}, \tag{6.20}$$

and

$$\rho^{(N+1)}(r) \underset{r\to\infty}{\rightarrow} e^{-2(2I_{N+1})^{1/2}r}, \tag{6.21}$$

where I_N and I_{N+1} are the ionization energies for the N and $N+1$-electron systems, respectively. Because the ionization energy for an $N+1$-electron system is smaller than that of an N-electron system we have

$$I_{N+1} < I_N, \tag{6.22}$$

and the fact (see Eq. (6.5)) that $\rho^{(N+\omega)}(r)$ is a linear combination of $\rho^{(N)}(r)$ and $\rho^{(N+1)}(r)$, we have

$$\rho^{(N+\omega)}(r) \underset{r\to\infty}{\rightarrow} \rho^{(N+1)}(r) \underset{r\to\infty}{\rightarrow} e^{-2(2I_{N+1})^{1/2}r}. \tag{6.23}$$

A comparison of Eq. (6.23) with (6.19) leads to

$$\epsilon_{N+1}^{(N+\omega)} = -I_{N+1} = \epsilon_{N+1}^{(N+1)} \ . \tag{6.24}$$

where the second equality is a consequence of the fact that the highest occupied eigenvalue of the s-system is minus the ionization potential [43]. Equation (6.24) also shows that the highest occupied eigenvalue is independent of the fractional charge ω

In order to show that $v_s^{(N+\omega)}(r)$ differs from $v_s^{(N)}(r)$ as ω approaches zero, let us consider a radius [73] $R(\omega)$ such that

$$\omega\rho^{(N+1)}(R) = (1-\omega)\rho^{(N)}(R) \ , \tag{6.25}$$

for $r=R(\omega)$. As ω approaches zero, $R(\omega)$ becomes infinite because of the fact that $\rho^{(N+1)}(R)$ decays more slowly than $\rho^{(N)}(R)$. As $v_s^{(N+\omega)}(r)$ and $v_s^{(N)}(r)$ generate the same density in the region $r<R(\omega)$ they can at most differ by a constant Δ in this region. For $r\rightarrow\infty$ both $v_s^{(N+\omega)}(r)$ and $v_s^{(N)}(r)$ become zero by definition. Therefore one has [74]

$$\begin{aligned} v_s^{(N+\omega)}(r) - v_s^{(N)}(r) &= \Delta \quad for \quad r<R(\omega) \\ & 0 \quad for \quad r \gg R(\omega) \ . \end{aligned} \tag{6.26}$$

In the limit $\omega\rightarrow 0$ the radius $R(\omega)$ becomes infinite and both potentials differ by a constant Δ everywhere. Employing Eq. (6.26) in the differential equation for the $(N+\omega)$-electron system, and that for small ω in the region $r<R(\omega)$ the orbitals $\phi_i^{(N+\omega)}(r) \sim \phi_i^{(N)}(r)$, we obtain

$$\epsilon_i^{(N+\omega)} = \epsilon_i^{(N)} + \Delta \quad for \quad \omega \to 0 \ . \tag{6.27}$$

In particular for $i = N+1$ we have

$$\Delta = \lim_{\omega \to 0} [\epsilon_{N+1}^{(N+\omega)} - \epsilon_{N+1}^{(N)}] = -I_{N+1} - \epsilon_{N+1}^{(N)} \tag{6.28}$$

where in the last step we have used Eq. (6.24). Since

$$v_H^{(N+\omega)}(r) = v_H^{(N)}(r) = 0 \quad for \ r \to \infty \ , \tag{6.29}$$

we finally have

$$\begin{aligned} \Delta &= \lim_{\omega \to 0} [v_{ee}^{(N+\omega)}(r) - v_{ee}^{(N)}(r)] \\ &= \lim_{\omega \to 0} [v_{xc}^{(N+\omega)}(r)) - v_{xc}^{(N)}(r)] \\ &= \epsilon_{N+1}^{(N+1)} - \epsilon_{N+1}^{(N)} \ , \end{aligned} \tag{6.30}$$

where we have employed $\epsilon_{N+1}^{(N+1)} = -I_{N+1}$. We thus see that the discontinuity Δ is finite.

If in Eq. (6.1) one employs the KS definitions of $v_{ee}^{(N+\omega)}(r)$ and $v_{xc}^{(N+\omega)}(r)$ as the functional derivatives $\delta E_{ee}^{KS}[\rho]/\delta\rho(r)\,|_{N+\omega}$ and $\delta E_{xc}^{KS}[\rho]/\delta\rho(r)\,|_{N+\omega}$, respectively, we see that in KS theory it is implicitly ***assumed*** that ***all*** the correlations present -- Pauli, Coulomb, and Correlation-Kinetic -- contribute to the discontinuity. That this is the case may also be surmized from Eq. (6.30), since these eigenvalues are generated via the ***full*** KS potential. What we show in this chapter via Q-DFT is that Pauli and Coulomb correlations do not contribute to the discontinuity, and that this intrinsic property of the s-system is *solely* a consequence of Correlation-Kinetic effects.

For this chapter to be self-contained, we next redefine the fields and potentials within Q-DFT with minor notational changes in order to distinguish between the N- and $(N+\omega)$-electron systems.

6.3. Definitions Within Quantal Density Functional Theory

The N-electron Schrödinger equation and that for the corresponding s-system are, respectively,

$$[-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2+\sum_{i=1}v(r_i)+\frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|r_i-r_j|}]\Psi^{(N)}(X) = E^{(N)}\Psi^{(N)}(X)\ , \qquad (6.31)$$

and

$$[-\frac{1}{2}\nabla^2+v(r)+v_{ee}^{(N)}]\,\phi_i^{(N)}(x) = \epsilon_i^{(N)}\phi_i^{(N)}(x)\ , \qquad (6.32)$$

where $\Psi^{(N)}(X)$ is the wavefunction, E the ground state energy, and $\phi_i(x)$ and ϵ_i the single particle orbitals and eigenenergies. (Here $X=x_1,\dots x_N$, $x=x\sigma$, and $\int dx=\sum_\sigma\int dr$.) The density $\rho^{(N)}(r)=\langle\Psi^{(N)}|\hat{\rho}(r)|\Psi^{(N)}\rangle = \langle\Phi\{\phi_i^{(N)}\}|\hat{\rho}|\Phi\{\phi_i^{(N)}\}\rangle$ $=\sum_{\sigma i}|\phi_i^{(N)}(x)|^2$, where $\hat{\rho} = \sum_i\delta(r_i-r)$, and $\Phi\{\phi_i^{(N)}\}$ the Slater determinant of the orbitals $\phi_i^{(N)}(x)$.

The work $v_{ee}^{(N)}(r)$ done to move an electron from a reference point at infinity to its position at r in the force of the conservative field $\mathcal{F}^{(N)}(r)$ is

$$v_{ee}^{(N)}(r) = -\int_{\infty}^{r} \mathcal{F}^{(N)}(r') \cdot dl' \,, \tag{6.33}$$

where

$$\mathcal{F}^{(N)}(r) = \mathcal{E}_{ee}^{(N)}(r) + \mathcal{Z}_{t_c}^{(N)}(r) \,. \tag{6.34}$$

The electron-interaction component field $\mathcal{E}_{ee}^{(N)}(r)$, which is representative of Pauli and Coulomb correlations, is obtained by Coulomb's law from its nonlocal source charge distribution $g^{(N)}(r,r')$, the pair-correlation density. Thus,

$$\mathcal{E}_{ee}^{(N)}(r) = \int \frac{g^{(N)}(r,r')(r-r')}{|r-r'|^3} dr' \,, \tag{6.35}$$

where $g^{(N)}(r,r') = \langle\Psi^{(N)}|\hat{P}(r,r')|\Psi^{(N)}\rangle / \rho^{(N)}(r)$, and $\hat{P} = \sum_{i \neq j}\delta(r_i - r)\delta(r_j - r')$.

The Correlation-Kinetic component field $Z_{t_c}^{(N)}(r)$ is defined in terms of the kinetic fields $z^{(N)}(r;[\gamma])$ and $z_s^{(N)}(r;[\gamma_s])$ for the interacting and s-system, respectively, as

$$Z_{t_c}^{(N)}(r) = [z_s^{(N)}(r;[\gamma_s]) - z^{(N)}(r;[\gamma])]/\rho^{(N)}(r) \,. \tag{6.36}$$

The nonlocal sources of the kinetic fields are the spinless single-particle $\gamma^{(N)}(r,r')$ and Dirac $\gamma_s^{(N)}(r,r')$ density matrices, respectively, where $\gamma^{(N)}(r,r') = \langle\Psi^{(N)}|\hat{X}|\Psi^{(N)}\rangle$ and $\gamma_s^{(N)}(r,r') = \langle\Phi\{\phi_i^{(N)}\}|\hat{X}|\Phi\{\phi_i^{(N)}\}\rangle = \sum_{\sigma i}\phi_i^{(N)*}(r\sigma)\phi_i^{(N)}(r'\sigma)$, and where $\hat{X}=\hat{A}+i\hat{B}$, $\hat{A}=\frac{1}{2}\sum_j[\delta(\boldsymbol{r}_j-\boldsymbol{r})T_j(\boldsymbol{a})+\delta(\boldsymbol{r}_j-\boldsymbol{r}')T_j(-\boldsymbol{a})]$, $\hat{B}=\frac{i}{2}\sum_j[\delta(\boldsymbol{r}_j-\boldsymbol{r})T_j(\boldsymbol{a})-\delta(\boldsymbol{r}_j-\boldsymbol{r}')T_j(-\boldsymbol{a})]$, $T_j(\boldsymbol{a})$ is a translation operator such that $T_j(\boldsymbol{a})\Psi(\cdots\boldsymbol{r}_j\cdots)=\Psi(\cdots\boldsymbol{r}_j+\boldsymbol{a},\cdots)$, and $\boldsymbol{a}=\boldsymbol{r}'-\boldsymbol{r}$. The kinetic fields are defined such that the component $z_\alpha^{(N)}(\boldsymbol{r})=2\sum_\beta\partial t_{\alpha\beta}(\boldsymbol{r};[\gamma])/\partial r_\beta$, where $t_{\alpha\beta}(\boldsymbol{r})=(1/4)[\partial^2/\partial r_\alpha{}'\partial r_\beta{}'' + \partial^2/\partial r_\beta{}'\partial r_\alpha{}'']\gamma^{(N)}(\boldsymbol{r}',\boldsymbol{r}'')|_{\boldsymbol{r}'=\boldsymbol{r}''=\boldsymbol{r}}$ is the kinetic energy density tensor. The field $z_s^{(N)}(\boldsymbol{r};[\gamma_s])$ is similarly defined in terms of the s-system tensor $t_{s,\alpha\beta}(\boldsymbol{r})$ and Dirac density matrix $\gamma_s^{(N)}(\boldsymbol{r},\boldsymbol{r}')$.

Within the Schrödinger theory framework, the fractionally charged $(N+\omega)$ case is treated in terms of an ensemble of the N- and $(N+1)$-electron systems. Thus, with the ensemble density matrix defined as in Eq. (6.3), the pair-correlation density, and the density matrix can be shown to be

$$\begin{aligned} g^{(N+\omega)}(\boldsymbol{r},\boldsymbol{r}') &= tr\{\hat{D}\hat{P}\}/\rho^{(N+\omega)}(\boldsymbol{r}) \\ &= [(1-\omega)\rho^{(N)}(\boldsymbol{r})g^{(N)}(\boldsymbol{r},\boldsymbol{r}') + \omega\rho^{(N+1)}(\boldsymbol{r})g^{(N+1)}(\boldsymbol{r},\boldsymbol{r}')]/\rho^{(N+\omega)}(\boldsymbol{r}) , \end{aligned} \tag{6.37}$$

and

$$\begin{aligned} \gamma^{(N+\omega)}(\boldsymbol{r},\boldsymbol{r}') &= tr\{\hat{D}\hat{X}\} \\ &= (1-\omega)\gamma^{(N)}(\boldsymbol{r},\boldsymbol{r}') + \omega\gamma^{(N+1)}(\boldsymbol{r},\boldsymbol{r}') . \end{aligned} \tag{6.38}$$

The local potential $v_{ee}^{(N+\omega)}(\boldsymbol{r})$ in Eq. (6.11) can be rewritten as the work done in a conservartive field $\mathcal{F}^{(N+\omega)}(\boldsymbol{r})$

$$v_{ee}^{(N+\omega)}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{F}^{(N+\omega)}(\mathbf{r}')\cdot d\mathbf{l}' \,, \tag{6.39}$$

with

$$\mathcal{F}^{(N+\omega)}(\mathbf{r}) = \mathcal{E}_{ee}^{(N+\omega)}(\mathbf{r}) + \tilde{\mathcal{Z}}_{t_c}^{(N+\omega)}(\mathbf{r}) \,. \tag{6.40}$$

The electron-interaction field $\mathcal{E}_{ee}^{(N+\omega)}(\mathbf{r})$ is obtained by Coulomb's law from its source charge $g^{(N+\omega)}(\mathbf{r},\mathbf{r}')$ as

$$\mathcal{E}_{ee}^{(N+\omega)}(\mathbf{r}) = [(1-\omega)\rho^{(N)}(\mathbf{r})\mathcal{E}_{ee}^{(N)}(\mathbf{r}) + \omega\rho^{(N+1)}(\mathbf{r})\mathcal{E}_{ee}^{(N+1)}(\mathbf{r})]/\rho^{(N+\omega)}(\mathbf{r}) \,, \tag{6.41}$$

The Correlation-Kinetic field $\tilde{\mathcal{Z}}_{t_c}^{(N+\omega)}(\mathbf{r})$ is defined as

$$\tilde{\mathcal{Z}}_{t_c}^{(N+\omega)}(\mathbf{r}) = [\tilde{z}_s^{(N+\omega)}(\mathbf{r};[\tilde{\gamma}_s^{(N+\omega)}]) - z^{(N+\omega)}(\mathbf{r};[\gamma^{(N+\omega)}])]/\rho^{(N+\omega)}(\mathbf{r}) \,, \tag{6.42}$$

where the kinetic field $z^{(N+\omega)}(\mathbf{r})$ is obtained from its source $\gamma^{(N+\omega)}(\mathbf{r},\mathbf{r}')$. The s-system kinetic field $\tilde{z}_s^{(N+\omega)}(\mathbf{r})$ is similarly obtained from the density matrix constructed from the orbitals $\phi_i^{(N+\omega)}(\mathbf{x})$ which is $\tilde{\gamma}_s^{(N+\omega)}(\mathbf{r},\mathbf{r}') = (1-\omega)\sum_{i=1}^{N}\sum_{\sigma}\phi_i^{(N+\omega)*}(\mathbf{r}\sigma)\phi_i^{(N+\omega)}(\mathbf{r}'\sigma) + \omega\sum_{i=1}^{N+1}\sum_{\sigma}\phi_i^{(N+\omega)*}(\mathbf{r}\sigma)\phi_i^{(N+\omega)}(\mathbf{r}'\sigma)$

We next prove that the discontinuity as defined by Eq. (6.1) is due to Correlation-Kinetic effects.

6.4. Analytical Proof

A. Electron-interaction component

From Eqs. (6.33) and (6.39) we have

$$\nabla[v_{ee}^{(N+\omega)}(r) - v_{ee}^{(N)}(r)] = -\Delta\mathcal{E}_{ee}(r) - \Delta Z_{t_c}(r) , \tag{6.43}$$

where

$$\Delta\mathcal{E}_{ee}(r) = \mathcal{E}_{ee}^{(N+\omega)}(r) - \mathcal{E}_{ee}^{(N)}(r) , \tag{6.44}$$

and

$$\Delta Z_{t_c}(r) = \tilde{Z}_{t_c}^{(N+\omega)}(r) - Z_{t_c}^{(N)}(r) . \tag{6.45}$$

From Eqs. (6.35) and (6.41), we have

$$\begin{aligned}\Delta\mathcal{E}_{ee}(r) = {} & [\{(1-\omega)\rho^{(N)}(r) - \rho^{(N+\omega)}(r)\}\mathcal{E}_{ee}^{(N)}(r) \\ & + \omega\rho^{(N+1)}(r)\mathcal{E}_{ee}^{(N+1)}(r)]/\rho^{(N+\omega)}(r) .\end{aligned} \tag{6.46}$$

Substituting for $(1-\omega)\rho^{(N)}(r) = \rho^{(N+\omega)}(r) - \omega\rho^{(N+1)}(r)$ into Eq. (6.46) leads to

$$\Delta\mathcal{E}_{ee}(r) = \omega\rho^{(N+1)}(r)[\mathcal{E}_{ee}^{(N+1)}(r) - \mathcal{E}_{ee}^{(N)}(r)]/\rho^{(N+\omega)}(r) . \tag{6.47}$$

It follows from Eq. (6.47) that $\lim_{\omega\to 0}\Delta\mathcal{E}_{ee}(r) = 0$. To see this consider the radius $R(\omega)$ defined such that $\omega\rho^{(N+1)}(R) = (1-\omega)\rho^{(N)}(R)$. For $r < R(\omega)$ and small ω, the density $\rho^{(N)}(r)$ dominates the ensemble density $\rho^{(N+\omega)}(r)$. Thus, in this region $\rho^{(N+\omega)}(r) \sim \rho^{(N)}(r)$, and $\Delta\mathcal{E}_{ee}(r)$ is linear in ω and vanishes as $\omega\to 0$. For $r \gg R(\omega)$, the ensemble density $\rho^{(N+\omega)}(r) \sim \omega\rho^{(N+1)}(r)$. Substitution into Eq. (6.47) shows that the ω's cancel. But in this region the difference $[\mathcal{E}_{ee}^{(N+1)}(r) - \mathcal{E}_{ee}^{(N)}(r)] \sim 1/r^2$ so that $\Delta\mathcal{E}_{ee}(r)$ once again vanishes. In the region $r \sim R(\omega)$, $\Delta\mathcal{E}_{ee}(r)$ vanishes essentially linearly with ω. We note, however, that

$\Delta\mathcal{E}_{ee}(r)$ is finite for positive definite ω, irrespective of how small ω is. It is only in the limit of vanishing ω that the Pauli and Coulomb correlation contributions to the discontinuity vanish. Finally, since the pair-correlation density may be written as $g^{(N)}(r,r') = \rho^{(N)}(r') + \rho_{xc}^{(N)}(r,r')$, where $\rho_{xc}^{(N)}(r,r')$ is the Fermi-Coulomb hole charge distribution, we have $\Delta\mathcal{E}_{ee}(r) = \Delta\mathcal{E}_{H}(r) + \Delta\mathcal{E}_{xc}(r)$, where $\Delta\mathcal{E}_{H}(r) = [\mathcal{E}_{H}^{(N+\omega)}(r) - \mathcal{E}_{H}^{(N)}(r)]$ and $\mathcal{E}_{xc}^{(N)}(r)$ are the Hartree and Pauli-Coulomb fields arising from the component charge distributions $\rho^{(N)}(r')$ and $\rho_{xc}^{(N)}(r,r')$, respectively. Substituting the ensemble definition of $\rho^{(N+\omega)}(r)$ into the expression for $\mathcal{E}_{H}^{(N+\omega)}(r)$ we have $\Delta\mathcal{E}_{H}(r) = \omega[\mathcal{E}_{H}^{(N+1)}(r) - \mathcal{E}_{H}^{(N)}(r)]$, so that $\lim_{\omega\to 0}\Delta\mathcal{E}_{H}(r) = 0$, and consequently the $\lim_{\omega\to 0}\Delta\mathcal{E}_{xc}(r) = 0$.

B. Correlation-Kinetic component

Since the quantum-mechanical electron-interaction contribution $\Delta\mathcal{E}_{ee}(r)$ in Eq. (6.47) vanishes in the $\lim \omega\to 0$, we have

$$\lim_{\omega\to 0}\Delta[v_{ee}^{(N+\omega)}(r) - v_{ee}^{(N)}(r)] = -\Delta Z_{t_c}(r) , \tag{6.48}$$

which proves the fact that the discontinuity is strictly a Correlation-Kinetic effect. Thus, the discontinuity Δ is then the work done

$$\Delta = -\int_{\infty}^{0} [\bar{Z}_{t_c}^{(N+\omega)}(r') - Z_{t_c}^{(N)}(r')]\cdot dl' . \tag{6.49}$$

From Eq. (6.48) it also follows that this work done is path-independent.

To understand more fundamentally, how Correlation-Kinetic effects contribute to the discontinuity, we next explain the structure of $\Delta Z_{t_c}(r)$ for small ω. We rewrite $\Delta Z_{t_c}(r)$ as

$$\begin{aligned}\Delta Z_{t_c}(r) &= \tilde{Z}_{t_c}^{(N+\omega)}(r) - Z_{t_c}^{(N)}(r) \\ &= A + B \ ,\end{aligned} \tag{6.50}$$

where

$$A = \frac{1}{\rho^{(N+\omega)}(r)} \tilde{z}_s^{(N+\omega)}(r) - \frac{1}{\rho^{(N)}(r)} z_s^{(N)}(r) \ , \tag{6.51}$$

$$B = -\frac{1}{\rho^{(N+\omega)}(r)} [(1-\omega) z^{(N)}(r) + \omega z^{(N+1)}(r)] + \frac{1}{\rho^{(N)}(r)} z^{(N)}(r) \ . \tag{6.52}$$

For $r < R(\omega)$, the region where $\rho^{(N)}(r)$ dominates [39, 73], $\tilde{\gamma}_s^{(N+\omega)}(r, r')$ $\sim \sum_{\sigma,i=1}^{N} \phi_i^{(N)*}(r\sigma) \phi_i^{(N)}(r'\sigma)$, so that $\tilde{z}_s^{(N+\omega)}(r) \sim z_s^{(N)}(r)$. Therefore $A = 0$. The term $B = 0$ since the terms linear in ω are negligible. Thus, in this region $\Delta Z_{t_c}(r) = 0$.

In the $r \to \infty$ limit, both $\tilde{Z}_{t_c}^{(N+\omega)}(r)$ and $Z_{t_c}^{(N)}(r)$ vanish, so that in this region $\Delta Z_{t_c}(r) = 0$.

For $r \gg R(\omega)$ but $r < \infty$, we have $\phi_i^{(N+\omega)}(r) \to \phi_i^{(N+1)}(r)$ [39, 73] so that $\tilde{\gamma}_s^{(N+\omega)}(r, r') \ \sim \omega \sum_{\sigma,i=1}^{N+1} \phi_i^{(N+1)*}(r\sigma) \phi_i^{(N+1)}(r'\sigma)$ and $\tilde{z}_s^{(N+\omega)}(r) \sim \omega z_s^{(N+1)}(r)$. Thus, $A \sim \ \{[z_s^{(N+1)}(r)/\rho^{(N+1)}(r)] - [z_s^{(N)}(r)/\rho^{(N)}(r)]\}$ and $B \sim -\{[z^{(N+1)}(r)/\rho^{(N+1)}(r)]$

$+[\mathbf{z}^{(N)}(\mathbf{r})/\rho^{(N)}(\mathbf{r})]\}$ so that $\Delta Z_{t_c}(\mathbf{r}) = Z_{t_c}^{(N+1)}(\mathbf{r}) - Z_{t_c}^{(N)}(\mathbf{r})$. Thus, in this region, $\Delta Z_{t_c}(\mathbf{r})$ is finite. In this limit as $\omega \to 0$, the radius $R(\omega)$ becomes infinite, and the difference $\Delta Z_{t_c}(\mathbf{r})$ stablizes.

We next demonstrate the above conclusions via two numerical examples.

6.5. Numerical Examples

As an example of the above conclusions, we consider the He^+ ion (atomic number $Z=2$, electron number $N=1$) as smaller and smaller fractional charge is added to the $1s$ shell. In our calculations we employ a 491-parameter correlated wavefunction [48] for the He atom. For the s-system the orbitals are

$$\phi_i^{(1+\omega)}(r) = [\{(1-\omega)\rho^{(1)}(r) + \omega\rho^{(2)}(r)\}/(1+\omega)]^{1/2} . \qquad (6.53)$$

The solutions for the He^+ ion are exactly known.

In Fig. 6.1 we plot the Hartree field difference $\Delta\mathcal{E}_H(\mathbf{r})$ for $\omega = 10^{-1}$, 10^{-2}, and 10^{-3}. As the fractional charge diminishes, the difference $\Delta\mathcal{E}_H(\mathbf{r})$ becomes negligible. The corresponding work $\Delta W_H(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \Delta\mathcal{E}_H(\mathbf{r}') \cdot d\mathbf{l}'$ is constant in the interior as expected (Fig. 6.1), but becomes smaller with decreasing fractional charge, although it is still finite at $\omega = 10^{-3}$. As ω is decreased further, however, both $\Delta\mathcal{E}_H(\mathbf{r})$ and $\Delta W_H(\mathbf{r})$ vanish. Thus, the Hartree component of the Coulomb interaction does not contribute to the discontiniuity.

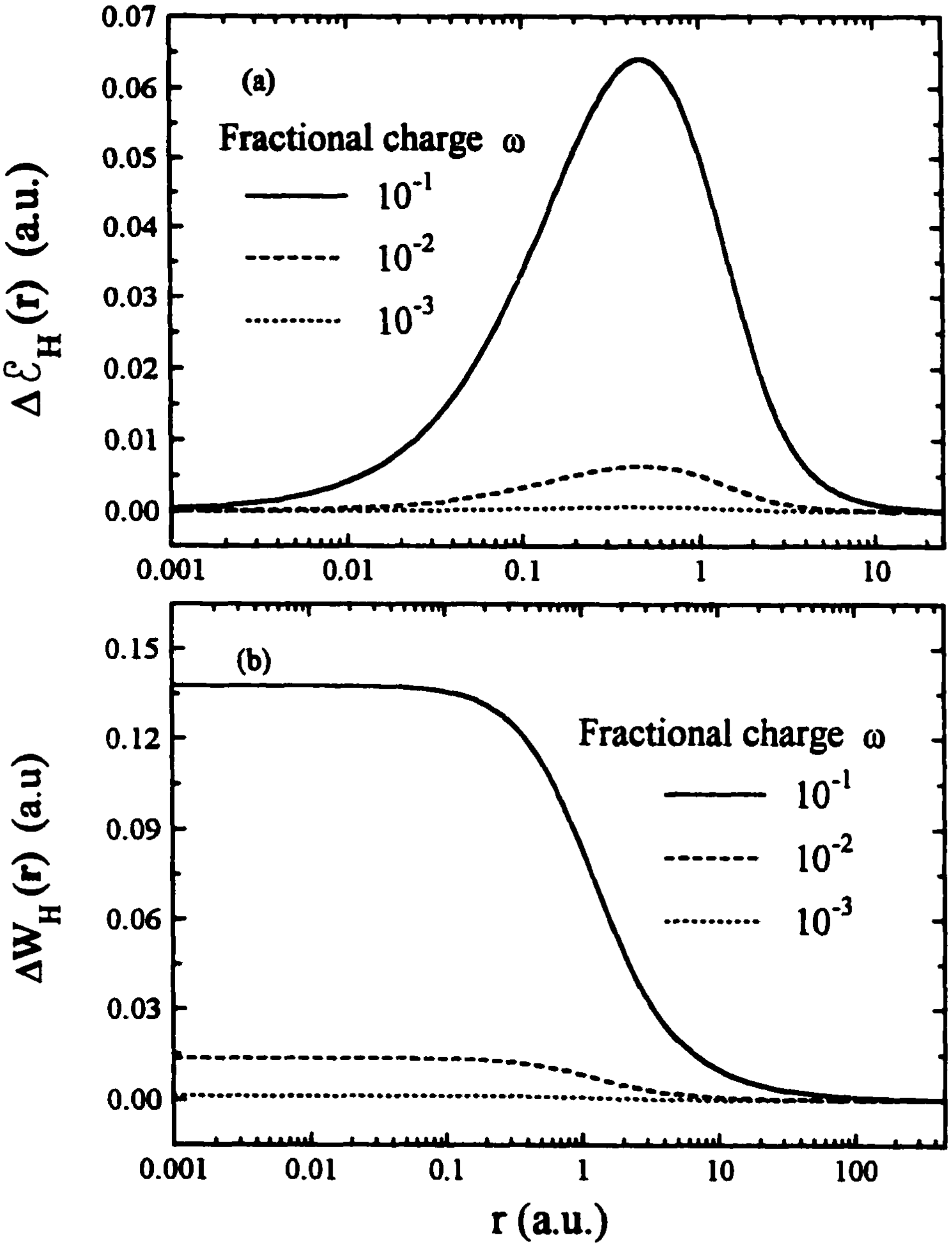


Figure 6.1: (a) Hartree field difference $\Delta\mathcal{E}_H(r)$ for different fractional charge ω. The integer charge system is He^+. (b) Work done $\Delta W_H(r)$ in the field $\Delta\mathcal{E}_H$

In Fig. 6.2, the difference in the Pauli-Coulomb fields $\Delta\mathcal{E}_{xc}(r)$ is plotted for fractional charge $\omega =$ 10^{-5}, 10^{-8}, and 10^{-10}. As expected it vanishes in the interior and is peaked in the surface region. It diminshes with decreasing ω, while simultaneously the peak moves further into the classically forbidden region where $\Delta\mathcal{E}_{xc}(r)$ decays as $(1-\omega)/r^2$ for finite ω. Thus, the corresponding work (Fig. 6.2) $\Delta W_{xc}(r) = -\int_{\infty}^{r}\Delta\mathcal{E}_{xc}(r')\cdot dl'$ is constant in the interior, with the region where this difference is constant increasing with decreasing ω, Furthermore, as expected the constant value of $\Delta W_{xc}(r)$ also diminishes with decreasing ω. For $\omega = 10^{-10}$ the constant value of $\Delta W_{xc}(r)$ in the interior is $0.052 a.u.$, Asymptotically, $\Delta W_{xc}(r)$ decays as $(1-\omega)/r$. With vanishing fractional charge, the Pauli-Coulomb contribution to the discontinuity will also vanish.

In Fig. 6.2 we plot the difference $\Delta Z_{t_c}(r)$ of the Correlation-Kinetic fields, for fractional charge $\omega =$ 10^{-2}, 10^{-5}, 10^{-8}, $10^{-10} a.u.$. As expected, this difference vanishes in the interior region. However, in the surface region, these curves are dramatically different from those of Figs. 6.1 and 6.2 in that as the fractional charge ω is decreased, the magnitude of these curves ***increases*** (Fig. 6.3). With a further decrease in ω, the structure essentially stablizes (Fig. 6.3) and remains finite, while simultaneously moving further out into the classically forbidden region. Thus, the constant value of the work $\Delta W_{t_c}(r) = -\int_{\infty}^{r}\Delta Z_{t_c}(r')\cdot dl'$ ***increases*** with decreasing fractional charge (Fig. 6.4) approaching the exact value of the discontinuity Δ from below. This value may be determined from the

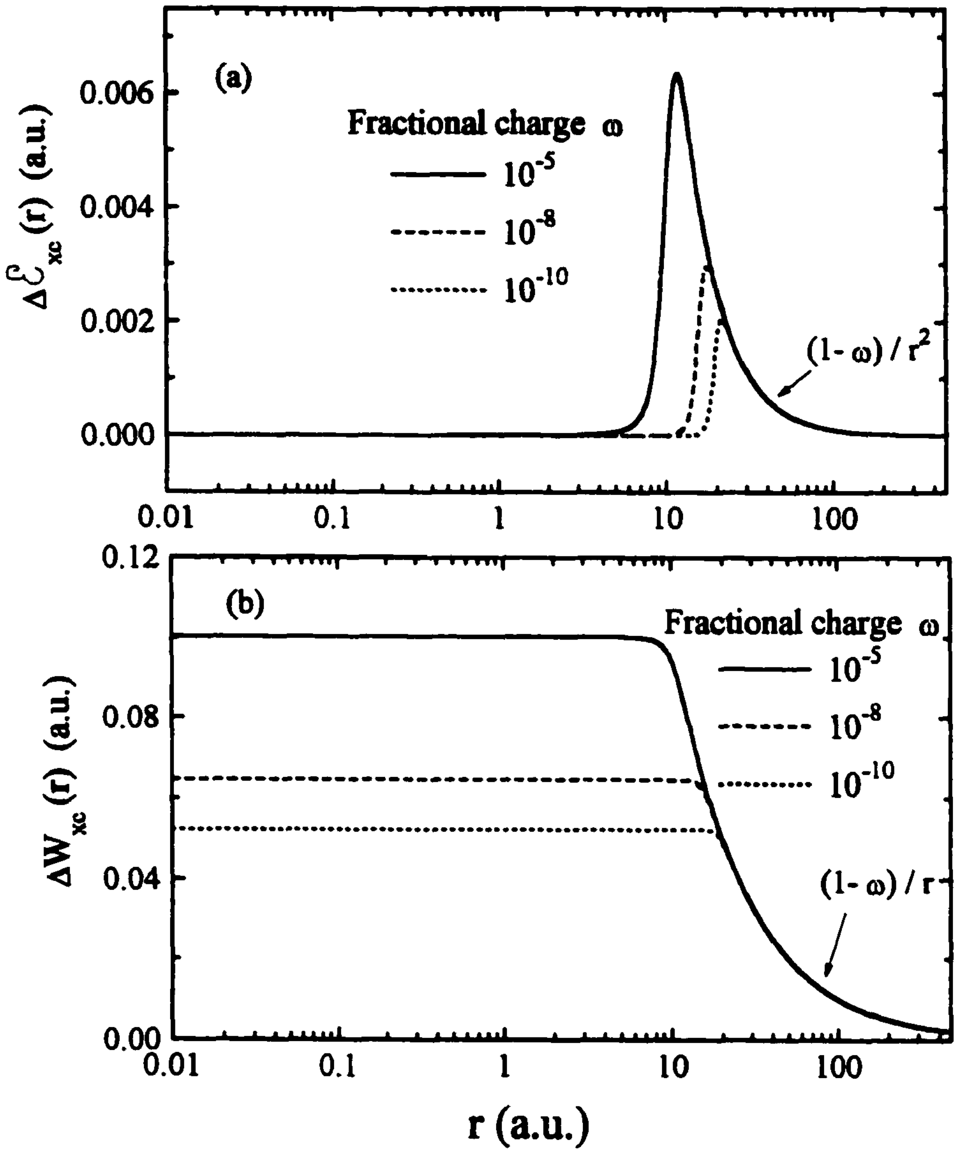


Figure 6.2: (a) Pauli-Coulomb field difference $\Delta\mathcal{E}_{xc}(r)$ for different fractional charge ω. The integer charge system is He^{+}. (b) Work done $\Delta W_{xc}(r)$ in the field $\Delta\mathcal{E}_{xc}(r)$.

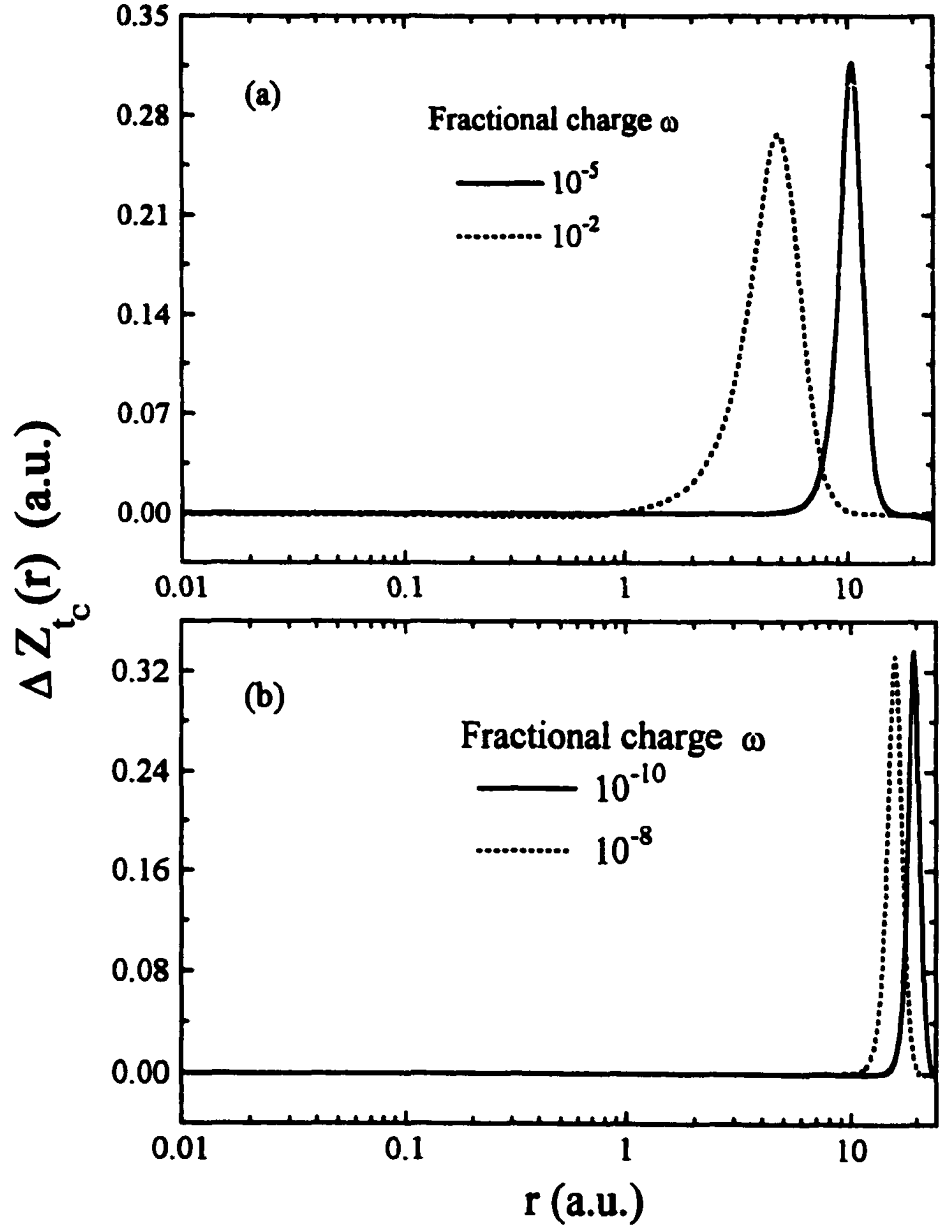


Figure 6.3: Correlation-Kinetic field difference $\Delta Z_{t_c}(r)$ for different fractional charge ω. The integer charge system is He^+.

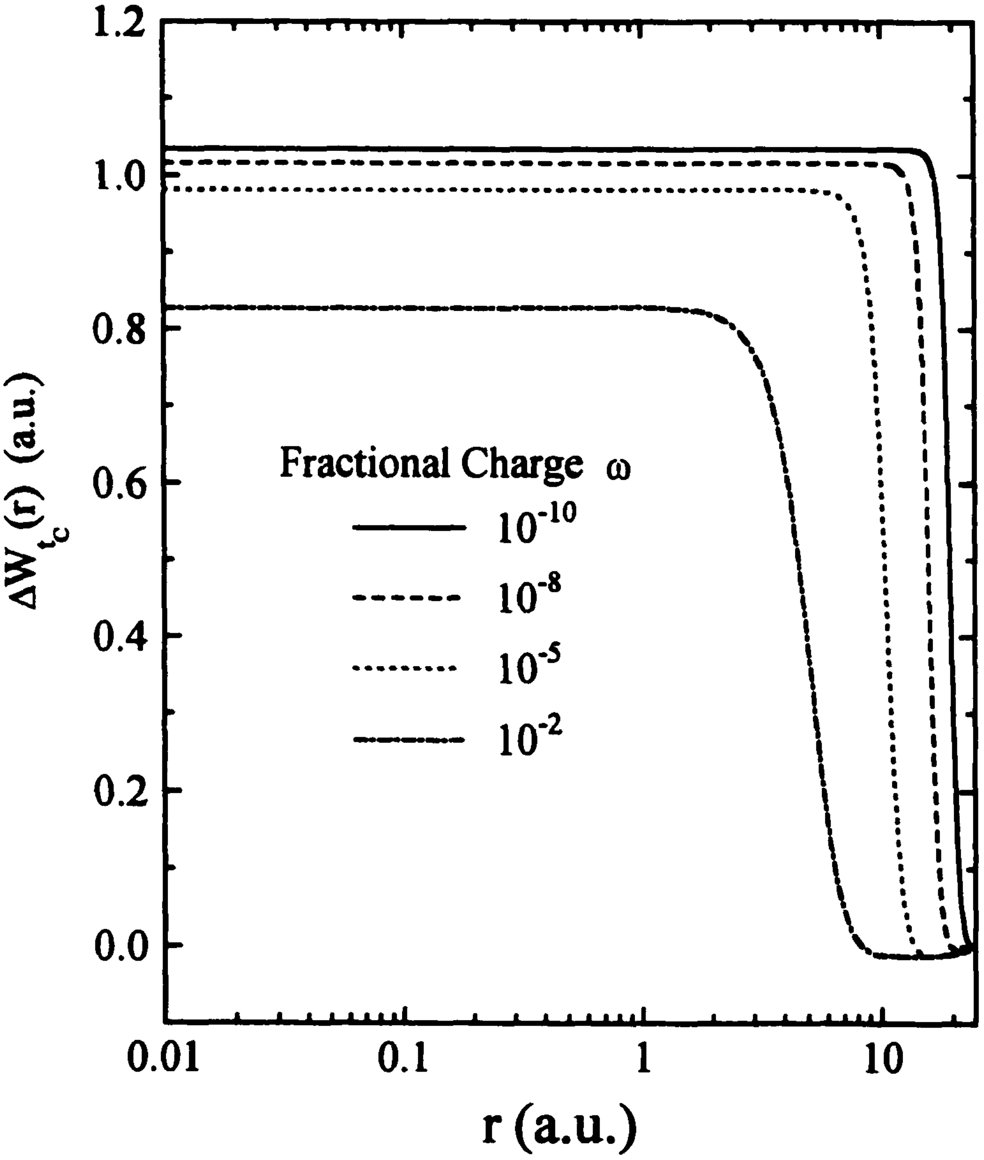


Figure 6.4: Work done $\Delta W_{t_c}(r)$ in the field $\Delta Z_{t_c}(r)$ of Fig. 6.3.

known result $\Delta = \epsilon_{N+1}^{(N+1)} - \epsilon_{N+1}^{(N)}$, and the fact the highest occupied eigenvalue of the s-system corresponds to minus the ionization potential. Taking into consideration the double occupancy of the $1s$ orbital, and that the ionization potentials of He and He^{+} are $0.903a.u.$ and $2a.u.$ respectively, we have $\Delta = 1.097a.u.$. The value of ΔW_{t_c} for $\omega = 10^{-10}$ is $1.035a.u.$. Adding the value of $\Delta W_{xc} = 0.052a.u.$ for the same ω value, we obtain $\Delta = 1.087a.u.$, which is essentially exact. In the limit of vanishing ω, the contribution from ΔW_{xc} will vanish and that due to ΔW_{t_c} will equal Δ. This confirms that the discontinuity in the electron-interaction potential is solely due to Correlation-Kinetic effects.

In the above example there are no exchange effects. To demonstrate that for finite fractional charge ω, irrespective of how small it is, there is a contribution to the discontinuity from Pauli correlations, we perform calculations at the lowest-order Q-DFT perturbation theory or equivalently the Work Formalism Hartree-Fock approximation [18, 19]. In this case the electron-interaction potential $v_{ee}(r)$ is $W_x(r)$, the work done in the Pauli field $\mathcal{E}_x(r)$ of the Fermi hole charge. For the $(N+\omega)$-electron system the Fermi hole is $\rho_x^{(N+\omega)}(r,r') = g_s^{(N+\omega)}(r,r') - \rho^{(N+\omega)}(r')$.

In Fig. 6.5 we plot the difference $\Delta\mathcal{E}_x(r) = \mathcal{E}_x^{(N+\omega)}(r) - \mathcal{E}_x^{(N)}(r)$ for the Na^{+} ion (atomic number $Z=11$, electron number $N=10$) for fractional charge of $\omega = 10^{-5}$, 10^{-10}, 10^{-15} filling the empty $3s$ subshell. These calculations are

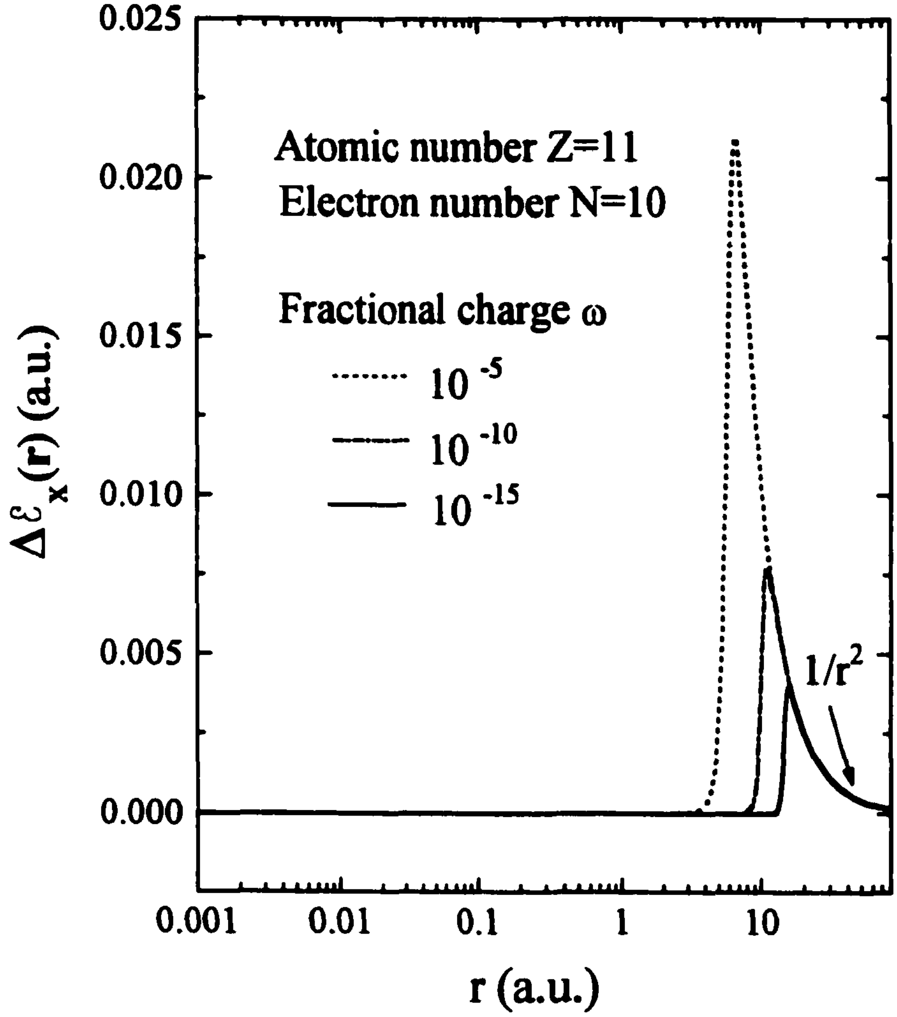


Figure 6.5: Variation of the difference $\Delta\mathcal{E}_x = \mathcal{E}_x^{(N+\omega)}(r) - \mathcal{E}_x^{(N)}(r)$ of the Pauli fields $\mathcal{E}_x^{(N+\omega)}(r)$ and $\mathcal{E}_x^{(N)}(r)$ for the $(N+\omega)$ fractionally charged and N-electron Na^+ ions, respectively. The fractional charge of $\omega = 10^{-5}$, 10^{-10}, 10^{-15}, partially fills the empty $3s$ subshell.

performed within the spin-unpolarized central field approximation. Observe that the difference vanishes except in the asymptotic region of the atom where it is peaked. Note also that as the fractional charge decreases, this peak moves further into the classically forbidden region as it must. The difference $\Delta\mathcal{E}_x(r)$ also decays asymptotically as $1/r^2$. In Fig. 6.6 we plot the corresponding Pauli potential $W_x(r)$ for the Na^+ ion for the case of the empty $3s$ subshell (dashed curve), and for the fractionally charged ion with fractional charge $\omega = 10^{-5}$ in the $3s$ subshell (solid curve). The difference $\Delta W_x(r) = W_x^{(N+\omega)}(r) - W_x^{(N)}(r)$ of the Pauli potentials for the $(N+\omega)$ fractionally charged and N-electron ions for $\omega = 10^{-5}$, 10^{-10}, 10^{-15} is plotted in Fig. 6.7. As is evident, the difference $\Delta W_x(r)$ is constant except in the asymptotic region where it decays as $1/r$. However, note that the constant value of $\Delta W_x(r)$ continues to diminish with decreasing ω as was the case for $\Delta W_{xc}(r)$ of Fig. 6.2. In the limit $\omega \to 0$, the difference $\Delta W_x(r)$ will vanish.

6.6. Connection to Kohn-Sham Theory

To make our conclusions better understood we describe here briefly the connection between Q-DFT and KS-DFT. This connection is explained more fully in the following chapter.

The relationship between Q-DFT and KS-DFT is established via adiabatic coupling constant perturbation theory [75]. The coupling constant λ varies the

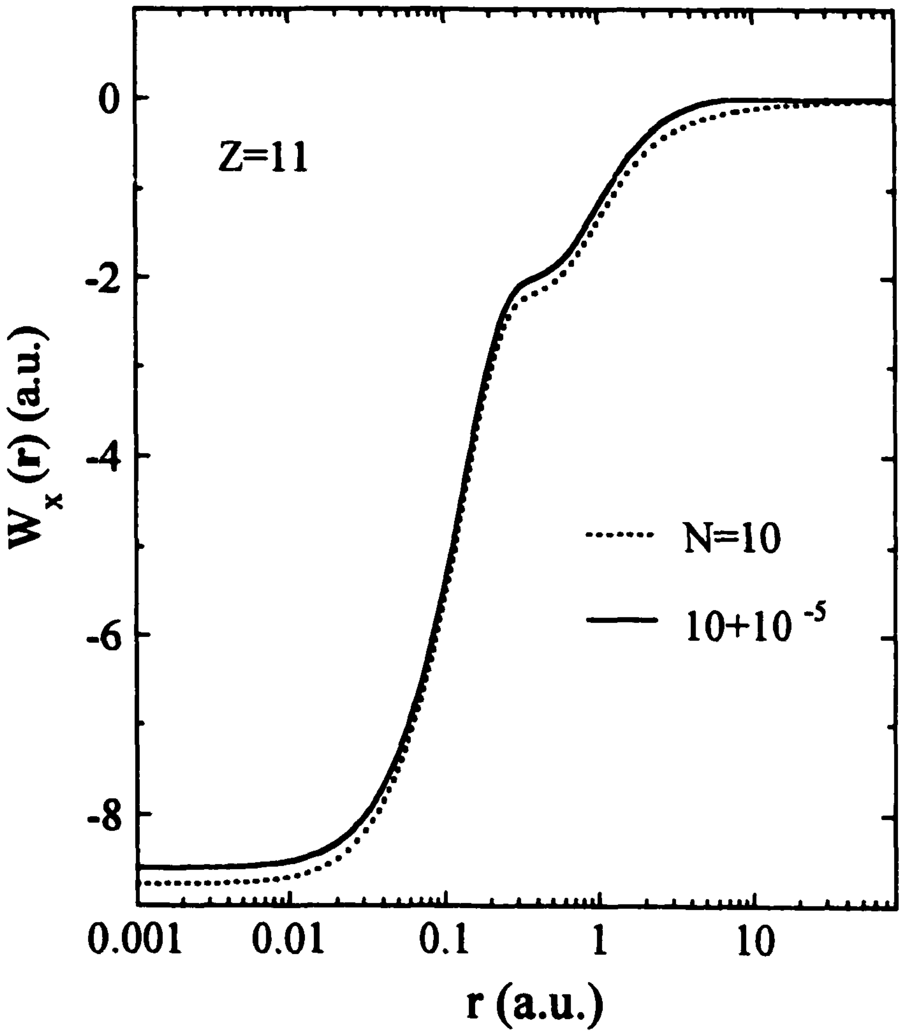


Figure 6.6: The Pauli potential for the Na^+ ion with integer number ($N=10$) of electrons (dashed curve), and with fractional charge ($10+10^{-5}$) (solid curve). The fractional charge 10^{-5} fills the empty $3s$ subshell

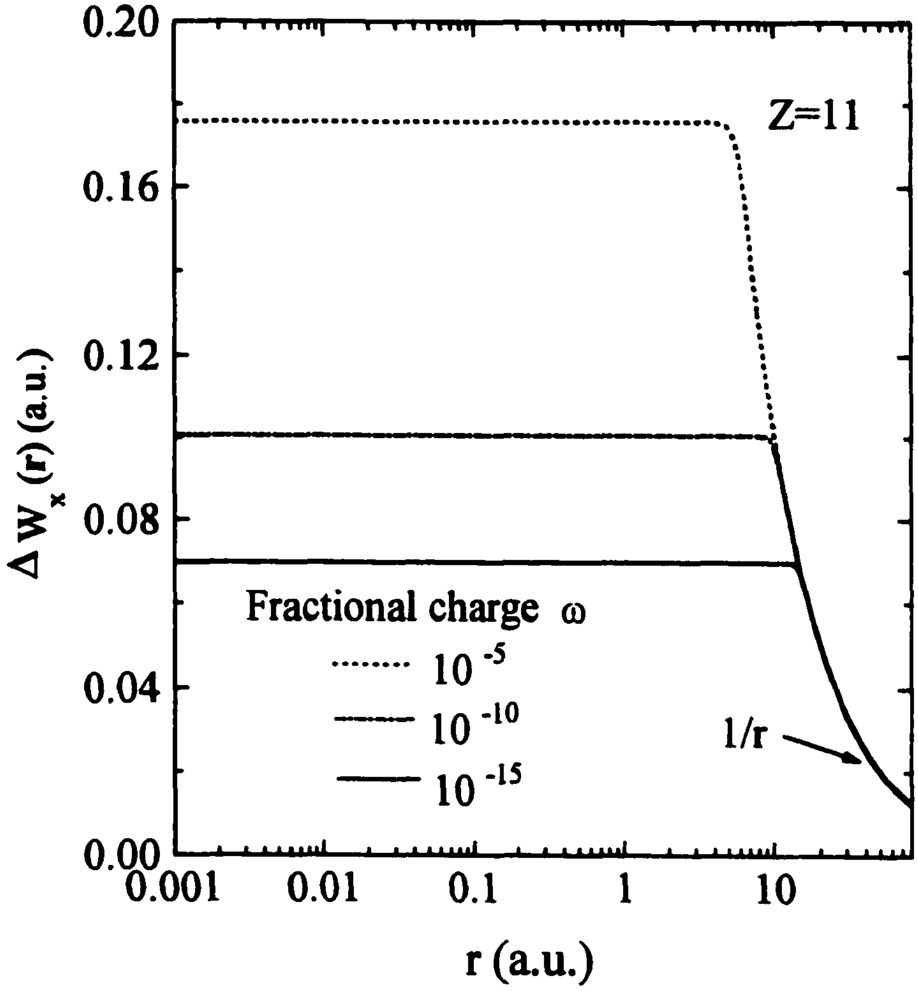


Figure 6.7: Variation of the difference $\Delta W_x(r) = W_x^{(N+\omega)}(r) - W_x^{(N)}(r)$ of the Pauli potentials $W_x^{(N+\omega)}(r)$ and $W_x^{(N)}(r)$ for the fractionally charged $(N+\omega)$- and N-electron Na^+ ions. respectively.

electron-electron interaction from the noninteracting s-system case of $\lambda = 0$ to the fully interacting $\lambda = 1$ case in such a manner that the ground-state density remains independent of the coupling strength. Now it can be show via this perturbation theory [51-53] that the KS exchange energy $E_x^{KS}[\rho]$ is linear in λ, while the KS correlation energy $E_c^{KS}[\rho]$ commences at $O(\lambda^2)$. As a consequence, the corresponding KS potentials $v_x(\boldsymbol{r})$ is of $O(\lambda)$ and $v_c(\boldsymbol{r})$ commences at $O(\lambda^2)$, respectively. Within Q-DFT, the Pauli component $\mathcal{E}_x(\boldsymbol{r})$ of the electron-interaction field $\mathcal{E}_{ee}(\boldsymbol{r})$ is of $O(\lambda)$ and the Coulomb field component $\mathcal{E}_c(\boldsymbol{r})$ commences at $O(\lambda^2)$. The Correlation-Kinetic field $\mathcal{Z}_{t_c}(\boldsymbol{r})$, however, commences at $O(\lambda)$. Thus, it follows that the KS exchange potential $v_x(\boldsymbol{r})$ is the work done in a conservative field $\boldsymbol{R}(\boldsymbol{r})$ which is the sum of the Pauli component $\mathcal{E}_x(\boldsymbol{r})$ and a Correlation-Kinetic component $\mathcal{Z}_{t_c}^{(1)}(\boldsymbol{r})$ which is the $O(\lambda)$ part of the field $\mathcal{Z}_{t_c}(\boldsymbol{r})$. Therefore, the KS potential $v_x(\boldsymbol{r})$ is representative of electron correlations due to the Pauli exclusion principle as well as part of the Correlation-Kinetic effect. Implicitly, via this potential and the orbitals generated by it, so is the exchange energy $E_x[\rho]$. The KS correlation energy $E_c^{KS}[\rho]$ and potential $v_c(\boldsymbol{r})$ are therefore representative of Coulomb correlation and the $O(\lambda^2)$ and higher-order Correlation-Kinetic contributions. From the above analysis, it is evident that the discontinuity in the KS exchange potential $v_x(\boldsymbol{r})$ in 'exchange-only' calculations [76, 77] which is then referred to as being due to exchange effects, is in fact due to Correlation-Kinetic effects arising from the field $\mathcal{Z}_{t_c}^{(1)}(\boldsymbol{r})$. Similarly, any discontinuity in the KS potential $v_c(\boldsymbol{r})$ is not due to Coulomb correlations, but rather the higher order Correlation-Kinetic effects.

6.7. Conclusions

In conclusion, we have shown that the discontinuity in the KS theory electron-interaction potential $v_{ee}(r)$ is due solely to Correlation-Kinetic effects. As such we have derived a new expression for the discontinuity and shown it to be the work done in a conservative field representative of this effect. However, for finite fractional charge, irrespective of how small it is, there will always be contributions to the discontinuity from Pauli and Coulomb correlation [39]. Thus, an accurate approximation to the discontinuity may be obtained by summing the various contributions for small fractional charge. Finally, since the discontinuity is a fundamental property of KS theory, the understanding of its physical origin should aid in the construction of accurate approximations to the energy functional $E_{ee}^{KS}[\rho]$. The Correlation-Kinetic contribution to the discontinuity and thus to properties such as the band gap etc., may be determined via Q-DFT many-body perturbation theory described in Chapter 4, or by the use of an approximate correlated wavefunction derived via the satisfaction of sum rules [96].

Chapter 7

TIME-DEPENDENT QUANTAL DENSITY-FUNCTIONAL THEORY

7.1. Description of Time-Dependent Local Effective Potential in Terms of Schrödinger Wave-Function.

Time-dependent (TD) density-functional theory [6-9] (DFT) has recently been put on a mathematically rigorous foundation [6, 78-80], and its development continues [9, 81, 82]. In TDDFT, for external TD potentials that are physically realistic with appropriate boundary conditions and expandable in a Taylor series about the initial time t_0, it has been shown that the TD Schrödinger wavefunction $\Psi(t)$ is a functional of the TD electronic density $\rho(\boldsymbol{r},t)$ unique to within a time-dependent phase. As such, the expectation of any operator representative of a physical observable, is a unique functional of the density, and independent of the phase. The explicit dependence of the wavefunction $\Psi(t)$ on $\rho(\boldsymbol{r},t)$ is, however, at present unknown. As in stationary-state KS DFT, one defines within its TD version a *local* electron-interaction potential $v_{ee}(\boldsymbol{r},t)$, which leads to the same electronic density $\rho(\boldsymbol{r},t)$ as that of Schrödinger theory. In recent work [83] noninteracting v-representability for TD theory has been proved. In other words, there exists a s-system of noninteracting Fermions confined by the local potential $v_{ee}(\boldsymbol{r},t)$ with density $\rho(\boldsymbol{r},t)$. The proof of noninteracting v-representability is valid for Taylor expandable external potentials.

Within TD KS DFT, the local electron-interaction potential $v_{ee}(r,t)$ is defined as the functional derivative of an electron-interaction functional $A_{ee}[\rho]$. The potential $v_{ee}(r,t)$ can also be defined [84] through its relationship to the self-energy $\sum(r\tau, r'\tau')$ of many-body theory (where τ is pseudotime) via the TD Sham-Schlüter integral equation. It is also defined [81, 85] by the integral equation of the TD optimized potential method, in which case it depends upon the functional derivative of an unknown action functional of the KS orbitals taken with respect to these orbitals. We refer the reader to the original literature for further details.

In this chapter [11, 12] we extend stationary-state quantal density-functional theory (Q-DFT) to the case of time-dependent external potentials that are local but arbitrary. Noninteracting v-representability for such external potentials will be ***assumed***. (As noted above, noninteracting v-representability has been proved for Taylor expandable external potentials [83]). By deriving the TD differential virial theorem for the Schrödinger and s systems, we obtain a simple formal line-integral expression for the potential $v_{ee}(r,t)$ in terms of a conservative TD field $\mathcal{F}(r,t)$. ***For each instant of time,*** the potential then has the ***physical*** interpretation of being the work done to move an electron in this field. The derivation of this interpretation shows that in addition to the correlations due to the Pauli principle, Coulomb repulsion, and Correlation-Kinetic effects, the field $\mathcal{F}(r,t)$ is also representative of Correlation-Current-

Density effects which are a consequence of the difference in current density of the Schrödinger and s-systems. We also derive various sum rules of the s-system within the context of TD Q-DFT. The relationship between TD KS DFT and TD Q-DFT is developed via TD adiabatic coupling constant perturbation theory. This then leads to an understanding of the electron correlations represented by the KS exchange and correlation potentials. Finally, from the differential virial theorems, integral virial theorems are derived.

7.2. Definitions within Schrödinger and s-systems

The TD Schrödinger equation (in atomic units) is

$$i\frac{\partial}{\partial t}\Psi(t)=\hat{H}(t)\Psi(t) \quad , \tag{7.1}$$

where the Hamiltonian $\hat{H}(t)=\hat{T}+\hat{U}+\hat{V}(t)$, $\hat{T}=\sum_i -\frac{1}{2}\nabla_i^2$ is the kinetic energy operator, $\hat{U}=(1/2)\sum_{i\neq j}1/|\mathbf{r}_i-\mathbf{r}_j|$ the electron-interaction operator, and $\hat{V}(t)=\sum_i v(\mathbf{r}_i,t)$ the TD external potential operator which is assumed to be real. The TD density is the expectation $\rho(\mathbf{r},t)=\langle\Psi(t)|\hat{\rho}|\Psi(t)\rangle$ with $\hat{\rho}=\sum_i\delta(\mathbf{r}_i-\mathbf{r})$ the density operator. The TD single-particle density matrix $\gamma(\mathbf{r},\mathbf{r}',t)=N\sum_\sigma\int\Psi^*(\mathbf{r}\sigma,\mathbf{x}_2,\cdots\mathbf{x}_N;t)\,\Psi(\mathbf{r}'\sigma,\mathbf{x}_2,\cdots\mathbf{x}_N;t)\;d\mathbf{x}_2\cdots d\mathbf{x}_N=\langle\Psi(t)|\hat{X}|\Psi(t)\rangle$, with the Hermitian operator $\hat{X}$ defined in Eq. (2.11). (Here $\mathbf{x}\equiv\mathbf{r}\sigma$; $\int d\mathbf{x}\equiv\sum_\sigma\int d\mathbf{r}$, with σ the spin coordinate). The TD current density

$$\begin{aligned} j(r,t) &= (i/2)N\sum_{\sigma}\int(\Psi\nabla\Psi^{*} - \Psi^{*}\nabla\Psi)dx_2\cdots dx_N \\ &= (i/2)\sum_{\sigma}[\nabla' - \nabla'']\gamma(x',x'')|_{x'=x''=x}\ . \end{aligned} \tag{7.2}$$

The corresponding TD differential equation for the noninteracting s-system is

$$i\frac{\partial}{\partial t}\phi_j(x,t) = [-\frac{1}{2}\nabla^2 + v(r,t) + v_{ee}(r,t)]\phi_j(x,t)\quad , \tag{7.3}$$

with $\rho(r,t) = \langle\Phi\{\phi_j\}|\hat{\rho}|\Phi\{\phi_j\}\rangle = \sum\limits_{j}\sum\limits_{\sigma}|\phi_j(x,t)|^2$, where the expectation is with respect to the Slater determinant $\Phi\{\phi_j\}$ of the s-system orbitals $\phi_j(x,t)$. The resulting TD Dirac density matrix $\gamma_s(r,r',t) = \sum_{\sigma}\sum_{i}\phi_i^{*}(r\sigma,t)\phi_i(r'\sigma,t)$, and current density

$$\begin{aligned} j_s(r,t) &= (i/2)\sum_{\sigma}\sum_{j}[\phi_j(r,t)\nabla\phi_j^{*}(r,t) - \phi_j^{*}(r,t)\nabla\phi_j(r,t)] \\ &= (i/2)\sum_{\sigma}[\nabla' - \nabla'']\gamma_s(x',x'')|_{x'=x''=x}\ . \end{aligned} \tag{7.4}$$

7.3. Q-DFT Interpretation of Electron-Interaction Potential $v_{ee}(r,t)$.

The formal expression for the local electron-interaction potential $v_{ee}(r,t)$ is

$$v_{ee}(r,t) = -\int_{\infty}^{r}\mathcal{F}(r',t)\cdot dl'\quad , \tag{7.5}$$

where $\mathcal{F}(r,t)$ is a conservative field. Since $\nabla\times\mathcal{F}(r,t) = 0$, this expression may be interpreted ***at each instant of time*** as the work done to move an electron from its reference point at infinity to its position at r in the field. This work done is

path-independent.

The field $\mathcal{F}(\boldsymbol{r},t)$ may in turn be written as a sum of three components: an electron-interaction field $\mathcal{E}_{ee}(\boldsymbol{r},t)$ representative of Pauli and Coulomb correlations, the Correlation-Kinetic field $Z_{t_c}(\boldsymbol{r},t)$ representative of Correlation-Kinetic effects, and the Correlation-Current-Density field $J_c(\boldsymbol{r},t)$ representative of correlation-current-density effects:

$$\mathcal{F}(\boldsymbol{r},t) = \mathcal{E}_{ee}(\boldsymbol{r},t) + Z_{t_c}(\boldsymbol{r},t) + J_c(\boldsymbol{r},t) \quad . \tag{7.6}$$

Note that the component fields are not necessarily conservative. Their sum, however, always is.

The field $\mathcal{E}_{ee}(\boldsymbol{r},t)$ is obtained via Coulomb's law from the TD pair-correlation density $g(\boldsymbol{r},\boldsymbol{r}',t)$ so that

$$\mathcal{E}_{ee}(\boldsymbol{r},t) = \int \frac{g(\boldsymbol{r},\boldsymbol{r}',t)\ (\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\, d\boldsymbol{r}' \ , \tag{7.7}$$

where $g(\boldsymbol{r},\boldsymbol{r}',t) = \langle\Psi(t)|\hat{P}(\boldsymbol{r},\boldsymbol{r}')|\Psi(t)\rangle\ /\rho(\boldsymbol{r},t)$, with $\hat{P}(\boldsymbol{r},\boldsymbol{r}') = \sum_{i\neq j}\delta(\boldsymbol{r}_i-\boldsymbol{r})\delta(\boldsymbol{r}_j-\boldsymbol{r}')$ the pair-correlation operator. Since $g(\boldsymbol{r},\boldsymbol{r}',t) = \rho(\boldsymbol{r}',t) + \rho_{xc}(\boldsymbol{r},\boldsymbol{r}',t)$, where $\rho_{xc}(\boldsymbol{r},\boldsymbol{r}',t)$ is the TD quantum-mechanical Fermi-Coulomb hole charge distribution, we have $\mathcal{E}_{ee}(\boldsymbol{r},t) = \mathcal{E}_H(\boldsymbol{r},t) + \mathcal{E}_{xc}(\boldsymbol{r},t)$, where the conservative Hartree field $\mathcal{E}_H(\boldsymbol{r},t)$ and Pauli-Coulomb field $\mathcal{E}_{xc}(\boldsymbol{r},t)$ are, respectively

$$\begin{aligned} \mathcal{E}_H(\boldsymbol{r},t) &= \int \frac{\rho(\boldsymbol{r}',t)(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}' \\ \textit{and} \quad \mathcal{E}_{xc}(\boldsymbol{r},t) &= \int \frac{\rho_{xc}(\boldsymbol{r},\boldsymbol{r}',t)(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\, d\boldsymbol{r}' . \end{aligned} \tag{7.8}$$

The correlation-kinetic field $\boldsymbol{Z}_{t_c}(\boldsymbol{r},t)$ is the difference of two fields $\boldsymbol{z}_s(\boldsymbol{r},t)$ and $\boldsymbol{z}(\boldsymbol{r},t)$ derived from the kinetic-energy-density tensors $t_{s,\alpha\beta}(\boldsymbol{r},t;[\gamma_s])$ and $t_{\alpha\beta}(\boldsymbol{r},t;[\gamma])$ corresponding to the non-interacting and interacting Schrödinger systems, respectively. The field $\boldsymbol{Z}_{t_c}(\boldsymbol{r},t)$ is

$$\boldsymbol{Z}_{t_c}(\boldsymbol{r},t) = \frac{1}{\rho(\boldsymbol{r},t)} \left[\, \boldsymbol{z}_s(\boldsymbol{r},t) - \boldsymbol{z}(\boldsymbol{r},t) \,\right] , \tag{7.9}$$

where the component $z_\alpha(\boldsymbol{r},t)$ of the field $\boldsymbol{z}(\boldsymbol{r},t)$ is

$$z_\alpha(\boldsymbol{r},t) = 2 \sum_\beta \frac{\partial}{\partial r_\beta}\, t_{\alpha\beta}(\boldsymbol{r},t\,;[\gamma]) , \tag{7.10}$$

with $t_{\alpha\beta}(\boldsymbol{r},t;[\gamma]) = (1/4)(\partial^2/\partial r'_\alpha \partial r''_\beta + \partial^2/\partial r'_\beta \partial r''_\alpha)\,\gamma(\boldsymbol{r}',\boldsymbol{r}'',t)|_{\boldsymbol{r}'=\boldsymbol{r}''=\boldsymbol{r}}$. The field $\boldsymbol{z}_s(\boldsymbol{r},t)$ is similarly defined in terms of $\gamma_s(\boldsymbol{r},\boldsymbol{r}',t)$.

Finally the correlation-current density field $\boldsymbol{J}_c(\boldsymbol{r},t)$ is defined as

$$\boldsymbol{J}_c(\boldsymbol{r},t) = \frac{1}{\rho(\boldsymbol{r},t)} \frac{\partial}{\partial t} [\boldsymbol{j}_s(\boldsymbol{r},t) - \boldsymbol{j}(\boldsymbol{r},t)] , \tag{7.11}$$

where the current densities $\boldsymbol{j}(\boldsymbol{r},t)$ and $\boldsymbol{j}_s(\boldsymbol{r},t)$ are defined previously.

The proof of the expression for $v_{ee}(r,t)$ of Eq. (7.5) is described here briefly. In Appendix C, we give the detailed derivation of the time-dependent differential virial theorems via which this expression is derived. We write the wavefunction as $\Psi(X,t) = \Psi^R(X,t) + i\Psi^I(X,t)$, where $\Psi^R(X,t)$, $\Psi^I(X,t)$ are the real and imaginary parts of the wavefunction, and $X = x_1, x_2, \cdots x_N$. On substituting $\Psi(X,t)$ into the Schrödinger Eq. (7.1) and performing the spatial and time derivatives, we obtain the differential virial theorem for TD Schrödinger theory as

$$\nabla v(r,t) = -F(r,t) \quad , \tag{7.12}$$

where

$$\begin{aligned} F(r,t) &= -\mathcal{E}_{ee}(r,t) \\ &+ \frac{1}{\rho(r,t)}\left[-\frac{1}{4}\nabla\nabla^2\rho(r,t) + z(r,t;[\gamma]) + \frac{\partial}{\partial t}j(r,t)\right] . \end{aligned} \tag{7.13}$$

Next we write the KS orbital as $\phi_j(r,t) = \phi_j^R(r,t) + i\phi_j^I(r,t)$, where $\phi_j^R(r,t)$, $\phi_j^I(r,t)$ are its real and imaginary components. Again on substitution of $\phi_j(r,t)$ into the s-system, we obtain for the non-interacting system the differential virial theorem

$$\nabla v(r,t) = -F_s(r,t) \quad , \tag{7.14}$$

where

$$\begin{aligned} F_s &= \nabla v_{ee}(r,t) \\ &+ \frac{1}{\rho(r,t)}\left[-\frac{1}{4}\nabla\nabla^2\rho(r,t) + z_s(r,t;[\gamma_s]) + \frac{\partial}{\partial t}j_s(r,t)\right] . \end{aligned} \tag{7.15}$$

On equating Eqs. (7.12) and (7.14), we obtain

$$\nabla v_{xc}(\boldsymbol{r},t) = -\mathcal{F}(\boldsymbol{r},t) \quad , \tag{7.16}$$

which proves the result of Eq. (7.5). We note that in the proof, the neglect of a surface term implies that the result is valid only for bound states for which the wavefunction decays asymptotically faster than $1/r$.

If the system in the presence of the TD external potential has a symmetry which reduces the problem to being one-dimensional, or when such a symmetry is imposed by application of the central field approximation, the interacting $j(\boldsymbol{r},t)$ and noninteracting $j_s(\boldsymbol{r},t)$ current densities are the same. This is because for such systems, both $\nabla\times[j_s(\boldsymbol{r},t)-j(\boldsymbol{r},t)]=0$ and $\nabla\cdot[j_s(\boldsymbol{r},t)-j(\boldsymbol{r},t)]=0$, the latter condition arising from the continuity equation. In this case then $J_c(\boldsymbol{r},t)=0$, and the expression for $v_{xc}(\boldsymbol{r},t)$ is precisely the same as in stationary state DFT, but with a time dependence. Furthermore, for systems of such symmetry, the fields $\mathcal{E}_{xc}(\boldsymbol{r},t)$ and $Z_{t_c}(\boldsymbol{r},t)$ are separately conservative so that $\nabla\times\mathcal{E}_{xc}=\nabla\times Z_{t_c}=0$. We can then write

$$v_{xc}(\boldsymbol{r},t) = W_{xc}(\boldsymbol{r},t) + W_{t_c}(\boldsymbol{r},t) \quad , \tag{7.17}$$

where

$$W_{ee}(\boldsymbol{r},t) = -\int_{\infty}^{\boldsymbol{r}} \mathcal{E}_{ee}(\boldsymbol{r}',t)\cdot d\boldsymbol{l}' \quad and \quad W_{t_c}(\boldsymbol{r},t) = -\int_{\infty}^{\boldsymbol{r}} \boldsymbol{Z}_{t_c}(\boldsymbol{r}',t)\cdot d\boldsymbol{l}' \tag{7.18}$$

are the work done in the fields $\mathcal{E}_{ee}(\boldsymbol{r},t)$, and $\boldsymbol{Z}_{t_c}(\boldsymbol{r},t)$, respectively, at each instant of time.

With the Coulomb hole defined as the difference $\rho_c(\boldsymbol{r},\boldsymbol{r}',t) = \rho_{xc}(\boldsymbol{r},\boldsymbol{r}',t) - \rho_x(\boldsymbol{r},\boldsymbol{r}',t)$, where the Fermi hole is defined as $\rho_x(\boldsymbol{r},\boldsymbol{r}',t) = -|\gamma_s(\boldsymbol{r},\boldsymbol{r}',t)|/2\rho(\boldsymbol{r},t)$, the Pauli-Coulomb field may be further subdivided into its Pauli $\mathcal{E}_x(\boldsymbol{r},t)$ and Coulomb $\mathcal{E}_c(\boldsymbol{r},t)$ components:

$$\mathcal{E}_{xc}(\boldsymbol{r},t) = \mathcal{E}_x(\boldsymbol{r},t) + \mathcal{E}_c(\boldsymbol{r},t) , \tag{7.19}$$

where

$$\begin{aligned} \mathcal{E}_x(\boldsymbol{r},t) &= \int \frac{\rho_x(\boldsymbol{r},\boldsymbol{r}',t)(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3} d\boldsymbol{r}' \\ and \quad \mathcal{E}_c(\boldsymbol{r},t) &= \int \frac{\rho_c(\boldsymbol{r},\boldsymbol{r}',t)(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3} d\boldsymbol{r}' . \end{aligned} \tag{7.20}$$

Thus, the field $\mathcal{F}(\boldsymbol{r},t)$ may be written in terms of its components, each representative of a different electron correlation, as

$$\mathcal{F}(\boldsymbol{r},t) = \mathcal{E}_H(\boldsymbol{r},t) + \mathcal{E}_x(\boldsymbol{r},t) + \mathcal{E}_c(\boldsymbol{r},t) + \boldsymbol{Z}_{t_c}(\boldsymbol{r},t) + \boldsymbol{J}_c(\boldsymbol{r},t) . \tag{7.21}$$

The Hartree field $\mathcal{E}_H(\boldsymbol{r},t)$ is conservative: $\nabla \times \mathcal{E}_H(\boldsymbol{r},t) = 0$. Thus, the work $W_H(\boldsymbol{r},t)$ done in this field is path-independent. Equivalently,

$\mathcal{E}_H(\boldsymbol{r},t) = -\nabla W_H(\boldsymbol{r},t)$ where $W_H(\boldsymbol{r},t) = v_H(\boldsymbol{r},t)$. As noted previously, the remaining fields are not separately conservative. Their sum always is. Again, for systems of certain symmetry, the individual fields, with the exception of $\mathcal{J}_c(\boldsymbol{r},t)$ which vanishes, are separately conservative. As such the work done in each of the remaining fields is path-independent. Therefore, under such circumstances

$$v_{ee}(\boldsymbol{r},t) = W_H(\boldsymbol{r},t) + W_x(\boldsymbol{r},t) + W_c(\boldsymbol{r},t) + W_{t_c}(\boldsymbol{r},t) \ . \qquad (7.22)$$

We note that any knowledge of the system wavefunction can, via the interpretation provided, lead to a corresponding understanding of the structure of the local potential $v_{ee}(\boldsymbol{r},t)$. However, within the Pauli-correlated approximation in which Correlation-Current-Density, Correlation-Kinetic and Coulomb correlation effects are neglected so that $\mathcal{F}^{app}(\boldsymbol{r},t) = \mathcal{E}_H(\boldsymbol{r},t) + \mathcal{E}_x(\boldsymbol{r},t)$, a fully self-consistent solution of the TD s-system equations can be achieved. As the Pauli field $\mathcal{E}_x(\boldsymbol{r},t)$ is not necessarily conservative, one would then employ its irrotational component to obtain a path-independent Pauli potential $W_x^{eff}(\boldsymbol{r},t) = \int d\boldsymbol{r}' \rho_x^{eff}(\boldsymbol{r}',t)/|\boldsymbol{r}-\boldsymbol{r}'|$, where $\rho_x^{eff}(\boldsymbol{r},t) = (1/4\pi)\nabla \cdot \mathcal{E}_x(\boldsymbol{r},t)$. If the field $\mathcal{E}_x(\boldsymbol{r},t)$ is spherically averaged, the Pauli potential would be the work done $W_x(\boldsymbol{r},t)$ at each instant in the averaged field. Note that $W_x^{eff}(\boldsymbol{r},t)$ and $W_x(\boldsymbol{r},t)$ are exactly known being explicitly defined in terms of the s-system orbitals through the Fermi hole charge. Since stationary state results for both the ground [19, 45] and excited states [19, 86-95] within the Pauli-correlated approximation are highly accurate, we expect those of the time-dependent calculations to be also, and particularly so in the linear-response regime, where the leading term for the Pauli potential $W_x(r,t)$ would be $W_x(r)$. Coulomb correlation, Correlation-Kinetic, and Correlation-Current-Density effects can also be introduced either by approximating the wavefunction directly or by employing approximate functionals [96] $\Psi^{app}[\rho]$. All these approximation schemes are independent of the strength of the perturbation.

7.4. Sum Rules

In this section we derive various sum rules within the context of TD Q-DFT.

A. We prove that in accordance with Newton's third law, the field $\mathcal{F}(r,t)$ representative of all the electron correlations exerts no net force on the system:

$$\int dr \rho(r,t) \mathcal{F}(r,t) = 0 \ , \tag{7.23}$$

To do so we prove that the electron-interaction $\mathcal{E}_{ee}(r,t)$, Correlation-Kinetic $Z_{t_c}(r,t)$, and Correlation-Current-Density $J_c(r,t)$ components of $\mathcal{F}(r,t)$ separately satisfy this sum rule.

Electron-interaction component

With the pair-correlation function $h(r,r',t)$ defined as $h(r,r',t) = g(r,r',t)/\rho(r',t)$, we have

$$\int d\mathbf{r}\rho(\mathbf{r},t)\mathcal{E}_{ee}(\mathbf{r},t) = \int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r},t)\rho(\mathbf{r}',t)h(\mathbf{r},\mathbf{r}',t)\frac{(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} \ . \tag{7.24}$$

On interchanging $\mathbf{r}$ and $\mathbf{r}'$, the right hand side of Eq. (7.24) is

$$\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r},t)\rho(\mathbf{r}',t)h(\mathbf{r}',\mathbf{r},t)\frac{(\mathbf{r}'-\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|^3} \ . \tag{7.25}$$

Since $h(\mathbf{r},\mathbf{r}',t) = h(\mathbf{r}',\mathbf{r},t)$, Eq. (7.24) is

$$\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r},t)\rho(\mathbf{r}',t)h(\mathbf{r},\mathbf{r}',t)\frac{(\mathbf{r}'-\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|^3} = -\int d\mathbf{r}\rho(\mathbf{r},t)\mathcal{E}_{ee}(\mathbf{r},t) \ , \tag{7.26}$$

so that

$$\int d\mathbf{r}\rho(\mathbf{r},t)\mathcal{E}_{ee}(\mathbf{r},t) = 0 \ . \tag{7.27}$$

Now together with

$$\int d\mathbf{r}\rho(\mathbf{r},t)\nabla v_H(\mathbf{r},t) = -\int d\mathbf{r}\rho(\mathbf{r},t)\mathcal{E}_H(\mathbf{r},t) = 0 \ , \tag{7.28}$$

and the symmetry of $h_s(\mathbf{r},\mathbf{r}',t) = g_s(\mathbf{r},\mathbf{r}',t)/\rho(\mathbf{r}',t)$, we have

$$\int d\mathbf{r}\rho(\mathbf{r},t)\mathcal{E}_x(\mathbf{r},t) = 0 \ , \tag{7.29}$$

and consequently

$$\int d\mathbf{r}\rho(\mathbf{r},t)\mathcal{E}_c(\mathbf{r},t) = 0 \ . \tag{7.30}$$

Correlation-Kinetic Component

We next prove

$$\int dr\rho(r,t)Z_{t_c}(r,t) = 0 \ . \qquad (7.31)$$

To prove this, let us first show that

$$\int drz(r,t) = 0 \quad and \quad \int drz_s(r,t) = 0. \qquad (7.32)$$

Consider the integral for the component $z_\alpha(r,t)$:

$$\int drz_\alpha(r,t) = 2\sum_\beta \int dr\frac{\partial}{\partial r_\beta}t_{\alpha\beta}(r,t,[\gamma]) \ . \qquad (7.33)$$

The integral

$$\int dydz \int dx\frac{\partial}{\partial x}t_{\alpha x}(r,t,[\gamma]) = 0 \ , \qquad (7.34)$$

etc., since the tensor vanishes at the boundary $x = +\infty, -\infty$. The same arguments apply to the integral of $z_{\alpha,s}(r,t;[\gamma_s])$. Thus, the sum rule of Eq. (7.31) is proved.

Correlation-Current-Density component

We next prove that

$$\int dr\rho(r,t)J_c(r,t) = 0 \ . \qquad (7.35)$$

Consider the integral

$$\int drj_x(r,t) = -\int dydzxdj_x = -\int dxdydzx\frac{\partial j_x}{\partial x} \ , \qquad (7.36)$$

where the second step is a consequence of the vanishing of the current density at the boundaries $x = +\infty, -\infty$. Now, because for the same reason

$$\int dxdydzx\frac{\partial j_y}{\partial y} = 0 \quad and \quad \int dxdydzx\frac{\partial j_z}{\partial z} = 0 \ , \tag{7.37}$$

we have

$$\int d\boldsymbol{r} j_x(\boldsymbol{r},t) = -\int d\boldsymbol{r} x\nabla\cdot\boldsymbol{j}(\boldsymbol{r},t) \ . \tag{7.38}$$

Therefore

$$\int d\boldsymbol{r}\rho(\boldsymbol{r},t)\boldsymbol{J}_c(\boldsymbol{r},t) = \frac{\partial}{\partial t}\int d\boldsymbol{r}\boldsymbol{r}\nabla\cdot[\boldsymbol{j}_s(\boldsymbol{r},t) - \boldsymbol{j}(\boldsymbol{r},t)] = 0 \ . \tag{7.39}$$

as a result of the continuity conditions

$$\nabla\cdot\boldsymbol{j}(\boldsymbol{r},t) = -\frac{\partial\rho(\boldsymbol{r},t)}{\partial t} \quad and \quad \nabla\cdot\boldsymbol{j}_s(\boldsymbol{r},t) = -\frac{\partial\rho(\boldsymbol{r},t)}{\partial t} \ . \tag{7.40}$$

Thus, the sum rule of Eq. (7.35) is proved. Furthermore, we have proved that the different correlations separately do not contribute to the force on the system.

Employing Eq. (7.16) in Eq. (7.23) leads to the equivalent result

$$\int d\boldsymbol{r}\rho(\boldsymbol{r},t)\nabla v_{ee}(\boldsymbol{r},t) = 0 \ . \tag{7.41}$$

and since $v_{ee}(\boldsymbol{r},t) = v_H(\boldsymbol{r},t) + v_{xc}(\boldsymbol{r},t)$ we have, from Eq. (7.28),

$$\int d\boldsymbol{r}\rho(\boldsymbol{r},t)\nabla v_{xc}(\boldsymbol{r},t) = 0 \ . \tag{7.42}$$

Alternate proofs of Eq. (7.42) are given in the literature [7, 97].

B. It is stated in the literature [7] that the torque of the s-system exchange-correlation potential $v_{xc}(\boldsymbol{r})$ vanishes. We prove this not to be the case. The correct sum rule is

$$\int d\boldsymbol{r}\rho(\boldsymbol{r},t)\times\nabla v_{xc}(\boldsymbol{r},t) = -\int d\boldsymbol{r}\rho(\boldsymbol{r},t)\boldsymbol{r}\times\boldsymbol{J}_c(\boldsymbol{r},t)\ . \tag{7.43}$$

The torque vanishes only for those systems of special symmetry as discussed previously for which $\boldsymbol{j}(\boldsymbol{r},t)=\boldsymbol{j}_s(\boldsymbol{r},t)$. We provide two proofs of Eq. (7.43)

(i) For the first of these proofs we require to show

$$\int d\boldsymbol{r}\rho(\boldsymbol{r},t)\boldsymbol{r}\times\boldsymbol{\mathcal{E}}_{ee}(\boldsymbol{r},t) = 0\ , \tag{7.44}$$

and

$$\int d\boldsymbol{r}\rho(\boldsymbol{r},t)\boldsymbol{r}\times\boldsymbol{Z}_{t_c}(\boldsymbol{r},t) = 0\ . \tag{7.45}$$

Eq. (7.44) is proved by once again employing the symmetry property of the pair-correlation fiunction $h(\boldsymbol{r},\boldsymbol{r}',t)$ as in subsection A above. Similarly, we have

$$\int d\boldsymbol{r}\rho(\boldsymbol{r},t)\boldsymbol{r}\times\nabla v_H(\boldsymbol{r},t) \equiv -\int d\boldsymbol{r}\rho(\boldsymbol{r},t)\boldsymbol{r}\times\boldsymbol{\mathcal{E}}_H(\boldsymbol{r},t) = 0\ . \tag{7.46}$$

To prove Eq. (7.45) we need to show

$$\int d\boldsymbol{r}\boldsymbol{r}\times\boldsymbol{z}(\boldsymbol{r},t) = 0 \quad and \quad \int d\boldsymbol{r}\boldsymbol{r}\times\boldsymbol{z}_s(\boldsymbol{r},t) = 0\ . \tag{7.47}$$

Consider the component

$$
\begin{aligned}
[\int d\mathbf{r}\,\mathbf{r}\times\mathbf{z}(\mathbf{r},t)]_i &= 2\int d\mathbf{r}\sum_{jkl}\epsilon_{ijk}r_j\frac{\partial}{\partial r_l}t_{kl}(\mathbf{r},t,[\gamma]) \\
&= -2\sum_{jk}\int d\mathbf{r}\,\epsilon_{ijk}t_{kj}(\mathbf{r},t,[\gamma]) = 0 \ ,
\end{aligned}
\tag{7.48}
$$

where we have again employed the vanishing of the tensor at the boundaries at infinity, and the properties $t_{kj}(\mathbf{r},t) = t_{jk}(\mathbf{r},t)$ and $\epsilon_{ijk} = -\epsilon_{ikj}$. This proves the first condition of Eq. (7.47). The second is similarly proved. Thus, the torque sum rule is proved.

(ii) The second proof is along the lines of Ref. [7] and employs the quantum mechanical equation of motion for the expectation value of an operator $\hat{Q}(t)$:

$$
\frac{d}{dt}\langle\Psi(t)|\hat{Q}(t)|\Psi(t)\rangle = \langle\Psi(t)|\frac{\partial\hat{Q}}{\partial t} - i[\hat{Q}(t),\hat{H}(t)]|\Psi(t)\rangle \ . \tag{7.49}
$$

For the angle operator $\hat{\phi} = \sum_i \mathbf{r}_i\times\mathbf{p}_i$ we have for the difference

$$
\begin{aligned}
&\frac{d}{dt}[\langle\Psi(t)|\hat{\phi}|\Psi(t)\rangle - \langle\Phi(t)|\hat{\phi}|\Phi(t)\rangle] \\
&= \int d\mathbf{r}\,\rho(\mathbf{r},t)\mathbf{r}\times\nabla v_{xc}(\mathbf{r},t) \ ,
\end{aligned}
\tag{7.50}
$$

where we have employed Eq. (7.46). Now

$$
\frac{d}{dt}\langle\Psi(t)|\hat{\phi}|\Psi(t)\rangle = -i\frac{d}{dt}\int\sum_i \mathbf{r}_i\times\Psi^*(X,t)\nabla_i\Psi(X,t)dX \ , \tag{7.51}
$$

with a similar equation for the s-system so that the left hand side of Eq. (7.50) is

$$= -\frac{\partial}{\partial t}\int d\mathbf{r}\,\mathbf{r}\times[\mathbf{j}_s(\mathbf{r},t) - \mathbf{j}(\mathbf{r},t)] \ , \tag{7.52}$$

which proves the torque sum rule.

C. In TD linear response theory [7, 98], the external potential is of the form $v(\mathbf{r},t) = v_0(\mathbf{r}) + v_1(\mathbf{r},t)\theta(t-t_0)$, where $\theta(t)$ is the Heavyside step function. For $t \le t_0$, the system is in its ground state with external potential $v_0(\mathbf{r})$ and density $\rho_0(\mathbf{r})$. In TD-DFT one defines the KS exchange-correlation kernel, in which all dynamic effects to linear order in the perturbing potential are incorporated, as

$$f_{xc}(\mathbf{r},t,\mathbf{r}',t';\rho_0) = \frac{\delta v_{xc}(\mathbf{r},t)}{\delta\rho(\mathbf{r}',t)}\Big|_{\rho_0} \ , \tag{7.53}$$

where $\rho(\mathbf{r},t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r},t)$, and $\delta\rho(\mathbf{r},t)$ is the deviation from the ground state density. Substitution of $\rho(\mathbf{r},t)$ into Eq.(7.43) leads to $O(\delta)$:

$$\begin{aligned}\int d\mathbf{r}\,\delta\rho(\mathbf{r},t)\mathbf{r}\times\nabla v_{xc}(\mathbf{r};\rho_0) + \int d\mathbf{r}\,\rho_0(\mathbf{r})\mathbf{r}\times\nabla\delta v_{xc}(\mathbf{r},t)\\ + \int d\mathbf{r}\,\rho_0(\mathbf{r})\mathbf{r}\times\delta\mathbf{J}_c(\mathbf{r},t) = 0 \ ,\end{aligned} \tag{7.54}$$

where we have used $\mathbf{J}_c(\mathbf{r},t)\big|_{t=t_0} = 0$. Employing the definition of the differential of a functional, we have

$$\delta v_{xc}(\mathbf{r},t) = \int \frac{\delta v_{xc}(\mathbf{r},t)}{\delta\rho(\mathbf{r}',t')}\delta\rho(\mathbf{r}',t')d\mathbf{r}'dt' \ , \tag{7.55}$$

with a similar expression for $\delta\mathbf{J}_c(\mathbf{r},t)$. Thus, Eq. (7.54) may be written as

$$\begin{aligned}&\int dr\,\delta\rho(r,t)\,r\times\nabla v_{xc}(r;\rho_0)+\int dr\,\rho_0(r)\,r\times\nabla\int f_{xc}(r,t;r',t')\\&\delta\rho(r',t')\,dr'\,dt'+\int dr\,\rho_0(r)\,r\times\int\frac{\delta J_c(r,t)}{\delta\rho(r',t')}\,\delta\rho(r',t')\,dr'\,dt'=0,\end{aligned}\tag{7.56}$$

or equivalently

$$\begin{aligned}&\int dt'\,dr'\,\delta(t-t')\,\delta\rho(r',t')\,r'\times\nabla' v_{xc}(r';\rho_0)\\&+\int dt'\,dr'\,\delta\rho(r',t')\int dr\,\rho_0(r)\,r\times\nabla f_{xc}(r,t;r',t')\\&+\int dt'\,dr'\,\delta\rho(r',t')\int dr\,\rho_0(r)\,r\times\mathfrak{J}_c(r,t;r',t')\;=\;0\;,\end{aligned}\tag{7.57}$$

where

$$\mathfrak{J}_c(r,t;r',t')\;=\;\frac{\delta J_c(r,t)}{\delta\rho(r',t')}\;.\tag{7.58}$$

From Eq. (7.57) it follows that

$$\begin{aligned}&\delta(t-t')\,r'\times\nabla' v_{xc}(r';\rho_0)\;+\;\int dr\,\rho_0(r)\,r\times\nabla f_{xc}(r,t;r',t')\\&+\int dr\,\rho_0(r)\,r\times\mathfrak{J}_c(r,t;r',t')\;=\;0\;.\end{aligned}\tag{7.59}$$

On Fourier transforming with respect to $(t-t')$ we have the sum rule

$$\begin{aligned}&r'\times\nabla' v_{xc}(r';\rho_0)\;+\;\int dr\,\rho_0(r)\,r\times\nabla f_{xc}(r,r',\omega)\\&+\int dr\,\rho_0(r)\,r\times\mathfrak{J}_c(r,r';\omega)\;=\;0\;.\end{aligned}\tag{7.60}$$

On multiplying by $\rho_0(r')$ and integrating over r' we have the sum rule

$$\begin{aligned}&\int d\boldsymbol{r}d\boldsymbol{r}'\,\rho_0(\boldsymbol{r})\rho_0(\boldsymbol{r}')\boldsymbol{r}\times\nabla f_{xc}(\boldsymbol{r},\boldsymbol{r}';\omega)\\ +&\int d\boldsymbol{r}d\boldsymbol{r}'\,\rho_0(\boldsymbol{r})\rho_0(\boldsymbol{r}')\boldsymbol{r}\times\mathfrak{F}_c(\boldsymbol{r},\boldsymbol{r}';\omega) = 0\ ,\end{aligned} \qquad (7.61)$$

where we have employed the stationary state sum rule [99] $\int d\boldsymbol{r}\rho_0(\boldsymbol{r})\,\boldsymbol{r}\times\nabla v_{xc}(\boldsymbol{r};\rho_0) = 0$. The terms involving $\mathfrak{F}_c(\boldsymbol{r},\boldsymbol{r}',\omega)$ in Eqs. (7.60) and (7.61) are absent from the sum rules in the literature [7, 98].

7.5. Relationship between Q-DFT and KS-DFT via the Adiabatic Coupling Constant Perturbation Expansion

In adiabatic coupling constant (λ) theory [100, 101], the Hamiltonian $H^{\lambda}(t)$ is defined as $H^{\lambda}(t) = T + V_{\lambda}(t) + \lambda U$ $(0 \leq \lambda \leq 1)$, where the operator $V_{\lambda} = \sum_i v_{\lambda}(\boldsymbol{r}_i, t)$ is constrained such that its addition to $\lambda\hat{U}$ leads to the density for the fully interacting system ($\lambda = 1$). Thus the wavefunction $\Psi^{\lambda}(\boldsymbol{X}, t)$ is such that the expectation $\langle\Psi^{\lambda}(t)\,|\,\hat{\rho}\,|\,\Psi^{\lambda}(t)\rangle = \rho^{\lambda=1}(\boldsymbol{r},t) = \rho(\boldsymbol{r},t)$. The $\lambda = 0$ case corresponds to the s-system. In this theory the density is independent of λ. Thus, we may also write the s-system potential as $v_s(\boldsymbol{r},t) = v_{\lambda}(\boldsymbol{r},t) + v_{ee}^{\lambda}(\boldsymbol{r},t)$. The corresponding Q-DFT equations Eqs. (7.5-7.16) are the same except that they are written with a superscript λ wherever appropriate.

To derive the relationship between Q-DFT and KS-DFT, we first express the fields in terms of the coupling constant perturbation expansion. (For the relationship between these theories in the time-independent case,we refer the reader to [53]). Following Levy and March [51], we expand the wavefunction $\Psi^{\lambda}(X,t)$ as

$$\Psi^{\lambda}(X,t) = \Phi\{\phi_i\}(X,t) + \lambda\Psi_1(X,t) + \lambda^2\Psi_2(X,t) + \cdots , \tag{7.62}$$

where $\Phi\{\phi_i\}$ is the Slater determinant of the s-system. The resulting pair-correlation density $g^{\lambda}(r,r^{\prime},t)$ and single-particle density matrix $\gamma^{\lambda}(r,r^{\prime},t)$ are

$$g^{\lambda}(r,r^{\prime},t) = g_s(r,r^{\prime},t) + \lambda g_1^c(r,r^{\prime} t) + \lambda^2 g_2^c(r,r^{\prime},t) + \cdots , \tag{7.63}$$

and

$$\gamma^{\lambda}(r,r^{\prime},t) = \gamma_s(r,r^{\prime},t) + \lambda\gamma_1^c(r,r^{\prime},t) + \lambda^2\gamma_2^c(r,r^{\prime},t) + \cdots , \tag{7.64}$$

where $g_s(r,r^{\prime},t)$ is as defined previously, and $O_1^c(r,r^{\prime},t) = \langle\Psi_1(t)|\hat{O}|\Phi(t)\rangle + \langle\Phi(t)|\hat{O}|\Psi_1(t)\rangle$ etc.. The fields $\mathcal{E}_{ee}^{\lambda}(r,t)$, $Z_{t_c}^{\lambda}(r,t)$, and $J_c^{\lambda}(r,t)$ which arise from these sources are

$$\mathcal{E}_{ee}^{\lambda}(r,t) = \lambda\mathcal{E}_H(r,t) + \lambda\mathcal{E}_x(r,t) + \lambda^2\mathcal{E}_{c,1}(r,t) + \lambda^3\mathcal{E}_{c,2}(r,t) + \cdots , \tag{7.65}$$

$$Z_{t_c}^{\lambda}(r,t) = -\lambda Z_{t_c,1} - \lambda^2 Z_{t_c,2}(r,t) - \lambda^3 Z_{t_c,3}(r,t) - \cdots , \tag{7.66}$$

and

$$J_c^{\lambda}(r,t) = -\lambda J_{c,1}(r,t) - \lambda^2 J_{c,2}(r,t) - \lambda^3 J_{c,3}(r,t) - \cdots , \tag{7.67}$$

where $\mathcal{E}_{c,1}(r,t) = \int dr^{\prime}\, g_1^c(r,r^{\prime},t)(r-r^{\prime})/|r-r^{\prime}|^3$, $Z_{t_c,1}(r,t) = z(r,t,\gamma_1^c)/\rho(r,t)$, and $J_{c,1}(r,t) = (\partial j(r,t;\gamma_1^c)/\partial t)/\rho(r,t)$ etc.. The expansion of these fields can then be employed to obtain the electron-interaction potential $v_{ee}^{\lambda}(r,t)$ to each order. For spherically symmetrized systems etc., the work done $W_{ee}^{\lambda}(r,t)$ and $W_{t_c}^{\lambda}(r,t)$ in the fields $\mathcal{E}^{\lambda}_{ee}(r,t)$ and $Z^{\lambda}_{t_c}(r,t)$, respectively, may then be expressed as

$$W^{\lambda}_{ee}(r,t) = \lambda W_H(r,t) + \lambda W_x(r,t) + \lambda^2 W_{c,1}(r,t) + \lambda^3 W_{c,2}(r,t) + \cdots \,, \qquad (7.68)$$

and

$$W^{\lambda}_{t_c}(r,t) = -\lambda W_{t_c,1}(r,t) - \lambda^2 W_{t_c,2}(r,t) - \cdots \,, \qquad (7.69)$$

where $W_{c,1}(r,t)$, $W_{t_c,1}(r,t)$ etc. are the work done in the fields $\mathcal{E}_{c,1}(r,t)$, $Z_{t_c,1}(r,t)$, respectively, etc.. We reiterate that for such systems, there is no contribution to the potential from Correlation-Current-Density effects.

In KS TD-DFT [7] the Hartree $A_H[\rho]$ and exchange $A_x[\rho]$ action functionals are defined, respectively as

$$A_H[\rho] = \frac{1}{2}\int_{t_0}^{t_1} dt \int dr dr' \frac{\rho(r,t)\rho(r',t)}{|r-r'|} \,, \qquad (7.70)$$

and

$$A_x[\rho] = \frac{1}{2}\int_{t_0}^{t_1} dt \int dr dr' \frac{\rho(r,t)\rho_x(r,r',t)}{|r-r'|} \,. \qquad (7.71)$$

The actions scale linearly in λ: $A^{\lambda}_H = \lambda A_H$, $A^{\lambda}_x = \lambda A_x$. Thus, the corresponding Hartree $v_H(r,t)$ and KS exchange $v_x(r,t)$ potentials also scale linearly:

$$v^{\lambda}_H(r,t) = \lambda v_H(r,t) \,, \qquad (7.72)$$

and

$$v_x^\lambda(r,t) = \lambda v_x(r,t) \ . \tag{7.73}$$

Now since $\nabla v_{ee}^\lambda(r,t) = -\mathcal{F}^\lambda(r,t)$ with $\mathcal{F}^\lambda(r,t) = \mathcal{E}_{ee}^\lambda(r,t) + Z_{t_c}^\lambda(r,t) + J_c^\lambda(r,t)$, we have on substituting the KS definition of $v_{ee}^\lambda(r,t)$ that

$$\nabla[v_H^\lambda(r,t) + v_x^\lambda(r,t) + v_c^\lambda(r,t)] = -[\mathcal{E}_{ee}^\lambda(r,t) + Z_{t_c}^\lambda(r,t) + J_c^\lambda(r,t)] \ . \tag{7.74}$$

On substitution of the expansions for the fields, and on equating terms of equal order, we obtain the components of the KS potential in terms of the fields as

$$\nabla v_H(r,t) = -\mathcal{E}_H(r,t) \tag{7.75}$$

$$\nabla v_x(r,t) = -[\mathcal{E}_x(r,t) - Z_{t_c,1}(r,t) - J_{c,1}(r,t)] \tag{7.76}$$

$$\nabla v_{c,2}(r,t) = -[\mathcal{E}_{c,1}(r,t) - Z_{t_c,2}(r,t) - J_{c,2}(r,t)] \tag{7.77}$$

$$\nabla v_{c,3}(r,t) = -[\mathcal{E}_{c,2}(r,t) - Z_{t_c,3}(r,t) - J_{c,3}(r,t)] \ , \ etc., \tag{7.78}$$

where $v_{c,2}(r,t)$, $v_{c,3}(r,t)$ etc., are the KS correlation potential components to $O(\lambda^2)$, $O(\lambda^3)$ etc.. Note that the KS correlation potential commences in second order.

Interpretation of KS exchange potential $v_x(r,t)$

From Eq. (7.76) we see that the KS exchange potential $v_x(r,t)$ is the work done to move an electron in a conservative field $R(r,t)$:

$$v_x(\boldsymbol{r},t) = -\int_{\infty}^{\boldsymbol{r}} \boldsymbol{R}(\boldsymbol{r}',t)\cdot d\boldsymbol{l}' \ , \qquad (7.79)$$

where $\boldsymbol{R}(\boldsymbol{r},t) = \boldsymbol{\mathcal{E}}_x(\boldsymbol{r},t) - \boldsymbol{Z}_{t_c,1}(\boldsymbol{r},t) - \boldsymbol{J}_{c,1}(\boldsymbol{r},t)$. Since $\nabla \times \boldsymbol{R}(\boldsymbol{r},t) = 0$, this work done is path-independent. We also see that the KS exchange potential $v_x(\boldsymbol{r},t)$ is representative not only of electron correlations due to the Pauli principle, but also of the lowest-order $O(\lambda)$ contributions due to Correlation-Kinetic and Correlation-Current-Density effects. For spherically symmetrized systems etc., the fields $\boldsymbol{\mathcal{E}}_x(\boldsymbol{r},t)$ and $\boldsymbol{Z}_{t_c,1}(\boldsymbol{r},t)$ are separately conservative and $\boldsymbol{J}_{c,1}(\boldsymbol{r},t) = 0$, so that we may write

$$v_x(\boldsymbol{r},t) = W_x(\boldsymbol{r},t) - W_{t_c,1}(\boldsymbol{r},t) \ , \qquad (7.80)$$

where $W_x(\boldsymbol{r},t)$ is the work done in the field $\boldsymbol{\mathcal{E}}_x(\boldsymbol{r},t)$ of the Fermi hole charge, and $W_{t_c,1}(\boldsymbol{r},t)$ the work done in the field $\boldsymbol{Z}_{t_c,1}(\boldsymbol{r},t)$.

Interpretation of KS correlation potential $v_c(\boldsymbol{r},t)$

From Eqs. (7.77) and (7.78), the KS correlation potential components $v_{c,2}(\boldsymbol{r},t)$, $v_{c,3}(\boldsymbol{r},t)$ etc., are separately the work done in conservative fields:

$$v_{c,2}(\boldsymbol{r},t) = -\int_{\infty}^{\boldsymbol{r}} [\boldsymbol{\mathcal{E}}_{c,1}(\boldsymbol{r}',t) - \boldsymbol{Z}_{t_c,2}(\boldsymbol{r}',t) - \boldsymbol{J}_{c,2}(\boldsymbol{r}',t)]\cdot d\boldsymbol{l}' \ , \qquad (7.81)$$

$$v_{c,3}(\boldsymbol{r},t) = -\int_{\infty}^{\boldsymbol{r}} [\boldsymbol{\mathcal{E}}_{c,2}(\boldsymbol{r}',t) - \boldsymbol{Z}_{t_c,3}(\boldsymbol{r}',t) - \boldsymbol{J}_{c,3}(\boldsymbol{r}',t)]\cdot d\boldsymbol{l}' \ , \ etc. \qquad (7.82)$$

The work done at each order is path-independent, and at each order, Coulomb correlation, Correlation-Kinetic, and Correlation-Current-Density effects contribute to the KS correlation potential.

Integral virial theorems

We next derive the integral virial theorem relating the components of the total energy to the local electron-interaction potential $v_{ee}^{\lambda}(r,t)$ for *arbitrary* coupling strength. Acting on the equation

$$-\nabla v_{ee}^{\lambda}(r,t) = \mathcal{E}_{ee}^{\lambda}(r,t) + Z_{t_c}^{\lambda}(r,t) + J_c^{\lambda}(r,t) , \tag{7.83}$$

with the operator $\int dr\rho(r,t)r\cdot$, we obtain

$$-\int dr\rho(r,t)r\cdot\nabla v_{ee}^{\lambda}(r,t) = E_{ee}^{\lambda}(t) + 2T_c^{\lambda}(t) + \int dr\rho(r,t)r\cdot J_c^{\lambda}(r,t) , \tag{7.84}$$

where

$$E_{ee}^{\lambda}(t) = \langle\Psi^{\lambda}(t)|\hat{U}|\Psi^{\lambda}(t)\rangle = \int dr\rho(r,t)r\cdot\mathcal{E}_{ee}^{\lambda}(r,t) , \tag{7.85}$$

is the quantum-mechanical electron-interaction energy, and

$$\begin{aligned} T_c^{\lambda}(t) &= \langle\Psi^{\lambda}(t)|\hat{T}|\Psi^{\lambda}(t)\rangle - \langle\Phi(t)|\hat{T}|\Phi(t)\rangle \\ &= \frac{1}{2}\int dr\rho(r,t)r\cdot Z_{t_c}^{\lambda}(r,t) , \end{aligned} \tag{7.86}$$

the Correlation-Kinetic energy.

Next we prove that

$$\int dr\rho(r,t)r \cdot J_c^\lambda(r,t) = 0 \ . \tag{7.87}$$

To do so we must prove that

$$\int drr \cdot \frac{\partial}{\partial t} j^\lambda(r,t) = \int drr \cdot \frac{\partial}{\partial t} j_s(r,t) \ . \tag{7.88}$$

Consider the integral

$$\begin{aligned} \int drxj_x^\lambda(r,t) &= \frac{1}{2}\int dydzj_x^\lambda(r,t)dx^2 \\ &= -\frac{1}{2}\int dydzx^2dj_x^\lambda(r,t) \\ &= -\frac{1}{2}\int drx^2\frac{\partial j_x^\lambda(r,t)}{\partial x} \ , \end{aligned} \tag{7.89}$$

where we have employed the vanishing of the current density $j_x^\lambda(r,t)$ at the boundaries at $x = +\infty, -\infty$. Now, since for the same reason

$$\int drx^2\frac{\partial j_y^\lambda(r,t)}{\partial y} = 0 \quad and \quad \int drx^2\frac{\partial j_z^\lambda(r,t)}{\partial z} = 0 \ , \tag{7.90}$$

we have

$$\int drxj_x^\lambda(r,t) = -\frac{1}{2}\int drx^2\nabla \cdot j^\lambda(r,t) \ , \tag{7.91}$$

and therefore

$$\int drr \cdot j^\lambda(r,t) = -\frac{1}{2}\int drr^2\nabla \cdot j^\lambda(r,t) = \frac{1}{2}\int drr^2\frac{\partial\rho(r,t)}{\partial t} \ , \tag{7.92}$$

where in the last step we have employed the continuity equation

$\nabla \cdot j^{\lambda}(r,t) = -\partial\rho(r,t)/\partial t$. For the s-system, the right hand side of Eq. (7.89) is the same. Hence Eq. (7.88) is proved as is the sum rule of Eq. (7.87). The integral virial theorem is then

$$E_{ee}^{\lambda}(t) \;+\; 2T_c^{\lambda}(t) \;=\; -\int dr\rho(r,t)r\cdot\nabla v_{ee}^{\lambda}(r,t)\ . \qquad (7.93)$$

Note that Correlation-Current-Density effects do not contribute explicitly to the energy. Their contribution is implicit via the potential $v_{ee}^{\lambda}(r,t)$. Of course, for spherically symmetrized systems etc., they contribute to neither.

For the fully interacting case $\lambda = 1$, the above theorem reduces to

$$E_{ee}(t) \;+\; 2T_c(t) \;=\; -\int dr\rho(r,t)r\cdot\nabla v_{ee}(r,t)\ , \qquad (7.94)$$

or equivalently

$$E_{xc}(t) \;+\; 2T_c(t) \;=\; -\int dr\rho(r,t)r\cdot\nabla v_{xc}(r,t) \qquad (7.95)$$

and

$$E_H(t) \;=\; \int dr\rho(r,t)r\cdot\mathcal{E}_H(r,t)\ . \qquad (7.96)$$

with

$$E_{xc}(t) \;=\; \int dr\rho(r,t)r\cdot\mathcal{E}_{xc}(r,t)\ . \qquad (7.97)$$

The KS exchange-correlation energy [18, 19] is defined as $E_{xc}^{KS}(t) \;=\; E_{xc}(t) \;+\; T_c(t)$, so that in KS language the sum rule is

$$E_{xc}^{KS}(t) + T_c(t) = -\int d\mathbf{r}\rho(\mathbf{r},t)\mathbf{r}\cdot\nabla v_{xc}(\mathbf{r},t) \ . \tag{7.98}$$

This sum rule has also been derived [102] via the Heisenberg equation of motion, the finiteness of the system being implicitly assumed.

For the s-system, $\lambda = 0$, and $E_{xc}^{KS,\lambda=0}(t) = E_x(t)$, and $v_{xc}^{\lambda=0}(\mathbf{r},t) = v_x(\mathbf{r},t)$, so that the KS exchange and correlation sum rules are

$$E_x(t) + \int d\mathbf{r}\rho(\mathbf{r},t)\mathbf{r}\cdot\nabla v_x(\mathbf{r},t) = 0 \ , \tag{7.99}$$

and

$$E_c^{KS}(t) + T_c(t) = -\int d\mathbf{r}\rho(\mathbf{r},t)\cdot\mathbf{r}\nabla v_c(\mathbf{r},t) \ . \tag{7.100}$$

On substituting for $\nabla v_x(\mathbf{r},t)$ from Eq. (7.76) into Eq. (7.99) and noting

$$E_x(t) = \int d\mathbf{r}\rho(\mathbf{r},t)\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_x(\mathbf{r},t) \ , \tag{7.101}$$

and that (from Eq. (7.87))

$$\int d\mathbf{r}\rho(\mathbf{r},t)\mathbf{r}\cdot\mathbf{J}_{c,i}(\mathbf{r},t) = 0 \ , \quad i = 1,\ 2,\ \ldots \tag{7.102}$$

we obtain the additional condition

$$\int d\mathbf{r}\rho(\mathbf{r},t)\mathbf{r}\cdot\mathbf{Z}_{t_c,1}(\mathbf{r},t) = 0 \ . \tag{7.103}$$

Thus, there is no ***explicit*** contribution of Correlation-Kinetic and Correlation-Current-Density effects to the KS exchange energy. These contributions are implicit via the orbitals generated by the potential $v_x(\mathbf{r},t)$.

Finally, for completeness we note that sum rules involving actions may be written by integrating the integral virial theorem of Eq. (7.93) over time. Thus, we have

$$A_{ee}^{\lambda} + 2A_{t_c}^{\lambda} = -\int_{t_0}^{t_1} dt \int d\boldsymbol{r}\rho(\boldsymbol{r},t)\boldsymbol{r}\cdot\nabla\frac{\delta A_{ee}^{\lambda}}{\delta\rho(\boldsymbol{r},t)} \ , \qquad (7.104)$$

where

$$A_{ee}^{\lambda} = \int_{t_0}^{t_1} dt \int d\boldsymbol{r}\rho(\boldsymbol{r},t)\boldsymbol{r}\cdot\mathcal{E}_{ee}^{\lambda}(\boldsymbol{r},t) \ , \qquad (7.105)$$

and

$$A_{t_c}^{\lambda} = \frac{1}{2}\int_{t_0}^{t_1} dt \int d\boldsymbol{r}\rho(\boldsymbol{r},t)\boldsymbol{r}\cdot\boldsymbol{Z}_{t_c}^{\lambda}(\boldsymbol{r},t) \ . \qquad (7.106)$$

From Eq. (7.104), the corresponding actions for the fully interacting ($\lambda = 1$) and s-systems ($\lambda = 0$) can be similarly written.

7.6. Summary of Conclusions

In conclusion we summarize the principal results of the chapter.

(i) For real, local, arbitrary TD external potentials $v(\boldsymbol{r},t)$ we have derived the differential virial theorem for both TD Schrödinger theory as well as for the corresponding noninteracting s-system of equivalent density $\rho(\boldsymbol{r},t)$.

(ii) As such we have obtained an ***exact*** integral expression for the TD electron-interaction potential $v_{ee}(r,t)$ of the TD s-system in terms of the system wavefunction that is independent of the choice of action. This expression has the physical interpretation at each instant of time as being the work done to move an electron in a conservative field $\mathcal{F}(r,t)$. Furthermore, the expression is independent of the strength of the TD external potential. We have thereby developed TD Q-DFT. (More recently [103] the TD differential virial theorem derived here has been shown to be equivalent to the Euler equation of quantum fluid dynamics [104]).

(iii) In addition to the expected Correlation-Kinetic effects, we have discovered that there exist Correlation-Current-Density effects in the potential $v_{ee}(r,t)$. These effects are explicitly defined through the components $Z_{t_c}(r,t)$ and $J_c(r,t)$ of the field $\mathcal{F}(r,t)$.

(iv) For systems which reduce to being one-dimensional, the Correlation-Current-Density effects vanish so that $J_c(r,t)=0$. Thus, for such systems, the description of the potential $v_{ee}(r,t)$ is the same as that of stationary-state Q-DFT but with a time-dependence.

(v) Finally, for time-independent external potentials, the interpretation reduces to that [18, 19] for the corresponding electron-interaction potential of

stationary-state Q-DFT.

Employing the field concepts of Q-DFT we have proved the following sum rules and properties of the s-system:

(vi) The electron-interaction (Pauli-Coulomb), Correlation-Kinetic, and Correlation-Current-Density components of the s-system electron-interaction potential $v_{ee}(\mathbf{r},t)$ ***separately*** exert no net force on the system.

(vii) The torque of the potential $v_{ee}(\mathbf{r},t)$ on the system is ***finite***, and is due ***entirely*** to Correlation-Current-Density effects via the representative field $\mathcal{J}_c(\mathbf{r},t)$. It is only when in the presence of the TD external potential the resultant system is one-dimensional so that [11, 12] $\mathcal{J}_c(\mathbf{r},t)=0$ does the torque vanish. The torque due to the electron-interaction and Correlation-Kinetic components of $v_{ee}(\mathbf{r},t)$ are proved to ***separately*** vanish.

(viii) Two sum rules involving the curl of the s-system electron-interaction kernel defined as the functional derivative of $v_{ee}(\mathbf{r},t)$ are derived. These sum rules incorporate a frequency-dependent term involving Correlation-Current-Density effects via the functional derivative of the field $\mathcal{J}_c(\mathbf{r},t)$. These terms vanish for systems of special symmetry for which $\mathcal{J}_c(\mathbf{r},t)=0$.

Through the adiabatic coupling constant (λ) connection between the Q-DFT and s-system definitions we have proved the following:

(ix) The s-system exchange potential $v_x(\boldsymbol{r},t)$ is the work done in a conservative field. This field is representative of electron correlations due to the Pauli principle and lowest-order $O(\lambda)$ Correlation-Kinetic and Correlation-Current-Density effects. The s-system correlation potential $v_c(\boldsymbol{r},t)$ commences in $O(\lambda^2)$. At each order the correlation potential is the work done in a conservative field representative of correlations due to Coulomb repulsion, Correlation-Kinetic, and Correlation-Current-Density effects of appropriate order. For systems of special symmetry, there are no Correlation-Current-Density Contributions to these potentials.

(x) From the differential virial theorem we have derived for ***finite*** coupling constant λ the integral virial theorem relating the s-system potential $v_{ee}^{\lambda}(\boldsymbol{r},t)$ to the electron-interaction and Correlation-Kinetic energy components. We show that there is no explicit Correlation-Current-Density contribution to the energy. The contributions of this effect are indirect via the potential $v_{ee}(\boldsymbol{r},t)$. The sum rule for the fully interacting ($\lambda = 1$) system is derived as a special case. For the noninteracting ($\lambda = 0$) case, we obtain the exchange-only sum rule relating the system exchange potential $v_x(\boldsymbol{r},t)$ to the exchange energy. We thereby see that there is no explicit Correlation-Kinetic contribution to the exchange energy. The

contribution is indirect via the potential $v_x(\mathbf{r}, t)$.

(xi) Finally, we note that via the finite λ integral virial theorem, it is possible to write expressions for the electron-interaction and Correlation-Kinetic action functionals in terms of the fields, from which the corresponding expressions for the $\lambda = 1$ and 0 cases can be readily obtained.

Chapter 8

CONCLUSIONS AND FUTURE WORK

Prior to the advent of Q-DFT, the one mathematically rigorous framework for the transformation of the Schrödinger equation to one of noninteracting Fermions with equivalent density $\rho(\mathbf{r}/\mathbf{r}t)$ -- the s-system -- was Hohenberg-Kohn-Sham DFT and its extension by Runge and Gross to the TD case. Although the density is a physical quantity [105], the definitions within this theory are intrinsically mathematical in that its description of the s-system is in terms of energy / action functionals of the density and of their derivatives. All the many-body effects are incorporated in the KS electron-interaction energy $E_{ee}^{KS}[\rho]$ / action $A_{ee}^{KS}[\rho]$ functionals, and therefore in their derivatives which constitute the KS definition of the local electron-interaction potential $v_{ee}(\mathbf{r}/\mathbf{r}t)$ of the s-system. How these many-body effects are incorporated in these functionals is not explained by the theory. Hence, although all the information about a system is implicitly contained within the density, the explicit details of the many-body effects have been integrated out.

Q-DFT, on the other hand, is a description of the s-system in terms of the system wavefunction. It thereby explains the physics underlying the transformation from Schrödinger theory to that of the equivalent density non-interacting system. Furthermore, within this independent framework, not only are the many-body effects ***separately*** delineated, they are ***explicitly*** defined. Hence, it is possible to determine fundamental properties of the s-system in terms of the different many-body effects. For example, there is a discontinuity in the electron-interaction potential $v_{ee}(r)$ of the s-system as the electron number passes through an integer value. Within the framework of KS theory, this means that the functional derivative $\delta E_{ee}^{KS}[\rho]/\delta\rho(r)$ exhibits a discontinuity. Now since the functional $E_{ee}^{KS}[\rho]$ is representative of all the many body effects, it is assumed that correlations due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects, all contribute to the discontinuity. In order, therefore to construct an approximate electron-interaction energy functional such that it exhibits the discontinuity, one would on the basis of KS theory incorporate contributions from each type of correlation into the functional. However, via Q-DFT we have shown that Pauli and Coulomb correlations do not contribute to the discontinuity, and that the discontinuity is solely a consequence of Correlation-Kinetic effects. As another example, it is commonly assumed that the KS theory exchange potential $v_x(r/rt)$ is representative strictly of Pauli correlations. However, this is not the case. Q-DFT shows that in the time-independent case there are in addition contributions from lowest-order Correlation-Kinetic effects to $v_x(r)$, and that in the time-dependent case there is a further lowest-order Correlation-Current-Density effect contribution to $v_x(rt)$. Consequently, the KS correlation potential $v_c(r/rt)$ is representative of Coulomb correlations and higher-order Correlation-Kinetic and Correlation-Current-Density effects. We have also shown via Q-DFT that the torque of the electron-interaction field $\mathcal{F}(rt)$ is due to Correlation-Current-Density effects, and that the force of this field on the system vanishes because its Pauli-Coulomb, Correlation-Kinetic, and Correlation-Current-Density components separately exert no force. As yet another example, we have derived the asymptotic structure of the KS exchange-correlation potential $v_{xc}(r)$ via Q-DFT and shown that the leading $O(1/r)$ term arises from the Fermi hole, the $O(1/r^4)$ term from the Coulomb hole, and the $O(1/r^5)$ term from the Correlation-Kinetic effect. No such explicit assignation of the correlations to the structure exists in the literature. These examples all demonstrate that Q-DFT provides a rigorous theoretical framework for an understanding of the s-system at a fundamental level.

In KS theory the functionals $E_{\alpha}^{KS}[\rho]$ / $A_{\alpha}^{KS}[\rho]$ are unknown and must be approximated. However, since the density $\rho(r/rt)$ depends on three / four variables, approximate KS theory readily lends itself to easy and therefore extensive application. This is a principal attribute of the theory. Hence, an additional key requirement in the construction of approximate functionals is that their form be such as to allow for easy functional differentiation, as is the case of the local density and various generalized gradient expansion approximations.

Q-DFT is in terms of the wavefunction which too is unknown. For purposes of application, therefore, we have developed a many-body perturbation theory within the context of Q-DFT. In this theory, there is a separate perturbation series for the Pauli-Coulomb correlations and Correlation-Kinetic effects. At the Pauli-correlated lowest-order, the bounds on the total energy are rigorous. Furthermore, at this order, for finite systems, the asymptotic stucture of the fully-correlated system is obtained exactly. This order of the perturbation theory is equivalent to the Work Formalism Hartree-Fock approximation which has been applied to the ground [45, 106, 107] and excited [86-95] states of atoms, ions [108-111], anion-positron binding [63], clusters [112], and metal surfaces [54, 55, 64, 67-70, 113]. The results obtained thereby are accurate in comparison with both the values of other theories as well as to experiment. Via the perturbation theory developed, the higher-order Coulomb correlation and Correlation-Kinetic contributions can now be separately and systematically determined and studied in these systems. The Pauli potential of the lowest-order perturbation theory can, however, also be employed in conjunction with approximate KS correlation energy functionals [90-94, 114].

Another approach [96] to the application of Q-DFT is to employ small parameter number correlated-determinantal wavefunction functionals of the density constructed in such a manner as to satisfy the Fermi-Coulomb hole sum rule at each electron position. For the value of the parameters determined by energy minimization, the orbitals and hence the density are obtained self-consistently. At the Pauli-correlated level, this method is equivalent to our lowest-order perturbation theory. The Coulomb correlation and Correlation-Kinetic components of the potential and energy can also be determined separately by this approach. Furthermore, at each level of correlation, the bound on the total energy is rigorous.

Finally, our extension of stationary state Q-DFT to the time-dependent domain allows for many additional applications. As the equations of TD Q-DFT are derived for arbitrary external potential, the theory is valid for the perturbative regime and beyond. Thus, problems such as the low frequency photoresponse of matter and the interaction of high intensity lasers with atoms can be addressed.

Undoubtedly, there is much theoretical work to be done for the further understanding and development of Q-DFT, and of its applicability. The basic framework, however, has been established. We note that the TD differential virial theorem derived by us has recently been employed [103] to prove the equivalence of Schrödinger theory to the Euler equation of quantum hydrodynamics [104]. This is of particular significance as the two equations are derived in distinctly different ways. The virial theorem has also been used [115] to provide an alternate discription of Schrödinger theory itself in terms of fields and quantal sources, thereby making the theory more tangible.

Appendix A

ANALYTICAL EXPRESSIONS FOR THE GROUND-STATE PROPERTIES OF THE HOOKE'S ATOM

In this appendix we give the analytical and semi-analytical expressions for various properties of the Hooke's atom in the ground state corresponding to a spring constant value of $k = 1/4$.

a. Electron density $\rho(\mathbf{r})$.

$$\rho(\mathbf{r}) = \frac{\pi\sqrt{2\pi}\,C^2}{r}\, e^{-r^2/2}\, \{\, 7r + r^3 + (8/\sqrt{2\pi})r\, e^{-r^2/2} + 4(1 + r^2)\, erf(r/\sqrt{2}) \,\} \tag{A1}$$

where

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2}\, dy \tag{A2}$$

is the error function [116].

b. Pair-correlation density $g(\mathbf{r},\mathbf{r}')$.

$$g(\mathbf{r},\mathbf{r}') = \frac{C^2}{2\rho(\mathbf{r})}\, e^{-(r^2 + r'^2)/2}\, (\, 2 + |\mathbf{r}-\mathbf{r}'|\,)^2 \,. \tag{A3}$$

c. Electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$.

$$\mathcal{E}_{ee}(r) = \frac{1}{r^2}\,\frac{C^2(\sqrt{2\pi})^3}{2\rho}\,e^{-r^2/2}\,\{\,(\,r^2+3\,)\,erf(r/\sqrt{2}) - 3\sqrt{2/\pi}\;r\,e^{-r^2/2} - 4\sqrt{2}\,daw(r/\sqrt{2}) + 4r\,\} \tag{A4}$$

where

$$daw(x) = e^{-x^2}\int_0^x e^{t^2}\,dt\ , \tag{A5}$$

is the Dawson's integral [116].

d. ***Hartree field*** $\mathcal{E}_H(r)$.

$$\mathcal{E}_H(r) = \frac{1}{r^2}\,(2\pi C)^2\,\{\,10\pi\,erf(r/\sqrt{2}) - 4\sqrt{2\pi}\,(\,3+r^2\,)\,e^{-r^2/2}\,erf(r/\sqrt{2}) + 16\sqrt{\pi}\,erf(r) - 8r\,e^{-r^2} - \sqrt{2\pi}\,(\,10r + r^3\,)\,e^{-r^2/2}\,\} \tag{A6}$$

e. ***Electron-interaction energy*** E_{ee}.

$$E_{ee} = (4\pi C)^2\,[\,\pi/2 + \sqrt{\pi}\,] = 0.447443\ a.u.\ . \tag{A7}$$

f. ***Coulomb self-energy*** E_H.

$$E_H = 4(2\pi C)^4\,\{\,\frac{20}{3}\pi^2 + \frac{507}{32}\pi^{3/2} + 9\sqrt{3}\,\pi + 4\sqrt{2\pi} + \sqrt{\pi}\,(\,23\arcsin\frac{7}{9} - 32\arcsin\frac{1}{3}\,)\,\} = 1.030250\ a.u.\ . \tag{A8}$$

g. ***External energy*** E_{ext}.

$$E_{ext} = \int \rho(r)\ \frac{1}{2}kr^2 dr = 2(\pi C)^2[9\pi + 14\sqrt{\pi}] = 0.888141\,a.u.\ . \qquad \textbf{(A9)}$$

h. ***Electron-interaction potential*** $W_{ee}(r)$.

$$W_{ee}(r) = -C^2(\sqrt{2\pi}\,)^3 \int_{\infty}^{r} \frac{1}{2r'^2\rho(r')} e^{-r'^2/2}\{\ (r'^2+3)\,erf(r'/\sqrt{2}) \qquad \textbf{(A10)}$$

$$-3\ \sqrt{2/\pi}\ \ r'e^{-r'^2/2} - 4\sqrt{2}\,daw(r'/\sqrt{2}) + 4r'\,\}\,dr'\ .$$

$$W_{ee}(0) = 0.65959\ a.u.\ . \qquad \textbf{(A11)}$$

i. ***Hartree potential*** $W_H(r)$.

$$W_H(r) = \frac{(2\pi C)^2\ \sqrt{2\pi}}{r}\ \{\ 5\sqrt{2\pi}\ \ erf(r/\sqrt{2})\ -\ 12e^{-r^2/2}\ erf(r/\sqrt{2}) \qquad \textbf{(A12)}$$

$$+\ 8\sqrt{2}\ \ erf(r)\ +\ 2\sqrt{2\pi}\ \ r(\ 1\ -\ erf^2(r/\sqrt{2})\ )\ -\ re^{-r^2/2}\ \}\ .$$

$$W_H(0) = (2\pi C)^2\,[9\sqrt{2\pi} + 4\pi + 8] = 1.442941\ a.u.\ . \qquad \textbf{(A13)}$$

j. ***Slater electron-interaction potential*** $V^S_{ee}(r)$.

$$V^S_{ee}(r) = \frac{\pi C^2}{r\rho(r)}\ e^{-r^2/2}\ \{\ 4\sqrt{2\pi}\ \ r\ +\ 2r\ e^{-r^2/2} \qquad \textbf{(A14)}$$

$$+\ \sqrt{2\pi}\ \ (\ 5\ +\ r^2\ )\ erf(r/\sqrt{2})\ \}\ .$$

$$V^S_{ee}(0) = \frac{4\ (\sqrt{2\pi}\ +\ 3)}{7\sqrt{2\pi}\ +\ 16} = 0.656598\ a.u.\ . \qquad \textbf{(A15)}$$

k. ***Single-particle density matrix*** $\gamma(r',r'')$.

$$\gamma(r',r'') = 2C^2 \, e^{-\frac{1}{4}(r'^2 + r''^2)} \cdot \int \left(1 + \frac{|r'-r|}{2}\right) \left(1 + \frac{|r''-r|}{2}\right) e^{-r^2/2} \, dr \quad . \tag{A16}$$

l. ***Dirac density matrix*** $\gamma_s(r',r'')$.

$$\gamma_s(r',r'') = \sqrt{\rho(r')\,\rho(r'')} \quad . \tag{A17}$$

m. ***Kinetic-energy-density tensor*** $t_{\alpha\beta}(r\ ;\ [\gamma])$.

$$t_{\alpha\beta}(r\ ;\ [\gamma]) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta}\, k(r) \ , \tag{A18}$$

where

$$f(r) = \frac{1}{8} \Big\{ r^2\rho(r) - \frac{4\pi C^2}{r^3} e^{-r^2/2} \Big[\sqrt{2\pi}\, r^5 - 2\sqrt{2\pi}\, r^2 (1 - r^2)\, erf(r/\sqrt{2}) + 4r^3 e^{-r^2/2} - 6\sqrt{\pi}\, daw(r/\sqrt{2}) - \sqrt{2\pi}\, r\,(r^2 - 3) \Big] \Big\} \quad . \tag{A19}$$

and

$$k(r) = \frac{(\sqrt{2\pi}\,)^3\, C^2}{4r^3} \left[r - \sqrt{2}\, daw(r/\sqrt{2}) \right] e^{-r^2/2} \ . \tag{A20}$$

n. ***Kinetic-energy-density tensor*** $t_{s,\alpha\beta}(r\ ;\ [\gamma_s])$.

$$t_{s,\alpha\beta}(r\ ;\ [\gamma_s]) = \frac{r_\alpha r_\beta}{r^2} h(r) \tag{A21}$$

where

$$h(r) = \frac{1}{8\rho}\,\left(\frac{\partial\rho}{\partial r}\right)^2 . \qquad \text{(A22)}$$

o. ***Kinetic field*** $z(r\ ;\ [\gamma])$.

$$\begin{aligned} z(r\ ;\ [\gamma]) = \frac{\pi C^2}{4r^2}\, e^{-r^2/2} \{ & \sqrt{2\pi}\ r\,(\,-\,r^6 + 3r^4 + 8r^2 + 16\,) \\ & - 4\sqrt{2\pi}\,(\,r^6 - 6r^4 + 5r^2 - 2\,)\ erf\,(r/\sqrt{2}) \\ & - 8r\,(\,r^4 - 7r^2 + 2\,)\, e^{-r^2/2} - 32\sqrt{\pi}\ daw\,(r/\sqrt{2})\ \}\ . \end{aligned} \qquad \text{(A23)}$$

p. ***Kinetic field*** $z_s(r\ ;\ [\gamma_s])$.

$$z_s(r\ ;\ [\gamma_s]) = \frac{1}{2\rho}\,\left(\frac{\partial\rho}{\partial r}\right)\,\left\{\,\frac{1}{r}\left(\frac{\partial\rho}{\partial r}\right) - \frac{1}{2\rho}\,\left(\frac{\partial\rho}{\partial r}\right)^2 + \frac{\partial^2\rho}{\partial r^2}\,\right\}\ . \qquad \text{(A24)}$$

q. ***Kinetic energy*** $T[\rho]$.

$$T\,[\rho] = \pi^2\, C^2\ [\ 14\pi + 20\sqrt{\pi}\ ] = 0.664418\ a.u.\ . \qquad \text{(A25)}$$

r. ***Expectations.***

$$\langle r\rangle = \int \rho(r)\ r dr = 2(2\pi C)^2[4\pi + 11\sqrt{2\pi} + 12] = 3.489025 a.u.\ . \qquad \text{(A26)}$$

$$\langle r^2\rangle = \int \rho(r) r^2 dr = (4\pi C)^2[9\pi + 14\sqrt{\pi}] = 7.105114 a.u.\ . \qquad \text{(A27)}$$

$$\left\langle\frac{1}{r}\right\rangle = \int \rho(r)\frac{1}{r}dr = (2\pi C)^2[4\pi + 9\sqrt{2\pi} + 8] = 1.442940 a.u.\ . \qquad \text{(A28)}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \int \rho(r) \, \frac{1}{r^2} \, dr = (2\pi C)^2 \left[\, 11\pi + 8\sqrt{\pi} + 4\sqrt{2\pi} \, \ln\left(1 + \sqrt{2}\right) \right] = 1.926359 \; a.u. \quad . \tag{A29}$$

$$\langle \delta(r) \rangle = \rho(0) = \pi C^2 \left[\, 7\sqrt{2\pi} + 16 \, \right] = 0.089319 \; a.u. \quad . \tag{A30}$$

Appendix B

DERIVATION OF THE KINETIC-ENERGY-DENSITY TENSOR FOR THE HOOKE'S ATOM

In this Appendix, we derive the kinetic-energy-density tensor for Hooke's atom.

The density matrix for a two-electron system is

$$\gamma(r', r'') = 2\sum_{\sigma} \int \Psi^*(r'\sigma, x_2)\Psi(r''\sigma, x_2)dx_2 \ , \tag{B1}$$

where $x_2 = r, \sigma$ and $\int dx_2 = \sum_{\sigma_2} \int dr_2$. Substituting the ground-state wavefunction of Eq. (3.2) into the above equation, we obtain,

$$\gamma(r', r'') = 2C^2 e^{-(r'^2 + r''^2)/4} \int [1 + \frac{|r' - r|}{2}][1 + \frac{|r'' - r|}{2}] e^{-r^2/2} dr \ . \tag{B2}$$

Now let us make the transformation to the coordinates

$$x = (r' + r'')/2 \ , \quad y = (r' - r'')/2 \ . \tag{B3}$$

Eq. (B2) then becomes

$$\gamma(r', r'') = 2Ce^{-(x^2+y^2)/2} \int [1 + |r - y|/2][1 + |r + y|/2] e^{-|r+x|^2/2} dr \ . \tag{B4}$$

Substitution of Eq. (B4) into Eq. (2.24) for the tensor then leads to

$$t_{\alpha\beta}(r,[\gamma]) = \frac{1}{8}\left[\frac{\partial^2}{\partial x_\alpha \partial x_\beta} - \frac{\partial^2}{\partial y_\beta \partial y_\alpha}\right]\gamma(r',r'')\big|_{x=r,y=0} \,. \tag{B5}$$

The first term on the right side of Eq. (B5) can be evaluated readily as

$$\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\gamma(r',r'')\big|_{x=r,y=0} = \frac{\partial^2}{\partial r_\alpha \partial r_\beta}\rho(r) \,. \tag{B6}$$

After complicated but straightforward algebra, the second term is evaluated as

$$-\frac{1}{2}\frac{\partial^2}{\partial y_\alpha \partial y_\beta}\gamma(r',r'')\big|_{x=r,y=0} = \delta_{\alpha\beta}C^2 e^{-r^2/2} I(r) + C^2 e^{-r^2/2} J_{\alpha\beta}(r) \,, \tag{B7}$$

where the integrals $I(r)$ and $J_{\alpha\beta}(r)$ are defined as

$$I(r) = \int [1 + r'/2 - 1/r'][1 + r'/2] e^{-|r'+r|^2/2} dr' \,, \tag{B8}$$

$$J_{\alpha\beta}(r) = \int \frac{r'_\alpha r'_\beta}{r'^3}(1 + r') e^{-|r+r'|^2/2} dr' \,, \tag{B9}$$

respectively. $J_{\alpha\beta}(r)$ can be further expressed as a sum of two integrals

$$J_{\alpha\beta}(r) = J_{1\alpha\beta}(r) + J_{2\alpha\beta}(r) \tag{B10}$$

where, respectively,

$$J_{1\alpha\beta}(r) = \int \frac{r'_\alpha r'_\beta}{r'^3} e^{-|r'+r|^2/2} dr' \,, \tag{B11}$$

and

$$J_{2\alpha\beta}(r) = \int \frac{r_\alpha' r_\beta'}{r'^2} e^{-|r+r'|^2/2} dr' \ . \qquad \textbf{(B12)}$$

The integrals $I(r)$, $J_{1\alpha\beta}(r)$, and $J_{2\alpha\beta}(r)$ are evaluated as

$$I(r) = 2\pi\{\frac{5}{4}\sqrt{2\pi} + \sqrt{2\pi}/4r^2 + 2e^{-r^2/2} + \sqrt{2\pi}\, r\, erf(r/\sqrt{2})\} \ , \qquad \textbf{(B13)}$$

$$\begin{aligned} J_{1\alpha\beta} &= -2\pi\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\{2e^{-r^2/2} + \sqrt{2\pi}\,(r+\frac{1}{r})\,erf(r/\sqrt{2})\} \\ &\quad + \delta_{\alpha\beta}(2\pi)^{3/2}\frac{1}{r}erf(r/\sqrt{2}) \ , \end{aligned} \qquad \textbf{(B14)}$$

and

$$J_{2\alpha\beta}(r) = e^{-r^2/2}\sqrt{2}(2\pi)^{3/2}\frac{\partial^2}{\partial r_\alpha \partial r_\beta}[e^{r^2/2} daw(r/\sqrt{2})/r] \ . \qquad \textbf{(B15)}$$

Thus, from Eqs. (B5-B7), and Eqs. (B10), (B13-B15), we obtain

$$t_{\alpha\beta}(r;[\gamma]) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta} k(r) \ , \qquad \textbf{(B16)}$$

where $f(r)$ and $k(r)$ are given by Eqs. (A19) and (A20) of Appendix A.

Appendix C

PROOF OF VIRIAL THEOREMS

The time-dependent Schrödinger equation is

$$\hat{H}(t)\Psi(X,t) = i\frac{\partial}{\partial t}\Psi(X,t) , \tag{C1}$$

where the Hamiltonian

$$\hat{H}(t) = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} v(r_i,t) + \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|r_i - r_j|} , \tag{C2}$$

$X = x_1, x_2, \cdots x_N$, $x = r\sigma$, and σ the spin coordinate. The quantal TD spinless single-particle $\gamma(r_1, r_1', t)$ and two-particle $\Gamma(r_1, r_2; r_1', r_2', t)$ density matrices are defined respectively as

$$\gamma(r_1,r_1',t) = N\sum_{\sigma}\int \Psi^*(r_1\sigma, X^{N-1},t)\Psi(r_1'\sigma, X^{N-1},t)dX^{N-1} , \tag{C3}$$

$$\begin{aligned}\Gamma(r_1,r_2;r_1',r_2',t) = \frac{N(N-1)}{2}\sum_{\sigma_1\sigma_2}\int &\Psi^*(r_1\sigma_1 r_2\sigma_2, X^{N-2},t) \\ &\Psi(r_1'\sigma_1, r_2'\sigma_2, X^{N-2},t)dX^{N-2} ,\end{aligned} \tag{B4}$$

where $X^{N-1} = x_2, x_3, \cdots x_N$ etc., $dX^{N-1} = dx_2, \cdots dx_N$ etc., and $\int dx = \sum_\sigma \int dr$. The diagonal matrix element $\gamma(r,r,t)$ is the TD density $\rho(r,t)$, and the diagonal matrix element $\Gamma(r,r';r,r',t) \equiv \Gamma(r,r',t)$ is related to the TD pair-correlation density defined as $g(r,r',t) = \langle\Psi(t)|\sum_{i\neq j}\delta(r_i - r)\,\delta(r_j - r')|\Psi(t)\rangle/\rho(r,t)$ by $g(r,r',t) = 2\Gamma(r,r',t)/\rho(r,t)$.

By writing the wavefunction as $\Psi(X,t)=\Psi^R(X,t)+i\Psi^I(X,t)$, where $\Psi^R(X,t)$ are its real and imaginary parts, we have on substitution into Eq. (C1)

$$\begin{aligned} & i\frac{\partial}{\partial t}\Psi^R(t)-\frac{\partial}{\partial t}\Psi^I(t) \\ & = [-\frac{1}{2}\sum_i \nabla_i^2+\sum_i v(r_i,t)+\frac{1}{2}\sum_{i\neq j}\frac{1}{|r_i-r_j|}](\Psi^R(t)+i\Psi^I(t)) \ , \end{aligned} \tag{C5}$$

where the dependence of Ψ on the electronic coordinates X is implicit. Equating the real parts of Eq. (C5) yields

$$\sum_i v(r_i,t)+\frac{1}{2}\sum_{i\neq j}\frac{1}{|r_i-r_j|}+\frac{1}{\Psi^R(t)}\frac{\partial}{\partial t}\Psi^I(t) = \frac{1}{2\Psi^R(t)}\sum_i \nabla_i^2\Psi^R(t) \ . \tag{C6}$$

On differentiating Eq. (C6) with respect to $r_{1\alpha}$, where $r_{1\alpha}$ is the α coordinate component of r_1, and then multiplying both sides by $(\Psi^R(t))^2$ we obtain

$$\begin{aligned} & \{\frac{\partial}{\partial r_{1\alpha}}[v(r_1,t)+\sum_{j=2}^{N}\frac{1}{|r_1-r_j|}]\}(\Psi^R(t))^2+(\Psi^R(t))^2\frac{\partial}{\partial r_{1\alpha}}(\frac{1}{\Psi^R(t)}\frac{\partial}{\partial t}\Psi^I(t)) \\ & =\frac{1}{2}\sum_{i\beta}\{\Psi^R(t)\frac{\partial^3\Psi^R(t)}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}}-\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}}\frac{\partial^2\Psi^R(t)}{\partial r_{i\beta}^2}\}. \end{aligned} \tag{C7}$$

Now since

$$\begin{aligned} \frac{1}{4}\frac{\partial^3(\Psi^R(t))^2}{\partial r_{i\beta}^2\partial r_{1\alpha}} & = \frac{1}{2}\frac{\partial^2\Psi^R(t)}{\partial r_{i\beta}^2}\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}} \\ & +\frac{\partial\Psi^R(t)}{\partial r_{i\beta}}\frac{\partial^2\Psi^R(t)}{\partial r_{i\beta}\partial r_{1\alpha}}+\frac{1}{2}\Psi^R(t)\frac{\partial^3\Psi^R(t)}{\partial r_{i\beta}^2\partial r_{1\alpha}} \ , \end{aligned} \tag{C8}$$

the right side of Eq. (C7) is

$$\frac{1}{2}\sum_{i\beta}\{\Psi^R(t)\frac{\partial^3\Psi^R(t)}{\partial r_{i\beta}{}^2\partial r_{1\alpha}}-\frac{\partial^2\Psi^R(t)}{\partial r_{i\beta}{}^2}\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}}\}$$
$$=\sum_{i\beta}\{\frac{1}{4}\frac{\partial^3(\Psi^R(t))^2}{\partial r_{i\beta}{}^2\partial r_{1\alpha}}-\frac{\partial}{\partial r_{i\beta}}(\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}}\frac{\partial\Psi^R(t)}{\partial r_{i\beta}})\}\ . \tag{C9}$$

Thus Eq. (C7) is

$$\{\frac{\partial}{\partial r_{1\alpha}}[v(r_1,t)+\sum_{j=2}^{N}\frac{1}{|r_1-r_j|}]\}(\Psi^R(t))^2+(\Psi^R(t))^2\frac{\partial}{\partial r_{1\alpha}}(\frac{1}{\Psi^R(t)}\frac{\partial}{\partial t}\Psi^I(t))$$
$$=\sum_{i\beta}\{\frac{1}{4}\frac{\partial^3(\Psi^R(t))^2}{\partial r_{i\beta}{}^2\partial r_{1\alpha}}-\frac{\partial}{\partial r_{i\beta}}(\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}}\frac{\partial\Psi^R(t)}{\partial r_{i\beta}})\}\ . \tag{C10}$$

A similar derivation from the imaginary part of Eq. (C5) leads to

$$\{\frac{\partial}{\partial r_{1\alpha}}[v(r_1,t)+\sum_{j=2}^{N}\frac{1}{|r_1-r_j|}]\}(\Psi^I(t))^2-(\Psi^I(t))^2\frac{\partial}{\partial r_{1\alpha}}(\frac{1}{\Psi^I(t)}\frac{\partial}{\partial t}\Psi^R(t))$$
$$=\sum_{i\beta}\{\ \frac{1}{4}\frac{\partial^3(\Psi^I(t))^2}{\partial r_{i\beta}{}^2\partial r_{1\alpha}}-\frac{\partial}{\partial r_{i\beta}}(\frac{\partial\Psi^I(t)}{\partial r_{1\alpha}}\frac{\partial\Psi^I(t)}{\partial r_{i\beta}})\}\ . \tag{C11}$$

Using the fact that

$$(\Psi^R(t))^2\frac{\partial}{\partial r_{1\alpha}}(\frac{1}{\Psi^R(t)}\frac{\partial}{\partial t}\Psi^I(t))-(\Psi^I(t))^2\frac{\partial}{\partial r_{1\alpha}}(\frac{1}{\Psi^I(t)}\frac{\partial}{\partial t}\Psi^R(t))$$
$$=\frac{\partial}{\partial t}[\Psi^R(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t)-\Psi^I(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t)]\ , \tag{C12}$$

we have on summing Eqs. (C10) and (C11), and then operating by $N\sum_{\sigma 1}\int dX^{N-1}$ on the resulting equation that

$$
\begin{aligned}
& N\sum_{\sigma_1} \int dX^{N-1}\{\frac{\partial}{\partial r_{1\alpha}}[v(r_1,t)+\sum_{j=2}^{N}\frac{1}{|r_1-r_j|}]\}|\Psi(t)|^2 \\
& +N\sum_{\sigma_1} \int dX^{N-1}\frac{\partial}{\partial t}\{\Psi^R(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t)-\Psi^I(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t)\} \\
& = \frac{1}{4}N\sum_{\sigma_1} \int dX^{N-1}\nabla_1{}^2\frac{\partial}{\partial r_{1\alpha}}|\Psi(t)|^2 \\
& -N\sum_{\sigma_1} \int dX^{N-1}\frac{\partial}{\partial r_{1\beta}}\sum_{\beta}\{(\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t))(\frac{\partial}{\partial r_{1\beta}}\Psi^R(t))+(\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t))(\frac{\partial}{\partial r_{1\beta}}\Psi^I(t))\} \\
& +N\sum_{\sigma_1} \int dX^{N-1}\sum_{j=2}^{N}\frac{\partial}{\partial r_{j\beta}}\{\frac{1}{4}\frac{\partial}{\partial r_{j\beta}}\frac{\partial}{\partial r_{1\alpha}}|\Psi(t)|^2 \\
& -(\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t))(\frac{\partial}{\partial r_{j\beta}}\Psi^R(t))-(\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t))(\frac{\partial}{\partial r_{j\beta}}\Psi^I(t))\} \ .
\end{aligned}
\tag{C13}
$$

On substituting the complex form of the wavefunction into the expression for $\gamma(r,r',t)$, the tensor may be written as

$$
\begin{aligned}
t_{\alpha\beta}(r,t) = \frac{1}{2}N\sum_{\sigma} \int dX^{N-1}\{ & \frac{\partial}{\partial r_\alpha}\Psi^R(r\sigma,X^{N-1},t)\frac{\partial}{\partial r_\beta}\Psi^R(r\sigma,X^{N-1},t) \\
& +\frac{\partial}{\partial r_\beta}\Psi^I(r\sigma,X^{N-1},t)\frac{\partial}{\partial r_\alpha}\Psi^I(r\sigma,X^{N-1},t)\} \ .
\end{aligned}
\tag{C14}
$$

Employing the definitions of Eqs. (7.10) and (C14), Eq. (C13) is then

$$
\begin{aligned}
&N\sum_{\sigma_1}\int dX^{N-1}\{\frac{\partial}{\partial r_{1\alpha}}[v(r_1,t)+\sum_{j=2}^{N}\frac{1}{|r_1-r_j|}]\}|\Psi(t)|^2 \\
&+\frac{N}{2}i\sum_{\sigma_1}\frac{\partial}{\partial t}\int dX^{N-1}\{\Psi(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^*(t)-\Psi^*(t)\frac{\partial}{\partial r_{1\alpha}}\Psi(t)\} \\
&= -z_\alpha(r_1,t)+\frac{1}{4}N\sum_{\sigma_1}\int dX^{N-1}\nabla_1^{\,2}\frac{\partial}{\partial r_{1\alpha}}|\Psi(t)|^2 \\
&+N\sum_{\sigma_1}\int dX^{N-1}\sum_{j=2}^{N}\sum_{\beta}\frac{\partial}{\partial r_{j\beta}}\{\frac{1}{4}\frac{\partial}{\partial r_{j\beta}}\frac{\partial}{\partial r_{1\alpha}}|\Psi(t)|^2 \\
&-(\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t))(\frac{\partial}{\partial r_{j\beta}}\Psi^R(t))-(\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t))(\frac{\partial}{\partial r_{j\beta}}\Psi^I(t))\}\ ,
\end{aligned}
\tag{C15}
$$

where we have employed the relation

$$
\begin{aligned}
&\Psi(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^*(t)-\Psi^*(t)\frac{\partial}{\partial r_{1\alpha}}\Psi(t) \\
&= 2i\{\Psi^I(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t)-\Psi^R(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t)\}\ .
\end{aligned}
\tag{C16}
$$

Since the wavefunction and its derivative vanish at infinity, the last term of Eq. (C15) vanishes on integration over $dr_{j\beta}$. Consequently, Eq. (C15) may be written in terms of the density $\rho(r,t)$, the diagonal matrix element $\Gamma(r,r',t)$ of the two-particle density matrix, and the current density $j(r,t)$ as

$$
\begin{aligned}
&\rho(r_1,t)\frac{\partial}{\partial r_{1\alpha}}v(r_1,t)+2\int dr_2\Gamma(r_1,r_2,t)\frac{\partial}{\partial r_{1\alpha}}\frac{1}{|r_1-r_2|}+\frac{\partial}{\partial t}j_\alpha(r_1,t) \\
&=\frac{1}{4}\nabla^2\frac{\partial}{\partial r_{1\alpha}}\rho(r_1,t)-z_\alpha(r_1,t)\ ,
\end{aligned}
\tag{C17}
$$

The differential virial theorem for TD Schrödinger theory is then

$$\nabla v(\mathbf{r},t) = -\mathbf{F}(\mathbf{r},t) \;, \tag{C18}$$

where $\mathcal{F}(\mathbf{r},t)$ is defined as in Eq. (7.6).

B. Time-dependent noninteracting Fermion system of equivalent density

We next derive the TD differential virial theorem for a system of noninteracting fermions with the same density $\rho(\mathbf{r},t)$ as that of the interacting Schrödinger system. Our proof is for arbitrary external potentials $v(\mathbf{r},t)$, and not restricted only to those that are expandable in a Taylor series about the initial time. The corresponding TD equations are

$$i\frac{\partial}{\partial t}\phi_j(\mathbf{r},t) = [-\frac{1}{2}\nabla^2 + v_s(\mathbf{r},t)]\phi_j(\mathbf{r},t) \;, \tag{C19}$$

Writing the orbitals as $\phi_j(\mathbf{r},t) = \phi_j^R(\mathbf{r},t) + i\phi_j^I(\mathbf{r},t)$, where $\phi_j^R(\mathbf{r},t)$ and $\phi_j^I(\mathbf{r},t)$ are its real and imaginary components, we have on equating the real and imaginary parts of the differential equation

$$v_s(\mathbf{r},t) + \frac{1}{\phi_j^R(t)}\frac{\partial}{\partial t}\phi_j^I(t) = \frac{1}{2}\frac{1}{\phi_j^R(t)}\nabla^2\phi_j^R(t) \;, \tag{C20}$$

$$v_s(\mathbf{r},t) - \frac{1}{\phi_j^I(t)}\frac{\partial}{\partial t}\phi_j^R(t) = \frac{1}{2}\frac{1}{\phi_j^I(t)}\nabla^2\phi_j^I(t) \;, \tag{C21}$$

Performing operations similar to those for the Schrödinger system leads to

$$|\phi_j(t)|^2 \frac{\partial}{\partial r_\alpha} v_s(r,t) + \frac{\partial}{\partial t}\{\phi_j^R(t)\frac{\partial}{\partial r_\alpha}\phi_j^I(t) - \phi_j^I(t)\frac{\partial}{\partial r_\alpha}\phi_j^R(t)\}$$

$$= \frac{1}{2}\sum_\beta\{\frac{\partial^3\phi_j^R(t)}{\partial r_\beta^2\partial r_\alpha}\phi_j^R(t) + \frac{\partial^3\phi_j^I(t)}{\partial r_\beta^2\partial r_\alpha}\phi_j^I(t) \qquad \text{(C22)}$$

$$- \frac{\partial^2\phi_j^R(t)}{\partial r_\beta^2}\frac{\partial\phi_j^R(t)}{\partial r_\alpha} - \frac{\partial^2\phi_j^I(t)}{\partial r_\beta^2}\frac{\partial\phi_j^I(t)}{\partial r_\alpha}\} .$$

On using the relations

$$\frac{1}{4}\frac{\partial^3(\phi_j^A(t))^2}{\partial r_\beta^2\partial r_{1\alpha}} - \frac{\partial}{\partial r_\beta}(\frac{\partial\phi_j^A(t)}{\partial r_\alpha}\frac{\partial\phi_j^A(t)}{\partial r_\beta})$$

$$= -\frac{1}{2}\{\frac{\partial^2\phi_j^A(t)}{\partial r_\beta^2}\frac{\partial\phi_j^A(t)}{\partial r_\alpha} - \phi_j^A(t)\frac{\partial^3\phi_j^A(t)}{\partial r_\beta^2\partial r_\alpha}\} , \qquad \text{(C23)}$$

with $A = R, I$, and

$$\phi_j^R(t)\frac{\partial}{\partial r_\alpha}\phi_j^I(t) - \phi_j^I(t)\frac{\partial}{\partial r_\alpha}\phi_j^R(t)$$

$$= \frac{i}{2}\{\phi_j(t)\frac{\partial}{\partial r_\alpha}\phi_j^*(t) - \phi_j^*(t)\frac{\partial}{\partial r_\alpha}\phi_j(t)\} , \qquad \text{(C24)}$$

in Eq. (C22), we obtain

$$|\phi_j(t)|^2\frac{\partial}{\partial r_\alpha}v_s(r,t) + \frac{i}{2}\frac{\partial}{\partial t}\{\phi_j(t)\frac{\partial}{\partial r_\alpha}\phi_j^*(t) - \phi_j^*\frac{\partial}{\partial r_\alpha}\phi_j(t)\}$$

$$= \frac{1}{4}\nabla^2\frac{\partial}{\partial r_\alpha}|\phi_j(t)|^2 - \sum_\beta\frac{\partial}{\partial r_\beta}\{\frac{\partial\phi_j^R(t)}{\partial r_\alpha}\frac{\partial\phi_j^R(t)}{\partial r_\beta} + \frac{\partial\phi_j^I(t)}{\partial r_\alpha}\frac{\partial\phi_j^I(t)}{\partial r_\beta}\} . \qquad \text{(C25)}$$

Now, for the noninteracting system

$$t_{s,\alpha\beta}(\boldsymbol{r},t) = \frac{1}{2}\sum_{\sigma}\sum_{j=1}^{N}\{\frac{\partial\phi_j^R(t)}{\partial r_\alpha}\frac{\partial\phi_j^R(t)}{\partial r_\beta} + \frac{\partial\phi_j^I(t)}{\partial r_\alpha}\frac{\partial\phi_j^I(t)}{\partial r_\beta}\} \ . \qquad \text{(C26)}$$

Finally, by operating on Eq. (C25) by $\sum_\sigma \sum_{j=1}^{N}$, we obtain the TD noninteracting system differential virial theorem as

$$\nabla v(\boldsymbol{r},t) = -\boldsymbol{F}_s(\boldsymbol{r},t) \ , \qquad \text{(C27)}$$

where $\boldsymbol{F}_s(\boldsymbol{r},t)$ is defined as in Eq. (7.15).

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