STUDIES IN HOHENBERG-KOHN

AND

QUANTAL DENSITY FUNCTIONAL THEORIES

by

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Abstract

Studies in Hohenberg-Kohn and Quantal Density Functional Theories

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This thesis is concerned with the first Hohenberg-Kohn (HK) theorem, its extension to the time-dependent case by Runge-Gross (RG), and the application and further extension of Quantal Density Functional theory (Q-DFT). According to the HK theorem, the ground state density $\rho(\mathbf{r})$ of a system uniquely determines its Hamiltonian H to within an additive constant C, and thus the physical system and its properties. In the RG extension, the density $\rho(\mathbf{r}t)$ uniquely determines the time-dependent Hamiltonian $H(t)$ to within a purely time-dependent function $C(t)$, and hence the system and its properties. We prove, by construction, the corollary that degenerate {time-independent/time-dependent} Hamiltonians $\{H/H(t)\}$ that represent different physical systems, but which differ by a {constant C/function $C(t)$}, and yet possess the same density $\{\rho(\mathbf{r})\ /\rho(\mathbf{r}t)\}$, cannot be distinguished on the basis of the HK/RG theorem.

Q-DFT is a local effective potential energy theory that maps the interacting system described by Schrödinger's equation to one of noninteracting Fermions such that the equivalent density $\{\rho(\mathbf{r})\ /\ \rho(\mathbf{r}t)\}$, energy $\{E/E(t)\}$, and ionization potential are obtained. This mapping is in terms of 'classical' fields and quantal sources representative of electron correlations the model system must account for,

viz. those due to the Pauli exclusion principle, Coulomb repulsion, Correlation-Kinetic and Correlation-Current-Density effects. The mapping contrasts with that of traditional Kohn-Sham (KS) DFT, which in the time-independent case, is in terms of an energy density functional for the ground state, and an energy bidensity functional for excited states, and of their functional derivatives. Here we apply time-independent Q-DFT to study the properties of the Hydrogen molecule in its ground state. We further extend time-independent nondegenerate Q-DFT to degenerate states for both ground and excited states, and for both pure state and ensemble densities. This further provides a rigorous physical interpretation of the energy density and bidensity functionals, and their derivatives, of degenerate state KS-DFT.

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CHAPTER 1

INTRODUCTION

One of the most extensively employed approaches to the determination of the electronic structure of matter is *local* (multiplicative) *effective potential energy theory.* The basic idea is to map the interacting system as described by the {time-independent/time-dependent} Schrödinger equation with Hamiltonian $\{H/H(t)\}$ to one of *noninteracting* fermions with *equivalent* density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$. The model system of noninteracting fermions, whose wave function is a Slater determinant $\{\Phi/\Phi(t)\}$, is referred to as the S system. From the S system, it is then possible to obtain the equivalent energy $\{E/E(t)\}$, where $E(t)$ is the non conserved time-dependent energy; and in the time-independent case, the ionization potential or electron affinity. The principal reason for the construction of the S systems is that it is easier to solve N single-particle equations than to solve the one Schrödinger equation for the N interacting electrons.

The mathematical basis for the construction of the S systems is the first Hohenberg-Kohn (HK) theorem [1] for the stationary state case, and its extension by Runge-Gross (RG) [2] to the time-dependent case. According to the $\{HK/RG\}$ theorems, for a system of N electrons in a local though *arbitrary* external potential represented by the operator $\{v(\mathbf{r}/v(\mathbf{r}t)\}$, there is a *one-to-one* correspondence between the electronic density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$ and the potential energy $\{v(\mathbf{r})/v(\mathbf{r}t)\}$

to within a {constant C/time-dependent function $C(t)$}. Thus, the density uniquely specifies the external potential energy of the electrons. With the kinetic energy operator known, and the operator for the interaction between the electrons also *assumed* known though *arbitrary*, a knowledge of the density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$ therefore fully defines the Hamiltonian $\{H/H(t)\}$ of the system. Solution of the corresponding Schrodinger equation then leads to the system wave function $\{\Psi(\mathbf{X})/\Psi(\mathbf{X}t)\}$ ($\mathbf{X} = \mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N; \mathbf{x} = \mathbf{r}\sigma$; σ =spin coordinate) for all states: ground and excited. As a consequence of the {HK/RG} theorems, the wave function $\{\Psi(\mathbf{X})/\Psi(\mathbf{X}t)\}$ is thus a functional of the density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$, unique to within a time-dependent phase in the time-dependent case. In the HK theorem, the density $\rho(\mathbf{r})$ corresponds to the *ground* state density. The RG theorem in turn is restricted to external potential energies $v(\mathbf{r}t)$ that are Taylor expandable about the initial time t_0. It is because the wave function is a functional of the density, and that all the information about a system is embedded in its density, that one is interested in constructing a model system of noninteracting fermions with *equivalent* density.

The mapping to the S system, of course, must be such that all the electron correlations of the interacting system are accounted for in the model system. The correlations are those due to the Pauli exclusion principle and Coulomb repulsion. However, there are additional correlations that must also be accounted for in the transformation to the S system. These are referred to as Correlation-Kinetic and Correlation-Current-Density contributions. They arise, respectively, because of

the difference in kinetic energy and current density between the interacting and noninteracting systems. Hence, it is only when all four types of correlations are represented in the local effective potential energy of the model fermions that their density will be the same as that obtained by Schrödinger theory.

It is only recently, within the framework of Quantal Density Functional Theory (Q-DFT) [3-16], that the mapping to the S system in terms of these correlations has been understood, and the contribution of each type of electron correlation *explicitly* given. Q-DFT is derived via the differential virial theorems for the interacting and noninteracting systems. It is a description of the S system in terms of 'classical' fields, and their quantal sources that are expectations of Hermitian operators. These expectations are taken with respect to the interacting $\{\Psi(\mathbf{X})/\Psi(\mathbf{X}t)\}$ and S system $\{\Phi/\Phi(t)\}$ wave functions. The fields are *separately* representative of the different electron correlations that must be accounted for by the S system. The local effective potential energy of the model fermions in time-independent Q-DFT is, in a manner similar to that of classical physics, the *work done* in the *sum* of these fields. In the time-dependent case, it is the corresponding *work done at each instant of time.* Again, as in classical physics, the energies $\{E/E(t)\}$ are expressed in terms of the quantal sources, or in integral virial form in terms of the fields. The description of both ground and excited states is the same within Q-DFT, with time-independent Q-DFT being a special case of the time-dependent theory.

The traditional approach to the mapping from the interacting to the model system with equivalent density is that of Kohn-Sham Density Functional Theory (KS-DFT) [1,2,17], the precursor to Q-DFT. In KS-DFT, the fact that the wave function $\{\Psi(\mathbf{X})/\Psi(\mathbf{X}t)\}$ is a functional of the density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$ is explicitly employed. In the time-independent case, the energy which is the expectation of the Hamiltonian H, is then a functional of the *ground* state density $\rho(\mathbf{r})$: $E = E[\rho]$. Thus, time-independent KS-DFT is a ground state theory. Now, according to the second HK theorem [1], the ground state energy functional obeys a variational principle with respect to arbitrary variations of the density, and therefore leads to the ground state energy for the true ground state density. Thus, the ground state density $\rho(\mathbf{r})$ can be obtained via the Euler equation $\delta E[\rho]/\delta\rho(\mathbf{r}) = 0$, subject to the constraint of charge conservation. A comparison of this Euler equation to that of the Schrödinger equation for the S system then leads to the definition of the local effective potential energy of the model fermions in KS-DFT as a *functional derivative*. Since the explicit dependence of $\Psi(\mathbf{X})$ on $\rho(\mathbf{r})$ is unknown, the energy functional $E[\rho]$ and its functional derivative are unknown. Thus, although it is *implicit* that $E[\rho]$ is representative of electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and Correlation -Kinetic effects, there is no explicit description within KS-DFT of how these correlations are incorporated in the energy functional or its derivative. There has been recent progress in time-independent KS-DFT for excited states [18]. For excited state KS-DFT, one is concerned with a *bidensity* energy functional of the ground and excited state densities: $E = E[\rho_0, \rho_i]$,

where (ρ_0, ρ_i) are the ground and excited state densities. The corresponding potential energy of the model fermions is then defined as a *functional derivative* taken at the excited state density.

In the time-dependent case, the wave function $\Psi(\mathbf{X}t)$, with some initial condition $\Psi(\mathbf{X}t_0)$, corresponds to a stationary point of a quantum-mechanical action integral A. Since the wave function is a functional of the density $\rho(\mathbf{r}t)$, this action integral too is a functional: $A = A[\rho]$. The action functional $A[\rho]$ must have a stationary point at the true density $\rho(\mathbf{r}t)$ with initial state $\Psi(\mathbf{X}t_0)$. Therefore, the true density may be obtained via the corresponding time-dependent Euler equation $\delta A[\rho]/\delta\rho(\mathbf{r}t) = 0$, with appropriate boundary conditions. Again, a comparison of this Euler equation with the time-dependent Schrödinger equation of the model fermions leads to their local effective potential energy within KS-DFT being defined as a functional derivative. And again, as the functional dependence of $\Psi(\mathbf{X}t)$ on $\rho(\mathbf{r}t)$ is unknown, the functional $A[\rho]$ and its derivative are unknown. As such, the manner in which the Pauli and Coulomb correlations, and the Correlation-Kinetic and Correlation-Current-Density effects, are incorporated into the action functional and its derivative are not described by KS-DFT.

Thus, although both Q-DFT and KS-DFT are founded on the first $\{HK/RG\}$ theorem, their route to and description of the S system are different. Both, of course, describe the same S system. However, as the Q-DFT description of the

potential energy of the model fermions and of the total energy is in terms of fields representative of the various electron correlations present, the theory provides a rigorous *physical* interpretation of the unknown { energy/action} functionals and functional derivatives of KS-DFT.

In Chapter 2 we give the basic equations of time-independent Schrodinger theory, the corresponding S system, Q-DFT, and KS-DFT. We also describe the two HK theorems and the RG theorem. Chapter 3 is a description of a corollary to the first HK theorem and to the RG theorem[19]. In Chapter 4 we apply Q-DFT to study the Hydrogen molecule in its ground state[20]. In Chapter 5 we extend nondegenerate Q-DFT to degenerate states for both ground and excited states, and for the cases of both pure state and ensemble densities[12]. Concluding remarks and possible directions for future research are made in Chapter 6.

CHAPTER 2

THE HOHENBERG-KOHN/RUNGE-GROSS THEOREMS AND DENSITY FUNCTIONAL THEORIES

2.1 Time-independent Schrödinger Theory

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

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

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

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

and the electron-interaction operator

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

and where $\Psi(\mathbf{X})$ is the wave function, E the energy, $\mathbf{X} = \mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N; \mathbf{x} = \mathbf{r}\sigma$; σ the spin coordinate. The energy E is the expectation of the Hamiltonian:

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

where the kinetic energy

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

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

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

The *density* $\rho(\mathbf{r})$ is N times the probability of a particle being at $\mathbf{r}$:

$$\rho(\mathbf{r}) = N \sum_i \int \Psi^*(\mathbf{r}\sigma, \mathbf{X}^{N-1}) \Psi(\mathbf{r}\sigma, \mathbf{X}^{N-1}) d\mathbf{X}^{N-1} = \langle \Psi | \hat{\rho} | \Psi \rangle, \tag{2.8}$$

where the density operator

$$\hat{\rho} = \sum_i \delta(\mathbf{r}_i - \mathbf{r}), \tag{2.9}$$

with $\mathbf{X}^{N-1} = \mathbf{x}_2, ..., \mathbf{x}_N$, $\int d\mathbf{X}^{N-1} = \int d\mathbf{x}_2, ... d\mathbf{x}_N$ and $\int d\mathbf{x} = \sum_\sigma \int d\mathbf{r}$. Integration of the density then leads to the electron number:

$$\int \rho(\mathbf{r}) d\mathbf{r} = N. \tag{2.10}$$

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

$$\gamma(\mathbf{r}, \mathbf{r}') = N \sum_\sigma \int \Psi^*(\mathbf{r}\sigma, \mathbf{X}^{N-1}) \Psi(\mathbf{r}'\sigma, \mathbf{X}^{N-1}) d\mathbf{X}^{N-1} = \langle \Psi | \hat{X} | \Psi \rangle, \tag{2.11}$$

where the operator

$$\hat{X} = \hat{A} + i\hat{B}, \tag{2.12}$$

is the sum of the Hermitian operators

$$\hat{A} = \frac{1}{2}\sum_j [\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) + \delta(\mathbf{r}_j - \mathbf{r}')T_j(\mathbf{a})], \tag{2.13}$$

and

$$\hat{B} = \frac{-i}{2}\sum_j [\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) - \delta(\mathbf{r}_j - \mathbf{r}')T_j(\mathbf{a})], \tag{2.14}$$

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

$$T_j(\mathbf{a})\Psi(..., \mathbf{r}_j ...) = \Psi(..., \mathbf{r}_j + \mathbf{a} ...), \tag{2.15}$$

and $\mathbf{a} = \mathbf{r}' - \mathbf{r}$. The diagonal matrix element of the density matrix is the density : $\rho(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r}')$.

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

$$g(\mathbf{r}, \mathbf{r}') = P(\mathbf{r}, \mathbf{r}')/\rho(\mathbf{r}) = \langle\Psi|\hat{P}(\mathbf{r}, \mathbf{r}')|\Psi\rangle/\rho(\mathbf{r}), \tag{2.16}$$

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

$$\hat{P}(\mathbf{r}, \mathbf{r}') = \sum_{i \neq j} \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}'). \tag{2.17}$$

The pair-correlation density satisfies the sum rule

$$\int g(\mathbf{r}, \mathbf{r}')d\mathbf{r}' = N - 1. \tag{2.18}$$

The pair-correlation density can also be interpreted as the density $\rho(\mathbf{r}')$ at $\mathbf{r}'$ plus the reduction in this density at $\mathbf{r}'$ due to electron correlations arising from the Pauli

exclusion principle and Coulomb repulsion. The reduction in the density at $\mathbf{r}'$ is the *quantum-mechanical Fermi-Coulomb hole charge* distribution $\rho_{xc}(\mathbf{r}, \mathbf{r}')$. Thus, we may rewrite the pair-correlation density as

$$g(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') + \rho_{xc}(\mathbf{r}, \mathbf{r}'), \tag{2.19}$$

and consequently the total charge of the Fermi-Coulomb hole for arbitrary electron position $\mathbf{r}$ is

$$\int \rho_{xc}(\mathbf{r}, \mathbf{r}')d\mathbf{r}' = -1. \tag{2.20}$$

Since the self-interaction contribution to the Fermi-Coulomb hole charge is cancelled by the density, the pair-correlation density 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:

$$E_{ee} = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})g(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{2.21}$$

From Eq.(2.19), the electron-interaction energy can be split further as

$$E_{ee} = E_H + E_{xc}, \tag{2.22}$$

where the Coulomb self-energy E_H is

$$E_H = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{2.23}$$

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

$$E_{xc} = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{2.24}$$

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

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

$$t_{\alpha\beta}(\mathbf{r};[\gamma]) = \frac{1}{4}[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r''_\alpha \partial r'_\beta}]\gamma(\mathbf{r}',\mathbf{r}'')|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}''}. \tag{2.25}$$

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

$$T = \int t(\mathbf{r})d\mathbf{r}. \tag{2.26}$$

2.2 The Hohenberg-Kohn Theorems

In this section we state without proof the two Hohenberg-Kohn[1] theorems, and provide a brief discussion of each. The theorems are for *nondegenerate ground* states.

Theorem 1. The ground state density $\rho(\mathbf{r})$ determines the external potential

energy $v(\mathbf{r})$ to within a trivial additive constant C.

In the proof of the theorem, the mapping between external potential energies $v(\mathbf{r})$ and ground state wave functions $\Psi(\mathbf{X})$ is shown to be injective (one-to-one) and therefore bijective (invertible). Then it is shown that the mapping between ground state wave functions $\Psi(\mathbf{X})$ and ground state densities $\rho(\mathbf{r})$ is also injective and hence bijective. Thus, for each nondegenerate ground state density $\rho(\mathbf{r})$, there exists one and only one ground state wave function $\Psi(\mathbf{X})$ that gives rise to this density. Since the map between $\Psi(\mathbf{X})$ and $\rho(\mathbf{r})$ is invertible, there then is a one-to-one correspondence between the ground state density $\rho(\mathbf{r})$ and the external potential energy $v(\mathbf{r})$.

The consequence of the theorem is that the ground state density $\rho(\mathbf{r})$ of a physical system determines that system via its Hamiltonian H, and hence all its properties by the solution $\Psi(\mathbf{X})$ of the corresponding Schrödinger equation Eq.(2.1). The integral of the electronic density leads to the electron number N (see. Eq. (2.10)). The cusps in the electron density which satisfy the electron-nucleus cusp condition determine the positions of the nuclei and their charge Z. With the kinetic energy T and electron-interaction potential energy $\hat{U}$ operators known, knowledge of the external potential energy $v(\mathbf{r})$ then fully defines the Hamiltonian H of the system to within a constant C.

Another consequence of the one-to-one correspondence between the wave function and the ground state density is that the wave function is a functional of the density: $\Psi(\mathbf{X}) = \Psi[\rho]$. Thus, all expectations of operators O are unique functionals of the density: $< \Psi[\rho]|O|\Psi[\rho] >$. Thus, the energy is a functional of the ground state density: $E = E[\rho]$.

Theorem 2. The ground state density $\rho(\mathbf{r})$ can be determined from the ground state energy functional $E[\rho]$ via the variational principle by variation only of the density.

Consider a trial ground state density $\rho'(\mathbf{r})$. From the first theorem, this density determines the corresponding external potential energy $v'(\mathbf{r})$, and trial ground state wave function $\Psi'(\rho')$. From the variational principle for the energy it follows that

$$E' = E[\rho'] = \langle \Psi'[\rho']|\hat{H}|\Psi'[\rho'] \rangle \; > \; E \; for \; \rho'(\mathbf{r}) \neq \rho(\mathbf{r})$$
$$= \; E \; for \; \rho'(\mathbf{r}) = \rho(\mathbf{r}). \qquad (2.27)$$

Thus, the exact ground state density can be determined by minimization of the functional $E[\rho]$ for arbitrary variations $\delta\rho(\mathbf{r})$ of the density. Introducing a Lagrange multiplier μ to ensure particle number conservation $\int \rho(\mathbf{r})d\mathbf{r} = N$, the stationary point is achieved via the variational principle at the vanishing of the first-order variation:

$$\delta\{E[\rho] - \mu[\int \rho(\mathbf{r})d\mathbf{r} - N]\} = 0. \qquad (2.28)$$

Equivalently, the ground state density may be obtained from the corresponding Euler-Lagrange equation

$$\frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = \mu. \tag{2.29}$$

Separating out the external potential energy component, the ground state energy functional $E[\rho]$ may be written as

$$E[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_{HK}[\rho], \tag{2.30}$$

where the functional

$$F_{HK}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{U} | \Psi[\rho] \rangle. \tag{2.31}$$

Note that F_{HK} is *universal* in the sense that it does not depend on $\hat{V}$. It is the same functional for arbitrary electron-interaction operators $\hat{U}$.

The statements on invertibility, variational access, and universality constitute the classic formulation of the theorems of Hohenberg and Kohn.

2.3 The Runge-Gross Theorem

The Runge-Gross theorem[2] is an extension of the first Hohenberg-Kohn theorem to time-dependent external potentials of the form $V(t) = \sum_i v(\mathbf{r}_i t)$. The time-

dependent Schrödinger equation is

$$i\frac{\partial\Psi(\mathbf{X}t)}{\partial t} = H(t)\Psi(\mathbf{X}t), \tag{2.32}$$

where $\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{U}$, and $\Psi(\mathbf{X}t)$ the system wave function with initial state $\Psi(t_0)$. The external potentials $v(\mathbf{r}t)$ are *assumed* expandable in a Taylor series about t_0.

Runge-Gross theorem. The density $\rho(\mathbf{r}t)$ corresponding to an initial state $\Psi(t_0)$ determines the external potential energy $v(\mathbf{r}t)$ to within a purely time-dependent function $C(t)$.

Together with the kinetic $\hat{T}$ and electron-interaction potential energy $\hat{U}$ operators, the Hamiltonian $\hat{H}(t)$ is consequently known. Thus the density $\rho(\mathbf{r}t)$ determines the Hamiltonian to within a time-dependent function $C(t)$. The Hamiltonian, via the Schrödinger equation Eq. (2.32), then determines the wave function $\Psi(\mathbf{X}t)$ to within a time-dependent phase $\alpha(t)$. In turn, the wave function determines the density $\rho(\mathbf{r}t)$, the phase factors canceling out.

The consequence of the one-to-one relationship between the density $\rho(\mathbf{r}t)$ and the potential energy $v(\mathbf{r}t)$, is that the wave function is a functional of the density and the initial state, unique to within an arbitrary time-dependent phase factor. The expectation value of any operator $\hat{O}(t)$ is therefore a unique functional of the density, the phase factor once again canceling out.

In the time-independent case, as a consequence of the second Hohenberg-Kohn theorem, the density $\rho(\mathbf{r})$ is determined by the Euler-Lagrange equation Eq. (2.29). In the time-dependent case, the solution $\Psi(\mathbf{X}t)$ corresponds to a *stationary point* of the quantum-mechanical action integral

$$A[\Psi] = \int_{t_0}^{t_1} \langle \Psi(t) | i\frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle \ . \tag{2.33}$$

Since the wave function is a functional of the density, there must exist some action functional of the density $A[\rho]$ that has a stationary point at the true time-dependent density $\rho(\mathbf{r}t)$ corresponding to the Hamiltonian $H(t)$ and initial state $\Psi(t_0)$. Thus, the correct density can be obtained by solving the Euler-Lagrange equation

$$\frac{\delta A[\rho; \Psi_0]}{\delta \rho(\mathbf{r}t)} = 0 \tag{2.34}$$

2.4 Noninteracting Fermions with Equivalent Density—the S system

In time-independent theory it is *assumed* that the S system of noninteracting fermions with density equivalent to that of the interacting system exists. The Schrödinger theory differential equation corresponding to the S system is

$$[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})]\phi_i(\mathbf{x}) = \varepsilon_i \phi_i(\mathbf{x}); \ i = 1, ..., N, \tag{2.35}$$

where

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_{ee}(\mathbf{r}), \tag{2.36}$$

$v_{ee}(\mathbf{r})$ is the local electron-interaction potential energy of the model fermions incorporating all the many-body correlations due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects, $\phi_i(\mathbf{x})$ the single-particle orbitals, and ε_i the corresponding eigenvalues. The resulting density is

$$\rho(\mathbf{r}) = \langle \Phi\{\phi_i\}|\hat{\rho}|\Phi\{\phi_i\}\rangle = \sum_{i\sigma} |\phi_i(\mathbf{r}\sigma)|^2, \tag{2.37}$$

where $\Phi\{\phi_i\}$ is the Slater determinant of the orbitals $\phi_i(\mathbf{x})$. *The state of the S system is arbitrary in that it may be in a ground or excited state.*

For the S system, the idempotent *Dirac density matrix* $\gamma_s(\mathbf{r},\mathbf{r}')$ is

$$\gamma_s(\mathbf{r},\mathbf{r}') = \langle \Phi\{\phi_i\}|\hat{X}|\Phi\{\phi_i\}\rangle = \sum_i \sum_\sigma \phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma), \tag{2.38}$$

and the *pair-correlation density* $g_s(\mathbf{r},\mathbf{r}')$ is

$$g_s(\mathbf{r},\mathbf{r}') = \langle \Phi\{\phi_i\}|\hat{P}|\Phi\{\phi_i\}\rangle/\rho(\mathbf{r}) = \rho(\mathbf{r}') + \rho_x(\mathbf{r},\mathbf{r}'), \tag{2.39}$$

where $\rho_x(\mathbf{r},\mathbf{r}')$ is the *nonlocal Fermi hole* charge defined as

$$\rho_x(\mathbf{r},\mathbf{r}') = -|\gamma_s(\mathbf{r},\mathbf{r}')|^2/2\rho(\mathbf{r}). \tag{2.40}$$

Since

$$\int g_s(\mathbf{r}\mathbf{r}')d\mathbf{r}' = N - 1, \tag{2.41}$$

the Fermi hole satisfies the following sum rule

$$\int \rho_x(\mathbf{r},\mathbf{r}')d\mathbf{r}' = -1. \tag{2.42}$$

The S system pair-correlation density is also self-interaction free. In a manner similar to that of the interacting system, one defines the S system *kinetic-energy density tensor* $t_{s,\alpha\beta}(\mathbf{r},[\gamma_s])$ in terms of $\gamma_s(\mathbf{r},\mathbf{r}')$ as

$$t_{s,\alpha\beta}(\mathbf{r};[\gamma]) = \frac{1}{4}[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r''_\alpha \partial r'_\beta}]\gamma_s(\mathbf{r}',\mathbf{r}'')|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}''}. \tag{2.43}$$

Thus the scalar kinetic energy density $t_s(\mathbf{r}) = \sum_\alpha t_{s,\alpha\alpha}(\mathbf{r})$ and the non-interacting kinetic energy is

$$T_s = \langle\Phi\{\phi_i\}|\hat{T}|\Phi\{\phi_i\}\rangle = \int t_s(\mathbf{r})d\mathbf{r}. \tag{2.44}$$

The total energy of the *interacting* system is then

$$E = T_s + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{ee} + T_c, \tag{2.45}$$

or

$$E = \sum_i \epsilon_i - \int v_{ee}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{ee} + T_c, \tag{2.46}$$

where T_c is the difference between the kinetic energy of the interacting and non-interacting systems, referred to as the *Correlation-Kinetic energy.*

The *nonlocal Coulomb hole* charge $\rho_c(\mathbf{r},\mathbf{r}')$ is defined via the S system Fermion hole as

$$\rho_c(\mathbf{r},\mathbf{r}') = \rho_{xc}(\mathbf{r},\mathbf{r}') - \rho_x(\mathbf{r},\mathbf{r}'), \tag{2.47}$$

so that the sum rule on the Coulomb hole charge is

$$\int \rho_c(\mathbf{r}, \mathbf{r}')d\mathbf{r}' = 0. \tag{2.48}$$

Employing the definitions of the Fermi and Coulomb holes, the electron interaction energy E_{ee} may also be expressed in terms of its Pauli and Coulomb components as

$$E_{ee} = E_H + E_x + E_c, \tag{2.49}$$

where E_H is the Coulomb self-energy, E_x the Pauli (exchange) energy, and E_c the Coulomb energy. The Pauli and Coulomb energies are the energies of interaction between the density and the Fermi and Coulomb hole charges, respectively:

$$E_x = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho_x(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{2.50}$$

and

$$E_c = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho_c(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{2.51}$$

Finally, the highest eigenvalue of the S system differential equation corresponds to minus the ionization potential or electron affinity[3,25-27]. The other eigenvalues have no physical meaning.

2.5 Quantal Density Functional Theory

As noted in the introduction, Quantal density-functional theory[3] (Q-DFT) maps the interacting to the S system of noninteracting Fermions. It does so in a

manner in which the contribution of the various electron correlations are *explicitly* defined. In this subsection we provide the key equations of time-independent *nondegenerate ground* and *excited* state Q-DFT, and refer the reader to Ref. [3] for those of time-dependent theory. Degenerate state Q-DFT for both ground and excited states is developed in chapter 5.

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

$$v_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{F}(\mathbf{r}') \cdot d\mathbf{l}'. \tag{2.52}$$

The work done is ***path-independent*** since $\nabla \times \mathcal{F}(\mathbf{r}) = 0$. The field $\mathcal{F}(\mathbf{r})$ is the sum of an of electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ representative of Pauli and Coulomb correlations, and a Correlation-Kinetic field component $\mathcal{Z}_{t_c}(\mathbf{r})$ representative of these effects :

$$\mathcal{F}(\mathbf{r}) = \mathcal{E}_{ee}(\mathbf{r}) + \mathcal{Z}_{t_c}(\mathbf{r}). \tag{2.53}$$

The fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_{t_c}(\mathbf{r})$ are not necessarily conservative. However, their sum always is.

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

$$\mathcal{E}_{ee}(\mathbf{r}) = \int \frac{g(\mathbf{r}, \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'. \tag{2.54}$$

The field $\mathbf{Z}_{t_c}(\mathbf{r})$ is the difference between two fields $\mathbf{Z}(\mathbf{r})$ and $\mathbf{Z}_s(\mathbf{r})$ where $\mathbf{Z}(\mathbf{r}) = \mathbf{z}(\mathbf{r};[\gamma])/\rho(\mathbf{r})$ and $\mathbf{Z}_s = \mathbf{z}_s(\mathbf{r};[\gamma_s])/\rho(\mathbf{r})$:

$$\mathbf{Z}_{t_c}(\mathbf{r}) = \mathbf{Z}_s(\mathbf{r}) - \mathbf{Z}(\mathbf{r}). \tag{2.55}$$

The 'forces' $\mathbf{z}(\mathbf{r};[\gamma])$ and $\mathbf{z}_s(\mathbf{r};[\gamma_s])$ are defined, respectively, in terms of their components as

$$z_\alpha(\mathbf{r}) = 2\sum_\beta \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r};[\gamma]), \tag{2.56}$$

and

$$z_{s,\alpha}(\mathbf{r}) = 2\sum_\beta \frac{\partial}{\partial r_\beta} t_{s,\alpha\beta}(\mathbf{r};[\gamma_s]). \tag{2.57}$$

The electron-interaction E_{ee} and correlation-kinetic T_c energy components of the total energy E (see Eqs. (2.45), (2.46)) may be expressed in integral virial form in terms of the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathbf{Z}_{t_c}$, respectively as

$$E_{ee} = \int \rho(\mathbf{r})\mathbf{r}\cdot\mathcal{E}_{ee}(\mathbf{r})d\mathbf{r}, \tag{2.58}$$

and

$$T_c = \frac{1}{2}\int \rho(\mathbf{r})\mathbf{r}\cdot\mathbf{Z}_{t_c}(\mathbf{r})d\mathbf{r}. \tag{2.59}$$

These energy expressions are independent of whether or not the fields $\mathcal{E}_{ee}(\mathbf{r})$ and

$\mathbf{Z}_{t_c}(\mathbf{r})$ are conservative.

For the systems such as spherically symmetries atoms, open-shell atoms in the central field approximation, jellium and structureless pseudopotential models of metal surfaces and clusters, etc., the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathbf{Z}_{t_c}$ are *separately* conservative. Thus, for such systems,

$$v_{ee}(\mathbf{r}) = W_{ee}(\mathbf{r}) + W_{t_c}(\mathbf{r}), \tag{2.60}$$

where

$$W_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{E}_{ee}(\mathbf{r}') \cdot d\mathbf{l}' \;\; and \;\; W_{t_c}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathbf{Z}_{t_c}(\mathbf{r}') \cdot d\mathbf{l}', \tag{2.61}$$

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

The electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ may be further subdivided into its Hartree $\mathcal{E}_H(\mathbf{r})$, Pauli-Coulomb $\mathcal{E}_{xc}(\mathbf{r})$, Pauli $\mathcal{E}_x(\mathbf{r})$, and Coulomb $\mathcal{E}_c(\mathbf{r})$ components as follows. Using the partition of $g(\mathbf{r}, \mathbf{r}')$ into its local $\rho(\mathbf{r}')$ and nonlocal $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ parts, and the further partition of $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ into its Fermi $\rho_x(\mathbf{r}, \mathbf{r}')$ and Coulomb $\rho_c(\mathbf{r}, \mathbf{r}')$ components, the field $\mathcal{E}_{ee}(\mathbf{r})$ may be written as

$$\mathcal{E}_{ee}(\mathbf{r}) = \mathcal{E}_H(\mathbf{r}) + \mathcal{E}_{xc}(\mathbf{r}) = \mathcal{E}_H(\mathbf{r}) + \mathcal{E}_x(\mathbf{r}) + \mathcal{E}_c(\mathbf{r}), \tag{2.62}$$

where

$$\mathcal{E}_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}', \tag{2.63}$$

$$\mathcal{E}_{xc}(\mathbf{r}) = \int \frac{\rho_{xc}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}', \tag{2.64}$$

$$\mathcal{E}_{x}(\mathbf{r}) = \int \frac{\rho_{x}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}', \tag{2.65}$$

$$\mathcal{E}_{c}(\mathbf{r}) = \int \frac{\rho_{c}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{2.66}$$

From the above equations of the fields, the Hartree (Coulomb self-energy) E_H, Pauli-Coulomb E_{xc}, Pauli E_x, and Coulomb E_c energies maybe be written in virial form as

$$E_H = \int \rho(\mathbf{r})\mathbf{r}\cdot\mathcal{E}_H(\mathbf{r})d\mathbf{r}, \tag{2.67}$$

$$E_{xc} = \int \rho(\mathbf{r})\mathbf{r}\cdot\mathcal{E}_{xc}(\mathbf{r})d\mathbf{r}, \tag{2.68}$$

$$E_x = \int \rho(\mathbf{r})\mathbf{r}\cdot\mathcal{E}_x(\mathbf{r})d\mathbf{r}, \tag{2.69}$$

$$E_c = \int \rho(\mathbf{r})\mathbf{r}\cdot\mathcal{E}_c(\mathbf{r})d\mathbf{r}. \tag{2.70}$$

For those systems for which the field $\mathcal{E}_{ee}(\mathbf{r})$ is conservative, its components $\mathcal{E}_{xc}(\mathbf{r})$, $\mathcal{E}_x(\mathbf{r})$, and $\mathcal{E}_c(\mathbf{r})$ are also separately conservative. The field $\mathcal{E}_H(\mathbf{r})$ is always conservative as it arises due to a local charge distribution, the density $\rho(\mathbf{r})$. Thus, for such systems, we may write the electron-interaction potential energy $v_{ee}(\mathbf{r})$ of the model Fermions as

$$\begin{aligned} v_{ee}(\mathbf{r}) &= W_H(\mathbf{r}) + W_{xc}(\mathbf{r}) + W_{t_c}(\mathbf{r}) \\ &= W_H(\mathbf{r}) + W_x(\mathbf{r}) + W_c(\mathbf{r}) + W_{t_c}(\mathbf{r}), \end{aligned} \tag{2.71}$$

where

$$W_H(\mathbf{r}) = -\int \mathcal{E}_H(\mathbf{r}') \cdot d\mathbf{l}' = \int \rho_H(\mathbf{r}') d\mathbf{r}' / |\mathbf{r} - \mathbf{r}'|, \tag{2.72}$$

$$W_{xc}(\mathbf{r}) = -\int \mathcal{E}_{xc}(\mathbf{r}') \cdot d\mathbf{l}', \tag{2.73}$$

$$W_x(\mathbf{r}) = -\int \mathcal{E}_x(\mathbf{r}') \cdot d\mathbf{l}', \tag{2.74}$$

$$W_c(\mathbf{r}) = -\int \mathcal{E}_c(\mathbf{r}') \cdot d\mathbf{l}'. \tag{2.75}$$

The above framework of Q-DFT is valid for transformation from both nondegenerate *ground* and *excited* states. As noted previously, the state of the S system is *arbitrary* in that it may be in a ground or excited state. The state of the S system, is governed solely by the Correlation-Kinetic field $\mathbf{Z}_{t_c}(\mathbf{r})$ or equivalently the kinetic field $\mathbf{Z}_s(\mathbf{r})$, because it is only in the expression for these fields that the orbitals $\phi_i(\mathbf{x})$ of the S system appear. We refer the reader to Refs.[9.10] for an example of the transformation of an *excited* state of the interacting system to two S systems, one in its *ground* state and the other in an *excited* state. For the transformation of a *ground* state of the interacting system to two S systems, one in its *ground* state

and the other in an *excited* state see Ref.[29]. For each S system, the same density and energy as that of the interacting system is obtained. Furthermore, the highest occupied eigenvalue of each S system corresponds to the first ionization potential of the interacting system.

2.6 Kohn-Sham Density Functional Theory

Kohn-Sham(KS) density functional theory (DFT), the precursor to Q-DFT, is based on the two theorems of Hohenberg and Kohn. Hence, it is a ground state theory: the mapping is from a *nondegenerate ground* state of the interacting system to an S system also in its *ground* state.

The starting point of the theory is the ground state energy functional expression Eq.(2.30). By adding and subtracting the kinetic energy functional $T_s[\rho]$ of the non-interacting Fermions from this expression, the ground state energy may be written as

$$E[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{ee}^{KS}[\rho], \tag{2.76}$$

where

$$E_{ee}^{KS}[\rho] = F_{HK}[\rho] - T_s[\rho]. \tag{2.77}$$

This defines the KS-DFT electron-electron interaction energy functional $E_{ee}^{KS}[\rho]$, in

which the Pauli and Coulomb correlations as well as Correlation-Kinetic effects are embedded. Since the Hartree energy $E_H[\rho]$ is a known functional of the density, the functional may be further partitioned as

$$E_{ee}^{KS}[\rho] = E_H[\rho] + E_{xc}^{KS}[\rho], \tag{2.78}$$

which then defines the KS-DFT 'exchange-correlation' energy functional $E_{xc}^{KS}[\rho]$. Note that this functional is representative of all correlations except that of the Hartree or Coulomb self-energy.

The functional $E_{xc}^{KS}[\rho]$ is usually further partitioned into an exchange E_x and KS 'correlation' energy functional $E_c^{KS}[\rho]$ components:

$$E_{xc}^{KS} = E_x[\rho] + E_c^{KS}[\rho]. \tag{2.79}$$

The functionals $T_s[\rho]$, $E_{ee}^{KS}[\rho]$, $E_{xc}^{KS}[\rho]$, $E_x[\rho]$, $E_c^{KS}[\rho]$ are all unknown. The kinetic energy T_s is determined directly from the orbitals of the S system. It is also customarily to replace $E_x[\rho]$ by the expression for the exchange energy of Hartree-Fock theory but to employ the S system orbitals instead. It can be shown [3] that $E_x[\rho]$ is representative of Pauli correlations and lowest-order Correlation-Kinetic effects, and that $E_c^{KS}[\rho]$ is representative of Coulomb correlations (minus the Coulomb self-energy) and second- and higher-order Correlation-Kinetic effects.

As a consequence of the Hohenberg-Kohn variational principle Eq.(2.29), the local electron-interaction potential energy $v_{ee}(\mathbf{r})$ is the defined as the functional derivative

of $E_{ee}^{KS}[\rho]$:

$$v_{ee}(\mathbf{r}) = \frac{\delta E_{ee}^{KS}[\rho]}{\delta \rho(\mathbf{r})}. \tag{2.80}$$

This potential energy may further be written in terms of its Hartree $v_H(\mathbf{r})$, KS 'exchange-Correlation' $v_{xc}(\mathbf{r})$, 'exchange' $v_x(\mathbf{r})$, and KS 'correlation' $v_c(\mathbf{r})$ components as

$$v_{ee}(\mathbf{r}) = v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) = v_H(\mathbf{r}) + v_x(\mathbf{r}) + v_c(\mathbf{r}), \tag{2.81}$$

where the Hartree potential energy is defined as

$$v_H(\mathbf{r}) = \frac{\delta E_H[\rho]}{\delta \rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r})'}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{2.82}$$

and

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}, \; v_x(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta \rho(\mathbf{r})}, \; v_c(\mathbf{r}) = \frac{\delta E_c[\rho]}{\delta \rho(\mathbf{r})}, \tag{2.83}$$

respectively. Thus, in contrast to Q-DFT, the KS-DFT is in terms of functionals of the ground state density and their derivatives.

CHAPTER 3

COROLLARY TO THE HOHENBERG-KOHN THEORY

3.1 Introduction and Corollary

In this chapter, we provide further insight[19] into the first theorem of Hohenberg and Kohn(HK), and of its extension to the time-dependent case due to Runge and Gross(RG), by deriving a corollary to the theorem.

According to the first HK theorem, for a system of N electrons in an external field $\mathcal{F}^{ext}(\mathbf{r}) = -\nabla v(\mathbf{r})$, the ***ground*** state electronic density $\rho(\mathbf{r})$ for a nondegenerate state determines the external potential energy $v(\mathbf{r})$ uniquely to within an ***unknown trivial additive constant*** C. Since the kinetic energy $\hat{T}$ and electronic-interaction potential energy $\hat{U}$ operators are known, the Hamiltonian $\hat{H}$ is explicitly known.

In the extension of the first HK theorem to the time-dependent case, Runge and Gross(RG) prove that for a system of N electrons in a time-dependent external field $\mathcal{F}^{ext}(\mathbf{r}t) = -\nabla v(\mathbf{r}t)$, such that the potential energy $v(\mathbf{r}t)$ is Taylor- expandable about some initial time t_0, the density $\rho(\mathbf{r}t)$ evolving from some fixed initial state $\Psi(t_0)$, determines the external potential energy uniquely to within an ***additive purely time-dependent function*** $C(t)$. Again, as the kinetic and electron-interaction potential energy operators are already defined, the Hamiltonian $\hat{H}(t)$ is

known.

In the preamble to their proof, $\{HK/RG\}$ consider Hamiltonians $\{\hat{H}/\hat{H}(t)\}$ that differ by an additive {constant C/function $C(t)$ }to be equivalent. In other words, the ***physical system*** under consideration as defined by the electronic Hamiltonian remains the ***same*** on addition of this {constant/function } which is ***arbitrary***. Thus, measurement of properties of the system, other than for example the total energy $\{E/E(t)\}$, remain invariant. The theorem then proves that ***each*** density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$ is associated with ***one*** and ***only one*** Hamiltonian $\{\hat{H}/\hat{H}(t)\}$ or physical system: the density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$ determines that *unique* Hamiltonian $\{\hat{H}/\hat{H}(t)\}$ to within an additive {constant C/function $C(t)$}.

{HK/RG}, however, did not consider the case of a set of Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ that represent ***different*** physical systems which differ by an ***intrinsic*** {constant C/function $C(t)$}, but which yet have the ***same*** density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$. By intrinsic {constant C/function $C(t)$ } we mean one that is inherent to the system and not extrinsically additive. Thus, this {constant C/function $C(t)$} helps distinguish between the different Hamiltonians in the set $\{\hat{H}\}/\{\hat{H}(t)\}$, and is consequently ***not arbitrary***. That the physical systems are ***different*** could, of course, be confirmed by experiment. Further, the density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$ would then not be able to distinguish between the different Hamiltonians $\{\hat{H}/\hat{H}(t)\}$ or physical systems, as it is the same for all of them.

In this chapter we construct a ***set*** of model systems with ***different*** Hamiltonians $\{\hat{H}/\hat{H}(t)\}$ that differ by a {constant C/function $C(t)$} but which ***all*** possess the same density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$. This is the Hooke's species: atom, molecule, all positive molecular ions with number of nuclei $\mathcal{N}$ greater than two. The { constants C/function $C(t)$ }contain information about the system, and are intrinsic to distinguishing between the different elements of the species.

The corollary to the {HK/RG} theorem is as follows: Degenerate Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ that differ by a {constant C/function $C(t)$} but which represent different physical systems all possessing the same density { $\rho(\mathbf{r})/\rho(\mathbf{r}t)$} cannot be distinguished on the basis of the {HK/RG} theorem. That is, for such systems, the density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$ cannot determine each external potential energy $\{v(\mathbf{r})/v(\mathbf{r}t)\}$, and hence each Hamiltonian of the set $\{\hat{H}\}/\{\hat{H}(t)\}$, uniquely.

In the following sections, we describe the Hooke's species for the time-independent and time-dependent cases to prove the above corollary.

3.2 Time-Independent Case

Prior to describing the Hooke's species, let us consider the following Coulomb species of two-electron systems and $\mathcal{N}$ nuclei: the Helium atom ($\mathcal{N} = 1$; atomic

number $Z = 2$), the Hydrogen molecule ($\mathcal{N} = 2$; atomic number of each nuclei $Z = 1$), and the positive molecular ions ($\mathcal{N} > 2$; atomic number of each nuclei $Z = 1$). (See Fig.1).

In atomic units, the Hamiltonian of the Coulomb species is

$$\hat{H}_{\mathcal{N}} = \hat{T} + \hat{U} + \hat{V}_{\mathcal{N}} \tag{3.1}$$

where $\hat{T}$ is the kinetic energy operator:

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{2} \nabla_i^2, \tag{3.2}$$

$\hat{U}$ the electron-interaction potential energy operator:

$$\hat{U} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{3.3}$$

and $\hat{V}_{\mathcal{N}}$ the external potential energy operator:

$$\hat{V}_{\mathcal{N}} = \sum_{i=1}^{2} v_{\mathcal{N}}(\mathbf{r}_i), \tag{3.4}$$

with

$$v_{\mathcal{N}}(\mathbf{r}) = \sum_{j=1}^{\mathcal{N}} f_C(\mathbf{r} - \mathbf{R}_j). \tag{3.5}$$

where

$$f_C(\mathbf{r} - \mathbf{R}_j) = -\frac{1}{|\mathbf{r} - \mathbf{R}_j|}. \tag{3.6}$$

Here $\mathbf{r}_1$ and $\mathbf{r}_2$ are positions of the electrons, $\mathbf{R}_j (j = 1, ...\mathcal{N})$ the positions of the nuclei, and $f_C(\mathbf{r} - \mathbf{R}_j)$ the Coulomb external potential energy function. Each

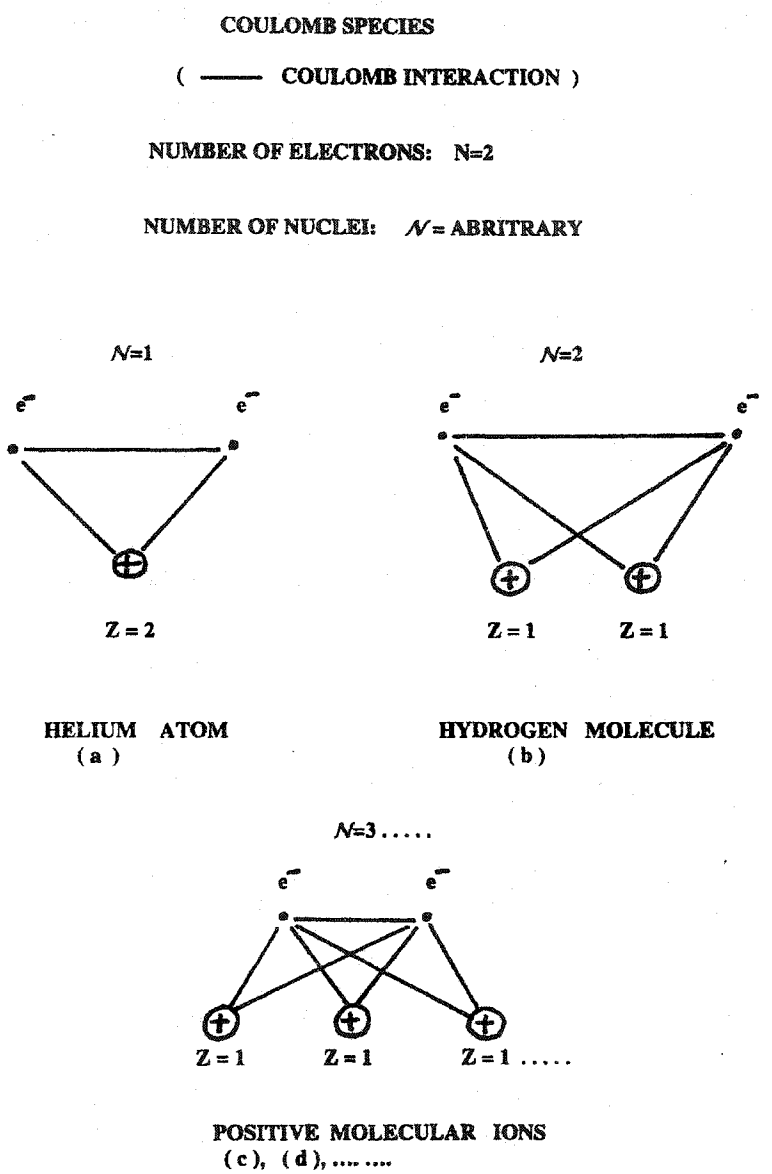

FIG. 1: The Coulomb species comprises of two electrons and an arbitrary number $\mathcal{N}$ of nuclei, the interaction between the electrons and that between the electrons and nuclei being Coulombic: (a)Helium atom; (b) Hydrogen molecule; (c), (d), ..., Positive molecular ions. Here $\mathcal{N}$ is the number of nuclei, Z the nuclear charge, e^- the electronic charge. Note that each element of the species corresponds to a different physical system .

element of the Coulomb species represents a ***different*** physical system. (The species could be further generalized by requiring each nuclei to have a different charge.)

Now suppose the ground state density $\rho(\mathbf{r})$ of the Hydrogen molecule were known. Then, according to the HK theorem, this density uniquely determines the external potential energy operator to within an additive constant C:

$$\hat{V}_{\mathcal{N}=2} = -\frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_2|}. \tag{3.7}$$

Thus, the Hamiltonian of the Hydrogen molecule is exactly known from the ground state density. Note that in addition to the functional form of the external potential energy, the density also explicitly defines the positions $\mathbf{R}_1$ and $\mathbf{R}_2$ of the nuclei.

The fact that the ground state density determines the external potential energy operator, and hence the Hamiltonian may be understood as follows. Integration of the density leads to the number N of the electrons: $\int \rho(\mathbf{r})d\mathbf{r} = N$. The cusps in the electron density which satisfies the electron-nucleus cusp condition [21-25], determine in turn the positions of the $\mathcal{N}$ nuclei and their charge Z. Thus, the external potential energy operator $\hat{V}_{\mathcal{N}} = \sum_i v_{\mathcal{N}}(\mathbf{r}_i)$, and therefore the Hamiltonian $\hat{H}$ are known.

The Hooke's species (see Fig.2)comprise of two electrons coupled harmonically to a variable number $\mathcal{N}$ of nuclei. The electrons are coupled to each nuclei with a different spring constants $k_j, j = 1...\mathcal{N}$. The species comprise of the Hooke's

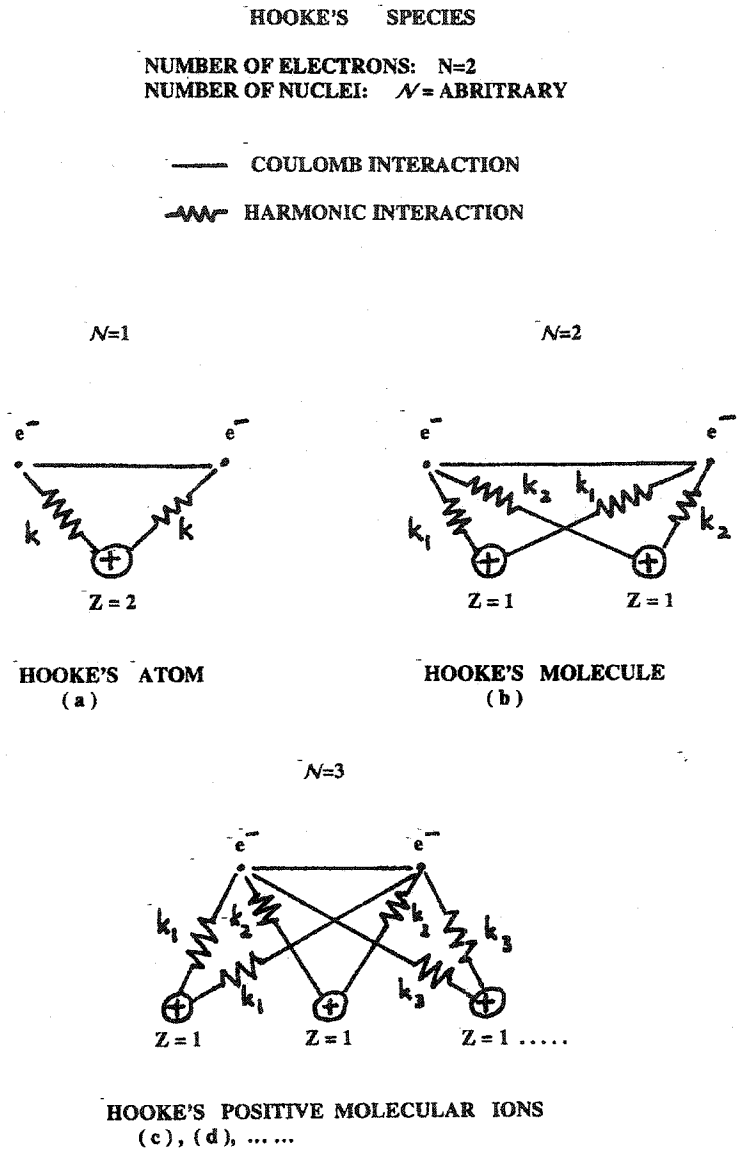

FIG. 2: The Hooke's species comprises of two electrons and an arbitrary number $\mathcal{N}$ of nuclei, the interaction between the electrons and nuclei being harmonic with spring constant k, k_1, k_2, ...$k_{\mathcal{N}}$. (a) Hooke's atom; (b) Hooke's molecule; (c), (d), ...Hooke's positive molecular ions. Here $\mathcal{N}$ is the number of nuclei, Z the nuclear charge, e^- the electronic charge. Note that each element of the species corresponds to a different physical system.

atom ($\mathcal{N} = 1$, atomic number $Z = 2$, spring constant k), the Hooke's molecule ($\mathcal{N} = 2$; atomic number of each nuclei $Z = 1$, spring constants k_1 and k_2), and the Hooke's positive molecular ions ($\mathcal{N} > 2$, atomic number of each nuclei $Z = 1$, spring constants $k_1, k_2, k_3 ... k_{\mathcal{N}}$). The Hamiltonian $\hat{H}_{\mathcal{N}}$ of this species is the same as that of the Coulomb species of Eq.(1) except that the external potential energy function is $f_H(\mathbf{r} - \mathbf{R}_j)$, where

$$f_H(\mathbf{r} - \mathbf{R}_j) = \frac{1}{2} k_j (\mathbf{r} - \mathbf{R}_j)^2. \tag{3.8}$$

Just as for the Coulomb species, each element of the Hooke's species represents a ***different*** physical system. Thus, for example, the Hamiltonian for Hooke's atom is

$$\hat{H}_a = -\frac{1}{2}{\nabla_1}^2 - \frac{1}{2}{\nabla_2}^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{2} k[(\mathbf{r}_1 - \mathbf{R}_1)^2 + (\mathbf{r}_2 - \mathbf{R}_1)^2], \tag{3.9}$$

and that of Hooke's molecule is

$$\begin{aligned} \hat{H}_m = & -\frac{1}{2}{\nabla_1}^2 - \frac{1}{2}{\nabla_2}^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{2}\{k_1[(\mathbf{r}_1 - \mathbf{R}_1)^2 + (\mathbf{r}_2 - \mathbf{R}_1)^2 \\ & + k_2[(\mathbf{r}_1 - \mathbf{R}_2)^2 + (\mathbf{r}_2 - \mathbf{R}_2)^2]\}, \end{aligned} \tag{3.10}$$

where $k \neq k_1 \neq k_2$, and so on for the various Hooke's positive molecular ions with $\mathcal{N} > 2$.

For the Hooke's species, however, the external potential energy operator $\hat{V}_{\mathcal{N}}$ which is

$$\hat{V}_{\mathcal{N}} = \frac{1}{2} \sum_{j=1}^{\mathcal{N}} [k_j (\mathbf{r}_1 - \mathbf{R}_j)^2 + k_j (\mathbf{r}_2 - \mathbf{R}_j)^2], \tag{3.11}$$

may be rewritten as

$$\hat{V}_{\mathcal{N}} = (\frac{1}{2}\sum_{j=1}^{\mathcal{N}} k_j)[(\mathbf{r}_1 - \mathbf{a})^2 + (\mathbf{r}_2 - \mathbf{a})^2] + C(\{k\}, \{\mathbf{R}\}, \mathcal{N}), \tag{3.12}$$

where the translation vector $\mathbf{a}$ is

$$\mathbf{a} = \sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j / \sum_{j=1}^{\mathcal{N}} k_j, \tag{3.13}$$

and the constant C is

$$C = b - d \tag{3.14}$$

with

$$b = \sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j^2, \tag{3.15}$$

$$d = (\sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j)^2 / \sum_{j=1}^{\mathcal{N}} k_j, \tag{3.16}$$

or

$$C = \frac{1}{2}\sum_{i,j=1}^{\mathcal{N}}{}' k_i k_j (\mathbf{R}_i - \mathbf{R}_j)^2 / \sum_{j=1}^{\mathcal{N}} k_j. \tag{3.17}$$

From Eq.(3.12) it is evident that the Hamiltonians $\hat{H}_{\mathcal{N}}$ of the Hooke's species are those of a Hooke's atom ($\sum_{j=1}^{\mathcal{N}} k_j = k$), (to within a constant $C(\{k\}, \{\mathbf{R}\}, \mathcal{N})$), whose center of mass is at $\mathbf{a}$. The constant C which depends upon the spring constants $\{k\}$, the positions of the nuclei $\{\mathbf{R}\}$, and the number $\mathcal{N}$ of the nuclei, differs from a trivial additive constant in that it is an ***intrinsic*** part of ***each*** Hamiltonian $\hat{H}_{\mathcal{N}}$, and distinguishes between the different elements of the species. It does so because the constant $C(\{k\}, \{\mathbf{R}\}, \mathcal{N})$ contains physical information about

the system such as the positions $\{\mathbf{R}\}$ of the nuclei.

Now according to the HK theorem, the ground state density determines the external potential energy, and hence the Hamiltonian, to within a constant. Since the density of ***each*** element of the Hooke's species is that of the Hooke's atom, it can only determine the Hamiltonian of a Hooke's atom and not the constant $C(\{k\},\{\mathbf{R}\},\mathcal{N})$. Therefore, it cannot determine the Hamiltonian $\hat{H}_{\mathcal{N}}$ for $\mathcal{N} > 1$. This is reflected by the fact that the density of the elements of the Hooke's species does not satisfy the electron-nucleus cusp condition.(It is emphasized that although the 'degenerate Hamiltonians' of the Hooke's species have a ground state wave function and density that corresponds to that of a Hooke's atom, each element of the species represents a ***different*** physical system. Thus, for example, a neutron diffraction experiment on the Hooke's molecule and Hooke's positive molecular ion would ***all*** give different results).

It is also possible to construct a Hooke's species such that the density of each element is the ***same***. This is most readily seen for the case when the center of mass is moved to the origin of the coordinate system, i.e. for $\mathbf{a} = 0$. This requires, from Eq.(3.13), the product of the spring constants and the coordinates of the nuclei satisfy the condition

$$\sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j = 0, \tag{3.18}$$

so that the external potential energy operator is then

$$\hat{V}_{\mathcal{N}}(\mathbf{r}) = \frac{1}{2}\sum_{j=1}^{\mathcal{N}} k_j \mathbf{r}^2 + \frac{1}{2}\sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j^2, \tag{3.19}$$

where $\mathbf{r}$ is the distance to the origin. If the sum $\sum_{j=1}^{\mathcal{N}} k_j$ is then adjusted to equal a particluar value of the spring constant k of Hooke's atom:

$$\sum_{j=1}^{\mathcal{N}} k_j = k, \tag{3.20}$$

then the Hamiltonian $\hat{H}_{\mathcal{N}}$ of any element of the species may be rewritten as

$$\hat{H}_{\mathcal{N}}(\{k\}, \{\mathbf{R}\}, \mathcal{N}) = \hat{H}_a(k) + C(\{k\}, \{\mathbf{R}\}, \mathcal{N}), \tag{3.21}$$

where $\hat{H}_a(k)$ is the Hooke's atom Hamiltonian and the constant $C(\{k\}, \{\mathbf{R}\}, \mathcal{N})$ is

$$C(\{k\}, \{\mathbf{R}\}, \mathcal{N}) = \sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j^2. \tag{3.22}$$

The solution of the Schrödinger equation and the corresponding density for ***each*** element of the species are therefore the ***same***.

As an example, again consider the case of Hooke's atom and molecule. For Hooke's atom $\mathcal{N} = 1, \mathbf{R}_1 = 0$, and let us assume $k = \frac{1}{4}$. Thus, the external potential energy operator is

$$v_a(\mathbf{r}) = \frac{1}{2} k r^2 = \frac{1}{8} r^2. \tag{3.23}$$

For this choice of k, the singlet ground state solution of the time-independent Schrödinger equation ($\hat{H}_{\mathcal{N}}\Psi = E_{\mathcal{N}}\Psi$) is analytical[30-31] :

$$\Psi(\mathbf{r}_1 \mathbf{r}_2) = D e^{-y^2/2} e^{-r^2/8}(1 + r/2), \tag{3.24}$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \mathbf{y} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, and $D = 1/[2\pi^{5/4}(5\sqrt{\pi}+8)^{1/2}]$. The corresponding ground state density $\rho(\mathbf{r}) = \langle\Psi|\hat{\rho}(\mathbf{r})|\Psi\rangle$, $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{2}\delta(\mathbf{r}-\mathbf{r}_i)$ is [6,31]

$$\rho(\mathbf{r}) = \frac{\pi\sqrt{2\pi}}{r}D^2 e^{-r^2/2}\{7r + r^3 + (8/\sqrt{2\pi})re^{-r^2/2} + 4(1+r^2)erf(r/\sqrt{2}\}, \quad (3.25)$$

where

$$erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-z^2}dz. \quad (3.26)$$

For the Hooke's molecule, $\mathcal{N} = 2, \mathbf{R}_1 = -\mathbf{R}_2$, and we choose $k_1 = k_2 = \frac{1}{8}$, so that the external potential energy operator is

$$v_m(\mathbf{r}) = \frac{1}{8}r^2 + \frac{1}{16}(R_1^2 + R_2^2) = \frac{1}{8}r^2 + \frac{1}{8}R^2, \quad (3.27)$$

where $|\mathbf{R}_1| = R$. Thus, the Hamiltonian for Hooke's molecule differs from that of Hooke's atom by only the constant $\frac{1}{8}R^2$, thereby leading to the ***same*** ground state wave function and density. However, the ground state energy of the two elements of the species differ by $\frac{1}{8}R^2$.

The above example demonstrating the equivalence of the density of the Hooke's atom and molecule is for a specific value of the spring constant k for which the wave function happens to be analytical. However, this conclusion is valid for arbitrary value of k for which solutions of the Schrödinger equation exist but are not necessarily analytical. For example, if we assume that for each element of the species ($\mathcal{N} \geq 2$), all the spring constants $k_j, j = 1, 2, ...\mathcal{N}$ are the same and designated by k', then for the three values of k for the Hooke's atom corresponding

to $k = \frac{1}{4}, \frac{1}{2}, 1$, the values of k' for which the Hooke's molecule and molecular ion ($\mathcal{N} = 3$) wave functions are the same are $k' = \frac{1}{8}, \frac{1}{12}$; $k' = \frac{1}{4}, \frac{1}{6}$; $k' = \frac{1}{2}, \frac{1}{3}$, respectively.

Thus, for the case where the elements of the Hooke's species are all made to have the ***same*** ground state density $\rho(\mathbf{r})$, the density cannot, on the basis of the HK theorem, distinguish bewteen the different physical elements of the species.

Corollary: *Degenerate time-independent Hamiltonians* $\{\hat{H}\}$ *that represent different physical systems, but which differ by a constant* C *, and yet possess the same density* $\rho(\mathbf{r})$*, cannot be distinguished on the basis of the Hohenberg-Kohn theorem.*

3.3 Time-Dependent Case

We next extend the above conclusions to the time-dependent HK theorem. Consider again the Hooke's species, but in this case let us assume that the positions of the nuclei are time-dependent, i.e. $\mathbf{R}_j = \mathbf{R}_j(t)$. This could represent, for example, the zero point motion of the nuclei. For simplicity we consider the spring constant strength to be the same (k') for interaction with all the nuclei. The external potential energy $v_{\mathcal{N}}(\mathrm{r}t)$ for an arbitrary member of the species which now is

$$v_{\mathcal{N}}(\mathrm{r}t) = \frac{1}{2}k' \sum_{j=1}^{\mathcal{N}} (\mathbf{r} - \mathbf{R}_j(t))^2, \tag{3.28}$$

may then be rewritten as

$$v_{\mathcal{N}}(\mathbf{r}t) = \frac{1}{2}\mathcal{N}k'r^2 - k'\sum_{j=1}^{\mathcal{N}}\mathbf{R}_j(t)\cdot\mathbf{r} + \frac{1}{2}k'\sum_{j=1}^{\mathcal{N}}\mathbf{R}_j^2(t), \tag{3.29}$$

where at some initial time t_0, we have $\mathbf{R}_j(t_0) = \mathbf{R}_{j,0}$. (Note that a spatially uniform time-dependent field $\mathbf{F}(t)$ interacting only with the electrons could be further incorporated by adding a term $\mathbf{F}(t)\cdot\mathbf{r}$ to the external potential energy expression.) The Hamiltonian of an element of the species governed by the number of nuclei $\mathcal{N}$ is then

$$\hat{H}_{\mathcal{N}}(\mathbf{r}_1\mathbf{r}_2t) = \hat{H}_{\mathcal{N},0} - k'\sum_{j=1}^{\mathcal{N}}[\mathbf{R}_j(t) - \mathbf{R}_{j,0}]\cdot(\mathbf{r}_1 + \mathbf{r}_2) + C(k',\mathcal{N},t), \tag{3.30}$$

where $\hat{H}_{\mathcal{N},0}$ is the time-independent Hooke's species Hamiltonian Eq.(3.21):

$$\hat{H}_{\mathcal{N},0} = \hat{H}_{\mathcal{N}}(k'), \tag{3.31}$$

and the time-dependent function

$$C(k',\mathcal{N},t) = k'\sum_{j=1}^{\mathcal{N}}[\mathbf{R}_j^2(t) - \mathbf{R}_{j,0}^2]. \tag{3.32}$$

Note that the function $C(k',\mathcal{N},t)$ contains physical information about the system: in this case, about the motion of the nuclei about their equilibrium positions. It also differentiates between the different elements of the species.

The solution of the time-dependent Schrödinger equation($\hat{H}_{\mathcal{N}}(t)\Psi(t) = i\partial\Psi(t)/\partial t$) employing the Harmonic Potential Theorem [3,32] is

$$\Psi(\mathbf{r}_1\mathbf{r}_2t) = exp\{-i\phi(t)\}exp[-i\{E_{\mathcal{N},0}t - 2S(t) - 2\frac{d\mathbf{z}}{dt}\cdot\mathbf{y}\}]\Psi_0(\overline{\mathbf{r}_1}\ \overline{\mathbf{r}_2}), \tag{3.33}$$

where $\overline{\mathbf{r}_i} = \mathbf{r}_i - \mathbf{z}(t), \mathbf{y} = (\mathbf{r}_1 + \mathbf{r}_2)/2$,

$$S(t) = \int_{t_0}^{t} [\frac{1}{2}\dot{\mathbf{z}}(t')^2 - \frac{1}{2}k\mathbf{z}(t')^2]dt', \tag{3.34}$$

the shift $\mathbf{z}(t)$ satisfies the classical harmonic oscillator equation

$$\ddot{\mathbf{z}}(t) + k\mathbf{z}(t) - k' \sum_{j=1}^{\mathcal{N}} [\mathbf{R}_j(t) - \mathbf{R}_{j,0}] = 0, \tag{3.35}$$

where the additional phase factor $\phi(t)$ is due to the function $C(k', \mathcal{N}, t)$,

$$\phi(t) = \int_{t_0}^{t} C(k', \mathcal{N}, t')dt', \tag{3.36}$$

and where at the initial time $\Psi(\mathbf{r}_1\mathbf{r}_2 t_0) = \Psi_0$ which satisfies $\hat{H}_{\mathcal{N},0}\Psi_0 = E_{\mathcal{N},0}\Psi_0$. Thus, the wave function $\Psi(\mathbf{r}_1\mathbf{r}_2 t)$ is the time-independent solution shifted by a time-dependent function $\mathbf{z}(t)$, and multiplied by a phase factor. The explicit contribution of the function $C(k', \mathcal{N}, t)$ to this phase has been separated out. The phase factor cancels out in the determination of the density $\rho(t) = \langle\Psi(t)|\hat{\rho}|\Psi(t)\rangle = \rho(\mathbf{r} - \mathbf{z}(t))$ which is the initial time-independent density $\rho(\mathbf{r}t_0) = \rho_0(\mathbf{r})$ displaced by $\mathbf{z}(t)$.

As in the time-independent case, the 'degenerate Hamiltonians' $\hat{H}_{\mathcal{N}}(\mathbf{r}_1\mathbf{r}_2 t)$ of the time-dependent Hooke's species can each be made to generate the ***same*** density $\rho(\mathbf{r}t)$ by adjusting the spring constant k' such that $\mathcal{N}k' = k$, and provided the density at the initial time t_0 is the ***same***. The latter is readily achieved as it constitutes the time-independent Hooke's species case discussed previously.

Thus, we have a set of Hamiltonians describing different physical systems but which can be made to generate the same density $\rho(\mathbf{r}t)$. These Hamiltonians differ

by the function $C(k', \mathcal{N}, t)$ that contains information which differentiates between them. In such a case, the density $\rho(\mathbf{r}t)$ cannot distinguish between the different Hamiltonians.

Corollary: *Degenerate time-dependent Hamiltonians* $\{\hat{H}(t)\}$ *that represent different physical systems, but which differ by a purely time-dependent function* $C(t)$, *and which all yield the same density* $\rho(\mathbf{r}t)$, *cannot be distinguished on the basis of the Runge-Gross theorem.*

3.4 Conclusions

The proof of the HK theorem is general in that it is valid for ***arbitrary*** local form (Coulombic, Harmonic, Yukawa, oscillatory, etc.) of external potential energy $\{v(\mathbf{r})/v(\mathbf{r}t)\}$. (In the time-dependent case, there is the restriction that $v(\mathbf{r}t)$ must be Taylor-expandable about some initial time t_0.) For their proof, {HK/RG} considered the case of potential energies , and hence Hamiltonians, that differ by an additive {constant C/function $C(t)$} to be equivalent:

$$v(\mathbf{r})/v(\mathbf{r}t) - v'(\mathbf{r})/v'(\mathbf{r}t) = C/C(t). \tag{3.37}$$

By equivalent is meant that the density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$ is the same. The fact that the {constant C/function $C(t)$ } is ***additive*** means that although the Hamiltonians differ, the physical system, however remains the ***same***. The theorem then shows that there is a one-to-one correspondence between a physical system (as described

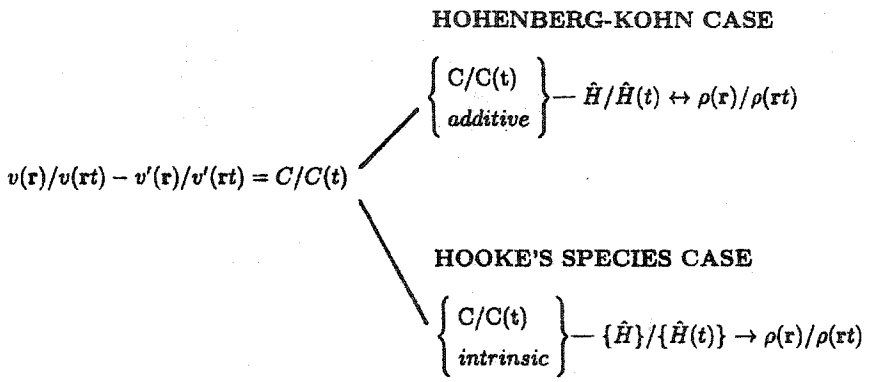

FIG. 3: A schematic representation of the Hohenberg-Kohn theorem and its corollary.

by all these equivalent Hamiltonians), and the corresponding density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$. The relationship between the basic Hamiltonian $\{\hat{H}/\hat{H}(t)\}$ describing a particular system and the density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$ is bijective or fully invertible. This case considered by {HK/RG} is shown schematically in Fig. 3 in which the invertibility is indicated by the double-headed arrow.

The case of a set of degenerate Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ that differ by a {constant C/function $C(t)$ } that is ***intrinsic*** such that the Hamiltonians represent ***different*** physical systems while yet ***all*** possessing the same density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$, was not considered by {HK/RG}. In such a case, the density ***cannot*** uniquely determine the Hamiltonian, and therefore ***cannot*** differentiate between the different

physical systems. This case, also shown schematically in Fig.3, corresponds to the Hooke's species. The relationship between the set of Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ and the density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$ which is not invertible is indicated by the single-headed arrow.

We conclude by noting that the Hooke's species, in both the time-independent and time-dependent cases, does not constitute a counter example to the {HK/RG} theorem. The reason for this is that the proof of the {HK/RG} theorem is ***independent*** of whether the {constant C/ function $C(t)$ } is additive or intrinsic. The Hamiltonians in either case still differ by a {constant C/ function $C(t)$}. A counter example would be one in which Hamiltonians that differ by more than a {constant C/ function $C(t)$} have the same density $\{\rho(\mathbf{r})/\rho(\mathbf{r}t)\}$.

CHAPTER 4

QUANTAL DENSITY FUNCTIONAL THEORY OF THE HYDROGEN MOLECULE

4.1 Introduction

In this chapter we analyze the Hydrogen molecule (H_2) in its ground-state electronic configuration $(\sigma_g 1s)^2$ from the perspective of time-independent Quantal density functional theory (Q-DFT). The *in principle exact* framework of Q-DFT for ground and excited states, both nondegenerate and degenerate, has been demonstrated by application to exactly solvable model atomic systems[6,9-12] as well as by the use of essentially exact atomic correlated wave functions [5,7,33]. In its approximate form, Q-DFT has been applied to atoms, atomic ions, atoms in excited states, and positron binding, as well as to the many-electron inhomogeneity at metallic surfaces and metallic clusters. We refer the reader to the review articles of Refs [5,34] for further references on these applications. This chapter constitutes a first step in the application of Q-DFT to molecules. Here we present the essentially exact analysis of the H_2 molecule via Q-DFT by employing the highly accurate correlated wave function of Kolos and Roothaan [35]. Beyond the understandings achieved, a principal attribute of the calculation is the knowledge that the structure of the corresponding Q-DFT properties for other diatomic molecules will then be qualitatively similar. Furthermore, these essentially exact properties can be used as

the basis for comparison and testing of various approximations within Q-DFT prior to their application to more complex molecules.

4.2 Wave functions, Orbitals, and Density

The purely electronic part of the Hamiltonian for H_2 in atomic units ($e = m = \hbar = 1$) is

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1a}} - \frac{1}{r_{2a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}}, \tag{4.1}$$

where 1 and 2 are the electrons, and a and b are the nuclei. As the wave function of the molecule in its ground state is unknown, we employ the essentially exact 51-parameter correlated wave function of Kolos-Roothaan in our calculations. The symmetric spatial part of the wave function is

$$\Psi(\mathbf{r}_1\mathbf{r}_2) = exp[-\delta(\xi_1 + \xi_2)] \sum_{mnjkl} C_{mnjkp}\,[\xi_1^m \xi_2^n \eta_1^j \eta_2^k + \xi_1^n \xi_2^m \eta_1^k \eta_2^j] r_{12}^p \tag{4.2}$$

with

$$\xi_1 = (r_{1a} + r_{1b})/R; \;\; \xi_2 = (r_{2a} + r_{2b})/R; \tag{4.3}$$

$$\eta_1 = (r_{1a} - r_{1b})/R; \;\; \eta_2 = (r_{2a} - r_{2b})/R, \tag{4.4}$$

where the variational parameters are δ and the coefficients C_{mnjkp}, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and $R = 2a$ is the internucleus separation. The values of the variational parameters are given in the Appendix. The total energy (inclusive of the internuclear potential

energy $V_{nn} = 1/R$) is $E_{tot}(H_2) = -1.174448$ (a.u.) at $a = 0.7005$ (a.u.). The kinetic energy $T = -E_{tot}$, and the total potential energy $E_{ext} + E_{ee} + V_{nn} = -2.348851$(a.u.). The virial theorem ratio, which is the ratio of the total potential energy to twice the total energy, is 0.999981. The electron interaction energy component $E_{ee} = 0.58737$(a.u.), and the external energy $E_{ext} = -3.65005$(a.u.). The total energy [36] of the Hydrogen molecular ion H_2^+ at the equilibrium internuclear separation of the Hydrogen molecule is $E_{tot}(H_2^+)|_{a=0.7005} = -0.56998$ (a.u.). Thus, the ionization potential of the H_2 molecule is $I = E_{tot}(H_2^+)|_{a=0.7005} - E_{tot}(H_2) = 0.60447$ (a.u.).

For two electron systems such as the Hooke's atom[30], Helium atom, or the Hydrogen molecule, the orbitals of the S system in its ground (singlet) state that lead to the interacting system density are known. These orbitals are $\phi_i(\mathbf{r}) = \sqrt{\rho(\mathbf{r})/2}, i = 1, 2$, and are therefore known to the same accuracy as the wave function or density.

The density $\rho(0, z)$ along the nuclear bond z-axis is plotted in Fig.4. The density is extremely accurate throughout space except at and very near each nucleus. Thus, although on the scale of this figure, it appears that the density satisfies the electron-nucleus cusp condition exactly, in fact it does not.

4.3. Fermi-Coulomb, Fermi, and Coulomb Holes

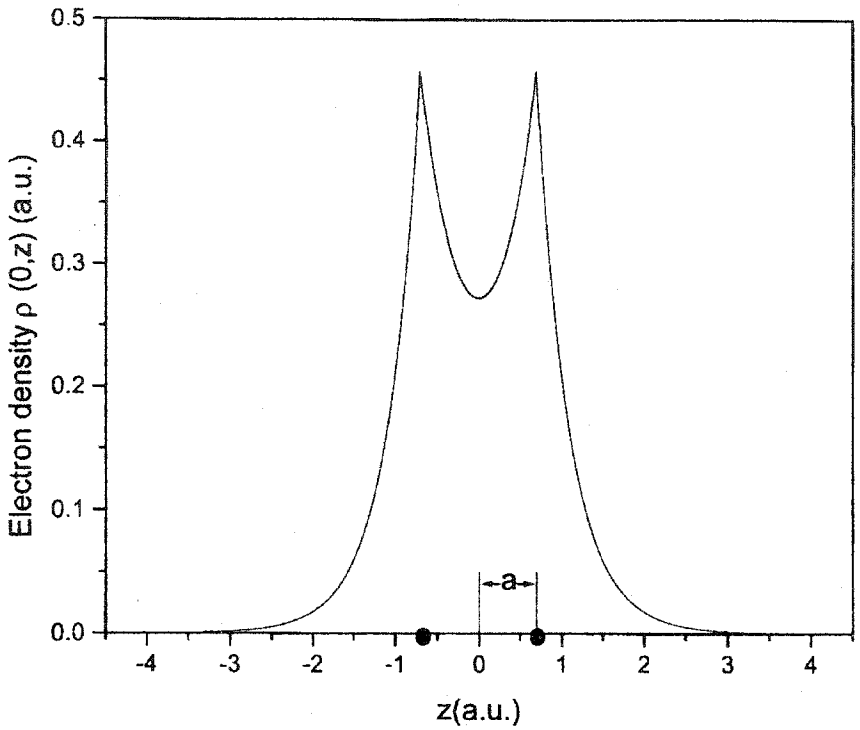

FIG. 4: The electron density $\rho(0, z)$ of the hydrogen molecule along the nuclear bond axis in atomic units (a.u.). The nuclei are on the axis at $a = 0.7005$ (a.u.) indicated by the two dots.

For the H_2 molecule in its singlet ground state, there are no correlations due to the Pauli exclusion principle as the two electrons have opposite spin. However, within the S system framework, it is customary in local effective potential energy theories to define the Fermi hole as $\rho_x(\mathbf{r}\mathbf{r}') = -\rho(\mathbf{r}')/2$. (This is because the pair-correlation density as determined from the corresponding S system wave function is $g(\mathbf{r}\mathbf{r}') = \rho(\mathbf{r}')/2$.)

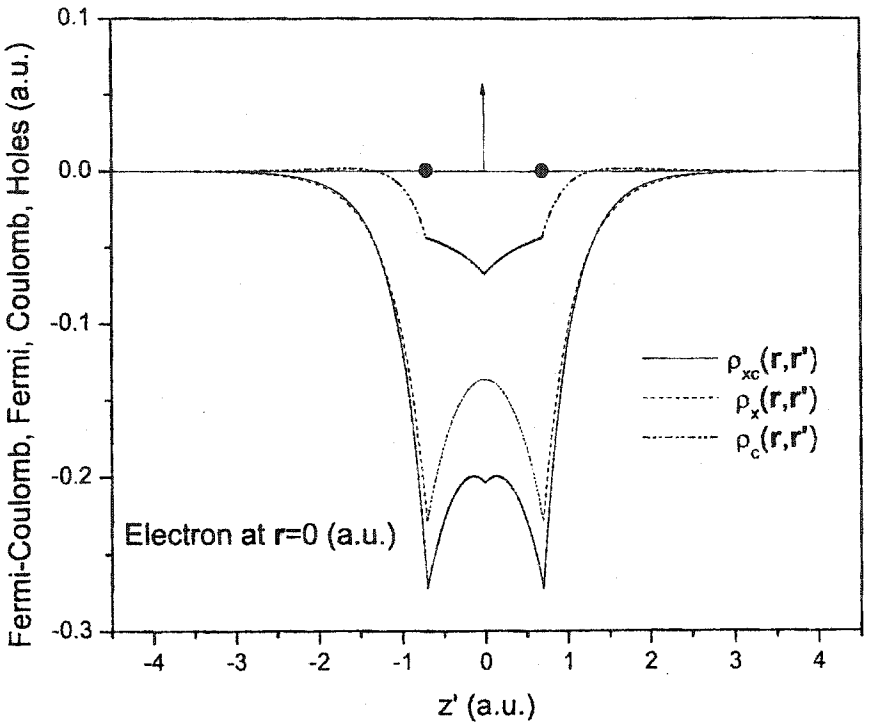

FIG. 5: Cross-sections of the Fermi-Coulomb $\rho_{xc}(\mathbf{r}\mathbf{r}')$, Fermi $\rho_x(\mathbf{r}\mathbf{r}')$, and Coulomb $\rho_c(\mathbf{r}\mathbf{r}')$ holes along the nuclear bond axis for an electron at the center $\mathbf{r} = (0,0)$ of the bond. The electron position is indicated by the arrow.

In Fig.5 we plot cross-sections through the Fermi-Coulomb $\rho_{xc}(\mathbf{r}\mathbf{r}')$, Fermi $\rho_x(\mathbf{r}\mathbf{r}')$, and Coulomb $\rho_c(\mathbf{r}\mathbf{r}')$ hole sources as a function of $\mathbf{r}' = (0, z')$ for an electron at the origin $\mathbf{r} = (0,0)$ at the center of the nuclear bond. (Because of the cylindrical symmetry of the molecule, cylindrical coordinates are employed throughout.) The electron position is indicated by the arrow. The three charge distributions, of course, have cylindrical symmetry about the bond axis. More significantly, they are symmetrical about the electron along the z' axis. Observe that at the electron

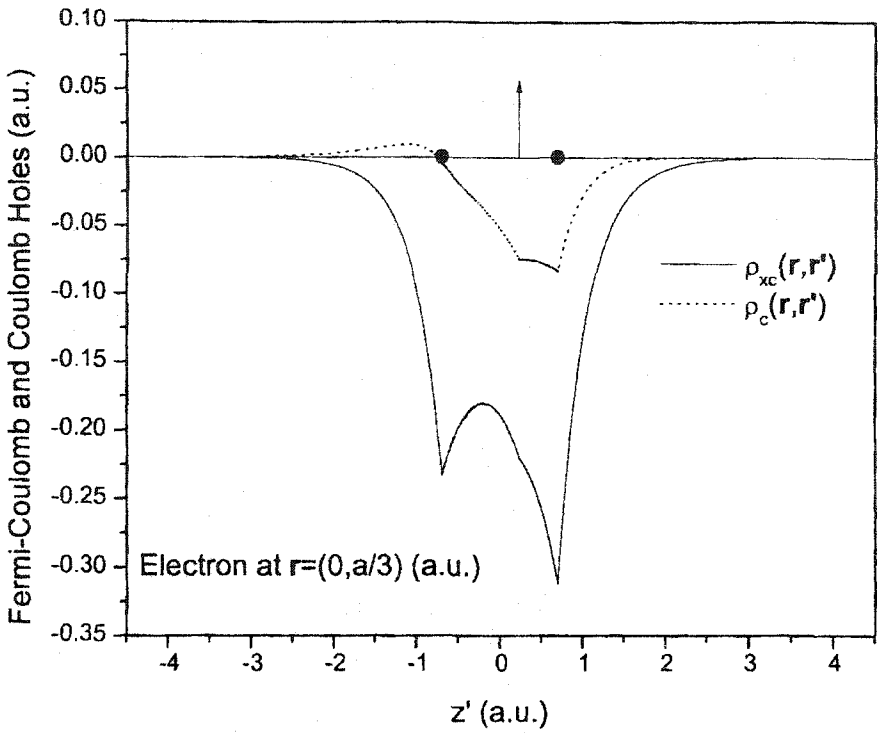

FIG. 6: Cross-sections of the Fermi-Coulomb $\rho_{xc}(\mathbf{r}\mathbf{r}')$ and Coulomb $\rho_c(\mathbf{r}\mathbf{r}')$ holes along the nuclear bond axis for an electron at the center $\mathbf{r} = (0, a/3)$ of the bond with the electron position indicated by the arrow.

position, both the Fermi-Coulomb and Coulomb holes exhibit a cusp corresponding to the electron-electron cusp condition. (Based on the work of Ref. [37] it is known that the wave function does not satisfy this cusp condition exactly. It obviously satisfies it to a good degree as evidenced by the figure.) As expected, at the electron position, the Fermi-Coulomb hole is more negative than the Fermi hole. Thus, in the region about the electron, the Coulomb hole is negative. (This is also the case for all the other electron positions considered.) As both the Fermi-Coulomb and Fermi

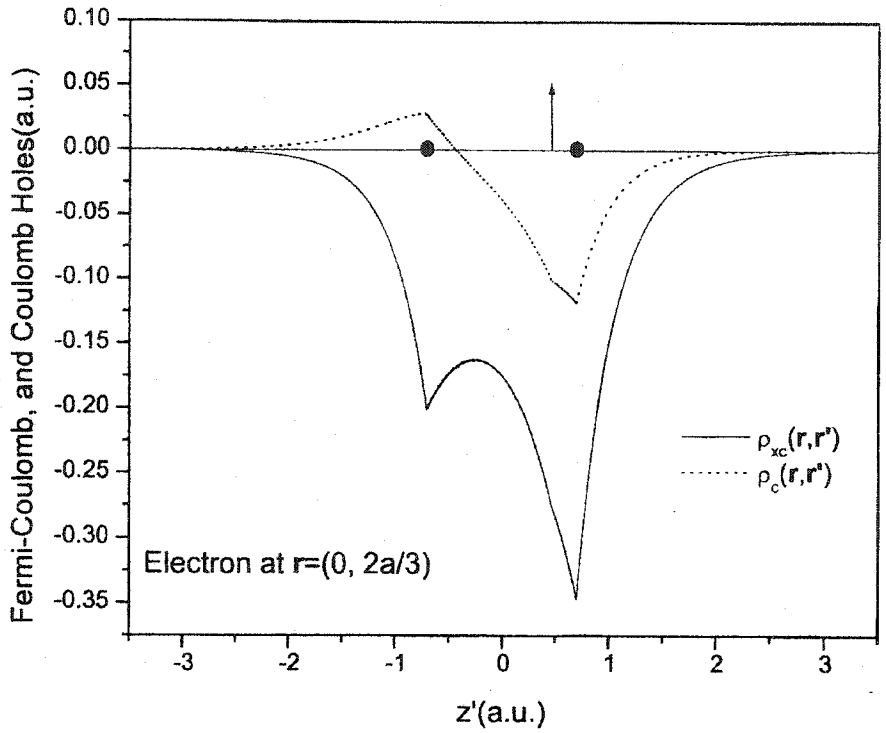

FIG. 7: The same as in Fig.6, but with the electron at $\mathbf{r} = (0, 2a/3)$.

holes satisfy the same charge conservation sum rule, there must then be regions where the former lies above the latter. This is clearly evident in the figure. Hence, in the outer and classically forbidden regions of the molecule, the Coulomb hole is positive. (The positive part of the Coulomb hole is more clearly evident in the figures that follow.) The Coulomb hole is both positive and negative as its total charge is zero. The positive part of the Coulomb hole is an indication that the other electron is equally likely to be in the classically forbidden region on either side of each nucleus.

As the Fermi hole is independent of electron position, we now focus on the

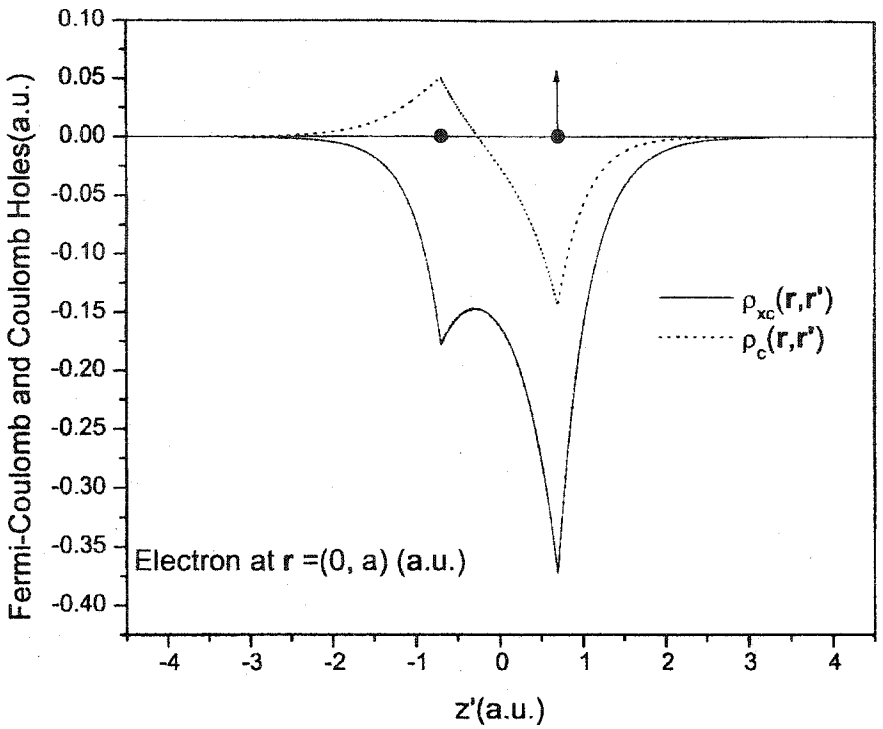

FIG. 8: The same as in Fig.6, but with the electron at $\mathbf{r} = (0, a)$.

Fermi-Coulomb and Coulomb holes. In Figs.6-8, we plot the cross-sections of these holes for electron positions at $\mathbf{r} = (0, a/3), \mathbf{r} = (0, 2a/3), \mathbf{r} = (0, a)$. Again, observe the cusp at the electron position for both the Fermi-Coulomb and Coulomb holes of each figure. Note also how the positive part of the Coulomb hole becomes more pronounced relative to the negative part as the electron is moved away from the center of the nuclear bond towards one nucleus. The positive part of the Coulomb hole is also largest about the other nucleus, thereby indicating that the second electron is about this nucleus.

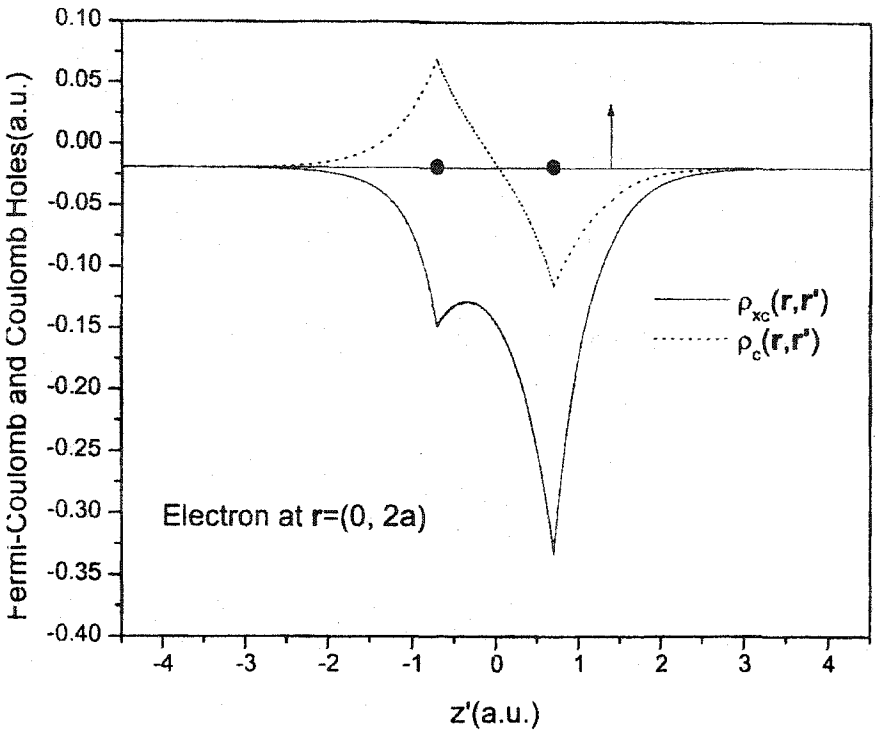

FIG. 9: The same as in Fig.6, but with the electron at $\mathbf{r} = (0, 2a)$.

In Figs.9-11, we plot the Fermi-Coulomb and Coulomb hole cross-sections for an electron in the classically forbidden region at $\mathbf{r} = (0, 2a)$, $\mathbf{r} = (0, 4a)$, and $\mathbf{r} = (0, 6a)$. The positive part of the Coulomb hole continues to increase about the left nucleus at the expense of the negative part as the electron is moved further from the molecule. Thus, even for the asymptotic position of an electron at $\mathbf{r} = (0, 6a)$, the other electron is still mainly about the left nucleus. For all electron positions, the Fermi-Coulomb hole $\rho_{xc}(\mathbf{r}\mathbf{r}')$ is negative.

(We note that the same cross-sections of the Fermi-Coulomb, Fermi, and

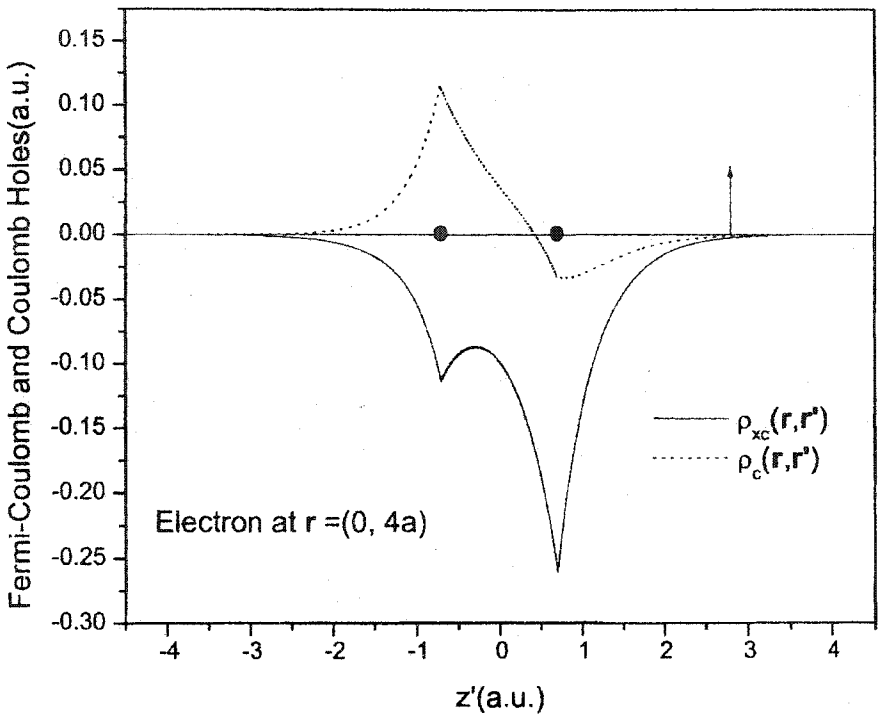

FIG. 10: The same as in Fig.6, but with the electron at $\mathbf{r} = (0, 4a)$.

Coulomb holes for an electron position 0.3 (a.u.) to the left of the right nucleus, which corresponds approximately to our Fig.7, has been plotted by Baerends et al [?] in their study of the dissociation of the molecule. However, in their figure, the electron-electron cusp in the Fermi-Coulomb and Coulomb holes is not present because the wave function employed by these authors is a configuration-interaction type wave function.)

4.4. Fields, Potential Energies, and Energies

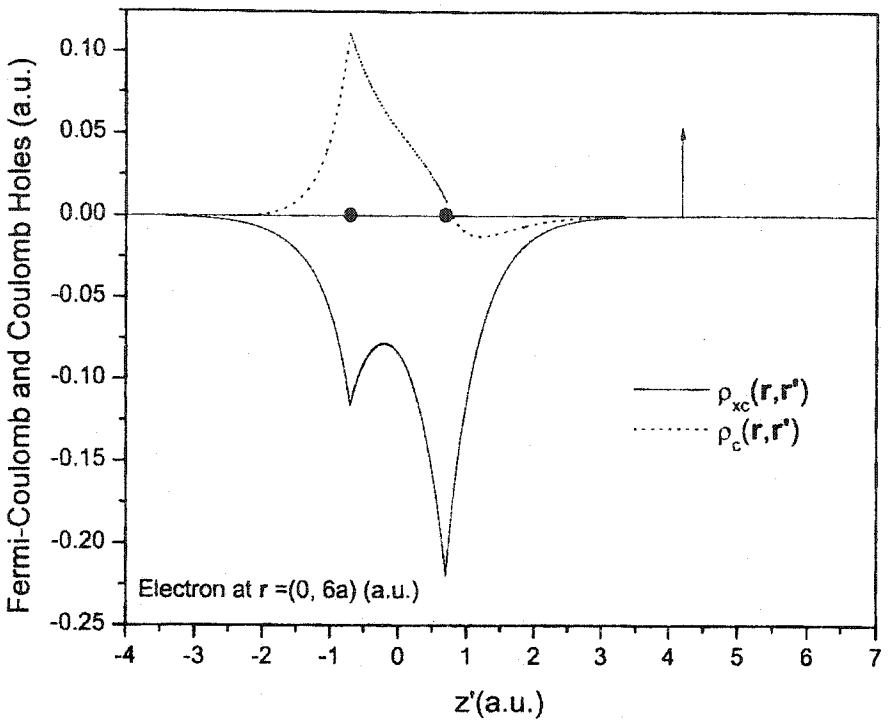

FIG. 11: The same as in Fig.6, but with the electron at $\mathbf{r} = (0, 6a)$.

The electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$, and its Hartree $\mathcal{E}_H(\mathbf{r})$ and Pauli-Coulomb $\mathcal{E}_{xc}(\mathbf{r})$ components along the nuclear bond axis are plotted in Fig.13. Observe that these fields all vanish at the center of the bond axis or origin. This is because their corresponding sources – the pair-correlation density $g(\mathbf{r}\mathbf{r}')$, the density $\rho(\mathbf{r})$, and the Fermi-Coulomb hole charge $\rho_{xc}(\mathbf{r}\mathbf{r}')$ — are symmetrical about the center of the nuclear bond for this electron position (see Figs.4 and 5). The existence (non-zero value) of these fields for all other electron positions is a consequence of the fact that their sources are *not symmetrical* about the electron (see Figs.4 and 6-11). The fields are also all *antisymmetric* about the center of the nuclear bond. (This is a

reflection of the symmetry about the x-y plane at the center of the nuclear bond. As such the potential energies obtained from these fields will be *symmetric* about this point.) In the positive half-space, there is a maximum in the electron-interaction and Hartree fields, and a minimum in the Pauli-Coulomb field. The Hartree and Pauli-Coulomb fields are of the same order of magnitude and opposite in sign. This is because their sources, $\rho(\mathbf{r})$ and $\rho_{xc}(\mathbf{r}\mathbf{r}')$ respectively, are of the same order of magnitude and opposite in sign. Asymptotically, in the z direction these fields decay as $\mathcal{E}_{ee}(\mathbf{r}) \sim 1/z^2$, $\mathcal{E}_H(\mathbf{r}) \sim 2/z^2$, and $\mathcal{E}_{xc}(\mathbf{r}) \sim -1/z^2$ as they must [6,33]. (It is interesting to note that with a slight translation to the right, the plots of the fields in the positive half-space, are strikingly similar to those of the Helium atom [5,33].)

The Pauli $\mathcal{E}_x(\mathbf{r})$ and Coulomb $\mathcal{E}_c(\mathbf{r})$ field components of the Pauli-Coulomb field $\mathcal{E}_{xc}(\mathbf{r})$ along the nuclear bond axis are plotted in Fig.13. Again, these fields vanish at the origin and are *antisymmetric* about it. Hence, the corresponding potential energies obtained from these fields will be symmetric. In the positive half space, the Pauli field $\mathcal{E}_x(\mathbf{r})$ is negative as its source is a negative charge. The Coulomb field $\mathcal{E}_c(\mathbf{r})$, on the other hand, is positive in the inter-nuclear region and negative throughout the region beyond the right nucleus. This structure is attributable to the fact that the Coulomb hole has both a positive and negative component. Asymptotically, the Pauli field decays as $\mathcal{E}_x(\mathbf{r}) \sim -1/z^2$, whereas the Coulomb field $\mathcal{E}_c(\mathbf{r})$ has essentially vanished by about $z = 5$ (a.u.). (Once again in the positive half-space, the structure of these fields when translated slightly to the right, is

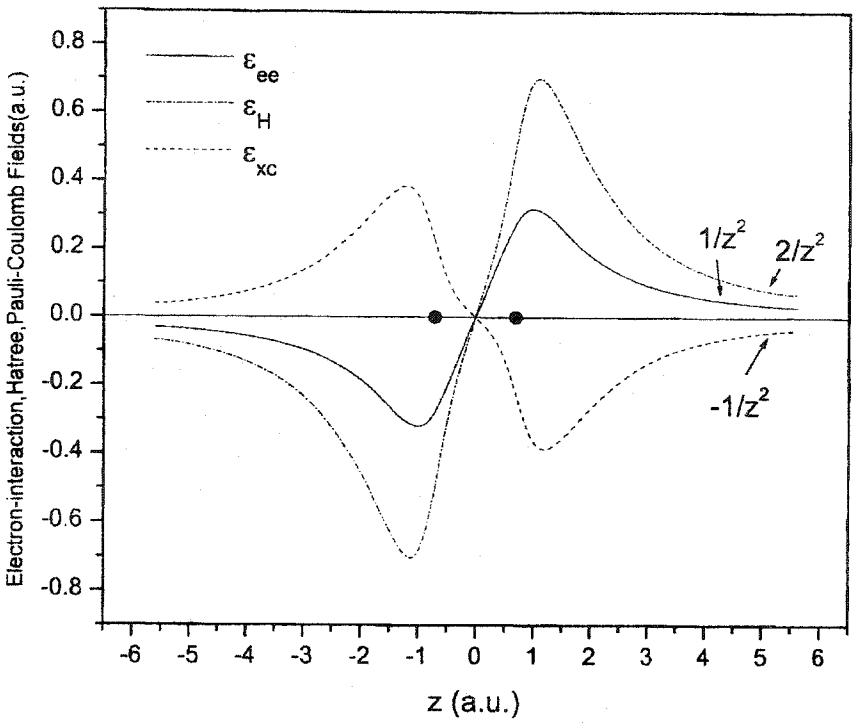

FIG. 12: The electron-interaction $\mathcal{E}_{ee}(0,z)$ field, and its Hartree $\mathcal{E}_H(0,z)$ and Pauli-Coulomb $\mathcal{E}_{xc}(0,z)$ components along the nuclear bond axis.

similar to those of the Helium atom. In particular, we note that the structure of the Coulomb holes of the Hydrogen molecule for electron positions $z > a$ (see Figs. 6-8) is very similar to those of the Helium atom for electron positions away from its nucleus (see Figs.3,4 of[33]).) As is the case for atoms, it turns out that the asymptotic structure along the nuclear bond axis of $\{\mathcal{F}(\mathbf{r}) - \mathcal{E}_H(\mathbf{r})\} \sim \mathcal{E}_x(\mathbf{r}) \sim -1/z^2$. Thus, the asymptotic structure of the electron-interaction potential energy $v_{ee}(\mathbf{r})$ minus the Hartree potential energy $W_H(\mathbf{r})$ is again due to Pauli correlations: $\{v_{ee}(\mathbf{r}) - W_H(\mathbf{r})\} \sim W_x(\mathbf{r}) \sim -1/z$ as shown in Fig. 14.

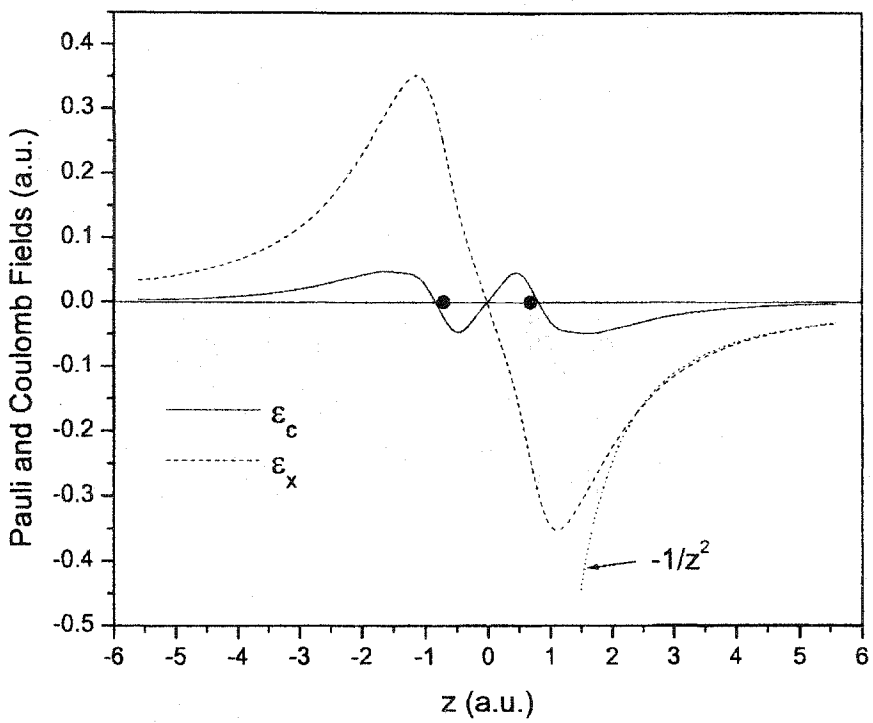

FIG. 13: The Pauli $\mathcal{E}_x(0,z)$ and Coulomb $\mathcal{E}_c(0,z)$ fields along the nuclear bond axis. The function $-1/z^2$ is also plotted.

Since in the S system description of two electron systems $\mathcal{E}_x(\mathbf{r}) = -\mathcal{E}_H(\mathbf{r})/2$, the curl of the Fermi field along the nuclear bond z axis direction vanishes: $\nabla \times \mathcal{E}_x(\mathbf{r})|_z = 0$, as it does in all directions. Hence, the work done $W_x(0,z)$ plotted in Fig. 14 is path independent. Along the nuclear bond axis, however, the $\nabla \times \mathcal{E}_c(\mathbf{r})|_z \neq 0$ and $\nabla \times \mathcal{Z}_{t_c}(\mathbf{r})|_z \neq 0$. But in this and all directions, the curl of the sum of the fields $\mathcal{E}_c(\mathbf{r})$ and $\mathcal{Z}_{t_c}(\mathbf{r})$ vanishes: $\nabla \times [\mathcal{E}_c(\mathbf{r}) + \mathcal{Z}_{t_c}(\mathbf{r})])|_z = 0$. Therefore, the work done in the sum of these fields in all directions, and hence

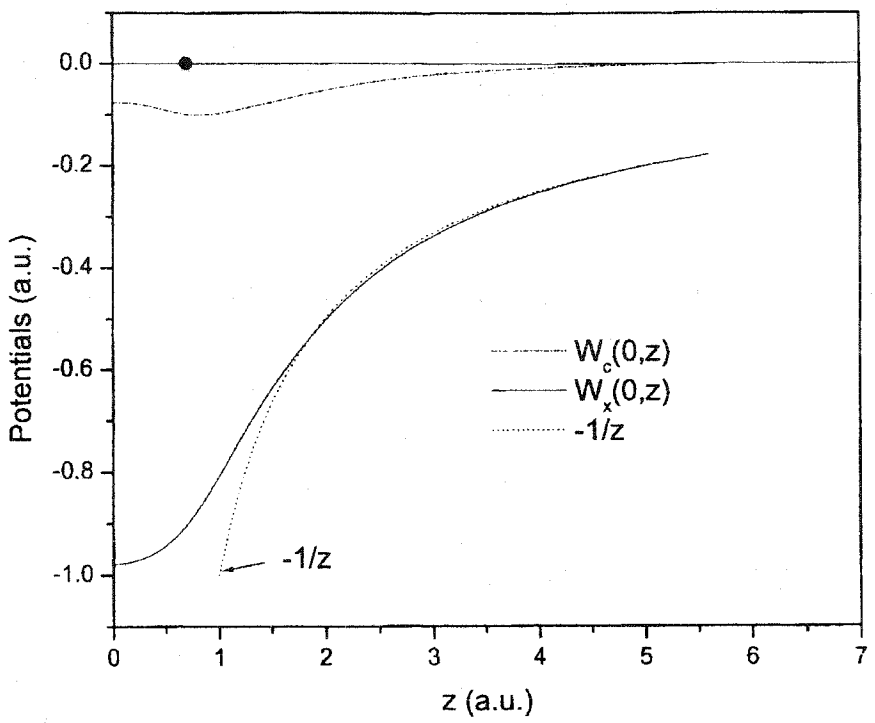

FIG. 14: The Pauli potential energy $W_x(0,z)$ along the nuclear bond axis. The work done $W_c(0,z)$ in this direction in the force of the Coulomb field $\mathcal{E}_c(0,z)$, and the function $-1/z$, are also plotted.

along the nuclear bond axis $v_c(0,z) = W_c(0,z) + W_{t_c}(0,z)$ is path independent. The calculation of the potential energy $v_c(0,z)$ is straightforward. However, our use of the Kolos-Roothaan wave function, in spite of its accuracy, leads to $v_c(0,z)$ being singular at the nucleus. This occurs due to the component $W_{t_c}(0,z)$ that requires a cancellation of the kinetic fields of the interacting and noninteracting systems. The underlying reason for the singularity, however, is that the wave function does not satisfy the *electron-nucleus* cusp condition exactly. In a recent paper [38], we have proved by employing the integral form of the electron-nucleus cusp condition , that

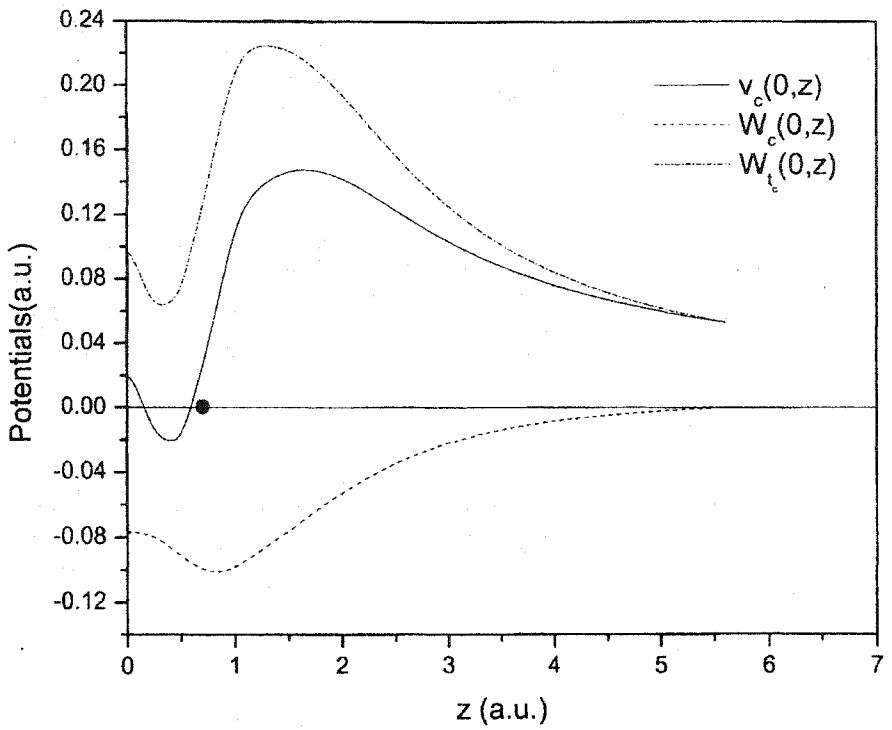

FIG. 15: The potential energy $v_c(0,z)$, the sum of the Coulomb and Correlation-Kinetic potential energies, along the nuclear bond axis. The work done $W_c(0,z)$ of Fig. 11, and the work done $W_{t_c}(0,z)$ in the force of the Correlation-Kinetic field $\mathcal{Z}_{t_c}(0,z)$ of Fig.13, are also plotted.

in local effective potential energy theories and for arbitrary symmetry, the potential energy $v_{ee}(\mathrm{r})$ is finite at the nucleus. Furthermore, it is shown that this finiteness is a direct consequence of the satisfaction of the electron-nucleus cusp condition by the Schrodinger wave function. (As a consequence, for example, this potential energy is singular at each nucleus when determined either from Gaussian geminal [38] or configuration interaction [39] wave functions.) Hence, in order to obtain $v_c(0,z)$, we have employed our calculated results in regions other than near the nucleus, and

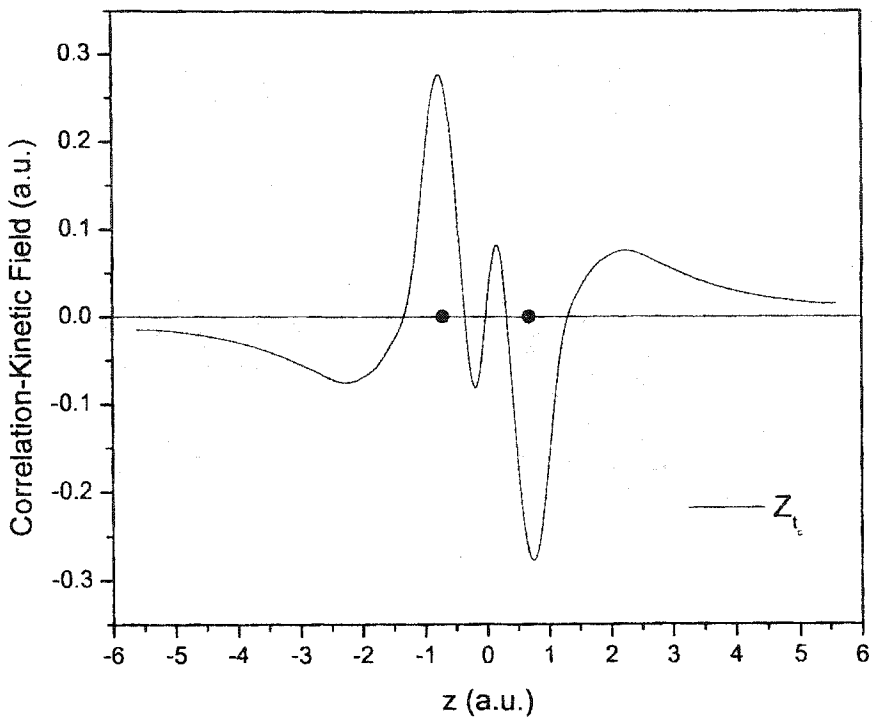

FIG. 16: The Correlation-Kinetic field $\mathcal{Z}_{t_c}(0,z)$ along the nuclear bond axis.

smoothed the curve through each nucleus.(A comparison of our results with the work of Gritsenko *et al*[40] who in their self-consistent calculations assumed $v_{ee}(\mathbf{r})$ to be finite at the nucleus show the two curves to be indistinguishable throughout space.) The potential energy $v_c(0,z)$ is plotted in Fig.15. Observe that $v_c(0,z)$, and thus the sum of the Coulomb and Correlation-Kinetic potential energies is an order of magnitude smaller than $W_x(0,z)$, the Pauli contribution. The potential energy $v_c(0,z)$ has considerable structure, is symmetric about the origin, and is mainly positive, indicating thereby that its principal contribution is Correlation-Kinetic. (Recall that the Coulomb field is principally negative in the right-half space (see

Fig. 13) so that the Coulomb potential energy $W_c(\mathbf{r})$ is negative.) The plot of $v_c(0,z)$ translated to the right nucleus is very similar in shape and magnitude to the corresponding potential energy $v_c(\mathbf{r})$ of the Helium atom (see Fig. 4 of [5]).

To obtain a quantitative sense of the separate Coulomb and Correlation-Kinetic contributions to $v_c(0,z)$, we plot in both Figs.14 and 15 the work done $W_c(0,z)$ along the path of the nuclear bond in the force of the Coulomb field $\mathcal{E}_c(\mathbf{r})$. From $v_c(0,z)$ and $W_c(0,z)$ we obtain $W_{t_c}(0,z)$ which is also plotted in Fig. 15. The corresponding Correlation-Kinetic field $Z_{t_c}(0,z)$ is shown in Fig.16. Note that this field too is antisymmetric about the origin. Once again, there is a striking similarity between the plots of $W_c(0,z)$, $Z_{t_c}(0,z)$, and $W_{t_c}(0,z)$ when translated to the right nucleus to those of the corresponding properties of the Helium atom [5]. The Coulomb correlation part $W_c(0,z)$ is negative throughout space and vanishes by about $z = 5$ (a.u.). The Correlation-Kinetic piece $W_{t_c}(0,z)$ is throughout positive and asymptotically decays more slowly. The field $Z_{t_c}(0,z)$ is principally positive throughout space. Thus, the Correlation-Kinetic energy T_c is positive: $T = 1.1745$ (a.u.), $T_s = 1.1414$ (a.u.), $T_c = 0.0331$ (a.u.) (The corresponding value of T_c for the Helium atom is 0.0365 (a.u.)[33]). (We note that the $W_c(0,z)$ and $W_{t_c}(0,z)$ do not each separately represent a potential energy. Their sum which is $v_c(0,z)$ does.)

4.5 Concluding Remarks

This work is the first application of the Q-DFT quantal source and field perspective to a molecule, and much has been learned as explained in the previous section. The symmetry of the H_2 molecule dictates that the individual fields $\mathcal{E}_x(\mathbf{r})$, $\mathcal{E}_H(\mathbf{r})$, $\mathcal{E}_c(\mathbf{r})$, $\mathcal{Z}_{t_c}(r)$ representative of the Pauli and Coulomb correlations, and Correlation-Kinetic effects respectively, must each be *antisymmetric* about the center of the nuclear bond. The corresponding electron-interaction potential energy $v_{ee}(\mathbf{r})$ representative of these correlations as determined by the work done in the force of these fields is then *symmetric* about this point as also dictated by the symmetry of the molecule. The potential energy $v_{ee}(\mathbf{r})$ is also finite at each nucleus, as must be the case [38]. The Hartree $\mathcal{E}_H(\mathbf{r})$ and Pauli $\mathcal{E}_x(\mathbf{r})$ fields are the largest in magnitude and opposite in sign, the former being positive and twice as large as the latter. As such the principal contributions to the electron-interaction energy E_{ee} and potential energy $v_{ee}(\mathbf{r})$ are due to the Hartree and the Pauli correlation terms. The Coulomb $\mathcal{E}_c(\mathbf{r})$ and Correlation-Kinetic $\mathcal{Z}_{t_c}(r)$ fields tend to cancel each other, so that the contribution of their sum to the potential energy $v_{ee}(\mathbf{r})$ is an order of magnitude smaller. However, as the potential energy component $v_c(\mathbf{r})$ representing the sum of these correlations is principally positive (see Fig. 12), it is evident that the Correlation-Kinetic effects are more significant. They are also more significant asymptotically, where the Coulomb correlation contributions to the potential energy vanish. Thus, Correlation-Kinetic effects play an important role in local effective potential energy theories of the H_2 molecule. We further note that in the construction of approximate KS-DFT 'exchange-correlation' and correlation

energy functionals $E_{xc}^{KS}[\mathbf{r}]$ and $E_{c}^{KS}[\mathbf{r}]$ for molecules, Correlation-Kinetic effects must be incorporated if an accurate S system representation of molecules is to be obtained.

On the basis of the Q-DFT results determined from the H_2 molecule, it is evident that the qualitative features of the quantal sources, fields, and potential energies for other diatomic molecules will be similar. However, the fields and hence the potential energies of these diatomics will have more structure as a consequence of the additional molecular subshells. We expect this added structure to be similar to that observed in atoms as the number of shells is increased. Finally, we note that the accuracy of approximation methods within Q-DFT and KS-DFT can be tested by comparison with these essentially exact results.

We conclude by reiterating the striking similarity between the Q-DFT properties of the Hydrogen molecule and the Helium atom for electron positions in the positive half space. It is interesting that in spite of the presence of a second nucleus, and therefore of a different symmetry, the quantal sources and fields representative of the various electron correlations in the Hydrogen molecule are so similar to those of the Helium atom. This speaks to the commonality of properties of these distinct quantum systems as exhibited within the framework of Q-DFT.

CHAPTER 5

QUANTAL DENSITY FUNCTIONAL THEORY OF DEGENERATE STATES

5.1 Introduction

In this chapter we develop the Quantal density functional theory of degenerate state for *both* the *ground* and *excited* state, and for the cases of *both* the *pure* and *ensemble* v-representable densities. To put our work in context, we note that the treatment of degenerate states within the context of Kohn-Sham density functional theory KS-DFT [17] is a problem of longstanding [18] and continued recent [41,42] interest. The basic idea underlying the KS-DFT methodology is the mapping from the interacting electronic system as described by Schrödinger theory to that of a system of *noninteracting fermions* such that the equivalent density and total energy are obtained. The existence of the model system is once again an assumption. Further, there is the distinction between the S system of noninteracting fermions whereby the equivalent density is obtained from a *single* Slater determinant, and the noninteracting system whose orbitals could be degenerate so that the density is obtained from a weighted sum of the Slater determinants constructed from the orbitals. Within KS-DFT, the following cases have been considered. The mapping from: (a) a *pure* degenerate ground state [43]; (b) a *pure* degenerate excited state[18]. In addition, maps to obtain the density and energy constructed from

(c) an *ensemble* of pure degenerate ground states[42], and (d) an *ensemble* of pure degenerate excited states[41], have been developed. The interest in the ensemble cases stems from a *ground* state theorem due to Levy [44] and Lieb [45]. According to the theorem, most ensemble densities constructed from pure degenerate ground states are not *interacting* v-representable. In other words, no *single* ground state wave function of the Schrödinger Hamiltonian will yield this ensemble density. Such ensemble densities are said to be *ensemble* v-representable. The translation of the theorem to the S system [44] means that there is no *single* Slater determinant that leads to this ensemble density. At this time, the question of interacting v-representability of the ensemble density of degenerate excited states is still unanswered [46]. In this chapter we propose a solution to the problem of mapping from the interacting degenerate system to that of the equivalent noninteracting fermion model within the unifying physical framework of quantal density functional theory (Q-DFT).

In contrast to the present work, the KS-DFT description of the noninteracting system is in terms of an energy functional of the density, and its functional derivative. For case (a), the energy is a functional of the degenerate ground state density; for (b), the energy is a *bidensity* functional of the ground and excited state densities, with the functional derivative taken at the excited state density; for (c), the energy, which is a functional of the ground state ensemble density, is constructed by the ensemble generalization of the coupling constant scheme; and for (d) the

energy is also a *bidensity* functional, in this instance of the ground state and excited state ensemble densities, with the functional derivative taken at the ensemble density.

We describe here the Q-DFT of *both ground* and *excited* degenerate states, and for the cases of *both* the *pure* state and *ensemble* v-representable densities. In Q-DFT, the interacting system *pure* state density, and *each* component of the *ensemble* density, are interacting v-representable as they are obtained by solution of the Schrödinger equation. The *assumption* of existence of an S system in Q-DFT therefore means that the *pure* state density and *each* component of the *ensemble* density are also *noninteracting v-representable.* (By an S system we mean a noninteracting fermion system whose wave function is a *single* Slater determinant, and which maybe in a ground or excited state). We begin by (*i*) describing the Q-DFT of the *individual* degenerate pure state. For the mapping from a degenerate *ground* state of the interacting system, the corresponding S system is in its *ground* state. For the mapping from a degenerate *excited* state, the state of the S system is *arbitrary* in that it may be in a *ground* or *excited* state. In either case, the highest occupied eigenvalue is the negative of the ionization potential. (The mapping from a nondegenerate excited state [9,10] is similar.) For the ground *and* excited state *ensemble* cases, we describe *two* different schemes within Q-DFT. Thus, (*ii*) in the first, the corresponding noninteracting system ensemble density is obtained by constructing g S systems, where g is the degeneracy of the state. Once again for excited states, the g S systems may either be in a *ground* or *excited* state or a

combination of the two. Next, (***iii***) we describe the Q-DFT whereby the ensemble density is obtained from a *single* noninteracting fermion system whose orbitals could be degenerate. The construction of this model system is a consequence of the linearity of the differential virial theorem. Here the highest occupied eigenvalue is degenerate, and the ensemble density is obtained from the resulting Slater determinants as described by Ullrich and Kohn [42] whose work in turn is based on that of Chayes et al [47]. Again for the mapping from an excited state, the noninteracting system may be in a ground or excited state. The Q-DFT description then (***iv***) provides the physics underlying *all* the various KS-DFT degenerate state energy density and bidensity functionals, and of their functional derivatives. Finally, (***v***) we present examples that demonstrate the above mappings within Q-DFT.

5.2 Q-DFT of the *individual* degenerate pure state

The Q-DFT of the bound *individual* degenerate *pure* state is as follows. The Schrodinger equation for a degenerate state whether ground or excited is

$$\hat{H}\Psi_{n,\eta}(\mathbf{X}) = [\hat{T} + \hat{V} + \hat{U}]\Psi_{n,\eta}(\mathbf{X}) = E_n\Psi_{n,\eta}(\mathbf{X}), \tag{5.1}$$

$\hat{T} = -\frac{1}{2}\sum_i {\nabla_i}^2$, $\hat{V} = \sum_i v(\mathbf{r}_i)$, $\hat{U} = \frac{1}{2}\sum'_{i,j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$, where $\Psi_{n,\eta}(\mathbf{X})$ and E_n are a bound degenerate state wave function and energy, n corresponds to the state, and $\eta = 1, ...g_n$ the degeneracy, $\mathbf{X} = \mathbf{x}_1, ...\mathbf{x}_\mathbf{N}, \mathbf{x} = \mathbf{r}\sigma$, with σ the spin coordinate. As the equations to follow are valid for arbitrary states, we drop the subscript n. The degenerate pure state density $\rho_\eta(\mathbf{r}) = \langle\Psi_\eta \mid \hat{\rho} \mid \Psi_\eta\rangle$, where $\hat{\rho} = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$, and the

energy $E_\eta = \langle \Psi_\eta \mid \hat{H} \mid \Psi_\eta \rangle$.

The corresponding differential equation for the S system of noninteracting fermions with the same density is

$$[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{ee,\eta}(\mathbf{r})]\phi_i(\mathbf{x}) = \varepsilon_i \phi_i(\mathbf{x}); \quad i = 1, ...N, \tag{5.2}$$

with

$$\rho_\eta(\mathbf{r}) = \langle \Phi_\eta\{\phi_i\} \mid \hat{\rho} \mid \Phi_\eta\{\phi_i\} \rangle = \sum_{i,\sigma} \mid \phi_i(\mathbf{x}) \mid^2, \tag{5.3}$$

and $\Phi_\eta\{\phi_i\}$ is the *single* Slater determinant of the orbitals $\phi_i(\mathbf{x})$. This is the S system wave function. The electron-interaction potential energy $v_{ee,\eta}(\mathbf{r})$ is representative of electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects. Correlation-Kinetic contributions to the potential energy are a consequence of the difference in kinetic energy between the interacting and noninteracting systems. The potential energy $v_{ee,\eta}(\mathbf{r})$ is the work done to move a model Fermion in the force of a conservative field $\mathcal{F}_\eta(\mathbf{r})$:

$$v_{ee,\eta}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \mathcal{F}_\eta(\mathbf{r}') \cdot d\mathbf{l}', \tag{5.4}$$

where $\mathcal{F}_\eta(\mathbf{r}) = \mathcal{E}_{ee,\eta}(\mathbf{r}) + \mathcal{Z}_{t_c,\eta}(\mathbf{r})$. The fields $\mathcal{E}_{ee,\eta}(\mathbf{r})$ and $\mathcal{Z}_{t_c,\eta}(\mathbf{r})$ are not necessarily conservative. Their sum always is. The electron-interaction field $\mathcal{E}_{\mathbf{ee},\eta}(\mathbf{r})$ is representative of Pauli and Coulomb correlation: $\mathcal{E}_{ee,\eta}(\mathbf{r}) = \mathbf{e}_{ee,\eta}(\mathbf{r})/\rho_\eta(\mathbf{r})$, where the electron-interaction 'force' $\mathbf{e}_{ee,\eta}(\mathbf{r})$ is obtained via Coulomb's law as $\mathbf{e}_{ee,\eta}(\mathbf{r}) = \int d\mathbf{r}' P_\eta(\mathbf{r}\mathbf{r}')(\mathbf{r} - \mathbf{r}')/ \mid \mathbf{r} - \mathbf{r}' \mid^3$, where $P_\eta(\mathbf{r}\mathbf{r}') = \langle \Psi_\eta | \hat{P}(\mathbf{r}\mathbf{r}') | \Psi_\eta \rangle$,

with $\hat{P}(\mathbf{r}\mathbf{r}') = \sum'_{i,j}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j)$. Equivalently, the field $\mathcal{E}_{ee,\eta}(\mathbf{r})$ may be thought of as being due to its quantal source, the pair-correlation density $g_\eta(\mathbf{r}\mathbf{r}') = P_\eta(\mathbf{r}\mathbf{r}')/\rho_\eta(\mathbf{r})$. The Correlation-Kinetic field $\mathcal{Z}_{t_c,\eta}(\mathbf{r}) = \mathcal{Z}_{s,\eta}(\mathbf{r}) - \mathcal{Z}_\eta(\mathbf{r})$, $\mathcal{Z}_\eta(\mathbf{r}) = \mathbf{z}_\eta(\mathbf{r};[\gamma_\eta])/\rho_\eta(\mathbf{r})$, $\mathcal{Z}_{s,\eta}(\mathbf{r}) = \mathbf{z}_{s,\eta}(\mathbf{r};[\gamma_{s,\eta}])/\rho_\eta(\mathbf{r})$, and where $\mathcal{Z}_\eta(\mathbf{r})$ and $\mathcal{Z}_{s,\eta}(\mathbf{r})$ are the interacting and S system kinetic fields, respectively. The kinetic 'force' $\mathbf{z}_\eta(\mathbf{r})$ is defined by its component $z_{\eta,\alpha} = 2\sum_\beta \partial t_{\alpha,\beta}/\partial r_\beta$, with $t_{\alpha,\beta}(\mathbf{r},[\gamma_\eta]) = \frac{1}{4}[\partial^2/\partial r'_\alpha \partial r''_\beta + \partial^2/\partial r'_\beta \partial r''_\alpha]\gamma_\eta(\mathbf{r}',\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}$ the kinetic energy density tensor. The source of the kinetic field $\mathcal{Z}_\eta(\mathbf{r})$ is the spinless single particle density matrix $\gamma_\eta(\mathbf{r},\mathbf{r}') = \langle\Psi_\eta|\hat{X}|\Psi_\eta\rangle$, $\hat{X} = \hat{A} + i\hat{B}$, $\hat{A} = \frac{1}{2}\sum_j[\delta(\mathbf{r}_j-\mathbf{r})T_j(\mathbf{a})+\delta(\mathbf{r}_j-\mathbf{r}')T_j(-\mathbf{a})]$, $\hat{B} = -\frac{i}{2}\sum_j[\delta(\mathbf{r}_j-\mathbf{r})T_j(\mathbf{a})-\delta(\mathbf{r}_j-\mathbf{r}')T_j(-\mathbf{a})]$, $T_j(\mathbf{a})$ is a translation operator, and $\mathbf{a} = \mathbf{r}' - \mathbf{r}$. The field $\mathcal{Z}_s(\mathbf{r})$ is defined in a similar manner in terms of the S system Dirac density matrix $\gamma_{s,\eta}(\mathbf{r},\mathbf{r}') = \langle\Phi_\eta\{\phi_i\}|\hat{X}|\Phi_\eta\{\phi_i\}\rangle = \sum_{i,\sigma}\phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma)$.

The proof of Eq.(5.4) follows by equating the differential virial theorems [3,9,11,13] for the interacting and S systems which are, respectively

$$\nabla v(\mathbf{r}) = -\mathbf{F}_\eta(\mathbf{r}) \;\; and \;\; \nabla v(\mathbf{r}) = -\mathbf{F}_{s,\eta}(\mathbf{r}), \tag{5.5}$$

where $\mathbf{F}_\eta(\mathbf{r}) = -\mathcal{E}_{ee,\eta}(\mathbf{r}) + \mathcal{D}_\eta(\mathbf{r}) + \mathcal{Z}_\eta(\mathbf{r})$, $\mathbf{F}_{s,\eta}(\mathbf{r}) = \nabla v_{ee,\eta}(\mathbf{r}) + \mathcal{D}_\eta(\mathbf{r}) + \mathcal{Z}_{s,\eta}(\mathbf{r})$, the differential density field $\mathcal{D}_\eta(\mathbf{r}) = \mathbf{d}_\eta(\mathbf{r})/\rho_\eta(\mathbf{r})$, $\mathbf{d}_\eta(\mathbf{r}) = -\frac{1}{4}\nabla\nabla^2\rho_\eta(\mathbf{r})$. Thus, one obtains

$$\nabla v_{ee,\eta}(\mathbf{r}) = -\mathcal{F}_\eta(\mathbf{r}), \tag{5.6}$$

from which the interpretation of Eq. (5.4) follows.

The total energy of the degenerate state η is then

$$E_\eta = T_{s,\eta} + \int \rho_\eta(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + E_{ee,\eta} + T_{c,\eta}, \tag{5.7}$$

where $T_{s,\eta} = \langle \Phi_\eta\{\phi_i\}|\hat{T}|\Phi_\eta\{\phi_i\}\rangle$ is the S system kinetic energy, and the electron-interaction $E_{ee,\eta}$ and Correlation-Kinetic $T_{c,\eta}$ energies in terms of the respective fields are

$$E_{ee,\eta} = \int d\mathbf{r} \rho_\eta(\mathbf{r}) \mathbf{r} \cdot \mathcal{E}_{ee,\eta}(\mathbf{r}), \ and \tag{5.8}$$

$$T_{c,\eta} = \frac{1}{2} \int d\mathbf{r} \rho_\eta(\mathbf{r}) \mathbf{r} \cdot \mathcal{Z}_{t_c,\eta}(\mathbf{r}). \tag{5.9}$$

These expressions are independent of whether the fields $\mathcal{E}_{ee,\eta}(\mathbf{r})$ and $\mathcal{Z}_{t_c,\eta}(\mathbf{r})$ are conservative or not.

The S system whereby the density and total energy equivalent to that of the interacting system degenerate state η is defined by Eqs.(5.2)-(5.4) and (5.7). If the degenerate state is excited , the S system may be constructed to be either in a ground or excited state. Since the electron-interaction field remains unchanged, the difference between the corresponding potential energies is independent of the Pauli principle and Coulomb repulsion and due entirely to the corresponding Correlation-Kinetic fields $\mathcal{Z}_{t_c,\eta}(\mathbf{r})$. Hence, the potential energy $v_{ee,\eta}(\mathbf{r})$ is different depending on whether the S system is in a ground or excited state. In either case, the highest occupied eigenvalue of the S system differential equation is the negative

of the ionization potential. This follows by equating the asymptotic structure of the density for the interacting and S systems.

In the transformation from an excited pure degenerate state to an S system in its ground state, the fact that the interacting system wave function has nodes is of no relevance. By construction, the S and interacting system density $\rho(\mathbf{r})$ are equivalent, and the density $\rho(\mathbf{r}) \geq 0$. Such a mapping for an excited pure nondegenerate state has been demonstrated in Ref. [9,11].

5.3 Q-DFT of the ensemble density of the degenerate states

Method 1

We next describe the first of *two* ways of obtaining the *ensemble* density and energy of the degenerate states via Q-DFT. The interacting system ensemble density matrix operator $\hat{D}(\mathbf{XX}')$ is defined as

$$\hat{D}(\mathbf{XX}') = \sum_{\eta=1}^{g} \omega_\eta \Psi_\eta^*(\mathbf{X}) \Psi_\eta(\mathbf{X}'); \quad \sum_{\eta=1}^{g} \omega_\eta = 1; \quad 0 \leq \omega_\eta \leq 1, \tag{5.10}$$

so that the ensemble density $\rho_{ens}(\mathbf{r})$ and energy E_{ens} are respectively

$$\rho_{ens}(\mathbf{r}) = tr(\hat{D}\hat{\rho}) = \sum_{\eta=1}^{g} \omega_\eta \rho_\eta(\mathbf{r}), \tag{5.11}$$

and

$$E_{ens} = tr(\hat{D}\hat{H}) = \sum_{\eta=1}^{g} \omega_\eta E_\eta, \tag{5.12}$$

with $\rho_\eta(\mathbf{r})$ and E_η as defined previously. (There are ensemble densities that cannot be represented by a single Slater determinant. However, its pure state component density can always be reproduced by an S system).

For *each* degenerate state η, the density $\rho_\eta(\mathbf{r})$ and energy E_η can be constructed from an S system as described in section 5.2. Thus, the ensemble density and energy of Eqs. (5.11) and (5.12) may be obtained from g S systems. Each S system contributing to the ensemble density may be in a ground or excited state. Note that the electron-interaction potential energy $v_{ee,\eta}(\mathbf{r})$ for *each* of the g S systems will be different. Further, $v_{ee,\eta}(\mathbf{r})$ will be different depending on whether the particular S system is in a ground or excited state as explained previously. Thus, the ensemble density and energy within Q-DFT are obtained by replacing the $\rho_\eta(\mathbf{r})$ and E_η on the right hand sides of Eqs. (5.11) and (5.12) by the corresponding S system equivalents of Eqs. (5.3) and (5.7), respectively.

Method 2

The ensemble density and energy may also be determined from a noninteracting fermion system whose orbitals could be degenerate as constructed within Q-DFT. According to Chayes et al[47], the ground state ensemble density may be determined as a unique weighted sum of squares of a finite number g of degenerate wave functions of this system. The potential energy $v_{ee}(\mathbf{r})$ of these noninteracting fermions is then determined via Q-DFT as follows. Rewrite the interacting and noninteracting system

differential virial theorems of Eq. (5.5) as

$$\rho_{ens}(\mathbf{r})\nabla v(\mathbf{r}) = \sum_{\eta=1}^{g} \omega_\eta \mathbf{f}_\eta(\mathbf{r}), \tag{5.13}$$

where $\mathbf{f}_\eta(\mathbf{r}) = \mathbf{e}_{ee,\eta}(\mathbf{r}) - \mathbf{d}_\eta(\mathbf{r}) - \mathbf{z}_\eta(\mathbf{r})$, and

$$\rho_{ens}(\mathbf{r})\nabla v(\mathbf{r}) = \sum_{\eta=1}^{g} \omega_\eta \mathbf{f}_{s,\eta}(\mathbf{r}), \tag{5.14}$$

where $\mathbf{f}_{s,\eta}(\mathbf{r}) = \rho_\eta(\mathbf{r})\nabla v_{ee,\eta}(\mathbf{r}) - \mathbf{d}_\eta(\mathbf{r}) - \mathbf{z}_{s,\eta}(\mathbf{r})$. Equating Eqs. (5.13) and (5.14) leads to

$$\sum_{\eta=1}^{g} \omega_\eta \rho_\eta(\mathbf{r})\nabla v_{ee,\eta}(\mathbf{r}) = \sum_{\eta=1}^{g} \omega_\eta \mathbf{q}_\eta(\mathbf{r}), \tag{5.15}$$

where $\mathbf{q}_\eta(\mathbf{r}) = \mathbf{e}_{ee,\eta}(\mathbf{r}) + \mathbf{z}_{t_c,\eta}(\mathbf{r})$, $\mathbf{z}_{t_c,\eta}(\mathbf{r}) = \mathbf{z}_{s,\eta}(\mathbf{r}) - \mathbf{z}_\eta(\mathbf{r})$. Eq. (5.15) is a consequence of the linearity of the differential virial theorem. As we require a *single* effective potential energy $v_s(\mathbf{r}) = v(\mathbf{r}) + v_{ee}(\mathbf{r})$, we replace $v_{ee,\eta}(\mathbf{r})$, in Eq. (5.15) by $v_{ee}(\mathbf{r})$ to obtain

$$\nabla v_{ee}(\mathbf{r}) = -\mathbf{Q}(\mathbf{r}), \tag{5.16}$$

where $\mathbf{Q}(\mathbf{r}) = -(\sum_{\eta=1}^{g} \omega_\eta \mathbf{q}_\eta(\mathbf{r}))/\rho_{ens}(\mathbf{r})$, Thus, the electron-interaction potential energy $v_{ee}(\mathbf{r})$ is the work done in the conservative field $\mathbf{Q}(\mathbf{r})$:

$$v_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathbf{Q}(\mathbf{r}') \cdot d\mathbf{l}'. \tag{5.17}$$

Note that the components $\mathbf{q}_\eta(\mathbf{r})$ are conservative so that $\mathbf{Q}(\mathbf{r})$ is conservative, and hence $v_{ee}(\mathbf{r})$ is path independent.

For the occupation of orbitals we follow Ullrich-Kohn [42]. Accordingly, all levels are occupied except the highest (h) which is q- fold degenerate and partially occupied. The number of the model fermions in these levels are $N^h \leq 2q$. The ensemble density which is a weighted sum of the degenerate Slater determinants is

$$\rho_{ens}(\mathbf{r}) = \sum_{i,\sigma}^{N-N^h} |\phi_i(\mathbf{x})|^2 + \sum_{i,\sigma}^{q} f_i |\phi_i^h(\mathbf{x}; R)|^2, \tag{5.18}$$

with $0 \leq f_i \leq 1$, and $f_i = \sum_{\eta=1}^{g} \omega_\eta \theta_{i,\eta}$ where $\theta_{i,\eta} = 1$ if the orbital $\phi_i^h(\mathbf{x}; R)$ occurs in the determinant $\Phi_\eta\{\phi_i\}$, and 0 otherwise. Here the $\phi_i^h(\mathbf{x}; R)$ are appropriately rotated (R) orbitals determined self-consistently together with the f_i and the lower lying orbitals leading to the ensemble density. The ensemble energy is obtained from the g Slater determinants as in Method 1. Once again for an excited state ensemble density, the corresponding noninteracting system may be in a ground or excited state.

Note that the methodology of construction of the g S systems of Method 1 also follows from Eq. (5.15). We believe that it is easier to construct the g S systems of Method 1 than it is to construct the single noninteracting system of Method 2. This is because each of the g S systems may be constructed independently.

5.4 Conclusions and Applications

From the above degenerate state Q-DFT description it is then possible to provide a rigorous physical interpretation for *each* energy functional and functional derivative of the corresponding KS-DFT. In each case, the local potential energy of the

model fermions is the work done in a conservative field. The energy in turn may be expressed in terms of the components of this field. Thus, for example, the KS-DFT degenerate *ground* state electron-interaction energy functional $E_{ee}^{KS}[\rho_{ens}]$[42] of the ensemble density is the ensemble sum of the electron-interaction $E_{ee,\eta}$ and Correlation-Kinetic $T_{c,\eta}$ energies. The functional derivative is the work done to move the model fermion in the conservative field $\mathbf{Q}(\mathbf{r})$. The *same* interpretation applies to the *bidensity* energy functional $E_{ee}^{KS}[\rho_{gr}, \rho_{ens}]$ [41] of degenerate *excited* state KS-DFT, and of its functional derivative.

The Q-DFT mapping from a pure degenerate excited state to an S system can be demonstrated via the first excited *triplet* state of the exactly solvable Hooke's atom [30]. This atom is comprised of two electrons with a harmonic external potential energy $v(\mathbf{r}) = \frac{1}{2}\omega r^2$. The triplet state wave functions are of the form

$$\Psi(\mathbf{r}_1\mathbf{r}_2) = C_0 e^{-\omega R^2} e^{-\omega r^2/4}[1 + C_1\sqrt{\frac{\omega}{2}}r + C_2(\frac{\omega}{2})r^2 + C_3(\frac{\omega}{2})^{3/2}r^3]Y_{l,m}(\theta,\phi), \qquad (5.19)$$

where $Y_{l,m}(\theta,\phi)$ is the spherical harmonic with $l = 1, m = -1, 0, 1, \mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1, \mathbf{R} = (\mathbf{r}_2 + \mathbf{r}_1)/2$, and C_0, C_1, C_2, C_3 are constants. For each degenerate wave function, the corresponding S system, in either a ground or excited state, can be determined in a manner similar to the transformation of the first excited *singlet* state [9,11]. These results will be presented elsewhere. The ensemble density of these degenerate states then follows from the 3 S systems. (Note that the ensemble density for this two electron model is v-representable. However, the methodology for constructing the g S systems is the same whether or not the ensemble density is v-representable.).

Another example is that of the noninteracting Be atom [42]. Here the ensemble density, which is not v-representable, is the weighted sum of the density of 4 S systems in the states $1s^2 2s^2, 1s^2 2p_i^2$ $(i = x, y, x)$. This latter model atom is also an example [42] of the noninteracting fermion system that leads to the ensemble density with appropriately rotated highest occupied orbitals.

In conclusion, we have described via Q-DFT the physics of mapping from a degenerate state of Schrödinger theory to that of a model system of noninteracting fermions such that the equivalent density and energy are determined. The cases of *both pure* and *ensemble* v-representable densities are explained. The framework is general and formally the *same* for *both* degenerate *ground* and *excited* states.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

This thesis is concerned primarily with the fundamental aspects of density functional theory. A Corollary to the first Hohenberg-Kohn theorem and the corresponding extension to the time-dependent case due to Runge-Gross have been derived. These corollaries lead to an understanding of the limitations of these fundamental theorems. In addition, the framework of Quantal density functional theory has been extended to degenerate states for both ground and excited states, and for the cases of both pure state and ensemble densities. This further provides a rigorous physical interpretation of the various energy density and bidensity functionals and functional derivatives of the corresponding Kohn-Sham density functional theories. Finally, we have applied Q-DFT to obtain properties of the Hydrogen molecule in its ground state. This is the first application of Q-DFT to molecular systems. The qualitative features of the results of this study will be the same for other diatomic molecules.

There are two areas of research in the context of Q-DFT currently being pursued. Thus far, the equations of time-dependent and independent Q-DFT have been derived within the Born-Oppenheimer approximation. We propose to extend Q-DFT to the case of multicomponent systems by incorporating the motion of different nuclei. This involves the derivation of the differential and integral virial

theorems for both the interacting system and the corresponding noninteracting system with equivalent electronic density. The special case when two S systems with equivalent electronic and nuclear densities are constructed will also be considered. The corresponding force and torque sum rules will also be derived.

A second thrust of research is the development of *approximate* Q-DFT in which the electron correlations due to the Pauli principle, Coulomb repulsion and Correlation-Kinetic effects are all incorporated. Briefly, the basic idea is to construct an approximate, *few-parameter* correlated *wave function functional* to be employed within the framework of Q-DFT. The wave function is a functional in that it depends on a set of functions χ: $\Psi = \Psi[\chi]$. The use of a wave function functional instead of a wave function helps reduce the number of parameters as the space of variations is increased. The form of the wave function functional being considered is that of the correlated-determinantal or Jastrow type. Thus, all three types of electron correlations can be accounted for. The wave function is determined by variational self-consistent solution of the Q-DFT S-system differential equation, the function χ being obtained by the satisfaction of a constraint such as normalization or the Fermi-Coulomb hole sum rule, or by the requirement that the wave function functional reproduce a physical observable such as the diamagnetic susceptibility or density. In this manner, both a rigorous upper bound to the energy, as well as a specific property of interest, are obtained accurately. For finite systems, Q-DFT intrinsically leads [3] to accurate highest occupied eigenvalues,

and thus to accurate ionization potentials. Finally, we are investigating the use of Fermi-Hypernetted-Chain (FHNSC) theory[48] in the context of Q-DFT since the starting point of FHNC theory is also the Jastrow ansatz.

APPENDIX: Wave function parameters

The values of the parameter δ and the coefficients c_{mnjkp} for the wave function of Eq.(4.2) are listed in the table I.

TABLE I: Variational parameters in the normalized 51-parameter correlated wave function for the ground state of H_2[35].

No. of terms					50
				$\delta =$	0.995
ξ_1	η_1	ξ_2	η_2	r_{12}	Coefficients
0	0	0	0	0	2.065908
0	0	0	2	0	1.282032
0	0	1	0	0	0.144619
0	1	0	1	0	−0.430253
0	0	0	0	1	0.787198
1	1	0	1	0	−0.235454
1	0	0	2	0	0.148273
0	0	2	0	0	0.109859
0	0	0	0	2	−0.212159
1	0	1	0	0	−0.081387
0	2	0	2	0	0.182892
0	0	0	2	1	0.198555
0	0	1	0	1	0.324658
1	1	1	1	0	−0.010794
0	0	1	0	2	0.077830
1	0	2	0	0	−0.055114
0	1	0	1	1	0.130714
0	1	0	1	2	−0.050854
1	0	2	0	1	0.014963
0	0	2	0	1	−0.132980
1	1	1	1	2	0.000362
0	0	2	0	2	0.006992
1	0	0	2	1	−0.050940
1	1	1	1	1	0.018027
1	0	1	0	1	0.017554
0	0	0	2	2	−0.014601
1	0	1	0	2	−0.015172
1	0	0	2	2	0.012656
1	2	3	0	0	−0.000202
2	0	3	0	0	−0.000856
0	0	1	2	0	−0.009469
0	0	3	0	0	0.036963
1	0	1	2	0	−0.022325
0	1	2	1	0	0.053233
1	0	3	0	0	0.004690
1	2	1	2	0	0.004707
1	1	2	1	0	−0.017531
0	2	3	0	0	0.017270
3	0	3	0	0	0.000082
2	1	2	1	0	0.000031
0	0	1	2	1	0.094436
0	0	3	0	1	0.001789
0	0	3	0	2	−0.000394
0	0	1	2	2	−0.004475
2	0	3	0	1	−0.000121
1	0	1	2	1	−0.014893
2	0	3	0	2	0.000011
1	0	1	2	2	0.001016
0	2	3	0	1	−0.003443
0	2	3	0	2	0.000225

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