Appendix A
Quantal Density Functional Theory of Degenerate States

In this appendix, the Q-DFT of both ground and excited degenerate states, and for the cases of both the pure state and the ensemble $v$-representable densities, is described [1]. The interest in the ensemble cases stems from a ground state theorem due to Levy [2] and Lieb [3]. 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 (2.1) will yield this ensemble density. Such ensemble densities are said to be ensemble $v$-representable. The translation of the theorem to the $S$ system 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. Within Q-DFT, the densities concerned are always those obtained from the solution of the Schrödinger equation (2.5). Thus, the pure state density, and each component of the ensemble density, are interacting $v$-representable. 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.

We begin by (1) describing the Q-DFT of the individual degenerate pure state. For the mapping from a degenerate ground or 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. For the ground and excited state ensemble cases, two different schemes within Q-DFT are described. Thus, (2) 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, the $g$ $S$-systems may either be in a ground or excited state or a combination of the two. Next, (3) 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 "Quantal Newtonian" first law. Here the highest occupied eigenvalue is degenerate, and the ensemble density is obtained from the resulting Slater determinants as described by Ullrich and Kohn [4] whose work in turn is based on that of Chayes et al. [5]. Again for the mapping from an excited state, the noninteracting system may be in a ground or excited state. Examples demonstrating the above mappings within Q-DFT are then given. Finally, in QDFT a rigorous
physical interpretation was provided of the energy functionals and functional derivatives of ground state Kohn–Sham density functional theory [6] (KS-DFT). The above mappings in turn explain the physics underlying all the various [4, 7, 9] Kohn–Sham theory degenerate state energy density and bidensity functionals and of their functional derivatives.

(1) The Q-DFT of the bound individual degenerate pure state is as follows. The Schrödinger equation for a degenerate state whether ground or excited is

\[
\hat{H} \Psi_{n,\eta}(X) = \left[ \hat{T} + \hat{V} + \hat{U} \right] \Psi_{n,\eta}(X) = E_n \Psi_{n,\eta}(X),
\]

\[
\hat{T} = \frac{1}{2} \sum_i \nabla_i^2, \quad \hat{V} = \sum_i v(r_i), \quad \hat{U} = \frac{1}{2} \sum_{i,j} (1/|r_i - r_j|),
\]

where \( \Psi_{n,\eta}(X) \) and \( E_n \) are a bound degenerate state wave function and energy, \( n \) corresponds to the state, and \( \eta = 1, \ldots, g \) the degeneracy, \( X = x_1, \ldots, x_N, x = r_\sigma \), with \( \sigma \) the spin coordinate. As the following equations are valid for arbitrary states, we drop the subscript \( n \). The degenerate pure state density \( \rho_\eta(r) = \langle \Psi_\eta | \hat{\rho} | \Psi_\eta \rangle \), where \( \hat{\rho} = \sum_\sigma \delta(r - r_\sigma) \), and the energy \( E_\eta = \langle \Psi_\eta | \hat{H} | \Psi_\eta \rangle \).

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

\[
\left[ -\frac{1}{2} \nabla^2 + v(r) + v_{ee,\eta}(r) \right] \phi_i(x) = \epsilon_i \phi_i(x);
\]

\[
i = 1, \ldots, N,
\]

with

\[
\rho_\eta(r) = \langle \Phi_\eta \{ \phi_i \} | \hat{\rho} | \Phi_\eta \{ \phi_i \} \rangle = \sum_{i,\sigma} |\phi_i(x)|^2,
\]

and \( \Phi_\eta \{ \phi_i \} \) is the single Slater determinant of the orbitals \( \phi_i(x) \). This is the \( S \) system wave function. The electron-interaction potential energy \( v_{ee,\eta}(r) \) 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 \( v_{ee,\eta}(r) \) is the work done to move a model fermion in the force of a conservative field \( \mathcal{F}_\eta(r) \):

\[
v_{ee,\eta}(r) = - \int_{-\infty}^r \mathcal{F}_\eta(r') \cdot d\ell',
\]

where \( \mathcal{F}_\eta(r) = \mathcal{E}_{ee,\eta}(r) + \mathcal{Z}_{tc,\eta}(r) \). The fields \( \mathcal{E}_{ee,\eta}(r) \) and \( \mathcal{Z}_{tc,\eta}(r) \) are not necessarily conservative. Their sum always is. The electron-interaction field \( \mathcal{E}_{ee,\eta}(r) \) is representative of the Pauli and Coulomb correlation: \( \mathcal{E}_{ee,\eta}(r) = e_{ee,\eta}(r)/\rho_\eta(r) \), where the electron-interaction “force” \( e_{ee,\eta}(r) \) is obtained via Coulomb’s law as

\[
e_{ee,\eta}(r) = \int d\ell' P_\eta(r,r') (r - r')/|r - r'|^3,
\]

where \( P_\eta(r,r') = \langle \Psi_\eta | \hat{P}(r,r') | \Psi_\eta \rangle \), with \( \hat{P}(r,r') = \sum_{i,j} \delta(r - r_i) \delta(r' - r_j) \). Equivalently, the field \( \mathcal{E}_{ee,\eta}(r) \) may be
thought as being due to its quantal source, the pair-correlation density \( g_\eta(r' r') = P_\eta(r' r')/\rho_\eta(r) \). The Correlation-Kinetic field \( \mathcal{Z}_{V,\eta}(r) = \mathcal{Z}_{s,\eta}(r) - \mathcal{Z}_\eta(r) \), \( \mathcal{Z}_\eta(r) = z_\eta(r; [\gamma_\eta])/\rho_\eta(r) \), \( \mathcal{Z}_{s,\eta}(r) = z_{s,\eta}(r; [\gamma_{s,\eta}])/\rho_\eta(r) \), and where \( \mathcal{Z}_\eta(r) \) and \( \mathcal{Z}_{s,\eta}(r) \) are the interacting and \( S \) system kinetic fields, respectively. The kinetic force \( z_\eta(r) \) is defined by its component \( z_{\eta, \alpha} = 2 \sum_\beta \partial t_{\alpha \beta}/\partial r_\beta \), with \( t_{\alpha \beta}(r; [\gamma_\eta]) = \frac{1}{2} [2 \partial^2 /\partial r'_\alpha \partial r''_\beta + 2 \partial^2 /\partial r''_\alpha \partial r'_\beta] \gamma_\eta(r' r'') \vert r' = r'' \) the kinetic energy density tensor. The source of the kinetic field \( \mathcal{Z}_\eta(r) \) is the spinless particle density matrix \( \gamma_\eta(r r') = \langle \Psi_\eta \vert \hat{X} \vert \Psi_\eta \rangle \), \( \hat{X} = \hat{A} + i \hat{B} \), \( \hat{A} = \frac{1}{2} \sum_j [\delta(r_j - r - r') \hat{T}_j(a) + \delta(r_j - r') \hat{T}_j(-a)] \), \( \hat{B} = -\frac{1}{2} \sum_j [\delta(r_j - r) \hat{T}_j(a) - \delta(r_j - r') \hat{T}_j(-a)] \), \( \hat{T}_j(a) \) is a translation operator, and \( a = r' - r \). The field \( \mathcal{Z}_\eta(r) \) is defined in a similar manner in terms of the \( S \) system Dirac density matrix \( \gamma_{s,\eta}(r r') = \langle \Phi_\eta \vert \hat{X} \vert \Phi_\eta \rangle \). The proof of (A.4) follows by equating the “Quantal Newtonian” first laws (2.11) and (3.5) for the interacting and \( S \) systems which are, respectively,

\[
\nabla v(r) = -F_\eta(r) \quad \text{and} \quad \nabla v(r) = -F_{s,\eta}(r),
\]

where \( F_\eta(r) = -\mathcal{E}_{ec,\eta}(r) + \mathcal{D}_\eta(r) + \mathcal{Z}_\eta(r) \), \( F_{s,\eta}(r) = \nabla v_{ec,\eta}(r) + \mathcal{D}_\eta(r) + \mathcal{Z}_{s,\eta}(r) \), the differential density field \( \mathcal{D}_\eta(r) = \mathcal{D}_\eta(r)/\rho_\eta(r) \), and \( \mathcal{D}_{s,\eta}(r) = -\frac{1}{2} \nabla \nabla \rho_\eta(r) \). Thus, one obtains

\[
\nabla v_{ec,\eta}(r) = -\mathcal{F}_\eta(r),
\]

from which the interpretation of (A.4) follows.

The total energy of the degenerate state \( \eta \) is then

\[
E_\eta = T_{s,\eta} + \int \rho_\eta(r) v(r) dr + E_{ec,\eta} + T_{c,\eta},
\]

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

\[
E_{ec,\eta} = \int \rho_\eta(r) r \cdot \mathcal{E}_{ec,\eta}(r),
\]

and

\[
T_{c,\eta} = \frac{1}{2} \int \rho_\eta(r) r \cdot \mathcal{Z}_{V,\eta}(r).
\]

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

The \( S \) system whereby the density and total energy equivalent to that of the interacting system degenerate state \( \eta \) is defined by (A.2)–(A.4) and (A.7). Irrespective of whether the interacting system is in a ground or excited state, 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 \( Z_{t,\eta}(r) \). Hence, the potential energy \( v_{\text{ee},\eta}(r) \) 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 (see Sect. 3.7).

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 \( S \) system and interacting system density \( \rho(r) \) are equivalent, and the density \( \rho(r) \geq 0 \). Such a mapping for an excited pure nondegenerate state is demonstrated in [10, 11] and in QDFT.

(2) 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 \( \hat{D}(XX') \) is defined as

\[
\hat{D}(XX') = \sum_{\eta=1}^{g} \omega_{\eta} \Psi_{\eta}^*(X)\Psi_{\eta}(X'); \quad \sum_{\eta=1}^{g} \omega_{\eta} = 1; \quad 0 \leq \omega_{\eta} \leq 1. \quad \text{(A.10)}
\]

where \( \omega_{\eta} \) is a weighting factor, and \( g \) the degeneracy. Then the ensemble density \( \rho_{\text{ens}}(r) \) and energy \( E_{\text{ens}} \) are, respectively,

\[
\rho_{\text{ens}}(r) = \text{tr}(\hat{D}\hat{\rho}) = \sum_{\eta=1}^{g} \omega_{\eta} \rho_{\eta}(r), \quad \text{(A.11)}
\]

and

\[
E_{\text{ens}} = \text{tr}(\hat{D}\hat{H}) = \sum_{\eta=1}^{g} \omega_{\eta} E_{\eta}(r), \quad \text{(A.12)}
\]

with \( \rho_{\eta}(r) \) and \( E_{\eta} \) 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 \( \eta \), the density \( \rho_{\eta}(r) \) and energy \( E_{\eta} \) can be constructed from an \( S \) system as described in part (1). Thus, the ensemble density and energy of (A.11) and (A.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 \( v_{\text{ee},\eta}(r) \) for each of the \( g \) \( S \)-systems will be different. Further, \( v_{\text{ee},\eta}(r) \) 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 \( \rho_{\eta}(r) \) and \( E_{\eta} \) on the right-hand sides of (A.11) and (A.12) by the corresponding \( S \) system equivalents of (A.3) and (A.7), respectively.
(3) 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. [5], 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 \( v_{ee}(r) \) of these noninteracting fermions is then determined via Q-DFT as follows. Rewrite the interacting and noninteracting system “Quantal Newtonian” first laws of (A.5) as

\[
\rho_{ens}(r) \nabla v(r) = \sum_{\eta=1}^{g} \omega_{\eta} f_{\eta}(r), \quad (A.13)
\]

where \( f_{\eta}(r) = e_{ee,\eta}(r) - d_{\eta}(r) - z_{\eta}(r) \), and

\[
\rho_{ens}(r) \nabla v(r) = \sum_{\eta=1}^{g} \omega_{\eta} f_{x,\eta}(r), \quad (A.14)
\]

where \( f_{x,\eta}(r) = \rho_{\eta}(r) \nabla v_{ee,\eta}(r) - d_{\eta}(r) - z_{x,\eta}(r) \). Equating (A.13) and (A.14) leads to

\[
\sum_{\eta=1}^{g} \omega_{\eta} \rho_{\eta}(r) \nabla v_{ee,\eta}(r) = \sum_{\eta=1}^{g} \omega_{\eta} \rho_{\eta}(r) \nabla v_{x,\eta}(r). \quad (A.15)
\]

where \( q_{\eta}(r) = e_{ee,\eta}(r) + z_{t,\eta}(r) \), and \( z_{t,\eta}(r) = z_{x,\eta}(r) - z_{\eta}(r) \). Equation (A.15) is a consequence of the linearity of the “Quantal Newtonian” first law. As we require a single effective potential energy \( v_{s}(r) = v(r) + v_{ee}(r) \), we replace \( v_{ee,\eta}(r) \), in (A.15) by \( v_{ee}(r) \) to obtain

\[
\nabla v_{ee}(r) = -Q(r), \quad (A.16)
\]

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

\[
v_{ee}(r) = -\int_{\infty}^{r} Q(r') \cdot d\ell'. \quad (A.17)
\]

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

For the occupation of orbitals we follow Ullrich-Kohn [4]. Accordingly, all levels are occupied except the highest (\( \ell \)) which is \( q \)-fold degenerate and partially occupied. The numbers of the model fermions in these levels are \( N^{\ell} \leq 2q \). The ensemble density which is a weighted sum of the degenerate Slater determinants is

\[
\rho_{ens}(r) = \sum_{i, \sigma}^{N-N^{\ell}} |\phi_{i}(x)|^2 + \sum_{i, \sigma}^{g} f_{i} |\phi_{i}^{h}(x; R)|^2, \quad (A.18)
\]
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 $\phi_{i}^\eta(x; R)$ occurs in the determinant $\Phi_{\eta}\{\phi_{i}\}$, and 0 otherwise. Here the $\phi_{i}^\eta(x; R)$ 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 part (2). 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 part (2) also follows from (A.15). We believe that it is easier to construct the $g$ $S$-systems of part (2) than it is to construct the single noninteracting system of part (3). This is because each of the $g$ $S$-systems may be constructed independently.

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 [12]. This atom is comprised of two electrons with a harmonic external potential energy $v(r) = \frac{1}{2} \omega r^2$. The triplet state wave functions are of the form

$$
\Psi(r_1 r_2) = C_0 e^{-\omega R^2} e^{-\omega r^2/4} \left[ 1 + C_1 \frac{\omega}{2} r + C_2 \left( \frac{\omega}{2} \right)^2 r^2 + C_3 \left( \frac{\omega}{2} \right)^{3/2} r^3 \right] Y_{l,m}(\theta, \phi), \tag{A.19}
$$

where $Y_{l,m}(\theta, \phi)$ is the spherical harmonic with $l = 1, m = -1, 0, 1, R = (r_2 + r_1)/2$, 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 [10, 11] (see QDFT). The ensemble density of these degenerate states then follows from the three $S$ 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 density is $v$-representable.)

Another example is that of the noninteracting Be atom [4]. Here the ensemble density, which is not $v$-representable, is the weighted sum of the density of four $S$ systems in the states $1s^22s^2, 1s^22p^2$ ($i = x, y, z$). This latter model atom is also an example [4] of the noninteracting fermion system that leads to the ensemble density with appropriately rotated highest occupied orbitals.

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. Within KS-DFT, the following cases have been considered: the mapping from (a) a pure degenerate ground state [7]; (b) a pure degenerate excited state [8]. In addition, maps to obtain the density and energy constructed from (c) an ensemble of pure degenerate ground states [4] and (d) an ensemble of pure degenerate excited states [9] have been developed. 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.

In each of the above cases, the local potential energy of the model fermion 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 $E_{\text{KS}}^{\text{ee}}(\rho_{\text{ens}})$ \[4\] of the ensemble density is the ensemble sum of the electron-interaction $E_{\text{ee},\eta}$ and Correlation-Kinetic $T_{\epsilon,\eta}$ 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 $E_{\text{KS}}^{\text{cc}}(\rho_{\text{gs}}, \rho_{\text{ens}})$ \[9\] of degenerate excited state KS-DFT, and of its functional derivative.
Appendix B
Generalization of the Runge–Gross Theorem of Time-Dependent Density Functional Theory

In this Appendix we generalize [1] the fundamental theorem of time-dependent (TD) density functional theory due to Runge and Gross [2] (RG) by a unitary or gauge transformation.

For a system of \( N \) electrons in a TD external field \( \mathcal{F}^{\text{ext}}(rt) \) such that \( \mathcal{F}^{\text{ext}}(rt) = -\nabla v(rt) \), with \( v(rt) \) a scalar external potential energy operator, the TD Schrödinger equation is

\[
\hat{H}(R_t)\Psi(X_t) = \frac{i}{\hbar}\frac{\partial\Psi(X_t)}{\partial t}, \tag{B.1}
\]

where \( \Psi(X_t) \) is the wave function, \( X = x_1, \ldots, x_N, x = r\sigma, r \) and \( \sigma \) are the spatial and spin coordinates, and \( R = r_1, \ldots, r_N \). The Hamiltonian \( \hat{H}(R_t) \) is the sum of the kinetic \( \hat{T} \), electron-interaction potential energy \( \hat{W} \), and external potential energy \( \hat{V} \) operators:

\[
\hat{H}(R_t) = \hat{T} + \hat{W} + \hat{V}, \tag{B.2}
\]

with \( \hat{T} = \sum_i (-\frac{1}{2} \nabla^2_i); \hat{W} = \frac{1}{2} \sum_{i,j} 1/|r_i - r_j|; \hat{V} = \sum_i v(r_i) \). The TD density \( \rho(rt) \) is the expectation

\[
\rho(rt) = \langle \Psi(X_t)|\hat{\rho}(r)|\Psi(X_t) \rangle, \tag{B.3}
\]

where \( \hat{\rho}(r) = \sum_i \delta(r - r_i) \) is the density operator.

The RG theorem is proved for the Hamiltonian \( \hat{H}(R_t) \) of (B.2). It is proved on the assumption that the scalar operator \( v(rt) \) is Taylor expandable about some initial time \( t_0 \). Furthermore, in the proof, the operators \( \hat{T} \) and \( \hat{W} \), and the initial many-particle state \( \Psi(t_0) \), are assumed known and kept fixed.

For fixed \( \hat{T}, \hat{W}, \) and \( \Psi(t_0) \), RG prove that the relationship between the density \( \rho(rt) \) and the external potential energy operator \( v(rt) \) to within a function \( C(t) \) is bijective: \( \rho(rt) \leftrightarrow v(rt) + C(t) \). Thus, knowledge of the density \( \rho(rt) \) of a system uniquely determines a Hamiltonian \( \hat{H}(R_t) \) to within \( C(t) \), and therefore via solution of the TD Schrödinger equation, the wave function \( \Psi(t) \). As a consequence of the bijectivity, the wave function is a functional of the density unique to within an arbitrary time-dependent phase factor \( \alpha(t) \). Hamiltonians that differ by \( C(t) \) are considered equivalent in the sense that they lead to the same density \( \rho(rt) \).
The TD unitary operator $U$ we employ is

$$
\hat{U} = e^{i\alpha(R_t)}.
$$

(B.4)

so that the transformed wave function $\Psi'(X_t)$ is

$$
\Psi'(X_t) = \hat{U}^\dagger \Psi(X_t),
$$

(B.5)

and the transformed density $\rho'(r_t) = \langle \Psi'(X_t)|\hat{\rho}(r)|\Psi'(X_t)\rangle = \rho(r_t)$. The unitary transformation thus preserves the density. The transformed Schrödinger equation is

$$
\hat{H}'(R_t)\Psi'(X_t) = i\frac{\partial \Psi'(X_t)}{\partial t},
$$

(B.6)

where the Hamiltonian $\hat{H}'(R_t)$ of the transformed system is

$$
\hat{H}'(R_t) = \hat{U}^\dagger \hat{H}(R_t)U + \frac{d\alpha(R_t)}{dt}
$$

(B.7)

$$
= \hat{H}(R_t) - \frac{1}{2} \sum_i \left[ \hat{U}^\dagger \left[ \nabla_i^2, \hat{U} \right] \right] + \frac{d\alpha(R_t)}{dt}.
$$

(B.8)

(Note that for the transformed system, the initial state and other boundary conditions too are transformed.) The solution of the commutator of (B.8) is the same as given in Sect. 4.3.1. Thus, the transformed Hamiltonian $\hat{H}'(R_t)$ is

$$
\hat{H}'(R_t) = \hat{H}(R_t) + \frac{d\alpha(R_t)}{dt} + \frac{1}{2} \sum_i (\hat{p}_i \cdot \hat{A}_i + \hat{A}_i \cdot \hat{p}_i + \hat{A}_i^2),
$$

(B.9)

where $\hat{p}_i = -i\nabla_i$ is the momentum operator, and where the vector potential energy operator is defined as $\hat{A}_i = \nabla_i \alpha(R_t)$ so that $\nabla \times \hat{A}_i = 0$.

The transformed Hamiltonian may also be written as

$$
\hat{H}'(R_t) = \frac{1}{2} \sum_i (\hat{p}_i + \hat{A}_i)^2 + \hat{W} + \hat{V}',
$$

(B.10)

where

$$
\hat{V}' = \hat{V} + \frac{d\alpha(R_t)}{dt}.
$$

(B.11)

Note that as is the case for the Hamiltonian $\hat{H}(R_t)$ of (B.2), there is no magnetic field in the transformed Hamiltonian $\hat{H}'(R_t)$. The vector potential energy operator $\hat{A}_i$ as defined above is curl-free.

That $\hat{H}(R_t)$ and $\hat{H}'(R_t)$ represent the same physical system may also be seen by performing the following gauge transformation of $\hat{H}(R_t)$ to obtain $\hat{H}'(R_t)$: $\hat{V} \rightarrow \hat{V}' = V + \frac{d\alpha(R_t)}{dt}$ and $\hat{A}_i \rightarrow \hat{A}_i' = \hat{A}_i + \nabla_i \alpha(R_t)$ with $\hat{A}_i = 0$ so that
The generalization of the fundamental theorem of density functional theory demonstrating the bijectivity between the density of a physical system and the infinite set of Hamiltonians representing that physical system. The figure is drawn for (a) the most general time-dependent form of the gauge function $\alpha(R_t)$. The figure reduces to the RG theorem for (b) when $\alpha(R_t) = \alpha(t)$. The figure further reduces to the most general form of the time-independent theorem when (c) $\alpha(R_t) = \alpha(R)$. Finally, the Hohenberg–Kohn theorem is recovered for (d) when $\alpha(R_t) = \alpha$, a constant.

$\hat{A}'_i = \nabla \alpha(R_t)$ and the magnetic field $B' = \nabla \times \hat{A}'_i = 0$. In quantum mechanics it is well known [3] that the more general gauge transformation above with nonzero magnetic field $B$ leaves the Schrödinger equation invariant provided the wave functions of the original and transformed Hamiltonians are related by the gauge transformation $\alpha(R_t)$ of (B.5).

The Hamiltonian $\hat{H}'(R_t)$ of (B.9), (B.10) is the most general form of the Hamiltonian for which the RG theorem is valid. It includes the scalar potential energy operator $V(r_t)$, the TD function $C(R_t) = d\alpha(R_t)/dt$, the momentum operator $\hat{p}_i$, and the TD curl-free vector potential energy operator $\hat{A}_i = \nabla \alpha(R_t)$. Pictorially the bijectivity of the RG Theorem in its general form is depicted in Fig. B.1. The bijectivity is $\rho(r_t) \leftrightarrow \hat{H}(R_t)$ with $\hat{H}(R_t)$ of (B.2), or equivalently $\rho(r_t) \leftrightarrow \hat{H}'(R_t)$ with $\hat{H}'(R_t)$ of (B.9), (B.10), depending on the gauge function $\alpha(R_t)$.

The Hamiltonian $\hat{H}(R_t)$ and the Hamiltonian $\hat{H}'(R_t)$ all correspond to the same physical system.

It is evident that the RG theorem in its original form is recovered from the above generalization for the special case when the gauge function $\alpha(R_t) = \alpha(t)$ (see Fig. B.1). The functions $C(t)$ of RG are linked to the gauge function: $C(t) = d\alpha(t)/dt$. Furthermore, the Hamiltonians $\hat{H}'(R_t) = \hat{H}(R_t) + C(t)$ all correspond to the same physical system because $\hat{H}'(R_t)$ is obtained from $\hat{H}(R_t)$ by a unitary or gauge transformation.
It is also clear from the unitary or gauge transformation that in the general case the wave function $\Psi(X_t)$ must be a functional of both the density $\rho(rt)$ and the gauge function $\alpha(R_t)$ i.e., $\Psi(X_t) = \Psi[\rho(rt); \alpha(R_t)]$. This functional dependence of the wave function functional on the gauge function $\alpha(R_t)$ ensures that it is gauge variant. Since the bijectivity is between the density $\rho(rt)$ of a system and the Hamiltonians representing the same physical system (see Fig. B.1), the choice of gauge function is arbitrary. Thus, the choice $\alpha(R_t) = 0$ is equally valid. Thus, in the RG case, the choice of $\alpha(t) = 0$ leads to a wave function functional that can be a functional only of the density $\rho(rt)$. In the RG case, Fig. B.1 shows that the bijectivity is between the density $\rho(rt)$ and the infinite number of Hamiltonians $\hat{H}(R_t) + C(t)$ representative of a physical system. Thus, the density uniquely determines the system Hamiltonian to within a function $C(t)$. It is, however, possible to construct [4], QDFT an infinite set of degenerate Hamiltonians $\{\hat{H}\}$ that differ by a function $C(t)$, represent different physical systems, but yet possess the same density $\rho(rt)$. In such a case, the density $\rho(rt)$ cannot distinguish between the different physical systems. For such systems, the RG theorem is not valid. (See Corollary to the RG theorem in QDFT.)

Finally, as a consequence of the unitary or gauge transformation, the following hierarchy exists in the fundamental theorem of density functional theory (see Fig. B.1). When the gauge function is $\alpha(R_t)$, one obtains the most general form of the time-dependent theorem. For the gauge function $\alpha(t)$, one recovers the original RG theorem. When the gauge function is $\alpha(R)$, one obtains the most general form of the time-independent theorem. Finally, when the gauge function is the constant $\alpha$, one recovers the original Hohenberg-Kohn theorem. (Note that the function $C(t)$ of the RG theorem does not reduce to the constant $C$ of the Hohenberg-Kohn theorem.) This hierarchy makes the role of the phase factor as significant in density functional theory as it is in quantum mechanics.
Appendix C

Analytical Asymptotic Structure of the Correlation-Kinetic Potential Energy in the Classically Forbidden Region of Atoms

In this Appendix, we derive [1] the analytical asymptotic structure of the Correlation-Kinetic potential energy $W_{c}(r)$ in the classically forbidden region of atoms. The derivation is in the framework of quasi-particle amplitudes as described by Almbladh and von Barth [2].

In second quantized notation, the single-particle density matrix $\gamma(xx')$ is

$$\gamma(xx') = \langle N|\psi'(x')\psi(x)|N \rangle,$$  \hspace{1cm} (C.1)

where $|N\rangle$ is the $N$-electron ground state wave function, $\psi(x)$, $\psi'(x')$ are respectively, the annihilation and creation field operators, and $x = r\sigma$. By inserting the complete set of the $(N - 1)$-electron system eigen states $\{|N - 1, s\}$ into (C.1) we have

$$\gamma(xx') = \sum_{s} f_{s}(x) f^{*}_{s}(x'),$$  \hspace{1cm} (C.2)

where the matrix elements

$$f_{s}(x) = \langle N - 1, s|\psi(x)|N \rangle$$  \hspace{1cm} (C.3)

are the quasi-particle amplitudes. These amplitudes are the interacting system counterparts of the one-electron orbitals of the noninteracting $S$ system. Following Almbladh and von Barth, the differential equation for these amplitudes is

$$\left[-\frac{1}{2}\nabla^{2} + v(x)\right] f_{s}(x) + \langle N - 1, s|\hat{v}_{H}(r)\psi(x)|N \rangle = \epsilon_{s} f_{s}(x),$$  \hspace{1cm} (C.4)

where $\epsilon_{s} = E_{0} - E_{1}^{(N-1)}$ (see (7.23)) is an exact one-particle excitation energy, $\hat{v}_{H}(r) = \int dr'\hat{\rho}(r')/|r - r'|$ the Hartree operator, and $\hat{\rho}(r) = \sum_{\sigma} \psi^\dagger(x)\psi(x) = \sum_{i} \delta(r - r_{i})$ is the density operator. By performing a multipole expansion of the
Coulomb interaction $1/|\mathbf{r} - \mathbf{r}'|$, one obtains

$$
\left[ -\frac{1}{2} \nabla^2 + v(x) + \langle N - 1|\hat{\mathbf{p}}(\mathbf{r})|N - 1 \rangle - \epsilon_x \right] f_s(x) \\
+ \left[ \frac{1}{r^2} \sum_{i} D_{s_2s_2}f_s(\hat{r}) + \frac{1}{r^3} \sum_{s'} Q_{s_2s_2}f_{s'}(x) \right] = 0, \quad (C.5)
$$

where $D_{s_2s_2}(\hat{r})$ and $Q_{s_2s_2}(\hat{r})$ are the dipole and quadrupole moment matrix elements defined as

$$
D_{s_2s_2}(\hat{r}) = \hat{r} \cdot \langle N - 1, s |d|N - 1, s' \rangle \quad (C.6)
$$

$$
Q_{s_2s_2}(\hat{r}) = \sum_{\alpha\beta} \hat{r}_\alpha r_\beta \cdot \langle N - 1, s |Q_{\alpha\beta}|N - 1, s' \rangle \quad (C.7)
$$

with

$$
d = \int \mathbf{r} \delta \hat{\rho}(\mathbf{r}) d\mathbf{r}, \quad (C.8)
$$

$$
\delta \hat{\rho}(\mathbf{r}) = \hat{\rho}(\mathbf{r}) - \langle N - 1|\hat{\rho}(\mathbf{r})|N - 1 \rangle, \quad (C.9)
$$

$$
\hat{Q}_{\alpha\beta} = \frac{1}{2} \int \left[ 3r_\alpha r_\beta - \delta_{\alpha\beta} r^2 \right] \delta \hat{\rho}(\mathbf{r}) d\mathbf{r}. \quad (C.10)
$$

and $\hat{r} = \mathbf{r}/r$. (In the asymptotic region, (C.5) and (7.22) are equivalent.) Equation (C.5) is the same as that derived by Almbladh and von Barth, but carried further to include the quadrupole moment term.

As we have seen in Chap. 7, to study the asymptotic structure of $v_{ee}(\mathbf{r})$ to $O(1/r^5)$, it is necessary to include the quadrupole term in the expansion of the Coulomb interaction. However, as also shown there, there is no quadrupole contribution of $O(1/r^5)$ to the asymptotic structure of $v_{ee}(\mathbf{r})$. Thus, in the derivations to follow, we drop the quadrupole terms, while simultaneously bearing in mind that the results are correct to $O(1/r^5)$. Following the same arguments as those below (7.24), we then have asymptotically

$$
f_s(x) \underset{r \to \infty}{\sim} -\frac{1}{r^2} \frac{D_{s_2s_2}(\hat{r})}{\omega_s} f_0(x), \quad (C.11)
$$

where $\omega_s = E_s^{(N-1)} - E_0^{(N-1)}$ is an excitation energy of the $(N - 1)$-electron system. This, of course, is the same as (7.26) but without the quadrupole moment term.

Substituting for $f_s(x)$ from (C.11) into (C.2), we obtain

$$
\gamma(x,x') \underset{r,r' \to \infty}{\sim} f_0(x)f_0^*(x') \left[ 1 + \sum_{s} \frac{1}{\omega^2_s} \frac{D_{s_2s_2}(\hat{r})D_{s_2s_2}(\hat{r}')}{r^2 r'^2} \right]. \quad (C.12)
$$
Now

\[
\sum_s \frac{D_{s0}(\mathbf{r}) D^*_{s0}(\mathbf{r}')} \omega_s^2 = \sum_{a\beta} \mathbf{\hat{r}}_a \mathbf{\hat{r}}'_\beta \sum_s \frac{\langle N-1 | d_\beta | N-1, s \rangle \langle N-1, s | d_\alpha | N-1 \rangle}{\omega_s^2} \\
= \sum_{a\beta} \mathbf{\hat{r}}_a \mathbf{\hat{r}}'_\beta \chi_{a\beta},
\]

where

\[
\chi_{a\beta} = \sum_s \frac{\langle N-1 | d_\beta | N-1, s \rangle \langle N-1, s | d_\alpha | N-1 \rangle}{\omega_s^2} \\
= \left\langle N-1 \right| d_\beta \frac{1 - P}{\left[H - E_0^{(N-1)}\right]^2} d_\alpha \left| N-1 \right>.
\]

\(\alpha, \beta\) are cartesian coordinates, \(\mathbf{\hat{r}}_\alpha\) is a component of the unit vector \(\mathbf{r}\), and \(P = \left| N-1 \right> \left< N-1 \right|\) is the projector onto the \((N-1)\)-electron ground state. Note that the coefficient \(\chi_{a\beta}\) is an expectation value with respect to the \((N-1)\)-electron ground state. Other than that, \(\chi_{a\beta}\) does not appear to have any physical interpretation. Thus,

\[
\gamma(x'x)_{r,r'\to\infty} \sim f_0(x) f_0^*(x') \left[ 1 + \frac{1}{r^2} \sum_{a\beta} \mathbf{\hat{r}}_a \mathbf{\hat{r}}'_\beta \chi_{a\beta} \right].
\]

As the \((N-1)\)-electron system is spherically symmetric, the coefficient \(\chi_{a\beta}\) is diagonal, \(\chi_{a\beta} = \delta_{a\beta} \chi\). Hence, the interacting system density matrix may be written as

\[
\gamma(x'x)_{r,r'\to\infty} \sim f_0(x) f_0^*(x') \left[ 1 + \frac{\chi}{r^2} \right].
\]

Next we determine the asymptotic structure of the kinetic-energy-density tensor \(t_{a\beta}(r; y)\) of (2.54):

\[
t_{a\beta}(r) = \frac{1}{4} \sum_{\sigma} \left[ \frac{\partial^2}{\partial r_\alpha' \partial r_\beta'} + \frac{\partial^2}{\partial r_\beta' \partial r_\alpha'} \right] \gamma(r'\sigma, r''\sigma) \bigg|_{r'=r''=r}.
\]

Substituting (C.18) into (C.19) we have

\[
t_{a\beta}(r) = \frac{1}{2} \left[ \frac{\partial^2}{\partial r_\alpha' \partial r_\beta'} + \frac{\partial^2}{\partial r_\beta' \partial r_\alpha'} \right] \times \left\{ f_0(x') f_0^*(x'') \left[ 1 + \frac{\chi}{r^2} \right] \right\} \bigg|_{r'=r''=r}.
\]
As the quasi-particle amplitude and wave function expansion methods are equivalent, we know from the derivation in QDFT that the asymptotic structure of \( f_0(x) \) depends only on \( r \) (see also [1–5]). This structure is

\[
\left. f_0(x) \right|_{r=\infty} \sim r^\lambda e^{-\kappa_0 r} (1 + A_1 r^{-1} + A_2 r^{-2} + A_3 r^{-3} + \ldots),
\]

where \( 1 + \lambda = Z_N - N + 1 \), \( Z_N \) is the total charge of the nuclei, \( \kappa_0^2/2 = E_0^{(N-1)} - E_0 \), and the \( A_i \) are coefficients. Using this fact and the relation \( \partial f(r)/\partial r = -E_0 f_0(x) \),
In (C.22) the tensor of the interacting system is

\[ t_{\alpha\beta}(r) = \frac{1}{2} \frac{r_{\alpha} r_{\beta}}{r^2} \left\{ \left( \frac{\partial f_0(x)}{\partial r} \right) \left( \frac{\partial f_0^*(x)}{\partial r} \right) \left( 1 + \frac{\chi}{r^4} \right) 
\right. \\
- \frac{2\chi}{r^5} \frac{\partial}{\partial r} \left[ f_0(x) f_0^*(x) \right] + \frac{3\chi}{r^8} f_0(x) f_0^*(x) \\
\left. + \frac{\chi}{2r^6} \delta_{\alpha\beta} f_0(x) f_0^*(x) \right\}. \quad (C.24) \]

We next need to determine the kinetic-energy-density tensor \( t_{s,\alpha,\beta}(r; \gamma_s) \) of the \( S \) system. The asymptotic structure of the density \( \rho(r) \) and Dirac density matrix \( \gamma_s(rr') \) are governed by the highest occupied eigenfunction \( \phi_N(x) \) of the \( S \) system differential equation. The diagonal element of the density matrix \( \gamma_s(rr') \) is then

\[ \rho(r) \xrightarrow{r \to \infty} \sum_\alpha f_0(x) f_0^*(x) \left[ 1 + \frac{\chi}{2r^4} \right], \quad (C.25) \]

so that asymptotically

\[ \phi_N(x) \xrightarrow{r \to \infty} f_0(x) \left[ 1 + \frac{\chi}{2r^4} \right]. \quad (C.27) \]

As such, asymptotically,

\[ \sum_\sigma \gamma_s(rr') = \sum_\sigma \phi_N(x) \phi_N^*(x') \quad (C.28) \]

\[ = \sum_\sigma f_0(x) f_0(x') \left[ 1 + \frac{\chi}{2r^4} \right] \left[ 1 + \frac{\chi}{2r^4} \right]. \quad (C.29) \]

The \( S \) system kinetic-energy-density tensor \( t_{s,\alpha,\beta}(r) \) which is defined as

\[ t_{s,\alpha,\beta}(r) = \frac{1}{4} \sum_\sigma \left[ \left( \frac{\partial^2}{\partial r'_\alpha \partial r'_\beta} + \frac{\partial^2}{\partial r'_{\alpha} \partial r'_{\beta}} \right) \gamma_s(r'; \sigma, r''; \sigma) \right] \left. \right|_{r'=r''=r}, \quad (C.30) \]

then reduces on performing the various partial derivatives in the above manner to

\[ t_{s,\alpha,\beta}(r) = \frac{1}{2} \frac{r_{\alpha} r_{\beta}}{r^2} \left\{ \left( \frac{\partial f_0(x)}{\partial r} \right) \left( \frac{\partial f_0^*(x)}{\partial r} \right) \left( 1 + \frac{\chi}{r^4} + \frac{\chi}{4r^8} \right) 
\right. \\
- \frac{2\chi}{r^5} \left( 1 + \frac{\chi}{2r^4} \right) \frac{\partial}{\partial r} \left[ f_0(x) f_0^*(x) \right] + \frac{4\chi^2}{r^{10}} f_0(x) f_0^*(x) \right\}. \quad (C.31) \]
Thus, on neglecting terms of $0(1/r^8)$ and higher-order, we have

$$t_{s, \alpha \beta}(r; [\gamma_s]) - t_{\alpha \beta}(r; [\gamma]) = -\frac{1}{2} \chi \left( \frac{3r_{\alpha \beta} r_{\beta \gamma}}{r^8} + \frac{\delta_{\alpha \beta}}{r^6} \right) f_0(x) f_0^*(x). \quad (C.32)$$

Observe the similarity of the interacting and noninteracting system tensors. An important difference, however, is the term with the delta function in the expression for $t_{s, \alpha \beta}(r; [\gamma_s])$ which is absent in $t_{s, \alpha \beta}(r; [\gamma_s])$. This term contributes to the kinetic-energy-density $t(r) = \sum_{\alpha} t_{\alpha \alpha}(r)$, and thus to the difference in kinetic energy of the two systems. Asymptotically, the difference $[t_s(r) - t(r)]$ is precisely $(-3 \chi/r^6) \sum_{\alpha} f_0(x) f_0^*(x)$.

Now the $\alpha$th component of the Correlation-Kinetic field $Z_{t_s}(r)$ is

$$\rho(r) Z_{t_s, \alpha}(r) = 2 \sum_{\beta=1}^3 \frac{\partial}{\partial r_{\beta \gamma}} \left[ t_{s, \alpha \beta}(r; [\gamma_s]) - t_{\alpha \beta}(r; [\gamma]) \right], \quad (C.33)$$

which on substituting for $f_0(x)$ from (C.23) becomes

$$8 \kappa_0 \chi \sum_{\beta=1}^3 |f_0(x)|^2 \frac{r_{\alpha \beta}}{r^8} \cdot \frac{r_{\beta \gamma}}{r}. \quad (C.34)$$

Since, asymptotically, $\rho(r) \sim \sum_{\alpha} |f_0(x)|^2$, we obtain the asymptotic structure of the field $Z_{t_s}(r)$ as

$$Z_{t_s}(r) \sim 8 \kappa_0 \chi \frac{r}{r^7}, \quad (C.35)$$

and the work done in this field as

$$W_{t_s}(r) = -\int_{r^\prime}^r Z_{t_s}(r^\prime) \, dr^\prime \quad (C.36)$$

$$= -8 \kappa_0 \chi \int_{r^\prime}^r \frac{1}{r^6} \, dr^\prime = \frac{8 \kappa_0 \chi}{2r^5}. \quad (C.37)$$

Thus, the Correlation-Kinetic potential energy decays as $0(1/r^5)$. 
Appendix D  
The Pauli Field $\mathcal{E}_x(r)$ and Potential Energy $W_x(r)$ in the Central Field Approximation

In this appendix, we derive [1] the expression for the Pauli field $\mathcal{E}_x(r)$ and potential energy $W_x(r)$ for open-shell atoms in the Central Field Approximation.

The Pauli field $\mathcal{E}_x(r)$ due to the Fermi hole charge $\rho_\chi(r'')$ is defined as (see 3.32)

$$\mathcal{E}_x(r) = -\int \rho_\chi(r') \nabla_{\mathbf{r}} \frac{1}{|r - r'|} dr'.$$

(D.1)

where (3.21)

$$\rho_\chi(r') = -\frac{|\gamma_\chi(r')|^2}{2 \rho(r)},$$

(D.2)

with $\gamma_\chi(r')$ the Dirac density matrix (3.12), and $\rho(r) = \gamma_\chi(r)$ the density. Employing the identity $i_{\mathbf{r}} \cdot \nabla_{\mathbf{r}} = \partial / \partial r$, the radial component of the Pauli field is

$$\mathcal{E}_{x,r}(r) = i_{\mathbf{r}} \cdot \mathcal{E}_x(r)$$

(D.3)

$$= -\int \rho_\chi(r') \frac{\partial}{\partial r'} \frac{1}{|r - r'|} dr'.$$

(D.4)

The spherical average of this radial component is then

$$\mathcal{E}_{x,r}(r) = -\frac{1}{4\pi} \int \rho_\chi(r') \frac{\partial}{\partial r'} \frac{1}{|r - r'|} dr' d\Omega,$$

(D.5)

which is spherically symmetric. For closed shell atoms, this is automatically the case. In the central field model of atoms, the single particle orbitals may be written as

$$\phi_{nlm}(r) = R_{nl}(r) Y_{lm}(\theta \phi),$$

(D.6)

where $R_{nl}(r)$ is the radial part of the orbital and $Y_{lm}(\theta \phi)$, the angular part, is the spherical harmonic of order $(lm)$.  


The Fermi hole \( \rho_\alpha(r') \) of (D.2) is then
\[
\rho_\alpha(r') = -\frac{2}{\rho(r)} \sum_{n/l,m} \sum_{n'/l',m'} R_{nl}(r)R_{nl}(r')R_{n'l'}(r') \times Y_{l'm'}^*(\Omega)Y_{l'm'}(\Omega)Y_{l'm'}(\Omega'), \quad (D.7)
\]
and the density \( \rho(r) \) is
\[
\rho(r) = \frac{1}{2\pi} \sum_{nl} (2l + 1) R_{nl}^2(r). \quad (D.8)
\]
Employing the expansion
\[
\frac{1}{|r - r'|} = 4\pi \sum_{l''m''} \frac{1}{2l'' + 1} Y_{l''m''}^*(\Omega)Y_{l''m''}(\Omega') \frac{r''}{r'' + 1} \quad (D.9)
\]
where \( r_<(r_>) \) is the smaller (larger) of \( |r| \) and \( |r'| \), the expression for the electric field becomes
\[
E_{x,r}(r) = \frac{2}{\rho(r)} \int \sum_{n/l,m} \sum_{n'/l',m'} \frac{1}{2l'' + 1} R_{nl}(r)R_{nl}(r')R_{n'l'}(r') \times \left[ \frac{\partial}{\partial r} \frac{r''}{r'' + 1} \right] r'' dr' \times \int Y_{l'm'}^*(\Omega)Y_{l'm'}(\Omega)Y_{l'm'}(\Omega') d\Omega \times \int Y_{l'm'}(\Omega')Y_{l'm'}(\Omega')Y_{l'm'}(\Omega') d\Omega'. \quad (D.10)
\]
Using the orthonormality condition of the spherical harmonics, which is [2]
\[
\int Y_{l'm'}(\Omega)Y_{lm}(\Omega) d\Omega = \delta_{ll'}\delta_{mm'}, \quad (D.11)
\]
and the coupling rule for the spherical harmonics, which is [2]
\[
Y_{l_1m_1}(\Omega)Y_{l_2m_2}(\Omega) = \sum_l \left[ \frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l + 1)} \right]^{1/2} \times C(l_1l_2; m_1m_2)C(l_1l_2; 000)Y_{l_1+m_1}(\Omega). \quad (D.12)
\]
where \( C \) are the Clebsch–Gordan [2] coefficients, the integrals over the solid angles in (D.10) which are complex conjugates of each other are
Substituting for these integrals, the expression for the spherically averaged field becomes
\[
\mathcal{E}_{x,r}(r) = \frac{1}{2\pi r} \int \sum_{\ell,m} R_{\ell m}(r) R_{\ell m}(r') R_{\ell m}(r') \frac{\partial}{\partial r'} \left[ \frac{r''}{r_{<}^{\ell+1}} \right] r'^2 dr' \\
\times \frac{(2l + 1)}{(2l' + 1)} C^2(l'';m',m'-m,m') C^2(l';l',000). \tag{D.14}
\]

For closed-subshell atoms, an occupancy of \(\ell\) is assumed in the above expression for the electric field. For open-subshell atoms, a partial occupancy of \(N_{\ell}/(2\ell + 1)\), where \(N_{\ell}\) is the number of electrons in the subshell, should be used.

Since the field \(\mathcal{E}_{x,r}(r)\) is spherically symmetric, its curl vanishes. Hence, the work done \(W_x(r)\) in this field is path-independent, spherically symmetric, and given by the integral
\[
W_x(r) = -\int_{\infty}^{r} \mathcal{E}_{x,r}(r') dr'. \tag{D.15}
\]

With the expressions for the density \(\rho(r)\) of (D.8) and the spherically averaged field \(\mathcal{E}_{x,r}(r)\) of (D.14), the Pauli energy \(E_x\) may then be obtained from (3.47).
Appendix E
Equations of the Irrotational Component Approximation as Applied to the Carbon Atom

In this appendix the analytical and integral expressions of the Irrotational Component Approximation as applied to the Carbon atom in its 1s\(^2\)2s\(^2\)2p\(^z\) degenerate state are given [1]. The orbitals employed are Hydrogenic as given by (12.6). To simplify the expressions we define

\[ \frac{q}{\text{DC}^2}; \quad \frac{q_0}{\text{DC}^2}; \quad \frac{z}{\text{DC}^2}; \quad \frac{z_0}{\text{DC}^2}; \quad \frac{p}{\text{DC}^2}; \quad \frac{p_0}{\text{DC}^2}. \]

The functions \( f_1(\text{rr}'); \ f_2(\text{qq}') \) up to \( f_5(\text{qq}') \) are defined as

\[ f_1(\text{rr}') = e^{-3r'}p - e^{-3r}p' \]  
\[ f_2(\text{qq}') = e^{-3r'}z' - e^{-3r}z \]  
\[ f_3(\text{qq}') = z'p - zp' \]  
\[ f_4(\text{qq}') = z - z' + 3z \left[ i_r \cdot (\text{rr}') \right] \]  
\[ f_5(\text{qq}') = z - z' + 3r \sin \theta \left[ i_{\theta} \cdot (\text{rr}') \right]. \]

The various vector dot products employed in the expressions are

\[ i_r \cdot (\text{rr}') = r - r' \left[ \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi') \right] \]  
\[ i_{\theta} \cdot (\text{rr}') = -r' \left[ -\sin \theta \cos \theta' + \cos \theta \sin \theta' \cos(\phi - \phi') \right] \]  
\[ i_{\phi} \cdot (\text{rr}') = -r' \sin \theta' \sin(\phi' - \phi) \]  
\[ i_{\theta} \cdot i_{\phi'} = \cos \theta \sin(\phi - \phi') \]  
\[ i_{\phi} \cdot i_{\phi'} = \cos(\phi - \phi') \]  
\[ i_r \cdot i_{\phi'} = \sin \theta \sin(\phi - \phi'). \]

E.1 Electron Density \( \rho(r) \)

The electronic density

\[ \rho(r) = 2 \sum_{i=1}^{3} |\phi_i(r)|^2 \]
has azimuthal symmetry so that
\[ \rho(r) = \rho(q) = \frac{432}{\pi} e^{-6\rho} A(q) \] (E.13)
where
\[ A(q) = e^{-6\rho} + \frac{1}{8} (p^2 + 9\zeta^2). \] (E.14)

**E.2 Fermi Hole \( \rho_x(rr') \)**

The Fermi hole (without the negative sign)
\[ \rho_x(rr') = |\gamma_x(rr')|^2 / 2 \rho(r) \] (E.15)
with
\[ \gamma_x(rr') = 2 \sum_{i=1}^{3} \phi_i^*(r)\phi_i(r') \] (E.16)
is independent of the azimuthal angles \( \phi \) and \( \phi' \) so that
\[ \rho_x(qq') = \frac{216}{\pi} e^{-6\rho'} B^2(qq') \frac{A(q)}{A(q)} \] (E.17)
where
\[ B(qq') = e^{-3(r+r')} + \frac{1}{8} (pp' + 9zz'). \] (E.18)

**E.3 Gradient of Fermi Hole \( \nabla \rho_x(rr') \)**

\[ \nabla \rho_x(qq') = i_r \frac{\partial \rho_x}{\partial r} + i_\phi \frac{1}{r} \frac{\partial \rho_x}{\partial \theta} \] (E.19)
where
\[ \frac{\partial \rho_x}{\partial r} = \frac{486 B}{\pi A^2} e^{-6\rho} \left[ \rho e^{-3\rho} f_1 + e^{-3\rho} (1 + 3\rho) f_2 \cos \theta + \frac{1}{8} f_3 \cos \theta \right] \] (E.20)
\[ \frac{1}{r} \frac{\partial \rho_x}{\partial \theta} = -\frac{486 B}{\pi A^2} e^{-6\rho} \left[ e^{-3\rho} f_2 \sin \theta + \frac{1}{8} p f_3 \sin \theta \right]. \] (E.21)
E.4 Pauli Field $\mathcal{E}_x(r)$

The Pauli field $\mathcal{E}_x(r)$ due to the Fermi hole $\rho_x(qq')$ of (E.17):

$$\mathcal{E}_x(r) = \frac{\rho_x(rr')}{|r - r'|^3} (r - r') dr'$$  \hspace{1cm} (E.22)

has azimuthal symmetry and does not have an azimuthal component. Thus

$$\mathcal{E}_x(q) = i_r \mathcal{E}_{x,r}(q) + i_\theta \mathcal{E}_{x,\theta}(q)$$  \hspace{1cm} (E.23)

where

$$\mathcal{E}_{x,r}(q) = \int \rho_x(qq') \frac{i_r \cdot (r - r')}{|r - r'|^3} dr'$$ \hspace{1cm} (E.24)

$$\mathcal{E}_{x,\theta}(q) = \int \rho_x(qq') \frac{i_\theta \cdot (r - r')}{|r - r'|^3} dr'.$$ \hspace{1cm} (E.25)

E.5 Scalar Effective Fermi Hole $\rho^\text{eff}_x(r)$

$$\rho^\text{eff}_x(r) = \frac{\rho(r)}{2} + \frac{1}{4\pi} \int \nabla \rho_x(rr') \cdot \frac{(r - r')}{|r - r'|^3} dr'$$ \hspace{1cm} (E.26)

$$\rho^\text{eff}_x(q) = \frac{\rho(q)}{2} + \frac{243}{2\pi^2 A^2} \int \frac{B e^{-6r'}}{|r - r'|^3} \left[ \left[ i_r \cdot (r - r') \right] r e^{-3r} f_1 + e^{-3r} f_2 f_4 + \frac{1}{8} f_3 f_5 \right] dr'.$$ \hspace{1cm} (E.27)

E.6 Vector Vortex Fermi Hole $\mathcal{J}_x(r)$

The curl of the Pauli field $\mathcal{E}_x(r)$ of (E.23) also has azimuthal symmetry but only an azimuthal component:

$$\nabla \times \mathcal{E}_x(r) = i_\phi \left[ \nabla \times \mathcal{E}_x(q) \right]_\phi$$ \hspace{1cm} (E.28)

where

$$\left[ \nabla \times \mathcal{E}_x(q) \right]_\phi = i_\phi \int \frac{\nabla \rho_x(qq') \times (r - r')}{|r - r'|^3} dr'.$$ \hspace{1cm} (E.29)
The vector vortex Fermi hole

\[ \mathbf{J}_x(r) = \frac{1}{4\pi} \nabla \times \mathbf{E}_x(r) \]  

(E.31)

is then

\[ \mathbf{J}_x(q) = i_\phi \mathcal{J}_{x,\phi}(q). \]  

(E.32)

### E.7 Irrotational Component \( \mathbf{E}^I_x(r) \) of the Pauli Field \( \mathbf{E}_x(r) \)

As with the Pauli field \( \mathbf{E}_x(r) \), its irrotational component

\[ \mathbf{E}^I_x(r) = \int \rho^\text{eff}_x(r') \frac{(r - r')}{|r - r'|^3} \, dr' \]  

(E.33)

has azimuthal symmetry, and only radial and theta components:

\[ \mathbf{E}^I_x(q) = i_r \mathbf{E}^I_{x,r}(q) + i_\theta \mathbf{E}^I_{x,\theta}(q) \]  

(E.34)

where

\[ \mathbf{E}^I_{x,r}(q) = \int \rho^\text{eff}_x(q') \frac{i_r \cdot (r - r')}{|r - r'|^3} \, dr' \]  

(E.35)

\[ \mathbf{E}^I_{x,\theta}(q) = \int \rho^\text{eff}_x(q') \frac{i_\theta \cdot (r - r')}{|r - r'|^3} \, dr'. \]  

(E.36)

### E.8 Solenoidal Component \( \mathbf{E}^S_x(r) \) of the Pauli Field \( \mathbf{E}_x(r) \)

The solenoidal component \( \mathbf{E}^S_x(r) \) of the Pauli Field \( \mathbf{E}_x(r) \) which is

\[ \mathbf{E}^S_x(r) = \int \mathcal{J}_x(r') \times \frac{(r - r')}{|r - r'|^3} \, dr' \]  

(E.37)

also has azimuthal symmetry and only radial and theta components:

\[ \mathbf{E}^S_x(q) = i_r \mathbf{E}^S_{x,r}(q) + i_\theta \mathbf{E}^S_{x,\theta}(q) \]  

(E.38)

where

\[ \mathbf{E}^S_{x,r}(q) = i_r \cdot \mathbf{E}^S_x(q) \]  

(E.39)
E.9 The Potential Energy $W^1_x(r)$

The (path-independent) potential energy

$$W^1_x(r) = \int \frac{\rho(q') \, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}$$

is

$$W^2_x(q) = \frac{1}{2} \int \frac{\rho(q')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + \frac{243}{2\pi^2} \int \frac{B(q'q'') e^{-6\mathbf{r}''}}{A^2(q') |\mathbf{r} - \mathbf{r}'| |\mathbf{r}' - \mathbf{r}''|^3} \times \left\{ \left[ i \cdot \cdot (\mathbf{r} - \mathbf{r}'') \right] r' e^{-3\mathbf{r}''} f_1(r' r'') 
+ e^{-3\mathbf{r}''} f_2(q' q'') f_4(q' q'') 
+ \frac{1}{8} f_5(q' q'') f_5(q' q'') \right\} \, d\mathbf{r}' \, d\mathbf{r}''.$$  

(E.44)

The six-dimensional integrals for the irrotational $E^1_x(r)$ and solenoidal $E^2_x(r)$ components of the field $E_x(r)$, and that for the potential energy $W^1_x(r)$ are performed by the Monte Carlo method [2].
Appendix F
Ground State Properties of the Helium Atom as Determined by the Kinoshita Wave Function

The Kinoshita [1] wave function for the ground state of the Helium atom, and various properties determined [2] from it are given in this appendix.

F.1 Wave Function $\psi (r_1 r_2)$

The Kinoshita wave function for the ground state of the Helium atom is

$$\psi (r_1 r_2) = \psi (stu) = c_N e^{-1.860556s} \sum_{i=-1}^{6} u^{(i)} T_i,$$  \hspace{1cm} (F.1)

where the Hylleraas [3, 4] coordinates are $s = r_1 + r_2$, $t = r_2 - r_1$, $u = |r_2 - r_1|$, and the normalization constant $c_N = 1.364931021$. The superscript $(i)$ represents the power of $u$ in each term of the summation, and the terms $T_i$ are

\begin{align*}
T_{-1} & = 0.001292r^2 + 0.002071t^2s, \\
T_0 & = 1 - 0.087026s + 0.030099t^2/s + 0.057891s^2 + 0.226660r^2 \\
& - 0.011656s^3 - 0.022154tr^2 + 0.001025s^4 + 0.005852s^2t^2 \\
& + 0.005555r^4 - 0.000200s^3t^2, \\
T_1 & = 0.467736 + 0.008079s - 0.155282r^2/s + 0.002128s^2 \\
& + 0.005221r^2 + 0.000252s^3, \\
T_2 & = -0.049206/s - 0.160571 + 0.039716r^2/s^3 + 0.028827s \\
& + 0.003594r^2/s - 0.002328s^2 + 0.003172r^2, \\
T_3 & = 0.076577/s + 0.014535 - 0.000112s - 0.001060r^2, \\
T_4 & = 0.013293/s^2 - 0.012758/s - 0.007997 - 0.000137s \\
& + 0.000105r^2, \\
T_5 & = 0.005655/s + 0.001326, \\
T_6 & = -0.000939/s - 0.000002.
\end{align*}
F.2 Electron Density $\rho(r)$

The electronic density is $\rho(r) = 2 \int \psi^2(r) \mathcal{L}_2 \, dr_2$. By performing the angular integration over $d\Omega_{r_2}$ analytically we obtain

$$\rho(r) = 4\pi c^2_N \int e^{-\frac{2}{\hbar} (1.86055663)} \left[ \sum_{k=-2}^{12} y_k(r) w_k(r) \right] r_2^2 \, dr_2,$$

where

$$y_{-2} = (lnb - lna)/(2rr_2),$$

$$y_{-1} = (\sqrt{b} - \sqrt{a})/(rr_2),$$

$$y_0 = 2,$$

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

$$y_k = \left[ \frac{b^{(k+2)/2} - a^{(k+2)/2}}{rr_2(k + 2)} \right]$$

$$a = r^2 + r_2^2 - 2rr_2,$$

$$b = r^2 + r_2^2 + 2rr_2,$$

and the terms $w_k$ are

$$w_{-2} = T_{1}^2,$$

$$w_{-1} = 2T_0T_{-1},$$

$$w_0 = T_0^2 + 2T_{-1}T_1,$$

$$w_1 = 2T_0T_1 + 2T_{-1}T_2,$$

$$w_2 = T_1^2 - 2T_0T_2 + 2T_{-1}T_3,$$

$$w_3 = 2T_0T_3 + 2T_{-1}T_4 + 2T_1T_2,$$

$$w_4 = T_2^2 + 2T_0T_4 + 2T_{-1}T_5 + 2T_1T_3,$$

$$w_5 = 2T_0T_5 + 2T_{-1}T_6 + 2T_1T_4 + 2T_2T_3,$$

$$w_6 = T_3^2 + 2T_1T_5 + 2T_2T_4 + 2T_0T_6,$$

$$w_7 = 2T_1T_6 + 2T_2T_5 + 2T_3T_4,$$

$$w_8 = 2T_2T_6 + 2T_3T_5 + T_4^2,$$

$$w_9 = 2T_3T_6 + 2T_4T_5,$$

$$w_{10} = T_5^2 + 2T_4T_6,$$

$$w_{11} = 2T_5T_6,$$

$$w_{12} = T_6^2.$$
The expression for $s$, $t$, and $u$ in $T_i$ above are the same as those given in Sect. F.1, but with $r_1$ replaced by $r$.

### F.3 Coulomb Hole $\rho_c(\mathbf{r}'')$

The Coulomb hole $\rho_c(\mathbf{r}'')$ is determined by (3.28), where the Fermi-Coulomb hole $\rho_{xc}(\mathbf{r}'') = [2|\psi(\mathbf{r}'')|^2/\rho(\mathbf{r})] - \rho(\mathbf{r})$, and the Fermi hole is $\rho_f(\mathbf{r}'') = -\rho(\mathbf{r}'')/2$ as discussed in Sect. 3.2.3. The expressions for $\psi(\mathbf{r}'')$ and $\rho(\mathbf{r})$ are given in Sects. F.1 and F.2, respectively.

### F.4 Coulomb Field $\mathcal{E}_c(\mathbf{r})$

The Coulomb force field $\mathcal{E}_c(\mathbf{r})$ due to the Coulomb hole is defined by (3.33). By performing the angular integration over $d\Omega_{r''}$ analytically, we obtain

\[
\mathcal{E}_c(\mathbf{r}) = \frac{i}{\mathbf{r}} \mathcal{E}_c(\mathbf{r}) = i \left[ \frac{4\pi e^2}{\rho(\mathbf{r})} \int e^{-2(1.8605\text{e6})r} \left( \sum_{k=-2}^{12} z_k (\mathbf{r}'') w_k(\mathbf{r}'') \right) (r'')^2 d\mathbf{r}' ight] - \frac{2\pi}{r^2} \int_0^r d\mathbf{r}' (r'')^2 \rho(\mathbf{r}''),
\]

where

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

\[
z_{-1} = \left[ h \left( 1 - a^{-1} \right) + d (\ln b - \ln a) \right] / (2rr'),
\]

\[
z_0 = \left[ h \left( 1 - a^{-1} \right) - 1/b^{-1} \right] + d \left( \sqrt{b} - \sqrt{a} \right) / (r''),
\]

\[
z_1 = [h (\ln a - \ln b) + d (a - b)] / (2rr'),
\]

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

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

where $h = \frac{r^2}{2} - (r'')^2$, and $d = \frac{1}{2\pi}$. The expressions for $s, a, b$ and $w_k$ are the same as those given previously, but with $r_2$ replaced by $r'$. 
F.5 Coulomb Potential Energy $W_c(r)$

The Coulomb potential energy $W_c(r)$ is then obtained from (3.75) as

$$W_c(r) = -\int_{\infty}^{r} \mathcal{E}_c(r')dr'.$$  \hspace{1cm} (F.38)
Appendix G
Approximate Wave Function for the Hydrogen Molecule

The value of the parameter $\delta$ and the coefficients $C_{mn\ell\pi}$ of the Kolos–Roothaan [1] wave function of (16.4) for the ground state of the hydrogen molecule are listed in Table G.1.

<table>
<thead>
<tr>
<th>No. of terms</th>
<th>$\delta = 0.995$</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi_1$ $\eta_1$ $\xi_2$ $\eta_2$ $r_{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 0</td>
<td>2.065908</td>
<td></td>
</tr>
<tr>
<td>0 0 0 2 0</td>
<td>1.282032</td>
<td></td>
</tr>
<tr>
<td>0 0 1 0 0</td>
<td>0.144619</td>
<td></td>
</tr>
<tr>
<td>0 1 0 1 0</td>
<td>-0.430253</td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 1</td>
<td>0.787198</td>
<td></td>
</tr>
<tr>
<td>1 1 0 1 0</td>
<td>-0.235454</td>
<td></td>
</tr>
<tr>
<td>1 0 0 2 0</td>
<td>0.148273</td>
<td></td>
</tr>
<tr>
<td>0 0 2 0 0</td>
<td>0.109859</td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 2</td>
<td>-0.212159</td>
<td></td>
</tr>
<tr>
<td>1 0 1 0 0</td>
<td>-0.081387</td>
<td></td>
</tr>
<tr>
<td>0 2 0 2 0</td>
<td>0.182892</td>
<td></td>
</tr>
<tr>
<td>0 0 0 2 1</td>
<td>0.198555</td>
<td></td>
</tr>
<tr>
<td>0 0 1 0 1</td>
<td>0.324658</td>
<td></td>
</tr>
<tr>
<td>1 1 1 1 0</td>
<td>-0.010794</td>
<td></td>
</tr>
<tr>
<td>0 0 1 0 2</td>
<td>0.077830</td>
<td></td>
</tr>
<tr>
<td>1 0 2 0 0</td>
<td>-0.055114</td>
<td></td>
</tr>
<tr>
<td>0 1 0 1 1</td>
<td>0.130714</td>
<td></td>
</tr>
<tr>
<td>0 1 0 1 2</td>
<td>-0.050854</td>
<td></td>
</tr>
<tr>
<td>1 0 2 0 1</td>
<td>0.014963</td>
<td></td>
</tr>
<tr>
<td>0 0 2 0 1</td>
<td>-0.132980</td>
<td></td>
</tr>
<tr>
<td>1 1 1 1 2</td>
<td>0.000362</td>
<td></td>
</tr>
<tr>
<td>0 0 2 0 2</td>
<td>0.006992</td>
<td></td>
</tr>
<tr>
<td>1 0 0 2 1</td>
<td>-0.050940</td>
<td></td>
</tr>
</tbody>
</table>

(continued)
Table G.1  continued

<table>
<thead>
<tr>
<th>No. of terms</th>
<th>50</th>
<th>$\delta = 0.995$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi_1$</td>
<td>$\eta_1$</td>
<td>$\xi_2$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>
Chapter 1

30. V. Fock, Z. Phys. 61, 126 (1930) R 1–2.
34. C. Møller, M.S. Plesset, Phys. Rev. 46, 618 (1934).
Chapter 2

2. E. Schrödinger, Ann Physik 79, 361, 489 (1925); 80, 437 (1926); 81, 109 (1926).

Chapter 3

References

15. Z. Qian, V. Sahni, Int. J. Quantum Chem. 78, 341 (2000)
17. V. Sahni in Electron Correlations and Materials Properties 2, ed. by A. Gonis et al. (Kluwer/Plenum, New York, 2003)
19. V. Fock, Z. Phys. 61, 126 (1930)

Chapter 4

15. Recent Advances in Density Functional Methods, Part II, ed. by D.P. Chong (World Scientific, Singapore, 1997)


25. V. Fock, Z. Phys. 61, 126 (1930)


46. V. Sahni in Recent Advances in Density Functional Methods, Part I, ed. by D.P. Chong (World Scientific, 1995).


49. Quantum Mechanics, H.A. Kramers (North-Holland, Amsterdam, 1957)

Chapter 5


<table>
<thead>
<tr>
<th>References</th>
<th>413</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Chapter 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. D.R. Hartree, Proc. Cambridge Philos. Soc. 24, 39 (1928); 24, 111 (1928); 24, 426 (1928)</td>
</tr>
<tr>
<td>6. V. Fock, Z. Phys. 61, 126 (1930)</td>
</tr>
<tr>
<td>7. J.C. Slater, Phys. Rev. 35, 210 (1930)</td>
</tr>
<tr>
<td>28. J.C. Slater, Phys. Rev. 81, 385 (1951)</td>
</tr>
<tr>
<td>34. A. Solomatin, V. Sahni, Int. J. Quantum Chem. 65, 893 (1997)</td>
</tr>
<tr>
<td>38. X.-Y. Pan, V. Sahni, L. Massa, Phil. Mag. 86, 2673 (2006)</td>
</tr>
</tbody>
</table>

Chapter 7

2. Z. Qian, V. Sahni, Int. J. Quantum Chem. 70, 671 (1998)

Chapter 8


Chapter 9

2. D.R. Hartree, Proc. Cambridge Philos. Soc. 24, 39 (1928); 24, 111 (1928); 24, 426 (1928)
5. V. Sahni, K.D. Sen, M. Slamet (unpublished)
19. T. Koopmans, Physica 1, 104 (1933)

**Chapter 10**

9. T. Koopmans, Physica 1, 104 (1933)
15. L. Brillouin, Art. Sci. Ind. No. 71 (1933); No. 159 (1934); No. 160 (1934)
16. C. Møller, M.S. Plesset, Phys. Rev. 46, 618 (1934)

**Chapter 11**

References

10. V. Fock, Z. Phys. 61, 126 (1930)

Chapter 12


Chapter 13

29. R. Singh (private communication)
36. T. Koopmans, Physica 1, 104 (1933)
37. J.C. Slater, Quantum Theory of Atomic Structure, Vol. 1 (McGraw-Hill, New York, 1960); sect. 5.4
47. Y.K. Ho, J. Phys. B 12, L543 (1979a)

Chapter 14

1. X.-Y. Pan and V. Sahni (unpublished)

Chapter 15

5. X.-Y. Pan, V. Sahni, L. Massa, e-print physics/0310128

Chapter 16


Chapter 17

2. J. Friedel, Phil. Mag. 7, 43 (1952); Nuovo Cimento 7, 287 (1958) (supplement)
3. V. Sahni, C.Q. Ma, Phys. Rev. B 22, 5987 (1980). (The product $\psi_1^*(x')\psi_1(x)\psi_1(x)$ is missing from (13))
17. H.J. Juretschke, Phys. Rev. 92, 1140 (1953)
30. E.G. McRae, Rev. Mod. Phys. 51, 541 (1979)
45. C.Q. Ma, V. Sahni, Phys. Rev. B 16, 4249 (1977)
52. L. Kleinman, V. Sahni, Adv. Quantum Chem. 21, 201 (1990)
References


Chapter 18

1. Z. Qian, V. Sahni (unpublished)
2. L. Massa, V. Sahni, X.-Y. Pan (unpublished)
3. C. Møller, M. S. Plesset, Phys. Rev. 46, 618 (1934) (As an aside we note that in their paper, Møller and Plesset also proved that the density and consequently the expectation of all other single-particle operators as determined within Hartree-Fock theory are correct to second-order.)
4. L. Brillouin, Actualités sci. et ind vol. 71 (1933); vol. 159 (1934); vol. 160 (1934)
5. S. Raimes, Many-Electron Theory (North-Holland, Amsterdam, 1972)

Appendix A

7. W. Kohn, in Highlights of Condensed Matter Theory, ed. by F. Bassani et al. (North-Holland, Amsterdam, 1985)
Appendix B

3. H.A. Kramers, Quantum Mechanics, North-Holland, Amsterdam (1957)

Appendix C


Appendix D


Appendix E


Appendix F

2. M. Slamet, V. Sahni (unpublished)
3. E.A. Hylleraas, Z. Phys. 48, 469 (1928)
4. X.-Y. Pan, V. Sahni, L. Massa, e-print physics/0310128

Appendix G

Index

Airy functions, 311
Airy Gas Model, 313
anion, 263
anion–positron complex, 263
Asymptotic structure at and near nucleus
kinetic “force” of S system, 164
Correlation-Kinetic field, 164
kinetic energy density of S system, 163
Kohn-Sham “exchange-correlation” potential, 165
of electron-interaction field, 159
of electron-interaction potential, 142
of kinetic “force”, 162
of kinetic energy density, 162
of the density, 157, 158
of the density matrix, 161
of wave function, 154, 156, 160
Asymptotic structure in the classically
forbidden region at metal–vacuum
interface
Coulomb and higher-order Correlation-
Kinetic potential, 344, 350
effective potential, 351
Kohn–Sham “correlation” potential, 344, 350
Kohn–Sham “exchange” potential, 340
Kohn–Sham “exchange-correlation” potential, 345
lowest-order Correlation-Kinetic potential, 339, 343
of density, 348
of Dirac density matrix, 348
of orbitals, 347
Pauli potential, 335
Slater function, 339
Asymptotic structure in the classically
forbidden region of atoms
of Correlation-Kinetic field, 138
of Correlation-Kinetic potential, 126, 387
of Coulomb potential, 126, 136
of density, 50
of density matrix, 131
of electron-interaction field, 134
of electron-interaction potential, 126
of Hartree field, 135
of Hartree potential, 126
of Pauli field, 135
of Pauli potential, 126, 136
of S system density, 49
of wave function, 130
pair-correlation density, 132
Atomic shell structure, 168, 196
Aufbau principle, 11, 168, 184, 188, 203, 207
Auger effect, 259
Autoionizing, 258
B system, 221
Correlation-Kinetic energy, 224
density matrix, 224
differential equation, 145, 222
effective field, 223
effective potential, 223
electron-interaction potential, 145, 224
kinetic “force”, 223
kinetic energy, 224
Bardeen-Friedel oscillations, 303, 314, 334
Bethe-Salpeter equation, 356, 360
bidensity energy functional, 250, 380
Born–Oppenheimer, 16
Brillouin’s theorem, 209, 355, 369
Central Field Approximation, 120, 393
chemical potential, 59
Clebsch–Gordan coefficients, 394
coalesscence constraints, 29
differential form, 31
integral form, 31
core charge, 177, 197
core radius, 177, 197
core–valence separations, 196
Correlated wave function
Drake (He), 277
Kinoshita, 276
Kinoshita (He), 403
Kolos–Roothaan (H$_2$), 290, 407
Komasa and Thakkar (H$_2$), 146
Pekeris (He), 277
Coulomb hole, 40, 277, 294
Coulomb species, 55
Coulson, 178
cusp coalescence condition, 31
density amplitude, 221
Dirac density matrix, 38
for uniform electron gas, 317
dynamic charge distribution, 21
Dyson equation, 345, 358
effective Fermi hole charge, 236
effective Fermi–Coulomb hole charge, 122
electron density, 18, 37
Energy
Correlation-Kinetic, 45
Coulomb, 44
electron-interaction, 16, 24
electrostatic, 308
external, 16, 45
external potential, 25
Hartree, 24
kinetic, 16, 25
Pauli, 44
Pauli–Coulomb, 24
ensemble density energy functional, 381
Euler’s theorem, 26
Euler–Lagrange equation, 59
Fermi hole, 39, 193
for uniform electron gas, 317
parallel to surface, 325
planar averaged, 317, 321
Fermi–Coulomb hole, 294
Fermi–Coulomb hole charge, 21
Field
Correlation-Kinetic, 43
Coulomb, 42
differential density, 23, 42
effective, 37, 41, 47
electron-interaction, 22, 192
external, 15
Hartree, 22, 192
internal, 17, 36
irrotational component, 121
kinetic, 23, 42
nonconservative, 119
Pauli, 41, 192
Pauli–Coulomb, 22
self-interaction correction, 104, 172
solenoidal component, 121
Finite Linear Potential model, 311
“Force”
differential density, 23
electron-interaction, 22
kinetic, 23
Fourier transform, 357
gauge invariance, 71
gauge transformation, 69, 385
gauge variance, 71
Green’s function, 345, 356
for interacting system, 345
for S system, 345
single-particle, 357
two-particle, 359
Hartree–Fock theory, 64, 108
Heisenberg picture, 357
Helmholtz’s theorem, 122
hierarchy within the fundamental theorem of
density functional theory, 386
Hohenberg–Kohn theorem
corollary, 57
generalization, 67
Hohenberg–Kohn theorems, 53
Hooke’s atom, 56, 76, 380
Hooke’s molecule, 56
Hooke’s species, 56
Hylleraas coordinates, 276, 403
idempotency, 38
image-potential-bound surface states, 353
integral virial theorem, 26
ionization potential, 50
Irrotational Component Approximation, 121,
235, 397
irrotational component of Pauli field, 242
jellium model, 303
kinetic-energy-density, 25, 45
kinetic-energy-density tensor, 23, 43
Kohn–Sham density functional theory, 59
“exchange” potential, 339
“correlation” energy functional, 63
“correlation” potential, 63
“exchange” energy functional, 62
“exchange” potential, 63
“exchange-correlation” energy functional, 62
“exchange-correlation” potential, 62
integral virial theorems, 63
electron interaction energy functional, 61
electron interaction potential, 61
Hartree energy functional, 62
Hartree potential, 62

Linear Potential model, 312
local charge distribution, 18
local density approximation, 315
local effective potential energy theory, 35

Madelung’s law, 168, 207
Metal surface models
Finite-Lineal Potential, 304, 311
Infinite Barrier Potential, 313
Linear Potential, 304, 312
Step Potential, 313
metal-vacuum interface, 303
mononegative ions, 214
multiplet structure, 256

N-representability, 59
node coalescence condition, 31
non idempotency, 19
noninteracting v-representability, 60
nonlocal charge distribution, 21

Operator
annihilation, 357
creation, 357
density, 18
density matrix, 19
electron-interaction potential energy, 15
external potential energy, 15
kinetic, 15
momentum, 69, 384
pair-correlation, 20
translation, 19
unitary, 384
vector potential, 69, 384
optimized potential method, 367

orbit силоп-dependent “exchange” function, 340, 368
orbit силоп-dependent Fermi hole, 340, 368, 369

pair-correlation density, 20
pair-correlation function, 21, 40
Pauli in Nobel lecture, 178
Perturbation theory
Møller-Plesset, 355
many-body, 355
pair-correlation density, 361
plasmon-pole approximation, 348
Poisson’s equation, 307
Polarizability
dipole, 217
quadrupole, 217
positron, 263
positron affinity, 263, 268
positronium, 264
positronium affinity, 264, 272
Potential
effective, 35
electron-interaction, 37, 47, 194
electrostatic, 307
Hartree, 48, 194
Pauli, 194
self-interaction correction, 105

Quantal density functional theory, 35, 113
Fully Correlated Approximation, 117, 275, 289
Hartree Uncorrelated Approximation, 106, 167
many-body perturbation theory, 355
Multi-Component Pauli Approximation, 263
Multi-Component theory, 263
of Hartree theory, 103
of Hartree–Fock theory, 108
of the density amplitude, 221
Pauli Approximation, 110, 187
Pauli–Coulomb Approximation, 114
perturbation series for Correlation-Kinetic field, 364
perturbation series for the electron-interaction field, 360
Pseudo Møller-Plesset perturbation theory, 356, 367
Quantal density functional theory of degenerate states
of ensemble densities, 375, 378
of pure Slater densities, 375
“Quantal Newtonian” first law, 17
“Quantal Newtonian” second law, 17
quasi-particle amplitudes, 387

radial probability density, 175, 196, 252
radiationless transition, 259
Runge–Gross time-dependent density functional theory
generalization of fundamental theorem, 383

S system, 35
meaning of highest occupied eigenvalue, 49
nonuniqueness of effective potential, 74
nonuniqueness of wave function, 75, 85
Schrödinger theory, 15
self-energy, 345
self-interaction correction charge, 104, 168
Sham and Schlüter equation, 366
single-particle density matrix, 18
Slater, 178
Slater’s diagonal sum rule, 256
solenoidal component of Pauli field, 242
spherical harmonics, 394

static charge distribution, 18
Sum Rules
for Coulomb hole, 40
for Fermi hole, 39
force, 48
torque, 48
sum rules for Fermi–Coulomb hole, 21
surface dipole barrier, 309
surface energy, 304, 309
Theophilou-Budd-Vannimenus theorem, 310
two-particle density matrix, 359
unitary transformation, 67
v-representability, 59
vector potential, 123
vector vortex Fermi hole, 239
vector vortex source, 124
virial theorem, 26
Wigner–Seitz radius, 306
work function, 304, 309, 310