

State Energy Functionals and Variational Equations in Density Functional Theory

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March 15, 1999

1. Dedication and Introduction

Prof. Reszo Gáspár was among the pioneers, along with Dirac, Thomas, Fermi, and Slater, of the part of many-Fermion theory that has become known as Density Functional Theory since the work of Hohenberg, Kohn, and Sham. We are honored to have the opportunity to present a portion of our work on formal Density Functional Theory in a volume dedicated to recognizing Prof. Gaspar's contributions.

In two recent papers [1,2] we have presented significant portions of an effort to provide a comprehensive mathematical basis for Density Functional Theory. The aim is to be both formally sound and to provide a structural framework for the development of improved approximations. The earlier paper addressed the relationship between symmetry breaking in Kohn-Sham solutions and the essential structure of the KS orbitals that emerges from general classification by spin-rotation and time-reversal symmetries. The later paper summarized a reformulation of the constrained-search construction of time-independent Hohenberg-Kohn functionals and their variational properties and, on that groundwork, presented a new formulation of time-dependent DFT based on the time-dependent variational principle. New and/or improved results for several major aspects of the time-independent problem were stated there without proof. Here we address those issues. We pay particular attention to rigorous definition of the functionals (including careful distinctions among them that often seem to be ignored), rigorous conditions for the existence of well-defined functional derivatives, conditions under which a density is associated with a one body potential (V-representability), and formulation of various kinds of one-particle functional equations (including but not limited to Kohn-Sham equations).

2. Mathematical Preliminaries

This section summarizes mathematical structures that are pertinent to our analysis of various energy functionals that can be used in DFT. *Note to the reader: the notation, in spite of our best efforts, is at points quite intricate. It is summarized in Appendix A.*

2.1 Operators and States

The objective of DFT may be stated succinctly as the characterization of quantum states by densities. To make full use of the representation of quantum states by density operators, we will be focusing upon two specific subsets of the set of all Bounded Operators, $\mathcal{B}(\mathcal{H})$, acting in a Hilbert space \mathcal{H} . The two subsets are the set of Trace Class Operators, $\mathcal{B}_1(\mathcal{H})$, and the set of Hilbert-Schmidt Operators $\mathcal{B}_2(\mathcal{H})$.

The set of bounded operators is rich in mathematical relationships between its elements. In particular it is a normed linear space with norm, for each operator $Z \in \mathcal{B}(\mathcal{H})$, defined by

$$\|Z\| = \sup_{\psi} \frac{\langle \psi | Z \psi \rangle}{\langle \psi | \psi \rangle}; \quad \psi \in \mathcal{H} \quad (2.1)$$

Its elements can be multiplied, thus giving it an algebraic structure. This multiplication is a continuous operation with respect to the norm in Eq.(2.1), as is the adjoint operation, and together they have the property

$$\|Z^\dagger Z\| = \|Z\|^2 = \|Z^\dagger\|^2 \quad (2.2)$$

Algebras with this property are called C^* -algebras [3].

The subset of trace class operators

$$\mathcal{B}_1(\mathcal{H}) = \left\{ X; Tr\left\{ (X^\dagger X)^{\frac{1}{2}} \right\} < \infty, X \in \mathcal{B}(\mathcal{H}) \right\} \quad (2.3)$$

with its norm defined as

$$\|X\|_1 = Tr\left\{ (X^\dagger X)^{\frac{1}{2}} \right\} \quad (2.4)$$

is not a C^* -algebra, but only a normed $*$ -algebra as Eq. (2.2) is not satisfied for all of its elements. This algebra is especially significant as it contains the set of quantum states, both mixed (ensemble) and pure, associated with the Hilbert space \mathcal{H} . Positive normalized trace class operators, D , called density operators represent these states

$$\mathcal{S} = \left\{ D; D \geq 0, Tr(D) = 1 \right\} \quad (2.5)$$

The set of states \mathcal{S} is convex i.e. $\sum_i \alpha_i D_i \in \mathcal{S}$; when $\sum_i \alpha_i = 1$ and $\alpha_i \geq 0$.

As the density operators are positive they always can be expressed as

$$D = QQ^\dagger \quad (2.6)$$

where Q is a Hilbert-Schmidt operator, an important relationship that will be used extensively in the material that follows.

The Hilbert-Schmidt operators comprise another subset of the set of Bounded Operators defined by

$$\mathcal{B}_2(\mathcal{H}) = \left\{ Q; Tr\{Q^\dagger Q\} < \infty, Q \in \mathcal{B}(\mathcal{H}) \right\} \quad (2.8)$$

They actually form a Hilbert space with an inner product defined by

$$(Q_1 | Q_2) = Tr\{Q_1^\dagger Q_2\} \quad (2.9)$$

which defines the Hilbert-Schmidt norm

$$\|Q\|_2 = (Q|Q)^{\frac{1}{2}} \quad (2.10)$$

Like the Trace Class operators the Hilbert-Schmidt operators also form a normed *-algebra.

In general, the sets of Trace Class operators and Hilbert-Schmidt operators are not contained in each other, but are connected in the following manner

$$\begin{aligned} Q_1, Q_2 \in \mathcal{B}_2(\mathcal{H}) &\Rightarrow Q_1 Q_2^\dagger \in \mathcal{B}_1(\mathcal{H}) \\ X \in \mathcal{B}_1(\mathcal{H}) &\Rightarrow X = Q_1 Q_2^\dagger; \quad Q_1, Q_2 \in \mathcal{B}_2(\mathcal{H}) \end{aligned} \quad (2.11)$$

It is the latter property that justifies Eq. (2.6). If the dimension of \mathcal{H} is finite all of these spaces of operators are identical.

2.2 Densities

The relevant Hilbert spaces, $\{\mathcal{H}^N\}$, describe the pure states of N -electron systems and are defined as N -fold antisymmetric tensor products of a Hilbert space of one-particle states \mathcal{H}^1 , which we will consider to be represented by square integral functions, $L_2(\mathbf{Y})$, of charge-spin variables $\mathbf{y} = (\mathbf{r}, \xi)$; $\mathbf{Y} = \{\mathbf{y} = (\mathbf{r}, \xi); \mathbf{r} \in \mathbb{R}^3, \xi \in \mathbb{C}^2\}$. In the original formulation of DFT the object of paramount interest was the electron charge density, $\rho(\mathbf{r})$, a function of position only. However it has become increasingly evident that generalizations involving spin are more flexible and powerful tools with which to construct functionals and describe the behavior of electronic systems. These extensions take the form of Spin-Polarized DFT [4] in which a two-component space density is considered $(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r}))$ one component associated with alpha-alpha spin interactions and one with beta-beta spin interactions, and the more general full spin DFT [5] that involves a three-component space density $(\rho_\alpha(\mathbf{r}), \rho_{\alpha\beta}(\mathbf{r}), \rho_\beta(\mathbf{r}))$ that also includes alpha-beta spin interactions. Though the three component form is more general it involves a spatial density $\rho_{\alpha\beta}(\mathbf{r})$ that *is not* a positive function.

In order to recover a general spin description, equivalent to spin DFT, while maintaining positivity we consider the full charge - spin number density, $\gamma(\mathbf{y})$, a function of three space and two spin variables. The linear map Ξ_N^1 that produces the full number density is a contraction map from the space of N -particle trace class operators into $L_1(\mathbb{R}^3 \times \mathbb{C}^2)$ the space of complex-valued absolute integrable functions of charge-spin variables

$$\Xi_N^1: \mathcal{B}_1(\mathcal{H}^N) \rightarrow L_1(\mathbb{R}^3 \times \mathbb{C}^2) \equiv L_1(\mathbf{Y}) \quad (2.12)$$

This map is defined in terms of Fermion field operators by

$$\zeta(\mathbf{y}) = \Xi_N^1(X)(\mathbf{y}) = Tr\{\Phi^\dagger(\mathbf{y})\Phi(\mathbf{y})X\} \in L_1(\mathbf{Y}). \quad (2.13)$$

The field operators used in this definition are given by

$$\Phi(\mathbf{y}) = \sum_{1 \leq i \leq r} \bar{\varphi}_i(\mathbf{y}) a_i \quad (2.14)$$

in terms of the discrete field operators, $\{\bar{a}_i, a_i^\dagger\}$ (overbars denote complex conjugation), in turn these are defined using a basis of \mathcal{H}^1 comprised of one-particle functions of space - spin variables $\{\varphi_i; 1 \leq i \leq r\}$ and their action on the vacuum vector $|\phi\rangle$

$$a_i^\dagger |\phi\rangle = |\varphi_i\rangle \quad (2.15)$$

The field operators satisfy the fermion anti-commutation relationships

$$\begin{aligned} [\Phi(\mathbf{y}), \Phi^\dagger(\mathbf{y}')]_+ &= \delta(\mathbf{y} - \mathbf{y}') \\ [a_i, a_j^\dagger]_+ &= \delta_{ij} \end{aligned} \quad (2.16)$$

The First Order Reduced Density Operator (FORDO), D^1 , which is defined in a similar fashion also can be used to define the density (Appendix B).

The kernel of the linear map Ξ_N^1 is a linear subspace of $\mathcal{B}_1(\mathcal{H}^N)$, which we can use to define an equivalence relationship on $\mathcal{B}_1(\mathcal{H}^N)$ by

$$X \sim Y \Leftrightarrow X - Y \in \text{Ker}\{\Xi_N^1\} \Leftrightarrow \Xi_N^1(X) = \Xi_N^1(Y) = \zeta \quad (2.17)$$

where the double arrow indicates equivalent statements. We denote these equivalence classes by $[\zeta]_N$ and note that

$$\text{if } \sum_i \alpha_i = 1 \text{ and } X_i \in [\zeta]_N \forall i \text{ then } \sum_i \alpha_i X_i \in [\zeta]_N \quad (2.18)$$

These equivalence classes are the essential tool for identifying states with densities.

The map Ξ_N^1 , when restricted to the convex set of N -particle states, \mathcal{S}_N , has values in the convex set, \mathcal{P}_{1N} , of positive functions in $L_1(\mathbf{Y})$ that are normalized to the value N

$$\mathcal{P}_{1N} = \{\gamma; \gamma(\mathbf{y}) \geq 0, \int \gamma(\mathbf{y}) d\mathbf{y} = N\} \quad (2.19)$$

Harriman [6] has shown that this map is "onto" i.e. any element of \mathcal{P}_{1N} comes from at least one element of \mathcal{S}_N . Note that this property does not rule out the possibility that an element of \mathcal{P}_{1N} can also come from operators *not* in \mathcal{S}_N . This "onto" property should be compared to the case that arises in the N -representability problem [7]. In it, not every positive two-particle operator comes from a state in \mathcal{S}_N so the corresponding contraction map does *not* have the "onto" property.

The equivalence classes $[\zeta]_N$ have a natural indexing by the functions $\{\zeta\}$ and can be expanded about a reference representative point

$$[\zeta]_N = X_{ref} + \text{Ker}\{\Xi_N^1\}; \quad X_{ref} \in [\zeta]_N \quad (2.20)$$

that is, given any single operator that maps to a specified density, all others that do so are determined by addition of elements of the kernel of the contraction map to this operator. If we restrict attention to $\gamma \in \mathcal{P}_{1N}$ then each $[\gamma]_N$ contains a convex set of states, $\mathcal{S}_N(\gamma)$ belonging to \mathcal{S}_N

$$\mathcal{S}_N(\gamma) = [\gamma]_N \cap \mathcal{S}_N \quad (2.21)$$

It is important to emphasize again that, even for densities γ , the equivalence class $[\gamma]_N$ can contain operators that are not positive i.e. *are not* states, as well as both pure and ensemble states.

The elements of the convex set $\mathcal{S}_N(\gamma)$ also can be expanded about a reference representative state

$$\mathcal{S}_N(\gamma) = D_{ref}^N + \mathcal{S}\Xi_N^1(\gamma, D_{ref}^N); \quad D_{ref}^N \in \mathcal{S}_N(\gamma) \quad (2.22)$$

where $\mathcal{S}\Xi_N^1(\gamma)$ is a convex set, contained in $Ker\{\Xi_N^1\}$, of state differences $\{D^N - D_{ref}^N; \quad D^N \in \mathcal{S}_N(\gamma)\}$ that depend *explicitly* on γ and D_{ref}^N .

2.3 Fiber Bundles

Though not exploited extensively in this paper, except for helping to visualize the mathematical connections in a more concrete fashion as shown in Figure 1, the set $\{\gamma, \mathcal{S}_N(\gamma)\}$ can be described mathematically in a convenient fashion as a fiber bundle [8], with fibers $\{\mathcal{S}_N(\gamma)\}$ and base space \mathcal{P}_{1N} , which we will denote by \mathfrak{D}^N .

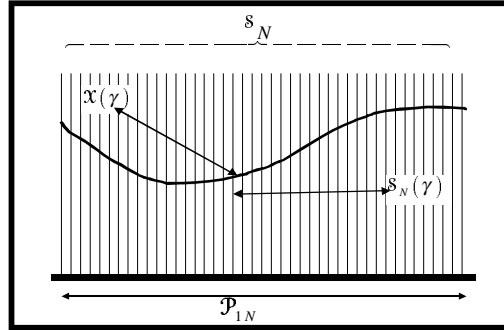


Figure 1: The vertical lines are the fibers $\mathcal{S}_N(\gamma)$; the curve is a path of states (fiber bundle vocabulary: cross-section); the thick horizontal line is the base space, in our case densities \mathcal{P}_{1N} . The complete collection of vertical lines is, in our case, the set of states \mathcal{S}_N .

The best known example of a fiber bundle used in physical applications is that of the set of tangent spaces (the fibers) associated with a nonlinear manifold (the base space) [9]. In that case, the fiber bundle is actually a vector bundle as the fibers are vector spaces, such is not the case here, however, as the fibers are the convex sets $\mathcal{S}_N(\gamma)$ which are *not* vector spaces. A cross section is a map from the base to a fiber. In the present case

$$\begin{aligned} \mathcal{X}: \mathcal{P}_{1N} &\rightarrow \mathcal{S}_N \\ \mathcal{X}(\gamma) &= D^N \in \mathcal{S}_N(\gamma) \end{aligned} \quad (2.23)$$

which associates a specific density with one specific operator in $\mathcal{S}_N(\gamma)$. Every different association determines a different \mathcal{X} . We call these cross sections **state paths** in \mathcal{S}_N . In the example of tangent spaces the cross-sections are vector fields.

3. Energy Functional Defined on Paths

The relationship between N -particle states, in which we include mixed states, represented by N -particle operators and the charge-spin density, $\gamma(\mathbf{y})$, as defined in Eq. (2.13), is not 1-1. This fact is a central issue in the rigorous formulation of DFT. The power and simplicity of DFT arise from the characterization of an N -Fermion system by a real positive semi-definite function (density) of a single 3D spatial variable and one 2D complex spin variable, but that characterization rests on the subtle details of just how the density determines a N -particle state.

In order to develop a framework in which to treat these topics rigorously for both time-dependent and independent systems, we have, as remarked in the Introduction, revisited the *constrained search* of Levy [10,11] to generate a well-defined energy functional of the density. As shown in detail in what follows, we then do a constrained optimization analysis of the problem as described, for example, by Hestenes [12]. These techniques provide a specification of paths (of N -particle density operators) that are defined in N -particle operator space such that they are labeled by densities in a 1-1 fashion. The expectation of the Hamiltonian with respect to N -particle states on those paths then becomes a well defined functional of the density $\gamma(\mathbf{y})$ and the ground state energy is the minimum value of this functional. We remark that this treatment bears some resemblance Kryachko and Ludeña's (KL) use of "orbits"[13]. It differs in two essential, specific ways: (a) The paths we use are determined by optimization criteria that guarantee the resulting functionals have well-defined functional derivatives irrespective of the topology of the density. KL, in contrast, identify orbits by employing the Bader density surface criterion[14]. Those orbits therefore are tied explicitly to the molecular point group symmetry but without any explicit criteria for existence of the required derivatives. Note also that molecular structure and bonding often involve changes in the point group symmetry, so the KL orbits intertwine chemical and mathematical properties that might better be left apart. (b) The analysis we use characterizes the states by the general charge-space density γ , not the charge density ρ , a point already mentioned that is treated in more detail below.

3.1 Energy Functionals

The energy functional defined by a Hamiltonian, H , given by

$$\begin{aligned} E_H: \mathcal{S}_N &\rightarrow \mathbb{R} \\ E_H(D^N) &= \text{Tr}\{HD^N\} \end{aligned} \tag{3.1}$$

does not have a unique value on a given convex set $\mathcal{S}_N(\gamma)$ as defined in Eq.(2.21), as many different D^N 's may give the same γ while producing different values $E_H(D^N)$. Thus E_H does not lead to a well-defined function on the space of equivalence classes of

density operators, a space whose elements are in 1-1 correspondence with densities. To obtain an energy functional that is well defined, we use the constrained search logic and define another functional in terms of the charge-spin density as

$$F_H(\gamma) = \underset{D^N \in \mathcal{S}_N(\gamma)}{\text{Min}} E_H(D^N) = E_H(D_*^N(\gamma)) \quad (3.2)$$

where $D_*^N(\gamma)$ is the minimizer of E_H in the set $\mathcal{S}_N(\gamma)$. Note that the case of a non-unique minimizer is excluded; see Savin [15] for a related discussion. Minimization in Eq. (3.2) involves three types of constraints, normalization, positivity and fixed density. Normalization and positivity can be handled by the factorization [recall Eq. (2.6)]

$$D^N = \frac{QQ^\dagger}{\text{Tr}\{QQ^\dagger\}}; Q \in \mathcal{B}_2(\mathcal{H}^N) \quad (3.3)$$

which leads to the energy functional form

$$F_H(\gamma) = \underset{QQ^\dagger \sim \gamma}{\text{Min}} \frac{\text{Tr}\{HQQ^\dagger\}}{\text{Tr}\{QQ^\dagger\}} = \underset{Q \in \langle \gamma \rangle_N}{\text{Min}} E_H(Q, Q^\dagger) = E_H(Q_*(\gamma), Q_*^\dagger(\gamma)) \quad (3.4)$$

The first *Min* is over all QQ^\dagger that correspond to γ , i.e. that yield that density or a constant multiplier of it. This correspondence also can be expressed by defining the set, $\langle \gamma \rangle_N$, of feasible Q 's by a constraint function, g , for a *fixed* γ as

$$\begin{aligned} g: \mathcal{B}_2(\mathcal{H}^N) &\rightarrow \mathcal{P}_{1N} \\ g(Q, Q^\dagger, \gamma) &= 0 \\ g(Q, Q^\dagger, \gamma) &= \Xi'_N \left(\frac{QQ^\dagger}{\text{Tr}\{QQ^\dagger\}} \right) - \gamma \end{aligned} \quad (3.5)$$

3.2 Minimization

The minimization in Eq. (3.4) subject to Eq. (3.5) can be carried out via a Lagrangian function

$$\mathcal{L}(Q, Q^\dagger, \lambda, \gamma) = E_H(Q, Q^\dagger) - \int_{\mathbf{y}} \lambda(\mathbf{y}) g(Q, Q^\dagger, \gamma, \mathbf{y}) d\mathbf{y} \quad (3.6)$$

Its stationary points

$$\begin{aligned} \nabla_Q \mathcal{L}(Q_*, Q_*^\dagger, \lambda_*, \gamma) &= \nabla_{Q^\dagger} \mathcal{L}(Q_*, Q_*^\dagger, \lambda_*, \gamma) = 0 \\ \Xi'_N \left(\frac{Q_* Q_*^\dagger}{\text{Tr}\{Q_* Q_*^\dagger\}} \right) &= \gamma \end{aligned} \quad (3.7)$$

determine the constrained extrema of $E_H(Q, Q^\dagger)$. (For the ground state obviously a minimum is required.) By considering the sensitivity of the minimizer $Q_*(\gamma)$ to variations in γ and checking that certain conditions on the first and second derivatives of $\mathcal{L}(Q, Q^\dagger, \lambda, \gamma)$, are satisfied (which we examine below), Hestenes [12] showed that one can define a *path* of solutions, $Q_*(\gamma)$, parameterized by γ , *not just a set of solutions*

indexed by γ . These paths in the parameter space $\mathcal{B}_2(\mathcal{H}^N)$ determine density operator

$$\text{paths } D_*^N(\gamma) = \frac{Q_*(\gamma)Q_*^\dagger(\gamma)}{\text{Tr}\{Q_*(\gamma)Q_*^\dagger(\gamma)\}} \text{ in } \mathcal{S}_N \subset \mathcal{B}_1(\mathcal{H}^N).$$

The energy functional $F_H(\gamma)$ developed in Eq. (3.4) now can be viewed as the energy functional E_H restricted to such paths i.e.

$$F_H(\gamma) = E_H(Q_*(\gamma), Q_*^\dagger(\gamma)) = E_H(D_*^N(\gamma)) \quad (3.8)$$

A further consequence of the Hestenes analysis is that one can define a Lagrange parameter functional $\lambda_*(\gamma)$ by setting $\lambda_*(\gamma)(\mathbf{y}) = \lambda_*(\mathbf{y})$ for each γ and its associated λ_* , obtained from solution of Eq. (3.7), and that this functional *can be identified rigorously* with the functional derivative $\frac{\delta F_H}{\delta \gamma}$ of $F_H(\gamma)$ *along the path* $Q_*(\gamma)$. Note that the energy is a 1-1 functional of the density on this path and simultaneously that the functional derivative is defined *on this* particular path. It is possible define other paths in \mathcal{S}_N on which the energy is also a 1-1 functional, but on those other paths the following crucial fact will not be true

$$E_0 = \text{Min}_{\gamma \in \mathcal{P}_{1N}} \{F_H(\gamma)\} \quad (3.9)$$

where E_0 is the ground state energy of the system.

The parameterization of state density operator paths by the paths $Q_*(\gamma)$, i.e.

$$D_*^N(\gamma) = \frac{Q_*(\gamma)Q_*^\dagger(\gamma)}{\text{Tr}\{Q_*(\gamma)Q_*^\dagger(\gamma)\}}, \text{ in general is redundant. That is, in general the association}$$

between parameters $Q_*(\gamma)$ and states. $D_*^N(\gamma)$ is not unique. The parameterization can be made non-redundant in a straightforward manner. For the purposes of this paper, however, the redundant parameterization is more convenient.

The explicit form of the functional F_H is at this point unknown, hence in practical applications has to be approximated. To facilitate creation of such approximations one decomposes F_H into a sum of other functionals that focuses essentially all the unknowns into one component, the exchange-correlation functional, F_{XC} .

$$F_H(\gamma) = F_C(\gamma) + F_{XC}(\gamma) + F_S(\gamma) + F_{eN}(\gamma) + F_{Ext}(\gamma) + F_T(\gamma) \quad (3.10)$$

(with subscripts C , XC , S , eN , Ext , and T denoting Coulomb, exchange-correlation, spin, electron-nuclear attraction, external, and kinetic energies respectively). We emphasize that Eq. (3.10) is *not* the Kohn-Sham decomposition familiar in prior presentations of DFT, because there is no KS auxiliary system involved in this decomposition. From the construction presented above it is clear that in order to maintain consistency and to define functional derivatives properly all the functionals in Eq. (3.10) must be defined on the same path in \mathcal{D}^N ; recall Figure 1. These two observations lead to what may be unfamiliar definitions for the kinetic energy functional and the exchange-correlation functional, as follows:

$$\begin{aligned}
F_C(\gamma) &= \frac{1}{2} \int \frac{\gamma(\mathbf{y})\gamma(\mathbf{y}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{y}d\mathbf{y}' \\
F_T(\gamma) &= Tr \left\{ -\frac{1}{2} \sum_i \nabla_i^2 D_*^N(\gamma) \right\} \equiv Tr \{ TD_*^N(\gamma) \} = E_T(D_*^N(\gamma)) \\
F_S(\gamma) &= Tr \{ H_S D_*^N(\gamma) \} = E_S(D_*^N(\gamma)) \\
F_{XC}(\gamma) &= Tr \left\{ \left(\sum_{1 \leq i < j \leq N} \frac{1}{r_{ij}} \right) D_*^N(\gamma) \right\} - F_C(\gamma) \equiv Tr \{ V_{12} D_*^N(\gamma) \} - F_C(\gamma) = E_{XC}(D_*^N(\gamma)) \quad (3.11) \\
F_{eN}(\gamma) &= - \int \gamma(\mathbf{y}) \sum_{i\mu} \frac{Z_\mu}{\|\mathbf{r}_i - \mathbf{R}_\mu\|} d\mathbf{y} \\
F_{Ext}(\gamma) &= \int \gamma(\mathbf{y}) \sum_i U_i(\mathbf{y}) d\mathbf{y}
\end{aligned}$$

(The H_S contribution is to allow for an explicitly spin-dependent Hamiltonian.) A particular point to observe that, unlike the familiar KS construction, this exchange-correlation functional does not involve the kinetic energy. From the perspective of the DFT literature, Eqs. (3.10) and (3.11) are a formulation of the Hohenberg-Kohn functional that is constructed to ensure that the functional derivatives required for variational minimization actually exist.

One can regroup the functionals in (3.11) into a universal electronic functional that describes the internal energetics of the electrons at prescribed γ ,

$$\begin{aligned}
F(\gamma) &= F_C(\gamma) + F_T(\gamma) + F_S(\gamma) + F_{XC}(\gamma) \\
&= E_C(D_*^N(\gamma)) + E_T(D_*^N(\gamma)) + E_S(D_*^N(\gamma)) + E_{XC}(D_*^N(\gamma)) = E(D_*^N(\gamma)) \quad (3.12)
\end{aligned}$$

and one describing the effects of the environment upon the electrons

$$F_V(\gamma) = F_{eN}(\gamma) + F_{Ext}(\gamma) \quad (3.13)$$

where the total single particle potential V is defined as

$$V(\mathbf{y}) = V(\mathbf{r}, \xi) \equiv V_{eN} + V_{ext} = \sum_{i\mu} \frac{Z_\mu}{\|\mathbf{r}_i - \mathbf{R}_\mu\|} - \sum_i U_i(\mathbf{y}) \quad (3.14)$$

It describes the interaction with the nuclear framework and other external fields and also could have a non-trivial *local* spin dependence. (It should be noted that it is possible, though unconventional, to formulate interactions with external magnetic fields in this manner. Note also that in many DFT papers, the “external” potential is just V_{eN} .)

A very significant property of $F_V(\gamma)$ is that it *is not* defined on a path in $\mathfrak{S}_N(\gamma)$ but directly on elements of \mathcal{P}_{1N} leading to the observation that E and E_H have the same minimizer in the set $\mathfrak{S}_N(\gamma)$ i.e.

$$E(D_*^N(\gamma)) = \underset{D^N \in \mathcal{S}_N(\gamma)}{\text{Min}} E(D^N) \quad (3.15)$$

while

$$E_H(D_*^N(\gamma)) = \underset{D^N \in \mathcal{S}_N(\gamma)}{\text{Min}} E_H(D^N) = E(D_*^N(\gamma)) - \int \gamma(\mathbf{y})V(\mathbf{y})d\mathbf{y} \quad (3.16)$$

This property *is not* shared by E_H with E_T , E_S and E_{XC} separately, thus the kinetic energy functional E_T minimizer $D_T^N(\gamma)$ given by

$$E_T(D_T^N(\gamma)) = \underset{D^N \in \mathcal{S}_N(\gamma)}{\text{Min}} E_T(D^N) \quad (3.17)$$

is not the same as the minimizer for the universal electronic energy functional E

$$\begin{aligned} E(D_*^N(\gamma)) &= \underset{D^N \in \mathcal{S}_N(\gamma)}{\text{Min}} \left\{ \text{Tr}\{(T + V_{12} + H_S)D^N\} \right\} = \text{Tr}\{(T + V_{12} + H_S)D_*^N(\gamma)\} \\ &\neq \text{Tr}\{(T + V_{12} + H_S)D_T^N(\gamma)\} \end{aligned} \quad (3.18)$$

3.3 Conditions for Existence of Paths and Derivatives

As stated in Eq. (3.7), a stationary point, $Q_*(\gamma)$, for the minimization problem Eq. (3.4) exists when one can find a Lagrange parameter function $\lambda_*(\gamma)$ such that

$$\nabla_P \mathcal{L}(Q_*, Q_*^\dagger, \lambda_*, \gamma) = \nabla_P E_H(Q_*, Q_*^\dagger) + \int_{\mathbf{Y}} \lambda_*(\mathbf{y}) \nabla_P g(Q_*, Q_*^\dagger, \gamma)(\mathbf{y}) d\mathbf{y} = 0 \quad (3.19)$$

$$\text{and } g(Q_*, Q_*^\dagger, \gamma) = 0; \text{ for } P = Q \text{ or } Q^\dagger$$

The energy gradients in Eq. (3.19) can be viewed as real valued linear maps

$$\nabla_P E_H(Q_*, Q_*^\dagger): \mathcal{B}_2(\mathcal{H}^N) \rightarrow \mathbb{R}; \quad P = Q \text{ or } Q^\dagger \quad (3.20)$$

which can be combined to form the total functional gradient ∇E_H that produces the first order variation δE_H in E_H with respect to the operators Q, Q^\dagger at the minimizing point Q_*, Q_*^\dagger

$$\delta E_H = \nabla E_H(Q_*, Q_*^\dagger)(P) = \nabla_Q E_H(Q_*, Q_*^\dagger)(P) + \nabla_{Q^\dagger} E_H(Q_*, Q_*^\dagger)(P^\dagger) \quad (3.21)$$

The constraint gradients in Eq. (3.19) can be viewed as linear maps and the components $\nabla_P g(Q_*, Q_*^\dagger, \gamma)$ can be combined to form the total constraint gradient $\nabla g(Q_*, Q_*^\dagger, \gamma)$ which can viewed as the linear map

$$\begin{aligned} \nabla g(Q_*, Q_*^\dagger, \gamma): \mathcal{B}_2(\mathcal{H}^N) &\rightarrow L_1(\mathbf{Y}) \\ \nabla g(Q_*, Q_*^\dagger, \gamma)(P) &= \nabla_Q g(Q_*, Q_*^\dagger, \gamma)(P) + \nabla_{Q^\dagger} g(Q_*, Q_*^\dagger, \gamma)(P^\dagger) \end{aligned} \quad (3.22)$$

One can conceptualize these maps more concretely via an operator basis

$\{ |\Psi_i\rangle\langle\Psi_j| \}$ in $\mathcal{B}_2(\mathcal{H}^N)$. Letting the dimension of \mathcal{H}^1 be r , we can expand the

operators $Q = \sum_{i,j=1}^{\binom{r}{N}} Q_{ij} |\Psi_i\rangle\langle\Psi_j|$ and $Q^\dagger = \sum_{i,j=1}^{\binom{r}{N}} \bar{Q}_{ji} |\Psi_i\rangle\langle\Psi_j|$ (again the overbars denote

complex conjugation) and express the energy gradient as

$$\nabla E(Q_*, Q_*^\dagger) \equiv \left(\frac{\partial E(Q_*, Q_*^\dagger)}{\partial Q_{11}}, \dots, \frac{\partial E(Q_*, Q_*^\dagger)}{\partial Q_{\binom{r}{N}\binom{r}{N}}}, \frac{\partial E(Q_*, Q_*^\dagger)}{\partial \bar{Q}_{11}}, \dots, \frac{\partial E(Q_*, Q_*^\dagger)}{\partial \bar{Q}_{\binom{r}{N}\binom{r}{N}}} \right) \quad (3.23)$$

and the constraint gradient as

$$\nabla g(Q_*, Q_*^\dagger, \gamma)(\mathbf{y}) \equiv \left(\frac{\partial g(Q_*, Q_*^\dagger)}{\partial Q_{11}}(\mathbf{y}), \dots, \frac{\partial g(Q_*, Q_*^\dagger)}{\partial Q_{\binom{r}{N}\binom{r}{N}}}(\mathbf{y}), \frac{\partial g(Q_*, Q_*^\dagger)}{\partial \bar{Q}_{11}}(\mathbf{y}), \dots, \frac{\partial g(Q_*, Q_*^\dagger)}{\partial \bar{Q}_{\binom{r}{N}\binom{r}{N}}}(\mathbf{y}) \right) \quad (3.24)$$

Noting the form of the constraint function g , Eq. (3.5), we see that

$$\frac{\partial g(Q_*, Q_*^\dagger, \gamma)}{\partial P_{ij}}(\mathbf{y}) = \frac{\partial \Xi_N^I \left(\frac{Q_* Q_*^\dagger}{\text{Tr}\{Q_* Q_*^\dagger\}} \right)}{\partial P_{ij}}(\mathbf{y}); \quad P_{ij} = Q_{ij} \text{ or } \bar{Q}_{ij} \quad (3.25)$$

leading to $\nabla g(Q_*, Q_*^\dagger, \gamma) = \nabla \Xi_N^I \left(\frac{Q_* Q_*^\dagger}{\text{Tr}\{Q_* Q_*^\dagger\}} \right)$, which explicitly does not depend on γ .

The central issue at this point is to determine conditions for existence of solution paths $\{Q_*(\gamma), \lambda_*(\gamma)\}$, i.e. continuous maps (defined with respect to the norms of $\mathcal{B}_1(\mathcal{H}^N)$ and $L_1(\mathbf{Y})$)

$$\begin{aligned} Q_*: \mathcal{P}_{1N} &\rightarrow \mathcal{B}_1(\mathcal{H}^N) \\ \lambda_*: \mathcal{P}_{1N} &\rightarrow L_1(\mathbf{Y}) \end{aligned} \quad (3.26)$$

not just a set of optimal values $\{D_*^N(\gamma), \lambda_*(\gamma); \gamma \in \mathcal{P}_{1N}\}$. By consideration of the implicit function theorem, Hestenes [12] has shown that sufficient conditions are:

I. The map $\nabla g(Q_*, Q_*^\dagger, \gamma)$ is nonsingular. This condition is equivalent

to $\left\{ \frac{\partial \Xi_N^1(Q_*(\gamma)Q_*^\dagger(\gamma))}{\partial Q_{ij}}; 1 \leq i, j \leq \binom{r}{N} \right\}$ being linearly independent as functions

in $L_1(\mathbf{Y})$, (recall Eq. (3.5): $g(Q, \gamma) = \Xi_N^1(QQ^\dagger) - \gamma$).

II. The map $\nabla^2 \mathcal{L}(Q_*, Q_*^\dagger, \lambda_*, \gamma): \mathcal{B}_2(\mathcal{H}^N) \rightarrow \mathcal{B}_2(\mathcal{H}^N)$ is nonsingular. This condition is equivalent to the Hessian matrix

$$\left\{ \frac{\partial^2 \mathcal{L}(Q_*, Q_*^\dagger, \lambda_*, \gamma)}{\partial P_{ij} \partial P_{kl}}; 1 \leq i, j, k, l \leq \binom{r}{N}; P_{ij} = Q_{ij}, \overline{Q_{ij}} \right\} \text{ being nonsingular.}$$

The formal resemblance of these conditions to those for a stable constrained minimum energy path on a multi-dimensional potential energy surface is clear. These two sets of conditions can be compressed into one by demanding that the augmented Hessian defined as

$$\mathfrak{H}(Q_*, Q_*^\dagger, \gamma) = \begin{pmatrix} \nabla^2 \mathcal{L}(Q_*, Q_*^\dagger, \gamma) & -\nabla g(Q_*, Q_*^\dagger, \gamma)' \\ \nabla g(Q_*, Q_*^\dagger, \gamma) & 0 \end{pmatrix} \quad (3.27)$$

be nonsingular.

Along paths on which these conditions are satisfied, the Lagrangian \mathcal{L} has the explicit dependence

$$\mathcal{L}(D_*^N(\gamma), \lambda_*(\gamma)) = E_H(D_*^N(\gamma)) + \int_{\mathbf{Y}} \lambda_*(\gamma)(\mathbf{y}) g(D_*^N(\gamma))(\mathbf{y}) d\mathbf{y} = E_H(D_*^N(\gamma)) \quad (3.28)$$

where again we have utilized the relationships $g(D_*^N(\gamma)) = \Xi_N^1(D_*^N(\gamma)) - \gamma = 0$ along a path and $D_*^N(\gamma) = Q_*(\gamma)Q_*^\dagger(\gamma)$. Differentiating Eq. (3.28) with respect to γ along a path, one obtains

$$\frac{\delta \mathcal{L}}{\delta \gamma(\mathbf{y})} = \frac{\delta E_H(D_*^N(\gamma))}{\delta \gamma(\mathbf{y})} + \int_{\mathbf{Y}} \left\{ \frac{\delta \lambda_*(\gamma(\mathbf{y}'))}{\delta \gamma(\mathbf{y})} g(D_*^N(\gamma))(\mathbf{y}') - \lambda_*(\gamma(\mathbf{y})) \delta(\mathbf{y} - \mathbf{y}') \right\} d\mathbf{y}' = 0 \quad (3.29)$$

This result follows from (3.19) by appeal to the implicit function theorem to give a path parameterized by γ , then confining the derivative of the Lagrangian to that path and

using the chain rule $\frac{\delta \mathcal{L}}{\delta \gamma} = \frac{\partial \mathcal{L}}{\partial D_*^N} \frac{\delta D_*^N}{\delta \gamma} = 0$. By the use of the constraint relationship along

a path yet again and integrating the delta function term in (3.29), one finds that the derivative of the energy functional along a path is equal to the Lagrange parameter function along that path i.e.

$$\lambda_*(\gamma(\mathbf{y})) = \frac{\delta E_H(D_*^N(\gamma))}{\delta \gamma(\mathbf{y})} = \frac{\delta F_H(\gamma)}{\delta \gamma(\mathbf{y})} \quad (3.30)$$

where the second equality follows from Eq. (3.8). Eq. (3.30) shows that the Lagrange parameter function is actually a measure of the sensitivity of the energy functional to changes in its argument γ .

3.4 Evaluation of Derivatives

One can examine the conditions just given in more detail by noting that the energy E_H , contraction map Ξ_N^1 , and constraint g are the following functions

$$\begin{aligned} E_H(Q, Q^\dagger) &= \frac{H(Q, Q^\dagger)}{S(Q, Q^\dagger)} = \frac{\text{Tr}\{HQQ^\dagger\}}{\text{Tr}\{QQ^\dagger\}} \equiv \frac{\mathcal{E}_H(QQ^\dagger)}{\text{Tr}\{QQ^\dagger\}} \\ \frac{\Xi_N^1(QQ^\dagger)(\mathbf{y})}{S(Q, Q^\dagger)} &= \frac{\text{Tr}\{\Phi^\dagger(\mathbf{y})\Phi(\mathbf{y})QQ^\dagger\}}{\text{Tr}\{QQ^\dagger\}} \\ g(Q, Q^\dagger, \gamma)(\mathbf{y}) &= \frac{\text{Tr}\{\Phi^\dagger(\mathbf{y})\Phi(\mathbf{y})QQ^\dagger\}}{\text{Tr}\{QQ^\dagger\}} - \gamma(\mathbf{y}) \end{aligned} \quad (3.31)$$

which have gradients

$$\left. \begin{aligned} \nabla_P E_H(Q, Q^\dagger) &= \frac{1}{S(Q, Q^\dagger)} \left(\nabla_P H(Q, Q^\dagger) - E_H(Q, Q^\dagger) \nabla_P S(Q, Q^\dagger) \right) \\ \nabla_P \Xi_N^1(QQ^\dagger) &= \frac{1}{S(Q, Q^\dagger)} \left(\nabla_P \Xi_N^1(QQ^\dagger)(\mathbf{y}) - \Xi_N^1(QQ^\dagger)(\mathbf{y}) \nabla_P S(Q, Q^\dagger) \right) \end{aligned} \right\} P = Q, Q^\dagger \quad (3.32)$$

Here the gradient functionals evaluated at the point (Q, Q^\dagger) are themselves linear maps of the argument X , that is

$$\begin{aligned} \nabla_Q H(Q, Q^\dagger)(X) &= \text{Tr}\{HXQ^\dagger\} \\ \nabla_{Q^\dagger} S(Q, Q^\dagger)(X) &= \text{Tr}\{XQ^\dagger\} \\ \nabla_Q \Xi_N^1(QQ^\dagger)|_{\mathbf{y}}(X) &= \text{Tr}\{\Phi^\dagger(\mathbf{y})\Phi(\mathbf{y})XQ^\dagger\} \end{aligned} \quad (3.33)$$

$$X \in \mathcal{B}_2(\mathcal{H}^N)$$

The subscript \mathbf{y} on the LHS of the third line of (3.33) is a reminder that the value lies in $L_1(\mathbf{Y})$. In order to check whether condition I is satisfied at a given $Q_*(\gamma)$, one needs to ascertain whether

$$\left\{ \text{Tr}\{\Phi^\dagger(\mathbf{y})\Phi(\mathbf{y})|\Psi_i\rangle\langle\Psi_j|Q_*^\dagger\}; 1 \leq i, j \leq \binom{r}{N} \right\}$$

and

$$\left\{ \text{Tr}\{\Phi^\dagger(\mathbf{y})\Phi(\mathbf{y})Q_*|\Psi_i\rangle\langle\Psi_j|\}; 1 \leq i, j \leq \binom{r}{N} \right\} \quad (3.34)$$

are sets of linearly independent functions in $L_1(\mathbf{Y})$. Condition II involves second derivatives that have the following form at *stationary points* $Q_*(\gamma)$

$$\begin{aligned}\nabla_{PP'}^2 \mathcal{L}(Q_*, Q_*^\dagger, \lambda_*, \gamma) &= \nabla_{PP'}^2 \left\{ \frac{\mathfrak{H}(Q_* Q_*^\dagger)}{S(Q_*, Q_*^\dagger)} \right\} \\ &= \frac{1}{S(Q_*, Q_*^\dagger)} \left(\nabla_{PP'}^2 \mathfrak{H}(Q_* Q_*^\dagger) - \mathcal{L}(Q_*, Q_*^\dagger, \lambda_*, \gamma) \nabla_{PP'}^2 S(Q_*, Q_*^\dagger) \right); \quad P = Q_*, Q_*^\dagger\end{aligned}\quad (3.35)$$

where we have introduced the unnormalized constraint Lagrangian \mathfrak{H} defined by

$$\mathfrak{H}(Q_* Q_*^\dagger) = \mathcal{E}_H(Q_* Q_*^\dagger) - \int_{\mathbf{Y}} \lambda(\mathbf{y}) \left(\mathcal{E}'_N(Q_* Q_*^\dagger)(\mathbf{y}) - \gamma(\mathbf{y}) \text{Tr} Q_* Q_*^\dagger \right) d\mathbf{y} \quad (3.36)$$

As the functions \mathfrak{H} and S are quadratic, their second derivatives are easy to evaluate. First, expand $\mathcal{E}_H(Q_* Q_*^\dagger)$ in terms of a matrix representation with respect to the basis $\{ |\Psi_i\rangle\langle\Psi_j| \}$ (recall the discussion just before Eq. (3.23))

$$\begin{aligned}\mathcal{E}_H(Q_* Q_*^\dagger) &= \text{Tr}\{H Q_* Q_*^\dagger\} = \sum_{ijkl} Q_{ij} \bar{Q}_{kl} \text{Tr}\{H |\Psi_i\rangle\langle\Psi_j| |\Psi_l\rangle\langle\Psi_k|\} \\ &= \sum_{ijkl} Q_{ij} \bar{Q}_{kl} \text{Tr}\{H |\Psi_i\rangle\langle\Psi_k| \delta_{jl}\} = \sum_{ijkl} Q_{ij} \bar{Q}_{kl} H_{ki} \delta_{jl} \equiv \sum_{ijkl} Q_{ij} \bar{Q}_{kl} H_{lkij}\end{aligned}\quad (3.37)$$

Similarly, one gets

$$\begin{aligned}\mathcal{E}'_N(Q_* Q_*^\dagger)(\mathbf{y}) &= \sum_{ijkl} Q_{ij} \bar{Q}_{kl} \text{Tr}\{\Phi^\dagger(\mathbf{y}) \Phi(\mathbf{y}) |\Psi_i\rangle\langle\Psi_j| |\Psi_l\rangle\langle\Psi_k|\} \\ &= \sum_{ijkl} Q_{ij} \bar{Q}_{kl} \text{Tr}\{\Phi^\dagger(\mathbf{y}) \Phi(\mathbf{y}) |\Psi_i\rangle\langle\Psi_k| \delta_{jl}\}\end{aligned}\quad (3.38)$$

and

$$\begin{aligned}\text{Tr}\{Q_* Q_*^\dagger\} &= \sum_{ijkl} Q_{ij} \bar{Q}_{kl} \text{Tr}\{ |\Psi_i\rangle\langle\Psi_j| |\Psi_l\rangle\langle\Psi_k|\} \\ &= \sum_{ijkl} Q_{ij} \bar{Q}_{kl} \delta_{ik} \delta_{jl}\end{aligned}\quad (3.39)$$

Then the matrix of second derivatives is

$$\begin{aligned}\left[\nabla^2 \mathfrak{H}(Q_* Q_*^\dagger) \right] &= \begin{bmatrix} \mathbf{0} & \mathbf{H} \\ \bar{\mathbf{H}} & \mathbf{0} \end{bmatrix} - \begin{bmatrix} \mathbf{0} & \mathfrak{D}(\lambda_*) \\ \mathfrak{D}(\lambda_*) & \mathbf{0} \end{bmatrix} \\ \mathfrak{D}(\lambda_*) &= \int_{\mathbf{Y}} \lambda_*(\mathbf{y}) \{ \mathbf{G}(\mathbf{y}) - \gamma(\mathbf{y}) \mathbf{1} \} d\mathbf{y}\end{aligned}\quad (3.40)$$

$$\nabla^2 S(Q_* Q_*^\dagger) = \begin{bmatrix} \mathbf{0} & \mathbf{1} \\ \mathbf{1} & \mathbf{0} \end{bmatrix}$$

Here the matrix of derivatives has elements $\nabla_{P_{ij}, P_{kl}}^2 \mathfrak{H}(Q_* Q_*^\dagger)$; $P_{rs} = Q_{rs}$ or \bar{Q}_{rs} . and the matrix \mathbf{G} is defined as

$$\mathbf{G}_{lkij}(\mathbf{y}) = \text{Tr}\{\Phi^\dagger(\mathbf{y}) \Phi(\mathbf{y}) |\Psi_i\rangle\langle\Psi_k| \delta_{jl}\} \equiv \gamma_{ki}(\mathbf{y}) \delta_{jl} \quad (3.41)$$

The map constructed from $\left\{ \nabla_{PP'}^2 \mathcal{L}(Q_*, Q_*^\dagger, \lambda_*, \gamma); P, P' = Q, Q^\dagger \right\}$ thus is singular when at least one vector

$$\mathbf{V} = \begin{pmatrix} \overline{\mathbf{W}} \\ \mathbf{W} \end{pmatrix}, \mathbf{W} \in \mathbb{C}^{\binom{r}{N}^2}$$

exists such that

$$\left(\begin{bmatrix} \mathbf{0} & \mathbf{H} \\ \overline{\mathbf{H}} & \mathbf{0} \end{bmatrix} - \begin{bmatrix} \mathbf{0} & \vartheta(\lambda_*, \gamma) \\ \vartheta(\lambda_*, \gamma) & \mathbf{0} \end{bmatrix} - E_H(Q_*(\gamma), Q_*^\dagger(\gamma)) \begin{bmatrix} \mathbf{0} & \mathbf{1} \\ \mathbf{1} & \mathbf{0} \end{bmatrix} \right) \mathbf{V} = \mathbf{0} \quad (3.42)$$

with the density dependence displayed explicitly. In other words if $E_H(Q_*(\gamma), Q_*^\dagger(\gamma))$ is a stationary state energy of the augmented Hamiltonian $H + \vartheta(\lambda_*(\gamma))$, then the Hessian of the Lagrangian is singular and the point $Q_*(\gamma)$ does not lie on a path of constrained minima of E_H .

In Section 3.2 Eqs. (3.15) and (3.16) we noted that the functionals E_H and E have the same constrained minimizer $Q_*(\gamma)$, though the Lagrange parameter function will be different. We can go further to note that, as $H = H_0 + V$, where V , defined in Eq. (3.14), is a local external one-body potential, the matrix representation of \mathbf{H} in Eq. (3.37) only differs from that of \mathbf{H}_0 by a constant matrix (keep in mind that this is for a stipulated γ). We thus can replace E_H and \mathbf{H} in Eqs. (3.31) - (3.40) by E and \mathbf{H}_0 , then ascertain whether the conditions are satisfied for $Q_*(\gamma)$ to lie on a path of solutions for E , again noting that we have a different Lagrange parameter function $\tilde{\lambda}_*$ associated with the constrained solution $Q_*(\gamma)$, and hence $\vartheta(\tilde{\lambda}_*) \neq \vartheta(\lambda_*)$. Using the analogous expression to Eq. (3.37) one thus can conclude that if $E(Q_*(\gamma), Q_*^\dagger(\gamma))$ is a stationary state energy of the augmented Hamiltonian $H_0 + \theta(\tilde{\lambda}_*(\gamma))$, the point $Q_*(\gamma)$ does not lie on a path of constrained minima of E . It is interesting to note that the test potential $\vartheta(\tilde{\lambda}_*)$ has matrix elements $\int_{\mathbf{Y}} \tilde{\lambda}_*(\mathbf{y}) \{ \gamma_{ki}(\mathbf{y}) - \gamma(\mathbf{y}) \delta_{ik} \} \delta_{jl} d\mathbf{y}$; in short, the difference of all possible densities with the stipulated one plays a decisive role in determining whether the Lagrange parameter function is a functional derivative.

3.5 V-Representability

The conditions for the existence of paths described in the preceding sections are intimately connected to the V-representability problem [16]. In fact, as we now shall show, the use of functionals defined on paths is actually equivalent to restricting attention to interacting V-representable densities and that the conditions for the existence of paths are in fact V-representability conditions. The V-representability problem is to specify conditions that guarantee a density, γ , to be a stationary state density for some

Hamiltonian $H = H_0 + V$, where V is an external potential in the sense of Eq. (3.14) and H_0 is as defined implicitly in Eq. (3.18).

Theorem: A density $\gamma' \in \mathcal{P}_{1N}$ is stationary-state V-representable if the augmented Hessian \mathfrak{R} (defined in Eq. (3.27)) is nonsingular both in a neighborhood of γ' and at γ' itself and if $E(Q_*(\gamma'), Q_*^\dagger(\gamma')) = \text{Min}_{Q \in \langle \gamma' \rangle_N} \{E(Q, Q^\dagger)\}$, where $E(Q, Q^\dagger) = \text{Tr}\{H_0 D^N\}$ and $D^N = \frac{QQ^\dagger}{\text{Tr}\{QQ^\dagger\}}$.

Proof

By assumption, the augmented Hessian \mathfrak{R} , Eq. (3.27), is nonsingular both at the constrained minimizer $Q_*(\gamma')$ and in a neighborhood of that γ' . Therefore, one can identify the Lagrange parameter function $\lambda_*(\gamma')$ with $\frac{\delta F(\gamma')}{\delta \gamma}$, [where $F(\gamma)$ is given by (3.12); its argument in the functional derivative indicates the evaluation function], define a local one-body potential as $V(\mathbf{y}) = -\frac{\delta F(\gamma')}{\delta \gamma(\mathbf{y})}$, and a Hamiltonian $H = H_0 + V$. Then the functional $F_H(\gamma) = E_H(Q_*(\gamma), Q_*^\dagger(\gamma))$ defined in a neighborhood of γ' follows by simple adding to F the energy contribution from V [recall Eqs. (3.10), (3.11)]. Immediately $\left. \frac{\delta F_H}{\delta \gamma} \right|_{\gamma=\gamma'} = 0$ and therefore γ' is stationary state representable for $V(\mathbf{y}) = \frac{\delta F(\gamma')}{\delta \gamma(\mathbf{y})}$.

Further if $F_H(\gamma') < F_H(\gamma)$ for all other densities associated with the path $Q_*(\gamma)$ then γ' is ground state V-representable.

4. Variation Principle for States Parameterized by Charge-Spin Densities

In this section we apply the constraint $\gamma \in \mathcal{P}_{1N}$ via parameterization of γ by "one particle functions" (i.e. functions of one space and one spin variable) in terms of quadratic expansions of various ranks. This procedure leads to one particle variational equations that determine the ground state density γ_0 and are equivalent to the HK equations. We then contrast these equations to those of Kohn-Sham type that arise from regrouping of the terms in the energy functional and the introduction of an auxiliary state. Finally we discuss the implications of using $\gamma(\mathbf{y})$ instead of $\rho(\mathbf{r})$, the significance of that choice for symmetry breaking, and the use of auxiliary states more general than single determinants. Some of these issues have been touched upon in our two previous papers; details omitted there are treated here.

4.1 Parameterization of γ

Recall from Eq. (3.10) that for well-defined paths the ground state energy is the solution to the minimization problem

$$E_0 = F_H(\gamma_0) = \text{Min}_{\gamma \in \mathcal{P}_{1N}} \{F_H(\gamma)\} \quad (4.1)$$

The constraint that $\gamma \in \mathcal{P}_{1N}$ can be handled in analogous fashion to that of $D^N \in \mathcal{S}_N$, namely parameterization of γ by elements of $L_2(\mathbf{Y})$.

$$\gamma = N \sum_i \alpha_i \frac{|\varphi_i\rangle\langle\varphi_i|}{\langle\varphi_i|\varphi_i\rangle}; \quad \varphi_i \in L_2(\mathbf{Y}); \quad \sum_i \alpha_i = 1; \quad \alpha_i \geq 0 \quad (4.2)$$

The functions $\{\varphi_i; 1 \leq i \leq r\}$ do not have to be orthogonal nor even linearly independent, though most often it is convenient to choose an orthogonal set. In the case of D^N we only used rank 1 expansions. In contrast, expansions of different ranks are useful in this case. The correspondence between γ and $\{\varphi_i; 1 \leq i \leq r\}$ is not unique, but as in the case of D^N and Q a non-redundant parameterization can be found. Once again it is convenient to work with unnormalized quantities, so we incorporate the expansion coefficients $\{\alpha_i\}$ and the number of particles N into the functions $\{\varphi_i\}$ and set

$$\gamma(\mathbf{y}) = \sum_{i=1}^r \langle \mathbf{y} | v_i \rangle \langle v_i | \mathbf{y} \rangle; \quad v_i \in L_2(\mathbf{Y}); \quad \langle v_i | v_i \rangle \leq N; \quad \sum_{i=1}^r \langle v_i | v_i \rangle = N \quad (4.3)$$

In terms of these parameter functions, denoted as the vector \mathbf{v} , and $F_H(\mathbf{v}) \equiv F_H(\gamma(\mathbf{v}))$, the minimization problem becomes

$$E_0 = \text{Min}_{\mathbf{v} \in \mathcal{K}} \{F_H(\mathbf{v})\} \quad (4.4)$$

The feasible region \mathcal{K} is defined by the constraints

$$\begin{aligned} h_N(\mathbf{v}) &\equiv \sum_{i=1}^r |v_i|^2 - N = 0 \\ h_{ii}(\mathbf{v}) &\equiv |v_i|^2 - N \leq 0 \\ h_{ij}(\mathbf{v}) &\equiv \langle v_i | v_j \rangle = 0; \quad i \neq j \end{aligned} \quad (4.5)$$

and the minimum of Eq. (4.4) can be obtained from the Lagrangian

$$\mathcal{L}(\mathbf{v}) = F_H(\mathbf{v}) - \sum_{1 \leq i, j \leq r} \lambda_{ij} h_{ij} - \mu h_N \quad (4.6)$$

that corresponds to (3.6). By virtue of

$$\gamma(\mathbf{y}) = \sum_{1 \leq i \leq r} \langle \mathbf{y} | v_i \rangle \langle v_i | \mathbf{y} \rangle \quad (4.7)$$

and the chain rule, one has

$$\begin{aligned} \frac{\delta F_H}{\delta \bar{v}_i(\mathbf{y})} &= \frac{\delta F_H}{\delta \gamma(\mathbf{y})} \frac{\delta \gamma}{\delta \bar{v}_i(\mathbf{y})} = \frac{\delta F_H}{\delta \gamma(\mathbf{y})} v_i(\mathbf{y}) \\ \frac{\delta F_H}{\delta v_i(\mathbf{y})} &= \frac{\delta F_H}{\delta \gamma(\mathbf{y})} \frac{\delta \gamma}{\delta v_i(\mathbf{y})} = \frac{\delta F_H}{\delta \gamma(\mathbf{y})} \bar{v}_i(\mathbf{y}) \end{aligned} \quad (4.8)$$

Notice that Eq. (4.8) defines the action of a local operator $\frac{\delta F_H}{\delta \gamma}: \mathcal{H}^1 \rightarrow \mathcal{H}^1$, that has

integral kernel $\frac{\delta F_H}{\delta \gamma(\mathbf{y})} \delta(\mathbf{y} - \mathbf{y}')$ and acts on \bar{v}_i to produce the function $\frac{\delta F_H}{\delta v_i(\mathbf{y})}$.

Eq. (4.6) plus the change of variables in Eq. (4.8), gives Euler equations $\frac{\delta \mathcal{L}}{\delta \bar{v}_i} = \frac{\delta \mathcal{L}}{\delta v_i} = 0$,

that correspond to the generalized eigenvalue problem

$$\left(\frac{\delta F_H}{\delta \gamma} - \mu \right) v_i = \sum_{1 \leq j \leq r} \lambda_{ij} v_j \quad (4.9)$$

and its complex conjugate. Exact (but, in several cases, not known explicitly) component potential functionals follow from functional derivatives of Eq. (3.10):

$\frac{\delta F_C}{\delta \gamma}$, $\frac{\delta F_T}{\delta \gamma}$, $\frac{\delta F_S}{\delta \gamma}$, $\frac{\delta F_{XC}}{\delta \gamma}$, $\frac{\delta F_{eN}}{\delta \gamma}$ and $\frac{\delta F_{ext}}{\delta \gamma}$. All these derivatives are evaluated on the same

path $D_*^N(\gamma)$, which again, leads to the definitions of $\frac{\delta F_T}{\delta \gamma}$, $\frac{\delta F_S}{\delta \gamma}$ and $\frac{\delta F_{XC}}{\delta \gamma}$ as local

potentials in the one-particle Eq. (4.9) for the density.

The minimization problem, Eqs. (4.4) and (4.5) and the resulting Euler Eq. (4.9) are for determining the density γ_0 that corresponds to the ground N -particle state $D_*^N(\gamma_0)$ in terms of the parameterization \mathbf{v} of γ and hence should be thought of as a reformulation of the Hohenberg-Kohn equations. Thus, as noted, Eqs. (4.5) and (4.9) are *not* conventional Kohn-Sham equations but an exact one-particle form of the Hohenberg-Kohn variation procedure with Hohenberg-Kohn potentials in the definition of the

effective one-particle Hamiltonian $\left(\frac{\delta F_H}{\delta \gamma} - \mu \right)$. Note in particular that very few

restrictions were placed on the form of the density expansion Eq. (4.3) save for its overall normalization. The parameterization of γ , Eq. (4.7), can be chosen to have any rank and to be in terms of any functions that belong to $L_2(\mathbf{Y})$ that satisfy Eq.(4.5) and then be used subsequently in the variational equation (4.9).

4.2 Kohn-Sham Type Procedures.

In contrast Kohn-Sham procedures are based on a strategy that introduces a partitioning and regrouping of the potential terms (functional derivatives) in Eq. (4.9) based on model auxiliary states that are related to the expansion Eq. (4.7). Examples include the treatment of generalized Kohn-Sham equations by Levy and Perdew[11].

Part of the incentive for this regrouping is found in the highly non-linear dependence of the variational equations upon the density. That dependence necessitates iterative solutions. Their convergence and stability obviously depend on the choice of starting potentials (which are density dependent). As the potentials are determined by states associated with densities, it is expedient to incorporate as much information as feasible about the form of solution states in those potentials. The other motivation for regrouping is to have as many terms as possible that are both large in magnitude (on physical grounds) and straightforward to compute. One strategy for such regrouping is to rearrange the sum of derivatives into combinations related to a well-studied type of quantum state. The choice of such an auxiliary state is dictated by a balance between (a) simplicity and (b) similarity of the auxiliary state to the solution state. In the standard

Kohn-Sham procedure (based on uncorrelated auxiliary states) most emphasis is placed on point (a), while for generalized Kohn-Sham formulations (based on correlated auxiliary states) the emphasis is more on (b).

For the case of a non-degenerate ground state the standard Kohn-Sham auxiliary state is well-characterized. (We put aside the degenerate case for now. It introduces issues of degeneracy at the Fermi level, fractional occupation and continuous non-integer electron number, etc. In many treatments those complications seem entangled with incompatible assumptions about single determinantal KS states.) For non-degenerate ground states, the standard KS auxiliary state is a real single determinant of singly occupied orbitals; any conventionally doubly occupied orbitals simply occur twice in the determinant. The KS determinant is an Independent Particle State (IPS). Its form is appealing because it explicitly incorporates anti-symmetry and N -representable, and because it is easy to manipulate.

Ordinarily, however, the KS procedure is developed in terms of the real-space charge density ρ , not the charge-spin density γ . A pertinent task therefore is to determine the kind of KS theory that arises from parameterization via γ . After developing such a γ -based theory in this Section, we will analyze its relationship to the more familiar theory based on ρ in Section 4.3.

Consider therefore $\mathcal{S}_{NIP}(\gamma)$, the set of all IPS corresponding to a given γ , and a rank N expansion of γ

$$\begin{aligned}\gamma(\mathbf{y}) &= \sum_{1 \leq i \leq N} \langle \mathbf{y} | \varphi_i \rangle \langle \varphi_i | \mathbf{y} \rangle \\ \langle \varphi_i | \varphi_j \rangle &= \delta_{ij}\end{aligned}\tag{4.10}$$

It is possible to restrict the form of the expansion in Eq. (4.10) by choosing $\{\varphi_i(\mathbf{y}) \in \mathbb{R}; 1 \leq i \leq N\}$ as is usually done in standard KS theory for $\rho(\mathbf{r})$ or by setting $\{\varphi_{2i} = \varphi_{2i-1}; 1 \leq i \leq \frac{N}{2}\}$ for even N or both but we will not impose either restriction. The N functions in Eq. (4.10) determine the first order reduced density operator (FORDO; recall Appendix B) of some N particle IPS. In general many such expansions are possible for a given γ , so the correspondence between a fixed γ and IPS's is one to many. However, in general there is at least one pure IPS that corresponds to any given γ , even if γ comes from an ensemble or highly correlated state [6].

The functional that is characteristic of KS procedures is an IPS kinetic energy, to wit

$$T_{KS}(\gamma) = \underset{D_{IP}^N \in \mathcal{S}_{NIP}(\gamma)}{\text{Min}} \text{Tr}\{TD_{IP}^N\} = E_T(D_{IP^\diamond}^N(\gamma))\tag{4.11}$$

where E_T is defined in Eq. (3.11) and $D_{IP^\diamond}^N(\gamma)$ is the N -particle IPS that minimizes this constrained optimization. If the conditions described in sections 3.4 and 3.5 are satisfied those minimizers form a path $D_{IP^\diamond}^N(\gamma)$ in \mathfrak{D}^N . It is imperative to recognize that, in general, the path $D_{IP^\diamond}^N(\gamma)$ is *completely* different from the path $D_*^N(\gamma)$. If we had applied other

restrictions to Eq. (4. 11), e.g. different rank expansions, different normalization for the functions, etc., yet other paths would have resulted.

The definitions in Eq. (3.11) can be transformed to KS form by regrouping and defining difference functionals between exact and independent particle paths. In so doing it is important to keep in mind that that the HK kinetic energy and XC terms involve a system-dependent path $D_*^N(\gamma)$ in N -particle state space whereas $D_{IP\phi}^N(\gamma)$ involves the kinetic energy of the IPS alone. Let

$$\widehat{F}_T(\gamma) = T_{KS}(\gamma) - F_T(\gamma) \equiv E_T(D_{IP\phi}^N(\gamma)) - E_T(D_*^N(\gamma)) \quad (4.12)$$

then

$$F_T(\gamma) = T_{KS}(\gamma) - \widehat{F}_T(\gamma) \quad (4.13)$$

The KS XC energy then is defined as

$$F_{XC,KS}(\gamma) = F_{XC}(\gamma) - \widehat{F}_T(\gamma) \quad (4.14)$$

which is equivalent to

$$F_T(\gamma) + F_{XC}(\gamma) = T_S(\gamma) + F_{XC,KS}(\gamma) \quad (4.15)$$

and thus the regrouping

$$F_H(\gamma) = T_{KS}(\gamma) + F_{XC,KS}(\gamma) + F_C(\gamma) + F_S(\gamma) + F_V(\gamma) \quad (4.16)$$

By construction, these KS functionals are well-defined and give well-defined functional derivatives, so their variation proceeds as in the preceding section and leads to standard KS equations strictly analogous with Eqs. (4.4), (4.5), and (4.9). The benefit of this formulation over the standard one is at least two-fold. It makes clear that the XC KS term is defined with the help of two distinct paths and that those paths are essential to the determination of conditions for the existence of the functional derivatives upon which the Euler equation (4.10) depends.

4.3 Parameterization in terms of $\rho(\mathbf{r})$ versus $\gamma(\mathbf{y})$

Conventionally both the HK and KS theories are based on the charge density ρ and not the more general charge-spin density γ . The standard formulation of spin density functional theory [4] extends the parameterization to include S_z -densities i.e. two positive spatial components $(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r}))$. The full spin-density also has been considered more than once [5] in the form of three spatial components $(\rho_\alpha(\mathbf{r}), \rho_{\alpha\beta}(\mathbf{r}), \rho_\beta(\mathbf{r}))$. However, in all earlier treatments (as far as we are aware) the alpha-beta cross term is dropped, perhaps because it is not a positive function. In contrast, the present formulation in terms of the full spin density is described completely in terms of $\gamma(\mathbf{y})$, which is positive. When describing systems that have non-trivial spin properties a theory based on ρ alone is inconvenient as it incorporates those spin properties implicitly in difficult-to-characterize potentials rather than explicitly in terms of the spin properties of γ . A general spin density formulation of DFT, based on positive densities, thus should treat γ as the basic parameter rather than ρ . As suggested by the remarks

about the alpha-beta cross term (and by the form of the KS kinetic energy), the appropriate object to consider is the FORDO (again, recall Appendix B).

The kernel of a FORDO can be expanded in terms of normalized functions as

$$D^1(\mathbf{y}, \mathbf{y}') = \sum_{1 \leq i, j \leq r} D_{ij}^1 \varphi_i(\mathbf{y}) \bar{\varphi}_j(\mathbf{y}') \quad (4.17)$$

where the set of functions of charge-spin variables $\{\varphi_i; 1 \leq i \leq r\}$ is a complete orthonormal basis for \mathcal{H}^1 . These basis functions always can be written as a product of orthonormal functions of spatial variables and orthonormal functions of spin variables

$$\begin{aligned} \varphi_i(\mathbf{y}) &= \chi_i(\mathbf{r}) \alpha(\xi); \quad 1 \leq i \leq s = \frac{r}{2} \\ \varphi_i(\mathbf{y}) &= \chi_i(\mathbf{r}) \beta(\xi); \quad s+1 \leq i \leq r \end{aligned} \quad (4.18)$$

so that Eq. (4.18) becomes

$$\begin{aligned} D^1(\mathbf{y}, \mathbf{y}') &= \sum_{1 \leq i, j \leq s} D_{\alpha\alpha ij}^1 \chi_i(\mathbf{r}) \bar{\chi}_j(\mathbf{r}') \alpha(\xi) \bar{\alpha}(\xi') \\ &+ \sum_{\substack{s+1 \leq i \leq 2s \\ 1 \leq j \leq s}} D_{\alpha\beta ij}^1 \chi_i(\mathbf{r}) \bar{\chi}_j(\mathbf{r}') \alpha(\xi) \bar{\beta}(\xi') + \sum_{\substack{1 \leq i \leq s \\ s+1 \leq j \leq 2s}} D_{\beta\alpha ij}^1 \chi_i(\mathbf{r}) \bar{\chi}_j(\mathbf{r}') \beta(\xi) \bar{\alpha}(\xi') \\ &+ \sum_{s+1 \leq i, j \leq 2s} D_{\beta\beta ij}^1 \chi_i(\mathbf{r}) \bar{\chi}_j(\mathbf{r}') \beta(\xi) \bar{\beta}(\xi') \end{aligned} \quad (4.19)$$

In turn this expression allows us to define *reducible*, (with respect to the action of the spin group SU(2)), spin component kernels as

$$\begin{aligned} D_{\alpha\alpha}^1(\mathbf{r}, \mathbf{r}') &= \sum_{1 \leq i, j \leq s} D_{\alpha\alpha ij}^1 \chi_i(\mathbf{r}) \bar{\chi}_j(\mathbf{r}') \\ D_{\alpha\beta}^1(\mathbf{r}, \mathbf{r}') &= \sum_{\substack{s+1 \leq i \leq 2s \\ 1 \leq j \leq s}} D_{\alpha\beta ij}^1 \chi_i(\mathbf{r}) \bar{\chi}_j(\mathbf{r}') \\ D_{\beta\alpha}^1(\mathbf{r}, \mathbf{r}') &= \sum_{\substack{1 \leq i \leq s \\ s+1 \leq j \leq 2s}} D_{\beta\alpha ij}^1 \chi_i(\mathbf{r}) \bar{\chi}_j(\mathbf{r}') \\ D_{\beta\beta}^1(\mathbf{r}, \mathbf{r}') &= \sum_{s+1 \leq i, j \leq 2s} D_{\beta\beta ij}^1 \chi_i(\mathbf{r}) \bar{\chi}_j(\mathbf{r}') \end{aligned} \quad (4.20)$$

and *irreducible* (that correspond to one and three dimensional irreps of SU(2) respectively) spin component kernels as

$$\begin{aligned} P(\mathbf{r}, \mathbf{r}') &= \frac{1}{2} \{ D_{\alpha\alpha}^1(\mathbf{r}, \mathbf{r}') + D_{\beta\beta}^1(\mathbf{r}, \mathbf{r}') \} \\ Q_{+1}(\mathbf{r}, \mathbf{r}') &= \frac{1}{2} \{ D_{\alpha\beta}^1(\mathbf{r}, \mathbf{r}') + D_{\beta\alpha}^1(\mathbf{r}, \mathbf{r}') \} \\ Q_0(\mathbf{r}, \mathbf{r}') &= \frac{1}{2} \{ D_{\alpha\alpha}^1(\mathbf{r}, \mathbf{r}') - D_{\beta\beta}^1(\mathbf{r}, \mathbf{r}') \} \\ Q_{-1}(\mathbf{r}, \mathbf{r}') &= \frac{1}{2i} \{ D_{\beta\alpha}^1(\mathbf{r}, \mathbf{r}') - D_{\alpha\beta}^1(\mathbf{r}, \mathbf{r}') \} \end{aligned} \quad (4.21)$$

The FORDO kernel therefore is expressible as

$$D^l(\mathbf{y}, \mathbf{y}') = P(\mathbf{r}, \mathbf{r}')\Theta_{00}(\xi, \xi') + Q_{+1}(\mathbf{r}, \mathbf{r}')\Theta_{11}(\xi, \xi') + Q_0(\mathbf{r}, \mathbf{r}')\Theta_{10}(\xi, \xi') + Q_{-1}(\mathbf{r}, \mathbf{r}')\Theta_{1-1}(\xi, \xi') \quad (4.22)$$

where the spin kernels are defined as

$$\begin{aligned} \Theta_{00}(\xi, \xi') &= (\alpha(\xi)\bar{\alpha}(\xi') + \beta(\xi)\bar{\beta}(\xi')); & \Theta_{10}(\xi, \xi') &= (\alpha(\xi)\bar{\alpha}(\xi') - \beta(\xi)\bar{\beta}(\xi')) \\ \Theta_{11}(\xi, \xi') &= (\alpha(\xi)\bar{\beta}(\xi') + \beta(\xi)\bar{\alpha}(\xi')); & \Theta_{1-1}(\xi, \xi') &= (\alpha(\xi)\bar{\beta}(\xi') - \beta(\xi)\bar{\alpha}(\xi')) \end{aligned} \quad (4.23)$$

The full charge-spin density in terms of these *irreducible* spin component kernels is

$$\begin{aligned} \gamma(\mathbf{y}) &= P(\mathbf{r}, \mathbf{r})\Theta_{00}(\xi, \xi) + Q_{+1}(\mathbf{r}, \mathbf{r})\Theta_{11}(\xi, \xi) \\ &\quad + Q_0(\mathbf{r}, \mathbf{r})\Theta_{10}(\xi, \xi) + Q_{-1}(\mathbf{r}, \mathbf{r})\Theta_{1-1}(\xi, \xi) \end{aligned} \quad (4.24)$$

while the charge density is given by

$$\rho(\mathbf{r}) = \int \gamma(\mathbf{y})d\xi = P(\mathbf{r}, \mathbf{r}) \quad (4.25)$$

Clearly $\rho \in \mathcal{P}_{1N}^{\mathbb{R}} \subset L_1(\mathbb{R}^3)$, hence could be used to index N -particle states in similar manner to γ , as was the case in the original HK formulation of DFT. As we have already remarked, however, the Q_{+1} and Q_{-1} contributions in (4.24) do not appear in ordinary spin-density functional theory.

The energy functional in terms of ρ is related to the functional in terms of γ by

$$\tilde{F}_H(\rho) = \underset{\gamma \in \mathcal{P}_{1N}(\rho)}{\text{Min}} \{F_H(\gamma)\} = \underset{\gamma \in \mathcal{P}_{1N}(\rho)}{\text{Min}} \{E_H(D_*^N(\gamma))\} = E_H(D_{\#}^N(\rho)) \quad (4.26)$$

where $\mathcal{P}_{1N}(\rho) = \{\gamma; \rho(\mathbf{r}) = \int \gamma(\mathbf{y})d\xi\}$ and $D_{\#}^N(\rho)$ is the constrained minimizer of the functional $E_H(D_*^N(\gamma))$; $\gamma \in \mathcal{P}_{1N}(\rho)$. If the conditions discussed previously in Sections 3.4 and 3.5 are satisfied Eq. (4.26) determines a path $D_{\#}^N(\rho)$ in \mathcal{S}_N . Once again, such paths in general are distinct from both the HK paths $D_*^N(\gamma)$ and the KS paths $D_{IP^0}^N(\gamma)$.

The values of component functionals referring to *one-particle, spin-free* observables have a constant value on the set $\mathcal{P}_{1N}(\rho)$. This fact is one of the appealing properties of the KS kinetic energy for example:

$$T_{KS}(\gamma) = T_{KS}(\rho) \quad \forall \gamma \in \mathcal{P}_{1N}(\rho) \quad (4.27)$$

This property does *not* hold in general for functionals associated with spin-free two-particle observables nor for spin dependent observables or external magnetic fields.

4.4 Spin-symmetry and Symmetry Breaking

In the case of a ρ -based DFT it is always possible, even when spin is involved nontrivially, to expand in terms of real functions of three spatial variables and in theory obtain an exact ground state energy, while for γ it is *not* possible to restrict the functions thusly. In addition the XC functional and potential in the ρ case cannot contain an explicit dependence on the spin density, as that has been factored out of γ in obtaining ρ . Thus the way that the ρ -based XC potential takes account of spin is very obscure except in the

simplest of configurations. Recall the earlier remark that conventional spin DFT omits (or else must attempt to reparameterize in an obscure way) two of the contributions in (4.24). As the XC potentials are in general unknown and must be approximated by physical and mathematical experience, most practitioners implicitly use the properties of γ , at least in some partial form. This distinction has not always been made clear in the DFT literature and has led to ambiguity, especially in discussions of symmetry breaking. For states with non-trivial spin characteristics, the form of parameterization assumes an important role with regard to symmetry breaking, notably when some of the potentials are not known exactly, as is invariably the case. In the discussion to follow, we remark on the ways an exact potential becomes a potential that is “not known exactly” by virtue of its exact spin-symmetry being different from the spin-symmetry of the problem to which it is applied.

In both the HK and KS cases it is possible to consider the minimization problem by means of functionals of ρ parameterized in terms of expansions of the type

$$\rho(\mathbf{r}) = \sum_{i=1}^{\lfloor \frac{N}{2} \rfloor} \chi_i(\mathbf{r})^2 \quad (4.28)$$

where $\lfloor \frac{N}{2} \rfloor = \frac{N}{2}$ for N even and $= \frac{N+1}{2}$ for N odd. The functions χ in general are different from those in (4.20). In the KS procedure the functions $\{\chi_i; 1 \leq i \leq \lfloor \frac{N}{2} \rfloor\}$ can be identified with the occupied orbitals of the KS IPS and a complementary set $\{\chi_i; \lfloor \frac{N}{2} \rfloor + 1 \leq i \leq s\}$ with the unoccupied ones. However only in the special case of a ground state, $D_{\#}^N(\rho_0)$, that is of the Fukutome [17] time reversal invariant singlet class can these orbitals be used in the natural expansion of its associated FORDO as

$$D_{\#}^1(\rho_0) = P_{\#}(\rho_0) = \sum_{i=1}^s n_i |\chi_i\rangle\langle\chi_i| \otimes (|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|); \quad \chi_i(\mathbf{r}) \in \mathbb{R}; \quad 0 \leq n_i \leq 1 \quad (4.29)$$

In those cases for which the ground state is *not* a time reversal invariant singlet, the FORDO *does not* equal $P_{\#}(\rho_0)$ and other components defined by Eq. (4.21) enter into its expansion. In these cases the $\lfloor \frac{N}{2} \rfloor$ real functions parameterizing ρ_0 *cannot* be identified with the functions that occur in the natural expansion of the FORDO. However they still can be used to define an auxiliary KS IPS that corresponds to a real restricted determinant (i.e., one that contains only doubly occupied, real-valued orbitals). If the corresponding functionals $\tilde{T}_{KS}(\rho)$, $\tilde{F}_{XC,KS}(\rho)$, $\tilde{F}_S(\rho)$, $\tilde{F}_V(\rho)$ were known exactly, this parameterization would lead to the exact ground state energy. This statement is the content of the original HK argument. However, if the functionals are to be approximated, it is possible to obtain better approximations to such ground states by letting $\{\chi_i; 1 \leq i \leq s\}$ be complex-valued functions and considering the more flexible, but equally valid, expansion

$$\rho(\mathbf{r}) = \sum_{i=1}^{\lfloor \frac{N}{2} \rfloor} |\chi_i(\mathbf{r})|^2 \quad (4.30)$$

in the variational process. The complex valued functions appearing in this expansion can, moreover, be identified with the natural orbitals of more general singlet states.

In order to use expansions in terms of functions that determine first order reduced density operators that belong to a general Fukutome class, one needs to consider complex valued functions that have the form of General Spin Orbitals (GSOs). Thus to construct a KS IPS that belongs to a general Fukutome class we consider the following expansion of the charge-spin density

$$\gamma(\mathbf{y}) = \sum_{i=1}^{\lfloor \frac{N}{2} \rfloor} |v_i(\mathbf{y})|^2; \quad v_i(\mathbf{y}) \in \mathbb{C} \quad (4.31)$$

where the "occupied" and "unoccupied" functions $\{v_i; 1 \leq i \leq r\}$ associated with this expansion belong to a particular Fukutome class. Suppose next that an approximation to $F_{XC,KS}$ were to be constructed for that class. Symmetry breaking would occur if a lower ground state energy could be achieved using that approximate functional and allowing the parameter functions $\{v_i; 1 \leq i \leq \lfloor \frac{N}{2} \rfloor\}$, which determine the KS IPS, to belong to a different Fukutome class. Of course one would not do this deliberately, but clearly it could occur for an approximation constructed without explicit consideration of the Fukutome class.

If one restricts attention to the Time Invariant Closed Shell (TICS) singlet class $\gamma = \rho\Theta_{00}$ for the parameterization of γ , one is essentially working with ρ . However, the functionals are based on the general form of γ *not* ρ , e.g. $F_{XC,KS}(\gamma)$ *not* $\tilde{F}_{XC,KS}(\rho)$. If we limit the parameterization of γ in this way we should write the functionals as, for example, $F_{XC,KS}(\gamma)|_{\gamma=\rho\Theta_{00}}$, which is the KS XC functional in the γ formulation of DFT, but with γ restricted to be in the Fukutome TICS class. In this case, the KS determinant can be formed from the real $\lfloor \frac{N}{2} \rfloor$ expansion of $\gamma = \rho\Theta_{00}$, and thus is a determinant formed by real orbitals with occupation numbers 1 or 2. This constraint has the effect of leading to an upper bound to the ground state energy, *even in the case of exact functionals*, if the ground state is not of TICS symmetry.

This symmetry classification has important implications for the adiabatic connection formulation of the KS XC potential [18]. In that treatment, the functional is found from a Pauli coupling constant integral which usually is said to connect from "the non-interacting ground state", i.e. the KS determinant, to the fully interacting ground state. If $F_{XC,KS}(\gamma)|_{\gamma=\rho\Theta_{00}}$ is used then, in general, the coupling constant integral will not connect from the ground state of the non-interacting system to the fully interacting ground state, but rather to an upper bound to the exact ground state.

4.5 Expansions of Rank $\neq \lfloor \frac{N}{2} \rfloor$

In the preceding discussion we expanded the density in terms of $\lfloor \frac{N}{2} \rfloor$ functions, which belonged to a Fukutome class, an expansion that was particularly suited for the construction of a KS auxiliary IPS and the use of the re-grouped exchange correlation

functional $F_{XC,KS}(\gamma)$. This expansion also could be used in solving the HK equation directly without the use of an auxiliary state and such a potential. There is however no compelling mathematical reason to have expansions of rank $\lfloor \frac{N}{2} \rfloor$ or to use IPS auxiliary states. The density γ can be parameterized as an expansion of any rank, $m =$ number of nonzero n_i , in terms of functions belonging to a suitable Fukutome class as

$$\gamma(\mathbf{y}) = \sum_{i=1}^m n_i |\psi_i(\mathbf{y})|^2; \quad \psi_i(\mathbf{y}) \in \mathbb{C}; \quad 0 \leq n_i \leq N; \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}; \quad \sum_{i=1}^m n_i = N \quad (4.32)$$

The reader should note that the limit on each of the positive numbers (weights) $\{n_i\}$ is N not 1, as would be the case if the weights were occupation numbers. These numbers also can be folded into the functions $\{\psi_i\}$ to produce functions $\{v_i\}$ normalized to $\{n_i\}$ i.e. $\langle v_i | v_j \rangle = n_i \delta_{ij}$ as we did in Eq. (4.3). The functions and weights $\{\psi_i, n_i\}$ can be used to parameterize γ in HK type equations or, in the case $\{0 \leq n_i \leq 1; 1 \leq i \leq r; \text{number of non-zero } n_i > N\}$, they can be used to define a correlated auxiliary state for a generalized KS type procedure. A re-grouped exchange correlation potential based on such a state would contain more information about the final N -particle state than an independent particle auxiliary state and thus might speed up iterative solutions of the variational equations. In the extreme case of $m = 1$ one can even express the density as $\rho = \omega \bar{\omega}$, where $\omega = \rho^{\frac{1}{2}}$ (one can take any branch of this function). This factorization leads to the Pauli potential [19], a particularly DFT scheme that we shall discuss elsewhere.

5. Acknowledgments

We have benefited from discussions with Andreas Görling, Mel Levy, John Perdew, and Andreas Savin.

Appendix A: Glossary of Mathematical Symbols

\mathfrak{S}_N	The convex set of N -particle states
$\mathfrak{S}_N(\gamma)$	The set of N -particle states that produce the same density γ
\mathfrak{S}_{N1}	The set of First Order Reduced Density Operators (FORDO's)
$\mathfrak{S}_{NIP}(\gamma)$	The set of Independent Particle FORDO's that produce the same density ρ
$\mathfrak{B}_1(\mathcal{H}^N)$	The space of trace class operators acting in the Hilbert space \mathcal{H}^N
\mathcal{H}^N	The Hilbert space of pure N -particle fermion states. It is an N -fold antisymmetric tensor product of the Hilbert space of pure one-particle states.
D^N	N -particle state operator, if it is not a projector onto a 1-dimensional subspace it represents a mixed N -particle state

$\mathcal{B}_2(\mathcal{H}^N)$	The Hilbert space of Hilbert Schmidt operators acting in \mathcal{H}^N
\mathcal{D}^N	Fiber Bundle with base space \mathcal{P}_{1N} and fibers $\mathcal{S}_N(\gamma)$
\mathcal{L}	Lagrangians
$\binom{r}{N}$	Combinatorial coefficient "r choose N"
$\gamma(\mathbf{y})$	Charge-spin density as a function of space and spin variables (\mathbf{r}, ξ)
\mathbf{Y}	$\mathbb{R}^3 \times \mathbb{C}^2$
$L_1(\mathbf{Y})$	Linear normed space of absolutely integrable complex-valued functions of 3 real and 2 complex variables.
$L_2(\mathbf{Y})$	Hilbert space of square-integrable complex-valued functions of 3 real and 2 complex variables.
Ξ_N^1	Linear map from the space of bounded N -particle operators to the space of absolutely integrable complex-valued functions of the variables \mathbf{y} .
$\Phi(\mathbf{y})$	Continuous Fermi field annihilation operator that depends on the charge-spin variable \mathbf{y} .
$\{a_i, a_i^\dagger\}$	Discrete Fermi field annihilation and creation operators
$\mathcal{B}_1(\mathcal{H}^N) / \text{Ker} \Xi_N^1$	Linear space of equivalence classes of Trace Class operators. The operators are equivalent if their difference lies in the kernel of Ξ_N^1
\mathcal{P}_{1N}	Positive cone of charge-spin densities derived from N -particle states.
E_H	Linear energy functional based on the Hamiltonian H ; it acts on the space of N -particle Trace Class operators.
E_T	Linear energy functional based on the Kinetic Energy operator.
E_{XC}	Linear energy functional based on the XC terms.
F_H	Nonlinear energy functional based on the Hamiltonian H ; it acts on the space of absolutely integrable complex valued functions of the variables \mathbf{y} .
$D_*^N(\gamma)$	Path of N -particle states; each state on the path corresponds to a density γ and is the minimum energy state for that density.
$D_{IP\phi}^N(\gamma)$	Paths of IP N -particle states.
$Q_*(\gamma)$	Path of Hilbert Schmidt operators

$[\zeta]_N$	Equivalence classes of N -particle Trace Class operators that all map to the same function ζ .
$\langle \rho \rangle_N$	Set of N -particle Hilbert-Schmidt operators that produce N -particle states associated with the same charge-spin density.
\mathbb{C}	The complex numbers
FORDO	First Order Reduced Density Operator
HK	Hohenberg-Kohn
KS	Kohn-Sham
NGSO	Natural General Spin Orbitals
\mathbb{R}	The real numbers

Appendix B: First Order Reduced Density Operator

The FORDO is defined by a linear contraction map, C_N^1 , given by the following

$$\begin{aligned}
C_N^1: \mathcal{B}_1(\mathcal{H}^N) &\rightarrow \mathcal{B}_1(\mathcal{H}^1) \\
D^1 &= C_N^1(D^N) \\
D_{ij}^1 &= Tr\{a_j^\dagger a_i D^N\} \\
D^1 &= \sum_{i,j=1}^r D_{ij}^1 a_i^\dagger a_j
\end{aligned} \tag{B.1}$$

The integral kernel of the FORDO is given by

$$\begin{aligned}
D^1(\mathbf{y}_1, \mathbf{y}_2) &= Tr\{\Phi^\dagger(\mathbf{y}_2)\Phi(\mathbf{y}_1)D^N\} \\
D^1 &= \iint_{\mathbf{Y} \times \mathbf{Y}} D^1(\mathbf{y}_1, \mathbf{y}_2)\Phi^\dagger(\mathbf{y}_1)\Phi(\mathbf{y}_2)d\mathbf{y}_1 d\mathbf{y}_2
\end{aligned} \tag{B.2}$$

and the density is thus the diagonal of this kernel, i.e. $\gamma(\mathbf{y}) = D^1(\mathbf{y}, \mathbf{y})$

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