Time-Dependent Variational Principle in

Density Functional Theory

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1. INTRODUCTION

Among the many ways in which explicit time dependence appears in the quantum mechanics of molecules is via double time propagators (1), notably the electron propagator and the polarization propagator. Some of the historical development regarding those quantities motivates and informs the present work, hence a summary is appropriate. Diverse decoupling schemes have been devised and used to generate approximations to both of those propagators (for example 2, 3). A major problem in the first order approximation for the polarization propagator, [equivalent to the Random Phase Approximation (RPA) - also known as the linearized Time-Dependent Hartree Fock (TDHF) approximation], is the inconsistency of the ground state involved in the definition of that propagator. The adjoints of the perturbationaly corrected excitation operators produced by RPA do not kill this ground state, as they should if the theory were consistent. Some time ago it was shown (4) that the nearest one can get to a consistent ground state is via states of the Antisymmetrized Geminal Power form. Subsequently the resulting generalized RPA theory was used to calculate the excitation spectra of small molecules (5).

The solution to the consistent ground state problem turns out to be closely related to the theory of coherent states and the theory of group representations. Taken together, the two topics involve the construction of group-related generalized phase spaces. Within this context, Öhrn and co-workers (6) have exploited the Time-Dependent Variational Principle (TDVP) as a means of obtaining approximate solutions to the Time-Dependent Schrödinger Equation (TDSE) for systems of electrons and nuclei (7). By application of this principle to coherent states of both electrons and nuclei, the Born-Oppenheimer approximation is avoided, hence the time evolution of electrons and nuclei can be treated efficiently without first finding electronic potential energy surfaces, then studying the coupled motion of nuclei on these surfaces. Typically, the variables used are nuclear coordinates and momenta and complex parameters labeling the electronic state. The approximate solutions to the TDSE are characterized by the evolution paths of these variables as determined by generalized classical equations of motion obtained from the TDVP.

Here we summarize our recent work to extend and apply these ideas to the powerful practical and conceptual tools of Density Functional Theory (8). Specifically, the formalism used in the TDVP is extended to include mixed states, with the states labeled by the densities as functions of electronic space and spin coordinates. (In the treatment presented here we do not explicitly consider the nuclei but consider them to be fixed. Elsewhere we shall show that it is indeed straightforward to extend our treatment in the same way as Öhrn et al. and obtain equations that avoid the Born-Oppenheimer approximation.) In

this article we obtain a formulation of *exact* equations for the evolution of electronic space-spin densities, which are equivalent to the Heisenberg equation of motion for the electrons in the system. Using the observation that densities can be expressed as quadratic expansions of functions, we also obtain *exact* equations for these one-particle functions. Not all the proofs and detailed analyses are given here, but enough is presented to delineate the entire formal structure.

A brief summary of motivation from the DFT perspective also may be helpful. On the whole, contemporary versions of Density Functional Theory are presented in two separate conceptual and logical frameworks, one each for time-independent and time-dependent DFT. Even within the constrained search formulation of time-independent DFT, there are several rather deep and interconnected questions. Commonly these are discussed in terms of symmetry (and symmetry breaking), occupation number distributions, and functional differentiability. Their resolution is important for both fundamental reasons and to provide pathways to more powerful and reliable DFT approximations. Implicit in them is the issue of mixed states. Because customary formulations of time-dependent DFT are separate, it is not evident how resolution of those issues in the time-independent case would carry over. Further, the importance of parameter-space metrics in the work of Öhrn et al. versus the absence of such metrics in conventional time-dependent DFT suggests strongly that a formulation directly from the TDVP would be beneficial and clarifying. Among other things, such a formulation would provide a rigorous basis for the use of dynamics in parameter space, including mixed states right from the start, as well as a significantly enhanced foundation for constructing approximations.

2. MIXED STATE TIME-DEPENDENT VARIATIONAL PRINCIPLE

Conventional presentations of DFT start with pure states but sooner or later encounter mixed states and densities (ensemble densities is the usual formulation in the DFT literature) as well. These arise, for example in formation or breaking of chemical bonds and in treatments of so-called "static correlation" (situations in which several different one-electron configurations are nearly degenerate). Much of the DFT literature treats these problems by extension and generalization from pure state, closed shell system results. A more inclusively systematic treatment is preferable. Therefore, the first task is to obtain the Time-Dependent Variational Principle (TDVP) in a form which includes mixed states.

In a landmark publication in 1981, Kramer and Saraceno (7) [hereafter "K&S" to distinguish from Kohn-Sham, usually denoted as "KS" in the DFT literature, a usage we follow] showed how to use the Time-Dependent Variational Principle to construct generalized classical equations of motion for

quantum mechanical state vectors in terms of labels that characterize those vectors parametrically. (Obviously, "classical" in this setting refers to the form of the equations, not the content.) This construction leads to equations that determine evolution paths in a parameter space. In the case of a parameterization that covers all of state space those equations are *entirely equivalent* to the exact Time-Dependent Equation Schrödinger Equation (TDSE) and to approximate TDSE's for parameterizations that label a subset of states in a continuous fashion. In their work they showed that in certain cases the parameters could be related to group coset spaces (9) and give rise to families of Coherent States (CS) (10-13), where the set of coherent states is generated by the action of a coset on a reference state. A familiar example is the set of single determinantal states, in which all the states are generated by the action of a coset of the group of one-particle unitary transformations acting on a given single determinantal reference state, leading to the Thouless parameterization of these states (14). In the case of group-generated CS's, the labels are complex variables that holomorphically (complex analytically) parameterize a set of N-particle states and the generalized dynamics takes place in the manifold of these states (which in general is nonlinear). In general not all N-particle states are produced by the action of the chosen group on the reference state. The resulting equations of motion correspond to the restriction of the TDSE to this submanifold. This formulation of approximate TDSE's has been examined at great length in many contexts (6,15-18).

The most general formulation is in terms of real parameters, as any complex parameterization can always expanded into real and imaginary parts, while the converse construction (complex parameters from combination of real ones) is not always possible. The real parameterization does not take one directly into the group and coherent state formalism. However in the context of DFT the real parameterization is particularly natural, since the pervasive perspective is that N-particle states are labeled by densities which are real-valued functions of space and spin variables.

The K&S treatment is in terms of pure N-particle states i.e. vectors in an N-particle Hilbert space. As noted, to encompass DFT in its most general form one must consider mixed N-particle states i.e. states described by N-particle Density Operators. Thus this section extends the K&S treatment to include mixed states by using the vector space structure of N-particle operator space and applying the K&S treatment to state "super vectors" in this operator vector space [If one can define a linear structure on a space of operators, then those operators can be viewed as *supervectors* and any map that maps a linear operator space into itself can be viewed as a *superoperator*. The terms *supervector* and *superoperator* were first introduced by Zwanzig (19)] Although most of the formal manipulations and expressions are identical in appearance (with those of K&S), the interpretation in terms of operators is quite different.

Note to the reader: the notation can be somewhat intricate, thus it is summarized in Appendix A.

2.1 States and Superoperators

The mixed and pure states of an N-particle fermion system can be described by positive and normalized operators, $\mathcal{S}_N$, which form a convex set contained in the space of Trace Class (Appendix B) operators $\mathcal{B}_1(\mathcal{H}^N)$ acting in the N-particle fermion Hilbert space $\mathcal{H}^N$.

$$\mathcal{S}_N = \left\{ D^N; D^N \geq 0; Tr\{D^N\} = 1; D^N \in \mathcal{B}_1(\mathcal{H}^N) \right\} \qquad (2.1)$$

where $\mathcal{H}^N$ is defined to be the N-fold antisymmetrized tensor product of the one-particle Hilbert space $\mathcal{H}^1$.

Positive elements, X, of the vector space of operators $\mathcal{B}_1(\mathcal{H}^N)$ can always be expressed as a product of a Hilbert-Schmidt operator (Appendix B) with its adjoint as $X=QQ^\dagger$. [The Harriman (20) decomposition of the density into positive sums of products of orbitals is in fact a very special case of this relationship, which will be important later.] One needs to keep in mind that this factorization is not unique however: QU for any unitary U produces the same X. Moreover UQ produces the same X for U belonging to the invariance group of X (Appendix C). The space of Hilbert-Schmidt operators, $\mathcal{B}_2(\mathcal{H}^N)$, is a Hilbert space that has an inner product defined in terms of the trace operation

$$(X|Y) = Tr\{X^\dagger Y\} \qquad (2.2)$$

This fact allows us to express the set $\mathcal{S}_N$ as the unit sphere in $\mathcal{B}_2(\mathcal{H}^N)$ as

$$\mathcal{S}_N = \left\{ Q;(Q|Q) = 1; Q \in \mathcal{B}_2(\mathcal{H}^N) \right\} \qquad (2.3)$$

The action of the Hamiltonian, H, can be expressed as a superoperator mapping the Hilbert space $\mathcal{B}_2(\mathcal{H}^N)$ into itself by

$$\hat{H}:Q \rightarrow HQ; \ Q \in \mathcal{B}_2(\mathcal{H}^N) \qquad (2.4)$$

The superoperator $\hat{H}$ inherits the unboundness of H and its domain is defined as

$$Dom(\hat{H}) = \left\{ Q, HQ \in \mathcal{B}_2(\mathcal{H}^N) \right\} \qquad (2.5)$$

In the following we consider Hamiltonians, $H(t)$, that are explicitly time dependent. The definitions Eq. (2.4)-(2.5) also hold without modification in these cases.

2.2 State Evolution Equations

Now consider operators Q that depend on real parameters $\mathbf{x}$, which can be considered as coordinates of points of a linear or nonlinear manifold $\mathcal{M}$ of operators Q contained in $\mathcal{B}_2(\mathcal{H}^N)$, [including $\mathcal{B}_2(\mathcal{H}^N)$ itself], i.e. the real coordinates $\mathbf{x}$ denote a point $Q \in \mathcal{M}$. Following K&S generalized classical equations of motion for evolution paths $\mathbf{x}(t)$ can be obtained for these operators, which are given by

$$\left.\begin{array}{l} \{x_i, \mathcal{E}\} = \dot{x}_i \\[8pt] \mathcal{E}(\mathbf{x}) = \dfrac{\mathcal{H}(\mathbf{x})}{\mathcal{S}(\mathbf{x})} = \dfrac{\left(Q(\mathbf{x}) \mid \hat{H} Q(\mathbf{x})\right)}{\left(Q(\mathbf{x}) \mid Q(\mathbf{x})\right)} \end{array}\right\} \tag{2.6}$$

The Poisson brackets are defined for functions $f: \mathcal{M} \to \mathbf{C}$ by

$$\{f, g\} = \sum_{i,j} \frac{\partial f}{\partial x_i} \xi_{ij} \frac{\partial g}{\partial x_j} \tag{2.7}$$

where the antisymmetric matrix that defines a "phase space" structure for the manifold was shown by K&S to be given by

$$\begin{array}{c} \xi_{ij} = \left(\eta^{-1}\right)_{ij} \\[8pt] \eta_{ij} = i\left\{\dfrac{\partial}{\partial x_i'}\dfrac{\partial}{\partial x_j} - \dfrac{\partial}{\partial x_i}\dfrac{\partial}{\partial x_j'}\right\} \ln\left\{\left(Q(\mathbf{x}')\mid Q(\mathbf{x})\right)\right\}\Bigg|_{\mathbf{x}'=\mathbf{x}} \end{array} \tag{2.8}$$

Note that for general parameterizations this metric matrix is *neither skew diagonal nor* constant; see below. The equations of motion expressed in Eq. (2.6) are obtained by using the Principle of Stationary Action, $\delta \mathcal{A} = 0$, with Lagrangian

$$\mathcal{L}\left(Q(\mathbf{x}(t)), Q(\mathbf{x}(t))^\dagger, t\right) = \mathrm{Re}\left\{\frac{\left(Q(\mathbf{x}(t))\left[i\dfrac{\hat{\partial}}{\partial t} - \hat{H}(t)\right]Q(\mathbf{x}(t))\right)}{(Q(\mathbf{x}(t)) \mid Q(\mathbf{x}(t)))}\right\} \tag{2.9}$$

and Action

$$\mathcal{A} = \int_{t_i}^{t_f} \mathcal{L}\left(Q(\mathbf{x}(t)), Q(\mathbf{x}(t))^\dagger, t\right) dt \tag{2.10}$$

where the end points $\left(x(t_i), x(t_f)\right)$ of the paths are held fixed. The "superoperator", $i\dfrac{\hat{\partial}}{\partial t}$, that produces i times the time rate of change of operators and is defined in a way analogous with $\hat{H}(t)$ in Eq. (2.4), is not self-adjoint on

the space $\mathcal{B}_2\left(\mathcal{H}^N\right)$. Therefore the process of taking the real part of the inner product in Eq. (2.9) is significant.

The metric term Eq. (2.8) is important for all cases in which the manifold-$\mathcal{M}$ has non-zero curvature and is thus nonlinear, e.g. in the cases of Time-Dependent Hartree-Fock (TDHF) and Time-Dependent Multi Configurational Self-Consistent Field (TDMCSCF) calculations. In such situations the metric tensor ξ varies from point to point and has a nontrivial effect on the time evolution. It plays the role of a time-dependent force (somewhat like the location-dependent gravitational force which arises in general relativity from the curvature of space-time). In the case of flat i.e. linear manifolds, as are found in Time-Dependent Configuration Interaction (TDCI) calculations, the metric is constant and does not have a significant effect on the dynamics.

If the inverse in Eq. (2.8) does not exist then the metric is singular, in which case the parameterization of the manifold of states is redundant. That is, the parameters are not independent, or splitting of the manifold occurs, as in potential curve crossing in quantum molecular dynamics. In both cases, the causes of the singularity must be studied and revisions made to the coordinate charts on the manifold (i.e. the way the operators are parameterized) in order to proceed with calculations.

The form of the action principle given above was first applied to quantum mechanics to describe the time evolution of pure states (i.e. wavefunctions) by Frenkel (21) and leads in the case that the manifold $\mathcal{M}$ is all of $\mathcal{H}^N$ to the TDSE. We have extended it to more general operator manifolds $\mathcal{M} \subseteq \mathcal{B}_2\left(\mathcal{H}^N\right)$ in the manner outlined above, and for the case $\mathcal{M} = \mathcal{B}_2\left(\mathcal{H}^N\right)$, have shown (22) that the equations of motion (2.6) are equivalent to the Heisenberg Equations of Motion (HEM) for the N-particle state operators D^N.

$$i\dot{D}^N = \left[H, D^N\right]; \quad D^N = QQ^\dagger; \quad Tr\left\{D^N\right\} = 1 \qquad (2.11)$$

In this particular case the $\mathbf{x} \equiv \left(\mathbf{x}_1, \mathbf{x}_2\right)$ parameters label the Q operators by

$$Q(\mathbf{x}) = Q\left(\mathbf{x}_1, \mathbf{x}_2\right) = \sum_{1 \leq k, l \leq d} c_{kl}\left|\Phi_k\right\rangle\left\langle\Phi_l\right| \qquad (2.12)$$

where $x_{1kl} = \mathrm{Re}\, c_{kl}$, $x_{2kl} = \mathrm{Im}\, c_{kl}$, $d = \binom{r}{N}$, the points $\mathbf{x} \equiv \left(\mathbf{x}_1, \mathbf{x}_2\right)$ lie on the hypersphere

$$\sum_{k,l=1}^{d}\left(x_{1kl}^2 + x_{2kl}^2\right) = 1 \qquad (2.13)$$

$$\left\{ \Phi_k; 1 \le k \le \binom{r}{N} \right\}$$ is a complete orthonormal basis for $\mathcal{H}^N$ and r is the dimension of one-particle space, which in the exact case is infinite.

The equations of motion (2.6) can be expressed compactly in matrix form as

$$\frac{d\mathbf{x}}{dt} = \eta^{-1} \frac{\partial \mathcal{E}}{\partial \mathbf{x}} \tag{2.14}$$

and solved by standard integration techniques (23).

The preceding evolution equations also can be used to generate equations for stationary states by setting the time derivative to zero giving the two equivalent forms (signified by the double arrow):

$$\{x_i, \mathcal{E}\} = 0; \text{ for all } i \Leftrightarrow \eta^{-1} \frac{\partial \mathcal{E}}{\partial \mathbf{x}} = \mathbf{0} \tag{2.15}$$

3. TIME INDEPENDENT DENSITY FUNCTIONAL THEORY

In order to apply the preceding development to states parameterized by densities we must first analyze the structure and properties of this type of parameterization.

3.1 Definition of the energy functional of the density

The relationship between N-particle states, in which we include mixed states, represented by N-particle operators as defined in Eq. (2.1), and the space-spin density $\rho(\mathbf{y})$ is not 1-1. Here and throughout the following development, $\mathbf{y}$ is the combined space-spin variable $(\mathbf{r}, \sigma)$. These facts are the essence of the power and simplicity of the density functional method and at the same time the source of its conceptual complexity and intricacy. The power and simplicity come from being able to characterize an N-particle system by a real positive semi-definite function of a single 3D spatial variable and one 2D complex spin variable, while the conceptual complexity and intricacy come from developing an explicit understanding of how such a density determines a N-particle state.

To develop a framework in which to treat these topics in a rigorous manner for both time-dependent and independent systems, we adapt the *constrained search* of Levy (24) to generate a well-defined energy functional of the density, then follow a constrained optimization analysis of the problem as described, for example, in the book by Hestenes (25). These techniques allow

one to specify the way paths of N-particle density operators can be defined in N-particle operator space such that they are labeled by densities in 1-1 fashion. The expectation of the Hamiltonian with respect to N-particle states on these paths then becomes a well-defined functional of the density $\rho(\mathbf{y})$ and the ground state energy is the minimum value of this functional. The treatment is somewhat akin to that of Kryachko and Ludeña's "orbits"(26) but differs (in an essential fashion) in determining the paths by optimization criteria which assure that the resulting functionals have well-defined functional derivatives irrespective of the topology of the density. Kryachko and Ludeña, in contrast, identify orbits by employing the Bader density surface criterion (27), which means that those orbits are connected inescapably with the molecular point group symmetry. Even at the time-independent level, molecular structure and bonding often involve changes in the point group symmetry, so that inescapable connection seems to intertwine two issues better left apart. Dynamics simply makes such conceptual and procedural issues harder.

First we define the linear map that produces the densities from N-particle states. It is a map from the space of N-particle Trace Class operators into the space of complex valued absolute integrable functions of space-spin variables

$$\Xi_N^1 : \mathcal{B}_1\left(\mathcal{H}^N\right) \to L_1\left(\mathbf{R}^3 \times \mathbf{C}^2\right) \equiv L_1(\mathbf{Y}) \tag{3.1}$$

defined by

$$\zeta(\mathbf{y}) = \Xi_N^1(X)(\mathbf{y}) = Tr\left\{\Phi^\dagger(\mathbf{y})\Phi(\mathbf{y})X\right\} \in L_1(\mathbf{Y}). \tag{3.2}$$

The field operators used in the definition above are given by

$$\Phi(\mathbf{y}) = \sum_{1 \leq i \leq r} \overline{\varphi}_i(\mathbf{y}) a_i \tag{3.3}$$

in terms of the discrete field operators, $\left\{a_i, a_i^\dagger\right\}$, which are defined using a basis of one-particle functions of space and spin $\left\{\varphi_i ; 1 \leq i \leq r\right\}$ and their action on the vacuum vector $|\phi\rangle$

$$a_i^\dagger|\phi\rangle = |\varphi_i\rangle \tag{3.4}$$

The field operators satisfy the fermion anti-commutation relationships

$$\left[\Phi(\mathbf{y}), \Phi^\dagger(\mathbf{y}')\right]_+ = \delta(\mathbf{y} - \mathbf{y}')$$

$$\left[a_i, a_j^\dagger\right]_+ = \delta_{ij} \tag{3.5}$$

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

$$X \sim Y \Leftrightarrow X - Y \in Ker\{\Xi_N^1\} \Leftrightarrow \Xi_N^1(X) = \Xi_N^1(Y) = \zeta \qquad (3.6)$$

where the doubled arrow indicates equivalent statements. We denote these equivalence classes by $[\zeta]_N$ and note that they form a linear space, in quotient notation, $\mathcal{B}_1(\mathcal{H}^N) \big/ Ker\Xi_N^1$. 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 integrate to the value N

$$\mathcal{P}_{1N} = \left\{ \rho; \rho(\mathbf{y}) \geq 0, \int \rho(\mathbf{y}) d\mathbf{y} = N \right\} \qquad (3.7)$$

Harriman (20) 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 (28) where not every positive two-particle operator comes from a state in $\mathcal{S}_N$ so the contraction map in that case does *not* have the "onto" property.

The energy functional defined by the Hamiltonian, *H*,

$$E_H : \mathcal{S}_N \rightarrow \mathbf{R}$$
$$E_H(D^N) = Tr\{HD^N\} \qquad (3.8)$$

is, however, not uniquely defined on the equivalence classes $[\rho]_N$, i.e. it is not defined on the space $\mathcal{B}_1(\mathcal{H}^N) \big/ Ker\Xi_N^1$ as many different D^N 's give the same ρ while producing different values $E_H(D^N)$. Thus E_H is not well-defined as it is multivalued on individual equivalence classes. In order to obtain an energy functional that is well-defined, we continue with the constrained search logic and define another functional in terms of the space-spin density as

$$F_H(\rho) = \underset{D^N \in \mathcal{S}_N(\rho)}{Min} E_H(D^N) = E_H(D_*^N(\rho)) \qquad (3.9)$$

where $\mathcal{S}_N(\rho) = [\rho]_N \cap \mathcal{S}_N$ is the set of N-particle states that produce the same density and $D_*^N(\rho)$ is the minimizer in the set $\mathcal{S}_N(\rho)$. Note that we exclude the case of a non-unique minimizer; see Savin (29) for a related discussion. The minimization of Eq. (3.9) contains three types of constraints, normalization, positivity and fixed density. The normalization and positivity constraints can be

handled by the factorization $D^N = \dfrac{QQ^\dagger}{Tr\{QQ^\dagger\}}$, which leads to the energy

functional definition

$$F_H(\rho) = \underset{QQ^\dagger \in \mathcal{S}_N(\rho)}{Min} \frac{Tr\{HQQ^\dagger\}}{Tr\{QQ^\dagger\}} = \underset{Q \in \langle \rho \rangle_N}{Min} E_H(Q)$$

(3.10)

$$= \underset{Q \in \langle \rho \rangle_N}{Min} \frac{\left(Q|\hat{H}Q\right)}{\left(Q|Q\right)} = E_H\left(Q_*(\rho)\right)$$

One can show (30) that densities are square integrable and thus belong to the Hilbert space $L_2(\mathbf{Y})$ of square integrable functions. This allows one to define the set, $\langle \rho \rangle_N$, of feasible Q's by a quadratic constraint function for a *fixed* ρ as

$$g: \mathcal{B}_2\left(\mathcal{H}^N\right) \to L_2(\mathbf{Y})$$

$$g(Q,\rho) = 0$$

(3.11)

$$g(Q,\rho) = \Xi_N^1\left(QQ^\dagger\right) - \rho$$

The variation in Eq. (3.10) can be carried out by using a Lagrangian function

$$\mathcal{L}(Q,\lambda,\rho) = E_H(Q) - \int_{\mathbf{Y}} \lambda(\mathbf{y})g(\mathbf{y})d\mathbf{y}$$

(3.12)

whose stationary points determine the constrained minima of $E_H(Q)$. By considering the sensitivity of the minimizer, $Q_*(\rho)$, to variations in ρ and checking that certain conditions on the first and second derivatives of $\mathcal{L}(Q,\lambda,\rho)$ are satisfied Hestenes (25) showed that one can define a path of solutions, $Q_*(\rho)$, parameterized by ρ. On this path one can define an energy functional

$$F_H(\rho) = E_H\left(Q_*(\rho)\right)$$

(3.13)

and a Lagrange parameter functional, $\lambda(\rho)$, which can be identified with the functional derivative $\frac{\delta F_H}{\delta \rho}$ of $F_H(\rho)$ along that path. 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 $\mathcal{B}_2\left(\mathcal{H}^N\right)$ on which the energy is also a 1-1 functional, but on those paths the following crucial fact will not be true

$$E_0 = \underset{\rho \in D}{Min} \{F_H(\rho)\}$$

$$D = \left\{\rho \mid \rho(\mathbf{y}) \geq 0; \int \rho(\mathbf{y})d\mathbf{y} = N\right\}$$

(3.14)

where E_0 is the ground state energy of the system. The paths $Q_*(\rho)$ clearly define paths in $\mathcal{B}_1(\mathcal{H}^N)$ by $D_*^N(\rho) = Q_*(\rho)Q_*(\rho)^\dagger$. The preceding construction of the energy functional is discussed in more detail in (30).

The explicit form of the functional F_H is of course unknown and in practical applications has to be approximated. In order to facilitate the creation of these approximations one decomposes F_H into a sum of other functionals that focuses all the unknowns into one component, the exchange-correlation functional, F_{XC}.

$$F_H(\rho) = F_C(\rho) + F_{XC}(\rho) + F_{eN}(\rho) + F_{Ext}(\rho) + F_T(\rho) \tag{3.15}$$

(with subscripts *C, XC, eN, Ext*, and *T* denoting Coulomb, exchange-correlation, electron-nuclear attraction, external, and kinetic energies respectively). It is crucial to remark that (3.15) is *not* the Kohn-Sham decomposition familiar in conventional presentations of DFT. There is no reference, model, nor auxiliary system involved in (3.15). From the construction presented above it is clear that in order to maintain consistency and to define functional derivatives properly all these functionals need to be defined on the same path in $\mathcal{B}_2(\mathcal{H}^N)$. These two observations lead to what may be unfamiliar definitions for the kinetic energy functional and the exchange-correlation functional, as follows:

$$F_C(\rho) = \frac{1}{2}\int \frac{\rho(\mathbf{y})\rho(\mathbf{y}')}{\|\mathbf{y}-\mathbf{y}'\|}d\mathbf{y}d\mathbf{y}'$$

$$F_T(\rho) = Tr\left\{-\frac{1}{2}\sum_i \nabla_i^2\{Q_*(\rho)Q_*(\rho)^\dagger\}\right\} \equiv Tr\left\{TQ_*(\rho)Q_*(\rho)^\dagger\right\} = E_T\left(D_*^N(\rho)\right)$$

$$F_{XC}(\rho) = Tr\left\{\left(\frac{1}{r_{12}}\right)Q_*(\rho)Q_*(\rho)^\dagger\right\} - F_C(\rho) = E_{XC}\left(D_*^N(\rho)\right)$$

(3.16)

$$F_{eN}(\rho) = -\int \rho(\mathbf{y})\sum_{i\mu} \frac{Z_\mu}{\|\mathbf{r}_i - \mathbf{R}_\mu\|}d\mathbf{y}$$

$$F_{Ext}(\rho) = \int \rho(\mathbf{y})\sum_i V(\mathbf{r}_i)d\mathbf{y}$$

Note in particular that the exchange-correlation functional that emerges here does not involve the kinetic energy. From the perspective of the DFT literature,

(3.16) is a formulation of the Hohenberg-Kohn functional that is constructed to ensure that the functional derivatives required for variational minimization actually exist. We return to these issues in Sect. 3.3. Also note that in the time dependent case the external potential $V(\mathbf{r}_i)$ is often considered to be explicitly time dependent and further, that if nuclear motions also are taken into account the eN term is also time dependent.

3.2 Factoring the Energy Functional through the First Order Reduced Density Operator.

An appealing way to apply the constraint expressed in Eq. (3.14) is to make connection with Natural Orbitals (31), in particular, to express ρ as a functional of the occupation numbers, *n*, and Natural General Spin Orbitals (NGSO's), $\{\psi_i\}$, of the First Order Reduced Density Operator (FORDO) associated with the N-particle state appearing in the energy expression Eq. (3.8). In order to introduce the variables *n* and $\{\psi_i\}$ in a well-defined manner, the constrained search process Eq. (3.9) needs to be factored into two stages. The first search is over all N-particle states that produce the same FORDO and hence produces an energy functional of the FORDO. The second search is over all FORDO's that correspond to a fixed density, thus producing an energy functional of the density. This sequential process constructs paths in N-particle state space that are labeled by FORDO's and paths in the set of FORDO's that are labeled by densities. On these paths there is 1-1 correspondence among N-particle states, FORDO's and densities.

FORDO's are determined by their occupation numbers and their NGSO's, a relationship that is only unique up to unitary transformations that mix NGSO's with the same occupation numbers. However one can parameterize this association to make it unique. Hence on the paths determined by the constrained energy functional, one has a 1-1 correspondence between $\{n_i, \psi_i\}$ and densities, and densities thus can be viewed as a functional of $\{n_i, \psi_i\}$. This construction leads to variational equations for the ground state energy in terms of occupation numbers and NGSO's.

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

$$C_N^1 : \mathcal{B}_1\left(\mathcal{H}^N\right) \rightarrow \mathcal{B}_1\left(\mathcal{H}^1\right)$$

$$D^1 = C_N^1\left(D^N\right)$$

$$D_{ij}^1 = Tr\left\{a_j^\dagger a_i D^N\right\} \tag{3.17}$$

$$D^1 = \sum_{i,j=1}^r D_{ij}^1 a_i^\dagger a_j$$

The energy functional, $O_H\left(D^1\right)$, of the FORDO is defined by

$$O_H\left(D^1\right) = \underset{D^N \in \mathcal{S}_N\left(D^1\right)}{Min} E_H\left(D^N\right) = E_H\left(D_\#^N\left(D^1\right)\right) \tag{3.18}$$

in terms of the energy E_H on the path $D_\#^N\left(D^1\right)$, where $\mathcal{S}_N\left(D^1\right) = \left[D^1\right]_N \cap \mathcal{S}_N$

is the set of N-particle states that contract to the same FORDO D^1. (Note that non-positive operators also contract to D^1 thus the content of $[D^1]_N$ is not limited to states.) The equivalence classes $\left[X\right]_N$; $X \in \mathcal{B}_1\left(\mathcal{H}^1\right)$ are defined in an

analogous manner to $\left[\rho\right]_N$, by replacing Ξ_N^1 by C_N^1, $L_1(\mathbf{Y})$ by $\mathcal{B}_1\left(\mathcal{H}^1\right)$ in Eqs. (3.1), (3.2), (3.6) and considering off-diagonal values in Eq. (3.2). The energy functional F_H from Eq. (3.9) then can be expressed as

$$F_H(\rho) = \underset{D^1 \in \mathcal{S}_{N1}(\rho)}{Min} O_H\left(D^1\right) = O_H\left(D_\#^1(\rho)\right) \tag{3.19}$$

in terms of O_H defined on the path $D_\#^1(\rho)$. Here $\mathcal{S}_{N1}(\rho) = \left[\rho\right]_1 \cap \mathcal{S}_{N1}$ is the set of FORDO's that produce the same density, $\mathcal{S}_{N1}$ is the set of N-Representable, FORDO's and $\left[\rho\right]_1$ the set of one-particle Trace Class operators that map to the density ρ. The equivalence classes $\left[\rho\right]_1$ in one-particle Trace Class operator space $\mathcal{B}_1\left(\mathcal{H}^1\right)$ are defined analogously to $\left[\rho\right]_N$, which are in N-particle operator space. The path $D_*^N(\rho)$ can then be expressed as the composition

$$D_*^N(\rho) = D_\#^N\left(D_\#^1(\rho)\right) = \left(D_\#^N \circ D_\#^1\right)(\rho) \tag{3.20}$$

A FORDO D^1 always can be expressed in natural form as

$$D^1 = \sum_{1 \le i \le r} n_i \left|\psi_i\right\rangle\!\left\langle\psi_i\right| = \sum_{1 \le i \le r} \left|v_i\right\rangle\!\left\langle v_i\right|$$

$$\left\langle\psi_i \middle| \psi_j\right\rangle = \delta_{ij}; \quad \left\langle v_i \middle| v_j\right\rangle = n_i \delta_{ij}; \ 0 \le n_i \le 1 \tag{3.21}$$

$$\sum_{1 \le i \le r} n_i = N$$

where we have introduced the occupation-number-normalized NGSO's $\{v_i\}$. On the path $D_\#(\rho)$ there is a 1-1 correspondence

$$\rho \leftrightarrow D_\#^1(\rho) \leftrightarrow \{v_i(\rho); 1 \leq i \leq r\} \equiv \mathbf{v}(\rho) \qquad (3.22)$$

As this relationship is 1-1, the density ρ can be expressed as a function of $\mathbf{v}$, i.e. $\rho = \rho(\mathbf{v})$, and both ρ and $\mathbf{v}$ can be treated as equivalent, but different, variables for the argument of the energy functional F_H. The minimization of Eq. (3.14) that determines the ground state energy then becomes

$$E_0 = \underset{\mathbf{v} \in \mathcal{K}}{Min}\{F_H(\mathbf{v})\} \qquad (3.23)$$

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

$$h_N(\mathbf{v}) = \sum_{i=1}^{r} |v_i|^2 - N = 0$$

$$h_{ii}(\mathbf{v}) = |v_i|^2 - 1 \leq 0 \qquad (3.24)$$

$$h_{ij}(\mathbf{v}) = \langle v_i | v_j \rangle = 0; \; i \neq j$$

and the constrained minimum of Eq. (3.23) can be obtained from the Lagrangian

$$\mathcal{L}_F(\mathbf{v}) = F_H(\mathbf{v}) - \sum_{1 \leq i,j \leq r} \lambda_{ij} h_{ij} - \mu h_N \qquad (3.25)$$

Noting that

$$\rho(\mathbf{y}) = \sum_{1 \leq i \leq r} \langle \mathbf{y} | v_i \rangle \langle v_i | \mathbf{y} \rangle \qquad (3.26)$$

one has, via the chain rule,

$$\frac{\delta F_H}{\delta \overline{v}_i} = \frac{\delta F_H}{\delta \rho} \frac{\delta \rho}{\delta \overline{v}_i} = \frac{\delta F_H}{\delta \rho} v_i \qquad (3.27)$$

It is useful to note that Eq. (3.27) defines the action of a local operator $\dfrac{\delta F_H}{\delta \rho} : \mathcal{H}^1 \to \mathcal{H}^1$ by

$$\frac{\delta F_H}{\delta \overline{v}_i}(\mathbf{y}) = \frac{\delta F_H}{\delta \overline{v}_i(\mathbf{y})} = \frac{\delta F_H}{\delta \rho(\mathbf{y})} v_i(\mathbf{y}) = \left[\frac{\delta F_H}{\delta \rho} v_i \right](\mathbf{y}) \qquad (3.28)$$

From Eq. (3.25) and the change of variables in Eq. (3.27), we obtain Euler equations $\dfrac{\delta \mathcal{L}_F}{\delta \overline{v}_i} = \dfrac{\delta \mathcal{L}_F}{\delta v_i} = 0$, which can be expressed as the generalized eigenvalue problem

$$\left(\frac{\delta F_H}{\delta \rho} - \mu \right) v_i = \sum_{1 \leq j \leq r} \lambda_{ij} v_j \qquad (3.29)$$

and its complex conjugate. The component potential functionals can be obtained by taking the functional derivatives of Eq. (3.16) leading to exact, but in some cases, unknown expressions for $\frac{\delta F_C}{\delta\rho}, \frac{\delta F_T}{\delta\rho}, \frac{\delta F_{XC}}{\delta\rho}, \frac{\delta F_{eN}}{\delta\rho}$ and $\frac{\delta F_{ext}}{\delta\rho}$. These derivatives are all evaluated on the same path $D_*^N(\rho) = \left(D_\#^N \circ D_\#^1\right)(\rho)$, which again, leads to the definitions of $\frac{\delta F_T}{\delta\rho}$ and $\frac{\delta F_{XC}}{\delta\rho}$ as local potentials in the one-particle Eq. (3.29) for the density.

3.3 Relation with the Conventional Kohn-Sham Procedure.

The reader should note that no restrictions were placed on the form of the density expansion Eq. (3.26); in particular there is no limit on the number of terms. As already noted, therefore Eqs. (3.29) are not conventional Kohn-Sham equations. Rather they are an exact one-particle form of the Hohenberg-Kohn variation procedure and use Hohenberg-Kohn potentials in the definition of the effective one-particle Hamiltonian $\left(\frac{\delta F_H}{\delta\rho} - \mu\right)$. They have some kinship with the generalized Kohn-Sham equations treated, for example, by Levy and Perdew (32) but there is still a key difference. Unlike Kohn-Sham procedures, in (3.16) no auxiliary state has been introduced to provide a partitioning and regrouping of the terms.

At least for the case of a non-degenerate ground state of a closed shell system, it is possible to delineate the standard Kohn-Sham procedure quite sharply. (The caveat is directed toward issues of degeneracy at the Fermi level, fractional occupation, continuous non-integer electron number, and the like. In many but of course not all works, these aspects of the theory seem to be intertwined in an unanalyzed way with incompatible assumptions about single determinantal KS states.) For that specific case, the standard KS auxiliary state is a single determinant of singly occupied orbitals, which is an Independent Particle State (IPS), (any conventionally doubly occupied orbitals simply occur twice). The form is appealing because it incorporates Pauli exclusion explicitly, and is explicitly N-representable while being easy to manipulate.

With these motivational remarks, we now recover standard KS theory (in the particular instance just defined) from Eq. (3.16) for this specific case but with an important new constraint. Let $\mathcal{S}_{N1IP}(\rho)$ be the set of all Independent Particle FORDO's corresponding to ρ with precisely N non-zero terms:

$$D_{IP}^1 = \sum_{1 \le i \le N} |\varphi_i\rangle\langle\varphi_i|$$

$$\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$$

(3.30)

By Harriman's theorem already cited there is always at least one such FORDO for each legitimate ρ. We now define the KS kinetic energy functional, which for a fixed number of particles is system independent, as

$$T_{KS}(\rho) = \underset{D_{IP}^1 \in S_{N1IP}(\rho)}{Min} Tr\{TD_{IP}^1\} = E_T\left(D_{IP\Diamond}^N(\rho)\right)$$

(3.31)

where E_T is defined in Eq. (3.16) and $D_{IP\Diamond}^N(\rho)$ is the unique Independent Particle N-particle state that corresponds to the minimizer $D_{IP\Diamond}^1(\rho)$ of this constrained optimization, which if the conditions described in (25) are satisfied determines paths $D_{IP\Diamond}^1(\rho)$ and $D_{IP\Diamond}^N(\rho)$ in $\mathcal{B}_1(\mathcal{H}^1)$ and $\mathcal{B}_1(\mathcal{H}^N)$ respectively. It should be noted that the paths $D_{IP\Diamond}^1(\rho)$ and $D_{IP\Diamond}^N(\rho)$ are in general *very* different from the paths $D_\#^1(\rho), D_*^1(\rho)$ and $D_*^N(\rho)$. The definitions in Eqs. (3.16) can then be transformed to standard KS form by regrouping and defining difference functionals between exact and independent particle paths in the following manner: (note that the HK kinetic energy and XC terms involve a system dependent path $D_*^N(\rho)$ in N-particle state space i.e. $F_T(\rho) = E_T\left(D_*^N(\rho)\right)$ and

$F_{XC}(\rho) = E_{XC}\left(D_*^N(\rho)\right)$)

$$\tilde{F}_T(\rho) = T_{KS}(\rho) - F_T(\rho) \equiv E_T\left(D_{IP\Diamond}^N(\rho)\right) - E_T\left(D_*^N(\rho)\right)$$

(3.32)

then

$$F_T(\rho) = T_{KS}(\rho) + \tilde{F}_T(\rho)$$

(3.33)

The KS XC potential term can then be defined by

$$F_{XC,KS}(\rho) = \tilde{F}_T(\rho) + F_{XC}(\rho)$$

(3.34)

leading to the identification

$$F_T(\rho) + F_{XC}(\rho) = T_S(\rho) + F_{XC,KS}(\rho)$$

(3.35)

By construction, KS functionals are well-defined, (but note that the XC KS term is defined with the help of two distinct paths) and give well-defined functional derivatives, so their variation proceeds as in the preceding section, leading superficially to the standard KS equations.

There is, however, an important distinction that seems to have been missed in most if not all of the DFT literature (29), (33). In essentially all presentations of the standard KS procedure, the functions corresponding to

$\{\varphi_i\}$ are restricted to the reals, usually implicitly. In fact this restriction cannot be true in general without either a violation of the constraints to the proper path or, alternatively, forcing the extremum of the constrained functional to lie above the actual energy minimum. (To illustrate the point, Harriman's construction of single-determinants associated explicitly with a specified density relied upon complex orbitals.) The proof is simple. Harriman's theorem provides at least one determinant for each feasible density but with the orbitals restricted only to $L_2(\mathbf{Y})$. Fukutome (34) has shown, however, that all possible single determinants with orbitals from $L_2(\mathbf{Y})$ separate into eight distinct classes according to spin and time reversal symmetries. Therefore all possible densities can be so classified (the densities associated with each class have a unique topology). Since some of the classes have orbital forms which are manifestly complex, it follows that to include all feasible densities in the paths and at the same time search them with a single KS determinant, the determinant must in general have complex orbitals.

There are two immediate consequences of this result. First, is a previously unappreciated ambiguity in the so-called adiabatic connection formulation of $F_{XC,KS}[\rho]$. 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 however, the KS determinant is restricted to real orbitals, then in general that coupling constant integral will not be connecting to the ground state of the non-interacting system but only an upper bound to its ground state. Secondly, in general, the exact KS potential will not be a pure real function, contrary to the unstated assumption in essentially all of the literature. Alternatively, if one insists on real orbitals, then the single KS determinant must be given up and replaced by a suitably chosen and characterized multi-determinantal auxiliary function. Taken together, these previously unnoticed aspects of KS theory also provide a significant opportunity for improvement in practical approximations, a topic that we address in Section 5.

In the preceding discussion we have expanded the density in terms of $N \leq M \leq r$ functions that belong to the one-particle Hilbert space $\mathcal{H}^1$ such that their norms are *less than or equal to one* and the trace of the density is equal to N. All these expansions could in principle be exact; there is no need for $M = r = \infty$, as is clearly demonstrated in the KS procedure, where $M = N$. If $M < \infty$ and $r = \infty$, then new forms of auxiliary states, i.e. different from single determinantal ones, are implicitly introduced.

Another class of expansions is also possible, but in these the functions cannot be interpreted as belonging to the Hilbert space of one-particle states,

even though they are functions of one space and one spin variable and do belong to a Hilbert space. In such expansions the norms of the functions are *less than or equal to N* and $1 \leq M \leq \infty$. In the extreme case of $M = 1$ one can even express the density as $\rho = \omega\overline{\omega}$, where $\omega = \rho^{\frac{1}{2}}$. This factorization leads to the Pauli potential (35); we shall discuss it in detail elsewhere (30). For each value of *M*, while $r = \infty$ one could choose a different partitioning of the XC and kinetic energy in a similar fashion to Eq. (3.35). Such choices would be closely related to the generalized KS schemes already mentioned.

4. TIME-DEPENDENT DFT.

4.1 Characterization of the Lagrangian as a function of the density

The definition of the Lagrangian in Eq. (2.9) in terms of the paths x(*t*) needs to be modified when time dependent densities $\rho(t)$ are considered as the variables x(*t*) in Eq. (2.9), as $\mathcal{L}$ is not a well-defined functional of $\rho(t)$. It is necessary to proceed somewhat parallel with the determination of paths in the preceding section in order to surmount this difficulty. In the context of K&S therefore, the Lagrangian which results will have no new content; rather, the analysis is restructured to make the functional dependence on the density precise and well-defined. First define an intermediate Lagrangian

$$\mathcal{L}_1\left(Q(t),Q(t)^\dagger,\rho(t),\lambda(t)\right) = \mathcal{L}\left(Q(t),Q(t)^\dagger,t\right) - \int_{\mathbf{Y}} \lambda(t,\mathbf{y})g(t,\mathbf{y})d\mathbf{y} \qquad (4.1)$$

where $\mathcal{L}\left(Q(t),Q(t)^\dagger,t\right)$ is the Lagrangian defined in Eq. (2.9), $\lambda(t)$ a time dependent Lagrange multiplier function and the constraint function $g(t)$ is defined for a *fixed* time-dependent ρ as

$$g(t,\mathbf{y}) = \Xi_N^1\left(Q(t)Q(t)^\dagger\right)(\mathbf{y}) - \rho(t,\mathbf{y}) = 0 \qquad (4.2)$$

The equality in the preceding constraint is in the sense of the $L_1(\mathbf{Y})$ norm for fixed *t*. The actual Lagrangian controlling the dynamics then is defined as

$$\mathcal{L}(\rho(t)) = \underset{Q(t)\in\mathcal{B}_2\left(\mathcal{H}^N\right)}{Min}\left\{\mathcal{L}_1\left(Q(t),Q(t)^\dagger,\rho(t),\lambda(t)\right)\right\}$$
$$= \mathcal{L}_1\left(Q_*(\rho(t)),Q_*(\rho(t))^\dagger,\lambda_*(\rho(t))\right) \qquad (4.3)$$

where the paths $Q_*(\rho(t)) \in \mathcal{B}_2(\mathcal{H}^N)$ are defined by the constrained minimization in the same manner as in the time-independent case. This Lagrangian is of the same form as in (7) modified only by constrained search considerations in order to get a well-defined functional of the time-dependent density.

4.2 Exact Equations of Motion in terms of the Density

With the Lagrangian in hand, the principle of stationary action

$$\delta \mathcal{A} = \int_{t_i}^{t_f} \delta \mathcal{L}(\rho(t)) dt = 0 \tag{4.4}$$

leads to the equation of motion

$$\{\rho, \mathcal{E}\} = \dot{\rho} \tag{4.5}$$

where the equivalent classical Hamiltonian is given by

$$\mathcal{E}(\rho(t)) = \frac{\mathcal{H}(\rho(t))}{\mathcal{S}(\rho(t))} = \frac{\left(Q_*(\rho(t)) | \hat{H} Q_*(\rho(t)) \right)}{\left(Q_*(\rho(t)) | Q_*(\rho(t)) \right)} \tag{4.6}$$

and the inner products in Eq. (4.6) are as defined in Eq. (2.2). The Poisson brackets are defined in a fashion similar to Eq. (2.7)

$$\{ f(t), g(t) \} = \int_{\mathbf{Y} \times \mathbf{Y}} \frac{\delta f(\rho(t))}{\delta \rho(\mathbf{y})} \xi(t, \mathbf{y}, \mathbf{y}') \frac{\delta g(\rho(t))}{\delta \rho(\mathbf{y}')} d\mathbf{y} d\mathbf{y}' \tag{4.7}$$

but now with a metric integral kernel, which depends on $\rho(t) \in L_1(\mathbf{Y})$ that is defined by $\xi(\mathbf{y}', \mathbf{y}) = (\eta^{-1})(\mathbf{y}', \mathbf{y})$, where

$$\eta(\mathbf{y}', \mathbf{y}) = i \left\{ \frac{\delta}{\delta \tilde{\rho}(\mathbf{y}')} \frac{\delta}{\delta \rho(\mathbf{y})} - \frac{\delta}{\delta \rho(\mathbf{y}')} \frac{\delta}{\delta \tilde{\rho}(\mathbf{y})} \right\} \ln \left(Q_*(\tilde{\rho}) | Q_*(\rho) \right) \Bigg|_{\tilde{\rho} = \rho} \tag{4.8}$$

The time-dependent Eq. (4.5) in terms of the density is *exact* and *equivalent to* the full Heisenberg equation of motion when no approximations or models are invoked. It is thus worthwhile to display it in more detail

$$\frac{d\rho(t)}{dt} = \int_{\mathbf{Y} \times \mathbf{Y}} \frac{\delta \rho}{\delta \rho(\mathbf{y})} \xi(t, \mathbf{y}, \mathbf{y}') \frac{\delta \mathcal{E}(\rho)}{\delta \rho(\mathbf{y}')} d\mathbf{y} d\mathbf{y}' \tag{4.9}$$

The first term in this integral is a delta function and produces pointwise equations

$$\frac{d\rho(t, \mathbf{y})}{dt} = \int_{\mathbf{Y}} \xi(t, \mathbf{y}, \mathbf{y}') \frac{\delta \mathcal{E}(\rho)}{\delta \rho(\mathbf{y}')} d\mathbf{y}' \tag{4.10}$$

4.3 Exact Equations of Motion in terms of one-particle Functions

The time-dependent density can be expressed as a sum of products of unnormalized, time-dependent NGSO's analogously with Eq. (3.26)

$$\rho(t, \mathbf{y}) = \sum_{1 \leq i \leq r} \langle \mathbf{y} | v_i(t) \rangle \langle v_i(t) | \mathbf{y} \rangle \tag{4.11}$$

and one can set up a 1-1 correspondence between $\rho(t)$ and $v(t) \equiv \{ v_i(t); 1 \leq i \leq r \}$. This correspondence allows us to express the

Lagrangian as a functional $\mathcal{L}(v,\overline{v})$. Note however that unlike functionals used in the Time-Dependent Hartree Fock approximation (6), this Lagrangian *is not* complex analytic in the variables $(v,\overline{v})$ separately.

The equation of motion Eq. (4.5) and Eq. (4.9) can be expressed in terms of the variables $v(t) \equiv \{v_i(t); 1 \leq i \leq r\}$

$$\{v_i, \mathcal{E}\} = \dot{v}_i \equiv \{\overline{v}_i, \mathcal{E}\} = \dot{\overline{v}}_i \tag{4.12}$$

In more detail these relations are

$$\frac{dv_i(t)}{dt} = \sum_{1 \leq j \leq r} \xi_{ij}(v(t)) \frac{\delta \mathcal{E}(v(t))}{\delta v_j}$$

$$\frac{d\overline{v}_i(t)}{dt} = \sum_{1 \leq j \leq r} \overline{\xi}_{ij}(v(t)) \frac{\delta \mathcal{E}(v(t))}{\delta \overline{v}_j} \tag{4.13}$$

where

$$\tag{4.14}$$

and $\xi_{ij} = (\eta^{-1})_{ij}$. Using Eq. (4.11) the components $\nabla_{v_i}\mathcal{E}$ of the gradient of the equivalent *classical energy* can be expanded as

$$\frac{\delta \mathcal{E}(v(t))}{\delta v_j} = \int_Y \frac{\delta \mathcal{E}(v(t))}{\delta \rho(\mathbf{y})} \frac{\delta \rho(\mathbf{y})}{\delta v_j} d\mathbf{y} = \int_Y \frac{\delta \mathcal{E}(v(t))}{\delta \rho(\mathbf{y})} \overline{v}_j(\mathbf{y}) d\mathbf{y} \equiv \frac{\delta \mathcal{E}(v)}{\delta \rho} \overline{v}_j \tag{4.15}$$

and

$$\frac{\delta \mathcal{E}(v(t))}{\delta v_j} = \frac{1}{\mathcal{S}(v(t))} \left\{ \frac{\delta \mathcal{H}(v(t))}{\delta v_j} - \mathcal{E}(v(t)) \frac{\delta \mathcal{S}(v(t))}{\delta v_j} \right\} \tag{4.16}$$

Using Eqs (4.11), (4.13), (4.15) and (4.16) one then can obtain time-dependent equations for the unnormalized NGSO's v

$$\frac{d\overline{v}_i}{dt} = \frac{1}{\mathcal{S}(v)} \sum_{1 \leq j \leq r} \xi_{ij}(v) \left\{ \frac{\delta \mathcal{H}(v)}{\delta \rho} - \mathcal{E}(v) \frac{\delta \mathcal{S}(v)}{\delta \rho} \right\} v_j \tag{4.17}$$

Note that the time-dependent version of the constraints of Eq. (3.24)

$$h_N(v(t)) = \sum_{i=1}^{r} |v_i(t)|^2 - N = 0$$

$$h_{ii}(v(t)) = |v_i(t)|^2 - 1 \leq 0 \tag{4.18}$$

$$h_{ij}(v(t)) = \langle v_i(t)|v_j(t)\rangle = 0; \ i \neq j$$

need to be maintained, which necessitates the use of time-dependent Lagrange parameters in a modified evolution equation based on Eq. (4.17).

Again we point out the rather remarkable fact that the coupled Eqs. (4.17) are *exact* and are equivalent to the full HEM if no other constraints, other than those of Eq. (4.18), are placed on ν, $\mathcal{H}$ nor $\mathcal{S}$. These coupled equations describe evolution paths in $\mathcal{H}^1 \equiv L_2(\mathbf{Y})$ and the local potentials $\dfrac{\delta \mathcal{H}}{\delta \rho}$ and $\dfrac{\delta \mathcal{S}}{\delta \rho}$ act as time dependent operators mapping $\mathcal{H}^1 \to \mathcal{H}^1$. The curvature tensor $\xi_{ij}(\nu)$ can be obtained either from the expression in Eq. (4.14) or from Eq. (4.8) by using the coordinate transformation Eq. (4.11) that introduces matrix elements of the operator defined by the kernel

$$\eta(\mathbf{y}',\mathbf{y}) = i \left\{ \frac{\delta}{\delta\widetilde{\rho}(\mathbf{y}')} \frac{\delta}{\delta\rho(\mathbf{y})} - \frac{\delta}{\delta\rho(\mathbf{y}')} \frac{\delta}{\delta\widetilde{\rho}(\mathbf{y})} \right\} \ln\left(Q_*(\widetilde{\rho})|Q_*(\rho)\right)\Bigg|_{\widetilde{\rho}=\rho} \quad (4.19)$$

between NGSO's $\{\nu_i(t); 1 \le i \le r\}$.

The local potential $\dfrac{\delta \mathcal{H}}{\delta \rho}$ can be expanded in terms of the component potentials Eq. (3.16), now considered as time dependent, leading to a time dependent exchange-correlation potential

$$\frac{\delta F_{XC}(\rho(t))}{\delta \rho} = \frac{\delta}{\delta \rho} \left\{ Tr\left\{ \left(\frac{1}{r_{12}}\right) Q_*(\rho(t)) Q_*(\rho(t))^\dagger \right\} - F_C(\rho(t)) \right\} \quad (4.20)$$

where the path $Q_*(\rho(t))$ is defined by Eq. (4.3).

4.4 Other Forms of Time-Dependent Density Functional Theory

Time-Dependent Density Functional theory (TDDFT) has been considered with increasing interest since the late 1970's and many papers have been published on the subject. The treatments presented by Runge and Gross (36) and Gross and Kohn (37) are widely cited in the discussion of the evolution of pure states. The evolution of mixed states has been considered by Rajagopal et al (38), but that treatment differs in many aspects from the form given here.

In essentially all of the prior formulations of TDDFT a complex Lagrangian is used, which would amount to using the full expectation value in Eq. (2.9), not just the real part as in our presentation. The form we use is natural for conservative systems and, if not invoked explicitly at the outset, emerges in some fashion when considering such systems. A discussion of the different forms of Frenkel's variational principle, although not in the context of DFT, can be found in (39).

Another place where we diverge from other developments of TDDFT is in the use of the *metric term* Eq. (2.9). These terms arise in a non-trivial manner

as the paths $Q_*(\rho)$ are manifestly nonlinear functionals of ρ and thus have significant affects on the evolution of the density. Regarding the Time-Dependent KS form of the theory as used by e.g. Theilhaber (40), it has been suggested (6) that the metric terms should cancel as in TDHF. However we do not concur with this suggestion as the overlap functional that appears in the Lagrangian that produces the one-particle equations depends on the paths $D_*^N(\rho), Q_*(\rho)$ in $\mathcal{B}_1(\mathcal{H}^N)$ and $\mathcal{B}_2(\mathcal{H}^N)$ respectively, not on independent particle paths. Independent particle paths are determined by these equations via the auxiliary KS single determinantal state, but *it is not* those auxiliary states that appear in the Lagrangian nor determine the generalized phase space metric. Our form of TDKS equations would modify Eqs. (17)-(18) to refer to only N one-particle functions, (thus each function must be normalized to 1), and use the kinetic and XC functionals $T_S(\rho)$ and $F_{XC,KS}(\rho)$ from Eq. (3.35) to generate the potentials in the evolution equations.

One could view the occurrence of the metric terms in the equations of motion as an annoying complication, but we hold a more positive view. First they assure that whatever the choice of parameters to be used as dynamical variables, that choice will not introduce unphysical artifacts. Second, the metric terms are another component of the theory with potential for providing guiding principles for development of XC models. Those terms also allow the mathematical origin of physical affects to be assigned.
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The mixed state TDDFT of Rajagopal et al (38) differs from our formulation in the aspects mentioned above and in the nature of the operator space where the *supervectors* reside. A particularly notable distinction is in the use of the factorization $D = QQ^\dagger$ of the state density operator that leads to unconstrained variation over the space of Hilbert-Schmidt operators, rather than to a constrained variation of the space of Trace-Class operators.

For a review of TDDFT the reader should consult (36) and Görling (41). In the latter work TDKS is developed and a fairly exhaustive list of TDDFT references is given.

4.5 Time-Independent NGSO Equations from Time-Dependent Theory

The critical points of the equivalent classical Hamiltonian $\mathcal{E}$ occur at stationary state energies of the quantum Hamiltonian H and correspond to stationary states in both the quantum and generalized classical pictures. These points are characterized by the constrained generalized eigenvalue equation obtained by setting the time variation to zero in Eq. (4.17)

$$\frac{d\overline{v}_i}{dt} = 0 = \frac{1}{\mathcal{S}(v)} \sum_{1 \le j \le r} \xi_{ij}(v) \left\{ \frac{\delta \mathcal{H}(v)}{\delta \rho} - \mathcal{E}(v) \frac{\delta \mathcal{S}(v)}{\delta \rho} \right\} v_j$$

$$\Rightarrow \left\{ \frac{\delta \mathcal{H}(v)}{\delta \rho} - \mathcal{E}(v) \frac{\delta \mathcal{S}(v)}{\delta \rho} \right\} v_j = 0; \ 1 \le j \le r \quad (4.21)$$

The ground state energy corresponds to the lowest value of $\mathcal{E}$ that satisfies Eq. (4.21) in a self-consistent manner. The variables v belong to the nonlinear manifold defined by the constraints expressed in Eq. (3.24). Often it is possible to find intrinsic coordinates for this manifold and convert the problem into an unconstrained one. Notice in particular that the N-particle state energy, $\mathcal{E}$, appears explicitly in Eq. (4.21), thus this equation can be used to determine the ground state energy, which is the lowest self consistent root of Eq. (4.21) or excited state energies given by higher self consistent roots. Techniques commonly used in geometry optimization to obtain saddle points could used be effectively in this latter context.

5. APPROXIMATIONS

5.1 Model Hamiltonians

In the preceding sections we have introduced effective one-particle equations, both time-dependent and time independent, for one-particle functions that determine the density through the expansion

$$\rho(t, \mathbf{y}) = \sum_{1 \le i \le M} \langle \mathbf{y} | v_i(t) \rangle \langle v_i(t) | \mathbf{y} \rangle; \ 1 \le M \le r \quad (5.1)$$

The time-independent case corresponds to fixed time $t=0$. The only constraints on this expansion are that the Hilbert space norm of the orthogonal functions $\{v_i\}$ should be less than or equal to one, *if the functions are to be interpreted as one-particle states* and less than or equal to N otherwise, and the integral of ρ over space and spin variables should equal the number of particles. The effective one-particle Hamiltonian that determines these functions in Eqs. (3.29) and (4.21) in general depends on the density and its derivatives and is composed of terms that make up the Hohenberg-Kohn energy functional. The equations we have displayed are exact and lead to the exact solutions of the quantum mechanical equations. However finding exact solutions is not possible in general as (a) the XC potential terms is not known, (b) the metric tensor is not known in the time dependent case, and (c) it is not feasible to solve the equations if the dimension of the space of functions is infinite and $M = \infty$ (i.e. the standard form of the equations that we have presented).

Approximations thus must be introduced that involve modeling both the XC potential and the metric tensor, and a truncation of the space within

which to choose the unknown functions $\{v_i\}$ to finite dimension $r < \infty$. The modeling is based on the restricted ansatz chosen for the form of states used to determine paths that approximate $D_*^N(\rho), D_\#^1(\rho)$ and $D_\#^N(D^1)$. It can be carried out, for example, by postulating and fitting functional forms involving the density, its derivatives and fitting parameters to match the properties of high quality CI calculations. If the expansion size $M \neq r$ then in analogy to the KS case the form of the exact potentials will be different and thus the chosen functional forms in the modeling/fitting procedure will have different properties.

Traditionally the expansion Eq. (5.1) used in the KS procedure has been in terms of $\frac{N}{2}$ real functions of space variables only. In order to allow some spin-polarized solutions this treatment is extended to allow N real space functions half associated with alpha spin and half with beta spin. Generalizations of the KS procedure would allow functions of a more general form and expansions with a greater number of functions than N in Eq. (5.1). Such generalizations would be based on auxiliary states other than a real restricted single determinant. Approximate forms of these *generalized* KS equations would correspond to the approximate forms of the time independent one-particle equations discussed in this article in the case when $M \neq r$. More detail is found in (42).

Approximate time-dependent KS formulations differ more sharply from approximations to our time-dependent formulation than do the time-independent ones as they do not explicitly refer to a time-dependent metric term. In time-dependent KS, these terms either are added implicitly to the approximate XC potential or combined with other potentials.

5.2 Symmetry Constraints

All of the approximation procedures noted above lead to density-dependent effective one-particle Hamiltonians. In such approximation schemes it is possible to obtain better results by relaxing some physical symmetry constraints on the form of approximate solutions i.e. allowing symmetry-broken solutions. The types of symmetry-broken solutions that are possible by relaxing spin and time-reversal symmetry have been discussed at length in (42), where we applied Fukutomes' analysis of the Hartree-Fock solutions to DFT. An alternative perspective on that same analysis is that, if more general solutions were included in the formulation of an approximate Hamiltonian, the resulting solutions would not be symmetry-broken. In short, an approximate Hamiltonian which does not have the generality discussed in the preceding subsection may yield an energetically favorable solution by breaking symmetry. Such symmetry breaking can be construed as a reintroduction of the missing flexibility

REFERENCES

1. Linderberg J., Öhrn Y., "Propagators in Quantum Chemistry"; Academic Press, London, 1973.
2. Öhrn Y., Born G., Adv. Quantum Chem., 1981, 13, 1.
3. Weiner B., Jensen H. J. Aa, Öhrn Y., J. Chem. Phys., 1983, 80, 2009.
4. Linderberg J., Öhrn Y., Int. J. Quantum Chem., 1977, 12, 161;
   Öhrn Y., Linderberg J., Int. J. Quantum Chem., 1979, 15, 343.
5. Ortiz J. V., Weiner B., Öhrn Y., Int. J. Quantum Chem., 1981, S15, 113;
   Jensen H. J. Aa, Weiner B., Öhrn Y., Int. J. Quantum Chem., 1982, S16, 615;
   Weiner B., Öhrn Y., J. Phys. Chem., 1987, 91, 563.
6. Deumens E., Diz A., Longo R., Ohrn Y., Rev. Mod. Phys. 1994, 66, 917.
7. Kramer P., Saraceno M., "Geometry of the Time-Dependent Variational Principle in Quantum Mechanics"; Springer, New York, 1981
8. Hohenberg H., Kohn W., Phys. Rev. B, 1964, 136, 864.
   Kohn W., Sham L. J., Phys. Rev A, 1965, 140, 1133.
   Dreizler R. M., Gross E. K. U., "Density Functional Theory"; Springer Verlag, Heidelberg, 1990.
   Parr R.G., Yang W., "Density Functional Theory of Atoms and Molecules"; Oxford University Press, 1989.
9. Zhang W., Feng D. H., Gilmore R., Rev. Mod. Phys. 1990, 62, 867.
10. Klauder J. R., Skagerstam B. S., "Coherent States. Applications in Physics and Mathematical Physics"; World Scientific, Singapore, 1985
11. Feng D. H., Klauder J. R., Strayer M. R., "Coherent States: Past, Present and Future"; World Scientific, Singapore, 1994.
12. Perelomov A. M., "Generalized Coherent States and their Applications"; Springer, New York, 1986.
13. Glauber R. J., Phys. Rev., 1963, 131, 2766.
14. Thouless D. J., "The Quantum Mechanics of Many-Body Systems"; Academic, New York, 1961.
15. Mechtly B., Shaw P. B., Weiner B., Phys. Rev. A, 1989, 40, 7275.
16. Blaziot J.P., Orland H., Phys. Rev. C, 1981, 24, 1740.
17. Deumens E., Ohrn Y., Weiner B., J. Math. Phys., 1991, 32, 1166.
18. Weiner B., Deumens E., Ohrn Y., J. Math. Phys., 1994, 35, 1139.
19. Zwanzig, R., Physica, 1964, 1109.
20. Harriman J., Phys. Rev. A, 1981, 24, 680.
21. Frenkel J. "Wave Mechanics: Advanced General Theory"; Clarendon, Oxford 1934.
22. Weiner B., Trickey S. B., "Mixed State TDVP" unpublished.
23. Press W. H., Flannery B. P., Teukolsky S. A., Vetterling W. T., "Numerical Recipes"; Cambridge University 1986.
24. Levy M., Proc. Natl. Acad. Sci., 1979, 76, 6062; Bull. Am. Phys. Soc., 1979, 24, 626; J. Chem. Phys., 1979, 70, 1573.

25. Hestenes M. R., "Optimization Theory"; Wiley, New York 1975.
26. Kryachko E. S., Ludeña E. V., "Energy Density Functional Theory of Many-Electron Systems"; Kluwer, Dordrecht, 1990.
27. Bader R. F. W., "Atoms in Molecules - A Quantum Theory"; Oxford University Press, Oxford, 1990.
28. Coleman A. J., Rev. Mod. Phys., 1963, 35, 668.
29. Savin A., In "Recent Developments and Applications of Modern Density Functional Theory", Seminario J. M., Ed., Elsevier, 1996, 327.
30. Weiner B., Trickey S. B., "Paths in DFT", unpublished.
31. Löwdin P. O., 1955, Phys. Rev. 97, 1474.
32. Levy M., Perdew J. P., In "Density Functional Methods in Physics", Dreizler R.M., da Providencia J., Eds. Plenum, New York, 1985, 11.
33. Theophilou A. K. 1998, In "Proceedings of 1997 Duke DFT Satellite Symposium", Levy M., Yang W., Trickey S. B., Eds. Int. J. Quantum Chem. (in press).
34. Fukutome H, Int. J. Quantum Chem., 1981, 20, 955.
35. March N.H., Phys. Lett., 1981, 84A, 319;
    Levy M., Perdew J.P., Sahni V., Phys. Rev. A, 1984, 30, 2745;
    Levy M. Ou-Yang H., Phys. Rev. A, 1988, A38, 625;
    Holas A., March N.H., Phys. Rev. A, 1991, 44, 5521;
    Nagy A., March N.H., Int. J. Quantum Chem., 1991, 39, 615;
    Flores J.A. , Keller J., Phys. Rev. A, 1992, 45, 6259.
36. Runge E., Gross E. K., Phys. Rev. Lett., 1884, 52, 997.
37. Gross E. K., Kohn W., Adv. Quantum Chem., 1990, 27, 255.
38. Rajagopal A. K., Bout F. A., Phys. Lett. A, 1994, 195, 312.
    Rajagopal A. K., Phys. Lett. A, 1994, 193, 363.
    Rajagopal A. K., Bout F. A., Phys. Rev E, 1994, 50, 721.
    Rajagopal A. K., Bout F. A., Phys. Rev A, 1995, 51, 1883.
39. Christiansen O., Jorgensen P., Hattig C., Int. J. Quantum Chem. (in press).
40. Theilhaber J., Phys. Fluids B (Plasma Phys.), 1992, 4, 2044;
    Phys. Rev. B, 1992, 46, 12990;
    Int. J. Quantum Chem., Quantum Chem. Symp., 1994, 28, 611.
41. Görling A., Phys. Rev. A, 1997, 55, 2630.
42. Weiner B., Trickey S. B., 1998, In "Proceedings of 1997 Duke DFT Satellite Symposium", Levy M., Yang W., Trickey S. B., Eds. Int. J. Quantum Chem. (in press).

APPENDIX A: GLOSSARY OF MATHEMATICAL SYMBOLS

$\mathcal{S}_N$	The convex set of N-particle states
$\mathcal{S}_N(\rho)$	The set of N-particle states that produce the same density ρ

$\mathcal{S}_{N1}$	The of First Order Reduced Density Operators (FORDO's)
$\mathcal{S}_{N1}(\rho)$	The set of FORDO's that produce the same density ρ
$\mathcal{S}_{N1IP}(\rho)$	The set of Independent Particle FORDO's that produce the same density ρ
$\mathcal{S}_{Np}$	The set of p-particle Trace Class operators that are N-Representable.
$\mathcal{B}_1(\mathcal{H}^N)$	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 1D subspace it represents a mixed N-particle state
$\mathcal{B}_2(\mathcal{H}^N)$	The Hilbert space of Hilbert Schmidt operators acting in $\mathcal{H}^N$
$\hat{H}$	The Hamiltonian super operator (the Hamiltonian represented as an operator acting on Hilbert Schmidt operators
$(\ \vert\ )$	Inner product in $\mathcal{B}_2(\mathcal{H}^N)$
$\mathcal{M}$	Submanifold (in general nonlinear) of operators in $\mathcal{B}_2(\mathcal{H}^N)$.
$\mathcal{E}(\mathbf{x})$	Equivalent classical Hamiltonian defined on $\mathcal{M}$; $\mathbf{x}$ is a coordinate system on $\mathcal{M}$ i.e. the points of $\mathcal{M}$ are states and the coordinates of these points are $\mathbf{x}$.
$\mathcal{S}(\mathbf{x})$	Normalization function of states in $\mathcal{M}$
$\{,\}$	Poisson Brackets defined on tangent spaces of $\mathcal{M}$
ξ	The symplectic metric tensor defined on the tangent spaces of $\mathcal{M}$
$\dfrac{\hat{\partial}}{\partial t}$	Superoperator acting on Hilbert-Schmidt operators producing their time derivative.
$\mathcal{L}$	Lagrangians
$\begin{pmatrix} r \\ N \end{pmatrix}$	Combinatorial coefficient "r choose N"
$\rho(\mathbf{y})$	Charge density as a function of space and spin variables $(\mathbf{r},\sigma)$
$\mathbf{Y}$	$\mathbf{R}^3 \times \mathbf{C}^2$
$L_1(\mathbf{Y})$	Linear normed space of absolutely integrable complex

	valued functions of 3 real and 2 complex variables. Arbitrary elements are denoted by ζ and densities by ρ
$L_2(\mathbf{Y})$	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 $\mathbf{y}$.
C_N^p	Contraction map from N-particle Trace Class Operators to p particle Trace Class operators.
$\Phi(\mathbf{y})$	Continuous Fermi field annihilation operator that depends on the space-spin variable $\mathbf{y}$.
$\left\{ a_i, a_i^\dagger \right\}$	Discrete Fermi field annihilation and creation operators
$\mathcal{B}_1\left(\mathcal{H}^N\right) \Big/ Ker\Xi_N^1$	Linear space of equivalence classes of Trace Class operators. The operators are equivalent if there difference lies in the kernel of Ξ_N^1
$\mathcal{P}_{1N}$	Positive cone of space-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 $\mathbf{y}$.
O_H	Nonlinear energy functional based on the Hamiltonian H, it acts on the space of one-particle Trace Class operators.
$D_*^N(\rho)$	Path of N-particle states, each state on the path corresponds to a density ρ and is the minimum energy state for that density.
$D_\#^N\left(D^1\right)$	Path of N-particle states, each state on the path corresponds to a fixed FORDO and is the minimum energy state for that FORDO.
$D_\#^1(\rho)$	Path of FORDO's, each FORDO on the path corresponds to a density ρ and is the FORDO that corresponds to the minimum energy state for that density.
$D_{IP\Diamond}^N(\rho)$ and $D_{IP\Diamond}^1(\rho)$	Paths of IP N-particle states and the unique FORDO's that correspond to these states.
$Q_*(\rho)$	Path of Hilbert Schmidt operators

$[\zeta]_N$	Equivalence classes of N-particle Trace Class operators that all map to the same function ζ.
$[\zeta]_1$	Equivalence classes of 1 particle Trace Class operators that all map to the same function ζ
$[X]_N$	The set of N-particle Trace Class operators that contract to the one-particle operator X.
$\langle\rho\rangle_N$	Set of N-particle Hilbert-Schmidt operators that produce N-particle states associated with the same space-spin density.
C	The complex numbers
CS	Coherent State
FORDO	First Order Reduced density Operator
HK	Hohenberg-Kohn
K&S	Kramer and Saraceno
KS	Kohn-Sham
NGSO	Natural General Spin Orbitals
R	The real numbers
TDHF	Time-Dependent Hartree-Fock
TDVP	Time-Dependent Variational Principle

APPENDIX B: SPACES OF OPERATORS

Bounded Operators $\mathcal{B}(\mathcal{H})$

The set of bounded operators acting in an Hilbert space $\mathcal{H}$ form a normed linear space. The norm is given by the bound on the operator

$$\|X\| = \sup_{\psi} \frac{\langle\psi\,|\,X\psi\rangle}{\langle\psi\,|\,\psi\rangle}; \quad \psi \in \mathcal{H} \tag{B1}$$

Trace Class Operators $\mathcal{B}_1(\mathcal{H})$

The set of trace class operators form a subset of the set of bounded operators, defined by

$$\mathcal{B}_1(\mathcal{H}) = \left\{ X; Tr\left\{\left(X^\dagger X\right)^{\frac{1}{2}}\right\} < \infty \right\} \tag{B2}$$

This set also forms a normed linear space with norm defined by

$$\|X\|_1 = Tr\left\{\left(X^\dagger X\right)^{\frac{1}{2}}\right\} \tag{B3}$$

Hilbert-Schmidt Operators $\mathcal{B}_2(\mathcal{H})$

The Hilbert Schmidt operators are another subset of the set of Bounded Operators, defined by

$$\mathcal{B}_2(\mathcal{H}) = \left\{ X;\ Tr\left\{ X^\dagger X \right\} < \infty \right\} \tag{B4}$$

This set forms a Hilbert space with an inner product defined by

$$\left(X|Y \right) = Tr\left\{ X^\dagger Y \right\} \tag{B5}$$

which defines the Hilbert-Schmidt norm

$$\left\| X \right\|_2 = \left(X|X \right)^{\frac{1}{2}} \tag{B6}$$

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

$$X \in \mathcal{B}_2(\mathcal{H}) \Rightarrow X^\dagger X \in \mathcal{B}_1(\mathcal{H}) \tag{B7}$$

If the dimension of $\mathcal{H}$ is finite all of these spaces of operators are identical.

APPENDIX C: INVARIANCE GROUPS

If X is an operator then its invariance group $Inv(X)$ is defined to be

$$Inv(X) = \left\{ U;\ UXU^\dagger = X;\ U^\dagger U = UU^\dagger = I \right\} \tag{C1}$$

If v is a vector then its invariance group $Inv(v)$ is defined by

$$Inv(v) = \left\{ U;\ Uv = v;\ U^\dagger U = UU^\dagger = I \right\} \tag{C2}$$