Fukutome Symmetry Classification of the Kohn–Sham Auxiliary One-Matrix and Its Associated State or Ensemble

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ABSTRACT: The Kohn–Sham (KS) procedure for variational minimization of the Hohenberg–Kohn density functional utilizes a one-particle reduced density matrix of assumed diagonal form, hence depends implicitly on a set of auxiliary states. Originally, the auxiliary state was assumed to be a single determinant with doubly occupied spin orbitals, i.e., of the same form as in ''restricted'' Hartree–Fock theory. The pragmatic and formal extension of the KS procedure to noninteger occupation numbers requires extension to more general forms of the auxiliary state or even its replacement by an auxiliary ensemble. Though attention has been given to the symmetry properties of the KS one-matrix, its spin and time-reversal symmetries have not been classified along the lines of Fukutome's treatment of the generalized Hartree–Fock problem. Here we show that, in the context of constrained search density functional theory (DFT), Fukutome's analysis goes through essentially unaltered. We then consider the broken symmetry consequences for the case that the KS one-matrix is restricted to a single-determinantal KS auxiliary state. © 1998 John Wiley & Sons, Inc. Int J Quant Chem 69: 451–460, 1998

Key words: broken symmetry; general spin orbitals; symmetry dilemma; spin symmetry; symmetry in density functional theory

Background

Treatments of the various symmetry properties of fermion density functional theory (DFT) seem to be relatively infrequent, though several subtle aspects of the theory are involved. The original DFT papers are Hohenberg and Kohn (HK) [1] and Kohn and Sham (KS) [2]; for general references see also Refs. [3–14].

Omitting the substantial but not directly relevant literature on the multiplet problem, early consideration of symmetry issues in DFT includes the observation that the $X\alpha$ approximation for the exchange–correlation (XC) potential does not have the spin symmetry of the full, nonrelativistic Hamiltonian [15, 16]. In both calculational and formal pursuits of this problem, Dunlap studied

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homonuclear diatomics with emphasis on broken-symmetry solutions of the Kohn–Sham (KS) equations, for example, Refs. [17, 18]. Subsequently he considered the problem more generally [19–21]. The first two focused on $X\alpha$-like formulations which are invariant under spin-space rotations. One of the two schemes tested in Ref. [18] actually has roots in the Fukutome classification of general determinantal wave functions [22] which we shall use. Unfortunately, that particular approximate DFT model is, as Dunlap said, ill-behaved. His 1995 paper is relevant here primarily in arguing that broken-symmetry KS solutions sometimes are inescapable and are related to fundamental issues of quantum mechanical preparation and measurement connected with bond breaking.

The common issue in those studies is an essential one. The symmetry of the KS Hamiltonian is that of the density (or, if explicitly spin-polarized systems are presumed from the outset, the spin densities), not the full Hamiltonian. The difference in symmetries has at least two consequences. The more-explored one is that apparent symmetry dilemmas can occur because of the difference. The less explored is that the symmetries of the KS system must be studied per se. For example, while it is commonly held that the appearance of broken-symmetry KS solutions with favorable energies is only a consequence of an approximate KS exchange–correlation model, it is possible (indeed straightforward, as we show below) to construct exact KS schemes which have a particular set of spin symmetries disallowed. Were such a scheme to be applied to a physical system having an incompatible symmetry, it could easily be the case that the energy minimum solution would be symmetry breaking.

Görling [23] addressed the issue of the relationship between the symmetry of the full and KS Hamiltonians by explicit construction of a constrained search DFT [24–26] symmetrized with respect to the direct product group comprised of the molecular point group and the spin rotations. The formulation is based upon using the totally symmetric part of a somewhat unusual appearing spin-density matrix. The result is a set of KS equations each of which is associated with only one irreducible representation of the group of the full Hamiltonian and which constrains the domain for energy minimization to the totally symmetric part of the density. (The restriction to a single irreducible representation of the group of the full Hamiltonian was introduced by Gunnarson and Lundqvist [27] in the course of generalizing spin density functional theory to excited states of differing symmetries.)

McWeeny [28] has criticized DFT as practiced (and, he claims, often as presented) on the grounds of failure to recognize the fundamental significance of permutation symmetry and with particular emphasis on the implications of considering only spin-up and spin-down interactions rather than spin coupling $\hat{S}(i) \cdot \hat{S}(j)$. The specific spin-symmetry problem associated with homonuclear diatomic bond breaking and its interpretation within local approximations (including gradient dependent ones) have been treated by Perdew, Savin, and Burke [29]; see below. Finally, Joubert [30] has shown the consequences of rotational (and translational) invariance for constraints on functional derivatives with respect to the density, while Ovchinnikov and Labanowski [31] have addressed the spin-contamination problem by a prescription for construction of a set of spin densities corresponding to a specified eigenvalue of S^2.

Issues

To delineate the issues further, the essential aspect of the KS minimization of the DFT energy functional is the assumption of an implicit auxiliary state (or, in some cases, ensemble) with certain key properties. Primary among those is the property that the auxiliary system is the ground state of an independent particle model whose ground-state electron number density matches the real system ground-state density. Originally, the auxiliary state was assumed to be a single determinant, since what went into the KS decomposition of the DFT functional was a one-particle reduced density matrix in natural orbital form [32] with integer occupancies.

However, one of the symmetry issues involves the so-called fractional occupancy problem. At least at the level of the local spin density approximation (LSDA), in either the Hedin–Lundqvist or Perdew–Zunger models, both atomic Fe and Co have DFT ground states with fractional s and d occupations. Neither can arise from a single determinant. Without explicit knowledge of the N-fermion state which yields the one-particle reduced density matrix that went into the KS equation (having such knowledge certainly is not the usual case), the most that can be said with certainty within DFT is

that such densities correspond to an auxiliary ensemble of determinants [33–37].

The problem appears to be fundamental. Levy and Perdew [26] long ago gave an argument that, for a density which is not noninteracting, ground-state v-representable (i.e., a density which cannot be realized as the ground-state density of a noninteracting N-fermion Hamiltonian), carrying through the KS procedure with a single auxiliary determinant always must lead either to fractional occupancy and/or a violation of the *aufbau prinzip* (so-called holes below the Fermi level).

When a KS determinant of restricted form (''restricted'' in the same technical sense as in Hartree–Fock theory: double occupancy of the spatial orbitals) is used to study dissociation, its spin symmetry provides a different example of the broken symmetry problem; see the introductory section of Perdew, Savin, and Burke [29]. Asymptotically the H_2 singlet ground state must have equal spin-up and spin-down densities (see, e.g., Ref. [38], sect. 2.4). However, for large internuclear separation, a spin-polarized H_2 LSDA calculation yields a spin-polarized atom on the right and a reverse-polarized atom on the left as the energetically favored description. Reference [29] describes this broken-symmetry solution as a dilemma because, they claim, there are only two standard interpretive choices (omitting, i.e., the one they propose), namely accept the energy and a ''qualitatively incorrect spin density'' or obtain a qualitatively correct spin density at the cost of a severe error in the total energy.

The issue is not unique to DFT, but occurs in ordinary wave-function-based theory. Emch [39] has pointed out that the proper framework for addressing the matter is in terms of preparation of a quantum mechanical system prior to measurement. The two measurements of spin density are for systems with very different preparations (asymptotic limit of a diatomic versus isolated atom). Though the energetics are indistinguishable, the symmetries are not. Any given isolated atom will have a specific spin state but an ensemble will have no net spin density. Goscinski [40] has given a most succinct summary. In particular he showed why symmetrized combinations of localized broken-symmetry solutions in a homonuclear diatomic molecule can be *de facto* indistinguishable from the localized solutions via an energy resolution criterion which he then related to the Mulliken approximation for the interaction energy between the two localized states. When that criterion is satisfied, he showed that the pure state projector which results is an equipartition ensemble of two broken-symmetry projectors.

Broken symmetries occur in Hartree–Fock theory whenever a single determinantal trial function yields a lower system energy upon removal of the constraint to restricted form. Since correlation energy is defined (except in DFT) with respect to the restricted Hartree–Fock (RHF) energy [32], the extent to which the correlation energy could be recovered by use of general Hartree–Fock (GHF) solutions has long attracted attention. It is known [41], for example, that one such GHF solution, cubic-lattice alternant molecular orbitals, gives a lower total energy than the RHF solution for the homogeneous electron gas (HEG) for all $r_s > 22$. Since the LSDA is based directly on the RHF solution for the HEG, this broken-symmetry HEG solution (and many others which we do not attempt to review here) signals the possibility of related solutions in both the LSDA and exact KS theory.

Thus there is good reason to study, not reject out of hand, broken-symmetry solutions of the KS equations. Fukutome [22] developed a systematic classification of all possible GHF solutions by identifying the inequivalent subgroups of the group of spin rotations and time reversal (an invariance group for any ordinary N-fermion Hamiltonian; see below). The classification was applied by Sykja and Calais [42, 43] and Calais [44]. A corresponding analysis of general symmetries of KS auxiliary states does not seem to have been done. Dunlap did cite Ref. [22] and commented (somewhat disapprovingly because of computational burden) on the complex orbitals which arise in GHF. Interestingly, Savin's recent paper [45] mentions the possible benefits of complex KS orbitals and the restoration of broken symmetry by constructing ensemble densities, but does not mention the Fukutome analysis nor the ensemble projector result of Goscinski [40]. This study represents the first steps in the general project of Fukutome-like analysis applied to DFT.

Equivalence Classes, Constrained Searches, Density Matrices, and Functionals

To establish basic equations, notation, and definitions in a way which makes no *a priori* assumptions about spin and time reversal symmetries, we

give a version of the now-standard constrained search formulation of Hohenberg–Kohn–Sham (HKS) theory which connects explicitly to full one-particle reduced density matrices. The original version of constrained search is due to Levy [25, 26], with extension to spin density functionals by Perdew and Zunger [46]. Portions of this section are similar to, but not identical with, developments presented in Refs. [8] and [9]. Note that the development does *not* presume an *a priori* spin-polarized form. One feature of the present development is that it returns to density functional theory but developed in terms of all the coordinates of the problem, not just the spatial ones.

For a system of N electrons in the presence of a fixed nuclear array and an arbitrary (reasonable) additional external potential, the total nonrelativistic Hamiltonian is the classical nuclear repulsion (omitted henceforth) plus the electronic Hamiltonian

$$H = T + V_{\mathrm{ne}} + V_{\mathrm{ee}} + V_{\mathrm{ext}}. \tag{1}$$

We also omit any possible external vector potential which would couple explicitly to the spins [46]. In HARTREE atomic units ($\hbar = m_e = e = 1$, 1 hartree = 27.2116 eV), the operators in order are the kinetic energy, nuclear-electronic potential energy, electron-electron Coulomb repulsion, and total external potential:

$$T = -\tfrac{1}{2}\sum_i \nabla_i^2, \tag{2}$$

$$V_{\mathrm{ne}}(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \sum_i V_{\mathrm{ne}}(\mathbf{r}_i) \equiv -\sum_{i\mu}\frac{Z_\mu}{|\mathbf{r}_i - \mathbf{R}_\mu|}, \tag{3}$$

$$V_{\mathrm{ee}}(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{4}$$

$$V_{\mathrm{ext}}(\mathbf{r}_1,\ldots,\mathbf{r}_N) \equiv \sum_i V_{\mathrm{ext}}(\mathbf{r}_i). \tag{5}$$

Sets in the following development are denoted as enclosed in braces $\{\cdots\}$, coordinate vectors are bold-faced (whether in $\mathbf{R}^3$ or in compound space-spin), matrices are underscored (with dimension determined by context), and equivalence classes are denoted by brackets $[\cdots]$. Therefore we do not use brackets to indicate the argument of a functional, the customary DFT notation, in what follows.

In terms of the compound space-spin coordinate $(\mathbf{r}, s) \equiv \mathbf{x}$, the set of admissible electron number densities $\mathscr{D}$ is comprised of scalar functions $n(\mathbf{x})$ such that

$$\int d\mathbf{x}\, n(\mathbf{x}) = N, \tag{6}$$

$$n(\mathbf{x}) \geq 0 \qquad \forall\, \mathbf{x}. \tag{7}$$

Note that all members of $\mathscr{D}$ are N-representable, i.e., correspond to some state in $\mathscr{H}^N$, the N-fermion Hilbert space; see Harriman [47]. They are not, in DFT terminology, necessarily ground-state N-representable, however, nor is their representation unique in general.

Each state Ψ in $\mathscr{H}^N$ has a one-particle reduced density kernel $\rho_\Psi(\mathbf{x}', \mathbf{x})$, another scalar, which in any suitable orthonormal basis $\{\phi\}$ has the development

$$\rho_\Psi(\mathbf{x}', \mathbf{x}) = \sum_{ij} \bar{\phi}_i(\mathbf{x}')\phi_j(\mathbf{x})\underline{D}^1(\Psi)_{ij}. \tag{8}$$

(For the sake of clarity we distinguish density kernels, which are functions of $\mathbf{x}, \mathbf{x}'$, from their matrix representations with respect to a basis; commonly but imprecisely both are called density matrices.) The sum may have finite or infinite upper limits, depending upon the basis. Though inconsequential for what follows, it is always true that there is at least one such development with finite upper limits, by reasoning akin to that which leads to the nonunique N-representability of the members of $\mathscr{D}$. The electron number density is

$$\rho_\Psi(\mathbf{x}, \mathbf{x}) = n_\Psi(\mathbf{x}). \tag{9}$$

Again it is important to note the deliberate absence of separation into spatial and spin densities; n_Ψ is a scalar function of the compound space-spin coordinates (the spin coordinates are themselves spinors, of course). The natural general spin orbitals $\{\psi\}$ are those one-particle functions which diagonalize the one-particle reduced density matrix $\underline{\mathscr{D}}^1(\Psi)$:

$$\rho_\Psi(\mathbf{x}', \mathbf{x}) = \sum_i \bar{\psi}_i(\mathbf{x}')\psi_i(\mathbf{x})n_i(\Psi). \tag{10}$$

Contact with constrained search DFT is made by defining an equivalence relation for Ψ_1 and Ψ_2 in $\mathscr{H}^N$:

$$\Psi_1 \overset{\mathrm{N}}{\sim} \Psi_2 \Leftrightarrow n_{\Psi_1} = n_{\Psi_2}, \tag{11}$$

which defines equivalence classes $[n]_N$ on $\mathscr{H}^N$ labeled by the densities in $\mathscr{D}$. Note that different states in a given equivalence class may have dif-

ferent symmetries. Now define a functional on $\mathscr{D}$:

$$F_H(n(\mathbf{x})) \equiv \min_{\Psi \in [n]_N} \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle. \quad (12)$$

F_H is universal in that its functional dependence on $n(\mathbf{x})$ is independent of the total one-body potential:

$$F_H(n(\mathbf{x})) = Q(n(\mathbf{x})) + \int d\mathbf{x}\, n(\mathbf{x})(V_{\text{ne}} + V_{\text{ext}}), \quad (13)$$

where

$$Q(n(\mathbf{x})) \equiv \min_{\Psi \in [n]_N} \frac{\langle \Psi | T + V_{\text{ee}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (14)$$

The variational principle for the ground-state electronic energy E_0 then is recast as a minimization over all equivalence classes

$$E_0 = \min_{n \in \mathscr{D}} F_H(n), \quad (15)$$

which is the essence of the generalized HK theorems. Note that unlike the original HK demonstration, constrained search developments are not restricted to nondegenerate ground states nor to v-representable spin densities.

In the present context, exact Kohn–Sham theory [26, 46] is an orbitally based procedure for formal variation of $F_{\text{HK}}(n)$ presuming that the exact density dependence of the functional Q is known explicitly (rather than implicitly through Ψ_i). It can be reached by introducing an equivalence relation for sets of functions $\{\varphi_1\}$ and $\{\varphi_2\}$ in the Hilbert space of one-particle functions $\mathscr{H}^1$:

$$\{\varphi_1\} \overset{1}{\sim} \{\varphi_2\} \Leftrightarrow \sum_i |\varphi_{1,i}(\mathbf{x})|^2 = \sum_i |\varphi_{2,i}(\mathbf{x})|^2 \qquad \forall \mathbf{x}. \quad (16)$$

(Because they belong to $\mathscr{H}^1$, the φ are complex-valued scalars over $\mathbf{x}$, not just spin-labeled real functions over $\mathbf{R}^3$.) This equivalence relation defines equivalence classes $[n]_1 \subset \mathscr{H}^1$ for functions which satisfy

$$\begin{aligned} \langle \varphi_{1,i} | \varphi_{1,j} \rangle &= n_{1,i}\delta_{ij}; \qquad 0 \le n_{1,i} \le 1 \\ \langle \varphi_{2,i} | \varphi_{2,j} \rangle &= n_{2,i}\delta_{ij}; \qquad 0 \le n_{2,i} \le 1 \\ \sum_i n_{1,i} &= \sum_i n_{2,i} = N. \end{aligned} \quad (17)$$

Each set $\{\varphi\}$ evidently defines multiple first-order reduced density matrices $\underline{\mathscr{D}}^1_\varphi$ also, though with a different norming than before. For a given set of matrices $\{\underline{\mathscr{D}}^1_\varphi\}$, select the subset $\{\underline{\mathscr{D}}^1_{\varphi,P}\}$ which arises from pure N-fermion states. Call that set of states $\mathscr{P}_\varphi$ and note that it is nonempty by the N-representability of all legitimate densities. Then define

$$O_H(\{\varphi\}) = O_H\left(\left\{\underline{D}^1_\varphi\right\}\right) = \min_{\Psi \in \mathscr{P}_\varphi} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (18)$$

It follows that

$$F_H(n) = \min_{\{\varphi\} \in [n]_1} O_H(\{\varphi\}) \quad (19)$$

and

$$E_0 = \min_{n \in \mathscr{D}} F_H(n) = \min_{\{\varphi\}} O_H(\{\varphi\}). \quad (20)$$

While both $F_H(n)$ and $O_h(\{\varphi\})$ are functionals which can achieve the ground-state energy, clearly they are not identical in general; note especially Eq. (19).

O_H is, in essence, the KS functional. The connection follows. Define the density functional for the ''noninteracting'' kinetic energy as

$$T_s(n) \equiv \min_{\{\varphi\} \in [n]_1} \sum_i \langle \varphi_i | T | \varphi_i \rangle \quad (21)$$

[bearing in mind the somewhat unconventional normalization in Eq. (17)]. Note that T_s is defined on $[n]_1$ but not on $\{\varphi\}$. As usual, the universal functional $Q(n)$ is decomposed into $T_s(n)$ plus the classical Coulomb interaction energy (including self-repulsion) and all the rest (in DFT identified as the XC energy; in general it includes kinetic energy (KE) and self-repulsion corrections in addition to exchange and Coulombic correlation contributions):

$$Q(n) = T_s(n) + E_{\text{ee}}(n) + E_{\text{xc}}(n). \quad (22)$$

Obviously E_{ee} is defined on $\{\varphi\}$:

$$E_{\text{ee}}(n) = E_{\text{ee}}(\{\varphi\}) \qquad \forall \{\varphi\} \in [n]_1 \quad (23)$$

as also are E_{ext} and E_{ne}. Because T_s is not defined there, neither is E_{xc}. Therefore, F_H remains a functional of the density, not of $\{\varphi\}$. Because T is a sum of one-body operators and E_{ee} is defined on $\{\varphi\}$, it

is obvious from Eq. (21) that two more functionals can be defined:

$$\tilde{T}_s(\{\varphi\}) = \min_{\Psi \in \mathscr{P}_\varphi} \frac{\langle \Psi | T | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{24}$$

$$= \sum_i \langle \varphi_i | T | \varphi_i \rangle \tag{25}$$

and

$$\tilde{Q}(\{\varphi\}) = \min_{\Psi \in \mathscr{P}_\varphi} \frac{\langle \Psi | T + V_{\mathrm{ee}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{26}$$

In terms of these

$$T_s(n) = \min_{\{\varphi\} \in [n]_1} \tilde{T}_s(\{\varphi\}) \tag{27}$$

and

$$Q(n) = \min_{\{\varphi\} \in [n]_1} \tilde{Q}(\{\varphi\}) \tag{28}$$

so that a consistent definition of

$$\tilde{E}_{\mathrm{xc}}(\{\varphi\}) = \tilde{Q}(\{\varphi\}) - \tilde{T}_s(\{\varphi\}) - E_{\mathrm{ee}}(\{\varphi\}) \tag{29}$$

is straightforward. As a result of all this maneuvering, Eq. (19) becomes

$$F_H(n) = \min_{\{\varphi\} \in [n]_1} E_{\mathrm{KS}}(\{\varphi\}), \tag{30}$$

where

$$E_{\mathrm{KS}}(\{\varphi\}) = \tilde{T}_s(\{\varphi\}) + E_{\mathrm{ee}}(\{\varphi\}) + \tilde{E}_{\mathrm{xc}}(\{\varphi\}) + E_{\mathrm{ne}}(\{\varphi\}) + E_{\mathrm{ext}}(\{\varphi\}). \tag{31}$$

Kohn–Sham Equation

The variation $\delta F_H / \delta n = 0$ to obtain the KS equations usually proceeds by variation of Eq. (30) over all the equivalence classes $[n]_1$. The details are not of immediate concern, except that, relative to the foregoing formulation, the variation proceeds in three steps. First, the orbital normalization is shifted to unity in order to reintroduce explicit occupation numbers n_i. Then the orbitals are varied, followed by determination of the occupation numbers. Enforcement of the orthonormalization and total particle number constraints by Lagrange multipliers leads to the well-known KS equation:

$$h_{\mathrm{KS}} \varphi_j \equiv \left[-\tfrac{1}{2}\nabla^2 + V_{\mathrm{ne}} + V_{\mathrm{ext}} + V_{\mathrm{ee}} + V_{\mathrm{xc}} \right] \varphi_j \tag{32}$$

$$= \varepsilon_j \varphi_j \tag{33}$$

with

$$V_{\mathrm{xc}}(\mathbf{x}) = \delta E_{\mathrm{xc}}(n(\mathbf{x})) / \delta n(\mathbf{x}). \tag{34}$$

Note that the exchange–correlation potential is always local for exact KS theory.

The occupation numbers are determined by an intermediate step, proof of the Janak–Slater theorem [48, 49] $\partial E / \partial n_j \equiv \varepsilon_j$ which yields the *aufbau prinzip* at the energy minimum

$$\varepsilon_j - \mu = 0 \Rightarrow \delta n_j \text{ arbitrary} \Rightarrow 0 < n_j < 1 \tag{35}$$

$$< 0 \Rightarrow \delta n_j \leq 0 \Rightarrow n_j = 1 \tag{36}$$

$$> 0 \Rightarrow \delta n_j \geq 0 \Rightarrow n_j = 0 \tag{37}$$

with μ the Lagrange multiplier for particle number N. It follows that within exact KS theory the highest occupied KS eigenvalue is the exact Fermi energy [50, 51]. Noninteger occupancy at the Fermi energy only occurs for degeneracies: $n_j = 1/f$ with f the degree of degeneracy.

As mentioned, constrained search, including the present development, can be extended to ensemble densities

$$\check{n}(\mathbf{x}) = \sum_j w_j n_j(\mathbf{x}), \tag{38}$$

where $0 \leq w_j \leq 1$, $\sum_j w_j = 1$, and n_j arises from a pure state (not necessarily a ground state). Note that the resulting functional $\check{F}_H$ differs in general from the pure state functional; for example, it is convex (see Ref. [36], sect. 4.B):

$$\check{F}_H[\check{n}] \leq \sum_j w_j \check{F}_H[n_j]. \tag{39}$$

Aside: In addition to the mathematical subtleties pointed out by Lieb in Ref. [36], the more-or-less conventional constrained search development summarized above has been criticized on at least two grounds. Weinert and Davenport [52] claim to show that use of noninteger occupation numbers requires adding a term to the variational energy expression. Their argument assumes the sequential, three-step variation sketched. Subsequently Valiev and Fernando [53] claim to invalidate the Janak–Slater theorem on grounds of nondifferen-

tiability of T_s with respect to arbitrary occupation numbers. We leave both of these apparently unresolved issues aside.

General Spin Orbital Symmetries

The symmetry group $\tilde{G}$ of a real, spin-independent molecular Hamiltonian such as Eq. (1) always includes $S \times T \times P$ where S is the group of rotations in spin space [$S \simeq$ SU(2)], T is time reversal, and P is the molecular point group. Variational prescriptions which yield effective Hamiltonians lead to the question of invariances with respect to $\tilde{G}$. Enforcement of full invariance in restricted HF theory leads to the symmetry dilemma.

Nothing in the formulation given guarantees that the KS one-body Hamiltonian is invariant with respect to $\tilde{G}$. Within DFT there does not seem be any reason why such a correspondence must occur, since the only symmetries which must arise from the KS equation are those of the densities. Rather than consider a symmetrized KS theory along the lines of Görling [23] therefore, we consider the possibility of symmetry classification according to invariance with respect to the subgroup $G = S \times T$. In a certain sense this choice is more general since there is no restriction to the properties of the point group P.

Frequently invariances with respect to G are addressed simply by restricting the domain of the effective one-fermion Hamiltonian h_{eff} to real functions which are distinguished with respect to spin by labels: ''different orbitals for different spins'' in the HF context. (Spin-polarized DFT is an analog.) Extension of HF to general spin orbitals (GSOs)

$$\varphi_i(\mathbf{r}, s) = \chi_{i\alpha}(\mathbf{r})\alpha(s) + \chi_{i\beta}(\mathbf{r})\beta(s) \tag{40}$$

is equivalent to changing the domain of h_{eff}. The effect would be nil for a real, spin-independent, local, one-body h_{eff}; the resulting exact fermion ground state is a restricted single determinant, i.e., with doubly occupied real orbitals. However, in the HF case, the change of domain is significant because h_{HF} is determined by the resulting Fock–Dirac one-particle reduced density kernel. Use of general spin orbitals leads [42] to h_{HF} explicitly in terms of a decomposition of the one-particle reduced density kernel

$$P\underline{1}\hat{Q} \cdot \underline{\hat{\sigma}} = \begin{bmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{bmatrix}, \tag{41}$$

where $\underline{\hat{\sigma}}$ is the vector of Pauli spin matrices, $\underline{1}$ is the 2×2 unit matrix, the number density kernel is

$$P(\mathbf{r}', \mathbf{r}) = \tfrac{1}{2}\big(\rho_{\alpha\alpha}(\mathbf{r}', \mathbf{r}) + \rho_{\beta\beta}(\mathbf{r}', \mathbf{r})\big), \tag{42}$$

and the components of the spin density kernel vector are

$$Q_1(\mathbf{r}', \mathbf{r}) = \tfrac{1}{2}\big(\rho_{\alpha\beta}(\mathbf{r}', \mathbf{r}) + \rho_{\beta\alpha}(\mathbf{r}', \mathbf{r})\big), \tag{43}$$

$$Q_2(\mathbf{r}', \mathbf{r}) = \frac{1}{2i}\big(\rho_{\beta\alpha}(\mathbf{r}', \mathbf{r}) - \rho_{\alpha\beta}(\mathbf{r}', \mathbf{r})\big), \tag{44}$$

$$Q_3(\mathbf{r}', \mathbf{r}) = \tfrac{1}{2}\big(\rho_{\alpha\alpha}(\mathbf{r}', \mathbf{r}) - \rho_{\beta\beta}(\mathbf{r}', \mathbf{r})\big). \tag{45}$$

The form of h_{HF} (omitted for brevity) depends explicitly on the *full* density kernel vector and not just the diagonal spin-labeled number densities $\rho_{\alpha\alpha}, \rho_{\beta\beta}$. Immediately, therefore, h_{HF} does not commute with all the elements of G, only with subgroups, whence those subgroups can be used to classify the determinants.

The summary of the HK functionals and KS procedure in the foregoing sections deliberately avoided introduction of diagonal spin densities as functional variables and worked instead with the full density as a function of the compound coordinate $\mathbf{x} \equiv (\mathbf{r}, s)$ and corresponding general spin orbitals in $\mathscr{H}^1$. The critical importance of this distinction now becomes apparent. Transcription of the theory to $\mathbf{R}^3$, i.e., to explicit spin orbitals, in general must yield an exchange–correlation potential V_{xc} which is dependent both on the number density and the spin density vector. By construction, there is no other place in the theory for explicit spin dependence to emerge. (Obviously, left aside are those approximate implementations which assume no dependence on any component of the spin density vector *a priori*.) Note that the XC potential is a scalar.

In general, therefore

$$h_{\text{KS}} = h_{\text{KS}}\big(P, \hat{Q}\big) \tag{46}$$

in the sense of being dependent on all the densities generated by $P, \hat{Q}$. The proof is by contradiction. Assume the contrary and consider a model system constructed such that its exact ground state is a nontrivial GHF state. Then the density dependence of the ground-state energy and the ground-state densities themselves as calculated from exact DFT applied to that model system must be identical with the corresponding GHF results. But that cannot happen if h_{KS} must depend fundamentally on

less than the full $P, \hat{Q}$ densities, which is a contra. Note that Gunnarsson and Lundqvist [27] earlier had demonstrated dependence on the full spin density matrix by means of a generalization of the original HKS proof by contradiction of the basic DFT theorems. Görling [23] also gets such dependence in his formulation by assuming an explicit general dependence on $P, \hat{Q}$ for the constrained search construction of the variational functional.

Because of Eq. (46), it is also true in general that h_{KS} will not commute with all the elements of G and the existence of nontrivial classification of the KS auxiliary state and its associated one-matrix by subgroups of G follows.

For simplicity and because the richness of the problem makes it prudent to proceed by well-delineated steps, we consider here the simplest case, namely the original assumption of a single KS determinant, but now with general spin orbitals and a corresponding general h_{KS}. Fukutome's classification of all possible single determinants according to their invariances with respect to the subgroups of G then can be carried over intact. Thus we need not repeat the analysis, only summarize; details are found in [22, 42–44].

In all there are eight subgroups: G itself, S, T, the trivial subgroup E, and four others. The other four separate into two, commonly denoted A and M, plus $A \times T$ and $A \times M$. It suffices therefore to summarize A and M. Let $U(g) \in \mathrm{SU}(2)$. The conventional parameterization of this spin-space rotation about a specified axis $\hat{v}$ (with $\hat{v} \cdot \hat{v} = 1$) through an angle θ is

$$u_s(\hat{v}, \theta) = \cos(\theta/2)\underline{1} + i \sin(\theta/2)\hat{v} \cdot \underline{\hat{\sigma}} \quad (47)$$

with 1 the two-dimensional unit matrix as before. The time reversal operator $U_a(g) \in T$ is realized as

$$u_a(g) = -i\underline{\sigma}_2 K, \quad (48)$$

where K is the operator of complex conjugation. Then the subgroups A and M are

$$A(\hat{v}) = \{u_s(\hat{v}, \theta); 0 \le \theta \le 4\pi; \hat{v} \text{ fixed}\}, \quad (49)$$

$$M(\hat{v}') = \{\underline{1}, u_a(g) \cdot u_s(\hat{v}', \pi); g \in T\}. \quad (50)$$

From the subgroups it is straightforward to work out the form of the density matrices with respect to the spatial orbitals. In density matrix form Eq. (41) becomes

$$\underline{P}\underline{1} + \underline{\hat{Q}} \cdot \underline{\hat{\sigma}} = \underline{D} = \begin{bmatrix} \underline{D}_{\alpha\alpha} & \underline{D}_{\alpha\beta} \\ \underline{D}_{\beta\alpha} & \underline{D}_{\beta\beta} \end{bmatrix}. \quad (51)$$

Recall that $\underline{\hat{Q}}$ is a vector of matrices $\underline{Q}_j$. The notation $\underline{P}\underline{1}$ and $\underline{Q}_j\underline{\sigma}_j$ signifies the matrix direct product. Let

$$\underline{P} = \underline{P}_R + i\underline{P}_I, \quad (52)$$

$$\underline{\hat{Q}} = \underline{\hat{Q}}_R + i\underline{\hat{Q}}_I, \quad (53)$$

$$\underline{\hat{Q}}_\perp = \underline{\hat{Q}} - \left(\hat{v} \cdot \underline{\hat{Q}}\right)\hat{v}, \quad (54)$$

where $\underline{P}_R, \underline{P}_I, \underline{\hat{Q}}_R, \underline{\hat{Q}}_I$ all are real matrices. Then the density matrices (names are taken from GHF; see the references cited) are:

Time reversal invariant closed shell:

$$\underline{D} = \underline{P}_R\underline{1}; \qquad \underline{P}_I = \underline{\hat{Q}} = 0, \quad (55)$$

Charge current waves:

$$\underline{D} = \underline{P}\underline{1}; \qquad \underline{\hat{Q}} = \underline{0}, \quad (56)$$

Axial spin current waves:

$$\underline{D} = \underline{P}_R\underline{1} + i\underline{\hat{Q}}_I(\hat{v} \cdot \hat{\sigma}), \quad (57)$$

Axial spin density waves:

$$\underline{D} = \underline{P}_R\underline{1} + i\underline{\hat{Q}}(\hat{v} \cdot \underline{\hat{\sigma}}), \quad (58)$$

Axial spin waves:

$$\underline{D} = \underline{P}\underline{1} + i\underline{\hat{Q}}(\hat{v} \cdot \underline{\hat{\sigma}}), \quad (59)$$

Torsional spin current waves:

$$\underline{D} = \underline{P}_R\underline{1} + i\underline{\hat{Q}}_I \cdot \underline{\hat{\sigma}}, \quad (60)$$

Torsional spin density waves:

$$\underline{D} = \underline{P}_R\underline{1} + i\underline{\hat{Q}}_I(\hat{v} \cdot \underline{\hat{\sigma}}) + \underline{\hat{Q}}_\perp \cdot \underline{\hat{\sigma}}, \quad (61)$$

Torsional spin waves:

$$\underline{D} = \underline{P}\underline{1} + \underline{\hat{Q}} \cdot \underline{\hat{\sigma}}. \quad (62)$$

For brevity, we make connections with the densities via the spatial part of the GSOs as follows:

$$\varrho(\mathbf{r}) = \sum_{ij} \bar{\chi}_i(\mathbf{r})\chi_j(\mathbf{r})\underline{P}_{ij}, \tag{63}$$

$$\hat{Q}(\mathbf{r}) = \sum_{ij} \bar{\chi}_i(\mathbf{r})\chi_j(\mathbf{r})\underline{\hat{Q}}_{ij}, \tag{64}$$

$$j(\mathbf{r}) = -i\sum_{ij}\left(\nabla\bar{\chi}_i(\mathbf{r})\chi_j(\mathbf{r}) - \bar{\chi}_i(\mathbf{r})\nabla\chi_j(\mathbf{r})\right)\underline{P}_{ij}, \tag{65}$$

$$\hat{j}_k(\mathbf{r}) = -i\sum_{ij}\left(\nabla\bar{\chi}_i(\mathbf{r})\chi_j(\mathbf{r}) - \bar{\chi}_i(\mathbf{r})\nabla\psi_j(\mathbf{r})\right)\underline{\hat{Q}}_{k,ij}. \tag{66}$$

Note that these are *not* in occupation number form.

Implicit in these density matrices and densities is the fact that each subgroup of $S \times T$ determines a particular form of the general spin orbitals for a single determinant. A clear, explicit tabulation of those forms is in Ref. [44], hence they need not be reproduced here.

Conclusions

Several new and/or differently delineated results have been presented. A general treatment of density functional theory in terms of all the fermion coordinates and not just the spatial ones shows that the KS effective Hamiltonian must depend upon all the densities determined by the auxiliary state one-particle reduced density kernel, not just the spin-labeled diagonal parts. Other presentations presume this to be the case in the way that the density variables are chosen; it emerges of necessity in this treatment. Therefore the $S \times T$ subgroup classification of the KS auxiliary state is nontrivial. That being the case, general complex KS orbitals are called for, even for a single-determinant KS auxiliary state. These results suggest strongly that attempts to build better approximate HK functionals should involve general spin orbitals *a priori*. The results also show that it is possible to have symmetry dilemmas for the case of exact KS theory. All that is required is knowledge of an exact KS model for a particular $S \times T$ subgroup and an attempt to solve that model exactly for a physical problem having densities which lie outside the subgroup.

We said at the outset that this is an initial report on a large project. At the least, the remaining work includes treatment of ensembles (hence, also, ensemble symmetrization of broken-symmetry solutions), stability analysis [54–56], $S \times T$ subgroup classification with respect to other auxiliary states of specified form, implications of $S \times T$ classification for the construction of V_{xc} given the densities, examination of the behavior of extant E_{xc} approximations, reexamination of the detailed steps of the functional variation that lead to the KS equations, and extension to time-dependent DFT.

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