Dyson Field: A Quasiparticle Mapping for Multi-State Density Functional Theory

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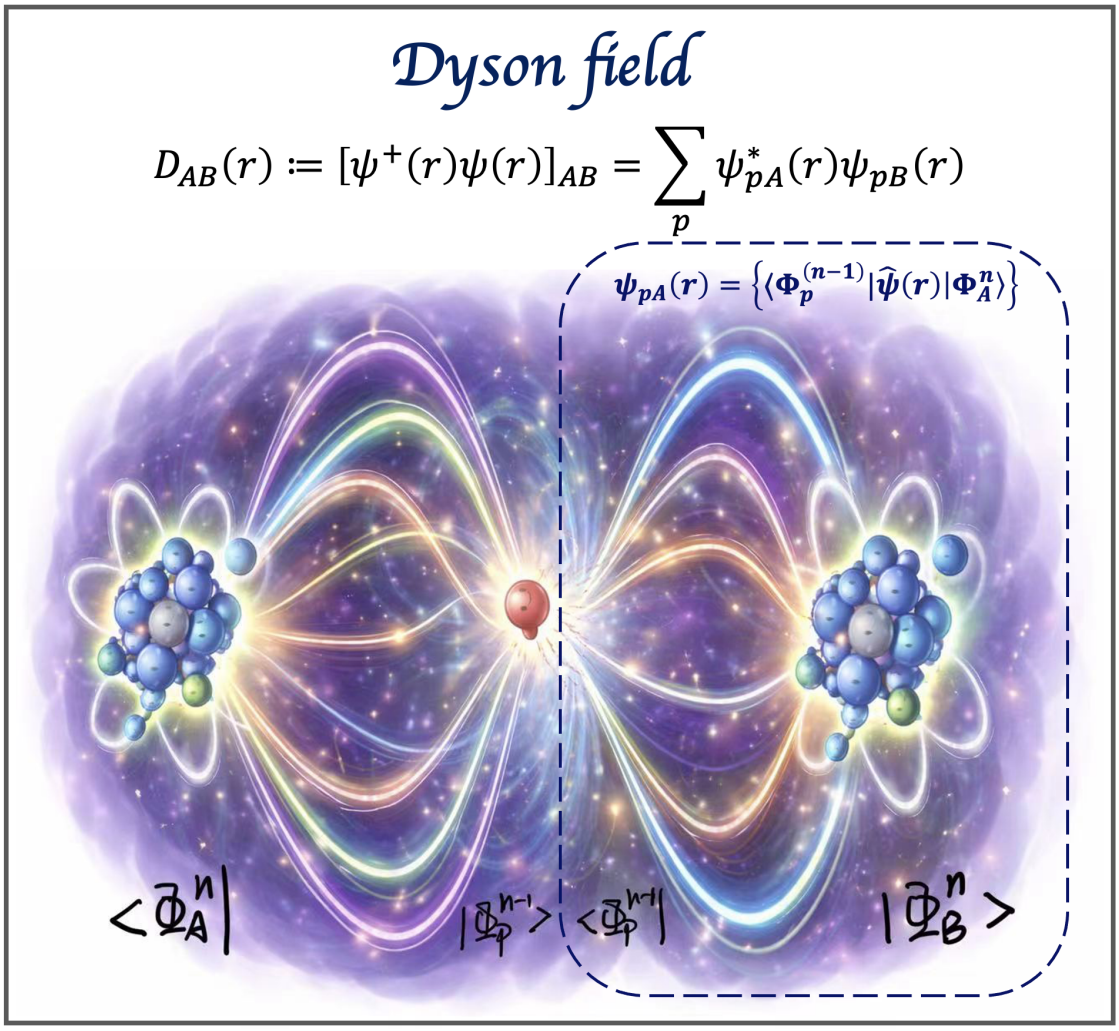
Abstract

Multistate density functional theory (MSDFT) provides a rigorous variational framework for the simultaneous description of multiple electronic states through a matrix density, but practical implementations have relied on multiconfigurational many-body wavefunctions. Here, we introduce the *Dyson field*, $\psi(\mathbf{r})$, an $L \times N$ matrix-valued function of the coordinate $\mathbf{r}$ that factorizes the matrix density as $\mathbf{D}(\mathbf{r}) = \psi^{\dagger}(\mathbf{r})\psi(\mathbf{r})$. The elements of $\psi(\mathbf{r}) = \{\psi_{pA}(\mathbf{r})\}$ are shown to be Dyson orbitals connecting the n-electron states of interest to $(n-1)$-electron ionization channels of size L, providing a direct physical interpretation of the matrix density in terms of electron removal amplitudes. Variational minimization of the MSDFT subspace energy with respect to the Dyson field yields a matrix Fock equation,

$$\left[-\tfrac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r})\right]\psi(\mathbf{r}) + \psi(\mathbf{r})\left[\mathbf{V}^{H}[\mathbf{D}](\mathbf{r}) + \mathbf{V}^{\mathrm{xc}}[\mathbf{D}](\mathbf{r})\right] = \psi(\mathbf{r})\mathcal{E},$$

in which the kinetic and external potential operators act locally, while Hartree and exchange–correlation effects appear as $N \times N$ matrix potentials, $\mathbf{V}^{H}[\mathbf{D}](\mathbf{r})$ and $\mathbf{V}^{\mathrm{xc}}[\mathbf{D}](\mathbf{r})$, that couple electronic states within the subspace. This formulation defines a quasiparticle reference system for MSDFT that is analogous to the Kohn–Sham orbitals in Hohenberg-Kohn DFT. In appropriate limits, the formalism reduces exactly to Kohn-Sham DFT for $N = 1$ and to the Tamm-Dancoff approximation of time-dependent DFT within the single-excitation manifold. More generally, the Dyson-field construction transforms MSDFT from a formally exact but wavefunction-dependent framework into an orbital-based theory, opening a practical route to self-consistent, density-based treatments of strongly correlated and electronically coupled states.



TOC Figure.

1. Introduction

A major challenge in electronic structure theory is the simultaneous and balanced description of multiple electronic states. A century after Erwin Schrödinger's formulation of the wave equation in 1926, electronic structure theory continues to evolve between wavefunction-based[1] and reduced-variable descriptions,[2–6] seeking both formal rigor and computational efficiency. The need to describe multiple, energetically close electronic states within a single consistent framework underlies a wide range of phenomena, from photochemistry and charge transfer to strongly correlated systems, where ground and excited states are intrinsically coupled.[7–15] Wavefunction-based methods provide, in principle, a systematic route, but their computational cost grows rapidly with system size and number of states, and the balanced treatment of dynamic and static correlation remains demanding.[16,17] Unfavorable scaling and imbalanced correlation treatment motivate density-based approaches that retain the advantages of density functional theory (DFT) while extending its scope beyond the ground state.[18–27]

The success of DFT lies in replacing the many-electron wavefunction with the electron density and introducing an auxiliary non-interacting reference system.[4,28,29] However, this framework is inherently single-state.[30–32] Extensions such as linear-response time-dependent DFT (LR-TDDFT) are based on perturbations of the ground state and do not provide a general variational description of multiple states.[33–35] This limitation is especially pronounced in strongly correlated, near-degenerate, and nonadiabatic regimes.[36,37]

Multistate density functional theory (MSDFT) addresses this limitation by elevating the basic variable to a matrix density defined within a finite-dimensional subspace of electronic states.[5,6] In this framework, state and transition densities are unified, and the Hamiltonian is expressed as a matrix functional of the density, yielding a rigorous, time-independent variational theory for multiple states.[5,38] A defining feature is subspace invariance, which leads to the "one-determines-all" (ODA) principle:[39,40] the Hamiltonian matrix functional is internally constrained such that all its elements can be generated from a single scalar

functional. Despite this formal foundation,[41] a key element of the DFT paradigm - the direct use of the density variable - has been missing.[16,27,38]

Here, we introduce a quasiparticle mapping of the matrix density through the Dyson field,[42–44] a matrix-valued function whose elements are Dyson orbitals connecting many-electron states to ionized configurations.[45,46] This factorization provides a direct physical interpretation in terms of electron removal amplitudes,[47,48] while defining an orbital representation that does not rely on auxiliary many-body wavefunctions. The Dyson field further establishes a non-interacting quasiparticle reference system for MSDFT: by expressing the kinetic energy and density in terms of this field, the multistate variational problem becomes a self-consistent optimization, leading to a generalized Fock equation in which inter-state coupling arises naturally through matrix-valued potentials, thereby defining a multistate analogue of the Kohn–Sham framework with intrinsic state coupling at the one-particle level. This Dyson-field mapping transforms MSDFT from a formally exact yet wavefunction-dependent framework into a practical, orbital-based theory; in appropriate limits, it reduces to Kohn–Sham DFT and the Tamm–Dancoff approximation to TDDFT, while more generally providing a nonperturbative variational formulation. Combined with spectral decomposition based on the ODA principle,[40] the exchange–correlation matrix functional reduces to scalar channel functions evaluated on a real-space grid. These results complete the structural foundation of MSDFT: the matrix density defines the basic variable, the Hamiltonian matrix functional defines the energy, and the Dyson field provides the quasiparticle representation enabling self-consistent computation. This framework opens a route to treating strongly coupled electronic states with efficiency and clarity comparable to Kohn-Sham DFT.

The remainder of this paper is organized as follows. Section 2 reviews the essential elements of MSDFT and the partition of the Hamiltonian matrix functional. Section 3 introduces the Dyson field, establishes its physical interpretation, and discusses the associated spectroscopic sum rules. Section 4 derives the Dyson-field SCF equation through constrained variational minimization. Section 5 examines key properties, including the re-

duction to Kohn–Sham theory and TDDFT. Section 6 describe computational algorithms, and Section 7 summarizes the main results and outlines future directions.

2. Multi-State Density Functional Theory

For an n-electron system, the Hamiltonian projected onto an N-dimensional Hilbert subspace $\mathbb{S}^N$ can be expressed as a matrix functional of the matrix density $\mathbf{D}(\mathbf{r})$:[5]

$$\mathcal{H}[\mathbf{D}] = \mathcal{F}[\mathbf{D}] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, \mathbf{D}(\mathbf{r}), \tag{1}$$

where $\mathcal{F}[\mathbf{D}]$ is a universal matrix functional, independent of the external potential $v_{\text{ext}}(\mathbf{r})$.[41] The rank-$N$ matrix density $\mathbf{D}(\mathbf{r})$ is defined through its matrix elements

$$D_{AB}(\mathbf{r}) = \langle \Phi_A | \hat{\rho}(\mathbf{r}) | \Phi_B \rangle, \quad A, B = 1, \ldots, N, \tag{2}$$

where $\hat{\rho}(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r})$ is the one-particle density operator with $\hat{\psi}^\dagger(\mathbf{r})$ and $\hat{\psi}(\mathbf{r})$ denoting the creation and annihilation operators, and $\{|\Phi_A\rangle\}$ forms an orthonormal basis spanning $\mathbb{S}^N$. $\mathbf{D}(\mathbf{r})$ can be obtained variationally by minimizing the trace of the Hamiltonian matrix:[5,38]

$$\mathbb{E}[v] = \frac{1}{N} \min_{\mathbf{D}(\mathbf{r})} \text{Tr}\{\mathcal{H}[\mathbf{D}]\}, \tag{3}$$

where $\mathbb{E}[v] = N^{-1} \sum_{I=1}^{N} E_I$ is the multistate energy, corresponding to the average energy of the lowest N eigenstates in the subspace.

A key feature of this formulation is its invariance under unitary transformations within the subspace.[39] Specifically, under the unitary transformation of state basis

$$\mathbf{D}(\mathbf{r}) \longmapsto \mathbf{D}'(\mathbf{r}) = \mathbf{U}^\dagger \mathbf{D}(\mathbf{r}) \mathbf{U}, \tag{4}$$

the Hamiltonian matrix functional transforms as

$$\mathcal{H}[\mathbf{U}^\dagger \mathbf{D} \mathbf{U}] = \mathbf{U}^\dagger \mathcal{H}[\mathbf{D}] \mathbf{U}. \tag{5}$$

with $\mathbf{U}$ being an arbitrary N-dimensional unitary matrix. This equivariant transformation property reflects the fact that physical observables are independent of the particular choice of basis in $\mathbb{S}^N$, and it imposes a necessary constraint on any admissible matrix functional of $\mathbf{D}(\mathbf{r})$.

3. Dyson Field and Quasiparticle mapping of $\mathbf{D}(\mathbf{r})$

The matrix density $\mathbf{D}(\mathbf{r})$ introduced above is defined in terms of multiconfigurational many-electron wave functions. In view of the success of Kohn–Sham density functional theory (KS-DFT), in which a non-interacting reference system through Kohn-Sham orbitals is constructed to reproduce the exact ground-state density, it is natural to ask whether an analogous representation exists for the multistate matrix density. Specifically, can one construct a quasiparticle, non-interacting-like reference framework that reproduces $\mathbf{D}(\mathbf{r})$ for a finite set of electronic states while retaining a one-electron, orbital-like structure?

The answer is affirmative at the level of representation. In the following, we show that the matrix density can be exactly factorized in terms of Dyson orbitals, leading to a Dyson-field description that provides a quasiparticle mapping of $\mathbf{D}(\mathbf{r})$. This construction establishes a formally exact correspondence between the multistate density and a set of one-electron objects with direct spectroscopic interpretation, thereby providing the multistate analog of the Kohn–Sham orbital representation in density functional theory.

Representing matrix density with Dyson orbitals

We begin by introducing the quasiparticle Dyson orbital, ψ_{pA}, defined as the overlap between an n-electron state $|\Phi_A^n\rangle$ and an $(n-1)$-electron ionic state $|\Phi_p^{n-1}\rangle$:[45,46]

$$\psi_{pA}(x_1) = \sqrt{n} \int \Phi_A^n(x_1, x_2, \ldots, x_n) \Phi_p^{n-1*}(x_2, \ldots, x_n)\, dx_2 \ldots dx_n \tag{6}$$

where $x_1 \equiv (r_1, \sigma_1)$ denotes the spatial and spin coordinates of the detached electron, and the remaining $n-1$ coordinates, $\int dx \equiv \sum_{\sigma=\alpha,\beta} \int \mathrm{d}\mathbf{r}$ are integrated out. In second quantization, this expression can be written compactly as

$$\psi_{pA}(x) \equiv \psi_{pA}(\mathbf{r}, \sigma) = \langle \Phi_p^{n-1} | \hat{\psi}(\mathbf{r}, \sigma) | \Phi_A^n \rangle, \tag{7}$$

The Dyson orbital describes the correlated distribution of the electron removed in an ionization process, incorporating the response of all remaining electrons.[49] In the absence of electron correlation, as in Hartree–Fock theory, the Dyson orbital reduces to the canonical molecular orbital from which the electron is removed. In general, the Dyson orbital ψ_{pA} is neither normalized nor orthogonal to each other. Its squared norm, $||\psi_{pA}||^2$, gives the pole strength associated with the ionization transition and is directly related to observables in photoemission and electron momentum spectroscopy.[47,48]

Inserting the resolution of identity in the $(n-1)$-electron space,

$$\hat{I}^{(n-1)} = \sum_{p=1}^{\infty} |\Phi_p^{n-1}\rangle\langle\Phi_p^{n-1}| \tag{8}$$

into the definition of the matrix density (2) yields

$$D_{AB}(\mathbf{r}) = \sum_{\sigma=\alpha,\beta} \sum_{p=1}^{\infty} \langle \Phi_A^n | \hat{\psi}^\dagger(\mathbf{r}, \sigma) | \Phi_p^{n-1} \rangle \langle \Phi_p^{n-1} | \hat{\psi}(\mathbf{r}, \sigma) | \Phi_B^n \rangle. \tag{9}$$

Recognizing the Dyson orbitals of eq (7) and noting that

$$\langle \Phi_A^n | \hat{\psi}^\dagger(\mathbf{r},\sigma) | \Phi_p^{n-1} \rangle = \psi_{pA}^*(\mathbf{r},\sigma), \tag{10}$$

the elements of the matrix density can be expressed exactly as a sum over all ionic states:

$$D_{AB}(\mathbf{r}) = \sum_{\sigma=\alpha,\beta} \sum_{p}^{\infty} \psi_{pA}^*(\mathbf{r},\sigma)\psi_{pB}(\mathbf{r},\sigma) \tag{11}$$

where the sum spans the complete spectrum of the $(n-1)$-electron system.

Quasiparticle mapping of $\mathbf{D}(\mathbf{r})$

The representation of eq (11) shows that, at each spatial point $\mathbf{r}$, the matrix density can be written exactly in the factorized form

$$\mathbf{D}(\mathbf{r}) = \mathrm{tr}_{\mathrm{spin}}\{\psi^\dagger(\mathbf{r},\sigma)\,\psi(\mathbf{r},\sigma)\} \equiv \psi^\dagger(\mathbf{r})\,\psi(\mathbf{r}), \tag{12}$$

where $\psi(\mathbf{r})$ is an $L \times N$ matrix-valued function, L being the number of ionizing channels for the N states of $\mathbf{D}(\mathbf{r})$. We refer to $\psi(\mathbf{r})$ as the **Dyson field**, whose elements $\psi_{pA}(\mathbf{r})$ constitute a set of *generalized* one-electron orbitals if we adopt a finite number L in eq (12) purely for representing $\mathbf{D}(\mathbf{r})$. We use the two expressions of ψ in eq (12) interchangeably: In the first expression, $\psi(\mathbf{r},\sigma)$, the spin coordinate σ is explicitly presented, whereas in the latter, $\psi(\mathbf{r}) = \{\psi_{pA}(\mathbf{r})\}$, the elements are spin-orbitals, in other words, the spin coordinate is part of the orbital index, which is frequently used in the second-quantization formalism.

The exact resolution of identity in the $(n-1)$-electron Hilbert space (Eq. (8)) formally involves an infinite set of ionic states, corresponding to a full configuration interaction (FCI) description. In practice, however, only a finite subset of ionizing channels carries significant spectral weight. For the matrix density $\mathbf{D}(\mathbf{r})$ associated with N states of an n-electron system, the sum rule (see below) implies that a minimal set of $L = n \times N$ generalized Dyson

orbitals is sufficient to reproduce the correct total electron number across the subspace.[6]

Equation (12) is the multistate analogue of the Kohn–Sham decomposition of the ground-state density,

$$\rho(\mathbf{r}) = \sum_{i=1}^{n} |\varphi_i(\mathbf{r})|^2, \tag{13}$$

but generalized to a matrix-valued density. In this sense, the Dyson field provides a natural multistate quasiparticle representation of $\mathbf{D}(\mathbf{r})$, in which the full many-body effects are encoded in the structure of the generalized orbitals.

In analogy with KS-DFT, where n orbitals reproduce the ground-state density, the truncated Dyson field, $\mathbf{D}(\mathbf{r}) = \psi^\dagger(\mathbf{r})\psi(\mathbf{r})$, provides a quasiparticle mapping of the matrix density onto a set of generalized one-electron orbitals. This mapping, which is constructed from a finite set of Dyson-like orbitals ($L = nN$) encoding correlated electron removal amplitudes, serves as a representation of $\mathbf{D}(\mathbf{r})$ rather than of the underlying many-electron wave functions.

In the context of density representation, the Dyson field defines an auxiliary quasiparticle, non-interacting-like framework that maps the multistate matrix density $\mathbf{D}(\mathbf{r})$ onto a finite set of generalized one-electron orbitals, without invoking a corresponding many-electron wavefunction. We emphasize that the purpose of this construction is not to approximate the underlying many-body states, but to provide an exact representation of $\mathbf{D}(\mathbf{r})$ in terms of a minimal set of Dyson-field components. While this mapping is formally exact in the complete Dyson expansion, its practical implementation relies on a controlled truncation, analogous to representing the ground-state density with a finite set of Kohn–Sham orbitals. This construction establishes the foundation of a quasiparticle framework for multistate density functional theory.

Physical interpretation

The factorization (12) is not merely a mathematical identity; its explicit form in Eq. (11) provides a clear physical interpretation of the Dyson field. Each component $\psi_{pA}(\mathbf{r},\sigma)$ represents the amplitude for removing an electron at position $\mathbf{r}$ from the n-electron state A, leaving the system in the $(n-1)$-electron ionic state p.[45,46] The matrix element $D_{AB}(\mathbf{r})$ is obtained by summing over all such ionization channels, corresponding to a process in which an electron is removed from state A into channel p and subsequently reinserted into state B.

In this way, the Dyson field encodes all one-electron removal and reinsertion pathways connecting states A and B, and thus provides a natural representation of the transition density between them. The summation over p reflects the completeness of the $(n-1)$-electron spectrum, ensuring that all ionization channels are included. As a result, the Dyson field is not only a formal construct but also has a direct spectroscopic interpretation: its elements correspond to amplitudes associated with electron removal processes, such as photoemission. It therefore furnishes a physically motivated orbital-like representation of the matrix density $\mathbf{D}(\mathbf{r})$.

Spectroscopic sum rule

Using the anticommutation relations of the fermionic field operators and the completeness of the $(n-1)$-electron states, the matrix density satisfies the sum rule

$$\int \mathrm{d}\mathbf{r}\; D_{AB}(\mathbf{r}) = \sum_{p} \int \mathrm{d}\mathbf{r}\; \psi^{*}_{pA}(\mathbf{r})\,\psi_{pB}(\mathbf{r}) = \langle \Phi^{n}_{A}|\hat{N}|\Phi^{n}_{B}\rangle, \tag{14}$$

where $\hat{N} = \int \mathrm{d}\mathbf{r}\,\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}(\mathbf{r})$ is the number operator. For an orthonormal set of n-electron states, one obtains

$$\int \mathrm{d}\mathbf{r}\; D_{AB}(\mathbf{r}) = n\,\delta_{AB}. \tag{15}$$

When $N = 1$, this reduces to the well-known sum rule

$$\sum_p S_p = n, \tag{16}$$

where $S_p = \|\psi_p\|^2$ is the spectroscopic factor associated with ionization channel p.

Illustrative examples of Dyson field

We illustrate the Dyson field mapping of the matrix density $\mathbf{D}(\mathbf{r})$ by two specific examples.

One-electron system. Consider the simplest system of one electron. With $\psi(\mathbf{r}) = \{c_{PA}^{\mu}\chi_\mu(\mathbf{r})\}$ and $\{\chi_\mu(\mathbf{r})\}$ being a complete set of basis orbitals, the matrix density $\mathbf{D}(r)$ is given by

$$D_{AB}(r) = \sum_p c_{pA}^{\mu *} c_{pB}^{\nu} \chi_\mu^*(r)\chi_\nu(r) \tag{17}$$

We illustrate with the special case of $N = 3$. An arbitrary 3-matrix density $\mathbf{D}(r)$ has the following generic form,

$$\mathbf{D}(r) = \begin{pmatrix} |\phi_1|^2 & \phi_1^*\phi_2 & \phi_1^*\phi_3 \\ \phi_2^*\phi_1 & |\phi_2|^2 & \phi_2^*\phi_3 \\ \phi_3^*\phi_1 & \phi_3^*\phi_2 & |\phi_3|^2 \end{pmatrix} \tag{18}$$

where $\{\phi_A(\mathbf{r}) = \sum_\mu c_{A\mu}\chi_\mu(\mathbf{r}); A = 1, \ldots, 3\}$ are one-electron orbitals. The normalization condition of the matrix density requires that $\int \mathrm{d}\mathbf{r}\, D_{AB}(\mathbf{r}) = \delta_{AB}$ with $A, B = 1, 2, 3$, which means that

$$\int \mathrm{d}\mathbf{r}\, \phi_A^*(\mathbf{r})\phi_B(\mathbf{r}) = \delta_{AB} \tag{19}$$

Hence, the corresponding orbital field can be given by

$$\psi(r) = \begin{pmatrix} \phi_1(\mathbf{r}) & \phi_2(\mathbf{r}) & \phi_3(\mathbf{r}) \\ 0 & 0 & 0 \\ \vdots & \vdots & \vdots \end{pmatrix} \tag{20}$$

In other words, a 1×3 Dyson field is sufficient to represent an arbitrary 3-matrix density, because it is an one-electron system and no electron correlation is involved.

Two-electron system. We consider a two-electron system ($n = 2$), such as the hydrogen molecule, using a minimal molecular orbital basis $\{\phi_1, \phi_2\}$ corresponding to the σ_g and σ_u^* bonds. All orbitals and coefficients are taken to be real.

We start with the four determinant configurations as the initial states:

$$\Phi_0 = |\phi_1(1)\bar{\phi}_1(2)\rangle, \quad \Phi_1 = |\phi_2(1)\bar{\phi}_2(2)\rangle,$$
$$\Phi_2 = |\phi_1(1)\bar{\phi}_2(2)\rangle, \quad \Phi_3 = |\phi_2(1)\bar{\phi}_1(2)\rangle$$

where ϕ_j and $\bar{\phi}_j$ ($j = 1, 2$) indicate the α and β-spin orbitals. Then, the $(n-1)$-ion states, since $n = 2$ here, simply correspond to the four spin-orbitals ($\phi_1, \bar{\phi}_1, \phi_2$ and $\bar{\phi}_2$), i.e., a total of four possible ionization channels. In this basis, the Dyson field has the following form:

$\boldsymbol{\psi}_{\mathrm{L\times N}} =$

Φ_{pA}^{n-1} channel	$\Phi_0(\sigma_g^2)$	$\Phi_1(\sigma_u^2)$	$\Phi_2(\sigma_g\bar{\sigma}_u)$	$\Phi_3(\sigma_u\bar{\sigma}_g)$
$\sigma_g(\mathbf{r})\alpha$	$\phi_1(\mathbf{r})$	0	$\phi_2(\mathbf{r})$	0
$\sigma_g(\mathbf{r})\beta$	$-\bar{\phi}_1(\mathbf{r})$	0	0	$-\bar{\phi}_2(\mathbf{r})$
$\sigma_u(\mathbf{r})\alpha$	0	$\phi_2(\mathbf{r})$	0	$\phi_1(\mathbf{r})$
$\sigma_u(\mathbf{r})\beta$	0	$-\bar{\phi}_2(\mathbf{r})$	$-\bar{\phi}_1(\mathbf{r})$	0

where the matrix entries are the Dyson orbitals, correponding to the overlap $\psi_{pA}(\mathbf{r}, \sigma) = \langle \Phi_p^{(1)} | \hat{\psi}(\mathbf{r}, \sigma) \Phi_A^{(2)} \rangle$ between the initial 2-electron state and the ion state. From the Dyson

field, we immediately obtain the matrix density in determinant basis

$$\mathbf{D}(\mathbf{r}) = \sum_{\sigma=\alpha,\beta} \psi^{\dagger}(\mathbf{r},\sigma)\psi(\mathbf{r},\sigma) = \begin{pmatrix} 2\phi_1^2 & 0 & \phi_1\phi_2 & \phi_1\phi_2 \\ 0 & 2\phi_2^2 & \phi_1\phi_2 & \phi_1\phi_2 \\ \phi_1\phi_2 & \phi_1\phi_2 & \phi_1^2+\phi_2^2 & 0 \\ \phi_1\phi_2 & \phi_1\phi_2 & 0 & \phi_1^2+\phi_2^2 \end{pmatrix} \tag{21}$$

In this example, the dimension $L = 4$, which is greater than $n = 2$. In general, the left dimension of the Dyson field is greater than the number of electrons, $L > n$; this is because the Dyson field not only gives the density of each state but also the transition density between states.

We now turn to an equivalent representation of the Dyson field in the basis of configuration state functions (CSF). Since both Φ_0 and Φ_1 are already eigenfunctions of $\hat{S}^2$, we just need to construct the spin-coupled singlet and triplet states with $S_z = 0$ through the unitary matrix,

$$\mathbf{U} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ 0 & 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \tag{22}$$

Then, we obtain the CSF states $\{\Phi_0, \Phi_1, \Phi_{S1}, \Phi_{T0}\}$, the singlet and triplet states are

$$\Phi_{S1} = \frac{1}{\sqrt{2}}\left(\Phi_2 + \Phi_3\right), \quad \Phi_{T0} = \frac{1}{\sqrt{2}}\left(-\Phi_2 + \Phi_3\right) \tag{23}$$

Under the rotated CSF basis, $\{\Phi_0, \Phi_1, \Phi_{S1}, \Phi_{T0}\}$, the Dyson field can be formulated through

$$\boldsymbol{\psi}^{\mathrm{CSF}} = \boldsymbol{\psi}\mathbf{U}$$

$$\boldsymbol{\psi}^{\mathrm{CSF}} = \begin{array}{c|cccc} \Phi_{pA}^{n-1}\text{ channel} & \Phi_0(\sigma_g^2) & \Phi_1(\sigma_u^2) & \Phi_{S1} & \Phi_{T0} \\ \hline \sigma_g\alpha(\mathbf{r}) & \phi_1(\mathbf{r}) & 0 & \frac{1}{\sqrt{2}}\phi_2(\mathbf{r}) & -\frac{1}{\sqrt{2}}\phi_2(\mathbf{r}) \\ \sigma_g\beta(\mathbf{r}) & -\bar{\phi}_1(\mathbf{r}) & 0 & -\frac{1}{\sqrt{2}}\bar{\phi}_2(\mathbf{r}) & -\frac{1}{\sqrt{2}}\bar{\phi}_2(\mathbf{r}) \\ \sigma_u\alpha(\mathbf{r}) & 0 & \phi_2(\mathbf{r}) & \frac{1}{\sqrt{2}}\phi_1(\mathbf{r}) & \frac{1}{\sqrt{2}}\phi_1(\mathbf{r}) \\ \sigma_u\beta(\mathbf{r}) & 0 & -\bar{\phi}_2(\mathbf{r}) & \frac{1}{\sqrt{2}}\bar{\phi}_1(\mathbf{r}) & -\frac{1}{\sqrt{2}}\bar{\phi}_1(\mathbf{r}) \end{array}$$

Now we see that all ionization channels enter in the columns of the open-shell singlet and triplet states.

Then, the matrix density is obtained from the CSF-Dyson field as follows, which is identical to that transformed accordingly: $\mathbf{D}^{\mathrm{CSF}}(\mathbf{r}) = \mathbf{U}^{\dagger}\mathbf{D}(r)\mathbf{U}$.

$$\mathbf{D}^{\mathrm{CSF}}(\mathbf{r}) = \sum_{\sigma=\alpha,\beta} \psi^{\mathrm{CSF}\dagger}(\mathbf{r},\sigma)\psi^{\mathrm{CSF}}(\mathbf{r},\sigma) = \begin{pmatrix} 2\phi_1^2 & 0 & \sqrt{2}\phi_1\phi_2 & 0 \\ 0 & 2\phi_2^2 & \sqrt{2}\phi_1\phi_2 & 0 \\ \sqrt{2}\phi_1\phi_2 & \sqrt{2}\phi_1\phi_2 & \phi_1^2+\phi_2^2 & 0 \\ 0 & 0 & 0 & \phi_1^2+\phi_2^2 \end{pmatrix} \tag{24}$$

Genearalization to multiconfiguraitonal wave function. The illustration above can be generalized to any multiconfiguraitonal state functions expressed in determinant basis; the latter is convenient for practical construction of the Dyson field. Let $\{|\Phi_A\rangle\}_{A=1}^{M}$ be determinants and $\{|\Psi_I\rangle\}_{I=1}^{N}$ be the N primary states of interest, expanded as

$$|\Psi_I\rangle = \sum_{A=1}^{M} C_{AI}|\Phi_A\rangle \tag{25}$$

where C_{AI} are elements of the $M \times N$ coefficient matrix, with the N states orthonormalized: $\mathbf{C}^{\dagger}\mathbf{C} = \mathbf{I}_N$.

In terms of the Dyson field, if we have constructed a determinant-column Dyson field,

$\psi_{pA}^{\mathrm{det}}(\mathbf{r}) = \langle \Phi_p^{n-1} | \hat{\psi}(\mathbf{r}) | \Phi_A^n \rangle$ such that the matrix density in determinant basis is given by

$$\mathbf{D}^{\mathrm{det}}(\mathbf{r}) = \boldsymbol{\psi}^{\mathrm{det},\dagger}(\mathbf{r}) \boldsymbol{\psi}^{\mathrm{det}}(\mathbf{r}). \tag{26}$$

Then, the Dyson field in multiconfiguration state (MS) basis is obtained by the same projection on the right:

$$\boldsymbol{\psi}^{\mathrm{MS}}(\mathbf{r}) = \boldsymbol{\psi}^{\mathrm{det}}(\mathbf{r}) \mathbf{C}, \tag{27}$$

which is now $L \times N$ with L being the ionization channels. Its columns correspond to the N states. Consequently, we obtain the N-matrix density as follows.

$$\mathbf{D}^{\mathrm{MS}}(\mathbf{r}) = \boldsymbol{\psi}^{\mathrm{MS},\dagger}(\mathbf{r}) \boldsymbol{\psi}^{\mathrm{MS}}(\mathbf{r}) = \mathbf{C}^\dagger \boldsymbol{\psi}^{\mathrm{det},\dagger}(\mathbf{r}) \boldsymbol{\psi}^{\mathrm{det}}(\mathbf{r}) \mathbf{C} = \mathbf{C}^\dagger \mathbf{D}^{\mathrm{det}}(\mathbf{r}) \mathbf{C} \tag{28}$$

4. Dyson-field Fock equation

Non-interacting kinetic, Coulomb and xc matrix functional

Given the Dyson-field representation of the matrix density, $\mathbf{D}(\mathbf{r}) = \psi^\dagger(\mathbf{r}) \psi(\mathbf{r})$, we define the quasiparticle kinetic matrix functional as

$$\mathbf{T}_s[\psi] = -\tfrac{1}{2} \int \mathrm{d}\mathbf{r}\ \psi^\dagger(\mathbf{r}) \nabla^2 \psi(\mathbf{r}). \tag{29}$$

This is the natural multistate generalization of the Kohn–Sham kinetic energy. Importantly, $\mathbf{T}_s[\psi]$ is a matrix-valued functional whose diagonal elements correspond to individual state kinetic energies, while off-diagonal elements describe inter-state couplings mediated by the Dyson field. In the orbital component form,

$$\left[\mathbf{T}_s\right]_{AB} = -\frac{1}{2} \sum_{p=1}^{L} \langle \psi_{pA} | \nabla^2 | \psi_{pB} \rangle. \tag{30}$$

The Hartree matrix functional is written as

$$\mathcal{E}^H[\mathbf{D}] = \frac{1}{2}\int \frac{\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\,\mathbf{D}(\mathbf{r})\,\mathbf{D}(\mathbf{r}'), \tag{31}$$

The definition of the Hartree matrix functional in eq (31) introduces products of matrix densities, which inherently generates cross-state Coulomb interactions within the N-state subspace. Unlike the conventional scalar Hartree energy in KS-DFT, this construction allows electrostatic coupling between different electronic states through the off-diagonal elements of $\mathbf{D}(\mathbf{r})$. This is not a trivial extension but a deliberate modeling choice that embeds interstate Coulomb correlations directly at the mean-field level.

The remaining contribution to electronic energy defines the exchange–correlation matrix functional,

$$\mathcal{E}^{xc}[\mathbf{D}] = \mathcal{F}[\mathbf{D}] - \mathbf{T}_s[\psi] - \mathcal{E}^H[\mathbf{D}], \tag{32}$$

which, by construction, includes the residual kinetic energy

$$\mathbf{T}_{\mathrm{res}}[\mathbf{D}] = \mathcal{T}[\mathbf{D}] - \mathbf{T}_s[\psi]. \tag{33}$$

where $\mathcal{T}[\mathbf{D}]$ is the exact kinetic matrix functional.

In the limit of $L \to \infty$, the Dyson field $\psi(\mathbf{r})$ not only reproduces the exact N-matrix density $\mathbf{D}(\mathbf{r})$ but also the multi-state density matrix $\mathbf{D}(\mathbf{r},\mathbf{r}')$ defined by

$$D_{AB}(\mathbf{r},\mathbf{r}') := \langle\Phi_A|\hat{\psi}(\mathbf{r})\hat{\psi}(\mathbf{r}')|\Phi_B\rangle = [\psi^\dagger(\mathbf{r})\psi(\mathbf{r}')]_{AB} \tag{34}$$

which gives the exact kinetic matrix,

$$\mathcal{T}[\mathbf{D}] = -\frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\,\delta(\mathbf{r}-\mathbf{r}')\nabla^2\mathbf{D}(\mathbf{r},\mathbf{r}') = -\tfrac{1}{2}\int \mathrm{d}\mathbf{r}\;\psi^\dagger(\mathbf{r})\nabla^2\psi(\mathbf{r}) \tag{35}$$

In this case, the residual kinetic energy vanishes, $\mathbf{T}_{\mathrm{res}}[\mathbf{D}] \to 0$.

Subspace energy functional

The subspace energy functional of MSDFT (3) can now be written in terms of the Dyson field as

$$E_S[\psi] = \frac{1}{N}\,\mathrm{Tr}\Big\{\mathbf{T}_s[\psi] + \int \mathrm{d}\mathbf{r}\, v_{\mathrm{ext}}(\mathbf{r})\,\mathbf{D}(\mathbf{r}) + \mathcal{E}^H[\mathbf{D}] + \mathcal{E}^{\mathrm{xc}}[\mathbf{D}]\Big\}. \tag{36}$$

To facilitate the variational treatment below, we define the Hartree matrix potential,

$$V^H_{AB}[\mathbf{D}](\mathbf{r}) = \int \frac{\mathrm{d}\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\, D_{AB}(\mathbf{r}'), \tag{37}$$

and the exchange–correlation matrix potential,

$$V^{\mathrm{xc}}_{AB}[\mathbf{D}](\mathbf{r}) = \frac{\delta}{\delta D_{BA}(\mathbf{r})} \sum_{A=1}^{N} \mathcal{E}^{\mathrm{xc}}_{AA} \tag{38}$$

where the transpose in the index ($\delta/\delta D_{BA}$ rather than $\delta/\delta D_{AB}$) ensures that $\mathbf{V}^{\mathrm{xc}}$ inherits the Hermiticity of $\mathbf{D}$.

Dyson-field Fock equation

We seek the Dyson field $\psi(\mathbf{r})$ that minimizes the subspace energy $E_S[\psi]$ (eq (36)) subject to the normalization constraint

$$\int \mathrm{d}\mathbf{r}\; \psi^\dagger(\mathbf{r})\psi(\mathbf{r}) = n\mathbf{I}_N. \tag{39}$$

where $\mathbf{I}_N$ is a rank N unit matrix. We construct the Lagrangian,

$$\mathcal{L} = NE_S[\psi] - \mathrm{Tr}\left[\mathbf{\Lambda}\left(\int \mathrm{d}\mathbf{r}\; \psi^\dagger\psi - n\mathbf{I}_N\right)\right]. \tag{40}$$

where $\mathbf{\Lambda}$ is an $N \times N$ Hermitian matrix of Lagrange multipliers.

The derivatives of the kinetic energy and the external potential terms can be obtained

directly:

$$\frac{\delta}{\delta\psi^*_{PA}(\mathbf{r})}\left(\mathrm{Tr}\ \mathbf{T}_s\right) = -\frac{1}{2}\nabla^2\psi_{PA}(\mathbf{r}). \tag{41}$$

and

$$\frac{\delta}{\delta\psi^*_{PA}(\mathbf{r})}\left(\mathrm{Tr}\int v_{\mathrm{ext}}\mathbf{D}\right) = v_{\mathrm{ext}}(\mathbf{r})\,\psi_{PA}(\mathbf{r}). \tag{42}$$

The trace of the Hartree and exchange-correlation functionals involve the relation $D_{AB}(\mathbf{r}) = \sum_Q \psi^*_{QA}(\mathbf{r})\,\psi_{QB}(\mathbf{r})$, and after straightforward application of the derivative chain rule (Appendix), we arrived at the expressions,

$$\frac{\delta}{\delta\psi^*_{PA}(\mathbf{r})}\left(\mathrm{Tr}\ \mathcal{E}^H\right) = \sum_B \psi_{PB}(\mathbf{r})\left[\mathbf{V}^H(\mathbf{r})\right]_{BA} = \left[\psi(\mathbf{r})\,\mathbf{V}^H(\mathbf{r})\right]_{PA}. \tag{43}$$

and

$$\frac{\delta}{\delta\psi^*_{PA}(\mathbf{r})}\left(\mathrm{Tr}\ \mathcal{E}^{\mathrm{xc}}\right) = \left[\psi(\mathbf{r})\,\mathbf{V}^{xc}(\mathbf{r})\right]_{PA}. \tag{44}$$

Importantly, for eqs (43)-(44), the $N \times N$ matrix functions $\mathbf{V}^H(\mathbf{r})$ and $\mathbf{V}^{\mathrm{xc}}(\mathbf{r})$ are multiplied to the right of the Dyson field since $\psi(\mathbf{r})$ is a $L \times N$ matrix function. Finally, the variation of the Lagrange-multiplier term yields

$$\frac{\delta}{\delta\psi^*_{PA}(\mathbf{r})}\,\mathrm{Tr}_N\left[\mathbf{\Lambda}\int \mathrm{d}\mathbf{r}'\ \psi^\dagger(\mathbf{r}')\psi(\mathbf{r}')\right] = \left[\mathbf{\Lambda}\,\psi(\mathbf{r})\right]_{PA}. \tag{45}$$

Combining Eqs. (41)–(45) and setting the stationary condition, we obtain the *generalized Fock equation* for the Dyson orbitals,

$$\left[-\tfrac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r})\right]\psi(\mathbf{r}) + \psi(\mathbf{r})\left[\mathbf{V}^H(\mathbf{r}) + \mathbf{V}^{\mathrm{xc}}(\mathbf{r})\right] = \psi(\mathbf{r})\mathbf{\Lambda}, \tag{46}$$

where $\mathbf{\Lambda}$ is an N-dimensional Hermitian matrix of generalized energies.

Equation (46) is a differential equation of matrix functions, which differs fundamentally from the Kohn-Sham equation. Here, the kinetic operator and external potential act element-wise on the elements of the Dyson field, governing spatial dynamics, while the Hartree and

xc matrix potentials act from the right, coupling the electronic states within the subspace. It provides the basis for a generalized mean-field theory in which inter-state coupling is treated on equal footing with single-particle motion. Equation (46) therefore defines a quasiparticle equation in a coupled-channel representation: although no explicit many-body interaction operator appears, the orbital components are coupled through the state-dependent matrix potential. In this sense, the Dyson-field formalism generalizes the Kohn-Sham construction from scalar orbitals to a matrix of quasiparticles, providing a multistate extension of one-particle density-based theory.

Equation (46) is the central result of this work.

Canonical Dyson field and orbitals

The Hermitian matrix $\mathbf{\Lambda}$ of eq (46) can be diagonalized by a unitary transformation such that

$$\mathbf{U}^\dagger \mathbf{\Lambda} \mathbf{U} = \mathrm{diag}(\mathcal{E}_1, \ldots, \mathcal{E}_N). \tag{47}$$

Defining the canonical Dyson field $\psi'(\mathbf{r}) = \psi(\mathbf{r})\mathbf{U}$, the matrix density transforms as $\mathbf{D}'(\mathbf{r}) = \mathbf{U}^\dagger \mathbf{D}(\mathbf{r})\mathbf{U}$. Under this transformation, the generalized Fock equation retains its form but is expressed in a basis in which the Lagrange multiplier matrix is diagonal. Writing $\psi' = (\psi_1, \cdots, \psi_N)$ in terms of its columns, eq (46) becomes

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r})\right] \psi_A(\mathbf{r}) + \sum_{B=1}^{N} \psi_B(\mathbf{r}) \left[\mathbf{V}^H(\mathbf{r}) + \mathbf{V}^{\mathrm{xc}}(\mathbf{r})\right]_{BA} = \mathcal{E}_A \psi_A(\mathbf{r}), \tag{48}$$

where we have dropped the prime symbol: $\psi_A(\mathbf{r}) \equiv \psi'_{.A}(\mathbf{r})$ which is the A-th column of ψ'. Each column $\psi_A(\mathbf{r})$ is an L-component vector function, and the equations remain coupled through the matrix potentials. Thus, the transformation diagonalizes the energy matrix but does not decouple the equations, reflecting the intrinsic coupling between electronic states.

Interpretation of eigenvalues

In ground-state Kohn-Sham theory, the highest occupied orbital energy is related to the ionization potential through Janak's theorem and related results.[50] The generalized eigenvalues obtained from eq (46) do not correspond to single-particle orbital energies in the Kohn–Sham sense. Instead, within the Dyson-field representation, they encode the energetics of electron removal from the multistate subspace.

The present Dyson-field formulation has an interpretation in terms of the projected electron-removal Green's function. For an n-electron state $|\Phi_A^n\rangle$ and a complete set of $(n-1)$-electron ionic states $\{|\Phi_p^{n-1}\rangle\}$, the removal spectral function is,[51,52]

$$A_{AB}^{(-)}(\mathbf{r},\mathbf{r}';\omega) = \sum_p \psi_{pA}^*(\mathbf{r}')\psi_{pB}(\mathbf{r})\,\delta\big[\omega - (E_B^n - E_p^{n-1})\big] \tag{49}$$

Integration over energy recovers the matrix density, $D_{AB}(\mathbf{r}) = \int d\omega\, A_{AB}^{(-)}(\mathbf{r},\mathbf{r};\omega)$, showing that $\mathbf{D}(\mathbf{r})$ is the zeroth moment of the projected removal spectrum (states within the subspace $\mathbb{S}^N$). Accordingly, the present generalized Fock equation may be viewed as a static density-functional approximation to the projected Dyson equation.[51,52] The generalized eigenvalues therefore represent effective quasiparticle removal energies, whereas the Dyson orbitals determine the corresponding spectral amplitudes in photoemission-type experiments.

Establishing a rigorous multistate analog of Janak's theorem, relating variations of the subspace energy to these generalized eigenvalues and to ionization processes and Green's function, remains an open theoretical problem and a promising direction for future work.

Self-consistent field procedure

Equations (12) and (46) must be solved self-consistently since $\mathbf{V}^H$ and $\mathbf{V}^{\mathrm{xc}}$ depend on $\mathbf{D}(\mathbf{r}) = \psi^\dagger(\mathbf{r})\psi(\mathbf{r})$, which in turn depends on $\psi(\mathbf{r})$.

A self-consistent-field (SCF) procedure proceeds as follows:

1. Construct an initial guess for the Dyson field $\psi^{(0)}(\mathbf{r})$.
2. Compute the k-th iterative Dyson field $\mathbf{D}^{(k)}(\mathbf{r}) = \psi^{(k)\dagger}(\mathbf{r})\psi^{(k)}(\mathbf{r})$.
3. Evaluate the matrix potentials $\mathbf{V}^H[\mathbf{D}^{(k)}]$ and $\mathbf{V}^{\rm xc}[\mathbf{D}^{(k)}]$.
4. Solve the generalized Fock equation (48) to obtain the updated Dyson field $\psi^{(k+1)}(\mathbf{r})$.
5. Normalize $\psi^{(k+1)}$ to satisfy the constraint of eq (39).
6. Check convergence; if not converged, return to step 2.

In a set of basis functions, $\{\chi_\mu(\mathbf{r})\}$, with $\psi_{pA}(\mathbf{r}) = \sum_\mu c^\mu_{pA}\chi_\mu(\mathbf{r})$, we obtain

$$\sum_{\mu B} c^\mu_{PB} F^{BA}_{\nu\mu} = \mathcal{E}_A \sum_\mu c^\mu_{PA} S_{\nu\mu}, \tag{50}$$

where $S_{\nu\mu} = \int \mathrm{d}\mathbf{r}\ \chi^*_\nu(\mathbf{r})\chi_\mu(\mathbf{r})$ is the overlap matrix and the Fock matrix elements are

$$F^{BA}_{\nu\mu} = \int \mathrm{d}\mathbf{r}\ \chi^*_\nu \left[\left(-\frac{1}{2}\nabla^2 + v_{\rm ext}\right)\delta_{BA} + (\mathbf{V}^H + \mathbf{V}^{\rm xc})_{BA}\right]\chi_\mu. \tag{51}$$

Subspace invariance

Consider a unitary transformation $\mathbf{U} \in \mathbf{U}(N)$ acting within the N-dimensional subspace $\mathbb{S}^N$. The Dyson field and matrix density transform as

$$\psi(\mathbf{r}) \ \rightarrow\ \psi'(\mathbf{r}) = \psi(\mathbf{r})\mathbf{U}, \qquad \mathbf{D}(\mathbf{r}) \ \rightarrow\ \mathbf{D}'(\mathbf{r}) = \mathbf{U}^\dagger\mathbf{D}(\mathbf{r})\mathbf{U}. \tag{52}$$

Since the Hartree and exchange–correlation matrix potentials are functionals of $\mathbf{D}(\mathbf{r})$, they transform covariantly as

$$\mathbf{V}^H[\mathbf{D}](\mathbf{r}) \ \rightarrow\ \mathbf{V}^H[\mathbf{D}'](\mathbf{r}) = \mathbf{U}^\dagger\mathbf{V}^H[\mathbf{D}](\mathbf{r})\mathbf{U}, \tag{53}$$

$$\mathbf{V}^{\rm xc}[\mathbf{D}](\mathbf{r}) \ \rightarrow\ \mathbf{V}^{\rm xc}[\mathbf{D}'](\mathbf{r}) = \mathbf{U}^\dagger\mathbf{V}^{\rm xc}[\mathbf{D}](\mathbf{r})\mathbf{U}. \tag{54}$$

The kinetic operator and the scalar external potential are invariant under this transformation.

Substituting these relations into the generalized Fock equation (46), we obtain

$$\begin{aligned}
&\left(-\tfrac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r})\right)\psi'(\mathbf{r}) + \psi'(\mathbf{r})\left(\mathbf{V}^H[\mathbf{D}'](\mathbf{r}) + \mathbf{V}^{\text{xc}}[\mathbf{D}'](\mathbf{r})\right) \\
&\quad = \left(-\tfrac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r})\right)\psi(\mathbf{r})\mathbf{U} + \psi(\mathbf{r})\mathbf{V}^H(\mathbf{r})\mathbf{U} + \psi(\mathbf{r})\mathbf{V}^{\text{xc}}(\mathbf{r})\mathbf{U} \\
&\quad = \psi(\mathbf{r})\mathbf{\Lambda}\mathbf{U} = \psi'(\mathbf{r})\left(\mathbf{U}^\dagger\mathbf{\Lambda}\mathbf{U}\right).
\end{aligned} \tag{55}$$

Thus, the generalized Fock equation is covariant under unitary transformations within the subspace: its form is preserved, with the eigenvalue matrix transforming as

$$\mathbf{\Lambda} \;\rightarrow\; \mathbf{\Lambda}' = \mathbf{U}^\dagger\mathbf{\Lambda}\mathbf{U}. \tag{56}$$

Since the subspace energy is given by the trace,

$$E_S = \frac{1}{N}\,\text{Tr}\{\cdots\}, \tag{57}$$

it remains invariant under such transformations. Therefore, the Dyson-field formulation satisfies the subspace invariance (or equivariance) condition of MSDFT (eq (5)).[39]

5. Connections to Kohn-Sham and Time-Dependent DFT

One-state reduction to Kohn–Sham theory

In the single-state limit $N = 1$, the matrix density reduces to the scalar ground-state density,

$$\mathbf{D}(\mathbf{r}) \;\rightarrow\; \rho_0(\mathbf{r}), \tag{58}$$

and the Dyson field $\psi(\mathbf{r})$ becomes an L-component column vector. To reproduce the correct electron number, the minimal representation corresponds to $L = n$, so that $\psi(\mathbf{r})$ may be identified (up to a unitary transformation) with a set of n orthonormal orbitals. Expanding $\psi(\mathbf{r})$ in an orthonormal set of orbitals $\{\varphi_i(\mathbf{r})\}_{i=1}^{n}$,

$$\psi(\mathbf{r}) = \big(\varphi_1(\mathbf{r}), \ldots, \varphi_n(\mathbf{r})\big)^T, \tag{59}$$

In this limit, all matrix-valued quantities collapse to scalars. The Hartree and exchange–correlation matrix potentials, $\mathbf{V}^H(\mathbf{r})$ and $\mathbf{V}^{\mathrm{xc}}(\mathbf{r})$, reduce to the usual scalar potentials $v^H(\mathbf{r})$ and $v^{\mathrm{xc}}(\mathbf{r})$, which commute with $\psi(\mathbf{r})$. Consequently, the generalized Fock equation (46) reduces to n independent equations of the form

$$\hat{h}^{\mathrm{KS}}\varphi_i(\mathbf{r}) = \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r}) + v^H(\mathbf{r}) + v^{\mathrm{xc}}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\,\varphi_i(\mathbf{r}), \tag{60}$$

which are just the Kohn–Sham equation, with the effective potential

$$v_{\mathrm{eff}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v^H(\mathbf{r}) + v^{\mathrm{xc}}(\mathbf{r}). \tag{61}$$

Thus, the present Dyson-field formulation of multistate density functional theory recovers standard Kohn–Sham theory as the single-state limit.

Connection to TDDFT

To give a concrete example of the Dyson-field SCF optimization, we reformulate the Tamm–Dancoff approximation (TDA) of linear-response time-dependent density functional theory (LR-TDDFT) within the present Dyson-field framework.

In LR-TDDFT, the ground state $|\Phi_0^n\rangle$ is represented by the Slater determinant with Kohn-Sham spin-orbitals, $|\Phi_0^n\rangle = |\Xi_0\rangle \equiv \det\{\varphi_1 \ldots \varphi_n\}$. Excited states are represented as

linear combinations of singly-excited determinants,[34,53]

$$|\Phi_A^n\rangle = \sum_i^{\text{occ}} \sum_a^{\text{vir}} X_{ia}^A \, \hat{c}_a^\dagger \hat{c}_i |\Phi_0^n\rangle, \qquad A \geq 1, \tag{62}$$

where X_{ia}^A are excitation amplitudes. The occupied, $\{\varphi_j; j = 1, \ldots, n\}$, and virtual orbitals, $\{\varphi_a; a = n+1, \ldots, n_v\}$, n being the number of electrons in the system and n_v being the number of virtual orbitals, are all determined by the Kohn-Sham equation,

$$\hat{h}^{\text{KS}} \varphi_p(\mathbf{r}) = \varepsilon_p^{\text{KS}} \varphi_p(\mathbf{r}), \tag{63}$$

where $\hat{h}^{\text{KS}}$ is the KS effective Hamiltonian.

To evaluate the Dyson field, one must also specify a set of $(n-1)$-electron states. We take the basis to consist of the set of hole states generated by removing an electron from the KS ground state,

$$|\Xi_j\rangle = \hat{c}_j |\Xi_0\rangle, \qquad j = 1, \ldots, n. \tag{64}$$

which yields $L = n$ ionization channels. The Dyson field elements are defined as

$$\psi_{jA}(\mathbf{r}) = \langle \Xi_j | \hat{c}(\mathbf{r}) | \Phi_A^n \rangle \tag{65}$$

For the ground state ($A = 0$), one obtains

$$\psi_{j0}(\mathbf{r}) = \varphi_j(\mathbf{r}), \tag{66}$$

so the ground-state column of the Dyson field reduces to the occupied KS orbitals. For excited states ($A \geq 1$), straightforward evaluation using second-quantized algebra gives

$$\psi_{jA}(\mathbf{r}) = \sum_a^{\text{vir}} X_{ja}^A \, \varphi_a(\mathbf{r}). \tag{67}$$

where $A = 1, \cdots, N-1$. Collecting both cases, the Dyson field can be written as

$$\psi_{jA}(\mathbf{r}) = \varphi_j(\mathbf{r})\,\delta_{A0} + (1-\delta_{A0})\sum_{a}^{\text{vir}} X_{ja}^{A}\,\varphi_a(\mathbf{r}). \tag{68}$$

The corresponding transition density is

$$D_{0A}(\mathbf{r}) = \sum_{jb} X_{jb}^{A}\,\varphi_j(\mathbf{r})\varphi_b(\mathbf{r}), \tag{69}$$

which coincides with the standard TDDFT transition density. We shall remark that, although the Dyson orbitals for the ground state, ψ_{j0}, are identical to Kohn-Sham orbitals (φ_j), the Dyson orbitals for excited states ψ_{jA} are neither normalized nor orthogonal to each other,

$$\langle\psi_{jA}|\psi_{jB}\rangle = \sum_{ab}^{\text{vir}} X_{ja}^{A*} X_{jb}^{B}\langle\varphi_a|\varphi_b\rangle = \sum_{a}^{\text{vir}} X_{ja}^{A*} X_{ja}^{B} \neq \delta_{AB} \tag{70}$$

The Dyson-field Fock equation (46) then reduces to

$$\hat{h}\psi_{jA}(\mathbf{r}) + \sum_{B=0}^{N-1}\psi_{jB}(\mathbf{r})\mathbf{V}_{BA}^{\text{Hxc}}(\mathbf{r}) = \sum_{B}\Lambda_{BA}\psi_{jB}(\mathbf{r}), \tag{71}$$

where $\hat{h} = -\frac{1}{2}\nabla^2 + v_{\text{ext}}(r)$ and $\mathbf{V}^{\text{Hxc}}[\mathbf{D}] = \mathbf{V}^{H}[\mathbf{D}] + \mathbf{V}^{\text{xc}}[\mathbf{D}]$ (eq (46)). We then expand the matrix density about the ground-state reference,

$$\mathbf{D}(\mathbf{r}) = \rho_0(\mathbf{r})\mathbf{I}_N + \delta\mathbf{D}(\mathbf{r}), \tag{72}$$

where $\rho_0(\mathbf{r})$ is the ground state density, and linearize the Hartree-exchange-correlation matrix potential,

$$\mathbf{V}_{BA}^{\text{Hxc}}[\mathbf{D}](\mathbf{r}) \approx v^{\text{Hxc}}[\rho_0](\mathbf{r})\delta_{BA} + \sum_{CJ}\int d\mathbf{r}'\,\mathcal{F}_{BA,CJ}^{\text{Hxc}}(\mathbf{r},\mathbf{r}')\,\delta D_{CJ}(\mathbf{r}'), \tag{73}$$

where $v^{\mathrm{Hxc}}[\rho_0] = v^H[\rho_0] + v^{\mathrm{xc}}[\rho_0]$ is the Kohn-Sham Hxc potential, and

$$\mathcal{F}^{\mathrm{Hxc}}_{BA,CJ}(\mathbf{r},\mathbf{r}') = \frac{\delta \mathbf{V}^{\mathrm{Hxc}}_{AB}[\mathbf{D}](\mathbf{r})}{\delta D_{CJ}(\mathbf{r}')}\Big|_{\mathbf{D}(\mathbf{r})=\rho_0(\mathbf{r})\mathbf{I}_N} \tag{74}$$

is the linearized multistate Hxc kernel.

Inserting the explicit expression (68) of the Dyson field into the Fock equation (71) gives

$$\begin{aligned} \hat{h}^{\mathrm{KS}}\varphi_j + \sum_{B=1}^{N-1}\sum_{b}^{\mathrm{vir}} X^B_{jb}\varphi_b \mathbf{V}^{\mathrm{Hxc}}_{B0} &= \Lambda_{00}\varphi_j + \sum_{A=1}^{N-1}\sum_{b}^{\mathrm{vir}} \Lambda_{0B} X^B_{jb}\varphi_b, \\ \mathbf{V}^{\mathrm{Hxc}}_{0A}\varphi_j + \sum_{b}^{\mathrm{vir}}\left(X^A_{jb}\hat{h}^{\mathrm{KS}} + \sum_{B=1,B\neq A}^{N-1} \mathbf{V}^{\mathrm{Hxc}}_{BA} X^B_{jb}\right)\varphi_b &= \sum_{B=1}^{N-1}\sum_{b}^{\mathrm{vir}} \Lambda_{AB} X^B_{jb}\varphi_b \end{aligned} \tag{75}$$

In LR-TDDFT, there is no coupling between the ground state and excited states, hence, we let $\Lambda_{0A} = \Lambda_{A0} = 0$. The second term on the left-hand-side of the first equation, $\sum_{B=1}^{N-1}\sum_{b}^{\mathrm{vir}} X^B_{jb}\varphi_b \mathbf{V}^{\mathrm{Hxc}}_{B0}$, comes from the contribution of the single-excited manifold to the ground state, which is also neglected. Multiply on the left of both sides of the first equation by $X^A_{ja}\varphi_j(\mathbf{r})$ and the second equation by $\varphi_a(\mathbf{r})$ and integrate over $\mathbf{r}$. Taking the difference of the resulting two equations yields

$$X^A_{ja}(\varepsilon^{\mathrm{KS}}_a - \varepsilon^{\mathrm{KS}}_j) + \int d\mathbf{r}\, \varphi_a(\mathbf{r})\varphi_j(\mathbf{r})\, \mathbf{V}^{\mathrm{Hxc}}_{0A}(\mathbf{r}) = \omega_A X^A_{ja}, \tag{76}$$

which employs $\hat{h}^{\mathrm{KS}}\varphi_p = \varepsilon^{\mathrm{KS}}_p\varphi_p$. ω_A are the eigenvalues of the excitation matrix, $\{\Lambda_{BC} - \mathcal{E}_0\delta_{BC}; B, C = 1, \ldots, N\}$, $\mathcal{E}_0$ being the Kohn-Sham ground-state energy.

If we identify the multi-state Hxc kernel as the Kohn-Sham xc kernel f_{xc},

$$\delta\mathbf{V}^{\mathrm{Hxc}}_{0A}(\mathbf{r}) = \int d\mathbf{r}' \left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')\right] D_{0A}(\mathbf{r}'), \tag{77}$$

and neglect the coupling between excited states ($\mathbf{V}^{\mathrm{Hxc}}_{BA} = 0$ for $A \neq B$), one obtains

$$(\varepsilon_a^{\mathrm{KS}} - \varepsilon_j^{\mathrm{KS}})\, X_{ja}^A + \sum_{kb} \left[(aj|kb) + K_{\mathrm{xc}}^{aj,kb}\right] X_{kb}^A = \omega_A X_{ja}^A, \tag{78}$$

where

$$(aj|kb) = \iint d\mathbf{r}\, d\mathbf{r}'\, \frac{\varphi_a(\mathbf{r})\varphi_j(\mathbf{r})\, \varphi_k(\mathbf{r}')\varphi_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{79}$$

and

$$K_{\mathrm{xc}}^{aj,kb} = \iint d\mathbf{r}\, d\mathbf{r}'\, \varphi_a(\mathbf{r})\varphi_j(\mathbf{r})\, f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')\, \varphi_k(\mathbf{r}')\varphi_b(\mathbf{r}'). \tag{80}$$

Equation (78) is exactly the Tamm–Dancoff approximation to Casida's equation.[54]

The full Casida's equation involves both excitation and de-excitation amplitudes and has the form of a non-Hermitian eigenvalue problem with forward (X) and backward (Y) components.[34] The present derivation recovers only the TDA (Hermitian) limit, since the so-built Dyson-field ansatz (69) includes only single-excitation (particle–hole) configurations. To recover the full Casida's equation, the Dyson-field representation needs to include de-excitation (hole–particle) components and the corresponding off-diagonal coupling blocks.

Scope and limitations. We can see from the above derivation that the TDA of TDDFT is a special case in the limit under a frozen KS reference, single-excitation truncation, and first-order linearization of the multistate xc functional in the Dyson-field formalism. The computed Dyson field (68) does not reproduce the full matrix density, lacking the density of each excited state and transition density between excited states, which are irrelevant for Casida's equation. The derivation in this section not only provides strong support for validity of the Dyson-field formalism, but also suggests possible directions overcoming limitations of linear-response approaches.

6. Evaluation of exchange-correlaton matrix functionals

The Dyson-field construction developed above provides a quasiparticle, orbital-based representation of the matrix density $\mathbf{D}(\mathbf{r})$ in an N-dimensional subspace and reduces the optimization of $\mathbf{D}(\mathbf{r})$ to solving a set of generalized Fock equations for the Dyson field $\psi(\mathbf{r})$. Once this representation is available, the remaining problem of practical MSDFT is to construct the exchange-correlation matrix functional and its contribution to the effective Hamiltonian matrix (i.e., the Fock matrix elements of eq (51)). In other words, the formal challenge shifts from representing $\mathbf{D}(\mathbf{r})$ to evaluating the matrix elements of $\mathcal{H}[\mathbf{D}]$, especially the exchange-correlation part, in a form suitable for self-consistent-filed computation.

A key simplification follows from the fact that the Hamiltonian matrix functional $\mathcal{H}[\mathbf{D}]$ is determined by the N-matrix density $\mathbf{D}(\mathbf{r})$, which are invariant in the subspace $\mathbb{S}^N$. Consequently, under the "one-determines-all" (ODA) principle, rather than designing all N^2 matrix elements independently, the full matrix functional can be obtained by spectral decomposition and recomposition based on a scalar exchange-correlation channel function.[40,41]

Spectral decomposition and grid-based evaluation

At each spatial grid point $\mathbf{r}$, the matrix density is diagonalized as

$$\mathbf{D}(\mathbf{r}) = \mathbf{P}(\mathbf{r})\,\mathbf{d}(\mathbf{r})\,\mathbf{P}^{\dagger}(\mathbf{r}), \qquad \mathbf{d}(\mathbf{r}) = \mathrm{diag}\big(d_1(\mathbf{r}), \ldots, d_N(\mathbf{r})\big), \tag{81}$$

where $\{d_i(\mathbf{r})\}$ are the local (grid point $\mathbf{r}$) eigendensities and $\mathbf{P}(\mathbf{r})$ is a unitary matrix of local eigenvectors. Any admissible (satisfying eq (5)) local or semilocal exchange–correlation matrix functional may then be constructed in the spectral frame from a scalar channel function g_{xc} and transformed back to the original (state-level) basis. For example, a local matrix functional may be written equivariantly as

$$\mathcal{E}^{\mathrm{xc}}[\mathbf{D}] = \int d\mathbf{r}\; \mathbf{P}(\mathbf{r})\,\mathrm{diag}\big(g_{\mathrm{xc}}(d_1), \ldots, g_{\mathrm{xc}}(d_N)\big)\,\mathbf{P}^{\dagger}(\mathbf{r}), \tag{82}$$

where $g_{xc}(d_j)$ is a scalar exchange-correlation function with the input densities of eq (81) (and gradients if a semilocal functional is used) and the corresponding matrix potential is obtained by functional differentiation,

$$\mathbf{V}^{\mathrm{xc}}(\mathbf{r}) = \frac{\delta \,\mathrm{Tr}\, \mathcal{E}^{\mathrm{xc}}[\mathbf{D}]}{\delta \mathbf{D}(\mathbf{r})}. \tag{83}$$

Equations (81)–(83) show that the computation of the N^2 matrix elements of $\mathcal{E}^{\mathrm{xc}}[\mathbf{D}]$ is reduced to N scalar function evaluations at the spectral channels (eq (81)),[40] providing a KS-DFT-like computational strategy for MSDFT. The numerical integration proceeds on a real-space grid exactly as in standard KS-DFT, except that the scalar density is replaced by the set of local eigendensities $\{d_i(\mathbf{r})\}_{i=1}^{N}$, together with any additional local invariants needed by the chosen approximation. Thus, at each grid point, one carries out the following operations:[40]

1. construct the matrix density $\mathbf{D}(\mathbf{r})$ from the present Dyson field;
2. diagonalize $\mathbf{D}(\mathbf{r})$ to obtain $\mathbf{P}(\mathbf{r})$ and $\{d_i(\mathbf{r})\}$ (eq (81));
3. evaluate the scalar channel function g_{xc} from the eigendensities (and, for semilocal forms, including their gradients and related invariants);
4. recompose the full matrix functional and matrix potential in the original basis using eq (82);
5. assemble the corresponding contribution to the generalized Fock equation (eq (51)).

In this way, the evaluation of a matrix exchange-correlation functional is reduced to a sequence of scalar evaluations followed by spectral recomposition.

From scalar channel functions to matrix functionals

The principal computational consequence of the spectral decomposition following the ODA principle is that any practical approximation for $\mathcal{E}^{\mathrm{xc}}[\mathbf{D}]$ reduces to the design of a scalar

exchange-correlation channel function analogous to approximations in KS-DFT. The matrix character of the theory is then recovered through the local eigenvectors $\mathbf{P}(\mathbf{r})$ and the spectral recomposition.[40] This suggests a direct route to importing standard density-functional approximations into the multistate setting.

The essential point is that the matrix functional does not need to be guessed element by element. Once a scalar channel function (e.g., the PBE approximate functional[55] with addition of multistate invariants) is specified at each grid point,[20] the full matrix exchange-correlation functional is generated by diagonalization of $\mathbf{D}(\mathbf{r})$, scalar evaluation on the eigendensities (and gradients in GGA functionals), and transformation back.[40] This provides both a conceptual unification and a practical algorithm for multistate exchange-correlation functionals.

Dyson-field constructions and practical starting points

The spectral decomposition framework[40] is independent of how the Dyson field for $\mathbf{D}(\mathbf{r})$ is represented in practice. The simplest realization is to construct the Dyson field from a frozen KS reference in the single-excitation manifold, as in the TDA/TDDFT limit discussed above. In that case, the Dyson-field columns are expressed in terms of occupied and virtual KS orbitals and excitation amplitudes, and the matrix density is obtained directly from these quantities. Combined with the spectral-grid construction described above, this yields a direct route to computing exchange–correlation matrix elements in a manner closely analogous to ordinary KS-DFT, but now for N coupled density channels.

This single-excitation construction should be viewed as the lowest level of practical approximations. Its value is twofold. First, it provides an explicit, computationally convenient initial representation of the Dyson field. Second, in the linearized frozen-reference limit, it connects directly to the Tamm–Dancoff approximation to TDDFT, thereby furnishing a transparent bridge between the present variational formalism and standard response theory. Third and importantly, although the construction of $\mathbf{D}(\mathbf{r})$ in Dyson field makes use

of single excitations in this lowest level approach, unlike TDDFT, the Hamiltonian matrix functional includes proper state coherence and thus state couplings, if not dropped, suitable for modeling photochemistry including conical intersections.

Significantly, the main advantage of the Dyson-field formulation is that it is not restricted to the frozen-reference or single-excitation regime. The Dyson orbitals may instead be optimized self-consistently through the generalized Fock equation, allowing the matrix density, the exchange-correlation matrix potential, and the quasiparticle orbitals to be determined variationally and simultaneously. Therefore, we obtain a set of consistent, orthonormal orbitals that respond both to static and dynamic correlation through the Hamiltonian matrix functional.

Beyond the single-excitation manifold

A natural next level approximation is to enlarge the space used to construct the Dyson field beyond single excitations. For example, one may adopt a CISD-like or more general multiconfigurational ansatz for the n-electron states and the associated $(n-1)$-electron ionization channels. The resulting Dyson field then carries a richer structure, which in turn yields a more flexible and accurate matrix density. The spectral decomposition strategy remains unchanged: once $\mathbf{D}(\mathbf{r})$ is constructed, the exchange-correlation matrix functional is still evaluated from a scalar channel function on the local eigendensities, repeating N times of KS-DFT-like calcualtions, one for each spectral channel density.

This separation between the representation of the Dyson field and the construction of the matrix functional is important. Improvements in the wavefunction-like structure used to generate $\psi(\mathbf{r})$ and improvements in the scalar channel function g_{xc}, i.e., the exchange-correlation function approximation, are logically distinct and can be pursued independently. In practical computations, this opens a hierarchy of approximations:

1. frozen-reference single-excitation Dyson fields combined with simple local or semilocal channel functions, no SCF is needed except that of the reference state;

2. self-consistent Dyson-field optimization within the single-excitation manifold;

3. enlarged Dyson-field manifolds, such as CISD-like or multiconfigurational constructions, combined with the same spectral functional framework;

4. systematic refinement of the scalar channel function from local to semilocal, meta-GGA, hybrid, or explicitly nonlocal forms.

Perspective

The practical significance of the Dyson-field construction is therefore twofold. At the representation level, it provides an orbital-based quasiparticle mapping of the multistate matrix density $\mathbf{D}(\mathbf{r})$. Here, any practical wave function methods such as configuration interaction (CI), many-body perturbation theory (MBPT) and multiconfigurational self-consistent-field (MCSCF) methods can be used and selected. This provides a direct connection to adopt computational algorithms already optimized in wave function theory. At the functional level, the spectral decomposition of $\mathbf{D}(\mathbf{r})$ reduces the construction of exchange-correlation matrix functionals to the design of a scalar channel function evaluated on local eigendensities. The result is a computational strategy closely analogous to KS-DFT in its use of grid-based scalar evaluations, but generalized to an N-channel density framework with explicit state coupling. Here, the challenge lies in the functional design that must include subspace invariant variables to account for subspace correlation.

From this perspective, the problem of practical MSDFT is no longer to invent matrix functionals in full generality, but to identify accurate and transferable scalar channel functions and suitable Dyson-field representations for the states of interest. The generalized Fock equation derived in the present work provides the self-consistent variational framework in which these approximations can be implemented, tested, and systematically improved.

7. Conclusions

We have introduced the Dyson field $\psi(\mathbf{r})$, a matrix-valued quasiparticle field that provides an orbital representation of multi-state density functional theory (MSDFT). The principal results of this work are summarized as follows:

1. **Factorization of the matrix density.** The positive semi-definiteness of the N-matrix density $\mathbf{D}(\mathbf{r})$ guarantees an exact factorization, $\mathbf{D}(\mathbf{r}) = \psi^\dagger(\mathbf{r})\psi(\mathbf{r})$, where $\psi(\mathbf{r})$ is an $L \times N$ matrix field (Sec.).

2. **Physical interpretation.** The elements, ψ_{PA}, are Dyson orbitals, which are electron-removal amplitudes connecting n-electron states to $(n-1)$-electron ionization channels, providing a direct physical interpretation of the matrix density (Sec.).

3. **Generalized Fock equation.** Variational minimization of the MSDFT subspace energy yields a self-consistent equation for the Dyson field, in which the kinetic and external potentials act locally, while Hartree and exchange–correlation contributions appear as matrix-valued potentials coupling the electronic states: $\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}\right)\psi + \psi\left(\mathbf{V}^H + \mathbf{V}^{\text{xc}}\right) = \psi\mathbf{\Lambda}$. This equation determines the matrix density without two-electron operators and explicit many-body wavefunctions (Sec.).

4. **Connections to Kohn-Sham and TDDFT.** In the single-state limit ($N = 1$), the formalism reduces exactly to the Kohn-Sham equations (Sec.). For $N > 1$, under a frozen-reference, single-excitation, and linearized exchange-correlation approximation, the projected Fock equation in the Dyson-field formulation recovers the Tamm-Dancoff approximation to Casida's equation (Sec.).

These results establish a quasiparticle, orbital-based formulation of MSDFT, transforming it from a formally exact but wavefunction-dependent framework into a practical, self-consistent theory.

The Dyson-field construction also suggests several directions for future work. The interpretation of the generalized eigenvalues in terms of electron removal processes points toward a multi-state generalization of Koopmans' and Janak's theorems.[50] The connection between Dyson orbitals and the one-body Green's function, where Dyson orbitals arise as residues at quasiparticle poles, indicates a natural link to many-body perturbation theory, including *GW* and related self-energy approaches,[56–62] which may guide the development of exchange-correlation matrix potentials. Equally important, the hierarchy of exchange-correlation matrix functional approximations from TDDFT-kernel-based constructions to nonperturbative local matrix density approximations and exact-exchange formulations provides a systematic pathway toward practical implementations. Combined with the spectral decomposition algorithm, these developments reduce the construction of matrix functionals to the design of scalar channel functions, enabling direct benchmarking against high-level wavefunction methods.

Appendix A. Derivation of the Hartree functional derivative

We provide the detailed derivation of Eq. (43). The trace of the Hartree matrix functional is

$$N \,\mathrm{Tr}\, \mathcal{E}^H[\mathbf{D}] = \frac{1}{2} \int \frac{\mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \sum_{A,B} D_{AB}(\mathbf{r})\, D_{BA}(\mathbf{r}'). \tag{84}$$

Since $D_{AB}(\mathbf{r}) = \sum_Q \psi^*_{QA}(\mathbf{r})\psi_{QB}(\mathbf{r})$, the functional derivative with respect to $\psi^*_{PA}(\mathbf{r})$ receives two contributions (one from each factor of D):

$$\frac{\partial D_{CD}(\mathbf{r}_1)}{\partial \psi^*_{PA}(\mathbf{r})} = \delta(\mathbf{r}_1 - \mathbf{r})\, \delta_{CA}\, \psi_{PD}(\mathbf{r}_1). \tag{85}$$

Applying this to Eq. (84):

$$\begin{aligned}\frac{\delta\ \mathrm{Tr}\ \mathcal{E}^H}{\delta\psi^*_{PA}(\mathbf{r})} &= \frac{1}{2}\sum_B \int \frac{\mathrm{d}\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\,\psi_{PB}(\mathbf{r})\,D_{BA}(\mathbf{r}') + \frac{1}{2}\sum_C \int \frac{\mathrm{d}\mathbf{r}'}{|\mathbf{r}'-\mathbf{r}|}\,D_{CA}(\mathbf{r}')\,\psi_{PC}(\mathbf{r}) \\ &= \frac{1}{2}\sum_B \psi_{PB}(\mathbf{r})\,\mathbf{V}^H_{BA}(\mathbf{r}) + \frac{1}{2}\sum_C \psi_{PC}(\mathbf{r})\,\mathbf{V}^H_{CA}(\mathbf{r}) \\ &= \sum_B \psi_{PB}(\mathbf{r})\,\mathbf{V}^H_{BA}(\mathbf{r}) = \psi(\mathbf{r})\,\mathbf{V}^H_{PA}(\mathbf{r}), \end{aligned} \tag{86}$$

where in the last step we used $\mathbf{V}^H_{BA} = \mathbf{V}^H_{CA}$ with C and B as dummy summation indices running over the same range, combined with the symmetry $|\mathbf{r}-\mathbf{r}'|^{-1} = |\mathbf{r}'-\mathbf{r}|^{-1}$. □

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