Local Spectral Formulation of the One-Determines-All (ODA) Principle for Multistate Density Functionals

Jiali Gao[*,†,‡,¶] and Yangyi Lu[*,‡]

†*School of Chemical Biology and Biotechnology, Beijing University Shenzhen Graduate School, Shenzhen 518055, China*

‡*Institute of Systems and Physical Biology, Shenzhen Bay Laboratory, Shenzhen 518107, China*

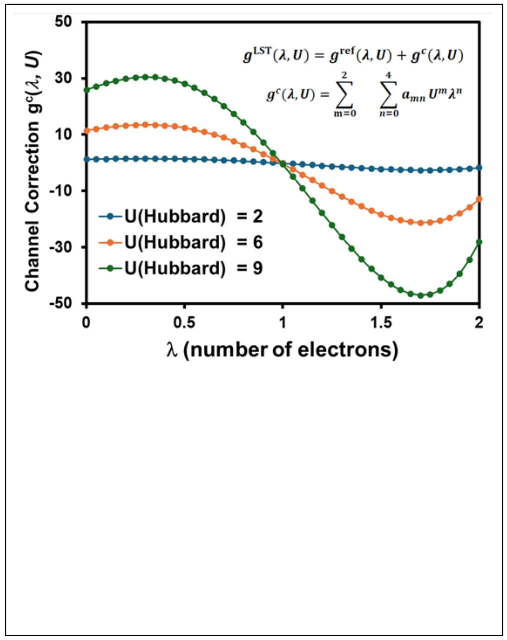
¶*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, USA*

E-mail: gao@jialigao.org; luyy@szbl.ac.cn

Abstract

Multistate density functional theory (MSDFT) generalizes Kohn–Sham density functional theory to a finite subspace of interacting states through a Hamiltonian matrix functional of the matrix density $\mathbf{D}(\mathbf{r})$. A central challenge is to construct matrix functionals that preserve subspace unitary invariance while encoding nontrivial state coupling. Here we show that any local, unitary-covariant matrix functional of $\mathbf{D}(\mathbf{r})$ must be co-diagonalizable with $\mathbf{D}(\mathbf{r})$, and is therefore completely specified by a scalar generator acting on its eigenvalues. This establishes a one-to-all mapping from a scalar generator to the full matrix functional. As a consequence, the construction of N^2 matrix elements is reduced to a single scalar mapping evaluated on the eigenvalue spectrum at each spatial grid point. The formalism is illustrated using a four-state Hubbard model, where exact reconstruction is achieved with a known scalar function, and deviations from this mapping can be systematically corrected within the spectral framework. The results provide a rigorous foundation for constructing local matrix exchange–correlation functionals with computational complexity comparable to Kohn–Sham DFT, and offer a practical route toward scalable MSDFT approximations.

TOC Graphic



Keywords

Local spectral decomposition, One-Determines-all, Matrix density functional, MSDFT

Multistate density functional theory (MSDFT) extends Kohn–Sham density functional theory (KS-DFT)[1,2] from a single ground state to a subspace of interacting electronic states, in which the Hamiltonian is expressed as a matrix functional of the matrix density $\mathbf{D}(\mathbf{r})$.[3,4] This formulation provides a rigorous framework for treating state interactions, enabling the simultaneous description of ground and excited states within a unified density-based theory. In contrast to conventional KS-DFT, where the energy is a scalar functional of the electron density, MSDFT requires the construction of a matrix-valued functional whose diagonal and off-diagonal elements encode both state energies and couplings.[5]

A central requirement of MSDFT is that the Hamiltonian matrix functional remains invariant under unitary transformations within the chosen subspace.[3,6] This subspace invariance ensures that physical observables are independent of the particular representation of the basis states. At the same time, the off-diagonal elements of the matrix functional must capture nontrivial state interactions, including electronic coupling and correlation effects. In practice, however, the construction of such functionals remains a major challenge:[7] for N states of primary interest, one must determine N^2 coupled matrix elements, with no general organizing principle to guide their approximation. As a result, most existing approaches rely on element-wise constructions or system-specific parameterizations,[4,8,9] which obscure the underlying structure of the theory.

In this work, we consider matrix functionals that are local in space and transform covariantly under unitary rotations within the subspace. Within this class, we show that any such functional must share the same spectral projectors (eigenvectors) with the matrix density $\mathbf{D}(\mathbf{r})$. Consequently, the matrix functional can be expressed in spectral form. Then, all matrix elements are generated from a single scalar function acting on the eigenvalues of $\mathbf{D}(\mathbf{r})$. This result provides a complete structural characterization of local, unitary-covariant matrix functionals, establishing a one-determines-all (ODA) mapping from a scalar generator to the full matrix functional.

The spectral formulation has immediate computational implications. Rather than constructing N^2 matrix elements independently, the evaluation of the matrix functional reduces to a scalar mapping applied to the eigenvalue spectrum of $\mathbf{D}(\mathbf{r})$ at each spatial grid point, followed by reconstruction of the matrix in the original basis. In this way, the computational structure closely parallels that of KS-DFT,[2,10] with a modest additional cost associated with diagonalizing a low-dimensional matrix density and the computation of the N spectral channel elements. This reduction provides a natural and efficient framework for the development of practical MSDFT approximations. While the theorem establishes the general structure of local matrix functionals, it does not uniquely determine the scalar generator (i,e,, function). Instead, it defines a systematic route for approximation, in which physically motivated scalar forms, depending on the eigenvalues of $\mathbf{D}(\mathbf{r})$ and additional local invariants, can be constructed and tested within the spectral representation. At the same time, we emphasize that more general functionals may require extensions beyond this local, covariant class, including additional variables or nonlocal dependence to capture effects not representable within a purely spectral form.

To illustrate the formalism, we consider a four-state Hubbard model.[11] Using the exact matrix density, the Hamiltonian is reconstructed through a known scalar rule, demonstrating internal consistency of the spectral representation. We further examine a distorted scalar form and show that systematic corrections can be introduced within the same framework to recover the model energies. These examples serve to demonstrate the practical implementation of the spectral construction and its flexibility for functional design. Together, these findings establish a rigorous and constructive approach for matrix functional development in MSDFT. By reducing the problem to the design of a scalar generator while preserving subspace invariance and state coupling, the spectral formulation provides a transparent and computationally efficient foundation for advancing multistate density functional approximations.

Background. Multistate density functional theory extends the KS-DFT from a single state to an N-dimensional Hilbert subspace spanned by the lowest-energy eigenstates.[3] The fundamental variable is the matrix density $\mathbf{D}(\mathbf{r})$,[3,5] whose elements are defined as

$$D_{AB}(\mathbf{r}) = \langle \Phi_A | \hat{\rho}(\mathbf{r}) | \Phi_B \rangle, \tag{1}$$

where Φ_A is an orthonormal basis of the N-dimensional subspace and $\hat{\rho}(\mathbf{r})$ is the one-particle density operator.[12] The Hamiltonian projected into this subspace is a matrix functional of $\mathbf{D}(\mathbf{r})$:

$$\mathcal{H}[\mathbf{D}] = \mathcal{F}[\mathbf{D}] + \int v(\mathbf{r})\mathbf{D}(\mathbf{r}), d\mathbf{r}, \tag{2}$$

where $\mathcal{F}[\mathbf{D}]$ is a universal matrix functional,[13] independent of the external potential $v(\mathbf{r})$. The universal term can be partitioned into kinetic, Hartree, exchange, and correlation contributions: $\mathcal{F}[\mathbf{D}] = \mathcal{T}[\mathbf{D}] + \mathcal{E}^H[\mathbf{D}] + \mathcal{E}^x[\mathbf{D}] + \mathcal{E}^c[\mathbf{D}]$. The energies of the N lowest eigenstates are obtained from the variational minimization of the multistate functional followed by diagonalization of the resulting Hamiltonian matrix.

A central structural property of MSDFT is subspace invariance.[6] If two orthonormal bases of the same Hilbert subspace are related by the unitary transformation $\mathbf{U}$, the corresponding matrix densities transform as

$$\mathbf{D}'(\mathbf{r}) = \mathbf{U}^\dagger \mathbf{D}(\mathbf{r}) \mathbf{U}, \tag{3}$$

and the Hamiltonian matrix functional must transform covariantly:

$$\mathcal{H}[\mathbf{U}^\dagger \mathbf{D} \mathbf{U}] = \mathbf{U}^\dagger \mathcal{H}[\mathbf{D}] \mathbf{U}. \tag{4}$$

The same subspace invariance condition applies to each component of the Hamiltonian matrix. Equation (4) therefore represents a necessary constraint on matrix functionals of multiple electronic states.[6]

Exploiting this invariance, Lu and Gao established that the elements of the correlation matrix functional are not independent, but are related through exact integro-differential relations involving their functional derivatives.[6] In particular, specifying a single diagonal correlation functional $E^c_{AA}[\mathbf{D}]$ uniquely determines all matrix elements of $\mathcal{E}^c[\mathbf{D}]$ within an N-dimensional subspace. In this sense, a diagonal element acts as a generator, while all off-diagonal and remaining diagonal elements are constrained by subspace invariance. Crucially, each matrix element depends on the full matrix density $\mathbf{D}(\mathbf{r})$, rather than on an individual state density alone. Consequently, this establishes a global ODA principle at the level of state-resolved functionals.

Here, we show that this global principle, originally defined in the state manifold, possesses a complementary formulation in real space. By analyzing matrix functionals pointwise in real space, we demonstrate that their structure can be expressed via the spectral representation of the density matrix, yielding a transparent and computationally tractable framework for functional construction.

Local Spectral Formulation of Matrix Functionals. At a given spatial position $\mathbf{r}$, the matrix density $\mathbf{D}(\mathbf{r})$ is Hermitian (or real symmetric in a real representation) and therefore can be expressed by the spectral decomposition[14,15]

$$\mathbf{D}(\mathbf{r}) = \sum_{i=1}^{m(\mathbf{r})} \lambda_i(\mathbf{r})\mathbf{P}_i(\mathbf{r}), \tag{5}$$

where $\lambda_i(\mathbf{r})$ are the m distinct eigenvalues and $\mathbf{P}_i(\mathbf{r})$ are the associated orthogonal spectral projectors. Each projector has a rank n_i such that $\sum_i^m n_i = N$. In the nondegenerate case, each projector simplifies to $\mathbf{P}_i(\mathbf{r}) = |u_i(\mathbf{r})\rangle\langle u_i(\mathbf{r})|$, where $|u_i(\mathbf{r})\rangle$ is the corresponding eigenvectors. More generally, in the presence of degeneracy, $\mathbf{P}_i(\mathbf{r})$ denotes the projector onto the entire eigenspace. This projector-based formulation ensures a unique decomposition regardless of the degeneracy of the spectrum.

A local matrix function $\mathcal{G}(\mathbf{D}(\mathbf{r}))$ is defined to be admissible if it depends only on the local matrix density and satisfies unitary covariance,

$$\mathcal{G}(\mathbf{U}^\dagger\mathbf{D}(\mathbf{r})\mathbf{U}) = \mathbf{U}^\dagger\mathcal{G}(\mathbf{D}(\mathbf{r}))\mathbf{U}, \tag{6}$$

for any unitary matrix $\mathbf{U}$. This condition is the local manifestation of subspace invariance and imposes a strong structural constraint on such functionals.

Theorem 1 (Local Spectral Covariance). *Let $\mathbf{D} = \mathbf{D}(\mathbf{r})$ be an $N \times N$ Hermitian matrix density at fixed $\mathbf{r}$, and let $\mathcal{G}(\mathbf{D})$ be an admissible local matrix function satisfying*

$$\mathcal{G}(\mathbf{U}^\dagger \mathbf{D} \mathbf{U}) = \mathbf{U}^\dagger \mathcal{G}(\mathbf{D}) \mathbf{U} \qquad \forall \mathbf{U} \in U(N). \tag{7}$$

If $\mathbf{D} = \sum_{i=1}^m \lambda_i \mathbf{P}_i$ is the spectral decomposition of $\mathbf{D}$, where λ_i are the distinct eigenvalues and $\mathbf{P}_i$ the corresponding orthogonal projectors at $\mathbf{r}$, then:

$$\mathcal{G}(\mathbf{D}) = \sum_{i=1}^{m} g_i(\mathbf{r}) \mathbf{P}_i(\mathbf{r}), \tag{8}$$

where $g_i(\mathbf{r})$ is a scalar eigenvalue of the output matrix $\mathcal{G}$ associated with the i-th eigenspace of $\mathbf{D}$ at position $\mathbf{r}$. Consequently,

$$[\mathcal{G}(\mathbf{D}), \mathbf{D}] = 0. \tag{9}$$

Proof. At fixed $\mathbf{r}$, we write $\mathbf{D} = \mathbf{D}(\mathbf{r})$. Since $\mathbf{D}$ is Hermitian and $\mathcal{G}$ is covariant, we can, without loss of generality, work in the eigenbasis of $\mathbf{D}$ such that

$$\mathbf{D} = \bigoplus_{i=1}^{m} \lambda_i \mathbf{I}_{n_i} \tag{10}$$

where n_i denotes the dimension of the i-th eigenspace and $\sum_i^m n_i = N$. Explicitly, eq (10) has the form

$$\mathbf{D} = \begin{pmatrix} \lambda_1 \mathbf{I}_{n_1} & 0 & \cdots & 0 \\ 0 & \lambda_2 \mathbf{I}_{n_2} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \lambda_m \mathbf{I}_{n_m} \end{pmatrix}.$$

Equivalently, $\mathbf{D} = \sum_{i=1}^m \lambda_i \mathbf{P}_i$, where $\mathbf{P}_i$ are the associated spectral projectors.

Let $W = \bigoplus_{i=1}^{m} W_i$, where $W_i \in U(n_i)$, be any unitary matrix that acts independently within each eigenspace of $\mathbf{D}$. By construction, $W^\dagger \mathbf{D} W = \mathbf{D}$. Admissibility implies,

$$\mathcal{G}(\mathbf{D}) = \mathcal{G}(W^\dagger \mathbf{D} W) = W^\dagger \mathcal{G}(\mathbf{D}) W \tag{11}$$

Thus, $\mathcal{G}(\mathbf{D})$ must commute with every such block-diagonal unitary W. Representing $\mathcal{G}(\mathbf{D})$ as a block matrix $(\mathbf{G}_{ij})$, the commutation requirement (11) yields

$$\mathbf{G}_{ij} = W_i^\dagger \mathbf{G}_{ij} W_j \qquad \forall W_i \in U(n_i), W_j \in U(n_j). \tag{12}$$

For the off-diagonal blocks $(i \neq j)$, we may choose $W_i = e^{i\theta_i}\mathbf{I}_{n_i}$ and $W_j = e^{i\theta_j}\mathbf{I}_{n_j}$. This leads to

$$\mathbf{G}_{ij} = e^{i(\theta_j - \theta_i)}\mathbf{G}_{ij}.$$

For this to hold for arbitrary phases $(\theta_j - \theta_i)$, we must have $\mathbf{G}_{ij} = 0$. Therefore, $\mathcal{G}[\mathbf{D}]$ does not mix distinct eigenspaces of $\mathbf{D}$.

For the diagonal blocks $(i = j)$, the condition (12) becomes

$$\mathbf{G}_{ii} = W_i^\dagger \mathbf{G}_{ii} W_i \qquad \forall W_i \in U(n_i)$$

Since the unitary group $U(n_i)$ acts irreducibly on the i-th eigenspace, Schur's Lemma dictates that $\mathbf{G}_{ii}$ must be a scalar multiple of the identity:[15]

$$\mathbf{G}_{ii} = g_i \mathbf{I}_{n_i}$$

Combining these results, we have

$$\mathcal{G}(\mathbf{D}) = \bigoplus_{i=1}^{m} g_i(\mathbf{r})\mathbf{I}_{n_i} = \sum_{i=1}^{m} g_i(\mathbf{r})\mathbf{P}_i(\mathbf{r}) \tag{13}$$

Because $\mathbf{D}$ and $\mathcal{G}(\mathbf{D})$ are expressed in the same set of orthogonal projectors, $\mathbf{D} = \sum_{i=1}^{m} \lambda_i \mathbf{P}_i$ and $\mathcal{G}(\mathbf{D}) = \sum_{i=1}^{m} g_i \mathbf{P}_i$ where $\mathbf{P}_i \mathbf{P}_j = \delta_{ij} \mathbf{P}_i$, it follows that

$$\mathcal{G}(\mathbf{D})\mathbf{D} = \sum_{i,j} g_i \lambda_j \mathbf{P}_i \mathbf{P}_j = \sum_{i} g_i \lambda_i \mathbf{P}_i = \mathbf{D}\mathcal{G}(\mathbf{D})$$

This proves the commutation:

$$[\mathcal{G}(\mathbf{D}), \mathbf{D}] = 0$$

□

In eq. (9), $[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA}$ denotes the standard matrix commutator.

This result shows that admissible local functionals are constrained to share the spectral structure of the matrix density, with no independent directional degrees of freedom beyond those encoded in $\mathbf{D}(\mathbf{r})$. As a consequence, the construction of a matrix functional is reduced from determining N^2 coupled matrix elements to specifying $m \leq N$ scalar quantities associated with the spectral components, where m denotes the number of degeneracy blocks of $\mathbf{D}$ ($n = N$ if $\mathbf{D}$ is nondegenerate). This reduction provides the foundation for a local realization of the ODA principle developed below. We note, however, that more general matrix functionals may involve nonlocal dependence or additional variables and need not be restricted to this spectral form.

Local Spectral One-Determines-All Theorem. In the spectral basis of $\mathbf{D}$, the $N \times N$ matrix density can be written as $\mathbf{D} = \mathrm{diag}(\lambda_1 \mathbf{I}_{n_1}, \ldots, \lambda_m \mathbf{I}_{n_m})$ (eq (10)). Under a permutation matrix $\mathbf{\Pi}$, the density transforms as

$$\mathbf{\Pi}^{\dagger}\mathbf{D}\mathbf{\Pi} = \mathrm{diag}(\lambda_{\pi(1)} \mathbf{I}_{n_{\pi(1)}}, \ldots, \lambda_{\pi(m)} \mathbf{I}_{n_{\pi(m)}}), \tag{14}$$

corresponding to a relabeling of the eigenvalues.

Admissibility further requires that the matrix $\mathcal{G}$ satisfy the same covariance condition,

$$\mathcal{G}(\mathbf{\Pi}^\dagger \mathbf{D} \mathbf{\Pi}) = \mathbf{\Pi}^\dagger \mathcal{G}(\mathbf{D}) \mathbf{\Pi}. \tag{15}$$

Thus, any permutation of the eigenvalues induces the same permutation of the spectral components of $\mathcal{G}(\mathbf{D})$.[15,16] This invariance implies that the output components cannot be independently specified, but must be generated from a common symmetric mapping.

Theorem 2 (Local Spectral ODA Theorem)**.** *Let $\mathcal{G}(\mathbf{D}(\mathbf{r}))$ be an admissible local matrix function. Then there exists a scalar mapping g such that, at each spatial point $\mathbf{r}$,*

$$\mathcal{G}(\mathbf{D}(\mathbf{r})) = \sum_{i=1}^{m(\mathbf{r})} g\left(\lambda_i(\mathbf{r}); \Lambda \setminus \{\lambda_i(\mathbf{r})\}\right) \mathbf{P}_i(\mathbf{r}), \tag{16}$$

where $\Lambda = \{\lambda_1, \cdots, \lambda_N\}$ is the multiset of all N eigenvalues of $\mathbf{D}$ at position $\mathbf{r}$. The mapping g is symmetric with respect to any permutation of the elements in the auxiliary set $\Lambda \backslash \{\lambda_i(\mathbf{r})\}$. Consequently, this scalar mapping uniquely determines the matrix functional through spectral recomposition across the spatial domain.

Proof. By Theorem 1, $\mathcal{G}(\mathbf{D})$ shares the spectral projectors with $\mathbf{D}$ at position $\mathbf{r}$ (eq (13)) and is diagonal in the same basis $\mathcal{G}(\mathbf{D}) = \mathrm{diag}(g_1 \mathbf{I}_{n_1}, \ldots, g_m \mathbf{I}_{n_m})$. This implies a functional relationship between the input and output spectra:

$$g_i = f_i(\lambda_1, \ldots, \lambda_N), \quad i = 1, \ldots, N. \tag{17}$$

or, the mapping $(\lambda_1, \ldots, \lambda_N) \mapsto (g_1, \ldots, g_N)$.

Permutation invariance (eq (15)) requires that for any $\pi \in \mathcal{S}^N$

$$f_{\pi(i)}(\lambda_1, \ldots, \lambda_N) = f_i(\lambda_{\pi(1)}, \ldots, \lambda_{\pi(N)}). \tag{18}$$

Equivalently, relabeling the input eigenvalues induces the same relabeling of the outputs.

$$(g_{\pi(1)}(\lambda_1,\ldots,\lambda_N),\ldots,g_{\pi(N)}(\lambda_1,\ldots,\lambda_N)) = (g_1(\lambda_{\pi(1)},\ldots,\lambda_{\pi(N)}),\ldots,g_N(\lambda_{\pi(1)},\ldots,\lambda_{\pi(N)}))$$

This condition of permutation equivariance implies that the functional form of each f_i must be identical ($f_i = f_j = g$) and that the value of g must be invariant under any permutation of the arguments other than the i-th one.

Consequently, the value g_i can be expressed as a single scalar mapping g that takes the i-th eigenvalue as its primary argument and the multiset $\Lambda \setminus \{\lambda_i\}$ as its auxiliary argument:

$$g_i = g\left(\lambda_i; \{\lambda_j\}_{j\neq i}\right). \tag{19}$$

Since the initial labeling of eigenvalues is arbitrary, and the output is equivariant, g is necessarily symmetric with respect to all elements in the auxiliary set. This establishes the spectral representation in eq (16). □

This result provides the local spectral realization of the ODA principle and complements the previously established state-level formulation.[6] In the state representation, subspace invariance imposes exact functional relations among matrix elements, such that a single diagonal generator determines the full matrix functional. This formulation is global and expressed in terms of matrix elements within an arbitrary orthonormal state-basis of the subspace.

By contrast, the present result is formulated pointwise operational in real space in the spectral frame of $\mathbf{D}(\mathbf{r})$. Here, the same principle emerges in an operational form: the full matrix functional at each spatial point is generated from a single symmetric scalar mapping acting on the local eigenvalue spectrum. The matrix structure is then recovered through spectral recomposition.

Taken together, the two formulations describe complementary aspects of the same underlying constraint imposed by subspace invariance: the state-level result establishes the global functional interdependence among matrix elements, while the local spectral formulation provides a canonical and computationally tractable realization of this principle. Accordingly, the construction of matrix functionals reduces to specifying a scalar mapping evaluated pointwise in real space, while retaining full coupling among states through the dependence on the complete local spectrum $\lambda_i(\mathbf{r})$. This yields a formulation that is spatially local yet intrinsically coupled in state space. We emphasize that this construction applies to local, unitary-covariant functionals; extensions beyond this class may require additional variables or nonlocal dependence.

Spatial Invariance and Universality. A natural question arises regarding the scalar mapping g in eq (16): does this mapping depend explicitly on the spatial coordinate $\mathbf{r}$, i.e., should it be written as $g = g(\mathbf{r}; \lambda_i, \{\lambda_{j\neq i}\})$?

For local and semilocal density functionals, the answer is no. This follows from the universality of the exchange-correlation functional: its mathematical form is determined by the nature of electron-electron interactions, which are independent of the external potential and the spatial origin.[10,13] Consequently, the local representation $\mathcal{G}(\mathbf{D})$ must act uniformly at every point $\mathbf{r}$. The position dependence of $g(\mathbf{r})$ enters only implicitly through the local values of its arguments. Consequently, the scalar mapping g in eq (16) is a universal function, common to all $\mathbf{r}$,

$$g_i(\mathbf{r}) = g\left(\lambda_i(\mathbf{r}); \{\lambda_j(\mathbf{r})\}_{j\neq i}\right). \tag{20}$$

This property is the matrix-functional analogue of locality in Kohn-Sham DFT, where the exchange-correlation functional is a universal mapping,[10] while the density varies in space. Similarly, in our multistate framework, the scalar mapping g is a system-independent rule. When semilocal descriptors such as density gradients are required, they enter as additional scalar arguments, preserving the universality of the functional form while extending the information content.

Within this framework, the scalar mapping g serves as the central object for constructing matrix functionals. The development of matrix exchange–correlation functionals is thereby reduced to specifying a universal scalar rule, from which the full matrix structure follows through spectral recomposition. This formulation provides a direct and constructive route for developing practical approximations within the multistate framework.[10,13]

Computational Construction. The local spectral formulation yields a practical protocol for evaluating a local, unitary-covariant matrix functional $\mathcal{G}(\mathbf{D})$ through a coupled spatial-state procedure.

At each integration grid point $\mathbf{r}$, the computation proceeds as follows:

- **Spectral Decomposition**. Diagonalize the $N \times N$ Hermitian matrix $\mathbf{D}(\mathbf{r})$,

$$\mathbf{D}(\mathbf{r}) = \mathbf{U}(\mathbf{r})\boldsymbol{\Lambda}(\mathbf{r})\mathbf{U}^{\dagger}(\mathbf{r}), \tag{21}$$

  to obtain its eigenvalues $\{\lambda_i(\mathbf{r})\}$ and corresponding spectral projectors $\{\mathbf{P}_i(\mathbf{r})\}$.

- **Scalar Functional Evaluation**. Evaluate the scalar mapping for each spectral component,

$$g_i(\mathbf{r}) = g\left(\lambda_i(\mathbf{r}); \{\lambda_j(\mathbf{r})\}_{j\neq i}\right), \tag{22}$$

  using the same functional rule for all i. The specific functional form of g is determined by the particular functional used. The dependence on the full local spectrum ensures that coupling among states is retained at each spatial point.

- **Spectral Reconstruction**. Reconstruct the matrix functional locally as

$$\mathcal{G}(\mathbf{D}(\mathbf{r})) = \sum_{i=1}^{N} g_i(\mathbf{r})\mathbf{P}_i(\mathbf{r}). \tag{23}$$

This procedure converts the evaluation of a matrix functional into a sequence of local operations that closely parallels standard Kohn–Sham DFT.[10] Instead of approximating N^2 coupled matrix elements independently, one specifies a single scalar mapping and applies it to the spectral components of $\mathbf{D}(\mathbf{r})$. The coupling among states is retained through the dependence of $g_i(\mathbf{r})$ on the complete local eigenvalue set $\lambda_j(\mathbf{r})$.

From a computational perspective, the dominant cost remains the real-space integration over the grid. The additional overhead arises from diagonalizing an $N \times N$ Hermitian matrix at each grid point. Although this step scales as $\mathcal{O}(N^3)$ per point, it is modest for the small subspace dimensions typically used in MSDFT. Consequently, the overall computational structure remains comparable to that of KS-DFT, with the principal added cost coming from the local spectral decomposition and reconstruction over a small number of state channels.

This formulation highlights the practical consequence of the local spectral representation: the full matrix functional is generated from a single scalar mapping while preserving the symmetry, invariance, and state-coupling structure imposed by the multistate formalism.

Illustration of Spectral Decomposition in Multistate Calculations. To assess the the spectral decomposition approach, we use the two-site, two-electron Hubbard model,[11,17] defined by the Hamiltonian $\hat{H} = -t \sum_\sigma c_{1\sigma}^\dagger c_{2\sigma} + c_{2\sigma}^\dagger c_{1\sigma} + U \sum_{i=1}^2 \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$, where t is set to unity. The first term of the Hamiltonian describes electron hopping between sites, while the second term represents the on-site electron-electron interaction with strength U. This model provides a minimal yet nontrivial testbed with four configurations (two doubly occupied and two singly occupied spin-coupled states), supporting both singlet and triplet states.

The numerical procedure for computing matrix functionals by spectral decomposition is given below.

- **Construction of the matrix density**. We first diagonalize the Hubbard Hamiltonian to obtain the four eigenvectors, from which the 4×4 matrix density $\mathbf{D}$ is constructed. For a given U/t, the matrix density at site $\mathbf{r}_i$ is

$$\mathbf{D}(\mathbf{r}_i) = \begin{pmatrix} 1 - U/R & 0 & 4t/R & 0 \\ 0 & 1 & 0 & 0 \\ 4t/R & 0 & 1 + U/R & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{24}$$

where $R = \sqrt{U^2 + 16t^2}$ and the basis is in the order $\{|I_+\rangle, |\Psi_C\rangle, |I_-\rangle, |\Psi_T\rangle\}$ where $|I_\pm\rangle = (|2,0\rangle \pm |0,2\rangle)/\sqrt{2}$, $|\Psi_C\rangle = (|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle)/\sqrt{2}$ and $|\Psi_T\rangle$ is the triplet state,.

- **Spectral decomposition of matrix density**. Diagonalization of $\mathbf{D}(\mathbf{r}_i)$ yields eigenvalues $\lambda = \{0, 1, 1, 2\}$, which are independent of U and t, while the associated spectral projectors depend on these parameters.

- **Local function and scalar interaction rule**. In the Hubbard model, the interaction operator is $\hat{G} = U \sum_{i=1}^{2} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$. For a local occupation number λ, the double-occupancy operator satisfies $\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} = 0.5\lambda_i(\lambda_i - 1)$, which counts electron pairs on a site. Consequently, the local interaction energy can be expressed as

$$g_i(\lambda_i, U) = \frac{1}{2} U \lambda_i(\lambda_i - 1) \tag{25}$$

  This provides the exact scalar mapping for the interaction functional in the spectral representation.

- **Spectral construction of the interaction functional**. Using the local spectral procedure (eqs (21)–(23)), the matrix interaction functional is constructed as

$$\mathcal{G}_{4\times4}(\mathbf{D}) = \sum_{s=1}^{2} \sum_{i=1}^{4} g_i(\lambda_i(\mathbf{r}_s), U)\mathcal{P}_i(\mathbf{r}_s) \tag{26}$$

Equation (26) corresponds to the matrix representation of the interaction operator $\hat{G}$ within the chosen subspace, which yields the exact matrix $\mathcal{G}((D)) = g(2, \{2, 2, 2\}) \cdot \mathbf{I}_4$.

The total Hubbard Hamiltonian is then reconstructed ($\mathbf{H} = \mathbf{T} + \mathcal{G}$) and diagonalized to yield the four $\hat{S}_z = 0$ eigenstates (three singlet and one triplet state).

Figure 1 shows that the spectral reconstruction reproduces all four eigenvalues exactly across the full range U/t = 0–10. This exact agreement reflects the fact that the scalar mapping $g(\lambda, U)$ is known analytically for this model. Importantly, the triplet state, although not explicitly distinguished in the scalar rule, is reproduced with the same accuracy as the singlet states. This demonstrates that the spectral construction recovers the full operator structure within the subspace, rather than selectively reproducing individual eigenvalues.

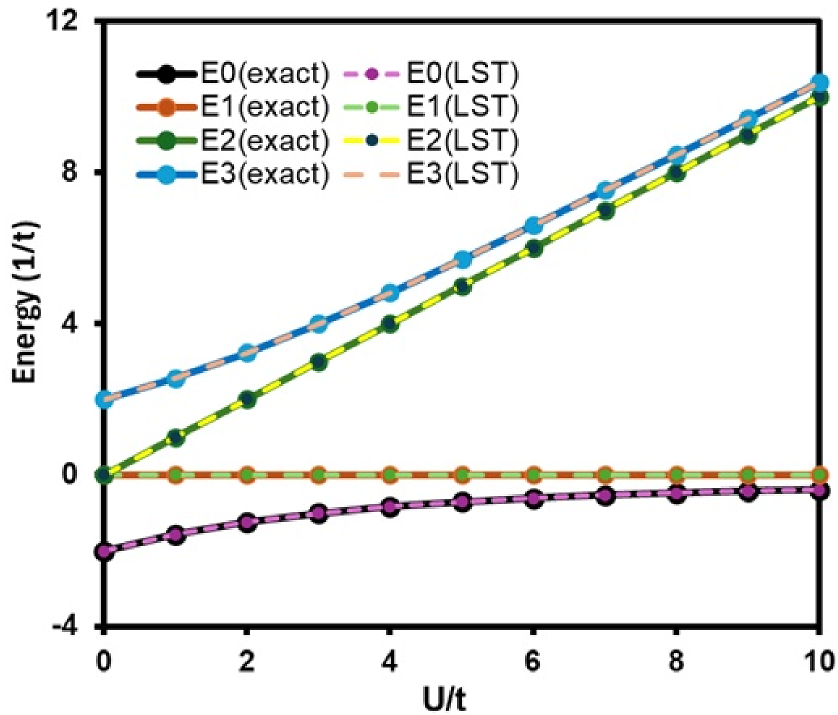


Figure 1: Analytical (exact) and spectrally reconstructed energies of the two-site, two-electron Hubbard model as a function of U/t. The local spectral construction employs the exact scalar interaction mapping $g(\lambda, U) = (1/2)U\lambda(\lambda - 1)$. All four eigenvalues (three singlet states and one triplet state) are reproduced exactly across the full range $U/t = 1-10$, demonstrating that the spectral formulation recovers the full interacting Hamiltonian within the subspace when the correct scalar mapping is used.

When the matrix functional, and thus the associated spectral scalar mapping, is unknown, as in exchange-correlation functionals for electronic systems, can one construct an approximate scalar function that reproduces the target ground- and excited-state energies?

To mimic this situation, we introduce a controlled distortion of the scalar mapping,

$$w^{ref}(\lambda, U) = \frac{1}{2}U\lambda(\lambda - 1) + 0.1\frac{U}{\lambda + 0.5} \tag{27}$$

This perturbation produces systematic deviations in all eigenvalues (Figure 2). To correct these deviations, we introduce a polynomial correction term,

$$g^{\mathrm{LST}}(\lambda, U) = g^{ref}(\lambda, U) + g^{c}(\lambda, U) \tag{28}$$

$$g^{\mathrm{c}}(\lambda, U) = \sum_{m=0}^{2}\sum_{n=0}^{4} a_{mn} U^{m} \lambda^{n} \tag{29}$$

where the coefficients a_{mn} are obtained by minimizing the least squre difference between the exact Hubbard energies and model results in the U/t range, piece-wise, of $[0, 4]$ and $[7, 10]$. Two "correlation" models are used, one depending on the spectral eigenvalue λ only $g^c(\lambda)$ and the second including coupling of charge and interaction strength $g^c(\lambda, U)$. The former is a special case by forcing $U = 1$, but the brute-force coupling of eq (29) is proposed in view of eq (27) containing both U and λ, but otherwise supposedly not knowing its detail.

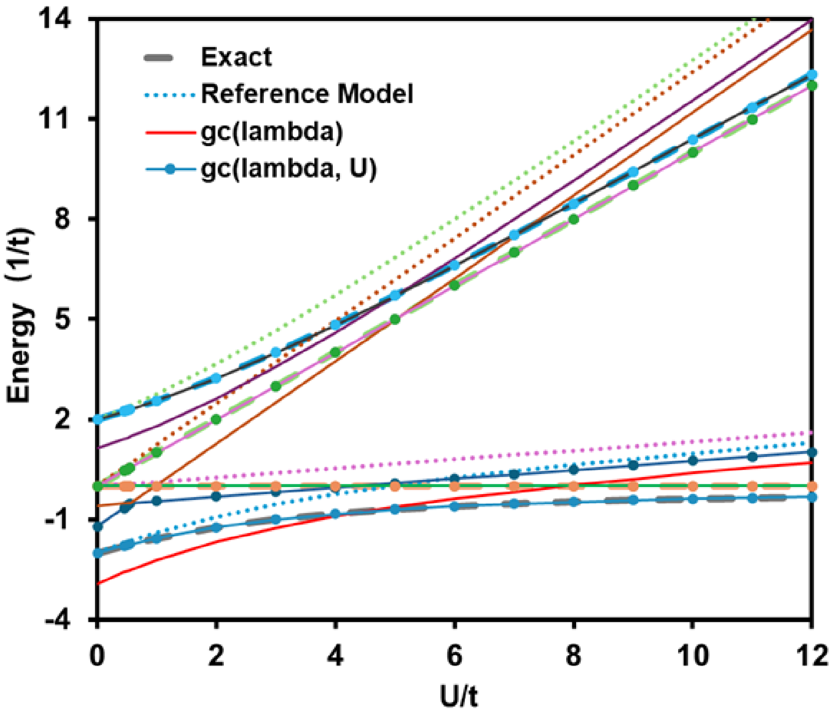


Figure 2: Exact (dashed), distorted reference (dotted), quartic correction (smooth thin), and $\lambda - U$ coupled $g^c(\lambda, U)$ (thin with data point) energies of the Hubbard model. The reference results (dotted) are obtained from a perturbed scalar mapping $g^{ref}(\lambda)$, which introduces systematic deviations in all eigenvalues (dashed). $g^c(\lambda)$ functional has large errors within the fitting range ($[0, 4], [7, 10]$) and outside. The $g^{\mathrm{LST}}(\lambda) = g^{ref}(\lambda) + g^c(\lambda, U)$ correlation restores the energies with negligible error.

The resulting energies are shown in Figure 2. We found that it was not possible to reproduce ground and excited state energies using $g^c(\lambda)$, either within the fitting range nor the expanded validation strength $[0, 12]$. On the other hand, the $g^c(\lambda, U)$-correlated scalar mapping recovers all four eigenvalues within the fitted range and areas outside the fitting with negligible errors (even for $U = 500$). Thus, for this system, the exact energies can be reproduced by using a scalar function of the density eigenvalues; however, the "real" physics requires only two parameters, 0.1 and 0.5 to compensate the effect of eq (27). Further discussion of the implications of this observation is beyond the scope of this article.

These results illustrate two key points. First, when the exact scalar mapping is known, the spectral construction reproduces the full interacting Hamiltonian within the subspace. Second, when the mapping is approximate, deviations can be systematically analyzed and reduced through refinement of the scalar function. This example demonstrates the practical implementation of the local spectral formulation and its potential as a framework for constructing approximate matrix functionals.

Discussion and Concluding Remarks. Several observations clarify the scope, interpretation, and implications of the local spectral formulation.

- The local spectral theorem applies to matrix functionals that are local and unitary-covariant with respect to the matrix density $\mathbf{D}(\mathbf{r})$. When additional variables are introduced such as density gradients, kinetic-energy densities, or nonlocal kernels, the functional dependence extends beyond the point-wise density. In such cases, the formulation remains applicable when expressed in terms of an appropriately enlarged set of local descriptors. Thus, the spectral representation is not restricted to strictly local approximations, but extends naturally to semilocal and generalized functional forms.

- Spectral degeneracies are treated at the level of projectors rather than individual eigenvectors. The requirement that the functional be diagonal in the eigenbasis is more precisely understood as invariance within each degenerate eigenspace. This condition ensures covariance under all unitary transformations that leave $\mathbf{D}(\mathbf{r})$ unchanged, and follows directly from Schur's Lemma.

- The local spectral ODA theorem (Theorem (2)) complements, rather than replaces, the state-level functional relations established in reference 6. The latter encodes global constraints among matrix elements arising from subspace invariance, whereas the former provides a pointwise representation in the spectral frame of $\mathbf{D}(\mathbf{r})$. In this sense, the state-level result is structural, while the local spectral formulation is operational, supplying a canonical ansatz class for constructing approximations consistent with local covariance and permutation symmetry.

- The scalar generating rule g may depend on additional symmetric invariants beyond the explicit eigenvalues. Any symmetric function of the spectrum, such as polynomial invariants or measures of spectral dispersion, contains equivalent information and may serve as alternative variables. This flexibility provides a systematic pathway for developing approximations within the spectral framework, while preserving the symmetry constraints imposed by admissibility.

- The local spectral theorem characterizes the commuting component of admissible matrix functionals, denoted $\mathcal{G}_{\|}[\mathbf{D}]$, which share the spectral projectors of $\mathbf{D}(\mathbf{r})$. In general, however, physically exact operators need not be fully contained within this commuting subspace. Deviations may arise from a non-commuting component, $\mathcal{G}_{\perp}[\mathbf{D}]$, which cannot be represented solely in terms of the local eigenvalue spectrum. This decomposition, $\mathcal{G} = \mathcal{G}_{\|} + \mathcal{G}_{\perp}$, provides a natural framework for analyzing the limitations of purely spectral approximations. The commuting component captures all information consistent with local covariance, while $\mathcal{G}_{\perp}$ encodes additional physical effects such as nonlocal exchange-correlation structure, long-range charge transfer, and excitonic coupling that are not reducible to local spectral data alone.

  Systematic improvement beyond the spectral approximation may therefore be achieved by introducing additional descriptors that resolve the non-commuting degrees of freedom. These may include gradient-dependent terms, transition density matrices, current densities, or other matrix-valued quantities that extend the functional domain. In this way, the local spectral formulation defines a controlled hierarchy: a minimal commuting approximation augmented by progressively richer representations of the nonlocal and noncommuting contributions.

In summary, we have established a local spectral formulation of the one-determines-all principle for multistate density functionals. By exploiting unitary covariance, the construction of a local matrix functional is reduced to defining a single scalar mapping function, from which the full matrix structure is constructed through spectral recomposition. The resulting formulation is spatially local yet intrinsically coupled in state space, ensuring consistency with subspace invariance while preserving universality in the functional form. From a computational perspective, the procedure closely parallels standard Kohn–Sham DFT, with only a modest additional cost associated with local matrix diagonalization. In this sense, the multistate functional problem is recast from the construction of N^2 coupled matrix elements to the design of a scalar functional defined on the local eigenvalue spectrum. Recent development of the partial-active-space multistate perturbation theory (PASPT2) with a similar dynamic-static structure could provide the necessary data for training multistate functionals.[18]

More broadly, this work provides both a rigorous structural foundation and a practical computational framework for multistate functional development. The spectral representation clarifies the internal organization of matrix functionals and enables their systematic construction in direct analogy to conventional density functional approximations. Extensions of this framework, including the development of approximate exchange–correlation matrix functionals, will be explored in future work. Together, these results define a coherent pathway toward density functional methods for excited states and strongly coupled electronic systems.

Supporting Information Available

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/. Numerical data for the figures used in the text in excel format.

AUTHOR INFORMATION

Corresponding Authors

Jiali Gao - School of Chemical Biology and Biotechnology, Shenzhen Graduate School Peking University, Shenzhen 518055, China; Institute of Systems and Physical Biology, Shenzhen Bay Laboratory, Shenzhen 518107, China; Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455, United States; orcid.org/0000-0003-0106-7154; Email: gao@jialigao.org

Yangyi Lu - Institute of Systems and Physical Biology, Shenzhen Bay Laboratory, Shenzhen 518107, China; orcid.org/0000-0002-1602-1661; Email: luyy@szbl.ac.cn

Notes

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