

Ensemble Reduced Density Matrix Functional Theory for Excited States and Hierarchical Generalization of Pauli's Exclusion Principle

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(Received 10 January 2021; revised 26 March 2021; accepted 2 June 2021; published 7 July 2021)

We propose and work out a reduced density matrix functional theory (RDMFT) for calculating energies of eigenstates of interacting many-electron systems beyond the ground state. Various obstacles which historically have doomed such an approach to be unfeasible are overcome. First, we resort to a generalization of the Ritz variational principle to ensemble states with fixed weights. This in combination with the constrained search formalism allows us to establish a universal functional of the one-particle reduced density matrix. Second, we employ tools from convex analysis to circumvent the too involved N -representability constraints. Remarkably, this identifies Valone's pioneering work on RDMFT as a special case of convex relaxation and reveals that crucial information about the excitation structure is contained in the functional's domain. Third, to determine the crucial latter object, a methodology is developed which eventually leads to a generalized exclusion principle. The corresponding linear constraints are calculated for systems of arbitrary size.

DOI: [10.1103/PhysRevLett.127.023001](https://doi.org/10.1103/PhysRevLett.127.023001)

Developing a comprehensive understanding of excitations in many-body systems is of utmost importance from both a fundamental and technological point of view. For instance, quantum excitations intervene in crucial processes such as vision [1], define the properties of advanced materials [2] and of states of matter in general [3–5] and give rise to distinctive functionalities of devices [6,7]. Although modern computational methodologies can determine the ground state energies of a wide range of systems relatively inexpensively and rather accurately [8], methodological innovations are called for handling excitations on an equal footing [9].

The workhorse of modern electronic structure calculations is the Kohn-Sham formulation [10] of density-functional theory (DFT) [11]. As far as excitations are concerned, its time-dependent extension could deal with them rigorously, at least in principle [12]. In practice, however, the widely used time-dependent DFT is not only blessed but unfortunately also cursed by the so-called adiabatic approximation [13–15]. Circumventing at least some of the deficiencies of adiabatic time-dependent DFT, ensemble DFT has become in recent years a promising alternative for calculating excitations [16–29]—for example, it can capture charge transfers, double excitations, and avoided or conical crossings.

From a general perspective, density functional theories are, however, not particularly well suited for the description of strongly correlated systems. The particle density, namely, does not directly reflect the correlation strength,

in striking contrast to the full one-particle reduced density matrix (1RDM) with fractional occupation numbers in case of strong correlations. This motivates one-particle reduced density matrix functional theory (RDMFT) [30] as a more suitable approach to strongly correlated quantum systems and explains why RDMFT has become an active field of research in recent years [31–44]. While the accuracy of ground state calculations compares favorably to those of DFT [45], no proper foundation for targeting excited states within RDMFT exists yet. For instance, a formal justification of a fully dynamical RDMFT is lacking and the approach based on an adiabatic approximation to be exploited through linear response techniques turns out to be technically involved and numerically rather demanding [34,46]. Most remarkably, the RDMFT analog of ensemble DFT for excited states has not even been considered yet, despite its numerous potential advantages over time-dependent functional theories.

In this Letter, we propose and work out the ensemble version of RDMFT for calculating the energies of (selected) low-lying excited states. For this, we put forward a generalization of the Ritz variational principle which together with the constrained search formalism leads to the definition of a universal functional. The crucial ingredient which makes this method viable is a convex relaxation scheme. It allows us to circumvent the corresponding too intricate one-body N -representability constraints and leads instead to an easy-to-calculate generalization of Pauli's exclusion principle for mixed states.

RDMFT in a nutshell and relevance of Valone's work.—We briefly recall ground state RDMFT. Here and in the following, we consider Hamiltonians of the form $H(h) = h + V$ on the N -fermion Hilbert space $\mathcal{H}_N \equiv \wedge^N [\mathcal{H}_1]$, where h is a one-particle Hamiltonian and V some fixed interaction (e.g., Coulomb pair interaction). We denote the set of pure states $\Gamma \equiv |\Psi\rangle\langle\Psi|$ by \mathcal{P}^N and the d -dimensional one-particle Hilbert space by \mathcal{H}_1 .

Calculating the ground state energy $E(h)$ of $H(h)$ via the Ritz variational principle leads immediately to a universal functional of the 1RDM [47,48],

$$\begin{aligned} E(h) &= \min_{\Gamma \in \mathcal{P}^N} \text{Tr}_N[(h + V)\Gamma] \\ &= \min_{\gamma \in \mathcal{P}_N^1} [\text{Tr}_1[h\gamma] + \mathcal{F}(\gamma)], \end{aligned} \quad (1)$$

where

$$\mathcal{F}(\gamma) \equiv \min_{\mathcal{P}^N \ni \Gamma \rightarrow \gamma} \text{Tr}_N[V\Gamma]. \quad (2)$$

Indeed, \mathcal{F} is universal in the sense that it depends only on the fixed interaction V but not on the one-particle Hamiltonian h . This version of RDMFT based on Eqs. (1), (2) has, however, not been practical at all. This is due to the fact that describing the functional's domain $\mathcal{P}_N^1 \equiv N\text{Tr}_{N-1}[\mathcal{P}^N]$ of pure N -representable 1RDMs γ has been an almost impossible task. Only recently, a formal solution to this problem has been found [49,50]. Yet, the corresponding generalized Pauli constraints defining \mathcal{P}_N^1 could be calculated so far only for systems of up to five electrons and eleven spin orbitals [49–52].

It has been Valone's crucial idea [53] to apply the constrained search formalism (1) by relaxing the Ritz variational principle from pure to *all* ensemble states $\Gamma \in \mathcal{E}^N$. In analogy to Eqs. (1), (2) this then leads to a universal functional

$$\bar{\mathcal{F}}(\gamma) \equiv \min_{\mathcal{E}^N \ni \Gamma \rightarrow \gamma} \text{Tr}_N[V\Gamma], \quad (3)$$

defined on the larger domain $\mathcal{E}_N^1 \equiv N\text{Tr}_{N-1}[\mathcal{E}^N]$ of ensemble N -representable 1RDMs. Since the latter is just described by the simple Pauli exclusion principle constraints [54], restricting the eigenvalues λ_i of γ as $0 \leq \lambda_i \leq 1$, Valone's work [53] has marked the starting point of RDMFT, at least from a practical perspective. Finally, we would like to stress that $\bar{\mathcal{F}}$ follows as the lower convex envelope of $\mathcal{F}(\gamma)$, $\bar{\mathcal{F}} \equiv \text{conv}(\mathcal{F})$ [36]. As the following will show, this key result has its origin in a fruitful geometrical structure which will be pivotal to our approach.

Ensemble-RDMFT for excited states.—To develop an RDMFT for targeting the excitation spectrum we resort to the generalization [55] of the Ritz variational principle to

ensemble states with fixed spectrum: let H be a Hermitian operator on a D -dimensional Hilbert space with increasingly ordered eigenvalues E_j and eigenstates $|\Psi_j\rangle$ and denote by $\mathcal{E}^N(\mathbf{w})$ the set of density operators Γ with decreasingly ordered spectrum $\mathbf{w} \equiv (w_1, \dots, w_D)$. Then, the following variational principle can be proven in a straightforward manner [55]

$$E_{\mathbf{w}} \equiv \sum_{j=1}^D w_j E_j = \min_{\Gamma \in \mathcal{E}^N(\mathbf{w})} \text{Tr}[H\Gamma], \quad (4)$$

and the minimizer of the right-hand side follows as $\Gamma_{H,\mathbf{w}} = \sum_{j=1}^D w_j |\Psi_j\rangle\langle\Psi_j|$.

At this point, it is crucial to appreciate that the knowledge of the function $E_{\mathbf{w}}$ would obviously allow one to determine various excitation energies E_j . In analogy to the derivation of ensemble DFT for excited states by Gross, Oliveira, and Kohn [55,56], the variational principle (4) is the key ingredient for establishing an RDMFT for excited states. Combining the constrained search (1) and the variational principle (4) with $H \equiv H(h)$ leads immediately to a universal functional of the 1RDM,

$$\mathcal{F}_{\mathbf{w}}(\gamma) \equiv \min_{\mathcal{E}^N(\mathbf{w}) \ni \Gamma \rightarrow \gamma} \text{Tr}_N[V\Gamma]. \quad (5)$$

In practice, one would restrict this \mathbf{w} -RDMFT to just a few finite weights w_1, \dots, w_r and the minimization of the total energy functional $\text{Tr}_1[h\gamma] + \mathcal{F}_{\mathbf{w}}(\gamma)$ would eventually yield the energy $E_{\mathbf{w}}$. It is also worth stressing, that pure *ground state* RDMFT is included in our general \mathbf{w} -RDMFT as the special case $\mathbf{w}_0 \equiv (1, 0, 0, \dots)$. This observation also implies, however, that finding a practically useful description of the underlying domain $\mathcal{E}_N^1(\mathbf{w})$ of \mathbf{w} -ensemble N -representable 1RDMs is impossible, at least for realistic system sizes [49,50,57].

This fundamental concern also explains why ensemble RDMFT for calculating excitation energies has never been established. It will therefore be a major achievement of our work to find and work out in the following a methodology for circumventing the too intricate one-body \mathbf{w} -ensemble N -representability constraints.

Convex relaxation.—Given the prominence of the Ritz variational principle in quantum physics, Valone's idea to apply the constrained search formalism to the larger set \mathcal{E}^N of ensemble states was rather natural. Since the generalization of this seminal idea to the variational principle (4) is less obvious, we take the relation $\bar{\mathcal{F}} \equiv \text{conv}(\mathcal{F})$ [36] in ground state RDMFT as an inspiration: A prominent concept in convex analysis explains that any minimization problem, at least in principle, can be turned into a convex one without altering the result. This exact convex relaxation applied in our context is illustrated in Fig. 1: First, one extends the “blue” domain of $\mathcal{F}_{\mathbf{w}}$ to its convex hull

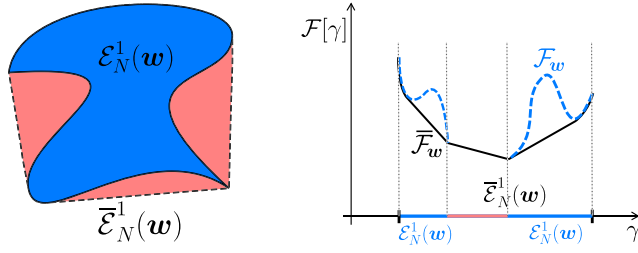


FIG. 1. Schematic illustration of the convex hull $\bar{\mathcal{E}}_N^1(\mathbf{w})$ of the blue set $\mathcal{E}_N^1(\mathbf{w})$ (left) and the convex envelope $\bar{\mathcal{F}}_w$ of \mathcal{F}_w (right). See text for more details.

$\bar{\mathcal{E}}_N^1(\mathbf{w}) = \text{conv}[\mathcal{E}_N^1(\mathbf{w})]$ by adding the “red” region and defining there $\mathcal{F}_w \equiv \infty$. Then, one replaces \mathcal{F}_w by its lower convex envelope

$$\bar{\mathcal{F}}_w \equiv \text{conv}(\mathcal{F}_w) \quad \text{on} \quad \bar{\mathcal{E}}_N^1(\mathbf{w}) \equiv \text{conv}[\mathcal{E}_N^1(\mathbf{w})]. \quad (6)$$

Per construction, the sought-after energy E_w can now be obtained by minimizing the energy functional $\text{Tr}_1[h\gamma] + \bar{\mathcal{F}}_w(\gamma)$ on the set $\bar{\mathcal{E}}_N^1(\mathbf{w})$,

$$E_w = \min_{\gamma \in \bar{\mathcal{E}}_N^1(\mathbf{w})} [\text{Tr}_1[h\gamma] + \bar{\mathcal{F}}_w(\gamma)], \quad (7)$$

rather than $\text{Tr}_1[h\gamma] + \mathcal{F}_w(\gamma)$ on $\mathcal{E}_N^1(\mathbf{w})$. This convex relaxation of \mathbf{w} -ensemble RDMFT has two pleasant and far-reaching consequences. As we will show below, a compact description of the convex set $\bar{\mathcal{E}}_N^1(\mathbf{w})$ can be found *and* the convexity of $\bar{\mathcal{F}}_w$ implies that the minimization cannot get stuck in local minima.

We conclude this section by presenting an equivalent but constructive expression for $\bar{\mathcal{F}}_w$. As it is shown in the Supplemental Material [58], the definition of the lower convex envelope leads in a straightforward (but technical) manner to

$$\bar{\mathcal{F}}_w(\gamma) \equiv \min_{\Gamma \in \mathcal{E}^N(\mathbf{w}) \ni \Gamma \rightarrow \gamma} \text{Tr}_N[V\Gamma]. \quad (8)$$

The underlying search space $\mathcal{E}^N(\mathbf{w})$ is nothing else than the convex hull of $\mathcal{E}^N(\mathbf{w})$, which can also be characterized as [58]

$$\bar{\mathcal{E}}^N(\mathbf{w}) \equiv \text{conv}(\mathcal{E}^N(\mathbf{w})) = \{\Gamma \in \mathcal{E}^N | \text{spec}(\Gamma) < \mathbf{w}\}. \quad (9)$$

Here, \mathbf{v} is said to be majorized by \mathbf{w} , $\mathbf{v} < \mathbf{w}$, if for all $k = 1, 2, \dots, D$ one has

$$v_1^\downarrow + \dots + v_k^\downarrow \leq w_1^\downarrow + \dots + w_k^\downarrow, \quad (10)$$

where $\mathbf{v}^\downarrow, \mathbf{w}^\downarrow$ denote the vectors with the same entries, but sorted in descending order. Intriguingly, relations (8) and (9) reveal that the functional $\bar{\mathcal{F}}_w$ could also have been defined in the spirit of Valone’s work [53] by replacing

in (4) the set $\mathcal{E}^N(\mathbf{w})$ by its convex hull $\bar{\mathcal{E}}^N(\mathbf{w})$. This modification of (4) can be seen as the historically missed variational principle for establishing a *viable* ensemble RDMFT for excited states. Moreover, since the partial trace $\text{Tr}_{N-1}[\cdot]$ is linear we obtain

$$\bar{\mathcal{E}}_N^1(\mathbf{w}) = N\text{Tr}_{N-1}[\bar{\mathcal{E}}^N(\mathbf{w})]. \quad (11)$$

Calculation of functional domain $\bar{\mathcal{E}}_N^1(\mathbf{w})$.—In general, without knowing the functional domain, the common process of developing more and more accurate and sophisticated approximations to the universal functional cannot be initiated. Also, having just a formal definition of $\bar{\mathcal{E}}_N^1(\mathbf{w})$ as in Eqs. (6) or (11) is actually not sufficient. Instead, a concrete description is needed, allowing one in minimization algorithms to easily check whether a given 1RDM γ belongs to $\bar{\mathcal{E}}_N^1(\mathbf{w})$. In the following, we achieve the ideal scenario: A description of $\bar{\mathcal{E}}_N^1(\mathbf{w})$ in terms of just a few linear inequalities is found, similar to the Pauli exclusion principle constraints in ground state RDMFT.

For this we resort to analytical tools some of which have extensively been used in quantum chemistry since the 1960s (see, e.g., Refs. [54,59] for a comprehensive introduction). The first one is a very well-known duality correspondence which is illustrated in Fig. 2 for a general convex, compact subset S of an Euclidean space: the minimization of a linear function $\langle \cdot, h \rangle$ on S means to shift the hyperplane of constant value $\langle \gamma, h \rangle$ (shown as red lines in the left panel) along its normal direction $-h$ until the boundary is reached. By realizing such minimizations for all possible “directions” $-h$, we obtain a complete characterization of S through its boundary points.

In our context, dual characterization of $\bar{\mathcal{E}}_N^1(\mathbf{w})$ means to study the minimization of $\text{Tr}_1[h\gamma]$ on the convex, compact set $\bar{\mathcal{E}}_N^1(\mathbf{w})$ for all Hermitian operators h on the one-particle Hilbert space \mathcal{H}_1 . It is exactly this aspect which reveals a fruitful equivalence of our theoretical problem of characterizing the set $\bar{\mathcal{E}}_N^1(\mathbf{w})$ and describing systems of N non-interacting fermions with a one-particle Hamiltonian h . Since $\bar{\mathcal{E}}_N^1(\mathbf{w})$ is invariant under unitary conjugation, $u\bar{\mathcal{E}}_N^1(\mathbf{w})u^\dagger = \bar{\mathcal{E}}_N^1(\mathbf{w})$, we can restrict to h with a fixed eigenbasis, $h = \sum_{i=1}^d h_i |i\rangle\langle i|$, and increasingly ordered

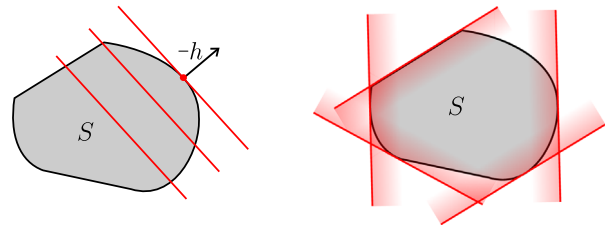


FIG. 2. Geometric illustration of the dual characterization of a convex, compact set S , based on the minimization of all possible linear functions (see text for more details).

energies h_j . To proceed, since the definition (11) of $\tilde{\mathcal{E}}_N^1(\mathbf{w})$ refers to the set $\tilde{\mathcal{E}}^N(\mathbf{w})$, we lift our minimization problem from the one- to the N -particle level, according to

$$\min_{\gamma \in \tilde{\mathcal{E}}_N^1(\mathbf{w})} \text{Tr}_1[h\gamma] = \min_{\Gamma \in \tilde{\mathcal{E}}^N(\mathbf{w})} \text{Tr}_N[h\Gamma]. \quad (12)$$

The minimizers of the right side of Eq. (12) then lead via

$$h \mapsto \Gamma_{h,\mathbf{w}} \mapsto \gamma_{h,\mathbf{w}} \mapsto \lambda_{h,\mathbf{w}} \quad (13)$$

to all extremal points $\lambda_{h,\mathbf{w}}$ of the polytope

$$\Sigma(\mathbf{w}) \equiv \text{spec}[\tilde{\mathcal{E}}_N^1(\mathbf{w})] \quad (14)$$

of natural occupation numbers $\lambda \equiv \text{spec}(\gamma)$. Just to recall, determining $\Sigma(\mathbf{w})$ is sufficient for the description of $\tilde{\mathcal{E}}_N^1(\mathbf{w})$ because of its unitary invariance.

To determine the required minimizers $\Gamma_{h,\mathbf{w}}$ of the right-hand side of Eq. (12), notice that the eigenstates of the one-particle Hamiltonian h are given by the configuration states $i \equiv |i_1, \dots, i_N\rangle$ with energies $\sum_{j=1}^N h_{i_j}$. Consequently, as explained by the variational principle (4), the minimizers follow as

$$\Gamma_{h,\mathbf{w}} = \sum_{j=1}^D w_j |i_j\rangle \langle i_j|, \quad (15)$$

where i_j is the N -fermion configuration with the j th lowest energy. Because of the noninteracting character, one can easily determine for any $\Gamma_{h,\mathbf{w}}$ its natural occupation numbers λ as required by Eq. (13).

To obtain the *vertex representation* of the polytope $\Sigma(\mathbf{w})$, it remains to determine for each choice $h_1 \leq \dots \leq h_d$ the corresponding sequence of eigenstates $|i_j\rangle$ ordered according to their energy. Since there are only finitely many different sequences, this amounts to a purely combinatorial problem. The example of $N = 3$ fermions with $r = 3$ finite weights, $\mathbf{w} = (w_1, w_2, w_3, 0, \dots)$, will be sufficiently representative for the general case. According to Eq. (15), we need to determine all possible sequences i_1, i_2, i_3 of the three energetically lowest configurations. Independent of the values of various h_j , the first two configurations are always given by $i_1 = (1, 2, 3)$ and $i_2 = (1, 2, 4)$. The third lowest will be either $(1, 2, 5)$ or $(1, 3, 4)$, depending on the ordering between $h_2 + h_5$ and $h_3 + h_4$. Consequently, there are in total two different minimizers $\Gamma_{h,\mathbf{w}}$ and according to Eq. (13) two vertices of decreasingly ordered natural occupation numbers,

$$\begin{aligned} \mathbf{v}^{(1)} &= (1, 1, w_1, w_2, w_3, 0, \dots), \\ \mathbf{v}^{(2)} &= (1, w_1 + w_2, w_1 + w_3, w_2 + w_3, 0, \dots). \end{aligned} \quad (16)$$

The polytope $\Sigma(\mathbf{w})$ is eventually obtained as the convex hull of $\mathbf{v}^{(1)}, \mathbf{v}^{(2)}$ and all their permutations. The supporting

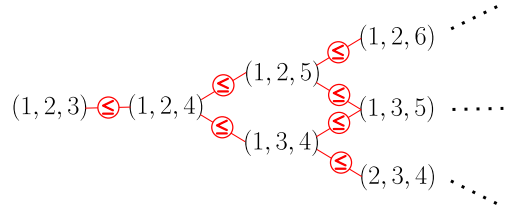


FIG. 3. Illustration of the excitation spectrum for the case of $N = 3$ fermions (see text for more details).

information [58] provides a graphical illustration of $\Sigma(\mathbf{w})$ for different \mathbf{w} .

As a help for dealing with larger numbers r of non-vanishing weights, we illustrate in Fig. 3 the so-called Gale order [60]. All configurations are systematically arranged, where the \leq -sign between two configurations i and j means that i has always a lower energy than j for all h . Figure 3 also confirms that the first two configurations are always given by $i_1 = (1, 2, 3)$, $i_2 = (1, 2, 4)$ and that the dimension d of the one-particle Hilbert space does not play any role. In addition, it shows that increasing the particle number from 3 to N will not change the excitation structure but just add another $N - 3$ ‘1’s at the very beginning of each spectral vector in Eq. (16).

Generalization of Pauli’s exclusion principle.—The vertex representation of the polytope $\Sigma(\mathbf{w})$ can also be turned into a *half-space representation*, leading according to Eq. (14) to the desired practical description of the domain $\tilde{\mathcal{E}}_N^1(\mathbf{w})$. This mathematical procedure for *arbitrary* r will be discussed in Ref. [61] and we present it here only for $r = 1, 2$. These two cases are particularly relevant from a physical point of view since the corresponding \mathbf{w} -RDMFT describes the ground state energy and its gap.

For $r = 1$ and $r = 2$, the permutation-invariant polytope $\Sigma(\mathbf{w})$ is generated by only one vertex, $(1, \dots, 1, 0, \dots)$ and $(1, \dots, 1, w_1, w_2, 0, \dots)$, respectively. According to Rado’s theorem [62], a vector λ lies in such distinctive polytope if and only if λ is majorized by the vertex $\mathbf{v}^{(1)}$, $\lambda < \mathbf{v}^{(1)}$. The definition (10) of majorization is nothing else than the half-space representation of $\Sigma(\mathbf{w})$.

Most remarkably, referring to different values r , there is a *hierarchy* of linear inequalities for $\Sigma(\mathbf{w})$ which generalize Pauli’s exclusion principle. On its lowest level, $r = 1$, one recovers the Pauli exclusion principle $\lambda_1^\downarrow \leq 1$. For $r = 2$, one additional constraint,

$$\sum_{j=1}^N \lambda_j^\downarrow \leq N - 1 + w_1, \quad (17)$$

occurs. This already manifests a generalization of the exclusion principle. Next, for $r = 3$ again one additional constraint emerges, namely,

TABLE I. Number of generating vertices $\mathbf{v}^{(k)}$ and inequalities of permutation-invariant polytope $\Sigma(\mathbf{w})$.

| r | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|------------------------|---|---|---|---|----|----|----|-----|------|
| No. $\mathbf{v}^{(k)}$ | 1 | 1 | 2 | 4 | 10 | 28 | 90 | 312 | 1160 |
| No. ineq | 1 | 2 | 3 | 4 | 8 | 13 | 23 | 42 | 88 |

$$2 \sum_{j=1}^{N-1} \lambda_j^\downarrow + \lambda_N^\downarrow + \lambda_{N+1}^\downarrow \leq 2N - 2 + w_1 + w_2. \quad (18)$$

The inequalities of this hierarchy for larger r are presented in Ref. [61], while in Table I we just list the number of generating vertices $\mathbf{v}^{(k)}$ and inequalities of $\Sigma(\mathbf{w})$ for $r \leq 9$. It is worth recalling that all these results are independent of the particle number N and the dimension d of the one-particle Hilbert space (provided $N \geq r - 1$, $d \geq N + r - 1$).

Outlook.—We have proposed and worked out in the form of \mathbf{w} -RDMFT a viable generalization of ground state RDMFT for targeting the energies of the first few excitations. The crucial ingredient has been a convex relaxation scheme which allowed us to overcome the obstacles which have historically doomed such an approach to be unfeasible. As a major achievement, our work has, namely, overcome the too involved one-body \mathbf{w} -ensemble N -representability constraints. Instead, a hierarchy of easy-to-calculate generalizations of Pauli's exclusion principle constraints has been revealed, providing a practical description of the functional domain $\tilde{\mathcal{E}}_N^1(\mathbf{w})$.

We expect a broad significance of those novel constraints across the quantum sciences. For instance, since they describe the compatibility of N -fermion and one-fermion density operators our work solves a certain class of quantum marginal problems. The latter play a crucial role, e.g., for quantum communication and quantum information processing [57,63]. Moreover, since realistic systems in nature are described by *mixed* states due to the *finite* temperature, it is primarily not Pauli's exclusion principle which dictates their physics but our generalized exclusion principle for mixed states. The spectral polytopes $\Sigma(\mathbf{w})$ are also strongly related to a possible generalization of the Fermi-Dirac distribution to *interacting* fermions: Increasing the temperature T of a system makes the spectrum $\mathbf{w}(T)$ of the Gibbs state $\Gamma(T) \propto e^{-H/k_B T}$ more mixed which in turn reduces the size of the polytope $\Sigma[\mathbf{w}(T)]$. In that sense the generalized exclusion principle constraints provide a tool to determine the maximal temperature of a system which is still compatible to given occupation numbers.

Equipped with the definition (8) of the universal functional $\tilde{\mathcal{F}}_{\mathbf{w}}$ and the practical description of its domain $\tilde{\mathcal{E}}_N^1(\mathbf{w})$, the common process of developing more and more accurate and sophisticated functional approximations can

be initiated. Actually, the ground state functional may serve as a first approximation to $\tilde{\mathcal{F}}_{\mathbf{w}}$, as it is explained in the Supplemental Material [58]: At least for weakly interacting systems, the energy difference $E_{\mathbf{w}} \leq E_{\mathbf{w}'}$ (where $\mathbf{w}' < \mathbf{w}$) is primarily a direct *geometrical* consequence, following from $\tilde{\mathcal{E}}_N^1(\mathbf{w}') \subset \tilde{\mathcal{E}}_N^1(\mathbf{w})$. In particular, knowing the boundary of $\tilde{\mathcal{E}}_N^1(\mathbf{w})$ is sufficient for determining approximately $E_{\mathbf{w}}$. Another promising and particularly sophisticated strategy would be to work out in the context of mixed states exactly the same three steps [64–66] that led to the rather accurate BBC ground state functionals.

We thank F.Castillo, J.-P.Labbé, and J.Liebert for helpful discussions. We acknowledge financial support from the Deutsche Forschungsgemeinschaft (Grant No. SCHI 1476/1-1) and the UK Engineering and Physical Sciences Research Council (Grant No. EP/P007155/1) (C.S.) and from the MIUR PRIN Grant No. 2017RKWTMY (S.P.).

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