Ensemble generalized Kohn–Sham theory: The good, the bad, and the ugly ^{EP}

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ABSTRACT

Two important extensions of Kohn–Sham (KS) theory are generalized: KS theory and ensemble KS theory. The former allows for non-multiplicative potential operators and greatly facilitates practical calculations with advanced, orbital-dependent functionals. The latter allows for quantum ensembles and enables the treatment of open systems and excited states. Here, we combine the two extensions, both formally and practically, first via an exact yet complicated formalism and then via a computationally tractable variant that involves a controlled approximation of ensemble “ghost interactions” by means of an iterative algorithm. The resulting formalism is illustrated using selected examples. This opens the door to the application of generalized KS theory in more challenging quantum scenarios and to the improvement of ensemble theories for the purpose of practical and accurate calculations.

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I. INTRODUCTION

Kohn–Sham^{1,2} (KS) density functional theory (DFT) has proven to be an indispensable tool for the first principles calculations across a wide range of disciplines.^{3,4} Many widely used density functional approximations (DFAs), e.g., Refs. 5–10, are “hybrid functionals,” i.e., they mix exact (Fock) exchange with KS exchange. These are almost always applied using the non-multiplicative Fock-exchange operator, which places them outside the realm of KS theory, but well within generalized Kohn–Sham (GKS) theory.^{11–14} The popularity of hybrid functionals reflects three useful properties of hybrids: first, the inclusion of exact Fermionic exchange allows for a systematically higher predictive accuracy;¹⁵ second, this is carried out in a numerically straightforward fashion, whereas the use of Fock exchange within “pure” KS theory must rely on difficult to calculate optimized effective potentials (OEPs);^{16–21} and third, the non-multiplicative potential allows for a reduction and, in some circumstances, even the elimination of the KS derivative discontinuity,²² allowing one to overcome notoriously difficult problems for KS theory such as the bandgap problem^{23,24} or the charge transfer excitation problem.^{25–27}

Recent years have seen renewed interest in ensemble KS (EKS) theory, which broadens the scope of traditional KS theory to include mapping to an ensemble of reference non-interacting electron states. EKS, thereby, extends the reach of DFT to a more diverse range of quantum scenarios, e.g., systems with non-integer electron number^{22,28–34} and mixtures of ground- and low-lying excited states.^{35–37} It can also improve the treatment of quantum systems that are technically within the reach of KS theory, such as those with significant spin-contamination.³⁸

Ensemble DFT (EDFT) is especially useful for addressing several classes of problems that are inaccessible to standard DFT. First, excited-state EDFT^{28,33,35–59} has attracted significant recent attention as a route to low cost prediction of charge transfer^{40,57} and double^{40,51,54} excitations, which are difficult to predict using traditional time-dependent KS theory. Second, approximations based on excited state EDFT have been introduced and employed to solve strong correlation problems in various complex chemical systems—see, e.g., Filatov’s review in 2015⁴¹ of such approaches. Third, ensemble theory of fractional ions²² and “N-centred”³³ mixtures offer direct access to fundamental and optical gaps at the Kohn–Sham level.^{29,30,33,34} Finally, the thermal

generalization of EDFT⁶¹ allows quantum systems to be studied at finite temperature, albeit with additional complexities compared to other applications of ensemble DFT.^{22,62}

To date, we are not aware of any formal theory that has been able to combine rigorously the attractive features of GKS and EKS theories, though some *ad hoc* solutions^{39,41} and approximations^{55,60} have been reported. This hampers the application of ensemble theories, which must be solved non-self-consistently or with less-sophisticated approximations or using OEPs.

Here, we demonstrate how to combine EKS and GKS theories into an ensemble GKS (EGKS) theory. We show, however, that the resulting approach is ill-suited to existing GKS implementations in its direct form. We then introduce simple, formally motivated approximations that make EGKS tractable without losing its good features.

II. BACKGROUND THEORY

A. Ensemble Kohn-Sham theory

We first briefly introduce EKS theory before turning to GKS and EGKS theory. For simplicity, we use a spin-unpolarized formalism throughout. To begin, we introduce the universal “Levy” ensemble density functional,

$$\mathcal{F}^\lambda[n, \mathbf{w}] = \min_{\hat{\Gamma}_w \rightarrow n} \text{Tr}[(\hat{T} + \lambda \hat{W})\hat{\Gamma}_w], \quad (1)$$

where $\lambda \in [0, 1]$ is an adjustable interacting-strength parameter. Here, n is the density, $\mathbf{w}$ is a set of statistical weights that define the ensemble, $\hat{T}$ is the kinetic energy operator, and $\hat{W}$ is the electron-electron interaction operator. The ensemble density matrix, $\hat{\Gamma}_w = \sum_\kappa w_\kappa |\kappa\rangle\langle\kappa|$, involves a weighted sum over orthonormal wave functions $|\kappa\rangle$. $\hat{\Gamma}_w \rightarrow n$ is short-hand for $\text{Tr}[\hat{n}(\mathbf{r})\hat{\Gamma}_w] = n(\mathbf{r})$, where $\hat{n}(\mathbf{r})$ is the electron-density operator. By varying the weights, $\mathbf{w}$, we can obtain useful properties (e.g., excitation energies) of the system that are inaccessible to ground-state DFT.

The Levy functional $\mathcal{F}^\lambda$ provides a versatile framework for defining key functionals in EKS,^{53,56,58} specifically the KS kinetic energy ($\mathcal{T}_s$), Hartree-exchange (Hx), and correlation (c) functionals, respectively:

$$\mathcal{T}_s[n, \mathbf{w}] = \mathcal{F}^0[n, \mathbf{w}], \quad (2)$$

$$\mathcal{E}_{\text{Hx}}[n, \mathbf{w}] = \lim_{\lambda \rightarrow 0^+} \frac{\mathcal{F}^\lambda[n, \mathbf{w}] - \mathcal{T}_s[n, \mathbf{w}]}{\lambda}, \quad (3)$$

$$\mathcal{E}_c[n, \mathbf{w}] = \mathcal{F}^1[n, \mathbf{w}] - \mathcal{T}_s[n, \mathbf{w}] - \mathcal{E}_{\text{Hx}}[n, \mathbf{w}]. \quad (4)$$

Each is a functional of the electron density n and weights $\mathbf{w}$, denoted by $[n, \mathbf{w}]$.

It has recently been shown that $\mathcal{T}_s[n, \mathbf{w}] \equiv \text{Tr}[\hat{\Gamma}_{s, \mathbf{w}}\hat{T}]$ and $\mathcal{E}_{\text{Hx}}[n, \mathbf{w}] \equiv \text{Tr}[\hat{\Gamma}_{s, \mathbf{w}}\hat{W}]$,⁵⁶ for some non-interacting ensemble density matrix $\hat{\Gamma}_{s, \mathbf{w}}$, which is formed on configuration state functions. $\mathcal{T}_s$ and $\mathcal{E}_{\text{Hx}}$ are, thereby, functionals of a set of orbitals, $\{\phi\}$,

$$\mathcal{T}_s[\{\phi\}] = \sum_i f_i^w \int d\mathbf{r} \phi_i^*(\mathbf{r}) \hat{t} \phi_i(\mathbf{r}) \equiv \sum_i f_i^w t_{i, \phi}, \quad (5)$$

$$\mathcal{E}_{\text{Hx}}[\{\phi\}] = \frac{1}{2} \sum_{ij} \{F_{ij}^{J, w} (ij|ij)_\phi^w + F_{ij}^{K, w} (ij|ji)_\phi^w\}, \quad (6)$$

involving electron-repulsion integrals $(ij|kl)_\phi^w = \int d\mathbf{r} d\mathbf{r}' W(\mathbf{r}, \mathbf{r}') \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}') \phi_k(\mathbf{r}) \phi_l^*(\mathbf{r}')$ with $W = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$.⁶³ The coefficients $f_i^w \in [0, 2]$ are average occupancies of orbitals i across the ensemble. The pair-coefficients, $F_{ij}^{J, w}$ and $F_{ij}^{K, w}$, encode all information about the non-interacting ensemble and are ensemble-specific. They are more complicated to obtain than f_i ; some examples are provided in the Appendix. Importantly, these pair-coefficients are not necessarily (scaled) products of f_i^w , i.e., generally, $F_{ij}^J \neq -2F_{ij}^K \neq f_i f_j$. Recent work has used the fluctuation-dissipation theorem to show that separated $\mathcal{E}_H$ and $\mathcal{E}_x$ also yield functionals of similar form to Eq. (6).⁵⁹ For pedagogical simplicity, we shall not consider the separated terms further.

Just as in KS theory, the EKS orbitals, $\phi_i[n, \mathbf{w}](\mathbf{r})$, are eigen-solutions of the KS equation,

$$\{\hat{t} + v + v_{\text{Hxc}}[n, \mathbf{w}]\} \phi_i[n, \mathbf{w}] = \epsilon_i[n, \mathbf{w}] \phi_i[n, \mathbf{w}]. \quad (7)$$

Here, $v_{\text{Hxc}}[n, \mathbf{w}] = \frac{\delta \mathcal{E}_{\text{Hx}}[n, \mathbf{w}]}{\delta n} + \frac{\delta \mathcal{E}_c[n, \mathbf{w}]}{\delta n}$ is the multiplicative Hxc effective potential of EKS theory, and v is the external potential.³⁶ The effective potential, $v_s := v + v_{\text{Hxc}}$, applied to the electrons, thus depends both on the overall ensemble density, n , and the set of weights, $\mathbf{w}$.

B. Generalized Kohn-Sham theory

We now turn to GKS theory. Seidl *et al.*¹¹ rigorously showed that the usual KS equation can be modified to include a non-local operator $\hat{v}_S$, which is usually of Fock-like form, without changing the fundamental properties of density functionals. The generalized KS equation,

$$[\hat{t} + v + \hat{v}_S + v_R[n]] \phi_i[n] = \epsilon_i[n] \phi_i[n], \quad (8)$$

where v is the external potential and v_R is a multiplicative effective potential, can then be used to find orbitals $\{\phi\}$ and the density n . We obtain different operators $\hat{v}_S$ and potentials v_R for different orbital functionals $S[\{\phi\}]$ that are invariant to unitary transformations of the orbitals. We use $\{\phi\}$ to indicate orbital solutions of Eq. (8), as opposed to $\{\phi\}$ of Eq. (7).

The existence of the GKS equation is deduced by defining $S[n] = \min_{\{\phi\} \rightarrow n} S[\{\phi\}]$ and $R_S[n] = F^1[n] - S[n]$, where we use non-calligraphic F^1 to represent the special case of Eq. (1) for pure ground states ($w_0 = 1$, $w_{k \neq 0} = 0$). Then, the ground-state energy, $E_0 = \min_n \{S[n] + R_S[n] + V[n]\} = \min_{\{\phi\}} \{S[\{\phi\}] + R_S[n_\phi] + V[n_\phi]\}$, is minimized for the density $n \equiv n_\phi \equiv n_0$. Uniqueness (in non-degenerate systems) follows from the external potential v being uniquely defined by the ground state density n_0 . Here, $V[n] = \int d\mathbf{r} n(\mathbf{r}) v(\mathbf{r})$, and we used $S + R_S = F^1$.

Importantly, almost all practical hybrid approximations can be re-expressed as functionals of the first-order reduced density matrix (1-RDM), $\gamma_1(\mathbf{r}, \mathbf{r}') = \sum_{i \in \text{occ}} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}')$. This includes all Hartree-Fock-like expressions, $S[\{\phi\}] := \langle \Phi | \hat{T} + \hat{W}_S | \Phi \rangle$, where Φ is a Slater determinant formed from $\{\phi\}$ and $\hat{W}_S$ is a (modified) interaction term involving interactions of form $0 < W_S(|\mathbf{r} - \mathbf{r}'|) \leq W(|\mathbf{r} - \mathbf{r}'|)$, which can be a simple fraction

$W_S = \alpha W$ of the full interaction term, or a more complex range-separated expression.^{8,64,65} Then,

$$S[\gamma_1] \equiv \int -\frac{1}{2} \nabla^2 \gamma_1(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} d\mathbf{r} + \int W_S(\mathbf{r}, \mathbf{r}') \left[n(\mathbf{r})n(\mathbf{r}') - \frac{1}{2} |\gamma_1(\mathbf{r}, \mathbf{r}')|^2 \right] \frac{d\mathbf{r}d\mathbf{r}'}{2}. \quad (9)$$

We restrict ourselves to this broad and popular class of hybrids, though many results derived below are general.

Our first step toward EGKS theory is to recognize that Eq. (9) can also accept more general 1-RDMs,

$$\gamma_1(\mathbf{r}, \mathbf{r}') = \sum_i f_i \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}'), \quad (10)$$

in which $f_i \in [0, 2]$ can be non-integer [note $n(\mathbf{r}) = \gamma_1(\mathbf{r}, \mathbf{r})$]. Such 1-RDMs appear naturally in ensemble theories, e.g., the 1-RDM for a lithium cation with a partial charge $+q$ is $\gamma_1(\mathbf{r}, \mathbf{r}') = 2\varphi_{1s}^*(\mathbf{r})\varphi_{1s}(\mathbf{r}') + (1-q)\varphi_{2s}^*(\mathbf{r})\varphi_{2s}(\mathbf{r}')$. Importantly, Eq. (9) can be obtained by the sum of Eqs. (5) and (6), for the special case of the product form $F_{ij}^J = -2F_{ij}^K = f_i f_j$. Conveniently, the self-consistent orbitals from Eqs. (9) and (10) always obey Eq. (8). This is because the functional chain rule ensures that orbital derivatives, $\frac{\delta S[\{\varphi\}]}{\delta \varphi_i^*} = \frac{\delta S[\gamma_1]}{\delta \gamma_1} \star \frac{\delta \gamma_1}{\delta \varphi_i^*} = f_i(\hat{t} + \hat{v}_S)\varphi_i$, attain the same form for all i . Here, $\hat{v}_S \varphi := \frac{\delta(S-T_S)}{\delta \gamma_1} \star \varphi$, where $\star$ indicates any necessary integrals. Similarly, $\frac{\delta \mathcal{R}_S}{\delta \varphi_i^*} := \frac{\delta E_R}{\delta n} \frac{\delta n}{\delta \varphi_i^*} \equiv f_i v_R \varphi_i$, and normalization leads to $\varepsilon_i f_i \varphi_i$ because the resulting operator equation is Hermitian. Division by f_i yields Eq. (8).

III. ENSEMBLE GENERALIZED KOHN-SHAM THEORY

A. Fundamental theory

We are now ready to tackle EGKS. The properly ensemblebized version of Eq. (9) is $S^e[\{\varphi\}, \mathbf{w}] := \mathcal{T}_s[\{\varphi\}, \mathbf{w}] + \mathcal{E}_{\text{Hx},S}[\{\varphi\}, \mathbf{w}]$, which uses the ensemble functionals given in Eqs. (5) and (6) [but with $W \rightarrow W_S$ in (6)]. We define the ensemble density functionals,

$$S^e[n, \mathbf{w}] := \min_{\{\varphi\} \rightarrow n} S^e[\{\varphi\}, \mathbf{w}], \quad (11)$$

$$\mathcal{R}_S^e[n, \mathbf{w}] := \mathcal{F}^1[n, \mathbf{w}] - S^e[n, \mathbf{w}], \quad (12)$$

where $\{\varphi\} \rightarrow n$ is short-hand for $\sum_i f_i |\varphi(\mathbf{r})|^2 = n(\mathbf{r})$. It is straightforward to show that Eqs. (11) and (12) are well-defined functionals: both are unique, bounded below ($\mathcal{T}_s[n] \leq S^e[n]$, $\mathcal{F}^1[n] - \mathcal{T}_s[n] - \mathcal{E}_{\text{Hx},S}[n] \leq \mathcal{R}_S^e[n]$), and have, at least, one valid solution ($\{\varphi\} = \{\varphi\}$).

Equation (11) is maximally free⁵⁶ of “ghost-interactions” (GI), namely, spurious interactions between electrons and their counterparts in different ensemble members⁶⁶ that are analogous to self-interactions in pure states. In other words, Eq. (11) will always yield the lowest possible energy for states that are consistent with the weights, $\mathbf{w}$. In contrast, $S[\gamma_1^w]$ of (9) generally exhibits GI errors.⁶⁶ Therefore, it has intrinsic positive energy errors even at the exact Hartree-exchange level and is inconsistent with Eq. (6).

We therefore define $S^{\text{GI}}[\{\varphi\}, \mathbf{w}] := S^e[\{\varphi\}, \mathbf{w}] - S[\gamma_1^w] \equiv \mathcal{E}_{\text{Hx}}[\{\varphi\}, \mathbf{w}] - E_{\text{Hx}}[\gamma_1^w] < 0$, or equivalently,

$$S^{\text{GI}}[\{\varphi\}, \mathbf{w}] := \frac{1}{2} \sum_{ij} [(F_{ij}^{J,w} - f_i^w f_j^w)(ij|ij)_{\varphi}^{W_S} + (F_{ij}^{K,w} + \frac{1}{2} f_i^w f_j^w)(ij|ji)_{\varphi}^{W_S}]. \quad (13)$$

This energy term accounts for differences between the GI-free orbital functional [Eq. (11)] and the 1-RDM energy functional [Eqs. (9) and (10)]. It is worth noting that Eq. (13) typically only has a small number of non-zero terms, as $F_{ij}^{J,w} = f_i^w f_j^w$ and $F_{ij}^{K,w} = -\frac{1}{2} f_i^w f_j^w$ for most combinations of i and j . Explicit dependence on $\mathbf{w}$ is, henceforth, dropped for brevity.

Owing to the GI correction term [S^{GI} , Eq. (13)], Eq. (11) cannot be written as a 1-RDM functional. Therefore, the series of steps leading to Eq. (8) cannot be reproduced fully for S^e . Instead, one must carry out explicit differentiation with respect to orbitals φ_i^* . We first write

$$\mathcal{C} = S^e[\{\varphi\}] + \mathcal{R}_S^e[n] - \sum_{ij} f_i \varepsilon_{ij} \left[\int \varphi_i^* \varphi_j d\mathbf{r} - \delta_{ij} \right] \quad (14)$$

as our functional to be minimized, where S^e and $\mathcal{R}_S^e$ are energies, the final term is the constraint that the orbitals be orthonormal, $\{f_i\}$ are average occupation factors, and $\{\varepsilon_{ij} = \varepsilon_{ji}^*\}$ are Lagrange multipliers. Next, we differentiate $\mathcal{C}$ with respect to φ_i^* (which can be treated as independent of φ_i) to obtain

$$\frac{\delta S^w}{\delta \varphi_i^*(\mathbf{r})} + f_i \varphi_i(\mathbf{r}) \frac{\delta \mathcal{R}_S^e}{\delta n(\mathbf{r})} - f_i \sum_j \varepsilon_{ij} \varphi_j(\mathbf{r}) = 0. \quad (15)$$

Finally, we rewrite (15) as a series of coupled orbital equations,

$$\hat{h}_i \varphi_i \equiv \{\hat{t} + v + \hat{v}_{S,i} + v_R\} \varphi_i = \sum_j \varepsilon_{ij} \varphi_j, \quad (16)$$

for all i, j with $f_i, f_j > 0$. Equation (16) must be simultaneously solved to obtain the minimum energy, $\mathcal{E}[n, \mathbf{w}]$. Importantly, because

$$\hat{v}_{S,i} \varphi_i := \frac{\delta \mathcal{E}_{\text{Hx},S}[\{\varphi\}]}{f_i \delta \varphi_i^*} \quad (17)$$

varies non-trivially with i , a separate one-body problem needs to be solved for each orbital, and Lagrange multipliers ε_{ij} are required to deal with normality and orthogonality (i.e., $\varepsilon_{ij}[\int \varphi_i^* \varphi_j d\mathbf{r} - \delta_{ij}]$, with $\varepsilon_{ij} = \varepsilon_{ji}^*$).

Before proceeding further, it is worth highlighting the similarity between Eq. (16) of the present text and Eqs. (11) and (12) of Filatov.⁴¹ Both these equations take on the same form as both arise from pair-coefficients that are not products of occupation factors. Here, these equations are derived from a rigorous EGKS theory. Filatov derived them by considering approximate solutions for the spin-restricted ensemble-referenced Kohn–Sham (REKS) approach for strongly correlated systems.

We are now ready to consider Eq. (16) in the titular framework. A solution provably exists and may, thus, formally be found. In this sense, Eq. (16) is a *good* result. However, it loses many of the appealing features (simple non-local operator, guaranteed orthogonal orbitals) that make GKS useful. Furthermore, it cannot easily be implemented using the existing GKS infrastructure, although more expensive infrastructure, e.g., that used in complete active space self-consistent field (CASSCF) calculations, may be useful. It is, thus, a *bad* result, in the sense of offering few obvious practical advantages over the existing approaches [using Eqs. (7) or (8)].

In the following, we show that an approximation that is amenable to solution using existing numerical approaches, while still maintaining the gains from both EKS and GKS theories, can be obtained by combining a non-multiplicative potential with an iterative algorithm. Such a theory could be viewed, in comparison to the parent EKS or GKS theory, as *ugly*. However, we show that it offers formal and practical advantages over existing approaches.

B. More amenable EGKS

In anticipation of further approximation, we first recast the exact result in a slightly different form. As discussed previously, $S[\gamma_1^w]$ lends itself to standard GKS treatment. We, therefore, “generalize” the KS formalism on this term separately from the difficult S^{GI} term [Eq. (13)]. The total energy may be written as

$$\mathcal{E}[\{\varphi\}] = S[\gamma_1] + \mathcal{S}^{\text{GI}}[\{\varphi\}] + \mathcal{R}_S^e[n] + V[n]. \quad (18)$$

This is an exact expression that partitions the straightforward 1-RDM part, $S[\gamma_1]$, in $S^e = S + \mathcal{S}^{\text{GI}}$ from the more difficult ghost interaction term, $\mathcal{S}^{\text{GI}}$.

Our goal is to find the orbitals that minimize $\mathcal{E}$, i.e., solutions of (16). The partitioning is preserved via differentiation, which lets us similarly partition the non-local potential operator,

$$\hat{v}_{S,i}^e \varphi_i = \hat{v}_S \varphi_i + \frac{\delta \mathcal{S}^{\text{GI}}[\{\varphi\}]}{f_i \delta \varphi_i^*} := \{\hat{v}_S + \hat{v}_i^{\text{GI}}\} \varphi_i. \quad (19)$$

Here,

$$\begin{aligned} \hat{v}_S \varphi_i &= \hat{v}_{\text{HF}}[\gamma_1] \varphi_i := v_{\text{H}} \varphi_i + \hat{v}_{\text{S}} \varphi_i \\ &= \int \frac{n(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \varphi_i(\mathbf{r}) - \frac{1}{2} \int \frac{\gamma_1(\mathbf{r}, \mathbf{r}') \varphi_i(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \end{aligned} \quad (20)$$

is the usual 1-RDM expression for Hartree–Fock theory that can be used in Eq. (8) without modification by assigning it an ensemble 1-RDM.

Our next step is to recognize that $\Delta F_{ij}^l = F_{ij}^l - f_i f_j$ and $\Delta F_{ij}^K = F_{ij}^K + \frac{1}{2} f_i f_j$ are zero for *almost* all combinations of i and j in all common types of ensembles, per the Appendix. Therefore, $\frac{\delta \mathcal{S}^{\text{GI}}}{\delta \varphi_i^*}$ is also zero for most values of i —including all doubly occupied orbitals with $f_i = 2$. We define a “doubly occupied space,” $\mathbb{D}$, for all orbitals with $f_i = 2$ and a “frontier space,” $\mathbb{F}$, for remaining orbitals with $f_i > 0$. Furthermore, we can eliminate most of the off-diagonal terms, $\varepsilon_{i \neq j}$ [in (16)], by recognizing that

$$\varepsilon_{ij} = \begin{cases} \varepsilon_i \delta_{ij}, & i, j \in \mathbb{D}, \\ \tilde{\omega}_j, & i \in \mathbb{D}, j \in \mathbb{F}, \\ \tilde{\omega}_i^*, & i \in \mathbb{F}, j \in \mathbb{D}, \\ \varepsilon_{ij}, & i, j \in \mathbb{F}, \end{cases} \quad (21)$$

which follows from the fact that $\hat{v}_S$ is Hermitian, $\varepsilon_{ij} = \varepsilon_{ji}^*$, and γ_1 and $S^{\text{1-RDM}}[\gamma_1]$ are invariant to unitary transformations among $i \in \mathbb{D}$.

It finally follows from Eqs. (13), (19), and (21) that

$$\hat{h}_{\text{1-RDM}} \varphi_i = \varepsilon_i \varphi_i + \sum_{j \in \mathbb{F}} \tilde{\omega}_j \varphi_j, \quad i \in \mathbb{D}, \quad (22)$$

$$\{\hat{h}_{\text{1-RDM}} + \hat{v}_i^{\text{GI}}\} \varphi_i = \sum_{j \in \mathbb{F}} \varepsilon_{ij} \varphi_j + \tilde{\omega}_i^* \sum_{j \in \mathbb{D}} \varphi_j, \quad i \in \mathbb{F}, \quad (23)$$

where $\hat{h}_{\text{1-RDM}} := \hat{t} + v + \hat{v}_S + v_R$ and

$$\begin{aligned} \hat{v}_i^{\text{GI}} &= \sum_j \frac{\Delta F_{ij}^l}{f_i} \int \frac{n_j(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \varphi_i(\mathbf{r}) \\ &+ \sum_j \frac{\Delta F_{ij}^K}{f_i} \int \frac{\varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \varphi_j(\mathbf{r}). \end{aligned} \quad (24)$$

Simultaneously solving Eq. (22) (for doubly occupied orbitals) and (23) (separately for each frontier orbital) yields the orbitals that minimize Eq. (18).

C. Practical approximations

Solving Eqs. (22) and (23) is difficult in general and cannot be trivially performed using standard iterative approaches to GKS theory implemented in quantum chemistry codes. We therefore propose two approximations that can be solved by using existing machinery directly, supplemented by simple linear algebra routines that are present in any quantum chemistry code.

A first, crude approximation is to assume that $\hat{v}_i^{\text{GI}}$ is of little consequence to the obtained EGKS orbitals and so can be set to zero. We therefore introduce the “1-RDM” approximation, in which the orbitals $\{\varphi\}_{\text{1-RDM}}$ are found using

$$\hat{h}_{\text{1-RDM}} \varphi_i^{\text{1-RDM}} = \varepsilon_i^{\text{1-RDM}} \varphi_i^{\text{1-RDM}}, \quad (25)$$

but energies are found by using $\{\varphi\}_{\text{1-RDM}}$ in Eq. (18). Here, the off-diagonal terms disappear naturally because $\hat{h}_{\text{1-RDM}}$ is Hermitian. The ensemble energy from this approximation provides an upper bound to the true EGKS energy.

On the positive side, the 1-RDM approximation is simple and convenient. On the negative side, it is uncontrolled, misses key ensemble physics, and even leads to asymptotically incorrect potentials—see the Li^{+q} example in Sec. IV. Nonetheless, it is a decent approximation in some cases, such as for the cation of HCN (shown in Fig. 1).

The second, “diagonal” approximation represents the titular ugly approach. It involves setting *all* off-diagonal terms in Eq. (21) to zero, not just the ones for $i, j \in \mathbb{D}$. That is, it involves solving

$$\hat{h}_{\text{1-RDM}}^{\text{diag}} \varphi_i^{\text{diag}} = \varepsilon_i^{\text{diag}} \varphi_i^{\text{diag}}, \quad i \in \mathbb{D}, \quad (26)$$

$$\{\hat{h}_{\text{1-RDM}} + \hat{v}_i^{\text{GI}}\} \varphi_i^{\text{diag}} = \varepsilon_i^{\text{diag}} \varphi_i^{\text{diag}}, \quad i \in \mathbb{F}, \quad (27)$$

and algorithmically imposing orthogonality. The resulting solution has better properties than the 1-RDM solution and, in almost all tested cases, gives lower energies. The orthogonalization and need to solve multiple equations, nonetheless, make it rather ugly compared to standard GKS theory of Eq. (8).

The difference between the 1-RDM and diagonal approximations is best illustrated using a finite M -element real basis set, so that $\varphi_i \rightarrow \mathbf{C}_i$ are the orbitals and $\gamma_1 = \sum_i f_i \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}') \rightarrow \mathbf{D} = \sum_i f_i \mathbf{C}_i \mathbf{C}_i^T$ is the 1-RDM. Then, $\hat{h}_{\text{1-RDM}}[\gamma_1] \rightarrow \mathbf{F}_{\text{1-RDM}}[\mathbf{D}]$ and $\hat{v}_i^{\text{GI}}[\{\varphi\}_i] \rightarrow \mathbf{V}[\{\mathbf{C}_i\}_i]^{\text{GI}}$ are symmetric matrix representations of effective Hamiltonian terms, expressed in the basis. We also introduce $\mathbf{S}$ as the $M \times M$ overlap matrix of our basis, to deal with non-orthogonal choices.

For both approximations we first solve

$$\mathbf{F}_{\text{1-RDM}} \mathbf{C}_i^{\text{1-RDM}} = \varepsilon_i \mathbf{S} \mathbf{C}_i^{\text{1-RDM}} \quad (28)$$

FIG. 1. Fractional anion energy curve of F (top) shown relative to the neutral atom energy of EGKS theory and fractional cation curve of HCN (bottom), shown relative to a straight line fit between the neutral and cation EGKS results. Here and in subsequent figures, we show 1-RDM in teal dash-dots, diag in orange dashes, and exact EGKS results in navy solid lines. Dots, where shown, indicate UHF values.

for all orbitals such that $C_i^{1\text{-RDM}}$ are guaranteed to be orthogonal. The 1-RDM approximation then involves updating $F_{1\text{-RDM}}$ using $D^{1\text{-RDM}}$ from these orbitals and solving to self-consistency. Similarly, in the diagonal approximation, the solutions, $C_{i \in \mathbb{D}}^{\text{diag}} := C_i^{1\text{-RDM}}$, are used for our doubly occupied orbitals. The difference comes because the solutions, $C_{i \in \mathbb{D}}^{1\text{-RDM}}$, are used to expand the frontier orbitals, $C_{i \in \mathbb{F}}^{\text{diag}}$, which are then solved separately.

To solve for $C_{i \in \mathbb{F}}^{\text{diag}}$, we must first impose an order on $i \in \mathbb{F}$, e.g., via $\varepsilon_i^{\text{diag}}$ from a previous step or the ground state. For the first $i \in \mathbb{F}$, we define $P^i = [C_i^{1\text{-RDM}}, C_{i+1}^{1\text{-RDM}}, \dots]$ (i.e., a matrix formed out of the frontier and virtual orbitals expressed as column vectors) that projects solutions onto the unoccupied space of Eq. (28). We then diagonalize

$$P^{i,T} \{F_{1\text{-RDM}} + V_i^{\text{GI}}\} P^i x_k = \varepsilon_k^i x_k, \quad (29)$$

to obtain $C_k^i := P^i x_k$, ordered for $k \geq 1$. Then, $C_i^{\text{diag}} := C_{k=1}^i$ is the next orbital for the diagonal approximation. We then set $P^{i+1} = [C_2^i, C_3^i, \dots]$ and solve Eq. (29) again for $i + 1$, until we have obtained all $i \in \mathbb{F}$. Once we have the full set of orbitals, we can use them to update $F_{1\text{-RDM}}[D^{\text{diag}}]$ and $V_i^{\text{GI}}[\{C_i^{\text{diag}}\}]$ and then use the new matrices to repeat the process starting from Eq. (28).

The approach, thus, gives us a set of orbitals, C_i^{diag} , that are guaranteed to be orthogonal to one another. Furthermore, the use of $\hat{v}_i^{\text{GI}}$ in the effective Hamiltonian for C_i^{diag} means that they, *prima facie*, have the correct asymptotics,⁶⁷ unlike the 1-RDM solutions. They may, thus, be expected to be better approximations to the real

solutions. Results (see Sec. IV) are almost always better than the 1-RDM, sometimes substantially so. Nevertheless, they can only form an upper bound to the true energy since $\varepsilon_{i \neq j} = 0$ is imposed via the diagonal approximation, rather than found from a true variational solution.

Of final note, it is obvious that the frontier orbitals, $C_{i \in \mathbb{F}}^{\text{diag}} \neq C_i^{1\text{-RDM}}$, differ from the 1-RDM approximation because they obey different effective Hamiltonians. However, it is also true that the doubly occupied orbitals, $C_{i \in \mathbb{D}}^{\text{diag}} \neq C_i^{1\text{-RDM}}$, are different despite both coming from Eq. (28). The difference comes from different 1-RDMs, $D^{\text{diag}} \neq D^{1\text{-RDM}}$, being used to form $F_{1\text{-RDM}}$.

D. Simplified EGKS theory

We next turn briefly to a less rigorous approximation recently introduced by one of the authors—the “simplified EGKS” (SEGKS) scheme⁶⁰—that is designed to efficiently approximate the EGKS solution of excited state ensembles. This approximation is based on an ansatz, $F \approx (1 - \mu)F_{\text{gs}} + \mu F_{h \rightarrow l}$, for the Fock matrix that interpolates between the ground state Fock matrix, F_{gs} , and a different Fock matrix, $F_{h \rightarrow l}$, formed by double promotion of the HOMO to the LUMO.

The physical intuition behind this ansatz is the idea that F_{gs} screens the HOMO more than the LUMO, whereas $F_{h \rightarrow l}$ does the reverse, which gives the model sufficient flexibility to optimize the orbitals. The precise amount of linear mixing is found by seeking μ^s , for which the resulting orbitals, C_i^s , minimize the total energy, $\mathcal{E}^s$, including the GI term. SEGKS provides an upper bound to the true EGKS energy.

E. A very slow route to exact solutions

Before concluding this section, we return to exact theory, where our goal is to find the orbitals, C_i^o , that minimize Eq. (18), to provide the best possible energy, $\mathcal{E}^o := \mathcal{E}[\{C_i^o\}] \leq \mathcal{E}[\{C_i\}]$, within the given finite basis. In all tested cases, we found that C_i^{diag} forms a good starting point for finding C_i^o , in the sense that we may write $C_i^o = \sum_j U_{ij} C_j^{\text{diag}}$, where the unitary matrix U (in our finite basis) is nearly an identity. Consequently, we may write $U \approx \prod_{i>j} \mathbf{u}_{ij}(\theta_{ij})$, where $\mathbf{u}_{ij}(\theta_{ij})$ are matrices that leave all orbitals unchanged except $C_i \rightarrow \cos(\theta_{ij})C_i - \sin(\theta_{ij})C_j$ and $C_j \rightarrow \sin(\theta_{ij})C_i + \cos(\theta_{ij})C_j$.

We are, thus, able to inefficiently find $\mathcal{E}^o$ by individually minimizing the energy with respect to rotations, θ_{ij} , for each combination of $j > i$ (including doubly occupied, frontier, and virtual orbitals but excluding double-double and virtual-virtual rotations as these leave the energy unchanged). This brute force approach leads to $O(N^2)$ calculations of $O(N^3)$ energies, for a very poor scaling of $O(N^5)$ that is unsuitable for large systems. In practice, we repeat the process several times until energies can no longer be reduced. We are, thus, able to find exact solutions, to within a few percent of an eV, for the small systems reported in Sec. IV.

IV. RESULTS

Having established both exact theory and useful approximate forms, we turn to examples. Throughout, we perform EGKS calculations corresponding to the ensemble exact exchange theory approximation⁵⁶ in EKS theory, i.e., we set $\mathcal{R}^e = 0$, $S^{1\text{-RDM}} \equiv S^{\text{HF}}$, and

$S^{\text{GI}} = \mathcal{T}_s + \mathcal{E}_{\text{Hx}} - S^{\text{HF}}$. As mentioned above, we use a spin-unpolarized formalism throughout so that potentials and orbitals are independent of spin, i.e., $\varphi_{i\uparrow} = \varphi_{i\downarrow}$ and $C_{i\uparrow} = C_{i\downarrow}$.

For the purpose of the present theoretical study, exact exchange represents an effective choice of density functional approximation as it lets us clearly delineate errors caused by the orbital approximations (1-RDM or diag) from those caused by the functional approximation. We are, thus, able to gain insights into the quality of approximations to the effective Hamiltonians (and orbitals), separate from other considerations. These calculations are denoted as “exchange-only” throughout, and the underlying orbital approximation (EGKS, diag, 1-RDM, or unrestricted Hartree–Fock) are mentioned separately. For a similar purpose, we also break spatial symmetries, by arbitrarily occupying selected degenerate orbitals in all cases, to avoid additional ensemble effects required to deal with them.^{28,38,68}

We begin with an analytic example: the fractional ion Li^{+q} , with $0 < q < 1$. This system is represented as an ensemble $\hat{\Gamma} \equiv q|1s^2\rangle\langle 1s^2| + (1-q)/2[|1s^2 2s^{\uparrow}\rangle\langle 1s^2 2s^{\uparrow}| + |1s^2 2s^{\downarrow}\rangle\langle 1s^2 2s^{\downarrow}|]$. It is straightforward to show (see Appendix) that the density is $n = 2|\phi_{1s}|^2 + (1-q)|\phi_{2s}|^2$, i.e., $f_{1s} = 2$ and $f_h \equiv f_{2s} = 1 - q$. Furthermore, the $2s$ orbital never interacts with itself, which gives $F_{2s2s}^{\text{I}} = F_{2s2s}^{\text{K}} = 0$ as the only pair-coefficient that contributes to

$$S^{\text{GI}}[\{\varphi\}] := S^{\text{GI}}[\phi_{2s}] = -\frac{f_{2s}^2}{2} E_{\text{H}}[n_{2s}]. \quad (30)$$

We are interested in the asymptotic behavior of the $2s$ orbital. By recognizing that for large r $\int \frac{\varphi_i^*(\mathbf{r}')\varphi_j(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \rightarrow \frac{\delta_{ij}}{r}$, we see [Eq. (20)] that $v_{\text{H}}^{\text{1-RDM}}\phi_{2s} = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \phi_{2s}(\mathbf{r}) \rightarrow \frac{f_{1s}+f_{2s}}{r} \phi_{2s}$ and $\hat{v}_{\text{x}}^{\text{1-RDM}}\phi_{2s} = -\int \frac{\gamma_1(\mathbf{r},\mathbf{r}')}{2|\mathbf{r}-\mathbf{r}'|} \phi_{2s}(\mathbf{r}') d\mathbf{r}' \rightarrow -\frac{f_{2s}}{2r} \phi_{2s}$ so that the 1-RDM approximation [Eq. (25)] yields

$$\lim_{r \rightarrow \infty} \hat{v}_s \phi_{2s} \rightarrow \frac{f_{1s} + \frac{f_{2s}}{2}}{r} \phi_{2s} = \frac{2 + \frac{1-q}{2}}{r} \phi_{2s}. \quad (31)$$

Including the GI term [Eq. (30) in (24)], whether in the exact theory or via the diagonal approximation [Eqs. (26) and (27)], gives an additional $\hat{v}_{2s}^{\text{GI}} \rightarrow -\frac{f_{2s}^2}{2f_{2s}r} = -\frac{f_{2s}}{2r}$, to yield

$$\lim_{r \rightarrow \infty} [\hat{v}_s + \hat{v}_{2s}^{\text{GI}}] \phi_{2s} \rightarrow \frac{f_{2s}}{r} \phi_{2s} = \frac{2}{r} \phi_{2s}. \quad (32)$$

Note that we have assumed $\lim_{r \rightarrow \infty} \phi_{1s}(\mathbf{r})/\phi_{2s}(\mathbf{r}) = 0$.

The outermost $2s$ electron, thus, “feels” the charge of the two $1s$ electrons only (i.e., no self-interaction) when the GI term is included, a result that is physical and consistent with previous findings of ensemble theories yielding the correct asymptotic behavior in ensembles.⁶⁸ By contrast, the 1-RDM approximation leads to an unphysical self-interaction in the outermost electron, with an effective charge $\frac{q-1}{2}$, and, thus, underbinds the $2s$ orbital. The total effective asymptotic potential (nuclear plus electronic) felt by the outermost electron is, thus, $-\frac{1}{r}$ for exact GKS and the diagonal approximation, but $-\frac{1-q}{2r}$ for the 1-RDM approximation.

The abovementioned result is not unique to the case $f_h \leq 1$. In general, exact EGKS theory and the diag approximation for fractional anions and cations will have asymptotic behavior in line with known OEP results.⁶⁸ This result follows from the fact that OEPs, exact GKS theory, and the diag approximation all reduce to the same

Slater potential in the limit $r \rightarrow \infty$ and, thus, have the same asymptotic behavior. However, this behavior is not necessarily that of a $\frac{-1}{r}$ decay.⁶⁸ The 1-RDM approximation always decays asymptotically as $\frac{-Z+N-f_h/2}{r}$ where Z is the nuclear charge and N is the total number of electrons.

We now turn to numerical examples, where we compare our two approximations (1-RDM and diag) against benchmark exchange-only solutions found by minimizing against unitary transformations of the orbitals, as described in Sec. III E. All calculations were performed using Gaussian type orbitals in the def2-TZVP basis set⁶⁹ and were implemented in a customized Python3 code using Psi4/numpy.^{70,71} We remind the reader that, in all examples, we have allowed spatial symmetries to break.

Table I reports errors for a selection of simple systems with degenerate ground states (triplet states, ts and doublet states, ds), shown relative to exact EGKS theory. In the case of CO, we show the excited triplet state. These systems have the advantage that not only can we compare exchange-only EGKS approximations against exact results but also compare exact and approximate EGKS against broken-symmetry unconstrained Hartree–Fock (UHF) theory. UHF is guaranteed to have an energy that is less than or equal to EGKS by virtue of having additional degrees of freedom. It is, therefore, included as a reference lower bound value for exchange-only theories.

We first notice that the diagonal approximation offers significant improvements over the 1-RDM approximation in all tested cases—an unsurprising success that is replicated in almost all tests reported here. Perhaps more surprisingly, we see that even exact EGKS theory can yield substantially larger energies than UHF, of up to 8.9 kcal/mol (0.38 eV) for the CO excited triplet state. Whether this should be considered an “error” of EGKS (which has the correct ground state degeneracy but higher energy) or UHF (which lowers energies via an unphysical breaking of fundamental symmetries) is a matter of taste that dates back to, at least, 1963 as Löwdin’s classic “symmetry dilemma.”⁷²

A more comprehensive example is provided by the full fractional ionization curve for the anion of the fluorine atom, which represents the zero temperature limit of a grand canonical ensemble. At net charge q , the ensemble describing this process is

$$\hat{\Gamma}_q = \frac{1+q}{2} [|F_{\uparrow}\rangle\langle F_{\uparrow}| + |F_{\downarrow}\rangle\langle F_{\downarrow}|] - q|F^{-}\rangle\langle F^{-}|, \quad (33)$$

which mixes equal amounts of the $\uparrow$ and $\downarrow$ dominant degenerate F doublet ground states with the singlet F^{-} ground state, to achieve the correct net charge. Results are shown in the top panel of Fig. 1.

TABLE I. Errors (in kcal/mol = 0.043 eV) for various EGKS approximations, with respect to exact EGKS energies, within exchange-only theory. Also shown are energies from UHF theory, for triplet state (ts) and doublet states (ds). Singlet states are identical in all theories.

	C(ts)	O(ts)	B(ds)	F(ds)	CO(ts)	Mean
1-RDM	11.6	15.6	5.2	8.3	14.1	11.0
Diag	4.0	7.7	0.0	0.1	6.3	3.6
Exact	0.0	0.0	0.0	0.0	0.0	0.0
UHF	−3.1	−3.9	−2.7	−2.9	−8.9	−4.3

In a correlated theory, this curve should be a straight line.²² Exchange-only theory introduces a substantial curvature as a function of charge.^{28,73,74} It is, nonetheless, clear that the diagonal approximation is nearly exact for all charges, whereas the 1-RDM approximation is only accurate when more than half an electron is added to the system; note that F^- is the closed shell pure state case for which standard 1-RDM theories apply so that exact, 1-RDM, and diag EGKS all become exactly equivalent to standard Hartree–Fock theory.

The bottom panel of Fig. 1 is similar to the top, but for the cation of HCN,

$$\hat{\Gamma}_q = \frac{q}{2} [|\text{HCN}_1^+\rangle\langle\text{HCN}_1^+| + |\text{HCN}_2^+\rangle\langle\text{HCN}_2^+|] + (1-q)|\text{HCN}\rangle\langle\text{HCN}|. \quad (34)$$

Rather than showing full energies, it reports errors relative to a straight line fit between exchange-only EGKS results for the cation and neutral molecule, i.e., it shows the curvature, so that difference between approximations are visible at the scale of the plot. Again diag is nearly exact, whereas 1-RDM has issues for positive charges of more than half an electron—here, the neutral system is the closed shell case.

EDFT can also be used to predict excitation energies. This is performed by forming an ensemble in which the excited states have weights less than or equal to the weights for the states that are lower in energy. We, therefore, next consider a relevant ensemble for predicting singlet–triplet excitations,

$$\hat{\Gamma}_w = (1-w)|S_0\rangle\langle S_0| + \frac{w}{3} \sum_{M_z} |T_{0,M_z}\rangle\langle T_{0,M_z}|, \quad (35)$$

which mixes different fractions of the singlet ground state (gs, S_0) with an equal mixture of the three lowest energy triplet states (ts, T_{0,M_z} , $M_z \in \{-1, 0, 1\}$). Here, $w = 0$ indicates a pure ground (singlet) state while $w = 1$ represents the state average of the degenerate triplets.

It is important to note here that the original Gross–Oliveira–Kohn theorem³⁵ that underlies excited state ensembles applies to systems with non-increasing weights, w_k , as a function of energy, E_k , and, thus, forbids the ensemble with $w > \frac{3}{4}$ because $w_{ts} = \frac{w}{3} > 1 - w = w_{gs}$ even though $E_{ts} > E_{gs}$. However, seamless inclusion of $w > \frac{3}{4}$ is allowed under generalized ensemble theorems³⁸ because the ensemble includes only the lowest energy state for each included spin symmetry.

Results are shown in Fig. 2 for Be, C, and O. In all cases, the diag approximation is substantially better than the 1-RDM, except for the pure singlet ground state where both approximations are exact. The diag results are nearly exact for mixings up to 60% of triplet, but then become poorer. We also include results from the SEGKS scheme.⁶⁰ In all cases, SEGKS outperforms 1-RDM slightly, especially for mid-range weights, but is worse than the diag approximation. Note that previous EDFT calculations of Be yielded a singlet–triplet excitation energy of between 2.3 eV and 3.5 eV,^{44,45} using a variety of exchange–correlation models. Although these are larger than the 1.5 eV found here, at least, some of the difference can be explained by the fact that correlations are completely neglected in our calculations.

The same scheme described above for triplet states can also be used to describe excitations between states of the same fundamental symmetry, which are not accessible to standard DFT. Ensembles that

FIG. 2. Energies (in eV) of mixtures of singlet and triplet states for Be (top), C (middle), and O (bottom).

provide access to the first and second excited states (for single and double excitations from $h \rightarrow l$) are

$$\hat{\Gamma}_{w \leq \frac{1}{2}} = (1-w)|S_0\rangle\langle S_0| + w|S_1\rangle\langle S_1|, \quad (36a)$$

$$\hat{\Gamma}_{\frac{1}{2} < w \leq 1} = \frac{2-w}{3} [|S_0\rangle\langle S_0| + |S_1\rangle\langle S_1|] + \frac{2w-1}{3} |S_2\rangle\langle S_2|, \quad (36b)$$

where again we use generalized ensemble theorems,³⁸ in this case to eliminate the triplets from the abovementioned ensembles. Here, setting $w \leq \frac{1}{2}$ gives mixtures of S_0 and S_1 only, whereas $\frac{1}{2} < w \leq 1$ mixes S_2 with an equal mixture of S_0 and S_1 . It, thus, provides a means of obtaining both single and double excitation energies. Ensembles of the form proposed for $w \leq \frac{1}{2}$ were recently used by one of the authors to obtain accurate singlet–singlet excitation energies of small molecules, using SEGKS together with standard density functional approximations.⁶⁰

Figure 3 shows results for excitations of HCN (top) and C_2 (bottom), the latter of which has very small gaps and a degenerate

FIG. 3. Energies (in eV) for mixtures of singlet excitations for HCN (top) and C_2 (bottom). The Ω values show extrapolated excitation energies in the different approaches, using the same colors and order as the legend.

HOMO, which we treat here as non-degenerate by breaking spatial symmetry (equivalent to applying an infinitesimal electric field in a direction perpendicular to the bond). In both cases, we see that diag outperforms 1-RDM for all values of w , with the diagonal approximation being nearly exact for HCN but a little poorer for double excitations of C_2 . SEGKS once again slightly out-performs 1-RDM, but is worse than diag. For HCN, the curvature is rather small compared to the overall energy, whereas for C_2 , it is significant.

Note that the categorization of S_0 , S_1 , and S_2 here is based on pure state orbital ordering, not energies. For C_2 in the exchange-only (and non-degenerate) approximation, the order is reversed, as seen by the negative energies in the figure. Further note that the nature of the ensemble used for these calculations changes discontinuously at $w = \frac{1}{2}$, at which point the second excited state is introduced. This leads to derivative discontinuities for properties that depend on w ; in our plots, this is revealed via discontinuities in the exact and approximate energies at $w = \frac{1}{2}$.

The abovementioned ensembles can be used further to estimate excitation gaps. This is performed via extrapolation, by using a quadratic fit to the energy to approximate the energy of a desired excited pure state.^{38,60} The energy, E_{S_0} , of the ground state S_0 is found by setting $w = 0$. We extrapolate results for $w \leq \frac{1}{2}$ to $w = 1$ to obtain the energy, E_{S_1} , of the S_1 state and extrapolate $\frac{1}{2} \leq w < 1$ to $w = 2$ to obtain the energy, E_{S_2} , of S_2 . The excitation energies, $\Omega_1 = E_{S_1} - E_{S_0}$ and $\Omega_2 = E_{S_2} - E_{S_0}$, are included in the curves, for each method. Keep in mind that these values are rather poor, due to our choice to use an exchange-only approximation that completely neglects any correlations. For this reason, we do not include exact values but rather

compare against the exchange-only benchmark value provided by EGKS theory.

Because the energy functional employed in all calculations reported here is the same, differences between approximations and with exact theories come from the orbitals. Thus, to further understand differences between the approximations, we show, in Fig. 4, the highest occupied and lowest unoccupied molecular orbital densities (HOMO and LUMO, h and l) of C_2 under the two approximations and in exact EGKS. We set $w = 1$ to obtain an equal mixing of S_0 , S_1 , and S_2 . The top panel shows contours (10^{-4} and 10^{-2}) of angular integrals, $\rho(z, r) = \frac{1}{2\pi} \int_0^{2\pi} \rho(r) d\theta$, while the bottom panel shows $\rho(z) = 2\pi \int_0^\infty r \rho(z, r) dr$.

It is clear that the diagonal approximation yields better densities than the 1-RDM, as expected from the better energies. What is interesting is that neither approximation manages to shift sufficient charge from outside the molecule to the bond, in the HOMO. This can be seen best by comparing the approximations against exact EGKS for $z \approx 0$, in the bottom panel. The diag does a better, albeit imperfect, job than the 1-RDM. The failure of the diag approximation suggests that GI effects can be quite complicated and non-local, since the only assumption in the diag approximation is that different orbitals do not couple together via $\hat{w}_i$ and $\epsilon_{i \neq j}$.

Finally, we turn to a rare example where the diag approximation is higher in energy than the 1-RDM: the first singlet-excitation of Be. Figure 5 shows the errors of the diag and 1-RDM approximations for the same excitation process as in Fig. 3. Here, the broken symmetry leads to a unique $2s2p_z$ singlet state, which we mix with a $2p_z^2$ doubly excited state by taking advantage of generalized ensemble theorems again.³⁸

When the amount of S_0 and S_1 is approximately equal ($w \rightarrow \frac{1}{2}$), the 1-RDM approximation is actually better than the diag, although it is worth noting that both approximations are within a few kcal/mol of the exact theory. Once S_2 is mixed in, this discrepancy disappears. Although surprising, such a result is not in contradiction to theory, since the diagonal approximation is not a guaranteed lower bound to the 1-RDM approximation. However, as expected

FIG. 4. HOMO and LUMO densities for C_2 . We retain the colors of previous figures (1-RDM in teal, diag in orange, and EGKS in navy) for the HOMO. LUMO are colored as cyan (1-RDM), red (diag), and blue (EGKS). In the lower panel, we also change the line styles (to dots, dashes, and solid, respectively) to improve clarity.

FIG. 5. Energy errors (eV) for singlet excitations of Be. The EGKS error is zero, by definition.

from the improved physics in the diag approximation, this was the only case where it was not a lower bound in practice. We speculate that it might be caused by an increased breaking of spatial symmetry in 1-RDM compared to diag.

V. CONCLUSIONS

To conclude, we showed that ensemble KS and generalized KS theories can be unified rigorously into EGKS theory—a *good* result. However, in doing so directly, one must optimize an energy functional [Eq. (13)] that is not expressible as a 1-RDM functional and, thus, not amenable to a standard GKS treatment—a *bad* result. We then showed that solutions to EGKS can be defined in its usual operator form [Eq. (16)], provided an orbital-dependent correction term is introduced to the GKS solutions for a small number of “frontier” orbitals that contribute “ghost interactions”—an *ugly* result. Still, the ghost interaction term can be dealt with via a “diagonal approximation” (Sec. III C) that is reasonably accurate and more amenable to efficient evaluation.

The approach was demonstrated on several analytical and numerical examples based on exchange-only approximations. The diagonal approximation was shown to successfully reproduce exact results (within an exchange-only formalism) and to consistently outperform a simpler 1-RDM approximation, except in one notable case. Our work, thus, demonstrates that not only is ensemble density functional theory formally amenable to a generalized Kohn–Sham framework but also the approach is both practical and advantageous.

Table I and Figs. 1–3 illustrate that both EGKS theory (relative to unrestricted Hartree–Fock) and the diagonal approximation are much better for the two doublet cases than for other cases. We suspect that this reflects the fact that, in doublets, only one electron (h) needs a GI correction, which is, therefore, easier to approximate than the other cases, which require that two electrons (h and l) be corrected. The general conditions under which the 1-RDM and/or diag approximations perform well should be scrutinized. Whether successes come from a relative lack of GI errors or a cancellation of GI errors should also be investigated.

It would also be useful to study and develop GKS theory for thermal EDFT⁶¹ in both infinite and finite bases. The finite basis case represents a more complex version of the problems discussed here and is amenable to present theory. However, the nature of thermal ensembles means that *every* excitation (plus promotion/removal of electrons, in the grand canonical case) is included in the ensemble, yielding $F_{ij}^l \neq f_i f_j \forall i, j$. Thus, all orbitals form part of $\mathbb{F}$,

and each requires its own GKS equation within the present framework. Whether the 1-RDM and diag approximation work well for such cases should be investigated.

Finally, recent work has shown that any hybrid approximation, $E_{\text{Hxc}} = E_H + \alpha E_x + (1 - \alpha) E_x^{\text{DFA}} + E_c^{\text{DFA}}$ (or range-separated variants), can be “enslaved,” by setting $E_{\text{Hxc}} = E_H + \alpha E_x + (1 - \alpha) E_x^{\text{DFA}} + E_c^{\text{DFA}}$,⁵⁹ and is, thus, amenable to the rigorous EGKS theory introduced here. Here, DFA stands for any standard density functional approximation, and $E_x^{\text{DFA}}/E_c^{\text{DFA}}$ are appropriate weighted averages. Furthermore, such functionals can out-perform time-dependent DFT using simplified EGKS schemes.⁶⁰ Logical next steps are, thus, to derive the equivalent of the diagonal approximation for general hybrid theories and to seek better ways of solving the exact theory. This is especially important since most previously evaluated gaps were overestimated,⁶⁰ suggesting that a full or better treatment of EGKS will improve results. Further work is ongoing.

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APPENDIX: PAIR-COEFFICIENTS

The appendix first derives pair-coefficients for the common ensembles and pure states considered in this work, including which orbitals belong to the double occupied space, $\mathbb{D}$, and the frontier space, $\mathbb{F}$. It then shows how these coefficients combine linearly to produce general ensemble formulae.

1. Pair-coefficients for singlet ground states

A singlet ground state represents a pure state,

$$\hat{S}_0 = |S_0\rangle\langle S_0| = |1^2 2^2 \dots h^2\rangle\langle 1^2 2^2 \dots h^2|, \quad (\text{A1})$$

in which all orbitals are doubly occupied or unoccupied. Thus, one trivially finds $f_i = 2$, $\forall i \leq h$ and

$$F_{ij}^l = f_i f_j = 4, \quad F_{ij}^K = -\frac{1}{2} f_i f_j = -2, \quad (\text{A2})$$

for the pair-coefficients. These systems, therefore, have no ghost interactions. All occupied orbitals, thus, belong to the doubly occupied space, $\mathbb{D} = \{i \leq h\}$, and the frontier space, $\mathbb{F} = \{\}$, is empty. Any coefficients not specified here, or in the remainder of the appendix, are zero.

2. Pair-coefficients for doublets

The next simplest ground state is a doublet, in which all electrons are paired except one, i.e., the state is $|1^2 2^2 \dots h^1\rangle$ or $\uparrow \rightarrow \downarrow$. Since our ensemble formalism treats all electrons in the same effective potential, these two states are degenerate (not so in unrestricted Hartree–Fock theory). The relevant ensemble is, thus,

$$\hat{D}_0 = \frac{1}{2} \left[|1^2 2^2 \dots h^1\rangle\langle 1^2 2^2 \dots h^1| + |1^2 2^2 \dots h^1\rangle\langle 1^2 2^2 \dots h^1| \right]. \quad (\text{A3})$$

We may, without any loss of generality, evaluate the density of the $\uparrow$ state to obtain the coefficients $f_{i<h} = 2$ and $f_h = 1$. The Hartree-Fock energy,

$$E_{\text{HX}}^D = \frac{1}{2} \sum_{i,j<h} [4(ij|ij) - 2(ij|ji)] + \frac{1}{2} \sum_{i<h} 2[2(ih|ih) - (ih|hi)], \quad (\text{A4})$$

then yields the pair-coefficients, which are

$$F_{ij}^I = -2F_{ij}^K = \begin{cases} f_{ij}, & i < h \text{ or } j < h, \\ 0, & i = j = h. \end{cases} \quad (\text{A5})$$

Thus, we see that most terms are in the usual product form, with only the hh term being different. For the purposes of EGKS calculations, $\mathbb{D} = \{i < h\}$ and $\mathbb{F} = \{h\}$, i.e., the doubly occupied orbitals are $i < h$ and the frontier orbital is h .

3. Pair-coefficients for triplets

An important property of most ensembles (including all we consider here) is that the KS pair-density, and, consequently, its pair-coefficients, must be independent of certain spin-properties of the system. This result follows from the fluctuation-dissipation theorem.⁵⁹ Thus, for the triplet state ensemble,

$$\hat{T}_0 = \frac{1}{3} \sum_{M_z \in \{-1, 0, 1\}} |T_{0,M_z}\rangle \langle T_{0,M_z}|. \quad (\text{A6})$$

We may pick any of the three triplet states to evaluate the pair-coefficients. Taking the $M_z = 1$ state, $|T_{0,1}\rangle = |1^2 2^2 \dots h^\uparrow l^\uparrow\rangle$, gives $f_{i<h} = 2, f_h = 1$. The Hartree-Fock energy for this state is

$$E_{\text{HX}}^{T_0} = \frac{1}{2} \sum_{ij} f_{ij} f_j (ij|ij) - \frac{1}{2} \sum_{ij \leq l} (ij|ji) - \frac{1}{2} \sum_{ij < h} (ij|ji), \quad (\text{A7})$$

where the first term is the Hartree energy and the second and third terms are the exchange of up and down electrons, respectively.

It is readily seen that, for $i, j < h$, we obtain $F_{ij}^I = f_{ij}$ and $F_{ij}^K = -2F_{ij}^I$, a result that also holds for ih, il, hi , and li , provided $i < h$. For the remaining states, we obtain

$$F_{fg}^I = -F_{fg}^K = 1, \quad \forall f, g \in \{h, l\}. \quad (\text{A8})$$

Thus, we again have only a small number of combinations of i and j for which $F_{ij}^I \neq -2F_{ij}^K \neq f_{ij}$ and, thus, contribute to the ghost interaction term. Thus, $\mathbb{D} = \{i < h\}$ and $\mathbb{F} = \{h, l\}$.

4. Pair-coefficients for singlet excitations

In this work, we consider single and double excitations, from h to l . The single excitation is represented by a state $|S_1\rangle = [1^2 2^2 \dots h^\uparrow l^\downarrow + 1^2 2^2 \dots h^\downarrow l^\uparrow]/\sqrt{2}$ and ensemble $\hat{S}_1 = |S_1\rangle \langle S_1|$. Application of the Slater-Condon rules yields

$$E_{\text{HX}}^{S_1} = E_{\text{HX}}^{T_0} + 2(hl|lh), \quad (\text{A9})$$

using results for the triplet state. Thus, $F_{ij}^I = f_{ij}$ and $F_{ij}^K = -2F_{ij}^I$, whenever $i < h$ or $j < h$, and

$$F_{fg}^I = F_{fg}^K = 1 - \delta_{fg}, \quad \forall f, g \in \{h, l\}. \quad (\text{A10})$$

Again, $\mathbb{D} = \{i < h\}$ and $\mathbb{F} = \{h, l\}$.

The double excitation is easier to treat, being in the form of a singlet state, $\hat{S}_2 = |S_2\rangle \langle S_2|$ and $|S_2\rangle = [1^2 2^2 \dots h^0 l^2]$. Thus, $f_i = 2, \forall i < h, f_h = 0$, and $f_l = 1$, and

$$F_{ij}^I = f_{ij} = 4, \quad F_{ij}^K = -\frac{1}{2}f_{ij} = -2, \quad (\text{A11})$$

for the pair-coefficients. Here, $\mathbb{D} = \{i < h, l\}$, and $\mathbb{F} = \{l\}$ is empty.

5. Pair-coefficients for general ensembles

Finally, we note that the piecewise linearity of ensembles also leads to piecewise linearity of pair-coefficients, provided one starts from an appropriate starting point, like those derived in previous sections.

Thus, for a general ensemble,

$$\hat{\Gamma}^w = \sum_{\kappa} w_{\kappa} \hat{\Gamma}_{\kappa}, \quad (\text{A12})$$

we obtain the general result $f_i = \sum_{\kappa} w_{\kappa} f_i^{\kappa}$, and

$$F_{ij}^{I,w} = \sum_{\kappa} w_{\kappa} F_{ij}^{I,\kappa}, \quad F_{ij}^{K,w} = \sum_{\kappa} w_{\kappa} F_{ij}^{K,\kappa}. \quad (\text{A13})$$

Importantly, if either $i \in \mathbb{D}$ or $j \in \mathbb{D}$ in *all* members of the ensemble, then, consequently, $F_{ij}^{I,w} = f_{ij}$ and $F_{ij}^{K,w} = -\frac{1}{2}f_{ij}$. If, however, both $i \in \mathbb{F}$ and $j \in \mathbb{F}$ (including $i = j$) in *any* member, κ , then the product form is no longer guaranteed.

For example, the fractional cation, Li^{+q} , is formed as $\hat{\Gamma} = q\hat{\Gamma}_{\text{Li}^+} + (1-q)\hat{\Gamma}_{\text{Li}}$, in terms of a singlet cation and doublet neutral atom. We, therefore, obtain $f_{1s} = 2, f_{2s} = q \times 0 + (1-q) \times 1 = 1-q$, and

$$\begin{aligned} F_{1s1s}^I &= -2F_{1s1s}^K = 4, \\ F_{1s2s}^I &= -2F_{1s2s}^K = 2(1-q) = F_{2s1s}^I = -2F_{2s1s}^K, \\ F_{2s2s}^I &= -2F_{2s2s}^K = 0. \end{aligned}$$

The fractional anion Li^{-q} is formed on $\hat{\Gamma} = q\hat{\Gamma}_{\text{Li}^-} + (1-q)\hat{\Gamma}_{\text{Li}}$, yielding $f_{1s} = 2, f_{2s} = q \times 2 + (1-q) \times 1 = 1+q$, and

$$\begin{aligned} F_{1s1s}^I &= -2F_{1s1s}^K = 4, \\ F_{1s2s}^I &= -2F_{1s2s}^K = 2(1-q) = F_{2s1s}^I = -2F_{2s1s}^K, \\ F_{2s2s}^I &= q \times 4 + (1-q) \times 0 = 4q, \\ F_{2s2s}^K &= q \times -2 + (1-q) \times 0 = -2q. \end{aligned}$$

In both cases, the $1s$ is always doubly occupied, so any term involving it has the product form. The $2s2s$ terms do differ from their product form. Thus, both cases have the same doubly occupied ($1s$) and frontier orbitals ($2s$). Sodium would have the same general form, except with more doubly occupied orbitals ($1s, 2s$, and $2p_{x,y,z}$) and a different frontier orbital ($3s$).

For mixtures, $\hat{\Gamma} = (1-w)\hat{\Gamma}_{S_0} + w\hat{\Gamma}_{T_0}$, or the lowest singlet and triplet state, we can use (A2) and (A8) to obtain $f_{i<h} = 2, f_h = \frac{3(1-w)}{2}$, and $f_l = \frac{1+3w}{2}$, for the occupation factors. The non-product pair-coefficients can be shown to be

$$F_{fg}^I = \begin{cases} 0, & hh, ll \\ w, & hl, lh, \end{cases} \quad F_{fg}^K = \begin{cases} 0, & hh, ll \\ -w, & hl, lh. \end{cases} \quad (\text{A14})$$

Here, $\mathbb{D} = \{i < h\}$ and $\mathbb{F} = \{h, l\}$.

A more complex example is the mixture of S_0 , S_1 , and S_2 used for the final figures, with $\hat{\Gamma} = \frac{1-w}{2} [|S_0\rangle\langle S_0| + |S_1\rangle\langle S_1|] + w|S_2\rangle\langle S_2|$. Combining results from Eqs. (A2), (A10), and (A11) gives $f_{i<h} = 2$, $f_h = \frac{3(1-w)}{2}$, and $f_l = \frac{1+3w}{2}$, for the occupation factors. The non-product pair-coefficients can be shown to be

$$F_{fg}^I = \begin{cases} \frac{5(1-w)}{2}, & hh, \\ \frac{(1+7w)}{2}, & ll, \\ 0, & hl, lh, \end{cases} \quad F_{fg}^K = \begin{cases} -(1-w), & hh, \\ -2w, & ll, \\ \frac{(1-w)}{2}, & hl, lh. \end{cases} \quad (\text{A15})$$

Once again, $\mathbb{D} = \{i < h\}$ and $\mathbb{F} = \{h, l\}$.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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