Ensemble generalized Kohn-Sham theory: the good, the bad, and the ugly

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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, e.g., open systems and excited states. Here, we combine the two extensions, both formally and practically, first via an exact yet complicated formalism, 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.

I. INTRODUCTION

Kohn-Sham[1,2] (KS) density functional theory (DFT) has proven to be an indispensable tool for 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 reflcts three useful properties of hybrids: first, the inclusion of exact Fermionic exchange allows for a systematically higher predictive accuracy;[15] second, this is done in a numerically straightforward fashion, whereas use of Fock exchange within "pure" KS theory must rely on difficult to calculate optimized effective potentials (OEPs);[16–21] third, the non-multplicative 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, and 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] Excited-state EDFT,[28,33,35–59] In particular, it has attracted significant recent attention as a route to low cost prediction of charge transfer[40,56] and double[40,50,53] excitations, which are hard to predict using traditional time-dependent KS theory.

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.[54,59] 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,

$$\mathcal{F}^{\lambda}[n,\mathbf{w}] = \min_{\hat{\Gamma}_{\mathbf{w}}\to n} \text{Tr}[(\hat{T}+\lambda\hat{W})\hat{\Gamma}_{\mathbf{w}}] \;, \tag{1}$$

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 energy operator. The ensemble density matrix, $\hat{\Gamma}_{\mathbf{w}} = \sum_{\kappa} w_{\kappa}|\kappa\rangle\langle\kappa|$, involves a weighted sum over orthonormal wave functions $|\kappa\rangle$. $\hat{\Gamma}_{\mathbf{w}} \to n$ is short-hand for $\text{Tr}[\hat{n}(\boldsymbol{r})\hat{\Gamma}_{\mathbf{w}}] = n(\boldsymbol{r})$, where $\hat{n}(\boldsymbol{r})$ 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[52,55,57], specifically the KS kinetic energy ($\mathcal{T}_s$), Hartree-exchange (Hx), and correlation (c), functionals, respectively:

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

$$\mathcal{E}_{\rm Hx}[n,\mathbf{w}] = \lim_{\lambda\to 0^+} \frac{\mathcal{F}^\lambda[n,\mathbf{w}] - \mathcal{T}_s[n,\mathbf{w}]}{\lambda} \ , \tag{3}$$

$$\mathcal{E}_{\rm c}[n,\mathbf{w}] = \mathcal{F}^1[n,\mathbf{w}] - \mathcal{T}_s[n,\mathbf{w}] - \mathcal{E}_{\rm Hx}[n,\mathbf{w}] \ . \tag{4}$$

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

It has recently been shown that $\mathcal{T}_s[n,\mathbf{w}] \equiv {\rm Tr}[\hat{\Gamma}_{s,\mathbf{w}}\hat{T}]$ and $\mathcal{E}_{\rm Hx}[n,\mathbf{w}] \equiv {\rm Tr}[\hat{\Gamma}_{s,\mathbf{w}}\hat{W}]$,[55] for some non-interacting ensemble density matrix $\hat{\Gamma}_{s,\mathbf{w}}$, which is formed on configuration state functions. $\mathcal{T}_s$ and $\mathcal{E}_{\rm Hx}$ are thereby functionals of a set of orbitals, $\{\phi\}$:

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

$$\mathcal{E}_{\rm Hx}[\{\phi\}] = \tfrac{1}{2}\sum_{ij} \left\{ F_{ij}^{J,\mathbf{w}}(ij|ij)_\phi^W + F_{ij}^{K,\mathbf{w}}(ij|ji)_\phi^W \right\} \ , \tag{6}$$

involving electron-repulsion integrals $(ij|kl)_\phi^W = \int d\boldsymbol{r}d\boldsymbol{r}'$ $W(\boldsymbol{r},\boldsymbol{r}')\phi_i^*(\boldsymbol{r})\phi_j(\boldsymbol{r}')\phi_k(\boldsymbol{r})\phi_l^*(\boldsymbol{r}')$ with $W = \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}$.[60] The coefficients $f_i^{\mathbf{w}} \in [0,2]$ are average occupancies of orbitals i across the ensemble. The pair-coefficients, $F_{ij}^{J,\mathbf{w}}$ and $F_{ij}^{K,\mathbf{w}}$, encode all information about the non-interacting ensemble and are ensemble-specific. They are more complicated to obtain – some examples are provided in appendix A. Importantly, these pair-coefficients are not necessarily (scaled) products of $f_i^{\mathbf{w}}$, i.e., generally $F_{ij}^J \neq -2F_{ij}^K \neq f_j f_j$. Recent work has used the fluctuation-dissipation theorem to show that separated $\mathcal{E}_{\rm H}$ and $\mathcal{E}_{\rm x}$ also yield functionals of similar form to Eq. (6).[58] For pedagogical simplicity we shall not consider the separated terms further.

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

$$\{\hat{t} + v + v_{\rm Hxc}[n,\mathbf{w}]\}\phi_i[n,\mathbf{w}] = \epsilon_i[n,\mathbf{w}]\phi_i[n,\mathbf{w}] \ . \tag{7}$$

Here, $v_{\rm Hxc}[n,\mathbf{w}] = \frac{\delta\mathcal{E}_{\rm Hx}[n,\mathbf{w}]}{\delta n} + \frac{\delta\mathcal{E}_{\rm c}[n,\mathbf{w}]}{\delta n}$ is the multiplicative Hxc effective potential of EKS theory, and v is the external potential.[36] The effective potential, $v_s := v + v_{\rm Hxc}$, 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 el[11] rigorously showed that the usual KS equation can be modified to include a non-local operator $\hat{v}_S$, which is usually of Hartree-Fock-like form, without changing the fundamental properties of density functionals. The generalized KS equation,

$$[\hat{t} + v + \hat{v}_S + v_R[n]]\varphi_i[n] = \varepsilon_i[n]\varphi_i[n] \ , \tag{8}$$

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

The existence of the GKS equation is deduced by defining: $S[n] = \min_{\{\varphi\}\to n} S[\{\varphi\}]$, 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 ($w_0 = 1, w_{\kappa\neq 0} = 0$). Then, the ground-state energy, $E_0 = \min_n\{S[n] + R_S[n] + V[n]\} = \min_{\{\varphi\}}\{S[\{\varphi\}] + R_s[n_\varphi] + V[n_\varphi]\}$, is minimized for the density $n \equiv n_\varphi \equiv n_0$. Uniqueness (in non-degenerate systems) follows from the *external* potential v being uniquely defined by the ground state density n_0. Here $V[n] = \int d\boldsymbol{r} n(\boldsymbol{r})v(\boldsymbol{r})$ 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), $\gamma_1(\boldsymbol{r},\boldsymbol{r}') = \sum_{i\sigma\in{\rm occ}} \varphi_{i\sigma}^*(\boldsymbol{r})\varphi_{i\sigma}(\boldsymbol{r}')$. This includes all Hartree-Fock-like expressions, $S[\{\varphi\}] := \langle\Phi|\hat{T} + \hat{W}_S|\Phi\rangle$, where Φ is a Slater determinant formed from $\{\varphi\}$, and $\hat{W}_S$ is a (modified) interaction term involving interactions of form $0 < W_S(|\boldsymbol{r}-\boldsymbol{r}'|) \leq W(|\boldsymbol{r}-\boldsymbol{r}'|)$, which can be a simple fraction $W_S = \alpha W$ of the full interaction term, or a more complex range-separated [8,61] expression.[12,62] Then,

$$\begin{aligned} S[\gamma_1] \equiv & \int -\tfrac{1}{2}\nabla^2\gamma_1(\boldsymbol{r},\boldsymbol{r}')|_{\boldsymbol{r}=\boldsymbol{r}'} d\boldsymbol{r} \\ & + \int W_S(\boldsymbol{r},\boldsymbol{r}')\big[n(\boldsymbol{r})n(\boldsymbol{r}') - \tfrac{1}{2}\big|\gamma_1(\boldsymbol{r},\boldsymbol{r}')\big|^2\big] \tfrac{d\boldsymbol{r}d\boldsymbol{r}'}{2} \ . \end{aligned} \tag{9}$$

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 recognise that Eq. (9) can also accept more general 1-RDMs,

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

in which $f_i \in [0,2]$ can be non-integer [note, $n(\boldsymbol{r}) = \gamma_1(\boldsymbol{r},\boldsymbol{r})$]. Such 1-RDMs appear naturally in ensemble theories, e.g., the 1-RDM for a lithium cation with a partial charge $+q$ is $\gamma_1(\boldsymbol{r},\boldsymbol{r}') = 2\varphi_{1s}^*(\boldsymbol{r})\varphi_{1s}(\boldsymbol{r}') + (1-q)\varphi_{2s}^*(\boldsymbol{r})\varphi_{2s}(\boldsymbol{r}')$. 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 Eq. (9) 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, $\frac{\delta R_S}{\delta\varphi^*} := \frac{\delta E_R}{\delta n}\frac{\delta n}{\delta\varphi_i^*} \equiv f_i v_R\varphi_i$, and normalisation 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 ensemblized version of Eq. (9) is $\mathcal{S}^e[\{\varphi\},\mathbf{w}] := \mathcal{T}_s[\{\varphi\},\mathbf{w}] + \mathcal{E}_{\text{Hx},S}[\{\varphi\},\mathbf{w}]$, which uses the ensemble functionals given in Eqs. (5) and (6) [but with $W \to W_S$ in (6)]. We define the ensemble density functionals,

$$\mathcal{S}^e[n,\mathbf{w}] := \min_{\{\varphi\}\to n} \mathcal{S}^e[\{\varphi\},\mathbf{w}], \tag{11}$$

$$\mathcal{R}^e_S[n,\mathbf{w}] :=\mathcal{F}^1[n,\mathbf{w}] - \mathcal{S}^e[n,\mathbf{w}], \tag{12}$$

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

Eq. (11) is maximally free[55] of "ghost-interactions" (GI), namely spurious interactions between electrons and their counterparts in different ensemble members[63] 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, $S[\gamma_1^{\mathbf{w}}]$ of (9) generally exhibits GI errors[63]. Therefore, it has intrinsic positive energy errors even at the exact Hartree-exchange level, and is inconsistent with Eq. (6).

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

$$\begin{aligned}\mathcal{S}^{\text{GI}}[\{\varphi\},\mathbf{w}] :=& \tfrac{1}{2}\sum_{ij} \big[(F^{J,\mathbf{w}}_{ij} - f^{\mathbf{w}}_i f^{\mathbf{w}}_j)(ij|ij)^{W_S}_{\varphi} \\ &+ (F^{K,\mathbf{w}}_{ij} + \tfrac{1}{2} f^{\mathbf{w}}_i f^{\mathbf{w}}_j)(ij|ji)^{W_S}_{\varphi}\big] \ .\end{aligned} \tag{13}$$

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

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

$$\mathcal{C} =\mathcal{S}^e[\{\varphi\}] + \mathcal{R}^e_S[n] - \sum_{ij} f_i \varepsilon_{ij} \Big[\int \varphi_i^* \varphi_j d\boldsymbol{r} - \delta_{ij}\Big] \tag{14}$$

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

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

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

$$\hat{h}_i \varphi_i \equiv \{\hat{t} + v + \hat{v}^e_{S,i} + v^e_R\} \varphi_i = \sum_j \varepsilon_{ij} \varphi_j \ , \tag{16}$$

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

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

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., $\varepsilon_{ij}[\int \varphi_i^* \varphi_j d\boldsymbol{r} - \delta_{ij}]$, with $\varepsilon_{ij} = \varepsilon_{ji}^*$).

Let us now consider (16) in the titular framework. A solution provably exists and may thus, formally, be found. In this sense (16) is a *good* result. But 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 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 existing approaches [using Eq. (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, $S[\gamma_1^{\mathbf{w}}]$ lends itself to standard GKS treatment. We therefore "generalize" the KS formalism on this term separately from the difficult, $\mathcal{S}^{\text{GI}}$ [Eq. (13)]. The total energy may be written as,

$$\mathcal{E}[\{\varphi\}] =S[\gamma_1] + \mathcal{S}^{\text{GI}}[\{\varphi\}] + \mathcal{R}^e_S[n] + V[n] \ . \tag{18}$$

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

$$\hat{v}^e_{S,i}\varphi_i = \hat{v}_S\varphi_i + \frac{\delta\mathcal{S}^{\rm GI}[\{\varphi\}]}{f_i\delta\varphi_i^*} := \{\hat{v}_S + \hat{v}_i^{\rm GI}\}\varphi_i \, . \tag{19}$$

Here,

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

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 recognise that $\Delta F^J_{ij} = F^J_{ij} - f_i f_j$ and $\Delta F^K_{ij} = F^K_{ij} + \frac{1}{2}f_i f_j$ are zero for *almost* all combinations of i and j in all common types of ensembles, per Appendix A. Therefore, $\frac{\delta\mathcal{S}^{\rm GI}}{\delta\phi_i^*}$ 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 recognising that

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

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

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

$$\hat{h}_{\text{1-RDM}}\varphi_i = \varepsilon_i\varphi_i + \sum_{j\in\mathbb{F}}\bar{\omega}_j\varphi_j \, , \qquad i\in\mathbb{D} \tag{22}$$

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

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

$$\begin{aligned}\hat{v}_i\varphi_i =& \sum_j \frac{\Delta F^J_{ij}}{f_i}\int \frac{n_j(\boldsymbol{r}')d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|}\varphi_i(\boldsymbol{r}) \\ &+ \sum_j \frac{\Delta F^K_{ij}}{f_i}\int \frac{\varphi_j^*(\boldsymbol{r}')\varphi_i(\boldsymbol{r}')d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|}\varphi_j(\boldsymbol{r}) \, ,\end{aligned} \tag{24}$$

Simultaneously solving Eqs. (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),(23) is difficult in general, and cannot be trivially done using standard iterative approaches to GKS theory implemented in quantum chemistry codes. We thus 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 $\hat{v}_i^{\rm GI}$ is of little consequence to the obtained EGKS orbitals so can be set to zero. We therefore introduce the "1-RDM" approximation, in which the orbitals $\{\varphi\}_{\text{1-RDM}}$ are found using:

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

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 Li^{+q} example in Section IV. Nonetheless, it is a decent approximation in some cases, such as for the cation of HCN (shown later in Figure 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,

$$\hat{h}_{\text{1-RDM}}\varphi_i^{\rm diag} = \varepsilon_i^{\rm diag}\varphi_i^{\rm diag} \, , \qquad i\in\mathbb{D} \, , \tag{26}$$

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

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 orthogonalisation and need to solve multiple equations nonetheless makes 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 $\varphi_i \to \boldsymbol{C}_i$ are the orbitals and $\gamma_1 = \sum_i f_i\varphi_i^*(\boldsymbol{r})\varphi_i(\boldsymbol{r}') \to \boldsymbol{D} = \sum_i f_i\boldsymbol{C}_i\boldsymbol{C}_i^T$ is the 1-RDM. Then, $\hat{h}_{\text{1-RDM}}[\gamma_1] \to \boldsymbol{F}_{\text{1-RDM}}[\boldsymbol{D}]$ and $\hat{v}_i^{\rm GI}[\{\varphi\}_i] \to \boldsymbol{V}[\{\boldsymbol{C}_i\}]_i^{\rm GI}$ are symmetric matrix representations of effective Hamiltonian terms, expressed in the basis. We also introduce $\boldsymbol{S}$ as the $M\times M$ overlap matrix of our basis, to deal with non-orthogonal choices.

For both approximations we first solve,

$$\boldsymbol{F}_{\text{1-RDM}}\boldsymbol{C}_i^{\text{1-RDM}} = \varepsilon_i\boldsymbol{S}\boldsymbol{C}_i^{\text{1-RDM}} \tag{28}$$

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

To solve for $\boldsymbol{C}_{i\in\mathbb{F}}^{\text{diag}}$ 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 $\boldsymbol{P}^i = [\boldsymbol{C}_i^{\text{1-RDM}}, \boldsymbol{C}_{i+1}^{\text{1-RDM}}, \cdots]$ (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 diagonalise,

$$\boldsymbol{P}^{i,T}\{\boldsymbol{F}_{\text{1-RDM}} + \boldsymbol{V}_i^{\text{GI}}\}\boldsymbol{P}^i\boldsymbol{x}_k = \varepsilon_k^i\boldsymbol{x}_k \ , \tag{29}$$

to obtain $\boldsymbol{C}_k^i := \boldsymbol{P}^i\boldsymbol{x}_k$, ordered for $k \geq 1$. Then, $\boldsymbol{C}_i^{\text{diag}} := \boldsymbol{C}_{k=1}^i$ is the next orbital for the diagonal approximation. We then set $\boldsymbol{P}^{i+1} = [\boldsymbol{C}_2^i, \boldsymbol{C}_3^i, \cdots]$ 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 $\boldsymbol{F}_{\text{1-RDM}}[\boldsymbol{D}^{\text{diag}}]$ and $\boldsymbol{V}_i^{\text{GI}}[\{\boldsymbol{C}_i^{\text{diag}}\}]$; and then use the new matrices to repeat the process starting from Eq. (28).

The approach thus gives us a set of orbitals, $\boldsymbol{C}_i^{\text{diag}}$ that are guaranteed to be orthogonal to one another. Furthermore, the use of $\hat{v}_i^{\text{GI}}$ in the effective Hamiltonian for $\boldsymbol{C}_i^{\text{diag}}$ means that they, *prima facie*, have the correct asymptotics,[64] unlike the 1-RDM solutions. They may thus be expected to be better approximations to the real solutions. Results (see Section 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, $\boldsymbol{C}_{i\in\mathbb{F}}^{\text{diag}} \neq \boldsymbol{C}_i^{\text{1-RDM}}$, differ from the 1-RDM approximation because they obey different effective Hamiltonians. However, it is also true that the doubly occupied orbitals, $\boldsymbol{C}_{i\in\mathbb{D}}^{\text{diag}} \neq \boldsymbol{C}_i^{\text{1-RDM}}$, are different despite both coming from Eq. (28). The difference comes from different 1-RDMs,the different $\boldsymbol{D}$, $\boldsymbol{D}^{\text{diag}} \neq \boldsymbol{D}^{\text{1-RDM}}$, being used to form $\boldsymbol{F}_{\text{1-RDM}}$.

D. Simplified EGKS theory

We next turn briefly to a less rigorous approximation recently introduced by one of the authors – the "simplified EGKS" (SEGKS) scheme.[59] – that is designed to efficiently approximate the EGKS solution of excited state ensembles. This approximation is based on an ansatz, $\boldsymbol{F} \approx (1-\mu)\boldsymbol{F}_{\text{gs}} + \mu\boldsymbol{F}_{h\to l}$, for the Fock matrix that interpolates between the ground state Fock matrix, $\boldsymbol{F}_{\text{gs}}$, and a different Fock matrix, $\boldsymbol{F}_{h\to l}$, formed by double promotion of the HOMO to the LUMO.

This physical intuition behind this ansatz is the idea that $\boldsymbol{F}_{\text{gs}}$ screens the HOMO more than the LUMO, whereas $\boldsymbol{F}_{h\to l}$ does the reverse which gives the model sufficient flexbility to optimize the orbitals. The precise amount of linear of mixing is found by seeking, μ^s, for which the resulting orbitals, $\boldsymbol{C}_i^s$, 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, $\boldsymbol{C}_i^o$, that minimize Eq. (18), to provide the best possible energy, $\mathcal{E}^o := \mathcal{E}[\{\boldsymbol{C}_i^o\}] \leq \mathcal{E}[\{\boldsymbol{C}_i\}]$ within the given finite basis. In all tested cases we found that $\boldsymbol{C}_i^{\text{diag}}$ forms a good starting point for finding $\boldsymbol{C}_i^o$, in the sense that we may write, $\boldsymbol{C}_i^o = \sum_j U_{ij}\boldsymbol{C}_j^{\text{diag}}$, where the unitary matrix $\boldsymbol{U}$ (in our finite basis) is nearly an identity. Consequently, we may write, $\boldsymbol{U} \approx \prod_{i>j}\boldsymbol{u}_{ij}(\theta_{ij})$ where, $\boldsymbol{u}_{ij}(\theta_{ij})$, are matrices that leave all orbitals unchanged except, $\boldsymbol{C}_i \to \cos(\theta_{ij})\boldsymbol{C}_i - \sin(\theta_{ij})\boldsymbol{C}_j$ and $\boldsymbol{C}_j \to \sin(\theta_{ij})\boldsymbol{C}_i + \cos(\theta_{ij})\boldsymbol{C}_j$.

We are thus able to inefficiently find $\mathcal{E}^o$ by individually minimzing 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 the next section.

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 approximation[55] in EKS theory, i.e., we set $\mathcal{R}^e = 0$, $\mathcal{S}^{\text{1-RDM}} \equiv \mathcal{S}^{\text{HF}}$ and $\mathcal{S}^{\text{GI}} = \mathcal{T}_s + \mathcal{E}_{\text{Hx}} - \mathcal{S}^{\text{HF}}$. 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 $\boldsymbol{C}_{i\uparrow} = \boldsymbol{C}_{i\downarrow}$.

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 thus orbitals), separate from other considerations. These calculations are denoted "exchange-only" throughout, and the underlying orbital approximation (EGKS, diag, 1-RDM or unrestricted Hartree-Fock) are mentioned separately.

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 A) 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 $F^J_{2s2s} = F^K_{2s2s} = 0$ as the only pair-coefficient that contributes to

$$\mathcal{S}^{\rm GI}[\{\varphi\}] := \mathcal{S}^{\rm GI}[\phi_{2s}] = -\frac{f_{2s}^2}{2} E_{\rm H}[n_{2s}]\,. \tag{30}$$

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

$$\lim_{r\to\infty} \hat{v}_S\varphi_{2s} \to \frac{f_{1s} + \frac{f_{2s}}{2}}{r}\varphi_{2s}\frac{2 + \frac{1-q}{2}}{r}\varphi_{2s}\,. \tag{31}$$

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

$$\lim_{r\to\infty} [\hat{v}_S + \hat{v}^{\rm GI}_{2s}]\varphi_{2s} \to \frac{f_{2s}}{r}\varphi_{2s} = \frac{2}{r}\varphi_{2s}\,. \tag{32}$$

Note that we have assumed $\lim_{r\to\infty}\varphi_{1s}(\boldsymbol{r})/\varphi_{2s}(\boldsymbol{r}) = 0$.

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 behaviour in ensembles.[65]. 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.

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 Section III E. All calculations were performed using Gaussian type orbitals in the def2-tzvp basis set,[66] and were implemented in a customized Python3 code using Psi4/numpy.[67,68] Note 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, we can 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.

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

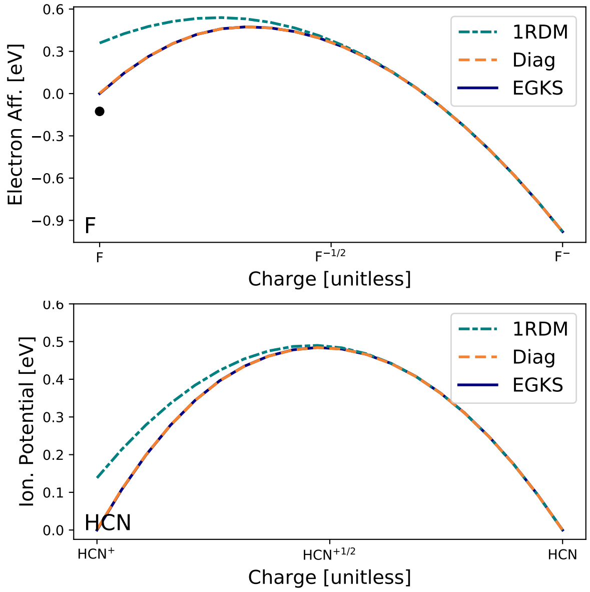

FIG. 1. Fractional anion energy curve of F (top) shown relative to the neutral atom energy of EGKS theory; and fractional cation curve of HCN (bottom), shown relative to a straight line fit between the neutral and cation EGKS results. Here and in subsequent figures we show 1-RDM in teal dash-dots, diag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

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".[69]

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,

$$\hat{\Gamma}_q = \tfrac{1+q}{2}[|\mathrm{F}_\uparrow\rangle\langle\mathrm{F}_\uparrow| + |\mathrm{F}_\downarrow\rangle\langle\mathrm{F}_\downarrow|] - q|\mathrm{F}^-\rangle\langle\mathrm{F}^-| \,, \tag{33}$$

which mixes equal amounts of the ↑ and ↓ 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 Figure 1.

In a correlated theory, this curve should look like a straight line.[22] Exchange-only theory introduces a substantial curvature as a function of charge.[28,70,71] 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 is similar to the top, but for the cation of HCN:

$$\begin{aligned}\hat{\Gamma}_q =& \tfrac{q}{2}[|\mathrm{HCN}^+_\uparrow\rangle\langle\mathrm{HCN}^+_\uparrow| + |\mathrm{HCN}^+_\downarrow\rangle\langle\mathrm{HCN}^+_\downarrow|] \\ &+ (1-q)|\mathrm{HCN}\rangle\langle\mathrm{HCN}| \,. \end{aligned} \tag{34}$$

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 netural system is the closed shell case.

EDFT can also be used to predict excitations energies. This is done 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,

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

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 triplets. Results are shown in Figure 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.[59] In all cases SEGKS outperforms 1-RDM slightly, especially for mid-range weights, but is worse than the diag approximation.

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

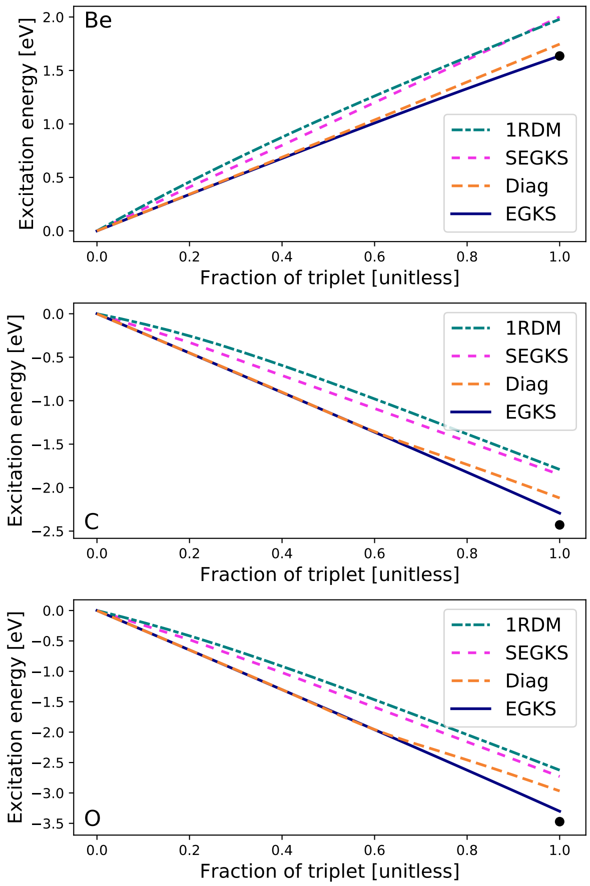

FIG. 2. Energies (in eV) of mixtures of singlet and triplet states for Be (top), C (middle) and O (bottom).

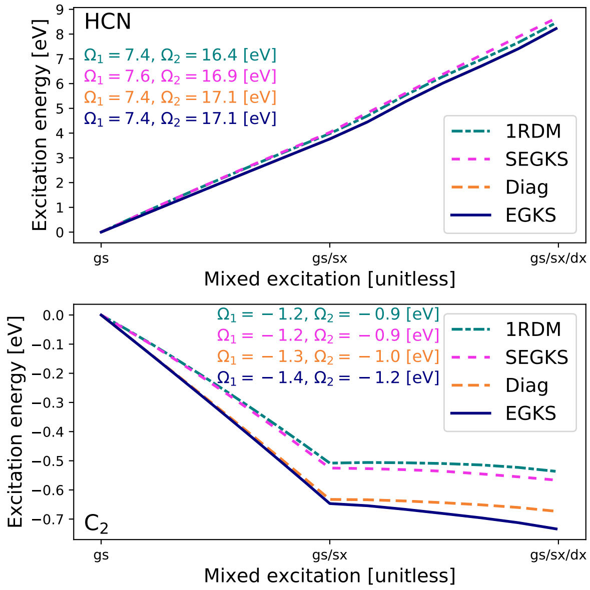

FIG. 3. Energies (in eV) for mixtures of singlet excitations for HCN (top) and C_2 (bottom). The Ω values show extrapolated excitation energies in the different approaches, using the same colours and order as the legend.

standard DFT. Ensembles that provide access to the first and second excited states (for single and double excitations from $h \to l$) are,

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

$$\begin{aligned}\hat{\Gamma}_{\frac{1}{2}<w\leq 1} =& \tfrac{2-w}{3}\left[|S_0\rangle\langle S_0| + |S_1\rangle\langle S_1|\right] \\ &+ \tfrac{2w-1}{3}|S_2\rangle\langle S_2| \,. \end{aligned}\tag{37}$$

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.[59]

Figure 3 shows results for excitations of HCN (top) and C_2 (bottom), the latter of which has very small gaps. 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, the categorisation 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 approximation the energies are reversed, as seen by the negative energies in the figure.

The above ensembles can be used further to estimate excitation gaps. This is done via extrapolation, by using a quadratic fit to the energy to approximate the energy of a desired excited pure state.[38,59] 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 Figure 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, $\rho(z,r) = \frac{1}{2\pi}\int_0^{2\pi} \rho(\boldsymbol{r})d\theta$, while the bottom panel shows, $\rho(z) = 2\pi\int_0^{\infty} r\rho(z,r)dr$.

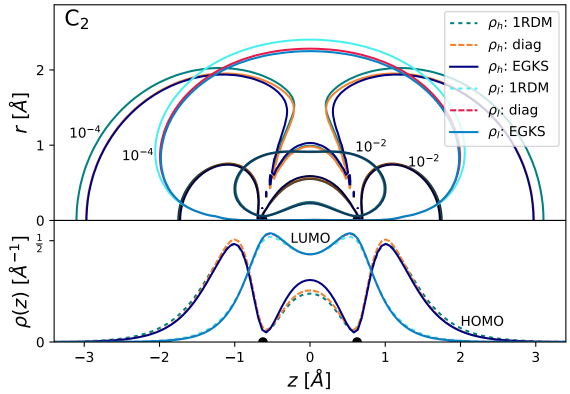

FIG. 4. HOMO and LUMO densities for C_2. We retain the colours of previous figures (1-RDM in teal, diag in orange and EGKS in navy) for the HOMO. LUMO are coloured as cyan (1-RDM), red (diag) and blue (EGKS). In the lower panel we also change the line styles (to dots, dashes, solid, respectively) to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

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.

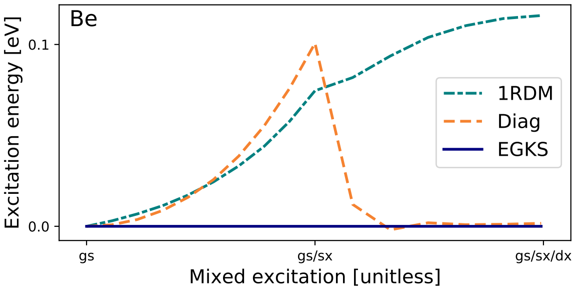

FIG. 5. Energy errors [eV] for singlet excitations of Be. The EGKS error is zero, by definition.

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. When the amount of S_0 and S_1 is approximately equal ($w \to \frac{1}{2}$) 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 from the improved physics in the diag approximation, this was the only case where it wasn't 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 that the approach is both practical and advantageous.

Table I and Figures 1 to 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 in which the 1-RDM and/or diag approximations perform well should be scrutinized.

Finally, recent work has shown that any hybrid approximation, $E_{\text{Hxc}} = E_H + \alpha E_{\text{x}} + (1-\alpha)E_{\text{x}}^{\text{DFA}} + E_{\text{c}}^{\text{DFA}}$ (or range-separated variants), can be "ensemblized", by setting $\mathcal{E}_{\text{Hxc}} = \mathcal{E}_{\text{H}} + \alpha\mathcal{E}_{\text{x}} + (1-\alpha)\mathcal{E}_{\text{x}}^{\text{DFA}} + \mathcal{E}_{\text{c}}^{\text{DFA}}$,[58] and are thus amenable to the rigorous EGKS theory introduced here. Here DFA stands for any standard density functional approximation and $\mathcal{E}_{\text{x}}^{\text{DFA}}/\mathcal{E}_{\text{c}}^{\text{DFA}}$ are appropriate weighted averages. Furthermore, such functionals can out-perform time-dependent DFT using simplified EGKS schemes.[59] 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,[59] suggesting that a full or better treatment of EGKS will improve results. Work is ongoing.

Appendix A: 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,

$$\hat{\Gamma}_{S_0} = |S_0\rangle\langle S_0| = |1^2 2^2 \cdots h^2\rangle\langle 1^2 2^2 \cdots h^2| \,, \tag{A1}$$

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

$$F_{ij}^J = f_i f_j = 4, \qquad F_{ij}^K = -\tfrac{1}{2} f_i f_j = -2, \tag{A2}$$

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 air paired except one, i.e. the state is, $|1^2 2^2 \cdots h^{\uparrow}\rangle$ or $\uparrow\,\to\,\downarrow$. 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,

$$\hat{\Gamma}_{D_0} = \tfrac{1}{2}\big[|1^2 2^2 \cdots h^{\uparrow}\rangle\langle 1^2 2^2 \cdots h^{\uparrow}| + |1^2 2^2 \cdots h^{\downarrow}\rangle\langle 1^2 2^2 \cdots h^{\downarrow}|\big] \,. \tag{A3}$$

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,

$$E_{\text{Hx}}^{D_0} = \tfrac{1}{2}\sum_{i,j<h}[4(ij|ij) - 2(ij|ji)] + \tfrac{1}{2}\sum_{i<h} 2[2(ih|ih) - (ih|hi)] \,, \tag{A4}$$

then yields the pair-coefficients, which are:

$$F_{ij}^J = -2F_{ij}^K = \begin{cases} f_i f_j, & i < h \text{ or } j < h \,, \\ 0 & i = j = h \end{cases} \tag{A5}$$

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 the spin-properties of the system. This result follows from the fluctuation-dissipation theorem.[58] Thus, for the triplet state ensemble,

$$\hat{\Gamma}_{T_0} = \tfrac{1}{3} \sum_{M_z \in \{-1,0,1\}} |T_{0,M_z}\rangle\langle T_{0,M_z}| \; . \tag{A6}$$

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

$$E^{T_0}_{\text{Hx}} = \tfrac{1}{2} \sum_{ij} f_i f_j (ij|ij) - \tfrac{1}{2} \sum_{i,j \leq l} (ij|ji) - \tfrac{1}{2} \sum_{i,j<h} (ij|ji) \; , \tag{A7}$$

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 $F^J_{ij} = f_i f_j = -2F^K_{ij}$, a result that also holds for ih, il, hi and li, provided $i < h$. For the remaining states, we obtain:

$$F^J_{fg} = -\, F^K_{fg} = 1, \quad \forall f, g \in \{h, l\} \; . \tag{A8}$$

Thus, we again have only a small number of combinations of i and j for which $F^J_{ij} \neq -2F^K_{ij} \neq f_i f_j$ and which 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, $|S_1\rangle = [|1^2 2^2 \cdots h^{\uparrow} l^{\downarrow}\rangle + |1^2 2^2 \cdots h^{\downarrow} l^{\uparrow}\rangle]/\sqrt{2}$ and ensemble $\hat{\Gamma}_{S_1} = |S_1\rangle\langle S_1|$. Application of the Slater-Condon rules yields,

$$E^{S_1}_{\text{Hx}} = E^{T_0}_{\text{Hx}} + 2(hl|lh) \; , \tag{A9}$$

using results for the triplet state. Thus, $F^J_{ij} = f_i f_j = -2F^K_{ij}$, whenever $i < h$ or $j < h$; and,

$$F^J_{fg} = F^K_{fg} = 1 - \delta_{fg}, \quad \forall f, g \in \{h, l\} \; . \tag{A10}$$

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, $\hat{\Gamma}_{S_2} = |S_2\rangle\langle S_2|$ and $|S_2\rangle = |1^2 2^2 \cdots h^0 l^2\rangle$. Thus, $f_i = 2, \forall i < h$, $f_h = 0$, $f_l = 1$, and,

$$F^J_{ij} = f_i f_j = 4, \qquad F^K_{ij} = -\, \tfrac{1}{2} f_i f_j = -2, \tag{A11}$$

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

$$\hat{\Gamma}^{\mathbf{w}} = \sum_{\kappa} w_{\kappa} \hat{\Gamma}_{\kappa} \; , \tag{A12}$$

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

$$F^{J,\mathbf{w}}_{ij} = \sum_{\kappa} w_{\kappa} F^{J,\kappa}_{ij} \; , \qquad F^{K,\mathbf{w}}_{ij} = \sum_{\kappa} w_{\kappa} F^{K,\kappa}_{ij} \; . \tag{A13}$$

Importantly, if either $i \in \mathbb{D}$ or $j \in \mathbb{D}$ in all members of the ensemble, then it follows that $F^{J,\mathbf{w}}_{ij} = f_i j_i$ and $F^{K,\mathbf{w}}_{ij} = -\frac{1}{2} f_i f_j$. 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 netural atom. We therefore obtain, $f_{1s} = 2$, $f_{2s} = q \times 0 + (1-q) \times 1 = 1 - q$, and,

$$\begin{aligned} F^J_{1s1s} &= -\, 2F^K_{1s1s} = 4, \\ F^J_{1s2s} &= -\, 2F^K_{1s2s} = 2(1-q) = F^J_{2s1s} = -2F^K_{2s1s}, \\ F^H_{2s2s} &= -\, 2F^K_{2s2s} = 0 \; . \end{aligned}$$

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

$$\begin{aligned} F^J_{1s1s} &= -\, 2F^K_{1s1s} = 4, \\ F^J_{1s2s} &= -\, 2F^K_{1s2s} = 2(1-q) = F^J_{2s1s} = -2F^K_{2s1s}, \\ F^J_{2s2s} &= q \times 4 + (1-q) \times 0 = 4q \; . \\ F^K_{2s2s} &= q \times -2 + (1-q) \times 0 = -2q \; . \end{aligned}$$

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 a more doubly occupied orbitals ($1s$, $2s$, $2p_{x,y,z}$) 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, $f_{i<h} = 2$, $f_h = \frac{3(1-w)}{2}$, $f_l = \frac{1+3w}{2}$, for the occupation factors. The non-product pair-coefficients can be shown to be,

$$F^J_{fg} = \begin{cases} 0 & hh, ll \\ w & hl, lh \end{cases} \; , \qquad F^K_{fg} = \begin{cases} 0 & hh, ll \\ -w & hl, lh \end{cases} \; , \tag{A14}$$

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

A more complex example 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 Eq. (A2), (A10) and (A11) gives, $f_{i<h} = 2$, $f_h = \frac{3(1-w)}{2}$, $f_l = \frac{1+3w}{2}$, for the occupation factors. The non-product pair-coefficients can be shown to be,

$$F^J_{fg} = \begin{cases} \frac{5(1-w)}{2} & hh \\ \frac{(1+7w)}{2} & ll \\ 0 & hl, lh \end{cases}, \quad F^K_{fg} = \begin{cases} -(1-w) & hh \\ -2w & ll \\ \frac{(1-w)}{2} & hl, lh \end{cases}, \tag{A15}$$

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

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AIP PUBLISHING DATA SHARING POLICY

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

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