Stationary conditions for excited states: the surprising impact of density-driven correlations

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Typical density functional theory (DFT) and approximations thereto solve the many-electron ground state problem by working from a non-interacting Kohn-Sham reference system. In practice, DFT benefits from useful minimization conditions that let approximate solutions iteratively approach the optimal energy and density. The present work reveals that stationary conditions also apply to all excited states of general electronic systems; and may be defined straightforwardly from ensemble extensions of DFT. However, it also reveals that the stationary condition for the non-interacting Kohn-Sham reference systems that make density functional theory numerically efficient is more complex than the ground state problem. The extra complexity reflects a contribution from density-driven correlations. Some implications for approximations and self-consistency are discussed.

In any given year, tens of thousands of papers will report "density functional theory" [1, 2] (DFT) results for chemical or material systems of interest to their authors. In reality, these papers are almost exclusively applications of self-consistent field theory applied to popular (e.g. Refs 3 and 4) density functional approximations (DFAs) for the purpose of deriving ground state energies and properties therefrom (including spectra).

The benefit of DFAs is certainly widely appreciated. What is less widely appreciated is the mathematical structure of DFT that allows convergence to self-consistent solutions. Specificially, the fact the self-consistent solution of the usual Kohn-Sham (KS) equations yields a minima for the energy; so that, when given a DFA (e.g. PBE [4]), computer codes can iteratively obtain an orbital solution (e.g. PBE densities and orbitals) that is a good approximation to the true interacting physics of electrons. In practice, it is this mathematical structure, together with the ability to capture ground state electronic physics, that makes DFAs so useful.

Given their excellent performance on ground states, it is not surprising that there is interest in adapting DFAs to *excited states*. Adaptation requires solving two interrelated problems: 1) determining how and when solutions can be converged to a genuine stationary solution; and 2) determining how DFAs for excited states can be designed to capture appropriate electronic structure physics, especially any differences from ground states.

Görling [5] provided a formal solution to the first problem in 1999, by showing that excited states within DFT are on firm theoretical footing via an extended density functional that involves both explicit and implicit conditions in its formal definition. Giarrusso and Loos [6] recently showed that "usual" variational principles may be applied directly and exactly to excited states of a two-site Hubbard model. Yang and Ayers extended Görlings work to additional excited states, [7] via a different formal approach. Various recent works – notably from the Levi and Head-Gordon groups [8–10] – have introduced practical methods for finding stationary solutions that yield useful excited state energies within a stationary DFT framework based on existing DFAs. Clearly, convergence of excited states is possible.

A solution to the second problem is enabled by recent advances in ensemble density functional theory (EDFT) that provide first principles density functionals, [11–15] as foundations for physics-based excited state DFAs. [16–19] Importantly, these works reveal that excited state functionals have contributions that are *not present* in ground states and that are therefore *neglected entirely* by existing ground state DFAs. Moreover, these terms can involve highly non-trivial functional forms, which makes them harder to deal with formally.

The fundamental problem therefore shifts from existence to effective adaptation. That is, how can existing formal and practical solutions be applied to DFAs that capture appropriate excited state physics? The rest of this work will therefore first derive generalized stationary conditions for excited state ensembles, and then use them to derive stationary conditions for individual excited states – both via EDFT. It will thus establish that approaches based on first principles EDFT and stationary conditions may yield both ground- and excited state energies within a useful density functional theory framework. It will then reveal how formal results transfer to the KS approach to DFT, which exposes some expected results as well as some surprises. Finally, some conclusions will be drawn.

Ensemble density functional theory: In standard DFT, one obtains the energy of an N-electron system in external potential v via $E[v] = \min_{\Psi\to N}\langle\Psi|\hat{T}+\hat{W}+\hat{v}|\Psi\rangle$. Here, $\hat{T}$ is the many-body kinetic energy operator, $\hat{W}$ is the electron-electron interaction operator and $\hat{v} = \int \hat{n}(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r} \equiv (\hat{n}, v)$ the operator for external potential, v. $E[v]$ and related quantities may then be used to define density functionals – for example one may define the density $n[v]$ as a functional of potential v or, conversely, the potential $v[n]$ as a functional of density, n.

Excited state EDFT works in much the same way, but replaces pure state expectation values, $O_\Psi = \langle\Psi|\hat{O}|\Psi\rangle$

by ensemble expectation values, $O_{\hat{\Gamma}} = \mathrm{Tr}[\hat{\Gamma}\hat{O}]$. Thus, the variational ensemble energy functional is, $\mathcal{E}^{\boldsymbol{w}}[v] := \inf_{v\to\hat{\Gamma}^{\boldsymbol{w}}} \mathrm{Tr}[\hat{\Gamma}^{\boldsymbol{w}}(\hat{T}+\hat{W}+\hat{v})]$, where $\hat{\Gamma} = \sum_\kappa w_\kappa |\Psi_\kappa\rangle\langle\Psi_\kappa|$ is an arbitrary ensemble of orthogonal wavefunctions, $\langle\Psi_\kappa|\Psi_{\kappa'}\rangle = \delta_{\kappa\kappa'}$, with weights $w_\kappa > 0$ obeying $\sum_\kappa w_\kappa = 1$. Theophilou [20] and Gross, Oliveira and Kohn [21, 22] (TGOK) showed that,

$$\mathcal{E}^{\boldsymbol{w}}[v] = \sum_\kappa w_\kappa E_\kappa[v] \leq \mathrm{Tr}[\hat{\Gamma}^{\boldsymbol{w}}\hat{H}[v]] \tag{1}$$

where $E_\kappa[v]$ are the eigenvalues of $\hat{H}[v] = \hat{T}+\hat{W}+\hat{v}$ organised from lowest to highest, w_κ are the weights organised from highest to lowest, and $\hat{\Gamma}$ is an arbitrary ensemble with the given weights. Furthermore, they showed that key density functional theory results, such as the mappings between densities and potentials, also hold for many ensembles. More recent work has extended the kinds of ensembles treated by EDFT [23] by exploiting symmetries. This work keep the number of electrons, N, fixed; although recent extensions of EDFT to excitations involving addition or removal of an electron should be addressable with minimal change. [24–26]

Consider now one restriction and one assumption that will be applied throughout this work to simplify treatment of degenerate states. Firstly, the degeneracy structure will be preserved by weighting all spatially degenerate interacting states equally, and restricting to potentials that have the same fundamental spatial symmetry as the external potential. [23] Manifolds of degenerate spin states (doublets, triplets etc) will also be treated similarly, yielding restricted orbitals. [11] These restrictions define a unique mapping,

$$n^{\boldsymbol{w}}[v] = \sum_\kappa w_\kappa n_\kappa[v] \equiv \sum_\kappa w_\kappa \langle\kappa[v]|\hat{n}|\kappa[v]\rangle \ , \tag{2}$$

from the potential to an ensemble density. [23] Here, $|\kappa[v]\rangle$ is a wave function associated with energy $E_\kappa[v]$ obeying $\hat{H}[v]|\kappa[v]\rangle = E_\kappa[v]|\kappa[v]\rangle$.

Secondly, assume that the set of ensemble v-representible densities, $n^{\boldsymbol{w}}[v]$, is sufficiently dense [27] in the space of all valid densities with the target symmetry. Then, any target density, $\tilde{n}$, may be defined by a series of potentials $\tilde{v}$ such that $\|n^{\boldsymbol{w}}[\tilde{v}] - \tilde{n}\| \to 0$. A similar result may be achieved by taking an appropriate limit of a regularization procedure. [28, 29] Either assumption yields a unique inverse mapping,

$$\tilde{v} \to v^{\boldsymbol{w}}[n] \text{ s.t. } \tilde{n} = n^{\boldsymbol{w}}[\tilde{v}] \to n \ . \tag{3}$$

The energy and universal ensemble functional may now be defined as, [30, 31]

$$\mathcal{E}^{\boldsymbol{w}}[v] := \inf_{\hat{\Gamma}^{\boldsymbol{w}}} \mathrm{Tr}[\hat{\Gamma}^{\boldsymbol{w}}(\hat{T}+\hat{W}+\hat{v})] = \sup_n \left\{\mathcal{F}^{\boldsymbol{w}}[n] + (n|v)\right\} \tag{4}$$

$$\mathcal{F}^{\boldsymbol{w}}[n] := \inf_{\hat{\Gamma}^{\boldsymbol{w}}\to n} \mathrm{Tr}[\hat{\Gamma}^{\boldsymbol{w}}(\hat{T}+\hat{W})] = \sup_v \left\{\mathcal{E}^{\boldsymbol{w}}[v] - (n|v)\right\} \tag{5}$$

where $\hat{\Gamma}^{\boldsymbol{w}}$ is an arbitrary ensemble with the weights, $\boldsymbol{w}$, and $(n|v) \equiv \int n(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r}$ is the usual pairing between densities and potentials. Here, $v \to \hat{\Gamma}^{\boldsymbol{w}}$ means the ensemble is formed on eigenstates of $\hat{T}+\hat{W}+\hat{v}$, whereas $\hat{\Gamma}^{\boldsymbol{w}} \to n$ means the ensemble obeys $\mathrm{Tr}[\hat{\Gamma}^{\boldsymbol{w}}\hat{n}] = n$. The right-most expressions yield,

$$\frac{\delta\mathcal{E}^{\boldsymbol{w}}[v]}{\delta v(\boldsymbol{r})} = n^{\boldsymbol{w}}[v](\boldsymbol{r}) \ , \qquad \frac{\delta\mathcal{F}^{\boldsymbol{w}}[n]}{\delta n(\boldsymbol{r})} = -v^{\boldsymbol{w}}[n](\boldsymbol{r}) \ , \tag{6}$$

using mappings from Eqs (2) and (3).

Eq. (6) leads to two very useful relationships: firstly, $\frac{\delta\mathcal{E}^{\boldsymbol{w}}[v]-(n'|v)}{\delta v(\boldsymbol{r})} = n^{\boldsymbol{w}}[v](\boldsymbol{r}) - n'(\boldsymbol{r})$ is zero whenever $n^{\boldsymbol{w}}[v] = n'$ or, equivalently, $v = v^{\boldsymbol{w}}[n']$; and secondly,

$$\frac{\delta\mathcal{F}^{\boldsymbol{w}}[n] + (n|v')}{\delta n(\boldsymbol{r})} = -v^{\boldsymbol{w}}[n](\boldsymbol{r}) + v'(\boldsymbol{r}) \tag{7}$$

is zero whenever $v^{\boldsymbol{w}}[n] = v'$ or $n = n^{\boldsymbol{w}}[v']$. Eq. (7) is especially important for self-consistency. Define, $\hat{\mathcal{E}}^{\boldsymbol{w}}[n,v] := \mathcal{F}^{\boldsymbol{w}}[n] + (n|v)$ to be the dual energy functional obtained by using an arbitrary density n in $\mathcal{F}$, but with an external arbitrary potential v that is unrelated to n. It follows from (7) that,

$$\frac{\delta\hat{\mathcal{E}}^{\boldsymbol{w}}[n,v]}{\delta n(\boldsymbol{r})} = v(\boldsymbol{r}) - v^{\boldsymbol{w}}[n](\boldsymbol{r}) \tag{8}$$

is zero when $n = n^{\boldsymbol{w}}[v]$. That is, the energy is stationary with respect to changes in the density when the ensemble density is consistent with the potential v. In fact, the energy, $\hat{\mathcal{E}}^{\boldsymbol{w}}[n,v]$ is a global minima when $v = v^{\boldsymbol{w}}[n]$ thanks to the TGOK variational principles. This result justifies the convergence of self-consistent mean-field calculations, since the minimum is a staionary point.

Resolution by state: Does (8) have a counterpart for individual excited states? As a first step toward an answer, note that despite the compact notation, each of eqs. (4)–(8) represents a different functional for each unique set of probabilistic (i.e. obeying $w_\kappa \geq 0$ and $\sum_\kappa w_\kappa = 1$) weights, $\boldsymbol{w}$. Furthermore, this family of functionals may be expanded by allowing $0 < \sum_\kappa w_\kappa < \infty$. [32]

As a second step, change from ensemble density functionals to ensemble potential functionals, via the dual potential functional,

$$\bar{\mathcal{E}}^{\boldsymbol{w}}[v,v'] = \bar{\mathcal{F}}^{\boldsymbol{w}}[v] + (n^{\boldsymbol{w}}[v],v') \ , \tag{9}$$

and its universal functional counterpart,

$$\bar{\mathcal{F}}^{\boldsymbol{w}}[v] = \mathcal{F}^{\boldsymbol{w}}[n^{\boldsymbol{w}}[v]] = \bar{\mathcal{E}}^{\boldsymbol{w}}[v,v'] - (n^{\boldsymbol{w}}[v],v') \ . \tag{10}$$

This resolves some ensemble-specific difficulties: 1) levels, κ, are only defined for eigenstates of a given potential, v, where they are ordered according to $E_\kappa[v]$; 2) degeneracies may be broken without careful construction of densities, n, but are preserved for appropriate potentals.

The third step is to adapt a very useful technique that Fromager [13] used to interpret correlations in ensembles – the application of weight-derivatives, ∂_{w_κ}, to resolve ensemble functionals into contributions from individual states. In fact, because the sum over weights is no longer constrained, weight derivatives of energy expressions may be taken *trivially* for cases where κ is non-degenerate, and thus used to establish state-resolved conditions for states, $|\kappa\rangle$. [33] Taking ∂_{w_κ} of (9) and (10) yields,

$$E_\kappa[v,v'] := \partial_{w_\kappa}\mathcal{E}^{\boldsymbol{w}}[v,v'] = \bar{F}_\kappa[v] + (n_\kappa[v],v') \;, \quad (11)$$

$$\bar{F}_\kappa[v] := \partial_{w_\kappa}\bar{\mathcal{F}}^{\boldsymbol{w}}[v] = E_\kappa[v] - (n_\kappa[v],v) \quad (12)$$

as the state-resolved counterparts of eqs. (9) and (10).

Next. take $\frac{\delta}{\delta v}$ of (9) to obtain,

$$\frac{\delta\bar{\mathcal{E}}^{\boldsymbol{w}}[v,v']}{\delta v(\boldsymbol{r})} = \frac{\delta\bar{\mathcal{F}}^{\boldsymbol{w}}[v]}{\delta v(\boldsymbol{r})} + \int \frac{\delta n^{\boldsymbol{w}}[v](\boldsymbol{r}')}{\delta v(\boldsymbol{r})} v'(\boldsymbol{r}')d\boldsymbol{r}' \;. \quad (13)$$

Then use (6) and the functional chain rule to find,

$$\frac{\delta\bar{\mathcal{F}}^{\boldsymbol{w}}[v]}{\delta v(\boldsymbol{r})} = \int \frac{\delta n^{\boldsymbol{w}}[v](\boldsymbol{r}')}{\delta v(\boldsymbol{r})}\frac{\delta\mathcal{F}^{\boldsymbol{w}}[n]}{\delta n(\boldsymbol{r}')}d\boldsymbol{r}' = -\int \frac{\delta n^{\boldsymbol{w}}[v](\boldsymbol{r}')}{\delta v(\boldsymbol{r})} v(\boldsymbol{r}')d\boldsymbol{r}'$$
$$:= -\int \chi^{\boldsymbol{w}}[v](\boldsymbol{r},\boldsymbol{r}')v(\boldsymbol{r}')d\boldsymbol{r}' \equiv -\chi^{\boldsymbol{w}}[v]\star v \;; \quad (14)$$

and finally,

$$\frac{\delta\bar{\mathcal{E}}^{\boldsymbol{w}}[v,v']}{\delta v} = \chi^{\boldsymbol{w}}[v]\star(v'-v) \;. \quad (15)$$

Because $n^{\boldsymbol{w}}[v] = \sum_\kappa w_\kappa n_\kappa[v]$, it follows from the linearity of derivatives that the density-response function of state κ obeys, $\partial_{w_\kappa}\chi^{\boldsymbol{w}}[v](\boldsymbol{r},\boldsymbol{r}') = \frac{\delta n_\kappa(\boldsymbol{r}')}{\delta v(\boldsymbol{r})}$. Combining this result with ∂_{w_κ} of (15) and (11) yields,

$$\frac{\delta E_\kappa[v,v']}{\delta v} = \chi_\kappa[v]\star(v'-v) \;. \quad (16)$$

It is thus clear that both $\frac{\delta\bar{\mathcal{E}}^{\boldsymbol{w}}}{\delta v} = 0$ and $\frac{\delta E_\kappa}{\delta v} = 0$ whenever $v' = v$ – i.e. both the ensemble- and state-energies are stationary to small changes around v.

Eq. (16) is the first major result of this work as it validates the use of stationary conditions for individual excited states. It shows that stationary points in the space of model potentials, v', can yield both ground and excited states of the true potential, v. They are, however, not necessarily minima, except when κ is the lowest energy state for a given fundamental symmetry.

Kohn-Sham density functional theory: While (16) is a helpful fundamental result, its practical benefit is limited as it deals with the potential for interacting electrons, not the effective KS potential, v_s, that is usually employed in DFT calculations. The first step toward a more practical result is to recognise that all previous steps may be repeated with only moderate modification for the case of a Hamiltonian $\hat{H} = \hat{T} + (\hat{n}|v_s)$. The equivalent of $\mathcal{F}^{\boldsymbol{w}}[n]$ in this case is the KS kinetic energy functional $\mathcal{T}_s^{\boldsymbol{w}}[n]$, and its density is $n[v_s] = \mathrm{Tr}[\hat{\Gamma}_s^{\boldsymbol{w}}\hat{n}] = \sum_i f_i^{\boldsymbol{w}}|\phi_i[v_s]|^2$ is a sum over non-interacting orbitals – $f_i^{\boldsymbol{w}}$ will be discussed shortly. It follows from Eq. (6) that $\frac{\delta\mathcal{T}_s}{\delta n} = -v_s[n]$.

Next, define $\bar{\mathcal{F}}_s^{\boldsymbol{w}}[v_s] = \mathcal{T}_s^{\boldsymbol{w}}[n[v_s]] + \mathcal{E}_{\mathrm{Hxc}}^{\boldsymbol{w}}[n[v_s]]$ and $\bar{\mathcal{E}}_s^{\boldsymbol{w}}[v_s,v] = \bar{\mathcal{F}}_s^{\boldsymbol{w}}[v_s] + (n[v_s]|v)$ to be the energy defined in terms of the KS system. Here, $\mathcal{E}_{\mathrm{Hxc}}^{\boldsymbol{w}}[n] := \mathcal{F}^{\boldsymbol{w}}[n] - \mathcal{T}_s^{\boldsymbol{w}}[n]$. Using $\frac{\delta}{\delta v_s} = \frac{\delta n}{\delta v_s}\star\frac{\delta}{\delta n} \equiv \chi_s\star\frac{\delta}{\delta n}$ yields,

$$\frac{\delta\bar{\mathcal{E}}_s^{\boldsymbol{w}}[v_s,v]}{\delta v_s} = \chi_s^{\boldsymbol{w}}\star(-v_s + v_{\mathrm{Hxc}}^{\boldsymbol{w}} + v) \quad (17)$$

which is zero if $v_s = v + v_{\mathrm{Hxc}}^{\boldsymbol{w}}$, where $v_{\mathrm{Hxc}}^{\boldsymbol{w}} := \frac{\delta\mathcal{E}_{\mathrm{Hxc}}^{\boldsymbol{w}}[n]}{\delta n}$. This is the expected generalization of the usual Kohn-Sham equations. [2] Taking a weight-derivative yields,

$$\frac{\delta E_{s,\kappa}[v_s,v]}{\delta v_s} = \chi_{s,\kappa}\star(v + v_{\mathrm{Hxc}}^{\boldsymbol{w}} - v_s) + \chi_s^{\boldsymbol{w}}\star\partial_{w_\kappa}v_{\mathrm{Hxc}}^{\boldsymbol{w}} \;, \quad (18)$$

however, where $v_{\mathrm{Hxc},\kappa} := \frac{\delta\mathcal{E}_{\mathrm{Hxc}}^{\boldsymbol{w}}}{\delta n}$ is the Hxc potential for the full ensemble. The extra term is a surprise as it means that the "naive" self-consistent relationship, $v_s = v + v_{\mathrm{Hxc}}^{\boldsymbol{w}}$, *does not* necessarily yield a variational minima. Eq. (18) is the second major result of this work.

Contextualising this term, and determining when it matters and when it can be ignored, requires an understanding of $\mathcal{E}_{\mathrm{Hxc}}^{\boldsymbol{w}} \equiv \mathcal{E}_{\mathrm{H}}^{\boldsymbol{w}} + \mathcal{E}_{\mathrm{x}}^{\boldsymbol{w}} + \mathcal{E}_{\mathrm{c}}^{\boldsymbol{w}}$. A series of recent papers [11–15] have provided key insights into the structure of exact density functionals for ensembles. Ref. 11 yields the following closed form functionals: $\mathcal{T}_s^{\boldsymbol{w}} := \sum_\kappa w_\kappa\langle\Phi_{s,\kappa}|\hat{T}|\Phi_{s,\kappa}\rangle$ (kinetic energy); and $\mathcal{E}_{\mathrm{Hx}}^{\boldsymbol{w}} := \sum_\kappa w_\kappa\langle\Phi_{s,\kappa}|\hat{W}|\Phi_{s,\kappa}\rangle$ (Hartree-exchange energy). Here, $|\Phi_{s,\kappa}[v_s]\rangle$ are the zeroth order renormalized orbital (ZORO) KS states that take the form [11] of configuration state functions; and are ordered by their energy on $\hat{T} + \hat{v}_s + \eta\hat{W}$ for $\eta \to 0^+$. They are formed out of non-interacting orbitals, $\phi_i[v_s]$, that are ordered by energy on $\hat{h} \equiv -\frac{1}{2}\nabla^2 + v_s$ (i.e. the KS potential). They are used to form an ensemble density, $n[v_s](\boldsymbol{r}) = \sum_\kappa w_\kappa\langle\Phi_{s,\kappa}|\hat{n}|\Phi_{s,\kappa}\rangle = \sum_i f_i^{\boldsymbol{w}}|\phi_i[v_s](\boldsymbol{r})|^2$, whose occupation factors, $f_i^{\boldsymbol{w}} = \sum_\kappa w_\kappa\theta_i^\kappa$, are weighted sums (over the ensemble) of the occupation factors, θ_i^κ, of individual non-interacting Fermionic states $|\Phi_{s,\kappa}[v_s]\rangle$.

If is readily seen from the weighted sum expressions that each of these terms can by trivially state-resolved by application of ∂_{w_κ}. Thus, the kinetic and Hx energy of ZORO state $|\Phi_{s,\kappa}\rangle$ are $T_{s,\kappa} := \langle\Phi_{s,\kappa}|\hat{T}|\Phi_{s,\kappa}\rangle$ and $E_{\mathrm{Hx},\kappa} := \langle\Phi_{s,\kappa}|\hat{W}|\Phi_{s,\kappa}\rangle$. Both the kinetic and Hx terms may therefore be expressed as direct functionals of v_s, via $|\Phi_{s,\kappa}[v_s]\rangle$ – indeed this is usually more useful in practice as their implicit functional dependence on ensemble densities is complicated to deal with. [34] Thus, we can write,

$$\frac{\delta E_{\mathrm{Hx},\kappa}}{\delta v_s} \equiv \frac{\delta n_{s,\kappa}}{\delta v_s}\star\frac{\delta E_{\mathrm{Hx},\kappa}}{\delta n_{s,\kappa}} \equiv \chi_{s,\kappa}\star v_{\mathrm{Hx},\kappa} \;, \quad (19)$$

and eliminate the weight derivative term on the right side of Eq. (18).

Indeed, any exact or approximate function defined only via a sum over contributions from ZORO states, $|\Phi_{s,\kappa}\rangle$, has this convenient property. This has important implications for ensemble density functional approximations (EDFAs). The energy approximation,

$$\mathcal{E}^{\boldsymbol{w}}_{\rm Hxc}[v_s] \approx \sum_\kappa w_\kappa E^{\rm DFA}_{{\rm Hxc},\kappa}[n_{s,\kappa}[v_s]] \tag{20}$$

where $n_{s,\kappa} = \langle\Phi_{s,\kappa}|\hat{n}|\Phi_{s,\kappa}\rangle$ has given good results in previous work. [19] By construction, the correlation *approximation* has the same properties as the H and x approximations, so self-consistency may be obtained via $v_s = v + v_{{\rm Hxc},\kappa}$ where $v^{\rm DFA}_{{\rm Hxc},\kappa} = \frac{\delta E^{\rm DFA}_{{\rm Hxc},\kappa}}{\delta n_{s,\kappa}}$. In practice the solution may be obtained via regular or ensemble generalized KS (EGKS) theory [5, 7, 34].

However, the true correlation energy is more complicated than the above approximation. Its state-resolved expression is,

$$\begin{aligned} E^{\boldsymbol{w}}_{{\rm c},\kappa} :=& \partial_{w_\kappa}\mathcal{E}^{\boldsymbol{w}}_{\rm c}[n^{\boldsymbol{w}}[v_s]] \equiv \partial_{w_\kappa}\mathcal{E}^{\boldsymbol{w}}_{\rm c}[\textstyle\sum_\kappa w_\kappa n_{s,\kappa}[v_s]] \\ =& (\partial_{w_\kappa}\mathcal{E}^{\kappa}_{\rm c})[n^{\boldsymbol{w}}[v_s]] + n_{s,\kappa}[v_s] \star v^{\boldsymbol{w}}_{\rm c}[n^{\boldsymbol{w}}[v_s]] \end{aligned} \tag{21}$$

where $v^{\boldsymbol{w}}_{\rm c} := \frac{\delta\mathcal{E}^{\boldsymbol{w}}_{\rm c}}{\delta n}$; and the individual terms also depend on both the set of weights, $\boldsymbol{w}$, and the ensemble density, $n^{\boldsymbol{w}}[v_s] = \sum_\kappa w_\kappa n_{s,\kappa}[v_s]$. The reason behind this surprising result is the presence of density-driven correlations [12–14] (DDCs) in the ensemble energy. A full discussion is beyond the scope of the present work, but essentially DDCs appear because the densities of states within an interacting ensemble are not the same as the densities of non-interacting states within the KS ensemble – the only restriction being that $\sum_\kappa w_\kappa n_{s,\kappa} = \sum_\kappa w_\kappa n_\kappa$. As a result, the total ensemble correlation energy depends explicitly and implicitly on $\boldsymbol{w}$. Thus, unlike the case of Hx where formal ensembles can be used to eliminate the extra weight derivative term, the correlation energy term contributes to both parts of Eq. (18)'s right side. The exceptions are the ground state, or lowest energy of a given spin-symmetry where we can set $n^{\boldsymbol{w}} = n_0 = n_{s,0}$ and thus eliminate extra contributions.

The last term of Eq. (18) may now be contextualised. Consider a *direct* attempt to find a stationary solution of the energy of state, κ. As discussed above, the H and x terms contribute trivially, via $\frac{\delta E^{\boldsymbol{w}}_{\rm Hx}}{\delta v_s} \equiv \chi_{s,\kappa} \star v_{{\rm Hx},\kappa}$ but correlation does not. Thus, the extra term in Eq. (18), $\chi^{\boldsymbol{w}}_s \star \partial_{w_\kappa} v_{{\rm Hxc},\kappa} \equiv \chi^{\boldsymbol{w}}_s \star \partial_{w_\kappa} v_{{\rm c},\kappa}$, must *come entirely* from the correlation physics that gives rise to the DDC energy. That is, given any set set of weights, $\boldsymbol{w}$, containing level κ, the self-consistent stationary solution ($\frac{\delta \bar{E}_s}{\delta v_s} = 0$) obeys,

$$v_s = v + v_{{\rm Hx},\kappa} + v^{\boldsymbol{w}}_{\rm c} + \chi^{-1}_{s,\kappa} \star \chi^{\boldsymbol{w}}_s \star \partial_{w_\kappa} v^{\boldsymbol{w}}_{\rm c} \,. \tag{22}$$

Note, $\chi_{s,\kappa}$ has a null space (e.g. for constant potential shifts) so the inverse excludes the null space.

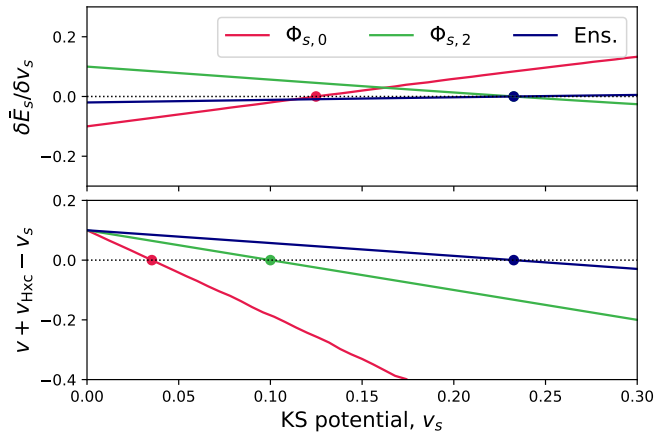

FIG. 1. Left hand side of Eq. (18) (top panel) and the difference between v_s and $v + v_{\rm Hxc}$ (bottom panel) from its right hand side. Dots indicate zero values. Results are shown for an ensemble (navy), and pure ground (red) and doubly excited (green) states of the two-site Hubbard model studied by Giarrusso and Loos [6] with $\Delta v = \frac{1}{10}$. Here, $\boldsymbol{w} \equiv (\frac{2}{5}, \frac{2}{5}, \frac{1}{5})$ and the state densities are $n_0 = -0.0342$, $n_1 = -0.1924$ and $n_2 = 0.2266$ (interacting) and $n_{s,1} = 0$ and $n_{s,2} = -n_{s,0} = 0.2266$ (KS).

Figure 1 shows [35] that this extra term can have an appreciable impact on calculations. The ensemble energy, $\bar{\mathcal{E}}^{\boldsymbol{w}}_s$ is minimized when $v^{\boldsymbol{w}}_s = v + v^{\boldsymbol{w}}_{\rm Hxc}$, as expected from (17). However, neither $v^{\boldsymbol{w}}_s$ nor the "naive" state-resolved potential, $v_{s,\kappa} = v + v_{{\rm Hxc},\kappa}$ using $v_{{\rm Hxc},\kappa} \equiv \partial_{w_\kappa} v^{\boldsymbol{w}}_{\rm Hxc}$, yield zeros for $\frac{\delta E_{s,\kappa}}{\delta v_s}$ when $\kappa = 0$, although $v^{\boldsymbol{w}}_s$ does for $\kappa = 2$. It should be noted that the DDC contribution is quite large in the example system (with $U = 1$, $t = \frac{1}{2}$, $\Delta v = \frac{1}{10}$) because the lattice model over-emphasises differences between interacting and non-interacting densities – notably the first excited KS state never changes density (hence its exclusion from the plot), whereas its interacting counterpart does.

More realistic chemical and material systems are likely to have much smaller contributions from DDCs and thus smaller differences between the naive and true optimal potentials. Nevertheless, any system that has a contribution from DDC *does not have* a trivial KS-like stationary condition, $v_s = v + v_{\rm Hxc}$. Rather, the contribution from (21) means that the stationary potential must obey Eq. (18). Note that Ref. 17 avoids this issue by obtaining stationary pure state energies via minimization (using EGKS potentials) of ensemble energies.

Conclusions: To conclude, this work has shown [eq. (16)] that all ground and excited states obey stationary conditions within density functional theory, for functional derivatives with respect to external potentials. However, when KS potentials are employed as the basic variable, the problem becomes more complicated. In these cases, density-driven correlations (DDCs) give rise to complications which mean that the extended Kohn-

Sham potential, $v_{s,\kappa} = v + v_{\mathrm{Hxc},\kappa}$, *does not necessarily* yield the variational minima of energies with respect to KS potentials, regardless of how v_{Hxc} is defined. Rather, an extended stationarity condition [Eq. (22)] must be employed for arbitrary excited states. The impact of this difference is illustrated on the Hubbard model [Figure 1].

All results apply to state-specific density functional approximations based on Kohn-Sham theory. Approximations which neglect DDCs [e.g. Eq. (20)] yield the usual self-consistent equations so may be solved in the usual way, up to any numerical instabilities or related issues. However, caution is required when treating more complicated EDFAs that include an explicit DDC approximation. The present work therefore justifies (or extends) the use of stationary conditions for excited state DFT. Due to the importance of excited state modelling, work is already progressing quickly on developing novel excited state functionals [16–19]; as well as on algorithms to solve for stationary conditions. [8–10] This work motivates accelerated development on both fronts.

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[32] A proof follow from the fact that $W\mathcal{E}^{\boldsymbol{w}'}[v]$ or $W\mathcal{F}^{\boldsymbol{w}'}[v]$ are equally valid functionals for all $0 < W < \infty$. Defining $w_\kappa = Ww'_\kappa$ (for $\sum_\kappa w'_\kappa = 1$) therefore has no fundamental impact on sums, constraints, or minimization principles. Thus, the restriction that $\sum_\kappa w_\kappa = 1$ may be generalized to $0 < \sum_\kappa w_\kappa < \infty$.

[33] The degenerate case may be dealt with by replacing ∂_{w_κ} by $\frac{1}{N_D}\sum_{\kappa\in D}\partial_{w_\kappa}$ – that is, taking the average derivative across the N_D degenerate states, $\kappa \in D$.

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