Freedom of ensemble density functionals from the excitation structure of strictly correlated electrons

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Ensemble density functional theory (EDFT) is a promising cost effective approach to address low-lying excitations in many-electron systems. Yet the corresponding functionals depend on the structure of the excitation in a challenging fashion; a fact which hinders a general and agile exploitation of the methodology. Here, we demonstrate that such a dependence become trivial as electrons become strictly correlated, because EDFT functionals become equivalent to pure ground state DFT functionals. This finding forms a most remarkable exact condition to deal with excitations in the low-density limit of all systems. An immediate consequence of which, excitations in Wigner systems can be dealt with non-empirically and universally.

Preamble. Ensemble (E) density functional theory (DFT) for excited states \[1, 2\] promises to bring cost-efficient techniques and well-developed approximations from ground state DFT to excited state problems, via a well-posed and rigorous formalism. The price of EDFT, however, is a deep deconstruction and reconstruction of the DFT framework, which has revealed additional constraints on key functionals: (i) the traditional definition of Hartree and exchange energy functionals must be abandoned in favor of extended forms able to handle auxiliary non-interacting, yet multi-configurational, excited states; (ii) recently discovered density-driven correlations must be understood and dealt with; (iii) an extended fluctuation dissipation theorem is instrumental for breaking the overall energy functional down into elemental contributions that may be tackled using (relatively) standard decompositions. Constraints (i-iii) are a byproduct of the intricate dependence of key functionals on the vast space of excitation physics and structure. Thus, despite impressive recent progress on single \[4, 5\] and double excitations, \[6\] a general agile implementation of EDFT remains challenging.

To make matters worse, interesting excitations often involve strong correlations which, as in all flavors of DFT, remain an outstanding challenge for approximations based on EDFT. \[15\] It is therefore of enormous interest if advances in understanding the strictly correlated limit of ground state DFT \[16–21\] could be transferred to ensemble problems. Strikingly, the present work reveals that strict correlations actually makes the ensemble problem easier, via an additional constraint:

(iv) when electrons are strictly correlated, the functional dependence on the excitation structure becomes trivial – specifically, the ensemble functional forms reduces to its ground state DFT form.

This condition applies in the low-density limit of all systems, a regime in which the electron-electron repulsion dominates over the kinetic energy and, thus, the positions of the electrons get strictly correlated. Below we give the derivation of such a remarkable finding and discuss the most immediate major consequences.

Theoretical framework. Because we are interested in a finite set of low-lying solutions of \[\hat{H}|\kappa\rangle = E_\kappa|\kappa\rangle\], we group them in an ensemble state \[\Gamma_w = \sum_\kappa w_\kappa|\kappa\rangle\langle\kappa|\] using some prescribed weights such that \[w_\kappa \geq 0\] and \[\sum_\kappa w_\kappa = 1\] (collectively, \[w\]). The average of an operator \(\hat{O}\), over \(\Gamma_w\) is given by \[\mathcal{S}_w := \text{Tr}[^\Gamma_w \hat{O}]\]. Crucially, choosing \(w_\kappa \leq w_{\kappa'}\) for \(E_\kappa \geq E_{\kappa'}\), ensures that \(\mathcal{E}_w\) fulfills an extended variational principle \[1\] according to which \[\mathcal{E}_w = \inf_{\Gamma_w} \text{Tr}[\mathcal{S}_w \hat{H}]\] where the argument for the infimum (usually a minimum), \(\Gamma_w\), involves prescribed weights, \(w\), and mutually orthonormal trial wavefunctions \(|\kappa\rangle\). For \(w_0 = 1\) and \(\Gamma^0 = |0\rangle\langle 0|\), the usual case of pure ground states is recovered. \[22\]

Density functionalizing the above variational principle in terms of the ensemble particle density, \(n\), yields, \[2, 9\]

\[\mathcal{E}_w = \min_n \left\{ \mathcal{T}_w[n] + \mathcal{E}_{\text{Hxc}}[n] + \int n(r)v_{\text{ext}}(r)dr \right\}. \tag{1}\]

Here, \(\mathcal{T}_w[n] = \min_{\Gamma_w} \text{Tr}[\mathcal{S}_w \hat{T}]\) is the kinetic energy of the Kohn-Sham (KS) system — i.e., an auxiliary systems reproducing the particle density of the ensemble; the minimum is attained at \(\Gamma_w = \sum_\kappa w_\kappa|\kappa\rangle\langle\kappa|\). \[24\] \(\mathcal{E}_{\text{Hxc}}[n]\) takes care of the remainder: the Hartree (H), the exchange (x), and the correlation (c) energies. We group them all into one term because, as mentioned in the preamble, these quantities individually look different...
than their familiar ground-state-only counterparts. Regular DFT forms are, of course, recovered when restricting to pure ground states.

Note, in Eq. (1), we use capital calligraphic letters to refer to energies of mixed states. We reserve capital Roman letters to refer to operators or energies of pure state, respectively. Superscripts w indicate quantities that explicitly depend on the weights. This compact notation masks an important fact about EDFT: eq. (1) describes different functionals for every choice of w! Varying w lets us access different types of excitations and different excitation structures, e.g., to obtain excitation energies.

Also, it is useful to recall that,

\[ F_\lambda,w[n] = \inf_{\Gamma^w \to n} \mathrm{Tr}[\hat{\Gamma}^w(\hat{T} + \lambda \hat{V}_{ee})] , \]  

is the universal energy functional for ensembles, where \( \lambda \) sets the strength of the interaction. \( \hat{T} \) is the kinetic energy operator and \( \hat{V}_{ee} \) is the Coulombic interaction operator. This functional is referred to as “universal” because the external potential, which specifies the molecule or solid we wish to treat, does not appear explicitly in its definition [the density being given and fixed in eq. (2)].

The Hxc functional is \( \mathcal{E}^{\text{Hxc}}_w := F^{1,w} - F^{0,w} \). In fact, we stress that, both \( F \) and \( \mathcal{E}^{\text{Hxc}}_w \) are multi-universal because each set of weights, w, defines a different excitation structure and, thus, a different universal functional. Our key results below show that such a multi-universality evolves into a simple universality in some non-trivial and very important limiting situations.

In what follows, our main objective is to determine the salient behavior of key ensemble density functionals in the so-called low-density (or strictly interacting) limit. In doing so, we shall extend to excited states concepts and core results which have previously been worked out for pure ground states only. These works can be understood as providing a generalization of the seminal work of Wigner [24] to inhomogeneous systems within DFT. Our current work completes the generalization to include excited inhomogeneous systems within EDFT.

Strictly-correlated electrons and excited states. In the parlance of modern density functional, the high- and low-density limits entail uniform scaling of the coordinates of the electrons, say, by \( \gamma > 0 \) in such a way \( n(r) \to \gamma^3 n(\gamma r) =: n_\gamma(r) \). To keep the discussion simple, we may think of a finite system like an atom, molecule or quantum dot. Scaling gives \( \hat{T} \to \gamma^{-2} \hat{T}_\gamma \) and \( \hat{V}_{ee} \to \gamma^{-1} \hat{V}_{ee,\gamma} \); so,

\[ F_\lambda,w[n_\gamma] = \gamma^2 F_\lambda/\gamma,w[n] . \]  

Because the scaled ensemble density is the density of a stationary ensemble of the Hamiltonian with interaction \( \lambda = 1/\gamma \), we see than that the high- and low-density limits are related to the weak- and strong-interaction limits, respectively. [20]

Let us first consider the high-density (i.e., weak interaction, \( \gamma \to \infty \)) limit. Scaling yields, [3]

\[ \lim_{\gamma \to +\infty} \frac{F^{1,w}[n_\gamma]}{\gamma} = T_w[n] , \quad \lim_{\gamma \to +\infty} \frac{\mathcal{E}^{\text{Hxc}}_w[n_\gamma]}{\gamma} = \mathcal{E}^{\text{Hxc}}_w[n] . \]  

Even in this “simple” case we find a complicated functional dependence on w. In fact, the exact \( \mathcal{E}^{\text{Hxc}}_w[n] \) is radically different from the usual ‘Hx’, as the underlying KS states are linear combination of Slater determinants, not just the usual single Slater determinants of regular DFT. Furthermore, symmetry adaptation is ultimately necessary to deal with multipoles consistently and generally. [11, 21]

Approaching a most striking, and previously unnoticed fact, let us turn to the the low-density (i.e., strong interaction, \( \gamma \to 0^+ \)) limit. We obtain,

\[ \lim_{\gamma \to 0^+} \frac{F^{1,w}[n_\gamma]}{\gamma} = \gamma \mathcal{E}^{\text{SCE},w}_w[n_\gamma] := \inf_{\Gamma^w \to n_\gamma} \mathrm{Tr}[\hat{\Gamma}^w \hat{V}_{ee}] , \]  

and, crucially,

\[ \mathcal{V}^{\text{SCE},w}_w[n_\gamma] \equiv \inf_{\Psi \to n_\gamma} \langle \Psi | \hat{V}_{ee} | \Psi \rangle \equiv \mathcal{V}^{\text{SCE}}_w[n] = \gamma \mathcal{V}^{\text{SCE}}_w[n] \]  

with \( \mathcal{V}^{\text{SCE}}_w[n] \) being the interaction energy of strictly correlated electrons at the ensemble particle density. This result says that, in the SCE limit, any dependence on weights disappears from both \( \mathcal{V}^{\text{SCE},w}_w[n_\gamma] \) and \( F^{1,w}[n_\gamma] \to \gamma \mathcal{V}^{\text{SCE}}_w[n] \). Dependence on the weights enters only via the particle density, \( n := \mathrm{Tr}[\hat{\Gamma}^w \hat{n}] = \sum_{\nu} u_{\nu} n_{\nu} \), of the ensemble. Eqs (6) [11], and their extension to next leading order in \( \gamma \) discussed later, are the central result of this work. In this context, the SCE result for ground states [16, 19] becomes a special case of the above more general result.

Proof of Eq. (6). Here, we shall guide the reader through the main steps and physics behind eq. (6). A

![FIG. 1. Ratio of quantum and classical interaction energies for two electrons in an Harmonic well. Shows six triplet (top) and singlet (bottom) energies. Scaled densities, 4πr^2n(r), of the states are also shown for the case λ = 50.](image-url)
full proof is reported in Section 1 of the Supplementary Material (Supp. Mat. Sec. 1).

The salient features of eq. (3) can be already grasped by observing the behaviour of an interacting system as interactions are increased. We choose two-electron Harmonium in which two electrons interact in an external potential \( e_{\text{ext}} = \frac{1}{2} r^2 \) with an interaction strength \( \lambda \).

The scaled classical interaction energy of this system is \( V_{\text{cl}} = 0.7937 A^{2/\beta} \). Quantum solutions may be found numerically. Details are in Supp. Mat. Sec. II. Figure 1 shows the interaction energies, \( V_{\text{cl}} := (\kappa | V_{\text{ee}} | \kappa) \), of six low-lying spherically symmetric triplet \((^3S)\) and singlet \((^1S)\) states. It is clear that quantum and classical interaction energies all become the same as \( \lambda \) is increased—i.e., all excitation tend toward the same classical limit.

To prove our result for EDFT we need to consider a similar physical setting (\( \lambda \to \infty \)), in which instead of fixing the external potential we fix the ensemble density, containing the excited states we want to treat. Proving eq. (3) then entails showing that the degeneracy behaviour carries through to systems in which the density is kept fixed. Our argument involves the expansion of wave functions for large but finite interaction strengths, \( 1 \geq 2 \) around the strictly correlated limit. In this effectively classical limit, which yields the leading term as \( \lambda \to \infty \) of the ground-state universal functional \( F'[n] \) \( ] \), the \( N \)-body distribution of an \( N \)-electron system is \( P_N[n](r_1 \cdots r_N) = \int \frac{n^N(s)}{N!} \prod_{i=1}^{N} \delta(r_i - f_i(s))ds \) which leads to \( F^{\lambda \to \infty}[n] \to \lambda V_{\text{ee}}^{SCE}[n] = \lambda \Sigma_{i=1}^{N} n(r_i) E_{\text{free},r}(r_i) \). Here, \( f_i(r) \) are co-motion maps that preserve the density and the indistinguishability of electrons. \( \frac{1}{2} [20] \)

At large but finite \( \lambda \) we construct orthonormal wave functions, \( |\kappa\rangle \), based on quantum harmonic oscillators (QHO) around the strictly-correlated distribution, \( P_N[n] \). \( \frac{1}{2} [22] \) The QHOS act on curvilinear coordinates orthogonal to the manifold parameterized by the co-motion functions; and contribute at \( O(\sqrt{\lambda}) \) in the kinetic and potential energies. Prima facie, the wave functions \( |\kappa\rangle \) have different densities. However, it is also possible to quantize along the manifold, which contributes only at \( O(1) \) in kinetic energy and is amenable to the Harmonian construction \( \frac{1}{2} [31] \) of orthogonal orbitals yielding density \( n \). We thereby obtain a countable number of orthonormal wavefunctions that all have the same density \( n \), and the same energy up to \( O(1) \). Thus, \( \lambda V_{\text{ee}}^{SCE}[n] = V_{\text{ee}}^{SCE}[n] \) and eq. (3) follows from the equivalence of \( \lambda \to 0^+ \) and \( \lambda \to \infty \) in eq. (3).

Implications. Having demonstrated the most fundamental result of this work, we turn below to the most immediate and far reaching consequences. We can extract the ensemble Hxc-energies in the SCE limit, as follows. First, consider

\[
\lambda V_{\text{ee}}^{\lambda,w}[n] = \lim_{n \to 0^+} \frac{F^{\lambda+w,\lambda,w}[n] - F^{\lambda,\lambda,w}[n]}{\eta} \geq 0 \quad \text{for} \quad \lambda \to 0^+ \quad (7)
\]

and note that the ‘Hx’ component is recovered as \( \lambda V_{\text{ee}}^{\lambda,w}[n] \geq V_{\text{ee}}^{\lambda,w}[n] \geq V_{\text{ee}}^{\text{SCE},w}[n] \). Integration yields,

\[
\lambda V_{\text{ee}}^{\lambda,w}[n] = \int_{0}^{1} V_{\text{ee}}^{\lambda,w}[n] d\lambda \quad (8)
\]

The latter is the adiabatic connection formula (ACF)—here, stated for excitation ensembles without singling out any pre-assumed Hartree. Scaling gives \( \lambda V_{\text{ee}}^{w}[n] = 2^{\frac{1}{2}} \int_{0}^{1} \gamma V_{\text{ee}}^{\lambda,w}[n] d\lambda \) and, thus, we conclude that

\[
\lim_{\gamma \to 0^+} \lambda V_{\text{ee}}^{1,w}[n] = \gamma V_{\text{ee}}^{SCE}[n] \quad (9)
\]

Eq. (9) shows that in the low-density limit (i.e., in the strictly correlated limit), not only \( \lambda V_{\text{ee}}^{w}[n] \) [see (5)] but also \( \lambda V_{\text{ee}}^{w}[n] \) depend on the excitation structure only trivially, via the ensemble particle density.

Let us demonstrate this result in an example, by constructing a proof-of-principle approximation that depends on it. The simplest local density approximation for ensembles (ELDA) involves setting,

\[
\lambda V_{\text{ee}}^{w}[n] := \lambda V_{\text{ee}}^{w}[n] + \int n(r) \epsilon_{xc}(n) d\gamma \quad (10)
\]

where \( \epsilon_{xc}(n) \) is a parametrisation of the homogeneous electron gas ground state energy; and the ensemble Hartree energy, \( \lambda V_{\text{ee}}^{w}[n] := \sum_{\kappa} \epsilon_{xc}(n_{\kappa}) \), is obtained using the fluctuation-dissipation theorem (FDT). \( \frac{1}{2} [6] \) \( \lambda V_{\text{ee}}^{w}[n] \) is the usual Hartree functional and \( \epsilon_{xc} \) are Kohn-Sham states.

However, this only minimally uses properties of the SCE and the behaviour uncovered here for the low density limit, via constraints on \( \epsilon_{xc} \). Eq. (10) and Eq. (9) provide scope for approximations that are tailored to low density systems. Therefore, let us instead write,

\[
\lambda V_{\text{ee}}^{w}[n] = \frac{\lambda V_{\text{ee}}^{w}[n] + \lambda V_{\text{ee}}^{SCE}[n]}{\lambda} \quad (11)
\]

where,

\[
\lambda V_{\text{ee}}^{w}[n] = \int_{0}^{1} \left( \lambda V_{\text{ee}}^{w}[n] - \lambda V_{\text{ee}}^{SCE}[n] \right) d\lambda \quad (12)
\]
We therefore make an LDA for eq. [12], using,
\[
\Delta \mathcal{E}_{\text{Hac}}^{\text{LDA, } w} [n] := \mathcal{E}_{\text{H, FDT}} [n] - E_{\text{H}} [n] + \int n(r) \left( e_{\text{sc}} (n) - e_{\text{sc}}^{\text{LSCF}} (n) \right) d\mathbf{r}, \tag{13}
\]
which we call the local SCE (LSCE) approximation. Here, the strictly correlated electron LDA, \( E_{\text{H}} [n] + E_{\text{xc}}^{\text{LDA-LSE}} [n] \), is subtracted from eq. [10]. Recent work [33, 34] rigorously established that \( e_{\text{sc}}^{\text{LSE}} (n) = -c_{\infty} n^{1/3} \) where \( c_{\infty} = 1.444 \) is the Madelung constant of the bcc Wigner crystal [35], which we also use in a modified PW92 [36] LDA parametrisation. \( V_{\text{exc}}^{\text{LSE}} [n] \) is evaluated per Ref. [16]. Technical details in Supp. Mat. Sec. III.

To test the performance of these two approximations [eqs. [10] and [13]], we investigate four-electron Harmonium for which high quality reference data [37] exists [eqs. (10) and (13)]. We furthermore show how recent progress in strongly correlated systems; and serve as a template for approximations can offer practical improvements in strongly correlated systems; and serve as a proof of concept of the immediate importance of the SCE limit in EDFT. In a more technical report to be submitted elsewhere, we will further show how recent progress for ground state DFT can be imported in EDFT to work also for excitations.

We next launch ourselves into suggesting a major change in the way EDFT may be formulated. To this end, first define \( \Delta \mathcal{E}_{\text{Hac}}^{\text{LDA}} := T^{\text{SCE, } w} - T_{s}^{w} \), which is to be contrasted with [12]. Hence, we may reformulate EDFT by using as an auxiliary reference a system of strictly-correlated electrons (SCE). In other words, we may write,
\[
\mathcal{F}^{1, w} [n] := T^{\text{SCE, } w} [n] + V_{\text{exc}}^{\text{SCE}} [n], \tag{14}
\]
where all ensemble effects are captured in the kinetic energy term, \( T^{\text{SCE, } w} \). Convenietly, we may evaluate,
\[
T^{\text{SCE, } w} [n] = \int_{1}^{\infty} \frac{T^{\lambda, w}}{\lambda^{2}} d\lambda, \tag{15}
\]
on an adiabatic connection, which can be verified using the (variational) identity \( T^{\lambda, w} = -\lambda^{2} \partial_{\lambda} T^{3, w} [\lambda] \). Eq. [15] generalizes results for the ground state-only case [39, 41] to the ensembles considered in this work.

Next, as anticipated, we want to show that \( T^{\lambda \to \infty} [\gamma \to 0] \) is independent of weights to leading order, which leads to \( T^{\text{SCE, } w} [n_{\gamma \to 0}] \) also independent of weights.

Next, as anticipated, we want to show that \( T^{\lambda \to \infty} [\gamma \to 0] \) is independent of weights to leading order, which leads to \( T^{\text{SCE, } w} [n_{\gamma \to 0}] \) also independent of weights. First, ensemblization of known results [17, 30, 42] gives \( T^{\lambda \to \infty, w} \to \frac{\lambda^{2}}{2} F^{\text{ZPE, } w} \), where \( F^{\text{ZPE, } w} \) involves \( \lambda \)-normalized zero point energy (ZPE) of the QHOs, \([\lambda^{i}]\), introduced earlier. Hence, \( T^{\lambda, w} \) becomes independent of weights if we can show that \( F^{\text{ZPE, } w} [\gamma \to 0] \) is independent of weights. Note, Supp. Mat. Sec. I naturally covers this case — for guidance, below, we touch on essential steps and consequences.

The Harriman construction introduced earlier (also, Supp. Mat. Sec. I B) yields \( \langle \gamma^{i} | T | \lambda^{i} \rangle = (0^{i} | \tilde{T} | 0^{i}) + O(1) \) for \( \lambda \to \infty \). Thus, \( T^{\lambda, w} = \sum_{\gamma} w_{\gamma} \langle \gamma^{i} | T | \lambda^{i} \rangle = (0^{i} | \tilde{T} | 0^{i}) + O(1) \) is independent of weights to leading order, giving weight-independent,
\[
F^{\text{ZPE, } w} [\gamma \to 0] = \lim_{\lambda \to \infty} 2 T^{\lambda, w} [\gamma \to 0] = F^{\text{ZPE}} [\gamma \to 0]. \tag{16}
\]
Here, \( F^{\text{ZPE}} [\gamma \to 0] \) is the well-studied ground state functional [17, 29, 30], but evaluated on the ensemble density. Using eq. [16] in [15], and applying scaling laws, finally yields,
\[
\lim_{\gamma \to 0^{+}} T^{\text{SCE, } w} [n_{\gamma}] = F^{\text{ZPE}} [n_{\gamma}] = \gamma^{3/2} F^{\text{ZPE}} [\gamma \to 0]. \tag{17}
\]
Thus, we conclude that \( T^{\text{SCE, } w} [n_{\gamma}] \) is independent of the ensemble weights in the low-density limit. Details of scaling are in Supp. Mat. Sec. IV.

Last but not least, it follows from eqs. [6], [14], [17], and a little additional work, that
\[
\mathcal{F}^{1, w} [n_{\gamma}] \to \gamma V_{\text{exc}}^{\text{SCE}} [\gamma] + \gamma^{3/2} F^{\text{ZPE}} [\gamma] + O(\gamma^{2}) \tag{18}
\]
is independent of the weights in its leading two terms. Weight dependence, unavoidably, appears at \( O(\gamma^{2}) \).

Summary and conclusions. This work has revealed an astonishing fact: as central as strong correlations can be for excitations, the tools needed to capture leading effects in the strictly correlated limit via ensemble DFT can be imported unchanged from progress made for ground states. Thus, we have proved that, in the low-density limit, the \( w \)-universal functional \( F^{\lambda, w} \) and its key components all approach weight-independent forms [see eqs. [6], [14], [17] — given by the corresponding ground state forms, but evaluated on ensemble densities. Next, we have illustrated how the aforementioned results on the universal functional transfer to the exchange-correlation energies of excitations. As proof of concept, we have derived an approximation (LSCE) built around the SCE limit, which out-performed a more conventional
ELDA for predicting excited states of four-electron Hamiltonian in the strongly-correlated regime.

As an additional implication, we rationalized a reformulation of EDFT in which the Kohn-Sham system for excited ensembles is replaced with a system of strictly-correlated electrons. This further adapts formal EDFT to apply non-empirically and universally on excitations in the low-density limit [eq. (18)] of all systems – of which, Wigner systems are an outstanding examples. Overall, the results presented here open constructive first principles pathways to novel ensemble density functional approximations, based on strictly correlated physics.

TG was supported by the Australian Research Council (ARC) Discovery Program (project DP200100033). DPK and PG-G were supported by the Netherlands Organisation for Scientific Research (NWO) under Vici grant 724.017.001.

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