Ensemblization of density-functional theory: Insight from the fluctuation-dissipation theorem

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Density functional theory can be generalized to mixtures of ground and excited states, for the purpose of determining energies of excitations using low-cost density functional approximations. Adapting approximations originally developed for ground states to work in the new setting would fast-forward progress enormously. But, previous attempts have stumbled on daunting fundamental issues. Here we show that these issues can be prevented from the outset, by using a fluctuation dissipation theorem (FDT) to dictate key functionals. We thereby show that existing exchange energy approximations are readily adapted to excited states, when combined with a rigorous *exact* Hartree term that is different in form from its ground state counterpart, and counterparts based on ensemble ansatzë. Applying the FDT to correlation energies also provides insights into ground state-like and ensemble-only correlations. We thus provide a comprehensive and versatile framework for ensemble density functional approximations.

Introduction: Averages and fluctuations are essential concepts to make sense of data of any sort. In physics, these quantities are also used to explore the formal relationships of theories and approximations. Via Feynman's path integrals [1], for example, classical physics itself can be seen to emerge in terms of an averaged path that, in the limit of $\hbar \rightarrow 0$, dominates over otherwise irreducible quantum fluctuations. In condensed-matter physics, to mention another important example, mean-field approximations are used to formalize the concept of the order parameters and their estimations; [2] consideration of fluctuations are then necessary to fully characterize second-order phase transitions.

Density functional theory (DFT) [3, 4] can also be conceptualized in terms of averages and fluctuations. In one and the same step [4] it overcomes the semiclassical Thomas-Fermi approximation [5] *and* the mean-field approximation by mapping the original many-body problem onto a one-electron problem capturing key fluctuations – the exchange and correlation (xc) terms in DFT parlance. Simple and effective xc approximations for these fluctuations have enabled DFT to become the workhorse of electronic structure calculations. [6]

In this Letter, we turn to a generalization of DFT through which excitation energies (not just the ground state energy) of a many-electron system can be computed; and invoke an extension of the (so-called) fluctuation dissipation theorem (FDT) to effectively deal with fluctuations relative to excited states. We shall refer to this formulation of DFT [7, 8] as "ensemble DFT" (EDFT) but, strictly, we deal with EDFT for

excited states (rather than other formulations such as the one that accounts for states with different particle numbers [9]). EDFT is a primary competitor of linear-response time-dependent DFT for the evaluation of excitation energies. Previous attempts at deriving improved approximations have, however, stumbled on a series of difficulties. Progress has recently attained a faster pace due to new fundamental and practical results [10–27].

Current wisdom stresses that ensembles are best dealt with by treating Hartree-Fock (Hartree-exchange, Hx, in DFT) energies as a "conjoint" unit. [10, 18] Indeed, two of the authors have previously strongly espoused this approach. [21] But, much of the progress in devising density functional approximations (DFA) for ground states has been enabled by treating Hartree (H) and exchange (x) components on different footings: with the former almost always employed in its exact form and the latter approximated in full, $E_{\text{Hxc}} \approx E_{\text{H}} + E_{\text{xc}}^{\text{DFA}}$, (standard approximations) or partially, $E_{\text{Hxc}} \approx \alpha E_{\text{Hx}} + (1-\alpha)(E_{\text{H}} + E_{\text{x}}^{\text{DFA}}) + E_{\text{c}}^{\text{DFA}}$ (hybrid approximations). DFAs of this form have been refined over decades to balance accuracy and practicality. It is imperative that we can transfer such experience to excited states. Attempts so far have been positive, but of somewhat narrow scope. Has the time come to surrender?

Quite on the contrary, here we show that the 'Hx' energy in EDFT can be split into disjoint Hartree-like and exchange-like contributions, which avoid the disastrous issues encountered in previous proposals. We derive this decomposition with the help of a generalization of the FDT to passive states – ensemble states whose weights

are non-increasing with increasing energy and are thereby amenable to EDFT treatment. [28] The same FDT also identifies key components of the corresponding correlation energy functional. Hence we draw a complete, user friendly, theoretical roadmap for developing novel approximations for excited states – which builds from fundamental principles without sacrificing previous work.

We begin with a brief introduction to EDFT for excited states; and illustrate the problem that is solved in this work. Then, we work out the details of the main results and see them in action on prototypical cases. We first work on the Hartree and exchange energy functionals, then complete the development by deriving corresponding results for correlations, before concluding.

Crash-course in EDFT: Consider the Hamiltonian $\hat{H} = \hat{T} + \hat{W} + \hat{V}_{\text{ext}}$ where $\hat{T}$ is the kinetic energy of the particles (electrons, in our case), $\hat{W}$ is the two-body interaction (typically the Coulomb interaction), and $\hat{V}_{\text{ext}}$ is an external potential (typically the scalar electric potential exerted by atomic nuclei on electrons).

We are often interested in a finite set of states with different energies (or symmetries when degenerate) but the same number of electrons – typically a handful of low-lying solutions of $\hat{H}|\kappa\rangle = E_\kappa|\kappa\rangle$. These form the ensemble described by the operator $\hat{\Gamma}^{\boldsymbol{w}} = \sum_\kappa w_\kappa|\kappa\rangle\langle\kappa|$ where a set of prescribed mixing weights $w_\kappa \geq 0$ (collectively, $\boldsymbol{w}$) are taken as non-increasing (i.e., $w_\kappa \leq w_{\kappa'}$ for $E_\kappa \geq E_{\kappa'}$) and normalised $\sum_\kappa w_\kappa = 1$. Such ensembles belong to the class of passive states [29]. Issues due to spurious breaking of symmetries are avoided by assigning equal weights to multiplets to obtain a totally symmetric passive state. [30] The average of an operator, $\hat{O}$, can be written as, $\text{Tr}[\hat{\Gamma}^{\boldsymbol{w}}\hat{O}]$.

$\hat{\Gamma}^{\boldsymbol{w}}$ fulfills an extended variational principle [28] according to which

$$\text{Tr}\big[\hat{\Gamma}^{\boldsymbol{w}}_{\text{trial}}\hat{H}\big] \geq \mathcal{E} = \text{Tr}\big[\hat{\Gamma}^{\boldsymbol{w}}\hat{H}\big] . \qquad (1)$$

Thus, $\mathcal{E} = \inf_{\hat{\Gamma}^{\boldsymbol{w}}_{\text{trial}}} \text{Tr}[\hat{\Gamma}^{\boldsymbol{w}}_{\text{trial}}\hat{H}]$ where the argument for the infimum (usually a minimum), $\hat{\Gamma}^{\boldsymbol{w}}_{\text{trial}} = \sum_\kappa w_\kappa|\kappa_t\rangle\langle\kappa_t|$, involves prescribed weights, $\boldsymbol{w}$, and mutually orthonormal trial wavefunctions $|\kappa_t\rangle$.

In EDFT we compute the average energy, $\mathcal{E}$, by minimizing the following functional of the ensemble-particle density, n, [7, 8]

$$\mathcal{E}^{\boldsymbol{w}}[n] = \mathcal{T}^{\boldsymbol{w}}_s[n] + \mathcal{E}^{\boldsymbol{w}}_{\text{Hxc}}[n] + \int n(\boldsymbol{r})v_{\text{ext}}(\boldsymbol{r})d\boldsymbol{r}. \qquad (2)$$

By analogy with standard DFT, $\mathcal{T}^{\boldsymbol{w}}_s[n] = \min_{\hat{\Gamma}^{\boldsymbol{w}}_{\text{trial}} \to n} \text{Tr}[\hat{\Gamma}^{\boldsymbol{w}}_{\text{trial}}\hat{T}]$, is the kinetic energy of the Kohn-Sham (KS) system reproducing the particle density of the ensemble; the minimum is attained at $\hat{\Gamma}_s \equiv \sum_\kappa w_\kappa|\kappa_s\rangle\langle\kappa_s|$. [31] $\mathcal{E}^{\boldsymbol{w}}_{\text{Hxc}}[n]$ subsumes the Hartree, exchange, and correlation energies for the ensemble. Note that in writing the energy functionals we use capital calligraphic letters to refer to energies of mixed states and capital Roman letters to refer to energies of pure state or their components, respectively. The superscript $\boldsymbol{w}$ indicates quantities that explicitly depend on the weights, meaning eq. (2) describes a different functional for every choice of $\boldsymbol{w}$. Varying $\boldsymbol{w}$ lets us, e.g., obtain excitation energies. The superscript shall henceforth be dropped for brevity.

Thus one can define a KS Hamiltonian $\hat{H}_s = \hat{T} + \hat{V}_s[n]$ which yields the same *ensemble* density, $n = \text{Tr}[\hat{\Gamma}_s\hat{n}] = \text{Tr}[\hat{\Gamma}\hat{n}]$, as the interacting system when the KS ensemble operator $\hat{\Gamma}_s \equiv \sum_\kappa w_\kappa|\kappa_s\rangle\langle\kappa_s|$ minimizes $\text{Tr}[\hat{\Gamma}_s\hat{H}_s]$. Following standard derivations one can show that the effective KS potential is given by $v_s \equiv v_{\text{ext}} + \frac{\delta\mathcal{E}_{\text{Hxc}}}{\delta n}$. We emphasize that ambiguities in constructing $\hat{\Gamma}_s$ due to extra (noninteracting) degeneracies are removed by choosing the κ_s's to belong to the same irreducible representation as the κ's; hence, the κ_s's may be configuration-state functions (CSFs) (i.e., finite linear combinations of Slater determinants). This allows us to preserve all the relevant symmetries, consistently. [32]

In particular, because we work at the level of totally symmetric ensembles, ensembles KS densities and corresponding KS kinetic energies can *still* be computed by referring to a "minimal" set of single Slater determinants, $\{\Phi_\kappa\}$, from which all the relevant $|\kappa_s\rangle$ states can be constructed. Therefore, $n \equiv \sum_i f_i|\phi_i|^2$, and, $\mathcal{T}_s = -\frac{1}{2}\sum_i f_i \int d\boldsymbol{r}\phi^*_i\nabla^2\phi_i$, involve one-body orbitals obeying the ensemble KS equation, $\{-\frac{1}{2}\nabla^2 + v_s[n](\boldsymbol{r})\}\phi_i(\boldsymbol{r}) = \epsilon_i\phi_i(\boldsymbol{r})$. Differences from ground state KS theory appear in the fractional occupation factors, $f_i = \sum_\kappa w_\kappa\theta_{i,\kappa}$, which are ensemble averages of total ($\uparrow$, $\downarrow$ or $\uparrow\downarrow$) occupation factors, $\theta_{i,\kappa}$, for orbital i in state Φ_κ; and also in the *form* of the Hxc energy functional, $\mathcal{E}_{\text{Hxc}}$ (see later).

A long standing struggle: Recall, in DFT we define the Hartree energy as,

$$E_{\text{H}}[n] \equiv \tfrac{1}{2} \int d\boldsymbol{r}d\boldsymbol{r}'\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \qquad (3)$$

and, correspondingly, the exchange energy as,

$$E_{\text{x}}[n] \equiv -\frac{1}{2} \int d\boldsymbol{r}d\boldsymbol{r}'\frac{|\rho_s(\boldsymbol{r}, \boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \equiv E_{\text{x}}[\rho_s] . \qquad (4)$$

Here, $\rho_s(\boldsymbol{r}, \boldsymbol{r}') = \sum_i f_i\phi^*_i(\boldsymbol{r})\phi_i(\boldsymbol{r}')$ is the KS one-body reduced density matrix (1-RDM) obeying $\rho_s(\boldsymbol{r}, \boldsymbol{r}) = n(\boldsymbol{r})$. Note that $\rho_s(\boldsymbol{r}, \boldsymbol{r}')$ is a functional of the particle density, $\rho_s(\boldsymbol{r}, \boldsymbol{r}') = \rho_s[n](\boldsymbol{r}, \boldsymbol{r}')$, because the KS orbitals have an implicit dependency on n.

A natural ansatz (Ans1) to extend the above equations to EDFT is to replace the density and 1-RDM by their ensemble versions. Then, $\mathcal{E}^{\text{Ans1}}_{\text{H}}[n] := E_{\text{H}}[\sum w_\kappa n_{s,\kappa}(\boldsymbol{r})] = E_{\text{H}}[\sum f_i|\phi_i(\boldsymbol{r})|^2]$ and $\mathcal{E}^{\text{Ans1}}_{\text{x}}[n] := E_{\text{x}}[\sum w_\kappa\rho_{s,\kappa}(\boldsymbol{r}, \boldsymbol{r}')] = E_{\text{x}}[\sum f_i\phi^*_i(\boldsymbol{r})\phi_i(\boldsymbol{r}')]$, where $\rho_{s,\kappa} = \langle\kappa_s|\hat{\rho}|\kappa_s\rangle$ (similarly for $n_{s,\kappa}$). Here, both $n_{s,\kappa}$ and $\rho_{s,\kappa}$ are functionals of the overall density n. Ans1 is appealing because it allows standard DFA to be readily reused in EDFT [7, 8].

But, in practice, Ans1 has disastrous consequences. "Ghost interaction errors" (GIE) badly affect both Hartree and exchange, but do not cancel each other. GIE can be understood as a generalization of the one-particle self-interaction error, in which electrons spuriously interact with 'ghost' counterparts in a *different* replica in the ensemble, leading to errors. GIE corrections have traditionally been worked out *ad hoc*. [13, 33, 34] Recent work [17, 26] has made interesting progress in using Ans1 together with weight-dependent xc-approximations.

GIE can sometimes be avoided by considering a different and, arguably, better ansatz (Ans2),

$$\mathcal{E}_{\mathrm{H}}^{\mathrm{Ans2}}[n] := \sum_{\kappa} w_{\kappa} E_{\mathrm{H}}[n_{s,\kappa}] \,, \qquad (5)$$

$$\mathcal{E}_{\mathrm{x}}^{\mathrm{Ans2}}[n] := \sum_{\kappa} w_{\kappa} E_{\mathrm{x}}[\rho_{s,\kappa}] \,. \qquad (6)$$

Ans2 is appealing, as it suggests that ground state functionals may be upgraded to ensembles via weighted averages of their "clones". Ans2, however, falls short in certain cases, such as difficult spin-multiplets (see below).

All issues with the previous definitions for $\mathcal{E}_{\mathrm{H}}[n]$ and $\mathcal{E}_{\mathrm{x}}[n]$ are resolved by working at the level of a *conjoint* $\mathcal{E}_{\mathrm{Hx}}[n]$ which is problem-free by construction: [21]

$$\mathcal{E}_{\mathrm{Hx}}[n] \equiv \lim_{\lambda \to 0^+} \frac{\mathcal{F}^{\lambda}[n] - \mathcal{T}_s[n]}{\lambda} \equiv \mathrm{Tr}[\hat{\Gamma}^{0^+}\hat{W}] \,. \qquad (7)$$

Eq. (7) is successful (and maximally GIE free) because it is written in terms of the well-defined universal functional $\mathcal{F}^{\lambda}[n] = \min_{\hat{\Gamma} \to n} \mathrm{Tr}[\hat{\Gamma}(\hat{T} + \lambda\hat{W})] \equiv \mathrm{Tr}[\hat{\Gamma}^{\lambda}(\hat{T} + \lambda\hat{W})]$, where $\hat{\Gamma}^{\lambda} = \sum_{\kappa} w_{\kappa}|\kappa^{\lambda}\rangle\langle\kappa^{\lambda}|$ involves eigen-solutions, $|\kappa^{\lambda}\rangle$, of $\{\hat{T} + \lambda\hat{W} + \hat{V}^{\lambda}\}|\kappa^{\lambda}\rangle = E_{\kappa}^{\lambda}|\kappa^{\lambda}\rangle$); with $v^{\lambda}[n]$ chosen to ensure $n = \mathrm{Tr}[\hat{\Gamma}^{\lambda}\hat{n}]$ regardless of λ. When totally symmetric ensembles are employed, $\hat{\Gamma}^{\lambda}[n]$, is also a unique functional of n and $\boldsymbol{w}$ [24] so we restrict to this useful case. We also assume that the ordering of states is preserved (or preservable) along the adiabatic path $0 < \lambda \leq 1$. [35] Note, we can now rigorously define $\hat{\Gamma}_s \equiv \lim_{\lambda \to 0^+} \hat{\Gamma}^{\lambda} \equiv \hat{\Gamma}^{0^+}$, $\mathcal{T}_s \equiv \mathcal{F}^0$ and $\mathcal{E}_{\mathrm{Hxc}} \equiv \mathcal{F}^1 - \mathcal{T}_s$.

The conjoint treatment leads to well-defined "ensemblized" versions of Hartree-exchange [21] and correlations [23], albeit with some additional complications compared to the ground state. But, *keeping 'H' and 'x' joint together loses the long experience gained in DFAs which treat them separately.* This is the most urgent drawback of eq. (7) as it hampers access to prior work.

Its impact can be easily seen by considering the following ensemble generalization of conventional DFAs:

$$\mathcal{E}_{\mathrm{xc}}^{\mathrm{DFA}}[n] := \sum_{\kappa} w_{\kappa} E_{\mathrm{xc}}^{\mathrm{DFA}}[n_{s,\kappa}] \,. \qquad (8)$$

Eq. (8) involves an ensemble average of a standard DFA (e.g. PBE) for xc, along the lines of Ans2. It can thus draw from decades of work on DFA development. But, it does not correct for *all* ghost interactions. Evaluating the ensemble energy, $\mathcal{E} = \mathcal{T}_s + \mathcal{E}_{\mathrm{H}} + \mathcal{E}_{\mathrm{xc}}^{\mathrm{DFA}} + \int d\boldsymbol{r}nv_{\mathrm{ext}} + \mathcal{E}_{\mathrm{c}}^{\mathrm{DD}}$ (the final term is discussed below) therefore requires choosing a GIE-free Hartree term to pair with eq. (8). Efforts to develop new approximations can thus be fast-forwarded, by ensuring that $\mathcal{E}_{\mathrm{H}}$ captures the energy components that would otherwise be missed. Below, we will show that the ideal $\mathcal{E}_{\mathrm{H}}$ *must* go beyond $\mathcal{E}_{\mathrm{H}}^{\mathrm{Ans2}}$. Furthermore, our derivation also sheds light on, $\mathcal{E}_{\mathrm{c}}^{\mathrm{DD}}$: the recently discovered "density-driven" correlation energy, [23] discussed in recent work. [23, 25]

Resolution: First, recall that the average of the interaction can be expressed as follows: $\mathrm{Tr}[\hat{\Gamma}^{\lambda}\hat{W}] \equiv \int \frac{d\boldsymbol{r}d\boldsymbol{r}'}{2|\boldsymbol{r}-\boldsymbol{r}'|} n_2^{\lambda}(\boldsymbol{r}, \boldsymbol{r}')$ where, $n_2^{\lambda}(\boldsymbol{r}, \boldsymbol{r}') = \mathrm{Tr}[\hat{\Gamma}^{\lambda}\hat{n}(\boldsymbol{r})\hat{n}(\boldsymbol{r}')] - n(\boldsymbol{r})\delta(\boldsymbol{r} - \boldsymbol{r}')$. The crucial second step is to use the FDT for passive states – stated and proved in the Supplementary Material [36] – to write,

$$\mathrm{Tr}[\hat{\Gamma}^{\lambda}\hat{n}(\boldsymbol{r})\hat{n}(\boldsymbol{r}')] = P^{\lambda}(\boldsymbol{r}, \boldsymbol{r}') - \int_{0^-}^{\infty} \frac{d\omega}{\pi} \Im\chi^{\lambda}(\omega, \boldsymbol{r}, \boldsymbol{r}') \,, \qquad (9)$$

in terms of the ensemble (retarded density-density) response, χ^{λ}, of the considered passive state, $\hat{\Gamma}^{\lambda}$; and a relevant pair-density,

$$P^{\lambda}(\boldsymbol{r}, \boldsymbol{r}') = \sum_{\kappa\kappa'} \min[w_{\kappa}, w_{\kappa'}] n_{\kappa\kappa'}^{\lambda}(\boldsymbol{r}) n_{\kappa'\kappa}^{\lambda}(\boldsymbol{r}') \,, \qquad (10)$$

where $n_{\kappa\kappa'}^{\lambda} \equiv \langle\kappa^{\lambda}|\hat{n}|\kappa'^{\lambda}\rangle$. Note, $P^{\lambda}(\boldsymbol{r}, \boldsymbol{r}') \equiv \sum_{\kappa} w_{\kappa} n_{\kappa\kappa}^{\lambda}(\boldsymbol{r}) n_{\kappa\kappa}^{\lambda}(\boldsymbol{r}') + \sum_{\kappa'<\kappa} w_{\kappa}[n_{\kappa\kappa'}^{\lambda}(\boldsymbol{r}) n_{\kappa'\kappa}^{\lambda}(\boldsymbol{r}') + \boldsymbol{r} \leftrightarrow \boldsymbol{r}']$ entails two terms: the first term resembles a typical mean-field-like contribution and involves products of pure state densities ($n_{\kappa\kappa}^{\lambda}$); the second involves *off-diagonal* matrix elements ($n_{\kappa\neq\kappa'}^{\lambda}$) which represent *extra* ensemble-specific fluctuations that are absent in pure ground states.

Next, by invoking the analogous FDT relationships from ground state DFT functionals we can establish the EDFT counterparts that account for degeneracies and excited states. Any non-degenerate ground state obeys $E_{\mathrm{x}} = -\int \frac{d\boldsymbol{r}d\boldsymbol{r}'}{2|\boldsymbol{r}-\boldsymbol{r}'|}[n(\boldsymbol{r})\delta(\boldsymbol{r} - \boldsymbol{r}') + \int_0^{\infty} \frac{d\omega}{\pi} \Im\chi_s(\omega, \boldsymbol{r}, \boldsymbol{r}')]$, where χ_s is the KS response of the ground state. This relationship is useful for constructing and understanding DFAs. It is therefore natural to similarly define,

$$\mathcal{E}_{\mathrm{x}}^{\mathrm{FDT}}[n] \equiv -\int \frac{d\boldsymbol{r}d\boldsymbol{r}'}{2|\boldsymbol{r}-\boldsymbol{r}'|}\bigg\{ n(\boldsymbol{r})\delta(\boldsymbol{r}-\boldsymbol{r}')$$
$$+ \int_{0^-}^{\infty} \frac{d\omega}{\pi} \Im\chi_s[n](\boldsymbol{r}, \boldsymbol{r}'; \omega)\bigg\} \,, \qquad (11)$$

where $\chi_s \equiv \chi^{\lambda=0^+}$ is the ensemble KS response function for the considered passive state, $\hat{\Gamma}^{0^+}$. Finally, using the FDT [eq. (9)] with eq. (7) dictates the form of the corresponding EDFT Hartree functional: $\mathcal{E}_{\mathrm{H}}^{\mathrm{FDT}} = \mathcal{E}_{\mathrm{Hx}} - \mathcal{E}_{\mathrm{x}}^{\mathrm{FDT}}$, or,

$$\mathcal{E}_{\mathrm{H}}^{\mathrm{FDT}}[n] = \int \frac{d\boldsymbol{r}d\boldsymbol{r}'}{2|\boldsymbol{r}-\boldsymbol{r}'|} P_s[n](\boldsymbol{r}, \boldsymbol{r}') \,. \qquad (12)$$

$P_s \equiv P^{\lambda=0^+}$ is defined via eq. (10) with $n_{s,\kappa\kappa'} \equiv n_{\kappa\kappa'}^{\lambda=0^+}$. Thus, only non-interacting KS states are involved. [21, 24] $P^\lambda[n]$ and $\chi^\lambda[n]$ are uniquely defined by $v^\lambda[n]$ and w, meaning eqs (9)–(12) are functionals of the density.

Eq. (12) reduces to the usual *semi-classical* mean-field approximation for a non-degenerate ground state (gs), with $P_s[n_{gs}](r, r') = n_{gs}(r)n_{gs}(r')$, since $w_{gs} = 1$ and $w_\kappa = 0$ otherwise. But in general, eq. (12) involves products between off-diagonal matrix elements of the density, from eq. (10). Disregarding these off-diagonal terms, i.e., replacing P_s by $\sum_\kappa w_\kappa n_{s,\kappa\kappa}(r)n_{s,\kappa\kappa}(r')$, reduces $\mathcal{E}_H^{FDT}$ to $\mathcal{E}_H^{Ans2}$ and involves direct integral terms only. The off-diagonal terms lead to additional exchange integrals in $\mathcal{E}_H^{FDT}$ which, because $\mathcal{E}_H^{FDT} + \mathcal{E}_x^{FDT} = \mathcal{E}_{Hx}$, must provide contributions that are missed by Ans2. Applying Slater-Condon rules to eq. (7) *must* give equivalent terms – the FDT assigns these terms unambiguously to H or x.

Last but not least, an additional nice property of $\mathcal{E}_H^{FDT}$ and $\mathcal{E}_x^{FDT}$ is that their integrands are invariant to rotations around axes of symmetry, in contrast to Ans2 which has an unphysical dependence on the choice of axes. Details are in the Supplementary Material. [36]

Illustrative examples: To keep the discussion of key results simple, let us work with a two electron system. In KS theory, the ground state has a doubly occupied orbital, ϕ_0, whereas the low-lying singlet/triplet excitations involve ϕ_0 and ϕ_1 together.

First, consider $\hat{\Gamma}_s^{ST} = w_S|S_0\rangle\langle S_0| + w_T\hat{\Gamma}_T$ consisting of the KS singlet ground state (S_0) and the lowest-lying KS triplet $\hat{\Gamma}_T = \frac{1}{3}\sum_{S_z=1,0,-1}|T_{S_z}\rangle\langle T_{S_z}|$ mixed with weights $w_T \leq \frac{1}{2}$ and $w_S = 1 - w_T$. Because $\hat{n}$ is spin independent, $\langle T_{S_z}|\hat{n}|S_0\rangle = 0$. Hence, eq. (12) yields $\mathcal{E}_{H,ST}^{FDT} = \mathcal{E}_{H,ST}^{Ans2}$.

Then, consider $\hat{\Gamma}_s^{SS} = w_{S_0}|S_0\rangle\langle S_0| + w_{S_1}|S_1\rangle\langle S_1|$, which mixes the ground (S_0) state, as above, with the first KS excited singlet state (S_1), with weights $w_{S_1} \leq \frac{1}{2}$ and $w_{S_0} = 1 - w_{S_1}$. This ensemble enables direct evaluation of excitations of the same symmetry. Eq. (12) yields,

$$\mathcal{E}_{H,SS} = \mathcal{E}_{H,SS}^{Ans2} + 4w_{S_1}E_H[\phi_0\phi_1] ; \qquad (13)$$

i.e., eq. (13) differs, in its final term, from the weighted average of Ans2. Ans2 and FDT both yield orbital functionals and thus require ensemble generalized Kohn-Sham theories [37], optimized-effective potentials (OEP) [38–40] or approximations. [17, 24, 27, 40]

Finally, consider the SS and ST ensembles when the ground state has the same weight $1 - w$. For simplicity, also allow the orbitals to be the same. It follows that $\mathcal{E}_{H,SS}^{FDT} = \mathcal{E}_{H,ST}^{FDT} + 4wE_H[\phi_0\phi_1]$. The Hartree difference for the SS and ST ensembles is the (weighted) spin splitting energy, $4E_H[\phi_0\phi_1]$, obtained at the level of CSFs – which is therefore captured when eq. (12) is combined with eq. (8). This is not surprising given that direct and exchange integrals appear in $\mathcal{E}_H^{FDT}$. In contrast, $\mathcal{E}_{H,SS}^{Ans2} = \mathcal{E}_{H,ST}^{Ans2}$ does not contain this term.

Let us now test how the choice of Hartree functional
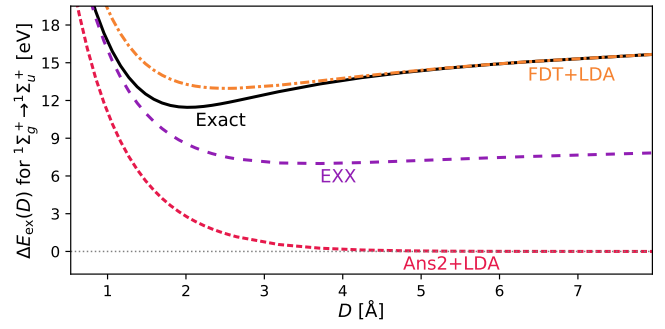
FIG. 1. SS excitation ($^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$) energies, $\Delta E_{ex}(D)$ for H_2, as a function of interatomic distance, D. Compares FDT+LDA (orange dash dot) and Ans2+LDA (red short dashes) against exact energies (black) and EXX (blue dashes).

affects energies. To this end, Figure 1 shows the SS excitation energy, ΔE_{ex}, of dissociating H_2 in a minimal basis set, using the local density approximation (LDA, E_{xc}^{LDA}) in eq. (8), paired with $\mathcal{E}_H^{FDT}$ (FDT+LDA) or $\mathcal{E}_H^{Ans2}$ (Ans2+LDA). This simple, non-trivial example illustrates differences between the two Hartree functionals but avoids complexities like weight-dependence and OEPs. Details are in the Supplementary Material. [36]

FDT+LDA has a clear (albeit imperfect) minima and agrees perfectly with exact calculations for large D ($\Delta E_{ex} \rightarrow 18$ eV). In contrast, Ans2+LDA predicts no minima and no gap for $D \rightarrow \infty$. Ans1, not shown, is nearly identical to Ans2. Exact exchange (EXX, $\mathcal{E}_{Hxc} \approx \mathcal{E}_{Hx}$) underestimates the asymptotic gap by a factor of two ($\Delta E_{ex} \rightarrow 9$ eV) and has an extremely shallow minima. For this example, it is clear that *only* FDT+LDA produces qualitatively correct physics.

General purpose ensemble DFAs must go beyond the LDA in eq. (8). They must also deal with density-driven correlations. [23, 25] The penultimate section thus applies the FDT to the correlation energy functional, $\mathcal{E}_c$, to reveal its inner components, for the purpose of devising and improving ensemble DFAs.

Correlations: Let us adiabatically connect the non-interacting ($\lambda = 0^+$) and fully interacting ($\lambda = 1$) systems. The Hellmann-Feynman theorem lets us write, $\mathcal{E}_{Hxc} \equiv \mathcal{F}^1 - \mathcal{F}^{0^+} = \int_{0^+}^1 d\lambda \frac{d\mathcal{F}^\lambda}{d\lambda} = \int_{0^+}^1 d\lambda \text{Tr}[\hat{\Gamma}^\lambda \hat{W}]$. We can then subtract the corresponding Hx contribution (derived earlier) to obtain the correlation energy,

$$\mathcal{E}_c[n] \equiv \int_{0^+}^1 d\lambda \int \frac{dr dr'}{2|r - r'|}\left\{\Delta P^\lambda(r, r')\right.$$
$$\left. - \int_{0^-}^\infty \frac{d\omega}{\pi}\Im\Delta\chi^\lambda(r, r'; \omega)\right\}. \qquad (14)$$

Therefore, we see that, $\mathcal{E}_c$ entails two key contributions: a contribution, $\Delta P^\lambda[n] = P^\lambda[n] - P_s[n]$, that naturally pairs with $\mathcal{E}_H^{FDT}$; and a second contribution, $\Delta\chi^\lambda[n] = \chi^\lambda[n] - \chi_s[n]$, that naturally pairs with $\mathcal{E}_x^{FDT}$.

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[30] By totally symmetric we mean, as usual, ensembles which are invariant under any symmetry operations of the considered Hamiltonian [24].

[31] To avoid ensemble v-representability concerns we consider only "well-behaved" densities here for which $v_s[n]$ exists.

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[35] Note, this assumption is usually made implicitly in Kohn-Sham EDFT. The results from this work thus may not apply in general but certainly cover all common applications of EDFT.

[36] Supplementary material may be found at XXXXXXXXX.

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