Approximately Self-Consistent Ensemble Density Functional Theory With All Correlations

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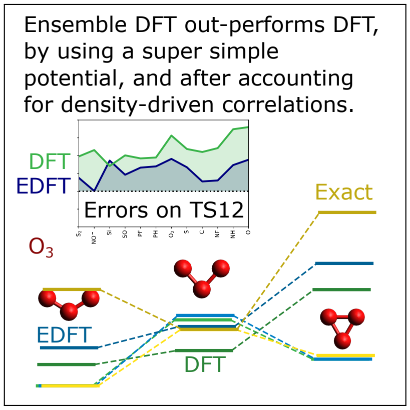
Abstract

The ability to predict low-lying excited states with the same ease as ground-states would represent a major advance in understanding interactions between light and chemistry, e.g. for solar cells or photocatalysis. Recent theory developments in ensemble density functional theory (EDFT) promise to bring decades of work for ground-states to the practical resolution of excited-state problem – provided newly-discovered "density-driven correlations" can be dealt with and adequate effective potentials can be found. This Letter introduces simple approximations to both the density-driven correlations and the potential; and shows that EDFT with the ωB97X density functional approximation outperforms ΔSCF DFT for singlet–triplet gaps in small atoms and molecules. It thus establishes EDFT as a vitally promising tool for low-cost but high-accuracy studies of excited states; and provides a clear route to practical EDFT implementation of arbitrary functional approximations.

Graphical TOC Entry



Ensemble DFT out-performs DFT, by using a super simple potential, and after accounting for density-driven correlations.

Quantum chemistry has improved our understanding of an enormous range of chemical systems, from biomolecules to battery materials. (Hybrid) density functional theory[1–3] (DFT) is the primary tool of quantum chemistry, due to its low computational cost and generally good accuracy. Recent developments have seen hybrid DFT calculations reach nearly chemical accuracy, across a wide range of tested systems.[4,5]

Unfortunately, DFT only treats electronic ground-states. This hampers its application to systems involving excited state processes, including those involving interactions with light such as photactivation and charge transfer. Excited state processes are likely to become a vitally important part of future chemistry, due to increasing control over light and the consequent ability to open up new applications. Thus, there is signifcant work on modelling excitation processes (see, e.g. various recent review articles[6–8]). Presently, however, much of this work is fairly high-level, in terms of its numerical cost and/or required expertise.

Time-dependent DFT (TDDFT), and ΔSCF DFT are two popular lower-level routes to excited states. In the latter case, ground-state calculations with restricted symmetries are used to find, e.g., the lowest-lying singlet and triplet energies, with the difference being the excitation energy; but this can be quite inaccurate because of "spin contamination" in triplet-states,[9,10] and cannot handle excitations of the same symmetry. TDDFT gives a range of excitation energies; but is significantly more costly than DFT, and has some limitations in treating charge transfers[11,12] and double excitations.[13]

Ensemble DFT (EDFT) for excited states[14–16] has recently enjoyed a resurgence as a promising alternative to DFT or TDDFT for treating low-level excited states, including charge transfer and double excitations.[17–33] In EDFT, the usual DFT approach of seeking a pure-state wavefunction $|\Phi\rangle$ and energy $E_\Phi = \langle\Phi|\hat{H}|\Phi\rangle$, is replaced by an equivalent quest for a statistical ensemble $\hat{\Gamma}^{\mathbf{w}} = \sum_\kappa w_\kappa |\kappa\rangle\langle\kappa|$ and its average energy $\mathcal{E}^{\mathbf{w}} = \sum_\kappa w_\kappa E_\kappa = \text{Tr}[\hat{\Gamma}^{\mathbf{w}}\hat{H}]$, for orthonormal quantum states $|\kappa\rangle$. ($\langle\kappa|\kappa'\rangle = \delta_{\kappa\kappa'}$). The set of weights $\mathbf{w} = \{w_\kappa\}$ obey $\sum_\kappa w_\kappa = 1$ and $w_\kappa \geq 0$.

EDFT is variational,[14,15] just like pure-state DFT. In terms of the versatile Levy constrained minimization[34] and adiabatic connection[35] conceptual picture, EDFT simply involves replacing the usual universal functional $F^\lambda[n] = \min_{|\Phi\rangle\to n}\langle\Phi|\hat{T} + \lambda\hat{W}|\Phi\rangle$ by

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

where $\hat{T}$ is the usual kinetic energy operator and $\hat{W}$ is the electron-electron Coulomb interaction. The average energy $\mathcal{E}^{\mathbf{w}}$ in external potential v can then be found by solving, $\mathcal{E}^{\mathbf{w}}[v] = \min_n \left\{\mathcal{F}^{1,\mathbf{w}}[n] + \int d\boldsymbol{r} n(\boldsymbol{r})v(\boldsymbol{r})\right\}$, where $n(\boldsymbol{r}) = \text{Tr}[\hat{\Gamma}^{\mathbf{w}}\hat{n}] = \sum_\kappa w_\kappa n_\kappa(\boldsymbol{r})$ is the average density of the ensemble. Variational principles give $E_\kappa \leq E_{\kappa'}$ for $w_\kappa > w_{\kappa'}$, i.e. the energies become ordered. Excitation energies can be found by varying weights, and taking differences or derivatives. Note, calligraphic letters indicate ensemble density functionals and explicit dependence on $\mathbf{w}$ is henceforth dropped for notational simplicity.

Recent work[24,29] showed how Eq. (1) can be used to provide EDFT analogs for the usual DFT functionals. EDFT has a kinetic energy,

$$\mathcal{T}_s[n] = \mathcal{F}^0[n] \equiv \sum_\kappa w_\kappa T_{s,\kappa} , \qquad (2)$$

and Hartree-exchange (Hx) functional,

$$\mathcal{E}_{\text{Hx}}[n] = \lim_{\lambda\to 0^+} \frac{F^\lambda[n] - \mathcal{T}_s[n]}{\lambda} \equiv \sum_\kappa w_\kappa \Lambda_{\text{Hx},\kappa} , \qquad (3)$$

like usual. Except: i) $T_{s,\kappa} = \langle\kappa_s|\hat{T}|\kappa_s\rangle$ and $\Lambda_{\text{Hx},\kappa} = \langle\kappa_s|\hat{W}|\kappa_s\rangle$ differ for each member $|\kappa_s\rangle$ of the KS ensemble; and ii) $\Lambda_{\text{Hx},\kappa}$ can inherit multi-configuration qualities to account for different spin symmetries.[24]

It also has a correlation energy term $\mathcal{E}_{\text{c}} = \mathcal{F}^1 - \mathcal{T}_s - \mathcal{E}_{\text{Hx}}$. However, unlike pure state DFT,

$$\mathcal{E}_{\text{c}}[n] = \mathcal{E}_{\text{c}}^{\text{SD}}[n] + \mathcal{E}_{\text{c}}^{\text{DD}}[n] , \qquad (4)$$

involves two terms: $\mathcal{E}_{\text{c}}^{\text{SD}}[n] = \sum_\kappa w_\kappa E_{\text{c},\kappa}^{\text{SD}}$ and $\mathcal{E}_{\text{c}}^{\text{DD}}[n] = \sum_\kappa w_\kappa E_{\text{c},\kappa}^{\text{DD}}$. The state-driven (SD) correlation energy terms $E_{\text{c},\kappa}^{\text{SD}}$ are like the usual

DFT correlation energy, and are invariant to $\mathbf{w}$ in certain cases, including those studied here. The density-driven (DD) terms $E^{\rm DD}_{{\rm c},\kappa}$ are unique to EDFT (i.e., $\mathcal{E}^{\rm DD}_{\rm c} = 0$ in pure-states) and carry a non-trivial dependence on $\mathbf{w}$ due to the inability of the KS ensemble members to simultaneously reproduce the densities and orbitals of all interacting ensemble members.[29]

Putting everything together gives,

$$\mathcal{E}[v] = \min_n \left\{ \mathcal{T}_s[n] + \mathcal{E}_{\rm Hxc}[n] + \int d\boldsymbol{r} n(\boldsymbol{r}) v(\boldsymbol{r}) \right\}, \tag{5}$$

where $\mathcal{E}_{\rm Hxc} = \mathcal{E}^{\rm SD}_{\rm Hxc} + \mathcal{E}^{\rm DD}_{\rm c}$ and

$$\mathcal{E}^{\rm SD}_{\rm Hxc} = \sum_\kappa w_\kappa [\Lambda_{{\rm Hx},\kappa} + E^{\rm SD}_{{\rm c},\kappa}] \equiv \sum_\kappa w_\kappa E^{\rm SD}_{{\rm Hxc},\kappa} \ , \tag{6}$$

Both $\Lambda_{{\rm Hx},\kappa}$ and $E_{{\rm c},\kappa}$ are pure-state-like. Thus, a useful strategy is to adapt existing density functional approximations (DFAs) for use in $E^{\rm SD}_{{\rm Hxc},\kappa}$. The key outstanding challenges are then how to modify existing approximations to deal with different ensemble members, and how to evaluate $\mathcal{E}^{\rm DD}_{\rm c}$. Both will be tackled later.

Once approximated, the energy functional, (5), must then be minimized on the density. Minimization of (5) involves finding a set of KS orbitals ϕ_i that obey the usual spin-independent KS equation,

$$\left[-\frac{1}{2}\nabla^2 + v_s[n](\boldsymbol{r}) \right] \phi_i(\boldsymbol{r}) = \epsilon_i \phi_i(\boldsymbol{r}) \ , \tag{7}$$

where $v_s = v + \frac{\delta \mathcal{E}_{\rm Hxc}}{\delta n}$. Then, $n(\boldsymbol{r}) = \sum_i f_i \phi_i(\boldsymbol{r})^2$, where $0 \leq f_i \leq 2$ is the average occupation factor of orbital ϕ_i, which obey $\sum_i f_i = N$ for N electrons, and which depend on $\mathbf{w}$.[24,36] Unfortunately, the EDFT density functional $\mathcal{E}_{\rm Hxc}$ has non-trivial dependencies on orbitals, whether treated exactly or approximately. Thus, unlike conventional DFT, direct density functional derivatives $\delta \mathcal{E}_{\rm Hxc}/\delta n$ cannot easily be found.

To circumvent this problem, one can use a generalized KS (GKS) formalism[37] or an optimized effective potential[38,39] (OEP). Both approaches have challenges. This work adopts a different approach – any GKS treatment required by the DFA is done as per the ground-state case. An additional potential is then introduced, which is approximated by a super simple OEP (SSOEP), introduced later. Consequently, Eq. (7) can be solved using existing machinery implemented in any molecular code.

The rest of this Letter proceeds as follows. First, a methodology is introduced to adapt the successful ωB97X DFA[40] to EDFT. This necessitates dealing with the DD correlation energy and SSOEP, which are discussed. Next, the method is assessed on several tests to illustrate how EDFT usually outperforms DFT for excitations, even when treated at the same level of theory. Finally, some conclusions are drawn.

Theory: Application of EDFT relies on approximating $\mathcal{E}_{\rm Hxc} = \mathcal{E}_{\rm Hx} + \mathcal{E}^{\rm SD}_{\rm c}$, like DFT. Ideally, one would use existing approximations, which have already been optimized for ground-states. This work extends the successful ωB97X functional of Chai and Head-Gordon[40] to EDFT. Thus, one obtains,

$$\mathcal{E}^{\rm SD} = \mathcal{T}_s + \sum_\kappa w_\kappa E^{\omega{\rm B97X}}_{{\rm Hxc},\kappa} + \int n v d\boldsymbol{r} \ . \tag{8}$$

for the SD energy, with Hxc terms,

$$E^{\omega{\rm B97X}}_{{\rm Hxc},\kappa} = \Lambda_{{\rm Hx},\kappa} - 0.8423 \Lambda^{\rm sr}_{{\rm x},\kappa} + E^{\rm DFA}_{{\rm xc},\kappa} \ . \tag{9}$$

The use of $\Lambda_{{\rm Hx},\kappa}$ indicates that spin symmetries are properly accounted for. The above and what follows can, of course, be adapted to any DFA of (hybrid) generalized-gradient approximation (GGA) character.

Any (range-separated) hybrid GGA requires three key inputs: densities n, spin-polarizations ζ, and (range-separated) Hartree and exchange energies $\Lambda_{\rm Hx}$. Each KS state $|\kappa_s\rangle$ is trivially associated with a density $n_{s,\kappa} = \langle \kappa_s | \hat{n} | \kappa_s \rangle$. However, $\zeta = 0$ in a spin-restricted formalism. Instead, $\zeta_{s,\kappa} = (1 - 2P_{2,\kappa}/n^2_{s,\kappa})^{\frac{1}{2}}$ is employed, per previous work,[29,41] where $P_{2,\kappa}$ is the KS on-top pair-density. Together, these terms are used to semi-locally approximate $E^{\rm DFA}_{{\rm xc},\kappa} \equiv E_{\rm xc}[n_{s,\kappa}, \zeta_{s,\kappa}]$ for short-range exchange and all correlations.

$\Lambda_{{\rm Hx},\kappa}$ is an orbital functional defined in eq. (3). The range-separated Hartree-exchange energy $\Lambda^{\rm sr}_{{\rm x},\kappa}$ is found by adopting the same functional form, but replacing the Coulomb potential $1/r$ by its short-range counterpart $\mathrm{erfc}(\omega r)/r$ (with $\omega = 0.3$ a.u.$^{-1}$). Then, $\Lambda^{\rm sr}_{{\rm x},\kappa} = \Lambda^{\rm sr}_{{\rm Hx},\kappa} - E^{\rm sr}_{\rm H}[n_{s,\kappa}]$ where $E_{\rm H}$ is the usual Hartree energy expression. Full details are in the Supporting Information.

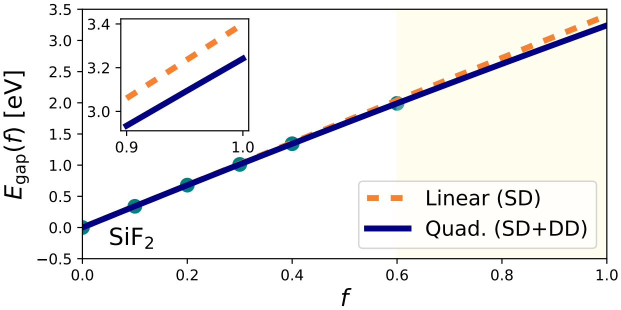


Figure 1: Illustration of the exrapolation procedure applied to SiF$_2$. The inset zooms into the DD contribution to the singlet–triplet gap. Light shading indicates the extrapolation region $W \geq 0.6$.

This establishes the SD energy approximation. However, DD correlations must also be accounted for. Previous work introduced a direct approximation for DD terms.[29] Here, $\mathcal{E}^{\rm DD}_{\rm c}$ is found by a parameter-free *extrapolation*, which is conceptually similar to a technique recently used to calculate DD correlations for S–P and S–S transitions in atoms.[30] A full derivation of the approach is rather long, so is left to the Supporting Information. Key steps are as follows: 1) Recognise that $\mathcal{E}^w = \mathcal{E}^{{\rm SD},w} + \mathcal{E}^{{\rm DD},w}_{\rm c}$ is linear in w so that the excitation energy $\Delta E = E_{\rm ts} - E_{\rm ss} = \partial_w \mathcal{E}^w$, $\forall w$ – where $\mathcal{E}^w \equiv \mathcal{E}^{\{1-w,w\}}$, $\mathcal{E}^{{\rm SD},w} \equiv \mathcal{E}^{\omega{\rm B97X},w}$ is evaluated using eq. (8), and $\mathcal{E}^{{\rm DD},w}_{\rm c}$ is unknown; 2) Approximate the SD excitation energy as $\Delta E^{\rm SD} = E^{\rm SD}_{\rm ts} - E^{\rm SD}_{\rm ss} = \partial_w \mathcal{E}^{\omega{\rm B97X},w}|_{w=0}$ so that it corresponds to a "typical" EDFT calculation using orbitals of the singlet ground-state; 3) Recognise that $\mathcal{E}^0 = \mathcal{E}^{\omega{\rm B97X},0}$ and $\mathcal{E}^1 = \mathcal{E}^{\omega{\rm B97X},1}$ in the pure-state limits.

This gives singlet–triplet gaps

$$\Delta E = \underset{w\to 1}{\rm ext}\, \mathcal{E}^{\omega{\rm B97X},w} - \underset{w\to 0}{\rm ext}\, \mathcal{E}^{\omega{\rm B97X},w} \;, \tag{10}$$

$$\Delta E^{\rm SD} = \partial_w \mathcal{E}^{\omega{\rm B97X},w}|_{w=0} \;, \tag{11}$$

so that the total DD contribution to the excitation is $\Delta\mathcal{E}^{\rm DD}_{\rm c} = \Delta E - \Delta E^{\rm SD}$. Here, ${\rm ext}_{w\to 1}$ involves fitting a quadratic (chosen to avoid over-fitting) to values of $\mathcal{E}^{\omega{\rm B97X},w_i}$ found for $w_i \in [0, 0.6]$, then extrapolating to $w = 1$ (for numerical consistency, the same fit is also used to calculate the singlet state at $w = 0$). This division into SD/DD differs very slightly from the formal definition,[29] but may be more suited to studying DFAs. The extrapolation is illustrated in Figure 1.

The final approximation is the super simple OEP (SSOEP), to account for the effective potential. This involves two steps: 1) try a variety of conventional DFAs (here, PBE,[42] PBE0[43] and ωB97X – in this last case, the effective Hamiltonian also includes GKS terms) to obtain a potential approximation $\tilde{v}^0_s$ (e.g., $\tilde{v}^0_s = \tilde{v}^{\rm PBE0}_s$) whose orbitals ϕ^0_i [using (7)] and densitiy n^0 give the lowest energy [using (8)]; 2) Find ξ such that the orbitals ϕ^ξ_i and density n^ξ [using (7)] from the potential

$$\tilde{v}^\xi_s(\boldsymbol{r}) = \tilde{v}^0_s(\boldsymbol{r}) + \xi \frac{n^0_{{\rm gs}'}(\boldsymbol{r})}{n^0(\boldsymbol{r})} \tag{12}$$

minimize the energy $\mathcal{E}^\xi$ [using (8)]. Here, $n^0_{{\rm gs}'}(\boldsymbol{r}) = \sum_{i\leq N/2} f_i \phi^0_i(\boldsymbol{r})^2$ is the ground-state-like density, with excited state orbitals excluded. This second step involves an ansatz for the potential inspired by a previous finding for *fractional* EDFT that the exact KS potential is approximately given by a similar expression – see eq. 15, of Gould and Toulouse.[44]

This approach avoids spin contamination when treating singlet or triplet states – unlike ΔSCF DFT, because $\phi_{i\uparrow}(\boldsymbol{r}) = \phi_{i\downarrow}(\boldsymbol{r})$ for all orbitals. It thus follows that DFT and EDFT results for singlet ground-states are the same; but triplet- states differ. Implementation requires only small modification of existing code, and iterates to a solution in around five steps.

Together, our approximations for the DD correlation energy and effective potential provide an overarching methodology that lets a general DFA (here ωB97X) be applied to EDFT problems with the same scaling as conventional DFT, albeit with a larger pre-factor from the density-driven correlations (×6, here) and SSOEP (×8, here). It is much cheaper than

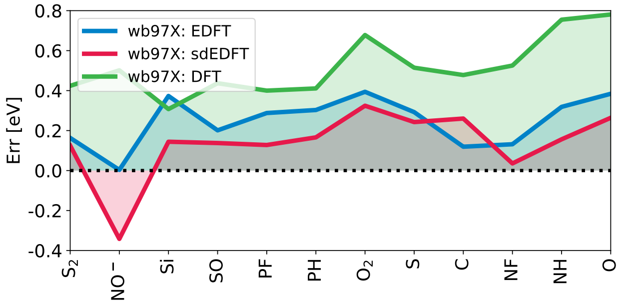


Figure 2: Errors [eV] in the triplet-singlet gap for the TS12 benchmark set in DFT (green), EDFT (blue) and sdEDFT (red).

the additional $O(N)$ overhead of TDDFT calculations. The approach is also "black box", making it easy to use without specifying active states or intuiting the processes involved.

Results: With the theory established, the approach is validated by applying it to various tests on small molecules. Tests are restricted to singlet–triplet gaps, as these allow direct comparison with ΔSCF DFT at the same level of theory.

The TS12 benchmark set of small triplet-singlet gaps in small molecules forms the first test.[46] The small gaps in these systems make them particularly problematic for DFT, as symmetry breaking can lead to substantial errors. [Note, the triplet-state is the ground-state in these systems. This does not change the formalism.]

Figure 2 shows errors from DFT (using ΔSCF), EDFT and state-driven EDFT calculations without DD correlations (sdEDFT). Overall, EDFT, with a mean absolute error (MAE) of 0.25 eV offers a two-fold improvement over DFT, with MAE 0.52 eV. EDFT without DD correlations slightly out-performs the full EDFT treatment, with MAE 0.19 eV.

It is clear from these results that EDFT can appropriately deal with excitations, as one would expect from its consistent treatment of ground- and excited-states. What is notable is that including the DD correlation energy does not always improve things, despite its formal justification. However, this is easy to explain. In these molecules the DD correlation energy is typically small (< 0.2 eV), which is smaller than the underlying error of the DFA. Thus, any small positive/negative DD correction to an over/underprediction by the DFAs will make things slightly worse. Importantly, in the one case (NO^-) where the DD term makes a big difference to the energy, it improves things.

To supplement TS12, vertical and adiabatic singlet–triplet gaps are calculated for three small molecules (SO_2, SiF_2, CHCl and CSHH) from the Loos-Jacquemin benchmark set[45] (LJ19). [Note, there is a mistake in the SO_2 triplet structure reported by Loos and Jacquemin. This work uses a structure provided by the authors.]

Results for vertical (using the ground-state geometry) and adiabatic (using the optimal geometries for ground- and excited states) excitations are reported in Table 1. On average, DFT slightly (by 0.06 eV on MAE) outperforms EDFT for vertical excitations. But, DFT does significantly better for adiabatic excitations (by 0.22 eV on MAE). The poor performance of EDFT for adiabatic excitations is mostly due to a very poor prediction for CSHH, which is out by around 40%. sdEDFT gives the worst results in all cases, meaning that, for these molecules, density-driven correlations are both quantitatively important and systematically beneficial.

Finally, a particularly challenging test is applied – predicting key excitations of strongly-correlated ozone. This involves computing singlet–triplet gaps at three selected geometries: open minimum (OM), transition state (TS) and ring minimum (RM). These represent key steps in the ozone excitation process that were recently benchmarked using high-level theory.[47] This problem represents the sort of application for which EDFT will likely prove most useful, e.g. to simultaneously predict multiple states for use in beyond-Born-Oppenheimer dynamics. The TS geometry is a very stringent test, due to the degeneracy of singlet- and triplet- states.

Figure 3 shows that EDFT clearly outperforms regular DFT and gives semi-quantitive agreement with the exact solution. EDFT almost predicts the degeneracy between the singlet- (ss) and triplet-states (ts) in TS, unlike DFT. By contrast, ΔSCF DFT does a poor job

Table 1: Vertical and adiabatic excitation energies [eV] from DFT, EDFT and sdEDFT (sdE). Benchmarks from LJ19.[45]

	Vertical							Adiabatic						
	Bench	DFT	Err	EDFT	Err	sdE	Err	Bench	DFT	Err	EDFT	Err	sdE	Err
SiF_2	3.30	3.76	0.46	3.50	0.20	3.76	0.46	3.20	3.26	0.06	3.38	0.18	3.63	0.43
SO_2	3.45	3.37	-0.08	3.51	0.06	3.62	0.17	3.03	2.88	-0.15	3.22	0.19	3.32	0.29
CSHH	1.96	1.70	-0.26	2.47	0.51	2.58	0.62	1.86	1.62	-0.24	2.58	0.73	2.68	0.82
CHCl	0.58	0.46	-0.12	0.98	0.40	1.14	0.56	0.24	0.11	-0.13	0.59	0.35	0.73	0.49
MAE			0.23		0.29		0.45			0.14		0.36		0.51

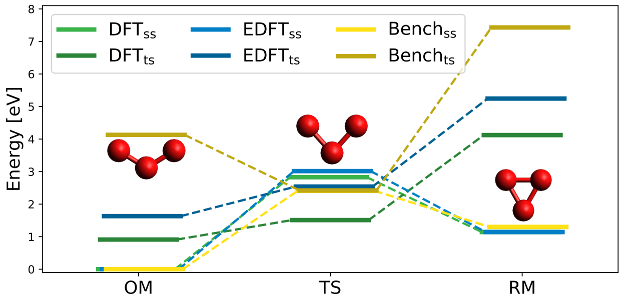


Figure 3: Energy levels for three geometries of ozone in DFT (green) and EDFT (blue) and benchmark[47] (yellow) calculations. Lighter colours indicate the ground-state (singlet) and darker colours indicate the excited state (triplet). Geometries are also shown.

of the triplet state in all cases. EDFT, unlike DFT, is thus useable for estimating dynamics. All relevant energies are shown in the Supporting Information. Note, in nearly-degenerate TS there is also a small (0.2 eV) difference between singlet states calculated using DFT and EDFT, because the latter are obtained using a quadratic fit on w.

sdEDFT (not shown) gives very similar results to full EDFT for OM and RM geometries. But for TS it predicts a significant gap of 5.1 eV, compared to a zero gap in the benchmark, and gaps of 0.13 eV for full EDFT and 1.3 eV for DFT. Thus, inclusion of the DD correlation energy term is vital.

Conclusions: In summary, this letter reports approximately self-consistent and fully correlated ensemble DFT (EDFT) calculations using the ωB97X DFA, and including recently-discovered density-driven (DD) correlation energy terms.[29] Obtaining these results required the introduction of two methodological innovations: 1) a way to deal with DD correlations [eq. (10)]; 2) a way to deal with self-consistency [eq. (12)].

Results showed that EDFT improved on ΔSCF DFT for the computation of low-lying excited states in almost all cases, and is thus a promising alternative for low-cost calculations. For the TS12 benchmark set, EDFT gave a two-fold improvement over DFT using the same ωB97X approximation. Small atom excitations (vertical and adiabatic) from LJ19 were reproduced reasonable well by both DFT and EDFT, except the latter failed badly for CSHH. Most promisingly, EDFT (but not sdEDFT) significantly out-performed DFT for difficult ozone excitations.

Including DD correlations in our ensemblised ωB97X calculations is vital in some systems, (e.g., NO^-, ozone TS) but slightly detrimental in others (e.g. Si, PF). Since these are small energies, and ωB97X is an “uncontrolled” (non-variational) approximation, some variation is to be expected. Results are certainly consistent with chemical intuition. A deeper conceptual understanding of DD terms (e.g., understanding when ground-state orbitals are poor for excited-states) might point the way to improved treatment of excitations generally, not just in EDFT – analogous to how a better understanding of dispersion corrections has improved treatment of weak binding generally. This problem should be investigated.

I speculate that the poor showing for EDFT in CSHH might reflect deficiencies in the super simple OEP. Better, low-cost solutions might be required for general cases. Theoretical and numerical work along these lines is being pursued.

Finally, unlike ΔSCF DFT, the EDFT scheme proposed here can handle singlet–singlet excitations as readily as singlet–triplet excitations.[30] Their quality will be investigated in future work, which must accommodate recent developments in Hartree theory for ensembles.[48]

Computational Methods

All calculations were performed in a custom Python3 code, based on `Psi4/NumPy`.[49,50] The code used standard routines therefrom wherever possible. Both DFT and EDFT calculations of the TS12 benchmark set were performed with the aug-cc-pVQZ basis set.[51] These calculations were repeated with aug-cc-pVTZ, which was found to give similar results (within 0.04 eV of aug-cc-pVQZ, except for NO^-). Since no other anions were tested, aug-cc-pVTZ was thus used for the remaining calculations. Spatial symmetries were allowed to break, to avoid the additional ensemble effects required to preserve them.[30]

EDFT calculations used ensemble weights $w \in \{0.0, 0.1, 0.2, 0.3, 0.4, 0.6\}$ in the quadratic extrapolation to $w = 1$. sdEDFT calculations used a finite difference $\partial_w E|_{w=0} \approx (E^{w=0.1} - E^{w=0.0})/0.1$ to approximate the gradient at $w = 0$.

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Supporting Information Available

Includes: 1) Full working for the implementation of the ωB97X density functional approximation for ensembles. 2) Details of the density-driven correlation calculation. 3) Tabulated data for calculations.

References

(1) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871.

(2) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.

(3) Kim, K.; Jordan, K. D. Comparison of Density Functional and MP2 Calculations on the Water Monomer and Dimer. *J. Phys. Chem.* **1994**, *98*, 10089–10094.

(4) Goerigk, L.; Hansen, A.; Bauer, C.; Ehrlich, S.; Najibi, A.; Grimme, S. A look at the density functional theory zoo with the advanced GMTKN55 database for general main group thermochemistry, kinetics and noncovalent interactions. *Phys. Chem. Chem. Phys.* **2017**, *19*, 32184–32215.

(5) Mardirossian, N.; Head-Gordon, M. Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. *Mol. Phys.* **2017**, *0*, 1–58.

(6) Crespo-Otero, R.; Barbatti, M. Recent Advances and Perspectives on Nonadiabatic Mixed Quantum–Classical Dynamics. *Chem. Rev.* **2018**, *118*, 7026–7068.

(7) Ghosh, S.; Verma, P.; Cramer, C. J.; Gagliardi, L.; Truhlar, D. G. Combining Wave Function Methods with Density Functional Theory for Excited States. *Chem. Rev.* **2018**,

(8) Lischka, H.; Nachtigallová, D.; Aquino, A. J. A.; Szalay, P. G.; Plasser, F.; Machado, F. B. C.; Barbatti, M. Multireference Approaches for Excited States of Molecules. *Chem. Rev.* **2018**, *118*, 7293–7361.

(9) Baker, J.; Scheiner, A.; Andzelm, J. Spin contamination in density functional the-

ory. *Chem. Phys. Lett.* **1993**, *216*, 380–388.

(10) Wittbrodt, J. M.; Schlegel, H. B. Some reasons not to use spin projected density functional theory. *J. Chem. Phys.* **1996**, *105*, 6574–6577.

(11) Maitra, N. T. Undoing static correlation: Long-range charge transfer in time-dependent density-functional theory. *J. Chem. Phys.* **2005**, *122*, 234104.

(12) Maitra, N. T. Charge transfer in time-dependent density functional theory. *J. Phys.: Cond. Matter* **2017**, *29*, 423001.

(13) Elliott, P.; Goldson, S.; Canahui, C.; Maitra, N. T. Perspectives on double-excitations in TDDFT. *Chem. Phys.* **2011**, *391*, 110–119.

(14) Gross, E. K. U.; Oliveira, L. N.; Kohn, W. Rayleigh-Ritz variational principle for ensembles of fractionally occupied states. *Phys. Rev. A* **1988**, *37*, 2805–2808.

(15) Gross, E. K. U.; Oliveira, L. N.; Kohn, W. Density-functional theory for ensembles of fractionally occupied states. I. Basic formalism. *Phys. Rev. A* **1988**, *37*, 2809–2820.

(16) Oliveira, L. N.; Gross, E. K. U.; Kohn, W. Density-functional theory for ensembles of fractionally occupied states. II. Application to the He atom. *Phys. Rev. A* **1988**, *37*, 2821–2833.

(17) Filatov, M.; Shaik, S. A spin-restricted ensemble-referenced Kohn–Sham method and its application to diradicaloid situations. *Chem. Phys. Lett.* **1999**, *304*, 429–437.

(18) Pribram-Jones, A.; Yang, Z.-h.; Trail, J. R.; Burke, K.; Needs, R. J.; Ullrich, C. A. Excitations and benchmark ensemble density functional theory for two electrons. *J. Chem. Phys.* **2014**, *140*.

(19) Yang, Z.-h.; Trail, J. R.; Pribram-Jones, A.; Burke, K.; Needs, R. J.; Ullrich, C. A. Exact and approximate Kohn-Sham potentials in ensemble density-functional theory. *Phys. Rev. A* **2014**, *90*, 042501.

(20) Filatov, M.; Huix-Rotllant, M.; Burghardt, I. Ensemble density functional theory method correctly describes bond dissociation, excited state electron transfer, and double excitations. *J. Chem. Phys.* **2015**, *142*, 184104.

(21) Senjean, B.; Knecht, S.; Jensen, H. J. A.; Fromager, E. Linear interpolation method in ensemble Kohn-Sham and range-separated density-functional approximations for excited states. *Phys. Rev. A* **2015**, *92*, 012518.

(22) Filatov, M. In *Density-Functional Methods for Excited States*; Ferré, N., Filatov, M., Huix-Rotllant, M., Eds.; Springer International Publishing: Cham, 2016; pp 97–124.

(23) Yang, Z.-h.; Pribram-Jones, A.; Burke, K.; Ullrich, C. A. Direct Extraction of Excitation Energies from Ensemble Density-Functional Theory. *Phys. Rev. Lett.* **2017**, *119*, 033003.

(24) Gould, T.; Pittalis, S. Hartree and Exchange in Ensemble Density Functional Theory: Avoiding the Nonuniqueness Disaster. *Phys. Rev. Lett.* **2017**, *119*, 243001.

(25) Senjean, B.; Fromager, E. Unified formulation of fundamental and optical gap problems in density-functional theory for ensembles. *Phys. Rev. A* **2018**, *98*, 022513.

(26) Sagredo, F.; Burke, K. Accurate double excitations from ensemble density functional calculations. *J. Chem. Phys.* **2018**, *149*, 134103.

(27) Filatov, M.; Min, S. K.; Kim, K. S. Non-adiabatic dynamics of ring opening in

cyclohexa-1, 3-diene described by an ensemble density-functional theory method. *Mol. Phys.* **2018**, 1–14.

(28) Gould, T.; Kronik, L.; Pittalis, S. Charge transfer excitations from exact and approximate ensemble Kohn-Sham theory. *J. Chem. Phys.* **2018**, *148*, 174101.

(29) Gould, T.; Pittalis, S. Density-Driven Correlations in Many-Electron Ensembles: Theory and Application for Excited States. *Phys. Rev. Lett.* **2019**, *123*, 016401.

(30) Gould, T.; Pittalis, S. Density Driven Correlations in Ensemble Density Functional Theory: Insights from Simple Excitations in Atoms. *Aus. J. Chem.; preprint on chemrxiv* **2020**,

(31) Fromager, E. Individual correlations in ensemble density-functional theory: State-driven/density-driven decompositions without additional Kohn-Sham systems. 2020.

(32) Loos, P.-F.; Fromager, E. A weight-dependent local correlation density-functional approximation for ensembles. 2020.

(33) Marut, C.; Senjean, B.; Fromager, E.; Loos, P.-F. Weight Dependence of Local Exchange-Correlation Functionals in Ensemble Density-Functional Theory: Double Excitations in Two-Electron Systems. 2020.

(34) Levy, M. Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6062–6065.

(35) Harris, J. Adiabatic-connection approach to Kohn-Sham theory. *Phys. Rev. A* **1984**, *29*, 1648–1659.

(36) Gould, T.; Dobson, J. F. The flexible nature of exchange, correlation, and Hartree physics: Resolving "delocalization" errors in a "correlation free" density functional. *J. Chem. Phys.* **2013**, *138*, 014103.

(37) Seidl, A.; Görling, A.; Vogl, P.; Majewski, J. A.; Levy, M. Generalized Kohn-Sham schemes and the band-gap problem. *Phys. Rev. B* **1996**, *53*, 3764–3774.

(38) Sharp, R. T.; Horton, G. K. A Variational Approach to the Unipotential Many-Electron Problem. *Phys. Rev.* **1953**, *90*, 317–317.

(39) Talman, J. D.; Shadwick, W. F. Optimized effective atomic central potential. *Phys. Rev. A* **1976**, *14*, 36–40.

(40) Chai, J.-D.; Head-Gordon, M. Systematic optimization of long-range corrected hybrid density functionals. *J. Chem. Phys.* **2008**, *128*, 084106.

(41) Becke, A.; Savin, A.; Stoll, H. Extension of the local-spin-density exchange-correlation approximation to multiplet states. *Theor. Chim. Acta* **1995**, *91*, 147–156.

(42) Perdew, J. P.; Burke, K.; ; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–68.

(43) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158–69.

(44) Gould, T.; Toulouse, J. Kohn-Sham potentials in exact density-functional theory at noninteger electron numbers. *Phys. Rev. A* **2014**, *90*, 050502.

(45) Loos, P.-F.; Jacquemin, D. Chemically Accurate 0-0 Energies with not-so-Accurate Excited State Geometries. *J. Chem. Theory Comput.* **2019**,

(46) Lee, J.; Head-Gordon, M. Two single-reference approaches to singlet biradicaloid problems: Complex, restricted

orbitals and approximate spin-projection combined with regularized orbital-optimized Møller-Plesset perturbation theory. *J. Chem. Phys.* **2019**, *150*, 244106.

(47) Chien, A. D.; Holmes, A. A.; Otten, M.; Umrigar, C. J.; Sharma, S.; Zimmerman, P. M. Excited States of Methylene, Polyenes, and Ozone from Heat-Bath Configuration Interaction. *J. Phys. Chem. A* **2018**, *122*, 2714–2722.

(48) Gould, T.; Stefanufucci, G.; Pittalis, S. Private communication. 2020.

(49) Parrish, R. M.; Burns, L. A.; Smith, D. G.; Simmonett, A. C.; DePrince III, A. E.; Hohenstein, E. G.; Bozkaya, U.; Sokolov, A. Y.; Di Remigio, R.; Richard, R. M. et al. Psi4 1.1: An open-source electronic structure program emphasizing automation, advanced libraries, and interoperability. *J. Chem. Theory Comput.* **2017**, *13*, 3185–3197.

(50) Smith, D. G.; Burns, L. A.; Sirianni, D. A.; Nascimento, D. R.; Kumar, A.; James, A. M.; Schriber, J. B.; Zhang, T.; Zhang, B.; Abbott, A. S. et al. Psi4NumPy: An interactive quantum chemistry programming environment for reference implementations and rapid development. *J. Chem. Theory Comput.* **2018**, *14*, 3504–3511.

(51) Kendall, R. A.; Dunning Jr, T. H.; Harrison, R. J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys* **1992**, *96*, 6796–6806.