Electronic excited states in extreme limits via ensemble density functionals

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Density functional theory (DFT) has greatly expanded our ability to affordably compute and understand electronic ground states, by replacing intractable ab initio calculations by models based on paradigmatic physics from high- and low-density limits. But, a comparable treatment of excited states lags behind. Here, we solve this outstanding problem by employing a generalization of density functional theory to ensemble states (EDFT). We thus address important paradigmatic cases of all electronic systems in strongly (low-density) and weakly (high-density) correlated regimes. We show that the high-density limit connects to recent, exactly-solvable EDFT results. The low-density limit reveals an unnoticed and most unexpected result – density functionals for strictly correlated ground states can be reused directly for excited states. Non-trivial dependence on excitation structure only shows up at third leading order. Overall, our results provide foundations for effective models of excited states that interpolate between exact low- and high-density limits, which we illustrate on the cases of singlet-singlet excitations in $H_2$ and a ring of quantum wells.

Preamble. Density functional theory (DFT) [1, 2] is best known as a computational modelling tool used in tens of thousands of applicative scientific papers every year. What is less widely known is that DFT offers a natural connection between quantum mechanics and paradigmatic physical conditions (high- and low-density limits) of matter, in which electronic correlations attain two quantitatively (weak and strong, respectively) and qualitatively different fundamental ends. In this context, DFT serves as a formal tool to understand the behaviour of ground state electronic structure via a rigorous constrained variational approach to the electronic structure problem. Understanding of paradigmatic conditions then informs model development, e.g. the popular “PBE” [3] approximation, and computational studies therefrom.

Unfortunately, DFT is only defined for ground states, so cannot elucidate the structure of excited states. This Letter will demonstrate that ensemble density functional theory (EDFT) for excited states [4, 5] can tackle this outstanding problem. We shall show that recently derived Hartree and exchange physics [6, 7] become exact in the high density (weak interaction); so high-density excited electronic states may be solved using these tools.

More importantly, we shall show that the low density (strong interaction) limit of excited states behaves exactly like a ground state. Therefore, the full suite of ground state strictly correlated electron (SCE) tools and approximations [8, 14] may be used to solve both ground and excited states of low-density many-electron systems.

Our work thereby improves understanding of excited states in paradigmatic limits and connects their behaviour to well-defined density functionals for which exact forms and approximations are available. It presents a crucial step toward efficient excited state approximations that capture important limits; and promises to accelerate and generalize recent progress on low cost modelling of single [14, 19] and double excitations [16, 20, 24] that may range from weakly to strongly correlated regimes.

The rest of this Letter proceeds as follows: First, we introduce EDFT and show how it can be used to understand the high- and low-density limits of interacting electrons in realistic inhomogeneous systems. Then, using as an illustration the strong interaction limit of electrons in an harmonic well, we derive the asymptotic properties of the density functionals for describing excitations in Wigner-like systems via EDFT. We then reveal that the second leading term in the low-density limit is also the same in ground and excited states, and that a non-trivial dependence only appears in the third leading term – which therefore describe more realistic correlated excitations. We then illustrate the importance of our findings for applications by studying excitations in two examples. Finally, we conclude.

Theoretical framework. Excited state EDFT is concerned with the behaviour of countable sets of excited states. In practice, a finite set of low-lying solutions of $H |\kappa\rangle = E_\kappa |\kappa\rangle$. These are grouped in an ensemble state $\Gamma^w = \sum_{\kappa} w_\kappa |\kappa\rangle\langle\kappa|$ using some prescribed weights [24] 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 $\mathcal{O}^w := \text{Tr}[\Gamma^w \hat{O}]$. Crucially, choosing $w_\kappa \leq \omega_\kappa$ for $E_\kappa \geq E_{\kappa'}$, ensures that $\Gamma^w$ fulfills an extended variational principle [4] according to which $\mathcal{E}^w = \inf_{\Gamma^w_{\text{trial}}} \text{Tr}[\Gamma^w_{\text{trial}} \hat{H}]$ where the argument for the infimum (usually a minimum),
Explicitly depend on their weights.

Capital calligraphic letters to refer to energies of mixed derivatives lets us address degenerate states. Varying weights (e.g. via partial limit discussion for further details) by equally weighting in terms of the ensemble particle density, excited states concepts and core results which have previously been worked out for pure ground states only. [8–13] These works can be understood as providing a generalization of the seminal work of Wigner [28, 29] to inhomogeneous systems within DFT. Our current work completes the generalization to include excited inhomogeneous systems within EDFT. It thus provides a complete treatment of electronic structure of two important paradigmatic and fundamentally different regimes, within a consistent and versatile approach.

High-density limit. 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,

\[
F^{\lambda,w}[n_\gamma] = \gamma^2 F^{\lambda,w}[n].
\]

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

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

\[
\lim_{\gamma \to \infty} F^{w}[n_\gamma] = F^{w}[n], \quad \lim_{\gamma \to \infty} \frac{\varepsilon^{w}_{\text{Hxc}}[n_\gamma]}{\gamma} = \varepsilon^{w}_{\text{Hxc}}[n],
\]

where the second result follows from the definition [9] of \( \varepsilon^{\text{Hxc}}_\text{H} \) as a gradient of \( F \). The high-density limit thus inherits good properties of \( \varepsilon^{\text{Hxc}}_\text{H} \): i) it preserves spin and spatial symmetries of the system; ii) the relevant KS states can be linear combinations of Slater determinants (SD) that are eigenstates of spin and proper generators of point groups, unlike the single SD of conventional spin-DFT treatments; iii) yet, it enable effective re-use of conventional spin-density functional approximations for exchange, via combination rules or on-top pair densities. [17, 19, 23]

Next, consider the adiabatic connection formula,

\[
\varepsilon^{w}_{\text{Hxc}}[n] = F^{w}[n] - F^{0,w}[n] = \int_0^1 \lambda \varepsilon^{\lambda}_\text{ee} [n] d\lambda,
\]

\[
\lambda \varepsilon^{\lambda}_\text{ee} [n] = \lim_{\eta \to 0^+} \frac{F^{\lambda + \eta,w} - F^{\lambda,w}}{\eta} := \text{Tr}[\hat{V}_{ee,\gamma} \hat{\Gamma}^{\lambda,w}] .
\]

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, \( 4\pi r^2 n(r) \), of the states are also shown for the case \( \lambda = 50 \).
The ‘Hx’ component is recovered as \( \mathcal{E}^{\text{Hx}}[n] = \gamma^{0,\text{Hx}}[n] \).
Scaling gives \( \mathcal{E}^{\text{Hxc}}[n_{\gamma}] = \gamma^{2} \int_{0}^{1/\gamma} \gamma^{0,\text{Hx}}[n] d\lambda \), from which (for finite systems) we get, \( \lambda \to \infty \):

\[
\mathcal{F}^{\gamma}[n_{\gamma}] \xrightarrow{\gamma \to \infty} \gamma^{2} \mathcal{F}_{\text{s}}^{\gamma}[n] + \gamma^{2} \mathcal{E}^{\gamma}_{\text{Hxc}}[n] + \mathcal{E}^{\gamma}_{\text{GL,2}}[n] + \ldots \tag{7}
\]

The first correlation contribution follows from Göring-Levy\(^2\)\(^2\) perturbation theory for ensembles,\(^3\)\(^3\) which must also be adapted for KS states in the form of linear combinations of SDs. Correlations may alternatively be captured by employing expressions previously reported in Ref.\(^7\)\(^4\) and \(5\)\(^5\) as in (e.g.) Ref.\(^3\)

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

\[
\lim_{\gamma \to 0^{+}} \mathcal{F}^{\gamma,\text{w}}[n_{\gamma}] = \lim_{\gamma \to 0^{+}} \mathcal{F}^{\gamma,\text{w}}[n_{\gamma}].
\]

Crucially,

\[
\lim_{\gamma \to 0^{+}} \mathcal{F}^{\gamma,\text{w}}[n_{\gamma}] = \mathcal{F}^{\gamma,\text{w}}[n_{\gamma}] = \mathcal{F}^{\gamma,\text{w}}[n_{\gamma}] = \mathcal{F}^{\gamma,\text{w}}[n_{\gamma}].
\]

where \(\mathcal{F}^{\gamma,\text{w}}[n_{\gamma}] = \inf_{\psi \to \gamma} (\mathcal{F}^{\gamma}[\psi] | \mathcal{F}^{\gamma}[\psi])\) is the known interaction energy functional of strictly correlated electrons in a ground state, but here evaluated at the ensemble particle density. This result says that, in the low-density limit, the functional dependence on weights disappears from both \(\mathcal{F}^{\gamma,\text{w}}[n_{\gamma}]\) and \(\mathcal{F}^{\gamma,\text{w}}[n_{\gamma}]\). Dependence on the weights enters only via the particle density, \(n := \text{Tr}[\Gamma^{\gamma} \hat{\rho}] = \sum_{i} w_{i} n_{i}\), of the ensemble. Eq. \(8\), and its extension to higher orders in \(\gamma\) discussed later, are the central result of this work. In this context, SCE results, analysis and understanding for ground states\(^8\)\(^1\) become special cases of the above more general result.

Proof of Eqs \(8\) and \(9\). Here, we shall guide the reader through the main steps and key physics. A full proof is reported in Section 1 of the Supplementary Material (Supp. Mat. Sec. I).

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

The scaled classical interaction energy of this system is \(V_{\text{cl}} = 0.7937 \lambda^{2/3}\).\(^{35}\) Quantum solutions may be found numerically. Details are in Supp. Mat. Sec. II. Figure \(1\) shows the interaction energies, \(V_{\lambda} := \langle \psi | V_{\text{cl}} | \psi \rangle\), of six low-lying spherically symmetric triplet \((\lambda S)\) and singlet \((1 S)\) states. It is clear that quantum and classical interaction energies all become the same as \(\lambda\) is increased – i.e., all excitations 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. \(9\) 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, \(9\)\(^3\)\(^7\) around the strictly correlated limit. In this effectively classical limit, which yields the leading term as \(\lambda \to 0\) of the ground-state universal functional \(F^{\gamma}[n]\)\(^1\)\(^1\), the \(N\)-body distribution of an \(N\)-electron system is \(P_{N}[\mathbf{r}_{1} \ldots \mathbf{r}_{N}] = \int \prod_{i=1}^{N} d r_{i} f_{i}(s) ds\) which leads to \(F^{\lambda \to \infty}[n] \to \lambda^{2} V_{\text{SCE}}[n] = \lambda^{2} \sum_{i=2}^{N} f_{i}(s) \int_{2/\rho}^{\infty} \frac{dr}{r} f_{i}(r)\).
Here, \(f_{i}(r)\) are co-motion maps that preserve the density and the indistinguishability of electrons.\(^3\)\(^2\)\(^1\)

At large but finite \(\lambda\) we construct orthonormal wave functions, \(\{\kappa_{\lambda}\}\), based on quantum harmonic oscillations (QHO) around the strictly-correlated distribution, \(P_{N}[\mathbf{r}]\).\(^9\)\(^3\)\(^7\) The QHOs act on curvilinear coordinates orthogonal to the manifold parametrized by the co-motion functions; and contribute at \(O(\sqrt{\lambda})\) in the kinetic and potential energies. \textit{Prima facie}, the wave functions \(\{\kappa_{\lambda}\}\) have different densities. However, it is also possible to quantize \(\lambda\) along the manifold, which contributes only at \(O(1)\) in kinetic energy and is amenable to the Harriman construction\(^3\)\(^9\) 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, \(\mathcal{F}^{\gamma,\text{w}}[\kappa_{\lambda}] = \sum_{\kappa} w_{\kappa} \mathcal{F}^{\gamma,\text{w}}[\kappa] = V_{\text{SCE}}[\kappa_{\lambda}]\) and eqs \(8\) and \(9\) follow from the equivalence of \(\gamma \to 0^{+}\) and \(\lambda \to \infty\) in eq. \(3\).

Next-leading terms in the low-density limit. To analyze the next leading terms, it useful to first rewrite \(\mathcal{F}^{\gamma}[\kappa_{\lambda}] = \mathcal{T}^{\gamma,\text{w}}[\kappa_{\lambda}] + V_{\text{SCE}}[\kappa_{\lambda}]\), taking SCE as the reference system and letting \(\mathcal{T}^{\gamma,\text{w}}[\kappa_{\lambda}]\) capture all the ensemble effects. Then an alternative adiabatic connection yields,

\[
\mathcal{T}^{\gamma,\text{w}}[\kappa_{\lambda}] = \int_{1}^{\infty} \mathcal{T}^{\gamma,\text{w}}[\kappa_{\lambda}] d\lambda.
\]

Here, we introduced, \(\mathcal{T}^{\gamma,\text{w}} = -\lambda^{2} \partial_{\lambda} \mathcal{E}^{\gamma,\text{w}} = \text{Tr}[\hat{T} \hat{T}^{\pm,\text{w}}]\), where the derivative and trace must be treated with caution, like in eq. \(6\). Eq. \(10\) generalizes known results for the ground state-only case\(^3\)\(^0\)\(^4\) to the ensembles considered in this work.

Next, we show that \(\mathcal{T}^{\gamma,\text{w}}[\kappa_{\lambda}]\) is independent of weights to leading order, which leads to \(\mathcal{T}^{\gamma,\text{w}}[\kappa_{\lambda}] = \mathcal{T}^{\gamma,\text{w}}[\kappa_{\lambda}]\) also independent of weights. Ensemblization of known results\(^9\)\(^3\)\(^7\) gives \(\mathcal{T}^{\gamma,\text{w}}[\kappa_{\lambda}] \to \frac{\lambda}{\sqrt{\lambda}} F_{\text{ZPE}}[\kappa_{\lambda}]\) where \(F_{\text{ZPE}}[\kappa_{\lambda}]\) involves \(\lambda\)-normalized zero point energy (ZPE) of the QHOS, \(\{\kappa_{\lambda}\}\), introduced earlier. Hence, \(\mathcal{T}^{\gamma,\text{w}}[\kappa_{\lambda}]\) becomes independent of weights if we can show that \(F_{\text{ZPE}}[\kappa_{\lambda}] \equiv \lim_{\lambda \to \infty} \frac{\lambda}{\sqrt{\lambda}} \mathcal{F}^{\gamma,\text{w}}[\kappa_{\lambda}]\) is independent of weights. 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. IB) yields \(\langle \kappa_{\lambda} | \mathcal{T} | \kappa_{\lambda} \rangle = \langle 0^{\lambda} | \mathcal{T} | 0^{\lambda} \rangle + O(1)\) for \(\lambda \to \infty\). Thus, \(\mathcal{T}^{\gamma,\text{w}} = \sum_{\kappa} w_{\kappa} \langle \kappa_{\lambda} | \mathcal{T} | \kappa_{\lambda} \rangle =\)
\( \langle 0^\lambda |\hat{\tau}|0^\lambda \rangle + O(1) \) is independent of weights to leading order, giving weight-independent, \( \mathcal{F}_\text{ZPE,}w[n] \equiv \lim_{\lambda \to \infty} \frac{2\mathcal{T}_\lambda^{w}[n]}{\sqrt{\lambda}} = \mathcal{F}_\text{ZPE}[n] \). Here, \( \mathcal{F}_\text{ZPE}[n] \) is the well-studied ground state functional \([29, 37, 38]\), but evaluated on the ensemble density. Using the latter result in \((10)\), and applying scaling laws, finally yields, \( \lim_{\gamma \to 0^+} \mathcal{T}^{\text{SCE,}w}[n,\gamma] = \mathcal{F}_\text{ZPE}[n\gamma] = \gamma^{3/2} \mathcal{F}_\text{ZPE}[n] \). Thus we conclude that \( \mathcal{T}^{w}[n] \) and \( \mathcal{T}^{\text{SCE,}w}[n] \) are independent of the ensemble weights in the low-density limit. \( \mathcal{F}_w[n,\gamma] \equiv \gamma V^{\text{SCE}}_{ee}[n] + \gamma^{3/2} \mathcal{F}_\text{ZPE}[n] \) is therefore also independent of weights to second leading order. Details of scaling are in Supp. Mat. Sec. III.

Where and how does the weight dependence appears in the low-density limit? Eqs (S31)–(S37) of Supp. Mat. Sec. IB reveal that it appears in the third leading term, \( \mathcal{F}_w[n_\gamma] \),

\[
\rightarrow \gamma V^{\text{SCE}}_{ee}[n] + \gamma^{3/2} \mathcal{F}_\text{ZPE}[n] + \gamma^2 \Delta T^{(2),w}[n] + \ldots \quad (11)
\]

The \( O(\gamma^2) \) term, \( \Delta T^{(2),w} = \sum \omega_k \Delta T_k^{(2)} \), has an explicit weight dependence on each excited state. It captures the energy of oscillations “perpendicular” to the collective ZPE modes, according to the metric dictated by the SCE manifold – see eq. (S36) and discussion for details. Note, a similar result was previously observed in the special case of Hubbard dimers. \([14]\)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Excitation energies, for dissociating \( \text{H}_2 \) (top); and seven random runs and the mean of 25 runs for a ring of wells with disorder (bottom). Shows ensemblized EXX (dots/green), GL2 (dashes/red), ISI (dash-dot/blue) and exact (lines/maroon) energies. GL2 errors in the ring are so large they cannot be shown in the lower panel.}
\end{figure}

Use of high- and low-density limits in approximations. We have so far derived series expansions in the high-density \([\text{eq. (2)}]\) and low-density \([\text{eq. (11)}]\) limits. Next, we shall illustrate their relevance in applications.

First, we remark that eqs \((3), (4)\) and \((11)\) imply that,

\[
\lim_{\gamma \to 0^+} c^{w}_{\text{Hxc}}[n,\gamma] = \gamma c^{w}_{\text{Hxc}}[n] + \gamma^{3/2} \mathcal{F}_\text{ZPE}[n] + \ldots, \quad (12)
\]

\[
\lim_{\gamma \to 0^+} c^{w}_{\text{Hxc}}[n] = \gamma V^{\text{SCE}}_{ee}[n] + \gamma^{3/2} \mathcal{F}_\text{ZPE}[n] + \ldots. \quad (13)
\]

Especially note that the low-density (strictly correlated) limit of both \( c_w[n] \) [see \((3)\)] and \( \mathcal{E}_w[n] \) depend on the excitation structure only trivially, via the ensemble particle density. Weight dependence appears at higher order.

To illustrate the usefulness of the limits, we first consider the lowest singlet-singlet excitation in dissociating \( \text{H}_2 \). This problem is a rather stringent test of density functionals – failed by time-dependent DFT approximations \([45, 46]\) because: i) the ground state is dynamically correlated near its minima but becomes strongly correlated when dissociated; ii) the first excited state is always dynamically correlated, thus cancellation of errors in the approximate excitation energy from the ground state may be unreliable during dissociation; iii) the first excited state in the KS ensemble involves a superposition of two SDs, and its symmetry and related properties are irreproducible by an adiabatic single-SD approach.

Figure 2 (top) reports the excitation energy \( \Delta E_{SS} = E_{S_1} - E_{S_0} \) of the lowest singlet states \((S_0 \text{ and } S_1)\) of \( \text{H}_2 \) using: EXact EXchange (EXX) energies – the leading term in the high-density series of eq. \((12)\); Görling-Levy \([32]\) (GL2) perturbation theory – the next leading term of \((12)\); and the Interaction Strength Interpolation (ISI) approximation \([33, 34]\) that uses high- and low-density limits – the latter via the harmonium point charge plus continuum (hPC) approximation \([35]\). Note, all approximations are ensemblized versions of ground states analogs, i.e. \( E_{\text{approx}}^{\text{SCE}} \rightarrow E_{\text{approx}}^{\text{Hxc}} \) is adapted for excited states. All relevant energy expressions and technical details on the calculations are in Supp. Mat. Sec. IV.

Only ISI performs well across the whole \( \text{H}_2 \) dissociation curve, which unambiguously highlights the benefit of using both eq. \((12)\) and eq. \((13)\) to construct approximations that capture different correlation regimes. In fact, using only eq. \((12)\) leads to very poor results for the ground state energy: EXX overestimates and GL2 drastically underestimates as correlations become stronger.

Next, we carry out similar calculations for four electrons in a ring of four quantum wells; see Supp. Mat. Sec. IV for further details. Lattice disorder in this system yields \( \Delta E_{SS} = 2.15 \text{ eV} \) on average, versus \( \Delta E_{SS} = 0.003 \text{ eV} \) of the ordered lattice. Results are shown in Figure 2 (bottom). Again, we see that the low-density behaviour included in ISI reduces errors: from 100% (EXX) down to -12% (ISI). GL2 energies (not shown) have orders of magnitude worse errors. This example (also, Ref. \([49]\)) thus suggests that seamless interpolation between high- and low-density limits may be crucial for predicting optical gaps in disordered nanostructures.

Summary and conclusions. The results presented in this work describe, via ensemble density functionals, the behaviour of excited many-electron states in the paradigmatic high- (weakly-) and low-density (strictly-correlated) limits (regimes) – summarized for the important \( \mathcal{E}_{\text{Hxc}} \) functional in eqs \((12)\) and \((13)\), respectively.

The high-density limit follows intuition and connects...
directly to previous results which use the ensemble Kohn-Sham system as reference system. The corresponding auxiliary pure states have the form of symmetry adapted combination of Slater determinants; and \( E_{\text{Hxc}} \) has strong weight-dependence. Approximations based on this limit have already successfully described weakly to moderately correlated excitations.

The low-density limit, in contrast, revealed an unexpected fact: the first two leading order terms of excited states may be described by existing tools used for strictly correlated ground states. Therefore the ensemblization of ground-state approximations is, for once, straightforward. Dependence of \( E_{\text{Hxc}} \) on the weights (and therefore excitation structure) only shows up in the third leading order term. The provided model applications illustrate that generally correlated regimes of excited states requires seamless treatment of both density regimes.

One immediate consequence of the present work is that electronic interaction models must interpolate between Fermionic mean-field like excitation-structure dependence at high-densities, and no excitation-structure dependence at low-densities. Not only is this of direct importance for traditional analytic-driven approximations, as seen in the examples reported here, it also provides constraints for data-driven methodologies based on machine learning. Ensemble-derived constraints were used to great success in the machine-learned “Deep Mind 21” ground state approximation [9] – our work promises to extend this success to excited states.

Natural next steps from the present results are to consider finite-temperature ensembles and magnetic interactions. Finite temperature imposes a \( \lambda \)-dependence on the weights. Prior work [10] showed that the high/low-density limit may be more relevant to the behavior of density functionals at low/high temperatures. Magnetic interactions require extra basic densities (e.g. spin-densities and currents) and related Hxc quantities; [11, 12] and must consistently fulfill gauge symmetries. [12] Further work along both lines is being pursued.

TG was supported by an Australian Research Council (ARC) Discovery Project (DP200100033) and Future Fellowship (FT210100663). DPK and PG-G were supported by the Netherlands Organisation for Scientific Research (NWO) under Vici grant 724.017.001. SP was partially supported by the MIUR PRIN Grant No. 2017RKWTMY.

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Note, to address degenerate states one must vary degenerate manifolds so that degenerate states remain equally weighted. E.g., addressing the first excited state of Be involves setting, $\Gamma = (1 - w)(1s^2 2s^2)(1s^2 2s^2) + \frac{\lambda}{2}(1s^2 2s 2p_x)(1s^2 2s 2p_y) + |1s^2 2p_x 2p_y| |1s^2 2s 2p_y| + |1s^2 2p_x 2p_y| |1s^2 2p_x 2p_y|$, and varying $w$. Then, perturbation theory is well-defined around the ensemble HX $\{\lambda \rightarrow 0^+\}$ limit.

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This is $V_{cl} = \frac{E_{cl}}{R_0}$ where $R_0$ minimizes the classical energy, $E_{cl}(R) = 2 \times \frac{1}{2} R^2 + \frac{\lambda}{2R}$, of two electrons interacting with $\frac{1}{R_0}$ when the two electrons are on opposite sides of the well.

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