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Domain Separation in Density Functional Theory

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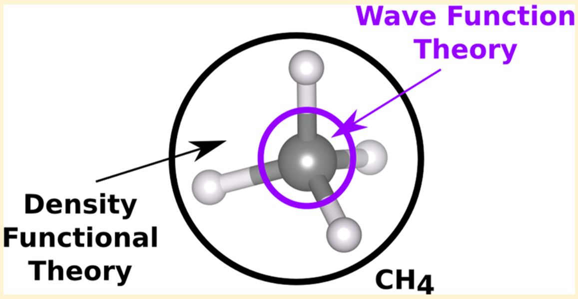
Martín A. Mosquera,[†] Leighton O. Jones,[†] Carlos H. Borca,[‡] Mark A. Ratner,[†]
and George C. Schatz*[,†]

[†]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States
[‡]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

Supporting Information



ABSTRACT: Research within density functional theory (DFT) has led to a large set of conceptual and computational methodologies to explore and understand the electronic structure of molecules and solids. Among the most commonly employed techniques in DFT are those of hybrid functionals, which are capable of producing accurate results for diverse properties, with notable exceptions. However, other techniques have been proposed to address limitations in the application of conventional hybrid functional techniques, especially to cases where a single reference is insufficient to achieve a proper description of the system of interest. In this paper we consider several previous developments in the field for the combination of local and nonlocal potentials and show that they can be formalized within the constrained-search Levy formalism, offering routes and ideas for the development of (nontraditional) density functionals, especially for treating strongly correlated regions of a molecule. The proposed formalism is centered around the idea of decomposing into domains the differential volume elements that are present in the definition of the electronic repulsion operator, which is contained in the electronic Hamiltonian, but this can also be applied to other operators as well. We show that the domain decomposition leads to a formulation that allows for the combination of different theories: DFT, correlated wave function theory, and Hartree−Fock, among others. This combination could accelerate the computation of electronic properties and allow for explicit inclusion, at the wave function level, of correlation effects, as in configuration-interaction theory. Our discussion covers both single- and multideterminantal methods. We demonstrate the approach through a simple application to the electronic structure of the methane and ethylene molecules, in which nonlocal exchange is applied to a given set of atoms, or domains, with the remaining atoms modeled with the local density approximation.

■ INTRODUCTION

Computing the electronic and conformational properties of molecules and solids has been the subject of continuing scientific efforts, with the main goals including speed-up of the algorithms while maintaining or increasing accuracy. Density functional theory (DFT) has played a significant role in this regard,[1] with its central objective being the determination of the electronic density and ground-state energy. The computation of electronic properties is often performed with Kohn−Sham (KS) wave functions, which provide a proper estimation of the kinetic energy and, through an XC functional approximation, of the ground-state electronic energy.

A formulation that is often employed in periodic calculations, to model crystals or solids with some degree of disorder, and in isolated-molecule computations is that proposed by Kohn and Sham.[2] In this model, the auxiliary electrons are subject exclusively to a local potential, which is determined by the semiclassical electron−electron repulsion (the Hartree potential), the exchange−correlation (XC) potential, and the electron−nuclear attraction. The computation of orbitals in this model tends to be tractable by standard high-performance computers. For molecules and solids, however, the inclusion of portions of nonlocal exchange is known to lead to improvements with respect to standard KS density functional approximations, such as the XC LDA or GGA, and orbital-free DFT methods,[3,4] especially in the accuracy of quantities such as ionization/affinity potentials, optimal geometries, excitation energies, etc.

There are situations where some ability to compute nonlocal exchange and/or including some explicit wave function correlation (a truncated configuration-interaction expansion, for example) is required.[5,6] Examples in this matter include molecular junctions[7] (where a better description could be achieved with hybrid functionals), transition metal complexes,[8] and molecular dissociation,[9−11] among others. In molecular electron transport,[12] revealing the effect of nonlocal

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interactions on the transmission spectrum of a molecular bridge remains an open topic. For transition metal complexes, explicit correlation, as in complete active space (CAS) methods, can provide crucial information about the interaction between the central transition metal atom and its ligands,[13] and magnetic properties of the molecule. Complexes with two, or more, mutually bonded transition metal atoms may even require more efforts toward their satisfactory quantum-chemical description.

In recent years, remarkable contributions have been made regarding some of the issues we mentioned above.[14−20] Toulouse, Savin, and collaborators[21−24] have illustrated how to introduce correlated wave functions to DFT algorithms. Their method is based on range separation of the Coulomb repulsion between the auxiliary electrons. This separation is global, as it is applied in terms of the relative distances between the electron coordinates. In this method, long-range interaction is treated at the correlated wave function level, while short-range contributions are modeled with a density functional approximation (DFA). An advantage of this approach is that the formalism is developed within the Levy constrained-search framework, providing a formalism for the exploration and development of alternative DFAs, which can be applied to problems in electronic structure. A theory derived from this framework was proposed recently by Fromager and collaborators.[25−28] But this approach is based on site (or orbital) occupations instead of the electronic density, in which the constrained search is applied to a single site that is embedded in a Hubbard chain, allowing for a description of strong correlation for the embedded site, as demonstrated by numerical simulations. The resulting eigenvalue equation for the embedded site involves a Hubbard repulsion term and an embedding potential that is obtained from a Hartree-XC function (in orbital-occupation space) that needs to be estimated. To treat a region of interest with correlated wave function methodologies, the Carter group[29−31] has designed and implemented embedding techniques. Within the fragment molecular orbital theory, Fedorov and Kitaura[32,33] have also demonstrated the possibility of treating a region of a molecule with CAS methods. Miller and co-workers[34−36] also developed methods in this direction that are based on projection operators. A powerful quantum-chemical methodology has been proposed by the Gagliardi group,[17] which can add dynamical correlation effects, via a density functional, to multiconfigurational calculations.

The present work concerns dividing the electronic repulsion operator for a molecule (or solid) into domains where one can control the type of electron−electron interaction for each of these domains: local, nonlocal, or correlated. By a correlated interaction we refer to the interaction arising from the inclusion of multideterminant wave functions that are created by exciting selected molecular orbitals. We refer to the theoretical framework described here as "domain separated density functional theory" (DS-DFT). DS-DFT is mainly based on three well-established tools: First, it uses the Levy constrained-search method,[37] which offers simple ways to define density functionals. Second, DS-DFT is formulated by employing the generalized Kohn−Sham (GKS) theory[38] that often leads to the development of range separated functionals but can also lead, as we suggest, to domain-separated interactions that can be treated as either local or nonlocal. Third, it is also motivated by the work of Toulouse et al.[21] and Fromager et al.,[25−28] which employs the Levy constrained-search similarly as in GKS theory, but we pursue a different focus, so explicit wave function correlation and/or Hartree−Fock (HF) exchange can be introduced to study the domains of interest in molecules and solids. We employ a trivial splitting of the differential volume elements that are part of the definition of the nonrelativistic Hamiltonian of the molecule (or solid). In this splitting, we suggest that expansion into a weighted set of volume elements can lead to a set of domain-separated operators that allows us to use different levels of theory to determine the electronic structure of the system of interest. In contrast to embedding theories that have been proposed in the literature, the methods presented in this work do not require embedding potentials. Instead, they need density-functional approximations that eliminate the local "DFT" interaction in the regions where nonlocal exchange or explicit electron correlation (wave function excitations) is applied. The domain separation may be performed in terms of space or energy, and it can lead, as discussed herein, to a vast family of algorithms to control explicit wave function correlation and the desired treatment of electron−electron interaction; this also includes the possibility of employing hybrid functionals for some domains while applying semilocal DFAs to others. For a choice of domain separation scheme, i.e., by choosing the proper weighing functions and with knowledge of the exact functionals, the formalisms we present here are exact in principle.

■ DOMAIN SEPARATION FOR A REGION OF INTEREST

In this section we consider the admixture of a DFT method (or DFA) with a wave function based technique (Hartree−Fock, or coupled cluster, for instance). Here the objective is to apply the wave function method to a single spatial region of interest and treat the complementary spatial domain to the region of interest with a DFA. The generalization to multiple domains is straightforward and will be briefly summarized in the Discussion section. Although the theory can be formulated in first quantization (in the Supporting Information we include some operators in this notation), we use second quantization as it is preferred for the development of correlated wave function methodologies.

The electron interaction operator is the object responsible for the explicit correlation in post-Hartree−Fock calculations. This operator can be written as follows:

$$\hat{W} = \frac{1}{2}\int \mathrm{d}^3\mathbf{r}\, \mathrm{d}^3\mathbf{r}'\, \hat{\psi}^{\dagger}(\mathbf{r}')\frac{\hat{\rho}(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\hat{\psi}(\mathbf{r}') \tag{1}$$

where the density operator is $\hat{\rho}(\mathbf{r}) = \hat{\psi}^{\dagger}(\mathbf{r})\,\hat{\psi}(\mathbf{r})$. Explicit (wave function) correlation, associated with this operator, is necessary to achieve high accuracy in electronic structure calculations, especially for strongly correlated systems (such as organometallic compounds for which standard DFAs perform poorly).

In the simplest domain decomposition one can consider, the electron−electron interaction is divided into an explicit operator for the region of interest (X) and a different one for the complementary region ($\bar{X}$), which is modeled with a density functional approximation. In this case we only introduce an explicit Coulomb repulsion for domain X, and all the other interactions (kinetic and electron-nuclei) are not separated into domains. We thus define the following domain-screened interaction operator:

$$\hat{W}_X = \frac{1}{2}\int d\mu_X(\mathbf{r})\, d\mu_X(\mathbf{r}')\, \hat{\psi}^\dagger(\mathbf{r}')\frac{\hat{\rho}(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\hat{\psi}(\mathbf{r}') \tag{2}$$

where $d\mu_X$ is the differential measure:

$$d\mu_X(\mathbf{r}) = d^3\mathbf{r}\, w_X(\mathbf{r}) \tag{3}$$

In the above equation $w_X(\mathbf{r})$ is a weighing function, which is preferably close to the unity inside the molecular domain X and close to zero otherwise. This function (w_X) can be conveniently defined in terms of Gaussians or other distribution functions that can allow for analytical computation of electron repulsion integrals. We thus assign the operator $\hat{W}_X$ to the region that needs to be studied with nonlocal exchange or explicit correlation. The complementary region is assumed to be modeled with a local effective potential, so the Coulomb operator $\hat{W}_{\bar{X}}$ is not needed for such region in practice.

More generally, the differential volume element can be decomposed into contributions from several domains. This can be used to generalize the theory discussed in this section to multiple domains or to develop formalisms to perform calculations within a fragment-based approach (by carrying out separate DFT or wave function calculations that are postprocessed to generate quantum chemical information about the system of interest[5]). This is briefly explored in Appendix A.

To derive density-functional approximations for the complementary domain $\bar{X}$, we introduce a density functional that includes the interaction operator that leads to explicit wave function correlation in domain X or allow for the application of nonlocal exchange to that domain, as we discuss below. This density functional reads

$$G_{l,X}[\rho] = \min_{\substack{\Phi\to\rho \\ \Phi\in\mathcal{L}}} \langle\Phi|\hat{T} + \hat{W}_X|\Phi\rangle \tag{4}$$

where $\hat{T}$ is the kinetic energy operator

$$\hat{T} = \frac{1}{2}\int d^3\mathbf{r}\, \nabla\hat{\psi}^\dagger(\mathbf{r})\cdot\nabla\hat{\psi}(\mathbf{r}) \tag{5}$$

$\mathcal{L}$ is a space of wave functions, for example, the space of Slater determinants ($\mathcal{S}$) or the space of fully correlated wave functions ($\mathcal{H}$). If $\mathcal{L} = \mathcal{S}$, we use the index l = s, and for the case $\mathcal{L} = \mathcal{H}$, we employ l = w to indicate search over correlated wave functions. The symbol ρ represents a given (physically meaningful) electronic density of the system. The constrained search that defines $G_{l,X}$ is a minimization under the condition that the wave functions considered must satisfy $\langle\Phi|\hat{\psi}^\dagger(\mathbf{r})\,\hat{\psi}(\mathbf{r})|\Phi\rangle = \rho(\mathbf{r})$ for all points in space. The above functional can be regarded as a variation of the constrained search defined within generalized KS theory[38] for the case of single determinants and of the method of Toulouse et al.[21] for DFT calculations based on multiple determinants and (global) range separation of the Coulombic electron repulsion.

The energy functional $G_{l,X}$ has contributions from the kinetic energy of the auxiliary electrons, and another contribution from the domain-screened interaction $\hat{W}_X$. In the following sections we express the total electronic energy functional in terms of $G_{l,X}$, a residual energy functional that we refer to as *partial* Hartree-exchange−correlation (HXC) energy, and the electron−nuclei attraction energy. The partial HXC energy is associated with the electron−electron repulsion energy of the complementary region $\bar{X}$. This partial HXC energy is required due to the functional $G_{l,X}$ accounting for an amount of the total electron−electron interaction energy that corresponds to region X.

The minimization shown on the right-hand side of eq 4 can be solved using the Lagrange multiplier method (Appendix B). This gives rise to a local potential (which is in turn a multiplier) that can be computed by adding to the electron−nuclei interaction the functional derivative of the partial HXC energy functional (Appendix B). In the next subsections we discuss the derivation of these functionals.

Expressions for Functionals Based on Single Determinants. In this subsection we suppose that $\mathcal{L} = \mathcal{S}$. Now, let us define the usual Levy functional:

$$F[\rho] = \min_{\Psi\to\rho}\langle\Psi|\hat{T} + \hat{W}|\Psi\rangle \tag{6}$$

Comparison between the above functional and $G_{s,X}$ leads us to the partial HXC functional:

$$\bar{E}^{s}_{Hxc}[\rho] = F[\rho] - G_{s,X}[\rho] \tag{7}$$

This functional is the HXC energy associated with domain $\bar{X}$, and it depends on the specific form of $\hat{W}_X$, which is determined by the measure $d\mu_X(\mathbf{r})$ that has been selected to define the molecular domain of interest. To express $\bar{E}^{s}_{Hxc}$ in a more convenient form, we first denote $\tilde{\Phi}$ and $\tilde{\Psi}$ as the wave functions that minimize the right-hand side of eqs 4 and 6, respectively. These two functions can also be regarded as functionals of the density (Supporting Information). Using these wave functions, we can write the functional $G_{s,X}$ as follows:[a]

$$G_{s,X}[\rho] = \langle\tilde{\Phi}|\hat{T} + \hat{W}|\tilde{\Phi}\rangle + E^{s,X}_{Hx}[\rho] - \langle\tilde{\Phi}|\hat{W}|\tilde{\Phi}\rangle \tag{8}$$

where $E^{s,X}_{Hx}[\rho] = \langle\tilde{\Phi}|\hat{W}_X|\tilde{\Phi}\rangle$. In the above equation the term $\langle\tilde{\Phi}|\hat{W}|\tilde{\Phi}\rangle$ is trivially inserted. Given that $F[\rho] = \langle\tilde{\Psi}|\hat{T} + \hat{W}|\tilde{\Psi}\rangle$, we find that the functional $\bar{E}^{s}_{Hxc}$ can be decomposed as follows:

$$\bar{E}^{s}_{Hxc}[\rho] = E^{s}_{Hx}[\rho] - E^{s,X}_{Hx}[\rho] + E^{s}_{c}[\rho] \tag{9}$$

where $E^{s}_{Hx}[\rho] = \langle\tilde{\Phi}|\hat{W}|\tilde{\Phi}\rangle$. The functional E^{s}_{Hx} accounts for the average electron−electron repulsion energy of the entire system, while $E^{s,X}_{Hx}$ quantifies such repulsion in the region labeled X. Since the expectation value $\langle\tilde{\Phi}|\hat{W}_X|\tilde{\Phi}\rangle$ only has Hartree and exchange contributions, the correlation energy remains a global quantity. This object reads

$$E^{s}_{c}[\rho] = \langle\tilde{\Psi}|\hat{T} + \hat{W}|\tilde{\Psi}\rangle - \langle\tilde{\Phi}|\hat{T} + \hat{W}|\tilde{\Phi}\rangle \tag{10}$$

It is important to note in this case that, due to the different nature of the constrained search defining $G_{s,X}$, the energy functionals E^{s}_{Hx} and E^{s}_{c}, strictly speaking, should be different from those used in standard KS theory. There is no analogue to $E^{s,X}_{Hx}$ or $\bar{E}^{s}_{Hxc}$ in KS-DFT. However, analytical formulas for the mentioned functionals can be derived from the study of the uniform electron gas. From a practical standpoint, assuming one would like to apply an explicit DFA to the complementary region, the functional $\bar{E}^{s}_{Hxc}$ would allow us to derive a local effective potential that would be felt not only mostly by the auxiliary electrons in the complementary region but also by domain X to a lower degree. In practical terms, this would be advantageous to model regions of the molecule where a standard KS DFA would perform well.

With the above formulas for the HXC energies, the ground-state energy (for the $X + \bar{X}$ system) may be obtained from minimizing the functional $E_v[\rho] = G_{s,X}[\rho] + \bar{E}^{s}_{Hxc}[\rho] + \int d^3\mathbf{r}$

$v(\mathbf{r})\,\rho(\mathbf{r})$, where $v(\mathbf{r})$ is the electron-nuclei attraction potential. By applying the minimization principle, we have (Appendix B):

$$\left\{-\frac{1}{2}\nabla^2 + 2\hat{j} - \hat{k}_X + \bar{u}^{\mathrm{s}}_{\mathrm{xc}}(\mathbf{r}) + v(\mathbf{r})\right\}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \tag{11}$$

where $\{\psi_i\}$ are the occupied orbitals of the system, $\hat{j}$ is the Coulomb operator,

$$\hat{j}\,\psi_i(\mathbf{r}) = \left(\int \mathrm{d}^3\mathbf{r}'\,\frac{\sum_j |\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\right)\psi_i(\mathbf{r}) \tag{12}$$

where the summation is carried out over all the occupied orbitals, and $\hat{k}_X$ is a domain-screened exchange operator:

$$\hat{k}_X\psi_i(\mathbf{r}) = \sum_j \left[\int \mathrm{d}\mu_X(\mathbf{r}')\,\frac{\psi_i(\mathbf{r}')\,\psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\right] w_X(\mathbf{r})\,\psi_j(\mathbf{r}) \tag{13}$$

In this formula real-valued orbitals are implied. The potential $\bar{u}^{\mathrm{s}}_{\mathrm{xc}}$ reads (Appendix B)

$$\bar{u}^{\mathrm{s}}_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta \bar{E}^{\mathrm{s}}_{\mathrm{xc}}}{\delta\rho(\mathbf{r})} \tag{14}$$

where $\bar{E}^{\mathrm{s}}_{\mathrm{xc}}$ is obtained by removing the Hartree contributions from eq 9:

$$\bar{E}^{\mathrm{s}}_{\mathrm{xc}}[\rho] = \bar{E}^{\mathrm{s}}_{\mathrm{Hxc}}[\rho] - \frac{1}{2}\left\{\int [\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{r}' - \mathrm{d}\mu_X(\mathbf{r})\,\mathrm{d}\mu_X(\mathbf{r}')]\frac{\rho(\mathbf{r}')\,\rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\right\} \tag{15}$$

With an approximation to the energy functional $\bar{E}^{\mathrm{s}}_{\mathrm{Hxc}}$, the above would lead to an estimate of the local potential $\bar{u}^{\mathrm{s}}_{\mathrm{xc}}$. In our theory the orbitals would be computed in a fashion similar to that in a standard hybrid functional (or a correlated-wave function) algorithm, but with differences in the construction of the energy matrices, as we discuss later on.

Expressions for Functionals Based on Correlated Wave Functions. Here we follow steps analogous to those discussed in the previous subsection, but with differences in detail, with the objective now being the study of the region of interest with explicit wave function correlation, and the derivation of the eigenvalue problem that has to be solved to estimate the auxiliary wave function of the system and related properties.

We start with the constrained-search functional, $G_{\mathrm{w},X}$, which is defined over the space of fully correlated wave functions (eq 4), so $\mathcal{L} = \mathcal{H}$. It is convenient to introduce a HXC functional for the region X, as it is an object that can be approximated. To this end, we first introduce the usual KS kinetic energy functional:

$$T_{\mathrm{s}}[\rho] = \min_{\substack{\Phi\to\rho\\ \Phi\in\mathcal{S}}}\langle\Phi|\hat{T}|\Phi\rangle \tag{16}$$

where the search is performed over the space of Slater determinants. With this definition, we introduce the HXC functional for region X:

$$E^{\mathrm{w},X}_{\mathrm{Hxc}}[\rho] = G_{\mathrm{w},X}[\rho] - T_{\mathrm{s}}[\rho] \tag{17}$$

This functional has properties similar to those of the standard HXC functional of KS-DFT. Let us denote $\tilde{\Phi}_{\mathrm{w}}$ and $\tilde{\Phi}_0$ as the wave functions that solve the constrained searches defining $G_{\mathrm{w},X}[\rho]$ and $T_{\mathrm{s}}[\rho]$, respectively. The functional $E^{\mathrm{w},X}_{\mathrm{Hxc}}[\rho]$ can be written as the sum

$$E^{\mathrm{w},X}_{\mathrm{Hxc}}[\rho] = E^{\mathrm{w},X}_{\mathrm{Hx}}[\rho] + E^{\mathrm{w},X}_{\mathrm{c}}[\rho] \tag{18}$$

where $E^{\mathrm{w},X}_{\mathrm{Hx}}[\rho] = \langle\tilde{\Phi}_0|\hat{W}_X|\tilde{\Phi}_0\rangle$, and $E^{\mathrm{w},X}_{\mathrm{c}}[\rho] = \langle\tilde{\Phi}_{\mathrm{w}}|\hat{T} + \hat{W}_X|\tilde{\Phi}_{\mathrm{w}}\rangle - \langle\tilde{\Phi}_0|\hat{T} + \hat{W}_X|\tilde{\Phi}_0\rangle$. These two functionals together account for the net electron−electron repulsion (including Hartree and XC effects) in domain X. The way the functional $E^{\mathrm{w},X}_{\mathrm{Hxc}}[\rho]$ is expressed, in terms of T_{s}, can be applied to the single-determinantal case discussed in the previous subsection; this is presented in the Supporting Information.

Now, the partial HXC energy for the complementary domain $(\bar{X})$ is written as

$$\begin{aligned}\bar{E}^{\mathrm{w}}_{\mathrm{Hxc}}[\rho] &= (F[\rho] - T_{\mathrm{s}}[\rho]) - (G_{\mathrm{w},X}[\rho] - T_{\mathrm{s}}[\rho])\\ &= E_{\mathrm{Hxc}}[\rho] - E^{\mathrm{w},X}_{\mathrm{Hxc}}[\rho]\end{aligned} \tag{19}$$

where E_{Hxc} is the traditional HXC energy functional from KS theory. Note that the KS kinetic functional (T_{s}) is trivially inserted in the above equation. It, however, allows us to express the partial energy $\bar{E}^{\mathrm{w}}_{\mathrm{Hxc}}$ in terms of HXC energies, where the energy $E^{\mathrm{w},X}_{\mathrm{Hxc}}[\rho]$ is an object that needs an approximation.

Using the above definitions, and analogously to the way we proceeded in the previous section, the ground-state energy functional reads

$$E_v[\rho] = G_{\mathrm{w},X}[\rho] + \bar{E}^{\mathrm{w}}_{\mathrm{Hxc}}[\rho] + \int \mathrm{d}^3\mathbf{r}\,v(\mathbf{r})\,\rho(\mathbf{r}) \tag{20}$$

In a fashion similar to that in the work of Toulouse et al.,[21] the minimization of the above density-functional can be solved through self-consistent solution of the equation (Appendix B):

$$\left\{\hat{T} + \hat{W}_X + \int \mathrm{d}^3\mathbf{r}\,[v(\mathbf{r}) + \bar{u}^{\mathrm{w}}_{\mathrm{Hxc}}(\mathbf{r})]\hat{\rho}(\mathbf{r})\right\}|\Phi_{\mathrm{w}}\rangle = E|\Phi_{\mathrm{w}}\rangle \tag{21}$$

where Φ_{w} is a correlated wave function and $\bar{u}^{\mathrm{w}}_{\mathrm{Hxc}}$ is obtained through functional differentiation:

$$\bar{u}^{\mathrm{w}}_{\mathrm{Hxc}}(\mathbf{r}) = \frac{\delta\bar{E}^{\mathrm{w}}_{\mathrm{Hxc}}}{\delta\rho(\mathbf{r})} \tag{22}$$

In eq 21, the operator $\hat{W}_X$, through orbital screening and within a configuration-interaction (or coupled cluster) picture, determines which orbital excitations need to be considered to construct the state $|\Phi_{\mathrm{w}}\rangle$. For example, excitations that involve promotion of orbitals that are far enough from domain X can be neglected (because the operator $\hat{W}_X$ is the object that couples these excitations, and it can be neglected in regions away from the domain determined by the weight w_X). In practice, for instance, this would lead to a reduced truncated CI space with respect to what would have been obtained if the entire system were treated with a CI method. Other possibilities would involve reduced excitation operators in coupled-cluster calculations. It is important to note that the solution of eq 21 should be performed self-consistently, and eq 37 can be used to construct the reference determinant(s).

To summarize, in practice, the elements that are needed to perform calculations using the present theory are (i), a choice of w_X that determines the domain of interest, X, (ii) an approximation to both density functionals $E_{\mathrm{Hxc}}[\rho]$ and $E^{\mathrm{w},X}_{\mathrm{Hxc}}[\rho]$, and (iii) a wave function methodology such as coupled cluster or complete active space, for example, to solve eq 21. To select the weighing function, w_X, we can choose domain X as a region of space where explicit correlation is required, and this weight (or domain function) could be based on linear combinations of Gaussian functions, as mentioned earlier. In addition, regarding the second item, a standard approximation could be chosen to the functional E_{Hxc}, whereas development of an estimate to $E_{\mathrm{Hxc}}^{\mathrm{w},X}$ is required. The mentioned points will be the subject of future work. The theory presented in this subsection is different from the previous one in that excited orbitals are needed to create the multideterminantal expansion of the ground-state auxiliary wave function, which in turn is required to evaluate the ground-state energy of the total system.

■ EXAMPLE AND DISCUSSION

Application of the Method Based on a Single Determinant. In this section we apply, with some approximations, the method based on single determinants and treat a region X of a molecule with (nonlocal) HF exchange, and the rest (the complementary region to X, which we refer to as $\overline{X}$) with the local density approximation (LDA). This combination of HF with a local DFA is of relevance for the construction of the reference determinant(s) needed to solve eq 21 (the solution of this equation will be the subject of future work). The examples are presented in order to illustrate the concepts introduced in the previous sections and to examine how adding HF exchange to hydrogen or to a carbon atom affects ground-state properties. A practical advantage of combining HF and LDA is the implication that, a hybrid functional assigned to certain domain could be combined with a GGA functional assigned to a different domain, which would be useful, for instance, to study molecular processes on electrode surfaces. This is where the application of a hybrid functional to the molecule's domain can eliminate charge delocalization.

Figure 1 shows two different domain decompositions for two different molecules, methane, and ethylene; we compute the electronic structure of these molecules separately. For the methane molecule, domain X consists of the carbon atom, whereas for ethylene the four hydrogen atoms define region X. We suppose that the function that defines region X is the weight $w_X(\mathbf{r})$, and we employ it implicitly, as shown below.

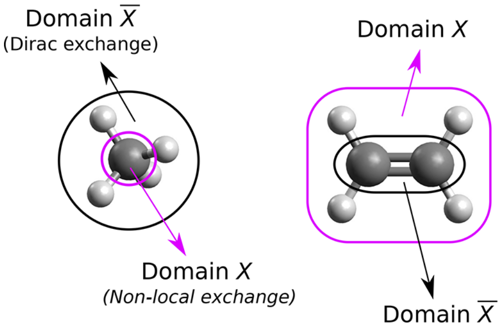

Figure 1. Ball-and-stick representation of a methane (left) and an ethylene (right) molecule, with domains indicated.

In the atomic orbital basis, the exchange matrix has the form

$$K_{X,\mu\nu} = \int \mathrm{d}\mu_X(\mathbf{r})\, \mathrm{d}\mu_X(\mathbf{r}')\, \phi_\mu(\mathbf{r}')\frac{\gamma(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_\nu(\mathbf{r}) \tag{23}$$

where $\{\phi_\mu\}$ is the basis set, $\gamma(\mathbf{r},\mathbf{r}')$ is the density matrix defined as $\sum_j \psi_j(\mathbf{r}')\, \psi_j(\mathbf{r})$, and the sum is performed over the occupied energy levels of the molecule. Now we define the following weighted density matrix:

$$\gamma_X(\mathbf{r}',\mathbf{r}) = w_X(\mathbf{r})\, w_X(\mathbf{r}')\, \gamma(\mathbf{r}',\mathbf{r}) \tag{24}$$

For the sake of the illustration, we assume that this function can be approximated as

$$\gamma_X(\mathbf{r}',\mathbf{r}) \approx \sum_{\mu\nu\in X} D_{X,\mu\nu}\phi_\mu(\mathbf{r}')\, \phi_\nu(\mathbf{r}) \tag{25}$$

where $D_{X,\mu\nu}$ is the density matrix in atomic orbital space: $D_{X,\mu\nu} = \sum_j C^j_\mu C^j_\nu$, if both indices μ and ν are associated with the atom (or atoms) contained in region X; otherwise, $D_{X,\mu\nu} = 0$ (the LCAO coefficients are denoted as $\{C^j_\mu\}$). Hence, we approximate the exchange matrix as follows:

$$K_{X,\mu\nu} = (\phi_\mu|\hat{k}_X|\phi_\nu) \approx \int \mathrm{d}^3\mathbf{r}\, \mathrm{d}^3\mathbf{r}'\, \phi_\mu(\mathbf{r}')\frac{\gamma_X(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_\nu(\mathbf{r}) \tag{26}$$

and the exchange energy for domain X reads

$$K_X = \sum_{\mu\nu} D_{\mu\nu}K_{X,\mu\nu} \tag{27}$$

where $\mathbf{D}$ is the standard (electronic) density matrix of the molecule $D_{\mu\nu} = \sum_j C^j_\mu C^j_\nu$, where the indices μ and ν run over the entire basis set.

To approximate the LDA exchange energy of domain X, we simply use the density $\rho_X(\mathbf{r}) = 2\gamma_X(\mathbf{r},\mathbf{r})$, and evaluate the Dirac exchange term at this density. Therefore

$$E_x^{s,X} = E_x^{\mathrm{LDA}}[\rho_X] = -c_x\int \mathrm{d}^3\mathbf{r}\, \rho_X{}^{4/3}(\mathbf{r}) \tag{28}$$

where $c_x = (3/\pi)^{1/3} \times (3/4)$. The density ρ_X is a functional of the total density of the system. In principle, the functional derivative of the above exchange energy could be computed as

$$\frac{\delta E_x^{s,X}}{\delta\rho(\mathbf{r})} = \int \mathrm{d}^3\mathbf{r}'\, \frac{\delta E_x^{s,X}}{\delta\rho_X(\mathbf{r}')}\frac{\delta\rho_X(\mathbf{r}')}{\delta\rho(\mathbf{r})} \tag{29}$$

For numerical simplicity, however, we assume that

$$u_x^{s,X}(\mathbf{r}) = \frac{\delta E_x^{s,X}}{\delta\rho_X(\mathbf{r})} \tag{30}$$

As an alternative form of eq 15, the partial XC energy reads

$$\bar{E}^{s}_{xc}[\rho] = E_x[\rho] - E_x^{s,X}[\rho_X] + E_c[\rho] \tag{31}$$

and the partial XC potential that we include in the single-particle Schrödinger equation (eq 37) is

$$\bar{u}_{xc}(\mathbf{r}) = u_{xc}(\mathbf{r}) - u_x^{s,X}(\mathbf{r}) \tag{32}$$

where u_{xc} is a standard XC potential from KS DFT. Finally, the ground-state energy is evaluated as

$$E_0 = \sum_i f_i \int \mathrm{d}^3\mathbf{r}\, \psi_i(\mathbf{r})\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r})\right]\psi_i(\mathbf{r}) + E_{\mathrm{H}}[\rho_0] - K_X + \bar{E}^{s}_{xc}[\rho_0] \tag{33}$$

where $\rho_0(\mathbf{r}) = \sum_i f_i|\psi_i(\mathbf{r})|^2$ is the ground-state electronic density, $f_i = 2$ for occupied levels, and E_{H} is the standard Hartree energy functional.

To summarize, the approximations we use are (i) the LDA for the functionals E_c, $E_x^{s,X}$, and E_x; (ii) eqs 25 and 26; and (iii) the functional derivative expressed in eq 30.

Table 1. Orbital Energies, Exchange and Ground-State Energies, and Hydrogen Dissociation Energies (DE_H) for the Methane and Ethylene Molecular Models Shown in Figure 1[a]

	CH_4			C_2H_4		
theory level	HF	LDA	LDA-nLE	HF	LDA	LDA-nLE
ϵ_{H-1}	−0.944 (I)	−0.617 (I)	−0.709 (I)	−0.494	−0.302	−0.301
ϵ_H	−0.542 (III)	−0.341 (III)	−0.316 (III)	−0.374	−0.240	−0.171
ϵ_L	0.254 (I)	0.094 (I)	0.189 (I)	0.175	−0.020	0.061
ϵ_{L+1}	0.322 (III)	0.146 (III)	0.251 (III)	0.260	0.091	0.181
$\epsilon_L - \epsilon_H$	0.796	0.435	0.505	0.549	0.260	0.232
K_X			4.966			0.586
$-E_x^{s,X}$			4.301			0.420
E_{ground}	−40.180	−40.090	−40.735	−78.003	−77.803	−77.928
DE_H (eV)	4.67	5.55	6.18	4.81	5.44	5.73

[a] Degeneracy indicated with Roman numerals. Energies expressed in atomic units, except DE_H, which is expressed in eV units.

Table 2. Comparison (Determined with Eq 34) between Frontier Orbitals Computed with Different Theories

	CH_4			C_2H_4		
T_A/T_B	LDA-nLE/HF	LDA-nLE/LDA	HF/LDA	LDA-nLE/HF	LDA-nLE/LDA	HF/LDA
$\Delta\psi_{H-1}$	0.033	0.085	0.009	0.074	0.061	0.021
$\Delta\psi_H$	0.071	0.103	0.119	0.033	0.007	0.040
$\Delta\psi_L$	0.015	0.062	0.062	0.118	0.002	0.116
$\Delta\psi_{L+1}$	0.036	0.089	0.095	0.083	0.053	0.075

We refer to the computations performed with the technique presented above as domain-separated LDA calculations with nonlocal exchange (LDA-nLE).[b]

For these calculations we employ the VWN-5 functional for the correlation energy[39] and Dirac exchange[40] (the geometries of these molecules were obtained from optimizations using the program NWChem[41] and the basis set 6-31G*). The basis set we use is 6-31G and convergence criterion 1×10^{-8} au for the total energy. The present computations were performed with the PyQuante suite.[42] Furthermore, to determine the difference between an orbital computed with theory level T_A and an orbital calculated with theory T_B, we use the L^2 norm:

$$\Delta\psi_j = \left\| \psi_j^{T_A} - \psi_j^{T_B} \right\|_2 = \left[2\left(1 - \int d^3\mathbf{r}\, \psi_j^{T_A}(\mathbf{r})\psi_j^{T_B}(\mathbf{r})\right)\right]^{1/2} \tag{34}$$

The eigenvalue solver can change the sign of the orbitals computed with a different theory level. For this reason, we compute the inner product using the molecular vectors produced by the eigenvalue solver and then change the sign of one of the orbitals and recompute and report the lowest value for the deviation.

Table 1 shows the results of applying our simplified method to the methane and ethylene molecules. For these molecules, we note that the orbital arrangement is preserved for all the levels considered. Interestingly, for the two molecules we note that the numerical values of the exchange energies K_X and $E_x^{s,X}$ are relatively close, with K_X being slightly larger in absolute value than $E_x^{s,X}$. This feature is due to the general trend by the Dirac exchange approximation to underestimate the exact exchange energy, leading to the well-known self-interaction error.

For the methane molecule we note that the orbital-energy level ordering is preserved after applying nonlocal exchange to the carbon atom. The highest occupied level is 3-fold degenerate, whereas the level right below it is nondegenerate, and this agrees with both the HF and LDA calculations. Regarding unoccupied levels, the lowest level is nondegenerate in our LDA-nLE, in agreement with the reference calculations. The 3-fold degeneracy of the level above the lowest unoccupied one is also preserved. For the ethylene molecule, the levels shown in Table 1 are nondegenerate, and the orbitals are close to the LDA orbitals (as confirmed by the comparison reported in Table 2, this is discussed below). In addition, because in this case we apply nonlocal exchange for the hydrogen atoms, potentially, this domain separation leads to some elimination of the self-interaction error (note that K_X is also larger than $-E_x^{s,X}$). We also observe that the LDA-nLE orbital eigenvalues are quite close to the LDA ones. This might be due to the low number of electrons being treated with HF exchange in the ethylene molecule, whereas in the methane this number is higher: for methane the density ρ_X integrates to 5.8 while in ethylene $\int d^3\mathbf{r}\, \rho_X(\mathbf{r}) = 2.7$.

In Table 2 we compare some LDA-nLE orbitals with HF and standard LDA orbitals. For the methane calculations, we observe that the considered LDA-nLE orbitals are closer to the HF orbitals than to the LDA ones (as the differences between LDA-nLE and LDA orbitals are similar to HF/LDA differences). In both comparisons, we note that the LDA-nLE orbitals, in terms of orbital energy, lie between pure LDA and pure HF orbitals, in agreement with the results presented in Table 1. As mentioned above, the LDA-nLE orbitals for ethylene are close to the LDA ones. The orbital energies computed with our method, however, are not expected to be an arithmetic average of LDA and HF orbital energies.

As an additional test of consistency for the calculations presented in this subsection, we computed the hydrogen dissociation energies for the two molecules:

$$\begin{aligned} &CH_4 \rightarrow CH_3 + H \\ &C_2H_4 \rightarrow C_2H_3 + H \end{aligned} \tag{35}$$

The dissociation energy is determined as the sum of ground-state energies of the hydrogen atom and the corresponding radical minus the energy of the methane or ethylene molecules.

The geometry of the methyl and vinyl radicals were kept frozen with respect to the geometries of their counterparts, so a hydrogen atom is simply eliminated from the methane and ethylene geometries. For these radicals we apply the domain-separation procedure we described in this subsection, but in spin-polarized form (in the Supporting Information we show additional details). The energy of the hydrogen atom is calculated with the same technique used for the molecule. For the dissociation energy calculation of the methane molecule, the ground-state energy of the hydrogen atom is computed with the Schrödinger equation with basis set 6-31G. But, for the case of ethylene, we included the correlation energy in the single hydrogen atom calculation.

As a same-basis reference we calculated the hydrogen dissociation energies with the CCSD(T)/6-31G technique, and with the NWChem program.[41] These energies are 5.28 and 5.29 eV for methane and ethylene, respectively. For both molecules we observe the computation with the LDA XC functional yields dissociation energies close to the CCSD(T)/6-31G values. In contrast, the LDA-nLE method, with the approximations made, produces results with a net deviation similar to that of Hartree–Fock/6-31G. While the latter underestimates the dissociation energies computed with CCSD(T) or LDA, the LDA-nLE results somewhat overestimate these numbers; such deviations can be corrected with the proper use of a domain function (w_X) and with better DFAs, as discussed below. We remark that, nonetheless, the domain separation approach produces physically meaningful results. The relatively moderate deviations, in combination with the other results presented in Tables 1 and 2, suggest the mixing of local and nonlocal exchange can potentially lead to orbitals and ground-state energies with properties similar to those that can be obtained from standard density functional or Hartree–Fock calculations.

The domain functions need to be included in order to perform computations that work in accordance to the DS-DFT formalism we discussed in this work. For example, we considered a domain X consisting of the two carbon atoms in ethylene and found that the imbalance between the approximated Dirac and the nonlocal exchange for domain X leads to the C–C σ orbital being the HOMO instead of the π orbital. In the present model we do not explicitly account for the domain function (w_X). Given the approximate nature of the steps we followed for these LDA-nLE calculations, this imbalance between the operators $\hat{k}_X$ and $u_x^{s,X}$ causes differences in the orbital-energy arrangement. As more electrons are computed with nonlocal exchange, a better estimation of the functional $E_x^{s,X}$ is required to ensure proper elimination of "DFT" exchange effects in the region of interest, so nonlocal exchange $\hat{k}_X$ is applied instead (including the domain function explicitly), and without modifying orbital level ordering. The proper balance can be accomplished by examining the domain-screened exchange energy in the electron gas limit, expressing it as a functional of density and then applying it to problems of interest. This will be subject of future work.

For problems where the application of hybrid-functional methods is sufficient, domain separation could also be useful to reduce computational costs. In such a case, the constrained search is defined in terms of the expectation value of the operator $\hat{T} + \lambda\hat{W}_X$, and the corresponding partial HXC energy has the form $\bar{E}^{s}_{\mathrm{Hxc}}[\rho] = E_{\mathrm{Hxc}}[\rho] - \lambda E^{s,X}_{\mathrm{Hx}}[\rho]$, where λ is the amount of HF exchange and Hx is the energy for domain X, which in this case formally reads $E^{s,X}_{\mathrm{Hx}}[\rho] = \langle\tilde{\Phi}[\rho]|\hat{W}_X|\tilde{\Phi}[\rho]\rangle$. As in the previous section, no correlation energy needs to be subtracted from the standard HXC energy (E_{Hxc}). The ground-state energy in this case can be written as follows:

$$E(\lambda) = \sum_i f_i \int \mathrm{d}^3\mathbf{r}\, \psi_i(\mathbf{r})\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r})\right]\psi_i(\mathbf{r}) + E_{\mathrm{H}}[\rho_0] - \lambda K_X + E_{\mathrm{xc}}[\rho_0] - \lambda E_{\mathrm{x}}^{\mathrm{s},X}[\rho_0] \tag{36}$$

And the equation for the orbitals is similar to eq 37:

$$\left\{-\frac{1}{2}\nabla^2 + 2\hat{j} - \lambda\hat{k}_X + u_{\mathrm{xc}}(\mathbf{r}) - \lambda u_{\mathrm{x}}^{\mathrm{s},X}(\mathbf{r}) + v(\mathbf{r})\right\}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \tag{37}$$

To compute the energy $E(\lambda)$, we applied the same approximations (LDA for XC functionals, density matrix, and functional derivative approximations) and adapted the steps discussed in the previous section.

To examine the effect of applying only a fraction of nonlocal exchange to the X-domains defined for the methane and ethylene molecules, we computed the total ground-state electronic energy as a function of λ, Figure 2. With respect to the LDA energies, we observe that the total ground-state energy almost linearly decreases as a function of λ. This near linearity indicates, besides the positive possibility of admixing with our method a hybrid functional with a local one, that for low values of λ quantities such as ground-state energies, orbital level ordering, etc. will be close to their LDA counterparts, so the domain separation is a smooth process. For instance, with $\lambda = 1/4$ we note that the hydrogen dissociation energy of methane and ethylene are estimated as 5.65 and 5.59 eV, correspondingly. In contrast with global quantities, however, properties sampled specifically from the region treated with the hybrid functional should behave as expected, using as reference traditional calculations with supramolecular hybrid functionals.

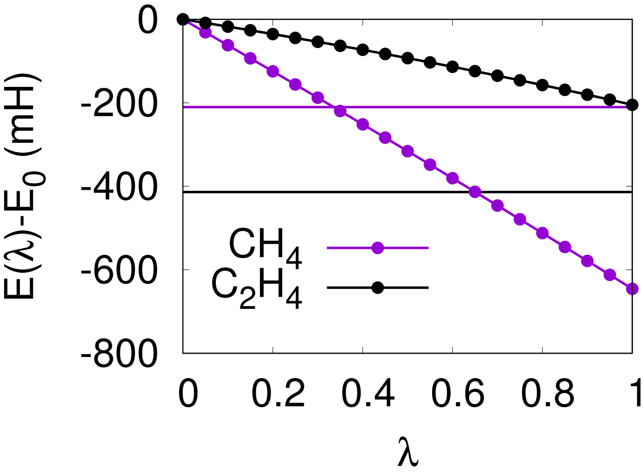

Figure 2. Difference between the hybrid LDA-nLE energy and the LDA energy vs amount of nonlocal exchange. Purple lines/solid-circles correspond to methane calculations and black lines/solid-circles to ethylene, the horizontal purple line indicates the CCSD(T) energy for methane, while the black horizontal line the CCSD(T) energy for ethylene.

For methane, because nonlocal exchange is assigned to the carbon atom, via elimination of the self-repulsion, only a fraction of nonlocal exchange is required to obtain an energy close to CCSD(T)/6-31G. For ethylene, the difference between CCSD(T) and LDA energies is larger. Given that nonlocal exchange is assigned to the hydrogen atoms in ethylene, even a 100% amount of this exchange is insufficient to obtain an energy closer to the reference CCSD(T) value.

Further Extensions. The domain separation methods we described so far are applicable to mixing standard KS calculations with tight-binding DFT. For such a case, we could decompose the kinetic energy operator as $\hat{T} = \sum_X \hat{T}_X$, where $\hat{T}_X = (1/2)\int \mathrm{d}\mu_X(\mathbf{r})\, \nabla\hat{\psi}^\dagger(\mathbf{r})\cdot\nabla\hat{\psi}(\mathbf{r})$. One (or more) of these operators can be replaced by $\hat{K}_{\mathrm{TB},X} = \sum_{\mu\nu\in X} t_{\mu\nu}\hat{c}_\mu^\dagger\hat{c}_\nu$, where $\hat{c}_\nu$ destroys an electron with orbital ν (where the indices run over atomic orbitals associated with domain X). This implies that the resulting correlation energy will have an important kinetic contribution that should be approximated appropriately, and this contribution must ensure that the electronic density of the whole system is properly described. This could have applications, for instance, in the study of molecules that interact with nanoparticles, where regions (like the nanoparticles) that are computationally demanding for standard DFT techniques (or DFAs) could be treated with tight-binding techniques, whereas the rest of the system could be modeled with higher-level methods such as standard KS-DFT or hybrid functionals. Domain separation in this context also implies that the region being modeled with a tight-binding approach has associated with it a local potential that has Hartree and XC components.

In addition to the above discussion, there is a diverse set of possibilities to employ weighing functions in alternative calculations and formalisms. For example, instead of partitioning the differential volume, one can split the creation/annihilation operators as $\hat{\psi}(\mathbf{r}) = \sum_X \hat{\psi}_X(\mathbf{r})$, where $\hat{\psi}_X(\mathbf{r}) = w_X(\mathbf{r})\,\hat{\psi}(\mathbf{r})$, express the Hamiltonian in terms of these, and use them to formulate new theories and methods.

To extend the theories described in previous sections to the time-dependent regime, and approach outstanding issues in the modeling of electron dynamics in strongly correlated systems,[43] a starting point is the variational principle applied to the action functional:

$$A[\Phi] = \int \mathrm{d}t\, \langle\Phi(t)|\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} - \hat{T} - \hat{W}_X - \int \mathrm{d}^3\mathbf{r}\, v_\mathrm{l}(\mathbf{r},t)\,\hat{\rho}(\mathbf{r})|\Phi(t)\rangle \tag{38}$$

where $\Phi(t) \in \mathcal{L}$. For wave function propagations, within the adiabatic approximation, for example, the local potential reads

$$v_\mathrm{l}(\mathbf{r},t) = \left.\frac{\delta\bar{E}^{1}_{\mathrm{Hxc}}[\rho']}{\delta\rho'(\mathbf{r})}\right|_{\rho'=\rho(\mathbf{r},t)} + v_0(\mathbf{r}) + v_\mathrm{D}(\mathbf{r},t) \tag{39}$$

where $v_0(\mathbf{r})$ represents the electron-nuclei attraction and v_D is some external perturbation. In the case the stationary point is sought in the space of correlated wave functions, the resulting TD equation is a simple extension of eq 21. For estimation of photoabsorption/emission spectra, the TD problem can be analyzed within the linear-response regime (for a weak driving field v_D), which would lead to an RPA-like equation that would include explicit wave function correlation (or nonlocal interactions if a single-determinantal approach is pursued).

The measure $\mathrm{d}\mu_X$ can be based on linear combinations of Gaussian functions. Integrating such a measure into current computational packages requires some adaptation of routines designed to compute electron-repulsion integrals (ERIs). We believe, however, that the resulting ERIs may be performed analytically. The rule stating that the product of Gaussian functions is a recentered Gaussian may be invoked to expand the corresponding weighted ERIs. Starting from a product of s-type Gaussian and its analytical ERI, one can take nuclear derivatives in order to find the formulas for integrals involving other types of Gaussians (p, d, etc.).

The methodologies we discussed in the previous sections for the case of two domains are generalizable to multiple ones. In general, the constrained search with the proper interactions included defines which regions are treated with nonlocal exchange,and which domains will be studied with wave function correlation. For example, one could start with a constrained-search functional (similar to $G_{\mathrm{l},X}$) based on the operator $\hat{T} + \sum_X \hat{W}_X$:

$$G_\mathrm{l}[\rho] = \min_{\substack{\Phi\to\rho\\ \Phi\in\mathcal{L}}} \langle\Phi|\hat{T} + \sum_X \hat{W}_X|\Phi\rangle \tag{40}$$

and follow the steps we discussed in this work to derive the corresponding, partial HXC energy functionals. The summation over potentials $\{\hat{W}_X\}$ would be performed over the multiple domains of interest. For example, in a periodic calculation of a supercell with several transition metals, the domains might be defined as spheres (but with smooth domain functions), or other shapes, around such metal atoms. In this matter, the calculations would share similarities with our computations modeling the electronic structure of the ethylene molecule.

The domain separation technique is also applicable to the energy or momentum space, which could be useful to separate core levels from valence ones (for instance, by assigning an orbital-free method to the core electrons, while the remaining electrons are modeled with KS DFT). To show this, it is sufficient to recall that the Hamiltonian of the system can also be written in terms of wave-vector-space volume elements. Therefore, the element $\mathrm{d}^3\mathbf{k}$ is conveniently expressed as $\sum_Z \mathrm{d}\tilde{\mu}_Z(\mathbf{k})$, where $\mathrm{d}\tilde{\mu}_Z(\mathbf{k})$ is now a measure with a weighing function in the wave-vector space, that also defines a domain, Z, in this space. With this idea, for example, frontier orbitals would be subject to nonlocal exchange, whereas the remaining levels to LDA exchange.

■ CONCLUSION

We presented a new variation of recent developments in the field of density functional theory that enables domain-separated calculations. The proposed formalism, DS-DFT, uses measures, or domain functions, that define regions of a molecule or solid that may be studied by different types of electron interaction operators (and thereby different levels of theory). This also leads to the possibility of performing calculations with multiple determinants, or references. For practical implementation of these methods, density functional approximations are needed to estimate, and subtract from the global HXC energy, the "DFT" Hartree-exchange or HXC energies that are associated with the regions that are to be computed with nonlocal interactions and/or explicit wave function correlation methods.

■ A. DIVIDING A HAMILTONIAN INTO SEPARATE CONTRIBUTIONS

Here we show a general expansion to divide a Hamiltonian into fragment Hamiltonians. This could be of interest for computations within a fragment-based approach, and without an embedding potential, i.e., using a global wave function for the entire system, but with different interaction operators (local and non-local) in the Hamiltonian, each used in a different region. For these types of calculations, it may be convenient to introduce some technique that decomposes objects such as the electronic density, Hamiltonian, or an energy functional, etc., into fragment contributions. This decomposition could also be of assistance to determine van der Waals forces between molecules that are not chemically interacting.

In previous work we studied auxiliary Hamiltonian operators that are partitioned into fragment-specific Hamiltonian operators that mutually commute.[44,45] The auxiliary operators include a coupling term that induces transfer of energy and charge between subsystems. This method, however, requires determination of a "coupling" (or "embedding") potential that could be obtained from a density functional, which has to be approximated.

An alternative approach could involve a direct partitioning of the real Hamiltonian of the system. For example, let us assume that the non-relativistic energy operator for the system of interest can be expressed as

$$\hat{H} = \int \mathrm{d}^3\mathbf{r} \left\{ \frac{1}{2} \nabla \hat{\psi}^{\dagger}(\mathbf{r}) \cdot \nabla \hat{\psi}(\mathbf{r}) + v(\mathbf{r})\, \hat{\rho}(\mathbf{r}) \right\} + \frac{1}{2} \int \mathrm{d}^3\mathbf{r}\, \mathrm{d}^3\mathbf{r}'\, \hat{\psi}^{\dagger}(\mathbf{r}') \frac{\hat{\rho}(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \hat{\psi}(\mathbf{r}') \tag{41}$$

As a starting point, let us decompose the differential volume element ($\mathrm{d}^3\mathbf{r}$) as follows:

$$\mathrm{d}^3\mathbf{r} = \sum_X \mathrm{d}\mu_X(\mathbf{r}) \tag{42}$$

where $\mathrm{d}\mu_X(\mathbf{r})$ reads

$$\mathrm{d}\mu_X(\mathbf{r}) = \mathrm{d}^3\mathbf{r}\, w_X(\mathbf{r}) \tag{43}$$

A molecular domain X is thus a region of space in which $w_X(\mathbf{r})$ is non-negligible. This function can then facilitate the screening of electrostatic repulsion integrals that involve the operator $\hat{W}_X$, which are needed to solve the ground-state or time-dependent problem of interest; neglecting insignificant integrals in the atomic orbital basis can reduce the computational costs by a significant margin.

The partition shown above requires that the sum of weighing functions equals the unity ($\sum_X w_X(\mathbf{r}) = 1$). Inserting this expansion into eq 41 gives

$$\hat{H} = \hat{H}_X + \sum_{X \neq Y} \hat{W}_{X,Y} \tag{44}$$

where

$$\hat{H}_X = \int \mathrm{d}\mu_X(\mathbf{r}) \left\{ \frac{1}{2} \nabla \hat{\psi}^{\dagger}(\mathbf{r}) \cdot \nabla \hat{\psi}(\mathbf{r}) + v(\mathbf{r})\, \hat{\rho}(\mathbf{r}) \right\} + \frac{1}{2} \int \mathrm{d}\mu_X(\mathbf{r})\, \mathrm{d}\mu_X(\mathbf{r}')\, \hat{\psi}^{\dagger}(\mathbf{r}') \frac{\hat{\rho}(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \hat{\psi}(\mathbf{r}') \tag{45}$$

and

$$\hat{W}_{X,Y} = \frac{1}{2} \int \mathrm{d}\mu_X(\mathbf{r})\, \mathrm{d}\mu_Y(\mathbf{r}')\, \hat{\psi}^{\dagger}(\mathbf{r}') \frac{\hat{\rho}(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \hat{\psi}(\mathbf{r}') \tag{46}$$

The operator $\hat{W}_{X,Y}$ is symmetric with respect to domain label exchange, $\hat{W}_{X,Y} = \hat{W}_{Y,X}$. This operator represents the repulsion between auxiliary electrons in different domains. For problems involving the computation of weak forces, a DS-DFT framework could be formulated in terms of a constrained search based on the operator $\hat{T} + \sum_{Y \neq X} \hat{W}_{X,Y}$.

B. LOCAL POTENTIAL AND SCHRÖDINGER-LIKE EQUATIONS

Let us consider the following Lagrange functional:

$$L[\Phi, v_1](E) = \langle \Phi | \hat{T} + \hat{W}_X | \Phi \rangle + \int \mathrm{d}^3\mathbf{r}\, v_1(\mathbf{r}) \{ \langle \Phi | \hat{\rho}(\mathbf{r}) | \Phi \rangle - \rho(\mathbf{r}) \} - E[\langle \Phi | \Phi \rangle - 1] \tag{47}$$

In the above equation, v_1 and E are the multipliers, and $\Phi \in \mathcal{L}$. If $\mathcal{L}$ is the space of Slater determinants, taking variations with respect to orbitals leads to the hybrid Hartree–Fock/Kohn–Sham equations. If $\mathcal{L}$ is the space of correlated wave functions, then variations with respect to Φ give eq 21. It can be shown that

$$\frac{\delta G_{1,X}}{\delta \rho(\mathbf{r})} = -v_1(\mathbf{r}) \tag{48}$$

this result is arbitrary by a constant. Similarly, $\delta F / \delta \rho(\mathbf{r}) = -v(\mathbf{r})$ at the ground state. Comparing this result with the above equation we obtain

$$\overline{u}^{1}_{\mathrm{Hxc}}(\mathbf{r}) = \frac{\delta \overline{E}^{1}_{\mathrm{Hxc}}}{\delta \rho(\mathbf{r})} \tag{49}$$

and $v_1(\mathbf{r}) = \overline{u}^{1}_{\mathrm{Hxc}}(\mathbf{r}) + v(\mathbf{r})$.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b01173.

> Operators in first quantization form, note on the wave functions $\tilde{\Psi}$, $\tilde{\Phi}$, $\tilde{\Phi}_0$, functional decomposition of $G_{s,X}$ based on KS-DFT, spin polarized single-determinantal method, additional hydrogen dissociation data (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: g-schatz@northwestern.edu. Phone: +1-847-491-5371.

ORCID

Martín A. Mosquera: 0000-0003-2170-5651
Leighton O. Jones: 0000-0001-6657-2632
Carlos H. Borca: 0000-0003-0683-7613
George C. Schatz: 0000-0001-5837-4740

Notes

The authors declare no competing financial interest.

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■ ADDITIONAL NOTES

[a]In the Supporting Information we show an alternative decomposition of this functional.

[b]If a different XC functional were used, like PBE, we would refer to it as PBE-nLE.

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