

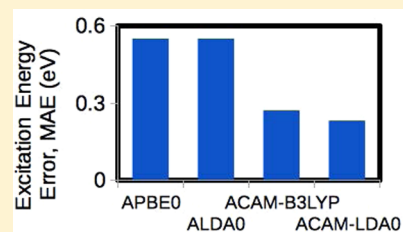
# Connection between Hybrid Functionals and Importance of the Local Density Approximation

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**ABSTRACT:** The exchange–correlation (XC) local density approximation (LDA) is the original density functional used to investigate the electronic structure of molecules and solids within the formulation of Kohn and Sham. The LDA is fundamental for the development of density-functional approximations. In this work we consider the generalized Kohn–Sham (GKS) theory of hybrid functionals. The GKS formalism is an extension of the Kohn–Sham theory for electronic ground states and leads to a vast set of alternative density functionals, which can be estimated by the LDA and related methods. Herein we study auxiliary electronic systems with parametrized interactions and derive (i) a set of exact equations relating the GKS XC energies in the parameter space and (ii) a formal relation between the parameters and the standard XC derivative discontinuity. In view of the new results and previously reported findings, we discuss why the inclusion of Fock exchange, and its long-range-corrected form (in the ground-state calculations and in linear-response Kohn–Sham equations), dominate over the generalized gradient corrections to enhance the quality of the fundamental gap and to enhance excitation-energy estimations. As an example, we show that the adiabatic CAM-LDA0 (a functional with 1/4 global and 1/2 long-range Hartree–Fock interaction, respectively, a range separation factor of 1/3, and pure LDA exchange and correlation) works for electronic excitations as well as the adiabatic CAM-B3LYP functional.



## INTRODUCTION

Calculations based on the theory of density functionals are customary in the study of electronic properties of materials. Unfortunately, the number of density-functional approximations grows, and grows, up to the point where the user (including the authors of this work) might be unsure about which functional should be used and why. Modern functionals are usually parametrized combinations of various objects including orbitals, gradients of the electronic and orbital densities, attenuated electron–electron interactions, etc. One can make matters more intricate by recombining already parametrized density functionals to propose a new approximation.

The work of Kohn and collaborators establishes the electronic density as a variable that can be used to determine *all* the properties of the system. The useful formalism of Kohn and Sham employs a single Slater determinant, where its orbitals, when subject to the exact exchange–correlation potential, yield the ground-state energy and electronic density of the system. Nowadays, many variations of the Kohn–Sham (KS) method are available, making accessible the calculations for molecular dynamics, thermodynamical statistics, and spectroscopy, among others.

The first density-functional approximation (DFA) within KS density-functional theory (DFT) includes correlation and is able to reproduce the ground-state properties of the homogeneous electron gas: a system where many electrons lie in a large periodic box, in such a way that they are properly described by plane waves and a continuum energy spectrum.

Such a functional is known as the local density approximation (LDA), and it is decomposed into kinetic, Hartree, and exchange–correlation (XC) contributions. To study molecules, the XC contribution is used within a set of single-particle Schrödinger equations. The XC LDA energy functional yields a local, multiplicative effective potential that the noninteracting electrons are subject to. This XC functional depends only on the electronic density.

The inclusion of a fraction of the Hartree–Fock orbital-exchange operator in the approximated KS equations helps to improve the estimation of binding energies,<sup>1</sup> lattice constants,<sup>2</sup> fundamental gaps,<sup>3</sup> and excitation energies.<sup>4</sup> The justification for addition of nonlocal exchange to improve the electronic structure calculations derives from the adiabatic connection formula<sup>1</sup> and density-functional perturbation theory.<sup>5</sup> An application of this justification is the famous recipe by Perdew et al.<sup>6</sup> to include 25% of Hartree–Fock exchange in the generalized gradient approximation (GGA) XC energy. If the GGA functional is the popular PBE,<sup>7</sup> then one obtains the PBE0 approximation,<sup>8,9</sup> an XC functional with only one parameter. In contrast, the most successful functionals are hybrids with more than three empirical parameters. The hybridization typically consists of combining different types of exchange and correlation functionals, leading to approximations like CAM-B3LYP.<sup>10</sup>

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The formulation of Kohn and Sham, strictly speaking, demands employing a local, multiplicative, XC potential, in other words, that all the orbitals (virtual and occupied) are subject to the same XC potential. We will refer to this formalism as *standard KS theory*. An alternative formal theoretical framework to incorporate Hartree–Fock (HF) exchange, or a fraction of it, in the single-particle Schrödinger equation is known as the generalized Kohn–Sham (GKS) method.<sup>11</sup> Instead of using an auxiliary model of noninteracting electrons, as in KS DFT, Seidl et al.<sup>11</sup> introduced a system of interacting electrons, where the interaction is described by means of a simplified functional of the orbitals, which can depend on parameters. An example of such a tractable interaction is the HF repulsion, often seen as “2J–K”. Then, the premise in GKS DFT is that one can approximate a residual functional, similar to the XC energy functional, that corrects the energy and density of the auxiliary system of interacting electrons in such a way that they are close to the corresponding true ground-state values. There is an uncountably infinite number of possible auxiliary systems of electrons, the KS electron system is one of them.

Within the generalization of KS DFT,<sup>11</sup> if a fraction of HF exchange is used, then the rest of the exchange energy is calculated using a fraction of the LDA exchange. In general, the GKS method allows us to split the energy into a residual and a nonlocal, parametrized energy. The LDA can be used to estimate the former. In other words, the residual energy is approximated using only an integral over a local function of the density. In the homogeneous electron gas limit, the parameters defining the nonlocal exchange are free. These parameters are related to the addition of nonlocal interactions, their splitting into long- and short-range contributions, and the mixings of different correlation functionals.

The GKS formalism is very broad, and its explicit formulas for the residual energies shown in this study for functionals like PBE0, or CAM-B3LYP, have not been highlighted elsewhere. The residual energies are weighted sums of exchange and correlation energy functionals. These functionals are different from those defined in standard KS theory. We derive a Koopmans’ theorem, and an exact relation between the parameters and the XC derivative discontinuity from standard KS theory. We show how the Coulomb-attenuated method (CAM) can be approached in the GKS framework. A new equation relating the exact XC energies in the parameter space is presented in this work. We suggest that, with respect to the generalized gradient corrections, the inclusion of a fraction of nonlocal exchange in the single-particle Schrödinger equations tends to be an overweighing factor to obtain improved excitation energies. In view of this, here we study: (i) A one-parameter method, consisting in mixing Dirac exchange with HF exchange, while using a 100% LDA correlation. The resulting functional is LDA0,<sup>12,13</sup> in essence PBE0 without gradient-dependent terms. (ii) A three-parameter method, i.e., the one-parameter method with Coulomb attenuation. We propose that the adiabatic CAM-LDA0 functional (exact for the homogeneous electron gas) can be used as a slightly less expensive alternative to the adiabatic CAM-B3LYP for linear-response calculations. A cautionary remark, the percentage of HF exchange is not *universal*, it varies depending of the type of application.<sup>14,15</sup> Thus, careful judgment and tuning of parameters are advised, as in the application of any other DFA.

The LDA0 is a functional with little use reported in the literature. We note that it has been used to study vacancies in

magnesium oxide<sup>12</sup> and irradiated silicon carbide.<sup>13</sup> On the contrary, the functional (adiabatic) CAM-LDA0 has not been considered previously.

## ■ BACKGROUND THEORY

Suppose  $n$  is a given electronic density. It can correspond to that of the true ground state, or a superposition of excited states. Define the energy ( $G_\lambda$ ) of a system of electrons, described by a single Slater determinant, which interact through a partial Coulomb interaction:<sup>16</sup>

$$G_\lambda[n] = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \lambda \hat{W} | \Phi \rangle \quad (1)$$

where  $\lambda > 0$  and  $\hat{T}$  and  $\hat{W}$  are the kinetic and repulsion energy operators, respectively. In second quantization,  $\hat{T}$  reads  $1/2 \int d^3\mathbf{r} \nabla \hat{\psi}^\dagger(\mathbf{r}) \cdot \nabla \hat{\psi}(\mathbf{r})$ , and  $\hat{W} = 1/2 \int d^3\mathbf{r} d^3\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}^\dagger(\mathbf{r}) w(|\mathbf{r}-\mathbf{r}'|) \hat{\psi}(\mathbf{r}) \hat{\psi}(\mathbf{r}')$ . The function  $w$  is the Coulomb repulsion potential. The value of the functional  $G_\lambda$  at  $n$  is obtained by a constrained minimization over single Slater determinants giving the density  $n$ . This minimization problem is solved using Lagrange multipliers and leads to a local potential  $u_s^\lambda$  and a set of orbital energies  $\{\epsilon_a^\lambda\}$ . The orbitals used to form the Slater determinant satisfy the following equation:

$$\left[ -\frac{1}{2} \nabla^2 + \lambda (\hat{j}(\mathbf{r}) + \hat{v}_{x,\lambda}(\mathbf{r})) + u_s^\lambda(\mathbf{r}) \right] \phi_a^\lambda(\mathbf{r}) = \epsilon_a^\lambda \phi_a^\lambda(\mathbf{r}) \quad (2)$$

where  $\hat{j}(\mathbf{r})$  and  $\hat{v}_{x,\lambda}(\mathbf{r})$  are the local Coulomb and HF exchange potential operators. The potential  $u_s^\lambda$  forces the orbital densities to satisfy  $\sum_a \nu_a |\phi_a^\lambda(\mathbf{r})|^2 = n(\mathbf{r})$ , for all  $\mathbf{r}$ ;  $\{\nu_a\}$  are the occupation numbers. We will denote the term enclosed by square brackets in the above equation as  $\hat{f}_\lambda$ , a Fock operator. The total number of electrons,  $N$ , satisfies  $N \geq 2$ ; otherwise,  $G_\lambda = G_0$ .

The electronic energy density functional is written as  $E_\nu[n] = F[n] + \int d^3\mathbf{r} v(\mathbf{r}) n(\mathbf{r})$ , where  $v$  is the one-body external potential.  $F$  is the Levy<sup>17</sup> constrained-search functional,  $F[n] = \min \{ \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle | \Psi \rightarrow n \}$ . This search is performed over the Hilbert space of fully correlated wave functions.

Denote  $\tilde{\Phi}_\lambda[n]$  as the optimal single Slater determinant that is the solution to the minimization problem shown in the right-hand side of eq 1. We can define a partial Hartree–XC (HXC) energy as follows:

$$E_{\text{HXC}}^\lambda[n] = (1 - \lambda) \langle \tilde{\Phi}_\lambda | \hat{W} | \tilde{\Phi}_\lambda \rangle + E_c^\lambda[n] \quad (3)$$

The interaction term  $\langle \tilde{\Phi}_\lambda | \hat{W} | \tilde{\Phi}_\lambda \rangle$  is a density functional, and it can be expanded as  $E_X^\lambda[n] + E_{\text{H}}[n]$ , where  $E_{\text{H}}[n]$  is the (usual) Hartree repulsion energy,  $1/2 \int d^3\mathbf{r}' d^3\mathbf{r} n(\mathbf{r}) n(\mathbf{r}') w(|\mathbf{r}-\mathbf{r}'|)$ . The *exact* exchange energy functional,  $E_X^\lambda$ , is thus given by the difference  $\langle \tilde{\Phi}_\lambda | \hat{W} | \tilde{\Phi}_\lambda \rangle - E_{\text{H}}[n]$ . Under these definitions, if we expand the Levy energy  $F$  as  $G_\lambda + E_{\text{HXC}}^\lambda$ , we find that the correlation energy reads<sup>18</sup>

$$E_c^\lambda[n] = \langle \tilde{\Psi} | \hat{T} + \hat{W} | \tilde{\Psi} \rangle - \langle \tilde{\Phi}_\lambda | \hat{T} + \hat{W} | \tilde{\Phi}_\lambda \rangle \quad (4)$$

Here  $\tilde{\Psi}$  is the optimal correlated wave function required to compute the  $F$  functional at  $n$ . The above expression is similar to the correlation energy defined in KS-DFT.  $E_c^\lambda$  corresponds to the usual correlation energy of KS-DFT if  $\lambda = 0$ . In general, within the exact framework,  $E_X^\lambda \neq E_X^0$  and  $E_c^\lambda \neq E_c^0$ , for  $\lambda > 0$ .

The LDA is exact for the uniform electron gas (UEG). In the UEG limit, the calculation of  $G_\lambda$  requires solution of the Hartree–Fock problem, where the charge of the electron is scaled by a factor of  $\sqrt{\lambda}$ . The functional  $G_\lambda[n]$  reads  $T^{\text{TF}}[n] + \lambda E_{\text{HX}}^{\text{LDA}}[n]$ , where  $T^{\text{TF}}$  is the Thomas–Fermi kinetic energy

functional, and  $n = N/V$  ( $V$  is the UEG volume). The partial LDA for the HXC energy is

$$E_{\text{HXC}}^{\text{LDA},\lambda}[n] = (1 - \lambda)(E_{\text{H}}[n] + E_{\text{X}}^{\text{LDA}}[n]) + E_{\text{c}}^{\text{LDA}}[n] \quad (5)$$

By adding  $G_{\lambda}$  and  $E_{\text{HXC}}^{\text{LDA},\lambda}$  together, we then recover the exact energy functional for the UEG limit for any value of  $\lambda$ .<sup>6</sup> Hence,  $E_{\text{HXC}}^{\text{LDA}}[n] = T^{\text{TF}}[n] + E_{\text{HXC}}^{\text{LDA}}[n]$ .

## COULOMB-ATTENUATED METHOD

Further parametrizations can be introduced for the auxiliary system of electrons. One can split the Coulomb interaction between two electrons using long- (lr) and short-range (sr) contributions. Such splitting requires an additional parameter,  $\mu$ . In general, one can write  $w(x) = w_{\mu}^{\text{lr}}(x) + w_{\mu}^{\text{sr}}(x)$ . If the error function is used to separate the Coulomb interaction, then  $w_{\mu}^{\text{lr}}(x) = \text{erf}(\mu x)/x$ , and  $w_{\mu}^{\text{sr}}(x) = \text{erfc}(\mu x)/x$ . To include a fraction of long-range Fock exchange, let us define the functional

$$G_{\lambda,\zeta}[n] = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \lambda \hat{W} + \zeta \hat{W}_{\mu}^{\text{lr}} | \Phi \rangle \quad (6)$$

$\hat{W}_{\mu}^{\text{lr}}$  is the lr electron–electron repulsion operator; this operator is obtained by replacing  $w$  by  $w_{\mu}^{\text{lr}}$  in the definition of  $\hat{W}$ . In this case, the constrained search is also carried out over the space of single Slater determinants. The corresponding partial HXC energy functional can be shown to be of the form

$$E_{\text{HXC}}^{\lambda,\zeta}[n] = E_{\text{c}}^{\lambda,\zeta}[n] + (1 - \lambda - \zeta)E_{\text{HX}}^{\lambda,\zeta}[n] + \zeta E_{\text{HX}}^{\text{sr},\lambda,\zeta}[n] \quad (7)$$

The definition of the functionals involved is as follows:  $E_{\text{c}}^{\lambda,\zeta}[n] = F[n] - \langle \tilde{\Phi}_{\lambda,\zeta} | \hat{T} + \hat{W} | \tilde{\Phi}_{\lambda,\zeta} \rangle$ ,  $E_{\text{HX}}^{\text{sr},\lambda,\zeta}[n] = \langle \tilde{\Phi}_{\lambda,\zeta} | \hat{W}_{\mu}^{\text{sr}} | \tilde{\Phi}_{\lambda,\zeta} \rangle$ ,  $E_{\text{HX}}^{\lambda,\zeta}[n] = \langle \tilde{\Phi}_{\lambda,\zeta} | \hat{W} | \tilde{\Phi}_{\lambda,\zeta} \rangle$ . The function  $\tilde{\Phi}_{\lambda,\zeta}$  is that which minimizes the expectation value required to calculate  $G_{\lambda,\zeta}$  at  $n$ .

Equation 7 is a weighted sum of exchange energies and 100% correlation. In general, if one accounts partially for exchange and/or correlation including orbital-dependent forms (in the calculation of a functional like  $G_{\lambda,\zeta}$ ), then the remaining portions of XC energy can be quantified using an explicitly density-dependent approximation, such as an LDA, or GGA. A remark: Definition of the auxiliary system is required prior to assigning the residual energy to be estimated with the LDA/GGA. For example, after setting  $\lambda$ ,  $\zeta$ , and  $\mu$ , one can apply the LDA/GGA to estimate  $E_{\text{HXC}}^{\lambda,\zeta}$ . But enhancing this approximation requires a new methodology because  $\tilde{\Phi}_{\lambda,\zeta}$ , in contrast to  $\tilde{\Phi}_{0,0}$  (from standard KS theory), describes the auxiliary system of electrons.

The use of parametrized interactions is an alternative to using standard KS orbitals as density functionals to calculate very accurate, and somewhat expensive, XC potentials, for instance, as in the exact exchange<sup>18</sup> and *ab initio* DFT methodologies.<sup>19</sup>

The above definitions encompass the Coulomb-attenuated method, formalized here within GKS theory. The parameters can be identified as  $\alpha = \lambda$  and  $\beta = \zeta$ . The long-range-corrected (LRC) method is obtained by simply setting  $\lambda = 0$  and  $\zeta = 1$ ; the only parameter is the separation factor  $\mu$ . In addition, extra parameters can be introduced to split the different functionals involved in eq 7 while obeying the UEG limit. For example, one can mix the LDA and GGA functionals:  $E_{\text{Y}}[n] = a_0 E_{\text{Y}}^{\text{LDA}}[n] + (1 - a_0) E_{\text{Y}}^{\text{GGA}}[n]$ , where  $Y$  is either “X” or “c”; the expansion is applicable to any of the different energy forms, sr, lr,  $\lambda$ , and/or  $\mu$  dependent. These types of mixed functionals are well studied with respect to training sets. Deciding which functional should be used can be challenging.<sup>20</sup>

The energy functional,  $E_{\nu}[n]$ , reads

$$E_{\nu}[n] = G_{\lambda,\zeta}[n] + E_{\text{HXC}}^{\lambda,\zeta}[n] + \int d^3\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) \quad (8)$$

The total electronic energy is independent of the parameters  $\lambda$ ,  $\zeta$ , and  $\mu$ . For instance, suppose that the density is fixed. Differentiation of both sides of the above equation with respect to  $\lambda$  leads to

$$\frac{\partial G_{\lambda,\zeta}}{\partial \lambda} = -\frac{\partial E_{\text{HXC}}^{\lambda,\zeta}}{\partial \lambda} \quad (9)$$

In a similar fashion one obtains  $\partial G_{\lambda,\zeta}/\partial \zeta = -\partial E_{\text{HXC}}^{\lambda,\zeta}/\partial \zeta$ .

Define the energy operator as

$$\hat{\mathcal{H}}_{\lambda,\zeta}[n] = \hat{T} + \lambda \hat{W} + \zeta \hat{W}_{\mu}^{\text{lr}} + \int d^3\mathbf{r} u_{\text{s}}^{\lambda,\zeta}[n](\mathbf{r}) \hat{n}(\mathbf{r}) \quad (10)$$

where  $\hat{n}(\mathbf{r})$  is the density operator and  $u_{\text{s}}^{\lambda,\zeta}[n]$  is the Lagrange multiplier required to solve the constrained search defining  $G_{\lambda,\zeta}[n]$ . Consider the following auxiliary energy functional:

$$\begin{aligned} \mathcal{E}_{\lambda,\zeta}[n] &= \langle \tilde{\Phi}_{\lambda,\zeta} | \hat{\mathcal{H}}_{\lambda,\zeta}[n] | \tilde{\Phi}_{\lambda,\zeta} \rangle \\ &= G_{\lambda,\zeta}[n] + \int d^3\mathbf{r} u_{\text{s}}^{\lambda,\zeta}[n](\mathbf{r}) n(\mathbf{r}) \end{aligned} \quad (11)$$

The wave function  $\tilde{\Phi}_{\lambda,\zeta}$  minimizes the expectation value of  $\hat{\mathcal{H}}_{\lambda,\zeta}[n]$  over the space of single Slater determinants (this minimization gives rise to the GKS equations, e.g., eq 2). Hence, invoking the Hellmann–Feynman theorem, we arrive at

$$\frac{\partial \mathcal{E}_{\lambda,\zeta}}{\partial \lambda} = \langle \tilde{\Phi}_{\lambda,\zeta} | \frac{\partial \hat{\mathcal{H}}_{\lambda,\zeta}[n]}{\partial \lambda} | \tilde{\Phi}_{\lambda,\zeta} \rangle \quad (12)$$

Expand both sides of this equation using eqs 10 and 11 and observe that

$$\frac{\partial G_{\lambda,\zeta}}{\partial \lambda} = \langle \tilde{\Phi}_{\lambda,\zeta} | \hat{W} | \tilde{\Phi}_{\lambda,\zeta} \rangle \quad (13)$$

If we set  $\zeta = 0$ , use the above result to integrate both sides of eq 9, and rearrange the result, we obtain

$$E_{\text{HXC}}^{\lambda,0}[n] = E_{\text{HXC}}[n] - \int_0^{\lambda} d\lambda' \langle \tilde{\Phi}_{\lambda',0} | \hat{W} | \tilde{\Phi}_{\lambda',0} \rangle \quad (14)$$

where  $E_{\text{HXC}} = E_{\text{HXC}}^{0,0}$  is the HXC energy of standard KS theory.

After applying the above analysis to the parameter  $\zeta$ , we can express  $E_{\text{HXC}}^{\lambda,0}$  in terms of  $\zeta$ . This yields

$$\begin{aligned} E_{\text{HXC}}^{\lambda,\zeta}[n] &= E_{\text{HXC}}[n] - \int_0^{\lambda} d\lambda' \langle \tilde{\Phi}_{\lambda',0} | \hat{W} | \tilde{\Phi}_{\lambda',0} \rangle \\ &\quad - \int_0^{\zeta} d\zeta' \langle \tilde{\Phi}_{\lambda,\zeta'} | \hat{W}_{\mu}^{\text{lr}} | \tilde{\Phi}_{\lambda,\zeta'} \rangle \end{aligned} \quad (15)$$

This equation can be further simplified by elimination of the Hartree energies, which are independent of  $\lambda$  and  $\zeta$ . The final result is

$$E_{\text{XC}}^{\lambda,\zeta}[n] = E_{\text{XC}}[n] - \int_0^{\lambda} d\lambda' E_{\text{X}}^{\lambda',0}[n] - \int_0^{\zeta} d\zeta' E_{\text{X}}^{\text{lr},\lambda,\zeta'}[n] \quad (16)$$

where  $E_{\text{X}}^{\text{lr},\lambda,\zeta}[n] = \langle \tilde{\Phi}_{\lambda,\zeta} | \hat{W}_{\mu}^{\text{lr}} | \tilde{\Phi}_{\lambda,\zeta} \rangle - E_{\text{H}}^{\text{lr}}[n]$ ; the lr Hartree energy is obtained after replacing  $w$  by  $w_{\mu}^{\text{lr}}$  in its definition formula. The above equation is an exact relation between XC energies in the parameter space. If the standard XC energy is known, then

subtracting from it the integrated, nonattenuated, and long-range exchange energies gives the XC energy for the auxiliary system defined by  $\lambda$  and  $\zeta$ .

Generally, if a functional  $G_z$  is defined, where the electron–electron interaction is parametrized in terms of a vector of parameters,  $\mathbf{z}$ , then  $G_z$  is related to the corresponding HXC energy by the equation  $\nabla E_{\text{HXC}}^z = -\nabla G_z$  (the gradient is taken with respect to the parameters). The integrated form of this relation is

$$E_{\text{HXC}}^{z_1} - E_{\text{HXC}}^{z_0} = -\int_{\gamma} d\mathbf{z} \cdot \nabla G_z \quad (17)$$

where  $\gamma$  is a trajectory in the parameter space connecting the points  $\mathbf{z}_0$  and  $\mathbf{z}_1$ . The difference between HXC energies is independent of the path because the integrand field is conservative:  $\oint d\mathbf{z} \cdot \nabla G_z = 0$ .

Equation 17 expresses the equivalence between different auxiliary electronic systems to calculate the exact ground-state electronic energy (regardless of the parametrization, the functional  $E_v$  is always the same). However, the electronic energy approximated by any hybrid DFA does indeed depend on the parametrization of the auxiliary system. Because of this, all the current, hybrid DFAs do not satisfy the condition shown in eq 17.

## ■ KOOPMANS' THEOREM AND THE FUNDAMENTAL GAP

Let us consider a system where the number of electrons is  $N$ , a positive even integer. The ground-state energy of the system is obtained by minimizing the energy functional  $E_v$  over densities that yield  $N$  electrons. For the ground-state density,  $n_{\text{H}}^{\text{gs}}$ , suppose that the local potential representing the density of the system is  $\tilde{u}_s^{\lambda}$ , and the auxiliary Slater determinant is  $\tilde{\Phi}_{N,\lambda}$ . It can be shown that this potential is given by  $\delta E_{\text{HXC}}^{\lambda} / \delta n(\mathbf{r}) + v(\mathbf{r})$ , where the functional derivative is evaluated at  $n_{\text{H}}^{\text{gs}}$ . The Lagrange multiplier,  $\tilde{u}_s^{\lambda}$ , has contributions from the partial Hartree–XC, and the one-body external potentials; the latter could be of the form  $-\sum_{\alpha} Z_{\alpha} / |\mathbf{r} - \mathbf{R}_{\alpha}|$ . Let us define the following electronic energy operator:

$$\hat{\mathcal{H}}_{\lambda} = \hat{T} + \lambda \hat{W} + \int d^3\mathbf{r} \tilde{u}_s^{\lambda}(\mathbf{r}) \hat{n}(\mathbf{r}) \quad (18)$$

Suppose that  $\tilde{u}_s^{\lambda}$  is frozen. It is straightforward to derive a Koopmans' theorem for the LUMO energy. This reads

$$\epsilon_{\text{L}}^{\lambda} = \langle \Phi'_{N+1,\lambda} | \hat{\mathcal{H}}_{\lambda} | \Phi'_{N+1,\lambda} \rangle - \langle \tilde{\Phi}_{N,\lambda} | \hat{\mathcal{H}}_{\lambda} | \tilde{\Phi}_{N,\lambda} \rangle \quad (19)$$

where  $\Phi'_{N+1,\lambda}$  is the single Slater determinant describing the auxiliary system where the LUMO (of the  $N$ -electron system in its ground state) is fully occupied.

A relevant result for the present, *exact* formulation is that the HOMO energy  $\epsilon_{\text{H}}^{\lambda}$  equals the negative of the vertical ionization energy.<sup>16,21,22</sup> This derives from the definition of the energy  $G_{\lambda}$ , which demands that the orbitals yield the ground-state density. In the asymptotic region of the real system of electrons, the exponential decreasing rate of the ground-state density is governed by the ionization energy.<sup>21</sup> For the auxiliary system of partially interacting electrons, the decreasing rate of the density is determined by the HOMO energy.<sup>23,24</sup> Therefore,<sup>16</sup>  $\epsilon_{\text{H}}^{\lambda} = -I$ .

In Hartree–Fock theory there is no correlation energy functional, and the Hartree–Fock HOMO–LUMO gap is larger than the fundamental one. Thus, an interaction strength  $0 < \lambda \leq 1$  could be appropriate to improve the gap estimation.

Although, strictly speaking, any positive real value of  $\lambda$  can be considered. Perhaps, large values of  $\lambda$  can be useful to study strongly correlated systems.

The LUMO energy is a function of the parameter  $\lambda$ . In standard KS-DFT  $\lambda = 0$ ; all the KS electrons are subject to the same local potential. Furthermore, practical calculations indicate that the KS HOMO–LUMO gap underestimates the fundamental gap of the system.<sup>25</sup> In the asymptotic region, for example, the exact HXC potential decays as  $(N - 1)/|\mathbf{r}|$ , this potential is felt by the LUMO level as well. On the contrary, if  $\lambda = 1$  the system displays a full dependency on the two-body interaction operator, which assigns different orbitals different interaction fields. The LUMO is screened by  $N$  electrons. Therefore, the LUMO energy with respect to the ionization energy is raised. For an in-depth discussion, see ref 26.

An analysis of the process of removal and addition of a very small amount of electron charge (using the grand canonical ensemble statistics) reveals that the affinity ( $A$ ) of the molecule is related to the LUMO energy ( $\lambda = 0$ ), and the XC potential, through the expression<sup>27</sup>  $(-A) = \epsilon_{\text{L}}^0 + \Delta_{\text{XC}}$ . The discontinuity of the XC potential,  $\Delta_{\text{XC}}$ , is  $\lim_{\Delta N \rightarrow 0^+} v_{\text{XC}}(N + \Delta N) - v_{\text{XC}}(N - \Delta N)$ . This quantity is required to widen the KS HOMO–LUMO gap, so it matches the fundamental gap of the system. Within the exact GKS formulation, one can find the best value of the mixing parameter ( $\lambda^*$ ) such that the GKS HOMO–LUMO gap matches the fundamental gap of the system.

Assuming  $\Delta_{\text{XC}}$  is given,  $\lambda^*$  is calculated by solving the root-finding problem:

$$\begin{aligned} \Delta_{\text{XC}} &= [\epsilon_{\text{L}}^{\lambda^*} - \epsilon_{\text{H}}^{\lambda^*}] - [\epsilon_{\text{L}}^0 - \epsilon_{\text{H}}^0] \\ &= \int_0^{\lambda^*} d\lambda \frac{d}{d\lambda} [\epsilon_{\text{L}}^{\lambda} - \epsilon_{\text{H}}^{\lambda}] \end{aligned} \quad (20)$$

The ionization theorem ( $\epsilon_{\text{H}}^{\lambda} = -I$ ) simplifies the root-finding problem as  $\Delta_{\text{XC}} = \int_0^{\lambda^*} d\lambda d\epsilon_{\text{L}}^{\lambda} / d\lambda$ . The LUMO energy,  $\epsilon_{\text{L}}^{\lambda}$  can be expressed as the expectation value  $\langle \phi_{\text{L}}^{\lambda} | \hat{\mathcal{H}}_{\lambda} | \phi_{\text{L}}^{\lambda} \rangle$ . Now, we have that (the Fock operator is hermitian)

$$\frac{d\epsilon_{\text{L}}^{\lambda}}{d\lambda} = \langle \phi_{\text{L}}^{\lambda} | \frac{d\hat{\mathcal{H}}_{\lambda}}{d\lambda} | \phi_{\text{L}}^{\lambda} \rangle + \left[ \langle \frac{d\phi_{\text{L}}^{\lambda}}{d\lambda} | \hat{\mathcal{H}}_{\lambda} | \phi_{\text{L}}^{\lambda} \rangle + \text{H.c.} \right] \quad (21)$$

Given that  $\hat{\mathcal{H}}_{\lambda} | \phi_{\text{L}}^{\lambda} \rangle = \epsilon_{\text{L}}^{\lambda} | \phi_{\text{L}}^{\lambda} \rangle$ , the terms in square brackets in the above equation can be written as  $\epsilon_{\text{L}}^{\lambda} d\langle \phi_{\text{L}}^{\lambda} | \phi_{\text{L}}^{\lambda} \rangle / d\lambda$ , which is null because the LUMO is normalized. Hence, we obtain the following relation:

$$\Delta_{\text{XC}} = \int_0^{\lambda^*} d\lambda \langle \phi_{\text{L}}^{\lambda} | \hat{v}_{\text{x},\lambda} - u_{\text{x}}^{\lambda} + \hat{o}_{\lambda} | \phi_{\text{L}}^{\lambda} \rangle \quad (22)$$

where  $\hat{o}_{\lambda}$  is a residual operator. It reads

$$\hat{o}_{\lambda} = (1 - \lambda) \frac{du_{\text{x}}^{\lambda}}{d\lambda} + \lambda \frac{d\hat{v}_{\text{x},\lambda}}{d\lambda} + \frac{du_{\text{c}}^{\lambda}}{d\lambda} \quad (23)$$

here  $u_{\text{x}}^{\lambda} = \delta E_{\text{x}}^{\lambda} / \delta n$  and  $u_{\text{c}}^{\lambda} = \delta E_{\text{c}}^{\lambda} / \delta n$ . Equation 22 is exact. It extends the first-order approximation of Seidl et al.,<sup>11</sup> which shows that the discontinuity depends on the difference between the orbital averages of the local and nonlocal *exchange* potentials.<sup>11</sup> Equation 22 suggests that the correlation effects manifest, implicitly, through the dependency on  $\lambda$  of the LUMO, correlation, and exchange potentials.

The LDA exchange and correlation potentials are independent of  $\lambda$ , then  $\hat{o}_{\lambda} = 0$ . Setting  $\lambda = 0$  in the integrand of the right-

hand side of eq 22 leads to the gross estimator  $\lambda^* \approx \Delta_{\text{XC}} / \langle \phi_{\text{L}}^0 | \hat{v}_{\text{x},0} - u_{\text{x}}^{\text{LDA}} | \phi_{\text{L}}^0 \rangle$ . In general, the value of  $\lambda^*$  used to reproduce the discontinuity is a function of the system because  $\Delta_{\text{XC}}$  and the ground-state orbitals are determined by the external potential and the number of electrons of the system. In practice, for solid structures it was found that the optimal amount of HF exchange correlates with the inverse of the dielectric constant, estimated by using a standard DFA such as PBE.<sup>28,29</sup>

Equation 20 is valid for any DFA, where the discontinuity reads<sup>30</sup>  $I^{\text{app}} - A^{\text{app}} - [\epsilon_{\text{L}}^0 - \epsilon_{\text{H}}^0]$ . The superscript “app” is used to indicate that the ionization, or affinity, potential is obtained from explicit calculations with the selected DFA; three self-consistent calculations are performed, each one for  $N - 1$ ,  $N$ , and  $N + 1$  electrons. In molecules, one can estimate the energy gap using any DFA by simply minimizing the ground-state energy of the molecule for different number of electrons. Within this approach there are errors in the ground-state energies associated with the size of the basis set and the self-interaction error (which is critical when the number of electrons changes). In solids, however, a direct calculation of the gap by changing the number of electrons, which does require adding/removing a very small charge to/from the unit cell, is very challenging because of the delocalization of charge. Unfortunately, due to the continuous differentiability of the LDA, and GGA, XC energies, the quasiparticle gap is underestimated, hence the need for  $\Delta_{\text{XC}}$ .

The relation between the parameters and the derivative discontinuity can also be generalized to the many-parameter case (assuming that the ionization theorem holds). Equation 20 can be written as

$$\Delta_{\text{XC}} = \int_{\gamma^*} \text{d}\mathbf{z} \cdot \langle \phi_{\text{L}}^z | \nabla_{\mathbf{z}} \hat{f}_{\text{z}} | \phi_{\text{L}}^z \rangle \quad (24)$$

where  $\gamma^*$  is a trajectory between the point where the interaction is absent ( $\mathbf{z} = 0$ ) and the point ( $\mathbf{z}^*$ ) that reproduces the discontinuity. The quantities on the right-hand side are functions of the auxiliary interaction. The specific evaluation of the Fock operator  $\hat{f}_{\text{z}}$  depends on the explicit form of the parametrization. It is possible that there is a large set of parameters satisfying the above equation, and that there are points in the parameter space where the LUMO energy is a nonanalytic function, which could be the case if there is orbital crossing (a situation where the integration can be trajectory-dependent).

## ■ DYNAMICS AND LINEAR RESPONSE

Suppose a local time-dependent (td) potential,  $u_{\text{s}}^{\lambda}(\mathbf{r}, t)$  is given. The Hamiltonian describing the auxiliary system of electrons is

$$\hat{\mathcal{H}}_{\lambda}[u_{\text{s}}^{\lambda}](t) = \hat{T} + \lambda \hat{W} + \int \text{d}^3\mathbf{r} u_{\text{s}}^{\lambda}(\mathbf{r}, t) \hat{n}(\mathbf{r}) \quad (25)$$

The evolution equations can be derived by stationarizing the action

$$\mathcal{A}[\Phi_{\text{N}}, u_{\text{s}}^{\lambda}] = \int_0^T \text{d}t \langle \Phi_{\text{N}}(t) | \text{i}\partial_t - \hat{\mathcal{H}}_{\lambda}[u_{\text{s}}^{\lambda}](t) | \Phi_{\text{N}}(t) \rangle \quad (26)$$

under the constraint that the state of the system is described at all times by a single td Slater determinant. The evolution equations for the orbitals are then of the form  $\text{i}\partial_t \phi_a(t) = \hat{f}_{\lambda}(t) \phi_a(t)$ , where  $\hat{f}_{\lambda}(t) = -1/2\nabla^2 + \lambda(\hat{j}(t) + \hat{v}_{\text{x},\lambda}(t)) + u_{\text{s}}^{\lambda}(t)$ .

For a given interaction strength,  $\lambda$ , and initial state,  $\Phi_{\text{N}}(0)$ , as a simple extension of the Runge–Gross theorem,<sup>31</sup> there is a one-to-one correspondence between the space of local, auxiliary td potentials and the space of electronic densities.<sup>32</sup> To reproduce the td electronic density of the real system of electrons, the orbitals are propagated self-consistently using a td potential  $\tilde{u}_{\text{s}}^{\lambda}(t) = u_{\text{HXC}}^{\lambda}(t) + v(t)$ , where  $v(t)$  is the total td one-body external potential of the system, which might include the driving scalar field, i.e., a laser field. One can introduce a proper XC action functional in such a way that

$$u_{\text{XC}}^{\lambda}(\mathbf{r}, t) = (1 - \lambda) \frac{\delta \mathcal{A}_{\text{x}}}{\delta n(\mathbf{r}, t)} + \frac{\delta \mathcal{A}_{\text{c}}}{\delta n(\mathbf{r}, t)} + g_{\text{XC}}(\mathbf{r}, t) \quad (27)$$

where  $g_{\text{XC}}$  is a memory term that vanishes in adiabatic approximations. The functional derivative symbol is defined as a symmetry operation in the Keldysh space that avoids a causality paradox.<sup>33</sup> The adiabatic approximation is obtained by replacing the actions in the above equation by the corresponding ground-state analogues. The resulting adiabatic, partial HXC potential is  $u_{\text{HXC}}^{\lambda}(\mathbf{r}, t) = (1 - \lambda)u_{\text{HX}}^{\text{gs}}[n(\mathbf{r}, t)] + u_{\text{s}}^{\text{gs}}[n(\mathbf{r}, t)]$ . For example, if Dirac exchange<sup>34</sup> is used, we find  $u_{\text{X}}^{\text{gs}}(\mathbf{r}, t) = -4/3C_{\text{x}}n^{1/3}(\mathbf{r}, t)$ ; the Hartree potential is adiabatic.

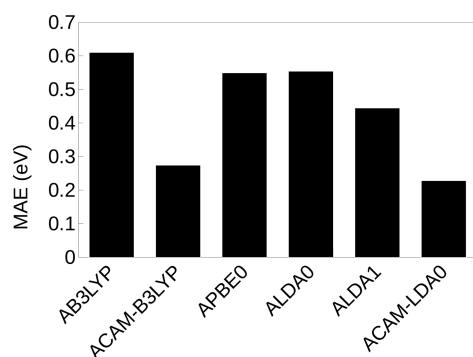
Equations 16 and 22 indicate that local and nonlocal exchange energies, and potentials, are quite relevant quantities to explore the relationship between the ground-state GKS XC energies, the XC derivative discontinuity, and the space of parameters. In addition, there is a close connection between the ground-state parametrized methods and their linear-response extensions. In a zero-order electronic transition, an electron is promoted from an occupied orbital to a virtual one. The linear-response formalism, roughly speaking, leads to the correction of this type of excitation, where the zero-order transition is shifted in the energy scale by the kernel. The approximated adiabatic kernels in general provide a small shift, usually insufficient to estimate electronic excitations in molecules: It is known that a purely local XC kernel in standard KS theory, like the adiabatic LDA, often produces an unsatisfactory optical gap. In both the td and ground-state cases, with respect to pure HF calculations, the relaxation and compression of the orbital levels caused by the XC LDA potential is excessive. The addition of an appropriate fraction of orbital exchange reduces these effects by inducing orbital-specific screening. Nonetheless, the gradient-based corrections to the XC LDA, present in functionals like PBE, do not seem to produce a significant change on this widening of orbital levels, as we report in the next section.

## ■ DISCUSSION

To study the effect of  $\lambda$ , and  $\zeta$ , we chose a subgroup of the benchmarking set previously reported by Peach et al.<sup>4</sup> The subset maintains an even balance between the number of charge-transfer and local excitations. Here we analyze the excitation energies of the following molecules: HCl, CO, 4-(*N,N*-dimethylamino)benzotrile (DMABN), dipeptide,  $\beta$ -dipeptide, *N*-phenylpyrrole (PP), anthracene, and some polyacetylene (PA) oligomers. To refer to td functionals, we affix an “A” to the acronym of their respective ground-state approximation. We compare the performance of the adiabatic functionals: APBE0 ( $\lambda = 0.25$ ), ALDA0 ( $\lambda = 0.25$ ), ALDA1 ( $\lambda = 0.3$ ), and ACAM-LDA0. Additionally, we include the data corresponding to AB3LYP and ACAM-B3LYP, calculated by Peach et al.<sup>4</sup>

First, we optimized all the molecular geometries employing the basis set 6-31G\* for each functional, PBE0, LDA0, and LDA1. In most cases, the excitation-energy calculations with a certain adiabatic DFA were performed at the molecular geometry obtained with its ground-state equivalent functional. For the calculations with ACAM-LDA0 we use the LDA0 geometry. And, for  $\beta$ -dipeptide the LDA0 optimal geometry was employed for all the excitation calculations. The linear-response TDDFT computations were carried out with the correlation-consistent, polarized, triple- $\zeta$  (cc-pVTZ) basis set, except for CO, for which we used d-aug-cc-pVTZ (as suggested in ref 4). Our calculations were run using the NWChem suite.<sup>35</sup>

We observed that convergence of the linear-response calculations with the adiabatic LDA0 functional is *twice as fast* as with APBE0; both functionals display very close mean absolute errors, Figure 1. The excitation energies from ALDA0



**Figure 1.** Performance comparison of DFAs in terms of mean absolute error, calculated using the reference values of Table 1.

are around 0.1 eV less than those obtained using APBE0. Also, for this set of excitation energies, both APBE0 and ALDA0 yield similar numbers as AB3LYP. Increasing the amount of Fock exchange raises the excitation energies with respect to APBE0. Consider, for example, LDA with  $\lambda = 0.3$ , which we denote<sup>b</sup> LDA1 (Table 1). ALDA1 gives a slightly better accuracy than ALDA0 (Figure 1). Note, however, that APBE0, ALDA0, and ALDA1 are unable to describe properly the charge-transfer (CT) excitation energies as the ACAM-B3LYP functional does. The solution to improve the description of such processes is the addition of the *long-range* HF exchange contribution. Why does this work? The addition of nonlocal exchange increases the excitation energies but does not raise the CT values high enough. One might try to further increase  $\lambda$ , but this would cause errors in the non-CT excitations. Long-range Fock exchange raises effectively the energy of the long-range excitations, which are essentially of the CT type. For local excitations, the long-range HF exchange has little effect.

The method of Yanai et al.<sup>10</sup> (the creators of CAM) is an extension of the work of Tsuneda et al.,<sup>37</sup> who showed that partitioning of the Coulombic interaction and use of Fock exchange for the lr interactions were of practical utility. These studies focus *only* on exchange interactions. The effect of nonlocal correlations is rather unexplored. Recently, hybrid functionals combining MP2 and local functionals have been proposed (we refer the reader to ref 38 for more information). The inclusion of MP2 can also be analyzed within the GKS framework.

*The gradient corrections to the adiabatic LDA0 functional have little effect on the excitation energies.* For example, we reduced

CAM-B3LYP to CAM-LDA0. This latter functional consists in setting  $\lambda = 1/4$ ,  $\zeta = 1/2$ , and  $\mu = 1/3$ , whereas the residual parts of exchange and correlation are treated with LDA only. The factor  $\mu = 1/3$  comes from the study of Tsuneda et al.,<sup>37</sup> and  $\zeta = 1/2$  derives from the work of Yanai et al.<sup>10</sup> The performance of ACAM-LDA0 agrees with that of ACAM-B3LYP, Figure 1. The former functional leads to computer times reduced by about 30% with respect to ACAM-B3LYP. The cost cannot be reduced further due to the use of the error function. In settings where computational resources are limited or need to be shared among many users, some reduction of power demands might be desired. Approximation and speed-up of exchange integrals is an ongoing field.<sup>39,40</sup> If a boosting algorithm can be applied to a functional like the adiabatic CAM-LDA0, then the savings could be increased.

The tendency of gradient-dependent terms to produce small contributions to the excitation energies, for the standard theory (no parameters,  $\lambda = 0$ ), can also be inferred from earlier studies. For instance, the data reported in refs 41–43 suggest that for low-lying excitation energies the results change by small amounts when switching from the adiabatic XC PBE functional to ALDA.

The purpose of the gradient corrections to the LDA XC energy is mainly to extend the LDA functional to the inhomogeneous electron gas case. To investigate atoms and molecules, the gradient-corrected functionals give slightly more accurate ground-state properties than the LDA. In a dissociation process, for example, the curvature of the density increases due to the reduction of the density in the bonding regions. Because the GGAs somewhat account for this, the binding energies are improved. In contrast, the LDA0, or CAM-LDA0, is less suited for describing binding energies.

A question that might come to mind is, “Should the ground-state XC potential be the same as the td one?” The answer depends on the type of application, the user needs, the hardware available, etc. For example, there are molecules for which combining LDA0 ground-state calculations with an excitation-energy analysis based on the ALDA0 XC potential could be enough. In addition, for calculation of forces and atomic motions, it can be convenient to use the same functionals with gradient corrections. On the contrary, there might be cases where one needs an accurate geometry from a different methodology and could simply use a functional like ALDA0, or its CAM version. From the perspective of rigorous TDDFT, however, it must be remarked that the improved, td XC potential should feature dependence on the initial state and the evolution of the electronic density, i.e., memory dependence. Thus, an improved, td XC potential should extend its ground-state counterpart and display a different algebraic structure.

The errors shown in Figure 1 indicate that introduction of the parameters  $\lambda$ ,  $\zeta$ , and  $\mu$  (alternatively,  $\alpha$ ,  $\beta$ , and  $\mu$ ) is useful to improve optical properties. Interestingly, the GKS formalism allows for inclusion of *many* types of auxiliary interactions between the auxiliary electrons to enhance the approximations in standard KS theory. It would be desirable to have a reference system where the value of the parameters  $\lambda$ ,  $\zeta$ ,  $\mu$  could be estimated. The concept of the electron gas, which offers a vast set of physical gapless systems, has been originally used to obtain local and semilocal approximations. The way it was traditionally used might discourage employing these systems to estimate parameters like  $\lambda$ ,  $\zeta$ , and  $\mu$ . However, downscaling the electron gas model to small volumes leads to non-negligible

Table 1. Calculated Excitation Energies by Using Several *Adiabatic* DFAs, Reference Values Included<sup>a</sup>

system	transition	type	B3LYP	CAM-B3LYP	PBE0	LDA0	LDA1	CAM-LDA0	ref
HCl	$\Pi$	CT	7.65	7.79	7.84	7.70	7.90	7.83	8.23
CO	$\Sigma^+$	R	10.97	11.79	11.23	11.40	11.60	12.37	12.40
	$\Pi$	R	10.19	10.90	10.53	10.69	10.87	11.45	11.53
	$\Sigma^+$	R	10.13	10.80	10.46	10.62	10.80	11.34	11.40
	$\Sigma^+$	R	9.80	10.37	10.10	10.26	10.42	10.87	10.78
	$\Delta$	L	10.03	10.08	10.05	10.00	10.23	9.98	10.23
	$\Sigma^-$	L	9.72	9.71	9.65	9.52	9.74	9.47	9.88
	$\Pi$	L	8.39	8.47	8.36	8.26	8.41	8.35	8.51
PA $m = 2$	$B_u$	L	5.88	6.04	5.89	5.83	5.97	5.99	5.92
PA $m = 3$	$B_u$	L	4.81	5.03	4.80	4.74	4.88	4.97	4.95
PA $m = 4$	$B_u$	L	4.13	4.39	4.67	4.63	4.19	4.63	4.41
PA $m = 5$	$B_u$	L	3.66	3.94	3.62	3.56	3.70	3.86	4.27
DMABN	$B_2$	L	4.44	4.72	4.43	4.35	4.52	4.70	4.25
	$A_2$	CT	4.64	4.91	4.74	4.67	4.83	4.96	4.56
PP	$B_2$	L	4.76	5.06	4.79	4.72	4.95	5.12	4.85
	$A_1$	L	4.96	5.12	4.86	4.79	5.00	5.19	5.13
	$B_2$	CT	4.58	5.27	4.91	4.83	5.04	5.46	5.47
	$A_1$	CT	4.64	5.92	5.15	5.08	5.34	6.28	5.94
anthracene	$B_{2u}$	L	4.38	4.67	4.46	4.40	4.56	4.71	4.88
	$B_{3u}$	L	4.47	4.62	4.55	4.48	4.64	4.63	4.46
$\beta$ -dipeptide	$n_1 \rightarrow \pi_2^*$	CT	7.26	8.38	6.96	6.92	7.33	9.05	9.13
	$\pi_1 \rightarrow \pi_2^*$	CT	7.20	8.01	6.73	6.66	6.92	8.37	7.99
	$n_1 \rightarrow \pi_1^*$	L	5.66	5.67	5.61	5.59	5.65	5.72	5.40
dipeptide	$n_2 \rightarrow \pi_2^*$	L	5.56	5.76	5.69	5.67	5.73	5.79	5.10
	$n_1 \rightarrow \pi_2^*$	CT	6.31	7.84	6.74	6.64	7.12	8.41	8.07
	$\pi_1 \rightarrow \pi_2^*$	CT	6.15	7.00	6.50	6.32	6.72	7.23	7.18
	$n_1 \rightarrow \pi_1^*$	L	5.55	5.69	5.76	5.64	5.88	5.78	5.63
	$n_2 \rightarrow \pi_2^*$	L	5.77	5.92	6.03	5.94	6.16	6.10	5.79
MAE			0.61	0.27	0.55	0.55	0.44	0.23	

<sup>a</sup>Excitation types: CT, charge transfer; L, local; R, Rydberg; MAE, mean absolute error. For the dipeptide molecules the subindexes 1 and 2 refer to the first and second carbonyl groups, respectively. The variable  $m$  is the number of units in the oligomer.

energy spacings in the spectrum. And, perhaps, at these scales the estimation of the parameters can be performed.

## CONCLUDING REMARKS

The GKS formalism allows us to regard XC functionals like PBE0, and LDA0, as part of a different flavor of KS theory that includes at least one parameter. In light of the GKS framework, we studied hybrid functionals and their associated, auxiliary, electronic systems. Also, some formal conditions that hybrid functionals should satisfy were shown. In principle, different systems require different amounts of nonlocal Fock exchange, which can motivate further work on transforming the parameters into purely *ab initio* quantities. Nonlocal exchange corrections in combination with the adiabatic LDA, e.g., the CAM-LDA0 form, can produce better charge-transfer excitation energies with respect to functionals like AB3LYP, and APBE0. This suggests that a portion of nonlocal exchange is a dominant factor for the enhancement of excitation energies. Nonetheless, we remark, discretion and insight by the user is required to properly set up the correct amount of orbital exchange, and related quantities. Knowledge deduced from reliable *ab initio* calculations and experimental measurements might assist in this matter.

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## Notes

The authors declare no competing financial interest.

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## ADDITIONAL NOTES

<sup>a</sup>A similar expression for the GKS correlation energy was defined by Görling and Levy.<sup>16</sup> Their formula, however, is different from eq 4 because their expansion of the partial HXC energy depends on the exchange energy of standard KS theory. <sup>b</sup>The GGA version of the XC LDA1 is in essence the PBE0-1/3 functional; see ref 36 for details.

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