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Adiabatic Connection for Range-Separated Hybrid Functionals

Rachel Garrick, Leeor Kronik,* and Tim Gould*

A generalized adiabatic connection that applies to any type of range-separated hybrid (RSH) functional employed within generalized Kohn–Sham (KS) theory is presented. This generalized relation is then used to derive a definition for a rigorous distinction between multiplicative exchange and correlation components. The developed adiabatic connection is defined in terms of both generalized and conventional KS orbitals. It is shown, however, that using only the KS orbitals produces an error that is $O(\epsilon^2)$, where ϵ is fully defined in terms of parameters in the RSH functional, and is found to be small in practical calculations. It is expected that this new adiabatic connection can assist in the development of new RSH functionals and the assessment of existing ones.

1. Introduction

The adiabatic connection formula^[1,2] of Kohn–Sham (KS) theory^[3] connects between the interacting many-electron system and the noninteracting KS system, by gradually “turning on/off” the electron–electron interaction through an infinite set of partially interacting systems. It has proven to be a useful tool in the analysis of formal properties of density functionals.^[4] Notably, it has served as the underlying rationale for the introduction of global hybrid functionals, which utilize a fraction of exact exchange.^[5–7]

While global hybrid functionals were motivated by KS theory, their practical use almost always involves a nonmultiplicative Fock potential,^[5,6] which actually places them outside KS theory. Instead, they can be rationalized within the rigorous framework of

generalized KS (GKS) theory.^[8,9] In recent work,^[10] we have defined an adiabatic connection formula for global hybrid functionals within GKS theory. We then used it to define exact multiplicative exchange and correlation components and analyze approximate global hybrid functionals in light of the exact results.

Range-separated hybrid (RSH) functionals^[11–13] are a more sophisticated class of hybrid functionals, in which different fractions of Fock exchange are employed at different inter-electron interaction ranges, allowing for a finer balance between exchange and correlation components. They are increasingly popular as they have proven to offer improved accuracy

for a wide range of electronic structure problems.^[14–20] In recent years, the KS adiabatic connection has been increasingly used to analyze and develop RSH functionals^[21,22] and other advanced hybrid functionals.^[23–27] It is therefore of interest to develop an adiabatic connection theorem, including an ensuing exchange and correlation component analysis, that is directly suitable for RSH functionals within the GKS framework in which they are used. In this article, we present such an appropriately generalized theory, illustrated by relevant numerical examples.

2. Synopsis of the Adiabatic Connection Approach


To begin our considerations, we recall that an adiabatic connection formula^[1,2] within KS theory is usually achieved by defining the many-body operator

$$\hat{H}_\lambda \equiv \hat{T} + \hat{V}_{\text{ext},\lambda} + \lambda \hat{W} \quad (1)$$

where $\hat{T} = -\frac{1}{2} \sum_i \nabla_i^2$ is the many-electron kinetic energy operator, $\hat{W} = \sum_{i<j} \frac{1}{|r_i - r_j|}$ is the many-electron Coulomb operator, $0 \leq \lambda \leq 1$ is a parameter, and $\hat{V}_{\text{ext},\lambda}$ is a λ -dependent external potential operator. $\hat{V}_{\text{ext},\lambda}$ is adjusted such that the ground-state many-electron wave-function, $|\Psi_\lambda\rangle$, corresponding to \hat{H}_λ , integrates to the original many-electron density for any λ .

As a special case of Equation (1), $\hat{V}_{\text{ext},1}$ is simply the external potential of the true many-electron system, \hat{H}_1 is the true many-electron Hamiltonian, and $|\Psi_1\rangle$ is the original many-electron wave-function, $|\Psi\rangle$. Similarly, $\hat{V}_{\text{ext},0}$ and \hat{H}_0 are the many-electron external potential operator and Hamiltonian corresponding to the KS potential, and $|\Psi_0\rangle$ is the KS determinant, $|\Phi_s\rangle$. The advantage, then, is, that mapping from $|\Psi\rangle$ to $|\Phi_s\rangle$ is no longer “abrupt”

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but rather can be obtained adiabatically by slowly “turning off” the electron–electron repulsion while retaining the overall density.

The many-electron and KS limits can be further connected by defining

$$F^\lambda[n] = \langle \Psi_\lambda | \hat{T} + \lambda \hat{W} | \Psi_\lambda \rangle \quad (2)$$

For $\lambda = 1$, $F^\lambda[n]$ becomes the universal Hohenberg–Kohn functional for the fully-interacting system, namely

$$F^{\text{HK}}[n] := F^1[n] = \min_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \quad (3)$$

where $n(\mathbf{r})$ is the electron density. For $\lambda = 0$, $F^\lambda[n]$ becomes the noninteracting kinetic energy function, $T_s[n]$, of KS theory, that is

$$T_s[n] := F^0[n] = \langle \Phi_s | \hat{T} | \Phi_s \rangle \quad (4)$$

The linear adiabatic connection formula for KS theory, as defined in Equation (2), does not apply to a global hybrid functional employed within GKS theory, for which the $\lambda = 0$ reference system is itself a partially-interacting functional of $n(\mathbf{r})$. As discussed in detail in our previous work,^[10] formulating an adiabatic connection theorem within the GKS framework is more challenging and less direct than in the KS case. This is because GKS theory involves an *ansatz* for the partially interacting system, which does not lend itself to continuous switching from off to on, as done for the interaction in Equation (2). Specifically, for a global hybrid the GKS system is described using

$$F_\alpha^{\text{GKS}}[n] := \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \alpha \hat{W} | \Phi \rangle := \langle \Phi_\alpha | \hat{T} + \alpha \hat{W} | \Phi_\alpha \rangle \quad (5)$$

as the reference “noninteracting” system, where $0 \leq \alpha \leq 1$. Here, we limit the minimization to Slater determinants with density $n(\mathbf{r})$, from which $|\Phi_\alpha\rangle$ minimizes $F_\alpha^{\text{GKS}}[n]$. The special case of $\alpha = 1$ is analogous to Hartree–Fock theory, but complemented by a correlation potential which makes it exact, while for the special case of $\alpha = 0$ the *ansatz* reduces to conventional KS theory.

In seeking an appropriate adiabatic connection density functional that can accommodate the *ansatz*, several criteria must be satisfied:

- (i) it must reduce to the GKS result when $\lambda = 0$;
- (ii) it must reduce to the fully interacting result when $\lambda = 1$;
- (iii) it must reduce to the adiabatic connection of KS theory for any choice of parameters for which $\alpha \hat{W} \rightarrow 0$, for all $\lambda \in [0, 1]$.

In order to be useful for defining the exchange and correlation components, we also ask that it:

- (iv) allow the attainment of the remainder Hartree-exchange (Hx) energy, $E_{\text{R,Hx};\alpha}[n]$, that is, the Hx contribution missing from the partial treatment of the Coulomb interaction in Equation (5), from a right derivative of the adiabatic functional with respect to λ at $\lambda = 0$. This means that the expression should involve only Slater determinants at $\lambda = 0^+$.

Based on these criteria we defined the adiabatic connection functional of Equation (6), where Φ_α is the GKS determinant for

the map with α as the global fraction of Fock exchange.

$$F_\alpha^\lambda[n] \equiv (1 - \lambda) [\langle \Phi_\alpha | \hat{T} + \alpha \hat{W} | \Phi_\alpha \rangle - \langle \Phi_s | \hat{T} | \Phi_s \rangle] + \langle \Psi_\lambda | \hat{T} + \lambda \hat{W} | \Psi_\lambda \rangle \quad (6)$$

which may also be expressed as $F_\alpha^\lambda[n] = (1 - \lambda)(F_\alpha^{\text{GKS}}[n] - T_s[n]) + F^\lambda[n]$.

Equation (6) may then be used to define key density functionals for hybrid schemes. By criterion (i), we have $F_\alpha^0[n] := F_\alpha^{\text{GKS}}[n]$, which is the definition of the GKS functional in Equation (5). By criterion (iv), we may define the remainder Hx energy as $E_{\text{R,Hx};\alpha} := \partial_\lambda^+ F_\alpha^\lambda$ (where ∂_λ^+ indicates a right-derivative). This yields

$$E_{\text{R,Hx};\alpha}[n] := \langle \Phi_s | \hat{T} + \hat{W} | \Phi_s \rangle - \langle \Phi_\alpha | \hat{T} + \alpha \hat{W} | \Phi_\alpha \rangle \quad (7)$$

We may then use criteria (ii) and (iii) to define the correlation energy

$$\begin{aligned} E_c[n] &:= F_\alpha^1[n] - F_\alpha^0[n] - E_{\text{R,Hx};\alpha}[n] \\ &= \langle \Psi_1 | \hat{T} + \hat{W} | \Psi_1 \rangle - \langle \Phi_s | \hat{T} + \hat{W} | \Phi_s \rangle \\ &= F^{\text{HK}}[n] - T_s[n] - E_{\text{Hx}}[n] \end{aligned} \quad (8)$$

where the last term on the right hand side of the above equation is the conventional (Hartree–Fock) expression for the Hartree and exchange energies. The correlation energy is then independent of α , and therefore takes its value from traditional KS theory. We note that an earlier, equally rigorous yet different partition between $E_{\text{R,Hx}}$ and E_c has been proposed by Görling and Levy,^[28] an issue we address further below in the context of RSH functionals.

Equation (7) is inconvenient from both a formal and a practical perspective, as it is defined in terms of both GKS (via $|\Phi_\alpha\rangle$) and KS (via $|\Phi_s\rangle$) orbitals. However, our previous work^[10] showed that

$$E_{\text{R,Hx};\alpha}[n] := (1 - \alpha) \langle \Phi_s | \hat{W} | \Phi_s \rangle + O(\alpha^2) \quad (9)$$

that is, the remainder Hx term can be expressed in terms of the KS orbitals alone, with errors of only $O(\alpha^2)$ in the global Fock exchange fraction, α . Therefore, errors from using the “wrong” orbitals are expected to be small.

3. Adiabatic Connection for Range-Separated Hybrid Functionals

RSH functionals partition the electron–electron interaction into long-range and short-range components, with different mixtures of Fock and semilocal exchange for each range.^[11–13] The partitioning between the long-range and short-range regimes is nonunique. A popular partitioning scheme uses the error functional^[15]

$$\frac{1}{r_{ij}} = \frac{\alpha + \beta \operatorname{erf}(\gamma r_{ij})}{r_{ij}} + \frac{1 - [\alpha + \beta \operatorname{erf}(\gamma r_{ij})]}{r_{ij}} \quad (10)$$

where α , β , and γ are free parameters and r_{ij} is the interelectronic distance of electrons i and j . A different partitioning scheme that

is not as common, but still in use, involves screening with the Yukawa potential^[12,21,29]

$$\frac{1}{r_{ij}} = \frac{\alpha + \beta(1 - e^{-\gamma r_{ij}})}{r_{ij}} + \frac{1 - [\alpha + \beta(1 - e^{-\gamma r_{ij}})]}{r_{ij}} \quad (11)$$

In (exact^[19,30] or approximate) RSH-based GKS theory, the first term in Equations (10) or (11) is treated using Fock exchange and the second term is treated using a multiplicative exchange potential. α is then the fraction of short-range exchange, $\alpha + \beta$ is the fraction of long-range exchange, and γ is the range-separation parameter (with units of inverse length).

As above, we wish to consider the exact remainder Hx energy, that is, the exact contribution to the Hartree and exchange energies that is missing owing to the explicit Hartree–Fock (HF) treatment of only the second term in Equation (10) or (11). To that end, we divide the many-electron Coulomb operator as

$$\hat{W} := \hat{W}_{\vec{\gamma}} + (\hat{W} - \hat{W}_{\vec{\gamma}}) \quad (12)$$

where $\hat{W}_{\vec{\gamma}}$ is the many-electron operator corresponding to a range-separated component of the overall Coulomb repulsion, that is

$$\hat{W}_{\vec{\gamma}} := \frac{1}{2} \int \hat{n}_2(\vec{r}, \vec{r}') W_{\vec{\gamma}}(\vec{r}, \vec{r}') d\vec{r} d\vec{r}' \quad (13)$$

where $\hat{n}_2(\vec{r}, \vec{r}')$ is the pair density operator and $\vec{\gamma}$ is short-hand notation for the parameters in the range-separated component, typically the above-defined α , β , and γ . Conventionally, range-separated potentials obey, $0 \leq W_{\vec{\gamma}}(\vec{r}_i, \vec{r}_j) \leq \frac{1}{r_{ij}}$ and we therefore require these bounds on $W_{\vec{\gamma}}$. We will also require $W_{\vec{\gamma}}(\vec{r}_i, \vec{r}_j) = W_{\vec{\gamma}}(\vec{r}_j, \vec{r}_i)$. Other than these two restrictions we shall not impose any other conditions on $W_{\vec{\gamma}}$.

The two range-separations defined above are special cases of the general form of Equation (13), defined by $W_{\vec{\gamma}}(r_{ij}) := \frac{\alpha + \beta \operatorname{erf}(\gamma r_{ij})}{r_{ij}}$,

and, $W_{\vec{\gamma}}(r_{ij}) := \frac{\alpha + \beta(1 - e^{-\gamma r_{ij}})}{r_{ij}}$ for Equations (10) and (11), respectively.

But the expression given in Equation (13) is even more general. For example,^[31] a “local hybrid”^[31] version of an RSH would be given by

$$W_{\vec{\gamma}}(\vec{r}_i, \vec{r}_j) := \frac{\alpha(\tilde{n}) + \beta(\tilde{n}) \operatorname{erf}[\gamma(\tilde{n})r_{ij}]}{r_{ij}} \quad (14)$$

are also of this general form, provided $0 \leq \alpha < 1$, $0 \leq \alpha + \beta \leq 1$, $\gamma > 0$, and $\tilde{n} := \tilde{n}(n(\vec{r}_i), n(\vec{r}_j)) = \tilde{n}(n(\vec{r}_j), n(\vec{r}_i))$.

In analogy to Equation (5), we describe the GKS system using

$$F_{\vec{\gamma}}^{\text{GKS}}[n] := \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \hat{W}_{\vec{\gamma}} | \Phi \rangle := \langle \Phi_{\vec{\gamma}} | \hat{T} + \hat{W}_{\vec{\gamma}} | \Phi_{\vec{\gamma}} \rangle \quad (15)$$

As before, this is minimized over Slater determinants with density n . Given the similarity of Equation (15) to Equation (5), we propose the following linear adiabatic connection for the case of RSH functionals

$$F_{\vec{\gamma}}^{\lambda}[n] = (1 - \lambda) [\langle \Phi_{\vec{\gamma}} | \hat{T} + \hat{W}_{\vec{\gamma}} | \Phi_{\vec{\gamma}} \rangle - \langle \Phi_s | \hat{T} | \Phi_s \rangle] + \langle \Psi_{\lambda} | \hat{T} + \lambda \hat{W}_{\vec{\gamma}} | \Psi_{\lambda} \rangle \quad (16)$$

Equation (16) differs from Equation (6) in that in the RSH case the electron–electron interaction operator is modified by all parameters of the RSH functional, rather than simply being multiplied by a constant fraction.

It can be easily verified that the first three criteria used to define the generalized adiabatic connection [Equation (6)] are satisfied by Equation (16):

- (i) For $\lambda = 0$ we obtain, $F_{\vec{\gamma}}^0 = \langle \Phi_{\vec{\gamma}} | \hat{T} + \hat{W}_{\vec{\gamma}} | \Phi_{\vec{\gamma}} \rangle - \langle \Phi_s | \hat{T} | \Phi_s \rangle + \langle \Psi_0 | \hat{T} | \Psi_0 \rangle = \langle \Phi_{\vec{\gamma}} | \hat{T} + \hat{W}_{\vec{\gamma}} | \Phi_{\vec{\gamma}} \rangle = F_{\vec{\gamma}}^{\text{GKS}}$, where we used $|\Phi_s\rangle := |\Psi_0\rangle$;
- (ii) For $\lambda = 1$ we obtain, $F_{\vec{\gamma}}^1 = \langle \Psi_1 | \hat{T} + \hat{W}_{\vec{\gamma}} | \Psi_1 \rangle = F^{\text{HK}}$;
- (iii) For $W_{\vec{\gamma}} = 0$ (denoted $\vec{\gamma} = 0$) we obtain, $F_{\vec{\gamma}=0}^{\lambda} = \langle \Phi_{\vec{\gamma}=0} | \hat{T} | \Phi_{\vec{\gamma}=0} \rangle - \langle \Phi_s | \hat{T} | \Phi_s \rangle + \langle \Psi_{\lambda} | \hat{T} + \lambda \hat{W}_{\vec{\gamma}} | \Psi_{\lambda} \rangle = \langle \Psi_{\lambda} | \hat{T} + \lambda \hat{W}_{\vec{\gamma}} | \Psi_{\lambda} \rangle$, where we used $|\Phi_{\vec{\gamma}=0}\rangle = |\Phi_s\rangle$

By taking the right-derivative at $\lambda = 0$, we obtain a rigorous definition for the Hx energy, in the form

$$E_{\text{R,Hx};\vec{\gamma}}[n] := \langle \Phi_s | \hat{T} + \hat{W} | \Phi_s \rangle - \langle \Phi_{\vec{\gamma}} | \hat{T} + \hat{W}_{\vec{\gamma}} | \Phi_{\vec{\gamma}} \rangle \quad (17)$$

which we show below is compatible with criterion (iv). The corresponding correlation energy then adopts its usual KS value [Equation (8)].

The physical origin of the remainder Hx is twofold. The first (and, as we shall show, typically largest) component reflects the fact that $\hat{W}_{\vec{\gamma}}$ is not the full Coulomb potential, \hat{W} , so there must be an additional energy term coming from the DFT treatment of the rest of the Coulomb potential. The second component reflects the fact that there is a difference between the KS and GKS Slater determinants $|\Phi_s\rangle \equiv |\Psi_0\rangle$ and $|\Phi_{\vec{\gamma}}\rangle$. The difference follows from the fact that even when the energy expression is the same in KS and GKS theory, the underlying orbitals are not, owing to the use of a multiplicative or a nonmultiplicative potential, respectively.

We now seek to derive a perturbation expression that would generalize Equation (9) to the case of RSH functionals. This would allow us to understand the relative magnitude of the second term in the remainder Hx expression. Our first step is to define a perturbation parameter, $\epsilon(\vec{\gamma})$, that lets us express the GKS Slater determinants as a perturbation about the KS Slater determinants

$$|\Phi_{\vec{\gamma}}\rangle = |\Phi_s\rangle + \epsilon(\vec{\gamma}) |\Delta\Phi_s\rangle \quad (18)$$

Here, $\epsilon(\vec{\gamma})$ is a function of all parameters in the hybrid functional and reduces $W_{\vec{\gamma}}(r_{12})$ to a scalar weight. To determine the value of $\epsilon(\vec{\gamma})$, we adopt the usual approach of expanding in terms of a scaled interaction energy, $\epsilon \hat{W}$. Specifically, we seek an ϵ for which

$$0 \leq \langle \Phi_{\vec{\gamma}} | \hat{W}_{\vec{\gamma}} | \Phi_{\vec{\gamma}} \rangle \leq \epsilon(\vec{\gamma}) \langle \Phi_n | \hat{W} | \Phi_n \rangle \quad (19)$$

for all Slater determinant wavefunctions, Φ_n , which yield the correct density. Then, any series expansion in $\epsilon \hat{W}$ is an upper bound to a series expansion in $\hat{W}_{\vec{\gamma}}$.

We start by recognizing that the Hx energy is less than the Hartree energy.

$$\langle \Phi_{\vec{\gamma}} | \hat{W}_{\vec{\gamma}} | \Phi_{\vec{\gamma}} \rangle \leq E_H^{\vec{\gamma}}[n_{\Phi_{\vec{\gamma}}}] = \frac{1}{2} \int W_{\vec{\gamma}}(|\vec{r} - \vec{r}'|) n(\vec{r}) n(\vec{r}') d\vec{r} d\vec{r}' \quad (20)$$

We may equivalently write this as

$$\langle \Phi_{\vec{\gamma}} | \hat{W}_{\vec{\gamma}} | \Phi_{\vec{\gamma}} \rangle \leq \epsilon(\vec{\gamma}) E_H[n] \quad (21)$$

so that our perturbation parameter can be chosen as

$$\epsilon(\vec{\gamma})[n] = \frac{\int W_{\vec{\gamma}}(\vec{r}, \vec{r}') n(\vec{r}) n(\vec{r}') d\vec{r} d\vec{r}'}{\int W(|\vec{r} - \vec{r}'|) n(\vec{r}) n(\vec{r}') d\vec{r} d\vec{r}'} \quad (22)$$

$E_H[n]$ is a good metric for the magnitude of \hat{W} as a functional of n . Therefore, Equation (22) defines a reasonable perturbation parameter for arbitrary $W_{\vec{\gamma}}$.

With ϵ established, we are ready to use Equation (18) in Equation (17), yielding

$$E_{R,Hx;\vec{\gamma}} = \langle \Phi_s | \hat{T} + \hat{W} | \Phi_s \rangle - \langle \Phi_s + \epsilon(\vec{\gamma}) \Delta \Phi_s | \hat{T} + \hat{W}_{\vec{\gamma}} | \Phi_s + \epsilon(\vec{\gamma}) \Delta \Phi_s \rangle \quad (23)$$

As our interest is in a perturbative series expansion, we next set $\hat{W}_{\vec{\gamma}} \approx \epsilon \hat{W}$, to obtain

$$\begin{aligned} E_{R,Hx;\vec{\gamma}} &\approx \langle \Phi_s | \hat{T} + \hat{W} | \Phi_s \rangle - \langle \Phi_s | \hat{T} + \epsilon \hat{W} | \Phi_s \rangle \\ &\quad - 2\epsilon \mathbb{R} \langle \Phi_s | \hat{T} + \epsilon \hat{W} | \Delta \Phi_s \rangle \\ &\quad - \epsilon^2 \langle \Delta \Phi_s | \hat{T} + \epsilon \hat{W} | \Delta \Phi_s \rangle \\ &= \langle \Phi_s | \hat{W} - \epsilon \hat{W} | \Phi_s \rangle - 2\epsilon \mathbb{R} \langle \Phi_s | \hat{T} | \Delta \Phi_s \rangle \\ &\quad - 2\epsilon^2 \mathbb{R} \langle \Phi_s | \hat{W} | \Delta \Phi_s \rangle - \epsilon^2 \langle \Delta \Phi_s | \hat{T} + \epsilon \hat{W} | \Delta \Phi_s \rangle \\ &= \langle \Phi_s | \hat{W} - \epsilon \hat{W} | \Phi_s \rangle + O(\epsilon^2) \end{aligned} \quad (24)$$

The last step uses the fact that $\langle \Phi_s | \hat{T} | \Phi_s \rangle$ is a variational minimum so may only be perturbed to $O(\epsilon^2)$.

We finally obtain

$$E_{R,Hx;\vec{\gamma}}[n] = \langle \Phi_s | \hat{W} - \hat{W}_{\vec{\gamma}} | \Phi_s \rangle + O(\epsilon^2) \quad (25)$$

where, to remind, $\epsilon(\vec{\gamma})$ is defined in Equation (22). Here we returned $\epsilon \hat{W}$ to its true value, $\hat{W}_{\vec{\gamma}}$. The dominant component of the remainder term therefore comes from the treatment of the interactions, $\hat{W} - \hat{W}_{\vec{\gamma}}$, that are outside of the GKS map. The secondary component, coming from the difference between $|\Phi_s\rangle$ and $|\Phi_{\vec{\gamma}}\rangle$, is only second order in $\epsilon(\vec{\gamma})$.

This result is analogous to the above-given previous result for global hybrids, Equation (9),^[10] where we have $\hat{W}_\alpha = \alpha \hat{W}$ and thus $E_{R,Hx}^{\text{global}} = (1 - \alpha) \langle \Phi_s | \hat{W} | \Phi_s \rangle + O(\alpha^2)$. Now, however, α has been replaced by a more general ϵ that is a function of $\vec{\gamma}$, the parameters of the RSH functional. Unlike, α , ϵ is itself a functional of the density, therefore changes based on the nature of the specific system are expected even within a given approximation.

Finally, we return to a rigorous definition of the remainder Hx term [cf., Equation (17)] and discuss the corresponding correlation energy. We recall that Görling and Levy^[28] defined the remainder Hx term of global hybrid theory using $\bar{E}_{R,Hx} = (1 - \alpha) E_{Hx}[n] = \langle \Phi_s | \hat{W} - \alpha \hat{W} | \Phi_s \rangle$, that is, in terms of the Hx energy

of the true KS system. The natural generalization of this to RSH functionals is

$$\bar{E}_{R,Hx;\vec{\gamma}} := \langle \Phi_s | \hat{W} - \hat{W}_{\vec{\gamma}} | \Phi_s \rangle := E_{R,Hx;\vec{\gamma}} - \Delta E_{R,Hx;\vec{\gamma}} \quad (26)$$

where

$$\Delta E_{R,Hx;\vec{\gamma}}[n] = \langle \Phi_s | \hat{W}_{\vec{\gamma}} | \Phi_{\vec{\gamma}} \rangle - \langle \Phi_s | \hat{W}_{\vec{\gamma}} | \Phi_s \rangle \quad (27)$$

is the difference between Equation (17) and $\bar{E}_{R,Hx;\vec{\gamma}}$. The correlation energy must always complement the other energy terms to the exact total energy. Therefore, $\bar{E}_c[n] = E_c[n] + \Delta E_{R,Hx;\vec{\gamma}}[n]$ must cancel out the difference in the remainder Hx term. Equation (25) reveals that $\Delta E_{R,Hx;\vec{\gamma}}[n]$ is $O(\epsilon^2)$, yielding

$$\bar{E}_{R,Hx;\vec{\gamma}} = E_{R,Hx;\vec{\gamma}} - O(\epsilon^2) \quad \bar{E}_{c;\vec{\gamma}} = E_{c;\vec{\gamma}} + O(\epsilon^2) \quad (28)$$

That is, the two partitions are the same up to $O(\epsilon^2)$. This shows that, as in global hybrids,^[10] the energy contribution due to differences between KS and GKS orbitals can legitimately be relegated to the correlation term. Here we generally preferred to avoid this, so that we can continue to define the remainder Hx energy as the right derivative of the functional at $\lambda = 0$, leading to Equation (17) directly.

4. Numerical Results

A practical interpretation of the results of Section 3 is that any density functional approximation (DFA) to the exact remainder Hx energy, $E_{R,Hx;\vec{\gamma}} \approx E_{R,Hx;\vec{\gamma}}^{\text{DFA}}$, will suffer from two sources of errors. First, it suffers from unavoidable and uncontrolled errors caused by the DFA, like almost all density functional calculations. Second, it suffers from controlled errors that are caused by differences between the KS and GKS wavefunctions. The second source of errors grows at second order with the effective amount [dictated by Equation (22)] of exact exchange, and is system dependent.

To illustrate the model and system dependence of the parameter, **Table 1** reports effective $\epsilon(\vec{\gamma})$ values for a series of small atoms and triatomic molecules from the W4-11 benchmark set.^[32] Results are shown for three error-function derived [cf., Equation (10)] range-separated hybrids: long-range corrected $\omega\text{B97x}^{[16]}$ with $W_{\vec{\gamma}} := \frac{0.1577+0.8423 \operatorname{erf}(0.30r_{ij})}{r_{ij}}$; CAM-B3LYP^[15] (CB) with $W_{\vec{\gamma}} := \frac{0.10+0.46 \operatorname{erf}(0.33r_{ij})}{r_{ij}}$; and short-range corrected HSE06^[14] with $W_{\vec{\gamma}} := \frac{0.25-0.25 \operatorname{erf}(0.11r_{ij})}{r_{ij}}$.

We see that the effective parameter is, unsurprisingly, very sensitive to the choice of range-separation parameters. It is also dominated by the long-range interaction, with short-range-only HSE06 having an order of magnitude smaller ϵ than the other two approaches. More surprisingly, it is also reasonably sensitive to the molecule itself. For example, O_3 has very different values to O across all three approaches, indicating a strong sensitivity to bonding.

Nevertheless, even in the worst case of Cl computed using ωB97x , we obtain $\epsilon^2 \leq \frac{2}{3}$, meaning the upper bound on KS/GKS orbital differences is fairly tight. We further note that, even with

Table 1. Effective $\epsilon(\bar{r})$ from Equation (22) for a series of atoms and triatomic molecules from W4-11,^[32] using ω B97x,^[16] which uses only long-range Fock exchange, HSE06, which uses only short-range Fock exchange,^[14] and CAM-B3LYP, which uses (different amounts of) both short- and long-range Fock exchange^[15] (CB). Results based on these popular approximate functionals are sorted in ascending order in the ω B97x parameter. Superscripts, where shown, indicate singlet or triplet.

Name	ω B97x	CB	HSE06	Name	ω B97x	CB	HSE06
H	0.604	0.417	0.049	O ₃	0.625	0.432	0.049
N ₂ O	0.625	0.432	0.049	NO ₂	0.626	0.433	0.049
FO ₂	0.629	0.435	0.049	CO ₂	0.629	0.435	0.049
F ₂ O	0.631	0.436	0.048	CF ₂	0.636	0.438	0.048
CCH	0.642	0.441	0.045	HCN	0.653	0.447	0.043
HNC	0.653	0.448	0.043	BeF ₂	0.655	0.450	0.047
N ₂ H	0.656	0.449	0.043	HCO	0.663	0.453	0.042
HNO	0.664	0.453	0.042	HOO	0.666	0.455	0.041
SO ₂	0.671	0.459	0.043	S ₃	0.671	0.461	0.047
HOF	0.673	0.459	0.041	S ₂ O	0.675	0.462	0.044
OCIO	0.676	0.462	0.042	CH ₂ ¹	0.680	0.463	0.040
CH ₂ ³	0.682	0.464	0.039	Cl ₂ O	0.682	0.467	0.044
OCS	0.684	0.467	0.043	CS ₂	0.692	0.472	0.044
CCl ₂	0.693	0.473	0.043	CICN	0.694	0.473	0.041
NH ₂	0.703	0.475	0.036	SSH	0.717	0.486	0.037
BeCl ₂	0.718	0.487	0.041	H ₂ O	0.725	0.488	0.033
HOCl	0.725	0.490	0.035	Be	0.735	0.495	0.033
B	0.735	0.495	0.033	C	0.744	0.499	0.031
N	0.756	0.506	0.029	O	0.769	0.513	0.027
F	0.782	0.521	0.025	H ₂ S	0.785	0.523	0.026
Al	0.808	0.537	0.023	Si	0.809	0.537	0.023
P	0.810	0.538	0.022	S	0.811	0.538	0.022
Cl	0.813	0.539	0.022				
Min	0.604	0.417	0.022	Max	0.813	0.539	0.049
Mean	0.697	0.473	0.039				

100% Fock exchange, both lithium and fluorine anions were found to have extremely similar KS and GKS orbitals.^[10] As these most likely represent extreme cases of orbital sensitivity, due to the weakly bound outermost electrons, we expect GKS and KS orbitals to be very similar in general; and the $O(\epsilon^2)$ term to be correspondingly small.

To further investigate the sensitivity of ϵ to bonding, **Figure 1** shows the energy and ϵ parameter for the stretched NF diatom (singlet state), using ω B97x. Interestingly, ϵ changes in a very similar fashion to the energy—it increases as the atoms are brought close together and as they are taken further apart. However, its minimum value occurs $\approx 30\%$ further out than the energy minima. The values are consistently lower than $\epsilon = 0.756$ for N, and $\epsilon = 0.782$ for F, which sit well outside the bounds on the figure. Note that $\epsilon^2 < \frac{1}{2}$ everywhere in the figure. Therefore, and given that even for pure HF calculations KS and GKS orbitals are similar,^[33,34] we do expect that in practice the remainder Hx term is only weakly affected by differences in KS and GKS orbitals, throughout the dissociation curve.

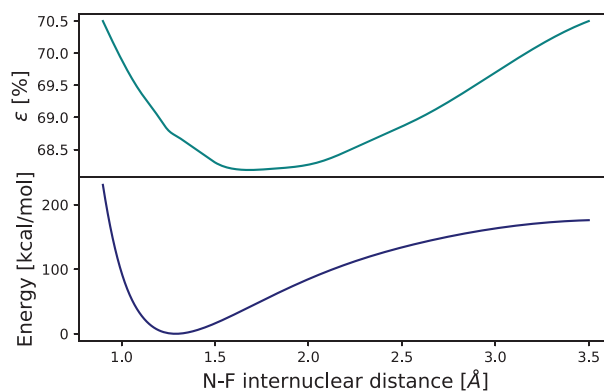


Figure 1. Energy (bottom) and $\epsilon(\bar{r})$ (top) expressed as a percent, for the stretched N-F dimer using ω B97x.

5. Alternative Adiabatic Connection

The linear adiabatic connection used to obtain the results of Section 3 is one way to connect between the fully interacting and KS systems, but it is not the only way. Other forms can also be chosen for an adiabatic connection formula. For example, an exponential (Yukawa-screened RSH) form^[21]

$$W_\lambda(r_{12}) = \frac{1 - e^{-\lambda \frac{r_{12}}{r_0}}}{r_{12}} \quad (29)$$

that explicitly depends on λ , can be specified, and has been found to be useful for proving various properties of RSH functionals.^[21] Here, r_0 is an arbitrary length parameter, while λ governs the interaction strength. The adiabatic connection then becomes

$$F_{\text{exp}}^\lambda[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W}_\lambda | \Psi \rangle := \langle \Psi_\lambda | \hat{T} + \hat{W}_\lambda | \Psi_\lambda \rangle \quad (30)$$

Then,

$$F_{\text{exp}}^0[n] = T_s[n], \quad F_{\text{exp}}^\infty[n] = F^{\text{HK}}[n] \quad (31)$$

follow from $W_0(r_{12}) = 0$, and $W_\infty(r_{12}) = \frac{1}{r_{12}}$, respectively. The upper bound is ∞ because the exponential form of the λ -dependence means we retrieve the fully interacting system at $\lambda = \infty$ rather than at $\lambda = 1$.

With some minor tweaks to account for $\lambda \in [0, \infty)$ instead of $[0, 1]$, we see that the first three criteria used to define Equations (6) and (16) are also satisfied by Equation (30). When we then take the right-derivative at $\lambda = 0$ to find the remainder Hx energy, we get

$$E_{\text{R,Hx;exp}} = \lim_{\lambda \rightarrow 0} \frac{F^\lambda - F^0}{\lambda} = \lim_{\lambda \rightarrow 0^+} \langle \Phi_s | \frac{\hat{W}_\lambda}{\lambda} | \Phi_s \rangle \quad (32)$$

Here we used a Hellmann–Feynman-like theorem, and $\hat{W}_0 = 0$, to obtain the second identity.

Equation (32) is, prima facie, compatible with criterion (iv) as it is expressed solely in terms of the KS Slater determinant. However, we shall proceed to show that it yields an unphysical defini-

tion of Hx so is incompatible in a practical sense. We first use Equations (13) and (29) to show

$$\begin{aligned} \lim_{\lambda \rightarrow 0^+} \frac{\widehat{W}_\lambda}{\lambda} &= \lim_{\lambda \rightarrow 0^+} \frac{1}{2} \int \widehat{n}_2(\vec{r}, \vec{r}') \frac{1 - e^{-\lambda|\vec{r}-\vec{r}'|/r_0}}{\lambda|\vec{r}-\vec{r}'|} d\vec{r}d\vec{r}' \\ &= \lim_{\lambda \rightarrow 0^+} \frac{1}{2} \int \widehat{n}_2(\vec{r}, \vec{r}') \frac{\lambda^{|\vec{r}-\vec{r}'|} r_0}{\lambda|\vec{r}-\vec{r}'|} d\vec{r}d\vec{r}' \\ &= \frac{1}{2r_0} \int \widehat{n}_2(\vec{r}, \vec{r}') d\vec{r}d\vec{r}' \end{aligned} \quad (33)$$

In the second step we have implicitly assumed that the operator will only ever act on wavefunctions that decay exponentially for $\vec{r} \rightarrow \infty$, and we therefore do not have to worry about orders of limits—additional care may need to be taken to deal with periodic systems. We then use Equation (33) in (32) to obtain

$$\begin{aligned} E_{R,Hx;exp} &= \langle \Phi_s | \frac{1}{2r_0} \int \widehat{n}_2(\vec{r}, \vec{r}') d\vec{r}d\vec{r}' | \Phi_s \rangle \\ &= \frac{1}{2r_0} \int n_{2,s}(\vec{r}, \vec{r}') d\vec{r}d\vec{r}' = \frac{N(N-1)}{2r_0} \end{aligned} \quad (34)$$

Here, $n_{2,s}(\vec{r}, \vec{r}') = \langle \Phi_s | \widehat{n}_2(\vec{r}, \vec{r}') | \Phi_s \rangle$ is the pair density of the KS system and $N = \int n(\vec{r}) d\vec{r}$ is the electron number.

Clearly, Equation (32) does not define a physical remainder Hx energy. It depends only on the number of electrons, N , and the length parameter, r_0 , rather than the form of the interaction, which follows from the fact that Equation (33) is equivalent to a spatially independent potential. However, we have already shown that Yukawa potentials can be dealt with in GKS theory, by using Equation (25), and that the adiabatic connection defined therein covers an enormous variety of RSH. The unphysicality therefore reflects the fact that the λ -gradient definition of $E_{R,Hx}$ is incompatible with the specific, exponential adiabatic connection of Equation (30), which fails criterion (iv) in practical terms of producing a useful remainder Hx.

This incompatibility, occurring for an otherwise useful and successful adiabatic connection, opens an interesting question about definitions in generalized adiabatic connections. The original purpose of using λ -gradients to define Hx energies was to resolve definitional issues in ensemble density functional theory^[35] that are inherited by GKS theory.^[36] These issues can certainly also appear in analyses based on Equation (30), or similar formulae. An interesting question for future research, then, is how the (remainder) Hx energy should be defined in such cases.

6. Conclusions

In Conclusion, we presented a generalized adiabatic connection that applies to any type of RSH functional, employed within GKS theory. We then used this generalized relation to derive a rigorous definition [Equation (17)] for the remainder Hx energy and thereby obtained a rigorous distinction between multiplicative exchange and correlation components.

The developed adiabatic connection was defined in terms of both GKS and KS orbitals. We showed, however, that using only the KS orbitals produces an error that is $O(\epsilon^2)$, where ϵ [given

in Equation (22)] is fully defined in terms of parameters in the RSH functional. Through numerical solutions of selected small systems using popular practical RSH functionals, we found ϵ to be small in practice.

We also considered whether we could identify a useful alternative definition of $E_{R,Hx}$ that is practically compatible with the exponential adiabatic connection, but showed that the above approach is incompatible with this case.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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