Exchange-only virial relation from the adiabatic connection ⊘

Andre Laestadius ✉ iD ; Mihály A. Csirik iD ; Markus Penz iD ; Nicolas Tancogne-Dejean iD ;
Michael Ruggenthaler iD ; Angel Rubio iD ; Trygve Helgaker iD

Check for updates

CrossMark

View
Online

Export
Citation

Exchange-only virial relation from the adiabatic connection

Andre Laestadius,[1,2,a]   Mihály A. Csirik,[1,2]   Markus Penz,[1,3]   Nicolas Tancogne-Dejean,[3]
Michael Ruggenthaler,[3,4]   Angel Rubio,[3,4,5]   and Trygve Helgaker[2]

AFFILIATIONS

[1] Department of Computer Science, Oslo Metropolitan University, 0130 Oslo, Norway
[2] Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, 0315 Oslo, Norway
[3] Max Planck Institute for the Structure and Dynamics of Matter and Center for Free-Electron Laser Science
  and Department of Physics, Luruper Chaussee 149, 22761 Hamburg, Germany
[4] The Hamburg Center for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany
[5] Center for Computational Quantum Physics, Flatiron Institute, 162 5th Avenue, New York, New York 10010, USA

Note: This paper is part of the JCP Festschrift for John Perdew.
[a] Author to whom correspondence should be addressed: andre.laestadius@oslomet.no

ABSTRACT

The exchange-only virial relation due to Levy and Perdew is revisited. Invoking the adiabatic connection, we introduce the exchange energy in terms of the right-derivative of the universal density functional w.r.t. the coupling strength λ at $\lambda = 0$. This agrees with the Levy–Perdew definition of the exchange energy as a high-density limit of the full exchange–correlation energy. By relying on v-representability for a fixed density at varying coupling strength, we prove an exchange-only virial relation without an explicit local-exchange potential. Instead, the relation is in terms of a limit ($\lambda \searrow 0$) involving the exchange–correlation potential v_{xc}^{λ}, which exists by assumption of v-representability. On the other hand, a local-exchange potential v_x is not warranted to exist as such a limit.

I. INTRODUCTION

Despite the long history of density functional theory (DFT) and research concerning its foundation, DFT still has many mathematical challenges remaining.[1–4] Addressing these contributes to the development of improved approximate functionals and enhances the overall understanding of DFT. The aim of this work is to investigate the exchange-only virial relation of Perdew and Levy from a mathematical standpoint, motivated by some recent developments in mathematical DFT.[5–9] It is with great enthusiasm we submit this contribution to the special issue honoring the great achievements of John Perdew in the field of quantum chemistry in general and DFT in particular.

Exact constraints play an important role in the development and testing of density functional approximations,[10–14] bearing in mind that semiempirical functionals can fail outside their training set.[15] These constraints are based on conditions that the exact exchange–correlation functional $E_{xc}[\rho]$ or its constituent exchange $E_x[\rho]$ and correlation $E_c[\rho]$ parts satisfy. For example, the second-order gradient expansion, aimed at improving on the local density approximation (LDA), can perform worse than LDA for real systems because LDA satisfies certain exact constraints that finite-order gradient expansions break.[16–18] In the generalized gradient approximation (GGA), these constraints are restored, leading to an overall better performance of the functionals.

One such constraint for GGA[19,20] follows from a physically appealing formula that arises as a consequence of the general virial theorem of quantum mechanics. In particular, Levy and Perdew[10] have proposed the exchange-only virial relation

$$E_x[\rho] = -\int \rho(\mathbf{r}) \, \mathbf{r} \cdot \nabla v_x(\mathbf{r}) \, d\mathbf{r}. \tag{1}$$

Relying on a different work of Levy and Perdew,[14] we define the exchange energy as the high-density limit of the exchange–correlation energy in the manner

$$E_x[\rho] = \lim_{\gamma \to \infty} \frac{1}{\gamma} E_{xc}[\rho_\gamma], \tag{2}$$

where the scaled density is given by $\rho_\gamma(\mathbf{r}) = \gamma^3 \rho(\gamma \mathbf{r})$. The exchange–correlation energy $E_{xc}[\rho]$ is defined in terms of the universal density functional $F[\rho]$ in the usual manner; see Eq. (33). Noting that $(\rho_\gamma)_\mu = \rho_{\gamma\mu}$, it follows directly from Eq. (2) that the exchange energy obeys the well-known[10,21] exact constraint $E_x[\rho_\gamma] = \gamma E_x[\rho]$.

There exists an alternative, equivalent definition for $E_x[\rho]$ that employs the adiabatic connection in DFT. This extremely useful concept not only relates the noninteracting system (with interaction strength $\lambda = 0$) with the fully interacting one ($\lambda = 1$) for a fixed, given density ρ, as it is customary in Kohn–Sham DFT, but also reveals the properties of the functionals for all intermediate values of the coupling strength λ. In the following, we study $F[\rho]$ as a function the interaction strength for a fixed, given density ρ, using the notation $\lambda \mapsto F(\lambda)$; see Eq. (8). The theory of convex analysis then provides multiple tools to study the adiabatic connection. Already from the definition of the universal density functional, many practical properties can be derived when considering it as a function of λ. The intuitive understanding of the exchange energy in this setting is then as the linear component of $\lambda E_{xc}(\lambda) = F(\lambda) - F(0) - \lambda E_H$, where E_H is the Hartree energy [see Eq. (32)].

Here, all derivations will be performed for general, mixed N-electron states, thus allowing for degeneracy at all coupling strengths, with the overall assumption of a v-representable density ρ at all coupling strengths $\lambda \in \mathbb{R}$ (a property henceforth called v^λ-representability). This comes as a form of minimal assumption, since, without v^λ-representability, the selected density cannot be assigned to a valid ground state of the system under consideration. On the other hand, it cannot be assumed that the universal density functional is functionally differentiable with respect to the density, nor does this need to hold for its individual parts such as the exchange functional. Equation (1) would then be the direct consequence of a functionally differentiable $E_x[\rho]$ (see Appendix B in the work of Tancogne-Dejean *et al.*[9] in the same special issue of this journal), but, unfortunately, the universal density functional is everywhere discontinuous.[5]

The principal aim of this paper to find a version of the exchange virial relation that holds without assuming functional differentiability. We shall find that this is indeed possible using a limit procedure and the main result, derived in Sec VII, is

$$E_x = -\lim_{\lambda \searrow 0} \int \rho(\mathbf{r}) \, \mathbf{r} \cdot \nabla v_{xc}^\lambda(\mathbf{r}) \, d\mathbf{r}, \tag{3}$$

as opposed to Eq. (1). Here, $v_{xc}^\lambda(\mathbf{r})$ is the corresponding exchange–correlation potential for interaction strength λ. However, this procedure does not provide us with a well-defined local-exchange potential $v_x(\mathbf{r}) = \lim_{\lambda \searrow 0} v_x^\lambda(\mathbf{r})$, as one would perhaps expect. Indeed, a general local-exchange potential need not exist, a finding that agrees with the force-based approach to DFT, where an additional vector potential is introduced to fulfill the exchange-only virial relation.[9] This also opens the possibility to a *nonlocal* limit potential.

We begin by giving the basic setting and some useful relations for the expectation values of the main components of the Hamiltonian. In atomic units, we consider a nonrelativistic system of N spinless particles in $\mathbb{R}^3$, for which the Hamiltonian at coupling strength $\lambda \in \mathbb{R}$ is given by

$$\hat{H}^\lambda[v] = \hat{T} + \lambda \hat{W} + \sum_{j=1}^{N} v(\mathbf{r}_j), \tag{4}$$

where $\hat{T}$ and $\hat{W}$ denote the kinetic and two-particle interaction operators, respectively:

$$\hat{T} = -\frac{1}{2} \sum_{j=1}^{N} \nabla_{\mathbf{r}_j}^2, \quad \hat{W} = \sum_{1 \le j < k \le N} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}. \tag{5}$$

Both operators are positive definite. We can bound the expectation value of $\hat{W}$ in terms of $\hat{T}$, for instance, by using the Hardy and the Cauchy–Schwarz inequalities, we have

$$\text{Tr } \hat{W}\Gamma \le C_N \sqrt{\text{Tr } \hat{T}\Gamma} \le \frac{C_N}{2} (1 + \text{Tr } \hat{T}\Gamma) \tag{6}$$

for some N-dependent constant $C_N > 0$.

If $v(\mathbf{r})$ is such that it admits a ground state with density $\rho(\mathbf{r})$, then the full virial relation for such a system can be derived from an application of the Ehrenfest theorem for mixed states. For a ground state Γ, it states that $i \text{Tr} [\hat{H}, \hat{A}] \Gamma = \partial_t \text{Tr } \hat{A}\Gamma = 0$ and we can apply this to the operator $\hat{A} = \sum_{j=1}^{N} \mathbf{r}_j \cdot \nabla_j$. This gives[22,23]

$$2 \text{Tr } \hat{T}\Gamma + \lambda \text{Tr } \hat{W}\Gamma = \int \rho(\mathbf{r}) \, \mathbf{r} \cdot \nabla v(\mathbf{r}) \, d\mathbf{r}, \tag{7}$$

where $\rho \hookleftarrow \Gamma$ is the ground-state density associated with the mixed state Γ. This expression forms the basis for our discussion of the virial relation in DFT.

II. COUPLING-STRENGTH DENSITY FUNCTIONALS

Central to DFT is the universal density functional, which, for a given coupling strength $\lambda \in \mathbb{R}$ and density ρ is defined as the constrained search over all density matrices that yield a given one-particle density ρ,

$$F(\lambda) = \inf_{\Gamma \mapsto \rho} \text{Tr} (\hat{T} + \lambda \hat{W}) \Gamma. \tag{8}$$

Since the density ρ is kept fixed in our discussion, we omit it as an argument to the functional. The only exception is when the scaled density ρ_γ rather than ρ is considered, always at $\lambda = 1$, in which case we write $F[\rho_\gamma]$. By Corollary 4.5 in Lieb,[24] for all "physical," N-representable densities ρ (non-negative, normalized, and of finite kinetic energy), there exists a minimizing (possibly nonunique) density matrix $\Gamma(\lambda)$ in Eq. (8) such that $\Gamma(\lambda) \mapsto \rho$ and

$$F(\lambda) = \text{Tr} (\hat{T} + \lambda \hat{W}) \Gamma(\lambda). \tag{9}$$

Although this corollary is formulated with $\lambda \ge 0$, it can easily be extended to all $\lambda \in \mathbb{R}$.[25] Existence of a minimizer in Eq. (8) ensures that $F(\lambda)$ is finite for all $\lambda \in \mathbb{R}$.

Since the minimizing density matrix $\Gamma(\lambda) \mapsto \rho$ in Eq. (9) is in general not unique, it is *a priori* unclear how to decompose the

function $\lambda \mapsto F(\lambda)$ uniquely into a kinetic and an interaction contribution. For every choice of minimizing $\Gamma(\lambda) \mapsto \rho$, however, we *do* have the decomposition

$$F(\lambda) = T(\Gamma(\lambda)) + \lambda W(\Gamma(\lambda)) \qquad (10)$$

with

$$T(\Gamma(\lambda)) = \text{Tr}\,\hat{T}\Gamma(\lambda), \qquad (11)$$

$$W(\Gamma(\lambda)) = \text{Tr}\,\hat{W}\Gamma(\lambda). \qquad (12)$$

As we shall now show, this decomposition becomes unique under the assumption of v-representability of the density ρ at interaction strength λ. Hence, instead of $T(\Gamma(\lambda))$ and $W(\Gamma(\lambda))$, we may write $T(\lambda)$ and $W(\lambda)$ and so

$$F(\lambda) = T(\lambda) + \lambda W(\lambda) \qquad (13)$$

holds.

To demonstrate uniqueness, we first note that v-representability for ρ means that we can find a potential $v^\lambda(\mathbf{r})$ such that there is a ground state $\Gamma(\lambda) \mapsto \rho$ for the Hamiltonian $H^\lambda[v^\lambda]$. By the virial theorem, Eq. (7), we then have

$$2T(\Gamma(\lambda)) + \lambda W(\Gamma(\lambda)) = \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v^\lambda(\mathbf{r})\,d\mathbf{r}. \qquad (14)$$

Subtracting $F(\rho)$ as given in Eq. (9) from both sides of this equation and using Eq. (13), we obtain

$$T(\Gamma(\lambda)) = \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v^\lambda(\mathbf{r})\,d\mathbf{r} - F(\lambda), \qquad (15)$$

whose right-hand side is uniquely determined by the density, i.e., it is independent of the choice of $\Gamma(\lambda)$. For $F(\lambda)$, this is clear while for $\nabla v^\lambda(\mathbf{r})$ it follows from the Hohenberg–Kohn Theorem,[26] which states that $v^\lambda(\mathbf{r})$ is determined uniquely up to a scalar by the ground-state density. Hence, $T(\lambda) := T(\Gamma(\lambda))$ is well defined (for all λ) and $W(\lambda) := W(\Gamma(\lambda))$ is also well defined (for $\lambda \neq 0$) via $\lambda W(\lambda) = F(\lambda) - T(\lambda)$, implying that *the universal density functional has a unique decomposition into kinetic and interaction contributions at each interaction strength where the density is v-representable.* Another possibility to achieve well-defined functions $T(\lambda)$ and $W(\lambda)$ is discussed in Sec. V. We will consider the case $W(0)$ later.

In the pure-state formulation, the functionals are defined as expectation values with $\Psi(\lambda) \mapsto \rho$ as the minimizer in the constrained-search functional. It is possible that this minimizing state is then uniquely given, and so the functionals are already defined unambiguously, but this does not seem to be guaranteed. Consequently, by the same argument as above, we rely on *pure-state v^λ-representability* to make sure that $\langle\Psi(\lambda)|\hat{T}|\Psi(\lambda)\rangle$ and $\langle\Psi(\lambda)|\hat{W}|\Psi(\lambda)\rangle$ have values that only depend on ρ for $\lambda > 0$. Only if $\Psi(0)$ is determined uniquely—for example, if ρ is noninteracting pure-state v-representable by a nondegenerate ground state—can also $W(0) = \langle\Psi(0)|\hat{W}|\Psi(0)\rangle$ be given, as it is the case in most presentations on the subject. Here, we aim to avoid such restrictions,

only demanding *ensemble v-representability* of ρ, defining $W(0)$ by a limit procedure that is laid out in Sec. IV.

III. BASIC PROPERTIES OF THE ADIABATIC CONNECTION

Recall that by our assumption of v^λ-representability of the considered density ρ and following the discussion in Sec. II, the individual parts $T(\lambda)$ and $W(\lambda)$ of the universal density functional $F(\lambda)$ are uniquely defined. We proceed by collecting important properties of the function $F(\lambda)$ that stem directly from its definition by Eq. (8). First, we relate $F(\lambda)$ with $\lambda = 1/\gamma > 0$ to the scaled density as[14]

$$\gamma^2 F(1/\gamma) = \inf_{\Gamma \mapsto \rho} \text{Tr}\,(\gamma^2 \hat{T} + \gamma \hat{W})\Gamma$$
$$= \inf_{\Gamma \mapsto \rho} \text{Tr}\,(\hat{T} + \hat{W})\Gamma_\gamma$$
$$= \inf_{\Gamma_\gamma \mapsto \rho_\gamma} \text{Tr}\,(\hat{T} + \hat{W})\Gamma_\gamma = F[\rho_\gamma], \qquad (16)$$

where $\Gamma_\gamma = \gamma^{3N}\Gamma(\gamma\cdot)$ is the coordinate-scaled density matrix that yields precisely ρ_γ.

Importantly, $F(\lambda)$ is concave, as follows easily from the super-additivity of the infimum—namely, for each $\lambda, \lambda' \in \mathbb{R}$ and $s \in [0, 1]$, we have

$$F(s\lambda + (1-s)\lambda') = \inf_{\Gamma \mapsto \rho} \text{Tr}\,(\hat{T} + (s\lambda + (1-s)\lambda')\hat{W})\Gamma$$
$$\geq s \inf_{\Gamma \mapsto \rho} \text{Tr}\,(\hat{T} + \lambda\hat{W})\Gamma$$
$$+ (1-s) \inf_{\Gamma \mapsto \rho} \text{Tr}\,(\hat{T} + \lambda'\hat{W})\Gamma$$
$$= sF(\lambda) + (1-s)F(\lambda'). \qquad (17)$$

Moreover, since the operator $\hat{W}$ is positive definite, we have that $W(\lambda)$ is strictly positive and thus $F(\lambda)$ is strictly monotonically increasing. Furthermore, it holds that

$$F(\lambda') = T(\lambda') + \lambda' W(\lambda')$$
$$\leq T(\lambda) + \lambda' W(\lambda) = F(\lambda) + (\lambda' - \lambda)W(\lambda), \qquad (18)$$

where the inequality stems from the fact that on the right-hand side, $T(\lambda)$ and $W(\lambda)$ are constructed from $\Gamma(\lambda)$, which in general is not a minimizer for $F(\lambda')$. From

$$F(\lambda') \leq F(\lambda) + (\lambda' - \lambda)W(\lambda), \qquad (19)$$

we see that $W(\lambda)$, $\lambda \neq 0$, is an element of the superdifferential of $F(\lambda)$. The individual elements of the set-valued superdifferential are called supergradients and they form tangents lying entirely on or above the respective concave function. Any choice of supergradients for different λ must be monotonically decreasing since $F(\lambda)$ is concave,[27] so this also holds for $W(\lambda)$. Then, by a generalization of the fundamental theorem of integral calculus,[27] we can write $F(\lambda) = F(0) + \int_0^\lambda f(\mu)\,d\mu$ for any choice of supergradient $f(\mu)$ of $F(\mu)$. By choosing $f(\mu) = W(\mu)$, we get, in particular,

$$F(\lambda) = F(0) + \int_0^\lambda W(\mu)\,d\mu. \qquad (20)$$

This result also follows as a direct consequence of the Hellmann–Feynman theorem[28] if one considers pure-state v^λ-representable densities. However, the Hellmann–Feynman theorem has to be at least handled with care in the case of degeneracies.[29–31]

IV. DIFFERENTIAL PROPERTIES OF THE ADIABATIC CONNECTION

Note that in Eq. (20) the choice of the integrand is not limited to $W(\lambda)$, but it can be any supergradient of $F(\lambda)$. A different choice would be the right-derivative

$$\partial^+ F(\lambda) = \lim_{\mu \searrow 0} \frac{F(\lambda + \mu) - F(\lambda)}{\mu}, \qquad (21)$$

where the limit always exists as $F(\lambda)$ is concave. The superdifferential of a concave function is always given as the closed interval from the right-derivative to the left-derivative, so we have for $\lambda \neq 0$

$$W(\lambda) \in [\partial^+ F(\lambda), \partial^- F(\lambda)]. \qquad (22)$$

Next, we will show how the right-derivative, that will be substantial for our later definition of the exchange energy, relates to the interaction energy $W(\lambda)$. From $F(\lambda) = T(\lambda) + \lambda W(\lambda)$ and $F(0) = T(0)$, we also have that

$$\frac{F(\lambda) - F(0)}{\lambda} - \frac{T(\lambda) - T(0)}{\lambda} = W(\lambda). \qquad (23)$$

The limit $\lambda \searrow 0$ is well defined for the first term in Eq. (23) since it equals the right-derivative of $F(\lambda)$. Since $W(\lambda)$ is monotone decreasing and finite as the subgradient of the concave and finite $F(\lambda)$, also here the limit exists and we *define* $W(0) = \lim_{\lambda \searrow 0} W(\lambda)$. An alternative way to see that $W(\lambda)$ is finite is through the bound of Eq. (6) that can be easily made into an estimate in terms of $F(\lambda)$. So far, we have defined $W(\lambda)$ only for $\lambda \neq 0$, see Eq. (12) and the discussion related to it. The limit $\lambda \searrow 0$ of Eq. (23) thus gives

$$\partial^+ F(0) - \partial^+ T(0) = W(0). \qquad (24)$$

The relations between the different functionals are illustrated in Fig. 1.

It is worth noting that for a ρ that is v-representable and has a certain regularity, the treatment in Sec. 4 of Lammert[5] shows that
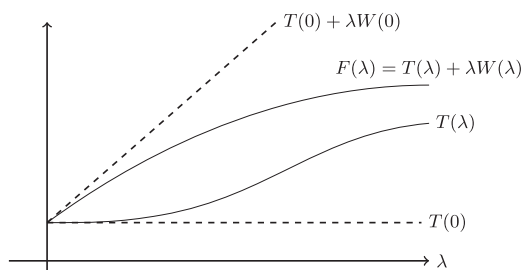

FIG. 1. Illustration of the different functionals with $F(\lambda) = T(\lambda) + \lambda W(\lambda)$ concave and strictly increasing.

$F[\rho_\gamma]$ is differentiable with respect to γ and thus also $F(\lambda)$ for that ρ is differentiable with respect to λ for $\lambda > 0$. This would be beneficial, since then the supergradient would always be unique for $\lambda > 0$, but we will continue here without any such assumption.

In the case when $F(\lambda)$ is differentiable on at least a small interval $(0, \lambda_0)$, the supergradient is unique and it thus holds that $\partial^+ F(\lambda) = W(\lambda)$ for all $\lambda \in (0, \lambda_0)$ since $W(\lambda)$ was found to be a supergradient. Consequently, in this case it holds that $\lim_{\lambda \searrow 0} \partial^+ F(\lambda) = \partial^+ F(0) = W(0)$ since the right-derivative is right-continuous (Sec. 1.8 in van Tiel[32]). If $F(\lambda)$ is not differentiable, then as a concave function it only has a countable number of points $\{\lambda_i\}_i$, $0 < \lambda_{i+1} < \lambda_i < \varepsilon$, where it is non-differentiable (again Sec. 1.8 in van Tiel[32]). If this is a finite number of points, then we will just be back to the previous case, since the smallest λ_i will then fill in the role for λ_0 from before. So, we are left with an infinite sequence of points $\{\lambda_i\}_i$ that has $\lim_{i \to \infty} \lambda_i = 0$ and where the following holds [Sec. 1.6–7 in van Tiel[32] but for a concave function, and using that $F(\lambda)$ is non-differentiable at λ_i and λ_{i+1} and thus right-derivative and left-derivative cannot agree]:

$$\partial^+ F(\lambda_i) < \partial^- F(\lambda_i) \leq \partial^+ F(\lambda_{i+1}) < \partial^- F(\lambda_{i+1}). \qquad (25)$$

$\partial^+ F(\lambda_i)$, as a convergent sequence with $\partial^+ F(\lambda_i) \to \partial^+ F(0) < \infty$, must have $\partial^+ F(\lambda_{i+1}) - \partial^+ F(\lambda_i) \to 0$. However, from Eq. (25) it then follows that also $\partial^- F(\lambda_i) - \partial^+ F(\lambda_i) \to 0$, and so no matter how $W(\lambda_i)$ is chosen from the superdifferential of $F(\lambda)$ at $\lambda = \lambda_i$ [cf. Eq. (22)], in the limit only the possibility $W(0) = \lim_{i \to \infty} W(\lambda_i) = \lim_{i \to \infty} \partial^+ F(\lambda_i) = \partial^+ F(0)$ remains. This is the main result in this section and helps to unambiguously define $W(0)$ in the given setting. From Eq. (24), it then follows that

$$\partial^+ T(0) = 0 \qquad (26)$$

and the above derived expression

$$W(0) = \lim_{\lambda \searrow 0} W(\lambda) = \partial^+ F(0) \qquad (27)$$

will yield the exchange energy, as demonstrated in the next section.

V. ADDITIONAL REMARKS ON $T(\lambda)$ AND $W(\lambda)$

In this section—which can be safely skipped at first reading as the rest of the paper is independent from it—we first want to mention an alternative route for the definition of the functions $T(\lambda)$ and $W(\lambda)$ that was suggested by the Anonymous Referee that avoids any assumption of v-representability. Let $\mathfrak{G}(\lambda)$ be the set of all minimizers $\Gamma(\lambda) \mapsto \rho$ for a fixed ρ in Eq. (8). This set is non-empty by the result quoted before Eq. (9). Then, for example, we can make the following choice in order to define $W(\lambda)$:

$$W(\lambda) = \inf_{\Gamma \in \mathfrak{G}(\lambda)} \mathrm{Tr}\, \hat{W} \Gamma. \qquad (28)$$

This then fixes $T(\lambda)$ for all $\lambda \neq 0$ by the relation of Eq. (13) as

$$T(\lambda) = \sup_{\Gamma \in \mathfrak{G}(\lambda)} \mathrm{Tr}\, \hat{T} \Gamma. \qquad (29)$$

If $\lambda = 0$, then $T(0) = F(0)$ anyway. Note that any other choice of the form

$$W(\lambda) \in \left[\inf_{\Gamma \in \mathfrak{G}(\lambda)} \operatorname{Tr} \hat{W}\Gamma, \sup_{\Gamma \in \mathfrak{G}(\lambda)} \operatorname{Tr} \hat{W}\Gamma \right] \tag{30}$$

in the interval between minimum and maximum is possible and would again fix $T(\lambda)$.

A second remark concerns Remark 3.1 in the work of Lewin *et al.*,[33] which states that not only $W(\lambda)$, but also the right-derivative and the left-derivative of $F(\lambda)$, and thus by convex combination all values in-between, come from $\operatorname{Tr} \hat{W}\Gamma(\lambda)$ with different minimizers $\Gamma(\lambda)$ from Eq. (8). This is equivalent to saying that the interval in Eq. (22) agrees with the one from Eq. (30). Since for v^λ-representable densities $\operatorname{Tr} \hat{W}\Gamma(\lambda)$ has a fixed value for all minimizers, as was noted in Sec. II, this would imply that the right-derivative and left-derivative agree and thus $F(\lambda)$ would be differentiable at λ. Nevertheless, we have note been able to provide a proof for this statement at this point, so we do not treat $F(\lambda)$ as differentiable here.

VI. ZERO-COUPLING LIMIT AND EXCHANGE ENERGY

We now continue with our main discussion and first establish a relation between the interaction term and the exchange energy. In the Kohn–Sham (KS) scheme, an interacting system ($\lambda > 0$) and a noninteracting system ($\lambda = 0$) are related by demanding that their ground-state densities are equal. This defines the Hartree-exchange–correlation energy,

$$\lambda E_{\mathrm{Hxc}}(\lambda) = F(\lambda) - F(0). \tag{31}$$

It is customary to separate out the Hartree mean-field term, defined as

$$E_{\mathrm{H}} = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}', \tag{32}$$

so that one remains with just the exchange–correlation energy

$$\lambda E_{\mathrm{xc}}(\lambda) = F(\lambda) - F(0) - \lambda E_{\mathrm{H}}. \tag{33}$$

Using the integral formula from Eq. (20), we readily obtain

$$\lambda E_{\mathrm{xc}}(\lambda) = \int_0^\lambda W(\mu) \, \mathrm{d}\mu - \lambda E_{\mathrm{H}}. \tag{34}$$

By substituting $\lambda = 1/\gamma > 0$ and by using the scaling relation of Eq. (16), we have

$$\begin{aligned}
E_{\mathrm{xc}}(1/\gamma) &= \frac{F(1/\gamma) - F(0)}{1/\gamma} - E_{\mathrm{H}} \\
&= \frac{1}{\gamma}\left(\gamma^2 (F(1/\gamma) - F(0)) - \gamma E_{\mathrm{H}} \right) \\
&= \frac{1}{\gamma}\left(F^{\lambda=1}[\rho_\gamma] - T^{\lambda=0}[\rho_\gamma] - E_{\mathrm{H}}[\rho_\gamma] \right) \\
&= \frac{1}{\gamma} E_{\mathrm{xc}}[\rho_\gamma]
\end{aligned} \tag{35}$$

and thus in the limit using Eq. (27),

$$\begin{aligned}
E_{\mathrm{x}} &= \lim_{\gamma \to \infty} \frac{1}{\gamma} E_{\mathrm{xc}}[\rho_\gamma] = \lim_{\lambda \searrow 0} E_{\mathrm{xc}}(\lambda) \\
&= \lim_{\lambda \searrow 0} \frac{F(\lambda) - F(0)}{\lambda} - E_{\mathrm{H}} \\
&= \partial^+ F(0) - E_{\mathrm{H}} = W(0) - E_{\mathrm{H}}. \tag{36}
\end{aligned}$$

This coincides exactly with the definition provided by Levy and Perdew[10] and beautifully relates the definition of the exchange energy as the high-density limit through coordinate scaling with its alternative definition as a zero-coupling limit. It further yields a third definition of the exchange energy as the right-derivative of the Lieb functional at zero coupling strength minus the Hartree energy. This also shows that if we split the exchange–correlation energy in the usual way,

$$E_{\mathrm{xc}}(\lambda) = E_{\mathrm{x}} + E_{\mathrm{c}}(\lambda), \tag{37}$$

then $E_{\mathrm{c}}(\lambda)$ carries all λ dependence of $E_{\mathrm{xc}}(\lambda)$, or, said differently, the linear (in λ) contribution to $\lambda E_{\mathrm{xc}}(\lambda)$ is exactly equal to E_{x} and at zero coupling it holds $E_{\mathrm{c}}(0) = 0$. This fact can be taken as a motivation to define E_{x} by Eq. (36) instead.

Note that in the presented setting, the exchange–correlation potential for different coupling strengths λ can be defined through (by assumption of v^λ-representability)

$$v^0(\mathbf{r}) = v^\lambda(\mathbf{r}) + \lambda v_{\mathrm{Hxc}}^\lambda(\mathbf{r}) = v^\lambda(\mathbf{r}) + \lambda v_{\mathrm{H}}(\mathbf{r}) + \lambda v_{\mathrm{xc}}^\lambda(\mathbf{r}), \tag{38}$$

where

$$v_{\mathrm{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}' \tag{39}$$

is the usual Hartree potential. In analogy to Eq. (36), it is then tempting to define the local-exchange potential as the zero-coupling limit $v_{\mathrm{x}}(\mathbf{r}) = \lim_{\lambda \searrow 0} v_{\mathrm{xc}}^\lambda(\mathbf{r})$ (since the usual definition as the functional derivative of E_{x} needs to be avoided) and introduce the split of the exchange–correlation potential $v_{\mathrm{xc}}^\lambda(\mathbf{r}) = v_{\mathrm{x}}(\mathbf{r}) + v_{\mathrm{c}}^\lambda(\mathbf{r})$. However, we cannot be sure about the existence of the zero-coupling limit for the xc potential. In the next section, we are only able to establish the limits for the energy expressions in the context of the virial relation.

VII. EXCHANGE-ONLY VIRIAL RELATION

In this section, we present our main result about the exchange-only virial relation [Eq. (3) from Sec. I, or Eq. (45) below]. By using the usual virial relation from Eq. (7), we arrive easily at the form given by Levy and Perdew[10] for $\lambda > 0$ and $\lambda = 0$,

$$F(\lambda) + T(\lambda) = \int \rho(\mathbf{r}) \, \mathbf{r} \cdot \nabla v^\lambda(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \tag{40}$$

$$F(0) + T(0) = \int \rho(\mathbf{r}) \, \mathbf{r} \cdot \nabla v^0(\mathbf{r}) \, \mathrm{d}\mathbf{r}. \tag{41}$$

We subtract those and divide by $\lambda \neq 0$ to get

$$\frac{1}{\lambda}(F(\lambda) - F(0)) + \frac{1}{\lambda}(T(\lambda) - T(0)) = -\int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v_{\mathrm{Hxc}}^{\lambda}(\mathbf{r})\,\mathrm{d}\mathbf{r}. \tag{42}$$

Here, we introduced the (λ- and ρ-dependent) Hartree-exchange–correlation potential $\lambda v_{\mathrm{Hxc}}^{\lambda}(\mathbf{r}) = v^0(\mathbf{r}) - v^{\lambda}(\mathbf{r})$, which of course relies on v^{λ}-representability again. In the limit $\lambda \searrow 0$, we then obtain that

$$\partial^+ F(0) + \partial^+ T(0) = -\lim_{\lambda \searrow 0} \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v_{\mathrm{Hxc}}^{\lambda}(\mathbf{r})\,\mathrm{d}\mathbf{r}. \tag{43}$$

Using Eqs. (26) and (36), and additionally the virial relation for the Hartree term that follows from direct computation,

$$E_{\mathrm{H}} = -\int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v_{\mathrm{H}}(\mathbf{r})\,\mathrm{d}\mathbf{r}, \tag{44}$$

that we have with $v_{\mathrm{Hxc}}^{\lambda}(\mathbf{r}) = v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{xc}}^{\lambda}(\mathbf{r})$ the exchange-only virial relation

$$E_{\mathrm{x}} = -\lim_{\lambda \searrow 0} \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v_{\mathrm{xc}}^{\lambda}(\mathbf{r})\,\mathrm{d}\mathbf{r}. \tag{45}$$

It is interesting to contrast this with the result from the force-based treatment presented in the work of Tancogne-Dejean et al.,[9] where the virial relation includes an additional transversal term next to the gradient of the force-based local-exchange potential v_{fx},

$$E_{\mathrm{x}} = \int \rho(\mathbf{r})\,\mathbf{r} \cdot (-\nabla v_{\mathrm{fx}}(\mathbf{r}) + \nabla \times \boldsymbol{\alpha}_{\mathrm{fx}}(\mathbf{r}))\,\mathrm{d}\mathbf{r}. \tag{46}$$

The necessary appearance of this additional term (within the integrand), which will be nonzero in all nontrivial situations, already makes it clear that we cannot expect $v_{\mathrm{fx}}(\mathbf{r}) = \lim_{\lambda \searrow 0} v_{\mathrm{xc}}^{\lambda}(\mathbf{r})$. We can, however, note that $\int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla \times \boldsymbol{\alpha}_{\mathrm{fx}}(\mathbf{r})\,\mathrm{d}\mathbf{r} = 0$ for spherically-symmetric systems,[9] which implies for such systems an equality between $\lim_{\lambda \searrow 0} \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v_{\mathrm{xc}}^{\lambda}(\mathbf{r})\,\mathrm{d}\mathbf{r}$ and $\int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v_{\mathrm{fx}}(\mathbf{r})\,\mathrm{d}\mathbf{r}$. Further results connecting to the force-based approach beyond this obvious observation is relegated to future work.

VIII. SUMMARY AND DISCUSSION

The adiabatic connection relates the different energy contributions of a quantum many-body system in its ground state with variable coupling strength λ and fixed one-particle density ρ. Central to our work is the assumption of v^{λ}-representability of ρ, which means that ρ is v-representable at each coupling strength $\lambda \geq 0$. This allowed us to assign unique values to the kinetic-energy function $T(\lambda)$ and the interaction-energy function $W(\lambda)$, see Sec. II. Various convex-analytic properties of the adiabatic connection were studied in Secs. III and IV. We found that $W(\lambda)$ is exactly a supergradient of $F(\lambda)$ at $\lambda \neq 0$ and if defined as $W(0) = \lim_{\lambda \searrow 0} W(\lambda)$ at $\lambda = 0$, then $W(0)$ is given by the right-derivative $\partial^+ F(0)$ of $F(\lambda)$ at $\lambda = 0$. We then confirmed the usual relation $E_{\mathrm{x}} = W(0) - E_{\mathrm{H}}$, which now alternatively allows a definition of the exchange energy through the adiabatic connection as $\partial^+ F(0) - E_{\mathrm{H}} = E_{\mathrm{x}}$. The last equation connects the zero-coupling limit to the high-density limit from coordinate scaling, since E_{x} is here defined through the latter.

In this context, it is natural to also ask for the virial relation (1) relating the exchange energy with an exchange potential and we examined this possibility in Sec. VII. While the zero-coupling limits in Eq. (43) can indeed be guaranteed to exist, this is unlikely to be the case for the associated exchange–correlation potential $v_{\mathrm{xc}}^{\lambda}$ without further assumptions. Although one would usually like to set $v_{\mathrm{x}} = \lim_{\lambda \searrow 0} v_{\mathrm{xc}}^{\lambda}$, only the limit of the corresponding virial integral in Eq. (45) is proven to exist to the exchange energy. This means that while we have a well-defined exchange energy $E_{\mathrm{x}}[\rho]$ for a v^{λ}-representable density ρ from Eq. (36), there might not be a general well-defined local-exchange potential from a similar limit or a functional derivative. This realization is in line with the results from the work of Tancogne-Dejean et al.[9] in the same special issue of this journal. In that work, following a definition of the exchange contribution in terms of force densities, one needs an additional vector potential to fulfill the exchange-only virial relation (1). That the exchange-only virial relation does not hold in general can also be seen from numerical evidence.[9] Of course, techniques like the optimized-effective potential (OEP) method[34–36] can still be used to get an approximate local-exchange potential.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Andre Laestadius: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Project administration (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Mihály A. Csirik**: Conceptualization (equal); Formal analysis (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Markus Penz**: Conceptualization (equal); Formal analysis (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Nicolas Tancogne-Dejean**: Conceptualization (equal); Validation (equal); Writing – review & editing (equal). **Michael Ruggenthaler**:

Conceptualization (equal); Validation (equal); Writing – review & editing (equal). **Angel Rubio**: Conceptualization (equal); Validation (equal); Writing – review & editing (equal). **Trygve Helgaker**: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

REFERENCES

[1] A. M. Teale, T. Helgaker, A. Savin, C. Adamo, B. Aradi, A. V. Arbuznikov, P. W. Ayers, E. J. Baerends, V. Barone, and P. Calaminici *et al.*, "DFT exchange: Sharing perspectives on the workhorse of quantum chemistry and materials science," Phys. Chem. Chem. Phys. **24**, 28700–28781 (2022).

[2] M. Penz, E. I. Tellgren, M. A. Csirik, M. Ruggenthaler, and A. Laestadius, "The structure of density-potential mapping. Part I: Standard density-functional theory," ACS Phys. Chem. Au **3**, 334–347 (2023).

[3] J. Wrighton, A. Albavera-Mata, H. F. Rodríguez, T. S. Tan, A. C. Cancio, J. W. Dufty, and S. B. Trickey, "Some problems in density functional theory," Lett. Math. Phys. **113**, 41 (2023).

[4] S. Crisostomo, R. Pederson, J. Kozlowski, B. Kalita, A. C. Cancio, K. Datchev, A. Wasserman, S. Song, and K. Burke, "Seven useful questions in density functional theory," Lett. Math. Phys. **113**, 42 (2023).

[5] P. E. Lammert, "Differentiability of Lieb functional in electronic density functional theory," Int. J. Quantum Chem. **107**, 1943–1953 (2007).

[6] S. Kvaal, U. Ekström, A. M. Teale, and T. Helgaker, "Differentiable but exact formulation of density-functional theory," J. Chem. Phys. **140**, 18A518 (2014).

[7] A. Laestadius, M. Penz, E. I. Tellgren, M. Ruggenthaler, S. Kvaal, and T. Helgaker, "Generalized Kohn–Sham iteration on Banach spaces," J. Chem. Phys. **149**, 164103 (2018).

[8] M. Penz, M. A. Csirik, and A. Laestadius, "Density-potential inversion from Moreau–Yosida regularization," Electron. Struct. **5**, 014009 (2023).

[9] N. Tancogne-Dejean, M. Penz, A. Laestadius, M. A. Csirik, M. Ruggenthaler, and A. Rubio, "Exchange energies with forces in density-functional theory," J. Chem. Phys. **160**, 024103 (2024).

[10] M. Levy and J. P. Perdew, "Hellmann–Feynman, virial, and scaling requisites for the exact universal density functionals. Shape of the correlation potential and diamagnetic susceptibility for atoms," Phys. Rev. A **32**, 2010–2021 (1985).

[11] R. O. Jones and O. Gunnarsson, "The density functional formalism, its applications and prospects," Rev. Mod. Phys. **61**, 689–746 (1989).

[12] H. Ou-Yang and M. Levy, "Nonuniform coordinate scaling requirements in density-functional theory," Phys. Rev. A **42**, 155–160 (1990).

[13] M. Levy and J. P. Perdew, "Tight bound and convexity constraint on the exchange-correlation-energy functional in the low-density limit, and other formal tests of generalized-gradient approximations," Phys. Rev. B **48**, 11638–11645 (1993).

[14] M. Levy and J. P. Perdew, "Density functionals for exchange and correlation energies: Exact conditions and comparison of approximations," Int. J. Quantum Chem. **49**, 539–548 (1994).

[15] S. Kurth, J. P. Perdew, and P. Blaha, "Molecular and solid-state tests of density functional approximations: LSD, GGAs, and meta-GGAs," Int. J. Quantum Chem. **75**, 889–909 (1999).

[16] O. Gunnarsson and B. I. Lundqvist, "Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism," Phys. Rev. B **13**, 4274–4298 (1976).

[17] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett. **77**, 3865–3868 (1996).

[18] J. P. Perdew, K. Burke, and Y. Wang, "Generalized gradient approximation for the exchange-correlation hole of a many-electron system," Phys. Rev. B **54**, 16533–16539 (1996).

[19] E. Engel and S. H. Vosko, "Exact exchange-only potentials and the virial relation as microscopic criteria for generalized gradient approximations," Phys. Rev. B **47**, 13164–13174 (1993).

[20] P. Borlido, J. Schmidt, A. W. Huran, F. Tran, M. A. L. Marques, and S. Botti, "Exchange-correlation functionals for band gaps of solids: Benchmark, reparametrization and machine learning," npj Comput. Mater. **6**, 96 (2020).

[21] A. D. Kaplan, M. Levy, and J. P. Perdew, "The predictive power of exact constraints and appropriate norms in density functional theory," Annu. Rev. Phys. Chem. **74**, 193–218 (2023).

[22] J. O. Hirschfelder, "Classical and quantum mechanical hypervirial theorems," J. Chem. Phys. **33**, 1462–1466 (1960).

[23] I. Theophilou, M. Penz, M. Ruggenthaler, and A. Rubio, "Virial relations for electrons coupled to quantum field modes," J. Chem. Theory Comput. **16**, 6236–6243 (2020).

[24] E. H. Lieb, "Density functionals for Coulomb systems," Int. J. Quantum Chem. **24**, 243–277 (1983).

[25] In the proof of Theorem 4.4 in Lieb[24], we replace $h^2 = \hat{T} + \lambda \hat{W} + 1$ by $h^2 = \hat{T} + \lambda \hat{W} + 1 + M_\lambda$, where $-M_\lambda$ is the lower bound of the combined operator $\hat{T} + \lambda \hat{W}$ given by Kato–Rellich theorem.[37]

[26] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," Phys. Rev. **136**, B864–B871 (1964).

[27] C. P. Niculescu and L.-E. Persson, *Convex Functions and Their Applications* (Springer, 2004).

[28] J. P. Perdew, M. Ernzerhof, and K. Burke, "Rationale for mixing exact exchange with density functional approximations," J. Chem. Phys. **105**, 9982–9985 (1996).

[29] G. P. Zhang and T. F. George, "Breakdown of the Hellmann–Feynman theorem: Degeneracy is the key," Phys. Rev. B **66**, 033110 (2002).

[30] R. Balawender, A. Holas, and N. H. March, "Comment on 'Breakdown of the Hellmann–Feynman theorem: Degeneracy is the key,'" Phys. Rev. B **69**, 037103 (2004).

[31] F. M. Fernández, "Comment on 'Breakdown of the Hellmann–Feynman theorem: Degeneracy is the key,'" Phys. Rev. B **69**, 037101 (2004).

[32] J. van Tiel, *Convex Analysis: An Introductory Text* (John Wiley & Sons Ltd., 1984).

[33] M. Lewin, E. H. Lieb, and R. Seiringer, "Universal functionals in density functional theory," in *Density Functional Theory* (Springer International Publishing, 2023), pp. 115–182.

[34] R. T. Sharp and G. K. Horton, "A variational approach to the unipotential many-electron problem," Phys. Rev. **90**, 317 (1953).

[35] J. D. Talman and W. F. Shadwick, "Optimized effective atomic central potential," Phys. Rev. A **14**, 36–40 (1976).

[36] W. Yang and Q. Wu, "Direct method for optimized effective potentials in density-functional theory," Phys. Rev. Lett. **89**, 143002 (2002).

[37] M. Reed and B. Simon, *II: Fourier Analysis, Self-Adjointness* (Elsevier, 1975), Vol. 2.