

Symmetrized Non-Decomposable Approximations of the Non-Additive Kinetic Energy Functional

Elias Polak,^{1,2, a)} Tanguy Englert,^{1, b)} Martin J. Gander,^{2, c)} and Tomasz A. Wesolowski^{1, d)}

¹⁾*Department of Physical Chemistry, University of Geneva, Quai Ernest-Ansermet 30, CH-1211 Genève 4, Switzerland*

²⁾*Section of Mathematics, University of Geneva, Rue du Conseil-Général 7-9, CP 64, CH-1211 Genève 4, Switzerland*

(Dated: April 11, 2023)

In subsystem density functional theory (DFT), the bottom-up strategy to approximate the multivariable functional of the non-additive kinetic energy (NAKE) makes it possible to impose exact properties on the corresponding non-additive kinetic energy potential (NAKEP). Such a construction might lead to a non-symmetric and non-homogeneous functional, which excludes the use of such approximations for the evaluation of the total energy. We propose a general formalism to construct a symmetric version based on a perturbation theory approach of the energy expression for the asymmetric part. This strategy is then applied to construct a symmetrized NAKE corresponding to the NAKEP developed recently [Polak et. al., J. Chem. Phys. 156, 044103 (2022)] making it possible to evaluate consistently the energy. These functionals were used to evaluate the interaction energy in several model intermolecular complexes using the formal framework of subsystem DFT. The new symmetrized energy expression shows a superior qualitative performance over common decomposable models.

I. INTRODUCTION

The non-additive kinetic energy functional (NAKE) is a component of the total energy in various formal frameworks of density functional theory¹ and it is a key bifunctional in many variants of the Frozen-Density Embedding Theory²⁻⁵. It is defined as:

$$T_s^{\text{nad}}[\rho_A, \rho_B] := T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B], \quad (1)$$

where the density functional of the non-interacting kinetic energy T_s is given via the constrained search⁶. Here, the admissible domain for pure state spin-unpolarized electron density functions ρ_A and ρ_B is the N_A - and N_B -representable function space⁷. They represent the density of the quantum many body problem for N_A and N_B electrons respectively. The separation of the full system into two subsystems A and B is non-unique and so is also the decomposition of any total density $\rho_{\text{tot}} = \rho_A + \rho_B$. Thus, the functionals in the Hohenberg-Kohn (HK) formalism for subsystem DFT³ impose further constraints on the density function spaces in order to be well-defined⁴.

The partial functional derivative of T_s^{nad} with respect to ρ_A provides the potential that describes a chemical system A embedded in a field generated by ρ_B electrons. It will be referred to as the non-additive kinetic energy potential (NAKEP):

$$\begin{aligned} v_T^{\text{nad}}[\rho_A, \rho_B] &:= \frac{\delta}{\delta \rho_A} T_s^{\text{nad}}[\rho_A, \rho_B] \\ &= \frac{\delta}{\delta \rho} T_s[\rho] \Big|_{\rho=\rho_{\text{tot}}} - \frac{\delta}{\delta \rho} T_s[\rho] \Big|_{\rho=\rho_A}. \end{aligned} \quad (2)$$

Its existence is subject to the admissibility of the chosen pairs of densities⁸. Minimizing the bifunctionals on an admissible domain leads to the true constrained HK energy and optimal embedded density of the subsystem formulation⁹. Applying the Kohn-Sham (KS) DFT framework¹⁰ provides a well-defined orbital-free solution procedure within FDET³. It carries a variational relation to the real HK energy of the total system.

In general, one has no access to the exact analytical expressions of the formulas (2) and (1), and consequently, practical considerations are limited to the use of approximations (denoted with a tilde $\tilde{v}_T^{\text{nad}}[\rho_A, \rho_B]$). There are two main paradigms for any semilocal framework of approximating the non-additive terms:

$$\begin{aligned} \text{top-down} &: \tilde{T}_s[\rho] \longrightarrow \tilde{T}_s^{\text{nad}}[\rho_A, \rho_B] \longrightarrow \tilde{v}_T^{\text{nad}}[\rho_A, \rho_B] \quad (3) \\ \text{or} & \\ \text{bottom-up} &: \tilde{v}_T^{\text{nad}}[\rho_A, \rho_B] \longrightarrow \tilde{T}_s^{\text{nad}}[\rho_A, \rho_B] \xrightarrow{\text{if decomposable } \tilde{T}_s^{\text{nad}}} \tilde{T}_s[\rho]. \end{aligned} \quad (4)$$

The top-down strategy uses some explicit approximate for the density functional T_s and applies it for Definition (1) and its functional derivative (2). The resulting non-additive kinetic bifunctional will be referred to as *decomposable* since the analytic form for the relevant kinetic energy component (\tilde{T}_s) is accessible. The accuracy of the approximant to the NAKEP is directly related to the quality of the approximation used to T_s ^{11,12}. Common embedding methods incorporate such a decomposable \tilde{T}_s^{nad} (see dedicated reviews in Ref. 8,9,13,14). In addition to the local and semilocal NAKEP models², non-local approximants have been used for the same purpose^{15,16}.

The alternative, bottom-up strategy starts with the construction of an approximation for the NAKEP. A corresponding density functional approximant \tilde{T}_s does not necessarily exist, see for example the models introduced in Refs. 17,18, the approximant from Lastra et. al¹⁹, or the more recent construction from Polak et. al.²⁰. These functionals are, therefore, denoted as *non-decomposable*. The potentials based on inverting the KS equation²¹⁻²⁵ also represent a bottom-up construction subject to the condition that the admissible densities are

^{a)}elias.polak@unige.ch

^{b)}tanguy.englert@etu.unige.ch

^{c)}martin.gander@unige.ch

^{d)}tomasz.wesolowski@unige.ch.

considered²⁶. The bottom-up approach has been further used in orbital-free DFT methods (OF-DFT) by Chai and Weeks²⁷. Here, exact physical conditions are used to modify the Euler equation from OF-DFT in case of a semilocal approximation to the kinetic energy. Similar to the non-decomposable model in subsystem DFT, the resulting densities yield superior properties compared to their counterparts in common local and semilocal models. However, Chai and Weeks emphasize that an immediate evaluation of the energy is not possible and continue to use a numerically tedious coupling parameter approach.

We use the following notation for an approximant to the NAKEP that is decomposable or non-decomposable: $\tilde{v}_T^{\text{nad}(x)}$, where x is a placeholder for the chosen model. It is enough if only a component of the approximant is non-decomposable such that the whole functional becomes non-decomposable, i.e. $\tilde{v}_T^{\text{nad}(\text{non-decomposable})}$. This particular component can be further identified as a non-decomposable potential $v_T^{\text{non-decomposable}}$. In the special case, where it does not depend on the embedded density ρ_A , a corresponding approximant to the NAKE is

$$\tilde{T}[\rho_A, \rho_B] := \int \rho_A v_T^{\text{non-decomposable}}[\rho_B]. \quad (5)$$

The left hand side of Eq. (5) is only decomposable if there exists a functional \tilde{T}_s such that each of the three terms on the right hand side of Eq. (1) can be evaluated and they reproduce \tilde{T} from Eq. (5) exactly. The non-decomposable potential can be obtained analytically upon partial functional differentiation with respect to ρ_A because the integral is homogeneous of degree 1 in ρ_A .

The formula in (5) is not guaranteed to obey symmetry upon interchanging the densities (i.e. $\tilde{T}_s^{\text{nad}}[\rho_A, \rho_B] \neq \tilde{T}_s^{\text{nad}}[\rho_B, \rho_A]$). The exact NAKE and any decomposable approximant derived from the top-down strategy are symmetric due to the symmetry property of Eq. (1). In particular, the total density should have the same resulting properties upon interchanging the labels A and B because it consists of the sum of the FDET optimized fragment densities ($\rho_{\text{tot}} = \rho_A + \rho_B$). Asymmetry is, thus, a visible defect, when one evaluates subsystem dependent different energy values. Imposing symmetry on the NAKE approximant with the bottom-up approach through a NAKEP approximant, is, however, a difficult endeavor. So far as we are aware, the possible lack of symmetry and its effects has gone undiscussed in the literature to date.

In this work, we propose an approach to “symmetrize” any semilocal bottom-up non-decomposable model, where the energy bifunctional expression given in Eq. (5) applies. In mathematics, the symmetrization of a multivariable functional is a process that converts any function into a symmetric function for any number of arguments. The result becomes indistinguishable upon permutation of all variables. There are several ways of constructing such a mapping; we are going to elaborate on a strategy that works in the spirit of perturbation theory. A first order correction to the approximant to the NAKE developed by the partial functional derivative ensures symmetry while retaining the desired properties of the associated non-decomposable approximant to the NAKEP.

In the next section, Sec. II, we introduce a general formalism for the symmetrization of any bifunctional. Section III displays the application on an already well-established semilocal non-decomposable model, the NDCS approximation. Here, we profit from the fact that the energy functional corresponding to the NDCS approximant to the NAKEP becomes available. Finally, in Sec. IV we present numerical results of the original asymmetric NDCS energy functional and the symmetrized NDCS (sym-NDCS) functional by discussing approximated interaction energies for a chosen set of chemical complexes.

II. SYMMETRIZATION OF AN ENERGY BIFUNCTIONAL CORRESPONDING TO A NON-DECOMPOSABLE \tilde{v}_T^{nad}

The symmetrization of a general energy bifunctional $F[\rho_A, \rho_B]$ for any admissible pair of densities (ρ_A, ρ_B) (i.e. the functional is well defined on a suitable domain) can be achieved in many ways. First, in order to elaborate on a correction to the functional, we need an estimation of the asymmetry:

$$F_{\text{asym}}[\rho_A, \rho_B] := F[\rho_B, \rho_A] - F[\rho_A, \rho_B]. \quad (6)$$

For a rigorous symmetrization, we assume that F_{asym} does not vanish on measurable volume spaces.

The simplest way to symmetrize a bifunctional is to take the arithmetic average: $F_{\text{sym}}[\rho_A, \rho_B] := \frac{1}{2} [F[\rho_A, \rho_B] + F[\rho_B, \rho_A]]$. Then,

$$F_{\text{sym}}[\rho_A, \rho_B] = F[\rho_A, \rho_B] + \frac{1}{2} F_{\text{asym}}[\rho_A, \rho_B]. \quad (7)$$

However, this strategy may not be physically realistic and lack the desired properties of the non-decomposable functional upon partial functional derivation. So we need a more rigorous representation of a correction to F that preserves the features of the bottom-up construction up to some order.

We propose a more refined approach in this work. It uses the partial functional derivative of the asymmetric term as a first order perturbation correction on the given approximant to the NAKEP. This approach utilizes the directional derivative along ρ_A (the choice of ρ_A is arbitrary but well motivated, since one performs an optimization in ρ_A while ρ_B is fixed) to compensate the variation caused by the asymmetric part. It should be emphasized that the existence of such a derivative is not essential and depends on the form of the energy functional. Our resulting formula with the perturbation correction reads

$$F_{\text{sym-p}}[\rho_A, \rho_B] := F[\rho_A, \rho_B] + C_{\text{sym}} \int \rho_A \frac{\delta}{\delta \rho_A} F_{\text{asym}}[\rho_A, \rho_A], \quad (8)$$

where C_{sym} is a real constant corresponding to the step size of the functional derivative. This constant in front of the correction should be set such that our formula is symmetric. We can use the advantage that the asymmetric part is fully accessible. Enforcing the simple symmetry condition on C_{sym} :

$F_{\text{sym-p}}[\rho_A, \rho_B] = F_{\text{sym-p}}[\rho_B, \rho_A]$ results in (see Appendix A),

$$C_{\text{sym}} = F_{\text{asym}}[\rho_A, \rho_B] \left[\int \rho_A \frac{\delta}{\delta \rho_A} F_{\text{asym}}[\rho_A, \rho_B] - \int \rho_B \frac{\delta}{\delta \rho_B} F_{\text{asym}}[\rho_B, \rho_A] \right]^{-1}. \quad (9)$$

In the next section, we are going to apply this symmetrization formalism to an established semilocal non-decomposable non-additive kinetic approximant as an illustration of the mathematical framework.

III. SYMMETRIZED NDCS ENERGY FUNCTIONAL

We will make use of the symmetrization framework from Sec. II to access the energy observable in the so-called NDCS model introduced in the work by Polak et. al.²⁰. The non-decomposable NDCS approximant to the NAKE or just NDCS energy functional (see Eq. (5)) reads

$$T^{\text{NDCS}}[\rho_A, \rho_B] := \int \rho_A f^{\text{NDCS}}[\rho_B] v^{\text{NDCS}}[\rho_B], \quad (10)$$

where the non-decomposable functional consists of a special potential

$$v^{\text{NDCS}}[\rho_B] := \frac{1}{8} [|\nabla \rho_B|^2 \rho_B^{-2} - \nabla^2 \rho_B \rho_B^{-1}], \quad (11)$$

which is controlled in a particular region of space by a multiplication with a switching function

$$f^{\text{NDCS}}[\rho_B] := (1 - e^{-\rho_B}). \quad (12)$$

The potential in Eq. (11) is derived by imposing some physically exact limit conditions and then modifying the formula due to the restriction to the complete space of admissible density functions. The associated switching function in (12) is supposed to restrict v^{NDCS} only to a certain domain of the volume space, where the said exact limit conditions are satisfied. We note that both formulas only depend on ρ_B . This feature permits a homogeneous energy expression of the NDCS approximant to the NAKE, see Eq. (10), that directly recovers the potential with the switching function upon taking the partial functional derivative,

$$\frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_A, \rho_B] = f^{\text{NDCS}}[\rho_B] v^{\text{NDCS}}[\rho_B]. \quad (13)$$

Now, the NDCS energy functional T^{NDCS} from (10) is a priori not symmetric because of the special form of the limit potential v^{NDCS} . Numerical estimates in Sec. IV will give an idea of how big the discrepancy can be in some cases. In order to use the perturbation correction framework from the previous section, we need an analytic expression of the asymmetric part and its functional derivative,

$$T_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] := T^{\text{NDCS}}[\rho_B, \rho_A] - T^{\text{NDCS}}[\rho_A, \rho_B], \quad (14)$$

which is equivalent to the definition given in (6). The corresponding potential, i.e. the functional derivative with respect to ρ_A , is given by

$$\begin{aligned} v_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] &:= \frac{\delta}{\delta \rho_A} T_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] \\ &= \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] - \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_A, \rho_B]. \end{aligned} \quad (15)$$

The second term on the right hand side is directly accessible due to (13), while the first term needs a very careful analysis because of the dependence on ρ_A in the switching function and in the potential. Its computation of the functional derivative with respect to ρ_A can be found in Appendix B. Here, several simplifications of complex terms result in a very compact expression. It confirms the applicability of the perturbation based symmetrization strategy. For the directional derivative of the first order perturbation correction term (see Eq. (8)) we need the following integral (see Eq. (B.14) in Appendix B),

$$\begin{aligned} \int \rho_A \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] &= \int \left[\rho_B |\nabla \rho_A|^2 (1 - f^{\text{NDCS}}[\rho_A]) (\rho_A^{-1} \right. \\ &\quad \left. - 1) - \nabla^2 \rho_B f^{\text{NDCS}}[\rho_A] \right]. \end{aligned} \quad (16)$$

In this special form, the NDCS switching function from (12) appears twice in opposite order. In volume elements, where one part is ‘‘switched off’’, the other one is ‘‘switched on’’. Hence, we shall expect a contribution of the perturbation term on the whole domain. Using Eqs. (15),(13) and (16), the final directional derivative of $T_{\text{asym}}^{\text{NDCS}}$ reads

$$\begin{aligned} \int \rho_A v_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] &= \int \rho_A \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] - \int \rho_A \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_A, \rho_B] \\ &= \int \rho_A \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] - T^{\text{NDCS}}[\rho_A, \rho_B] \\ &= \int \left[\rho_B |\nabla \rho_A|^2 (1 - f^{\text{NDCS}}[\rho_A]) (\rho_A^{-1} - 1) - \nabla^2 \rho_B f^{\text{NDCS}}[\rho_A] \right] \\ &\quad - T^{\text{NDCS}}[\rho_A, \rho_B]. \end{aligned} \quad (17)$$

Then, the new symmetry perturbation correction of the NDCS energy functional (sym-NDCS) is given by (see Eqs. (8) and (17))

$$\begin{aligned} T^{\text{sym-NDCS}}[\rho_A, \rho_B] &:= T^{\text{NDCS}}[\rho_A, \rho_B] + C_{\text{sym}} \int \rho_A v_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] \\ &= T^{\text{NDCS}}[\rho_A, \rho_B] + C_{\text{sym}} \left(\int \left[\rho_B |\nabla \rho_A|^2 (1 - f^{\text{NDCS}}[\rho_A]) \right. \right. \\ &\quad \left. \left. \times (\rho_A^{-1} - 1) - \nabla^2 \rho_B f^{\text{NDCS}}[\rho_A] \right] - T^{\text{NDCS}}[\rho_A, \rho_B] \right) \\ &= (1 - C_{\text{sym}}) T^{\text{NDCS}}[\rho_A, \rho_B] + C_{\text{sym}} \int \left[\rho_B |\nabla \rho_A|^2 (1 - f^{\text{NDCS}}[\rho_A]) \right. \\ &\quad \left. \times (\rho_A^{-1} - 1) - \nabla^2 \rho_B f^{\text{NDCS}}[\rho_A] \right]. \end{aligned} \quad (18)$$

Finally, the symmetry constant is derived with Eqs. (9), (17) and (14):

$$\begin{aligned}
C_{\text{sym}} &= T_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] \left[\int \rho_A \frac{\delta}{\delta \rho_A} T_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] \right. \\
&\quad \left. - \int \rho_B \frac{\delta}{\delta \rho_B} T_{\text{asym}}^{\text{NDCS}}[\rho_B, \rho_A] \right]^{-1} \\
&= T_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] \left[\int \rho_A \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] - T^{\text{NDCS}}[\rho_A, \rho_B] \right. \\
&\quad \left. - \int \rho_B \frac{\delta}{\delta \rho_B} T^{\text{NDCS}}[\rho_A, \rho_B] + T^{\text{NDCS}}[\rho_B, \rho_A] \right]^{-1} \\
&= T_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] \left[T_{\text{asym}}^{\text{NDCS}}[\rho_A, \rho_B] + \int \rho_A \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] \right. \\
&\quad \left. - \int \rho_B \frac{\delta}{\delta \rho_B} T^{\text{NDCS}}[\rho_A, \rho_B] \right]^{-1}. \tag{20}
\end{aligned}$$

We remark from the above formula that the symmetry constant does not necessarily have to be a half as in Eq. (7). Its value depends only on the magnitude of the asymmetric discrepancy $T_{\text{asym}}^{\text{NDCS}}$. In particular, the contribution from both directional derivatives play an important role. If one experiences a significant energy difference when interchanging the subsystems, then this odd behavior is reflected in the magnitude of the symmetry constant C_{sym} . This concerns cases where the opposite labeling of A and B might violate the imposed exact conditions on the limit potential²⁰. The symmetry constant finds then the best correction contribution to enforce symmetry.

The final full approximant of the NAKEP in the NDCS model is constructed by a combination of a decomposable approximant to the NAKEP and the non-decomposable NDCS functional from Eq. (13),

$$\tilde{v}_T^{\text{nad(NDCS)}}[\rho_A, \rho_B] := \tilde{v}_T^{\text{decomposable}}[\rho_A, \rho_B] + f^{\text{NDCS}}[\rho_B] v^{\text{NDCS}}[\rho_B]. \tag{21}$$

Typical decomposable NAKE approximants are provided by the gradient expansion framework^{8,13,14}. If \tilde{T}_s is local or semilocal in ρ , the potential is analytically derivable²⁸. The local case is referred to as a local density approximation (LDA) and can be described with the Thomas-Fermi (TF) model for the uniform electron gas^{29,30}. Its kinetic energy expression is given by

$$\tilde{T}_s^{\text{TF}}[\rho] := C_{\text{TF}} \int \rho^{5/3}, \tag{22}$$

[where $C_{\text{TF}} = \frac{3}{10} (3\pi^2)^{2/3}$] and the corresponding non-additive formula, which is decomposable, reads

$$\tilde{T}_s^{\text{nad(TF)}}[\rho_A, \rho_B] := C_{\text{TF}} \int \left((\rho_A + \rho_B)^{5/3} - \rho_A^{5/3} - \rho_B^{5/3} \right). \tag{23}$$

The resulting approximant for the NAKEP is the functional derivative,

$$\begin{aligned}
\tilde{v}_T^{\text{nad(TF)}}[\rho_A, \rho_B] &:= \frac{\delta}{\delta \rho_A} \tilde{T}_s^{\text{nad(TF)}}[\rho_A, \rho_B] \\
&= \frac{5}{3} C_{\text{TF}} \left((\rho_A + \rho_B)^{2/3} - \rho_A^{2/3} \right). \tag{24}
\end{aligned}$$

For the decomposable approximant in formula (21), the TF NAKEP (24) is applied because the NDCS limit potential is used to address the flaws by any LDA approach²⁰,

$$\tilde{v}_T^{\text{nad(NDCS)}}[\rho_A, \rho_B] := \tilde{v}_T^{\text{nad(TF)}}[\rho_A, \rho_B] + f^{\text{NDCS}}[\rho_B] v^{\text{NDCS}}[\rho_B], \tag{25}$$

and the resulting full approximant to the NAKE reads

$$\tilde{T}_s^{\text{nad(NDCS)}}[\rho_A, \rho_B] = \tilde{T}_s^{\text{nad(TF)}}[\rho_A, \rho_B] + T^{\text{NDCS}}[\rho_A, \rho_B]. \tag{26}$$

From now on, we can use the sym-NDCS expression given in (19) as the NDCS energy functional in (26),

$$\tilde{T}_s^{\text{nad(sym-NDCS)}}[\rho_A, \rho_B] = \tilde{T}_s^{\text{nad(TF)}}[\rho_A, \rho_B] + T^{\text{sym-NDCS}}[\rho_A, \rho_B]. \tag{27}$$

The final functional, $\tilde{T}_s^{\text{nad(sym-NDCS)}}$, constructed above satisfies the desired relation

$$\tilde{v}_T^{\text{nad(NDCS)}}[\rho_A, \rho_B] = \frac{\delta}{\delta \rho_A} \tilde{T}_s^{\text{nad(sym-NDCS)}} + \text{small correction}, \tag{28}$$

where the small correction is due to the higher order corrections in perturbation theory and $\tilde{v}_T^{\text{nad(NDCS)}}$ is the approximant to the NAKEP introduced in Ref.²⁰.

IV. NUMERICAL ILLUSTRATIONS

In this section, we discuss the errors in energy obtained using densities obtained by means of the NDCS approximant (see Eq. (25)) for the NAKEP. The analyses are made for the same set of weakly bound intermolecular complexes as the ones considered in the Ref. 20 in which the errors of the NDCS approximant for the NAKEP were analysed. We start by showing the asymmetry discrepancy due to the corresponding NDCS energy functional (see Eq. 14) and then discuss the performance of the approximant to the NAKE with the symmetrized energy functional, sym-NDCS (see Eq. 27), in comparison to the energy obtained with optimized densities by means of the TF approximant of the NAKEP (see Eq. (24)) and the KS energy reference of the total system.

To determine, the errors in the quantities derived from a given approximation to the NAKE (and NAKEP), the procedure introduced for the same purpose in Ref³¹ was used for NDCS and sym-NDCS approximants. It consists of performing subsystem DFT calculations, in which the densities ρ_A and ρ_B are optimized in “freeze-and-thaw” (F&T) iterations, and comparing the results to the corresponding ones obtained from the conventional KS calculations. Note that the notion of embedded subsystem and environment becomes irrelevant if the two densities are optimized. Although the subsystem DFT¹ has its fundamental flaw (the subsystem densities are ill-defined in exact formulation⁸), if applied using the same approximation for the exchange-correlation functional and the same finite basis sets in both subsystem-DFT and reference KS calculations, it provides a tool to “measure” the quality of a given approximation to the NAKE (and NAKEP). Any discrepancy between the total density obtained from subsystem DFT and from the corresponding reference KS densities can

be uniquely attributed to the errors in the approximation to the NAKEP. Discrepancies of energies, on the other hand, are due to both errors in the approximation to NAKEP and to NAKE.

We denote further any densities ρ_A and ρ_B as the solution to the F&T protocol described above. The total energy in the subsystem DFT¹ for two interacting systems reads³

$$E_{v_{AB}}^{\text{KS-FDET}}[\rho_A, \rho_B] := E_{v_A}^{\text{KS}}[\rho_A] + E_{v_B}^{\text{KS}}[\rho_B] + T_s^{\text{nad}}[\rho_A, \rho_B] + E_{xc}^{\text{nad}}[\rho_A, \rho_B] + J[\rho_A, \rho_B] + V_A[\rho_B] + V_B[\rho_A], \quad (29)$$

where the general KS energy functional^{10,32} is defined as

$$E_v^{\text{KS}}[\rho] := T_s[\rho] + E_{xc}[\rho] + J[\rho] + V[\rho], \quad (30)$$

with the non-interacting kinetic energy T_s defined via the constrained search⁶, the exchange-correlation energy of an interacting system E_{xc} ¹⁰, the Coulomb functional J ³³, which is also used in its bifunctional form,

$$J[\rho_A, \rho_B] := \iint \frac{\rho_A(\mathbf{r})\rho_B(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \quad (31)$$

and finally, the energy functional of an external potential v , $V[\rho] := \int v\rho$. For two subsystems, the total external potential is considered as a direct sum $v_{AB} := v_A + v_B$, while the functionals are given with their density counterpart,

$$V_A[\rho_B] = \int v_A\rho_B, \quad V_B[\rho_A] = \int v_B\rho_A. \quad (32)$$

The non-additive functionals in Eq. (29) consists then of the common kinetic and exchange-correlation functionals in the KS formalism (30), see Eq. (1) and

$$E_{xc}^{\text{nad}}[\rho_A, \rho_B] := E_{xc}[\rho_A + \rho_B] - E_{xc}[\rho_A] - E_{xc}[\rho_B]. \quad (33)$$

Our computation will access the energy upon complexation by subtracting the KS energy of the isolated subsystems,

$$E_{\text{int}}[\rho_A, \rho_B] := E_{v_{AB}}^{\text{KS-FDET}}[\rho_A, \rho_B] - E_{v_A}^{\text{KS}}[\rho_A^{\text{iso}}] - E_{v_B}^{\text{KS}}[\rho_B^{\text{iso}}], \quad (34)$$

where ρ_A^{iso} and ρ_B^{iso} correspond to an isolated KS treatment of system A and B respectively. This interaction energy $E_{\text{int}}[\rho_A, \rho_B]$ will be used in this work as a global measure of quality for the evaluated KS-FDET energies (see (29)) from the optimized densities. The use of approximations to the non-additive functionals and to the exchange-correlation energy is indicated by the tilde notation $\tilde{E}_{\text{int}}^x[\rho_A, \rho_B]$, where x is a placeholder for the chosen approximant to the NAKE, e.g. $x=\text{NDCS}$.

For the numerical evaluation and discussion of a NAKEP approximant generated error, a representative set of intermolecular complexes has been chosen. Their geometries were implemented at the equilibrium structure obtained from a KS GGA/6-311G(d,p) calculation with the Gaussian software package³⁴: (i) the 1996 exchange functional and gradient-corrected correlation functional of Perdew, Burke and Ernzerhof (PBE)^{35,36} as the generalized gradient approximation of the exchange-correlation functional, and (ii) the 6-311G(d,p)

people basis set^{37,38}. For the F&T computations within the FDET multiscale method, we use the FDETaco library³⁹ based on the PySCF⁴⁰ program. The embedding potential approximants are numerically implemented using functions from PySCF. Thereby, the density of each subsystem is expanded in a supermolecular manner¹¹ with the same basis set as that in (ii). For the non-additive exchange-correlation functional the same approximant as in (i) is used.

In Sections IV A and IV B, we report the interaction energies of the optimized densities, which are obtained after successful convergence of the self-consistent supercycle of calculations (F&T). The corresponding KS reference values are extracted from a KS computation of the total system within the same methodology.

IV.A. Asymmetric Interaction Energies

The formula for the NDCS energy functional (see Eq. (14)) has an asymmetric character. Applying the $\tilde{T}_s^{\text{nad(NDCS)}}$ in Eq. (29) may yield a total energy, which differs upon exchanging the F&T optimized ρ_A and ρ_B . We can observe this difference in Table I.

Table I. Interaction energies in kcal/mol from Eq. (34) using the non-symmetrized approximation to the NAKE given in Eq. (26) obtained from F&T optimized ρ_A and ρ_B for two assignments of labels A and B for the subsystems. $\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_A, \rho_B]$ shows the values, where the symmetry from the first two columns is used. $\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_B, \rho_A]$ shows the result upon the interchange of the subsystem densities ρ_A and ρ_B . $E_{\text{int}}^{\text{KS}}$ is the reference interaction energy from KS calculations for the whole complex.

Complex		Interaction energies from subsystem DFT		
A	B	$\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_A, \rho_B]$	$\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_B, \rho_A]$	$E_{\text{int}}^{\text{KS}}$
Li ⁺	H ₂ O	-39.82	-37.90	-37.48
Li ⁺	CO ₂	-21.87	-20.72	-21.47
Li ⁺	F ⁻	-194.80	-188.32	-187.56
Li ⁺	Cl ⁻	-162.07	-157.22	-153.57
Li ⁺	OH ⁻	-195.79	-189.80	-191.69
K ⁺	F ⁻	-131.51	-140.90	-141.83
K ⁺	Cl ⁻	-112.80	-119.64	-116.62
K ⁺	OH ⁻	-138.21	-140.80	-142.08
Mg ²⁺	O ²⁻	-696.66	-670.52	-666.35
Mg ²⁺	H ₂ O	-87.24	-83.96	-85.21
Be ²⁺	O ²⁻	-947.31	-883.99	-857.56
Be ²⁺	H ₂ O	-176.28	-153.96	-149.97

$\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_A, \rho_B]$ corresponds to the original labeling of embedded subsystem A and subsystem B , while $\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_B, \rho_A]$ stands for the inverse. It is also evident that all functionals that are used in calculating the interaction energies apart from the NDCS approximant, are completely symmetric upon this interchange (see formula (34) and (29)). Thus, any difference can be directly appointed to the discrepancy obtained from

the asymmetric component of the NDCS kinetic energy functional (see Eq. (14)). Although the notion of embedded subsystems A and B becomes irrelevant after the F&T procedure, we can still distinctly choose the optimized subsystem densities by counting the even and odd number of F&T supercycles. The last column shows the KS reference interaction energies for a direct comparison.

We observe that the total asymmetry ranges from a difference of about 2kcal/mol in the case of $\text{Li}^+-\text{H}_2\text{O}$ (-39.82kcal/mol for $\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_A, \rho_B]$ and -37.90kcal/mol for $\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_B, \rho_A]$) up to about 64kcal/mol in the case of $\text{Be}^{2+}-\text{O}^{2-}$ (-947.31kcal/mol for $\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_A, \rho_B]$ and -883.99kcal/mol for $\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_B, \rho_A]$). This difference has to be observed on top of the reference KS interaction energy, which represents a relative effective change of about 2% – 7%. In many cases it seems that $\tilde{E}_{\text{int}}^{\text{NDCS}}[\rho_B, \rho_A]$ provides more accurate interaction energies by being closer to the KS reference. This is attributed to the fact that the original NDCS model is introduced for subsystems B , which represent tightly bound electrons to the nuclei²⁰. This trend is, however, not consistent as in some systems the two symmetries are showing results, which overshoot the KS reference in one symmetry, and undershoot it in the other one (see for example the case of K^+-Cl^-). Nevertheless, a robust model should not depend on the choice of the labeling, or more precisely, display such a significant variation in the energy results upon interchange.

In the next subsection, Sec. IV B, we will apply the symmetrized NDCS energy functional for the evaluation of the interaction energies on the same set of chemical systems.

IV.B. Symmetric Interaction Energies

In Table II we show the approximated interaction energy results with the use of the symmetrized NDCS energy functional (sym-NDCS) for the full NDCS approximant to the NAKE (see Eq. (27)). In addition to that, computed interaction energies with the TF approximant for the NAKE (see Eq. (23)) as well as the KS reference values are printed. Relative percentage errors to the reference value are given in parentheses to display the performance.

Since the approximants used are now completely symmetric by construction, we can omit the notion of A and B , and concentrate the discussion of the F&T results on the respective chemical complexes. The relative interaction energy error decreases by a factor of 3.5 in the case of Li^+-OH^- (from 2.82% for TF to 0.79% for sym-NDCS) or in the case of $\text{Be}^{2+}-\text{H}_2\text{O}$ by at least a factor of 2 (from 24.36% for TF to 11.63% for sym-NDCS). In addition to the fact that the new symmetrized NDCS formula provides symmetric energies, it also outperforms in all cases the decomposable local density functional. We already know that NDCS provides more accurate densities²⁰, and thus, the evaluated energy functionals are expected to be closer to the reference value. Hereby, the approximated interaction energy improves in some cases more than just by a margin, see for example Li^+-CO_2 . NDCS also stays robust by providing small errors in complexes, where

Table II. Interaction energies in kcal/mol from Eq. (34) using the TF approximant given in Eq. (23), $x=\text{TF}$, and the sym-NDCS approximant, $x=\text{sym-NDCS}$, given in Eq. (27), to the NAKE, obtained from F&T optimized densities. $E_{\text{int}}^{\text{KS}}$ is the reference interaction energy from KS calculations for the whole complex. For comparison, the absolute relative percentage errors ($|\tilde{E}_{\text{int}}^x - \tilde{E}_{\text{int}}^{\text{KS}}|/\tilde{E}_{\text{int}}^{\text{KS}} * 100\%$) are given in parentheses.

Complex		Interaction energies from subsystem DFT		
		TF	sym-NDCS	KS
Li^+	H_2O	-40.66	-39.02	-37.48
		(8.48)	(4.11)	
Li^+	CO_2	-22.41	-21.39	-21.47
		(4.37)	(0.37)	
Li^+	F^-	-196.75	-192.04	-187.56
		(4.90)	(2.39)	
Li^+	Cl^-	-164.08	-160.05	-153.57
		(6.84)	(4.22)	
Li^+	OH^-	-197.09	-193.20	-191.69
		(2.82)	(0.79)	
K^+	F^-	... ^a	-136.94	-141.83
		(...)	(3.45)	
K^+	Cl^-	... ^a	-116.77	-116.62
		(...)	(0.13)	
K^+	OH^-	... ^a	-139.80	-142.08
		(...)	(1.61)	
Mg^{2+}	O^{2-}	-691.91	-684.44	-666.35
		(3.84)	(2.71)	
Mg^{2+}	H_2O	-89.21	-85.94	-85.21
		(4.69)	(0.85)	
Be^{2+}	O^{2-}	-954.86	-920.58	-857.86
		(11.31)	(7.31)	
Be^{2+}	H_2O	-186.51	-167.41	-149.97
		(24.36)	(11.63)	

^a No converged results are available.

the TF model does not converge. These challenging system are similar to the ones reported in the publication about the NDCS model in Ref. 20. Future orbital and graphical analysis about the potassium complexes and other systems, which experience charge leak issues, will give more detailed insight about the superior performance of NDCS.

Finally, we want to compare the sym-NDCS interaction energies in Table II to the asymmetric ones in Table I. The symmetrized values are not equal to the average of both symmetry results. In fact, averaging would provide interaction energies with a higher relative error in most cases. The sym-NDCS interaction energies use a symmetry constant C_{sym} (see Eq. (20)) in order to find a more sophisticated portion of the correction to the functional, which results in a specific value lying in between the two symmetry results. The computation of C_{sym} can be done after the F&T optimization of the subsys-

tem densities ρ_A and ρ_B because it only depends on the value of the asymmetry functional $T_{\text{asym}}^{\text{NDCS}}$ and its functional derivative. Therefore, we can evaluate the constant without further effort after the F&T procedure when calculating the energies, and directly obtain a symmetrized result.

V. CONCLUSIONS

As shown in our previous works, non-decomposable approximants for the NAKEP provide more robust and superior electron densities than the decomposable ones constructed from local or semilocal approximants for T_s in subsystem DFT. We attribute this to the imposed exact physical and mathematical properties on the NAKEP approximant. They can be useful for properties which are available numerically as expectation values evaluated for the embedded wavefunction or in extensions of FDET for excited states^{41,42}, which do not involve the evaluation of the total energy. Unfortunately, the corresponding non-decomposable approximant to the NAKE (see Eq. (5)) is not suitable for the evaluation of energies because it might violate the symmetry of the non-additive kinetic energy. The issue of asymmetry can always occur when using a bottom-up strategy to construct an approximant to the NAKEP, whereas the exact NAKE or approximations derived from the top-down strategy are always symmetric.

In this work, we propose a new formally sound framework to symmetrize a non-decomposable approximant to the NAKE. Sec. II describes a symmetrization procedure, which can be applied to any density functional expression by using a perturbation theory approach for the evaluation of the energy. The resulting formula (see Eq. (8)) only needs access to the asymmetric part of the functional and its functional derivative to provide a completely symmetric expression for the energy functional. Computing the derivative results in a compact formula for a bottom-up constructed approximant, which is physically motivated (see Appendix B). Meanwhile, the optimized embedded density continues to profit from the fact that it is obtained through a supercycle of self-consistent computations within an embedding potential, which includes the non-decomposable approximant to the NAKEP.

The application to the recently developed NDCS model shows the numerical validation of symmetric interaction energies for a set of charge transfer complexes in Sec. IV. It retains a superior performance over local decomposable models when using the sym-NDCS functional for the NDCS approximant to the NAKE (see Eq. (27)). Other non-decomposable approximants to the NAKEP, where the corresponding approximant to the NAKE violates the symmetry, use the proposed symmetrization framework (Sec. II) to gain access to the energies. Future applications beyond bifunctionals, such as to multivariable models that lack symmetry, are also possible. In principle, the construction of symmetric NAKE consistent with a given non-decomposable approximant for the NAKEP proposed in this work is also applicable for NAKEPs obtained from inverting the KS equation. Such a construction would, however, involve an additional intermediate step - expressing a given potential as a density functional.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY STATEMENT

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

Appendix A: First Order Symmetry Correction

In this section, we will present the derivation of the symmetry constant in (9) from the enforced symmetry condition:

$$\begin{aligned}
F_{\text{sym-p}}[\rho_A, \rho_B] &= F_{\text{sym-p}}[\rho_B, \rho_A] & (\text{A.1}) \\
\Leftrightarrow F[\rho_A, \rho_B] + C_{\text{sym}} \int \rho_A \frac{\delta}{\delta \rho_A} F_{\text{asym}}[\rho_A, \rho_B] \\
&= F[\rho_B, \rho_A] + C_{\text{sym}} \int \rho_B \frac{\delta}{\delta \rho_B} F_{\text{asym}}[\rho_B, \rho_A] \\
\Leftrightarrow C_{\text{sym}} \left[\int \rho_A \frac{\delta}{\delta \rho_A} F_{\text{asym}}[\rho_A, \rho_B] - \int \rho_B \frac{\delta}{\delta \rho_B} F_{\text{asym}}[\rho_B, \rho_A] \right] \\
&= F[\rho_B, \rho_A] - F[\rho_A, \rho_B] \\
\stackrel{(6)}{\Leftrightarrow} C_{\text{sym}} &= F_{\text{asym}}[\rho_A, \rho_B] \left[\int \rho_A \frac{\delta}{\delta \rho_A} F_{\text{asym}}[\rho_A, \rho_B] \right. \\
&\quad \left. - \int \rho_B \frac{\delta}{\delta \rho_B} F_{\text{asym}}[\rho_B, \rho_A] \right]^{-1}.
\end{aligned}$$

The term in the denominator does not vanish because the general functional F is conditioned not to be symmetric.

Appendix B: Functional derivative of $T^{\text{NDCS}}[\rho_B, \rho_A]$

The following section will show the full derivation of the functional derivative of $T^{\text{NDCS}}[\rho_B, \rho_A]$ with respect to ρ_A . The main difference to the simple differentiation of the original NDCS functional (13) is the interchanged argument. Therefore, the switching function (12) and NDCS limit potential (11) both depend now on ρ_A ,

$$\frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] = \frac{\delta}{\delta \rho_A} \int f^{\text{NDCS}}[\rho_A] v^{\text{NDCS}}[\rho_A] \rho_B. \quad (\text{B.1})$$

We are going to apply the well known variational method to find the functional derivative (B.1). For any differentiable functional F , a variation represented by a test function η provides the descriptor of the directional derivative⁴³,

$$\int \frac{\delta}{\delta \rho} F[\rho] \eta = \frac{d}{d\epsilon} \left[F[\rho + \epsilon \eta] \right]_{\epsilon=0}. \quad (\text{B.2})$$

Hence, we obtain the following formula for the functional derivative from (B.1) with (10),

$$\begin{aligned}
\int \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] \eta &= \frac{d}{d\varepsilon} \left[T^{\text{NDCS}}[\rho_B, \rho_A + \varepsilon \eta] \right]_{\varepsilon=0} \\
&= \frac{d}{d\varepsilon} \int f^{\text{NDCS}}[\rho_A + \varepsilon \eta] v^{\text{NDCS}}[\rho_A + \varepsilon \eta] \rho_B \Big|_{\varepsilon=0} \\
&= \int \underbrace{\frac{d}{d\varepsilon} \left[f^{\text{NDCS}}[\rho_A + \varepsilon \eta] \right]_{\varepsilon=0}}_{(I)} v^{\text{NDCS}}[\rho_A] \rho_B \\
&\quad + \int f^{\text{NDCS}}[\rho_A] \underbrace{\frac{d}{d\varepsilon} \left[v^{\text{NDCS}}[\rho_A + \varepsilon \eta] \right]_{\varepsilon=0}}_{(II)} \rho_B. \quad (\text{B.3})
\end{aligned}$$

We calculate the derivatives (I) and (II) separately. The first one is obtained directly due to the simple form of the

switching function (see Eq. (12)),

$$(I) = \frac{d}{d\varepsilon} \left[\left(1 - e^{-(\rho_A + \varepsilon \eta)} \right) \right]_{\varepsilon=0} = \eta e^{-\rho_A}. \quad (\text{B.4})$$

The second one needs a more careful treatment of the terms in the special form of the NDCS limit potential (see Eq. (11)),

$$\begin{aligned}
(II) &= \frac{d}{d\varepsilon} \left[|\nabla(\rho_A + \varepsilon \eta)|^2 (\rho_A + \varepsilon \eta)^{-2} \right. \\
&\quad \left. - \nabla^2(\rho_A + \varepsilon \eta) (\rho_A + \varepsilon \eta)^{-1} \right]_{\varepsilon=0} \\
&= \left[2\nabla(\rho_A + \varepsilon \eta)^\top \nabla \eta (\rho_A + \varepsilon \eta)^{-2} \right. \\
&\quad \left. - 2\nabla(\rho_A + \varepsilon \eta)^\top \nabla(\rho_A + \varepsilon \eta) (\rho_A + \varepsilon \eta)^{-3} \eta \right. \\
&\quad \left. - (\nabla^2 \eta (\rho_A + \varepsilon \eta)^{-1} - \nabla^2(\rho_A + \varepsilon \eta) \eta (\rho_A + \varepsilon \eta)^{-2}) \right]_{\varepsilon=0} \\
&= -\nabla^2 \eta \rho_A^{-1} + \nabla^2 \rho_A (\rho_A)^{-2} \eta + 2\nabla \rho_A^\top \nabla \eta \rho_A^{-2} \\
&\quad - 2\nabla \rho_A^\top \nabla \rho_A \rho_A^{-3} \eta. \quad (\text{B.5})
\end{aligned}$$

Thus, due to (B.5) and (B.4), (B.3) is composed out of the following two integrals:

$$\begin{aligned}
\int [(I)v^{\text{NDCS}}[\rho_A] + f^{\text{NDCS}}[\rho_A](II)] \rho_B &= \int e^{-\rho_A} [|\nabla \rho_A|^2 \rho_A^{-2} - \nabla^2 \rho_A \rho_A^{-1}] \eta \rho_B \\
&\quad + \underbrace{\int (1 - e^{-\rho_A}) [-\nabla^2 \eta \rho_A^{-1} + \nabla^2 \rho_A (\rho_A)^{-2} \eta + 2\nabla \rho_A^\top \nabla \eta \rho_A^{-2} - 2\nabla \rho_A^\top \nabla \rho_A \rho_A^{-3} \eta] \rho_B}_{(III)}. \quad (\text{B.6})
\end{aligned}$$

For the application of the formula (B.2), we need the test function η to appear without its derivatives. The first integral on the right hand side obeys this property, whereas the second integral (which denoted as (III)) does have higher order derivatives of η . A common strategy to replace these is to use the Greens identity (see for instance 44) for twice differentiable functions, which vanish at infinity,

$$\int \nabla \rho_A^\top \nabla \rho_B = - \int \rho_A \nabla^2 \rho_B. \quad (\text{B.7})$$

We group the terms in the integral (III) according to the order of the derivative,

$$\begin{aligned}
(III) &= \underbrace{\int (1 - e^{-\rho_A}) [\nabla^2 \rho_A \rho_A^{-2} - 2|\nabla \rho_A|^2 \rho_A^{-3}] \rho_B \eta}_{(i)} \\
&\quad + 2 \underbrace{\int (1 - e^{-\rho_A}) \rho_A^{-2} \rho_B \nabla \rho_A^\top \nabla \eta}_{(ii)} \\
&\quad - \underbrace{\int (1 - e^{-\rho_A}) \rho_A^{-1} \rho_B \nabla^2 \eta}_{(iii)}. \quad (\text{B.8})
\end{aligned}$$

Now, (i) does not require any more calculus because there are no derivatives of η involved. In (ii), however, we need to

apply Greens identity (B.7) once,

$$\begin{aligned}
(ii) &= -2 \int \nabla \left[(1 - e^{-\rho_A}) \rho_B \nabla \rho_A^\top \rho_A^{-2} \right] \eta = -2 \int \left[e^{-\rho_A} \rho_B \nabla \rho_A^\top \nabla \rho_A \rho_A^{-2} \right. \\
&\quad \left. + (1 - e^{-\rho_A}) \nabla \rho_B^\top \nabla \rho_A \rho_A^{-2} + (1 - e^{-\rho_A}) \rho_B \nabla^2 \rho_A \rho_A^{-2} \right. \\
&\quad \left. + (1 - e^{-\rho_A}) \rho_B \nabla \rho_A^\top \nabla \rho_A (-2) \rho_A^{-3} \right] \eta \\
&= \int \left[4(1 - e^{-\rho_A}) \rho_B |\nabla \rho_A|^2 \rho_A^{-3} - 2e^{-\rho_A} \rho_B |\nabla \rho_A|^2 \rho_A^{-2} \right. \\
&\quad \left. - 2(1 - e^{-\rho_A}) \nabla \rho_B^\top \nabla \rho_A \rho_A^{-2} - 2(1 - e^{-\rho_A}) \rho_B \nabla^2 \rho_A \rho_A^{-2} \right] \eta \\
&= \int \left[\nabla \rho_B^\top \nabla \rho_A (-2(1 - e^{-\rho_A})) \rho_A^{-2} + \rho_B \left((1 - e^{-\rho_A}) (4|\nabla \rho_A|^2 \rho_A^{-3} \right. \right. \\
&\quad \left. \left. - 2\nabla^2 \rho_A \rho_A^{-2}) + e^{-\rho_A} (-2|\nabla \rho_A|^2 \rho_A^{-2}) \right) \right] \eta.
\end{aligned}$$

In the last expression for (ii), we have grouped the terms inside the bracket according to the appearance of ρ_B . This formula has no derivatives of η involved. The third integral (iii) needs twice the application of Greens identity (B.7) because of $\nabla^2 \eta$,

$$\begin{aligned}
(\text{iii}) &= \int \left[\nabla \left((1 - e^{-\rho_A}) \rho_B \rho_A^{-1} \right)^\top \right] \nabla \eta \\
&= \int \left[e^{-\rho_A} \rho_B \rho_A^{-1} \nabla \rho_A^\top + (1 - e^{-\rho_A}) \rho_A^{-1} \nabla \rho_B^\top + (1 - e^{-\rho_A}) \rho_B (-1) \rho_A^{-2} \nabla \rho_A^\top \right] \nabla \eta \\
&= - \int \nabla \left[e^{-\rho_A} \rho_B \rho_A^{-1} \nabla \rho_A^\top + (1 - e^{-\rho_A}) \rho_A^{-1} \nabla \rho_B^\top - (1 - e^{-\rho_A}) \rho_B \rho_A^{-2} \nabla \rho_A^\top \right] \eta \\
&= \int \left[e^{-\rho_A} |\nabla \rho_A|^2 \rho_B \rho_A^{-1} - e^{-\rho_A} \nabla^2 \rho_A \rho_B \rho_A^{-1} - e^{-\rho_A} \nabla \rho_B^\top \nabla \rho_A \rho_A^{-1} + e^{-\rho_A} |\nabla \rho_A|^2 \rho_B \rho_A^{-2} - e^{-\rho_A} \nabla \rho_B^\top \nabla \rho_A \rho_A^{-1} \right. \\
&\quad \left. - (1 - e^{-\rho_A}) \nabla^2 \rho_B \rho_A^{-1} + (1 - e^{-\rho_A}) \nabla \rho_B^\top \nabla \rho_A \rho_A^{-2} + e^{-\rho_A} \nabla \rho_A^\top \nabla \rho_B \rho_A^{-2} + (1 - e^{-\rho_A}) \nabla \rho_B^\top \nabla \rho_A \rho_A^{-2} \right. \\
&\quad \left. - 2(1 - e^{-\rho_A}) \rho_B \rho_A^{-3} |\nabla \rho_A|^2 + (1 - e^{-\rho_A}) \rho_B \rho_A^{-2} \nabla^2 \rho_A \right] \eta \\
&= \int \left[-\nabla^2 \rho_B \rho_A^{-1} (1 - e^{-\rho_A}) + \nabla \rho_B^\top (\nabla \rho_A (1 - e^{-\rho_A}) [2\rho_A^{-2}] + \nabla \rho_A e^{-\rho_A} [-2\rho_A^{-1}]) \right. \\
&\quad \left. + \rho_B ((1 - e^{-\rho_A}) [\nabla^2 \rho_A \rho_A^{-2} - 2|\nabla \rho_A|^2 \rho_A^{-3}] + e^{-\rho_A} [2|\nabla \rho_A|^2 \rho_A^{-2} - \nabla^2 \rho_A \rho_A^{-1} + |\nabla \rho_A|^2 \rho_A^{-1}]) \right] \eta,
\end{aligned}$$

This final expression seems to have blown up because of the many products from the derivative in Greens identity. Nevertheless, the result is an integral that has now no derivatives

in η . To see how these terms do simplify with the ones from the other integrals, we sum now step by step everything back together. At first **(ii)** and **(iii)**,

$$\begin{aligned}
&(\text{ii}) + (\text{iii}) \\
&= \int \left[-\nabla^2 \rho_B \rho_A^{-1} (1 - e^{-\rho_A}) + \nabla \rho_B^\top (\nabla \rho_A (1 - e^{-\rho_A}) [2\rho_A^{-2}] + \nabla \rho_A e^{-\rho_A} [-2\rho_A^{-1}]) \right. \\
&\quad \left. - 2|\nabla \rho_A|^2 \rho_A^{-3} + 4|\nabla \rho_A|^2 \rho_A^{-3} - 2\nabla^2 \rho_A \rho_A^{-2} \right] + e^{-\rho_A} \left[2|\nabla \rho_A|^2 \rho_A^{-2} - \nabla^2 \rho_A \rho_A^{-1} + |\nabla \rho_A|^2 \rho_A^{-1} - 2|\nabla \rho_A|^2 \rho_A^{-2} \right] \eta \\
&= \int \left[-\nabla^2 \rho_B \rho_A^{-1} (1 - e^{-\rho_A}) + \nabla \rho_B^\top \nabla \rho_A e^{-\rho_A} [-2\rho_A^{-1}] + \rho_B ((1 - e^{-\rho_A}) [2|\nabla \rho_A|^2 \rho_A^{-3} - \nabla^2 \rho_A \rho_A^{-2}] + e^{-\rho_A} [-\nabla^2 \rho_A \rho_A^{-1} + |\nabla \rho_A|^2 \rho_A^{-1}]) \right] \eta,
\end{aligned}$$

where some terms in the last two brackets canceled out each other. It is left to add **(i)** to get back to (B.8),

$$\begin{aligned}
(III) &= (\text{i}) + (\text{ii}) + (\text{iii}) \\
&= \int \left[-\nabla^2 \rho_B \rho_A^{-1} (1 - e^{-\rho_A}) + \nabla \rho_B^\top \nabla \rho_A e^{-\rho_A} [-2\rho_A^{-1}] \right. \\
&\quad \left. + \rho_B ((1 - e^{-\rho_A}) [2|\nabla \rho_A|^2 \rho_A^{-3} - \nabla^2 \rho_A \rho_A^{-2} + \nabla^2 \rho_A \rho_A^{-2} \right. \\
&\quad \left. - 2|\nabla \rho_A|^2 \rho_A^{-3}] + e^{-\rho_A} [-\nabla^2 \rho_A \rho_A^{-1} + |\nabla \rho_A|^2 \rho_A^{-1}]) \right] \eta \\
&= \int \left[-\nabla^2 \rho_B \rho_A^{-1} (1 - e^{-\rho_A}) + \nabla \rho_B^\top \nabla \rho_A e^{-\rho_A} [-2\rho_A^{-1}] \right. \\
&\quad \left. + \rho_B (e^{-\rho_A} [-\nabla^2 \rho_A \rho_A^{-1} + |\nabla \rho_A|^2 \rho_A^{-1}]) \right] \eta. \quad (\text{B.9})
\end{aligned}$$

Here again, the simplification lead to a more compact final integral formula for (III), which allows the use of the functional derivative representation from (B.2). The last step is to add this integral back to (B.6) with the use of (B.9),

$$\begin{aligned}
&\int \frac{\delta}{\delta \rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] \eta \\
&= \int e^{-\rho_A} [|\nabla \rho_A|^2 \rho_A^{-2} - \nabla^2 \rho_A \rho_A^{-1}] \eta \rho_B + (III) \\
&= \int \left[-\nabla^2 \rho_B \rho_A^{-1} (1 - e^{-\rho_A}) + \nabla \rho_B^\top \nabla \rho_A e^{-\rho_A} [-2\rho_A^{-1}] \right. \\
&\quad \left. + \rho_B (e^{-\rho_A} [-\nabla^2 \rho_A \rho_A^{-1} + |\nabla \rho_A|^2 \rho_A^{-1} + |\nabla \rho_A|^2 \rho_A^{-2} \right. \\
&\quad \left. - \nabla^2 \rho_A \rho_A^{-1}]) \right] \eta \\
&= \int \left[-\nabla^2 \rho_B \rho_A^{-1} (1 - e^{-\rho_A}) + \nabla \rho_B^\top \nabla \rho_A e^{-\rho_A} [-2\rho_A^{-1}] \right. \\
&\quad \left. + \rho_B (e^{-\rho_A} [|\nabla \rho_A|^2 (\rho_A^{-2} + \rho_A^{-1}) - 2\nabla^2 \rho_A \rho_A^{-1}]) \right] \eta \\
&= \int \left[-\nabla^2 \rho_B \rho_A^{-1} (1 - e^{-\rho_A}) + \rho_B e^{-\rho_A} |\nabla \rho_A|^2 (\rho_A^{-2} + \rho_A^{-1}) \right. \\
&\quad \left. - 2e^{-\rho_A} [\nabla \rho_B^\top \nabla \rho_A \rho_A^{-1} + \rho_B \nabla^2 \rho_A \rho_A^{-1}] \right] \eta. \quad (\text{B.10})
\end{aligned}$$

In the last equation, we group the terms in a more compact way. The formula for the functional derivative of T^{NDCS} with respect to ρ_A is given in the big brackets inside the integral,

$$\frac{\delta}{\delta\rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] = -\nabla^2 \rho_B \rho_A^{-1} (1 - e^{-\rho_A}) + \rho_B e^{-\rho_A} |\nabla\rho_A|^2 \times (\rho_A^{-2} + \rho_A^{-1}) - 2e^{-\rho_A} [\nabla\rho_B^T \nabla\rho_A \rho_A^{-1} + \rho_B \nabla^2 \rho_A \rho_A^{-1}]. \quad (\text{B.11})$$

We are also able to derive the directional derivative,

$$\int \rho_A \frac{\delta}{\delta\rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] = \int \left[-\nabla^2 \rho_B (1 - e^{-\rho_A}) + \rho_B e^{-\rho_A} |\nabla\rho_A|^2 (\rho_A^{-1} + 1) - 2e^{-\rho_A} [\nabla\rho_B^T \nabla\rho_A + \rho_B \nabla^2 \rho_A] \right]. \quad (\text{B.12})$$

With the help of Greens identity (B.7), we can further rewrite the first of the last two terms in (B.12),

$$\begin{aligned} -2 \int e^{-\rho_A} \nabla\rho_B^T \nabla\rho_A &= 2 \int \rho_B \nabla (e^{-\rho_A} \nabla\rho_A) \\ &= \int 2\rho_B (e^{-\rho_A} \nabla^2 \rho_A - e^{-\rho_A} |\nabla\rho_A|^2). \end{aligned} \quad (\text{B.13})$$

Therefore, equation (B.12) even more simplifies to

$$\begin{aligned} &\int \rho_A \frac{\delta}{\delta\rho_A} T^{\text{NDCS}}[\rho_B, \rho_A] \\ &\stackrel{(\text{B.13})}{=} \int \left[-\nabla^2 \rho_B (1 - e^{-\rho_A}) + \rho_B e^{-\rho_A} |\nabla\rho_A|^2 \rho_A^{-1} + \rho_B e^{-\rho_A} |\nabla\rho_A|^2 \right. \\ &\quad \left. + e^{-\rho_A} [2\rho_B \nabla^2 \rho_A - 2\rho_B |\nabla\rho_A|^2 - 2\rho_B \nabla^2 \rho_A] \right] \\ &= \int \left[-\nabla^2 \rho_B (1 - e^{-\rho_A}) + \rho_B e^{-\rho_A} |\nabla\rho_A|^2 (\rho_A^{-1} - 1) \right] \\ &\stackrel{(\text{12})}{=} \int \left[\rho_B |\nabla\rho_A|^2 (1 - f^{\text{NDCS}}[\rho_A]) (\rho_A^{-1} - 1) - \nabla^2 \rho_B f^{\text{NDCS}}[\rho_A] \right], \end{aligned} \quad (\text{B.14})$$

where we reintroduced in the last equation the switching function f^{NDCS} . This final compact formula (B.14) corresponds to the result given in (16).

REFERENCES

- ¹P. Cortona, *Physical Review B* **44**, 8454–8458 (1991).
- ²T. A. Wesolowski and A. Warshel, *The Journal of Physical Chemistry* **97**, 8050–8053 (1993).
- ³T. A. Wesolowski, *Physical Review A* **77**, 012504 (2008).
- ⁴K. Pernal and T. A. Wesolowski, *Int. J. Quantum Chem.* **109**, 2520–2525 (2009).
- ⁵T. A. Wesolowski, *Journal of Chemical Theory and Computation* **16**, 6880–6885 (2020), pMID: 32986425.
- ⁶M. Levy, *Phys. Rev. A* **26**, 1200–1208 (1982).
- ⁷T. L. Gilbert, *Phys. Rev. B* **12**, 2111–2120 (1975).
- ⁸T. A. Wesolowski, in *Computational Chemistry: Reviews of Current Trends*, Vol. 10, edited by J. Leszczynski (World Scientific, 2006) pp. 1–82.
- ⁹T. A. Wesolowski, S. Shedge, and X. Zhou, *Chemical Reviews* **115**, 5891–5928 (2015).
- ¹⁰W. Kohn and L. J. Sham, *Physical Review* **140**, A1133–A1138 (1965).
- ¹¹T. A. Wesolowski, *The Journal of Chemical Physics* **106**, 8516–8526 (1997).
- ¹²T. A. Wesolowski and F. Tran, *The Journal of Chemical Physics* **118**, 2072–2080 (2003).
- ¹³C. R. Jacob and J. Neugebauer, *WIREs Comput. Mol. Sci.* **4**, 325–362 (2014).
- ¹⁴A. Krishtal, D. Sinha, G. Alessandro, and M. Pavanello, *Journal of Physics: Condensed Matter* **27** (2015), 10.1088/0953-8984/27/18/183202.
- ¹⁵W. Mi and M. Pavanello, *Physical Chemistry Letters* **11**, 272–279 (2020).
- ¹⁶X. Shao, W. Mi, and M. Pavanello, *Journal of Chemical Theory and Computation* **17**, 3455–3461 (2021), pMID: 33983729.
- ¹⁷K. Jiang, J. Nafziger, and A. Wasserman, *The Journal of Chemical Physics* **148**, 104113 (2018).
- ¹⁸K. Jiang, J. Nafziger, and A. Wasserman, *The Journal of Chemical Physics* **149** (2018).
- ¹⁹J. M. G. Lastra, J. W. Kaminski, and T. A. Wesolowski, *The Journal of Chemical Physics* **129**, 074107 (2008).
- ²⁰E. Polak, C. E. González-Espinoza, M. J. Gander, and T. A. Wesolowski, *The Journal of Chemical Physics* **156**, 044103 (2022).
- ²¹A. Savin and T. A. Wesolowski, “Orbital-free embedding effective potential in analytically solvable cases,” in *Advances in the Theory of Atomic and Molecular Systems: Conceptual and Computational Advances in Quantum Chemistry*, edited by P. Piecuch, J. Maruani, G. Delgado-Barrio, and S. Wilson (Springer Netherlands, Dordrecht, 2009) pp. 311–326.
- ²²J. D. Goodpaster, N. Ananth, F. R. Manby, and T. F. Miller, *The Journal of Chemical Physics* **133**, 084103 (2010).
- ²³S. Fux, C. R. Jacob, J. Neugebauer, L. Visscher, and M. Reiher, *The Journal of Chemical Physics* **132**, 164101 (2010).
- ²⁴P. de Silva and T. A. Wesolowski, *The Journal of Chemical Physics* **137**, 094110 (2012).
- ²⁵M. Banafsheh, T. A. Wesolowski, T. Gould, L. Kronik, and D. A. Strubbe, *Physical Review A* **106**, 042812 (2022).
- ²⁶T. A. Wesolowski, *The Journal of Chemical Physics* **157**, 081102 (2022).
- ²⁷J.-D. Chai and J. D. Weeks, *Journal of Physical Chemistry B* **108**, 6870–6876 (2004).
- ²⁸P. Golub and S. Manzhos, *Physical Chemistry Chemical Physics* **21**, 378–395 (2019).
- ²⁹L. H. Thomas, *Mathematical Proceedings of the Cambridge Philosophical Society* **23**, 542 (1927).
- ³⁰E. Fermi, *Zeitschrift für Physik* **48**, 73–79 (1928).
- ³¹T. A. Wesolowski and J. Weber, *Chemical Physics Letters* **248**, 71–76 (1996).
- ³²E. H. Lieb, *International Journal of Quantum Chemistry* **24**, 243–277 (1983).
- ³³P. Hohenberg and W. Kohn, *Physical Review* **136**, B864–B871 (1964).
- ³⁴M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuse-

- ria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Men-
nucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, "Gaussian-16 Revision A.03," (2016), gaussian Inc. Wallingford CT.
- ³⁵J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- ³⁶J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **78**, 1396–1396 (1996).
- ³⁷J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, and L. Radom, *J. Chem. Phys.* **107**, 5016–5021 (1997).
- ³⁸R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650–654 (1980).
- ³⁹C. E. González-Espinoza and M. Scheurer, "Fdetaco," <https://github.com/crisely09/taco-1> (2021).
- ⁴⁰Q. Sun, T. C. Berkelbach, N. S. Blunt, G. H. Booth, S. Guo, Z. Li, J. Liu, J. D. McClain, E. R. Sayfutyarova, S. Sharma, S. Wouters, and G. K. Chan, "PySCF: the Python-based simulations of chemistry framework," *Wiley Interdisciplinary Reviews: Computational Molecular Science* **8**, e1340 (2017).
- ⁴¹T. A. Wesolowski, *Journal of the American Chemical Society* **126**, 11444–11445 (2004).
- ⁴²T. A. Wesolowski, *The Journal of Chemical Physics* **140**, 18A530 (2014).
- ⁴³E. Engel and R. M. Dreizler, *Appendix A from Density Functional Theory: An Advanced Course*, 1st ed. (Springer Berlin, Heidelberg, 2011).
- ⁴⁴W. Strauss, *Partial Differential Equations: An Introduction.*, 2nd ed. (John Wiley & Sons, Inc., 2008) Chap. 7.