A non–decomposable approximation on the complete density function space for the non–additive kinetic potential

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A new non–decomposable approximation of the non–additive kinetic energy potential (NAKEP) is constructed starting from the same exact property in the limit ($\rho_A \to 0$ and $\int \rho_B = 2$) as introduced in [Lastra et al, J. Phys. Chem. 129, (2008) 074107]. In order to cover the complete function space for exponentially decaying densities, the kernel of a differential operator $D_\gamma[\rho]$ is introduced and analyzed in dependence of γ. The conclusive choice of $\gamma = 1$ assures that the solution functions span the complete space of molecular electron densities. As a result, the new approximant preserves the desired feature of the older approximation, which is the reciprocal singularity if the electron density decays exponentially, and eliminates artificial shallow wells (holes), which were responsible for an artificial "charge leak". Numerical considerations using the standard validation procedure introduced by Wesolowski and Weber, Chem. Phys. Letters 248, (1996) 71, demonstrate the numerical performance of the developed approximation, which increases the range of applicability of semilocal functionals.

I. INTRODUCTION

Treating a chemical system numerically has been a challenge for many decades now. The tradeoff between computational cost and accuracy will always be a guiding force for the development of any new methodology in this domain. One of the first accomplishments in this field has been the well known adiabatic approximation from Born and Oppenheimer[1] which established the fully electronic treatment of any chemical system. Any nuclei geometry dependence can be hence omitted throughout the notation due to the fixed external nuclear potential. When it comes to improve the accuracy only in specific areas without increasing heavily the overall computational cost, multiscale methods, such as the commonly known QM/MM, provide many advantages. Especially the electronic structure can be modeled in some well–defined region in space of direct relevance. The effect of the chemical system outside of this selected region is taken into account by an embedding potential. Such a division is adequate to simulate ionic solids, liquids, molecular crystals, and clusters of molecules, for instance, where the system of interest is embedded in an environment. The quantum chemical theory consists in many strategies how the environment is modeled properly, i.e. how the embedding potential is constructed.

In the following expressions, atomic units are applied in all formulas which are given for the spin–unpolarized case. Separating the total system to the embedded species A and the environment B represented by its densities ρ_A and ρ_B, one can use the Hohenberg–Kohn (HK) theorems[2] and apply the Kohn–Sham (KS) formalism[3]. The underlying density function spaces are exactly determined by the properties of the HK energy functional[4]: $\rho_A^{1/2}, \rho_B^{1/2} \in H^1 = \{\rho \in L^2 | \nabla\rho \in (L^2)^3\}$. ($L^2$ is the space of functions which are square integrable). For a given external potential v_{AB} and a frozen ρ_B, the minimization of the HK energy functional $E_{v_{AB}}^{HK}[\rho_A + \rho_B]$ with respect to the embedded density ρ_A, can be achieved by a suitable multiplicative potential[5-7]. Here, the constrained search within Frozen Density Embedding Theory (FDET) leads to an exact expression of such an embedding potential which is orbital–free, i.e. it does not involve other descriptors of the environment than its electron density[5,6]:

$$v_{emb(v_B)}^{FDET}[\rho_A, \rho_B](\boldsymbol{r}) := v_B(\boldsymbol{r}) + \int \frac{\rho_B(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta}{\delta\rho_A} E_{xcT}^{nad}[\rho_A, \rho_B](\boldsymbol{r}).$$
(1)

For a given nuclear potential ($v_B(\boldsymbol{r})$) generated by subsystem B, $v_{emb(v_B)}^{FDET}[\rho_A, \rho_B](\boldsymbol{r})$ is an explicit functional evaluated at every point in space $\boldsymbol{r} \in \mathbb{R}^3$. We also recognize in definition (1) the electrostatic contribution by the electronic density of system B and the functional derivative with respect to the embedded density ρ_A of the non–additive exchange–correlation kinetic energy contribution. Let us have a closer look at the last term; it consists of two functionals, the non–additive exchange–correlation energy and the non–additive kinetic energy (NAKE), which are implicitly defined after the Levy constrained search[8]:

$$E_{xcT}^{nad}[\rho_A, \rho_B] := E_{xc}^{nad}[\rho_A, \rho_B] + T_s^{nad}[\rho_A, \rho_B] \quad \text{with}$$

$$E_{xc}^{nad}[\rho_A, \rho_B] := E_{xc}[\rho_A + \rho_B] - E_{xc}[\rho_A] - E_{xc}[\rho_B], \quad (2)$$

$$T_s^{nad}[\rho_A, \rho_B] := T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B]. \quad (3)$$

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We define the non–additive exchange–correlation and non–additive kinetic energy potential (NAKEP) as the derivative with respect to ρ_A

$$v_{\mathrm{xc}}^{\mathrm{nad}}[\rho_A,\rho_B] := \frac{\delta}{\delta\rho_A} E_{\mathrm{xc}}^{\mathrm{nad}}[\rho_A,\rho_B]$$

$$= \frac{\delta}{\delta\rho} E_{\mathrm{xc}}[\rho]\Big|_{\rho=\rho_A+\rho_B} - \frac{\delta}{\delta\rho} E_{\mathrm{xc}}[\rho]\Big|_{\rho=\rho_A}, \quad (4)$$

$$v_t^{\mathrm{nad}}[\rho_A,\rho_B] := \frac{\delta}{\delta\rho_A} T_s^{\mathrm{nad}}[\rho_A,\rho_B]$$

$$= \frac{\delta}{\delta\rho} T_s[\rho]\Big|_{\rho=\rho_A+\rho_B} - \frac{\delta}{\delta\rho} T_s[\rho]\Big|_{\rho=\rho_A}. \quad (5)$$

Both are given in the functional derivative of the non–additive exchange–correlation kinetic energy contribution

$$\frac{\delta}{\delta\rho_A} E_{\mathrm{xcT}}^{\mathrm{nad}}[\rho_A,\rho_B] = v_{\mathrm{xc}}^{\mathrm{nad}}[\rho_A,\rho_B](\boldsymbol{r}) + v_t^{\mathrm{nad}}[\rho_A,\rho_B](\boldsymbol{r}). \quad (6)$$

This orbital–free functional is used in many multiscale methods. Such simulations aim for the electronic properties of a target subsystem A whereas the environment is simplified with respect to various representations of ρ_B[9–15]. Other traditional wave–function based models can be combined with the use of an orbital–free effective embedding potential[6]. In general the non–additive kinetic energy and exchange–correlation components constitute the most important and crucial difference between KS potentials and the multiscale FDET approach.

However the exact analytic expressions of $v_t^{\mathrm{nad}}[\rho_A,\rho_B]$ and $v_{\mathrm{xc}}^{\mathrm{nad}}[\rho_A,\rho_B]$ are not known and consequently we are limited to the use of approximations (in this work denoted with a tilde $\tilde{v}_t^{\mathrm{nad}}[\rho_A,\rho_B]$ or $\tilde{v}_{\mathrm{xc}}^{\mathrm{nad}}[\rho_A,\rho_B]$). As a result one has to deal with non–electrostatic induced errors. Those affect all quantities which are directly obtained by the inner product with the optimized density, e.g. electronic properties such as total dipole moments. In other words, the Levy constrained search on function spaces is governed by the applied approximated potential, which determines the range of admissible electron densities. We will focus on the approximation of NAKEs and NAKEPs in our work.

Typically NAKEPs are derived from semilocal or local kinetic energy density functionals[9,16,17], which we call top–down models. Here the parent functional is given and the corresponding terms such as the NAKEP and the NAKE can be computed directly. There has been also recent development on nonlocal expansion of the functional[18,19]. In the present work we want to explore the bottom-up strategy for semilocal functional derivatives and their functionals. The objective is not the approximation of the NAKEP $v_t^{\mathrm{nad}}[\rho_A,\rho_B](\boldsymbol{r})$ evaluated for some particular $\rho_A(\boldsymbol{r})$ and $\rho_B(\boldsymbol{r})$, but an approximation to the functional, i.e. to the correspondence between the $v_t^{\mathrm{nad}}[\rho_A,\rho_B](\boldsymbol{r})$ and the pair of functions $\rho_A(\boldsymbol{r})$ and $\rho_B(\boldsymbol{r})$. This precludes the use of any explicit dependency on position in such approximations.

The idea of a bottom up approach dates, for instance, back to the work of Leeuwen and Baerends[20], where an exchange–correlation potential was introduced in order to impose the correct asymptotic behavior. Their paradigm of the direct construction of a potential by targeting certain observable properties was the starting point for the future scientific development on this strategy. Later, a direct modification to the kinetic energy potential was proposed by Chai and Weeks[21]. They manage to prove that replacing the contribution of unphysical terms with a proper choice of parameters improves globally the obtained densities. It was not until in the work of Lastra et al.[22] that a so–called non–decomposable ansatz was introduced and discussed in an embedded scheme method. Imposing exact limit conditions created a new non–decomposable approximant for the NAKEP depending on first and second order derivatives (NDSD) $\tilde{v}_t^{\mathrm{nad(NDSD)}}[\rho_A,\rho_B]$. Even if the NAKE could be obtained for the original NDSD potential, a corresponding parent functional $\tilde{T}_s[\rho]$ is analytically not derivable. Thus, this bottom–up construction is not top–down reversible. Its theoretical principles provide the background motivation in the current work. More recent developments[23] also show that non–decomposable methods provide very good results when analyzing specific properties directly related to the embedded electron density.

The above considerations suggest the two following approaches for the development of approximations:

$$\mathrm{top-down}: \qquad \tilde{T}_s[\rho] \longrightarrow \tilde{T}_s^{\mathrm{nad}}[\rho_A,\rho_B] \longrightarrow \tilde{v}_t^{\mathrm{nad}}[\rho_A,\rho_B] \quad (7)$$

or

$$\mathrm{bottom-up}: \quad \tilde{v}_t^{\mathrm{nad}}[\rho_A,\rho_B] \longrightarrow \tilde{T}_s^{\mathrm{nad}}[\rho_A,\rho_B] \overset{\text{if decomposable } \tilde{T}_s^{\mathrm{nad}}}{\longrightarrow} \tilde{T}_s[\rho] \quad (8)$$

The Top–down strategy starts by constructing an approximant $\tilde{T}_s[\rho]$ and uses it for the formulas (3) and (5). The resulting non–additive kinetic bifunctional will be referred to as decomposable since the analytic form for the relevant kinetic energy component ($\tilde{T}_s[\rho]$) is accessible. On the other hand, a direct bottom–up definition of approximants $\tilde{v}_t^{\mathrm{nad}}[\rho_A,\rho_B]$ and $\tilde{T}_s^{\mathrm{nad}}[\rho_A,\rho_B]$ is called non–decomposable if the corresponding parent functional, i.e. the kinetic energy approximant $\tilde{T}_s[\rho]$, is analytically not derivable.

In section II, we illustrate approximants for a decomposable NAKE (and NAKEP) from the literature. In subsection II.B we will show the derivation of the NDSD potential from reference [22] along with its undesired features. The next section III deals with the analysis of a ordinary differential operator and its kernel space. As a result, in section IV, we propose a new bottom–up construction of a NAKEP approximant. In subsection IV.A, we develop a suitable switching function, while in subsection IV.B, we present the final new non–decomposable potential. In section V, we discuss our new approximant in comparison to other models. Finally, in section VI, numerical considerations with several systems of interest will be used to evaluate the performance compared to other semilocal approximations.

II. DECOMPOSABLE AND NON–DECOMPOSABLE APPROXIMATIONS

In this section, we will highlight some main NAKEs and NAKEPs approximations and then focus on the non–decomposable NDSD functional from the Lastra et al. publication[22], which will be derived and discussed in a mathematically detailed manner.

II.A. Decomposable Approximants from gradient expansion

We will briefly review the most important aspects for gradient expansion based constructions of NAKEP approximants. All those potentials have in common that the functional for the approximation of the kinetic energy is given explicitly and the associated analytic expression for $\tilde{v}_t^{\mathrm{nad}}[\rho_A, \rho_B]$ is derived beforehand. For kinetic energy approximants which are local or semilocal in ρ, the computation of the functional derivative (see eq. (5)) can be performed directly. There has been continuous effort in developing approximations to the kinetic energy functional $T_s[\rho]$ in orbital–free models. It dates back to the scientific achievements of Thomas and Fermi[24,25]. Truncation up to higher order gradients leads to the first steps of expansion methods, see for example the formulas up to fourth order in the work from Golub and Manzhos[26].

The Thomas–Fermi[24,25] (TF) kinetic energy functional, which is exact for the uniform electron gas,

$$\tilde{T}_s^{\mathrm{TF}}[\rho] := C_{\mathrm{TF}} \int \rho^{5/3}, \qquad (9)$$

(where $C_{\mathrm{TF}} = \frac{3}{10}(3\pi^2)^{2/3}$) provides a sophisticated theory for a decomposable NAKE approximant,

$$\tilde{T}_s^{\mathrm{nad(TF)}}[\rho_A, \rho_B] := C_{\mathrm{TF}} \int \left((\rho_A + \rho_B)^{5/3} - \rho_A^{5/3} - \rho_B^{5/3} \right). \qquad (10)$$

The resulting approximant for the NAKEPs reads

$$\tilde{v}_t^{\mathrm{nad(TF)}}[\rho_A, \rho_B] := \frac{5}{3} C_{\mathrm{TF}} \left((\rho_A + \rho_B)^{2/3} - \rho_A^{2/3} \right). \qquad (11)$$

For one–electron ($\int \rho = 1$) or two–electron spin–compensated ($\int \rho = 2$) systems, the so–called von Weizsäcker[27,28] functional

$$\tilde{T}_s^{\mathrm{W}}[\rho] := \frac{1}{8} \int \frac{|\nabla \rho|^2}{\rho} \qquad (12)$$

is exact. The corresponding non–additive terms[29] are

$$\tilde{T}_s^{\mathrm{nad(W)}}[\rho_A, \rho_B] = -\frac{1}{8} \int \frac{|\rho_A \nabla \rho_B - \rho_B \nabla \rho_A|^2}{\rho_A \rho_B (\rho_A + \rho_B)} \qquad (13)$$

and the associated functional derivative is

$$\tilde{v}_t^{\mathrm{nad(W)}}[\rho_A, \rho_B] = \frac{1}{8} \left[\frac{|\nabla(\rho_A + \rho_B)|^2 - 2(\rho_A + \rho_B)\nabla^2(\rho_A + \rho_B)}{(\rho_A + \rho_B)^2} \right.$$
$$\left. - \frac{|\nabla \rho_A|^2 - 2\rho_A \nabla^2 \rho_A}{\rho_A^2} \right], \qquad (14)$$

which can be also found in reference [5].

For slowly varying densities, the gradient expansion approximation up to second order[5] (GEA2) is given as

$$\tilde{T}_s^{\mathrm{GEA2}}[\rho] := \tilde{T}_s^{\mathrm{TF}}[\rho] + \frac{1}{9} \tilde{T}_s^{\mathrm{W}}[\rho], \qquad (15)$$

where we use the expression from (9) and (12). For the non–additive formula we just need to combine the definitions (10) and (13):

$$\tilde{T}_s^{\mathrm{nad(GEA2)}}[\rho_A, \rho_B] := \tilde{T}_s^{\mathrm{nad(TF)}}[\rho_A, \rho_B] + \frac{1}{9} \tilde{T}_s^{\mathrm{nad(W)}}[\rho_A, \rho_B] \qquad (16)$$

and the total functional derivative becomes

$$\tilde{v}_t^{\mathrm{nad(GEA2)}}[\rho_A, \rho_B] = \tilde{v}_t^{\mathrm{nad(TF)}}[\rho_A, \rho_B] + \frac{1}{9} \tilde{v}_t^{\mathrm{nad(W)}}[\rho_A, \rho_B]. \qquad (17)$$

Overall those conventional models satisfy the following two exact conditions:

(a) $T_s^{\mathrm{nad}}[\rho_A, \rho_B] = 0$ for nonoverlapping ρ_A and ρ_B.

(b) For uniform ρ_A and ρ_B, they recover the exact analytical expression for $T_s^{\mathrm{nad}}[\rho_A, \rho_B]$.

Note that so far we have not made any comments about the overlap between the electronic densities of the embedded system ρ_A and the environement ρ_B. In particular, having nonoverlapping densities is not a necessary condition in the exact functional case in order to satisfy the Hohenberg–Kohn theorems. They are sufficient however for the approximations of the non–additive functionals since those ought to vanish in that limit case[30]. Thus the desire to satisfy rigorously those conditions arises naturally.

Now all of those decomposable approaches, i.e. choices of approximant $\tilde{T}_s[\rho]$, lack (or just partly recover) the exact analytic form in the limit characteristic[22]. Such local conditions for $v_t^{\mathrm{nad}}[\rho_A, \rho_B]$ cannot be directly imposed on the parent energy functional approximant $\tilde{T}_s[\rho]$. The bottom–up approach of the construction of $\tilde{v}_t^{\mathrm{nad}}[\rho_A, \rho_B]$ is able to impose those conditions within a non–decomposable framework.

II.B. Building–in the exact local behavior of the NAKEP

The main motivation to use a bottom–up approach is the fact that exact properties of $v_t^{\mathrm{nad}}[\rho_A, \rho_B]$ can be satisfied a priori by generating a desired potential $\tilde{v}_t^{\mathrm{nad}}[\rho_A, \rho_B]$. The conditions are then automatically induced on the resulting electron densities due to the Levy–constrained search formalism[8]. Furthermore, recent studies on gradient–depending expansions have also shown that there is no correlation between the accuracy of $\tilde{T}_s^{\mathrm{nad}}[\rho_A, \rho_B], \tilde{v}_t^{\mathrm{nad}}[\rho_A, \rho_B]$ and the errors in the parent gradient–dependent approximation to $\tilde{T}_s[\rho]$[13]. We only demand the conditions for the exact analytic form (a)

and (b) to be obeyed and hence the construction can arise from already existing decomposable gradient expansion based NAKEP approximants.

Now as a key element for a non–decomposable approximant, we will use the following additional limit conditions[22]:

(c) Local exactness of $v_t^{\mathrm{nad}}[\rho_A,\rho_B]$ for vanishing embedded density $\rho_A \to 0$.

(d) Two tightly bound electrons in the environment $\int \rho_B = 2$.

Starting from the general definition for $v_t^{\mathrm{nad}}[\rho_A,\rho_B]$ in (5), one can apply directly condition (c)

$$v_t^{\mathrm{nad}}[\rho_A,\rho_B] \overset{(c)}{\to} v_t^{\mathrm{nad}}[0,\rho_B] = \frac{\delta}{\delta\rho}T_s[\rho]\Big|_{\rho=\rho_B},$$

$$v_t^{\mathrm{limit}}[\rho_B] := \frac{\delta}{\delta\rho}T_s[\rho]\Big|_{\rho=\rho_B} \qquad (18)$$

where we defined the limit potential $v_t^{\mathrm{limit}}[\rho_B]$. It should be stressed here that this limit approximant does only depend on ρ_B, thus it is completely independent of the embedded system. The result in (18) allows us now to directly derive that limit potential as the functional derivative of $\tilde{T}_s[\rho]$ evaluated at any environmental electronic density obeying condition (d). For instance, in two–electron–spin–compensated systems the exact kinetic energy is the von-Weizsäcker functional[27,28] (see eq. (12))

$$\tilde{T}_s[\rho] = \tilde{T}_s^W[\rho] = \frac{1}{8}\int\frac{|\nabla\rho|^2}{\rho} \qquad \text{for } \int\rho = 2. \quad (19)$$

Therefore using functional calculus yields

$$v_t^{\mathrm{limit}}[\rho_B] \overset{(d)}{=} \frac{\delta}{\delta\rho}\tilde{T}_s^W[\rho]\Big|_{\rho=\rho_B} = \frac{1}{8}\frac{|\nabla\rho|^2 - 2\rho_B\nabla^2\rho_B}{\rho_B^2}. \quad (20)$$

This limit form for the NAKEP is exact in the domain where the desired local properties (c) and (d) hold. If ρ_B is represented by a doubly occupied hydrogenic $1s$ function, i.e. it is spherical symmetric ($\rho_B(\boldsymbol{r}) = \rho_B(r)$, where r denotes the euclidean norm of $\boldsymbol{r}\in\mathbb{R}^3$ as the distance to the nucleus in B), one can evaluate $v_t^{\mathrm{limit}}[\rho_B](\boldsymbol{r})$ explicitly at any point in space,

$$v_t^{\mathrm{limit}}[\rho_B](\boldsymbol{r}) = \frac{1}{8}\frac{|\nabla\rho(\boldsymbol{r})|^2 - 2\rho_B(\boldsymbol{r})\nabla^2\rho_B(\boldsymbol{r})}{\rho_B(\boldsymbol{r})^2}$$

$$= \frac{1}{8}\frac{\rho_B'(r)\rho_B'(r) - 2\rho_B(r)\rho_B''(r)}{\rho_B(r)^2} - \frac{1}{2}\left(\frac{\rho_B'(r)}{\rho_B(r)}\right)\frac{1}{r}. \quad (21)$$

Especially for $\rho_B^{1s}(\boldsymbol{r}) := \rho_B^{1s}(r) = 2(\zeta^3/\pi)\exp(-2\zeta r)$ the formula simplifies to

$$v_t^{\mathrm{limit}}[\rho_B^{1s}](r) = \frac{\zeta}{r} - \frac{\zeta^2}{2}. \quad (22)$$

The former derivation with the effective nuclear charge ζ was similarly discussed in the publication by Lastra et al.[22]. It provides a local repulsive behavior for $r < 2/\zeta$ which is desired for the compensation of the Coulomb attraction due to the nuclear charge near the nuclear cusp. As a result, the following NAKEP approximant (denoted as NDSD) was first published in equation (22) in the work of Lastra et al.[22],

$$\tilde{v}_t^{\mathrm{nad(NDSD)}}[\rho_A,\rho_B] := \tilde{v}_t^{\mathrm{nad(TF)}}[\rho_A,\rho_B] + f^{\mathrm{NDSD}}(\rho_B)v_t^{\mathrm{limit}}[\rho_B]. \quad (23)$$

The approximant consists of a decomposable part, here the TF NAKEP. It lacks the desired limit conditions (c) and (d) and thus, NDSD provides a well–proven attempt to improve upon semilocal models. Furthermore, it incorporates a switching function $f^{\mathrm{NDSD}}(\rho_B)$ which restricts the activation of the limit potential to a local volume space. This feature ensures that any physical exact characteristic in the limit case which is missing in the decomposable potential, can be overcome by "activating" the limit potential. The restriction is also due to the fact that the reciprocal property is locally limited because of the negative constant shift in formula (22), which leads to a nonphysical well after the nuclear cusp. As a consequence, artificial charge leak might cause numerical instability with charged subsystems. On the other hand, the limit potential (21) shows clearly which term is responsible for the well in dependence of ρ_B. Therefore, a careful analysis of the functional and its density function domain, needs to be done.

III. ORDINARY DIFFERENTIAL OPERATOR D_γ

In this section, we consider a more general functional. Let

$$D_\gamma[\rho] := (\rho')^2 - \gamma\rho\rho'' \quad (24)$$

be an ordinary differential operator on the space of appropriate density functions[4] $H^1(\mathbb{R}_0^+)$ with $\gamma \in \mathbb{R}$. The attentive reader might have noticed now that this operator appears in the first term of the formula for the limit potential given in eq. (21) with $\gamma = 2$

$$v_t^{\mathrm{limit}}[\rho_B](r) = \frac{1}{8}\frac{D_2[\rho_B](r)}{\rho_B(r)^2} - \frac{1}{2}\left(\frac{\rho_B'(r)}{\rho_B(r)}\right)\frac{1}{r}. \quad (25)$$

In order to ensure that D_γ is well defined, we restrict the domain to at least twice continuous differentiable functions. Furthermore, we consider with the limit condition (d) a spherical symmetric electron density which reduces the volume space to the positive axis of real values.

Now the purpose of this new operator is to find its kernel, $\ker(D_\gamma)$, in dependence of γ. Then the first term on the right hand side in equation (25) will vanish. What is left will be the desired attractive potential without any unphysical well. In more general terms, this strategy

corresponds to the search of a homogeneous solution of a particular partial differential equation for the electron density. The condition for a ρ to be in $\ker(D_\gamma)$ is

$$0 = D_\gamma[\rho] = \rho'\rho' - \gamma\rho\rho'', \qquad (26)$$

which is nothing else then a second–order nonlinear ordinary differential equation on the one dimensional space. In the following, we are going to compute the general solution for different cases of γ. The result will give us some insight on how the parameter γ should be chosen in accordance with the given electron density function space.

Firstly, we exclude any trivial solution ($\rho \equiv 0$) since we are only interested in non–trivial densities. In the following derivation we use a similar methodology as it was used in reference [31]. Remember the derivative of a logarithmic function is given by $(\ln(\rho))' = \rho'/\rho$. Thus dividing (26) by $\rho\rho'$ we obtain

$$\frac{\rho'}{\rho} = \gamma\frac{\rho''}{\rho'} \;\Leftrightarrow\; (\ln(\rho))' = \gamma\big(\ln(\rho')\big)'.$$

Now, integrating on both sides yields

$$\ln(\rho) = \gamma(\ln(\rho') + C_1), \qquad C_1 \in \mathbb{C}$$

We introduce another constant for the second therm on the right side, since it is stationary in ρ: $\ln(k) = C_1$ for some $k \in \mathbb{C}\setminus\{0\}$. Hence

$$\ln(\rho) = \gamma\big(\ln(\rho') + \ln(k)\big) = \ln((\rho'\cdot k)^\gamma)$$
$$\Leftrightarrow \qquad \rho = (\rho'\cdot k)^\gamma \qquad\qquad (27)$$

and due to the fact that the electron density is a positive function[4], we have to restrict the constant to the real space $k \in \mathbb{R}\setminus\{0\}$. Eq. (27) is now a first–order non–linear differential equation in ρ which can be solved in dependence of γ. There will be several cases for γ to account for:

(i) $\gamma = 0$.

It follows from eq. (27) $\rho = (\rho'\cdot k)^0 = 1$ and thus the general solution has to be a constant function $\rho(r) = C$ for $C \in \mathbb{R}$.

(ii) $\gamma = 1$.

We can use again the derivative of the logarithm for eq. (27)

$$\rho = (\rho')\cdot k \;\Leftrightarrow\; k^{-1} = \rho'/\rho \;\Leftrightarrow\; k^{-1} = (\ln(\rho))'.$$

Both sides can be integrated with respect to $r \in \mathbb{R}_0^+$

$$rk^{-1} = \ln(\rho) + C_2, \qquad C_2 \in \mathbb{R}.$$
$$\Leftrightarrow \rho(r) = e^{r/k - C_2} = e^{r/k}\cdot K,$$

where we substituted the constant $e^{-C_2} = K \in \mathbb{R}$. Thus, the general solution for $\gamma = 1$ has to be

$$\rho(r) = Ke^{r/k} \text{ with } K \in \mathbb{R} \text{ and } k \in \mathbb{R}\setminus\{0\}, \qquad (28)$$

i.e. all solutions to eq. (27) with $\gamma = 1$ are given by a linear combination of (28).

(iii) $\gamma \in \mathbb{R}\setminus\{0,1\}$.

This third and last case for γ involves a differential equation (27) which can be solved by separation of variables. For this strategy we first divide both sides with ρ and then isolate the constant term on one side: $\rho = (\rho'\cdot k)^\gamma \Leftrightarrow \frac{\rho'^\gamma}{\rho} = k^{-\gamma} \Leftrightarrow \frac{\rho'}{\rho^{1/\gamma}} = k^{-1}$. Now one can integrate on both sides and use the substitution rule for integrals

$$\int^\rho u^{-\frac{1}{\gamma}}du \;=\; \int^r k^{-1}ds$$
$$\overset{\gamma\neq 1}{\Leftrightarrow} \left(1 - \tfrac{1}{\gamma}\right)^{-1}\rho^{1-\frac{1}{\gamma}} = (rk^{-1} + C_3), \qquad C_3 \in \mathbb{R}$$
$$\Leftrightarrow \left(\tfrac{\gamma-1}{\gamma}\right)^{-1}\rho^{\frac{\gamma-1}{\gamma}} = (rk^{-1} + C_3)$$
$$\Leftrightarrow \rho^{\frac{\gamma-1}{\gamma}} = \left(\tfrac{\gamma-1}{\gamma}\right)\big[(rk^{-1} + C_3)\big]$$
$$\Leftrightarrow \rho = \rho(r) = \left[\left(\tfrac{\gamma-1}{\gamma}\right)\big[(rk^{-1} + C_3)\big]\right]^{\frac{\gamma}{\gamma-1}}.$$

Finally, the general solution are power functions

$$\rho(r) = A\left[\left(\frac{\gamma-1}{\gamma}\right)\big[rk^{-1} + C_3\big]\right]^{\gamma/(\gamma-1)} \qquad (29)$$

with $A \in \mathbb{R}$. For instance if $\gamma = 2$ (corresponding to the case in eq. (25)) the solution space consists of quadratic functions of the form

$$\rho(r) = A\left(\frac{r}{2k} + \frac{1}{2}C_3\right)^2.$$

So far, we concentrated only on densities which are twice differentiable but we need to maintain also the restriction of the integrability in order to find the kernel in the set of appropriate density functions. In the first case (i), it is quite obvious that the constant function has to be trivial ($\rho \equiv 0$) if the solution ought to be integrable on the whole real axis. A similar result ($\rho \equiv 0$) is obtained in the last case (iii) because the exponent of the power functions is either strictly positive or negative.

Only in the second case (ii) we can find a nontrivial integrable solution because the functions are exponentially decaying if the constant in the exponent k is negative. Using $k^+ := -k$ the general solution becomes

$$\rho(r) = Ke^{-r/k^+}, \qquad K \in \mathbb{R}.$$

Consequently, only the following kernel function space for $\gamma = 1$

$$\ker(D_1) = \{\rho \geq 0 |\; \rho(r) = Ke^{-r/k^+}, K \in \mathbb{R} \text{ and } k^+ > 0\} \qquad (30)$$

displays the nontrivial part of the domain of our differential operator $D_1[\rho]$, but this result is far more than a mathematical triviality.

We introduced $D_\gamma[\rho]$ inside the limit potential $v_t^{\text{limit}}[\rho_B]$ in order to tackle the unphysical well caused by the first term (see eq. (25)). Here $\gamma = 2$ was used, although the corresponding kernel space $\ker(D_2)$ consists only of trivial functions (see consequence of case (iii)). Thus, the electron density function determines the vanish of the unphysical term (see eq. (22)) provided that it lies in the associate kernel space. Only $\gamma = 1$ is applicable in order to allow nontrivial functions. In fact, we obtain more than that if we observe the exact decay of electronic densities. Every density function which is optimized in terms of the Levy–constrained search[8] obeys an exponential decay[32]. Its exact form is not as relevant as the immediate implication for such a density in the domain of $D_1[\rho]$. Clearly, the kernel $\ker(D_1)$ contains all exponentially decaying functions (see (30)) so every appropriate electron density will be in the kernel as well. The conclusive choice of $\gamma = 1$ respects the exact function space for environmental electron densities ρ_B in the limit case which will lead to $D_1[\rho_B] = 0$, and thus, it avoids any unphysical well. It is also worthwhile to notice that the kernel of an operator plays an important role for the potential in a self–consistent manner[8] because it is connected to its range. In the following section, we will implement that choice $\gamma = 1$ in a formula for an approximant of $v_t^{\text{nad}}[\rho_A, \rho_B]$.

IV. CONSTRUCTION OF A NEW NON–DECOMPOSABLE NAKEP

While our construction maintains the non–decomposable nature, we move the paradigm from imposing limit conditions to respecting admissible density function spaces. This bottom–up strategy builds on mathematical results about the involved operators, such as it has been shown in section III.

We apply the same formula as for the NDSD approximant (see eq. (23)), which was first published in equation (15) in the work of Lastra et al.[22],

$$\tilde{v}_t^{\text{nad}}[\rho_A, \rho_B] := \tilde{v}_t^{\text{decomposable}}[\rho_A, \rho_B] + f[\rho_A, \rho_B]v_t^{\text{limit}}[\rho_B]. \tag{31}$$

All the above functionals ought to be local or semilocal in ρ_A and ρ_B. The $v_t^{\text{limit}}[\rho_B]$ potential is referred to (20) in section II.B by imposing the exact limit conditions (c) and (d). The first term on the right side in eq. (31) $\tilde{v}_t^{\text{decomposable}}[\rho_A, \rho_B]$ is a placeholder for any conventional decomposable potential presented in section II.A. Lastly, the physical meaning of the functional $f[\rho_A, \rho_B]$ is a function that switches the limit potential "on" and "off".

In our model, we replace the non–decomposable limit potential $v_t^{\text{limit}}[\rho_B]$ with the one which uses the general expression with the γ parameter

$$v^\gamma[\rho_B] := \frac{1}{8}\frac{|\nabla\rho|^2 - \gamma\rho_B\nabla^2\rho_B}{\rho_B^2}, \tag{32}$$

and with a spherical symmetric density this potential becomes explicit in r,

$$v^\gamma[\rho_B](r) = \frac{1}{8}\frac{D_\gamma[\rho_B](r)}{\rho_B(r)^2} - \frac{\gamma}{4}\left(\frac{\rho_B'(r)}{\rho_B(r)}\right)\frac{1}{r}, \tag{33}$$

where we used the differential operator $D_\gamma[\rho]$ from (24). The resulting parametrized NAKEP approximant becomes

$$\tilde{v}_t^{\text{nad}(\gamma)}[\rho_A, \rho_B] := \tilde{v}_t^{\text{decomposable}}[\rho_A, \rho_B] + f[\rho_A, \rho_B]v^\gamma[\rho_B]. \tag{34}$$

In section III, we established a value of $\gamma = 1$ in order to postulate a nontrivial kernel of $D_\gamma[\rho]$, which lies in the space of admissible electron density functions. Hence, our new potential in (32) will be

$$v^1[\rho_B] = \frac{1}{8}\frac{|\nabla\rho_B|^2 - \rho_B\nabla^2\rho_B}{\rho_B^2} \tag{35}$$

or in the explicit form (see eq. 33)

$$v^1[\rho_B](r) = -\frac{1}{4}\left(\frac{\rho_B'(r)}{\rho_B(r)}\right)\frac{1}{r}. \tag{36}$$

With the fixed choice of $\gamma = 1$, the new NAKEP approximant from (34) reads

$$\tilde{v}_t^{\text{nad}(\gamma=1)}[\rho_A, \rho_B] = \tilde{v}_t^{\text{decomposable}}[\rho_A, \rho_B] + f[\rho_A, \rho_B]v^1[\rho_B], \tag{37}$$

where the non–decomposable part $v^1[\rho_B]$ will now obey the complete space of admissible densities. Formula (37) presents now a new non–decomposable NAKEP approximant which was build with the bottom–up strategy using mathematical results about the density function spaces. Note that this new approximant $\tilde{v}_t^{\text{nad}(\gamma=1)}[\rho_A, \rho_B]$ does not obey the exact limit conditions (c) and (d), which were used for the NDSD model (see section V). In the next step, we will design a suitable switching functional $f[\rho_A, \rho_B]$.

IV.A. Developing a suitable switching function f

It is important to note that our goal is to construct a function $f = f[\rho_A, \rho_B]$ and not just a functional. For the attentive reader the difference is nontrivial because a functional just projects a function space on the real (or complex) axis. On the other hand, the range of a function provides another function space which can be explicitly evaluated at any point in space. The latter is desired in the definition of the approximant $\tilde{v}_t^{\text{nad}(\gamma)}[\rho_A, \rho_B]$ (see eq. (34)) since the potential itself is also a function in ρ_A and ρ_B. By its appearance in equation (37), the role of the switching function is completely determined and thus, it has to satisfy some important rigorous properties along the new functional $v^1[\rho_B]$:

(i) From the formula for $v^1[\rho_B]$ in equation (35) one can detect a singular behavior in volume spaces where

the environmental density ρ_B is getting small. Here the factor role of the function $f[\rho_A, \rho_B]$ can help to avoid this issue by "switching off" the potential where ρ_B is small:

$$f \to 0 \qquad \text{if} \qquad \rho_B \to 0.$$

This condition implies that the switching function can only depend on ρ_B: $f[\rho_A, \rho_B] = f[\rho_B]$, which is similar to the potential $v^1[\rho_B]$. Dependence on ρ_A is not needed in order to switch off the potential in regions where ρ_B is small.

(ii) The range of the switching function $f[\rho_A, \rho_B](\boldsymbol{r})$ should be between 0 to 1. Since FDET can also be used to obtain forces[13], a smooth switching is preferable. We demand continuity not only in ρ_B but also when evaluating $f[\rho_A, \rho_B](\boldsymbol{r})$ in every point $\boldsymbol{r}$ in volume space.

(iii) Stationary points at the edges

$$\nabla_{\boldsymbol{r}} f[\rho_A, \rho_B](\boldsymbol{r})\Big|_{r \to \infty} = 0 \text{ and } \nabla_{\boldsymbol{r}} f[\rho_A, \rho_B](\boldsymbol{r})\Big|_{r \to 0} = 0,$$

affirm that the switching happens only in the desired volume space and that anything outside is fixed to one state. Note that this property is directly related to the form of the density function because the explicit computation of the gradient happens after the realization of the function with a given ρ_B. So far we have not made any restrictions on the shape of ρ_B apart from the affiliation to appropriate integrable function spaces. Here it is convenient for the final construction of $f(\rho_B)$ to consider exponentially decaying densities[32].

(iv) There exists only one inflection point $\boldsymbol{r}_0 \in \mathbb{R}^3$ for $f[\rho_A, \rho_B](\boldsymbol{r})$. As a result, the switching takes place only once and it is bound to a specific volume range. Furthermore this condition limits the second spatial derivative in the relevant space.

We now define a suitable switching function obeying all the above properties. One remarks that the conditions (ii)–(iv) infer a specific class of mathematical functions which are called sigmoid-like smooth step functions. There exists already a good theoretical foundation as well as many applications, such as deep learning[33], for this famous class of functions. In particular, the Fermi–Dirac statistics formula corresponds to this class as well. It was used in the work of Lastra et al.[22]. We focus here on a different $f[\rho_B]$ whose construction is based on the use of the new potential $v^1[\rho_B]$. It does not need any special restriction on the volume space apart from the one given by (i) and thus, we can choose a switching function with as few parameters as possible. Furthermore, its performance should not depend on the choice of ρ_B, i.e. it

should be chemical environment independent. Our final and simplest form for $f[\rho_B]$ reads

$$f[\rho_B] := \left(1 - e^{-\rho_B}\right). \tag{38}$$

One can easily check that the properties (i)–(iv) are satisfied by this switching function for the appropriate class of exponentially decaying electronic densities. In the next section we present the final form of the new NAKEP approximant.

IV.B. The NDCS potential

For the decomposable part in (37) we will use TF NAKEP from (11) because of the same reasoning as in the work by Lastra et al.[22]. We denote the final expression of the approximant as the NDCS functional, which is non–decomposable and satisfies the complete space of admissible density functions.

$$\tilde{v}_t^{\text{nad(NDCS)}}[\rho_A, \rho_B] := \tilde{v}_t^{\text{nad(TF)}}[\rho_A, \rho_B] + f^{\text{NDCS}}[\rho_B]v^1[\rho_B], \tag{39}$$

where $\tilde{v}_t^{\text{nad(TF)}}[\rho_A, \rho_B]$ is given in eq. (11), $f^{\text{NDCS}}[\rho_B] := f[\rho_B]$ is defined in (38) and $v^1[\rho_B]$ is from formula (35).

Since the switching function $f^{\text{NDCS}}[\rho_B]$ also only depends on ρ_B, its evaluation will have the same effort as $v^1[\rho_B]$. Furthermore, one can derive directly an analytic expression for the NAKE $\tilde{T}_s^{\text{nad(NDCS)}}[\rho_A, \rho_B]$ which yields $\tilde{v}_t^{\text{nad(NDCS)}}[\rho_A, \rho_B]$ after functional differentiation with respect to ρ_A,

$$\tilde{T}_s^{\text{nad(NDCS)}}[\rho_A, \rho_B] = \tilde{T}_s^{\text{nad(TF)}}[\rho_A, \rho_B] + \int f^{\text{NDCS}}[\rho_B]v^1[\rho_B]\rho_A + C[\rho_B], \tag{40}$$

where the first term on the right side is the TF NAKE in equation (10). $C[\rho_B]$ is a constant in ρ_A and for dissociation limit reasons it must vanish. We observe that $\tilde{T}_s^{\text{nad(NDCS)}}[\rho_A, \rho_B]$ satisfies rigorously conditions (a) and (b). The bottom–up definitions in (39) and (40) are non–decomposable because there exists no analytic parent kinetic energy functional $\tilde{T}_s[\rho]$. Although formula (40) can be used in order to study energy level effects, any discussion with energies compared to decomposable models is unsuitable here. All discrepancies can be attributed independently to the used NAKEP approximant or the used parent kinetic energy approximant. This is due to the non–electrostatic part not beeing homogeneous[34] and thus, it can not be evaluated directly with the embedding potential approximant.

V. COMPARISON TO OTHER APPROXIMANTS

The difference between the former NDSD approach in the work of Lastra et al.[22] and the present model is determined by the choice of γ. The small mathematical variation of the parameter from $\gamma = 2$ to $\gamma = 1$ leads to a significant change in the space of computed electron densities, or more precisely, spans the complete solution space for molecular electron densities. This reasoning highlights the alternative non–decomposable approach by imposing well–defined mathematical conditions, such as the density function space. The new functional $v^1[\rho_B]$ in the NDCS approximant is able to overcome the issue about unphysical wells while acting on this complete functional space of exponentially decaying environment densities. Although it does not satisfy rigorously the limit conditions (c) and (d), we still recover the desired reciprocal characteristic for exponentially decaying densities, while resolving the problematic about "charged holes" where the embedded electrons could leak into[35]. As a consequence, the NDCS model provides a numerically robust alternative within the non–decomposable framework.

Furthermore, we briefly elaborate on the bottom–up strategy from Chai and Weeks[21] concerning the Orbital-Free DFT methodology. They improved the TF model for the kinetic energy by an extension similar to the GEA2 model. Gradient dependent terms are introduced with a general parameter instead of the 1/9 factor in GEA2 (see formula (17)). Its final choice resembles our choice of $\gamma = 1$, although the final kinetic energy potentials are not similar. However, their derivation is physically motivated and does not involve any multiscale scheme and thus no non–additive terminology. In hindsight the result also yields exponentially decaying densities.

Recent developments have shown that nonlocal NAKEs[19] approximants improve computed interaction energies in comparison to conventional decomposable semilocal NAKEs approximants. In our work however, the NDCS functional establishes an extension of non–decomposable semilocal NAKEs approximants. It aims to improve direct properties related to the computed electron density while maintaining numerical robustness. Implementing nonlocal functionals in the same non–decomposable framework can not be done in a straight forward manner because it is not possible to identify a similar ordinary differential operator $D_\gamma[\rho]$ from (24). The derivation of an appropriate kernel from $v^1[\rho_B]$ needs, thus, to be considered. A careful analysis of this approach is currently addressed in our lab.

The functional $\tilde{v}_t^{\mathrm{nad(NDCS)}}[\rho_A, \rho_B]$ given in eq. (39) can now be evaluated explicitly in any point of space for the optimization of the embedded density function. Numerical validations, such as metrical distances or induced dipole moments, will provide the ground for a conclusive discussion in the upcoming sections.

VI. NUMERICAL VALIDATION AND DISCUSSION

The aim of this section is to measure the quality of the newly presented model by comparing the results to already established methods. We consider practical applications of eq. (41), where the embedded density depends on the environment as well as self–consistently on the approximant to the embedding potential. For the latter we can use the general procedure from one of our earlier publications[10,13] which was also established in the numerical validation of the work of Lastra et al.[22]. The two frameworks of Cortona[9] and Kohn and Sham[3] with fully variational formal results are applied for the numerical discussion of the approximant to the NAKEP $\tilde{v}_t^{\mathrm{nad}}[\rho_A, \rho_B]$. Thus, this FDET scheme constrains the optimization domain on v–representable noninteracting and pure–state densities[6]. As a result, we have to solve common one–electron eigenvalue equations (equations (20) and (21) in reference [5]),

$$\left[-\frac{1}{2}\nabla^2 + v^{\mathrm{KS}}[\rho_A] + v_{\mathrm{emb}(v_B)}^{\mathrm{FDET}}[\rho_A, \rho_B] \right] \phi_i^A = \varepsilon_i^A \phi_i^A \quad (41)$$

for $i = 1, \ldots, N^A$, where the resulting density of system A is constructed by $\rho_A = \sum_i^{N^A} |\phi_i|^2$ and $v^{\mathrm{KS}}[\rho_A]$ denotes the effective KS potential for system A evaluated at ρ_A. The FDET embedding potential $v_{\mathrm{emb}(v_B)}^{\mathrm{FDET}}[\rho_A, \rho_B]$ is given in eq. (1). Now the sum of those functionals in the eigenvalue equation (41) underline the difference to other effective potentials, e.g. the original KS model for the total system with ρ_{tot} ($v^{\mathrm{KS}}[\rho_{\mathrm{tot}}]$) or for the isolated system with ρ_{iso} ($v^{\mathrm{KS}}[\rho_{\mathrm{iso}}]$). With the use of approximations to the NAKEP in the formula for the embedded potential (6), we can solve now the eigenvalue problem (41) in dependence of the chosen approximant.

Other technical parameters, such as approximant to the exchange–correlation functional, basis sets for expanding orbitals, algorithms to calculate matrix elements, can be set equal for the direct link of any discrepancy to the NAKEP approximants. In order to obtain the final electron densities ρ_A^0 and ρ_B^0, which minimize the total energy in Cortona's type of calculations, a self–consistent supercycle of embedding calculations, Freeze-and-Thaw[11] (F&T), is performed. Here the one–electron equations for embedded orbitals (41) are solved in every iteration step, where ρ_A and ρ_B exchange their roles. The resulting F&T iterations continue until self–consistency. As a result, the notion of embedded system and environment becomes redundant since both densities are treated equally variational. This F&T method can be used to fully assess the $\tilde{v}_t^{\mathrm{nad}}[\rho_A, \rho_B]$ approximant.

It is important to point out here that this strategy is bound to the use of approximation models and thus, does not provide exact solutions a priori.

All computations are performed with one of the following NAKEP approximants: The original TF approximant $\tilde{v}_t^{\mathrm{nad(TF)}}[\rho_A, \rho_B]$ (see eq. (11)), the second order gradient expansion GEA2 $\tilde{v}_t^{\mathrm{nad(GEA2)}}[\rho_A, \rho_B]$ (see eq. (17)), the

NDSD approximant used in the work of Lastra et al.[22] $\tilde{v}_t^{\mathrm{nad(NDSD)}}[\rho_A,\rho_B]$ (see eq. (23)), and the new NDCS potential $\tilde{v}_t^{\mathrm{nad(NDCS)}}[\rho_A,\rho_B]$ (see eq. (39)).

We want to stress that the quality of the final FDET energy (see for instance formula (12) in reference [36]) is not directly correlated to the potential because the non–electrostatic functional $E_{\mathrm{xcT}}^{\mathrm{nad}}[\rho_A,\rho_B]$ is not homogeneous[34]. Other approximations to the exchange–correlation $(\tilde{v}_{\mathrm{xc}}^{\mathrm{nad}}[\rho_A,\rho_B])$ or the final choice of ρ_B contribute as well to the total energy error. On the other hand, the quality of a final electronic density will be directly determined by the approximant $\tilde{v}_t^{\mathrm{nad}}[\rho_A,\rho_B]$. As a consequence, we focus our study only on direct properties of the resulting densities.

The upcoming subsections will deal with different measures of quality as far as they are accessible from numerical methods, because in practice all quantities can only be obtained on a bounded volume space. Only global properties from the solution densities, such as the total norm of the difference or total dipole moments, will be observed. For numerical evaluation of the $\tilde{v}_t^{\mathrm{nad}}$–generated error, a representative set of intermolecular complexes including charged and non–charged examples is analyzed. All geometries were used at their equilibrium structure obtained from KS LDA/cc-pVTZ calculations with the Gaussian software package[37]: (i) LDA approximation of the exchange–correlation functional: The Slater exchange, $\rho^{4/3}$ with theoretical coefficient of $2/3$, also referred to as Local Spin Density exchange[2,3,38] and Functional V from reference [39] which fits the Ceperly-Alder solution to the uniform electron gas[40], and (ii) cc-pVTZ Dunning's correlation consistent basis set[41]. For the F&T computations within the FDET multiscale method we used the FDETaco library[42] based on the PySCF[43] program. The kinetic embedding potential approximants were numerically implemented using functions from PySCF. Thereby the density of each subsystem was expanded in a supermolecular manner[17] with the same basis set as in (ii). Also the same exchange-correlation functional as in (i) was used.

In the following sections we report the values, which are obtained after a successful convergence of the self–consistent supercycle of calculations (F&T). Consequently, the discussed observables corresponding to direct computational properties of the optimized densities, belong also to the conception of converged values.

VI.A. Acurracy of the NDCS densities

In this section, we are going to introduce a quality measure which is related to the mathematical object of a density function. The main motivation for this analysis comes from the derivation of the new potential $v^1[\rho_B]$ (35) in section III and IV. Here, considerations about the admissible function space provided the optimal value for the parameter $\gamma = 1$. Therefore, it seems natural to continue in the same spirit and use a mathematical tool in order to discuss the resulting functions in a global manner.

We recall from the Introduction I that the functional spaces for the densities are determined by the properties of the exact Hohenberg–Kohn energy functional, i.e. $\rho^{1/2} \in H^1$. Now it is a convenient fact that the so–called Sobolev space[44] H^1 is an inner product space with a given norm for integrable functions. In order to measure "distances" in the sense of functions, we can simply use the square of the H^1-norm[44] of the difference function. (Note that taking the square does preserve all desired norm properties.) For $\rho_1^{1/2}, \rho_2^{1/2} \in H^1$ this would be

$$\|(\rho_1-\rho_2)^{1/2}\|_{H^1}^2 = \int \left(|(\rho_1-\rho_2)^{\frac{1}{2}}|^2 + |\nabla(\rho_1-\rho_2)^{\frac{1}{2}}|^2 \right)$$
$$= \|(\rho_1-\rho_2)^{\frac{1}{2}}\|_{L^2}^2 + \|\nabla(\rho_1-\rho_2)^{\frac{1}{2}}\|_{L^2}^2. \quad (42)$$

As a simplification we will only use the first term on the right side in eq. (42) because the L^2–norm itself induces as well an inner product space $L^2(\mathbb{R}^3)$ of square integrable functions. It is worthwhile to point out that the information covered by the norm of the gradient is not negligible, especially in cases where the decaying behavior of the functions is significant. However, in our study we only investigate density functions which all ought to obey an exponential decay[32] so the L^2–norm expects to cover all conclusive deviation effects for a global measure of quality.

For the comparison between the full chemical system calculation and the two subsystems with the embedding potential, the total electronic density of interest needs to be evaluated. We set $\rho_{AB} = \rho_A + \rho_B$ (we leave it as an exercise to show $\rho_{AB}^{1/2} \in H^1$) as the electronic density of the total system using the subsystem densities ρ_A and ρ_B. ρ_{tot} will be referred to as the reference density obtained by a Kohn–Sham treatment of the total system. In numerical terms the subsystem densities are optimized by the supercycle of computations (F&T), evaluated on the same grid as the reference system and then combined for the generation of ρ_{AB}. The final distance measure reads

$$d(\rho_{AB},\rho_{\mathrm{tot}}) := \|(\rho_{AB}-\rho_{\mathrm{tot}})^{1/2}\|_{L^2}^2$$
$$= \int |\rho_{AB}-\rho_{\mathrm{tot}}| = \|\rho_{AB}-\rho_{\mathrm{tot}}\|_{L^1}. \quad (43)$$

The following results report the first four digits of this computed norm in atomic units for electron densities.

Tables I and II show the obtained $d(\rho_{AB},\rho_{\mathrm{tot}})$ values for a set of chosen charged and neutral systems, respectively. For comparison, we printed also the result for a completely isolated treatment of the subsystems. Any variational model which includes the electrostatic effect from the subsystems on each other ought to push the summed F&T density ρ_{AB} to the reference one ρ_{tot}. Thus we are able to observe the performance of the used approximant by analyzing the magnitude of this improvement. Thereby a lower value of the distance measure indicates a higher similarity between the density functions or in simpler words, the global error is smaller.

Table I. Distance measure (43) between the sum of the subsystem densities obtained from the F&T calculation and the total Kohn–Sham (KS) density. The multiscale optimization was performed with five different models $\tilde{v}_t^{\mathrm{nad}(x)}[\rho_A,\rho_B]$, where x is a placeholder for the chosen approximation (x =TF as in eq. (11), x =GEA2 as in eq. (17), x =NDSD as in eq. (23), x =NDCS as in eq. (39)) and x =ISO for isolated optimized subsystem densities. Values are given in atomic units. In bold are the best results.

| | | Freeze and Thaw | | | | |
A	B	TF	GEA2	NDSD	NDCS	ISO
Li^+	H_2O	0.0620	0.1227	0.0508	**0.0447**	0.3675
Be^{2+}	H_2O	0.5149	0.7295	0.3951	**0.2422**	1.0457
Na^+	H_2O	0.0200	0.0711	0.0174	**0.0168**	0.2879
Mg^{2+}	H_2O	0.0942	0.2487	0.0695	**0.0489**	0.7177
K^{+a}	H_2O	0.0678	$-^b$	$-^b$	**0.0322**	0.2418
Rb^{+c}	$H2O$	0.4949	0.5185	0.5461	**0.4906**	0.6546
Mg^{2+}	He	0.0145	0.0679	**0.0129**	0.0176	0.2398
Be^{2+}	He	0.1401	$-^b$	0.1002	**0.0582**	0.3857
Li^+	CO_2	0.0316	0.0797	0.0273	**0.0270**	0.4544
K^{+a}	CO_2	0.0197	0.0630	$-^b$	**0.0173**	0.2926
Li^+	F_2	0.0279	0.0463	0.0222	**0.0205**	0.3031

a For potassium the basis set $6-311G(d,p)^{45,46}$ was used.
b No converged results are available.
c For rubidium the basis set ANORCCVTZP$^{47-52}$ was used.

Some of the calculations do not have converged results available with the used basis set and for the considered approximation for the density functionals. This concerns especially chemical systems with the potassium cation. The possible reason for this behavior is an incorrect distribution of charges via the electronic density. Due to unphysical properties in the used approximant to the NAKEP, there are charged holes where the electrons can leak into. Thus, a density distribution might appear in volume spaces where a rapid exponential decay should be expected. However, with the new NDCS approximant $\tilde{v}_t^{\mathrm{NDCS}}[\rho_A,\rho_B]$ we are able to overcome any of those issues. A similar feature is hence also expected in more systems of interest with charge leak problems.

We also want to underline the strength of the distance norm method because it will record any global error, independent of the system or associated volume geometry. As a consequence one can discuss the overall performance of the method and does not need to worry about any artificial fine tuning mechanism which might drive the result to the reference value. On the other hand, the downside of a global well defined mathematical norm is that local properties stay undetected. For example, the local impact of the activation of the limit potential in a specific volume space or the disparity of the involved density

Table II. Distance measure (43) between the sum of the subsystem densities obtained from the F&T calculation and the total Kohn–Sham (KS) density. The multiscale optimization was performed with five different models $\tilde{v}_t^{\mathrm{nad}(x)}[\rho_A,\rho_B]$, where x is a placeholder for the chosen approximation (x =TF as in eq. (11), x =GEA2 as in eq. (17), x =NDSD as in eq. (23), x =NDCS as in eq. (39)) and x =ISO for isolated optimized subsystem densities. Values are given in atomic units. In bold are the best results.

| | | Freeze and Thaw | | | | |
A	B	TF	GEA2	NDSD	NDCS	ISO
H_2O	H_2O	0.0210	0.0311	**0.0209**	0.0224	0.0914
Li^+	F^-	0.2044	0.2839	0.1670	**0.1465**	0.4440
Li^+	Cl^-	0.2623	0.3788	0.2148	**0.1843**	0.6088
Li^+	Br^-	0.2969	0.4300	0.2440	**0.2075**	0.6736
Na^+	F^-	0.0691	0.1583	0.0578	**0.0479**	0.3592
Na^+	Cl^-	0.0619	0.1893	0.0505	**0.0416**	0.5231
Na^+	Br^-	0.0615	0.2071	0.0490	**0.0404**	0.5926
Ne	CO_2	**0.0107**	0.0200	0.0109	0.0119	0.0190
He	CO_2	**0.0062**	0.0179	0.0062	0.0066	0.0131
Be^{2+}	O^{2-}	1.1169	1.2709	0.9723	**0.8114**	2.1072
Mg^{2+}	O^{2-}	0.2988	0.5172	0.2205	**0.1531**	2.1176
HF	HF	0.0537	**0.0441**	0.0539	0.0591	0.1504
K^{+a}	Cl^-	$-^b$	$-^b$	$-^b$	**0.1969**	0.4279
K^{+a}	F^-	$-^b$	$-^b$	$-^b$	**0.1929**	0.4916

a For potassium the basis set $6-311G(d,p)^{45,46}$ was used.
b No converged results are available.

functions at the important area of the nuclear cusp can not be discussed.

In general, a decreasing trend can be seen when comparing the results for the different self–consistent models, i.e. the first four columns in both tables concerning the F&T computations in Tables I and II. The range varies from 0.0620 for TF, 0.1227 for GEA2, 0.0508 for NDSD to 0.0447 for NDCS while the overall distance measure for isolated subsystems lies at 0.3675 in the case of Li^+-H_2O. And from 0.5149 for TF, 0.7295 for GEA2, 0.3951 for NDSD to 0.2422 for NDCS while the overall distance measure for isolated subsystems lies at 1.0457 in the case of $Be^{2+}-H_2O$. The last case shows a good example for the possible improvement when using non–decomposable models. Conventional methods are only able to capture around half of the overall error. Imposing exact limit conditions pushes this error capture estimation up to two–thirds and with satisfaction of the desired function space for electron densities we get even up to three–fourths of the overall error. For neutral systems this reduction is less significant especially if the subsystems are not charged. Their distance measures are much

closer to the isolated density case, thus the effect here is almost negligible. Note that we cannot compare the results between different systems in a straight forward manner because many factors on the electronic density influences the magnitude of the norm. So one obtains quite high values of 1.1169 for TF, 1.2709 for GEA2, 0.9723 for NDSD and 0.8114 for NDCS in the case of $Be^{2+}-O^{2-}$ where the overall distance measure for isolated subsystems lies at 2.1072. Whereas for the Na^+-H_2O complex the numbers are some orders of magnitude lower; 0.0200 for TF, 0.0711 for GEA2, 0.0174 for NDSD and 0.0168 for NDCS while the overall distance measure for isolated subsystems lies at 0.2879. The overall decreasing trend indicates that using a non–decomposable NAKEP approximants in order to account for the exact limit behavior (NDSD) reduces the distance from the original TF method. The reduction is, in particular, much more significant if imposing density function space based properties on the non–decomposable NAKEP approximants. Further we observe a "poor" behavior of the conventional GEA2 method in comparison to the standard TF model, which was already predicted in former publications[5]. It should be pointed out here that the truncation by higher order derivatives[26] may also be the pattern to improvement since for quickly varying density functions the low order expansions are poorly approximating the NAKEs. This lies at the origin of the bad performance of the second-order gradient expansion decomposable approximation $\tilde{v}_t^{\mathrm{nad}(\mathrm{GEA2})}[\rho]$ (see eq. (17)).

VI.B. Accuracy of the NDCS dipole moments

The choice of induced dipole moments as another measure of quality comes naturally from the fact that the local behavior of $\tilde{v}_t^{\mathrm{nad}}[\rho_A, \rho_B]$ near the nuclei directly affects the electron distribution between the two subsystems. A not repulsive enough potential at the nuclear cusp might cause an artificial electron transfer which is reflected in the dipole moment of the total system. Therefore, $\tilde{v}_t^{\mathrm{nad}}$–dependent total dipole moments on the same set of systems were analyzed. We report the relevant number of digits, which were used to compute the relative error. A similar discussion with induced dipole moments has been performed in the work of Lastra et al.[22] on an equivalent set of complexes.

In Tables III and IV we collect the total complexation induced dipole moment from the set of charged and neutral systems, respectively. The overall trend of the results in both tables show that imposing the exact conditions in the limit case (NDSD) decreases the $\tilde{v}_t^{\mathrm{nad}}$-generated errors. Furthermore, the use of our new NDCS potential (see eq. (39)) amplifies this effect. The magnitude of the reduction in the relative errors for charged systems depends on the case such as in Na^+-H_2O (from -1.39% for TF or -10.35% for GEA2 to -0.66% for NDSD and to 0.38% for NDCS) or such as in $Be^{2+}-H_2O$ (from -27.17% for TF or -40.43% for GEA2 to -20.37%

Table III. Total dipole moments (μ in Debye) obtained from the F&T calculation using four different approximants $\tilde{v}_t^{\mathrm{nad}(x)}[\rho_A, \rho_B]$, where x is a placeholder for the chosen approximation ($x =$TF as in eq. (11), $x =$GEA2 as in eq. (17), $x =$NDSD as in eq. (23) or $x =$NDCS as in eq. (39)). The target Kohn-Sham (KS) results are in the last column. For comparison the relative percentage errors ($[\mu^x - \mu^{\mathrm{KS}}]/\mu^{\mathrm{KS}} \cdot 100\%$) are given in parentheses. Those are based on the respective total dipole moments computed with the according method along the principle axis of the subsystems. In bold are the results which are closest to the KS target.

| A | B | Freeze and Thaw | | | | KS |
		TF	GEA2	NDSD	NDCS	
Li^+	H_2O	3.744 (-4.83)	3.502 (-10.98)	3.807 (-3.22)	**3.866** (-1.73)	3.934
Be^{2+}	H_2O	3.930 (-27.17)	3.214 (-40.43)	4.296 (-20.37)	**4.845** (-10.20)	5.396
Na^+	H_2O	2.210 (-1.39)	2.009 (-10.35)	2.226 (-0.66)	**2.250** (0.38)	2.241
Mg^{2+}	H_2O	3.889 (-7.04)	3.271 (-21.82)	3.993 (-4.54)	**4.139** (-1.04)	4.183
K^{+a}	H_2O	0.755 (-26.25)	$-^b$ (–)	$-^b$ (–)	**0.968** (-5.45)	1.023
Rb^{+c}	$H2O$	**0.445** (4.92)	0.547 (28.86)	0.852 (100.88)	0.400 (-5.70)	0.424
Mg^{2+}	He	1.878 (-1.94)	1.681 (-12.21)	1.897 (-0.94)	**1.928** (0.68)	1.915
Be^{2+}	He	3.145 (-13.49)	$-^b$ (–)	3.281 (-9.74)	**3.478** (-4.34)	3.635
Li^+	CO_2	9.834 (-0.78)	9.618 (-2.96)	9.880 (-0.33)	**9.926** (0.14)	9.912
K^{+a}	CO_2	7.561 (-0.70)	7.367 (-3.25)	$-^b$ (–)	**7.627** (0.16)	7.615
Li^+	F_2	7.166 (0.92)	6.954 (-2.07)	7.138 (0.52)	**7.111** (0.14)	7.101

[a] For potassium the basis set $6-311G(d,p)^{45,46}$ was used.
[b] No converged results are available.
[c] For rubidium the basis set ANORCCVTZP$^{47-52}$ was used.

for NDSD and to -10.20% for NDCS). In general, when investigating the overall influence with NDCS, one remarks that the relative error tends from negative values to zero or further to positive values. A similar trend can be found in Table IV with the neutral systems, although here the effect on the errors is rather negligible. Whereas for some charged subsystems we observe that the former NDSD model provides slightly better relative errors (see for example the case of $Mg^{2+}-O^{2-}$ or Na^+-Cl^-). The new NDCS approximant overshoots in those cases the target total dipole moment (positive relative error). This effect is due to the switching function because it controls where the non–decomposable potential is "switched on".

Table IV. Total dipole moments (μ in Debye) obtained from the F&T calculation using four different approximants $\tilde{v}_t^{\mathrm{nad}(x)}[\rho_A,\rho_B]$, where x is a placeholder for the chosen approximation ($x=$TF as in eq. (11), $x=$GEA2 as in eq. (17), $x=$NDSD as in eq. (23) or $x=$NDCS as in eq. (39)). The target Kohn-Sham (KS) results are in the last column. For comparison the relative percentage errors ($\left[\mu^x - \mu^{\mathrm{KS}}\right]/\mu^{\mathrm{KS}}\cdot 100\%$) are given in parentheses. Those are based on the respective total dipole moments computed with the according method along the principle axis of the subsystems. In bold are the results which are closest to the KS target.

		Freeze and Thaw				
A	B	TF	GEA2	NDSD	NDCS	KS
H_2O	H_2O	**4.3533** (-0.07)	4.3529 (-0.08)	4.3531 (-0.07)	4.3510 (-0.12)	4.3563
Li^+	F^-	5.444 (-8.05)	5.100 (-13.86)	5.591 (-5.56)	**5.713** (-3.50)	5.921
Li^+	Cl^-	5.682 (-14.53)	5.086 (-23.5)	5.894 (-11.35)	**6.072** (-8.68)	6.649
Li^+	Br^-	5.573 (-18.49)	4.868 (-28.81)	5.816 (-14.93)	**6.017** (-11.99)	6.837
Na^+	F^-	7.539 (-1.18)	7.103 (-6.90)	7.593 (-0.47)	**7.651** (0.29)	7.629
Na^+	Cl^-	8.271 (-1.32)	7.516 (-10.34)	**8.348** (-0.41)	8.440 (0.69)	8.382
Na^+	Br^-	8.346 (-1.55)	7.441 (-12.23)	**8.436** (-0.49)	8.543 (0.78)	8.477
Ne	CO_2	0.14902 (-0.45)	0.11988 (-19.92)	**0.14914** (-0.37)	0.14908 (-0.41)	0.14969
He	CO_2	0.0445 (-20.07)	0.0313 (-43.80)	0.0454 (-18.58)	**0.0457** (-17.94)	0.0557
Be^{2+}	O^{2-}	3.968 (-31.32)	3.577 (-38.08)	4.167 (-27.87)	**4.491** (-22.26)	5.777
Mg^{2+}	O^{2-}	6.419 (-2.27)	5.714 (-13.00)	**6.547** (-0.32)	6.714 (2.22)	6.568
K^{+a}	Cl^-	_b (-)	_b (-)	_b (-)	**9.418** (-5.18)	9.932
K^{+a}	F^-	_b (-)	_b (-)	_b (-)	**6.683** (-2.42)	6.849

[a] For potassium the basis set $6-311$G(d,p)[45,46] was used.
[b] No converged results are available.

In those complexes $f^{\mathrm{NDCS}}[\rho_B]$, given in formula (38), contributes on volume spaces where ρ_B is already small (see condition (i)). Consequently $v^1[\rho_B]$, given in formula (35), is activated in a too wide volume space. Since the exponential decay of the switching function is connected to the environmental electron density, we expect some room for improvement. The final goal is a model which behaves system independent using global quantities such as electronic densities. Nevertheless, the NDCS results are still outperforming the ones from the original

TF model and thus, the origin of the total error may lie somewhere else than in the approximant to the NAKEP for neutral systems.

Similar to the results with the distance norm, in several complexes we did not obtain converged results, especially in systems with potassium. The total dipole moment shows in those cases only robust results for the NDCS model. Finally, we want to point out as well the very poor relative error results of the GEA2 model. In comparison to the conventional TF model, the error is increased by a significant magnitude, which indicates that the gradient expansion method is far from suitable to model properly the NAKEP in the limit volume spaces.

VII. CONCLUSIONS

The approximation of the non–additive kinetic potential $v_t^{\mathrm{nad}}[\rho_A,\rho_B]$ and its influence on the obtained electron density functions was subject of our work in this publication. Conventional top–down (7) construction of an approximant needs a decomposable NAKE functional. For gradient–expansion models the resulting potentials lack exact limit properties or do not obey the complete space of admissible densities.

The bottom–up approach (8) provides a method, where one can impose mathematical or physical conditions beforehand in order to construct a suitable approximant $\tilde{v}_t^{\mathrm{nad}}[\rho_A,\rho_B]$. The existence of a corresponding parent functional $\tilde{T}_s[\rho]$ is not necessary and thus the approximant to the NAKE functional can be non–decomposable. One is only restricted by the corresponding density function space and the resulting dual space for appropriate potentials[4]. This strategy has the ability to yield more accurate electron densities with improved direct properties. Hence, non–decomposable bi–functionals are proven to be essential in order to overcome certain sources of error in embedding theory.

In the NDSD model[22], the limit conditions (c) and (d) lead to a limit potential which is used in the approximant to the NAKEP (see eq. 31). It comprises the desired local reciprocal singularity for exponentially decaying environment densities. Taking into account the exact admissible space of electron density functions leaves only $\gamma = 1$ as the best choice for the ordinary differential operator $D_\gamma[\rho_B]$ from section III. As a result, a new potential $v^1[\rho_B]$ (see formula (35)) was defined which replaces the limit potential in equation (37). Although it does not satisfy the limit conditions (c) and (d), we still recover the desired reciprocal characteristic and furthermore, we do not encounter any unphysical wells. With this change of paradigm in the bottom–up construction of an approximant to the NAKEP, we propose a new non–decomposable approximant $\tilde{v}_t^{\mathrm{nad(NDCS)}}[\rho_A,\rho_B]$ (see definition (39)) as a mathematical sound alternative to gradient expansion based decomposable and non–decomposable strategies. Its advantages can be summed up as follows:

- Theory: $\tilde{v}_t^{\mathrm{nad(NDCS)}}[\rho_A, \rho_B]$ reproduces the desired reciprocal characteristic at the nucleus as well as avoids any unphysical wells (as in the case of NDSD) which cause an artificial charge leak, while permitting the admissible function space for exponentially decaying densities. A corresponding approximant to the NAKE exists and can be directly evaluated (see eq. (40)).

- Practical: The numerical results show a clear reduction in the error in comparison to other methods. NDCS provides also a robust model whose applicability is not limited by any arbitrary choice of the environmental density. Especially in systems where the original TF approximation, higher order truncation GEA2 or the NDSD model are numerically not stable, the NDCS variant ensures a successful optimization.

- Numerical: Evaluating the NDCS potential and the corresponding switching function has the same complexity as other conventional decomposable methods from gradient–expansion models. It uses only the electron density quantity up to second order derivatives. The magnitude of the improvement varies from system to system. While the relative error in neutral subsystems is rather negligible, in charged cases the NDCS approximant gives statistically the best results.

We want to conclude with some outlook for more work on non–decomposable approaches. In order to study the local effects on the solution density from the NAKEP approximant, one needs to adapt more measures of quality with higher resolution. For instance, the initial H^1–norm (see eq. (42)) would be a suitable mathematical candidate as an expansion to the discussed distance norm. A graphical analysis of the electron density in real space will detect the local volume spaces which are crucial at the nuclear cusp. Especially in those cases where former models fail because of the charge leak problem. Here, a detailed study of orbital level shifts for several systems of interest is necessary to discuss the electronic distribution. Preliminary results indicate that the $v^1[\rho_B]$ component of $\tilde{v}_t^{\mathrm{nad(NDCS)}}[\rho_A, \rho_B]$ (see eq. (39)) leads to the desired effect on orbital energies.

Finally, the decomposable part in the formula for $\tilde{v}_t^{\mathrm{nad(NDCS)}}[\rho_A, \rho_B]$ might also be exchanged with other conventional approximants. A detailed trial with gradient–expanded approximations will enlighten the overall effect of a non–decomposable addition.

DISCLOSURE STATEMENT

The authors have no conflicts to disclose.

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DATA AVAILABILITY STATEMENT

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

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