

## Methods to generate reference total and Pauli kinetic potentials

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We have derived a method which allows us to compute the full and the Pauli reference kinetic potentials for atoms and molecules in a real-space representation. This is done by applying the optimized effective potential (OEP) method to the Kohn-Sham noninteracting kinetic energy expression. Additionally, we have also derived a simplified OEP variant based on the common energy denominator approximation which has proven to give much more stable and robust results than the original OEP. Moreover, we have also proved that at the solution point our approach is formally equivalent to the commonly used Bartolotti-Acharya formula.

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### I. INTRODUCTION

The most natural and straightforward realization of density-functional theory (DFT) [1,2] is the so-called orbital-free (OF) DFT [3,4]. The theory describes the ground-state electronic properties of any electron system via the knowledge of the electron density  $\rho$  that is obtained as the solution of the Euler equation [5],

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} = \mu, \quad (1)$$

where  $v_{\text{ext}}$  is the external/nuclear potential,  $v_H$  is the Hartree potential,  $\mu$  is a Lagrange multiplier fixed from the normalization condition  $\int d\mathbf{r} \rho(\mathbf{r}) = N$ , and  $E_{\text{xc}}$  and  $T_s$  are the exchange correlation (XC) and noninteracting kinetic energy (KE) functionals, respectively. The latter two quantities are very important to describe many-body fermionic effects. However, despite that the existence of both functionals is guaranteed by the first Hohenberg-Kohn theorem [1] and that they can be formally defined within the Levy's constrained search procedure [2], their explicit expression in terms of the electron density is unknown. Therefore, one needs to approximate both quantities.

In the case of the XC functional, many useful approximations have been proposed (see, e.g., Refs. [6–8] and references therein). On the other hand, for the KE term, this task is much more difficult due to two facts: (i) the KE contribution is much larger than the XC one (it has the same order of magnitude as the total energy [9,10]); (ii) it includes highly nonlocal Pauli contributions [11–14], which account for all fermionic effects. Nonetheless, different approximate KE functionals have been developed (see, e.g., Refs. [13,15–41]). In numerous cases, these have been developed mimicking the exchange functional

construction, according to the *conjointness conjecture* hypothesis [42–45]. In other cases, specific KE properties have been considered such as the exact constraint satisfaction [17,19,46] or the use of information from the linear response of the uniform electron gas [3]. In all cases, however, the approximate KE functionals still show, in general, poor accuracy and/or transferability [25,47,48].

For these reasons, OF-DFT calculations are rarely employed in practice. The most popular computational realization of DFT, the Kohn-Sham (KS) method [49], avoids the direct use of the KE functional by introducing an auxiliary noninteracting system of fermionic particles where both the density and the KE terms are expressed in terms of single-particle orbitals  $\{\phi_i\}$ . Thus, we have

$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 \quad (2)$$

$$T_s = -\frac{1}{2} \sum_i^N \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}). \quad (3)$$

Note that the KE can be alternatively written as

$$T_s = \int d\mathbf{r} \tau(\mathbf{r}), \quad (4)$$

where  $\tau(\mathbf{r}) = 1/2 \sum_i^N |\nabla \phi_i(\mathbf{r})|^2$  is the positive-definded KE density. Throughout this paper, we label with  $i, j$  the occupied KS orbitals, with  $a, b$  the unoccupied ones, and with  $p, q$  the general (occupied or unoccupied) ones. All equations are written in spin-restricted form.

The KE functional given by Eq. (3) is usually separated in two main contributions, namely the von Weizsäcker (VW) [50] ( $T^W$ ) and the Pauli ( $T^P$ ) term:

$$T_s[\rho] = T^W[\rho] + T^P[\rho]. \quad (5)$$

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The former has a simple semilocal expression written in terms of the density and its gradient, which reads

$$T^W[\rho] = \int d\mathbf{r} \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho(\mathbf{r})}, \quad (6)$$

and is exact for any one- and two-electron spin-singlet state systems. Due to its explicit density dependence, the corresponding kinetic potential can be easily derived using standard functional derivatives as

$$v^W(\mathbf{r}) = \frac{\delta T^W[\rho]}{\delta\rho(\mathbf{r})} = \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho^2(\mathbf{r})} - \frac{\nabla^2\rho(\mathbf{r})}{4\rho(\mathbf{r})}. \quad (7)$$

On the other hand, the Pauli term can only be expressed exactly via the KS orbitals [51–54] as

$$T_s^P[\rho] = \int d\mathbf{r} \tau^P(\mathbf{r}) \quad (8)$$

with

$$\tau^P(\mathbf{r}) = \frac{1}{2\rho(\mathbf{r})} \sum_{i<j} |\phi_i(\mathbf{r})\nabla\phi_j(\mathbf{r}) - \phi_j(\mathbf{r})\nabla\phi_i(\mathbf{r})|^2 \quad (9)$$

being the Pauli kinetic-energy density according to Ref. [53].

The KS method, via Eq. (3) [or Eq. (4)], provides a direct way to calculate the noninteracting KE of any electron system. Therefore, this information can be, and indeed is, used to assess and improve approximate KE functionals. On the other hand, the KS method makes no use of the kinetic potential,  $\delta T_s[\rho]/\delta\rho(\mathbf{r})$ , and provides no direct way to obtain it. For this reason, the kinetic potential has long been an overlooked quantity and almost no effort has been made to assess and optimize the approximate KE functionals against this quantity. However, the kinetic potential is the main ingredient in the Euler equation [Eq. (1)] and its importance is nowadays increasingly recognized [47,48,55–60]. Thus, methods to generate the kinetic potential from reference KS input quantities, or more generally from any input set of orbitals, are of great importance to allow a direct knowledge of this fundamental quantity.

The simplest way to generate the total kinetic potential is to directly use Eq. (1). If the ground-state density  $\rho(\mathbf{r})$  is already determined and we fix the corresponding XC potential (e.g., from standard KS calculations [49], *ab initio* DFT [61–68] or some “reverse-engineering” approach [54,69,70]), then it is clear that at the solution point the kinetic potential can be obtained as the negative of the effective potential shifted by a constant

$$v_k(\mathbf{r}) = \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} = -v_s[\rho](\mathbf{r}) + \mu, \quad (10)$$

where with  $v_k(\mathbf{r})$  we denote the total kinetic potential. The constant  $\mu$  is commonly taken [5,71] to be the negative of the first ionization potential  $\mu = -IP$  or approximately the orbital energy of the highest occupied molecular orbital (HOMO) ( $\mu = \varepsilon_H$ ), which can be calculated in various manners [72].

To compute the Pauli potential one simply needs to subtract the Weizsäcker kinetic potential given by Eq. (7) from Eq. (10) getting

$$v^P(\mathbf{r}) = -v_s[\rho](\mathbf{r}) - v^W(\mathbf{r}) + \mu. \quad (11)$$

Another commonly used method to generate reference Pauli potentials [52,53,73–76] is the one derived by Bartolotti and Acharya (BA) in Ref. [52]. The formula

$$v^P(\mathbf{r}) = \frac{\tau(\mathbf{r}) - \tau^W(\mathbf{r})}{\rho(\mathbf{r})} + \sum_i^N (\varepsilon_H - \varepsilon_i) \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \quad (12)$$

utilizes the occupied orbitals and the orbital energies from an arbitrary self-consistent field (SCF) method [including Hartree-Fock (HF)]. The full derivation of Eq. (12) can be found in Refs. [52,53]. However, for clarity of this paper, it is also briefly sketched in Appendix A.

Formally, Eq. (12) is equivalent to Eq. (11) with a corrected VW term (see Ref. [18], Sec. III A, and Appendix A for more details). Once the Pauli potential is available, the total kinetic potential can be calculated as

$$v_k(\mathbf{r}) = v^W(\mathbf{r}) + v^P(\mathbf{r}). \quad (13)$$

In this paper, we introduce a method based on the optimized effective potential (OEP) [77,78] approach, allowing us to generate the noninteracting kinetic potentials (full and Pauli terms) for different atoms and molecules in a real space representation. Additionally, we compare and discuss the proposed method with the aforementioned approaches utilized up to date.

## II. THEORY

In this section, we introduce a method based on the OEP technique that allows us to generate the full and the Pauli kinetic potentials from any set of reference orbitals ( $\phi_p$ ) and orbital energies ( $\varepsilon_p$ ); in addition, we describe the common energy denominator approximation of the method that is numerically simpler and more stable.

### A. Kinetic potential using the OEP method

In this subsection, we consider a method to obtain the kinetic potential. For simplicity, we will describe it for the total kinetic functional; however, it can also be applied in exactly the same way for the Pauli kinetic term [see Eq. (9)].

To start, consider the KS noninteracting kinetic energy functional given in Eq. (3). Because it displays an explicit orbital dependence, while it is only an implicit functional of density, the direct computation of the kinetic potential through functional derivative is impossible. Thus, to calculate the potential, alike in the case of the orbital dependent exchange [77–84] and correlation [61–67,85,86] energy functionals, one can employ the OEP method [77,78]. Hence, we can define the functional derivative of Eq. (3) using the following chain rule:

$$v_k(\mathbf{r}) = \sum_p \int d\mathbf{r}' d\mathbf{r}'' \left\{ \frac{\delta T_s[\{\phi_q\}]}{\delta\phi_p(\mathbf{r}')} \frac{\delta\phi_p(\mathbf{r}')}{\delta v_s(\mathbf{r}'')} \frac{\delta v_s(\mathbf{r}'')}{\delta\rho(\mathbf{r})} + \text{c.c.} \right\}. \quad (14)$$

In the above equation, the first term in brackets is easily derived (see Appendix C) to be zero when  $p$  indexes an unoccupied orbital, while for  $p$  indexing an occupied orbital we find

$$\frac{\delta T_s[\{\phi_q\}]}{\delta\phi_p(\mathbf{r}')} = -\frac{1}{2} \nabla^2 \phi_p(\mathbf{r}') - \frac{1}{2} \nabla^2 \phi_p^*(\mathbf{r}'). \quad (15)$$

In the case of real orbitals, as often happens, this is just  $-\nabla^2\phi_p(\mathbf{r}')$ . The second term can be obtained from first-order perturbation theory considering an infinitesimal perturbation of the effective potential ( $\delta v_s$ ) introduced into the KS equation. Thus, we have

$$\frac{\delta\phi_p(\mathbf{r})}{\delta v_s(\mathbf{r}')} = \sum_{q \neq p} \frac{\phi_p(\mathbf{r}')\phi_q^*(\mathbf{r}')}{\varepsilon_p - \varepsilon_q} \phi_q(\mathbf{r}). \quad (16)$$

The last term is the inverse ( $X^{-1}(\mathbf{r}', \mathbf{r})$ ) of the static KS linear response function of a system of noninteracting particles expressed through KS orbitals and eigenvalues:

$$X(\mathbf{r}', \mathbf{r}) = 2 \sum_{ia} \frac{\phi_i^*(\mathbf{r}')\phi_a(\mathbf{r}')\phi_a^*(\mathbf{r})\phi_i(\mathbf{r})}{\varepsilon_i - \varepsilon_a} + \text{c.c.} \quad (17)$$

Inserting Eqs. (15) and (16) into Eq. (14), after some algebra we obtain

$$v_k^{\text{OEP}}(\mathbf{r}) = \sum_{i,a} \left[ \frac{(T_s)_{ia}}{\varepsilon_i - \varepsilon_a} \int d\mathbf{r}' \phi_i(\mathbf{r}')\phi_a^*(\mathbf{r}')X^{-1}(\mathbf{r}, \mathbf{r}') + \text{c.c.} \right], \quad (18)$$

where  $(T_s)_{pq} = \langle \phi_p | -\frac{1}{2}\nabla^2 | \phi_q \rangle$  are the KE matrix elements. Note that the above procedure is partially similar to the one used in the self-consistent implementation of meta-GGA XC functionals depending on the local kinetic energy density [8,87,88].

### B. Common energy denominator approximation

Since the OEP procedure described above is numerically involved and not very stable (see Sec. IV for more details), we introduce here an approximation based on the common energy denominator method (CEDA) [89–91]. This leads to a simpler and well-behaving equation for the kinetic potential that yields basically the same results as the full OEP variant [Eq. (18)].

To obtain our approximation, we start by multiplying Eq. (18) by Eq. (17) and integrating over  $\mathbf{r}$  to obtain

$$\sum_{ia} \left[ \frac{(v_k)_{ia}}{\varepsilon_i - \varepsilon_a} \phi_i(\mathbf{r})\phi_a^*(\mathbf{r}) + \text{c.c.} \right] = \sum_{ia} \left[ \frac{(T_s)_{ia}}{\varepsilon_i - \varepsilon_a} \phi_i(\mathbf{r})\phi_a^*(\mathbf{r}) + \text{c.c.} \right], \quad (19)$$

where

$$(v_k)_{pq} = \int d\mathbf{r} \phi_p^*(\mathbf{r})v_k(\mathbf{r})\phi_q(\mathbf{r}). \quad (20)$$

This is just another representation of the OEP equation [92]. Now we assume that all the energy differences in the denominator of Eq. (19) can be approximated by a constant mean energy ( $\Delta \approx \varepsilon_i - \varepsilon_a$ ), getting

$$\sum_{ia} \left[ (v_k)_{ia}\phi_i(\mathbf{r})\phi_a^*(\mathbf{r}) + \text{c.c.} \right] = \sum_{ia} \left[ (T_s)_{ia}\phi_i(\mathbf{r})\phi_a^*(\mathbf{r}) + \text{c.c.} \right]. \quad (21)$$

At this point, we can use on both sides of Eq. (21) the relation

$$\sum_a \phi_a^*(\mathbf{r})\phi_a(\mathbf{r}') + \sum_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (22)$$

to obtain

$$\begin{aligned} \rho(\mathbf{r})v_k(\mathbf{r}) - \sum_{i,j} (v_k)_{ij}\phi_i(\mathbf{r})\phi_j^*(\mathbf{r}) + \text{c.c.} \\ = -\frac{1}{2} \sum_i \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r}) - \sum_{i,j} (T_s)_{ij}\phi_i(\mathbf{r})\phi_j^*(\mathbf{r}) + \text{c.c.} \end{aligned} \quad (23)$$

Finally, using the identity [8]

$$-\frac{1}{2} \sum_i \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r}) = \tau(\mathbf{r}) - \frac{1}{4}\nabla^2\rho(\mathbf{r}), \quad (24)$$

we find the kinetic potential approximation

$$v_k(\mathbf{r}) = \frac{\tau(\mathbf{r})}{\rho(\mathbf{r})} - \frac{\nabla^2\rho(\mathbf{r})}{4\rho(\mathbf{r})} + \sum_{i,j} [(v_k)_{ij} - (T_s)_{ij}] \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})}{\rho(\mathbf{r})}. \quad (25)$$

This equation expresses the kinetic potential in the CEDA.

A further approximation can be obtained following the idea of Krieger-Li-Iafrate (KLI) [91], neglecting in the summation all the terms with  $i \neq j$ . Indeed, numerical investigations support the fact that the off-diagonal terms in the sum provide only a minor contribution with respect to the diagonal ones. In this way, we obtain the KLI approximation of Eq. (18), which reads

$$v_k(\mathbf{r}) = \frac{\tau(\mathbf{r})}{\rho(\mathbf{r})} - \frac{\nabla^2\rho(\mathbf{r})}{4\rho(\mathbf{r})} + \sum_i [(v_k)_{ii} - (T_s)_{ii}] \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})}. \quad (26)$$

Inserting the definition  $\tau(\mathbf{r}) = \tau^W(\mathbf{r}) + \tau^P(\mathbf{r})$  into Eq. (26) and removing the VW potential of Eq. (7), one obtains the Pauli potential

$$v^P(\mathbf{r}) = \frac{\tau^P(\mathbf{r})}{\rho(\mathbf{r})} + \sum_i [(v_k)_{ii} - (T_s)_{ii}] \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})}. \quad (27)$$

One can prove that for density and orbitals corresponding to the SCF solution of the KS and Euler equations (i.e., at the solution point) the above formula is formally equivalent to Eq. (12) (see Appendix B for more details).

### III. COMPUTATIONAL DETAILS

All methods have been implemented in a local version of the ACESII [93] software package. The kinetic potentials have been computed for fixed reference densities obtained from various methods, such as OEPx [78,79], OEP2-sc [62], HF [94], Perdew-Burke-Ernzerhof (PBE) [95] in post-SCF fashion. Here OPEX denotes exact-exchange OEP calculations, OEP2-sc denotes second-order correlated OEP calculations with a semicanonical transformation of the orbitals. We remark that a similar approach was already successfully utilized in some studies [96–98] to investigate the most relevant features of the XC potentials. To calculate the kinetic potentials

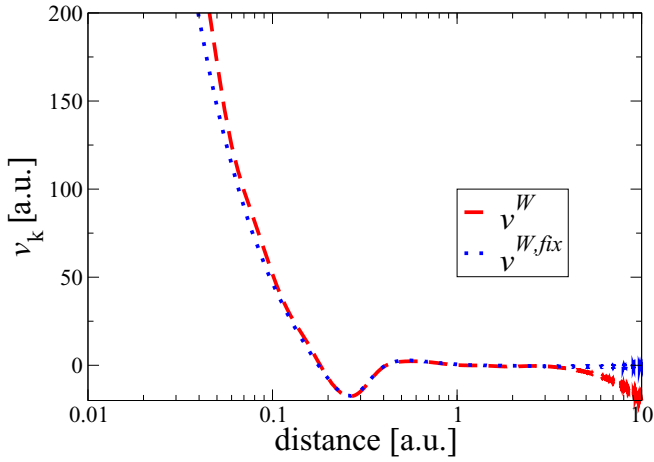


FIG. 1. The Weizsäcker kinetic potential without and with oscillatory profile correction calculated for Ne atoms in the cc-pVTZ basis set.

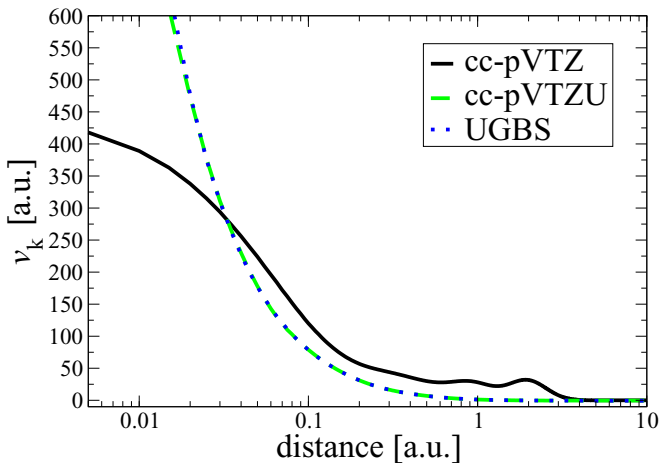
with the OEP method, in practice, we have employed the finite-basis set procedure of Ref. [79], which was also used in our previous studies to generate exchange and correlation potentials [67,98–104]. Thus, the kinetic OEP potential is expanded in the same primitive Gaussian basis set which is used to represent the orbitals in the SCF procedure. In the case of exchange and correlation potentials, this procedure led to the reduction of numerical instabilities in the solution of OEP equation [105–107]. In all calculations, the cutoff for the truncated singular-value decomposition (SVD) was set to  $10^{-6}$ .

In the following subsection, we recall some problems related to representation in real space of von Weizsäcker and Pauli potentials and describe the details related to the implementation of the OEP method and the KLI approximation.

### A. Asymptotic-corrected VW potential

In principle, the far-distance asymptotic behavior of the VW potential is

$$v^W(\mathbf{r}) \propto \varepsilon_H, \quad (28)$$



where  $\varepsilon_H$  is the HOMO energy. This property is readily obtained by using the asymptotic density behavior [108]  $\rho(r) \propto Ae^{-2\sqrt{-2\varepsilon_H}r}$  into Eq. (7). However, in many calculations, the electron density is expanded in Gaussian basis functions. Thus, the asymptotic density behavior is not the true one but rather  $\rho(\mathbf{r}) \propto e^{-\alpha r^2}$ , with  $\alpha$  being the exponent of the most diffuse primitive basis function. Consequently, the VW potential is found to behave as

$$v^W(\mathbf{r}) \propto -\frac{1}{2}\alpha^2 r^2 + \frac{1}{2}\alpha. \quad (29)$$

Then, the VW potential incorrectly diverges. In a similar way, the use of contracted Gaussian functions to represent the electron density may lead to oscillations in the core region of atoms, due to inaccuracies in the description of the Laplacian term in Eq. (7) [109]. These issues have been studied by several groups [109–114] and are basically related to the truncation error of the basis set.

One possible remedy to reduce these basis set artifacts is to use a smoothing procedure as described in Ref. [112]. This allows, in an effective manner, to eliminate the oscillations and divergences in the VW potential computed using Gaussian basis set densities by utilization of a basis-set oscillation profile [109,112] defined as

$$\Delta v_{\text{osc}}(\mathbf{r}) = -\frac{1}{\rho(\mathbf{r})} \sum_{i=1}^N \phi_i^*(\mathbf{r}) \delta_i(\mathbf{r}) \quad (30)$$

with

$$\delta_i(\mathbf{r}) = \left[ -\frac{1}{2}\nabla^2 + v_s(\mathbf{r})[\rho] \right] \phi_i(\mathbf{r}) - \varepsilon_i \phi_i(\mathbf{r}). \quad (31)$$

Note that since the oscillation profile is directly linked with a measure of basis set incompleteness [109], for a complete basis set all  $\delta_i(\mathbf{r})$  vanish and thus so does the oscillation profile.

Employing Eq. (30), the corrected VW potential can be computed as

$$v^{W,\text{fix}}(\mathbf{r}) = v^W(\mathbf{r}) - \Delta v_{\text{osc}}(\mathbf{r}). \quad (32)$$

Figure 1 shows the VW potential of the Ne atom, computed with a Gaussian basis set (cc-pVTZ [115]) with and without

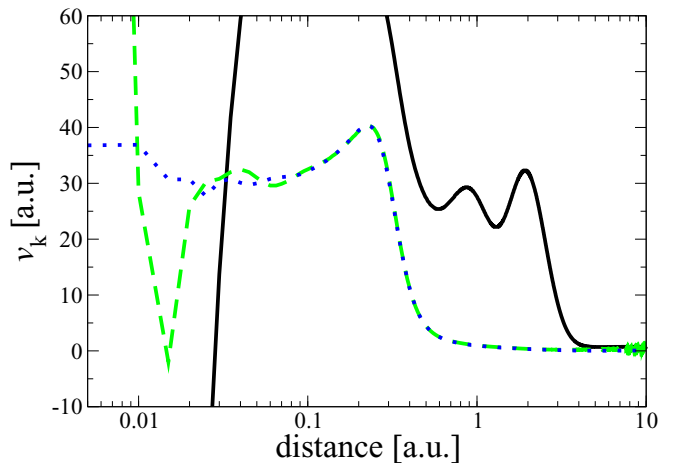


FIG. 2. Total (left) and Pauli (right) kinetic potential calculated using OEP method described in Sec. II A on top of OEPx converged quantities the Ne atom in various basis sets (see text).

the oscillation profile correction. We see that the impact of the correction is observed both in core and asymptotic regions that might be very important from the computational point of view when a Gaussian-type basis set is employed in the calculation.

### B. Numerical implementation of OEP method

In principle, likewise for the exchange potential, Eq. (18) could be solved numerically [78,84]. However, in general it is better to transform the OEP equation [Eq. (18)] into an algebraic problem like in Refs. [79,80]. This is done by expanding the kinetic potential and Eq. (17) on an auxiliary, orthonormal, and  $M$ -dimensional basis set  $\{f_p(\mathbf{r})\}_{p=1}^M$  as

$$v_k^{\text{OEP}}(\mathbf{r}) = \sum_p c_p f_p(\mathbf{r}), \quad (33)$$

and

$$X(\mathbf{r}, \mathbf{r}') = \sum_{p,q} (\mathbf{X})_{pq} f_p^*(\mathbf{r}) f_q(\mathbf{r}'), \quad (34)$$

where

$$\begin{aligned} (\mathbf{X})_{pq} &= \int f_p^*(\mathbf{r}) X(\mathbf{r}, \mathbf{r}') f_q(\mathbf{r}') d\mathbf{r}' d\mathbf{r} \\ &= \sum_{i,a} \left( \frac{(ia|p)(ia|q)^*}{\varepsilon_i - \varepsilon_a} + \text{c.c.} \right), \end{aligned} \quad (35)$$

while

$$(rs|q) = \int d\mathbf{r}' \phi_s(\mathbf{r}') \phi_r^*(\mathbf{r}') f_q(\mathbf{r}').$$

This step allows us to turn the solution of Eq. (18) into an algebraic problem in which the expansion coefficients ( $c_p$ ) are obtained from the solution of the OEP equation in the form

$$(\mathbf{X})_{qp} \mathbf{c}_p = \mathbf{Y}_q, \quad (36)$$

with

$$\mathbf{Y}_q = \sum_p \sum_{i,a} \left[ \left\{ \frac{(T_s)_{ia}}{\varepsilon_i - \varepsilon_a} (ai|q) \right\} + \text{c.c.} \right]. \quad (37)$$

Note that since the density-density response matrix is singular [105], to solve Eq. (36), one needs to employ a truncated SVD in the OEP procedure to calculate the pseudoinverse of the density-density response matrix,  $(\mathbf{X}^{-1})_{qp}$ , which is an essential step for determining stable and physically meaningful OEP potentials [66,83,105].

### C. Numerical implementation of KLI method

To obtain the total kinetic potential given by Eq. (26), one needs to find the matrix elements  $[c_i = (v_k)_{ii} - (T_s)_{ii}]$  which depend explicitly on the total kinetic potential itself. Thus, similarly as in the case of the KLI method applied to the exchange potential [91,116], one can solve this problem turning Eq. (26) into the linear algebraic equations taking the form

$$[\mathbf{I} - \mathbf{M}] \mathbf{c} = \mathbf{t}, \quad (38)$$

where

$$(\mathbf{M})_{kl,i} = \int d\mathbf{r} \frac{\phi_k^*(\mathbf{r}) \phi_l(\mathbf{r}) \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})}{\rho(\mathbf{r})} \quad (39)$$

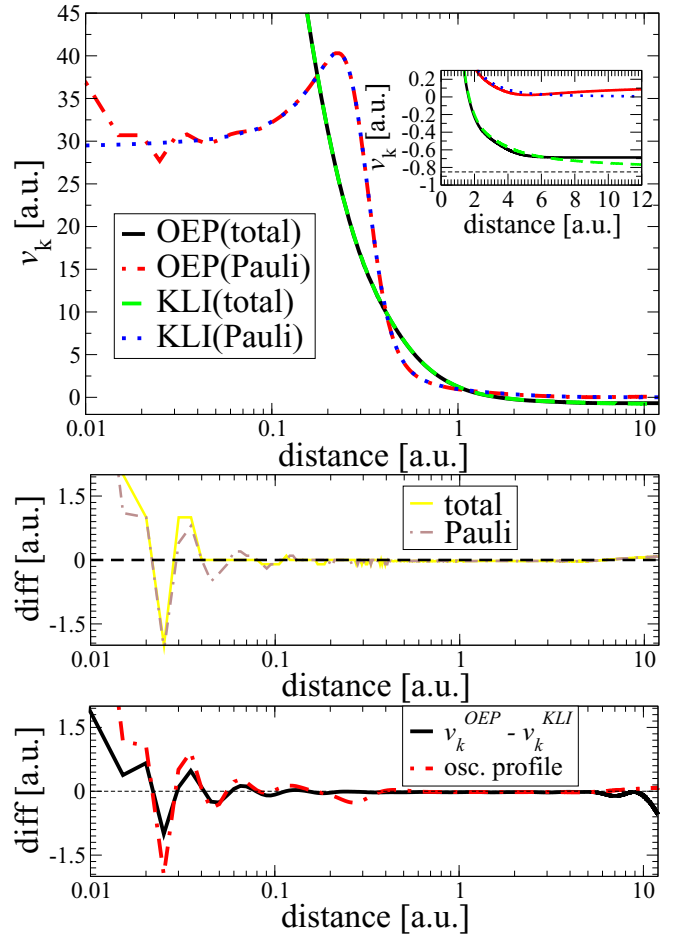


FIG. 3. Top: Comparison of total and Pauli kinetic potentials calculated with OEP and KLI methods on top of OEPx SCF quantities using the UGBS basis set. The inset presents the asymptotic behavior of the potential. The dashed horizontal line denotes the HOMO energy ( $\varepsilon_H = -0.8507$  a.u.). Middle: The difference in the total and Pauli kinetic potential between the OEP and KLI methods. Bottom: The comparison of the difference in the total kinetic potential ( $v_k^{\text{OEPx}} - v_k^{\text{KLI}}$ ) and the oscillatory profile [see Eq. (30)] calculated for the same computational setup.

and

$$(\mathbf{t})_{kl} = \langle \phi_k | \frac{1}{2} \nabla^2 - \frac{\tau(\mathbf{r})}{\rho(\mathbf{r})} + \frac{\nabla^2 \rho(\mathbf{r})}{4\rho(\mathbf{r})} | \phi_l \rangle. \quad (40)$$

The matrix equation [Eq. (38)] can be efficiently solved using standard numerical routines with respect to the  $c_i$  coefficients which then can be used to compute the potential via Eq. (26).

## IV. RESULTS

In this section, we show the total and Pauli kinetic potentials generated using various methods for some representative systems. More examples (for several atoms and molecules) are provided in the Supplemental Material [117]. Because we have proved analytically the equivalence of the inverted Euler equation, the BA formula, and the KLI approach, in the

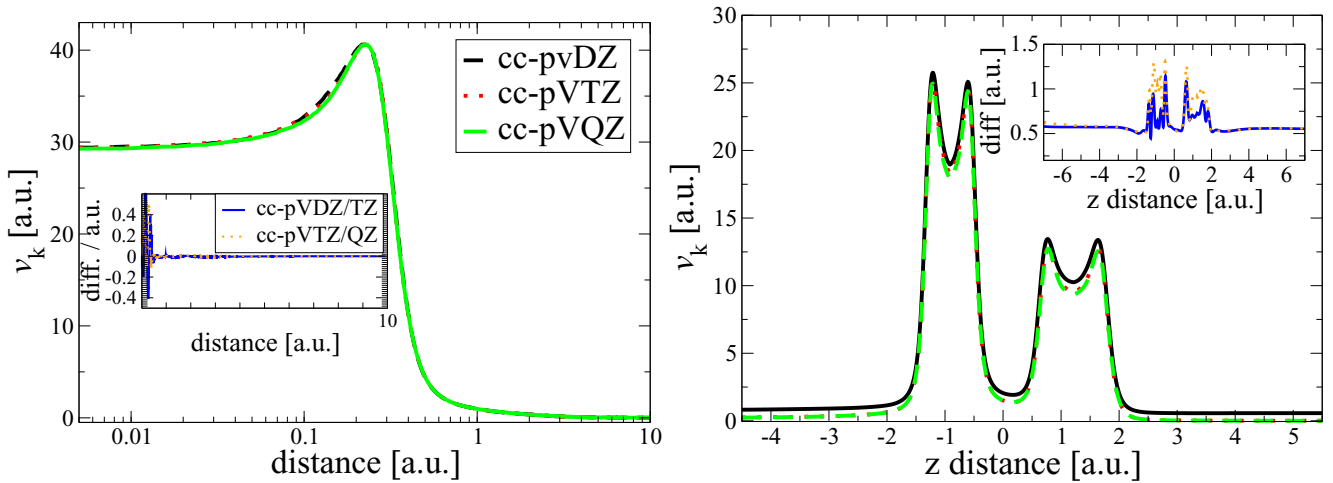


FIG. 4. Pauli potential calculated using the KLI method described in Sec. II B on top of OEPx converged quantities for the Ne atom (left) and the CO molecule (right, plotted along bond axis) for the cc-pVXZ ( $X = D, T, Q$ ) family of basis sets. The inset presents the differences between the Pauli potentials calculated for two successive basis sets in cc-pVXZ family.

following we will show and discuss only the OEP and KLI results.

In Fig. 2, we report the total (left) and Pauli (right) kinetic potentials obtained using the OEP procedure for the Ne atom in few basis sets. One can note that for both kinetic potentials generated using the cc-pVTZ [115] basis set, we get a nonphysical course of the potential in the asymptotic and the core region. Moreover, in the valence region, we observe strong oscillations, especially visible in the case of the Pauli potential. Similar results (not reported) were also obtained employing the cc-pVDZ and cc-pVQZ Dunning [115] basis sets. These issues are due to the fact that these basis sets are not flexible enough to represent the kinetic potentials and the response matrix, thus the OEP equation cannot yield a satisfactory solution. Uncontraction of the cc-pVTZ basis set (cc-pVTZU) makes it sufficiently flexible, especially in the atomic core regions, leading to a significant improvement in the shape of both potentials. In fact, in this case, the kinetic potential exhibits a much better behavior in that region. This fact resembles what is observed in the case of the OEP procedure applied to exchange and exchange-correlation potentials [96,105,106]. Nevertheless, even if the cc-pVTZU basis set definitely improves the description of the total kinetic potential, looking at the Pauli potential, which is more sensitive to numerical issues, one can still observe a moderate oscillatory behavior in the core region. This probably has the same origin as the one observed in Ref. [106] in the case of exchange potentials. Those oscillations can be removed by a careful choice of the basis set. For example, the utilization of a larger uncontracted basis set, namely, the universal Gaussian basis set [118] (UGBS), leads to a further improvement of the Pauli kinetic potential such that the oscillations are largely reduced.

A more effective way to avoid the basis set artifacts and obtain stable and well-behaving kinetic potentials turns out to be the utilization of the KLI approximation described in Sec. II B. In the top of Fig. 3, we show in fact a comparison of the total and Pauli kinetic potentials generated using the KLI and the OEP methods (with the UGBS basis set). Additionally,

in the middle panel of Fig. 3, we report the difference in the total ( $v_k^{\text{OEPx}} - v_k^{\text{KLI}}$ ) and Pauli kinetic potentials between the OEP and KLI methods. One can readily see that the KLI approximation yields virtually the same potentials as the OEP procedure but without the unphysical oscillations. The largest differences can be seen mostly in the core and asymptotic regions probably due to the superposition of two problems related to (i) the basis set incompleteness and oscillatory profile and (ii) the expansion of OEP kinetic potential in the finite Gaussian basis set. This actually can be confirmed comparing the ( $v_k^{\text{OEPx}} - v_k^{\text{KLI}}$ ) difference with the oscillatory profile. This is reported in the bottom panel of Fig. 3. One can note that in the major part these two quantities are largely proportional to each other, meaning that the difference between the kinetic potential generated by the OEP and the KLI methods lays basically in the incompleteness of the basis set used to expand both orbitals (thus the density) and the kinetic potential. Moreover, the KLI approximation appears to incorporate the oscillation profile correction thus the quality of the total and Pauli potentials are much better. For example, in the asymptotic region, the KLI method performs much better than the OEP potential (see the inset in the upper panel) which is not decaying correctly to  $\varepsilon_H$  for large values of  $r$  (and as  $1/r^2$  [76] to zero in case of the Pauli potential). This, in fact, is related to the Gaussian basis (used to expand the OEP kinetic potential) which goes rapidly to zero in this region. A similar behavior was also observed in the case of the exchange OEP potential [83,105]. Moreover, we note that, in the case of the KLI approximation, the description of the core region is highly improved. The occurrence of rapid oscillations in the OEP potential in this region probably has the same origin as the one observed in Ref. [106] in the case of the exchange potential and can be cured by a proper balancing the auxiliary basis set in the OEP procedure.

One more advantage of the KLI method is that the quality of the results is also preserved when standard, relatively small basis sets are used. This is shown in Fig. 4, where we report the Pauli potentials for a Ne atom and CO molecule generated

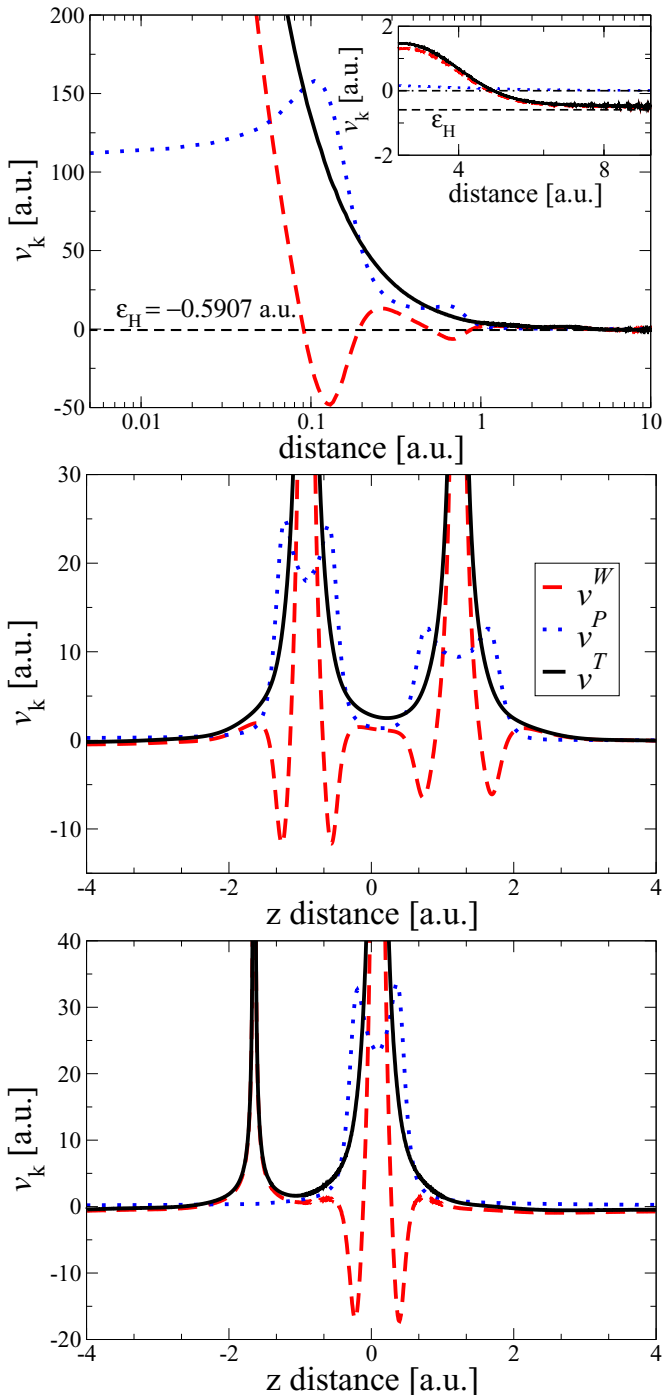


FIG. 5. Total, Weizsäcker, and Pauli kinetic potentials for Ar (top) atom and CO (middle) and HF (bottom) molecules (plotted along bond axis). Data are generated on top of OEPx SCF results in cc-pVTZ basis set using the method described in Sec. II B.

using the family of Dunning [115] cc-pVXZ basis sets (where  $X = D, T, Q$ ). The plots show that indeed the potential is only marginally dependent on the basis set and, in any case, no numerical artifacts appear. This shows that the KLI approach for the description of the kinetic potential is really a robust numerical procedure.

In Fig. 5, we report the total, von Weizsäcker, and Pauli kinetic potentials generated using the KLI method and the

cc-pVTZ [115] basis set for three representative systems, namely the Ar (top) atom and the CO (middle) and HF (bottom) molecules. The same quantities are reported for several other atomic and molecular systems in the Supplemental Material (see Ref. [117]). First, we note the smooth course of all kinetic potentials. This further supports the conclusion that the KLI method is stable and can generate reference potentials for any type of system. Second, the Pauli potential is always non-negative, giving a finite value at the core [119] and decays to zero asymptotically [76]. Moreover, at the bond (see, e.g., the HF and CO cases, as well as other molecules in Ref. [117]), the Pauli potential gives a non-negative contribution to the total kinetic potential which may play quite an important role in some cases. Furthermore, we see that in the iso-orbital regions, the Pauli potential goes correctly to zero (see, e.g., the H side in the HF molecule). The Pauli potential also exhibits a similar shell structure as the one visible in the Weizsäcker kinetic potential case. We note that the total kinetic potential does not have such features, meaning that those must almost cancel mutually. This is an important fact which should be taken into account in the construction of KE functionals and potentials for OF-DFT. Finally, we note that the total and Weizsäcker kinetic potentials show the correct behavior at the nuclei and in the asymptotic region where they decay to  $\epsilon_H$  (see the insets in Fig. 5, Ar atom).

Finally, we have assessed the impact of the reference SCF orbitals on the shape of total and Pauli kinetic potentials. Thus, in Fig. 6 we report the aforementioned quantities calculated on top of OEPx [78,79], OEP2-sc [62], HF [94], and PBE [95] orbitals in the post-SCF fashion for a Ne atom and CO molecule in the cc-pVTZ basis sets [115]. One can readily see that all the orbitals generate virtually the same Pauli potentials. A closer look (see the inset of Fig. 6 where we present the differences between PBE, HF, and OEPx results and the one obtained from OEP2-sc method) reveals that some differences appear mostly in the core regions. Note that the Pauli potential obtained from HF orbitals also behaves in line with others. This is somehow contradictory to the results reported in Ref. [120] (see Fig. 2 in the paper). However, the closer inspection reveals that the Pauli potential in Ref. [120] was obtained using the BA formula which, in contrary to our KLI method, also incorporates effects related to the nonlocality of the exchange operator (see Appendix B for more details). This can be also seen in Table I where we report the expansion coefficients calculated using the BA formula ( $\epsilon_H - \epsilon_i$ ) and the KLI method for Be and Ne atom in the UGBS basis set. One can immediately note that in the case of the OEPx orbitals, the expansion coefficients are identical. On the other hand, in the case of the HF orbitals, there is quite a large discrepancy between the coefficients. As was mentioned before, this is due to the fact that the BA coefficients obtained for the HF orbitals also take into account the energy shift ( $\langle \phi_i^{\text{HF}} | v_x - \hat{v}_x^{\text{NL}} | \phi_i^{\text{HF}} \rangle$ ) related to the difference between the local and nonlocal exchange potentials. In the KLI case, the utilization of HF quantities leads to a purely local kinetic potential which does not include any additional effect related to the exchange potential (see Appendix B) and thus the coefficients are much more similar to the ones obtained from the OEPx method.

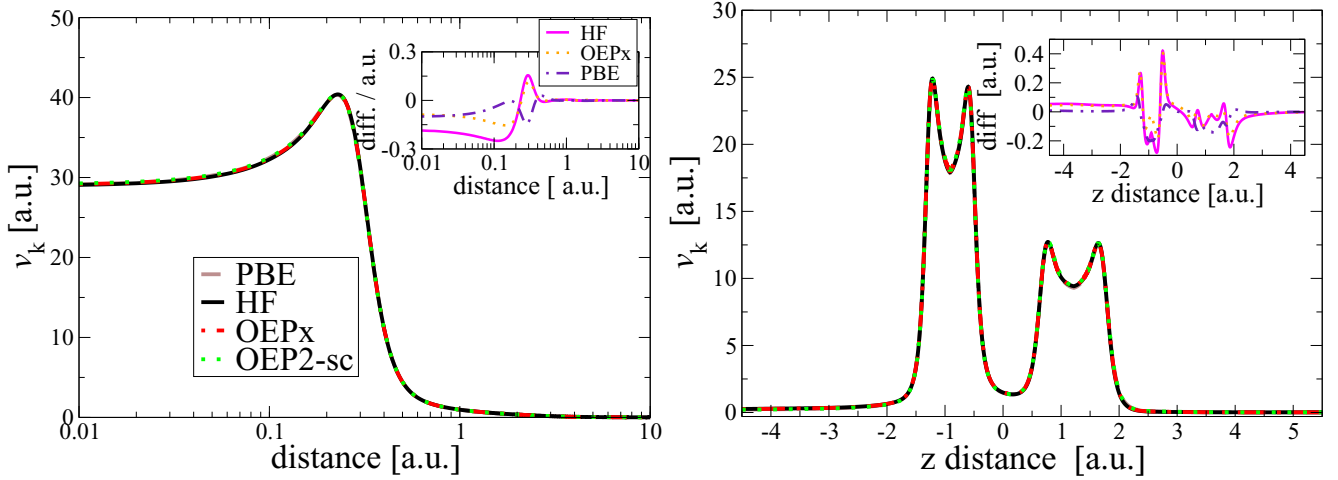


FIG. 6. Pauli potential calculated using the KLI method described in Sec. II B on top of PBE, HF, OEPx, and OEP2-sc converged quantities for the Ne atom (left) and the CO molecule (right, plotted along bond axis) for the cc-pVTZ basis set. The inset presents the differences between PBE, HF, and OEPx results and those obtained from OEP2-sc method.

## V. CONCLUSIONS

We have introduced a method that allows one to generate a real-space representation of the total and Pauli kinetic potentials via the utilization of the OEP method [77,78], taking as a starting point the KS noninteracting kinetic energy expression. Moreover, we have reviewed in detail all the presently utilized methods used to compute the aforementioned quantities. The OEP based method, however, leads to similar numerical problems as those encountered in the case of the exchange and exchange-correlation OEP calculations. Thus, we have derived a common energy denominator approximation to the kinetic OEP method and then its KLI variant which has proven to give much more stable and robust results than the original OEP one. Additionally, we have proved that when the SCF density and orbitals are employed, at the solution point, our KLI method is formally equivalent to commonly used BA formula [52] when KS reference orbitals are considered. Nevertheless, our KLI approach seems to be superior to the BA one because it can also be employed starting from HF orbitals (whereas in this case, the BA formula includes some undesired nonlocal contributions). We hope that the present paper will shed some light on the future development of

total and Pauli kinetic potentials for OF-DFT and allow us to improve existing [121] semilocal expressions for the latter.

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## APPENDIX A: BARTOLOTTI-ACHARYA FORMULA

Consider the KS equation

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}). \quad (\text{A1})$$

Multiplication by  $\phi_i^*$  and sum over  $i$  yields

$$\frac{\tau_L(\mathbf{r})}{\rho(\mathbf{r})} + v_s(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_i^N \varepsilon_i |\phi_i(\mathbf{r})|^2, \quad (\text{A2})$$

where  $\tau_L(\mathbf{r}) = -(1/2) \sum_i \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$ . Using Eq. (24) and the fact that  $\tau(\mathbf{r}) = \tau^W(\mathbf{r}) + \tau^P(\mathbf{r})$ , we find

$$\frac{\tau^W}{\rho} - \frac{\nabla^2 \rho}{4\rho} + \frac{\tau^P}{\rho} + v_s(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_i^N \varepsilon_i |\phi_i(\mathbf{r})|^2. \quad (\text{A3})$$

TABLE I. The expansion coefficients calculated using Bartolotti-Acharya formula (BA) and the one obtained from KLI method described in Sec. II B (KLI). For all systems, the UGBS basis set was used.

orb.	OEPx orbitals			HF orbitals		
	orb. energy	BA ( $\varepsilon_H - \varepsilon_i$ )	KLI	orb. energy	BA ( $\varepsilon_H - \varepsilon_i$ )	KLI
Be						
1s	-4.125	3.816	3.816	-4.733	4.423	3.861
2s	-0.309	0.000	—	-0.309	0.000	—
Ne						
1s	-30.820	29.969	29.969	-32.772	31.922	29.961
2s	-1.718	0.867	0.867	-1.930	1.080	0.858
2p	-0.851	0.000	—	-0.850	0.000	—



On the other hand, the Euler equation [Eq. (1)] reads

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v_s(\mathbf{r}) = \mu. \quad (\text{A4})$$

By subtracting Eq. (A3) from Eq. (A4), after some algebra we obtain

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = \frac{\tau^W}{\rho} - \frac{\nabla^2 \rho}{4\rho} + \frac{\tau^P}{\rho} + \frac{1}{\rho(\mathbf{r})} \sum_i^N (\mu - \varepsilon_i) |\phi_i(\mathbf{r})|^2, \quad (\text{A5})$$

Now if we remove the von Weizsäcker kinetic potential from both sides, we easily retrieve Eq. (12).

It is also easy to show that the BA formula can be alternatively derived starting from the oscillation profile corrected Pauli potential

$$v^{P,\text{fix}}(\mathbf{r}) = -v_s(\mathbf{r}) - v^W(\mathbf{r}) + \Delta v_{\text{osc}}(\mathbf{r}) + \mu, \quad (\text{A6})$$

that is directly derivable from Eq. (32). Taking into account that the  $\Delta v_{\text{osc}}(\mathbf{r})$  can be rewritten as

$$\Delta v_{\text{osc}}(\mathbf{r}) = \frac{\tau^W(\mathbf{r})}{\rho(\mathbf{r})} - \frac{\nabla^2 \rho(\mathbf{r})}{4\rho(\mathbf{r})} + \frac{\tau^P(\mathbf{r})}{\rho(\mathbf{r})} + v_s(\mathbf{r}) - \frac{1}{\rho(\mathbf{r})} \sum_i^N \varepsilon_i |\phi_i(\mathbf{r})|^2, \quad (\text{A7})$$

one arrives at

$$v^P(\mathbf{r}) = \frac{\tau^P(\mathbf{r})}{\rho(\mathbf{r})} - \frac{1}{\rho(\mathbf{r})} \sum_i^N \varepsilon_i |\phi_i(\mathbf{r})|^2 + \mu, \quad (\text{A8})$$

that is exactly Eq. (12).

### APPENDIX B: EQUIVALENCE OF BARTOLOTTI-ACHARYA FORMULA AND KLI APPROXIMATION

From the KS equation, we easily find

$$\varepsilon_i = \langle \phi_i | -\frac{1}{2}\nabla^2 + v_s | \phi_i \rangle. \quad (\text{B1})$$

On the other hand, multiplying the Euler equation [Eq. (A4)] by  $|\phi_i(\mathbf{r})|^2$  and integrating over the whole space, one arrives at

$$\mu = \langle \phi_i | \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v_s | \phi_i \rangle. \quad (\text{B2})$$

Now, subtracting Eqs. (B1) and (B2), we get

$$\mu - \varepsilon_i = \langle \phi_i | \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + \frac{1}{2}\nabla^2 | \phi_i \rangle = (v_k)_{ii} - (T_s)_{ii}. \quad (\text{B3})$$

Finally, inserting Eq. (B3) into Eq. (A5) and removing from both sides the VW potential, we recover Eq. (27).

Alternatively, starting from the HF equations, we find

$$\varepsilon_i^{\text{HF}} = \langle \phi_i^{\text{HF}} | -\frac{1}{2}\nabla^2 + v_{\text{ext}} + v_{\text{H}} + \hat{v}_x^{\text{NL}} | \phi_i^{\text{HF}} \rangle, \quad (\text{B4})$$

where  $\hat{v}_x^{\text{NL}}$  is a nonlocal HF exchange operator. Multiplying now the Euler equation [Eq. (A4)] by  $|\phi_i^{\text{HF}}(\mathbf{r})|^2$  and integrating over the whole space, one arrives at

$$\mu = \langle \phi_i^{\text{HF}} | \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v_s | \phi_i^{\text{HF}} \rangle. \quad (\text{B5})$$

Subtracting Eqs. (B4) and (B5), we get

$$\mu - \varepsilon_i^{\text{HF}} = \langle \phi_i^{\text{HF}} | \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + \frac{1}{2}\nabla^2 | \phi_i^{\text{HF}} \rangle + \langle \phi_i^{\text{HF}} | v_x - \hat{v}_x^{\text{NL}} | \phi_i^{\text{HF}} \rangle. \quad (\text{B6})$$

Finally, inserting Eq. (B6) into Eq. (A5) and removing from both sides the VW potential, one obtains the expression for the Pauli kinetic potential. Note, however, that Eq. (27) does not include the  $\langle \phi_i^{\text{HF}} | v_x - \hat{v}_x^{\text{NL}} | \phi_i^{\text{HF}} \rangle$  term which additionally accounts in the  $\mu - \varepsilon_i^{\text{HF}}$  difference for the nonlocal effect related to the HF exchange operator.

### APPENDIX C: DERIVATION OF $\frac{\delta T_s[\{\phi_q\}]}{\delta \phi_p(\mathbf{r}' )}$

The derivative of the orbital-dependent KE functional given by Eq. (15) with respect to the orbitals reads

$$\begin{aligned} \frac{\delta T_s[\{\phi_q\}]}{\delta \phi_p(\mathbf{r}')} &= -\frac{1}{2} \sum_i^N \int d\mathbf{r} \frac{\delta \phi_i^*(\mathbf{r})}{\delta \phi_p(\mathbf{r}')} \nabla_r^2 \phi_i(\mathbf{r}) \\ &\quad - \frac{1}{2} \sum_i^N \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla_r^2 \left( \frac{\delta \phi_i(\mathbf{r})}{\delta \phi_p(\mathbf{r}')} \right) \\ &= -\frac{1}{2} \sum_i^N \int d\mathbf{r} \delta(\mathbf{r} - \mathbf{r}') \delta_{pi} \nabla_r^2 \phi_i(\mathbf{r}) \\ &\quad - \frac{1}{2} \sum_i^N \int d\mathbf{r} \delta_{pi} \phi_i^*(\mathbf{r}) \nabla_r^2 (\delta(\mathbf{r} - \mathbf{r}')). \end{aligned} \quad (\text{C1})$$

Clearly, whenever  $\phi_p$  denotes an unoccupied orbital, we have  $\delta T_s/\delta \phi_p = 0$ . In the opposite case ( $\phi_p$  being an occupied orbital), a nonzero value is obtained. After some algebra, Eq. (C1) reduces to

$$\frac{\delta T_s[\{\phi_q\}]}{\delta \phi_p(\mathbf{r}')} = -\frac{1}{2} \nabla_r^2 \phi_p(\mathbf{r}') - \frac{1}{2} \int d\mathbf{r} \phi_p^*(\mathbf{r}) \nabla_r^2 (\delta(\mathbf{r} - \mathbf{r}')). \quad (\text{C2})$$

Now, utilizing the following relation:

$$\int d\mathbf{r}' f(\mathbf{r}') \nabla_r^2 \delta(\mathbf{r} - \mathbf{r}') = \int d\mathbf{r}' \delta(\mathbf{r} - \mathbf{r}') \nabla_r^2 f(\mathbf{r}') = \nabla_r^2 f(\mathbf{r}), \quad (\text{C3})$$

on the right-hand side of Eq. (C2), we recover Eq. (15).

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