# Exchange energies with forces in density-functional theory

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We propose exchanging the energy functionals in DFT with physically equivalent exact force expressions as a promising route towards efficient yet accurate approximations to the exchangecorrelation potential. In analogy to the usual energy-based procedure, we split the force difference between the interacting and auxiliary system into a Hartree, an exchange and a correlation force. The corresponding potentials are obtained by solving a Poisson equation. The explicit expression of the exchange potential overcomes conceptual issues of previous force-based approaches and compares well with the numerically more involved optimized effective-potential method.

Density-functional theory (DFT) [1], with its many variants [2–9], is the workhorse of first-principle simulations in chemistry, solid state physics and materials science. Most of DFT simulations are performed using the Kohn–Sham (KS) scheme, where the density of the interacting system is predicted by solving an auxiliary non-interacting system. The exact KS potential that generates the interacting density is then determined by the underlying density-potential mappings  $v(\mathbf{r}) \stackrel{1:1}{\leftrightarrow} \rho(\mathbf{r})$  for *v*representable (one-body) densities  $\rho(\mathbf{r})$  of the interacting and non-interacting system, respectively.

It is common practice to derive approximations for this (in general unknown) potential by re-expressing the universal energy functional as a sum of non-interacting kinetic, Hartree and exchange-energy functionals as well as the unknown correlation-energy functional [10] and then to assume Gâteaux differentiability [11] with respect to the density. While for energy functionals explicitly given in terms of the density, approximate potentials can be determined this way, for implicit functionals this is no longer possible in general [12]. To make matters worse, it has been shown that the exact energy functionals of DFT are not Gâteaux differentiable with respect to the usual function spaces [13], questioning this common way of deriving approximations to the KS potential. We note that the theoretical setting of an exact regularization procedure is available [14, 15], but with unclear practical implications at the moment.

However, from a physical point of view one can exchange a description in terms of energies by a description based on forces. Indeed, the exact exchange-correlation potential of DFT can be expressed directly in terms of the difference in force densities between the interacting and the auxiliary non-interacting system [16, 17], thus bypassing differentiation and related issues. In this work we show that this force-based approach is not only conceptually very appealing but also practically relevant. Specifically, we show that besides the usual Hartree potential we also find the explicit form of the local-exchange potential and highlight that this approach overcomes conceptual issues of previous functional approximations based on

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forces. The form of the local exchange potential is consistent with current-density-functional theory (CDFT) and we discuss its connections to the time-dependent case. In the context of DFT we then show that the explicit force-based exchange approximation performs similarly to the numerically more involved optimized effective potential (OEP) approach in exchange approximation. We finally comment on ways to approximate the remaining correlation force densities.

We consider the N-particle Hamiltonian (in Hartree atomic units  $e = \hbar = m_e = (4\pi\epsilon_0)^{-1} = 1$ )

$$\hat{H} = \underbrace{-\frac{1}{2} \sum_{k=1}^{N} \nabla_k^2}_{\hat{T}} + \underbrace{\sum_{k=1}^{N} v(\mathbf{r}_k)}_{\hat{V}[v]} + \underbrace{\sum_{k>l} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}}_{\hat{W}}, \quad (1)$$

with  $v(\mathbf{r})$  some external one-particle potential. For antisymmetric wave functions  $\Psi(\mathbf{x}_1,...,\mathbf{x}_N)$ , where  $\mathbf{x}_k = (\mathbf{r}_k \sigma_k)$ , we then define the spin-summed  $p^{\text{th}}$ -order reduced density matrix

$$\rho^{(p)}(\mathbf{r}_{1},\ldots,\mathbf{r}_{p},\mathbf{r}_{1}',\ldots,\mathbf{r}_{p}') = \frac{N!}{p!(N-p)!} \sum_{\substack{\sigma_{1}\ldots\sigma_{p}\\\sigma_{1}'\ldots\sigma_{p}'}} \int \Psi(\mathbf{x}_{1},\ldots,\mathbf{x}_{p},\mathbf{x}_{p+1},\ldots,\mathbf{x}_{N}) \quad (2)$$
$$\Psi^{*}(\mathbf{x}_{1}',\ldots,\mathbf{x}_{p}',\mathbf{x}_{p+1},\ldots,\mathbf{x}_{N}) \,\mathrm{d}\mathbf{r}_{p+1}\ldots \,\mathrm{d}\mathbf{r}_{N}.$$

We can then use these reduced density matrices and the exact density  $\rho(\mathbf{r}) = \rho^{(1)}(\mathbf{r}, \mathbf{r})$  to express the equation of motion of the (paramagnetic) current density

$$\mathbf{j}(\mathbf{r}) = \frac{1}{2i} \left( \nabla \rho^{(1)}(\mathbf{r}, \mathbf{r}') - \nabla' \rho^{(1)}(\mathbf{r}, \mathbf{r}') \right) \Big|_{\mathbf{r}' = \mathbf{r}}$$
(3)

for an eigenstate, for which the current density does not change in time, as [17, 18]

$$0 = -\rho(\mathbf{r})\nabla v(\mathbf{r}) + \mathbf{F}_T(\mathbf{r}) + \mathbf{F}_W(\mathbf{r}).$$
(4)

This expression introduces the exact interaction-stress and momentum-stress forces, respectively,

$$\mathbf{F}_W(\mathbf{r}) = -2 \int (\nabla |\mathbf{r}' - \mathbf{r}|^{-1}) \rho^{(2)}(\mathbf{r}, \mathbf{r}', \mathbf{r}, \mathbf{r}') \,\mathrm{d}\mathbf{r}', \quad (5)$$

$$\mathbf{F}_T(\mathbf{r}) = \left. \frac{1}{4} (\nabla - \nabla') (\nabla^2 - \nabla'^2) \rho^{(1)}(\mathbf{r}, \mathbf{r}') \right|_{\mathbf{r}' = \mathbf{r}}.$$
 (6)

Here,  $(\nabla |\mathbf{r}' - \mathbf{r}|^{-1})$  indicates that the gradient *only* acts on the Coulomb interaction term. In the following we indicate the terms coming from the solution of the fully interacting problem as  $\mathbf{F}_W[\Psi]$  and  $\mathbf{F}_T[\Psi]$  and the terms coming from the auxiliary non-interacting KS problem (Eq. (1) without  $\hat{W}$  and with a different single-particle potential  $v_s(\mathbf{r})$ ) as  $\mathbf{F}_T[\Phi]$ . Analogously to Eq. (4), we then have for an eigenstate of the auxiliary noninteracting system

$$0 = -\rho_s(\mathbf{r})\nabla v_s(\mathbf{r}) + \mathbf{F}_T([\Phi], \mathbf{r}).$$
(7)

If we now impose that both systems generate the same ground-state density, i.e.,  $\rho_s(\mathbf{r}) = \rho(\mathbf{r})$ , we find with the definition of the Hartree exchange-correlation (Hxc) potential  $v_{\text{Hxc}}(\mathbf{r}) = v_s(\mathbf{r}) - v(\mathbf{r})$  the local force-balance equation

$$\rho \nabla v_{\text{Hxc}} = -\mathbf{F}_{\text{Hxc}}[\Phi, \Psi] = \mathbf{F}_T[\Phi] - \mathbf{F}_T[\Psi] - \mathbf{F}_W[\Psi], \quad (8)$$

which defines  $\mathbf{F}_{\text{Hxc}}$ . By virtue of the Hohenberg–Kohn theorem [19] the Slater determinant  $\Phi$  as well as the the interacting wave function  $\Psi$  are given solely in terms of the density, which makes all the force densities determined by the density only. Equation (8) implies that

$$\nabla v_{\rm Hxc}(\mathbf{r}) = -\frac{\mathbf{F}_{\rm Hxc}(\mathbf{r})}{\rho(\mathbf{r})} = -\mathbf{f}_{\rm Hxc}(\mathbf{r})$$
(9)

is a purely longitudinal vector field. We can thus recast the equation for  $v_{\text{Hxc}}$  into a Poisson equation  $-\nabla^2 v_{\text{Hxc}} = \nabla \cdot \boldsymbol{f}_{\text{Hxc}}$  by applying the divergence such that the solution, using the corresponding Green's function, is given by

$$v_{\rm Hxc}(\mathbf{r}) = \int \frac{\nabla' \cdot \boldsymbol{f}_{\rm Hxc}(\mathbf{r}')}{4\pi |\mathbf{r} - \mathbf{r}'|} \,\mathrm{d}\mathbf{r}'.$$
 (10)

Next, we split up the Hxc force in analogy to the partition of the energy usual in DFT as

$$\mathbf{F}_{\mathrm{Hxc}}[\Phi, \Psi] = \mathbf{F}_{W}[\Phi] \tag{11}$$
$$+ \underbrace{\mathbf{F}_{T}[\Psi] - \mathbf{F}_{T}[\Phi] + \mathbf{F}_{W}[\Psi] - \mathbf{F}_{W}[\Phi]}_{\mathbf{F}_{c}[\Phi, \Psi]},$$

where  $\mathbf{F}_{W}[\Phi]$  is the Hartree-exchange (Hx) force and  $\mathbf{F}_{c}[\Phi, \Psi]$  the correlation force. This partition leads to the respective force-based potentials,  $v_{\text{fHx}}$  and  $v_{\text{fc}}$ , that add up to the exact Hxc potential,

$$v_{\rm Hxc}(\mathbf{r}) = \underbrace{\int \frac{\nabla' \cdot \boldsymbol{f}_{\rm Hx}(\mathbf{r}')}{4\pi |\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}'}_{v_{\rm fHx}(\mathbf{r})} + \underbrace{\int \frac{\nabla' \cdot \boldsymbol{f}_{\rm c}(\mathbf{r}')}{4\pi |\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}'}_{v_{\rm fc}(\mathbf{r})}.$$
 (12)

Here, we have denoted  $\mathbf{f}_{\text{Hx}} = \mathbf{F}_{W}[\Phi]/\rho$  and  $\mathbf{f}_{\text{c}} = \mathbf{F}_{\text{c}}[\Phi, \Psi]/\rho$ . Since the Hx force is given in terms of the KS wave function only, we know this part explicitly and we can directly calculate the exact Hx potential for a given KS wave function.

To make the resulting Hx potential more explicit, we rely on the standard assumption that  $\Phi$  is a single, closedshell Slater determinant with spin-space orbitals  $\varphi_k(\mathbf{x})$ , such that we can express [20, Eq. (2.5.19)]

$$\rho_{s}^{(2)}(\mathbf{r}, \mathbf{r}', \mathbf{r}, \mathbf{r}') = \frac{1}{2} \left( \rho(\mathbf{r}) \rho(\mathbf{r}') - \frac{1}{2} \left| \rho_{s}^{(1)}(\mathbf{r}, \mathbf{r}') \right|^{2} \right), \quad (13)$$

where  $\rho_s^{(1)}(\mathbf{r},\mathbf{r}') = \sum_{k,\sigma} \varphi_k(\mathbf{r}\sigma) \varphi_k^*(\mathbf{r}'\sigma)$ . We therefore have

$$\mathbf{F}_{W}[\Phi] = -\rho(\mathbf{r})\nabla\int\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\mathbf{r}' \\ +\underbrace{\frac{1}{2}\int(\nabla|\mathbf{r} - \mathbf{r}'|^{-1})\left|\rho_{s}^{(1)}(\mathbf{r}, \mathbf{r}')\right|^{2}\,\mathrm{d}\mathbf{r}'}_{\mathbf{F}_{\mathbf{x}}[\Phi]}.$$
(14)

We can thus identify the usual Hartree potential

$$v_{\rm H}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \,\mathrm{d}\mathbf{r}' \tag{15}$$

and the force-based local-exchange potential

$$v_{\rm fx}(\mathbf{r}) = -\int \frac{\nabla' \cdot \int (\nabla' |\mathbf{r}'' - \mathbf{r}'|^{-1}) \bar{\rho}_{\rm x}(\mathbf{r}'' |\mathbf{r}') \,\mathrm{d}\mathbf{r}''}{4\pi |\mathbf{r} - \mathbf{r}'|} \,\mathrm{d}\mathbf{r}',\tag{16}$$

where we used the definition of the exchange hole [20, Eq. (2.5.27)]

$$\bar{\rho}_{\mathbf{x}}(\mathbf{r}'|\mathbf{r}) = -\frac{1}{2} \frac{|\rho_s^{(1)}(\mathbf{r}, \mathbf{r}')|^2}{\rho(\mathbf{r})}.$$
(17)

For a numerically more convenient form of  $v_{\rm fx}$  in terms of the Slater-exchange potential plus correction terms we refer to App. A. We note that in the homogeneous limit, Eq. (16) reduces to the well-known exchange-only localdensity approximation and we give details in App. B. The form of Eq. (16) resembles the exchange potential introduced by Harbola and Sahni [21]. However, in contrast to the Harbola–Sahni potential, it does not involve any line integrals or the assumption of conservative forces (see also the discussion after Eq. (21)). Moreover, the missing correlation potential is given uniquely in terms of the force-density difference  $\mathbf{F}_{c}[\Phi, \Psi]$  and a simple Coulomb integral (see Eq. (12)).

Based on the above explicit form of the local-exchange potential we can highlight some advantages of the forcebased approach. In the common energy-based approach, the potential is found via a functional variation of the energy expression with respect to the density. In the exchange case one considers the functional derivative of

$$E_{\mathbf{x}}[\rho] = \langle \Phi[\rho] | \hat{W} | \Phi[\rho] \rangle - E_{\mathrm{H}}[\rho]$$
  
=  $-\frac{1}{4} \int \frac{\left| \rho_s^{(1)}(\mathbf{r}, \mathbf{r}') \right|^2}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}',$  (18)

where  $E_{\rm H}[\rho] = \frac{1}{2} \int v_{\rm H}(\mathbf{r})\rho(\mathbf{r}) \,\mathrm{d}\mathbf{r}$  is the Hartree energy. As was pointed out by van Leeuwen [12], for an implicit density functional the (generalization of the) functional derivative is not straightforward and might not exist in certain cases. If the functional derivative exists, then by construction it obeys a virial relation of the form (see App. C)

$$E_{\mathbf{x}}[\rho] = -\int \rho(\mathbf{r}) \,\mathbf{r} \cdot \nabla \frac{\delta E_{\mathbf{x}}[\rho]}{\delta \rho(\mathbf{r})} \,\mathrm{d}\mathbf{r}.$$
 (19)

In practice, the derivative is determined by the OEP approach [22, 23]. Yet, OEP exchange potentials in general do not obey Eq. (19) and sometimes this relation is additionally imposed, e.g., in Ref. [24] (also compare Tab. I). On the other hand, in the force-based approach we have

$$\boldsymbol{f}_{\mathrm{x}}(\mathbf{r}) = \frac{\mathbf{F}_{\mathrm{x}}(\mathbf{r})}{\rho(\mathbf{r})} = -\nabla v_{\mathrm{fx}}(\mathbf{r}) + \nabla \times \boldsymbol{\alpha}_{\mathrm{fx}}(\mathbf{r}), \qquad (20)$$

where by applying the Helmholtz decomposition into a longitudinal (curl-free) and a transverse (divergencefree) vector-field component [25, §3.9], we find that (see App. C for details)

$$E_{\mathbf{x}}[\rho] = \int \mathbf{r} \cdot \mathbf{F}_{\mathbf{x}}(\mathbf{r}) \, \mathrm{d}\mathbf{r}$$
(21)  
=  $-\int \rho(\mathbf{r}) \, \mathbf{r} \cdot \nabla v_{\mathrm{fx}}(\mathbf{r}) \, \mathrm{d}\mathbf{r} + \int \rho(\mathbf{r}) \, \mathbf{r} \cdot (\nabla \times \boldsymbol{\alpha}_{\mathrm{fx}}(\mathbf{r})) \, \mathrm{d}\mathbf{r}.$ 

Here, the last term due to the curl vanishes for spherically symmetric densities (see App. C and Tab. I). Hence, the local-exchange potential satisfies a virial relation of the form of Eq. (19) for spherically symmetric systems, but in general we have the more involved Eq. (21) including a transverse component. This most notably implies that the local-exchange potential from the force-balance approach derived here is in general *different* from an exchange potential defined as the exact exchange-energy derivative. It is interesting to observe that this transverse (and thus path-dependent) component of Eq. (20) has to be cancelled exactly by the transverse component of the correlation force  $f_{\rm c} = \mathbf{F}_{\rm c}/\rho$ , since their sum  $f_{\rm x} + f_{\rm c}$ is purely longitudinal by Eq. (9) and since the Hartree contribution is a gradient field given by  $-\nabla v_{\rm H}$ . This gives a rationale for omitting the transverse part altogether from the exchange-only force  $f_x$  and taking only  $v_{\rm fx}$  as an exchange potential. We further note that the local-exchange potential given by Eq. (16) also obeys the usual coordinate scaling relations (see App. C).

The generalized virial relation Eq. (21) also highlights the connection of the force-based approach to CDFT. If besides the density  $\rho$  we also intend to control the current density **j**, then we would need a transverse exchangecorrelation vector potential as well, where  $\alpha_{fx}$  contributes to the exchange vector potential [17]. We even find that  $v_{fx}$  can be chosen to be the exchange potential of CDFT and of time-dependent CDFT [17]. This makes  $v_{fx}$  nicely compatible with different variants of DFT. Furthermore, there is a direct connection from  $v_{fx}$  to time-dependent DFT (TDDFT), since the second time derivative of the densities is controlled by the Hxc potential. The fundamental equation of TDDFT is [5]

$$\nabla \cdot [\rho(\mathbf{r}, t) \nabla v_{\text{Hxc}}(\mathbf{r}, t)] = -\nabla \cdot \mathbf{F}_{\text{Hxc}}(\mathbf{r}, t) \qquad (22)$$

and the exchange potential in TDDFT is now determined from the exchange forces not by solving a Poisson equation but by inverting a Sturm–Liouville equation. So in general, the exchange potential in TDDFT will be different from  $v_{\rm fx}$ , yet the difference can be determined from the transverse parts of  $\mathbf{F}_{\rm x}$  [26].

Finally, let us consider the force-balance equation in exchange approximation (FBEx), i.e., we take  $v_{\rm fx}$  from Eq. (16) and assume  $v_{\rm fc} = 0$  in every KS iteration step, and check how this performs in comparison to common exchange approximations numerically. We have implemented the force-based local-exchange potential in the real-space code Octopus [27] and ran simulations for a set of atoms using norm-conserving pseudopotentials [28], a grid spacing of 0.15 Bohr, and a radius of 10 Bohr for Be and Ne, a radius of 12 Bohr for Mg, Ar, and Zn, and a radius of 14 Bohr for Ca. Indeed, FBEx performs similar to the much more involved OEP in exact-exchange approach (OEPx) or its approximation OEPx-KLI [29] (see Fig. 1). All exchange functionals considered in this work, pure Slater potential, FBEx and OEPx-KLI, share the same computational scaling as Hartree–Fock, while OEPx additionally only works as an iterative procedure. Further-



Figure 1. The exchange potential obtained for different functionals and different atoms.

more, we demonstrate that the local-exchange potential adheres to the virial relation of the form of Eq. (19) up to numerical inaccuracies (see Tab. I) because of spherical symmetry, while the OEPx and the OEPx-KLI violate this relation. Further numerical tests and comparisons, also for small molecules, can be found in App. D.

In conclusion, we have shown that defining the Hxc potential of KS DFT by forces is not only conceptually beneficial, but also has certain advantages in practice over the common energy-based approach. It is numerically straightforward to construct the corresponding potential from a given force density, the method allows to avoid various problems of the energy-based approach such as determining implicit functional derivatives, and it further provides an explicit form for the exchange potential.

| Atom | Slater | FBEx   | OEPx-KLI | OEPx   |
|------|--------|--------|----------|--------|
| Li   | 245.3  | -0.049 | 0.647    | -1.464 |
| Be   | 415.2  | 0.037  | 32.87    | 17.97  |
| Ne   | 208.2  | -0.001 | 30.94    | 33.139 |
| Na   | 896.1  | 0.080  | -22.08   | -36.4  |
| Mg   | 1328.1 | 0.353  | 60.40    | -19.49 |
| Ar   | 221.95 | 0.000  | 7.61     | 8.21   |
| Ca   | 603.4  | -0.011 | 17.51    | -1.52  |
| Zn   | 6225.1 | 4.31   | 24.58    | -88.72 |

Table I. Difference  $\Delta E_{\rm x} = E_{\rm x}^{\rm eig} - E_{\rm x}^{\rm virial}$ , in mHa, between the exchange energy computed from the orbitals (or the density) and from the exchange energy obtained from the potential using the virial relation for different local-exchange potentials.

The non-explicit correlation potential is defined uniquely by the correlation force density and in contrast to the energy-based approach we also have a straightforward connection to the current-density variant of DFT and to the time-dependent case. Furthermore, the approach can be seamlessly applied to atomic, molecular and solidstate systems. Finally, we have shown that the explicit Hx approximation performs similarly as the much more involved OEP approach in an exchange approximation. The exchange potential of Eq. (16) performs much better than the Slater potential, which currently serves as a basis for many existing functionals. We therefore expect that our potential could lead to a new class of more accurate functional approximations.

In order to address the still unknown correlation force density, the interaction part  $\mathbf{F}_{W}[\Psi] - \mathbf{F}_{W}[\Phi]$  can be expressed by the correlation hole [26], while the kinetic part  $\mathbf{F}_{T}[\Psi] - \mathbf{F}_{T}[\Phi]$  might be expressed as the difference between the interacting and the non-interacting one-body reduced density matrix close to the diagonal [26]. One can therefore either try to build approximate models of these quantities based on physical intuition [30], derive expressions for these terms for specific cases (e.g., the homogeneous limit) from wave-function methods potentially augmented by modern machine-learning techniques [31], or devise perturbative expansions on top of the KS Slater determinants. Even though the force densities are three-dimensional vector fields and thus more involved than simple energy functionals, the previously successful application of such approaches to construct correlation-energy functionals makes it plausible that similar methods are well applicable to the force-based approach to KS DFT. One possible strategy follows directly from the observation that the transverse parts in  $f_{\rm x} + f_{\rm c}$  cancel: Modify the exchange hole in Eq. (14) with a correlation function such that  $\mathbf{F}_{W}[\Phi]/\rho$  becomes (almost) purely longitudinal. Another approach could employ an additional auxiliary vector potential consistent with CDFT [17] to include correlations in the KS system.

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## Appendix A: Numerically convenient forms of the exchange potential

In order to bring the local-exchange potential into a numerically more convenient form, we perform a partial integration in Eq. (16) and find

$$v_{\rm fx}(\mathbf{r}) = v_{\rm SL}(\mathbf{r}) + \int \frac{\nabla' \cdot \int |\mathbf{r}'' - \mathbf{r}'|^{-1} \nabla' \bar{\rho}_{\rm x}(\mathbf{r}'' |\mathbf{r}') \,\mathrm{d}\mathbf{r}''}{4\pi |\mathbf{r} - \mathbf{r}'|} \,\mathrm{d}\mathbf{r}',\tag{A1}$$

where  $v_{\rm SL}(\mathbf{r}) = \int |\mathbf{r} - \mathbf{r}'|^{-1} \bar{\rho}_{\mathbf{x}}(\mathbf{r}|\mathbf{r}') \, \mathrm{d}\mathbf{r}'$  is the Coulomb potential generated by the exchange hole, i.e., the well-known Slater exchange potential. The second term can be computed using

$$\int |\mathbf{r}'' - \mathbf{r}'|^{-1} \nabla' \bar{\rho}_{\mathbf{x}}(\mathbf{r}'' | \mathbf{r}') \, \mathrm{d}\mathbf{r}'' = \sum_{ij} \left( \nabla' \frac{\rho_{ij}^*(\mathbf{r}')}{\rho(\mathbf{r}')} \right) \int |\mathbf{r}'' - \mathbf{r}'|^{-1} \rho_{ij}(\mathbf{r}'') \, \mathrm{d}\mathbf{r}'', \tag{A2}$$

where we defined the co-density  $\rho_{ij}(\mathbf{r}) = \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})$ .

This form has a few advantages. First, we only need to solve one Poisson equation and compute one gradient per pair of indices i, j. Therefore, the numerical cost only increases by one gradient pair of indices i, j compared to the Slater potential. Further, it provides an analytical expression for beyond-Slater approximations and might such serve as the starting point for the development of novel functionals. Finally, from this expression it is also clear that in the single orbital case  $\rho_{ij}^*(\mathbf{r}')/\rho(\mathbf{r}')$  is uniformly equal to 1 and then the second term vanishes.

There is still a subtle numerical issue when implementing this expression. When evaluating  $\rho_{ij}^*(\mathbf{r}')/\rho(\mathbf{r}')$  close to the border of the simulation box we obtain the unity, as in the one-electron limit only the highest occupied state contributes to the density. Having zero-boundary conditions at the border of the box leads to a step function irrespective of the size of the simulation box. Consequently, the evaluation of the gradient on the real-space grid by finite differences leads to a non-zero contribution at the surface of the simulation box. This "surface charge" leads to a uniform potential which is not physical. In order to circumvent this issue, we simply used the Leibniz product rule

$$\nabla' \frac{\rho_{ij}^*(\mathbf{r}')}{\rho(\mathbf{r}')} = \frac{\rho(\mathbf{r}')\nabla'\rho_{ij}^*(\mathbf{r}') - \rho_{ij}^*(\mathbf{r}')\nabla'\rho(\mathbf{r}')}{\rho(\mathbf{r}')^2} \,. \tag{A3}$$

The numerator is computed first and the two contributions exactly cancel, which leads to the correct long-range numerical value of the potential.

#### Appendix B: Local-density approximation from the local-exchange potential and its virial relation

In Tchenkoue *et al.* [17, IV.B] it was demonstrated how the usual Slater X $\alpha$  [32] and local-density approximation (LDA) [20, §7.4] formulas for the local-exchange potential can be derived directly from the exchange-force expression Eq. (14). Since the approximated  $f_x(\mathbf{r})$  is purely longitudinal, the exact same derivation can also be started immediately from the local-exchange potential expression of Eq. (16). This directly connects the most fundamental functional approximations of DFT with the present formalism.

For completeness, we further show that the exchange LDA also still fulfils a virial relation of the form of Eq. (19). The exchange energy for the LDA is [20, (6.1.20)]

$$E_{\rm x}^{\rm LDA}[\rho] = C_{\rm x} \int \rho({\bf r})^{4/3} \, \mathrm{d}{\bf r}, \qquad C_{\rm x} = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3},$$
 (B1)

which by functional differentiation gives the LDA exchange potential

$$v_{\mathbf{x}}^{\mathrm{LDA}}(\mathbf{r}) = \frac{\delta E_{\mathbf{x}}^{\mathrm{LDA}}}{\delta\rho(\mathbf{r})} = \frac{4}{3}C_{\mathbf{x}}\rho(\mathbf{r})^{1/3}.$$
 (B2)

Now putting this into the right-hand side of the virial relation Eq. (19), we get by partial integration

$$I[\rho] = -\int \rho(\mathbf{r})\mathbf{r} \cdot \nabla v_{\mathbf{x}}^{\text{LDA}} \, \mathrm{d}\mathbf{r} = -\frac{4}{9}C_{\mathbf{x}} \int \rho(\mathbf{r})^{1/3}\mathbf{r} \cdot \nabla \rho(\mathbf{r}) \, \mathrm{d}\mathbf{r} = \frac{4}{3}C_{\mathbf{x}} \int \rho(\mathbf{r})^{4/3} \, \mathrm{d}\mathbf{r} - \frac{1}{3}I[\rho]. \tag{B3}$$

This means  $I[\rho] = C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$ , which is exactly the expression of  $E_x^{\text{LDA}}[\rho]$ , so the LDA fulfills the virial relation. Furthermore, it has the correct scaling,  $v_{x,\lambda}^{\text{LDA}}(\mathbf{r}) = \lambda v_x^{\text{LDA}}(\lambda \mathbf{r})$ , as can easily be checked. Such scaling relations will be further discussed for the local-exchange potential in App. C.

## Appendix C: Scaling behavior and virial relation

If one uses the coordinate-scaled densities

$$\rho_{\lambda}(\mathbf{r}) = \lambda^{3} \rho(\lambda \mathbf{r}), \quad \rho_{\lambda}^{(1)}(\mathbf{r}, \mathbf{r}') = \lambda^{3} \rho^{(1)}(\lambda \mathbf{r}, \lambda \mathbf{r}'), \tag{C1}$$

one finds  $v_{fx,\lambda}(\mathbf{r}) = \lambda v_{fx}(\lambda \mathbf{r})$ , where  $v_{fx,\lambda}$  is the expression from Eq. (16) with  $\rho \mapsto \rho_{\lambda}$  and  $\rho^{(1)} \mapsto \rho_{\lambda}^{(1)}$  replaced. Similarly one finds  $E_x[\rho_{\lambda}] = \lambda E_x[\rho]$  directly from Eq. (18). This is the correct scaling behaviour for the exchange energy [20, §11.1] and together with the assumption of functional differentiability of  $E_x[\rho]$  this suffices to derive the virial relation of Eq. (19). By virtue of the chain rule of functional calculus we have

$$E_{\mathbf{x}}[\rho] = \left. \frac{\mathrm{d}E_{\mathbf{x}}[\rho_{\lambda}]}{\mathrm{d}\lambda} \right|_{\lambda=1} = \int \frac{\delta E_{\mathbf{x}}[\rho]}{\delta\rho(\mathbf{r})} \left. \frac{\mathrm{d}\rho_{\lambda}(\mathbf{r})}{\mathrm{d}\lambda} \right|_{\lambda=1} \,\mathrm{d}\mathbf{r} = \int \frac{\delta E_{\mathbf{x}}[\rho]}{\delta\rho(\mathbf{r})} (3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla\rho(\mathbf{r})) \,\mathrm{d}\mathbf{r} = -\int \rho(\mathbf{r})\mathbf{r} \cdot \nabla \frac{\delta E_{\mathbf{x}}[\rho]}{\delta\rho(\mathbf{r})} \,\mathrm{d}\mathbf{r}, \quad (C2)$$

where the last step involves partial integration and the easy identity  $\nabla \cdot \mathbf{r} = 3$ . It needs to be stressed that this form of the virial relation depends of the assumption of functional differentiability and that  $v_x(\mathbf{r}) = \delta E_x[\rho]/\delta\rho(\mathbf{r})$  defines in general a *different* exchange potential than  $v_{fx}(\mathbf{r})$  given by a force-based approach in Eq. (16) or by OEPx.

Next, we prove the virial relation between  $E_{\mathbf{x}}$  and  $\mathbf{F}_{\mathbf{x}}$  by direct computation. Starting with the exchange-energy expression Eq. (18), we use the identity  $(\mathbf{r} - \mathbf{r}') \cdot \nabla |\mathbf{r} - \mathbf{r}'|^{\alpha} = \alpha |\mathbf{r} - \mathbf{r}'|^{\alpha}$  (that is also central for deriving the usual *virial theorem*) with  $\alpha = -1$  and the symmetry of the whole expression in  $\mathbf{r} \leftrightarrow \mathbf{r}'$ .

$$E_{\mathbf{x}} = -\frac{1}{4} \int \frac{\left|\rho_{s}^{(1)}(\mathbf{r},\mathbf{r}')\right|^{2}}{|\mathbf{r}-\mathbf{r}'|} \,\mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}' = \frac{1}{4} \int \left((\mathbf{r}-\mathbf{r}')\cdot\nabla|\mathbf{r}-\mathbf{r}'|^{-1}\right) \left|\rho_{s}^{(1)}(\mathbf{r},\mathbf{r}')\right|^{2} \,\mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}'$$

$$= \frac{1}{4} \int \left((\mathbf{r}\cdot\nabla+\mathbf{r}'\cdot\nabla')|\mathbf{r}-\mathbf{r}'|^{-1}\right) \left|\rho_{s}^{(1)}(\mathbf{r},\mathbf{r}')\right|^{2} \,\mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}' = \frac{1}{2} \int \mathbf{r}\cdot(\nabla|\mathbf{r}-\mathbf{r}'|^{-1}) \left|\rho_{s}^{(1)}(\mathbf{r},\mathbf{r}')\right|^{2} \,\mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}' \qquad (C3)$$

$$= \int \mathbf{r}\cdot\mathbf{F}_{\mathbf{x}}(\mathbf{r}) \,\mathrm{d}\mathbf{r}$$

In order to extend the relation towards  $v_{\text{fx}}$ , in Eq. (16) we first switch  $\nabla'$  over to the term  $1/(4\pi |\mathbf{r} - \mathbf{r}'|)$  by partial integration and then switch  $\nabla' \to -\nabla$  by symmetry.

$$v_{\rm fx}(\mathbf{r}) = \frac{1}{2} \nabla \cdot \int \frac{(\nabla' |\mathbf{r}'' - \mathbf{r}'|^{-1})}{4\pi |\mathbf{r} - \mathbf{r}'|} \frac{|\rho_s^{(1)}(\mathbf{r}', \mathbf{r}'')|^2}{\rho(\mathbf{r}')} \,\mathrm{d}\mathbf{r}' \,\mathrm{d}\mathbf{r}'' \tag{C4}$$

Now putting this into the right hand side of a virial relation of the type of Eq. (C2) we get

$$-\int \rho(\mathbf{r})\mathbf{r} \cdot \nabla v_{\mathrm{fx}}(\mathbf{r}) \,\mathrm{d}\mathbf{r} = -\frac{1}{2} \int \rho(\mathbf{r})\mathbf{r} \cdot \nabla \left( \nabla \cdot \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|} (\nabla' |\mathbf{r}'' - \mathbf{r}'|^{-1}) \right) \frac{|\rho_s^{(1)}(\mathbf{r}', \mathbf{r}'')|^2}{n(\mathbf{r}')} \,\mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}' \,\mathrm{d}\mathbf{r}''$$

$$= -\frac{1}{2} \int \rho(\mathbf{r})\mathbf{r} \cdot \underbrace{\left(\Delta \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|}\right)}_{-\delta(\mathbf{r} - \mathbf{r}')} (\nabla' |\mathbf{r}'' - \mathbf{r}'|^{-1}) \frac{|\rho_s^{(1)}(\mathbf{r}', \mathbf{r}'')|^2}{n(\mathbf{r}')} \,\mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}' \,\mathrm{d}\mathbf{r}'' \tag{C5}$$

$$- \frac{1}{8\pi} \int \rho(\mathbf{r})\mathbf{r} \cdot \left(\nabla \times \left((\nabla |\mathbf{r} - \mathbf{r}'|^{-1}) \times (\nabla' |\mathbf{r}'' - \mathbf{r}'|^{-1})\right)\right) \frac{|\rho_s^{(1)}(\mathbf{r}', \mathbf{r}'')|^2}{n(\mathbf{r}')} \,\mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}' \,\mathrm{d}\mathbf{r}'',$$

where the vector calculus identities  $\nabla(\nabla \cdot \mathbf{A}) = \Delta \mathbf{A} + \nabla \times (\nabla \times \mathbf{A})$  and  $\nabla \times f(\mathbf{r})\mathbf{C} = (\nabla f(\mathbf{r})) \times \mathbf{C}$  were used. Now the first part gives exactly  $E_x$  while the second line appears as an additional term in a virial relation between  $E_x$  and  $v_{fx}$ . But since it appears as the curl of a vector expression it cannot be equal to the gradient of a scalar potential, so the difference comes from the transverse part of  $\mathbf{f}_x$  while  $v_{fx}$  corresponds only to the longitudinal part of  $\mathbf{f}_x$ . The nice thing is that this gives an explicit form for the transverse part of  $\mathbf{f}_x$ , while the longitudinal part is already given by  $-\nabla v_{fx}$ . We thus find the following Helmholtz decomposition,

$$\mathbf{f}_{\mathbf{x}}(\mathbf{r}) = \frac{\mathbf{F}_{\mathbf{x}}(\mathbf{r})}{\rho(\mathbf{r})} = -\nabla v_{\mathbf{f}\mathbf{x}}(\mathbf{r}) + \nabla \times \boldsymbol{\alpha}_{\mathbf{f}\mathbf{x}}(\mathbf{r}), \tag{C6}$$

$$v_{\rm fx}(\mathbf{r}) = \frac{1}{4\pi} \int (\nabla' |\mathbf{r} - \mathbf{r}'|^{-1}) \cdot (\nabla' |\mathbf{r}'' - \mathbf{r}'|^{-1}) \bar{\rho}_{\rm x}(\mathbf{r}'' |\mathbf{r}') \,\mathrm{d}\mathbf{r}' \,\mathrm{d}\mathbf{r}'', \tag{C7}$$

$$\boldsymbol{\alpha}_{\mathrm{fx}}(\mathbf{r}) = \frac{1}{4\pi} \int (\nabla' |\mathbf{r} - \mathbf{r}'|^{-1}) \times (\nabla' |\mathbf{r}'' - \mathbf{r}'|^{-1}) \bar{\rho}_{\mathrm{x}}(\mathbf{r}'' |\mathbf{r}') \,\mathrm{d}\mathbf{r}' \,\mathrm{d}\mathbf{r}'', \tag{C8}$$

| Atom    | Slater | FBEx   | OEPx-KLI | OEPx  |
|---------|--------|--------|----------|-------|
| Li      | -29.34 | 1.496  | 1.234    | 0.787 |
| Be      | -39.33 | -2.255 | 0.040    | 0.909 |
| Ne      | -27.51 | -7.411 | -1.981   | 2.505 |
| Na      | -98.07 | 2.112  | 2.756    | 4.400 |
| Mg      | -118.2 | -2.106 | -0.467   | 4.099 |
| Ar      | -22.34 | 2.417  | 0.856    | 0.081 |
| Ca      | -91.12 | 0.113  | 1.903    | 1.508 |
| Zn      | -365.6 | 81.26  | 55.97    | 9.688 |
| MARE(%) | 1.49   | 0.116  | 0.077    | 0.035 |

Table II. Deviation from the Hartree–Fock exchange energy, in mHa, for different exchange functionals. We also report the mean absolute relative error (MARE) for each functional.

| Atom | Slater | FBEx  | OEPx-KLI | OEPx  | $_{ m HF}$ |
|------|--------|-------|----------|-------|------------|
| Li   | 0.101  | 0.086 | 0.082    | 0.082 | 0.082      |
| Be   | 0.325  | 0.311 | 0.307    | 0.307 | 0.307      |
| Ne   | 0.900  | 0.859 | 0.843    | 0.845 | 0.844      |
| Na   | 0.118  | 0.083 | 0.074    | 0.074 | 0.074      |
| Mg   | 0.285  | 0.260 | 0.253    | 0.253 | 0.253      |
| Ar   | 0.622  | 0.585 | 0.590    | 0.590 | 0.590      |
| Ca   | 0.224  | 0.201 | 0.195    | 0.195 | 0.195      |
| Zn   | 0.368  | 0.332 | 0.300    | 0.300 | 0.300      |

Table III. Eigenvalues  $-\epsilon_n$ , in Ha, of the highest occupied orbitals for different functionals.

and the extended virial relation

$$E_{\mathbf{x}} = \int \mathbf{r} \cdot \mathbf{F}_{\mathbf{x}}(\mathbf{r}) \, \mathrm{d}\mathbf{r} = -\int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_{\mathrm{fx}}(\mathbf{r}) \, \mathrm{d}\mathbf{r} + \int \rho(\mathbf{r}) \mathbf{r} \cdot (\nabla \times \boldsymbol{\alpha}_{\mathrm{fx}}(\mathbf{r})) \, \mathrm{d}\mathbf{r}.$$
(C9)

If in certain situations it holds that the second term above is zero than the virial relation between  $E_x$  and  $v_{fx}$  holds in the form of Eq. (C2). We show that for spherically symmetric densities  $\rho(\mathbf{r}) = \rho(|\mathbf{r}|)$  this indeed is the case. For this we take the last integral of Eq. (C9) and perform integration by parts with the curl and vanishing boundary terms to get

$$\int \rho(\mathbf{r})\mathbf{r} \cdot (\nabla \times \boldsymbol{\alpha}_{fx}(\mathbf{r})) \, \mathrm{d}\mathbf{r} = \int (\nabla \times \rho(\mathbf{r})\mathbf{r}) \cdot \boldsymbol{\alpha}_{fx}(\mathbf{r}) \, \mathrm{d}\mathbf{r} = \int (\rho(\mathbf{r})(\nabla \times \mathbf{r}) + (\nabla \rho(\mathbf{r})) \times \mathbf{r}) \cdot \boldsymbol{\alpha}_{fx}(\mathbf{r}) \, \mathrm{d}\mathbf{r}.$$
(C10)

But now  $\nabla \times \mathbf{r} = 0$  and  $(\nabla \rho(\mathbf{r})) \times \mathbf{r} = (\mathbf{r} \times \mathbf{r})\rho'(|\mathbf{r}|)/|\mathbf{r}| = 0$ , so the above expression evaluates as zero.

## Appendix D: Numerical results for the FBEx functional

Here, we show further numerical comparisons of the local-exchange potential to well-established exchange potentials in DFT. Firstly, we investigate how the local-exchange potential compares to the Hartree–Fock energies. Since the local-exchange potential is not derived directly from the exchange-energy expression of Eq. (18), it is not designed to approximate the non-local Hartree–Fock exchange-energy expression. Still, the resulting energies of the local-exchange potential determined from Eq. (18) together with the respective orbitals (see Tab. II) are in good agreement with the Hartree–Fock exchange energies.

In Tab. III, we further report the eigenvalue of the highest occupied orbital for different exchange functionals. While OEPx-KLI and OEPx are yielding similar ionization energies as Hartree–Fock, within a meV precision, the local-exchange potential leads to slightly different results. The Slater potential shows a stronger deviation from the Hartree–Fock values.

| Molecule        | Slater | FBEx    | OEPx-KLI | OEPx   |  |
|-----------------|--------|---------|----------|--------|--|
| $N_2$           | 93.34  | -134.7  | -276.4   | -235.4 |  |
| $\mathrm{CO}_2$ | 13.64  | -520.9  | -1157    | -660.1 |  |
| $\mathrm{CH}_4$ | 72.36  | -12.517 | -38.66   | -19.15 |  |

Table IV. Same as Tab. I but for small molecules.

| Molecule        | Slater | FBEx  | OEPx-KLI | OEPx  | HF    |
|-----------------|--------|-------|----------|-------|-------|
| $N_2$           | 0.635  | 0.607 | 0.629    | 0.630 | 0.617 |
| $\mathrm{CO}_2$ | 0.619  | 0.586 | 0.545    | 0.544 | 0.546 |
| $CH_4$          | 0.566  | 0.540 | 0.543    | 0.545 | 0.546 |

Table V. Same as Tab. III but for small molecules.

Tab. IV lists the difference in exchange energy computed from the orbitals and the virial relation of Eq. (19) for small molecules. This shows that for non-spherically-symmetric systems, this virial relation is not respected by the local-exchange potential either. For N<sub>2</sub>, we employed a N-N distance of 1.09769Å. For CO<sub>2</sub>, we considered a C-O bond length of 1.16Å. For CH<sub>4</sub>, we considered a C-H bond length of 1.087Å. In all cases, we employed a grid spacing of 0.15 Bohr and a simulation box made of atom-centered spheres of radii 12 Bohr.

The corresponding ionization energies for these molecules are given in Tab. V. Similar to the atomic case, we find that the local-exchange potential performs much better than the Slater potential and yields ionization energies close to the ones obtained from Hartree–Fock or OEPx.