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Optimizing a parametrized Thomas-Fermi-Dirac-Weizsäcker density functional for atoms[†]

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Because of issues with accuracy and transferability of existing orbital-free (OF) density functionals, OF functionals development remains an active research area. However, due to numerical difficulties, all-electron self-consistent assessment of OF functionals is limited. Using an all-electron radial OFDFT code, we evaluate the performance of a parametrized OF functional for a wide range in parameter space. Specifically, we combine the parametrized Thomas-Fermi-Weizsäcker kinetic model (λ and γ for the fractions of Weizsäcker and Thomas-Fermi functionals, respectively) with a local density approximation (LDA) for the exchange-correlation functional. In order to obtain converged results for λ values other than $\lambda = 1$, we use the potential scaling introduced in previous work. Because we work within a wide region in parameter space, this strategy provides an effective route towards better understanding the parameters interplay that allow to achieve good agreement with the Khon-Sham (KS) model. Here, our interest lies in total energy, Euler equation eigenvalue, and electronic densities when the parameters are varied between 0.2 and 1.5. We observe that a one-to-one relation between λ and γ defines a region in parameter space that allows the atomic energies to be approximated with a very small average error (less than 3% percent for all the atoms studied) with respect to the KS reference energies. For each atom, the reference KS HOMO eigenvalue can also be reproduced with a similar error, but the one-to-one correspondence between λ and γ belongs to a different region of the same parameter space. Contrary to both properties, the atomic density behaves more smoothly and the error in reproducing the KS reference densities appears more insensitive to variation of the parameters (with mostly an average integrated difference of 0.15–0.20 $|e|$ per electron). These results pave the way towards testing of parameter transferability and the further systematic improvement of OF density functionals.

1 Introduction

The Hohenberg-Kohn theorems[1] state that for an N-electron system in an external potential v the electronic density determines all the ground state properties of the system, such as the wave function and any observable. In theory, in order to find the ground-state energy of the N-electron system, it would suffice to apply the variational principle to the energy functional $E[n]$:

$$E[n] = T[n] + V_{ee}[n] + + \underbrace{\int \mathrm{d}\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r})}_{V[n]} . \tag{1}$$

In practice, the exact form of $E[n]$ for the many-body system is unknown and must be approximated. The Kohn-Sham (KS) approach[2], the most widely used approximation to DFT, works by introducing an equivalent non-interacting electron system for which the kinetic energy can be calculated exactly. We can define the KS kinetic functional T_S by the constrained-search formulation[3] as

$$T_s[n] = \min_{\sum|\psi_i|^2 = n} \sum_{i=1}^{N} \int \mathrm{d}\mathbf{r}\, \psi_i^*(\mathbf{r})(-\frac{1}{2}\nabla^2)\psi_i(\mathbf{r}), \tag{2}$$

where the equivalent non-interacting total wave function is constructed as a Slater determinant from the single-particle orbitals ψ_i. Because the kinetic term is the dominant contribution to the total energy expression, introducing the exact kinetic functional ensures that the remaining terms (which need to be approximated) are comparatively small and easier to handle. This strategy allows to derive KS density functional approximations of reasonable accuracy, especially when the balance between required computational resources and accuracy is taken into account. More precisely, in the KS method we introduce the kinetic functional T_s, the classical electron-electron repulsive Coulombic interaction

$$J[n] = \frac{1}{2} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{3}$$

with the remaining contribution to the total energy denoted as “exchange correlation”. Thus, we rewrite the KS DFT energy

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functional as

$$E_{\mathrm{KS}}[n] = T_{\mathrm{s}}[n] + J[n] + \underbrace{V_{ee}[n] - J[n] + T[n] - T_S[n]}_{E_{\mathrm{xc}}[n]} + V[n]. \tag{4}$$

In the spirit of the Hohenberg-Kohn theory, we can also introduce a kinetic functional that is explicitly density-dependent[4]. This leads directly to an orbital-free (OF) formulation of the same unknown energy functional. For example, we can introduce the exact single-electron kinetic functional that is equivalent to the Weizsäcker functional $T_{\mathrm{W}}[n]$[5]

$$\begin{aligned} E_{\mathrm{OF}}[n] = \underbrace{\int d\mathbf{r}\, n^{1/2}\left(-\frac{1}{2}\nabla^2\right)n^{1/2}}_{T_{\mathrm{W}}[n]} + J[n] + V[n] \\ + V_{ee}[n] - J[n] + T[n] - T_{\mathrm{W}}[n]. \end{aligned} \tag{5}$$

Another approach consists in expressing $E_{\mathrm{OF}}[n]$ in terms of the KS kinetic functional T_S and KS exchange-correlation functional E_{xc}[4,6]:

$$\begin{aligned} E_{\mathrm{OF}}[n] = \int d\mathbf{r}\, n^{1/2}\left(-\frac{1}{2}\nabla^2\right)n^{1/2} + J[n] + V[n] \\ E_{\mathrm{xc}}[n] + \underbrace{T_s[n] - T_{\mathrm{W}}[n]}_{T_\theta[n]}, \end{aligned} \tag{6}$$

where the final term is known as the Pauli functional T_θ. The minimum of the energy functional is found by a functional derivative subject to the constraint that the density integrates to the number of electrons N using the Lagrange multiplier ε_{OF}. The resulting single Euler equation is then[4]:

$$\begin{aligned} \left(-\frac{1}{2}\nabla^2 + \frac{\delta J[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})} + \frac{\delta T_\theta[n]}{\delta n(\mathbf{r})} + v(\mathbf{r})\right) n^{1/2}(\mathbf{r}) \\ = \varepsilon_{\mathrm{OF}} n^{1/2}(\mathbf{r}). \end{aligned} \tag{7}$$

The eigenvalue ε_{OF} is equal to minus the ionization potential for the exact energy functional[4]. Relying on quantities borrowed from KS theory is obviously not the only possible choice, but it allows to build on accumulated knowledge of the widely used KS functionals. After introducing T_s and E_{xc} in the OF formulation of the total energy functional, the remaining task to achieve an accuracy comparable to the parent KS method is to obtain an orbital-free approximation to T_s that approaches the exact orbital-dependent KS limit.

A number of OF kinetic functionals have been proposed over the years. Typically they are a combination of two exact ubiquitous kinetic functionals: the Thomas-Fermi[7,8] and Weizsäcker[5] kinetic functionals, defined as

$$T_{\mathrm{TF}}[n] = \frac{3}{10}(3\pi^2)^{2/3}\int d\mathbf{r}\, n^{5/3}(\mathbf{r}) \tag{8}$$

$$T_{\mathrm{W}}[n] = \frac{1}{8}\int d\mathbf{r}\, \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}. \tag{9}$$

The Thomas-Fermi kinetic functional is the exact kinetic functional of the homogeneous electron gas and therefore correctly reduces to T_s in the constant density limit. To improve the description of atomic and molecular densities, Weizsäcker derived T_{W} as a correction to the Thomas-Fermi kinetic functional[5]. This correction was later derived from gradient expansion techniques with a different prefactor[9]. The first two terms in the gradient expansion are denoted as the $TF\lambda W$ functional:

$$T_{\mathrm{TF}\lambda\mathrm{W}}[n] = T_{\mathrm{TF}}[n] + \lambda T_{\mathrm{w}}[n], \tag{10}$$

with the parameter $\lambda = 1/9$[10,11]. Weizsäcker initially proposed the value $\lambda = 1$, whereas later work proposed the value $\lambda = 1/5$ by optimizing atomic and small molecule energies[12]. Other proposed values include $\lambda = 0.186$ for the limit of large atomic number[13] and $\lambda = 0.12$ from post-KS optimization of small molecules energies[14] .

It is also reasonable to treat T_{W} as the first term in the expansion of the KS kinetic functional T_s and include a parametrized Thomas-Fermi contribution as a correction[9,15,16]. In the general form, the Thomas-Fermi functional is multiplied by a function dependent on the number of electrons N:

$$T_{\gamma\mathrm{TFW}}[n] = T_{\mathrm{W}}[n] + \gamma(N) T_{\mathrm{TF}}[n]. \tag{11}$$

Issues with accuracy and convergence are why the development of OF kinetic functionals remains an active area of research. There are excellent recent reviews to which we refer the reader for further information on such developments[6,17–22]. Here, we briefly mention a few. For example, a family of kinetic functionals has been established in analogy with the development of generalized gradient approximations (GGA) for exchange-correlation functionals. The kinetic GGA form uses in its formulation the reduced density gradient $s = \frac{1}{2(3\pi^2)^{(1/3)}}\frac{|\nabla n|}{n^{4/3}}$, a Weizsäcker contribution, and a modified Thomas-Fermi functional with an enhancement factor. From the proposed GGA kinetic functionals, we can cite forms with empirical and non-empirical parameters in the enhancement factor[23–25]. Moreover, the general combination of T_{TF} and T_{W} is also derived from quantization from classical considerations or information theoretic arguments[15,26,27]. Similarly, non-local kinetic energy functionals include a sum of T_{TF} and T_{W} functionals that is corrected with a non-local two-point functional[18]. Finally, we mention there is also a family of functionals developed and tested for embedding applications with frozen density approaches[28,29].

In examining the performance of kinetic functionals, most studies have relied on the use of what could be considered good trial densities, typically from Hartree-Fock theory or KS LDA (local density approximation) calculations in non-self-consistent or post-KS treatments. While one can extract some useful information from such methods (for example, we can rule out functionals based on failures at this level), these studies have a fundamental limitation to assess the true performance of the kinetic functional, given that the self-consistent density will differ from the density actually employed. Moreover, many applications of OFDFT functionals rely on the use of pseudo-potentials that must overcome difficult problems, stemming from the essential relationship between the method and separation of orbitals on core and valence electrons[18,22].

Due to numerical difficulties, self-consistent all-electron assessment of OF functionals typically have focused on atoms or diatomic molecules and only a small number of OF functionals have been tested[6,30–36]. For example, in Chan et al.[32], the kinetic TFλW functional is used in addition to the LDA exchange for a few values of λ ($\lambda = 1, 1/5, 1/9, 2$) in self-consistent all-electron calculations using a Gaussian basis. Out of the λ values studied, the best agreement to Hartree-Fock energies is obtained for $\lambda = 1/5$, as in earlier work[12]. The ionization energies increase with increasing λ, and the values computed oscillate around the experimental values. For the Ne atom, the progressive effect of increasing λ is to lower the value at the origin (position of the nucleus) and increase the density value in the valence region. From the binding energies of molecules the authors conclude that, indeed, the addition of a gradient term such as $T_{\rm W}$ allows for a small binding of the molecules. This binding increases with increasing λ, but none of the tried parameters gives a satisfactory description because the errors in the atomic energy increase drastically. These binding energies of molecules are reproduced by two later studies[6,35], using different methods. The first one uses a non-modified nuclear potential and both a Gaussian and grid basis, and the second study uses the PAW transformation and a grid basis. Notably, with the use of the PAW method bulk simulations were reported at the same level of theory[35].

We have chosen to extend the benchmark data of OF all-electron self-consistent calculations for atoms. Using an all-electron radial atomic OFDFT code to compute all-electron values, we study a wide region of the parameter space of the parametrized Thomas-Fermi-Weizsäcker kinetic model. To achieve convergence for values of λ other than $\lambda = 1$, we use the potential scaling from our previous work[35]. By working within this wide region in parameter space, we can achieve a deeper understanding of the interplay between the fractions of $T_{\rm TF}$ and $T_{\rm W}$ contained in the model that yield good agreement with the reference KS calculation. Here, total energy, eigenvalue, and all-electron densities are of interest, particularly when the parameters λ and γ are varied between 0.2 and 1.5. We choose to compare the OFDFT results to reference KS calculations because, for the ideal case of an exact kinetic functional, all the quantities should agree. These results will bridge the way to improving parameter transferability from atomic to dimeric systems, and in general to the overall improvement OF kinetic functional derivation.

2 Results and discussion

In order to define an OF model in the KS-like form described in the introduction, we must work under approximations for the KS kinetic and exchange-correlation functionals. Here we use a parametrized kinetic functional[37] that we denote as $T_{\gamma{\rm TF}\lambda{\rm W}}$ in an extension of the naming convention used in the introduction, and an LDA exchange-correlation functional[38,39]. The parametrized orbital-free functional we study here is therefore:

$$E_{\rm OF}[n;\lambda,\gamma] = \lambda T_{\rm W}[n] + \gamma T_{\rm TF}[n] + J[n] + V[n] + E_{\rm xc}^{\rm LDA}[n] \tag{12}$$

Using the partitioning introduced in Equation (6), we obtain the KS-like equation to solve by setting:

$$T_\theta[n] = (\lambda - 1)\, T_{\rm W}[n] + \gamma T_{\rm TF}[n], \tag{13}$$

$$E_{\rm xc}[n] = E_{\rm xc}^{\rm LDA}[n], \tag{14}$$

in Equation (7). The Weizsäcker term in the Pauli functional can be expanded in its Laplacian form and combined back with the first term so that the final KS-like equation to solve is:

$$\left(-\frac{\lambda}{2}\nabla^2 + \underbrace{\frac{\delta J[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})} + \gamma\frac{\delta T_{\rm TF}[n]}{\delta n(\mathbf{r})} + v(\mathbf{r})}_{v_{\rm eff}(\mathbf{r})}\right) n^{1/2}(\mathbf{r}) = \varepsilon_{\rm OF}\, n^{1/2}(\mathbf{r}), \tag{15}$$

or in the convenient scaled form used in previous work[35]:

$$\left(-\frac{1}{2}\nabla^2 + \frac{v_{\rm eff}(\mathbf{r})}{\lambda}\right) n^{1/2}(\mathbf{r}) = \frac{\varepsilon_{\rm OF}}{\lambda} n^{1/2}(\mathbf{r}). \tag{16}$$

2.1 Total energy

In the ideal limit where the exact form of the KS kinetic energy functional is retrieved, both OF and KS energy functionals as defined in equations (4) and (6) are equal. We therefore explore the evolution of the total energy of the different atoms in the first three rows of the periodic table as the two parameters that define the OF kinetic energy functional introduced here are varied. By comparing the KS and OF total energies throughout this parameter space, one can determine which combinations of λ and γ yield good agreement between the two methods. A good OF kinetic functional, $T_{\gamma{\rm TF}\lambda{\rm W}}$, can then be obtained by minimizing the difference between the KS and OF predicted total energies (or other properties) with respect to the choice of λ and γ. In practice, this can be done by studying the quantity

$$\Delta E(\lambda,\gamma) = \frac{E_{\rm OF}(\lambda,\gamma) - E_{\rm KS}}{E_{\rm KS}}, \tag{17}$$

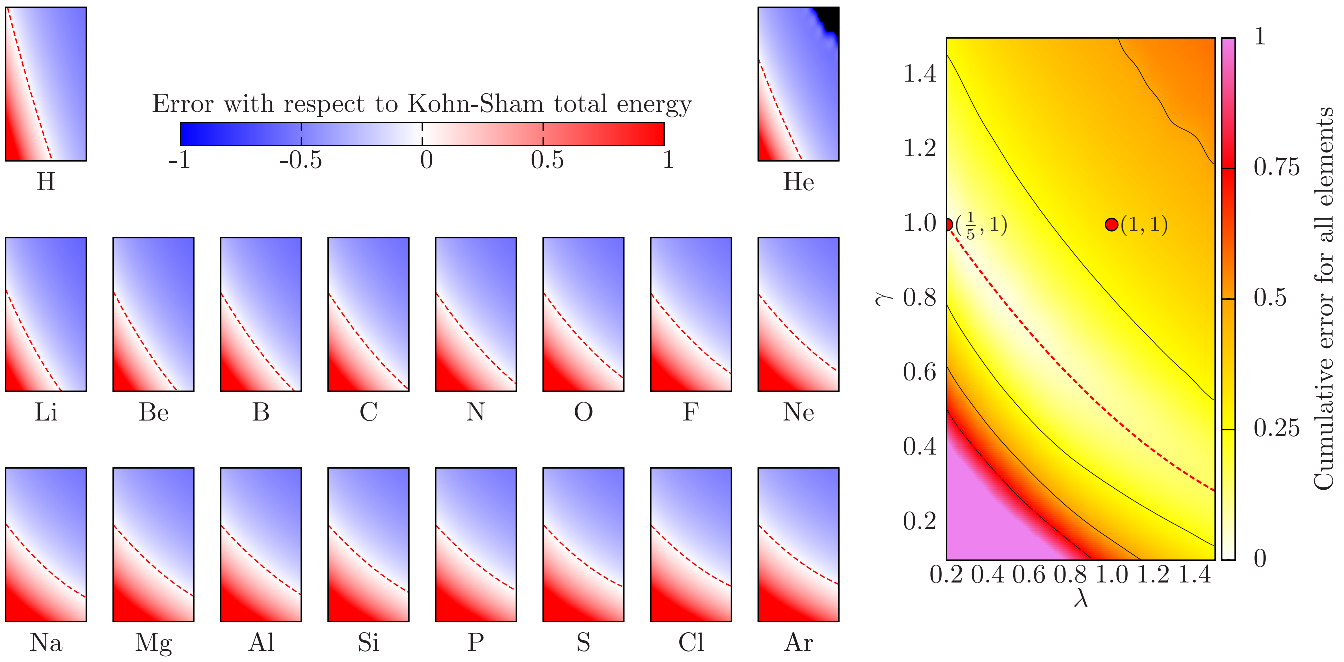

Fig. 1 Evolution of the relative error in OF total energies with respect to KS reference total energies calculated for all the atoms in the first three rows of the periodic table, cf. equation 17 for a definition. The cumulative error is calculated as the combined average error for the whole set, $\frac{1}{N_a}\sum_a |\Delta E_a|$. The OF kinetic functional used is $\lambda T_W[n] + \gamma T_{TF}[n]$ and the exchange-correlation is a LDA functional (cf. equation 12 for the complete energy functional). The parameters λ and γ are varied in the same range for all plots. The black region in the top-right corner for He is due to the impossibility to bring the corresponding calculations to convergence.

which for each atom gives the relative error in the OF total energy E_{OF}, taking the KS value E_{KS} as a reference, as a function of λ and γ. One can then extend this analysis to a wider set of elements by studying the cumulative error, which is simply given as the average relative error $\frac{1}{N_a}\sum_a |\Delta E_a|$ where a is an atom index and N_a is the number of atoms included in the set. The error for each atom and the cumulative error as defined above are presented in Figure 1. Previous work indicates the average error in the atomic energy at parameters $(\lambda, \gamma) = (1/5, 1)$ is very small[12,32]. We also find the average error in the atomic total energies calculated at $(\lambda, \gamma) = (1/5, 1)$ to be very small. In this OF model, which differs from the cited work by the inclusion of LDA correlation, the average error for the present atomic set is only of 3 percent deviation from the KS reference values. This (λ, γ) combination is, however, not singular. It belongs to a whole region in parameter space of good agreement between the OF and KS energies, denoted by white and the superimposed dashed lines in the figure. For the H atom such region includes the limit $(\lambda, \gamma) = (1, 0)$ for which the Weizsäcker term is the exact kinetic energy functional. The evolution of these regions of good agreement as the atomic number increases is smooth, so that there still exists a well-defined region of overall good agreement between the OF and KS energies. We note that for every atom the (λ, γ) values corresponding to the region of good agreement can be described by means of a second-order polynomial fitting, valid within the ranges shown. These second-order expressions give optimum γs for any given λ in terms of reproducing the KS values: $\gamma_{\text{opt}}(\lambda) = a_2\lambda^2 + a_1\lambda + a_0$. The fitting coefficients for all the atoms studied are given in Table 1.

A simple correlation between the two components of the kinetic functional can be observed. As the fraction of Weizsäcker functional added to the model increases so does the need to decrease the fraction of Thomas-Fermi functional in order to achieve a good description of the total energy. As previously discussed, this correlation is not linear and it can be clearly observed how the total energy values become more insensitive to an increase of the von Weizsäcker functional contribution as the number of electrons in the system increases.

2.2 Eigenvalues

The fundamental chemical properties of atoms are determined by the process of acceptance or removal of electrons. In this context, the chemical reactivity of molecular systems and atoms in particular is a desired quantity to be addressed by means of the OF model. In the KS model the highest occupied molecular orbital (HOMO) eigenvalue of the KS equations has

Table 1 Fitting parameters for the second-order polynomial $\gamma_{\mathrm{E}}(\lambda) = a_2\lambda^2 + a_1\lambda + a_0$. This polynomial gives the combination of (λ, γ) yielding the OF total energies that better agree with the reference KS total energies of the different atoms. The fitted curves are shown as dashed lines in Figure 1.

Atom	a_2	a_1	a_0
H	0.372	−2.386	2.032
He	0.272	−1.614	1.347
Li	0.305	−1.428	1.301
Be	0.207	−1.175	1.236
B	0.162	−1.013	1.195
C	0.145	−0.928	1.180
N	0.128	−0.859	1.166
O	0.145	−0.851	1.167
F	0.135	−0.796	1.147
Ne	0.129	−0.768	1.136
Na	0.165	−0.799	1.145
Mg	0.127	−0.718	1.122
Al	0.108	−0.672	1.109
Si	0.119	−0.676	1.112
P	0.113	−0.651	1.104
S	0.147	−0.689	1.117
Cl	0.128	−0.649	1.106
Ar	0.135	−0.648	1.108

a special physical significance[40,41]. The KS HOMO eigenvalue determines the decaying behaviour of the electronic density and equals minus the ionization potential using the exact energy functional[40]. The Euler equation eigenvalue in the OF model also determines the decaying behaviour of the density and equals minus the ionization potential for the exact functional[4]. When having an exact approximation for the KS kinetic functional in OF model, the two eigenvalues should coincide[4,42]. Despite the poor description of the KS frontier eigenvalues, observed for both local and semi-local exchange-correlation approaches, reproducing the KS results is a first step in the construction of better kinetic functionals for the OF model. In this section, we study the behaviour of the OF eigenvalue for the same atomic species surveyed in the previous section, and compare it to the KS HOMO eigenvalue. The error is defined in a similar way to the total energy case as a relative deviation from the KS reference for different values of λ and γ, writing the eigenvalue as $\varepsilon(\lambda, \gamma)$, it reads

$$\Delta\varepsilon(\lambda,\gamma) = \frac{\varepsilon_{\mathrm{OF}}(\lambda,\gamma) - \varepsilon_{\mathrm{KS/HOMO}}}{|\varepsilon_{\mathrm{KS/HOMO}}|}, \tag{18}$$

where the cumulative error is defined in a similar way to the error in the total energy as the average relative error $\frac{1}{N_a}\sum_a |\Delta\varepsilon_a|$. Here, a is an atom index and N_a is the number of atoms in the set. Figure 2 shows the error in the eigenvalue for each atomic species. The results show that the best set of parameters behave differently compared to the error in the total energy. For low values of the parameter γ, there already exists an underestimation of the OF eigenvalue (the error is negative) and no value of λ can decrease the error. However at moderate and high values of γ and at low λ the eigenvalue error is positive so that the OF eigenvalues are an overestimation of the KS eigenvalue. Increasing λ decreases the OF eigenvalue up to the point where it matches the KS eigenvalue. If λ is further increased, the OF eigenvalue just continues to deviate from the KS value.

Another striking difference between the total energy and the eigenvalue is that the calculated region of best agreement strongly depends on the atom. In particular, the best region for H and He show a distinctly different behaviour when compared to the other atoms. This is because both species are single-orbital systems and they are well described by the Weizsäcker model, which corresponds to values of $(\lambda, \gamma) = (1, 0)$. In general, a best set of parameters can be chosen to describe elements with similar chemical properties (with the same number of valence electrons, i.e. elements in the same column of the periodic table). The superposition therefore does lead to a high average error (more than 40 percent) in comparison to the total energy. It is interesting to note that the error at the pair of parameters $(\lambda, \gamma) = (1/5, 1)$ is quite high (48 percent). Furthermore, this parameter pair does not belong to the fitted region of best agreement that can be observed in the cumulative graph. For each atomic species, the parameter region of lowest error has been fitted, as the energy, to a second-order polynomial (red-dashed line), and the coefficients are included in Table 2.

We can then conclude that achieving small errors for *both* energy and eigenvalue is not possible with this simple parameterization. In order to achieve the best possible chemical accuracy for a specific problem of interest, one can however optimize this parametrization such that the resulting functional minimizes both errors per each atom or for a small set of atoms.

2.3 Electronic density

The OF and the KS electronic densities should coincide if an exact approximation of the KS kinetic functional is used in the OF functional. To characterize the error we have used the following definition:

$$\Delta n(\lambda,\gamma) = \frac{\int \mathrm{d}\mathbf{r}\, |n_{OF}(\mathbf{r};\lambda,\gamma) - n_{KS}(\mathbf{r})|}{\int \mathrm{d}\mathbf{r}\, n_{OF}(\mathbf{r};\lambda,\gamma) + \int \mathrm{d}\mathbf{r}\, n_{KS}(\mathbf{r})} \tag{19}$$

where the denominator reduces to $2Z$ for the neutral atomic densities considered here (where Z is the atomic number). The cumulative error is defined as earlier by $\frac{1}{N_a}\sum_a \Delta n_a$, where a is an atom index and N_a is the number of atoms in the set. From the definition we expect that the regions of high density will

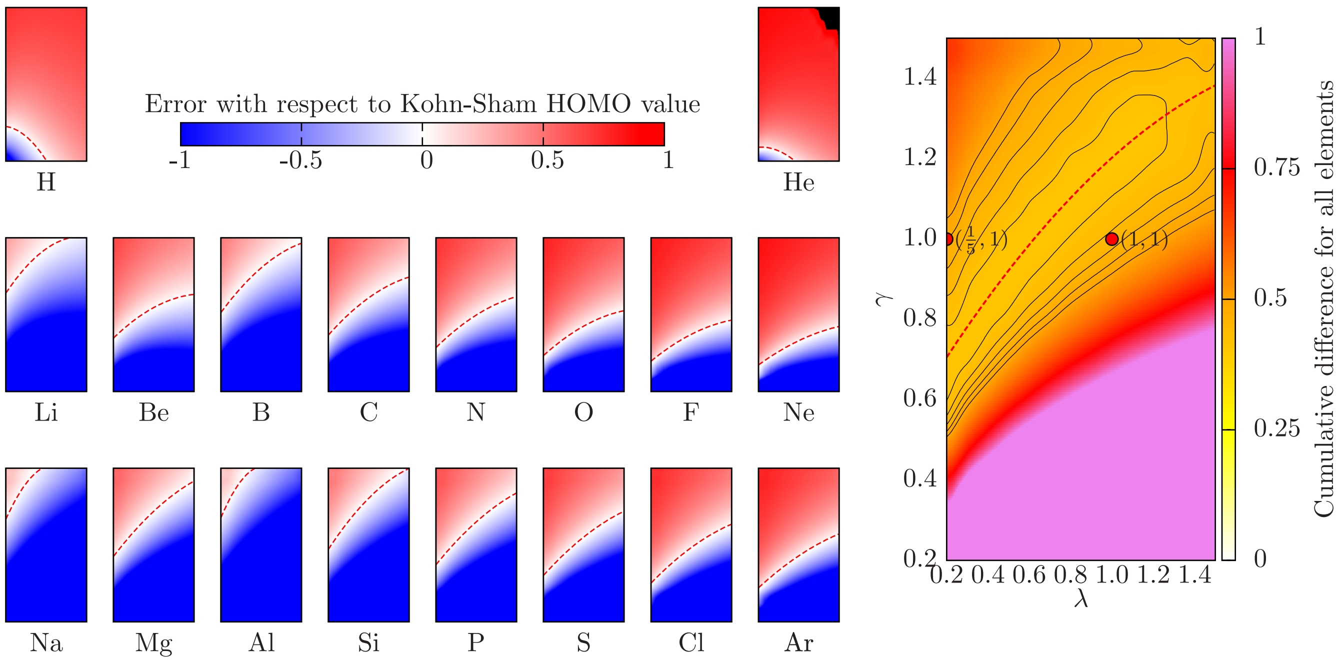

Fig. 2 Evolution of the relative error in OF eigenvalue with respect to KS HOMO calculated for all the atoms in the first three rows of the periodic table, cf. equation 18 for a definition. The cumulative error is calculated as the combined average error for the whole set, $\frac{1}{N_a}\sum_a |\Delta\varepsilon_a|$. The OF kinetic functional used is $\lambda T_W[n] + \gamma T_{TF}[n]$ and the exchange-correlation is a LDA functional (cf. equation 12 for the complete energy functional). The parameters λ and γ are varied in the same range for all plots

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dominate this integrated error and therefore the error will reflect the core density error rather than the error in the decaying tail.

As is the case for the total energy error, Figure 3 shows there is a different dependence for each atom of the region of best agreement. However, it tends to quickly converge when increasing the number of electrons. The average error is therefore quite homogeneous (at 0.15 to 0.20 $|e|$ per electron). Contrary to the total energy and eigenvalue cases, a wide range of parameters allow to approach the KS density with a similar error. The maximum possible deviation is 1 so that it can also interpreted as a percentage (multiplying the error by 100). An average error of 15 to 20 percent is a poor feature that was similarly encountered in the eigenvalue error. We can therefore conclude that for the present parametrization and for atoms, the integrated density error is a quantity that can be omitted from a fitting procedure without much loss with respect to improving the functional. Other density-dependent error quantities may be more sensitive to the parameters and further exploration is required.

2.4 N_2 molecule

We focused on the nitrogen dimer as an example of diatomic molecule where we can study the error in the molecule formation using parameters coming from our previous atomic results. The nitrogen dimer is also studied in detail in one of the OF all-electron works we use as reference[32]. In that all-electron reference, they proved that adding the Weizsäcker functional in the kinetic functional helped to overcome the no-binding failure of the Thomas-Fermi kinetic model. However, with the parameters $(\lambda,\gamma) = (1/5, 1)$ fitted to atomic energies the binding energy obtained was very small and the bond distance was completely overestimated with respect to a HF calculation. By increasing λ, and using $(\lambda,\gamma) = (2, 1)$, they obtained a good value for the bond length but at the price of having a binding energy overestimated. Here, we use parameters coming from our own fits γ_E (coefficients from the energy fit in Table 1 for N atom) and γ_ε (coefficients from the eigenvalue fit from Table 2 for N atom) to study the binding energy, bond length distance and eigenvalue of the N_2 molecule. We use `rcut` $= 1.0$ Bohr and grid spacing `h` $= 0.14 Å$ in the setup generation and GPAW calculation respectively.

Table 3 summarizes the N_2 results. We tested first two pairs of parameters with same λ but different γ, one γ fitted to reproduce the KS atomic energy and the other γ fitted to reproduce the KS HOMO eigenvalue. The result is that the kinetic functional with parameters fitted to reproduce the atomic KS eigenvalue reproduces better the dimer KS bond distance (the

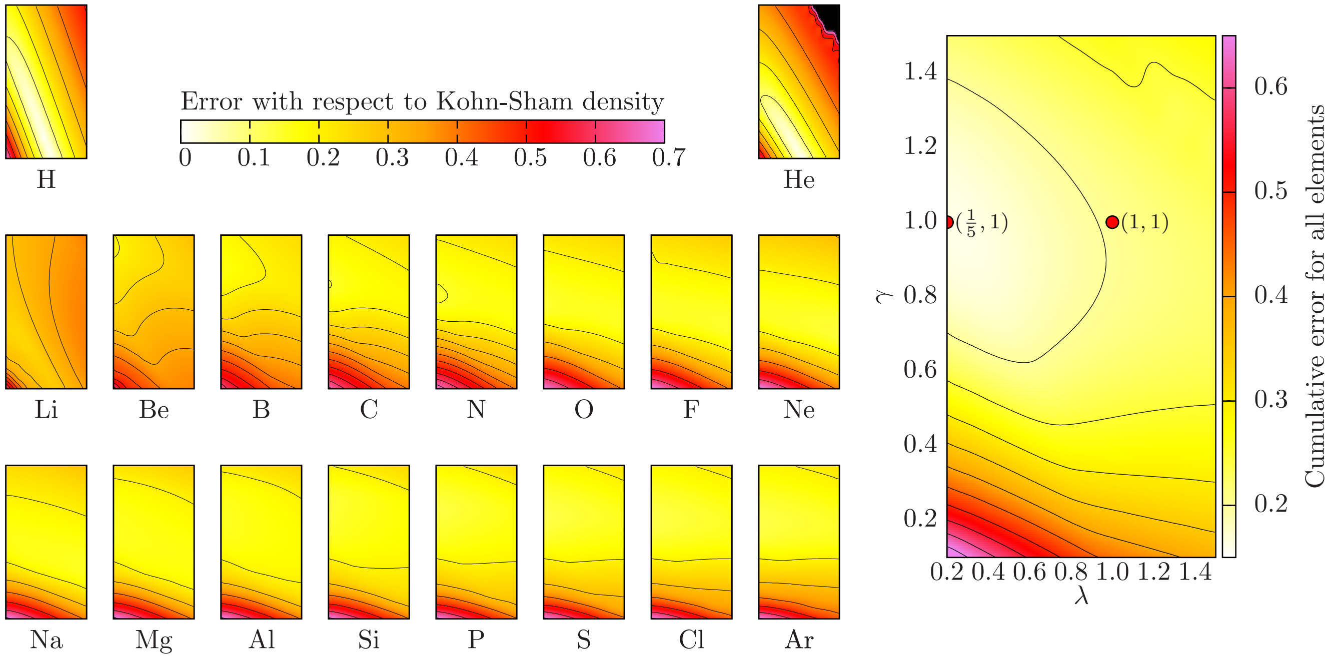

Fig. 3 Deviation of the OF density with respect to the KS density for atoms. The maximum deviation is 1 and it would correspond to a situation of complete no overlap of the densities. On the right-hand side the combined cumulative error (or mean error) for the set of atoms is included. The OF kinetic functional used is $\lambda T_W[n] + \gamma T_{TF}[n]$ and the exchange-correlation is a LDA functional (cf. equation 12 for the complete energy functional). The parameters λ and γ are varied in the same range for all plots

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error is 0.1 Å while the other one gives an error of 0.6 Å). We tested another value of γ, this time close to the value reported in the reference. Setting $\lambda = 2$, the γ_ε fitted to reproduce the KS HOMO eigenvalue equals to 1.007, a value very close to the one reported by Chan et al[32]. With those parameters, we obtained good bond distances but again bad binding energies. The error is 0.08 Åand 26 eV for bond and binding respectively. Finally, we used the parameters in the intersection of the two optimum curves and obtained simultaneously a lower error in both quantities, 0.2 Åand 2.7 eV for bond and binding respectively. For practical applications however, the errors obtained with the parameters optimized for energy and eigenvalue simultaneously are unacceptable. With applications in mind, we should still decrease the error by fine-tuning the parameters or even trying other equivalent training sets (for example electronegativity, electron affinity or direct evaluation of ionization potential). Our main conclusion here is that in order to improve the kinetic functional transferability from atoms to molecules, the kinetic functional must correctly describe the tendency to donate electrons at the atomic level. This conclusion requires now a systematic exploration using more molecules, molecular properties and using a wider range of parameter space.

2.5 Convergence tests

In our calculations, we have used the all-electron radial atomic code that is included in the DFT code GPAW[43] and that was previously modified to solve self-consistently the OF minimization problem[35]. The atomic all-electron code in GPAW is used as a generator of the atomic all-electron orbitals necessary for the generation of the PAW transformation. In our previous work[35] we presented the parameters for the calculations of a small set of atoms. Here we extend systematically our convergence tests to the atoms in the first two rows of the periodic table. We have used in the calculations presented in the previous sections the GPAW parameters `gpernode` and `mix` set to 800 and 0.01, respectively, in the all-electron atomic code. These parameters determine the number of points in the atomic radial grid and the degree of mixing between old and new potentials during the self-consistency cycle. In order to test the energy deviation with respect to reference all-electron values[32] for the selected atoms, the λ and γ values were set to 0.2 and 1.0, respectively. Taking the energy value E from literature[32] as a reference, the deviation ΔE of the calculated total energy $E_{\rm OF}$ for an atom can be expressed as

$$\Delta E = E_{\rm OF} - E. \qquad (20)$$

Table 2 Fitting parameters for the second-order polynomial $\gamma_\varepsilon(\lambda) = a_2\lambda^2 + a_1\lambda + a_0$. This polynomial gives the combination of (λ, γ) yielding the OF eigenvalue that better agree with the reference KS HOMO of the different atoms. The fitted curves as shown as dashed lines in Figure 2.

Atoms	a_2	a_1	a_0
H	-0.607	0.161	0.407
He	-0.422	0.202	0.203
Li	-0.351	0.992	0.811
Be	-0.188	0.625	0.469
B	-0.215	0.852	0.657
C	-0.179	0.710	0.479
N	-0.152	0.616	0.383
O	-0.152	0.573	0.319
F	-0.136	0.519	0.278
Ne	-0.109	0.455	0.255
Na	-0.794	1.579	0.751
Mg	-0.162	0.803	0.542
Al	-0.955	1.726	0.742
Si	-0.230	0.958	0.578
P	-0.151	0.759	0.474
S	-0.137	0.682	0.392
Cl	-0.131	0.636	0.331
Ar	-0.109	0.563	0.302

Table 3 Binding energies in eV (BE=2E(N)-E(N_2)), optimized bond length in Åand eigenvalue in eV of the N_2 molecule for various parameters in the kinetic OF functional $\lambda T_W + \gamma T_{TF}$. The LDA exchange-correlation functional is composed of Dirac exchange and PW correlation[38,39]. The KS reference values are calculated with the same exchange-correlation in spin-polarized formalism using GPAW.

Method and Parameters	BE	r_e	Eigenvalue
OF $(\lambda, \gamma_E) = (1.000, 0.435)$	87.488	0.534	-21.829
OF $(\lambda, \gamma_\varepsilon) = (1.000, 0.847)$	21.062	0.991	-8.172
OF $(\lambda, \gamma_\varepsilon) = (2.000, 1.007)$	37.398	1.010	-9.294
OF $(\lambda, \gamma_E \cap \gamma_\varepsilon) = (0.599, 0.697)$	14.383	0.903	-8.057
KS LDA	11.663	1.093	-10.418

Note that in this section we use Bohr units for `rcut` (the radius of the PAW augmentation sphere), because these are the units used in the PAW setup generation. The grid calculation energy values are given in eV.

As seen from Figure 4 the energy deviation for selected atoms does not exceed the absolute value of 0.007 eV. Thus, the `gpernode` $= 800$ value was used for extending the convergence tests to the PAW setup generator.

We can use the benchmark data we have produced in addition to data from the literature to study the PAW generation parameter `rcut` and the parameters for the evaluation of this model on the grid using the PAW transformation (grid spacing `h`). The `rcut` parameter determines the size of the augmentation sphere and therefore the size of the region where the PAW transformation will be defined. For each atom, we study the set of parameters $(\lambda, \gamma) = (1, 1)$.

The total energy deviation obtained from equation (20) for the H and O atoms as a function of `rcut` is presented in Figure 5. It is found that for the first and second row elements of the periodic table the energy deviation converges to the reference value with an `rcut` value equal to 1.2 Bohr, for all the tested grid spacings. For instance, for the H atom, at `rcut` $= 1.2$ Bohr the maximum energy deviation was found about 0.007 eV for `h` $= 0.2$ Å, compared to 0.005 eV for `h` $= 0.12$ Å, while the computation time was about one order of magnitude shorter. Above `rcut` $= 1.2$ Bohr the grid atomic energy shows very little dependence on the grid spacing. In conclusion, a grid spacing of 0.18 Å could be used to save computational time with such `rcut`. Below `rcut` $=$ 1.2 Bohr, the grid spacing needs to be decreased until convergence of the atomic energy is achieved. In this region the energy deviation increases as one goes to heavier atoms. As seen in Figure 5 (b) for the example for the O atom, using an `rcut` equal to 1.0 Bohr the energy deviation is found to converge at `h` $= 0.14$ Å (energy difference of -0.017 eV). To test the parameters for the PAW generation for systems other than atoms and below `rcut` $= 1.2$ Bohr one needs to test the convergence of energy differences (such as binding energy)[43]. This is exactly the case of the N_2 molecule studied in the last section. The LDA bond leght (and expected bond lenght) is of only 1.093 Å. An `rcut` $= 1.0$ Bohr (=0.53 Å) therefore, would not induce augmentation sphere superposition errors at such distance. We test then with respect to the all-electron binding energy reference[32] the deviation when varying the grid parameter `h`. We obtained with grid spacing the error is -0.075, -0.081 and -0.082 eV with grid spacing of 0.18, 0.14 and 0.12 Å respectively. We obtained then that binding energy is converged for grid spacing of 0.14 Å and that the error with respect to all-electron reference is small. We have therefore chosen the grid spacing of 0.14 Å for our dimer calculations. A systematic study of binding energy convergence for a wider set of molecules will be presented in our next study.

3 Conclusions

Using an all-electron radial atomic orbital-free DFT code[35], we have studied the performance of a parametrized OF model. In the model we include a parametrized Thomas-Fermi-Weizsäcker kinetic functional, where λ and γ determine the amount of Weizsäcker and Thomas-Fermi functionals added to the model, respectively, in addition to an LDA exchange-correlation. We have studied the interplay between λ and γ in terms of achieving agreement between the OF calculation and the corresponding KS calculation. We have compared the

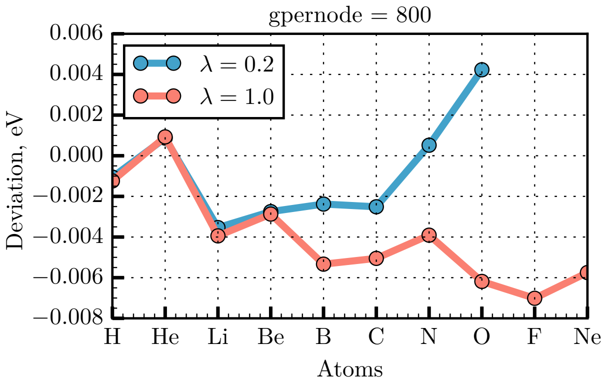

Fig. 4 Energy deviation with respect to reference value[32] calculated for the first and second row elements for `gpernode` $= 800$, $\lambda = 0.2, 1.0$, `rcut` $= 1.2$ Bohr.

OFDFT results to the equivalent KSDFT results following the rationale that for a perfect KS kinetic functional approximation, quantities such as total energy, Euler equation eigenvalue and electronic density should agree completely.

As the fraction of the Weizsäcker functional added to the model increases so does the need to decrease the fraction of Thomas-Fermi functional in order to achieve a good description of the total energy. In contrast, the best region of agreement for the eigenvalue strongly depends on the particular atom. The atomic density error shows a similar dependence but converges fast towards a homogenous error when the atomic number increases.

For the total energy and eigenvalue, we have fitted the regions of best agreement with a γ function that is not linear but quadratic. The fitted parameters for the total energy and eigenvalue interpolation formulas are essentially different. We can use the fitted coefficients to derive a small set of parameters per atom or for a small set of atoms that minimze both total energy and eigenvalue errors. However, any pair of parameters in this parametrized functional form will present large errors *in average* for the eigenvalue and the density of the different elements/molecules belonging to any sizeable system set. As an application of the atomic analysis, we tested a dimer formation with kinetic functionals fitted to reproduce atomic total energy and eigenvalue. We obtained that a kinetic functional fitted to simultaneously energy and eigenvalue gave a smaller error in binding energy, bond length and eigenvalue that kinetic functionals fitted to reproduce only one of the atomic properties.

These results on the performance of a parametrized OF functional within a wide region in parameter space can now open the way to test parameter transferability and overall accuracy of parametrized OF density functionals.

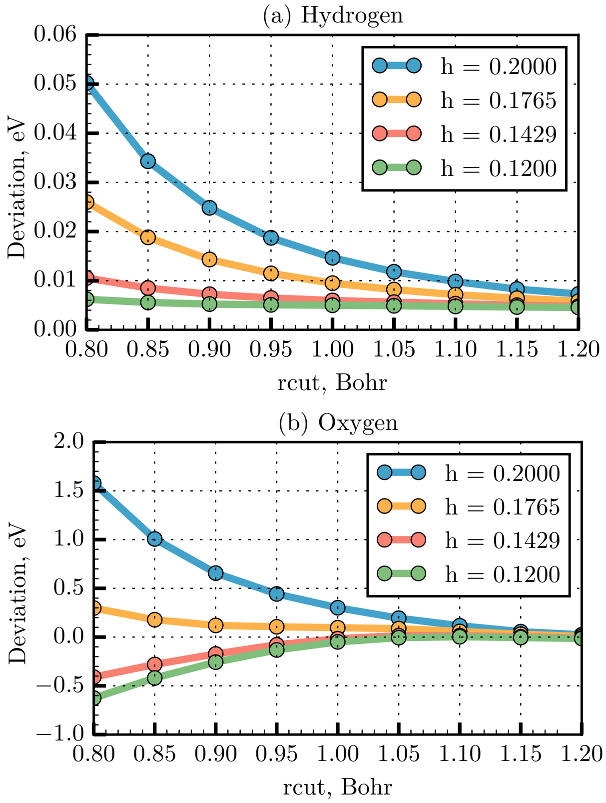

Fig. 5 Convergency of total energy with respect to all-electron energy using TFD1W theory for various `rcut` values and different grid spacings, calculated for the H (a) and O (b) atoms, respectively.

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