On the upper bound of the electronic kinetic energy in terms of density functionals

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Abstract
We propose a simple density-functional expression for the upper bound of
the kinetic energy for electronic systems. Such a functional is valid in the
limit of slowly varying density, its validity outside this regime is discussed by
making a comparison with upper bounds obtained in the previous work. The
advantages of the functional proposed for applications to realistic systems are
briefly discussed.

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1. Introduction

Kinetic energy functionals of the electron density have been since long a subject of intense
investigation. Starting with the pioneering work of March [1] through the monumental work
of Lieb (see e.g. [2–5]), the aim was to construct functionals which are accurate enough to
properly describe physical and chemical properties and at the same time simple enough to allow
a feasible computation. There has been a period of intense activity around this subject across
the 1970s until the end of the 1980s, during which many interesting results were produced.
After about a decade of lesser activity, the interest in the subject has got a new vigour (see e.g.
the interesting work of Ludeña and co-workers [6–9] and the topical review of March [10]).
The reason of this renewed interest lies in the fact that in the meanwhile novel computational
schemes for quantum calculations, where the kinetic functional plays a key role, have been
developed. Of particular interest is the linear-scaling real-space kinetic energy functional
method, where the kinetic energy is calculated as a functional of the electron density. The
electron wavefunctions are no longer required and for this reason the method is called orbital-
free density-functional theory (OFDFT) (see e.g. [11–16]). Since neither the diagonalization
of the electronic Hamiltonian nor the reciprocal space sampling are required, such techniques
allow for studies of relatively large systems compared to those treatable with the standard
Kohn–Sham based approaches. Moreover, the fact that the calculations are done only in real
space allows for the development of efficient quantum–classical interfaces which in current
research are highly desirable within the emerging multiscale modelling techniques. For this

reason, we turned our attention to the derivation of a simple and physically well-founded kinetic functional. We start from the most general polar form of the electron wavefunction and derive an upper bound which is exact in the limit of slowly varying density; we discuss its validity beyond such an approximation by comparing our results with those available in the literature. A first interesting result is that our functional is potentially a better bound compared to some of those available in the literature and by now well established; it is also universal, i.e. does not show explicit dependence on N, the number of electrons, differently from most of those found in the literature. Next, we combine our upper bound with the well-known lower bound of Lieb and Thirring. By doing so, we conclude that a valid functional is likely to have the form of a Thomas–Fermi–Weizsacker type (with different constants), where the multiplicative constant of the Weizsacker term is the only free parameter. To our knowledge, this is the first time that a universal functional containing a Thomas–Fermi-like term and the Weizsacker one is obtained within the same derivation, and not by separate schemes. Moreover, the link we find between the wavefunction phase factor and the kinetic functional suggests an operative way to estimate the unknown constant.

2. The kinetic energy

Let us consider a system of N electrons in a $3N$-dimensional volume Ω^N. The general N-particle wavefunction in polar form is $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \theta(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \, e^{iS(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)}$, where $\theta(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and $S(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ are real functions in Ω^N. We also require $\theta(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ to be antisymmetric with respect to any pair permutation, i.e. $\theta(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_N) = -\theta(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N)$ and $S(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ symmetric. In this way, the wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is antisymmetric as should be for a system of fermions. For simplicity, the spin variables are not explicitly considered. We define the one-electron density $\rho(\mathbf{r})$ in Ω as $\rho(\mathbf{r}) = N \int_{\Omega^{N-1}} [\theta(\mathbf{r}_1, \ldots, \mathbf{r}_{i-1}, \mathbf{r}_i, \mathbf{r}_{i+1}, \ldots, \mathbf{r}_N)]^2 \, d\mathbf{r}_1 \cdots d\mathbf{r}_{i-1} \, d\mathbf{r}_{i+1} \cdots d\mathbf{r}_N$, where the index i is arbitrary and can take any value from 1 to N; for the case $i = 1$, $d\mathbf{r}_{i-1}$ is not considered while for $i = N$, $d\mathbf{r}_{i+1}$ is not considered. The one-electron density, in turn, satisfies the condition $\int_{\Omega} \rho(\mathbf{r}) \, d\mathbf{r} = N$. We will use atomic units $\hbar = 1$, the electron mass $m = 1$ and the electron charge $e = 1$. Let us consider the average kinetic energy for the state ψ:

$$T_\psi = -\frac{1}{2} \int_{\Omega^N} \psi^* \nabla^2 \psi \, d^N \omega, \tag{1}$$

where $d^N \omega = \Pi_{i=1}^N d\mathbf{r}_i$ and $\nabla = \sum_{i=1}^N \nabla_i$. The expression above can also be written as (see e.g. [3])

$$T_\psi = \frac{1}{2} \int_{\Omega^N} |\nabla \psi|^2 \, d^N \omega. \tag{2}$$

Substituting the expression $\psi = \theta \, e^{iS}$ into equation (2), one obtains

$$T_\psi = \int_{\Omega^N} \left[\frac{\theta^2 |\nabla S|^2}{2} + \frac{|\nabla \theta|^2}{2} \right] d^N \omega. \tag{3}$$

The integrand on the rhs of equation (3) is a $3N$-dimensional function; the goal is to reduce it, as rigorously as possible, to a simple three-dimensional functional of $\rho(\mathbf{r})$.

2.1. Upper bound to $|\nabla S|$ in the slowly varying density limit

The average over Ω^n of the $3N$-dimensional momentum vector of the system is defined as

$$\langle \psi | \mathbf{m} | \psi \rangle_{\Omega^N} = \int_{\Omega^N} \text{Im}[\psi^* \nabla \psi] \, d^N \omega. \tag{4}$$

Substituting the polar form of ψ into equation (4), we obtain

$$\int_{\Omega^N} \text{Im}[\psi^* \nabla \psi] \, d^N\omega = \int_{\Omega^N} [\psi^* \nabla S \psi] \, d^N\omega. \tag{5}$$

Through equation (5) we find the relation $\langle \psi | \mathbf{m} | \psi \rangle_{\Omega^N} = \langle \psi | \nabla S | \psi \rangle_{\Omega^N}$, which suggests an interpretation of ∇S as a $3N$-dimensional quantum velocity field. Such an interpretation would not be new, and can be often found in the literature (see e.g. [17–19]), above all in the context of a fluid dynamics formulation of quantum mechanics [20]. If we interpret ∇S as a quantum velocity field then, in the limit of $\rho(\mathbf{r})$ being a slowly varying function[1], we can make the following conjecture for the absolute value of ∇S:

$$\langle \psi | |\nabla S| | \psi \rangle \leqslant \langle \psi | |\mathbf{P}_{F_N}| | \psi \rangle, \tag{6}$$

which explicitly reads

$$\int_{\Omega^N} \theta^2 \left| \sum_{i=1}^{N} \nabla_i S \right| d^N\omega \leqslant \int_{\Omega^N} \theta^2 \left| \sum_{i=1}^{N} \mathbf{P}_{F_i} \right| d^N\omega. \tag{7}$$

Here $\mathbf{P}_{F_N} = \sum_i^N \mathbf{P}_{F_i}$, with $\mathbf{P}_{F_i} = \mathbf{P}_F(\mathbf{r}_i)$, where $P_F(\mathbf{r})$ is the Fermi momentum, i.e. the maximum momentum a particle can reach in the limit of slowly varying density. Since equation (7) must hold for any arbitrary subvolume of Ω^N, we obtain

$$|\nabla S| \leqslant |\mathbf{P}_{F_N}|, \qquad \forall \mathbf{R} \in \Omega^N \tag{8}$$

and thus

$$|\nabla S|^2 \leqslant |\mathbf{P}_{F_N}|^2, \qquad \forall \mathbf{R} \in \Omega^N. \tag{9}$$

From the inequality (9), we have

$$\int_{\Omega^N} (\psi^* |\nabla S|^2 \psi) \, d^N\omega \leqslant \int_{\Omega^N} \left(\psi^* |\mathbf{P}_{F_N}|^2 \psi \right) d^N\omega \tag{10}$$

or equivalently

$$\int_{\Omega^N} \theta^2 |\nabla S|^2 \, d^N\omega \leqslant \int_{\Omega} \rho(\mathbf{r}) |\mathbf{P}_F(\mathbf{r})|^2 \, d\mathbf{r}. \tag{11}$$

The second term on the rhs of equation (11) is obtained in the following way:

$$\int_{\Omega^N} (\psi^* |\mathbf{P}_F|^2 \psi) \, d^N\omega = \sum_{i=1}^{N} \int_{\Omega_i} |\mathbf{P}_{F_i}|^2 \, d\mathbf{r}_i \int_{\Omega^{N-1}} \theta^2 \, d^{N-1}\omega = \sum_{i=1}^{N} \int_{\Omega_i} \frac{\rho(\mathbf{r}_i)}{N} |\mathbf{P}_{F_i}|^2 \, d\mathbf{r}_i. \tag{12}$$

If we go back to equation (3), since $|\mathbf{P}_F(\mathbf{r})| = C_F[\rho(\mathbf{r})]^{1/3}$, where C_F is a constant, $(C_F)^2 = (3\pi^2)^{2/3}$ (see footnote 1), we have

$$\int_{\Omega^N} \theta^2 \frac{|\nabla S|^2}{2} \, d^N\omega + \int_{\Omega^N} \frac{1}{2} \sum_{i=1}^{N} |\nabla_i \theta|^2 \, d^N\omega \leqslant \int_{\Omega} \frac{C_F^2}{2} [\rho(\mathbf{r})]^{5/3} + \int_{\Omega^N} \frac{1}{2} \sum_{i=1}^{N} |\nabla_i \theta|^2 \, d^N\omega. \tag{13}$$

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[1] In this context, the hypothesis of $\rho(\mathbf{r})$ being a slowly varying quantity must be interpreted in the same spirit of the Thomas–Fermi approximation, i.e. $\rho(\mathbf{r})$ describes a system which can be reasonably approximated by the statistics of a Fermi uniform electron gas at 0 K. Within this approximation, the Fermi momentum, $|\mathbf{P}_F|$, is the maximum value possible for the single-electron momentum and, according to the Fermi statistics, is proportional to $\rho^{1/3}(\mathbf{r})$. In fact, in the ground state of the Fermi electron gas, N electrons fill all the states up to the Fermi energy E_F. This means that in the momentum space all the states up to a certain momentum $|P_F|$ are occupied, i.e. the Fermi electron gas fills a sphere in the momentum space of radius $|P_F|$ (the Fermi sphere). Within the formalism of the Fermi statistics, it can be easily proved (see e.g. p. 308 of [21]) that $\frac{1}{3\pi^2} V |P_F|^3 = N$, i.e. $|P_F| = [3\pi^2 \rho(\mathbf{r})]^{1/3}$, under the hypothesis that $\rho(\mathbf{r})$ does not deviate significantly from a uniform density $\frac{N}{V}$.

In this way, we have determined an upper bound to T_ψ, where the first term is written as a functional of $\rho(\mathbf{r})$. We shall now also reduce the other term into a three-dimensional expression, possibly as a functional of $\rho(\mathbf{r})$. One may wonder why one should study the phase factor S for atoms and molecules in their ground states. Indirectly, this work suggests an unconventional answer; strictly speaking, $S = 0$ for the ground state of atoms and molecules, and this would mean that, in principle, the only kinetic functional term is the Weizsacker term, as discussed by Sears *et al* [22], Herring [23] and Luo [24]. However in [23, 24] it is discussed and shown that this result would not be correct and there must be an additional term to the kinetic energy coming from some angular part of the wavefunction which factorizes, i.e. something related to a phase factor. At the same time if $\psi = \theta\,\mathrm{e}^{\mathrm{i}S}$ is a solution, also $\psi^* = \theta\,\mathrm{e}^{-\mathrm{i}S}$ is a solution with the same energy; this also holds for linear combinations of the two. For atoms and molecules one can always choose, without loss of generality, linear combinations of ψ and ψ^* that lead to real wavefunctions. In this case, as it can be verified by a straightforward calculation, the rhs of equation (13) is still an upper bound to the kinetic energy.

2.2. Weizsacker and non-local information functional

The term $\int_{\Omega^N} |\nabla\theta|^2\,\mathrm{d}^N\mathbf{r} = \sum_{i=1}^N \int_{\Omega^N} |\nabla_i\theta|^2\,\mathrm{d}^N\mathbf{r}$ is what Sears *et al* [22] refer to as the *multivariate kinetic functional* and can be written as

$$\frac{1}{2}\sum_{i=1}^N \int_{\Omega^N} |\nabla_i\theta|^2\,\mathrm{d}^N\mathbf{r} = \frac{1}{8}\int_\Omega \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}\,\mathrm{d}\mathbf{r}$$

$$+ \frac{1}{8}\sum_{i=1}^N \int_{\Omega^N} \frac{\rho(\mathbf{r}_i)}{N} \frac{|\nabla_i f(\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r}_{i+1},\ldots,\mathbf{r}_N/\mathbf{r}_i)|^2}{f(\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r}_{i+1},\ldots,\mathbf{r}_N/\mathbf{r}_i)}\,\mathrm{d}^N\mathbf{r}, \tag{14}$$

where the first term on the rhs is the well-known Weizsacker term and $i \in [1, N]$ with $f(\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r}_{i+1},\ldots,\mathbf{r}_N/\mathbf{r}_i)$ is proportional to the conditional density, i.e. the probability density of finding a certain spatial configuration for $N - 1$ particles once the position of the ith particle is assigned (see also [25]). Following the work of [22], we can write

$$\frac{1}{2}\sum_{i=1}^N \int_{\Omega^N} |\nabla_i\theta|^2\,\mathrm{d}^N\mathbf{r} = \frac{1}{8}\int_\Omega \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}\,\mathrm{d}\mathbf{r} + \frac{1}{8}\int_\Omega \rho(\mathbf{r})I(\mathbf{r})\,\mathrm{d}\mathbf{r}, \tag{15}$$

where

$$\int_\Omega \rho(\mathbf{r})I(\mathbf{r})\,\mathrm{d}\mathbf{r} = \int_\Omega \rho(\mathbf{r})\left[\int_{\Omega^{N-1}} \frac{|\nabla_\mathbf{r} f(\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N/\mathbf{r})|^2}{f(\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N/\mathbf{r})}\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\cdots\mathrm{d}\mathbf{r}_N\right]\mathrm{d}\mathbf{r}, \tag{16}$$

with $I(\mathbf{r})$ being the well-known non-local *information functional* within Fisher information theory. An exact expression for $I(\mathbf{r})$ is difficult to find, however, one can note that $I(\mathbf{r})$ would be equivalent to write in local form some kinetic correlation effects which are usually considered negligible [7]. Combining the results above with those of the previous section, we obtain

$$T_\psi \leqslant \frac{[C_\mathrm{F}]^2}{2}\int_\Omega [\rho(\mathbf{r})]^{5/3} + \frac{1}{8}\int_\Omega \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}\,\mathrm{d}\mathbf{r} + \frac{1}{8}\int_\Omega \rho(\mathbf{r})I(\mathbf{r})\,\mathrm{d}\mathbf{r}. \tag{17}$$

3. Beyond the slowly varying density regime

In this section, by comparing the result of equation (17) with upper bounds to T_ψ available in the literature, we will discuss the validity of our results for the general case. For simplicity,

we will neglect the non-local information functional term since, as said before, it represents a non-relevant correction. Under this hypothesis, equation (17) becomes

$$T_\psi \leqslant \frac{[C_F]^2}{2} \int_\Omega [\rho(\mathbf{r})]^{5/3} + \frac{1}{8} \int_\Omega \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \, d\mathbf{r}. \tag{18}$$

It is encouraging to note that the same functional form for the upper bound, with a slightly different multiplicative constant for the first term, was conjectured, following arguments different from ours, by Lieb [4]. March and Young obtained a result similar to ours but the constant multiplying the $\int \rho^{5/3} \, d\mathbf{r}$ must be determined for each atom [1]. Gazquez and Robles [26] derived a kinetic energy functional of the form: $T_\psi = C_1 \left(1 - \frac{C_0}{N^{1/3}}\right) \int \rho^{5/3} \, d\mathbf{r} + \frac{1}{8} \int \frac{|\nabla\rho|^2}{\rho} \, d\mathbf{r}$, the same functional was independently proposed by Acharya et al [27]. This functional has explicit dependence on N, the number of particles, thus it is not universal; however, in the thermodynamic limit, i.e. N large, it has the same functional form of the functional we derived (with, again, a slightly different constant for the first term). Moreover, our result is fully consistent with the estimate of the *relative-phase-energy* term of Herring [23] where he concludes that the upper bound must be something which has the same form as our functional. Even better comparison can be made for the simpler, one-dimensional case; now the term $\int \rho^{5/3} \, d\mathbf{r}$ in equation (18) becomes $\int \rho^3 \, dx$ because in our derivation $P_F \sim \rho$ in one dimension. The resulting upper limit has the same functional form for T_ψ obtained by Harriman [28] using the special equidensity orbitals (SEDOs) construction for ψ (see also [29]). Moreover, it represents an upper bound, in the limit of large N, to the rigorous functional found by March and Young in one dimension: $T_\psi \leqslant \text{const} \times \int \rho^{3/2} \, dx + \int \frac{|\nabla\rho|^2}{\rho} \, dx$. The arguments above, although they do not represent an explicit proof, suggest that the functional we propose may indeed be a valid upper bound beyond the slowly varying density approximation. An intuitive argument to support the validity of our hypothesis is the following. In the slowly varying density regime, our upper bound condition on the momentum of the single electron is rather 'large'. In fact, we approximate the momentum of each electron with the maximum value possible instead of distributing among the N electrons all the states available from $|\mathbf{m}| = 0$ to $|\mathbf{m}| = |\mathbf{P}_F|$. By slowly moving from this regime to an intermediate one, for a large number of particles, despite the fact that $\mathbf{P}_F$ slowly loses its physical meaning, the upper bound hypothesis $|\nabla S| \leqslant \text{const} \times \rho^{1/3}$ is likely to still hold for an extended range of densities. Moreover, the larger N, the more extended the range of validity; in the thermodynamic limit, one can expect such an upper limit to be always valid, as the comparison with the functional of Gazquez and Robles [26] and of Acharya et al [27] suggests. Interestingly, if this was the case, we would have found a better upper bound to T_ψ compared to that of Zumbach [30]:

$$T_\psi \leqslant [1 + C_{Zu} N^{2/3}] \frac{1}{8} \int \frac{|\nabla\rho|^2}{\rho} \, d\mathbf{r}, \qquad C_{Zu} = 15(4\pi)^2 \frac{3}{5} \left(\frac{1}{5}\right)^{2/3}, \tag{19}$$

which was obtained using a SEDOs-like construction of ψ and is considered of general validity, although its explicit dependence on N makes it non-universal. In fact, as it is discussed by Pathak and Gadre [31], and also reported by Zumbach [30], by using the Schwartz inequality and then applying one Sobolev inequality in three dimensions, it is possible to obtain the following relation:

$$\int \rho^{5/3} \, d\mathbf{r} \leqslant C_{PG} \times N^{2/3} \frac{1}{8} \int \frac{|\nabla\rho|^2}{\rho} \, d\mathbf{r}, \tag{20}$$

where C_{PG} is a constant (see [31]); if now we compare equation (18) with equation (19) via equation (20), we obtain

$$T_\psi \leqslant \frac{[C_F]^2}{2} \int_\Omega \rho^{5/3} + \frac{1}{8} \int_\Omega \frac{|\nabla\rho|^2}{\rho} \, d\mathbf{r} \leqslant [1 + C_{Zu} N^{2/3}] \frac{1}{8} \int \frac{|\nabla\rho|^2}{\rho} \, d\mathbf{r}, \quad (21)$$

since $C_{PG} \times C_F^2 \ll C_{Zu}$.

4. Upper and lower bounds for T_ψ

An interesting property of our upper bound can be obtained by relating it to the Lieb–Thirring inequality and the consequent lower bound to T_ψ [2, 3, 5, 32, 33]:

$$T_\psi \geqslant \frac{C_{LT}}{2} \int \rho^{5/3} \, d\mathbf{r}. \quad (22)$$

From [3, 32, 33] it follows that C_F^2 of equation (18) is very close to C_{LT} of equation (22). In fact, $C_F^2 \approx 9.57$ while $C_{LT} \approx 9.11$. Actually Lieb in [3] argues that numerical calculations improve C_{LT} to 9.578. If we consider $C_F^2 \approx C_{LT}$, then we can write in good approximation the following relation:

$$C \times \int \rho^{5/3} \, d\mathbf{r} \leqslant T_\psi \leqslant C \times \int \rho^{5/3} \, d\mathbf{r} + \frac{1}{8} \int_\Omega \frac{|\nabla\rho|^2}{\rho} \, d\mathbf{r}, \quad (23)$$

where C is a constant whose value is between that of $C_F^2/2$ and $C_{LT}/2$, thus very close to both. The implications of equation (23) are very interesting; it suggests that a valid approximation for T_ψ can be written as

$$T_\psi \approx C \times \int \rho^{5/3} \, d\mathbf{r} + q \times \frac{1}{8} \int_\Omega \frac{|\nabla\rho|^2}{\rho} \, d\mathbf{r}, \quad (24)$$

where $0 \leqslant q \leqslant 1$, is the only free parameter. A possible way to obtain a first guess for q would be by estimating ∇S numerically for some simple model systems. However, already at this stage, equation (24) represents a very interesting result, as it has been previously discussed in the introduction, in connection with current quantum-based computational schemes.

5. Discussion and conclusions

We have used the polar form of a many-particle electron wavefunction to derive a simple functional for the kinetic energy. Such a functional represents an upper bound to the true kinetic energy and it is exact in the limit of slowly varying density. We have discussed its validity beyond such an approximation by making a comparison with functionals obtained in the previous work. The novelty of our derivation presents different aspects; we obtain within the same theoretical framework a kinetic functional containing both a Thomas–Fermi-like functional and the Weizsacker functional. These are usually determined by following separate procedures under different physical approximations. This result provides a physical justification to a highly desirable upper bound functional which was heuristically conjectured by Lieb [4]. Another advantage is that it does not show explicit dependence on N, differently from most of the upper bounds available in the literature, and represents a better bound compared to other well-established functionals. Finally, combined with the Lieb–Thirring lower bound leads to the conclusion that a valid functional, which can well approximate the true one, could be determined by simply tuning the multiplicative constant (between 0 and 1) of the Weizsacker term. This result is very interesting above all for applications to

condensed matter systems within free orbital density-functional schemes. In fact, it provides not only a theoretical background to justify the kinetic functional currently employed, but also a possible procedure to determine new ones. Approaches such as the one shown in this paper are crucial for the development of computationally efficient and theoretical flexible quantum mechanical techniques for modern multiscale simulations. As discussed in the introduction, the computational apparatus is available and new ideas, which can improve the energy functionals currently available or suggest new ones, are strongly required. In this respect, our contribution suggests a possible way to proceed.

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