We propose a simple gradient-dependent bound for the exchange-correlation energy (sLL), based on the recent non-local bound derived by Lewin and Lieb. We show that sLL is equivalent to the original Lieb-Oxford bound in rapidly-varying density cases but it is tighter for slowly-varying density systems. We apply the sLL bound to revisit the construction of both semilocal and non-local exchange and correlation functionals. In both cases improved results, with respect to the use of Lieb-Oxford bound, are obtained.

\[ E_{xc}[n_\lambda] \geq E_{xc}[\lambda n_\lambda] \] for any \( \alpha \leq 2 \), and where \( s = |\nabla n_\lambda|/|2(3\pi^2)^{1/3}n_\lambda^{4/3}| \) and \( t_\lambda = |\nabla n_\lambda|/[2(3/\pi)^{1/6}n_\lambda^{7/6}] \) are the reduced gradients for exchange and correlation respectively (note that \( s \) is invariant under the uniform scaling while \( t_\lambda \) and \( \beta \) are the second order expansion coefficient for correlation. We recall that \( \beta \) is known only in the high-density limit, and in the metallic range\(^{19}(a.i.) \) for \( 2 \leq r_\alpha \leq 6 \), with \( r_\alpha = [3/(4\pi n)]^{1/3} \) being the bulk parameter). The last inequality uses the fact that \( s \leq 1 \) in the considered limit. Eq. (3) suggests that in the low-density limit, a gradient-dependent term may play an important role to the bound, similar with the LL expression.

On the other hand, starting form the LL bound and using the Hölder inequality we find

\[ E_{xc}[n_\lambda] \geq -1.45 \int n_\lambda^{4/3} dr - 0.516 \int n_\lambda^{4/3} s^{1/4} dr \ . \] (4)

This provides a slightly tighter bound than LL (not mathematically rigorous but in the spirit of Ref. 13 as explained below), and it can be used together with Eq. (3) to obtain a more useful formula for the bound.

In fact, a comparison of Eqs. (3) and (4) suggests that the correct bound could be

\[ sLL[n_\lambda] = -1.45 \int n_\lambda^{4/3} dr - C \int n_\lambda^{4/3} s^{1/4} dr \ , \] (5)

with \( 0.09 \leq C \leq 0.52 \) (to be fixed later). This ansatz is also supported by a further analysis of the XC energy...
under the uniform scaling to the low-density limit at any value of \( s \) (note that instead Eq. (3) holds only for \( s < 1 \)). To see this, consider the partitioning the XC energy as

\[
E_{xc}[\rho] = E_{xc}^{LDA}[\rho] + E_{xc}^{GE2}[\rho] + \delta E_{xc},
\]

where \( LDA \) denotes the local density approximation, \( GE2 \) denotes the second-order gradient expansion terms, and \( \delta E_{xc} \) and \( \delta E_c \) indicate higher-order exchange and correlation contributions. Because in this limit \( t \to 0 \) we can set \( \delta E_c \approx 0 \). Moreover, following Ref. 8, we can assume that \( E_{xc}^{GE2}[\rho] \approx 0 \) for \( \lambda \to 0 \). Hence,

\[
E_{xc} \approx E_{xc}^{LDA}[\rho] + \delta E_{xc}[\rho] = -1.44 \int n^{4/3}_x dr - C_x \int \frac{n^{4/3}_x}{r_x} f_{xc}^{exact}(s) - 1) dr,
\]

with \( C_x = -(3/4)(3/\pi)^{1/3} \) and \( f_{xc}^{exact} \) is the exact exchange enhancement factor. Noting that at large gradients \( f_{xc}^{exact} - 1 \geq 0 \), Eq. (6) shows that a tighter LO bound may fail in the low-density regime (where both LDA correlation and exchange scale similarly, as \( \sim 1/r_x \)) and an s-dependent term is instead required.

To fix the parameter \( C \), we consider a tough case for the semilocal sLL bound: the beryllium isoelectronic series up to \( Be^{140+} \). This is in fact a rapidly-varying high-density limit case with strong correlation (\( E_{xc} \to -\infty \) for highly charged ions\(^{20} \)). While the original LO bound gives \( LO/E_{xc} \approx 1.9 \), the LL bound is much looser, having \( LL/E_{xc} \approx 2.3 \) (note that all results are practically independent on the nuclear charge). Hence, our constraint is that \( sLL \approx LO \) for such a case (that is representative for rapidly-varying density regime). In this way we obtain \( C = 0.245 \).

The bound of Eq. (5) can be tested for different systems. In case of atoms, ions, molecules, and solids this test is trivial because sLL is slightly looser than the local bound of Odashima and Capelle\(^{22} \) which was already verified for these cases. Hence, we consider here a few additional possibilities, based on interesting model systems.

For slowly-varying density cases the sLL bound is surely verified in the low-density limit, because \( C = 0.245 \geq 0.091 \). For other density regimes we consider in Fig. 1 jellium spheres with 40 electrons and bulk parameters included in the interval \( 1 \leq r_s \leq 20 \), as well as two interacting jellium slabs of thickness and separation distance equal to the Fermi wave length (similar results are obtained also for other thicknesses and distances) and \( 1 \leq r_s \leq 20 \). In all cases the exchange energy is computed exactly, whereas the correlation energy is estimated using the JS functional\(^{23,24} \) (similar results are given also by PBE\(^8 \) and TPSS\(^2 \)). We note that these systems were not considered in the investigation of Ref. 13. Moreover they are relevant to understand the significance on the bound of quantum oscillations in ordinary matter. Inspection of Fig. 1 shows that in all cases the sLL bound is respected \( (sLL/E_{xc} \geq 1) \) and it is tighter than LO. On the other hand, the non-local LL bound is always rather loose. Finally, comparison with uniform electron gas results shows that quantum oscillations and surface effects have a negligible effect on the LO bound, which does not depend on the gradient, while they give a little weakening of the semilocal sLL bound.

As a different example we consider the one-electron densities

\[
n_{H}(r) = \frac{e^{-2r}}{\pi} ; \quad n_{G}(r) = \frac{e^{-r^2}}{\pi^{3/2}}.
\]

These are models for rapidly-varying density systems and have been shown to be relevant for bonding properties of molecules\(^{22} \). In these cases all calculations are analytical and we readily find: \( LO/E_{XC} = 1.55, LL/E_{XC} = 1.82, \) and \( sLL/E_{xc} = 1.56 \) for H; \( LO/E_{XC} = 1.54, LL/E_{XC} = 1.80, \) and \( sLL/E_{xc} = 1.54 \) for G. Thus, the LO and sLL bounds have the same quality, both outperforming the LL bound. The coincidence of LO and sLL for these model systems is reminiscent of the fact that, to fix \( C \) in Eq. (5), we constrained sLL to reproduce LO for the Be series, which presents rapidly-varying densities. However, notably in the present case there is no contribution from correlation, whereas for the Be series correlation tends to infinity.

To conclude our analysis we consider finally the opposite case of slowly-varying strong-correlated systems. One example of such systems is given by the point-charge-plus-continuum (PC) model\(^{23,24} \). At small reduced gradients \( s \leq 1 \), the XC energy is

\[
E_{xc}^{PC}[n] = -1.45 \int n^{4/3} dr + 0.203 \int n^{4/3} s^2 dr.
\]

We observe that the local term is exactly the one entering in the LL and sLL bounds and is very close to the numerical estimation of Odashima and Capelle\(^{22} \), although this latter bound is formally broken for \( s \to 0 \). This shows that this model is the true limit for constant densities. On the other hand, because the second-order XC contribution is positive, all the examined bounds are valid for the PC model for \( 0 < s \leq 1 \).
Another interesting example of slowly-varying strongly correlated system can be obtained by considering the strong-correlation scaling of the density

\[ n_\lambda(r) = \lambda^{-2}n(\lambda^{-1}r) \]

in the limit \( \lambda \to \infty \). Under this scaling the reduced gradients behave as \( s_\lambda(r) = \lambda^{-1/3}s(\lambda^{-1}r) \) and \( t_\lambda(r) = \lambda^{-2/3}t(\lambda^{-1}r) \). The XC energy is dominated by the local terms, while the second-order contributions decay as \( \lambda^{-1/3} \). On the other hand, we have \( s_{LL} = -1.45\lambda^{1/3} \int n^{1/3}dr - 0.245\lambda^{1/4} \int n^{1/3}s^{1/3}dr \). Therefore, for \( \lambda \to \infty \) sLL provides a good bound to the XC energy (note that the local part of sLL is almost the exact limit for the local XC energy). Moreover, we note that in this limit \( s_{LL} \leq LO \), being a tighter bound for the XC energy of slowly-varying strongly-correlated systems.

To employ the sLL bound in a practical tool we consider its application in the construction of an XC functional. Following the idea used to build the PBE functional we can thus consider an exchange enhancement factor

\[ F_x = 1 + \kappa - \frac{\kappa}{[1 + (\mu/\kappa)s^2]} \]

and fix \( \kappa \) by requiring the respect of the sLL bound at any point in space. This gives

\[ \kappa = 0.559 + 0.279s^{1/4} \].

Concerning the choice of \( \mu \) we simply consider here the value 10/81 coming from the second-order gradient expansion of the exchange energy. Other choices will be considered in future work. The so defined exchange functional resembles the PBEsol one, except for the new bound. Hence, we associate it with the correlation functional having the correlation energy per particle given by the formula

\[ \epsilon_c = \epsilon_c^{LDA} + \phi^{\alpha t^3} H^{PBE}(\beta = 0.045) \],

where \( \epsilon_c^{LDA} \) is the LDA correlation energy per particle, \( \phi = ((1+\zeta)^{2/3}+(1-\zeta)^{2/3})/2 \), with \( \zeta = (n_\uparrow-n_\downarrow)/n \) being the spin polarization, and \( H^{PBE} \) is a PBE-like correlation generalized gradient correction, where the parameter \( \beta = 0.045 \) (note that in PBEsol \( \beta = 0.046 \) is fixed from jellium surfaces. The term \( \phi^{\alpha t^3} \) is a spin-dependent correction designed to improve cohesive properties and \( \alpha = 4.0 \) is optimized as explained in Ref. \[22\]. The final XC functional is named zPBEsol-b.

In Fig. 2 we show a comparison of the exchange enhancement factors. Note that any exchange functional that recovers the local LO bound (e.g. PBEsol, TPSS meta-GGA) satisfies also the local sLL bound. On the other hand, PBEsol-b violates the local LO bound.

To test the zPBEsol-b functional and assess the importance of the sLL bound we performed different tests comparing with PBEsol, PBEsol-b, and zPBEsol results. In Table I we report the mean absolute errors (MAEs) for solid-state tests on 24 bulk solids including Al, Ca, K, Li, Na (simple metals); Ag, Cu, Pd, Rh, V (transition metals); LiCl, LiF, MgO, NaCl, NaF (ionic solids); AlN, BN, BP, C (insulators); GaAs, GaP, GaN, Si, SiC (semiconductors). We see that zPBEsol-b performs remarkably well even slightly improving overall over PBEsol and zPBEsol. We recall that PBEsol is one of the most used semilocal functional in solid-state physics and, to our knowledge, one of the best for this test set. Additionally, we report in Table II the MAEs for several tests on molecular properties that are relevant for semilocal functionals. Even more clearly than for bulk solids, the results of zPBEsol-b are systematically better than the zPBEsol ones and definitely much better than PBEsol results. The results of Tables I and II thus indicate the importance of the sLL bound for the construction of semilocal functionals.

To complete our investigation we consider the hyper-
The correlation energies of the atoms from He to Ar as well as of jellium spheres (with 2, 8, 18, 20, 34, 40, 58, 92, and 106 electrons and various $r_s$), computed with these functionals, are reported in Table III. The hyper(sLL) functional systematically improves over hyper(LO), showing that the sLL bound may be an interesting tool in the construction of non-local functionals.

In conclusion, we showed a new simple gradient-dependent bound (sLL), which has the same quality as the Lieb-Oxford (LO) bound for systems where the density varies rapidly but is significantly tighter for slowly-varying density cases. It is also the exact limit for slowly-varying strongly correlated systems. To indicate the utility of this new bound we applied it to both semilocal

non-local DFT, showing how it can be employed to construct improved exchange and correlation functionals. In particular, we build a generalized gradient approximation functional (zPBEsol-b) which gives a better accuracy than PBEsol and zPBEsol for a broad pallet of molecular properties and solid-state properties. In addition, we showed that the sLL bound can be fruitfully employed in the construction of hyper-GGAs, thus being an important tool for future developments in the field of non-local density functionals.

Acknowledgments. We thank Prof. Andreas Savin for useful discussions.

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