

## Violation of a local form of the Lieb-Oxford bound

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In the framework of density-functional theory, several popular density functionals for exchange and correlation have been constructed to satisfy a *local* form of the Lieb-Oxford bound. In its original global expression, the bound represents a rigorous lower limit for the indirect Coulomb interaction energy. Here we employ exact-exchange calculations for the G2 test set to show that the local form of the bound is violated in an extensive range of both the dimensionless gradient and the average electron density. Hence, the results demonstrate the severity in the usage of the local form of the bound in functional development. On the other hand, our results suggest alternative ways to construct accurate density functionals for the exchange energy.

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### I. INTRODUCTION

Density-functional theory [1] (DFT) is one of the most popular electronic structure methods that, for a large variety of systems, produces accurate results with a relatively small computational cost. Functionals used for the exchange and correlation energy  $E_{xc}[n]$  and potential  $V_{xc}[n]$  play a central role in DFT [2]. In fact, DFT became a mainstream method in quantum chemistry only after significant developments beyond the local-density approximation (LDA), first and foremost the generalized-gradient approximations (GGAs).

Most GGAs are built in a way that  $E_{xc}[n]$  satisfies a set of known exact conditions. These conditions, together with an ansatz of the gradient form, enable GGAs to account for inhomogeneities in the electronic density and thus improve upon the LDA in most cases. Two of the most prominent examples of the GGA are that of Becke from 1988 [3] (B88) and the Perdew-Burke-Ernzerhof [4] (PBE) functional. In the latter, seven known exact conditions to the  $E_{xc}[n]$  are imposed to a simple ansatz. The result is an outstandingly accurate functional that performs well on a wide range of systems. Currently, PBE is the most popular functional for material applications, whereas B88—embedded in the B3LYP hybrid functional [5]—is the most popular functional in quantum chemistry [6].

An important exact condition for  $E_{xc}[n]$  is the Lieb-Oxford (LO) bound [7]. The bound sets a rigorous lower limit for the indirect (quantum mechanical) part of the total Coulomb interaction energy. Hence, on one hand, the LO bound is a fundamental condition in many-particle physics and relates to the analysis of the stability of matter [8]. On the other hand, the LO bound must be satisfied by all density functionals. In DFT this requirement can be conveniently formulated through

the expression of the bound in terms of the LDA exchange energy (see below).

Levy and Perdew [2,9] have suggested that in order to satisfy the LO bound, the *exchange-energy density* (exchange-energy integrand) must also be bounded. This local condition, however, is stronger than the global LO bound. In spite of the ambiguity, several functionals such as PBE rely on this local form to impose an extra constraint on the functional. In fact, to the best of our knowledge, the LO bound has been applied solely in its local form in the development of functionals [2].

The use of the local LO bound has been questioned in several works [10,11], but the severity of the approximation, i.e., the extent to which the local bound is violated, has not been explored until now [12]. Addressing the similarities and differences between the global and local LO bound would be of particular importance in view of recent studies on the tightening of the LO bound [13,14] and the consequent developments or revisions of density functionals.

In this work we use the well-known G2 test set [15] to analyze to which extent, and in which range of parameters, the local form of the LO bound is violated. The G2 set of 148 molecules is commonly used to gauge the accuracy and predictive abilities of a given computational method, and it represents a broad range of chemical environments [15,16].

Our analysis is carried out in the following order. In Sec. II we review and address the differences between the global and local forms of the LO bound within DFT. In Sec. III we present our results for closed-shell molecules in the G2 set; here we solve exact exchange (EXX) energies within the Krieger-Li-Iafrate [17] (KLI) approximation and demonstrate the violation of the local bound. In the same context, we assess the local performance of different density functionals with respect to the enhancement factor. In addition, we compare the relation between the violation of the local bound and the distance from the global LO bound, and consider the spatial dependence of the violation of the local bound. Finally, in Sec. IV we summarize our findings and discuss how our results could be used in the development of density functionals.

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## II. LIEB-OXFORD BOUND

### A. Global bound

The LO bound in its original, global form applies to all three-dimensional (3D) nonrelativistic, Coulomb-interacting systems. The bound can be expressed in terms of the indirect part of the interaction energy as

$$W_{xc}[\Psi] \equiv \langle \Psi | \hat{V}_{ee} | \Psi \rangle - E_H[n] \geq -C \int d^3r n^{4/3}(\mathbf{r}), \quad (1)$$

where  $\hat{V}_{ee} = \sum_{i>j} |\mathbf{r}_i - \mathbf{r}_j|^{-1}$  is the Coulombic interaction operator and  $E_H[n]$  is the classical Hartree energy. The expectation value of  $\hat{V}_{ee}$  is calculated over any normalized many-body wave function  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  with the corresponding density  $n(\mathbf{r})$ . For the prefactor  $C$ , Lieb [18] originally found a value  $C^L = 8.52$ , but this was later refined by Lieb and Oxford [7] to  $C^{LO} = 1.68$  and numerically by Chan and Handy [19] to  $C^{CH} = 1.64$ . Recently, using nonrigorous but physical arguments the bound was tightened further to  $C = 1.44$  (Ref. [14]).

Remarkably, the right-hand side of Eq. (1) has a form similar to the LDA for the exchange energy, i.e.,

$$E_x^{\text{LDA}}[n] = -A \int d^3r n^{4/3}(\mathbf{r}) \quad (2)$$

with  $A = 3^{4/3}\pi^{-1/3}/4$ . Moreover, the left-hand side of Eq. (1) can be expressed as a density-functional  $W_{xc}[n]$  corresponding to the minimization of  $\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$ , so that the ground-state density  $n(\mathbf{r})$  is produced. Following the definition of the exchange-correlation energy  $E_{xc}$  we can now write

$$W_{xc}[n] \leq W_{xc}[n] + T_c[n] \equiv E_{xc}[n] \leq E_x[n], \quad (3)$$

where the first inequality is justified by the fact that the kinetic-energy part of the correlation energy is always non-negative, i.e.,  $T_c \geq 0$ . The second inequality follows from the negative nature of the correlation energy  $E_c[n] = E_{xc}[n] - E_x[n] \leq 0$ . This is straightforward to see in the constrained-search definition of the correlation functional [20].

Combining the above relations leads to a simple expression of the global bound:

$$E_x[n] \geq \lambda E_x^{\text{LDA}}[n], \quad (4)$$

or, alternatively,

$$\frac{E_x[n]}{E_x^{\text{LDA}}[n]} \leq \lambda, \quad (5)$$

where  $\lambda = C/A$ . We note that in this definition,  $\lambda$  is a *number* that in principle is universal. Recent studies [14,21] on the LO bound have focused on finding maximum values for a density-functional  $\lambda[n]$  or function  $\lambda(N)$ , with an aim to tighten the universal value for  $\lambda$ . Indeed, the procedure in Ref. [14] led to a conclusion that the bound can be tightened to  $\lambda \approx 1.96$ , corresponding to  $C = 1.44$ . In the following, however, we will refer to the original LO value of  $C^{LO} = 1.68$  corresponding to  $\lambda = 2.27$ .

### B. Local bound

Before introducing the local bound it is useful to write the exchange-correlation energy in the form of the standard GGA

ansatz, i.e.,

$$E_{xc}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{\text{3DEG}}[n] \mathcal{F}_{xc}[n, \nabla n, \dots], \quad (6)$$

where  $\epsilon_{xc}^{\text{3DEG}}$  is the exchange-correlation energy per particle in the 3D homogeneous electron gas (3DEG), and  $\mathcal{F}_{xc}$  is the enhancement factor including the corrections to the LDA. By definition it is non-negative, as well as its components  $\mathcal{F}_x$  and  $\mathcal{F}_c$ . In the standard GGA ansatz,  $\mathcal{F}_{xc}$  is written as a functional of  $n$  and  $\nabla n$ , or more conveniently, in terms of the dimensionless density gradient  $s = |\nabla n| / (2k_F n)$  [with  $k_F = (3\pi^2 n)^{1/3}$  being the Fermi momentum] and the Wigner-Seitz radius  $r_s = 3^{1/3}(4\pi n)^{-1/3}$ . As indicated by the symbol “...” in Eq. (6),  $\mathcal{F}_{xc}$  generally depends on other quantities and thus the expression refers to the *exact*  $E_{xc}[n]$ .

Combining the above integral form for  $E_{xc}$  and the relations of the previous section, we can rewrite the *global* LO bound as

$$\int d^3r n(\mathbf{r}) |\epsilon_x^{\text{3DEG}}[n]| \mathcal{F}_x \leq \lambda \int d^3r n(\mathbf{r}) |\epsilon_x^{\text{3DEG}}[n]|, \quad (7)$$

where we take the absolute values to deal with only non-negative quantities. The *local* bound suggested by Levy and Perdew [2,20] (originally expressed for  $\mathcal{F}_{xc}$ ) is written for the integrands of Eq. (7), i.e.,

$$\mathcal{F}_x \leq \lambda. \quad (8)$$

If this local condition is satisfied, the global inequality in Eq. (7) is trivially satisfied as well. However, the reverse implication obviously does not hold. In other words, Eq. (8) may be violated without the violation of the global bound. In particular, the local bound in Eq. (8) might be considerably too strict to be a well-reasoned condition in the development of density functionals. This will be explicitly demonstrated in the following section.

## III. RESULTS

We use the OCTOPUS code [22] to calculate the EXX energies and the corresponding EXX energy densities (per particle)  $\epsilon_x^{\text{EXX}}$  for closed-shell molecules in the G2 test set. We use the norm-conserving Hartwigsen-Goedecker-Hutter pseudopotentials [23]. The EXX results are obtained from the optimized-effective-potential [24] (OEP) scheme within the KLI approximation that neglects the so-called orbital shifts in the full OEP. Apart from special cases such as long atomic chains [25], the KLI approximation has been shown to be extremely accurate with respect to the full OEP [26].

The obtained EXX energy density per particle is directly related to the exchange enhancement factor through  $\epsilon_x^{\text{EXX}} = \epsilon_x^{\text{3DEG}} \mathcal{F}_x$ . Hence, after calculating both the EXX and LDA results we can visualize the distribution of the enhancement factors with respect to the local bound given in Eq. (8). The procedure is the following. For every coordinate  $\mathbf{r}_i$ , within every molecule, we collect the values  $r_s(\mathbf{r}_i)$ ,  $s(\mathbf{r}_i)$ , and  $\mathcal{F}_x(\mathbf{r}_i)$ , so that we can make a statistical count histogram of  $\mathcal{F}_x$  as a function of  $s$  or  $r_s$ . Figure 1 visualizes the situation as a function of  $s$ . The local LO bound is shown as a horizontal red (dark gray) line, so that all the values *above* the line at  $\mathcal{F}_x > 2.27$  violate the local bound according to Eq. (8). We find significant

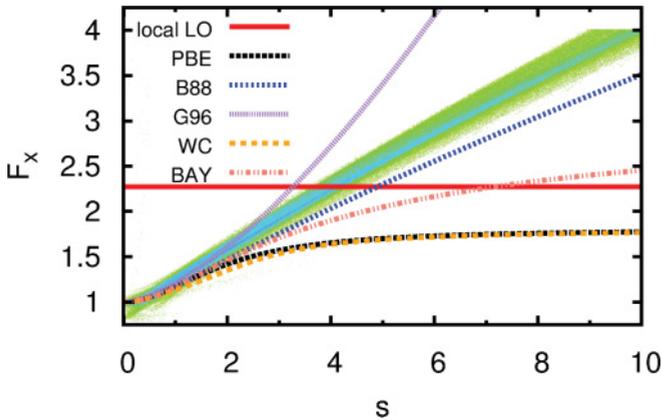


FIG. 1. (Color online) Count histogram of exact enhancement factors for the electronic exchange as a function of the dimensionless gradient in the G2 test set. The results are compared to the enhancement factors of several density functionals. The line shows the local Lieb-Oxford bound that is violated for  $\mathcal{F}_x > 2.27$ .

violation at  $s \gtrsim 3$ . This range of the dimensionless gradient, estimating the ratio of the density variation in the Fermi wavelength scale, corresponds to the tail of the electronic density. The local dependence is studied in more detail below.

In Fig. 1 we also assess the enhancement factors of several popular general density functionals with respect to the EXX results and to the local bound. The functionals include PBE (exchange only), B88, Gill's functional from 1996 [27] (G96), Wu's and Cohen's functional from 2006 [28] (WC), and a Bayesian fit for the enhancement factor by Mortensen and co-workers [29] (BAY). In Fig. 1 we can find a large variance in the behavior of different functionals, especially at large  $s$ , that corresponds to the asymptotic exponential tail of the atomic or molecular charge distribution.

As expected, PBE and WC obey the local bound *by definition*. However, they are relatively far from the histogram of exact results when  $s \gtrsim 2$  and thus miss the correct asymptotic behavior of  $\mathcal{F}_x$ . BAY has a similar trend but follows the EXX to larger values of  $s$ , as it is a Padé fit to experimental atomization energies of a subset of the G2 test set.

Interestingly, B88 performs best of all the tested approximations. This is due to the fact that B88 has a parameter chosen to reproduce the Hartree-Fock exchange energies for atomic systems that are conceptually similar to the G2 test set considered here. B88 also by construction obeys the correct asymptotic behavior of the exchange energy per particle, i.e.,  $\epsilon_x(r) \rightarrow -1/(2r)$  as  $r \rightarrow \infty$ . G96 does not obey this limit and strongly deviates from the EXX results at large  $s$ .

Figure 2 shows the distribution of the EXX enhancement factors as a function of the Wigner-Seitz radius  $r_s$ . The local bound is violated at  $r_s \gtrsim 5$ , corresponding to densities around  $n \lesssim 0.002 \text{ bohr}^{-3}$ . Considering a local version of a recently proposed tighter global bound [14] with  $\lambda = 1.96$  (instead of the LO one) would lead to violation already at  $r_s \sim 4$  ( $n \sim 0.004 \text{ bohr}^{-3}$ ). In any case, the violation clearly seems to occur in the tail of the electronic density, as shown explicitly below.

In Fig. 3 we have a closer look at the enhancement factor as a function of  $s$  for four diatomic molecules including  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{Na}_2$ , and  $\text{Li}_2$ .  $\text{H}_2$  and  $\text{Cl}_2$  violate the local LO bound more

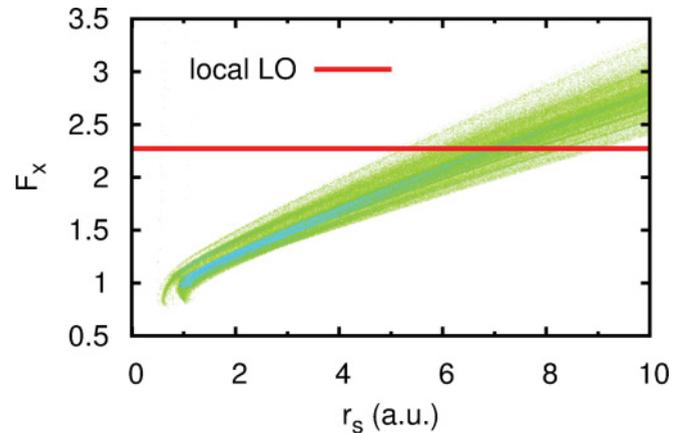


FIG. 2. (Color online) Same as Fig. 1 but as a function of the Wigner-Seitz radius  $r_s = 3^{1/3}(4\pi n)^{-1/3}$ .

rapidly than  $\text{Na}_2$  and  $\text{Li}_2$ . It is interesting to compare these results with the *distance from the global bound* considered by Odashima and Capelle [30]. In their study  $\text{H}_2$  was found to be closest to the global bound with  $\lambda[n] \approx 1.25$ . Therefore the high tendency of  $\text{H}_2$  to violate the local bound in Fig. 3 is plausible and unlikely to be purely accidental, although obviously there is no rigorous implication from the global to local bound, as discussed in Sec. II. In fact, in Ref. [30]  $\text{Li}_2$  and  $\text{Cl}_2$  were found to have  $\lambda[n] \approx 1.21$  and  $1.11$ , respectively, whereas the local bound-breaking tendency is much higher in the latter system (Fig. 3). Therefore, the spatial distribution of  $\mathcal{F}_x$  has an important role, so that there is no clear correlation in the sensitivity of a particular molecule to the global and local bounds. As discussed above, the only rigorous implication is the fact that if the local bound is obeyed (as in PBE), the global bound is obeyed as well.

Finally we give an example of the spatial dependence of the enhancement factor. Figure 4 shows  $\mathcal{F}_x$  along the molecular axis of  $\text{CO}_2$ , plotted together with the density and the dimensionless gradient (in arbitrary units). The arrows mark the position of the atoms. Furthermore, for clarity we removed the points inside the cores of the pseudopotentials.

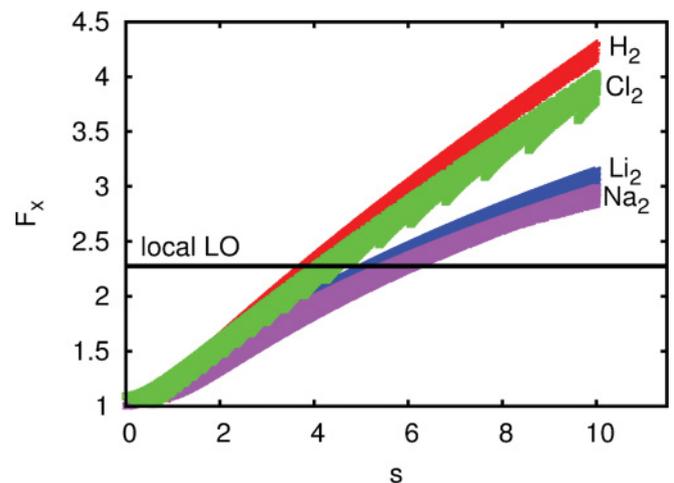


FIG. 3. (Color online) Enhancement factor as a function of the dimensionless gradient  $s$  for four diatomic molecules.

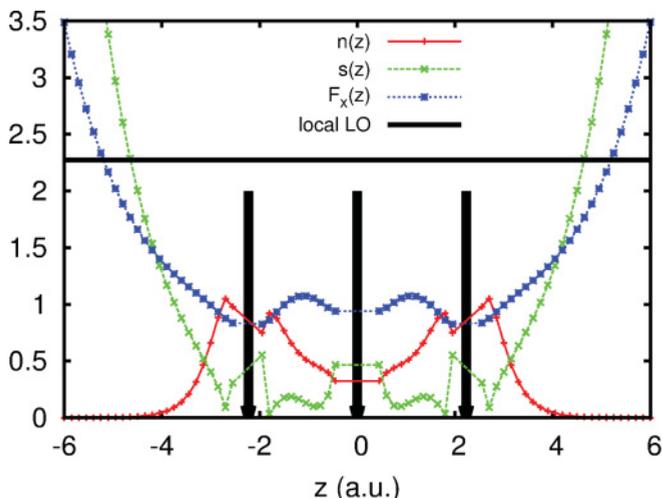


FIG. 4. (Color online) Spatial behavior of the enhancement factor across the molecular axis of  $\text{CO}_2$ . The density  $n$  and dimensionless gradient  $s$  are also shown (in arbitrary units). The arrows mark the position of the atoms.

The figure confirms our statement within Fig. 1 that the local bound is violated in the tail of the electronic density where  $n$  is small and  $s$  is large. Similar spatial behavior was found in all the cases that we checked in this detail.

#### IV. CONCLUSIONS AND OUTLOOK

We have explicitly studied the conceptual difference between the universal Lieb-Oxford bound and its local interpretation used in the development of density functionals. Our molecular examples in the G2 test set demonstrate that the local bound is broadly violated when exact exchange enhancement factors are considered. Therefore the use of the local bound in

the development of functionals, e.g., in generalized-gradient approximations, is questionable, even if the condition is straightforward to implement and the fulfillment of the global Lieb-Oxford bound is guaranteed. In short, the local bound is simply much stricter than has been previously thought.

Our exact-exchange results pinpoint the violation of the local bound to  $s \gtrsim 3$  or  $r_s \gtrsim 5$ , corresponding to the tail of the electronic density. We find no clear correlation between the distance from the global bound and the degree of violation of the local bound; this demonstrates the complexity of the enhancement factor in the tail region throughout the ensemble of molecules.

The surprisingly uniform distribution of the exact enhancement factors in Figs. 1 and 2 suggests a construction of a density functional according to the observed  $\mathcal{F}_x(s)$ . This could be done with a fitting procedure or, better, by tailoring a physically motivated ansatz in the (meta-)generalized-gradient fashion that is able to reproduce the exact  $\mathcal{F}_x(s)$  to a reasonable extent. Such an ability is of particular importance when describing physical properties that depend on the correct description of the tail of the electronic density, e.g., ionization and Rydberg excitations, etc. Within the construction, however, a simultaneous implementation of the *global* Lieb-Oxford bound is a tedious (if not practically impossible) task. These aspects will be studied in detail in our future works.

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