

Testing and using the Lewin-Lieb bounds in density functional theory

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(Dated: December 9, 2014)

Lewin and Lieb have recently proven several new bounds on the exchange-correlation energy that complement the Lieb-Oxford bound. We test these bounds for atoms, for slowly-varying gases, and for Hooke's atom, finding them usually less strict than the Lieb-Oxford bound. However, we also show that, if a generalized gradient approximation (GGA) is to guarantee satisfaction of the new bounds for all densities, new restrictions on the exchange-correlation enhancement factor are implied.

I. INTRODUCTION

The Lieb-Oxford (LO) bound [1] is a cornerstone of exact conditions in modern density functional theory.[2] Rigorously proven for non-relativistic quantum systems, the LO bound provides a strict upper bound on the magnitude of the exchange-correlation energy, E_{xc} , of any system relative to a simple integral over its density. The constant in the LO bound was built into the construction of the PBE generalized gradient approximation[3], one of the most popular approximations in use in density functional theory (DFT) today.[4] The use of the bound to construct approximations remains somewhat controversial, as most systems' E_{xc} does not come close to reaching this bound.[5]

Recently, Lewin and Lieb [6] have proven several alternative forms for the bound that are distinct from the original LO bound. In each, some fraction of the density integral is traded for an integral over a density gradient. Thus, the new bounds are tighter for uniform and slowly varying gases, and could be hoped to be tighter for real systems. If so, they would be more useful than the LO bound in construction and testing of approximate density functionals. We show below that they are not tighter for atoms or for Hooke's atom (two electrons in a parabolic well). However, they do lead to new restrictions on the enhancement factor in GGAs that are constructed to guarantee satisfaction of the bounds for all possible densities.

To begin, the LO bound can be written as

$$E_{xc} \geq -C_{LO} \int d^3r n^{4/3}(\mathbf{r}) \quad (1)$$

where C_{LO} is a constant that Lieb and Oxford[1] showed is no larger than 1.68 (Chan and Handy showed it to be no larger than 1.6358).[7] For simplicity we define the following density integrals:

$$I_0 = \int d^3r n^{4/3}(\mathbf{r}), \quad (2)$$

$$I_1 = \int d^3r |\nabla n(\mathbf{r})|, \quad (3)$$

$$I_2 = \int d^3r |\nabla n^{1/3}(\mathbf{r})|^2. \quad (4)$$

Two new families of bounds are derived by Lewin and Lieb[6]:

$$U_{xc} \geq -C_{LL} I_0 - \alpha I_0 - c_p I_p / \alpha^{k-1}, \quad p = 1, 2 \quad (5)$$

where $C_{LL} = 3(9\pi/2)^{1/3}/5 \approx 1.4508$, $c_1 = 1.206 \times 10^{-3}$, $c_2 = 0.2097$, $k = 5 - p$, and α is any positive number. Here U_{xc} is the potential energy contribution to the exchange-correlation energy.

We can convert these to a family of conditions on E_{xc} with several simple steps. We utilize the adiabatic connection formula[8, 9] in terms of the scaled density:

$$E_{xc} = \int_0^1 d\lambda \lambda U_{xc}[n_{1/\lambda}], \quad (6)$$

where $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$ is the density scaled uniformly[10, 11] by positive constant γ . Examining each of the integrals in the LL bounds, we find

$$I_p[n_\gamma] = \gamma I_p[n], \quad (7)$$

so that applying the bounds to every value of λ between 0 and 1 yields a bound on the DFT exchange-correlation energy directly:

$$E_{xc} \geq -C_{LL} I_0 - \alpha I_0 - c_p I_p / \alpha^{k-1}, \quad p = 1, 2. \quad (8)$$

There is a Faustian dilemma when it comes to the value of α : A very small value makes the first term smaller in magnitude than that of the LO bound, but increases the of the gradient additions. A very large value will make those additions negligible, but also make the first term larger than that of LO bound. Choosing α in each case to maximize the right-hand-side, Lewin and Lieb find

$$E_{xc} \geq -C_{LL} I_0 - \tilde{c}_p I_p^{1/k} I_0^{1-1/k} \quad p = 1, 2 \quad (9)$$

where

$$\tilde{c}_p = \frac{k}{k-1} ((k-1)c_p)^{1/k}. \quad (10)$$

This yields $\tilde{c}_1 = 4(3c_1)^{1/4}/3 \approx 0.3207$ and $\tilde{c}_2 = 3(2c_2)^{1/3}/2 \approx 1.1227$. Lewin and Lieb report a third

bound by combining the $p = 2$ case with the Schwarz inequality:

$$E_{xc} \geq -C_{LL} I_0 - \tilde{c}_3 I_2^{1/8} I_0^{7/8} \quad (11)$$

where $\tilde{c}_3 = ((3^{1/4} c_1)^{2/5})(c_2^{3/5}) \approx 0.7650$. We refer to these as the optimized LL bounds with LL1 and LL2 given by (9) with $p = 1, 2$ respectively. LL3 is given by (11).

II. LEWIN-LIEB BOUNDS FOR SPHERICALLY SYMMETRIC ATOMS

To test each of these bounds, we performed calculations using the non-relativistic atomic OEP code of Engel.[12] We used the PBE functional[3] to find self-consistent atomic densities, and evaluated all I_p . We did this for a simple subset of atoms for which highly accurate correlation energies are available.[13] The results are fully converged with respect to the radial grid. We use accurate E_{xc} from Ref. 14

In Table I, we list the results. We see immediately that, unfortunately, the new bounds are less restrictive than the current LO bound. Atoms have gradients that are sufficiently large as to make the corrections larger than the density-integral term.

Z	E_{xc}	LO	LL1	LL2	LL3	$-C_{ll}I_0$	I_1	I_2
1	-0.3125	-1.200	-1.395	-3.131	-2.159	-1.036	3.978	12.73
2	-1.069	-1.991	-2.318	-4.514	-3.302	-1.719	6.739	10.99
4	-2.758	-5.255	-6.095	-11.19	-8.401	-4.538	16.82	21.26
10	-12.51	-25.01	-28.56	-43.09	-35.35	-21.60	62.18	31.64
12	-16.47	-33.20	-37.83	-56.93	-46.80	-28.67	79.85	40.82
18	-30.97	-63.36	-71.82	-101.2	-85.64	-54.72	139.5	49.76
20	-36.11	-74.16	-83.97	-118.6	-100.3	-64.04	160.4	58.77
30	-71.22	-149.1	-167.6	-220.0	-192.3	-128.8	284.1	68.21
36	-95.79	-201.5	-225.9	-298.8	-256.0	-174.0	365.7	76.26
38	-104.0	-219.2	-245.5	-316.2	-278.9	-189.3	393.2	84.90
48	-151.7	-321.9	-359.3	-446.9	-400.2	-278.0	542.4	92.74
54	-182.2	-388.0	-432.4	-531.7	-478.7	-335.1	635.9	100.6
56	-192.4	-410.1	-456.8	-563.8	-506.9	-354.2	667.1	109.3
70	-281.1	-603.6	-669.6	-799.6	-729.4	-521.3	911.6	117.9
80	-350.5	-755.4	-836.1	-981.7	-902.0	-652.3	1096	124.9
86	-393.0	-848.5	-938.1	-1096	-1009	-732.7	1210	132.5
88	-405.2	-879.3	-972.0	-1139	-1048	-759.3	1246	141.0

TABLE I. Exchange-correlation energies for neutral spherical atoms, bounds, and integrals.

To be sure that *no* atom behaves differently, we examine the large- Z limit, where Thomas-Fermi theory applies.[15, 16] It has recently been shown[14] that

$$E_{xc} \rightarrow -C_x Z^{5/3} - A Z \ln Z + B_{xc} Z + \dots \quad (12)$$

for atoms, where $C_x = 0.2201$, $A = 0.020\dots$, and $B_{xc} \approx 0.039$. The dominant term, which is an exchange contribution, was proven by Schwinger[17], and can be easily

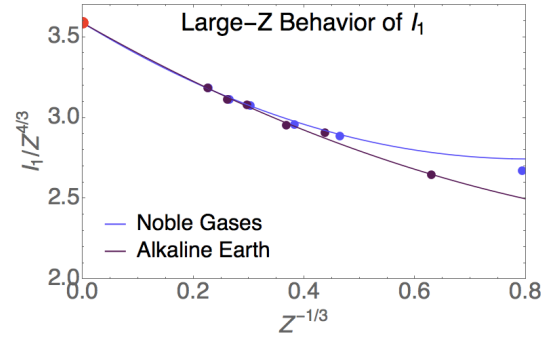


FIG. 1. I_1 (see text) for noble gas and alkaline earth atoms. The red dot indicates the limiting value as $Z \rightarrow \infty$

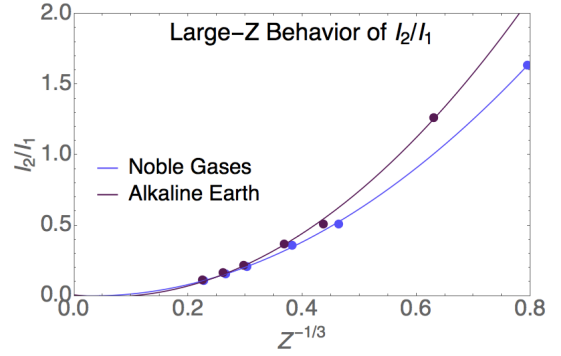


FIG. 2. I_2/I_1 ratio (see text) for noble gas and alkaline earth atoms.

calculated by inserting the TF density[16] into the local approximation for E_x . Since

$$E_x^{\text{LDA}} = -A_x I_0 \quad (13)$$

where $A_x = \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \approx 0.738$, this easily satisfies all bounds, including any LL bound with the gradient terms ignored. In Fig. 1, we plot I_1 as a function of $Z^{-1/3}$, to show that it approaches its large Z limit, which can be extracted from the TF density:

$$I_1[n^{\text{TF}}] = d_1^{\text{TF}} Z^{4/3} \quad (14)$$

where we find $d_1 = 3.58749$. In Fig. 2, we plot the ratio I_2/I_1 , showing that, although I_2 diverges in TF theory (as noted by Lewin and Lieb), it appears to vanish relative to I_1 in this limit. Thus all the additions in the LL bounds become relatively small in this limit, and no change in behavior occurs. As $Z \rightarrow \infty$, the LL1 bound eventually becomes more restrictive than the LO bound, but only at unrealistically [18] large values of Z .

III. HOOKE'S ATOM AND THE SLOWLY-VARYING ELECTRON GAS

We also performed calculations on the model system of two electrons in a harmonic potential, the Hooke's

atom.[19] One might imagine that, for higher or lower densities, the bounds might tighten, or their order reverse, given the different external potential. We report three distinct results. For $k \rightarrow \infty$, where k is the spring constant, the density becomes large, and $E_{\text{XC}} \rightarrow E_{\text{X}}$. All energies and integrals scale as $\omega^{1/2}$, where $\omega = \sqrt{k}$. The first line of Table II shows the results, which are analogous to those of the two-electron ions (with different constants). The order of the bounds remains the same as in Table I. In the next line, we report actual energies for the largest value of k for which there exists an analytic solution, $k = 1/4$. Again we see the same behavior.

The most interesting case is the low-density limit, $k \rightarrow 0$. In this limit, the kinetic energy becomes negligible, and the electrons arrange themselves to minimize the potential energy, on opposite sides of the center. This regime provides a system where correlation energy becomes comparable to exchange energy. The third line of Table II shows that none of the bounds is tight in this limit (the XC energy vanishes relative to any of them) and that the LL bounds diverge relative to the LO bound.

k	scale	E_{xc}	LO	LL1	LL2	LL3
∞	$k^{1/4}$	-1.37	-1.5513	-1.7879	-3.1804	-2.4255
$\frac{1}{4}$	1	-0.554	-1.0031	-1.1558	-2.0682	-1.5740
0	$k^{11/36}$	$-0.0042 k^{1/36}$	-1.85	$-1.6 - \frac{.44}{k^{1/24}}$	$-1.6 - \frac{3.34}{k^{1/6}}$	$-1.6 - \frac{1.8}{k^{19/144}}$

TABLE II. Hooke's atom (two electrons in a harmonic potential) ranging over all values of the spring constant, k .

IV. EFFECTS ON F_{XC}

In the rest of this paper, we show how the LL bounds can be used to derive interesting and new restrictions on the enhancement factor of generalized gradient approximations (GGA's). Begin with the definition of the enhancement factor for a GGA for spin unpolarized systems:

$$E_{\text{XC}}^{\text{GGA}} = \int d^3r e_{\text{X}}^{\text{unif}}(n(\mathbf{r})) F_{\text{XC}}(r_{\text{s}}(\mathbf{r}), s(\mathbf{r})), \quad (15)$$

where $e_{\text{X}}^{\text{unif}}(n) = -A_{\text{X}} n^{4/3}$ is the exchange energy density of a spin-unpolarized uniform gas, $r_{\text{s}} = (3/(4\pi n))^{1/3}$ is the local Wigner-Seitz radius, and $s = |\nabla n|/(2k_{\text{F}}n)$ is the (exchange) dimensionless measure of the gradient, where $k_{\text{F}} = (3\pi^2 n)^{1/3}$ is the local Fermi wavevector. Most famously, the PBE approximation was constructed to ensure it satisfies the LO bound for any density. A sufficient condition to guarantee this is

$$F_{\text{X}}(s) \leq 1.804. \quad (16)$$

Here we digress slightly, to correct a popular misconception in the literature.[20] The LO bound applies to the XC energy. There is no unique choice of XC energy

density, and more than one choice was used in the derivation of PBE.[21] Thus the enhancement factor in PBE should not (and does not) correspond to *any* choice of energy density. No bound has ever been defined, much less proven, for a specific energy density. As others[5] and Table I have shown, real systems do not come close to saturating the LO bound. In fact, the B88 exchange functional does not satisfy Eq. (16) due to the logarithmic dependence on s . But for the present purposes, B88 gives exchange energies almost identical to PBE and very close to exact exchange energies for atoms. While one can design densities that cause B88 to violate the LO bound, they look nothing like densities of real systems.[22]

Now we apply the logic of PBE to the LL bounds. We wish to find conditions on the enhancement factor that guarantee satisfaction of those bounds for all possible densities. In this context, the optimum bounds are not useful, since they contain denominators different from the local term. Dividing each term of Eq. (8) by $e_{\text{X}}^{\text{unif}}$, we find that

$$F_{\text{XC}} \leq \tilde{C}_{\text{LL}} + A_{\text{X}}^{-1}(\alpha + c'_p s^p / \alpha^{k-1}) \quad (17)$$

is a sufficient condition to ensure satisfaction of the LL bounds for any density, with $\tilde{C}_{\text{LL}} = C_{\text{LL}}/A_{\text{X}} = 6(2\pi/3)^{2/3}/5 = 1.9643\dots$, and

$$c'_p = 2(4-p) \left(\frac{\pi}{3}\right)^{2p/3} c_p. \quad (18)$$

We now find the most restrictive value of α for each value of s , to yield

$$F_{\text{XC}} \leq \tilde{C}_{\text{LL}} + \tilde{d}_p s^{p/(5-p)}, \quad (19)$$

where

$$\tilde{d}_p = \frac{k}{k-1} ((k-1)c'_p)^{1/k}. \quad (20)$$

Writing these out explicitly yields

$$F_{\text{XC}} \leq 1.9643 + 2.76755 s^{1/4}, \quad (\text{LL1}) \quad (21)$$

and

$$F_{\text{XC}} \leq 1.9643 + 3.06212 s^{2/3}, \quad (\text{LL2}) \quad (22)$$

in contrast to the LO bound

$$F_{\text{XC}} \leq 2.273. \quad (\text{LO}) \quad (23)$$

In Fig 3, we plot all three bounds and see that for small values of s , the LL2 bound is tighter than the LO bound. We therefore define the new Lieb-Oxford-Lewin (LOL) bound to be the LL2 bound for small s and the old LO bound otherwise. This new bound is more restrictive than the LO bound when s is less than 0.032. The existence of a tighter bound on the enhancement factor for all s has been empirically suggested.[23] We also plot the

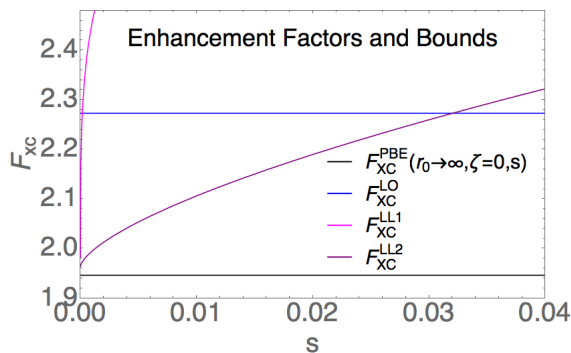


FIG. 3. F_{XC} for LL and LO compared with PBE density for small s .

PBE enhancement factor, showing that it satisfies the LOL bound, but is much closer for small s than the old LO bound.

Spin-polarization is handled different for exchange than for correlation. For exchange-correlation together, it does not raise F_{XC} beyond its maximum for unpolarized systems, as that is achieved in the low-density limit, which is independent of spin. But in the opposite, high-density limit, exchange dominates, and its spin-dependence is determined by the exact spin-scaling relation for exchange:

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}(E_x[2n_\uparrow, 0] + E_x[0, 2n_\downarrow]) \quad (24)$$

which implies

$$F_x^{pol}(s) = 2^{1/3} F_x^{unpol}(s) \quad (25)$$

Thus $F_x^{unpol} < \tilde{C}_{LO}/2^{1/3}$ to ensure F_x^{pol} satisfies the LO bound, which is the origin of Eq. (16).

V. CONCLUSION

In summary, we have tested the optimum LL bounds (which have already been applied to DFT by other groups[24]) for a variety of simple systems, finding they are less restrictive for those systems than the LO bound. However, the LL bounds are clearly more restrictive for a uniform gas, and the family of bounds that the LL bounds come from can be used to place limits on the enhancement factor of GGA's. With this in mind, we constructed the combined LOL bound and we recommend that the LOL bound be used whenever relevant for all future functional development and testing of GGAs.

VI. ACKNOWLEDGEMENTS

We thank Mathieu Lewin and Elliott Lieb for bringing their new bounds to our attention, and Eberhard Engel for developing the OPMKS atom code. This work was supported by NSF under grant CHE-1112442.

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