

Tightened Lieb–Oxford Bound for Systems of Fixed Particle Number

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Abstract: The Lieb–Oxford bound is a constraint upon approximate exchange-correlation functionals. We explore a nonempirical tightening of that bound in both universal and electron number-dependent form. The test functional is PBE. Regarding both atomization energies (slightly worsened) and bond lengths (slightly improved), we find the PBE functional to be remarkably insensitive to the value of the Lieb–Oxford bound. This both rationalizes the use of the original Lieb–Oxford constant in PBE and suggests that enhancement factors more sensitive to sharpened constraints await discovery.

I. Background

$$\lambda_{\text{LO}} = 2.273 \quad (3)$$

Construction of approximate exchange-correlation (XC) functionals in DFT without reliance on empirical data is an important task, both conceptually and practically. Perhaps the most widely used constraint-based approximate XC functional today is the extremely popular Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA).³ One of the constraints on which the PBE GGA XC functional (and some others also) is based is the Lieb–Oxford bound.⁵ In the DFT literature, this bound commonly is expressed as

$$\frac{E_{\text{xc}}[n]}{E_{\text{x}}^{\text{LDA}}[n]} \leq \lambda_{\text{LO}} \quad (1)$$

where

$$E_{\text{x}}^{\text{LDA}}[n] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d^3r n^{4/3}(\mathbf{r}) \quad (2)$$

The LO value for the constant is

The possibility of tightening this bound has been the subject of recurrent interest in DFT. A slightly tighter value $\lambda_{\text{CH}} = 2.215$ was found by Chan and Handy.⁶ Vela⁷ later reported that using a spatially varying implementation of the LO bound, which always is tighter than λ_{LO} , improved the results for a test set of light inorganic and organic molecules calculated using constraint-based GGAs.

Shortly thereafter and independently, two of us (OC hereafter)^{8,9} gave numerical evidence from exact and near-exact calculations on atoms, small molecules, and model systems that the true bound is much tighter. That analysis proceeded by defining the *functional* $\lambda[n]$

$$\lambda[n] = \frac{E_{\text{xc}}[n]}{E_{\text{x}}^{\text{LDA}}[n]} \quad (4)$$

with both numerator and denominator evaluated on the actual density of each system. In general, this functional cannot be evaluated exactly, because neither E_{xc} nor the density is known exactly. However, it can be evaluated to high accuracy for systems for which near-exact XC energies and system densities are known from configuration interaction or quantum Monte Carlo calculations. The result^{8,9} is that

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real systems typically have $\lambda[n] \in (1.1 \dots 1.3)$. The higher end of the interval typically corresponds to more rarefied, diffuse density distributions, while the lower end corresponds to more compact densities. Values above 1.3 were only found for extreme low-density limits of model Hamiltonians: the $k \rightarrow 0$ limit of Hooke's atom has $\lambda[k \rightarrow 0] = 1.489$, and the $r_s \rightarrow \infty$ limit of the homogeneous electron gas has $\lambda[r_s \rightarrow \infty] = 1.9555 := \lambda_{\text{HEG}}$.

On the basis of these results, OC conjectured^{8,9} that further tightening of the LO bound, beyond that obtained by Chan and Handy, can be achieved and suggested that for real systems (excluding unphysical limits of model Hamiltonians) $\lambda_{\text{OC1}} = 1.35$ may provide the tightest upper limit, whereas for arbitrary systems $\lambda_{\text{OC2}} = 2.00 \approx \lambda_{\text{HEG}}$ is the upper limit.

OC also speculated that system-specific upper limits could be found, thereby providing upper limits for all systems sharing some common properties. Earlier, there was other evidence for system-specific limits. Novikov et al.¹⁰ used a reduced κ parameter (defined below) in the PBE XC functional to some benefit. This reduction (see our discussion below) is equivalent to a reduced LO bound. The numerical rationalization for this was published somewhat later by Peltzer y Blanca et al.¹¹ Translating to effective values of λ , broadly they found that 3d metals do better with $\lambda \approx \lambda_{\text{LO}}$, 4d metals benefit from $\lambda \approx 1.81 \rightarrow 1.94$, and 5d metals benefit from $\lambda \approx 1.69 \rightarrow 1.84$. The notable exception was Fe, where the effective λ was 2.8, an illustration of the fact that all the limitations of a specified XC form cannot be corrected by a single parameter fix. (Recently, there has also been a study of reduced κ in the PBE functional but the reduction is done in such a way as to respect the original Lieb–Oxford bound,¹² and is not directly related to the issue at hand.)

Other than this one empirical example, the available data did not allow any general characterization of λ -value classes. Here, we propose and explore a generally applicable, entirely nonempirical way to characterize classes of systems with a common maximum value of $\lambda[n]$. This characterization is based on a rarely mentioned part of the original Lieb–Oxford article, in which they show that tighter estimates of the upper limit on $\lambda[n]$ can be achieved by restricting the λ functional to densities that integrate to a specified particle number N . We therefore introduce the *function* $\lambda(N)$, which for a given value of N provides a universal upper limit upon $\lambda[n]$ valid for all systems such that $\int d^3r n(\mathbf{r}) = N$. The maximum value of $\lambda(N)$, attained for $N \rightarrow \infty$, is the value λ_{LO} used in common density functionals. The function $\lambda(N)$ assigns to each class of systems of common particle number an upper limit $\lambda(N) \leq \lambda_{\text{LO}}$.

In construction of constraint-based functionals, the fact that the upper limit can be tightened universally (from λ_{LO} to λ_{CH} and perhaps on to λ_{OC2}) or in a system-specific way (e.g., using $\lambda(N)$) has not been taken into account, and the consequences of a replacement of λ_{LO} by one of the lower values in currently popular functionals are unknown. We study some of those consequences here.

II. Construction of a Particle-Number-Dependent Bound

To explore the system-specific bound provided by the function $\lambda(N)$ requires facing the problem that, while Lieb and Oxford proved the existence of this function and deduced some of its properties, they did not obtain a closed analytical expression for all N . We thus propose a simple approximation to $\lambda(N)$, compatible with all known information on the universal LO bound. The following facts are known about $\lambda(N)$:^{5,8,9}

- (i) Its value at $N = 1$ is $\lambda(N = 1) = 1.48 := \lambda_1$.
- (ii) Its value at $N = 2$ is not known, but is above $\lambda_{\text{min}}(N = 2) = 1.67$.
- (iii) The function $\lambda(N)$ is monotonic, that is, $\lambda(N + 1) \geq \lambda(N)$.
- (iv) Its value at $N = \infty$ is not known, but must be less than or equal to $\lambda_{\text{max}}(N \rightarrow \infty) := \lambda_{\infty}$. Different proposals for the value of λ_{∞} are $\lambda_{\text{LO}} = 2.273$, $\lambda_{\text{CH}} = 2.215$, and $\lambda_{\text{OC2}} = 2.00 \approx \lambda_{\text{HEG}}$.
- (v) The largest value of $\lambda[n]$ found for any system studied specifically is that for the extreme low-density limit of the homogeneous electron gas $\lambda_{\text{HEG}}(r_s \rightarrow \infty) = 1.9555$. For real physical systems, $\lambda[n]$ typically ≤ 1.3 . These values provide empirical lower bounds on the function $\lambda(N)$.

Note that standard density functionals either do not make use of the Lieb–Oxford bound at all (and some can violate it)^{13–16} or exploit only property (iv), normally with the weakest value for λ_{∞} , namely λ_{LO} . To construct a model for the function $\lambda(N)$, we exploit properties (i) (value at $N = 1$), (iii) (monotonicity), and (iv) (value at $N \rightarrow \infty$). We use properties (ii) (theoretical lower limit at $N = 2$) and (v) ($\lambda[n]$ for model and real systems) as consistency tests for the construction. With all this in mind, we propose the simple interpolation:

$$\lambda(N) = \left(1 - \frac{1}{N}\right)\lambda_{\infty} + \frac{\lambda_1}{N} \quad (5)$$

where λ_{∞} is λ_{LO} , λ_{CH} , or λ_{OC2} . By construction this interpolation obeys properties (i), (iii), and (iv). Direct inspection shows that it also respects properties (ii) and (v).

Figure 1 illustrates this function for the three different choices of λ_{∞} and compares it to the known value at $N = 1$, the lower limit at $N = 2$, and some representative data for atoms, molecules, and the homogeneous electron gas.

We note that the function $\lambda(N)$ is a global multiplicative factor and as such can be applied in the context of both the global and the local LO bound. As PBE makes use of the local form,¹⁶ we here explore consequences of the N -dependence of λ in this context, but as a matter of principle, the issue of tightening the bound and/or making it N -dependent applies to the global bound as well.

III. Implementation and Computational Protocols

A. Modification of PBE GGA. To explore these ideas, we implemented the various possible replacements of λ_{LO} in the PBE GGA. At the outset, we remark that, on the basis

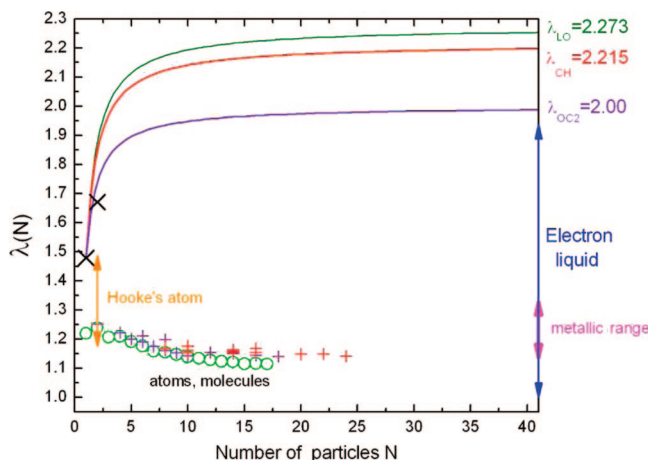


Figure 1. Interpolation function $\lambda(N)$ for three different choices of λ_∞ , compared to known theoretical results and empirical data. Black crosses represent the exact value at $N = 1$ and the lower bound at $N = 2$. Values at $N \rightarrow \infty$ are indicated on the right vertical axis. The three continuous curves are our interpolation (eq 5) using the three alternative choices for λ_∞ . All other data represent ranges or values for selected real systems, providing empirical lower bounds.

of previous experience with the revPBE functional,¹⁶ we expect that lowering λ in PBE will have a detrimental effect on atomic total energies. (In revPBE, an *increase* of λ was shown to improve atomic total energies and molecular atomization energies, at the expense of worsened bond lengths.)

Since the actual values of $\lambda[n]$ for physical systems are known to fall far below λ_{LO} , and the theoretical information available from the CH numerical tightening and from the function $\lambda(N)$ both indicate that lower values of λ are appropriate, this detrimental effect must be considered a severe shortcoming of the GGA. An important issue of energetics, therefore, is whether the atomization energies are improved when tightened LO bounds are used in a GGA. Further investigation is needed to see if meta-GGA functionals⁴ suffer from the same problem, but that is beyond the scope of this study. Because the quality of predicted equilibrium energies and system geometries is the first prerequisite for any generally useful approximate XC functional, the effects of tightening the LO bound upon Kohn–Sham orbitals (e.g., their utility as frontier orbitals) and eigenvalues also will be considered separately.

In any event, there are five possibilities for tightening, pertaining to two categories. Category I is a simple replacement of the constant value λ_{LO} by the alternative lower constants λ_{CH} or λ_{OC2} . Category II replaces the constant by the function $\lambda(N)$, with the three possible choices for λ_∞ . The resulting five choices are to be compared to the original choice λ_{LO} , made in the construction of PBE.

In the original PBE GGA, the LO bound is enforced locally (but not pointwise) through the choice of the parameter κ in the exchange enhancement factor:

$$F_x^{\text{PBE}} := 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa} \quad (6)$$

with the dimensionless reduced gradient given by:

$$s(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla n(\mathbf{r})|}{n(\mathbf{r})^{4/3}} \quad (7)$$

Taking spin-polarization into account, satisfaction of eq 2 by the enhancement factor in eq 6 for all densities (a sufficient condition) is equivalent to

$$F_x[n, s] \leq \frac{\lambda_{LO}}{2^{1/3}} = 1.804 \quad (8)$$

Since $\lim_{s \rightarrow \infty} F_x[n, s] = 1 + \kappa$, the result is

$$\kappa_{\text{PBE}} = 0.804 \quad (9)$$

Of course, the simple choice of a different universal bound leads to

$$\kappa(\lambda_\infty) = \frac{\lambda_\infty}{2^{1/3}} - 1 \quad (10)$$

The equivalent modification to include the N -dependent LO bound (eq 5) is

$$\kappa(N, \lambda_\infty) = \frac{\lambda(N, \lambda_\infty)}{2^{1/3}} - 1 \quad (11)$$

The result of considering such altered LO bounds is five variants of the PBE exchange functional:

PBE(λ_{CH}): PBE96 exchange but with $\lambda_\infty = \lambda_{CH} = 2.215$.

PBE(λ_{OC2}): PBE96 exchange but with $\lambda_\infty = \lambda_{OC2} = 2.00$.

PBE($\lambda_{LO}(N)$): PBE96 exchange but with $\lambda(N, \lambda_\infty)$ and $\lambda_\infty = \lambda_{LO} = 2.273$.

PBE($\lambda_{CH}(N)$): PBE96 exchange but with $\lambda(N, \lambda_\infty)$ and $\lambda_\infty = \lambda_{CH} = 2.215$.

PBE($\lambda_{OC2}(N)$): PBE96 exchange but with $\lambda(N, \lambda_\infty)$ and $\lambda_\infty = \lambda_{OC2} = 2.00$.

The first two, along with the original PBE = PBE(λ_{LO}), comprise category I, the latter three, category II. We denote the six variants collectively as PBE(λ) in what follows.

It is important for clarity of interpretation of our results to note that the five new variants alter *only* the value of the LO bound that is enforced and *not* the way in which the bound is enforced. In both original PBE and our variations, the bound is enforced locally as a sufficient condition. Whether global enforcement is better is a distinct question not considered here. Note also that, just as with original PBE, while the enforcement is local it is not pointwise (we do not have $\lambda(\mathbf{r})$).

B. Protocols. All five variants were introduced in the code deMon2k, development version 2.4.2,¹⁷ by systematic modification of the exchange–correlation modules. Subsequently, the implementation was validated by comparison of atomic calculations done with hard-coded modifications of the code soatom.f.¹⁸ Throughout, we used the full PBE correlation functional, not the deMon cutoff version (i.e., we used the deMon2k “PBESSF” option), for all PBE(λ). Because deMon2k uses variational Coulombic fitting, there is a choice of density fitting (auxiliary) basis sets and of the method for evaluating XC matrix elements. Initially, we used the so-called A2 density fitting basis (deMon2k option “AUXIS(2)”) and the option to do the numerical integrals for the XC

Table 1. Comparison of Effects of Various Lieb–Oxford Bounds in the PBE Exchange Functional for the Li_2 Molecule^a

functional	E_{atom}	E_{Li_2}	ΔE	R_e
PBE(λ_{LO})	−7.460992748	−14.953949056	20.06	2.7236
PBE(λ_{CH})	−7.457436406	−14.946932892	20.01	2.7218
PBE(λ_{OC2})	−7.441633876	−14.915640294	20.31	2.7155
PBE($\lambda_{\text{LO}}(N)$)	−7.442385785	−14.937217688	32.91	2.7196
PBE($\lambda_{\text{CH}}(N)$)	−7.439006265	−14.930264047	32.79	2.7181
PBE($\lambda_{\text{OC2}}(N)$)	−7.424518016	−14.899876726	31.90	2.7131

^a See text for notation about functionals. E_{atom} and E_{Li_2} are total energies in hartrees. ΔE is the total atomization energy in kilocalories per mole, and R_e is the equilibrium bond length in angstroms.

Table 2. Values of the PBE Exchange Functional Parameter $\kappa(N, \lambda_{\infty})$ for the PBE(λ) Functionals for $N = 3$ (Li Atom) and $N = 6$ (Li_2 Molecule)

functional	$\kappa(3, \lambda_{\infty})$	$\kappa(6, \lambda_{\infty})$
PBE(λ_{LO})	0.804319	0.804319
PBE(λ_{CH})	0.757967	0.757967
PBE(λ_{OC2})	0.587401	0.587401
PBE($\lambda_{\text{LO}}(N)$)	0.594439	0.699379
PBE($\lambda_{\text{CH}}(N)$)	0.563537	0.660752
PBE($\lambda_{\text{OC2}}(N)$)	0.449826	0.518614

quantities using the fitted (auxiliary) density (deMon2k “AUXIS” option). We return to these options below.

For development of a suitable protocol (Kohn–Sham basis, fitting basis) we first studied the Li_2 molecule in a triple- ζ -plus-polarization (TZVP) KS basis. The results are in Table 1. Note that ΔE is the total atomization energy, $2E_{\text{Li,atom}} - E_{\text{Li}_2}$ (not the cohesive energy per atom). Regarding the quality of the calculation, observe that for the unmodified PBE functional, our results are almost identical with those given by Ernzerhof and Scuseria,¹⁹ $\Delta E = 20$ kcal/mol, $R_e = 2.727$ Å. (For reference, they quote experimental values as 26 kcal/mol and 2.673 Å.)

As would be expected from naïve use of a particle-number-dependent model, the results in Table 1 show a clear size-inconsistency problem, signaled by the big shift in ΔE between the N -independent models, PBE(λ), and the N -dependent models, PBE($\lambda(N)$). The fact that there is no such

Table 4. O and O_2 (Triplet) Total Energies (E_{H}), Molecular Atomization Energy (kcal/mol), and Equilibrium Bond Length (Å) for the Ordinary PBE XC Functional As Calculated in deMon2k, TZVP Basis (“deMon-TZVP”); Gaussian 03, 6311+G(3df,2p) Basis (Ref 19 “ES”); ACES-II, aug-cc-PVTZ (Ref 25 “AP”); and deMon2k, aug-cc-PVTZ Basis (“deMon-aug”)

calcd	$E_{\text{tot,O}}$	$E_{\text{tot,O}_2}$	ΔE	R_e
deMon-TZVP	−75.00612438	−150.23282532	138.4	1.23491
ES			143	1.217
AP	−75.00773627	−150.24372619	143.2	1.21996
deMon-aug	−75.00781596	−150.24387554	143.2	1.22008

shift in the R_e values is a clear sign that the problem is in the comparison with the isolated atom. Equation 11 illustrates the point. In a naïve application of the N -dependent models, the Li atom has $\lambda(3, \lambda_{\infty})$ while the Li_2 molecule has $\lambda(6, \lambda_{\infty})$ (with the three choices of λ_{∞}). The result is a separated atom limit of the diatomic molecule which is not the same as the isolated atom. Table 2 shows the very substantial difference in the PBE parameter κ for these two situations.

Table 3 shows how a size-consistent set of parameters, here for $N = 6$, resolves the problem. (For clarity, note that we made the common choice throughout all these calculations and ignored the DFT spin-symmetry problem. Thus, the separated atoms are spin-polarized even though the molecule has multiplicity of one.) Throughout this study, we used this same size-consistent procedure, namely applying to the separated atoms the modified LO constants proper for the value of N of the aggregated system (molecule) in question. For heteronuclear molecules, especially hydrides, this protocol results in a rather disparate enforcement of the LO bound for atoms of substantially different N , a matter for later study and refinement. (We note that the use of the original PBE functional implies the most disparate enforcement of all, as it amounts to using the largest $N \rightarrow \infty$ value of λ for all finite N .)

Table 3 also compares the effect of the two different options in deMon2k for evaluation of the XC matrix elements. First is the deMon A2 density fitting basis (deMon2k option “AUXIS(2)”) and the aforementioned deMon2k option (“AUXIS”) for evaluation of XC quantities

Table 3. Comparison of Effects of Various Lieb–Oxford Bounds in the PBE Exchange Functional for the Li_2 Molecule^a

functional	E_{atom}	E_{Li_2}	ΔE	R_e
PBE(λ_{LO})	−7.460992748	−14.953949056	20.06	2.7236
PBE(λ_{CH})	−7.457436406	−14.946932892	20.01	2.7218
PBE(λ_{OC2})	−7.441633876	−14.915640294	20.31	2.7155
PBE($\lambda_{\text{LO}}(N)$)	−7.452520577	−14.937217688	20.19	2.7196
PBE($\lambda_{\text{CH}}(N)$)	−7.449007723	−14.930264047	20.24	2.7181
PBE($\lambda_{\text{OC2}}(N)$)	−7.433703689	−14.899876726	20.37	2.7131
PBE(λ_{LO})	−7.460613173	−14.953310471	20.13	2.7304
PBE(λ_{CH})	−7.457076546	−14.946319641	20.18	2.7277
PBE(λ_{OC2})	−7.441303732	−14.915029100	20.34	2.7181
PBE($\lambda_{\text{LO}}(N)$)	−7.452179554	−14.936623118	20.25	2.7244
PBE($\lambda_{\text{CH}}(N)$)	−7.448674591	−14.929672255	20.28	2.7222
PBE($\lambda_{\text{OC2}}(N)$)	−7.433359029	−14.899212818	20.39	2.7143
reference values ^{20–23}	−7.47806	−14.9938	26	2.673

^a N -dependent functionals done with $N = 6$ size-consistent parameters. TZVP KS basis. Upper set is the A2 fitting basis with AUXIS XC evaluation option, lower set is GEN-A2 and BASIS option. See text for details as well as notation for functionals. E_{atom} and E_{Li_2} are total energies in hartrees. ΔE is the total atomization energy in kilocalories per mole. R_e is the equilibrium bond length in angstroms.

Table 5. As in Table 3 but for Triplet O₂ and for Two Different Basis Sets TZVP/GEN-A2 (Upper Set), aug-cc-PVTZ/GEN-A2* (Lower Set)

functional	E_{atom}	E_{O_2}	ΔE	R_e
PBE(λ_{LO})	-75.00612438	-150.23282532	138.4	1.2349
PBE(λ_{CH})	-74.99689680	-150.21624772	139.6	1.2343
PBE(λ_{OC2})	-74.95432779	-150.13915494	144.6	1.2315
PBE($\lambda_{\text{LO}}(M)$)	-74.99835094	-150.21886346	139.4	1.2344
PBE($\lambda_{\text{CH}}(M)$)	-74.98900193	-150.20202494	140.6	1.2338
PBE($\lambda_{\text{OC2}}(M)$)	-74.94639261	-150.12467907	145.5	1.2310
PBE(λ_{LO})	-75.00781596	-150.24387554	143.2	1.2201
PBE(λ_{CH})	-74.99853463	-150.22722985	144.4	1.2195
PBE(λ_{OC2})	-74.95571887	-150.14986185	149.6	1.2167
PBE($\lambda_{\text{LO}}(M)$)	-74.99998015	-150.22985618	144.3	1.2196
PBE($\lambda_{\text{CH}}(M)$)	-74.99059055	-150.21295118	145.4	1.2189
PBE($\lambda_{\text{OC2}}(M)$)	-74.94774275	-150.13534295	150.5	1.2162
reference values ^{20–23}	-75.0674	-150.2770	118	1.208

Table 6. Comparison of Effects of Various Lieb–Oxford Bounds in the PBE Exchange Functional upon the Atomization Energies (kcal/mol) of Various Small Molecules

species	2S + 1	PBE(λ_{LO})	PBE(λ_{CH})	PBE(λ_{OC2})	PBE($\lambda_{\text{LO}}(M)$)	PBE($\lambda_{\text{CH}}(M)$)	PBE($\lambda_{\text{OC2}}(M)$)	expt ²²
Li ₂	1	20.13	20.18	20.34	20.25	20.28	20.39	26
Be ₂	1	9.71	9.95	10.94	10.12	10.35	11.28	2.3
B ₂	3	76.7	77.3	80.1	77.6	78.2	80.8	71.3
C ₂	1	142.3	143.4	147.9	143.6	144.6	148.9	146
N ₂	1	235.5	236.7	241.7	236.7	237.9	242.6	227
O ₂	3	138.4	139.6	144.6	139.4	140.6	145.5	118
F ₂	1	51.56	52.46	56.30	52.23	53.12	56.90	38
Ne ₂	1	0.1279	0.1438	0.2236	0.1385	0.1549	0.2369	0.0839
Ar ₂	1	0.1377	0.1631	0.2998	0.1462	0.1732	0.3122	0.2846
HF	1	142.645	143.161	145.401	143.356	143.864	146.037	142
LiH	1	54.53	54.54	54.57	54.57	54.57	54.54	58
OH	2	110.361	110.762	112.458	110.976	111.365	112.981	107
NH	3	88.95	89.18	90.07	89.34	89.55	90.36	88
NiH	2	74.05	75.05	76.63	74.86	75.21	76.79	58.8
H ₂ O	1	235.9	236.8	240.5	237.1	237.9	241.5	235
NH ₃	1	305.686	306.664	310.761	307.029	307.976	311.882	297
CH ₄	1	427.184	428.245	432.736	428.641	429.673	433.983	420
C ₆ H ₆	1	1423.74	1430.39	1458.48	1425.84	1432.45	1460.30	1362

using the fitted (auxiliary) density on a numerical grid. Second is the richer GEN-A2 fitting basis and evaluation of the XC quantities from the density formed straightforwardly from the KS orbitals also on the numerical grid (“BASIS” option). In principle, the latter procedure is the more accurate and is the one we adopted. Nevertheless, the trends in the PBE(λ) series are essentially the same in the less-accurate procedure.

Our other exploratory test was the O₂ molecule, a triplet ground-state system. The TZVP PBE atomization energy (see the first two lines of Table 4) is about 3% off from the published result of Ernzerhof and Scuseria,¹⁹ who used the substantially richer basis 6311+G(3df,2p). An ACES-II²⁴ calculation using another rich basis (aug-cc-PVTZ) matched the deMon2k results with that same KS basis and the richer density-fitting basis (“GEN-A2*” option). These results, in the third and fourth lines of Table 4, calibrate the effects of basis set differences. Results for the PBE(λ) series in the aug-cc-PVTZ/GEN-A2* basis sets also are in Table 5. The relative shifts among the six PBE variants are the same irrespective of basis sets, but the richer basis sets make the atomization energies larger and bond lengths slightly shorter. Ernzerhof and Scuseria¹⁹ quote the experimental data as $\Delta E = 118$ kcal/mol and $R_e = 1.208$ Å. Thus, all six PBE variants

(original plus five new) give too deep a binding energy at slightly elongated bond lengths.

The preceding discussion makes clear that systematic comparison of the six PBE variants generally does not require a fully saturated basis set. Rare gas dimers, discussed below, are an exception. Therefore, except for rare gas dimers, we adopted the following protocol: (i) use TZVP for the KS basis, (ii) use GEN-A2 or GEN-A3 algorithms to generate the fitting-function basis (and thereby minimize the effect of the variational Coulombic fitting, which gives a lower bound to the Coulombic repulsion that can be deceptive with a poorly chosen fitting basis), and (iii) use the deMon2k BASIS option for evaluation of the XC matrix elements. This protocol combines a reasonably rich KS basis with an abundance of caution in treating the XC quantities.

For the rare gas dimers, test calculations on Ar₂ with both a DZVP and a 6-311++G(3df,3pd) KS basis set demonstrated that these do not reproduce known, large-basis PBE results for this dimer.^{26,27} Since those two calculations were completely independent and gave essentially identical values, $\Delta E = 0.138$ kcal/mol, $R_e = 4.00$ Å, it is essential to reproduce them. Therefore, we shifted to the aug-cc-pVTZ KS basis,²⁸ as used by Zhao and Truhlar, and the deMon2k GEN-A3 fitting function basis. This combination gives the

Table 7. Comparison of Effects of Various Lieb–Oxford Bounds in the PBE Exchange Functional upon the Bond Lengths (Å) and Bond Angles (deg) of Various Small Molecules^a

species	PBE(λ_{LO})	PBE(λ_{CH})	PBE(λ_{OC2})	PBE($\lambda_{LO}(N)$)	PBE($\lambda_{CH}(N)$)	PBE($\lambda_{OC2}(N)$)	expt ²³
Li ₂	2.7304	2.7277	2.7181	2.7244	2.7222	2.7143	2.673
Be ₂	2.4409	2.4379	2.4259	2.4355	2.4328	2.4218	2.45
B ₂	1.6208	1.6198	1.6159	1.6194	1.6185	1.6148	1.590
C ₂	1.2595	1.2590	1.2567	1.2590	1.2584	1.2562	1.243
N ₂	1.1112	1.1108	1.1091	1.1108	1.1104	1.1087	1.098
O ₂	1.2349	1.2343	1.2315	1.2344	1.2338	1.2310	1.208
F ₂	1.4301	1.4290	1.4242	1.4293	1.4282	1.4235	1.412
Ne ₂	3.0808	3.0418	2.8709	3.0546	3.0162	2.8550	3.091
Ar ₂	3.99907	3.9124	3.6964	3.9469	3.8929	3.6841	3.7565
HF	0.9385	0.9385	0.9385	0.9385	0.9385	0.9385	0.917
LiH	1.6065	1.6058	1.6029	1.6039	1.6033	1.6012	1.595
OH	0.9899	0.9899	0.9898	0.9899	0.9899	0.9897	0.971
NH	1.0549	1.0549	1.0548	1.0549	1.0549	1.0548	1.036
NiH	1.4580	1.4594	1.4553	1.4599	1.4590	1.4549	1.477
H ₂ O, R	0.9750	0.9749	0.9747	0.9749	0.9749	0.9746	0.959
H ₂ O, θ	104.21	104.24	104.39	104.25	104.29	104.43	103.9
NH ₃ , R	1.0252	1.0252	1.0245	1.0250	1.0249	1.0244	1.012
NH ₃ , θ	106.40	106.44	106.62	106.45	106.49	106.67	106.7
CH ₄	1.0990	1.0989	1.0984	1.0988	1.0987	1.0982	1.086
C ₆ H ₆ , R _{CC}	1.3995	1.3990	1.3965	1.3994	1.3988	1.3963	1.397
C ₆ H ₆ , R _{CH}	1.0947	1.0946	1.0943	1.0947	1.0946	1.0943	1.084

^a The NH₃ bond angle is θ_{HNNH} . See text for notation about functionals. CH₄ was done with T_d symmetry enforced.

same PBE results as the foregoing two references. We treated Ne₂ with the corresponding aug-cc-pVTZ KS basis and GEN-A3 fitting function basis.

IV. Results and Discussion

For PBE(λ), Table 6 gives the atomization energies for 18 light molecules, while Table 7 gives bond lengths and bond angles for those same systems. (As a technical aside, note that NiH is a difficult system to treat.) Absolute relative errors in the atomization energy are shown in Figure 2, and the corresponding bond length data are in Figure 3.

Several features stand out from these results. With a few exceptions, the general pattern is that both atomization energies and bond lengths are remarkably insensitive to changes in the enforcement of the LO bound. This outcome is consistent with what one might have inferred from Figure 1. The $\lambda(N)$ that we are justified in using (in the sense that our interpolation respects the known constraints) is substantially larger than the λ values imputed for actual molecules. Thus, one might conclude that a more refined way of implementing the LO bound in a GGA is needed.

However, two systems, Ne₂ and Ar₂, are notably sensitive to the value of λ in the atomization energies. Be₂ is somewhat similar in sensitivity. A coherent interpretation by classes of molecules is possible: unlike the other atoms, Ne and Ar are closed-shell atoms and the Be atom is similar in having $l = 0$ symmetry. Thus, we may suspect that the well-known peculiarities of closed-shell interactions are the source of the distinct behavior. (We do not venture any remarks on the validity and limitations of GGA XC functionals for such molecules.) For the equilibrium bond lengths, Ne₂ and Ar₂ still stand out from all other systems by being most sensitive to changes in λ (Figure 3). However, the classification of Be₂ with Ne₂ and Ar₂ is at least consistent in that the Be₂ bond-length variation is at odds with all the other open-shell systems. The behavior of Be₂ does not seem to be traceable to being from the rapidly varying part of the $\lambda(N)$ function,

since Li₂ is in that region also and it is insensitive in both bond length and atomization energy.

To display the effects of imposition of the size-consistent molecular N values on the LO bounds in atoms, we also calculated some isolated atom total energies at their intrinsic $N = Z$ values. For H, C, N, O, and F, Table 8 displays the results for the intrinsic value versus the results for the highest N molecule in which each element was used in the present study. As would be expected from the interpolation in eq 5 and the constraints on which it is based, the total energy of the H atom exhibits the largest percentage variation between intrinsic and molecular values for the three N -dependent variants PBE($\lambda(N)$).

V. Concluding Remarks

Our results show that PBE is rather insensitive to changes in λ for covalently and ionically bound small molecules when measured by atomization energies and bond lengths. The total energies are notably more sensitive, presumably because of the large s contributions from the density tails. Overall, a reduced, and thus, in principle, better, value of λ produces slightly worsened energies and slightly improved bond lengths. This insensitivity explains why PBE can be successful even though it uses the λ_∞ value even for small N . In this sense, the present study provides additional insight into the success of PBE for small systems. On the other hand, a suitably designed, constraint-based functional should give improved results when the constraints it incorporates are sharpened. The failure of PBE to meet this expectation must be considered a limitation of the PBE functional form.

In the case of the closed-shell systems, we find a more pronounced λ dependence than in the covalent and ionic systems. Because of the delicate nature of binding in these systems, more detailed investigation would be needed to make conclusive statements. In the spirit of the preceding paragraph, it would appear to be more productive to focus

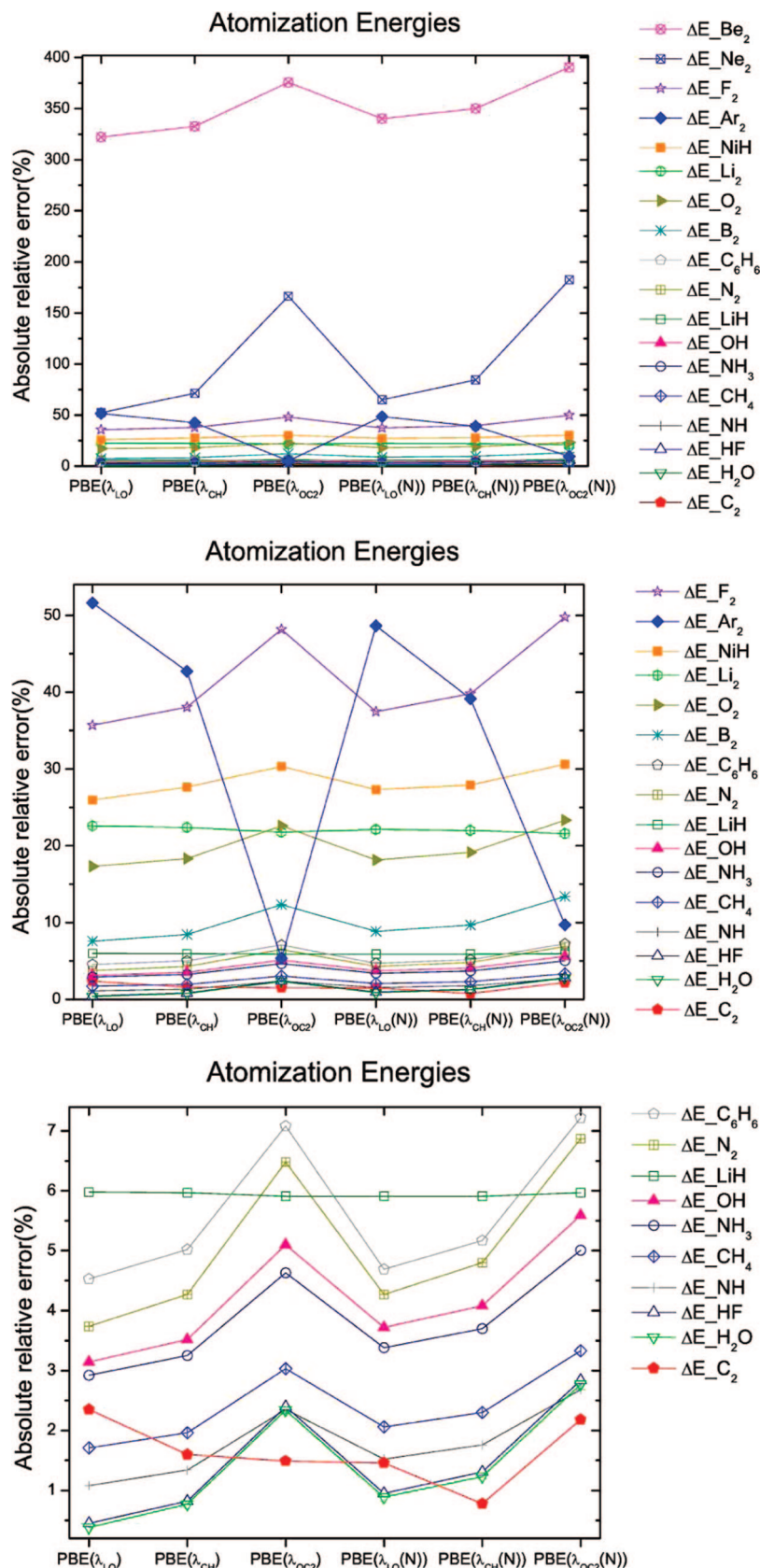


Figure 2. Top panel: Absolute relative errors in atomization energies for all 18 molecules for original PBE and the five variants. Middle panel: As in the upper panel but with the worst two cases (Be_2 , Ne_2) removed to allow a finer scale. Bottom panel: As in the middle panel but with the worst six cases of that panel (F_2 , Ar_2 , NiH , Li_2 , O_2 , B_2) removed to allow a finer scale.

on developing enhancement factors that are more sensitive to sharpening of constraints.

An appealing thought is that the insensitivity found here may also have to do with the way that the LO bound is

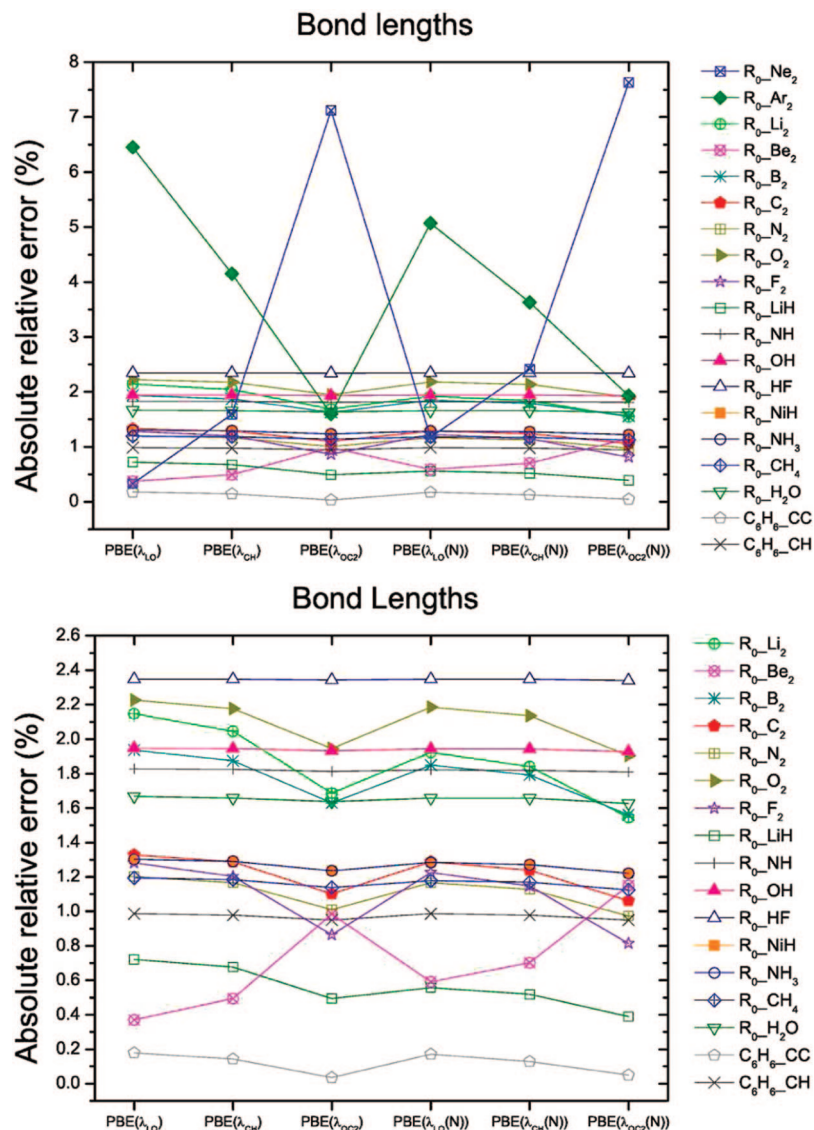


Figure 3. Upper panel: Absolute relative errors in bond lengths for all 18 molecules for the original PBE and the five variants. Lower panel: As in the upper panel but with the two most sensitive cases (Ar_2 , Ne_2) removed to allow a finer scale.

Table 8. Total Energies (Hartree au) for Five Chemically Important Atoms from Various Lieb–Oxford Bounds in the PBE Exchange Functional^a

XC	H	C	N	O	F
PBE(λ_{LO})	−0.498147969	−37.794851185	−54.530389203	−75.006124382	−99.664580137
PBE(λ_{CH})	−0.497515476	−37.787528107	−54.522145702	−74.996896796	−99.654626939
PBE(λ_{OC2})	−0.494726517	−37.754129975	−54.484419695	−74.954327792	−99.608420218
PBE($\lambda_{\text{LO}}(N)$) (intrinsic N)	−0.481206885	−37.777286824	−54.513676785	−74.989918352	−99.649171204
PBE($\lambda_{\text{LO}}(N)$) (highest N)	−0.497950959	−37.792580522	−54.52240237	−74.99835094	−99.65716700
PBE($\lambda_{\text{CH}}(N)$) (intrinsic N)	−0.481206885	−37.769885027	−54.505322010	−74.980521867	−99.639010126
PBE($\lambda_{\text{CH}}(N)$) (highest N)	−0.497316032	−37.785199634	−54.51406717	−74.98900193	−99.64707222
PBE($\lambda_{\text{OC2}}(N)$) (intrinsic N)	−0.481206885	−37.736869483	−54.467831152	−74.937949507	−99.592621018
PBE($\lambda_{\text{OC2}}(N)$) (highest N)	−0.494539297	−37.751826019	−54.47640949	−74.94639261	−99.60074422
exact ²⁰	−0.5	−37.8450	−54.5893	−75.0674	−99.7341

^a Results for the N -dependent functionals are given both for the values of N intrinsic to the specific atom and for the highest molecular N used: 42 for H, 42 for C, 14 for N, 16 for O, 18 for F.

implemented in DFT in general. The original LO bound is for the Coulombic exchange and correlation energy W_{xc} and

does not include the correlation kinetic energy, $T_{\text{c}} = T - T_{\text{s}} \geq 0$, which contributes to E_{xc} . As a result, $E_{\text{xc}} \geq W_{\text{xc}}$ and

the functional $\lambda[n] = E_{xc}[n]/E_x^{LDA}[n]$ which was evaluated in refs 8 and 9 is smaller than the functional

$$\lambda_w[n] = \frac{W_{xc}[n]}{E_x^{LDA}[n]} \quad (12)$$

If the effect of T_c were large enough, it might explain at least part of the large difference between the values of $\lambda[n]$ and $\lambda(N)$ in Figure 1. What limited numerical evidence we have, however, suggests that $\lambda_w[n]$ is only about 10% larger than $\lambda[n]$, a very modest shift compared to the difference in Figure 1.

The more general point, however, that the LO bound is a constraint on exchange and correlation together, seems to be sustained by our findings, in that the PBE form enforces the bound purely on exchange. One speculation is that the insensitivity found here is in part a consequence of that restricted use of the LO bound.

Finally, we consider aspects of N -dependence and chemical classification for enforcement of the LO bound. The first insight is that, in retrospect, N -dependent satisfaction of the LO bound actually arose very early in DFT, before the LO proof. In Slater's $X\alpha$ model, E_{xc} is modeled by scaling E_x^{LDA} . (From a modern perspective, $X\alpha$ is a one-parameter XC model that gains simplicity at the cost of violating correct scaling for C.) The α -parameter is N -dependent²⁹ and exhibits very clear shell structure.^{30,31} For $X\alpha$, the LO functional $\lambda[n]$ of eq 4 is just $3\alpha/2$. With typical values of α ,^{30,31} this gives $\lambda[n] = 1.0745$ for H ($N = 1$) to 1.0387 for Rn ($N = 86$). Comparison with Figure 1 shows that these values are slightly smaller than the highly accurate empirical values found in refs 8 and 9.

The importance of shell-dependent classification was evident in the modern work of refs 8 and 9. The numerical results of this study also leave a strong suggestion that such classification would be helpful. An advantage of the present classification of λ with respect to N alone is that it can be done in an entirely nonempirical way, as it relies only upon exact properties of the function $\lambda(N)$. (This is a clear distinction from all parametrized approaches.) Of course, the choice of interpolating function is not unique, but the fact that the upper limit on λ depends on N is completely general, as are the properties of $\lambda(N)$ used in the construction of our interpolation. What this means is that whatever shell-dependent classification might be invented, it must somehow be an addition to (or incorporate) classification by particle number, not supplant it. Because that classification will have to avoid size inconsistency, we suspect that the formulation will require additional insight, including additional constraints.

Dedication. John Perdew has contributed major insights to both fundamental and computational aspects of density functional theory. A consistent feature of his work is to prove relationships and apply them as rigorous constraints in the construction of approximate functionals. For those general reasons as well as a particular one, we are pleased to present this article in celebration of John's work and his contributions as part of this birthday festschrift. The particular reason is that the constraint we consider here was introduced to DFT

by John,¹ further analyzed by him in collaboration with Mel Levy,² and incorporated in John's GGA³ and meta-GGA⁴ functionals.

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