

Interrogating the **Becke05** density functional for non-locality information

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Abstract

In two papers, Becke [J. Chem. Phys. **119**, 2972 (2003) and **122**, 064101 (2005)] introduced Kohn-Sham density-functional approximations for static and dynamical correlation to be partnered with 100 percent exactly-computed exchange. Known as “B05”, this was the first non-local correlation model designed to work with the full non-locality of exact (or Hartree-Fock) exchange. Non-locality issues, often referred to as the “delocalization” problem, are among the most vexing problems in DFT today. How much exact exchange should be used in a hybrid functional? What value of the range parameter

should be used in a long-range corrected functional? Questions such as these abound, and the answers are system dependent. The physics of non-locality is built into the B05 functional in a natural way and one wonders, therefore, if B05 might provide a mechanism to answer such questions. Here we explore a variational procedure, “B05min”, to do so. We compute dipole moments of 52 small molecules and find that B05min delivers better moments than parent hybrid and long-range corrected functionals. Furthermore, B05min provides *a priori* optimum exact-exchange mixing fractions and range parameters for the parent functionals, whose values agree with literature values fit to experimental data.

1. Introduction

Kohn-Sham^{1,2} density-functional theory (DFT) attained its great popularity in the late 1980s and early 1990s with the rise of “generalized gradient” approximations (GGAs) for exchange-correlation (XC) energy³. GGAs employ local density and density-gradient in their integrands in order to approximate exchange and correlation energies. They are therefore “local” in the sense that the underlying exchange and correlation model holes are localized to regions of roughly atomic size. The first widely available XC GGA was BLYP (Becke⁴-Lee-Yang-Parr⁵) thanks to its implementation^{6,7} in the GAUSSIAN92/DFT program.

Becke observed in 1993^{8,9} that the non-interacting limit of the *adiabatic connection* or *coupling-strength integration* formula of Kohn-Sham DFT (see Ref. 3 for a discussion and references to the original literature) has the characteristics of *Hartree-Fock* exchange, namely that the hole generally extends over several atoms in molecular systems and hence is “*non-local*” or multi-center. He proposed that exact Hartree-Fock exchange be mixed with GGA exchange to improve DFT efficacy. Such mixed functionals are known as “hybrid” functionals and, with typically a small amount of exact exchange (about 20 percent), these afford significant general improvement over pure GGAs. The “B3LYP” hybrid was the first popular density-functional approximation (DFA) of this class^{9,10}. It is important to note that the amount of exact-exchange mixing has historically been determined by fits to experimental data⁹, since there is no known theoretical handle on its value (see, however, Ref. 11 for an attempt). Furthermore the exact-exchange mixing fraction is certainly system dependent, not global (meaning position and system independent) as has been presumed in the past.

The roughly 20 percent non-locality of hybrid functionals was later found to be insufficient for problems involving long-range charge transfer,¹² and a second class of non-local DFAs was developed for this purpose: “long-range corrected” (LC) functionals¹³⁻¹⁵. LC separates the $1/r_{12}$ Coulomb repulsion between electron pairs into a short-range and a long-range part, with the short-range part being treated by GGA-type DFAs and the long-range part treated by exact-exchange (Hartree-Fock) methodologies. In the present work we focus on the BLYP GGA, the earliest popular DFA, and its long-range corrected variant LC-BLYP.¹⁶ Its hybrid variant will be denoted h-BLYP.

GGA, and their hybrid and LC variants, work well in closed-shell chemical problems. They can fail dramatically, however, in odd-electron (radical) systems. The dissociation curve of the simplest conceivable molecule, H_2^+ , is a famous disaster³ for GGAs and hybrid functionals, falling to an erroneous asymptote almost as deep as the binding-energy well itself! Only 100 percent exact (Hartree-Fock) exchange, with zero GGA component, can cure this severe illness. Unfortunately, the high non-locality of Hartree-Fock exchange needs to be partnered with equally *non-local correlation* functionals, with explicit modeling of “static” or “nondynamical” correlation included. These are very challenging to design. The first successful exact-exchange (EXX) based static correlation functional was “B05”, whose opposite-spins part was published in 2003¹⁷ and its parallel-spins part in 2005¹⁸. B05 is exact for any one-electron system, such as H_2^+ , and significantly better than previous DFAs for radical systems in general.^{19,20} Other EXX-based functionals soon followed.²¹⁻²⁴ In 2013 an extension of B05 was published²⁵ (“B13”) incorporating strong correlations as encountered in highly multi-reference problems.

Another strength of EXX-based correlation functionals is their conceptual simplicity. GGA so-called “exchange” functionals model both exchange *and static correlation* through their inherent locality.^{3,9} This was the foundation of their great rise in popularity thirty years ago. Simulation of static correlation by X-GGA locality is, however, haphazard and out of control. The result is a growing trend to parameterize XC-GGAs against experimental data with increasingly numerous parameters,²⁶⁻²⁸ a frustrating

task that might eventually destroy the rigor of DFAs. Exact exchange, on the other hand, is cleanly defined and not open to parameterization. Indeed, B05 is essentially a parameter free, non-empirical functional as argued in Section 2.

B05 was initially implemented¹⁸ in a post-LSDA manner (i.e. non-self-consistently). Its complicated functional form makes self-consistent implementation extremely difficult. In the present work, therefore, we explore a variational approach to the determination of B05 orbitals and densities. This “B05min” approach is introduced in Section 2. In Section 3 we test B05min densities on the dipole moments of 52 small molecules. Moreover, B05min can be used to inform previous hybrid and LC functionals by predicting values of their non-locality parameters in an *a priori* manner (as opposed to fitting to experimental data). The ultimate purpose of this work, though, is to encourage the development of efficient self-consistent B05 technology, currently in its early stages²⁹⁻³².

2. B05min

The B05 exchange-correlation energy has the form

$$E_{XC}^{B05} = E_X^{exact} + a_{statC}^{opp} U_{statC}^{opp} + a_{statC}^{par} U_{statC}^{par} + a_{dynC}^{opp} E_{dynC}^{opp} + a_{dynC}^{par} E_{dynC}^{par} \quad (1)$$

where static and dynamical correlation energies are denoted by subscripts “statC” and “dynC”, and each is explicitly modeled by an opposite-spins and a parallel-spins part

(superscripts “opp” and “par”). Details are given in Refs. 17 and 18. Our implementation in this work is precisely as in Ref. 18, notwithstanding minor notation changes that should be obvious to readers. The static terms U_{statC}^{opp} and U_{statC}^{par} are *potential* energy models, whereas E_{dynC}^{opp} and E_{dynC}^{par} are *total* energy models incorporating kinetic energy through the Kohn-Sham adiabatic connection³. Thus the prefactors a_{statC}^{opp} and a_{statC}^{par} should have value 1/2 in accordance with the virial theorem, and a_{dynC}^{opp} and a_{dynC}^{par} should have value 1. We adopt these theoretical values throughout this work, making B05 an essentially *non-empirical* correlation model. On the 222 heats of formation of the G3 thermochemical benchmarks,³³ the post-LSDA basis-set-limit mean absolute error is 4.5 kcal/mol, compared to 3.0 kcal/mol with the fitted prefactors in Ref. 18. The difference is acceptably small.

B05 is a functional of density, density gradient, kinetic-energy density, Laplacian of the density, and the Coulomb (spin) potential of the exact exchange hole, also known as the Slater potential:

$$V_{X\sigma}^{Slater}(\mathbf{r}_1) = -\frac{1}{\rho_{\sigma}(\mathbf{r}_1)} \sum_{ij} \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{j\sigma}(\mathbf{r}_1) \int \frac{\psi_{i\sigma}(\mathbf{r}_2) \psi_{j\sigma}^*(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|} d^3\mathbf{r}_2 \quad (2)$$

It is the Slater potential that communicates non-locality information to the B05 correlation model, through a renormalized local exchange-hole reconstruction introduced in Refs. 17 and 18. Unfortunately, this potential leads to serious complications in the self-consistent implementation of B05. Nevertheless an “optimized effective potential” (OEP) implementation has been reported by Arbuznikov and Kaupp²⁹ and a conventional SCF implementation has been reported by Proynov et al.³⁰⁻³²

In the present work, an alternative variational approach is introduced that we shall call “B05min”. We perform B05 energy computations on a manifold of input orbitals, created by strategies described momentarily, and the lowest energy set of orbitals is deemed the B05min variational solution. Since it is explicitly non-local and 100 percent EXX-based, we expect B05min to reflect delocalization effects in a flexible and natural manner, *provided that the manifold of input orbitals reflects a wide spectrum of “delocalized character”*. What we mean by this is discussed below.

“Delocalized character” has, in existing density functionals, been associated with the amount of exact exchange a_x in hybrid functionals:

$$E_{XC}^{hybrid} = a_x E_X^{exact} + (1 - a_x) E_X^{GGA} + E_C^{GGA} \quad (3)$$

or the value of the range-separation parameter ω in the interelectronic Coulomb potential of LC functionals:

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\omega r_{12})}{r_{12}} + \frac{\text{erf}(\omega r_{12})}{r_{12}} \quad (4)$$

Varying a_x or ω over their typical domains (0 through 1) changes the non-local character of the resulting orbitals. Therefore a wide “non-local orbital space” can be represented by scanning over a_x and/or ω in hybrid DFT and LC DFT computations and using the orbitals as B05min inputs.

The above is computationally exorbitant. Indeed, we are not recommending B05min as a routine alternative to self-consistency. Our purpose is rather to encourage

others beyond the groups of Kaupp²⁹ and Kong,³⁰⁻³² to develop self-consistent B05 technologies. An additional, and perhaps more interesting theoretical purpose, is to determine exact-exchange fractions a_x in hybrid functionals and range parameters ω in LC functionals *a priori*. In the past, these have been treated as global parameters and have been fit to experimental data. They are not, however, global. They are fundamentally system dependent. B05min offers an *a priori* method to determine a_x or ω from theory.

3. Computations

In this work we focus on the BLYP GGA and its hybrid and LC versions, h-BLYP and LC-BLYP. The h-BLYP variant is defined by Eq.(3). LC-BLYP is defined as in Refs. 15 and 16. Note that h-BLYP is not quite the same functional as B3LYP^{9,10} since the latter contains two more parameters in the exchange and correlation gradient terms. All h-BLYP and LC-BLYP orbitals are obtained from the GAUSSIAN09 program³⁴ using the aug-cc-pVTZ basis set³⁵ and written to WFN files. An in-house “postG09” interface program built on our NUMOL (NUMerical MOLEcules) grid-based methods^{36,37} is then used to read the WFN files and calculate B05 energies.

Computations have been carried out on 52 di-atomic and tri-atomic molecules having known experimental dipole moments as compiled by NIST³⁸ in order to assess

B05min densities. Experimental geometries were used³⁸ and open shell computations were spin unrestricted. Dipole moments from experiment, and for Hartree-Fock, BLYP, B3LYP (having an exact-exchange fraction of 0.20), and LC-BLYP (with $\omega=0.33$ as recommended in Ref. 16) are tabulated in Table S1 of the Supplemental Information. CCSD (coupled-cluster singles and doubles) dipole moments are included as well, without frozen cores. We noticed large discrepancies between experiment and CCSD in molecules such as BF and HOF, in excess of 0.3 Debye (D). Therefore CCSD moments are taken as our reference values for the mean absolute error (MAE) and mean error (ME) statistics given in the table and throughout this paper. CCSD has recently been employed in a fascinating benchmark study of DFT densities in atoms by Medvedev et al³⁹ and in molecules by Brorsen et al.⁴⁰

A B05min search over the a_x parameter in h-BLYP was performed for each molecule in increments of 0.02. The minimum-energy solutions will be called “h-B05min”. See Table S2 in the Supplemental Information for the h-B05min dipole moment, along with the minimizing value of a_x , for each molecule. Table 1 summarizes MAEs and MEs for all functionals of this work. The h-B05min moments are overall slightly better (MAE = 0.078 D) than B3LYP (MAE = 0.081 D), signifying that our variational a_x search for each molecule slightly outperforms the global parameterization in B3LYP.

Perhaps even more interesting is the *average* h-B05min a_x value over all 52 molecules, given in Table 2. The standard deviation is given as well. Its value, $a_x = 0.20$,

is identical to the B3LYP value of 0.20 obtained by fitting to experimental thermochemical data.⁹ It is gratifying that our averaged *a priori* non-locality parameter a_x concurs with fits to experiment.

Next, a B05min search over the ω parameter in LC-BLYP was performed for each molecule in increments of 0.02. The minimum-energy solutions will be called “LC-B05min”. See Table S2 for the LC-B05min dipole moment and minimizing value of ω for each molecule. The LC-B05min moments (MAE = 0.077 D) are clearly superior to those of the parent LC-BLYP functional (MAE = 0.106 D) as seen in Table 1. Yet the average LC-B05min $\omega = 0.34 \text{ bohr}^{-1}$ over all 52 molecules, in Table 2, is very near the value 0.33 recommended in Ref. 16. Again our averaged *a priori* non-locality parameter, in this case ω , concurs with fits to experiment.

In order to explore an even wider non-local orbital space, *two*-dimensional searches over *both* the a_x and ω parameters have been undertaken, in increments of 0.02 for each. Figure 1, for the molecule CN, depicts a typical B05 energy landscape. The minimum-energy point, located at $a_x = 0.20$ and $\omega = 0.32 \text{ bohr}^{-1}$ (blue dot in the figure), will be called the “hLC-B05min” solution. The *one*-dimensional h-B05min and LC-B05min searches for this particular molecule minimize at $a_x = 0.34$ and $\omega = 0.42 \text{ bohr}^{-1}$ on the y axis and the x axis, respectively, the yellow and red dots in the figure.

The hLC-B05min dipole moments and minimizing values of a_x and ω for all of our 52 molecules are listed in the last columns of Table S2. The hLC-B05min moments

(MAE = 0.068 D and ME = 0.001 D in Table 1) are the best among all the functionals considered here. Also, the averaged hLC-B05min a_x and ω values (see Table 2) are quite reasonable, with a_x being slightly lower than the h-B05min average, and ω being slightly lower than the LC-B05min average. This makes sense, because both parameters “add” to provide non-local character in the combined hLC search. There is no global two-dimensional hLC-BLYP parameterization in the literature with which to compare our averaged hLC-B05min a_x and ω .

4. Conclusions and future work

The 100 percent exact-exchange-based B05 correlation functional of Ref. 18 handles exchange-correlation non-locality in a natural, physically satisfying way. However, self-consistent B05 orbitals are very difficult to obtain.²⁹⁻³² We have shown in this work that B05 (*partially*) *variationally-minimized* orbitals (i.e. orbitals from existing non-local density-functional forms that minimize the B05 energy) produce dipole moments superior to those of the parent functionals. There is no guarantee of this at the outset; it implies that B05 is an excellent functional. Additionally, our averaged a_x and ω non-locality parameters concur well with global parameterizations in the literature. In other words, we have here presented an *a priori* method for prediction of non-locality parameters in conventional hybrid and long-range corrected functionals, without appealing to experimental data. A non-empirical scheme for determining the range

parameter in LC functionals is known⁴¹, but B05min is the first non-empirical scheme for determining a_x in hybrid functionals.

We hope this work will stimulate continuing development of self-consistent B05 (and B13²⁵) technologies. Meanwhile, the present “B05min” variational approach will be used in future studies to further explore densities and non-locality parameters in diverse chemical contexts. The issues of “density driven error” versus “functional driven error” raised by Burke et al,⁴² may thereby be addressed.

Supplementary Material

[See Supplementary Tables S1 and S2 for full listings of dipole moments and B05min optimized exact-exchange fractions and LC range parameters.](#)

Acknowledgements

The authors gratefully acknowledge the support of the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Killam Trusts of Dalhousie University and the Canada Council for the Arts. Computing support has been provided by ACEnet, the Atlantic Computational Excellence Network.

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Table 1: Mean absolute errors (MAE) and mean errors (ME) of dipole moments with respect to CCSD, in Debye (D).

	MAE	ME
HF	0.216	0.123
BLYP	0.167	-0.108
B3LYP	0.081	-0.037
LC-BLYP	0.106	0.071
h-B05min	0.078	-0.038
LC-B05min	0.077	0.006
hLC-B05min	0.068	0.001

Table 2: Non-locality parameters a_x and ω . B05min values are averaged over the test set (with standard deviation σ).

	a_x	ω (bohr ⁻¹)
HF	1	---
BLYP	0	---
B3LYP	0.20	---
LC-BLYP	---	0.33
	$a_x \pm \sigma$	$\omega \pm \sigma$
h-B05min	0.20 ± 0.033	---
LC-B05min	---	0.34 ± 0.103
hLC-B05min	0.19 ± 0.026	0.24 ± 0.057

Figure 1: Two-dimensional hLC-B05min energy landscape for the CN molecule. See Section 3 for full description.

