

短距離と長距離を補正した密度汎関数法 (LCgau-DFT) の開発

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An improved long-range corrected hybrid exchange-correlation functional (LCgau-BOP) is presented with the inclusion of a short-range two-parameter Gaussian attenuation. We show that LCgau-BOP provides a consistently more accurate description of thermochemistry, chemical reactions and excitation energies than other existing Coulomb-attenuated functionals.

1 Introduction

Recently, we developed the Long-range Corrected Density Functional Theory (LC-DFT), where the exchange functional is partitioned with respect to the inter-electronic separation into long-range and short-range parts using a standard error function.¹ The LC approach was shown to clearly solve many of the problems which conventional DFT confronted: for example, the underestimation of Rydberg excitation energies and corresponding oscillator strengths,¹ the poor reproduction of charge-transfer excitations in time-dependent DFT calculations,¹ and the poor description of van der Waals interactions² as well as accurate reaction enthalpies and barrier heights.³

However, these LC-DFT functionals still have room for improvement. For example, it was found that LC-DFT could not produce atomization energies of the same quality as the B3LYP hybrid functional in spite of its more sophisticated inclusion of exact exchange, dependent on the inter-electronic distance.⁴

Recently, Savin *et al.* suggested the so-called erfgau interaction which combines a Gaussian correction to the error function to describe the long-range--short-range separation of the Coulomb operator.⁵

In this paper we extend this work by investigating the erfgau interaction in the context of generalized-gradient-approximation (GGA) calculations on molecules.

2 Theory

In the LC scheme,¹ the electron repulsion operator, $1/r_{12}$, is divided into short- and long-range parts using a standard error function:

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

The first term of Eq. (1) is the short-range interaction term, and the second term is the long-range interaction term. The DFT exchange

functional is included through the first term, and the long range orbital-orbital exchange interaction is described using the HF exchange integral.

The erfgau interaction of Savin *et al.*⁵ modifies the partitioning with a Gaussian correction, such that the long-range part takes the form

$$\frac{\text{erf}(\mu r)}{r} - \frac{2\mu}{\sqrt{\pi}} e^{-(1/3)\mu^2 r^2}$$

with an obvious modification to the complementary short-range part.

However, we took the pragmatic approach of introducing 2 extra parameters. We replaced the exponent, 1/3, by a parameter, 1/ a , and multiplied the prefactor by a parameter, k , to give the long-range form

$$\frac{\text{erf}(\mu r)}{r} - k \frac{2\mu}{\sqrt{\pi}} e^{-(1/a)\mu^2 r^2}$$

with the obvious modification to the complementary short-range part. We named this short- and long-range corrected method LCgau-DFT.

3 Result and Discussion

We employed a 50%-50% summation of atomization energy and barrier height errors and obtained an optimized parameter set with $\mu=0.42$, $a=0.011$, and $k=-18.0$, which gave an RMS error of 5.3 kcal/mol, which is significantly better than LC-BOP (10.3 kcal/mol) and even B3LYP (7.5 kcal/mol) and gave slightly improved barrier heights (2.43 kcal/mol RMS error) compared to LC-BOP (2.53 kcal/mol). As a result, the errors of LCgau-BOP for both atomization energies and barrier heights were lower than those of B3LYP and LC-BOP. This shows that the inclusion of HF exchange in the short-range part is of significant importance in calculating both the atomization energies and the barrier heights.

Concerning the reaction enthalpies of Database/3, LCgau-BOP also gives smaller errors (2.00 kcal/mol) than LC-BOP (2.18 kcal/mol) and B3LYP

(3.03 kcal/mol).

In addition, LCgau-BOP gave the most accurate reproduction of the optimized bond lengths and bond angles.

Finally, LCgau-BOP is also seen to improve excitation energy calculations, giving generally improved errors of the valence, Rydberg, and total excitation energies compared to other LC functionals (Table.2).

Table.1: Results from 148 atomization energies (kcal/mol), 329 bond lengths (Å), and 271 bond angles (degrees) in the G2 test set, plus 72 calculated barrier heights and 26 reaction enthalpies (kcal/mol) from Database/3. Root mean square (RMS) and mean signed errors (MSE) are given for all calculations using the 6-311++G(2d,2p) basis set and optimized geometries.

	μ	k	a	G2 set			Database/3		
				Atom Energy	Bond Length	Bond Angle	Barrier Height	Reaction Enthalpy	
				RMS	RMS	RMS	MSE	RMS	RMS
B3LYP				7.5	0.0244	1.5581	-3.91	4.74	3.03
LC-BOP	0.33			21.0	0.0235	1.5421	-3.77	4.92	3.27
	0.47			10.1	0.0244	1.5798	0.48	2.53	2.18
LCgau-BOP	0.42	-18.0	0.01	5.3	0.0233	1.5087	-0.95	2.43	2.00

Table.2: Mean absolute Errors of Vertical excitation energies of the molecule set calculated by TDDFT. Error of SAC-CI is also shown for comparison. All calculations used an augmented Sadlej pVTZ basis set.

State	# of state	LCgau-BOP	LC-BOP	BOP	B3LYP	SAC-CI
		$\mu=0.42$	$\mu=0.33$	$\mu=0.47$		
		$a=0.011$				
		$k=-18.0$				
Mean absolute deviation of excitation energies of N ₂ (eV)						
Valence	(8)	0.44	0.37	0.52	0.40	0.53
Rydberg	(4)	0.19	0.79	0.17	2.37	1.14
Total	(12)	0.35	0.51	0.40	1.06	0.73
Mean absolute deviation of excitation energies of CO (eV)						
Valence	(7)	0.20	0.19	0.21	0.28	0.35
Rydberg	(7)	0.07	0.64	0.23	2.06	1.15
Total	(15)	0.14	0.41	0.22	1.17	0.75
Mean absolute deviation of excitation energies of H ₂ CO (eV)						
Valence	(4)	0.21	0.30	0.22	0.23	0.18
Rydberg	(8)	0.15	0.47	0.29	1.66	0.83
Total	(12)	0.17	0.41	0.27	1.18	0.62
Mean absolute deviation of excitation energies of C ₂ H ₄ (eV)						
Valence	(2)	0.41	0.31	0.47	0.47	0.45
Rydberg	(12)	0.16	0.15	0.32	1.41	0.96
Total	(14)	0.19	0.17	0.34	1.28	0.88
Mean absolute deviation of excitation energies of C ₆ H ₆ (eV)						
Valence	(6)	0.32	0.23	0.37	0.28	0.25
Rydberg	(10)	0.50	0.29	0.64	1.00	0.56
Total	(16)	0.43	0.27	0.54	0.73	0.44

4 Conclusion

We have presented a new hybrid exchange-correlation functional based on the LC scheme, named LCgau-BOP, which we have demonstrated to be consistently superior to other

such functionals, including LC-BOP, CAM-BLYP, and B3LYP, in terms of the reproduction of atomization energies, barrier heights, reaction enthalpies, geometrical properties, and excitation energies (including charge-transfer excitations) over a wide range of molecular systems. The key feature is the introduction of a two-parameter Gaussian function to the Coulomb attenuation which allows a more flexible description of exact exchange at short-range inter-electronic separations. The new partitioning preserves 100% exact exchange in the long range, which is known to be important for the success of the LC-scheme, with an asymptotic attenuation described by a standard error function with parameter 0.42. The LCgau partitioning was optimized for the reproduction of atomization energies and reaction barrier heights over large fitting sets and the results highlight the importance of including a substantial portion of exact exchange in the short range.

Reference

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