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A Semiempirical Long-Range Corrected Exchange Correlation Functional Including a Short-Range Gaussian Attenuation (LCgau-B97)

Jong-Won Song,^[a,b,c] Daoling Peng,^[a,b] and Kimihiko Hirao^{*[a,b]}

We applied an improved long-range correction scheme including a short-range Gaussian attenuation (LCgau) to the Becke97 (B97) exchange correlation functional. In the optimization of LCgau-B97 functional, the linear parameters are determined by least squares fitting. Optimizing μ parameter (0.2) that controls long-range portion of Hartree-Fock (HF) exchange to excitation energies of large molecules (Chai and Head-Gordon, *J Chem Phys* 2008, 128, 084106) and additional short-range Gaussian parameters ($a = 0.15$ and $k = 0.9$) that controls HF exchange inclusion ranging from short-

range to mid-range (0.5–3 Å) to ground state properties achieved high performances of LCgau-B97 simultaneously on both ground state and excited state properties, which is better than other tested semiempirical density functional theory (DFT) functionals, such as ω B97, ω B97X, BMK, and M0x-family. We also found that while a small μ value (~ 0.2) in LC-DFT is appropriate to the local excitation and intramolecular charge-transfer excitation energies, a larger μ value (0.42) is desirable in the Rydberg excitation-energy calculations. © 2011 Wiley Periodicals, Inc. *J Comput Chem* 32: 3269–3275, 2011

Keywords: density functional theory • long-range correction • range separation • Gaussian short-range Hartree-Fock exchange • semiempirical density functional theory • charge transfer excitation • Becke97

Introduction

The long-range correction (LC)^[1–5] scheme has been applied in various features^[6–16] of the present density functional theory (DFT). The DFT functional combined with LC scheme overcomes fatal problems that conventional DFT functionals have confronted, such as the overestimation of linear and nonlinear polarizabilities of long-chain molecules,^[17–19] the underestimation of barrier heights,^[5] and the underestimations of Rydberg excitation energies and the corresponding oscillator strengths, as well as the underestimations of charge-transfer excitations using the time-dependent (TD) scheme.^[4] Additionally, combined with C_6/R^6 dispersion interaction correlation functional, LC-DFT showed improvement on a poor description of van der Waals interactions of conventional DFT functionals^[20,21] as well as on the overestimations in the energy calculations of increasing linear alkanes.^[22] In our recent report, the orbital energies of the DFT including the LC scheme were shown to follow Koopman's theorem in a high accuracy.^[23]

This LC approach is characterized as the combination of an exchange functional for the interelectronic short-range distance with the Hartree-Fock (HF) exchange integral for the long-range distance using the standard error function,

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

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between electrons 1 and 2 and μ is a parameter that controls the proportion between the two ranges depending on the value of r_{12} .

Recently, Head-Gordon group applied LC scheme to Becke97 (B97)^[24] exchange correlation functional (ω B97 and ω B97X)^[13] and determined the linear parameters of B97 functional using

least squares fitting on the ground state properties, such as G3 set atomization energies,^[25–27] reaction barrier heights, ionization potential, electron affinities, and so on. As a result, ω B97 and ω B97X showed improved performances on ground state property with long-range properties maintained, compared with other semiempirical exchange correlation functionals, such as M0x-series^[28,29] and Boese and Martin's τ -dependent hybrid functional (BMK).^[30] However, in the recent assessments on excitation energies of especially large molecules using TD scheme, ω B97 and ω B97X showed unexpectedly high errors of excited state energies on local transitions like $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$.^[31]


Recently, we proposed an improved LC scheme that includes an additional short-range Gaussian HF exchange, which is named as LCgau.^[8,9] Using LCgau scheme, we found

[a] J.-W. Song, D. Peng, K. Hirao
Next-generation Molecular Theory Unit, Advanced Science Institute, RIKEN 2-1, Hirosawa, Wako, Saitama 351-0198, Japan
E-mail: hirao@riken.jp

[b] J.-W. Song, D. Peng, K. Hirao
CREST, Japan Science and Technology Agency, Saitama 332-0012, Japan

[c] J.-W. Song
Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan

Contract/grant sponsor: Japan Science and Technology Agency [(JST) Core Research for Evolutional Science and Technology Program, "High Performance Computing for Multi-Scale and MultiPhysics Phenomena"], Japan Society for the Promotion of Science [(JSPS); post-doctoral fellowship to J.-W.S.].

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that a short-range HF inclusion to exchange functional is quite efficient and that the flexible inclusion of short-range HF exchange through a Gaussian function enables us to improve the performances of LC-DFT on excitation energies as well as ground state energies. We rationalized that the inclusion of short-range HF exchange plays a role in decreasing self-interaction error of DFT abiding near the core region.^[10,11] In our recent report of the DFT calculations on the isomerization energy of organic molecules, it was shown that the short-range Gaussian exchange inclusion is crucial to the energy calculations of ring-strained molecules.^[32]

In this article, we will apply the LCgau scheme to B97 functionals and will address the problem, which ω B97 and ω B97X confront, in the category of LCgau-B97.

Theory

Becke97 functional

In the B97 functional, the exchange energy is expressed as

$$E_x^{\text{B97}} = \sum_{\sigma} \int e_{x\sigma}^{\text{LDA}}(\rho_{\sigma}) g_{x\sigma}(s_{\sigma}^2) d^3\mathbf{R}. \quad (2)$$

Here, $e_{x\sigma}^{\text{LDA}}(\rho_{\sigma})$ is the local density approximation (LDA) exchange energy density for σ spin,

$$e_{x\sigma}^{\text{LDA}}(\rho_{\sigma}) = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3} \rho_{\sigma}^{4/3}(\mathbf{r}). \quad (3)$$

$g_{x\sigma}$ is expressed as the polynomials of the expansion function $u_{x\sigma}$, which depends on the dimensionless reduced spin density gradient $s_{\sigma} = |\nabla \rho_{\sigma}|/\rho_{\sigma}^{4/3}$ like

$$g_{\sigma}(s_{\sigma}^2) = \sum_{i=0}^m c_{x\sigma,i} u_{x\sigma}^i, \quad (4)$$

$$u_{x\sigma} = \gamma_{x\sigma} s_{\sigma}^2 / (1 + \gamma_{x\sigma} s_{\sigma}^2), \quad (5)$$

$$\gamma_{x\sigma} = 0.004. \quad (6)$$

The correlation energy functional part of B97 functional can also be expressed with the same form of the exchange energy part, which can be decomposed into same-spin $E_{c\sigma\sigma}^{\text{B97}}$ and opposite-spin $E_{c\sigma\sigma}^{\text{B97}}$ components as $E_{c\sigma\sigma}^{\text{B97}} = \sum_{\sigma} E_{c\sigma\sigma}^{\text{B97}} + E_{c\alpha\beta}^{\text{B97}}$. For the same-spin terms,

$$E_{c\sigma\sigma}^{\text{B97}} = \int e_{c\sigma\sigma}^{\text{LDA}}(\rho_{\sigma}) g_{c\sigma\sigma}(s_{\sigma}^2) d^3\mathbf{R}, \quad (7)$$

$$g_{c\sigma\sigma}(s_{\sigma}^2) = \sum_{i=0}^m c_{c\sigma\sigma,i} u_{c\sigma\sigma}^i, \quad (8)$$

$$u_{c\sigma\sigma} = \gamma_{c\sigma\sigma} s_{\sigma}^2 / (1 + \gamma_{c\sigma\sigma} s_{\sigma}^2), \quad (9)$$

$$\gamma_{c\sigma\sigma} = 0.2. \quad (10)$$

and for the opposite-spin terms,

$$E_{c\alpha\beta}^{\text{B97}} = \int e_{c\alpha\beta}^{\text{LDA}}(\rho_{\alpha}, \rho_{\beta}) g_{c\alpha\beta}(\bar{s}_{\text{avg}}^2) d^3\mathbf{R}, \quad (11)$$

$$g_{c\alpha\beta}(\bar{s}_{\text{avg}}^2) = \sum_{i=0}^m c_{c\alpha\beta,i} u_{c\alpha\beta}^i, \quad (12)$$

$$u_{c\alpha\beta} = \gamma_{c\alpha\beta} \bar{s}_{\text{avg}}^2 / (1 + \gamma_{c\alpha\beta} \bar{s}_{\text{avg}}^2), \quad (13)$$

$$\gamma_{c\alpha\beta} = 0.006, \quad (14)$$

$$\bar{s}_{\text{avg}}^2 = \frac{1}{2} (s_{\alpha}^2 + s_{\beta}^2). \quad (15)$$

$e_{\alpha\alpha}^{\text{LDA}}$ and $e_{\alpha\beta}^{\text{LDA}}$ are parallel-spin and opposite-spin correlation energy densities, which are extracted from total LDA correlation energy density e_c^{LDA} using the approach of Stoll et al.^[33,34]

$$e_{\alpha\alpha}^{\text{LDA}}(\rho_{\alpha}, \rho_{\beta}) = e_c^{\text{LDA}}(\rho_{\alpha}, 0), \quad (16)$$

$$e_{c\alpha\beta}^{\text{LDA}}(\rho_{\alpha}, \rho_{\beta}) = e_c^{\text{LDA}}(\rho_{\alpha}, \rho_{\beta}) - e_c^{\text{LDA}}(\rho_{\alpha}, 0) - e_c^{\text{LDA}}(0, \rho_{\beta}). \quad (17)$$

e_c^{LDA} can be obtained using Perdew–Wang parametrization^[35] of the LDA correlation energy.

LCgau scheme

In the LC scheme, 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 through the second term. In the LC scheme, the short-range exchange functional may be computed by modifying the usual exchange energy expression from of Eq. (2) to

$$E_x^{\text{sr,eff}} = \sum_{\sigma} \int e_{x\sigma}^{\text{LDA}}(\rho_{\sigma}) g_{x\sigma}(s_{\sigma}^2) \times \left\{ 1 - \frac{8}{3} a_{\sigma} \left[\sqrt{\pi} \operatorname{erf} \left(\frac{1}{2a_{\sigma}} \right) + 2a_{\sigma}(b_{\sigma} - c_{\sigma}) \right] \right\} d^3\mathbf{R}, \quad (18)$$

where a_{σ} , b_{σ} , and c_{σ} are defined as

$$a_{\sigma} = \frac{\mu}{(2k_{\text{F}\sigma})}, \quad (19)$$

$$b_{\sigma} = \exp \left(-\frac{1}{4a_{\sigma}^2} \right) - 1, \quad (20)$$

and

$$c_{\sigma} = 2a_{\sigma}^2 b_{\sigma} + \frac{1}{2}, \quad (21)$$

where $k_{\text{F}\sigma} \equiv (6\pi^2 \rho_{\sigma}(\mathbf{r}))^{1/3}$ is the local Fermi wave factor.

In LCgau scheme,^[8,9] the electron repulsion operator, $1/r_{12}$, is divided using a standard error function augmented by an additional Gaussian function,

$$\frac{1}{r_{12}} = \frac{\operatorname{erfc}(\mu r_{12})}{r_{12}} - k \frac{2\mu}{\sqrt{\pi}} e^{-(1/a)\mu^2 r_{12}^2} + \frac{\operatorname{erf}(\mu r_{12})}{r_{12}} + k \frac{2\mu}{\sqrt{\pi}} e^{-(1/a)\mu^2 r_{12}^2}. \quad (22)$$

where the DFT exchange functional is included through the first two terms of Eq. (22), and the HF exchange integral is

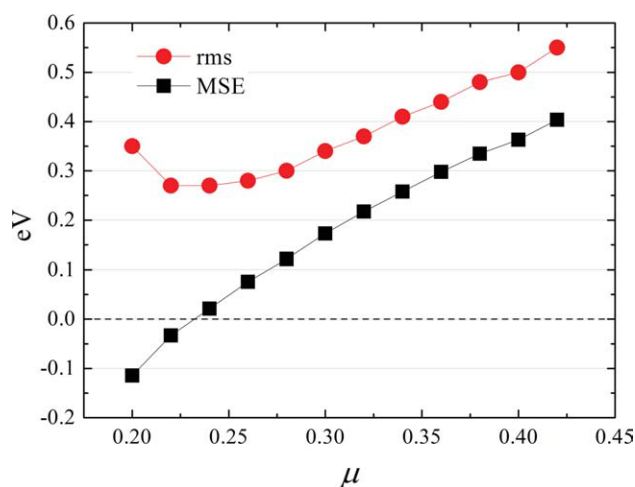


Figure 1. The mean signed (MSE) and rms errors on 94 local transitions of LCgau-B97 whose μ is changed from 0.20 to 0.42 with a and k fixed to 0.011 and 18.0, respectively.

included through the second two terms. Note that the sign of the parameter k is positive, which is contrary to the convention of previous publications.^[8,10] The Gaussian correction part gives an additional contribution to the short-range exchange energy of a very similar form to Eq. (18)

$$E_x^{\text{sr,gau}} = -k \sum_{\sigma} \int e_{x\sigma}^{\text{LDA}}(\rho_{\sigma}) g_{x\sigma}(s_{\sigma}^2) \times \frac{8}{3} a_{\sigma} \left[\sqrt{\pi} \operatorname{erf}\left(\frac{1}{2d_{\sigma}}\right) + (2d_{\sigma} - 16d_{\sigma}^3)e_{\sigma} - 4d_{\sigma} \right] d^3\mathbf{R} \quad (23)$$

where d_{σ} and e_{σ} are defined as

$$d_{\sigma} = \frac{a_{\sigma}}{\sqrt{a}}, \quad (24)$$

$$e_{\sigma} = \exp\left(-\frac{1}{4d_{\sigma}^2}\right) - 1, \quad (25)$$

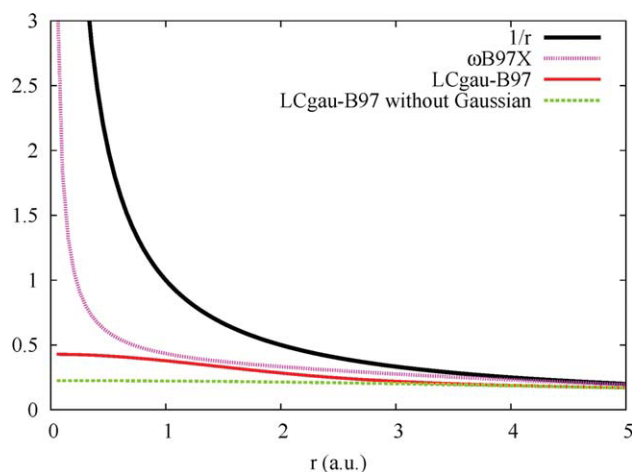


Figure 2. Modified forms of the $1/r_{12}$ operator for the HF exchange contributions in ω B97X ($\mu = 0.3$ and $C_{x\sigma,0} = 0.842294$), LCgau-B97 ($\mu = 0.2$, $a = 0.15$, and $k = 0.9$), and LCgau-B97 without Gaussian ($\mu = 0.2$ and $k = 0.0$).

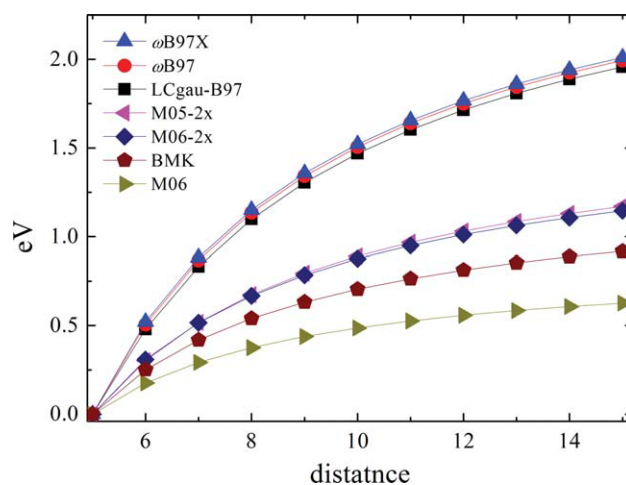


Figure 3. The lowest CT excitation energy of $\text{C}_2\text{H}_4\text{-C}_2\text{F}_4$ dimer for long intermolecular distances (in Å) calculated by TD-DFT employing various types of functionals. Calculated SAC-CI results are also shown for comparison. For all methods, the excitation energy at 5.0 Å is set to zero.

and the total short-range DFT exchange energy of the LCgau scheme can be obtained as a summation of two contributions ($E_x^{\text{sr}} = E_x^{\text{sr,erf}} + E_x^{\text{sr,gau}}$).

In the case of the LC scheme, exact HF exchange is incorporated in the long-range region via integrals such as

$$E_x^{\text{lr,LC}} = -\frac{1}{2} \sum_{\sigma} \sum_i^{\text{occ}} \sum_j^{\text{occ}} \int \int \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{j\sigma}^*(\mathbf{r}_1) \left[\frac{\operatorname{erf}(\mu r_{12})}{r_{12}} \right] \psi_{i\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2, \quad (26)$$

and, in the case of the LCgau scheme,

$$E_x^{\text{lr,LCgau}} = -\frac{1}{2} \sum_{\sigma} \sum_i^{\text{occ}} \sum_j^{\text{occ}} \int \int \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{j\sigma}^*(\mathbf{r}_1) \left[\frac{\operatorname{erf}(\mu r_{12})}{r_{12}} + k \frac{2\mu}{\sqrt{\pi}} e^{-(1/a)\mu^2 r_{12}^2} \right] \psi_{i\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2, \quad (27)$$

where $\psi_{i\sigma}$ is the i th σ -spin molecular orbital.

Detail of Optimizing Parameters

Typically, the empirical linear parameters ($C_{x\sigma,i}$, $C_{\sigma\sigma,i}$, and $C_{\alpha\beta,i}$) of B97 functional were fitted against the ground state properties. As for the fitting process of linear parameters, we followed the optimization process used when the parameters of ω B97 and ω B97X functionals were determined.^[13,36] That is, we performed least squares fittings of linear parameters of LCgau-B97 functional using 6-311G++(3df,3pd) basis set to the experimental values of reaction enthalpy (G3/99 set; 233 molecules),^[25–27,37] ionization potential (G2-1 set^[38]; 40 molecules except for SH_2 [$^2\text{A}_1$] and N_2 [$^2\Pi$]), electron affinity (G2-1 set; 25 molecules), proton affinity (G2-1 set; eight molecules), reaction barrier height set consisting of hydrogen transfer and non-hydrogen transfer sets (HTBH38/04 and NHTBH38/04

Table 1. Optimized parameters for LCgau-B97.

μ	0.2
A	0.15
K	-0.9
$C_{\chi\sigma,0}$	1.000000
$C_{\chi\sigma,1}$	0.907206
$C_{\chi\sigma,2}$	1.359944
$C_{\chi\sigma,3}$	-6.115681
$C_{\chi\sigma,4}$	12.067180
$C_{c\sigma\sigma,0}$	1.000000
$C_{c\sigma\sigma,1}$	-5.572448
$C_{c\sigma\sigma,2}$	23.738570
$C_{c\sigma\sigma,3}$	-37.828107
$C_{c\sigma\sigma,4}$	19.079116
$C_{c\alpha\beta,0}$	1.000000
$C_{c\alpha\beta,1}$	1.148502
$C_{c\alpha\beta,2}$	-7.992061
$C_{c\alpha\beta,3}$	11.093747
$C_{c\alpha\beta,4}$	-12.778365

sets,^[39–41] respectively; overall 68 reactions), and noncovalent interaction (the S22 set),^[42] with nonlinear range separation parameters (μ , a , and k) of LCgau scheme fixed. In the least squares fitting, all data were equally weighted. In all the cases, the geometries and zero-point energies were obtained using B3LYP/6-31G(2df,p).

In G3set atomization energy, scaling factor for zero-point energy (0.9854) was used^[37] and experimental spin-orbital corrections for the atoms were also used.^[25] All the calculations of the S22 set were corrected for basis set superposition errors by counterpoise method. However, we found that the S22 set calculations are so time consuming that it looks impossible to fit both nonlinear and linear parameters with including the S22 set. Therefore, for the time being, we fitted linear parameters excluding the S22 set. Then, after the nonlinear

parameters were optimized, we added the S22 set to the test set in optimizing linear parameters.

As mentioned in Introduction section, it was reported that the excited state energies of large molecules calculated using ω B97 and ω B97X are quite underestimated and smaller value of μ than 0.4 or 0.3 may be desirable.^[31] In our preliminary tests, we found that long-range parameter, μ , has a high impact on the excited state properties while the short-range HF exchange inclusion has low influences. Therefore, to check the dependency of excited state energies on μ parameter in LCgau-B97, we scanned μ from 0.2 to 0.42 with the step of 0.2 and fitted the linear parameters on each μ value with $a = 0.011$ and $k = 18.0$ fixed. Then, we applied these optimized LCgau-B97 functionals to local transition excitation energy benchmark set of large molecule,^[31] which Schreiber et al. compiled. In local transition excitation energy benchmark set calculations, we performed the calculations of 94 vertical excitation energies of 25 molecules using TD scheme with aug-cc-pVTZ basis set. Note that, in Ref. [31], Rohrdanz et al. skipped several excitations due to the problems in assigning the states, but we added 10 more higher-lying excitation states of the nucleic acid base among the omitted excitations to the excitation energy fitting set.

Figure 1 shows the errors on local excited state energy depending on the μ value. As expected, in smaller value ($\mu = 0.22$) than that previously used, the minimum of error was found. Then, with the optimized μ value fixed, we optimized a and k values to the experimental ground state energies. With a and k values changed, the linear parameters were fitted. In summary, μ value is optimized to excited state energy and the other parameters (a , k , and 12 linear parameters) are fitted against ground state properties.

As a result, we obtained the parameter set of $\mu = 0.22$, $a = 0.16$, and $k = 0.8$, which makes unexpectedly different pattern

Table 2. Statistical errors (in kcal/mol) of the training set tested in Ref. [13].

Benchmark set	Error	LCgau-B97	ω B97	ω B97X	M05-2x	M06	M06-2x	BMK
G3 set (223)	MSE	0.00	-0.24	-0.15	2.07	2.53	0.46	1.98
	MAE	1.99	2.68	2.16	3.68	3.57	2.32	3.31
	Rms	2.69	3.66	2.94	4.84	5.18	3.41	4.19
IP (40)	MSE	0.23	-0.50	-0.15	1.14	-0.80	0.19	0.90
	MAE	2.97	2.67	2.70	3.30	3.42	2.43	3.60
	rms	3.80	3.62	3.62	4.57	4.33	3.57	4.96
EA (25)	MSE	-0.60	-1.53	-0.47	-0.24	-1.18	-1.38	-0.38
	MAE	2.01	2.70	2.03	2.46	2.22	2.55	2.43
	rms	2.51	3.10	2.55	3.21	2.70	3.05	3.02
PA (8)	MSE	1.90	0.67	0.56	-1.26	-0.04	-1.22	-1.44
	MAE	1.90	1.48	1.21	1.52	1.72	2.04	1.96
	rms	2.38	2.18	1.71	1.89	1.94	2.23	2.08
BH (68)	MSE	-1.40	0.07	-0.70	-0.29	-2.12	-0.47	0.62
	MAE	2.21	2.11	2.04	1.64	2.44	1.39	1.61
	rms	2.68	2.55	2.39	2.08	3.23	1.75	1.97
S22 (22)	MSE	0.88	0.15	0.52	0.73	1.00	0.27	2.77
	MAE	1.10	0.59	0.86	0.87	1.00	0.39	2.77
	rms	1.72	0.77	1.28	1.19	1.26	0.55	3.29
All (394)	MSE	-0.17	-0.25	-0.21	1.26	0.98	0.10	1.45
	MAE	2.08	2.43	2.09	3.00	3.08	2.07	2.92
	rms	2.73	3.23	2.77	3.95	4.30	2.92	3.71

For all cases, single-point calculations are performed using the 6-311++G(3df,3pd) basis set.

Table 3. Statistical errors (in eV) in calculated local transitions,^[49] charge transfer transitions,^[48] and Rydberg excitations.^[8]

Benchmark set	Error	LCgau-B97	ω B97	ω B97X	M05-2x	M06	M06-2x	BMK
Local transition (94)	MAE	0.22	0.38	0.32	0.30	0.43	0.25	0.26
Intramolecular CT ^[a] (13)	MAE	0.19	1.01	0.56	0.28	1.10	0.23	0.40
Rydberg excitation ^[b] (31)	MAE	0.44	0.28	0.24	0.20	1.36	0.40	0.44

In parentheses, the numbers of calculated transitions are shown. Details of calculated results are provided as Supporting Tables.

[a] Intramolecular CT excitation energies of dipeptide, β -dipeptide, tripeptide, *N*-phenylpyrrole, and 4-(*N,N*-dimethylamino) benzonitrile. [b] Rydberg excitation energies of CO, N₂, H₂CO, and C₂H₄. An augmented Sadlej pVTZ was used as a basis set.

of short-range HF exchange inclusion from those in LCgau-BOP (Becke88 exchange^[43] + One parameter correlation^[44] functionals). However, we noticed that the change of the short-range HF exchange inclusion can affect somewhat the performance on excited state energy. For example, LCgau-B97 optimized with $\mu = 0.22$, $a = 0.16$, and $k = 0.8$ showed 0.30 eV root mean square (rms) error of 94 local transitions while LCgau-B97 optimized with $\mu = 0.22$, $a = 0.011$, and $k = 18.0$ showed 0.27 eV rms error. Therefore, we flexibly optimized the parameters, a and k , on additional values of μ near to 0.22. Then, slightly lower value of $\mu = 0.20$ and its following short-range values, $a = 0.15$ and $k = 0.9$, were found to be optimal. Its following linear parameter set is shown in Table 1.

For comparison, we also performed all the related calculations using ω B97, ω B97X, M05-2x, M06, M06-2x, and BMK, which are semiempirical DFT functionals reported to give high performances on various properties. We used a development version of the Gaussian03 program^[45] as for the LCgau-B97 functional and, as for other functionals, the official version of Gaussian09 program.^[46]

Results and Discussion

Table 2 shows the errors of overall calculated ground state properties of LCgau-B97. Consequently, compared with other semiempirical functionals, LCgau-B97 functional shows relatively higher performances on overall ground state property calculations over 394 training set than any other functionals.

Investigation of the shape of optimized HF exchange inclusion in Figure 2 presents physical reasoning of the accomplished improvement. On the surface, the inclusion of HF exchange attributed to an additional Gaussian function seems to make no contributions to optimized LCgau-B97. However, when separating HF exchange of LCgau-B97 into the contributions from Gaussian function and that from error function, we can find that a Gaussian part of LCgau-B97 plays a role in controlling the additional HF exchange inclusion in the short-range and mid-range regions (0.5–3 Å), which mainly contributes to the performances on ground state properties.^[47]

The first line of Table 3 shows the errors of various semiempirical functionals on 94 local excitation energies of large molecules of Ref. [31]. LCgau-B97 shows best performance on the local excitation energy calculations. In addition, we performed the calculations of intramolecular charge transfer (CT) energy of Ref. [48] using cc-pVTZ (Dunning's Triple-zeta correlation consistent basis set) and its optimized geometries. The second line of the table shows the errors of calculated intramolecular CT excitation energy. LCgau-B97 functional also shows better performances on CT excitations than other functionals. These results show that small μ is desirable to reproduce the intramolecular CT excitation energy at least in the category of tested excitation energies. However, the third line of the table shows that small μ value is not appropriate in the calculations of Rydberg excitation energies in Ref. [32]. In detail, ω B97 and ω B97X using a large μ value (0.4 and 0.3, respectively) shows better performances on Rydberg excitation energy calculations (0.28 and 0.24 eV, respectively). In addition, in the previous study, LCgau-BOP which uses a μ value of 0.42 also showed

Table 4. Statistical errors in calculated atomization energies (in kcal/mol), optimized bond length (in Å), and optimized bond angle (in °) of G2 set,^[8,9,25] atomization energy of G3/05 set^[13,50,51] (in kcal/mol), and reaction enthalpies (in kcal/mol) of NHTBH38/04 and HTBH38/04.^[13,39–41]

Benchmark set	Property	# of data	Error	LCgau-B97	ω B97	ω B97X	M05-2x	M06	M06-2x	BMK
G2 set ^[a]	Atomization energy	(148)	rms	4.2	4.5	4.3	5.0	3.2	4.5	4.0
	Bond length	(326)	rms	0.0132	0.0132	0.0132	0.0133	0.0132	0.0132	0.0148
	Bond angle	(271)	rms	0.9326	0.8996	1.0591	0.9308	0.9342	0.9342	0.9605
G3/05 set ^[b]	Atomization energy	(48)	MSE	0.64	1.20	0.68	−0.09	3.13	−2.98	−0.49
			MAE	3.01	4.10	3.39	5.05	5.72	5.14	3.52
			rms	4.18	5.40	4.53	6.92	8.55	6.85	5.15
NHTBH38/04 + HTBH38/04 ^[c]	Reaction enthalpy	(30)	MSE	−0.16	0.06	−0.09	−0.86	−0.25	−0.58	−0.55
			MAE	1.81	1.95	1.72	1.64	2.22	1.22	1.66
			rms	2.24	2.36	2.11	2.28	3.08	1.84	2.10

In parentheses, the numbers of calculated data are shown.

[a] Geometries optimized using each DFT functional with 6-311++(2d,2p) basis set were used. [b] Geometries optimized using B3LYP/G3LargeXP and its frequencies with scaling factor 0.9854 were used. The enthalpy of formation at 0 K for gaseous Br atom, ΔH_f^0 (0 K), is 28.19 kcal/mol and the temperature correction ($H^{298} - H^0$) of Br atom is 1.481 kcal/mol and spin-orbit correction of Br atom is −5.6 mhartrees in NIST-JANAF thermochemical Tables.^[55]

[c] Single-point calculations were performed using 6-311++G(3df,3pd) basis set.

0.15 eV in mean absolute error (MAE). Therefore, we can find that small μ value is appropriate for the calculations of local and intramolecular CT excitations, while large μ value is desirable for those of Rydberg excitations. In addition, it is found that μ , which determines the ratio of HF exchange inclusion in long range, strongly influences the excitation energy calculations, while a and k influence the ground state energy calculations.

Figure 3 shows the dependency on the CT distances of the intermolecular CT energy of various semiempirical functionals. The figure shows that the intermolecular CT result using the functionals including LC scheme are similar with that using Symmetry Adapted Cluster/Configuration Interaction (SAC-CI), but that of other functionals, M0x family and BMK, show larger underestimation as the distance becomes longer.

We notice that the overall error on ground state properties of LCgau-B97 optimized using our fitting process is not so different from that of LCgau-B97 with global optimization. For example, only in the category of our incomplete test fittings, we found that the lowest rms error on ground state properties without the S22 set, 2.79 kcal/mol, was seen in LCgau-B97 optimized with $\mu = 0.28$, $a = 0.11$ and $k = 0.7$ while LCgau-B97 provided 2.80 kcal/mol rms error with the same calculations. This shows that the inclusion of short-range HF exchange is substantially helpful to optimize LC-DFT functionals satisfying simultaneously performances on ground and excited state energies.^[8,31]

Table 4 shows the results of various DFT functionals including LCgau-B97 on other ground state properties, which are not used in the fitting process of the parameters of LCgau-B97 functional, such as atomization energy, optimized bond length, and optimized bond angle of G2 set,^[8,9,25] atomization energy of G3/05 set,^[13,50,51] and reaction enthalpy of NHTBH38/04 and HTBH38/04.^[13,39–41] LCgau-B97 functional shows better performances on overall tested properties. Specially, except the reaction enthalpy, LCgau-B97 shows lower errors than ω B97X.

Finally, we mention that ω B97XD^[52] may show affirmative performances on excited state energy calculations, in that ω B97XD also uses small μ value (0.2), even though we did not assess here. However, we hope to compare LCgau-B97 with ω B97XD as for not only the ground state properties and excitation energies but also various dispersion interactions when we study the combination of LCgau-B97 functional with dispersion interaction in future work, such as local response dispersion theory.^[53,54]

Conclusion

LCgau scheme was applied to B97 functional. In the optimizing process, μ parameter was fitted against local excitation energies and the other nonlinear and linear parameters were fitted against ground state properties. LCgau-B97 shows simultaneously high performances on intramolecular CT energy and local excitation energy as well as ground state properties. We found that a mixing of HF exchange ranging from 0.5 to 3.0 Å

significantly affects the calculation performances on ground state property while the local and CT excitation energy calculation performances are mainly dependent on the inclusion ratio of HF exchange in the range of more than 3.0 Å, which can be adjustable using μ value. We found that small μ value has an advantage on the calculations for local and intramolecular CT excitations, but, on the other hand, shows a disadvantage on Rydberg excitation energy calculations.

Acknowledgments

The numerical calculations were conducted on the RIKEN Cluster of Clusters (RICC).

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Received: 15 June 2011
Revised: 25 July 2011
Accepted: 25 July 2011
Published online on 26 August 2011