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REGULAR ARTICLE

Analytical optimization of orbital exponents in Gaussian-type functions for molecular systems based on MCSCF and MP2 levels of fully variational molecular orbital method

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Abstract We have analyzed the basis function series in molecular systems by optimization of orbital exponents in Gaussian-type functions (GTFs) including the electron correlation effects with multiconfiguration self-consistent field (MCSCF) and Møller–Plesset second-order perturbation (MP2) methods. First, we have derived and implemented the gradient formulas of MCSCF and MP2 energies with respect to GTF exponent, as well as GTF center and nuclear geometry, based on the fully variational molecular orbital (FVMO) method. Second, we have applied these electron-correlated FVMO methods to H_2, LiH, and hydrocarbon (CH_4, C_2H_6, C_2H_4, and C_2H_2) molecules. We have clearly demonstrated that the optimized exponent values with electron-correlated methods are different from those with simple Hartree–Fock method, since adequate basis functions for adequate virtual orbitals are indispensable to describe the accurate wave function and geometry for electron-correlated calculations.

Keywords Gaussian-type function · Orbital exponent in GTF · Fully variational molecular orbital (FVMO) · Electron correlation effect

1 Introduction

According to the rapid developments of theoretical methodology and high-performance computers, ab initio molecular orbital (MO) calculations of molecular system composed of thousands of atoms become possible [1–6]. Nowadays, ab initio MO calculations are used as a kind of experimental equipments, as well as the conventional experimental techniques, to obtain various properties for huge molecules. For example, the elongation method [1, 2] and fragment molecular orbital (FMO) method [3] have theoretically made it possible to calculate the structure and properties of large molecules, such as DNA and proteins. For more improvement of the estimation of various physical properties, the adequate basis functions with high accuracy for larger or fragment molecules would be expected.

As well known, although the Hartree–Fock (HF) method [7] yields about more than 99% of total electronic energies in ab initio MO methods, it often fails to obtain sufficient accuracy, and thus, the electron correlation methods [8–12] are indispensable for the accurate evaluation of some physical properties. The linear combination of atomic orbital (LCAO) expansion is widely used in MO calculation, and the Gaussian-type functions (GTFs) are often used in these basis or AO sets due to the convenience of the analytical integral calculations. According to the concept of LCAO approximation, many basis functions, such as the correlation consistent [13, 14] and polarization consistent [15, 16] basis sets, have been already proposed. We note here that in the conventional MO calculations such GTF exponents were already determined to obtain the best for the electronic ground state of each atom or small molecule and they are generally fixed during the variational procedure, in which only LCAO coefficients are optimized. Such conventional basis functions are, however, not always

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Dedicated to Professor Akira Imamura on the occasion of his 77th birthday and published as part of the Imamura Festschrift Issue.

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sufficient, and sometimes there are questions as to whether they are appropriate for the molecular calculations including electron correlation effect.

To answer these questions, we have already proposed the fully variational MO (FVMO) method [17], which is based on the optimization of all parameters under the variational principle. According to the FVMO scheme, all the variational parameters, such as the GTF exponents and centers, are simultaneously optimized as well as the nuclear geometries and LCAO coefficients. In addition, we have extended the energy gradient of FVMO method to the full-configuration interaction (CI) wave function [18] and applied to the calculation of low-lying singlet and triplet excited states of hydrogen molecule. We have found that the conventional basis functions are not so bad for the ground state of hydrogen molecule in HF level of calculation, while they cannot even qualitatively describe the excited states where the adequate basis functions for virtual orbitals are required. For example, the appropriate basis functions for π orbitals were essential for the full-CI calculation of each ground and excited state. However, it is not possible to employ such full-CI calculation even for medium-sized molecules, and other electron-correlated FVMO methods are needed for the applicable calculation.

In this article, thus, we would focus on other electron correlation methods, such as Møller–Plesset second-order perturbation (MP2) [8] and complete active space self-consistent field (CASSCF) [9] of multiconfiguration self-consistent field (MCSCF) methods. In the next section, we have derived the gradient formulas of the MP2 and MCSCF energies with respect to nuclear geometry, GTF center and exponent, based on the FVMO scheme. In Sect. 3, as test examples, we have applied our MP2 and MCSCF levels of the FVMO method to the H_2, LiH, and hydrocarbon (CH_4, C_2H_6, C_2H_4, and C_2H_2) molecules and optimized the orbital exponent values in GTFs, which are compared with the results under the HF to clarify the characteristic feature of electron correlation effect. Finally, some concluding remarks are shown in Sect. 4.

2 Theory

The μth Cartesian GTF (CGTF) is represented as follows:

$$\chi(\alpha_\mu, \mathbf{R}_\mu) = N(\alpha_\mu)(x - X_\mu)^{l_\mu}(y - Y_\mu)^{m_\mu}(z - Z_\mu)^{n_\mu} \exp\left\{-\alpha_\mu(\mathbf{r} - \mathbf{R}_\mu)^2\right\}, \qquad (1)$$

where N(α_μ) is a normalization factor. The notations of (α_μ) and $\mathbf{R}_\mu = \{X_\mu, Y_\mu, Z_\mu\}$ are GTF exponent and coordinate of CGTF center, respectively. Hereafter, we denote all parameters of (α_μ) and $\mathbf{R}_\mu$ are denoted as Ω. We note here that the quantum-mechanically virial [19] and Hellmann–Feynman [20] theorems are completely satisfied when one employs the optimization of the GTF exponents and centers, respectively.

The total electronic energy and energy gradient with respect to Ω under HF level of calculation are expressed as follows:

$$E_{\mathrm{HF}}^{\mathrm{elec}} = 2\sum_{i}^{\mathrm{IMO}} f_i h_{ii} + \sum_{ij}^{\mathrm{IMO}} \{a_{ij}(ii|jj) + b_{ij}(ij|ji)\}, \qquad (2)$$

$$\frac{\partial E_{\mathrm{HF}}^{\mathrm{elec}}}{\partial \Omega} = 2\sum_{i}^{\mathrm{IMO}} f_i h_{ii}^{\Omega} + \sum_{ij}^{\mathrm{IMO}} \left\{a_{ij}(ii|jj)^{\Omega} + b_{ij}(ij|ji)^{\Omega}\right\} - 2\sum_{ij}^{\mathrm{IMO}} S_{ij}^{\Omega}\varepsilon_{ij}, \qquad (3)$$

where f_i is the occupation number of the ith molecular orbital. The coefficients a_{ij} and b_{ij} are the coupling constants of Coulomb $(ii|jj)$ and exchange $(ij|ji)$ molecular integrals, respectively, and ε_{ij} is the Lagrangian matrix. The notations of S_{ij}^{Ω}, h_{ij}^{Ω}, and $(ij|kl)^{\Omega}$ are so-called skeleton derivatives of the overlap, one-electron, and two-electron molecular integrals, defined as follows:

$$S_{ij}^{\Omega} = \sum_{\mu\nu}^{\mathrm{IAO}} C_{\mu}^{i} C_{\nu}^{j} \frac{\partial S_{\mu\nu}}{\partial \Omega}, \qquad (4)$$

$$h_{ij}^{\Omega} = \sum_{\mu\nu}^{\mathrm{IAO}} C_{\mu}^{i} C_{\nu}^{j} \frac{\partial h_{\mu\nu}}{\partial \Omega}, \qquad (5)$$

$$(ij|kl)^{\Omega} = \sum_{\mu\nu\rho\sigma}^{\mathrm{IAO}} C_{\mu}^{i} C_{\nu}^{j} C_{\rho}^{k} C_{\sigma}^{l} \frac{\partial(\mu\nu|\rho\sigma)}{\partial \Omega}, \qquad (6)$$

where C_{μ}^{i} is the LCAO coefficient, IMO and IAO are the numbers of molecular and atomic orbitals, respectively.

The MCSCF energy in molecular orbital basis can be written down as

$$E_{\mathrm{MCSCF}}^{\mathrm{elec}} = \sum_{IJ}^{\mathrm{Nconf}} C_I C_J H_{IJ} = \sum_{ij}^{\mathrm{IMO}} \gamma_{ij} h_{ij} + \sum_{ijkl}^{\mathrm{IMO}} \Gamma_{ijkl}(ij|kl), \qquad (7)$$

and the corresponding energy gradient of $E_{\mathrm{MCSCF}}^{\mathrm{elec}}$ with respect to Ω in atomic orbital basis is expressed as follows:

$$\frac{\partial E_{\mathrm{MCSCF}}^{\mathrm{elec}}}{\partial \Omega} = \sum_{\mu\nu}^{\mathrm{IAO}} \gamma_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial \Omega} + \sum_{\mu\nu\rho\sigma}^{\mathrm{IAO}} \Gamma_{\mu\nu\rho\sigma} \frac{\partial(\mu\nu|\rho\sigma)}{\partial \Omega} - \sum_{\mu\nu}^{\mathrm{IAO}} W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial \Omega}, \qquad (8)$$

where C_I is the CI coefficient, γ_{ij} and Γ_{ijkl} ($\gamma_{\mu\nu}$ and $\Gamma_{\mu\nu\rho\sigma}$) are the one- and two-electron reduced density matrices in molecular orbital (atomic orbital) basis, and $W_{\mu\nu}$ is the energy weighted density matrix in atomic orbital basis [21].

The MP2 energy, for a closed shell system, can be written in terms of sums over spatial orbital as

$$E_{\mathrm{MP2}}^{\mathrm{corr}} = 2\sum_{ab}^{\text{d.o.}}\sum_{rs}^{\text{virt.}}\frac{(ar|bs)^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} - \sum_{ab}^{\text{d.o.}}\sum_{rs}^{\text{virt.}}\frac{(ar|bs)(as|br)}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}, \tag{9}$$

where a, b and r, s are occupied and virtual molecular orbitals, respectively. The energy gradient of $E_{\mathrm{MP2}}^{\mathrm{corr}}$ with respect to Ω is expressed as follows:

$$\frac{\partial E_{\mathrm{MP2}}^{\mathrm{corr}}}{\partial\Omega} = 2\sum_{ab}^{\text{d.o.}}\sum_{rs}^{\text{virt.}}\frac{2(ar|bs)-(as|br)}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\frac{\partial(ar|bs)}{\partial\Omega} - \sum_{ab}^{\text{d.o.}}\sum_{rs}^{\text{virt.}}\frac{(ar|bs)\{2(ar|bs)-(as|br)\}}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)^2}\left(\frac{\partial\varepsilon_a}{\partial\Omega}+\frac{\partial\varepsilon_b}{\partial\Omega}-\frac{\partial\varepsilon_r}{\partial\Omega}-\frac{\partial\varepsilon_s}{\partial\Omega}\right). \tag{10}$$

We note here that the coupled perturbed HF (CPHF) equation [22] is required for the calculation of $\frac{\partial\varepsilon_a}{\partial\Omega}$ and $\frac{\partial(ar|bs)}{\partial\Omega}$. The MCSCF and MP2 optimization algorithms based on the FVMO method are shown in Figs. 1 and 2, respectively. We have utilized the method by McMurchie and Davidson [23] to evaluate the overlap, one- and two-electron integrals with CGTF and corresponding gradient formulas. The energy gradient with respect to GTF exponents has been evaluated in the scale of their natural logarithms. The updated Hessian matrix is constructed from the analytical gradients using the Davidon, Fletcher, and Powell method [24] to find the stationary point on energy hypersurface. The convergence of optimization is judged when the maximum value and the root mean square of gradients become less than 1×10^{-5} and 5×10^{-6}, respectively.

Our developed FVMO schemes for MCSCF and MP2 have made it possible to perform simultaneous optimization not only for nuclear geometry but also for GTF center and exponent. Meanwhile, in this article, we focused on the optimization of only GTF exponent and nuclear geometry, while all CGTF centers were fixed on each nuclear position through the optimization procedure. We calculated H_2, LiH, and hydrocarbon (CH_4, C_2H_6, C_2H_4, and C_2H_2) molecules, as test examples, to analyze the optimum basis sets with electron correlation effect under the CASSCF and MP2 levels of wave functions. At the practical point of view, we note here that the computational cost for our scheme is time-consuming especially due to the derivative of two-electron integrals with respect to GTF exponents. All calculations are carried out using our own program package of the MC_MO [25].

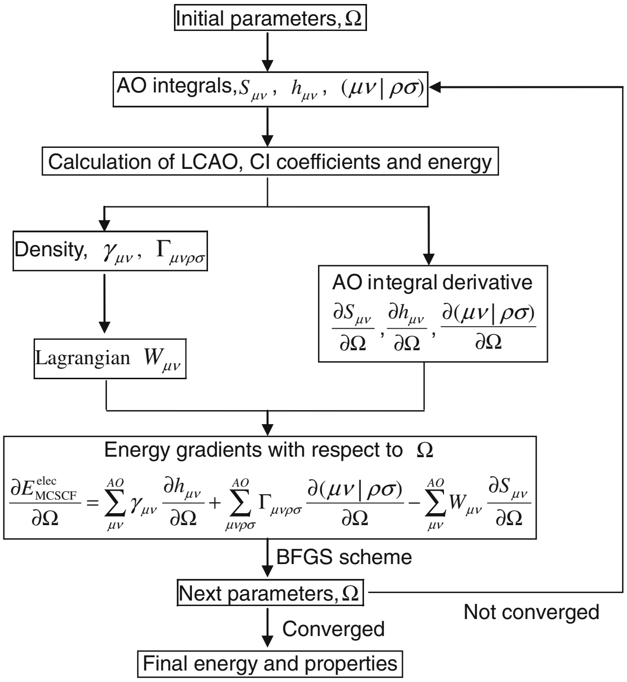

Fig. 1 Optimization algorithm for MCSCF method

3 Results and discussion

3.1 H_2 molecule

First, we calculate H_2 molecule with HF, MP2, CAS(2,2) (two electrons in $1\sigma_g$ and $1\sigma_u$ orbitals), CAS(2,6) (two electrons in $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, $1\pi_u$, and $1\pi_g$ orbitals), and full-CI levels using uncontracted [4s1p] GTFs. Table 1 shows the optimized results of GTF exponents, total energies, relative energies from HF level, and optimized internuclear distance by each level of calculation. The values in parentheses are the ratios of the optimized exponent values by electron correlation and HF methods ($\alpha^{\mathrm{corr}}/\alpha^{\mathrm{HF}}$). The initial values of the exponents of [4s1p] GTFs are taken from the values of Huzinaga's [4s] basis set [26] scaled by the conventional universal factor 1.2, and the initial exponent value of p-type GTF as a polarization function is set to 1.0000. The HF energy with the initial [4s1p] basis set is −1.131269 au.

First, we have optimized GTF exponents and geometry under HF level, and the energy is −1.131590 au which does not change so much compared with the initial set (−1.131269 au). Actually, the optimized value of the exponent of p-type GTF, 1.0268, is very close to the conventional initial one, 1.0000. Then, we have optimized GTF exponents and geometry under electron-correlated levels. The s-type GTF exponent values ([4s] part of basis function) optimized with MP2, CASSCF, and full-CI levels are very similar to those optimized with HF level.

Fig. 2 Optimization algorithm for MP2 method

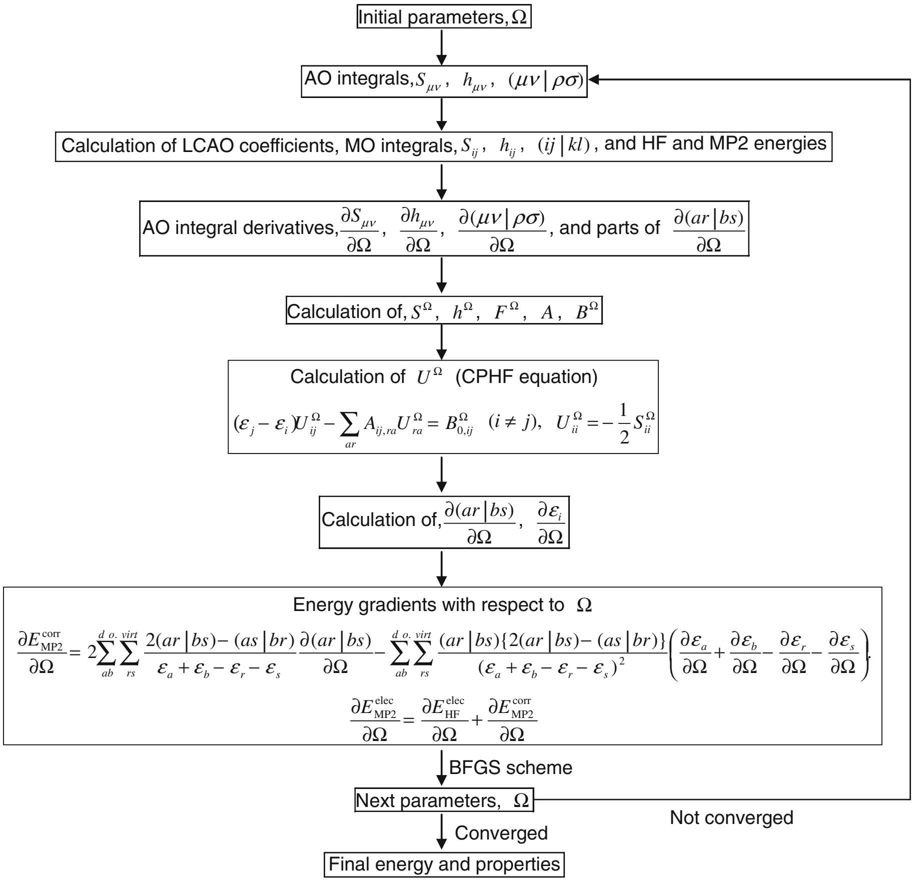

Table 1 Optimized GTF exponent values of uncontracted [4s1p] GTF basis set for H in H_2 molecule with HF, MP2, CASSCF, and full-CI levels

	HF	MP2	CAS(2,2)	CAS(2,6)	Full-CI
s1	15.9835	15.9506 (1.00)	16.1789 (1.01)	17.1863 (1.08)	16.5475 (1.04)
s2	2.4041	2.4588 (1.02)	2.4337 (1.01)	2.6227 (1.00)	2.5391 (1.06)
s3	0.5508	0.5846 (1.06)	0.5645 (1.02)	0.6144 (1.12)	0.6007 (1.09)
s4	0.1506	0.1580 (1.05)	0.1540 (1.02)	0.1624 (1.08)	0.1606 (1.07)
p1	1.0268	0.7866 (0.77)	1.1078 (1.08)	0.6918 (0.67)	0.7157 (0.70)
Energy (au)	−1.131590	−1.159433	−1.150372	−1.166212	−1.167562
ΔE (kcal/mol)	0.00	−17.47	−11.79	−21.73	−22.57
R_{HH} (au)	1.3870	1.3949	1.4271	1.4090	1.4080

Total energies, relative energies from HF approximation (ΔE), and optimized internuclear distances (R_{HH}) are also shown. Values in parentheses are ratio of the optimized exponent values by electron correlation method and HF ($\alpha^{\mathrm{corr}}/\alpha^{\mathrm{HF}}$)

Meanwhile, the tendency of the optimized p-type GTF is drastically different from that of the s-type GTFs, that is, the optimized exponent value with MP2 is 0.77 times smaller than that by HF. This result indicates that in the calculation of MP2 the diffusive character of basis functions is required for the virtual π orbitals. Similar trends are obtained by the CAS(2,6) and full-CI wave functions, while the optimized p-type exponent value with CAS(2,2) where no π orbitals are included in active space is very similar to that with HF level.

Table 1 clearly shows that the internuclear distances of H_2 molecule calculated with the electron correlation methods (MP2, CAS(2,6), and full-CI) are close to the experimental value (1.4010 au) [27] within 0.01 au, due to the optimization of exponent values in GTFs even though the small number of basis functions. Contrary to them, the internuclear distance by CAS(2,2) is quite longer than the experimental value, due to the overestimation of the contribution for the anti-bonding $1\sigma_u$ orbital. The adequate basis functions for adequate virtual orbitals are indispensable for electron correlation calculations to obtain the accurate wave function, the total energy, and the reproduction of the molecular geometry.

3.2 LiH molecule

The optimized exponent values of [6s3p/3s] GTFs for LiH molecule are shown in Table 2. The initial values of the exponents are taken from the primitive values of Pople's STO-3G basis set [28]. The optimized exponent values of GTFs in inner part become greater than those of the initial sets, due to the nuclear-electron cusp. To clarify the electron correlation effect for basis sets, we have compared the results optimized by MP2 and CASSCF methods with those by HF.

For LiH molecule, we performed the optimization with MP2, CAS(4,5) (four electrons in 1–3σ and 1–2π orbitals), and CAS(4,9) (four electrons in 1–5σ and 1–4π orbitals) levels of calculation. Table 3 shows the total energies, relative energies from HF energy, and optimized internuclear distances. The total energy obtained by MP2 was found to be close to that one by CAS(4,9). Figure 3 shows the values of the ratios $\alpha^{\mathrm{corr}}/\alpha^{\mathrm{HF}}$, where the similar trends are observed among MP2 and CASSCF calculations. Especially, the optimized exponent values of p-type functions are much greater than those of HF. Strictly speaking, the inner s-type GTF exponent values on Li (Li1s and Li2s) by MP2 calculation are a little smaller than those by HF. Contrary, the outer s-type GTF exponent values on Li by MP2 calculation are same or a little greater.

We also calculated the dipole moment as an example of physical properties with the optimized GTF exponent values. These results are also shown in Table 3. Contrary to the case of total energy and geometrical parameter, focused on this article, we cannot obtain the improved results for the dipole moment. As shown in the previous articles

Table 2 Optimized GTF exponent values of uncontracted [6s3p/3s] basis set for LiH molecule under HF level

		LiH
Li	s1	262.7889
	s2	39.5467
	s3	8.9365
	s4	2.4157
	s5	0.7075
	s6	0.0558
	p1	1.3747
	p2	0.2474
	p3	0.0486
H	s1	6.1358
	s2	0.9181
	s3	0.1904

Table 3 Total energies, relative energies from HF approximation (ΔE), optimized internuclear distances (R_{LiH}), and dipole moment for LiH molecule obtained by HF, MP2, and CASSCF

	HF	MP2	CAS(4,5)	CAS(4,9)
Energy (au)	−7.979088	−8.022399	−7.998329	−8.024656
ΔE (kcal/mol)	0.00	−27.18	−12.07	−28.59
R_{LiH} (au)	3.0276	3.0190	3.0208	3.0697
Dipole moment (D)	5.874	5.886	5.544	5.528

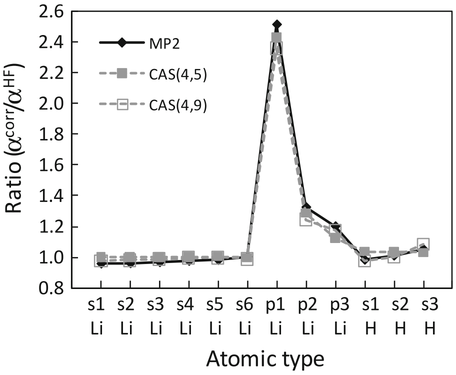

Fig. 3 Ratios of the optimized exponent values by electron correlation method (MP2 and CASSCF) and HF ($\alpha^{\mathrm{corr}}/\alpha^{\mathrm{HF}}$) for LiH molecule

Table 4 Optimized GTF exponent values of uncontracted [10s4p/4s] basis set for C/H in CH_4, C_2H_6, C_2H_4, and C_2H_2 molecules under HF level

		CH_4	C_2H_6	C_2H_4	C_2H_2
C	s1	15077.95	14707.70	14651.20	14410.34
	s2	2260.332	2204.937	2196.414	2160.353
	s3	514.4552	501.8678	499.9172	491.7302
	s4	145.6532	142.109	141.5511	139.2520
	s5	47.4122	46.2771	46.0885	45.3593
	s6	16.9481	16.5612	16.4862	16.2462
	s7	6.4566	6.03292	6.2943	6.2246
	s8	2.5276	2.4918	2.4744	2.4613
	s9	0.5137	0.4926	0.5048	0.5338
	s10	0.1966	0.1803	0.1749	0.1655
	p1	12.5941	11.8775	10.8688	10.3515
	p2	2.7078	2.5438	2.3223	2.2223
	p3	0.7157	0.6706	0.6052	0.5978
	p4	0.2224	0.2060	0.1623	0.1617
H	s1	20.1881	21.0453	21.9643	23.1085
	s2	3.0714	3.2018	3.3314	3.5197
	s3	0.6608	0.6797	0.6977	0.7614
	s4	0.1356	0.1444	0.1962	0.2069

Table 5 Total energies, relative energies from HF approximation (ΔE), and optimized geometrical parameters (R_{CH} and R_{CC}) for CH_4, C_2H_6, C_2H_4, and C_2H_2 molecules obtained by HF and MP2

	HF	MP2	MP2[a]	MP2[b]	Exptl.[c]
CH_4					
Energy (au)	−40.208939 (−39.726863)	−40.421722 (−39.783524)	−40.360175	−40.411666	
ΔE (kcal/mol)	0.00 (0.00)	−90.48 (−35.56)			
R_{CH} (au)	2.0444 (2.0466)	2.0481 (2.0772)	2.0778	2.0512	2.0541
C_2H_6					
Energy (au)	−79.251306 (−78.306180)	−79.653256 (−78.414269)	−79.537475	−79.629908	
ΔE (kcal/mol)	0.00 (0.00)	−173.83 (67.83)			
R_{CC} (au)	2.8735 (2.9058)	2.8560 (2.9385)	2.8912	2.8800	2.9026
R_{CH} (au)	2.0501 (2.0523)	2.0574 (2.0846)	2.0836	2.0566	2.0617
C_2H_4					
Energy (au)	−78.051683 (−77.073955)	−78.423394 (−77.196284)	−78.315302	−78.389306	
ΔE (kcal/mol)	0.00 (0.00)	−167.98 (−76.76)			
R_{CC} (au)	2.4833 (2.4680)	2.5090 (2.5413)	2.5427	2.5174	2.5303
R_{CH} (au)	2.0331 (2.0447)	2.0433 (2.0756)	2.0689	2.0418	2.0522
C_2H_2					
Energy (au)	−76.838525 (−75.856280)	−77.189113 (−76.004660)	−77.082680	−77.159196	
ΔE (kcal/mol)	0.00 (0.00)	−168.98 (−93.11)			
R_{CC} (au)	2.2324 (2.2080)	2.2852 (2.3022)	2.3237	2.2890	2.2733
R_{CH} (au)	1.9928 (2.0133)	2.0070 (2.0421)	2.0326	2.0060	2.0088

Results of the conventional geometry optimization with the initial GTF exponent values are in parentheses

[a] MP2/cc-pVDZ

[b] MP2/cc-pVTZ

[c] Taken from Refs. [33, 34]

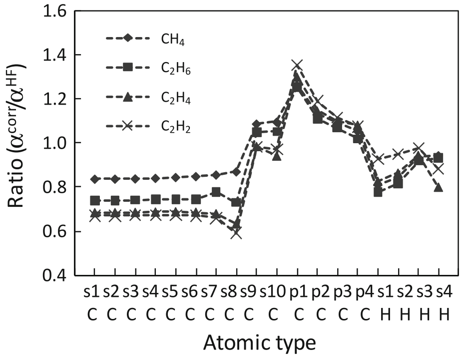

Fig. 4 Ratios of the optimized exponent values by electron correlation method (MP2) and HF ($\alpha^{corr}/\alpha^{HF}$) for hydrocarbon molecules (CH_4, C_2H_6, C_2H_4, and C_2H_2)

[29, 30], further development is necessary to improve the various physical properties.

3.3 Hydrocarbon molecules

Finally, we show the optimized exponent values of [10s4p/4s] GTFs for CH_4, C_2H_6, C_2H_4, and C_2H_2 under the HF level in Table 4. The optimized exponent values of GTFs in inner part become greater than those with the initial sets [31]. To clarify the electron correlation effect for basis sets, here, we compared the results obtained by MP2 method with those ones by HF [32].

Table 5 shows the total energies, relative energies from HF level, and optimized geometrical parameters obtained by MP2. To see the effect of optimization of GTF exponent along with the geometry, the results of the conventional geometry optimization by MP2 with the initial GTF exponent values (in parentheses), conventional cc-pVDZ, and cc-pVTZ are also shown in Table 5. These results clearly show that the total energy is drastically improved due to the optimization of GTF exponents, and actually our energy is lower than the conventional MP2/cc-pVDZ and MP2/cc-pVTZ levels of calculation. The geometrical parameters, especially C–H bond distances, along with the optimization of exponent values are actually found to be 0.02–0.03 au close to the corresponding experimental values [33, 34]. One of the reasons for such improvement of the total energy and geometry are due to the adequate description of different sp^3-, sp^2-, and sp-hybrid characters of carbon atom.

The values of the ratios $\alpha^{corr}/\alpha^{HF}$ are shown in Fig. 4. The optimized exponent values in s-type GTFs on carbon atom by MP2 tend to be smaller than those by HF. The difference of the ratio among each hydrocarbon molecule is caused by the difference of sp^3-, sp^2-, and sp-hybrid characters. Interestingly, the ratios of sp^3-hybrid character in CH_4 and C_2H_6 are greater than those of sp^2- and sp-hybrid characters in C_2H_4 and C_2H_2. Contrary, the optimized exponent values in p-type GTFs on carbon atom by MP2 tend to be greater than those by HF. The optimization of GTF exponent values is, thus, effective to describe adequate basis functions for each atom in molecular systems.

The optimization of the exponent values of polarization and diffusive functions for excited states or triplet states should be quite interesting subjects. In addition, the applications to chemical reaction including hetero and heavy atoms are also our next targets by using our FVMO method. Meanwhile, in this article, we have reported only singlet ground state molecules with small basis functions, as the first step of the electron-correlated FVMO method. Although, at the practical point of view, the actual computational cost for our scheme is quite time-consuming, especially due to the derivative of two-electron integrals with respect to GTF exponents, we believe that such molecular-optimized basis sets under the electron correlation calculations would be necessary for the more accurate description of geometry parameters, and various physical and chemical properties. We also believe that such molecular-optimized basis sets are suitable for the calculation with elongation [1] or FMO [3] methods. Such studies are now in progress.

4 Conclusions

To develop suitable basis functions in molecular systems for electron correlation calculation, we have derived the energy gradient of MCSCF and MP2 with respect to nuclear geometry, GTF center and exponent, based on the FVMO method. Our developed methods are applied to the H_2, LiH, and hydrocarbon (CH_4, C_2H_6, C_2H_4, and C_2H_2) species, as test molecules. In the case of H_2 molecule, optimized exponent values of s- and p- type functions in GTFs under the MP2 and CASSCF are greater and smaller, respectively, than those one under the HF. In LiH and hydrocharbon molecules, we have also demonstrated the difference of basis function for HF and post-HF (MP2 and CASSCF) methods, because the optimized exponent values are drastically changed. Our developed methods are effective to analyze and determine basis functions for each atom in molecular systems of the post-HF calculations. The adequate exponents for excited states or triplet states are now in progress.

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