Practical electronic ground- and excited-state calculation method for lanthanide complexes based on frozen core potential approximation to 4f electrons *

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Abstract

A practical electronic ground- and excited-state calculation method for lanthanide complexes is proposed by introducing frozen core potential (FCP) approximation to 4f electrons of a lanthanide atom ion (Ln^{3+}). Based on the fact that the FCP method is formally equivalent to the elongation method, the 4f-frozen FCP calculations of Ln^{3+} complexes were successfully performed using the elongation method implemented in GAMESS quantum chemistry program. By comparing the 4f-frozen FCP calculation results of several lanthanide complexes with the results of the standard calculations, it was confirmed that the excitation energies by these calculations are comparable. Also, the SCF convergence and stability were significantly improved by the FCP approximation. We further propose a method to relax the rotational degrees of freedom for the frozen 4f orbitals. This relaxation slightly improves the accuracy of the excitation energies for f-f transitions.

Keywords: Frozen 4f core potential approximation, Lanthanide complexes, Elongation method

*This article is dedicated to Prof. János Pipek.

1 Introduction

A series of the molecular orbital (MO) theories [1] has been widely utilized, as compared to the valence bond (VB) theory [2, 3] and related generalized VB [4] or geminal wavefunction theories [5–7], as the practical calculation methods for obtaining molecular electronic structures. A disadvantage of the MO theory and related Kohn–Sham (KS) density functional theory (DFT) [8, 9] against the VB theory is that the methods give extremely delocalized canonical MOs. The concept of the localized MOs first introduced by Boys [10] and developed by Edmiston and Ruedenberg [11] and Pipek and Mezey [12] has been used not only as the analysis technique of the electronic structures but also in the acceleration of the electron correlation calculations [13]. The elongation method [14–16] is another example of utilizing localized MOs for the calculation of large-scale systems. Large-scale molecular calculations based on the local canonical MOs, the concept of which was inspired by the localized MOs, have also been developed drastically for last two decades [17–25].

Lanthanide complexes are widely known as luminescent compounds with characteristic narrow emission bands and long emission lifetimes derived from f-f transition, and they have been put into a practical use as various luminescent materials [26, 27]. Since 4f electrons exist in the core and are hardly affected by chemical environment, the emission wavelength originating from f-f transition is characterized almost independent of the ligands. On the other hand, the luminance and the emission quantum yield may be affected by the other electronic excited states such as the ligand excited states and ligand-to-metal/metal-to-ligand charge-transfer (LMCT/MLCT) states [28–30]. For adequately investigating them, relative energy levels of all the relevant states as well as those of their crossing points should be determined. Although an electronic state calculation based on a multi-reference wave function is required for accurate description of multiple potential energy surfaces, the application of conventional methods to actual lanthanide complexes is still difficult in terms of computational costs. In addition, even if a single-reference theory or DFT calculation is used, a serious problem arises in the convergence of self-consistent field (SCF) calculation because lanthanide complexes often have pseudo-degenerate electronic states owing to the open shell 4f electrons.

Hatanaka and Morokuma [31] proposed a strategy called the energy shift method for estimating the crossing points between the f-f excited state and the other excited states. In this method, the potential energy surface of the f-f excited state is approximated to be parallel to the ground state due to the fact that the change of the 4f electronic states hardly affect the valence electronic stracture. Although this method is a powerful tool to identify the crossing point between the ligand excited and f-f excited states, it should refer to the experimental f-f transition energy as the offset of these two states.

In this study, we propose a simple calculation method for treating both electronic ground and excited states of lanthanide complexes by introducing frozen core potential (FCP) [32] approximation to 4f electrons of Ln^{3+} (Ln = La–Lu) in order to overcome the above mentioned problems. Here, we utilized the fact that the FCP method is formally equivalent to the elongation method [14–16], which has been developed for calculations of large polymeric systems and is implemented in the

GAMESS program package [33, 34]. The elongation method starts from the calculation of a small molecule, which is called the starting monomer. The next fragment (attacking monomer) is sequentially added one by one so as to follow the polymerization reaction of the polymer, and finally the calculation of the entire polymer is achieved. After an attacking monomer is added, the localized MOs are constructed and those far from the attacking monomer are then frozen. This frozen process can be diverted to the fixing of the 4f orbitals in the present FCP calculation. To realize the variation in the restricted variational space excluding the fixed orbitals, the elongation method utilizes so-called Huzinaga–Cantu equation [35], which is the basic equation in the FCP method.

The organization of this paper is the following. The present FCP approximation and its realization using the elongation program are denoted in Section 2. Numerical assessment of the method was performed for the calculation of CeF diatomic molecule and several lanthanide complexes in Section 3. Finally the concluding remarks will be addressed in Section 4.

2 Methods

2.1 FCP method using the program of elongation method

Here, we summarize the theoretical and computational aspects of the present method. Since our calculations were performed using the module of the elongation method [15] implemented in GAMESS program, our FCP scheme is explained in terms of the elongation method. We assume that the inner-core Ln electrons (1s to 4d) are treated with the model core potential (MCP) [36].

In the present method, the calculation of a mononuclear lanthanide complex is initiated by the Hartree–Fock (HF) or KS calculation of Ln^{3+} with adopting MCP for 1s to 4d electrons (the charge of the Ln atom is not necessarily set to +3, depending on the electronic structure one wants to obtain).

$$\mathbf{F}^{\mathrm{Ln}}\mathbf{C}^{\mathrm{Ln}} = \mathbf{S}^{\mathrm{Ln}}\mathbf{C}^{\mathrm{Ln}}\boldsymbol{\varepsilon}^{\mathrm{Ln}}. \tag{1}$$

Here, $\mathbf{F}^{\mathrm{Ln}}$ and $\mathbf{S}^{\mathrm{Ln}}$ are the Fock/KS and overlap matrices for Ln^{3+} system. According to the procedure of the elongation method, the atomic orbitals (AOs) of the Ln atom is divided into A and B *regions*, where the A region includes 7 (or 10 in case of Cartesian Gaussian basis) 4f orbitals and the B region includes the remaining orbitals. From the density matrix $\mathbf{D}^{\mathrm{Ln}}$, whose elements are given by,

$$D^{\mathrm{Ln}}_{\mu\nu} = \sum_{i}^{\mathrm{occ}} C^{\mathrm{Ln}}_{\mu i} C^{\mathrm{Ln}*}_{\nu i}, \tag{2}$$

one can obtain so-called regional localized molecular orbitals (RLMOs), among which those corresponding to the A region will be fixed as the frozen core orbitals during the following calculation of the complex. Note that the obtained 4f RLMOs are not only expanded by the 4f AOs but also has contribution from the other AOs (especially p orbitals for symmetrical reason).

Then, the lanthanide complex is calculated with fixed 4f orbitals. In the terminology of the elongation method, all ligands of the lanthanide complex is treated as the *attacking monomer* or M region. For removing the 4f orbitals from the variational space, the transformed Fock matrix is adopted during the calculation of complex:

$$F_{pq}^{\mathrm{cmplx}} = \sum_{\mu\nu} L_{\mu p}(\mathrm{B}+\mathrm{M}) F_{\mu\nu}^{\mathrm{AO,cmplx}} L_{\nu q}(\mathrm{B}+\mathrm{M}), \tag{3}$$

$\mathbf{L}(\mathrm{B}+\mathrm{M})$ is a rectangular transformation matrix from the AO basis to an orthogonal basis corresponding to B+M region. Note that the virtual 4f RLMOs are also removed from the variational space. In the FCP method, this treatment is realized by solving so-called Huzinaga–Cantu equation [35]. The HF/KS equation for the lanthanide complex is then given by the following:

$$\mathbf{F}^{\mathrm{cmplx}}\mathbf{U}^{\mathrm{cmplx}} = \mathbf{U}^{\mathrm{cmplx}}\boldsymbol{\varepsilon}^{\mathrm{cmplx}}. \tag{4}$$

Solving eq. (4) is fairly easier than solving the original HF/KS equation of the lanthanide complex since quasi-degenerate 4f orbitals, which usually cause slow SCF convergence, are fixed during the SCF procedure. The MOs other than the frozen 4f orbitals are expressed in the AO basis with $\mathbf{L}$ and $\mathbf{U}^{\mathrm{cmplx}}$ by

$$C_{\mu i}^{\mathrm{other}} = \sum_{p} L_{\mu p}(\mathrm{B}+\mathrm{M}) U_{pi}^{\mathrm{cmplx}}. \tag{5}$$

2.2 Relaxation of the rotational degrees of freedom in FCP calculation

In the present FCP method, the 4f orbitals of lanthanide complexes, which create pseudo-degenerate electronic states leading severe SCF convergence, are fixed with the orbitals obtained from the calculations of lanthanide ions. Although the inner-shell 4f electrons are considered to be hardly affected by the ligand field, there still remains a room to optimize the direction of the frozen 4f orbitals in the FCP approximation. Therefore, we further conducted the optimization of the rotational degrees of freedom in the FCP approximation.

In the rotational optimization, the rotation matrix is applied to the orbital coefficients of the 4f orbitals obtained by the calculation of the lanthanide ion and obtained orbitals are used in the following FCP calculation of the lanthanide complex. In the present implementation, this optimization is achieved by numerically locating the minimum energy point by optimizing roll, pitch, and yaw angles, θ_z, θ_y, and θ_x, separately and iteratively. For fixed rotational angles, the rotation matrix $\mathbf{R}$ is expressed with these angles by

$$\mathbf{R} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta_x & -\sin\theta_x \\ 0 & \sin\theta_x & \cos\theta_x \end{pmatrix} \begin{pmatrix} \cos\theta_y & 0 & \sin\theta_y \\ 0 & 1 & 0 \\ -\sin\theta_y & 0 & \cos\theta_y \end{pmatrix} \begin{pmatrix} \cos\theta_z & -\sin\theta_z & 0 \\ \sin\theta_z & \cos\theta_z & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{6}$$

For p-type AOs mixed in the 4f orbitals, the coefficients of the rotated orbital, $\{\mathbf{c}'\}$, are straightforwardly obtained by

$$\begin{pmatrix} c'_x \\ c'_y \\ c'_z \end{pmatrix} = \begin{pmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{zy} & R_{zz} \end{pmatrix} \begin{pmatrix} c_x \\ c_y \\ c_z \end{pmatrix}. \tag{7}$$

For f-type AOs, the coefficients are obtained by, e.g.,

$$\begin{aligned} c'_{xxx} =& R^3_{xx}c_{xxx} + R^3_{xy}c_{yyy} + R^3_{xz}c_{zzz} + \sqrt{3}R_{xy}R^2_{xx}c_{xxy} + \sqrt{3}R_{xz}R^2_{xx}c_{xxz} \\ &+ \sqrt{3}R_{xx}R^2_{xy}c_{yyx} + \sqrt{3}R_{xz}R^2_{xy}c_{yyz} + \sqrt{3}R_{xx}R^2_{xz}c_{zzx} \\ &+ \sqrt{3}R_{xy}R^2_{xz}c_{zzy} + \sqrt{6}R_{xx}R_{xy}R_{xz}c_{xyz}, \end{aligned} \tag{8}$$

$$\begin{aligned} c'_{xxy} =& \sqrt{3}R^2_{xx}R_{yx}c_{xxx} + \sqrt{3}R^2_{xy}R_{yy}c_{yyy} + \sqrt{3}R^2_{xz}R_{yz}c_{zzz} \\ &+ [2R_{xx}R_{xy}R_{yx} + R^2_{xx}R_{yy}]c_{xxy} + [2R_{xz}R_{xx}R_{yx} + R^2_{xx}R_{yz}]c_{xxz} \\ &+ [2R_{xx}R_{xy}R_{yy} + R^2_{xy}R_{yx}]c_{yyx} + [2R_{xy}R_{xz}R_{yy} + R^2_{xy}R_{yz}]c_{yyz} \\ &+ [2R_{xz}R_{xx}R_{yz} + R^2_{xz}R_{yx}]c_{zzx} + [2R_{xy}R_{xz}R_{yz} + R^2_{xz}R_{yy}]c_{zzy} \\ &+ \sqrt{2}(R_{xy}R_{xz}R_{yx} + R_{xz}R_{xx}R_{yy} + R_{xx}R_{xy}R_{yz})c_{xyz}, \end{aligned} \tag{9}$$

and

$$\begin{aligned} c'_{xyz} =& \sqrt{6}R_{xx}R_{yx}R_{zx}c_{xxx} + \sqrt{6}R_{xy}R_{yy}R_{zy}c_{yyy} + \sqrt{6}R_{xz}R_{yz}R_{zz}c_{zzz} \\ &+ \sqrt{2}\{[R_{xx}R_{yy} + R^2_{xy}R_{yx}]R_{zx} + R_{xx}R_{yx}R_{zy}\}c_{xxy} \\ &+ \sqrt{2}\{[R_{xx}R_{yz} + R^2_{xz}R_{yx}]R_{zx} + R_{xx}R_{yx}R_{zz}\}c_{xxz} \\ &+ \sqrt{2}\{[R_{xx}R_{yy} + R^2_{xy}R_{yx}]R_{zy} + R_{xy}R_{yy}R_{zx}\}c_{yyx} \\ &+ \sqrt{2}\{[R_{xy}R_{yz} + R^2_{xz}R_{yy}]R_{zy} + R_{xy}R_{yy}R_{zz}\}c_{yyz} \\ &+ \sqrt{2}\{[R_{xx}R_{yz} + R^2_{xz}R_{yx}]R_{zz} + R_{xz}R_{yz}R_{zx}\}c_{zzx} \\ &+ \sqrt{2}\{[R_{xy}R_{yz} + R^2_{xz}R_{yy}]R_{zz} + R_{xz}R_{yz}R_{zy}\}c_{zzy} \\ &+ \{[(R_{xy}R_{yz} + R_{xz}R_{yy}]R_{zx} + [(R_{xx}R_{yz} + R_{xz}R_{yx}]R_{zy} \\ &+ [(R_{xx}R_{yy} + R_{xy}R_{yx}]R_{zz}\}c_{xyz}. \end{aligned} \tag{10}$$

3 Numerical Assessments

In this manuscript, all the quantum chemical calculations were performed by utilizing the elongation method program implemented in the GAMESS package [33, 34], while the rotational optimization was performed by the hand-made python code. The MCP-DZP basis set [36, 37] was used for lanthanide atoms while the cc-pVDZ set [38, 39] was adopted for the other elements.

3.1 CeF molecule

The method above was first examined in calculation of CeF diatomic molecule, which is considered to be formed by the ionic interaction between Ce^+ and F^-. In small lanthanide molecules, consideration of the spin-orbit coupling is essential for the accurate determination of electronic states [40, 41]. However, since the present method is oriented toward the calculation of large lanthanide complexes, the spin-orbit coupling effect is not treated in this manuscript. According to our accurate quantum chemical calculation [40], the ground-state configuration of Ce^+ in the CeF molecule is $[Xe]4f^15d^16s^1$. Therefore, in the FCP calculation, Ce^+ with $[Xe]4f^15d^16s^1$ configuration was adopted as the A+B region included in the initial calculation. Figure 1 shows the potential energy curve obtained by the standard and FCP HF calculations. Here, the standard calculation refers to the default HF computation by GAMESS program. The potential energy curve was analyzed by Vibrot program of Molcas [42] to obtain equilibrium bond length and harmonic vibrational frequency, which were summarized in Table 1. The total energy for r = 5.40 Å by the standard calculation was set to zero. The total energy by the FCP calculation shows good agreement with that by the standard calculation for the elongated system. At r = 5.40 Å, the difference between FCP and standard calculations is 0.08 eV. However, the energy difference becomes larger as the bond length decreases due to the FCP approximation: the difference is 1.57 eV at r = 2.11 Å. Accordingly, the calculated equilibrium bond length, r_e, and the harmonic frequency, ω_e, by the FCP method was about 15 pm longer and 110 cm^{-1} smaller than those by the standard method, respectively. In this diatomic case, the environment of 4f electrons in Ce is strongly anisotropic due to the unidirectional Coulombic interaction from F^-. Therefore, the FCP approximation causes large discrepancy from the non-approximate result. In case of lanthanide complexes with seven or more coordination, this discrepancy may be reduced because the environment of 4f electrons is considered to be more isotropic.

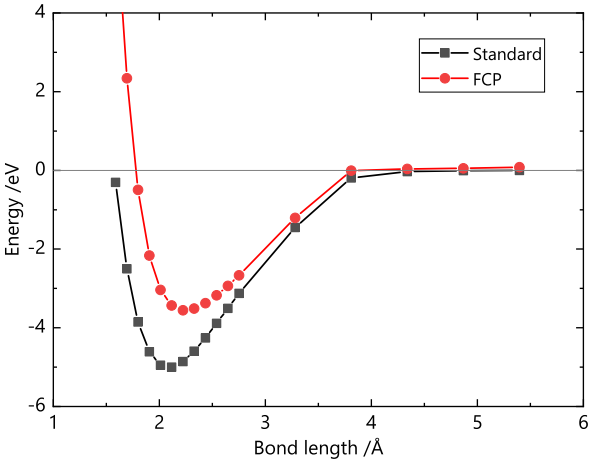

Fig. 1 Potential energy curve of CeF by the standard and FCP HF methods.

Table 1 Harmonic vibrational frequency (ω_e) and equilibrium bond length (r_e) of CeF calculated by the standard and FCP HF methods.

Method	Frequency ω_e / cm^{-1}	Equilibrium bond length r_{eq} / pm
Standard	564.4	208
FCP	454.0	224

We further applied the rotational optimization to the FCP result with r = 2.01 Å. Fig. 2(a) shows the occupied 4f orbital of CeF by the standard HF calculation. The orbital is perpendicular to the molecular axis and forms the π-type bonding interaction with the p orbital of F atom. By adopting the FCP approximation, the frozen occupied 4f orbital is represented as given in Fig. 2(b). Since the orbital is obtained from the spherical Ce^+ calculation, the orbital cannot mix with any AOs of F atom and its direction is purely random. Consequently, the total energy by the FCP approximation is 1.88 eV higher than that by the standard calculation. After applying the rotational optimization, the lobe of occupied 4f orbital is directed to F atom. The orbital represents the σ-type interaction rather than the π-type one, which is contrary to the standard calculation. This can be interpreted as the consequence of avoiding the repulsion with the occupied 5d orbital, which expands perpendicular to the molecular axis. By the rotational relaxation, the energy is stabilized by 0.11 eV.

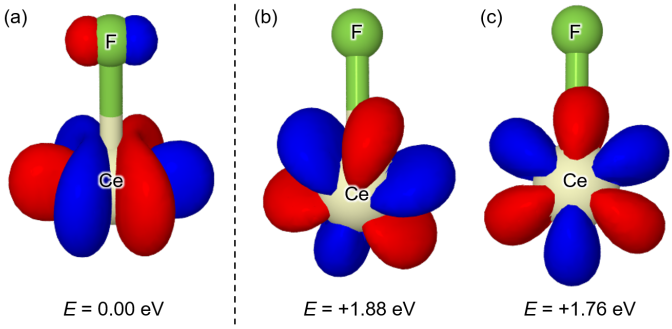

Fig. 2 Occupied 4f orbital of CeF obtained by (a) the standard HF method, (b) the FCP HF method without the rotational optimization, and (c) the FCP HF method with the rotational optimization. The relative total energy is also given at the bottom.

3.2 Lanthanide complexes

Next, the FCP method is applied to several lanthanide complexes, namely, $Eu(tmh)_3(tppo)$ [43] (tmh = 2,2,6,6-tetramethylheptane-3,5-dionate, tppo = triphenylphosphine oxide), $Gd(NO_3)_2(acac)(tpy)$ [44] (acac = acetylacetonate, tpy = terpyridine), $Tb(tmh)_3(tppo)$ [43], $Sm(dbm)_3(phen)$ [45] (dbm = dibenzoylmethanate, phen = 1,10-phenanthroline), and $Dy(dbm)_2(dtc)(phen)$ [46] (dtc = diethyldithiocarbamate). We here compare the excitation energy from the ground state to the spin-flip 4f-4f excited state, where both electronic structures are obtained from the SCF calculations of different spin multiplicity. In the FCP calculation, the frozen 4f orbitals

of each state are first obtained from the calculation of Ln^{3+} with corresponding spin multiplicity, and then the remaining ligands are attached to obtain the energy of the complex. The geometries of these complexes used in the calculations are obtained from the X-ray structures published in the reference mentioned above. In addition, the FCP method allows us to calculate spin-flip 4f-4f excited state and ligand T_1 excited state separately in the SCF scheme by using different Ln^{3+} FCP with the same overall spin multiplicity. Therefore, we also conducted the calculations of ligand T_1 excited states for Sm, Eu, and Tb complexes.

Table 2 lists the energies of ground and excited states of these complexes obtained by the standard and FCP HF calculations. For Sm, Eu, and Tb complexes, the rotational optimization of FCP was also applied, the result of which was given in "FCP-rot" row. The excitation energy by each method is given together in parentheses. Comparing the energies of each state of the complex between standard and FCP calculations, the difference is 3 eV or more, which is rather larger than the difference in CeF diatomic molecule. However, the f-f excitation energies by the FCP approximation only differ from those by the standard method by 0.1 eV or less. The excitation energy difference for the ligand triplet excitation energy is slightly larger, probably due to the mixing of undesired electronic configuration in the converged state in the standard calculation. It was confirmed that the FCP scheme provides a practical and accurate way of expressing energy levels of different states. The total energy change by the rotational optimization of FCP is less than 0.1 eV and the change in excitation energy is further small. Therefore, the rotational optimization of FCP is not mandatory for constructing the potential energy profile by the FCP method. In addition, the calculations of Eu complex in the f-f excited states and Dy complex in the ground state by the standard method did not converge when using the default MO guess. In such cases, the orbitals obtained by the FCP calculation were used as the initial guess orbital, leading the standard calculation to converge successfully. Therefore, it can also be stated that our computational scheme greatly improves the SCF convergence of the lanthanide complexes even when the FCP approximation is finally not adopted.

Table 3 lists the energies by the standard and FCP DFT calculations with B3LYP functional [47, 48]. As for the Sm complex, the story is almost similar to the HF case, namely, the excitation energy difference between standard and FCP calculations is only 0.01 eV. However, the excitation energy differences in the Tb complex is about 0.75 eV. To investigate the origin of the discrepancy, the difference electron density maps between ground and 4f-4f excited states were depicted in Fig. 3. In the case of Sm complex, where the excitation energy difference between standard and FCP B3LYP calculations is small, both methods show that the density change is concentrated on the 4f electrons of the central Sm atom. On the other hand, in the case of Tb complex with large energy difference, the electron density change by the standard calculation expands to a tmh ligand while that by the FCP calculation is concentrated on the central Tb atom. Since this is due to the mixing of 4f orbitals with ligand orbitals, the improvement by rotational optimization of FCP orbitals will be limited.

Table 2 Energies of the ground state (GS), spin-flip 4f-4f excited state (ES), and ligand T_1 ES of lanthanide complexes calculated by standard and FCP HF methods. The excitation energies are also given in parentheses

Complex	Method	GS energy / eV	4f-4f ES energy / eV	Ligand T_1 ES energy / eV
$Sm(dbm)_3(phen)$	(term)	(S_0-^{6}H)	(S_0-^{4}G)	(T_1-^{6}H)
	Standard	-76778.75	-76775.98 (2.77)	-76774.47 (4.28)
	FCP	-76771.63	-76768.93 (2.71)	-76767.32 (4.31)
	FCP-rot	-76771.66	-76768.93 (2.74)	-76767.37 (4.29)
$Eu(tmh)_3(tppo)$	(term)	(S_0-^{7}F)	(S_0-^{5}D)	(T_1-^{7}F)
	Standard	-79824.37	-79820.66 (3.72)	-79820.55 (3.82)
	FCP	-79817.56	-79813.94 (3.62)	-79813.92 (3.64)
	FCP-rot	-79817.59	-79813.95 (3.64)	-79813.97 (3.63)
$Tb(tmh)_3(tppo)$	(term)	(S_0-^{7}F)	(S_0-^{5}D)	(T_1-^{7}F)
	Standard	-80748.33	-80744.38 (3.95)	-80745.37 (2.96)
	FCP	-80742.81	-80738.87 (3.94)	-80739.65 (3.16)
	FCP-rot	-80742.86	-80738.94 (3.92)	-80739.72 (3.15)
$Gd(NO_3)_2(acac)(tpy)$	(term)	(S_0-^{8}S)	(S_0-^{6}I)	
	Standard	-47650.74	-47645.59 (5.15)	
	FCP	-47647.51	-47642.41 (5.10)	
$Dy(dbm)_2(dtc)(phen)$	(term)	(S_0-^{6}H)	(S_0-^{4}F)	
	Standard	-87336.83	-87333.73 (3.11)	
	FCP	-87333.30	-87330.19 (3.11)	

Table 3 Energies of the ground state (GS) and spin-flip 4f-4f excited state (ES) of lanthanide complexes calculated by standard and FCP B3LYP methods. The excitation energies are also given in parentheses

Complex	Method	GS energy / eV	4f-4f ES energy / eV
$Sm(dbm)_3(phen)$	(term)	(S_0-^{6}H)	(S_0-^{4}G)
	Standard	-77297.93	-77295.64 (2.29)
	FCP	-77291.71	-77289.43 (2.29)
$Tb(tmh)_3(tppo)$	(term)	(S_0-^{7}F)	(S_0-^{5}D)
	Standard	-81286.20	-81283.08 (3.12)
	FCP	-81280.91	-81277.03 (3.88)

4 Concluding Remarks

In this study, we applied the frozen-core potential approximation to fixing the 4f orbitals of the lanthanide atom, which often cause serious problem on the SCF convergence, to establish a practical method for the calculation of the ground and excited states of lanthanide complexes. Practically, the method is realized by utilizing the elongation method program in the GAMESS package since the elongation method is formally equivalent to the FCP method. Numerical assessment in several lanthanide complexes revealed that the method improves the SCF convergence and can accurately reproduce the excitation energies by the standard method, while the difference in the total energy is relatively large. Also, a method to optimize the direction of the 4f orbitals was proposed. The effect of the rotational optimization was examined in CeF diatomic molecule and the lanthanide complexes. In case of small CeF molecule, the

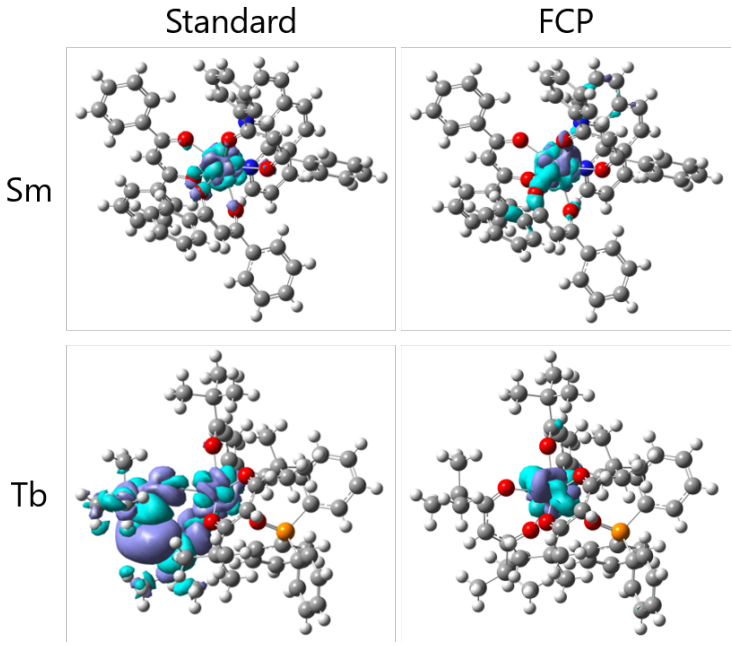

Fig. 3 The difference electron density maps between the ground and excited states of Sm and Tb complexes by the standard and FCP B3LYP methods.

optimized occupied 4f orbital was directed to F atom, which is not consistent with the orbitals obtained by the standard calculation but is reasonable if considering the fact that the orbital interaction with the F atom is neglected in the FCP approximation.

Note that the present scheme does not consider the multi-configuration effect nor the f-electron occupation change. Even in the case of lanthanide ions (Ln^{3+}), f orbitals are partially occupied and then the single determinant description of these systems is not always adequate. Our approach as well as the other DFT approaches are an approximate treatment for calculating large lanthanide complex with many ligands, where the accurate treatment considering multi-configuration and relativistic effects is costly. However, if one accepts this approximation, since 4f electrons are shielded by the valence electrons, their energy levels are hardly affected by ligands.

To achieve the location of the energy levels of different electronic states, the geometry of the complex for each electronic state has to be optimized appropriately. The application of the present FCP scheme to the energy gradient calculation is now under consideration. Then, this method can be applied to the calculation of elementary reaction processes from excitation to luminescence of lanthanide complexes, and will be used to elucidate their luminescent properties.

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