

Electronic structure of CeF from frozen-core four-component relativistic multiconfigurational quasidegenerate perturbation theory

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We have investigated the ground state and the two lowest excited states of the CeF molecule using four-component relativistic multiconfigurational quasidegenerate perturbation theory calculations, assuming the reduced frozen-core approximation. The ground state is found to be $(4f^1)(5d^1)(6s^1)$, with $\Omega=3.5$, where Ω is the total electronic angular momentum around the molecular axis. The lowest excited state with $\Omega=4.5$ is calculated to be 0.104 eV above the ground state and corresponds to the state experimentally found at 0.087 eV. The second lowest excited state is experimentally found at 0.186 eV above the ground state, with $\Omega=3.5$ based on ligand field theory calculations. The corresponding state having $\Omega=3.5$ is calculated to be 0.314 eV above the ground state. Around this state, we also have the state with $\Omega=4.5$. The spectroscopic constants R_e , ω_e , and $\nu(1-0)$ calculated for the ground and first excited states are in almost perfect agreement with the experimental values. The characteristics of the CeF ground state are discussed, making comparison with the LaF⁺ and LaF molecules. We denote the d - and f -like polarization functions as d^* and f^* . The chemical bond of CeF is constructed via $\{\text{Ce}^{3.6+}(5p^6d^{*0.3}f^{*0.1})\text{F}^{0.6-}(2p^{5.6})\}^{3+}$ formation, which causes the three valence electrons to be localized at $\text{Ce}^{3.6+}$. © 2008 American Institute of Physics. [DOI: 10.1063/1.2924118]

I. INTRODUCTION

The lanthanide atoms are well characterized by their localized $4f$ electrons. The light lanthanides are more reactive than the heavier ones because of the near degenerate $4f$, $5d$, and $6s$ binding energies. The ground states of most lanthanide atoms have $(4f)^n(6s)^2$ configurations, except for the La, Ce, and Gd atoms, which have $(5d)^1(6s)^2$, $(4f)^1(5d)^1(6s)^2$, and $(4f)^7(5d)^1(6s)^2$, respectively. The ordinary electron configuration of the monovalent free cations is $(4f)^n(6s)^1$ but those of La, Ce, and Gd are $(5d)^2$, $(4f)^1(5d)^2$, and $(4f)^7(5d)^1(6s)^1$.¹

The bonding of lanthanide monofluoride molecules (LnF) is ionic, and the lanthanide is regarded as a cation. The ground states predicted for the LnF molecules according to the ligand field theory^{2,3} (LFT) have the configurations $(4f)^{n-1}(6s)^2$ for LaF, GdF, TbF, DyF, HoF, ErF, TmF, and LuF, $(4f)^n(6s)^1$ for NdF, PmF, SmF, EuF, and YbF, and $(4f)^{n-1}(5d)^1(6s)^1$ for the CeF and PrF molecules. The experimental assignments to the ground states run parallel to those of LFT. The ground state configurations for LaF⁴, CeF⁵, and GdF⁶ have also been confirmed by a four-component relativistic method of Moriyama *et al.*,⁴ Wasada-Tsutsui *et al.*,⁵ and Tatewaki *et al.*⁶ The presence of the F atom leads to complicated configurations in the LnF molecules; for example, La⁺ in LaF is not $(5d)^2$ but $(6s)^2$, and Ce⁺ in CeF is not

$(4f)^1(5d)^2$ but $(4f)^1(5d)^1(6s)^1$. Careful treatment is necessary for these states when these $4f$, $5d$, and $6s$ spinors have similar energies.

Recently, Wasada-Tsutsui *et al.*⁵ have investigated the lower excited states of CeF by using the four-component relativistic Dirac–Fock–Roothaan (DFR) and configuration interaction (CI) methods with the reduced frozen-core approximation (RFCA).^{7,8} Dolg and Stroll⁹ and Dai *et al.*¹⁰ respectively applied the pseudopotential and density functional theory to consider the electronic structure of CeF. We now summarize the experimental results and outstanding theoretical problems in the assignments of CeF spectra.

The band transition in the CeF molecule was first recorded by Lumley.¹¹ This is a red-degraded band at 17 610 cm⁻¹ (2.181 eV). Rotational analysis of this band yielded R_e and other spectroscopic constants of the upper (excited) and lower (ground) states.¹² The band was assigned as $\Omega'=4.5 \leftarrow \Omega''=3.5$ based on the magnetic rotation and doppler-free laser-fluorescence spectroscopies,^{13,14} here, Ω is the total electronic angular momentum around the molecular axis. Two more low-lying excited states were observed with excitation energies T_0 of 0.087 eV ($\Omega=4.5$) and 0.186 eV (tentatively assigned $\Omega=3.5$) using selectively detected fluorescence excitation and dispersed fluorescence spectroscopy;¹⁵ the symmetry of the higher state ($\Omega=3.5$) was not experimentally determined and the results of the LFT were used for this assignment. Consequently, only three electronic excited states are observed at 0.087, 0.186, and 2.181 eV above the ground state and having $\Omega=4.5$, 3.5, and

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4.5, respectively. Theoretically, approximately 35 states should be found in this energy region.⁵ Wasada-Tsutsui *et al.*⁵ showed that the theoretical excited states corresponding to experiment have excitation energies of 0.319 ($\Omega=4.5$), 0.518 ($\Omega=3.5$), and 2.197 eV ($\Omega=4.5$). Although the calculated spectroscopic constants (R_e and $\nu(1-0)$) show almost exact agreement, the differences between the experimental and theoretical excitation energies in the two lower excited states are large. In the present work, we have carefully studied the ground state and two lowest excited states. It will be shown that the present calculation gives excitation energies of 0.104 and 0.312 eV for the $\Omega=4.5$ and $\Omega=3.5$ states, respectively, which are much closer to experiment than those given by Wasada *et al.*⁵ Furthermore, the state with $\Omega=4.5$ is found near to the $\Omega=3.5$ state as LFT.¹⁵

In Sec. II, we set out the method of calculation, including four-component relativistic complete active space configuration interaction (CASCI) calculation¹⁶ and second-order multiconfigurational quasidegenerate perturbation^{17,18} (MC-QDPT) calculations. Section III sets out the excitation energies, spectroscopic constants, and the characteristics of the excited states. We also discuss the bonding properties of the ground state. It will be shown that the outermost three electrons, which move in the field given by $\text{Ce}^{3.6+}\text{F}^{0.6-}$, are expressed as $(4f)^1(5d)^1(6s)^1$. Concluding remarks are given in Sec. IV.

II. METHOD OF CALCULATION

A. RFCA and basis set

It is time consuming and difficult to treat all the 58 electrons of the Ce atom, so we used the RFCA proposed by Matsuoka and Watanabe throughout the present work.^{7,8} We first performed self-consistent field calculation. Previous studies of LaF^+ and LaF indicated that, to make sense of the spectra, it is vital to include correlation effects from the electrons in the $4s$, $4p$, $4d$, $5s$, and $5p$ spinors, and from the valence electrons of the $4f$, $5d$, $6s$, and $6p$ spinors.⁴ It is also necessary to include correlations from the F $2s$ and $2p$ electrons. We divided the electron shell groups into four categories: (1) frozen core, in which the spinors are fixed to the atomic ones, (2) active cores from which one and two electron excitations are allowed, but are not treated as valence shells in CASCI, (3) the valence shells, and (4) the virtual shells, which are given as f -core $\{\text{Zn}^{2+}(28)+\text{He}(2)\}+a$ -core $\{(4s^24p^64d^{10}5s^25p^6)+(2s^22p^6)\}+valence(4f, 5d, 6s, 6p)+virtual$ (the remaining 135 spinors).

The frozen core (f -core) in Ce is a Zn^{2+} -like ion core of Ce with 28 electrons, and a He-like ion core of F with 2 electrons. The active core (a -core) consists of $\text{Ce}(4s^2\cdots5p^6)$ and $\text{F}(2s^22p^6)$. The number of electrons in the active core is 34. The valence shell is composed of three electrons, which are distributed in the CAS spanned with $4f$, $5d$, $6s$, and $6p$ spinors. For the virtual shells, one- and two-electron excitations of the a -core and valence shell electrons are allowed in the perturbation calculations.

The basis set is $\text{Ce}[1*6/1*5+(11)/1*6+(11)/1*7/1*10/(11)]+\text{F}[21/422/(1)]$, where the slash separates the symmetries s , p_- , p_+ , d_+ , f_+ , and g_+ ; $1*n$ im-

plies that n primitive Gaussian-type functions (pGTFs) are used, and numbers 2 and 4 indicate that the contracted GTFs (cGTF) are spanned with two and four primitives, respectively. The (11), (11), and (11) for Ce are two p_- , p_+ ,¹⁹ and two g_+ -type polarization functions with exponents 3.460(g_+), 1.730(g_+), 3.408(g_-), and 1.7043(g_-), whereas (1) for F is a single d_+ -type polarization function.¹⁹ The total number of molecular spinors generated is 168.

The Ce pGTFs in parentheses are those of the most diffuse GTFs in the respective atomic spinors given by Koga, Tatewaki, and Matsuoka (KTM).²⁰ The Ce p_{\pm} polarization functions have similar diffuseness (exponents 0.042, 0.012) to those of the s -type pGTFs for the $6s$ atomic spinor (exponents are 0.056, 0.023), so that we have not added further p primitives. For the F a -core, cGTFs are constructed from the atomic spinors given by KTM.²¹

B. CASCI and MC-QDPT

To calculate the electronic states of the neutral CeF molecule, we first performed RFCA DFR calculations for the neutral CeF molecule and the CeF^+ cation so as to prepare molecular spinors for CASCI. We call these two spinor sets the spinor-set(N) and spinor-set(C), respectively. Second, using the no-virtual-pair approximation,²²⁻²⁷ we performed CASCI (Ref. 16) calculations with the CeF^+ or CeF 16 virtual (valence) spinors as valence spinor sets. Three electrons are filled in the respective valence spinors. Third, to consider electron correlation effects among the valence electrons and between the valence and active-core electrons, we performed MC-QDPT (Refs. 17 and 18) calculations, taking into account the one- and two-electron excitations from the active-core and valence shells to all the valence and virtual spinors. The effective Hamiltonian obtained through second-order MC-QDPT is expressed as

$$H_{\mu\nu} = E_{\mu}^{\text{CASCI}} \delta_{\mu\nu} + \frac{1}{2} \left\{ \sum_{I \in \text{CAS}} \frac{\langle \mu | H_{\text{DC}} | I \rangle \langle I | H_{\text{DC}} | \nu \rangle}{E_{\nu}^{(0)} - E_I^{(0)}} + \text{H.c.} \right\}, \quad (1)$$

where $|\mu\rangle$ and $|\nu\rangle$ denotes the CASCI eigenfunctions and H.c. is the Hermitian conjugate. $E_{\nu}^{(0)}$ and $E_I^{(0)}$ are the zeroth order energies for the states ν and I , respectively, which are defined as

$$E_{\nu}^{(0)} = \sum_p \varepsilon_p \langle \nu | a_p^{\dagger} a_p | \nu \rangle, \quad E_I^{(0)} = \sum_p \varepsilon_p \langle I | a_p^{\dagger} a_p | I \rangle. \quad (2)$$

An anomaly involving the intruder states²⁸⁻³⁰ is carefully checked in this investigation. The CAS spanned by the 16 valence spinors of CeF^+ and CeF was used. However, the present CAS and MC-QDPT programs independently treat the two strings of subspecies due to time reversal symmetry so that we actually used 32 valence spinors (16 Kramers pairs).

C. Numerov's method

Using the potential curves given by MC-QDPT, we obtained the spectroscopic constants of R_e and ω_e and two excitation energies of T_e (the difference between the potential

TABLE I. Effect of the energy-denominator shift Δ on excitation energies (eV) calculated with MC-QDPT/spinor-set(N) at $R=3.75$ bohrs. The MC-QDPT/spinor-set(N) total energies for the ground state with $\Omega=3.5$ are $-8962.214\,986$, $-8962.215\,056$, $-8962.215\,042$, $-8962.214\,919$, and $-8962.213\,542$ hartrees for $\Delta=0.0$, $0.000\,08$, $0.000\,40$, $0.002\,00$, and 0.0200 , respectively. The numbers after Ω denote the order of the electronic energy state; for example, 3.5-1 is the first electronic state with $\Omega=3.5$.

Ω/Δ	0.000 00	0.000 08	0.000 40	0.002 00	0.020 00
3.5-1	0.0 (eV)	0.0 (eV)	0.0 (eV)	0.0 (eV)	0.0 (eV)
2.5-1	0.019	0.021	0.022	0.022	0.026
1.5-1	0.046	0.049	0.052	0.059	0.091
4.5-1	0.144	0.147	0.149	0.154	0.170
2.5-2	0.313	0.309	0.309	0.310	0.319
3.5-2	0.375	0.344	0.339	0.342	0.364
1.5-2	0.445	0.448	0.450	0.454	0.465
4.5-2	0.450	0.392	0.368	0.362	0.389
4.5-3	0.541	0.553	0.558	0.566	0.614
3.5-3	0.796	0.808	0.813	0.823	0.864
1.5-3	0.814	0.818	0.826	0.840	0.874
2.5-3	0.966	0.968	0.970	0.973	1.003

minima of the ground and excited states) and T_0 (the difference between the lowest vibrational energy of the ground state and that of the excited state), by solving the one-dimensional Schrödinger equation with Numerov's method,^{31,32} which requires many values from the potential curve. These values are obtained from the cubic natural spline³³⁻³⁵ fitted to the MC-QDPT potential curves. Six to eight vibrational levels are determined. Values of ω_e , $\omega_e x_e$, and $\omega_e \nu_e$ are calculated using the lowest three vibrational states of the respective symmetries. We compiled only ω_e , $\omega_e x_e$, and $\nu(1-0)$ [the vibration transition energy from $\nu(0)$ to $\nu(1)$ of the respective electronic states] in the present work.

III. RESULTS

A. Intruder states

Using the ground state DFR spinors, we solved for CASCI; the dimension was 4960. We selected around 20 lowest CASCI solutions as the reference functions in MC-QDPT for the respective Ω 's. In the MC-QDPT calculations, we encountered intruder states²⁸⁻³⁰ in many states. We therefore abandoned using such large numbers of references such

as 20. Instead we selected the lowest two to six solutions of CASCI for the respective Ω 's, and performed MC-QDPT for $R=3.25$, 3.50 , 3.75 , 4.00 , 4.25 and 4.50 bohrs. We also introduced an energy-denominator shift Δ to deal with the contamination of the intruder state; we replaced the denominator $E_v^{(0)} - E_I^{(0)}$ with $E_v^{(0)} - E_I^{(0)} + \Delta / (E_v^{(0)} - E_I^{(0)})$.³⁰ We found that (1) six reference functions are necessary to discuss the excitation energies lower than ~ 1.0 eV and (2) the $\Omega=0.5$ and 5.5 states are contaminated with intruder states. We shall ignore the results given by the $\Omega=0.5$ and 5.5 states.

Table I shows the dependence of the excitation energies on Δ at $R=3.75$ bohrs. The MC-QDPT total energies of the ground state for $\Delta=0.0$, $0.000\,08$, $0.000\,40$, $0.002\,00$, and 0.0200 are shown in the caption of Table I. They are almost independent of the changes in Δ at least when Δ is in the range of $0.0-0.002$. The same is true for the total energies of the excited states and, therefore, is also true for the excitation energies. We note that the order of the excitation energy is reversed only for the 1.5-2 and 4.5-2 states at $\Delta=0.000\,08$. The excitation energy of 4.5-2 keeps a constant value in $0.0008 \leq \Delta \leq 0.002$, however. Thus, we fix Δ to $0.000\,08$ and examine the electronic structure of CeF.

TABLE II. Spectroscopic constants of CeF calculated with MC-QDPT/spinor-set(N). The numbers after Ω denote the order of the electronic energy state; for example 3.5-1 is the first electronic state with $\Omega=3.5$.

No.	Sym. (Ω)	R_c (bohrs)	$\omega/2$ (cm^{-1})	TE(elect) (hartrees)	T_c (eV)	TE(elect+ $\omega/2$) (hartrees)	T_0 (eV)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
0	3.5-1	3.846	306.9	-8962.216 314	0.000	-8963.214 916	0.000	618.5	9.6
1	2.5-1	3.805	329.7	-8962.214 729	0.043	-8962.213 227	0.046	664.5	10.2
2	1.5-1	3.830	304.4	-8962.214 081	0.061	-8962.212 694	0.060	613.3	8.9
3	4.5-1	3.846	312.4	-8962.211 100	0.142	-8962.209 677	0.143	637.4	25.4
4	4.5-2	3.947	283.3	-8962.204 962	0.309	-8962.203 671	0.306	565.9	-1.3
5	3.5-2	3.883	263.0	-8962.204 356	0.325	-8962.203 158	0.320	529.8	7.5
6	2.5-2	3.752	285.6	-8962.203 711	0.343	-8962.202 410	0.340	568.2	-5.9
7	1.5-2	3.848	317.0	-8962.200 013	0.444	-8962.198 569	0.445	640.3	12.8
8	4.5-3	3.831	351.2	-8962.196 062	0.551	-8962.194 462	0.557	720.4	36.2
9	1.5-3	3.899	294.7	-8962.188 535	0.756	-8962.187 192	0.754	599.6	20.4
10	3.5-3	3.858	333.4	-8962.187 347	0.788	-8962.185 828	0.792	675.0	16.5
11	2.5-3	3.904	290.1	-8962.182 996	0.907	-8962.181 674	0.905	588.0	15.5

TABLE III. Spectroscopic constants of CeF calculated with MC-QDPT/spinor-set(C). The numbers after Ω denote the order of the electronic energy state; for example 3.5-1 is the first electronic state with $\Omega=3.5$.

No.	Sym. (Ω)	R_e (bohrs)	$\omega/2$ (cm^{-1})	TE(elect) (hartrees)	T_c (eV)	TE(elect+ $\omega/2$) (hartrees)	T_0 (eV)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
0	3.5-1	3.882	273.5	-8962.219 028	0.000	-8962.217 782	0.000	548.1	2.0
1	4.5-1	3.877	267.4	-8962.215 164	0.105	-8962.213 946	0.104	534.5	-0.6
2	2.5-1	3.838	293.6	-8962.213 514	0.150	-8962.212 176	0.153	588.2	2.1
3	1.5-1	3.886	267.1	-8962.212 099	0.189	-8962.210 882	0.188	534.6	1.0
4	4.5-2	3.974	256.3	-8962.209 526	0.259	-8962.208 358	0.256	515.1	5.3
5	3.5-2	3.925	259.4	-8962.207 498	0.314	-8962.206 316	0.312	519.1	0.8
6	2.5-2	3.822	293.2	-8962.202 574	0.448	-8962.201 238	0.450	587.0	1.3
7	1.5-2	3.896	274.2	-8962.201 665	0.472	-8962.200 416	0.473	549.0	1.3
8	4.5-3	3.849	252.0	-8962.199 946	0.519	-8962.198 798	0.517	499.9	-8.4
9	1.5-3	3.952	268.2	-8962.190 573	0.774	-8962.189 351	0.774	537.4	1.9
10	3.5-3	3.901	293.5	-8962.187 497	0.858	-8962.186 160	0.860	588.1	2.1
11	2.5-3	3.928	277.2	-8962.185 891	0.902	-8962.184 628	0.902	558.8	8.7

B. Spinor-set(N) of CeF or spinor-set(C) of CeF⁺

The total energies, spectroscopic constants, and the excitation energies T_e and T_0 are shown in Table II, which are given by MC-QDPT with spinor-set(N) of the neutral CeF. We designate this computational scheme as MC-QDPT/spinor-set(N). The first $\Omega=3.5$ state (denoted as 3.5-1 in Table II) is the ground state, which is consistent with experiment. The first observed state has a symmetry of $\Omega=4.5$. The first calculated excited state is not the state having $\Omega=4.5$ (4.5-1), but is the 2.5-1 state. The calculated 4.5-1 state is found to be the third excited state.

Since the molecular spinors (MOs) of the cation are known to give better descriptions of molecular correlations,³⁶ we performed MC-QDPT with spinor-set(C) of CeF⁺, setting $\Delta=0.000\ 08$. The results are shown in Table III. Comparison between Tables II and III indicates that MC-QDPT/spinor-set(N) gives lower total energies only for 1.5-1, 2.5-1, and 2.5-2 than MC-QDPT/spinor-set(C). (The ground state is again the first $\Omega=3.5$ (3.5-1) state, as shown in Table III.) Moreover, spinor-set(C) gives much better spectroscopic constants than spinor-set(N): for example, $\nu(1-0)$ for the

ground state; experiment, 544 cm^{-1} ; spinor-set(C); 544 cm^{-1} ; spinor-set(N), 599 cm^{-1} ; $\nu(1-0)$ for the $\Omega=4.5-1$ state; experiment, 540 cm^{-1} ; spinor-set(C), 537 cm^{-1} ; spinor-set(N), 587 cm^{-1} . We therefore use the results obtained using spinor-set(C) to consider the electronic structure including spectroscopic constants.

C. Spectroscopic constants

The calculated spectroscopic constants are compared to those of the experiment in Tables IV(A) and IV(B); the observed values are in parentheses. Figure 1 shows the potential curves. The experimental equilibrium nuclear distance and the dissociation energy for the ground state are 3.871 bohrs and 6.03 ± 0.44 eV, and the calculated values are 3.882 bohrs and 5.873 eV. The vibrational transition from $\nu=0$ to $\nu=1$ is correctly reproduced by the present calculation. Since $\omega_e x_e$ is near to 0, the potential curve for the ground state is accurately quadratic and $\nu(1-0)$ therefore is close to ω_e . The same is true for the first excited state. For the lowest two states, the experimental spectroscopic con-

TABLE IV. Spectroscopic constants of CeF calculated with MC-QDPT/spinor-set(C) with 6 reference functions. The dissociation energy is calculated assuming that the CeF molecule is correlation to $C_{\infty v}$ atoms; CeF($\Omega=3.5$) \rightarrow Ce($\Omega=3$) with $-8862.336\ 257 + F(\Omega=0.5)$ with $-99.666\ 924$ hartrees and CeF($\Omega=4.5$) \rightarrow CeF($\Omega=3$) with $-8862.336\ 257 + F(\Omega=1.5)$ with $-99.666\ 140$ hartrees.

No.	Sym (Ω)		R_e (bohrs)		D_e (eV)		T_0 (cm^{-1})		$\omega_e(\text{cm}^{-1})$ Calc.	$\omega_e x_e$ Calc.	$\nu(1-0)$ (cm^{-1})	
	Expt.	Calc	Expt.	Calc	Expt.	Calc	Expt.	Calc			Expt.	Calc
(A) Spectroscopic constant with counterpoise correction												
0	3.5	3.5	3.871 ^a	3.882	6.03 ^b	5.873	0.000	0.000	548.1	2.0	544 ^a	544.2
1	4.5	4.5	3.868 ^a	3.877		5.790	0.087 ^a	0.104	534.5	-0.6	540 ^a	535.7
4	4.5			3.974		5.636		0.256	515.1	5.3		504.6
5	3.5	3.5		3.925		5.560	0.186 ^a	0.312	519.1	0.8		517.5
(B) Spectroscopic constant with counterpoise correction												
0	3.5	3.5	3.871 ^a	3.901	6.03 ^b	5.394	0.000	0.000	548.3	3.2	544 ^a	541.9
1	4.5	4.5	6.868 ^a	3.896		5.269	0.087 ^a	0.147	550.6	1.6	540 ^b	547.4
4	4.5			3.988		5.123		0.291	526.9	5.6		515.7
5	3.5	3.5		3.944		5.084	0.186 ^a	0.308	522.2	2.0		518.2

^aSee Ref. 15. The error range for ν of the first excited state is given as 540 ± 20 cm^{-1} .^bSee Ref. 37. The error range for D_e is given as 6.03 ± 0.44 eV.

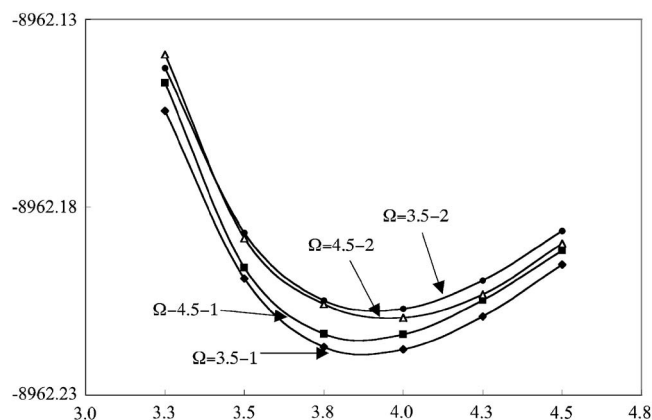


FIG. 1. Potential curves for the ground state (first $\Omega=3.5$ state), the first and second $\Omega=4.5$ states, and the second $\Omega=3.5$ state of CeF, calculated with the MC-QDPT/spinor-set(C). The reference function number is 6 and the energy-denominator shift is $\Delta=0.0008$. Solid diamonds, solid squares, open triangles, and solid circles indicate states with $\Omega=3.5-1$, $4.5-1$, $4.5-2$, and 3.5 , respectively.

stants including the excitation energy are almost perfectly reproduced by the present calculation. (The results are too perfect, we feel that some fortunate cancellation of errors causes these.)

The experimental second lowest state is tentatively assigned as $\Omega=3.5$ and it is 0.186 eV above the ground state. The state with $\Omega=3.5$ appeared as the calculated fifth excited state found at 0.312 eV above the ground state, whereas the state with $\Omega=4.5$ appeared as the calculated fourth excited state. Since as shown in Table I, the energy-denominator shift Δ gives around 10% ambiguity in the excitation energies, a more precise investigation is necessary to confirm the energetic position of the second $\Omega=3.5$ and 4.5 states.

One may be interested in the basis set superposition error^{38–40} (BSSE) and prolapse which is peculiar to the four-component relativistic calculations.^{41–45} We estimate them by the counterpoise method, assuming the full basis set given in Sec. II A as ghost orbitals. The results given by MC-QDPT are shown in the second part of Tables IV(A) and IV(B). The geometrical structure and the vibrational constants with counterpoise corrections almost agree with the values without them. A little differences are observed in energetics, however. For example, the ground state D_e 's with and without the correction are 5.39 and 5.87 eV, respectively. The 90% of reduction in D_e arises from the energy lowering in F; the large ghost basis set replaced at Ce leads to a large counter-

poise correction for F. Since we use the basis sets that give near numerical DF energies especially for F, and since the He core in F and the Zn^{2+} core in Ce are frozen to the respective atomic-ion cores, the BSSE and the prolapse should be small. Moreover, the counterpoise method in MC-QDPT includes the molecular extra correlation energies (MECEs) which are brought by electron pairs in F/Ce being scattered into Ce/F virtual spinors, indicating again that the BSSEs in the counterpoise corrections are unrealistically too much exaggerated; MECE is one of the origin to make a stable chemical bond. The counterpoise corrections might be unneeded under the use of the RFCA with the sizes of the present basis set.

One may doubt sufficiency of the nondynamical correlation effects among valence electrons. We enlarge the valence spinors by 50% (16 spinors \rightarrow 24 spinors) and performed the CASCI and MC-QDPT calculations in order to see the effects of increasing the nondynamical correlation effects on the physical quantities. Results are collected in Table V. The calculated spectroscopic constants in Table V are close to those of Table IV(A), but the latter gives slightly better agreement with experiment. The larger T_0 's in Table V than those in Table IV(A) indicate that enlargement of the CASCI space (the valence spinors) works better for the ground state than for the excited states. We always encounter the imbalance of estimated correlation energies. The T_0 's of second $\Omega=4.5$ and 3.5 states in Table V become closer to each other than those in Table IV(A), indicating again the necessity of further investigations to confirm the relative position of the two states.

D. Characters of the respective state

The spinor energies and gross atomic orbital populations⁴⁶ (GAOPs) calculated with MC-QDPT/spinor-set(C) are given in Table VI. Figure 2 shows the density contour maps for the spinor. Important CSFs and approximate GAOPs in MC-QDPT, which are given by the following equation, are set out in Table VII:

$$\text{GAOP}_\lambda = \sum_I C_I^2 \text{GAOP}_{I\lambda}, \quad (3)$$

where λ , I , and C_I denote the symmetry of the atomic spinor, the configuration, and mixing configurational coefficients, respectively.

TABLE V. Spectroscopic constants of CeF calculated with extended CASI/spinor-set(C). The dissociation energy is calculated assuming that the CeF molecule is correlated to $C_{\infty v}$ atoms; $\text{CeF}(\Omega=3.5) \rightarrow \text{Ce}(\Omega=3) + \text{F}(\Omega=0.5)$ with $-8862.335733 + \text{F}(\Omega=0.5)$ with -99.666924 hartrees and $\text{CeF}(\Omega=4.5) \rightarrow \text{CeF}(\Omega=3) + \text{F}(\Omega=1.5)$ with $-8862.335733 + \text{F}(\Omega=1.5)$ with -99.666140 hartrees.

Sym (Ω)		R_e (bohrs)		D_e (eV)		T_0 (cm^{-1})		ω_e (cm^{-1})	$\omega_e x_e$	$\nu(1-0)$ (cm^{-1})	
Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
3.5	3.5-1	3.871 ^a	3.882	6.03 ^b	5.884	0.000	0.000	552.8	2.0	544 ^a	548.9
4.5	4.5-1	3.868 ^b	3.874		5.762	0.087 ^a	0.144	555.5	1.8	540 ^a	551.9
	4.5-2		3.965		5.557		0.346	500.8	2.7		495.4
3.5	3.5-2		3.915		5.532	0.186 ^a	0.351	522.9	0.9		521.1

^aSee Ref. 15. The range for $\nu(1-0)$ of the first excited state is given as $540 \pm 20 \text{ cm}^{-1}$.

^bSee Ref. 37. The range for D_e is given as $6.03 \pm 0.44 \text{ eV}$.

TABLE VI. Spinor energies (hartrees) and GAOPs of CeF⁺ at 3.882 bohrs. The configuration for CeF⁺ consists of 11, 5, and 1 closed shell and 0, 1, and 1 open shells for the $e_{1/2}$, $e_{3/2}$, and $e_{5/2}$ symmetries, respectively.

No.	Spinor energy	Ω	Ce s_+	Ce p_-	Ce p_+	Ce d_-	Ce d_+	Ce f_-	Ce f_+	F s_+	F p_-	F p_+	
12	-1.3469	1/2	0.001	1.921	0.004	0.002	0.000	0.000	0.000	0.052	0.001	0.019	
13	-1.2348	1/2	0.003	0.001	1.847	0.001	0.003	0.000	0.000	0.072	0.039	0.034	
14	-1.2028	3/2	0.000	0.000	1.989	0.000	0.000	0.000	0.000	0.000	0.000	0.011	
15	-0.7524	1/2	0.000	0.007	0.008	0.037	0.039	0.017	0.016	0.000	1.385	0.491	
16	-0.7506	3/2	0.000	0.000	0.017	0.015	0.058	0.009	0.023	0.000	0.000	1.877	
17	-0.7483	1/2	0.015	0.025	0.073	0.068	0.080	0.012	0.013	0.007	0.431	1.275	
	Σ GAOP _i ($i=1, 17$)		4.010	4.005	8.000	4.126	6.186	0.040	0.054	1.987	1.865	3.724	
	Total GAOPs				Ce(...5s ² 5p ⁶ 5d ¹):26.421						F(2s ² 2p ⁵):7.576		
18	-0.7168	5/2	0.000	0.000	0.000	0.000	0.000	0.975	0.025	0.000	0.000	0.000	
21	-0.4306	3/2	0.000	0.000	0.000	0.873	0.120	0.007	0.001	0.000	0.000	0.000	
	Total GAOPs				Ce: 2.000						F: 0.000		
26	-0.1747	1/2	1.733	0.087	0.138	0.017	0.028	0.000	0.000	-0.002	0.000	-0.001	
19	-0.6950	5/2	0.000	0.000	0.000	0.000	0.001	0.051	1.949	0.000	0.000	0.000	
20	-0.5190	5/2	0.000	0.000	0.000	0.000	1.998	0.000	0.002	0.000	0.000	0.000	
22	-0.3969	3/2	0.000	0.000	0.095	0.197	1.533	0.034	0.090	0.000	0.000	0.032	
23	-0.3018	3/2	0.000	0.000	0.356	0.010	0.003	1.631	0.000	0.000	0.000	0.001	
24	-0.2937	3/2	0.000	0.000	0.861	0.009	0.012	0.181	0.936	0.000	0.000	0.000	
25	-0.2658	3/2	0.000	0.000	0.655	0.030	0.157	0.147	0.986	0.000	0.000	0.026	
27	-0.1559	5/2	0.000	0.000	0.000	0.000	1.998	0.000	0.002	0.000	0.000	0.000	
28	-0.1456	3/2	0.000	0.000	1.987	0.005	0.004	0.001	0.003	0.000	0.000	0.000	
29	-0.1324	3/2	0.000	0.000	0.002	1.287	0.709	0.001	0.001	0.000	0.000	0.000	
30	-0.1231	1/2	0.004	0.977	0.212	0.655	0.132	0.007	0.002	0.000	0.003	0.008	

The present ground state (entry No. 0) is expressed approximately as $\{(4f_-)_{5/2}(5d_-)_{3/2}(6s_+)_{1/2}\}_{7/2}$, where i indicates the Kramers partner of the spinor i and the suffix after (i) is the spinor angular momentum around the molecular axis. The suffix after the configuration in braces is Ω . This configuration is in accord with the experimentally assigned $(4f)(5d)(6s)$ configuration and is the same as the designation of Wasada-Tsutsui *et al.*⁵

The first experimental excited state (entry No. 1) is $(4f)(5d)(6s)$ with $\Omega=4.5$, located 0.087 eV above the ground state.¹⁵ The calculated state corresponding to this is found at 0.104 eV and is approximately expressed as $\{(4f_-)_{5/2}(5d_-)_{3/2}(6s_+)_{1/2}\}_{9/2}$. The results seem to be satisfactory. Wasada-Tsutsui *et al.* gave the same configuration as here, but their excitation energy is rather large (0.319 eV). Their calculation is a single and double excitation configuration interaction (SDCI) using a single reference function. Entry No. 1 in Table VII shows that the weight of the main configuration is large. This implies that a single reference SDCI calculation is adequate. The difference between the two calculations probably originates from the differences in the active core; the present calculation uses $4s^2 4p^6 4d^{10} 5p^6$ and Wasada-Tsutsui *et al.* used $5p^6$.

Referring to the LFT,¹⁵ the second experimental excited state located 0.186 eV above the ground state was tentatively assigned as $(4f)(5d)(6s)$ with $\Omega=3.5$. In our study, the calculated state with $\Omega=3.5$ (entry No. 5) is found 0.314 eV above the ground state. The configuration of this state is $0.4\{(4f_-)_{5/2}(5d_+)_{3/2}(6s_+)_{1/2}\}_{7/2} + 0.3\{(4f_+)_{5/2}(5d_-)_{3/2}(6s_+)_{1/2}\}_{7/2}$, where the numbers before the configuration indicate the weight. We also have a state near to this. It exists 0.259 eV (entry No. 4) above the ground state. The configuration of the state is $0.6\{(4f_-)_{5/2}(5d_+)_{3/2}(6s_+)_{1/2}\}_{9/2}$

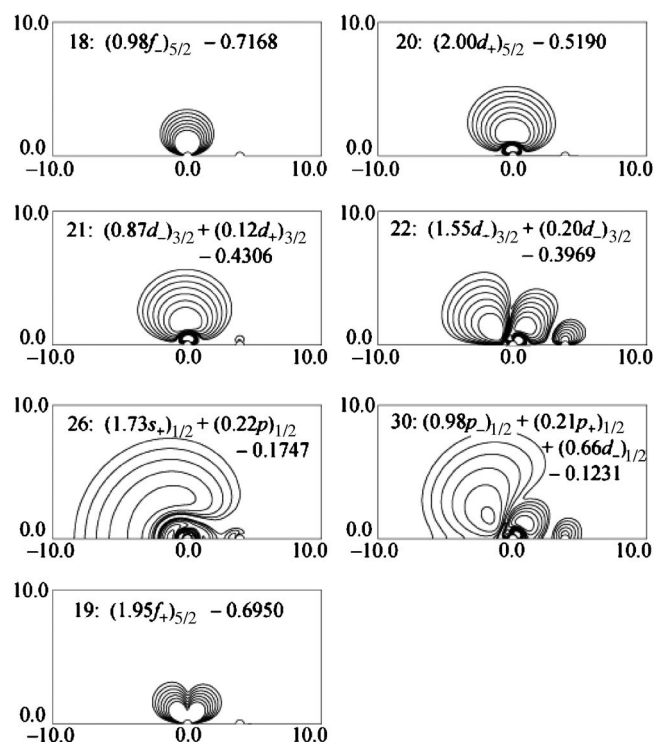


FIG. 2. Density contour maps of the valence (virtual) spinors of CeF⁺ from Table VII. The order of the contours 18, 21, 26, 19, 20, 22, and 30 is arranged as the orders of the Slater determinants which use them (see Table VIII). The first four spinors (18, 21, 26, and 19) are in the determinants for the ground state (entry No. 0), the spinors 20, 22, and 30 are in the first excited state (entry No. 1), and the fourth (entry No. 4), and ninth (entry No. 9) excited states. The spinor numbers (No.), the characters with GAOPs (\dots), and the spinor energies (ϵ) are given in the respective contour maps as No. (\dots), ϵ . The circles on the z axis indicate the Ce and F nuclei located at (0.0, 0.0, 0.0) and (0.0, 0.0, 3.882) bohrs. The outermost contour on the map is $0.0001 e \text{ bohrs}^{-3}$. The value of each inner line is twice as large as that of the neighboring outer line. The electron numbers inside the outermost line are appropriately at 0.98–1.00.

TABLE VII. MC-QDPT/spinor-set(C) wavefunction analysis at $R=3.882$ bohrs with threshold $\Delta=0.00008$. The numbers after Ω are the order of the electronic energy state; for example, 3.5-1 means the first electronic state in $\Omega=3.5$.

No.	Ω	TE (hartrees) Core	Ce_s	Ce_p	Ce_d	Ce_f	Sum-Ce	F_s	F_p	Sum F	Wavefunction in spinor numbers ^a $Ce^{3.4+}F^{0.6-} \leftarrow Ce^{3+}(\dots 5p^6 4f^1) + F(2s^2 2p^5)$
0	3.5-1	-8962.219 175	0.86	0.12	1.01	1.01	3.00	0.00	0.00	0.00	$0.95^* 18\ 21\ 26 + 0.20^* 21\ 26\ 19 $
1	4.5-1	-8962.215 434	0.85	0.12	1.01	1.01	3.00	0.00	0.00	0.00	$0.91^* 18\ 21\ 26 - 0.31^* 18\ 26\ 20 $
2	2.5-1	-8962.213 271	1.49	0.28	0.18	1.03	2.99	0.00	0.00	0.00	$0.72^* 18\ 26\ 26 - 0.52^* 18\ 26\ 26 $
3	1.5-1	-8962.212 442	0.85	0.13	1.01	1.00	2.99	0.00	0.00	0.00	$0.83^* 18\ 21\ 26 - 0.49^* 21\ 26\ 19 $
4	4.5-2	-8962.209 249	0.83	0.18	0.90	1.07	2.98	0.00	0.01	0.01	$0.75^* 18\ 26\ 22 + 0.45^* 21\ 26\ 19 $
5	3.5-2	-8962.207 497	0.85	0.23	0.88	1.03	2.99	0.00	0.01	0.01	$0.66^* 21\ 26\ 19 + 0.53^* 18\ 26\ 22 $
6	2.5-2	-8962.202 146	1.48	0.28	0.19	1.03	2.99	0.00	0.00	0.00	$0.70^* 26\ 26\ 19 - 0.55^* 26\ 26\ 19 $
7	1.5-2	-8962.201 731	0.85	0.13	1.01	1.00	2.99	0.00	0.00	0.00	$0.83^* 21\ 26\ 19 + 0.49^* 18\ 21\ 26 $
8	4.5-3	-8962.200 298	0.82	0.15	1.02	1.00	2.99	0.00	0.00	0.00	$0.57^* 26\ 19\ 20 + 0.55^* 21\ 26\ 19 $
9	1.5-3	-8962.190 364	0.82	0.43	0.65	1.09	2.98	0.00	0.01	0.01	$0.68^* 18\ 26\ 22 + 0.60^* 18\ 26\ 30 $
10	3.5-3	-8962.187 667	0.77	0.45	0.74	1.03	2.99	0.00	0.00	0.00	$0.60^* 18\ 26\ 30 - 0.58^* 21\ 26\ 19 $
11	2.5-3	-8962.185 117	0.82	0.66	0.52	0.99	2.99	0.00	0.01	0.01	$0.69^* 18\ 26\ 30 - 0.50^* 18\ 26\ 30 $

^aThe symbol \bar{i} in the Slater determinants denotes Kramers partner of the spinor i .

+0.2 $\{(4f_+)^{5/2}(5d_-)^{3/2}(6s_+)^{1/2}\}_{9/2}$. Wasada-Tsutsui *et al.*⁵ assigned the calculated state at 0.518 eV as the second experimental state and gave the configuration as $\{(4f_-)^{3/2}(5d_-)^{3/2}(6s_+)^{1/2}\}_{7/2}$. The larger excitation energy of Wasada-Tsutsui *et al.* is due to their smaller active core and use of a single reference SDCI. Further investigations are necessary to confirm the designation for the second experimental excited state.

E. Chemical bond in CeF

Table VIII summarizes the MC-QDPT/spinor-set(C) GAOPs and spectroscopic constants for the ground state of CeF, together with those of LaF⁺ and LaF. The ion cores of LaF⁺, LaF, and CeF can be schematically represented as $\{Ln^{2.5+}$ or $3.5+(5p^6 d^{*0.4} f^{*0.1})F^{0.5-}(2p^{5.5})\}^{2+}$ or $3+$, where Ln = La and Ce. Here, d^* and f^* are the polarization functions which allow F 2p electrons to seep deeply into the Ce ionic core. The valence electrons are almost entirely localized at the Ln ion in LaF⁺, LaF, and CeF.

For the LaF⁺ ground state $^2\Delta$ ($\Omega=3/2$), the valence electrons are populated in the atomiclike La 5d spinor. If the attraction potential in LaF⁺ is strong compared to the electron-electron repulsive potential, $4f_{5/2}$ almost degener-

ates to $4d_{5/2}$. In this case the electron occupies $4f_{5/2}$. We see that the valence electron is in the 5d spinor. The attraction potential in $(La^{2.5+}F^{0.5-})^{2+}$ is not strong enough to hold the 4f electron, but not so weak as to hold the 6s electron. For the LaF ground state, two electrons are in the s-d hybridized spinors localized at La^{2.5+}. The attraction potential in the ground state given by $(La^{2.5+}F^{0.5-})^{2+}$ is not strong enough to hold two 5d-like electrons, as does the La³⁺(5p⁶) in the gaseous La⁺ ion. In a similar manner, the attractive potential of Ce^{3.6+}F^{0.6-} in CeF gives the ground state $(4f)^1(5d)^1(6s)^1$ since the potential is not strong enough to hold $(4f)^1(5d)^2$.

The chemical bond in LaF⁺ and LaF is constructed via a $\{La^{2.5+}(5p^6 d^{*0.4} f^{*0.1})F^{0.5-}(2p^{5.5})\}^{2+}$ formation which results from the interaction between La²⁺(5p⁶5d¹) and F(2p⁵). The resulting attractive potential produced by La^{2.5+} and the repulsive potential produced by F^{0.5-} localize the valence electrons around the La^{2.5+} ion core. In that case, the spectroscopic constants R_e , ω_e , and D_e of LaF should be close to those of LaF⁺. The values in Table VIII verify this hypothesis. In the same way the chemical bond in CeF is constructed by forming $\{Ce^{3.6+}(5p^6 d^{*0.3} f^{*0.1})F^{0.6-}(2p^{5.6})\}^{3+}$ from Ce³⁺(5p⁶5f¹) + F(2p⁵), which causes the three valence electrons to be localized at Ce^{3.6+}. By considering the com-

TABLE VIII. MC-QDPT GAOPs for LaF⁺ (see Ref. 4), LaF (see Ref. 4), and LaF.

Spinor	Ln_s	Ln_p	Ln_d	Ln_f	F_s+	F_p
LaF ⁺ Σ GAOP _{<i>il</i>} (<i>i</i> =1, 17)	4.01	11.99	10.42	0.12	1.99	5.47
<i>a</i> -core: La ^{2.5+} (<i>d</i> [*]) ^{0.4} (<i>f</i> [*]) ^{0.1} F ^{0.5-} (2p) ^{5.5}		La:26.53			F:7.47	
Valence: 5d ^{1.0}	0.00	0.00	1.00	0.00	0.00	0.00
Spectroscopic constant		R_e 2.002 Å, ω_e 522 cm ⁻¹ , D_e 5.86 eV				
LaF Σ GAOP _{<i>il</i>} (<i>i</i> =1, 17)	4.01	12.00	10.34	0.11	1.99	5.56
<i>a</i> -core: La ^{2.5+} (<i>d</i> [*]) ^{0.3} (<i>f</i> [*]) ^{0.1} F ^{0.5-} (2p) ^{5.5}		La:26.45			F:7.55	
Valence: 4f ^{0.05} 5d ^{0.5} 6s ^{1.4} 6p ^{0.1}	1.38	0.11	0.48	0.02	0.00	0.00
Spectroscopic constant		R_e 2.052 Å, ω_e 534 cm ⁻¹ , D_e 5.72 (6.23) eV				
CeF Σ GAOP _{<i>il</i>} (<i>i</i> =1, 17)	4.01	12.01	10.31	0.09	1.99	5.59
<i>a</i> -core: Ce ^{3.6+} (<i>d</i> [*]) ^{0.3} (<i>f</i> [*]) ^{0.1} F ^{0.6-} (2p) ^{5.6}		Ce:26.42			F:7.58	
Valence: 4f ^{1.0} 5d ^{1.0} 6s ^{0.9} 6p ^{0.1}	0.86	0.12	1.01	1.01	0.00	0.00
Spectroscopic constant		R_e 2.054 Å, ω_e 548 cm ⁻¹ , D_e 5.87 (6.03) eV				

pounds of CeX such as CeF₄, it is plausible that all three valence electrons move into the ligand X and Ce becomes Ce^{3.6+}(5p⁶d*^{0.3}f*^{0.1})-like. The d* and f* polarization functions make up the molecular spinors with the ligand spinors, for example with F 2p. The electrons in d* and f* can be regarded as the ligand electrons backdonated through these Ce spinors. Thus, the Ce ion in the compound can be considered as and behave as the tetravalent in CeX, such as CeF₄.

IV. CONCLUSION

We have investigated the ground state and the two lowest excited states using the four-component CASCI and second-order MC-QDPT calculations, assuming the RFCA.^{7,8} All of the states investigated states arise approximately from the same configuration (4f)¹(5d)¹(6s)¹ but with differing electron angular momentum with respect to the molecular spinors, and with different total electron angular momentum around the molecular axis (Ω). The lowest excited state is experimentally found at 0.087 eV. The corresponding calculated state was 0.104 eV above the ground state, having {(4f₋)_{5/2}(5d₋)_{3/2}(6s₊)_{1/2}}_{9/2}. For this state, the calculated spectroscopic constants all agree with the experimental values.

The second lowest excited state is experimentally found 0.186 eV above the ground state. The experimental Ω value for this state is tentatively given as 3.5, based on the ligand field theory (LFT) calculation.¹⁵ (The LFT gives excitation energies of 0.214 and 0.273 eV for the Ω=3.5 and 4.5 states, respectively.) In the present calculation, the state corresponding to Ω=3.5 is found 0.314 eV above the ground state having 0.4{(4f₋)_{5/2}(5d₊)_{3/2}(6s₊)_{1/2}}_{7/2} + 0.3{(4f₊)_{5/2}(5d₋)_{3/2}(6s₊)_{1/2}}_{7/2}, where the numbers before the braces are the weights of the respective configurations. We also have a state with Ω=4.5 at 0.256 eV above the ground state. More precise calculations are necessary to confirm the assignment of the second lowest excited states.

The characteristics of the CeF molecule have also been discussed, comparing the LaF⁺ and LaF molecules. The chemical bond of CeF is constructed via a formation of {Ce^{3.6+}(5p⁶d*^{0.3}f*^{0.1})F^{0.6-}(2p^{5.6})}³⁺, which causes the three valence electrons to be localized around Ce^{3.6+}.

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