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# Molecular Spinors Suitable for Four-Component Relativistic Correlation Calculations: Studies of LaF<sup>+</sup> and LaF Using Multiconfigurational Quasi-Degenerate Perturbation Theory

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**ABSTRACT:** Multiconfigurational second-order quasidegenerate perturbation theory (MCQDPT) calculations were performed for the LaF<sup>+</sup> molecule, with one LaF<sup>2+</sup> and four LaF<sup>+</sup> Dirac–Fock–Roothaan (DFR) spinor sets. The best spinor set was that of LaF<sup>2+</sup>, which gave the lowest total energies and also the best excitation energies for any state considered. The MCQDPT calculations with the cation and neutral molecular spinors were also performed for LaF. The MCQDPT with the cation spinors gave the lowest total energies for all states under consideration, and the calculated excitation energies compared best with experiment. We prefer the LaF<sup>+</sup> spinor set to those of LaF. These calculations indicate that the DFR spinor set for the (*n*–1) electron system is adequate for treating the molecular electronic system having *n* electrons. © 2009 Wiley Periodicals, Inc. *Int J Quantum Chem* 109: 1898–1904, 2009

**Key words:** four-component relativistic calculation; CASCI; MCQDPT; LaF

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## Introduction

For accurate calculation of the electronic structure of molecules, including heavy atoms such as lanthanides, it is necessary to account for electron correlations and relativistic effects. One of the most accurate treatments is the four-component relativistic multireference configuration interaction method, but this is scarcely practical in most cases because of the huge dimension of the configuration interaction (CI) expansion method. Perturbation methods, such as complete-active-space second-order perturbation theory (CASPT2) [1] and multi-configurational second-order quasidegenerate perturbation theory (MCQDPT) [2] are often suitable for treating four-component relativistic problems at reasonable cost while retaining accuracy.

When performing relativistic CASPT2 or MCQDPT calculations, it may be adequate to use the four-component spinors generated by CASSCF [3]. Unfortunately, no publicly available programs provide CASSCF spinors for atoms and molecules. CASSCF also suffers sometimes from convergence difficulties. Recently, Abe et al. [4] argued that improved virtual orbitals (IVOs) [5, 6] are adequate for four-component relativistic CASPT2. We show later that for MCQDPT calculations [7] the Dirac-Fock-Roothaan (DFR) molecular spinors of the  $(n-1)$  electron system are superior to those of the  $n$  electron system in describing the  $n$  electron system. Programs for the DFR calculations are by Watanabe and Matsuoka [8, 9] and for the MCQDPT calculations by Miyajima et al. [7]. We scarcely met intruder states: one exception is found in the  $\text{LaF}^+$  calculation which would be given in Table II.

## Method of Calculation

Since it is time-consuming to treat all the electrons of  $\text{La}^+/\text{La}$ , we used the reduced frozen-core approximation proposed by Watanabe and Matsuoka [8, 9].

The molecular basis sets are those of La [ $1^*6/1^*5+(11)/1^*6+(11)/1^*7/1^*8/(1)$ ] + F [ $21/422/(1)$ ], where the slash symbol separates the  $s_+$ ,  $p_-$ ,  $p_+$ ,  $d_{\pm}$ ,  $f_{\pm}$ , and  $g_{\pm}$  symmetries, and  $1^*n$  implies that  $n$  primitive Gaussian type functions (pGTFs) are used; the numbers 2 and 4 indicate that the contracted GTFs (cGTF) are spanned with two and four primitives, respectively. The pGTFs in the square brackets are those of the most diffuse GTFs founded by Koga et al.

[10, 11]. The eight f-type primitives and one g-type polarization function have been generated previously [12]. The symbols (11) and (1) in La denote two p-[13] and one g-type polarization function, and (1) for F is a single  $d$ -type polarization function [13].

We first perform the DFR calculations. The electron shells are put into four categories: (1) a frozen-core consisting of La ( $1s^2 \dots 3d^{10}$ ) and F ( $1s^2$ ), where the spinors are fixed to the atomic ones; (2) active-core consisting of La ( $4s^2 4p^6 4d^{10} 5s^2 5p^6$ ) and F ( $2s^2 2p^6$ ), from which one- and two-electron excitations are allowed but are not treated as valence shells in CASCI; (3) the valence shells (4f, 5d, 6s, 6p) from which CAS are constructed; and (4) virtual shells to which one or two electron excitations from the active-core and the valence shell are permitted, involving all spinors not included in the active-core and the valence shell.

Employing the no-virtual-pair-approximation [14, 15], we next performed four-component relativistic CASCI [7] calculations using the DFR valence spinors, filling one or two electrons in the respective spinors. Then, to take account of correlation effects among the valence electrons and between the valence and active-core electrons, we performed four-component relativistic MCQDPT [7] calculations.

## Results

### $\text{LaF}^+$

Table I sets out the relativistic MCQDPT total energies (TEs) at the experimental  $\text{LaF}^+$  ground state equilibrium nuclear distance of  $R = 3.78$  bohr [16] having symmetry  $\Omega$  (total angular momentum around the molecular axis). The molecular basis sets for MCQDPT are those for (0000), (1000), (0100), (0010), and (0001), where (0100) (for example) stands for  $\text{LaF}^+(\dots 5p^6 1e_{1/2}^0 1e_{3/2}^1 1e_{5/2}^0 1e_{7/2}^0)$ . This configuration is also abbreviated as  $1e_{3/2}^1$ . The  $\text{LaF}^+$  ground state is known to be  $(1e_{3/2}^1; 5d_-)^1$ , with  $\Omega = 3/2$ . The MCQDPT TE for this state given by (0000) is  $-8594.435719$  hartrees, and the value given by (1000) is  $-8594.415015$  hartrees. The set for (0000) gives the lowest TE for any states under consideration, including the ground state. Moreover, the vertical excitation energies using (0000) give the best agreement with experiment [17], as shown in Table II. Table II also shows the valence shell configuration from the approximate gross atomic populations (GAOPs) [12]. (A forthcoming paper (H. Moriyama et al., in preparation) will show that the vertical excitation energies

**TABLE I**

**Total energies (hartrees) at  $R = 3.78$  bohr for  $\text{LaF}^{2+}$  calculated with one  $\text{LaF}^{2+}$  and three  $\text{LaF}^+$  DFR sets, denoted as (0000), (1000), (0100), (0010), and (0001).**

$\Omega$	(0000)		(1000)		(0100)		(0010)		(0001)	
	NO	TE	NO	TE	NO	TE	NO	TE	NO	TE
1/2	3	-0.424740	3	-0.405528	3	-0.388054	3	-0.388766	2	-0.380835
1/2	4	-0.404991	4	-0.382727	4	-0.366724	4	-0.367593	4	-0.372374
1/2	6	-0.378303	6	-0.345143	6	-0.327494	6	-0.328285	6	-0.330755
1/2	11	-0.340005	9	-0.311795	7	-0.308791	7	-0.287702	8	-0.303950
1/2	13	-0.314298	13	-0.271790	13	-0.286578	14	-0.259485	11	-0.243802
1/2	14	-0.288060	14	-0.261285	15	-0.258845	15	-0.244548	13	-0.235304
3/2	1	-0.435719	1	-0.415015	1	-0.397873	1	-0.398903	1	-0.379362
3/2	5	-0.401572	5	-0.379460	5	-0.363699	5	-0.364251	5	-0.346880
3/2	8	-0.361065	10	-0.328492	8	-0.304817	10	-0.306876	9	-0.275576
3/2	12	-0.338916	11	-0.306778	11	-0.280750	12	-0.281935	12	-0.253720
3/2	15	-0.285199	15	-0.267641	14	-0.254733	13	-0.255135	16	-0.120645
5/2	2	-0.430170	2	-0.409560	2	-0.392926	2	-0.393439	3	-0.373455
5/2	7	-0.365539	7	-0.333588	9	-0.296652	8	-0.298442	7	-0.314218
5/2	10	-0.352223	12	-0.319134	10	-0.106571	9	-0.271036	17	-0.085452
7/2	9	-0.354522	8	-0.322086	12	-0.227646	11	-0.297920	10	-0.254580

From all TEs, -8,594 hartrees have been subtracted.

given in Table II are close to calculated  $T_0$  and  $T_e$ .) Since the basis set for La does not include the p-type pGTFs suitable for 6p, agreement with experiment for the excitation energies of the 6p dominant states is not good.

Consider why (0000) gives good energetics. We write the electronic potential as  $V(X)$ , where  $X$  is the electronic configuration or electron number. Upon solving the CI matrix composed of  $\langle \dots 5p^6 m_{e_i}^1 | H[V\{\text{LaF}^{2+}(\dots 5p^6)\}] \dots 5p^6 m_{e_i}^1 \rangle$ , the DFR

determines the virtual spinors for (0000). The resulting  $\text{LaF}^{2+}$  virtual spinors are all equivalent to the IVOs of  $\text{LaF}^+$ . More accurately, since the matrix elements are calculated with average configurations, the resulting spinors are equivalent to average IVOs. When  $1e_i$  is occupied, the spinors  $m_{e_i}$  are determined by  $V\{\text{LaF}^{2+}(\dots 5p^6)\}$ , the same as  $1e_i$ , so that  $m_{e_i}$  is suitable for correlating calculations. Spinors for other symmetries are determined by  $V\{\text{LaF}^+(\dots 5p^6 1e_i^1)\}$ , making their shapes inade-

**TABLE II**

**MCQDPT vertical excitation energies (eV) calculated with the (1000), (0100), (0010), (0001), and (0000) sets and valence configuration calculated with (0000) for  $\text{LaF}^+$  at  $R = 3.78$  bohr.**

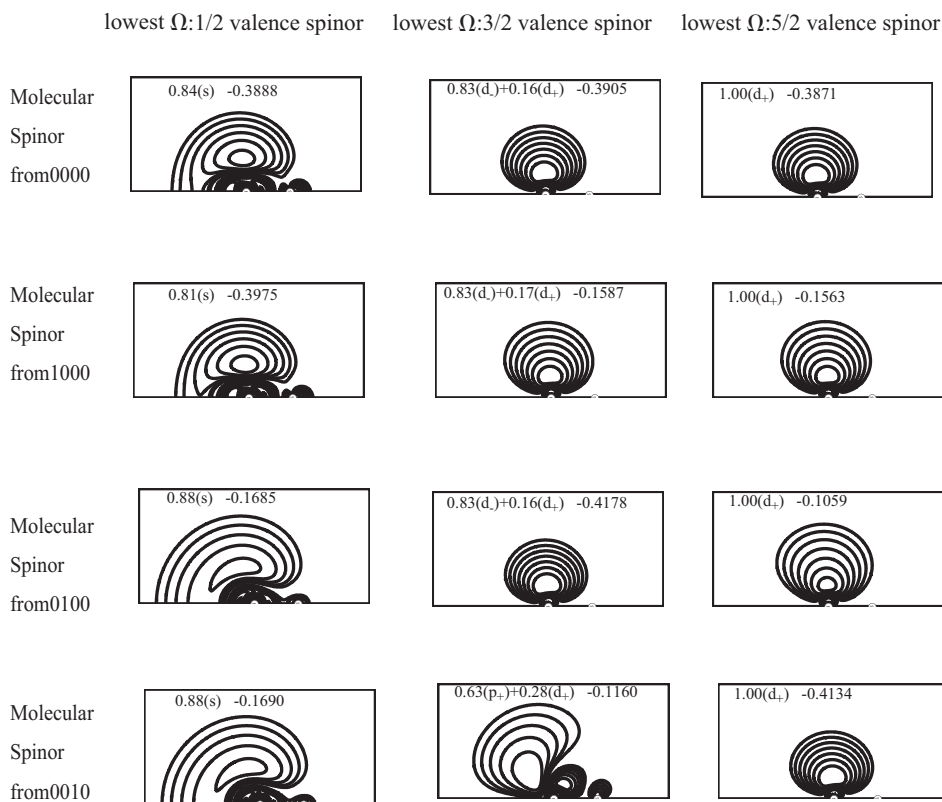
Sym.	Exptl. <sup>a</sup>	(1000)	(0100)	(0010)	(0001) <sup>b</sup>	(0000)	(0000) La val. config. <sup>c</sup>
3/2	0.00	0.00	0.00	0.00	0.00	0.00	$6s^{0.00}6p^{0.00}5d^{0.99}4f^{0.01}$
5/2	0.03	0.15	0.13	0.15	0.16	0.15	$6s^{0.00}6p^{0.00}5d^{1.00}4f^{0.01}$
5/2	2.05	2.22	2.42	2.72	1.77	1.91	$6s^{0.00}6p^{0.00}5d^{0.00}4f^{1.00}$
7/2	2.12	2.53	4.50	2.75	3.40	2.21	$6s^{0.00}6p^{0.00}5d^{0.00}4f^{1.00}$
1/2	3.75	3.90	3.78	3.79	3.69	4.02	$6s^{0.08}6p^{0.73}5d^{0.05}4f^{0.13}$
3/2	3.77	4.01	3.89	3.91	3.42	4.10	$6s^{0.00}6p^{0.76}5d^{0.05}4f^{0.18}$

The GAOPs for the active-core ( $\text{LaF}^{2+}$ ) are 26.53 and 7.47 for La and F.

<sup>a</sup>  $T_e$ ; See Ref. [17]

<sup>b</sup> Only in this calculation we found the intruder states. We therefore set the energy-denominator shift = 0.00008 to deal with the contamination [7].

<sup>c</sup> La valence configuration calculated from the MCQDPT wavefunctions given by (0000).



**FIGURE 1.** Density contour maps of the valence (virtual) spinors of (0000), (1000), (0100), and (0010). The spinor characters with GAOPs and the spinor energies ( $\varepsilon$ ) are given in the respective contour maps as GAOP $\times$ (character),  $\varepsilon$ . Circles on the z-axis indicate the La and F nuclei, which are located at (0.0, 0.0, 0.0) and (0.0, 0.0, 3.78) bohr respectively. The outermost contour of the map is at 0.0001 e bohr<sup>-3</sup>. The value at each inner contour is twice as large as that of the adjacent outer contour.

quate for correlating calculations. Figure 1 shows the charge densities. The  $1e_i$  of (0000) mimics the  $1e_i$  of  $1e_i^1$ , but  $1e_{i,s}$  of (0100) and (0010) does not.

For the virtual spinors, when considering molecules with  $n = 2m + 1$  electrons, we can use virtual spinors of the cation as a substitute for the IVO of the molecule, since the virtual spinors are determined by the potential  $V(2m)$ .

### LaF

The relativistic MCQDPT TEs at  $R = 3.82$  bohr (the experimental ground state  $R_e$  [18]) for the respective  $\Omega$ s are set out in Table III. The molecular basis sets are those of (1000), (2000), (1100), and (1010), which indicate the electron configurations of  $1e_{1/2}^1$ ,  $1e_{1/2}^2$ ,  $1e_{1/2}^1 1e_{3/2}^1$ , and  $1e_{1/2}^1 1e_{5/2}^1$ . Figure 2 shows the charge densities given by these sets.

The results in Table III run parallel to those for LaF<sup>+</sup>; the MCQDPT TEs given by (1000) are always

lower than the corresponding TEs given by any neutral set.

Table IV sets out the excitation energies and assignments at  $R = 3.82$  bohr calculated with the cation and neutral spinor sets. The (1000) set gives excitation energies comparable to those of neutral sets, which closely match the experimental values [18, 19], although the internuclear distance is fixed at  $R_e$ . (The forthcoming paper (H. Moriyama et al., in preparation) will show that the vertical excitation energies are close to the calculated  $T_e$  and  $T_0$ .) In details, the (1100) and (1010) spinors give slightly better agreement with experiment than (1000) and (2000), and the largest errors for the states are around 0.2 eV. The (1000) and (2000) spinors also give reasonable excitation energies, however, with largest errors around 0.3 eV. Appendix shows that the (1000) spinors give the best spectroscopic constants for the ground state, including the dissociation en-

**TABLE III**

Total energies (hartrees) at  $R = 3.82$  bohr for LaF calculated with one LaF<sup>+</sup> and three LaF DFR sets, denoted as (1000), (2000), (1100), and (1010).

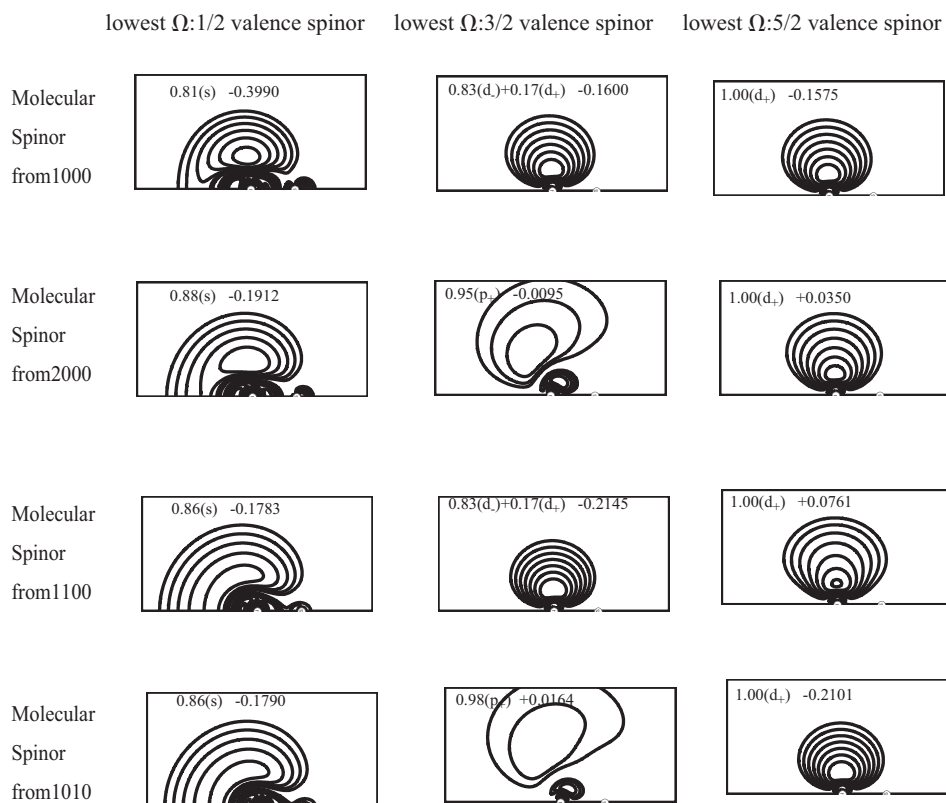
$\Omega$	(1000)		(2000)		(1100)		(1010)	
	NO	TE	NO	TE	NO	TE	NO	TE
0 <sup>+</sup>	1	-0.639588	1	-0.624949	1	-0.612760	1	-0.613495
0 <sup>+</sup>	7	-0.600985	7	-0.586574	7	-0.576139	7	-0.576940
0 <sup>-</sup>	6	-0.601159	6	-0.586737	6	-0.576315	6	-0.577111
1	2	-0.630131	2	-0.616588	2	-0.602963	2	-0.605131
1	8	-0.599644	8	-0.585243	8	-0.575015	8	-0.575624
1	10	-0.590175	10	-0.577348	10	-0.566794	10	-0.567569
2	3	-0.628251	3	-0.614663	3	-0.601449	4	-0.602547
2	5	-0.607621	5	-0.595559	5	-0.584396	5	-0.584790
2	9	-0.597428	9	-0.583096	9	-0.573044	9	-0.573402
3	4	-0.625862	4	-0.612142	4	-0.600095	3	-0.599373

From all TEs -8,594, hartrees have been subtracted.

ergy ( $D_e$ ), H. Moriyama et al. (in preparation) will show that it also gives the best  $R_e$ s for all states under consideration. Since (1000) gives the best spectroscopic constants for the ground state and

gives reasonable excitation energies, the (1000) set is most reliable.

It could be said that the MCQDPT method is based on second-order perturbation theory, and



**FIGURE 2.** Density contour maps of the valence (virtual) spinors of (1000), (2000), (1100), and (1010). Circles on the z-axis indicate the La and F nuclei, located at (0.0, 0.0, 0.0) and (0.0, 0.0, 3.82) bohr. The outermost contour of the map is at 0.0001 e bohr<sup>-3</sup>. The value at each inner contour is twice as large as that of the adjacent outer contour.

TABLE IV

MCQDPT vertical excitation energies (eV) calculated with the (2000), (1100), (1010), and (1000) sets and valence configuration calculated with (1000) for LaF at  $R = 3.82$  bohr.

Sol.	Exptl. <sup>a</sup>	(2000)	(1100)	(1010)	(1000)	(1000) La val. config. <sup>b</sup>
0 <sup>+</sup>	0.00	0.00	0.00	0.00	0.00	6s <sup>1.39</sup> 6p <sup>0.13</sup> 5d <sup>0.46</sup> 4f <sup>0.01</sup>
1	0.18	0.23	0.27	0.23	0.26	6s <sup>0.76</sup> 6p <sup>0.07</sup> 5d <sup>1.14</sup> 4f <sup>0.02</sup>
2	0.23	0.28	0.31	0.30	0.31	6s <sup>0.76</sup> 6p <sup>0.07</sup> 5d <sup>1.14</sup> 4f <sup>0.02</sup>
3	0.29	0.35	0.34	0.38	0.37	6s <sup>0.76</sup> 6p <sup>0.07</sup> 5d <sup>1.14</sup> 4f <sup>0.02</sup>
2	0.68 <sup>c</sup>	0.80	0.77	0.78	0.87	6s <sup>0.61</sup> 6p <sup>0.20</sup> 5d <sup>1.15</sup> 4f <sup>0.03</sup>
0 <sup>-</sup>	0.82	1.04	0.99	0.99	1.05	6s <sup>0.76</sup> 6p <sup>0.49</sup> 5d <sup>0.70</sup> 4f <sup>0.03</sup>
0 <sup>+</sup>	0.82	1.04	1.00	0.99	1.05	6s <sup>0.76</sup> 6p <sup>0.49</sup> 5d <sup>0.71</sup> 4f <sup>0.03</sup>
1	0.86	1.08	1.03	1.03	1.09	6s <sup>0.76</sup> 6p <sup>0.48</sup> 5d <sup>0.72</sup> 4f <sup>0.03</sup>
2	0.92	1.14	1.08	1.09	1.15	6s <sup>0.75</sup> 6p <sup>0.46</sup> 5d <sup>0.74</sup> 4f <sup>0.03</sup>
1	1.05	1.30	1.25	1.25	1.34	6s <sup>0.59</sup> 6p <sup>0.48</sup> 5d <sup>0.88</sup> 4f <sup>0.03</sup>

The GAOPs for the active-core (LaF<sup>2+</sup>) are 26.46 and 7.54 for La and F.

<sup>a</sup>  $T_e$ : See Refs. [19] and [20].

<sup>b</sup> La valence configuration calculated from the MCQDPT wavefunctions given by (1000).

<sup>c</sup>  $T_o$ .

that it overestimates the correlation energies. Our discussion also overemphasizes TE. We already see that  $D_e$  calculated using the (1000) set is the largest, but is still smaller than experiment by 0.6 eV (see Appendix), suggesting that MCQDPT overestimates the correlation energies of the molecule compared to the accurate values, but does not give larger  $D_e$  than experiment. Difficulty may arise from the complete replacement of the occupied spinors of the excited states with the virtual spinors of (1000), and difficulty in calculating the correlation energies among the open shells. The slightly better excitation energies given by the excited state spinor sets arise by sacrificing the accuracy of the description of the ground state, as seen, for example, in the poor  $D_e$  values. The problem is which set to choose. We prefer the cation set, since it gives the best values for the spectroscopic constants of the ground state and for the excitation energies comparable to neutral sets, although a tiny discrepancy remains. Tatewaki and coworkers [21] recently calculated the electronic structure of the CeF molecule using the cation and neutral sets for MCQDPT, and found that the cation set gives much better results for the spectroscopic constants and excitation energies than the neutral set. The cation MOs giving the better description of molecular correlation energies in CI calculations is summarized by Shavitt [22].

In the ordinary CI calculations, the excitation energies are often calculated by using optimum (SCF) MOs for the respective excited states. If the (2000) spinors are used for the  $\Omega = 0$  ground state

and the (1100) spinors for the first  $\Omega = 1$  and  $\Omega = 2$ , the resulting excitation energies are respectively 0.60 and 0.64 eV, as calculated from the TEs given in Table III. They are far from the experimental values of 0.18 and 0.23 eV, indicating the inappropriateness of using the respective optimum (SCF) spinors for the corresponding state in MCQDPT; the optimum spinors cannot give sufficient correlation energies, in contrast to the cation set.

The electronic potentials in (1000) are  $V\{\text{LaF}^{2+}(\dots 5p^6)\}$  for the valence and virtual spinors having  $e_{1/2}$ , and  $V\{\text{LaF}^+(\dots 5p^6 1e_{1/2}^1)\}$  for virtual spinors other than  $e_{1/2}$ . Except for the  $e_{1/2}$  spinors, (1000) gave spinors equivalent to the LaF IVOs. It is well known that electron correlation causes the correlating orbitals to be tighter than the Hartree-Fock (HF) orbitals. The use of the contracted  $e_{1/2}$  spinors given by (1000) may be equivalent to taking account of the correlation effects in advance. The cation set (1000) can therefore act as a reasonable set for the neutral molecules. We have already seen that this set gives good excitation energies, and gives the lowest TE and the best spectroscopic constants for the ground state. The potentials for the valence and virtual spinors in (2000) are  $V\{\text{LaF}(\dots 5p^6 1e_{1/2}^2)\}$ . We see from Figure 2 that  $1e_{3/2}$  and  $1e_{5/2}$  of (2000) are diffuse compared to the corresponding spinors of (1100) and (1010), suggesting that  $ne_{3/2}s$  and  $me_{5/2}s$  in (2000) are inadequate as the valence and correlated spinors. Similar considerations apply to virtual spinors in  $1e_i^1 1e_j^1$ , where spinors other than



$e_i$  and  $e_j$  are diffuse because of the potential  $V\{\text{LaF}(\dots 5p^6 1e_i^1 1e_j^1)\}$ .

We now summarize the discussion of the spinors, taking account of correlation. In considering a molecule with  $n = 2m$  electrons, we can use virtual spinors of the molecule with  $2m-1$  electrons as a substitute for the IVO except for spinors which have the same symmetry of a single electron occupancy, since the virtual spinors are determined by  $V(2m-1)$ . Spinors having the same symmetry as the single electron occupancy are determined by  $V(2m-2)$ ; see the discussion in the previous paragraph. Finally, IVO orbitals are equivalent to the pseudo-restricted Hartree-Fock (PRHF) orbitals given by one of the present authors (HT) [23].

## Conclusions

MCQDPT calculations were performed for the  $\text{LaF}^+$  molecule with one  $\text{LaF}^{2+}$  and four  $\text{LaF}^+$  DFR spinor sets. The best spinor set was that of  $\text{LaF}^{2+}$ , which gave the lowest MCQDPT TEs and gave excitation energies in good agreement with experiment. Similar calculations were performed for  $\text{LaF}$ . The  $\text{LaF}^+$  spinor set gives the lowest MCQDPT TEs, and excitation energies comparable to the neutral ground state spinors. These calculations indicate that it is best to use the DFR spinors for the  $(n-1)$  electron problem when considering the  $n$  electron correlated system.

## APPENDIX

**We list here the spectroscopic constants for the ground state of  $\text{LaF}$ . The spinors of  $\text{LaF}^+$  give the best values.**

Sol.	$\omega_e(\text{cm}^{-1})$	$R_e(\text{bohrs})$	$D_e(\text{eV})$
Exptl. <sup>a</sup>	575.2	3.823	6.23
(1000)	573.0	3.867	5.64
(2000)	544.3	3.873	5.24
(1100)	531.0	3.861	4.91
(1010)	534.2	3.859	4.93

<sup>a</sup> See Refs. [18] and [19].

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