

Ab Initio Correlated All Electron Dirac-Fock Calculations for Eka-Francium Fluoride (E119F)

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Resultados obtidos por cálculos Dirac-Fock correlacionados de 4 componentes para o fluoreto do elemento E119 (Eka-Frâncio) com base estável e precisa, livre de prolapso variacional, são reportados neste trabalho. No nível CCSD(T), a distância de equilíbrio R_e , frequência harmônica ω_e e energia de dissociação D_e são 2,432 Å, 354,97 cm^{-1} e 116,92 kcal mol^{-1} , respectivamente. Também são reportados base livre de prolapso variacional de 4 componentes para o elemento 119, uma curva analítica de energia potencial precisa e o espectro vibracional a partir dos dados obtidos no nível CCSD(T). Nossos resultados sugerem que a molécula E119F deva ser menos iônica que seus fluoretos alcalinos homólogos mais leves, em contraste com o senso químico comum baseado nas propriedades periódicas - era de se esperar nesta molécula a ligação química mais iônica possível. Também encontramos que a correção do tipo modelo de carga para negligenciar as integrais do tipo SS resulta em erros insignificantes e acelera os cálculos cerca de 3 vezes no nível CCSD(T) e cerca de 4 vezes no nível DFT/B3LYP.

Results obtained with correlated 4-component Dirac-Fock calculations for element E119 (eka-francium) fluoride with stable and accurate basis set (prolapse-free) are reported in this work. At CCSD(T) level, the equilibrium distance R_e , harmonic frequency ω_e and dissociation energy D_e are 2.432 Å, 354.97 cm^{-1} and 116.92 kcal mol^{-1} , respectively. A 4-component prolapse free basis set for E119, an accurate analytical potential energy curve and vibrational spectra from CCSD(T) data are also reported. Our results suggest that E119F should be less ionic than lighter alkaline fluoride homologues, in contrast to the common chemical belief based on periodic trends - it would be expected in this molecule the most ionic bond possible. We also found that the charge model correction to neglect SS integrals leads to negligible errors and speed up calculations close to three times at CCSD(T) level and close to 4 times at DFT/B3LYP level.

Keywords: super heavy elements (SHE), 4-component relativistic molecular calculations, 4-component gaussian basis sets, relativistic effects in chemistry

Introduction

The quest for super heavy nuclei began in 1940's with the synthesis of new elements with an atomic number greater than uranium, and the search for new elements was boosted with the prediction of an "island of stability"¹ for super heavy elements (SHE) with atomic numbers 114, 120 and 126.²⁻⁴ Some predictions estimate half-lives for isotopes

with special combination of proton and neutron numbers as long as 10^8 years, as for $^{290}\text{Sg}_{184}$.^{5,6} Recently, the production of the super heavy elements 112 through 118 using "hot" fusion reactions attained special chemical interest since the reported half-lives are in order of seconds, orders of magnitude longer than those of isotopes produced by "cold" fusion reactions. In addition to short half-lives, the drawback of low production rates also makes chemical experiments expensive, difficult and hard to perform since macrochemical properties should be inferred on the basis

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of single atom events.⁷ The question about the inertness of element 112,^{8,9} named copernicium,¹⁰ is a good example of the difficulty to characterize chemically the SHE.

The theoretical chemical research on SHE is not easier to perform since accurate quantum molecular calculations should be based on relativistic framework in order to obtain reliable properties.^{11,12} Due to strong relativistic effects, it is also known that the behavior of the SHE does not necessarily follows the known trends for lighter homologues in chemical groups, and forecasting of properties and trends based on simple extrapolations of properties of lighter homologues may result in erroneous predictions.¹³ In fact, the chemistry of SHE may be a lot of different to what is known due to these strong relativistic effects¹⁴ and perform relativistic calculations is often the only source of useful chemical information.⁷ From all possible options used for the inclusion of relativistic effects, the most reliable is the 4-component relativistic method,^{12,15} where the relativistic effects of interest for chemistry as spin-orbit or mass-velocity are included from the onset.

Relatively few all electron relativistic and highly correlated calculations exist for SHE,¹⁶ and this is particularly true for elements of the 8th period. To the best of our knowledge, there are just three articles regarding 4-component relativistic quantum chemical calculations for such elements, one¹⁷ for E126F, other¹⁸ for both E119H and E120H⁺ and another¹⁹ for intermetallic dimers including E119Au and (E119)₂. It is worth to mention that the calculations for E126F were performed without electron correlation, the calculations on E119H and E120H⁺ were performed neglecting the SS integrals using a charge model developed by Visscher²⁰ probably due to the huge computational cost inherent to 4-component calculations (in general two orders of magnitude higher than the non-relativistic ones) and the calculations on E119Au and (E119)₂ were performed at DFT level using the B88/P86 functional.^{21,22}

One way to overcome the huge computational cost of 4-component calculations is to include the relativistic effects using relativistic core potentials (RECPs).²³ Nevertheless, to develop a RECP for a SHE is very difficult:²⁴ there is only large core RECPs available for element 119, where the potential substitutes 110 inner core electrons and the basis set represents the 9 outmost valence electrons^{25,26}, and it is known that large core pseudo potentials usually give poor results on calculations.^{24,25}

Besides the “large core” difficulty, another drawback to include relativistic effects by employing approximate methods like Douglas-Kroll (two component) hamiltonian is that finite order two-component methods should use very high orders of *n* (*n* is the order of expansion) in

order to achieve reasonable accuracy. The Douglas-Kroll hamiltonian of order two, the order usually implemented in popular codes as Gaussian²⁹ and NWChem,³⁰ leads to results considerably depart from 4-component values for super heavy elements.³¹ Due to these limitations for the applicability of approximate methods to include relativistic effects to study SHE, it was pointed¹² that lack of “proper basis sets make *ab initio* DF (Dirac-Fock) methods of limited use in studies of heavy element systems”.

Now, the synthesis of element E117 last year³² made the element E119 the next target for nuclear chemists and the first element of the 8th period of periodic table to be discovered, probably an alkaline metal. Nevertheless, synthesize E117 is an experimental “tour de force” since it is necessary to obtain 97 protons from the devilishly-hard-to-synthesize berkelium, and E119 will require einsteinium, an element even more difficult to synthesize.³³ As a consequence, it is reasonable to expect that maybe it will take some years until the element E119 be synthesized.

In this work, we developed an accurate and stable 4-component relativistic basis set for E119, and applied it on all electron 4-component relativistic and correlated molecular calculations in order to obtain chemical and spectroscopic information from E119F, a molecule that should have in principle the most ionic bond according the periodic trends. The main goals were: (i) to obtain reliable spectroscopic constants for E119F at different electron correlation levels and compare with those obtained neglecting the SS integrals using the point charge model in order to evaluate its accuracy on SHE’s molecular calculations; (ii) to investigate the relativistic effects (on these constants and on bonding character) and (iii) to obtain an accurate analytical form for the ground state’s potential energy curve and the vibrational spectra derived from this analytical form. The results obtained were also compared with those lighter alkaline fluoride analogues of E119F from literature data.

Methodology

All numerical calculations on E119 atom have been carried out with a modified version of GRASP,³⁴ on which the Gaussian nuclear model³⁵ was introduced. Atomic relativistic calculations using basis sets were performed with the aid of the DRFATOM software developed by Matsuoka and Watanabe.³⁶ The basis set was generated using the polynomial version of the generator coordinate Dirac-Fock method³⁷ (p-GCDF) and minimized using the downhill simplex (DS) method.³⁸ The E119 basis set comprising a total of 34s31p23d18f uncontracted basis functions is prolapsed-free,³⁹ a condition that seems

important when calculating dissociation energies at 4-component correlated calculations.⁴⁰ The atomic mass adopted for E119 was 318 a.u. since it seems the mass of the most stable isotope for this element.⁶

All relativistic Dirac-Hartree-Fock (DHF) and nonrelativistic Hartree-Fock (HF) molecular calculations were performed with the DIRAC04 software.⁴¹ For nonrelativistic calculations, we employed the nonrelativistic limit.^{42,43} We introduced correlation at different levels, such as perturbation theory (MP2), coupled cluster single and doubles (CCSD), coupled cluster single and doubles with perturbative contribution of connected triples, CCSD(T), and with the aim of density functional theory (DFT) using the hybrid functional B3LYP. The kinetically balanced scheme was used and the basis set was uncontracted on all calculations. For fluorine atom, an aug-cc-pVTZ basis set⁴⁴ was used. The active orbital space included the 6s, 6p, 7s, 6d, 7p, and 8s orbitals for E119 atom and 2s and 2p orbitals for F atom, with the virtual space truncated above 10 a.u. due to limitations of our computational resources. Breit or quantum electrodynamics (QED) effects were not included since it is known that although not negligible, they are “of minor importance for chemical properties of super heavy elements”.¹ For example, Breit correction for transition energies (electron affinity, ionization potential) of element 121 is known to be below 0.02 eV,⁴⁵ *i.e.*, less than 0.5 kcal mol⁻¹, so it is far beyond the purposes of this work investigate it.

In order to obtain a reliable analytical form, the E119F potential energy curve was fitted using the following Rydberg function⁴⁶ of the tenth order,

$$E_{Ryd} = -D_e \left(1 + \sum_{i=1}^{10} a_i \left(R - R_{eq} \right)^i \right) e^{-a_i [R - R_{eq}]} \quad (1)$$

where D_e is the dissociation energy, R is the distance between E119 and F nuclei and R_{eq} , the equilibrium distance. The fitting of the Rydberg function parameters was obtained using the genetic algorithm.^{47,48}

The rovibrational spectroscopic constants were determined for $J=0$ and 1 to rovibrational energies ($E_{v,J}$),^{49,50} obtained via solution of the Schrödinger nuclear equation by means of discrete variable method,⁵¹ and the following equation,

$$E_{v,J} = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \dots + \left[B_e - \alpha_e \left(v + \frac{1}{2} \right) + \dots \right] J(J+1) \quad (2)$$

where $B_e = \frac{h}{8\pi^2 c I_e}$ is the rotational constant, I_e denoting

the moment of inertia, c is the velocity of light, h is the Planck's constant, and v and J are the vibrational and rotational quantum numbers, respectively.

Spectroscopic constants were obtained with the aid of the Vibrot software included on Molcas⁵² 7.4 package. The Bader volumes, based on atoms in molecules⁵³ (AIM) framework, were obtained with the aid of Henkelman's code⁵⁴ and Molekel⁵⁵ programs from densities generated by DIRAC program. Bader critical points were not calculated since programs used to calculate them such as AIM2000⁵⁶ use non-relativistic wave functions with point nucleus model.

Results and Discussion

First, it is convenient to explain how a relativistic 4-component basis set is developed. It is known that the relativistic 4-component basis set expansion method can suffer from the variational collapse problem, which results in a calculated energy lower than the corresponding numerical value when the basis set does not follow the kinetic balance or the minimax theorem. Some years ago, Faegri developed⁵⁷ 4-component basis sets and he found for the heaviest elements a small variational collapse and named it variational prolapse, or simply prolapse. Basis sets with prolapse usually have total energies below the numerical values of reference and it occurs due to the basis set deficiency, the behavior of core electrons may exhibit large nonphysical deviations whose effects on atomic and molecular properties are not completely understood. The prolapse may interfere in the self-consistent-field (SCF) convergence procedure, it may lead to wrong results when relativistic molecular calculations are performed, such as predicting incorrectly the binding energy of GdF,⁵⁸ or it can produce substantial deviations for dissociation energies at correlated calculations.⁴⁰ So several cautions should be taken when one develops a reliable relativistic basis set: in a basis set optimization procedure, it means that one should find a set with the smallest number of exponents that represents the inner core electrons very well, and that obeys both the kinetic balance and the minimax theorem. The basis set developed and used in this work takes into account all these concerns, it has total energy difference between the numerical calculation and the energy obtained by DHF close to 0.7 milli-Hartree, or less than 0.5 kcal mol⁻¹. The basis set's Gaussian exponents are shown in Table 1. The prolapse test, as explained in reference 39, reveals a small prolapse for S symmetry of 0.003 milli-Hartree, which is negligible for practical purposes. The orbital (spinors)

Table 1. Optimized gaussian basis set exponents generated for E119 under 4-component framework

Exponent Number	S	P	D	F
1	292537106000.00000	64256310.60000	694530.74700	31256.59250
2	2452664740.00000	22679199.60000	205423.29000	15504.13640
3	610698516.00000	8476300.44000	67672.89120	7855.84415
4	166834382.00000	3342760.66000	24597.76080	4057.99545
5	49735302.20000	1386047.72000	9772.39832	2132.73926
6	16092183.40000	602113.94700	4203.78443	1138.16590
7	5620651.86000	273061.47600	1939.64546	615.52978
8	2107804.84000	128818.15100	950.94600	336.66840
9	844105.24900	62991.53780	490.73824	185.86581
10	359034.17900	31814.82390	264.06657	103.36526
11	161323.81000	16537.60590	146.77612	57.79121
12	76161.43650	8815.87038	83.48044	32.41866
13	37574.76370	4802.42771	48.12940	18.20995
14	19267.81020	2663.87106	27.86387	10.22202
15	10213.95470	1499.25645	16.04673	5.72286
16	5567.13119	853.10533	9.10657	3.18913
17	3103.09764	489.04298	5.04493	1.76542
18	1759.28572	281.42501	2.70269	0.96889
19	1009.03159	161.99562	1.38704	
20	582.30577	92.94423	0.67552	
21	336.29922	52.96314	0.30928	
22	193.32123	29.86833	0.13187	
23	110.01773	16.61069	0.05187	
24	61.64896	9.07732		
25	33.83134	4.85707		
26	18.08396	2.53566		
27	9.36482	1.28695		
28	4.67291	0.63276		
29	2.23464	0.30032		
30	1.01862	0.13710		
31	0.44020	0.05999		
32	0.17938			
33	0.06855			
34	0.02444			

properties for energy and for mean values radius are shown in Table 2, confirming the good accuracy of the basis set. The largest deviation in energy was verified for 1s spinor, value in the order of magnitude of 10^{-5} hartrees.

In Table 3, the spectroscopic constants obtained for relativistic and nonrelativistic calculations are shown. First, it was observed that at the 4-component relativistic framework the contraction due to electron correlation is close to 0.015 Å, where R_c at DHF and DHF+CCSD(T) are 2.448 Å and 2.432 Å, respectively. The contraction is

smaller than the nonrelativistic counterpart, where R_c on HF and HF+CCSD(T) are 2.447 Å and 2.406 Å, respectively, and the contraction is close to 0.04 Å. Interestingly, when we compare the relativistic and nonrelativistic values at CCSD(T) level, it is suggested that relativity expands the bond length instead of contracting it as one might expect.⁵⁹

It seems that the effect on bond length is almost negligible when we compare results without inclusion of electron correlation: R_c for DHF and HF are almost the same, the deviation is close to 0.001 Å. This trend

Table 2. Spinor energies (in hartrees) and mean values of orbital parameters $\langle r^{-1} \rangle$ (in \AA^{-1}) and $\langle r \rangle$ (in \AA) obtained by numerical integration and Dirac-Fock-Roothan (DFR) with basis set developed in this work

Spinor	E (numerical)	$\langle r^{-1} \rangle$ (numerical)	$\langle r \rangle$ (numerical)	E (DFR)	$\langle r^{-1} \rangle$ (DFR)	$\langle r \rangle$ (DFR)
1s	-8386.450136	220.259110	0.008664	-8386.450100	220.259121	0.008664
2s	-1769.386849	60.526223	0.035458	-1769.386600	60.526226	0.035458
2p-	-1733.600158	62.611943	0.026808	-1733.599700	62.611899	0.026808
2p	-1161.447440	30.940644	0.041551	-1161.447200	30.940644	0.041551
3s	-486.103615	20.697715	0.095173	-486.103340	20.697716	0.095173
3p-	-466.743774	21.073750	0.087193	-466.743450	21.073737	0.087193
3p	-326.053758	12.734066	0.113418	-326.053470	12.734066	0.113418
3d-	-293.927920	12.604426	0.096433	-293.927630	12.604425	0.096433
3d	-272.122418	11.545672	0.103263	-272.122130	11.545672	0.103263
4s	-146.185193	8.667640	0.204620	-146.184880	8.667644	0.204620
4p-	-136.161667	8.685190	0.199309	-136.161370	8.685186	0.199310
4p	-94.923774	5.921408	0.245595	-94.923496	5.921407	0.245596
4d-	-78.914622	5.744830	0.236497	-78.914347	5.744828	0.236497
4d	-72.738671	5.362291	0.248287	-72.738401	5.362290	0.248287
4f-	-51.872711	5.147622	0.227143	-51.872438	5.147621	0.227143
4f	-50.041787	5.007153	0.232573	-50.041515	5.007152	0.232573
5s	-41.845153	3.975197	0.402694	-41.844796	3.975191	0.402697
5p-	-37.068482	3.900011	0.406260	-37.068213	3.900011	0.406260
5p	-24.806926	2.856224	0.492655	-24.806641	2.856223	0.492656
5d-	-17.660683	2.658387	0.514198	-17.660411	2.658387	0.514198
5d	-15.982436	2.503171	0.538097	-15.982163	2.503172	0.538097
5f-	-7.224114	2.176020	0.593474	-7.223841	2.176023	0.593472
5f	-6.829079	2.119187	0.606937	-6.828806	2.119193	0.606933
6s	-9.736356	1.838457	0.793270	-9.735947	1.838417	0.793292
6p-	-7.768021	1.744895	0.829683	-7.767731	1.744893	0.829684
6p	-4.663434	1.287468	1.034742	-4.663135	1.287469	1.034743
6d-	-2.107500	1.074133	1.220932	-2.107193	1.074137	1.220931
6d	-1.808447	1.004285	1.292257	-1.808134	1.004289	1.292256
7s	-1.563469	0.767795	1.746180	-1.563073	0.767761	1.746305
7p-	-0.954844	0.682657	1.945546	-0.954517	0.682650	1.945576
7p	-0.434780	0.470068	2.704700	-0.434487	0.470067	2.704306
8s	-0.158964	0.240419	5.200111	-0.158866	0.240821	5.183724

was also observed for lighter alkali fluorides,^{60,61} where the relativistic and correlation effects also demonstrated small influence on R_e . Dyall and Partridge⁶⁰ suggested that the properties of alkali fluorides change very little due to relativistic effects probably because the outermost spinors differ from the nonrelativistic ones, but these results were obtained in a context of lack of electron correlation, as in the case DHF and HF just mentioned above.

In addition, the changes due to correlation and/or relativity are also not negligible on ω_e and especially on

dissociation energies D_e and D_0 . Concerning the relativistic calculations, ω_e increases when we compare the DHF and the DHF+CCSD(T) results: they are 351.49 cm^{-1} and 354.97 cm^{-1} , respectively, and the difference is close to 3.5 cm^{-1} . The increase is even larger when we compare nonrelativistic results: 300.11 cm^{-1} and 318 cm^{-1} for HF and HF+CCSD(T) respectively, an increase of almost 18 cm^{-1} . Substantial deviation is also observed when we compare DHF+CCSD(T) and HF+CCSD(T), an increase of 36.91 cm^{-1} when relativistic effects are included at

Table 3. Bond lengths R_e (in Å), harmonic vibrational frequencies ω_e (in cm^{-1}) and anharmonic terms $\omega_e x_e$ and $\omega_e y_e$ (in cm^{-1}), dissociation energies D_e and D_0 (in kcal mol^{-1}), rotational constant B_e (in cm^{-1}) and rotation-vibration interaction constant α_e (in cm^{-1}) for E119F in this work

This Work	R_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	D_e	D_0	$B_e/(10^{-1})$	$\alpha_e/(10^{-3})$
Relativistic								
DHF	2.448	351.49	-4.69	2.07	127.53	127.07	1.574	1.720
DHF+MP2	2.431	356.94	-3.78	1.19	124.99	124.53	1.593	1.564
DHF+CCSD	2.434	354.12	-3.47	1.35	111.85	111.15	1.589	1.518
DHF+CCSD(T)	2.432	354.97	-3.37	1.25	116.92	116.46	1.592	1.493
DFT (B3LYP)	2.443	337.41	-1.43	1.76	94.09	93.63	1.577	1.101
Non-Relativistic								
HF	2.447	300.11	-3.17	2.41	104.93	104.47	1.573	1.464
HF+MP2	2.407	321.84	-1.89	0.52	114.61	114.15	1.624	1.108
HF+CCSD	2.413	314.08	-2.11	0.74	111.85	111.38	1.617	1.194
HF+CCSD(T)	2.406	318.06	-1.81	0.51	113.92	113.46	1.626	1.090
DFT (B3LYP)	2.412	301.35	-2.31	0.61	112.31	111.85	1.617	1.110

Table 4. Deviations observed on molecular properties when calculations were performed with charge model correction to neglect SS integrals. The units are the same as in Table 3

	R_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	D_e	D_0	B_e	α_e
DHF+CCSD(T)	-0.07	0.3520	0.0244	-0.0346	-0.2744	-0.2767	0.0001	0.0000
DFT (B3LYP)	-0.05	0.0900	0.0517	-0.0292	-0.4866	-0.4889	0.0001	0.0000

CCSD(T) level. It is also interesting to observe that although the bond length is almost the same for DHF and HF, the harmonic frequency has an increase of more than 51 cm^{-1} due to relativity. Concerning the dissociation energies D_e and D_0 , we have to consider the fluorine's electron affinity problem, the primary source of the poor dissociation energies of alkali monofluorides.⁶¹ This problem can be minimized with the inclusion of triple excitations, so we will focus only the results obtained at CCSD(T) level. The inclusion of relativity increases the dissociation energy D_0 from $113.46 \text{ kcal mol}^{-1}$ to $116.46 \text{ kcal mol}^{-1}$, an increase of $3.00 \text{ kcal mol}^{-1}$. Similar results are found for D_e .

The worst relativistic results, *i.e.*, larger deviations related to CCSD(T), were obtained at DFT/B3LYP level: the harmonic frequency was underestimated by 17.6 cm^{-1} and the dissociation energies D_e and D_0 by almost 23 kcal mol^{-1} . On the other hand, other spectroscopic constants as $\omega_e y_e$, B_e and α_e presented small absolute deviations when correlation and relativistic effects were taken into account.

The deviations on molecular properties due to the substitution of SS integrals using the point charge model (labeled as LVCOOR in the Dirac program) are shown on Table 3. Based on these results one can conclude that the deviations for practical purposes are negligible. For example, the deviations at DHF+CCSD(T) level for R_e ,

ω_e , $\omega_e x_e$ and D_e are -0.07 Å , 0.35 cm^{-1} , 0.0244 cm^{-1} and $-0.27 \text{ kcal mol}^{-1}$, respectively. Similar results were also found for calculations performed at DHF/B3LYP level. If we observe that the speed-ups observed are close to 3 at DHF+CCSD(T) and close to 4 at DHF/B3LYP levels, it becomes clear that it is a major advantage to apply this methodology.

In Table 5 we can observe Rydberg parameters obtained from fitting. These parameters, along with equation 1 generates an accurate potential energy curve fitted from DHF+CCSD(T) results for E119F's ground state. In this fitting, we used 35 DHF+CCSD(T) energies as well as the fixed equilibrium bond length (2.4322 Å) and dissociation energy ($116.92 \text{ kcal mol}^{-1}$). The obtained root mean square deviation was about 1.9789×10^{-5} hartree and it indicates the good description obtained by our analytical form for electronic energies as a function of the internuclear distances.

In Table 6 the vibrational spectra for E119F's ground state are shown. The zero point energy is close to 176 cm^{-1} and the level spacings (neighborhood transitions) are close to 338 cm^{-1} on average. These values were obtained solving the Schrodinger nuclear equation considering the internuclear distance varying from 2.00 Å (strong interaction region) to 10.00 Å (asymptotic region). The reduced mass value for the E119F system is 32667.89822 a.u.

Table 5. The Rydberg parameters needed to generate accurate potential energy curve for E119F

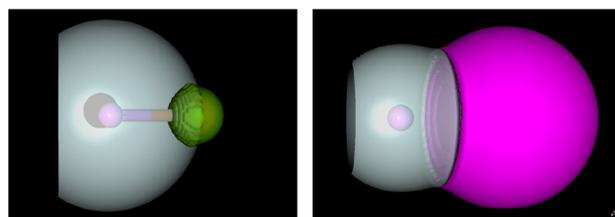
Parameters	Value	Unit
a_1	$0.234795347459 \times 10^1$	\AA^{-1}
a_2	$0.166254782038 \times 10^1$	\AA^{-2}
a_3	$0.104027972256 \times 10^1$	\AA^{-3}
a_4	$0.358992878527 \times 10^0$	\AA^{-4}
a_5	$0.134568262671 \times 10^0$	\AA^{-5}
a_6	$0.538425791164 \times 10^{-1}$	\AA^{-6}
a_7	$-0.127123705033 \times 10^{-2}$	\AA^{-7}
a_8	$-0.267747493846 \times 10^{-1}$	\AA^{-8}
a_9	$0.176335973708 \times 10^{-1}$	\AA^{-9}
a_{10}	$-0.379678115170 \times 10^{-2}$	\AA^{-10}

Table 6. The vibrational energies and transitions (in cm^{-1}) calculated at 4-component CCSD(T) level for E119F (see text for details)

Level	Value / cm^{-1}
$v = 0$	176.22
$v = 1$	526.41
$v = 2$	873.76
$v = 3$	1218.31
$v = 4$	1560.05
$v = 5$	1899.02
$v = 6$	2235.22
$v = 7$	2568.67
$v = 8$	2899.39
Neighborhood transitions	
$1 \rightarrow 0$	350.19
$2 \rightarrow 1$	347.36
$3 \rightarrow 2$	344.54
$4 \rightarrow 3$	341.75
$5 \rightarrow 4$	338.96
$6 \rightarrow 5$	336.20
$7 \rightarrow 6$	333.45
$8 \rightarrow 7$	330.72
$9 \rightarrow 8$	328.01
Transitions to ground state	
$1 \rightarrow 0$	350.19
$2 \rightarrow 0$	697.55
$3 \rightarrow 0$	1042.09
$4 \rightarrow 0$	1383.83
$5 \rightarrow 0$	1722.80
$6 \rightarrow 0$	2059.00
$7 \rightarrow 0$	2392.45
$8 \rightarrow 0$	2723.17
$9 \rightarrow 0$	3051.18

In Figure 1 the Bader volumes obtained from large components densities with density contour of 0.001 a.u. for both KF and E119F are shown (the fluorine atoms have gray translucent color). We calculated the Bader volumes

only for large components densities since it is known that the small component density is rather localized in the vicinity of the nucleus and vanishes fast as the radial distance increases.⁶² As an example,⁶³ the electron densities represented by small components are negligible compared with those by large components for valence electrons of Uranium (less than 0.03%) although 15% of the electron density is due to small component for the 1s electrons.

**Figure 1.** Bader volumes for KF (left) and E119F (right) obtained with contour density of 0.001 a.u.

First, we can observe that fluorine volume on KF is larger than the corresponding of E119F and maybe this fact can be understood as follows. Bader⁶⁴ found that for first row hydrides, the large charge transfer from one atom to another is accompanied by a polarization of the electronic charge in a direction counter to that of the charge transfer; the electronic charge distribution of the negative ion is polarized toward the cation, while the charge distribution of the cation is polarized away from the anion, being the cation polarization small. Since the transferred density in the ionic bond should be almost symmetrically placed around the nucleus and in the covalent bond the primary contribution to the binding is from the overlap density, he concluded that a strong ionic nature results in an almost spherical contour and a covalent nature should result in a more elliptical shape, as seen respectively in KF and E119F. This suggestion agrees with benchmark calculations of electron affinities (EA) of alkali atoms performed by Landau and co-workers.^{65,45} They found, using the intermediate hamiltonian Fock-space coupled-cluster (IHFS-CC) method, that element E119 should have the highest electron affinity in the 1A family with value of 15.27 kcal mol⁻¹. It is much higher than its lighter homologues francium (11.32 kcal mol⁻¹), cesium (10.94 kcal mol⁻¹), rubidium (11.31 kcal mol⁻¹), potassium (11.68 kcal mol⁻¹) or sodium (12.63 kcal mol⁻¹). In fact the electron affinity of E119 has almost the same value of some transition metal's EA, like cobalt (15.21 kcal mol⁻¹) or chromium (15.36 kcal mol⁻¹). So it is reasonable to expect that E119F should have a higher covalent nature than the lighter alkaline fluorides, and this expectation was recently reinforced since it seems¹⁹ that E119Au should have the smallest dipole moment and should be the weakest out of all group-1 MAu (M = K, Rb, Cs, Fr and E119).

The Mülliken population analysis may explain the observed expansion on bond length due to relativity. The bonding is mainly due to $7p_z$ orbital of E119 and $2p_z$ orbital of F, with small contributions of $2s$ of F and $8s$, $7p_x$, $7p_y$ and $6d_z^2$ of E119 (the relative weights are: (0.47) $7p_z$, (0.10) $7p_x$, (0.10) $7p_y$, (0.02) $8s$ and (0.03) $6d_z^2$ from E119 atom, and (0.01) $2s$ and (0.27) $2p_z$ from F atom), on the contrary of s - elements like Au and Hg where the s valence electrons participate in the bonding and are available to mix with d orbitals.⁶⁶ So the bond expansion observed may be explained as follows: the p orbitals suffer a demixing of $p_{1/2}$ and $p_{3/2}$ components due to the mass velocity and large spin-orbit splitting in E119 and as a result this demixing forces the bonding electrons into the orbital with the largest radial extend, an explanation found for the relativistic bond expansion of hydrate of the p -block element Uus.⁶⁷ This phenomenon was also found in a lesser extend to another p block element, HAt, where a small “ p ” expansion in bond length was also observed.⁶⁸

Conclusions

Although Dirac-Hartree-Fock level leads to a reasonable value for R_e and ω_e , the inclusion of correlation at 4-component CCSD(T) level is mandatory to obtain reliable results for dissociation energy D_e and D_0 . The E119F molecule should have a higher covalent nature than its lighter homologues, in contrast to what is regularly seen on textbooks or to common chemical belief based on periodic trends that suggests that E119F should have the most ionic bond possible. This deviation from periodic trends should be understood as a consequence of the strong relativistic effects on E119. We also found that the largest deviations from relativistic CCSD(T) were obtained using DFT with hybrid functional B3LYP, so its use to obtain spectroscopic constants on SHE should be done with caution. Finally, it is also worth to neglect the (SS|SS) integrals using Visscher’s Coulomb correction due to significant time savings and negligible loss of accuracy.

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