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Abstract. In this work we investigate the possibility to create cold Fr_2, RbFr, and CsFr molecules through photoassociation of cold atoms. Potential curves, permanent and transition dipole moments for the Francium dimer and for the RbFr and RbCs molecules are determined for the first time. The Francium atom is modelled as a one valence electron moving in the field of the Fr^+ core, which is described by a new pseudopotential with averaged relativistic effects, and including effective core polarization potential. The molecular calculations are performed for both the ionic species Fr_2^+, $RbFr^+$, $CsFr^+$ and the corresponding neutral, through the CIPSI quantum chemistry package where we used new extended gaussian basis sets for Rb, Cs, and Fr atoms. As no experimental data is available, we discuss our results by comparison with the Rb_2, Cs_2, and RbCs systems. The dipole moment of CsFr reveals an electron transfer yielding a Cs^+Fr^- arrangement, while in all other mixed alkali pairs the electron is transferred towards the lighter species. Finally the perturbative treatment of the spin-orbit coupling at large distances predicts that in contrast with Rb_2 and Cs_2, no double-well excited potential should be present in Fr_2, probably preventing an efficient formation of cold dimers via photoassociation of cold Francium atoms.

1. Introduction

As discussed for instance by Sprouse *et al* [1] the recent development of laser cooling and trapping of radioactive atoms opens ways for new investigations like the search for the electric dipole moment (EDM), β decay, cold atom-atom collisions, Bose-Einstein condensation and more precise atomic clocks. As the heaviest alkali-metal atom, Francium offers a sensitive test of the influence of relativistic and quantum electrodynamic effects (QED) on the atomic structure. It is also an excellent system to study weak interactions in atoms such as atomic parity non-conservation (PNC) [2, 3].

However, none of the Francium istopes is stable. The longest-lived isotope is ^{223}Fr with a half-time of 21.8 min, while the shortest-lived isotope ^{215}Fr has a half-time of 0.12 μs. Several groups have been successful in trapping long-lived isotopes in a magneto-optical trap (MOT): in 1995, Simsarian *et al* captured ^{210}Fr atoms (half-time 3.2 min) produced at the Stony Brook LINAC [4, 5]; a collaboration between the groups of C. Wieman from the University of Colorado and H. Gould from Lawrence Berkeley Laboratory lead to the trapping of ^{221}Fr (half time 4.8 min) [6]; more recently, a ^{210}Fr MOT has been set up in Legnaro (Italy) [7], but to our knoweledge its optimization is still under way.

Even if the spectroscopy of Francium atom is not yet fully investigated, a noticeable amount of experimental and theoretical data is now available for energy levels, hyperfine splittings, and transition dipole moments. In contrast, experimental conditions allowing to form Francium dimers have not yet been achieved, and the availability of cold Francium atoms in MOT's may allow one day to perform the photoassociation spectroscopy of such radioactive molecules. The creation of a mixed species cold atom trap involving Francium and Rubidium or Cesium appears as a closer possibility [8], which would allow to explore the RbFr or CsFr heteronuclear molecules.

On the theoretical side, no potential curves have been published yet on these molecular systems. To our knowledge, the only results concern the bond length and the dissociation energy of Fr_2 which have been determined by Lim *et al* [9] using various approaches based on relativistic coupled-cluster method or functional density theory. Also the van der Waals interactions between Fr, Rb, and Cs atoms have been computed by Derevianko *et al* [10].

The purpose of this paper is to calculate the electronic properties of Fr_2, RbFr, and CsFr and of their cations, including potential curves, permanent and transition dipole moments. Our aim is also to predict the rates for the photoassociation and for the formation of cold molecules, as we did previously for all mixed alkali dimers involving Li to Cs atoms [11]. Such predictions should be useful for upcoming experimental investigations. Our theoretical method relies on effective potentials for modelling the Fr^+ ionic core, as in our previous paper (hereafter identified as paper I) [12] devoted to the accurate determination of permanent dipole moments of heteronuclear alkali dimers.

The combination of large-core pseudopotentials (namely one active valence electron per alkali atom), complemented by core-polarization pseudopotentials (CPP) following

the idea of Müller and Meyer [13] has proved up to now to be one of the most successful approaches to accurately deal with the electronic structure of alkali pairs, even up to cesium [14, 15, 16, 17, 18, 19]. One of the advantage of the large-core+CPP approach is that it allows full configuration interaction (CI) even in large basis sets for the valence electrons (reduced to 2 in the case of alkali diatomics), and that the core polarization mimics the effect of coupled core-valence double excitations that otherwise should be calculated in the CI. Moreover, even for compounds including cesium, most calculations were performed within the framework of the so-called scalar (i.e. spin-orbit averaged) pseudopotentials, or averaged relativistic pseudopotentials (AREP) [20, 21, 22], which take into account scalar relativistic effects (mass correction, Darwin term) [23]. The definition of quasi-relativistic pseudopotentials is actually closely linked to the way electrostatic and spin-orbit coupling are treated. AREP's are very convenient for molecular calculations, as configuration interaction is achieved in a first step, whereas spin-orbit coupling responsible for multiplicity splitting is accounted for a-posteriori. Other schemes have been implemented in the case of heavy elements where spin-orbit coupling is large, namely two-component schemes [24] in the basis of spinors which treat electrostatic and spin-orbit coupling on an equal footing in the configuration interaction. Four-component CI calculations are also sometimes feasible [25] but still require a heavy computational effort with respect to the other methods. Detailed and recent overviews of the various techniques can be found in references [26, 27, 28, 25, 29, 30, 31, 32]. In alkali diatomics, spin-orbit coupling does not directly concern the ground state but only the excited states, and it therefore remains relatively small, even for lowest excited states of the heavy elements: the Cs($6p$) fine structure splitting is 554 cm^{-1}, and the one of Fr($7p$) is 1686 cm^{-1} [33], to be compared for instance with the one of iodine, close to 1 eV. Core-valence correlation is a larger effect in heavy alkalis, especially for the lowest valence states, closer to the core. Even more important is the two-electron valence correlation in alkali diatomics which must be treated accurately. This is why quasi-relativistic calculations with averaged relativistic large-core pseudopotentials complemented by CPP's proved to be very accurate for complexes of alkali atoms at least up to cesium [34].

Given this ability, it is appealing to extend this simple scheme to systems including the heaviest atom of the series, namely Francium. We have therefore determined a spin-orbit-averaged semi-local pseudopotential for francium in the large-core approach, namely with a single external electron, using the shape-consistent norm-conserving technique of Durand and Barthelat [35, 36], complemented with core-polarization pseudopotentials (CPP). We describe in detail in section 2 the chosen model, that we compare to the model potential approach of Klapisch [37]. We recall in section 3 the main steps of the molecular calculations, and our results for molecular ions and neutral diatomics of Francium coumpounds. Atomic units will be used throughout the text, except otherwise stated.

2. Atomic structure calculations and pseudopotential determination

In 1939, M. Perey of the Curie Institute in Paris discovered a new radioactive element that she named Francium [38]. The optical spectrum of Francium remained unknown until 1978 when the D_2 line of francium was detected by Liberman *et al* at CERN on the on-line mass separator ISOLDE [39]. Then the precise spectroscopy of francium isotopes was performed by the same group still at CERN [40, 33], while the properties of Fr highly excited states were explored at Moscow University [41]. After 1995, spectroscopic studies were carried on with cold trapped Francium atoms [4, 6, 42, 5, 1]. Hyperfine splittings [33, 43] and radiative lifetime measurements [42, 44] became then available. Among the energy levels, s levels and Rydberg d series have been the most investigated using two-step or two-photon excitation from the $7p$ manifold [41, 40, 33, 45], as well as the $7p_j$ and $8p_j$ multiplets. An ionization potential of $32848.972(9)\text{cm}^{-1}$ has been determined from the quantum defects of ns and nd Rydberg levels [33]. However the lowest $6d_{\,3/2,5/2}$ levels have not been observed yet, even if their location has been predicted using quantum defects fits of nd_j energies [46]. Levels of higher symmetry (f, g) as well as p levels beyond $n = 7, 8$ remain unknown.

On the theoretical side, Dzuba *et al* [47, 48] used relativistic Hartree-Fock and many-body perturbation theory to calculate the transition energies, fine structure intervals, electric transition amplitudes, and addressed the issue of parity violation in this atom. Eliav *et al* [49] calculated ground and excited transition energies as well as ionization potentials and electron affinities [50, 51] for all alkali atoms including Fr, with the relativistic coupled-cluster method. Relativistic many-body calculations of transition energies, hyperfine constants, electric-dipole matrix elements and static polarizabilites were performed by Safronava *et al* for all alkali atoms [52]. Derevianko *et al* [53] used many-body perturbation theory (MBPT) and model-potential calculations to investigate low-energy photoionization parameters for Fr. The same model-potential approach has been adopted by Marinescu [54] to compute long-range parameters for all alkali pairs but Fr and by Marinescu *et al* [55] for a Francium atom pair. More recently, long-range parameters for homonuclear and heteronuclear alkali dimers including Fr have been calculated by Derevianko *et al* [56, 10] using relativistic coupled-cluster method.

All these data represent a rich starting point for our molecular calculations which first impliy the determination of an accurate effective potential for the representation of the Francium ionic core. We performed three different atomic calculations. We first implemented for Francium the parametric energy-adjusted model potential (MP) proposed by Klapisch [37], further improved to involve ℓ-dependent parameters (with ℓ the orbital moment of the valence electron), core polarization effects, and spin-orbit terms [57]. Accurate atomic energy levels are obtained, allowing the use of MP predicted levels to check the quality of the pseudopotential described below. However, the Klapisch type model potentials conserve the nodal structure of the wavefunctions even within the core region, which is not very convenient for molecular calculations, especially in such heavy elements. In line with previous works on alkali diatomics, we preferred

to use a pseudopotential approach which yields nodeless atomic wave functions in the core region. We thus adopted a mean-field approach extraction. We first performed relativistic Dirac-Fock SCF calculations (DF) with Desclaux's package [58], to obtain single electron energies and spin-orbitals considered as reference data for subsequent pseudopotential determination. We then determined a spin-orbit-averaged semi-local pseudopotential (PP) for Francium within the large-core approach, complemented with core-polarization pseudopotential (CPP) which will be used in molecular calculations of section 3.

2.1. Parametric model potential (MP)

Such a model is known to be efficient for instance to calculate multiphoton cross sections of heavy alkali atoms K and Cs [59, 60] and complicated spectra of heavy alkaline-earth atoms [57]. A similar model potential without spin-orbit has been also used by other authors for the determination of the van der Waals interaction between alkali atoms [61], or of photoionization parameters in Fr [53]. The semi-local model potentiel accounting for the interaction between the ionic core and the external electron depends on the empirical parameters α_i^ℓ and contains a polarization term involving the static dipole polarizability (core- polarization contribution) of the ionic core α_d:

$$V_\ell(r) = -\frac{1}{r}\{1+(Z-1)\exp(-\alpha_1^\ell r)+\alpha_2^\ell r\exp(-\alpha_3^\ell r)\}-\frac{\alpha_d}{2r^4}\{1-\exp[-(r/r_c^\ell)^6]\} \quad (1)$$

where Z is the nuclear charge, and r_c^ℓ are cut-off radii truncating the polarization potential at short electronic distances r. We use the theoretical value for α_d=20.38 au [62] obtained with fully relativistic coupled cluster method, in very good agreement with the value α_d=20.41 au computed using relativistic random phase approximation [56]. The one-electron radial function $P_{n\ell j}$ (where j is the total angular momentum of the external electron) is the solution of the radial Schrödinger equation with eigenvalue $\epsilon_{n\ell j}$:

$$[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{\ell(\ell+1)}{2r^2}+V_\ell(r)+V_{so}^{s\ell j}(r)-\epsilon_{n\ell j}]P_{n\ell j}=0 \quad (2)$$

The spin-orbit scalar operator $V_{so}^{s\ell j}(r)$ is explicitely included and is approximated by:

$$V_{so}^{s\ell j}(r) = \frac{\alpha^2}{2}\vec{s}.\vec{\ell}\frac{1}{r}\frac{dV}{dr}\left(1-\frac{\alpha^2}{2}V(r)\right)^{-2} \quad (3)$$

where α is the fine structure constant. The last factor suggested by the Dirac equation [63] is included, to ensure that the solutions of the radial Schrödinger equation are well-defined when $r \to 0$. The empirical parameters α_i^ℓ and r_c^ℓ are adjusted until the energies $\epsilon_{n\ell j}$ agree with the experimental atomic energies (table 1).

Atomic binding energies of Francium obtained by the MP approach are compared with experimental values and with several other computations in table 2: the MPBT calculations of Dzuba *et al* performed whithin the Bruckner expansion [48], the

ℓ	α_1^ℓ	α_2^ℓ	α_3^ℓ	r_c^ℓ
0	4.29673059	13.58990866	1.54459081	1.35534853
1	4.10987255	5.87755911	1.36939901	1.22513294
2	3.39019850	0.78543635	0.92256617	1.96472431

Table 1. Empirical parameters involved in the model potential of eq.1 describing the Francium ionic core. The value α_d =20.38 a.u. [62] is introduced in the polarization potential.

Level	Exp	MP Present work	ΔE	[48]	ΔE	[49]	ΔE	[52]	ΔE	[53](1)	[53](2)
7s	-32848.87	-32848.87	0.05	-32762	86	-32839	9.8	-32735	113		
7p-	-20611.46	-20613.03	-1.5	-20654	-42	-20584	27	-20583	28		
6d-		-16684.56		-16623		-16370					
6d+		-16412.47		-16423		-16194					
7p+	-18924.87	-18922.33	2.5	-18926	-1.2	-18913	11	-18907	17		
8s	-13116.62	-13116.39	0.2	-13082	35	-13121	-4	-13051	65		
8p-	9735.91	-9730.38	5.55	-9742	-6	-9719	17	-9712	23		
8p+	9190.56.0	-9199.62	-9.0	-9188	-29	-9158	32	-9176	14		
7d-	-8604.04	-8605.25	-1.2	-8663	-58						
7d+	-8515.57	-8514.55	1.0	-8574	-58						
9s	-7177.85	-7177.94	-0.09	-7160	18			-7148	29		
9p-		-5733.61		-5736				-5724		-5748	-5737
9p+		-5493.70		-5485				-5480		-5496	-5487
8d-	-5248.22	-5246.58	1.6	-5261	-12						
8d+	-5203.50	-5204.42	-0.9	-5218	-15						
10p-		-3787.81						-3782		-3800	-3790
10p+		-3658.66						-3650		-3662	-3655
10s	-4538.26	-4538.29	-0.03	-4534	4			-4522	16		

Table 2. Theoretical binding energies of Francium (in cm^{-1}) obtained with the present MP approach, compared with other relativistic calculations and experimental energies from refs. [33, 46]. Differences ΔE between calculated and experimental energies are also displayed. Levels labelled with a $\pm$ sign means $j = \ell \pm 1/2$.

relativistic coupled-cluster (CC) calculations of Eliav *et al* [49], the relativistic many-body calculations of Safronova *et al* [52], and the results of the Quantum Defect Theory (QDT) combined with MBPT and model potential calculations of Derevianko *et al* [53].

The present MP energies are found in good agreement with the available observed energies, and are generally more accurate than the other theoretical predictions. The fine structure splitting of the $6d$ level, $\Delta E_{so} = 272.1$ cm^{-1}, is found larger than in the CC value of ref.[49], $\Delta E_{so} = 200$ cm^{-1}, and also disagrees with the values predicted using quantum defects fits of nd_J energies [46] ($\Delta E_{so} = 188$ cm^{-1}). Our predictions for all the other unobserved np_j levels agree with other theoretical values, giving in particular similar fine-structure splitting for $8p$ to $10p$ levels. These predictions for energy levels will be used in the next paragraph.

ℓ	$\alpha_{i,\ell}$	$c_{i,\ell}$	$n_{i,\ell}$
0	0.784936	14.194790	1
1	0.170429	0.352240	0
	0.170429	0.309530	1
2	0.258663	-3.442104	0
	0.258663	4.652569	-1

Table 3. Parameters of the pseudopotential of eq.4 representing the Francium core, implemented in the present work.

2.2. Pseudopotential approach (PP)

We actually used this approach to perform the molecular calculations for Fr_2 and RbFr and CsFr compounds. The ionic core is described by a semi-local ℓ-dependent pseudopotentiel (PP) [35, 36] employed in paper I:

$$W_\ell(r) = -1/r + \sum_i C_{i,\ell} r^{n_{i,\ell}} \exp(-\alpha_{i,\ell} r^2) \tag{4}$$

As explained in paper I, and in contrast with the MP approach, the parameters $C_{i\ell}$ and $\alpha_{i\ell}$ in equation 4 for Rb and Cs ionic cores are adjusted to reproduce the energies and valence orbitals of an all-electron Hartree-Fock Self-Consistent Field (SCF) calculation for the atomic ground state.

The Francium PP parameters (table 3) are chosen in order to match the results of the all-electron relativistic Dirac-Fock (DF) SCF calculations performed with Desclaux's package [58]. More precisely, we determine the large components of the Dirac-Fock solutions for the valence levels $7s_{1/2}$, $7p_{1/2,3/2}$, $6d_{3/2,5/2}$ and $5f_{5/2,7/2}$, and we adjust the PP parameters to match the corresponding *spin-orbit-averaged* orbitals. Relativistic corrections to atomic radial wave functions such mass-velocity, and the Darwin terms are automatically introduced in Dirac-Fock orbitals and thus in the pseudopotential [23], which keeps the simple expression of equation 4. As discussed by several authors on Cs or Fr exemples [47, 48, 52], zero-order Dirac-Fock energies do not include correlation effects necessary to reproduce the atomic energy level structure, taken in account through MPBT in ref.[47, 48, 52, 49]. However, while intra-core correlation effects are hardly accessible via CI, inter-shell core-valence correlation effects can be described via the core-polarization operator. Let us note finally that an *ab initio* small-core pseudopotential (involving an ionic core with 78 electrons, instead of 86 in the present work) including relativistic effects has been obtained by Ermler [64], and further used by Lee *et al* to compute ground state potential energy curves of MO oxydes with (M=Rb,Cs,Fr) [65]. However the authors have not extended their investigations towards francium-alkali pairs.

The Dirac-Fock orbitals for the fine structure doublets $7p_{1/2,3/2}$, $6d_{3/2,5/2}$, and $5f_{5/2,7/2}$ are plotted in figure 1. It is clear that even if differences between $7p_j$ orbitals are visible, this figure suggests that spin-orbit averaged orbitals can be used to set up

Figure 1. Dirac-Fock orbitals for the (a) $7p_{1/2,3/2}$, (b) $6d_{3/2,5/2}$, (c) $5f_{5/2,7/2}$ levels of Francium. The orbital with the lowest (largest) j value is drawn with full (dotted) line.

Figure 2. Spin averaged orbitals for the (a) $7s$, (b) $7p$, (c) $6d$ levels of Francium, calculated with various approaches: Dirac-Fock (dashed line), present pseudopotential (red full line), present model potential (blue dotted line).

a pseudopotential for the Francium ionic core with averaged relativistic effects. Such orbitals are drawn in figure 2 for the $7s$, $7p$, and $6d$ levels, as computed via the present MP, DF, and PP approaches. As expected, the mean-field PP pseudo-orbitals perfectly match the DF spin-orbit averaged orbitals in the region outside the core, i.e. the outer lobe of the wave function is well reproduced. In contrast, the MP orbitals are shifted inwards with respect to the DF orbitals, except for the 7s wavefunction. The same trend (not shown here) is actually observed with the nodeless PP pseudo-orbitals when the core polarization effects (see next section for the modelling of these effects) are included, compared to those pseudo-orbitals without core polarization. As the MP orbitals intrinsically contain core polarization effects, we suspect that this explains their observed pattern.

2.3. PP results for atoms

The external electron in each atom (Rb, Cs, or Fr) is described with a Gaussian basis set. In order to check the accuracy against the size of the basis set, we proceed as in paper I, defining two basis sets for Rb and Cs: we first use a $[7s4p5d]$ contracted to a $[6s4p4d]$ basis, identical to the one introduced by Pavolini *et al* [14] previously refered to as basis "A" in paper I. Then we consider for Rb the large $[9s6p6d4f]$ basis of uncontracted Gaussian functions resulting in 138 molecular orbitals (basis "B" in paper I), and we elaborate a similar $[9s6p6d4f]$ basis for Cs refered to as "B'" in the following (table 4). For the Fr atom, we use a large uncontracted $[9s9p9d]$ Gaussian basis set yielding 162 molecular orbitals (table 4). Molecular calculations for RbFr and CsFr then combine the Fr basis with one of the above basis sets for Rb and Cs.

Core-valence correlation is treated by adding a phenomenological core polarization operator W_{CPP} to the Hamiltonian of the valence electrons [13] in the field of the M^+ and M'^+ ionic cores, and :

$$W_{CPP} = -\frac{1}{2}\alpha_d^{M^+}\vec{f_M}^{\,2} - \frac{1}{2}\alpha_d^{M'^+}\vec{f'_M}^{\,2} \tag{5}$$

where $\alpha_d^{M^+}$ is the static dipole polarizability of the M^+ ion, and $\vec{f}_M$ (resp. $\vec{f}'_M$) is the total electric field seen by M^+ (resp. M'^+) due to the two electrons i and the partner ion M'^+ (resp. M^+):

$$\vec{f}_M = \sum_{i=1,2} -\frac{\vec{r}_{iM}}{r_{iM}^3}\Theta(r_{iM}) + \frac{Z_{M'}\vec{R}_{M'M}}{R_{M'M}^3} \tag{6}$$

Atom	Basis	ℓ	Exponents
Cs	$[9s6p6d4f]$	s	2.35,1.492561,0.824992,0.5,0.234682,0.032072,0.013962,0.005750,0.0025
		p	0.22,0.128,0.040097, 0.03,0.014261,0.004850
		d	0.29,0.12,0.096036,0.026807,0.009551,0.004
		f	0.2,0.1,0.05,0.005
Fr	$[9s9p9d]$	s	1.8,0.480468,0.369521,0.2,0.11230,0.053409,0.018240,0.006,0.002
		p	0.22,0.120,0.0655,0.03,0.0162,0.008,0.00443,0.002,0.001
		d	1.3,0.6,0.30,0.196894,0.067471,0.027948,0.010712,0.00300,0.001

Table 4. Exponents of the Gaussian functions introduced in the $[9s6p6d4f]$ basis for Cesium (basis "B'"), and the $[9s9p9d]$ basis for Francium.

Atom	Series	$\alpha_d^{M^+}$	ρ_s	ρ_p	ρ_d
Fr	A	20.38 [62]	3.16372	3.045	3.1343
	B	23.2[53]	3.343	3.435	3.292
Rb	A	9.245	2.5213	2.279	2.511
	B	9.245	2.5538	2.3498	2.5098
Cs	A	15.117	2.6915	1.8505	2.807
	B'	16.33	2.0081	2.6865	2.83518

Table 5. Dipole polarizabilities $\alpha_d^{M^+}$ and cutoff parameters ρ_ℓ introduced in the effective core polarization potential (CPP) for M^+ =Fr, Rb, Cs. Values for Rb (basis A and B) and Cs (basis A) are recalled from paper I, while new values for the Cs B' basis are reported.

Experimental values for $\alpha_d^{M^+}$ are available for Cs and Rb as reported in paper I. We introduce a dependence on the electronic orbital momentum ℓ in the effective core polarization potential [34], through the cut-off functions Θ_ℓ to prevent the CPP matrix elements from diverging at the origin. As in ref. [34], Θ_l is taken as a step function vanishing below the ℓ-dependent cut-off radii ρ_ℓ.

For each basis set and a fixed value of $\alpha_d^{M^+}$, the cut-off radii are adjusted to reproduce the experimental energies [67, 68, 69] of the lowest s, p and d levels of Cs and Rb (Table 5). As no experimental determination for the Fr^+ polarizability is available, we use like in the previous MP approach $\alpha_d^{Fr^+}$ =20.38 a.u. [62]. Another estimate $\alpha_d^{Fr^+}$ =23.2 a.u. was obtained from an extrapolation of known core polarizabilities of the lighter alkali atoms [53], and we will discuss in the next section the influence of this parameter. As for Rb and Cs, the cut-off radii are adjusted on the experimental atomic energies [33, 46], for each above value of $\alpha_d^{Fr^+}$ (Table 5). The sensitivity of the results with the cut-off radii values is such that the influence of the polarizability can be balanced to provide a good representation of energy levels with both sets A and B.

Level	Exp	with $\alpha_d^{Fr^+}$ =20.38 a.u.	ΔE	with $\alpha_d^{Fr^+}$ =23.2 a.u.	ΔE
$7s$	-32848.87	-32848.87	0.002	-32848.87	0.002
$7p$	-19487.07	-19486.93	0.143	-19487.18	-0.110
$6d$	-16471.07	-16470.92	0.147	-16470.94	0.128
$8s$	-13116.62	-13161.02	-44.	-13136.97	-20.
$8p$	-9372.35	-9448.16	-76.	-9424.96	-53.
$7d$	-8550.96	-8394.77	156.	-8371.59	179.
$9s$	-7177.85	-7161.96	16.	-7151.28	26.
$9p$	-5573.18	-5619.67	-46.	-5605.27	-32.
$8d$	-5221.39	4981.02	240	4963.01	258

Table 6. Computed binding energies of atomic Francium atom in cm^{-1} with the two available Fr^+ polarizabilities, compared to experimental values [33, 46], and corresponding energy differences ΔE. For the unobserved $9p$ level our reference is the spin-averaged value predicted by the model-potential approach described earlier in the text.

3. Molecular calculations

As in paper I, we used an automatized procedure based on the CIPSI package [71]. The molecular orbitals are determined by restricted single electron calculations including the CPP [34], namely corresponding to $[XY]^+$ systems, providing the potential curves for the relevant molecular cations. A full valence configuration interaction (CI) is then performed for each involved molecular symmetry, providing potential curves and permanent and transition dipole moments. In the case of neutral pairs, two-electron full CI is achieved in the framework of a single-component scheme. Clearly, further investigations using two- and four component schemes or larger cores would be interesting, although not easily tractable even at present, especially in the case of excited states, if one wants to include excitations corresponding to core polarization effects. Such calculations would anyway imply the use of two- or four-component pseudopotentials, which was not achieved here.

In addition to the explicit above calculations, it is also important to estimate the magnitude of the deviation from the Coulomb repulsion of core-core interactions, which could be significant for the heavier and larger alkali atoms. The most significant effect is the repulsive overlap of the cores, which can be either extrapolated from exponential formulas valid for the lighter species [14], or derived from a calculation of $[XY]^{++}$ at the Hartree-Fock level, for instance within the frozen core approximation [17, 18, 72] which is adapted here as the core polarization is accounted for through an effective potential. The main influence of this term is to make the short-range repulsive part of the potentials steeper, while it dies out in the region of the minimum of the ground state. According to ref.[72], this term contributes for about 15 cm^{-1} at the equilibrium distance of the ground state of Na_2, K_2, Rb_2 and Cs_2, and slightly more ($\approx$40 cm^{-1}) for RbCs. A comparable estimation is probably appropriate for the Francium compounds

studied here.

The contribution of the core-core dispersion energy can be estimated via the London formula (see for instance ref.[14]):

$$V_{cc}^{disp}(R) = -\frac{3\alpha_d^{X^+}\alpha_d^{Y^+}}{2R^6}\frac{E_I^{X^+}E_I^{Y^+}}{E_I^{X^+}+E_I^{Y^+}} \tag{7}$$

where $E_I^{X^+}$ and $E_I^{Y^+}$ are the ionisation energies of the X^+ and Y^+ ions respectively. At the equilibrium distance of the ground state, this term deepens the potential by about 27, 16 and 18 cm^{-1} for Fr_2, RbFr and CsFr respectively. It basically compensates the core-core term above.

3.1. Potential curves of Fr_2^+, $RbFr^+$, $CsFr^+$

We display in figure 3 the potentiel curves of the ground state $(1)^2\Sigma_g^+$ and the lowest $(1)^2\Sigma_u^+$ state of Fr_2^+. We see in figure 3a that the choice of the large Fr^+ polarizability $\alpha_d^{Fr^+}$ =23.2 a.u. induces a potential well deeper by about 16 cm^{-1} than with $\alpha_d^{Fr^+}$ =20.38 a.u. . Its effect is then rather small, possibly within the usual inaccuracy which was previously observed for this type of quantum chemistry calculations.

Since no experimental result is presently available, we qualitatively compare our results for the Fr_2^+ ground state with those of Rb_2^+ and Cs_2^+ in the main panel of Figure 3, and in Table 7. The well depth of the ground state indeed decreases for increasing mass of the atom, as it can be observed over the whole sequence of homonuclear alkali ions. In contrast the Fr_2^+ equilibrium distance is found slightly smaller the Cs_2^+ one, and larger than that of Rb_2^+. Note that a similar trend was also found by Lim *et al* [9], but the large dispersion of the dissociation energy found by these authors does not allow an easy comparison with our results. These results illustrate that the properties of the Fr atom are not reducible to extrapolations from the lightest ones due to relativistic effects. This is fingerprinted by the size evolution of the lowest ns valence orbital, the $7s$ orbital of Francium being more contracted than the $6s$ one of cesium, whenever relativistic effects are taken into account. Indeed, Dirac-Fock calculations yields averaged radii values of 5.91 a_0 for the $7s$ orbital in Francium and 6.08 a_0 for the $6s$ orbital in cesium, while the non-relativistic HF calculation reverses this hierarchy yielding 6.25 a_0 for Francium $7s$, and 5.85 a_0 for Cesium 6s. Such orbital contractions were illustrated on atoms by Desclaux [70]. In the case of alkali's, these contractions are further correlated with an increase of the atomic ionization potentials as discussed later on in the paper. This behaviour illustrates on francium compounds the influence of relativistic effects on the chemical bonding whenever heavy atoms are involved.

A similar pattern is observed for the $(1)^2\Sigma_u^+$ state (3b). It is interesting to note that such a shallow long-range potential well is predicted for all ionic alkali dimers including heteronuclear ones [73, 74, 75], and could be used as an alternative route for the detection through resonant ionization of ultracold molecules [12, 76].

We performed the same analysis for the two lowest states of $RbFr^+$ and $CsFr^+$ compared with those of $RbCs^+$ (figure 4and Table 7). Among the three atoms, Rb

Figure 3. Main panel: potential curves of the ground state $1^2\Sigma_g^+$ (full lines) and the lowest $1^2\Sigma_u^+$ state (dashed lines) of Fr_2^+ (black lines), compared with those of Rb_2^+ (red lines with open circles) and Cs_2^+ (blue lines with closed circles). All curves are referenced to the same dissociation energy taken as the origin. (a) Comparison of calculations with $\alpha_d^{Fr^+}$ =20.38 a.u. [62] (full line) and with $\alpha_d^{Fr^+}$ =23.2 a.u. [53] (dot-dashed line). (b) Blow up of the long-range well predicted in the $1^2\Sigma_u^+$. The main and (b) panels display calculations with $\alpha_d^{Fr^+}$ =20.38 a.u., and with basis B and B' for Rb_2^+ and Cs_2^+ repectively.

Figure 4. Potential curves of the ground state $(1)^2\Sigma^+$ (panel a) and of the $(2)^2\Sigma^+$ state (panel b) of $RbFr^+$ (black lines) and $CsFr^+$ (full red lines with open circles), compared with those of $RbCs^+$ (blue lines with closed circles). The energy origin is taken in both cases at the dissociation limits of the potentials. Calculations reported in panels a and b are performed with $\alpha_d^{Fr^+}$ =20.38 a.u. [62], and basis B and B' for Rb and Cs respectively. (c) Ground state of the $RbFr^+$ ion: calculations with $\alpha_d^{Fr^+}$ =20.38 a.u. and basis A for Rb (full line), with $\alpha_d^{Fr^+}$ =23.2 a.u. [53] and basis A (Rb) (black dot-dashed line), and with $\alpha_d^{Fr^+}$ =20.38 a.u. and basis B (Rb) (full line with circles). (d) Same as (c) for $CsFr^+$ ion.

has the largest ionization potential and Cs the lowest one. The ground state $(1)^2\Sigma^+$ of $RbFr^+$ (resp. $CsFr^+$) is correlated to Rb(5s)+Fr^+ (resp. Fr(7s)+Cs^+) and the $(2)^2\Sigma^+$ to Fr(7s)+Rb^+ (resp. Cs(6s)+Fr^+). There is no clear trend for the hierarchy among well depths of the three systems. An analysis of the ground state of the whole ensemble of heteronuclear alkali molecular ionic species [74] shows that the $NaLi^+$ has the deepest well (more than 8000 cm^{-1}) with the smallest equilibrium distance (around $6.5a_0$). The $RbCs^+$, KCs^+ and KRb^+ ions have comparable well depth (in the 5000-6000 cm^{-1} range) and equilibrium distances (around 8.5-$9a_0$), while the remaining species exhibit well depth ranging between 3500 and 5000 cm^{-1}, with comprable equilibrium distance around 8-$9a_0$. The $RbFr^+$ and $CsFr^+$ ions fit into the second category. As already found for $RbCs^+$ in ref.[73], a shallow long-range well is present in the $(2)^2\Sigma^+$ potential curve of $RbFr^+$ and $CsFr^+$ ions (figure 4b) similar to the well of $(1)^2\Sigma_u^+$ potential of homonuclear dimers. The difference induced by the different choices of parameters within these compounds is illustrated in figure 4c,d. As in Fr_2^+, the larger Francium polarizability yields a deeper potential well. Increasing the size of the Rb basis has the same effect, as the $RbFr^+$ well depth is increased by about 11 cm^{-1}. In contrast, increasing in the same way the size of the Cs basis slightly changes the $CsFr^+$ equilibrium distance, but not its depth.

3.2. Potential curves and permanent dipole moments for Fr_2, RbFr, CsFr lowest states

As no experimental data are available, the neutral systems involving Fr are analyzed along the same lines than the molecular ions in the previous section. Figure 5 shows

$(1)^2\Sigma_g^+$	Basis	D_e (cm^{-1})	R_e (a_0)
Fr_2^+	(a)	5537	9.61
	(b)	5552	9.65
Rb_2^+	A	6138	9.08
	B	6208	9.05
Cs_2^+	A	5950	9.75
	B'	5977	9.85
$((1)^2\Sigma_u^+$	Basis	D_e (cm^{-1})	R_e (a_0)
Fr_2^+	(a)	72.3	24.0
	(b)	72.6	24.0
Rb_2^+	A	81.7	23.0
	B	82.1	23.0
Cs_2^+	A	82.7	24.3
	B'	84.6	24.3
$(1)^2\Sigma^+$	Basis	D_e (cm^{-1})	R_e (a_0)
$RbFr^+$	A	5439	9.3
	B	5450	9.3
$CsFr^+$	A	5054	9.68
	B'	5052	9.72
$RbCs^+$	A,A	5053	9.40
	B,B'	5090	9.41
$((2)^2\Sigma^+$	Basis	D_e (cm^{-1})	R_e (a_0)
$RbFr^+$	A	205.9	19.65
	B	206.1	19.65
$CsFr^+$	A	291.3	19.07
	B'	295.7	19.06
$RbCs^+$	A,A	381.6	17.83
	B,B'	389.5	17.84

Table 7. Well depth D_e and equilibrium distance R_e (a_0=0.0529177 nm) of the potential wells obtained in the present work for the two lowest $^2\Sigma$ states of Fr ionic compounds. Results for Rb_2^+, Cs_2^+ and $RbCs^+$ are also displayed for comparison. (a) and (b) results for Fr_2^+ correspond to $\alpha_d^{Fr^+}$ =20.38 a.u. [62] and with $\alpha_d^{Fr^+}$ =23.2 a.u. [53] respectively. Results for heteronuclear systems are obtained with $\alpha_d^{Fr^+}$ =20.38 a.u.. Note that results with basis B' for Cs_2^+ and (B,B') basis results for $RbCs^+$ are new, while those Rb_2^+ were already given in ref.[11].

the lowest Fr_2 potential curves dissociating into $7s + 7s$, compared with those of Rb_2 and Cs_2. The influence of the value of the Fr^+ polarizability is clearly larger than in the molecular ion, as two electrons now contribute to the polarization of the cores (Figure 5b,d): the depth obtained with $\alpha_d^{Fr^+}$ =23.2 a.u. [53] is larger by about 80 cm^{-1}, and by about 12 cm^{-1} for the $(1)^1\Sigma_g^+$ ground state and for the $(1)^3\Sigma_u^+$ state respectively.

Figure 5. Potential curves of the ground state $(1)^1\Sigma_g^+$ (panel a) and the lowest $(1)^3\Sigma_u^+$ state (panel b) of Fr_2 (full line with circles) calculated with $\alpha_d^{Fr^+}$ =20.38 a.u. [62], compared with those of Rb_2 with basis B (blue dot-dashed line) and Cs_2 with basis B' (red dashed line). The energy origin is taken at the dissociation limits of the potentials. (b) Ground state of the Fr_2 dimer obtained with with $\alpha_d^{Fr^+}$ =20.38 a.u. (full line), and with $\alpha_d^{Fr^+}$ =23.2 a.u. [53] (dashed line). (d) Same as (b) for the $(1)^3\Sigma_u^+$ state.

Figure 6. Potential curves of the ground state $(1)^1\Sigma^+$ (panel a) and the lowest $(1)^3\Sigma^+$ state (panel b) of RbFr (full black line) and CsFr (dashed red line), compared with those of RbCs (blue dots). The energy origin is taken at the dissociation limit of the potentials. We used $\alpha_d^{Fr^+}$ =20.38 a.u. and basis B and B' for Rb abd Cs respectively.

As for molecular ions the the well depth increases with increasing mass, while and the equilibrium distance increases along the series Rb_2, Fr_2, Cs_2, again in agreement with ref.[9].

The lowest potential curves of RbFr and CsFr are displayed in Figure 6, compared with RbCs ones. In contrast with the related molecular ions, the RbCs ground state and lowest triplet state are found deeper than those of the Fr compounds. This suggests that the overall energy associated to the core polarization strongly depends not only on the polarizability of the individual atoms, but also on the difference of their ionization potentials, in a somewhat irregular way along the series of mixed alkali dimers. The characteristics of these wells are reported in Table 8, including those for Rb_2, Cs_2, RbFr, CsFr, and RbCs. As in the previous section, Rb_2 results of type B were already shown in paper I, while those for Cs_2 and RbCs are new.

The permanent dipole moment of RbFr and CsFr are given in Figure 7 for the ground state and the lowest triplet state, respectively and compared with the results from paper I for RbCs. Note that results are not significantly different when using bais A or B and B' for Rb and Cs.The sign of charge transfer in the ground state of an XY diatomic molecule can be roughly determined by comparing the asymptotic energy costs $\Delta(XY) = IP(X) - EA(Y)$ versus $\Delta(YX) = IP(Y) - EA(X)$ describing ionization (IP stands for ionization potential) combined with electron attachement (EA stands for electron affinity) at dissociation. For alkali atoms from Li to Cs, the heavier the alkali atom, the smaller the ionization potential (43487, 41449, 35009, 33691, and 31406 cm^{-1}) and the larger the electron affinity (experimental values are 4984, 4403, 4043, 3020, and 3803 cm^{-1}), for Li, Na, K, Rb and Cs, respectively [49]. It is easy to show that in heteronuclear alkali diatomics including atoms up to Cs, the electron transfer from the heavy atom towards the light one is expected to be more favorable, due to the regular decrease of the IP's with increasing atom size which is not compensated by the corresponding variation of electron affinities. This is indeed confirmed for instance in our results from paper I, where we chose the convention of a negative sign of the ground state dipole moment in XY molecules corresponding to a X^-Y^+ configuration where the X atom is lighter than the Y atom [12]. This model is no longer valid for Fr. Indeed,

$(1)^1\Sigma_g^+$	Basis	D_e (cm^{-1})	R_e (a_0)
Fr_2	(a)	3498	8.45
	(b)	3576	8.45
Rb_2	A	3861	7.9
	B	4039	7.9
Cs_2	A	3703	8.65
	B'	3787	8.69
$(1)^3\Sigma_u^+$	Basis	D_e (cm^{-1})	R_e (a_0)
Fr_2	(a)	188.5	12.5
	(b)	200.8	12.5
Rb_2	A	233.6	11.6
	B	258.9	11.6
Cs_2	A	255.0	12.0
	B'	286.8	12.0
$(1)^1\Sigma^+$	Basis	D_e (cm^{-1})	R_e (a_0)
RbFr	A	3654	8.2
	B	3690	8.2
CsFr	A	3553	8.55
	B'	3576	8.57
RbCs	A,A	3655	8.27
	B,B'	3921	8.29
$((1)^3\Sigma^+$	Basis	D_e (cm^{-1})	R_e (a_0)
RbFr	A	207.2	12.0
	B	209.8	12.0
CsFr	A	209.5	12.36
	B'	217.9	12.33
RbCs	A,A	253.7	11.70
	B,B'	273.1	11.65

Table 8. Well depth D_e and equilibrium distance R_e of the potential wells obtained in the present work for the ground state and the lowest triplet state of Fr neutral compounds. Results for Rb_2, Cs_2 and RbCs are also displayed for comparison. (a) and (b) results for Fr_2 correspond to $\alpha_d^{Fr^+}$ =20.38 a.u. [62] and with $\alpha_d^{Fr^+}$ =23.2 a.u. [53] respectively. Results for heteronuclear systems are obtained with $\alpha_d^{Fr^+}$ =20.38 a.u.. . Note that results with basis B' for Cs_2 and with (B,B') basis for RbCs are new, while those Rb_2 were already given in paper I.

the ionization potential IP(Fr)=32848 cm^{-1} is larger by 1442 cm^{-1} than the one of Cs, almost half-way between IP(Cs) and IP(Rb), whereas the electron affinity EA(Fr)=3920 cm^{-1} [51] (see also ref. [77]) exceeds EA(Cs) by only 117 cm^{-1}. This IP increase is clearly related to the decrease of the orbital radius mentionned above. The energy cost $\Delta(CsFr)$ is lower than $\Delta(FrCs)$ by 1559 cm^{-1}, while $\Delta(RbCs)$ is larger than $\Delta(CsRb)$

Figure 7. Permanent dipole moment functions of the ground state $(1)^1\Sigma^+$ (panel a) and the lowest $(1)^3\Sigma^+$ state (panel b) of RbFr (black dashed line) and CsFr (red dot-dashed line, ompared with those of RbCs (blue full line). A negative dipole moment corresponds to a X^-Y^+ configuration. We used $\alpha_d^{Fr^+}$ =20.38 a.u. and basis A for Rb abd Cs.

by about the same amount. The charge transfer in CsFr is then expected to be Cs^+Fr^-, which is confirmed by the positive sign of the dipole moment. The situation of RbFr is more ambiguous since the difference $\Delta(RbFr) - \Delta(FrRb) = -57$ cm^{-1} is quite small, predicting a Rb^+Fr^- arrangement. But the dipole moment is found negative and of small magnitude negative, compatible with a very weak electron transfer to form a Rb^-Fr^+ arrangement. This apparent disagreement may be due to an uncertainty on the calculated electron-affinity of Francium [51], but it most probably demonstrates the role of the polarization forces occurring at finite distance, resulting from the subtle and self-consistent unscreening of the ion electric field by the one of the electrons.

The equilibrium distance of the lowest triplet state is large, and the state behaves like a neural state due to spin-forbidden electron transfer. The dipole moment then remains very weak, but we remark that its variation for RbCs is opposite to the RbFr and RbCs ones. At shorter distances, the magnitudes of the dipole moments may be increased due to overlapping atomic distributions.

3.3. Excited states of Fr_2, RbFr, CsFr and prospects for photoassociation and cold molecule formation

It is also interesting to look at the Fr_2 excited states dissociating to the $7s + 7p$ limits in order to verify if the Fr_2 system behaves similarly to the Cs_2 and Rb_2 species. For instance the existence of long-range molecular wells [78] has been decisive in the formation process of Cs_2 and Rb_2 molecules [79, 80]. Excited potential curves of *gerade* and *ungerade* symmetry correlated to the $7s+7p$ limit are reproduced in Figure 8. Their overall variation is similar to the one for all homonuclear alkali pairs, with for instance a crossing at short distances between the $(1)^1\Sigma_u^+$ and $(1)^3\Pi_u$ curves, which gives rise to an avoided crossing when spin-orbit interaction is introduced.

The magnitude of the atomic spin-orbit coupling is reported in the figure, showing that it will be the dominant interaction down to quite short internuclear distances ($R \approx 20a_0$). Assuming that a constant spin-orbit interaction is a reasonably good approximation for $R > 20a_0$ (as it was the case in Cs_2, see for instance ref.[81]), we can diagonalize the electronic Hamiltonian including spin-orbit (also given in ref.[81]), yielding the curves reported in Figure 9. In contrast with the Cs_2 [82] and Rb_2 [81] molecules, the spin-orbit interaction is so strong in Francium that it dominates the electrostatic interaction over a range of internuclear distances such that it prevents the occurence of long-range potential wells in the 0_g^- and 1_u symmetries, resulting respectively from the interaction between the $^3\Pi_g$ and $^3\Sigma_g^+$ states, and between the $^3\Pi_u$,

Figure 8. Excited potential curves of *gerade* (panel a) and *ungerade* (panel c) symmetry correlated to the Fr($7s$)+Fr($7p$) dissociation limit, obtained with $\alpha_d^{Fr^+}$ =20.38 a.u.. Panel b and d focus on the long-range part of these curves.

Figure 9. Same as Figure 8, but including now the fine structure induced by the atomic spin-orbit interaction.

$^1\Pi_u$, and $^3\Sigma_u^+$ states. For the same reason, the expected avoided crossing generated by the interaction between the $(1)^1\Sigma_u^+$ and $(1)^3\Pi_u$ states is no more well localized so that the resulting 0_u^+ curves are almost uncoupled.

The photoassociation rate for cold Francium atoms can be estimated by comparison with the cesium one, assuming that similar experimental conditions could be achievable. Following the model developed in ref.[83], we consider a PA transition close to an atomic D line. The photoassociation rate R_{PA} is then proportional to the product of characteristic constants $\lambda_D^3 \mu^{-1/2} C_3^{2/3} \tau_D^{-1}$, where λ_D is the wavelength of the D transition, μ the reduced mass of the atom pair, C_3 the effective long-range coefficient of the PA state, and τ_D the radiative lifetime of the D line. Then the ratio of PA rates is estimated according to:

$$\frac{R_{PA}(Fr)}{R_{PA}(Cs)} = \left(\frac{\lambda_D(Fr)}{\lambda_D(Cs)}\right)^3 \left(\frac{\mu_{Cs}}{\mu_{Fr}}\right)^{1/2} \left(\frac{C_3^{Fr}}{C_3^{Cs}}\right)^{2/3} \frac{\tau_D(Cs)}{\tau_D(Fr)} \tag{8}$$

where the effective C_3 coefficient for Francium has been roughly estimated [84] from the atomic lifetime of the D2 line [42]. Equation 8 results in a factor of about 0.7, meaning that PA is expected to be almost as efficient in Francium than in Cesium. On the other hand, the absence of double-well potential, or of a significant interaction between the two 0_u^+ curves (labelled as resonant coupling in ref.[85]) will probably prevent the efficient formation of cold Francium dimers in deeply bound levels of the ground state or of the lowest triplet state (see refs. [79, 85] for a full description of these mechanisms), leaving molecules only in the uppermost bound vibrational levels. Moreover, the van der Waals coefficient of ground state Francium C_6^{Fr} =5226 a.u. is smaller than the one of Cesium C_6^{Cs} =6851 a.u.[10]. The corresponding dimer potential curves have a shorter range, which also does not favor the stabilization of long-range PA molecules by radiative decay towards these states.

The excited potential curves correlated to the two lowest $s+p$ dissociation limits in RbFr and CsFr are drawn in Figure 10, as obtained with $\alpha_d^{Fr^+}$ =20.38 a.u., and with basis B and B' for Rb and Cs. In contrast with all other the mixed pairs, the smallest excitation energy is now for the lightest atom, which is another characteristic which illustrates the unusual character of the Francium atom compared to the rest of the alkali series. In RbFr, the spin-orbit is expected to strongly mix both $5p+7s$ and $5s+7p$ asymptotes (see the dashed and dotted boxes in Figure 10, which cannot be represented by the perturbative approach employed for Fr_2, and multiple-well structures may probably be expected. The CsFr asymptotes are more spaced than in RbFr, so

Figure 10. Excited potential curves for (a) FrRb and (b) FrCs molecules correlated to the two lowest $s+p$ dissociation limits, obtained with $\alpha_d^{Fr^+}$ =20.38 a.u., and with basis B and B' for Rb and Cs respectively. The dashed and dotted area indicate respectively the atomic fine structure splitting for Rb and Fr (in panel a), and for Cs and Fr (in panel b). Full lines: singlet states. Dashed lines: triplet states. Black lines: Σ states. Red lines with circles: Π states. The energy origin is taken at the $5p+7s$ and $6p+7s$ limit for RbFr and CsFr respectively.

Figure 11. Transition dipole moments from the ground state towards the first excited (a) $^1\Sigma^+$ states and (b) $^1\Pi$ in Francium compounds. Full black lines: $X \rightarrow (1)^1\Sigma_u^+(7s+7p)$ and $X \rightarrow (1)^1\Pi_u(7s+7p)$ in Fr_2. Full red lines with closed circles: $X \rightarrow (1)^1\Sigma^+(5p+7s)$ and $X \rightarrow (1)^1\Pi^(5p+7s)$ in RbFr. Dashed red lines with closed circles: $X \rightarrow (2)^1\Sigma^+(5s+7p)$ and $X \rightarrow (2)^1\Pi(5s+7p)$ in RbFr. Full blue lines with open circles: $X \rightarrow (1)^1\Sigma^+(6p+7s)$ and $X \rightarrow (1)^1\Pi(6p+7s)$ in CsFr. Dashed blue lines with open circles: $X \rightarrow (2)^1\Sigma^+(6s+7p)$ and $X \rightarrow (2)^1\Pi(6s+7p)$ in CsFr.Calculations are performed with $\alpha_d^{Fr^+}$ =20.38 a.u., and with basis A for both Rb and Cs.

that the perturbative approach may be valid at large distances, but strong mixing will probably occur at short interatomic distances.

The van der Waals coefficients for these systems, C_6^{RbFr} =4946 a.u. and C_6^{CsFr} =5968 a.u. have the same magnitude than the RbCs one C_6^{RbCs} =5663 a.u.[10], so that the stabilization of PA molecules by radiative decay should be as efficient as in RbCs [86].

Finally we present in Figure 11 the transition dipole moments between the ground state and the first excited $^1\Sigma^+$ states and $^1\Pi$ in Francium compounds. Here also results are equivalent when using basis A or basis B and B' for Rb and Cs respectively. In the upper panel, one sees that the RbFr and CsFr dipole moments for the transition towards the lowest Σ excited state are superimposed onto the Fr_2 function between 7 and $12a_0$, suggesting that in this range, the electrons are closer to the Francium cores confirming the discussion about permanent dipole moments above. The same pattern is observable in panel b as well, but over a shorter range (8 to 10 a_0). The presence of a strong avoided crossing between the $^1\Pi$ states in RbFr and CsFr is visible here as the two transition dipole moment functions cross each other at the position of the avoided crossing.

4. Conclusion

In this work we investigated the possibility to create cold Fr_2, RbFr, and CsFr molecules through photoassociation of cold atoms. Indeed, the creation of dense samples of cold Francium atoms may become available experimentally, as well as the mixing with cold Rubidium or Cesium atoms. We predict that under comparable experimental conditions, photoassociation of cold Francium atoms should be as efficient as with cold cesium atoms. In contrast the formation of ultracold Fr_2 molecules will probably be weaker as the formation processes known in Cs_2, relying on the presence of long-range potential

wells or resonant coupling, are not expected in Fr_2. However, the formation of ultracold RbFr or CsFr molecules is probably as efficient as in RbCs, which could be worthwhile to try experimentally as dense cold Rb and Cs samples are widely available.

To extract these results, we performed the first calculations of the electronic structure of the Fr_2, RbFr, and CsFr molecules, yielding potential curves, permanent and transition dipole moments. A new scalar (ie spin-orbit averaged) pseudopotential has been determined to represent the interaction of the valence electron with the large Fr^+ core complemented with core-polarization operators. Through a comparison with the closest heavy alkali dimers Rb_2, Cs_2 and RbCs, we found that our results yield a realistic representation of the Fr_2, FrCs and FrRb molecules. It would be interesting to check the present results with two-component pseudopotential configuration interaction schemes [87], but they only exist in the framework of small core pseudopotential (ie 10 valence electrons or more in he case of Francium. This would allow in particular to estimate errors of the present calculation which ignore spin-orbit induced polarization effects. However, we provided a description of the molecular fine structure via an empirical atom-in molecules schemes, which suggests that the behaviour of excited Fr_2 molecular states involved in photoassociation and cold molecule formation is different from Rb_2 and Cs_2 cases. Here again, it would be interesting to compare with more refined ab initio spin-orbit calculations which are in progress. An interesting conclusion of the present work is that, while the nature and the quantitative behaviour of the ground state and metastable triplet state potential curves of the francium compounds are generally comparable with other previously studied alkali diatomics, the ground state polarity of hetero-atomic molecules cannot be extrapolated from the other alkali pairs, due to the influence of relativistic effect which affect atomic properties, especially the ionization potential(correlated with the outer *s* orbital radius). We hope that the present work will stimulate experimental spectroscopic studies on those short-lived species, which would also help to discuss further the accuracy of the present results.

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References

[1] G. D. Sprouse, R. P. Fliller, J. S. Grossman, L. A. Orozco, and M. R. Pearson. *Nucl. Phys. A*, 701:597, 2002.

[2] J.A. Behr, S.B. Chahn, S.B. Dutta, A. Görlitz, A.Ghosh, G.Gwinner, L.A. Orozco, G.D. Sprouse, and F.Xu. *Hyperfine Interactions*, 81:197, 1993.

[3] M. A. Bouchiat and C. Bouchiat. *Rept. Prog. Phys.*, 60:1351, 1997.

[4] J. E. Simsarian, A. Ghosh, G. Gwinner, L. A. Orozco, G. D. Sprouse, and P. A. Voytas. *Phys. Rev. Lett.*, 76:3522, 1996.
[5] G. D. Sprouse, L. A. Orozco, J. E. Simsarian, and W. Z. Zhao. *Nucl. Phys. A*, 630:316, 1998.
[6] Z.-T. Lu, K. L. Corwin, K. R. Vogel, C. E. Wieman, T. P. Dinneen, J. Maddi, and H. Gould. *Phys. Rev. Lett.*, 79:994, 1997.
[7] S. N. Atutov, R. Calabrese, V. Guidi, B. Mai, E. Scansani, G. Stancari, L. Tomassetti, L. Corradi, A. Dainelli, V. Biancalana, A. Burchianti, C. Marinelli, E. Mariotti, L. Moi, and S. Veronesi. *J. Opt. Soc. Am. B*, 20:953, 2003.
[8] L. Orozco. *private communic.*, 2005.
[9] I. S. Lim, P. Schwerdtfeger, T. Söhnel, and H. Stoll. *J. Chem. Phys.*, 122:134307, 2005.
[10] A. Derevianko, J. F. Babb, and A. Dalgarno. *Phys. Rev. A*, 63:052704, 2001.
[11] S. Azizi, M. Aymar, and O. Dulieu. *Eur. Phys. J. D*, 31:195, 2004.
[12] M. Aymar and O. Dulieu. *J. Chem. Phys.*, 122:204302, 2005.
[13] M. Müller and W. Meyer. *J. Chem. Phys.*, 38:283, 1983.
[14] D. Pavolini, T. Gustavsson, F. Spiegelmann, and J.-P. Daudey. *J. Phys. B*, 22:1721, 1989.
[15] R. Poteau and F. Spiegelmann. *J. Molec. Spect.*, 171:299, 1995.
[16] A.R.Allouche, M.Korek, K.Fakherddine, A.Chaalan, M.Dagher, F.Taher, and M.Aubert-Frécon. *J. Phys. B*, 33:2307, 2000.
[17] S. Rousseau, A.R. Allouche, and M. Aubert-Frécon *J. Mol. Spectr.*, 203:235, 2000.
[18] M. Korek, A.R. Allouche, K. Fakhreddine, and A. Chaalan *Can. J. Phys.*, 78:977, 2000.
[19] M. Korek, A. R. Allouche, M. Kobeissi, A. Chaalan, M. Dagher, K. Fakherddin, and M. Aubert-Frécon. *Chem. Phys.*, 256:1, 2000.
[20] W. C. Ermler, Y. S. Lee, P. A. Christiansen, and K. S. Pitzer. *Chem. Phys. Lett.*, 81:70, 1981.
[21] C. Teichteil, M. Pélissier, and F. Spiegelman. *Chem. Phys.*, 81:373, 1983.
[22] M.M. Hurley, L.F. Pacios, P.A. Christiansen, R.B. Ross, and W.C. Ermler. *J. Chem. Phys.*, 84:6840, 1986.
[23] R. D. Cowan. *J. Opt. Soc. Am. B*, 66:1010, 1976.
[24] P. A. Christiansen, K. Balasubramanian, and K. S. Pitzer. *J. Chem. Phys.*, 76:5087, 1982.
[25] P. Pykkö. Relativistic theory of atoms and molecules. Vol. 41, Springer Verlag, Berlin, 1986.
[26] K. Balasubramian. Relativistic effects in quantum chemistry, Part I, Theory and Techniques and Relativistic effects in Chemistry John Wiley and Sons, New York, 1997.
[27] B. A. Hess and C. Marian. Relativistic effects in the calculations of electronic energies. in P. Jensen, P. R. Bunker (Eds), Computational Molecular Spectroscopy, p. 169 John Wiley and sons, Sussex, 2000.
[28] M. Dolg. Relativistic effective core potentials in Relativistic Electronic Structure Theory, Part I., Fundamentals, Ch. 14, pp 7983, Elsevier, Amsterdam, 2002.
[29] P. Pykkö. Relativistic theory of atoms and molecules. Vol. 60, Springer Verlag, Berlin, 1993.
[30] P. Pykkö. Relativistic theory of atoms and molecules. Vol. 76, Springer Verlag, Berlin, 2000.
[31] P. Schwerdfeger. Relativistic Electronic Structure Theory, Part I, Fundamentals, Elsevier, Amsterdam, 2002.
[32] C. Teichteil, L. Maron, and V. Vallet. Relativistic pseudopotential calculations for electronic excited states. Elsevier, Amsterdam, 2004.
[33] E Arnold, W Borchers, H T Duong, P Juncar, J Lermé, P Lievens, W Neu, R Neugart, M Pellarin, J Pinard, J L Vialle, K Wendt, and ISOLDE. *J. Phys. B*, 23:3511, 1990.
[34] M. Foucrault, Ph. Millié, and J.P. Daudey. *J. Chem. Phys.*, 96:1257, 1992.
[35] P. Durand and J.C. Barthelat. *Chem. Phys. Lett.*, 27:191, 1974.
[36] P. Durand and J.C. Barthelat. *Theor. chim. Acta*, 38:283, 1975.
[37] M. Klapisch. PhD thesis, 1969. Université Paris-Sud (France).
[38] M. Perey. *Comptes Rendus Acad. Sci. Paris*, 208:97, 1937.
[39] S. Liberman, J. Pinard, H. T. Duong, P. Juncar, J.-L. Vialle, P. Jacquinot, G. Huber, F. Touchard, S. Büttgenbach, A. Pesnelle, C. Thibault, and R. Klapisch. *Comptes Rendus Acad. Sci. Paris*,

286:253, 1978.
[40] E. Arnold, W. Borchers, M. Carré, H. T. Duong, P. Juncar, J. Lermé, S. Liberman, W. Neu, R. Neugart, E.W. Otten, M. Pellarin, A. Pesnelle, J. Pinard, J.-L. Vialle, and K. Wendt. *J. Phys. B*, 22:L391, 1989.
[41] S. V. Andreev, V. S. Letokhov, and V. I. Mishin. *Phys. Rev. Lett.*, 59:1274, 1987.
[42] J. E. Simsarian, L. A. Orozco, G. D. Sprouse, and W. Z. Zhao. *Phys. Rev. A*, 57:2448, 1998.
[43] J. S. Grossman, L. A. Orozco, M. R. Pearson, J. E. Simsarian, G. D. Sprouse, and W. Z. Zhao. *Phys. Rev. Lett.*, 83:935, 1999.
[44] J. M. Grossman, R. P. Fliller III, L. A. Orozco, M. R. Pearson, and G. D. Sprouse. *Phys. Rev. A*, 62:062502, 2000.
[45] J. E. Simsarian, W. Shi, L. A. Orozco, G. D. Sprouse, and W. Z. Zhao. *Opt. Lett.*, 21:1939, 1996.
[46] J. M. Grossman, R. P. Fliller III, T. E. Mehlstäubler, L. A. Orozco, M. R. Pearson, G. D. Sprouse, and W. Z. Zhao. *Phys. Rev. A*, 62:052507, 2000.
[47] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov. *Phys. Lett. A*, 95:230, 1983.
[48] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov. *Phys. Rev. A*, 51:3454, 1995.
[49] E. Eliav, U. Kaldor, and Y. Ishikawa. *Phys. Rev. A*, 50:1121, 1994.
[50] A. Landau, E. Eliav, Y. Ishikawa, and U. Kaldor. *J. Chem. Phys.*, 115:2389, 2001.
[51] E. Eliav, M. J. Vilkas, Y. Ishikawa, and U. Kaldor. *J. Chem. Phys.*, 122:224113, 2005.
[52] M. S. Safronova, W. R. Johnson, and A. Derevianko. *Phys. Rev. A*, 60:4476, 1999.
[53] A. Derevianko, W. R. Johnson, and H. R. Sadeghpour. *Phys. Rev. A*, 61:022506, 2000.
[54] M. Marinescu, H. R. Sadeghpour, and A. Dalgarno. *Phys. Rev. A*, 49:982, 1994.
[55] M. Marinescu, D. Vrinceanu, and H. R. Sadeghpour. *Phys. Rev. A*, 58:R4259, 1998.
[56] A. Derevianko, W. R. Johnson, M. S. Safronova, and J. F. Babb. *Phys. Rev. Lett.*, 82:3589, 1999.
[57] M. Aymar, C. H. Greene, and E. Luc-Koenig. *Rev. Mod. Phys.*, 68:1015, 1996.
[58] J. P. Desclaux. *Comp. Phys. Comm.*, 9:31, 1975.
[59] M. Aymar and M. Crance. *J. Phys. B*, 14:3585, 1981.
[60] M. Aymar and M. Crance. *J. Phys. B*, 15:719, 1982.
[61] M. Marinescu. *Phys. Rev. A*, 50:3177, 1994.
[62] I. S. Lim, J. K. Laerdahl, and P. Schwerdtfeger. *J. Chem. Phys.*, 116:172, 2002.
[63] E. U Condon and G.H. . Shortley. *The Theory of Atomic Atomic spectra*. Cambridge University Press, 1935.
[64] W. C. Ermler, R B Ross, and P A Christiansen. *Intern. J. Quantum Chem.*, 40:829, 1991.
[65] E. P F Lee, J. Lozeille, P. Soldan, S. E. Daire, J. M. Dyke, and T. G. Wright. *Phys. Chem. Chem. Phys.*, 3:4863, 2001.
[66] M. Dolg, H. Stoll, and H. Preuss. *J. Chem. Phys.*, 90:1730, 1989.
[67] C.E. Moore. *Atomic energy levels, vol. 1 (Hydrogen through Vanadium).* U.S. Government Printing Office, Washington, 1949.
[68] C.E. Moore. *Atomic energy levels, vol. 2 (Chromium through Niobium).* U.S. Government Printing Office, Washington, 1952.
[69] C.E. Moore. *Atomic energy levels, vol. 3.* US Government Printing Office, Washington, 1958.
[70] J. P. Descaux, At. Data, Nucl. Data Tables, 12: 311 (1973).
[71] B. Huron, J.-P. Malrieu et P.Rancurel, J. Chem. Phys. 58:5745 (1973); S. Evangelisti, J. P. Malrieu and J. P. Daudey, Chem. Phys. 75:91 (1983);
[72] G-H. Jeung. *J. Molec. Spect.*, 182:113, 1997.
[73] M. Aymar, S. Azizi, and O. Dulieu. *J. Phys. B*, 36:4799, 2003.
[74] S. Azizi. PhD thesis, 2006. Université Paris-Sud (France).
[75] S. Magnier and F. Masnou-Seeuws. *Mol. Phys.*, 89:711, 1996.
[76] C. M. Dion, O. Dulieu, D. Comparat, W. de Souza Melo, N. Vanhaecke, P. Pillet, R. Beuc, S. Milošević, and G. Pichler. *Eur. Phys. J. D*, 18:365, 2002.
[77] C.H. Greene. *Phys. Rev. A*, 42:1405, 1990.
[78] W. C. Stwalley, Y. H. Uang, and G. Pichler. *Phys. Rev. Lett.*, 41:1164, 1978.

[79] A. Fioretti, D. Comparat, A. Crubellier, O. Dulieu, F.Masnou-Seeuws, and P. Pillet. *Phys. Rev. Lett.*, 80:4402, 1998.

[80] C. Gabbanini, A. Fioretti, A. Lucchesini, S. Gozzini, and M. Mazzoni. *Phys. Rev. Lett.*, 84:2814, 2000.

[81] R. Gutterres, C. Amiot, A. Fioretti, C. Gabbanini, M. Mazzoni, and O. Dulieu. *Phys. Rev. A*, 66:024502, 2002.

[82] A. Fioretti, D. Comparat, C. Drag, C. Amiot, O.Dulieu, F. Masnou-Seeuws, and P. Pillet. *Eur. Phys. J. D*, 5:389, 1999.

[83] P. Pillet, A. Crubellier, A. Bleton, O. Dulieu, P. Nosbaum, I. Mourachko, and F. Masnou-Seeuws. *J. Phys. B*, 30:2801, 1997.

[84] C. Amiot, O. Dulieu, R. F. Gutterres, and F. Masnou-Seeuws. *Phys. Rev. A*, 66:052506, 2002.

[85] C.M. Dion, C. Drag, O. Dulieu, B. Laburthe Tolra, F.Masnou-Seeuws, and P. Pillet. *Phys. Rev. Lett.*, 86:2253, 2001.

[86] A. J. Kerman, J. M. Sage, S. Sainis, T. Bergeman, and D. DeMille. *Phys. Rev. Lett.*, 92:153001, 2004.

[87] W. C. Ermler *J. Chem. Phys.*, 116:172, 2002.