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# Core repulsion effects in alkali trimers

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**Abstract.** The present paper is related to a talk presented during the Symposium on Coherent Control and Ultracold Chemistry held during the Sixth Congress of the International Society for Theoretical Chemical Physics (ISTCP-VI, July 2008). The talk was entitled "Electronic structure properties of alkali dimers and trimers. Prospects for alignment of ultracold molecules". Here we report on the electrostatic repulsion forces of the ionic cores at short separation, involved when the potential energy surfaces of alkali trimers are calculated with a quantum chemistry approach based on effective large-core potentials for ionic core description. We demonstrate that such forces in the triatomic molecule can be obtained as the sum of three pairwise terms. We illustrate our results on the lowest electronic states of  $\text{Cs}_3$ , which are computed for the first time within a full configuration interaction based on a large Gaussian basis set. As a preliminary section, we also propose a brief introduction about the importance of alkali trimer systems in the context of cold and ultracold molecules.

## 1. Introduction: a brief overview on cold molecules

The research field on translationally cold ( $\approx 1\text{K}$  and lower) and ultracold ( $\approx 1\text{mK}$  and lower) molecules is continuously expanding in many directions, involving an increasing number of groups throughout the world. The availability of gaseous samples of cold neutral molecules opens entirely new avenues for fascinating researches, offering the possibility to control all degrees of freedom of a quantum system. Molecular ions can also be trapped and cooled down inside atomic ion traps behaving like ionic crystals, where each ion is kept at a specific position with a residual motion equivalent to a temperature smaller than 1 K [1]. Cold neutral molecules brought new perspectives in high-resolution molecular spectroscopy [2, 3, 4, 5]. The expected accuracy of the envisioned measurements with ultracold molecules makes them appear as a promising class of quantum systems for precision measurements related to fundamental issues: the existence of the permanent electric dipole moment of the electron [6, 7, 8, 9] related to CP-parity violation [10, 11, 12], and the time-independence of the electron-to-nuclear and nuclear-to-nuclear mass ratios [13, 14, 15, 16, 17, 18], or of the fine-structure constant [19]. Various proposals have been suggested for achieving quantum information devices [20, 21, 22, 23] based on cold polar molecules (i.e. molecules exhibiting a permanent electric dipole moment). Elementary chemical reactions at very low temperatures could be manipulated by external electric or magnetic fields, therefore offering an extra flexibility for their control [24]. The large anisotropic interaction between cold polar molecules is also expected to give rise to quantum magnetism [25], and to novel quantum phases [26, 27]. The achievement of quantum degeneracy with cold molecular gases [28, 29, 30, 31, 32, 33, 34, 35] together with the mastering of optical lattices [36] built a fantastic bridge between condensed matter and dilute matter physics. Indeed, the smooth crossover between the Bose-Einstein condensation (BEC) of fermionic atomic pairs and the Bardeen-Cooper-Schrieffer (BCS) delocalized pairing of fermions related to superconductivity and superfluidity, has been observed experimentally [35, 37, 38, 39].

Cold and ultracold neutral molecules can be formed along two paths:

- Existing molecules in their vibrational ground state can be slowed down and cooled by various means, such as interactions with external electric and magnetic fields, or by collision with surrounding particles (see for instance the review articles in refs.[40, 24, 41]. This approach concerns a broad variety of small molecules (OH, NH, NO, SO<sub>2</sub>, ND<sub>3</sub>, CO, YbF, C<sub>7</sub>H<sub>5</sub>N, H<sub>2</sub>CO, LiH, CaH,...), but is currently limited to the production of molecules with a translational temperature around 10 mK.
- Pairs of trapped ultracold atoms can be associated using laser fields (photoassociation, or PA) [3], or time-varying magnetic fields (magneto- or Feshbach- association) [42]. Translational temperatures as low as a few tens of microKelvins can be reached, and even lower when quantum degeneracy is achieved. In contrast to the previous case, these results are up to now limited to alkali diatomic molecules which are most often formed in highly-excited vibrational levels, i.e. with high internal

energy.

In the latter case, a breakthrough occurred in 2008, when the possibility to create ultracold bialkali molecules in the lowest vibrational level of their ground state or their lowest metastable triplet state, has been demonstrated. Caesium dimers have been created in their ground state  $v = 0$  level after a PA step followed by spontaneous emission and further vibrational pumping, using a sequence of shaped laser pulses [43]. Dipolar molecules, namely LiCs, have been observed in their absolute ground state rovibrational level  $v = 0, J = 0$  after PA and spontaneous emission [44]. Samples close to the degeneracy regime of ultracold molecules in the  $v = 0$  level of their ground state have been observed for Cs<sub>2</sub> [45, 46], and KRb [47], and in the  $v = 0$  level of their lowest triplet state for Rb<sub>2</sub> [48], using the STIRAP technique (Stimulated Rapid Adiabatic Passage) to transfer the population from initial high-lying vibrational levels.

## 2. Motivation of the present work

The growing availability of ultracold samples of alkali diatomics brings the possibility to observe and study their interactions with neighboring ultracold atoms and molecules. In two independent - and almost simultaneous- experiments, inelastic rate constants for atom-molecule and molecule-molecule collisions have been extracted, using optically trapped Cs<sub>2</sub> molecules created by PA and spontaneous emission [49, 50]. The rate constants have been found independent from the initially populated rovibrational level. A resonant feature observed in the loss rate after collisions between trapped ultracold Cs<sub>2</sub> molecules created by Feshbach association has been interpreted as Cs<sub>2</sub>-Cs<sub>2</sub> bound states [51]. Inelastic atom-molecule collisions in a trapped sample of RbCs molecules have been studied for both RbCs-Cs and RbCs-Rb cases [52]. No systematic dependence on the internal state of the molecule has been probed within the experimental precision.

Theoretical knowledge of the electronic structure of alkali triatomic systems is strongly needed for theoretical dynamical studies, which would support these experiments. There has been a significant research activity concerning the theoretical study of the structure and dynamical properties of homonuclear alkali-metal trimers. Non-additive effects in spin-polarized alkali-metal trimers were studied by Soldán *et.al.* [53] and the three-dimensional potential energy surfaces for the lowest quartet states were constructed for Li<sub>3</sub> [54, 55], Na<sub>3</sub> [56, 57], K<sub>3</sub> [58] and Rb<sub>3</sub> [59]. These were then used to study the corresponding spin-polarized reactive atom-dimer collisions at very low temperatures [55, 58, 60, 61, 62, 63, 64, 65, 66, 67]. General trends for the lowest quartet state of homonuclear alkali trimers - correlated to three spin-polarized alkali atoms - have been described by Hutson and Soldán [68]. One of the main characteristic of these systems is the importance of non-additive three-body forces, which are predicted to be large especially close to the equilibrium geometries [53]. Much less has been done in the case of heteronuclear alkali-metal trimers. One of us has actually started with a systematic study the lowest quartet states of Li<sub>2</sub>A mixed systems (with A=Na, K, Rb, Cs) [69]. He concluded that the single-reference coupled-cluster approach, which

has been successfully used for homonuclear alkali-metal trimers [58, 69], would be for various reasons very difficult to employ for calculations of the potential energy surfaces of heteronuclear alkali-metal trimers, and that an alternative approach to the problem should be sought.

In the present paper, we present such an alternative approach. We extend our previous works on effective two-electron diatomic molecules like alkali dimers [70, 71, 72] and alkali hydrides [73] to alkali trimers. We propose a preliminary study of the potential energy surfaces of the heaviest alkali trimer,  $\text{Cs}_3$ , modeled as an effective three-electron molecule. Our approach is based on large-core effective core potentials (ECP) with core polarization potentials (CPP). We focused our work on two aspects: (i) the estimation of repulsion effects between the three  $\text{Cs}^+$  ionic cores at short distances within the present ECP+CPP approach; (ii) the comparison of the results with the results obtained by the MOLPRO package for *ab-initio* calculations.

### 3. Method of calculation

#### 3.1. *Ab initio methods and basis sets*

The potential energies were calculated making use of the CIPSI package (Configuration Interaction by Perturbation of a multiconfigurational wave function Selected Iteratively) [74]. As in our previous studies on alkali dimers, the alkali atom A is described by an  $\ell$ -dependent Effective Core Potential (ECP) for the ionic core  $\text{A}^+$  [75, 76] including effective core polarization potential (CPP) terms [77, 78], and by a large set of uncontracted Gaussian functions for the valence electron. The atom is modeled as an effective one-electron system, permitting us to perform Full Configuration Interaction (FCI) calculations for any alkali dimer or trimer, considered as an effective two-electron or three-electron system, respectively.

As the distance between different cores becomes smaller than the equilibrium distance of the system, it is well known that their electrostatic repulsion is not accounted for by this effective large-core potential. At the same time, the addition of the CPP term leads to a non-physical attractive behavior at short distances. For diatomic molecules, an empirical repulsion term is usually added to the calculation (see e.g. Refs. [79, 80, 81, 82]). If this short-range repulsive interaction in the triatomic molecule can be treated as the sum of pairwise interaction terms, computation of the potential surfaces would be greatly simplified. In order to check if such an approximation could be justified, we calculated the core-core repulsion at the Hartree-Fock level making use of the MOLPRO 2006.1 Quantum Chemistry Package [83]. For lithium and sodium, the all-electron correlation-consistent polarized core-valence quadruple- $\zeta$  cc-pCVQZ basis sets [84] were used. For potassium, rubidium, and caesium, the small-core scalar relativistic effective core potentials ECP10MDF, ECP28MDF, and ECP46MDF, respectively, together with the corresponding uncontracted valence basis sets [85] were employed.

For the caesium dimer and trimer, the counterpoise-corrected dimer interaction energies were optimized using an algorithm implemented in MOLPRO. In this algorithm the interaction energies were calculated at the coupled-clusters level making use of a single-reference restricted open-shell variant [86] of the coupled cluster method [87] with single, double and non-iterative triple excitations [RCCSD(T)]. The small-core scalar relativistic effective core potentials ECP46MDF was employed together with its uncontracted valence basis set, which was augmented by one set of diffuse function in an even-tempered manner (aug-ECP46MDF). All electrons from the “outer-core”  $5s5p$  orbitals were included in the RCCSD(T) calculations. The full counterpoise correction of Boys and Bernardi [88] was applied to all the interaction energies in order to compensate for the basis set superposition errors.

### 3.2. Core Polarization Potential for a triatomic molecule

The core polarization potential (CPP) is given by [77]:

$$V_{CPP} = -\frac{1}{2} \sum_c \alpha_c \mathbf{f}_c \cdot \mathbf{f}_c \quad (1)$$

The electric field  $\mathbf{f}_c$  is the one produced at point  $\mathbf{r}_c$  by all the other electrons and the ionic cores with static dipole polarizability  $\alpha_c$ :

$$\mathbf{f}_c = \sum_i \frac{\mathbf{r}_{ci}}{r_{ci}^3} h(r_{ci}, \rho_c) - \sum_{c' \neq c} \frac{\mathbf{R}_{cc'}}{R_{cc'}^3} Z_{c'} \quad (2)$$

where  $\mathbf{r}_{ci}$  is the position vector from core  $c$  to electron  $i$ ,  $\mathbf{R}_{cc'}$  the one between cores  $c$  and  $c'$ . The cutoff function  $h(r, \rho)$  ensures the convergence of the integral over electronic coordinates. The  $V_{CPP}$  term contains a purely geometrical part  $v_{nn}$  depending only on the relative positions of the nuclei:

$$v_{nn} = -\frac{1}{2} \sum_c \alpha_c \sum_{c', c'' \neq c} \frac{\mathbf{R}_{cc'} \cdot \mathbf{R}_{cc''}}{R_{cc'}^3 R_{cc''}^3} Z_{c'} Z_{c''} \quad (3)$$

For a diatomic molecule,  $v_{nn}$  is given by the familiar formula:  $v_{nn} = -\frac{Z_2^2 \alpha_1 + Z_1^2 \alpha_2}{2R^4}$ . For a triatomic system, we have:

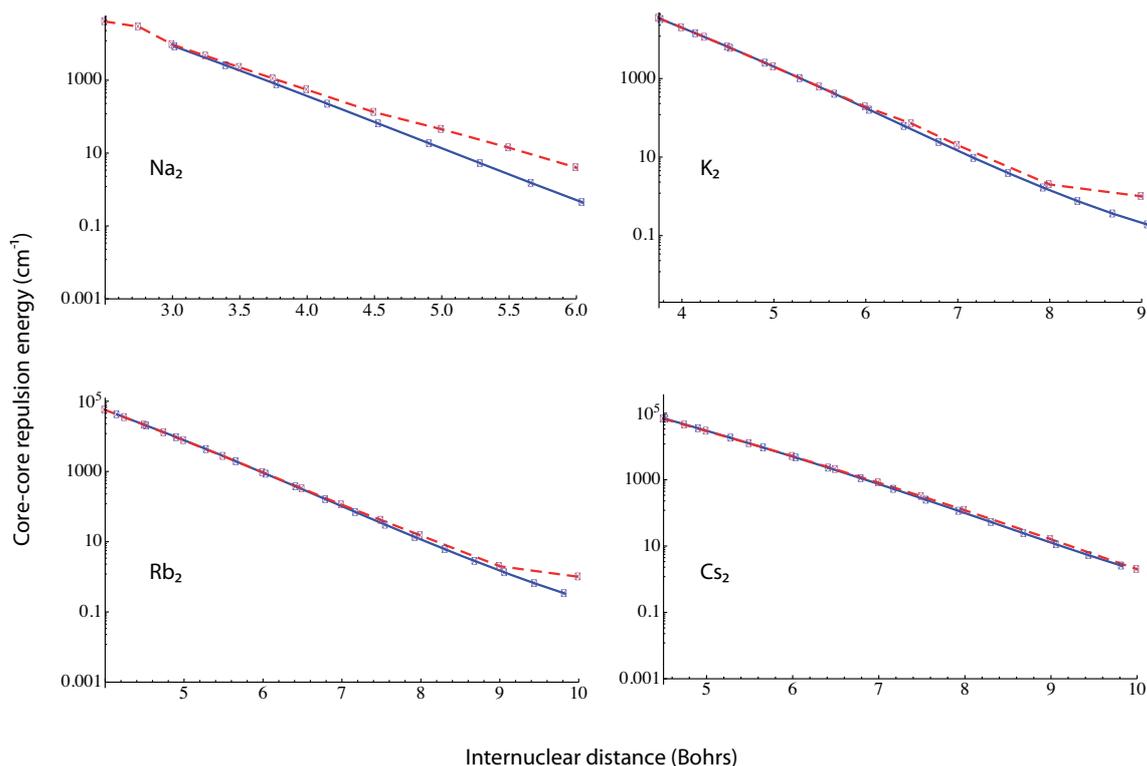
$$v_{nn} = -\frac{Z_2^2 \alpha_1 + Z_1^2 \alpha_2}{2R_{12}^4} - \frac{Z_3^2 \alpha_1 + Z_1^2 \alpha_3}{2R_{13}^4} - \frac{Z_3^2 \alpha_2 + Z_2^2 \alpha_3}{2R_{23}^4} \\ - \frac{Z_2 Z_3 \alpha_1 \mathbf{R}_{12} \cdot \mathbf{R}_{13}}{R_{12}^3 R_{13}^3} - \frac{Z_1 Z_3 \alpha_2 \mathbf{R}_{12} \cdot \mathbf{R}_{23}}{R_{12}^3 R_{23}^3} - \frac{Z_1 Z_2 \alpha_3 \mathbf{R}_{13} \cdot \mathbf{R}_{23}}{R_{13}^3 R_{23}^3} \quad (4)$$

In those formulas,  $Z_i$  and  $\alpha_i$  are, respectively, the net charge and static polarizability of ion core  $i$ . This term is independent of the *ab initio* calculation itself and is added *a posteriori*.

#### 4. Volume effect for triatomic systems

The part of the interaction between two nuclei other than the point charge repulsion has been dubbed “volume effect” by Jeung in his 1997 paper on alkali diatomics [89]. Here, we are interested in this volume effect for alkali triatomic systems. More precisely, we investigate whether it can be reasonably approximated as a sum of two-body terms.

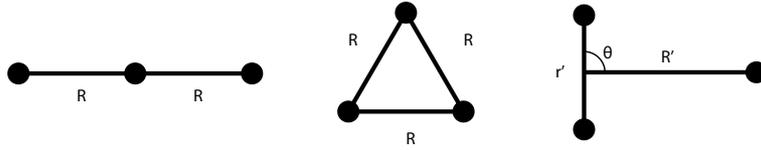
The two-body repulsion energies  $V_{cc}$  are calculated for all the alkali homonuclear diatomic molecules. The three-body repulsion energies  $V_{ccc}$  are calculated for particular geometries, namely for  $D_{\infty h}$  and  $D_{3h}$  symmetries, to provide a representative investigation. Calculations are done at the Hartree-Fock level of theory starting with the orbitals of the free atoms. Those orbitals are kept frozen as the internuclear distance is shortened. In this respect, our calculations for the two-body term are similar to those of the “A” column from the tables of ref. [89]. This comparison is shown in Figure 1 in logarithmic scale. Apart from a slight discrepancy in the case of  $\text{Na}_2$ , there is a good agreement between both calculations, and it is seen that the two-body core repulsion term could be well fitted by an exponential form, as already stated in ref.[80].



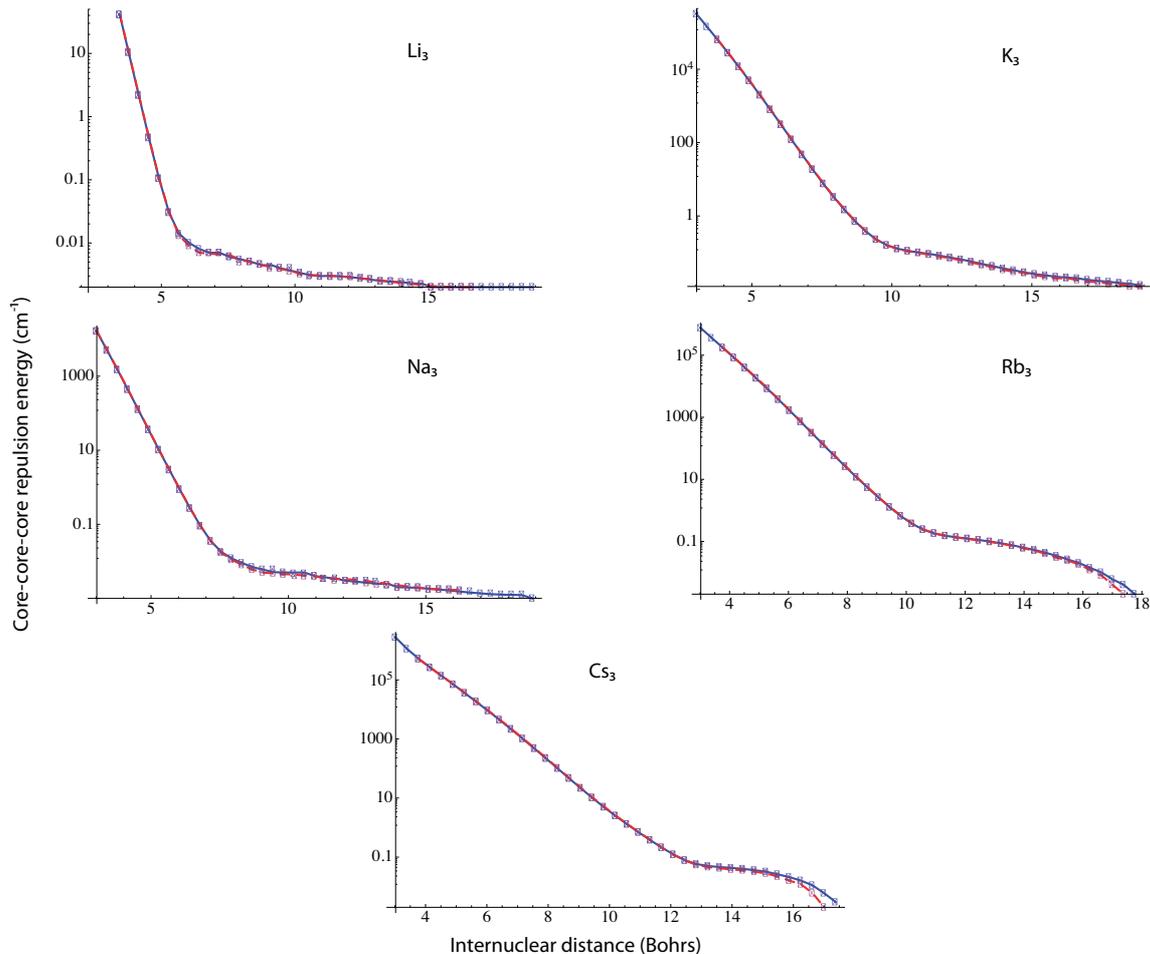
**Figure 1.** Two-body core repulsion energies for alkali dimers. Blue : our work. Red dashed : Ref. [89]. Note the logarithmic scale used for the potential energy axis.

Three-body core repulsion energies have been calculated for all homonuclear alkali trimers at linear symmetric and equilateral geometries according to the schemes of Figure 2. In Figure 3, we compare the three-body core repulsion term for linear geometries  $V_{ccc}^{lin}(R)$  (the internuclear distance  $R$  being defined in Figure 2), with the sum

of two-body term  $2V_{cc}(R) + V_{cc}(2R)$ . In the same manner, we compare in Figure 4 the three-body repulsion term for equilateral geometries  $V_{ccc}^{eq}(R)$  to  $3V^{(2)}(R)$ . In both cases, it is seen that the three-body core repulsion term is well described by a pairwise additive lemma, up to the region where it becomes negligible. Therefore, just like for alkali dimers, the  $V_{ccc}$  term can be added *a posteriori* to the potential surface calculations, whatever the chosen grid is for them.



**Figure 2.** Linear ( $D_{\infty h}$ ) and equilateral ( $D_{3h}$ ) geometries at which the three-body core repulsion term have been calculated. The Jacobi coordinates  $\{r', R', \theta\}$  used in the calculation of the potential energy surfaces of  $\text{Cs}_3$  are also presented.



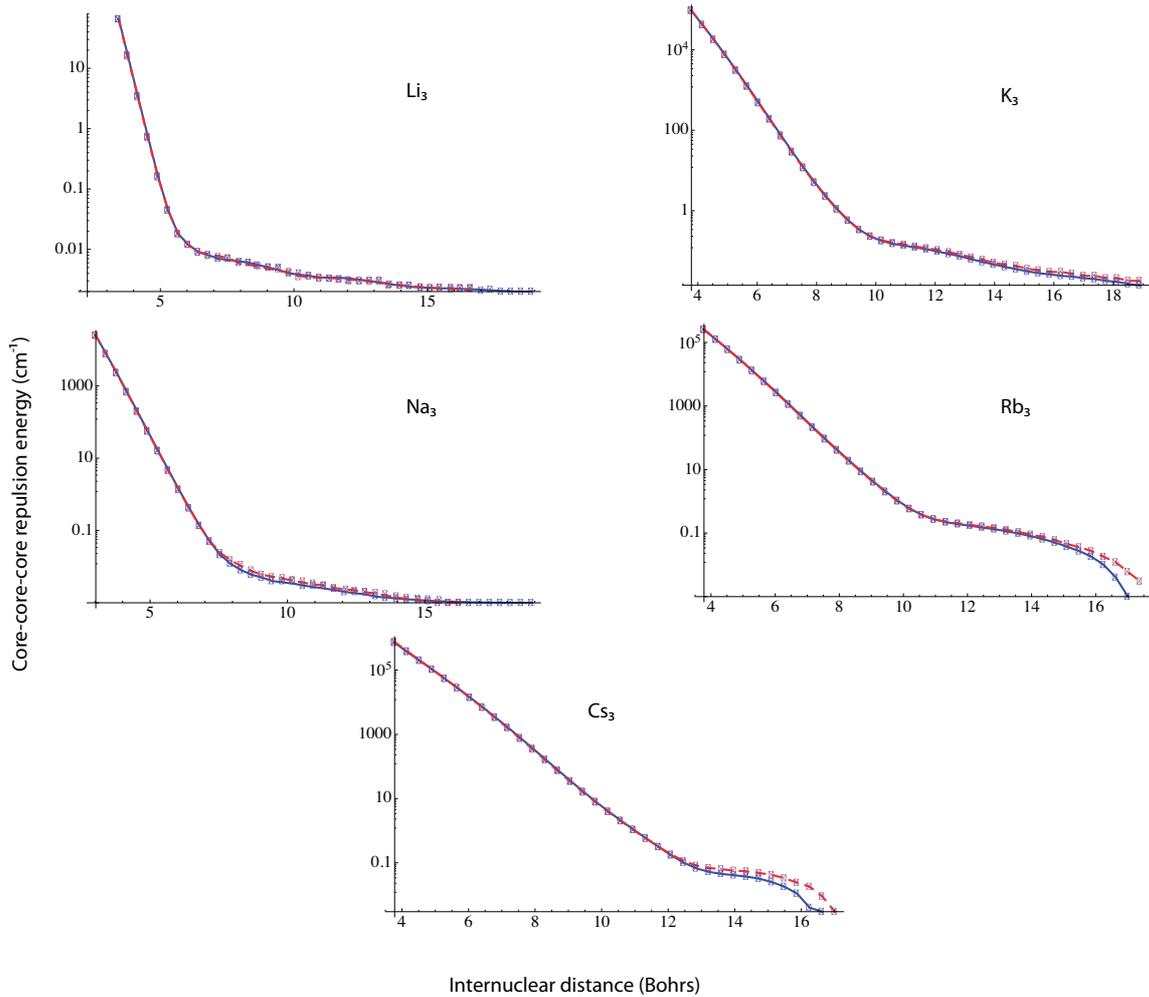
**Figure 3.** Additivity of the three-body core repulsion term for linear geometries. Blue : Three-body term  $V_{ccc}^{lin}(R)$ . Red dashed : sum of the relevant two-body terms  $2V_{cc}(R) + V_{cc}(2R)$  (see text).

## 5. Preliminary application to caesium trimer

The inclusion of the three-body core repulsion term is considered in preliminary calculations concerning the  ${}^4A'_2$  state of  $\text{Cs}_3$  which correlates to three spin-polarized caesium atoms. The used basis set is kept relatively small to maintain reasonable size for the FCI, reaching 152 532 Slater determinants in  $C_s$  symmetry in which the calculation is performed. The basis set ( $5s3p4d/4s3p3d$ ) is detailed in Table 1. We use  $\ell$ -dependent CPP's [78] which allow us to adjust the calculated atomic energies to the experimental ones for the  $6s\ {}^2S$ ,  $6p\ {}^2P$  and  $5d\ {}^2D$  atomic states of caesium. This is achieved by tuning the cutoff radii  $\rho_\ell$  of Eq. 2 to the values displayed in Table 2.

### 5.1. The triplet state of $\text{Cs}_2$

With these basis set and cut-off radii, we first calculate the lowest  ${}^3\Sigma_u^+$  potential energy curve for  $\text{Cs}_2$  dissociating into  $\text{Cs}(6s)+\text{Cs}(6s)$  in the framework of our ECP+CC-FCI



**Figure 4.** Additivity of the three-body core repulsion term for equilateral geometries. Blue : Three-body term  $V_{ccc}^{eq}(R)$ . Red dashed : sum of the relevant two-body terms  $3V^{(2)}(R)$  (see text).

method. We found an equilibrium internuclear distance  $R_e = 11.82 a_0$  and a well depth of  $D_e = 380.6 \text{ cm}^{-1}$ . These numbers can be compared to our optimized results obtained at the RCCSD(T)/aug-ECP46MDF level  $R_e = 12.19 a_0$  and  $D_e = 256.4 \text{ cm}^{-1}$  and the results from Ref. [53, 68], who obtained  $R_e = 12.44 a_0$  and  $D_e = 246.8 \text{ cm}^{-1}$  at the RCCSD(T)/ECP46MWB level of theory. The MOLPRO calculation yields a potential well which is deeper by is a more than  $140 \text{ cm}^{-1}$  than the one of the ECP+CC-FCI calculation. Apparently, the small-core ECP in combination with a rich valence basis set in the RCCSD(T) calculations provides more realistic description of the interaction energy than the large-core ECP in combination with a smaller valence basis set used in the FCI calculations (see also the discussion in Section 6). The potential energy well of the triplet state results from the competition between the exchange energy at short distances and the attractive dispersion forces at long distances and is very sensitive to the quality of the basis. For this  ${}^3\Sigma_u^+$  curve, the inclusion of the two-body core repulsion

Angular momentum	Exponent	Contraction coefficients
s	0.347926	0.411589
s	0.239900	-0.682422
s	0.050502	1.
s	0.036900	1.
s	0.00515	1.
p	0.1837	1.
p	0.0655	1.
p	0.0162	1.
d	0.2106894	0.18965
d	0.065471	0.22724
d	0.021948	1.
d	0.011200	1.

**Table 1.** Gaussian basis set used on each caesium atom in the ECP+CPP-FCI approach.

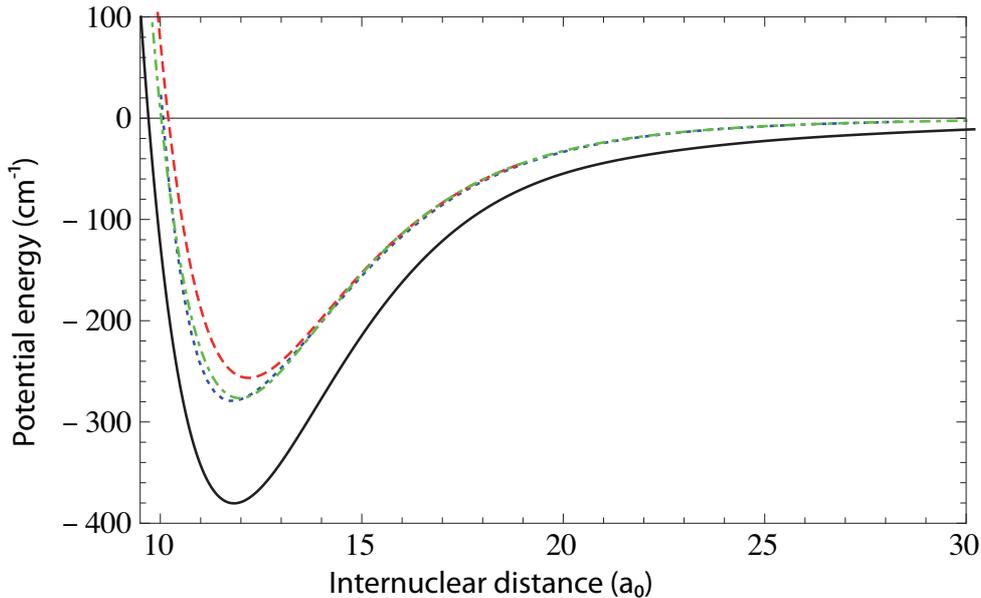
$\ell$	$\rho_\ell$
s	2.6248
p	1.87
d	2.8111

**Table 2.**  $\ell$ -dependent cutoff radii  $\rho_\ell$  (in units of  $a_0$ ) used in the core polarization potential. The polarization for  $\text{Cs}^+$  ionic core of  $16.33 a_0^3$  is taken from Ref [90].

term does not change the characteristics of the well but ensures a correct exponential behavior at short internuclear distances (Figure 5).

### 5.2. Quartet state of $\text{Cs}_3$

We then calculate the potential energy surface of the lowest quartet state of  $\text{Cs}_3$ . Calculations are carried out in Jacobi coordinates  $\{r', R', \theta\}$  (depicted in Figure 2) with the angle  $\theta$  fixed at  $\pi/2$  in order to explore  $C_{2v}$  nuclear geometries, as a representative geometry. We have computed 984 points on a grid where  $4.4 a_0 < r' < 40 a_0$  and  $4 a_0 < R' < 40 a_0$ . The minimum of the surface is found at a  $D_{3h}$  geometry with a bond length of  $R'_e = 10.72 a_0$  and a well depth of  $D_e = 1518 \text{ cm}^{-1}$  with the inclusion of the pairwise three-body core repulsion term, which ensures a realistic short-range repulsive wall. These numbers can be compared to our optimization results obtained at the RCCSD(T)/aug-ECP46MDF level  $R'_e = 11.18 a_0$  and  $D_e = 1208 \text{ cm}^{-1}$  and to the results from Ref. [53, 68], who obtained  $R'_e = 11.33 a_0$  and  $D_e = 1139 \text{ cm}^{-1}$  at the RCCSD(T)/ECP46MWB level of theory. It is worth noting that as the minimum of the quartet potential well is located at shorter distances than the minimum of the  $\text{Cs}_2$



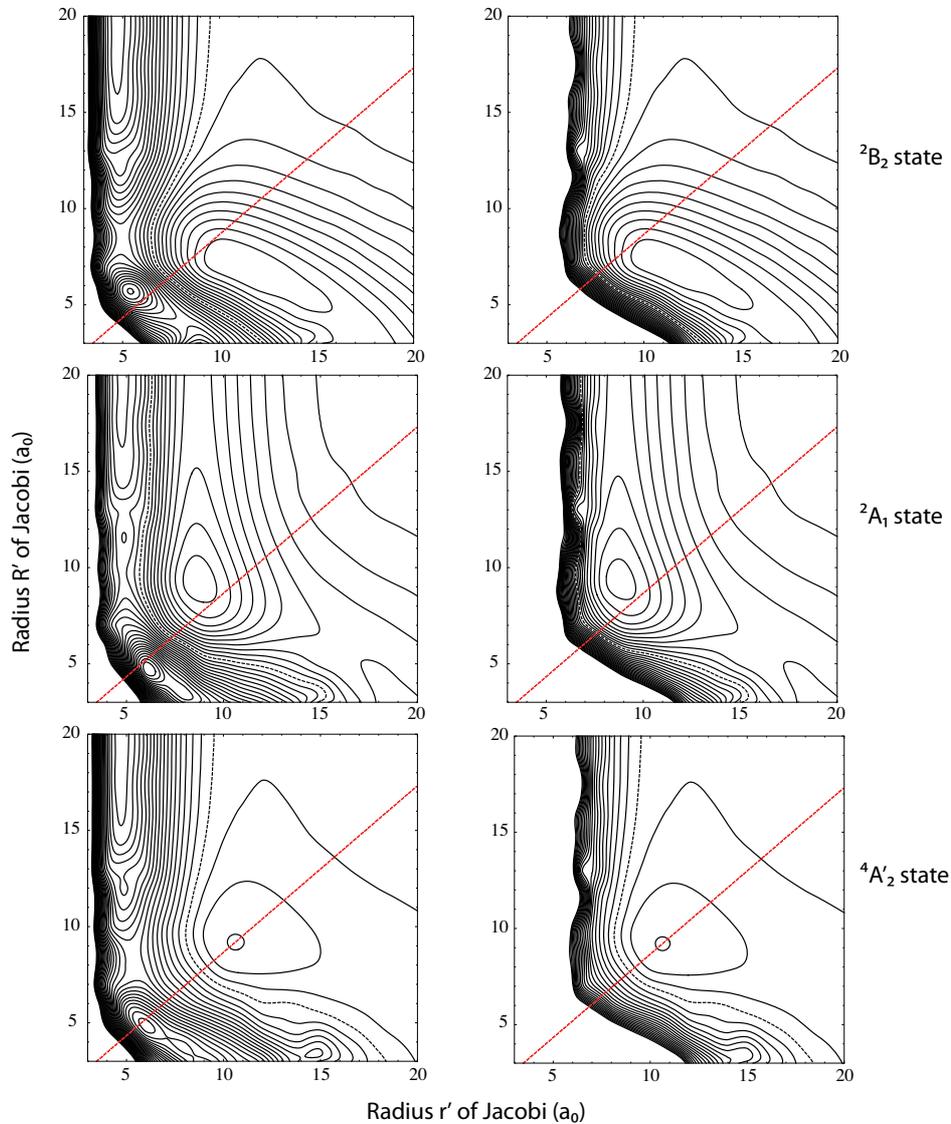
**Figure 5.** Calculated potential energy curves for the lowest  ${}^3\Sigma_u^+$  state of  $\text{Cs}_2$ . Black plain curve : ECP+CPP-FCI calculation with the basis detailed in Table 1. Red dashed curve : obtained at the RCCSD(T)/aug-ECP46MDF level. Green chain dotted curve : ECP+CPP full CI result obtained with basis set “A” from Ref. [70] (see the discussion in Section 6). Blue dotted curve : Multiparameter Morse Long Range fitting to spectroscopic data measured by Xie *et al* [91].

triplet state, the  $V_{ccc}$  term indeed contributes to the depth of the well, and not only in the region of the repulsive wall. However, the magnitude of  $V_{ccc}$  is still small, as the equilibrium internuclear distance is  $R'_e = 10.7 a_0$  and the well depth is  $D_e = 1522 \text{ cm}^{-1}$  if we neglect it. As expected from the diatomic calculations above, we obtain a difference of about  $300 \text{ cm}^{-1}$  on the well depth of the quartet state of  $\text{Cs}_3$  compared to the MOLPRO calculations. This confirms the limited quality of our basis set at the current level of our computations.

### 5.3. Doublet states of $\text{Cs}_3$

The three lowest potential surfaces for  $\text{Cs}_3$  are presented in Figure 6. The  ${}^2B_2$  and  ${}^2A_1$  states are the two components of a  ${}^2E'$  state at  $D_{3h}$  symmetry subjected to Jahn-Teller effect. The left (resp. right) column shows the surfaces without (resp. with) the addition of the core repulsion term. Note the strongly unphysical attractive behavior in the region  $r' < 5 a_0$ , which is removed when  $V_{ccc}$  is added. The global ground state  ${}^2B_2$  is characterized by a well depth of  $5437.1 \text{ cm}^{-1}$  at the geometry  $\{r' = 10.58 a_0, R' = 7.36 a_0\}$  with the inclusion of the core repulsion term. This changes to a well depth of  $5489 \text{ cm}^{-1}$  at  $\{r' = 10.57 a_0, R' = 7.3 a_0\}$  without the core repulsion term. Once again, the effect of  $V_{ccc}$  is larger than in the dimer, as the equilibrium distance is shorter. The other component  ${}^2A_1$  is characterized by a well depth of

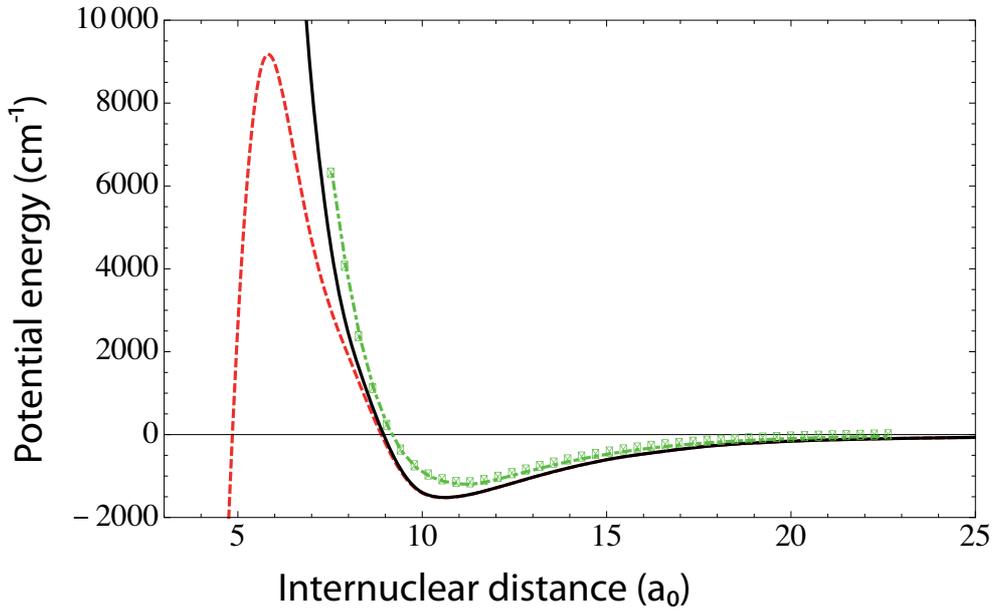
5258.2 cm<sup>-1</sup> at  $\{r' = 8.75 a_0, R' = 9.28 a_0\}$  with the core repulsion term (5312 cm<sup>-1</sup> at  $\{r' = 8.66 a_0, R' = 9.26 a_0\}$  without it).



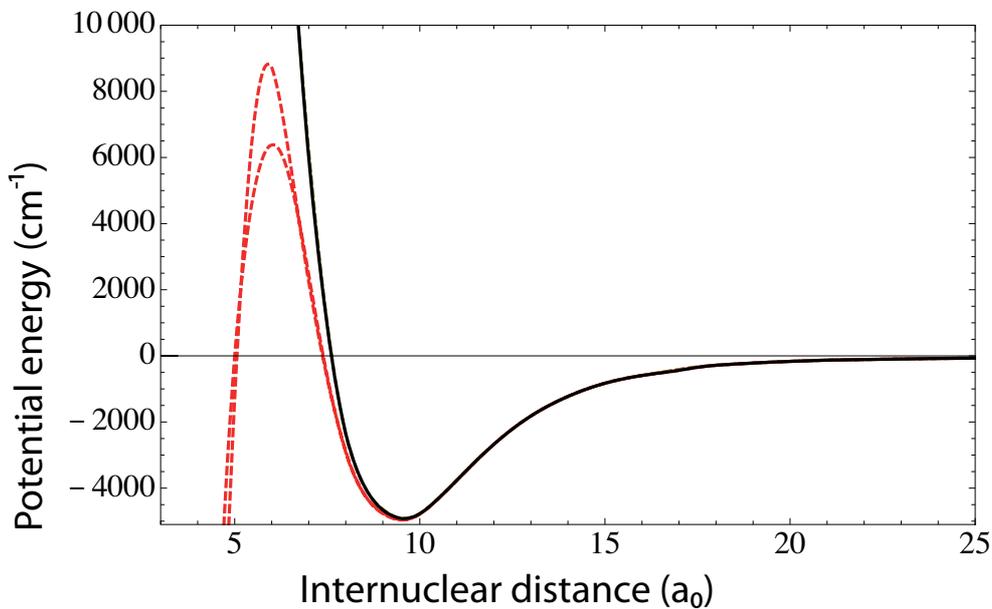
**Figure 6.** Lowest three calculated surfaces for Cs<sub>3</sub> in Jacobi coordinates with fixed  $\theta = \pi/2$ . Left (resp. right) column : without (resp. with) the inclusion of the cores repulsion term  $V_{ccc}$ . The red dashed curve locates the equilateral  $D_{3h}$  geometry  $R' = \frac{\sqrt{3}}{2}r'$ . Contours are distant of 500 cm<sup>-1</sup> and the dashed contour is the energy of the dissociation  $\text{Cs}(^2S) + \text{Cs}(^2S) + \text{Cs}(^2S)$ .

We present in Figures 7 and 8 the cut through the  $D_{3h}$  geometry of the previous surfaces. We recall that in the  $D_{3h}$  symmetry point group, the two doublet states  $^2B_2$  and  $^2A_1$  discussed before correlates to the two components of a doubly degenerate  $^2E'$  state. We clearly see in these figures the abrupt attractive behavior which occurs at short distances and that the addition of the core repulsion term gives us back a realistic

repulsive wall of potential.



**Figure 7.** Cut through the  $D_{3h}$  geometry for the lowest quartet states of  $Cs_3$ . Plain black (resp. red dashed) curve : with (resp. without) the core repulsion term  $V_{ccc}^{eq}(R)$ . Green chain dotted curve : quartet state on the RCCSD(T)/aug-ECP46MDF level of theory (see the discussion in section 6).



**Figure 8.** Cut through the  $D_{3h}$  geometry for the lowest doublet states of  $Cs_3$ . Plain black (resp. red dashed) curve : with (resp. without) the core repulsion term  $V_{ccc}^{eq}(R)$ . Both components of the  ${}^2E'$  state are represented.

## 6. Future prospects

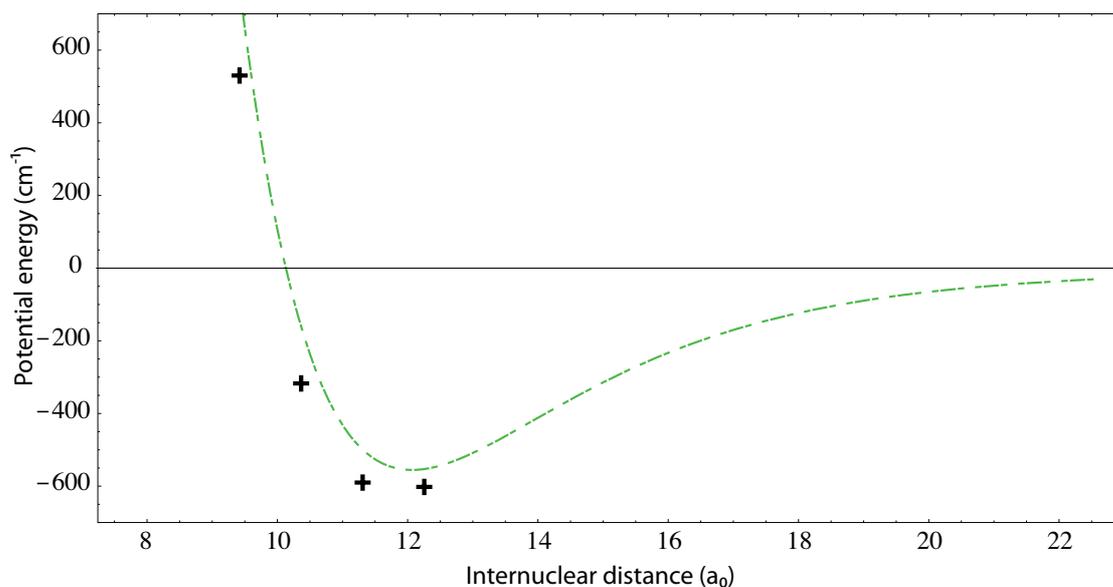
Preliminary potential energy surfaces for doublet and quartet states of the  $\text{Cs}_3$  molecule have been computed in the framework of a ECP+CPP-FCI quantum chemistry approach. The core repulsion interaction has been taken into account as an additional empirical correction as it is routinely done for diatomic molecules calculations. We showed that this term is well described by a sum of two-body terms. As mentioned before in ref. [80], it can be fitted by an exponential formula. Therefore, this term needs not to be calculated at each point of the three dimensional grid spanned by the degrees of freedom of a triatomic molecule on which the *ab initio* calculations are performed. It can easily be added *a posteriori* to cancel any non-physical behavior which might occur at short internuclear distances.

To estimate the quality of this basis set, we have compared our calculations to high level ones which uses a different method than ours, with the MOLPRO package. Such a comparison between different methods is crucial to assess their accuracy and their consistency, as no spectroscopic data are available for the  $\text{Cs}_3$  system, as well as for most of the triatomic alkali systems. The calculations presented here are exploratory in nature: the small basis set used (Table 1) makes the calculation time short enough to generate over a thousand *ab initio* points. Figure 5 shows the limitation of this basis set where the well depth of the triplet state of  $\text{Cs}_2$  is overestimated by more than  $100 \text{ cm}^{-1}$ . For the quartet state of  $\text{Cs}_3$ , our calculated well depth is consequently  $300 \text{ cm}^{-1}$  lower than the RCCSD(T) calculations. If we employ the basis set previously used for the caesium dimer [70] in the ECP+CPP-FCI method, this yields a very good agreement with the RCCSD(T) calculations, as the difference is now found at about  $20 \text{ cm}^{-1}$  between them (Figure 5). The agreement is even more spectacular with the potential curve extracted from the spectroscopy of the lowest triplet state of  $\text{Cs}_2$  [91].

We are currently calculating a comprehensive set of *ab initio* points with the ECP+CPP-FCI with this extended basis for the  $\text{Cs}_3$  molecule which will be the subject of a future paper. Such FCI calculations now involve more than 500,000 Slater determinants. In Figure 9, we display the first calculated points for the  $D_{\infty h}$  symmetry of the lowest  $\text{Cs}_3$  quartet state, compared to the MOLPRO calculation as described in Section 5. The figure suggests that the results are in good agreement with each other as the position of the minimum looks similar. The point calculated around  $12.3 a_0$  with the ECP+CCP full CI method is deeper than the minimum of the MOLPRO curve by about  $40 \text{ cm}^{-1}$ , while the difference between corresponding triplet potential curves in Figure 5 is seen to be about  $20 \text{ cm}^{-1}$ . This suggests that pairwise additivity of the forces is a reasonably good approximation in this case.

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**Figure 9.** Quartet  ${}^4\Sigma_u^+$  state of  $\text{Cs}_3$  in  $D_{\infty h}$  symmetry. Green chain dotted curve : calculation at the RCCSD(T)/aug-ECP46MDF level of theory. Plus signs : preliminary calculations with the ECP+CPP-FCI approach using basis set “A” from Ref. [70].

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