



## Treating $I^-$ anion as a zero-electron system: the $LiI^-$ and $CsI^-$ alkali halides anions.

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The accuracy of a full core treatment of  $\text{I}^-$  anion based on a zero-electron pseudo-potential (*ZEP*) including core polarization pseudo-potential (*CPP*) is examined on reference compounds  $\text{LiI}^-$  and  $\text{CsI}^-$  considered as one-electron systems. The results are compared to *ab initio* CASPT2 calculations involving 8 active electrons on iodine and 3 (respectively 9) on lithium (respectively cesium). An original scheme is proposed to build a pseudo-potential describing the short-range electron- $\text{I}^-$  interaction beyond the point charge approximation. The importance of the *ZEP* in one-electron calculations is estimated for the mentioned anions.

## I. INTRODUCTION

The quantum mechanical determination of electronic properties of large molecules and sophisticated materials has become one of the major challenges in the *ab initio* community of theoretical chemists. However, the use of quantum chemical approaches has long been limited to small systems due, in particular, to the number of electrons which are to be taken into account. Therefore, much effort was devoted to reduce the number of active electrons in the calculations. It is known that chemical bonding as well as most chemical properties essentially depend on the valence electrons. Such observation has lead theoreticians either to freeze the inner electrons as in their mean-field description or to elaborate so-called Model Potentials (*MP*), effective core potentials (*ECP*) or pseudo-potentials (*PP*) theories. These ideas date back to early pioneering works<sup>1-4</sup> and have been extensively developed in atomic physics and electronic collisions<sup>5-11</sup>, quantum chemistry<sup>12-16</sup> and solid state physics calculations<sup>17-20</sup>. It is noticeable that the nowadays derivations of *ECP*'s and *PP*'s allow one to reach quantitative accuracy for many systems in their ground and excited states. Extensions of the *PP* theory has made available the incorporation of scalar relativistic effects leading to an accurate and still tractable treatment of molecules including heavy atoms<sup>16,21,22</sup>. Furthermore, overpassing the strictly frozen scheme, techniques have also been proposed to restore the core polarization and core-valence correlation in an operatorial form<sup>23</sup>.

Beyond these standard and now routine determination and use of valence *ECP*'s, different strategies have been developed to entirely replace inert atoms and ions, and even more recently functional groups<sup>24</sup>, by pseudo-potentials. The former approach corresponds to zero-electron pseudo-potentials (*ZEP*), with two main fields of applications. The first one involves the treatment of rare-gas atoms in molecules, clusters and even embedding matrices. Rare-gas complexes are indeed of interest as prototypes for solvation models. In the con-

text of collisional or spectroscopic studies, many authors have put much effort to derive model potentials (*MP*) or pseudo-potentials for rare-gas atoms in alkali rare-gas molecules. The early studies suggested empirical or *l*-independent *MP*'s<sup>5,8,10</sup>. More recent versions include the *l*-dependency of the *PP*'s and were extracted by fitting electron rare-gas elastic differential cross sections<sup>9,27</sup>. Recent works have demonstrated the power of these *PP* treatments since quasi-spectroscopic accuracy has been reached on alkali rare-gas and rare-earth rare-gas diatomics<sup>25,26</sup>. The second class of applications for atomic *ZEP* involves halogen negative ions (isoelectronic to rare-gas atoms), met in essentially ionic materials. These systems include condensed matter compounds as well as ionic clusters for which local spectroscopy is widely investigated<sup>29</sup>. The description of inert ions in periodic systems has attracted some theoretical interest in the *ab initio* community. Indeed, *ab initio* spectroscopic techniques are limited to finite systems. Therefore, embedded fragment models must be considered in order to simultaneously restrict the quantum chemical calculation to a small number of atoms and properly describe the fragment spectroscopy in its crystalline environment. Few groups have tried to address the important issue of surrounding effects modeling<sup>28</sup>. Specific *PP* techniques have been developed to account for the influence of the rest of the crystal on the fragment under consideration<sup>29</sup>. One main achievement is the so-called *Ab Initio* Model Potential (*AIMP*) method suggested by Seijo and Barandíaran in which material specific *PP* are derived from periodic Hartree-Fock calculations<sup>30</sup>. This scheme is particularly interesting since it allows the treatment of both anions and cations on the same footing with equal effort. However, the main drawback is that the use of the *PP* is constrained to the structural conditions in which it has been extracted. Hence, applications in a dynamical context or in situations for which the geometry is *a priori* unknown, seem to be limited. Similarly, such approach is not adapted to the study of surfaces, nor clusters in which the local geometry may strongly differ from the bulk situation. In the investigation of structural and electronic properties of alkali halide clus-

ters with excess electrons<sup>31</sup> (namely  $M_nX_p$ ,  $M$  alkali,  $X$  halogen), the  $X^-$  ions were usually considered as simple point charges<sup>32,33</sup>. Such approximations might be questionable for heavy halogen atoms. Indeed, one may think that an extra pseudo-potential is required to account for the electron- $X^-$  short-range additional repulsion. *Ab initio* calculations using the perturbed ion model with correlations contributions have been recently presented on similar systems<sup>34</sup>. However, this type of approach has a very high computational cost.

The scope of the present work is to investigate the reliability of a zero-electron treatment of the  $I^-$  ion. As benchmark calculations, we consider the smallest molecules which can be described as one-electron systems for which *ab initio* reference calculations can still be achieved, namely the diatomic alkali halogen anions. We have chosen the  $LiI^-$  and  $CsI^-$  diatomics, as examples of light-heavy and heavy-heavy compounds. We will hereafter examine the reliability of one-electron calculations achieved within both the point-charge, and point charge+extra short-range pseudo-potential approximations. For the latter, a zero-electron pseudo-potential (*ZEP*) extraction scheme is suggested for the  $I^-$  ion.

While system-independent zero-electron cations pseudo-potentials (*ZEP*) can easily be determined using similar methods as those derived for standard *ECP*'s, the situation is much less favorable for anions. Indeed, the reference system including one extra electron does not usually exist. One could think of using differential electron-anion cross sections for this purpose. However, those are most of the time not available as such, neither experimentally nor theoretically, in contrast with the situation for rare-gas atoms. In the scope of theoretically understanding the chemistry of silver-bromide surfaces<sup>35</sup>, Flad *et al.* derived a pseudo-potential for the  $Br^-$  anion. In order to stabilize the  $Br^{2-}$  species, they embedded the anion in a gaussian-shaped auxiliary potential.

Following a similar inspiration, we propose to stabilize of the extra electron via a positively charged surrounding. In addition to the repulsive *PP*, core polarization effects will be included using the scheme developed by Müller *et al.*<sup>23</sup>. Section II is devoted to the *PP* extraction procedure and internal checks of its transferability. Section III details the test calculations on alkali-iodine diatomic neutrals and anions. The potential energy curves of neutrals are indeed required as core-core contributions in the one-electron treatment of anions.

## II. METHOD

The  $I^-$  zero-electron pseudo-potential will be constructed according to the  $l$ -dependent semi-local expression of Barthelat and Durand<sup>12</sup>

$$\hat{W} = \frac{1}{r} + \sum_l W_l \hat{P}_l \quad (1)$$

with

$$W_l = \sum_i C_{li} e^{-\alpha_{li} r^2} r^{n_{li}} \quad (2)$$

and

$$\hat{P}_l = \sum_{m=-l}^{m=l} |lm\rangle \langle lm| \quad (3)$$

$\hat{P}_l$  is the projector on the usual spherical harmonics  $|lm\rangle$ . It should be reminded that in the present study, the local part is repulsive. The *PP* operator is expected to mimic the interaction of extra electrons with the  $I^-$  ion. Therefore, a reference system including at least one extra electron has to be considered. Quantum chemical standard procedures for *PP* extractions are based on the existence of atomic bound states of the reference system, from which orbital energies, pseudo-orbitals and finally pseudo-potentials can be determined. Here, the main issue stems from the unstable character of  $I^{2-}$  species. We therefore imposed an artificial constraint on the system in order to stabilize the extra electron. This goal was achieved by embedding the  $I^{2-}$  anion within a positively charged cage of sodium cations. The choice of the cage is obviously partly arbitrary. However, several criteria have guided our choice. First, the wave function of the extra electron must keep a non-vanishing density close to the  $I^-$  core. Second, the symmetry of the cage has been taken octahedral so that it preserves the degeneracy of the  $p$  orbitals, which correspond to the highest  $l$  components of the *PP* considered in the present work. One should note that the  $d$  orbitals of iodine split in such an octahedral environment. A cage of higher symmetry should be used to evaluate the pseudo-potentials  $d$  components. The iodine-sodium distance  $R_{I-Na}$  was set to  $6.0 a_0$  as compared to the equilibrium distance  $5.2 a_0$  in the  $NaI$  diatomics<sup>36</sup>. As long as the information from the wave-function is transferable, this particular distance should not be a critical parameter. This important issue is discussed later in the text. Thus, our procedure consists in constructing a *PP* from an Hartree-Fock calculation for an extra electron in the field of  $I^-(Na^+)_6$ . Usual valence relativistic *PP*'s were used to describe both the iodine anion<sup>37</sup> (8 active electrons) and sodium cations<sup>38</sup> (1 active electron per sodium) in order to avoid the collapse of the extra electron on the surrounding ions.

The reference calculation of this system was achieved as follows. First, we performed an Hartree-Fock calculation on  $I^-$ . The resulting orbitals were left frozen,  $I^-$  being the reference core system. This procedure prevents the core electrons from being polarized or delocalized with the inclusion of the cage in the following step. Then, the calculation of the full  $I^{2-}(Na^+)_6$  system was performed and the resulting orbitals and orbital energies were taken as references. Third, for each  $l$ -manifold, the standard methodology was used : i) determination of the nodeless, normalized and shape-consistent pseudo-orbitals, ii) inversion of the one-electron Schrödinger equation and determination of the pseudo-potential.

Since the potential generated by the six  $\text{Na}^+$  cations does not have a spherical symmetry, we were lead to use an adapted least-square minimization procedure in order to extract the  $PP$ . Within each symmetry, the calculated norm  $L_l$  in the least-square procedure reads

$$L_l = \left\| \left( \hat{F} + \hat{W}_l \right) \hat{\varphi}_l - \varepsilon_l \hat{\varphi}_l \right\| \quad (4)$$

where  $\hat{\varphi}_l$  is the reference pseudo-orbital in each symmetry  $l$ . A rather large uncontracted basis set of Gaussian-type orbitals (9s and 9p uncontracted primitives) was used. The  $L_l$  minimization with respect to  $\hat{W}_l$  leads to  $L_l \approx 10^{-2} \text{ a.u.}$  The pseudo-potential parameters in semi-local representation are listed in Table I.

$l$	$\alpha_{li}$	$C_{li}$	$n_{li}$
0	0.19022	0.15536	1
	11.92021	11.18667	-1
1	0.13759	0.28112	1

TABLE I: Zero-electron pseudo-potential parametrization for  $\text{I}^-$ .  $\alpha_{li}$ ,  $C_{li}$  and  $n_{li}$  are defined in Eq. 2.

In order to roughly evaluate the zero-electron pseudo-potential transferability, one can look into the Lagrangian  $L = \sum_l L_l$  variations under distortions of the  $(\text{Na}^+)_6$  cage. The deviation from the reference value  $L_{ref} = 7.9 \times 10^{-2}$  enables to validate this important criterion. Two types of deformations characterized by the modification of the  $R_{I-\text{Na}}$  distances were considered, either according to an homothetic expansion preserving the  $O_h$  symmetry, or to an axial  $D_{4h}$  distortion. The results are presented in Table II. For the  $D_{4h}$  distortion the four equatorial  $\text{I} - \text{Na}$  distances are set equal to the original value  $6.0 a_0$ . One immediately sees that the variations of  $L$  are less than 20% of its nominal value, that is an order of magnitude less than the error in the  $PP$  extraction.

$R_{I-\text{Na}} \text{ (a.u.)}$	$10^2 \times L \text{ (a.u.)}$	
	$O_h$	$D_{4h}$
5.0	10	8.2
5.5	9.2	7.9
6.5	8.3	7.8
7.0	10	8.3

TABLE II: Variations of the Lagrangian under  $O_h$  and  $D_{4h}$  deformations of the cage  $(\text{Na}^+)_6$ . The reference value is  $L_{ref} = 7.9 \times 10^{-2}$ .

The  $\text{I}^-$  ion being quite polarizable, it is necessary to introduce a  $CPP$  operator in order to recover the core polarization and core-valence correlation effects. It should be emphasized that the previously mentioned freezing of the  $\text{I}^-$  orbitals avoids the double counting of these contributions. Following Müller *et al.*<sup>23</sup>, the core polarization

potential  $\hat{V}_{CPP}$  ( $CPP$ ) is incorporated as :

$$\hat{V}_{CPP} = -\frac{1}{2} \alpha_{I^-} \mathbf{f}_{I^-} \cdot \mathbf{f}_{I^-} \quad (5)$$

where  $\alpha_{I^-}$  stands for the  $\text{I}^-$  polarizability and  $\mathbf{f}_{I^-}$  is the electric field produced by the single valence electron and all other cores acting on  $\text{I}^-$ . The electric field integrals cutoff radius,  $\rho_c$ , has been taken as a step function, accordingly to the work of Foucrault *et al.*<sup>39</sup>.

The dipole polarizability has been previously calculated to be  $69 a_0^3$  from time-dependent second-order Möller-Plesset perturbation theory<sup>40</sup>. Based on electronic excitations experiments of salt clusters<sup>32</sup>, the polarization terms have been estimated to a rather different value,  $40 a_0^3$ . In our study, the *ab initio* polarizability value has been assumed. The cutoff radius  $\rho_c$  was determined to make contact between the ionization energy of the embedded  $\text{I}^{2-}$  species and the one-electron energy computed from the combined  $ZEP + CPP$  approach. Therefore, we first performed reference  $CASPT2$  calculations on  $\text{I}^-$  and  $\text{I}^{2-}$  in the  $(\text{Na}^+)_6$  environment. Then, a one-electron calculation including dynamical polarization effects by means of the  $CPP$  was adjusted to the  $CASPT2$  energies difference. The  $CPP$  parametrization and the energetic contribution of the  $CPP$  correction on the ionization energy of embedded  $\text{I}^{2-}$  are given in Table III.

Energetic contribution	IE (a.u.) for $\text{I}^{2-}$	Parametrization
$PP$ contribution	.5886	8s, 8p
$CPP$ contribution	.0011	$\alpha_{I^-} = 69$ $\rho_c = 3.50$

TABLE III:  $CPP$  parameters and energetic contributions to the embedded  $\text{I}^{2-}$  ionization energy (IE). All values are given in atomic units.

### III. CALCULATIONS WITHIN A $ZEP$ TREATMENT

Since transferability is a main concern in our study, in this section we investigate the potential energy curves of two model systems, namely  $\text{LiI}^-$  and  $\text{CsI}^-$ . Let us remind that the  $ZEP$  was extracted in an octahedral environment. Within the  $C_{\infty v}$  symmetry, the degeneracy of the  $p$  orbitals is obviously lifted. Thus, both the local symmetry and the chemical environment are different from the pseudo-potential extraction conditions.

Based on our  $ZEP + CPP$  parametrization, the energy curves of  $\text{LiI}^-$  and  $\text{CsI}^-$  were computed and compared to reference *ab initio* calculations. In the  $ZEP + CPP$  scheme the  $(\text{MI})^-$  system is represented by a one electron hamiltonian

$$\hat{h} = -\frac{1}{2} \hat{\Delta} - \frac{1}{r_{M^+}} + \hat{W}_{M^+} + \hat{W}_{M^+}^{CPP} \quad (6)$$

$$+\frac{1}{r_{I^-}} + \hat{W}_{I^-} + \hat{W}_{I^-}^{CPP} + \hat{V}_{M^+I^-}(R)$$

where  $R$  is the  $M-I$  distance,  $r_{M^+}$  and  $r_{I^-}$  are the electron-nuclei distances,  $\hat{W}_{M^+}$  and  $\hat{W}_{I^-}$  the mean-field  $ZEP$ , and  $\hat{W}_{M^+}^{CPP}$  and  $\hat{W}_{I^-}^{CPP}$  the core polarization pseudo-potentials of  $M^+$  and  $I^-$ , respectively.  $\hat{V}_{M^+I^-}(R)$  is a classical potential representing the core-core rigid-ion interaction between the  $M^+$  and  $I^-$  ions.  $\hat{V}_{M^+I^-}(R)$  models the interaction of the zero-electron ( $M^+, I^-$ ) system, excluding the ions polarization already accounted for in the  $CPP$  operator. The MI systems, from which the core-core  $V_{M^+I^-}(R)$  potentials were extracted, and the reference anions  $MI^-$  were computed using a Complete Active Space Self Consistent Field plus second order perturbation theory (*CASPT2*, MOLCAS Version 5<sup>41</sup>). The type of  $CI$  method was motivated by the multiconfigurational character of the wave-function including at least the ion pair and the covalent configurations. For the sake of consistency, the same  $CI$  treatment was applied to the molecular anions. The calculations were performed using a  $11s5p3d$ ,  $7s6p4d3f$  and  $5s5p4d3f$  basis sets for Li, Cs and I, respectively. The iodine and cesium core electrons were treated via relativistic effective core potential with 7 valence electrons for iodine and 9 for cesium<sup>42</sup>. Conversely, the  $1s$  electrons of lithium were explicitly considered in the calculations. The active space consisted of 8 and 9 electrons in 8 orbitals for the neutral and ionic compounds, respectively. Thus, the active space includes the molecular orbitals (MO) derived from the  $5s$  and  $5p$  atomic orbitals (AO's) of iodine, those correlated with the  $6s$  (or  $2s$ ) AO of cesium (or lithium) and the four next higher virtual MO's. The inner MO's ( $5s$ ,  $5p$  for cesium,  $1s$  for lithium) were left inactive in the active space, but were considered in the perturbative procedure.

Let us note that a major part of the core-valence correlation effects (last inner shell, valence) is treated at the perturbative level. Under these conditions, the calculated ionization potentials (IP's) of Li and Cs are 5.31 and 3.66 eV, to be compared with the experimental values 5.39 eV and 3.89 eV<sup>43</sup>. The electron affinity (EA) of  $I^-$  is calculated to be 3.15 eV, slightly overestimating the experimental value of 3.06 eV<sup>46</sup>. Figure 1 displays the *CASPT2* potential energy curves of Li I, Li  $I^-$  (Fig. 1a) and Cs I, Cs  $I^-$  (Fig. 1b). The spectroscopic constants of the neutrals potential energy curves are given in Table IV. They are in fairly good agreement with the experimental data (see Table IV).

The equilibrium distances absolute errors are smaller than  $0.05 a_0$ , whereas the dissociation energies, determined relatively to the ions pairs  $M^+ + I^-$  are underestimated by  $\approx -1700$  and  $\approx -2100 \text{ cm}^{-1}$  for Li I and Cs I, respectively. One should point out that the adiabatic dissociation yields to the neutral fragments  $M + X$ . The spectroscopic constants  $\omega_e$  are also very close to the experimental data (490 versus  $498 \text{ cm}^{-1}$  for Li I, 115 versus  $119 \text{ cm}^{-1}$  for Cs I). *CCSD(T)* calculations on Li I have been recently reported<sup>47</sup>, exhibiting an equilibrium dis-

systems	source	$R_e (a_0)$	$D_e (\text{cm}^{-1})$	$\omega_e (\text{cm}^{-1})$	$EA (\text{eV})$
Li I	expt.	4.52 <sup>a</sup>	48390 <sup>a</sup>	498 <sup>a</sup>	0.75 <sup>c</sup>
	<i>CASPT2</i>	4.56	46620	490	0.65
	<i>Coulomb</i>				0.82
	<i>ZEP</i>				0.76
Cs I	expt.	6.25 <sup>b</sup>	35490 <sup>b</sup>	119 <sup>b</sup>	0.62 <sup>c</sup>
	<i>CASPT2</i>	6.30	33360	115	0.55
	<i>Coulomb</i>				0.54
	<i>ZEP</i>				0.58
Li $I^-$	<i>CASPT2</i>	4.84	10100	370	
	<i>Coulomb</i>	4.95	10450	367	
	<i>ZEP</i>	4.91	9950	361	
	expt.		10960		
Cs $I^-$	<i>CASPT2</i>	6.77	7380	86.3	
	<i>Coulomb</i>	6.89	6870	79.3	
	<i>ZEP</i>	6.91	6700	78.2	
	expt.		9110		

TABLE IV: Spectroscopic analysis of Li I, Li  $I^-$ , Cs I and Cs  $I^-$ . <sup>a</sup>Ref. 43. <sup>b</sup>Ref. 44. <sup>c</sup>Ref. 47.

tance  $R_e=4.57 a_0$  almost identical to our *CASPT2* value.

Those potential energy curves have been fitted using an expression including the Born-Mayer repulsion (exponential form), the electrostatic and polarization contributions

$$\begin{aligned}
 E_{M^+I^-}^{CASPT2} &= V_{M^+I^-}(R) - \frac{\alpha_{I^-} + \alpha_{M^+}}{2R^4} \\
 &= A \exp(-aR) - \frac{1}{R} - \frac{\alpha_{I^-} + \alpha_{M^+}}{2R^4} \quad (7)
 \end{aligned}$$

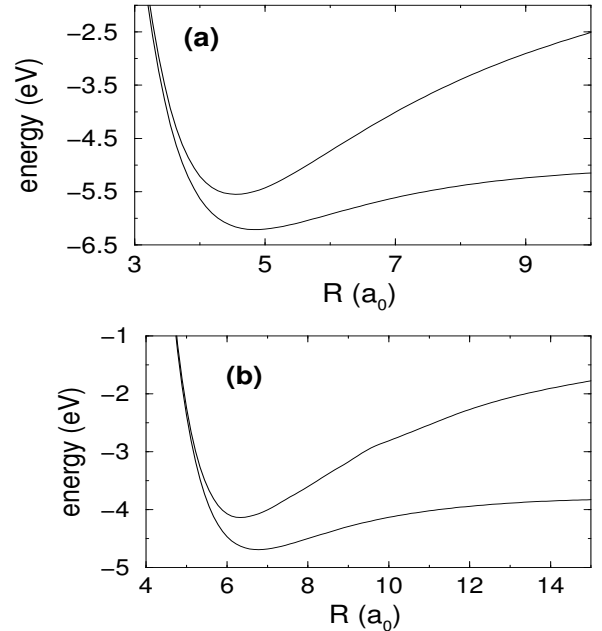


FIG. 1: Potential energy curves of a) Li I and Li  $I^-$ ; b) Cs I and Cs  $I^-$ . The zero energy corresponds to the dissociated pairs  $M^+ + I^-$ .

where  $V_{M+I^-}(R)$  is the rigid-ion energy defined above, whereas the *CASPT2* obviously includes the polarization effects on each ion, due to the presence of the other one. The Born-Mayer parameters in atomic units are given in Table V. Since the dissociation energies of the ions pairs are underestimated with respect to experiment (see above), we have also determined “experimental” Born-Mayer parameters in order to avoid the propagation of such error in the core-core contribution of the  $MX^-$  anions in the *ZEP* approach.

LiI	CsI
$A = 91.526/89.714$	$A = 140.450/134.047$
$a = 1.5994/1.5788$	$a = 1.3292/1.3126$

TABLE V: Born-Mayer parameters in atomic units. The first data refer to the fit of the *CASPT2* values, the second to experimental dissociation energies<sup>44,45</sup>(Eq. 7).

The *CASPT2* potential energy curves for the anions are also displayed in Fig. 1 and the calculated spectroscopic constants given in Table IV. Partial experimental data can be extracted from the above  $MX$  experimental spectroscopic data, the molecular electron affinities<sup>48</sup> (0.62 eV for LiI, 0.75 eV for CsI), and the ionization potential of M. Estimated experimental values are  $D_e = 10960$  and  $9110 \text{ cm}^{-1}$  for  $LiI^-$  and  $CsI^-$ , respectively. The *CASPT2*  $D_e$  values are found to be 10100 and  $7380 \text{ cm}^{-1}$ . The discrepancy with experiment seems to be much larger for the  $CsI^-$  anion ( $\approx -1600 \text{ cm}^{-1}$ ) than for  $LiI^-$  ( $\approx -800 \text{ cm}^{-1}$ ).

We now turn to the single electron description using the combined *ZEP* + *CPP* + *core-core* scheme. The anions  $LiI^-$ ,  $CsI^-$  potential energy curves are readily determined by the diagonalization of the one-electron hamiltonian, complemented by the Born-Mayer term (using the “experimental” parameters in Table V).

$$E((MI)^-) = V_{M+I^-}(R) + \varepsilon \quad (8)$$

where  $\varepsilon$  is the single-electron energy of  $MI^-$ .

In this one-electron picture, we used rather large basis sets, namely  $6s4p3d$ ,  $5s5p4d$  and  $8s8p7d$  for Li, Cs and I, respectively. Figure 2 reports the reference *CASPT2* potential energy curves, the *ZEP* + *CPP* calculations and those assuming  $MI^-$  being a one-electron systems without the  $\hat{W}_{I^-}$  pseudo-potential. In this particular approach, the electron- $I^-$  repulsion is only described by the  $1/r_{I^-}$  term. The calculated spectroscopic constants are summarized in Table IV. In both systems, the increase of the equilibrium distances with respect to the  $MX$  systems exhibited by the *CASPT2* results, is fairly reproduced in the one-electron approaches. In the case of  $LiI^-$ , the dissociation energies with and without the short range *PP* operator (coulombic repulsion only) are 9950 and  $10450 \text{ cm}^{-1}$ , respectively. Both values are smaller than the experimental estimations ( $\approx 1.36 \text{ eV}$

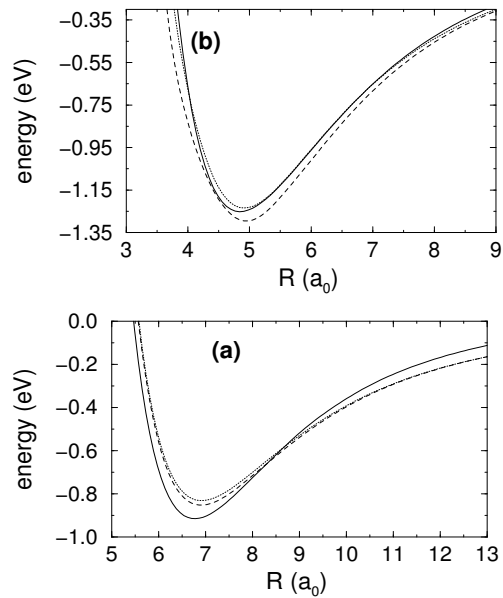


FIG. 2: Potential energy curves of a)  $LiI^-$ ; b)  $CsI^-$ . Solid lines are the *CASPT2* reference; dashed lines the purely coulombic calculations, and dotted lines the *ZEP* + *CPP*. The zero energy corresponds to the dissociated pairs  $M + I^-$ .

or  $10960 \text{ cm}^{-1}$ ). However, the total *ZEP* result occurs to be in good agreement with the *CASPT2* reference value. The effect of the short-range pseudo-potential is to reduce  $D_e$  by  $\approx 500 \text{ cm}^{-1}$ . On the other hand, the results are slightly less accurate for  $CsI^-$ , since the energies with and without short range *PP* are 6700 and  $6870 \text{ cm}^{-1}$ , respectively. The effect of the *PP* is smaller than in  $LiI^-$  since the equilibrium distance is significantly larger, reducing the role of the  $I^-$ -centered *PP*. An overall  $600\text{-}800 \text{ cm}^{-1}$  underestimation of  $D_e$  with respect to the *CASPT2* result is observed. However, the three theoretical calculations provide smaller dissociation energies than the experimental estimation. This discrepancy remains to be clarified. Finally, let us note that in  $CsI$ , the *PP* correction is smaller than the residual errors in all calculations.

#### IV. CONCLUSION

In this paper, we have developed an original strategy to parametrize a zero-electron pseudo-potential (*ZEP*) for an anionic species. As long as core-valence correlation (*CPP*) and core-core interaction effects are introduced, a very satisfactory level of accuracy is reached within this *ZEP* formalism for  $LiI^-$ . The effect of the short range *PP* is to decrease the dissociation energy by  $\approx 500 \text{ cm}^{-1}$  with respect to a pure coulombic treatment of the halogen. The effect is only  $\approx 200 \text{ cm}^{-1}$  for  $CsI^-$ . The results are slightly less satisfactory since the one-electron dissociation energies are in error by roughly 10%

with respect to the *ab initio CASPT2* reference calculation. Obviously, monitoring the cut-off radius to adjust the *CASPT2* result could be done. However, such procedure would hinder the *ab initio* extraction philosophy and would require transferability controls on larger systems. The *CASPT2* dissociation energy value might be improved by increasing the already large basis set and performing *CI* calculations. Nevertheless, the one-electron results on both systems turn out to be fairly consistent with the *ab initio CASPT2* references. The computational cost in *ZEP* calculations is obviously much reduced with respect to a standard approach relying on a seven-electron description of iodine. Since the chemical environments of the diatomic systems we considered are very different from the extraction situation, we believe that transferability, a major concern, is achieved. Therefore, such a formalism might be extremely useful to re-

duce the number of active electrons without any tremendous lost of accuracy. In this respect, the limit on the number of electrons in large systems such as ionic clusters is significantly moved. It might also be worth comparing the present *PP* extraction strategy with previous parametrization of electron-Ar pseudo-potentials relying on scattering properties<sup>27</sup>. A very similar approach is now being carried on for counter-ions  $\text{Cl}^-$  and  $\text{Br}^-$  which are frequently met in crystal structures of solid state compounds. Finally, one should mention that similar *ZEP*'s could be extracted within the *DFT* framework extensively used to investigate large systems. Their efficiency should however be checked consistently with the ability of various functionals. Besides, the implementation of *CPP*'s for several valence electrons within density-based formalism remains to be developed.

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