

Evaluation of the adiabatic correction for LiH, RbH and CsH molecules

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Abstract

The evaluation of the first and second derivative of the non adiabatic coupling between the several $^1\Sigma^+$ adiabatic states of LiH, RbH and CsH molecules, is considered from accurate diabatic and adiabatic data. Such derivatives of the electronic wave function are determined through a numerical differentiation of the rotational matrix connecting the diabatic and adiabatic representations. The first as well as the second derivative presents many peaks, related to ionic–neutral and neutral–neutral coupling between the $^1\Sigma^+$ states. Such radial coupling has been exploited to calculate the first adiabatic correction, which corresponds to the diagonal term of the second derivative divided by the reduced mass, for the ground and some excited states of the three molecules. The second adiabatic correction has been determined using the Virial theorem.

The first adiabatic correction was added to the adiabatic potential energy curves to re-determine the corrected spectroscopic constants and vibrational energy levels. The vibrational shift, which is the difference between the corrected and the adiabatic levels, has been calculated for X, A, C and D $^1\Sigma^+$ states of the three molecules. A shift of some 10 cm^{-1} is observed for some vibrational levels showing the breakdown of the Born–Oppenheimer approximation.

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1. Introduction

The development of theoretical methods to evaluate the nonadiabatic coupling has long been a topic of considerable interest [1–7]. The first theoretical calculation of the adiabatic correction for heteronuclear molecules was carried out for the HeH^+ molecule [8–12] composed of two electrons, then for a more complex system which is the LiH molecule [7,13–18]. Such coupling can be evaluated in the adiabatic representation by using numerical methods [19–24] or analytical expressions [25–27]. In our approach the coupling is determined through a numerical differentia-

tion of the rotational matrix connecting the diabatic and adiabatic representations.

The Born–Oppenheimer (BO) approach is generally a good approximation; however it breaks down by nonadiabatic interaction, as occurs in avoided crossings. In such regions of space, transition between potential energy surfaces can take place. These interactions bring about some processes like predissociation, collisions or radiationless transitions. It is always possible to use this approximation, but it is then necessary to take into account the couplings and the corrections neglected in the Born–Oppenheimer approximation. The radial coupling rises from the action of the kinetic energy operator on the electronic wave function which presents a parametric dependence with the interatomic distance. The first adiabatic correction corresponds to the second derivative of the electronic wavefunction versus R the nuclear coordinate divided by the reduced

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mass. However, the second adiabatic correction, developed in the body fixed frame, rise from a nucleus motion compensating the electronic motion to maintain fixed the centre of mass of the system.

In this work, both corrections have been evaluated in a simple way using the adiabatic and diabatic representations. The two adopted equivalent adiabatic and diabatic representations were well explained in our previous works [18,28–30]. In the diabatic representation we have purely potential coupling where the diagonal terms represent the diabatic potential energy, while in the adiabatic one the coupling is established by the kinetic energy operator of the nuclei. This coupling may become almost particular in the vicinity of avoided crossings. This work is focussed on the evaluation of the adiabatic corrections for several states of $^1\Sigma^+$ symmetry for LiH, RbH and CsH molecules. Furthermore, the effect of the correction on the spectroscopic constants and the vibrational energy levels will be analysed. The adiabatic and diabatic potential energy curves and also the diabatisation method were presented and analysed previously [18,29–34].

This paper is organized as follows. In Section 2, the computational method to evaluate the radial couplings and the adiabatic corrections, is presented. Section 3 is devoted to the results. Finally, we conclude in Section 4.

2. Computational method

2.1. The diatomic Hamiltonian

Various choices of coordinates [10,12,13] were developed in the past to separate the translation movement from the centre of mass of the system. In the system of internal coordinates [12], the Hamiltonian of diatomic molecules is written as:

$$H = -\frac{1}{2M} \Delta_{XYZ} - \frac{1}{2\mu} \Delta_{\vec{R}} - \frac{1}{2} \sum_{i=1}^n \Delta_{\vec{r}_i} - \frac{1}{2(M_a + M_b)} \left(\sum_{i=1}^n \vec{\nabla}_{\vec{r}_i} \right)^2 + V(R, r_i) \quad (1)$$

$$V(R, r_i) = \frac{Z_a Z_b}{R} - \sum_{i=1}^n \frac{Z_a}{|\vec{r}_i - \frac{1}{2}\vec{R}|} - \sum_{i=1}^n \frac{Z_b}{|\vec{r}_i + \frac{1}{2}\vec{R}|} + \sum_{i,j=1}^n \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (2)$$

We adopted the system of internal coordinates for two reasons. The first is the absence, in this reference, of the term of coupling between the electronic and nuclear gradients. The second is that it seems more logical to fix the origin of all the coordinates at the centre of mass of the system.

Therefore, the adiabatic correction is composed of two terms. The first is proportional to the second derivative of the electronic wave function divided by 2μ and the second one is the electronic kinetic energy divided by the sum of the nuclear masses.

2.2. First adiabatic correction

Our method is based primarily on the analysis of the results of the diabatisation presented in Refs. [18,23,28–30]. The derivation, in our case, is related to the rotational matrix which connects the adiabatic and the diabatic representations.

The evaluation of the first adiabatic correction needs the calculation of the first and the second derivative matrixes. Such correction corresponds to the diagonal term of the second derivative divided by 2μ :

$$-\frac{1}{2\mu} \left\langle \Psi_i \left| \frac{\partial^2}{\partial R^2} \Psi_i \right. \right\rangle \quad (3)$$

2.2.1. First derivative

We have calculated the radial coupling using two methods by making the assumption that the residual coupling in the diabatic basis is null.

- (i) Numerical differentiation of the rotational matrix.

$$\langle \Psi_i | \frac{\partial}{\partial R} | \Psi_j \rangle = \sum_{\alpha} C_{i\alpha} \frac{\partial C_{\alpha j}}{\partial R} \quad (4)$$

$|\Psi_i\rangle$ and $|\Phi_k\rangle$ denote, respectively, the adiabatic and the diabatic states and are connected by the unitary rotational matrix C ($C_{ki} = \langle \Phi_k | \Psi_i \rangle$).

- (ii) Hellmann–Feynman expression:

$$\langle \Psi_i | \frac{\partial}{\partial R} | \Psi_j \rangle = (E_j - E_i)^{-1} \langle \Psi_j | \frac{\partial H}{\partial R} | \Psi_i \rangle \quad (5)$$

where the electronic Hamiltonian is assumed to be known in and restricted to the diabatic basis ($H_{kl} = \langle \Phi_k | H_{el} | \Phi_l \rangle$).

As expected, both methods here lead to the same result. In both cases the matrix elements H_{ij} were interpolated by cubic spline in the first step and we determined the C matrix by diagonalization at all distances required by the three-point numerical differentiation. Interpolation of the rotational matrix C leads to numerical instability due to the loss of unitarity and should be avoided. The evaluation by the method Hellman–Feynman is more stable.

2.2.2. Second derivative

Like the first derivative, the second one is a second term neglected in the approximation of Born–Oppenheimer. It is often neglected in the calculation of the nonradiative lifetimes. The knowledge of diabatic and adiabatic representations, as well as the rotational matrix, simplify the calculation of the second derivative. It has shown that this term is not negligible and it will be able consequently to have contributions on the nonradiative lifetimes [18,30,35,36]. The derivation of the rotational matrix C leads to:

$$\begin{aligned} \frac{dC}{dR} &= \frac{d}{dR} \langle \Psi | \frac{d}{dR} | \Psi \rangle = \left\langle \frac{d}{dR} \Psi \left| \frac{d}{dR} \Psi \right. \right\rangle \\ &+ \langle \Psi | \frac{d^2}{dR^2} | \Psi \rangle = C^+ C + \langle \Psi | \frac{d^2}{dR^2} | \Psi \rangle \end{aligned} \quad (6)$$

We can thus easily express the second derivative according to the first one and of its derivative:

$$\langle \Psi | \frac{d^2 C}{dR^2} | \Psi \rangle = C^2 + \frac{dC}{dR} \quad (7)$$

2.3. Second adiabatic correction

The Hamiltonian presenting the second correction is given by

$$H_2 = -\frac{1}{2(M_a + M_b)} (\vec{\nabla}_{r_1} + \vec{\nabla}_{r_2})^2 \quad (8)$$

The term $\vec{\nabla}_{r_1} \vec{\nabla}_{r_2}$ cannot be calculated using our simple approach based on the diabatic and adiabatic results. In contrast, the term $-\frac{1}{2(M_a + M_b)} (\Delta_{r_1} + \Delta_{r_2})$, corresponding to our second adiabatic correction, is evaluated using the Virial theorem.

Finally our second adiabatic correction is given by

$$-\frac{1}{2(M_a + M_b)} (\Delta_{r_1} + \Delta_{r_2}) = -\frac{1}{M_a + M_b} \left(E + R \left(\frac{\partial E}{\partial R} \right) \right) \quad (9)$$

3. Results

3.1. Diabatic and adiabatic results

The results of the diabatisation method [23,28] which are used here are based on effective Hamiltonian theory combined to an effective overlap matrix. The diabatisation method was tested, first, for the CsH molecule [23,28] and applied later for the LiH, NaH, KH and RbH systems [18,29–34]. Such method was well explained in the previous works [23,28].

The determination of the diabatic states, which are linear combination of the adiabatic states, is founded on the condition that the wave function derivative is equal to zero, by choice of the basis. This forms the criterion of diabatisation. It is difficult to satisfy this condition, but one can approach zero, which corresponds to quasidiabatic states. For the CsH molecule, the residual radial coupling was calculated and found to be about 10^{-4} au [28].

The spectroscopic constants and the vibrational energy spacing were already presented and compared with the available theoretical and experimental studies showing the high accuracy of our calculations. To better the agreement with the experimental results, a correction related to the electroaffinity of hydrogen has been added to the ionic diabatic curve. This correction accounts for an underestimation of the hydrogen electroaffinity error due to the

basis set limitation and can be cast in the diabatic representation.

Furthermore, the diabatic curves were used for the LiH molecule to determine the non radiative lifetimes for the first time using the close coupling method [18,30] and the optical potential approach [35,36]. This work is essentially focussed on the exploitation of such results to determine the adiabatic corrections.

3.2. Radial coupling: first and second derivatives

The evaluation of the radial coupling between the $^1\Sigma^+$ states for LiH, RbH and CsH, was performed using the accurate adiabatic and diabatic data produced and published previously following the formalism detailed before.

Fig. 1 shows the first derivative radial coupling ($\langle \Psi_i | \partial / \partial R | \Psi_j \rangle$, $|i-j|=1$) between neighbour adiabatic $^1\Sigma^+$ states for the three molecules LiH, RbH and CsH. The radial couplings between $^3\Sigma^+$ adiabatic states and the other between $^1\Sigma^+$ and $^3\Sigma^+$ adiabatic states are not reported here. We observe many peaks at short and intermediate distances related to the avoided crossings between adiabatic curves and real crossings between diabatic curves. The inner peaks are due to the neutral–neutral crossings, while the outer are related to ionic–neutral crossings. In contrast to the radial coupling between the electronic states of the LiH molecule which were presented previously [18], the coupling for the RbH and CsH is presented here for the first time. The accuracy of the calculated first derivative radial coupling for LiH has been demonstrated by the comparison with the work of Mendez et al. [38] in a previous work [37]. Mendez et al. have used various techniques to compute directly the radial coupling between the $^1\Sigma^+$ adiabatic LiH electronic states. The radial coupling between the electronic states (as shown in Fig. 1) are very similar in shape and magnitude to this completely different calculation. Since the radial coupling is known to be very sensitive to the details of the adiabatic wave functions, this similarity brings a confirmation for the results themselves and also a new confirmation of the validity of the diabatisation procedure we used.

Fig. 2 presents the first derivative radial coupling between next-neighbour ($\langle \Psi_i | \partial / \partial R | \Psi_j \rangle$, $|i-j|=2$) $^1\Sigma^+$ states for the three molecules LiH, RbH and CsH. In contrast to the coupling between neighbour states, the peaks at intermediate distance are less intense. However the peaks at short distance are still important. They are related to the fact that the Li(2s)H, Rb(5s)H and Cs(6s)H diabatic states are more repulsive than the Rydberg diabatic states. All these peaks result from the intricate crossings of the repulsive part of the diabatic states. These crossings provide a contribution to the first adiabatic correction and vanish for large R , its order of magnitude is the wave length.

The peaks related to the first derivative radial coupling could also be important for high energy collisions where the repulsive part of the curves has a dominant role. It should be emphasised that most of these peaks in the radial

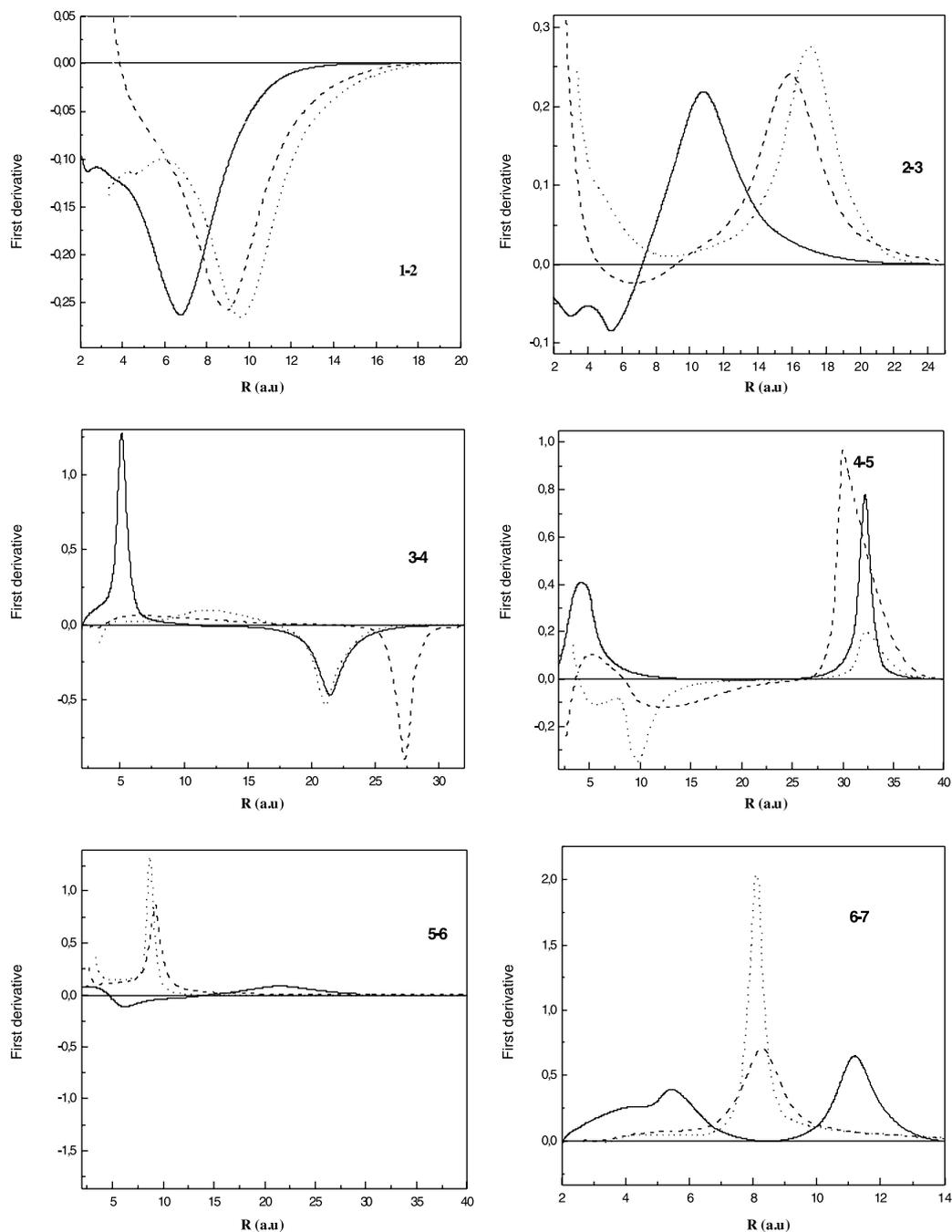


Fig. 1. First derivative ($\langle \Psi_i | \frac{\partial}{\partial R} | \Psi_j \rangle, j = i + 1$) for LiH (full line), RbH (dashed line) and CsH (dotted line).

coupling are rather unexpected from the shape of the adiabatic curves.

The second derivative radial coupling was neglected in the past. Its calculation, here, does not present any difficulty as we exploited the existing first derivative and rotational matrix for the three molecules. As expected, this quantity is as important as the first derivative. As shown in Fig. 3, the second derivative coupling between neighbour states presents many peaks which can be related to neutral–neutral and ionic–neutral crossings in the diabatic picture. Furthermore, such coupling vanishes at internuclear distances corresponding to avoided crossings in the adiabatic picture.

3.3. Adiabatic correction

The full adiabatic correction has been determined for LiH by various authors [17,19]. Their works were focussed on analytical and numerical derivation of the resulting ab initio electronic wave functions. Our approach is simple and based on the produced data in both adiabatic and diabatic representations.

The first adiabatic correction, which is proportional to the diagonal term of the second derivative of the electronic wave function, is positive. As can be seen in Fig. 4, which presents the first adiabatic correction for X, A, C and D

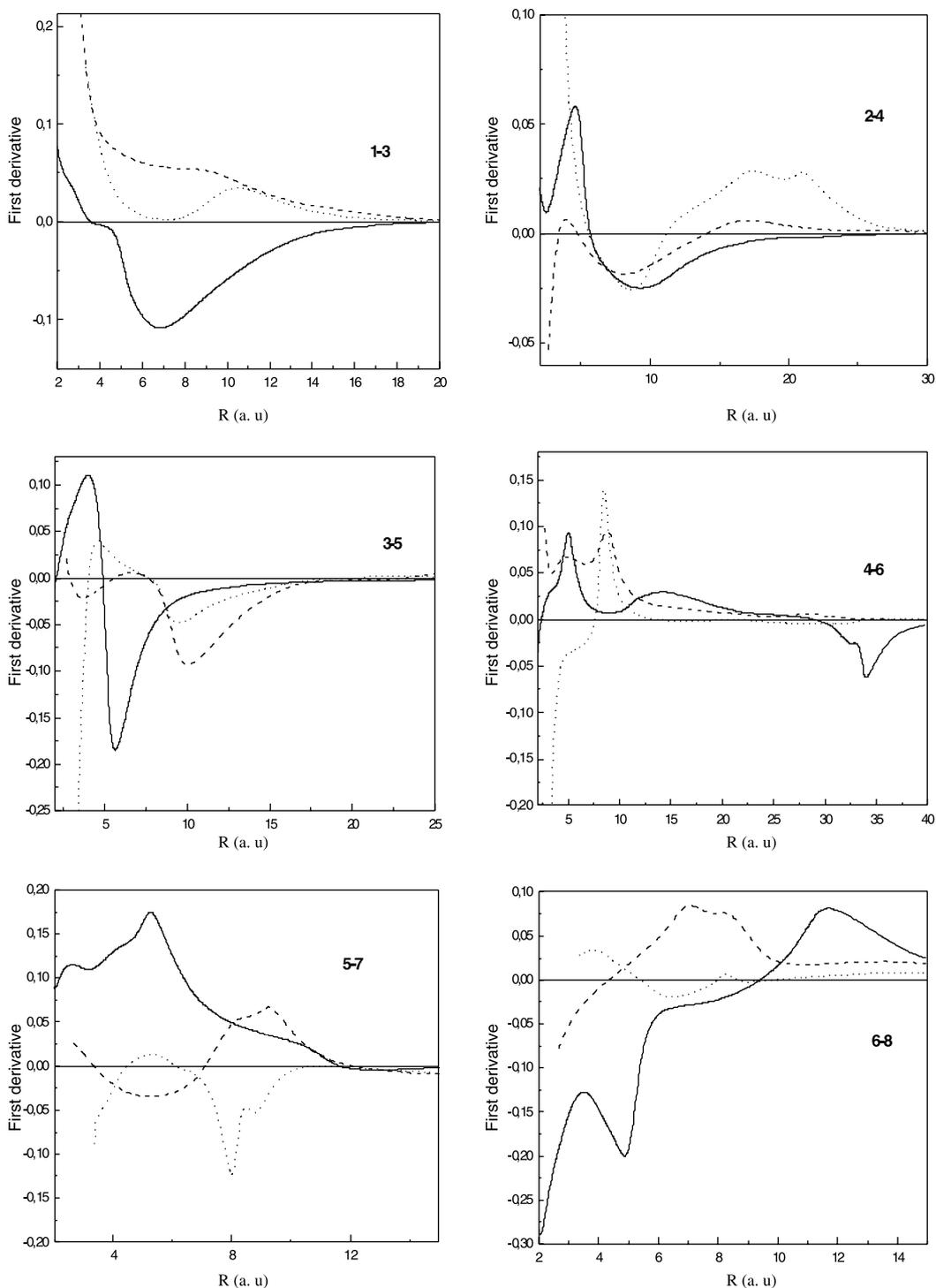


Fig. 2. First derivative $\langle \Psi_i | \frac{\partial}{\partial R} | \Psi_j \rangle, j = i + 2$ for LiH (full line), RbH (dashed line) and CsH (dotted line).

$^1\Sigma^+$ states for LiH, RbH and CsH molecules, the variation is unusual. It has a minimum corresponding to the equilibrium distance, and then it presents a peak in the vicinity of the avoided crossing. It is not surprising that the correction is minimal at the equilibrium distance as it is the distance where the Born–Oppenheimer can represent perfectly any molecular system. We remark that, for the three molecules, the first adiabatic correction has the same feature. It pre-

sents a peak related to the avoided crossing with their neighbours. This explain why we get only one peak for the $X^1\Sigma^+$ state, which has only one avoided crossing with the $A^1\Sigma^+$ state. In contrast, the first correction for the $A^1\Sigma^+$ state and for the three molecules, presents two peaks related to the positions of avoided crossings with X and C neighbour $^1\Sigma^+$ states. It is important to note that the peaks positions' are shifted to larger distances when the

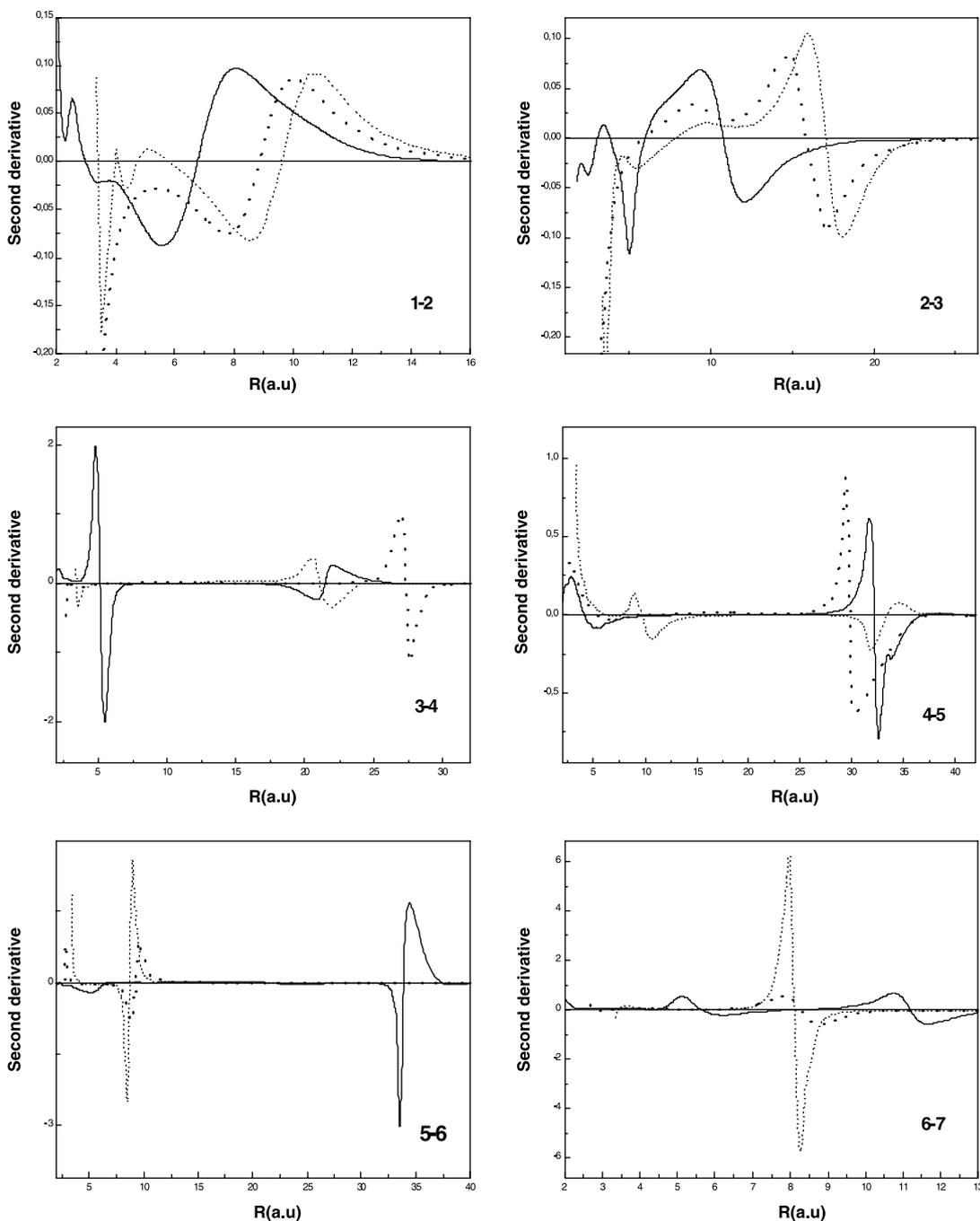


Fig. 3. Second derivative $\langle \Psi_i | \frac{\partial^2}{\partial R^2} | \Psi_j \rangle, j = i + 1$ for LiH (full line), RbH (dashed line) and CsH (dotted line).

size of the alkali atom increases. Thus also explains the closed positions of peaks for RbH and CsH molecules. The size of their nuclei is of the same order if we compare them to that of the lithium nucleus. The first correction is about some cm^{-1} for X and A $^1\Sigma^+$ states, whereas it is about tens and hundreds cm^{-1} for higher excited states. For example the correction is around 120 cm^{-1} at short distance for the C and D $^1\Sigma^+$ states of the LiH system as illustrated in the Fig. 4. The order of correction for these states decreases to tens of cm^{-1} for the RbH and CsH states but it is still important. Here also the correction

peaks are shifted to larger distance for the two mentioned molecules relative to LiH. Furthermore, the first correction becomes zero at large distance, because the electronic wave function is independent of the internuclear distance.

Fig. 5 presents our second adiabatic correction for X, A, C and D $^1\Sigma^+$ states for LiH, RbH and CsH molecules. This correction is related to the radial dependence of the derivative of the electronic energy in the diabatic representation. It is significant at short internuclear distances. At large distances, it corresponds to the asymptotic electronic energy divided by the sum of the nuclear masses of the two atoms.

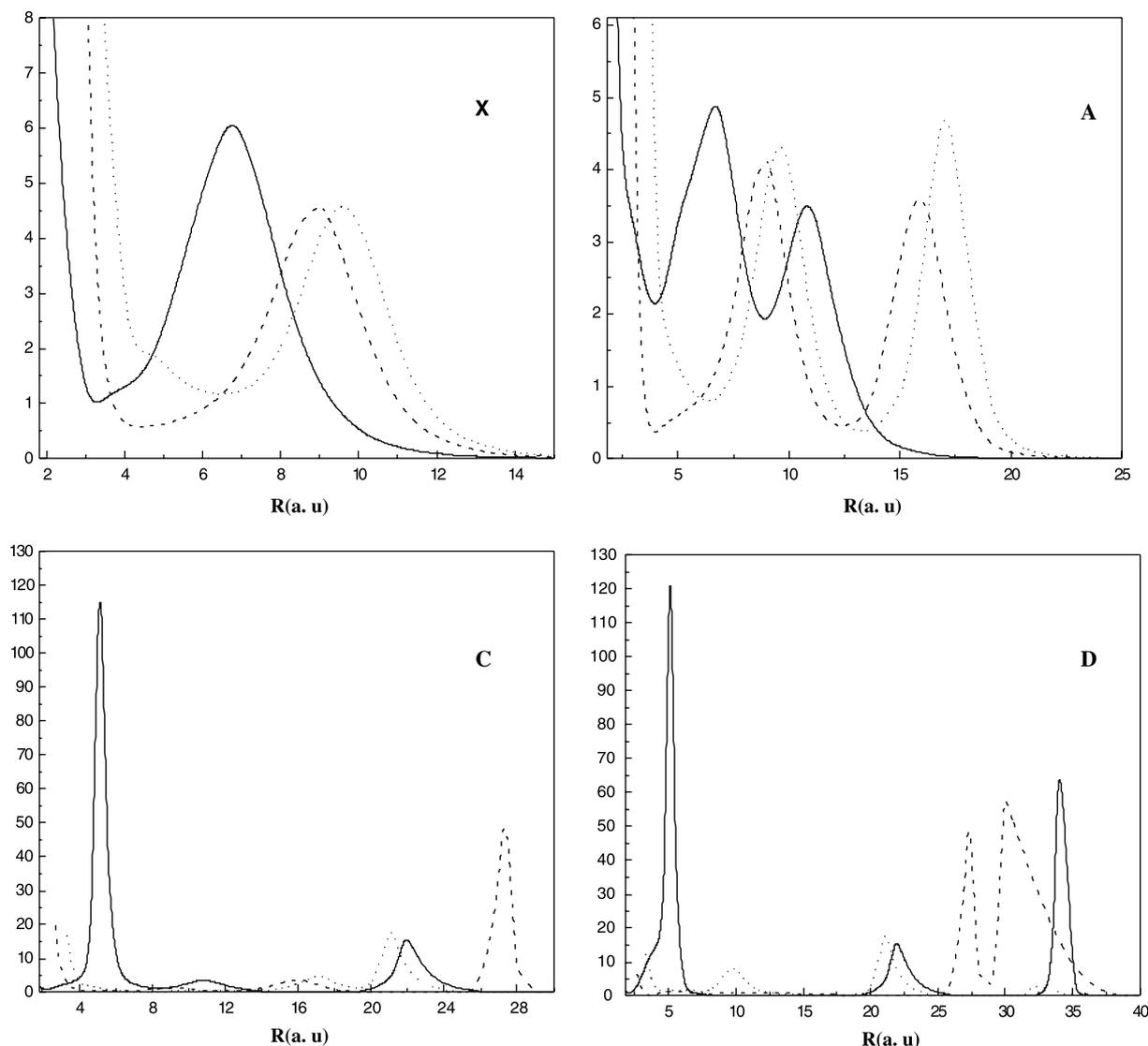


Fig. 4. First adiabatic correction for X, A, C and D states for LiH (full line), RbH (dashed line) and CsH (dotted line) molecules.

The feature of the correction is similar for the three systems and for each state: X, A, C and D. At short range, the second correction depends strongly on the internuclear position, while, it is constant at large distance. We find approximately the same correction for the X, A, C and D $^1\Sigma^+$ states for each molecule. The order of such correction is, respectively, 10 cm^{-1} , 1 cm^{-1} and 0.6 cm^{-1} for LiH, RbH and CsH. We remark that this second adiabatic correction is inversely proportional to the size of the molecule. The second adiabatic correction of the X state of LiH molecule is compared to the results given by Jenson and Yarkony [7] (see Table 1). In fact, we compare the difference between the corrections at R and at the equilibrium distance R_e taken at 3 au. We remark that we are in good agreement with their analytical calculation. However, our correction is slightly larger (in absolute value) than the Jenson and Yarkony [7] one. They have computed analytically the correction using accurate electronic wave functions,

while in our work we have only applied the Virial theorem on our accurate diabatic potential energy.

The total adiabatic correction for LiH, RbH and CsH systems is presented in Fig. 6 for the ground and the first excited states. In fact, in our case and according to the development of Jenson and Yarkony [7], we do not have the third term of the correction. This term corresponds to the rotation of the molecule and includes the orbital momentum operator. The estimation of this term in our approach was not possible as it was the case for the first and the second terms. It should be noted that our main objective was to consider the adiabatic correction by exploiting the diabatic representation and the high accuracy of the potential energy curves.

3.3.1. Shift on spectroscopic constants

The first adiabatic correction can be included to re-determine the spectroscopic constants for all $^1\Sigma^+$ states of

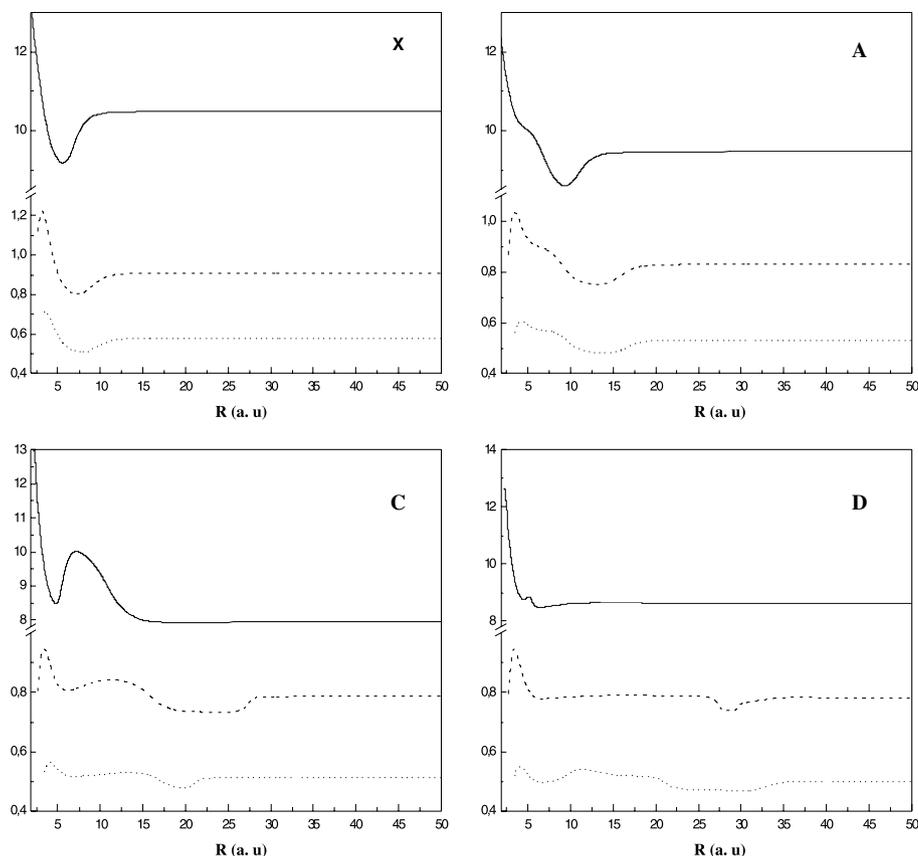


Fig. 5. Second adiabatic correction for X, A, C and D states for LiH (full line), RbH (dashed line) and CsH (dotted line) molecules.

Table 1
The second adiabatic correction of the X state for the LiH molecule

R (au)	Our work (cm^{-1})	Jenson and Yarkony [7] (cm^{-1})
2.5	1.83	1.43
3	0.0	0.0
3.5	-1.19	-1.02
4.5	-2.4	-2.15
5	-2.65	-2.42
5.5	-2.74	-2.54
7.5	-2.01	-2.01

the three molecules and therefore the shift in the equilibrium positions (R_e) due to the adiabatic correction. The equilibrium distance of the ground state of LiH, is shifted by about 10^{-4} au to be compared with the values reported by Kleinman and Wolfsberg [39] (7.18×10^{-4} au) and Jenson and Yarkony [7] (7.27×10^{-4} au). It is important to note that our shift is due only to the first adiabatic correction, while their shift is corresponding to the total adiabatic correction. The shift for the ground state of RbH and CsH systems, which is about 10^{-5} au, is smaller than that found for the LiH molecule. This is not surprising as the adiabatic correction is more important for LiH. The shift for the excited states and for the three molecules becomes more important as well as the adiabatic correction. This shift is of an order of 10^{-1} au for the D $^1\Sigma^+$ electronic state of LiH.

The same thing is observed for the well depth D_e , which is shifted by few cm^{-1} for the ground and the lower excited states and by some 10 cm^{-1} for the higher excited states having minima located at large distances. For example, the D $^1\Sigma^+$ and H $^1\Sigma^+$ states of LiH are shifted by 64 cm^{-1} and 77 cm^{-1} . It is important to note that the adiabatic correction for several states has produced other local equilibrium distances with well depths of 10–100 of cm^{-1} . The vertical transition energy is slightly shifted by few cm^{-1} . It seems to be not affected by the adiabatic correction. This can be explained by the fact that the adiabatic correction for the ground state near the equilibrium distance is of this order.

3.3.2. Shift on vibrational energy levels

The vibrational energy levels have been recomputed by taking into account the first adiabatic correction. The latter was added to the adiabatic potential energy curves of the $^1\Sigma^+$ electronic states of LiH, RbH and CsH molecules. The vibrational shift is defined as the difference between the corrected and the adiabatic (BO) levels. Fig. 7 presents the determined shift for the X, A and C $^1\Sigma^+$ states of LiH, RbH and CsH molecules. We remark that the shift for the energy levels associated to the ground state ($X^1\Sigma^+$) presents the same behaviour for the three molecules. It is maximum at vibrational level $v = 18, 20, 22$, respectively, for LiH, RbH and CsH. It seems that the high vibrational

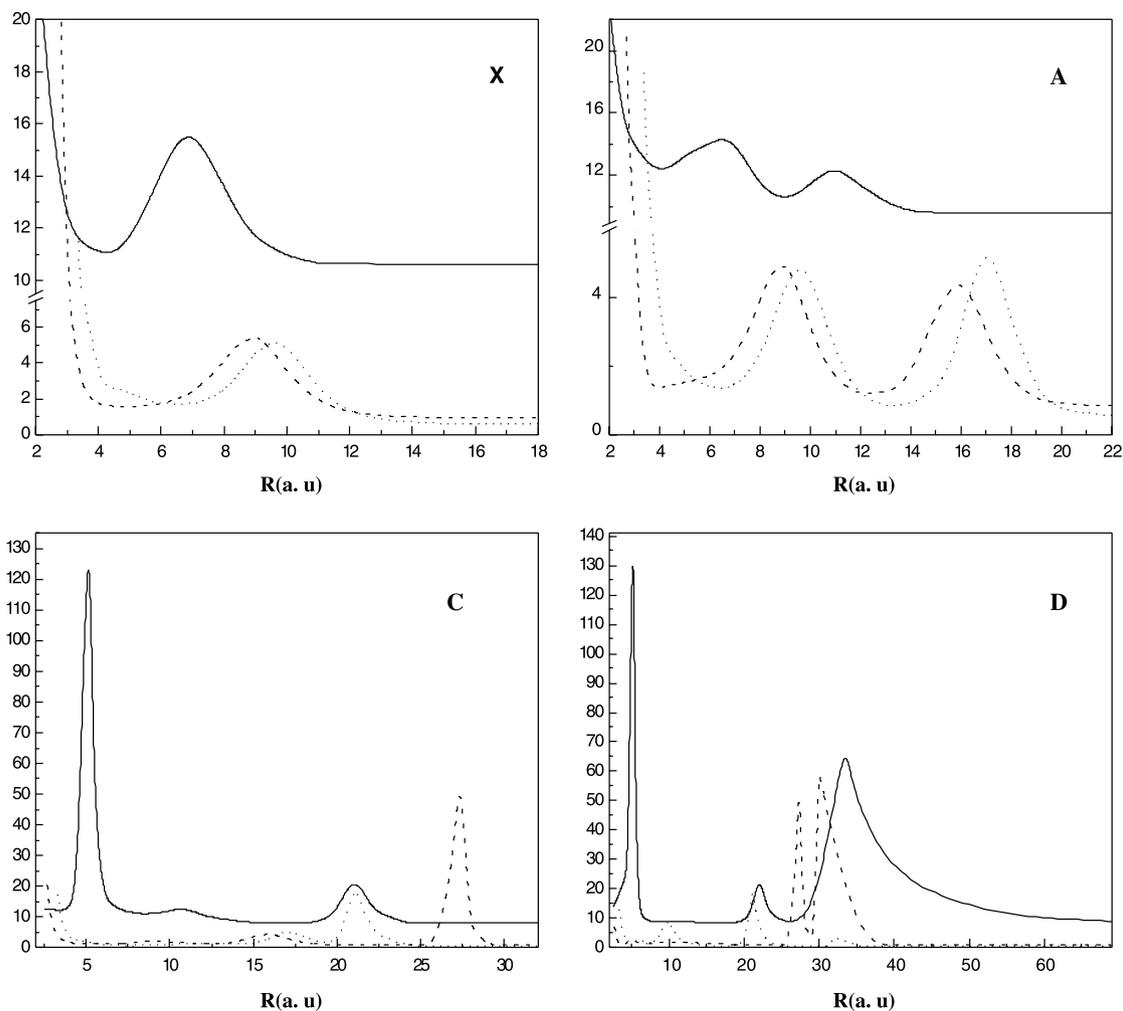


Fig. 6. Total adiabatic correction for X, A, C and D states for LiH (full line), RbH (dashed line) and CsH (dotted line) molecules.

energy levels are not shifted, which can be explained by the absence of the first adiabatic correction at large distance. However, the shift is more important for LiH compared to RbH and CsH. The maxima of displacement for the vibrational energy positions for the ground state of LiH, RbH and CsH systems are, respectively, 4.6, 3.5 and 3.4 cm^{-1} . The shift of the vibrational levels of the first excited state ($A^1\Sigma^+$) is still of the same order of magnitude, few cm^{-1} , and vanishes for higher levels. The shift of the vibrational levels trapped by the $C^1\Sigma^+$ state of the LiH molecule presents many maxima located at $v = 34, 38$ and 42. In contrast, the CsH vibrational displacement is maximum for $v = 28$ and 29, while the shift for the RbH system is maximum for $v = 54$. For the C state the corrected vibrational levels are shifted for some levels by about 18 cm^{-1} , which shows again the breakdown of the Born–Oppenheimer approximation.

4. Conclusion

The radial coupling and the adiabatic corrections to the Born–Oppenheimer potential energy curves of the ground

and the lowest $^1\Sigma^+$ excited states of LiH, RbH and CsH molecules is performed. We have used a simple approach based on exploiting the accurate diabatic and adiabatic results determined previously [18,29–34]. We have used computationally efficient method to determine the non adiabatic radial coupling matrix elements, which corresponds to the first and the second derivative of the electronic wave function. This method is essentially based on a numerical differentiation of the rotational matrix connecting the diabatic and adiabatic representations. The numerical advantages of this approach are evident. The electronic Hamiltonian in the diabatic basis can be easily interpolated and its derivatives computed since all matrix elements present smooth variations. Then the necessary diagonalisation of this small matrix and the eventual differentiations can be easily performed for many points as necessary. Thus the determination of the radial coupling between the adiabatic states presents no numerical difficulty, even for sharp peaks. The main difficulty is of course the obtention of the electronic Hamiltonian in the diabatic basis.

The calculated radial coupling for the lowest $^1\Sigma^+$ are found to be very similar in shape, location and intensities

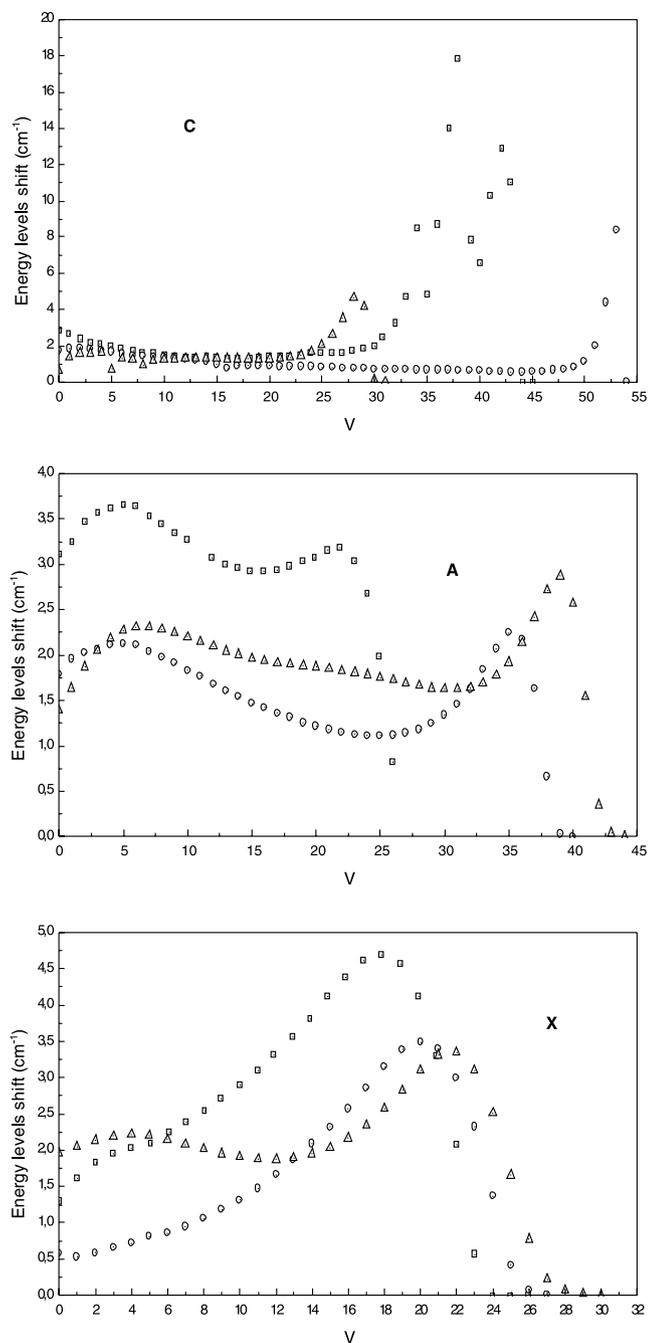


Fig. 7. Vibronic shift for X, A, C state of LiH (square), RbH (circle) and CsH (triangle) molecules.

to other, more conventional ab initio calculations involving different techniques specifically devoted to such problems. This success for the adiabatic singlet states shows the validity of our approach and grounds the diabatisation method used previously. The peaks of the radial coupling can easily be assigned to crossings between diabatic states. Most of these crossings are due to an over-repulsiveness of the valence diabatic states as compared to the Rydberg ones, and is a common feature in the alkali hydrides. Such peaks could be important in medium and high energy collisions. At intermediate internuclear distances, in addition

to the well known neutral–ionic peaks which play a dominant role in the mutual neutralization process, we observe some intense peaks, also related to neutral–neutral interactions.

The radial coupling is exploited to determine the first adiabatic correction for several electronic states of LiH, RbH and CsH molecules. Such correction was found to be of few cm^{-1} and more significant for the excited states. This correction was also added to the Born–Oppenheimer potential energy curves to estimate the change in spectroscopic constants and the shift of the vibrational energy levels trapped by the X, A and C $^1\Sigma^+$ states. It is important to note that the spectroscopic constants (R_e , D_e and T_e) are affected by the adiabatic correction. Such effect is more significant for the higher excited states, which is not surprising as the correction for such states is larger.

The second adiabatic correction was evaluated using the Virial theorem. This correction for the X state of the LiH molecule was compared with the work of Jensen and Yarkony [7]. A reasonable agreement between the two works is found.

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