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Game of basis sets pinpointing charge transfer states: Example for LiH

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Abstract

Considering the LiH case study, an semi-quantitative approach is presented to locate the energy and interatomic ranges of charge transfer states. Using basis sets of increasing size, it is shown how their effect on the quality of description of neutral and anionic hydrogen can be used to determine the ionic nature of the ground and excited electronic states. The results are satisfactorily compared to those obtained from the permanent dipole moment analysis.

1 Introduction

The study of the physical nature of the chemical bonding has been a central problem of quantum chemistry since the beginning of quantum physics[1]. It was soon understood that the interaction between electronic wave functions leads to stabilisation or destabilisation. For an interesting discussion see [2, 3]. However the standard of the covalent bond, in H₂, is known to be some mixing between neutral and ionic (H⁺ H⁻) configurations. In many cases, even for simple diatomics, neutral and ionic configurations interact, some times at large distances as for example in LiF[4, 5] or NaI[6, 7], or at much shorter distances as for the LiH molecule[8, 9, 10].

Made of the two lightest atoms, LiH is well known, among the simplest molecules for its earlier formation in the universe and interesting molecular physics properties such as neutralization cross sections ($\text{Li}^+ + \text{H}^- \rightarrow \text{Li}^* + \text{H}$), dissociative recombination ($\text{LiH}^+ + e^- \rightarrow \text{LiH}^* \rightarrow \text{Li}^* + \text{H}$), associative recombination ($\text{Li}^* + \text{H} \rightarrow \text{LiH}^* \rightarrow \text{LiH} + \text{photon}$), ... and it has been thoroughly studied both theoretically and experimentally[11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26]. It represents a simple molecule but a complex system where covalent and ionic states strongly interact, its ground state is neutral at dissociation ($\text{Li}(2s) + \text{H}(1s)$) but largely ionic at the equilibrium geometry as shown by an important permanent dipole moment, and therefore it is a challenging system for many theoretical theories such as DFT[20], diabatisation approaches[8, 9],... Powerful diabatisation studies have been performed for LiH and it has been shown that shifting the ionic diabatic state down in energy by the error in the H electron affinity strongly improves the adiabatic energies, the molecular spectroscopy and molecular physics properties. The D_e of the ground state is improved and all the vibrational spacings for the A, C, D,... states are decreased and the experimental spacings bracketed by the results with and without the correction. Comparing the adiabatic energies with and without the correction immediately highlights the ionicity of the adiabatic states since only the ionic component of the wave function is affected[27, 28, 29, 30, 31]. It was also shown that the permanent dipole moments gives a direct illustration of the ionic character of the various adiabatic wave functions[32].

This correction was based on the diabatisation procedure which was very performant for LiH and the whole series of alkalis heteroatomic diatomics but is not easily applicable to general molecules. Having in mind this correction effects which reveals the ionic component of the adiabatic states we imagine here a strategy which can be easily extended to general molecules and only involves standard adiabatic calculations but in a quite specific way. We would try to answer the question did a given adiabatic state contain strong ionic, charge transfer component, at which energies, for which internuclear distances or geometries. It is the purpose of this work to investigate if the approach proposed, which is applicable to general molecules, did work for the well studied LiH molecule.

The general motivation for the identification of charge transfer states is at least two folds:

i) A deeper understanding of the nature of the electronic states yields physical insight in the system and could allow for further analysis and extrapolations to other systems.

ii) As shown for LiH, it opens the way to specific corrections or requirements. For example, for the ground state of LiH, the molecule is largely ionic at short distances and neutral at dissociation. Thus, to get an accurate D_e it is necessary to have a very good description of H^- otherwise the D_e will be underestimated. The knowledge of the real nature of the molecular system reveals the challenge the calculations are facing and may allow to compensate some deficiencies.

In the charge transfer states there are anions and cations. The basic idea of the method is that anionic states are much more difficult to compute and therefore the residual errors are much larger than for the other species. Therefore analyzing the sensitivity of the energies with respect to quality of the anionic description could give an idea of the ionic components. For LiH, we should just look at the sensitivity of the adiabatic energies and dipoles to the quality of the H⁻ description. It is often difficult to get highly accurate results but it is quite easy to deteriorate them and we will do so in a controlled way, by varying the size of the H basis set while keeping fixed the one for Li. The challenge is to correlate the variation of the adiabatic potential curves and dipole moments with the H basis set and the ionicity of the adiabatic states, pinpointing which state is ionic and where.

The presentation is organized as follows; In Section 2, the method used for calculations is presented. Section 3 is devoted to the presentation of the results and discussion. Concluding remarks are reported in Section 4.

2 Methods

We have used the Molpro package[33, 34, 35] in up to date but standard approaches. For all calculation full valence CI have been performed while the Li core was kept frozen at the RHF level. A very large basis was used for Lithium (*spdfg* AV5Z[36]) able to describe the whole Rydberg states involved in the low-lying states of the LiH molecule, in ¹Σ symmetry, *ie*, the X, A and C states.

For Hydrogen we have used four standard AVxZ basis sets from Dunning[37]. The corresponding electronic affinities at the FCI level are given in Table 1

Table 1: Energies and electro-affinities of hydrogen

Basis set	H	H ⁻	E _a (eV) [†]
sp AVDZ	-0.49933432	-0.52402863	0.6720
spd AVTZ	-0.49982118	-0.52656215	0.7277
spdf AVQZ	-0.49994832	-0.52713929	0.7399
spdfg AV5Z	-0.49999478	-0.52742896	0.7465

[†]Experimental value: 0.754195 eV[38]

3 Results and discussion

3.1 Global overview of potentials and permanent dipole moments

As mentioned before, we have fixed the basis set for Li to a huge basis as needed for the various excited states of LiH dissociating to the low Rydberg states of Li, while for H which is only as a neutral H (*1s*) or ionic H⁻, we

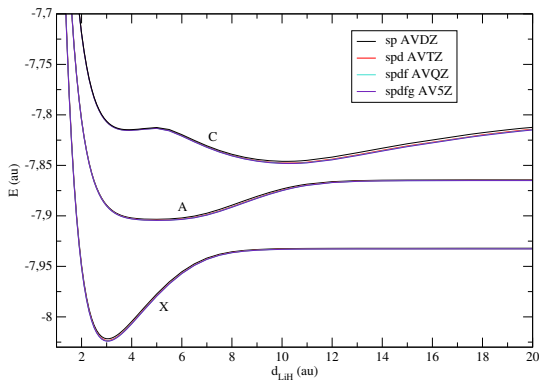


Figure 1: LiH potential curves (Li basis set is *spdfg* AV5Z from Dunning

have used four basis sets ranging from a rather reduce one involving only s and p gaussians to a quite large one involving s , p , d , f and g gaussians. These four basis sets are rather standard ones and can be used for very wide studies. The energy for H and H^- is reported in Table 1 for the four basis sets. The corresponding errors can be easily deduced since the non relativistic converged energy is known both for H (*ie* -0.5 a.u.) and H^- (-0.527716 a.u.[38]). This table gives also an idea of the kind of variations we can expect for a neutral state involving H and an ionic one involving H^- . The energy of H is much easier to improve than the one of H^- .

In Figure 1, the adiabatic energies are reported for the 3 lowest states of LiH: the ground state X, the first excited one A and the second excited state C, resulting from full valence CI using the four H basis sets and the same AV5Z basis set for Li. Noteworthy, clear differences appear, not everywhere but at small distances for X, somewhat larger ones for A and larger ones for C. In previous studies diabatic ionic energies were shifted by the H electron affinity error and the diabatic matrix diagonalised to get improved adiabatic energies. Comparison with these previous results reveals quite similar changes in the same energy and distance ranges; a very promising result for the present much simpler approach. In Figure 2 the corresponding permanent dipole moments are plotted for the four H basis sets. It was emphasized in reference [32] that for LiH the permanent dipole moment gives a good illustration of the ionic character of the wave function. In a point charge model, a behaviour in $-d$ (green curve in Figure 2) is expected for the ionic state permanent dipole moment. This behaviour was nicely seen for the diabatic ionic state, giving strong confidence in the diabaticization method, while it was shown that the adiabatic dipole moments reproduce piecewise this $-d$ curve and it was established that their crossing points correspond to the related avoided crossings in adiabatic

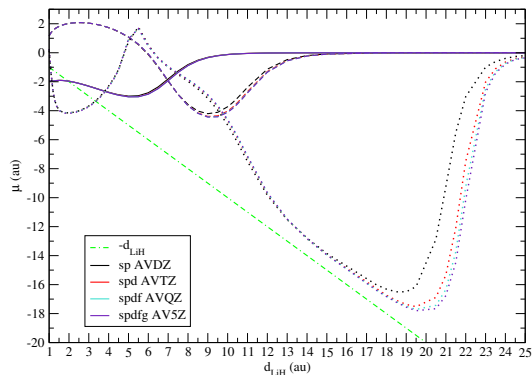
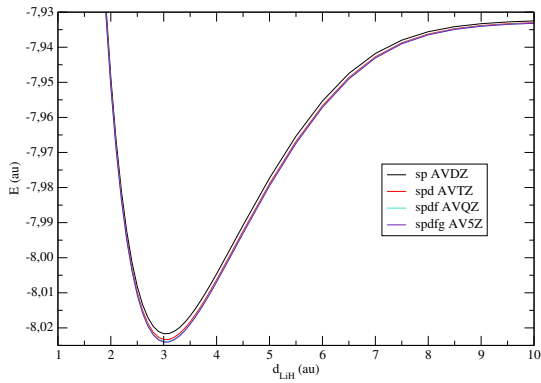


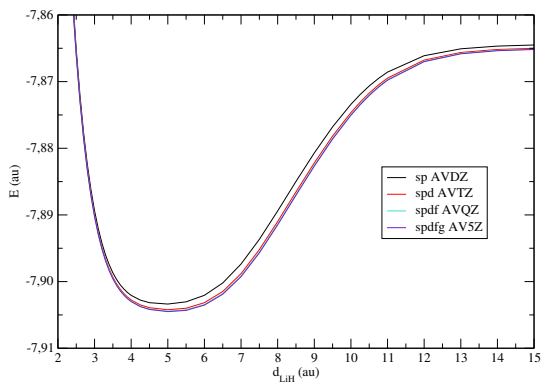
Figure 2: Permanent dipole moments of LiH (full line: ground state, dash: A state and dot: C state). The green line corresponds to the point charge model.

energy landscape. Here, we clearly observe a similar picture, with increasing absolute values of the permanent dipole moment as the distance increases, and a global piecewise reproduction of the linear behaviour with R . Interestingly, when enlarging the H basis sets, the crossings of the permanent dipole moments shift to slightly larger distances, as when correcting the diabatic ionic energy and recomputing the adiabatic permanent dipole moments[32]. Here also, for larger distances, we see sharper behaviours around the crossings for the permanent dipole moment, and related less avoided crossings for the adiabatic energy. This is consistent with a global decrease of the electronic coupling between the underlying diabatic states and particularly between the ionic state and the various neutral ones.

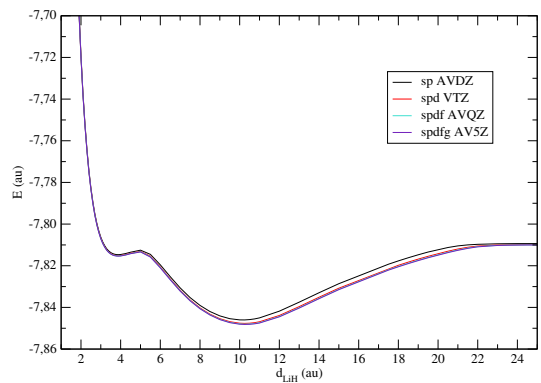
From Figures 1 and 2, we can clearly conclude that it is possible to identify the charge transfer state involving H^- (and therefore Li^+) just by comparing the adiabatic results of the energy resulting from the various basis sets for H. In the region where we see a clear variation we have a charge transfer state, at short distances and low energies for X, at somewhat larger distances and higher energies for A, and larger ones for C. Therefore the analysis of the adiabatic energies variations when varying the H basis sets allows to identify where in energy and distance we have an ionic state, not only for the ground state, but also for the excited states. This important information is moreover corroborated by the variations seen for the permanent dipole moment. To see better the variations, the adiabatic energy results are plotted in adapted enlarged ranges in Figure 3 (a) to (c) for the ground state, for A, and for C, respectively. We see more quantitatively that these variations are well related to the energy and d range where we have an ionic state consistently to what is known for LiH. In the following sections, we will try to see if this successful semiquantitative analysis can be made more quantitative.



(a)



(b)



(c)

Figure 3: Details of X (a), A (b) and C (c) potentials

3.2 Energies differences

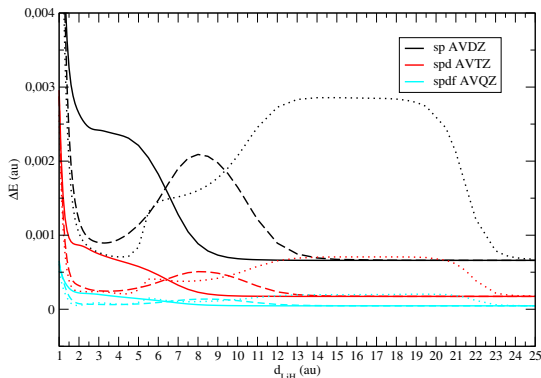
To go further, we need to have a closer look at the energy differences between the various basis sets. We know the errors for H and H⁻ resulting from the four basis sets used for H and therefore the asymptotic error. However, the error in the molecular calculation is not so well known since many molecular effects can contribute. The error can be estimated since the exact energy for H and H⁻ are known, however for a general molecule this is not the case. Therefore the best we can do is to compare the various calculations to the best one, *ie* the one with the larger basis set for H. The energy differences, ΔE , of the results using the three other basis sets with respect to the one using the basis *spdfg* AV5Z are reported in Figure 4 for a global picture involving the 3 states X, A and C, and magnified in Figure 5 (a) to (c) for X, A and C respectively. The asymptotic ΔE constants are also plotted in consistent colors.

Naively one would expect that when the state is mainly neutral we would observe a ΔE close to the asymptotic one of H, while when the state is mainly ionic we would observe a ΔE close to the one of H⁻. Effectively, it is more or less the case which allows to clearly identify where the X, A and C states are ionic or not. Quantitatively, we can see in Figures 4 and 5 that while that works at larger distances, at short distances the situation is more involved. Clearly, at short distance, particularly for the X state (Figure 5(a)), but also somewhat for the A state (Figure 5(b)), ΔE remains below its ΔE asymptotic corresponding value, while for the C state (Figure 5(c)), it almost reaches it.

To made more quantitative comparison between the information given by the permanent dipole moment and the one given by ΔE , let us define two distances R_I (for R interior) and R_E (for R exterior) such that the state is considered as ionic (charge transfer) between these two distances. From the adiabatic energy landscape, it is difficult to determine these distances because we have avoided crossings, however from the permanent dipole moment and the ΔE data, it is easier because we do have real crossings. These distances are thus given at the crossings between two states either for the permanent dipole moments or for ΔE which presents a similar behaviour. For the ground state we have only R_E because for smaller distances it remains ionic. For the C state, as we have not computed the D state, at large distance, there is no crossing. In that case, we define R_E at the distance were we observe a decrease by 50% of the largest value for smaller distances, somewhat in the same spirit than the half width for spectroscopic line profiles. The resulting data is reported in table 2. For all these distances, all the states and all the basis sets, we observe a good agreement between the data obtained with the permanent dipole moment and the one obtained with ΔE , which firmly grounds the new method. We see now quantitatively that the crossings where the ionic character is transferred from one adiabatic state to the other, is shifted to somewhat larger distances when the H basis is increased, clearly related to a better description of the H⁻ component. The ΔE data gives slightly smaller distances, in almost all cases, however it should be emphasized that these distances correspond to where the charge transfer state is equally shared between two adiabatic states. These

Table 2: Inner and outer border of the ionic character of the electronic states

State	Basis	AVDZ		AVTZ		AVQZ		AV5Z
		μ	ΔE	μ	ΔE	μ	ΔE	μ
X	R_E	6.95	6.36	6.99	6.41	7.00	6.43	7.00
	R_I	6.95	6.36	6.99	6.41	7.00	6.43	7.00
A	R_I	9.55	9.37	9.74	9.54	9.79	9.63	9.80
	R_E	9.55	9.37	9.74	9.54	9.79	9.63	9.80
C	R_I	21.13	21.41	21.87	21.80	22.05	21.97	22.19
	R_E	21.13	21.41	21.87	21.80	22.05	21.97	22.19

**Figure 4:** Energy differences relative to the largest *spd*fg AV5Z basis set (Full line: ground state, dash: A state and dot: C state)

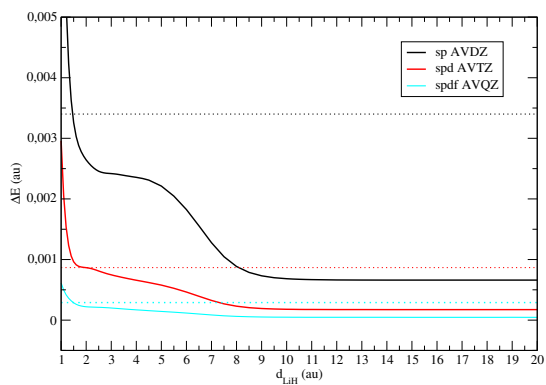
criteria give slightly different results, since the wave function is not tested directly but through an observable, either the energy or the dipole moment. Reversely, we see how important it is to have very good descriptions of the anionic species when ionic states are involved, even for neutral molecules.

We will try to understand in the following sections how the ΔE asymptotic value is affected by some molecular effects and could thus be corrected. The main problem now is to estimate whether the ΔE asymptotic value needs molecular corrections or if it is related to the effect of decreasing ionicity percentage.

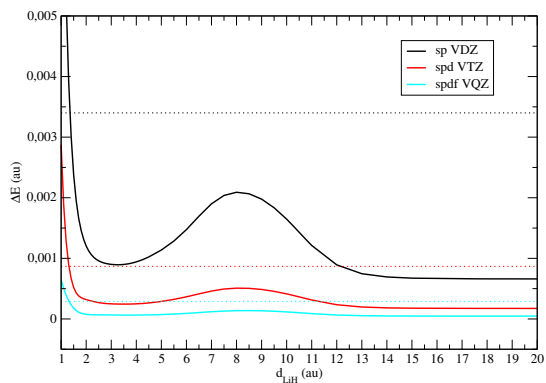
3.3 Going further

3.3.1 Basis set superposition error effects

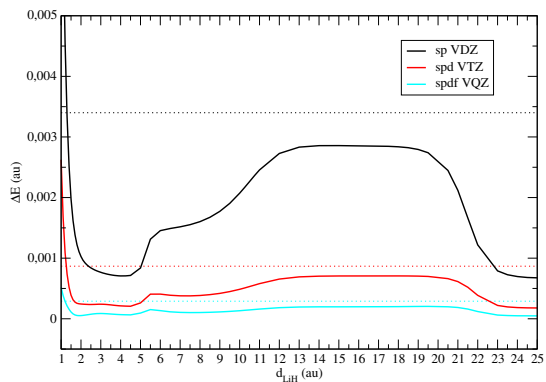
The first molecular effect we can think about is the basis set superposition error (BSSE). In a molecular calculation of an AB molecule deficiencies in the basis set of atom A (here H) is in part compensated by the basis set of atom B. This effect is often estimated by the counterpoise method [39] and incorporated as a repulsive correction. Here we want to estimate the BSSE effect on the energies of H and H^- , therefore a full CI approach is performed for H^- with



(a)



(b)



(c)

Figure 5: Energy differences relative to the *spdfg* AV5Z basis set for the X (a), A (b) and C (c) states. The horizontal lines show the energy difference of H^-

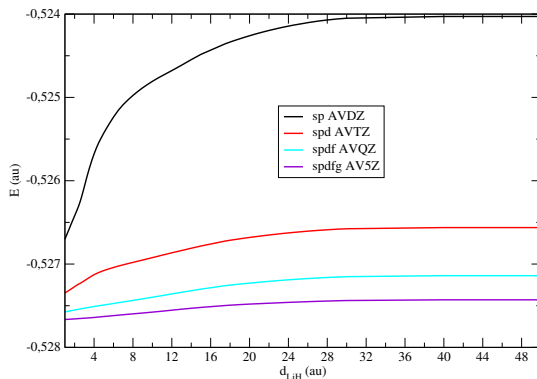


Figure 6: BSSE for H^- in presence of Li *spdfig* AV5Z basis set

the four H basis sets and the basis set of Li is also present as a dummy center at distance d . The procedure is thus very similar to the one used for the LiH calculation, however Li is just a dummy center, without pseudopotential and without core or valence electrons. We thus want to estimate how the energy of H^- is lowered by the presence of the Li basis set. Of course, when the basis set used for H is large, the asymptotic error is small and there is less room for BSSE effects. The resulting energy for H^- are reported in Figure 6 as a function of d . As d decreases, we see a rather strong decrease of the error. Obviously, this BSSE effect only acts when there is some overlap between the two basis sets and decreases at large distance.

The ΔE is plotted again in Figure 7 as a function of d for the three smaller H basis sets and compared now not only to the constant asymptotic ΔE , but also to the one including the BSSE effect for H^- . Clearly BSSE effects play an important role and the asymptotic ΔE should be replaced by this BSSE improved ones, rather than considered as constants. BSSE effects allow to decrease the asymptotic error by a factor larger than 2 around the equilibrium distance for the ground state.

For the three basis sets, the ΔE results for the three states are compared to the BSSE corrected H^- energy differences in Figure 8. The ΔE results now fit rather well the H^- ΔE BSSE improved when the state is ionic, however we see now that some overshoot is observed for the X state at rather short distances.

We may consider two explanation: i) there is more than one charge transfer in these region, *ie* we have a situation like $\text{Li}^{+q} + \text{H}^{-q}$ with q larger than 1; ii) other molecular effects should be considered that balance the BSSE ones. It is hard to believe that a charge larger than one can be transferred because H^- is stable but, to our knowledge, not with a charge larger than one. Moreover to made a hole, even partially, in the Li core seems very difficult because the core electrons of Li are very strongly bound, much more than the valence electron. Therefore we must consider some other molecular effect.

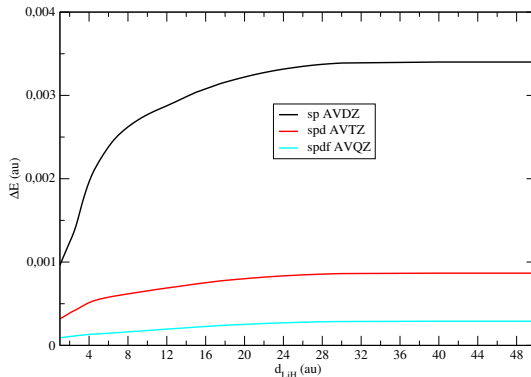


Figure 7: Energy differences of H^- including BSSE

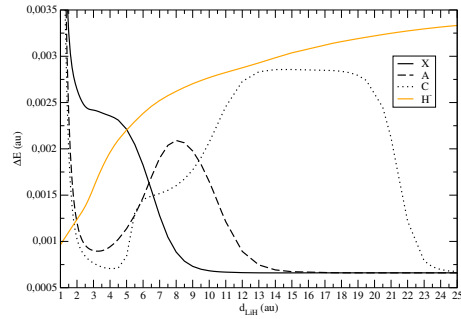
3.3.2 H^- polarisabilities effects

The main molecular effect which can act against BSSE is that of the polarisability of H^- due to the field created by Li^+ being badly computed with the small H basis sets. To estimate this polarisability lack, we have performed FCI calculations of H^- , with the four H basis sets and a point charge +1 at distance d without any basis set. The result of this energy are plotted in Figure 9. Asymptotically we have the various H^- energies and we see a behaviour in $-1/d$ with corrections in $-A/2d^4$ as expected.

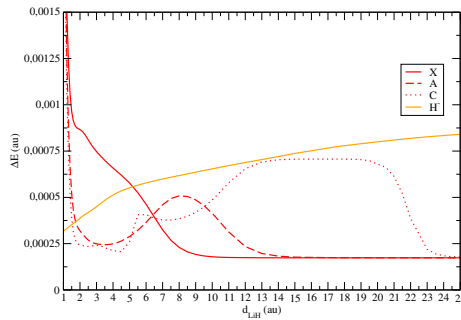
We fitted the the long-range part (from $d=10$ to 1000 bohr) of H^- energy with the model function $-\frac{Qq}{d} - \frac{\alpha}{2d^4} + E_{FCI}(H^-)$ where d is the distance between the anion and the positive point charge. Table 3 shows the results for the different basis sets used in the present work. The estimated polarisabilities for H^- given in Table 3 are quite far from the exact dipolar polarisability of H^- , estimated in reference [40] to be about 200 au³. The energy of H^- is difficult to compute and needs very extended basis sets, its polarisability is even more difficult to compute, it is thus not so surprising that standard basis as used here for H lead to quite poor results for this H^- polarisability. A more dramatic behaviour can be seen at short distances: we observe some unexpected repulsive effect between H^- and a point charge. In fact these results at short distances are polluted by some kind of H_2 calculation. Although no basis set has been given to the point charge, some kind of BSSE is acting to localise an electron around the point charge producing a poor H_2 calculation.

Table 3: Long-range fit of H- energies polarised by the +1 point charge

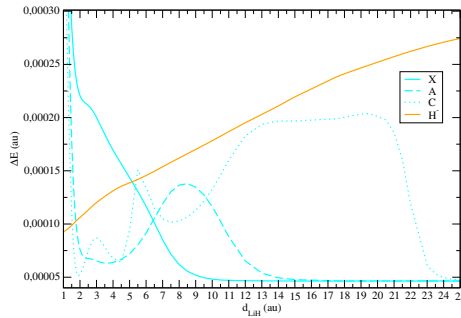
Basis set	Q_q	α
AVDZ	-1.00004	15.24
AVTZ	-1.00004	28.38
AVQZ	-1.00000	39.44
AV5Z	-0.99997	48.70



(a) sp AVDZ



(b) spd AVTZ



(c) spdf AVQZ

Figure 8: Energy difference for state X, A and C compared to H^- energy difference including BSSE for different H basis sets

The ΔE data for H^- corresponding to the energy of Figure 9 is plotted in Figure 10. The main behaviour in $-1/d$ is not dependent of the basis set used and vanishes in the difference while polarisability effects which are strongly sensitive to the basis set used remain. Now these curves are much above the asymptotic constant, while for BSSE they were below. Clearly there is some competition between these two effects. The polarisability effects are an order of magnitude larger and clearly dominate over BSSE effects, but as they are

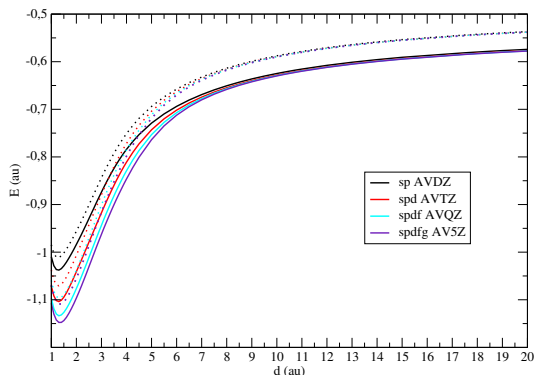


Figure 9: H^- energy including point charge polarisability. Full line: FCI, dot: HF.

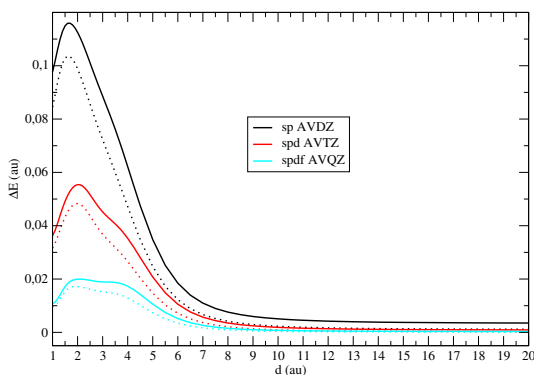


Figure 10: Energy difference of H^- including point charge polarisability effects. Full line: FCI, dot: HF

polluted by the poor H_2 estimation they may be questionable at short and intermediate intermolecular distance. It can be seen in figures 9 and 10 that this is not specific to FCI as the same behaviour is present at HF level.

In a last attempt to include both BSSE and polarisability effects together directly, we have performed calculations for H^- with on one side at $-d$ a dummy atom with the Li basis set on the other side at the same distance d , a point charge. The results both for the energy of H^- and ΔE are quite similar to the one of Figure 9 and 10 where there was only the point charge at distance d , and not reported here. However, the pollution by a poor H_2 calculation is much worse now because the extended basis set of Li, although at distance $2d$, combined to the one of H (at a distance d) from the point charge, allows some more electron localisation around the point charge.

4 Conclusion

Using a series of basis sets for H and keeping a single large one for Li, in adiabatic, state of the art calculations, we have tested the possibility to identify the charge transfer state Li^+H^- which was shown to imprint the low energy spectrum of LiH. We have tested here the approach for the ground state X, and the two first excited ones of the same symmetry, the A and C states. The energy differences between the adiabatic energies obtained with the various H basis sets with respect to the largest one, nicely indicates which state is ionic (Li^+H^-) at which energy and interatomic distance. This important information is moreover consistent with the results obtained previously by analysing the permanent dipole moments and energies in adiabatic and diabatic representations and gives confidence to the much simpler method we proposed here for the identification of a charge transfer state. The new method can be used widely for molecules larger than diatomics since it relies on adiabatic standard calculations.

In the new method the energy differences are compared to the asymptotic ones where the atomic charges are well controlled. In order to go somewhat beyond, we have further tested some molecular effects. First of all, BSSE ones, and see that the error for H^- is reduced by a factor larger than 2, compared to the asymptotic one, at distances around the ground state equilibrium geometry, thanks to the basis set of Li. We have further tested the polarisability of H^- in presence of a point charge. It is of course better computed with the larger H basis sets and found that this effect competes with BSSE ones in the ΔE and are generally much larger. Furthermore, because of the huge sensitivity of the adiabatic calculations to the basis sets, particularly for the underlying anionic species, even for a neutral molecule, to get accurate results a specific care should be taken not only to the asymptotic energies, but also to the molecular effects like polarisabilities or BSSE.

This method found some limitation at very short distances where for all states we see an exponential increase of the ΔE . Small basis sets lead to overestimate the repulsion at short range due to an underestimation of the correlation energy.

In the present contribution, taking benefit of the huge sensitivity of the anion H^- with respect to the basis sets, we have shown that the energy difference with respect to the largest basis can be used to identify where in energy and distance the adiabatic states can be considered as charge transfer ones involving H^- and Li^+ . On the discussion about the large applicability of the method, various points can be considered. The method can be easily extended to molecules, either charged or neutral, involving H and alkali atoms which have a similar behaviour. For other atoms X, the main question is: with standard basis sets, is there a large difference between the calculation of the various charged species X^+ , X, X^- . If it is the case, the method can be applied and should work. In other words, the method can be intended for molecules where it is possible to discriminate the charge of the atom, just by evaluating the sensitivity of the adiabatic calculation with the basis sets. In further

works, we plan to test the method for molecules like CaH, and other alkaline-earth - alkali molecules or molecules containing halogen atoms or the diborane molecule, molecules where little is known on the charge transfer state imprint and interesting challenges could be investigated.

Declarations

Authors declare no conflict of interest.

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