

Ab initio adiabatic and diabatic permanent dipoles for the low-lying states of the LiH molecule. A direct illustration of the ionic character

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Abstract

The permanent dipole moments of the eight low-lying $^1\Sigma$ states of the LiH molecule are calculated by an ab initio approach for both the adiabatic and the diabatic representations. The results shed light on the interplay between the ionic and the neutral states producing a direct illustration of the ionic character of the electronic wavefunction. Our results suggest that the location and the width of the avoided crossings for the potential energy curves could be experimentally derived.

The LiH molecule is known to be ionic (Li^+H^-) in nature at its equilibrium geometry and neutral at the lowest dissociation limit ($\text{Li}(2s) + \text{H}(1s)$). As the internuclear coordinate increases, the interplay between the various neutral channels ($\text{Li}(2s \text{ to } 4p) + \text{H}(1s)$) and the ionic one leads to a series of avoided crossings which become less and less avoided. This pattern has been largely studied, within the adiabatic representation, in order to determine, for example, the neutralisation cross-section, for which the radial coupling also needs to be estimated. The ground state and the first excited state of $^1\Sigma$ symmetry (labeled A) have been thoroughly studied both experimentally [1–4] and theoretically [5–7]. For a review see Ref. [8].

Recently, we have computed [7] a manifold of eight low-lying diabatic states dissociating in the neutral asymptotes $\text{Li}(2s, 2p, 3s, 3p, 3d, 4s, 4p) + \text{H}(1s)$ and the ionic one (Li^+H^-) together with the 8 low-lying $^1\Sigma$ adiabatic states. The calculation uses a diabatisation procedure [9] which allows for a direct

ab initio determination of the diabatic states defined as an R dependent unitary transform of a set of adiabatic states. We used an effective metric for the overlap between the atomic basis sets together with variational effective Hamiltonian techniques [10]. These diabatic potential curves reveal the expected behaviour, namely an ionic curve which varies roughly as $1/R$ at large interatomic distances and crosses one after the other all the neutral diabatic states.

The ionic character of the molecule around its equilibrium geometry is known from the measured permanent dipole results, 2.3141 au [11,12] for $v = 0$. Since the ground state vibrational wavefunction has limited extension around the equilibrium distance ($R = 3.015$ bohr) [13], it is clear that the charge transfer from Li to H is large – in atomic units the dipole of the pure ionic species is directly R , the internuclear distance which is also the charge separation.

The permanent dipole has been calculated by

various groups [5,14,15] together with the related transition moment only for the ground state and A state. These calculations were devoted to the comprehension of the intense $X \rightarrow A$ absorption spectrum. From the diabatic curves, we expected a particular feature for the permanent dipole when considering the low-lying adiabatic states all together. Only the ionic state has a large dipole, so that we expect the permanent dipole to give an illustration of the ionic character of these adiabatic states.

In order to get some insight into the interplay between the neutral and the ionic species for LiH, we propose calculated permanent dipole moments for both adiabatic and diabatic representations. The calculation has been performed with the same basis set as in our preceding study [7] and using similar methods both for the diabatic and adiabatic ap-

proaches. The details of this new and more complete calculation will be published elsewhere [16] together with additional information directly related to the absorption or emission spectrum (position, intensity and width of the lines).

The accuracy of our calculation can be checked by a comparison with the important measurements of dipole moments for various vibrational levels of the A state by Brieger et al. [17,18]. For the vibrational levels $v = 2, 4$ and 5 ($j = 1$), they measured $\mu = 0.61, 0.23$ and 0.06 (in au), respectively, while we get $0.638, 0.256$ and 0.069 ($j = 0$). The agreement is thus good and illustrates the accuracy of our adiabatic results.

The results for the permanent dipoles are presented in Fig. 1 for the adiabatic representation and in Fig. 2 for the diabatic one. We considered a large

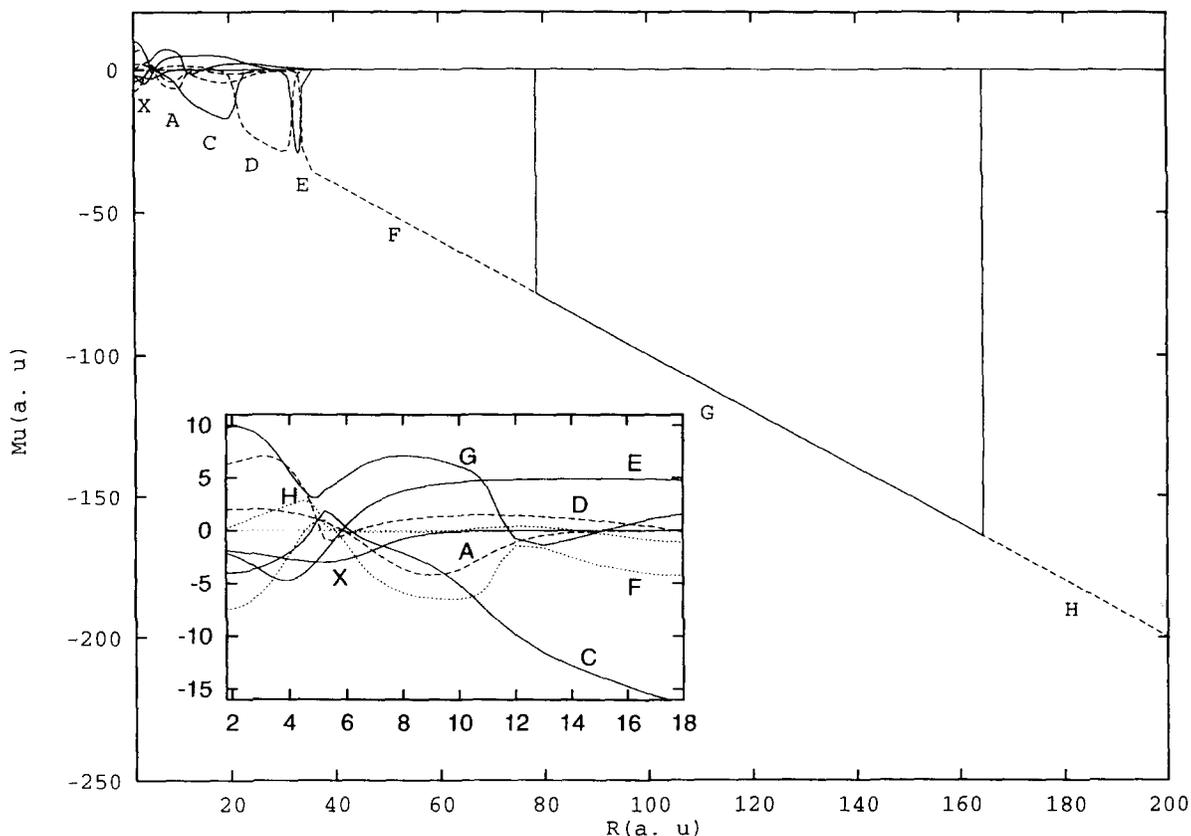


Fig. 1. Permanent dipole moment for the eight low-lying $^1\Sigma$ adiabatic states of the LiH molecule, as a function of the internuclear distance (all in au). Alternating solid and dashed lines correspond to X, A, C, D, E, F, G, H.

range of internuclear distances because we expected new features to arise from a global picture also involving the highly excited states. In effect, these latter ones become ionic at large internuclear distances only. Let us consider the diabatic results. This is the first direct evaluation of the dipole for the diabatic states. As expected, for the dipole of the ionic diabatic state, we get a straight line, while the neutral diabatic state dipole rapidly drops to zero as R increases. This behaviour is nicely consistent with a purely ionic diabatic state and grounds our diabatisation approach on physical properties.

For the adiabatic representation we observe that, one after the other, each adiabatic states has its dipole that goes up to the R curve and then drops to zero. When combined these curves reproduce piecewise the whole R curve characteristic of the ionic dipole and cross forming nodes between consecutive

pieces. The curves seem to relay each other to this R line. This particular behaviour can be easily understood from the diabatic potential and dipole curves. The permanent dipole gives us a direct illustration of the ionic character of the adiabatic electronic wavefunction. We then access directly to a visualisation of the R dependence of the charge distribution of the wavefunction. The distance for which two consecutive adiabatic states have the same dipole locates the crossing of the ionic diabatic state with the corresponding neutral one. The sharpness of the slopes around the node for the dipole is closely related to the weakness of the avoided crossing for energy.

An interesting point is that the R dependence of the dipole can be experimentally derived if the expectation value of the dipole is measured for a sufficiently large number of vibrational levels. Thus, when measured for various adiabatic states, such

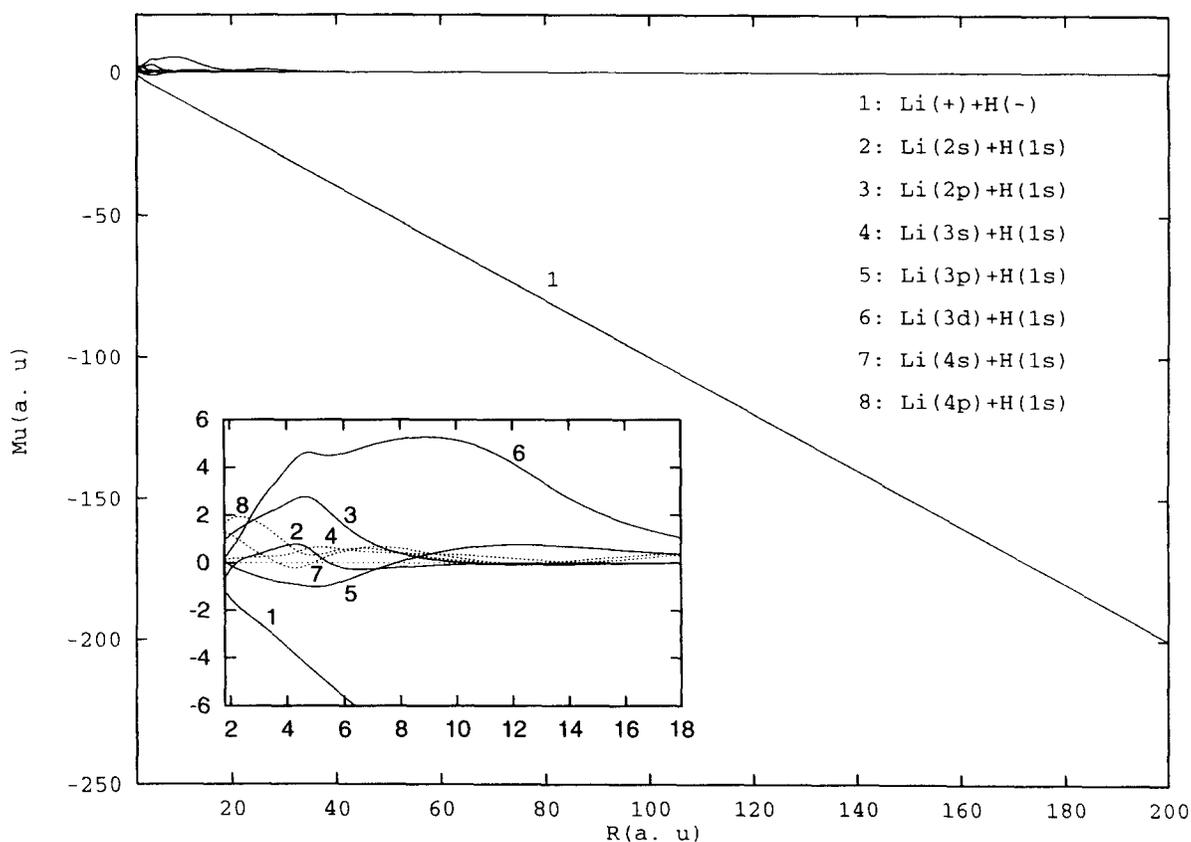


Fig. 2. Permanent dipole moment for the eight low-lying $^1\Sigma$ diabatic states of the LiH molecule, as a function of the internuclear distance (all in au).

information should lead to an experimental determination of the diabatic neutral–ionic crossings and to the related avoided crossings for the potential curves.

Another interesting aspect of the present results is related to the outer repulsive branch of the wells of the excited states, corresponding to the ionic species. It exhibits a considerable dipole (a few tenths of atomic units) due to the prominent charge separation in the ionic state. These unusually large values for the dipole should lead to interesting physical effects and to specific spectral signatures, in particular, for the infrared spectrum.

In conclusion, we have calculated here the permanent dipole of LiH, in both the adiabatic and diabatic representations, for a complete manifold of low-lying $^1\Sigma$ states and for a large range of internuclear distances. For the diabatic ionic state, the dipole behaves as a straight line. For the adiabatic states, we have curves which relay each other to this line, illustrating their ionic inprint. These results can be easily understood from the physical nature of the diabatic states and they shed light on the interplay between the ionic and neutral species that dominate the alkali hydride potential curves. Consequently, we suggest that it seems possible to determine experimentally the location and width of these avoided crossings.

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