

## Supplementary information

# Three states global fittings with improved long range: Singlet and Triplet states of $\text{H}_3^+$ .

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## A Long range interaction: $\text{H}_2 + \text{H}^+$

In figure A.1 is plotted the approaching of  $\text{H}^+$  to the centre of mass of a fixed  $\text{H}_2$  molecule ( $r=1.4$  a.u.), for several angles, using Jacobi coordinates for the lowest Singlet state. The Jacobi angle is specified in each panel. In the left panels (first column) are compared the *ab initio* points with the DIM, DIM + Long range terms of equations 9 and 10, the fit of Polyansky and coworkers (*Philos Trans A Math Phys Eng Sci*, 2012, **370**, 5014-27), the fit of Ghosh and coworkers (*J. Chem. Phys.*, 2017, **147**, 074105) and the fit of this study. In the second and third columns are plotted the differences between the *ab initio* points and the fit, for intermediate distances (second column) and for long distances (third column). The errors remain lower than  $1 \text{ cm}^{-1}$  for Jacobi distances larger than 9.0 a.u. The fits of Polyansky and Ghosh do not lie next to the points, probably because the long range has been left to be described by the DIM matrix and long range of the diatomic molecules. The DIM approximation, as well included in the figure, has a smooth behaviour and it describes correctly the long range, specially for the angles near the perpendicular approach of  $\text{H}^+$  to the  $\text{H}_2$  molecule. When we add the long range terms of equations 9 and 10 to the DIM approximation the line lies on top of the points showing that the description of the intermediate and long range have been enhanced mainly with the adding of these terms.

## B Long range interaction: $\text{H}_2^+ + \text{H}$

The new terms given in eq. 10 were not necessary for the description of the long range in the channel of  $\text{H}_2^+ + \text{H}$ , since the DIM approximation reproduces correctly this channel. An analysis of the long range in this channel, in the lowest Triplet state, is presented in Figure A.2 using Jacobi coordinates. The coordinate  $r$  is fixed at 2.0 a.u., and the angles are specified in each plot. In the left panels are presented the comparisons of DIM, with and without long range terms of Eq. 9, the global fit and the *ab initio* points as a function of the  $R$  Jacobi distance. The right panels present the energy difference between the global fit and the *ab initio* points. The DIM approximation and the DIM

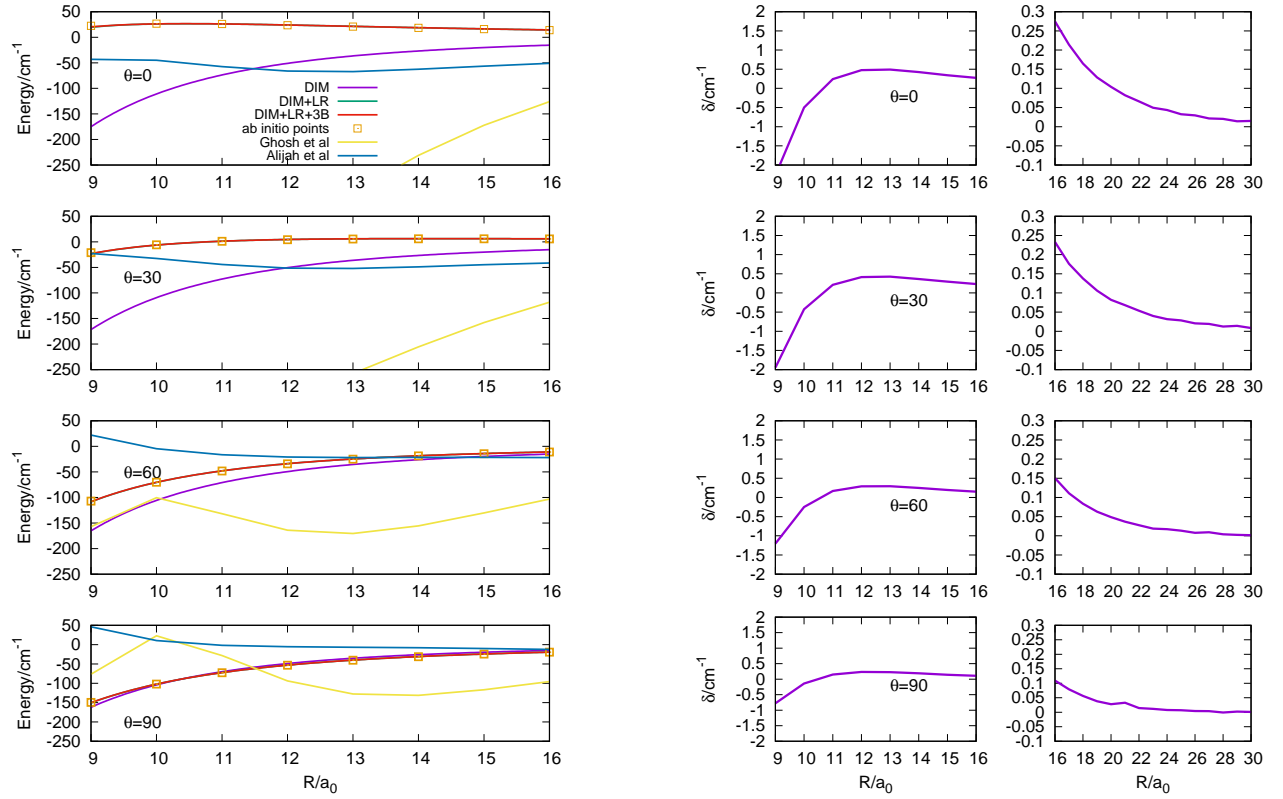


Figure A.1: The plots in the left column represent the intermediate interaction potential energy curves of the lowest Singlet state for the Jacobi coordinate  $R$ , for the DIM, DIM + LR, DIM + LR + 3B and *ab initio* points, and Ghosh *et al* potential and Alijah *et al* potentials. The two columns on the right represent the energy difference between the fit and the *ab initio* points for intermediate distances (second column) and long distances (third column). In all panels the Jacobi coordinate  $r$  is fixed on 1.4 a.u. and the angles are specified in each plot.

plus the long range terms are not distinguishable, proving that the long range of the diatomic fragments, included in the DIM matrix, are crucial for this channel.

## C Derivatives and non-adiabatic couplings

The global fit explained in the previous section provides a full description of all the elements of the potential matrix, in a diabatic representation of the three first singlet, and triplet states. The diagonalisation of this matrix gives, as eigenvalues, the adiabatic energies and the eigenvectors needed to obtain the non-adiabatic coupling matrix elements (NACMEs), and the derivative of the adiabatic energies.

The procedure used to obtain the derivatives and the NACMEs employs the Hellmann-Feynman theorem and is described in detail in Ref. 28. Briefly here are presented the equations that produce the derivatives of the adiabatic energies and the NACMEs. The derivative of the adiabatic energies, diagonal values ( $n = n'$ ) in which NACMEs are zero, are obtained as

$$\frac{\partial W_n}{\partial \alpha} = \sum_{mm'} (T_n^{m'})^\dagger (T_n^m) \frac{\partial V_{mm'}}{\partial \alpha} \quad (1)$$

where  $W_n$  are the adiabatic energies after the diagonalization of the potential matrix of equation 1,  $T_n^m$  are the eigenvectors obtained from this diagonalisation,  $V_{mm'}$  are the terms of the matrix  $\tilde{V}$  in equation 1 and  $\alpha$  stands for each internuclear coordinate,  $R_\alpha$ .

The NACMEs are obtained as

$$\left\langle \phi_{n'} \left| \frac{\partial}{\partial \alpha} \right| \phi_n \right\rangle = \frac{1}{W_n - W_{n'}} \sum_{mm'} (T_{n'}^{m'})^\dagger (T_n^m) \frac{\partial V_{mm'}}{\partial \alpha}, \quad (2)$$

which correspond to the non-diagonal with  $n \neq n'$ .

The potential matrix defined in equation 1 requires the fitting of all the diatomic molecules appearing in the DIM matrix, and for the second term the three body terms for each of the elements of the matrix. The diatomic molecules are fitted independently but all the three body elements are fitted simultaneously.

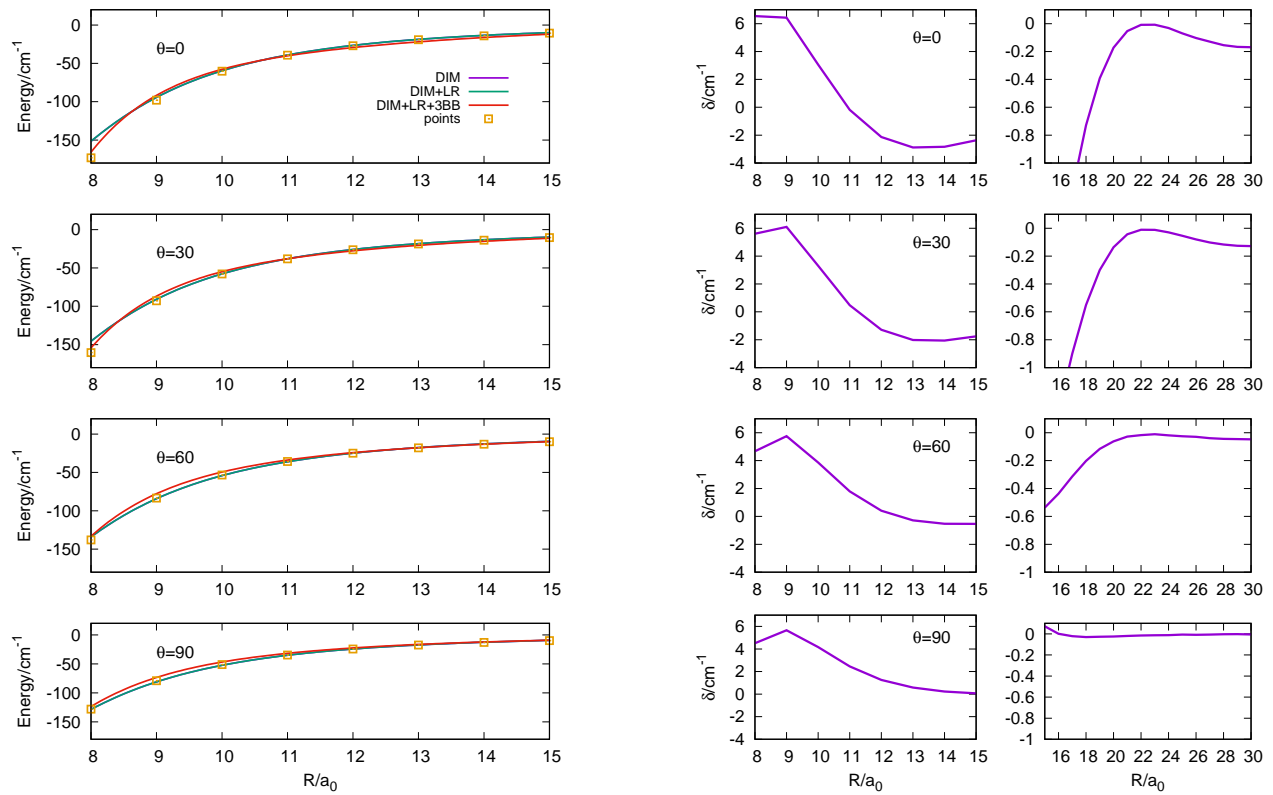


Figure A.2: The plots in the left column represent the intermediate interaction potential energy curves of the lowest Triplet state for the Jacobi coordinate  $R$  for the DIM, DIM + LR, DIM + LR + 3B. The two columns on the right represent the energy difference between the fit and the *ab initio* points for intermediate distances (second column) and long distances (third column). In all panels the Jacobi coordinate  $r$  is fixed on 2.0 a.u. and the angles are specified in each plot.