

# Total Position-Spread tensor in Mixed-Valence Systems: *an indicator of charge transfer processes*

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## Abstract

The behavior of the Position-Spread Tensor ( $\Lambda$ ) in a series of mixed-valence systems is investigated at a Full Configuration Interaction, and CASSCF level. This tensor, which is the second moment cumulant of the total position operator, is invariant with respect to molecular translations, while its trace is also rotationally invariant. Moreover, the tensor is additive in the case of non-interacting subsystems, and can be seen as an intrinsic property of a molecule. In the present work, it is shown that the Position Spread shows a marked maximum peak in the region of the avoided crossing where the wavefunction is more delocalized.

## Introduction

- ▶ Mixed-valence compounds are characterized by intervalence charge transfer between two or more redox sites existing in different oxidation states.
- ▶ Robin and Day classified mixed-valence compounds in three categories:
  - ▷ redox centers are completely localized (class I).
  - ▷ intermediate electronic coupling between the mixed-valence centers exists, and the charge is partly localized (class II).
  - ▷ coupling is so strong that the system is completely delocalized.
 Intermediate redox states have to be attributed to the redox centers (class III).
- ▶ According to Marcus, the potential energy surface (PES) of a degenerate mixed-valence system can be constructed from parabolic functions, each representing a diabatic, noninteracting, state.
- ▶ The Total Position Spread tensor (TPS) can be used as a tool to describe and monitor the charge transfer process.

## The Total Position Spread, $\Lambda$

- ▶ It is defined as the second moment cumulant of the total electron position operator.
- ▶ It considers the position operator and its tensorial square:

$$\hat{r}_\beta = \sum_{p=1}^n \hat{\beta}(p) \quad (1)$$

$$\hat{r}_\beta \hat{r}_\gamma = \sum_{p,q=1}^n \hat{\beta}(p) \hat{\gamma}(q) \quad (2)$$

where the sums run over the electrons ( $n$  is the total number of electrons) and  $\beta, \gamma$  represent one of the Cartesian coordinates ( $x, y$ , and  $z$ ).

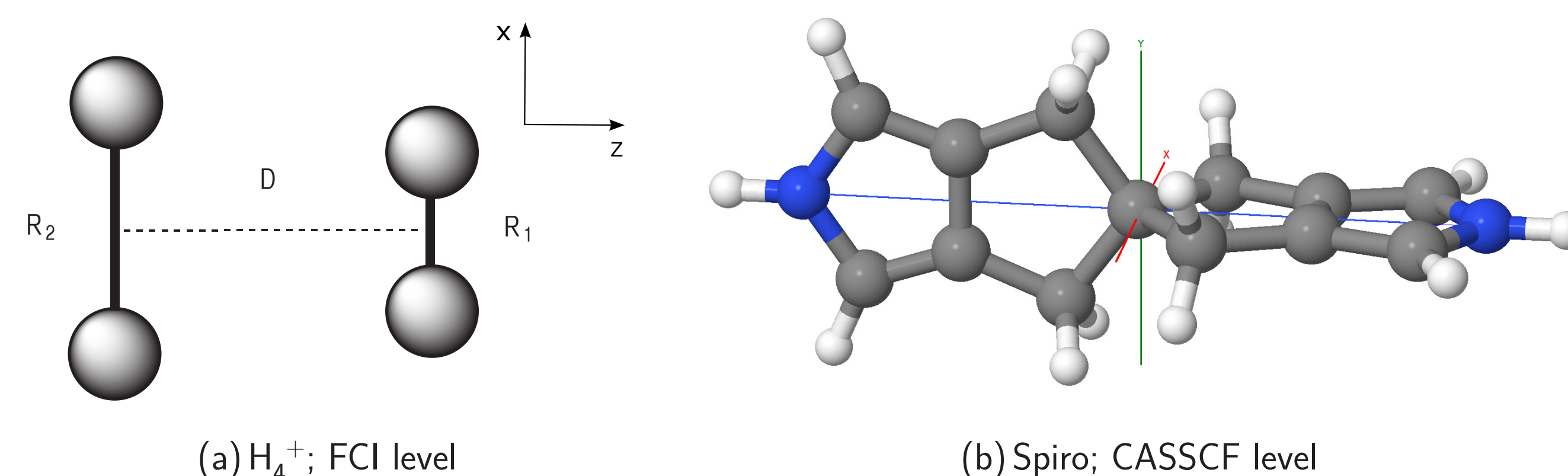
- ▶ Finally, the cumulant of the quadratic fluctuation of the electron position is:

$$\langle \hat{r}_\beta \hat{r}_\gamma \rangle_c = \Psi \hat{r}_\beta \hat{r}_\gamma \Psi - \Psi \hat{r}_\beta \Psi \Psi \hat{r}_\gamma \Psi \quad (3)$$

## Computational Details

- ▶ We investigated at Full Configuration Interaction (FCI) level, and CASSCF level the behavior of the ground state position-spread tensor for  $H_4^+$  and the Spiro  $\pi$ - $\sigma$ - $\pi$  system **5, 5' (4H, 4H')-spirobi[cyclopenta[c]-pyrrole] 2, 2', 6, 6'** tetrahydro molecule respectively.
- ▶ We employed the ANO basis sets optimized by Roos and the following contractions: **2s1p** for  $H_4^+$ ; and **STO-3G, VDZP** basis sets for the spiro molecule.
  - ▷  $H_4^+$ 
    - ▶ Initial Hartree-Fock calculations were performed using the quantum chemistry package DALTON.
    - ▶ Then the atomic one- and two-electron integrals recovered were transformed to the molecular basis set using the Ferrara code.
    - ▶ The energy and the TPS were computed with NEPTUNUS code.
  - ▷ Spiro
    - ▶ State-average calculations were performed.
    - ▶ The valence  $\pi$  electron CAS was used to compute the energies and the TPS in MOLPRO.

## Mixed-valence systems



## Results

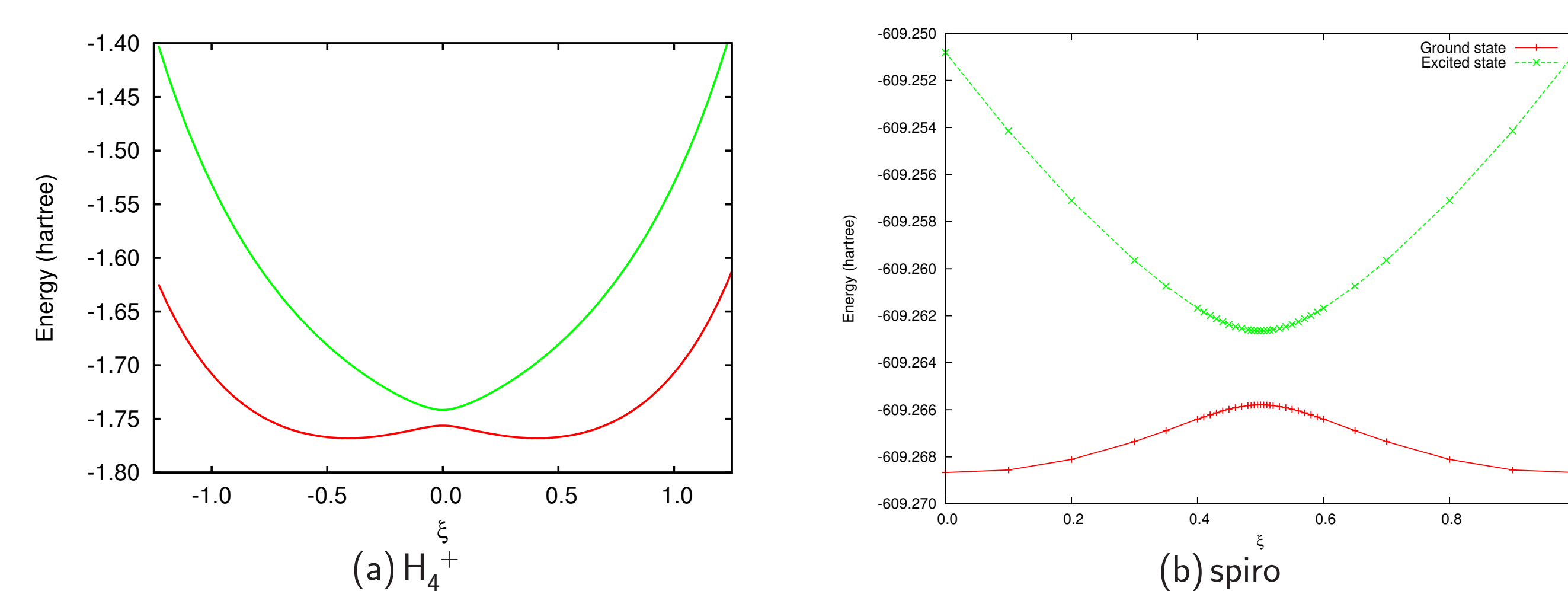


Figure 1: Potential energy surfaces for the  $H_4^+$  and the cationic spiro molecule.

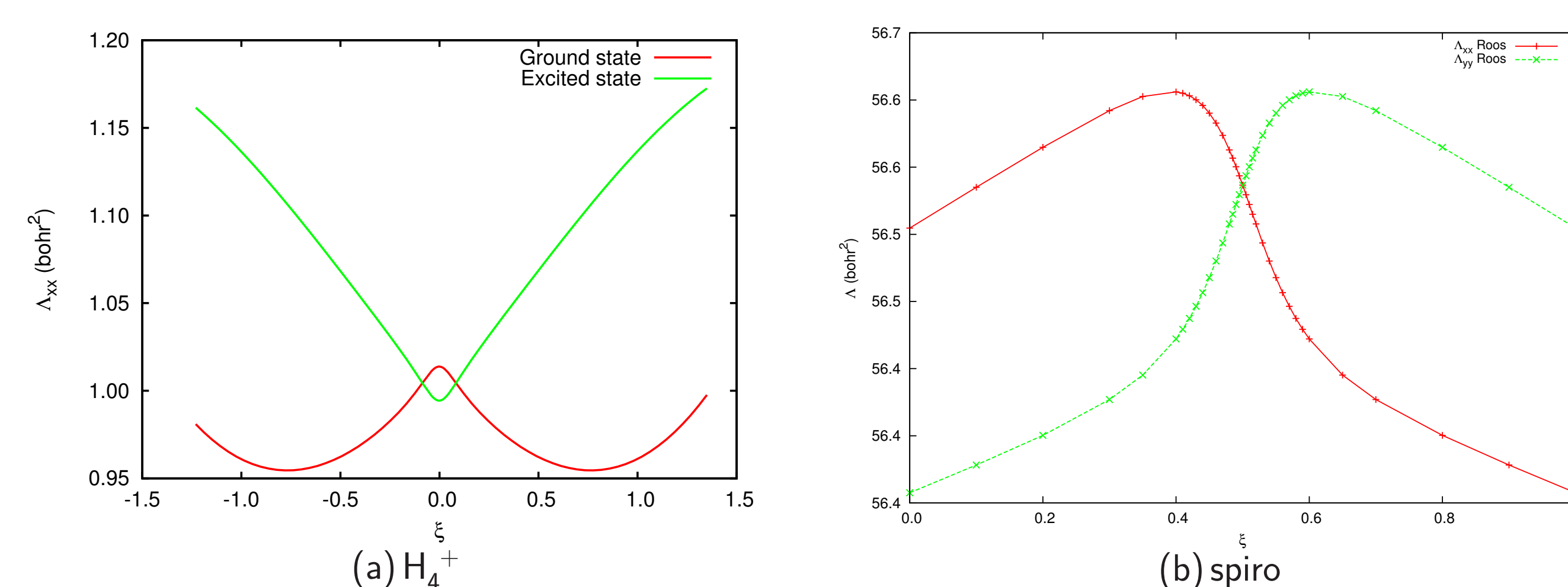


Figure 2: Perpendicular component of the TPS tensor for the  $H_4^+$  and the cationic spiro molecule.

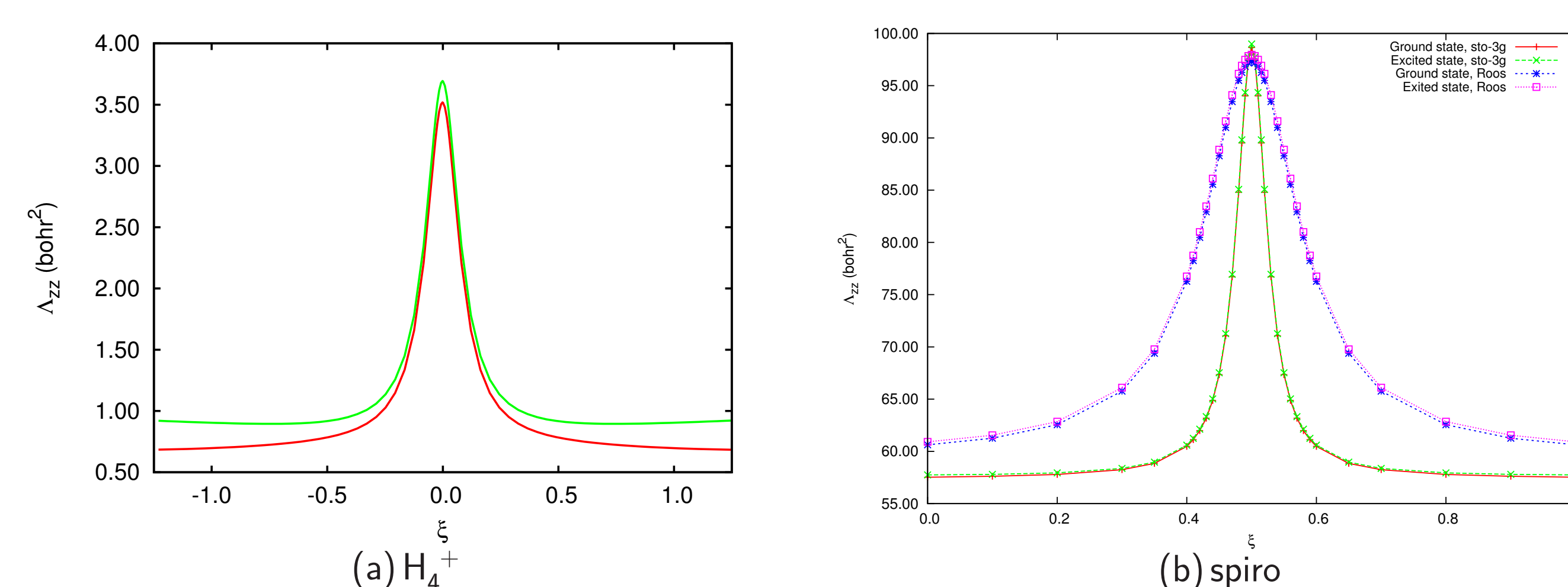


Figure 3: Longitudinal component of the TPS tensor for the  $H_4^+$  and the cationic spiro molecule.

## Conclusions

- ▶  $H_4^+$  molecule shows a class II character and it can be used as model to understand mixed-valence compounds. In spite of its simplicity, it shows the features of more realistic systems.
- ▶ The TPS tensor is able to describe the delocalized nature of the mobile electrons (or holes) during the charge transfer process. It shows a marked maximum peak in the transition state-region.
- ▶ The largest magnitude of the tensor is present in the longitudinal component of the mixed-valence compounds.

## Bibliography

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