The behavior of the Position-Spread Tensor in Diatomic Systems

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Introduction

► The "Localization Tensor" **(LT)** is a quantity introduced in the context of the theory of Kohn (1964) to characterize the electrical conductivity properties. Kohn realized that the electrical conductivity is more related to a properly delocalization of the wavefunction.[1]

► Resta and coworkers (1999), with the introduction of the localization tensor, provided an important tool to give a quantitative formulation of this localization (a per electron quantity).[2]

► In the molecular studies, the full quantity (not divided by the number of electrons) seems more appropriate since one is interested in the analysis of the molecular wavefunction. For this reason, we introduce the Total Position-Spread (TPS) tensor, Λ, defined as the second moment cumulant of the total electron position operator (2013).

► In this work, the behavior of Λ for a series of diatomic molecules and ions has been investigated, as a function of the internuclear distance R.

The Total Position Spread, Λ

► It is defined as the second moment cumulant of the total electron position operator.

► It considers the position operator and its tensorial square:

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

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

where the sums run over the electrons (n is the total number of electrons) and β, γ represent one of the Cartesian coordinates (x, y, and z).

► Finally, the cumulant of the quadratic fluctuation of the electron position is:

$$\langle \hat{r}_{\beta}\hat{r}_{\gamma}\rangle_{c} = \Psi\hat{r}_{\beta}\hat{r}_{\gamma}\Psi - \Psi\hat{r}_{\beta}\Psi\,\Psi\hat{r}_{\gamma}\Psi \qquad (3)$$

Computational Details

► We investigated at Full Configuration Interaction (FCI) level the behavior of the ground state position-spread tensor for the next series of diatomic systems: H_2, He_2, Li_2, Be_2, N_2, F_2, LiF, HeH^- and BeH^-. Where the singlet ground states are $^1\Sigma_g^+$ for homonuclear and $^1\Sigma^+$ for heteroatomic systems.

► We employed the ANO basis sets optimized by Roos and the following contractions: H_2, $7s3p3d3f$; Li_2, $7s6p4d3f$; LiF, $3s2p$-$3s2p$; He_2, $7s4p3d$; HeH^-, $7s4p3d$-$6s4p3d$; Be_2, $7s7p4d3f$; BeH^-, $7s7p4d3f$-$6s4p3d$; N_2 and F_2, $3s2p$.

► 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 Full-CI calculations were performed using our FCI algorithm implemented in the NEPTUNUS code.

► The $1s$ electrons were kept frozen at the Hartree-Fock level for all atoms but Hydrogen and Helium. However, they were taken into account through a generalization of the formalism.

Results

► Total Position Spread values for the diatomic molecules close to the dissociation limit (50 bohr) except for LiF (40 bohr), compared to the sum of their corresponding values for the isolated atoms.

Molecule	Value at Dissociation (50 bohr)		Isolated Atoms (sum of the atomic values)	
	$\Lambda_{\parallel}$	$\Lambda_{\perp}$	$\Lambda_{\parallel}$	$\Lambda_{\perp}$
H_2	2.000742	2.000639	2.000668	2.000668
Li_2	12.439117	12.415638	12.423086	12.423086
N_2	6.441467	6.441315	6.440920	6.440920
F_2	5.050114	5.040229	5.050058	5.040210
LiF ($1^1\Sigma$)	8.805411	8.799939	8.804686	8.799762
LiF ($2^1\Sigma$)	3.986952	3.985769	3.986199	3.986199
He_2	1.506416	1.506392	1.506400	1.506400
HeH^-	6.870093	6.869880	6.869950	6.869950
Be_2	8.152292	8.148845	8.149992	8.149992
BeH^-	10.193261	10.191089	10.191746	10.191746

Results

(a) Be_2 (b) BeH^-
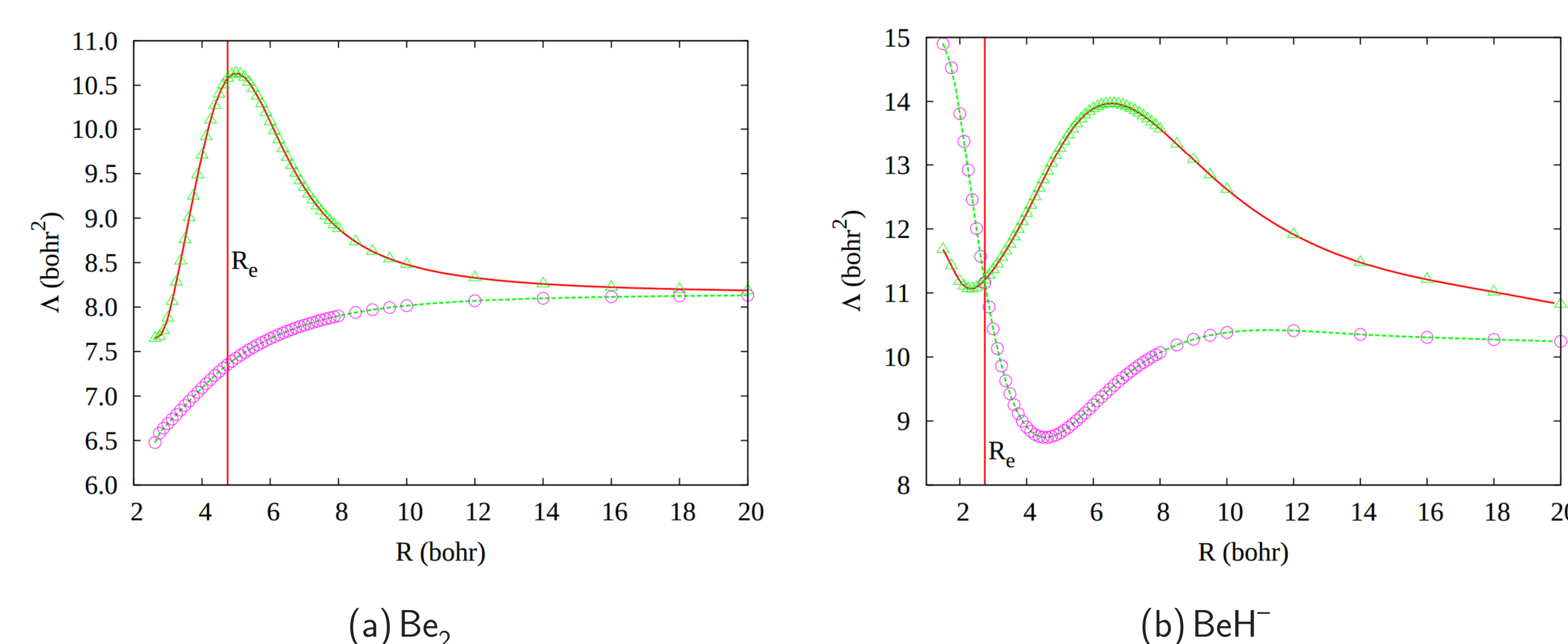
Figure 1 : Total Position Spread, Λ, for the molecular anions and weakly bonded systems ($\Lambda_{\parallel}$, red full line; $\Lambda_{\perp}$, green line/circles; R_e equilibrium distance).


(a) H_2 (b) N_2
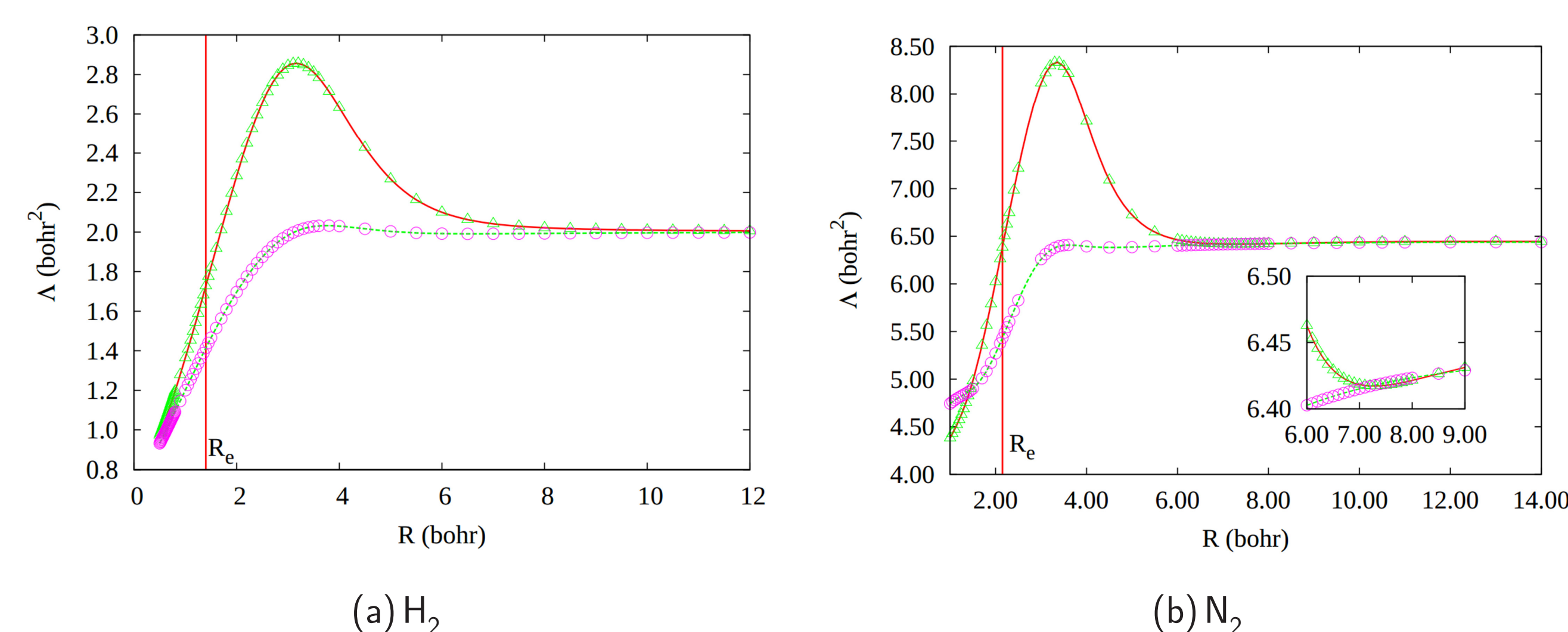
Figure 2 : Total Position Spread, Λ, for the covalent systems ($\Lambda_{\parallel}$, red full line; $\Lambda_{\perp}$, green line/circles; R_e equilibrium distance).
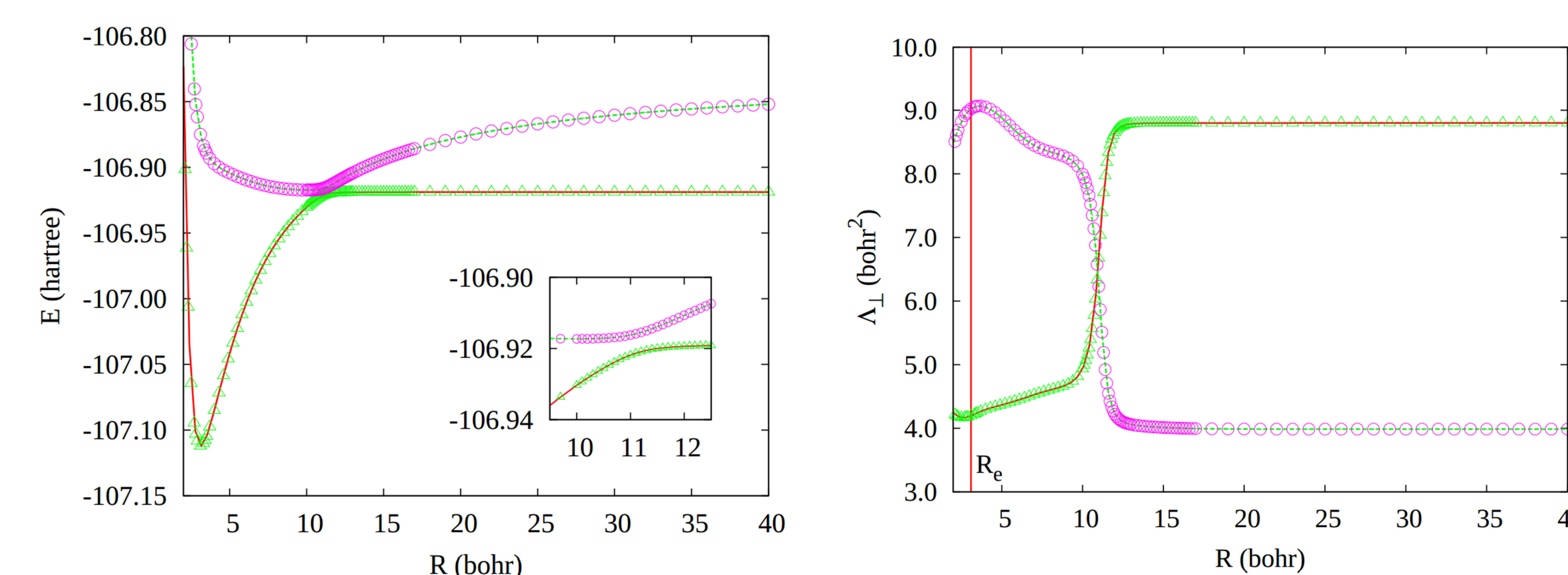
(a) PES (GS, $1^1\Sigma$: red full line; ES, $2^1\Sigma$: green line/circles)

(b) TPS, $\Lambda_{\perp}$(GS, $1^1\Sigma$: red full line; ES, $2^1\Sigma$: green line/circles)
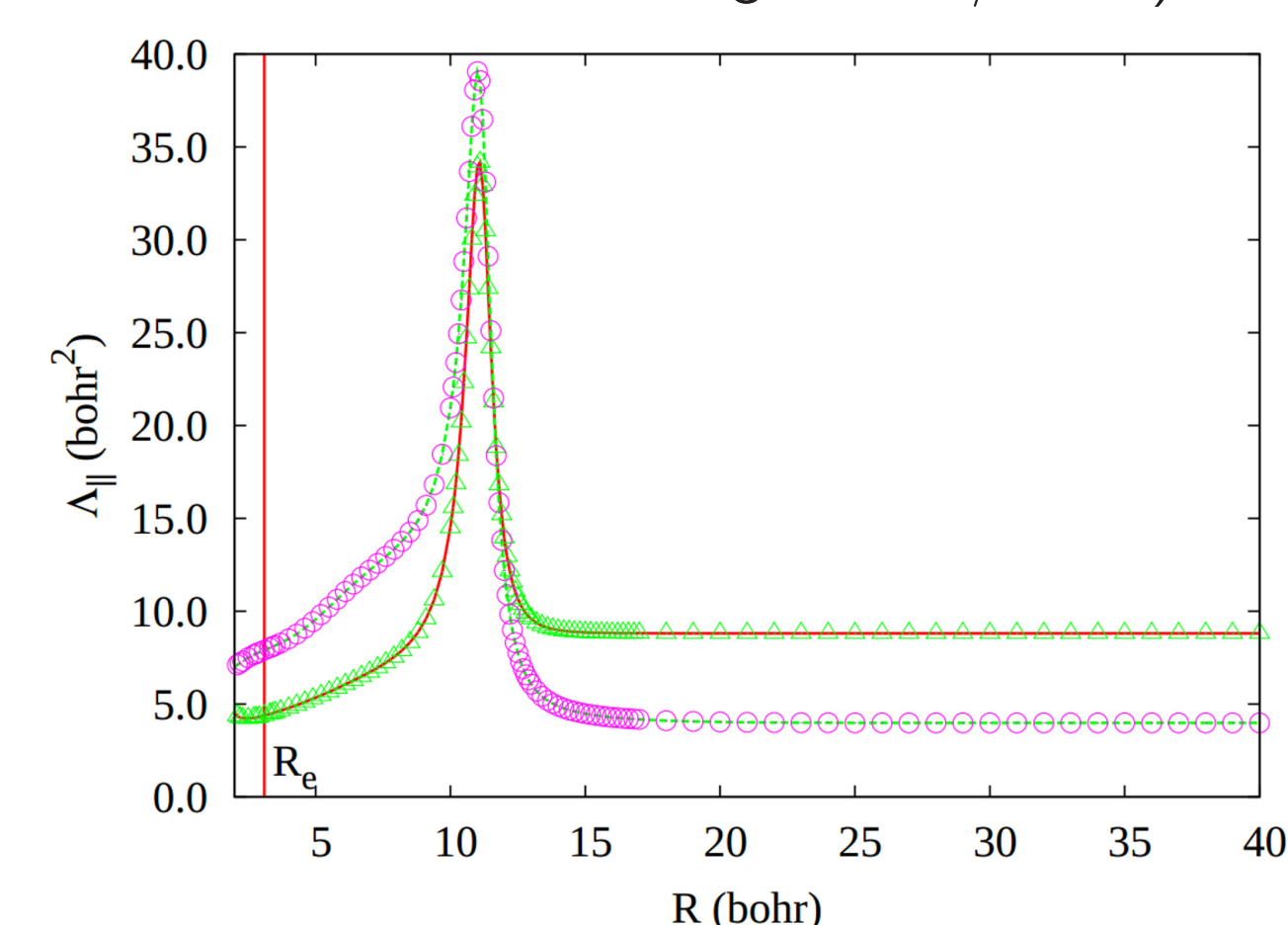
(c) TPS, $\Lambda_{\parallel}$(GS, $1^1\Sigma$: red full line; ES, $2^1\Sigma$: green line/circles)

Figure 3 : Potential energy surface (a), and Total Position Spread (b),(c) for the LiF diatomic molecule.

Conclusions

► The results presented in this work confirm the fact that the TPS tensor is a powerful indicator of electronic rearrangements in a molecular wavefunction.

► In the region where the bond is in formation (for R between R_e and the distance where the bond is broken) is characterized by a relatively large extension of the mutual influence of the electrons, while outside this region such influence is more "short range".

► The TPS tensor is able to describe the delocalized nature of the mobile electrons (or holes) during the transfer process. Together with the mean value of the position operator, this gives an interesting description of the transfer mechanism.

► With the aim to apply the strategy here reported to larger systems, we are currently working on the implementation of the algorithm in the **MOLPRO** code, in particular for the case of **CAS-SCF** wavefunctions.

Bibliography

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