On the Total Position Spread Tensor, **Λ**, in some model systems

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Group seminars @ AG-Paulus
Freie Universität Berlin

October 2013

Outline

1 Introduction

2 Total Position Spread Tensor, Λ
Theory
Implementation in MOLPRO

3 Our Results/Contribution
Diatomic molecules (FCI level)
Mixed-valence systems

Introduction

- Metal and Insulators. Distinction proposed by Bethe, Sommerfeld and Bloch (1928).

- What is a metal-insulator transition?
  The process to change from a metal state to an insulator one.

- Why to study them?
  * Yet one of the fundamentally least understood problems in condensed matter physics.
  * Electronic components are getting into the low dimensional regime.

Introduction

- Why is it important?
  - Many applications: eg.: microelectronics, molecular electronics.
  - Physical and chemical properties changes dramatically in such transitions.
- Why is the MIT a difficult problem to study?
  - A good metal and a good insulator are very different physical systems.

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Theory

- 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.

- 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).

$$\lambda_{\beta\gamma}^2 = \frac{< \hat{r}_\beta \hat{r}_\gamma >_c}{n} \tag{1}$$

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Theory

- 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. (Ángyán, Int. J. Quant. Chem. 2009, 109, 2340)

$$\Lambda = < \hat{r}_\beta \hat{r}_\gamma >_c \tag{2}$$

- What is a cumulant?
  A combination of moments that vanishes when some subset of the variables is independent of the others.
  (R. Kubo, J. Phys. Soc. Jpn., 17, 1100 (1962))

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Theory

On the cumulants (1)

This mathematical object has many interesting characteristics:

- They can be explicitly represented only by moments of lower or equal order.

| Order	Moment	Cumulant
1	$< \hat{r}_\beta >$	$< \hat{r}_\beta >$
2	$< \hat{r}_\beta \hat{r}_\gamma >$	$< \hat{r}_\beta \hat{r}_\gamma > - < \hat{r}_\beta >< \hat{r}_\gamma >$
3	$< \hat{r}_\beta \hat{r}_\gamma \hat{r}_\delta >$	$< \hat{r}_\beta \hat{r}_\gamma \hat{r}_\delta > - < \hat{r}_\delta >< \hat{r}_\beta \hat{r}_\gamma >$
		$- < \hat{r}_\beta >< \hat{r}_\delta \hat{r}_\gamma > - < \hat{r}_\gamma >< \hat{r}_\beta \hat{r}_\delta >$
		$+2 < \hat{r}_\beta >< \hat{r}_\gamma >< \hat{r}_\delta >$

- They are a linear combination of the products of these moments of lower or equal order so they are additive (size consistency).

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Theory

On the cumulants (2)

- The trace of the tensor is rotational invariant, for cumulants of second order.
- A diagonal element of the cumulant tensor is the variance, and it is always a positive value.
- They also are invariant under translation of the origin of cumulants of order ≥ 2.

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1. Introduction

2. **Total Position Spread Tensor, Λ**
   Theory
   Implementation in MOLPRO

3. Our Results/Contribution
   Diatomic molecules (FCI level)
   Mixed-valence systems

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Implementation in MOLPRO
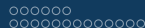
The position spread (1)

- The total position operator:

$$\hat{r}_\beta = \sum_{p=1}^{n} \hat{\beta}(p) \qquad (3)$$

- We also consider its tensorial square.

$$\hat{r}_\beta \hat{r}_\gamma = \sum_{p,q=1}^{n} \hat{\beta}(p)\hat{\gamma}(q) \qquad (4)$$

- The cumulant of the quadratic fluctuation of the position is:

$$\langle \hat{r}_\beta \hat{r}_\gamma \rangle_c = <\Psi|\hat{r}_\beta \hat{r}_\gamma|\Psi> - <\Psi|\hat{r}_\beta|\Psi><\Psi|\hat{r}_\gamma|\Psi> \qquad (5)$$

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Implementation in MOLPRO
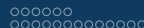
The position spread (2)

The implementation done in MOLPRO that calculates the TPS on a CASSCF wavefunction needed:

- The bielectronic operator, $\hat{r}_\beta \hat{r}_\gamma$, is evaluated with the second order reduced density matrix.
- The monoelectronic operators are evaluated with the first order reduced density matrix.
- We validated our implementation by comparing our results with the implementation of **Λ** already made in NEPTUNUS.

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Implementation in MOLPRO

The position spread (3)

- What were our motivations?
    - Study bigger molecular systems.
    - At CASSCF level, MOLPRO treats very well situations where state averaged calculations are needed.
- What our implementation calculate is:
    - The total position spread, **Λ**.
    - It prints the different contributions: core-core-, active-core, active-active.

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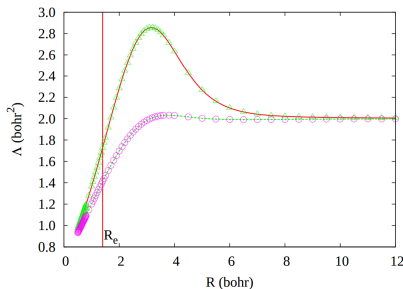
Covalent systems (1)

(a) $H_2(7s3p3d3f)$
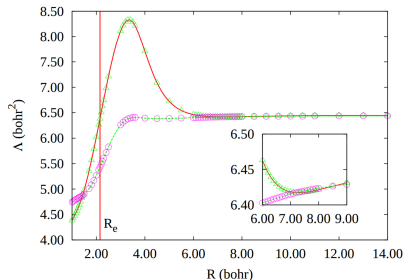
(b) $N_2(3s2p)$

Figure 1 : Total Position Spread, **Λ**, for the covalent systems ($\Lambda_\parallel$, red full line; $\Lambda_\perp$, green line/circles; R_e equilibrium distance).
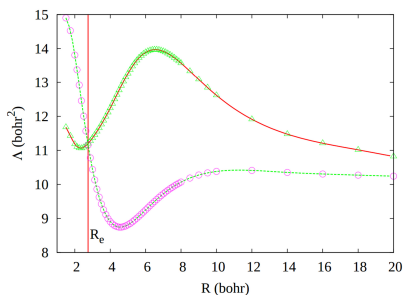
Weakly bounded systems
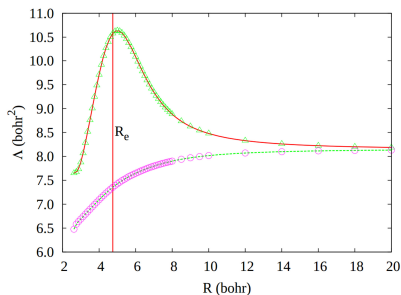
(a) Be$_2$ ($7s7p4d3f$)

(b) BeH$^-$ ($7s7p4d3f - 6s4p3d$)

Figure 2 : Total Position Spread, **Λ**, for the molecular anions and weakly bonded systems (Λ$_\parallel$, red full line; Λ$_\perp$, green line/circles; R_e equilibrium distance).
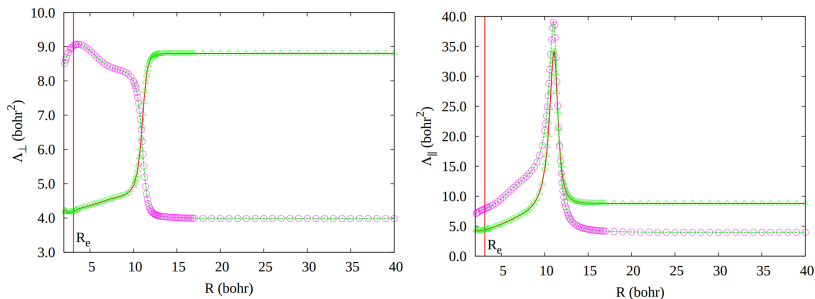
Ionic systems (1)
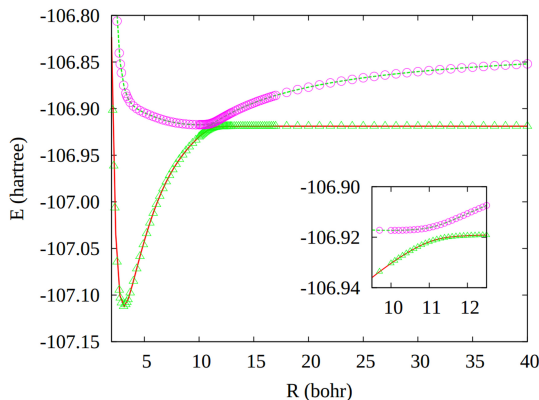
Figure 3 : Potential energy surface for LiF (GS, $1^1\Sigma$: red full line; ES, $2^1\Sigma$: green line/circles) ($3s2p$).

Ionic systems (2)

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

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

Figure 4 : Total Position Spread, **Λ**, for the LiF molecule.

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Diatomic molecules (FCI level)

Take home messages about diatomic molecules:

- The TPS tensor is a powerful indicator of the electronic rearrangements in a molecular wavefunction.

- When a bond is stretched from its equilibrium distance, the longitudinal component of the TPS tensor increases rapidly. Once the bond is broken, the TPS decreases abruptly to the atomic values.

- Possible application of this technique to the study of mixed-valence systems (?).

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Mixed-valence systems
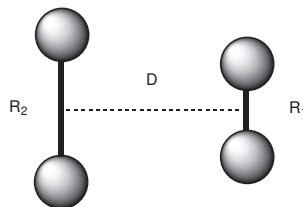
H_4^+ model system (1) (FCI level)

Figure 5 : The H_4^+ model structure (Submitted to JCC)

• The average geometry: $\mathbf{R}(\xi, D) \equiv \{R_1(\xi, D), R_2(\xi, D)\}$

$$R_1(\xi, D) = (1/2 - \xi)R_+(D) + (1/2 + \xi)R_0(D) \qquad (6)$$

$$R_2(\xi, D) = (1/2 + \xi)R_+(D) + (1/2 - \xi)R_0(D) \qquad (7)$$

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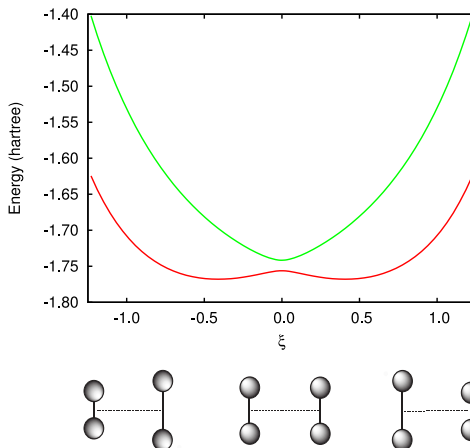Mixed-valence systems

H_4^+ model system (2) (FCI level)

Figure 6 : The potential energy curves of the two lowest states as a function of the mixing parameter ξ, for a fixed intermolecular distance $D = 6.0$ bohr.
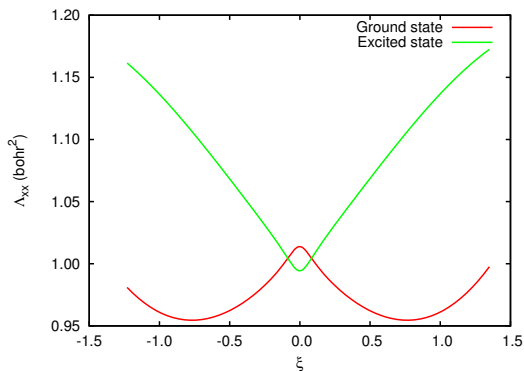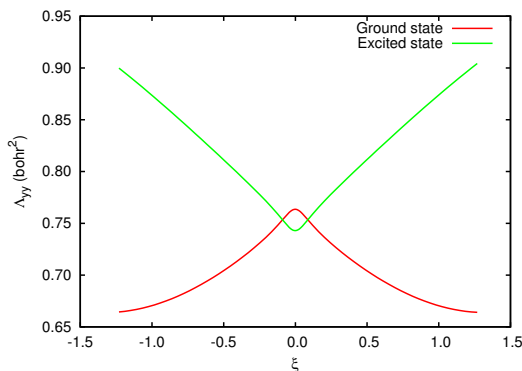
H_4^+ model system (3) (FCI level)

Figure 7 : The *xx* component of the Localization-Spread Tensor for the two lowest states as a function of the mixing parameter ξ, for a fixed intermolecular distance $D = 6.0$ bohr.

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Mixed-valence systems

H$_4^+$ model system (4) (FCI level)

Figure 8 : The *yy* component of the Localization-Spread Tensor for the two lowest states as a function of the mixing parameter ξ, for a fixed intermolecular distance $D = 6.0$ bohr.
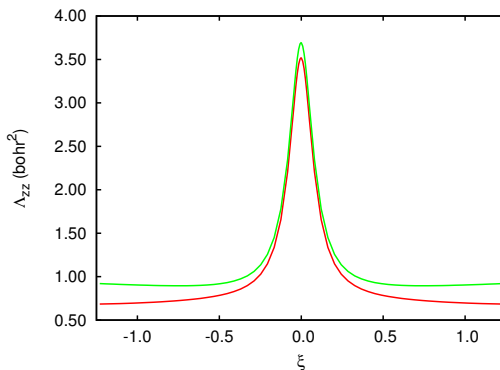
H_4^+ model system (5) (FCI level)

Figure 9 : The *zz* component of the Localization-Spread Tensor for the two lowest states as a function of the mixing parameter ξ, for a fixed intermolecular distance $D = 6.0$ bohr.

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Mixed-valence systems

Take home messages about H_4^+:

- It shows the character of mixed-valence compounds of Class II.
- Even being a simple system, it presents many features of realistic and much larger systems.
- The TPS shows a marked maximum in the transition-state region where the charge is very delocalized.

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Mixed-valence systems

The spiro molecule (1) (CASSCF level)
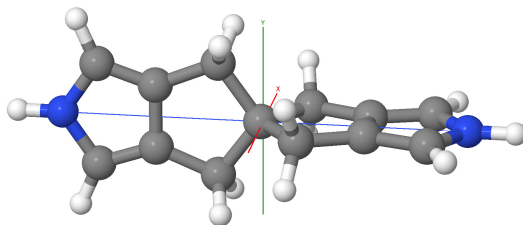
Figure 10 : The structure of the Spiro π-σ-π system
$5, 5'(4H, 4H')$-spirobi[cyclopenta[c]-pyrrole]$2, 2', 6, 6'$ tetrahydro molecule.
CAS(11,12); state averaged calculation. (submitted to Chem. Phys. Lett.).

- The mixing parameter employed:

$$Q(\xi) = (\xi)Q_A + (1 - \xi)Q_B \tag{8}$$

The spiro molecule (2) (CASSCF level)
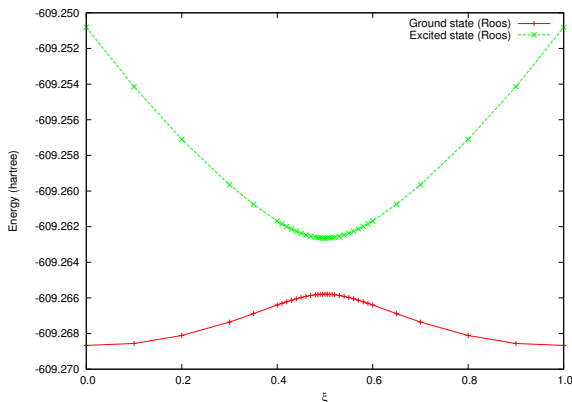
Figure 11 : Potential energy surfaces of the Spiro cation for the ground state and first lower excited state ($3s2p1d$) using a CAS(11,12).
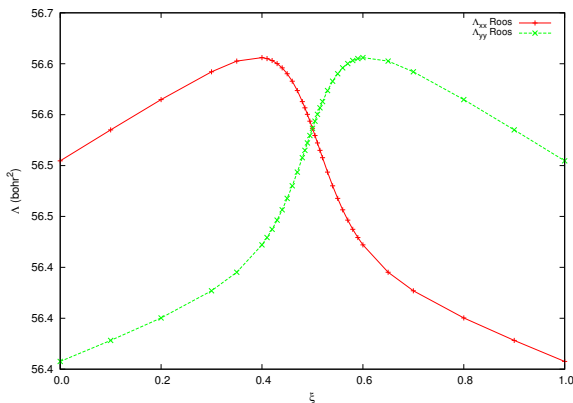
Mixed-valence systems

The spiro molecule (3) (CASSCF level)

Figure 12 : The TPS Λ_{xx} and Λ_{yy} components represented in bohr^2 as a function of the chosen mixing parameter ξ (GS).
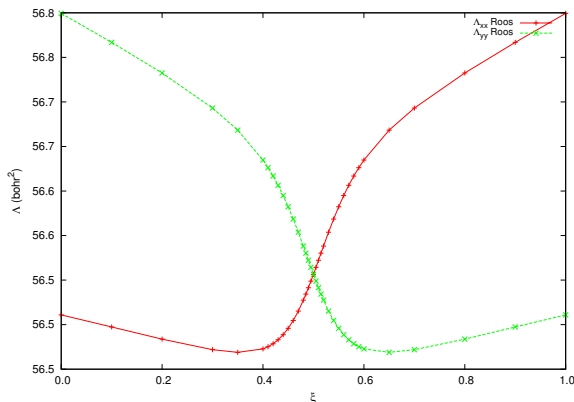
The spiro molecule (4) (CASSCF level)

Figure 13 : The TPS Λ_{xx} and Λ_{yy} components represented in bohr^2 as a function of the chosen mixing parameter ξ (ES).

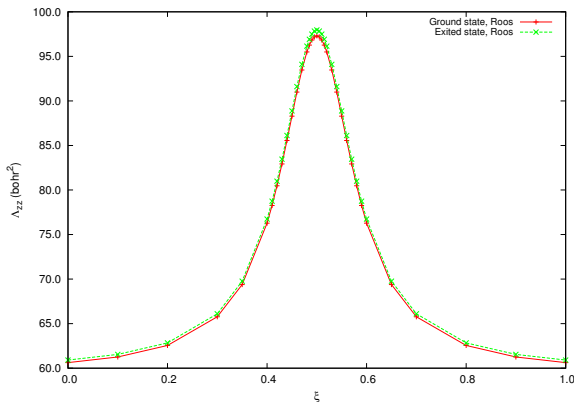# The spiro molecule (5) (CASSCF level)

Figure 14 : The TPS Λ_{zz} component represented in bohr^2 as a function of the chosen mixing parameter ξ (GS & ES).

Take home messages about the implementation of the TPS in MOLPRO:

- The evaluation of the TPS in bigger systems is now possible.
- Averaged orbitals required to describe correctly charge transfer processes in mixed-valence systems can be done using state-avaraged calculations at CASSCF level.

Summary

- The TPS is very sensitive to the change of the WF.
- The TPS is able to describe the delocalized nature of the electrons.

- Outlook
  - The Implementation of the TPS to be computed on a MRCI WF.
  - Application to graphenes.
  - Study of conducting polymers.
  - Definition of the Local Position Spread Tensor.
- Download these slides: http://muammar.me/files/chemistry/

Acknowledgment

Thanks for your attention

"Und wenn du lange in einen Abgrund blickst, blickt der Abgrund auch in dich hinein"

Friedrich Nietzsche

On the cumulants (1)

- They are a linear combination of the products of these lower moments so they are additive (size consistency).

Consider two fragments A and B (well separated and with their own orthonormal basis set of spin-orbitals).

$$\Psi_{AB} = \Psi_A \Psi_B \tag{9}$$

Given that the total position is represented by:

$$\hat{R} = \sum_{i=1}^{n} \hat{r}_i \tag{10}$$

And written in the second quantization as:

$$\hat{R} = \hat{R}_A + \hat{R}_B = \sum_{ij \epsilon A} < i|\hat{R}|j > a_i^\dagger a_j + \sum_{ij \epsilon B} < i|\hat{R}|j > a_i^\dagger a_j \tag{11}$$

On the cumulants (2)

The moment generating function is defined by:

$$F(t) = < \Psi | exp(t * R) | \Psi > \tag{12}$$

Finally the exponential factorize:

$$F(t) = F_A(t)F_B(t); \quad G(t) = G_A(t) + G_B(t) \tag{13}$$