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On the Total Position Spread Tensor, Λ

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Outline

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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1. Introduction

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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).

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

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

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

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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 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.

The position spread (3)

- What were our motivations?
    - Study bigger molecular systems.
    - 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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Diatomic molecules (FCI level)

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3. **Our Results/Contribution**
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Covalent systems (1)
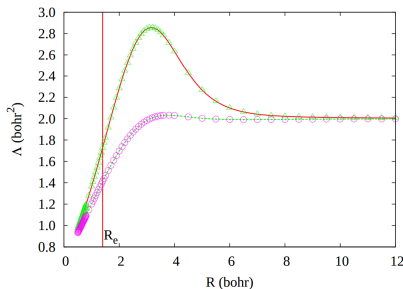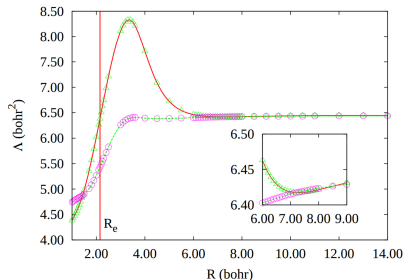
(a) $H_2(7s3p3d3f)$ (b) $N_2(3s2p)$

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
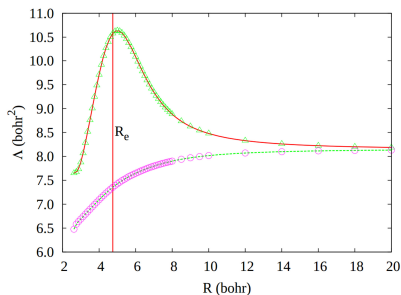
(a) Be$_2$ ($7s7p4d3f$)
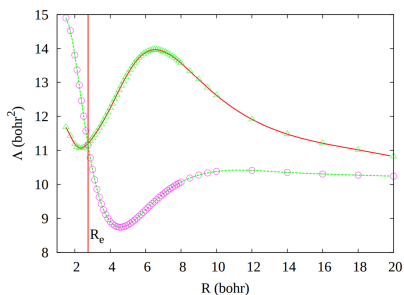
(b) BeH$^-$ ($7s7p4d3f - 6s4p3d$)

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)
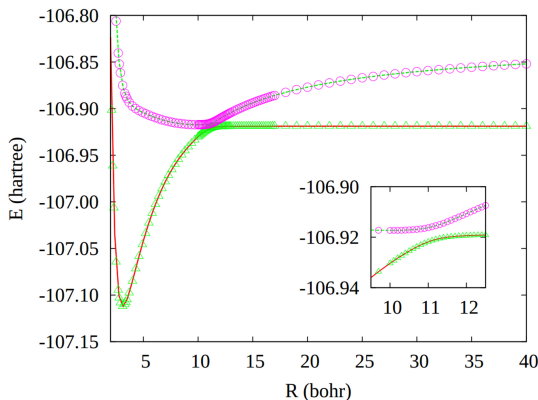
Figure 3 : Potential energy surface for LiF (GS, $1^1\Sigma$: red full line; ES, $2^1\Sigma$: green line/circles) ($3s2p$).

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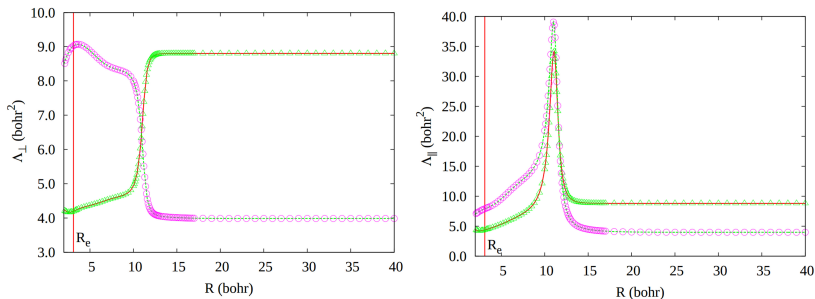
(a) TPS, $\Lambda_\perp$ (GS, $1^1\Sigma$: red full line; ES, $2^1\Sigma$: green line/circles

(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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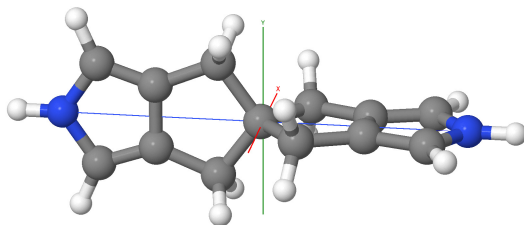Mixed-valence systems (CASSCF level)

The spiro molecule (1)

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

• The mixing parameter employed:

$$Q(\xi) = (\xi)Q_A + (1 - \xi)Q_B \tag{6}$$

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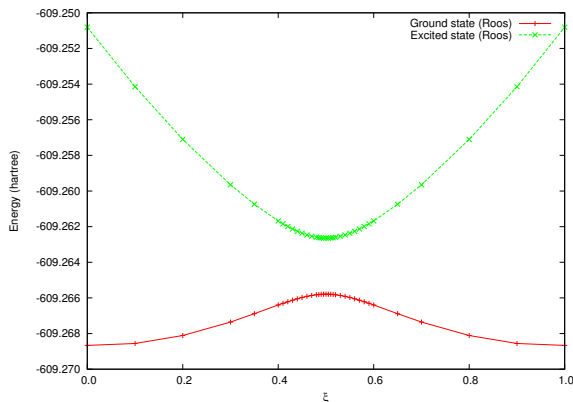Mixed-valence systems (CASSCF level)

The spiro molecule (2)

Figure 6 : Potential energy surfaces of the Spiro cation for the ground state and first lower excited state ($3s2p1d$) using a CAS(11,12).
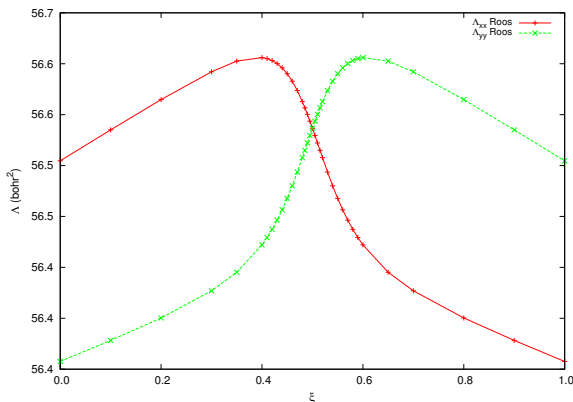
The spiro molecule (3)

Figure 7 : The TPS Λ_{xx} and Λ_{yy} components represented in bohr^2 as a function of the chosen mixing parameter ξ (GS).

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Mixed-valence systems (CASSCF level)

The spiro molecule (4)

Figure 8 : The TPS Λ_{xx} and Λ_{yy} components represented in bohr^2 as a function of the chosen mixing parameter ξ (ES).

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Mixed-valence systems (CASSCF level)
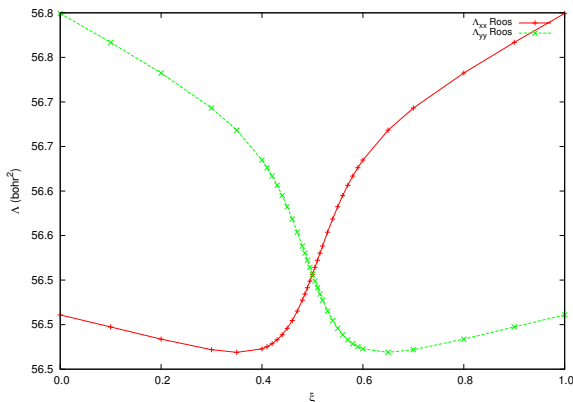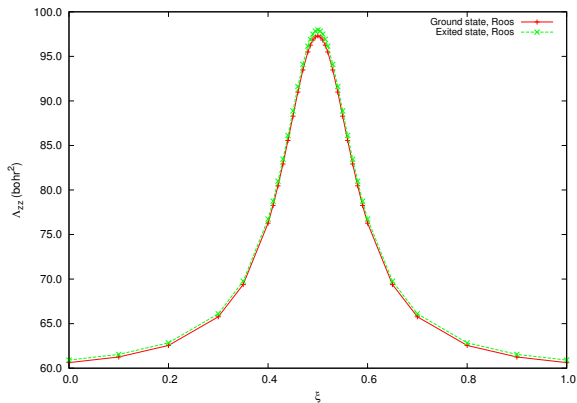
The spiro molecule (5)

Figure 9 : The TPS Λ_{zz} component represented in bohr^2 as a function of the chosen mixing parameter ξ (GS & ES).

Summary

- The TPS is very sensible 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.
    - Complete the studies on stack benzenes for approaching graphenes.
- Download these slides: http://muammar.me/files/chemistry/

Acknowledgment

Thanks for your attention

"When you look into an abyss, the abyss also looks into you."
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).

$$\Psi_{AB} = \Psi_A \Psi_B \tag{7}$$

Given that the total position is represented by:

$$\hat{R} = \sum_{i=1}^{n} \hat{r}_i \tag{8}$$

And written in the second quantization as:

$$\hat{R} = \hat{R}_A + \hat{R}_B = \sum_{ij \epsilon A} <i|\hat{R}|j> a_i^\dagger a_j + \sum_{ij \epsilon B} <i|\hat{R}|j> a_i^\dagger a_j \tag{9}$$

On the cumulants (2)

The moment generating function is defined by:

$$F(t) = <\Psi|exp(t*R)|\Psi> \tag{10}$$

Finally the exponential factorize:

$$F(t) = F_A(t)F_B(t); \quad G(t) = G_A(t) + G_B(t) \tag{11}$$