

# CHARACTERIZATION OF METALLIC AND INSULATING PROPERTIES OF LOW-DIMENSIONAL SYSTEMS

M. El Khatib<sup>a</sup>, S. Evangelisti<sup>a†</sup>, T. Leininger<sup>a†</sup>

<sup>a</sup> *Laboratoire de Chimie et Physique Quantiques LCPQ/IRSAMC. Université de Toulouse (UPS) et CNRS (UMR-5626). Cedex France.*

<sup>†</sup> *Thesis supervisors.*

We carried out a theoretical study to characterize metallic and insulating properties of low-dimensional systems using wave function methods. Low-dimensional systems are particularly important because they allow an understanding that can be extrapolated to higher dimensional systems. We have employed a new tool based on the theory of conductivity of Kohn that we have named: *total position-spread tensor* (TPS)[1]. The TPS is defined as the second moment cumulant of the total position operator:

$$\Lambda = \langle \Psi | \hat{X}^2 | \Psi \rangle - \langle \Psi | \hat{X} | \Psi \rangle^2, \quad (1)$$

where  $\hat{X} = \sum_{i=1}^n \hat{x}_i$ . The tensor divided by the number of electrons diverges when the wave function is delocalized (high fluctuation of electrons' positions), and it takes finite values for localized ones. In this way, the electrical conductivity is related to the proper delocalization of the wave function. In addition, the tensor can be divided in spin-summed (SS-TPS) and spin-partitioned tensors (SP-TPS). The latter one becomes a powerful tool to the study of strongly correlated systems.

In this dissertation, we started to investigate at full configuration interaction (FCI) level diatomic molecules showing different types of bond. The TPS presented a marked maximum before the bond was broken and in the asymptotic limit one recovers the TPS values of isolated atoms (size consistency). For the case of diatomic systems showing avoided-crossing electronic states, the TPS diverges evidencing the high delocalization of the wave function[1, 2]. Therefore, the SS-TPS is capable of monitoring and characterizing molecular wave functions.

We considered mixed-valence systems that are often distinguished by a double-well potential energy surface presenting an avoided-crossing. Thus, such a configuration possesses a strongly multireference nature involving at least two states of the same symmetry. Two different systems were investigated: *i*) two weakly interacting hydrogen dimers that were investigated at Full CI level[3], and *ii*) a spiro like molecule where the TPS tensor was evaluated in a CAS-SCF state-averaged wave function using our implementation of the SS-TPS formalism in MOLPRO[4]. We found that the tensor's component in the direction of the electron transfer (ET) shows a marked maximum in the avoided-crossing region, evidencing the presence of a high electron mobility.

The formalisms of the SS- and SP-TPS was applied to one dimensional systems composed by three types of half-filled hydrogen chains: *i*) equally-spaced chains, *ii*) fixed-bond dimerized chains, and

*iii*) homothetic dimerized chains[5, 6]. Both the SS- and SP-TPS showed different signatures associated to the three types of systems. Equally-spaced chains have metallic wave functions and a high spin delocalization in the strongly correlated regime. In contrast, fixed-bond dimerized chains have an insulating character and a restricted spin delocalization. Finally, homothetic dimerized chains dissociate very quickly which renders them in the insulating state but with a high spin delocalization. We also studied half-filled chains by using the Hubbard and the Heisenberg Hamiltonians. On the one hand, we were able to depict the response of the SS- and SP-TPS by varying the ratio between the hopping and electron-electron repulsion ( $-t/U$  parameter) of topological connected sites. On the other hand, the ferromagnetic and anti-fermagnetic character of the wave functions were evaluated by varying the coupling constant ( $J$ ) in the strongly correlated systems.

A theoretical study of closed polyacenes (PAH) structures was performed at CAS-SCF and NEVPT2 level [7, 8]. Our methodology for choosing the active space using the Hückel Hamiltonian was able to characterize the ground state of the systems that indeed fulfilled the Ovchinnikov rule. Finally, we applied the SS-TPS to understand the nature of the wave functions of these PAHs.

## References

- [1] O. Brea, M. El Khatib, C. Angeli, G. L. Bendazzoli, S. Evangelisti, and T. Leininger, "Behavior of the Position-Spread Tensor in Diatomic Systems," *J. Chem. Theory Comput.*, vol. 9, pp. 52865295, 2013.
- [2] M. El Khatib, G. L. Bendazzoli, S. Evangelisti, W. Helal, T. Leininger, L. Tenti, and C. Angeli, "Beryllium dimer: a bond based on non-dynamical correlation.," *J. Phys. Chem. A*, vol. 118, no. 33, pp. 666473, 2014.
- [3] G. L. Bendazzoli, M. El Khatib, S. Evangelisti, and T. Leininger, "The total Position Spread in mixed-valence compounds: A study on the  $H_4^+$  model system," *J. Comput. Chem.*, vol. 35, no. 10, pp. 802808, 2014.
- [4] M. El Khatib, T. Leininger, G. L. Bendazzoli, and S. Evangelisti, "Computing the Position-Spread tensor in the CAS-SCF formalism," *Chem. Phys. Lett.*, vol. 591, pp. 5863, 2014.
- [5] M. El Khatib, O. Brea, E. Fertitta, G. L. Bendazzoli, S. Evangelisti, and T. Leininger, "The total position-spread tensor: Spin partition," *J. Chem. Phys.*, vol. 142, no. 9, p. 094113, 2015.
- [6] M. El Khatib, O. Brea, E. Fertitta, G. L. Bendazzoli, S. Evangelisti, T. Leininger, and B. Paulus, "Spin delocalization in hydrogen chains described with the spin-partitioned total position-spread tensor," *Theor. Chem. Acc.*, vol. 134, no. 3, pp. 1El Khatib, M., Brea, O., Fertitta, E., Bendazzol, 2015.
- [7] M. El Khatib, S. Evangelisti, T. Leininger, and G. L. Bendazzoli, "A theoretical study of closed polyacene structures.," *Phys. Chem. Chem. Phys.*, vol. 14, no. 45, pp. 1566676, 2012.
- [8] M. El Khatib, S. Evangelisti, T. Leininger, and G. L. Bendazzoli, "Partly saturated polyacene structures: A theoretical study," *J. Mol. Model.*, vol. 20, no. 7, p. 2284, 2014.