Quantum similarity index: Generalization and applications in multielectronic systems

J. C. Angulo[a,b], J. Antolín[b,c] and P. A. Bouvrie[a,b]

[a]*Departamento de Física Atómica, Molecular y Nuclear, Universidad de Granada, Spain*

[b]*Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada, Spain*

[c]*Departamento de Física Aplicada, Universidad de Zaragoza, Spain*

A Generalized Quantum Similarity Index is defined, quantifying the similarity among density functions [1]. The generalization includes, as new features (i) comparison among an arbitrary number of functions, (ii) its ability to modify the relative contribution of different regions within the domain, and (iii) the possibility of assigning different weights to each function according to its relevance on the comparative procedure. The similarity among atomic one-particle densities in both conjugated spaces, and neutral–cation similarity in ionization processes are analyzed. The results are interpreted attending to shell-filling patterns, and also in terms of experimentally accessible quantities of relevance in ionization processes.

The recent explosion in knowledge-based chemical research has created a surge of interest in chemical similarity. Molecular modeling and molecular similarity [2] are simple examples of such an interest. More recently the molecular quantum similarity framework has been used to provide a new set of quantum quantitative structure–properties relationship procedures (QQSPR) [3].

For the case of molecules or atoms this kind of similarity measures have been defined as the scalar product between the first order density functions weighted with a bielectronic definite positive operator. The simplest choice, the Dirac delta operator, leads to the well-known Quantum Similarity Index (QSI) [4]. Recent applications of the QSI to the analysis of atomic structure [5] and the changes suffered by the electronic cloud as a consequence of ionization [6] have been carried out. A relevant conclusion arising from those studies is the essential role played by the density in momentum space, as compared to the position one, in order to get non-trivial information from the atomic QSI values. The generalized QSI provides complementary results from a position-space-based study, which are masked when dealing with the pioneering QSI.

A detailed numerical analysis is presented, from which it is clearly established the relationship between valence subshell properties of the systems under comparison and the generalized similarity values, as well as the detection of the presence of systems suffering from anomalous shell-filling.

[1] P. A. Bouvrie, J. Antolín and J.C. Angulo, *Chem. Phys.Lett.* **506**, 326 (2011).

[2] J. Cioslowski and A. Nanayakkara, *J. Am. Chem. Soc.* **115,** 11213 (1993).

[3] R. Carbó-Dorca and S. van Damme, *Theor. Chem. Acc*. **118,** 673 (2007).

[4] R. Carbó-Dorca, J. Arnau and L. Leyda, *Int. J. Quantum Chem*. **17,** 1185 (1980).

[5] J. C. Angulo and J. Antolín, *J. Chem. Phys*. **126**, 044106 (2007).

[6] J. Antolín and J. C. Angulo, *Eur. J. Phys. D* **46,** 21 (2008).