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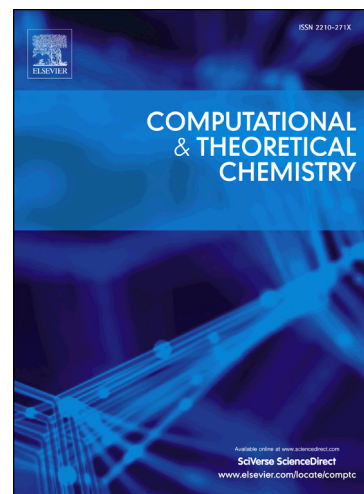
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Relationships between charge density response functions, exchange holes and localized orbitals

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Abstract

The charge density response function and the exchange hole are closely related to each other via the fundamental fluctuation-dissipation theorem of physics. A simple approximate model of the static response function is visually compared on several examples in order to demonstrate this relationship. This study is completed by illustrating the well-known isomorphism between the exchange hole and the square of the dominant localized orbital lying in the space region of the reference point of the exchange hole function. The implications of these relationships for the interpretation of common chemical concepts, such as delocalization, are discussed.

Keywords: charge density response function, Fermi-hole, localized orbitals, electron localization, topological analysis

1. Introduction

To establish links between the wave function and chemical concepts characterizing the structure and reactivity of atoms, molecules, solids and interfaces has always been a considerable challenge for computational and theoretical chemistry. Although this is a subject which has been in the focus of scientists since the very beginning of quantum chemistry, the development of Conceptual Quantum Chemistry tools remains even in our days a dynamically developing domain, producing new ideas and leading to a deeper understanding of old concepts. This research activity betrays a natural need for having a sound basis of quantitative or semi-quantitative characterization of chemical objects and their interaction in the framework of concepts, which are most often deeply rooted in chemical thinking. Technically it means that one has to extract specific parameters from many-electron wave functions of high complexity, which are able to quantify or illustrate concepts.

If we are to identify some trends in the evolution of conceptual tools over the decades, one of the most remarkable feature is that the definition of extracted quantities become more and more independent of any specific approximation scheme and are rooted more and more in true observables. On the one hand, at the beginning, quantities like bond orders and atomic populations were constructed directly from intermediate quantities of popular quantum chemical approximations (molecular orbitals, populations analysis in a given basis set, valence bond configurations, . . .) which could not be interpreted outside the scope of a given computational scheme. On the other hand, in the course of the last 20 years, researchers made an effort to define generally applicable conceptual measures and indices, which are valid independently of any quantum chemical approximation method. Emblematic examples of such approximation-independent concepts are atomic multipoles defined on the basis of the topological partitioning of the electron density [1], delocalization indices between topologically defined atoms [2–6] or, more recently, the total position spread (TPS) [7], based on the localization tensor of Resta [8]. Various measures of electron localization, like the electron localization function (ELF) [9–11], and other analogous functions of the three-dimensional space [12–14] are also defined in a universal manner, without referring to specific notions which would be valid only in the realm of a particular approximate electronic structure method. Such a philosophy has not only the advantage of making possible a judicious comparison of results obtained from different electronic structure methods (e.g. atomic charges obtained from Gaussian and plane-wave basis set calculations), but opens the way to the comparison of theoretical values directly with the experiment. For instance, atomic charges and Laplacians derived from the QTAIM (Quantum Theory of Atoms In Molecules) of Bader can be derived not only from computed, but also from experimental electron densities obtained from high-resolution X-ray diffraction data [15–18].

Inspired by the works of Parr and his coworkers [19], a whole family of functions have been defined in the framework of the Conceptual Density Functional Theory, leading to a formally rigorous interpretation of the chemical potential of an electronic system as the functional derivative of the electronic energy with respect to the number of electrons, and of the linear charge density response function as the functional derivative of

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