Charge Decomposition Analysis of the Electron Localizability Indicator: A Bridge between the Orbital and Direct Space Representation of the Chemical Bond

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Abstract: The novel functional electron localizability indicator is a useful tool for investigating chemical bonding in molecules and solids. In contrast to the traditional electron localization function (ELF), the electron localizability indicator is shown to be exactly decomposable into partial orbital contributions even though it displays at the single-determinantal level of theory the same topology as the ELF. This approach is generally valid for molecules and crystals at either the single-determinantal or the explicitly correlated level of theory. The advantages of the new approach are illustrated for the argon atom, homonuclear dimers N₂ and F₂, unsaturated hydrocarbons C₂H₄ and C₆H₆, and the transition-metal-containing molecules Sc₂⁺ and TiF₄.

Keywords: bond theory · chemical bonds · electron localizability indicator · ELF (electron localization function) · localized orbitals

Introduction

The electron localization function (ELF) originally defined by Becke and Edgecombe[1] for a Hartree-Fock (HF) wavefunction has proven to be a valuable quantum mechanical tool for bonding analysis in position space. One drawback to its use has been the unknown physical content of this function as it has been defined in axiomatic manner employing an arbitrary division of the position-dependent, spherically averaged conditional pair probability density by that of a reference model system, namely, the free electron gas. Another problem, in fact connected with the first one, is the difficulty of uniquely defining the ELF at a correlated level of theory. Recently, a functional termed the electron localizability indicator[2] (ELI) was derived directly from the electron-pair density without any reference system using a novel scheme that can be generalized to yield the restricted populations approach.[3] The ELI was initially designed to depict the position-dependent fraction of a same-spin electron pair per fixed fraction of a same-spin electron pair, was derived and applied in momentum space.[4,5] Being quite generally defined for the correlated pair density of a time-dependent many-body wavefunction for the case of a time-independent single-determinantal wavefunction, the ELI-D formally simplifies to the inverse of the relevant kernel of the ELF. For this reason it has an identical topology to the ELF. However, the ELI-D should not be considered as a generalization of the ELF formula, but a separate though related quantity that represents one possible physical interpretation of the ELF kernel at a correlated level of theory. Other physical interpretations of the ELF kernel may lead to different expressions at a correlated level of theory.[6] Adopting the ELI-D interpretation of the ELF kernel gives rise to both 1) new concepts on how to work with it as well as 2) strict limitations of applicability beyond which the physical content will be lost.

In this contribution we will elaborate the method for orbital decomposition of the ELI-D in direct space. The orbital concept is widely used in chemistry and physics and orbital decomposition of the ELI-D will enable a bridge to be built between the Hilbert and direct space representations of the chemical bond.

Charge decomposition of the ELI-D

In the following, the basic theory underlying the definition of the ELI-D is briefly reviewed in order to familiarize the