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Review

Exploring excited states using Time Dependent Density Functional Theory and density-based indexes

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ABSTRACT

The recent advances in the development and application of density-based indexes for the description of the nature and the quantification of the extent of charge transfer associated with a given electronic transition are here reviewed.

Starting from the basic definition of the indexes, a brief overview of their potential as indicators of potentially problematic cases in the description of charge transfer excitations using Time Dependent Density Functional Theory (TD-DFT) will be first given together with their possible application for comparing TD-DFT results to post Hartree–Fock (post-HF) calculations.

After this methodological part, several examples of the application of density-based indexes to describe, from a quantitative and qualitative point of view, the charge transfer character (for instance in push–pull systems) or to map excited state reaction pathways (for instance in the case of Excited State Proton Transfer reactions) will be given to exemplify the insights that these indexes may bring to the description and design of new compounds of potential technological relevance.

1. Introduction

Recent developments in quantum mechanical methods have enabled the description of Excited State Potential Energy Surfaces (ES-PES) and have opened the route to many investigations aimed at the description, and prediction, of several different excited state phenomena of both fundamental and more applicative relevance.

Many of these studies make use of Density Functional Theory (DFT) rooted approaches [1] and more specifically of Time Dependent-DFT (TD-DFT) protocols [2], mainly due to their extremely favorable accuracy to cost ratio [3]. Nonetheless, these approaches suffer from several identified flaws in their description of excited state energetic and nature, mainly ascribable to the underlying exchange correlation functional used, that call for the setup of internal indicators of their accuracy. On the other hand,

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the alternative presented by post-Hartree–Fock methods (although having indeed increased significantly in efficiency in the last years so to enable the description of relatively complex systems) is still far more computationally expensive than TD-DFT and still somehow suffers from the lack of simple, yet chemically sound, descriptors of the computed excited state nature and character.[4]

With the objective to develop a descriptor that is able to link between TD-DFT results and chemical intuition, several different indexes were recently developed primarily to spot potentially problematic descriptions provided at TD-DFT level.

With this primary diagnostic aim, several descriptors, mainly computed from orbitals, were derived. In this context it is worth to mention the seminal work of Gritsenko and Baerends [5] followed by the development of the Tozer index [6,7] or, more recently, those derived by Guido and Adamo [8,9] or Assfeld and collaborators [10,11]. Indeed, even if these last two indexes were also used to define the spatial extent associated with a given electronic transition, the use of all these indexes to measure charge transfer is still very limited [8–11].

In this general context, we developed in 2011 an index, the so called D_{CT}, with the primary aim of quantifying the spatial extent associated with a given electronic transition in order to be able, for instance, to compare the strength in charge separation obtained in different families of donor–acceptor push–pull dyes ([D–A]) [12].

This index, contrary to the previous ones, is fully computed from the density associated with the ground and the excited state, and for this reason is directly extendable to any quantum chemical method, DFT or post-HF based, thus enabling a direct comparison of the results obtained with different approaches [13,14].

The strengths and weaknesses of the index are indeed both related to its very simple conception. The D_{CT} quantifies the CT distance associated with a given electronic transition simply as the distance between the barycenters of the density depleted and density augmented zones associated with the electronic transition. Therefore, contrary to the Charge Displacement Analysis for excited states proposed by Tarantelli et al. [15], it condenses the information on charge reorganization upon electronic excitation to a CT distance. Interestingly, the D_{CT} index is very similar to the distance between the electron and hole probability distributions lately defined by Faber et al. using GW calculations [16].

Thus, the strength of D_{CT} is its ability to directly convey the simple chemical picture that, upon excitation, an electron is transferred in a molecule from one group (or atom) to another as is, for instance, represented by the $[D^+–A^-]^*$ excited state formulation in the case of push–pull dyes. It thus condenses and quantifies the information that one may derive for the analysis of the orbitals involved in the most relevant one electron excitations and describes a given excited state directly obtained at quantum chemical level. For this reason, this index has been largely applied for the description of CT excitation strength and extent in many molecular systems ranging from simple molecules to Push–Pull systems and dyes (including transition metal complexes) used for various applications such as, for instance, Dye Sensitized Solar Cells, NLO materials, fluorescent probes and sensors [17–60].

Nonetheless, the main drawback of the index also relies on its simplicity when condensing the information. If, from a theoretical point of view, the index formulation has the clear advantage of making no arbitrary choice in the localization scheme adopted, indeed the D_{CT} is, by construction, vanishing for symmetric systems since the barycenters of density depleted and incremented zones coincide. The index is thus unsuitable to describe all centrosymmetric molecules such as, for instance, antenna systems of great photophysical relevance. This point has been also clearly underlined by Sun et al. [61] in their study of the electronic properties (band gap) of conjugated oligomers.

Nonetheless, beside this important weakness, the original D_{CT} index has indeed been extensively applied not only to characterize molecular systems but also, more recently to follow excited state reactivity [54]. To this aim, a modified version of the index has also been proposed to analyze the evolution of the Excited State Potential Energy Surface (ES-PES) in the case of Excited State Proton Transfer reactions (ESPT) [54].

This work demonstrates its potential interest in the definition of suitable reaction coordinates for reaction occurring at the excited state.

In order to give a flavor of the possible application of the density-based index in the description of excited state nature and evolution essentially in combination with TD-DFT calculations, the review is organized as follows: after a description of the density indexes developed (Section 2), different examples of their application are summarized in the following sections.

First (Section 3), the more methodologically oriented applications of D_{CT} as an indicator of possible pathologic cases for TD-DFT or to more easily compare TD-DFT results with post-HF methods is given. Next (Section 4) examples of relevance of its application to the description of excited state nature and character are provided and finally, in section 5, examples of application of density indexes in the description of the excited state behavior and reactivity are briefly reported. Finally, some general conclusions about current limitations and strength of the indexes are given (Section 6).

2. The density-based index for the description of ES nature and evolution

Here we will briefly review the definition of the density-based indexes as derived in Ref. [12,54].

Let us define $\rho_{GS}(r)$ and $\rho_{EX}(r)$ as the electronic densities computed for the ground and the excited state, respectively. The density change associated with an electronic transition from the ground to the excited state is thus given by:

$$\Delta\rho(r) = \rho_{EX}(r) - \rho_{EX}(r) - \rho_{GS}(r) \quad (1)$$

Two functions, $\rho_+(r)$ and $\rho_-(r)$, can be defined collecting, respectively, the points in space where an augmentation or depletion of the electronic density upon absorption is produced. That is:

$$\rho_+(r) = \begin{cases} \Delta\rho(r) \text{ if } \Delta\rho(r) > 0 \\ 0 \text{ if } \Delta\rho(r) < 0 \end{cases} \quad (2)$$

$$\rho_-(r) = \begin{cases} \Delta\rho(r) \text{ if } \Delta\rho(r) < 0 \\ 0 \text{ if } \Delta\rho(r) > 0 \end{cases} \quad (3)$$

and $\int \rho_-(r)dr = -\int \rho_+(r)dr$.

The barycenters (referred in the following as R_+ and R_-) of the spatial regions associated with $\rho_+(r)$ and $\rho_-(r)$, can thus be defined and computed, for instance by discretizing them on a 3D grid around the molecule, as:

$$R_+ = \frac{\int r\rho_+(r)dr}{\int \rho_+(r)dr} = (x_+, y_+, z_+) \quad (4)$$

$$R_- = \frac{\int r\rho_-(r)dr}{\int \rho_-(r)dr} = (x_-, y_-, z_-) \quad (5)$$

The original D_{CT} index was thus defined as the spatial distance between these two barycenters of density distributions as:

$$D_{CT} = \left|R_+ - R_-\right| \quad (6)$$

Integrating over all space $\rho_+(r)$ or $\rho_-(r)$ additionally provides the net transferred charge (q_{CT}) associated with the transition. Additionally, from the D_{CT} and q_{CT} terms defined above, the norm of the