Using Density Based Indexes to Characterize Excited States Evolution

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With the aim of offering new computational tools helping in the description of photochemical reactions and phenomena occurring at the excited state, we present in this work the capability of a density based index (Π) in locating decay channels from higher to lower excited states. The Π index, previously applied to disclose non-radiative decay channels from the first excited state to the ground state, is very simple in its formulation and can be evaluated, practically with no extra computational cost, and coupled to any quantum method able to provide excited states densities. Indeed, this index relies only on the knowledge of energetics and electronic densities of the different electronic states involved in the decay. In the present work, we show the proficiency of the Π index in the general case of decay between excited states by applying it to two model systems well characterized both theoretically and experimentally. In both cases, this descriptor was successful in spotting the regions where excited states are more likely to decay, thus suggesting its potential interest for further application in the design of new compounds.

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Introduction

In the last few decades, the study of excited states (ESs) reaction pathways, beyond the simple analysis of vertical excitations within the Franck-Condon region, has increasingly attracted research interest.[1-4] Indeed, localizing the most stable reaction intermediates, as well as shading some light on the reaction pathways associated to photochemical processes, is still a challenge for quantum methods nowadays available. Nevertheless, to gain some knowledge from theory and computational approaches on photophysical and photochemical properties of photoactive molecules or materials used for optoelectronic devices,[5] becomes essential not only for the understanding of their basic working principles but also for their design.

In this respect, developing tools enabling one to describe the evolution of the potential energy surfaces (PES) associated to selected electronic ESs becomes of fundamental interest.[6-11] However, the concept of PESs implies that the Born-Oppenheimer approximation (BOA) holds,[12,13] which is generally true for reactions occurring at the ground state but may break down at the ES.[14,15]

In particular, in the case of many photoinduced processes occurring even in simple molecular systems, for specific nuclear coordinates two or more electronic ESs can get close enough so that their coupling cannot anymore be neglected, thus determining the breakdown of the BOA.[14,16] These nuclear conformations for which the PESs of different states are very close or even cross are commonly defined as “funnel” regions, and they are indeed extremely important for the photochemical and photophysical behavior of such systems. In particular, they play a key role in defining their non-radiative decay pathways as well as their reactivity at the ES.

Setting up simple approaches to identify these regions would therefore greatly help in the description of phenomena occurring at the ES.

Two basic ingredients are indeed necessary: an accurate quantum chemical method enabling the description of the different ESs (often of multideterminantal nature) and a protocol enabling the characterization of their coupling. Recently, in several works we have shown that combining robust and reliable density functional theory (DFT) approaches and simple descriptors based on the electron density, it is possible to provide a fair description of the PES at the ES both from a quantitative (energy landscape) and a qualitative (hole-electron distance and charge transfer (CT) character) point of view.[6,17,18] Furthermore, we have shown in a previous work that electron density descriptors can also be used in conjunction with any electronic structure method, as long as it provides accurate densities of ground and ESs.[19]

In the present contribution, starting from an index recently proposed to qualitatively spot the regions of non-radiative decay from the first ES (S1) to the ground state (S0), namely the Π index,[20] we have extended its use to locate regions of potential decay between ESs. In the same line of thought as the previous work, this new formulation of the Π index can also be rationalized in terms of classical electromagnetism, since this density-based index can be correlated to the inverse of the work (WCT) necessary to interconvert two electronic ESs of interest. The Π index will be tested considering two model systems that are (1) a simple Excited State Intramolecular Proton Transfer reaction (ESIPT) and (2) the analysis of the ESs PES of the dimethylamino-benzo nitrile (DMABN, Scheme 1) molecule. For the first case, both a multiconfigurational—namely CASSCF/CASPT2—and a Time-dependent DFT (TD-DFT) approach will be used in conjunction with the same density based descriptor.

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while for the second only the TD-DFT results will be presented in the discussion.

The paper is organized as follows: after a brief description of the theoretical approach used, results obtained for the photoinduced proton transfer occurring in 1-cyclopropylldiazoo-2-naphtol aromatic azo compound (CPDNO, Scheme 1) will be discussed. Next, the ES-PES surfaces of the DMABN system will be analyzed and some conclusions on the potential use of the II density based index to locate decay regions will be drawn.

**Density Based Indexes and Computational Approaches**

In order to describe the PES at the ES we will make use of a density based descriptor (the so-called II), originally designed to qualitatively locate regions in the PES where a non-radiative decay between the first singlet ES and the ground state is most likely to occur. However, contrary to its original formulation, in the present contribution, we will generalize this definition to the broader case of decay occurring between two ESs. In this context, it is common to explore PESs of selected states by means of their relative energies, computed dipole moments, and density-based indexes such as the $D_{\text{II}}$. Indeed, the probability of an electronic transition from an initial state ($\hat{f}_i$) to a final state ($\hat{f}_j$) ($i, j = 1, ..., n \in \mathbb{R}$) is dictated by the energy gap between the states and the transition dipole moment. The former is given by the energy difference between the stationary states involved in the transition. The quantum mechanical expression for the transition dipole is

$$\mu_{ij} = \langle f_j | M | f_i \rangle,$$

the square of the length of $M$ being proportional to the integrated transition density. Conversely, the difference in dipole moment between two states ($M^{\hat{f}_i} - M^{\hat{f}_j}$) can be expanded as the product of the actual hole-particle transferred charge (hereafter $q_{\text{CT}}$) and the effective length associated with a given electronic transition ($D_{\text{CT}}$). With this in mind, the II index is defined as

$$\Pi = \frac{1}{|\Delta E|^2 D_{\text{CT}} q_{\text{CT}}}.$$

This index qualitatively satisfies also some conditions that can be drawn based on chemical intuition. Indeed, one may expect that the closest the energy between the states, the higher the probability for the system to undergo a non-radiative relaxation. Besides, if the total electronic density is similarly distributed in the two states involved, the probability of interconversion will be maximal. The first criterion translates in an inverse dependence of the probability of state crossing on the two states energy gap. Hence, II will diverge in the case that two states are degenerate. Conversely, the $q_{\text{CT}}$ term accounts for a complementary and intuitive interpretation, namely the fact that the interconversion will occur more easily if the electronic density redistribution associated with the transition from one state to another is the least. In other words, although the energy gap between the two states will be the leading term for many photochemical reactions implying a crossing of states, for a given energy gap a decay will actually be more efficient the most akin the electronic densities of the starting and final states are. This is a different way of saying that the smaller the electron reorganization between the states will be, the more likely the decay will be.

Since, quantitatively the $D_{\text{CT}}$ value calculated between two states with equivalent charge distributions equals zero, the product $q_{\text{CT}}D_{\text{CT}}$ may be the leading term to identify radiationless pathway, that may be responsible of peculiar photo-reactivity.

Indeed, a classical picture of the II is to consider that the work ($W_{\text{CT}}$) necessary to redistribute an ensemble of charges in an electromagnetic field is defined as the integral over the space of the product between the charges moved, the field, and the infinitesimal displacement. More precisely, this work associated to an electronic transition from $S_n$ to $S_{n+1}$ state is a function of the rearranged electronic charge ($q_{\text{CT}}$), of the $D_{\text{CT}}$, that represents the charge displacement, and of the electric field in which the rearrangement occurs, the latter being proportional to the transition energy $\Delta E$. Using the II index, which is proportional to the inverse of the work associated with the reorganization of a density distribution, we suggest that decay channels appear in those regions of PESs where the work needed to interconvert two different ESs is the lowest.

To investigate the efficiency of the II descriptor in locating funnel regions, two different molecules have been considered as models, namely the CPDNO and the DMABN (Scheme 1), essentially due to their limited size allowing both the use of wavefunction and density-based methods. Moreover, these molecules have been extensively studied in literature, as they display a complex behavior of different states along ESs PES. For the first molecule (CPDNO), CASSCF/CASPT2 calculations are reported in literature (see Ref. 21 of Cui and collaborators) pointing out a competition between a cis-trans photo-isomerization and a photo-induced proton-transfer reaction. Cui and co-workers characterized the PES of $S_0$, $S_1$, and $S_2$ and some of the crossings between them. In the present work, only the crossing between the $\pi\pi^*$ and the $n\pi^*$ ES (Fig. 1) occurring during the photo-induced proton-transfer reaction is discussed. More in detail, starting from the structures reported in Ref. 21, we have focused on the description of the relaxed minimum energy proton-transfer profile occurring along...
Results and Discussion

Inspired by the work of Cui et al.,\cite{21} we decided to monitor, by means of the II index, the S1/S2 state crossing, occurring along the ESIPT in the CPDNO molecule. In the work of Cui et al.,\cite{21} it has been pointed out that the reaction evolves almost barrierless along the PES of the bright 1ππ* state, connecting the ES enol* and the keto* forms (Scheme 1). Hence, to analyze their evolution by means of the II index, the 1nπ* and 1ππ* states have been computed at the same level of theory reported in Ref. 21, starting from the published relaxed optimized structures. For each point along the minimum energy 1ππ* potential energy profile, the 1nπ* PES has been vertically computed, revealing a crossing between the 1ππ* and 1nπ* ESs. More in detail, we have computed single point energies and associated densities for eight relaxed geometries corresponding to an N–H length (d_{N-H}) varying from 1.8 to 1.1 Å in steps of 0.1 Å. We have calculated the minimum energy ES proton transfer profile along the 1ππ* and 1nπ* states using the same SA-CASSCF (14,10) active space reported in Ref. 21. Specifically, 14 π electrons in 10 π orbitals where chosen for the diabatic 1ππ* state, 10 π and 4 lone-pair electrons in 8 π orbitals. These active spaces consist of 14 π electrons in 10 π orbitals in the case of the 1ππ* ES, whereas for the correct description of the 1nπ* ES, the active space used consists of 10 π and 4 lone-pair electrons in 8 π and 2 lone-pair orbitals. These calculations were carried out using the Pople’s valence-double-ζ basis set with one set of d polarization functions for all atoms but hydrogens (6-31G(d)).\cite{22–24} The imaginary shift technique\cite{25} (0.2 a.u.) was employed to avoid the presence of intruder states, as described in Ref. 21. All these post-Hartee–Fock calculations (CASSCF and CASPT2) were performed using the MOLCAS 8.0\cite{26} quantum package. TD-DFT calculations were also performed on the same structures (Scheme 1) using the global hybrid PBE0\cite{27} functional and the same basis set (6-31G(d)). All calculations have been performed in the gas phase using the Gaussian code.\cite{28}

The same level of theory was applied to analyze the behavior of the 4-(N,N-dimethylamino)benzonitrile (DMABN) molecule at the TD-DFT level.

With the aim of mapping the crossing of the first two ESs of DMABN a 2D grid was generated, optimizing 60 homogeneously distributed structures at the ground state with two constrained degrees of freedom namely the dihedral angles D1(C1N2C4C5) and D2(C3N2C4C6), as depicted in Scheme 1. These two dihedral defines, respectively, a twisting (τ) and a symmetric wagging (δ) motion of the di-methyl amino substituent with respect to the aromatic ring. In particular, the structures were generated varying the τ dihedral angle from 0° to 10° in increments of 10°, and the δ dihedral from 0° to 25° in increments of 5°. This scan allows one to encompass the formation of the local excited (LE) ππ* state and the first CT state. A more detailed description on how the grid was constructed is given in Section “Results and Discussion,” along with the results.

The II index [eq. (2)] was computed at each structure with all the methods described above.
and 2 lone-pair orbitals for the diabatic \(1\,n_x\pi^*\) state, situated in the H6–N1 plane (Supporting Information Figure S1).

At the Franck–Condon geometry, that is for a N–H distance around 1.8 Å, the \(1\,n_x\pi^*\) state (depicted in red in Fig. 1) is lower in energy with respect to the \(1\,\pi\pi^*\) state by 10.7 kcal/mol. As the proton moves toward the nitrogen, the \(1\,\pi\pi^*\) state decreases in energy. For a N–H distance around 1.6 Å the two states become very close in energy while for shorter N–H distances, the \(1\,\pi\pi^*\) state (in green in Fig. 1) becomes the lowest in energy. In order to characterize the nature of each state along the reaction profile, the \(D_{CT}\) index has been computed. Here we have used the notation \(D_{CT}^{\text{final}}\) to indicate the initial and final states that we consider when computing the \(D_{CT}\).

The dark \(1\,n_x\pi^*\) state, is mainly related to an HOMO-2 (n) to LUMO (\(\pi^*\)) excitation. As shown in Figures S2 and S3 (Supporting Information), both these orbitals are mainly localized on the diazeylenophenyl moiety. As a consequence, the associated \(D_{CT}\) values along the computed profile are relatively low, ranging from 0.04 Å, for a \(d_{N-H}\) of 1.3 Å to 0.7 Å at \(d_{N-H}\) of 1.2 Å, thus fully reflecting the localized nature of the transition. Conversely, the \(1\,\pi\pi^*\) bright ES is predominantly stemming from a HOMO–LUMO excitation and is accompanied by a significant CT from the naphthalene fragment to the diazenyl part.

Accordingly, the \(D_{CT}^{\text{exp}}\) values range from 0.553 Å at an N–H distance of 1.8 to a maximum value of 2.338 Å occurring at \(d_{N-H}\) 1.3 Å. Upon excitation in the enol region, the \(1\,n_x\pi^*\) state is first populated. This latter may evolve to the keto tautomer after interconversion to the \(1\,\pi\pi^*\) state or keep on the \(1\,\pi\pi^*\) state and turn back to the enol tautomer.

The calculated \(\Pi\) value along the \(1\,n_x\pi^*\) to \(1\,\pi\pi^*\) interconversion trajectory (middle panel in Fig. 1) shows that the \(\Pi\) function displays one distinct peak corresponding to the \(1\,n_x\pi^*/1\,\pi\pi^*\) crossing region. This is expected due to the presence of the vanishing \(\Delta E\) term in the \(\Pi\) index expression. More generally, as expected a crossing point in the PES will always be spotted by the \(\Pi\) index, which is in this case dominated by the energetic contribution. It is interesting to note that the maximum value is located close to the Franck–Condon region, suggesting that the preferred path is indeed the one leading back to the enol tautomer rather than to the photoproduct.

This finding is in agreement with the experimental results\(^{29}\) showing that an efficient internal conversion path to the ground state is opened upon absorption, and that, once the equilibrium condition is restored, a consistent fraction of the CPDNO molecules (84%) is in the enol-form. However, as soon as enough energy is provided for the proton to move towards the nitrogen, at about 1.6 Å, the \(1\,\pi\pi^*\) state is accessed, and the interconversion to the keto conformer form occurs without any barrier. Indeed, the statistical distribution in terms of Boltzmann population of the two states calculated with respect to the potential energy profile of the bright diabatic \(1\,\pi\pi^*\) state is monotonically increasing (bottom panel in Fig. 1). Thus, once the \(1\,\pi\pi^*\) state is accessed, the likelihood that this state remains populated increases. On the contrary, the probability that the system turns back to the dark \(1\,n_x\pi^*\) state drops.

In the following, we consider the same reaction profile at the TD-DFT level. In an analogous fashion to what has been performed at post-HF level, first-relaxed- and second-vertical- ES energies were computed. As previously, these states correspond to the Franck–Condon region of the \(1\,n_x\pi^*\) and \(1\,\pi\pi^*\), respectively. Unsurprisingly, looking at the system at large N–H distances before the intersection occurs, \(S_1\) consists of \(a\,n_x\pi^*\) and \(S_2\) is a pure HOMO–LUMO excitation of \(\pi\pi^*\) character. In analogy with the post-HF results, this picture is reversed at shorter N–H distances, as indicated by the associated \(D_{CT}\) values. The \(D_{CT}\) for the \(1\,\pi\pi^*\) state changes from 0.587 Å to 0.256 Å as the N–H distance is shortened from 1.7 Å to 1.5 Å. Correspondingly, the \(D_{CT}\) value for the \(1\,\pi\pi^*\) state increases from 1.268 to 1.698 Å, thus reflecting its CT character. Once more, we analyzed the energy profiles associated to the two ESs, w.r.t. the ground state minimum (top panel in Fig. 2).

Contrary to the previous case, the potential energy profile associated to the \(1\,\pi\pi^*\) state is not monotonically decreasing, with a small barrier around a \(d_{N-H}\) value of 1.2 Å (top panel in Fig. 2).

A possible reason for this discrepancy is the use of CASSCF optimized structures as starting point also for TD-DFT ES calculations. Nonetheless, despite this slight difference, the actual photophysical behavior predicted for CPDNO at density functional level is the same as the one obtained using wavefunction methods. This is easily verified by inspecting the Boltzmann distribution of each state: at the Franck–Condon geometry the \(1\,n_x\pi^*\) state is by far more likely populated than the \(1\,\pi\pi^*\) one. However, the proton transfer only occurs once the \(1\,\pi\pi^*\) state is accessed. Again, the \(\Pi\) profile (in the middle panel in Fig. 2) correctly points out the \(d_{N-H}\) at which the inversion between the two states occurs. As a result, the crossing at a N–H distance of 1.6 Å is unveiled and resolved in the peaked \(\Pi\) function, again related to the leading \(\Delta E\) term in the index expression.

In order to further proof the potentiality of the \(\Pi\) index in the description of ES evolution, this latter has been applied to characterize the ES interconversion occurring for the DMABN molecule. In the last two decades, this molecule has been the object of numerous experimental\(^{30–43}\) and theoretical\(^{32–34,38,40,43–47}\) studies, devoted to uncovering the origin of its dual emissive properties\(^{30,40,49}\) the references chosen are an essential but relevant collection. Several models have been proposed\(^{40,46,49–56}\) in literature, which reveal the presence of different states accounting for the peculiar photophysical properties, depending on specific reaction coordinates. Among all the proposals, the one allowing better fitting with the experimental evidences is the so-called twisted intramolecular charge transfer (TICT) model proposed by Grabowski and co-workers in 1973.\(^{30}\) According to the TICT model, the initially promoted planar and LE state interconverts radiationless to a CT state— from the amino-donor to the benzonitrile acceptor—upon rotation of 90° of the dialkylamino group with respect to the benzonitrile plane, yielding a conformation where the donor and acceptor groups of the molecule are perpendicular. According to the TICT model the dual-emissive properties of the DMABN are ascribed to the twisting coordinate.\(^{49,53}\)

Roughly 20 years later (in 1993), a different model was proposed by Zachariasse, the so-called planar intramolecular CT
(a) Relaxed (\(1\pi^*\)) and vertical (\(1n\pi^*\)) minimum energy proton-transfer profile as a function of the N–H distance, computed at the PBE0/6-31G(d) level of theory. b) \(1n\pi^*\) to \(1\pi^*\) II index evolution computed along the relaxed scan. c) Normalized Boltzmann factors computed for the \(1n\pi^*\) state (red), \(1\pi^*\) state (green). [Color figure can be viewed at wileyonlinelibrary.com]

This model predicts the formation of a quinoidal intramolecular CT (ICT) state promoted by the pyramidalization of the natively planar \(-\text{NMe}_2\) group. This model implies that the H distance, computed at the PICT model of the \(D_2\) and \(P\) structural features above, that are the torsion (for the TICT) and the wagging (for the PICT) modes, but also highlight other zones on the PES in which a decay may be likely to occur even in presence of a finite energy difference (i.e., non zero) between the two ESs involved.

Starting from the planar ground state optimized geometry, we performed a relaxed scan, individually changing a linear combination of the two dihedral angles (\(D_L\) and \(D_W\), respectively, the \(D_T\) and \(D_P\)) of the same geometrical structure, the highest crossing probability is at this point, providing us with an unequivocal interpretation of the crossing occurring at the same spot in the PES.
Interestingly, the decomposition of the II index map endorses a step forward in the interpretation, yielding a clear and intuitive picture of the crossing at different twisted/wagged geometries. Figure 3c shows the distribution of the $1/\Delta E$ function along the two reaction coordinates. Close to the region of $0^\circ \delta$ and $40^\circ \tau$, the inverse of the energy has the same behavior as the II function, scaled by a factor of roughly a third. The $D_{CT}^{\delta}$ displays a minimum in the same region. In antithesis to the distribution of the $1/\Delta E$ surface, this shallow region propagates in the same range of twisting values over the whole range of wagging angles, revealing a decay pathway connecting the $0^\circ \delta/40^\circ \tau$ region to the $25^\circ \delta/10^\circ \tau$ one.

The II index, in fact, represents a magnitude proportional to the work that needs to be accomplished in order to rearrange two charge distributions, relative to two different ESs. In turn, the II function points out the portion of the reaction space where the work needed to reorganize the density is the least, and the LE to CT transition is more likely to occur. Indeed, a large wagging motion of $25^\circ \delta$ strongly increases the possibility of the decay to occur at small twisting angles, around $10^\circ$. However, as soon as the twist becomes larger, the wagging motion reduces the probability of a non-radiative relaxation and with it the likelihood of the CT state to be populated. In agreement with previous theoretical and experimental findings, we can assert that, while the twisting coordinate remains predominant, the wagging motion contributes to convey the system toward in the ICT state (where the emission occurs). Not only our index individuates the $S_1/S_2$ crossing at the correct position, but it also helps to identify other non-radiative decay channels, highlighting the role of the inverstion mode on the ICT process in a simple and unequivocal manner, analysis that could not be performed using only energetics arguments (that is on the basis of the sole $1/\Delta E$ term).

**Conclusions**

In this work, we have tested on two model systems, characterized by a complex photochemical behavior, and well-studied both theoretically and experimentally, an index enabling to locate decay channels between PESs of ESs. Relying both on relative energy and on the electron densities similarity of the electronic states involved, the II index can be used to locate decay regions on the PES.

In principle, qualitative screening based only on the location of minimal energy gap zones may not be sufficient to correctly...
locate all the regions on the PESs leading to potential decay. Indeed, a decay from a higher to a lower energy ES is likely to appear in regions where either the energy gap between ESs involved is small or the charge distributions of the two states involved are similar, or in regions where both these conditions are satisfied.

Due to its simple formulation, the II index can be coupled to any quantum chemical method, from density functional to wavefunction methods offering a simple qualitative tool to screen along PES of complex photoactive systems.

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