Visualization application domains—Scientific visualization; The study of electronic transitions in molecules due to absorption or emission of light is a complex quantum mechanical process. Their study plays an important role in the design of novel materials. A common yet challenging task in the study is to determine the nature of those electronic transitions, i.e. which subgroups of the molecule are involved in the transition by donating or accepting electrons, followed by an investigation of the variation in the donor-acceptor behavior for different transitions or conformations of the molecules. In this paper, we present a novel approach towards the study of electronic transitions based on the visual analysis of a bivariate field, namely the electron density in the hole and particle Natural Transition Orbital (NTO). The visual analysis focuses on the continuous scatter plots (CSPs) of the bivariate field linked to their spatial domain. The method supports selections in the CSP visualized as fiber surfaces in the spatial domain, the grouping of atoms, and segmentation of the density fields to peel the CSP. This peeling operator is central to the visual analysis process and helps identify donors and acceptors. We study different molecular systems, identifying local excitation and charge transfer excitations to demonstrate the utility of the method.

Index Terms: Human-centered computing—Visualization—Visualization application domains—Scientific visualization;

1 INTRODUCTION

The study of electronic transitions in molecules due to absorption or emission of light, called molecular spectroscopy, is crucial for understanding their chemical and physical properties. Electrons are distributed within a series of available orbitals in a molecule. When a photon is absorbed by a molecule, electrons are excited from occupied orbitals to unoccupied orbitals resulting in a change in the electronic structure of the molecule. The process is reversed for emission of light. The orbital vacated by the electron is named as hole and the orbital that gets filled by the electron is named as particle. The Natural Transition Orbital (NTO) is a compact representation of electronic excitations. It considers a linear combination of orbitals involved in a specific electronic transition to describe where the electrons are excited (hole NTO) and to where they are promoted (particle NTO). Our objective is to develop a solution for a problem of interest to a theoretical chemist, namely the analysis of the nature of electronic transitions in molecules. A typical study of electronic transitions poses questions related to the transfer of charge within and between molecular subgroups such as: Which subgroup is a donor / acceptor for a particular excited state of the molecule? How do the donor / acceptor strengths (charge transfer) vary with different molecular conformations? How do donor / acceptor behavior vary within a family of complexes? Can a given state be classified as presenting a local excitation or charge transfer character?

Related work. The electron density fields are often studied individually via isosurfaces together with ball-and-stick model representations of the molecule and additional annotations to indicate charge transfer [12,20]. These techniques are useful for the study of orbitals within a given state and rely on side-by-side comparisons to understand transitions [10]. The analysis of transfer of charge between the molecular subgroups and their classification as donor-acceptor is a key step towards the study of electronic transitions. A few studies employ quantitative approaches towards the study of charge transfer. Garcia et al. [3,8] propose a set of indexes based on point wise difference in charge density field to capture the amount of charge transfer and change in dipole moment, and later also interpreted as hole-electron distance [9,11]. In recent work, Masood et al. [17] present an automated method for quantifying charge distribution and transitions based on a spatial segmentation of the electronic density field. They formulate charge transfer as a constrained optimization problem by modeling the molecular subgroups as nodes in a graph and describe methods for visualizing the charge distribution and transfer at the atomic and subgroup level.

Generalization of discrete scatter plots to continuous scalar fields and of isosurfaces to fiber surfaces have led to new directions in bivariate and multivariate field visualization. Carr et al. [4] highlighted the applicability of fiber surface to electron density fields. Subsequent work focused on improving the correctness and efficiency of fiber surface computation and various applications [4,19,21]. Tierny et al. [21] segment the domain based on the Reeb space and use them to peel the continuous scatter plot (CSP) to reveal its connected structures. Lehmann et al. [13] investigate discontinuities in CSPs to establish a relationship with the number of connected components in the spatial domain.

We propose a new approach that analyzes the bivariate field consisting of the hole NTO and particle NTO to directly capture the nature of electronic transitions. We employ visualization techniques...
2 BIVARIATE ANALYSIS OF ELECTRONIC TRANSITIONS

Molecular orbitals provide an approximate solution for the electron distribution in molecules. Typically they are calculated using Density Functional Theory (DFT), applying programs like Gaussian [7]. DFT methods also support the simulation of electronic transitions. Functional Theory (DFT), applying programs like Gaussian [7]. Molecular orbitals provide an approximate solution for the electron distribution in molecules. Typically they are calculated using Density Functional Theory (DFT), applying programs like Gaussian [7].

Figure 2 presents an overview of the visual analysis pipeline that processes the input electron density fields together with the molecular structure (atom locations, radii, bond information).

**Segmentation.** A molecular subgroup is represented by a subset of atoms that constitute the molecule. Following previous work [17], a weighted Voronoi tessellation [1] of a point set is computed to partition the molecule into atomic regions. The point location and weights correspond to the atom location and radii. A molecular subgroup is represented as a union of atomic regions. Other geometric
or topology-based segmentation may be used if they are deemed appropriate. Atoms that constitute the various subgroups of interest are assumed to be available as input to the visualization pipeline.

**Continuous scatter plot (CSP) and fiber surfaces.** The CSP of the bivariate field \((\phi_h, \phi_p)\) is computed and displayed to provide an overview. It may be explored interactively by specifying query line segments and extracting the corresponding fiber surfaces, the preimage of the line segments. Extraction and visualization of fiber surfaces is one approach towards studying and understanding the domain and range space of the bivariate field. \(^{[2]}\)

**CSP peeling.** A detailed analysis of the CSP is provided via CSP peeling. This is the computation of CSP for the field restricted to a region of interest within the spatial domain to study and compare characteristic patterns. \(^{[4]}\)

### 4 Interpreting a Peeled CSP

If the peeled CSP aligns with the X-axis or specifically consists of the region satisfying \(|\phi_h| > |\phi_p|\), then we classify the subgroup as a donor. A horizontal line \(\phi_p = 0\) implies that the particle NTO equals zero within the corresponding region in the domain and there is no charge gain. Rather, this region has lost charge because hole NTO \(\neq 0\). Similarly, if the CSP aligns with the Y-axis, then the corresponding region in the domain represents an acceptor. In Fig. 1 Cu and PHEOME are classified as donors while PHE as an acceptor.

A large difference in the area covered by the CSP of subgroups may help infer which subgroup is a stronger donor or acceptor, as appropriate. Alternatively, a consistent CSP for a subgroup within different complexes indicates a unique property of the subgroup. For example, we compare the behavior of copper within different complexes in Fig. 4. Peeling also helps identify the nature of the electronic transition. Local excitation refers to the scenario where both hole and particle NTOs are located within a subgroup, and charge transfer excitation where they are located within different subgroups. Local excitation may be identified by comparing CSPs of individual subgroups. If the contribution from all subgroups except one is small then we may conclude that the electronic transition is local to a subgroup. For example, we identify State 10 as a local excitation state in Cu-PHE-PHEOME, see Fig. 5.

### 5 Results

We now present results of two case studies where CSP peeling reveals the donor-acceptor behavior, how it varies with geometric conformations or with varying ligands in a family of complexes. The hole and particle NTOs for these case studies are calculated using the Gaussian software package \(^{[7]}\) while the CSPs and fiber surfaces are computed using the topology toolkit \(^{[22]}\).

#### 5.1 Case Study 1: Thiophene-Quinoxaline

The first case study investigates different geometric conformations of a molecule that can be divided into two subgroups, Thiophene and Quinoxaline, first row in Fig. 3. Our analysis focuses on the first excited state of the molecule. Thiophene (the 5-member ring) is generally considered to be a donor subgroup but, as our study shows, this property varies depending on the dihedral angle between the subgroups. The \(\pi\)-bond conjugation (delocalization of electrons over the molecule) can be broken (at 90°) which results in different types of excitation, local vs. charge transfer, for different angles. The CSP analysis results are shown in Fig. 3.

The \(\pi\)-bond conjugation is maximum in 0° and 180° as the orbitals are fully delocalized over the molecule. The CSPs for these two angles are near identical, and hence capture the similarity between the two conformations. The peeled CSPs corresponding to Thiophene for 0° and 180° are aligned along the X-axis implying that Thiophene is the donor subgroup, the Quinoxaline CSPs are more aligned along the Y-axis suggesting that it is the acceptor in both conformations. The area covered by Thiophene CSP shrinks towards origin from 0° to 60° and reduces to a minimum at 90°.
This suggests that both hole and particle NTOs for Thiophene reduce and hence the charge transfer from Thiophene to Quinoxaline also decreases as the dihedral angle increases. Such a behavior is expected because the π-bond conjugation is minimum at 90°. The area increases when the dihedral angle increases further to 120°. Quinoxaline CSP for 60° and 90° is similar to the CSP of the molecule, while Thiophene CSP covers a small region near the origin. This suggests local excitation in these conformations, primarily within Quinoxaline. The behavior changes towards charge transfer excitation again at 120°. In the relaxed geometry, where the molecule is at an energy optimal dihedral angle (35.3°), we observe that Thiophene acts as a donor, which is again the expected behavior.

### 5.2 Case Study 2: Copper complexes

In this case study, we consider copper complexes consisting of a copper subgroup, a fixed ligand (PHE), and a second ligand that varies between PHE, PHEOME and XANT.

**Varying ligands.** First, we study the effect of varying the second ligand with a focus on the first excited state of each molecule, see Fig. 4. Copper behaves as a donor in all configurations with similar strength. This is an expected behavior for copper. PHE behaves as an acceptor. An interesting observation is that the charge transfer is expected to be symmetric in Cu-PHE-PHE, from Cu to both PHE ligands. This behavior is observable from the CSPs of the individual PHE ligands. In Cu-PHE-PHEOME, both Cu and PHEOME are donors. Cu is expected to be a stronger donor. Copper covers a larger span on the X-axis indicating larger values of φh in its atomic region. However, a visual inspection of the CSPs is not sufficient to claim that copper is indeed the stronger donor. CSPs for Cu and PHEOME appear to be similarly close to origin, but a quantification step is necessary in order to confirm that the point densities are indeed similar. In Cu-PHE-XANT, both Cu and XANT behave as donors. XANT is expected to be a stronger donor than Cu but a visual inspection is again not sufficient to make such a claim.

**Characterizing excitations.** We now compare the behavior of two complexes, Cu-PHE-PHEOME and Cu-PHE-XANT, within different excitation states. The aim is to characterize the nature of excitation, local or charge transfer. Fig. 5 shows the results of the CSP peeling based visual analysis. For Cu-PHE-PHEOME, we observe a charge transfer excitation in state 9. The Cu and PHE CSPs exhibit donor and acceptor behaviors, respectively. We may conclude that a significant charge transfer happens from Cu to PHE. However, in state 10, CSPs of the molecule and that of PHE are similar. Further, contributions from other subgroups appear to be low indicating local excitation within PHE. In state 3 of Cu-PHE-XANT, we observe a charge transfer from Cu and XANT to PHE, and in state 10 a local excitation within XANT.

### 6 Conclusions

This paper presented a simple and effective approach to bivariate data analysis for visually interpreting electronic transition data. The case studies demonstrated the use of CSP peeling for identifying and comparing donor-acceptor behavior of molecular subgroups across different geometric conformations. Topics for future work include investigation of other segmentation methods and quantification of the peeled CSPs.

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