A Quantitative Analysis of Light-Driven Charge Transfer Processes Using Voronoi Partitioning of Time Dependent DFT-Derived Electron Densities

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Introduction

Molecular photophysical processes can be described conceptually with a Jablonski diagram and an energy profile that plots surfaces for ground and excited states S₀, S₁, ... (Fig. 1). Hence, experimentally determined energies can be predicted theoretically with time-dependent density functional theory (TD-DFT), thereby enabling in silico design of photoactive materials. In the past decade such calculations have been conducted on large molecules (~<200 atoms) to explore the effect of light absorption on the reorganization of electron density, which is relevant to the design of light-driven molecular motors[1] and switches,[2] singlet[3a] and triplet[3b] photocatalysts, and light-harvesting architectures.[4]

Electron density difference isosurface plots can be used for the purpose of obtaining an in-depth atomistic view (Fig. 2) of photoexcitation, but such analyses are only qualitative and give no information about the magnitude of the change in density. Moreover, electron density difference isosurfaces are poorly defined when nuclear positions are affected by the photophysical process, which hampers a proper description of the relaxation process.

In this pursuit, Le Bahers, Adamo, and Ciofﬁni[5] pioneered a quantitative analysis that has been useful in the analysis of light-absorbing organic chromophores.[6] In their approach the charge transferred (q_CT) in a photochemical transition is calculated from the sum of all per-atom differences in partial atomic charges (PAC) having the same sign. The associated vector d_CT, across which charge is transferred, is computed between the geometric barycenters of the positive and negative PAC difference. The difference in electron density is used to compute PACs, but any method of obtaining partial charges can in principle be applied. Jacquemin et al. investigated the relative merits of various PAC schemes to calculate Δ_CT/D_CT.[5c]

This CT index has been adapted to also include excitation-induced geometrical changes, thereby enhancing its utility in, for example, excited-state proton transfer processes.[7]

Other indices that quantify electron density differences, such as the density overlap index ϕ,[8a] or the molecular orbital-derived hole-electron difference Δ[8b] have been developed as well. These approaches provide global quantitative data on a molecular system. However, from such single (per-molecule) values or indices, no fine-grained information on per-atom charge differences can be obtained.

We felt the need to develop a mathematically straightforward method capable of describing at the atomic level the effect of electronic transitions and relaxations on charge distribution. Atomic charges computed for the initial state of a photochemical process are then subtracted from those at the final state. By subtracting state-speciﬁc electron densities for atoms (or groups of atoms) that are numerically integrated over the Voronoi polyhedra, we arrive at a quantitative description of charge transfer in vertical excitations and relaxations.

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These results appear more robust compared with other space-partitioning (Bader and Hirschfeld) and wavefunction-based partitioning (Mulliken) methods.

Approach

Summing electron density of atom-centered Voronoi cells has been used previously to obtain ground-state electronic charges.\[^9\] We forego the inclusion of a promolecule density in our calculations for reasons of simplicity (Had we employed the VDD by Bickelhaupt et al., the promolecule density would eventually cancel out in the equation $Q = Q_{\text{final}} - Q_{\text{initial}}$). The electron density is computed for each point of interest on the ground and excited state of the potential energy surfaces. The atomic Voronoi charge $Q_{\text{Voronoi}}^{\text{Atom}}$ for all atoms is defined according to eq. (1), which integrates electron density over atom-centered Voronoi polyhedra, and is expressed in units of charge as fraction of the charge of one electron. The $Q_{\text{Voronoi}}^{\text{Atom}}$ charges must be computed separately for the initial and final states to determine the $Q_{\text{VECD}}^{\text{Atom}}$ values for each atom in a photochemical step, according to eq. (2). For emission $Q_{\text{VECD}}^{\text{E}}$ the Voronoi charges at the excited state $S_1$ must then be subtracted from the ground state charges $S_0$ both calculated at the excited state geometry (denoted by superscript E). It is important to recognize that there does not exist a unique set of Voronoi charges at the excited state. In these cases, direct integration of the density difference $\Delta \rho(r)$ in eq. (1) would be an undefined operation, making obvious the use of eq. (2). Finally, for a group of atoms R, the summed Voronoi charge $Q_{\text{VECD}}^R$ is defined by eq. (3).

$$\begin{align*}
Q_{\text{Voronoi}}^{\text{Atom}} &= \int_{\text{Voronoi polyhedra of the atom}} \rho(r) \, dr \\
Q_{\text{VECD}}^{\text{Atom}} &= Q_{\text{Voronoi}}^{\text{Atom, final}} - Q_{\text{Voronoi}}^{\text{Atom, initial}} \\
Q_{\text{VECD}}^R &= \sum_{\text{atom A in R}} Q_{\text{VECD}}^{\text{Atom}}
\end{align*}$$

Method validation

Other methods to calculate PAC, such as Bader,\[^{10}\] Hirschfeld,\[^{11}\] and Mulliken\[^{12}\] charge analyses are also readily obtained with DFT software packages. For arbitrary PAC frameworks, a straightforward extension to excitation charge difference is to subtract the excited state charge for each atom A from that of its ground state. For example, we define Bader excitation charge differences (BECD) as in eq. (4). Other quantities such as $Q_{\text{BECD}}^{\text{Atom}}$ are defined in an analogous manner.

$$Q_{\text{BECD}}^{\text{Atom}} = Q_{\text{Bader}}^{\text{Atom, final}} - Q_{\text{Bader}}^{\text{Atom, initial}}$$

The Bader (BECD), Hirschfeld (HECD), Mulliken (MECD), and Voronoi (VECD) charge differences were compared for vertical transitions of diatomic and other small molecules with varying dipole moments using Dunning’s correlation-consistent polarized basis sets of double, triple, quadruple and quintuple zeta quality, with and without diffuse functions, i.e., cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z).

The results for the $n \rightarrow \pi^*$ excitation of formaldehyde are plotted in Figure 4, showing computed charge as a function of basis set. The $Q_O/Q_C$ ratio is expected to be near unity, because the hydrogen atoms do not participate in the pi-bond affected by this excitation (see also the left panel of Fig. 2). The Mulliken $Q_O/Q_C$ charge ratios are highly dependent on the basis set in accordance with prior observations.\[^9\] The Bader-derived values predict an accumulation of charge on carbon, with $Q_O/Q_C$ ratios fluctuating between 50% and 60%. The Hirschfeld ratios perform better and show a convergence...
to nearly 80%, but the Voronoi QO/QC ratio goes beyond 90% even though its partitioning is arguably the most simple one. The slightly inferior ratio obtained using Hirshfeld may be due to the ‘sharing factor’ that ‘smoothes’ partial charges across neighboring atoms.

The basis set dependency on the entire set of test molecules can be quantified using the standard deviation across all basis sets ($\sigma_A$) for all atoms (A). The sum $\Sigma \sigma_A$ reflects the performance with higher values indicating poorer consistency between basis sets (e.g., for nitrous oxide $\Sigma \sigma_{\text{NNO}} = \sigma(\text{N}_1) + \sigma(\text{N}_2) + \sigma(\text{O})$ where $\sigma(\text{N}_1), \sigma(\text{N}_2), \ldots$ is the standard deviation of $Q^{\text{VECD}}$ over all the used basis sets, for an atom). Figure 5 displays the performance of PACs across the molecules in the test set; a comprehensive table is given in the Supporting Information. Again, the Voronoi charge difference analysis outperforms that of the Hirshfeld analysis. The results are worse on using the Bader approach, with higher basis set dependence for all compounds in the test set. The large standard deviation in this case is possibly due to use of zero-flux surfaces as a basis for spatial partitioning, since these are inherently dependent on the chosen electronic state (Bader analysis has to compute, for every given electron density, the Bader surfaces that partition space into atomic volumes. For Voronoi, every set of Cartesian coordinates has one and only one partitioning that is independent on electron density). Mulliken charges are highly variable and are clearly unsuited for performing the desired charge difference calculations. Due to its superior performance Voronoi-based charge differences are used in the rest of this study.

It is relevant to address the practical aspects of calculating the $Q^{\text{VECD}}$ values. Most quantum chemical software packages give electron densities as voxel files in which a series of volume elements (voxels) describe the density around the molecule. Assignment of subtracted charge density to the nearest neighboring atom is straightforward and entails computing the nearest atom to the position of the current voxel, subtracting the two charge densities, accumulating the resulting number on the nearest nucleus, and advancing one position. A script written in the Python language that performs these

Figure 3. Ground- and excited-state geometries of formaldehyde at B3LYP/aug-cc-pVTZ (top) with atomic $Q^{\text{VECD}}$ charges (bottom) for the $n\rightarrow \pi^*$ excitation-emission cycle. A negative value denotes the rearrangement of electron density toward the nucleus. The non-zero sum of charges are due to rounding errors, see Supporting Information. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 4. Plot of the ratio between accumulated charge on oxygen and carbon as a function of basis set, computed using a subtraction of Voronoi, Bader, Hirshfeld, and Mulliken charges for $n\rightarrow \pi^*$ excitation of formaldehyde. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 5. Effect of various schemes for computing PAC on $\Sigma \sigma_A$ for 14 test molecules, plotted on a logarithmic scale. Larger values indicate a higher basis set dependence. [Color figure can be viewed at wileyonlinelibrary.com]
Voronoi Charge Difference Analysis for Formaldehyde $\pi - \pi^*$ Excitation

We start with formaldehyde and examine the excitation from its non-bonding lone pair centered on oxygen to the $\pi^*$ orbital. A four-step cycle describes the photon absorption, geometry relaxation of the excited molecule, photon emission, and geometrical relaxation on the ground state surface (Fig. 3). For each of these steps the change in charge distribution on every atom was calculated with eqs. (1) and (2).

The computed atomic $Q^{\text{VECD}}$ values concur with the isocontour map of Figure 2, as charge is removed from the oxygen atom-centered lone pair on excitation and returned on emission; the influence from the hydrogen atoms is small because they do not contribute to the $\pi^*$ orbital. A small but relevant charge difference is observed on relaxation of both the excited ($S_1^\ast$) and ground-state ($S_0^\ast$) structures. Clearly, compared to density isocontour plots, the Voronoi Charge Difference method gives a comprehensive analysis of the entire photochemical cycle.

Relaxation-Induced Charge Transfer in Trans-Azobenzene

In contrast to the limited nuclear motion possible in the small and rigid formaldehyde molecule, more significant relaxation-associated nuclear motions are expected when studying compounds with a larger number of degrees of freedom. Such a well-studied chromophore is azobenzene, which famously undergoes reversible photoisomerization from the more stable trans conformer to the cis conformer. Its rich excited state photochemistry has been the cornerstone of molecular designs such as light-driven molecular motors, photochemically controlled molecular switches or design into light-responsive functional materials. Thus, it is of interest to probe the $Q^{\text{VECD}}$ values on the process from photoexcited trans-azobenzene, through an intermediate excited-state geometry, to cis-azobenzene.

The photochemical process under study is based on the assumption that $trans - cis$ isomerization occurs by means of vertical excitation from the ground-state $trans$ geometry to $S_1$, followed by relaxation on the $S_1$ energy surface to an intermediate excited-state geometry, and finally nonradiative decay to the cis-azobenzene ground state geometry.

We have based this pathway, shown in Figure 6, on spectroscopic investigations that conclude that isomerization takes place from the $S_1$ energy surface. As such, probing electron density rearrangement during azobenzene isomerization should initially target the vertical excitation from ground state to $S_1$.

Second, for azobenzene, there are no well-defined energy minima on $S_1$ to which the excited compound can be said to relax, as the $S_1 - S_0$ surfaces have been shown to contain crossing seams and conical intersections via which nonradiative relaxation proceeds directly to ground state cis-azobenzene. Due to these complications, a thorough computational treatment of the isomerization process is beyond the scope of this work. We define an excited state geometry that is intermediate between the two ground state structures by applying some torsion to one of the C-C-N-N dihedral angles (see Fig. 6, top), with the caveat that other intermediate geometries can and probably do exist. This structure is optimized in the $S_1$ excited state using TD-DFT to suitable convergence of energy, density and gradient. Experimental work by Satzger et al.

**Figure 6.** Energy diagram for the excitation–relaxation–nonradiative decay process for trans-azobenzene isomerization to cis-azobenzene (black arrows). Experimental energies taken from literature. Both experimental and (TD)-DFT derived energies are translated to correspond to 0.00 eV at trans-azobenzene, the lowest energy state. The captions shown correspond to the groups of atoms used to tabulate results in Table 1. Dotted red lines indicate the shape of the potential energy surfaces. [Color figure can be viewed at wileyonlinelibrary.com]
serves to validate our computed energies, also showing that the energy of the intermediate conforms to the cis-azobenzene ground state as computed.

Table 1. Computed Q^{VECD} values of each step in the above isomerization process, for the separate nitrogen atoms and summed over each phenyl group, as described for the latter in eq. (3).

| Process step description | Ph₁ | Ph₂ | N₁ | N₂ |
|-------------------------|-----|-----|----|----|
| trans S_{20} to trans S_{cis} | -0.058 | -0.058 | +0.059 | +0.058 |
| trans S_{20} to S_{cis} | +0.206 | -0.129 | -0.019 | -0.059 |
| S_{cis} to cis S_{20} | -0.104 | +0.250 | -0.098 | -0.048 |
| Overall trans to cis | +0.044 | +0.063 | -0.058 | -0.048 |
| cis S_{20} to cis S_{0} | +0.016 | +0.016 | -0.016 | -0.016 |
| cis S_{20} to S_{1} | +0.088 | -0.266 | +0.144 | +0.064 |
| S_{1} to trans S_{0} | -0.148 | +0.187 | -0.040 | -0.000 |
| Overall cis to trans | -0.044 | -0.063 | +0.058 | +0.048 |

[a] Vertical excitation from trans-azobenzene. [b] Relaxation to S_{0}^\text{cis} the excited state intermediate structure as defined in the text. [c] Non-radiative decay to the cis-azobenzene ground state. [d] Process steps for the back-reaction from cis-azobenzene to trans-azobenzene, via an identical excitation-relaxation-decay pathway. Negative values signify net accumulation of electrons.

To quantify the influence of the distance between donor and acceptor on charge transfer in photoactive chromophores, we examine in this section the applicability of Q^{VECD} calculations to increasingly larger linear donor-acceptor dyes and test the conformity of our results to what is expected for such molecules. trans-4-[4-(Dimethylamino)styryl]-N-methylpyridinium iodide (DAMPI, Fig. 7) is a versatile light-absorbing dye used in non-linear optics,[18] spectroscopy,[19] and zeolite morphology research.[20] Two absorption maxima are observed in organic solvents, one around 500 nm and one upwards of 300 nm.[21] The molecular structure suggests push-pull behavior in which electrons move from the aniline moiety to its electron-poor pyridinium group.[22] Fluorescent emission (aqueous solvents) shows a redshift from 470 to 600 nm,[23] suggesting excited-state relaxation behavior.

The cam-B3LYP/cc-pVTZ (COSMO) optimized ground and excited state structures of DAMPI (in DCM) were analyzed by single point TDDFT calculations for the vertical S₀ → S₁ excitation (corresponding to a push-pull, HOMO → LUMO, π → π* transition), relaxation, and emission. A long-range hybrid functional was used to accommodate the excited-state properties of the push-pull chromophore.[24] The Q^{VECD} values are summed into ‘donor’, ‘bridge’, and ‘acceptor’ parts (see color coding in Fig. 7) according to eq. (3), listed in Table 2, and displayed in Figure 8.

The parent DAMPI (n = 1) is indeed a charge transfer chromophore with negative charge being moved from the dimethylamino donor to the N-methylpyridinium acceptor on excitation. The bridge accumulates only 10% of charge on the two olefinic carbons. Subsequent relaxation enhances the charge transfer significantly due to additional polarization of the donor and acceptor sites. The graphical presentation of the Q^{VECD} values for the photochemical cycle in Figure 8 illustrates that relaxation of the excited state maximizes the polarization, which largely reverses on emission and disappears on subsequent relaxation, as it should.
Next, the influence of differently sized bridges ($n = 0, 1, 2, 3$ in Fig. 7) was evaluated for the vertical excitation induced charge transfer from the dimethylaminophenyl donor to the methylpyridine acceptor using cam-B3LYP/cc-pVTZ. To assess the charge transfer efficiency of the DAMPI homologues, we computed the charge transfer vectors $D^{CT}$ according to Ciofini et al. The results show that for every 2.5 Å added to the length of the compound, which is the size of a repeating ethylene unit, the charge transfer distance increases by only ~0.3 Å. This observation concurs with earlier studies on linear donor-acceptor systems where it was found that elongation can decrease the donor-to-acceptor charge transfer efficiency. The $Q^{VECD}$ values for these DAMPI homologues, listed in Table 3, show a decrease in charge transfer on elongation of the olefinic bridge. The transferred charge decreases by 60% on going from $n = 0$ to $n = 3$. We attribute this behavior to increased Coulomb interaction concomitant with the increase in donor-acceptor distance, causing the oligoethylene spacer to become involved in charge transfer as shown for similar linear donor-bridge-acceptor systems. From the $Q^{VECD}$ calculations valuable numerical insights are gained into the magnitude of charge accumulated across the ends of the homologues.

**Electron Transfer in Chromophoric Metallosalphen Compounds**

Finally, in this section we explore $Q^{VECD}$ as a design tool for the preparation of organometallic pigments. Recently, we reported on the synthesis of DAZnS (Fig. 9) as building block for supramolecular light-harvesting architectures. This flat molecule that contains a conjugated naphthalene diimide fused to a Zn$^{II}$-binding tetradentate ‘salphen’ moiety was shown to emit from a singlet excited state on photoexcitation. Supramolecular binding of a fifth ligand to the zinc cation appears to have no effect on the photophysical properties of DAZnS, leading to the conclusion that the metal site serves a purely structural purpose. Replacing the inert d$^{10}$ Zn$^{II}$ cation for other d-block metals of different redox activity may, however, affect the chromophoric properties. We investigate the effect of different metals on the absorption properties using $Q^{VECD}$ calculations.

To this end, we examined the first-row d-block Ni$^{II}$, Fe$^{II}$, Cu$^{I}$, Co$^{II}$, and Co$^{III}$ analogues, having the generic abbreviation DATMS. Their choice was based on the synthetic accessibility of the parent salphen complexes and their $S = 0$ spin state, which also simplifies the TDDFT calculations (see Supporting Information for details). We investigated for each compound the first singlet excitation with non-zero oscillator strength. Table 4 shows the TDDFT-derived orbital configurations of the singlet excitations under study.

Table 4 lists the computed $Q^{VECD}$ charges for the DATMS series as sums of the atomic charge differences (eq. (3)) found on the naphthalene diimide (NDI), phenylene bridge, salphen ligand arms and metal atom (see Fig. 9). They allow for an evaluation of the degree and direction of the charge transfer in the chromophore with respect to the electropositive character of the d-block metal. The three neutral analogues with a formally dicaticonic metal (Fe$^{II}$, Ni$^{II}$, and Zn$^{II}$) have virtually identical properties. The $Q^{VECD}$ charges are accumulated in the NDI unit, ranging from $-0.118$ to $-0.111$, and originate in equal degrees from the salphen and phenylene bridge. Clearly, moving from a d$^{10}$ configuration (Zn$^{II}$) to a low-spin d$^6$ (Fe$^{II}$) has little influence on the magnitude of charge transfer, the absorption wavelength, and the orbital configuration of the optical transition. This indicates that the charge transfer behavior for the neutral compounds is determined by the properties of the organic ligand and not by the metal.

![Figure 8. $Q^{VECD}$ charges on DAMPI donor, bridge, and acceptor groups, for the four steps of the photochemical cycle. Positive values signify net charge depletion and negative ones net accumulation of electrons.](image)

![Figure 9. Molecular structure of DATMS. The shaded areas indicate the grouping of $Q^{VECD}$ charges according to eq. (3). The naphthalene diimide is at the left (green), the bridging phenylene in the middle (blue), and the salphen ligand arms (red) on the right, chelating a metal cation (M; black). Red atoms: oxygen, gray: carbon, blue: nitrogen, black: metal; hydrogen atoms are omitted for clarity.](image)
A different picture emerges for the charged analogues. Comparing the d^{10} anionic DATCuS to DATZnS shows an approximate threefold increase of charge depletion on the salphen ligands (Q^{VECD} = -0.219), and a twofold increase of charge transfer to the electron-accepting NDI moiety (Q^{VECD} = -0.265). The electron transfer for this CuI congener results from excitation from the ligand-based HOMO-1 to the LUMO, which is located at the NDI (similar to DATZnS, see isocontour plots in Fig. 10), showing DATCuS^{-1} as an improved version of the original Zn-containing chromophore.

In contrast, d^{8} anionic DATCoS^{-1} shows negligible charge transfer to the NDI on photoexcitation. Instead, charge is transferred to the salphen ligands (Q^{VECD} = -0.091) and removed from the metal atom (Q^{VECD} = +0.112). As the MLCT state does not extend appreciably past the salphen arms it appears that the more electropositive CoI is not capable (like CuI) of donating to the NDI’s LUMO. Here, numerical analysis using Q^{VECD} allows to precisely pinpoint the results of substituting the parent compound with a less electronegative metal.

Remarkably, cationic d^{6} compound DATCoS^{+1} shows a complete reversal of the photodriven charge transfer, namely from the NDI (Q^{VECD} = +0.125) to the salphen (Q^{VECD} = -0.140; see also Fig. 10). The ligand-to-metal charge transfer concurs with the expected behavior for electropositive metals. This umpolung of the NDI redox chemistry, where the usually electron-demanding NDI is changed from a reductor to an oxidant, is in line with literature reports that show the use of an NDI as cation sensor capable of undergoing one-electron reduction.[28]

The directionality of charge transfer is clear: the electron-rich metal complexes transfer charge away from the metal, whilst the electron poor CoII complex transfers charge toward the metal. Using Voronoi charge differences, these qualitative descriptions can be assigned a numerical quantity, which will clearly be of benefit to exploratory and explanatory molecular research.

**Conclusions**

The presented method that makes use of atom-centered Voronoi polyhedra to calculate charge differences for photoinduced excitations and emissions provides an easily obtainable, novel, and relevant quantity to describe charge transfer processes at the atomic level. Because electron charge is integrated over atomic volumes before subtracting the initial state properties from the final state properties, both vertical processes and those that incur geometrical changes can be assessed using the Q^{VECD} formalism.

There is a direct correspondence of Q^{VECD} values with the well-known, intuitive but strictly qualitative electron density isocontour plots, as showcased for formaldehyde. For a series of donor-bridge-acceptor chromophores, Q^{VECD} values are shown to be consistent with existing methods of assessing photodriven charge transfer. Computation of the Voronoi excitation charge difference can be employed as a design tool to optimize charge transfer processes, as shown for a series of chromophoric metal complexes. By quantifying the amount of...
charge moving across the donor-acceptor axis of the molecule, direct comparison across a homologous series of compounds is possible. We believe this to be an excellent example of the value of QVECD calculations as a design tool for photoactive organic compounds. Furthermore, the calculations add quantitative insight to the qualitative description available through MO theory.

The chosen Voronoi partitioning scheme is density-independent, that is, the obtained atomic volumes depend only on atomic coordinates and not on the DFT-derived electron density. As such, this method is expected to be equally applicable to processes in singlet, triplet or open-shell systems, which is a topic for future study.

In reflecting on the Bader versus Voronoi approach, we note that Tognetti and Joubert et al. have shown that charge transfer vector (DCT and DFT) calculations based on integration over Bader volumes are much improved on taking into account the positive atomic charge Z. For our QVECD calculations on vertical processes, Z would simply vanish from the equation, but changes in geometry cause changes in integrated volumes. Hence, the role of atomic dipoles in QVECD calculations on processes with changing nuclear positions is an intriguing topic for further study.

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Keywords: time-dependent density functional theory · atomic charges · charge analysis · molecular design

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Additional Supporting Information may be found in the online version of this article.

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