

Optimal Transport Distances to Characterize Electronic Excitations

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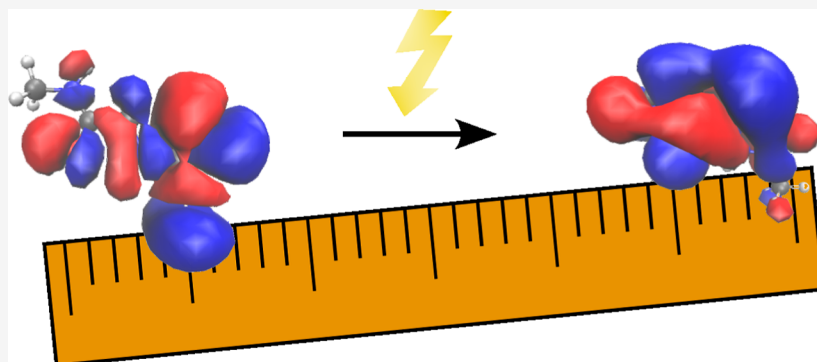
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ABSTRACT: Understanding the character of electronic excitations is important in computational and reaction mechanistic studies, but their classification from simulations remains an open problem. Distances based on optimal transport have proven very useful in a plethora of classification problems and, therefore, seem a natural tool to try to tackle this challenge. We propose and investigate a new diagnostic Θ based on the Sinkhorn divergence from optimal transport. We evaluate a k -NN classification algorithm on Θ , the popular Λ diagnostic, and their combination, and assess their performance in labeling excitations, finding that (i) the combination only slightly improves the classification, (ii) Rydberg excitations are not separated well in any setting, and (iii) Θ breaks down for charge transfer in small molecules. We then define a length-scale-normalized version of Θ and show that the result correlates closely with Λ for results obtained with Gaussian basis functions. Finally, we discuss the orbital dependence of our approach and explore an orbital-independent version. Using an optimized combination of the optimal transport and overlap diagnostics together with a different metric is in our opinion the most promising for future classification studies.

1. INTRODUCTION

Electronic excitations drive various processes, for example, in light harvesting or solar cells, which are important in the exploration of alternative energy sources.^{1,2} There is consequently significant theoretical interest in calculating excited states and their energies, which could then be used to drive nonadiabatic dynamics and design novel materials. However, excited state calculations are computationally expensive problems, and various approximations have been introduced to obtain solutions at lower costs. Similar to the ground state problem, methods based on density functional theory (DFT) have become highly popular as they come at a relatively low computational cost but have a solid theoretical foundation, except for approximations that have to be made to the density functional.³ Despite decades of effort, there is no “one-fits-all” density functional.⁴ In particular, for electronic excitations in time-dependent DFT (TDDFT),⁵ where transition energies are calculated within the linear response setting, it has become clear that a functional’s performance can depend heavily on the character of the excitation.⁶

This is one of the main motivations behind exploring diagnostics that split TDDFT-calculated excitations into

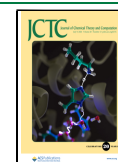
different types,^{7,8} of which there are three. First, Rydberg excitations to energetically high lying and diffuse Rydberg states. Second, charge-transfer (CT) excitations from a donor to an acceptor, which is spatially separated from the donor, either within the same molecule (intramolecular) or in different molecules (intermolecular). CT excitation can carry especially large errors in TDDFT calculations.⁶ The third group is local excitations, which encompass excitations that fit neither of the other two categories. With a classifier, one can decide a posteriori whether the chosen density functional was suitable and if not, repeat the calculation with a higher-level functional. However, such a classification might prove useful beyond picking the right functional. Assigning a label to a new excitation can be a very tedious process, during which one relies on chemical intuition or has to inspect wave functions

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and/or localized orbitals visually. With a quantitative method to decide on the character of the excitation, this step could be extremely simplified.⁹

To this end, Peach et al. took advantage of the decomposition of an electronic excitation into single orbital transitions within the TDDFT framework and studied a weighted average of the overlap between initial and final orbitals.⁷ While they did not establish a classification of excitation types, they showed a correlation between their overlap diagnostic and the associated error in excitation energy. The same trends have been observed in other systems and the overlap diagnostic has been widely applied since its introduction.^{10–12} In a similar spirit, Guido et al. studied the difference between the electron's centroid in the initial and final orbitals within a single orbital transition.¹³ The centroid difference is better able to differentiate between CT and valence excitations than the overlap diagnostic, although they stress that the best results were obtained when using them in combination.

An alternative interpretation of electronic excitations is via the formation of an electron–hole pair (the exciton). The resulting exciton formalism opens the door for a multitude of other descriptors like the distance between electron and hole, d_{he} , the electron/hole sizes, σ_e/σ_h , respectively, and the size of the exciton d_{exc} . All have been used to characterize excited states^{8,14} and the overlap diagnostic has been combined with d_{he} and d_{exc} for classification.⁵

Going back to a density picture in the TDDFT framework, Moore et al. consider the modulus of the change in electron density between the initial and final orbitals, which they argue is better suited for a classification.¹⁵ However, this diagnostic suffers from a similar problem as the overlap: If the sets of points where the initial and final orbitals are nonzero, which will also be referred to as their “supports”, become disjoint, there is a plateau value for both of them, and they are agnostic to any variations in the orbitals beyond that point.

In this work, we seek to improve the classification of excitations by considering optimal transport properties of electron densities, which promise to avoid the plateau problem. The paper is structured as follows. After laying out the necessary theory on TDDFT and optimal transport in Section 2, we cover the computational details in Section 3. In Section 4, we present the results, both confirming previous studies on the overlap diagnostic and new results using descriptors from optimal transport. Finally, we summarize our findings in Section 5 and propose future directions.

2. THEORY

2.1. TDDFT and the Λ Diagnostic. The Kohn–Sham (KS) ground state for an N -electron system is a Slater determinant

$$\Psi_s(\mathbf{x}_1, \dots, \mathbf{x}_N) = \mathcal{A} \prod_{i=1}^N \varphi_i(\mathbf{x}_i) \quad (1)$$

where \mathcal{A} antisymmetrizes and normalizes the wave function, \mathbf{x}_i is the space-spin coordinate of the i th electron, and φ_i is the i th KS orbital.³ The orbitals are solutions to the (time-independent) KS equations¹⁶

$$\left[-\frac{1}{2} \Delta + v_s(\mathbf{r}) \right] \varphi_i(\mathbf{x}) = \varepsilon_i \varphi_i(\mathbf{x}) \quad (2)$$

The ground state is composed of KS orbitals φ_i with the lowest energies ε_i (the occupied orbitals). Excited states within linear-response TDDFT are linear combinations of Slater determinants with single orbital excitations into previously unoccupied (or virtual) orbitals φ_a .⁵ The excitation energy and the contribution of a single orbital transition can be determined in the linear response picture by solving the Casida equations¹⁷

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \Omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \quad (3)$$

The eigenvalues Ω are the excitation energies and the eigenvectors X , Y contain the excitation and de-excitation amplitudes, respectively. Although eq 3 looks simple, the entries of A and B depend on the exact ground state of the system as well as on the exact form of the exchange correlation functional. Neither of these is currently attainable, but there are various approximations to the exchange–correlation functional with which excitation energies can be obtained.¹⁸ However, TDDFT excitation energies can vary greatly in accuracy between different excitation characters and between different functionals.⁶

It is generally difficult to assign one of the labels “CT”, “local”, or “Rydberg” to a given electronic excitation. Peach et al. investigated energy errors in electronic excitations based on the overlap of the single orbital transitions⁷

$$\Lambda = \frac{\sum_{i,a} c_{ia} \langle |\varphi_a| |\varphi_i| \rangle}{\sum_{i,a} c_{ia}} \quad (4)$$

where $c_{ia} = X_{ia}^2 + Y_{ia}^2$ is the contribution of the excitation $\varphi_i \rightarrow \varphi_a$ and $\langle |\varphi_a| |\varphi_i| \rangle$ is the overlap of the (modulus of the) orbitals. They studied a set of 11 molecules with the PBE, B3LYP, and CAM-B3LYP functionals and evaluated Λ for a total of 59 excitations. While Λ gives some insights into the expected error magnitude for different DFT functionals, it is not possible to distinguish between the different excitation types without prior knowledge: Though the Λ values of local and Rydberg excitations are well separated, CT excitations fall across almost the whole range of Λ . Hence, one cannot make conclusions about the excitation type based on Λ alone. Optimal transport might be able to help.

2.2. Optimal Transport Diagnostic. At the heart of optimal transport lies the problem of finding a plan to transport a source probability density into a target probability density.¹⁹ Imagine a pile of soil next to a hole in the ground. With a wheelbarrow, one can—with some physical effort—carry the soil over and fill the hole. When the hole is entirely filled, the total work that was necessary is the invested “cost”. For this process, the optimal transport problem would be to plan the wheelbarrow transport so as to minimize the work. As we will be looking at electronic orbitals $\varphi_{i,a}$, it is only natural to use the probability densities $\rho_{i,a} = |\varphi_{i,a}|^2$. The (entropically regularized) optimal transport problem is²⁰

$$\begin{aligned} W_{2,\varepsilon}^2(\rho_i, \rho_a) = & \min_{\pi \in \Pi(\rho_i, \rho_a)} \int_{\mathbb{R}^3 \times \mathbb{R}^3} c(\mathbf{r}, \mathbf{r}') \pi(\mathbf{r}, \mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \\ & + \varepsilon \text{KL}(\pi | \rho_i \otimes \rho_a) \end{aligned} \quad (5)$$

where c is called a cost function, $\Pi(\rho_i, \rho_a)$ is the set of joint probability densities π with marginals ρ_i and ρ_a

$$\int_{\mathbb{R}^3} \pi(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = \rho_i(\mathbf{r}) \quad \int_{\mathbb{R}^3} \pi(\mathbf{r}, \mathbf{r}') d\mathbf{r} = \rho_a(\mathbf{r}') \quad (6)$$

and we use the regularized optimal transport problem with the Kullback–Leibler divergence

$$\begin{aligned} \text{KL}(\pi|\nu) &= \int_{\mathbb{R}^3 \times \mathbb{R}^3} \pi(\mathbf{r}, \mathbf{r}') \log \frac{\pi(\mathbf{r}, \mathbf{r}')}{\nu(\mathbf{r}, \mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\ &+ \int_{\mathbb{R}^3 \times \mathbb{R}^3} (\nu(\mathbf{r}, \mathbf{r}') - \pi(\mathbf{r}, \mathbf{r}')) d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (7)$$

for computational efficiency.²⁰ Because of the entropic regularization, eq 5 can unintuitively be nonzero even if the orbitals φ_i and φ_a are identical, which can be fixed by defining the Sinkhorn divergence²¹

$$S(\rho_i, \rho_a) = \mathcal{W}_{2,\varepsilon}^2(\rho_i, \rho_a) - \frac{1}{2} [\mathcal{W}_{2,\varepsilon}^2(\rho_i, \rho_i) + \mathcal{W}_{2,\varepsilon}^2(\rho_a, \rho_a)] \quad (8)$$

which will therefore be used from here on. The Sinkhorn divergence S has the same units as the cost function c . Depending on the application, different cost functions are appropriate. Here, we will always use the squared Euclidean cost, $c(\mathbf{r}, \mathbf{r}') = \|\mathbf{r} - \mathbf{r}'\|^2$, for which S has units of length squared. Note that π has units of length⁻⁶, since it is a joint probability density of two position vectors. ε also needs to have the same units as c , since the Kullback–Leibler divergence is dimensionless.

Figure 1 motivates the use of the Sinkhorn divergence to study electronic excitations: Consider the case where the target

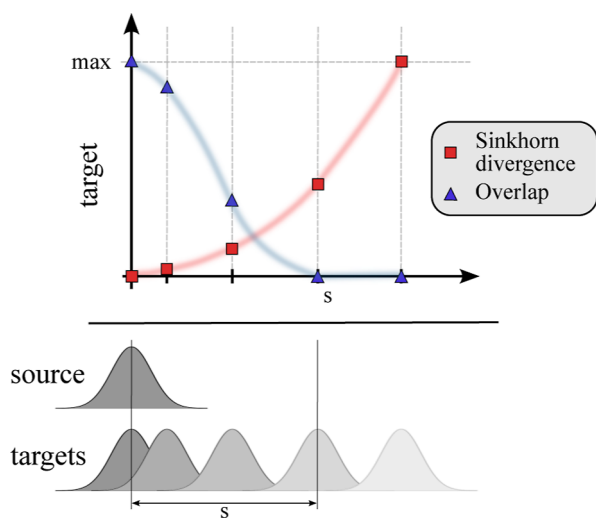


Figure 1. (Qualitative) demonstration of overlap measurements and the Sinkhorn divergence when studying translations, here for Gaussian source and target densities.

density (ρ_a in eq 5) is a translation of the source density ρ_i . This could be a crude model of CT with an increasing number of linker fragments between the donor and acceptor, for which Mewes and Dreuw have already found a linear dependence of exciton-based diagnostics.¹⁴ As soon as the supports of source and target density become disjointed, the overlap is zero and stays zero for any larger translations. It is in that sense blind to translations above some threshold, and Λ will tend toward zero. The optimal transport-derived quantities are expected to behave very differently. If the regularization parameter ε goes

to 0, the squared Wasserstein distance $\mathcal{W}_{2,0}^2$ would be quadratic in the displacement. While the Sinkhorn divergence S overestimates the Wasserstein distance, it should behave similarly for a small enough ε .

The Sinkhorn divergence's sensitivity for translations motivates us to propose a new diagnostic

$$\Theta = \frac{\sum_{i,a} c_{ia} S(\rho_i, \rho_a)}{\sum_{i,a} c_{ia}} \quad (9)$$

with the single orbital contribution c_{ia} as in eq 4.

3. COMPUTATIONAL DETAILS

We calculated Λ and Θ for the same set of molecules as studied by Peach et al. because their data set includes many examples of the three different excitation types.⁷ The set includes the four small molecules N_2 , CO, HCl, and formaldehyde, five larger molecules [dipeptide, β -dipeptide, tripeptide, *N*-phenylpyrrole, and 4-(*N,N*-dimethylamino)-benzotrile], and conjugated polymer systems: acenes (1–5 monomers) and polyacetylene (PA) oligomers (2–5 monomers), all of which are shown in Figure S1. Calculating Λ allowed us to verify our data before studying the new diagnostic Θ . Electronic excitation energies were calculated with Turbomole,²² using the *d*-aug-cc-pVTZ basis set for N_2 , H_2CO , and CO and the cc-pVTZ basis set for the remaining molecules.^{23–27} The SCF convergence threshold was 10^{-7} and the multiple grid m3 was used for the DFT calculation.²⁸ At the end of a converged TDDFT calculation, Turbomole prints a list of single orbital contributions c_{ia} (for $c_{ia} > 0.05$) and the involved orbitals, which can be obtained on a grid. The grid data is then used to calculate Λ by numerical quadrature and Θ with the geomloss package (version 0.2.5).²⁹ In order to calculate Sinkhorn divergences, the orbital grids have to be chosen large enough to contain all electronic density (in practice, we chose the grids big enough to contain at least 99% of the density). We used an equidistant grid with a spacing of 0.8 bohr for all molecules.

In order to gain some quantitative understanding of the degree of separation into excitation types, we use a *k*-nearest neighbor classifier. The data points are first separated into a training and a test set. For each point in the test set, we consult the excitation type of its *k*-nearest neighbors in the training set. The data point is then labeled with the excitation type that the most neighbors belong to. Here, the $k = 13$ nearest neighbors are consulted, which corresponds approximately to the square root of the training set size. Contrary to other learning algorithms, there is no iterative training procedure since the training set does not change.

4. RESULTS AND DISCUSSION

4.1. Data Set. The calculated excitation energies and Λ and Θ values are available in the Supporting Information. The energies and Λ s agree very well with previously reported values except for the PBE excitation in the third PA oligomer, where our Λ s seem swapped, and the CAM-B3LYP $D^1\Delta$ and $I^1\Sigma^-$ excitations in CO, where our Λ s are much smaller in the Turbomole results. In the other cases, any deviations are likely due to differences between different quantum chemistry programs, different grids, or different convergence thresholds for the SCF iterations.

4.2. Optimal Transport Results. The regularization parameter ϵ in eq 5 is determined based on the maximum value of the cost function d_{\max}

$$\epsilon = 10^{-\sigma} d_{\max} \quad (10)$$

with integer σ . In order to determine a suitable σ , we calculated Θ for the dipeptide and N_2 molecules at different σ , the results of which are included in the Supporting Information (Table S1). These molecules have drastically different grid sizes and are therefore good edge cases to test σ . For $\sigma = 4$, Θ is captured to within 2% of its true value, which is sufficient for the purpose of this article and was therefore used in all further calculations.

To start, we compare both Θ and Λ with the error in the electronic excitation energy (Figure 2), analogously to Figure 2

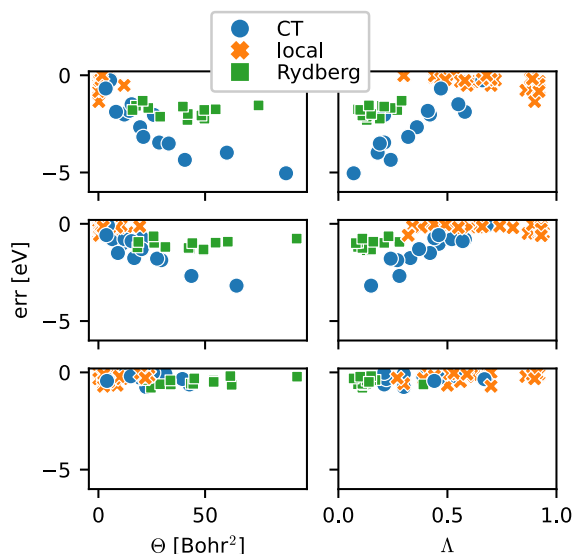


Figure 2. Comparison of Θ (left) and Λ (right) with the error in excitation energy. From top to bottom, the TDDFT functionals are PBE, B3LYP, and CAM-B3LYP.

in ref 7. The two diagnostics exhibit opposite trends: Θ increases, while Λ decreases with the excitation error. Furthermore, Θ is generally large for Rydberg excitations and small for local excitations. The inverse is true for Λ , which we can reason as follows: In Rydberg excitations, the electron is excited to a very diffuse and highly delocalized orbital. On the one hand, it will only have very small density within the support of the initial orbital and Λ is small. On the other hand, in order to satisfy the marginals, the transport plan π will have nonzero entries far away from its diagonal, resulting in a large Θ . In contrast, local excitations have a high overlap between the initial and final orbitals, which results in a large Λ . Simultaneously, little overall density has to be transported over a small distance, and therefore Θ will be small.

Turning our attention to CT excitations, we note that, contrary to our expectations, the CT Θ values lie between Rydberg and local values, similar to the Λ values. This makes both Λ and Θ unlikely to be suitable classifiers, which is also apparent from the results of a k -nearest neighbors classifier trained using either Θ or Λ (Figure 3, first two panels): The Λ classifier (Figure 3a) performs well for both local and Rydberg excitations but labels almost all CT excitations wrong. The Θ classifier (Figure 3b) performs better for CT excitations but is

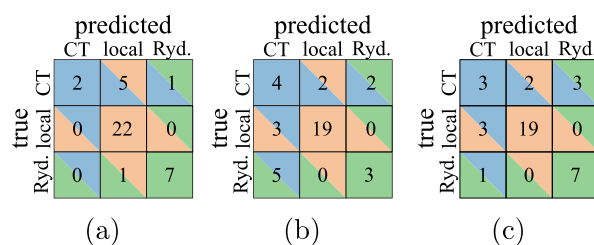


Figure 3. Confusion matrix of a k -NN classification using Λ only (a), Θ only (b) and both (c). A cell in the i th row and j th column gives the total number of points in group i that was classified as group j . Hence, the diagonal elements are all correctly identified data points.

worse for the other excitation types. It should be noted that we are trying to classify imbalanced data, as our data set contains significantly more local excitations than CT or Rydberg ones, which might incur additional errors. However, it is clear from Figure 2 that even imbalanced learning would not produce a very good classifier: The CT excitations are simply too spread out to allow for this.

Instead, we could take advantage of the opposite trends of Θ and Λ and train a classifier on the joint Θ and Λ values. Its confusion matrix is shown in Figure 3c. The two-dimensional classification can only partially recover the advantages of each of the one-dimensional classifiers: It is as good as the Λ classifier for Rydberg excitations and as good as the Θ classifier for local excitations (therefore worse than if we were to use Λ) and lies between the other classifiers for CT excitations.

To understand better why, let us consider the regions of overlap of CT excitations with local and Rydberg excitations, respectively. Rydberg and CT excitations might be difficult to distinguish with the diagnostics used here because there is a property that is completely ignored: diffusivity. We do not have the ability to discern an excitation into a diffuse orbital from an excitation into a translated orbital. Additional metrics that can identify Rydberg orbitals, such as the average distance of the electron to the center of the molecule or higher-order moments, might provide a better classification in combination with Θ . In the same spirit, Hirose et al. previously used a combination of Λ and the electron–hole distance relative to the exciton size to classify excitations.⁹

One good example of coinciding CT and local excitations are the CT excitations in the HCl molecule. Since the excitations only take place across one hydrogen–chloride bond, the associated Sinkhorn divergences are very small (Θ on the order of 4 bohr²) and similar to typical Θ values for local excitations in the same molecule. This is in fact not the only molecule where CT excitations are associated with surprisingly low values of Θ but rather a common situation that occurs in all molecules with CT excitation considered here.

We have now pointed out multiple times that there are opposite trends in Θ and Λ . For two Gaussian densities with the same variance, there is even an explicit relation between them

$$\log \Lambda + \frac{\Theta}{4\sigma^2} = C \quad (11)$$

with a constant C , which motivates us to define a new optimal transport diagnostic where the Sinkhorn divergence is normalized by the variance of the electron position

$$\Theta' = \frac{1}{\sum_{i,a} c_{ia}} \sum_{i,a} c_{ia} \frac{S(\rho_i, \rho_a)}{\sqrt{\langle r^2 \rangle_i \langle r^2 \rangle_a}} \quad (12)$$

with

$$\langle r^2 \rangle_x = \int_{\mathbb{R}^3} r^2 \rho_x \, d\mathbf{r} \quad (13)$$

and we have assumed that the center of the molecule lies at the origin. Note that Θ' is now dimensionless. Plotting the new Θ' against $\log \Lambda$ (Figure 4) reveals a close correlation between

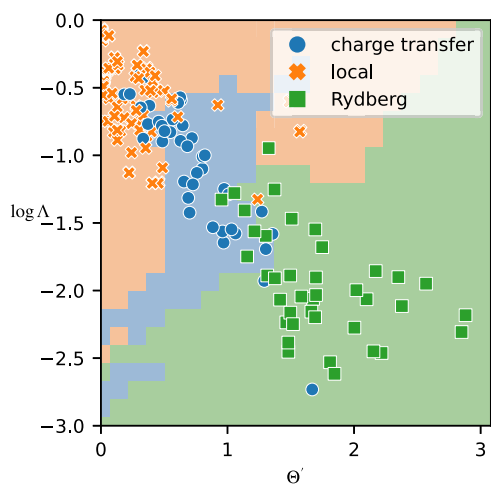


Figure 4. Combined plot of Θ' and $\log \Lambda$ for the present set of excitations. The background colors correspond to the boundaries from a k -NN classification.

the two, which confirms that they capture the same information. Note that Turbomole uses Gaussian basis sets, which may have an influence on the striking correlation in Figure 4 and we reserve the study of other basis functions for future work.

Figure 5 shows the confusion matrices for k -NN classifiers trained on the $\Theta' - \log \Lambda$ data set. While the $\log \Lambda$ classifier

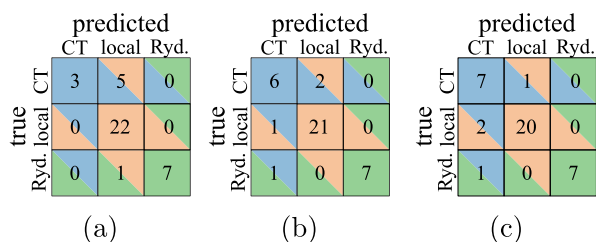


Figure 5. Confusion matrix of a k -NN classification using $\log \Lambda$ only (a), Θ' only (b), and both (c). For an explanation of the confusion matrices, see the caption of Figure 3.

(Figure 5a) does not improve significantly on the Λ classifier (Figure 3a), we see a much better performance of the Θ' classifier (Figure 5b) on Θ (Figure 3b). Again, the combination does not seem to offer much additional improvement, but the current data set is too small to allow for quantitative conclusions.

4.3. Orbital Dependence. Λ , Θ , and Θ' are calculated from the Kohn–Sham orbitals obtained in the DFT calculation. These orbitals are not always useful to assess electronic excitations, as they can be significantly delocalized

over the system. Up to now, we followed the same strategy used for the Λ diagnostic in order to have a straightforward comparison. However, modern developments have focused on natural transition orbitals, which give a physically more reasonable picture of the excitation on an orbital level,³⁰ on densities and density matrices, where orbital dependence is avoided altogether,^{31–33} and on the exciton formalism.^{9,32,34,35} The difference between orbital- and density-based descriptors has also been discussed elsewhere.³⁶ In particular, Savarese et al. conclude that natural transition orbitals are much better suited for CT diagnostics than molecular orbitals.³⁶ We next briefly discuss some of these newer developments.

For the ground and excited state densities, ρ_0 and ρ_X , respectively, Le Bahers et al. consider the density variation associated with a specific excitation³¹

$$\Delta\rho = \rho_X - \rho_0 \quad (14)$$

Positive values of $\Delta\rho$ correspond to an increment in density upon excitation, and negative values correspond to a depletion. They define a measurement for the CT length, D_{CT} , as the difference between the barycenters of the positive and negative part of $\Delta\rho$. Furthermore, they define the spread of the regions associated with positive and negative changes in the density variation and combine them with D_{CT} to find a diagnostic for the breakdown of lower-level TDDFT functionals in CT excitations.

Alternatively, we can start from the density matrices $\hat{\rho}_0$ and $\hat{\rho}_X$ of the ground and excited state. We follow Etienne et al. in defining the difference matrix³³

$$\hat{\Delta} = \hat{\rho}_X - \hat{\rho}_0 \quad (15)$$

If the excited state consists of singly excited Slater determinants, the difference matrix is block-diagonal with an occupied–occupied and a virtual–virtual block.³⁷ The detachment density matrix $\hat{\Gamma}$ corresponds to the occupied–occupied block and the attachment density matrix $\hat{\Lambda}$ to the virtual–virtual block.³⁷ From these density matrices, we can define the attachment and detachment densities

$$\rho_\tau(\mathbf{r}) = \sum_{\mu,\nu} \hat{\tau}_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu^*(\mathbf{r}) \quad (16)$$

where $\tau = \Gamma, \Lambda$. Etienne et al. define the overlap of the attachment and detachment densities

$$\phi_S = \mathfrak{D}^{-1} \int_{\mathbb{R}^3} \sqrt{\rho_\Gamma(\mathbf{r}) \rho_\Lambda(\mathbf{r})} \, d\mathbf{r} \quad (17)$$

where $\mathfrak{D} = \frac{1}{2} \int_{\mathbb{R}^3} \sum_{\tau \in \{\Lambda, \Gamma\}} \rho_\tau(\mathbf{r}) \, d\mathbf{r}$ and show that they can make similar conclusions as for the Λ diagnostic but with the benefit of orbital independence.³³

Since the attachment and detachment densities hold the same mass, it is straightforward to apply our optimal transport formalism. We simply evaluate the Sinkhorn divergence for the attachment and detachment densities, for which our diagnostic can be written as

$$\Theta' = \frac{S(\rho_\Lambda, \rho_\Gamma)}{\sqrt{\langle r^2 \rangle_\Lambda \langle r^2 \rangle_\Gamma}} \quad (18)$$

Note that, if the attachment and detachment densities have the same overall shape, the Sinkhorn divergence would reduce to the distance between the centroids of the densities (for

small enough ε) and would be closely related to D_{CT} . In Figure 4, we compared Θ' to the overlap-based Λ . In a similar spirit, we compare Θ' to ϕ_S in the context of densities (see Figure 6).

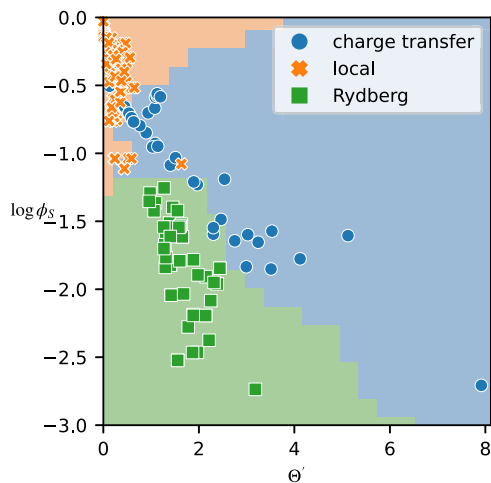


Figure 6. As Figure 4 but for Θ' and ϕ_S calculated for attachment and detachment densities.

Compared to those in Figure 4, the CT and Rydberg excitations are clustered very differently, showing the orbital dependence of our previous results. At the same overlap value, the Sinkhorn divergence is larger for CT excitations than for Rydberg excitations, leading to a diagonal separating plane, whereas in Figure 4, the CT excitations were squeezed between the other two regions. The improved separation between the excitation types is also reflected in the associated confusion matrix (Figure 7), where we reach a near perfect classification.

		predicted		
		CT	local	Ryd.
true	CT	6	1	0
	local	1	23	0
	Ryd.	1	0	5

Figure 7. Confusion matrix of a k -NN classification using $\log \phi_S$ and Θ' for attachment and detachment densities. For an explanation of the confusion matrices, see the caption of Figure 3.

In future work, Θ' should therefore be applied either in the manner of eq 18 or in the manner of eq 12 but with natural transition orbitals. Both of these strategies mitigate the extent of orbital dependence.

In Figure 6, there are still data points that lie close to the boundary between the excitation types. In particular, in these boundary cases, it is sensible to think of these diagnostics as measuring the extent of an excitation character rather than assigning a definite label. In such cases, it may be useful to introduce a fractional decomposition into excitation characters. We can now also question the labels in our data set based on the results in Figure 6. For example, the 1B_1 excitation in formaldehyde ($\Theta' = 1.6$, $\log \phi_S = -1.0$) is labeled as a local excitation in our data set but clearly lies in the CT labeled region, an indication that the excitation carries significant CT character.

Finally, let us touch on diagnostics derived from the exciton formalism. The electron and hole sizes from the exciton formalism are useful to analyze Rydberg states.³⁴ Furthermore, the exciton size d_{exc} has been shown to be large for CT and Rydberg excitations.³² d_{exc} also works well for centrosymmetric molecules,³⁵ which have proven challenging for other diagnostics like the electron–hole distance d_{eh} and the CT length D_{CT} .^{9,31} It can be expected that optimal transport diagnostics would also struggle with centrosymmetric molecules.

5. CONCLUSIONS

There is currently no reliable way to classify electronic excitations into CT, Rydberg, and local excitations. In this report, we studied two diagnostics, the overlap-based Λ ⁷ and the optimal-transport-based Θ and their combination to classify an electronic excitation via its k -nearest neighbors. There are strengths and issues in both Λ and Θ , and their combination gives a compromise, but it still does not give a viable classifier. We argued that CT excitations can be similar to local excitations in Θ and Λ if the donor and acceptor are close together, especially in small molecules. We further argued that Θ and Λ cannot distinguish between CT and Rydberg excitations because neither of them captures the diffusivity of the final orbital in a Rydberg excitation.

We then showed that there is a relation between $\log \Lambda$ and a modified diagnostic Θ' , which is a length-scale-corrected version of Θ . The combination of Θ' and $\log \Lambda$ gives the best classifier explored in this work which is purely based on KS orbitals, but more studies are necessary into whether Θ' is also a sensible diagnostic in programs that use non-Gaussian orbitals. We also discuss the orbital dependence in Θ' and propose a density-matrix-based version, which compares attachment and detachment densities. We compare this modification to the overlap between the two densities³³ and observe a very different clustering of the data points which leads to a significant improvement in the classification. This suggests that the orbital choice has a significant impact. In future work, we also want to compare Θ' diagnostics with other modern CT diagnostics,^{8–10,13–15,31,32,34,35} to learn more about its strengths and weaknesses. Modern diagnostics will additionally help in the differentiation between CT and Rydberg excitations.

While this work was being finalized, a study that shares similar ideas has appeared.³⁸ The study focuses on the density difference defined in eq 14 and looks at the optimal transport between the regions of density depletion ($\Delta\rho < 0$) and density enhancement ($\Delta\rho > 0$). We reach similar conclusions, but we have also key differences, like the use of the entropic regularization to accelerate calculations and a different look at possible classifications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.4c00289>.

Molecules considered here, convergence of Θ with the regularization parameter σ , and link to a GitHub repository (PDF)

Data needed to reproduce the results here (XLSX)

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Notes

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