Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information: Density-based descriptors and exciton analyses for visualizing and understanding the electronic structure of excited states

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1 Electron-hole correlation plots of first five singlet excited states of *para*-Nitrodimethylaniline

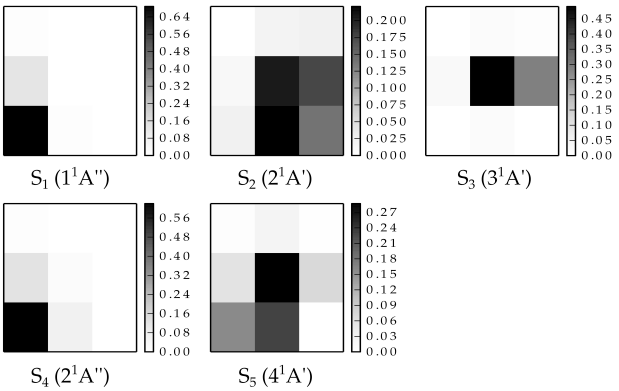

Figure 1: Electron-hole correlation plots of S_1 to S_5 of *para*-nitrodimethylaniline calculated at the ADC(2)/6-311G(d,p) level of theory.

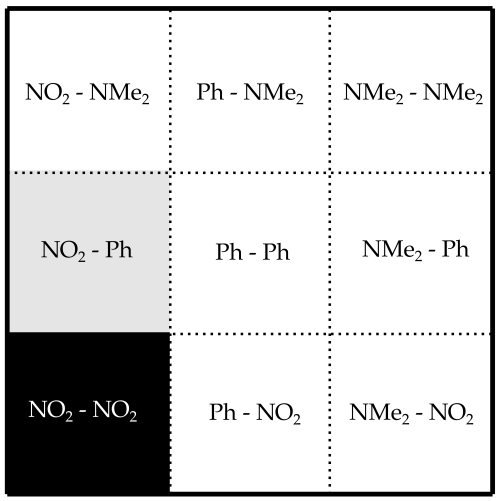

Figure 2: Explanatory electron-hole correlation plot of S_1 of *para*-nitrodimethylaniline: Electron density is shifted between fragments in terms of donor - acceptor scheme as indicated in the boxes with probability given in grey scale.

2 Definitions of excited-state descriptors

2.1 Analysis of detachment and attachment densities

In the following, the basic equations and concepts underlying the descriptor ζ designed by Etienne *et al.* are reviewed.[1] The approach is built upon the detachment and attachment density matrices Γ and Λ. First, the overlap between detachment and attachment densities computed from detachment and attachment density matrices Γ,Λ is obtained by integrating over all three spatial coordinates ξ and the index ϕ_S is defined as

$$\phi_S = \vartheta^{-1} \int_{R^3} d^3\xi \sqrt{\varrho_\Gamma(\xi)\varrho_\Lambda(\xi)}; \tag{1}$$

$$\vartheta \equiv \frac{1}{2}\left[\int_{R^3} d^3\xi \sum_{\tau=\Gamma,\Lambda} \varrho_\tau(\xi)\right], \tag{2}$$

where $\varrho_{\Gamma,\Lambda}$ are the detachment and attachment densities. The index ϕ_S ranges between 0 and 1, and quantifies the amount of charge-transfer character of the electronic transition.

In order to measure the distance between the charge centroids, the individual attachment/detachment density centroid coordinates ζ_i^τ with $i = x, y, z$ are determined as

$$\zeta_i^\tau = \vartheta_\tau^{-1} \int_{R^3} d^3\xi \varrho_\tau(\xi)\xi_i \quad \tau \equiv \Gamma, \Lambda. \tag{3}$$

Hence, the intercentroid distance ζ can be calculated as

$$\zeta = \left(\sum_{i=\{x,y,z\}} (\xi_i^\Lambda - \xi_i^\Gamma)^2\right)^{1/2} \tag{4}$$

In general, ζ is a measure for the amount of charge-transfer character of an excited state and referres to the Hilbert space.

2.2 Analysis of difference densities

A derivation of the descriptor D_{CT} developed by Le Baher, Adamo and Ciofini[2] is reviewed in the following: First, the difference density between excited (ES) and ground state (GS) is calculated according to

$$\Delta\rho(r) = \rho_{ES}(r) - \rho_{GS}(r) \tag{5}$$

This quantity is split into negative and positive contributions, where ρ^+ corresponds to an increase in density and ρ^- a density decrease upon excitation

$$\rho^+ = \begin{cases} \Delta\rho(r), & \text{if } \Delta\rho(r) > 0 \\ 0, & \text{if } \Delta\rho(r) < 0 \end{cases} \tag{6}$$

and the charge centroids (R^+, R^-) can be calculated as

$$R^+ = \left(x^+, y^+, z^+\right) = \frac{\int r\rho^+(r)dr}{\int \rho^+(r)dr}\,. \tag{7}$$

The distance between the charge centroids can then be calculated according to

$$D_{CT} = \left|R^+ - R^-\right| \tag{8}$$

The densities used to calculate the difference density can be either relaxed (${}^{R}D_{CT}$) or unrelaxed (${}^{U}D_{CT}$) yielding two different descriptors.

3 Data of Figures 4 and 7

Excitation energies and electron-hole separation, exciton sizes and correlation coefficients of α-$(NMe_2)\omega(NO_2)(phenylene)_n$

functional	system n	ΔE (eV)	$d_{h\to e}$ (Å)	d_{exc} (Å)	R_{eh}
B3LYP	1	3.85	3.01	4.57	-0.03
	2	2.98	6.18	7.38	0.00
	3	2.67	9.70	10.71	0.01
	4	2.55	13.60	14.45	0.00
	5	2.49	17.23	18.07	0.00
PBE0	1	3.97	2.87	4.47	-0.01
	2	3.16	5.86	7.16	0.01
	3	2.90	9.24	10.37	0.02
	4	2.83	13.08	14.06	0.00
	5	2.77	16.61	17.59	-0.01
CAM-B3LYP	1	4.12	0.68	2.40	0.02
	2	3.87	3.80	5.71	0.14
	3	3.89	4.82	7.13	0.21
	4	4.00	4.58	7.61	0.40
	5	3.95	3.72	7.31	0.52

4 Data of figure 8

Excited-state descriptors and complementary information describing the (first) singlet excited state of α-(NMe_2)ω(NO_2)(phenylene)$_n$ with $n = 1 - 5$. Systems are enumerated according to number of phenyl rings.

method	descriptor	**1**	**2**	**3**	**4**	**5**
ref.	NN-distance (Å)	5.64	9.94	14.25	18.55	22.87
B3LYP	${}^{U}\mathrm{D}_{\mathrm{CT}}$ (Å)	4.12	7.41	10.78	14.43	18.27
	${}^{R}\mathrm{D}_{\mathrm{CT}}$ (Å)	2.23	3.95	5.75	7.60	9.53
	$d_{h\to e}^{\mathrm{1TDM}}$ (Å)	3.01	6.18	9.70	13.60	17.23
PBE0	${}^{U}\mathrm{D}_{\mathrm{CT}}$ (Å)	3.98	7.15	10.40	13.97	17.74
	${}^{R}\mathrm{D}_{\mathrm{CT}}$ (Å)	2.25	3.95	5.72	7.55	9.48
	$d_{h\to e}^{\mathrm{1TDM}}$ (Å)	2.87	5.86	9.24	13.08	16.61
CAM-B3LYP	${}^{U}\mathrm{D}_{\mathrm{CT}}$ (Å)	0.90	5.77	7.61	2.58	2.58
	${}^{R}\mathrm{D}_{\mathrm{CT}}$ (Å)	0.58	3.59	4.86	2.10	5.17
	$d_{h\to e}^{\mathrm{1TDM}}$ (Å)	0.68	3.80	4.82	4.58	3.72
ADC(2)/S_1	$d_{h\to e}^{\mathrm{1TDM}}$ (Å)	0.71	3.23	0.52		
	$d_{h\to e}^{\mathrm{1DDM}}$ (Å)	0.46	1.83	0.34		
ADC(2)/CT	$d_{h\to e}^{\mathrm{1TDM}}$ (Å)	2.31	3.23	4.56		
	$d_{h\to e}^{\mathrm{1DDM}}$ (Å)	1.30	1.83	2.60		

5 Data of figure 11: Benchmark of *para*-Nitrodimethylaniline

state	method	ΔE (eV)	f_{osc}	Ω	d_{exc}	$d_{h\to e}$	σ_h	σ_e	R_{eh}
1^1A"	ADC(3)	4.14	0.00	0.83	2.30	0.59	1.40	1.76	0.02
	ADC(2)	3.89	0	0.85	2.41	0.71	1.40	1.85	0.02
	EOM-CCSD	4.23	0.00	0.80	2.24	0.56	1.40	1.72	0.04
	B3LYP	3.97	0.00	1.00	2.69	0.94	1.42	2.09	0.01
	PBE0	4.04	0.00	1.00	2.63	0.89	1.41	2.05	0.01
	CAM-B3LYP	4.12	0.00	1.00	2.40	0.68	1.40	1.84	0.02
2^1A'	ADC(3)	4.26	0.55	0.80	3.66	1.74	2.36	2.52	0.13
	ADC(2)	4.13	0.59	0.82	4.01	2.31	2.39	2.50	0.10
	EOM-CCSD	4.59	0.60	0.77	3.78	1.98	2.37	2.53	0.13
	B3LYP	3.85	0.43	1.03	4.56	3.01	2.45	2.33	-0.03
	PBE0	3.97	0.45	1.03	4.47	2.87	2.45	2.37	-0.01
	CAM-B3LYP	4.29	0.51	1.02	4.01	2.23	2.40	2.45	0.06
3^1A'	ADC(3)	4.47	0.02	0.81	2.93	0.44	2.18	2.05	0.06
	ADC(2)	4.48	0.02	0.84	3.08	0.84	2.29	1.99	0.05
	EOM-CCSD	4.65	0.02	0.79	2.97	0.62	2.22	2.01	0.06
	B3LYP	4.48	0.01	1.01	3.25	1.04	2.33	2.17	0.07
	PBE0	4.58	0.01	1.01	3.22	1.00	2.34	2.12	0.06
	CAM-B3LYP	4.65	0.00	1.00	2.40	0.58	1.45	1.86	0.03

6 Molecular geometries

6.1 *para*-Nitrodimethylaniline ($\alpha(NMe_2)\omega(NO_2)$phenylene)

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0 1
C 0.5455965053 -1.2180111595 0
C -0.8600945767 -1.2106729862 0
C -1.5761592098 -0.0045423393 0
C -0.8574053406 1.1965000861 0
C 0.5434380682 1.2018714787 0
C 1.2960568042 -0.0062830422 0
H 1.0094991299 -2.1851267258 0
H -1.3927713496 -2.1548636474 0
H -1.3848320763 2.142921781 0
H 1.0009046659 2.1694526366 0
N -3.0105358434 0.0026539742 0
O -3.6212117689 -1.02368031 0
O -3.6095082256 1.037002228 0
N 2.7673307202 0.0010744429 0
C 3.5599377604 1.2308504797 0
C 3.5767169772 -1.2171087146 0
H 3.0320114467 -2.1677187676 0
H 4.2373310689 -1.2219379478 0.89513
H 4.2373310689 -1.2219379478 -0.89513
H 3.0066287394 2.1753663143 0
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H 4.2167855976 1.2477736125 0.89692
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Molecular Point Group       Cs    NOp =  2
Largest Abelian Subgroup    Cs    NOp =  2
Nuclear Repulsion Energy =  671.0321563244 hartr.
```

6.2 $\alpha(\mathbf{NMe_2})\omega(\mathbf{NO_2})(\mathbf{phenylene})_2$

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C 3.0166852536 1.2011471185 -0.0044229354
C 1.620385094 1.1967958095 -0.0071083618
C 0.8856438816 -0.0169497643 -0.0044435939
H 1.1584717864 -2.1890441135 0.0040264898
H 3.5631393427 -2.1536927208 0.0083346637
H 3.5348874553 2.1520431547 -0.0065314356
H 1.1437386496 2.1587313798 -0.0112145897
N 5.1699931212 0.0128355717 0.003879236
O 5.7829266654 -1.0120061475 0.0085219211
O 5.7651170977 1.0488767793 0.00139594
C -0.640272739 -0.0194160562 -0.0060450315
C -1.3753089247 1.1898820585 -0.0063127897
C -1.3843627023 -1.225271541 -0.0060020099
C -2.7853295877 -1.2161604287 -0.0047972584
C -3.5055251582 -0.0044507966 -0.0027679699
C -2.7705868461 1.1952762052 -0.0043925976
N -4.9527130448 0.0115143586 0.0029747602
C -5.7113069643 -1.232388147 -0.0019819043
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H -6.8079608781 -1.0560918417 0.0082316231
H -5.4648083297 -1.8305961862 0.9002637735
C -5.6784318976 1.2758993113 0.0166739266
H -6.7792884369 1.132868759 0.0219661016
H -5.4261119641 1.8670368618 -0.8891268491
H -5.4152913032 1.8527138772 0.9287401326
H -0.9086293735 -2.1897272186 -0.0061771578
H -3.297735416 -2.1679718313 -0.0039432936
H -0.8986128136 2.1516180749 -0.0067357701
H -3.2674637322 2.1543260771 -0.0035661819
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Molecular Point Group      C1    NOp =  1
Largest Abelian Subgroup   C1    NOp =  1
Nuclear Repulsion Energy = 1174.4204897666 hart.
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6.3 $\alpha(\mathbf{NMe_2})\omega(\mathbf{NO_2})(\mathbf{phenylene})_3$

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C 5.9942944993 -0.0247040036 -0.0180022123
C 5.3054246113 1.1995951503 -0.0181770257
C 3.9025082117 1.2370923277 0.003267596
C 3.1386680209 0.04296062 0.0255965651
H 3.3737693589 -2.1392741481 0.042203141
H 5.7534548191 -2.1713298932 0.0053508434
H 5.8556450756 2.1320985454 -0.0355397268
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C 0.8775325038 -1.1416287296 0.0575106499
C -0.5122797923 -1.1567146149 0.0718489371
C -1.2733637043 0.0314024028 0.0757469542
C -0.5510431817 1.2504424912 0.0672041963
C -2.9108804936 0.1283011389 -0.026994343
C -3.5940627284 -1.1108751615 -0.0383562955
C -3.7095469542 1.2959625922 -0.0109263082
H 1.3518221926 -2.1027924658 0.0538886665
H -0.9615638311 -2.1290336321 0.0790551116
H 1.3413018654 2.229159279 0.0451788006
H -1.0547950964 2.2032814918 0.0692847439
C -5.114392067 1.2173216044 -0.0080222488
C -5.7860988675 -0.0298723695 -0.0207033754
C -4.9849904727 -1.1886202953 -0.0353468807
N -7.2418073856 -0.0962837803 -0.0219221365
C -8.0311811622 1.126592542 -0.0269519301
H -7.8173688978 1.722911815 0.8843404624
H -9.1225168201 0.9060555937 -0.0312002879
H -7.8093806403 1.7195032471 -0.9387217636
C -7.9949293437 -1.3502546861 -0.0212532891
H -7.4028155986 -2.2730788807 -0.0112664693
H -8.6376213376 -1.3965012481 -0.9262811893
H -8.647900592 -1.388831462 0.8766835082
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Molecular Point Group      C1    NOp =  1
Largest Abelian Subgroup   C1    NOp =  1
Nuclear Repulsion Energy = 1721.1477626252 hart.
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6.4 $\alpha(\mathbf{NMe_2})\omega(\mathbf{NO_2})(\mathbf{phenylene})_4$

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C 7.4738186504 -1.2242312595 0.1417976594
C 8.1925709421 -0.0231062057 0.2425287704
C 7.4819683943 1.1847221807 0.2070826577
C 6.0855070297 1.1983750624 0.0688240928
C 5.3373549205 -0.0052739471 -0.0411274725
H 5.5985587089 -2.1806033863 -0.0663879266
H 7.9976541396 -2.172669696 0.1700006046
H 8.0113586042 2.1271434539 0.2866302488
H 5.6163573259 2.1644973426 0.0520723457
N 9.6205875738 -0.0320401918 0.3776315714
O 10.2206233144 -1.0629769057 0.4015315734
O 10.2257762465 0.9970024122 0.4573437344
C 3.8025189128 0.0079881513 -0.1886233508
C 3.0658655447 1.2171031231 -0.2279480273
C 3.0514866834 -1.1876250636 -0.2802566844
C 1.6452449929 -1.1757899354 -0.3801497296
C 0.9034912597 0.0340241028 -0.3952717599
C 1.6590444394 1.2299810733 -0.3293442027
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N -9.4234312338 -0.0580649449 0.391936354
C -10.1737244343 1.1874593973 0.5033610328
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C -0.6451291429 0.0457957104 -0.4245205555
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C -1.3930933388 -1.1537017128 -0.3734189546
C -2.8110309488 1.2503608882 -0.3863795987
C -2.798850943 -1.1536975025 -0.3076216539
C -3.5521794318 0.0460047319 -0.2890862057
H -3.2714598892 -2.1162614236 -0.2464412597
H -0.9122428103 -2.1149907203 -0.3543493039
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H -0.9101445129 2.2097275525 -0.5050001582
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Molecular Point Group      C1    NOp =  1
Largest Abelian Subgroup   C1    NOp =  1
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6.5 $\alpha(\mathbf{NMe_2})\omega(\mathbf{NO_2})(\mathbf{phenylene})_5$

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0 1
C 8.0256414003 -1.1201234473 -0.4540139897
C 9.409689343 -1.1364709757 -0.4493912345
C 10.0885070501 -0.0193410717 0.0129097237
C 9.4189158626 1.1059714048 0.4688865808
C 8.0347825717 1.1059994913 0.4614868095
C 7.31339455 -0.0030091194 0.0011019965
H 7.4854295279 -1.9781381406 -0.8382108262
H 9.9732685915 -1.9897560726 -0.8045190443
H 9.9893606632 1.9525196948 0.8291129276
H 7.5013381886 1.9701341706 0.841381635
N 11.5552615834 -0.0281944549 0.0199190287
O 12.1120426034 -1.0336046637 -0.3724728451
O 12.1203424011 0.9689142627 0.4215415128
C 5.8376251057 0.0042244927 -0.0033695127
C 5.122257616 1.1666406826 -0.3063261029
C 5.1108710239 -1.1515617077 0.2969234468
C 3.7259311475 -1.1444856895 0.2948912406
C 3.008172475 0.0170771027 -0.0084209927
C 3.7372760136 1.1720970587 -0.3093967788
C -7.0870643946 0.014193821 -0.0260773696
C -7.8140876905 -1.1101998196 -0.427620836
C -7.8268946861 1.1309090546 0.374264855
H 5.6376652926 -2.0648325844 0.5536296745
H 3.1891315586 -2.0608626197 0.5174845188
H 5.6580382497 2.0756011128 -0.5596392006
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C -9.9385231092 0.0020183583 -0.0391102642
C -9.1973327065 -1.1265573057 -0.4352539203
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C -12.0379411326 1.09755194 0.5275804971
H -11.7996493107 1.2375381574 1.5923183216
H -13.1077650809 0.9086837469 0.4417919088
H -11.8268674876 2.0386103506 0.0069706455
C -12.0091396182 -1.2409976131 -0.3154794923
H -11.7589467659 -1.6404698261 -1.3045021234
H -13.0829967308 -1.0573513416 -0.2996943483
H -11.7800800964 -2.0157658273 0.4315479653
H -7.3074276555 2.0163563444 0.7273965879
H -7.2848908993 -1.9947434355 -0.7681369094
H -9.7045826265 -2.0257228344 -0.762102031
H -9.7274217303 2.0232809177 0.7122337292
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C 1.5330625462 0.0219832078 -0.0097936247
C 0.8113816109 0.7838135426 -0.9341162476
C 0.8076367896 -0.7366538285 0.9140104521
C -0.5737110594 0.7842754941 -0.93595324
C -0.5772688468 -0.7334004857 0.9137051727
C -1.3007339137 0.0256901864 -0.0121285063
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H -1.1040945609 1.3554488156 -1.6911265204
H 1.3437395607 1.3557711032 -1.6875598931
C -2.7755488689 0.0248893077 -0.0143222973
C -3.5024743229 1.1791328447 -0.3225594372
C -4.8876334992 1.1750725407 -0.3281505569
C -3.4990430585 -1.1319639186 0.2917594339
C -4.8839464217 -1.13389993 0.2914141744
C -5.6138525476 0.0187383878 -0.0207150056
H -2.966986559 -2.0503267249 0.5196104536
H -5.41196868 -2.0441464664 0.5564251899
H -2.9733438874 2.1002600461 -0.5461000551
H -5.4188628144 2.0834987966 -0.5930560555
----
Molecular Point Group      C1    NOp =  1
Largest Abelian Subgroup   C1    NOp =  1
Nuclear Repulsion Energy = 3022.6451444728 hartr.
```

References

(1) Etienne, T.; Assfeld, X.; Monari, A. *J. Chem. Theory Comput.* **2014**, *10*, 3906–3914.

(2) Le Bahers, T.; Adamo, C.; Ciofini, I. *J. Chem. Theory Comput.* **2011**, *7*, 2498–2506.