

# Non-adiabatic MD analysis for TURBOMOLE

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## 1 Introduction

The theoretical formalism used to compute observables from the trajectory data of non-adiabatic molecular dynamics (NAMD) simulations is outlined in this document. The particular example used here is that of a dually fluorescent molecule 4-(Dimethylamino)benzonitrile (DMABN) in the gas phase, where emission occurs from a locally excited (LE) state and a charge transfer (CT) excited state.

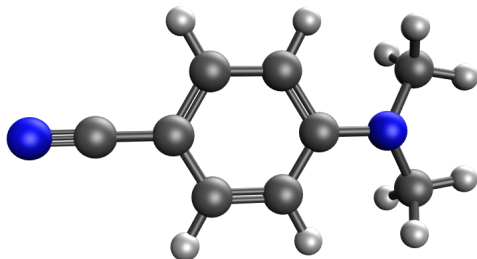


Figure 1: 4-(Dimethylamino)benzonitrile (DMABN)

## 2 Computational Details

Twenty NAMD trajectories were propagated for 1.5 ps starting from the bright  $S_2$  state, with initial conditions sampled from a 10 ps long ground-state molecular dynamics trajectory. Electronic structure calculations were performed using density functional theory (DFT) with the  $\omega$ B97X-D [1] functional and the def2-SVP basis set [5] for all atoms. Excited state properties were computed using time-dependent density functional theory (TDDFT). All calculations were performed with the TURBOMOLE program suite, Version V7.5 [2].

State	Excitation energy (eV)	f
S <sub>1</sub> (L <sub>b</sub> )	4.76	0.03
S <sub>2</sub> (L <sub>a</sub> )	5.03	0.55

Table 1: Vertical excitation energies (eV) and oscillator strengths in the length gauge of DMABN computed at the TDDFT/ $\omega$ B97X-D level of theory at the ground state minimum energy geometry with the experimental band origins in parenthesis

### 3 Population analysis

The population of the electronically excited state  $k$  at time  $t$ , was computed as  $p_k(t) = \frac{N_k(t)}{N_{\text{traj}}}$ , where  $N_k(t)$  is the number of trajectories that are evolving on the state  $k$  at time  $t$  and  $N_{\text{traj}}$  is the total number of trajectories.

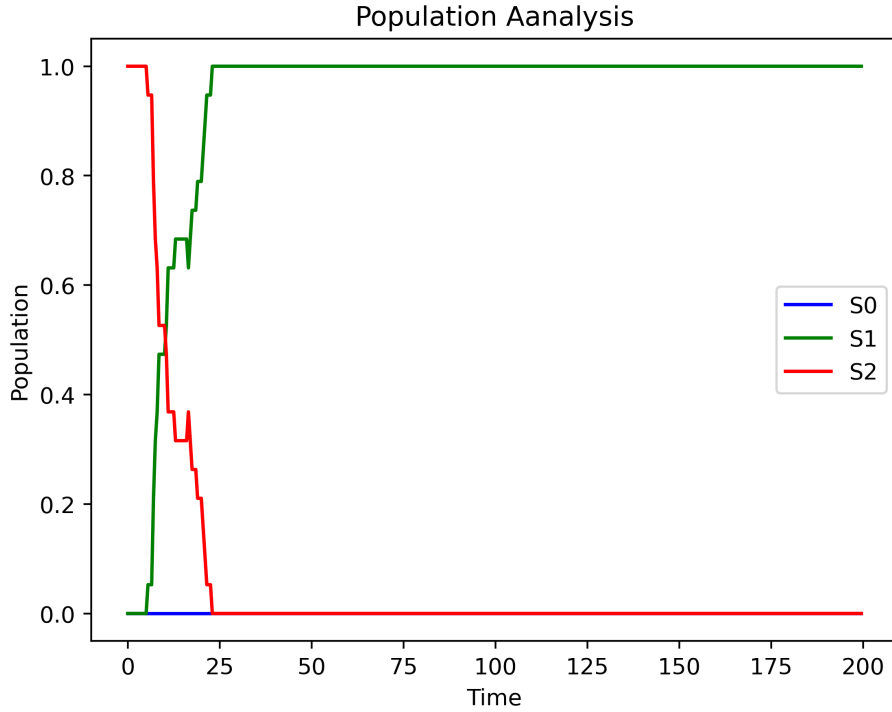


Figure 2: Population analysis of the swarm of NAMD trajectories of DMABN after initial excitation to the S<sub>2</sub> state.

## 4 Steady state fluorescence spectrum

Spectroscopic observables are obtained by ensemble averaging over the set of trajectories after an equilibration period of 0.5 ps. The steady-state fluorescence spectrum is constructed from the NAMD simulations using the following lineshape function [4],

$$\sigma_{em}(\omega) = \frac{1}{N} \sum_{j=1}^N f_{j,a} \omega_{j,a}^2 G(\omega_{j,a} - \omega) \quad (1)$$

where  $f_{j,a}$  is the oscillator strength of the active state  $a$  of the trajectory,  $\omega$  is the excitation energy,  $N$  is the total number of time steps from the trajectories after the equilibration period and  $G$  is a Gaussian or Lorentzian broadening function.

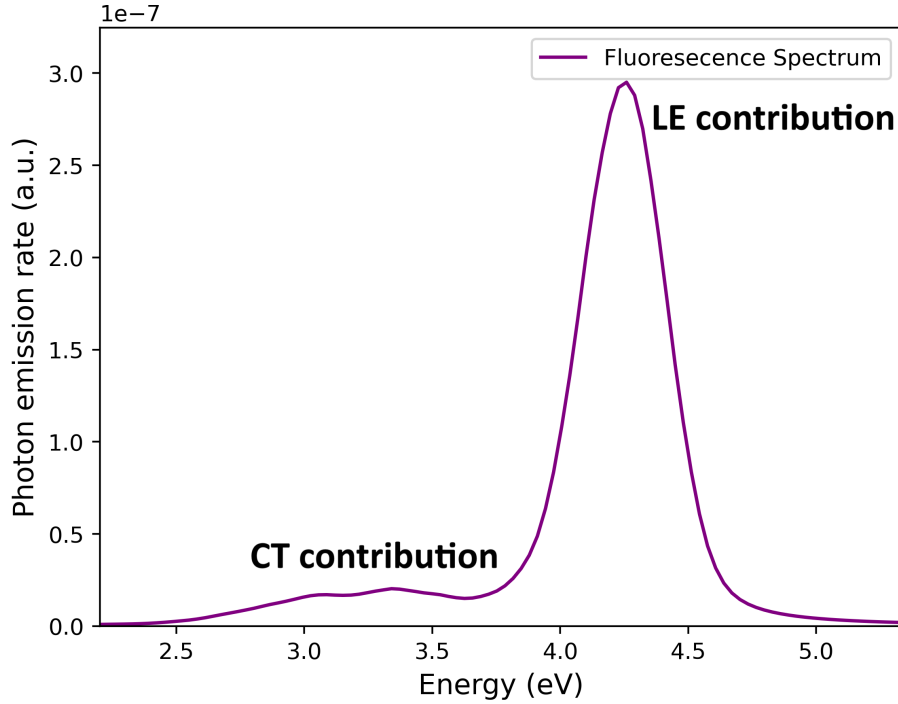


Figure 3: The steady state fluorescence spectrum of DMABN computed from the NAMD trajectories using a Gaussian lineshape function of linewidth 0.05 eV exhibiting emission from the locally excited (LE) state and the charge transfer (CT) state.

## 5 Time resolved fluorescence spectrum

The time-resolved fluorescence spectrum is computed using the following lineshape function [3],

$$I^{TRF}(\omega, t) = \frac{1}{N_{traj}} \sum_{j=1}^{N_{traj}} f_{j,a}(t) \omega_{j,a}(t)^2 G(\omega_{j,a} - \omega) \quad (2)$$

Work in Progress!!!

## References

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- [2] Yannick J Franzke et al. “TURBOMOLE: Today and tomorrow”. In: *Journal of chemical theory and computation* 19.20 (2023), pp. 6859–6890.
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- [5] Florian Weigend and Reinhart Ahlrichs. “Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy”. In: *Physical Chemistry Chemical Physics* 7.18 (2005), pp. 3297–3305.