

Electronic Supplementary Information: Excited State Born-Oppenheimer Molecular Dynamics through a coupling between Time Dependent DFT and AMOEBA

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1 Forces in a link-atom scheme

When computing the gradients of the energy with respect to the QM or MM atoms used to define \mathbf{r}_H , we get the following expressions

$$\begin{aligned} \frac{d}{d\mathbf{R}_{\text{MM}}}\mathcal{E}(\mathbf{r}_{\text{QM}}, \mathbf{R}_{\text{MM}}, \mathbf{r}_H(\mathbf{r}_{\text{QM}}, \mathbf{R}_{\text{MM}})) &= \frac{\partial\mathcal{E}}{\partial\mathbf{R}_{\text{MM}}} + \frac{\partial\mathcal{E}}{\partial\mathbf{r}_H} \frac{\partial\mathbf{r}_H}{\partial\mathbf{R}_{\text{MM}}} = \\ &= \frac{\partial\mathcal{E}}{\partial\mathbf{R}_{\text{MM}}} - k \frac{\hat{\mathbf{d}}_{\text{MM-QM}}}{|\mathbf{d}_{\text{MM-QM}}|} \left(\frac{\partial\mathcal{E}}{\partial\mathbf{r}_H} \cdot \hat{\mathbf{d}}_{\text{MM-QM}} \right) + \frac{k}{|\mathbf{d}_{\text{MM-QM}}|} \frac{\partial\mathcal{E}}{\partial\mathbf{r}_H}, \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{d}{d\mathbf{r}_{\text{QM}}}\mathcal{E}(\mathbf{r}_{\text{QM}}, \mathbf{R}_{\text{MM}}, \mathbf{r}_H(\mathbf{r}_{\text{QM}}, \mathbf{R}_{\text{MM}})) &= \frac{\partial\mathcal{E}}{\partial\mathbf{r}_{\text{QM}}} + \frac{\partial\mathcal{E}}{\partial\mathbf{r}_H} \frac{\partial\mathbf{r}_H}{\partial\mathbf{r}_{\text{QM}}} = \\ &= \frac{\partial\mathcal{E}}{\partial\mathbf{r}_{\text{QM}}} + k \frac{\hat{\mathbf{d}}_{\text{MM-QM}}}{|\mathbf{d}_{\text{MM-QM}}|} \left(\frac{\partial\mathcal{E}}{\partial\mathbf{r}_H} \cdot \hat{\mathbf{d}}_{\text{MM-QM}} \right) + \left(1 - \frac{k}{|\mathbf{d}_{\text{MM-QM}}|} \right) \frac{\partial\mathcal{E}}{\partial\mathbf{r}_H}. \end{aligned} \quad (2)$$

The term $\frac{\partial\mathcal{E}}{\partial\mathbf{r}_H}$ is the gradient with respect to \mathbf{r}_H , which is computed by the QM package. The two expressions can be used as rules to project this fictitious gradient on the real atoms.

2 Density analysis

Given the large amount of MM molecules and the short simulation times, we decided to not use boundary conditions, expecting an almost constant density in the inner region where the DMABN molecule resides. The assumption has been validated by measuring the density of the inner core (a sphere of radius 10 \AA) along 3 ps of equilibration and 2 ps of excited state dynamics. From the results, shown in fig. 1 it appears that the density fluctuates slightly around the average value of 0.80 g/cm^3 without showing clear negative drifts.

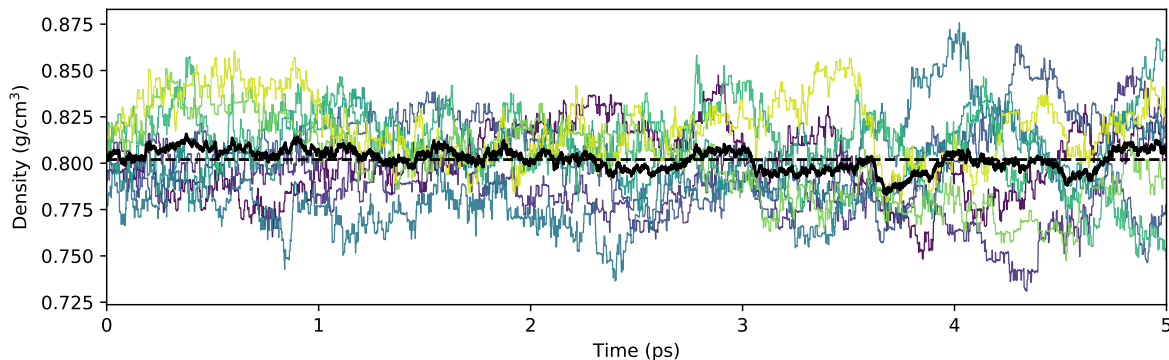


Figure 1: Density of the inner 10 \AA core computed during the equilibration and excited state dynamics. The average value among the trajectories is reported as a black solid line. The average value among trajectories and time is reported as a dashed black line.

3 Trajectory data

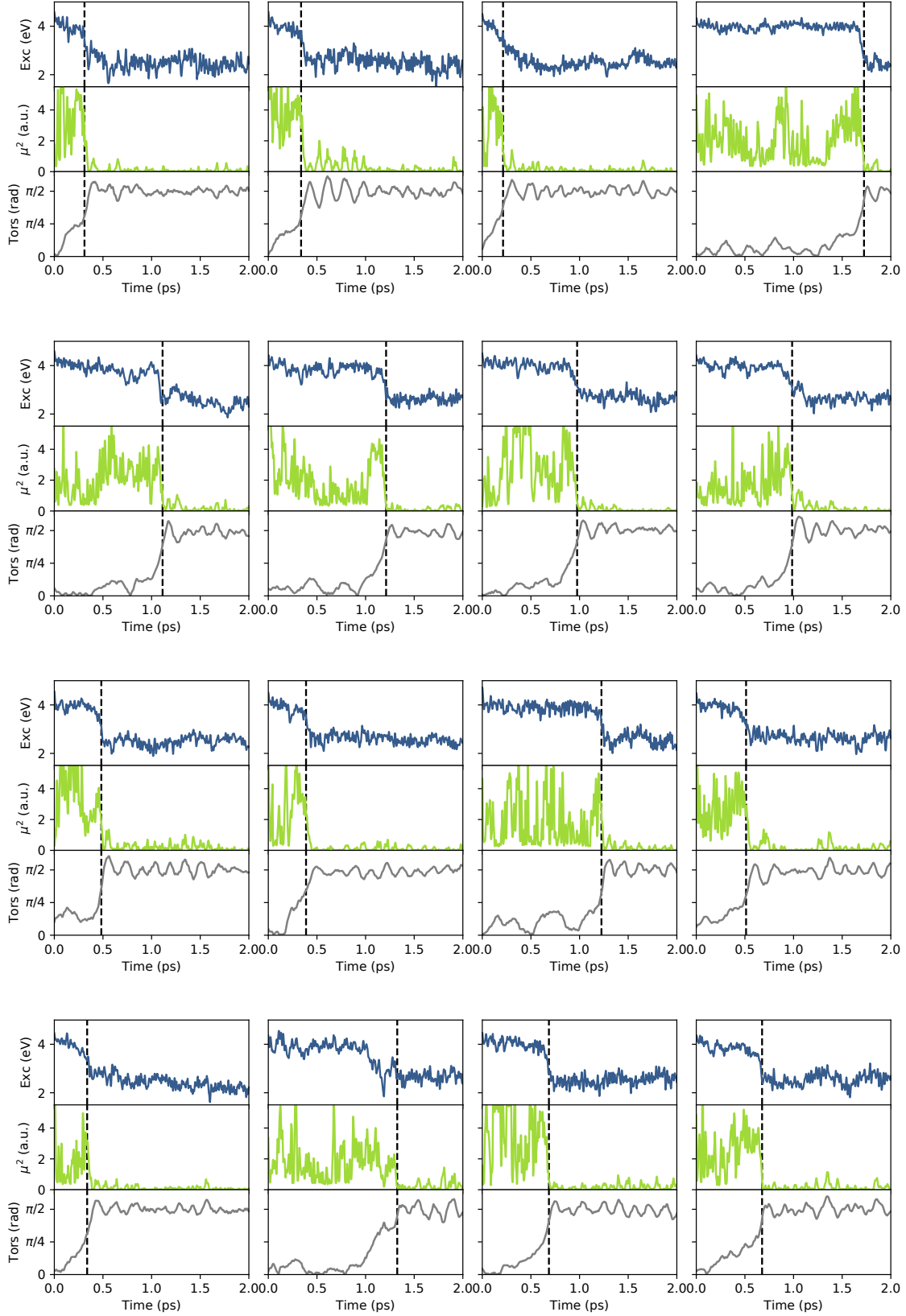


Figure 2: Properties computed along the 16 excited state trajectories. The times at which the LE-ICT interconversion takes place are shown with vertical dashed lines.