Supplementary Information

Atomistic non-adiabatic dynamics of the LH2 complex with a GPU-accelerated *ab initio* exciton model

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Table of Contents

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Section S1. Full Gradient Expressions

In what follows, we write full expressions for gradients of all the elements in the exciton Hamiltonian. The gradient of the ground state Hamiltonian matrix element, E_0, within the dipole-dipole approximation to the ground state energy, can be expressed as:

$$\frac{\partial E_0}{\partial R} = \sum_i \frac{\partial \varepsilon_{(i,0)}}{\partial R} + \frac{1}{\varepsilon_r} \sum_{j>i} \frac{\partial}{\partial R} \left[\frac{\vec{\mu}_{(j,0)} \cdot \vec{\mu}_{(i,0)} - 3\left(\vec{n}_{ij} \cdot \vec{\mu}_{(j,0)}\right)\left(\vec{n}_{ij} \cdot \vec{\mu}_{(i,0)}\right)}{R_{ij}^3} \right]$$

$$= \sum_i \frac{\partial \varepsilon_{(i,0)}}{\partial R} + \frac{1}{\varepsilon_r} \sum_{j>i} \left[\begin{array}{l} \left(\vec{\mu}_{(j,0)} \cdot \vec{\mu}_{(i,0)} - 3\left(\vec{n}_{ij} \cdot \vec{\mu}_{(j,0)}\right)\left(\vec{n}_{ij} \cdot \vec{\mu}_{(i,0)}\right)\right)\frac{\partial\left(1/R_{ij}^3\right)}{\partial R} + \frac{\dfrac{\partial \vec{\mu}_{(j,0)}}{\partial R} \cdot \vec{\mu}_{(i,0)}}{R_{ij}^3} + \frac{\vec{\mu}_{(j,0)} \cdot \dfrac{\partial \vec{\mu}_{(i,0)}}{\partial R}}{R_{ij}^3} \\[2em] -3\left(\vec{n}_{ij} \cdot \vec{\mu}_{(j,0)} \left(\dfrac{\dfrac{\partial \vec{n}_{ij}}{\partial R} \cdot \vec{\mu}_{(i,0)}}{R_{ij}^3} + \dfrac{\vec{n}_{ij} \cdot \dfrac{\partial \vec{\mu}_{(i,0)}}{\partial R}}{R_{ij}^3} \right) + \vec{n}_{ij} \cdot \vec{\mu}_{(i,0)} \left(\dfrac{\dfrac{\partial \vec{n}_{ij}}{\partial R} \cdot \vec{\mu}_{(j,0)}}{R_{ij}^3} + \dfrac{\vec{n}_{ij} \cdot \dfrac{\partial \vec{\mu}_{(j,0)}}{\partial R}}{R_{ij}^3} \right) \right) \end{array} \right]$$

The derivatives of the diagonal matrix elements H_{22}, H_{33}, …, H_{NN}, can be computed as:

$$\frac{\partial E_{(i,k)}}{\partial R} = \sum_{j\neq i}\frac{\partial \varepsilon_{(j,0)}}{\partial R} + \left(\frac{\partial \varepsilon_{(i,k)}}{\partial R}+\delta\right) +$$

$$\frac{1}{\varepsilon_r}\sum_{j\neq i}\frac{\partial}{\partial R}\left[\frac{\vec{\mu}_{(j,0)}\cdot\vec{\mu}_{(i,k)}-3\left(\vec{n}_{ij}\cdot\vec{\mu}_{(j,0)}\right)\left(\vec{n}_{ij}\cdot\vec{\mu}_{(i,k)}\right)}{R_{ij}^3}\right] + \frac{1}{\varepsilon_r}\sum_{j>l,j,l\neq i}\frac{\partial}{\partial R}\left[\frac{\vec{\mu}_{(j,0)}\cdot\vec{\mu}_{(l,0)}-3\left(\vec{n}_{ij}\cdot\vec{\mu}_{(j,0)}\right)\left(\vec{n}_{ij}\cdot\vec{\mu}_{(l,0)}\right)}{R_{ij}^3}\right]$$

$$= \sum_{j\neq i}\frac{\partial \varepsilon_{(j,0)}}{\partial R} + \left(\frac{\partial \varepsilon_{(i,k)}}{\partial R}+\delta\right) + \frac{1}{\varepsilon_r}\sum_{j\neq i}\left[\vec{\mu}_{(j,0)}\cdot\vec{\mu}_{(i,k)}\frac{\partial\left(1/R_{ij}^3\right)}{\partial R} + \frac{\frac{\partial\vec{\mu}_{(j,0)}}{\partial R}\cdot\vec{\mu}_{(i,k)}}{R_{ij}^3} + \frac{\vec{\mu}_{(j,0)}\cdot\frac{\partial\vec{\mu}_{(i,k)}}{\partial R}}{R_{ij}^3}\right]$$

$$+\frac{1}{\varepsilon_r}\sum_{j>l;j,l\neq i}\left[\vec{\mu}_{(j,0)}\cdot\vec{\mu}_{(l,0)}\frac{\partial\left(1/R_{ij}^3\right)}{\partial R} + \frac{\frac{\partial\vec{\mu}_{(j,0)}}{\partial R}\cdot\vec{\mu}_{(l,0)}}{R_{ij}^3} + \frac{\vec{\mu}_{(j,0)}\cdot\frac{\partial\vec{\mu}_{(l,0)}}{\partial R}}{R_{ij}^3}\right]$$

$$-3\sum_{j\neq i}\left[\begin{array}{c}\vec{n}_{ij}\cdot\vec{\mu}_{(j,0)}\left(\vec{n}_{ij}\cdot\vec{\mu}_{(i,k)}\frac{\partial\left(1/R_{ij}^3\right)}{\partial R} + \frac{\frac{\partial\vec{n}_{ij}}{\partial R}\cdot\vec{\mu}_{(j,0)}}{R_{ij}^3} + \frac{\vec{n}_{ij}\cdot\frac{\partial\vec{\mu}_{(i,k)}}{\partial R}}{R_{ij}^3}\right)+ \\[2em] \vec{n}_{ij}\cdot\vec{\mu}_{(i,k)}\left(\vec{n}_{ij}\cdot\vec{\mu}_{(i,k)}\frac{\partial\left(1/R_{ij}^3\right)}{\partial R} + \frac{\frac{\partial\vec{n}_{ij}}{\partial R}\cdot\vec{\mu}_{(i,k)}}{R_{ij}^3} + \frac{\vec{n}_{ij}\cdot\frac{\partial\vec{\mu}_{(i,k)}}{\partial R}}{R_{ij}^3}\right)\end{array}\right]$$

$$-3\sum_{j>l;j,l\neq i}\left[\begin{array}{c}\vec{n}_{ij}\cdot\vec{\mu}_{(j,0)}\left(\vec{n}_{ij}\cdot\vec{\mu}_{(l,0)}\frac{\partial\left(1/R_{ij}^3\right)}{\partial R} + \frac{\frac{\partial\vec{n}_{ij}}{\partial R}\cdot\vec{\mu}_{(l,0)}}{R_{ij}^3} + \frac{\vec{n}_{ij}\cdot\frac{\partial\vec{\mu}_{(l,0)}}{\partial R}}{R_{ij}^3}\right)+ \\[2em] \vec{n}_{ij}\cdot\vec{\mu}_{(l,0)}\left(\vec{n}_{ij}\cdot\vec{\mu}_{(j,0)}\frac{\partial\left(1/R_{ij}^3\right)}{\partial R} + \frac{\frac{\partial\vec{n}_{ij}}{\partial R}\cdot\vec{\mu}_{(j,0)}}{R_{ij}^3} + \frac{\vec{n}_{ij}\cdot\frac{\partial\vec{\mu}_{(j,0)}}{\partial R}}{R_{ij}^3}\right)\end{array}\right]$$

That is, the gradient of the kth excitation on the ith chromophore is given as the sum of gradients of all other chromophores on the ground state and that of the kth excitation on the ith chromophore. Ground and excited state gradients on individual chromophores are readily computed from TDDFT at a small cost beyond the energy calculation. Obtaining gradients of the

off-diagonal matrix elements is slightly more complicated. The derivative of the coupling elements between the ground and excitonic states, within the dipole-dipole approximation, is given as:

$$\frac{\partial V_{(0)(jJ)}}{\partial R} = \frac{1}{\varepsilon_r} \sum_{j \neq i} \frac{\partial}{\partial R} \left[\frac{\bar{\mu}_{(i,0)} \cdot \overline{M}_{(jJ)} - 3\left(\bar{n}_{ij} \cdot \bar{\mu}_{(i,0)}\right)\left(\bar{n}_{ij} \cdot \overline{M}_{(jJ)}\right)}{R_{ij}^3} \right]$$

$$= \frac{1}{\varepsilon_r} \sum_{j \neq i} \left[\begin{array}{l} \left(\bar{\mu}_{(i,0)} \cdot \overline{M}_{(jJ)} - 3\left(\bar{n}_{ij} \cdot \bar{\mu}_{(i,0)}\right)\left(\bar{n}_{ij} \cdot \overline{M}_{(jJ)}\right)\right)\dfrac{\partial\left(1/R_{ij}^3\right)}{\partial R} + \dfrac{\dfrac{\partial\bar{\mu}_{(i,0)}}{\partial R} \cdot \overline{M}_{(jJ)}}{R_{ij}^3} + \dfrac{\bar{\mu}_{(i,0)} \cdot \dfrac{\partial\overline{M}_{(jJ)}}{\partial R}}{R_{ij}^3} \\ -3\left(\bar{n}_{ij} \cdot \overline{M}_{(jJ)}\left(\dfrac{\dfrac{\partial\bar{n}_{ij}}{\partial R} \cdot \bar{\mu}_{(i,0)}}{R_{ij}^3} + \dfrac{\bar{n}_{ij} \cdot \dfrac{\partial\bar{\mu}_{(i,0)}}{\partial R}}{R_{ij}^3}\right) + \bar{n}_{ij} \cdot \bar{\mu}_{(i,0)}\left(\dfrac{\dfrac{\partial\bar{n}_{ij}}{\partial R} \cdot \overline{M}_{(jJ)}}{R_{ij}^3} + \dfrac{\bar{n}_{ij} \cdot \dfrac{\partial\overline{M}_{(jJ)}}{\partial R}}{R_{ij}^3}\right)\right) \end{array} \right]$$

The derivatives of the off-diagonal matrix elements coupling excited states within the exciton Hamiltonian (i.e., $i \neq 1$ and $j \neq 1$) can be expressed as:

$$\frac{\partial V_{(i,k)(jJ)}}{\partial R} = \frac{1}{\varepsilon_r} \frac{\partial}{\partial R} \left[\frac{\overline{M}_{(i,k)} \cdot \overline{M}_{(jJ)} - 3\left(\bar{n}_{ij} \cdot \overline{M}_{(i,k)}\right)\left(\bar{n}_{ij} \cdot \overline{M}_{(jJ)}\right)}{R_{ij}^3} \right]$$

$$= \frac{1}{\varepsilon_r} \left[\begin{array}{l} \left(\overline{M}_{(i,k)} \cdot \overline{M}_{(jJ)} - 3\left(\bar{n}_{ij} \cdot \overline{M}_{(i,k)}\right)\left(\bar{n}_{ij} \cdot \overline{M}_{(jJ)}\right)\right)\dfrac{\partial\left(1/R_{ij}^3\right)}{\partial R} + \dfrac{\dfrac{\partial\overline{M}_{(i,k)}}{\partial R} \cdot \overline{M}_{(jJ)}}{R_{ij}^3} + \dfrac{\overline{M}_{(i,k)} \cdot \dfrac{\partial\overline{M}_{(jJ)}}{\partial R}}{R_{ij}^3} \\ -3\left(\bar{n}_{ij} \cdot \overline{M}_{(jJ)}\left(\dfrac{\dfrac{\partial\bar{n}_{ij}}{\partial R} \cdot \overline{M}_{(i,k)}}{R_{ij}^3} + \dfrac{\bar{n}_{ij} \cdot \dfrac{\partial\overline{M}_{(i,k)}}{\partial R}}{R_{ij}^3}\right) + \bar{n}_{ij} \cdot \overline{M}_{(i,k)}\left(\dfrac{\dfrac{\partial\bar{n}_{ij}}{\partial R} \cdot \overline{M}_{(jJ)}}{R_{ij}^3} + \dfrac{\bar{n}_{ij} \cdot \dfrac{\partial\overline{M}_{(jJ)}}{\partial R}}{R_{ij}^3}\right)\right) \end{array} \right]$$

The first term depends simply on the derivative of the distance between the centers of mass for each chromophore. However, the remaining terms involve differentiation of the transition dipole vectors of each excitation on each chromophore in turn.

Section S2. Cartesian Gradients of the Transition Dipole and Excited State Dipole Moments
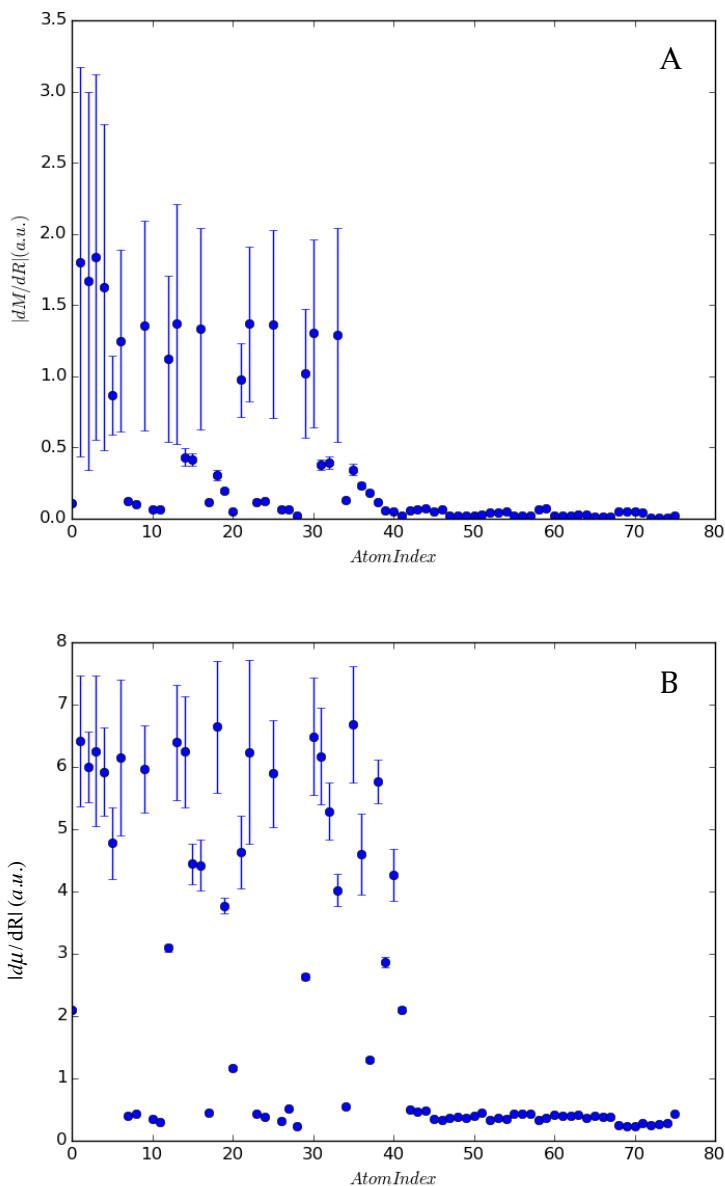

Figure S1 1: a) Magnitudes of the Cartesian transition dipole gradient vector $|dM/dR_i|$ in a.u., of each of the 27 BChla chromophores in the LH2 complex averaged over 10 MD conformations. These are used to calculate on-the-fly transition dipole gradients in the surface hopping trajectories as described in the text. 2σ standard error bars are also shown, obtained from the ensemble of snapshots used to calculate $|dM/dR_i|$. b) Average magnitudes of the Cartesian excited state dipole gradient vector $|d\mu/dR_i|$ in a.u.

Figure 2 shows the ground and excited state gradients calculated using this approximation compared to the same gradients calculated using TDDFT of a 6-chromophore subset of LH2 over a range of conformations. The results in Figure 2 are obtained by computing the dot product of

the 3N exciton gradient on each electronic state and the TDDFT gradient for the same conformation. Scaling this quantity by the magnitude of the TDDFT gradient vectors allows for the agreement to be assessed, with values close to one indicating good agreement. As shown in Figure 2, the agreement between atomic xyz gradients obtained using the exciton model and TDDFT for the first six singlet states is very good. In Figure 3, this approximation is compared to the exact off-diagonal coupling derivative expressions in which the transition dipole derivatives are calculated for each chromophore state at each timestep. The difference between the 'static' approximation and the 'dynamic' (exact) calculation is less than 5 meV over a 100fs simulation.
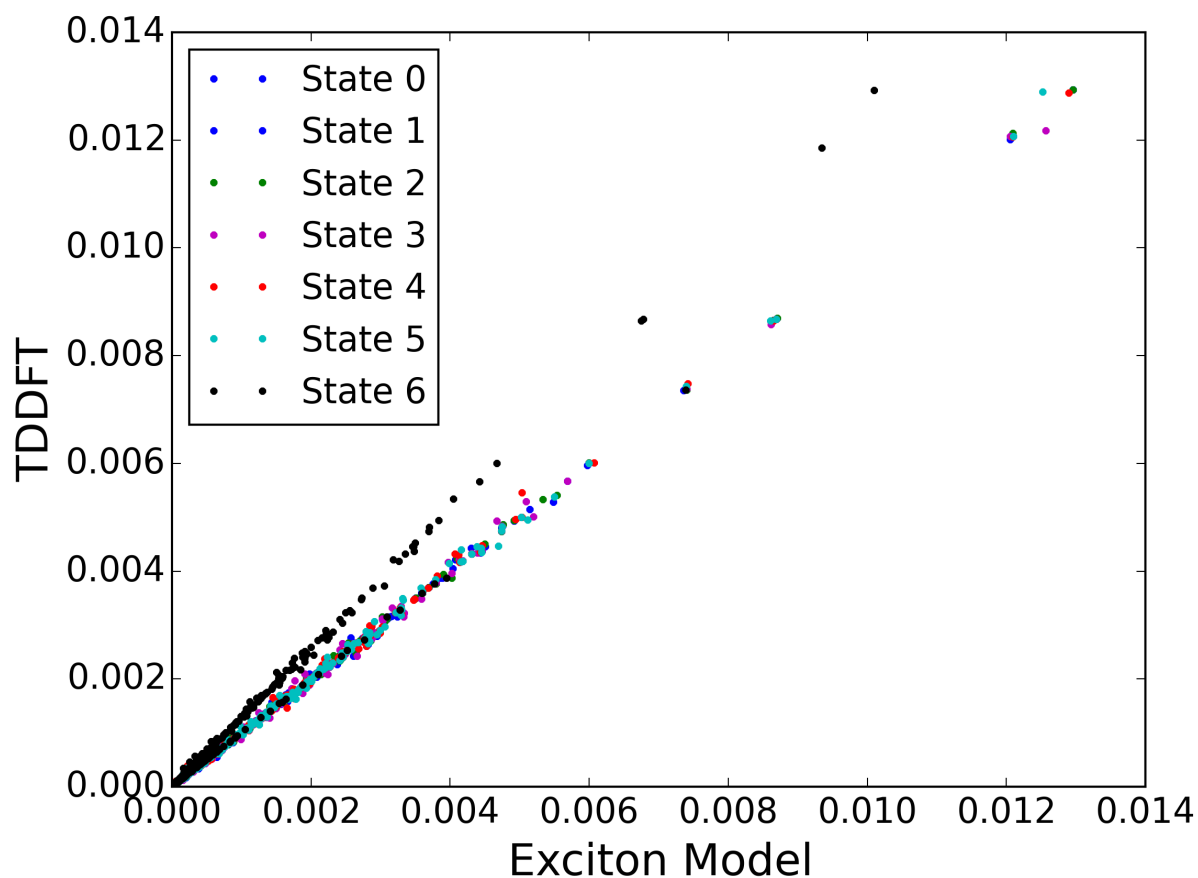

Figure S2: Correlation plot of the exciton model gradient vector with the gradient calculated using TDDFT at varying geometry snapshots. The ground and first six excited state gradient projections are shown. Perfect agreement between the TDDFT and the exciton model would place points strictly along the diagonal.
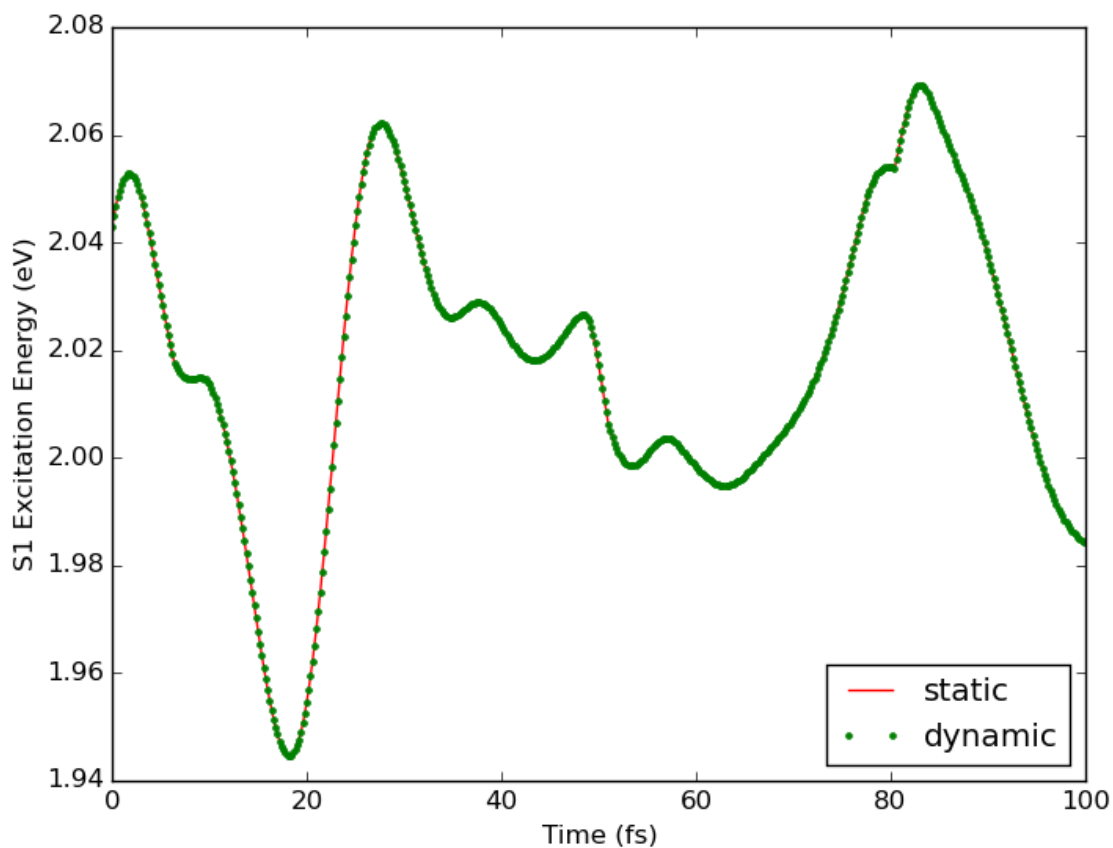
Figure S3: Comparison of a non-adiabatic dynamics trajectory of a BChla dimer in the 850-800 configuration, with static and dynamic transition dipole derivatives. Static refers to the approximation described in the text, while dynamic refers to explicit calculation of the transition dipole derivatives at each timestep.

Section S3: Cinema 4D movie-making instructions

To illustrate how to generate an excitonic dynamics movie, we have provided a file which may be opened in Cinema 4D (C4D): Graham_2fk2_series2_normlzdToS2maxEqualSelf_MD_v2_1.c4d. Having opened this file, you can render a movie that shows the time evolution of both the atomic dynamics and excitonic amplitudes. Two typical tasks which you may want to carry out include reading a time series of (1) excitonic amplitudes or (2) atomic coordinates.

To read in a time series of excitonic amplitudes:
1   Prepare the amplitude data in a format similar to monoWfn1D_2_v2_1_TDT_1w.txt, a tab-delimited file formatted as follows:
   a   Column 1 lists the time from the simulation. This column should have sequences of 27 consecutive rows all with identical times (for each of the 27 sites)
   b   Column 2 lists the amplitude at a specified excitonic site at a specific time.
   c   Column 3 lists the column 2 data multiplied by some arbitrary scaling factor F. This is necessary owing to the fact that this data will later be stored within C4D as vertex vectors, with a precision limited to 10^{-6}.
2   Record the max value of the Column 3 data, which will be used to normalize the data.
3   Should you want to change the data stored in this AmplitudeData_S2, do the following:
   a   In the Object Manager of C4D (on the upper right panel in the default user interface), select the object towards the bottom of the hierarchical list called "AmplitudeData_S2". This object contains an array of vertices where the Y coordinate is used to store the "Column 3" data discussed above.
   b   With AmplitudeData_S2 selected on the far right of the C4D interface, select the tab labeled "Structure" to open C4D's structure manager.
      i   Be sure the Structure Manager menu: Mode is set to points to be able to see and change the data.
      ii   Select all the old data and delete to remove
      iii   File/Import ASCII data to import the Tab delimited file (be sure that the line endings of the text file are properly formatted for the operating system you are using).
      iv   When the data is loaded, return to the object manager by selecting the "Objects" Tab on the far right of the C4D interface.
   c   To normalize the data, C4D needs the maximum value discussed above. This is stored in the name of the Null object that is the first and only child of the AmplitudeData_S2 object in the hierarchical Object Manager. In the provided *.c4d file, this object has the value 97583.809 (the maximum intensity from the simulations was 0.97583809 which was then multiplied by $F = 10^5$ as described above).

To read in a time series of Cartesian atomic coordinates:
1   Export the MD simulation data as a concatenated PDB file or *.trj file.
2   Import the data using ePMV as follows:
   a   If using a concatenated PDB file, then import the file using ePMV (epmv.scripps.edu) b   Else if using a *.trj trajectory file, open this file in the ePMV data
3   player. Select "Line" for the style and thicken the lines for the desired representation
4   In the C4D interface Object Manager, select the "Line" object generated by ePMV and use the technique described in the ePMV tutorial (www.mesoscope.org/workshops/ami-epmv-scripting-workshop-2015 for transmembrane ligand binding) to keyframe the atomic motion.

Section S4: Chimera movie-making instructions

We also provide files and associated python scripts which illustrate how to generate an excitonic dynamics movie using Chimera, a molecular visualization package which is better known to the chemistry and biochemistry communities than C4D. The latest daily build of Chimera can be downloaded and installed from https://www.cgl.ucsf.edu/chimera/download.html.

Within Chimera, open the movie_glow_2.cmd file. Upon opening this file, Chimera will automatically execute the constituent python scripts (included in the /chimera folder) required to open the file and generate a movie. All of the parameters within the *.cmd file and the accompanying Python scripts can be adjusted in order to modify the visualization settings. One important setting which requires modification is the output path for the rendered movie file (this path may be found within the *.cmd file).

References

1. Johnson, G. T.; Autin, L.; Goodsell, D. S.; Sanner, M. F.; Olson, A. J. Epmv Embeds Molecular Modeling into Professional Animation Software Environments. *Structure* **2011**, *19*, 293.