Quantum modeling of photosynthetic light harvesting

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https://github.com/OrlaneZang/MEMAQUAN_2022

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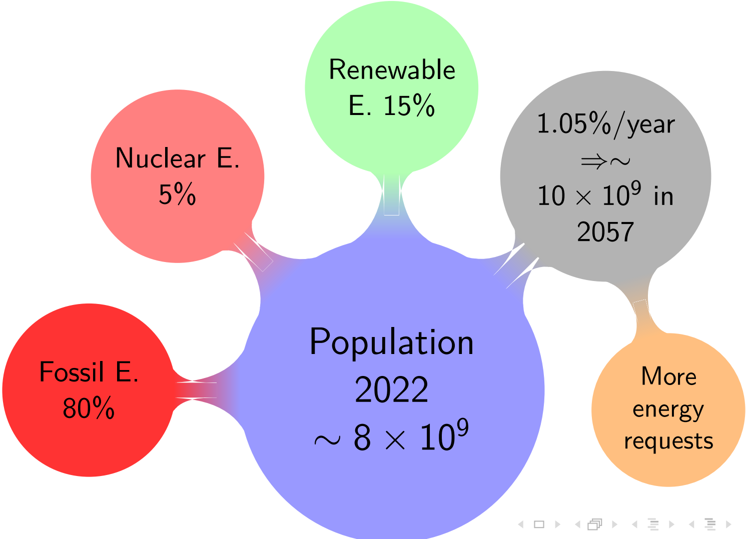
MEMAQUAN - Bénin, July 11-15 2022

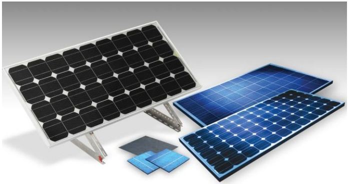
Setting the context

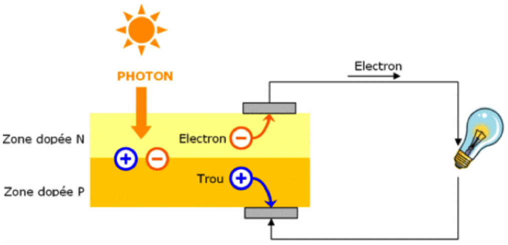
Energy production problem



Setting the context

Solar energy - inorganic solar cells

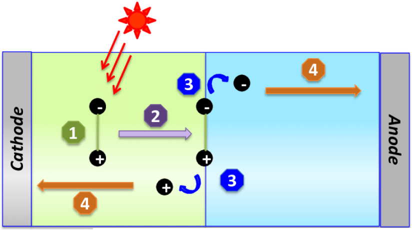


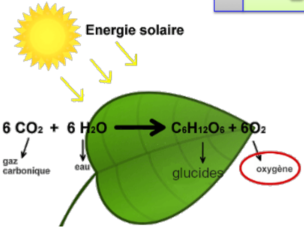


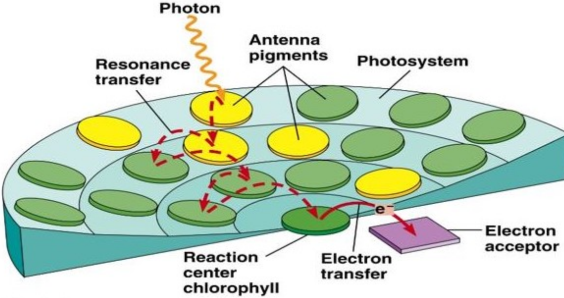
Rendement $\approx$ 27%, gros inconvénient : cout élevé

Setting the context

Solar energy - organic solar cells

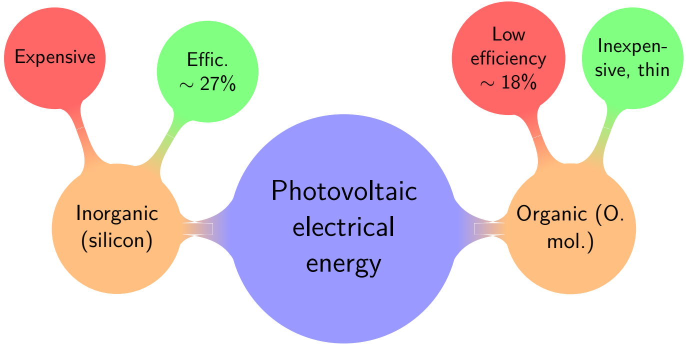






Setting the context

Problem of the current photovoltaic cells



Research question

How to simulate in a reasonable time the dynamics of LHCs in order to contribute to the improvement of OPV performance ?

Setting the context

General and specific objectives

General objective

Model the dynamics of the FMO (Fenna-Matthews-Olson) complex using the Lindblad master equation theory

Specific objectives

- Write the Hamiltonian of the FMO complex considered as an open system
- Derive the general form of its Lindblad master equation
- Make a comparison between the *gold standard* method (HEOM) and the master equation method

Continuation of the presentation

1. FMO complex - Open quantum system (OQS)
2. Dynamics of the FMO complex
3. Why Lindblad for our work ?

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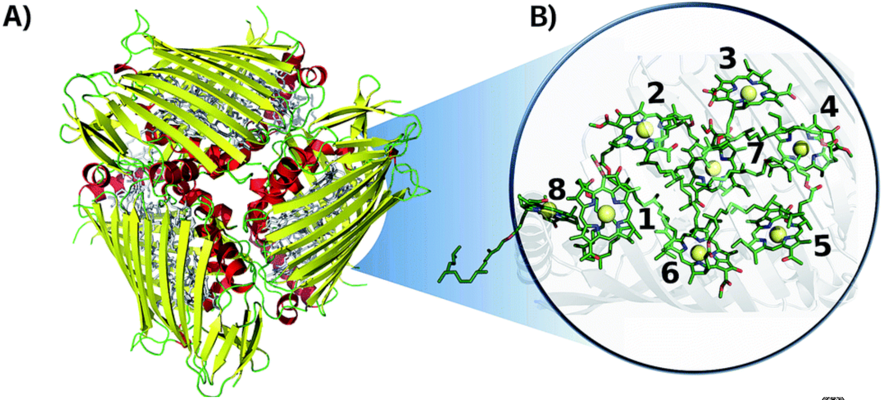
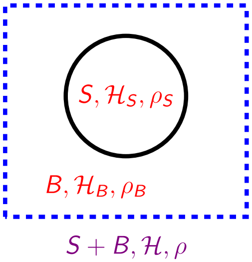
FMO complex - Open quantum system (OQS)

Frenkel Hamiltonian



FMO - OQS

Hamiltonian of the OQS



$$\mathrm{H} = \mathrm{H}_S + \mathrm{H}_\mathrm{B} + \mathrm{H}_{int} \quad (1)$$

$$= \mathrm{H}_S + \mathrm{H}_\mathrm{B} + \mathrm{H}_\mathrm{SB} + \mathrm{H}_\mathrm{reorg} \quad (2)$$

$$\mathrm{H}_S = \sum_{i=1}^{n} |i\rangle\langle i| E_i + \sum_{i \neq j=1}^{n} |i\rangle\langle j| V_{ij}$$

$$\mathrm{H}_\mathrm{B} = \sum_{i=1}^{n} \sum_{k=1} \left(\frac{1}{2} \mathbf{P}_{k,i}^2 + \frac{1}{2} \omega_{k,i}^2 \mathbf{Q}_{k,i}^2 \right)$$

$$\mathrm{H}_\mathrm{SB} = - \sum_{i=1}^{n} \sum_{k=1} |i\rangle\langle i| c_{k,i} \mathbf{Q}_{k,i}$$

$$\mathrm{H}_\mathrm{reorg} = \sum_{i} |i\rangle\langle i| \lambda_i$$

Dynamics of the FMO complex

Hierarchical equations of motion (HEOM) - Gold standard

- At low temperatures,

$$\frac{d}{dt}\sigma_{\mathbf{n}} = \left(\mathcal{L}_S - \sum_{i=1}^{N}\sum_{k=0}^{K} n_{ik}\nu_{ik}\right)\sigma_{\mathbf{n}} - i\sum_{i=1}^{N}\left[\mathcal{V}_i, \sum_{k=0}^{K}\sigma_{n_{ik}}^{+}\right] - \sum_{i=1}^{N}\sum_{k=0}^{K} n_{ik}\left(c_k\mathcal{V}_i\sigma_{n_{ik}}^{-} - c_k^{*}\sigma_{n_{ik}}^{-}\mathcal{V}_i\right) \tag{3}$$

$$\mathbf{n} = \{\{n_{10}, n_{11}, \ldots, n_{1k}, \ldots, n_{1K}\}, \ldots, \{n_{i0}, n_{i1}, \ldots, n_{ik}, \ldots, n_{iK}\}, \ldots, \{n_{N0}, n_{N1}, \ldots, n_{Nk}, \ldots, n_{NK}\}\} \tag{4}$$

$$\sigma_{\mathbf{n}=0} = \rho_S(t) \tag{5}$$

Dynamics of the FMO complex

Hierarchical equations of motion (HEOM) - Gold standard

- Hierarchical level

$$L = \sum_{i=1}^{N} \sum_{k=0}^{K} n_{ik} \tag{6}$$

- Required number of auxiliary density matrices

$$N_{number}(ADMs) = \frac{(N+L)!}{N!L!} \tag{7}$$

- For example, if N=3 and K=4,

$$\begin{aligned} L = {} & n_{10} + n_{11} + n_{12} + n_{13} + n_{14} + n_{20} + n_{21} \\ & + n_{22} + n_{23} + n_{24} + n_{30} + n_{31} + n_{32} + n_{33} + n_{34} \end{aligned}$$

$$N_{number}(ADMs) = \frac{(3+15)!}{3!15!} = 816 \tag{8}$$

Accurate results but Large computation times!

Separability

At t=0, (S) and (B) are separable

$$\rho(0) = \rho_S(0) \otimes \rho_B(0) \implies \rho(t) = \rho_S(t) \otimes \rho_B(t) + \rho_{\text{correl}}$$

Born approximation

(B) is very large so that it is negligibly affected by (S), and therefore $\rho_{\text{correl}} \approx 0$

$$\rho(t) \approx \rho_S(t) \otimes \rho_B(t)$$

Markov Approximation

(B) relaxes much faster than the system evolves

$$\rho(t) \approx \rho_A(t) \otimes \rho_B(0).$$

Dynamics of an open system

Derivation of the Lindblad equation

- Isolated system : Schrödinger equation (9) or Liouville - Von-Neumann equation (10)

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \mathtt{H}(t)|\psi(t)\rangle \tag{9}$$

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}[\mathtt{H}, \rho(t)] = \mathcal{L}\rho(t) \tag{10}$$

- Rewriting the total Hamiltonian

$$\mathtt{H} = \mathtt{H}_S \otimes \mathbb{I}_B + \mathbb{I}_S \otimes \mathtt{H}_B + \alpha \mathtt{H}_I \tag{11}$$

- Without loss of generality, we can decompose

$$\mathtt{H}_I = \sum_i S_i \otimes B_i \tag{12}$$

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Dynamics of an open system

Derivation of the Lindblad equation

- Picture interaction

$$\tilde{O}(t) = e^{\frac{i}{\hbar}(\mathrm{H}_S+\mathrm{H}_B)t} O e^{\frac{-i}{\hbar}(\mathrm{H}_S+\mathrm{H}_B)t} \quad (13)$$

- Evolution equation of ρ in the picture interaction

$$\frac{d}{dt}\tilde{\rho}(t) = -\frac{i}{\hbar}\alpha[\tilde{\mathrm{H}}_I(t), \tilde{\rho}(t)] \quad (14)$$

- Integration of the equation (14)

$$\tilde{\rho}(t) = \tilde{\rho}(0) - \frac{i}{\hbar}\alpha \int_0^t ds[\tilde{\mathrm{H}}_I(s), \tilde{\rho}(s)] \quad (15)$$

- (15) in (14) (taking $\hbar = 1$)

$$\frac{d}{dt}\tilde{\rho}(t) = -i\alpha[\tilde{\mathrm{H}}_I(t), \tilde{\rho}(0)] - \alpha^2 \int_0^t ds[\tilde{\mathrm{H}}_I(t), [\tilde{\mathrm{H}}_I(s), \tilde{\rho}(s)]] \quad (16)$$

Dynamics of an open system

Derivation of the Lindblad equation

- The operation is repeated

$$\frac{d}{dt}\tilde{\rho}(t) = -i\alpha[\tilde{\mathrm{H}}_I(t), \tilde{\rho}(0)] - \alpha^2 \int_0^t ds[\tilde{\mathrm{H}}_I(t), [\tilde{\mathrm{H}}_I(s), \tilde{\rho}(s)]] + O(\alpha^3)$$

- First approximation : interaction force between S and B is weak, so terms in $O(\alpha^3)$ are negligible

$$\frac{d}{dt}\tilde{\rho}(t) = -i\alpha[\tilde{\mathrm{H}}_I(t), \tilde{\rho}(0)] - \alpha^2 \int_0^t ds[\tilde{\mathrm{H}}_I(t), [\tilde{\mathrm{H}}_I(s), \tilde{\rho}(s)]] \tag{17}$$

- Evolution of system S : partial trace on B

$$\begin{aligned}\frac{d}{dt}\tilde{\rho}_S(t) = \mathrm{Tr}_B\left(\frac{d}{dt}\tilde{\rho}(t)\right) &= -i\alpha \mathrm{Tr}_B[\tilde{\mathrm{H}}_I(t), \tilde{\rho}(0)] \\ &\quad -\alpha^2 \int_0^t ds \mathrm{Tr}_B[\tilde{\mathrm{H}}_I(t), [\tilde{\mathrm{H}}_I(s), \tilde{\rho}(s)]]\end{aligned} \tag{18}$$

Dynamics of an open system

Derivation of the Lindblad equation

- Second and third approximations :
  - At t=0, S and B are not correlated

$$\rho(0) = \rho_S(0) \otimes \rho_B(0) \tag{19}$$

  - The initial state of B is assumed to be thermal

$$\rho_B(0) = exp(-\mathrm{H}_B/T)/\mathrm{Tr}\left[exp(-H_B/T)\right] \tag{20}$$

- Using these approximations and the equation (12), we compute the first right-hand term of (18)

$$\mathrm{Tr}_B[\tilde{\mathrm{H}}_I(t), \tilde{\rho}(0)] = \sum_i \Big(\tilde{S}_i(t)\tilde{\rho}_S(0)\mathrm{Tr}_B\left[\tilde{E}_i(t)\tilde{\rho}_B(0)\right] - \tilde{\rho}_S(0)\tilde{S}_i(t)\mathrm{Tr}_B\left[\tilde{\rho}_B(0)\tilde{E}_i(t)\right]\Big) \tag{21}$$

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Dynamics of an open system

Derivation of the Lindblad equation

- By setting $\langle E_i \rangle = \mathrm{Tr}[E_i \rho_B(0) = 0$ from

$$\mathtt{H} = (\mathtt{H}_S + \alpha \sum_i \langle E_i \rangle S_i) + \mathtt{H}_B + \alpha \Big(\sum_i S_I \otimes (E_i - \langle E_i \rangle) \Big) \quad (22)$$

- Then the terms of (21) are zero and the evolution equation (18) becomes

$$\frac{d}{dt}\tilde{\rho}_S(t) = -\alpha^2 \int_0^t ds \mathrm{Tr}_B[\tilde{\mathtt{H}}_I(t), [\tilde{\mathtt{H}}_I(s), \tilde{\rho}(s)]] \qquad (23)$$

- New approximations
  - S and B assumed uncorrelated throughout the evolution
  - Correlation time scale τ_{corr} and rexalation time scale τ_{rel} assumed $\ll \tau_{\mathrm{sys}}$.

$$\tilde{\rho}(t) = \tilde{\rho}_s(t) \otimes \tilde{\rho}_B(0) \qquad (24)$$

Dynamics of an open system

Derivation of the Lindblad equation

- (23) becomes

$$\frac{d}{dt}\tilde{\rho}_S(t) = -\alpha^2 \int_0^t ds \mathrm{Tr}_B[\tilde{\mathrm{H}}_I(t), [\tilde{\mathrm{H}}_I(s), \tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)]] \tag{25}$$

- By setting t to ∞ and $s \to t - s$ we obtain a Markovian equation : Redfield equation

$$\frac{d}{dt}\tilde{\rho}_S(t) = -\alpha^2 \int_0^\infty ds \mathrm{Tr}_B[\tilde{\mathrm{H}}_I(t), [\tilde{\mathrm{H}}_I(s-t), \tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)]] \tag{26}$$

- Disadvantage of this equation : possibility of having non-positive OS

Dynamics of an open system

Derivation of the Lindblad equation

- New approximation to solve the previous problem

$$\tilde{\mathrm{H}}_S A = [\mathrm{H}_S, A] \tag{27}$$

- Eigenvectors of $\tilde{\mathrm{H}}_S A$ form a basis of $\mathcal{H}_S$
- In this basis, we write

$$S_i = \sum_{\omega} S_i(\omega) \tag{28}$$

and

$$[\mathrm{H}_S, S_i(\omega)] = -\omega S_i(\omega), [\mathrm{H}_S, S_i^{+}(\omega)] = +\omega S_i^{+}(\omega) \tag{29}$$

- We return to the Schrödinger representation by writing

$$\tilde{S}_k = e^{it\mathrm{H}_S} S_k e^{-it\mathrm{H}_S} \tag{30}$$

Dynamics of an open system

Derivation of the Lindblad equation

$$\tilde{\mathrm{H}}_I(t) = \sum_{k,\omega} e^{-i\omega t} S_k(t) \otimes \tilde{E}_k(t) = \sum_{k,\omega} e^{-i\omega t} S_k^{+}(t) \otimes \tilde{E}_k(t) \tag{31}$$

- Expansion of the commutator in (26)

$$\begin{aligned}\frac{d}{dt}\tilde{\rho}_S(t) = -\alpha^2 \mathrm{Tr}\Big[\int_0^\infty ds \tilde{\mathrm{H}}_I(t)\tilde{\mathrm{H}}_I(t-s)\tilde{\rho}_S(t)\otimes\tilde{\rho}_B(0)\Big] \\ - \int_0^\infty ds \tilde{\mathrm{H}}_I(t)\tilde{\rho}_S(t)\otimes\tilde{\rho}_B(0)\tilde{\mathrm{H}}_I(t-s) \\ - \int_0^\infty ds \tilde{\mathrm{H}}_I(t-s)\tilde{\rho}_S(t)\otimes\tilde{\rho}_B(0)\tilde{\mathrm{H}}_I(t) \\ + \int_0^\infty ds \tilde{\rho}_S(t)\otimes\tilde{\rho}_B(0)\tilde{\mathrm{H}}_I(t-s)\end{aligned}$$

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- From eigenvalue decomposition + permutation property of the trace + $[\mathrm{H}_B, \rho_B(0)] = 0$, we obtain

$$\frac{d}{dt}\tilde{\rho}_S(t) = \sum_{\omega,\omega',k,l}\Big(e^{i(\omega'-\omega)t}\Gamma_{kl}(\omega)\Big[S_l(\omega)\tilde{\rho}_S(t), S_k^+(\omega')\Big] + e^{i(\omega'-\omega)t}\Gamma^*_{kl}(\omega')\Big[S_l(\omega), \tilde{\rho}_S(t)S_k^+(\omega')\Big]\Big) \tag{32}$$

- The effect of B was absorbed by

$$\Gamma_{kl} \equiv \int_0^\infty ds e^{i\omega S}\mathrm{Tr}_B\Big[\tilde{E}_k^+(t)\tilde{E}_l(t-s)\rho_B(0), \tilde{E}_l(t) = e^{i\mathrm{H}_B t}E_l e^{-i\mathrm{H}_B t}$$

$$\frac{d}{dt}\tilde{\rho}_S(t) = \sum_{\omega,k,l}\Big(\Gamma_{kl}(\omega)\Big[S_l(\omega)\tilde{\rho}_S(t), S_k^+(\omega')\Big] + \Gamma^*_{kl}(\omega')\Big[S_l(\omega), \tilde{\rho}_S(t)S_k^+(\omega')\Big]\Big) \tag{33}$$

Dynamics of an open system

Derivation of the Lindblad equation

- Decomposition of Γ_{kl}

$$\Gamma_{kl}(\omega) = \frac{1}{2}\gamma_{kl}(\omega) + i\pi_{kl}(\omega) \tag{34}$$

$$\pi_{kl}(\omega) = -\frac{i}{2}\Big(\Gamma_{kl}(\omega) - \Gamma^{*}_{kl}(\omega),\ \gamma_{kl}(\omega) = \Gamma_{kl}(\omega) + \Gamma^{*}_{kl}(\omega)$$

- Back to the Shrödinger representation, we obtain

$$\begin{aligned} \frac{d}{dt}\tilde{\rho}_S(t) = {} & -i[\mathrm{H}_S + \mathrm{H}_{reorg}, \rho_S(t)] + \sum_{\omega,k,l} \gamma_{kl}(\omega)\Big(S_l(\omega)\rho_S(t)S^{+}_{k}(\omega) \\ & - \frac{1}{2}\Big\{S^{+}_{k}S_l(\omega), \rho_S(t)\Big\} \end{aligned} \tag{35}$$

Dynamics of an open system

Derivation of the Lindblad equation

- The equation (35) is the first form of the master equation for open quantum systems
- To obtain the Lindblad equation itself, we diagonalize the matrix formed by the coefficients $\gamma_{kl}(\omega)$.
- The general form of Lindblad is thus

$$\frac{d}{dt}\tilde{\rho}_S(t) = -i[\mathrm{H}_S + \mathrm{H}_{reorg}, \rho_S(t)] + \sum_{i,\omega}\Big(L_i(\omega)\rho_S(t)L_i^{+}(\omega) - \frac{1}{2}\Big\{L_i^{+}L_i(\omega), \rho_S(t)\Big\}\Big) \tag{36}$$

- The most accurate model is the local thermalising of the Lindblad master equation

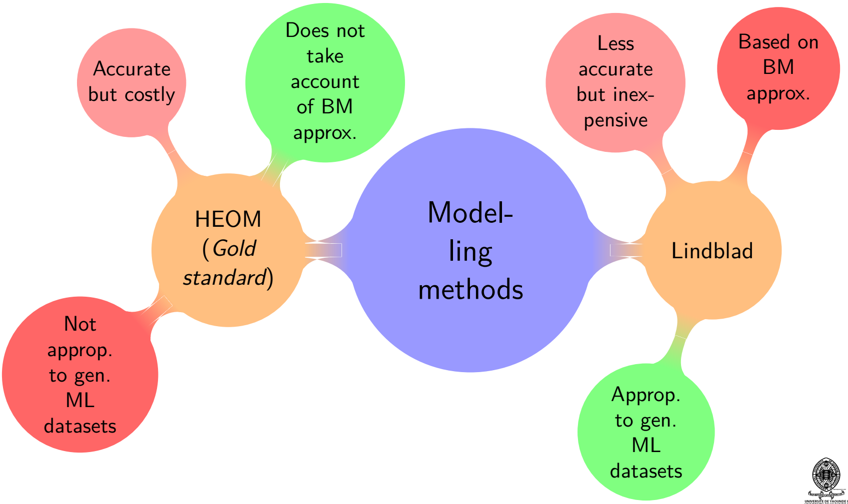
1. FMO complex - Open quantum system (OQS)

2. Dynamics of the FMO complex

3. Why Lindblad for our work ?

HEOM - Lindblad

ML datasets generation

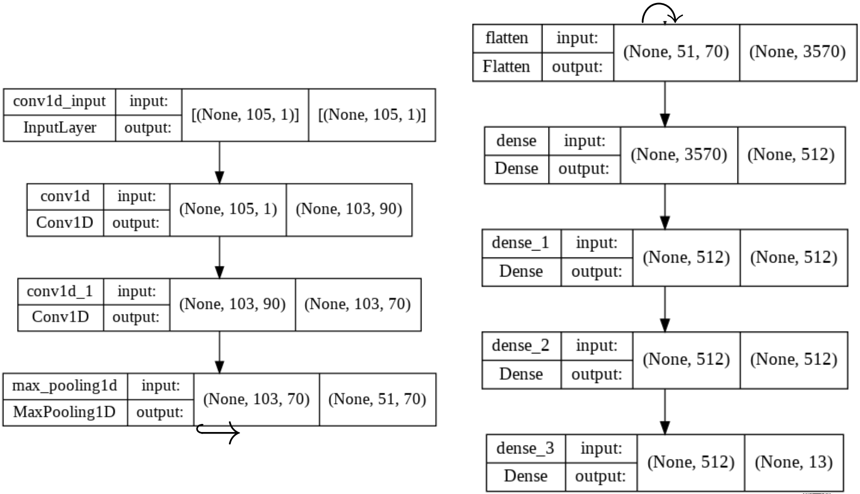


ML=Machine Learning

Datasets for our work

- For our work we have generated, with the local thermalising Lindblad model, 3960 trajectories (site 1 + site 6 initial excited sites) : 1000 for the training, 200 for the validation and 2760 for the test
- Each dataset is a D-space consisting of data on the reorganization energy, the relaxation rate, the temperature, the number of sites, the first excited site as well as the time which is introduced in the form of a temporal functional
- By using a convolutional neural network (CNN) for our ML model, and simulating the EET for both short and long time periods in the FMO complex, we found that our model is able to capture the coherent EET of short time dynamics and also predict the asymptotic limit

CNN architecture used



Acknowledgements