



# Singlet fission in carotenoids

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## Carotenoid excited states

Carotenoids are a family of linear polyenes found abundantly in plants and algae.

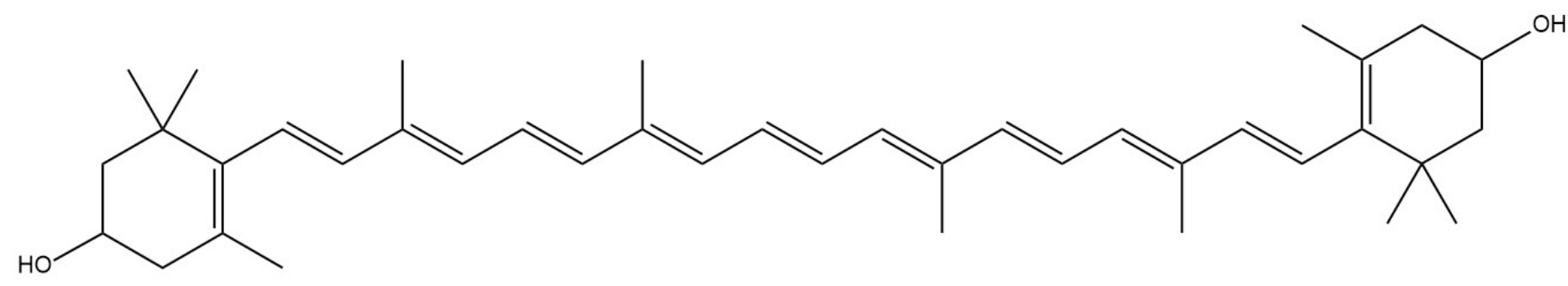


Figure 1: Structural formula of zeaxanthin, a naturally occurring carotenoid.

The quasi one-dimensional geometry of carotenoids gives rise to enhanced electron-electron and electron-nuclear interactions. An important consequence of these interactions is that the optically excited  $1^1B_u^+$  state ( $S_2$ ) is above the optically dark  $2^1A_g^-$  state ( $S_1$ ).

## Singlet fission

Due to the energetic reversal of the  $S_2$  and the  $S_1$  states, carotenoids can undergo singlet fission. Singlet fission is a process by which a photoexcited state dissociates into two uncorrelated triplets. In carotenoids, singlet fission proceeds via a correlated singlet triplet-pair state.



Using the density matrix renormalization group (DMRG) method to solve the Pariser-Parr-Pople-Peierls (PPPP)  $\pi$ -electron Hamiltonian, we showed there exists a family of polyene triplet-pair states ( $2^1A_g^-$ ,  $1^1B_u^-$ ,  $3^1A_g^-$ , ...), differentiated by the center-of-mass kinetic energies.<sup>1</sup>

## Aim of the project

We now seek to characterise the nature of this singlet triplet-pair state  ${}^1(TT)$  via dynamical simulations.

## Model : UV-Peierls Hamiltonian

$$\begin{aligned}\hat{H} &= \hat{H}_{UVP} + \hat{H}_e \\ \hat{H}_{UVP} &= \hat{H}_{UV} + \hat{H}_{e-n} + \hat{H}_{elastic} \\ \hat{H}_{UV} &= -t \sum_{n,\sigma} \left( \hat{c}_{n,\sigma}^\dagger \hat{c}_{n+1,\sigma} + \hat{c}_{n+1,\sigma}^\dagger \hat{c}_{n,\sigma} \right) \\ &\quad + U \sum_n \left( \hat{N}_{n\uparrow} - \frac{1}{2} \right) \left( \hat{N}_{n\downarrow} - \frac{1}{2} \right) \\ &\quad + V \sum_n \left( \hat{N}_n - 1 \right) \left( \hat{N}_{n+1} - 1 \right) \\ \hat{H}_{e-n} &= -\alpha \sum_{n,\sigma} (u_{n+1} - u_n) \left( \hat{c}_{n\sigma}^\dagger \hat{c}_{n+1\sigma} + \hat{c}_{n+1\sigma}^\dagger \hat{c}_{n\sigma} \right) \\ \hat{H}_{elastic} &= \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 \\ \hat{H}_e &= \sum_n \epsilon_n \left( \hat{N}_n - 1 \right)\end{aligned}$$

$t$  is the electron hopping integral for a uniform chain,  $U$  is the on-site Coulomb interaction,  $V$  is the nearest neighbour Coulomb repulsion,  $\alpha$  is the electron-nuclear coupling parameter,  $K$  is the nuclear spring constant, and  $\epsilon_n$  is the on-site potential energy of site  $n$ .

## Symmetry breaking, adiabatic and diabatic states

Symmetry breaking term  $\hat{H}_e$  facilitates internal conversion from positive particle-hole  $1^1B_u^+$  state to negative particle-hole triplet-pair states. We define two types of eigenstates.

$$\begin{aligned}\text{diabatic states : } \hat{H}_{UVP} |\Phi_i\rangle &= E_{\Phi_i} |\Phi_i\rangle, \Phi_i \in \{1^1A_g^-, 2^1A_g^-, 1^1B_u^+, \dots\} \\ \text{adiabatic states : } \hat{H} |S_i\rangle &= E_i |S_i\rangle, i \in \{0, 1, 2, \dots\}\end{aligned}$$

## Time propagation of the electronic wavefunction

Electronic wavefunction evolves under the time dependent Schrödinger equation.

$$|\Psi(t + \delta t)\rangle = e^{-i\hat{H}\delta t/\hbar} |\Psi(t)\rangle, |\Psi(t=0)\rangle = |S_2\rangle$$

Since  $\hat{H} = \sum_n \hat{H}_{n,n+1}$  is a pairwise operator, time evolution operator  $e^{-i\hat{H}\delta t/\hbar}$  can be decomposed via Suzuki-Trotter decomposition.<sup>2,3</sup>

$$\begin{aligned}e^{-i\hat{H}\delta t/\hbar} &= e^{-i\hat{H}_{1,2}\delta t/2\hbar} \dots e^{-i\hat{H}_{N-1,N}\delta t/2\hbar} \\ &\times e^{-i\hat{H}_{N-1,N}\delta t/2\hbar} \dots e^{-i\hat{H}_{1,2}\delta t/2\hbar} + O(\delta t^3)\end{aligned}$$

## TD-DMRG algorithm<sup>2,3</sup>

Link operator :  $\hat{U}_{n,n+1} = e^{-i\hat{H}_{n,n+1}\delta t/2\hbar}$

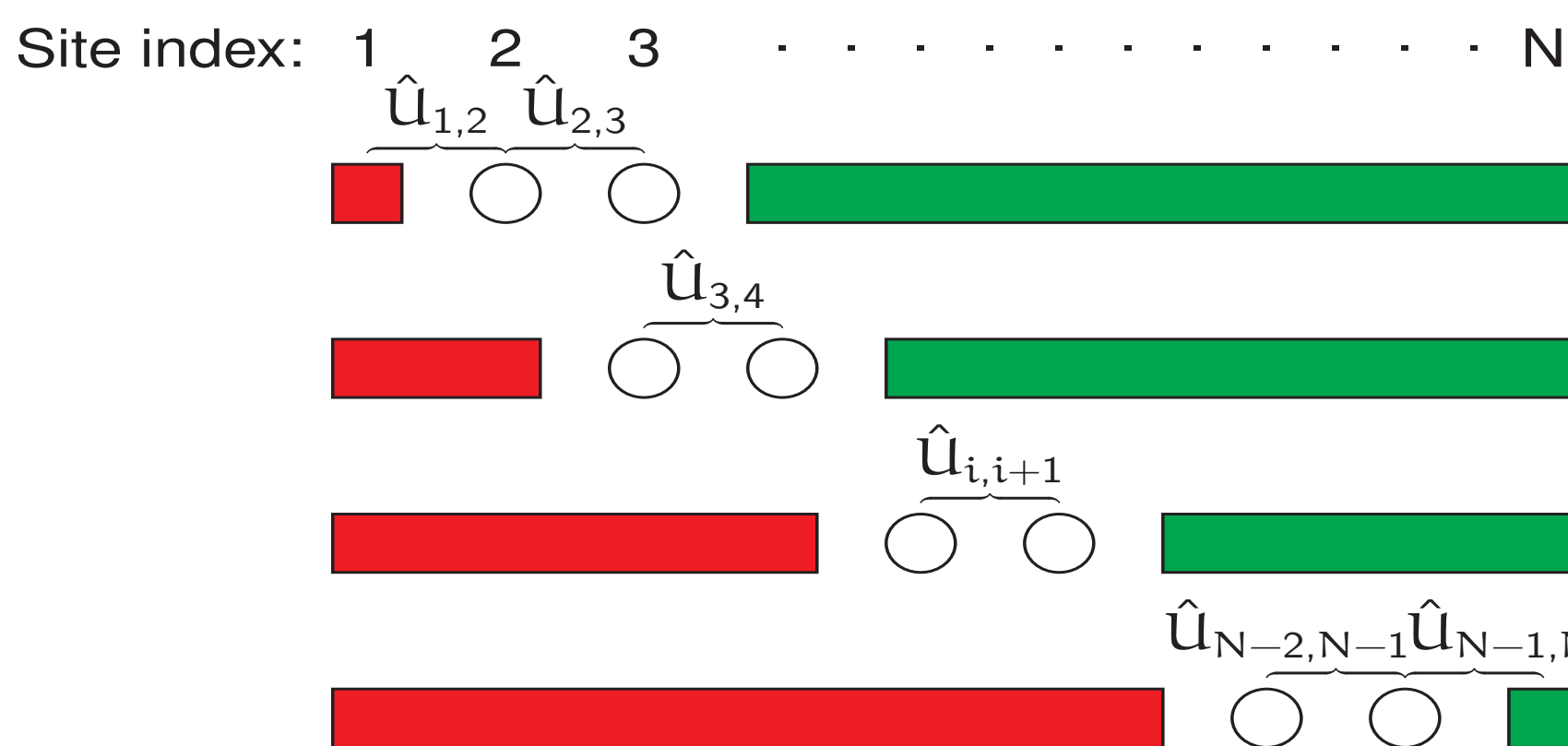


Figure 2: Schematic diagram for TD-DMRG algorithm.

## Nuclear dynamics

Nuclear dynamics is treated classically via Ehrenfest equations of motion.

## Dynamical simulations of zeaxanthin

As a model study, we performed a dynamical simulation of the photoexcited state of zeaxanthin.<sup>4</sup>

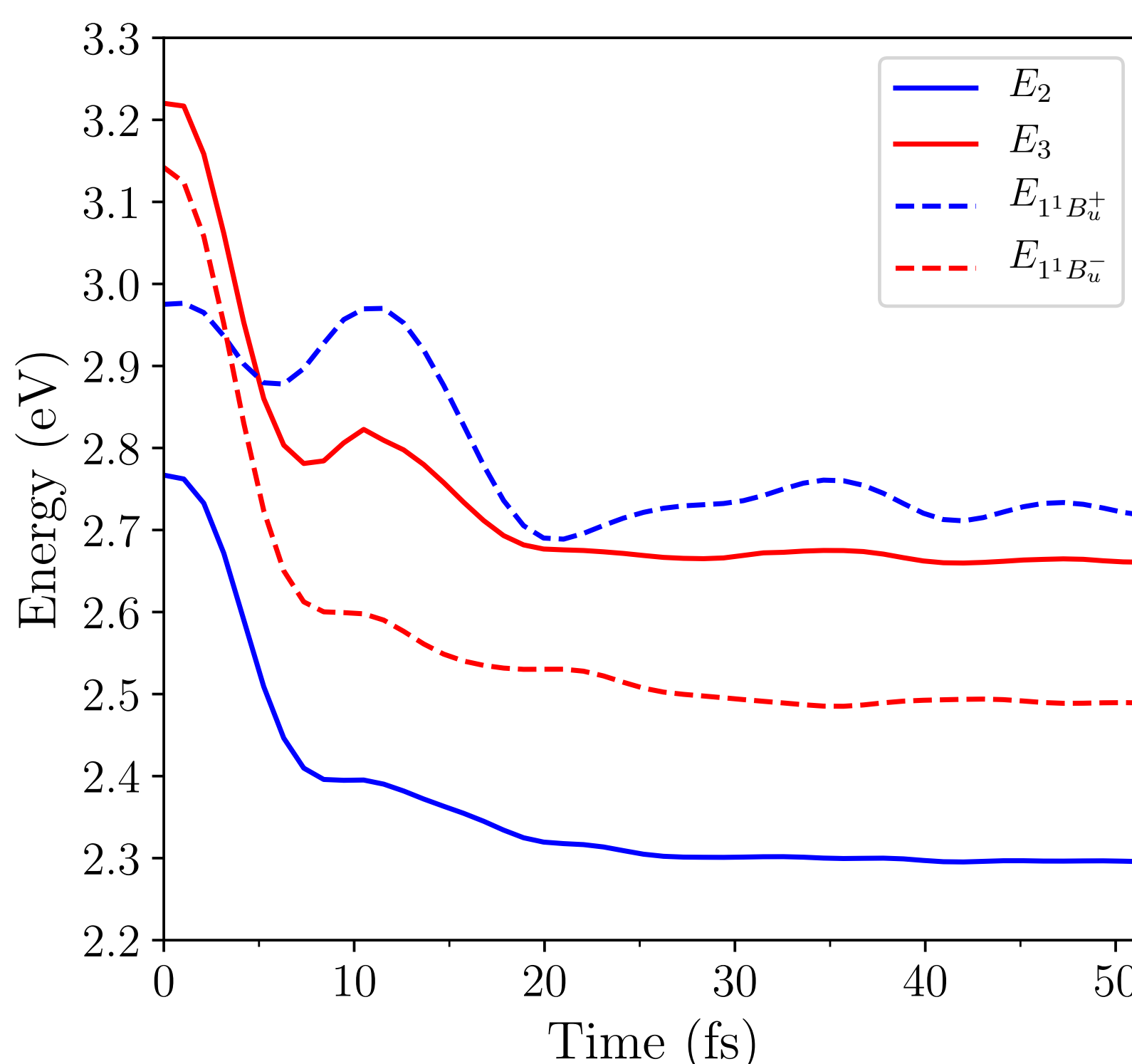


Figure 3: Excitation energies as a function of time of the diabatic  $1^1B_u^-$  and  $1^1B_u^+$  states, and second and third excited adiabatic singlet states  $S_2$  and  $S_3$  for zeaxanthin.  $1^1B_u^-$  and  $1^1B_u^+$  states exhibit a diabatic crossover within 5 fs.

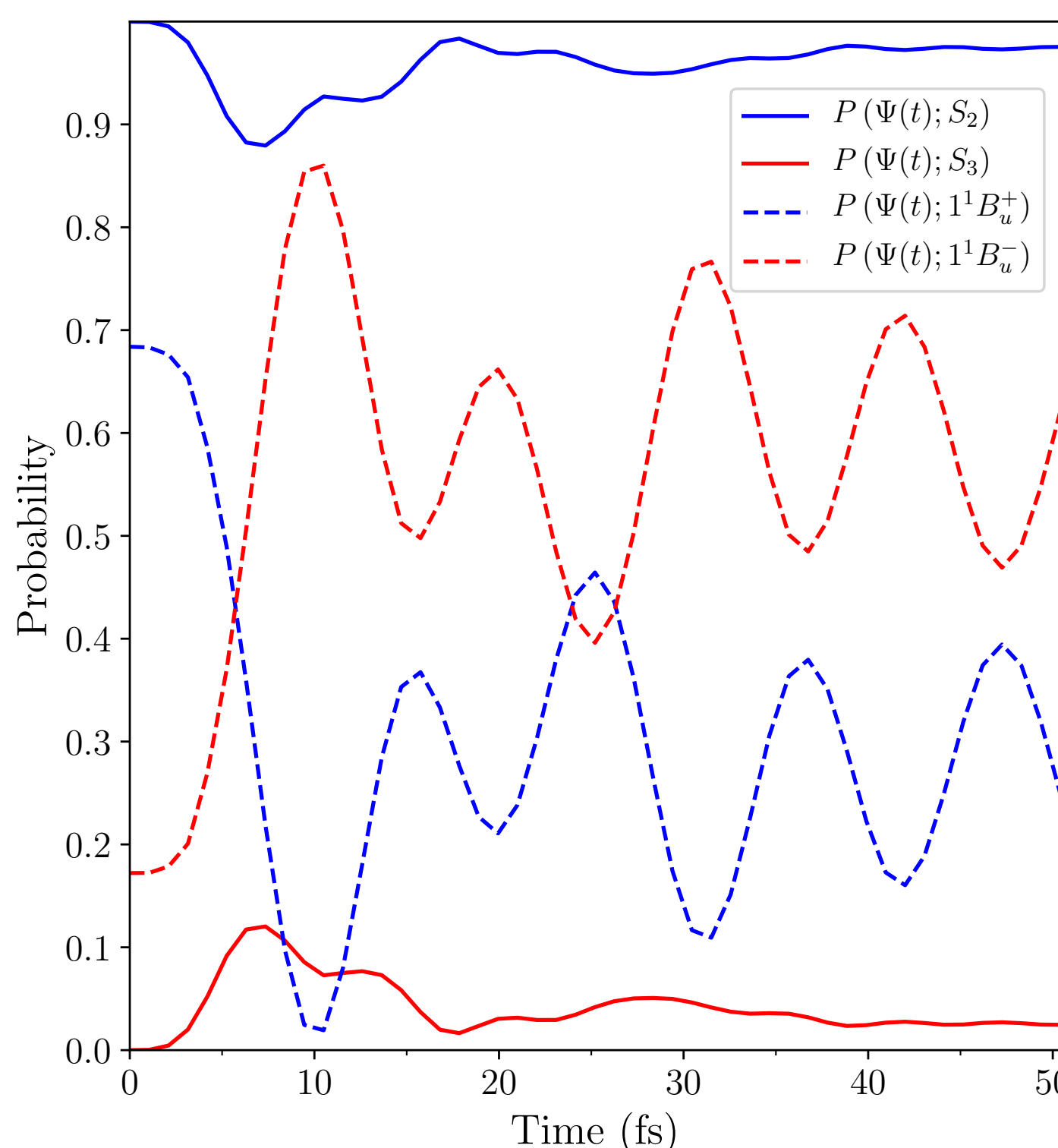


Figure 4: Probabilities that the system described by  $\Psi(t)$  occupies the adiabatic excited singlet states  $S_2$  and  $S_3$ , and diabatic states  $1^1B_u^-$  and  $1^1B_u^+$ .

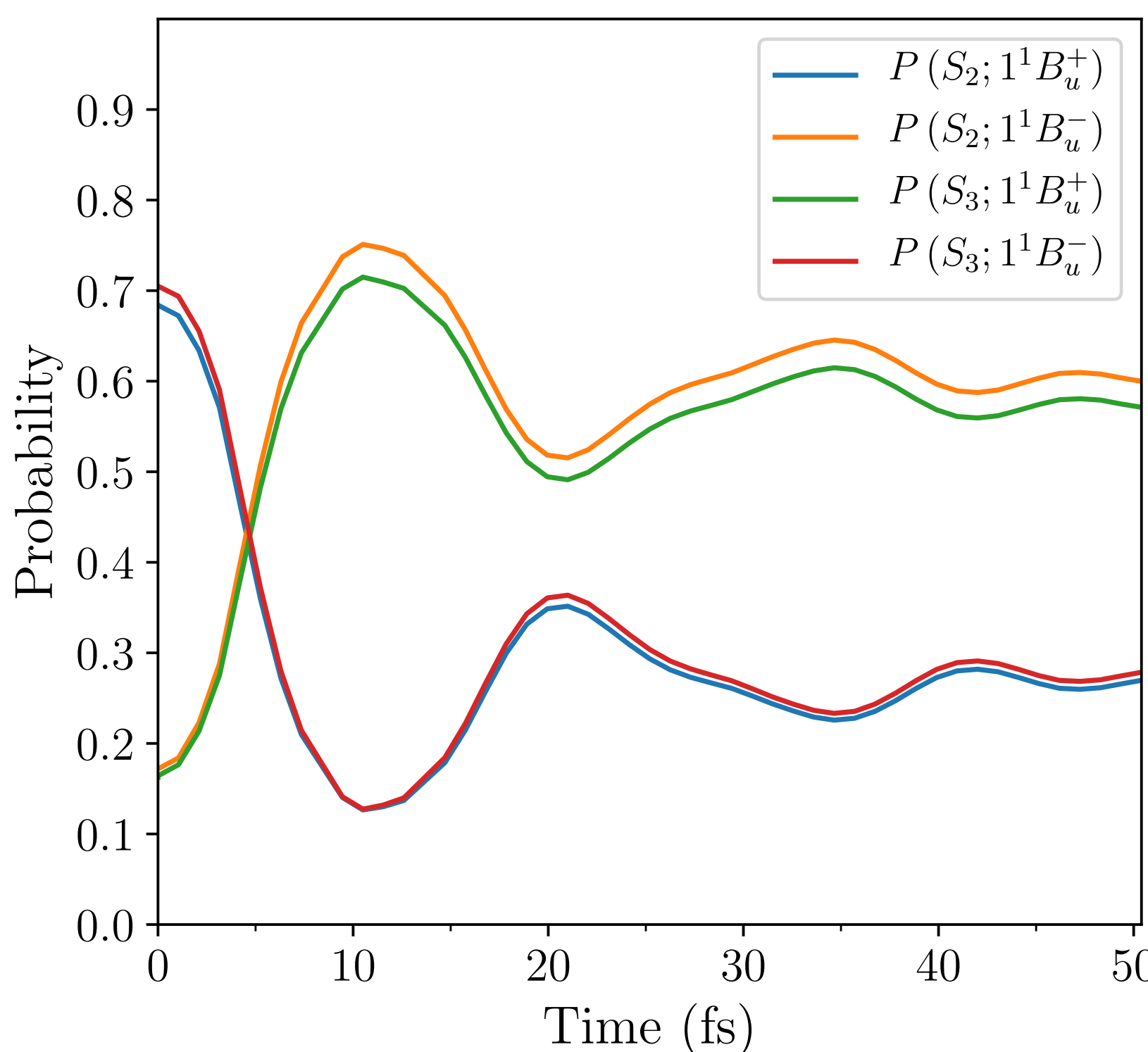


Figure 5: Probabilities that the adiabatic states,  $S_2$  and  $S_3$ , occupy the diabatic states,  $1^1B_u^-$  and  $1^1B_u^+$ . At time  $t = 0$ ,  $S_2$  is the primary photoexcited state, which predominately occupies the exciton state,  $1^1B_u^+$ . Within 50 fs,  $S_2$  predominately occupies the triplet-pair state  $1^1B_u^-$ .

We observe internal conversion to  $1^1B_u^-$  triplet-pair state via an adiabatic transition within 5 fs. A triplet-pair ( $1^1B_u^-$ ) yield of 60% is predicted.

## Dynamical simulations of a series of carotenoids

We performed dynamical simulations on the series of carotenoids reported in ref 5 using two sets of Coulomb ( $U, V$ ) parameterisations to facilitate diabatic energy level crossover between  $1^1B_u^+$  and two triplet-pair states  $1^1B_u^-$  and  $2^1A_g^-$ .

Sym.	Diabatic state crossover	
	$1^1B_u^+ \rightarrow 1^1B_u^-$	$1^1B_u^+ \rightarrow 2^1A_g^-$
$C_{2h}$	Adiabatic dynamics Fast transition to $1^1B_u^-$ $1^1B_u^-$ prominent at long times	Non-adiabatic dynamics System remains in $1^1B_u^+$
	Adiabatic and non-adiabatic dynamics Fast transition to $1^1B_u^-$ Slow non-adiabatic dynamics to $2^1A_g^-$	Adiabatic dynamics Fast transition to $2^1A_g^-$ $2^1A_g^-$ prominent at long times

## Singlet fission via torsional relaxation

Torsional relaxation ( $\theta_0$ ) can promote intermolecular singlet fission from the  $2^1A_g^-$  state.

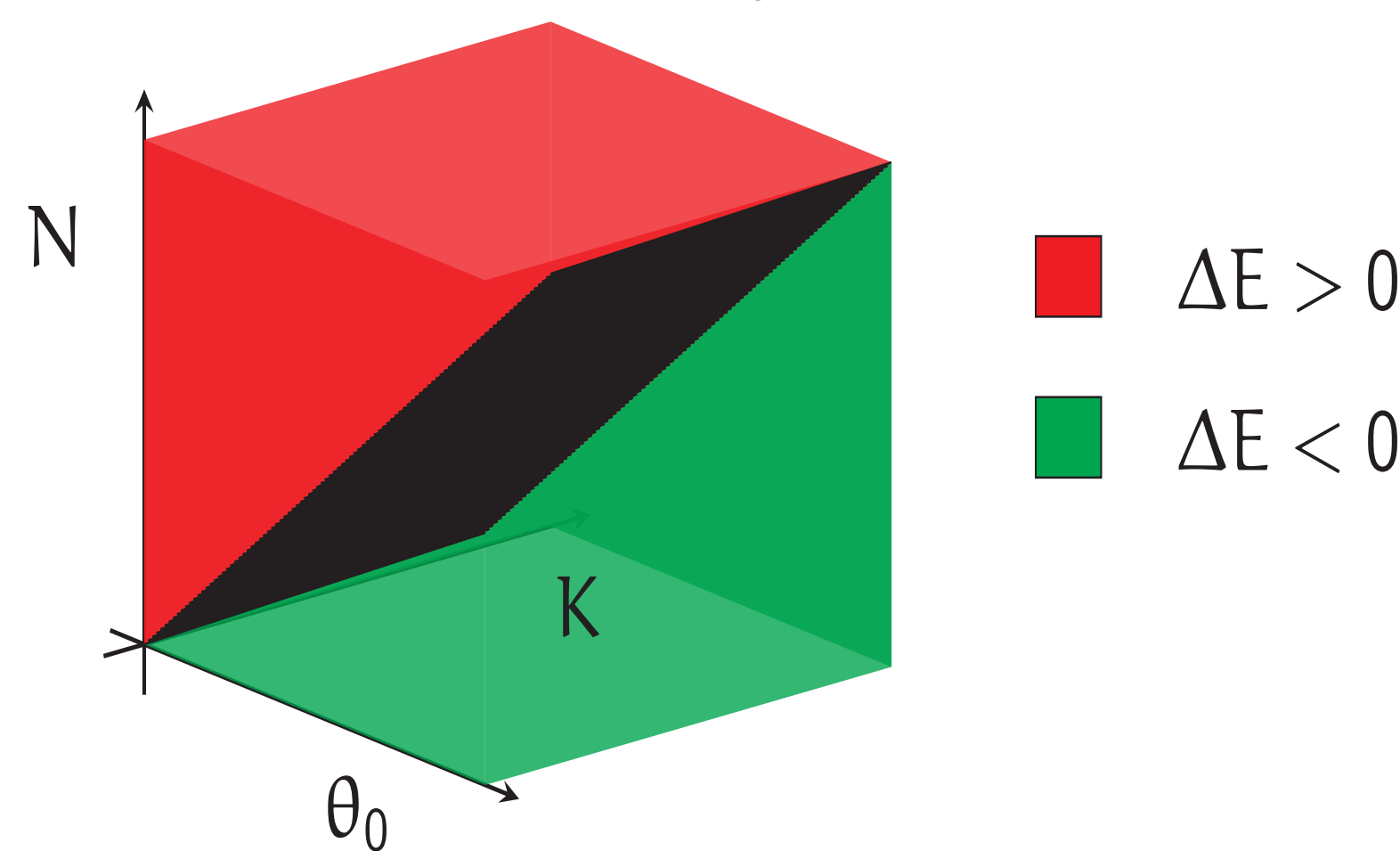


Figure 6: Schematic representation of the variation of triplet binding energy with the torsional angle ( $\theta_0$ ), chain length ( $N$ ) and torsional elastic constant ( $K$ ). Triplet binding energy is defined as  $\Delta E = 2 \times E_{T_1} - E_{2^1A_g^-}$ . Red regions correspond to positive triplet binding energies and green regions correspond to negative triplet binding energies.

For fixed  $N$  and  $K$ ,  $\Delta E$  decreases with  $\theta_0$ .  
For fixed  $N$  and  $\theta_0$ ,  $\Delta E$  increases with  $K$ .  
For fixed  $\theta_0$  and  $K$ ,  $\Delta E$  increases with  $N$ .

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