A Structure Based Model of Slow Excitation Quenching in the major Photosystem II antenna complex of Plants

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Supplementary Material

A discussion of the origin of weak chlorophyll-carotenoid couplings and the role of the exchange and overlap interactions

The *a priori* neglect of the exchange contribution to resonant couplings in light-harvesting complexes is often justified due to its exponential distance dependence. In the case of the interactions between the allowed transitions of the chlorophylls this Coulomb part is often simplified to a transition dipole or transition monopole/charge description. In this work we have neglected the exchange interaction while adopting a reasonable description of the 3D transition density cloud of the donor and acceptor molecules (TDC approach).

However, when considering interactions involving the dark S_1 state, in which appreciable Coulomb coupling occurs only for closely associated pigments, this neglect is less justifiable and the exchange contribution may be significant. However, it is possible to argue that the neglect of the exchange interaction is reasonable (or at least as reasonable as it is in the case of the chlorophyll-chlorophyll couplings).

The overlap correction is similarly neglected here and we present an argument that this is actually less important for the carotenoid-chlorophyll interactions than the chlorophyll-chlorophyll interactions.

For a donor-acceptor pair we define our basis states as

$$|I\rangle = |EX_D\rangle|GS_A\rangle$$

$$|F\rangle = |GS_D\rangle|EX_A\rangle$$

(S1)

where the initial state $|I\rangle$ describes an excited donor and a ground state acceptor and $|F\rangle$ describes the state following energy transfer. If these two basis states are orthogonal, then total (relevant) coupling is composed only of Coulomb, J_{DA}, and exchange parts, K_{DA}. The Coulomb coupling is defined,

$$J_{DA} = \sum_{\substack{i,j \in D \\ k,l \in A}} J'_{ijkl} T^D_{ij} T^A_{kl}$$

(S2)

where the Latin indices denote atomic orbitals (AOs) and Greek indices (see below) label spin. T^D_{ij} and T^A_{kl} are the elements of the transition density matrix in the AO basis,

$$T^D_{ij} = \sum_{\sigma} \left\langle EX_D \middle| c^{\dagger}_{i\sigma} c_{j\sigma} \middle| GS_D \right\rangle$$

$$T^A_{kl} = \sum_{\sigma'} \left\langle GS_A \middle| c^{\dagger}_{k\sigma'} c_{l\sigma'} \middle| EX_D \right\rangle$$

(S3)

with $c^{(\dagger)}_{i\sigma}$ being the AO (creation) annihilation operators. Lastly,

$$J'_{ijkl} = \iint d^3r d^3r' \phi^*_i(r) \phi_j(r) \frac{1}{|r - r'|} \phi^*_k(r') \phi_l(r')$$

(S4)

For singlet-singlet transfer the exchange contribution is defined,

$$K_{DA} = -\frac{1}{2} \sum_{\substack{i,j \in D \\ k,l \in A}} K'_{ijkl} T^D_{ij} T^A_{kl}$$

(S5)

where,

$$K'_{ijkl} = \iint d^3r d^3r' \phi^*_i(r) \phi_j(r') \frac{1}{|r - r'|} \phi^*_k(r') \phi_l(r)$$

(S6)

The total coupling is therefore,

$$W_{DA} = \sum_{\substack{i,j \in D \\ k,l \in A}} T^D_{ij} T^A_{kl} \left\{ J'_{ijkl} - \frac{1}{2} K'_{ijkl} \right\}$$

(S8)

The carotenoid S$_1$ state is optically dark due to two factors: inversion symmetry and its multi-electron character. Inversion symmetry arises from the bulk geometry of the molecule and is only (approximately) valid for *all trans* polyenes. The multi-electron character, however, arises from strong-electron correlations, depends on bond length alternation and places strict limits on how strongly the S$_1$ state can interact with transitions of other chromophores.

In our approach both ground and S$_1$ states of the chromophores are described as multi-electron CI expansion,

$$|\Psi\rangle = C_0|\psi_0\rangle + \sum_{\substack{a\in occ.\\ r\in virt.\\ \sigma}} C_{a_\sigma}^{r_\sigma} a_{r\sigma}^{\dagger} a_{a\sigma}|\psi_0\rangle + \sum_{\substack{a,b\in occ.\\ r,t\in virt.\\ \sigma,\sigma'}} C_{a_\sigma b_{\sigma'}}^{r_\sigma t_{\sigma'}} a_{t\sigma'}^{\dagger} a_{b\sigma'} a_{r\sigma}^{\dagger} a_{a\sigma}|\psi_0\rangle + \ldots \tag{S9}$$

where $|\psi_0\rangle$ is the references determinant from the initial self-consistent field (SCF) calculation, $\{C\}$ are the CI coefficients and $a_{r\sigma}^{(\dagger)}$ are molecular orbital, MO, (creation) annihilation operators. Calculating T_{ij}^{X} involves evaluating a large number of cross terms. However, this is simplified by Slater's rule, which states that the matrix elements between determinants that differ by more than one orbital are zero. Therefore,

$$T_{ij}^{X} = \sum_{\substack{A,R\\ \psi'\\ \sigma}} C_{\psi'} C_{A_\sigma}^{R_\sigma} \beta_{Ai}^{*} \beta_{Rj}$$

(S10)

where $|\psi'\rangle$ is any determinant featuring in the CI-expansion of the ground state and,

$$|\psi_{A_\sigma}^{R_\sigma}\rangle = a_{R\sigma}^{\dagger} a_{A\sigma}|\psi'\rangle$$

(S11)

For the carotenoid co-factors $|GS_{Car}\rangle \approx |\psi_0\rangle$ ($C_0 > 0.9$) and so,

$$T_{ij}^{Car} \approx \sum_{\substack{a\in occ.\\ r\in virt.\\ \sigma}} C_{a_\sigma}^{r_\sigma} \beta_{ai}^{*} \beta_{rj}$$

(S12)

Moreover the predominant contribution to $|S_1\rangle$ is the two-electron HOMO-LUMO determinant ($C_{H_\downarrow H_\uparrow}^{L_\downarrow L_\uparrow} \sim 0.6$) with a relatively small contribution from one-electron terms. The result of this is that the S$_1$ state (having a strong two-electron character) is associated with a vanishingly small transition density[1]. This puts the severe limits on the chlorophyll carotenoid couplings in our model of LHCII and explains why even 9-*cis* neoxanthin (which is asymmetric under inversion) has a vanishing transition dipole moment and a similarly restricted coupling to neighbouring chlorophylls.

In our model, we have neglected the exchange contribution to our inter-molecular couplings based on its steep distance dependence. Indeed, for any pair of chromophore transitions (dark or otherwise) this is the only consideration,

$$\frac{K_{DA}}{J_{DA}} = -\frac{K_{ijkl}^{'}}{2J_{ijkl}^{'}}$$

(S13)

In the densely packed interior of LHCII it is likely that the exchange interaction makes some contribution to the couplings between co-factors. However, this contribution depends only on distances and relative orientations of the co-factors (if both transitions are computed with the same AO basis set). We would therefore expect the exchange correction to be as relevant for the closely-associated chlorophyll clusters for the appreciable chlorophyll-carotenoid pair interaction. Previous ‘chlorophyll-only’ models of LHCII have also assumed $K_{DA} = 0$ while reproducing all steady-state and time resolved spectra and given the reasonable agreement between the lifetime of our model and the measured lifetime of the quenched part of the crystal[2] we argue that our model is at least qualitatively reasonable. Moreover, in bacterial systems it has been argued that only the Coulomb interaction makes a significant contribution to the bacteriochlorophyll-carotenoid (S_1) interaction[3].

If the basis states (S1) are not orthogonal, then an overlap correction for W_{DA} is required[4],

$$W^{overlap}_{DA} = \frac{1}{1 - {S_{DA}}^2}\left\{W_{DA} - \frac{1}{2}(\varepsilon_D + \varepsilon_A)S_{DA}\right\}$$

(S14)

where,

$$S_{DA} = -\frac{1}{N^e_{DA}}\sum_{\substack{i,j \in D \\ k,l \in A}} T^D_{ij}T^A_{kl}S_{ik}S_{jl}$$

(S15)

where N^e_{DA} is the total number of electrons in our dimer and,

$$S_{ik} = \int dr\phi^*_i(r)\phi_k(r)$$

where $i \in D$ and $k \in A$. If we assume that the pigment landscape in LHCII is broadly iso-energetic, then due to the two-electron character of the carotenoid S_1 state we expect the relative overlap correction for the chlorophyll-carotenoid couplings to be significantly smaller than for the chlorophyll-chlorophyll couplings ($T^{Cart}_{ij} \ll T^{Chl}_{ij}$).

Supplementary references

[1] K. Schulten, I. Ohmine and M. Karplus, *Journal of Chemical Physics*, 1976, 64, 4422-4441.
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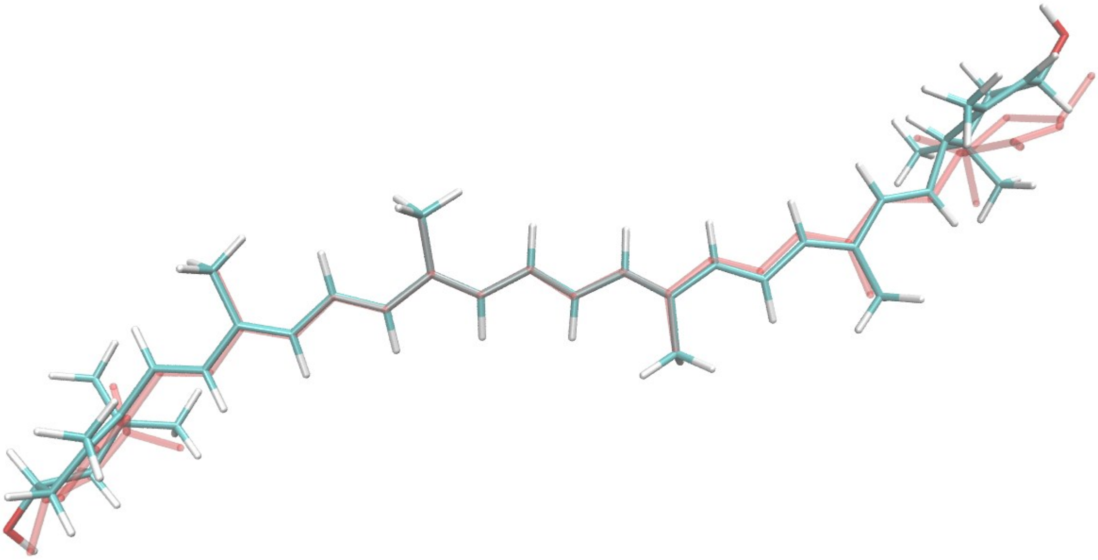
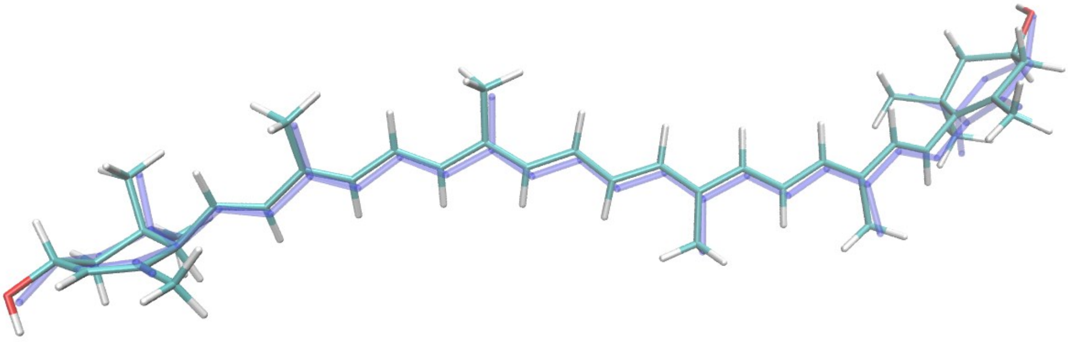
[3] T. Ritz, A Damjanović and K Schulten, *Chem. Phys. Chem.* 2002, 3, 243-248.
[4] P.-O. Löwdin, *J. Chem. Phys.*, 1950, 18, 365.

Supplementary Figures

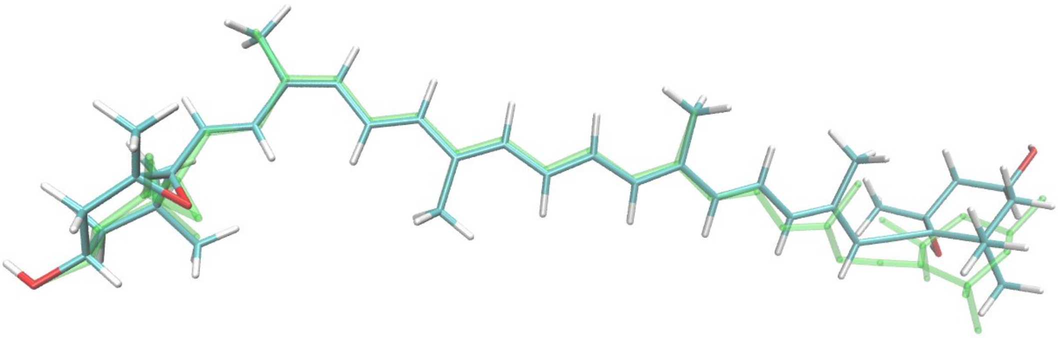
Sup. Figure 1 | A comparison between the crystal structure and the post cage optimised structure of Lutein620. Deviations fall within the resolution of the crystal structure. The largest differences are with some slight rotations to the head groups.



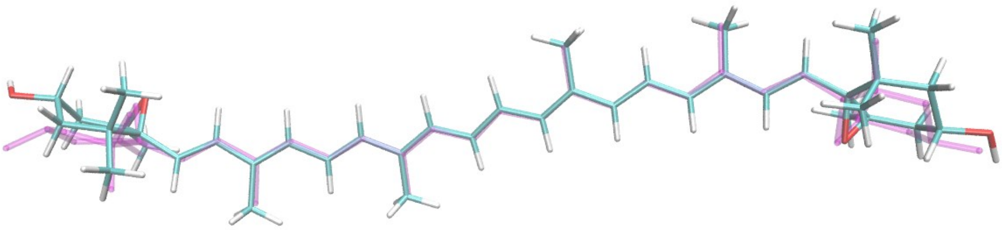
Sup. Figure 2 | A comparison between the crystal structure and the post cage optimised structure of Lutein621.



Sup. Figure 3 | A comparison between the crystal structure and the post cage optimised structure of Neoxanthin. There is some deviation at one end but this is the end that extends past the edges of the protein and as such has very little difference to any couplings due to the short-range nature of the carotenoid-chlorophyll coupling interactions.



Sup. Figure 4 | A comparison between the crystal structure and the post cage-optimised structure of Violaxanthin.



Sup. Figure 5 | A bond length alternation plot of vacuum and cage optimised Lut620 as well as a vacuum optimised Lut620 with the dihedrals along the backbone of the carotenoid frozen. δ_n is defined as $\delta = (-1^n) \times (\bar{n} - (\bar{n} + 1))$ where n is the bond number and $\bar{n}$ is the bond length.