Supporting Information

Bridge-mediated excitation energy transfer pathways through protein media: a Slater determinant-based electronic coupling calculation combined with localized molecular orbitals

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A. Electronic coupling with super-exchange mechanism

Here, we derive the formula for the electronic coupling calculation with Green's function technique using Slater determinants. The following equations are mostly similar to their one-electron counterparts; the present formula employs Slater determinants instead of one-electron orbitals in the previous formula.[1] The system was divided into donor, bridge, and acceptor (D-B-A). We adopted LMOs, $\{\phi_r\}$, for one-electron orbitals, and they are orthonormal each other, $\langle\phi_r|\phi_s\rangle = \delta_{rs}$. Slater determinant, $\Phi_p = |\phi_1\phi_2\cdots\phi_N|$, is constructed using the LMOs. If the index p is D and A, an exciton (or electron for the ET case) is localized at donor (D) and acceptor (A), respectively. In the other cases, Φ_p represents an exciton in the bridge or CT excitations. The initial- and final-state wave functions were described as a linear combination of the determinants, $\Psi_I = \sum_{p\neq A} C_p^I \Phi_p$ and $\Psi_F = \sum_{p\neq D} C_p^F \Phi_p$, respectively. We put a limitation in the linear expansion, $C_p^I = C_q^F = 0$ ($p \in A, q \in D$); the initial- and final-state wave functions do not involve the acceptor and donor determinants, respectively. Because of the orthonormality in the one-electron orbitals, the determinants are also orthonormal $\langle\Phi_p|\Phi_q\rangle = \delta_{pq}$. We also introduce notation for Hamiltonian matrix element as $\langle\Phi_p|H|\Phi_q\rangle = H_{pq}$.

We do not consider nuclear motions here and instead employ the Born-Oppenheimer and Condon approximations following Marcus theory.[2] Under these approximations, EET occurs when the initial and final electronic states have the same energy E. In this situation, a two-state Schrödinger equation is written as

$$\left(\hat{H} + \hat{V}\right)\begin{pmatrix}\Psi_I\\ \Psi_F\end{pmatrix} = E\begin{pmatrix}\Psi_I\\ \Psi_F\end{pmatrix}, \qquad \text{(A1)}$$

where $\hat{V}$ denotes the interaction between the initial and final state, and $\hat{H}$ denotes the non-interacting part of the Hamiltonian. From the Schrödinger equation (A1), the interaction between the initial and final state is

$$\langle \Psi_I | \hat{V} | \Psi_F \rangle = \langle \Psi_I | E - \hat{H} | \Psi_F \rangle. \quad \text{(A2)}$$

The secular equations for determining $\{C_q^I\}$ are $\{C_q^F\}$ are

$$\langle \Psi_I | \hat{H} - E | \Phi_p \rangle = C_{D_0}^I H_{D_0 p} + \sum_{q \neq A, q \neq D_0} C_q^I (H_{qp} - E\delta_{qp}) = 0, \quad \text{(A3)}$$

$$\langle \Phi_p | \hat{H} - E | \Psi_F \rangle = H_{pA_0} C_{A_0}^F + \sum_{q \neq D, q \neq A_0} (H_{pq} - E\delta_{pq}) C_q^F = 0, \quad \text{(A4)}$$

where we use intermediate normalization, $C_{D_0}^I = C_{A_0}^F = 1$. D_0 and A_0 are the most dominant determinant in the donor and acceptor states. After solving the linear equations A3 and A4, coefficients for the CI-level wave functions of the initial and final states can be written as

$$C_q^I = -C_{D_0}^I \sum_{p \neq A, p \neq D_0} H_{D_0 p} G_{pq}, \quad \text{(A5)}$$

$$C_q^F = -C_{A_0}^F \sum_{p \neq D, p \neq A_0} G_{qp} H_{pA_0}, \quad \text{(A6)}$$

where $G_{pq} = (1/H - EI)_{pq}$. These equations show that interactions between the dominant and other determinants are included. Ψ_I and Ψ_F are then normalized as:

$$\bar{C}_p^I \equiv C_p^I / \sqrt{P_I}, \quad P_I \equiv \sum_q |C_q^I|^2,$$

$$\bar{C}_p^F \equiv C_p^F / \sqrt{P_F}, \quad P_F \equiv \sum_q |C_q^F|^2. \quad \text{(A7)}$$

These normalization factors involve a self-energy correction for the D_0 and A_0 configurations from a higher order of configuration interaction that is neglected in the above secular equations.[1,3]

Finally, the electronic coupling can be written as[4]

$$T_{IF}(E) = \langle \Psi_I | E - \hat{H} | \Psi_F \rangle = \sum_{pq} \bar{C}_p^I (EI - H)_{pq} \bar{C}_q^F$$

$$= \sum_p \bar{C}_p^I H_{qA_0} \bar{C}_{A_0}^F = \sum_q \bar{C}_{D_0}^I H_{D_0 q} \bar{C}_q^F. \quad \text{(A8)}$$

This equation includes the super-exchange effect from bridge configurations with second-order perturbations of the H_{Dp} and H_{qA} interactions as well as a direct interaction between the donor and acceptor configurations.

B. Configuration density tunneling flux analysis for excitation energy transfer

Here, we retain the tunneling current analysis.[5] Because we study the flux of the configuration density instead of the electron flux, we refer to this object as the tunneling flux rather than the current. The time-dependent two-state wave function is written as

$$\Psi = \begin{pmatrix} \cos(\omega t)\,\Psi_I \\ -i\sin(\omega t)\,\Psi_F \end{pmatrix}. \tag{B1}$$

Using $\Psi_I = \sum_p \bar{C}_p^I \Phi_p$ and $\Psi_F = \sum_p \bar{C}_p^F \Phi_p$, it is divided with components of p as

$$\Psi = \sum_p \begin{pmatrix} \cos(\omega t)\bar{C}_p^I \Phi_p \\ -i\sin(\omega t)\,\bar{C}_p^F \Phi_p \end{pmatrix} \equiv \sum_p \Psi_p. \tag{B2}$$

The time evolution of the population matrix element is given by

$$\begin{aligned} \frac{\partial P_{pq}}{\partial t} &= \frac{\partial \langle \Psi_p | \Psi_q \rangle}{\partial t} = \frac{\partial \langle \Psi_p |}{\partial t} |\Psi_q\rangle + \langle \Psi_p | \frac{\partial |\Psi_q\rangle}{\partial t} \\ &= -\frac{1}{i\hbar} \langle \Psi_p | \hat{H}^{ts} | \Psi_q \rangle^* + \frac{1}{i\hbar} \langle \Psi_p | \hat{H}^{ts} | \Psi_q \rangle = \frac{2}{i\hbar} \mathrm{Im} \langle \Psi_p | \hat{H}^{ts} | \Psi_q \rangle, \end{aligned} \tag{B3}$$

and

$$\begin{aligned} \langle \Psi_p | \hat{H}^{ts} | \Psi_q \rangle &= \bar{C}_p^I \bar{C}_q^I \langle \Phi_p | \hat{H}^{ts} | \Phi_q \rangle \cos(\omega t)^2 + \bar{C}_p^F \bar{C}_q^F \langle \Phi_p | \hat{H}^{ts} | \Phi_q \rangle \sin(\omega t)^2 \\ &\quad -i\left(\bar{C}_p^I \bar{C}_q^F \langle \Phi_p | \hat{H}^{ts} | \Phi_q \rangle - \bar{C}_p^F \bar{C}_q^I \langle \Phi_p | \hat{H}^{ts} | \Phi_q \rangle \right) \sin(\omega t)\cos(\omega t), \end{aligned} \tag{B4}$$

where $\hat{H}^{ts} = E\hat{I} - \hat{H}$ is the two-state Hamiltonian, E is the tunneling energy, and $\hat{H}$ is the single-state electronic Hamiltonian. Substituting (B4) into (B3), the tunneling flux (defined as components of the time evolution of the population) becomes

$$\frac{\partial P_{pq}}{\partial t} = \frac{1}{\hbar}\left(\bar{C}_p^I \bar{C}_q^F - \bar{C}_p^F \bar{C}_q^I \right) (\mathbf{H} - E\mathbf{I})_{pq} \sin(2\omega t) \equiv J_{pq}(t) \equiv J_{pq} \sin(2\omega t). \tag{B5}$$

The diagonal term J_{pp} is zero, allowing us to write the amplitude factor as

$$J_{pq} = \frac{1}{\hbar}\left(\bar{C}_p^I \bar{C}_q^F - \bar{C}_p^F \bar{C}_q^I\right) H_{pq}. \quad \text{(B6)}$$

J_{pq} indicates the contribution of the tunneling pathway between two configurations to the electronic coupling at energy E.

C. Distance dependence of bridge-mediated indirect electronic coupling

Here we consider a one-dimensional donor-bridge-acceptor system with N bridge sites. The distance between the donor and acceptor is defined as R_0.

(1) We compare the distance dependence between the single-step (direct) term and the two-step term. Here we assume a site-site interaction is proportional to R^{-n}, where R and n are the distance between the sites and a positive real value, respectively. Because of the one-dimensional bridge, a two-step term in the electronic coupling, T_2 with the site-site distances r and (R_0-r) is given by

$$T_2 = C\, r^{-n}(R_0 - r)^{-n}, \tag{C1}$$

where C is a constant. The slope of T_2 on a log-log scale is given by

$$\frac{\partial \log T_2}{\partial \log R_0} = -n\left(\frac{R_0}{R_0 - r}\right). \tag{C2}$$

When the right-hand side of (C2) is smaller than –n, the T_2 term decays faster than R^{-n}. In the long distance limit ($R_0 \gg r$), the T_2 term polynomially decays with distance R_0. We conclude here that the two-step term decays faster than the single-stem when the site-site interaction is proportional to R^{-n}. This discussion can also apply to the comparison between the n-step term and the (n+1)-term.

(2) Next, we discuss the dependence on the number of site when the distance between the donor and acceptor is kept constant, R_0. Using site-site distance r_s, the donor-acceptor distance is written as $R_0 = (N+1)\cdot r_s$. In our assumption, site-site interaction decays with r_s^{-n} (n equals 3 for the case of a dipole-dipole interaction). N-step interaction is

$$T_{N+1} = C'\gamma^{N+1} = C'\left(\frac{\beta(N+1)^n}{R_0^n}\right)^{N+1}, \tag{C3}$$

where one-step decay factor $\gamma = \beta/r_s^n = \beta(N+1)^n/R_0^n$. β is a factor of the site-site interaction divided by the tunneling barrier. C' is the tunneling barrier. Differentiating the T_{N+1} with respect to N, we get

$$\frac{\partial T_{N+1}}{\partial N} = T_{N+1}(\log\gamma + n). \qquad \text{(C4)}$$

Eq. (C4) is smaller than zero and T_{N+1} decays with N for weak-coupled bridging sites, $\gamma < e^{-n}$. For a limit of constant γ (n=0), T_N decays exponentially with N.

References

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