Electronic Supplementary Information (ESI) Available:

Direct sampling of discretized Feynman paths (Appendix A); Derivation of the charge transfer rate formula with the saddle point approximation from Fermi gold rule (Appendix B)

Influences of molecular packing on the charge mobility of organic semiconductors: from quantum charge transfer rate theory beyond the first-order perturbation

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Appendix A: Direct sampling of discretized Feynman paths

In this appendix, we give a detailed description of the Monte Carlo calculation of the imaginary time correlation functions. This is basically a simplified version of the calculation of real time correlation functions by Cao *et al*.[43] Given two terminal points x_0^j and x_τ^j of the vibrational-mode paths as specified by the boundary conditions of the *j*-th vibrational-mode path integration, one has the imaginary time propagator in the discretized form[33]

$$\left\langle x_\tau^j \middle| \exp\left(-\tau \frac{H_{vib}^j}{\hbar}\right) \middle| x_0^j \right\rangle = \left[\frac{m_j\omega_j}{2\pi\hbar\sinh\left(\omega_j\tau\right)}\right]^{P/2} \prod_{n=1}^{P-1} \int dx_n^j \ \exp\left\{-S\left(\left[x_n^j\right]\right)/\hbar\right\}, \quad \text{(A1)}$$

and the $S\left(\left[x_n^j\right]\right)$ has the form

$$S\left(\left[x_n^j\right]\right) = \frac{m_j\omega_j}{2\sinh\left(\omega_j\varepsilon\right)} \sum_{n=1}^{P} \left[\left(x_{n-1}^{j2} + x_n^{j2}\right)\cosh\left(\omega_j\varepsilon\right) - 2x_{n-1}^j x_n^j\right]. \quad \text{(A2)}$$

In Eqs. (A1) and (A2), we have denoted the number of discretized time slices as P, $x_P^j = x_\tau^j$, $\tau = \beta\hbar$ and thus the increment of the discretized time slice is $\varepsilon = \tau/P$. H_{vib}^j in Eq. (A1) is the Hamiltonian of *j*-th intramolecular normal mode and is given in Eq. (15). Introducing the classical trajectory $x_{cl}^j\left(\tau'\right)$ and the discretized Fourier modes $\left\{a_l^j\right\}$, one can decompose the path as

$$x_n^j = x_{cl}^j\left(\tau_n\right) + \sum_{l=1}^{P-1} a_l^j \sin\left(l\pi n/P\right), \quad \text{(A3)}$$

where the classical solution connecting the two end points is given by

$$x_{cl}^j\left(\tau'\right) = \frac{x_\tau^j \sinh\left(\omega_j\tau'\right) + x_0^j \sinh\left[\omega_j\left(\tau-\tau'\right)\right]}{\sinh\left(\omega_j\tau\right)}, \quad \text{(A4)}$$

and the Fourier modes diagonalize the quadratic action functional. Consequently, the imaginary action functional, Eq. (A2), becomes the form

$$S\left(\left[x_n^j\right]\right)=S_\beta\left(x_0^j,x_\tau^j;\tau\right)+\sum_{l=1}^{P-1}\frac{m_j\bar{\tau}_j}{2}\left\{2\left[1-\cos\left(\pi l/P\right)\right]\frac{P^2}{\bar{\tau}_j^2}+\bar{\omega}_j^2\right\}\frac{a_l^{j2}}{2}. \tag{A5}$$

Here, $\bar{\tau}_j$ and $\bar{\omega}_j$ are defined as

$$\bar{\tau}_j=\tau\frac{\sinh\left(R_j\right)}{R_j}, \tag{A6}$$

$$\bar{\omega}_j=\omega_j\frac{1}{\cosh\left(R_j/2\right)} \tag{A7}$$

with $R_j=\omega_j\tau/P$. Then, Eq. (A1) is written as

$$\left\langle x_\tau^j\left|\exp\left(-\tau\frac{H_{vib}^j}{\hbar}\right)\right|x_0^j\right\rangle=\left[\frac{m_j\omega_j}{2\pi\hbar\sinh\left(\omega_j\tau\right)}\right]^{P/2}\exp\left\{-S_\beta\left(x_0^j,x_\tau^j;\tau\right)/\hbar\right\}$$
$$\times\prod_l^{P-1}\int da_l^j\ \exp\left\{-\sum_{l=1}^{P-1}\frac{m_j\bar{\tau}_j}{2\hbar}\left\{2\left[1-\cos\left(\pi l/P\right)\right]\frac{P^2}{\bar{\tau}_j^2}+\bar{\omega}_j^2\right\}\frac{a_l^{j2}}{2}\right\}. \tag{A8}$$

The above equation is for the *j*-th vibrational mode. When all of the modes are considered, we can get

$$\left\langle x_\tau\left|\exp\left(-\tau\frac{H_{vib}}{\hbar}\right)\right|x_0\right\rangle=\prod_{j=1}^{N}\left(\left[\frac{m_j\omega_j}{2\pi\hbar\sinh\left(\omega_j\tau\right)}\right]^{P/2}\exp\left\{-S_\beta\left(x_0^j,x_\tau^j;\tau\right)\right\}\right)$$
$$\times\left(\prod_{l=1}^{P-1}\prod_{j=1}^{N}\int da_l^j\right)\exp\left\{-\sum_{l=1}^{P-1}\sum_{j=1}^{N}\frac{m\bar{\tau}_j}{2\hbar}\left\{2\left[1-\cos\left(\pi l/P\right)\right]\frac{P^2}{\bar{\tau}_j^2}+\bar{\omega}_j^2\right\}\frac{a_l^{j2}}{2}\right\} \tag{A9}$$

with $\left|x_0\right\rangle=\left|x_0^1\cdots x_0^N\right\rangle$ and $\left|x_\tau\right\rangle=\left|x_\tau^1\cdots x_\tau^N\right\rangle$. It is useful to define

$$\omega_l^{j2}=\frac{m_j\bar{\tau}_j}{2\hbar}\left\{2\left[1-\cos\left(\pi l/P\right)\right]\frac{P^2}{\bar{\tau}_j^2}+\bar{\omega}_j^2\right\}. \tag{A10}$$

Cao *et al* have found a linear transformation from $\left\{a_l^j\right\}$ to a_l and its orthogonal set $\left\{y_l^j\right\}$[80]

$$\sum_{j=1}^{N}\frac{1}{2}\omega_l^{j2}a_l^{j2}=\frac{1}{2}\omega_l^2a_l^2+\sum_{i=1}^{N-1}\frac{1}{2}\bar{\omega}_i^2\left(y_l^i+\frac{\bar{c}_i}{\bar{\omega}_i^2}a_l\right)^2 \tag{A11}$$

and the following the relationship

$$\sum_{j=1}^{N} g_j a_l^j = a_l, \tag{A12}$$

with

$$g_j = c_j \Big/ \sqrt{\sum_{j=1}^{N} c_j^2} \tag{A13}$$

and

$$\omega_l^2 = \left(\sum_{j=1}^{N} \frac{g_j^2}{\omega_l^{j2}} \right)^{-1}. \tag{A14}$$

Eq. (A9) then turns out to be

$$\left\langle x_\tau \left| \exp\left(-\tau \frac{H_b}{\hbar} \right) \right| x_0 \right\rangle = \Gamma\left(\left\{ m_j, \bar{\omega}_j, x_0^j, x_\tau^j \right\} \right) \times \prod_{l=1}^{P-1} \int da_l \; \exp\left\{ -\frac{1}{2} \omega_l^2 a_l^2 \right\}. \tag{A15}$$

Here, the prefactor $\Gamma\left(\left\{ m_j, \bar{\omega}_j, x_0^j, x_\tau^j \right\} \right)$ appears in both the denominator and numerator of Eq. (18) and can be canceled out. By combining Eqs. (A3), (A4), (A12) and (A13), we can obtain the Eq. (16) at the discretized time slices which is required in Eq. (18).

If we define $\Sigma = \sum_{j=1}^{N} c_j x_j$, then $H(u)$ has the form

$$H(u) = \begin{pmatrix} -\Sigma & V \\ V & \Sigma \end{pmatrix}. \tag{A16}$$

For every step of propagation in Eq. (18), that is $e^{-H \cdot du/\hbar}$, we can easily get that

$$\exp\left(-\frac{H}{\hbar} du \right) = A \begin{pmatrix} \exp\left(-\frac{\Delta}{\hbar} du \right) & 0 \\ 0 & \exp\left(\frac{\Delta}{\hbar} du \right) \end{pmatrix} A^{-1}. \tag{A17}$$

Here, A is the transformation matrix

$$A = \begin{pmatrix} 1 & 1 \\ \frac{\Delta + \Sigma}{V} & \frac{-\Delta + \Sigma}{V} \end{pmatrix} \tag{A18}$$

with $\Delta = \sqrt{\Sigma^2 + V^2}$. The matrix A has not been normalized because the normalized factor can be cancelled from the denominator and numerator in Eq. (18). The imaginary-time propagation goes on with Eqs. (A17) and (A18).

In summary, the imaginary-time FFCF can be evaluated as follows: (i) sample the terminal points of the vibrational path according to the Gaussian distribution of Eq. (19); (ii) sample the intermediate time slices according to the Gaussian distribution of Eq. (20) or Eq. (A15) to obtain Eq. (16); (iii) use Eqs. (A17) and (A18) to propagate the denominator and numerator of Eq. (18); (iv) repeat steps (i), (ii) and (iii) to obtain enough samplings for the vibrational-mode path average.

To obtain the reliable imaginary-time FFCF, the error estimate is required. When M imaginary-time FFCFs $\left\{C_{ff}^{n}(\tau)\right\}\big|_{n=1}^{M}$ have been obtained, the average imaginary-time FFCF is

$$\bar{C}_{ff}(\tau) = \frac{\sum_{n=1}^{M} C_{ff}^{n}(\tau)}{M} . \tag{A19}$$

Then, the error estimate is be defined as

$$\delta = \sqrt{\frac{\sum_{n=1}^{M} C_{ff}^{n2} - M\bar{C}_{ff}^{2}}{M(M-1)}} . \tag{A20}$$

M has to be large enough to make sure that δ is very small. Finally, $\bar{C}_{ff}(\tau)$ at the dominant saddle point τ_{st} is used into Eq. (12) to evaluate the quantum CT rates.

Appendix B: Derivation of the charge transfer rate formula with the saddle point approximation from Fermi gold rule

The CT rate formalism from Fermi gold rule is given as[14,81]

$$k = \frac{1}{\hbar^2}|V|^2 \int_{-\infty}^{\infty} dt \exp\left\{ i\omega_{fi}t - \sum_j S_j\left[\left(2\overline{n}_j + 1\right) - \overline{n}_j e^{-i\omega_j t} - \left(\overline{n}_j + 1\right)e^{i\omega_j t}\right]\right\}. \quad \text{(B1)}$$

Here, $\overline{n_j} = \frac{1}{e^{\hbar\omega_j / k_B T} - 1}$ denotes the population of the *j*-th normal mode and ω_j is its frequency. $S_j = \lambda_j / \hbar\omega_j = \frac{1}{2}\hbar^{-1}\omega_j(\Delta Q_j)^2$ is the Huang-Rhys factor measuring the charge-phonon coupling strength and λ_j is the reorganization energy of the *j*-th mode. $\hbar\omega_{fi}$ is the energy difference of the reactants and products. For the present hole self-exchange CT reaction, $\omega_{fi} = 0$. It is useful to define that

$$G(t) = \exp\{-\phi(t)\}$$

$$= \exp\left\{ -\sum_j S_j\left[\left(2\overline{n}_j + 1\right) - \overline{n}_j e^{-i\omega_j t} - \left(\overline{n}_j + 1\right)e^{i\omega_j t}\right]\right\}. \quad \text{(B2)}$$

If τ_{st} is the dominant saddle point at the imaginary time axis, the integral in Eq. (B1) can be translated to an integral over the line $t^{'} = \tau_{st} + t$ through the standard contour integral methodology:

$$k = \frac{1}{\hbar^2}|V|^2 \int_{\tau_{st}-\infty}^{\tau_{st}+\infty} G(\tau_{st} - t)\, dt\,. \quad \text{(B3)}$$

From Eqs. (B2) and (B3), we can easily obtain

$$\phi(\tau_{st} - t) = \sum_j S_j\left[\left(2\overline{n}_j + 1\right) - \overline{n}_j e^{-i\omega_j(\tau_{st}-t)} - \left(\overline{n}_j + 1\right)e^{i\omega_j(\tau_{st}-t)}\right]. \quad \text{(B4)}$$

In the self-exchange reaction, $\tau_{st} = i\beta\hbar/2$. After introducing the Wick's rotation $t \to -i\tau$, the CT rate becomes

$$k = \frac{1}{\hbar^2}|V|^2 \,\mathrm{Im}\int G(\tau_{st} + i\tau)\, d\tau \quad \text{(B5)}$$

and Eq. (B4) is

$$\phi(\tau_{st} + i\tau) = \sum_j S_j\left[\left(2\overline{n}_j + 1\right) - \overline{n}_j e^{\omega_j(\beta\hbar/2+\tau)} - \left(\overline{n}_j + 1\right)e^{-\omega_j(\beta\hbar/2+\tau)}\right]. \quad \text{(B6)}$$

Expanding $\phi(\tau_{st} + i\tau)$ at the dominant saddle point τ_{st}, we have

$$\phi(\tau) = \phi(\tau_{st}) - \frac{1}{2}\phi''(\tau_{st})\tau^2 . \qquad \text{(B7)}$$

Here,

$$\phi(\tau_{st}) = \sum_j S_j \left[\left(2\bar{n}_j + 1\right) - \bar{n}_j e^{\beta\hbar\omega_j/2} - \left(\bar{n}_j + 1\right) e^{-\beta\hbar\omega_j/2} \right]$$

$$= \sum_j S_j \tanh\left(\frac{1}{4}\hbar\beta\omega_j\right), \qquad \text{(B8)}$$

and

$$\phi''(\tau_{st}) = \sum_j S_j \omega_j^2 \left[\bar{n}_j e^{\beta\hbar\omega_j/2} + \left(\bar{n}_j + 1\right) e^{-\beta\hbar\omega_j/2} \right]$$

$$= \sum_j S_j \omega_j^2 \operatorname{csc} h\left(\frac{1}{2}\hbar\beta\omega_j\right). \qquad \text{(B9)}$$

The CT rate with the SPA from Fermi golden rule is then obtained as

$$k_{FGR-SPA} = \frac{1}{\hbar^2}|V|^2 \exp\left[-\phi(\tau_{st})\right]\sqrt{\frac{2\pi}{\phi''(\tau_{st})}} , \qquad \text{(B10)}$$

which is abbreviated as FGR-SPA rate formula in the present paper. We note that a similar result was obtained in the case of a continuous bath.[82]