Frenkel-Exciton Kinetics

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1 Model

photoinduced excited state kinetics are considered in a complex of two-level molecules; the computations shall be based on

$$H(t) = H_{\rm exc} + H_{\rm field}(t) \tag{1}$$

the standard exciton Hamiltonian is written as

$$H_{\rm exc} = E_g + \sum_m E_m B_m^+ B_m + \sum_{m,n} J_{mn} B_m^+ B_n \tag{2}$$

the B_m^+ are transition operators

$$B_m^+ = |\varphi_{me}\rangle\langle\varphi_{mg}| \tag{3}$$

from the ground-state $|\varphi_{mg}\rangle$ to the excited state $|\varphi_{me}\rangle$ of molecule m; be aware of the important relation (completeness relation for a two-level system)

$$B_m^+ B_m + B_m B_m^+ = |\varphi_{me}\rangle\langle\varphi_{me}| + |\varphi_{mg}\rangle\langle\varphi_{mg}| = 1 \tag{4}$$

we use the excitonic coupling in dipole approximation

$$J_{mn} = \frac{1}{|\mathbf{R}_{mn}|^3}\big([\mathbf{d}_m \mathbf{d}_n^*] - 3[\mathbf{d}_m \mathbf{n}][\mathbf{n}\mathbf{d}_n^*]\big) \tag{5}$$

$\mathbf{d}_m$ denotes the transition dipole moment of molecule m and $\mathbf{R}_{mn}$ is the center of mass distances between molecule m and n; we set $\mathbf{d}_m = d_m \mathbf{e}_m$, $|\mathbf{R}_{mn}| = R_{mn}$ and get

$$J_{mn} = \frac{\kappa_{mn} d_m d_n}{R_{mn}^3} \tag{6}$$

with the orientation factor

$$\kappa_{mn} = [\mathbf{e}_m \mathbf{e}_n] - 3[\mathbf{e}_m \mathbf{n}][\mathbf{n}\mathbf{e}_n] \tag{7}$$

the coupling to the radiation takes the form

$$H_{\rm field}(t) = -\mathbf{E}(t) \sum_m \mathbf{d}_m B_m^+ + \mathrm{H.c.} \tag{8}$$

the electric-field strength

$$\mathbf{E}(t) = \mathbf{n}E(t)e^{-i\omega_0 t} + \text{c.c.} \tag{9}$$

describes a single pulse with pulse envelope

$$E(t) = E_0 \exp\big(-4\ln 2(t-t_\text{p})^2/\tau_\text{p}^2\big) \tag{10}$$

to simplify the notation we introduce the so-called Rabi energy

$$R_m(t) = -[\mathbf{E}(t)\mathbf{d}_m] = -[\mathbf{n}\mathbf{d}_m]E(t)e^{-i\omega_0 t} + \text{c.c.} \tag{11}$$

it follows (note $E_g = 0$)

$$H(t) = \sum_k E_k B_k^+ B_k + \sum_{k,l} J_{kl} B_k^+ B_l + \sum_k (R_k B_k^+ + R_k^* B_k) \tag{12}$$

2 Basic Equations of Motion

kinetic equations are derived for expectation values of different arrangements of the B_m^+ and B_n; we introduce the arbitrary operator $\hat{O}$ and get

$$O(t) =< \hat{O} >= \mathrm{tr}\{\hat{\rho}(t)\hat{O}\} \tag{13}$$

equation of motions are derived from the quantum master equation

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[H(t), \hat{\rho}(t)]_- - \mathcal{D}\hat{\rho}(t) \tag{14}$$

dissipation appears due to excitation decay

$$\mathcal{D}\hat{\rho}(t) = \sum_m \frac{k_m}{2}\Big(\big[B_m^+ B_m, \hat{\rho}(t)\big]_+ - 2B_m\hat{\rho}(t)B_m^+\Big) \tag{15}$$

the excited state decay rate referring to molecule m is k_m; noting the quantum master equation we may write

$$\frac{\partial}{\partial t} < \hat{O} >= \mathrm{tr}\{\frac{\partial}{\partial t}\hat{\rho}(t)\hat{O}\} = \frac{i}{\hbar} < [H(t), \hat{O}]_- > - < \tilde{\mathcal{D}}\hat{O} > \tag{16}$$

the modified dissipative superoperator follows as

$$\tilde{\mathcal{D}}\hat{O} = \sum_m \frac{k_m}{2}\Big(\big[B_m^+ B_m, \hat{O}\big]_+ - 2B_m^+\hat{O}B_m\Big) \tag{17}$$

to get equations of motion for $O(t) =< \hat{O} >$ one has to compute $< [H, \hat{O}]_- >$ and $< \tilde{\mathcal{D}}\hat{O} >$; if $\hat{O}$ factorizes according to $\hat{O} = \hat{O}_1\hat{O}_2$ we may use

$$[H, \hat{O}_1\hat{O}_2]_- = [H, \hat{O}_1]_-\hat{O}_2 + \hat{O}_1[H, \hat{O}_2]_- \tag{18}$$

we also note

$$[H, \hat{O}^+]_- = -\Big([H, \hat{O}]_-\Big)^+ \tag{19}$$

2.1 Important Commutator Relations

we calculate $[H,\hat{O}]_-$ for different types of $\hat{O}$; case $\hat{O}=B_m^+$

$$
\begin{aligned}
&[H,B_m^+]_- = \Big[\sum_k E_k B_k^+ B_k + \sum_{k,l} J_{kl} B_k^+ B_l + \sum_k (R_k B_k^+ + R_k^* B_k), B_m^+\Big]_- \\
&= \sum_k E_k (B_k^+ B_k B_m^+ - B_m^+ B_k^+ B_k) + \sum_{k,l} J_{kl} (B_k^+ B_l B_m^+ - B_m^+ B_k^+ B_l) \\
&+ \sum_k R_k^* (B_k B_m^+ - B_m^+ B_k) \\
&= E_m (B_m^+ B_m B_m^+ - B_m^+ B_m^+ B_m) + \sum_l J_{ml} (B_m^+ B_l B_m^+ - B_m^+ B_m^+ B_l) \\
&+ \sum_k J_{km} (B_k^+ B_m B_m^+ - B_m^+ B_k^+ B_m) + R_m^* (B_m B_m^+ - B_m^+ B_m) \\
&= E_m B_m^+ + \sum_k J_{km} B_k^+ (B_m B_m^+ - B_m^+ B_m) + R_m^* (B_m B_m^+ - B_m^+ B_m) \qquad (20)
\end{aligned}
$$

in a first step we notized that the commutator deviates from zero only if $m=k$ or $m=l$ (be aware of the fact that $k \neq l$); further we took into consideration, for example $B_m^+ B_m^+ = |\varphi_{me}\rangle\langle\varphi_{mg}||\varphi_{me}\rangle\langle\varphi_{mg}| = 0$; if we note $B_m B_m^+ - B_m^+ B_m = 1 - 2B_m^+ B_m$ we may write

$$
\begin{aligned}
[H,B_m^+]_- &= E_m B_m^+ + \sum_k J_{km} B_k^+ (1 - 2B_m^+ B_m) + R_m^* (1 - 2B_m^+ B_m) \\
&= E_m B_m^+ + \sum_k J_{km} B_k^+ + R_m^* - 2\sum_k J_{km} B_k^+ B_m^+ B_m - 2R_m^* B_m^+ B_m \qquad (21)
\end{aligned}
$$

we meet two new types of operators $\hat{O}=B_m^+ B_m$ and $\hat{O}=B_k^+ B_m^+ B_m$; case $\hat{O}=B_m^+ B_m$

$$
\begin{aligned}
&[H,B_m^+ B_m]_- = [H,B_m^+]_- B_m + B_m^+ [H,B_m]_- = [H,B_m^+]_- B_m - B_m^+ \big([H,B_m^+]_-\big)^+ \\
&= \Big(E_m B_m^+ + \sum_k J_{km} B_k^+ (1 - 2B_m^+ B_m) + R_m^* (1 - 2B_m^+ B_m)\Big) B_m \\
&- B_m^+ \Big(E_m B_m^+ + \sum_k J_{km} B_k^+ (1 - 2B_m^+ B_m) + R_m^* (1 - 2B_m^+ B_m)\Big)^+ \\
&= \Big(E_m B_m^+ B_m + \sum_k J_{km} B_k^+ (1 - 2B_m^+ B_m) B_m + R_m^* (1 - 2B_m^+ B_m) B_m\Big) \\
&- B_m^+ \Big(E_m B_m + \sum_k J_{mk} (1 - 2B_m^+ B_m) B_k + R_m (1 - 2B_m^+ B_m)\Big) \\
&= \sum_k (J_{km} B_k^+ B_m - J_{mk} B_m^+ B_k) + R_m^* B_m - R_m B_m^+ \qquad (22)
\end{aligned}
$$

we continue in considering the case $\hat{O} = B_m^+ B_n$ (note $m \neq n$) and get

$$[H, B_m^+ B_n]_- = \Big(E_m B_m^+ B_n + \sum_k J_{km} B_k^+ (1 - 2B_m^+ B_m) B_n + R_m^* (1 - 2B_m^+ B_m) B_n\Big)$$

$$-B_m^+ \Big(E_n B_n + \sum_k J_{nk} (1 - 2B_n^+ B_n) B_k + R_n (1 - 2B_n^+ B_n)\Big)$$

$$= (E_m - E_n) B_m^+ B_n + \sum_k J_{km} (1 - 2B_m^+ B_m) B_k^+ B_n - \sum_k J_{nk} B_m^+ B_k (1 - 2B_n^+ B_n)$$

$$+R_m^* (1 - 2B_m^+ B_m) B_n - R_n B_m^+ (1 - 2B_n^+ B_n) \quad (23)$$

2.2 Important Dissipative Terms

we calculate different terms of the type $\tilde{\mathcal{D}}\hat{O}$; case $\hat{O} = B_m^+$

$$\begin{aligned}\tilde{\mathcal{D}}B_m^+ &= \sum_k \frac{k_k}{2}\Big(\big[B_k^+ B_k, B_m^+\big]_+ - 2B_k^+ B_m^+ B_k\Big)\\ &= \frac{k_m}{2}\Big(B_m^+ B_m B_m^+ + B_m^+ B_m^+ B_m - 2B_m^+ B_m^+ B_m\Big) = \frac{k_m}{2} B_m^+\end{aligned} \tag{24}$$

case $\hat{O} = B_m^+ B_m$

$$\tilde{\mathcal{D}}B_m^+ B_m = \frac{k_m}{2}\Big(B_m^+ B_m B_m^+ B_m + B_m^+ B_m B_m^+ B_m - 2B_m^+ B_m^+ B_m B_m\Big) = k_m B_m^+ B_m \tag{25}$$

case $\hat{O} = B_m^+ B_n$ $(m \neq n)$

$$\begin{aligned}\tilde{\mathcal{D}}B_m^+ B_n &= \sum_k \frac{k_k}{2}\Big(\big[B_k^+ B_k, B_m^+ B_n\big]_+ - 2B_k^+ B_m^+ B_n B_k\Big)\\ &= \frac{k_m}{2}\Big(B_m^+ B_m B_m^+ B_n + B_m^+ B_n B_m^+ B_m - 2B_m^+ B_m^+ B_n B_m\Big)\\ &+ \frac{k_n}{2}\Big(B_n^+ B_n B_m^+ B_n + B_m^+ B_n B_n^+ B_n - 2B_n^+ B_m^+ B_n B_n\Big) = \frac{k_m + k_n}{2} B_m^+ B_n\end{aligned} \tag{26}$$

2.3 Equations of Motion

2.3.1 Equation for $< B_m^+ >$

we obtain

$$\frac{\partial}{\partial t} < B_m^+ >= \frac{i}{\hbar} E_m < B_m^+ > + \frac{i}{\hbar} \sum_k J_{km} < B_k^+ (1 - 2B_m^+ B_m) >$$
$$+ \frac{i}{\hbar} R_m^* < (1 - 2B_m^+ B_m) > - \frac{k_m}{2} < B_m^+ > \quad (27)$$

this is not a closed equation for $< B_m^+ >$; we introduce abbreviations

$$P_m =< B_m^+ B_m > \quad (28)$$

2.3.2 Equation for $< B_m^+ B_m >$

$$\frac{\partial}{\partial t} < B_m^+ B_m >= \frac{i}{\hbar} \sum_k (J_{km} < B_k^+ B_m > - J_{mk} < B_m^+ B_k >)$$
$$+ \frac{i}{\hbar} R_m^* < B_m > - \frac{i}{\hbar} R_m < B_m^+ > - k_m < B_m^+ B_m > \quad (29)$$

introducing the abbreviations together with

$$W_{mn} = (1 - \delta_{m,n}) < B_m^+ B_n > \quad (30)$$

2.3.3 Equation for $< B_m^+ B_n >$

$$\frac{\partial}{\partial t} < B_m^+ B_n >= \frac{i}{\hbar} (E_m - E_n) < B_m^+ B_n >$$
$$+ \frac{i}{\hbar} \sum_k J_{km} < (1 - 2B_m^+ B_m) B_k^+ B_n > - \frac{i}{\hbar} \sum_k J_{nk} < B_m^+ B_k (1 - 2B_n^+ B_n) >$$
$$+ \frac{i}{\hbar} R_m^* < (1 - 2B_m^+ B_m) B_n > - \frac{i}{\hbar} R_n < B_m^+ (1 - 2B_n^+ B_n) > - \frac{k_m + k_n}{2} < B_m^+ B_n >$$
$$(31)$$