COHERENCE EFFECTS IN REDOX CHEMICAL REACTIONS

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Abstract. Nonstochastic formulation of the electron-transfer problem (via time-convolutionless generalized master equations or Tokuyama–Mori approach) is argued to lead, for any electronic system with a site-local coupling to the bath taken into account up to the second order, to equations providing a rigorous basis for the generalized stochastic Liouville equation model. Its application to an asymmetric dimer shows that the usual transition from the nonactivated to activated (Arrhenius-type) Marcus long-time reaction kinetics is obtained. Coherence effects make, however, the usual long-time markovian description of the population kinetics based on the golden rule formula unjustified.

Key words: redox reactions, coherence, electron transfer.

1. INTRODUCTION

Since the pioneering works by Primas [1] and Haken and Strobl [2] (see also [3] for extensive discussion and further references), the stochastic Liouville equation model (SLEM) has proved to be a reliable method providing a qualitatively reasonable interpolation between coherent and fully incoherent regimes of carrier (electron, exciton) transport. Because the standard approach to the electron transfer in redox chemical kinetics is based on usual markovian kinetic equations (Pauli master equations with golden rule transfer rates) describing the incoherent transfer, SLEM might serve as an ideal tool to scrutinize the chemical kinetics theory. Soon, on the other hand, it became also clear that the basic assumption of SLEM, i.e. the replacing of a true responsive thermodynamic bath (phonons) by a nonresponsive stochastic field, is problematic. A rederivation of the corresponding system of equations in [4] via time-convolution generalized master equation (TC-GME) and the Born–Markov

approximation in the interaction picture or via the second-order time-convolutionless generalized master equation (TCL-GME) as in [5] (in both cases taking into account properly quantum and responsive character of the bath), however, leads (apart from some lacking symmetries among coefficients) to the same system of equations. These equations (forming a basis of the so-called generalized stochastic Liouville equation model – GSLEM) admit, at least formally, the same type of parametrization as known from [2] (see also, e.g., [3], the so-called Haken–Strobl–Reineker model).

When derived as usual by expanding in powers of the electron coupling to the thermodynamic bath, SLEM as well as GSLEM do not explicitly contain polaron effects. In order to involve these and to keep the structure of GSLEM, a new method has been devised in [6, 7]. It allows working with untransformed (to the small polaron basis) quantities like the bare (undressed) electron density matrix $\rho_{mn}(t)$, while the coefficients in the corresponding time-local equations remain appropriately transformed. As this type of theory is then sufficiently general as well as flexible for scrutinizing the role of coherent effects in the electron transfer (reduction–oxidation chemical reactions), we shall generalize it here to a nonperiodic situation to check the basic results of the standard chemical reaction theory.

2. HAMILTONIAN AND STARTING EQUATIONS

In this paper, we shall work with the standard Hamiltonian

$$H = H_e + H_{ph} + H_{e-ph}, \tag{1a}$$

$$H_e = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m \neq n} J_{mn} a_m^\dagger a_n, \tag{1b}$$

$$H_{ph} = \sum_{\vec{k}} \hbar \omega_{\vec{k}} b_{\vec{k}}^\dagger b_{\vec{k}}, \tag{1c}$$

$$H_{e-ph} = \frac{1}{\sqrt{N}} \sum_r \sum_{\vec{k}} G_{\vec{k}}^r \hbar \omega_{\vec{k}} a_r^\dagger a_r (b_{\vec{k}} + b_{-\vec{k}}^\dagger). \tag{1d}$$

Here, ϵ_m, $J_{mn} = J_{nm}$, $\omega_{\vec{k}}$, and $G_{\vec{k}}^r$ are the electron site energies, transfer (resonance or hopping) integrals, phonon frequencies and carrier-phonon coupling constants. Only one electron will be assumed throughout the study.

There is a lot of physics concerning the possibility of modelling the electron transfer in, e.g., solutions, by this Hamiltonian. However, as it is too complicated, we postpone the discussion to a next publication. Let us only mention that the most decisive point concerns the fact that in real situations, the electron interacts not only with phonons but also with virtual Frenkel excitons (due to polarization of its surroundings) thus forming a new quasiparticle – electron-polaron [8].

One comment concerning the Hamiltonian, though is worth making. Here, we fully refrain from the off-diagonal part of H_{e-ph} (if any). So, like in the original Marcus theory of chemical kinetics [9, 10], we take the bath (solvent) not as an active medium, being perhaps also partly responsible for some real transitions, but only as a passive (though quantum, i.e. responsive) one hindering the transitions caused by transfer integrals in H_e but making simultaneously these transitions real owing to dephasing.

With our Hamiltonian (1a-d) we first introduce an operator known from the small polaron canonical (displacement) transformation:

$$S = -S^\dagger = \frac{1}{\sqrt{N}} \sum_{\vec{k}} \sum_n G_{\vec{k}}^m a_n^\dagger a_n (b_{\vec{k}} - b_{-\vec{k}}^\dagger). \tag{2}$$

Further, we shall assume the initial state (initial full electron–phonon density matrix)

$$\varrho(0) = e^{\lambda S} a_1^\dagger |vac\rangle \langle vac| a_1 \otimes \rho_{ph} e^{-\lambda S}, \tag{3}$$

$$\rho_{ph} = \frac{e^{-\beta H_{ph}}}{\mathrm{Tr}_{ph} e^{-\beta H_{ph}}}. \tag{4}$$

Here, one should assume that the site designated as 1 in (3) is arbitrary in the system; it designates the site where the carrier is initially located with the polaron cloud (of the degree λ) formed around. The degree λ (being a real number) may also be taken as arbitrary; the choices $\lambda = 0$ or 1 correspond to a no-polaron cloud and a small full polaron cloud, respectively. On the other hand, higher (or even negative) values of λ are not excluded.

Now, let us choose the projection superoperator

$$\mathcal{P} \ldots = \sum_{mn} a_m^\dagger a_n \frac{1}{\langle \Theta_m^\dagger \Theta_n \rangle} \mathrm{Tr}^{(1)} (e^{\lambda S} \rho_{ph} a_n^\dagger a_m e^{-\lambda S} \ldots),$$

$$\Theta_m = \exp\left\{ \frac{\lambda}{\sqrt{N}} \sum_{\vec{k}} G_{\vec{k}}^m (b_{\vec{k}} - b_{-\vec{k}}) \right\}, \quad \langle \ldots \rangle = \mathrm{Tr}_{ph}(\rho_{ph} \ldots). \tag{5}$$

Applying this projector to the Tokuyama–Mori identity [11], choosing as a set (column) of operators of interest the operators $a_m^\dagger a_n$, multiplying the identity from the left by $\varrho(0)$ from (3) and, finally taking the trace, one obtains for the carrier (single-particle) density matrix

$$\rho_{nm}^{(1)}(t) = \mathrm{Tr}(\varrho(0) a_m^\dagger a_n) \tag{6}$$

the set of equations

$$\frac{d}{dt} \rho_{nm}^{(1)}(t) = \sum_{pq} i\omega_{nm,qp}(t) \rho_{qp}^{(1)}(t) + f_{nm}(t). \tag{7a}$$

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Here the inhomogeneous term

$$f_{nm}(t) = 0, \qquad (7b)$$

provided that λ and β in (5) are the same as those in (4) (as will be taken henceforth). The coefficients, to the second order in H_{e-ph}, result

$$i\omega_{nm,qp}(t) = i\Omega_{nm,qp} + i \cdot \delta\Omega_{nm,qp}(t), \qquad (8a)$$

$$i\Omega_{nm,qp} = \frac{i}{\hbar}[\delta_{pm}\delta_{nq}(\epsilon_m - \epsilon_n) + J_{pm}\delta_{nq} - J_{nq}\delta_{mp}], \qquad (8b)$$

$$i \cdot \delta\Omega_{nm,qp}(t) = -i\delta_{mp}\delta_{nq}\frac{\lambda}{N}\sum_{\vec{k}}\omega_{\vec{k}}(G_{\vec{k}}^m - G_{\vec{k}}^n)(G_{-\vec{k}}^m + G_{-\vec{k}}^n)-$$

$$- \int_0^t \sum_{uv} M_{nm,uv}(\tau)\langle a_u^\dagger a_v a_q^\dagger(\tau)a_p(\tau)\rangle \, d\tau + \mathcal{O}(G^4), \qquad (8c)$$

$$\langle a_u^\dagger a_v a_q^\dagger(\tau)a_p(\tau)\rangle = \mathrm{Tr}_e(a_u^\dagger a_v e^{i\mathcal{L}_e\tau}a_q^\dagger a_p). \qquad (8d)$$

Here, we designate the Liouville superoperators as

$$\mathcal{L}\ldots = \frac{1}{\hbar}[H,\ldots], \quad \mathcal{L}_e\ldots = \frac{1}{\hbar}[H_e,\ldots], \quad \mathcal{L}_{e-ph}\ldots = \frac{1}{\hbar}[H_{e-ph},\ldots] \qquad (9)$$

and the projector as

$$\mathcal{Q} = 1 - \mathcal{P}. \qquad (10)$$

Our quantity $M_{nm,uv}(\tau)$ in (8) then reads:

$$M_{nm,vu}(\tau) = -w_{nm,vu}(\tau) =$$

$$= \mathrm{Tr}(e^{\lambda S}\rho_{ph}a_v^\dagger a_u e^{-\lambda S}\mathcal{L}e^{i\mathcal{Q}\mathcal{L}\tau}\mathcal{Q}\mathcal{L}_{e-ph}a_m^\dagger a_n)/\langle\Theta_u^\dagger\Theta_v\rangle \qquad (11)$$

and designates nothing but the second-order kernel of Mori's [12] theory for the same problem or, up to the opposite sign, the second-order memory function $w_{nm,vu}(\tau)$ from the TC-GME formulation of the same problem. One should add that the same equations may be obtained also starting from TCL-GME as in [6].

By a direct expansion up to the second order in H_{e-ph} we obtain

$$i \cdot \delta\Omega_{nm,qp}(t) = -i\delta_{mp}\delta_{nq}\frac{\lambda}{N}\sum_{\vec{k}}\omega_{\vec{k}}(G_{\vec{k}}^m - G_{\vec{k}}^n)(G_{-\vec{k}}^m + G_{-\vec{k}}^n)-$$

$$- \int_0^t \sum_{uv}\left\{\frac{1-\lambda}{N}\sum_{\vec{k}}\omega_{\vec{k}}^2(G_{-\vec{k}}^m - G_{-\vec{k}}^n) \times\right.$$

$$\times(G_{\vec{k}}^{ru}[[1 + n_B(\hbar\omega_{\vec{k}})]e^{i\omega_{\vec{k}}\tau} + n_B(\hbar\omega_{\vec{k}})e^{-i\omega_{\vec{k}}\tau}]-$$

$$-G_{\vec{k}}^v[n_B(\hbar\omega_{\vec{k}})e^{i\omega_{\vec{k}}\tau} + [1 + n_B(\hbar\omega_{\vec{k}})]e^{-i\omega_{\vec{k}}\tau}])\langle a_v^\dagger a_u a_m^\dagger(\tau)a_n(\tau)\rangle+$$

$$+\frac{\lambda}{N}\sum_{\vec{k}}\omega_{\vec{k}}(G^m_{-\vec{k}}-G^n_{-\vec{k}})\frac{1}{\hbar}\sum_r J_{ur}(G^r_{\vec{k}}-G^u_{\vec{k}})\times$$

$$\times[[1+n_B(\hbar\omega_{\vec{k}})]e^{i\omega_{\vec{k}}\tau}-n_B(\hbar\omega_{\vec{k}})e^{-i\omega_{\vec{k}}\tau}]\langle a^\dagger_v a_r a^\dagger_m(\tau)a_n(\tau)\rangle+$$

$$+\frac{\lambda}{N}\sum_{\vec{k}}\omega_{\vec{k}}(G^m_{-\vec{k}}-G^n_{-\vec{k}})\frac{1}{\hbar}\sum_r J_{rv}(G^r_{\vec{k}}-G^v_{\vec{k}})\times$$

$$\times[n_B(\hbar\omega_{\vec{k}})e^{i\omega_{\vec{k}}\tau}-[1+n_B(\hbar\omega_{\vec{k}})]e^{-i\omega_{\vec{k}}\tau}]\langle a^\dagger_r a_u a^\dagger_m(\tau)a_n(\tau)\rangle\}\times$$

$$\times\langle a^\dagger_u a_v a^\dagger_q(\tau)a_p(\tau)\rangle\,d\tau. \tag{12}$$

(Here n_B designates the Bose–Einstein distribution for phonons.) Designating the eigenvectors and the eigenvalues of H_e by $|\nu\rangle$ and E_ν, respectively, (12) may be turned to the form

$$i\cdot\delta\Omega_{nm,qp}(t)=-\delta_{nq}\delta\mathcal{A}^p_{mn}(\lambda,t)-\delta_{mp}\delta\mathcal{A}^q_{nm}(\lambda,t)^*, \tag{13a}$$

$$\delta\mathcal{A}^p_{mn}(\lambda,t)=\int_0^t\frac{1-\lambda}{N}\sum_{\vec{k}}\omega^2_{\vec{k}}(G^m_{-\vec{k}}-G^n_{-\vec{k}})\times$$

$$\times\sum_r G^r_{\vec{k}}\sum_{\nu_1,\nu_2}\langle r|\nu_1\rangle\langle\nu_1|m\rangle\langle p|\nu_2\rangle\langle\nu_2|r\rangle\times$$

$$\times\exp\{\frac{i}{\hbar}(E_{\nu_1}-E_{\nu_2})\tau\}[[1+n_B(\hbar\omega_{\vec{k}})]e^{i\omega_{\vec{k}}\tau}+n_B(\hbar\omega_{\vec{k}})e^{-i\omega_{\vec{k}}\tau}]\,d\tau-$$

$$-\int_0^t\frac{\lambda}{N}\sum_{\vec{k}}\omega_{\vec{k}}(G^m_{-\vec{k}}-G^n_{-\vec{k}})\times$$

$$\times\sum_r G^r_{\vec{k}}\sum_{\nu_1,\nu_2}\frac{1}{\hbar}(E_{\nu_1}-E_{\nu_2})\langle r|\nu_1\rangle\langle\nu_1|m\rangle\langle p|\nu_2\rangle\langle\nu_2|r\rangle\times$$

$$\times\exp\{\frac{i}{\hbar}(E_{\nu_1}-E_{\nu_2})\tau\}[[1+n_B(\hbar\omega_{\vec{k}})]e^{i\omega_{\vec{k}}\tau}-n_B(\hbar\omega_{\vec{k}})e^{-i\omega_{\vec{k}}\tau}]\,d\tau+$$

$$+i\delta_{mp}\frac{\lambda}{2N}\sum_{\vec{k}}\omega_{\vec{k}}(G^m_{-\vec{k}}-G^n_{-\vec{k}})(G^m_{\vec{k}}+G^n_{\vec{k}}). \tag{13b}$$

Now, let the time t exceed (after first performing the infinite bath limit $N\to+\infty$ in order to get rid of the Poincaré cycles) the time needed for the reconstruction of the polaron cloud around the carrier, i.e. the phonon dephasing time $t_D\approx\hbar/\Delta W_{ph}$ (with ΔW_{ph} being the width of the relevant phonon band). What is really pleasant is that then (as it physically should be) all the λ-dependence disappears from $i\delta\Omega_{nm,qp}(t)$ simultaneously with all the time-dependence. We obtain

$$i\cdot\delta\Omega_{nm,qp}(t)\xrightarrow{t\to+\infty}=-\delta_{nq}\mathcal{A}^p_{mn}-\delta_{mp}\mathcal{A}^q_{nm}{}^*, \tag{14a}$$

$$\mathcal{A}_{mn}^p = \frac{i\hbar}{N} \sum_{\vec{k}} \omega_{\vec{k}}^2 (G_{-\vec{k}}^m - G_{-\vec{k}}^n) \sum_r G_{\vec{k}}^r \sum_{\nu_1,\nu_2} \langle \nu_2|r\rangle\langle r|\nu_1\rangle\langle \nu_1|m\rangle\langle p|\nu_2\rangle \times$$

$$\times \left\{ \frac{1 + n_B(\hbar\omega_{\vec{k}})}{E_{\nu_1} - E_{\nu_2} + \hbar\omega_{\vec{k}} + i\epsilon} + \frac{n_B(\hbar\omega_{\vec{k}})}{E_{\nu_1} - E_{\nu_2} - \hbar\omega_{\vec{k}} + i\epsilon} \right\}. \tag{14b}$$

Here, as usual, ϵ is an infinitesimal positive quantity understood to turn to zero after converting, e.g., $1/N \sum_{\vec{k}} \dots$ into an integral.

3. ASYMMETRIC DIMER AND THE MARCUS FORMULA

As already mentioned above, we omit completely the site-off-diagonal part of the carrier–bath interaction. So, physically and speaking in terms of virtual processes, the bath takes just a passive role in, e.g., electron transfer. This might seem to imply that there should be no reason for the 'up-and-down' asymmetry in transition rates. It should be stressed, however, that the bath in our treatment is nevertheless a quantum (responsive) one, leading to spontaneous processes. Irrespective of the fact that our sites are not the eigenstates of H_e, the latter processes do consequently cause the above-mentioned asymmetry in the transition rates as well as the long-time electron distribution, known since Einstein [13, 14] who phenomenologically introduced these processes to get the above-mentioned asymmetry.

Assume for simplicity the carrier Hamiltonian H_e in (1b) of the asymmetric dimer by choosing

$$J_{12} = J_{21} = J, \ \epsilon_1 = \epsilon, \ \epsilon_2 = 0. \tag{15}$$

This Hamiltonian can easily be diagonalized. For $t \gg t_D$, we then obtain from (7), (8), and (14)

$$\frac{d}{dt} \begin{pmatrix} \rho_{11}^{(1)}(t) \\ \rho_{22}^{(1)}(t) \\ \rho_{12}^{(1)}(t) \\ \rho_{21}^{(1)}(t) \end{pmatrix} = \frac{i}{\hbar} J \begin{pmatrix} 0 & 0 & 1 & -1 \\ 0 & 0 & -1 & 1 \\ 1 & -1 & -\epsilon/J & 0 \\ -1 & 1 & 0 & \epsilon/J \end{pmatrix} \cdot \begin{pmatrix} \rho_{11}^{(1)}(t) \\ \rho_{22}^{(1)}(t) \\ \rho_{12}^{(1)}(t) \\ \rho_{21}^{(1)}(t) \end{pmatrix} +$$

$$+ \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -X - \frac{i}{\hbar}J \cdot 2W & -Y + \frac{i}{\hbar}J \cdot 2W & -C_1 - \frac{i}{\hbar}\Delta\epsilon & 0 \\ -X + \frac{i}{\hbar}J \cdot 2W & -Y - \frac{i}{\hbar}J \cdot 2W & 0 & -C_1 + \frac{i}{\hbar}\Delta\epsilon \end{pmatrix} \cdot \begin{pmatrix} \rho_{11}^{(1)}(t) \\ \rho_{22}^{(1)}(t) \\ \rho_{12}^{(1)}(t) \\ \rho_{21}^{(1)}(t) \end{pmatrix} \tag{16}$$

Here

$$X \equiv \mathrm{Re}\,\mathcal{A}_{21}^1 =$$

$$= \frac{\pi J}{\hbar N} \sum_{\vec{k}} |G_{\vec{k}}^1 - G_{\vec{k}}^2|^2 \delta\left(\hbar\omega_{\vec{k}} - 2\sqrt{(\epsilon/2)^2 + J^2}\right) \times$$

$$\times \left\{ \frac{\epsilon}{2}[1 + 2n_B(\hbar\omega_{\vec{k}})] + \sqrt{(\epsilon/2)^2 + J^2} \right\}, \tag{17a}$$

$$Y \equiv \mathrm{Re}\,\mathcal{A}_{12}^2 =$$

$$= \frac{\pi J}{\hbar N} \sum_{\vec{k}} |G_{\vec{k}}^1 - G_{\vec{k}}^2|^2 \delta\left(\hbar\omega_{\vec{k}} - 2\sqrt{(\epsilon/2)^2 + J^2}\right) \times$$

$$\times \left\{ -\frac{\epsilon}{2}[1 + 2n_B(\hbar\omega_{\vec{k}})] + \sqrt{(\epsilon/2)^2 + J^2} \right\}, \tag{17b}$$

$$C_1 \equiv 2\,\mathrm{Re}\,\mathcal{A}_{21}^2 = 2\,\mathrm{Re}\,\mathcal{A}_{12}^1 =$$

$$= 2\frac{\pi J^2}{\hbar N} \sum_{\vec{k}} |G_{\vec{k}}^1 - G_{\vec{k}}^2|^2 \delta\left(\hbar\omega_{\vec{k}} - 2\sqrt{(\epsilon/2)^2 + J^2}\right)[1 + 2n_B(\hbar\omega_{\vec{k}})], \tag{17c}$$

$$2W = \frac{1}{N} \sum_{\vec{k}} |G_{\vec{k}}^1 - G_{\vec{k}}^2|^2 [1 + 2n_B(\hbar\omega_{\vec{k}})], \tag{17d}$$

$$\Delta\epsilon = \frac{\hbar}{N} \sum_{\vec{k}} \omega_{\vec{k}}(G_{-\vec{k}}^2 - G_{-\vec{k}}^1)(G_{\vec{k}}^2 + G_{\vec{k}}^1). \tag{17e}$$

In (16)–(17), we have also assumed for simplicity that the carrier is slow compared to the bath, i.e. J is much less than the relevant phonon bandwidth.

Now we designate

$$\tilde{J} \equiv J \exp\{-W\} \approx J\sqrt{1 - 2W}. \tag{18}$$

In W, one can easily recognize the Debye–Waller factor responsible for the small-polaron renormalization of the carrier transfer (resonance or hopping) integral J; the accuracy in (18) is the same as that of the theory, i.e. up to the lowest (second) order in the carrier–bath coupling. With that, setting in (17) $\epsilon = \Delta\epsilon = 0$, $X = Y$, one can return to the symmetric case discussed sufficiently in, e.g., [7]. In a slow carrier regime, the solution then describes a very slow left-right relaxation corresponding to the overdamped oscillator behaviour. Without underestimating the importance of this case, we are here rather interested in the limit of the pronounced asymmetry. In order to understand the situation, let us assume for a while a very small and practically negligible $\tilde{J}$ (tendency of suppressing $\tilde{J}$ in (24) is also strongly enhanced by increasing temperature) and small but not necessarily

negligible J. Then the characteristic equation (determining the decay of particular exponential solutions to (16))

$$x\left[x(C_1 - x)^2 - 4\left(\frac{\tilde{J}}{\hbar}\right)^2 (C_1 - x) - 2(Y - X)\frac{J}{\hbar}\frac{\bar{\epsilon}}{\hbar} - x\left(\frac{\bar{\epsilon}}{\hbar}\right)^2\right] = 0,$$

$$\bar{\epsilon} = \epsilon + \Delta\epsilon \tag{19}$$

has one root,

$$x \approx -2\left(\frac{J}{\hbar}\right)^2\frac{\pi\hbar}{N}\sum_{\vec{k}}|G_{\vec{k}}^1 - G_{\vec{k}}^2|^2\delta\left(\hbar\omega_{\vec{k}} - 2\sqrt{(\epsilon/2)^2 + J^2}\right)\cdot$$

$$\cdot\left[1 + 2n_B(2\sqrt{(\epsilon/2)^2 + J^2})\right], \tag{20}$$

which is small for small J. Under these conditions, the validity of the Markov approximation is currently assumed. Let us therefore return to the general case and exclude as usual the off-diagonal elements $\rho_{12}^{(1)}(t)$ and $\rho_{21}^{(1)}(t)$ from (16). This yields

$$\frac{d}{dt}\rho_{11}^{(1)}(t) = -\frac{d}{dt}\rho_{22}^{(1)}(t) = \frac{i}{\hbar}e^{-C_1 t}[\rho_{12}^{(1)}(0)e^{-i\bar{\epsilon}t/\hbar} - C.C.]-$$

$$-2\left(\frac{\tilde{J}}{\hbar}\right)^2\int_0^t e^{-C_1\tau}\cos(\bar{\epsilon}\tau/\hbar)[\rho_{11}^{(1)}(t - \tau) - \rho_{22}^{(1)}(t - \tau)]\,d\tau-$$

$$-2\frac{J}{\hbar}\int_0^t e^{-C_1\tau}\sin(\bar{\epsilon}\tau/\hbar)[X\cdot\rho_{11}^{(1)}(t - \tau) + Y\cdot\rho_{22}^{(1)}(t - \tau)]\,d\tau. \tag{21}$$

Now, because the validity of the markovian kinetics is one of the basic assumptions in, e.g., the theory of reaction kinetics [9], let us apply the usual Markov approximation to (21). We obtain

$$\frac{d}{dt}\rho_{11}^{(1)}(t) = -\frac{d}{dt}\rho_{22}^{(1)}(t) \approx W_{1\leftarrow 2}\rho_{22}^{(1)}(t) - W_{2\leftarrow 1}\rho_{11}^{(1)}(t), \tag{22a}$$

with the transition rates

$$W_{1\leftarrow 2} = 2\left(\frac{\tilde{J}}{\hbar}\right)^2\int_0^{+\infty} e^{-C_1\tau}\cos(\bar{\epsilon}\tau/\hbar)\,d\tau - 2\frac{J}{\hbar}Y\int_0^{+\infty} e^{-C_1\tau}\sin(\bar{\epsilon}\tau/\hbar)\,d\tau =$$

$$= 2\left(\frac{\tilde{J}}{\hbar}\right)^2\frac{C_1}{(\bar{\epsilon}/\hbar)^2 + C_1^2} - 2\frac{J}{\hbar}Y\frac{\bar{\epsilon}/\hbar}{(\bar{\epsilon}/\hbar)^2 + C_1^2}, \tag{22b}$$

and

$$W_{2\leftarrow 1} = 2\left(\frac{\tilde{J}}{\hbar}\right)^2\int_0^{+\infty} e^{-C_1\tau}\cos(\bar{\epsilon}\tau/\hbar)\,d\tau + 2\frac{J}{\hbar}X\int_0^{+\infty} e^{-C_1\tau}\sin(\bar{\epsilon}\tau/\hbar)\,d\tau =$$

$$= 2\left(\frac{\tilde{J}}{\hbar}\right)^2 \frac{C_1}{(\bar{\epsilon}/\hbar)^2 + C_1^2} + 2\frac{J}{\hbar}X\frac{\tilde{\epsilon}/\hbar}{(\bar{\epsilon}/\hbar)^2 + C_1^2}. \tag{22c}$$

So far, we have assumed a slow carrier regime

$$|J| \ll \Delta W_{ph} \tag{23a}$$

(in the opposite regime, the polaron renormalization would not appear in such a simple manner or at all) and the long-time approximation

$$t \gg t_D \approx \frac{\hbar}{\Delta W_{ph}} \tag{23b}$$

(a time large as compared to the bath dephasing time). For the validity of the Markov approximation (22) to (21), one further needs

$$W_{1\leftarrow 2} + W_{2\leftarrow 1} \ll C_1 \tag{23c}$$

(condition of slow kinetics as compared to the decay of memory) and

$$t \gg 1/C_1. \tag{23d}$$

Solution to (22a) reads:

$$\rho_{11}^{(1)}(t) = 1 - \rho_{22}^{(1)}(t) =$$
$$= \frac{W_{1\leftarrow 2}}{W_{1\leftarrow 2} + W_{2\leftarrow 1}} + e^{-(W_{1\leftarrow 2}+W_{2\leftarrow 1})t}\left[\rho_{11}^{(1)}(0) - \frac{W_{1\leftarrow 2}}{W_{1\leftarrow 2} + W_{2\leftarrow 1}}\right]. \tag{24}$$

Thus, the long-time asymptotics (equilibrium solution) is

$$\rho_{11}^{(1)}(+\infty) = 1 - \rho_{22}^{(1)}(+\infty) = \frac{W_{1\leftarrow 2}}{W_{1\leftarrow 2} + W_{2\leftarrow 1}} \tag{25}$$

and the rate of approaching it is

$$W_{1\leftarrow 2} + W_{2\leftarrow 1} = \left(\frac{\tilde{J}}{\hbar}\right)^2 \frac{4C_1}{(\bar{\epsilon}/\hbar)^2 + C_1^2} + 2\frac{J}{\hbar}\frac{\bar{\epsilon}/\hbar}{(\bar{\epsilon}/\hbar)^2 + C_1^2}(X - Y). \tag{26}$$

Worth noticing is that (26) really turns (apart from the opposite sign) into (20), provided that $\tilde{J}$ term is negligible and (as usual) $\bar{\epsilon}/\hbar \gg C_1$. Under these conditions

$$\frac{\rho_{11}^{(1)}(+\infty)}{\rho_{22}^{(1)}(+\infty)} = \frac{W_{1\leftarrow 2}}{W_{2\leftarrow 1}} \approx -\frac{Y}{X} = e^{-\beta\epsilon}, \tag{27}$$

exactly as required by the equilibrium statistical mechanics in the absence of any renormalization. Specifying, e.g., $\tilde{\epsilon} > 0$ (this specifies the direction of asymmetry), we then obtain from (22b) and for $|J| \ll \tilde{\epsilon}$

$$W_{1\leftarrow 2} \propto n_B(\tilde{\epsilon}) \approx e^{-\beta\epsilon}, \tag{28}$$

which is essentially the reaction rate k_1 of Marcus [9]. Clearly, (28) can immediately be compared with the result of [9] for the reaction rate

$$k_1 = Z \exp(-\Delta F^*/(k_B T)), \tag{29}$$

where Z is 'the collision number in the solution' and ΔF^* is 'the contribution to the free energy of the formation of the intermediate state X^* from the isolated reactants in the dielectric medium'. Also, our result (28) yields the activated form. The difference between ΔF^* in (29) and the corresponding change of energy (the latter quantity to be identified with our $\tilde{\epsilon}$ in (28)) is (minus) the product of temperature and the change of entropy which changes only the pre-exponential term in (29). Concerning Z in (29), we can hardly identify it with any quantity in our general result (22b). The point is that

- our theory (being a strictly quantum one) does not involve such vaguely defined (and in our context only semiclassical) notions as the collision number in solution whose (e.g.) temperature dependence is hard to estimate;

- our theory does not involve any notion like 'reaction path', 'an intermediate state' or nonequilibrium thermodynamic notions like 'free energy of the intermediate state' (irrespective of possible justifications of the latter [15]); it is purely microscopic and automatically involves all possible (given by the Hamiltonian) intermediate states which are in general taken as (up to an arbitrary degree) nonstationary;

- our theory yields the exponential form (28) only at strictly defined conditions (see the text above) which we consider to be physically correct; in our opinion, this corresponds well to other more recent results and conclusions [16, 17].

Anyway, though these results are encouraging, one should be extremely careful. The point is that one of the assumptions underlying the application of the Markov approximation to (21) and the very markovian character of the kinetics assumed by Marcus [9], in particular (23c), is not fulfilled. This may be verified by a direct inspection of (17a–c). Thus, the markovian description of, in particular, the electron kinetics – in fact, the basic assumption of the usual reaction rate theory, to our knowledge never questioned so far in, e.g. the chemical literature and currently used in reviews, textbooks and monographs on reaction theory [18, 19] – is actually invalid. So, the inclusion of quasicoherent effects, i.e. finite memory as in (21), when treating the time-dependence of the electron kinetics, seems to be inevitable.

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KOHERENTSUSEFEKTID KEEMILISTES REDOKSREAKTSIOONIDES

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On näidatud, et elektronülekande probleemi mittestohhastiline formuleering (alates ajalise sidumita üldistatud juhtvõrrandeist või Tokuyama–Mori lähendusest) annab iga reservuaariga lokaalses seoses oleva elektronsüsteemi tarvis võrrandid, mis on aluseks üldistatud stohhastilise Liouville'i võrrandi rangele mudelile. Võrrandite asümmeetrilisele dimeerile rakendamise tulemuseks on pikaajaline Marcuse reaktsioonikineetika üleminekuga mitteaktiveeritud tüübilt aktiveeritule. Koherentsusefektide korral aga harilik kvantmehaanika kuldreeglil põhinev pikaajaline Markovi asustuskineetika ei kehti.

ЭФФЕКТЫ КОГЕРЕНТНОСТИ В ХИМИЧЕСКИХ
ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫХ РЕАКЦИЯХ

Владислав ЧАПЕК

Показано, что нестохастическая формулировка проблемы электронного переноса (начиная с обобщенных управляющих уравнений без свертки или подхода Токуяма–Мори) ведет к уравнениям, лежащим в основе строгой модели обобщенного стохастического уравнения Лиувилля для каждой электронной системы, имеющей локальную связь с резервуаром. Для несимметрического димера в кинетике Маркуса в пределах больших времен наблюдается переход между активационным и неактивационным поведением. Эффекты когерентности приводят к тому, что обыкновенная марковская кинетика заселения электронных состояний, основанная на золотом правиле квантовой механики, неоправданна.