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Quantum dynamics of interacting excitonic-vibronic dimer

V. Čápek[a]

Institute of Physics of Charles University, Faculty of Mathematics and Physics, Ke Karlovu 5, 121 16 Prague 2, Czech republic

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Abstract. A carrier on a symmetric dimer with a weak hopping integral, interacting (*via* a site-local coupling) strongly with on-site oscillators is considered. It is shown that the dynamics of the low excited nonstationary states is, owing to strong carrier-oscillator correlations, incompatible with that of the nonlinear Liouville equation theory. The oscillators are, owing to carrier-oscillator correlations, fully relaxed to the instantaneous rather than to the mean carrier position and need no time-delay or relaxation mechanism to respond to the shifted carrier's position, in contrast to the usual Holstein and Davydov picture. The origin of the standard Debye-Waller renormalization is scrutinized using the Tokuyama-Mori theory including all the excited states of the oscillators and rigorous statements are made concerning its form. Limitations on the time interval of applicability of the semiclassical description resulting from the carrier dynamics are discussed.

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1 Introduction

For discussion of time-development of interacting electron- (or exciton-) phonon systems, one can apply different types of kinetic approaches using, *e.g.*, different types of projection formalisms. Usual projection methods can yield either time-convolution [1–3] (TC-GME) or time-convolutionless [4–7] (see also [8] for equivalence of seemingly different approaches) generalized master equations (TCL-GME) for, *e.g.*, matrix elements of the electron or exciton (carrier henceforth) density matrix. Another class of theories are those developed by Mori [9] and Tokuyama with Mori [10] for time-development of operators in the Heisenberg picture. The Nakajima-Zwanzig TC-GME method has recently been proved to be equivalent to that one by Mori [11]; the same applies to the TCL-GME and Tokuyama-Mori methods [12].

Simultaneously, other methods for treating the problem of interacting systems have been developed. The first one goes back to Holstein [13] and Davydov [14,15] and is based on representing the main effect of phonons (or, more generally the bath) on the carrier, *i.e.* selftrapping, by a nonlinear term in the (nonlinear) Schrödinger equation. Kenkre with his collaborators as well as others have developed the method further [16–18]. The method has recently been heavily criticized [19] but no *elementary* reason has been given so far why this theory, sometimes yielding entirely different results to other approaches, should fail. Recently, Salkola, Bishop, Kenkre and Raghavan [20] came to the conclusion that for the interacting carrier-phonon problem, the discrete nonlinear Schrödinger equation (or Liouville equation) approach is well justified only in a highly limited regime.

The second treatment which became very popular recently in connection with the notion of chaos, is based on a classical or semiclassical picture of the interacting carrier-oscillator model [21,22]. Correspondence with the above nonlinear Schrödinger equation can be then easily found in the so-called discrete selftrapping approximation but a semiclassical description of the total carrier-oscillator complex is in at least the simplest situations possible [22]. The latter approach, though undoubtedly correct in the high temperature limit, has, however, also unpleasant limitations. The first one is connected with time: detailed quantum calculations for the carrier-oscillator problem performed by, *e.g.*, Steib [23] have proved recently that classical equations of motion say very little about real quantum behaviour of the system, except for initially separable carrier-oscillator states and for such limited time intervals for which this separation persists. The second type of limitations comes from the very applicability of the high-temperature classical description in standard situations: In, *e.g.*, Anthracene as a typical organic molecule, intramolecular vibrational modes have energy quanta $\hbar\omega$ between 0.0149 eV and 0.372 eV. Thus, at room and lower temperatures, we always have $\hbar\omega \gtrsim k_{\mathrm{B}}T$ (with k_{B} being the Planck constant and T the temperature).

[a] e-mail: capek@karlov.mff.cuni.cz

This does not allow the classical treatment requiring necessarily $\hbar\omega \ll k_{\rm B}T$. Thus, in order to estimate the value of both the above (nonlinear Schrödinger as well as classical) approaches, a rather detailed quantum analysis of the effect of the carrier interaction with surroundings is needed.

The present work involves only analytical methods. Anyway, in connection with the fully quantum numerical work by Steib above [23], one should also mention that plenty of other numerical works exist on quantum dynamics of particles coupled to a finite number of modes which are on the other hand usually devoted to other aims and problems. We have in mind first of all papers [24–27]. Extensions of these works (devoted to or at least partly inspired by fast dynamics in concrete molecular systems) by including coupling to the thermodynamic bath [28,29] or even external driving fields [30] exist. The most usual form of including the thermodynamic bath is provided by so called spin-boson model [31–33]. These generalizations will not be mentioned in more detail here, however, as the bath can be practically included by approximate methods only. Open questions then remain concerning lack of correspondence of the most usual approximate treatments [33–35] with more advanced approximate ones [36] or even rigorous statements especially (but not only) in the long-time domain [37–39]. The most advanced computer-exact methods enabling to project off the bath (reducing the dynamical problem to relatively low-dimensional ones of the linear algebra) and work with unexpectedly high accuracy in its coupling to the system [40–42] still wait for applications to a broader class of realistic models.

2 Model

We shall work with a coupled carrier-vibronic system consisting of a symmetric pair of sites (dimer) for the carrier, interacting *via* a linear local and symmetric coupling, with two identical harmonic oscillators coupled each to one of the respective sites. This is the simplest model allowing still reliable analytical treatment but able already to discuss connection to both the above (nonlinear Schrödinger and classical) methods. Ignoring for simplicity any possible coupling of the system to the bath, the Hamiltonian of this standard model reads

$$\begin{aligned} H = & - V(c_1^\dagger c_2 + c_2^\dagger c_1) \\ & + \frac{1}{2m}(p_1^2 + p_2^2) + \frac{1}{2}m\omega^2(q_1^2 + q_2^2) \\ & + \gamma(q_1 c_1^\dagger c_1 + q_2 c_2^\dagger c_2). \end{aligned} \tag{1}$$

Here c_r ($c_r^\dagger$), $r = 1,\ 2$ are the annihilation (creation) operators of the carrier on individual sites, m and ω are the oscillator mass and frequency, γ is the carrier-oscillator coupling constant and V (usually taken as a positive number in order to get the bonding state symmetric) is the carrier hopping (resonance or transfer) integral due to an overlap between the localized site (*e.g.* atomic) states.

As usual, we introduce the centre-of-mass (plus) and relative (difference or minus) oscillators with coordinates and momenta

$$\begin{aligned} q_+ = \frac{1}{2}(q_1 + q_2),\ q_- = q_2 - q_1, \\ p_+ = p_1 + p_2,\ p_- = \frac{1}{2}(p_2 - p_1). \end{aligned} \tag{2}$$

This turns (1) to

$$\begin{aligned} H = & - V(c_1^\dagger c_2 + c_2^\dagger c_1) \\ & \times \left[\frac{1}{2(2m)}p_+^2 + \frac{1}{2}(2m)\omega^2(q_+ + \frac{1}{2m\omega^2}\gamma)^2\right] \\ & + \left[\frac{1}{2(\frac{m}{2})}p_-^2 + \frac{1}{2}\frac{m}{2}\omega^2(q_- + \frac{1}{m\omega^2}\gamma(c_2^\dagger c_2 - c_1^\dagger c_1))^2\right] \\ & - \frac{\gamma^2}{2m\omega^2}\,. \end{aligned} \tag{3}$$

Here, we have used the fact that we work with just one carrier, *i.e.* $(c_2^\dagger c_2 - c_1^\dagger c_1)^2 = c_2^\dagger c_2 + c_1^\dagger c_1 = 1$.

Except for the centre-of-mass oscillator which is fully decoupled, this is a problem whose analytical solution is unknown but whose *stationary* states are well studied and can be found with numerically arbitrary accuracy [43–45]. Here, however, in order to allow for an *analytical* treatment of the *dynamics*, we shall choose a special regime given by inequalities

$$\frac{\gamma^2}{2m\omega^2} \gg \hbar\omega \gg |V|. \tag{4}$$

The first one means that the polaron well depth is much greater that the phonon energy and may also be written as $\gamma/(m\omega^2) \gg \sqrt{(2\hbar/(m\omega))}$, *i.e.* that polaron shift of the equilibrium position of the minus-oscillator is much greater than the radius of its ground-state. That means that the unshifted, left-shifted and right-shifted ground states of the oscillator all have very little overlap, *i.e.* the renormalization of the hopping integral V by the Debye-Waller factor (to be discussed below) is appreciable and quantum effects are thus expected to be quite strong. The second inequality in (4) allows us to treat, for low excited states and low degrees of excitation characterized by, *e.g.*, effective temperatures fulfilling

$$k_{\rm B}T_{\rm eff} \ll \hbar\omega, \tag{5}$$

the dynamics analytically[1].

[1] Even outside equilibrium, one can (for such purposes) well define such temperatures expressing the difference of the mean and ground state energies, *i.e.* the mean excitation energy as $k_{\rm B}T_{\rm eff}$.

Owing to (4), the ground and the first excited states (up to corrections of the order $|V|/(\hbar\omega)$) read

$$|\Psi_\pm\rangle = \frac{1}{\sqrt{2}}\Big[c_1^\dagger|\mathrm{vac_{car}}\rangle \otimes \left(\frac{m\omega}{2\pi\hbar}\right)^{1/4} \exp[-\frac{1}{4}\frac{m\omega}{\hbar}(q_- - \frac{\gamma}{m\omega^2})^2] \pm c_2^\dagger|\mathrm{vac_{car}}\rangle \otimes \left(\frac{m\omega}{2\pi\hbar}\right)^{1/4} \exp[-\frac{1}{4}\frac{m\omega}{\hbar}(q_- + \frac{\gamma}{m\omega^2})^2]\Big] \otimes \left(\frac{2m\omega}{\pi\hbar}\right)^{1/4} \exp[-\frac{m\omega}{\hbar}(q_+ + \frac{\gamma}{2m\omega^2})^2]. \quad (6)$$

The corresponding eigenenergies (up to corrections of the order $|V|^2/(\hbar\omega)$) read

$$E_\pm = 2\frac{1}{2}\hbar\omega - \frac{\gamma^2}{2m\omega^2} \mp \tilde{V}, \qquad \tilde{V} = V\exp\left[-\frac{1}{2}\frac{\gamma^2}{m\hbar\omega^3}\right]. \quad (7)$$

In approximate treatments, such states are commonly used as basis states of the small polaron theory [46]. It is, however, not difficult to see that in the above regime (4), these states asymptotically coincide with the lowest eigenstates first derived by Wagner and Koengeter [43]. For such Wagner and Koengeter eigenstates, it is in general typical that with, *e.g.*, the carrier on the left (site 1) and, *e.g.* positive γ, the wave function of the minus-oscillator is not simply localized on the same (left) side but also has a local maximum on the opposite (right) one reminiscent, in a dynamical language, of the (carrier's) previous hop from the right to the left. During this hop the state of the minus-oscillator remained unchanged and did not succeed (up to the measurement time) in accommodating to the new carrier position. Such a behaviour would, however, become pronounced only for sufficiently large $|V|$. From the energy arguments, one can guess that such local maxima on the opposite side could (for $\gamma/(m\omega) \gg (2\hbar/(m\omega))^{1/2}$) be well distinguished in, *e.g.*, the ground state for $|V| \gtrsim \gamma^2/(m\omega^2)$ only, *i.e.* certainly not in our regime (4). The same applies to a possibility of obtaining unrelaxed minus-oscillator states. Both such possibilities do, however, exist among higher excited states [43,44]. The fact that, with a high accuracy, at least the ground state to (1) in our regime (4) reads as (6), has recently been very well illustrated also by Zhao *et al.* [51,52].

Let us now specify initial condition for our dynamical problem. The state which at time $t = 0$ was

$$|\Psi(t=0)\rangle = c_1^\dagger|\mathrm{vac_{car}}\rangle \otimes \left(\frac{m\omega}{2\pi\hbar}\right)^{1/4} \exp[-\frac{1}{4}\frac{m\omega}{\hbar}(q_- - \frac{\gamma}{m\omega^2})^2] \otimes (\frac{2m\omega}{\pi\hbar})^{1/4} \exp[-\frac{m\omega}{\hbar}(q_+ + \frac{\gamma}{2m\omega^2})^2], \quad (8)$$

i.e. the state with the initial oscillator polarizations

$$\langle q_1\rangle(t=0) = \langle q_+ - \frac{1}{2}q_-\rangle(t=0) = -\frac{\gamma}{m\omega^2}, \qquad \langle q_2\rangle(t=0) = \langle q_+ + \frac{1}{2}q_-\rangle(t=0) = 0 \quad (9)$$

reads at $t > 0$

$$\begin{aligned}|\Psi(t)\rangle =& \frac{1}{\sqrt{2}}[|\Psi_+\rangle \mathrm{e}^{-iE_+t/\hbar} + |\Psi_-\rangle \mathrm{e}^{-iE_-t/\hbar} \\ =& \Big\{c_1^\dagger|\mathrm{vac_{car}}\rangle \otimes \left(\frac{m\omega}{2\pi\hbar}\right)^{1/4} \times \exp[-\frac{1}{4}\frac{m\omega}{\hbar}(q_- - \frac{\gamma}{m\omega^2})^2]\cos(t\tilde{V}/\hbar) \\ &+ ic_2^\dagger|\mathrm{vac_{car}}\rangle \otimes \left(\frac{m\omega}{2\pi\hbar}\right)^{1/4} \times \exp[-\frac{1}{4}\frac{m\omega}{\hbar}(q_- + \frac{\gamma}{m\omega^2})^2]\sin(t\tilde{V}/\hbar)\Big\} \\ &\times \mathrm{e}^{-i(\hbar\omega - \gamma^2/(2m\omega^2))t/\hbar}\left(\frac{2m\omega}{\pi\hbar}\right)^{1/4} \times \exp[-\frac{m\omega}{\hbar}(q_+ + \frac{\gamma}{2m\omega^2})^2]. \end{aligned} \quad (10)$$

Clearly, in the sense given by (5), this is (owing to (4)) a low-excited state. With (8) and according to what has been already said above, corrections to (10) are formally of the first order in $V/(\hbar\omega)$ in the wave function amplitudes and of the second order in energies as prefactors of time. Correspondingly, for discussions of, *e.g.*, the mean position of the carrier, they are in our regime (4) irrelevant. (The importance of these corrections becomes, however, amplified when correlation functions are examined - see Sect. 4 below.) There are several things typical of the above quantum regime which should be stressed in connection with dynamics described by (10) and the above (nonlinear Schrödinger and classical) approaches to be discussed below:

- We never have a full self-localization; the carrier moves coherently back and forth; the lack of damping is owing to lack of the genuine bath in our simple model.
- The coherent oscillations of the site occupation probabilities have a frequency Ω which is strongly renormalized by the coupling to the oscillators ($\Omega = 2|\tilde{V}|/\hbar$ instead of $2|V|/\hbar$). The renormalization is, as seen from (7), due to the standard Debye-Waller factor.
- There is *no* separation of the wave function to the carrier and the oscillatory part[2] as assumed in the soliton theories [13–15]. The wave function contains as many components (with the carrier on one of the sites) as the number of these sites. Each of the components has its own form of the oscillator wave functions which (in the above regime (4)) strongly differ for different possible (instantaneous) carrier positions. Thus, there is, during the time development connected with the carrier motion, *no* relaxation of the oscillator system to the *mean* carrier position which may slowly develop with increasing time (as it corresponds to the soliton picture by Davydov [15]) but rather an 'instantaneous' relaxation of the site oscillators to the *instantaneous* carrier position. One should thus strongly distinguish

[2] With the former one being extended over more than one site.

between the notions of the instantaneous and the mean carrier positions.

- Concerning the relaxation process: the minus- as well as site oscillators remain fully relaxed to the instantaneous position of the carrier in the sense that for each possible position of the carrier found (*i.e.* individual component of the wave function (10)), there is a corresponding state of the oscillators *already relaxed* to this position. (There is no time-delay for the oscillator relaxation; that is why this relaxation can be taken as 'instantaneous'.) With the carrier transfer in space, there is *no* relaxation of the oscillators to a new *mean* carrier position in, *e.g.*, the Davydov sense (*i.e.* simultaneously in all the wave-function components). In other words, oscillator relaxation to the instantaneous carrier position is, in our situation, *neither* dynamical *nor* kinematical process but a correlation phenomenon. The oscillator wave functions in the individual components remain fully unchanged with increasing time. What changes with t is only a weight of the wave-function components. That is the reason why we can have a full accommodation of the oscillators to the moving carrier without any oscillations of the oscillators around new (shifted with time when the carrier moves away) equilibrium positions though we have, in our model, no real relaxation mechanism (owing to, *e.g.*, a coupling of the oscillators with a true thermodynamic bath) making such a relaxation feasible as a real dynamical process.

At least some of these features of our solution contradict the usual understanding of the process of the dynamical reconstruction of the lattice near a moving carrier (polaron).

3 Correspondence with the nonlinear Schrödinger equation picture

The above mentioned impossibility of writing (in the above regime (4) and the low-excited state of the system) the total (carrier + oscillators) function (10) as a product of the carrier wave function multiplied by the oscillatory one which should accommodate to the mean carrier position, means that the original arguments leading to the nonlinear Schrödinger equation for the carrier only and, consequently, to, *e.g.*, solitons or selflocalization picture must necessarily break. Thus, one should scrutinize the standard derivation to find formally where problems on the way to the nonlinear Schrödinger equation appear.

From (1), we can write equations of motion for momentum operators of both the site oscillators

$$\dot{p}_1 = -m\omega^2 q_1 - \gamma c_1^\dagger c_1, \qquad \dot{p}_2 = -m\omega^2 q_2 - \gamma c_2^\dagger c_2. \tag{11}$$

If we now assume as usual that the lattice relaxes so fast to the mean carrier position (or, in our picture, that it is always relaxed) that the time derivatives of momenta on the left hand side of (11) become negligible, one can then express q_1 and q_2 from (11) as

$$q_r(t) \approx -\frac{\gamma}{m\omega^2} c_r^\dagger c_r,\ r = 1, 2 \tag{12}$$

and introduce the result to (1). Neglecting then the kinetic energy of the oscillators (*i.e.* again their momenta), (1) reduces to

$$H = -V(c_1^\dagger c_2 + c_2^\dagger c_1) - \frac{\gamma^2}{2m\omega^2}[(c_1^\dagger c_1)^2 + (c_2^\dagger c_2)^2]. \tag{13}$$

Here, one should mention that approximation (12) breaks the commutational rules between q_r and $c_r^\dagger$ or c_r. Hence other orders in the product of the creation and annihilation operators in the nonlinear term in (13) are imaginable as far as we rearrange the order of (still commuting) operators in (1) before applying (12). They, however, yield no nonlinearity as, *e.g.*, $(c_r^\dagger)^2$ as well as $(c_r)^2$, $r = 1, 2$ should, in our situation with only one carrier, be considered as zero. One should remember here that $c_r^\dagger$ and c_r are still operators. With (13), however, the situation is then similar as (again for operators) $(c_r^\dagger c_r)^2 = c_r^\dagger c_r$ so that all the nonlinearity is lost. Thus, one is led to understanding (12) rather as

$$q_r(t) \approx -\frac{\gamma}{m\omega^2}\langle c_r^\dagger c_r\rangle,\ r = 1, 2. \tag{14}$$

Then, from (1) and (14), we get (upon neglecting the kinetic energy of the oscillators)

$$H = -V(c_1^\dagger c_2 + c_2^\dagger c_1) - \frac{\gamma^2}{m\omega^2}[\langle c_1^\dagger c_1\rangle c_1^\dagger c_1 + \langle c_2^\dagger c_2\rangle c_2^\dagger c_2] + \frac{\gamma^2}{2m\omega^2}[(\langle c_1^\dagger c_1\rangle)^2 + (\langle c_2^\dagger c_2\rangle)^2]. \tag{15}$$

This, as a quantum Hamiltonian, contains no nonlinearity but (owing to the presence of the mean values $\langle \dots \rangle$) leads to a selfconsistency in equations of motion for matrix elements of the carrier density matrix

$$\rho_{mn}(t) = \langle c_n^\dagger c_m\rangle \tag{16}$$

derived from (15). The same applies to Schrödinger equation for site-occupation amplitudes. In other words, these equations become nonlinear. That is the source of nonlinearity in the non-linear Schrödinger equation [13–16] which, on the other hand, can yield selflocalization on a dimer [16,17]. This selflocalization (selftrapping) is, however, in sharp contradiction to the above solution (10). Already this observation, of course, questions approximation (14) as well as the nonlinear Schrödinger equation on at least dimer. In order to understand why this approximation is so misleading, let us, therefore examine (14) in detail.

Necessary but still insufficient condition for (14) to be reliable is equality of the right hand side and the mean

value of the left hand side. It really is, using (10),

$$\begin{aligned}\langle q_1\rangle(t) &\equiv \langle\Psi(t)|q_1|\Psi(t)\rangle \\ &= -\frac{\gamma}{2m\omega^2}[1+\cos(2t\tilde{V}/\hbar)] = -\frac{\gamma}{m\omega^2}\langle c_1^\dagger c_1\rangle(t), \\ \langle q_2\rangle(t) &= -\frac{\gamma}{2m\omega^2}[1-\cos(2t\tilde{V}/\hbar)] \\ &= -\frac{\gamma}{m\omega^2}\langle c_2^\dagger c_2\rangle(t), \end{aligned} \tag{17}$$

so that (14) is reliable in the mean value sense. This fact is tempting to interpret as an argument in favour of the usual Holstein-Davydov assumption that the site oscillator polarizations follow the mean carrier position. As already mentioned above, this of course contradicts the structure of (10). The fact that off-diagonal elements of q_r, $r = 1, 2$ fully neglected by the c-number approximation (14) make this approximation unacceptable can be best illustrated by calculating the mean value of the Hamiltonian. Really, from (10), we get

$$\begin{aligned}\langle c_1^\dagger c_1\rangle(t) &= \frac{1}{2}[1+\cos(2t\tilde{V}/\hbar)], \\ \langle c_2^\dagger c_2\rangle(t) &= \frac{1}{2}[1-\cos(2t\tilde{V}/\hbar)], \\ \langle q_1 c_1^\dagger c_1\rangle(t) &= \langle q_1\rangle(t) = -\frac{\gamma}{2m\omega^2}[1+\cos(2t\tilde{V}/\hbar)] \\ \langle q_2 c_2^\dagger c_2\rangle(t) &= \langle q_2\rangle(t) = -\frac{\gamma}{2m\omega^2}[1-\cos(2t\tilde{V}/\hbar)] \\ \langle q_1^2\rangle(t) &= \frac{\hbar}{2m\omega} + \frac{\gamma^2}{2m^2\omega^4}[1+\cos(2t\tilde{V}/\hbar)] \\ \langle q_2^2\rangle(t) &= \frac{\hbar}{2m\omega} + \frac{\gamma^2}{2m^2\omega^4}[1-\cos(2t\tilde{V}/\hbar)] \end{aligned} \tag{18}$$

so that from (1), we obtain

$$\langle H\rangle(t) = \frac{1}{2}\hbar\omega - \frac{\gamma^2}{2m\omega^2}\,. \tag{19}$$

On the other hand, from (15), we get

$$\langle H\rangle(t) = \frac{1}{2}\hbar\omega - \frac{\gamma^2}{4m\omega^2}[1+\cos(2t\tilde{V}/\hbar)^2]. \tag{20}$$

This is a time-dependent mean value which immediately offers an idea of the relation between the degree of this time-dependence and the tendency of self-trapping (self-localization) inherent to (15) [16,17]. The difference between (19) and (20) illustrates the deficiency of (14) leading to the nonlinear Schrödinger or Liouville equation corresponding to the Hamiltonian (15) above, at least in our situation and in the above regime (4). Specifically, we get that the nonlinear Schrödinger equation connected with Hamiltonian (15) can be applied, in our situation, at most for $0 \le t \ll \hbar/\tilde{V}^3$. This hinders its application to, *e.g.*, the localization or self-trapping problem.

Two comments are still worth mentioning. First, one often argues in favour of (15) by a virtual transition to the classical description. That would mean replacing mean values of products of operators by the product of the corresponding mean values or *vice versa*. The invalidity of this assumption is, in our situation, easily seen already from (18). It is certain that

$$\begin{aligned}\langle q_r c_r^\dagger c_r\rangle(t) &\neq \langle q_r\rangle(t)\langle c_r^\dagger c_r\rangle(t), \\ \langle q_r^2\rangle &\neq [\langle q_r\rangle(t)]^2. \end{aligned} \tag{21}$$

The second nonequality is certainly not only due to the finite radius of the oscillator ground states. The second comment is that the deficiency of the approximation (14) can be also easily verified even for its possible application in the quantum equations of motion

$$\begin{aligned}\frac{\mathrm{d}c_1}{\mathrm{d}t} &\equiv \frac{i}{\hbar}[H, c_1] = \frac{i}{\hbar}(Vc_2 - \gamma c_1 q_1) \\ &\approx \frac{i}{\hbar}(Vc_2 - \gamma c_1\langle q_1\rangle(t)). \end{aligned} \tag{22}$$

Multiplying (22) from the left by $c_1^\dagger$ and taking average in our state (10), we would get approximate equality

$$-\gamma\langle c_1^\dagger c_1 q_1\rangle(t) \approx -\gamma\langle c_1^\dagger c_1\rangle(t)\langle q_1\rangle(t). \tag{23}$$

From (18), it is easily seen that (23) is, in our regime and situation, invalid.

4 Origin of renormalization and correspondence with classical description

For the classical description, it is undoubtedly true (as a consequence of the Bohr correspondence principle) that it should be well justified at high enough temperatures. These temperatures could, on one hand, be much higher than room temperatures as argued above. On the other one, with our low-temperature theory, we have no possibility of direct comparison. That is why we are limited here just to qualitative arguments using the fact that quantum equations of motion (applicable at high as well as low temperatures) have the same (though operator) form as the corresponding classical equations (applicable at high enough temperatures) for the corresponding classical quantities (mean values of the quantum operators).

In order to be specific, let us first introduce three Bloch operators or quantum variables (instead of four operators $c_r^\dagger c_s$, $r = 1, 2$ fulfilling, in our single carrier space, the identity $c_1^\dagger c_1 + c_2^\dagger c_2 = 1$) as

$$\begin{aligned} x &= c_2^\dagger c_1 + c_1^\dagger c_2, \\ y &= i(c_1^\dagger c_2 - c_2^\dagger c_1), \\ z &= c_2^\dagger c_2 - c_1^\dagger c_1. \end{aligned} \tag{24}$$

Defining then, for an arbitrary (for simplicity explicitly time-independent) operator in the Schrödinger picture, A, the time derivative operator $\dot{A} \equiv \mathrm{d}A/\mathrm{d}t = \frac{i}{\hbar}[H, A]$,

[3] This is an important criterion which will appear below again.

we have

$$\dot{x} = -\frac{\gamma}{\hbar} q_- y, \tag{25}$$

$$\dot{y} = \frac{\gamma}{\hbar} q_- x + 2\frac{V}{\hbar} z, \tag{26}$$

$$\dot{z} = -2\frac{V}{\hbar} y, \tag{27}$$

$$\dot{q}_- = 2p_-/m, \tag{28}$$

$$2\dot{p}_- = -m\omega^2 q_- - \gamma z. \tag{29}$$

The same equations apply, however, for the operators in the Heisenberg picture with the usual meaning of the time-derivative. As these equations are exact and apply in the high (*i.e.* classical) as well as low temperature regions (including our regime (4-5)), at least two open questions appear in connection with the above discussion:

- If renormalization of the above back-and-forth site-occupation-probability oscillation frequency $\Omega = 2\tilde{V}/\hbar$ (instead of $\Omega = 2V/\hbar$) is a genuine really existing effect in our regime (4-5) as illustrated above and if the above equations (25-29) apply in all the regimes, how is it possible that the very form of (25-29) does not indicate such a renormalization? In other words, where (in (25-29)) does the renormalization $V \to \tilde{V}$ formally come from? One should add here that the form of (25-29) can hardly be questioned in general as these equations are undoubtedly correct in the classical regime. In the classical regime, on the other hand, hardly any renormalization of the carrier dynamics by the Debye-Waller factor is expected (notice that in the last equation in (7) defining the renormalized transfer integral $\tilde{V}$, there is the Planck constant $\hbar$ in the exponential indicating quantum character of the renormalization).
- As shown above, at low excitation levels and in our regime (4) at least, the surroundings (represented here by the minus-oscillator) is undoubtedly relaxed to the *instantaneous* carrier position. By that we mean as usual that we can find the carrier on various places but finding it (in a measurement process) on one specific site, we can be sure that the surroundings is already accommodated to this specific carrier position as if the carrier were (for a sufficiently long time) kept to this position before the act of measurement, needing (in our regime) even no time (following the previous carrier position experiment) to relax to such a state. This certainly contradicts the original semiclassical Holstein and Davydov picture of the dynamical state of the carrier + bath system where the wave function was factorized into a product of the carrier and bath wave functions with the former one *not* being localized to a single site only and the second one describing accommodation of the surroundings to the mean carrier position in the carrier wave packet in question [13–15]. Thus we can perhaps accept the usual conjecture that the semi-classical Holstein-Davydov assumption (leading to solitons) about approximate factorizability of the wave function for the above dynamical process, *i.e.* about the lattice accommodation to the mean (instead of the instantaneous) carrier position *during the carrier transfer* becomes justified at most at higher excitation levels (temperatures). If so, a question then arises how then this change of behaviour of the solution to (25-29) follows from structure of (25-29).

In our opinion, perhaps the semiclassical (Holstein and Davydov like) character of the solution to (25-29) is connected with a character of the initial state of the dynamical process as one can hardly expect, *e.g.*, a soliton creation in chains in all situations. Postponing detailed discussion of this problem to a later publication, we shall limit our attention here to just the first question above.

Let us first turn our attention to (25-26) as these two equations contain the influence of the site oscillators which should cause the above Debye-Waller renormalization reflected in the carrier dynamics. With our state (10), we can take the average obtaining that

$$\langle q_- x\rangle(t) = \langle q_- y\rangle(t) = 0. \tag{30}$$

This looks like as if there were no effect of the coupling to the site oscillators on the carrier propagation as seen in the site occupation probabilities. This is of course not true and the reason for failure of (30) is that corrections to (10) and consequently to (30) not taken properly here are formally of the first order in $|V|$. This makes the approximate result (30) insufficiently exact to discuss, *e.g.*, the effect of renormalization (*i.e.* partial cancelling of the effect) of the second term on the right hand side of (26).

One should realize that in our regime (4), the first and second terms on the right hand side of (26) may be viewed as formally (when determined by the relative values of the corresponding multiplicative constants $\gamma/\hbar$ and $V/\hbar$) the dominating and small terms, respectively. Hence a high accuracy is needed when investigating partial cancelation of the second (formally small) term by the dominating one which, however, disappears in the lowest order in V. We shall even show that the first (from the point of view of multiplicative prefactor in our regime) 'big' or 'dominating' term on the right hand side of (26) plays, in our low-temperature regime (4) and for the above carrier dynamics, just a minor role of only a small renormalization correction to the second ('small') term proportional to the small parameter $V/\hbar$. Thus care is needed in general in estimating the role of dominating or small terms only *via* values of the multiplicative constants.

Arguments for such a picture may be best taken from the above treatment and solution (10). Another formalism capable of describing the effect of removing (projecting off) formally big terms on the dynamics otherwise caused by formally small terms, is provided by the Tokuyama-Mori operator method [53]. For our model of a dimer interacting with the polarization oscillator, such a theory has so far not been presented. Here, we shall therefore limit ourselves to just a simple perturbational reasoning postponing a more detailed treatment based on the Tokuyama-Mori method to the next Section.

In view of the assumed smallness of V in our regime (4), we shall limit to the first order corrections in V and, for simplicity, we shall include only the first excited states in each adiabatic potential well[4]. In addition to $\Psi_\pm$ in (6), we have to extend our Hilbert space by including states

$$\begin{aligned}|\Phi_\pm\rangle =&\frac{1}{\sqrt{2}}\Big[c_1^\dagger|\mathrm{vac_{car}}\rangle\otimes\left(\frac{m\omega}{2\pi\hbar}\right)^{1/4}\sqrt{\frac{m\omega}{\hbar}}(q_- - \frac{\gamma}{m\omega^2})\\ &\times\exp[-\frac{1}{4}\frac{m\omega}{\hbar}(q_- - \frac{\gamma}{m\omega^2})^2]\\ &\pm c_2^\dagger|\mathrm{vac_{car}}\rangle\otimes\left(\frac{m\omega}{2\pi\hbar}\right)^{1/4}\sqrt{\frac{m\omega}{\hbar}}(-q_- - \frac{\gamma}{m\omega^2})\\ &\times\exp[-\frac{1}{4}\frac{m\omega}{\hbar}(q_- + \frac{\gamma}{m\omega^2})^2]\Big] \end{aligned} \quad (31)$$

(here, for simplicity, we ignore the above plus-oscillator which has no influence on the carrier transfer processes). Then, to the lowest order in V, the lowest two eigenstates $|\Psi'_\pm\rangle$, replacing $|\Psi_\pm\rangle$ read

$$|\Psi'_\pm\rangle = |\Psi_\pm\rangle \mp \frac{\tilde{V}}{\hbar\omega}\frac{\gamma}{m\omega^2}\sqrt{\frac{m\omega}{\hbar}}|\Phi_\pm\rangle. \quad (32)$$

For simplicity, we assume the initial condition

$$|\Psi(t=0)\rangle = \frac{1}{\sqrt{2}}[|\Psi'_+\rangle + |\Psi'_-\rangle], \quad (33)$$

we have the time-dependent solution

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}}[|\Psi'_+\rangle \mathrm{e}^{-iE_+t/\hbar} + |\Psi'_-\rangle \mathrm{e}^{-iE_-t/\hbar}] \quad (34)$$

(for our purposes to the first order in V here, there is no need to include the first order corrections to $E_\pm$). With that, one can proceed to calculation of the above correlation functions. After straightforward though lengthy calculations, one finds that

$$\frac{\gamma}{\hbar}\langle q_- x\rangle \approx \frac{2\tilde{V}}{\hbar}\frac{\gamma^2}{m\hbar\omega^3}\exp\left(-\frac{\gamma^2}{m\hbar\omega^3}\right)\cos\left(\frac{2\tilde{V}t}{\hbar}\right). \quad (35)$$

This is to be compared with

$$\frac{2V}{\hbar}\langle z\rangle \approx -\frac{2V}{\hbar}\cos\left(\frac{2\tilde{V}t}{\hbar}\right). \quad (36)$$

The fact that for all the times, (35) and (36) have the opposite signs (both of them being proportional to V) illustrates, in the regime (4), the above mentioned renormalization of the 'small' term by the 'big' one.

An interesting comment is, however, also worth mentioning here. Comparing (32) with (6), one can see that γ may also serve as a small parameter in our generalization of our treatment in Section 2 here. Then the sum of (35) and (36), *i.e.* the solution to (26), can be approximated to the second order in γ as

$$\langle \dot{y}\rangle \approx -\frac{2V}{\hbar}\cos\left(\frac{2\tilde{V}t}{\hbar}\right)\exp\left(-\frac{\gamma^2}{m\hbar\omega^3}\right). \quad (37)$$

This means a double-renormalization as compared to the (physically justified) renormalization of V in (7). The solution of this seeming contradiction is, however, that in addition to the renormalization (slowing) of the dynamics coming from the $V\to\tilde{V}$ renormalization in the $\cos(2\tilde{V}t/\hbar)$ factor, we have an additional overlap of the q_- oscillator states relaxed to different carrier positions hidden in the very definition of the mean value $\langle y\rangle$. This situation is analogous to that one found in [54] where this 'double renormalization' was due to the fact that there is no way to renormalize, in an manner analogous to above, by mutual compensation of several terms, V on the right hand side of (27). Detailed discussion then yields that solution to (26-27) gives together the oscillations properly renormalized as in (7) [54][5].

5 Tokuyama-Mori approach to renormalization

We have already mentioned several reasons why one cannot expect the $V\to\tilde{V}$ renormalization whenever accepting the classical picture (*i.e.* the c-number character of (25-29)) for the minus- (polarization) oscillator. Let us remember that

- its physical origin consists in overlap of the oscillator states accommodated to different carrier positions and the notion of "overlap" does not appear in any classical theory;
- the quantum Planck constant $\hbar$ enters the Debye-Waller factor in $\tilde{V}$ in (7).

In order to show that and how the $V\to\tilde{V}$ renormalization in the left-right carrier transition results from quantum equations of motion (25-29) we invoke the Tokuyama-Mori approach [53]. This time-local theory starts from general quantum equations of motion for operators

$$\frac{\mathrm{d}}{\mathrm{dt}}A(t) = \frac{i}{\hbar}[H, A(t)] \quad (38)$$

(Eqs. (25-29) being just particular cases of (38)) and applies a properly chosen projector. We have found it useful and technically very simple to apply a new Mori-like projector

$$\mathcal{P}\ldots = y\,\mathrm{Tr}(\rho(0)y\ldots) + z\,\mathrm{Tr}(\rho(0)z\ldots) \quad (39)$$

[4] This of course means that we can pretend to at most a qualitative accuracy henceforth in this section.

[5] Here, one should notice that we have got the $V\to\tilde{V}$ renormalization in expressions for *mean* values of our observables but not in operator solutions of the corresponding quantum equations of motion. So one should comment on the first question posed above that this (and not a full replacement $V\to\tilde{V}$ in the time-dependent operators in (25-29)) is the real meaning of the Debye-Waller renormalization.

with the initial (carrier + the polarization oscillator) density matrix

$$\rho(0) = |\Psi(t=0)\rangle\langle\Psi(t=0)| = |1\rangle\langle 1| \otimes \rho_{\rm ph} \qquad (40)$$

(see Eq. (8)) where $\rho_{\rm ph}$ is the phonon density matrix expressing the initial state of both the q_+ and the q_- (polarization) oscillators ($\mathrm{Tr}_{\rm ph}\rho_{\rm ph} = 1$). We do not need to specify necessarily here whether we mean the initially relaxed or unrelaxed phonon system around the carrier situated, at $t = 0$, at site 1. This yields from the general Tokuyama-Mori identity [53]

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{dt}}G(t) &= \mathrm{e}^{i\mathcal{L}t}\mathcal{P}i\mathcal{L}G(0) + \mathrm{e}^{i\mathcal{L}t}\mathcal{P}\mathcal{T}(t)\mathcal{Q}i\mathcal{L}G(0) \\
&\quad + \mathrm{e}^{i\mathcal{Q}\mathcal{L}t}\mathcal{V}(t)\mathcal{Q}i\mathcal{L}G(0), \\
\mathcal{T}(t) &= \mathcal{S}(t)[1-\mathcal{Q}\mathcal{S}(t)]^{-1},\ \mathcal{V}(t) = [1-\mathcal{Q}\mathcal{S}(t)]^{-1}, \\
\mathcal{S}(t) &= 1-\mathrm{e}^{-i\mathcal{L}t}\mathrm{e}^{i\mathcal{Q}\mathcal{L}t},\ \mathcal{Q}=1-\mathcal{P},\ G(t)=\mathrm{e}^{i\mathcal{L}t}G \qquad (41)
\end{aligned}$$

the set of Tokuyama-Mori equations

$$\frac{\mathrm{d}}{\mathrm{dt}}\begin{pmatrix} x_2(t) \\ x_3(t) \end{pmatrix} = \begin{pmatrix} \omega_{22}(t)\ \omega_{23}(t) \\ \omega_{32}(t)\ \omega_{33}(t) \end{pmatrix}\begin{pmatrix} x_2(t) \\ x_3(t) \end{pmatrix} + \begin{pmatrix} f_2(t) \\ f_3(t) \end{pmatrix}. \qquad (42)$$

With our initial condition (40), we have $\langle f_m(t)\rangle \equiv \mathrm{Tr}(\rho(0)f_m(t)) = 0$. For the 'frequencies' $\omega_{mn}(t)$ determining oscillations of $\langle x_2(t)\rangle$ and $\langle x_3(t)\rangle$, we have general formulae

$$\begin{aligned}
\omega_{mn}(t) &= \Omega_{mn} + \delta\Omega_{mn}(t), \\
\Omega_{mn} &= \mathrm{Tr}(\rho(0)x_n i\mathcal{L}x_m), \\
\delta\Omega_{mn}(t) &= \mathrm{Tr}(\rho(0)x_n[1-\mathrm{e}^{-i\mathcal{L}t}\mathrm{e}^{i(1-\mathcal{P})\mathcal{L}t}] \\
&\quad \times [1-(1-\mathcal{P})[1-\mathrm{e}^{-i\mathcal{L}t}\mathrm{e}^{i(1-\mathcal{P})\mathcal{L}t}]]^{-1} \\
&\quad \times (1-\mathcal{P})i\mathcal{L}x_m). \qquad (43)
\end{aligned}$$

Everywhere in (42-43), $x_2 \equiv y$ and $x_3 \equiv z$ and $\mathcal{L}\ldots = [H,\ldots]/\hbar$ is the Liouville superoperator. In general, in order to get hermitian $y(t)$ and $z(t)$ from hermitian $y(0)$ and $z(0)$, the frequencies $\omega_{mn}(t)$ should be real. This is not the case for Ω_{mn} and $\delta\Omega_{mn}(t)$ separately, however. As only the sum $\Omega_{mn} + \delta\Omega(t)_{mn}(t)$ has a meaning, we henceforth take only real parts of Ω_{mn} and $\delta\Omega_{mn}(t)$ into account.

Let us take for a while all (even highly excited) oscillator states into account. One then gets easily that the Ω-matrix reads

$$\Omega = \begin{pmatrix} 0 & 2V/\hbar \\ -2V/\hbar & 0 \end{pmatrix} \qquad (44)$$

so that all the oscillation-frequency renormalization (if any) comes from $\delta\Omega_{mn}(t)$. Calculation of the latter quantities is, however, nontrivial. Easily, one gets that

$$\delta\Omega_{3n}(t) = 0,\ n = 2,\ 3 \qquad (45)$$

as $(1-\mathcal{P})y = 0$. As for the $\delta\Omega_{2n}(t)$ terms, no way has been found how to find them explicitly. One can verify by direct calculation, however, that these terms also turn to zero (as a consequence of the identity $(x-iy)|1\rangle = 2c_1^\dagger c_2|1\rangle = 0$) *provided* that we neglect all oscillator coordinate or momenta fluctuations identifying (like in the classical treatment), *e.g.*, $\langle q^r\rangle$ with $\langle q\rangle^r$ *etc.* That means that in order to get the $V \to \tilde{V}$ renormalization in (42), one must inevitably take the quantum character of q and p into account.

As already indicated above, this is a difficult task provided that we take all the oscillator excited states into account. Instead, therefore, in order to overcome such difficulties but to include nevertheless the accommodation of the oscillator system to the carrier position, we limit as usual (and as above in the second section) to a subspace of the total Hilbert space spanning the lowest excited states of the problem. That means, in our situation, to work in just the basis of states

$$\begin{aligned}
|\phi_1\rangle &= c_1^\dagger|\mathrm{vac_{car}}\rangle \otimes \left(\frac{m\omega}{2\pi\hbar}\right)^{1/4}\exp[-\frac{1}{4}\frac{m\omega}{\hbar}(q_- - \frac{\gamma}{m\omega^2})^2] \\
&\quad \otimes \left(\frac{2m\omega}{\pi\hbar}\right)^{1/4}\exp[-\frac{m\omega}{\hbar}(q_+ + \frac{\gamma}{2m\omega^2})^2], \\
|\phi_2\rangle &= c_2^\dagger|\mathrm{vac_{car}}\rangle \otimes \left(\frac{m\omega}{2\pi\hbar}\right)^{1/4}\exp[-\frac{1}{4}\frac{m\omega}{\hbar}(q_- + \frac{\gamma}{m\omega^2})^2] \\
&\quad \otimes \left(\frac{2m\omega}{\pi\hbar}\right)^{1/4}\exp[-\frac{m\omega}{\hbar}(q_+ + \frac{\gamma}{2m\omega^2})^2], \qquad (46)
\end{aligned}$$

(compare (6) above). Then, in the matrix representation,

$$H = \text{ const. } + \begin{pmatrix} 0 & -\tilde{V} \\ -\tilde{V} & 0 \end{pmatrix} \qquad (47)$$

so that (in the basis of states $|mn) = |m\rangle\langle n|$ in the Liouville space arranged as $|11)$, $|22)$, $|12)$ and $|21)$):

$$\begin{aligned}
\mathcal{L} &= \frac{1}{\hbar}\begin{pmatrix} 0 & 0 & \tilde{V} & -\tilde{V} \\ 0 & 0 & -\tilde{V} & \tilde{V} \\ \tilde{V} & -\tilde{V} & 0 & 0 \\ u-\tilde{V} & \tilde{V} & 0 & 0 \end{pmatrix}, \\
\mathcal{P} &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \\
\rho(0) &= \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \otimes \rho_{\rm ph}. \qquad (48)
\end{aligned}$$

Here, however, $\rho_{\rm ph}$ in (48) refers to the phonon density matrix *initially relaxed* around the carrier located, at $t = 0$, at site 1. Then, unlike above but after a simple matrix algebra, we get that $\delta\Omega_{mn}(t) = 0$, $\Omega_{22} = \Omega_{33} = 0$ while $\Omega_{23} = -\Omega_{32} = 2\tilde{V}/\hbar$. Thus, (42) yields in this case

$$\frac{\mathrm{d}}{\mathrm{dt}}\begin{pmatrix} \langle y\rangle(t) \\ \langle z\rangle(t) \end{pmatrix} = \frac{2\tilde{V}}{\hbar}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\cdot\begin{pmatrix} \langle y\rangle(t) \\ \langle z\rangle(t) \end{pmatrix}. \qquad (49)$$

The oscillation frequency of the solution is then properly renormalized by the Debye-Waller factor as usual. Thus, the quantum equations of motion (25-29) *do*, in contrast to their classical counterparts, in principle include the renormalization of the oscillation frequency[6]. The above treatment thus answers the first question posed in Section 4 above. One should anyway add a comment here saying that the above renormalization is not due to the above limitations to the approximate wave functions (6). In fact, this form of the wave functions has not been utilized here. It may be, on the other hand, interpreted as being due to the limitation to the same subspace (spanned on states (6) or (46)) of the total Hilbert space. In order to avoid this interpretation and beat off similar objections regarding the existence, origin and form of the renormalization, one must continue the discussion as we are going to do below.

The solution (49) also allows an estimate of the time-interval of applicability of the classical solution to our dimer + oscillator problem. In the classical solution to (the classical counterpart of) (25-29), the typical time of the left-right oscillations is $\approx \hbar/(2|V|)$ while, in our regime, for the quantum solution to (25-29), this time reads $\approx \hbar/(2|\tilde{V}|)$. Thus, owing to the inequality $|\tilde{V}| \ll |V|$ assumed to be valid in our regime (4) (compare (7)), the latter time should in our situation be appreciably longer. Hence, when starting from the same initial condition, one cannot expect the classical solution to describe behaviour of the quantum system once the time becomes comparable with $\approx \hbar/(2|V|)$, *i.e.* once the classical solution starts to indicate a left↔right transition. The situation on the other hand changes (even in our regime (4)) once we appreciably increase the degree of excitation, *i.e.* effective temperatures $T_{\rm eff}$ so that (5) becomes disturbed. If we require even more, namely the high-excitation regime with

$$k_{\rm B}T_{\rm eff} \gg \frac{\gamma^2}{4m\omega^2}, \tag{50}$$

(on the right hand side, we have the adiabatic potential barrier to be overcome in the adiabatic left-right transitions), one can view the carrier-oscillator coupling as only a weak perturbation. Then the relevant oscillator states will be practically uninfluenced by this coupling so that the Debye-Waller renormalization (as a consequence of accommodation of the polarization oscillator to the left- or right position of the carrier) is expected to disappear. Thus the classical and quantum typical times for the right-left transfer become identical in such a classical domain and limitations *of the above type* on applicability of the classical description of the polarization oscillator disappear too. One should mention the existence of other time-limitations on the classical description of quantum systems (see, *e.g.*, [55]).

These results concerning the origin of the $V \to \tilde{V}$ renormalization are in accord with the standard picture of the influence of the small polaron formation on the carrier dynamics as well as the standard explanation of the physical origin of the Debye-Waller renormalization. A word of warning is, however, necessary here. From (44) and (45), we get that $\omega_{32} = -2V/\hbar$ while in (49), $\omega_{32} = -2\tilde{V}/\hbar$. Checking the difference between above two approaches starting from the same Hamiltonian (1), one can ascribe this difference to just inclusion of higher excited oscillator (*i.e.* also dimer + oscillators) states in (44) and (45). Technically, one should notice that $\omega_{mn}(t)$ is given by a trace which should not be changed by choosing another basis as far as a *complete* set of states is used as a basis for calculation of traces. For other models, higher excited states are in general (owing to possible virtual up- and down-transitions) known to influence (enhance) appreciably the dynamics even at low excitation levels [56–59]. For the small polaron model of the present type, no such detailed treatment exists so far. In order to settle finally the question about the real existence or non-existence of the Debye-Waller renormalization, we have found a trick to include *all higher excited oscillator states*. Physically, this means not to pose the question about time dependence of mean values $\langle y\rangle(t)$ and $\langle z\rangle(t)$ but rather that of $\langle {\rm e}^{i\Gamma Pz} y {\rm e}^{-i\Gamma Pz}\rangle(t)$ and $\langle z\rangle(t)$. Here

$$\Gamma = \frac{\gamma}{\sqrt{2m\hbar\omega^3}}, \quad P = -\frac{i}{\sqrt{2}}(b - b^\dagger) \tag{51}$$

(with b and $b^\dagger$ being the annihilation and creation operators for the difference oscillator). This means using, instead of the above projectors, rather

$$\begin{aligned}\mathcal{P}\ldots = {\rm e}^{i\Gamma Pz} y {\rm e}^{-i\Gamma Pz} {\rm Tr}(\rho(0) {\rm e}^{i\Gamma Pz} y {\rm e}^{-i\Gamma Pz} \ldots) \\ + z{\rm Tr}(\rho(0) z \ldots).\end{aligned} \tag{52}$$

Here, limiting our attention to the low excited states, we assume for the initial density matrix the form with the minus oscillator relaxed around the carrier located initially at site 1, *i.e.*

$$\rho(0) = {\rm e}^{i\Gamma Pz}|1\rangle\langle 1| \otimes \rho_{\rm ph} {\rm e}^{-i\Gamma Pz} \tag{53}$$

with $\rho_{\rm ph}$ being the unrelaxed canonical phonon density matrix $\rho_{\rm ph} = {\rm e}^{-\beta H_{\rm ph}}/{\rm Tr}_{\rm ph}{\rm e}^{-\beta H_{\rm ph}}$. Again, (42-43) applies with, however, $x_2 = {\rm e}^{i\Gamma Pz} y {\rm e}^{-i\Gamma Pz}$ and $x_3 = z$. Calculation of all the coefficients in (43) is easy using the identity that ${\rm Tr}_{\rm ph}(\rho_{\rm ph}{\rm e}^{2i\Gamma P}) = {\rm e}^{-\Gamma^2(1+2n_{\rm B})}$ with $n_{\rm B} = 1/({\rm e}^{\beta\hbar\omega} - 1)$. We get that $\Omega_{12} = -\Omega_{21} = 2\tilde{V}/\hbar$, $\Omega_{11} = \Omega_{22} = 0$ and $\delta\Omega_{mn}(t) = \mathcal{O}(V^2)$. So, with the coefficients to the first order in V but including all the excited states of the minus oscillator, we have

$$\begin{aligned}\frac{\rm d}{{\rm d}t}\begin{pmatrix}\langle {\rm e}^{i\Gamma Pz} y {\rm e}^{-i\Gamma Pz}\rangle \\ \langle z\rangle\end{pmatrix} \approx \begin{pmatrix}0 & 2\tilde{V}/\hbar \\ -2\tilde{V}/\hbar & 0\end{pmatrix} \\ \times \begin{pmatrix}\langle {\rm e}^{i\Gamma Pz} y {\rm e}^{-i\Gamma Pz}\rangle \\ \langle z\rangle\end{pmatrix} + \mathcal{O}(V^2).\end{aligned} \tag{54}$$

This provides the rigorous statement about existence and form of the Debye-Waller renormalization of the back-and-forth oscillation frequency of the carrier even when *all*

[6] One should realize here that choosing $\mathcal{P} = 1$ in (41) with the corresponding choice of G's, (41) reduces to the quantum equations of motion (25-29).

the oscillator states are taken into account. A comment is worth mentioning here that in the derivation of (54), we have never used any condition for temperature. Thus, even temperatures $T \gg \max(\hbar\omega/k_{\rm B}, \gamma^2/(4mk_{\rm B}\omega^2))$ are admissable (notice that our initial oscillator temperature $T = 1/(k_{\rm B}\beta)$ with β entering $\rho_{\rm ph}$, *i.e.* $\rho(0)$, T plays the role of the effective temperature $T_{\rm eff}$ in (50) defined above as a degree of excitation). This on the other hand contradicts the picture according to which, the carrier-oscillator coupling should, at $T \gg \gamma^2/(4mk_{\rm B}\omega^2)$, be just a small perturbation and all the Debye-Waller renormalization effects should disappear. In our opinion, the explanation of this seeming contradiction lies in higher order terms in (54): the asymptotic form (as $V \to 0$) of all the coefficients in (54) as in (54) is correct. On the other hand, for finite value of V, corrections (of the order $\sim V^2$ and higher) to the lowest order coefficients in (54) become, however, more and more important with increasing T. This observation can make both the above seemingly contradicting statements compatible.

In connection with (54) as a basis for the above statement about existence and form of the Debye-Waller renormalization, one should add a word of warning, however. First, the above renormalization appeared in coefficients in *one particular type* of theory determining time-development of mean values of $e^{i\Gamma Pz} y e^{-i\Gamma Pz}$ and z. That means that in the mean occupation probabilities, one should in reality always (under the conditions of applicability of our expansion to just the lowest order in V) see the Debye-Waller renormalization. Seeing this renormalization in the time-dependence of the solution for, *e.g.*, $\langle z\rangle(t)$ means, however,

- neither that any theory starting from, *e.g.*, the wave-function expansion in terms of unshifted oscillator states must include the Debye-Waller factors from the very beginning in, *e.g.*, matrix elements involved[7],
- nor that the unrenormalized back-and-forth transfer frequencies $2|V|/\hbar$ should be completely absent in the contingent solution for such matrix elements of the Bloch operators which do not enter the mean values of, *e.g.*, $e^{i\Gamma Pz} y e^{-i\Gamma Pz}$ and z.

On the contrary, we believe that the latter matrix elements should involve terms oscillating with the above unrenormalized frequencies. That could be the explanation why it is, as mentioned above, technically so difficult to amend (49) or (42) with $x_2 = y$ and $x_3 = z$ by including all the higher (shifted or unshifted) oscillator states.

6 Where and how the semiclassical description may also fail

By semiclassical picture, we mean here as usual a kind of description of our model in which the dimer is treated in a quantum fashion while the polarization (minus) oscillator is taken as classical. From (3), one can see that the plus oscillator fully separates having thus no influence on the carrier dynamics while the dynamics of the minus oscillator can be then viewed as classical oscillations around $-z\gamma/(m\omega^2)$. Here, z is an operator (not a c-number mean value of z) with two eigenvalues ± 1 having the meaning of the carrier position. (In this way we deviate from another possible model treatment where, in the equations of motion for the oscillator, z as an operator is replaced by the mean value of z [60] - compare (29).) Thus, the oscillations are, up to a numerical factor $-\gamma/(m\omega^2)$, viewed as those around *instantaneous* (not mean) values of the carrier position.

In order to check the consistency of this approach, we calculate equations of motion of exact correlation functions. For the Hamiltonian, we take

$$H = -Vx + \frac{p_-^2}{m} + \frac{1}{4}m\omega^2(q_- + \frac{\gamma}{m\omega^2}z)^2 + \sum_k \hbar\omega_k b_k^\dagger b_k + \frac{1}{2\sqrt{N}}\sum_k \hbar\omega_k G_k z(b_k + b_{-k}^\dagger). \quad (55)$$

Here $G_k = g_k^2 - g_k^1$ is difference of site local coupling constants of the carrier to the respective site oscillators, ω_k are bath oscillator frequencies for N bath modes with bosonic creation and annihilation operators $b_k^\dagger$ and b_k. As usual, we take k as a plane-wave vector of the running mode in the bath but working with standing modes is also possible. The bath and its interaction with the dimer has been added here in order to include possible relaxation processes. We need that in order

- to verify the possibility and find limits of applicability of the semiclassical picture (classical oscillator and quantum dimer) even for always existing coupling of the dimer to the bath,
- to show that the limits of applicability of this picture are not essentially influenced by this coupling.

As for the plus oscillator, it is decoupled from the dimer in (3) and is entirely ignored here.

Quantum operator equations of motion $\mathrm{d}/(\mathrm{d}t)\hat{A} = (i/\hbar)[\hat{H}, \hat{A}]$ for operators b_k and $b_k^\dagger$ can be readily solved. Introducing the result into those for x, y and z yields

$$\frac{\mathrm{d}}{\mathrm{d}t}x(t) = -\frac{\gamma}{\hbar}q(t)y(t) + \frac{1}{2N}\sum_k \omega_k^2|G_k|^2\int_0^t \sin(\omega_k(t-\tau))\{z(\tau), y(t)\}\,\mathrm{d}\tau - \frac{1}{2\sqrt{N}}\sum_k \omega_k G_k\{e^{-i\omega_k t}b_k(0) + e^{i\omega_k t}b_{-k}^\dagger(0), y(t)\},$$

[7] The renormalization should appear only in the solution for, *e.g.*, $\langle z\rangle(t)$.

$$\frac{\mathrm{d}}{\mathrm{d}t}y(t) = \frac{2V}{\hbar}z(t) + \frac{\gamma}{\hbar}q(t)x(t)$$
$$- \frac{1}{2N}\sum_k \omega_k^2|G_k|^2 \int_0^t \sin(\omega_k(t-\tau))\{z(\tau), x(t)\}\,\mathrm{d}\tau$$
$$+ \frac{1}{2\sqrt{N}}\sum_k \omega_k G_k\{\mathrm{e}^{-i\omega_k t}b_k(0) + \mathrm{e}^{i\omega_k t}b^\dagger_{-k}(0), x(t)\},$$
$$\frac{\mathrm{d}}{\mathrm{d}t}z(t) = -\frac{2V}{\hbar}y(t),$$
$$\frac{\mathrm{d}}{\mathrm{d}t}q(t) = \frac{2}{m}p(t),$$
$$\frac{\mathrm{d}}{\mathrm{d}t}p(t) = -\frac{1}{2}m\omega^2 q(t) - \frac{\gamma}{2}z(t). \qquad (56)$$

Here the time-argument at operators designates that the corresponding operators are in the Heisenberg picture; $\{\ldots,\ldots\}$ designates an anti-commutator. Usually, one performs here, *e.g.*, a kind of a Markovian approximation in order to bring the relaxation terms owing to the carrier-bath coupling in a more tractable form. This leads to so-called Bloch equations [61]. In contrast to that type of reasoning in standard situations, we

- do not know (owing to presumably even strong exciton *vs.* polarization oscillator coupling) the time-development of the dimer (exciton) operators if the coupling to the bath is negligible which complicates the standard Markovian, rotating wave *etc.* approximations,
- do not need for what follows to resort to any approximations at all.

So we shall stay at the level given by (56) and calculate directly the quantities of interest.
Using (56), we get easily

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle[q(t)\pm i\frac{2}{m\omega}p(t)]z(t)\rangle = -\frac{2V}{\hbar}\langle[q(t)\pm i\frac{2}{m\omega}p(t)]y(t)\rangle$$
$$\mp\frac{i\gamma}{m\omega} \mp i\omega\langle[q(t)\pm i\frac{2}{m\omega}p(t)]z(t)\rangle,$$
$$\frac{\mathrm{d}}{\mathrm{d}t}\langle[q(t)\pm i\frac{2}{m\omega}p(t)]y(t)\rangle \approx \frac{2V}{\hbar}\langle[q(t)\pm i\frac{2}{m\omega}p(t)]z(t)\rangle$$
$$+\frac{\gamma}{2\hbar}\langle\{q(t)\pm i\frac{2}{m\omega}p(t), q(t)\}x(t)\rangle$$
$$\mp i\omega\langle[q(t)\pm i\frac{2}{m\omega}p(t)]y(t)\rangle. \qquad (57)$$

Here, in the second equation, we have omitted explicitly the terms which depend on the (presumably weak) coupling to the bath. In what follows, they will be, however, fully taken into account. From (56), one also gets

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle y(t) + iz(t)\rangle = -i\frac{2V}{\hbar}\langle y(t) + iz(t)\rangle + \frac{\gamma}{\hbar}\langle q(t)x(t)\rangle$$
$$- \frac{1}{2N}\sum_k \omega_k^2|G_k|^2 \int_0^t \sin(\omega_k(t-\tau))\langle\{z(\tau), x(t)\}\rangle\,\mathrm{d}\tau$$
$$+ \frac{1}{2\sqrt{N}}\sum_k \omega_k G_k\langle\{\mathrm{e}^{-i\omega_k t}b_k(0) + \mathrm{e}^{i\omega_k t}b^\dagger_{-k}(0), x(t)\}\rangle, \qquad (58)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle y(t) - iz(t)\rangle = +i\frac{2V}{\hbar}\langle y(t) - iz(t)\rangle + \frac{\gamma}{\hbar}\langle q(t)x(t)\rangle$$
$$- \frac{1}{2N}\sum_k \omega_k^2|G_k|^2 \int_0^t \sin(\omega_k(t-\tau))\langle\{z(\tau), x(t)\}\rangle\,\mathrm{d}\tau$$
$$+ \frac{1}{2\sqrt{N}}\sum_k \omega_k G_k\langle\{\mathrm{e}^{-i\omega_k t}b_k(0) + \mathrm{e}^{i\omega_k t}b^\dagger_{-k}(0), x(t)\}\rangle, \qquad (59)$$

while from (57) (but writing now the terms dependent on the interaction with the bath explicitly)

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t)][y(t)+iz(t)]\rangle =$$
$$- i\frac{2V}{\hbar}\langle\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t)][y(t)+iz(t)]\rangle$$
$$+ \frac{\gamma}{2\hbar}\langle\{\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t), q(t)\}x(t)\rangle$$
$$- \frac{1}{2N}\sum_k \omega_k^2|G_k|^2 \int_0^t \sin(\omega_k(t-\tau))$$
$$\times\langle\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t)]\{z(\tau), x(t)\}\rangle\,\mathrm{d}\tau$$
$$+ \frac{1}{2\sqrt{N}}\sum_k \omega_k G_g\langle\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t)]$$
$$\times\{\mathrm{e}^{-i\omega_k t}b_k(0) + \mathrm{e}^{i\omega_k t}b^\dagger_{-k}(0), x(t)\}\rangle, \qquad (60)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t)][y(t)-iz(t)]\rangle =$$
$$+ i\frac{2V}{\hbar}\langle\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t)][y(t)-iz(t)]\rangle$$
$$+ \frac{\gamma}{2\hbar}\langle\{\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t), q(t)\}x(t)\rangle$$
$$- \frac{1}{2N}\sum_k \omega_k^2|G_k|^2 \int_0^t \sin(\omega_k(t-\tau))$$
$$\times\langle\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t)]\{z(\tau), x(t)\}\rangle\,\mathrm{d}\tau$$
$$+ \frac{1}{2\sqrt{N}}\sum_k \omega_k G_g\langle\mathrm{e}^{\pm i\omega t}[q(t)\pm i\frac{2}{m\omega}p(t)]$$
$$\times\{\mathrm{e}^{-i\omega_k t}b_k(0) + \mathrm{e}^{i\omega_k t}b^\dagger_{-k}(0), x(t)\}\rangle. \qquad (61)$$

In a similar way, one can proceed also to higher correlation functions. The reason for our writing down such complicated expressions consists in the observation that (58) is compatible with (60) and, similarly, (59) is compatible with (61) provided that we approximate

$$q(t) \pm i\frac{2}{m\omega}p(t) \approx A\,\mathrm{e}^{\mp i\omega t} - \frac{\gamma}{m\omega^2}z(t). \qquad (62)$$

Notice that (62) involves neither any information about the bath nor that about its coupling to the dimer. It is to be stressed here that in (62), A is a c-number, not an operator. Equation (62) means therefore, physically, that irrespective of the above coupling of the dimer to the bath, the polarization oscillations can be treated as classical oscillations around the instantaneous (but understood as quasi-static) value of $-(\gamma/(m\omega^2))z(t)$. (Standard semiclassical approximation where the polarization oscillations are around mean values of $\frac{\gamma}{m\omega^2}z(t)$ determined by the mean carrier position results from (62) upon averaging over the latter. Limitations obtained for this form of the theory are, however, the same.) Equation (62) can also be derived from the last two equations of (56) *provided* that one can neglect the term $\frac{\mathrm{d}}{\mathrm{d}t}z(t)$. This imposes the following conditions on applicability of the classical description of the polarization oscillator:

$$|V| \ll \hbar\omega \qquad (63)$$

(which is compatible with our regime (4)) and for not very strong coupling to the bath (because a typical time entering time-dependence of $z(t)$ remains then $\approx \hbar/(2|V|)$) also

$$0 \leq t \ll \hbar/(2|V|). \qquad (64)$$

Only in the vicinity of equilibrium and in single-time correlation functions where the usual (Debye-Waller) renormalization $V \to \tilde{V}$ is expected to appear, one might argue that the right hand side of (64) could perhaps be substituted by $\hbar/(2|\tilde{V}|)$. This is, however, true only when we ask about mean values of, *e.g.*, y and z in low excited states. In other situations and in general matrix elements of these operators, unrenormalized frequencies of the order $\hbar/(2|V|)$ necessarily appear as it follows from (25-29). The problem is, on the other hand that there is no Debye-Waller renormalization in the semiclassical theory (the physical origin of this renormalization is due to overlaps of the polarization oscillator states accommodated to different exciton locations). So, equations (63-64) are, for our semiclassical model describing the oscillator classically and the quantum dimer *via* the density matrix, limitations on the time and regime of the transport (slow exciton regime). One should add that describing the oscillator classically but the exciton on the dimer by the usual wave function [60], the limitations could be less restrictive.

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