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Collective coordinates for semiclassical femtosecond dissipative dynamics in Liouville space

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Abstract

A semiclassical path-integral algorithm for propagating the reduced density matrix of a quantum-particle coupled to a harmonic bath with an arbitrary temperature and distribution of timescales is developed. Using a canonical transformation of the action in Liouville space, a unique prescription is provided for constructing collective bath coordinates for a given nuclear spectral density. The number of relevant collective coordinates depends on the structure of the spectral density and increases at lower temperatures. © 1998 Elsevier Science B.V. All rights reserved.

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The motion of a quantum-particle interacting with a harmonic bath is of considerable interest, with a broad range of applications including tunneling in semiconductor devices [1,2], biological long-range electron and energy transfer [3-9] chemical and nuclear reactions [10], nonadiabatic transitions [12-14] and nonlinear femtosecond spectroscopy of dyes in liquids [15,16]. Path integral techniques developed by Feynmann [17-19] and Caldeira-Leggett [20,21] allow a rigorous formal elimination of the bath degrees of freedom, and result in a reduced description for the particle coordinates alone. However, evaluating the necessary path integrals using the resulting nonlocal action in the particle's phase space remains a complex task. The problem is simplified considerably when all bath correlation times are fast compared with the

relevant particle motions, and the temperature is sufficiently high. In this case, one may use the simple model of Ohmic spectral density for the bath $J(\omega) = M\gamma\omega$, the action becomes local, and the particle dynamics may be described using a Fokker-Planck equation. Many applications of the theory have been therefore made in this limit.

NonOhmic spectral densities have been incorporated in the instanton theory of dissipative tunneling [22,23] (see also Ref. [24] for an excellent overview of the reaction-rate theory). However, the approach of Ref. [22,23] is based on the assumption that the system (which includes the bath as well) remains in thermal equilibrium. Deviations from thermal equilibrium can be accounted for using the approach introduced by Larkin and Ovchinnikov [25] and later pursued by several authors. However, the deviation is the result of a competition between bath-induced equilibration inside the

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barrier and escape from the barrier region due to tunneling. The bath degrees of freedom are fully integrated out: effects of the bath show up in relaxation rates which are calculated semiclassically rather than perturbatively in the system-bath coupling. Both approaches constituting an important and substantial contribution to the reaction-rate theory, are based on the assumption of the thermally equilibrated bath. Formally, arbitrary bath timescale and nonohmic spectral densities can be treated using multidimensional hierarchies of kinetic equations [26–28]. However, these equations are numerically expensive and do not offer a clear physical insight.

In this letter we develop a semiclassical propagation algorithm which applies for a bath with an arbitrary distribution of timescales and allows us to calculate ultrafast dynamics when the bath relaxation timescales are comparable to those of the primary system. The procedure developed here can be used to predict the nonlinear optical response of systems such as solvated dyes and of light-harvesting complexes [9,29–31] in which the timescales of electronic and nuclear relaxation are comparable. The key element in the present approach is the construction of a less-reduced description in which the effect of the bath on the particle is described using a few collective bath variables. Our calculation uses the nuclear spectral density as the main input: spectral densities representing intermolecular and intramolecular nuclear motions are currently available from optical Kerr and Raman echo measurements in liquids (such as alcohols and water), in glasses, and in proteins [32,33].

A systematic procedure for identifying the relevant collective coordinates for a given bath spectral density is developed. The path-integral representation then allows us to apply semiclassical techniques [10,11,34–40] to calculate the necessary propagators. By generalizing the semiclassical expression for the propagator [34–40] to allow for a complex Liouville-space action we derive closed expressions for the Liouville-space propagator in a dissipative system.

We consider a quantum particle which can occupy several electronic states. It is further coupled to an anharmonic nuclear coordinate Q , which in turn interacts with a harmonic bath. In electronic

spectroscopy, the various states are coupled by the electric field through the dipole operator. Expanding the density matrix perturbatively in the incoming fields, we can represent the optical response functions (or susceptibilities) as sums over Liouville-space paths. Each path is represented by a sequence of given time intervals between successive interactions with the radiation field in which the left (ket) and the right (bra) components of the density matrix assume one of the possible electronic states. The time evolution in each interval is determined by the purely molecular Hamiltonian (with no fields). The signal is then obtained by time integrations over the field amplitudes and by summation over all possible Liouville-space pathways [41]. Since the left (right) components of the density matrix can be in different electronic states at a given time, they evolve using different potentials $V_L(Q)$ ($V_R(Q)$), and the evolution of the density matrix is determined by a Liouville operator $L\rho = H_L\rho - \rho H_R$ with different left and right Hamiltonians.

For a given path, these have the form

$$H_{L,R} \equiv \frac{p^2}{2M} + V_{L,R}(Q) + \sum_j \left[\frac{p_j^2}{2m_j} + \frac{m_j\omega_j^2}{2} \left(q_j - \frac{c_j}{m_j\omega_j} Q \right)^2 \right]. \quad (1)$$

Here q_j , p_j , m_j and c_j represent the coordinate, momentum, mass, and coupling strength of the j th bath degree of freedom, and the adiabatic Born–Oppenheimer approximation for separating electronic and nuclear motions is assumed.

The path-integral representation of Liouville-space evolution involves integrations over left and right trajectories $Q_L(\tau)$, $Q_R(\tau)$, $q_{jL}(\tau)$, $q_{jR}(\tau)$, of $\exp\{iS^{(K)}[Q_L(\tau), Q_R(\tau), q_{jL}(\tau), q_{jR}(\tau)]\}$, with the Liouville-space (Schwinger–Keldysh) action $S^{(K)} = S^{(L)}[Q_L(\tau), q_{jL}(\tau)] - S^{(R)}[Q_R(\tau), q_{jR}(\tau)]$ with

$$S^{(L,R)}[Q(\tau), q_j(\tau)] \equiv \int d\tau \left\{ \frac{M\dot{Q}^2}{2} - V_{L,R}(Q) + \sum_j \left[\frac{m_j\dot{q}_j^2}{2} - \frac{m_j\omega_j^2}{2} \left(q_j - \frac{c_j}{m_j\omega_j} Q \right)^2 \right] \right\}. \quad (2)$$

The Caldeira–Leggett nonlocal action is obtained by integrating $\exp(iS^{(K)})$ over the bath variables

$q_{jL}(\tau)$ and $q_{jR}(\tau)$. All relevant bath information is contained in the spectral density $J(\omega)$ which is expanded as a sum of terms representing overdamped Brownian oscillators [42],

$$J(\omega) \equiv \sum_j \frac{c_j^2}{4m_j\omega_j} 2\pi[\delta(\omega - \omega_j) - \delta(\omega + \omega_j)]$$

$$= M \sum_{\alpha=1}^{N_0} \frac{\gamma_\alpha A_\alpha^2 \omega}{\omega^2 + A_\alpha^2}. \quad (3)$$

The key step in the present work is the introduction of a new effective Liouville-space action $S^{(e)}[Q_L(\tau), Q_R(\tau), q_x(\tau)]$ which depends on a set of collective variables q_x rather than on the original macroscopic number of variables q_j .

$$S^{(e)}[\mathbf{x}(\tau)] = \int d\tau \left[\frac{M\dot{Q}_L^2}{2} - \frac{M\dot{Q}_R^2}{2} - V_L(Q_L) + V_R(Q_R) \right. \\ \left. + \frac{1}{2}(\dot{Q}_L + \dot{Q}_R)p + (Q_L - Q_R)q \right] \\ + \sum_x S_x[q_x(\tau)], \quad (4)$$

where $\mathbf{x} \equiv (Q_L, Q_R, q)$, q and p are some bath coordinates. Our goal is to replace the full action $S^{(K)}$ by $S^{(e)}$. By requiring the integration of $\exp(iS^{(e)})$ over the collective bath variables q_x should lead to the Caldeira–Leggett action, we guarantee that the particle dynamics represented by $S^{(K)}$ and $S^{(e)}$ is identical, once the bath coordinates are eliminated.

To accomplish this goal we first represent that action $S^{(K)}$ (Eq. (2)) in a form of Eq. (4) where the last term on the r.h.s. of Eq. (4) represents the action of bath variables q_j rather than collective variables q_x . This can be done by applying a simple Liouville-space canonical transformation $q'_{jL,R} = q_{jL,R} - (c_j/2m_j\omega_j^2)(Q_L + Q_R)$. The nonlocal part of the Caldeira–Leggett action is fully determined by the correlation functions of p and q calculated with respect to the bath action entering Eq. (4). These correlation functions are in turn fully determined by the spectral density and in the case of the spectral density of Eq. (3) are given by a superposition of exponential functions $\exp(-A_x|\tau|)$. Each term can be represented by a single harmonic oscillator with coordinate q_x . We describe each oscillator by a general action bilinear in q_x and \dot{q}_x with arbitrary

coefficients and represent p as a linear combination of q_x and \dot{q}_x . The coefficients can be found by requiring that the correlation functions of p_x and q_x represent the x th contributions to the bath correlation functions which are proportional to $\exp(-A_x|\tau|)$. This leads to the following collective variables action:

$$S_x[q_x(\tau)] = i \int d\tau \left(\frac{\dot{q}_x^2}{4\sigma_x A_x} + \frac{1}{2\sigma_x} q_x \dot{q}_x + \frac{A_x q_x^2}{4\sigma_x} - \frac{A_x}{2} \right) \quad (5)$$

and

$$q(\tau) \equiv \sum_{x=1}^N q_x(\tau),$$

$$p(\tau) \equiv iM \sum_{x=1}^{N_0} \frac{\gamma_x}{2\sigma_x} [\dot{q}_x(\tau) + A_x q_x(\tau)]. \quad (6)$$

Altogether we need $N = N_0 + N_1$ collective variables. The first N_0 variables are overdamped oscillators as suggested by the expansion [Eq. (3)], with $\sigma_x \equiv \frac{1}{2}M\gamma_x A_x^2 \cot(A_x/2kT)$ for $\alpha = 1, \dots, N_0$, A_x is the relaxation rate and γ_x is the coupling strength of the x th oscillator. The remaining Matsubara oscillators $\alpha = N_0 + 1, \dots, N$ have

$$A_x \equiv 2\pi(\alpha - N_0)kT,$$

$$\sigma_x \equiv \sum_{\beta=1}^{N_0} M\gamma_\beta A_\beta^2 \frac{4\pi(\alpha - N_0)(kT)^2}{(2\pi(\alpha - N_0)kT)^2 - A_\beta^2},$$

T and k are the temperature and Boltzmann constant, respectively. The necessary number of Matsubara oscillators N_1 depends on temperature, as will be discussed below.

The physical significance of the collective variables q_x is clear: they represent the relevant bath information one needs to keep, i.e. those bath degrees of freedom which evolve on the same time-scale of the primary system (represented by Q) and may not be eliminated (as opposed to fast variables). In other words, q_x represent relevant slow variables representing the dynamics of the bath variables q_j after the fast variables have been eliminated. The complete evolution of the system described by Eq. (1) is given by the Liouville equation. The collective description represented by the action of Eq. (4) is formally exact provided we keep

all Matsubara oscillators. Thus, the only approximations made are (i) expanding the spectral density in a form of Eq. (3), and (ii) keeping a finite number (N_1) of Matsubara oscillators.

Our approach is conceptually similar to Feynmann's treatment of the polaron problem [43] who represented the effective action using a model system of an electron coupled to an additional particle mass by a spring. The difference is that in Ref. [43] the effective action in the Hilbert space with periodic imaginary time has been used to treat equilibrium properties at finite temperatures whereas we consider the Liouville-space Caldeira–Leggett effective action which can describe relaxation processes. Our approach is also reminiscent of the way memory effects in the generalized Langevin equation are eliminated by introducing additional variables [44]. Note, however, that the present procedure which starts from the full Liouville equation is more general; although the nonlocal Caldeira–Leggett action can be calculated explicitly, we may not generally write a closed equation of motion for the primary variables, even if we allow for a memory.

We shall recast the complex action given by Eqs. (4)–(6) in the form

$$S^{(c)}[\mathbf{x}(\tau)] = \int d\tau L^{(c)}(\mathbf{x}, \dot{\mathbf{x}}, \tau) \\ = \int d\tau \left[\frac{1}{2} \sum_{ij} P_{ij} \dot{\mathbf{x}}_i \dot{\mathbf{x}}_j + \sum_j A_j(\mathbf{x}) \dot{\mathbf{x}}_j - U(\mathbf{x}) \right], \quad (7a)$$

where the Hermitian part of the mass matrix P_{ij} is positive definite, i.e., the real parts of eigenvalues of P are all positive. The local nature of our new collective action immediately allows us to develop a semiclassical approximation for the reduced Liouville-space propagator $K(\mathbf{x}'', \mathbf{x}'; t)$ by a straightforward generalization of the real action case [38–40]:

$$K(\mathbf{x}'', \mathbf{x}'; t) = (2\pi i)^{-(d/2)} \sum_{\mathbf{x}} \{ \bar{M}[\mathbf{x}] \}^{-1/2} \exp\{iS^{(c)}[\mathbf{x}]\}. \quad (7b)$$

Here $d = N + 2$ is the dimensionality of \mathbf{x} , and the summation is performed over all classical trajectories

which satisfy the condition $\delta S^{(c)}/\delta \mathbf{x}(\tau) = 0$, with the boundary conditions $\mathbf{x}(0) = \mathbf{x}'$, $\mathbf{x}(t) = \mathbf{x}''$. $\bar{M}(\mathbf{x}) \equiv \det\{M_{ij}[\mathbf{x}]\}$ is the determinant of the stability matrix $M_{ij}(\mathbf{x}) \equiv \partial \mathbf{x}_i(\tau)/\partial \xi_j(0)$, where ξ_j is the canonical quasimomentum $\xi_j \equiv \partial L^{(c)}/\partial \dot{\mathbf{x}}_j = \sum_k P_{jk} \dot{\mathbf{x}}_k$. We refer to ξ_j as quasimomenta, since they are not related to the physical momenta of the system (which are conjugate to $Q_L - Q_R$). Since $L^{(c)}$ is complex, $\bar{M}[\mathbf{x}]$ in Eq. (7b) adopts complex values and one needs to define its square root properly. This can be done by an analytical continuation of the variation of $\bar{M}([\mathbf{x}], \tau) \equiv \det(\partial \mathbf{x}_i(\tau)/\partial \xi_j(0))$ along the trajectory obtained by defining $\{\bar{M}([\mathbf{x}], \tau)\}^{1/2}$ for $\tau \rightarrow 0$, where $M_{ij}([\mathbf{x}], \tau) \approx \tau(P^{-1})_{ij}$. At $t \rightarrow 0$ the semiclassical expression of Eq. (7b) is asymptotically correct; on the other hand, $K(\mathbf{x}'', \mathbf{x}', t)$ at $t \rightarrow 0$ can be easily calculated using its operator representation. Comparing the latter expression with Eq. (7b), and setting $\mathbf{x}'' = \mathbf{x}'$, we obtain the following prescription: at $\tau \rightarrow 0$, $\{\bar{M}([\mathbf{x}], \tau)\}^{1/2}$ is the product of square roots of eigenvalues of the stability matrix $M_{ij}([\mathbf{x}], \tau)$ taken with positive real parts. When the imaginary part of $L^{(c)}$ vanishes, the procedure will reproduce the expression for the semiclassical real action propagator, including the term related to the Maslov index [38–40].

Eqs. (7a) and (7b) provide a closed semiclassical prescription for calculating the reduced Liouville-space propagator, where the classical trajectories are given by

$$M \left(\ddot{Q}_L + i \sum_x \frac{\gamma_x}{\sigma_x} \dot{q}_x \right) + iM \sum_x \frac{\gamma_x A_x}{\sigma_x} \dot{q}_x \\ + \frac{\partial V_L}{\partial Q_L} - \sum_x q_x = 0, \quad (8a)$$

$$\frac{1}{2\sigma_x A_x} \ddot{q}_x + \frac{M \gamma_x}{\sigma_x} (\ddot{Q}_L + \ddot{Q}_R) - \frac{M \gamma_x A_x}{\sigma_x} (\dot{Q}_L + \dot{Q}_R) \\ - \frac{A_x}{2\sigma_x} q_x + i(Q_L - Q_R) = 0. \quad (8b)$$

The equation for Q_R is obtained from Eq. (8a) by a substitution $L \leftrightarrow R$ and $i \rightarrow -i$. In the case of harmonic potential $V(Q)$, the semiclassical expression [Eq. (7b)] becomes exact and the result can be alternatively derived using the solution of the dis-

placed Brownian oscillator model (see e.g. Ref. [41]).

Pervious semiclassical calculations of nonlinear response were based on a single reference trajectory for each Liouville-space path [41]. However, the choice of the reference potential is not unique, since the system evolves with different potentials from the left and from the right. This ambiguity is resolved here by using distinct “left” and “right” trajectories [12–14]. The optical response is given by the expectation value of the dipole operator $\hat{\mu}$ at time $\tau = t$ for the system driven by the external fields, $\mu(t) = \int d\mathbf{x}' d\mathbf{x}'' \mu(\mathbf{x}'') K(\mathbf{x}'', \mathbf{x}'; t) \rho(\mathbf{x}')$, where $\rho(\mathbf{x}')$ represents the equilibrium density matrix. Using the semiclassical expression for K [Eq. (7b)], and switching to integration over initial quasimomenta ξ instead of final coordinates \mathbf{x}'' we obtain

$$\mu(t) = (2\pi i)^{-(d/2)} \int d\mathbf{x}' d\xi \mu(\mathbf{x}''(\mathbf{x}', \xi; t)) \{ \bar{M}[\mathbf{x}(\mathbf{x}', \xi)] \}^{1/2} \times \exp\{iS[\mathbf{x}(\mathbf{x}', \xi)]\} \rho(\mathbf{x}'), \quad (9)$$

where $\mathbf{x}(\mathbf{x}', \xi)$ denotes the classical trajectory which starts at point \mathbf{x}' and quasimomentum ξ at $\tau = 0$, and $\mathbf{x}''(\mathbf{x}', \xi; t)$ stands for the value of the set of coordinates on this trajectory at time $\tau = t$. The equations of motion which yield classical trajectories entering Eq. (9) can be integrated in the (\mathbf{x}, ξ) space directly or alternatively in the $(\mathbf{x}, \dot{\mathbf{x}})$ space by making use of a simple linear connection between ξ and \mathbf{x} . This semiclassical expression for the response only involves integrations over initial conditions. Note that the trajectories are complex (\mathbf{x}'' is, in general, complex even for real values of \mathbf{x}' and ξ); this does not cause any difficulty, since \mathbf{x}'' is an analytical function of ξ , and one can always deform the contour of integration over ξ to make $\mathbf{x}''(\mathbf{x}', \xi; t)$ real, without affecting the integral.

In the fast-bath and high-temperature limit, we can approximate $J(\omega)$ by the ohmic spectral density $J(\omega) = M\gamma\omega$ where $\gamma = \sum_{\alpha} \gamma_{\alpha}$. In this case we can totally eliminate the bath variables and obtain a closed expression for the propagator in the particle phase space. Eq. (8b) can be solved for q_{α} by adopting the Markovian approximation. Substituting q_{α} expressed in terms of $Q_{L,R}$ and $\dot{Q}_{L,R}$ into

Eqs. (8a) and (8b) and into the expressions for the stability matrix $M_{ij}[\mathbf{x}]$ and for the actions, we obtain the equations of motion

$$M\ddot{Q}_L + \frac{\partial V_L}{\partial Q_L} + \gamma M\dot{Q}_R - i\gamma MkT(Q_L - Q_R) = 0 \quad (10)$$

and a second equation is obtained from Eq. (10) by $L \leftrightarrow R$ and $i \rightarrow -i$. The action is now given by Eq. (4), where the last three terms are replaced by $[i\gamma MkT(Q_L - Q_R)^2 - (\gamma M/2)(Q_L - Q_R)(\dot{Q}_L + \dot{Q}_R)]$. The same action can be alternatively obtained by making the Markovian approximation in the Caldeira–Leggett action. The semiclassical propagator is given by Eq. (7b) with $d = 2$, $\mathbf{x} = (Q_L, Q_R)$. In this limit the particle density matrix satisfied the Fokker–Planck equation and our propagator represents the semiclassical solution of this equation.

Finally, consider the case when the motion of the primary particle is overdamped (fast dephasing) so that Q_L is close to Q_R at all times. Changing variables to $Q \equiv \frac{1}{2}(Q_L + Q_R)$, $Q_- \equiv Q_L - Q_R$ and eliminating Q_- we obtain the equation of motion

$$\frac{\gamma M}{2kT} \ddot{Q} - \frac{1}{2\gamma MkT} \frac{\partial^2 V_-}{\partial Q^2} \frac{\partial V_+}{\partial Q} - i \frac{\partial V_-}{\partial Q} = 0 \quad (11)$$

and the action assumes the form

$$S^{(c)}[\mathbf{x}(\tau)] = i \int d\tau \left[\frac{\gamma M}{4kT} \dot{Q}^2 + \frac{1}{2kT} \frac{\partial V_+}{\partial Q} \dot{Q} + \frac{1}{4\gamma MkT} \left(\frac{\partial V_+}{\partial Q} \right)^2 + iV_- \right], \quad (12)$$

where $V_- \equiv V_L - V_R$, $V_+ \equiv \frac{1}{2}(V_L + V_R)$. Eq. (7b) with $\mathbf{x} = Q$ then represents the semiclassical propagator of the Smoluchowski equation.

Our algorithm interpolates between the weak and strong system–bath coupling limits. In the former case, the system of equations for classical trajectories [Eqs. (8a) and (8b)] factorizes to uncoupled equations for trajectories of collective bath variables and equations for left and right trajectories in the primary coordinates space, which corresponds to the semiclassical treatment of closed systems. Stronger system–bath coupling causes rapid dephasing, which leads to vanishing of contributions from trajectories in Liouville space with different left and right paths of particle coordinates.

In the high temperature and strongly overdamped particle motion limits, these trajectories merge to form a single trajectory which satisfies Eq. (11). This limit has been considered in the theory of quantum measurements as a manifestation of decoherence [45].

In summary, our reduced description of the dynamics of a quantum-particle coupled to a harmonic bath, which holds for an arbitrary spectral density of the system–bath coupling and temperature, is based on identifying a finite set of relevant collective bath coordinates. This type of reduced description can only be developed in Liouville space and may not be obtained using any reduced Hilbert space, since the collective coordinates operate in the reduced Liouville space and do not have a conjugated momentum. Each collective coordinate q_α represents a bath timescale $t_\alpha \equiv A_\alpha^{-1}$. For $\alpha = 1, \dots, N_0$ these timescales are directly related to the spectral density $J(\omega)$ [Eq. (3)], and reflect the frequencies of bath oscillators coupled to the particle. For $\alpha > N_0$ the timescales t_α are related to Matsubara frequencies, which constitute an important additional set of bath timescales. The Matsubara timescales increase as the temperature is lowered, and at sufficiently low temperatures, the bath is no longer fast no matter how fast are the timescales related to the spectral density. At high temperatures, the Matsubara timescales become fast, and the corresponding stochastic variables q_α , $\alpha > N_0$ can be eliminated. In the intermediate case one needs to keep a finite number of Matsubara oscillators as necessary to satisfy the relation $A_{N_0+N_1} > A_\alpha$ for $\alpha = 1, \dots, N_0$. This number increases as the temperature is lowered. In the fast and high-temperature bath limit, when collective bath variables can be eliminated, this leads to a reduced description in terms of particle variables alone [Eq. (10)], which is equivalent to the Fokker–Planck equation. Our description, which explicitly includes additional collective bath variables, goes far beyond the Fokker–Planck level. The present approach has several advantages over the multidimensional hierarchies of kinetic equations used to generalize the Fokker–Planck equations [26–28]: it provides a clear physical picture of the system–bath evolution, representing the bath by a set of collective relevant variables, and further

makes it possible for us to adopt powerful path-integral approximate methods for solving the basic equations. The present formalism should lend itself naturally to numerical calculations using real-time path-integral simulation techniques [46,47] and Monte Carlo procedures [14]. Semiclassical approximation to the path-integral representation yields closed expressions for observables [Eqs. (7b) and (9)]. Numerical calculations using Eqs. (7b) and (9) are based on calculating classical trajectories; the same numerical procedures are used in the absence of the bath or for a fast bath, when a reduced description in terms of particle variables alone is possible [34–37]. The only difference is that the action and the variables are not complex.

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