

Choice of dynamics for spin-crossover systems

Nikolay Klinduhov,¹ Dmitry Chernyshov,² and Kamel Boukheddaden³

¹*St.-Petersburg State University, 199034 St. Petersburg, Russia*

²*Swiss-Norwegian Beam Lines at ESRF, 6 rue Jules Horowitz, BP 220, 38043 Grenoble, France*

³*Groupe d'Etudes de la Matière Condensée, UMR-CNRS 8635, Université de Versailles St-Quentin, 45 Av. des Etats Unis, 78035 Versailles, France*

(Received 25 November 2009; revised manuscript received 20 January 2010; published 8 March 2010)

We present a generalized version of the Ising-type Hamiltonian describing the spin-crossover (SC) solids, accounting for the tunneling effect, lattice phonons, and spin-phonon interactions. We show that under Lang-Firsov-type transformation, the model becomes isomorphic to an effective Ising-type Hamiltonian in which the “exchange” coupling between the spin operators originates from a multiphonon interaction, thus explaining the origin of the elastic interaction between the SC units. In addition, we investigated theoretically the quantum nonequilibrium version of the present model in the frame of the Born-Oppenheimer approach. As a result, we could derive naturally a Glauber-type master equation with Arrhenius-type dynamics that agrees with experimental data. The present theory gives the microscopic origin of the Arrhenius-type dynamics which is usually set phenomenologically in most of the models describing the dynamics of spin-crossover phenomena.

DOI: [10.1103/PhysRevB.81.094408](https://doi.org/10.1103/PhysRevB.81.094408)

PACS number(s): 75.30.Wx, 63.20.K-, 64.60.De

I. INTRODUCTION

Spin-crossover (SC) solids, mostly based on molecular complexes with Fe(II) ions, show on heating a gradual or abrupt conversion from the low-spin ground state (LS, $S=0$, singlet $t_{2g}^6 e_g^0$) to a high-spin state (HS, $S=2$, quintet $t_{2g}^4 e_g^2$). Similar effect has been observed at low temperatures under light irradiation; the process of light-induced switching of the spin state is found to be reversible.¹ This so-called direct and inverse light-induced excited spin-state trapping effect has been suggested to be useful for future applications of spin-crossover compounds as optical memories or as molecular switching devices or displays.²

The light-induced excited HS state at low temperatures is a metastable one. Its metastable character is due to the existence of an elastic intramolecular energy barrier (related to the volume change in the molecule upon the SC transition) which is usually enhanced by a macroscopic contribution due to intermolecular elastic interactions between the SC units. Under heating, or with time, the system of spin-active molecular units relaxes back to the LS ground state. The relaxation has been found to be of a sigmoidal shape. This nonlinear character in relaxation has been attributed to the effect of interactions; a fact which has been proposed and accounted in the first phenomenological model proposed by Hauser.³ Results of more detailed theoretical studies can be found in the followed papers of Boukheddaden *et al.*⁴ where a cooperative dynamics of the Ising-type Wajnflasz⁵ Hamiltonian describing the equilibrium properties of the spin-crossover solids has been derived from the Glauber stochastic scheme.⁶ A choice of the microscopic dynamics of Arrhenius type has been finally made in order to respect experimental observations. It has also been shown that the other types of dynamics such as genuine Glauber and Metropolis ones provide the same equilibrium state as Arrhenius type but give the relaxation a linear character at low temperature; this would completely disagree with the experimental data. It has also been shown that Arrhenius dynamics does

allow to reproduce the observed nonlinear sigmoidal shape of the relaxation curves from HS to LS states after photoexcitation; the choice of dynamics has, however, been done on the phenomenological basis and microscopic reasons remain unclear. On the other hand, the problem is somewhat similar to a time evolution of a many-body system in contact with phonon reservoirs that has been studied in details earlier.^{7,8} It was found that, depending on the coupling with phonon bath, the phonon-assisted rates may differ significantly from what is expected for genuine Glauber dynamics.

In the present work, we study theoretically the low-temperature dynamics and we focus on the specific problem of relaxation of the spin-crossover systems from the metastable photoinduced HS to the thermally stable LS states, which we describe in the frame of a quantum nonequilibrium approach. We show that by accounting for interaction of spin states with phonon subsystem one obtains Glauber type of master equation and Arrhenius-type dynamics that so far has been set phenomenologically. The paper is organized as follows: Sec. II introduces the Hamiltonian of the SC solid combining spin, lattice, and spin-lattice interaction. Section III is devoted to the examination of the dynamic of the model. There, we derive the master equation of the spin system. The transitions rates between the spin states, induced by the phonon transitions, are calculated in Sec. IV, where they are compared with the available data of literature. Finally, Sec. V summarizes our results and outlines the interesting questions for future work.

II. MODEL

The SC problem is well known as phenomenon which combines both electronic and lattice changes at the solid state under various constraints, such as, light, pressure, magnetic field, and so on. Thus, it is basically an electrovibrational problem, in which lattice and electronic properties of the molecules are strongly coupled. The change in molecular and unit-cell volumes upon the transition from the LS to the

HS state may serve as an example for this coupling. Thus, we start with the following general Hamiltonian of the (fictitious) spin and phonon (lattice) systems:

$$H = H_s + H_{ph} + H_{s-ph}, \quad (1)$$

where H_s is the spin part, H_{ph} is free phonon contribution, and H_{s-ph} accounts for interaction between spin and phonon subsystems, that could be termed by the ‘‘magnetoelastic’’ or, more precisely, ‘‘spin state—phonon’’ coupling having in mind that fictitious spin operators relate not to magnetic spins but to occupation numbers distinguishing HS or LS states.⁹

We consider the spin subsystem as consisting of noninteracting fictitious spins, σ^z , with temperature-dependent bias $\Delta(T) = \Delta_0 - \frac{kT}{2} \ln(g_{HS}/g_{LS})$, which contains the ligand-field energy Δ_0 (Ref. 10) and an entropic term, $(kT/2) \ln(g_{HS}/g_{LS})$, where g_{LS} and g_{HS} are the effective degeneracies of the LS and HS states, respectively.⁹ Here, we assume that these degeneracies are temperature independent. We also add in this intramolecular part a weak transverse field, $\Omega\sigma^x$, which accounts for a tunneling contribution originating from a high-order spin-orbit coupling.¹¹ In addition, we assume that the tunneling constant Ω does not depend on the spin states. The intramolecular Hamiltonian of the SC molecules is then written as

$$H_s = \Delta(T) \sum_l \sigma_l^z + \Omega \sum_l \sigma_l^x = \left[\Delta_0 - \frac{kT}{2} \ln \left(\frac{g_{HS}}{g_{LS}} \right) \right] \sum_l \sigma_l^z + \Omega \sum_l \sigma_l^x, \quad (2)$$

where the standard definition for the Pauli matrices σ^i ($i=x, y, z$) is assumed.

We model the lattice as a set of independent harmonic oscillators, the Hamiltonian of which is given by

$$H_{ph} = \sum_q \omega_q b_q^\dagger b_q, \quad (3)$$

in the normal-modes representation. There, b_q and b_q^\dagger are the usual annihilation and creation operators and ω_q is the frequency of q th normal mode. In the following we will assume for simplicity that LS and HS states can be described by the same set of normal-mode coordinates and frequencies; such an assumption implies that both molecular and crystal symmetries do not change upon the spin transition.

Next, we consider that the main effect of the phonon environment on the spin system is to induce fluctuations in the asymmetry of the double-well potential of HS and LS states; the tunneling constant Ω stays substantially unaffected. We also restrict ourselves to the linear contributions in oscillator coordinates in the spin-lattice interaction. Thus, the spin-lattice interaction Hamiltonian, H_{s-ph} , takes the form

$$H_{s-ph} = \sum_{lq} \gamma_{ql} \sigma_l^z (b_q^\dagger + b_q) = \sum_{lq} \gamma_{ql} \sigma_l^z u_q, \quad (4)$$

where γ_{ql} is the electron-distortion coupling constant, assumed here to be independent of the spin states.

Finally, the total Hamiltonian of the system becomes

$$H = \Delta(T) \sum_l \sigma_l^z + \Omega \sum_l \sigma_l^x + \sum_q \omega_q b_q^\dagger b_q + \sum_{lq} \gamma_{ql} \sigma_l^z (b_q^\dagger + b_q). \quad (5)$$

In the case where there is no tunneling contribution (transverse field), the total Hamiltonian (5) can be diagonalized with the following unitary polaron Lang-Firsov-type transformation:^{12,13}

$$U = \exp \left[- \sum_{lq} \frac{\gamma_{ql}}{\omega_q} \sigma_l^z (b_q^\dagger - b_q) \right]. \quad (6)$$

The transformation of Hamiltonian (5) leads to the following form:

$$H = \Delta(T) \sum_l \sigma_l^z + \sum_l V_l \sigma_l^x + \sum_q \omega_q b_q^\dagger b_q - \sum_{lm} J_{lm} \sigma_l^z \sigma_m^z, \quad (7)$$

in which we recognize the effective tunneling constant, $V_{\ell'}$, and the appearance of an exchange term, $J_{\ell'm}$, given by

$$V_l = \Omega \exp \left[- 2 \sum_q \frac{\gamma_{ql}}{\omega_q} \sigma_l^z (b_q^\dagger - b_q) \right] \quad \text{and} \quad J_{lm} = \sum_q \frac{\gamma_{qm} \gamma_{ql}}{\omega_q}. \quad (8)$$

It is worth to notice that Hamiltonian (7) can be seen as a generalization of the usual Ising-type Hamiltonian, widely used in literature to describe the thermodynamic properties of spin-crossover solids, since important similarities can be found at least in their spin structures related to the spin contributions. If we neglect the tunneling term, which is not so relevant in the static properties, it becomes possible to investigate the thermal properties of such model, in which the interaction between the spin states take place through the multiphonon transitions, by using similar methods as those already developed for the Ising-type Hamiltonian. This interesting part will be addressed elsewhere in a close future.

III. DYNAMICS

Among the interesting properties of SC solids, their dynamics, and particularly the study of the relaxation of the metastable photoinduced high-spin states have taken an important part in the experimental and theoretical investigations, due to the nonlinear nature of the shape of the observed relaxation curves. Although, this problem has been widely studied in the literature, it has been postulated in most of the microscopic models^{3,4,14,15} considering interacting SC particles, that the adequate transition rates allowing to describe and to reproduce the experimental shapes of the relaxation curves of HS fractions is of Arrhenius type. Here, we aim to show that this important result can be deduced naturally from the present theoretical approach.

Let us assume, as already reported in literature,^{3,4} that the tunneling contribution in Hamiltonian (1) is weak, i.e., the constant Ω is small in comparison with the ligand-field energy, for example. Then, it becomes possible to split the Hamiltonian (1) into an unperturbed Hamiltonian

$$H_0 = \Delta(T) \sum_l \sigma_l^z + \sum_q \omega_q b_q^\dagger b_q - \sum_{lm} J_{lm} \sigma_l^z \sigma_m^z \quad (9)$$

and a small perturbation

$$\Delta H = \sum_l V_l \sigma_l^x. \quad (10)$$

Next, we assume that the coupling between spins (S) and phonons (R) subsystems is small enough to apply Born approximation.¹⁶ Thus, the total density matrix, ρ , is written as $\rho(0) = \rho_S(0) \rho_R(0)$ at time $t=0$, and it is given at time t by

$$\rho(t) = \rho_S(t) \rho_R(0) + \Delta \rho. \quad (11)$$

Here $\Delta \rho$ is a small parameter in order of ΔH . In Eq. (11), the quantities $\rho_S = \text{tr}_R \rho$ and $\rho_R = \text{tr}_S \rho$ are the reduced density matrices for spin and phonon subsystems, respectively, which will be used later to calculate averages such as $\langle \bullet \rangle_S = \text{tr}(\rho_S \bullet)$ and $\langle \bullet \rangle_R = \text{tr}(\rho_R \bullet)$.

For the interaction representation of the reduced density, the matrix associated with the spin subsystem writes $\rho_{SI}(t) = U_1^\dagger(t) \rho_S(t) U_1(t)$ (in first order of $\Delta \rho$), where $U_1(t) = \exp(-iH_0 t)$.

The equation of motion for the spin density matrix in the interaction representation, ρ_{SI} , follows directly from the Liouville equation:

$$\begin{aligned} \dot{\rho}_{SI}(t) = & -i \text{Tr}_R[\Delta H(t), \rho_S(0) \rho_R(0)] \\ & - \int_0^\infty \text{Tr}_R\{\Delta H(t), [\Delta H(\tau), \rho_{SI}(\tau) \rho_R(0)]\} d\tau, \end{aligned} \quad (12)$$

in which we have invoked the Markov approximation to set $\rho_{SI}(t-\tau) \approx \rho_{SI}(t)$ and the upper limit of the integration is set as infinite in the time integral Eq. (12).

These assumptions remain true as far as the reduced density matrix $\rho_{SI}(t)$ does not change substantially on the time scale τ_{mem} (memory time), which is a characteristic time related to the correlation time of the reservoir correlation function.

The first term in Eq. (12) has the form

$$-i \sum_l [\sigma_l^x(t), \rho_S(0)] \langle V_l(t) \rangle_R \quad (13)$$

and therefore it is nonzero. Using the same procedure as for hydrogen-transfer reactions in condensed media,¹⁷ we now reorder H_0 and ΔH and introduce fluctuations of the perturbation V around the thermal average, $F = V - \langle V \rangle_R$, which leads to

$$H_0 = \Delta(T) \sum_l \sigma_l^z + \sum_l \langle V_l \rangle \sigma_l^x + \sum_q \omega_q b_q^\dagger b_q - \sum_{lm} J_{lm} \sigma_l^z \sigma_m^z, \quad (14)$$

$$\Delta H = \sum_l F_l \sigma_l^x. \quad (15)$$

Thus, Eq. (12) for the spin density matrix in the modified interaction representation now writes

$$\begin{aligned} \dot{\rho}_{SI}(t) = & - \sum_{lm} \int_0^\infty ([\sigma_l^x(t), \sigma_m^x(\tau) \rho_S(t)] \langle F_l(t) F_m(\tau) \rangle_R \\ & - [\sigma_l^x(t), \rho_S(t) \sigma_m^x(\tau)] \langle F_m(\tau) F_l(t) \rangle_R) d\tau. \end{aligned} \quad (16)$$

It should be noted that the corresponding time-evolution operator U'_1 (different from U_1) is now given by

$$U'_1 = \exp \left\{ -i \left[\Delta(T) \sum_l \sigma_l^z + \sum_l \langle V_l \rangle \sigma_l^x + \sum_q \omega_q b_q^\dagger b_q - \sum_{lm} J_{lm} \sigma_l^z \sigma_m^z \right] \right\}, \quad (17)$$

where the relation $U'_1{}^\dagger \sigma^x U'_1 = U_1{}^\dagger \sigma^x U_1$ follows from the smallness of Ω .

For the diagonal elements of density matrix $\langle \sigma_1 \dots \sigma_N | \rho_S(t) | \sigma_1 \dots \sigma_N \rangle = P(\{\sigma\}, t)$ Eq. (16) can be written as Pauli master equation¹⁸

$$\begin{aligned} \dot{P}(\{\sigma\}, t) = & -P(\{\sigma\}, t) \sum_{\{\sigma'\} \neq \{\sigma\}} W(\{\sigma'\} | \{\sigma\}) \\ & + \sum_{\{\sigma'\} \neq \{\sigma\}} P(\{\sigma'\}, t) W(\{\sigma\} | \{\sigma'\}), \end{aligned} \quad (18)$$

where $W(\{\sigma'\} | \{\sigma\})$ is the transition rate from the spin configuration $|\sigma_1 \dots \sigma_N\rangle = |\{\sigma\}\rangle$ to $|\sigma'_1 \dots \sigma'_N\rangle = |\{\sigma'\}\rangle$. The latter can be expressed in the frame of a Fermi Golden Rule,¹⁹ since it implies a transition from some initial state into the manifold of final states. It is given by

$$\begin{aligned} W(\{\sigma'\} | \{\sigma\}) = & \sum_{\{n\} | \{n'\}} |\langle \{\sigma'\}, \{n\} | \Delta H | \{\sigma\}, \{n'\} \rangle|^2 \\ & \times \langle \{n'\} | \rho(0)_R | \{n'\} \rangle \delta(E_{\{n'\}} - E_{\{n\}} - E_{\{\sigma\}} + E_{\{\sigma'\}}), \end{aligned}$$

where the delta function appearing in the rate expression can be interpreted as the energy-conservation law for the transition. Moreover, the sum over all phonon subsystem states, $|n_1 \dots n_M\rangle = |\{n\}\rangle$, indicates that we have considered that the phonon bath equilibrates in a time scale shorter than that of the molecular spin states.

Using now the exact form of ΔH , we naturally arrive to the master equation of Glauber⁶ type

$$\begin{aligned} \dot{P}(\{\sigma\}, t) = & -P(\{\sigma\}, t) \sum_l W_l(\sigma_l) + \sum_l W_l(-\sigma_l) P(\sigma_1 \dots \\ & - \sigma_l \dots \sigma_N, t) \end{aligned} \quad (19)$$

with transition rate $W_l(\sigma_l)$ for l th pseudospin flips from the value σ_l to $-\sigma_l$ while the others remain momentarily fixed,

$$W_l(\sigma_l) = \int_{-\infty}^\infty d\tau \exp[-2i\tau E_l \sigma_l] (\langle V_l(\tau) V_l^\dagger \rangle_R - \langle V_l \rangle_R^2). \quad (20)$$

Here, E_l is a local field that depends on the neighborhood of a l th spin and is given²⁰ by

$$E_l = -\Delta(T) + \sum_{l \neq m} J_{lm} \sigma_m.$$

IV. TRANSITION RATE

Accounting for the expressions for averages $\langle V \rangle_R$ and $\langle V(\tau)V^+ \rangle_R$ derived in appendix, the transition rate writes

$$W_I(\sigma_I) = \Omega^2 \exp\left(-\sum_q \frac{4\gamma_{ql}^2}{\omega_q^2} [2\langle n_q \rangle + 1]\right) \int_{-\infty}^{\infty} d\tau \exp\left[-2i\tau E_I \sigma_I\right] \exp\left\{\left(\sum_q \frac{4\gamma_{ql}^2}{\omega_q^2} \frac{\cos\omega_q\left(\tau + \frac{i}{2T}\right)}{\sinh\frac{\omega_q}{2T}}\right) - 1\right\}. \quad (21)$$

Changing variables $t' = \tau + i/2T$, which leads to $\lim_{t \rightarrow \infty} \int_{-t}^t dt' \rightarrow \lim_{t \rightarrow \infty} \int_{-t+i/2T}^{t+i/2T} dt'$, and assuming that ω_q belongs to a phonon branch with associated dispersion $\Delta\omega$,^{13,21} the above expression for $W(\sigma)$ writes

$$W_I(\sigma_I) = \Omega^2 \exp\left[-\frac{E_I \sigma_I}{T}\right] \exp\left(-\sum_q \frac{4\gamma_{ql}^2}{\omega_q^2} \times \coth\left(\frac{\omega_q}{2T}\right)\right) \int_{-\infty}^{\infty} d\tau \exp[-2i\tau E_I \sigma_I] \times \left\{\exp\left(\sum_q \frac{4\gamma_{ql}^2}{\omega_q^2} \frac{\cos(\omega_q \tau)}{\sinh\left(\frac{\omega_q}{2T}\right)}\right) - 1\right\}. \quad (22)$$

Next, we assume that $E_I \sigma_I$ is much more smaller than $\min(\omega_q)$, which is, in particular, true when ω_q belongs to the optical branch with dispersion relation $\omega_q^2 + \omega_0^2 = \Delta\omega^2 \cos(q)$. Then, $4E_I^2 (\sigma_I^2 = 1) \ll \omega_0^2 - \Delta\omega^2$, and it follows that $\exp(-2iE_I \sigma_I)$ is a slowly varying function in comparison with the rest of the integrand in Eq. (22), which makes possible to replace it with unity.

Although the master Eq. (19) and the transition rate Eq. (22) allow the calculation of the equations of motion at all temperature, here, we are particularly interested in the low-temperature regime where the relaxation of the photoinduced metastable HS fraction is usually observed. In this limit, we set $\coth(\omega_q/2T) \approx 1$ and so $1/\sinh(\omega_q/2T) \approx \exp(-\omega_q/2T)$ and also expand the expression $\exp\left(\sum_q \frac{4\gamma_{ql}^2}{\omega_q^2} \frac{\cos(\omega_q \tau)}{\sinh\left(\frac{\omega_q}{2T}\right)}\right)$ as a power series in $\exp(-\omega_q/2T)$ up to the second order. The integrand of Eq. (22) then takes the form

$$\begin{aligned} & \exp\left(\sum_q \frac{4\gamma_{ql}^2}{\omega_q^2} \frac{\cos(\omega_q \tau)}{\sinh\left(\frac{\omega_q}{2T}\right)}\right) - 1 \\ &= \sum_q \frac{4\gamma_{ql}^2}{\omega_q^2} e^{-\omega_q/2T} \times \cos(\omega_q \tau) \\ &+ \sum_{qq'} \frac{2\gamma_{ql}^2 \gamma_{q'l}^2}{\omega_q^2 \omega_{q'}^2} e^{-(\omega_q + \omega_{q'})/2T} \cos(\omega_q \tau) \cos(\omega_{q'} \tau). \quad (23) \end{aligned}$$

Now it is easy to evaluate the integral appearing in Eq. (22) as follows:

$$\begin{aligned} & \int_{-\infty}^{\infty} \left[\sum_q \frac{4\gamma_{ql}^2}{\omega_q^2} e^{-\omega_q/2T} \cos(\omega_q \tau) \right. \\ & \left. + \sum_{qq'} \frac{2\gamma_{ql}^2 \gamma_{q'l}^2}{\omega_q^2 \omega_{q'}^2} e^{-\omega_q + \omega_{q'}/2T} \cos(\omega_q \tau) \cos(\omega_{q'} \tau) \right] d\tau \\ &= \sum_q \frac{4\gamma_{ql}^2}{\omega_q^2} e^{-\omega_q/2T} \delta(\omega_q) + \\ &+ \sum_{qq'} \frac{2\gamma_{ql}^2 \gamma_{q'l}^2}{\omega_q^2 \omega_{q'}^2} e^{-\omega_q + \omega_{q'}/2T} \frac{\delta(\omega_q + \omega_{q'}) + \delta(\omega_q - \omega_{q'})}{2}. \quad (24) \end{aligned}$$

The first term here is actually zero if we assume that $\omega_q \neq 0$ (for example, for optical phonons with $\Delta\omega < \omega_0$) and so one-phonon (emissive) transition is forbidden. The second term represents two-phonon processes in which both phonons are emitted or absorbed, or in which one phonon is emitted and the other is absorbed. The condition $\omega_q + \omega_{q'} = 0$ cannot be realized and only the latter process remains.

Finally, the expression for the rate takes the following simple form:

$$W_I(\sigma_I) = \exp\left[-\frac{E_I \sigma_I}{T}\right] \Omega^2 \sum_q \frac{\gamma_{ql}^4}{\omega_q^4} e^{-\omega_q/T} = A(T) \exp\left[-\frac{E_I \sigma_I}{T}\right], \quad (25)$$

where $A(T)$ is a parameter that depends on phonon and pseudospin—phonon coupling and temperature.

It is worth to mention that Eq. (25) does not reproduce the tunnelling regime of the relaxation, in which the transition rate becomes temperature independent at very low temperature. This is due to the fact that the intramolecular part of the on-site Hamiltonian (2) misses the intramolecular vibrations originating from the vibronic structure of the molecule. As a consequence, the reorganization energy related to the rigidity of the molecule is also absent. It follows that, we do not have any contribution of Franck-Condon overlapping between the vibrational functions associated with the LS and HS states, as in Ref. 11. However, the model allows such an extension which can be performed in a forthcoming paper.

Equation (25) clearly shows that the rate of transition from one spin configuration (LS or HS) to the another one is of Arrhenius type, as set phenomenologically in most of the SC models,^{22–26} which have addressed the dynamics of the SC problem. There is a certain similarity of the relaxation process studied here with a time evolution of magnetization relaxation investigated earlier within generalized Blume-Capel model.⁸ At variance with those detailed investigations we do not consider explicitly the transitions between degenerated states but also obtain the necessity to account for two-phonon processes.

As a matter of fact, in the pioneering works, it was checked that the Glauber and Metropolis transitions rates were inadequate to describe the relaxation of the SC solids.

Indeed, while Glauber and Metropolis transition rates depend only on the initial and final energy states, the present transition probability is induced by the phonons, at the origin of the interaction between the SC units. The effect of the phonons results on an effective energy barrier which depends itself on temperature. In the pioneering works on the dynamics of SC using microscopic models, this barrier was introduced through an intramolecular energy barrier created by the distortion of the molecule when it passes from the LS to HS states and reversibly.

An interesting case for the transition rate Eq. (25) to mention here is that when γ_{ql} has a maximum at $q=q_1$ and changes much more faster than ω_q , which leads Eq. (25) to be rewritten in the form

$$W_l(\sigma_l) = \frac{\Omega^2}{\omega_1^4} e^{(-\omega_1 - E_l \sigma_l / T)} \sum_q \gamma_{ql}^4,$$

where $\omega_1 = \omega(q_1)$ corresponds to a phonon giving maximal coupling. So ω_1 can be interpreted as a phonon contribution to some effective intramolecular energy barrier of the spin-crossover molecule, which must also contain an intrinsic intramolecular contribution.

V. CONCLUSION

Based on the ideas of previous works on spin-crossover solids, we have constructed a new type of an Ising-like Hamiltonian for a two-level system of pseudospins accounting for the tunneling effects, phonons, and interactions between phonons and pseudospins. We show that under Lang-Firsov-type transformation this model allows to find out the usual phenomenological Ising-type model in which the “exchange” interaction between different sites comes from the pseudospin—phonon coupling. A somewhat similar Hamiltonian has also been proposed for the Invar effect,²⁷ where, alike to spin crossover, coupling between electronic states and local-deformation results to an effective interaction between different atomic sites. A mean-field model of spin crossover based on elasticity theory,²⁸ where the effective interactions have been expressed via elastic properties, in frame of the proposed approach would correspond to a long-wave limit where the interaction is mediated by acoustic phonons. It is patently obvious that the present model merges also the restricted number of models describing the SC phenomenon as based on local elastic interactions, and which can mimics in a realistic way the complex behavior of SC solids.^{22–26} At variance with the previous models, the proposed model also provides with a microscopic meaning of cooperative interactions which are now a function of phonon spectra and coupling constants; these parameters can be potentially obtained via “*ab initio*” calculations.

Arrhenius-type dynamics has been observed experimentally and suggested phenomenologically for the relaxation of the photoinduced phase in spin-crossover materials.^{3,4} Under realistic assumption on weak tunneling our model allows to obtain the Glauber-type master equation, that naturally results in the Arrhenius-type dynamics. On top of that, the model provides an interesting and not yet explored opportu-

nity of numerical modeling by variational methods as well as kinetic Monte Carlo simulations based on the derived transition rates.²⁹ We have identified two possible interesting extensions of the present model related to: (i) the introduction of the spin-state dependence of the normal-mode frequencies and (ii) the accounting for the intramolecular aspects in order to retrieve the behavior of the transition rate in the tunneling regime. The development of the model along these lines will be done in forthcoming papers.

Finally, we conclude with a note on more general problems in the field of spin crossovers to be addressed in a future using the proposed model. The role of the lattice in the existence of the first-order transition is one of such generic problems that could be clarified through investigations of the equilibrium thermodynamic properties. The other interesting study would be a theoretical investigation of the photoinduced effect on lattice and spin systems with the future possibility to rationalize the domino effect.

APPENDIX: DERIVATION OF $\langle V \rangle_R$ AND $\langle V(\tau) V^+ \rangle_R$

We start from the $\langle V \rangle$ average (here and after we will neglect “*R*” subscript for averages). Using Veil formula

$$e^{\hat{F}} e^{\hat{G}} = e^{\hat{F} + \hat{G}} e^{1/2[\hat{F}, \hat{G}]}$$

for operators we have commutator as a number (that is true for both creation and annihilation operators) and therefore

$$\begin{aligned} e^{\Gamma(b^+ - b)} &= e^{\Gamma b^+} e^{-\Gamma b} e^{-\Gamma^2/2[b^+, -b]} = e^{\Gamma b^+} e^{-\Gamma b} e^{-\Gamma^2/2} \\ &= e^{-\Gamma^2/2} \left(1 + \Gamma b^+ + \frac{\Gamma^2 (b^+)^2}{2} + \dots \right) \\ &\quad \times \left(1 - \Gamma b + \frac{\Gamma^2 b^2}{2} - \dots \right), \\ &= e^{-\Gamma^2/2} \left\langle 1 + \sum_{lm} (-1)^m \frac{\Gamma^{l+m}}{l!m!} (b^+)^l b^m \right\rangle, \end{aligned}$$

where it has been taken into account that averages $\langle (b^+)^l b^m \rangle$ are nonzero only when $l=m$.

According to the Bloch-Wick-Dominis theorem the average of product of even number of creation and annihilation operators $\langle a_1 \dots a_{2p} \rangle$ is the sum of all possible pairings $\langle a_l a_m \rangle$, $l < m$; in order to apply the theorem to $\langle (b^+)^l b^m \rangle$ we note that there are only three types of pairings: $\langle b^+ b \rangle$, $\langle (b^+)^2 \rangle$, and $\langle b^2 \rangle$. The last two equals to zero, the number of $\langle b^+ b \rangle$ permutations is equal to the number of permutations from m and so is $m!$. Thus

$$\langle e^{\Gamma(b^+ - b)} \rangle = e^{-\Gamma^2/2} \left(1 + \sum_m (-1)^m \frac{\Gamma^{2m}}{m!} \langle b^+ b \rangle^m \right).$$

From the other side $\langle (b^+ - b)^2 \rangle = -2\langle b^+ b \rangle - 1$, and

$$\langle e^{\Gamma(b^+ - b)} \rangle = e^{1/2\Gamma^2 \langle (b^+ - b)^2 \rangle} = e^{-\Gamma^2/2} e^{-\Gamma^2 \langle b^+ b \rangle}.$$

So for $\langle V \rangle$ we have

$$\begin{aligned}\langle V_l \rangle &= \Omega \left\langle \exp \left(-2 \sum_q \frac{\gamma_{ql}}{\omega_q} \sigma_l^z (b_q^+ - b_q) \right) \right\rangle = \Omega \prod_q \left\langle \exp \left(-2 \frac{\gamma_{ql}}{\omega_q} \sigma_l^z (b_q^+ - b_q) \right) \right\rangle = \Omega \prod_q \exp \left(\frac{2\gamma_{ql}^2 \langle (b_q^+ - b_q)^2 \rangle}{\omega_q^2} \right) \\ &= \Omega \prod_q \exp \left(-\frac{2\gamma_{ql}^2}{\omega_q^2} [2\langle b_q^+ b_q \rangle + 1] \right) = \Omega \exp \left(-\sum_q \frac{2\gamma_{ql}^2}{\omega_q^2} [2\langle b_q^+ b_q \rangle + 1] \right).\end{aligned}$$

Now we use this approach to calculate the $\langle V(t)V^+ \rangle$ averages. Using the relationships $b^+(\tau) = \exp(-iH_0) b^+ \exp(-iH_0) = \exp(i\omega\tau)b^+$, and $b(\tau) = \exp(-iH_0)b \exp(-iH_0) = \exp(-i\omega\tau)b$ we can write

$$e^{\Gamma(b^+ - b) - \Gamma[b^+(\tau) - b(\tau)]} = e^{\Gamma[b^+(\tau) - b^+] - \Gamma[b(\tau) - b]} = \exp[\Gamma b^+(e^{-i\omega\tau} - 1) - \Gamma b(e^{i\omega\tau} - 1)] = \exp[\Gamma(\tau)b^+ - \Gamma^*(\tau)b].$$

where $\Gamma(\tau) = \Gamma[\exp(i\omega\tau) - 1]$.

Again using Veil formula and Bloch-Wick-Dominis theorem one gets

$$\langle e^{\Gamma(\tau)b^+ - \Gamma^*(\tau)b} \rangle = e^{-\Gamma(\tau)^2/2} \left(1 + \sum_m (-1)^m \frac{\Gamma(\tau)^{2m}}{m!} \langle b^+ b \rangle^m \right) = e^{1/2\Gamma(\tau)^2 \langle (b^+ - b)^2 \rangle} = e^{\phi(\tau, T) - \phi(0, T)}$$

with $\phi(t, T) = \Gamma^2[\langle b^+ b \rangle \exp(i\omega t) + (\langle b^+ b \rangle + 1) \exp(-i\omega t)]$. Finally

$$\begin{aligned}\langle V_l(\tau)V_l^+ \rangle &= \left\langle \Omega^2 \exp \left\{ -2 \sum_q \frac{\gamma_{ql}}{\omega_q} [b_q^+(\tau) - b_q(\tau)] \right\} \exp \left[2 \sum_{q,q'} \frac{\gamma_{q'l}}{\omega_{q'}} (b_{q'}^+ - b_{q'}) \right] \right\rangle = \Omega^2 \prod_{qq'} \left\langle \exp \left\{ -2 \frac{\gamma_{ql}}{\omega_q} [b_q^+(\tau) - b_q(\tau)] \right\} \exp \left[2 \frac{\gamma_{q'l}}{\omega_{q'}} (b_{q'}^+ - b_{q'}) \right] \right\rangle \\ &= \Omega^2 \prod_q \left\langle \exp \left\{ -2 \frac{\gamma_{ql}}{\omega_q} [b_q^+(\tau) - b_q(\tau)] \right\} \exp \left[2 \frac{\gamma_{ql}}{\omega_q} (b_q^+ - b_q) \right] \right\rangle \\ &= \Omega^2 \prod_q e^{\phi_q(\tau, T) - \phi_q(0, T)} = \Omega^2 e^{\sum_q \phi_q(\tau, T) - \phi_q(0, T)},\end{aligned}$$

$$\phi_q(t, T) = 4 \frac{\gamma_{ql}^2}{\omega_q^2} [\langle b_q^+ b_q \rangle e^{i\omega t} + (\langle b_q^+ b_q \rangle + 1) e^{-i\omega t}].$$

While replacing double product with qq' to the product with q it has been taken into account that all averages $\langle b_q^+ b_{q'} \rangle$ are zero if $q \neq q'$.

-
- ¹A. Hauser, Chem. Phys. Lett. **124**, 543 (1986).
²J.-F. Letard, P. Guionneau, and L. Goux-Capes, Top. Curr. Chem. **235**, 221 (2004).
³A. Hauser, J. Chem. Phys. **94**, 2741 (1991).
⁴K. Boukheddaden, I. Shteto, B. Hôo, and F. Varret, Phys. Rev. B **62**, 14796 (2000); **62**, 14806 (2000).
⁵J. Wajntasz, Phys. Status Solidi **40**, 537 (1970).
⁶R. J. Glauber, J. Math. Phys. **4**, 294 (1963).
⁷K. Saito, S. Takesue, and S. Miyashita, Phys. Rev. E **61**, 2397 (2000).
⁸K. Park, Phys. Rev. B **77**, 104420 (2008).
⁹S. Miyashita, Y. Konishi, H. Tokoro, M. Nishino, K. Boukheddaden, and F. Varret, Prog. Theor. Phys. **114**, 719 (2005).
¹⁰A. Hauser, Top. Curr. Chem. **233**, 49 (2004).
¹¹Y. Ogawa, T. Ishikawa, S. Koshihara, K. Boukheddaden, and F. Varret, Phys. Rev. B **66**, 073104 (2002); E. Bukhs, G. Navon, M. Bixon, and J. Jortner, J. Am. Chem. Soc. **80**, 2918 (1980).
¹²I. G. Lang and Y. A. Firsov, Zh. Eksp. Teor. Fiz. **43**, 1843 (1962).
¹³I. Goychuk and P. Hänggi, Adv. Phys. **54**, 525 (2005).
¹⁴A. Desaix, O. Roubeau, J. Jeftic, J. G. Haasnoot, K. Boukheddaden, E. Codjovi, J. Linares, M. Nogues, and F. Varret, Eur. Phys. J. B **6**, 183 (1998).
¹⁵H. Romstedt, A. Hauser, and H. Spiering, J. Phys. Chem. Solids **59**, 265 (1990).
¹⁶H. Carmichel, *An Open Systems Approach to Quantum Optics* (Springer-Verlag, Berlin, 1991).
¹⁷A. Suárez and R. Silbey, J. Chem. Phys. **94**, 4809 (1991).
¹⁸K. Blum, *Density Matrix Theory and Its Applications* (Plenum, New York, 1981).
¹⁹I. Goychuk, chemically driven electron tunneling pumps, <http://arxiv.org/abs/physics/0604177v1>
²⁰M. Suzuki and R. Kubo, J. Phys. Soc. Jpn. **24**, 51 (1968).
²¹T. Holstein, Ann. Phys. (N.Y.) **8**, 325 (1959).
²²K. Boukheddaden, M. Nishino, S. Miyashita, and F. Varret, Phys. Rev. Lett. **100**, 177206 (2008).
²³K. Boukheddaden, S. Miyashita, C. Chong, and M. Nishino, Phys. Rev. B **75**, 094112 (2007).
²⁴S. Miyashita, Y. Konishi, M. Nishino, H. Tokoro, and P. A. Rikvold, Phys. Rev. B **77**, 014105 (2008).
²⁵C. Enachescu, L. Stoleriu, and A. Stancu, Phys. Rev. Lett. **102**, 257204 (2009).
²⁶W. Nicolazzi, S. Pillet, and C. Lecomte, Phys. Rev. B **78**, 174401 (2008).

²⁷D. I. Khomskii and F. V. Kusmartsev, Phys. Rev. B **70**, 012413 (2004).

²⁸H. Spiering and N. Willenbacher, J. Phys.: Condens. Matter **1**,

10089 (1989).

²⁹S. Miyashita, P. A. Rivold, T. Mori, Y. Konishi, M. Nishino, and H. Tokoro, Phys. Rev. B **80**, 064414 (2009).