Secular non-secular master equation

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(Dated: October 6, 2017)

Redfield non-secular master equation governing relaxation of a spin in weak interaction with a thermal bath is studied. Using the fact that the relaxation follows the exponential law, we prove that in most cases the semi-secular approximation is sufficient to find the system relaxation rate. Based on this, a “secular” form of the non-secular master equation is for the first time developed which correctly set up one of most fundamental equations in relaxation investigation. This key secular form allows us to derive a general formula of the phonon-induced quantum tunneling rate which is valid for the entire range of temperature regardless of the basis. In incoherent tunneling regime and localized basis, this formula reduces to the ubiquitous incoherent tunneling rate. Meanwhile, in eigenstates basis, this tunneling rate is demonstrated to be equal to zero. From this secular form, we end the controversy surrounding the selection of basis for the secular approximation by figuring out the conditions for using this approximation in localized and eigenstates basis. Particularly, secular approximation in localized basis is justified in the regime of high temperature and small tunnel splittings. In contrast, a large ground doublet’s tunnel splitting is required for the secular approximation in eigenstates basis. With these findings, this research lays a sound foundation for any treatments of the spin-phonon relaxation under any conditions provided that the non-secular master equation is relevant.
I. INTRODUCTION

Real physical systems are always in contact with its surroundings, and spin system is not an exception. In non-equilibrium state, a spin in thermal contact with a reservoir will undergo a process of relaxation where its energy is exchanged with environment of which quantized particles of the lattice vibrations, phonons, is one of the most important contributions. Understanding this spin-phonon relaxation process is thus crucial for many fundamental problems and applications such as quantum coherence/decoherence in spin-based qubits\textsuperscript{1–4}, implementation of spintronics devices\textsuperscript{5–8}, or high-density information storage/quantum computing using single-molecule/single-atom magnets\textsuperscript{9–13}.

Of all the possible scenarios, a spin in weakly coupling with the phonon bath is one of the most often occurred. In this scenario, the equation of motion of the spin reduced density matrix, so-called Redfield master equation, can be derived using Born approximation of weakly coupling and Markov approximation of short memory\textsuperscript{14,15}. From this, characteristics of the relaxation process can be figured out.

Formulated in the operators form, the Redfield master equation can be represented by different specific matrix forms depending on the basis. In molecular magnetism generally and single-molecule/single atom magnets particularly, up to now existing works can be divided into two groups\textsuperscript{7,16–22}: one uses the localized (natural) basis and the other uses eigenstates (diagonal) basis. In principle, the matrix forms of the Redfield master equation in these two bases are equivalent\textsuperscript{17}. However, due to its complexity in practice, most of the theoretical works only used the secular approximation matrix form of the master equation in either localized basis or eigenstates basis. Unfortunately, these secular master equations are not equivalent to each other. Moreover, the conditions for their application are also ambiguous. As a consequence, the results and interpretations of involved physical quantities are unreliable and varied between these bases.

Playing a vital role in single-molecule/single-atom magnets relaxation, phonon-induced quantum tunneling effect has been rigorously investigated using the master equation since the early days of single-molecule magnets (SMMs). By treating SMM relaxation using the secular form in localized basis, a formula for the \textit{incoherent} spin tunneling rate at (near) resonance has been proposed\textsuperscript{16,18,23}. From then, this formula is ubiquitously used in a wide range of temperatures\textsuperscript{24–27}, even when the incoherence condition is unjustified. These will bias the interpretation of data and lead to inaccurate explanation of the physical reasons causing fast/slow relaxation. Accordingly, tactics for SMMs improvement is likely inadequate. In combination with the mentioned weakness of the secular approximation, these urge for the necessity of a new formula of the phonon-induced quantum tunneling rate derived from the non-secular Redfield master equation which can accurately describe the effect in any circumstance.

In order to elucidate these problems, in this work, we start from the most general equation governing the relaxation process in the system, Redfield non-secular master equation, then develop an unique unprecedented secular form for it. Having this form, we apply it to the localized and eigenstates basis to find the conditions for the secular approximation in these bases. During this process, the issue concerning the general formula for the phonon-induced quantum tunneling rate is also tackled. The paper is then organized into 5 sections. In particular, we devote Section II for derivation of the “secular” form of the non-secular master equation regardless of the basis. A general formula for the phonon-induced quantum tunneling rate is also introduced in this section. Equipped with these, Section III concentrates on the detailed form of the developed “secular” non-secular master equation and accordingly quantum tunneling rate in the localized basis. Meanwhile, the master equation in eigenstates basis and related quantities are investigated in Section IV. As usual, implications and conclusions are given in the last section.

II. SECULAR FORM OF NON-SECULAR MASTER EQUATION

Relaxation of a spin system with Hamiltonian $\mathcal{H}$ in a thermal bath can be described by the Redfield master equation\textsuperscript{14,17}:

$$\frac{d\rho}{dt} = -i [\mathcal{H}, \rho] + \hat{R}\rho,$$

where $\hat{R}$ is the Redfield super-operator. In a specific basis $\{|m\}$, the above equation becomes

$$\frac{d\rho_{mn}}{dt} = \sum_{k,l} R'_{mn,kl}\rho_{kl},$$

where

$$R'_{mn,kl} = R_{mn,kl} + i (\delta_{mk} \mathcal{H}_{ln} - \mathcal{H}_{mk}\delta_{ln}).$$
Here $R_{mn,mm} = - \sum_{n \neq m} R_{mn,mm}$ is the rate of population loss from state $|m\rangle$ to all other $|n\rangle \neq |m\rangle$; $R_{mn,nn} \equiv \Gamma_{mn} \forall n \neq m$ is the population transition rate from $|n\rangle$ to $|m\rangle$; $R_{mn,mm} \equiv -\gamma_{mn}$ is the coherence dephasing rate of $\rho_{mn}$; and other $R_{mn,kl}$ represents the coherence transfer rate at which the varied amplitude of the density matrix $\rho_{kl}$ influencing the element $\rho_{mn}$.

It is clear that solution of equation Eq. (2) is a linear combination of time exponentials where exponents $\lambda_i$ are eigenvalues of the matrix $\hat{R}$. Since this system of equation describes the relaxation of a physical system, there exists one eigenvalue, so-called $\lambda_0$, corresponding to the equilibrium states and thus equal to 0. Meanwhile, one of its eigenvalue, so-called $\lambda$, describes the “slow” relaxation of the spin system. Other eigenvalues are usually large and fast damped. Without loss of generality, we can assume that the solution of Eq. (2) is approximately of the form:

$$\rho_{mn} = A_{mn} e^{-\lambda t} + B_{mn}.$$  \hspace{1cm} (4)

Insert this form into Eq. (2) then identify those terms with the exponent $\lambda$ and solve for $A_{mn}$, we obtain

$$A_{mn} = \frac{1}{1 - \frac{|R'_{mn,mm}|^2}{|R'_{mn, mm} + \lambda|^2}} \frac{1}{R'_{mn, mm} + \lambda} \sum_{(kl) \notin \{mn, nm\}} \left( \frac{R'_{mn,mm} R'_{mn,kl}}{R'_{mn, mm} + \lambda} - R'_{mn,kl} \right) A_{kl},$$ \hspace{1cm} (5)

where we have taken into account the fact $A_{nm} = A_{nn}^*$ and $R'_{mn,kl} = R_{nm,lk}$ (see Appendix A).

In a basis where $|m\rangle$ and $|n\rangle$ mainly reside in the subspace of different $m$th and $n$th doublet/singlet, $R'_{mn,mm}$ can be approximated as:

$$R'_{mn,mm} = R_{mn,mm} + i \omega_{mn},$$ \hspace{1cm} (6)

where $\omega_{mn} = \varepsilon_m - \varepsilon_n$ is the energy gap between these two doublets/singlets. Since $|\omega_{nm}|$ is effectively much larger than any $R_{mn,kl}$, $A_{mn}$ thus becomes negligible. The only noticeable components are $A_{mm'}$ where $|m\rangle$ and $|m'\rangle$ mainly resides in the same $m$th doublet’s subspace. A critical consequence of this property is that the semi-secular approximation is always sufficient in finding the dynamics of $\rho_{mm}$ and $\rho_{mm'}$ as long as the above condition of the basis is satisfied, i.e. we can approximate:

$$\frac{d\rho_{mm}}{dt} \approx \sum_n \left( R'_{mm,nn} \rho_{nn} + R'_{mm,nn'} \rho_{nn'} \right),$$ \hspace{1cm} (7)

$$\frac{d\rho_{mm'}}{dt} \approx \sum_n \left( R'_{mm',nn} \rho_{nn} + R'_{mm',nn'} \rho_{nn'} \right).$$ \hspace{1cm} (8)

These form a closed system of equations. In order to have a closed “secular” system of equations of the diagonal density matrix elements only, we simplify $A_{mm'}$ using the semi-secular approximation version of Eq. (5) to obtain

$$A_{mm'} = C_{mm'} (A_{mm} - A_{m'm'}) + \sum_k D_{mm',kk} A_{kk} + \sum_{k \neq m, m'} D_{mm',kk'} A_{kk'},$$ \hspace{1cm} (9)

where

$$C_{mm'} \equiv -\frac{1}{1 - \frac{|R'_{mm',mm'}|^2}{|R'_{mm', mm'} + \lambda|^2}} \frac{i}{R'_{mm', mm'} + \lambda} \left( \frac{R_{mm',m'm'} H_{m'm'} + H_{mm'}}{R'_{mm', mm'} + \lambda} \right),$$ \hspace{1cm} (10)

$$D_{mm',kl} \equiv -\frac{1}{1 - \frac{|R'_{mm',mm'}|^2}{|R'_{mm', mm'} + \lambda|^2}} \frac{1}{R'_{mm', mm'} + \lambda} \left( \frac{R_{mm',m'm'} R_{m'm',kl} + H_{m'm'} - H_{mm'}}{R'_{mm', mm'} + \lambda} \right),$$ \hspace{1cm} (11)

$$R'_{mm',mm'} = R_{mm',mm'} + i (H_{m'm'} - H_{mm'}).$$ \hspace{1cm} (12)

Apparently, Eq. (9) is self-consistent. Drawing a similar expression for $A_{kk'}$ and inserting back, finally we reach

$$A_{mm'} = \sum_k \left[ F_{mm',kk'} (A_{kk} - A_{k'k'}) + G_{mm',kk} A_{kk} \right],$$ \hspace{1cm} (13)
where

\[ F_{mm',kk'} \equiv C_{mm'} \delta_{mk} \delta_{mk'} + \sum_{l \neq m,m'} D_{mm',ll'} C_{ll'} \delta_{lk} \delta_{lk'} + \sum_{l \neq m,m'} \sum_{p \neq l,l'} D_{mm',ll'} D_{ll',pp} C_{pp'} \delta_{pk} \delta_{p'k'} + \ldots , \quad (14) \]

\[ G_{mm',kk} \equiv D_{mm',kk} + \sum_{l \neq m,m'} D_{mm',ll'} D_{ll',kk} + \sum_{l \neq m,m'} \sum_{p \neq l,l'} D_{mm',ll'} D_{ll',pp} D_{pp',kk} + \ldots . \quad (15) \]

Denoting \( A \) as the expression of \( A_{nn} \) and \( A_{nn'} \) corresponding to the right-hand side of Eq. (13), and simplifying with the help of Eq. (13), we obtain

\[ A = \sum_{k} \Gamma_{m}^{k}(A_{kk} - A_{k'k'}) + \sum_{k \neq m} \left[ R_{mm, kk} + R_{mm, kk}^{(corr)} \right] A_{kk}, \quad (16) \]

where

\[ \Gamma_{m}^{k} \equiv i \left[ H_{m'} (F_{mm', kk'} - F_{mm', k'k}) - H_{m'} (F_{mm', kk'} - F_{mm', k'k}) \right], \quad (17) \]

\[ R_{mm, kk}^{(corr)} = \Gamma_{m}^{(corr)} \equiv i \left( H_{m'} G_{mm', kk} - H_{m'} G_{mm', kk} \right) + \sum_{n} R_{mm, nn'} \left( G_{nn', kk} + F_{nn', kk'} - F_{nn', k'k} \right). \quad (18) \]

Since \( R_{mm, mm} = - \sum_{k \neq m} R_{kk, mm} \) and \( R_{mm, mm}^{(corr)} = - \sum_{k \neq m} R_{kk, mm}^{(corr)} \) (see proof in Appendix A), Eq. (10) can be rewritten as:

\[ A = \sum_{k} \Gamma_{m}^{k} (A_{kk} - A_{k'k'}) + \sum_{k \neq m} \left[ \left( \Gamma_{mk} + \Gamma_{mk}^{(corr)} \right) A_{kk} - \left( \Gamma_{km} + \Gamma_{km}^{(corr)} \right) A_{mm} \right]. \quad (19) \]

Converting back to \( \rho_{mm} \) yields the most important result of this work:

\[ \frac{d \rho_{mm}}{dt} = \sum_{k} \Gamma_{m}^{k} (\rho_{kk} - \rho_{k'k'}) + \sum_{k \neq m} \left[ \left( \Gamma_{mk} + \Gamma_{mk}^{(corr)} \right) \rho_{kk} - \left( \Gamma_{km} + \Gamma_{km}^{(corr)} \right) \rho_{mm} \right] + C, \quad (20) \]

where \( C \) is a constant dependent on the initial and equilibrium value of the diagonal density matrix elements. Since this constant could be removed by a trivial change of variable and does not affect to the relaxation rate, its detailed form is neglected.

The non-secular density matrix equation now reduces to the form of a self-consistent "secular" one containing only the diagonal density matrix elements. From these diagonal density matrix elements, off-diagonal elements can be easily calculated using Eq. (14).

As can be seen from Eq. (20), \( \Gamma_{m}^{k} = - \Gamma_{m}^{k'} = - \Gamma_{m}^{k}, \) plays the role of the transition rate of population difference from doublet/singlet \( k \)-th representative by \( |k| \) (or \( |k'| \)) to state \( |m| \). In particular, \( \Gamma_{m}^{m} = \Gamma_{m}^{m} \) can be considered as the general quantum tunneling rate between two states \( |m| \) and \( |m'| \). Meanwhile, \( \Gamma_{k}^{(corr)} \) \( k \neq k' \) is a correction to the transition rate \( \Gamma_{kl} \) resulting from the semi-secular/non-secular approximation where the time-dependence of off-diagonal density matrix elements is taken into account.

It is worthy to note that due to \( C_{m'm'} = - C_{mm'} \) and \( D_{mm',kk} = D_{mm',kl} \), we have \( G_{mm', kk} = G_{mm', kk}^{*} \) and \( F_{mm', k'k} = - F_{mm', kk}^{*} \). As a corollary, both \( \Gamma_{m}^{k} \) and \( \Gamma_{m}^{(corr)} \) are real as expected for any quantity representing a population transition rate.

Since \( A_{mm}, \forall m \) and \( A_{kk} \forall k \) are definite, it is obvious from Eq. (13) that the series \( F_{mm', kk'} \) and \( G_{mm', kk} \) must converge. Consequently, terms in those series should monotonically decrease. Zeroth-order approximation of those series then are \( F_{mm', kk'} \approx C_{mm'} \delta_{mk} \delta_{mk'} \) and \( G_{mm', kk} \approx D_{mm', kk} \). Accordingly, the zeroth-order approximation of \( d \rho_{mm}/dt \) takes the form:

\[ \frac{d \rho_{mm}}{dt} = \Gamma_{m}^{(0)} (\rho_{mm'} - \rho_{mm}) + \sum_{k \neq m} \left[ \left( \Gamma_{mk} + \Gamma_{mk}^{(corr)(0)} \right) \rho_{kk} - \left( \Gamma_{km} + \Gamma_{km}^{(corr)(0)} \right) \rho_{mm} \right], \quad (21) \]

where we have ignored the constant \( C \) and denoted

\[ \Gamma_{m}^{(0)} = -i \left( H_{m'm} C_{mm'} + H_{mm'} C_{m'm} \right), \quad (22) \]

\[ \Gamma_{mk}^{(corr)(0)} = \left( i H_{m'm} D_{mm', kk} + R_{mm', kk} C_{kk'} + \sum_{n} R_{mm, nn'} D_{mm', kk} \right) + h.c. \forall k \neq m, \quad (23) \]
where h.c. is the Hermitian conjugate. As is clear, in zeroth-order approximation, only the quantum tunneling rate between \( |m\rangle \) and \( |m'\rangle \) enters the rate equation of \( \rho_{mm} \) whereas other \( \Gamma_m^{(k)} \forall k \neq m \) is zero. This fact underlines the important role of the doublet internal tunneling in relaxation of a spin system compared to the contribution from the population difference of other doublets.

Since the vast majority of the relaxation studies uses the localized and eigenstates basis, detailed form of the quantum tunneling rate as well as the correction to other transition rate in these bases are indispensable. Therefore, in the following, we will consecutively apply our developed formulas specifically for these bases. However, for the sake of simplicity, hereinafter we only retain the zeroth-order approximation of \( d\rho_{mm}/dt \).

### III. “Secular” Non-Secular Master Equation in Localized Basis

Localized basis vectors \( |m\rangle \) and \( |m'\rangle \) corresponding to \( m^{th} \) doublet of a spin system are defined as \( ^{28} \).

\[
|m\rangle = \frac{1}{\sqrt{2}} \left( |+^{(0)} m\rangle - |-^{(0)} m\rangle \right),
\]

\[
|m'\rangle = \frac{1}{\sqrt{2}} \left( |+^{(0)} m\rangle + |-^{(0)} m\rangle \right),
\]

where \( |\pm^{(0)} m\rangle \) are eigenstates of the spin Hamiltonian in zero external magnetic field corresponding to the \( m^{th} \) doublet. In the presence of an external magnetic field, the Hamiltonian in the subspace of this doublet can take the form:

\[
\mathcal{H}_{\{m, m'\}} = \frac{W_{mm'}}{2} (|m\rangle \langle m'| + \langle m'| m\rangle) \]

\( \Delta m_{mm'} \)

where \( W_{mm'} \) is the energy bias between \( |m\rangle \) and \( |m'\rangle \) and \( \Delta m_{mm'} \) is the tunnel splitting of \( m^{th} \) doublet. Without loss of generality, these two quantities can be assumed to be real. From this, we can easily have

\[
C_{mm'} = \frac{i \Delta m_{mm'}}{2} \left( \gamma'_{mm'} - \lambda \right) - i \left( W_{mm'} + \gamma''_{mm'} - R_{mm'} m_{mm'} \right)
\]

\[
D_{mm', kl} = \frac{R_{mm', mm'} R_{mm', kl} + R_{mm', kl} \left( \gamma'_{mm'} - \lambda \right) - i \left( W_{mm'} + \gamma''_{mm'} \right)}{\left( \gamma'_{mm'} - \lambda \right)^2 + \left( W_{mm'} + \gamma''_{mm'} \right)^2 - \left| R_{mm', mm'} \right|^2}
\]

where \( \gamma'_{mm'} \) and \( \gamma''_{mm'} \) denote the real and imaginary part of \( \gamma_{mm'} \) respectively. Substituting these into Eq. \( ^{22} \) and \( ^{28} \) results in

\[
\Gamma_m^{(0)} = \frac{\Delta_{mm'}^2}{2} \frac{\left( \gamma'_{mm'} - \lambda \right) - (R_{mm', mm'} + R_{mm', mm'})}{\left( \gamma'_{mm'} - \lambda \right)^2 + \left( W_{mm'} + \gamma''_{mm'} \right)^2 - \left| R_{mm', mm'} \right|^2}
\]

and

\[
\Gamma_{mk}^{(corr)(0)} = \left\{ \begin{array}{l}
\frac{i \Delta_{mm'}^2}{2} \frac{R_{mm', mm'} R_{mm', kk} + R_{mm', kk} \left( \gamma'_{mm'} - \lambda \right) - i \left( W_{mm'} + \gamma''_{mm'} \right)}{\left( \gamma'_{kk'} - \lambda \right)^2 + \left( W_{kk'} + \gamma''_{kk'} \right)^2 - \left| R_{kk', kk'} \right|^2} \\
+ \frac{i \Delta_{kk'}^2}{2} \frac{R_{mm', kk'} \left( \gamma'_{kk'} - \lambda \right) - i \left( W_{kk'} + \gamma''_{kk'} \right)}{\left( \gamma'_{kk'} - \lambda \right)^2 + \left( W_{kk'} + \gamma''_{kk'} \right)^2 - \left| R_{kk', kk'} \right|^2} \\
\sum_{n, n'} R_{mm', nn'} \frac{R_{nn', mm'} R_{nn', kk'} + R_{nn', kk'} \left( \gamma'_{nn'} - \lambda \right) - i \left( W_{nn'} + \gamma''_{nn'} \right)}{\left( \gamma'_{nn'} - \lambda \right)^2 + \left( W_{nn'} + \gamma''_{nn'} \right)^2 - \left| R_{nn', nn'} \right|^2} \end{array} \right\} + \text{h.c. } \forall k \neq m.
\]

As all Redfield operator elements \( R_{mm', km} \) are functions of temperature, both \( \Gamma_m^{(0)} \) and \( \Gamma_{mk}^{(corr)(0)} \), and accordingly \( \Gamma_m' \) and \( \Gamma_{mk}' \), also depend on temperature.

For excited doublet, since the conditions \( \gamma'_{mm'} \gg \lambda, \gamma''_{mm'} \gg \left| R_{mm', mm'} \right| \), and \( \gamma_{mm'}' \gg \left( R_{mm', mm'} + R_{mm', mm''} \right) \) are usually satisfied over nearly entire temperature range, a simpler version of Eq. \( ^{22} \) can be used to find the quantum tunneling rate inside these excited doublet

\[
\Gamma_m^{(0)} = \frac{\Delta_{mm'}^2}{2} \frac{\gamma'_{mm'}'}{\gamma''_{mm'} + \left( \gamma''_{mm'} + W_{mm'} \right)^2},
\]

\( ^{31} \).
which is basically similar to the well-known incoherent tunneling rate\textsuperscript{16,18}.

However, for the ground doublet at low temperature, since those mentioned conditions are now hardly fulfilled, a direct application of Eq. 31 can lead to an inaccurate result. In that circumstance, a full treatment of the quantum tunneling rate $\Gamma_m^{(0)}$ is essential. At high temperature though, the validity of the incoherent tunneling rate for the ground doublet is subject to the relative magnitude between the dephasing rate $\gamma_{mn}$ and $\lambda$.

Similarly to the quantum tunneling rate, we can also approximate $\Gamma_m^{(0)}$ at high temperature by neglecting $\lambda$ in Eq. 32. However, it becomes interesting when the temperature is sufficiently high such that the coherence transfer rates are much smaller than the dephasing rates, i.e. $R_{nn',n'n}, R_{nn',kk} \ll |\gamma_{nn'}|$ $\forall n, k$. Under this condition, $\Gamma_m^{(0)}$ becomes

$$\Gamma_m^{(0)} \approx \frac{i}{2} \left( \frac{\Delta_{mm'}R_{mm',kk}}{\gamma_{mm'} + iW_{mm'}} + \frac{\Delta_{kk'}R_{mm',kk'}}{\gamma_{kk'} + iW_{kk'}} \right) + \text{h.c. } \forall k \neq m. \tag{32}$$

As is clear, even at high temperature, this correction may still not be small compared to $\Gamma_m$ except for the case when the spin system is out of resonance or $\Delta_{nn'}/\gamma_{nn'}$ $\forall n$ is large enough. This fact indicates that the correction to the transition rate $\Gamma_m^{(0)}$, besides the quantum tunneling rate $\Gamma_m^{(0)}$, must be taken into account even at high temperature. Moreover, from the above formula we can also deduce the condition for applying the secular approximation in localized basis, i.e. all the corrections can be ignored. Specifically, Eq. 32 shows that the secular approximation in localized basis is valid only at high temperature and small tunneling splitting. Intriguingly, the latter condition is quite opposite to the one for the secular approximation in eigenstates basis which will be derived in the next section.

As a limiting case, out of resonance, both quantum tunneling rate and the corrections to the transition rates becomes negligible. Accordingly, the “secular” non-secular master equation reduces to the non-tunneling secular master equation as expected.

\section*{IV. “SECULAR” NON-SECULAR MASTER EQUATION IN EIGENSTATES BASIS}

In eigenstates basis, the Hamiltonian of the spin system is diagonal:

$$\mathcal{H} = \sum_{\alpha\beta} \left( \varepsilon_\alpha |\alpha\rangle \langle \alpha| + \varepsilon_{\alpha'} |\alpha'\rangle \langle \alpha'| + \right), \tag{33}$$

where $|\alpha\rangle$ and $|\alpha'\rangle$ belong to the same doublet $\alpha^{th}$. In this basis, $\gamma_{\alpha\alpha'} = \gamma_{\alpha'}\alpha$ is real\textsuperscript{12} and

$$D_{\alpha\alpha',\beta\gamma} = \frac{R_{\alpha\alpha',\alpha'\beta}R_{\alpha'\beta,\gamma} + R_{\alpha\alpha',\beta\gamma} (\gamma_{\alpha\alpha'} - \lambda - i\omega_{\alpha\alpha'})}{(\gamma_{\alpha\alpha'} - \lambda)^2 + \omega_{\alpha\alpha'}^2 - |R_{\alpha\alpha',\alpha'\beta}|^2}, \tag{34}$$

Thus,

$$\Gamma_{\alpha}^{(0)} = 0 = \Gamma_{\alpha'}^{(0)} \forall \beta, \tag{35}$$

$$\Gamma_{\alpha\beta}^{(0)} = \sum_{\delta\delta'} R_{\alpha\alpha,\delta\delta'} R_{\delta\delta',\alpha'\beta} R_{\delta\delta',\beta\gamma} + R_{\delta\delta',\alpha'\beta} R_{\delta\delta',\beta\gamma} (\gamma_{\delta\delta'} - \lambda - i\omega_{\delta\delta'}) + \text{h.c. } \forall \beta \neq \alpha. \tag{36}$$

Strikingly, the phonon-induced quantum tunneling rate is non-existent when working in the eigenstates basis. Since for excited doublets $\sqrt{\gamma_{gg'} + \omega_{gg'}}$ often dominates over $\lambda$ and other coherence transfer rates, $\Gamma_{\alpha\beta}^{(0)}$ can be further approximated as:

$$\Gamma_{\alpha\beta}^{(0)} = \frac{R_{\alpha\beta,gg} R_{gg',g'g} R_{g'g',\alpha'\beta} R_{gg',\beta\gamma} (\gamma_{gg'} - \lambda - i\omega_{gg'})}{(\gamma_{gg'} - \lambda)^2 + \omega_{gg'}^2 - |R_{\alpha\beta,\alpha'\beta}|^2} + \text{h.c. } \forall \beta \neq \alpha, \tag{37}$$

where only contribution from the ground doublet $g^{th}$ survives in the expression of $\Gamma_{\alpha\beta}^{(0)}$. Moreover, in the case the tunnel splitting of the ground doublet $\Delta_{gg'}$ is large, this contribution from the ground doublet also becomes negligible. As a consequence, the “secular” non-secular master equation reduces to the secular one. From this, we can conclude that a preeminent ground doublet’s tunnel splitting in comparison to the coherence transfer rates is the sufficient condition for using the secular master equation in eigenstates basis at a particular temperature.
At low temperature where only the ground doublet is populated, it is likely that the secular approximation for the Redfield master equation in eigenstates basis is also a good approximation. This results from the fact that in this regime, all the coherence transfer rates entering the expression of $E_{\alpha\beta,\gamma\delta}^{(corr)(0)}$ appears to be miniature compared to $|\omega_{\delta\beta'}|$. In contrast, when localized basis is considered in the same regime, the semi-secular approximation has to be used instead. This stresses the difference between using these two common bases in relaxation problem.

V. CONCLUSIONS

In summary, the present study has demonstrated that the semi-secular approximation for the Redfield master equation is mostly sufficient to deduce the relaxation rate. In order to find this rate, a self-consistent secular form of the non-secular/semi-secular master equation has also been developed. Containing much less number of equations, this secular form of the semi-secular approximation allows to reduce considerably the amount of effort in calculating the relaxation rate as well as facilitates different approximations to the master equation depending on the investigated regimes. Based on this finding, for the first time, a general formula of the phonon-induced quantum tunneling rate and correction to other transition rates regardless of working basis are proposed. Surprisingly, applying the general “secular” form of the non-secular/semi-secular approximation for localized basis, we found that a proper treatment of the spin relaxation must take into account the corrections to both familiar incoherent quantum tunneling rate and population transition rates between localized states. Meanwhile, in eigenstates basis, our “secular” non-secular master equation shows that the phonon-induced quantum tunneling rate in this basis is always equal to zero. Moreover, the conditions for applying secular approximation in both localized and eigenstates basis are also elucidated. In particular, secular approximation in localized basis is justified in the regime of high temperature and small tunnel splittings. On the contrary, a large ground doublet’s tunnel splitting is required for the secular approximation in eigenstates basis. At intermediate conditions, the semi-secular approximation (in any basis) is essential for extracting the relaxation rate. This finding thus settles the debate over which basis should be used in the secular master equation. On the whole, by establishing an accurate “secular” non-secular master equation, our research serves as a sturdy base for the exploration of the relaxation phenomenon in any condition provided that the Redfield non-secular master equation is relevant. Last but not least, it is important to stress that the “secular” non-secular master equation is also valid for describing the relaxation of not just spin but also any general system in weak interaction with a thermal bath as well.

ACKNOWLEDGMENTS

L. T. A. H. would like to acknowledge financial support from the Flemish Science Foundation (FWO).

Appendix A: Properties of the relaxation matrix elements in an arbitrary basis

- Relaxation matrix elements $R_{\alpha\beta,\alpha'\beta'}$ in the eigenstates basis can be calculated from the spin-phonon Hamiltonian $V^{12}$.

\[
R_{\alpha\beta,\alpha'\beta'} = \frac{\pi}{\hbar Z_b} \sum_{w,w'} \left\{ - \sum_{\gamma} e^{-E_w/kT} \delta (\varepsilon_{\alpha'} - \varepsilon_{\gamma} + E_w - E_{w'}) V_{\alpha\gamma,w} V_{\gamma\alpha',w'} \delta_{\beta\beta'} \\
- \sum_{\gamma} e^{-E_{w'}/kT} \delta (\varepsilon_{\beta'} - \varepsilon_{\gamma} + E_{w'} - E_w) V_{\beta'\gamma,w'} V_{\gamma\beta,w} \delta_{\alpha\alpha'} \\
+ e^{-E_{w'}/kT} \left[ \delta (\varepsilon_{\beta} - \varepsilon_{\beta'} + E_w - E_{w'}) + \delta (\varepsilon_{\alpha} - \varepsilon_{\alpha'} + E_{w'} - E_w) \right] V_{\alpha\beta',w'} V_{\beta'\alpha,w} \right\},
\]

where $|w\rangle$ and $|w'\rangle$ designate the eigenstates of the thermal bath and $Z_b$ is the bath partition function.

- Relaxation matrix elements $R_{mn,kl}$ in an arbitrary basis $\{|m\rangle\}$ are related to the elements $R_{\alpha\beta,\gamma\delta}$ in the eigenstates basis as follows $^{12}$.

\[
R_{mn,kl} = \sum_{\alpha,\beta,\gamma,\delta} \langle m | \alpha \rangle \langle \beta | n \rangle \langle \gamma | k \rangle \langle \delta | l \rangle R_{\alpha\beta,\gamma\delta}, \quad (A4)
\]

and vice versa,

\[
R_{\alpha\beta,\gamma\delta} = \sum_{m,n,k,l} \langle \alpha | m \rangle \langle n | \beta \rangle \langle k | \gamma \rangle \langle \delta | l \rangle R_{mn,kl}. \quad (A5)
\]
• $R_{m,n,k,l}^* = R_{n,m,k,l}^*$ — Proof: this property can be easily derived from the relation between $R_{m,n,p,q}$ and $R_{\alpha,\beta,\gamma,\delta}$ above. Indeed,

$$
R_{m,n,k,l}^* = \sum_{\alpha,\beta,\gamma,\delta} \langle m|\alpha \rangle^* \langle \beta|n \rangle^* \langle \gamma|k \rangle^* \langle l|\delta \rangle R_{\alpha,\beta,\gamma,\delta}^{*}
$$

$$
= \sum_{\beta,\alpha,\gamma,\delta} \langle n|\beta \rangle \langle \alpha|m \rangle \langle \delta|l \rangle \langle k|\gamma \rangle R_{\beta,\alpha,\gamma,\delta} = R_{n,m,k,l}.
$$

(A6)

From this, it is straightforward to show that $R_{m,n,k,l}^* = R_{n,m,k,l}^*$, $C_{m,m} = -C_{m,n,n}$, and $D_{m,m',k} = D_{m',k}$.

• $\sum_m R_{m,m,k,l} = 0$ — Proof: from the property $\sum_\gamma R_{\alpha,\gamma,\delta} = 0$, we have

$$
\sum_m R_{m,m,k,l} = \sum_{m} \sum_{\alpha,\beta,\gamma,\delta} \langle m|\alpha \rangle \langle \beta|m \rangle \langle \gamma|k \rangle \langle l|\delta \rangle R_{\alpha,\beta,\gamma,\delta}
$$

$$
= \sum_{\alpha,\beta,\gamma,\delta} \delta_{\alpha\beta} \langle \gamma|k \rangle \langle l|\delta \rangle R_{\alpha,\beta,\gamma,\delta}
$$

$$
= \sum_{\gamma,\delta} \langle \gamma|k \rangle \langle l|\delta \rangle \left( \sum_\alpha R_{\alpha,\gamma,\delta} \right) = 0.
$$

(A7)

As a result, $R_{m,m,m} = -\sum_{k \neq m} R_{kk,m,m}$.

• $\sum_k R_{k,k,m,m}^{(corr)} = 0$ — Proof:

$$
\sum_k R_{k,k,m,m}^{(corr)} = i \sum_k (H_{k,k}G_{k,k,m,m} - H_{k,k}G_{k,k,m,m}^*) + \sum_n \left( \sum_k R_{k,k,n,n} \right) (G_{n,n,m,m} + F_{n,n,m,m} - F_{n,n,m,m}^*)
$$

$$
= \sum_{k,k'} \left[ (H_{k,k}G_{k,k',m,m} - H_{k,k}G_{k,k',m,m}^*) + (H_{k,k}G_{k,k',m,m} - H_{k,k}G_{k,k',m,m}^*) \right] = 0
$$

(A8)

(A9)

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