MEAN RELAXATION TIME DESCRIPTION OF QUASI-DISSIPATIVE BEHAVIOR IN FINITE-STATE QUANTUM SYSTEMS

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An approximately single-exponential decay of an initially prepared non-stationary state can occur in quantum systems even if there are only a finite number of states. The time scale τ of the decay is then much shorter than the recurrence time T of the system. We describe here a method for calculating the probability amplitude of the non-stationary state, observed on a time scale γ^{-1}, by a *mean relaxation time approximation*. In many cases the resulting decay constant $\Gamma(\gamma)$ is almost independent of γ for $\tau \ll \gamma^{-1} \ll T$, and the value found for it in this regime constitutes the actually observed decay constant.

1. Introduction

The exponential decay of a quantum state coupled to a continuum of states is a well-known phenomenon. Under certain assumptions, e.g., an unbounded continuum with density $\rho(E)$ and weak coupling between the unstable state and the continuum states with the coupling element $v(E)$ depending only on the energy E, this behavior can be derived theoretically [1,2]. The resulting decay constant Γ is given by the *golden rule* formula

$$\Gamma = 2\pi |v(E_0)|^2 \rho(E_0) , \qquad (1)$$

where E_0 is the mean energy of the initial state, and we have set $\hbar$ equal to unity. However, even in quantum systems with only a finite number of states, where eq. (1) no longer is valid, an approximately exponential decay can often be observed [3,4].

This quasi-dissipative decay on a time scale τ is followed by quantum recurrences on a much longer time scale T, related to the non-zero spacing ΔE of the spectrum. Such a behavior may occur, for example, in the case of quantum chaos [5]. More importantly here, it is also encountered in the theoretical description of intramolecular relaxation processes. If, for example, a vibrational/rotational wave packet of states in an isolated polyatomic molecule is excited optically to a high enough energy, a quasi-dissipative and almost exponential decay of this "state" can be observed experimentally [6,7]. For intermediate excitation energies damped quantum beats are observed also [6].

The theoretical description of this situation commonly starts with a representation of the system in terms of a large but finite number of zeroth-order basis states from which a matrix Hamiltonian **H** is derived [8]. In this approach the probability of a non-stationary state decreases initially as $1-\sigma^2 t^2$, σ^2 being the spread in energy of the initial wave packet, and shows the above mentioned recurrences at long times. An approximate exponential decay in such a finite-state system is, therefore, a phenomenon which occurs at an intermediate time scale. It cannot be derived exactly, but is the result of some approximate phenomenological description.

A direct way to determine the decay constant for an excited state from the given Hamiltonian **H** of a polyatomic molecule would be, in principle, to calculate the time evolution of an initial state $|\psi(0)\rangle$ explicitly, using the diagonalized Hamiltonian, and to fit an exponential function to the decaying part of its occupation probability. In contrast, we seek a method that avoids the diagonalization and yields an approximate decay constant in terms of some

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general properties of the Hamiltonian, like the golden rule formula does in the case of a continuum of states. In the following we investigate whether the *mean relaxation time* description used successfully for correlation functions in stochastic systems [#1] can provide a simplified phenomenological approximation for the intermediate time-scale quasi-dissipative decay in finite-state quantum systems.

2. Theory

In order to separate in the present theoretical description the expected decay of the non-stationary inital state $|\psi(0)\rangle$ from the quantum recurrences, we assume that the state is observed experimentally on a time scale γ^{-1} (e.g., a radiative time scale). The probability to remain in $|\psi(0)\rangle$ is then given by

$$p(t)=|\langle\psi(0)|\psi(t)\rangle|^2\exp(-\gamma t)\,. \tag{2}$$

For $\gamma>T^{-1}$ the recurrences will be largely damped out by the exponential in eq. (2), and only the quasi-dissipative decay will be visible in $p(t)$. In quantum mechanics the underlying quantities are, of course, the *probability amplitudes*, the one corresponding to $p(t)$ being given by $\langle\psi(0)|\psi(t)\rangle\exp(-\frac{1}{2}\gamma t)$. The *mean relaxation time* (in our case complex-valued) of this amplitude is given by [9]

$$\tau(\gamma)=\int_0^\infty\langle\psi(0)|\psi(t)\rangle\exp(-\tfrac{1}{2}\gamma t)\,\mathrm{d}t\,. \tag{3}$$

Using $|\psi(t)\rangle=\exp(-\mathrm{i}\delta\mathbf{H}t)\,|\psi(0)\rangle$ the mean relaxation time can be expressed as matrix element of a resolvent operator,

$$\tau(\gamma)=\langle\psi(0)|(\tfrac{1}{2}\gamma\mathbf{I}+\mathrm{i}\delta\mathbf{H})^{-1}|\psi(0)\rangle\,, \tag{4}$$

where $\mathbf{I}$ is the identity matrix. We have used the shifted Hamiltonian $\delta\mathbf{H}=\mathbf{H}-\langle\mathbf{H}\rangle$ in eq. (4), $\langle\mathbf{H}\rangle$ being the mean energy of the inital state, $\langle\mathbf{H}\rangle=\langle\psi(0)|\mathbf{H}|\psi(0)\rangle$. This shift is useful for the determination of long-time properties [10]. The *mean relaxation time approximation* of the probability amplitude is a single-exponential description [9], resulting in

$$p(t)\approx|\exp[-t/\tau(\gamma)]|^2=\exp[-\Gamma(\gamma)t] \tag{5a}$$

for the probability itself, with the decay constant

$$\Gamma(\gamma)=2\,\mathrm{Re}(1/\tau(\gamma))\,. \tag{5b}$$

Eq. (5a) is the phenomenological form for $p(t)$ that we are seeking. As argued above, this phenomenological description should reproduce the decaying part of the probability for $\gamma>T^{-1}$.

By a suitable choice of basis states, or by employing a simple unitary transformation, the matrix Hamiltonian $\delta\mathbf{H}$ can always be cast into a form such that the initial wave-packet is given by the first basis state, i.e. where the initial wave packet can be written as

$$|\psi(0)\rangle=\begin{pmatrix}1\\ \mathbf{0}\end{pmatrix}, \tag{6a}$$

$\mathbf{0}$ denoting the zero vector, and

$$\delta\mathbf{H}=\begin{pmatrix}0 & \boldsymbol{v}^+\\ \boldsymbol{v} & \delta\mathbf{H}_\mathrm{B}\end{pmatrix}. \tag{6b}$$

$\boldsymbol{v}$ is a vector describing the interactions of the initial state with the remaining states which we denote as "bath" B, $\boldsymbol{v}^+$ is its transpose, and $\delta\mathbf{H}_\mathrm{B}$ is the matrix Hamiltonian of the bath. Employing eqs. (4) to (6) we can determine the phenomenological decay constant $\Gamma(\gamma)$ to be

$$\Gamma(\gamma)=\gamma\{1+\boldsymbol{v}^+[(\tfrac{1}{2}\gamma)^2\mathbf{I}+\delta\mathbf{H}_\mathrm{B}^2]^{-1}\boldsymbol{v}\}\,. \tag{7}$$

As can be seen in the appendix, eq. (7) reduces to the golden rule, eq. (1), in the limit $\gamma\to0$, upon using the continuum approximation for the bath. We note, in passing, that renormalizations of the golden rule formula due to tiers of mutually coupled continua [11] can also be derived from eq. (7).

The qualitative properties of $\Gamma(\gamma)$ for a finite-state system can readily be investigated with a model of the Bixon–Jortner type [3], i.e. a diagonal $(2M+1)$-state bath Hamiltonian $\delta\mathbf{H}_\mathrm{B}$ with eigenvalues $E_j=\Delta E_0+j\Delta E$, $j=-M,\ \ldots,\ M$, and a constant coupling v, i.e. $(\boldsymbol{v})_j=v$. ΔE_0 is the energy shift between the center of the bath spectrum and the mean energy of the initial state, and ΔE is the spacing of the spectrum. For large values of the density $\rho=1/\Delta E$ this

[#1] The quantity called here the *mean relaxation time* is commonly used in the field of statistical mechanics, sometimes under different names like *linear relaxation time*. Some references are given in ref. [9].

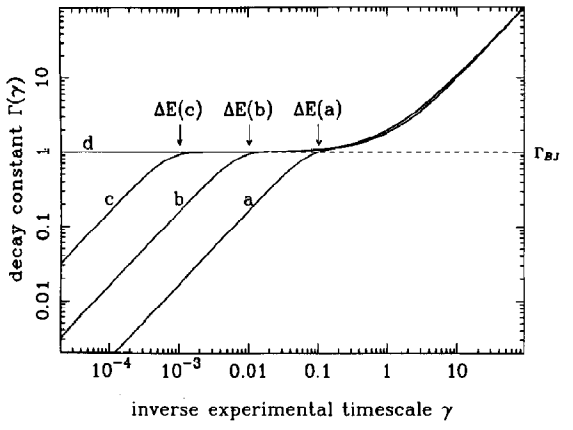

Fig. 1. Decay constant $\Gamma(\gamma)$ versus inverse experimental time scale γ in Bixon–Jortner models; parameters: (a) $\Delta E=10^{-1}$, (b) $\Delta E=10^{-2}$, (c) $\Delta E=10^{-3}$, (d) $\Delta E\to 0$; $M=2/\Delta E$, $\Delta E_0=\frac{1}{2}\Delta E$ and $v^2=\Delta E/2\pi$ in each case; (dashed line) golden rule value $\Gamma=1$; (dotted line) asymptotic behavior $\Gamma(\gamma)=\gamma$ for large γ.

model exhibits an approximate exponential decay of the initial state with the decay constant determined by eq. (1) [3,4]. The behavior of $\Gamma(\gamma)$ for this model is shown in fig. 1 for different values of v and of the spacing ΔE of the bath spectrum. The parameters ΔE and v are chosen in such a way that they lead to the same golden rule decay constant Γ, eq. (1), in each case. For large γ the experimental damping dominates over the actual decay and, therefore, $\Gamma(\gamma)=\gamma$ holds asymptotically. For small γ the recurrences are simply superimposed on a decay curve with rate constant γ, thereby leading to $\Gamma(\gamma)\propto\gamma$ as asymptotic behavior. As can be seen from fig. 1, $\Gamma(\gamma)$ exhibits a stationary behavior, $\Gamma(\gamma)\approx\Gamma$, for values of γ between $\gamma\approx T^{-1}=\Delta E$ and $\gamma\approx\tau^{-1}=\Gamma$. This result demonstrates that the approximation eq. (5) is, indeed, independent of the experimental time scale in this regime of $\Gamma(\gamma)$, and that the value of $\Gamma(\gamma)$ in the stationary regime gives a good estimate for the actually observed decay constant. For comparison, curve (d) in fig. 1 shows the dependence of $\Gamma(\gamma)$ on γ in the limit of vanishing spacing, where $\Gamma(\gamma)=\gamma+2\pi|v|^2\rho$ holds. As is seen clearly, in the limit $\gamma\to 0$ the phenomenological decay constant $\Gamma(\gamma)$ goes to a finite value which is given by the golden rule formula.

In the case of Bixon–Jortner models the numerical evaluation of eq. (7) is straightforward due to the use of a diagonal bath Hamiltonian. For a general Hamiltonian a method similar to the low-frequency expansion approach, presented by us recently [10], can be employed. We can expand the matrix contribution in eq. (7) formally for small γ, i.e.

$$\boldsymbol{v}^+[(\tfrac{1}{2}\gamma)^2\mathbf{I}+\delta\mathbf{H}_B^2]^{-1}\boldsymbol{v}\sim\sum_{n=0}^{\infty}(-\tfrac{1}{2}\gamma)^{2n}\mu_{-2n-2}\,, \quad (8)$$

with the *generalized moments*

$$\mu_{-2n}=\boldsymbol{v}^+\delta\mathbf{H}_B^{-2n}\boldsymbol{v} \quad (9)$$

as expansion coefficients. The μ_{-2n} can be obtained by solving numerically the hierarchy of linear equations $\delta\mathbf{H}_B\boldsymbol{\mu}_{-n}=\boldsymbol{\mu}_{-n+1}$ for the vectors $\boldsymbol{\mu}_{-n}$, with $\boldsymbol{\mu}_0=\boldsymbol{v}$ as starting rhs vector, and evaluating $\mu_{-2n}=|\boldsymbol{\mu}_{-n}|^2$. Using the first two expansion coefficients in eq. (8), μ_{-2} and μ_{-4}, one can construct a lowest-order Padé approximation to $\Gamma(\gamma)$ of the form

$$\Gamma_1(\gamma)=\gamma\left(1+\frac{\mu_{-2}^2/\mu_{-4}}{(\frac{1}{2}\gamma)^2+\mu_{-2}/\mu_{-4}}\right). \quad (10)$$

We note that $\Gamma_1(\gamma)$ provides a lower bound for the exact $\Gamma(\gamma)$ [10], i.e. $\Gamma_1(\gamma)\leqslant\Gamma(\gamma)$.

Although $\Gamma_1(\gamma)$ is not a very accurate approximation for $\Gamma(\gamma)$ in the quasi-stationary regime (see below, section 3), it offers the possibility of determining approximately the location of the quasi-stationary regime of $\Gamma(\gamma)$ on the γ-axis. The quasi-stationary regime contains an inflection point in a $\log\Gamma(\gamma)$ versus $\log\gamma$ plot. We can, therefore, determine the experimental time scale γ^* at which we have to evaluate our phenomenological approximation $\Gamma(\gamma)$ as the solution of

$$\frac{\mathrm{d}^2}{\mathrm{d}(\log\gamma)^2}\log\Gamma(\gamma)\bigg|_{\gamma=\gamma^*}=0\,. \quad (11)$$

For the lowest-order approximant to $\Gamma(\gamma)$, $\Gamma_1(\gamma)$, this equation yields

$$\gamma_1^*=2(1+\mu_{-2})^{1/4}\sqrt{\mu_{-2}/\mu_{-4}}\,. \quad (12)$$

In our current experience γ_1^* has usually been a reliable empirical estimate for the regime of experimental time scales where $\Gamma(\gamma)$ exhibits its quasi-stationary behavior. An intuitive justification for this result stems from the properties of $\Gamma_1(\gamma)$. $\Gamma_1(\gamma)$ describes correctly the leading behavior of $\Gamma(\gamma)$ for small and large values of γ, i.e. $\Gamma(\gamma)=(1+\mu_{-2})\gamma$ and $\Gamma(\gamma)=\gamma$, respectively (cf. fig. 1 above and fig. 2 be-

low). The plateau or pseudo-plateau regime of $\Gamma(\gamma)$ connects those asymptotic regimes. Since $\Gamma_1(\gamma)$ also interpolates between those asymptotic properties, it will have an inflection point γ_I^* in this plateau-like region and, so, may give a reasonable estimate for γ^*.

The actual decay constant can then be obtained by evaluating $\Gamma(\gamma_I^*)$. The best way of obtaining the latter numerically is comparable to the procedure for determining the generalized moments [10]: the linear equation

$$[(\tfrac{1}{2}\gamma_I^*)^2\mathbf{I}+\delta\mathbf{H}_B^2]\boldsymbol{x}=\boldsymbol{v} \qquad (13)$$

is solved for $\boldsymbol{x}$ and, via eq. (7), the actual decay constant is obtained from

$$\Gamma(\gamma_I^*)=\gamma_I^*(1+\boldsymbol{v}\cdot\boldsymbol{x})\,. \qquad (14)$$

The term in parentheses is usually much larger than unity.

3. Example

We have employed the technique introduced above to approximate the quasi-dissipative decay of a high energy excitation in the model molecule C_a–C_b–M–CD_2–C_c, where M represents a heavy mass barrier (Si in this case) for the energy transfer between the lhs and the rhs of the molecule, and C_a, C_b, and C_c have masses of CH_3, CH_2 and CD_3, respectively [12]. The basis set employed for the analysis was determined by an artificial intelligence approach that selects those zeroth-order states that are important for the time evolution of the particular initial state for the given Hamiltonian [13]. In fig. 2 the beharior of $\Gamma(\gamma)$ is shown for a 15-quantum excitation of a lhs anharmonic normal mode in the molecule [12]. An almost stationary behavior of $\Gamma(\gamma)$ in the range $10^{-5}<\gamma<7\times10^{-5}$ au can be seen. The approximate experimental time scale for the quasi-stationary behavior of $\Gamma(\gamma)$ is $\gamma_I^*=1.4\times10^{-5}$ au for this case, resulting in $\Gamma(\gamma_I^*)=4.1\times10^{-4}$ au. The latter value is very close to the actual average value of Γ in the plateau regime, which is about 4.5×10^{-4} au. The single-exponential approximation, eq. (5), for the decay of $p(t)$ following from this value of $\Gamma(\gamma_I^*)$ is compared with the exact behavior of $p(t)$ in fig. 3. It is seen that our approximate decay constant $\Gamma(\gamma_I^*)$, eqs. (13) and (14), gives a good description of the apparent decay of $p(t)$.

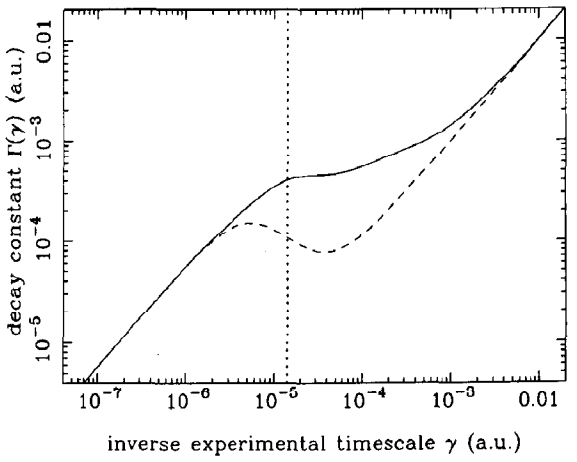

Fig. 2. Quasi-dissipative behavior in the heavy mass barrier problem (see text): (solid line) decay constant $\Gamma(\gamma)$ versus inverse experimental time scale γ; (dashed) first-order approximation $\Gamma_1(\gamma)$, eq. (10); the dotted line denotes γ_I^*.

For comparison, a heuristic application of the golden rule formula, eq. (1), is included in fig. 3. For this purpose we have used for $\rho(E_0)$ the averaged smoothed density of zeroth-order states in the neighbourhood of the enery of the initial state. This choice for $\rho(E_0)$ is often possible, since the smoothed density in this energy regime shows little variation. Since

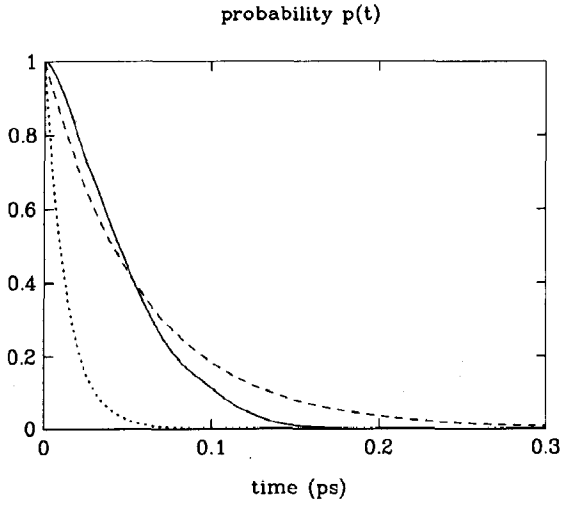

Fig. 3. Quasi-dissipative behavior in the heavy mass barrier problem (see text): (solid line) exact $p(t)$ for the 15-quantum excitation; (dashed line) single-exponential description with $\Gamma(\gamma_I^*)$; (dotted line) approximation based on a heuristic evaluation of the golden rule formula (see text).

the couplings in the present model are sparse and the magnitude fluctuates strongly, the same approach is not possible for the coupling element contribution to eq. (1). Instead, we have used for $|v(E_0)|^2$ an average squared coupling element, determined by averaging over the states directly coupled to the initial state. It is seen from the results presented in fig. 3 that the heuristic golden rule interpretation we use overestimates the real apparent decay constant.

There is always a certain arbitrariness in applying formulas such as eq. (1) to systems with discrete states. It may well be possible to choose other interpretations of eq. (1) that underestimate instead of overestimate the real decay constant, or, perhaps, even give a reasonable result for the particular case discussed above. This arbitrariness formed part of the reason for the approach presented in section 2.

4. Discussion

An approach has been presented here for the approximate description of quasi-dissipative behavior in finite-state quantum systems. Approaches that lead to golden rule type formulas have the disadvantage that the assumption of a continuum of states has to be introduced at one level or another [1,2,11]. This assumption can lead to difficulties when such formulas are applied to quantum systems with a finite number of discrete states in the practical treatment of quantum dynamics of molecules. The heuristic application of the golden rule formula eq. (1) in section 3 provides an example for this problem. The present approach presents one way of overcoming this difficulty by introducing an apparent decay constant that depends on the experimental time scale for the observation of the system in question, and then determining at which experimental time scale the apparent decay constant should be evaluated.

The example in section 3 demonstrates that the present approach can be used successfully for the determination of the approximate decay constant for a quantum state. However, this approach is not foolproof. For example, we encountered one case that exhibited multiple quasi-stationary behavior of $\Gamma(\gamma)$. In such a case the present approach can fail since the wrong plateau may be selected.

A perhaps surprising by-product of the present research is the result that a heuristic application of the golden rule formula still gives a relatively good result for decay constants, correct within an order of magnitude. The choice of which method to use for the actual determination of an apparent decay constant depends then on the desired accuracy. Naturally, the method presented here is numerically more demanding than the simplified approach based on eq. (1). However, an important advantage of the present approach is that it is model-independent, in the sense that the specific structure of the Hamiltonian is irrelevant for the application of the method.

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Appendix

In the continuum approximation eq. (7) has the form

$$\Gamma(\gamma)=\gamma+2\int \mathrm{d}E\,\frac{\frac{1}{2}\gamma}{(\frac{1}{2}\gamma)^2+(E-E_0)^2}\,|v(E)|^2\rho(E)\,, \tag{A1}$$

where we have assumed that the bath Hamiltonian is diagonalized and that the coupling depends on the energy only. The first term in the integral of (A1) is a representation of the δ-function [2], i.e.

$$\lim_{\epsilon\to 0}\frac{\epsilon}{\epsilon^2+x^2}=\pi\delta(x)\,. \tag{A2}$$

By using this relation eq. (1) follows immediately from (A1) in the limit $\gamma\to 0$.

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