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Study of some approximation schemes in the spin-boson problem

V.M. Kenkre *, L. Giuggioli

Consortium of the Americas for Interdisciplinary Science and Department of Physics and Astronomy, University of New Mexico, 800 Yale Blvd, Albuquerque, NM 87131, USA

Abstract

Some approximation schemes used in the description of the evolution of the spin-boson system are studied through numerical and analytic methods. Among the procedures investigated are semiclassical approximations and the memory function approach. An infinitely large number of semiclassical approximations are discussed. Their two extreme limits are shown to be characterized, respectively, by effective energy mismatch and effective intersite transfer. The validity of the two limits is explored by explicit numerical calculations for important regions in parameter space, and it is shown that they can provide good descriptions in the so-called adiabatic and anti-adiabatic regimes, respectively. The memory function approach, which provides an excellent approximation scheme for a certain range of parameters, is shown to be connected to other approaches such as the non-interacting blip approximation. New results are derived from the memory approach in semiclassical contexts. Comments are made on thermal effects in the spin-boson problem, the discrete non-linear Schroedinger equation, and connections to the areas of dynamic localization, and quantum control.
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1. Introduction

A pursuit of central importance in theoretical physics is the study of models constructed to incorporate, at the same time, enough physical content to represent essential features of observed phenomena, and enough simplification to make meaningful quantitative analysis possible. The harmonic oscillator model, the Ising model, and linear chain models are examples. The spin-boson model, which the present collection of articles addresses, belongs to this family, has enormous scope and application, and continues to be at the forefront of theoretical research because it is rich in content (see Fig. 1), and because it possesses features in its dynamics which are not fully understood. Our own purpose in the

*Corresponding author. Tel.: +1-505-277-4846; fax: +1-505-277-1520.

E-mail addresses: kenkre@unm.edu (V.M. Kenkre), giuggiol@unm.edu (L. Giuggioli).

present article is to focus on a small and specific aspect of the area: the validity of certain approximation procedures that have been used to study the model. Because the subject is so vast, it is inevitable that our bibliography will be found to be narrow in scope and to fail to refer to important investigations reported in areas of research less familiar to us.

Our paper is structured as follows. In the rest of this Section we mention one of the physical contexts in which the spin-boson system arises naturally, and set out the Hamiltonian and the notation. In Section 2, we address the validity of a set of approximation procedures (the Semiclassical Approximation) widely used in the literature. Their importance stems from the complexity of the full quantum mechanical problem, and consequently from the hoped-for simplification provided by treating one part classically. Countless papers have been written on the basis of the approximation [1]. Nevertheless, issues about its validity, and the validity of related entities such as the discrete non-linear Schroedinger equation
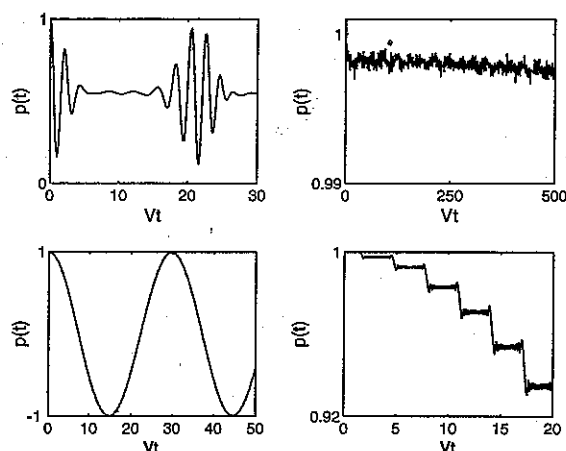
Fig. 1. Richness of phenomena arising in the simple spin-boson system illustrated by the time evolution of the probability difference $p(t)$ of the spin system. Mere variation of the coupling constant and oscillator frequency produces, respectively, the so-called 'silent runs' during which there is no transfer, self-trapping, simple ringing, and locking of the spin followed by transfer spurts. The first three follow from the basic quantum Hamiltonian, the last from a semiclassical approximation.

[1,2], have been raised continually [3–7]. In our analysis of this issue, we emphasize the obviously correct, but often forgotten, fact that there is no single semiclassical approximation whose validity one may question, establish, or explore. There are several, indeed an arbitrary number of, such approximations, flanked by at least two natural limiting cases. The rest of Section 2 focuses on the two limiting cases of the Semiclassical Approximation, and on the extent of their agreement with the exact solutions of the full quantum mechanical problem.

In Section 3, we discuss an approximation procedure which arises in the fully quantum treatment of the spin-boson model, and has nothing to do with semiclassical assumptions. It is known as the Memory Function approach [6]. Memory function formalisms appear in many places in physics [8–10]. In the context of the spin-boson problem, the memory function approach was set out a number of years ago [11,12] and used successfully for practical calculations of excitation transfer [13] and the mobility of photoinjected electrons in aromatic hydrocarbon crystals [14] (see [15] for a review with emphasis on experimental aspects of the application). The approach was reintroduced a few years ago for the analysis of formal issues [6] when it was realized that it could yield much greater accuracy than semiclassical approximations in useful parameter regimes. We present here calculations of the memory function obtained approximately for the full quantum version of the spin-boson model and exactly for some semiclassical versions.

In Section 4, we present a summary and mention several miscellaneous topics. They include the description of thermal effects in the semiclassical spin-boson

system via the Gibbs procedure as well as via Brownian motion approaches, relation to dynamic localization and quantum control areas of research, and validity of the discrete non-linear Schroedinger equation with relation to the Bose–Einstein condensation field.

In one condensed-matter context, the spin-boson problem arises from the field of electron transport in organic or molecular crystals in which the Hamiltonian may be written as

$$H = \sum_m E_m a_m^+ a_m + \sum_{m,n} V_{mn} a_m^+ a_n + \sum_q \hbar \omega_q \left(b_q^+ b_q + 1/2 \right)$$
$$+ N^{-1/2} \sum_{m,q} \hbar e^{iqm} a_m^+ a_m \left[\omega_q g_q \left(b_q^+ + b_{-q} \right) \right]. \quad (1)$$

Eq. (1) describes charge carriers (electrons or holes) of site energy E_m created by operators a_m^+ at sites m of a crystal, moving via intersite transfer matrix elements V_{mn} among the N sites of the crystal, and interacting via coupling constants g_q with a band of phonons characterized by wavevectors q, frequencies ω_q, and creation operators b_q^+. Consider the 'crystal' to be tiny, indeed composed of only two sites ($N = 2$), and the electron to be shuttling back and forth between the two sites via V and interacting via g with a single oscillator mode of frequency ω. The resultant *dimer* Hamiltonian (with $\hbar = 1$) then takes the form

$$H = V\hat{r} + g\omega\hat{y}\hat{p} + (\omega/2)\left(\hat{y}^2 + \hat{\pi}_y^2\right). \quad (2)$$

We have here the spin-boson Hamiltonian. The bosons are the excitations of the oscillator mode. The electron represents the 'spin' system. The dimensionless displacement and momentum of the harmonic oscillator whose excitations form the boson field are, respectively,

$$\hat{y} = (b + b^+)/\sqrt{2}, \quad \hat{\pi}_y = i(b^+ - b)/\sqrt{2}, \quad (3)$$

and satisfy the commutation relation $[\hat{y}, \hat{\pi}_y] = i$. The electron (or 'spin') operators

$$\hat{p} = a_1^+ a_1 - a_2^+ a_2, \quad \hat{q} = i(a_1^+ a_2 - a_2^+ a_1),$$
$$\hat{r} = a_1^+ a_2 + a_2^+ a_1, \quad (4)$$

are trivially related to the Pauli spin matrices, and satisfy $[\hat{p}, \hat{q}] = 2i\hat{r}$, $[\hat{r}, \hat{p}] = 2i\hat{q}$, and $[\hat{q}, \hat{r}] = 2i\hat{p}$. The physical meaning of $\hat{p}$ is obvious: its expectation value is the probability difference of the occupation of the two sites by the electron. Its time evolution is the focus of our investigations.

2. The semiclassical approximation is obviously not unique

Exact analytical solutions of (1), (2) are not known. Consequently, the Semiclassical Approximation (SCA) is routinely employed to analyze the evolution described

by these equations. By the SCA in this context is meant a procedure wherein the moving electron (spin) is considered quantum mechanical but the boson field (oscillator mode) is treated classically. It has been often thought, expressed, or implied in the literature that this statement defines the SCA uniquely. Specifically, it has been assumed that, given parameter regimes and/or initial conditions, one may state the validity, or the lack of validity, of replacing the oscillator part of the system by its classical counterpart. This is certainly incorrect, and it is simple to understand why. Transformations of variables are ubiquitous in physics: they are invoked whenever one wishes to reduce the strength of interaction terms in a new (transformed) space. Normal mode transformations in classical small-oscillation theory provides an elementary example. Discrete Fourier transforms in periodic lattices provides another. In the spin-boson or polaronic context, a frequently used transformation [16] replaces the bare spin and the bare boson field by dressed counterparts made up of superpositions of bare operators. The dressed system corresponds, simultaneously, to a *displaced* oscillator and a *rotated* spin vector. The reasoning behind making a semiclassical approximation is to reduce the complexity of the problem by treating one part (oscillator) via c-numbers. But should we impose the c-number replacement on the original (bare) oscillator or on the displaced (dressed) oscillator? Surely, both are viable candidates. Because the dressed oscillator contains within itself a part of the bare spin (as well as a part of the bare oscillator), considering it classical is *by no means* equivalent to considering the bare oscillator classical.

There are, thus, at least two extreme semiclassical approximations. Traditionally, what has been called the SCA is the approximation in which the *bare* boson field is replaced by a field of c-numbers. In this paper, we will call it the bare semiclassical approximation: BSCA. The SCA, in which the fully *dressed* boson field is instead replaced by a field of c-numbers, will be called here the dressed semiclassical approximation: DSCA. We will learn below that the BSCA and the DSCA have *opposite* domains of validity: the latter (former) improves in applicability as the oscillator frequency increases (decreases). We will also see that there are, additionally, an infinite number of physically relevant intermediate semiclassical approximations.

2.1. The bare semiclassical approximation: traditional SCA

The full quantum mechanical evolution of the system (2) may be written in terms of the Heisenberg equations of motion for the electron and the oscillator operators:

$$\mathrm{d}\widehat{p}/\mathrm{d}t = -2V\widehat{q},$$
$$\mathrm{d}\widehat{q}/\mathrm{d}t = 2V\widehat{p} - 2g\omega\widehat{y}\widehat{r},$$
$$\mathrm{d}\widehat{r}/\mathrm{d}t = 2g\omega\widehat{y}\widehat{q},\tag{5}$$
$$\mathrm{d}\widehat{y}/\mathrm{d}t = \omega\widehat{\pi}_y,$$
$$\mathrm{d}\widehat{\pi}_y/\mathrm{d}t = -\omega\widehat{y} - g\omega\widehat{p}.$$

The BSCA, which has been called *the* semiclassical approximation in the literature, consists of replacing the oscillator operators wherever they appear in the spin operator evolution equations by their (c-number) expectation values. The replacement of $\widehat{y}$ and $\widehat{\pi}_y$ with c-numbers y and π_y, respectively, followed by taking the expectation values of the resulting equations, yields

$$\mathrm{d}p/\mathrm{d}t = -2Vq,$$
$$\mathrm{d}q/\mathrm{d}t = 2Vp - 2g\omega yr,\tag{6}$$
$$\mathrm{d}r/\mathrm{d}t = 2g\omega yq,$$

for the expectation values p, q, r of the electron operators, and

$$\mathrm{d}y/\mathrm{d}t = \omega\pi_y, \quad \mathrm{d}\pi_y/\mathrm{d}t = -\omega y - g\omega p,\tag{7}$$

for the oscillator displacement and momentum expectation values.

2.2. The polaron transformation and the dressed SCA

Let us now return to the fully quantum mechanical description provided by the Hamiltonian (2) and introduce the polaron transformation. For any bare operator $\widehat{f}$, the dressed operator $\widehat{F}$ is defined through the unitary transformation

$$\widehat{F} = \mathrm{e}^{\mathrm{i}g\widehat{\pi}_y\widehat{p}}\widehat{f}\mathrm{e}^{-\mathrm{i}g\widehat{\pi}_y\widehat{p}}.\tag{8}$$

This results in

$$\widehat{P} = \widehat{p},$$
$$\widehat{Q} = \widehat{q}\cos\left(2g\widehat{\pi}_y\right) - \widehat{r}\sin\left(2g\widehat{\pi}_y\right),$$
$$\widehat{R} = \widehat{r}\cos\left(2g\widehat{\pi}_y\right) + \widehat{q}\sin\left(2g\widehat{\pi}_y\right),\tag{9}$$
$$\widehat{Y} = \widehat{y} + g\widehat{p},$$
$$\widehat{\Pi}_Y = \widehat{\pi}_y.$$

The dressed operators all maintain the commutation relations that the bare counterparts possess. The Hamiltonian (2) may be rewritten in terms of the dressed operators as

$$H = V\left[\widehat{R}\cos\left(2g\widehat{\Pi}_Y\right) - \widehat{Q}\sin\left(2g\widehat{\Pi}_Y\right)\right]$$
$$+ (\omega/2)\left(\widehat{Y}^2 + \widehat{\Pi}_Y^2\right) - (g^2\omega/2)\widehat{I},\tag{10}$$

where $\widehat{I}$ is the identity operator.

The cosine and sine operators in the second and third equations of each set are the so-called *phonon cloud* operators. This terminology corresponds to the fact that

they contain (via series expansions) products of all possible numbers of phonons. Typically, they are expressed in terms of exponential quantities. Our usage [6] of trigonometric forms was introduced to emphasize the rotational character of the transformation [17]. It is clear from the first three of Eq. (9) that the polaron transformation brings about a rotation of the spin vector around the $\hat{p}$ axis through an 'angle' $2g\hat{\Pi}_Y$. The last two equations in (9) show that the transformation simultaneously produces a translation of the oscillator through a 'displacement' $g\hat{p}$. The quotes that we have put around the words 'angle' and 'displacement', because those quantities in (9) are operators, might be removed if we make the semiclassical approximation and replace the operators by c-numbers.

The quantum mechanical Heisenberg equations of motion for the dressed operators that result from (10) are

$$\frac{d\hat{P}}{dt} = -2V\left[\hat{Q}\cos\left(2g\hat{\Pi}_Y\right) + \hat{R}\sin\left(2g\hat{\Pi}_Y\right)\right],$$

$$\frac{d\hat{Q}}{dt} = 2V\hat{P}\cos\left(2g\hat{\Pi}_Y\right),$$

$$\frac{d\hat{R}}{dt} = 2V\hat{P}\sin\left(2g\hat{\Pi}_Y\right),$$

$$\frac{d\hat{Y}}{dt} = -2gV\left[\hat{Q}\cos\left(2g\hat{\Pi}_Y\right) + \hat{R}\sin\left(2g\hat{\Pi}_Y\right)\right] + \omega\hat{\Pi}_Y,$$

$$\frac{d\hat{\Pi}_Y}{dt} = -\omega\hat{Y}.$$

(11)

If we make the semiclassical approximation on these dressed operators in the same way described above for the bare operators, we obtain, for the (dressed) oscillator displacement and momentum expectation values,

$$dY/dt = -2gV[Q\cos(2g\Pi_Y) + R\sin(2g\Pi_Y)] + \omega\Pi_Y,$$

$$d\Pi_Y/dt = -\omega Y.$$

(12)

The dressed semiclassical approximation could thus consist of the coupled Eq. (12) for the displaced oscillator, and

$$dP/dt = -2V[Q\cos(2g\Pi_Y) + R\sin(2g\Pi_Y)],$$

$$dQ/dt = 2VP\cos(2g\Pi_Y),$$

$$dR/dt = 2VP\sin(2g\Pi_Y),$$

(13)

for the spin vector. In exploring the validity of this (dressed) SCA in various parameter regimes, we discover something peculiar. While it has a tendency to get better in the high frequency limit (large ω/V), the approximation consistently predicts a *shift in the evolution* of the probability difference. We exhibit one of these comparisons in Fig. 2. Unlike the BSCA (Eqs. (6) and (7)), which self-traps the spin in this parameter regime used in Fig. 2 and is thus hopelessly different from the exact solution, we see that this dressed SCA (Eqs. (12)
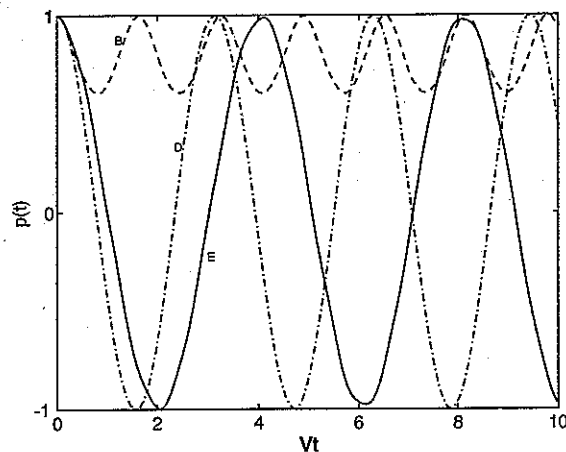

Fig. 2. Qualitative agreement accompanied by the presence of a *shift* between the exact probability difference $p(t)$ (shown by curve E) and the dressed semiclassical approximation (curve D). The bare counterpart (BSCA) is represented by curve B and is way off. Parameters are $g = 0.5$ and $\omega/V = 10$.

and (13)) matches qualitatively the exact evolution. However, there is a clear shift in the curves. Through an exhaustive study, we have found that the amount of shift depends exponentially on the square of the coupling constant g. What could be the reason for this systematic discrepancy? Our study of the literature uncovered a lucid argument [18] of the dangers of conducting a dressed SCA in the perhaps natural, but incorrect, manner described above, and, simultaneously provided an excellent explanation of the shift in the evolution.

In contrast to the BSCA case, the semiclassical procedure of replacing the boson operators by c-numbers has a double approximation effect. Approximating

$$\cos\left(2g\hat{\Pi}_Y\right) \approx \cos\left(2g\langle\hat{\Pi}_Y\rangle\right)$$

not only involves the replacement of the operator $\hat{\Pi}_Y$ by its expectation value, but the replacement of all powers of $\hat{\Pi}_Y$, resident in the cosine, by their expectation values as well. On the basis of the time-dependent variational principle [19], the authors of [18] have suggested a correction. The time-dependent variational principle is an approximation procedure involving the variation of an action functional and the requirement that the functional be stationary under free variation of the time-dependent state. Following the prescription of [18], one is led to replacing V in the semiclassical approximation Eqs. (13) and (12) by the reduced quantity Ve^{-g^2}. The (Huang–Rhys) reduction factor arises from the overlap of displaced oscillator states and is related to the well-known identity (for thermal averages)

$$\langle\exp(\theta b + \phi b^+)\rangle = \exp[\theta\phi(\langle b^+ b\rangle + 1/2)],$$

where θ and ϕ are c-numbers [20]. We find that the replacement produces excellent quantitative matching with the exact evolution for the parameters of Fig. 2 for the parameter ranges we checked. We will therefore use,

for our investigation of validity of SCA's, the alternative suggested in [18].

We will reserve the term 'Dressed Semiclassical Approximation' (DSCA) to mean

$$dP/dt = -2Ve^{-g^2}[Q\cos(2g\Pi_Y) + R\sin(2g\Pi_Y)],$$
$$dQ/dt = 2Ve^{-g^2}P\cos(2g\Pi_Y), \qquad (14)$$
$$dR/dt = 2Ve^{-g^2}P\sin(2g\Pi_Y),$$

for the spin, along with

$$dY/dt = -2gVe^{-g^2}[Q\cos(2g\Pi_Y) + R\sin(2g\Pi_Y)] + \omega\Pi_Y,$$
$$d\Pi_Y/dt = -\omega Y, \qquad (15)$$

for the dressed oscillator.

2.3. Effective energy mismatch and effective intersite transfer: respective characteristics of the two SCA's

The spin-boson system exhibits remarkable features in its time evolution. They include a self-trapping tendency whereby the probability difference $p(t)$ can oscillate *not* symmetrically between the two sites, thus signifying localization, and 'silent runs' during which the probability hardly changes, followed by transfer in spurts, or even in some cases collapses of transfer [4–6,21,22]. Fig. 1 illustrates these observations. It has been argued [6] that these phenomena arise from an effective time-dependent energy mismatch and an effective time-dependent intersite transfer matrix element. Although the dimer sites are degenerate in energy, the interaction with the oscillator produces an effective energy mismatch in the electron site states. Similarly, although the interaction transfer V is actually constant, the interaction with the oscillator produces an effectively time-dependent V. We now show that these conjectured explanations can be made quantitatively transparent. For this purpose we ask what the two sets of equations representing the two SCA's mean from the viewpoint of electron transfer between the two dimer sites. To answer the question, we recast (14) as the torque equation for the precession of a rigid rotator. Focusing on the evolution of the spin alone, we see that the dimer is subjected to an effective time-dependent $V(t)$. Following a calculation given earlier [21] (see Eq. (5) of that reference), we can rewrite the evolution (14) in the form

$$\frac{d}{dt}\begin{pmatrix} P \\ Q \\ R \end{pmatrix} + \begin{pmatrix} 0 & 2\mathrm{Re}[V(t)] & 2\mathrm{Im}[V(t)] \\ -2\mathrm{Re}[V(t)] & 0 & 0 \\ -2\mathrm{Im}[V(t)] & 0 & 0 \end{pmatrix} \times \begin{pmatrix} P \\ Q \\ R \end{pmatrix} = 0. \qquad (16)$$

We see at once that in the DSCA the (dressed) electron shuttles between two degenerate states with an effective

complex and time-dependent intersite transfer which depends on the momentum of the (dressed) oscillator:

$$V(t) = Ve^{-g^2}e^{i2g\Pi_Y(t)}. \qquad (17)$$

The intersite transfer is reduced by the factor e^{-g^2}, and is, additionally, not only time-dependent but *complex as well*. Furthermore, it is possible for the $V(t)$ to periodically collapse, and thereby produce the 'silent runs'. If the momentum $\Pi_Y(t)$ of the dressed oscillator varies sinusoidally in time [22], the effective intersite transfer $V(t)$ will be given by an exponential of i times a trigonometric function. The intersite transfer can thus vary in time, drop effectively to zero for extended intervals, leading to little or no transfer for those intervals. This can be followed by spurts of transfer. The connection between the qualitative discussion of such behavior given in [6] and the quantitative derivation based on exact memory functions for fields externally applied to a spin [21], thus clearly emerges from the dressed picture for the full (semiclassical) spin-boson system. Indeed, the effective transfer can exhibit collapses under certain Bessel root conditions [23]. Dynamic localization at Bessel root conditions has appeared in solid state problems [23,24] theoretically as well as experimentally [25] in problems as varied as electron transport, magnetic systems, and quantum optics [26,27]. Collapses in transfer, well-known in quantum optics systems [27,28] can arise in semiclassical driven problems [21]. How it might arise in the fully quantum mechanical spin-boson problem has been commented on via numerical solutions [29]. A derivation of its onset has been recently provided [22] on the basis of a clear action-angle variables analysis.

What about the BSCA? Eq. (6), cast in the form of (16), give

$$\frac{d}{dt}\begin{pmatrix} p \\ q \\ r \end{pmatrix} + \begin{pmatrix} 0 & 2V & 0 \\ -2V & 0 & 2E(t) \\ 0 & -2E(t) & 0 \end{pmatrix}\begin{pmatrix} p \\ q \\ r \end{pmatrix} = 0, \qquad (18)$$

and show that, in the BSCA, the (bare) electron shuttles with constant intersite transfer V between two *energetically mismatched* states. The effective mismatch $2E(t)$ is time-dependent and proportional to the displacement of the bare oscillator:

$$E(t) = g\omega y(t). \qquad (19)$$

It is well-known [2,30] that an energy mismatch in the dimer leads to probability oscillations which are not complete, thus signifying self-trapping.

The disruption of transfer (localization) can thus occur in two ways. The explanation [6] of the occurrence of these two factors (the effective energy mismatch and the effectively reduced intersite transfer) in the spin-boson problem is now complemented by our present demonstration that *the bare picture is representative of*

energy mismatch while the dressed picture is representative of reduced intersite transfer. By 'reduced' in the latter expression we mean, not only the Huang–Rhys factor e^{-g^2}, but also, and particularly, the time variation which can periodically collapse the effective transfer. Other than making the respective semiclassical ansatz in each of the two cases, no approximation has been necessary to arrive at this conclusion.

It is important to realize that, even beyond the fact that the Huang–Rhys factor appears in the DSCA but not in the BSCA, the two semiclassical approximations are not identical to each other. The probability differences P and p are equal to each other. So are the momenta Π_Y and π_y. But Q, R, Y are different from their bare counterparts. More to the point, the equations of motion are not all identical. Thus, the predictions (for instance for $p(t) = P(t)$) can be profoundly different. To appreciate this explicitly, note that a search for the stationary states by putting all time derivatives equal to zero produces the possibility of self-trapping, i.e., nonzero p's in the bare case provided $g^2\omega > 2V$. On the other hand, in the dressed case, the averages of P thus obtained always vanish.

2.4. Infinite number of additional semiclassical approximations: the ISCA

It is clear that the two SCA's we have mentioned are only extremes and that an infinite number of semiclassical approximations, each with some energy mismatch and some time-dependent transfer, are possible. To make this clear, we use a transformation which displaces the oscillator only *partially*, i.e., with a displacement proportional not to the coupling constant g which appears in the Hamiltonian (2) but to G where $0 \leqslant G \leqslant g$. Such partial dressing has appeared earlier in variational treatments of the polaron problem [31]. With the transformation

$$\widehat{F} = e^{iG\widehat{\pi_y}\widehat{p}}\widehat{f}e^{-iG\widehat{\pi_y}\widehat{p}} \tag{20}$$

for any bare operator $\widehat{f}$, the Hamiltonian is rewritten as

$$\widehat{H} = V\left[\widehat{R}\cos\left(2G\widehat{\Pi}_Y\right) - \widehat{Q}\sin\left(2G\widehat{\Pi}_Y\right)\right]$$
$$+ (g - G)\omega\widehat{Y}\widehat{P} + \frac{\omega}{2}\left(\widehat{Y}^2 + \widehat{\Pi}_Y^2\right) - G\omega\left(g - \frac{G}{2}\right)\widehat{I}. \tag{21}$$

Here the partially dressed operators $\widehat{P}$, $\widehat{Q}$, $\widehat{R}$, $\widehat{Y}$ and $\widehat{\Pi}_Y$ are defined as in (9) but with G in place of g. Eq. (21) becomes Eq. (2) or (10) in the limit when $G \to 0$ or $G \to g$, respectively. It is straightforward to write the Heisenberg equations of motion. We call the corresponding semiclassical approximation the *intermediate semiclassical approximation*: ISCA. Under this ISCA, the partially dressed semiclassical equations of motion are

$$dP/dt = -2V_{\text{int}}[Q\cos(2G\Pi_Y) + R\sin(2G\Pi_Y)],$$
$$dQ/dt = 2V_{\text{int}}P\cos(2G\Pi_Y) - 2(g - G)\omega YR, \tag{22}$$
$$dR/dt = 2V_{\text{int}}P\sin(2G\Pi_Y) + 2(g - G)\omega YQ,$$

for the electron system, and

$$dY/dt = -2GV_{\text{int}}[Q\cos(2G\Pi_Y) + R\sin(2G\Pi_Y)] + \omega\Pi_Y,$$
$$d\Pi_Y/dt = -\omega Y - (g - G)\omega P, \tag{23}$$

for the oscillator system. By V_{int} is meant a quantity intermediate between the BSCA limit V and the BSCA limit Ve^{-g^2}, whose magnitude, which can be obtained through the time-dependent variational principle, appears to be simply Ve^{-G^2}. The electron equations are easily cast in the form

$$\frac{d}{dt}\begin{pmatrix} P \\ Q \\ R \end{pmatrix} + \begin{pmatrix} 0 & 2\text{Re}[V(t)] & 2\text{Im}[V(t)] \\ -2\text{Re}[V(t)] & 0 & 2E(t) \\ -2\text{Im}[V(t)] & -2E(t) & 0 \end{pmatrix}$$
$$\times \begin{pmatrix} P \\ Q \\ R \end{pmatrix} = 0, \tag{24}$$

showing that, under the ISCA, the electron system develops *both* an energy mismatch and a time-dependent complex intersite transfer (see (17) and (19)):

$$E(t) = (g - G)\omega Y(t),$$
$$V(t) = V_{\text{int}}\exp(i2G\Pi_Y). \tag{25}$$

2.5. Numerical exploration of the extreme SCA's and graphical representation of their validity

The subject of the validity of approximation techniques employed in the spin-boson system is rather large. We have chosen to touch upon only a small aspect of it in the present paper. Rather than engage in purely analytic considerations such as those employed by the authors of [4], we restrict ourselves to direct numerical investigation of the extreme SCA's. We consider only low energy initial excitation of the oscillator. We calculate the exact quantum evolution by explicit numerical diagonalization of matrices of finite size as in [5,6]. The size, which represents the semi-infinite energy manifold of the harmonic oscillator, is increased until convergence is obtained. We calculate the semiclassical evolution by several different numerical procedures to solve the coupled set of differential equations representing the BSCA. The electron is initially localized on one of the two sites. The oscillator initial state for the quantum evolution is precisely that in the ground state of the full Hamiltonian. In the semiclassical calculation it is the equilibrium state of the displaced oscillator. (For a detailed discussion of the initial states, see [5]).

We carry out our validity studies in two parts. In the first, we calculate an objectively obtained least-squares error between the exact evolution and the approximations, focusing on time scales that are not too long ($Vt < 100$). We report particularly on two regions in $g - \omega$ space. In the first, the oscillator frequency ω is varied relative to the intersite transfer from $w/V = 10^{-1}$ to $w/V = 10^2$ and the coupling constant g from 0 to 14. In the second, g is varied between 0.1 and 3 and ω/V from 10^{-2} to 10^3. The second part of our validity studies is based on an inspection of the explicit time dependence (exact and approximate) for different parameter sets and time scales.

The results of the first studies are displayed in Fig. 3. We have plotted the 'discrepancy factor' η, which is the least-squares error corresponding to the departure of the BSCA/DSCA prediction from the quantum evolution. It is calculated by averaging the square of the difference of $p(t)$ from the respective approximation for a large number of t values and normalizing it appropriately via the constant C:

$$\eta = C^{-1} \sqrt{\sum_i \left[\frac{p_{\text{exact}}(t_i) - p_{\text{SCA}}(t_i)}{|p_{\text{exact}}(t_i)| + |p_{\text{SCA}}(t_i)|} \right]^2}.$$

For the BSCA, the error is plotted versus g for different values of ω/V. For the DSCA, it is plotted versus ω/V for different values of g. At $g = 0$, the BSCA prediction and the exact evolution coincide since the coupling vanishes. On increasing the coupling constant, η increases, whatever the value of ω, until it reaches a plateau. With a further increase in g, beyond a value g_0 which depends on the frequency ω (the higher the ω the

smaller the g_0), η decreases and tends to zero. The BSCA and the exact evolution tend towards each other. This latter situation corresponds to the electron being self-trapped. Moreover, the span of the plateau region, where a change in the coupling does not appreciably change the validity of the approximation scheme, shrinks and shifts to smaller values of g, as ω is increased. The dip in the discrepancy factor around $g = 1$ and the oscillations in the plateau are interesting features that merit further study. In checking the validity of the DSCA in (b) we restrict ourselves to coupling constants that are not too large ($g < 3$). We notice that the discrepancy factor η starts from a non-zero value (except at $g = 0$), first remains flat, and then decreases as the value of ω is increased. As the ratio ω/V increases, the DSCA gets better, eventually becoming indistinguishable from the exact solution.

An examination of the explicit time dependence of the probability variation forms the basis of the second part of our validity investigations. See Fig. 4 in which we plot $p(t)$ for $g = 1.7$ and four values of ω/V. The low frequency case ($\omega/V = 0.01$) shows that the exact evolution and the BSCA coincide for the entire time range shown while the DSCA is way off. The exact evolution can be checked to be, for all practical purposes, $p(t) = \cos(2Vt)$, which can also be obtained as the small-ω limit of Eqs. (6) and (7): that limit uncouples the spin from the bosons. Thus, the BSCA is excellent and the DSCA is inapplicable if the oscillator frequency is small. The high frequency case ($\omega/V = 5$) shows practical coincidence of the DSCA with the exact evolution while the BSCA is way off: it shows self-trapping and thus hardly changes from the initial value. One can easily
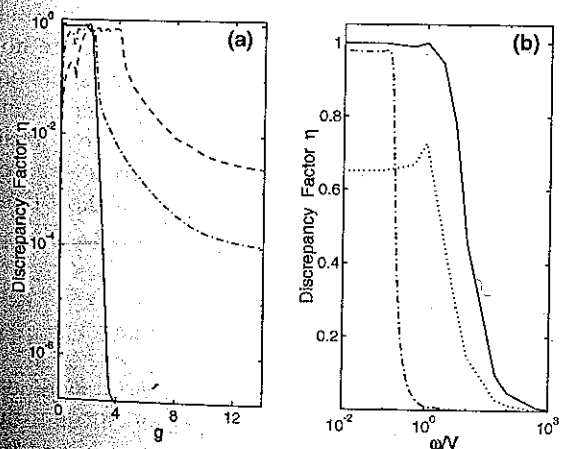

Fig. 3. Investigation of the validity of the (a) BSCA and (b) the DSCA. In each case we plot the discrepancy factor η calculated (see text) by considering the least-squares error computed for short times ($Vt < 100$) over a region of coupling constants g and of ω/V. For the BSCA we show in (a) the dependence of the error on g for $\omega/V = 0.1$ (dashed line), 0.5 (dash-dotted line), and 100 (solid line). For the DSCA we show in (b) the dependence of the error on ω/V for $g = 0.1$ (dotted line), 0.5 (solid line), and 3 (dash-dotted line). The constant C is chosen so that the largest value of η is normalized to 1 in each case.
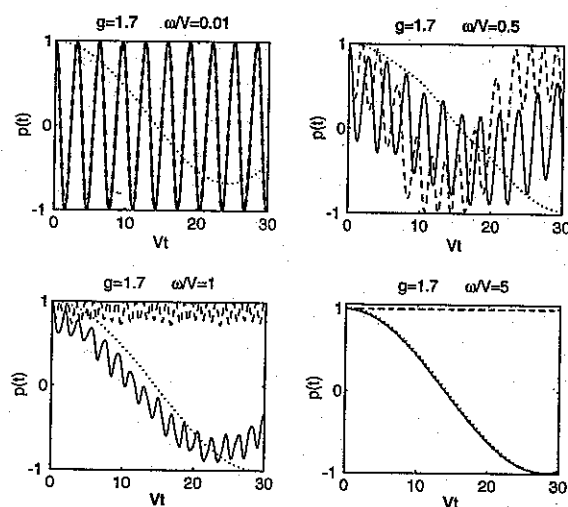

Fig. 4. Time evolution of the probability difference in the interval $0 < Vt < 30$ showing that the BSCA (DSCA) provides a good approximation for small (large) oscillator frequencies. The coupling constant $g = 1.7$ and ω/V varies as shown. The BSCA is identical to the exact evolution for $\omega/V = 0.01$ while the DSCA coincides with the exact evolution for $\omega/V = 5$.

check in this case that the exact evolution is given by $p(t) = \cos(2Ve^{-g^2}t)$. Therefore, the DSCA is excellent and the BSCA is bad if the oscillator frequency is large. Fig. 4 also shows clearly that, for intermediate values of ω/V, the reliability of the approximation procedure passes from the BSCA to the DSCA as the frequency grows. In all cases, the exact evolution is denoted by a solid line, the DSCA by a dotted line and the BSCA by a dashed line. The same conclusions can be drawn on inspection of the evolution for other values of g which we have not shown here. The simple result that emerges is that the dressed semiclassical approximation improves in validity as the oscillator frequency becomes large whereas the reverse is true for the bare semiclassical approximation. The time span used in Fig. 4 is relatively small: $0 < Vt < 30$. To ensure that the conclusions drawn do not depend on the time span, we examined the evolution for spans larger by several orders of magnitude. Precisely the same behavior as discussed above occurs, it being only necessary to decrease(increase) ω/V by an appropriate factor to ensure the practical coincidence of the BSCA (DSCA) for all times in the corresponding figures.

The general improvement in validity of the BSCA as ω/V decreases is compatible with the 'massive oscillator limit' discussed in [5]. On the other hand, the improvement in the DSCA as ω/V increases appears to agree well with a recently published analysis [22]. It is shown in [22] that a separation of the boson and the spin subsystems occurs better for this case, a noteworthy feature of that work being that it provides an explicit series expansion in inverse powers of ω/V. We hope that future work will clarify whether the ISCA's we have discussed above will provide better description for intermediate ω/V.

In order to examine the applicability of the two SCA's in extreme time scale limits, we provide Fig. 5. The probability difference $p(t)$ is plotted for the two extremes (short and long times) for $g = 3$ and $\omega/V = 10$. The short-time evolution is shown in the inset while the overall picture, which makes clear the long-time evolution, is the main plot. Although the BSCA is not able to reproduce the 'silent runs' of the exact evolution during which the probability changes very little, it predicts self-trapping oscillations within the precise limits shown by the exact curve. Thus, for the parameter values specified, the BSCA does a fine job at short times. However, it fails utterly at long times. The reverse appears true for DSCA. It fails to reproduce the apparent self-trapping on the short-time scale exhibited by the exact evolution (and by the BSCA) but does an excellent job of describing the overall tunneling from one site to the other via the reduced matrix element Ve^{-g^2}. The simple conclusion to be drawn is that, whenever the exact evolution shows apparent self-trapping at short times (this corresponds to values of g and ω/V that are
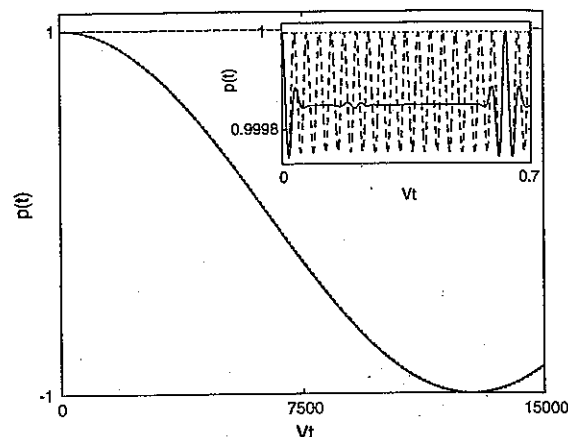

Fig. 5. Comparison of the exact evolution (solid line) and the SCA's showing that the BSCA (dashed line) provides a reasonable description (see inset) of the apparent self-trapping behavior of the exact evolution for short times while the DSCA (dotted line) describes excellently the tunneling (see main figure) at long times. In each time limit, the other approximation fares poorly. At short times the DSCA (dotted line) remains essentially unchanged at the top of the inset, while at long times the BSCA appears essentially unchanged at the top of the main plot. Note that the short time scale ($0 < Vt < 0.7$) and the long time scale ($0 < Vt < 15000$) are considerably apart.

not too small), the BSCA tends to describe the spin-boson system well at short times and the DSCA at long times.

We would also like to point out that the BSCA result shown in the inset of Fig. 5, which approximates rather well the exact evolution on the short time scale, is practically *indistinguishable* from the prediction of the non-linear dimer [2]. That prediction for the case of Fig. 5 is $p(t) = dn(\chi t/2, 4V/\chi)$ where dn is the Jacobian elliptic function with argument $\chi t/2 = g^2 \omega t$ and elliptic parameter (whose square is the elliptic modulus) $4V/\chi = 2V/g^2\omega$ [2]. This means that the discrete non-linear Schroedinger equation [1,2] depicts the short time evolution very well so long as demand is not made on it to describe tunneling – a long time phenomenon outside its reach. This fact, that the DNLSE provides an excellent fit to the exact quantum evolution at short times, may come as a surprise to some.

3. Memory function approach and its validity

Memory formalisms constitute a powerful method of description of time evolution problems in statistical mechanics [8–13]. They employ a projection operator $\mathcal{P}$ which, through its action on whichever operator it acts, coarsegrains that operator and extracts its diagonal part in a given representation. This results in memory functions which, easily and conveniently, describe crucial characteristics of the evolution of the coarsegrained probabilities. Starting from the von Neumann equation for the density matrix, one obtains [8–10]

$$\frac{d\rho'(t)}{dt} = -i\mathscr{P}L\rho'(t) - \mathscr{P}L\int_0^t e^{-i(t-s)(1-\mathscr{P})L}(1-\mathscr{P})$$
$$\times L\rho'(s)ds - i\mathscr{P}Le^{-it(1-\mathscr{P})L}[\rho(0) - \rho'(0)],$$
$$(26)$$

where ρ' is the projected part of the density matrix (i.e., coarsegrained with off-diagonal elements removed), and L is the Liouville–von Neumann operator which evaluates the commutator of the Hamiltonian with the operator on which it acts. The first term on the right hand side of (26) is identically zero because of the successive action in it of L and $\mathscr{P}$ on a diagonal operator, while the last term vanishes identically if the unprojected part of ρ is zero at the initial instant of time. The surviving term is integrodifferential in nature and contains the memory function.

The application of this memory formalism to the spin-boson problem was carried out long ago [11,12] for practical computational reasons, and has long served as a tool for describing observationally important systems such as photoinjected charge carriers and electronic excitation in organic crystals [14,15]. That work appears to have been missed, and independently rederived, in the more formalistic literature. Eq. (26) yields [9], for the spin-boson system, an integrodifferential equation for the probability difference $p(t)$ in the spin-boson system:

$$\frac{dp(t)}{dt} + 2\int_0^t \mathscr{W}(t-s)p(s)ds = 0. \qquad (27)$$

The only assumption made is that the initial density matrix of the spin-boson system is a product state in spin and boson spaces, respectively, and that the spin state is initially diagonal in the representation in which the difference in the diagonal elements of the density matrix is $p(t)$.

Eq. (26) shows that knowledge of the spin-boson Hamiltonian, and therefore of L, allows the computation of the memory $\mathscr{W}(t)$, at least in principle. Practical computation requires that one disentangle the action of the numerous projection operators in the integrand. Knowing $\mathscr{W}(t)$, the probability evolution $p(t)$ is known in principle via Laplace transforms. There are two explicit advantages of the memory approach. First, general conclusions about the p evolution can be drawn directly from knowledge of the memory [9]. Second, perturbative calculation of the memory followed by use in (27) has shown [6] remarkably close agreement with numerically exact solutions in the spin-boson system for physically relevant parameter regimes. We comment on both points below.

3.1. Perturbatively calculated memory and agreement with exact results

Explicit calculation of the memory function $\mathscr{W}(t)$ requires further assumptions. Let us consider that the

initial density matrix is of product type in the spin and boson spaces *after* the polaron (dressing) transformation (8) is carried out, that the electron is fully on one of the two sites, meaning that $p(0) = \pm 1$, and that the (displaced) oscillator is initially in the thermal equilibrium state. A perturbative calculation in orders of the transfer term of the Hamiltonian (first term in (10)), whose validity assumes the smallness of $2V/g^2\omega$, produces the memory function $\mathscr{W}(t)$:

$$\mathscr{W}(t) = 2V^2 e^{h(t)-h(0)} + c.c., \qquad (28)$$

$$h(t) = 2\sum_q g_q^2 [n_q e^{i\omega_q t} + (n_q + 1)e^{-i\omega_q t}]. \qquad (29)$$

Here n_q is the Bose factor $(e^{\omega_q/kT} - 1)^{-1}$. We have shown here the result valid for a spin interacting with a large number of boson modes as in (1). For the case of zero temperature and a single mode of vibration, the memory reduces to

$$\mathscr{W}(t) = 2V^2 e^{-2g^2(1-\cos\omega t)} \cos(2g^2 \sin\omega t). \qquad (30)$$

Although simple in form, this memory function is rich in content. Much can be learnt about the spin dynamics from a mere inspection of the memory [6] and the interplay of its several characteristic time constants. The memory function is not based on any semiclassical assumptions and therefore bypasses all questions about SCA validity. The agreement of the memory formalism results with exact evolution is quite impressive, which makes it often preferable to SCA approaches. Because these matters are already clear in the literature [6,10], we do not display examples in this paper.

The generalized form this memory function takes for finite temperatures and multiple vibrational modes does not seem to be widely known. In the case appropriate to optical phonons centered around frequency ω with a narrow width σ, the memory can be written down as

$$\mathscr{W}(t) = 2V^2 e^{-2g^2 \coth(\omega/2kT)(1-\zeta(t)\cos\omega t)} \cos(2g^2\zeta(t)\sin\omega t),$$
$$(31)$$

where $\zeta(t)$ is the Fourier transform of the phonon density of states, typified by a Gaussian $\exp(-\sigma^2 t^2)$. The general memory reduces to the single-mode zero-temperature expression (29) in the appropriate limits. Plots of (29) in the zero-temperature single-mode case may be found in [6] and those of the generalization (31) to many modes and finite temperature may be found in [10]. Eq. (31) shows that the memory has several characteristic times which are directly reflected in the evolution of the probability difference. The characteristic times become, in simple limits, reciprocals of $g^2\omega$, $g\omega$, ω, and Ve^{-g^2}. General conclusions about amount of intersite transfer can also be easily drawn from the integral $\int_0^t \mathscr{W}(s)$ of the memory function. A detailed discussion is available elsewhere [21].

3.2. Relation of the memory formalism to other approaches

We mention briefly several relations of the memory formalism to other approaches and phenomena: to the BSCA, the Bessel root collapse, the discrete non-linear Schroedinger equation (DNLSE), and the non-interacting blip approximation. First, consider that the frequency (more appropriately ωt) is small enough to allow the approximation $1 - \cos \omega t \approx \omega^2 t^2/2$, and $\sin \omega t \approx \omega t$ in the memory (30). The memory becomes a product of a Gaussian of time constant $1/g\omega$ and a cosine of frequency $g^2\omega$. The further limit $\omega \to 0$, $g \to \infty$, $g^2\omega = $ const. connects the memory formalism to the BSCA, which exhibits self-trapping.

Next, rewrite the exponential and cosine factors in (30) via Bessel function expansions to get

$$\mathscr{W}(t) = 2V^2 e^{-2g^2} \left[I_0(2g^2) + 2\sum_{m=1}^{\infty} I_m(2g^2) \cos(m\omega t) \right]$$
$$\times \left[J_0(2g^2) + 2\sum_{m=1}^{\infty} J_{2m}(2g^2) \cos(2m\omega t) \right], \quad (32)$$

and note that neglect of oscillating factors in the limit of large ωt yields the proportionality of the memory to $J_0(2g^2)$. This means the possibility of temporary collapse of transfer at values of $2g^2$ which are roots of $J_0(2g^2)$. A more careful analysis as in [22] shows, in the case of high initial excitation of the oscillator, the need to replace $2g^2$ by the product of g and the initial vibrational amplitude.

The relation of memory functions to the discrete non-linear Schroedinger equation has been explained in [21] and mentioned passingly in the next section where it is shown that the pendulum equation for the time integral of the probability difference emerges naturally from the memory formalism.

The most interesting relation is to the so-called 'non-interacting blip approximation' [32], and a non-linear memory function result derived more recently [4]. Eq. (2.17) of the first of [4], recast in our present notation, has the form

$$\frac{\mathrm{d}p(t)}{\mathrm{d}t} + 2\int_0^t \mathscr{W}(t,s,p(s))p(s)\mathrm{d}s = 0, \quad (33)$$

which is similar to (27) but differs in two regards: the memory contains p within itself and is thus non-linear, and it is *not* of the convolution type. Under the approximation of strong coupling, a replacement is made in [4] of $p(s)$ by 1 in the memory. As a consequence, the non-interacting blip approximation equation, which is equation (4.33) of [32], is obtained. This is *precisely* our memory result of (28) derived for practical computations of excitation transfer in molecular crystals [11,12], and applied for charge transport in organics [14,15].

3.3. Exact evaluation of the memory for the semiclassical dimer under driving fields

We have seen that the evolution of the spin-boson system may be viewed 'from the spin side' as the evolution of the spin with time-varying fields imposed. These imposed fields have a quantum (operator) nature and are non-linear in the sense that they depend on the spin operators also. The semiclassical approximations take the imposed fields to be classical. The idea of the effective energy mismatch and effective intersite transfer explained in earlier sections suggests that it is important to calculate the evolution of the spin in such classical (generally non-linear) imposed fields. Let us first take them to be independent of the spin variables. For the case of a time-dependent energy difference $2E(t)$, and a generally complex $V(t)$, the von Neumann equation for the dimer leads to the 'torque equation' (24). We now make explicit use of the projection operator technique [8], follow the method of [21], and arrive, *without approximation* at a new and useful result. Eq. (26) reduces exactly to

$$\frac{\mathrm{d}p(t)}{\mathrm{d}t} + 2\int_0^t \mathscr{W}(t,s)p(s)\mathrm{d}s = 0, \quad (34)$$

which is a generalization of (27) in that the memory is not of the convolution type. The memory is given by

$$\mathscr{W}(t,s) = V(t)V^*(s)e^{-\mathrm{i}\int_s^t [2E(t')]\mathrm{d}t'} + \text{c.c.} \quad (35)$$

It is important to note that this involves an exact derivation. No weak coupling approximation is made. Eq. (35) is a direct consequence of (24) if initially $p = P = \pm 1$. It is straightforward to write explicit expressions for the driving terms in (27) if the initial condition is more general.

Consider two extreme limits of (35). In one case, let $V(t)$ be a constant V. In the other, let $E(t) = 0$ and $V(t)$ be complex and time-dependent,

$$V(t) = V e^{\mathrm{i}\psi(t)}. \quad (36)$$

We see that the forms the memory takes in the two respective cases,

$$\mathscr{W}(t,s) = 2V^2 \cos \left[2\int_s^t E(t')\mathrm{d}t' \right], \quad (37)$$

$$\mathscr{W}(t,s) = 2V^2 \cos[\psi(t) - \psi(s)], \quad (38)$$

are identical to each other if $2E(t) = \mathrm{d}\psi/\mathrm{d}t$. This means that precisely the same spin evolution results from a time-dependent intersite transfer (36) with no energy mismatch as from a constant transfer ($\psi = 0$ in (36)) and a time-dependent energy mismatch $2E(t) = \mathrm{d}\psi/\mathrm{d}t$. Eq. (37) has been derived earlier [21] while (38) is a new result. Notice the relation to the BSCA and the DSCA. Consider, thus, the DSCA in which, as the result of the arguments presented in [22], we may assume the time

dependence of $\Pi_y(t)$ to be $J\sin\omega t$. Our Eqs. (17) and (38) show that the memory is $\mathcal{W}(t,s) = 2V^2\cos J$ $[\sin\omega t - \sin\omega s]$. The variety of phenomena such as the so-called AH structures [27] and collapse [23] can be understood immediately from this result. Consider, next, the BSCA in which the oscillator amplitude varies as $J\cos\omega t$. From (19) and (37), we get exactly the same memory $\mathcal{W}(t,s) = 2V^2\cos J[\sin\omega t - \sin\omega s]$. For small frequencies, the memory becomes of the convolution form, while for large frequencies it shows the possibility of collapse at Bessel roots.

What happens if we make the imposed fields depend on spin variables? Let us, for instance, take $E(t)$ as proportional to the probability difference $p(t)$. Such an assumption is typical of slaving arguments wherein time scale disparity might lead us to write $y(t) = -gp(t)$. If $E(t) = -g^2\omega p(t)$ is substituted in (37), one obtains a *non-linear* memory function

$$\mathcal{W}(t,s) = 2V^2\cos\left[2g^2\omega\int_s^t p(t')\mathrm{d}t'\right]$$
$$= 2V^2\cos\left[2g^2\omega(Q(t) - Q(s))\right], \qquad (39)$$

where $Q(t)$ is defined as the *integral* of $p(t)$. Differentiation of (34) with the memory given by (39) gives the pendulum equation for $Q(t)$

$$\frac{\mathrm{d}^2 Q(t)}{\mathrm{d}t^2} + \left(\frac{2V^2}{g^2\omega}\right)\sin[2g^2\omega Q(t)] = 0. \qquad (40)$$

It is straightforward to show that the sinusoidal non-linearity in the integral of $p(t)$ leads, exactly, to the cubic non-linearity in $p(t)$ itself. The discrete non-linear Schroedinger equation [2] and consequent self-trapping related to its *cn–dn* transition [2] follow in this fashion from the memory formalism, provided slaving arguments can be used.

4. Conclusions

The question of the validity of approximation procedures in the spin-boson system is much more complex than might be thought at first glance. We might ask if the procedure under investigation is valid for particular initial states, and/or for particular combinations of system parameters. In the first category, necessary conditions for validity might be simply high initial (boson) excitations, or they might have to do with the detailed nature of the boson excitation, such as whether the oscillator is in a coherent state, a Fock state, a thermal state (of *either* the bare *or* the displaced oscillator state, and, if the latter, fully or partially displaced), or some other state altogether. There is a tendency in some circles to dismiss the problem of the validity of the semiclassical approximation with the comment that Bohr's

complementary principle ensures that the higher the initial boson excitation, the more valid the semiclassical approximation. After all, quantum systems are said to look classical as the quantum number increases. The actual situation may, however, be more complicated. We have also seen (see, e.g., Fig. 7b of [6]) that even at low excitations, the *nature* of the boson excitation has intriguing consequences on the spin evolution. It is also possible that the initial phase of the spin system [30,36] affects the validity.

The second category of validity conditions has to do with system parameter combinations. Our studies reported in the present paper, as well as the investigations of many others in the condensed matter field, have focused on this second category. The question here is whether the approximation under investigation is good for small or large values of the spin-boson coupling constant g, and/or for small or large values of the ratio ω/V of spin versus boson time scales. Sharp changes are expected to occur in validity regimes as g crosses the value 1. Also, there is an additional time-scale ratio: $g^2\omega/2V$ which measures the polaronic binding energy relative to the electron bandwidth. It appears that the perturbative memory approximation (29) is good for large values of $g^2\omega/2V$ often irrespective of the value of ω/V. This condition that $g^2\omega/2V$ is much larger than 1 seems well satisfied for charge or excitation transport in many molecular or organic crystals. In those systems, the coupling constant is believed to lie between 1 and 2, the V is often of the order of a few wavenumbers, while ω can range from a hundred to thousands of wavenumbers depending on whether one is dealing with acoustic, optical, or intramolecular vibrations. The situation is quite different in inorganic metals or semiconductors in which V is huge, i.e., of the order of an electron volt, while there are often no intramolecular vibrations of higher frequency to couple to them. On the other hand, in these inorganic systems, the standard text-book Born–Oppenheimer separation scheme applies. It is based on ω/V being small, *not large as in organic systems*. The large mass of the nucleii makes them sluggish and the nimbler electrons adapt to their motion. In organic materials, the small intersite transfer interactions for the electrons means that the quick adapters are the oscillators: the situation is thus reversed.

It is an interesting paradox that the indisputably best methodology to adopt in studying the validity of approximation procedures involves finding the exact solution and therefore presupposes no need to have the approximation procedures in the first place. One alternative is the theoretical querying on the basis of clear computation of neglected terms as exemplified for the spin-boson system by the Wigner-function procedures developed in [4]. Another, more modest, alternative is to carry out a blend of theoretical enquiry and numerical

procedures. We have adopted here the latter and reported on some parameter ranges. We have arrived at two clear conclusions. The first is that the BSCA improves as the oscillator frequency decreases while the DSCA gets worse in this limit, as well as that the exactly opposite behavior occurs as the oscillator frequency increases (Fig. 4). The second is that the BSCA (DSCA) tends to be a good short-time (long-time) approximation to the exact evolution (Fig. 5), whenever the exact evolution shows apparent self-trapping at short times. We have also extracted some additional information from the error plots (Fig. 3), which is, to some extent, preliminary. In future publications we hope to give complete pictures of the validity over the entire g–ω terrain, and to relate the findings to the results of investigations such as those of [4–6,22,29].

In studying the validity of the semiclassical approximation, one must not confuse making the classical approximation with invoking a time scale separation. The latter is valid whenever there is disparity between time scales as in systems with sluggish or nimble nucleii or electrons. The validity of the former is much more complicated as it refers to the approximation of an expectation value of a product of operators, $\langle \hat{f}_1 \hat{f}_2 \rangle$ by the product of expectation values, $\langle \hat{f}_1 \rangle \langle \hat{f}_2 \rangle$.

We touch upon, very briefly, three miscellaneous topics in this Section. The first is the description of thermal effects in the spin-boson system. It derives its importance from intense debates that have occurred [33] about stability of the Davydov soliton (and related non-linear structures) against thermal fluctuations. Some have expressed the opinion that the 'original soliton proposal does not work at biological temperatures' and others have stated that 'thermal vibrations not only do not prevent the soliton transport of energy but... become its necessary condition.' Amid the myriads of papers that have been published on this topic, we would like to draw the attention of the reader to some attempts based on a non-equilibrium approach [34], and some on an equilibrium procedure [35]. The former introduces effects of finite temperature into the spin-boson system by augmenting an appropriate set of semiclassical equations through the addition of noise terms and arrives at a powerful (so-called 'ecumenical') equation of evolution for the density matrix. Within its domain of validity, it predicts fascinating phenomena such as Hopf bifurcations and thermally induced limit cycles for the spin-boson system. The Gibbs procedure [35] proceeds quite differently. An analogy with a ferromagnet suggests the study of a spin-boson observable which exhibits an increase as the temperature is increased, followed by a decrease, thus exhibiting both a thermal enhancing of the non-linear structure and, at higher temperatures still, its thermal destruction. We refer the reader to the literature [35] for details. In light of the improved understanding of the validity of semiclassical approximations

attempted in the present paper and planned for the near future, it might be worthwhile to return to the problem of the construction of thermal extensions of the SCA's initiated in [34] and [35].

Dynamic localization which occurs at Bessel function roots [23–25] and the possibility of quantum control [37] in low-temperature coherent systems such as optical lattices and Bose–Einstein condensates, have received considerable experimental attention in recent times. Studies of the spin-boson system resulting in dramatic effects such as the ones in Fig. 1 are relevant to these phenomena [21,26]. Driven systems may be controlled by fields with time dependence which is not only sinusoidal but of much more general character. Characteristic observables can be the extent of transfer during spurts, the length of the quiescent plateau, and the extent of oscillations. In addition to optical trap systems, magnetic macromolecules in giant-spin materials [38] provide further interesting examples of phenomena of this kind.

Finally, we mention in passing the discrete non-linear Schroedinger equation (DNLSE) [1,2,33,34]. Much has been written about this equation. Applications have been made from it, objections have been raised against it, and validity issues have been discussed concerning it. Some authors appear to have given up on it being ever possible to justify the DNLSE for the spin-boson case and have expressed the opinion that the DNLSE may be useful only in 'intrinsically non-linear' systems such as Bose–Einstein condensates. In the latter [39], the cubic non-linearity arises from the inherent interactions among the material particles, whereas in the spin-boson case, it was/is supposed to arise in the spin evolution from the elimination of the boson field. Despite old [3] and new [4,5,7] criticisms of the equation, we have begun to wonder recently whether the DNLSE might not be much more useful than recently thought. We have seen in the present paper (Fig. 5) that the original elliptic function description [2] agrees remarkably well on the short-time scale with the exact quantum evolution. Also, the issue of the validity of the DNLSE might be more closely related to initial conditions of the boson system which have not been systematically explored. We hope that such work will be carried out in the future.

We feel that much still remains to be done in the spin-boson system in spite of the activity that the system has seen over the years. Among the large number of excellent methods developed by various authors for the purpose, we would like to draw the attention of the reader especially to four: the explicit calculation of correction terms carried out by Grigolini and collaborators [4], the use of the time-dependent variational principle for developing the correct dressed semiclassical approximation by Reineker and collaborators [18], the action-angle variable analysis showing a clean separa-

tion of the spin and boson time scales given recently by Dunlap and collaborators [22], and our own memory function approach [6,10,21,26] which bypasses concerns with the semiclassical approximations and is identical to the non-interacting blip approximation. The confirmation of the validity conclusions drawn in the present paper, the extension of the investigation to arbitrary initial boson and spin states and to all regions of the parameter space, and a fundamental understanding of all these issues from the Hamiltonian are among the issues that need to be addressed.

Acknowledgements

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