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Two-level system with nonlinear coupling

Pedro de Vries and Ad Lagendijk
Natuurkundig Laboratorium, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

Hans De Raedt
Department of Physics, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium
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We present a numerical study of a two-level system coupled quadratically to a harmonic oscillator. The possibility of an instability as a function of the coupling strength is studied. The model might be relevant for the behavior of quadratically coupled polarons in solids. In the adiabatic limit the thermodynamical properties of the system can be calculated exactly over the whole coupling range. In addition, we discuss computations based on a discrete path-integral representation for the partition function. In the adiabatic limit there is a transition as a function of the coupling strength from the weak-coupling regime to a state where the oscillator mode is soft.

I. INTRODUCTION

Two-level systems are often used to describe in some approximate way the behavior of several models in solid-state physics. Many systems with linear coupling have been studied this way, e.g., the molecular polaron[1–5] and impurities embedded in a crystal lattice.[5–7] In those models the description is restricted to the two lowest energy levels of the unperturbed system. Such an approximation is adequate if the higher levels are not thermally occupied.

In this paper we study the model Hamiltonian

$$H=-h\sigma^x+p^2/2M+\tfrac{1}{2}M\Omega^2x^2+\lambda x^2\sigma^z\ , \qquad (1.1)$$

where σ^μ are the Pauli spin-$\frac{1}{2}$ matrices. The coupling constant λ, which we choose to be nonnegative, has to be smaller than or equal to $\frac{1}{2}M\Omega^2$, so that the Hamiltonian is bounded from below. The case of negative and positive λ are equivalent, since they can be mapped onto one another. This model may represent for instance a molecular system in which one electron can be on either of two sites on a molecule and where the electron is coupled to a harmonic rotational mode. Then the first factor in (1.1) describes the (free) hopping motion of the electron in terms of pseudospin operators. The next two terms represent a harmonic degree of freedom and the last part of the Hamiltonian is a quadratic coupling.

A quadratic coupling is not very common and would apply in those cases where the linear term vanishes because of symmetry or where the linear term is very small. Gutfreund and Weger have suggested[8] that the quadratic coupling of electrons to librons in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) type compounds is important in understanding the transport properties. The coupling they propose is more complicated than ours. We do not know yet of a physical realization where the quadratic coupling has the form as in (1.1). We will study the Hamiltonian (1.1) on its merits, being a simple but nontrivial quantum model. In particular, we will address the question of a possible phase transition as a function of the coupling strength.

The possibility of a transition in (1.1) will be studied in the adiabatic limit ($M\to\infty$, $M\Omega^2$ finite). Taking this limit is equivalent to neglecting the kinetic energy of the oscillator. The energy scale of the unperturbed two-level system is consequently taken to be much larger than the one of the harmonic degree of freedom. We expect that the adiabatic limit shows qualitatively the same behavior as the nonadiabatic limit. An advantage of working in the adiabatic limit is that now all thermodynamical properties can be computed numerically to any desired precision for every coupling parameter λ and temperature T.

If there is no coupling the spin will oscillate with frequency $2h$ between the states $|s_z=+\frac{1}{2}\rangle$ and $|s_z=-\frac{1}{2}\rangle$. In the weak-coupling range the periodic motion still persists. In the corresponding linear models there is a ground-state phase transition at a certain critical value of the coupling strength.[1–5] The effective flipping rate vanishes, so that flipping of the spin does not occur. The system is effectively confined to one of the s_z states. In polaron theory this is called a self-trapped state.[1–5]

We will perform exact numerical calculations and, in addition, we will apply a discrete path-integral method to our model. Results from calculations based on a discrete path-integral representation of the partition function will be compared with the exact results. In this way we will have a nontrivial check on the path-integral method. This is very useful because this method is applied to many systems whose exact solution cannot be obtained.

In general, the use of path integrals is ideally suited to study systems containing a small number of particles coupled to a bath of phonons. Since the phonon variables appear quadratically in the Hamiltonian, they can be eliminated analytically in a path-integral formulation.[9,10] In this way the number of variables can be reduced greatly. Furthermore, this representation is very appropriate for numerical evaluation and allows the computation of all model properties over the whole coupling range in a unified manner. Going beyond the adiabatic limit we are

only able to use this approach.

In Sec. II we give some analytical results and we derive the discrete path-integral expressions for the partition function and some observable quantities. In Sec. III we present exact numerical results and results obtained from calculations based on discrete path-integrals. The conclusions drawn can be found in Sec. IV.

II. THEORY

A. $T=0$

First we discuss the case for temperature $T=0$. In the adiabatic limit the spin ground-state properties are readily calculated. Exact diagonalization of the Hamiltonian with respect to the spin coordinates and minimalization of the energy with respect to the x variable gives:

$$E_0=-h\ , \tag{2.1a}$$

$$|0\rangle=|s_x=+\tfrac{1}{2}\ ,x=0\rangle\ . \tag{2.1b}$$

The magnetization in the z direction is

$$\langle\sigma^z\rangle=0\ . \tag{2.2}$$

Equations (2.1) and (2.2) are independent of the coupling parameter λ. We conclude that this quadratic model does not exhibit a ground-state phase transition as a function of λ.

B. $T\neq 0$

To study the adiabatic limit for $T\neq 0$ we perform exact numerical calculations and computations based on a path-integral formulation of (1.1). To perform the former type of calculations we first eliminate analytically the spin degree of freedom, and get the following expression for the partition function:

$$Z=\int dx\{\exp(-\beta\tfrac{1}{2}M\Omega^2x^2)2\cosh[\beta(h^2+\lambda^2x^4)^{1/2}]\}\ , \tag{2.3}$$

where we have neglected the kinetic energy of the oscillator. Similar expressions can be obtained for the energy, the specific heat, the magnetization in the z direction, etc. These thermodynamical quantities can now be computed numerically for arbitrary model parameters. This is a nice feature of the adiabatic limit.

The derivatives of the free energy with respect to the coupling λ are of special interest. The first derivative of the free energy is the expectation value of the coupling term of the Hamiltonian:

$$\partial F/\partial\lambda=\langle x^2\sigma^z\rangle\ . \tag{2.4}$$

The second derivative is a measure for the fluctuation of the coupling energy. A discontinuity in $\partial F/\partial\lambda$ or $\partial^2F/\partial\lambda^2$ as a function of λ would mean that the free energy is not an analytical function of λ and, in analogy with the theory of phase transitions, this indicates that the system undergoes a transition.

To derive a discrete path-integral representation for the partition function we use Trotter's formula[11,12] and obtain

$$Z\equiv\mathrm{Tr}(e^{-\beta H})=\lim_{m\to\infty}Z_m\ , \tag{2.5a}$$

$$Z_m=\mathrm{Tr}(e^{-\tau H_1}e^{-\tau H_2})^m\ , \tag{2.5b}$$

where $\tau=\beta/m$ and where, in the adiabatic limit, H_1 and H_2 represent the first and last two terms of (1.1), respectively. From an operational point of view the adiabatic limit is equivalent to neglecting the kinetic energy of the oscillator. Inserting complete sets of states (for the spin we use the eigenstates of σ^z) in (2.5) and working out all resulting matrix elements, we find

$$Z_m=[\tfrac{1}{2}\sinh(2\tau h)]^{m/2}\int dx\sum_{\{s_i\}}\exp(-S)\ , \tag{2.6a}$$

$$S=\sum_{i=1}^{m}[-Js_is_{i+1}+\tau x^2(\tfrac{1}{2}M\Omega^2+\lambda s_i)]\ . \tag{2.6b}$$

Here we used the identities

$$\langle s_i|e^{\tau h\sigma^x}|s_{i+1}\rangle=[\tfrac{1}{2}\sinh(2\tau h)]^{1/2}\exp(Js_is_{i+1})\ , \tag{2.7a}$$

$$J=\tfrac{1}{2}\ln\coth(\tau h)\ . \tag{2.7b}$$

Now the boson variable can be eliminated analytically from (2.6) to obtain for the mth approximant of the spin partition function Z_m^S (in the following we shall factor out the boson part of the partition function and only calculate the spin properties):

$$Z_m^S=\sum_{\{s_i\}}\left[1+C\sum_{i=1}^{m}s_i/m\right]^{-1/2}\exp\left[J\sum_{i=1}^{m}s_is_{i+1}\right]\ , \tag{2.8}$$

where $C\equiv 2\lambda/M\Omega^2$ (range of C: $0\le C\le 1$). Equation (2.8) resembles the partition function of an Ising system. However, the spin-spin interaction constant J is size (m) dependent. From (2.6) and (2.8) we see that the system tends to become polarized in the negative z direction.

From (2.8) it is straightforward to derive the mth approximants for the related thermodynamical quantities. For example, the expressions for the spin energy E^S and the first derivative of the free energy with respect to the normalized coupling constant C are

$$E_m^S=-h\coth(2\tau h)+h\left\langle\sum_i s_is_{i+1}/m\right\rangle\Big/\sinh(2\tau h)\ , \tag{2.9a}$$

$$\frac{\partial}{\partial C}(F_m^S)=\tfrac{1}{2}\beta^{-1}\left\langle\frac{\sum_i s_i/m}{1+C\sum_i s_i/m}\right\rangle\ . \tag{2.9b}$$

In practice one can never take the limit $m\to\infty$ ($\tau\to 0$), so taking a finite value for m constitutes the only approximation being made in this approach. The sum over spin states can easily be done exactly for m values up to 20. Thus results presented here for $m\le 20$ are numerically exact. For larger m values (appropriate for lower temperatures) we have performed Monte Carlo simulations.[13]

The case $m=1$ is of special interest. It is an appropriate description for the high-temperature limit ($m=1$ and $\tau\to 0$ imply $T\to\infty$). In our model we can calculate

analytically the $m=1$ approximants. We summarize a few results:

$$E_1^S = -h\tanh(\beta h) \underset{T\to\infty}{\longrightarrow} -h^2\beta\ , \tag{2.10a}$$

$$\langle\sigma^z\rangle_1 = \frac{(1+C)^{-1/2}-(1-C)^{-1/2}}{(1+C)^{-1/2}+(1-C)^{-1/2}}\ , \tag{2.10b}$$

$$\frac{\partial}{\partial C}(F_1^S) = \tfrac{1}{2}\beta^{-1}\frac{(1+C)^{-3/2}-(1-C)^{-3/2}}{(1+C)^{-1/2}+(1-C)^{-1/2}}\ . \tag{2.10c}$$

In the limit $\Delta C=(1-C)\to 0$, the last two quantities behave like

$$\langle\sigma^z\rangle_1 \to -1+(2\Delta C)^{1/2}\ , \tag{2.11a}$$

$$\partial F_1^S/\partial C \to -\tfrac{1}{2}(\beta\Delta C)^{-1}\ . \tag{2.11b}$$

We see that, in the high temperature limit, $C=1$ is a critical value and that $\partial F_1^S/\partial C$ diverges as $(\Delta C)^{-1}$.

The $m=2$ approximants are also easily calculated and give the first temperature-dependent corrections on (2.11). For the magnetization in the z direction we find

$$\langle\sigma^z\rangle_{m=2} = \frac{(1+C)^{-1/2}-(1-C)^{-1/2}}{(1+C)^{-1/2}+(1-C)^{-1/2}+2\tanh^2(\beta h/2)}\ . \tag{2.12}$$

An analogous correction holds for $\partial F_2^S/\partial C$.

C. Perturbation theory

In this subsection we consider the case where the coupling is weak and calculate the partition function by means of perturbation theory. The Hamiltonian of the noninteracting system is

$$H_0 = -h\sigma^x + p^2/2M + \tfrac{1}{2}M\Omega^2x^2\ , \tag{2.13a}$$

and the interaction is given by

$$H_i = \lambda x^2\sigma^z\ . \tag{2.13b}$$

To second order in C the Taylor expansion of the partition function reads

$$Z(C) = Z_0 + Z_2\ , \tag{2.14a}$$

$$Z_0 = \mathrm{Tr}(e^{-\beta H_0})\ , \tag{2.14b}$$

$$Z_2 = \tfrac{1}{2}\beta\int_0^\beta dy\,\mathrm{Tr}(e^{(y-\beta)H_0}H_i e^{-yH_0}H_i)\ . \tag{2.14c}$$

The first-order term is zero because $\langle\sigma^z\rangle_0=0$. Using standard techniques we obtain in the adiabatic limit

$$Z_2/Z_0 = 3C^2\tanh(\beta h)/8\beta h\ . \tag{2.15}$$

To second order in C the interaction energy is given by

$$E_2 = -\frac{\partial}{\partial\beta}(Z_2/Z_0)\ , \tag{2.16}$$

and with (2.15) we find

$$E_2 = 3C^2[\tanh(\beta h)-\beta h/\cosh^2(\beta h)]/8\beta^2 h\ . \tag{2.17}$$

Calculating the z magnetization to lowest order in C we obtain

$$\langle\sigma^z\rangle = -\tfrac{1}{2}C\tanh(\beta h)/\beta h\ . \tag{2.18}$$

In the high-temperature limit, (2.18) agrees with (2.10b) to lowest order in C. Analogous results can be found for $\partial F^S/\partial C$.

III. NUMERICAL RESULTS

In our calculations we have set h as the energy unit. The system can then be characterized by two parameters: the temperature T/h and the coupling $C\equiv 2\lambda/M\Omega^2$, see Eqs. (2.7b) and (2.8)–(2.12). First we discuss the expected behavior. At sufficiently low temperatures we expect that there is a weak-coupling regime for every C (for $T=0$ the energy is independent of C). As the temperature is raised we anticipate that for $C\approx 1$ the system rapidly becomes polarized ($\langle\sigma^z\rangle\to -1$) and the oscillator mode will become soft. For smaller values of C the system will be adequately described by means of perturbation theory. As a function of C therefore we expect an instability to occur for $C\to 1$. For $C>1$ the Hamiltonian is not bounded from below.

Besides performing exact numerical calculations we have used discrete path integrals to study (1.1). In general, the convergence as a function of m should be studied for any set of parameters. Different thermodynamical quantities will have different convergence rates. Since in this case we can also calculate the thermodynamical quantities exactly from (2.3) we shall not make extrapolations to $m=\infty$ but shall compare our finite m results directly with the exact ones. In all figures, drawn lines represent exact results.

In Fig. 1 we plot the spin energy E^S for $C=0$ and $C=0.8$ as a function of temperature. We have also shown the weak-coupling results for $C=0.8$. We see that, besides for temperatures $T/h<0.1$, the system is not in the weak-coupling regime.

Results for the coupling energy $\partial F^S/\partial C$ [see Eq. (2.4)] as a function of the coupling are presented in Fig. 2 for $T/h=0.1$. At this low temperature we have found that the system can adequately be described by perturbation theory for C values up to 0.7 as expected. When C approaches 1 the coupling energy increases rapidly, it exhibits a divergency for $C=1$.

In Fig. 3 the coupling energy is shown as a function of temperature for $C=0.5$ and $1-10^{-4}$. It turns out that the results for the temperatures $T/h<0.1$ and $T/h<1$, for $C=1-10^{-4}$ and 0.5, respectively, agree exactly with results from perturbation theory. We conclude that for all C there is a weak-coupling regime at sufficiently low temperatures. For C not too close to 1 the behavior changes smoothly to the high-temperature regime. As $C\to 1$ the system becomes polarized ($\langle\sigma^z\rangle\to -1$, see Fig. 5) and the oscillator mode becomes soft. Then at a certain temperature (which becomes lower if C is closer to 1, see Fig. 4) the derivative of the free energy begins to increase sharply. Clearly there is an instability for $C=1$. In this intermediate regime the derivative shows a divergence as a function of the coupling C. The high-temperature behavior corresponds exactly with the result we have calculated for the $m=1$ approximant (2.10c), which is valid for large T/h. Calculations of the second derivative,

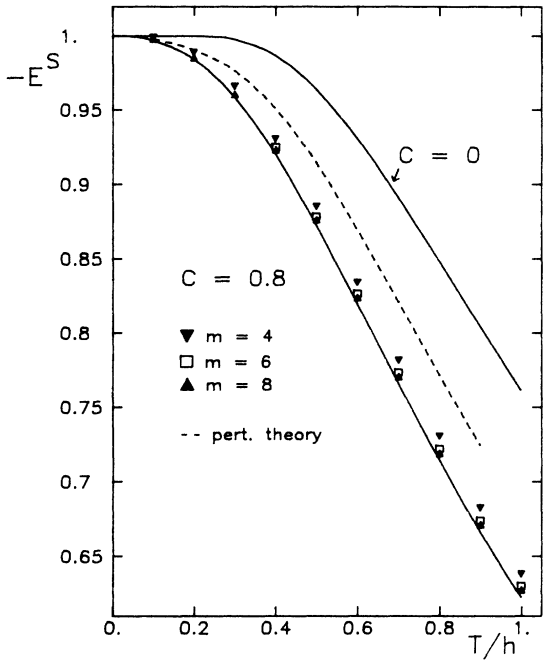

FIG. 1. The spin energy $-E^S$ as a function of the temperature T/h for $C=0.8$. Drawn lines represent exact results (the zero-coupling results are also shown). Symbols represent data from discrete path-integral calculations for $m=4$, 6, 8. Weak-coupling results are given by the dashed line for $C=0.8$.

which is a measure of the fluctuations in the coupling energy, show the same general behavior.

In Fig. 4 we focus on the behavior of the coupling energy as a function of ΔC in the regime of the instability. We conclude that in this regime ($T/h=0.1$) the first derivative of the free energy goes like $(\Delta C)^{-1.49(1)}$ for the range presented. The lower the temperature, the longer the weak-coupling regime persists for smaller ΔC. At higher temperatures $\partial F^S/\partial C$ still exhibits a divergence as a function of C [see Eq. (2.11b)] which is less steep though. The derivative then behaves like $(\Delta C)^{-1}$.

Exact results for the z magnetization as a function of C are presented in Fig. 5 for $T/h=0.4$ and $T/h\rightarrow\infty$. The latter is the $m=1$ approximant (2.10b) for the magnetization. In the temperature regime where the derivative of the free energy with respect to C has the strongest ΔC dependence the magnetization grows slowly as a function of C and rises very rapidly to the value -1 as C approaches 1. In the high-temperature limit the C dependence of $\langle\sigma^z\rangle$ is more continuous.

We now compare our exact data with the results obtained from calculations using discrete path integrals. In Fig. 1 we observe that the energy converges from below: ($E_n^S<E_m^S$ for $n<m$). We also see that small m values are sufficient to obtain accurate results. It can be shown,[14] that for $C=0$ the exact values can be reproduced for any m. For $C\neq 0$ we therefore expect the m value required for accuracy to increase with C. Leaving the weak-

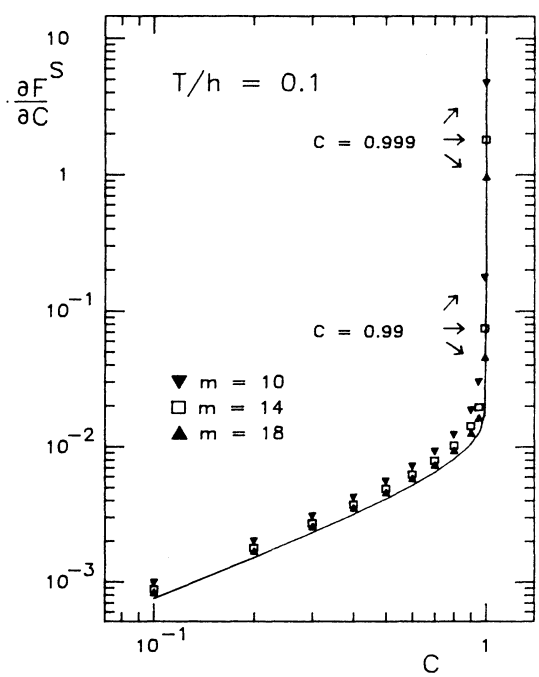

FIG. 2. Coupling dependence of the derivative of the free energy with respect to the coupling C for the temperature $T/h=0.1$. Exact results (drawn line) and results for different values of m (symbols) are shown.

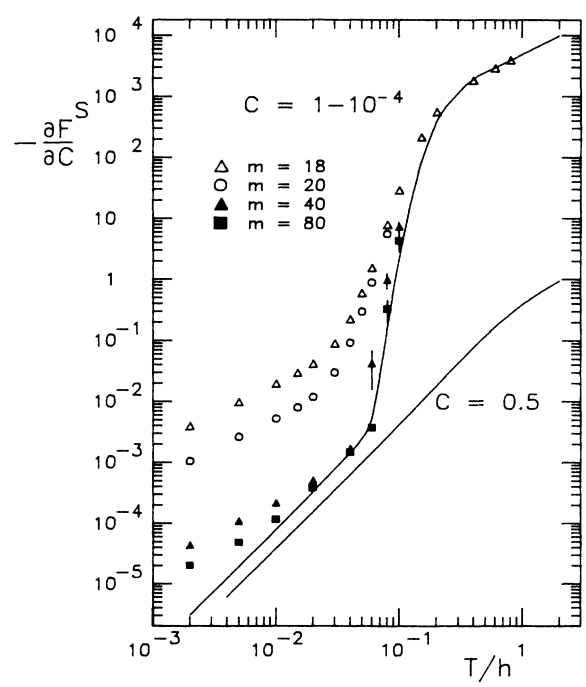

FIG. 3. The derivative of the free energy with respect to the coupling constant C for $C=0.5$ and 0.9999 as a function of T/h. For the latter discrete path-integral results are included. Open symbols: exact summations for $m=18,20$. Closed symbols: Monte Carlo results for $m=40,80$ (error bars not shown have the size of symbols). Drawn lines: exact results.

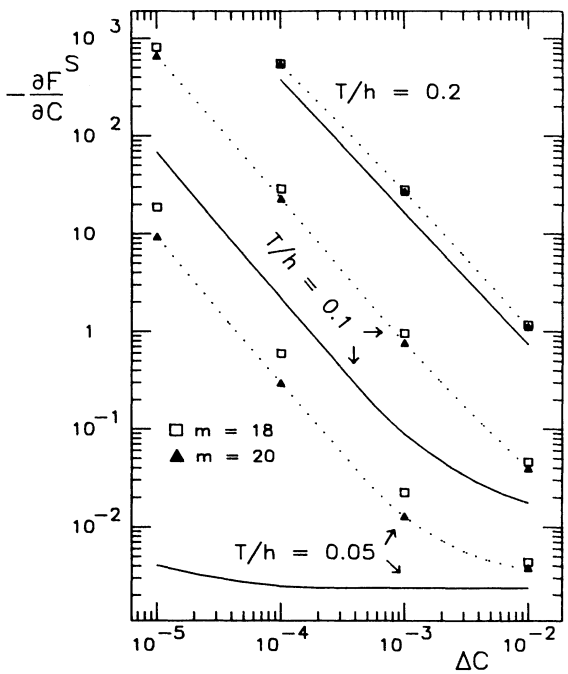

FIG. 4. The coupling energy $\partial F/\partial C$ as a function of $\Delta C \equiv 1-C$ for different values of the temperature. In the regime of the instability the coupling energy shows a power dependence of -1.49(1) on ΔC for $T/h=0.1$. Dotted lines are guides to the eyes only.

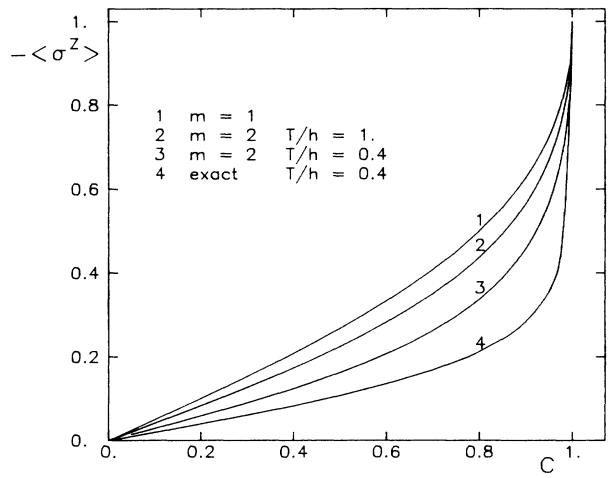

FIG. 5. Coupling dependence of the z magnetization. The exact results for $T/h=\infty$ and $T/h=0.4$ (curves 1 and 4) are given. The Trotter approximants for $m=2$ are shown for $T/h=1$ and $T/h=0.4$ (2 and 3).

coupling regime by increasing the temperature requires larger m values for accuracy, compare the $m=4$, 8 results in Fig. 1.

Comparing the m-values of Fig. 2 with the ones of Fig. 1 we see the expected difference in convergence rate for different thermodynamical quantities. We also observe that the convergence becomes slower if $C \rightarrow 1$.

Results from exact summations of spin states ($m=18,20$) and Monte Carlo simulations ($m=40,80$) are presented in Fig. 3. Most of the Monte Carlo data were obtained from runs of 50 000 samples per spin each. At low temperatures we observe that for $m=18,20$ the deviations from the exact results are enormous. This is an intrinsic property of the finite m approximation. Letting the temperature go to zero implies that we must take the limit of m to infinity first. Also the qualitative behavior deviates from exact results at low temperatures. As the temperature is increased the convergence as a function of m increases. For $T/h>1$ the $m=1$ results for the first two derivatives of the free energy with respect to C are within 10^{-3} of the exact values. This not only holds for C close to one but for all C. However, the other thermodynamical quantities, in particular for large C, are not well described by their $m=1$ approximants for $T/h \geq 1$. This is because of differences in convergence rates. A $m=1$ description of the system is only reliable when $T/h \gg 1$.

The qualitative behavior of the discrete path-integral data in Fig. 4 is identical to the exact behavior for the temperature range in which the instability occurs. Increasing the temperature we see that the convergence as a function of m increases.

Results for the z magnetization as a function of C are presented in Fig. 5. Besides the exact result for $T/h=0.4$ the $m=1$ and 2 approximants of $\langle\sigma^z\rangle$ have been plotted, the former is valid for $T/h \rightarrow \infty$ and the latter for $T/h=0.4$, 1 respectively. The $m=2$ results show the temperature-dependent corrections on the $m=1$ case.

IV. CONCLUSIONS

We have discussed the global features of a two-level model with a quadratic coupling, see the Hamiltonian (1.1). For $C=1$ the system exhibits an instability. There is a transition from the weak-coupling regime to a state in which the system is nearly fully magnetized in the z direction and where the oscillator mode has become soft.

Application of discrete path-integral methods and comparison with exact results have shown that, using these methods, the model properties can be calculated accurately in a systematic way.

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