Phase Diagram of a Heisenberg Spin-Peierls Model with Quantum Phonons

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Using a new version of the density-matrix renormalization group we determine the phase diagram of a model of an antiferromagnetic Heisenberg spin chain where the spins interact with quantum phonons. A quantum phase transition from a gapless spin-fluid state to a gapped dimerized phase occurs at a nonzero value of the spin-phonon coupling. The transition is in the same universality class as that of a frustrated spin chain, to which the model maps in the diabatic limit. We argue that realistic modeling of known spin-Peierls materials should include the effects of quantum phonons.

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Challenged by the discovery of high-temperature superconductivity in doped antiferromagnets, our understanding of quantum magnetism in low dimensions has increased significantly over the past decade [1]. However, the effect of the interaction of quantum spin systems with further degrees of freedom such as disorder, phonons, and holes produced by doping is still poorly understood. Interest in models of spins interacting with phonons has increased significantly since the discovery of a spin-Peierls transition in the inorganic compound $CuGeO_3$ [2]. The availability of large, high-quality single crystals has led to much more extensive experimental studies [3] than on the organic spin-Peierls materials studied in the 1970s [4].

The fact that a spin-1/2 antiferromagnetic Heisenberg chain is unstable to a *static* uniform dimerization [4,5] is known as the spin-Peierls instability. This occurs because dimerization opens a gap Δ in the spin excitation spectrum and lowers the total magnetic energy by a greater amount than the increase in elastic energy due to the dimerization. Until very recently, almost all theoretical treatments have used this *static* picture which assumes that the frequency ω of the phonon associated with the dimerization is much smaller than Δ and the antiferromagnetic exchange integral J. It has recently been pointed out that $CuGeO_3$ is not in this adiabatic regime [6–8], stimulating several numerical studies of models with dynamical phonons [8,9].

In this Letter, we study a model of a spin-1/2 antiferromagnetic Heisenberg chain interacting with quantum phonons using a powerful new numerical technique that allows an essentially exact treatment of *both* the spins and the phonons at a fully quantum-mechanical level. Our main result is the phase diagram in Fig. 1 in which the adiabaticity parameter J/ω varies over several decades. We find that the spin-phonon coupling must be larger than some nonzero critical value for the spin-Peierls instability to occur. This is in contrast to the static case ($\omega/J \to 0$) for which dimerization occurs for any value of the coupling. Hence, quantum lattice fluctuations can destroy Heisenberg spin-Peierls order. We find that the quantum phase transition from the spin-fluid state to the gapped state is in the same universality class as the dimerization transition of the J_1-J_2 frustrated spin chain. Our results have important implications for the modeling of spin-Peierls materials.

The model we study is one of the simplest possible. It consists of a local phonon on each site and the antiferromagnetic exchange on neighboring sites varies linearly with the difference between the phonon amplitudes on the two sites. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N}[J + g(b_{i+1} + b_{i+1}^{\dagger} - b_i - b_i^{\dagger})]\vec{S}_i \cdot \vec{S}_{i+1} + \omega \sum_{i=1}^{N} b_i^{\dagger} b_i \,. \tag{1}$$

Here $\vec{S}_i$ is the $S = 1/2$ spin operator on site i and b_i destroys a phonon of frequency ω on site i. We assume a periodic chain of N sites.

Insight into this model can be obtained by considering the diabatic limit ($\omega \gg J$). One can then integrate out the phonon degrees of freedom to obtain the following effective Hamiltonian for the spin degrees of freedom [10:

$$\mathcal{H}_{\text{eff}} = J_1 \sum_{i=1}^{N} \vec{S}_i \cdot \vec{S}_{i+1} + J_2 \sum_{i=1}^{N} \vec{S}_i \cdot \vec{S}_{i+2} \,, \tag{2}$$

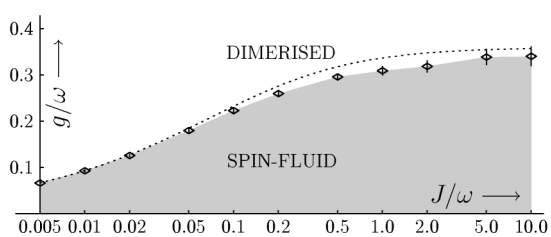

FIG. 1. Zero temperature phase diagram of the spin-Peierls antiferromagnetic chain of spins interacting with quantum phonons [Eq. (1)]. For small spin-phonon coupling g the system is a gapless spin-fluid. For large g the system is dimerized and has an energy gap. The diamonds with error bars denote the phase boundary from this DMRG study. The dotted line is [Eq. (5)] the phase boundary which results from an approximate mapping onto the J_1-J_2 model [frustrated antiferromagnetic chain, Eq. (2)] which becomes exact in the diabatic limit $J/\omega \to 0$.

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where $J_1 = J + g^2/\omega$ and $J_2 = g^2/2\omega$. Uhrig [6] recently obtained the same Hamiltonian, calculating J_1 and J_2 to next order in J/ω.

$$J_1 = J + g^2/\omega - 3g^2J/2\omega^2 + \cdots, \tag{3}$$

$$J_2 = g^2/2\omega + 3g^2J/2\omega^2 + \cdots. \tag{4}$$

The frustrated spin chain Eq. (2) or J_1-J_2 model has been extensively studied and is well understood. If $\alpha \equiv J_2/J_1$ then at a critical value of $\alpha = \alpha_c = 0.241\,167(5)$ the model undergoes a quantum phase transition from a gapless spin-fluid state with quasi-long-range antiferromagnetic order to a gapped phase with long-range dimer order [11,12]. Uhrig pointed out that this implies that in the diabatic regime (1) possesses a *nonzero* critical coupling g_c. To second order in J/ω,

$$g_c^2/\omega = \frac{\alpha_c J}{1/2 - \alpha_c + 3(1 + \alpha_c)J/2\omega}. \tag{5}$$

We have confirmed this result numerically (see Fig. 1). Furthermore, this nonzero critical coupling g_c still occurs well into the adiabatic regime. It is interesting that although (5) is valid only to second order in J/ω it gives a good description of g_c up to $J/\omega \sim 1$.

Models such as (1), which involve bosons are a challenge to study numerically due to the large number of degrees of freedom per site. The density matrix renormalization group (DMRG) method [13] has the potential for obtaining definitive results for these models by studying very large systems. Several schemes based on the DMRG have recently been developed to treat models involving phonons [14–16]. We employ a new "four-block" DMRG method [16] which allows us to treat the phonons and spins on an equal footing and to study systems as large as 256 sites. This is in contrast to some recent exact diagonalization studies of spin-phonon models that were limited to small systems and/or used uncontrolled truncations of the phonon degrees of freedom [8,9]. We previously used this method to obtain the phase diagram of the Holstein model with spinless fermions [17].

The four-block method can be used to calculate the ground state energy E_0 and the singlet and triplet gaps Δ_{ss} and Δ_{st} for periodic systems [16]. Table I shows the DMRG convergence of the gaps with the *single* truncation parameter ϵ [18] for a representative parameter set. It can be seen that the gaps are sufficiently well resolved to be useful for finite-size scaling analyses. The error of around 0.1% in the $N = 128$ site system is typical of the error in the largest systems studied for a given set of parameters.

We determine the critical coupling using the gap-crossing method used by Okamoto and Nomura [12] to determine the critical coupling α_c in the frustrated Heisenberg model (2). The convergence of the crossover coupling $\alpha_c(N)$ with N is rapid due to the absence of logarithmic corrections at the critical point [11,12,19]. If the system is gapless with quasi-long-range Néel order for $0 \le g \le g_c$, the lowest excitation is the triplet state, i.e., $\Delta_{st} < \Delta_{ss}$ (for sufficiently large N) and $\Delta_{st}, \Delta_{ss} \to 0$ as $N \to \infty$. If for $g > g_c$ the system has a nonzero gap Δ and is dimerized with a doubly degenerate ground state, then the first excited singlet state becomes degenerate with the ground state in the bulk limit [19]. That is, $\Delta_{ss} < \Delta_{st}$ (for sufficiently large N), $\Delta_{ss} \to 0$, and $\Delta_{st} \to \Delta > 0$ as $N \to \infty$. A finite lattice crossover coupling $g_c(N)$ is defined by $\Delta_{st} = \Delta_{ss}$. As shown in Table II, $g_c(N)$ rapidly approaches a limit as $N \to \infty$. This limit is the critical coupling g_c separating gapless and gapped phases. For the $J/\omega > 1$ cases, where the N dependence is substantial, $g_c(N)$ is well described by the functional form $g_c(N) \sim g_c - A\exp(-BN)$ and nonlinear fitting is used to determine g_c [20]. The resulting phase boundary is plotted in Fig. 1. The DMRG, discretization, and fitting errors in g_c are estimated to be no greater than a few percent.

From conformal invariance the finite-size energies of the spin-fluid should satisfy [12]:

$$E_0 \sim N\epsilon_\infty + \frac{\pi v_0}{6N} + \cdots, \tag{6}$$

$$\frac{1}{4}(3\Delta_{st} + \Delta_{ss}) \sim \frac{\pi v_1}{N}(1 + \cdots), \tag{7}$$

TABLE I. Four-block DMRG convergence of the singlet and triplet gaps Δ_{ss} and Δ_{st} of the spin-Peierls model (1) with the truncation parameter ϵ for various periodic lattices of size N, where $J/\omega = 1$ and $g/\omega = 0.4$.

N	ϵ	Δ_{ss}/ω	Δ_{st}/ω
8	10^{-15}	0.313 749 61	0.518 325 1
8	10^{-20}	0.313 728 89	0.518 325 4
8	10^{-22}	0.313 728 70	0.518 325 4
32	10^{-13}	0.076 478 2	0.133 925
32	10^{-15}	0.076 595 8	0.133 785
32	10^{-16}	0.076 593 3	0.133 778
128	10^{-10}	0.014 909	0.040 09
128	10^{-11}	0.014 817	0.038 56
128	10^{-13}	0.014 619	0.037 90
128	10^{-14}	0.014 648	0.037 75

TABLE II. Convergence of the crossover coupling $g_c(N)/\omega$ with lattice size N for various values of the adiabaticity parameter J/ω. $g_c(N)$ is defined by $\Delta_{ss} = \Delta_{st}$ and converges to the critical coupling g_c as $N \to \infty$.

	J/ω				
N	0.005	0.1	1.0	2.0	10.0
4	0.0692	0.237	0.1201	⋯	⋯
8	0.0681	0.228	0.2735	0.092	⋯
16	0.0671	0.225	0.3021	0.274	⋯
32	⋯	0.223	0.3087	0.310	⋯
64	⋯	⋯	0.3092	0.318	0.249
128	⋯	⋯	⋯	⋯	0.318
256	⋯	⋯	⋯	⋯	0.339

where ϵ_∞ is the bulk ground state energy density and $v_0 = v_1 = v_\sigma$ is the spin wave velocity. The combination of the gaps in Eq. (7) is chosen to cancel the logarithmic corrections.

We have performed a number of consistency checks on our results. First, v_σ as determined from Eq. (6) and our DMRG calculations for $J/\omega = 0.005$ and $g/\omega < 0.05$ agrees with results for the same quantity determined for the corresponding J_1-J_2 model, again using DMRG techniques. This confirms the mapping between the two models in the diabatic regime. Second, we note that the DMRG results for the phase boundary agree well with the result (5) from the mapping in the diabatic limit (see the dotted line in Fig. 1). Third, for general phonon frequencies, we calculate the ratio v_0/v_1 which should equal unity. At $g = g_c$ it is one within errors expected from corrections to scaling and DMRG truncation, over the range of frequencies studied. Values vary from 0.98 ± 0.04 for $J/\omega = 0.005$ to 1.07 ± 0.10 for $J/\omega = 10$.

For a Kosterlitz-Thouless (KT) transition, the gap $\Delta = \lim_{N\to\infty} \Delta_{st}$ is expected to have an essential singularity at $g = g_c$. In Fig. 2, Δ_{st} is plotted as a function of g for various N in a case of intermediate coupling $J/\omega = 1$. Two-point linear extrapolations (in $1/N$) to $N = \infty$ are included in the plot. These estimates of Δ are shown to be well fitted by the KT form [12] $\Delta \sim Af(g)\exp\{-B[f(g)]^2\}$ where $f(g) \equiv (g - g_c)^{-1/2}$. Note that the gap crossover method (Table II) is substantially more accurate than this fitting procedure for determining g_c, the latter tending to overestimate g_c [16].

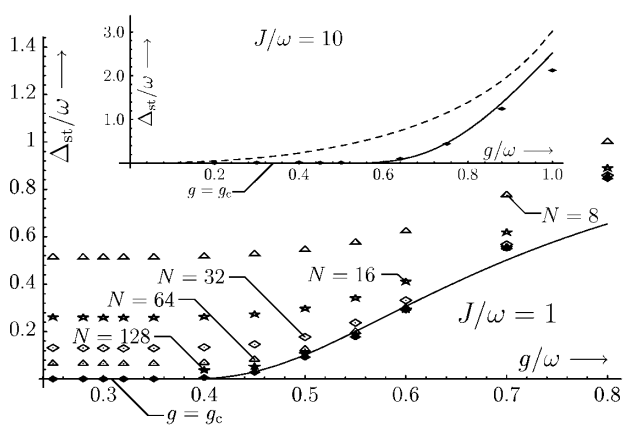

FIG. 2. The singlet-triplet gap Δ_{st} of the spin-Peierls model as a function of the coupling g for various lattice sizes N for an intermediate phonon frequency $J/\omega = 1$. Extrapolations (in $1/N$, using the two largest values of N) to $N = \infty$ are given by the solid diamonds. These are fitted to the KT form $Af(g)\exp[-Bf(g)^2]$, where $f(g) \equiv (g - g_c)^{-1/2}$ (solid line). The critical coupling g_c is not obtained from this fit. It is substantially more accurate to use the gap crossover method (see Table III). The inset shows the extrapolated gap (using $N = 32$ and 64) for a small phonon frequency (adiabatic regime) $J/\omega = 10$. The dashed line is the result for the static limit where the quantum phonon fluctuations are neglected [21].

In the adiabatic regime ($\omega \ll J$) there is strong mixing between spin singlet and phonon excitations. An analogous effect was observed for the Holstein model [17]. In the case of (1) this is manifested in nonlinear corrections to the scaling of Δ_{ss}. That is, Δ_{ss} is found to be phonon like (flat in $1/N$) until the characteristic spin energy $2\pi J/N$ decreases below the bare phonon frequency ω, at which point Δ_{ss} begins to vanish, as $1/N$ ($0 \le g \le g_c$), or exponentially ($g > g_c$). This can be seen in Table II from the slow convergence of $g_c(N)$ with N for the $J/\omega = 10$ case.

Next, we consider the validity of the static approximation in the adiabatic regime, where the phonon operators b_i in (1) are replaced by the constant dimerization $(-1)^i\delta$, the total energy is minimized as a function of δ then the gap is calculated for this optimal value of δ. This calculation was performed by using the four-block DMRG method to solve for the ground state energy and gap in the dimerized Heisenberg model [21]. The resulting adiabatic curve is compared in Fig. 2 to the extrapolated gap Δ found from our numerical results for $J/\omega = 10$. We see that even in this adiabatic region treating the phonons in the mean-field approximation is not fully reliable, particularly for the purposes of quantitatively extracting the coupling g from the experimental triplet gap. The situation is far worse for phonon frequencies relevant to $CuGeO_3$. For example, for the $J/\omega = 1$ case in Fig. 2, the adiabatic curve would not fit on the same scale as the curve from the fully dynamical model.

To consider our results in the context of experiment, estimates of a number of parameters for various spin-Peierls compounds are listed in Table III. It can be seen from these estimates and our results that the static approximation is highly questionable for $CuGeO_3$, and may not be valid for the organic spin-Peierls materials. A related question is the use of an explicit next-neighbor (J_2, frustration) term in adiabatic spin-phonon models of $CuGeO_3$ [27,28]. The value of J_2 required to achieve agreement with susceptibility and magnetic specific heat data is generally very large ($J_2/J_1 \approx 0.3$). Attempts have been made to justify the inclusion of a J_2 term on the basis of Cu-O-O-Cu superexchange paths [28]. However, Ref. [6] and the present analysis suggests that an explicit J_2 term may not be required in order to describe experimental results if the phonons are treated

TABLE III. Estimates of the exchange J, phonon frequency ω, and energy gap Δ for various spin-Peierls materials. All are given in units of degrees kelvin. (We are unaware of any other measurements of the frequencies of the dimerization phonon in organic materials.)

Material	J	ω	Δ	Ref.
$CuGeO_3$	100	150, 300	20	[2,22]
$TTFCuS_4C_4(C_3F)_4$	70	? [24]	20	[4,23]
(MEM) $(TCNQ)_2$	50	100	60	[25,26]

quantum mechanically since the phonons induce a next-nearest neighbor interaction.

To conclude, we have numerically determined the phase diagram of a spin-Peierls model (1) with high accuracy. Our results are consistent with a mapping of the model to the frustrated spin chain (2) in the diabatic limit (large phonon frequency). For a wide range of phonon frequencies compared to the exchange there is a phase transition at a nonzero value of the coupling g from a gapless spin-fluid state to a gapped dimer phase [29]. The transition is in the same universality class as the Kosterlitz-Thouless transition in the frustrated antiferromagnetic chain (2). Quantum phonon fluctuations are important in known spin-Peierls materials.

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