Insights into phase transitions and entanglement from density functional theory

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Abstract
Density functional theory (DFT) has met great success in solid state physics, quantum chemistry and in computational material sciences. In this work we show that DFT could shed light on phase transitions and entanglement at finite temperatures. Specifically, we show that the equilibrium state of an interacting quantum many-body system which is in thermal equilibrium with a heat bath at a fixed temperature is a universal functional of the first derivatives of the free energy with respect to temperature and other control parameters respectively. This insight from DFT enables us to express the average value of any physical observable and any entanglement measure as a universal functional of the first derivatives of the free energy with respect to temperature and other control parameters. Since phase transitions are marked by the nonanalytic behavior of free energy with respect to control parameters, the physical quantities and entanglement measures may present nonanalytic behavior at critical point inherited from their dependence on the first derivative of free energy. We use two solvable models to demonstrate these ideas. These results give new insights for phase transitions and provide new profound connections between entanglement and phase transitions in interacting quantum many-body physics.

1. Introduction

The electronic density functional theory (DFT) developed by Hohenberg and Kohn [1] and Kohn and Sham [2] in 1964–1965 has shown tremendous success in solid state physics, quantum chemistry and in computational material sciences [3, 4]. The central idea of DFT is a transformation of the dependence of the properties of a system of interacting many-body system on their single-particle potential to a dependence on the ground state density, which provides a practical method to calculate ground state properties of electronic systems [3, 4]. David Mermin generalized the DFT formalism to calculate finite temperature properties [5] and Runge and Gross extended DFT further to calculate time-dependent properties and hence the excited state properties of electronic systems [6].

Phase transitions are one of the most intriguing phenomena in many-body physics because it indicates emergence of new states of matter. In recent years, there are a great deal of interest in studying the relations between entanglement and phase transitions in many-body systems [7]. An inspiring result on the relations between entanglement and quantum phase transitions is from DFT perspective [8]. It was also shown that DFT provides new insights for quantum phase transitions [9, 10]. Here, we demonstrate that DFT sheds new light on phase transitions at any temperatures and provides rigorous connections between phase transitions and entanglement at arbitrary temperatures.

In this work we show that DFT provides insights for finite temperature phase transitions. We prove that the equilibrium state of a quantum many-body system, which is in thermal equilibrium with a heat bath, is a universal functional of the first derivative of the free energy with respect to the control parameters. This finding explains how the non-analytic behavior of free energy at critical point affects the expectation values of physical observable at phase transition point. Since entanglement in quantum many-body systems is a functional of expectation value of observable, the finding also introduces a direct link between entanglement and the first
derivatives of free energy, leading to a deep connection between entanglement and phase transitions. The organization of this paper is as follows. We prove a few theorems for establishing the relation between thermodynamic equilibrium state and first derivatives of free energy from DFT in section 2. In section 3, we prove a theorem for connecting phase transitions and entanglement. In section 4 we study two solvable models to demonstrate our central ideas and finally we give a summary.

2. Insight into phase transitions from DFT

Let us consider an interacting quantum many-body system with Hamiltonian

\[ H(\lambda) = H_0 + \sum_{i=1}^K \lambda_i H_i, \]

where \( \{ \lambda_i \} = (\lambda_1, \lambda_2, \ldots, \lambda_K) \) are the control parameters of the system. For example, in spin models, the magnetic field \( h = \lambda_1 \), the nearest coupling \( J = \lambda_2 \) and the next to nearest neighbor coupling \( J' = \lambda_3 \), etc. We assume that any two terms in the Hamiltonian do not commute, \([H_i, H_j] \neq 0 \) for \( i \neq j \). We shall work in the canonical ensemble, where the many-body system is in contact with a heat bath at a fixed temperature and finally they reach thermal equilibrium. The thermodynamic equilibrium state of the many-body system can be obtained from maximizing the entropy [11, 12]

\[ S = -\text{Tr}[\rho \ln \rho], \]

under two constraints. The first constraint is that the average energy of the system is fixed,

\[ \text{Tr}[\rho H] = \langle E \rangle, \]

which is because the system is in thermal equilibrium with the heat bath and there is no macroscopic energy flow between them. The second constraint is that the density matrix is normalized, namely

\[ \text{Tr}[\rho] = 1. \]

By maximizing the entropy under above two constraints, one obtain the equilibrium state of the system with density matrix,

\[ \rho_0 = \frac{e^{-\beta H(\lambda, \ldots, \lambda_K)}}{Z(T, \lambda_1, \ldots, \lambda_K)}, \]

where \( \beta \equiv 1/T \) and \( Z(T, \lambda_1, \ldots, \lambda_K) \equiv \text{Tr}[e^{-\beta H(\lambda_1, \ldots, \lambda_K)}] \) being the canonical partition function. We take the Boltzmann constant \( k_B \equiv 1 \). One can see from equation (5) that the thermal density matrix is fully characterized by the set of parameters \((T, \lambda_1, \lambda_2, \ldots, \lambda_K)\). To establish our central theorem, we shall prove two Lemmas:

**Lemma 1.** There is a one-to-one map between the canonical density matrix of a quantum many-body system with Hamiltonian \( H = H_0 + \sum_{i=1}^K \lambda_i H_i \), which is in thermal equilibrium state with a heat bath at temperature \( T \), and the set of control parameters \((T, \lambda_1, \lambda_2, \ldots, \lambda_K)\).

**Proof.** In the above we show that the equilibrium state is described by the canonical density matrix \( \rho_0 = e^{-\beta H}/Z(T, \lambda_1, \lambda_2, \ldots, \lambda_K) \), which is determined by the set of control parameters \((T, \lambda_1, \lambda_2, \ldots, \lambda_K)\). Now we have to prove that the canonical density matrix \( \rho_0 \) determines these control parameters. This means only one set of control parameters corresponds to the equilibrium density matrix \( \rho_0 \). The proof is done by reductio and absurdum. We assume that there are two different sets of control parameters \((T, \lambda_1, \lambda_2, \ldots, \lambda_K)\) and \((T', \lambda_1', \lambda_2', \ldots, \lambda_K')\) correspond to the same equilibrium state \( \rho_0 \). Then we have

\[ \text{Tr}[\rho_0 H(\lambda, \lambda_2, \ldots, \lambda_K)] = \langle E \rangle, \]

\[ \text{Tr}[\rho_0 H(\lambda', \lambda_2', \ldots, \lambda_K')] = \langle E' \rangle. \]

Note that the average energy of the system \( \langle E \rangle \) is fixed by the temperature of the thermal bath. Subtracting equation (6) from (7), we get

\[ \sum_{i=1}^K (\lambda_i - \lambda_i') \text{Tr}[\rho_0 H_i] + \langle E \rangle - \langle E' \rangle = 0. \]

Thus we have

\[ \lambda_i = \lambda_i', \ i = 1, 2, \ldots, K. \]

\[ \langle E \rangle = \langle E' \rangle. \]

Equation (10) means that \( T = T' \). This contradicts the assumption. Thus we proved lemma 1. Note that the non-uniqueness, the density matrix is not uniquely determined by the control parameters, in the generalization
Lemma 1 means that the thermal density matrix is uniquely fixed by the control parameters, namely
\[ \rho_0 \leftrightarrow (T, \lambda_1, \lambda_2, \ldots, \lambda_K). \]  
(11)

From the equilibrium density matrix \( \rho_0 \), we can evaluate all physical quantities, in particular, the quantities conjugate to the control parameters. For example, the entropy, which is conjugate to temperature, is given by
\[ S_0 = -\text{Tr}[\rho_0 \ln \rho_0]. \]  
(12)

The density \( \langle H_i \rangle \) which is conjugate to \( \lambda_i \) is
\[ \langle H_i \rangle = \text{Tr}[\rho_0 H_i], \quad i = 1, 2, \ldots, K. \]  
(13)

Lemma 1 implies that the set of control parameters \( (T, \lambda_0, \lambda_2, \ldots, \lambda_K) \) determine the set of densities \( (S_0, \langle H_0 \rangle, \langle H_2 \rangle, \ldots, \langle H_K \rangle) \). We shall prove the converse is also true in lemma 2.

To establish lemma 2, we record a minimum property of the free energy at finite temperature in analogous to that of the ground state energy. If we define a free energy functional
\[ F[T, \{ \lambda_i \}, \rho] = \text{Tr}[\rho S(H(\{ \lambda_i \}) + T \ln \rho)], \]  
(14)

then this functional satisfies
\[ F[T, \{ \lambda_i \}, \rho] > F[T, \{ \lambda_i \}, \rho_0], \quad \rho \neq \rho_0 \]  
(15)

for all positive definite density matrices \( \rho \) with unit trace and \( \rho_0 \) is the canonical density matrix corresponds to the control parameters \( (T, \{ \lambda_i \}) \). In the appendix A we prove that \( F[T, \{ \lambda_i \}, \rho] \) is bounded below by \( F[T, \{ \lambda_i \}, \rho_0] \) for general quantum many-body systems. Given this property, we can prove

**Lemma 2.** For an interacting quantum many-body system with Hamiltonian, \( H = H_0 + \sum_{i=1}^{K} \lambda_i H_i \), which is in thermal equilibrium with a heat bath at fixed temperature \( T \), there is a one-to-one map between the set of control parameters \( (T, \lambda_0, \ldots, \lambda_K) \) and thermal equilibrium densities, \( (S_0, \langle H_0 \rangle, \ldots, \langle H_K \rangle) \).

**Proof.** For simplicity of notation, we denote the set of control parameters by \( \Lambda \equiv (T, \lambda_0, \ldots, \lambda_K) \). Let us consider two different sets of parameters \( \Lambda \neq \Lambda' \) and assume that their corresponding equilibrium density matrices are \( \rho_0 \) and \( \rho_0' \), respectively. From their density matrices, we can obtain the sets for thermal densities
\[ D_\Lambda \equiv \{ S_0, \langle H_0 \rangle, \ldots, \langle H_K \rangle \} \text{ and } D_{\Lambda'} \equiv \{ S_0', \langle H_0 \rangle', \ldots, \langle H_K \rangle' \} \text{ where } S_0 = -\text{Tr}[\rho_0 \ln \rho_0], \]  
(16)

\[ \langle H_i \rangle = \text{Tr}[\rho_0 H_i], \quad i = 1, 2, \ldots, K \text{ and } S_0' = -\text{Tr}[\rho_0' \ln \rho_0'], \quad \langle H_i \rangle' = \text{Tr}[\rho_0' H_i], \quad i = 1, 2, \ldots, K. \]

We assume two different sets of control parameters \( \Lambda \) and \( \Lambda' \) produce the same set for thermal equilibrium densities, namely \( D_\Lambda = D_{\Lambda'} \). According to the minimum property of free energy, equation (15), we have
\[ F[\Lambda, \rho_0] = \text{Tr} \left[ \rho_0 \left( H_0 + \sum_{i=1}^{K} \lambda_i H_i + T \ln \rho_0 \right) \right], \]  
(17)

\[ < F[\Lambda, \rho_0'], \]  
(18)

\[ = \text{Tr} \left[ \rho_0' \left( H_0 + \sum_{i=1}^{K} \lambda_i H_i + T \ln \rho_0' \right) \right], \]  
(19)

so that
\[ F[\Lambda, \rho_0] < F[\Lambda', \rho_0'] + \sum_{i=1}^{K} (\lambda_i - \lambda_i') \langle H_i \rangle' + (T - T')S_0', \]  
(20)

But the reasoning of equation (16) to equation (19) remains valid when the set for parameters \( \Lambda \) and \( \Lambda' \) are interchanged, yielding
\[ F[\Lambda', \rho_0'] < F[\Lambda, \rho_0] + \sum_{i=1}^{K} (\lambda_i' - \lambda_i) \langle H_i \rangle + (T' - T)S_0. \]  
(21)

Adding equations (20) and (21) and using the assumptions lead to the contradiction
\[ F[\Lambda, \rho_0] + F[\Lambda', \rho_0'] < F[\Lambda, \rho_0] + F[\Lambda', \rho_0'], \]  
(22)

and therefore a set of control parameters \( \Lambda = \{ T, \lambda_0, \ldots, \lambda_K \} \) can only result in a set of thermal densities \( D_\Lambda = \{ S_0, \langle H_0 \rangle, \ldots, \langle H_K \rangle \} \), i.e. the control parameters are unique function of the equilibrium densities.
Lemma 2 is proved. Lemma 2 means that
\[(T, \lambda_1, \lambda_2, \ldots, \lambda_K) \iff (S_0, \langle H_1 \rangle, \langle H_2 \rangle, \ldots, \langle H_K \rangle). \quad (23)\]
An immediate consequence of lemma 2 is that we can use the thermal densities instead of control parameters as a fundamental variable of the equilibrium state, \(\rho_0(S_0, \langle H_1 \rangle, \langle H_2 \rangle, \ldots, \langle H_K \rangle).\) In real applications, it is always useful to vary only one of the control parameters while keeping all the others fixed. Then lemma 2 actually implies that the following one-to-one correspondence relations,
\[T \iff S_0, \quad (24)\]
\[\lambda_i \iff \langle H_i \rangle, \text{ for } i = 1, 2, \ldots, K. \quad (25)\]

Now we are ready to establish the following central theorem:

**Theorem 1.** If an interacting many-body system with Hamiltonian \(H(\lambda_1, \ldots, \lambda_K) = H_0 + \sum_{i=1}^{K} \lambda_i H_i\) is in thermal equilibrium with a heat bath at temperature \(T\), then the equilibrium density matrix of the many-body system is a unique functional of the first order derivatives of the free energy with respect to control parameters, namely
\[\rho_0 = \rho_0 \left( \frac{\partial F}{\partial T}, \frac{\partial F}{\partial \lambda_1}, \ldots, \frac{\partial F}{\partial \lambda_K} \right), \quad (26)\]

**Proof.** According to lemma 2, we have one-to-one correspondence relations between thermal densities and the corresponding control parameters. Thus we can express the control parameter as function of their conjugate density, namely
\[T = f_0(S_0), \quad (27)\]
\[\lambda_i = f_i(\langle H_i \rangle), \quad i = 1, 2, \ldots, K, \quad (28)\]
where \(f_0, f_1, f_2, \ldots, f_K\) are some unknown functions. Because the thermal densities are all first derivatives of free energy, for example, entropy is the first derivative of free energy with respect to temperature \(S_0 = -\frac{\partial F}{\partial T}\) and \(\langle H_i \rangle = \frac{\partial F}{\partial \lambda_i}, \quad i = 1, 2, \ldots, K,\) this means that
\[T = f_0 \left( \frac{\partial F}{\partial T} \right), \quad (29)\]
\[\lambda_i = f_i \left( \frac{\partial F}{\partial \lambda_i} \right), \quad i = 1, 2, \ldots, K, \quad (30)\]

In addition, lemma 1 tells us that the canonical density matrix is uniquely fixed by the control parameters, i.e. \(\rho_0(T, \lambda_1, \lambda_2, \ldots, \lambda_K).\) Combing with equations (29) and (30) with lemma 1, we proved theorem 1. Theorem 1 means that we can use the first derivative of free energy with respect to control parameters as a fundamental variable.

According to theorem 1, the thermal expectation value of any observable \(A\) of the many-body system is given by
\[\langle A \rangle = \text{Tr} \left[ A \rho_0 \left( \frac{\partial F}{\partial T}, \frac{\partial F}{\partial \lambda_1}, \ldots, \frac{\partial F}{\partial \lambda_K} \right) \right], \quad (31)\]
Phase transitions are marked by the discontinuity of the free energy with respect to temperature \(T\) or other control parameters \(\lambda_i, \quad i = 1, 2, \ldots, K:\)

(1) For first order phase transitions, the first order derivatives of the free energy, such as \(\frac{\partial F}{\partial T}\) or \(\frac{\partial F}{\partial \lambda_i}, \quad i = 1, 2, \ldots,\) is discontinuous across a phase boundary, then expectation value of an arbitrary observable \(A\) also presents discontinuity across phase boundary from equation (31).

(2) For second order phase transitions, the first derivatives of free energy with respect to parameters are continuous and the second order derivatives of the free energy, such as \(\frac{\partial^2 F}{\partial T^2}\) and \(\frac{\partial^2 F}{\partial \lambda_i^2},\) are discontinuous or diverge and we should examine the derivatives of the observable \(A, \) which are
\[\frac{\partial \langle A \rangle}{\partial T} = \text{Tr} \left[ A \rho_0 \left( \frac{\partial \rho_0}{\partial T} \right) \times \frac{\partial S_0}{\partial T} = -\frac{\partial \langle A \rangle}{\partial S_0} \times \frac{\partial^2 F}{\partial T^2}, \quad (32)\]
\[\frac{\partial \langle A \rangle}{\partial \lambda_i} = \text{Tr} \left[ A \rho_0 \left( \frac{\partial \rho_0}{\partial \lambda_i} \right) \times \frac{\partial \langle H_i \rangle}{\partial \lambda_i} = \frac{\partial \langle A \rangle}{\partial \langle H_i \rangle} \times \frac{\partial^2 F}{\partial \lambda_i^2}, \quad i = 1, 2, \ldots, K. \quad (33)\]
Equations (32) and (33) show that the first order derivative of arbitrary observable \( A \) with respect to a control parameter is proportional to the second order derivative of free energy with respect to the same control parameter. While at second order thermal phase transitions point, \( \partial^2_F F \) and \( \partial^2_{F_i} F \), \( i = 1, 2, \ldots, K \) are discontinuous or diverge, thus the first derivative of an arbitrary observable \( \partial_T \langle A \rangle \) and \( \partial_{\lambda_i} \langle A \rangle \) present discontinuous or divergence at second order phase transition point. Analogously, one needs to detect \((n - 1)\)-th order derivative of physical quantity for \( n \)-th order phase transitions. It should be emphasized that for those phase transitions which can not be described by singularities in the free energy, then the theory in this work does not apply.

3. Relations between entanglement and phase transitions from DFT

Entanglement is a unique feature in quantum mechanics. It was found that entanglement measures present non-analytic behavior at phase transition point \([7, 16]\). Wu et al [8] found that DFT provide intriguing relationship between entanglement and quantum phase transitions. Local density type approximate functionals was developed to study quantum entanglement in various physical systems \([17–20]\). Now we show that DFT provides relations between entanglement and phase transitions in many-body systems at any temperatures. We can prove the following theorem:

**Theorem 2.** Any finite temperature entanglement measure \( M \) can be expressed as a unique functional of the set of first derivatives of the free energy:

\[
M = M(S_0, \langle H_1 \rangle, \langle H_2 \rangle, \cdots, \langle H_K \rangle)
\]

\[
= M \left( \frac{\partial F}{\partial T}, \frac{\partial F}{\partial \lambda_1}, \frac{\partial F}{\partial \lambda_2}, \cdots, \frac{\partial F}{\partial \lambda_K} \right).
\]

**Proof.** The proof follows from the fact that, according to lemma 1 and lemma 2, the thermal equilibrium density matrix is a unique functional of \( S_0, \langle H_1 \rangle, \langle H_2 \rangle, \cdots, \langle H_K \rangle \) and also \( \rho_0 \) provides the complete information of the thermal equilibrium state, everything else is a unique functional of \((S_0, \langle H_1 \rangle, \langle H_2 \rangle, \cdots, \langle H_K \rangle)\). Formally let us consider an \( n \)-partite entanglement in spin-1/2 systems. For other cases, the proof can be generalized immediately. First of all any entanglement measure of \( n \) qubits is always a function of the matrix elements of the reduced density matrix of these qubits, \( \rho_{12 \cdots n} \). For spin-1/2 systems, the \( n \)-body reduced density matrix can be written as

\[
\rho_{12 \cdots n} = \sum_{a_1, a_2, \cdots, a_n = 0, x, y, z} C_{a_1 a_2 \cdots a_n} \sigma_1^{a_1} \sigma_2^{a_2} \cdots \sigma_n^{a_n}.
\]

with

\[
C_{a_1 a_2 \cdots a_n} = \text{Tr}_{12 \cdots n} \rho_{12 \cdots n} \sigma_1^{a_1} \sigma_2^{a_2} \cdots \sigma_n^{a_n},
\]

\[
= \text{Tr}[\rho_0 \sigma_1^{a_1} \sigma_2^{a_2} \cdots \sigma_n^{a_n}],
\]

\[
= \langle \sigma_1^{a_1} \sigma_2^{a_2} \cdots \sigma_n^{a_n} \rangle,
\]

where \( a_1, a_2, \cdots, a_n = 0, x, y, z \) with \( \sigma^0 = I \). Thus \( M = M(\langle \sigma_1^{a_1} \sigma_2^{a_2} \cdots \sigma_n^{a_n} \rangle) \). According to lemma 2, thermal expectation value of any observable can be taken as a functional of \((S_0, \langle H_1 \rangle, \langle H_2 \rangle, \cdots, \langle H_K \rangle)\). Therefore

\[
M = M(S_0, \langle H_1 \rangle, \cdots, \langle H_K \rangle) = M \left( \frac{\partial F}{\partial T}, \frac{\partial F}{\partial \lambda_1}, \cdots, \frac{\partial F}{\partial \lambda_K} \right).
\]

Theorem 2 is proved.

One can immediately see that for first order phase transition, where the first derivative of free energy is discontinuous, the entanglement measure presents non-analytic behavior. For second order phase transitions, we need to examine the first derivative of the entanglement,

\[
\frac{\partial M}{\partial T} = \frac{\partial M}{\partial S_0} \frac{\partial S_0}{\partial T} = - \frac{\partial M}{\partial S_0} \frac{\partial^2 F}{\partial S_0 \partial T^2}.
\]

\[
\frac{\partial M}{\partial \lambda_i} = \frac{\partial M}{\partial \langle H_i \rangle} \frac{\partial \langle H_i \rangle}{\partial \lambda_i} = \frac{\partial M}{\partial \langle H_i \rangle} \frac{\partial^2 F}{\partial \langle H_i \rangle \partial \lambda_i^2}, \ i = 1, 2, \cdots, K.
\]

These equations show that first derivative of any entanglement is proportional to the second order derivative of free energy. Using entanglement measures, the second order thermal phase transitions can be identified through nonanalytic or vanishing values of \( \partial M / \partial T \) at the thermal critical point.
4. Model study

4.1. LMG model study

To demonstrate the above ideas, we first study a spin model with finite temperature phase transitions, namely the Lipkin–Meshkov–Glick (LMG) model \[21–23\] with Hamiltonian

\[
H(\lambda) = -\frac{J}{N} \sum_{1 \leq i < j \leq N} (\sigma_i^x \sigma_j^x + \gamma \sigma_i^y \sigma_j^y) - \lambda \sum_{i=1}^{N} \sigma_i^z, \quad \equiv H_0 + \lambda H_0
\]

where \(J\) is the ferromagnetic coupling strength between arbitrary two pauli spins \(s_i^\rho\) and \(s_j^\rho\) while \(\gamma\) describes the anisotropy of the coupling in the \(y\) direction. The LMG model has been experimentally simulated in trapped ion systems \[24–26\].

The LMG model can be simplified by defining a collective spin operator \(S^\alpha = \sum_{j=1}^{N} s^\alpha_j\) where \(\alpha = x, y, z\) and it is simple to show that the collective spin operators satisfy the ordinary spin angular momentum commutation relations. In terms of collective spin operators, the Hamiltonian \(H\) can be rewritten as,

\[
H_S = -\frac{2J}{N} (S_x^2 + \gamma S_y^2) - 2\lambda S_z + \frac{J(1 + \gamma)}{2}.
\]

It is obvious that the collective spin angular momentum squared is a conserved quantity, \(\{S^2, H_S\} = 0\). Thus we can make use of the quantum number of the collective spin operator squared \(S^2\) to classify the total Hilbert into different blocks, each of the block takes a fixed quantum number of the collective spin angular momentum squared, which can take values \(-S, -S + 1, \ldots, S\). Moreover, each collective spin block is highly degenerate and the degeneracy of collective spin-\(S\) block is

\[
D_S = \frac{C_N^{N/2-S} - C_N^{N/2-S-1}}{C_N^{N/2-S} (2S + 1) / (N/2 + S + 1)}.
\]

By such a mapping, the many-body problem of \(H\) in LMG model is simplified into diagonalising a series of small large spins with Hamiltonian \(H_S\). Then the partition function of the spin system with Hamiltonian \(H\) can be calculated by

\[
Z(T, \lambda) = \sum_{S=0}^{N/2} D(S) Tr_S [e^{-\beta H_S(\lambda)}].
\]

From the partition function we then can get the free energy

\[
F(T, \lambda) = -T \ln Z(T, \lambda).
\]

Thus all the thermodynamic quantities can be evaluated from free energy.

For infinite system, \(N \to \infty\), mean field theory becomes exact \[27\] and we show mean field phase diagram of LMG model in figure 1. At thermodynamic limit, \(N \to \infty\), when \(0 < \gamma < 1\), we obtain (See appendix B for derivations) the temperature is a universal function of thermodynamic entropy,

\[
T = \begin{cases} 
\frac{\varepsilon^2}{2 - \varepsilon^2} - \frac{\gamma^2}{N}, & T < T_c; \\
\frac{\lambda^2}{2} - \frac{\gamma^2}{N}, & T > T_c,
\end{cases}
\]

where \(\varepsilon = \sqrt{M_0^2 + \lambda^2}\). Also the control parameter \(\lambda\) is a universal function of the density \(\langle \sigma_i^z \rangle\),

\[
\lambda = \begin{cases} 
\frac{\langle \sigma_i^z \rangle}{N}, & T < T_c; \\
\frac{1}{2} \tanh^{-1} \frac{\langle \sigma_i^z \rangle}{N}, & T > T_c.
\end{cases}
\]

When \(\gamma > 1\), the temperature is given in terms of the entropy by

\[
T = \begin{cases} 
\frac{\varepsilon^2}{\sqrt{1 - \varepsilon^2} \gamma^2} - \frac{S_z}{N}, & T < T_c; \\
\frac{\lambda^2}{\sqrt{1 - \lambda^2} \gamma^2} - \frac{S_z}{N}, & T > T_c.
\end{cases}
\]
The control parameter $\lambda$ is given in terms of its density $\rho$ by

$$
\lambda = \begin{cases} 
\frac{\langle H \rangle}{N}, & T < T_c; \\
\frac{1}{\beta} \tanh^{-1} \frac{\langle H \rangle}{N}, & T > T_c.
\end{cases}
$$

These results support lemma 2.

In Figure 2, we show the equilibrium entropy per spin $s_0 \equiv S_0/N$ in the LMG model at $\lambda = 0.5J$ and $\gamma = 0.5$ as a function of the temperature for different system sizes, $N = 50, 200, \infty$. We can see that the entropy is monotonic function of the temperature, which thus supports lemma 2. From Figure 2, one can see that the range of density $s_0 \equiv S_0/N$ ($0 < s_0 < 1$) is much smaller than the range of the corresponding control parameter, temperature ($0 < T < \infty$).

Figure 3 presents the equilibrium density per spin $h_1 \equiv \langle H \rangle/N$ in the LMG model at temperature $T/J = 0.8$ as a function of the control parameter $\lambda$ for different system sizes, $N = 50, 200, \infty$. We can see that the density $h_1$ is a monotonic function of the control parameter $\lambda$ and it thus supports the lemma 2. From figure 3, we can see that the range of density $h_1 \equiv \langle H \rangle/N$ ($-1 < h_1 < 1$) is much smaller than the range of the corresponding control parameter, magnetic field ($-\infty < \lambda < \infty$).

In Figure 4, we show the behavior of order parameter as a function of entropy, where we use entropy as a fundamental variable. In Figure 4(a), we present $\langle \sigma \rangle$ as a function of entropy per spin $s_0 \equiv S_0/N$ in the LMG model at $N \to \infty$ with $\lambda = 0.5J$ and $\gamma = 0.5$. One can see that the order parameter vanishes when entropy approaches a critical value $s_0 = 0.562335$ which corresponds to the critical temperature $T_c = \lambda/\tanh^{-1} \lambda$ with $\lambda = 0.5$. Since the phase transitions in LMG model are of second order, according to theorem 3, one need to evaluate the first derivative of physical observable. In figure 4(b), we show $\partial \langle \sigma \rangle / \partial s_0$ versus $s_0$ in the LMG model at $N \to \infty$ with $\lambda = 0.5J$ and $\gamma = 0.5$. One can see that $\partial \langle \sigma \rangle / \partial s_0$ diverges when entropy approaches a critical value $s_0 = 0.562335$.

In Figure 5, we use density $\langle H \rangle$ as a fundamental variable. In figure 5 (a), we show the order parameter $\langle \sigma \rangle$ as a function of density per spin $h_1 \equiv \langle H \rangle/N$ in the LMG model at $N \to \infty$ with $T = 0.8J$ and $\gamma = 0.5$. One can
see that the order parameter vanishes as density approaches a critical value $h_1 = 0.710412$ which corresponds to the critical fields at temperature $T = 0.8J$ and $\gamma = 0.5$. In figure 5(b), we present $\partial \langle \sigma^x_1 \rangle / \partial h_1$ as a function of density per spin $\langle h_1 \rangle / N$ in the LMG model at $N \to \infty$ with $T = 0.8J$ and $\gamma = 0.5$. One can see that $\partial \langle \sigma^x_1 \rangle / \partial h_1$ diverges when $h_1$ approaches a critical value $h_1 = 0.710412$.

Compared to the traditional field dependence approach [27, 29], using the density as a fundamental variable has some advantages. First, the range of the density is much smaller than the range of corresponding control parameter (See figures 2 and 3). Second, it is more clear that the non-analytic behavior of the physical observable at phase transition point is inherited from the non-analytic behavior of the free energy (equations (32) and (33)).

Now we evaluate an entanglement measure, namely the concurrence of two spins in the LMG model at zero magnetic field, which is given by (See appendix C for derivations)

$$M = \max[0, C_1, C_2],$$

where

$$C_1 = |C| - |A| = \langle \sigma^x_1 \sigma^y_1 \rangle + \langle \sigma^z_1 \sigma^z_1 \rangle - \langle \sigma^x_1 \sigma^x_1 \rangle - \frac{1}{4},$$

$$C_2 = |D| - |B|,$$

$$= \begin{cases} 
\frac{1}{4} + \frac{4N^2 - 3N}{N^2 - N} & \langle \sigma^z_1 \sigma^z_1 \rangle < \frac{1}{4}, \\
\frac{4N^2 - 3N}{N^2 - N} & \langle \sigma^z_1 \sigma^z_1 \rangle > \frac{1}{4}. 
\end{cases}$$
We can see that the concurrence is a universal functional of the first derivatives of the free energy, $\partial_l F$ and $\partial_T F$, this supports our theorem 2.

4.2. One-dimensional quantum XY model

Here we study a short range spin model, namely, the one-dimensional (1D) quantum transverse field XY model. The Hamiltonian of the 1D quantum XY model is

$$
H = J \sum_{j=1}^{N} (\sigma_j^x \sigma_{j+1}^x + \gamma \sigma_j^y \sigma_{j+1}^y + \lambda \sigma_j^z),
$$

where $J$ is the coupling strength between nearest neighbor spins and we set $J = 1$ for simplicity, $\lambda$ is a dimensionless parameter measuring the strength of transverse field along $z$ direction, $\sigma_j^\alpha (\alpha = x, y, z)$ is the Pauli operator acting at the $j$th spin and periodic boundary conditions are imposed by requiring that $\sigma_0 = \sigma_N$.

The critical points of this model are given by the points $\lambda = \pm 1$.

The 1D quantum transverse XY model can be diagonalized through three consecutive transformations, i.e. the Jordan–Wigner transformation, Fourier transformation and Bogoliubov transformation [30, 31]. The Hamiltonian finally becomes a collection of quasi-free fermions in momentum space,

$$
H (\lambda) = \sum_k \epsilon_k (b_k^\dagger b_k - 1/2),
$$

where $b_k$, $b_k^\dagger$ are the fermion annihilation and creation operators of momentum $k$,

$$
\epsilon_k = 2\sqrt{(1 + \gamma) \cos k - \lambda^2 + (1 - \gamma)^2 \sin^2 k}
$$

is the excitation spectrum. Then the partition function can be evaluated,

$$
Z (\beta, \lambda) = \prod_k 2 \cosh [\beta \epsilon_k / 2].
$$

From the partition function we can evaluate all the physical quantities. The density that corresponds to control parameters $\lambda$ and $T$ are respectively given by

![Figure 4. Entropy as a fundamental variable: (a). Order parameter $\langle \sigma_j^x \rangle$ as a function of entropy per spin $s_0 = \frac{S}{N}$ in the LMG model at $N \to \infty$ with $\lambda = 0.5$ and $\gamma = 0.5$. (b). $\partial_s \langle \sigma_j^x \rangle$ versus $s_0 = \frac{S}{N}$ in the LMG model at $N \to \infty$ with $\lambda = 0.5$ and $\gamma = 0.5$. The critical value of the entropy per spin is $s = 0.562335$ which corresponds to the critical temperature $T_c = \lambda / \tanh^{-1} \lambda$ with $\lambda = 0.5$.](image-url)
\[ \langle H_h \rangle = \sum_k \frac{(1 + \gamma) \cos k - \lambda}{\sqrt{(1 + \gamma) \cos k - \lambda^2 + (1 - \gamma)^2 \sin^2 k}} \tanh[\beta \epsilon_k/2], \] (56)

and

\[ S_0 = \sum_k \ln(2 \cosh(\beta \epsilon_k/2)) = \sum_k (\epsilon_k/2T) \tanh(\beta \epsilon_k/2). \] (57)

The nearest neighbor correlation function can be calculated to be,

\[ \langle \sigma^x_j \sigma^x_{j+1} \rangle = -\frac{1}{Nf} \left[ -\sum_k \frac{\epsilon_k}{2} \tanh[\beta \epsilon_k/2] \right. \]
\[ + \sum_k \tanh[\beta \epsilon_k/2] \frac{\gamma \cos 2k - (2\gamma + 1) \lambda \cos k + \gamma^2 + \lambda^2}{\sqrt{(1 + \gamma) \cos k - \lambda^2 + (1 - \gamma)^2 \sin^2 k}} \left. \right]. \] (58)

In figure 6, we show the nearest neighbor correlation function \( \langle \sigma^x_j \sigma^x_{j+1} \rangle \) as a function of entropy in the 1D quantum XY model, where we use entropy as a fundamental variable. In figure 6(a), we present \( \langle \sigma^x_j \sigma^x_{j+1} \rangle \) as a function of entropy per spin \( s_0 \equiv S_0/N \) in the XY model at \( N \to \infty \) with \( \lambda = 0.5 \) and \( \gamma = 0.5 \). One can see that the correlation function decreases as entropy increases because the ferromagnetic correlation decreases as the temperature increases. In figure 6(b), we show \( \partial \langle \sigma^x_j \sigma^x_{j+1} \rangle / \partial s_0 \) versus \( s_0 \) in the XY model at \( N \to \infty \) with \( \lambda = 0.5 \) and \( \gamma = 0.5 \). One can see that \( \partial \langle \sigma^x_j \rangle / \partial s_0 \) is a smooth function when entropy increases because there is no finite temperature phase transitions in the quantum XY model. Or one may say that the critical temperature in the quantum XY model is 0. According to equation (32), the nonanalytic behavior in the correlation function is inherited from the nonanalytic behavior of free energy as a function of temperature \( \partial F / \partial T \).

In figure 7, we use density \( \langle H_h \rangle \) as a fundamental variable. In figure 7 (a), we show the nearest neighbor correlation function \( \langle \sigma^x_j \sigma^x_{j+1} \rangle \) as a function of density per spin \( h_1 \equiv \langle H_h \rangle / N \) in the XY model at \( N \to \infty \) with \( T = 0.001 \) and \( \gamma = 0.5 \). One can see that the correlation decreases as density increases. In figure 7(b), we...
present $\partial (\sigma_j^x \sigma_{j+1}^x) / \partial h_1$ as a function of density per spin $h_1 \equiv (H_1) / N$ in the XY model at $N \to \infty$ with $T = 0.001$ and $\gamma = 0.5$. One can see that $\partial (\sigma_j^x \sigma_{j+1}^x) / \partial h_1 = 0$. According to equation (33), the nonanalytic behavior in the correlation function is inherited from the nonanalytic behavior of free energy as a function of magnetic field $\frac{\partial F}{\partial N}$ (figure 8).

Now we calculate an entanglement measure, the concurrence in the quantum XY model, which is given by (See appendix D for derivations)

$$M \equiv \max[0, C_1, C_2],$$

where

$$C_1 = \langle \sigma_j^x \sigma_{j+1}^x \rangle - \langle \sigma_j^x \rangle \langle \sigma_{j+1}^x \rangle + \langle \sigma_j^y \sigma_{j+1}^y \rangle - \frac{1}{4},$$

$$= -\frac{1}{4} - \frac{1}{N^2} \left[ F + T \frac{\partial F}{\partial T} - (1 + \gamma) \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right] + \frac{1}{N^2} \left[ \left( \frac{\partial F}{\partial \lambda} \right)^2 - \frac{\partial F}{\partial \gamma} \left( F + T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right) \right],$$

$$C_2 = \langle \sigma_j^x \sigma_{j+1}^x \rangle + \langle \sigma_j^y \sigma_{j+1}^y \rangle - \sqrt{(1/4 + \langle \sigma_j^x \sigma_{j+1}^x \rangle^2 - \langle \sigma_j^y \rangle^2)},$$

$$= -\frac{1}{N^2} \left[ F + T \frac{\partial F}{\partial T} - (1 - \gamma) \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right] - \sqrt{\left[ \frac{1}{4} + \frac{1}{N^2} \left( \frac{\partial F}{\partial \lambda} \right)^2 - \frac{\partial F}{\partial \gamma} \left( F + T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right) \right] + \left( \frac{1}{N^2} \frac{\partial F}{\partial \lambda} \right)^2}.$$

Figure 6. Entropy as a fundamental variable: (a). Nearest neighbor correlation function $\langle \sigma_j^x \sigma_{j+1}^x \rangle$ as a function of entropy per spin $s_0 \equiv s / N$ in the quantum XY model at $N \to \infty$ with $\lambda = 0.5$ and $\gamma = 0.5$. (b) $\partial (\sigma_j^x \sigma_{j+1}^x) / \partial h_1$ versus $s_0 \equiv s / N$ in the quantum XY model at $N \to \infty$ with $\lambda = 0.5$ and $\gamma = 0.5$. The critical value of the entropy per spin is $s = 0$ which corresponds to the critical temperature $T_c = 0$. 

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Thus one can see that the concurrence is a universal functional of the first derivatives of the free energy, \( \partial_x F, \partial_y F \) and \( \partial_t F \); this supports our theorem 2.

4.3. Discussions

In the above, we have investigated two simple models (analytic solvable) to demonstrate the central ideas in sections 2 and 3. For more realistic physical systems, such as the Heisenberg model or Hubbard models in various dimensions, our central results (theorems 1 and 2) are also valid. For example for the anisotropic...
Heisenberg model of interacting spins in an arbitrary lattice,
\[
H(\Delta) = -\sum_{\langle ij \rangle} [\sigma_i^x \sigma_j^x + \sigma_i^y \sigma_j^y + \Delta \sigma_i^z \sigma_j^z],
\]
(60)
\[
\Delta = H_0 + \Delta H_i.
\]
(61)
According to lemma 2, finite temperature average \(\sum_{\langle ij \rangle} \langle \sigma_i^x \sigma_j^x \rangle\) and \(\Delta\) are one-to-one mapped, then one can use \(\sum_{\langle ij \rangle} \langle \sigma_i^x \sigma_j^x \rangle\) as a fundamental variable in place of \(\Delta\). For the anisotropic Heisenberg model, theorem 1 reveals that the canonical density matrix is a universal function of the first derivative free energy with respect to temperature and \(\Delta\), i.e. \(\rho_0(\partial F/\partial T, \partial F/\partial \Delta)\). Then the nonanalytic behavior of an arbitrary physical observable \(O\), which satisfies \([O, H] \neq 0\), is inherited from the nonanalytic behavior of the free energy if \(\partial \langle O \rangle / \partial (H_i) \neq 0\) and \(\partial \langle O \rangle / \partial S_0 = 0\), both of which can be extracted from the experimental measurement of \(\langle H_0 \rangle, \langle O \rangle, S_0\). Similarly, for the anisotropic Heisenberg model, theorem 2 states that any entanglement measure is a universal function of the first derivative free energy with respect to temperature and \(\Delta\), i.e. \(M(\partial F/\partial T, \partial F/\partial \Delta)\), the nonanalytic behavior of the free energy with respect to parameters shall leave a footprint in the entanglement measure.

In this work, we focused on the canonical ensemble. It should be also possible to study a quantum many-body system in the grand canonical ensemble. Besides temperature and the control parameters in the Hamiltonian, one needs to consider the chemical potential as a new control parameter. Then formulation of theorems 1 and 2 in the grand canonical ensemble is straightforward.

5. Summary

In summary, we show that DFT provides insights for phase transitions and entanglement at finite temperatures. We proved that the equilibrium state of an interacting quantum many-body system which is in thermal equilibrium with a heat bath at a fixed temperature is a universal functional of the first derivatives of the free energy with respect to temperature and other control parameters. This insight from DFT enables us to express the average value of any observable and any entanglement measures at nonzero temperature in terms of the first derivatives of the free energy with respect to temperature and other control parameters. These results from DFT give new insights for phase transitions and provide new profound connections between entanglement and phase transition in interacting quantum many-body physics.

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Appendix A. Proof the free energy functional is lower bounded by the equilibrium free energy

In this appendix we show that the free energy functional
\[
F[T, \{ \lambda_i \}, \rho] = \text{Tr}[\rho(H(\{ \lambda_i \}) + k_B T \ln \rho)],
\]
(62)
satisfies
\[
F[T, \{ \lambda_i \}, \rho] > F[T, \{ \lambda_i \}, \rho_0], \rho \equiv \rho_0
\]
(62)
for all positive definite density matrices \(\rho\) with unit trace and \(\rho_0\) is the equilibrium state corresponds to the control parameters \((T, \{ \lambda_i \})\). To prove the inequality, we first define an assistant parameter \(g\) dependent density matrix, \(\rho_g \equiv \frac{e^{-\beta[H(\{\lambda_i\}) + gO]}}{\text{Tr}[e^{-\beta[H(\{\lambda_i\}) + gO]}]}\),
(63)
with
\[
O \equiv -\frac{1}{\beta} \ln \rho - H(\{ \lambda_i \}).
\]
(64)
Note that \(g\) is an assistant parameter and moreover,
\[
\rho_{g=0} = \rho_0 = \frac{e^{-\beta[H(\{\lambda_i\})]}}{\text{Tr}[e^{-\beta[H(\{\lambda_i\})]}]},
\]
(65)
\[
\rho_{g=1} = \rho.
\]
(66)
We want to show that if $r \neq 0$, 
\[ F[T, \{ \lambda_i \}, \rho] > F[T, \{ \lambda_i \}, \rho_0]. \] (A7)
For simplicity of notation, we shall not write out explicitly the control parameter dependence in the free energy hereafter as they are fixed. Because
\[ F[\rho] - F[\rho_0] = \int_0^\beta \frac{\partial F[\rho_k]}{\partial g} \, dg. \] (A8)
To evaluate $\partial_2 F[\rho_k]$, we write out
\[ F[\rho_k] = \text{Tr}[\rho_k (H (\{ \lambda_i \}) + k_B T \ln \rho_k)]. \] (A9)
Thus
\[ \partial_2 F[\rho_k] = \text{Tr}[\partial_2 \rho_k (H (\{ \lambda_i \}) + k_B T \ln \rho_k)], \] (A10)
\[ = -g \text{Tr}[O \partial_2 \rho_k]. \] (A11)
Using the operator identity [28]
\[ \frac{\partial}{\partial g} e^{-\beta (H + g O)} = -e^{-\beta (H + g O)} \int_0^\beta du O(u), \] (A12)
where $O(u) \equiv e^{u(H + g O)} O e^{-u(H + g O)}$, we have
\[ \partial_2 \rho_k = -\int_0^\beta du \rho_k O(u) + \rho_k \int_0^\beta du \text{Tr}[\rho_k O(u)], \] (A13)
So
\[ \partial_2 F[\rho_k] = -g \text{Tr}[O \partial_2 \rho_k], \] (A14)
\[ = g \int_0^\beta du \text{Tr}[\rho_k O(u) O] - g \text{Tr}[\rho_k O] \int_0^\beta du \text{Tr}[\rho_k O(u)], \] (A15)
\[ = g \int_0^\beta du \{ \langle O(u) O \rangle_k - \langle O(u) \rangle_k \langle O \rangle_k \}, \] (A16)
\[ = g \int_0^\beta du \{ \langle O(u) O \rangle_k - \langle O \rangle_k \langle O \rangle_k \}, \] (A17)
\[ = g \int_0^\beta du \{ \langle O(u/2) O(u/2) \rangle_k - \langle O \rangle_k \}, \] (A18)
Note that all the expectation values are performed with respect to $\rho_k$. Therefore we finally have
\[ F[\rho] - F[\rho_0] = g \int_0^\beta du \{ \langle O(u/2) - \langle O \rangle_k \rangle_k O(u/2) - \langle O \rangle_k \}, \geq 0. \] (A19)
The equality holds if and only if $O \propto I$, in this case $\rho = \rho_0$.

**Appendix B. Mean field theory of LMG model**

Here we give the mean field theory of LMG model. We consider the LMG model with Hamiltonian
\[ H(\lambda) = -\frac{1}{N} \sum_{1 \leq i < j \leq N} (\sigma_i^x \sigma_j^x + \gamma \sigma_i^z \sigma_j^z) - \lambda \sum_j \sigma_j^z, \] (B1)
Defining $M_n \equiv \langle \sum_j \sigma_j^n \rangle / N$, $\alpha = x, y, z$, the Hamiltonian can be rewritten as
\[ H(\lambda) = -\frac{1}{2N} \sum_{ij} [(\sigma_i^x - M_x)(\sigma_j^x - M_x) + \gamma (\sigma_i^z - M_z)(\sigma_j^z - M_z)] + M_x (\sigma_i^x + \sigma_j^x) + \gamma M_y (\sigma_i^z + \sigma_j^z) - (M_x^2 - \gamma M_y^2) - \lambda \sum_j \sigma_j^z. \] (B2)
Making mean field approximations and setting the quadratic term vanishes, we get the mean field Hamiltonian
\[ H_{MF} = -\sum_j M_x \sigma_j^x + \gamma M_y \sigma_j^z - \frac{1}{2} (M_x^2 + \gamma M_y^2) + \lambda \sigma_j^z, \] (B3)
where we set $f = 1$. The mean field Hamiltonian is set of decoupled single Pauli spins and can be easily solved with the following eigenvalues

$$E_{k} = \pm \sqrt{M_{x}^{2} + \gamma^{2}M_{y}^{2} + \lambda^{2}} \equiv \pm \varepsilon. \quad (B4)$$

The corresponding eigenvectors are

$$|\psi_{+}\rangle = \frac{-(M_{x} - i\gamma M_{y})|\uparrow\rangle + (E_{x} + \lambda)|\downarrow\rangle}{\sqrt{M_{x}^{2} + \gamma^{2}M_{y}^{2} + (E_{x} + \lambda)^{2}}} , \quad (B5)$$

$$|\psi_{-}\rangle = \frac{-(M_{x} + i\gamma M_{y})|\uparrow\rangle + (E_{x} - \lambda)|\downarrow\rangle}{\sqrt{M_{x}^{2} + \gamma^{2}M_{y}^{2} + (E_{x} - \lambda)^{2}}} . \quad (B6)$$

Then the self consistent equations for $M_{x}$, $M_{y}$, $M_{z}$ are, respectively

$$M_{x} = \frac{M}{\varepsilon} \tanh[\beta \varepsilon], \quad (B7)$$

$$M_{y} = \frac{\gamma M}{\varepsilon} \tanh[\beta \varepsilon], \quad (B8)$$

$$M_{z} = \frac{\lambda}{\varepsilon} \tanh[\beta \varepsilon]. \quad (B9)$$

Now the phase diagram can be extracted:

**B.1. Physical quantities at $0 < \gamma < 1$**

For $T < T_{c}$, the system is in a Ferromagnetic state along $x$ directions, $M_{y} = 0$ and $M_{x} \neq 0$, then the self-consistent equations reduce to

$$\frac{\tanh[\beta \sqrt{M_{x}^{2} + \lambda^{2}}]}{\sqrt{M_{x}^{2} + \lambda^{2}}} = 1,$$

$$M_{x} = \lambda. \quad (B10)$$

The critical temperature $T_{c}$ is obtained by making $M_{x} \rightarrow 0$, which is

$$T_{c} = \frac{\lambda}{\tanh^{-1} \lambda}. \quad (B12)$$

For $T > T_{c}$, $M_{x} = M_{y} = 0$, and the self consistent equations reduce to

$$M_{z} = \tanh \beta \lambda. \quad (B13)$$

Thus the control parameter is given by

$$\lambda = \begin{cases} \frac{(H_{0})}{N}, & T < T_{c}; \\ \frac{1}{\beta} \tanh^{-1} \left( \frac{(H_{0})}{N} \right), & T > T_{c}. \end{cases} \quad (B14)$$

The entropy per spin for $T < T_{c}$ is

$$s = \frac{S}{N} = -\frac{\varepsilon^{2}}{T} + \ln \left[ \frac{2}{\sqrt{1-\varepsilon^{2}}} \right], \quad (B15)$$

where $\varepsilon = \sqrt{M_{x}^{2} + \lambda^{2}}$. If $T > T_{c}, \varepsilon = \lambda$, the entropy becomes

$$s = \frac{S}{N} = -\frac{\lambda^{2}}{T} + \ln \left[ \frac{2}{\sqrt{1-\lambda^{2}}} \right]. \quad (B16)$$

Thus the temperature is given in terms of entropy by

$$T = \begin{cases} \frac{\varepsilon^{2}}{\ln \left( \frac{2}{\sqrt{1-\varepsilon^{2}}} \right) - \frac{S}{N}}, & T < T_{c}; \\ \frac{\lambda^{2}}{\ln \left( \frac{2}{\sqrt{1-\lambda^{2}}} \right) - \frac{S}{N}}, & T > T_{c}. \end{cases} \quad (B17)$$
B.2. Physical quantities at $\gamma > 1$

For $T < T_c$, the system is in a Ferromagnetic state along $y$ direction, $M_y = 0$ and $M_x = 0$, then the self consistent equations reduce to

$$1 = \frac{\gamma \tanh[\beta \sqrt{\gamma^2 M_y^2 + \lambda^2}]}{\sqrt{\gamma^2 M_y^2 + \lambda^2}},$$

$$M_z = \frac{\lambda}{\gamma}.$$  \hspace{1cm} (B18)

The critical temperature is obtained by making $M_y \to 0$, which is

$$T = \frac{\lambda}{\tanh^{-1}(\lambda/\gamma)}.$$  \hspace{1cm} (B20)

For $T > T_c$, the system is a paramagnetic state, i.e. $M_x = M_y = 0$, the self consistent equations become

$$M_z = \tanh[\beta \lambda].$$  \hspace{1cm} (B21)

Thus the control parameter is given by

$$\lambda = \begin{cases} \frac{\gamma \langle H_i \rangle}{N}, & T < T_c; \\ \frac{1}{\beta} \tanh^{-1} \frac{\langle H_i \rangle}{N}, & T > T_c. \end{cases}$$ \hspace{1cm} (B22)

The entropy per spin for $T < T_c$ is

$$s = \frac{S}{N} = -\frac{\varepsilon^2}{\gamma^2 T} + \ln \left[\frac{2}{\sqrt{1 - \varepsilon^2/\gamma^2}}\right],$$

where $\varepsilon = \sqrt{M_y^2 + \lambda^2}$. If $T > T_c$, $\varepsilon = \lambda$, the entropy becomes

$$s = \frac{S}{N} = -\frac{\lambda^2}{\gamma^2 T} + \ln \left[\frac{2}{\sqrt{1 - \lambda^2/\gamma^2}}\right].$$ \hspace{1cm} (B24)

Thus the temperature is given in terms of entropy by

$$T = \begin{cases} \frac{\varepsilon^2/\gamma^2}{\ln \frac{2}{\sqrt{1 - \varepsilon^2/\gamma^2}} - \frac{s}{N}}, & T < T_c; \\ \frac{\lambda^2/\gamma^2}{\ln \frac{2}{\sqrt{1 - \lambda^2/\gamma^2}} - \frac{s}{N}}, & T > T_c. \end{cases}$$ \hspace{1cm} (B25)

Appendix C. Derivation of thermal concurrence of two spins in LMG model

Here we give the derivation of thermal concurrence of two spins in LMG model. We consider the LMG model at zero magnetic field with Hamiltonian

$$H = -\frac{J}{N} \sum_{i<j} \sigma_i^z \sigma_j^z + \gamma \sigma_i^z \sigma_j^z.$$ \hspace{1cm} (C1)

To calculate the concurrence, we first reconstruct the two-body reduced density matrix. According to the symmetry of the LMG model, the reduced density matrix for two sites can be written as

$$\rho_{ij} = \begin{pmatrix} A & 0 & 0 & D \\ 0 & B & C & 0 \\ 0 & C & B & 0 \\ D & 0 & 0 & A \end{pmatrix},$$ \hspace{1cm} (C2)

where

$$A = \frac{1}{4} + \langle \sigma_i^z \sigma_j^z \rangle,$$ \hspace{1cm} (C3)

$$B = \frac{1}{4} - \langle \sigma_i^z \sigma_j^z \rangle,$$ \hspace{1cm} (C4)
All the correlation functions can be obtained from free energy
\[ \langle \sigma_j^+ \sigma_{j+1}^- \rangle = -\frac{2}{(N-1)} \left[ F + T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} \right], \]
\[ \langle \sigma_j^- \sigma_{j+1}^+ \rangle = -\frac{2}{(N-1)} \frac{\partial F}{\partial \gamma}, \]
\[ \langle \sigma_j^x \sigma_{j+1}^y \rangle = \frac{4\langle S_j^z \rangle - 3N}{N^2 - N} + \frac{2}{(N-1)} \left[ F + T \frac{\partial F}{\partial T} + (1 - \gamma) \frac{\partial F}{\partial \gamma} \right]. \]

So the matrix elements of the two-body reduced density matrix is
\[ A = \frac{1}{4} + \frac{4\langle S_j^z \rangle - 3N}{N^2 - N} + \frac{2}{(N-1)} \left[ F + T \frac{\partial F}{\partial T} + (1 - \gamma) \frac{\partial F}{\partial \gamma} \right], \]
\[ B = \frac{1}{4} - \frac{4\langle S_j^z \rangle - 3N}{N^2 - N} - \frac{2}{(N-1)} \left[ F + T \frac{\partial F}{\partial T} + (1 - \gamma) \frac{\partial F}{\partial \gamma} \right], \]
\[ C = -\frac{2}{(N-1)} \left[ F + T \frac{\partial F}{\partial T} + (1 - \gamma) \frac{\partial F}{\partial \gamma} \right], \]
\[ D = -\frac{2}{(N-1)} \left[ F + T \frac{\partial F}{\partial T} + (1 + \gamma) \frac{\partial F}{\partial \gamma} \right]. \]

Then the thermal concurrence is given by [29]
\[ M \equiv \max \{0, C_0, C_1\}, \]

where
\[ C_0 = |C| - |A| = \langle \sigma_j^+ \sigma_{j+1}^+ \rangle - \langle \sigma_j^- \sigma_{j+1}^- \rangle - \frac{1}{4}, \]
\[ C_1 = |D| - |B|, \]
\[ \langle \sigma_j^x \sigma_{j+1}^y \rangle < \frac{1}{4}; \]
\[ \langle \sigma_j^z \sigma_{j+1}^z \rangle > \frac{1}{4}. \]

**Appendix D. Derivation of thermal concurrence of two nearest neighbor spins in the quantum XY model**

Here we give the derivation of thermal concurrence of two spins in LMG model. We consider the LMG model at zero magnetic field with Hamiltonian
\[ H = -J \sum_{j=1}^{N} [\sigma_j^x \sigma_{j+1}^x + \gamma \sigma_j^y \sigma_{j+1}^y + \lambda \sigma_j^z], \]

To calculate the concurrence, we first reconstruct the two-body reduced density matrix of two nearest neighbor spins. According to the symmetry of the XY model, the reduced density matrix for two nearest neighbor sites can be written as
\[ \rho_{j,j+1} = \begin{pmatrix} A & 0 & 0 & G \\ 0 & B & C & 0 \\ 0 & C & B & 0 \\ G & 0 & 0 & D \end{pmatrix}, \]

where
\[ A = \frac{1}{4} + 2 \langle \sigma_j^+ \rangle + \langle \sigma_j^+ \sigma_{j+1}^+ \rangle, \]

\[ B = \frac{1}{4} - 2 \langle \sigma_j^- \rangle + \langle \sigma_j^- \sigma_{j+1}^- \rangle, \]

\[ C = -\frac{1}{4} \]
\[ D = -\frac{1}{4} \]
\[ G = \frac{1}{4} \]
\[ H = -\frac{1}{4} \]
\[ J = -\frac{1}{4} \]
\[ K = -\frac{1}{4} \]
\[ L = -\frac{1}{4} \]
\[ M = -\frac{1}{4} \]
\[ N = -\frac{1}{4} \]
\[ O = -\frac{1}{4} \]
\[ P = -\frac{1}{4} \]
\[ Q = -\frac{1}{4} \]
\[ R = -\frac{1}{4} \]
\[ S = -\frac{1}{4} \]
\[ T = -\frac{1}{4} \]
\[ U = -\frac{1}{4} \]
\[ V = -\frac{1}{4} \]
\[ W = -\frac{1}{4} \]
\[ X = -\frac{1}{4} \]
\[ Y = -\frac{1}{4} \]
\[ Z = -\frac{1}{4} \]
\[ B = \frac{1}{4} - \langle \sigma_j^z \sigma_{j+1}^z \rangle, \quad \text{(D4)} \]
\[ C = \langle \sigma_j^x \sigma_{j+1}^x \rangle + \langle \sigma_j^y \sigma_{j+1}^y \rangle. \quad \text{(D5)} \]
\[ D = \frac{1}{4} - 2 \langle \sigma_j^z \rangle + \langle \sigma_j^z \sigma_{j+1}^z \rangle, \quad \text{(D6)} \]
\[ G = \langle \sigma_j^x \sigma_{j+1}^x \rangle - \langle \sigma_j^x \sigma_{j+1}^x \rangle. \quad \text{(D7)} \]

All the correlation functions can be obtained from free energy
\[ \langle \sigma_j^z \rangle = -\frac{1}{N J} \frac{\partial F}{\partial \lambda}, \quad \text{(D8)} \]
\[ \langle \sigma_j^x \sigma_{j+1}^x \rangle = -\frac{1}{N J} \left[ F - T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right], \quad \text{(D9)} \]
\[ \langle \sigma_j^y \sigma_{j+1}^y \rangle = -\frac{1}{N J} \frac{\partial F}{\partial \gamma}, \quad \text{(D10)} \]
\[ \langle \sigma_j^z \sigma_{j+1}^z \rangle = \frac{1}{N J^2} \left[ \left( \frac{\partial F}{\partial \lambda} \right)^2 - \frac{\partial F}{\partial \gamma} \left( F + T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right) \right]. \quad \text{(D11)} \]

So the matrix elements of the two-body reduced density matrix is
\[ A = \frac{1}{4} - \frac{2}{N J} \frac{\partial F}{\partial \lambda} + \frac{1}{N J^2} \left[ \left( \frac{\partial F}{\partial \lambda} \right)^2 - \frac{\partial F}{\partial \gamma} \left( F + T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right) \right], \]
\[ B = \frac{1}{4} - \frac{1}{N J^2} \left[ \left( \frac{\partial F}{\partial \lambda} \right)^2 - \frac{\partial F}{\partial \gamma} \left( F + T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right) \right], \]
\[ C = -\frac{1}{N J} \left[ F - T \frac{\partial F}{\partial T} + (1 - \gamma) \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right], \]
\[ D = \frac{1}{4} - \frac{2}{N J} \frac{\partial F}{\partial \lambda} + \frac{1}{N J^2} \left[ \left( \frac{\partial F}{\partial \lambda} \right)^2 - \frac{\partial F}{\partial \gamma} \left( F + T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right) \right], \]
\[ G = -\frac{1}{N J} \left[ F - T \frac{\partial F}{\partial T} + (1 + \gamma) \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right]. \]

Then the thermal concurrence is given by [29]
\[ M = \max \{0, C_1, C_2\}, \quad \text{(D12)} \]

where
\[ C_1 = \langle \sigma_j^x \sigma_{j+1}^x \rangle - \langle \sigma_j^x \sigma_{j+1}^x \rangle + \langle \sigma_j^x \sigma_{j+1}^x \rangle - \frac{1}{4}, \]
\[ = \frac{1}{4} - \frac{1}{N J} \left[ F + T \frac{\partial F}{\partial T} + (1 - \gamma) \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right], \]
\[ + \frac{1}{N J^2} \left[ \left( \frac{\partial F}{\partial \lambda} \right)^2 - \frac{\partial F}{\partial \gamma} \left( F + T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right) \right], \]
\[ C_2 = \langle \sigma_j^x \sigma_{j+1}^x \rangle + \langle \sigma_j^x \sigma_{j+1}^x \rangle - \sqrt{\frac{1}{4} + \langle \sigma_j^x \sigma_{j+1}^x \rangle^2} - \langle \sigma_j^x \sigma_{j+1}^x \rangle, \]
\[ = \frac{1}{N J} \left[ F + T \frac{\partial F}{\partial T} + (1 - \gamma) \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right], \]
\[ - \left( \frac{1}{4} + \frac{1}{N J^2} \left[ \left( \frac{\partial F}{\partial \lambda} \right)^2 - \frac{\partial F}{\partial \gamma} \left( F + T \frac{\partial F}{\partial T} - \gamma \frac{\partial F}{\partial \gamma} - \lambda \frac{\partial F}{\partial \lambda} \right) \right] \right) \right)^{1/2}. \]

References

[1] Hohenberg P and Kohn W 1964 Inhomogenous electron gas Phys. Rev. 136 B864
[2] Kohn W and Sham L J 1965 Self-consistent equations including exchange and correlation effects Phys. Rev. 140 A1133
[3] Jones R O 2015 Density functional theory: its origins, rise to prominence, and future Rev. Mod. Phys. 87 897
[4] Zangwill A 2015 A half-century of density functional theory Phys. Today 68 34
[5] Mermin N D 1965 Thermal properties of inhomogeneous electron gas Phys. Rev. 137 A1441
[6] Runge E and Gross E K U 1984 Density-Functional theory for time–dependent Systems Phys. Rev. Lett. 52 997
[7] Amico L, Fazio R, Osterloh A and Vedral V 2008 Entanglement in many-body systems Rev. Mod. Phys. 80 517
[8] Wu L A, Sarandy M S, Lidar D A and Sham L J 2005 Linking entanglement and quantum phase transitions from density-functional theory Phys. Rev. A 74 052335
[9] Nagy A, Calixto M and Romera E 2013 A density-functional view of quantum phase transitions J. Chem. Theory Comput. 9 1068
[10] Nagy A and Romera E 2013 Quantum phase transitions via density-functional theory: extension to the degenerate cases Phys. Rev. A 88 042515
[11] Jaynes E T 1957 Information theory and statistical mechanics Phys. Rev. 106 620
[12] Jaynes E T 1957 Information theory and statistical mechanics. II Phys. Rev. 108 171
[13] Capelle K and Vignale G 2001 Nonuniqueness of the potentials of spin-density-functional theory Phys. Rev. Lett. 86 5546
[14] Ulrich C A 2005 Nonuniqueness in spin-density-functional theory on lattices Phys. Rev. B 72 073102
[15] Capelle K and Vignale G 2002 Nonuniqueness and derivative discontinuities in density-functional theories for current-carrying and superconducting systems Phys. Rev. B 65 113106
[16] Iaconis J, Inglis S, Kallin A B and Melko R G 2013 Phys. Rev. B 87 195134
[17] Franca V V and Capelle K 2008 Entanglement in spatially inhomogeneous many-fermion systems Phys. Rev. Lett. 100 070403
[18] Capelle K and Campos V I Jr 2013 Density functionals and model hamiltonians: pillars of many-particle physics Phys. Rep. 528 91
[19] Coe J P, Sudbery A and D’Amico I 2008 Entanglement and density-functional theory: testing approximations on Hooke’s atom Phys. Rev. B 77 205122
[20] Coe J P, Franca V V and D’Amico I 2010 Hubbard model as an approximation to the entanglement in nanostructures Phys. Rev. A 81 052321
[21] Lipkin H J, Meshkov N and Glick A J 1965 Validity of many-body approximation methods for a solvable model: (I). Exact solutions and perturbation theory Nucl. Phys. 62 188
[22] Meshkov N, Glick A J and Lipkin H J 1965 Validity of many-body approximation methods for a solvable model: (II). Linearization procedures Nucl. Phys. 62 199
[23] Lipkin H J and Meshkov N 1965 Validity of many-body approximation methods for a solvable model: (III). Diagram summations Nucl. Phys. 62 211
[24] Porras D and Cirac J I 2004 Effective quantum spin systems with trapped ions Phys. Rev. Lett. 92 207901
[25] Friedenauer A, Schmitz H, Glueckert J T, Porras D and Schaeetz T 2008 Simulating a quantum magnet with trapped ions Nature Phys. 4 757
[26] Islam R et al 2011 Onset of a quantum phase transition with a trapped ion quantum simulator Nature comm. 2 377
[27] Quan H T and Cucchietti F M 2009 Quantum fidelity and thermal phase transitions Phys. Rev. E 79 031101
[28] Wilcoxon R M 1967 Exponential operators and parameter differentiation in quantum physics J. Math. Phys. 8 962
[29] Matera J M, Rossignoli R and Canosa N 2008 Thermal entanglement in fully connected spin systems and its RPA description Phys. Rev. A 78 012316
[30] Lieb E, Schultz T and Mattis D 1961 Two soluble models of an antiferromagnetic chain Ann. Phys. 16 407
[31] Suzuki M 1971 Relationship among exactly soluble models of critical phenomena. i: 2D Ising model, dimer problem and the generalized xy-model Prog. Theor. Phys. 46 1357