Modified Barrett formula near the neutral-ionic quantum phase transition

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Abstract. A quantum version of the Blume-Emery-Griffiths (BEG) model is investigated by mean-field theory in order to characterize the newly-found neutral-ionic (NI) quantum phase transition in pressured-DMTTF-QBr$_4$ (4,4'-dimethyltetrathiafulvalene-p-bromanil). In the quantum BEG model, a finite tunneling between neutral and ionic states changes the quantum NI transition of first order in the BEG model into that of second order. In the vicinity of this continuous NI quantum critical point, the dielectric permittivity in the neutral phase is shown to follow the Barrett formula characteristic of quantum paraelectricity. These features in the quantum BEG model are in good agreement with the experimental results, which suggests the importance of quantum NI fluctuations in DMTTF-QBr$_4$.

In organic mixed-stack charge-transfer paraelectrics 4,4'-dimethyltetrathiafulvalene-p-bromanil (DMTTF-QBr$_4$), a novel neutral-ionic (NI) phase transition of continuous nature takes place by substituting Cl for Br or by applying hydrostatic pressure[1, 2, 3, 4]. This is remarkable contrast to temperature- or pressure-induced discontinuous NI phase transitions in TTF-CA[5, 6]. In the neutral ground state of DMTTF-QBr$_4$, substantial ionicity still remains at the lowest temperature measured, which may suggest the importance of charge-transfer fluctuations of π electrons between the DMTTF donor and the QBr$_4$ acceptor molecules. Concerning the dielectric properties of pressured-DMTTF-QBr$_4$, a paraelectric to an anti-ferroelectric phase transition is observed at the same time with the NI transition. This is because the ionic state is always accompanied with donor(D)-acceptor(A) lattice dimerizations, implying strong interplay between charge and lattice degrees of freedom. In the vicinity of the NI quantum critical point (QCP), more interestingly, the temperature ($T$) dependence of the dielectric permittivity $\varepsilon(T)$ in the neutral phase follows the Barrett formula characteristic of quantum paraelectricity.

The Barrett formula is derived from the quantum Ising model defined by:

$$H_{\text{qIsing}} = - J \sum_{\langle i,j \rangle} \sigma^z_i \sigma^z_j - H \sum_i \sigma^x_i - E \sum_i \sigma^z_i,$$

where $\vec{\sigma}'s$ are the SU(2) Pauli matrices and $\sigma^z = \pm 1$ specifies the direction of local electric dipole. Applying the mean-field approximation to Eq. (1), the Barrett formula for dielectric permittivity is obtained to be:

$$\varepsilon(T) = \lim_{E \to 0} \frac{\langle \sigma^z \rangle}{E} = \frac{1}{H \coth(H/T) - 2J},$$

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where \( z \) is the coordination number. Note that the conventional notations of the Barrett formula correspond to \( H = T_{J}/2 \) and \( zJ = T_{0} \). In the high-temperature region, thermal fluctuations always overcome quantum fluctuations \( H \) to give the Curie-Weiss type of \( \epsilon(T) \sim 1/(T - zJ) \). With decreasing temperature, \( \epsilon(T) \) develops gradually but does not show any diverging behavior when \( H > zJ \), and saturates to the value of \( 1/(H - zJ) \) at \( T = 0 \). This is the typical dielectric behavior in quantum paraelectric systems, which is also observed in the neutral phase of DMTTF-QBr₄.

The spin-one analogue of the Ising model, so-called the Blume-Emery-Griffiths (BEG) model defined by Eq. (3) with \( H = 0 \), was originally introduced to investigate the superfluid-normal transition (\( \lambda \) transition) in \( ^{3}\text{He}-^{4}\text{He} \) mixture[7]. In that case, a \( ^{3}\text{He} \) atom and superfluid phases of \( ^{4}\text{He} \) are represented by \( S^{z} = 0 \) and \( \pm 1 \), respectively. In the application of the BEG model to NI systems[8, 9, 10], the spin-1 operator \( S^{z}_{i} \) specifies a neutral \( D^{\mp\rho_{N}}A^{\pm\rho_{N}} \) (\( S^{z}_{i} = 0 \)) or an ionic state with positive \( D^{\pm\rho_{N}}A^{-\rho_{N}} \) (\( S^{z}_{i} = +1 \)) or negative polarization \( A^{\pm\rho_{N}}D^{\pm\rho_{N}} \) (\( S^{z}_{i} = -1 \)), where the underlined DA pairs are dimerized so that the intra-dimer distance is shorter than that of the inter-dimer. \( \rho_{N} \) and \( \rho_{I} \) are the ionicity in neutral and ionic phases, respectively. It is well known that the mean-field analysis of the BEG model demonstrates many prototypical features of phase transition, such as critical points, tricritical points, and triple points, which characterize the superfluid-normal transition in \( ^{3}\text{He}-^{4}\text{He} \) mixture[7] or the NI transition in TTF-CA[8, 9].

After the example of the quantum Ising model, we have introduced a quantum version of the Blume-Emery-Griffiths (q-BEG) model defined by;

\[
\mathcal{H}_{\text{q-BEG}} = -J \sum_{(ij)} S^{x}_{i} S^{x}_{j} - K \sum_{(ij)} (S^{y}_{i})^{2} (S^{y}_{j})^{2} - P \sum_{i} (S^{z}_{i})^{2} - H \sum_{i} S^{z}_{i} - E \sum_{i} S^{z}_{i}, \tag{3}
\]

where \( S^{x}_{i} = (|1\rangle\langle 1| - | - 1\rangle\langle -1|)/\sqrt{2} \), \( S^{z}_{i} = (|1\rangle\langle 0| + |0\rangle\langle 1|)/\sqrt{2} \), and \( J(K) \) is the nearest-neighbor dipolar (quadrupolar) interaction. The energy difference between N and I states are specified by \( P \). The \( H \) and \( E \) terms denote the NI quantum tunneling and the external electric field, respectively. In the pressure-induced NI transition of DMTTF-QBr₄, hydrostatic or chemical pressure contracts average DA distances, which stabilizes the local ionic site more than the neutral one due to the Madelung-energy gain. Therefore, we assume that the experimental pressure effect can be taken in the q-BEG model by such a simplified interpretation that the larger \( P \) corresponds to higher pressure.

The ionic ground state for pressured-DMTTF-QBr₄ is of an antiferroelectric type, where the ferroelectric one-dimensional (1D) DA chains in \( c \) direction arrange in the staggered manner between neighboring chains, resulting the ordering vector of \( (\pi, \pi, 0) \). Experimental results indicate that the present system is a quasi-1D insulator and that inter-chain interactions such as \( J_{\perp} \) and \( K_{\perp} \) are expected to be small compared with those within each chain. In such a situation, \( J_{\perp} \) and \( K_{\perp} \) terms can be treated by chain mean-field theory only to give self-consistent fields in addition to \( E \) and \( H \) in the 1D model. Neglecting quantitative corrections due to \( J_{\perp} \) and \( K_{\perp} \) for simplicity, therefore, the 1D ferroelectric q-BEG model of Eq.(3) with \( J > 0 \) and \( z = 2 \) is investigated in the present study. When \( K \gg J \) the number of the neutral sites is negligible, which is inconsistent with the experimental situation. Accordingly, \( K/J \) is always assumed at 0.2 throughout this paper and \( E/J = 0 \) if not mentioned. Applying the uniform mean-field approximation to the 1D q-BEG model, we introduce the self-consistent fields of \( szJ + E \) and \( tzK + P \) each coupled to \( S^{z}_{i} \) and \( (S^{z}_{i})^{2} \), where \( s \equiv \langle S^{z}_{i} \rangle \) and \( t \equiv \langle (S^{z}_{i})^{2} \rangle \) measure the magnitudes of ferroelectricity and ionicity, respectively. Numerical diagonalization of the mean-field Hamiltonian is performed and we have determined the self-consistent order parameters of \( s \) and \( t \) as a function of \( P \), \( H \), and \( T \).

First of all, let us review results for the BEG model corresponding to the \( H = 0 \) case. In this case, a discontinuous quantum NI transition occurs at \( P_{c} = z(J + K)/2 \), which is inconsistent
with the experimental continuous phase transition in pressur ed-DMTTF-QBr$_4$. The ionicity at zero Kelvin is either zero or unity depending on $P < P_c$ or $P > P_c$, since no fluctuations between N and I states survive at $T = H = 0$. As is well known for the property of the BEG model[7], a tricritical point separates the NI phase boundary into the high-$T$ continuous and low-$T$ discontinuous parts. Around this tricritical point, the dielectric permittivity in the neutral phase shows a broad bump and does not follow the Barrett formula. This is because, in general, a susceptibility diverges at the second-order phase boundary, but does not when crossing the first-order transition line. These results strongly suggest the importance of quantum NI fluctuations, the $H$ term, which hybridizes N and I states even at zero temperature.

When the $H$ term is incorporated in the BEG model, the tricritical point is gradually suppressed to lower temperature. Generally in $H \gtrsim zJ$ regions, the tricritical point disappears and the NI phase boundary becomes the continuous line of second order as shown in Fig.1 for $H = 2.2J > zJ$. Around the NI QCP, the ionicity takes a fractional value between 0 and 1 even at zero temperature due to the quantum tunneling $H$ between N and I. In the neutral phase just below the NI transition line, furthermore, $\bar{\varepsilon}(T)$ follows the Barrett formula which is consistent with the experimental results. When $K = P = 0$, there is no local potential barrier between N and I states and thus the quantum tunneling between $S_z = 1$ and -1 is given by $H$ in analogy with the quantum Ising model. Accordingly, the Barrett formula modified due to the presence of the neutral state is obtained in the following analytic form:

$$\bar{\varepsilon}(T) = \frac{1}{2(1-\bar{t})} \coth \left( \frac{H}{T} \right) - zJ, \quad \text{where} \quad \bar{t} = \frac{1 + \cosh \left( \frac{H}{T} \right)}{1 + 2 \cosh \left( \frac{H}{T} \right)}. \quad (4)$$

In the $K = P = 0$ limit, therefore, $0 = H - zJ$ defines the QCP separating the N-paraelectric

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**Figure 1.** $(P,T)$ phase diagram for $H = 2.2J$ and $K = 0.2J$. The solid line indicates the 2nd order phase transition line. The QCP is located at $P_c = H - zJ - zK/2 = 0$ for $z = 2$. The inset graphs display the typical temperature dependence of $(s, t, \bar{\varepsilon})$ in the neutral ($P/J = -0.5$) and the ionic ($P/J = 1.0$) phases.
(H > zJ) and the I-ferroelectric (H < zJ) phases, as in the quantum Ising model. When the K and P terms are included, the effective NI potential barrier \( P + tzK \) should be compared with \( H - zJ \), as long as \( H \sim zJ \), in order to determine the NI phase boundary. In fact, the relation \( P_c = H - zJ - tzK \) is approximately confirmed at the quantum critical point around \( H = zJ \) (see Fig.1). Note that the quantity \( t_c \) is equal to 1/2 when \( H = zJ \), because in this case all effective mean fields, \( P_c + tzK \) and \( E_c + s_czK \), vanish and only the \(-HS_c \) term remains in the mean-field Hamiltonian, which gives the \((\langle |1| + \sqrt{2}\langle 0| + \langle | -1| \rangle)/2 \) ground state with \( s_c = 0 \) and \( t_c = 1/2 \).

In Fig. 2 shown are the pressure dependences of ferroelectricity (s), ionicity (t), and dielectric permittivity (e) as a function of temperature. Here we put \( H = 3.3J \) and \( K = 0.2J \). P is varied from 0 to 2.0 so as to get across the QCP of \( P_c \sim 1.1J \). In addition, a finite electric field of \( E = 0.07J \) is applied to prevent differential dielectric permittivity \( \varepsilon = ds/dE \) from diverging at \( T = T_c \) in order to compare with the experimental results. The shape of \( \varepsilon(T) \) in Fig.2 is quite similar to the experimentally observed dielectric permittivity in DMTTF-QBr\(_4\) under pressure[1]. In particular, the Barrett type \( \varepsilon(T) \) is obtained in the N phase, which follows the continuous peak evolution in \( \varepsilon(T) \) with further increase of \( P \) beyond \( P_c \). When we set \( J = 15K \), \((zJ, 2JH) = (30K, 99K) \) roughly corresponds to the experimental results of \( T_0 = 33K \) and \( T_1 = 96K \), although the peak positions in the ionic phase are factor 2 or 3 times smaller than those of the experimental results. This quantitative differences may originate from a difference between our \( P \) variable and experimental pressure and/or the inter-chain couplings we have neglected.

![Figure 2](image-url)

**Figure 2.** Order parameters (s, t) and dielectric permittivity \( \varepsilon(T) \) as a function of temperature \( T/J \), where \( H = 3.3J, K = 0.2J, E = 0.07J \) and \( P/J \) is varied with a step of 0.4 from 0 to 2.0. The arrows indicate the increment of applied pressure \( P \).

In conclusion we have studied the pressure-induced neutral-ionic quantum phase transition observed in quasi-1D mixed-stack organic complex DMTTF-QBr\(_4\). The conventional BEG model, which successfully describes the first-order NI phase transition in TTF-CA, fails to describe the continuous NI phase transition as well as the Barrett-type dielectric permittivity in the neutral phase of DMTTF-QBr\(_4\). Since the finite charge transfer experimentally observed even in the neutral phase suggest the importance of quantum fluctuations between N and I states, we have introduced the quantum tunneling \( H \) term between the N and the I states into the BEG model. The inclusion of \( H \) brings a finite mixing between the ground states and the meta-stable states, resulting in the second-order NI quantum phase transition when \( H \) exceeds the potential barrier between N and I states. Numerically, \( H \geq zJ \) is large enough to destroy the first-order transition and the continuous quantum phase transition takes place. Moreover, the
dielectric permittivity in the neutral phase close to this NI phase boundary roughly follows the Barrett formula which is consistent with the experimental findings. The detailed whole $H$-$P$-$T$ phase diagram will be published elsewhere.

In the present phenomenological model, the importance of the $H$ term is evident. However, the microscopic origin of such a quantum tunneling is still unclear. The $S_z$ variable in the q-BEG model consists of both charge transfer and lattice displacement in a $D^+\rho A^-\rho$ pair. Within the model, therefore, we cannot distinguish between charge dynamics and quantum phonon fluctuations, which may be possible origin of the $H$ term. Theoretical study for a microscopic model, dealing with both charge and lattice degrees of freedom separately, will be highly desired.

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