Quantum critical dynamics of electric dipoles in two-dimensions

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In the vicinity of the quantum critical point (QCP), thermodynamic properties diverge toward zero temperature, governed by universal exponents. Although this fact is well known, how it is reflected in quantum dynamics has never been addressed before. An ideal laboratory platform to test the issue is the organic Mott dielectrics because the dielectric degrees of freedom, a quantum electric dipole, is described by the transverse Ising model which has a QCP. We track the dynamics of the model by constructing a kinetic protocol based on the quantum Monte Carlo method. The dynamical susceptibility takes the form of the Debye function and shows a significant peak-narrowing in approaching a QCP due to the divergence of the relaxation timescale. It resembles the anomaly of dielectric constants observed in the organic materials $\kappa$-ET$_2$X dimer Mott insulating phase, indicating that the material is very near the ferroelectric QCP.

I. INTRODUCTION

Criticality is a phenomenon characterized by an algebraically growing fluctuation that spreads throughout the system and eventually manifests as a scale invariance of the physical properties. There, the thermodynamic properties such as specific heat and susceptibility diverge as the system approaches the second order phase transition point. In quantum many body systems, exponents of such divergence near the quantum critical point (QCP) is well known to follow the universality that has one extra dimension higher than the space dimension, where this additional dimensional degrees of freedom called imaginary time is responsible for the quantum fluctuation. The knowledge about the static criticality is thus established in both quantum and classical systems, providing reasonable interpretations to the the experimental observations in laboratories.

However, when we look at the dynamical properties, we do not know how they react to the enhanced quantum fluctuation near the QCP. The difficulty stems primarily from a lack of theoretical tools for evaluating linear response functions in quantum many body systems. Although it is naively expected that the dynamical exponents will also follow the universality with one extra dimension, quantum relaxation still remains hard to access even numerically.

In experiments, the dynamical response measurement in an applied field is a formally well-established technique. Observations at very low temperatures that appear to be influenced by quantum criticality have been reported from time to time, while unfortunately, they cannot be understood within the framework of available theories. One of the intriguing examples is the anomalous dielectric response in a series of triangular lattice Mott insulators, $\kappa$-(ET)$_2$X, $X=$Cu$_2$(CN)$_3$ and Cu[N(CN)$_2$]Cl. In these materials, the ET molecules are structurally dimerized and form a triangular lattice in the two dimensional (2D) conducting layer as shown in Fig. 1(a). Each dimer accommodates a single charge in a Mott insulating phase at low temperature due to strong intra-dimer electronic correlation. The former material is famous as possibly hosting a quantum spin liquid state in the same Mott insulating phase. Deep inside this Mott insulating phase, the dielectric function shows a peak at temperature that shifts significantly as the frequency is varied. Although such behaviour is reminiscent of relaxer ferroelectrics found typically in PMN, the frequency where the peak-shift is observed ranges much wider over more than two orders of magnitudes. Physically, the peak temperature roughly indicates the energy scale dominating the system, and a single divergent peak structure generally suggests a ferroelectric phase transition at that temperature. The observation of frequency dependent non-divergent peaks indicates a coexisting broad range distribution of characteristic time and energy scales. In relaxer ferroelectrics, this phenomenon had been attributed to the polar-nano region induced by the artificial impurity doping. However, the organic crystals are almost free of impurities.

The source of this Mott dielectrics in organic crystals is the quantum electric dipole – the degree of freedom of charge to stay at either of the dimerized two molecular orbitals. A good description of this degrees of freedom is provided by the transverse Ising (TRI) model, a canonical model of quantum computation and annealing as well as of condensed matter theory. Each charge fluctuates back and forth within the dimer by a quantum tunnelling (transfer integrals) (Fig. 1(a)), serving as a transverse field on the dipole, and the Coulomb interactions between the charges (dipoles) are the Ising interactions. If they align in the same direction, they yield a quantum ferroelectricity. The question is, what could be the reason for the coexisting massive range of energy scales within a uniform system at low temperature?, and could we clarify it via bottom up microscopic calculation on the TRI model without the aid of simplified and idealized phenomenology.

In the present article, we construct a kinetic protocol using quantum Monte Carlo (QMC) method, and obtain a dynamic susceptibility, $\chi(q = 0, \omega)$, of the TRI.
Due to the peak-narrowing of the Debye function, it takes a maximum at some $T$ dielectrics in the vicinity of the ferroelectric QCP critical dynamics, which is indeed detected in the organic material. Our results thus provide a signature of quantum invariance of the system. Therefore, we could access the experimentally observed phenomena without assumption once we get a reasonable

As shown in advance in Fig. 1(c), it takes the form of the Debye function at each fixed temperature $k_B T$ near QCP. Since its width and the height are given by $\tau^{-1}$ and $\chi_0$, respectively, the peak becomes high and sharp as the temperature is lowered toward QCP, as relaxation time $\tau$ and static susceptibility $\chi_0$ diverge algebraically. Accordingly, if we fix $\omega$ and plot the $k_B T$ dependence of the functions, it takes a maximum at some $T_m(\omega)$. Due to the peak-narrowing of the Debye function, $T_m(\omega)$ shifts significantly to lower temperature whenever we decrease $\omega$. The wide variation of $T_m(\omega)$ indicates the scale invariance of the system which is nothing but a criticality. Our results thus provide a signature of quantum critical dynamics, which is indeed detected in the organic dielectrics in the vicinity of the ferroelectric QCP.

II. MODEL AND FORMULATION

Let us introduce the TRI model in a two-dimensional anisotropic triangular lattice;

$$
H = \sum_{(i,j)} -J_{ij} \sigma_i^x \sigma_j^x - \Gamma \sum_i \sigma_i^z.
$$

The $z$-component of the Pauli operator, $\sigma_i^z = \pm 1$, accounts for the location of charges in the $i$-th lattice site representing a dimer, which we call either “pseudo-spin” or “quantum dipole”. The transverse field, $\Gamma$ flips the pseudo spins up and down via $\sigma_i^z = \sigma_i^+ + \sigma_i^-$ where $\sigma_i^\pm$ is the raising and lowering operators. We consider the Ising interactions between quantum dipoles, $J_{ij}$, between neighboring pairs of dimers, $i$ and $j$. In the anisotropic triangular lattice, we take $J_{ij} = J$ and $J'$ for the two directions and the other one directions of the lattice, as shown in Fig. 1(a). This model is obtained by the strong coupling perturbation theory at the lowest order from the so-called extended Hubbard model, a basic model of $\kappa$-(ET)$_2$X, which includes the on-site and inter-site Coulomb interaction between electrons and the transfer integrals.

Since different configuration of electric dipoles on neighboring dimers will give different Coulomb energies between them, $J_{ij}$ is described by the difference between interaction parameters (Appendix A). From the first principles calculation, the actual parameter values of the extended Hubbard model are precisely evaluated, which is transformed to our $J_{ij}$ and $\Gamma$ (see Appendix A). Therefore, we could access the experimentally observed phenomena without assumption once we get a reasonable
The dynamical response to a spatially uniform external field $h(t)$, namely the response to the time-dependent perturbative term $H'(t) = -\sigma^z_j h(t)$ added in the Hamiltonian Eq.(1) is calculated by the Kubo formula.$^3$ The susceptibility then reads,

$$\chi(q, \omega) = \chi(q, 0) + i \omega \int_0^\infty dt e^{i\omega t} \Psi(q, t)$$  \hspace{1cm} (2)

which is directly interpreted as the dielectric function, $\epsilon(q, \omega)/\epsilon_0 = 1 + \chi(q, \omega)$, where $\epsilon_0$ is the permittivity of free space, or variational Monte Carlo calculations. Here, $\Psi(q, t)$ is the relaxation function described in the imaginary and real-time connected form,

$$\Psi(q, \omega) = \int_0^\beta d\lambda (\sigma^z_q (i\hbar\lambda) \sigma^z_q (t))$$  \hspace{1cm} (3)

where $\sigma^z_q = e^{-i\beta \sum_j \sigma^z_j e^{-iqr}} e^{-i\hbar \lambda}$ is the interaction picture of the Ising operator of wave number $q$ and real time $t$, where replacing $t$ with $i\hbar\lambda$ gives the imaginary time, $\lambda$ that runs from zero to inverse temperature $1/\beta = (k_B T)^{-1}$ (where $T$ denotes the temperature and $k_B$ the Boltzmann constant). As we are considering the ferroelectric orders of the quantum dipoles, we focus on the $q = 0$ quantities in the following.

Conventionally, the calculation of Eq.(3) is given by the finite temperature Green’s function using the analytic continuation from $\lambda$ to $t$, but it is reliable enough only when the analytic form of the Green’s function is available, which is not the case of strongly correlated quantum systems.$^9$ Tracking real-time dynamics using numerical time evolution is limited to very small system sizes in the exact diagonalization, and to one dimensional system by the density matrix renormalization group$^{15}$ and matrix product construction$^{20}$ but basically only short timescales are available. Recently, the imaginary time evolution is adopted in the quantum Monte Carlo study$^{21,22}$ illustrating that the nonadiabatic quantum dynamics at a leading order could be similar to the real-time ones$^{22}$. The generalized dynamical scaling of the susceptibility-like quantity obtained averaged along the imaginary time is found to show a good collapse.$^{23}$

Another approach is to regard the Monte Carlo steps as a pseudo real-time evolution by restricting the updating of the Ising pseudo-spin configurations locally in real space direction while allowing for a global update in the imaginary time$^{22}$. We call this a kinetic TRI protocol, as it is a quantum analogue of a so-called kinetic Ising model or Glauber dynamics already established in classical systems based on the Master’s equation.$^{23}$ The kinetic TRI model is empirically found to realize the intrinsic relaxation process, and the dynamical scaling relation is well reproduced.$^{23}$ Similar protocol is applied to quantum annealing$^{26,27}$, whereas Ref.$^{27}$ includes the loop update, and Ref.$^{26}$ the simultaneous flipping of a variable along the whole imaginary time. Particularly in the latter the relaxation process may change and shall be discriminated from Ref.$^{24}$. We briefly note that there are some other trials like phenomenological extension of the Glauber dynamics to quantum systems.$^{28}$ or variational Monte Carlo approaches regarding time evolution.$^{29}$

In adopting the kinetic TRI protocol, we perform the continuous imaginary time QMC calculation by applying the segment update only in the imaginary time direction. The evaluation of Eq.(3) using this protocol is straightforward, whose details are given in Appendix$^{11}$. The QMC calculation is given in a $N = L \times L$ site cluster with $L = 8, 16, 32, 64, 128$, while taking $L \times k_B T = 8, 4, 1, 0.5$. This is because near the QCP, the correlation length diverges in powers and the minimum temperature that captures the relatively size-free ($L > \xi$) results is limited at each $L$. We made a Binder plot of the pseudo-spin expectation value, $\langle \sum_j \sigma^z_j \rangle$ to evaluate the phase diagram of Fig.2(a), and compared it with the anomaly of the specific heat. The value of $\chi_0$ in our kinetic protocol is strictly the same quantity as the ones obtained from the standard QMC. We use a Bayesian scaling method in our finite size scaling analysis.$^{20}$

In the vicinity of the quantum criticality point (QCP), the relaxation timescale $\tau$ obtained by this protocol diverges in powers of the critical exponents. We further show that the kinetic TRI protocol yields the same QCP and the 3D Ising-type critical exponents of the original TRI. The state-of-art roadmap of the relaxation time $\tau$ and static susceptibility $\chi_0$ that characterizes this quantum criticality is clarified for the first time.

III. RESULTS

A. Phase diagram and susceptibility

We first overview the low temperature properties of the TRI model on an anisotropic triangular lattice. In overall, at large enough Ising interactions, $J_{ij}/\Gamma$, the system is in a conventional ordered phase, whereas fluctuates the pseudo-spins and makes the system disordered. The phase transition between the two is of second-order, and the wave function of the disordered phase in this class of model is well-known as a typical product state, a trivial state in the context of topological classification.$^{31}$ The $k_B T J - J'$ phase diagram is shown in Figure 2(a) in unit of $\Gamma = 1$. The ordered phase expands from large $J, J' > 0$ region toward slightly antiferromagnetic $J'$. The case of the square lattice ($J' = 0$) is well studied$^{21,22}$ and the quantum critical point (QCP), namely the phase boundary at $k_B T = 0$, is evaluated as, $J_c/\Gamma = 0.3284$. From a series of first principles calculation, the $\kappa(ET)_{2\times 2}$ is located at around $J' \sim 0.1, J' \sim 0.5$ (Appendix$^{18}$), which is marked in the phase diagram Fig.2(a). One finds that it is near the QCP. Although the nature of the phase diagram is clear-cut, the dynamic responses near the QCP is highly nontrivial, as it should be governed by the quantum many body effects.
Let us explain the derivation of $\chi(q=0,\omega)$ from our dynamical susceptibility, $\chi(q=0,\omega)$, in the thermodynamic limit when the parameters $J$ and $J'$ fall on QCP (The 3D line in Fig. 2(a)). The similar frequency dependent shift of the peak temperature is observed when $J'$ is off QCP toward the ordered phase (see Fig. 7), while the frequency dependence of $\tau$ fall near the blue point ($J \sim 0.1, J' \sim 0.5$) in the diagram at $k_B T = 0$. The right panel shows the cross section of the phase diagram at $J = 0.1$ at low $k_B T$ in the vicinity of QCP. The case of square lattice ($J' = 0$) in green cross section is given in Appendix C. (b) Relaxation function $\Psi(q=0,t)$ obtained by the QMC calculation at $L = 64$ and $J' = 0.47$, $J = 0.1$ for several choices of $k_B T$. (c) $\tau_L$ and $\chi_{0;L}$ extracted from the relaxation function at several $L$, plotted as functions of $k_B T$. The envelope line $\tau = c_1(k_B T)^{-\gamma}, \chi_0 = c_2(k_B T)^{-\gamma}$ are the values in the thermodynamic limit. For the 3D critical exponents, we obtain $c_1 = 4.34, c_2 = 4.61$, which is almost the same with the case of square lattice (Appendix C, Fig. 6). (d,e) Dynamical susceptibility as functions of $\omega$ and $k_B T$ (cross sections of Fig. 6(c)).

### B. Relaxation function and critical exponents

We already introduced in Fig. 1(c) our dynamical susceptibility, $\chi(q=0,\omega)$, in the thermodynamic limit when the parameters $J$ and $J'$ fall on QCP (The 3D line in Fig. 2(a)). The similar frequency dependent shift of the peak temperature is observed when $J'$ is off QCP toward the ordered phase (see Fig. 7), while the frequency dependence of $T_m(\omega)$ is slightly suppressed as we discuss shortly.

Let us explain the derivation of $\chi(q=0,\omega)$ from our calculation. In the disordered phase relatively near the phase boundary, the response function $\Psi(q=0,t)$ shows a clear exponential decay as a function of MC time step, $t$, typically as in Fig. 2(b). The relaxation time, $\tau_L$, and the static uniform susceptibility, $\chi_{0;L}$, are the only two parameters characterizing the response function at a given $k_B T$ and $J, J'$ and system size $L$ as,

$$\Psi(q=0,t) = \chi_{0;L} \exp(-t/\tau_L).$$

The extracted values of $\chi_{0;L}$ and $\tau_L$ are plotted in Fig. 2(c) for $L = 8, 16, 32$ and 64 as functions of $k_B T$ at $J' = J_c$. Curves belonging to different $L$ together form an envelope function, and each curve falls off the envelope at low $k_B T$, namely, when the correlation length $\xi$ exceeds $L$. The envelope function thus gives the value of thermodynamic limit, which we denote $\tau$ and $\chi_0$.

Since the system is near QCP, $\tau$ and $\chi_0$ diverges in powers toward the ordered phase as (see the inset of Fig. 1(c)),

$$\kappa(k_B T) = c_1(k_B T)^{-\gamma}, \chi_0(k_B T) = c_2(k_B T)^{-\gamma}$$

where $\gamma$ and $\gamma$ are the dynamical and magnetic critical exponents, respectively, and $c_1$ is the constant coefficients. This could be understood as follows: Consider a quantum 2D system of size $L \times L$ with an additional axis in the imaginary time direction, $\lambda = 0 \sim \beta$, that characterizes the quantum fluctuation. As the system approaches QCP, the correlation length $\xi$ diverges. Suppose that $L$ is large enough to assume $L > \xi$, and then $\beta$
becomes the upper bound of the effective system length. Thus, for moderately low temperature, $\xi$ cannot develop larger than $\beta$. From the scaling theory, we immediately find $\tau \propto \xi^z = (k_B T)^{-z}$. The form Eq. (5) is applied to laboratory systems as well as to theoretical models.

On the basis of the conformal field theory, the criticality at the very QCP and off QCP in the ordered region follow that of the 3D and 2D Ising universality classes \( \xi^z \approx (k_B T)^{-z} \), and their exponents are evaluated as \( (z, \gamma, \nu) = (2.0^{\pm 0.3}, 2.03^{+0.03}_{-0.02}, 1.237, 0.629^{+0.05}_{-0.03}) \) and \( (2.16^{+0.2}_{-0.05}, 2.13^{+0.02}_{-0.04}, 1.75, 1) \), respectively. We analytically in the Lorenzian form as,

\[
\chi(q = 0, \omega) = \chi_0 \frac{\tau^{-2}}{\omega^2 + \tau^{-2}}.
\]

This is a so-called Debye function in dielectrics. The cross sections of plots Fig. 2(c) at fixed values of $\omega$ and $k_B T$ of are shown in Fig. 2(d) and Fig. 2(e), respectively. A remarkable aspect is that such frequency dependence of $T_m(\omega)$ near QCP is nearly scale free. If we take the temperature range one orders of magnitude higher than that of the main panel of Fig. 2(e), the almost same functional form is observed by shifting the frequency to the higher energy (inset of Fig. 2(e)). From Eq. (6), we find that, $T_m(\omega) \propto \omega^z$ thus the frequency dependent peak is indeed dominated by the dynamical critical exponent.

By precisely evaluating Eq. (3) by the QMC calculation, and from the system size scaling, we obtain a set of $(\chi_0, \tau)$ over the whole region of the phase diagram. Their contour map is given in Fig. 3. One can regard the region $\tau < 10$ of being no longer critical, namely either quantum mechanically or classically disordered, which is marked as a region outside the red line in Fig. 1(b) (For the corresponding actual value of the square lattice, see Appendix Fig. 6). The naive and schematic description of the crossover lines of the QCP region is generally given as in the yellow broken line of Fig. 1(b), which however turned out to be only qualitative and valid at extremely low temperature.

C. Finite size scaling analysis

The similarities of the present kinetic TRI protocol and the original TRI model could be further tested by the generalized dynamical finite size scaling analysis; the
scale invariance is expected in the dynamical critical phenomena, which results in the finite size scaling form of the relaxation timescale,

$$\tau_{\text{int}}(J^*, L) = L^2 \phi((J^* - J_0) L^{1/2})$$

(7)

near the QCP. For this purpose, we evaluate $\tau_{\text{int}}$ at low temperatures available in a series of $k_B T = \Gamma / 2 L$, down to $k_B T = 0.0078125 \Gamma$, by varying $J^*$ in the phase diagram of Fig. 1(b). We use the following integral,

$$\tau_{\text{int}} = \int_0^\infty \frac{\Psi(t)}{\Psi(0)} dt$$

(8)

which gives the value independent of the detailed functional form of $\Psi(q = 0, t)$. Fig. 4 shows the finite size scaling plot using $L = 8, 16, 32$ and 64. One finds an almost perfect collapse of the data points into a single functional form. The exponent obtained by this plot is $J_c / \Gamma = 0.4700, (z, 1/\nu) = (2.095, 1.56(3))$, which is fully consistent with our Binder analysis of TRI and the fitting of exponents on the kinetic TRI. We thus think it to be properly interpreted as a 3D universality class.

IV. SUMMARY AND DISCUSSION

We have clarified how the quantum criticality appears in the dynamics of the quantum many-body system. As an ideal and realistic platform, we chose the transverse Ising model on triangular and square lattices, whose Ising degrees of freedom represent the quantum electric dipole degrees of freedom in the dimer Mott insulating phase of the organic crystal, $\kappa$-ET$_2$X. The model is known to exhibit a quantum criticality and can be almost exactly solved numerically by the state-of-art quantum Monte Carlo method. We developed a kinetic TRI protocol to study the quantum dynamics of the transverse Ising model in two-dimension, which is built on the local quantum Monte Carlo update that is known to capture the intrinsic real-time Glauber types of dynamics of the model. In this protocol, by analyzing the Monte Carlo time dependence of the correlation functions, we obtained the dynamical susceptibility, and showed that they have Debye functional form with its peak heights and inverse of width diverging algebraically in approaching QCP. This led to a significant peak-narrowing, and the obtained temperature dependence of the dynamical susceptibility is found to show a frequency-dependent peak shift, reminiscent of the relaxor-ferroelectric like behavior observed in many experimental studies of organic dimer Mott materials.

We briefly refer to some theoretical studies discussing this relaxor-ferroelectric-like behavior of $\kappa$-ET$_2$X. The extended Hubbard model in one dimension is shown to be described in the mean-field level using the phase Hamiltonian, which they aim to describe the cross-section line of the two-dimensional systems. They discussed that the kinks (the domains in 2D) as the origin of frequency-dependent peaks, and by evaluating the dynamical correlation function of kinks, showing that their relaxation timescale shall vary with frequency by orders of magnitudes. This may give a simplified phenomenological interpretation of the phenomena, although they do not explain a temperature-dependent characteristic dynamical susceptibility and seems to have no relevance to the criticality we observed.

The authors in Ref. 10 extended our effective model for $\kappa$-ET$_2$X by including all nearest neighbor interactions, which have lead to the additional terms that couple the electron spin and dipole degree of freedom in a more complicated manner than Ref. 11. Then, they discarded the quantum fluctuation term and performed the classical Monte Carlo study by explicitly dealing with the electron spin as a classical SO(3) vector and electric dipole as Ising pseudo-spins, showing that the couplings of these two will generate a dynamical (classical) disorder to each other. The dipole susceptibility shows broad peaks in lowering the temperatures, which they attributed to the glassiness, which may be relevant to the glassy behavior of $\kappa$-ET$_2$Cu$_2$(CN)$_3$ at $T < 6 K$. Indeed, the coupling of two different degrees of freedom can be a driving force of glassiness. Recently, one of the authors and collaborators showed that in a three-dimensional frustrated pyrochlore lattice, the model including the spin and lattice-displacement coupling can exhibit a thermodynamic glass transition at finite temperature even without quenched disorder, which explained the long-standing puzzle on the origin of the disorder-free spin glass in Yb$_2$Mo$_2$O$_7$. Since the classical model in Ref. 10, is two-dimensional, the fluctuation disturbs the true glass transition and the system remains glassy. If one deals with it quantum mechanically, there shall be room for the true glass transition.

We now compare the overall behaviour of $\chi(q = 0, \omega)$ with the experimentally observed dielectric constant $\epsilon'(\omega)$ of $\kappa$-(ET)$_2$X. The material at ambient temperature is a good conductor. At temperatures below 100K, the conducting charges start to lose its spatial coherence and localize on each dimer, and a quantum electric dipole is spontaneously formed supported by strong electronic correlation. We emphasize that this kind of dipole itself is already exotic as it is of quantum mechanical origin, namely it emerges due to the special modulation of wave function and the resultant modification of the charge distribution, which should be strictly discriminated from the conventional and semiclassical lattice-displacement-type of dielectrics. As the frequency is varied from 1kHz to 100kHz, of $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$ shifts from about 20K to 50K. By extracting $\epsilon'(\omega)$ within this temperature window and fitting them by Eq. (6), we find a series of Debye curves belonging to different $T$, that crosses in a manner comparable to Fig. 2(e) (Appendix E). In the case of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl, with only slight variation of $T_m(\omega) \sim 25 - 30$K, contrastingly shows no such crossings, and is considered to locate off the QCP.

One remaining issues is that we cannot directly deter-
mine the laboratory timescale that corresponds to the Monte Carlo timestep. Still, we may safely assume that for each temperature, \( t = a(T) \) lab holds, where \( a(T) \) could become smaller with lowering the temperature by few factors. If we plot the extracted of \( \kappa \)-(ET)\(_2\)Cu\(_2\)(CN)\(_3\) against \((T - T_\text{c})\), taking \( T_\text{c} = 6\text{K} \) where the Curie tail of \( \varepsilon'(\omega) \) diverges, we obtain \( \tau_\text{lab} \propto (T - T_\text{c})^{-2} \) with \( \tau_\text{lab} \sim 2 - 3 \) (Appendix Fig. 5) not too different from that of 2D Ising ones expected for the case with finite.

Although there had been a dispute on whether such seemingly subtle dipole really exist, further examination on \( \kappa \)-(ET)\(_2\)Cu\(_2\)(CN)\(_3\)Cl after Ref [25] for many samples supported the picture of order-disorder type of ferroelectrics [26]. The dipoles have further proven to be present in \( \beta \)-(ET)\(_2\)ICl\(_2\), a similar 2D material showing the same critical dynamics, via observation of pyrocurrents [27], collective modes [28], and the polarization curve [29]. Similar dynamics is quite relevant near the phase transition in a series of quasi-one-dimensional organic materials TMTSF\(_2\)X [20,22] based on dimerized molecules, although its criticality was not really discussed before.

Quantum nature of dielectrics has become a topic in a series of materials: A geometrical frustration induced quantum paraelectric nature is found in the conventional displacement-type of dipoles in a hexaferrite BaFe\(_2\)O\(_4\) [30]. Critical behaviour of the static dielectric function has been discussed in another displacement-type of quantum paraelectrics, SrTiO\(_3\), on the basis of a phenomenological \( \phi ^4 \)theory which explains well the experimental observation in such a three dimensional system with moderate quantum fluctuation [31]. Then finally, the present study reached the dynamics of dipoles in the presence of strong quantum fluctuation characteristic of two dimension. The TRI model adopted here may serve as the basis of the first principles calculation reported by one of the authors for almost a whole family of these materials [18]. Figure 5 shows the schematic description of the two dimensional conducting layer of \( \kappa \)-ET\(_2\)X, where circle represents an ET molecular orbital (we call here “site”) and oval the dimer. There are four sites and two dimers in the unit cell. This family of material has an old history, and its variety of electronic states are already well known to be described by the extended Hubbard model in unit of molecular orbitals as [33].

\[
H = \sum_{\langle i,j \rangle} \sum_{\sigma = \uparrow, \downarrow} -t_{ij} \left( c_{i\sigma}^\dagger c_{j\sigma} + H. c. \right) + \sum_{i = 1}^N U_{n_i^\uparrow n_i^\downarrow} + \sum_{\langle i,j \rangle} V_{ij} n_i n_j \tag{A1}
\]

where \( c_{i\sigma}^\dagger c_{i\sigma} \) is the creation/annihilation operator of electrons on site \( i \) and spin \( \sigma \), and \( n_i \sigma = c_{i\sigma}^\dagger c_{i\sigma} \) are their number operators. The transfer integrals \( t_{ij} \) are evaluated from the latest first principles calculation as (Table I and II of Ref. [16]),

\[
(t_1, t_2, t_3, t_4) = (0.46, 0.43, -0.08) \text{ and } (0.34, 0.51, -0.21) \text{ for } X = \text{Cu}_2(\text{CN})_3 \text{ and } \text{Cu}[\text{N}(\text{CN})_2]\text{Cl, respectively, in unit of } t_1 \text{, showing that the geometry of } t \text{'s depends on materials. The intra-dimer transfer integral is, by contrast, not that different between materials; } t_1 = 199 \text{ meV and } 207 \text{ meV for } X = \text{Cu}_2(\text{CN})_3 \text{ and } \text{Cu}[\text{N}(\text{CN})_2]\text{Cl, respectively, and distributes within a narrow range, } 195 - 209 \text{meV for all other } \kappa \text{-ET}_2\text{X. The on-site Coulomb } U \text{ and the inter-site Coulomb interactions } V_{ij} \text{ are also evaluated on the basis of the molecular distances (X-ray structure) referring to the abinitio down-folding[21], which are } U = 8, \text{ } (V_1, V_2, V_3, V_4) = (4.0, 2.0, 2.4, 2.0) \text{ in unit of } t_1 = 200 \text{ meV (or } V_2 = 0.4 \text{meV from the abinitio study[22]), also almost independent of } X. \text{ The absolute values of these interactions are rather overestimated, but we consider that the ratio between these interactions are reliable enough. Let us consider the strong coupling case, } U, V_1 \gg V_i, t_i, \text{ where the large Coulomb interactions, } U \text{ and } V_1 \text{ hinder the electrons to occupy the same site and the dimer, respectively. Originally, there are } 4^2 = 16 \text{ basis state in a unit dimer, but is reduced to four in the strong coupling case (see Fig. 5(b)). One of the authors have derived the effective Hamiltonian by the perturbation up to fourth order[11], where the second order perturbation is responsible for the coupling of the spin and charge degrees of freedom. Whereas, the leading order (namely first order in } t_{ij} \text{) does not include the spin operator, as the spins can only hop within dimers to keep the constraint of having one particle per dimer. Therefore, taking only the lowest order reduces the number of basis per dimer to two, in which the configuration of charge degrees of freedom in the dimer is represented via up and down of pseudo spins, } \sigma^z = \pm 1/2. \text{ The effective Hamiltonian is thus reduced to the representation of } m = 1 \sim 2^N \text{ basis,}
\]

\[
H_{\text{eff}}^{(1)} = \sum_{m, m'} \langle m | H_{mn} | m' \rangle = \sum_{i = \uparrow, \downarrow} -J_{ij} \sigma^z_i \sigma^z_j + \Gamma \sum_{i = 1}^N \sigma^z_i \tag{A2}
\]

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Appendix A: Microscopic derivation of the model parameters

We evaluate the model parameters of \( \kappa \)-ET\(_2\)X on the basis of the first principles calculation reported by one of the authors for almost a whole family of these materials [18].
we find $J' = V_2/4$. The relation, $J = (V_3 - V_4)/4$, is also constructed in the same manner as a linear combination of the two connections $V_3$ and $V_4$.

Substituting the first principles values of $V$'s to the above relation yields, $J'/\Gamma \sim 0.1$ and $J'/\Gamma \sim 0.5$ for $\Gamma \sim 200$ meV, and $X = Cu_{2}(CN)_{2}$ has slightly larger values than $Cu[N(CN)_{2}]Cl$. Coincidentally, it falls on to the very vicinity of the QCP ($J'/\Gamma = 0.1$, $J'/\Gamma = 0.47$, which continues in the vicinity) in the phase diagram we obtained in Fig.1b.

We briefly not that Ref.[40] performing a higher order perturbation with extra terms included compared to Ref.[11]. In our model, however, we neglect the electron spin degrees of freedom and only focus on the charge (dipole) degrees of freedom, and at this level the two give the same form.

### Appendix B: Kinetic protocol

In the following, we consider a lattice system of size $N = L \times L$, where the $i$-th lattice site is located at $r_i$ in the two dimensional plane. Suppose that we are in the disordered phase ($\langle \sigma_i^z \rangle = 0$) in the equilibrium. Consider an external field, $h(r_i, t)$, as a time-dependent perturbation, which gives the additional term to the original Hamiltonian as $\mathcal{H} + \mathcal{H}'(t)$.

$$\mathcal{H}'(t) = -\sum_{i=1}^{N} \sigma_i^z h(r_i, t) = -\int \frac{d\omega}{2\pi} e^{-i\omega t + \delta \omega} \frac{1}{N} \sum_{q} \sigma_q^z h(q, \omega),$$

$$h(r_i, t) = \int \frac{d\omega}{2\pi} \frac{1}{N} \sum_{q} h(q, \omega) e^{iqr_i - i\omega t + \delta \omega},$$

$$\sigma_i^z = \frac{1}{N} \sum_{q} \sigma_q^z e^{iqr_i}. \tag{B1}$$

The induced polarization is given within linear response theory as,

$$\sigma_i^{\text{ind}}(t) \equiv \langle \sigma_i^z \rangle_t = \int_{-\infty}^{t} ds \sum_{j=1}^{N} \Phi(r_i - r_j, t - s) h(r_j, s)$$

$$\Phi(r_i - r_j, t - s) = -\frac{i}{\hbar} \langle [\sigma_j^z(s), \sigma_i^z(t)] \rangle_{\text{eq}},$$

$$\sigma_i^z(t) = e^{i\mathcal{H}t/\hbar} \sigma_i^z e^{-i\mathcal{H}t/\hbar} \tag{B2}$$

where $\Phi(r, t)$ is the response function, $\sigma_j^z(t)$ is the interaction picture using the unperturbed Hamiltonian (Eq.(1)), and $\langle \cdot \rangle_t$ is the expectation values in an external field at time $t$. The thermal average in the equilibrium state is, $\langle \cdot \rangle = \text{Tr} (\cdot \rho)$, using the density matrix operator, $\rho = e^{-\beta \mathcal{H}}/Z$, where $Z$ is the partition function. The Fourier transform of the above form yields,

$$\sigma_i^{\text{ind}}(\omega) = \chi(q, \omega) h(q, \omega),$$

$$\sigma_q^{\text{ind}}(\omega) = \int dt \sum_{i=1}^{N} \sigma_i^{\text{ind}}(t) e^{-iqr_i + i\omega t}.$$
\begin{align}
\sigma^{\text{ind}}(t) &= \frac{1}{2\pi} \int \! d\omega \, \frac{1}{N} \sum_q \sigma_q^{\text{ind}}(\omega) \, e^{iqr - i\omega t + i\delta t}, \quad \text{(B3)}
\end{align}

where the susceptibility is given as
\begin{align}
\chi(q, \omega) &= \int_0^\infty \! dt \, \sum_{i=1}^N \Phi(r_i, t) \, e^{-iqr + i\omega t} \\
&= \frac{i}{\hbar} \int_0^\infty \! e^{i\omega t - \delta t} \langle \left[ \sigma_q^z(t), \sigma_q^z(0) \right] \rangle_{\text{eq}} \, dt \\
&= -\int_0^\infty \! Q^R(q, t) e^{i\omega t - \delta t} \, dt.
\end{align}

In general, the retarded Green’s function \(Q^R(q, t) = -\frac{i}{\hbar} \langle \left[ \sigma_q^z(t), \sigma_q^z(0) \right] \rangle_{\text{eq}}\) is obtained from the analytic continuation \((i\omega_i \rightarrow z = \hbar\omega_i)\) of the finite temperature Green’s function, \(Q(q, u) = -\langle T \sigma_q^z(u) \sigma_q^z(0) \rangle\), by calculating \(Q(q, i\omega_i) = \int_0^\beta Q(q, u) e^{i\omega_i u} \, du\) in terms of Matsubara frequency, \(\omega_i = \frac{2\pi i}{\beta}\). Whereas, due to the lack of analytic form of \(Q(q, u)\) in the strongly correlated quantum lattice model, a sparse numerical data at low temperature for large spacings of \(\omega_i\), the information to properly construct the response function particularly at low frequencies and low temperature is lacking. This has long been a bottleneck of the calculation of dynamical quantities.

Here, as one of the complementary treatment, we introduce a protocol that evaluates \(\chi(q, \omega)\) along the evolution of Monte Carlo simulation time within the equilibrium.

Suppose that we continuously apply a field at \(t = -\infty \sim t_0\) and turning it off, \(h(s) = \theta(-(s - t_0))\), which will give a response at \(t > t_0\) as,
\begin{align}
\sigma^{\text{ind}}_i(t) &= \int_{-\infty}^t \! ds \, \Phi(t - s) \theta(-(s - t_0)) \\
&= \int_{t_0}^t \! ds \, \Phi(t - s) = \int_{t_0}^\infty \! dt' \, \Phi(t') \\
&= \int_t^\infty \! dt' \, \Phi(t' - t_0) \equiv \Psi(t - t_0)
\end{align}

where \(\Psi(t)\) is a relaxation function that fulfills
\begin{align}
\lim_{t \rightarrow \infty} \Psi(r, t) = 0 \quad \text{and} \quad \Phi(r, t) = -\frac{d}{dt} \Psi(r, t).
\end{align}

Using the following relation,
\begin{align}
\frac{i}{\hbar} \int_0^\beta \! d\lambda e^{\lambda H} \frac{dA}{dt} e^{-\lambda H} &= -e^{\beta H} [A, e^{\beta H}] \\
\rightarrow -i\hbar\rho_{\text{eq}} &\int_0^\beta \! d\lambda \dot{A}(-i\hbar\lambda) = [A, \rho]
\end{align}

we find,
\begin{align}
\Phi(r_i - r_j, t) &= -\frac{i}{\hbar} \text{Tr} \left( \rho_{\text{eq}} \, [\sigma_j^z(0), \sigma_i^z(t)] \right) \\
&= \int_0^\beta \! d\lambda \langle -i\hbar\lambda \sigma_j^z(t) \rangle_{\text{eq}} \\
&= \int_0^\beta \! d\lambda \langle e^{\lambda H} [\sigma_j^z, \mathcal{H}] e^{-\lambda H} \sigma_i^z(t) \rangle_{\text{eq}}
\end{align}

The susceptibility is rewritten in the form,
\begin{align}
\chi(q, \omega) &= -\int_0^\infty \! dt \, e^{i\omega t} \sum_{i=1}^N \frac{d}{dt} \Psi(r_i, t) \\
&= \chi(q, 0) + i\omega \int_0^\infty \! dt \, e^{i\omega t} \Psi(q, t)
\end{align}

where we used the following Fourier forms of the two functions,
\begin{align}
\Psi(r_i - r_j, t) &= \int_0^\beta \! d\lambda \langle -i\hbar\lambda \sigma_j^z(t) \rangle_{\text{eq}} \\
\Psi(q, t) &= \int_0^\beta \! d\lambda \langle -i\hbar\lambda \sigma_q^z(t) \rangle_{\text{eq}}
\end{align}

The equations given so far are the summary of the Kubo formula. Now, we introduce our protocol to evaluate Eq. (B5). First, notice that Eq. (B5) is an imaginary time(\(\lambda\)) and real time(\(t\)) connected form. Whereas, in the present protocol we approximate these two time evolutions to be independent and denote the two time variables explicitly as, \(\sigma_j^z(\lambda, t)\). Further, the real-time \(t\) is replaced with the Monte Carlo step \(t_{MC}\), which is already empirically confirmed to reproduce the physically intrinsic timescale, when the Monte Carlo update process is restricted to the spatially local one. Then, the evaluation of \(\langle \sigma_j^z(\lambda, u) \sigma_q^z(0, u + t) \rangle_{\text{eq}}\) is given between \(\sigma_j^z\) of \(t_{MC} = s\) at imaginary time \(\lambda\), and that of \(t_{MC} = s + t\) and imaginary time 0, where the integration of \(\lambda = 0 \sim \beta\) is made independent of \(t_{MC}\). We take an average over \(M\) time steps in the equilibrium, namely the Monte Carlo process has already reached the equilibrium manifold of states as;
\begin{align}
\Psi(r_i - r_j, t) &= \int_0^\beta \! d\lambda \langle \sigma_j^z(\lambda, 0) \sigma_q^z(0, t_{MC}) \rangle_{\text{eq}} \\
\Psi(q, t) &= \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N \sum_{s=0}^M \int_0^\beta \! d\lambda \langle \sigma_j^z(\lambda, s) \sigma_q^z(0, s + t) \rangle_{\text{eq}}
\end{align}

In the actual calculation, we averaged over 16 runs each taking \(M = 10^7\) time steps. Near QCP the time correlation (similarly, \(\tau_L\)) extends to more than \(10^6\) steps.

\section*{Appendix C: Square lattice transverse Ising model}

Although the results presented in the main text are the ones for the anisotropic triangular lattice model in the certain parameter range to compare with \(\kappa\)-ET\(_2\)X materials, the phase diagram in Fig.1b has larger parameter space than we have discussed. Particularly, the case
of the square lattice ferromagnetic transverse Ising model is realized at $J' = 0$. We show basically the same results are obtained for the square lattice. Figures (a) and (b) are the $k_B T$ dependences of $\tau_L$ and $\chi_{0,L}$ to be compared with Figs. 2(b). Here, we show both the case at QCP and just off QCP, which basically follow the exponents of 3D and 2D Ising universality classes, respectively. The plots of $\tau$ and $\chi_0$ on the plane of $J$ and $k_B T$ are also shown for wider temperature range than Fig.3 in the main text. Although the contour lines are rather different, the overall tendency does not depend on the parameters $J$ and $J'$. Also, $\tau$ and $\chi_0$ extracted from the envelope function of Figs. (a) and (b) at QCP of the square lattice almost coincides with that of the anisotropic triangular lattice including the constant coefficients.

We here note that the temperature dependences of $\tau$ and $\chi_0$ at $J' > J_c$, namely when $T_c > 0$, are different from those of the quantum critical point discussed in Eq. (5) in the main text. They follow,

\[
\tau \propto (T - T_{c})^{-\nu}, \quad \chi_0 \propto (T - T_{c})^{-\gamma}
\]  

(C1)

with $z \sim 2.18$, $\nu = 1$, and $\gamma = 1.75$ (see the main text) following those of the 2D Ising universality class. When fixing the temperature and approaching the phase boundary by varying the model parameters, $g = J$ or $J'$, they also follow,

\[
\tau \propto |g - g_c|^{-\nu}, \quad \chi_0 \propto |g - g_c|^{-\gamma}
\]  

(C2)

where $g_c = J_c$ or $J'_c$ are the phase boundaries.
FIG. 8. Dielectric constant $\epsilon'(\omega)$ in unit of $\epsilon_0$ of (a)$\kappa$-ET$_2$ Cu$_2$(CN)$_3$ and (b)$\kappa$-ET$_2$ Cu [N(CN)$_2$]Cl, reported in Refs.\ 56. Data is provided by the courtesy of T. Sasaki and P. Lunkenheimer. Solid lines are the Lorenzian fit (Eq.(6)), and the value of $\tau_{lab}$ for (a) is given in the inset as functions of $(T - T_c)$ with $T_c = 6K$. The solid/broken lines in the inset shows the function, $(T - T_c)^{-\nu}$ with $\nu = 1.05$, and $\nu = 1$ respectively.

Appendix D: Dynamical susceptibility off QCP

We here show in Fig.7 and 8 the dynamical susceptibility, $\chi(q, \omega)$, as a function of $k_BT$, when the model parameter is slightly off QCP. The one at QCP for the square lattice is given together in Fig.7(a), which is almost the same as that of Fig.2e in the main text. In the case off QCP, $\chi_0$ and $\tau$ diverges toward $T_c > 0$, and below $T_c$, enter the ferro ordered phase. The similar behavior as that of the QCP is observed, but their critical exponents are that of the 2D universality class, which we actually confirmed in the calculation in Fig.6.

Appendix E: Reexamination of the experimental results by Abdel-Jawad, et. al and Lunkenheimer, et. al

On the basis of our theoretical findings, we here re-examine the previous reports on the dielectric measurements of $\kappa$-ET$_2$ Cu$_2$(CN)$_3$ by Majed, et. al and $\kappa$-ET$_2$ Cu [N(CN)$_2$]Cl by Lunkenheimer, et. al. In these measurements, the dielectric constants in unit of $\epsilon_0$ shows a peak at temperature, $T_m(\omega)$, which distributes at 20-50 K in the former and 25-30K in the latter material, when the frequency varies from the order of 1Hz to 100kHz (see the insets of Fig.8). These results shall be qualitatively compared to our $\chi(q = 0, \omega)$ in Fig.1e besides the constant and the possible experimental background values of $\epsilon'$s from different origin. Let us fix the value of $T$ and extract the experimental data from these figures, and by plotting them against $\omega$ we find Figs.8a and 8b. In the case of $\kappa$-ET$_2$ Cu$_2$(CN)$_3$, the successive crossing of lines belonging to different $T$ takes place over the frequency range of 10-500 kHz, to be compared with Fig.2c, which is indeed the origin of the large frequency dependence of $T_m$. These lines are Lorenzian fit following Eq.(5) in the main text, and the resultant $\tau_{lab}$ (inset of Fig.8a, in unit of (kHz)$^{-1}$) varies by one orders of magnitude during the temperature change of 10K. We plot $\tau_{lab}$ against $(T - T_c)$ with $T_c = 6 K$, and draw a line proportional to $(T - T_c)^{-\zeta(T)}$ with $\nu = 1.05$. While we cannot precisely determine the exponents as we are not able to extract reliable error bars in fitting $\epsilon'$ with relatively small numbers of data points, the data seems to fall between $\zeta_{lab} \sim 2.18(2D$ critical exponent, solid line)-3(broken line). By contrast, in the case of $\kappa$-ET$_2$ Cu [N(CN)$_2$]Cl, such crossing does not take place, and $\tau$ stays extremely small of order-$10^{-6}$ (Hz)$^{-1}$ with no significant variation against $T$.

We thus consider that $\kappa$-ET$_2$ Cu$_2$(CN)$_3$ in the critical region of the phase diagram, and the frequency dependence in overall understood as a signature of the dynamical criticality. Whereas, the interpretation of $\kappa$-ET$_2$ Cu [N(CN)$_2$]Cl is not straightforward. The almost frequency independent behavior indicates that the system is in the disordered phase slightly of the critical region, whereas $\tau$ is very large. One way to reconcile these two tendency is to notice that $\kappa$-ET$_2$ Cu [N(CN)$_2$]Cl has a Néel order at 27K, which may be related to the dielectric ordering. If the system is near but off the critical point, the coupling of dipoles with spin degrees of freedom may work as a perturbation to drive the system to the first order transition of dipoles and magnetism. These couplings indeed emerge in the model one of the authors discussed previously\ 11. In fact, $\kappa$-ET$_2$ Cu$_2$(CN)$_3$ does not show magnetic ordering down to lowest temperature, which supports this scenario. The first principles calculation shows that $\Gamma = t_1$ is slightly larger, namely $J/\Gamma$ is smaller, for $\kappa$-ET$_2$ Cu [N(CN)$_2$]Cl than $\kappa$-ET$_2$ Cu$_2$(CN)$_3$. This is also consistent with the fact that the former is off the critical point.
