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Introduction

The basic motivation of modern condensed matter physics is to explore new physics that emerges out of complexity in a collection of large number (\(\sim\) Avogadro number \(\sim 10^{23}\)) of interacting non-relativistic particles. The “fundamental Hamiltonian” in a condensed matter system is usually known. It consists of a collection of atoms interacting via coulomb interaction. But when a system with such a large number of particles is exposed to thermal fluctuations or enters in a quantum domain or both and when the system parameters are tuned to certain values, many novel features can emerge. Formation of crystal structure, superfluidity, superconductivity are few examples of such novel phenomena. Such emergent behavior may not be adiabatically connected to the phases that appear in either side of those special points in a parameter space\([1, 2]\). It is difficult to capture such novel behavior in a standard perturbation theory and one needs a new mechanism, such as spontaneous symmetry breaking for phase transition\([3]\) and new calculational scheme, such as renormalization group\([4]\) scheme for critical phenomena to explain such behavior. Such a scenario is observed when the system undergoes a transition between two phases at zero temperature as a result of changes in some non-thermal parameter and is dubbed as \textit{quantum phase transition}\([5]\). At a certain value of a non-thermal tuning parameter where a quantum phase transition of a continuous kind occurs is called a quantum critical point. At a quantum critical point system properties even at finite temperature, are governed mainly by quantum critical fluctuations. Finite temperature properties near a quantum critical point shows novel power law behaviors which are beyond the realm of any zero temperature limit of a classical theory. Such an emergent scenario drew lot of attentions in the past.
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and has been experimentally observed in case of itinerant magnets, He\textsuperscript{3}, etc.[6]. As a result of experimental findings, most of the earlier works in this area were directed mostly toward quantum phase transition either in quantum spin systems or in metallic magnets. Though classical phase transitions in insulating dielectric materials are well studied, there has not been any study in context of quantum phase transition. In this thesis we emphasis that the effect of quantum fluctuations can as well be observed in case of certain insulating dielectric materials, namely quantum paraelectrics such as SrTiO\textsubscript{3}, KTaO\textsubscript{3} etc. In these materials a quantum phase transition occurs as a result of isotopic substitution and it involves softening of an optical mode. Thus a quantum generalization of the soft mode picture of phase transition in classical ferroelectrics is realized in these materials. A theory of quantum phase transition in these materials can be described by a continuum model which includes transverse optical modes near zone center as the most relevant degrees of freedom. It shares some similarity with the effective theory of spin fluctuations in metals. At the technical level the effective theory for quantum paraelectric to ferroelectric transition is similar to a undamped Bosonic version of the effective theory of quantum paramagnet-ferromagnetic transition in a metallic magnet. Theoretically these systems are much simpler than their magnetic counterparts to deal with, and moreover many features are experimentally observable. Thus these systems can become good playgrounds for studying some general aspects of quantum phase transitions such as finite temperature properties, disorder effects etc.

Before going into the details of the issues related to the quantum phase transition in the above mentioned materials, a brief excursion through these concepts would set a background for the present study. More detail discussions on some of the concepts if needed, will be presented in the corresponding chapter.

1.1 Quantum phase transition

Quantum phase transition is a phase transition induced by quantum fluctuations at zero temperature. Unlike the classical phase transition where the tuning parameter is temperature, one looks for a quantum phase transition by tuning a non-thermal parameter such as hydrostatic pressure, impurity concentrations, etc. Whereas a
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classical phase transition corresponds to non-analyticity in the free energy as a function of temperature, a quantum phase transition involves non-analyticity in the ground state energy as a function of some non-thermal external parameter. In a strict sense, a quantum phase transition is defined only at zero temperature. However it affects finite temperature properties of a systems over a finite temperature range. Though the temperature range over which quantum critical fluctuations dominate is specific to the system, the emergent behavior at a quantum critical point is universal. The finite temperature properties depend on system dimension, order parameter dimension and symmetry, range of interaction and the dynamic scaling exponent. The concept of dynamic scaling exponent will be introduced in the next section. Consequences of being in the vicinity of a quantum phase transition has been observed in many systems like itinerant magnets, H\textsc{e}^4, ferroelectrics etc. and are argued in other systems like high T\textsc{c} superconductors. Before going into the detail of issues of a quantum phase transition relevant to the system we study, we now briefly introduce a path integral formulation of quantum statistical mechanics.

1.1.1 Quantum Statistical Mechanics

To calculate any physical properties of a statistical system in equilibrium we need to know its Partition function. In a statistical system quantum fluctuations become important when its temperature is much lower than its characteristic energy scale. In a quantum domain many system can be described by a Hamiltonian in operator form as $\hat{H} = \hat{T} + \hat{V}$. Where $\hat{T}$ and $\hat{V}$ are the kinetic and potential energies respectively in the operator form. With this Hamiltonian, its partition function at a finite temperature can be written as,

$$Z = Tr \exp(-\beta \hat{H}).$$  \hspace{1cm} (1.1)

Here $\beta$ is the inverse temperature. If we describe the state of system in terms of a complete set of eigen states $\{|\phi_i>\}$ of some operator $\hat{\phi}$, with corresponding eigen values ($\{\phi_i\}$), then the partition function in the path integral formalism\cite{7} can be
re-written as,

\[ Z = \int d\phi_a < \phi_a | \exp(-\beta \hat{H}) | \phi_a >. \quad (1.2) \]

On the other hand in quantum mechanics, the transition amplitude for a system in returning to its initial state \( \phi_a \) after a time \( t \) is given by,

\[ < \phi_a | \exp(-it\hat{H}) | \phi_a > = \int_{\phi(x,t)=\pm\phi_a(x)} d\phi e^{i \int_0^t dt \int dx \mathcal{L}(\phi, \frac{\partial \phi}{\partial t})}. \quad (1.3) \]

Here \( \mathcal{L} \) is the Lagrangian of the system. The boundary conditions are periodic for Bosons and anti-periodic for Fermions. It is now quite evident that one can write the expression for the partition function (eqn. (1.2)) using the expression for quantum mechanical transition amplitude (eqn. (1.3)) through an Wick rotation of the time axis to the imaginary direction. This leads to the following correspondence,

\[ \beta = \frac{1}{T} \equiv it. \quad (1.4) \]

At \( T = 0 \), i.e., at \( \beta = \infty \) system acquires a complete “extra dimension”. Above mathematical correspondence has interesting consequences. Firstly an equilibrium quantum statistical system in \( d \)-dimension is mapped on-to a \( d + 1 \)-dimensional classical statistical system. Secondly the information about the dynamics of a classical system enters into the description of the corresponding quantum system. Given the knowledge of dynamics of the system, quantum-classical mapping is extremely helpful in calculating quantum fluctuations in a systematic manner. When the interaction part contains terms beyond quadratic form, an exact calculation of a quantum partition function (eqn. (1.2)) is not possible. One needs to use some systematic and controlled truncation scheme.

### 1.1.2 Quantum critical point

Quantum phase transition follows a similar classification as thermal phase transition. A point in parameter space where a continuous phase transition occurs at zero temperature is called a quantum critical point. Near this point the system is describable by a vanishing characteristic energy scale or a diverging correlation
length which becomes the only relevant length scale near this point. As a result, at or near the quantum critical point various physical quantities follow power laws and such behavior can be explained by scaling arguments similar to that of the classical phase transitions[8, 9].

Dynamic scaling at $T = 0$: In general, an action in the path integral representation of a partition function can have terms with different powers of time derivative and space derivative of the field configurations. Thus in general, the scaling behavior of the characteristic time scale ($\tau$) and the correlation length ($\xi$) becomes anisotropic near a quantum critical point. Near a quantum critical point a new quantity, namely dynamic scaling exponent $z$ needs to be introduced. Dynamic scaling exponent characterizes the scaling behavior of the characteristic time scale ($\tau$) with the correlation length ($\xi$) and is defined as

$$\tau \sim \xi^z,$$  \hspace{1cm} (1.5)

with $z$ positive\footnote{Negative $z$ would mean smaller relaxation time for larger size system which is unphysical.} but not necessarily $= 1$. Such anisotropic scaling is used in other systems also. In case of dynamic critical phenomena where one studies the dynamics of a system near a critical point, one needs to consider such anisotropic space-time scaling to find out scaling behavior of various time dependent quantities near a critical point[10]. Similar situation also arises in case of a Lifshitz transition. In that case one considers critical phenomena in an anisotropic system and the critical properties depends on anisotropic scaling in the different directions[11]. Introduction of a dynamic scaling exponent has many consequences. A system in $d$–spatial dimension and near a quantum phase transition can be thought of as a
classical system of dimension $d+z$. The upper critical dimension\textsuperscript{2} of the quantum system is reduced by $z$, fluctuation effects becomes less relevant and the theory becomes more mean field like. However in a critical system whether it is classical or quantum, fluctuation corrections are always important and a naive perturbation theory can not have the correct answers. One needs to go beyond that and needs to invoke ideas like scaling hypothesis, various self-consistent scheme etc. In the scaling hypothesis that holds in case of a second order phase transition, any physical quantity near a quantum critical point can be written in a scaled form as follows,

$$\mathcal{O}(k, \omega, T = 0) = \xi^{\nu} \mathcal{F}(k\xi, \omega\xi^z, 0).$$

(1.6)

where $\mathcal{O}$ is some physical quantity, observed at a momenta $k$ and frequency $\omega$. The correlation length $\xi$ is the only important length scale in this hypothesis. $\mathcal{F}$ is the scaling function and $\nu$ is the scaling exponent. It is to be noted that though the scaling exponent is universal, the scaling function is not. Predictions based on such scaling hypothesis can be established by various theoretical schemes like self-consistent mean field theory, renormalization group theory etc.

**Finite size scaling at $T \neq 0$:** Since in a strict sense, a quantum critical point is defined only at zero temperature, it is not experimentally observable. However, a quantum critical point has its effects at finite $T$ also. At a low but non-zero temperature, any physical quantity of a quantum critical system should obey power law behavior in temperature and such behavior can be obtained using the previous scaled form as shown in equation (1.6). At a non-zero temperature, a quantum critical system behaves like a finite size system of size $T^{-1}$ in the “time direction”. In this case the correlation length can not diverge but can be extended up-to a size $T^{-z}$. Thus we can put $\xi = T^{-z}$ in the expression eqn. (1.6) and thus in the limit $T \to 0$,

$$\mathcal{O}(\omega = 0, k = 0, T) = T^{-z\nu} \mathcal{F}(0, 0, 1).$$

(1.7)

\textsuperscript{2}Upper critical dimension is defined as the critical value of the space dimension above which fluctuation effects does not play any major role and a mean field theory gives sufficiently correct result.
Above expression is the most experimentally relevant feature of a quantum critical point and is experimentally observed in many systems like itinerant magnets, $He_4$, ferroelectrics etc. The case of quantum criticality in ferroelectrics will be discussed in the next chapter where these power laws will be derived in a self-consistent mean field scheme.

1.1.3 First order quantum phase transition

Like classical phase transitions, a quantum phase transition can become first order because of the coupling to other degrees of freedom, disorder etc. A first order quantum phase transition can be observed through discontinuity of the order parameter at the transition point. A system undergoing a first order transition, evolves from its parent phase to resulting phase through a metastable state. In the intermediate phase a system shows coexistence of both the parent phase and the final phase. Classic example of a phase coexistence is the water-vapor phase transition and can be detected by some light scattering experiment. Thus in some sense a phase coexistence is also a signature of a first order transition. Many features of a first order transition can be described in Landau mean field description. In this case the free energy density for an one component system can be written as a variational form as,

$$f(\phi, r, \{\lambda_i\}) = r\phi^2 + \lambda_3\phi^3 + \lambda_4\phi^4 + \lambda_5\phi^5 + \lambda_6\phi^6 + .... \quad (1.8)$$

Here $\phi$ is the expectation value of some field configuration whose fluctuations are neglected completely. Such an approximation works well when the system is above its upper critical dimension and/or when order parameter dimensionality is very high. If one has the privilege to do so, the free energy density is dictated only by the symmetry of the system. The above expression is a small $\phi$ expansion of the variational form and the actual free energy can be found by minimizing the above expression with respect to $\phi$ followed by a substitution of the corresponding value of $\phi$ in the expression for variational ansatz. If the transformation which changes $\phi$ to $-\phi$ is a symmetry of the system, then terms with odd powers of $\phi$ are not allowed and one can truncate the free energy density at the lowest $i^{th}$ order term.
with positive $\lambda_i$. In case of positive $\lambda_4$, the Landau free energy density looks like

$$f(\phi, r, \lambda_4) = r\phi^2 + \lambda_4\phi^4. \tag{1.9}$$

Above free energy density shows a continuous phase transition at $r = 0$. For $r < 0$, order parameter is non-zero and is given by $\sqrt{-r}$ which smoothly goes to zero at the phase transition point.

On the other hand if it turns out that $\lambda_4 < 0$, one needs to truncate Landau free energy density at some higher power of $\phi$ with a positive coefficient. Let us consider the simplest possible case when $\lambda_6 > 0$. In this case the Landau free energy density looks like,

$$f(\phi, r, \lambda_4, \lambda_6) = r\phi^2 + \lambda_4\phi^4 + \lambda_6\phi^6. \tag{1.10}$$

In this case a non-zero value of the order parameter corresponding to a metastable

![Diagram](figure.png)

Figure 1.2: Typical Landau free energy profile for a first order transition. Eqn. (1.8) corresponds to such free energy profile when $0 \neq \lambda_3 < 0$.

minima of the Landau free energy profile develops at some positive value of $r$. At the phase transition point i.e. $r = 0$ order parameter has a discontinuity in its non-zero value $\sim \sqrt{-\frac{\lambda_4}{\lambda_6}}$ which corresponds to a first order transition.

However using Landau theory for a first order transition has many limitations. Firstly the Lanadu expansion is appropriate for small values of order parameter. Thus it can not incorporate the case of strong first order transition where the order parameter exhibits a large discontinuity at the phase transition point. On
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the other hand for weak first order transition, i.e. in the limit $\lambda_1 \to 0$ one needs to consider the fluctuation corrections in the effective coupling constant for the quartic term which is also missing in a traditional Landau expansion. The later case will be considered here and will be discussed in detail in this thesis in context of weak first order transition in ferroelectrics.

1.1.4 Effects of disorder

Introduction of disorder makes a system inhomogeneous. Coupling constants in a disordered system varies from point to point. As a result system becomes a collection of ordered and non-ordered regimes. Thus one is interested in average behavior of various physical properties with a meaningful averaging scheme. If in a particular scheme, the mean of the averaged physical quantities are greater than their variances, we can say that the averaging scheme is meaningful. In such a situation, a single large system is sufficient to represent the whole ensemble and is called self-averaging. At a pure critical point randomness is classified as relevant if it leads to a change in the critical behavior (i.e., the critical exponents) of the pure system. Such systems are non self-averaging with respect to a pure critical point scenario. The relevancy of disorder for a pure critical point can be estimated using a field theoretical language as follows. Let us consider a disordered parameter $\delta r(x)$ of quenched type (no dynamics) which has a Gaussian distribution with variance $g$, couples to some field variable $\mathcal{O}(x, \tau)$ with scaling dimension $\eta_0$ as

$$\int d^d x d\tau \delta r(x) \mathcal{O}(x, \tau). \quad (1.11)$$

Integration of the Gaussian disorder will generate a term

$$g^2 \int d^d x d\tau_1 d\tau_2 \mathcal{O}(x, \tau_1) \mathcal{O}(x, \tau_2). \quad (1.12)$$

The above term will generate the effective disorder effect in a disordered system. Now if we use a dimensional analysis to look for the relevancy of the above term near a critical point, we see that at the zeroth order perturbation theory the coupling constant $g^2$ has the scaling dimension $d + 2z - 2\eta_0$. Thus near a critical point where low energy and long wave length fluctuations are most dominant, the
coupling constant $g^2$ becomes relevant if

$$d + 2z - 2\eta_0 > 0.$$  \hspace{1cm} (1.13)

This is the criteria for relevancy of certain kind of disorder in a quantum phase transition. When disorder couples to energy density whose scaling dimension of the associated coupling constant is $1/\nu$, and so the dimension of the energy operator is $\eta_0 = d + z - 1/\nu$. Thus the criterion for its relevance becomes above relation becomes

$$\nu < \frac{2}{d + z}.$$ \hspace{1cm} (1.14)

In literature this relation is known as Harris criteria[5]. Above criterion is derived on the basis of a dimensional analysis which neglects the effects of the interaction and the effects of spatial inhomogeneity as well. However it sets a criterion for the breakdown of a pure critical behavior. When certain kind of disorder is found to be relevant, one needs to consider the spatial inhomogeneity which is not included in a theory of critical phenomena in a pure system. Such a consideration needs some technique beyond standard perturbation theory. Vector breaking of the replica symmetry is such a candidate and is used to analyze the effects of disorder in ferroelectrics near a quantum phase transition in this thesis.

### 1.2 Quantum paraelectrics

In the previous section we have introduced some basic ideas regarding the quantum statistical mechanics and the quantum phase transitions. Now we introduce some dielectric materials where those theoretical concepts can be experimentally observed. Insulating materials such as SrTiO$_3$ and KTaO$_3$ are ABO$_3$ type perovskites and have interesting dielectric behavior. They are known to remain paraelectric down to any experimentally accessible low temperature. However, the $q = 0$ optic mode which consists of Ti or Ta motion along a diagonal of the cubic perovskite unit cell against oxygen octahedra becomes very nearly unstable as temperature approaches to zero. Perfect softening of this optic mode would lead to a ferroelectric transition as occurs in other structurally similar materials like BaTiO$_3$. Thus at low temperature ($< 10K$ for SrTiO$_3$), these materials end up in a state
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Figure 1.3: An unit cell of a ABO₃ type perovskite structure. Filled black circles are A-atom at the corners, circle filled with dashed line is the B-atom at the center and Oxygen atoms are shown with un-filled circles.

of incipient ferroelectrics, characterized by a very high, temperature independent static dielectric constant ($\mathcal{O}(10^4)$ for SrTiO₃) and no spontaneous polarization. Dielectric properties of these materials are being studied since long ago and they are widely known as quantum paraelectrics in the literature[16]. The correspondence between the high static dielectric susceptibility and the softening of an optic mode is also confirmed by the neutron scattering experiments[17, 18]. Thus it is evident that the quantum paraelectric systems are of displacive type and the dielectric behavior of these systems are dominated by a nearly soft $q = 0$ transverse optic mode fluctuations. A theoretical understanding of the dielectric behavior of these materials needs a proper account of not only thermal fluctuations but also quantum fluctuations arising from the optic modes near zone center. The lack of physical content of earlier theoretical works on this material, particularly regarding its vicinity to a quantum phase transition is one of the motivations for recent studies on this materials. In an earlier attempt to explain the dielectric behavior of such systems, Barrett [19] proposed a semi-phenomenological theory, which essentially recasts the Curie-Weiss formula with a replacement of temperature $T$ there, by average energy, thereby the inverse of dielectric susceptibility could be written as, $\chi^{-1} \propto T_1 \coth(T_1/T) - T_c$, where $T_c$ is classically calculated critical temperature and $T_1$ is a quantum scale $\sim (h/mass)$. This theory, in the high temperature limit, reproduces the Curie Weiss law. To match experimental data in SrTiO₃ the Barretts' formula has been found inadequate as one single constant quantum scale $T_1$ can not trace the full curve. The formula has since been modified
Figure 1.4: Temperature-dependent phonon modes in SrTiO$_3$ measured by Shirane G and Yamada Y, Phys. Rev. 177, 858 (1969). The 111°K transition is caused by the soft mode at the zone boundary. Soft mode near the origin is due to incipient ferroelectricity.

in various ways, for example, by introducing an extra exponent [20], that is, by writing $\chi^{-1}$ as $(T_1 \coth(T_1/T) - T_c)^{-\nu}$, and by making $T_1$ temperature dependent with an extra scale [21], to take care of various “anomalies”, for example the one near 40K. There has been a proposal of attributing this extra energy scale to the structural transition which occurs at 110K [22]. These proposals either follow an order parameter expansion similar to the Landau expansion or some modifications thereof, hence they do not introduce any new microscopic description. Moreover these attempts considers fluctuations arising from $q = 0$ mode only and misses a fact that the characteristic energy scale in this systems are very low, i.e. these systems are near a quantum phase transition. We assume that the would be quantum phase transition from a paraelectric phase to a ferroelectric phase in this materials to a continuous transition and will show that analysis based on such a view point can capture many features of the dielectric behavior of these system which were untouched by the previous theories.

We analyze the fluctuation effects in such systems within a self consistent mean field approximation. The theory involves a lowest order perturbation expansion of
a continuum theory with a momentum cut-off and self consistent conditions[23]. Results depend on the choice of the cut-off and we have shown that a choice of temperature dependent cut-off at/near a quantum critical point can lead to a novel $T^{-2}$ behavior of the static dielectric susceptibility which is argued by scaling analysis[24] and also verified by recent experiment[25]. Motivated by the success of the assumption of nearness of these materials to a quantum critical point we discuss the effects of strain coupling, magneto-electric coupling and the quenched disorder in these materials. Each case will be analyzed by a minimal action and suitable mean-field scheme. Analysis are mostly analytic and are motivated to capture the basic physics rather than exact matching with the experimental data. Moreover due the universality of the behavior near a quantum critical point many of these analysis will also be useful for analyzing the quantum critical behavior of a large class of Bosonic systems with undamped dynamics.

The thesis is organized in the following manner. In this chapter, basic concepts related to quantum phase transitions, phase transitions in ferroelectrics and some experimental facts about some incipient ferroelectrics such as SrTiO$_3$ and KTaO$_3$ are introduced. In the next chapter we will explore the possibility of quantum critical phenomena and its consequences in these materials. Attempts are made
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to analyze low temperature behavior of these system with the assumption of its nearness to a quantum critical point. It is followed by a theory of weak first order quantum phase transition observed in SrTiO$_3$ which is assumed to be a result of the strain coupling. Analysis is based on a self-consistent scheme for vertex corrections at non-zero polarization. Predictions are made on the discontinuity in the non-zero polarization both at zero and non-zero temperature and are in accord with experiments. Chapter four is an account of dielectric behavior of an incipient ferroelectric EuTiO$_3$ where ferroelectric fluctuations are coupled to anti-ferromagnetic fluctuations. Invoking a self-consistent scheme similar to the first chapter in presence of magneto-electric coupling and external magnetic field, predictions are made about new power law behavior of the static dielectric behavior at finite temperature. Predictions are new and worth further experimental investigations. Next chapter is an account of the effects of disorder in quantum critical paraelectrics. Discussions are based on semi-phenomenological Ginzburg-Landau theory with self-consistent mean field analysis. In this case a replica formalism is invoked to take account of fluctuations from locally ordered regimes. A prediction broad power law distribution of the instability points and its consequences on the temperature dependence of the static dielectric behavior are made.