Third order dielectric susceptibility in a model quantum paraelectric

R. Martoňák\textsuperscript{a,b,c}, E. Tosatti\textsuperscript{b,c,d}

\textsuperscript{a}Johannes-Gutenberg Universität, Institut für Physik, WA 331, D-55099 Mainz, Germany
\textsuperscript{b}International Centre for Theoretical Physics (ICTP), P.O. Box 586, 34014 Trieste, Italy
\textsuperscript{c}International School for Advanced Studies (S.I.S.S.A.), Via Beirut 2–4, 34014 Trieste, Italy
\textsuperscript{d}Istituto Nazionale Fisica della Materia, Unità Trieste SISSA, Italy

Abstract

In the context of perovskite quantum paraelectrics, we study the effects of a quadrupolar interaction $J_q$, in addition to the standard dipolar one $J_d$. We concentrate here on the nonlinear dielectric response $\chi_P^{(3)}$, as the main response function sensitive to quadrupolar (in our case antiquadrupolar) interactions. We employ a 3D quantum four-state lattice model and mean-field theory. The results show that inclusion of quadrupolar coupling of moderate strength ($J_q \sim \frac{1}{4}J_d$) is clearly accompanied by a double change of sign of $\chi_P^{(3)}$ from negative to positive, near the quantum temperature $T_Q$ where the quantum paraelectric behaviour sets in. We fit our $\chi_P^{(3)}$ to recent experimental data for SrTiO$_3$, where the sign change is identified close to $T_Q \sim 37K$. 
I. INTRODUCTION

Classical perovskite ferroelectrics such as BaTiO$_3$ are very widely studied. As is well brought out by recent quantitative ab-initio studies [1–3], formation of a local dipole moment corresponds to formation of a shorter, partially covalent Ti-O bond while dipole-dipole interaction is partly of Coulomb origin (long-range) and partly resulting from the overlap of atomic orbitals (short-range).

The situation is considerably more open and interesting in those cases, mainly SrTiO$_3$ (also KTaO$_3$) where quantum fluctuations are important to the extent that they actually suppress ferroelectricity altogether (”quantum paraelectrics” - Müller and Burkhard [4]). Experimentally, the onset of quantum paraelectric regime in SrTiO$_3$ at a ”quantum temperature” $T_Q \sim 30 \div 40$ K has revealed a variety of intriguing features. They are connected in particular with a surprisingly abrupt off-center local displacement of the transition metal ion, without ferroelectric or structural long-range order, leading to phase transition-like features in EPR [5], EXAFS [6], X-ray [7] and sound velocity [8–10]. A similarly abrupt phenomenon has been observed also in NMR studies of KTaO$_3$ [11]. In SrTiO$_3$, various spectroscopic anomalies have also been found in Raman and Brillouin studies [12].

The reason why quantum fluctuations are so important here is not because the ions are particularly light. Rather, it is because the lattice packing is so tight, as compared, e.g. to BaTiO$_3$, to leave very little room for the Ti ion to move off-center and form a preferential Ti-O dipole. As the lattice is compressed, the classical ferroelectric Ti off-center equilibrium displacement gets smaller and smaller, and the system approaches the classical displacive limit, characterized by a vanishing classical Curie temperature $T_c$. In SrTiO$_3$, the extrapolated classical off-center Ti displacement and Curie temperature are $\sim 0.03\AA$ and $\sim 37$ K respectively, against $\sim 0.1\AA$ and $\sim 400$ K in BaTiO$_3$. In such a situation, quantum fluctuations, even if due to a heavy ion such as Ti, can well remove the ferroelectric long-range order and cause a persistence of the paraelectric state down to $T \to 0$. We have previously discussed this scenario in some detail [22] and also provided a quantum Monte Carlo study
of a lattice model illustrating this phenomenon [21]. A very recent ab-initio quantum Monte Carlo study of SrTiO$_3$ and BaTiO$_3$ has moreover indicated that the exquisite sensitivity of the ferroelectric order parameter to this kind of quantum fluctuations is likely to be related to the very anisotropic, quasi-one-dimensional electric dipole correlations, which are absent for other ”neutral” structural order parameters [13].

The theoretical study of structural phase transitions and ferroelectricity has so far mostly been conducted on models with an anharmonic on-site potential and a bilinear intercell interaction (standard model of structural phase transition, [14,15]), as well as on more specific shell models [16,17]. Likewise, the studies of quantum paraelectricity have been performed within this model [18,19], or some approximate version of it, like the Ising model in transverse field [20] or the quantum 4-state clock model [21]. All these studies predict the existence of a critical value for the strength of quantum fluctuations, above which static ferroelectricity disappears in the ground state. The crossover from the high temperature classical paraelectric to low temperature quantum paraelectric is predicted to be a smooth crossover, without any sharp features. These models are therefore unable to account for the experimentally observed abrupt phenomena at $T_Q \sim 30 \div 40$ K in SrTiO$_3$.

While a thorough understanding of what is going on is still missing, it seems clear that on cooling below $T_Q$ the individual Ti ions move off-center inside their cell with surprising abruptness, whereas their mutual ordering between different cells only progresses slowly as $T$ is lowered and never becomes total, down to the lowest temperatures [22]. An abrupt onset of the local ferroelectric lattice distortion is not well explained by the standard model even if the local coupling of the polarization to the lattice strain is taken into account, as done for example by Zhong and Vanderbilt [13]. In the latter quantum study, no particular sharp features have been observed on cooling the system down to $T \sim 5$ K, contrary to the experimental observations. It therefore appears highly probable that in order to achieve a satisfactory description of low temperature regime of SrTiO$_3$, the extension of the standard model to include some physically new ingredient is required.

A very natural extension is, apart from introducing a coupling of the soft mode to other
phonon modes, to drop the limitation of a simple, dipolar interaction \( \cos(\phi_i - \phi_j) \) and take into account also higher angular terms (\( \phi_i \) is the phase angle of a 2-component XY order parameter in cell \( i \), see section 2). The next order term with square symmetry has an angular dependence \( \cos 2(\phi_i - \phi_j) \), typical of the quadrupolar interactions.

This paper is devoted to a study of the effects of such a quadrupolar-type of interaction on the onset of quantum paraelectricity in SrTiO\(_3\). Deferring to section 2 a more detailed presentation of a simplified lattice Hamiltonian which takes both dipolar and quadrupolar coupling into account, we note that the impact of the new coupling might be of qualitative importance. In fact, as we pointed out in [22], quantum effects in a quadrupolar system are very different from those in a dipolar system. A purely quadrupolar quantum system exhibits reentrance in its phase diagram, while a dipolar one does not. Reentrance in quantum quadrupolar systems is beautifully exemplified by the data of Silvera et al. on ordering of HD under pressure [23]. It also appears very straightforwardly in simple models, at least in the mean-field theory [22,24].

The ferroelectric perovskites, unlike HD, are unlikely to be dominated by the quadrupolar interaction. Our point, however, will be that they exhibit features which cannot be explained by purely dipolar couplings. Experimentally, direct detection of quadrupolar couplings in a ferroelectric system is not completely straightforward, since the main quantity, the linear dielectric susceptibility \( \chi_1 \), is unaffected by them, at least on the mean-field level [23]. However, the third order nonlinear dielectric susceptibility \( \chi^{(3)}_P \), defined by \( P = \chi^{(1)}_PE + \chi^{(3)}_PE^3 + \ldots \), turns out to be very sensitive to quadrupolar couplings. In particular Morin and Schmitt [25] (in a completely parallel magnetic context) showed that \( \chi^{(3)}_P \) will change sign from negative to positive, as a system reaches a temperature region where quadrupolar effects become important, while it will stay negative so long as they are unimportant.

1This is not the full form of the true Coulomb quadrupole-quadrupole interaction, much as \( \cos(\phi_i - \phi_j) \) is not that of a true dipole-dipole interaction. These forms are adopted here for their simplicity.
Very recently, new detailed data have been obtained by Hemberger, Lunkenheimer, Viana, Böhmer and Loidl [26], who measured $\chi^{(3)}_P$ in SrTiO$_3$. They find strong structures in $\chi^{(3)}_P$ between 30 and 60 K, precisely in the region near $T_Q$, where the Ti ions suddenly move off-center on cooling, giving rise to quantum fluctuating local dipoles, and quantum paraelectricity sets in.

In this paper we study this problem, and show that the behaviour of $\chi^{(3)}_P$ can be understood if we assume the existence of quadrupolar interactions in SrTiO$_3$, besides the standard dipolar ones. In section 2, we first introduce a simple quantum lattice model including dipolar as well as and quadrupolar couplings. In section 3 we calculate $\chi^{(3)}_P$ within mean-field theory, and find that depending on the relative strength of the quadrupolar and dipolar interactions, $\chi^{(3)}_P$ exhibits a rich behaviour as a function of temperature. In section 4 we consider the application of this calculation to the case of SrTiO$_3$. By comparing the calculated temperature dependence of the third order dielectric susceptibility to the observed data [26] we estimate the strength of effective quadrupolar interactions in SrTiO$_3$. The results indicate that in SrTiO$_3$ a double change of sign of $\chi^{(3)}_P$ should take place, above and below $T \sim T_Q$, with decreasing temperature. The upper one from negative to positive $\chi^{(3)}_P$ is related to onset of quadrupolar effects; the lower one from positive back to negative $\chi^{(3)}_P$, to the onset of quantum paraelectricity. Before concluding, in section 5, we shall briefly discuss the possible origin of the quadrupolar interactions in connection with the lattice dynamics of SrTiO$_3$.

II. SIMPLIFIED LATTICE MODEL OF SRTIO$_3$

The hamiltonian is quite generally a function of $3 \times 5 = 15$ continuous coordinates per cell in the cubic phase (5 atoms per unit cell) or of even more coordinates in the tetragonal antiferrodistorted state. Even simplifying to include only polarization, strain and antiferrodistortive degrees of freedom, we are still forced to include at least $3+3+3 = 9$ degrees of freedom per cell. A proper quantum treatment, for example via PIMC of
so many continuous degrees of freedom is at present very demanding. A quantum lattice model, although much less realistic, and incapable of describing the displacive behaviour of a perovskite in its classical regime \((T \gg T_Q)\) is more directly amenable to study either via PIMC, or, much more simply, via mean-field theory.

In this section we introduce a simplified discrete lattice model of a QPE system including dipolar as well as quadrupolar interactions. A discussion of these simple models in the context of quantum paraelectricity of \(\text{SrTiO}_3\) has already been presented in Ref. \([21,22]\), where a variety of lattice models has been introduced and considered. For convenience we briefly repeat here the main ideas.

We start from the experimentally observed XY-character of the incipient ferroelectricity in tetragonal \(\text{SrTiO}_3\). The physical reason why at zero stress and field the polarization is confined to the \((x,y)\) plane is given by the presence (below 105 K) of the antiferродistortive order parameter, which expands the lattice in \((x,y)\) plane, while contracting it along the \(z\)-axis, taken along (001). The onset of ferroelectric polarization is favored in the expanded \((x,y)\) plane, and disfavoured in the contracted \(z\)-direction. In the \((x,y)\) plane, the polarization has four easy directions, namely \((\pm 100), (0\pm 10)\). The corresponding quantum four-state clock model introduced first in \([21]\) and considered in various versions in \([22]\) appears thus to be a minimal model for the description of \(\text{SrTiO}_3\) at sufficiently low temperatures. The model neglects the radial degrees of freedom associated with the continuous displacement of the Ti ion from the center of the oxygen cage in the cell \(i\) of the crystal. It assumes that the displacement is of fixed magnitude and can be completely characterized by a discrete plane rotor angular variable \(\phi_i\). This variable is allowed four possible values \(\phi_i = 0, \pi/2, \pi, -\pi/2\), and the corresponding four quantum states labeled as \(|0\rangle, |1\rangle, |2\rangle, |3\rangle\) constitute a basis of the on-site Hilbert space. The quantum effects are mimicked by allowing the clock variable \(\phi_i\) to hop onto its two nearest orientations, i.e. from \(\phi_i\) into \(\phi_i \pm \frac{\pi}{2}\) with amplitude \(-t\). This is expressed by a hamiltonian term \(H_{i\text{hop}}\), represented in the site basis by the matrix
For simplicity, interaction between different cells $i \neq j$ is limited to nearest neighbours, and the adjacent cells are supposed to interact via the usual ”dipole” interaction

$$H^d = -J_d \sum_{(ij)} \cos(\phi_i - \phi_j),$$  \hspace{1cm} (2)$$
as well as via a ”quadrupole” interaction

$$H^q = -J_q \sum_{(ij)} \cos 2(\phi_i - \phi_j).$$  \hspace{1cm} (3)$$

While the origin of $H^d$ is widely discussed, that of $H^q$ is not, and this is to our knowledge the first place where such a term is invoked for a displacive ferroelectric. The strength of the $H^q$ term in SrTiO$_3$ will be estimated in section 4 and its possible origin will be discussed in section 5. We note that the classical four-state model $H = H^d + H^q$ is the well-known Ashkin-Teller model [28]. The 2D classical A-T model is already considerably richer than the XY model [8]. For the sake of simplicity, we shall treat our model on a 3D cubic lattice, and use a mean-field theory. This approximation, while far from accurate, is at least not totally unacceptable in (3+1)D and is attractive due to its great simplicity.

The complete hamiltonian that will be considered in the following is then given by

$$H = \sum_i H^\text{hop}_i + H^d + H^q.$$  \hspace{1cm} (4)$$

III. MEAN FIELD THEORY OF THIRD ORDER DIELECTRIC SUSCEPTIBILITY

In this section we start from our microscopic hamiltonian (4) and derive a free energy expansion, using a mean-field approximation. From the free energy expansion we then
calculate the third order dielectric susceptibility $\chi_P^{(3)}$ as a function of temperature. Our treatment will parallel very closely that of Morin & Schmitt [25] for the magnetic case. We will show that the behaviour of $\chi_P^{(3)}$ at low and intermediate temperatures relative to the quantum temperature $T_Q$ is profoundly modified by the presence of the quadrupolar interactions.

We take as our mean-field hamiltonian a sum of on-site mean-field hamiltonians,

$$H^0 = \sum_i H_i^0 = \sum_i (H_{i\text{hop}}^0 - eP_{xi} - qR_i), \quad (5)$$

corresponding to a single quantum rotor in external fields $e$ and $q$, coupling to the on-site polarization and quadrupole moment $P_{xi}$ and $R_i$, respectively. For simplicity, we shall assume from now on that the polarization component $P_y$ is always zero and omit the subscript $x$ on $P_x$; we also set $|t| = 1$ as the energy and temperature scale. The matrix of the on-site hamiltonian (5) in the basis of the 4 states |1⟩, |2⟩, |3⟩, |4⟩ reads

$$H_i^0 = \begin{pmatrix}
q & -1 & 0 & -1 \\
-1 & e - q & -1 & 0 \\
0 & -1 & q & -1 \\
-1 & 0 & -1 & -e - q
\end{pmatrix}. \quad (6)$$

The trial free energy $F_t(e, q)$ per site as a function of the mean-field variational parameters $e, q$ is given by

$$F_t(e, q) = F_0 + \langle H - H^0 \rangle_0 = F_0 - 6J_d \frac{1}{2} P^2 - 6J_q \frac{1}{2} R^2 + eP + qR, \quad (7)$$

where

$$F_0 = -\frac{1}{\beta} \text{Tr} \ e^{-\beta H^0}, \quad (8)$$

and $P, R$ are now a ferroelectric and a quadrupolar order parameter. The hamiltonian (5) cannot be diagonalized analytically, but the expansions of the energy levels in powers of the fields $e, q$ around their zero values (we assume that our system, like SrTiO$_3$ in the absence of fields, is paraelectric) can be found by perturbation theory. For our purpose it is sufficient to
find the expansion to fourth order in $e$ and to second order in $q$. The following expressions are found for the eigenvalues of $H^0$

$E_0 = -2 - \frac{1}{4}e^2 + \frac{1}{64}e^4 - \left(\frac{1}{4} + \frac{3}{32}e^2\right)q^2 + \frac{1}{4}e^2q + \ldots$  \hspace{1cm} (9)

$E_1 = -q$  \hspace{1cm} (10)

$E_2 = (1 - \frac{1}{2}e^2)q + \ldots$  \hspace{1cm} (11)

$E_3 = 2 + \frac{1}{4}e^2 - \frac{1}{64}e^4 + \left(\frac{1}{4} + \frac{3}{32}e^2\right)q^2 + \frac{1}{4}e^2q + \ldots$  \hspace{1cm} (12)

whence the power expansion of free energy (8) can be calculated,

$F_0 = -\frac{1}{2}\chi^{(1)}_0 e^2 - \frac{1}{2}\chi_2 q^2 - \chi^{(2)}_2 e^2q - \frac{1}{4}\chi^{(3)}_0 e^4 + \ldots$,  \hspace{1cm} (13)

where

$\chi^{(1)}_0 = \frac{1}{2}\tanh\beta$

$\chi^{(3)}_0 = \frac{1 + 4\beta e^{2\beta} - e^{4\beta}}{16(1 + e^{2\beta})^2}$

$\chi_2 = -\frac{1 - 4\beta e^{2\beta} - e^{4\beta}}{2(1 + e^{2\beta})^2}$

$\chi^{(2)}_2 = -\frac{1}{4}\tanh^2\beta$. \hspace{1cm} (14)

The polarization and quadrupolar order parameters $P$ and $R$ can now be calculated as derivatives of (13) with respect to the fields $e$ and $q$

$P = -\frac{\partial F_0}{\partial e} = \chi^{(1)}_0 e + 2\chi^{(2)}_2 e q + \chi^{(3)}_0 e^3 + \ldots$ \hspace{1cm} (15)

$R = -\frac{\partial F_0}{\partial q} = \chi_2 q + \chi^{(2)}_2 e^2 + \ldots$. \hspace{1cm} (16)

In order to obtain an expansion of the free energy term $F_0$ in terms of the order parameters $P, R$, we must invert the expansions (15) and (16) and express the fields $e, q$ in terms of powers of $P$ and $R$. We find the expressions

$e = \frac{1}{\chi^{(1)}_0} P - \frac{2\chi^{(2)}_2}{(\chi^{(1)}_0)^2 e^{\chi_2}} P R - \frac{1}{(\chi^{(1)}_0)^4} \left(\chi^{(3)}_0 - \frac{2(\chi^{(2)}_2)^2}{\chi_2}\right) P^3 + \ldots$ \hspace{1cm} (17)

$q = \frac{1}{\chi_2} R - \frac{\chi^{(2)}_2}{(\chi^{(1)}_0)^2 e^{\chi_2}} P^2 + \ldots$. \hspace{1cm} (18)
which after substituting to (13) yields the desired form

\[
F_0 = -\frac{1}{2}(\chi_0^{(1)})^{-1} P^2 - \frac{1}{2}(\chi_2)^{-1} R^2 + \frac{2\chi_2^{(2)}}{(\chi_0^{(1)})^2 \chi_2} P^2 R + \left( \frac{3}{4} \frac{\chi_0^{(3)}}{(\chi_0^{(1)})^4} - \frac{3}{2} \frac{(\chi_2)^2}{\chi_2 (\chi_0^{(1)})^4} \right) P^4 + \ldots .
\] (19)

At this point, we can express the full free energy \(F_t\) (7) as an expansion in powers of the order parameters, namely polarization \(P\) and quadrupole moment \(R\). It reads

\[
F_t(P, R) = \frac{1}{2}[(\chi_0^{(1)})^{-1} - 6J_d] P^2 + \frac{1}{2}[(\chi_2)^{-1} - 6J_q] R^2 - \frac{\chi_2^{(2)}}{(\chi_0^{(1)})^2 \chi_2} P^2 R
\]

\[\] 

\[-\frac{1}{4} \frac{1}{(\chi_0^{(1)})^4} \left( \chi_0^{(3)} - 2 \frac{(\chi_2)^2}{\chi_2} \right) P^4 .
\] (20)

As in real SrTiO\(_3\) at zero stress and field, we assume \(P = R = 0\). In the neighbourhood of this minimum of \(F_t\), we now wish to eliminate \(R\), yielding an effective free energy expansion in powers of the polarization \(P\) alone. Minimizing (20) with respect to \(R\), we obtain

\[
R = \frac{\chi_2^{(2)}}{(\chi_0^{(1)})^2 (1 - 6J_q \chi_2)} P^2 ,
\] (21)

and after substituting this expression back to (20) we obtain the expansion of \(F_t\) in terms of \(P\) only

\[
F_t(P) = \frac{1}{2}[(\chi_0^{(1)})^{-1} - 6J_d] P^2 - \frac{1}{4} \frac{1}{(\chi_0^{(1)})^4} \left( \chi_0^{(3)} + \frac{12J_q (\chi_2)^2}{1 - 6J_q \chi_2} \right) P^4 .
\] (22)

Now it is worth noticing that the coefficient of \(P^4\) has been renormalized downwards (i.e. towards negative values) by the quadrupolar coupling \(J_q\). This follows because \(\chi_0^{(3)}\) is negative definite, while the other term dependent on \(J_q\) is positive as long as \(J_q < (6 \chi_2)^{-1}\).

By adding an interaction term \(-EP\), corresponding to an external electric field \(E\), to the free energy (22) and minimizing with respect to the polarization \(P\), we can calculate the first order (linear) and third order (nonlinear) dielectric susceptibilities \(\chi_1^{(1)}\) and \(\chi_3^{(3)}\), defined as usual by the expansion

\[
P = \chi_1^{(1)} E + \chi_3^{(3)} E^3 + \ldots .
\] (23)

In our model we find
\[ \chi^{(1)}_P = \frac{\chi_0^{(1)}}{1 - 6J_d\chi_0^{(1)}} \]  
\[ \chi^{(3)}_P = \frac{1}{(1 - 6J_d\chi_0^{(1)})^4} \left( \chi_0^{(3)} + \frac{12J_q(\chi_2^{(2)})^2}{1 - 6J_q\chi_2} \right). \]  

The nonlinear susceptibility (25) can also be written in a slightly more transparent form

\[ \chi^{(3)}_P = \chi^{(3)}_P(J_q = 0) + \frac{12J_q(\chi_0^{(1)})^4}{1 - 6J_q\chi_2}, \]  

where we made use of the relation \((\chi_2^{(2)})^2 = (\chi_0^{(1)})^4\), verified by Eq.(14). While the first order dielectric susceptibility \(\chi^{(1)}_P\), in the mean field approximation, is independent of \(J_q\), we see that the third order susceptibility \(\chi^{(3)}_P\) is a sum of its original value in the absence of quadrupolar coupling which is always negative, and of an additional positive term. The latter can eventually overbalance the negative term and reverse the sign of \(\chi^{(3)}_P\), if \(J_q\) is large enough. The temperature dependences of \(\chi^{(3)}_P\) for \(J_d = 0.273\) and a series of values of quadrupolar coupling \(J_q\) are plotted on Fig.1. We see that a) the effect of renormalization of \(\chi^{(3)}_P\) is most strongly pronounced at intermediate temperatures \(T \sim T_Q\), and b) there is a region of values of \(J_q\) where \(\chi^{(3)}_P\) now turns positive at intermediate temperatures, while staying negative at sufficiently high and low temperatures. Finally, if \(J_q\) is stronger, there is a temperature where \(\chi^{(3)}_P \to \infty\) and an independent (anti)quadrupolar ordering takes place.

We point out here that positive \(\chi^{(3)}_P\), which means a negative overall coefficient in front of \(P^4\) term in (22) would imply the ferroelectric transition at the classical level to be of first order. The QPE state for positive \(\chi^{(3)}_P\) can therefore be seen as a frustrated first order transition.

**IV. APPLICATION TO THE CASE OF SRTIO\(_3\)**

We now wish to apply the above results to the case of SrTiO\(_3\). As mentioned in the introduction, SrTiO\(_3\) belongs rather to the class of displacive than to the order-disorder ferroelectrics. The use of a continuous model should thus be preferred to a discrete one, if a realistic comparison to experiment is to be attempted. However, the main purpose of this
paper is to pursue the qualitative differences induced in the behaviour of $\chi^{(3)}_P$ by a presence of a quadrupolar interaction with its different angular dependence, and these features should be correctly reproduced also by a discrete model, which in turn has the big advantage of being easily analytically tractable on a simple mean-field level. It is clearly beyond the possibilities of such a discrete model to describe the sharp dipole onset observed at $T_Q \sim 37$ K, since the local off-center displacement is described just by the radial part of the local mode which is left out completely in the present discrete model.

Before attempting any comparison between experimental data \cite{26} and our results \cite{24} and \cite{25}, we have to convert the latter formulas from dimensionless units back to normal ones. We consider first the linear dielectric susceptibility. If the displacement of the Ti ion from the center of the cage is associated with a dipole moment $\mu$, the dipole density per unit volume being $n$, then $\chi^{(1)}_P$ can be conventionally written in form of the familiar Barrett formula

$$\chi^{(1)}_P = \frac{n\mu^2}{2k_B\epsilon_0} \left( \coth \frac{T}{T_1} - \frac{1}{2} \right),$$

derived in many different contexts \cite{29,4}. The temperatures $T_0$ and $T_1$ are given by $T_0 = 3J_d/k_B, T_1 = 2t/k_B$, and have the meaning of classical Curie temperature and of quantum temperature, respectively. This formula has been used to fit the $\chi^{(1)}_P$ data on SrTiO$_3$ \cite{3,26}, and produces a reasonable fit over a temperature range from 0 to 100 K with $T_1 \sim 88$ K, $T_0 \sim 36$ K, and $\frac{n\mu^2}{2k_B\epsilon_0} \sim 10^5$ K. The microscopic hamiltonian parameters corresponding to these values of $T_0$ and $T_1$ are $J_d = 12$ K, $t = 44$ K. We note in particular that the ratio $J_d/t = 0.273$ is not far from the critical mean-field value of $(J_d/t)_c = 1/3$, where our model undergoes a transition from para ($J < J_c$) to ferro ($J > J_c$).

A problem arises, however, with the prefactor $\frac{n\mu^2}{2k_B\epsilon_0}$, since with one dipole per cell $n = 1/a^3 = 1.68 \times 10^{28}$ m$^{-3}$, where $a = 3.9\AA$ is the lattice constant of SrTiO$_3$, the required value of the dipole moment per cell is $\mu = 3.4 \times 10^{-29}$ Cm. If we take the effective charge to be $Z^* \sim 8$ \cite{30}, the corresponding displacement should be $d \sim 0.26\AA$, which is an order of magnitude larger than the value of $\sim 0.03\AA$ realistically estimated in Ref. \cite{4}, as well as
in ab-initio calculations [3]. The discrepancy is, in our opinion, related to the quantitative inadequacy of the discrete model to SrTiO$_3$, as well as to the mean-field treatment. The Barrett formula reproduces the essential features of the temperature behaviour of the linear susceptibility well enough, but fails at the quantitative level.

Let us now come to the nonlinear susceptibility, and the related quadrupolar effects. The complete expression we have just obtained for $\chi^{(3)}_P$ is

$$\chi^{(3)}_P = \frac{n\mu_0^4}{(t - 6J_d\chi^{(1)}_0)^4} \left( \chi^{(3)}_0 + \frac{12J_q(\chi^{(2)}_2)^2}{t - 6J_q\chi_2} \right),$$

(28)

where $\beta = t/(k_B T)$. We can now try to fit this formula to the $\chi^{(3)}_P$ data measured on SrTiO$_3$ [26]. For this purpose, however, the form in which the data are presented in Ref. [26], namely log $|\chi^{(3)}_P|$ vs. temperature plot is not so well suited, since the mere knowledge of the magnitude of the complex quantity $|\chi^{(3)}_P|$ without its phase angle, mixes together the real and imaginary part and conceals the desired information about the sign of the real part. Our static mean-field theory produces, of course, a real static $\chi^{(3)}_P$. We have therefore attempted to extract Re $\chi^{(3)}_P$ from the data [26], making use of the corresponding phase angles kindly provided by J. Hemberger [31]. The resulting experimentally derived Re $\chi^{(3)}_P$ (corresponding to the lowest electric field intensity $E_0 = 50$ V/mm) is shown on Fig.2 as a function of temperature. While at low temperatures this quantity is negative, on heating it crosses zero at $T = 33$ K where it becomes positive, passes through a maximum at $T = 45$ K and then approaches zero again, from the positive values. Above $T \approx 60$ K, it probably turns small and negative again, although experimental uncertainty appears larger in this regime. With hindsight, we re-examined also some old data of Fleury and Worlock [32] for SrTiO$_3$ and found that evidence for a positive $\chi^{(3)}_P$ at $T = 40$ K can be evinced there, too (Fig. 5 b, Ref. [32]).

Having in mind the difficulties related to the prefactor, encountered in case of $\chi^{(1)}_P$, we decided to allow this to be a free parameter. Anticipating that the best fit of $\chi^{(3)}_P$ does not necessarily have to lead to the same values of $J_d$ and $t$ as the fit of $\chi^{(1)}_P$, we decided to preserve the value of $J_d/t = 0.273$ and allow for $J_q$ and $t$ to be free parameters. The result of
this fitting is the curve on Fig.2, which corresponds to $t = 75$ K, $J_d = 0.273t = 20.5$ K and $J_q = 4.8$ K. With these values, the positive maximum of $\chi_P^{(3)}$ is well fitted, although at lower temperatures the fit is less perfect within the present theory. At higher temperatures on the other hand it is hard to assess the agreement between the theory and data; in any case the theory predicts $\chi_P^{(3)}$ to become negative again at high temperatures and approach zero from below. From Fig.2 it is clear that by assuming a quadrupolar interaction of strength about 5 K, the theory can qualitatively account for the temperature dependent double change of sign of $\chi_P^{(3)}$. Quantitatively, the agreement is worse than in case of $\chi_P^{(1)}$, which is perhaps not surprising for a thermodynamic quantity which is a higher order derivative of the free energy. The required value of $t$ is now larger by $\sim 70$ % and the value of the displacement required in order to obtain the necessary value of the prefactor is even an order of magnitude larger than in case of $\chi_P^{(1)}$, namely 2.3 Å, which is clearly unphysical. As in the case of $\chi_P^{(1)}$, we attribute these discrepancies to the crudeness of the model. On the other hand, a firm result of this calculation and fit is that the presence of $J_q$ appears to be crucial in order to account for a positive $\chi_P^{(3)}$ at intermediate temperatures.

V. POSSIBLE ORIGIN OF THE QUADRUPOLAR INTERACTION IN PEROVSKITES

Before closing, we discuss the possible microscopic origin of the effective (anti)-quadrupolar interaction $J_q$ in perovskites. Recently, we did in fact invoke for SrTiO₃ [22] the possible importance of an effective quadrupolar coupling $J_q$ between the dipoles in different cells, in addition to the dipolar one $J_d$. The sign of this interaction $J_q$ is negative (”antiquadrupolar”), such that dipoles prefer to be either parallel or antiparallel, to being orthogonal. One physical source anticipated in Ref. [22] could be related to a lattice strain effect, as follows. When a dipole bond appears in one cell, it will cause an elongation of that cell along the dipole direction, and a shrinking in the orthogonal direction via electrostriction. This deformation, to avoid strain gradients, will extend to the neighbouring cells where
it will favor equally well a parallel or an antiparallel dipole orientation, but will disfavor the orthogonal one. The coupling then arises so as to reduce strain gradients associated with orthogonal dipoles, but absent for parallel or antiparallel dipoles. In order to estimate the strength of the resulting interaction, these intuitive considerations have to be formalized.

Formally, the term representing the coupling between the local polarization and strain is, for a perovskite structure, linear in strains and quadratic in polarizations, and according to Ref. [3] it reads

\[ H_{int} = \frac{1}{2} \sum_i \sum_{\alpha\beta} B_{i\alpha\beta} \eta_i(\vec{R}_i) u_\alpha(\vec{R}_i) u_\beta(\vec{R}_i), \]  

(29)

while the elastic energy is given by

\[ H_{el} = \frac{1}{2} \sum_i \sum_{lk} C_{lk} \eta_i(\vec{R}_i) \eta_k(\vec{R}_i), \]  

(30)

where \( \eta_i(\vec{R}_i) \) and \( u_\alpha(\vec{R}_i) \) are the strain and local soft mode amplitude components at site \( i \), respectively, \( B_{i\alpha\beta} \) are the strain-ferroelectric soft mode coupling constants and \( C_{lk} \) are the elastic constants. The total strain at site \( i \) consists of the homogeneous component arising from the uniform deformation of the whole system as well as of the inhomogeneous local strain. Both components have to be taken into account in a different way, because the 6 local strain components per cell are not in fact independent quantities, but rather suitable linear combinations of the 3 independent acoustic displacement components per cell. To proceed, one has to express the local strains in both (29) and (30) in terms of the acoustic displacements. Integrating out the acoustic displacements from the total hamiltonian, one finds the effective interaction between the polarizations in different cells, which turns out to be fourth order in polarizations and contains also the quadrupolar interaction which we are interested in. In our case, however, such procedure would not be as straightforward as in the corresponding classical case, because the complete hamiltonian contains the quantum kinetic energy term which does not commute with the coupling term containing the polarization. The simpler classical calculation should, however, provide at least a rough estimate of the strength of the effective \( J_q \) induced in this way.
Before doing this calculation in detail, however, it is actually possible to estimate an upper limit to the strength of the effective $J_q$ by means of a simple argument. The induced *intersite* interaction term of the form $(\vec{u}(\vec{R}_i) \cdot \vec{u}(\vec{R}_j))^2 = \frac{1}{2} u(\vec{R}_i)^2 u(\vec{R}_j)^2 (1 + \cos 2(\phi_i - \phi_j)), i \neq j$ certainly must be weaker than an analogous induced term for $i = j$, $(\vec{u}(\vec{R}_i) \cdot \vec{u}(\vec{R}_i))^2 = u^4(\vec{R}_i)$, which represents a renormalization of the on-site quartic term $u^4(\vec{R}_i)$. This renormalization is clearly of the order of $\frac{B_{l\alpha\beta}^2}{C_{lk}}$. In order to get an upper estimate for the interaction strength $J_q$, we must also multiply by $\frac{1}{2} d^4$, where $d$ is the typical value of the local displacement. Taking the typical values of $B_{l\alpha\beta} \sim 1.4$ hartree/bohr$^2$ and $C_{lk} \sim 5$ hartree (from Ref. [3]), together with the displacement $d \sim 0.03\AA$, we arrive at a value about 0.5 K, which is an order of magnitude lower than the value of 5 K estimated in the previous section to be necessary to explain $\chi^{(3)}_P$ in SrTiO$_3$.

A more accurate classical calculation of $J_q^{\text{strain}}$ is most conveniently performed in the Fourier representation, due to the translational invariance of the hamiltonian. The long-wavelength limit of the problem has been studied in the 70’s when it was shown that the resulting interaction is nonanalytical in $k$-space and has a long-range tail in the real space [3,14]. A similar 2D calculation of indirect strain-induced coupling has been performed for the case of SrTiO$_3$ [34], taking into account all the Fourier components from the Brillouin zone, which allows extraction of the induced interaction for each pair of lattice sites $i \neq j$. We will not go here into the full detail of that calculation and merely quote the main result, which is that the strength of the induced interaction is of the order of 0.1 K, a factor of five lower than the previous upper limit estimate. We conclude that the origin of the effective quadrupolar interactions of the required strength is not likely to be elastic, and should be sought elsewhere.

Another possible source could be long-range interactions. Coupling one cell with further neighbours will generally yield terms with higher angular Fourier components. The soft phonon mode dispersion away from $k = 0$ is in fact very non-sinusoidal, precisely due to Coulomb interactions [35]. A third possibility might finally arise from anharmonic terms like $(\vec{u}(\vec{R}_i) \cdot \vec{u}(\vec{R}_j))^2$ of non-strain origin. At this stage we are not in a position to decide...
among these possibilities. It would therefore be highly desirable to extend ab-initio studies similar to those in Ref. [3] beyond the lowest order considered there ("local anharmonicity approximation"), and try to determine also the required higher order terms of the energy expansion.

Because of the close relationship between these expansions and the harmonic and anharmonic phonon properties, which in case of KTaO$_3$ and KNbO$_3$ are also quite well reproduced by extended shell models [36], it might also be possible to use them for this purpose.

VI. CONCLUSIONS

In conclusion, we have considered the nonlinear dielectric susceptibility $\chi^{(3)}_P$, and its behaviour with temperature for a model system exhibiting quantum paraelectricity below a "quantum temperature" $T_Q$. The model is chosen so as to include a quadrupolar coupling in addition to the normal dipolar one. It is found that the effect of the quadrupolar couplings is to cause a temporary switch of sign of $\chi^{(3)}_P$ from negative, well above and well below $T_Q$, to positive at $T \sim T_Q$. Recent data for $\chi^{(3)}_P$ of SrTiO$_3$ appear to agree well with this predicted behaviour implying an effective quadrupolar coupling $J_q \sim \frac{1}{4} J_d$. Work which remains to be done includes

a) better understanding of the true microscopic origin of $J_q$, presently still unclear
b) understanding the possible relationship of this new coupling to the exciting and largely unexplained phenomenology observed near $T_Q$, in Müller’s original experiments [4], and those which followed it. For the time being, we have noted that a positive $\chi^{(3)}_P$ at $T_Q$ implies that the QPE state results due to quantum frustration of an otherwise first-order ferroelectric transition.

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* Permanent address: Department of Physics, Faculty of Electrical Engineering, Slovak Technical University, Ilkovičova 3, 812 19 Bratislava, Slovakia.

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FIGURES

Fig.1. Third order nonlinear dielectric susceptibility $\chi_P^{(3)}$ as a function of temperature for a fixed value of dipolar coupling $J_d$ and various values of quadrupolar coupling $J_q$.

Fig.2. Fitting of the experimentally measured $\text{Re}(\chi_P^{(3)})$ [26,31,37] of SrTiO$_3$ with formula (28). Full points correspond to experimental data, solid line to the theoretical curve.
Fig. 1

\[ \chi_p^{(3)} \]

- \( J_d = 0.273 \)
- \( t = 1 \)

Values:
- \( J_q = 0 \)
- 0.0833
- 0.07
- 0.0637
- 0.033
$\text{Re}(\chi^{(3)}_p) \quad [(V/mm)^{-2}]$

$T[K]$

$t = 75 \text{ K}$

$J_d = 20.5 \text{ K}$

$J_q = 4.8 \text{ K}$