Quantum susceptibility for structural transitions based on exact solutions of the Schrödinger equation

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The static susceptibility of a quantum system is considered to discuss the structural phase transition.   The linear response theory is applied with assuming a mean field treatment for the interaction between unit cells.   The energy eigen state is solved exactly for the Schrödinger equation of a single particle within a two-Morse type self-potential.   The parameter dependence of the transition temperature is discussed analytically, which will give a general insight into the structural phase transition. The pressure-temperature phase diagram for KDP-type crystal is constructed theoretically.

Keywords exact solution of the Schrödinger equation; zero point energy; energy barrier; two-Morse potential; susceptibility; Barrett equation; *p-T* phase diagram

Introduction

A phase transition is characterized by divergence of the static susceptibility[1, 2], which can be calculated by the linear response theory[3].   The non-linearity in the self-potential of a particle and the interaction between particles are indispensable to the phase transition[4], but these prevent usually to derive analytic relations.   If an exact solution would be solved, we could view the nature of the phase transition straightforwardly.

The general formalism of the structural transition was presented by Onodera for a classical system[5].   Recently, a single particle susceptibility has been reinvestigated by using quantum mechanics[6, 7] to discuss the pressure-temperature phase diagram of KH_2PO_4[8], which is famous for a proton tunneling[9].   The Barrett equation[10] has been derived for the static susceptibility, and the pressure dependence of the transition line was calculated[7]. However, the single particle states were obtained by numerical solutions for the Schrödinger equation.

Here we present exact ground and first excited state wave-functions for a one dimensional

motion of a quantum particle within a two-Morse potential function.   The analytic form of the eigen energy is helpful to discuss the parameter dependence of the phase transition.

Susceptibility and T_c

   The thermodynamic properties of a crystal system can be described by a susceptibility χ, which relates the thermodynamic variable with the conjugate external field[2].   In dielectric crystals, for example, the Polarization P is induced by an electric field E as

$$P = \chi E \quad . \tag{1}$$

The polarization stems from a displacement of ions with charge q_j from the equilibrium position by x_j: $P = \sum_j q_j x_j$.   According to the linear response theory[3], χ is calculated by using the equilibrium density matrix ρ by the formula

$$\chi = \int_0^\beta d\lambda \, Tr(\rho e^{\lambda H} x e^{-\lambda H} x) \quad . \tag{2}$$

Here H is the Hamiltonian of the system without the external field and $\beta = 1/k_B T$, where k_B is the Boltzman constant and T is temperature.   The density matrix is related to the partition function Z as

$$\rho = e^{-\beta H} / Z \quad , \text{ and } \quad Z = Tr \, e^{-\beta H} \quad . \tag{3}$$

   Now let's consider a particle within a one-dimensional local potential $V(x)$.   The Schrödinger equation permits discrete energy levels ε_n for a localized wave function $\psi_n(x)$;

$$\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\}\psi_n = \varepsilon_n \psi_n \quad . \tag{4}$$

With representing the eigen states as $|n>$, single particle susceptibility can be explicitly written as [3, 6];

$$\chi_S = \frac{1}{Z} \sum_{j,k} \frac{\exp(-\beta\varepsilon_j) - \exp(-\beta\varepsilon_k)}{\varepsilon_k - \varepsilon_j} \left|\langle j|x|k\rangle\right|^2 . \tag{5}$$

If only two eigen states are predominant, then the single particle susceptibility is represented as

$$\chi_S = \frac{2x_0^2}{\hbar\omega_1} \tanh\frac{\beta\hbar\omega_1}{2} \quad , \tag{6}$$

where $\hbar\omega_1 = \varepsilon_1 - \varepsilon_0$ is the gap energy, and $x_0 = \left|\langle 0|x|1\rangle\right|$ is the transition element.   At high

temperature, the susceptibility obeys the classical relation of $\chi_S = \dfrac{x_0^2}{k_B T}$.

Now let's introduce an interaction between the particles as

$$-\gamma \sum_{j<k} x_j x_k \ , \tag{7}$$

and apply a mean field approximation to get the susceptibility [5];

$$\chi = \frac{\chi_S}{1 - \gamma \chi_S} \ . \tag{8}$$

By using (6), we obtain the Barrett equation

$$\chi = \frac{x_0^2 / k_B}{\dfrac{T_1}{2} \coth(\dfrac{T_1}{2T}) - T_0} \ , \tag{9}$$

where $k_B T_0 = \gamma x_0^2$ is the interaction energy, and $k_B T_1 = \hbar \omega_1$ is the gap energy. At high temperature, the susceptibility can be approximated by a Curie-Weiss relation: $\chi = x_0^2 / k_B (T - T_0)$. The susceptibility diverges at $T=T_c$; the transition temperature is given by [7]

$$T_c = \frac{T_1}{\log(\dfrac{2T_0 + T_1}{2T_0 - T_1})} \ . \tag{10}$$

Once the Schrödinger equation (4) is solved, the static susceptibility and the transition temperature would be given explicitly.

The two-Morse potential and the exact solution for the Schrödinger equation

It is widely accepted that a harmonic force cannot induce the transition. In order to consider the phase transition, we adopt a two-Morse potential[6, 7]

$$V(x) = 2D\left(e^{-2ad} \cosh(2ax) - 2e^{-ad} \cosh(ax)\right) \ , \tag{11}$$

which is constructed from the usual Morse potential by back-to-back location with a splitting distance of $2d$. The potential actually takes two minimum if $ad > \log 2$.

Generally, the exact solution for this local potential is not written analytically. But for a special value of D, we can write an analytic form of wave functions and eigen values. With scaling the space coordinate by $2/a$ and putting

$$\lambda = 8e^{-ad}, \tag{12}$$

the Schrödinger equation is written as

$$-\frac{\partial^2}{\partial x^2}\psi_n = \frac{2mD}{\hbar^2 a^2}\left\{\frac{4}{D}\varepsilon_n + \lambda(2-\frac{\lambda}{8}) - \left(\lambda^2 \sinh^4 x - \lambda(4-\lambda)\sinh^2 x\right)\right\}\psi_n \tag{13}$$

It can be shown straightforwardly that the following wave functions are ground and first excited states, if $2mD/\hbar^2 a^2 = 1$;

$$\varepsilon_0 = \frac{D}{4}(\frac{\lambda^2}{8} - \lambda - 1), \quad \psi_0 = N_0 \cosh(x)\exp(-\tfrac{\lambda}{2}\sinh^2 x), \tag{14a}$$

$$\varepsilon_1 = \frac{D}{4}(\frac{\lambda^2}{8} + \lambda - 1), \quad \psi_1 = N_1 \sinh(x)\exp(-\tfrac{\lambda}{2}\sinh^2 x). \tag{14b}$$

Here N_j is a normalization factor. Figure 1 displays the two-Morse potential and these wave functions. In this figure the scaled potential

$$4V(x)/D = \lambda^2/8 \cdot \cosh(4x) - 2\lambda \cosh(2x) \tag{15}$$

is shown for λ=5, 1, 0.1 and 0.01, as well as their normalized wave functions. The scaled potential takes a minimum value $-4 - \lambda^2/8$ at $x = \pm\ln(\dfrac{\sqrt{4-\lambda}+\sqrt{4+\lambda}}{\sqrt{2\lambda}})$ if λ<4. The barrier energy at x=0 is $-2\lambda + \lambda^2/8$. The ground state wave function becomes a single-peak shape if $\lambda \ge 1$, while the wave function takes two peaks at $x = \pm\ln(\dfrac{1+\sqrt{1-\lambda}}{\sqrt{\lambda}})$

if $\lambda < 1$. It should be noted that the ground state wave function is single peaked both for the single minimum potential($\lambda \ge 4$) and for the double minimum potential if the zero point energy is above the barrier level(4>λ>1).

Here we define a scaled temperature $\tau = 4k_B T/D$. From (10), the transition temperature is estimated, if λ/τ_0 is small:

$$\tau_c = 2\lambda/\log\frac{\tau_0 + \lambda}{\tau_0 - \lambda} \cong \tau_0\{1 - \tfrac{1}{3}(\frac{\lambda}{\tau_0})^2\}. \tag{16}$$

At a classical limit, the last approximation is appropriate. On the other hand, the transition disappears logarithmically at $\lambda_0 \ge \tau_0$: quantum paraelectricity. The scaled transition temperature τ_c/τ_0 is plotted against λ/τ_0 in Fig. 2.

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Discussions

Now we discuss how the transition temperature depends on potential parameters. This would describe the phase diagram of the system, since parameter d, for example, will shrink with applying the hydrostatic pressure p as $d = d_0 - d_1 p$. So the parameter λ is given by $\lambda_0 \exp(ad_1 p)$. Figure 3 gives the pressure dependence of the transition temperature. The phase diagram coincides qualitatively with the pressure-temperature phase diagram of KDP[8, 11, 12].

The result of the present report is equivalent to the previous publication[7]. However, the exact solutions of the Schrödinger equation allow us analytical discussions. One of the consequences is the criterion of the peak of the nuclear density. Even if the self-potential has two minima, the nuclear density takes a single-peaked form when the zero-point energy exceeds the potential barrier.

Finally it should be noted that the exact solutions (14) are restricted to the condition of $2mD/\hbar^2 a^2 = 1$; the nuclear mass cannot be changed freely. If d is 0.5A, a=5A^{-1}, and D=2eV[7], then m is too lighter than proton. Strictly speaking, the solution cannot be applied to KDP, but the qualitative behavior of the quantum particle is described in the present model.

REFERENCES

[1] T. Mistui, I. Tatsuzaki and E. Nakamura, "*An Introduction to the Physics of Ferroelectrics*", Translated by Y. Ishibashi *et al*. (Taylor and Francis, London, 1981).
[2] Y. Ishibashi, Ferroelectrics **267**, 191 (2002).
[3] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[4] M. E. Lines and A. M. Glass, "*Principles and applications of ferroelectrics and related materials*", (Oxford University Press, Oxford, 1977).
[5] Y. Onodera, Progr. Theor. Phys. **44**, 1477 (1970).
[6] H. Mashiyama, J. Phys. Soc. Jpn. **73**, 3466 (2004).
[7] H. Mashiyama, J. Korean Phys. Soc. **46**, 63 (2005).

[8] G. A. Samara, Ferroelectrics **7**, 221 (1974).

[9] R. Blinc, J. Phys. Chem. Solids **13**, 204 (1960).

[10] J. H. Barrett, Phys. Rev. **86**, 118 (1952).

[11] S. Endo, K. Deguchi and M. Tokunaga, Phys. Rev. Lett. **88**, 35503 (2002).

[12] M. Tokunaga, K. Deguchi and S. Endo, Ferroelectrics **267**, 263 (2002).

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Figure captions

Fig. 1   The two-Morse potential and wave functions for λ=5, 1, 0.1 and 0.01, in (a), (b), (c) and (d), respectively.   The energy levels are shown by dashed lines.

Fig. 2   Transition temperature as a function of parameter λ.   The longitudinal and the abscissa axes are T_c / T_0 and $\lambda D / 4 k_B T_0$, respectively.

Fig. 3   Transition temperature as a function of pressure p.   The longitudinal and the abscissa axes are T_c / T_0 and $a d_1 p$, respectively, where λ_0 / τ_0 is set to 0.9.
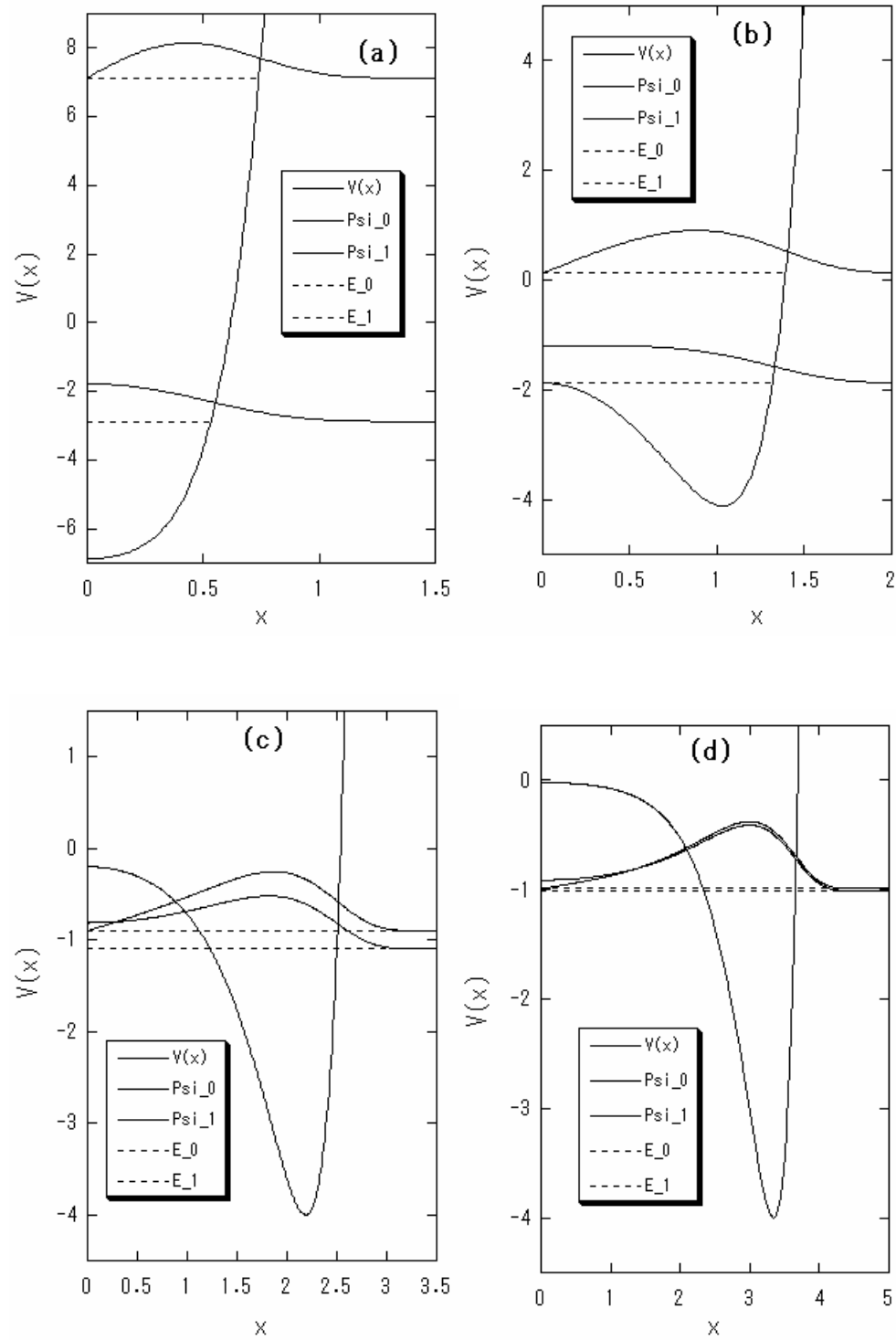
Figure 1   M. Ashida and H. Mashiyama
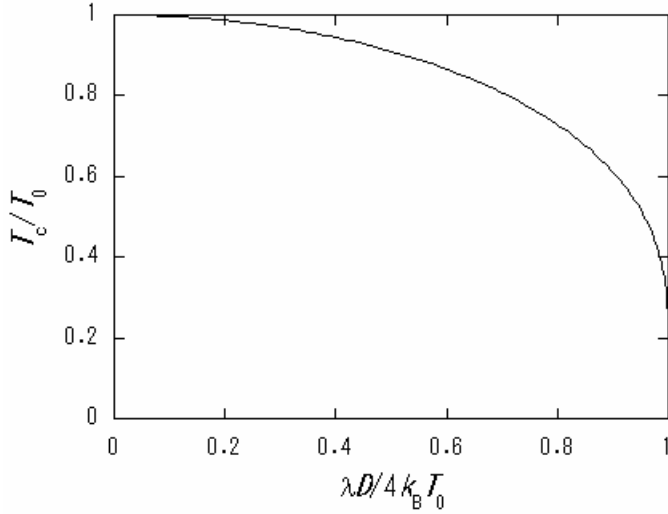
Figure 2   M. Ashida and H. Mashiyama

Figure3　　M. Ashida and H. Mashiyama