CHAPTER I

INTRODUCTION

I.1 The Polaron Problem

The problem concerning an electron moving in an ionic
crystal has been of constant theoretical and experimental
interest since the beginning of the systematic development of
solid state physics. The earliest direct approach to this
problem was made by Landau in 1933, when he introduced the
idea of self-trapping of an electron in the sodium chloride
crystal[1]. The principal idea is that as the electron moves
through the ionic crystal it distorts the ion lattices in its
neighbourhood by virtue of the coulomb interaction and thus
produces a polarization. This polarization constitutes a
potential field surrounding the electron, which is then trapped
in the potential minimum. Furthermore, the electron always
carries with it the polarization field and hence possesses a
specific self energy as it moves through the crystal. Since
the lattice ions are much heavier than the electron, they will
not return to their equilibrium positions during a half period
of the electronic motion in the trapping potential.

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[1] H. Fröhlich, "Introduction to the Theory of the
Polaron.", in Polarons and Excitons, Eds.C.G. Kuper, and G.D.
Whitfield, Edinburgh and London: Oliver and Boyd (1962) 1.

The combination of the electron and the accompanying self-consistent polarization field can be thought of as a quasi-particle, and this quasi-particle is called a "polaron". The concept of a polaron[2] was first introduced explicitly by Pekar in 1954.

The principal effect of the polarization field on the electron is that its self energy is lower than that of a bare electron. Since its inertia is greater, it will have an effective mass larger than the electron rest mass. Since the polaron provides a particularly simple model of a particle interacting with a quantum field, it is certainly of great theoretical interest and indeed it was the first specific problem of solid state physics to which the method of quantum field theory has been applied.

The polaron which we shall consider arises from the strong coulomb interaction between a single slow electron and the lattice of a perfect crystal. In this case the polarization field is due to the deformation of the lattice. There are two extreme types of polaron distinguished by its size as measured by the extension of the lattice distortion[3]. First, one has

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[2] J. Appel, "Polarons.", in Solid State Physics, 21, Eds. F.Seitz, D.Turnbull, and H.Ehrenreich, New York and London: Academic Press (1968) 194.

[3] D. Adler, "Electronic Phase Transitions.",1,in,Essays in Physics, Eds. G.K.T.Conn, and G.N.Fowler, London and New York: Academic Press (1970) 33.

the <u>large</u> polaron that extends over a distance much larger than
a lattice spacing, and for which one can therefore treat the
lattice as a dielectric continuum. This is the particular form
of polaron which we are going to study in detail. Secondly,
one has the <u>small</u> polaron where the lattice distortion is res-
tricted to the immediate vicinity of the electron. In this case
the atomicity of the lattice must be taken into account and a
suitable treatment is the tight binding approximation.

Polaron properties have been investigated by a number
of authors using different methods. The problem of fundamental
theoretical interest is its self energy and mobility. In the
present research, the polaron self energy will be studied by
using the Feynman[4] path integration technique in spite of its
rather tedious mathematical formulation, for the following
reasons. First, it is the only formulation that covers the
whole range of the electron-lattice coupling constant $\propto$, and
this differs essentially from most other theories such as the
perturbation theory, which are only applicable to the polaron
with weak coupling constant. Secondly, the value of the polaron
self energy given by the path integration has shown a very good
agreement with or is lower than those of the other theories
which have hitherto been published.

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[4] A.P. Feynman, and A.R. Hibbs, <u>Quantum Mechanics and
Path Integrals</u>, New York: McGraw-Hill (1965) 26.

In order to evaluate the polaron self energy, it is
appropriate to consider first the behaviour of a single slow
electron in a perfect ionic crystal. As an electron moves
through an ionic crystal, it always interacts with the lattice
ions in its neighbourhood, the positive and negative ions of
the lattice being respectively attracted to and pushed away
from the equilibrium points, and thus producing the polarization
field. In the theory, it is usual to make the simplifying
assumption that the lattice ions are undeformable and rigidly
fixed to their equilibrium positions. By using this assumption,
the single slow electron can therefore be considered as a free
electron moving in a periodic field of force with kinetic energy
$E(k)$ expressible as a quadratic function of the momentum $\hbar k$,

$$E(k) = \frac{\hbar^2 k^2}{2m^*} \quad , \tag{1.1}$$

where the periodicity is admitted by replacing the electron
mass by an effective mass m^*.

Owing to the fact that the electron energy is suffi-
ciently low, the electronic wave function changes only very
little in one unit lattice distance. In this way, the crystal
lattice can be treated as a dielectric continuum and the
displacement vectors become a continuous function of position.
Furthermore, the electron interacts strongly with the polariza-
tion field arising from the longitudinal optical modes of lattice
vibrations, which are assumed to be characterized by a constant
frequency ω_L. This description of the polaron was idealized

by Fröhlich[5] in 1954.

I.2 Outline of the Thesis

Generally, the Hamiltonian of a physical system is the appropriate basis for the energy calculation. However, in dealing with the path integration, the Lagrangian of the system is the fundamental for the solution of the problem. Therefore a derivation of the Lagrangian of the polaron system, as idealized by Fröhlich, will be given in the remaining section of this chapter.

Principal ideas of constructing the Feynman path integral, the method of writing the propagator in the form of a path integral and its application to the forced harmonic system will be presented in Chapter II. It will also be shown that the propagator is essentially equivalent to the density matrix, and its relation to the ground state energy will be presented in Section II.3.

In Chapter III, the original Feynman polaron theory[6], which gives the formulation suitable for an evaluation of the polaron ground state energy at absolute zero temperature, will be introduced. This theory is extremely powerful, and indeed

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5 H. Fröhlich, "Electron in Lattice Fields.", Advances in Physics, 3 (1954) 325.

6 R.P. Feynman, " Slow Electrons in a Polar Crystal.", Physical Review, 97 (1955) 660.

it has been shown by Schultz[7] that the ground state energy thus obtained is lower than those calculated from other theories [8-9]. Various properties of the polaron have since been studied by the same method[10-12]. Recently, the Feynman polaron theory has been improved by Abe and Okamoto[13] by introducing two additional parameters. However, the subsequent corrections are very small[14].

7 T.D. Schultz, " Slow Electrons in Polar Crystals: Self Energy, Mass, and Mobility.", Physical Review,116 (1959)526.

8 T.D. Lee, and D. Pines, "Interaction of a Nonrelativistic Particle with a Scalar Field with Application to Slow Electrons in Polar Crystal.", Physical Review, 92 (1953) 883.

9 E.P. Gross, "Small Oscillation Theory of the Interaction of a Particle and Scalar Field.", Physical Review, 100 (1955) 1571.

10 P.M. Platzman, "Ground-State Energy of Bound Polarons.", Physical Review, 125 (1962)6.

11 R.W. Hellwarth, and P.W. Platzman, "Magnetization of Slow Electrons in a Polar Crystal.", Physical Review, 128 (1962) 1599.

12 J.T. Marshall, and M.S. Chawla, "Feynman Path-Integral Calculation of the Polaron Effective Mass." Physical Review B, 2 (1970) 4283.

13 R. Abe, and K. Okamoto, "An Improvement of the Feynman Action in the Theory of Polaron.I", Journal of the Physical Society of Japan, 31 (1971) 1337.

14 K. Okamoto, and R. Abe, "An Improvement of the Feynman Action in the Theory of Polaron.II", Journal of the Physical Society of Japan, 33 (1972) 343.

The reasons why this problem should again assume great significance, some physical ideas of the recent improvements, and the detailed evaluation of the ground state energy by the new treatment, will be presented in Chapter IV.

In Chapter V, the Feynman polaron theory, which is restricted to the case of polaron state at absolute zero temperature, will be extended to the case at finite temperatures by using the model Lagrangian proposed by Osaka[15,16]. It seems therefore of interest to attempt to improve the polaron theory at finite temperatures, and this will be discussed in Chapter VI.

Finally, in Chapter VII, the results of the polaron self energy calculated by different methods for various situations, as obtained from the previous chapters, will be presented and compared with the corresponding results of other workers.

I.3 Lagrangian of the System

To obtain the Lagrangian of the polaron system, the Fröhlich idealized model as described in Section I.1 must be recalled for further consideration. The induced polarization

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[15] Y. Osaka, "Polaron State at a Finite Temperature.", Progress of Theoretical Physics, 22 (1959) 437.

[16] M.A. Krivoglaz, and S.I. Pekar, "The Method of Traces for Conduction Electrons in Semiconductors.", Bull Acad. Sci. USSR. Phys. Ser. (English Transl.), 21 (1957) 1,13.

field at the position vector $\underset{\sim}{r}$ is related to the electric displacement $\underset{\sim}{D}(\underset{\sim}{r})$ and the electric field $\underset{\sim}{E}(\underset{\sim}{r})$ by

$$\underset{\sim}{D}(\underset{\sim}{r}) \;=\; \underset{\sim}{E}(\underset{\sim}{r}) + 4\pi \cdot \underset{\sim}{P}(\underset{\sim}{r}) \qquad , \qquad (1.2)$$

where the electric displacement represents the external field acting on the polarization of the crystal.

If the source of $\underset{\sim}{D}(\underset{\sim}{r})$ is the single free electron in the crystal with the position vector $\underset{\sim}{r}_{el}$, the electric displacement $\underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el})$ is defined by

$$\underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el}) \;=\; \underset{\sim}{\nabla} \frac{e}{|\underset{\sim}{r}-\underset{\sim}{r}_{el}|} \qquad . \qquad (1.3)$$

Therefore, $\operatorname{curl} \underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el}) = 0, \quad \underset{\sim}{\nabla} \cdot \underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el}) = 4\pi \cdot e\delta(\underset{\sim}{r}-\underset{\sim}{r}_{el}), (1.4)$ and $\underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el}) = 0$ in the absence of the electron.

The electric dipole moment of an infinitesimal volume $d^3\underset{\sim}{r}$ around $\underset{\sim}{r}$ is $\underset{\sim}{P}(\underset{\sim}{r})d^3\underset{\sim}{r}$, and it thus follows that the interaction energy between the electron and the lattice displacement is

$$-\int \underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el}) \cdot \underset{\sim}{P}(\underset{\sim}{r})d^3\underset{\sim}{r} \qquad ,$$

where $\underset{\sim}{P}(\underset{\sim}{r})$ is defined as follows:

$$4\pi\underset{\sim}{P}(\underset{\sim}{r}) \;=\; \underset{\sim}{\nabla}\,\phi(\underset{\sim}{r}) \qquad . \qquad (1.6)$$

On substituting $\underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el})$ and $\underset{\sim}{P}(\underset{\sim}{r})$ from (1.3) and (1.6), respectively, into (1.5), we obtain

$$-\frac{1}{4\pi}\int \underset{\sim}{\nabla} \frac{e}{|\underset{\sim}{r}-\underset{\sim}{r}_{el}|} \cdot \underset{\sim}{\nabla}\phi(\underset{\sim}{r})d^3\underset{\sim}{r} \;=\; -e\phi(\underset{\sim}{r}_{el}) \qquad . \qquad (1.7)$$

The polarization $\underset{\sim}{P}(\underset{\sim}{r})$ has two principal contributions:

$$\underset{\sim}{P}(\underset{\sim}{r}) \;=\; \underset{\sim}{P}_0(\underset{\sim}{r}) + \underset{\sim}{P}_{1r}(\underset{\sim}{r}) \;, \tag{1.8}$$

where $\underset{\sim}{P}_0(\underset{\sim}{r})$ arises from a deformation of the electric orbitals of the lattice ions, and $\underset{\sim}{P}_{1r}(\underset{\sim}{r})$ is due to the displacement of whole ions and is also due in part to the component of the motion of the electrons which adiabatically follows any ionic movement. Each component of $\underset{\sim}{P}(\underset{\sim}{r})$ corresponds to an optical absorption in the ultraviolet and infrared region, respectively; and in the external field $\underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el})$ they each satisfy the forced harmonic equations of motion

$$\underset{\sim}{\ddot{P}}_{ir}(\underset{\sim}{r}) + \omega^2 \underset{\sim}{P}_{ir}(\underset{\sim}{r}) \;=\; \underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el})/\gamma \;, \tag{1.9}$$

$$\underset{\sim}{\ddot{P}}_0(\underset{\sim}{r}) + \omega_0^2 \underset{\sim}{P}_0(\underset{\sim}{r}) \;=\; \underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el})/\delta \;, \tag{1.10}$$

where γ and δ are constants for the respective displacements which we are going to determine.

On substituting into Eq.(1.2) the relation $\underset{\sim}{D}(\underset{\sim}{r}) = \epsilon(w)\underset{\sim}{E}(\underset{\sim}{r})$, we obtain

$$4\pi\left(\underset{\sim}{P}_0(\underset{\sim}{r}) + \underset{\sim}{P}_{ir}(\underset{\sim}{r})\right) \;=\; \left(1 - \frac{1}{\epsilon(\omega)}\right)\underset{\sim}{D}(\underset{\sim}{r}) \;. \tag{1.11}$$

Now consider in turn the static and the high frequency cases, for which the electron is either at rest or oscillates with a frequency ω_∞, where $\omega_{ir} \ll \omega_\infty \ll \omega_0$. On applying the former limiting case to Eq.(1.11), we obtain

$$4\pi\left(\underset{\sim}{P}_0(\underset{\sim}{r}) + \underset{\sim}{P}_{ir}(\underset{\sim}{r})\right) \;=\; \left(1 - \frac{1}{\epsilon_s}\right)\underset{\sim}{D}(\underset{\sim}{r}) \;. \tag{1.12}$$

For the high frequency case, $P_{1r}(r)$ can no longer follow the electron adiabatically. Its value is very small compared with $P_0(r)$ and can thus be neglected. Eq.(1.11) is then reduced to

$$4\pi P_0(r) = (1 - \frac{1}{\epsilon_\infty})D(r) , \qquad (1.13)$$

where ϵ_s and ϵ_∞ are, respectively, the static and the high frequency dielectric constants. Hence $P_{1r}(r)$ can be obtained by elimination of $P_0(r)$ in (1.12) with the use of (1.13), and thus

$$4\pi P_{1r}(r) = (\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s})D(r) . \qquad (1.14)$$

The parameters γ and δ can be obtained by considering (1.9) and (1.10) for the static case, where $\ddot{P}_0(r) = \ddot{P}_{1r}(r) = 0$, with a substitution of $P_0(r)$ and $P_{1r}(r)$ as given by (1.14) and (1.15):

$$\frac{1}{\gamma} = \frac{\omega^2}{4\pi}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right) , \qquad (1.15)$$

$$\frac{1}{\delta} = \frac{\omega_0^2}{4\pi}\left(1 - \frac{1}{\epsilon_\infty}\right) . \qquad (1.16)$$

For a slowly moving electron, $P_0(r)$ will always be excited, independently of the electronic motion; and consequently its interaction potential will be stationary and lattice periodic. Hence it can be included in the effective mass approximation (1.1), and we can therefore leave it out from further discussion. Born and Huang[17] have suggested that the frequency dependence of the dielectric constant in the infrared region is of the

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[17] M. Born, and K. Huang, Dynamical Theory of Crystal Lattices, Oxford: Clarendon Press (1956) 91.

form illustrated in Fig.1 and the dispersion curves are of
the form illustrated in Fig.2. From the dispersion relation,
it follows that, at all wavelengths in the region being
considered, longitudinal vibrations are only excited at the
single frequency ω_L which is related to ω_r, the maximum fre-
quency of the transverse wave in the infrared region, by the
relation

$$\omega_L = \left(\frac{\epsilon_s}{\epsilon_\infty}\right)^{\frac{1}{2}} \omega_r \quad . \qquad (1.17)$$

We shall thus justifiably identify the infrared frequency ω_{ir}
with the unique and constant frequency ω_L.

The equations of motion of the polaron are clearly the
same as that of the polarization field (1.9) associated with
the electronic motion, which can be immediately re-expressed
in terms of the interaction energy (1.7) as

$$m^*\ddot{\underset{\sim}{r}}_{el} = e \underset{\sim el}{\nabla} \phi(\underset{\sim}{r}_{el}) \quad . \qquad (1.18)$$

The classical Lagrangian that describes the polaron
equations of motion (1.9) and (1.18) is

$$L = \frac{1}{2} m^* \dot{\underset{\sim}{r}}_{el}^2 + \frac{1}{2} \gamma \int [\dot{\underset{\sim}{P}}_{ir}^2(\underset{\sim}{r}) - \omega_L^2 \underset{\sim}{P}_{ir}^2(\underset{\sim}{r})] d^3\underset{\sim}{r} + \int \underset{\sim}{D}(\underset{\sim}{r},\underset{\sim}{r}_{el}) \underset{\sim}{P}_{ir}(\underset{\sim}{r}) d^3\underset{\sim}{r} , \qquad (1.19)$$

where the independent variables are the three components
of $\underset{\sim}{r}_{el}$ and one of $\underset{\sim}{P}_{ir}(\underset{\sim}{r})$ at the field position $\underset{\sim}{r}$. In solving
the polaron problem, the Fröhlich Lagrangian of the form (1.19)
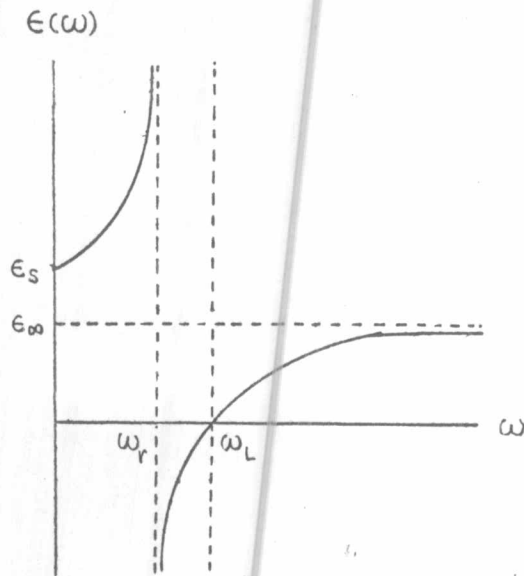must first be written in the form of a quantum mechanical

$\epsilon(\omega)$

ϵ_S

ϵ_∞

ω_r ω_L

ω

Fig.1 The frequency dependence of the dielectric constant.

ω

T

L

ω_L
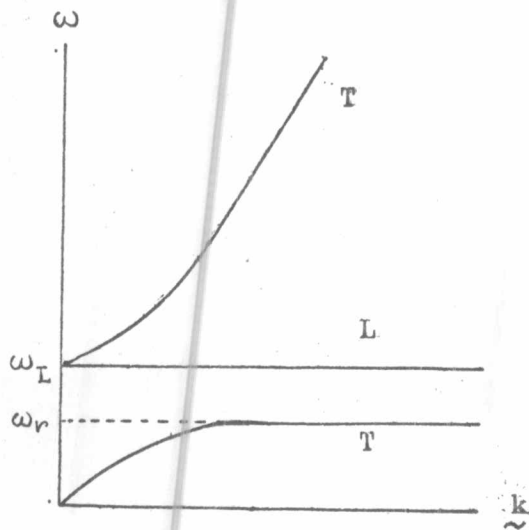
ω_r

T

$\underset{\sim}{k}$

Fig.2 Dispersion curves of lattice vibrations.

Lagrangian, and then the equations of motion can be expressed as a path integral. The details of this formulation will be presented in Chapter III.